Inorg. Chem. **1982**, *21*, 1921-1927

Contribution from the Department of Chemistry, University of Virginia,
Charlottesville, Virginia 22901

Boranometallacarboranes. 1. Synthesis and Characterization of Borane–Cobalt–Carborane Sandwich Complexes[1]

LESTER BORODINSKY and RUSSELL N. GRIMES*

Received September 22, 1981

The first known examples of borane–metal–carborane sandwich complexes, in which a metal atom simultaneously occupies vertices in a metallaborane and a metallacarborane framework, have been obtained from reactions of $B_5H_8^-$ or $B_9H_{14}^-$ ions with $CoCl_2$ in THF, followed by addition of $R_2C_2B_4H_5^-$ ion (R = CH_3 or C_2H_5). With $B_5H_8^-$ and $(C_2H_5)_2C_2B_4H_5^-$, the characterized products are $[2,3\text{-}(C_2H_5)_2C_2B_4H_4]\text{-}2\text{-}Co[B_5H_{10}]$ (I), $[2,3\text{-}(C_2H_5)_2C_2B_4H_4]\text{-}5\text{-}Co[B_9H_{12}\text{-}1\text{-}O(CH_2)_4]$ (II), and $[2,3\text{-}(C_2H_5)_2C_2B_3H_5]\text{-}5\text{-}Co[B_9H_{12}\text{-}1\text{-}O(CH_2)_4]$ (III). With $B_9H_{14}^-$ as the borane reagent, the products are $[2,3\text{-}(C_2H_5)_2C_2B_3H_5]\text{-}6\text{-}Co[B_9H_{12}\text{-}2\text{-}O(CH_2)_4]$ (IV) and $[1,2\text{-}(C_2H_5)_2C_2B_7H_7]\text{-}6\text{-}Co[B_9H_{12}\text{-}2\text{-}O(CH_2)_4]$ (V), as well as traces of I, II, and III. Except for I, an orange oil, all products are crystalline solids. Products I–V were characterized from their FT NMR spectra obtained at 360 MHz for ^1H and 115.5 MHz for ^{11}B, their IR and mass spectra, and X-ray diffraction studies on II, III, and V, which are reported in the accompanying paper. The syntheses of I–V are highly sensitive to reaction conditions; simultaneous addition of the borane, carborane, and metal reagents does not give boranometallacarboranes (as shown in an earlier study by Hosmane and Grimes). The yields of I–V are maximized by short (~20 min) reaction periods and low temperatures (~−20 °C) for the $CoCl_2$/borane interaction prior to addition of carborane.

Introduction

The insertion of metals into borane and carborane frameworks generates metallaboranes[2] and metallacarboranes,[3] respectively. These two compound classes encompass an enormous variety of species and constitute two large and quite distinct fields. While the metallaboranes and metallacarboranes have much in common structurally and obey the same electron-counting rules (which in fact extend to numerous nonboron clusters as well),[4] their synthetic origins are entirely different and their respective chemistries have developed along separate paths. As a general observation, interactions of metal reagents with carborane substrates are, to a degree, more predictable and stereospecific than are metal–borane reactions. Moreover, the cage atoms in metallacarboranes provide loci for functional groups that permit the synthesis of specifically "tailored" derivatives; an elegant recent example is the preparation by Hawthorne and co-workers[5] of powerful metallacarborane catalysts for homogeneous hydrogenation. Rational development of metallaborane chemistry has proceeded more slowly, but this has been compensated by the discovery of a variety of novel structural features and unanticipated cage geometries, which have aided the evolution of structural and bonding theory in clusters.

This paper is concerned with the interface between the metallaborane and metallacarborane fields and describes the synthesis and characterization of the first borane–metal–carborane complexes, or boranometallacarboranes, in which a metal atom occupies vertices in metallaborane and metallacarborane frameworks simultaneously. Our interest in such species was stimulated by the possibility of effecting fusion of borane and carborane cages under mild conditions, in a manner similar to that previously demonstrated for bis(carborane) complexes of cobalt and iron.[2d,6] Although a previous study involving interactions of metal ions with the $2,3\text{-}(CH_3)_2C_2B_4H_5^-$ and $B_5H_8^-$ ions simultaneously[6c] did not lead to isolable borane–metal–carborane complexes, further investigation revealed that under proper conditions such mixed species can indeed be isolated. Here we report the synthesis and spectroscopic characterization of several boranometallacarboranes derived from *nido*-$R_2C_2B_4H_5^-$ (R = CH_3 or C_2H_5) and $B_5H_8^-$ or $B_9H_{14}^-$ ions. X-ray crystal structure determinations on three of these products are described in the following article.[7]

Results and Discussion

The choice of *nido*-$2,3\text{-}R_2C_2B_4H_5^-$ ions as the carborane substrates in this work was based on the facility with which these ions form η^5 complexes with transition-metal ions,[2d,e,3b,6] their easy accessibility,[8] and the demonstrated propensity of $(R_2C_2B_4H_4)_2MH_x$ complexes (R = CH_3, C_2H_5, or C_3H_7; M = Fe, x = 2; M = Co, x = 1) to undergo fusion, forming $R_4C_4B_8H_8$ carboranes in high yield.[2d,6] As borane reagents, the $B_5H_8^-$ and $B_9H_{14}^-$ ions, both of which interact with transition metals to generate metallaboranes,[2] were utilized in separate experiments. In earlier published work from this laboratory,[6c] the *simultaneous* interaction of $CoCl_2$ with $B_5H_8^-$ and $(CH_3)_2C_2B_4H_5^-$ ions in tetrahydrofuran (THF) solution at room temperature gave, as the sole isolated product (21% yield), the mixed-carborane complex $[2,3\text{-}(CH_3)_2C_2B_4H_4]\text{-}CoH[2,3\text{-}(CH_3)_2C_2B_7H_7]$, a yellow, air-stable solid. In the present study, $B_5H_8^-$ ion and $CoCl_2$ were permitted to react first, with the carborane substrate added later; this procedure gave entirely different results and produced several borane–metal–carborane complexes (which, in fact, had been the original synthetic objective of the earlier investigation).

Reaction of $Na^+B_5H_8^-$ and $CoCl_2$ Followed by $Na^+R_2C_2B_4H_5^-$ (R = CH_3, C_2H_5). As described elsewhere,[9] the formation of $B_5H_8^-$ on treatment of B_5H_9 with NaH in

---

[1] Taken in part from: Borodinsky, L. Ph.D. Thesis, University of Virginia, 1982.

[2] Reviews: (a) Greenwood, N. N.; Ward, I. M. *Chem. Soc. Rev.* **1974**, *3*, 231. (b) Wegner, P. A. In "Boron Hydride Chemistry"; Muetterties, E. L., Ed.; Academic Press: New York, 1975, Chapter 12. (c) Greenwood, N. N. *Pure Appl. Chem.* **1977**, *49*, 791. (d) Grimes, R. N. *Acc. Chem. Res.* **1978**, *11*, 420. (e) Grimes, R. N. *Coord. Chem. Rev.* **1979**, *28*, 47.

[3] Reviews: (a) Dunks, G. B.; Hawthorne, M. F. Reference 2b, Chapter 11. (b) Grimes, R. N. *Organomet. React. Synth.* **1977**, *6*, 63; also see ref 2d,e.

[4] (a) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1. (b) Rudolph, R. W. *Acc. Chem. Res.* **1976**, *9*, 446. (c) Mingos, D. M. P. *Nature (London), Phys. Sci.* **1972**, *236*, 99.

[5] Delaney, M. S.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1981**, *20*, 1341.

[6] (a) Maxwell, W. M.; Miller, V. R.; Grimes, R. N. *Inorg. Chem.* **1976**, *15*, 1343. (b) Maxwell, W. M.; Miller, V. R.; Grimes, R. N. *J. Am. Chem. Soc.* **1976**, *98*, 4818. (c) Hosmane, N. S.; Grimes, R. N. *Inorg. Chem.* **1980**, *19*, 3482.

[7] Borodinsky, L.; Sinn, E.; Grimes, R. N., *Inorg. Chem.*, companion paper in this issue.

[8] Hosmane, N. S.; Grimes, R. N. *Inorg. Chem.* **1979**, *18*, 3294.

[9] (a) Savory, C. G.; Wallbridge, M. G. H. *J. Chem. Soc., Dalton Trans.* **1973**, 179. (b) Leach, J. B.; Toft, M. A.; Himpsl, F. L., Shore, S. G. *J. Am. Chem. Soc.* **1981**, *103*, 988.

0020-1669/82/1321-1921$01.25/0

Table I. Boranometallacarborane Products

compd	color	R_f[a]	mp, °C
$[2,3\text{-}(C_2H_5)_2C_2B_4H_4]\text{-}2\text{-}Co[B_5H_{10}]$ (I)	orange	0.78	*b*
$[2,3\text{-}(C_2H_5)_2C_2B_4H_4]\text{-}5\text{-}Co[B_9H_{12}\text{-}1\text{-}O(CH_2)_4]$ (II)	brown	0.45	89–91
$[2,3\text{-}(C_2H_5)_2C_2B_3H_5]\text{-}5\text{-}Co[B_9H_{12}\text{-}1\text{-}O(CH_2)_3$ (III)	orange	0.60	141–143
$[2,3\text{-}(C_2H_5)_2C_2B_3H_5]\text{-}6\text{-}Co[B_9H_{12}\text{-}2\text{-}O(CH_2)_4]$ (IV)	burgundy	0.52	125–127
$[1,2\text{-}(C_2H_5)_2C_2B_7H_7]\text{-}6\text{-}Co[B_9H_{12}\text{-}2\text{-}O(CH_2)_4]$ (V)	black-brown	0.48	150 dec
$[2,3\text{-}(C_2H_5)_2C_2B_3H_5]\text{–}CoH\text{–}[2',3'\text{-}(C_2H_5)_2C_2B_4H_4]$[c] (VI)	yellow	0.82	*b*

[a] Chromatography on silica gel 60 TLC plates in 1:1 CH_2Cl_2/hexane. [b] Oil. [c] The tetra-*C*-methyl analogue of this compound has been reported.[6b]

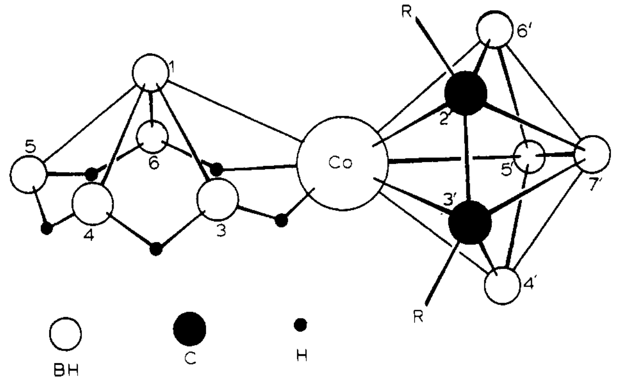

Figure 1. Proposed structure of $[2,3\text{-}(C_2H_5)_2C_2B_4H_4]\text{-}2\text{-}Co[B_5H_{10}]$ (I).

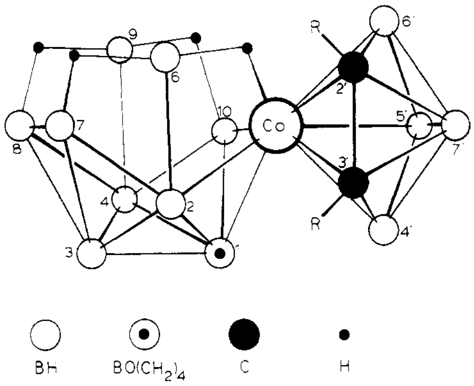

Figure 2. Established structure[7] of $[2,3\text{-}(C_2H_5)_2C_2B_4H_4]\text{-}5\text{-}Co[B_9H_{12}\text{-}1\text{-}O(CH_2)_4]$ (II).

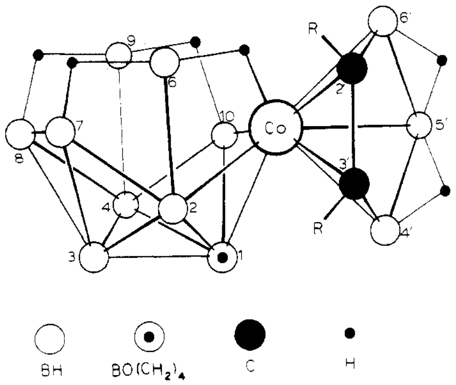

Figure 3. Established structure[7] of $[2,3\text{-}(C_2H_5)_2C_2B_3H_5]\text{-}5\text{-}Co[B_9H_{12}\text{-}1\text{-}O(CH_2)_4]$ (III).

THF unavoidably generates some $B_9H_{14}^-$ as a byproduct; however, at low temperature (<–30 °C) and in the presence of at least a 2.5-fold excess of NaH over B_5H_9, this complication is minimized[10] and the borane ion formed is predominantly (>90 mol %) $B_5H_8^-$. Under these conditions the se-

Table II. 115.5-MHz ^{11}B FT NMR Data ($CDCl_3$ Solution)

compd	δ (*J*, Hz)[a]	rel area
I	34.1 (112),[b] 13.1 (151),[c] 5.5 (139),[d] 2.2 (161),[e] –47.7 (148)[f]	2, 3, 2, 1, 1
II	36.6,[g] 20.6 (110), 142 (128), 7.5 (139), 5.3 (133), –0.4 (105), –3.5 (151), –11.5 (128), –27.1 (139), –39.2 (151)	1, 1, 1, 2, 2, 2, 1, 1, 1, 1
III	36.7,[g] 19.2 (110), 7.0 (128), 3.2,[h] 1.4,[h] –0.7,[h] –2.2 (116), –3.2,[h] –12.8 (103), –26.4 (116), –38.8 (140)	1, 1, 1, 2, 1, 1, 1, 1, 1, 1, 1
IV	10.7 (124), 8.3 (140), 4.4,[h] 1.7,[h] –3.1 (130), –6.5 (147), –38.4 (154)	2, 2, 3, 1, 2, 1, 1
V	78.8 (165), 10.7 (141), 8.5 (126), 7.3,[h] 3.0,[g] –2.1 (130), –3.9 (124), –9.3 (156), –18.8 (137), –22.9 (151), –24.8 (140), –34.9 (148)	1, 1, 2, 1, 2, 2, 2, 1, 1, 1, 1, 1

[a] $BF_3{\cdot}O(C_2H_5)_2$ shift is 0; positive shifts downfield. [b] Assigned to B(3,6). [c] Assigned to B(4,5) and B(5') (superimposed). [d] Assigned to B(4',6'). [e] Assigned to B(7'). [f] Assigned to B(1). [g] Singlet in coupled spectrum; assigned to $B\text{–}O(CH_2)_4$. [h] J_{BH} not measurable owing to peak overlap.

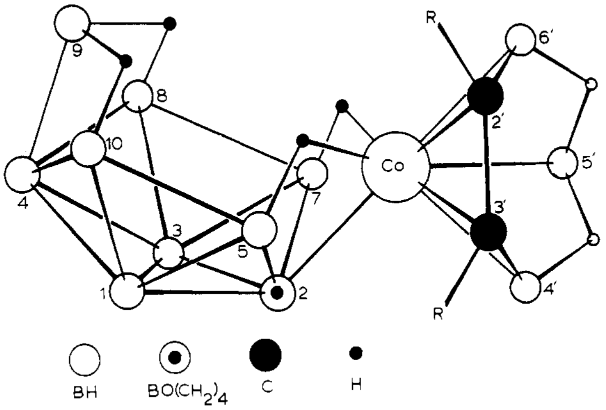

Figure 4. Proposed structure of $[2,3\text{-}(C_2H_5)_2C_2B_3H_5]\text{-}6\text{-}Co[B_9H_{12}\text{-}2\text{-}O(CH_2)_4]$ (IV).

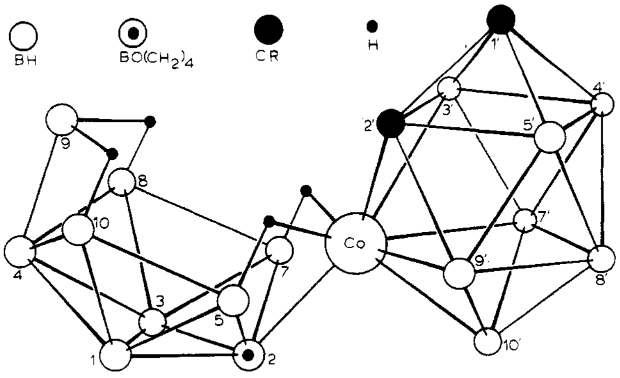

Figure 5. Established structure[7] of $[1,2\text{-}(C_2H_5)_2C_2B_7H_7]\text{-}6\text{-}Co[B_9H_{12}\text{-}2\text{-}O(CH_2)_4]$ (V).

---

(10) Venable, T. L.; Grimes, R. N. *Inorg. Chem.*, in press.

Table III. 360-MHz ^1H FT NMR Data ($CDCl_3$ Solution)[a]

compd	δ[b]	rel area	assignt
I	2.17 q ($J_{H-H} = 8$)	4	CH_2
	1.15 t ($J_{H-H} = 8$)	6	CH_3
	−1.12 br	c	B-H-B
	−5.19 br s	2	B-H-B
	−10.13 br q ($J_{H_b-H_t} = 77$)	2	Co-H-B
II	4.51 m	4	THF
	2.80 m	4	THF
	2.19 m	4	CH_2
	1.35 t ($J_{H-H} = 8$)	6	CH_3
	−2.46 br s	1	B-H-B
	−3.99 br s	1	B-H-B
	−4.15 br s	1	B-H-B
	−15.33 br s	1	Co-H-B
III	4.40 m	4	THF
	2.41 m	4	THF
	2.09 unres s	4	CH_2
	1.26 unres s	6	CH_3
	−2.29 br s	1	B-H-B
	−4.00 br s	2	B-H-B
	−4.87 br s	1	B-H-B
	−5.60 br s	1	B-H-B
	−14.57 br s	1	Co-H-B
IV	4.25 m	4	THF
	2.16 m	4	THF
	2.08 q ($J_{H-H} = 8$)	4	CH_2
	1.03 t ($J_{H-H} = 8$)	6	CH_3
	−3.78 br s	2	B-H-B
	−5.58 br s	2	B-H-B
	−8.70 br q ($J_{H_b-H_t} = 88$)	2	Co-H-B
V	4.31 m	4	THF
	3.04 m	4	THF
	2.07 m	4	CH_2
	1.61 t ($J_{H-H} = 8$)	3	CH_3
	0.41 t ($J_{H-H} = 8$)	3	CH_3
	−5.53 br s	2	B-H-B
	−12.99 br s	2	Co-H-B

[a] ^{11}B coupled. [b] Shifts referenced to $(CH_3)_4Si$; all *J* values in hertz. Key to abbreviations: s, singlet; t, triplet, q, quartet; m, multiplet; br, broad; unres, unresolved. [c] Signal overlapped with several H_t quartets.

Table IV. Infrared Absorptions (cm^{-1})[a,b]

I	2980 s, 2940 s, 2880 m, 2860 s, 2580 s, 1880 w, 1585 w, 1470 m, 1455 m, 1420 w, 1390 m, 1380 m, 1070 sh, 1050 m, 1010 m, 930 m, 910 w, 875 m, 710 m, 690 sh, 630 w
II	2976 s, 2940 s, 2880 m, 2560 s, 1880 w, 1530 sh, 1450 s, 1380 m, 1360 m, 1340 sh, 1190 sh, 1150 w, 1110 w, 1045 s, 1020 sh, 940 s, 915 s, 900 sh, 875 m, 790 m, 670 m
III	2975 s, 2940 s, 2880 m, 2860 m, 2540 s, 1875 m, 1560 sh, 1470 sh, 1460 m, 1450 m, 1380 w, 1370 sh, 1355 w, 1115 sh, 1105 w, 1070 sh, 1045 m, 930 s, 915 s, 890 w, 780 w, 670 w
IV	2980 s, 2940 s, 2935 s, 2880 m, 2870 m, 2570 s, 1875 w, 1580 m, 1460 w, 1380 w, 1360 w, 1260 w, 1050 m, 1015 sh, 1005 m, 960 m, 930 m, 915 m, 825 w, 765 w, 725 m, 715 m, 690 w, 660 w, 625 w
V	2980 s, 2940 s, 2884 s, 2850 sh, 2570 s, 1880 m, 1815 m, 1540 sh, 1455 s, 1430 sh, 1380 m, 1360 m, 1190 sh, 1135 sh, 1115 w, 1065 m, 1050 m, 965 w, 930 sh, 915 s, 875 m, 770 w, 690 w, 660 w

[a] CCl_4 solution vs. CCl_4. [b] Key. s = strong, m = medium, w = weak, sh = shoulder.

quence shown by Scheme I is observed. The yields shown are calculated from carborane employed; the corresponding *C*,*C'*-dimethyl products are obtained from $(CH_3)_2C_2B_4H_5^-$ ion in essentially the same yields. The isolated products I, II, and III, all air stable, were purified via thick-layer and preparative high-pressure column chromatography and characterized from their ^{11}B and ^1H FT NMR spectra obtained at 115.5 and 360 MHz, respectively, and from IR and mass spectra (Tables I–V), as discussed below. In addition, X-ray crystal structure determinations were conducted on II and III.[7] Figures 1–3 present the assigned structures of all three species.

Table V. High-Resolution Mass Measurements

compd	parent ion	mass	
		calcd	obsd
I	$^{59}Co^{12}C_6{}^{11}B_9{}^1H_{24}{}^+$	254.2047	254.2050
II	$^{59}Co^{16}O^{12}C_{10}{}^{11}B_{13}{}^1H_{34}{}^+$	372.3151	372.3157
III	$^{59}Co^{16}O^{12}C_{10}{}^{11}B_{12}{}^1H_{35}{}^+$	362.3136	362.3149
IV	$^{59}Co^{16}O^{12}C_{10}{}^{11}B_{12}{}^1H_{35}{}^+$	362.3136	362.3149
V	$^{59}Co^{16}O^{12}C_{10}{}^{11}B_{16}{}^1H_{37}{}^+$	408.3666	408.3698

Scheme I

$$B_5H_8^- + CoCl_2 \xrightarrow[\text{20 min, −23 °C}]{\text{THF}} [\text{dark green soln}] \xrightarrow[\text{THF, 7 h}]{Et_2C_2B_4H_5^-} [\text{dark brown soln}] \xrightarrow[O_2]{H_2O}$$

$[(C_2H_5)_2C_2B_4H_4]$-2-Co$[B_5H_{10}]$ (I) 6.9%
$[(C_2H_5)_2C_2B_4H_4]$-5-Co$[B_9H_{12}$-1-O$(CH_2)_4]$ (II) 3.6%
$[(C_2H_5)_2C_2B_3H_5]$-5-Co$[B_9H_{12}$-1-O$(CH_4)]$ (III) 1.5%

This reaction also generated a trace of [2,3-$(C_2H_5)_2C_2B_3H_5$]CoH[2,3-$C_2H_5)_2C_2B_4H_4$], analogous to the known complex $[(CH_3)_2C_2B_3H_5]CoH[(CH_3)_2C_2B_4H_4]$,[6b] which was isolated and identified from its NMR spectra.

The yields of products I–III are sensitive to the length of time elapsed between the initial reaction of $B_5H_8^-$ with $CoCl_2$ and the introduction of the carborane anion. When this period is held to 20 min, the yields are as indicated above, but longer intervals result in progressively lower yields for all three species; thus, when the $B_5H_8^-/CoCl_2$ mixture is stirred at −23 °C for 4 h before addition of carborane, the quantities of I–III are reduced by an order of magnitude or more. Temperature is also a significant factor in this system. When the $B_5H_8^-/CoCl_2$ reaction mixture is maintained at −78 °C for 20 min, the yields of I, II, and III increase slightly to 7.3, 4.7, and 1.6%, respectively.

Reaction of $Na^+B_9H_{14}^-$ and $CoCl_2$ Followed by $Na^+R_2C_2B_4H_5^-$ (R = CH_3, C_2H_5). Since the $B_9H_{14}^-$ ion is readily generated from B_5H_9 and NaH at room temperature (with minimal amounts of other borane species present),[9] a sequence (see Scheme II) analogous to that described above was employed with $B_9H_{14}^-$. The major products, IV and V, are species *not* obtained in the $B_5H_8^-$ reaction; however, small quantities of I, II, and III are also obtained. The spectroscopic and other characterization data for IV and V are given in Tables I–V, and a crystal structure analysis of V is reported in the following article.

Scheme II

$$B_9H_{14}^- + CoCl_2 \xrightarrow[\text{30 min, −45 °C}]{\text{THF}} [\text{dark brown soln}] \xrightarrow[\text{THF, 5 h}]{Et_2C_2B_4H_5^-} [\text{black soln}] \xrightarrow[O_2]{H_2O}$$

$[(C_2H_5)_2C_2B_3H_5]$-6-Co$[B_9H_{12}$-2-O$(CH_2)_4]$ (IV) 5.0%
$[(C_2H_5)_2C_2B_7H_7]$-6-Co$[B_9H_{12}$-2-O$(CH_2)_4]$ (V) 1.8%
traces of I, II, and III

Structural Characterization of Products. The proposed geometry of I (Figure 1), the major isolable product of the reaction of $B_5H_8^-$, $(C_2H_5)_2C_2B_4H_5^-$, and $CoCl_2$, is consistent with both the NMR data and the synthetic origin. The ^{11}B and ^1H spectra indicate *local* mirror symmetry in the CoB_5 (cobaltaborane) and CoC_2B_4 (cobaltacarborane) cage systems; as we have previously noted in other mixed-ligand sandwich complexes,[6c] the ligands do not perturb each other's chemical shifts to a detectable extent, and thus the relative orientation of the two ligands is not revealed by NMR evidence alone. However, the "twisted" arrangement in Figure 1 is consistent with the crystallographically determined structures[7] of II, III, and V, all of which lack a molecular mirror plane.

Strong evidence for the proposed structure is given by the presence of ^1H NMR signals corresponding to two equivalent Co–H–B, two equivalent B–H–B, and a unique B–H–B bridge. Moreover, the *nido*-CoB_5H_{10} grouping exhibits ^{11}B and ^1H spectra very similar to those of the established compounds 2-$(CO)_3FeB_5H_9$,[11] 2-$(\eta^5$-$C_5H_5)FeB_5H_{10}$,[12] and 2-$(CO)_3MnB_5H_{10}$,[13] all of these species being structural analogues of hexaborane(10), B_6H_{10}. After assignment of the ^{11}B signals arising from the $B_5H_{10}^-$ ligand (Table II), the remaining 1:1:2 pattern can be attributed to the $(C_2H_5)_2C_2B_4H_4^{2-}$ group, whose spectrum resembles that of the well-characterized $(\eta^5$-$C_5R_5)CoR'_2C_2B_4H_4$ species (R = H, CH_3; R' = H, CH_3, C_2H_5).[14] The presence of only one set of C_2H_5 peaks in the ^1H spectrum indicates apparent equivalence of the two *C*-ethyl units but, as noted above, does not imply *overall* mirror symmetry in the molecule.

Compound I can be viewed as two polyhedra (closo 7-vertex and nido 6-vertex) sharing a common vertex or, equivalently, as a sandwich complex of Co^{3+} with $[\eta^5$-$(C_2H_5)_2C_2B_4H_4]^{2-}$ and $[\eta^3$-$B_5H_{10}]^-$ ligands. The proposed structure represents an interesting illustration of Wade's electron-counting rules,[4] in that it incorporates both $(2n + 4)$-electron (nido) and $(n + 2)$-electron (closo) frameworks.[15]

Compound II is formulated from its mass spectra and NMR data as a THF-substituted derivative of a $[(C_2H_5)_2C_2B_4H_4]Co[B_9H_{13}]^-$ parent species; formal replacement of a terminal $:H^-$ by $:O(CH_2)_4$ generates II as a neutral derivative. The ^1H and ^{11}B patterns are consistent with the presence of a *closo*-CoC_2B_4 cage, as in I, and the ^1H spectrum reveals three B–H–B and one Co–H–B signal (identified from its high-field resonance), placing cobalt in the 5-position of a *nido*-CoB_9 cage. In order to establish the structure and precisely locate the THF substituent group, an X-ray diffraction study was undertaken,[7] which disclosed the cage geometry shown in Figure 2. In this molecule, the 7-vertex $Co(C_2H_5)_2C_2B_4H_4$ unit is identical with that in I, while the 5-CoB_9H_{12}-$O(CH_2)_4$ moiety is structurally analogous to 5-$(\eta^5$-$C_5H_5)CoB_9H_{13}$, which was crystallographically characterized several years ago;[16a] both of these 10-vertex CoB_9 frameworks formally contain 24 $(2n + 4)$ skeletal valence electrons and hence are nido cages, structurally similar to $B_{10}H_{14}$.

The molecule contains no overall symmetry plane, but as in I, the NMR spectra indicate local mirror symmetry in the carborane cage (particularly striking is the apparent equivalence of the two C_2H_5 groups). The ^{11}B NMR assignments in Table II are based, in part, on accumulated data from other CoB_9 and Co_2B_8 cage systems[10,16,17] and trends perceived in the earlier work; the ^{11}B spectrum of $B_{10}H_{14}$ itself[18] is also relevant. As expected,[19] substitution of a THF ligand for a terminal hydrogen produces a substantial shift of the corresponding ^{11}B resonance to lower field.

Viewed as a sandwich complex of Co^{3+}, the ligands in II are $[\eta^5$-$(C_2H_5)_2C_2B_4H_4]^{2-}$ and $[\eta^4$-B_9H_{12}-$O(CH_2)_4]^-$. Further discussion of the structure of II appears in the accompanying article.[7]

The third product, III, is identifiable from its NMR and mass spectra as $[(C_2H_5)_2C_2B_3H_5]$-5-$Co[B_9H_{12}$-$O(CH_2)_4]$ (Figure 3), analogous to II with an $R_2C_2B_3H_5^{2-}$ ligand replacing $R_2C_2B_4H_4^{2-}$; thus the cobaltacarborane cage is a *nido*-CoC_2B_3 (pentagonal-pyramidal) unit. The borane ligand is again $[B_9H_{12}$-1-$O(CH_2)_4]^-$, identical with that in II. These deductions are based on the close similarity in ^{11}B and ^1H NMR spectra of II and III (Tables II and III), and on the fact that base degradation of II produces III by removal of B(7')–H from the former (vide infra). Conclusive proof of this structure is given by an X-ray diffraction analysis whose details are reported in the following paper.[7]

The 360-MHz proton NMR spectrum of III clearly reveals the resonances of all six bridging protons, two of which [H(56') and H(45')] are equivalent, owing to the local mirror plane in the C_2B_3 ring ligand, and are assigned to the area-2 signal at δ −4.00.

The $R_2C_2B_3H_5^{2-}$ ligand in III is isoelectronic with $C_5H_5^-$ and has previously been observed in the crystallographically characterized species 1-$(CO)_3FeC_2B_3H_7$[20] and $[(CH_3)_2C_2B_4H_4]Co[(CH_3)_2C_2B_3H_5]^-$.[21] As in the case of I and II, III can be described either in cluster terms (6- and 10-vertex nido cages linked at a common vertex) or as a sandwich of Co^{3+} with $[\eta^5$-$(C_2H_5)_2C_2B_3H_5]^{2-}$ and $[\eta^4$-B_9H_{12}-$O(CH_2)_4]^-$ ligands.

Product IV, obtained from $B_9H_{14}^-$ ion as described above, is an isomer of III in which the cobalt atom occupies the 6-position in the CoB_9 cage (Figure 4). This produces local mirror symmetry in both the CoB_9 and CoC_2B_3 frameworks and results in considerable simplification of the NMR spectra as compared to those of III. The location of cobalt in the cobaltaborane cage is established by the presence of two equivalent Co–H–B and two equivalent B–H–B bridges, as revealed by NMR. While the THF substituent could be attached to B(2), B(4), or B(9) and still preserve the local mirror symmetry, placement on B(2) is most consistent with the NMR data in comparison with those of the established structures II and III; moreover, attack of THF on MB_9-type metallaborane cages invariably occurs at a boron adjacent to the metal.[22] The proton and boron NMR data on the CoC_2B_3 fragment correlate well with those of the corresponding portion of the established structure, III. Similarly, the signals arising from the 6-CoB_9 cage closely resemble the spectra of known 6-$(\eta^5$-$C_5R_5)CoB_9H_{13}$ species (R = H[23] and CH_3[10]).

Compound V, the other major product of the $B_9H_{14}^-$ reaction, is unique among the compounds obtained in this study, in that the carborane ligand is a C_2B_7 rather than a C_2B_3 or C_2B_4 system. The ^{11}B NMR spectrum exhibits 12 distinct resonances and is too complex for unambiguous interpretation. From the ^1H spectrum one can deduce the presence of two Co–H–B and two B–H–B bridges in equivalent pairs; with the assumption that the cobaltaborane cage is once again a $B_{10}H_{14}$-like CoB_9 system, this places the metal in the 6-position. However, definitive structural assignment of this molecule required an X-ray diffraction study,[7] which established the

---

(11) Shore, S. G.; Ragaini, J. D.; Smith, R. L.; Cottrell, C. E.; Fehlner, T. P. *Inorg. Chem.* **1979**, *18*, 670.

(12) Weiss, R.; Grimes, R. N. *Inorg. Chem.* **1979**, *18*, 3291.

(13) Fischer, M. B.; Gaines, D. F. *Inorg. Chem.* **1979**, *18* 3200.

(14) Grimes, R. N.; Beer, D. C.; Sneddon, L. G.; Miller, V. R.; Weiss, R. *Inorg. Chem.* **1974**, *13*, 1138.

(15) BH and CR units contribute two and three valence electrons, respectively, to the framework, bridging hydrogen atoms contribute one electron, and cobalt contributes a total of three (of its total of nine valence electrons, six are assigned to "nonbonding" orbitals in the usual fashion;[4] the remaining three are available for skeletal bonding). Of the three Co skeletal electrons, assignment of two to the CoC_2B_4 cage and one to the CoB_5 framework produces electron counts of 16 $(2n + 2)$ and 16 $(2n + 4)$, respectively.

(16) (a) Pipal, J. R.; Grimes, R. N. *Inorg. Chem.* **1977**, *16*, 3251. (b) Miller, V. R.; Weiss, R.; Grimes, R. N. *J. Am. Chem. Soc.* **1977**, *99*, 5646.

(17) Venable, T. L.; Sinn, E.; Grimes, R. N. *Inorg. Chem.*, in press.

(18) Clouse, A. O.; Moody, D. C.; Roseberry, T.; Schaeffer, R. *J. Am. Chem. Soc.* **1973**, *95*, 2496.

(19) Eaton, G. R.; Lipscomb, W. N. "NMR Studies of Boron Hydrides and Related Compounds"; W. A. Benjamin: New York, 1969.

(20) Brennan, J. P.; Grimes, R. N.; Schaeffer, R.; Sneddon, L. G. *Inorg. Chem.* **1973**, *12*, 2266.

(21) Pipal, J. R.; Maxwell, W. M.; Grimes, R. N. *Inorg. Chem.* **1978**, *17*, 1447.

(22) (a) Lott, J. W.; Gaines, D. F.; Shenhav, H.; Schaeffer, J. *J. Am. Chem. Soc.* **1973**, *95*, 3042. (b) Lott, J. W., Gaines, D. F. *Inorg. Chem.* **1974**, *13*, 2261.

(23) Zimmerman, G. J.; Hall, L. W.; Sneddon, L. G. *Inorg. Chem.* **1980**, *19*, 3642.

geometry shown in Figure 5. As can be seen, the complex consists of closo 10-vertex CoC_2B_7 and nido 10-vertex CoB_9 cages sharing a common vertex at cobalt. The CoC_2B_7 unit, however, has an abnormally long C(2′)–B(3′) distance [2.192 (9) Å], which suggest a weak bonding interaction; this may reflect electronic influence of the B_9 ligand, as discussed in the accompanying report.[7]

A variety of other *closo*-MC_2B_7 metallacarborane systems has been reported,[3] but in none of these do the carbon atoms occupy the 1,2-vertices as in V. Curiously, even in the complex $[(CH_3)_2C_2B_4H_4]CoH[(CH_3)_2C_2B_7H_7]$, which was obtained in a closely related earlier study of the $CoCl_2/B_5H_8^-/(CH_3)_2C_2B_4H_5^-$ "simultaneous" reaction[6c] (see Introduction), the CoC_2B_7 cage is different from that in V; although X-ray confirmation of the earlier compound is not available, its ^{11}B NMR spectrum lacks a low-field signal corresponding to that at δ 78.8 in V. Furthermore, the ^1H NMR spectrum of the above-mentioned bis(carborane) complex shows that the C–R units in the CoC_2B_7 cage are equivalent, in contrast to those of V.

The ^{11}B and ^1H NMR spectra of V are fully compatible with the X-ray-determined structure; assignment of the individual ^{11}B peaks is not obvious, other than for B(2)–THF (a singlet resonance) and B(10′)–H, which is a low-coordinate BH unit adjacent to cobalt and probably generates the low-field (δ 78.8) signal.

Degradation of II to III. In light of the structures established for products II and III, which differ only by the presence of a "capping" BH group (i.e., B(7′)] in II that is replaced by two bridging hydrogen atoms in III, it appeared likely that III is formed by removal of B(7′)–H from II during workup in aqueous media. Accordingly, treatment of II with acidified aqueous THF was found to give III in 82% yield. Such conversions of *closo*-C_2B_4 to *nido*-C_2B_3 ligands by base attack at the apex boron have been noted elsewhere: $[(CH_3)_2C_2B_4H_4]_2CoH$ is similarly degraded to $[(CH_3)_2C_2B_4H_4]CoH[(CH_3)_2C_2B_3H_5]$,[6b] and $(\eta^5\text{-}C_5H_5)CoR_2C_2B_4H_4$ species are readily converted to $(\eta^5\text{-}C_5H_5)CoR_2C_2B_3H_5$ complexes.[24]

These observations raise the question of the origin of compound IV, which also contains an $R_2C_2B_3H_5^{2-}$ ligand. It can be assumed that this species forms similarly via degradation of the corresponding $R_2C_2B_4H_4^{2-}$ complex, i.e, $[(C_2H_5)_2C_2B_4H_4]\text{-}6\text{-}Co[B_9H_{12}\text{-}2\text{-}O(CH_2)_4]$; however, this latter species has not been observed. It seems a reasonable presumption that this compound is formed in the original reaction of $(C_2H_5)_2C_2B_4H_5^-$, $CoCl_2$, and $B_9H_{14}^-$ in THF and during workup in aqueous THF undergoes complete conversion to product IV, which is subsequently isolated.

Finally, we note that treatment of compounds I and V (both of which also incorporate an $R_2C_2B_nH_n^{2-}$ ligand) with aqueous THF does *not* lead to characterizable compounds, giving only intractable substances.

Reaction of $B_3H_8^-$ with $CoCl_2$ and $R_2C_2B_4H_5^-$. Investigation of the borane/$CoCl_2$/$R_2C_2B_4H_5^-$ reaction system (R = CH_3) with $B_3H_8^-$ as the borane substrate, following the sequence used in the $B_5H_8^-$ reaction, gave compounds II and III together with some $(R_2C_2B_4H_4)_2Co^-$, in very low yields; no I, IV, or V were observed. When BH_4^- was employed as the borane reagent, the only isolable product was the known compound $(2,3\text{-}R_2C_2B_3H_5)CoH(2,3\text{-}R_2C_2B_4H_4)$. These results can be contrasted with earlier observations on the borane/$FeCl_2$/$(CH_3)_2C_2B_4H_5^-$ reactions in which the isolable products and yields were essentially independent of whether $B_5H_8^-$ or $B_3H_8^-$ was employed as the borane reagent.[6c]

Reaction of $[2,3\text{-}(CH_3)_2C_2B_4H_4]_2CoH$ with $B_5H_8^-$. As a control experiment, the carborane anion $(CH_3)_2C_2B_4H_5^-$ was permitted to react first with $CoCl_2$, generating the well-characterized red complex[6b] $[(CH_3)_2C_2B_4H_4]_2CoH$, which was then stirred in THF solution with $B_5H_8^-$, and the products were worked up in aqueous THF in air. No evidence of reaction was observed, other than degradation to $[(CH_3)_2C_2B_4H_4]CoH[(CH_3)_2C_2B_3H_5]$ during workup.

Conclusions

This work affords the first known examples of borane–metal–carborane mixed-ligand complexes or boranometallacarboranes and in the process reveals some useful information which may guide future efforts at synthesizing mixed-ligand species. It is evident that Co^{2+} interacts with $R_2C_2B_4H_5^-$ carborane anions much more rapidly than with $B_5H_8^-$ (a similar conclusion was reached earlier[6c] regarding $FeCl_2$ with the same substrates); hence, a prerequisite for obtaining mixed-ligand products is that the metal–borane reaction be conducted prior to introduction of the carborane reagent. Simultaneous interaction of all three reactants leads only to bis(carborane) metal complexes (though the presence of the borane anion gives rise to larger carborane ligands[6c] such as $R_2C_2B_5H_5^{2-}$ and $R_2C_2B_7H_7^{2-}$). The nature of the metallaboranes generated initially in reactions of metal halides with $B_5H_8^-$ in THF has not been established, although their extreme reactivity and their activity as hydrogenation catalysts have been reported.[25]

Since borane and carborane ligands in monometallaborane and-metallacarborane complexes usually carry a formal 2– charge, bis(ligand) complexes of cobalt(III) would normally be monoanions. In both past and present work in this laboratory, however, we have been fortunate to isolate neutral products generated either by protonation to give such species as $[R_2C_2B_4H_4]_2Co^{III}H$,[6b] or, as in the present study, by substitution of THF for a terminal hydrogen to give electrically neutral molecules that are soluble in organic media and can often be sublimed under vacuum.

The products obtained from $B_5H_8^-$ and from $B_9H_{14}^-$ in this work, viewed together with earlier investigations involving interactions of these ions with $CoCl_2$ and $C_5R_5^-$ (R = H, CH_3),[2d,10,16b] reveal a clear structural pattern, which seems to have mechanistic implications. When the reagent is $B_5H_8^-$, a variety of cobaltaborane products are obtained, often including 10-vertex CoB_9 species; with $B_9H_{14}^-$, the products are invariably *nido*-CoB_9 and/or -Co_2B_8 cage systems. Thus far without exception, *the CoB_9 products obtained from $B_5H_8^-$ have the metal in the 5-position, while in those generated from $B_9H_{14}^-$ the metal occupies the 6-position.* Earlier studies by Gaines et al.,[13,22] on manganaboranes are consistent with these trends. We think it likely, therefore, that the 6-substituted species, which include IV and V in this work and $6\text{-}[\eta^5\text{-}C_5(CH_3)_5]CoB_9H_{13}$,[10] are formed by direct, stereospecific insertion of cobalt into the $B_9H_{14}^-$ ion; the 5-CoB_9 complexes, which include II and III in this study as well as $5\text{-}(\eta^5\text{-}C_5H_5)CoB_9H_{13}$,[16b] evidently are generated by attack of $B_5H_8^-$ on a CoB_4 or CoB_5 species present in the reaction mixture. This suggestion is consistent with the fact that the principal species obtained from $B_5H_8^-$ in the present study is I, a CoB_5 complex.

Finally, compound I merits comment. That the major product of the $B_5H_8^-/CoCl_2/R_2C_2B_4H_5^-$ reaction is a mixed complex incorporating $B_5H_{10}^-$ and $R_2C_2B_4H_4^{2-}$ ligands would perhaps be unremarkable, except for the fact that in no previous study of cobalt–$B_5H_8^-$ interactions[6c,10,16b] has a CoB_5 species been isolated (the vapor-phase reaction of (C_5H_5)-

---

[24] Grimes, R. N.; Beer, D. C.; Sneddon, L. G.; Miller, V. R.; Weiss, R. *Inorg. Chem.* **1974**, *13*, 1138.

[25] (a) Bonny, A.; Beard, W. R.; Misener, C. M.; Kennedy, F. G.; Grimes, R. N. "Abstracts of Papers", 180th National Meeting of the American Chemical Society, Las Vegas, NV, Aug 1980; American Chemical Society: Washington, D.C., 1980; INOR 252. (b) Grimes, R. N. *Pure Appl. Chem.* **1982**, *54*, 43.

$Co(CO)_2$ with B_5H_9 does, however, give $1\text{-}(C_5H_5)CoB_5H_9$[26]). In reactions of $B_5H_8^-$ with $CoCl_2$ and $C_5H_5^-$ or $C_5(CH_3)_5^-$, for example,[10,16b] the major products obtained are $2\text{-}(C_5R_5)CoB_4H_8$ (R = H, CH_3), which are presumed to have formed from an unstable $(C_5R_5)CoB_5H_x$ precursor, but no such intermediate has been found. Thus, the isolation of I as a stable product suggests that the $R_2C_2B_4H_5^-$ carborane anion intercepts and stabilizes a CoB_5 intermediate species (perhaps dislodging one B_5H_x ligand from a bis(ligand) cobaltaborane formed in the $CoCl_2/B_5H_8^-$ reaction). Two inherent properties of $R_2C_2B_4H_5^-$ are of value here: the presence of an acidic bridging proton that is readily transferable to other ligands in a metal sandwich complex, and the capacity of the dinegative $R_2C_2B_4H_4^{2-}$ pyramidal ligand to bind strongly to metal ions via its C_2B_3 face. Both properties of the $R_2C_2B_4H_5^-$ anions are currently being exploited in our laboratory as a tool in the synthesis of new arene hydrocarbon ligands and metal–arene sandwich complexes.[27]

Experimental Section

Materials. 2,3-Dimethyl-2,3-dicarbahexaborane(8), $2,3\text{-}(CH_3)_2C_2B_4H_6$, was prepared from B_5H_9, $(CH_3)_2C_2$, and $(CH_3CH_2)_3N$ as described elsewhere.[8] 2,3-Diethyl-2,3-dicarbahexaborane(8), $2,3\text{-}(C_2H_5)_2C_2B_4H_6$, was similarly prepared from B_5H_9, $(CH_3CH_2)_2C_2$, and $(CH_3CH_2)_3N$. Triethylamine was freed of primary and secondary amine impurities first by reflux and then by distillation from phthalic anhydride and then dried by distillation from BaO under a nitrogen atmosphere. 2-Butyne and 3-hexyne were purified by twice stirring over metallic sodium and distillation under nitrogen. Pentaborane(9), B_5H_9, (U.S. Government stockpile), was utilized as received after assay by infrared spectroscopy. $(CH_3)_4NB_3H_8$ was prepared from $NaBH_4$ and I_2 as described elsewhere.[28] $CoCl_2$ was dried at high temperature in vacuo, and tetrahydrofruan (THF) was rigorously dried over $LiAlH_4$ prior to use. NaH (Alfa, 50% in mineral oil) was washed twice with pentane prior to use. All other chemicals were reagent grade and were used as received. Column chromatography utilized silica gel 60 (Merck), and thin- and preparative-layer chromatography (TLC and PLC, respectively) were conducted on precoated plates of silica gel F-254 (Brinkman Instruments, Inc.).

Instrumentation. ^{11}B (115.5 MHz) and ^1H (360 MHz) pulse Fourier transform NMR spectra were recorded on a Nicolet NT-360 spectrometer equipped with a 118OE/293B data processor. Broadband heteronuclear decoupling of ^1H was employed in recording the ^{11}B spectra, but the ^1H spectra were obtained without ^{11}B decoupling. Unit resolution mass spectra (EI) were obtained on a Hitachi Perkin-Elmer RMU-6E mass spectrometer at 70 eV. High-resolution mass measurements[29] (EI) were conducted on a VG Micromass 70/70 HS mass spectrometer at 70 eV, with a source temperature of 230 °C. Peak matching vs. perfluorokerosene as an internal reference was employed. Infrared spectra were recorded on a Beckman IR-8 instrument. Preparative-scale high-pressure liquid chromatography (HPLC) was performed on a Prep-500 LC (Waters Associates), with use of a refractive index detector and a PrePAK 500/silica gel cartridge. Melting ranges were determined on a Thomas-Hoover Unimelt capillary melting point apparatus (Thomas Co.) or a Fisher-Jones melting point apparatus (Fisher Scientific Co.).

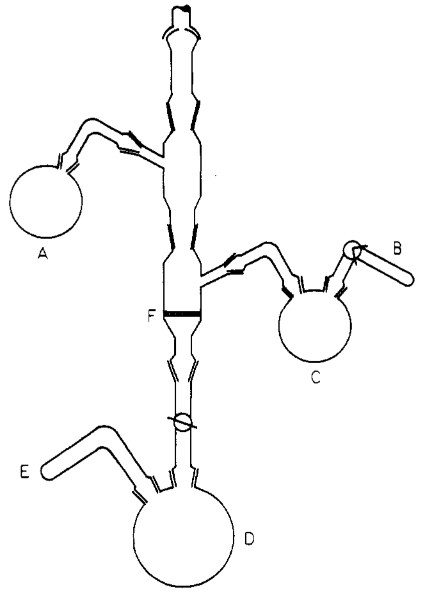

Figure 6. Apparatus for reaction of $Na^+R_2C_2B_4H_5^-$ (R = CH_3 or C_2H_5), Na^+ $B_5H_8^-$, and $CoCl_2$: A, 100-mL round-bottom flask; B, 1 × 16.5 cm storage tube fitted with a Teflon stopcock; C, 100-mL round-bottom flask; D, 250-mL two-neck round-bottom flask; E, 1.5 × 8 cm tube; F, coarse frit.

Reaction of $B_5H_8^-$ and $CoCl_2$ Followed by $(C_2H_5)_2C_2B_4H_5^-$. Into storage tube B (Figure 6) was placed 1.235 g of $2,3\text{-}(CH_3CH_2)_2C_2B_4H_6$ (9.40 mmol), which was degassed andd evacuated. The tip-in side-arm flasks were charged with 1.0222 g of NaH (42.6 mmol) and 0.5736 g of NaH (23.9 mmol) in flasks A and C, respectively. A tip-in side-arm tube (E) was charged with 1.2238 g of anhydrous $CoCl_2$ (9.43 mmol). The apparatus was assembled as in Figure 6 and evaucated. Flask A was cooled to −196 °C, and 1.187 g of B_5H_9 (18.8 mmol) with about 35 mL of dry THF were condensed in vacuo into it. The flask was warmed enough to liquefy the contents and was quickly immersed in a −30 °C bath. Hydrogen gas was evolved over the course of 1.5 h. The flask was cooled to −196 °C and the H_2 pumped away, after which the contents of flask A were warmed to liquefaction and quickly filtered into flask D, kept at −78 °C. Stirring was begun at −78 °C, and the $CoCl_2$ in tube E was tipped into flask D. The solution became blue immediately and after 2 min became green-brown; essentially no gas was evolved. Flask D was cooled to and maintained at −196 °C. Flask C was then cooled to −196 °C, the contents of tube B were tipped in, and about 35 mL of dry THF was therein condensed in vacuo. The flask was warmed to room temperature, and the contents evolved H_2 gas. When effervescence ceased (after 1 h), the flask was cooled to −196 °C, the H_2 pumped away, and the flask rewarmed to liquefy its contents. The $(C_2H_5)_2C_2B_4H_5^-$ solution was filtered in vacuo into flask D, which was then warmed to liquefaction. A −78 °C bath was then placed arund the reaction flask, and the reaction resumed. The reaction mixture rapidly became black-brown and remained that color for the ensuing 7 h. Partial solvent removal was begun in vacuo, and after 1.5 h a thick brown slurry remained in flask D. The reaction flask was filled with N_2 and removed from the rest of the apparatus. Its contents were exposed to the air, and to it was added 75 mL of a 2:1 mixture of H_2O and THF; the mixture was stirred in the air for 30 min, which produced some effervescence and gave a dark brown suspension. This mixture was extracted with three 50-mL aliquots of a 1:1 CH_2Cl_2/hexane mixture to yield a brown organic phase and a dark pink aqueous phase. The solvent of the organic layer was removed on a rotary evaporator, and the residue remaining was dissolved in a small amount of 10% CH_2Cl_2 in hexane. This solution was loaded onto a 4.5 × 14 cm silica gel column packed in hexane and was eluted with 100-mL portions of 0%, 10%, 25%, 50%, and 100% CH_2Cl_2 in hexane. A red-orange band was eluted in 10–50% CH_2Cl_2/hexane and further purified by PLC in 1:1 CH_2Cl_2/hexane, giving primarily I (161.9 mg, 6.9% yield). A brown band was eluted in 50–100% CH_2Cl_2/hexane. This solution was rotary evaporated to dryness and separated by PLC in 1:1 CH_2Cl_2/hexane. This gave primarily orange III (51.2 mg, 1.5% yield) and brown II (125.6 mg, 3.6%).

Reaction of $B_9H_{14}^-$ and $CoCl_2$ Followed by $(C_2H_5)_2C_2B_4H_5^-$. Storage tube B (Figure 6) was charged with 1.111 g of $2,3\text{-}(CH_3CH_2)_2C_2B_4H_6$ (8.45 mmol), degassed, and evacuated. The tip-in side-arm flasks A and C were charged with 0.2268 g of NaH (9.45 mmol) and 0.4709 g of NaH (19.6 mmol), respectively. Side-arm tube E was charged with 1.1018 g of anhydrous $CoCl_2$ (8.49 mmol). The apparatus was assembled as in Figure 6 and evacuated. Flask A was cooled to −196 °C, and 1.187 g of B_5H_9 (18.8 mmol) and about 35 mL of dry THF were condensed in vacuo into it. The flask was warmed to ambient temperature and allowed to react for 12 h, during which H_2 was evolved and the solution became yellow with an off-white flocculent

---

(26) Wilczynski, R.; Sneddon, L. G. *Inorg. Chem.* **1979**, *18*, 864.

(27) Maynard, R. B.; Grimes, R. N., "Abstracts of Papers", 182nd National Meeting of the American Chemical Society, New York, NY, Aug 1981; American Chemical Society: Washington, D.C., 1981; INOR 11.

(28) Nainan, K. C.; Ryschkewitsch, G. E. *Inorg. Nucl. Chem. Lett.* **1970**, *6*, 765.

(29) Harvey Analytical Laboratories, Charlottesville, VA.

material in suspension. The flask was cooled to −196 °C and the H_2 pumped away, after which it was warmed to 24 °C and the $B_9H_{14}^-$ solution filtered into flask D, maintained at −78 °C. An additional 15 mL of dry THF was condensed into flask A to rinse the insoluble material, and this washing was also filtered into flask D. Stirring was begun at −78 °C, but much of the solid remained undissolved; consequently, the temperature was raised to −45 °C, which caused all of the solid material to dissolve. The $CoCl_2$ was tipped in, and a blue solution immediately formed. The solution, which turned light brown after 5 min, after 30 min was dark brown. The reaction flask was cooled to −196 °C and maintained at that temperature. Flask C was then cooled to −196 °C, the contents of tube B were tipped in, and into it about 35 mL of dry THF was condensed in vacuo. The flask was warmed to room temperature, and the contents evolved H_2. After about 1 h, effervescence ceased, and the flask was cooled to −196 °C. The H_2 was pumpted off, the flask rewarmed to liquefaction, and the 2,3-$(CH_3CH_2)_2C_2B_4H_5^-$ solution filtered into flask D. The reaction flask was warmed to liquefaction and immersed in a −45 °C bath, resulting in a black-brown solution. Stirring was resumed and continued for 5 h, at which point partial removal of the solvent was begun in vacuo. A thick brown slurry remained in the flask after 1.5 h. The reaction system was filled with N_2, the reaction flask (D) was separated from the remainder of the apparatus, and its contents were exposed to the air. Into it was placed 75 mL of a 2:1 mixture of H_2O and THF, and the resulting mixture was stirred in air for 30 min with slight bubbling, producing a dark brown suspension. This mixture was extracted three times with 50-mL portions of a 1:1 CH_2Cl_2/hexane mixture to yield a brown organic phase and a dark pink aqueous phase. The organic phase was placed on a rotary evaporator and the solvent removed. The residues remaining were dissolved in a small amount of 10% CH_2Cl_2 in hexane. This solution was placed atop a 4.5 × 14 cm silica gel column packed in hexane and eluted with 250 mL of hexane, 300 mL of 10% $CHCl_2$ in hexane, 300 mL of 50% CH_2Cl_2 in hexane, and 200 mL of CH_2Cl_2. An organge band was eluted in 10% CH_2Cl_2 in hexane and purified via TLC in 1:1 CH_2Cl_2/hexane, producing orange I (8 mg, 0.4% yield). A brown band was eluted in 50–100% CH_2Cl_2 in hexane, rotary evaporated to dryness, and separated by PLC in 1:1 CH_2Cl_2/hexane, giving primarily orange III (4 mg, 0.1% yield), burgundy IV (153 mg, 5.0%), black-brown V (41 mg, 1.8%), and brown II (6 mg, 0.2%).

Reaction of 2,3-$(CH_3)_2C_2B_4H_5^-$, $(CH_3)_4N^+B_3H_8^-$, and $CoCl_2$. A tipping storage tube was charged with 0.871 g of 2,3-$(CH_3)_2C_2B_4H_6$ (7.81 mmol) and degassed. A tip-in side-arm flask was charged with 0.4641 g of NaH (19.3 mmol), and another tip-in side-arm tube was filled with 1.0143 g of anhydrous $CoCl_2$ (7.81 mmol). The reaction flask was charged with 2.686 g of $(CH_3)_4N^+B_3H_8^-$ (23.4 mmol). The apparatus was assembled and evacuated. About 40 mL of dry THF was condensed in vacuo into the reactor, warmed to liquefaction, and immersed in a −23 °C bath, and stirring began. The solid salt would not completely dissolve, and hence the temperature was raised to 24 °C, which effected solution. The $CoCl_2$ was tipped into the reactor, and the solution became blue immediately but gradually became green and evolved H_2 gas; after 45 min the solution had become very dark green. The flask was then cooled to −196 °C and kept at that temperature. The NaH and carborane were combined at −196 °C, and 35 mL dry THF was condensed in vacuo. The flask was warmed to room temperature, and H_2 evolution ensued. When effervescence had ceased (after 1 h), the flask was cooled to −196 °C and then H_2 removed. The flask was warmed to liquefy the contents, and the $(CH_3)_2C_2B_4H_5^-$ solution was filtered into the reaction vessel. The reaction flask was warmed to −23 °C, and stirring was resumed at that temperature for 3 h, at which point the solution was greenish brown-black. The solvent was partially removed in vacuo, with a thick brown slurry remaining after 1 h. The flask was flooded with N_2, and its contents were exposed to the air; to the flask was added 25 mL of THF, and then slowly and carefully 50 mL of H_2O was introduced. The mixture exhibited much effervescence upon the initial additions of H_2O, but gas evolution decreased after addition of the first 10 mL. Stirring this mixture for 20 min in the air gave a chocolate brown suspension, which was extracted with two 50-mL aliquots of a 1:1 CH_2/hexane mixture. The resulting brown organic phase was rotary evaporated to dryness, and the solids remaining were dissolved in a small amount of 1:1 CH_2Cl_2/hexane. The solution was placed atop a 4.5 × 14 cm silica gel column packed in hexane. The column was eluted with 175 mL of hexane, 175 mL of 20%, 175 mL of 60%, and 200 mL of 100% CH_2Cl_2 in hexane, and finally 200 mL of acetone. A yellow band was eluted in 20% CH_2Cl_2 in hexane and purified by TLC in 1:1 CH_2Cl_2/hexane to give yellow VI (12 mg). A brown band was eluted in 60–100% CH_2Cl_2 in hexane, and this solution was separated via TLC in 1:1 CH_2Cl_2/hexane, giving primarily orange III (2 mg) and brown II (4 mg). The acetone eluted an orange band, which was rotary evaporated to dryness. The resulting crystalline material was recrystallized by slow evaporation of 10% acetone in CH_2Cl_2 and was shown to be $(CH_3)_4N^+$ (2,3-$(CH_3)_2C_2B_4H_4)_2Co^-$ (32 mg).

Reaction of I with THF/Acidified Ethyl Acetate. A 95.3-mg sample of I (0.378 mmol) was dissolved in 5 mL of acidified ethyl acetate (prepared by shaking 25 mL of ethyl acetate with 5 mL of concentrated aqueous HCl and pipetting off the ethyl acetate layer), to give an orange solution. After about 15 min, no color change was observed. A 5-mL aliquot of THF was added to the solution. After another 10 min, the solvent was removed on a rotary evaporator, leaving a brown solid that was insoluble in hexane, CH_2Cl_2, and acetone and was not further investigated.

Reaction of II with THF/Acidified Ethyl Acetate. A 11.6-mg quantity of II (31.6 μmol) was dissolved in 5 mL of acidified ethyl acetate (prepared as above), to give a brown solution. After 15 min of stirring in the air, no color change was observed. To this stirring solution was added 5 mL of THF. After an additional 10 min of stirring, the solvent was removed on a rotary evaporator, and the brown residue was separated by TLC in 1:1 CH_2Cl_2/hexane to give orange III (3.1 mg, 82% yield based on starting material consumed) and unreacted II (7.7 mg).

Reaction of V with THF/Acidified Ethyl Acetate. A 25.2-mg quantity of V (62.2 μmol) was dissolved in 5 mL of acidified ethyl acetate (prepared as above), to give a brown solution. After 10 min of stirring, a black precipitate had formed. To this was added 5 mL of THF, causing the formation of additional black precipitate. After an additional 10 min of reaction, the solvent was removed by rotary evaporation. The solid residue was not appreciably soluble in hexane, CH_2Cl_2, or acetone.

Acknowledgment. This work was supported by the Office of Naval Research. We thank T. L. Venable for recording the high-resolution NMR spectra. The 360-MHz cryogenic NMR spectrometer utilized in this work was obtained by the Department of Chemistry with partial support from a major instrument grant by the National Science Foundation.

Registry No. I, 80583-51-3; II, 80583-52-4; III, 80593-35-7; IV, 80643-03-4; V, 80612-07-3; VI, 80593-36-8; $(CH_3)_4N^+$(2,3-$(CH_3)_2C_2B_4H_4)_2Co^-$, 80583-54-6; 2,3-$(CH_3CH_2)_2C_2B_4H_6$, 80583-48-8; B_5H_9, 19624-22-7; 2,3-$(CH_3)_2C_2B_4H_6$, 20741-68-8; $(CH_3)_4N^+B_3H_8^-$, 12386-10-6.