NMR spectra of *cis*-bis(phosphine) complexes.[39,40] Certainly the effect of $^2J_{PP'}$ is seen in both types of spectra and when properly recognized leads to no real interpretation problems. Admittedly, ^1H spectra of $X_nAA'X'_n$ systems do lead to more complex spectra than ^{13}C spectra which are of an AXX′ type, but the two types of spectra are complementary.

Registry No. (2,2-dm-1,3-dppp), 80326-98-3; (2,2-dm-1,3-dpap), 80326-99-4; $Mo(CO)_4$(2,2-dm-1,3-dppp), 80327-49-7; $Mo(CO)_4$-(2,2-dm-1,3-dpap), 80327-48-6; $W(CO)_4$(2,2-dm-1,3-dppp), 80327-47-5; $W(CO)_4$(2,2-dm-1,3-dpap), 80327-46-4; $Mn(CH_3CO)(CO)_3$-(2,2-dm-1,3-dppp), 80327-65-7; $Mn(CH_3CO)(CO)_3$(2,2-dm-1,3-dpap), 80327-64-6; $Mn(CH_3)(CO)_3$(2,2-dm-1,3-dppp), 80327-63-5; $Mn(CH_3)(CO)_3$(2,2-dm-1,3-dpap), 80327-62-4; $MnCl(CO)_3$(2,2-dm-1,3-dppp), 80327-61-3; $MnCl(CO)_3$(2,2-dm-1,3-dpap), 80327-60-2; $MnBr(CO)_3$(2,2-dm-1,3-dppp), 80327-59-9; $MnBr(CO)_3$(2,2-dm-1,3-dpap), 80327-58-8; $MnI(CO)_3$(2,2-dm-1,3-dppp), 80327-57-7; $MnI(CO)_3$(2,2-dm-1,3-dpap), 80327-56-6; $Fe(CO)_3$(2,2-dm-1,3-dppp), 80327-55-5.

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

(Pentamethylcyclopentadienyl)cobaltaboranes Derived from the $B_5H_8^-$ and $B_9H_{14}^-$ Ions: Studies in Synthesis and Structure[1]

T. LEON VENABLE and RUSSELL N. GRIMES*

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The reactions of $B_5H_8^-$ and $B_9H_{14}^-$ ions (both generated from B_5H_9 and NaH in THF solution under different conditions) with $CoCl_2$ and $Li^+[C_5(CH_3)_5]^-$ in THF were examined. The two reaction systems generate entirely different cobaltaborane products, which were isolated as air-stable, colored crystalline solids and characterized by ^{11}B and ^1H FT NMR spectroscopy at 115.5 and 360 MHz, respectively, by unit- and high-resolution mass spectrometry and infrared spectra, and (in five cases) by X-ray diffraction studies which are reported in the following two papers. From the $B_9H_{14}^-$ reaction four products were characterized, all of which are 10-vertex CoB_9 or Co_2B_8 nido cages analogous to $B_{10}H_{14}$; the major species, 6-$[C_5(CH_3)_5]CoB_9H_{13}$, was obtained in 25% yield. Minor products were 6,9-$[C_5(CH_3)_5]_2Co_2B_8H_{12}$, 5,7-$[(C_5(CH_3)_5]_2Co_2B_8H_{12}$, and the 6-chloro derivative of the latter compound. The $B_5H_8^-$ reaction generates a larger and structurally more diverse series of products, none in greater than 5% yield. The major products obtained after a 2-h reaction period at room temperature are 2-$[C_5(CH_3)_5]CoB_4H_8$, 1,2-$[C_5(CH_3)_5]_2Co_2B_4H_6$, and 1,2,3-$[C_5(CH_3)_5]_3Co_3B_4H_4$, all of which are analogous to cyclopentadienyl complexes obtained in the reaction of $B_5H_8^-$ with $CoCl_2$ and $C_5H_5^-$ reported earlier. Minor products, which do *not* have known C_5H_5 counterparts, consist of 1,2-$[C_5(CH_3)_5]_2Co_2B_5H_7$, $[C_5(CH_3)_5]_2Co_2B_5H_9$, and 5,9-$[C_5(CH_3)_5]_2Co_2B_8H_{12}$. The structures deduced for these species are, respectively, pentagonal bipyramidal (closo), nido, and nido; the last species is isomeric with the Co_2B_8 complexes obtained from $B_9H_{14}^-$. Thermal rearrangement of 2-$[C_5(CH_3)_5]CoB_4H_8$, a nido cage analogous to B_5H_9, gave the 1-isomer. Thermolysis of 1,2-$[C_5(CH_3)_5]_2Co_2B_5H_7$ resulted in loss of hydrogen to give $[C_5(CH_3)_5]_2Co_2B_5H_5$, a 2*n*-electron cage system that has been assigned a capped-octahedral geometry.

Interactions of transition-metal cations with the $B_5H_8^-$ anion have proved to be a remarkably fertile source of metallaborane clusters. In earlier work,[2] the reaction of $CoCl_2$, NaB_5H_8, and NaC_5H_5 in cold tetrahydrofuran (THF) was found to give, following workup in air, a series of crystalline, air-stable, structurally interesting cobaltaboranes of general formula $[(C_5H_5)Co]_n(BH)_mH_p$ where $1 \leq n \leq 4$. This reaction generated the first known examples of *closo*-metallaboranes (exclusive of metallacarboranes), of electron-hyperdeficient (hypercloso) metallaboranes, of tetrametallic boron clusters, and of partial incorporation of a cyclopentadienyl ring into a boron cage. In addition, two of the products $[(C_5H_5)_2Co_2B_4H_6$ and $(C_5H_5)_3Co_3B_3H_5]$ were shown to have face-bridging hydrogen atoms associated with the metals,[2,3] a feature not previously established in boron chemistry although it had been postulated in certain metallacarboranes from NMR data. In all of these cases, molecular structures of key compounds have been established by X-ray crystallography,[3-7] and the results in general are in agreement with the Wade electron-counting rules for clusters[8] (an exception, however, is $(C_5H_5)_4Co_4B_4H_4$[6]).

These findings on the $CoCl_2/B_5H_8^-/C_5H_5^-$ reaction system pointed to several lines of further study, including (1) interactions of other metal cations with $B_5H_8^-$ and $C_5H_5^-$, (2) reactions of metal cations with $B_5H_8^-$ in the *absence* of $C_5H_5^-$ or other ligands, and (3) reactions in which another coordinating ligand is employed in place of $C_5H_5^-$. With respect to (1), we have reported that $FeCl_2$[9] and $NiBr_2$[10] in the presence of $B_5H_8^-$ and $C_5H_5^-$ generate isolable metallaboranes that differ markedly in composition and structure from those obtained with $CoCl_2$ and from each other. Studies relating to the second point are in progress; complexes formed from $B_5H_8^-$ and metal halides of iron, cobalt, nickel, ruthenium, and rhodium are ionic and difficult to characterize, but THF solutions containing these species exhibit significant catalytic activity in the homogeneous hydrogenation of alkynes and alkenes under mild conditions.[11]

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The work described in this paper was designed to address point 3, via the reaction of $CoCl_2$, $B_5H_8^-$, and $C_5(CH_3)_5^-$ (pentamethylcyclopentadienide) ion. In contrast to $C_5H_5^-$, a highly reactive species that not only serves as a capping ligand for cage metal atoms but clearly has other functions as well (for example, substitution on the cage and even incorporation into it),[2a] $C_5(CH_3)_5^-$ must be essentially restricted to a metal-capping role. Moreover, $C_5(CH_3)_5^-$ is less reactive than $C_5H_5^-$ (failing, for example, to give decamethylcobaltocene under our reaction conditions). It has also been shown to stabilize complexes whose C_5H_5-containing counterparts are unstable or nonexistent;[12,13] in boron chemistry, the synthesis[14] of $[\eta^5\text{-}C_5(CH_3)_5]_2Co_3(CH_3)_4C_4B_8H_7$ is a case in point. Hence we anticipated that use of the $C_5(CH_3)_5^-$ ion would minimize side reactions and polymer formation[15,16] and accordingly increase the yield of isolable metallaboranes. Further, the bulkiness of this ligand seemed likely to favor products having nonvicinal $(\eta^5\text{-}C_5R_5)$–metal groups in the cage, contrary to the tendency toward Co–Co bond formation which is evident in the $CoCl_2/B_5H_8^-/C_5H_5^-$ reaction.

For these reasons, replacement of $C_5H_5^-$ by $C_5(CH_3)_5^-$ was expected to have significant stereochemical consequences and prompted the present investigation. In the course of this work, an unexpected complication arose: we found that our solutions of "$B_5H_8^-$" ion, generated from the reaction of B_5H_9 with NaH, contained high concentrations of $B_9H_{14}^-$ unless special precautions were taken to minimize the latter species; investigation disclosed that the formation of $B_9H_{14}^-$ from B_5H_9 is even more facile than had been indicated in earlier reports.[17,18] Hence our study was broadened to include reactions involving $B_9H_{14}^-$ as well as $B_5H_8^-$, with major consequences in terms of synthetic and structural findings.

This article describes the synthesis and spectroscopic characterization of a variety of (pentamethylcyclopentadienyl)cobaltaboranes, some of which are analogous to known C_5H_5-containing species while others are new cage systems; X-ray crystallographic studies on five of these complexes are reported in the two following papers.

Results and Discussion

Generation of the $B_5H_8^-$ and $B_9H_{14}^-$ Anions from B_5H_9. Pentaborane(9) is easily bridge-deprotonated by sodium hydride or other nucleophiles in THF to produce the $B_5H_8^-$ anion,[19] but other species, including $B_9H_{14}^-$, are also formed.[17,18] In the early stages of this work we proceeded on the assumption that the formation of $B_9H_{14}^-$ would be minimal provided low temperatures (−20 °C or below), short reaction periods, and the presence of excess NaH were maintained. However, the cobaltaborane products obtained on reaction of the presumed $B_5H_8^-$ solution with $CoCl_2$ and $Li^+[C_5(CH_3)_5]^-$ were primarily 10-vertex $[C_5(CH_3)_5]CoB_9H_{13}$ and $[C_5(CH_3)_5]_2Co_2B_8H_{12}$ species (vide infra), leading us to suspect that these complexes actually originated from metal attack on $B_9H_{14}^-$ rather than $B_5H_8^-$. This indeed proved to be the case, and the species produced from $B_9H_{14}^-$ can in general be clearly distinguished from those originating from $B_5H_8^-$.

Table I. Cobaltaborane Products

compd	color	mp, °C	R_f[a]
Complexes Obtained from $B_9H_{14}^-$			
$6\text{-}[C_5(CH_3)_5]CoB_9H_{13}$ (I)	burgundy	250 dec	0.32
$6,9\text{-}[C_5(CH_3)_5]_2Co_2B_8H_{12}$ (II)	green	175 dec	0.06
$5,7\text{-}[C_5(CH_3)_5]_2Co_2B_8H_{12}$ (III)	olive brown	229 dec	0.24
$6\text{-Cl-}5,7\text{-}[C_5(CH_3)_5]_2Co_2B_8H_{11}$ (IV)	olive brown	220 dec	0.33
Complexes Obtained from $B_5H_8^-$			
$2\text{-}[C_5(CH_3)_5]CoB_4H_8$ (V)	red-orange	92–94	0.51
$1,2\text{-}[C_5(CH_3)_5]_2Co_2B_4H_6$ (VI)	violet	72–74	0.32
$1,2,3\text{-}[C_5(CH_3)_5]_3Co_3B_4H_4$ (VII)	yellow	230 dec	0.32[b]
$1,2\text{-}[C_5(CH_3)_5]_2Co_2B_5H_7$ (VIII)	burgundy	160 dec	0.07[b]
$[C_5(CH_3)_5]_2Co_2B_5H_9$ (IX)	violet	205 dec	0.27[b]
$5,9\text{-}[C_5(CH_3)_5]_2Co_2B_8H_{12}$ (X)	light brown	190 dec	0.11[b]
Complexes Obtained by Thermolysis			
$1\text{-}[C_5(CH_3)_5]CoB_4H_8$ (XI)	pale yellow	117	*c*
$1,2\text{-}[C_5(CH_3)_5]_2Co_2B_5H_5$ (XII)	red-yellow	118	0.30[b]

[a] Chromatography on silica gel-60 TLC plates in 1:1 CH_2Cl_2/hexanes. [b] Eluted with 1:1 CH_2Cl_2/hexane. [c] Follows solvent front.

Formation of $B_9H_{14}^-$ from B_5H_9 and NaH in THF is rapid when the $NaH:B_5H_9$ mole ratio is less than 1:1; even at a 1.15:1 ratio, after 90 min the concentration of $B_9H_{14}^-$ is ~28% compared to 45% $B_5H_8^-$ as determined from ^{11}B NMR experiments. For the minimization of the production of $B_9H_{14}^-$, a large excess of NaH over B_5H_9 (at least 2- to 3-fold) is required, and the solution temperature is maintained at −30 °C or below. Under these conditions the concentration of $B_5H_8^-$, as measured by NMR, exceeds 90% while that of $B_9H_{14}^-$ is less than 8%. To *maximize* $B_9H_{14}^-$ formation, one has only to use excess B_5H_9 and conduct the reaction with NaH at room temperature for several hours; as previously reported,[18] this affords $B_9H_{14}^-$ in over 90% yield.

Reaction of $B_9H_{14}^-$ with $CoCl_2$ and $[C_5(CH_3)_5]^-$. Addition of $CoCl_2$ to a solution of $Li^+[C_5(CH_3)_5]^-$ in THF, followed by the introduction of a THF solution of $Na^+B_9H_{14}^-$ at −76 °C, produced no color change; on warming to room temperature, however, the solution became greenish brown. Following removal of solvent in vacuo, extraction of the residue with dichloromethane–hexane mixtures, and separation by preparative thick-layer chromatography on silica, several air-stable, diamagnetic, crystalline products were isolated and characterized (yields shown are based on B_5H_9 employed):

$$\begin{aligned} &CoCl_2 + C_5(CH_3)_5^- + B_9H_{14}^- \xrightarrow{\text{THF}} \\ &\quad \underset{\text{I}}{6\text{-}[C_5(CH_3)_5]CoB_9H_{13}}\ (25\%) + \\ &\quad \underset{\text{II}}{6,9\text{-}[C_5(CH_3)_5]_2Co_2B_8H_{12}}\ (<1\%) + \\ &\quad \underset{\text{III}}{5,7\text{-}[C_5(CH_3)_5]_2Co_2B_8H_{12}}\ (<1\%) + \\ &\quad \underset{\text{IV}}{6\text{-Cl-}5,7\text{-}[C_5(CH_3)_5]_2Co_2B_8H_{11}}\ (2\%) \end{aligned}$$

These compounds were structurally characterized from their ^{11}B and ^1H FT NMR spectra at 115.5 and 360 MHz, respectively, from their unit- or high-resolution mass spectra and IR spectra, and from single-crystal X-ray diffraction analyses on all four compounds.[20] Relevant characterization data are presented in Tables I–IV and in the Experimental Section.

Structures and NMR Spectra of CoB_9 and Co_2B_8 Complexes. Products I–IV are all 10-vertex, 24-electron ($2n + 4$) nido cage systems, based on the well-known electron-counting scheme[8] which assigns two electrons from each BH and $Co(C_5R_5)$ unit

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

compd	δ (J, Hz)[a]	rel area
6-$[C_5(CH_3)_5]CoB_9H_{13}$ (I)	20.5 (107), 15.4 (136), 5.2 (143), −1.2 (143), −12.4 (139), −29.8 (148)	2, 2, 1, 2, 1, 1
6,9-$[C_5(CH_3)_5]_2Co_2B_8H_{12}$ (II)	20.8 (116), 2.3 (134)	6, 2
5,7-$[C_5(CH_3)_5]_2Co_2B_8H_{12}$ (III)	57.3,[b] 24.4 (109), 6.0,[b] −7.4 (~105), −40.3 (139)	1, 3, 2, 1, 1
6-Cl-5,7-$[C_5(CH_3)_5]_2Co_2B_8H_{11}$ (IV)	49.9,[c] 23.1 (124), 19.4 (94), 7.1,[b] −7.1,[b] −40.7 (141)	1, 2, 1, 2, 1, 1
2-$[C_5(CH_3)_5]CoB_4H_8$ (V)	2.7 (137), −13.6 (135)	1, 3
1,2-$[C_5(CH_3)_5]_2Co_2B_4H_6$ (VI)	63.8 (140), [B(4,6)], 17.4 (127) [B(3,5)]	2, 2
1,2,3-$[C_5(CH_3)_5]_3Co_3B_4H_4$ (VII)	154.1[b] [B(7)], 91.0 (140) [B(4,5,6)]	1, 3
1,2-$[C_5(CH_3)_5]_2Co_2B_5H_7$ (VIII)	31.5 (102) [B(4,5)],[d] 26.3 (89) [B(3,6)],[d] 17.5 (122) [B(7)]	2, 2, 1
$[C_5(CH_3)_5]_2Co_2B_5H_9$ (IX)	62.5 (137) [B(4,5) and B(2)], 28.3[b] [B(6)], 18.4 (112) [B(7)]	3, 1, 1
5,9-$[C_5(CH_3)_5]_2Co_2B_8H_{12}$ (X)	32.7 (140), 30.3,[b] 27.9,[b] 24.6,[b] 16.3 (128), 8.6 (93), −1.4 (128), −2.3 (116)	1, 1, 1, 1, 1, 1, 1, 1
1-$[C_5(CH_3)_5]CoB_4H_8$ (XI)	−2.9 (158)	
1,2-$[C_5(CH_3)_5]_2Co_2B_5H_5$ (XII)	135.6 (~174) [B(7)], 96.3 (140) [B(5)], 76.6 (140) [B(4,6)], 2.9 (128) [B(3)]	1, 1, 2, 1

[a] $BF_3 \cdot O(C_2H_5)_2$ shift is 0; positive shifts are downfield. [b] J_{BH} coupling not measurable. For discussion of assignments, see text. [c] Singlet resonance [B(6)−Cl]. [d] Tentative assignment.

and one from each bridge hydrogen to framework bonding. These complexes are structural and electronic analogues of $B_{10}H_{14}$ and may be regarded as derivatives of that borane in which one or two BH units are replaced by $Co[C_5(CH_3)_5]$ groups. The cage skeletons and numbering are shown in Figure 1. In all cases the ^{11}B and ^{1}H NMR spectra conform to the X-ray determined structures, although some coincidental superposition of peaks appears even in the 115-MHz ^{11}B spectrum; for example, compound II exhibits a 6:2 rather than the 4:2:2 pattern expected from its structure (the 100-MHz ^{1}H spectrum, however, does reveal three distinct terminal H–B resonances in a 4:2:2 ratio). In all instances the peaks arising from B–H–Co and B–H–B bridging protons are distinguishable (Table III).

The ^{11}B NMR spectra of the 5,7-isomers III and IV differ rather sharply from that of the 6,9-isomer (II). The appearance of an area-1 signal at low field (δ ~50) in III and IV, and its absence in the spectra of II as well as those of I and all other known $B_{10}H_{14}$-type metallaboranes containing metals in the 6(9) position(s), suggests that this resonance arises from B(6); this boron is semiisolated from the other boron nuclei, being directly linked only to B(2). Similarly, the unusually deshielded H–B resonance at δ 6.66 in the 100-MHz ^{11}B-decoupled ^{1}H spectrum of III can be assigned to the corresponding terminal hydrogen, H(6). Unequivocal proof of these assignments is given by IV, the 6-chloro derivative of III, whose B–Cl singlet resonance at δ 49.9 can be assigned to B(6) on the basis of the X-ray structure determination[20] on that compound.

The structurally related species 5-$(C_5H_5)CoB_9H_{13}$ has been reported earlier.[2,5] Unfortunately, its $C_5(CH_3)_5$ counterpart is not known, nor is the cyclopentadienyl analogue of III [i.e., 5,7-$(C_5H_5)_2Co_2B_8H_{12}$] available; hence, direct spectroscopic comparison is not possible. With the assumption, however, that the ^{11}B NMR spectra of 5-$(C_5R_5)CoB_9H_{13}$ species are not greatly affected by replacement of C_5H_5 with $C_5(CH_3)_5$ (as is borne out in general by comparison of NMR data), it is noteworthy that the ^{11}B shift of B(6) to low field in the spectra of III and IV is less pronounced (by 30 ppm) in 5-$(C_5H_5)CoB_9H_{13}$.[2a] This is taken to reflect the presence of only one cobalt atom adjacent to B(6) in 5-$(C_5H_5)CoB_9H_{13}$, as compared to two such cobalts in III and IV. Observations of this kind are important in the development of reliable structural assignments from NMR evidence, as, obviously, crystal structure determinations of new metallaborane species are not feasible or practical in all cases.

Formation of Products I–IV and Relation to Other Clusters. Compound I is a counterpart of 6-$(C_5H_5)CoB_9H_{13}$ obtained by Sneddon et at.[21] via the reaction of cobalt vapor, cyclopentadiene, and $B_{10}H_{14}$. The proposed geometry of the latter species, based on NMR spectra,[21] can be regarded as confirmed by the X-ray analysis of I, since the ^{11}B NMR spectra of the two compounds are closely similar. Two other $(C_5H_5)CoB_9H_{13}$ isomers, having the metal in the 5- and 2-vertices, respectively, have been reported. In the case of 5-$(C_5H_5)CoB_9H_{13}$[2] the structure was confirmed crystallographically,[5] and the 2-isomer[22] can be taken as established since its NMR pattern distinguishes it from the still-unknown 1-$(C_5H_5)CoB_9H_{13}$, the only other possible isomer based on a $B_{10}H_{14}$-type structure.

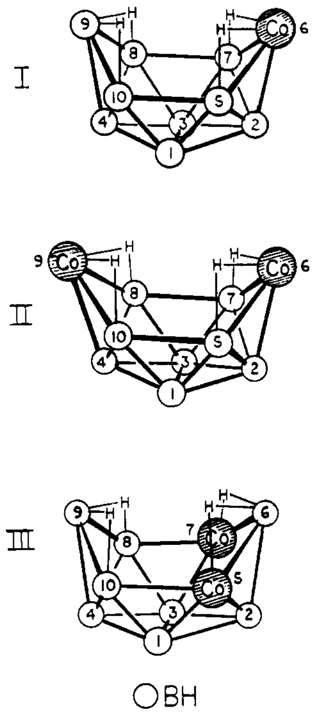

Figure 1. Cage frameworks of 6-CoB_9, 6,9-Co_2B_8, and 5,7-Co_2B_8 systems, corresponding to products I, II, and III, respectively (IV is a 6-chloro derivative of III).

The formal $B_9H_{13}^{2-}$ ligand also appears in several mixed-ligand carborane–cobalt–borane complexes which have been isolated and crystallographically characterized in our laboratory.[23] In these complexes the metal atom occupies either the 5- or 6-vertex in the CoB_9 cage. In addition, several analogous manganese and rhenium species having the general formula 6-$(CO)_3MB_9H_{12}R$ [R = H, THF, $(C_2H_5)_2O$, or $(C_2H_5)_3N(CH_2)_4O$] have been characterized by Gaines and

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Table III. 360-MHz ^{1}H FT NMR Data ($CDCl_3$ Solution)

compd	δ^a	rel area	assignt
I	1.89	15	$C_5(CH_3)_5$
	4.3		BH
	3.7		BH
	2.7		BH
	0.8		BH
	−3.3	2	B-H-B
	−11.8 (35 Hz)^b	2	Co-H-B
II	1.80	30	$C_5(CH_3)_5$
	4		BH overlapped quartets
	−11.65	4	Co-H-B
III	1.63	30	$C_5(CH_3)_5$
	3.5		BH } overlapped quartets
	2.2		BH
	−2.6	2	B-H-B
	−21.0	2	Co-H-B
IV	1.60	30	$C_5(CH_3)_5$
	3		BH } overlapped quartets
	−0.5		BH
	−2.4	2	B-H-B
	−20.0	2	Co-H-B
V	1.9	15	$C_5(CH_3)_5$
	3.2	4	BH overlapped quartets
	−3.8	2	B-H-B
	−14.2 (67 Hz)^b	2	Co-H-B
VI	1.9	30	$C_5(CH_3)_5$
	5.8	2, 2	BH overlapped quartets
	−13.0	2	Co-H-Co
VII	1.62	45	$C_5(CH_3)_5$
	11.8	1	BH
	8.4	3	BH
VIII	1.71	15	$C_5(CH_3)_5$
	1.36	15	$C_5(CH_3)_5$
	5.0	4	BH } overlapped quartets
	−0.5	1	BH
	−14.6	2	Co-H-Co
IX	1.9	30	$C_5(CH_3)_5$
	5	5	BH overlapped quartets
	−12.4	2	Co-H-B
	−14.1	2	Co-H-B
X	1.81	15	$C_5(CH_3)_5$
	1.76	15	$C_5(CH_3)_5$
	4	8	BH overlapped quartets
	−4.25	1	B-H-B
	−10.7	1	Co-H-B
	−14.2	1	Co-H-B
	−19.5	1	Co-H-B
XI	1.79	15	$C_5(CH_3)_5$
	3.30 2.86 2.42 1.98	4	B-H quartet, $J_{BH} = 158$
	−4.04	4	B-H-B
XII	1.71	30	$C_5(CH_3)_5$
	10.1	1	BH
	8.4	1	BH
	7.0	2	BH
	−0.8	1	BH

^{a} Shifts referenced to $Me_4Si = 0$. ^{b} $J(H_{bridge}-H_{terminal})$.

co-workers.[24] Further discussion of structure in the MB_9 and M_2B_8 nido cage systems is given elsewhere.[20]

The dicobalt complexes II–IV are the first examples of metallaborane analogues of $B_{10}H_{14}$ containing more than one metal atom. That the metals occupy nonadjacent vertices might be attributed to steric repulsion of the bulky $C_5(CH_3)_5$ ligands, but the observation that several products of the $B_5H_8^-$ reaction (vide infra) *do* contain adjacent $Co[C_5(CH_3)_5]$ units undermines such arguments. From the static structure of $B_9H_{14}^-$, which corresponds to $B_{10}H_{14}$ with the 6-vertex missing,[25] it can be conjectured that the major isolable product, I, forms via insertion of cobalt into the vacant 6-position; similarly, the loss of B(9)–H from I and its subsequent replacement by $Co[C_5(CH_3)_5]$ could generate II. Since the metal atoms in II are only 3-coordinate with respect to the cage while those in III are 4-coordinate, rearrangement of II to III may be favored thermodynamically although this has not been demonstrated. The chloro derivative IV apparently forms from III during workup in dichloromethane solution; halogenation under such circumstances has been observed previously in metallaborane chemistry.[6]

Reaction of $B_5H_8^-$ with $CoCl_2$ and $[C_5(CH_3)_5]^-$. Treatment of a THF solution containing 90–95 mol % $Na^+B_5H_8^-$ (relative to all borane species present) with $CoCl_2$ and $Li^+[C_5(CH_3)_5]^-$ at −76 °C followed by slow warming to room temperature gave a red-brown solution, in sharp contrast to the $B_9H_{14}^-$ reaction described above. Removal of THF, extraction with CH_2Cl_2, and separation on silica plates gave a series of cobaltaborane products, none of which correspond to species obtained from $B_9H_{14}^-$:

$$CoCl_2 + C_5(CH_3)_5^- + B_5H_8^- \xrightarrow[2\ \mathrm{h}]{\mathrm{THF}}$$

$$\underset{\mathrm{V}}{2\text{-}[C_5(CH_3)_5]CoB_4H_8}\ (4.2\%)\ +$$

$$\underset{\mathrm{VI}}{1,2\text{-}[C_5(CH_3)_5]_2Co_2B_4H_6}\ (1.6\%,^a\ 3.5\%^b)\ +$$

$$\underset{\mathrm{VII}}{1,2,3\text{-}[C_5(CH_3)_5]_3Co_3B_4H_4}\ (\sim 1\%)\ +$$

$$\underset{\mathrm{VIII}}{1,2\text{-}[C_5(CH_3)_5]_2Co_2B_5H_7}\ (<1\%,^a\ 2\%^b)\ +$$

$$\underset{\mathrm{IX}}{[C_5(CH_3)_5]_2Co_2B_5H_9}\ (0.1\%)\ +$$

$$\underset{\mathrm{X}}{5,9\text{-}[C_5(CH_3)_5]_2Co_2B_8H_{12}}\ (0.1\%)$$

The superscripts *a* and *b* refer to yields at reaction times of 2 h and 15 min, respectively. All of these compounds are apparently air-stable, diamagnetic crystalline solids. The relative yields of the products are sensitive to reaction time; when the reaction is terminated at an early stage (<30 min), the yields of VI and VIII increase significantly, while longer periods (hours) favor the formation of V. These observations suggest that V may form by loss of cobalt from VI although this has not been confirmed.

The corresponding reaction[2] of $B_5H_8^-$ with $CoCl_2$ and $C_5H_5^-$ in THF generates primarily $2\text{-}(C_5H_5)CoB_4H_8$ (a counterpart of V) in ~5% yield, together with much smaller amounts of $1,2\text{-}(C_5H_5)_2Co_2B_4H_6$ and $1,2,3\text{-}(C_5H_5)_3Co_3B_4H_4$ (analogues of VI and VII, respectively). Other minor products of the $C_5H_5^-$ reaction include $(C_5H_5)_3Co_3B_3H_5$ and $(C_5H_5)_4Co_4B_4H_4$, whose $C_5(CH_3)_5$ counterparts have not been detected. The overall yield of isolable, air-stable cobaltaborane products in the $C_5(CH_3)_5^-$ reaction is comparable to that obtained in the $C_5H_5^-$ system, but the formation of $1,2\text{-}[C_5(CH_3)_5]_2Co_2B_4H_6$ in much larger yield than of its C_5H_5 analogue[2] is important in terms of future synthetic work.

Characterization of Products. Spectroscopic and other data are given in Tables I–IV and in the Experimental Section. Products V–VII (Figure 2) were readily identified by comparison of their ^{11}B and ^{1}H NMR spectra with those of the analogous cyclopentadienyl complexes. In the case of the tricobalt species VII, however, we were skeptical of the assignment of a capped-octahedral structure corresponding to that established[3b] for $(C_5H_5)_3Co_3B_4H_4$, in which the three metal atoms form a triangular face on a Co_3B_3 polyhedron

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[24] (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. (c) Gaines, D. F.; Calabrese, J. C. *Ibid.* **1974**, *13*, 2419.

[25] Greenwood, N. N.; Gysling, H. J.; McGinnety, J. A.; Owen, J. D. *J. Chem. Soc., Chem. Commun.* **1970**, 505.

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

I	2996 w, 2966 w, 2925 m, 2580 s, 2520 s, 2500 s, 1470 s, br, 1375 s, 1357 s, 1075 m, 1081 m, 1022 m, 1011 m, 996 s, sh, 770 sh
II	2950 m, 2910 s, 2850 m, 2470 s, br, 1725 m, br, 1465 s, br, 1375 s, sh, 1280 m, br, 1080 w, 1020 s, 990 s, 915 w, 860 m, 795 m, 740 s, sh
III	2985 m, 2960 m, 2910 s, 2860 m, 2550 s, 2505 s, 2450 s, 2420 s, 1475 s, br, 1375 s, 1250 s, 1160 m, 1070 m, 1030 m, 1010 s, 1020 s, 985 m, 960 m, 870 m, 690 s
IV	2950 m, 2920 s, 2860 m, 2545 s, 2495 s, 2430 s, 1450 s, br, 1375 s, 1220 m, br, 1150 w, 1070 w, 1020 m, 985 m, 975 m, 850 m, 780 m, 770 m, 740 s
V	2990 s, 2960 s, 2915 s, 2855 s, 2560 s, 2530 s, 2500 s, 1800 w, br, 1720 m, br, 1530 w, 1450 s, 1375 s, 1270 m, br, 1210 w, 1130 w, 1065 m, 1025 s, 950 s, 855 s, 815 m, 750 w, 690 m, 675 m, 650 m
VI	2910 s, br, 2850 s, 2460 s, br, 1720 m, br, 1460 m, br, 1370 s, 1270 m, br, 1015 s, br, 780 w, br, 740 s, br, 620 m
VII	2920 s, sh, 2850 m, sh, 2440 m, 1440 m, br, 1365 m, 1010 m, 840 m
VIII	2985 w, 2885 w, 2850 w, 2485 m, 2450 m, 2400 m, 1465 m, br, 1420 m, 1370 sh, s, 1065 m, 1015 s, 975 s, 885 m, 810 m, 790 w, 750 w, 630 m
IX[b]	2990 m, 2965 m, 2910 s, 2860 m, 2490 s, br, 1530 w, br, 1480 m, 1450 m, 1425 w, 1380 s, 1070 m, br, 1030 s, 810 w, 715 m, 680 m
X	2980 w, 2940 m, sh, 2930 m, 2500 w, 2480 m, 2460 w, 1720 w, 1655 m, 1630 m, 1615 m, 1515 m, sh, 1460 s, br, 1440 s, br, 1380 s, sh, 1190 m, 1080 w, 1070 w, 1020 w, 805 m, br, 650
XI	2990 w, 2960 w, 2900 m, 2850 w, sh, 2530 m, 1805 m, br, 1790 m, br, 1710 w, 1500 w, sh, 1495 m, sh, 1470 m, 1430 m, 1380 s, 1130 w, 1070 w, 1030 m, 1010 m, 895 s, 830 w, 725 s, 680 s, 650 s
XII	2970 m, 2900 s, 2860 m, 2500 s, 2460 s, sh, 1440 s, br, 1370 s, sh, 1065 m, 1020 s, sh, 875 s, 780 s, 775 m, br, 740 m, 675 m

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

with the fourth boron capping the Co_3 array. Despite the NMR data on VII, which pointed to a similar capped-octahedral geometry, it appeared doubtful that the large steric requirements of the three $Co[C_5(CH_3)_5]$ groups could be accommodated in such an arrangement. However, an X-ray crystal structure determination on VII (second following paper) confirmed this cage geometry, which is indeed analogous to $(C_5H_5)_3Co_3B_4H_4$ except for moderate lengthening of the three Co–Co distances (Figure 2).[26]

The structure of the dicobalt complex VI is also remarkable, in that the $Co[C_5(CH_3)_5]$ units adopt the 1,2- (adjacent-vertex) configuration rather than the 1,6-geometry; clearly, whatever repulsions may exist between $C_5(CH_3)_5$ ligands are not sufficient to prevent formation of adjacent-metal complexes (still other examples of such species are discussed below). The assignments of ^{11}B and ^{1}H resonances in VI (Tables II and III) are based on those of $1,2\text{-}(C_5H_5)_2Co_2B_4H_6$,[2a] which are unambiguous owing to the availability of B-substituted derivatives[2a] of that complex. The Co–H–Co ^{1}H resonances in VI are readily assigned from their high-field shifts and are closely similar to those in the corresponding C_5H_5 complex.

Products VIII–X, obtained in very small yields, are new cobaltaborane systems whose C_5H_5 analogues are unknown. Indeed, VIII and IX are the first five-boron cobaltaboranes to be obtained from $B_5H_8^-$; in the $B_5H_8^-/CoCl_2/C_5H_5^-$ reaction,[2] the absence of any such species among the characterized products was surprising. The proposed structure of VIII, shown in Figure 3, is assigned from the NMR data and from the electron-counting rules,[8] which dictate closo geometry for this 7-vertex, 16-electron cage. With the assumption of a pentagonal-bipyramidal cage, the nonequivalence of the $Co[C_5(CH_3)_5]$ groups and the 2:2:1 ^{11}B pattern uniquely identifies the 1,2-geometry shown. In addition, the "extra" hydrogen atoms can be assigned to equivalent Co–Co edge-bridging (or Co_2B face-bridging) locations, on the basis of the high-field ^{1}H resonance. Complex VIII is isoelectronic and isostructural with the crystallographically characterized[27] metallacarboranes $1,2,4,5\text{-}(C_5H_5)_2Co_2(CH_3)_2C_2B_3H_3$ and $1,2,4,5\text{-}(C_5H_5)_2CoFe$-

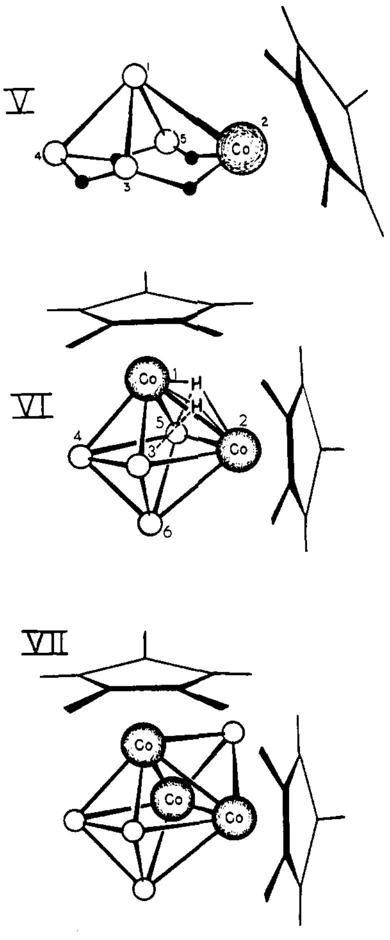
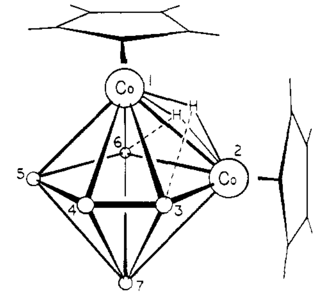


Figure 2. Structures of $2\text{-}[C_5(CH_3)_5]CoB_4H_8$ (V), $1,2\text{-}[C_5(CH_3)_5]_2Co_2B_4H_6$ (VI), and $1,2,3\text{-}[C_5(CH_3)_5]_3Co_3B_4H_4$ (VII). One $C_5(CH_3)_5$ ligand is omitted in VII for clarity. The structure of VII was confirmed in an X-ray structure determination;[26] those of V and VI are analogous to the crystallographically established structures of $2\text{-}(C_5H_5)CoB_4H_8$[4] and $1,2\text{-}(C_5H_5)_2Co_2B_4H_6$,[3a] respectively.



VIII

Figure 3. Proposed structure of $1,2\text{-}[C_5(CH_3)_5]_2Co_2B_5H_7$ (VIII).

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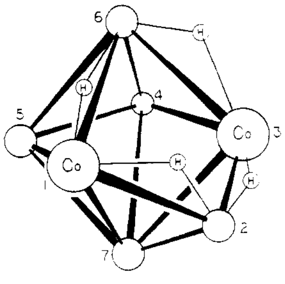
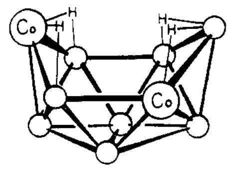
(27) Grimes, R. N; Sinn, E.; Maynard, R. E. *Inorg. Chem.* **1980**, *19*, 2384.



IX

Figure 4. Proposed structure of $[C_5(CH_3)_5]_2Co_2B_5H_9$ (IX), omitting $C_5(CH_3)_5$ groups.



X

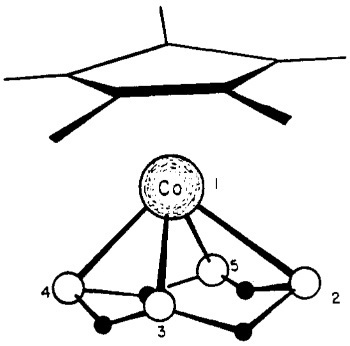
Figure 5. Proposed structure of 5,9-$[C_5(CH_3)_5]_2Co_2B_8H_{12}$ (X), omitting $C_5(CH_3)_5$ ligands for clarity. See Figure 1 for cage numbering.

$(H)(CH_3)_2C_2B_3H_3$. In addition, VIII can be viewed as a diprotonated derivative of the hypothetical $[C_5(CH_3)_5]_2Co_2B_5H_5^{2-}$ ion, which would be analogous to the known[28] species $B_7H_7^{2-}$. The behavior of VIII at elevated temperature is novel, as described below.

Compound IX is a 7-vertex, 18-electron ($2n + 4$) cage system, which should adopt a nido structure according to Wade's rules.[8] Assuming such a geometry, derived from a closo 8-vertex polyhedron by removal of one low-coordinate vertex, it is possible to assign the structure shown in Figure 4. The ^{11}B and ^1H NMR spectra indicate the presence of a mirror plane, which in the proposed structure passes through B(2), B(6), and B(7); the 3:1:1 pattern of ^{11}B resonances can be interpreted as involving superposition of an area-1 and an area-2 signal.

The ^{11}B assignments given in Table II are tentative but can be reconciled nicely with the proposed structure. The low-field resonance is attributed in part to B(4) and B(5), which are "trans" to the cobalt atoms (as in complex VI and its counterpart[2a] 1,2-$(C_5H_5)_2Co_2B_4H_6$); superimposed on this is the signal from B(2), which is a low-coordinate boron adjacent to two cobalt nuclei.[29] The high-coordinate B(7) would be expected to produce a high-field resonance and is assigned accordingly. Finally, placement of the cobalt atoms on the open face, rather than in vertices 4 and 5, is indicated by the presence of four metal–hydrogen interactions (in equivalent pairs) as revealed by their distinctive proton resonances at high field.

It should be noted that IX is formally analogous to the unknown[30] borane B_7H_{11}; since unsubstituted, uncomplexed[31] heptaboranes have not been isolated, the existence of IX testifies to the stabilizing influence of $Co(C_5H_5)$ or $Co[C_5(CH_3)_5]$ when substituted for BH in a borane framework.[2a]



XI

Figure 6. Structure of 1-$[C_5(CH_3)_5]CoB_4H_8$ (XI), which is analogous to that of 1-$(C_5H_5)CoB_4H_8$, confirmed in an X-ray investigation.[32]

Complex X, another very minor product, was characterized as an additional isomer of the $[C_5(CH_3)_5]_2Co_2B_8H_{12}$ series already represented by the 6,9- and 5,7-isomers (products II and III of the $B_9H_{14}^-$ reaction described above). The NMR spectra indicate an absence of any symmetry in the molecule, and the ^1H spectrum reveals the presence of three Co–H–B and one B–H–B bridge. These data uniquely locate the cobalt atoms in the 5- and 9-vertices as depicted in Figure 5. It is worthy of note that the signal at δ −19.5 in the ^1H NMR spectrum is typical of Co–H–B bridging protons where the cobalt occupies the 5-vertex in a $B_{10}H_{14}$-type cage, as revealed in the spectra of 5-$(C_5H_5)CoB_9H_{13}$[2a] as well as those of 5,7-$[C_5(CH_3)_5]_2Co_2B_8H_{12}$ and its 6-Cl derivative (compounds III and IV in this work). When cobalt is in the 6(9)-position(s), the Co–H–B resonance is at lower field (near δ −12) as in 6-$(C_5H_5)CoB_9H_{13}$,[21] 6-$[C_5(CH_3)_5]CoB_9H_{13}$ (I), and 6,9-$[C_5(CH_3)_5]_2B_8H_{12}$ (II); this correlates nicely with the presence of signals at δ −10.7 and −14.2 in the spectrum of X.

Thermal Isomerization of 2-$[C_5(CH_3)_5]CoB_4H_8$ (V). Previous work[2a] has established that red 2-$(C_5H_5)CoB_4H_8$ rearranges to pale yellow 1-$(C_5H_5)CoB_4H_8$ in the vapor phase at 180 °C. The 1-isomer contains a $B_4H_8^{2-}$ cyclic ligand, which is isoelectronic with cyclobutadienide ($C_4H_4^{2-}$); hence this complex is a direct analogue of $(\eta^5\text{-}C_5H_5)Co(\eta^4\text{-}C_4H_4)$. This structure, originally assigned from NMR evidence,[2a] has recently been confirmed by X-ray diffraction.[32] In the present study it was found that red 2-$[C_5(CH_3)_5]CoB_4H_8$ undergoes a similar rearrangement, though at a higher temperature (225 °C), to give pale yellow 1-$[C_5(CH_3)_5]CoB_4H_8$ (XI). The sandwich structure of this species (Figure 6) is clearly supported by its lone ^{11}B resonance and the equivalence of the four terminal and four bridging hydrogen atoms in the ^1H NMR spectrum, all of which exhibit shifts similar to those of their counterparts in the spectra of 1-$(C_5H_5)CoB_4H_8$.[2a]

Thermolysis of 1,2-$[C_5(CH_3)_5]_2Co_2B_5H_7$ (VIII). Rearrangement of compound VIII at elevated temperature was expected to generate the 1,7-isomer, which would have a planar central borane ligand, formally $B_5H_5^{6-}$, isoelectronic with $C_5H_5^-$. Such a species would be a triple-decker complex analogous to the well-known metallacarborane triple-deckers 1,7,2,3- and 1,7,2,4-$(C_5H_5)_2Co_2C_2B_3H_5$[33] in which the central ring is formally $C_2B_3H_5^{4-}$; no complex of planar $B_5H_5^{6-}$ is known as yet. The proposed rearrangement of VIII to the

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(30) Mass spectroscopic evidence for B_7H_{11} has been reported: McLaughlin, E.; Rozett, R. W. *Inorg. Chem.* **1972**, *11*, 2567. However, there is no indication of its existence as a characterizable species.

(31) The complex $(CO)_4FeB_7H_{12}^-$ has been prepared and crystallographically characterized: Mangion, M.; Clayton, W. R.; Hollander, O.; Shore, S. G. *Inorg. Chem.* **1977**, *16*, 2110.

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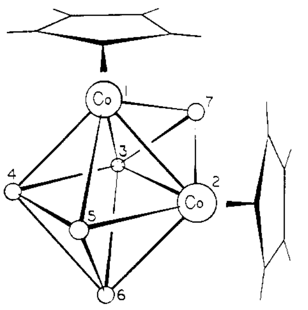

XII

Figure 7. Proposed structure of 1,2-$[C_5(CH_3)_5]_2Co_2B_5H_5$ (XII).

1,7-isomer would be directly analogous to the known isomerization[34] of 1,2,3,5-$(C_5H_5)_2Co_2C_2B_3H_5$ to the 1,7,2,4-complex, in which the equatorial (2) cobalt moves to the apex (7) location of the pentagonal bipyramid. To our surprise, however, compound VIII on thermolysis did not produce the 1,7-isomer but instead lost 1 molar equiv of hydrogen and generated a new cage system, XII:

$$\underset{\text{VIII}}{[C_5(CH_3)_5]_2Co_2B_5H_7} \xrightarrow{\Delta} \underset{\text{XII}}{[C_5(CH_3)_5]_2Co_2B_5H_5} + H_2$$

Since the new compound XII is a $2n$-electron (7-vertex, 14-electron) cage, a capped-octahedral structure analogous to VII is indicated. The geometry shown in Figure 7 is strongly supported by the ^{11}B and ^1H NMR spectra of XII, which reveal (1) the presence of a mirror plane, which renders the cobalts equivalent, and (2) an extremely low-field ^{11}B resonance (δ 135.6) that can be assigned to a boron capping a Co_2B face. Actually, from symmetry requirements alone the only other capped-octahedral geometry that could be considered is one in which a B_3 face, rather than a Co_2B face, is capped; however, the low-field ^{11}B signal is more compatible with a boron adjacent to metal atoms, as found in VII (see above) and in the C_5H_5 analogue of VII, whose corresponding ^{11}B signal[2a] appears at δ 141.4. All other arrangements based on a capped octahedron would have nonequivalent cobalt atoms and can be ruled out.

Complex XII together with its tricobalt counterparts VII and $(C_5H_5)_3Co_3B_4H_4$ are electronic analogues of a hypothetical B_7H_7 borane. Again, as with other cobaltaboranes reported here (notably VIII and IX), the ability of $Co(C_5R_5)$ units to stabilize geometries that are untenable in the parent borane series is quite evident.

The conversion of VIII to XII is to our knowledge the first example of a closo → capped-closo thermal conversion induced by ejection of hydrogen (nido-to-closo processes are known such as the formation of $C_2B_4H_6$ from $C_2B_4H_8$ at elevated temperature[35]). A likely mechanism for the VIII–XII conversion, suggested in Figure 8, involves merely breakage of an apex-equatorial B–B bond with concurrent linkage of two equatorial atoms as shown. Among the interesting questions this poses for future investigation is whether it might be possible to reverse the process by addition of hydrogen to XII; also, there is the possibility that the thermal rearrangement of VIII in the presence of H_2 might cause it to take a different course, perhaps producing 1,7-$[C_5(CH_3)_5]_2Co_2B_5H_5$ as originally intended.

Conclusions

This work, taken together with previous studies, affords two kinds of comparisons: that between the isolable $B_5H_8^-$/$CoCl_2$/$C_5H_5^-$ and $B_5H_8^-$/$CoCl_2$/$C_5(CH_3)_5^-$ reaction products and that between the two borane–cobalt reactions described in this paper. As to the first point, it need only be noted that replacement of $C_5H_5^-$ with $C_5(CH_3)_5^-$ produced several complexes that are directly analogous to those obtained with $C_5H_5^-$ (these being the main products) while at the same time also forming several species (VIII–X) whose C_5H_5 counterparts are unknown at present. The increase in yield of 1,2-$(C_5R_5)_2Co_2B_4H_6$ for R = CH_3 compared to that obtained when R = H represents a significant difference in the two systems.

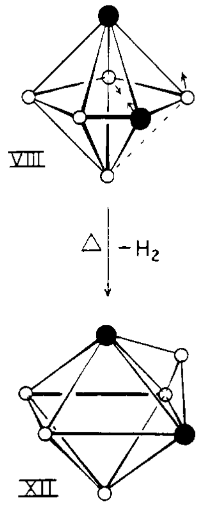

Figure 8. Possible pathway for rearrangement of VIII to XII: ○, BH; ●, $Co[C_5(CH_3)_5]$.

The second comparison, involving the reactions of two different borane anions with the same metal ion under essentially the same conditions, is more striking. The contrast in product distributions is sharp: with $B_9H_{14}^-$, all of the isolable cobaltaboranes in this work are 10-vertex nido cages, whereas $B_5H_8^-$ produced a much wider variety of species containing up to three cobalt and four to eight boron atoms and including nido, closo, and capped-closo cage systems. This supports the indications from earlier work in our laboratory on $B_5H_8^-$–transition-metal reactions,[2,9,10] and by Gaines on $B_9H_{14}^-$–metal systems,[24] that the behavior of $B_5H_8^-$ toward metals is much more stereochemically complex. Indeed, the isolable products obtained from different metals (e.g., Fe, Co, and Ni) are quite distinct. In contrast, interactions of the $B_9H_{14}^-$ ion with metal reagents invariably produce MB_9 or M_2B_8 cage systems, suggesting that attack of metal ions on that substrate is relatively stereospecific. Our own NMR observations on the 360-MHz instrument confirm that solutions of $Na^+B_9H_{14}^-$ in THF are quite stable at room temperature, in contrast to those of $B_5H_8^-$, as discussed earlier.

The new cobaltaboranes described here provide further support for the structure/electron-count correlation in clusters,[8] and especially for the generalization that $Co(C_5H_5)$ and $Co[C_5(CH_3)_5]$ can function as electronic substitutes for BH in polyhedral boranes; the structural similarity between the cobaltaboranes and their boron hydride analogues is quite remarkable (although certain species such as VII and IX have no known borane counterparts). Those products that are obtained in substantial quantities (especially VI) present opportunities for extensive studies of cage systems that heretofore were not readily available. Finally, the $[C_5(CH_3)_5]_2Co_2B_5H_x$ species XII, VIII, and IX, in which x is 5, 7, or 9 and the proposed structures are respectively capped closo, closo, and nido, exhibit a type of structural relationship not previously seen in metallaborane chemistry and which bears further investigation.

Experimental Section

Materials. $CoCl_2·6H_2O$ (Baker) was dehydrated under vacuum at 160 °C. Pentaborane(9) from U.S. Government stockpiles was used as received after infrared analysis indicated high purity. Pen-

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[34] Miller, V. R.; Grimes, R. N. *J. Am. Chem. Soc.* **1975**, *97*, 4213.

[35] Onak, T. P.; Gerhart, F. J.; Williams, R. E. *J. Am. Chem. Soc.* **1963**, *85*, 3378.

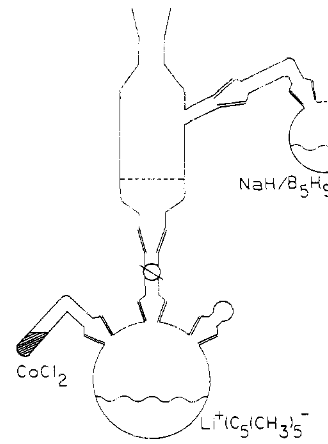

Figure 9. Diagram of the apparatus employed in reactions of $CoCl_2$ and $Li^+[C_5(CH_3)_5]^-$ with $B_5H_8^-$ and $B_9H_{14}^-$ ions.

tamethylcyclopentadiene (Strem, Alfa) was used without further purification. Sodium hydride was obtained as a 50% dispersion in mineral oil and used as received. *n*-Butyllithium was purchased from Alfa as a hexane solution and standardized by the method of Silveira et al.[36] All solvents were reagent grade; tetrahydrofuran (THF) was dried over sodium and distilled from $LiAlH_4$ prior to use.

Spectra and Chromatography. Boron-11 and proton FT NMR spectra were recorded at 115.5 and 360 MHz, respectively, on a Nicolet superconducting spectrometer with the samples at ambient temperature. Infrared spectra were obtained on a Beckman IR-8 instrument, unit-resolution mass spectra were run on a Hitachi-Perkin-Elmer RMU-6E spectrometer, and high-resolution mass spectra were provided by Harvey Analytical Laboratories, Charlottesville, Va. Chromatographic separations were achieved on packed silica gel (Merck 70/230 mesh) columns, thin- (0.25 mm) and preparative- (2 mm) layer precoated silica gel chromatographic plates (E.M. Reagents, F-254), and on a Waters Associates Prep-500 liquid chromatograph employing prepacked, radially compressed silica columns.

Mass Spectra. The unit-resolution spectra of all of the cobaltaborane products exhibit an intense peak at *m/e* 194 arising from $Co[C_5(CH_3)_5]^+$, as well as strong parent groupings. In the spectra of the CoB_9 and Co_2B_8 clusters (I–IV), all of which contain four bridging hydrogens, extensive hydrogen loss is exhibited in the parent region. Unlike the spectra of C_5H_5–cobaltaboranes, in which peaks corresponding to $Co(C_5H_5)_2^+$ are invariably seen for compounds containing more than one cobalt,[2a] no $Co[C_5(CH_3)_5]_2^+$ peaks were evident in these spectra. However, peaks arising from doubly charged parent ions were observed in the spectra of dicobalt and tricobalt species.

Reaction of $Li^+[C_5(CH_3)_5]^-$, $CoCl_2$, and $Na^+B_9H_{14}^-$. Typically, a solution of $Li^+[C_5(CH_3)_5]^-$ in THF was prepared by the addition, under N_2, of a 2 M solution of *n*-butyllithium (15 mmol) in hexane to a stirred solution of $C_5(CH_3)_5H$ (2.0048 g, 14.7 mmol) at 0 °C over a 5-min period. This solution was maintained at 0 °C for 4.5 h after which time the reaction mixture was a viscous yellow slurry. To the reaction vessel was attached another flask containing anhydrous $CoCl_2$ (2.50 g, 19.3 mmol), and the assembled reaction apparatus was attached to the vacuum line (see Figure 9). The hexane was removed under vacuum, the flask was immersed in liquid nitrogen, and THF was condensed on top of the $Li^+C_5(CH_3)_5^-$. The mixture was warmed to room temperature to dissolve the salt, and the $CoCl_2$ was added in small portions. This slightly exothermic reaction produced a dark olive-green solution after stirring for 2 h. At this point the reaction mixture was frozen in liquid nitrogen.

Concurrent with the above procedure, a solution of $Na^+B_9H_{14}^-$ was prepared. A separate flask containing NaH (0.373 g of a 50% dispersion in oil, 7.77 mmol), washed with pentane to remove the oil, was attached to the vacuum line. Following evacuation, B_5H_9 (6.0 mmol) and THF (~50 mL) were condensed in the flask at −196 °C and the mixture was warmed to ~−20 °C to generate the anion. After 2 h, evolution of H_2 had ceased, indicating completion of the reaction. The reaction mixture was frozen in liquid nitrogen and H_2 pumped away. The THF solution of $CoCl_2/Li^+[C_5(CH_3)_5]^-$ in the lower flask was immersed in a dry ice/isopropyl alcohol bath, and the solution of $B_9H_{14}^-$, after warming to room temperature for 2 h, was filtered into the lower flask and the solution was stirred at dry ice temperature for 2 h during which time no color change was apparent. The solution was then allowed to warm gradually to room temperature, which caused the solution to change to greenish brown. (In early experiments, the reaction mixture at this stage was exposed to air and stirred for an additional 2 h; later it was found that this step did not materially affect the product distribution, and it was subsequently omitted.) The THF was removed under vacuum, and the brown residue was extracted with CH_2Cl_2/hexane. This solution was filtered to remove the considerable insoluble material and concentrated by partial evaporation of solvent prior to preparative separation.

The concentrated extract was developed on preparative-layer silica gel plates with a 1:1 CH_2Cl_2/hexane solvent system. This yielded three major bands, two of which constituted mixtures. The major fraction (R_f = 0.46–0.53) was composed of two compounds that proved irresolvable by plate chromatography. Separation of these products 6-$[C_5(CH_3)_5]CoB_9H_{13}$ (I) and 6-Cl-5,7-$[C_5(CH_3)_5]_2Co_2B_8H_{11}$ (IV) was achieved by preparative high-pressure liquid chromatography with a 28% CH_2Cl_2/hexane solvent system on silica gel columns. The other unresolved band (R_f = 0.14–0.23) was a complex mixture that yielded one predominant product, 6,9-$[\eta^5\text{-}C_5(CH_3)_5]_2Co_2B_8H_{12}$, after TLC on silica gel with repetitive development using a 5:3 CH_2Cl_2/hexane eluant. The third band (R_f = 0.37) proved to be 5,7-$[C_5(CH_3)_5]_2Co_2B_8H_{12}$. (Note: the R_f values given in Table I represent measurements on pure compounds in a common solvent system.) Yields of I and IV were, respectively, 229 mg (25% based on B_5H_9 employed) and 31 mg (2%); complexes II and III were isolated in less than 1% each. Exact mass determinations: calcd for $^{12}C_{10}{}^{11}B_9{}^{59}Co^1H_{28}^+$ (I) 306.2361, found 306.2372; calcd for $^{12}C_{20}{}^{11}B_8{}^{59}Co_2{}^1H_{42}^+$ (III) 488.2695, found 488.2703.

Reaction of $Li^+[C_5(CH_3)_5]^-$, $CoCl_2$, and $Na^+B_5H_8^-$. A solution of $Li^+[C_5(CH_3)_5]^-$ in THF was prepared and combined with $CoCl_2$ as in the above $B_9H_{14}^-$ reaction, with use of identical quantities of reagents; after 2 h of stirring, the mixture was frozen in liquid nitrogen. A solution of $Na^+B_5H_8^-$ was separately prepared by condensing 6.0 mmol of B_5H_9 and 50 mL of THF onto 20.7 mmol of pentane-washed NaH (obtained from 0.995 g of a 50% dispersion in mineral oil) in the upper flask (Figure 9), which was cooled in liquid nitrogen. The mixture was warmed to −20 °C and subsequently maintained between −20 and −30 °C. Under these conditions the principal borane species present is $B_5H_8^-$ (90–95 mol %) as shown from ^{11}B NMR spectra;[37] the important factors in maximizing $B_5H_8^-$ concentration are the use of a large (3:1) excess of NaH and the maintenance of the solution below −20 °C.

The $CoCl_2/Li^+[C_5(CH_3)_5]^-$ solution in the lower flask was immersed in dry ice/isopropyl alcohol, the $Na^+B_5H_8^-$ solution was filtered into the lower flask, and the same procedure as in the $B_9H_{14}^-$ reaction was followed, except that reaction times were varied from 15 min to 2 h in different experiments. As explained earlier, the longer period favors formation of compound V while shorter periods favor VI and VIII. In contrast to the $B_9H_{14}^-$ reaction, the solution color in the $B_5H_8^-$ reaction was red-brown. After removal of THF under vacuum, the residue was extracted with CH_2Cl_2/hexane, filtered, and concentrated on a rotary evaporator.

The CH_2Cl_2/hexane extract was placed on a silica gel column and eluted with hexane followed by solvent mixtures of hexane gradually enriched with CH_2Cl_2 and finally with 100% CH_2Cl_2. Four bands were eluted from the column and then subjected to additional purification by TLC. The first band, yellow-orange, proved to be largely V along with traces of $C_5(CH_3)_5H$ and VII. The second band, brown, proved to be predominantly a mixture of V and VI. The third band, violet, and the fourth, burgundy, were essentially pure VI and VIII, respectively. Products IX and X were isolated as trace materials during the TLC separations.

In a reaction quenched after 15 min, the major isolated products were 1,2-$[C_5(CH_3)_5]_2Co_2B_4H_6$ (VI) (97 mg, 3.5%) and 1,2-$[C_5(CH_3)_5]_2Co_2B_5H_7$ (VIII) (54.8 mg, 1.9%); the other products were isolated in individual yields of 5–10 mg. For 2-h reactions, the major isolated products were 2-$[C_5(CH_3)_5]CoB_4H_8$ (V) (64 mg, 4.2%) and

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(36) Silveira, A., Jr.; Bretherick, H. D.; Negishi, Ei-ichi *J. Chem. Educ.* **1979**, *56*, 560.

(37) Venable, T. L. Ph.D. Dissertation, University of Virginia, 1982.

VI (44 mg, 1.6%), with 10–15 mg of each of the other species. Exact mass determinations: calcd for $^{12}C_{20}{}^{11}B_5{}^{59}Co_2{}^{1}H_{37}^{+}$ (VIII) 450.2024, found 450.2013.

Isomerization of 2-[$C_5(CH_3)_5$]CoB_4H_8 (V). A 21.9-mg sample of V dissolved in pentane was placed in a 1-L Pyrex bulb and attached to the vacuum line. After removal of the pentane under vacuum, the bulb was sealed (via a vacuum stopcock fitted with Viton or Buna-N O-rings) and heated in an oven to 180 °C for 5.5 h and then at 200 °C overnight. When the contents cooled, both red and yellow crystals were visible. As the two isomers are less volatile than their (C_5H_5)CoB_4H_8 counterparts, they were removed from the bulb with pentane and transferred to an evacuated 0.5 × 20 cm Pyrex tube. Separation of pale yellow 1-[$C_5(CH_3)_5$]CoB_4H_8 (XI) from the red V that remained was accomplished by slow sublimation in the Pyrex tube at ~37 °C, which caused crystals of the more volatile XI (5.5 mg, 25%) to collect at the opposite (room-temperature) end. Some decomposition also occurred, as evidenced by the formation of nonvolatile dark solids.

Thermolysis of 1,2-[$C_5(CH_3)_5$]$_2Co_2B_5H_7$ (VIII). A 15-mg sample of VIII dissolved in dichloromethane was placed in a Pyrex reactor, the reactor was attached to the vacuum line, and the solvent was removed under vacuum, after which the bulb was sealed under vacuum and placed in an oven at 225 °C for 17 h. The contents were removed with CH_2Cl_2 in air and filtered to remove decomposed material. The filtrate was developed on TLC plates to give three bands. The first band (R_f = 0.51) contained a trace of a green compound formulated from mass spectra as [$C_5(CH_3)_5$]$_2Co_2B_6H_6$ (mol wt 460) but was not further characterized. The second band (R_f = 0.46) was yellow-red 1,2-[$C_5(CH_3)_5$]$_2Co_2B_5H_5$ (XII) (8.4 mg, 56%), and the third band (R_f = 0.32) was a trace of violet VI, identical with the complex isolated in the $CoCl_2$/$Li^+[C_5(CH_3)_5]^-$/$Na^+B_5H_8^-$ reaction.

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Registry No. I, 80145-59-1; II, 80145-60-4; III, 80145-65-9; IV, 80145-66-0; V, 80127-20-4; VI, 80145-61-5; VII, 80145-67-1; VIII, 80145-62-6; IX, 80127-21-5; X, 80160-30-1; XI, 80127-22-6; XII, 80145-63-7; B_5H_9, 19624-22-7.

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

Cobaltaborane Analogues of $B_{10}H_{14}$. Crystal and Molecular Structures of 6-[η^5-$C_5(CH_3)_5$]CoB_9H_{13}, 6,9-[η^5-$C_5(CH_3)_5$]$_2Co_2B_8H_{12}$, 5,7-[η^5-$C_5(CH_3)_5$]$_2Co_2B_8H_{12}$, and 6-Cl-5,7-[η^5-$C_5(CH_3)_5$]$_2Co_2B_8H_{11}$[1]

T. LEON VENABLE, EKK SINN, and RUSSELL N. GRIMES*

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Crystal and molecular structures have been determined for the title compounds, which were obtained from the reaction in THF of $Li^+C_5(CH_3)_5^-$, $CoCl_2$, and $Na^+B_9H_{14}^-$ (generated during the deprotonation of B_5H_9 with NaH) followed by workup in air, as described in the preceding paper. All four compounds exhibit 10-vertex nido cage structures analogous to $B_{10}H_{14}$ with one or two BH units replaced by Co[η^5-$C_5(CH_3)_5$], and the observed solid-state geometries are compatible with ^{11}B and ^{1}H FT NMR spectra in solution. In each case the four bridging hydrogens, present as B–H–B and Co–H–B groups, occupy locations equivalent to those in $B_{10}H_{14}$ itself; the Co–H–B bridges are unsymmetrical, with the hydrogen closer to boron than cobalt. The dicobalt complexes are the first structurally characterized metallaborane analogues of $B_{10}H_{14}$ having more than one metal atom in the cage. The molecular parameters are compared with those of the previously reported compounds 5-(η^5-C_5H_5)CoB_9H_{13}, 5-THF-6-(CO)$_3MnB_9H_{12}$, and $B_{10}H_{14}$. Crystal data: 6-[$C_5(CH_3)_5$]CoB_9H_{13}, mol wt 305, space group $P2_12_12_1$, $Z = 4$, $a = 10.535$ (3) Å, $b = 12.830$ (3) Å, $c = 13.037$ (3) Å, $V = 1762$ Å^3, $R = 0.028$ for 1427 reflections having $F_o^2 > 3\sigma(F_o^2)$; 6,9-[$C_5(CH_3)_5$]$_2Co_2B_8H_{12}$, mol wt 487, space group $P2_1/n$, $Z = 4$, $a = 8.543$ (2) Å, $b = 14.636$ (8) Å, $c = 20.88$ (2) Å, $\beta = 90.38$ (4)°, $V = 2611$ Å^3, $R = 0.059$ for 1418 reflections having $F_o^2 > 3\sigma(F_o^2)$; 5,7-[$C_5(CH_3)_5$]$_2Co_2B_8H_{12}$, mol wt 487, space group $P2_1/n$, $Z = 4$, $a = 9.236$ (4) Å, $b = 20.229$ (9) Å, $c = 13.681$ (6) Å, $\beta = 98.05$ (4)°, $V = 2531$ Å^3, $R = 0.076$ for 2501 reflections having $F_o^2 > 3\sigma(F_o^2)$; 6-Cl-5,7-[$C_5(CH_3)_5$]$_2Co_2B_8H_{11}$, mol wt 521, space group $P\bar{1}$, $Z = 2$, $a = 9.842$ (8) Å, $b = 11.693$ (6) Å, $c = 12.154$ (8) Å, $\alpha = 68.93$ (6)°, $\beta = 84.95$ (4)°, $\gamma = 86.85$ (4)°, $V = 1300$ Å^3, $R = 0.063$ for 3870 reflections having $F_o^2 > 3\sigma(F_o^2)$.

Introduction

The preceding article[2] describes the reaction of $CoCl_2$, $Li^+[C_5(CH_3)_5]^-$, and $Na^+B_5H_8^-$ in cold tetrahydrofuran (THF), in which it was shown that $B_5H_8^-$, under surprisingly mild reaction conditions, forms $B_9H_{14}^-$ ion in significant concentration. Under these conditions the major isolable product following workup in air was 6-[η^5-$C_5(CH_3)_5$]CoB_9H_{13}, a burgundy crystalline solid obtained in 25% yield. Isolated in much smaller quantities were dark green 6,9-[η^5-$C_5(CH_3)_5$]$_2Co_2B_8H_{12}$, dark brown 5,7-[η^5-$C_5(CH_3)_5$]$_2Co_2B_8H_{12}$, the 6-chloro derivative of the latter complex, and several other (pentamethylcyclopentadienyl)cobalt metallaboranes having one to three metal atoms in the cage.

The CoB_9 and Co_2B_8 products were characterized from high-resolution ^{11}B and ^{1}H pulse Fourier transform NMR spectra and assigned $B_{10}H_{14}$-like nido cage structures in which the cobalt atoms occupy verticles on the open face and participate in Co–H–B bridging groups. In order to rigorously establish the proposed structures of these compounds (which are the first known metallaboranes containing the $C_5(CH_3)_5$ ligand[3]) and also to obtain molecular parameters of interest,

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(1) Taken in part from the Ph.D. dissertation of T.L.V., University of Virginia, 1982.

(2) Venable, T. L.; Grimes, R. N. *Inorg. Chem.* preceding paper in this issue.

(3) Metalla*carboranes* utilizing the pentamethylcyclopentadienyl ligand have been reported from this laboratory: (a) Finster, D. C.; Grimes, R. N. *Inorg. Chem.* **1981**, *20*, 863. (b) Finster, D. C.; Sinn, E.; Grimes, R. N. *J. Am. Chem. Soc.* **1981**, *103*, 1399.