Polyhedral Cobaltaboranes. Versatile Replacement of BH Groups by Co(η^5-C_5H_5) Units in Boron Hydride Frameworks. Borane–Metal Cluster Hybrid Molecules

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Abstract: A series of air-stable crystalline cobaltaboranes has been isolated from the reaction of $Na^+B_5H_8^-$, $CoCl_2$, and $Na^+C_5H_5^-$ in THF below −20 °C. The major products were red 2-(η^5-C_5H_5)CoB_4H_8 (an analogue of B_5H_9) and the known orange complex 1,3-cyclohexadienecobalt(II) cyclopentadiene, (C_6H_8)Co(C_5H_5). The pyrolysis of 2-(η^5-C_5H_5)CoB_4H_8 at 200 °C produced yellow 1-(η^5-C_5H_5)CoB_4H_8, cobalt moving to the apex position. The other structurally characterized products were: red 5-(η^5-C_5H_5)CoB_9H_{13} (a $B_{10}H_{14}$ analogue); violet 1,2-(η^5-C_5H_5)$_2$$Co_2B_4H_6$ and its 3- and 4-cyclopentyl derivatives, for which octahedral structures were assigned; brown 1,2,3-(η^5-C_5H_5)$_3$$Co_3B_3H_5$, octahedral; yellow ($\eta^5$-$C_5H_5$)$_3$$Co_3B_4H_4$, a capped octahedron; green (η^5-C_5H_5)$_4$$Co_4B_4H_4$, a D_{2d} dodecahedron, and red μ(2,3)-1,3-C_3H_4-1,7,2,3-(η^5-C_5H_5)$_2$$Co_2C_2B_3H_3$, a derivative of the known triple-decked sandwich metallocarborane 1,7,2,3-(η^5-C_5H_5)$_2$$Co_2C_2B_3H_5$, in which the central C_2B_3 ring is fused on an edge to a cyclopentadiene ring. The compounds were characterized from ^{11}B and ^1H pulse Fourier Transform NMR, unit- and high-resolution mass spectra, and infrared spectra, supported by x-ray diffraction data on (C_5H_5)CoB_9H_{13}, (C_5H_5)$_3$$Co_3B_3H_5$, ($C_5H_5$)$_3$$Co_3B_4H_4$, and μ-C_3H_4-(C_5H_5)$_2$$Co_2C_2B_3H_3$, and an earlier x-ray study of 2-(C_5H_5)CoB_4H_8. The structures are classified into three groups based on the presence of $2n + 4$, $2n + 2$, or $2n$ valence electrons in the skeletal frameworks, and provide further support for the skeletal electron-count theory in polyhedral clusters. The metal-rich di-, tri-, and tetracobalt systems are viewed as hybrids linking the boron hydride and metal cluster areas. Various aspects of the formation, structures, bonding, and properties of these compounds are discussed.

An important recent development in inorganic chemistry is the perception[1] of a close structural and electronic relationship between the polyhedral boranes and other types of cage compounds such as the metal clusters. Following the first clear exposition of this analogy by Wade[1a] in 1971 there has been a rapidly growing body of evidence to support it, including the synthesis of many heteroboranes containing transition metal or main group atoms in the polyhedral framework. In the metallocarborane family, many of the known species consist of 12-vertex icosahedral cages, and a few larger examples having 13 or 14 vertices have been reported.[2] It is the smaller species, however, which provide the most direct analogy between the borane and metal cluster areas, since few of the latter class have more than six cage atoms. The only known metallocarboranes having as few as six vertices are (η^5-C_5H_5)$CoC_2B_3H_5$ and $(CO)_3FeC_2B_3H_5$, both of which are assigned[3] octahedral structures from ^{11}B and ^1H NMR data; the octahedral geometry is as expected,[1,4] in accordance with their 14 skeletal valence electrons (two from each BH unit, three from each CH, and two from the (η^5-C_5H_5)Co or $(CO)_3Fe$ groups). These molecules are isoelectronic with octahedral clusters such as $(C_2H_5)_2C_2Co_4(CO)_{10}$,[5] each having n framework atoms and $2n + 2$ framework electrons utilized in bonding.

In the area of metalloboranes (species having only metal and boron atoms in the cage), a number of open-cage systems have been reported in recent years,[6] but no closed polyhedra of any size were known when the present work was initiated. Following our report[7] of the first such species, (η^5-C_5H_5)$_2$$Co_2B_4H_6$, it appeared likely that an entire family of polyhedral cobaltaboranes as small as five or six vertices could be prepared; also, we speculated that some of these might be metal-rich systems having as many or more metal as boron atoms in the cage, thus constituting borane–metal cluster "hybrids". Meanwhile, in a related study, Hawthorne's group[8] synthesized the 12-vertex icosahedral clusters (η^5-C_5H_5)$_2$$Ni_2B_{10}H_{10}$ and (η^5-C_5H_5)$NiB_{11}H_{11}^-$, and two isomers of the closo ten-vertex (η^5-C_5H_5)$NiB_9H_9^-$ system.

The work to be described here concerns the preparation from a single reaction, that of $Na^+B_5H_8^-$, $CoCl_2$, and $Na^+C_5H_5^-$, of a series of cobaltaborane cage compounds which exhibit a variety of structures, compositions, and stereochemically novel features. We have presented two short reports[7,9] of some of these findings and wish now to give a complete account of the work and a discussion of some of its implications.

Results and Discussion

Description of the Reaction System. All of the compounds described in this paper were obtained from the reaction of the $B_5H_8^-$ ion with $CoCl_2$ and $C_5H_5^-$ in THF at −20 °C or below, with subsequent workup in air. Although the choice of reaction conditions (particularly the order of addition of reagents) has some influence on relative yields, the same compounds were obtained in each instance. The two principal products were red (η^5-C_5H_5)CoB_4H_8 (I) and orange 1,3-cyclohexadienylcobalt(II) cyclopentadiene, (C_6H_8)Co(C_5H_5), an organometallic sandwich species which was originally prepared[10] several years ago from (η^5-C_5H_5)$Co(CO)_2$ and 1,3-cyclohexadiene; we have no good explanation for the formation of the latter complex in our reaction (it will be noted that no evidence was seen for any other cyclohexadienyl products).

Compound I and the remaining cobaltaboranes, which were isolated in much smaller yield than I, were separated by column and thick-layer chromatography on silica gel as described in the Experimental Section. All of these compounds, listed with R_f values in Table I, are colored crystalline solids which are readily handled in air.

Characterization of the Products. The structures of the cobaltaborane products, as determined from x-ray studies or deduced from ^{11}B and ^1H NMR spectra, IR spectra, unit-resolution mass spectra, and exact mass measurement (Tables II–V), are illustrated in Figures 1–3. The compounds fall into three categories: nido (open-cage) systems containing $2n + 4$ skeletal valence electrons, closo systems (polyhedra with all faces triangular) having $2n + 2$ electrons, and $2n$-electron systems which are electron hyperdeficient and normally adopt capped polyhedral geometry. All of these species contain formal cobalt(III) as shown by the normal NMR spectra, which are indicative of diamagnetic spin states.

Nido Systems ($2n + 4$ electrons). The major product obtained under all conditions studied was a red solid, 2-(η^5-C_5H_5)CoB_4H_8 (I), whose structure as originally proposed[7]

Table I. Cobaltaborane Products

Compd	Color	R_f value^a
$(2n + 4)$-Electron Systems		
2-$(\eta^5\text{-}C_5H_5)CoB_4H_8$ (I)	Red	0.72
1-$(\eta^5\text{-}C_5H_5)CoB_4H_8$ (II)^b	Yellow	*c*
5-$(\eta^5\text{-}C_5H_5)CoB_9H_{13}$ (III)	Red	0.41
$(2n + 2)$-Electron Systems		
1,2-$(\eta^5\text{-}C_5H_5)_2Co_2B_4H_6$ (IV)	Violet	0.43
3-σ-C_5H_9-1,2-$(\eta^5\text{-}C_5H_5)_2Co_2B_4H_5$ (IVa)	Violet	0.63
4-σ-C_5H_9-1,2-$(\eta^5\text{-}C_5H_5)_2Co_2B_4H_5$ (IVb)	Violet	0.69
1,2,3-$(\eta^5\text{-}C_5H_5)_3Co_3B_3H_5$ (V)	Brown	0.33
C_5H_7-$(\eta^5\text{-}C_5H_5)_3Co_3B_3H_4$ (Va)	Brown	0.45
μ(2,3)-C_3H_4-1,7,2,3-$(\eta^5\text{-}C_5H_5)_2Co_2C_2B_3H_3$ (VI)	Red	0.34
$2n$-Electron Systems		
$(\eta^5\text{-}C_5H_5)_3Co_3B_4H_4$ (VII)	Yellow	0.42
$(\eta^5\text{-}C_5H_5)_4Co_4B_4H_4$ (VIII)	Green	0.51

[a] Elution in 50% benzene/hexane. [b] Obtained by thermal rearrangement of I (see text). [c] R_f not measurable; very near solvent front.

Table II. 32.1-MHz ^{11}B FT NMR Data ($CDCl_3$ solution)

Compd	δ,^{a} ppm (J, Hz)	Rel area
I	6.2 (154), −15.9 (136)	1,3
II	−4.4 (162)	
III	30.2 (170), 25.1 (200), 12.3 (160), 8.0 (160), 2.2 (160), −2.9 (160), −16.0 (160), −36.4 (160)	1,1,1,2, 1,1, 1,1
IV	61.1 (151), 19.4 (146)	2,2
IVa	59.3 (149), 39.2,^{b} 18.7 (122)	2,1,1
IVb	76.2,^{b} 55.9 (142), 17.7 (129)	1,1,2
V	62.7 (~112)	
Va	99.8 (228), 63 (225), 61^b	1,1,1
VI	64.4 (130), 4.2^c	1,2
VII	141.4,^{c} 86.6 (146)	1,3
VIII	121.4 (137)	

[a] Chemical shifts referenced to boron trifluoride etherate, with *positive values indicating shift to lower field* (*less shielding*), in conformity with the new sign convention adopted at the Third International Meeting on Boron Chemistry, Munich and Ettal, West Germany, July 1976. [b] Singlet. [c] Broad resonance, J_{HB} not measurable.

Table III. 100-MHz ^1H FT NMR Data, ^{11}B-Decoupled ($CDCl_3$ solution)

Compd	δ,^{a} ppm (rel area)	Assignment
I	5.13 (5)	C_5H_5
	3.64 (1)	H-B
	2.79 (1)	H-B
	1.70 (2)	H-B
	−3.59 (2)	B-H-B
	−15.28 (2)^b	B-H-Co
II	5.01 (5)	C_5H_5
	2.82 (4)^c	H-B
	−4.30 (4)	B-H-B
III	5.39 (5)	C_5H_5
	−2.5 (3)	B-H-B
	−19.2 (1)	B-H-Co
IV	5.21 (10)	C_5H_5
	6.30 (2)	H-B
	3.14 (2)	H-B
	−12.58 (2)	Co-H
IVa	5.13 (10)	C_5H_5
	6.18 (2)	H-B
	3.12 (1)	H-B
	−12.60 (2)	Co-H
	1.56,^{d} 1.22^d	C_5H_9
IVb	5.18 (5)	C_5H_5
	5.09 (5)	C_5H_5
	6.00 (1)	H-B
	3.12 (2)	H-B
	−12.67	Co-H
	1.54^d	C_5H_9
V	4.90 (15)	C_5H_5
	7.11 (3)	H-B
	−14.48 (2)	Co-H
VI	4.28 (10)	C_5H_5
	6.75 (1)	H-B
	3.75 (1)	H-B
	3.52 (1)	H-B
	7.34 (1)^e	C_3H_4
	6.88 (1)^e	C_3H_4
	3.84 (2)^f	C_3H_4
VII	4.65	C_5H_5
	14.45 (1)	H-B
	9.40 (3)	H-B
VIII	4.49 (20)	C_5H_5
	11.83 (4)	H-B

[a] Parts per million relative to $(CH_3)_4Si$, with positive sign indicating shift to lower field (less shielding). [b] $J_{H_{bridge}-H_{terminal}} = 72$ Hz. [c] $J_{HB} = 160$ Hz. [d] Largest peak of multiplet. [e] Center peak of multiplet. [f] Apparent (not true) triplet.

Table IV. High-Resolution Mass Measurements

Compd	Formula^a	Calcd mass	Obsd mass
I	$^{12}C_5{}^{11}B_4{}^{59}Co{}^1H_{13}{}^+$	176.0721	176.0721
III	$^{12}C_5{}^{11}B_9{}^{59}Co{}^1H_{18}{}^+$	236.1577	236.1585
IV	$^{12}C_{10}{}^{11}B_4{}^{59}Co_2{}^1H_{16}{}^+$	298.0287	298.0285
V	$^{12}C_{15}{}^{11}B_3{}^{59}Co_3{}^1H_{21}{}^{+\,b}$	410.9918	410.9899
	$^{12}C_{15}{}^{11}B_3{}^{59}Co_3{}^1H_{20}{}^+$	409.9840	409.9815
VI	$^{12}C_{15}{}^{11}B_3{}^{59}Co_2{}^1H_{20}{}^{+\,b}$	351.0508	351.0530
	$^{12}C_{15}{}^{11}B_3{}^{59}Co_2{}^1H_{19}{}^+$	350.0430	350.0446
VII	$^{12}C_{15}{}^{11}B_4{}^{59}Co_3{}^1H_{20}{}^{+\,b}$	420.9933	420.9923
	$^{12}C_{15}{}^{11}B_4{}^{59}Co_3{}^1H_{19}{}^+$	419.9855	419.9867
VIII	$^{12}C_{20}{}^{11}B_4{}^{59}Co_4{}^1H_{25}{}^{+\,b}$	544.9657	544.9646
	$^{12}C_{20}{}^{11}B_4{}^{59}Co_4{}^1H_{24}{}^+$	543.9578	543.9546

[a] Parent ion except where otherwise indicated. [b] Protonated parent ion (M + 1).

(Figure 1) was later confirmed in an x-ray study by Sneddon and Voet.[11] This square-pyramidal molecule is a direct analogue of B_5H_9 in which a $(C_5H_5)Co$ group replaces a basal BH unit, each group being a formal two-electron donor to the cage framework. The similarity to B_5H_9 is underlined by a comparison of bond distances: in B_5H_9[12] the apex-to-basal B-B length is 1.69 Å, vs. 1.66 and 1.69 Å for B(1)-B(3) and B(1)-B(4), respectively, in I; in B_5H_9 the basal B-B distance is 1.80 Å, compared to 1.76 Å in I. Complex I, however, is far more stable to hydrolysis and oxidation than is B_5H_9, an observation which appears to reflect a general trend. We shall return to this point later.

Pyrolysis of I in the gas phase at 200 °C for 30 min resulted in some decomposition and produced a 10% yield of a new isomer, 1-$(\eta^5\text{-}C_5H_5)CoB_4H_8$ (II), in which the $(C_5H_5)Co$ group has moved to the apex position. The structure shown in Figure 1 is virtually certain, given the NMR equivalence of all four BH units and of all B-H-B bridging protons as well as the synthesis from I. Compound II and its analogue, 1-$(CO)_3FeB_4H_8$,[13] are key metalloborane species, in that they not only are directly related to B_5H_9 by formal replacement of BH with a metal group, but also can be viewed as analogues of metal cyclobutadiene complexes. Thus, the square planar $B_4H_8{}^{2-}$ ligand is isoelectronic with $C_4H_4{}^{2-}$, so that II is analogous to

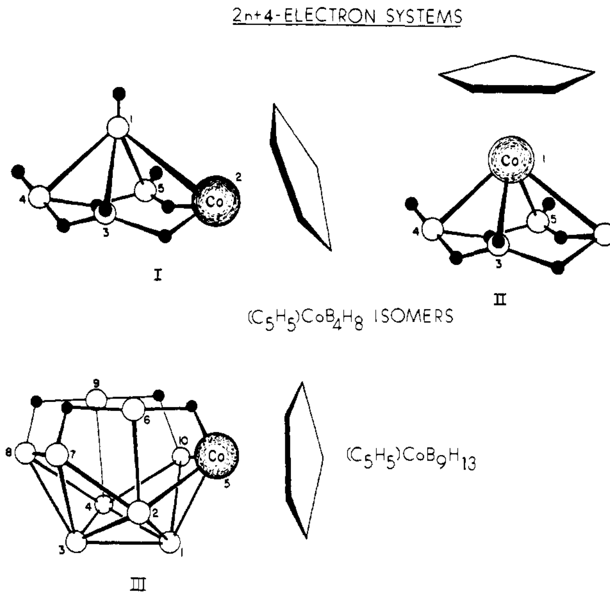

Figure 1. Structures of $(2n + 4)$-electron (nido) cobaltaboranes.

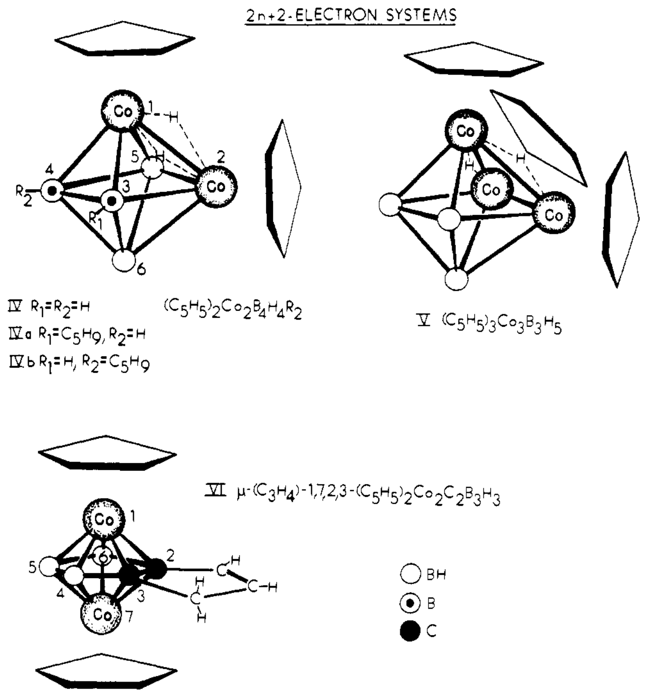

Figure 2. Structures of $(2n + 2)$-electron (closo) cobaltaboranes. Those of V and VI are established, and the others are proposed from ^{11}B and ^{1}H NMR data. The indicated locations of bridge hydrogens in IV, IVa, and IVb are suggested; those in V are supported by crystallographic evidence.

Table V. Infrared Absorptions[a]

I	3119(w), 3041(w), 2550(s), 1980(w), 1825(m), 1791(m), 1705(m), 1669(m), 1545(m), 1470(m), 1409(s), 1378(m), 1342(m), 1113(m), 1066(m), 1018(m), 999(m), 951(s), 862(s), 832(s), 671(m)
II	3114(w), 2921(w), 2451(s), 1812(m), 1484(m), 1416(w), 1113(w), 1007(m), 897(m), 824(m), 662(w)
III	3116(w), 3014(w), 2925(m), 2852(w), 2548(s), 1710(w), 1465(w), 1369(w), 1092(w), 1039(m), 999(m), 931(w), 835(m), 802(sh)
IV	3114(w), 2924(w), 2506(s), 1820(w), 1753(w), 1415(m), 1110(sh), 1075(m), 1046(m), 1007(m), 825(s), 666(m)
IVa	3105(w), 2942(m), 2858(m), 2500(s), 1815(w), 1735(w), 1668(w), 1450(w), 1415(w), 1098(m), 1045(m), 1007(m), 821(s)
IVb	3112(w), 2941(s), 2860(m), 2494(s), 1816(w), 1741(w), 1667(w), 1448(w), 1415(m), 1131(sh), 1075(m), 1027(m), 1007(s), 820(s), 654(w)
V	3109(w), 3040(w), 2976(w), 2925(m), 2473(s), 2300(w), 1726(w), 1413(m), 1248(w), 1108(m), 1070(m), 1041(m), 1002(m), 888(w), 833(m), 820(m), 809(m), 700(m)
VII	3040(m), 2927(s), 2854(m), 2683(w), 2480(s), 2302(w), 1809(w), 1729(w), 1548(w), 1414(m), 1245(m), 1154(w), 1110(w), 1004(m), 989(m), 954(m), 927(m), 914(s), 695(s)
VIII	3045(m), 2978(m), 2919(m), 2855(w), 2685(w), 2440(s), 2301(w), 1730(w), 1415(m), 1250(m), 1113(w), 1007(w), 890(w), 834(s), 823(s), 798(s), 700(s)

[a] CH_2Cl_2 solution vs. CH_2Cl_2, in cm^{-1}.

$(\eta^5\text{-}C_5H_5)Co(\eta^4\text{-}C_4H_4)$ while 1-$(CO)_3FeB_4H_8$ is a counterpart of $(CO)_3Fe(\eta^4\text{-}C_4H_4)$. It is clear that these metalloboranes play a central role in tying together the once disparate classes of metallocenes and boron hydrides. In this connection, the recent isolation[14] of $(CO)_3FeB_5H_9$, an analogue of B_6H_{10} in which an $Fe(CO)_3$ group replaces a basal BH, is an important recent contribution.

The only other nido species isolated in this study was a red trace material which was characterized as 5-$(\eta^5\text{-}C_5H_5)$-CoB_9H_{13} (III) and assigned the structure shown in Figure 1. The original elucidation[7] of this geometry from ^{11}B and ^{1}H NMR strikes us as a timely illustration of the value of the skeletal electron-count theory[1,4] in synthetic chemistry. With 24 skeletal valence electrons (two from $(C_5H_5)Co$, two from each BH unit, and one from each extra hydrogen), the molecule is a nido system analogous to $B_{10}H_{14}$; assuming the $B_{10}H_{14}$ skeletal framework, the complete asymmetry indicated by the NMR data fixed the location of the $(C_5H_5)Co$ group as the 5-position (equivalent to 7, 8, and 10). This geometry has been confirmed in a recent x-ray investigation[15] whose details again reveal a close similarity to the parent boron hydride. Thus, ignoring the B–Co bonds, a comparison of the B–B distances in III with the corresponding ones in $B_{10}H_{14}$[16] (employing a common numbering scheme) shows an average difference of only 0.019 Å, or less than three standard deviations; the largest differences occur at B(3)–B(4) and B(2)–B(6), where the bond lengths in III are shortened by 0.039 and 0.034 Å, respectively (~2%), compared to $B_{10}H_{14}$. From these findings it can be said accurately that III is a $B_{10}H_{14}$ molecule with the B(5)–H group replaced by $Co(\eta^5\text{-}C_5H_5)$.

Compound III is also closely related to the species of the $(CO)_3MB_9H_{12}R$ type prepared by lott and Gaines,[17] where M = Mn or Re and R = THF or $(C_2H_5)_3N(CH_2)_4O$.[18] These complexes are also $B_{10}H_{14}$ analogues, but interestingly the metal occupies the 6(9) position (using our numbering system) rather than the 5-vertex as in III.

Closo Systems (2*n* + 2 electrons). The reaction products included the closo octahedral cages 1,2-$(\eta^5\text{-}C_5H_5)_2Co_2B_4H_6$ (IV) and 1,2,3-$(\eta^5\text{-}C_5H_5)_3Co_3B_3H_5$ (V); perhaps surprisingly, there was no evidence for the hypothetical six-vertex monocobalt system, $(\eta^5\text{-}C_5H_5)CoB_5H_7$. In addition to the parent compounds, two cyclopentyl-substituted derivatives of IV (IVa and IVb) and an apparent cyclopentenyl-substituted derivative of V (Va) were isolated. Both IV and V are 14-electron systems with two electrons from each BH or $Co(C_5H_5)$ unit and two from the extra hydrogens, and are electronic analogues of the known octahedral species $B_6H_6^{2-}$, $C_2B_4H_6$, CB_5H_7, $(C_5H_5)CoC_2B_3H_5$, and $(CO)_3FeC_2B_3H_5$. For both IV and V, there are only two possible arrangements for cobalt and boron in an octahedral cluster and the NMR data permit assignment of the structures in Figure 2. In addition, an x-ray investigation[15] has confirmed the gross geometry proposed[9] for V.

The dicobalt species IV, as deduced from the spectroscopic observations, has C_{2v} symmetry with the twofold axis bisecting the Co(1)-Co(2) and B(4)-B(6) bonds, as a result of which Co(1)-Co(2), B(4)-B(6), and B(3)-B(5) are equivalent pairs. The "extra" hydrogen atoms are assigned bridging locations on the polyhedral surface, in either edge or face locations, but in close association with the metal atoms. The bonding to cobalt is indicated not only from the high-field ^{1}H NMR signals, typical of transition metal-hydrogen interaction, but also from x-ray data on the closely related species V (vide infra). Tautomeric exchange of these hydrogens among several locations is possible, although not required by the NMR spectra. The widely separated ^{11}B resonances at δ 61.1 and 19.4 are assigned to the equivalent pairs B(4), B(6) and B(3), B(5), respectively, as required by the proton and ^{11}B spectra of the derivatives IVa and IVb, described below. The fact that B(4) and B(6), which are adjacent to only one metal atom, exhibit a boron resonance at lower field than do B(3) and B(5), which are linked to two metals, suggests an antipodal effect involving those borons trans to the cobalt nuclei; this phenomenon supersedes, in this case, the usual observation[19,20] that ^{11}B signals of four-coordinate BH groups adjacent to two metal atoms appear at extremely low field. Significantly, the only known octahedral metallocarboranes, $(\eta^5\text{-}C_5H_5)CoC_2B_3H_5$ and $(CO)_3\text{-}FeC_2B_3H_5$, exhibit similar evidence of an antipodal effect in their ^{11}B NMR spectra.[3]

Characterization of the cyclopentyl derivatives IVa and IVb is unequivocal from the ^{11}B and ^{1}H NMR spectra, with substitution occurring at B(3) (or the equivalent location B(5)) in IVa, and at B(4) (B(6)) in IVb. In each case the presence of two BH environments in a 2:1 area ratio is shown in both the ^{11}B NMR and the ^{11}B-decoupled proton NMR spectra, with the ^{11}B resonance of the substituted boron shifted sharply downfield 15-20 ppm in both derivatives, compared to the parent compound.

The tricobalt closo system V contains as many metal as boron atoms in the framework, and thus constitutes a hybrid species linking the metal clusters and the boranes. Except for compound Va, the only other known example of an M_nB_n-type cage of any sort is the tetracobalt system VIII, described below (however, the boron-capped species VII, while not an M_nB_n cage, has a close structural relationship to V). The structure of V was deduced originally from NMR data, which distinguishes the geometry indicated in Figure 2 from the alternative arrangement, which would place the cobalt groups at vertices 1, 2, and 6. This geometry has been confirmed crystallographically with the details to be reported in a subsequent article.[15] As observed by NMR in solution, the molecule has C_{3v} symmetry with three equivalent $Co(C_5H_5)$ groups and three equivalent BH units. As in the case of the dicobalt homologue IV, there are two extra protons on the polyhedral surface, and once again the proton NMR resonance of these protons is indicative of metal-hydrogen binding. The C_{3v} symmetry on the NMR time scale implies tautomerism of the bridge hydrogens among several positions, and the x-ray data strongly suggest that *in the solid state structure* the bridge hydrogens preferentially occupy disordered locations on the three cobalt-cobalt edges.

The red species VI was originally observed only as a trace product from its mass spectrum, but was subsequently isolated and spectroscopically characterized. The elemental composition and NMR data on this compound first suggested the formula $\sigma\text{-}C_5H_5\text{-}(\eta^5\text{-}C_5H_5)_2Co_2B_3H_2$, i.e., a cyclopentadienyl-substituted derivative of the unknown system $(\eta^5\text{-}C_5H_5)_2Co_2B_3H_3$, which presumably would be a five-vertex closo (trigonal bipyramidal) system. However, we were troubled by the fact that such a polyhedron would have only ten skeletal electrons as opposed to the 12 required by theory[1,4] (and found in $C_2B_3H_5$). An x-ray structure determination[15] resolved the problem and yielded the geometry depicted in Figure 2. As shown, the "extra" C_5 ring is not a σ-bonded substituent, but has become partly incorporated into the polyhedron so that two of its carbon atoms combine with the three borons to form a planar C_2B_3 ring system sandwiched between the two $(\eta^5\text{-}C_5H_5)$Co moieties. The result is a *C,C′*-(1,3-propenylene)-disubstituted derivative of the known[21] "triple-decked sandwich" species, $1,7,2,3\text{-}(\eta^5\text{-}C_5H_5)_2Co_2\text{-}C_2B_3H_5$.[21]

The isolation of VI from this reaction has two highly unusual aspects deserving comment. First, although many reported syntheses of metallocarboranes utilize the $C_5H_5^-$ ion,[2] this appears to be the first instance of its incorporation into the polyhedral cage proper. Many examples are known of carboranes or metallocarboranes containing exopolyhedral rings fused onto the carborane cage system;[22] perhaps the most relevant here are the bis(1,2-μ-trimethylene) derivatives of $(C_2B_9H_{11})_2Ni$ complexes,[23] benzo-[24] and naphthocarborane,[25] and metallocarboranes derived from the latter two species.[26] However, all of these compounds were obtained by C,C′-disubstitution on an existing carborane polyhedron, and did not involve ring insertion into a borane cage. The second point is that the synthesis of a metallocarborane other than from a carborane is extremely rare, having been reported only twice: the reaction of $B_{10}H_{13}^-$ with $M(CO)_6$ to give $(B_{10}H_{10}COH)\text{-}M(CO)_4^-$ (M = Cr, Mo, W)[27a] and the insertion of C_2H_2 into I to give $(\eta^5\text{-}C_5H_5)CoC_2B_3H_7$.[27b]

The central $C_5B_3H_7$ fused-ring system in VI is planar with C-C distances consistent with the bond system shown; thus, the exo polyhedral ring double-bond C-C length is 1.347 (5) Å with J_{HCCH} = 5.2 Hz as calculated from the first-order proton NMR spectrum. Further discussion of this compound will be given elsewhere.[15]

Capped Closo Systems (2*n* electrons). The final two products to be described are electron-hyperdeficient species, so-called[28] because the number of skeletal valence electrons is less than the $2n + 2$ required for normal closed polyhedral (closo) systems. Both experimental[28-30] and theoretical considerations[31,32] indicate that in such circumstances the geometry adopted is a closo polyhedron in which one or more faces is capped. A simple explanation[29,31,32] is that the number of bonding molecular orbitals in a closo polyhedron ($n + 1$) is left unchanged by capping a face of that polyhedron; thus, an n-vertex capped polyhedron will require the same number of skeletal bonding electrons ($2n$) as an uncapped ($n - 1$)-vertex polyhedron.

In this study, the clearest illustration of this effect occurs in the yellow product $(\eta^5\text{-}C_5H_5)_3Co_3B_4H_4$ (VII). The ^{11}B and ^{1}H NMR spectra indicate a threefold symmetry axis, and are incompatible with any structure based on a pentagonal bipyramid, the normal seven-vertex geometry. The C_{3v} symmetry can be obtained by capping a Co_3B_3 octahedron like that in V with a fourth BH group, either on the Co_3 or the B_3 face. The structure shown in Figure 3, with a capped Co_3 face, was originally proposed[9] on the basis of the unique BH signal in the ^{11}B NMR spectrum at extremely low field, which is consistent with a low-coordinate BH adjacent to several cobalt nuclei. The alternate structure, in which the B_3 rather than the Co_3 octahedral face is capped, could not be altogether eliminated by this argument, since a BH group in a three-coordinate polyhedral vertex would be expected to exhibit resonance at moderately low field even if it were not adjacent to a metal. Thus, the unique three-coordinate BH in trigonal bipyramidal $C,3\text{-}(CH_3)_2\text{-}2,3\text{-}C_2B_3H_3$[33] displays a boron resonance 53 ppm to low field of boron trifluoride etherate. However, the resonance at δ 141.4 in VII appeared more compatible with the Co_3-capped structure, and this geometry has been verified by an x-ray structural study.[15] This system constitutes, to our knowledge, the only polyhedral borane in which a boron atom

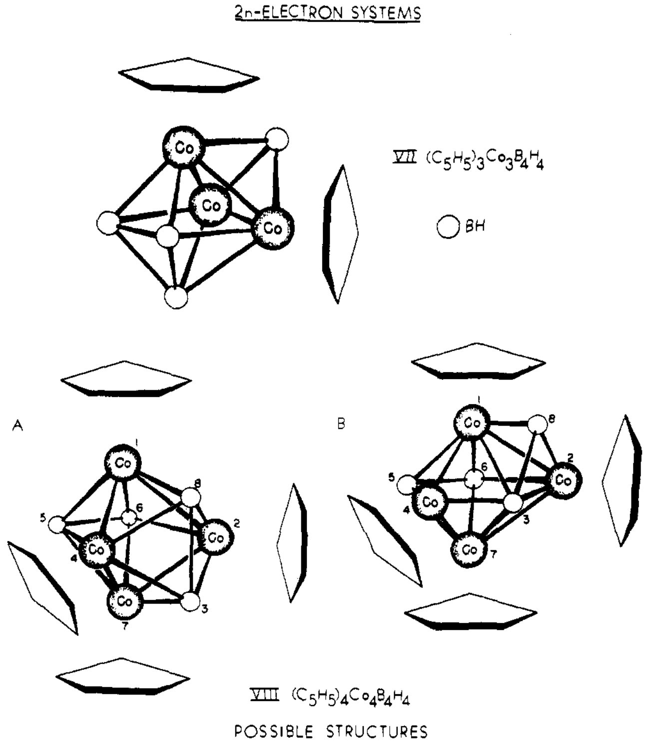

Figure 3. Structures of $2n$-electron cobaltaboranes, including the established geometry of VII and two suggested possibilities for VIII.[41] One C_5H_5 ring in VII has been omitted for clarity.

is isolated from all other borons in the molecule, and the chemistry of the unique BH should therefore be of unusual interest. In this connection VII could be regarded as a borane counterpart of the well-known family of tricobalt-carbon clusters,[34] $RCCo_3(CO)_9$, with HB and (C_5H_5) replacing RC and $(CO)_3$, respectively.

Compound VIII, a green solid characterized as $(\eta^5\text{-}C_5H_5)_4Co_4B_4H_4$, is unique among boron cage species in having four metal atoms in the framework. The 16 skeletal valence electrons suggest a capped closo structure for this system, but the NMR data rule out any such geometry, at least in a fixed sense. Structure A shown in Figure 3 has D_{2d} symmetry and is compatible with the ^{11}B and ^1H NMR observations, but is the geometry expected for an 18-electron, eight-vertex ($2n + 2$) system such as $C_2B_6H_8$ or $(\eta^5\text{-}C_5H_5)_2Co_2C_2B_4H_6$, rather than the hyperdeficient cage which VIII is presumed to have. If structure A is correct, it may be that there are trans-cage metal-metal bonding interactions (Co(1)-Co(7) and Co(2)-Co(4)) which compensate for the deficiency of two skeletal electrons and stabilize the system. (Indeed, structure A differs only in degree from a Co_4 tetrahedron with each face capped by a BH group; the latter geometry can be formally generated from A by making the four Co-Co distances equal and breaking the two B-B bonds).

Alternatively, the capped pentagonal bipyramidal structure B would be consistent with a $2n$-electron eight-vertex species, but obviously conflicts with the NMR data, which indicate equivalence of all four boron atoms and of all four $Co(C_5H_5)$ groups. Such a molecule might, however, undergo rapid fluxional rearrangement in solution, with cleavage of the Co(1)-B(3) and formation of a Co(4)-B(8) bond (or their equivalents), so that the dodecahedral structure A is perceived as a time-averaged geometry on the NMR time scale. An x-ray investigation to resolve the solid-state structure of VIII has thus far been prevented by a lack of suitable crystals.[41]

Conclusions

The reaction described here raises many questions of mechanistic, structural, stereochemical, and theoretical interest, of which we can indicate only a few. It is notable, considering the use of $B_5H_8^-$ as the borane reagent, that no five-boron products were isolated. The product distribution suggests that the major process occurring is the replacement of a boron atom in $B_5H_8^-$ by cobalt to give I, with subsequent addition of up to three more cobalts to produce the metal-rich species. There is no question that the $C_5H_5^-$ ion plays a major role in this reaction; the formation of several cyclopentyl and cyclopentenyl B-substituted species and the curious product VI suggests direct attack of the Lewis base $C_5H_5^-$ on one or more borane substrates during the course of the reaction. Furthermore, when $CoCl_2$ and NaB_5H_8 were allowed to react in the absence of cyclopentadiene, no isolable metalloboranes were found. We suspect that $C_5H_5^-$ facilitates the extraction of boron from, and introduction of additional metal atoms into, the monocobalt species initially formed. These mechanistic problems were not directly probed in this work, but certainly warrant further investigation.

Aside from the question of how it comes about kinetically, the ability of cobalt to replace boron in polyhedral borane systems, as evidenced here, strikes us as truly remarkable. It has long been clear in metallocarborane chemistry[2] that cobalt, particularly the $(\eta^5\text{-}C_5H_5)Co$ moiety, is a highly versatile structural member, and that cobaltacarboranes generally resemble their carborane analogues; indeed, cobalt is by far the most extensively used transition metal in metallocarboranes. However, in all types of metalloboron cluster compounds prior to this work there did seem to be a *de facto* limit of three metal atoms per cage, with this number attained only in large polyhedra such as $(\eta^5\text{-}C_5H_5)_3Co_3C_2B_7H_9$,[35] $(\eta^5\text{-}C_5H_5)_3Co_3C_2B_5H_7$,[3] $[(CO)_3Fe]_2(\eta^5\text{-}C_5H_5)Co(CH_3)_2C_2B_4H_4$,[36] and $(\eta^5\text{-}C_5H_5)_3Ni_3CB_5H_6$.[37] None of these species approaches the 1:1 metal/nonmetal ratio found in V and VIII. It now seems likely that, in some polyhedra at least, replacement of boron by cobalt (and perhaps other metals) can occur without limit to generate a continuum of clusters of composition $[(C_5H_5)Co]_m(BH)_n$. This is probably not attainable in large (e.g., 12-vertex) cages, given the absence of any examples of icosahedral metal clusters, but it is quite plausible for small (six to eight vertex) polyhedra.

The cobalt-boron replacement phenomenon has other aspects worthy of comment, one of which is the greatly increased hydrolytic stability of at least some of the cobaltaboranes compared to their borane analogues. All of the new compounds are resistant to attack by air and water, with degradation noticeable only after several months' exposure.[38] The stability of the $(\eta^5\text{-}C_5H_5)CoB_4H_8$ isomers I and II is especially noteworthy, since they differ from B_5H_9, a highly pyrophoric material which reacts violently with air, only by substitution of one C_5H_5Co group for a BH unit. Somewhat similar, though less dramatic, increases in stability occur when carboranes are converted to metallocarboranes, as in the replacement of the apex BH in 2,3-$C_2B_4H_8$ by $Co(\eta^5\text{-}C_5H_5)$ to give $(\eta^5\text{-}C_5H_5)CoC_2B_3H_7$.[21b] An exploration of the chemistry of the cobaltaboranes has only just begun, but it can be speculated that the combination of increased stability with retention of borane cage geometry could provide a basis for new synthetic pathways to boranes and carboranes. In addition, the presence of Co-H-B and/or Co-H-Co groups in several of these compounds suggests possible utilization as homogeneous catalysts. These and many other facets of this area are deserving of investigation.

Experimental Section

Materials. Pentaborane(9) was purchased from Callery Chemical Co., Callery, Pa., and purified by trap-to-trap distillation in vacuo. Anhydrous cobalt(II) chloride was obtained from $CoCl_2 \cdot 6H_2O$ (Baker) by dehydration in vacuo at 160 °C. Cyclopentadiene was distilled from dicyclopentadiene (Aldrich) under a nitrogen atmosphere. Sodium hydride was obtained as a 50% dispersion in mineral oil (Alfa) and used as received. All solvents were reagent grade, and tetrahydrofuran (THF) was dried over lithium aluminum hydride before use.

Spectra and Chromatography. Boron-11 and proton pulse Fourier transform NMR spectra at 32.1 and 100 MHz, respectively, were obtained on a JEOL PS-100P spectrometer interfaced to a JEOL-Texas Instruments EC-100 computer system. Unit-resolution mass spectra were obtained on a Hitachi-Perkin Elmer RMU-6E mass spectrometer. High-resolution mass spectra were recorded on an AEI MS-902 double-focusing instrument equipped with an SRI chemical ionization source. All high-resolution spectra were obtained under chemical ionizing conditions. Infrared spectra were recorded on a Beckman IR-8 spectrometer. Thin layer and preparative layer chromatography were conducted in air on precoated plates of silica gel F-254 purchased from Brinkmann Instruments, Inc. Column chromatography was accomplished on silica gel (Merck, 70-230 mesh).

Reaction of $Na^+B_5H_8^-$ with $CoCl_2$ and $Na^+C_5H_5^-$. In the course of this work, this reaction was run many times under varying conditions with essentially the same qualitative results. Initially, the salt $Na^+B_5H_8^-$ was prepared separately from B_5H_9 and NaH in THF, cooled to −196 °C, and excess $CoCl_2$ and $Na^+C_5H_5^-$ were added, followed by slow warming to room temperature. Later it was found more convenient to add $CoCl_2$ and B_5H_9 to a previously prepared solution containing $Na^+C_5H_5^-$ in large excess, part of which was consumed in deprotonating B_5H_9 to $B_5H_8^-$ [39] while the remainder was available as a ligand for cobalt. The following procedure was typical: A 50% NaH-mineral oil dispersion (103.2 mmol) was placed in a Pyrex reactor and washed with 20 mL of pentane. The reaction vessel was evacuated and 106 mmol of C_5H_6 was vacuum-distilled onto the NaH. Approximately 50 mL of dry THF was then condensed on top of this mixture at −196 °C. The mixture was allowed to warm to room temperature and maintained at that temperature until H_2 evolution had ceased; meanwhile hydrogen was removed periodically. The solution of $Na^+C_5H_5^-$ was frozen at −196 °C, the reactor evacuated, and 29.1 mmol of B_5H_9 was condensed into the flask. Anhydrous $CoCl_2$ (51.9 mmol) was also added at this time together with some additional THF. The reaction mixture was warmed to ∼−20 °C to effect solution and then was cooled to −78 °C and held at that temperature overnight with stirring. The reaction mixture was warmed to −23 °C and the solvent was removed under vacuum, after which the reactor was filled with dry nitrogen and 50 mL of dry silica gel was added. The reaction vessel and silica gel were washed with 125 mL of CH_2Cl_2 and filtered, and the filtrate was placed in a 200-mL round-bottom flask containing 7 mL of dry silica gel. The solvent was then evaporated under reduced pressure and the remaining silica gel was placed on the top of a previously prepared chromatographic column of silica gel and eluted with progressively varying solvent mixtures, starting with pure hexane, continuing with mixtures of hexane gradually enriched with benzene, then benzene-CH_2Cl_2, and finally pure CH_2Cl_2.

Six major fractions were collected from this first chromatographic separation. Each of these fractions was then subjected to additional separation via preparative TLC, with R_f values as given in Table I. The yield of 2-(η^5-C_5H_5)CoB_4H_8 (I) was 300 mg (1.36 mmol, 4.7% based on B_5H_9 used) and that of $(C_6H_8)Co(C_5H_5)$, identified from its mass spectrum and its published ^{1}H NMR and IR spectra,[10] was 202 mg. The remaining cobaltaboranes were isolated in far smaller amounts in yields of 90 mg (1%) for IV and 1-10 mg for each of the others.[40] The unit-resolution mass spectra of all products displayed intense peaks at *m/e* 124 corresponding to $(C_5H_5)Co^+$; in addition, compounds having two or more $(C_5H_5)Co$ units also exhibited an intense peak at *m/e* 189 corresponding to $(C_5H_5)_2Co^+$. The mass spectra indicated some loss of hydrogen in all cases, particularly those in which bridge hydrogens are known to be present.

Thermolysis of 2-(η^5-C_5H_5)CoB_4H_8. A 30-mg sample of I was heated at 200 °C in an evacuated Pyrex tube for 30 min to yield 3 mg of yellow 1-(η^5-C_5H_5)CoB_4H_8 (II), which was obtained as a pure solid by TLC on silica plates. The remaining products were nonvolatile, essentially insoluble residues.

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(39) In a separate experiment in the absence of $CoCl_2$ it was demonstrated that $C_5H_5^-$ reacts with B_5H_9 to give C_5H_6 and $B_5H_8^-$.

(40) Many of these cobaltaborane products, including IV, V, VII, and VIII, were obtained in substantially improved total yield (∼20% of purified products) by allowing the $(C_5H_5)CoB_4H_7^-$ ion (obtained by bridge deprotonation of I with NaH) to react with $CoCl_2$ and NaC_5H_5. These results and other aspects of the chemistry of I, presently under study, will be described in subsequent reports.

(41) **Note Added in Proof.** Since this manuscript was written, an x-ray study of VIII has established the correct structure as that of A in Figure 3: J. R. Pipal and R. N. Grimes, to be submitted for publication.