Synthesis of Four-, Five-, and Six-Boron Metallocarboranes from Polyhedral $C_2B_5H_7$

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Abstract: A series of new cobalt(III)–small carborane sandwich complexes, of which eight have been structurally characterized and a number of others identified as to composition, has been prepared from *closo*-$C_2B_5H_7$ *via* reduction with sodium naphthalide in THF, followed by reaction with $CoCl_2$ and NaC_5H_5 and air oxidation. Separation on silica gel columns and tlc plates has given $(\pi\text{-}C_2B_4H_6)Co(\pi\text{-}C_5H_5)$, $(\pi\text{-}C_2B_5H_7)Co(\pi\text{-}C_5H_5)$, $(\pi\text{-}C_2B_6H_8)Co(\pi\text{-}C_5H_5)$, $(\pi\text{-}C_2B_4H_6)Co_2(\pi\text{-}C_5H_5)_2$, $(\pi\text{-}C_2B_5H_7)Co_2(\pi\text{-}C_5H_5)_2$, $(\pi\text{-}C_2B_6H_8)Co_2(\pi\text{-}C_5H_5)_2$, $[\pi\text{-}(\sigma\text{-}C_2B_5H_6)C_2B_4H_5]Co(\pi\text{-}C_5H_5)$, and $[\pi\text{-}(\sigma\text{-}C_{10}H_7)C_2B_4H_5]Co(\pi\text{-}C_5H_5)$, all of which are air-stable sublimable solids. The characterization is based on boron-11 and proton nmr, infrared, and high resolution mass spectra. The formal $C_2B_5H_7^{2-}$, $C_2B_4H_6^{4-}$, and $C_2B_5H_7^{4-}$ ligands are novel, and the formal $C_2B_4H_6^{2-}$, $C_2B_6H_8^{2-}$, and $C_2B_6H_8^{4-}$ ligands in these complexes represent new structural isomers of previously reported ligands. Mass spectroscopic evidence has also been obtained for a number of additional metallocarboranes. The nature of the processes occurring in the reaction is discussed and possible mechanisms are considered.

Metallocarboranes (defined as boron–carbon cage systems containing one or more metal atoms bound into the framework) have been known since 1965, when Hawthorne and associates prepared transition metal π complexes of the $C_2B_9H_{11}^{2-}$ ion.[1] The early synthetic work in this field[2] utilized the base-induced extraction of a boron atom from a closed polyhedral carborane (*e.g.*, 1,2-$C_2B_{10}H_{12}$) to create an open-faced ligand such as $C_2B_9H_{11}^{2-}$, into which a metal could be inserted to give complexes of the type $M(\pi\text{-}C_2B_9H_{11})_2^{n}$ or $(\pi\text{-}C_2B_9H_{11})M(\pi\text{-}C_5H_5)^{n+1}$. In similar fashion, base removal of boron from a metallocarborane followed by metal ion insertion has given bimetallic cage species.[3] Alternatively, open-cage carboranes such as $C_2B_9H_{13}$,[4] $C_2B_4H_8$,[5] $C_2B_3H_7$,[6] and $C_3B_3H_6(CH_3)$[7] have been employed as metallocarborane precursors involving transition or main-group metals.

In a somewhat different approach developed recently,[8] a polyhedral carborane reacts with an electron-donating reagent *without* cage degradation to yield a presumed open-cage dianion into which a metal ion can be inserted to generate a metallocarborane. Since the end product of such a sequence is a cage system having one more atom than the original carborane, the discoverers of this reaction have labeled it "polyhedral expansion."[8b] At this writing, this method has been utilized in the synthesis of 9-, 10-, 11-, and 13-atom polyhedral metallocarboranes from 1,6-$C_2B_6H_8$,[8a] 1,6-$C_2B_8H_{10}$,[8b] and 1,2-$C_2B_{10}H_{12}$.[8c]

As a part of our exploration of small metallocarborane chemistry we have examined the application of the polyhedral expansion technique to *closo*-$C_2B_5H_7$, a pentagonal bipyramidal cage in which the carbons are in equatorial, nonadjacent positions. The results indicate an exceedingly complex reaction system in which net cage expansion occurs to a partial extent but the predominant characterized products, like the original carborane, consist of seven-atom polyhedra. In our initial paper on this reaction we describe the characterization of a number of the metallocarborane products, with additional findings, including evidence for reaction mechanisms, to be presented in subsequent reports.

Results and Discussion

General Observations. The reaction of $C_2B_5H_7$ with 2 mol equiv of sodium naphthalide at 25° in tetrahydrofuran (THF) proceeds without evolution of H_2 or other volatiles, yielding a dark orange solution. Treatment of this material with NaC_5H_5 and anhydrous $CoCl_2$ in THF at 25° under a nitrogen atmosphere produces an initially blue-green solution which gradually changes to dark brown over a period of several hours. Subsequent evaporation of most of the THF, treatment with a water–acetone mixture, and exposure to air followed by separation of the products *via* column and thin-layer chromatography on silica gel have disclosed more than 20 neutral metallocarborane products. Ionic products of the reaction, including the expected biscarboranyl cobalt(III) species $[(\pi\text{-}C_2B_{n-2}H_n)_2Co^-]$, have not been investigated and are not dealt with in this report, which is concerned only with neutral metallocarboranes.

Eight compounds have been structurally characterized by ^{11}B and ^1H nmr, infrared, and mass spectra. In addition, it is clear from mass spectroscopic evidence that a large number of additional metallocarboranes—at least 20—are present in small quantities. Many of these trace materials have been tentatively identified as to composition from their molecular ion masses and

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[1] M. F. Hawthorne, D. C. Young, and P. A. Wegner, *J. Amer. Chem. Soc.*, **87**, 1818 (1965).

[2] For recent reviews, see (a) M. F. Hawthorne, *Pure Appl. Chem.*, **29**, 547 (1972); (b) L. J. Todd, *Advan. Organometal. Chem.*, **8**, 87 (1970); (c) R. N. Grimes, "Carboranes," Academic Press, New York, N. Y., 1970, pp 207–232.

[3] J. N. Francis and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **90**, 1663 (1968), and subsequent papers.

[4] (a) G. Popp and M. F. Hawthorne, *ibid.*, **90**, 6553 (1968); (b) D. A. T. Young, G. R. Willey, M. F. Hawthorne, M. R. Churchill, and A. H. Reis, Jr., *ibid.*, **92**, 6663 (1970).

[5] (a) R. N. Grimes, *ibid.*, **93**, 261 (1971); (b) R. N. Grimes and W. J. Rademaker, *ibid.*, **91**, 6498 (1969); (c) R. N. Grimes, W. J. Rademaker, M. L. Denniston, R. F. Bryan, and P. T. Greene, *ibid.*, **94**, 1865 (1972); (d) L. G. Sneddon and R. N. Grimes, *ibid.*, **94**, 7161 (1972).

[6] D. A. Franz, V. R. Miller, and R. N. Grimes, *ibid.*, **94**, 412 (1972).

[7] (a) J. W. Howard and R. N. Grimes, *ibid.*, **91**, 6499 (1969); (b) J. W. Howard and R. N. Grimes, *Inorg. Chem.*, **11**, 263 (1972).

[8] (a) G. B. Dunks and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **92**, 7213 (1970); (b) W. J. Evans and M. F. Hawthorne, *ibid.*, **93**, 3063 (1971); (c) G. B. Dunks, M. M. McKown, and M. F. Hawthorne, *ibid.*, **93**, 2541 (1971).

Table I. Molecular Ion Masses of Metallocarboranes[a]

Compound	Ion[b]	Calcd mass	Measd mass
I	$^{12}C_7{}^{11}B_4{}^1H_{12}{}^{59}Co^+$ (P + 1)	199.0643	199.0637
	$^{12}C_7{}^{11}B_4{}^1H_{11}{}^{59}Co^+$	198.0564	198.0556
	$^{12}C_7{}^{11}B_3{}^{10}B{}^1H_{11}{}^{59}Co^+$	197.0609	197.0605
II	$^{12}C_7{}^{11}B_5{}^1H_{13}{}^{59}Co^+$ (P + 1)	211.0812	211.0807
	$^{12}C_7{}^{11}B_5{}^1H_{12}{}^{59}Co^+$	210.0733	210.0745
	$^{12}C_7{}^{11}B_4{}^{10}B{}^1H_{12}{}^{59}Co^+$	209.0769	209.0775
III	$^{12}C_7{}^{11}B_6{}^1H_{14}{}^{59}Co^+$ (P + 1)	223.0985	223.0991
	$^{12}C_7{}^{11}B_6{}^1H_{13}{}^{59}Co^+$	222.0907	222.0906
	$^{12}C_7{}^{11}B_5{}^{10}B{}^1H_{13}{}^{59}Co^+$	221.0933	221.0944
IV	$^{12}C_{12}{}^{11}B_4{}^1H_{17}{}^{59}Co_2{}^+$ (P + 1)	323.0366	323.0345
	$^{12}C_{12}{}^{11}B_4{}^1H_{16}{}^{59}Co_2{}^+$	322.0288	322.0280
	$^{12}C_{12}{}^{11}B_3{}^{10}B{}^1H_{16}{}^{59}Co_2{}^+$	321.0324	321.0341
V	$^{12}C_{12}{}^{11}B_5{}^1H_{18}{}^{59}Co_2{}^+$ (P + 1)	335.0537	335.0570
	$^{12}C_{12}{}^{11}B_5{}^1H_{17}{}^{59}Co_2{}^+$	334.0458	334.0448
	$^{12}C_{12}{}^{11}B_4{}^{10}B{}^1H_{17}{}^{59}Co_2{}^+$	333.0495	333.0472
VI	$^{12}C_{12}{}^{11}B_6{}^1H_{18}{}^{59}Co_2{}^+$ [c]	346.0630	346.0664
	$^{12}C_{12}{}^{11}B_6{}^{10}B{}^1H_{18}{}^{59}Co_2{}^+$	345.0666	345.0632
VII	$^{12}C_9{}^{11}B_9{}^1H_{17}{}^{59}Co^+$ (P + 1)	283.1500	283.1500
	$^{12}C_9{}^{11}B_9{}^1H_{16}{}^{59}Co^+$	282.1422	282.1489[d]
	$^{12}C_9{}^{11}B_8{}^{10}B{}^1H_{16}{}^{59}Co^+$	281.1459	281.1535[e]
VIII	$^{12}C_{17}{}^{11}B_4{}^1H_{18}{}^{59}Co^+$ (P + 1)	325.1111	325.1105
	$^{12}C_{17}{}^{11}B_4{}^1H_{17}{}^{59}Co^+$	324.1034	324.1070
	$^{12}C_{17}{}^{11}B_3{}^{10}B{}^1H_{17}{}^{59}Co^+$	323.1070	323.1061

[a] Chemical ionization spectra obtained in Ar–H_2O atmosphere; only peaks corresponding to species containing 1 or 0 ^{10}B atoms are shown. [b] (P + 1) species are protonated parent ions. [c] P + 1 peak not available. [d] Intense peak arising from overlapping contributions of $^{12}C_9{}^{11}B_9{}^1H_{16}{}^{59}Co^+$ and $^{12}C_9{}^{11}B_8{}^{10}B{}^1H_{17}{}^{59}Co^+$ (calculated $m/e = 282.1534$). [e] Intense peak arising from overlapping contributions of $^{12}C_9{}^{11}B_8{}^{10}B{}^1H_{16}{}^{59}Co^+$ and $^{12}C_9{}^{11}B_7{}^{10}B_2{}^1H_{17}{}^{59}Co^+$ (calculated $m/e = 281.1571$).

Table II. Infrared Absorptions (cm^{-1}, CCl_4 *vs.* CCl_4)

I	II	III	IV	V	VI	VII	VIII
3940 (w)	3940 (w)	3940 (w)	3940 (w)	3935 (w)	2525 (vs)	3940 (w)	3940 (w)
3115 (w)	2560 (vs)	3115 (w)	3110 (w)	3115 (w)	1416 (m)	3120 (w)	3100 (sh)
3055 (w)	1828 (w)	3085 (w)	3020 (w)	3030 (w)	1126 (m)	3100 (w)	3050 (m)
2570 (vs)	1766 (w)	2565 (vs)	2535 (vs)	2545 (vs)	1061 (m)	3050 (s)	3005 (w)
1825 (w)	1680 (w)	1829 (w)	1804 (w)	2495 (vs)	1029 (m)	2610 (vs)	2570 (vs)
1761 (w)	1424 (sh)	1760 (w)	1735 (w)	1827 (w)	1009 (m)	1831 (w)	1825 (w)
1681 (w)	1416 (m)	1676 (w)	1657 (w)	1756 (w)	904 (m)	1767 (w)	1760 (w)
1422 (sh)	1318 (m)	1421 (m)	1417 (m)	1655 (w)	885 (s)	1689 (w)	1680 (w)
1414 (m)	1156 (m)	1143 (s)	1350 (w)	1414 (w)	864 (m)	1413 (m)	1595 (w)
1155 (s)	1114 (m)	1112 (s)	1115 (m)	1113 (s)	659 (m)	1355 (s)	1467 (m)
1136 (sh)	1097 (s)	1093 (s)	1086 (s)	1085 (s)		1186 (m)	1424 (m)
1113 (m)	1057 (s)	1060 (m)	1018 (m)	1009 (s)		1112 (m)	1413 (m)
1038 (s)	1030 (m)	1010 (s)	1010 (m)	992 (sh)		1036 (m)	1371 (m)
1004 (m)	1008 (m)	917 (s)	1003 (m)	934 (w)		1012 (w)	1337 (s)
908 (m)	975 (m)	855 (sh)	962 (m)	871 (sh)		1005 (w)	1299 (s)
862 (s)	913 (w)	825 (s)	820 (m)	851 (s)		913 (m)	1269 (w)
709 (w)	884 (w)	797 (m)	697 (m)	700 (w)		865 (m)	1235 (m)
694 (s)	761 (w)			687 (w)		834 (s)	1195 (m)
	732 (m)					707 (m)	1134 (s)
	714 (w)						1111 (m)
	649 (w)						1035 (s)
							1010 (m)
							936 (w)
							909 (m)
							855 (s)
							829 (s)
							715 (m)
							660 (m)

intensity profiles, but further characterization has not been attempted in this study, and the emphasis in this paper is on the eight well-characterized species I–VIII.

The major product, a yellow solid obtained in 20–25% yield, has been characterized as (π-$C_2B_4H_6$)Co(π-C_5H_5) (I). Formed in much smaller yields are the additional monocobalt species (π-$C_2B_5H_7$)Co(π-C_5H_5) (II, orange) and (π-$C_2B_6H_8$)Co(π-C_5H_5) (III, red); the dicobalt species (π-$C_2B_4H_6$)Co_2(π-C_5H_5)$_2$ (IV, red), (π-$C_2B_5H_7$)Co_2(π-C_5H_5)$_2$ (V, red-brown), and (π-$C_2B_6H_8$)Co_2(π-C_5H_5)$_2$ (VI, red-brown); a carboranyl-substituted complex, [π-(σ-$C_2B_5H_6$)$C_2B_4H_5$]Co(π-C_5H_5) (VII, yellow); and a naphthyl derivative, [π-(σ-$C_{10}H_7$)$C_2B_4H_5$]Co(π-C_5H_5) (VIII, yellow). All of the compounds I–VIII are sublimable and air-stable (some decomposition of II has been noted during chromatography on silica gel) and all are diamagnetic from nmr evidence and hence assumed to contain formal Co(III). The formal $C_2B_5H_7{}^{2-}$, $C_2B_4H_6{}^{4-}$, and $C_2B_5H_7{}^{4-}$ ligands have not been reported previously, while the $C_2B_4H_6{}^{2-}$, $C_2B_6H_8{}^{2-}$, and $C_2B_6H_8{}^{4-}$ ligands are evidently new structural isomers of carborane ligands described earlier (*vide infra*).

The presence of trace amounts of larger polyhedral species is clearly indicated in the mass spectra of several tlc fractions. Thus, ($C_2B_7H_9$)Co(C_5H_5), ($C_2B_8H_{10}$)Co(C_5H_5), and ($C_2B_9H_{11}$)Co(C_5H_5) are identifiable from their sharp cutoffs at *m/e* 234, 246, and 258, respectively, and corresponding seven-, eight-, and nine-boron profiles, but in the absence of nmr data it cannot be ascertained whether these products are identical with previously reported complexes having the same compositions.[8b,9]

Structural Characterization. Compounds I–VIII exhibit strong mass spectroscopic parent peaks, and in each case the intensities in the parent region are in very close agreement with the calculated composition based on known isotopic distributions. In addition,

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(9) (a) M. F. Hawthorne and T. A. George, *J. Amer. Chem. Soc.*, **89**, 7114 (1967); (b) T. A. George and M. F. Hawthorne, *ibid.*, **90**, 1661 (1968); **91**, 5475 (1969); (c) M. F. Hawthorne, D. C. Young, T. D. Andrews, D. V. Howe, R. L. Pilling, A. D. Pitts, M. Reintjes, L. F. Warren, and P. A. Wegner, *ibid.*, **90**, 879 (1968).

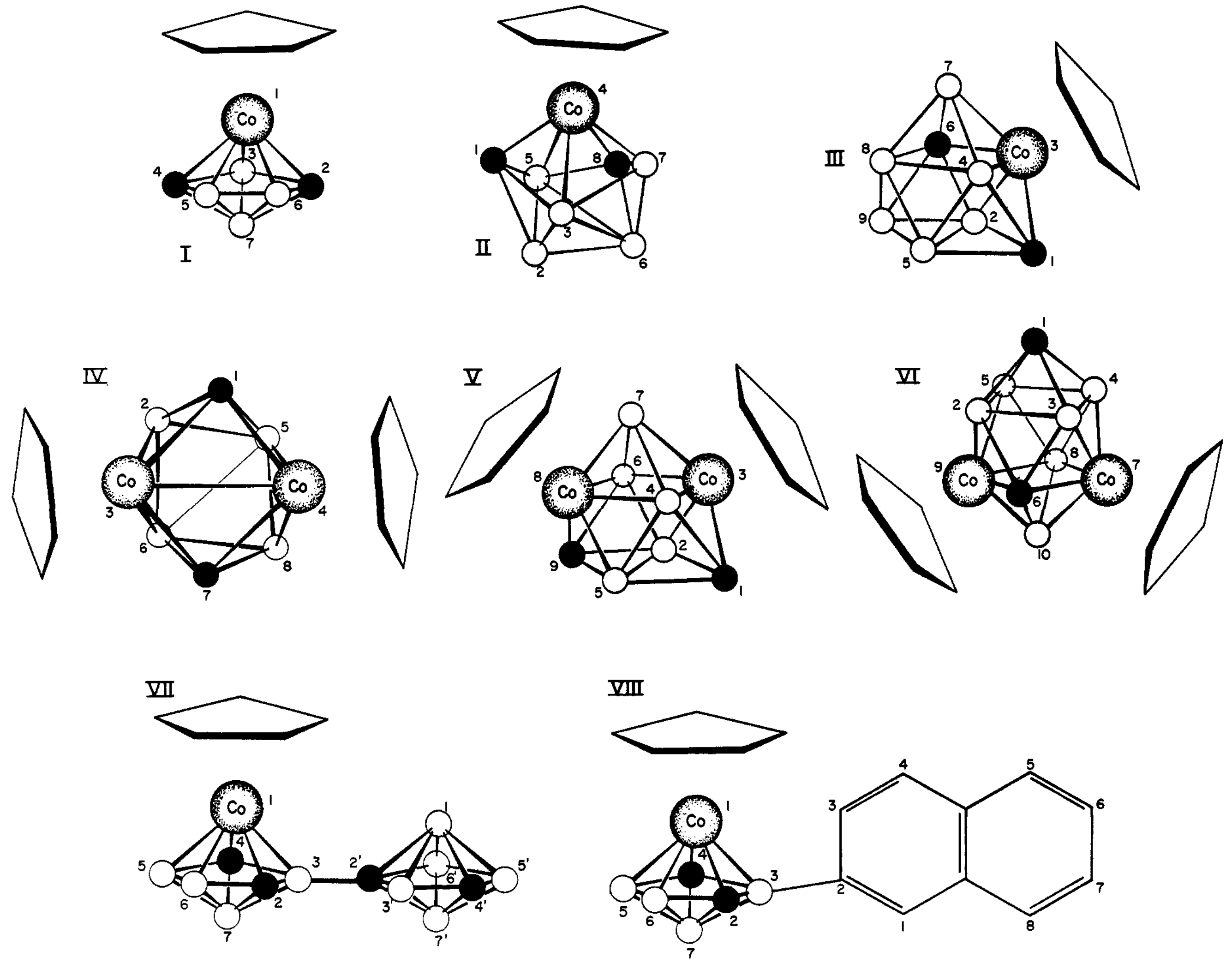

Figure 1. Proposed structures of metallocarboranes I–VIII. Solid circles represent carbon, open circles boron; hydrogen atoms are omitted for clarity.

the elemental composition of each complex has been confirmed by exact mass determination on a high-resolution spectrometer (Table I). In all cases, the masses of ions corresponding to various combinations of boron isotopes have been measured in addition to the usual boron-11 monoisotopic species, thus providing additional proof of composition (for reasons of space limitation, Table I lists only three ions per compound). The mass spectrum of each metallocarborane contains an intense peak at *m/e* 124 corresponding to $^{59}Co^{12}C_5{}^1H_5{}^+$, and the dicobalt complexes also exhibit a very strong peak at *m/e* 189 corresponding to $^{59}Co(^{12}C_5{}^1H_5)_2{}^+$. The infrared spectra of I–VIII (Table II) exhibit B–H stretching bands as well as absorptions attributed to cyclopentadienyl and carboranyl C–H groups.

Table III. 32.1-MHz ^{11}B Nmr Data

Complex	δ, ppm (*J*, Hz)[a]	Area ratio
I	−6.7 (166), −1.4 (170)	3:1
II[b]	−56.5 (172), −12.8 (144), +1.8 (166), +15.7 (158), +21.0 (177)	1:1:1:1:1
III	−66.5 (155), −4.2 (177), +3.6 (186), +9.3 (168), +16.0 (141), +20.7 (158)	1:1:1:1:1:1
IV	−56.2 (159), +6.1 (154)	2:2
V	−116.3 (156), −4.0 (165), +11.6 (161)	1:2:2
VI	−81 (143), +3.4 (147), +5.9 (141), +15 (∼150)	1:2:2:1
VII	−8.8 (177), 7.0 (163), −4.5, +1.9 (162), +20.4 (175)	2:3:1:1:2[c]
VIII	−10.1, −7.7 (155), −2.8 (155)	1:2:1[c]

[a] Chemical shifts in ppm relative to $BF_3 \cdot O(C_2H_5)_2$. All spectra were obtained in CCl_4 solution. [b] Sample contained distinguishable impurities. [c] Estimated from overlapping peaks.

The nmr data presented in Tables III and IV are consistent with the geometries in Figure 1, but in several cases alternative isomeric structures cannot be ruled out at this stage (the suggested structures are based on idealized polyhedra having seven–ten vertices and are analogous to isoelectronic carboranes and metallocarboranes whose structures are known from X-ray studies[2]). In the following discussion, it is assumed *a priori* that the cobalt atoms occupy only five-coordinate vertices in the polyhedral frameworks (coordination sites other than 4 and 5 do not occur in the polyhedra under discussion), a limitation which sharply reduces the number of isomeric structures that must be considered. A basic premise is that the carborane ligands are six-electron donors analogous to the $C_5H_5{}^-$ and $C_2B_9H_{11}{}^{2-}$ (dicarbollide) ions; in the case of bifunctional ligands such as $C_2B_4H_6{}^{4-}$, six electrons are donated to each of two metal atoms. It appears unlikely that a d^6 metal atom would adopt four-coordina-

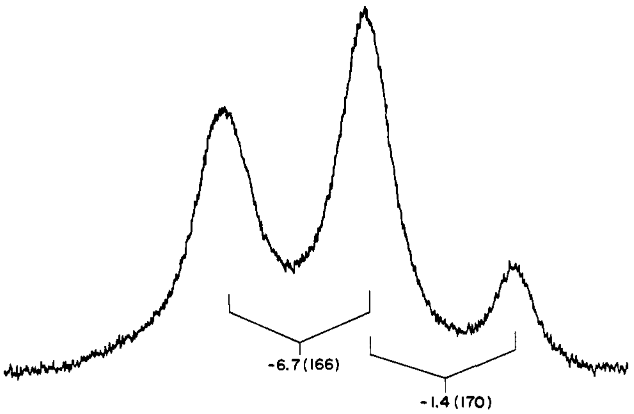

Figure 2. The 32-MHz ^{11}B nmr spectrum of (π-2,4-$C_2B_4H_6$)-Co(π-C_5H_5) (I) in CCl_4 solution. Chemical shifts are in ppm relative to $BF_3 \cdot O(C_2H_5)_2$ and coupling constants are in parentheses.

Table IV. 100-MHz ^1H Nmr Data

Complex	δ, ppm[a] C_5H_5	δ, ppm[a] Carborane CH	Area ratio
I	−4.86	−3.90	5:2
II	−4.86	−4.40 −3.94	5:1:1
III	−4.91	−5.79 −3.70	5:1:1
IV	−4.46	−2.76	10:2
V	−4.81	−3.88	10:2
VI	−4.88	−4.68 −4.44	10:1:1
VII	−4.80	−3.73[b,c] −5.75	5:2:1
VIII	−4.68	−4.33[d,c] −7.45[e,f] −7.86[e,f] −8.38[e]	5:2:2:4:1

[a] Chemical shifts relative to $(CH_3)_4Si$; all spectra were obtained in CCl_4 solution. H–B quartets are largely masked by the H–C peaks. [b] Doublet, $J = 5$ Hz. [c] Attributed to H–H coupling (see text). [d] Doublet, $J = 6$ Hz. [e] Naphthyl peaks. [f] Most intense peak of multiplet (see Figure 7).

tion in preference to an available five-coordinate site, and no such metallocarborane has been reported.

A more tentative general assumption is that the cage carbon atoms occupy nonadjacent vertices in the polyhedra. The basis of this postulate is that the carbons are nonadjacent in the $C_2B_5H_7$ precursor as well as in the major product, (π-$C_2B_4H_6$)Co(π-C_5H_5) (complex I), for which unequivocal structural data are available as discussed below. We have used this assumption as a guiding principle in assigning probable structures, but in no sense suggest it as a rigid rule.

Finally, the presence of peaks at extremely low field (−57 to −116 ppm relative to $BF_3 \cdot (C_2H_5)_2O$) in the ^{11}B nmr spectra of II–VI is interpreted as arising from BH groups occupying four-coordinate positions in eight-, nine-, and ten-atom polyhedra and bonded to one or more cobalt atoms. Although four-coordinate vertices occur in other cases (*e.g.*, seven-atom polyhedra), examination of models suggests that those in the eight- to ten-atom cages involve smaller polyhedral angles and are significantly more exposed. Indeed, boron atoms occupying four-coordinate positions in the carboranes $C_2B_6H_8$, $C_2B_7H_9$, and $C_2B_8H_{10}$ and their alkyl derivatives exhibit moderately low-field resonances ($\delta \sim -25$ to -7).[10] The much greater downfield shift in compounds II–VI is surely attributable to the metal atoms, which consequently are presumed to be adjacent to the BH groups in question. The structural assignments are summarized as follows.

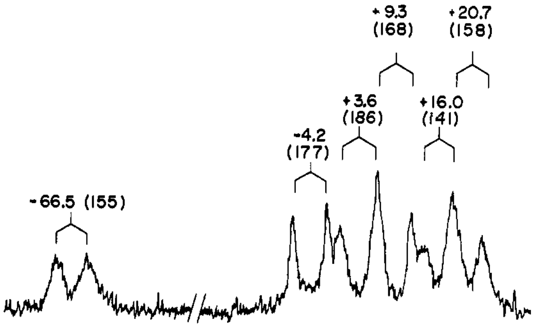

Figure 3. The 32-MHz ^{11}B nmr spectrum of (π-$C_2B_6H_8$)Co(π-C_5H_5) (III) in CCl_4 solution. Data are given as in Figure 2.

Complex I. The proton nmr spectrum indicates that the CH groups are equivalent; hence both are equatorial. Although the nmr data alone do not distinguish between two isomers in which the cage carbons are adjacent and nonadjacent, respectively, the structure of I has been established as (π-(1)-2,4-$C_2B_4H_6$)Co(π-C_5H_5) (Figure 1)[11] by the independent synthesis[12] of the alternative isomer, (π-(1)-2,3-$C_2B_4H_6$)Co(π-C_5H_5) from $Na^+[2,3\text{-}C_2B_4H_7^-]$, $CoCl_2$, and NaC_5H_5. The ^{11}B nmr spectrum of I (Figure 2) exhibits two overlapping doublets in an apparent 3:1 area ratio; since there cannot be three equivalent borons in the molecule, the larger doublet must consist of superimposed resonances from nonequivalent BH groups.[13]

Compounds containing the 2,4-$C_2B_4H_6^{2-}$ ligand have been previously unknown, although formal 2,3-$C_2B_4H_6^{2-}$ exists in (π-$C_2B_4H_6$)Fe(CO)$_3$,[5a] (π-$C_2B_4H_6$)Fe(π-C_5H_5),[5d] and 1-$CH_3GaC_2B_4H_6$.[5b,c]

Complex II. A polyhedron containing five nonequivalent borons and two nonequivalent carbons is indicated, with two four-coordinate BH groups of which one is adjacent to cobalt (*vide supra*). These considerations lead to a unique structure, (π-(4)-1,8-$C_2B_5H_7$)-Co(π-C_5H_5). (It should be noted that the (4)-7,8 isomer would have equivalent carbon atoms and an equivalent (3,5) pair of borons, both of which are inconsistent with the nmr data.)

Complex III. The ^{11}B nmr (Figure 3) and ^1H nmr spectra indicate that all six borons and both carbons are nonequivalent, with one four-coordinate BH adjacent to cobalt; the remaining four-coordinate vertex adjacent to the metal is then occupied by carbon. Assuming nonadjacent carbon atoms, three isomers are possible, but (π-(3)-1,6-$C_2B_6H_8$)Co(π-C_5H_5) is slightly

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

(11) The number in parentheses indicates the position of the metal atom in the polyhedron, and the other numbers designate the cage carbon atoms.

(12) L. G. Sneddon and R. N. Grimes, manuscript in preparation.

(13) Coincidental superposition of nonequivalent boron resonances has been observed in other four-boron metallocarboranes, including (π-$C_2B_3H_7$)Fe(CO)$_3$,[5a] whose structure has been established in an X-ray study.[14]

(14) See ref 6, footnote 11a.

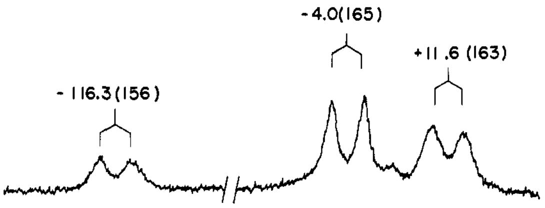

Figure 4. The 32-MHz ^{11}B nmr spectrum of (π-$C_2B_5H_7$)Co_2(π-C_5H_5)$_2$ (V) in CCl_4 solution. Data are given as in Figure 2.

favored inasmuch as both carbons are bonded to the metal.

The (π-$C_2B_6H_8$)$Mn(CO)_3^-$ ion reported by George and Hawthorne[15] contains a different formal $C_2B_6H_8^{2-}$ ligand in which both cage carbons are proposed to occupy four-coordinate apex positions.

The presence of a second ($C_2B_6H_8$)Co(C_5H_5) isomer among the reaction products has been established from its mass spectrum, which is nearly identical with that of III, and its tlc elution rate on silica, which differs considerably from that observed for III. Nmr data have not been obtained for the second isomer due to insufficient sample.

Complex IV. The simple ^{11}B nmr spectrum, which contains two widely separated doublets of equal area, suggests a symmetrical structure containing equivalent pairs of four-coordinate and five-coordinate BH groups. The CH and Co(C_5H_5) groups are also in equivalent pairs, as shown from the ^1H nmr data. The only such D_{2d} polyhedral structure having nonadjacent carbons is (π-(3,4)-1,7-$C_2B_4H_6$)Co_2(π-C_5H_5)$_2$ (Figure 1), but the (π-(3,5)-1,2-$C_2B_4H_6$)Co_2(π-C_5H_5)$_2$ isomer with adjacent carbons is also consistent with the nmr data.

Complex V. The ^{11}B nmr (Figure 4) and proton nmr data, combined with the arguments presented above, lead to a favored structure, (π-(3,8)-1,9-$C_2B_5H_7$)-Co_2(C_5H_5)$_2$, depicted in Figure 1. This isomer contains a C_2 symmetry axis which generates equivalent pairs of borons (2,5 and 4,6) as well as equivalent CH and Co(C_5H_5) groups. The extremely low-field ^{11}B nmr resonance at δ -116 is assigned to the unique four-coordinate B(7)–H unit adjacent to both cobalt atoms.

Complex VI. The (π-(7,9)-1,6-$C_2B_6H_8$)Co_2(π-C_5H_5)$_2$ isomer (Figure 1) is indicated from the symmetry requirements implied by the nmr data and by the assignment of the ^{11}B nmr resonance at δ -81 to an apex BH adjacent to two metal atoms. Since there are no other ^{11}B nmr peaks at even moderately low field, it is highly probable that the other apex is occupied by carbon, and the assumption of nonadjacent carbons leads uniquely to the structure shown. This compound is isomeric with, but not identical with, a previously reported[8a] ($C_2B_6H_8$)Co_2(C_5H_5)$_2$ species whose ir, ^{11}B nmr, and ^1H nmr spectra are distinct from those of VI.

Complex VII. The ^{11}B nmr (Figure 5) and ^1H nmr spectra indicate the structure σ-3-(2′,4′-$C_2B_5H_6$)-[π-(1)-2,4-$C_2B_4H_5$]Co(π-C_5H_5), shown in Figure 1. A linked-cage structure is virtually certain, since a single 14-atom CoC_4B_9 polyhedron is not plausible. Moreover, the ^{11}B nmr spectrum is strongly suggestive of a combination of the spectra of (π-(1)-2,4-$C_2B_4H_6$)Co(π-C_5H_5) (complex I) and 2,4-$C_2B_5H_7$;[10] alternative possibilities such as σ-($C_2B_4H_5$)-[π-$C_2B_5H_6$]Co(π-C_5H_5) are more difficult to reconcile with the nmr data. In addition, since complex I is the major product and 2,4-$C_2B_5H_7$ is the starting material in the overall reaction, a linked complex derived from these cage systems is not unreasonable. The high-field doublet of area 2 is assigned to the B(1′,7′)-H apex groups in the $C_2B_5H_6$ cage, which are rendered equivalent by free rotation about the σ bond linking the two polyhedra.

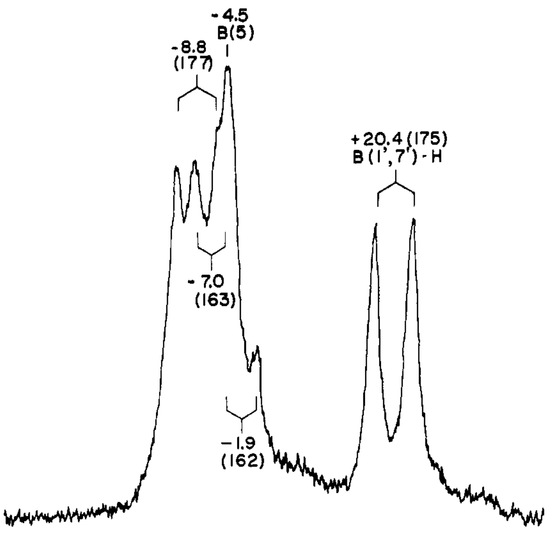

Figure 5. The 32-MHz ^{11}B nmr spectrum σ-3-(2,4-$C_2B_5H_6$)-[π-(1)-2,4-$C_2B_4H_5$]Co(π-C_5H_5) (VII) in CCl_4 solution. Data are given as in Figure 2.

The 100-MHz ^1H nmr spectrum contains carboranyl C–H resonances with a total area of 3, indicating that the cages are linked by a C–B bond (B–B or C–C links would give cage C–H peaks with total areas of 4 or 2, respectively). Since the C–H resonances near δ -3.7 are in the region of the C-H peaks in the spectrum of I, while the area 1 resonance at δ -5.75 is close to the C–H peak in the spectrum of parent 2,4-$C_2B_5H_7$ (δ -5.5), it is concluded that the $C_2B_5H_6$ ligand contains only one C–H moiety, with the other carbon involved in the intercage C–B link.

Originally, the pair of peaks at δ -3.71 and -3.76 were interpreted as arising from nonequivalent CH groups in the metallocarborane cage. However, we have established that in fact these peaks constitute a doublet centered at δ -3.73 with $J = 5$ Hz, the coupling constant being identical in the 100- and 60-MHz nmr spectra. This resonance (of total area 2) is assigned to magnetically *equivalent* CH groups in the metallocarborane cage, requiring that the $C_2B_5H_6$ ligand be attached either at B(3) as suggested in Figure 1 (VII) or at B(7). The splitting of carboranyl C–H resonances has apparently not been observed previously, but we have found this effect in the 60- and 100-MHz ^1H nmr spectra of several other small metallocarboranes, all of which contain four or fewer boron atoms per cage (*e.g.*, compound VIII described below and the triple-decked sandwiches (π-$C_2B_3H_5$)Co_2(π-C_5H_5)$_2$[16]). We attribute the splitting to H–B–C–H proton–proton

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(15) A. D. George and M. F. Hawthorne, *Inorg. Chem.*, **8**, 1801 (1969).

(16) D. C. Beer, V. R. Miller, L. G. Sneddon, R. N. Grimes, M. Mathew, and G. J. Palenik, *J. Amer. Chem. Soc.*, in press.

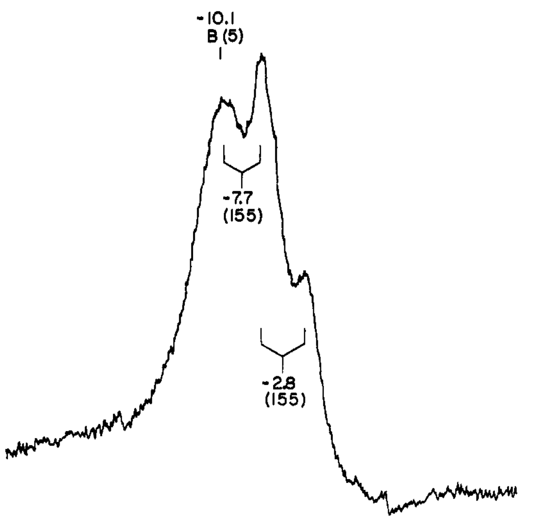

Figure 6. The 32-MHz ^{11}B nmr spectrum of σ-3-(2-$C_{10}H_7$)-[π-(1)-2,4-$C_2B_4H_5$]Co(π-C_5H_5) (VIII) in CCl_4 solution. Data are given as in Figure 2.

coupling between hydrogen atoms attached to adjacent boron and carbon atoms. This effect is currently under study and will be more fully discussed at a later date.

Several additional reaction products having a probable linked-cage structure have been detected from mass spectroscopic evidence, and the following compositions are indicated from parent peaks (*m*/*e* given in parentheses) and intensity profiles: ($C_2B_5H_6$)–($C_2B_5H_6$)Co(C_5H_5) (294), (C_5H_5)Co($C_2B_4H_5$)–($C_2B_4H_5$)Co(C_5H_5) (394), (C_5H_5)Co($C_2B_4H_5$)–($C_2B_5H_6$)Co(C_5H_5) (406), (C_5H_5)Co($C_2B_5H_6$)–($C_2B_5H_6$)Co(C_5H_5) (418), (C_5H_5)Co($C_2B_5H_6$)–($C_2B_6H_7$)Co(C_5H_5) (430).

Complex VIII. The ^{11}B nmr spectrum (Figure 6) is consistent with a σ-bonded derivative of I but is otherwise basically uninformative. However, the ^1H nmr spectrum (Figure 7) contains a carboranyl C–H doublet with $J = 6$ Hz, very similar to compound VII described above. Accordingly, the CH groups in the cage are equivalent and the naphthyl ligand is attached at either B(3) or B(7). The spectrum is more consistent with 2-naphthyl than 1-naphthyl substitution, in that the pattern of naphthyl resonances is very closely similar to that of 2-$NO_2C_{10}H_7$ but unlike that of 1-$NO_2C_{10}H_7$[17] (the nitro and carboranyl groups are both electron-withdrawing substituents and assumed to be comparable for this purpose).

Apparently similar naphthyl-substituted species, ($C_{10}H_7$)($C_2B_5H_6$)Co(C_5H_5) and ($C_{10}H_7$)($C_2B_6H_7$)Co(C_5H_5), have been identified in trace quantities from their mass spectroscopic parent peaks at *m*/*e* 336 and 348, respectively, and their respective five- and six-boron profiles in the parent region.

Possible Mechanisms. Aside from the unexpected variety of metallocarboranes formed, the most surprising aspect of these findings is the dominance of products incorporating the formal $C_2B_4H_6{}^{2-}$ ligand. Indeed, the (π-$C_2B_5H_7$)Co(π-C_5H_5) species, which was the anticipated major product based on polyhedral expansion of $C_2B_5H_7$, has been obtained only in low yield and was the most difficult of the compounds I–VIII to isolate and characterize. Thus, in net effect at least,

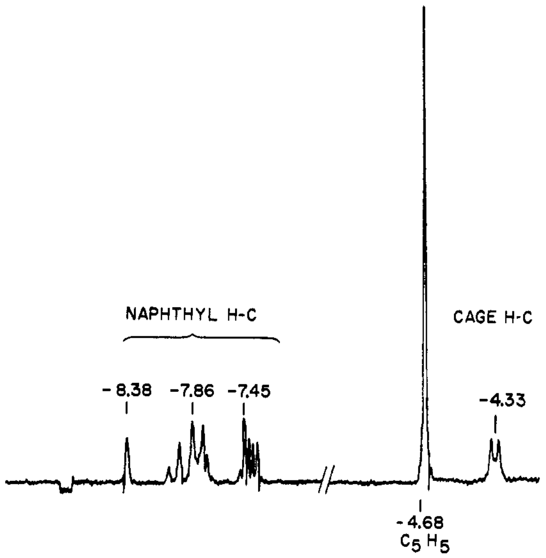

Figure 7. The 100-MHz ^1H nmr spectrum of σ-3-(2-$C_{10}H_7$)-[π-(1)-2,4-$C_2B_4H_5$]Co(π-C_5H_5) (VIII) in CCl_4 solution. Chemical shifts are relative to $(CH_3)_4Si$.

this system does not constitute primarily a polyhedral expansion reaction and stands in contrast to the earlier studies of 8-, 10-, and 12-atom carboranes cited above.

While details of the mechanism are not now available pending further studies presently in progress, the nature of the products and the reaction conditions are consistent with (but certainly not unique to) the following sequence: (1) formation of a $C_2B_5H_7{}^{2-}$ anion from $C_2B_5H_7$ and sodium naphthalide; (2) formation of the (π-$C_2B_5H_7$)Co^{II}(π-C_5H_5)$^-$ anion from $CoCl_2$, NaC_5H_5, and $C_2B_5H_7{}^{2-}$; (3) reaction of the (π-$C_2B_5H_7$)Co^{II}(π-C_5H_5)$^-$ ion with $C_2B_5H_7{}^{2-}$ *via* (a) electron transfer and (b) base degradation to produce, respectively, the open-cage metallocarborane ions (π-$C_2B_5H_7$)Co^{II}(π-C_5H_5)$^{3-}$ and (π-$C_2B_4H_6$)Co^{II}(π-C_5H_5)$^{3-}$; (4) insertion of Co^{2+} ions into the some of the open-cage metallocarborane anions, forming dicobalt complexes; (5) air oxidation of the cobalt(II) anions produced in (2), (3), and (4), to give neutral cobalt(III) metallocarboranes, (π-$C_2B_{n-2}H_n$)Co(π-C_5H_5) and (π-$C_2B_{n-2}H_n$)Co_2(π-C_5H_5)$_2$; (6) side reactions including deprotonation of carborane species and subsequent linkage to give σ-bonded derivatives such as VII and VIII. It is important to note that each of the processes 1 through 5 has precedent in metallocarborane chemistry, except for the suggested function of a carborane dianion ($C_2B_5H_7{}^{2-}$) as an electron-donating reagent. Thus, the formation of open-cage species from polyhedral carboranes and metallocarboranes *via* electron transfer and base extraction, as well as the subsequent insertion of metal atoms to produce mono- or dimetallocarboranes, have all been demonstrated elsewhere (see introductory section). The principal novelty in the scheme suggested above, as compared with other metallocarborane syntheses, is the postulate of a highly reactive $C_2B_5H_7{}^{2-}$ intermediate which acts as a cage-opening agent.

An alternative possibility is that the $C_2B_5H_7{}^{2-}$ anion disproportionates to $C_2B_4H_6{}^{2-}$, $C_2B_6H_8{}^{2-}$, and other species prior to the introduction of metal ions to the system. While this hypothesis directly accounts for the formation of the monocobalt complexes, generation of the dicobalt species requires an additional process

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(17) P. R. Wells and P. G. E. Alcorn, *Aust. J. Chem.*, **16**, 1108 (1963).

such as cage-opening *via* $C_2B_5H_7^{2-}$ attack as suggested above or intermolecular exchange of $Co(C_5H_5)^+$ moieties in solution. Evidence that the latter process may be significant has been obtained in preliminary studies of the chemistry of $(\pi\text{-}C_2B_4H_6)Co(\pi\text{-}C_5H_5)$, which readily forms dicobalt complexes in the presence of sodium naphthalide without the addition of metal ions.[18] Direct formation of the dicobalt complexes from tetranegative anions of the $C_2B_{n-2}H_n^{4-}$ type (*e.g.*, $C_2B_6H_8^{4-}$) is improbable since such highly charged small ions are unlikely to have a stable existence, and indeed none has been characterized.

Neither of the proposed schemes adequately accounts for the preponderance of the $(\pi\text{-}C_2B_4H_6)Co(\pi\text{-}C_5H_5)$ species and its σ-bonded derivatives. A current study of the immediate products of the reaction of $C_2B_5H_7$ with sodium naphthalide is expected to provide some additional insight into the problem.

Experimental Section

Materials. Dicarba-*closo*-heptaborane(7) ($C_2B_5H_7$) was obtained from Chemical Systems, Inc. and purified by glpc (30% Apiezon L on Chromosorb W at 35°). Cobalt(II) chloride was obtained from $CoCl_2 \cdot 6H_2O$ (Baker Reagent) by dehydration *in vacuo* at 160°. Cyclopentadiene was distilled from dicyclopentadiene (Aldrich). All solvents were reagent grade, and tetrahydrofuran (THF) was dried over lithium aluminum hydride before use. Naphthalene (Fisher) was used as received.

Spectra. Boron-11 nmr spectra at 32.1 MHz and proton nmr spectra at 100 MHz were obtained on a Varian HA-100 nmr spectrometer. Infrared spectra were run in solution (*vs.* pure solvent) on a Beckman IR-8 instrument. 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 and interfaced to a PDP-8I computer. All high-resolution spectra were obtained under chemical ionizing conditions using an argon–water matrix, which characteristically produced intense P + 1 peaks due to protonation of parent ions. Each significant ion mass was accompanied by a computer printout indicating all possible compositions for the given mass within preset limits and based on selected isotopic masses which included ^{59}Co, ^{12}C, ^{11}B, ^{10}B, ^{1}H, and ^{16}O. In virtually every instance (each peak of each spectrum), only one chemically significant composition was found within acceptable limts of error.

Procedure. Sodium cyclopentadienide (NaC_5H_5) was prepared by distilling *in vacuo* approximately 170 mmol of C_5H_6 into 120 mg-atoms of divided sodium in 40 ml of THF and allowing the reaction to proceed until all the sodium was consumed. The sodium naphthalide was prepared *in vacuo* by allowing 53 mg-atoms of divided sodium to react with 53 mmol of naphthalene in 70 ml of THF overnight. To this dark green solution was added by vacuum distillation 26 mmol of $C_2B_5H_7$. After standing overnight at 25° this solution was dark orange in color with no formation of noncondensables. The carborane and NaC_5H_5 solutions were taken into a drybox, mixed (with slight gas evolution), and added dropwise over 30 min to a stirred mixture of 145 mmol anhydrous $CoCl_2$ in 500 ml of THF. The dark blue solution turned very dark brown. After stirring for 20 hr at 25°, most of the THF was distilled off under reduced pressure. The residue was suspended in a solution of 500 ml of H_2O and 50 ml of acetone and stirred for 4 hr under a stream of air. After distilling off most of the acetone and remaining THF, the solution was filtered and the solid extracted with several portions of acetone. The combined acetone fraction was reduced in volume by evaporation at reduced pressure and diluted with hexanes, after which the solution was decanted off and the solvent removed at reduced pressure. The compounds I–VIII reported herein were obtained from this residue by a combination of column and thin layer chromatography. The order of elution from a silica gel column with hexanes is II, III, VII, I, IV, V, VIII, and VI. On the plates hexanes was used to separate I, II, III, and VII while 5% THF in hexanes was used to separate IV, V, VI, and VIII. Compounds I, III, and VII were crystallized by cooling the hexane solution at −78° while IV and VIII were crystallized from heptane using slight warming and then cooling at 0°.

Approximate yields of the isolated compounds were the following: I, 1000 mg (20% of theory); II, 20 (0.5); III, 90 (2); IV, 20 (0.2); V, 20 (0.2); VI, 20 (0.2); VII, 100 (2); VIII, 150 (2).

Acknowledgment. We are grateful for a gift of mixed lower carboranes from Chemical Systems, Inc., through the courtesy of Drs. J. F. Ditter and R. E. Williams. This work was supported by the Office of Naval Research.

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[18] R. Weiss and R. N. Grimes, unpublished results.

Polar and Free-Radical Halogenation of Amine–Boranes with Halocarbons

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Contribution from the Department of Chemistry, University of Florida,
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Abstract: Amine–boranes will react cleanly with halocarbons to give amine–haloboranes and an alkane. Polar reactions are observed with organic halides, such as chlorotriphenylmethane, which form carbonium ions readily, with reactivity increasing with the stability of the carbonium ion. Free-radical reactions are observed with CCl_4 or CCl_3Br; they can be initiated with benzoyl peroxide. 4-Methylpyridine–monochloroborane and –dichloroborane have been synthesized.

In a recent paper[1] evidence was presented which suggested that substitution of halogen for hydrogen in amine–boranes may proceed either by a polar or by a free-radical pathway, depending on the nature of the chlorinating agent. During a subsequent investigation of the reaction between dimethylchloramine and amine–boranes,[2] it was observed that the solvent, CCl_4, could become involved in the reaction and act as a chlorinat-

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[1] J. W. Wiggins and G. E. Ryschkewitsch, *Inorg. Chim. Acta*, **4**, 33 (1970).

[2] V. R. Miller, G. E. Ryschkewitsch, and S. Chandra, *Inorg. Chem.*, **9**, 1427 (1970).