and 3-Sn-1,2-$B_9C_2H_{11}$[1] were prepared according to literature procedures. Triphenylphosphine and $SnCl_2$ were obtained from Matheson Coleman and Bell; GeI_2, *n*-butyllithium, and trimethylamine were purchased from Rocky Mountain Research Chemicals, Alfa Inorganics, and Eastman Organics, respectively; these reagents were used without further purification.

3-Ge-1,7-$B_9C_2H_{11}$. In a 100-ml three-necked flask, equipped with a condenser, nitrogen inlet, rubber septum, magnetic stirrer, and heating mantle were placed 1.0 g (5.16 mmol) of Me_3NH^+ 7,9-$B_9C_2H_{12}^-$ and 50 ml of benzene. Before heating, 5.0 ml of 2.28 *M* *n*-butyllithium was added with a syringe through the septum. The mixture was then stirred at reflux for 12 hr with a slow purge of N_2 to remove NMe_3 and form the 7,9-$B_9C_2H_{11}^{2-}$ ion. GeI_2 (1.83 g) was then added and the mixture stirred at reflux for an additional 54 hr before it was poured into a Soxhlet thimble and extracted with benzene for 24 hr. After rotary evaporation of the solvent the solid was further purified by vacuum sublimation at 55° to give 0.210 g of 3-Ge-1,7-$B_9C_2H_{11}$. *Anal.* Calcd for $B_9C_2GeH_{11}$: B, 47.44; C, 11.71; Ge, 35.43; H, 5.41. Found: B, 49.61; C, 11.21; Ge, 33.17; H, 5.48. The compound was not observed to melt when heated to 310° in a sealed capillary.

When 3-Ge-1,2-$B_9C_2H_{11}$ was vacuum sublimed through 20-mm o.d. Vycor tubing which was maintained at 600° for a 100-mm length, the sublimate was observed to be a mixture of 3-Ge-1,2-$B_9C_2H_{11}$ and 3-Ge-1,7-$B_9C_2H_{11}$ by infrared spectroscopy.

2,3-$B_9C_2H_{11}$. In a typical pyrolytic preparation a 20 mm o.d. Pyrex tube was charged with 730 mg of 3-Sn-1,2-$B_9C_2H_{11}$ and about 100 mm above the sample a 200 mm length of the tube was loosely packed with degreased glass wool. The tube was attached to a high vacuum system through a standard taper joint and outgassed at 300° by heating for 1 hr with a furnace placed around the packed portion. The furnace temperature was then raised to 450° and the 3-Sn-1,2-$B_9C_2H_{11}$ was sublimed up the tube by placing a 200° oil bath at the bottom. As the stannacarborane sublimed through the packed tube the 2,3-$B_9C_2H_{11}$ formed was pumped into a tared trap held at −196°. The yield was 380 mg (98%) [*m*/*e*] 134, $^{11}B_9{}^{12}C_2{}^1H_{11}{}^+$].

The *in situ* preparation of 2,3-$B_9C_2H_{11}$ was effected in the following manner. A benzene solution of the 7,9-$B_9C_2H_{11}^{2-}$ ion was generated from 1.0 g of Me_2NH^+ 7,9-$B_9C_2H_{12}^-$ (*vide supra*) before adding 1.07 g (5.65 mmol) of anhydrous $SnCl_2$. Within a few minutes the mixture showed incipient blackening and stirring was continued at reflux for 24 hr. The product could be recovered by removal of the Sn and NaCl by filtration and evaporation of the filtrate *in vacuo*; however, rather than recover the 2,3-$B_9C_2H_{11}$, it was usually treated *in situ* with other reagents (*vide infra*).

7,9-$B_9C_2H_{11} \cdot P(C_6H_5)_3$, A freshly prepared solution of 2,3-$B_9C_2H_{11}$ (*vide supra*) was cooled to 25° and 1.47 g (5.60 mmol) of $(C_6H_5)_3P$ was added before continuing reflux and stirring for 24 hr. More conveniently, $(C_6H_5)_3P$ was added to a freshly prepared benzene solution of 7,9-$B_9C_2H_{11}^{2-}$ along with the $SnCl_2$. In this case, blackening was noted immediately and stirring was continued at reflux for 24 hr. Recovery of the crude product was accomplished by removal of Sn and NaCl by filtration and evaporation of the benzene. The crude product was extracted with heptane to removed unreacted $(C_6H_5)_3P$, dried, and finally either recrystallized from benzene–heptane or vacuum sublimed (180°) to give 1.57 g (4.01 mmol) of the pure material (78% yield). *Anal.* Calcd for $B_9C_{20}H_{26}P$: B, 24.67; C, 60.90; H, 6.59; P, 7.85. Found: B, 24.64; C, 60.10; H, 6.39; P, 7.62 [*m*/*e* 396, $B_9C_{20}H_{26}P^+$, mp 188–189°].

7,9-$B_9C_2H_{11} \cdot N(CH_3)_3$. A reaction flask containing a fresh benzene solution of 7,9-$B_9C_2H_{11}^{2-}$ prepared from 1.0 g of Me_3NH^+ 7,9-$B_9C_2H_{12}^-$ (*vide supra*) was fitted with a bubbler and anhydrous $SnCl_2$ (1.07 g) was added to the mixture. Anhydrous trimethylamine (7 g, 120 mmol) was then bubbled through the refluxing solution over a 1-hr period. After the addition was complete, stirring was continued at reflux for 3 hr. The work-up was the same as for $(C_6H_5)_3P \cdot B_9C_2H_{11}$. The product sublimes at 170° *in vacuo*. *Anal.* Calcd for $B_9C_5H_{20}N$: B, 50.86, C, 31.38; H, 10.54; N, 7.31. Found: B, 50.01; C, 30.34, H, 10.11; N, 7.25 [*m*/*e* 193, $B_9C_5H_{20}N^+$, mp 264° dec].

7,9-$(CH_3)_2$-7,9-$B_9C_2H_9 \cdot OC_2H_6^-$. Phosphoric acid (85%, 30 ml) was added to 1.33 g (4.5 mmol) of Cs^+ 7,8-$(CH_3)_2$-7,8-$B_9C_2H_{10}^-$ in 30 ml of toluene and the mixture stirred at reflux under nitrogen for 6 hr. The toluene layer was then decanted and the solvent removed on a rotary evaporator until a thick oil remained. The oil was treated, under nitrogen, with 50 ml of 1 *M* ethanolic KOH and stirred for 10 min before adding 15 ml of aqueous saturated $(CH_3)_4N^+Cl^-$ to precipitate the product. Pure product was obtained upon recrystallization from ethanol–water by slow evaporation of the ethanol (yield 0.40 g, 32%).

Acknowledgment, We thank the NSF (GP-28619) and the Research Corporation for partial support of this research, and Professors Riley Schaeffer and Lee Todd and Mr. Art Clouse, Indiana University, for the 70.6-MHz ^{11}B nmr spectra.

Synthesis of Metallocarboranes by Polyhedral Expansion[1]

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Received January 8, 1973

Abstract: The reduction of the closo carboranes 1,7-$C_2B_6H_8$, 4,5-$C_2B_7H_9$, 1,6-$C_2B_8H_{10}$, 1,10-$C_2B_8H_{10}$, and 2,3-$C_2B_9H_{11}$ with Na followed by complexation with $CoCl_2$ and NaC_5H_5 produces metalloboranes of the following types: $C_5H_5CoC_2B_nH_{n+2}$, $(C_5H_5Co)_2C_2B_nH_{n+2}$, and $C_5H_5CoC_2B_nH_{n+1}(C_2B_nH_{n+1})$. Similarly, addition of $FeCl_2$ and NaC_5H_5 to the anions derived from the reduction of 1,7-$C_2B_6H_8$ and 1,6-$C_2B_8H_{10}$ results in new ferracarboranes. The preparation, characterization, and proposed structures of these metalloboranes are discussed.

Since 1965 a large number of metallocarboranes have been prepared *via* the following three steps carried out in succession: (1) basic or oxidative degradation of a carborane, (2) deprotonation of the degradation product with a base such as sodium hydride, and (3) complexation of the resulting anion with a transition metal ion. In this manner metallocarboranes containing the $C_2B_9H_{11}^{2-}$,[2] $C_2B_7H_9^{2-}$,[3] and $C_2B_6H_8^{2-}$[4] moieties have been prepared. This work has been recently reviewed,[5] and the following equations serve as an example.[2]

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(1) Presented in part at the 14th International Conference on Coordination Chemistry, Toronto, Ontario, Canada, June 1972.

(2) M. F. Hawthorne, D. C. Young, T. D. Andrews, D. V. Howe, R. L. Pilling, A. D. Pitts, M. Reintjes, L. F. Warren, Jr., and P. A. Wegner, *J. Amer. Chem. Soc.*, **90**, 879 (1968).

(3) T. A. George and M. F. Hawthorne, *ibid.*, **91**, 5475 (1969).

(4) M. F. Hawthorne and A. D. Pitts, *ibid.*, **89**, 7115 (1967).

(5) M. F. Hawthorne, *Accounts Chem. Res.*, **1**, 281 (1968); M. F. Hawthorne and G. B. Dunks, *Science*, **178**, 462 (1972).

$$C_2B_{10}H_{12} \xrightarrow[C_2H_5OH]{KOH} C_2B_9H_{12}^- \xrightarrow[-H_2]{NaH} C_2B_9H_{11}^{2-}$$

$$C_2B_9H_{11}^{2-} \xrightarrow[2.\ [O]]{1.\ CoCl_2,\ NaC_5H_5} C_5H_5CoC_2B_9H_{11}$$

Another method of metallocarborane synthesis involves the degradation of a metallocarborane itself to produce a smaller metallocarborane or a polymetallic species. Several new cobalt complexes have been synthesized in this manner.[6,7]

Although these methods allow the synthesis of a wide range of metallocarboranes, they remain dependent on the availability of suitable carborane anion intermediates and suitable cobalt metallocarboranes. In the general synthetic route which we now report, a polyhedral carborane itself is directly involved as a reactant, as shown in the general equation[8]

$$C_2B_nH_{n+2} \xrightarrow{2e^-} [C_2B_nH_{n+2}]^{2-} \xrightarrow[2.\ [O]]{1.\ M(II),\ NaC_5H_5} C_5H_5MC_2B_nH_{n+2}$$

We have termed this reaction "polyhedral expansion"[9] since the polyhedral framework of the primary product is one vertex larger than that of the starting carborane. The procedure vastly increases the potential number of metallocarboranes which can be synthesized since variation of the carborane as well as variation of the transition metal is possible. The generality of this reaction extends beyond the application to carboranes alone, however, for indeed the polyhedral expansion of monometallocarboranes to form species containing more than one metal has been accomplished.[10,11]

$$C_5H_5MC_2B_nH_{n+2} \xrightarrow[\substack{2.\ M'(II),\ NaC_5H_5 \\ 3.\ [O]}]{1.\ 3e^-} (C_5H_5M)(C_5H_5M')C_2B_nH_{n+2}$$

The polyhedral expansion reaction applied to carboranes as reported here and then sequentially applied to metallocarboranes establishes a basis for the rational synthesis of a large number of the variations of the general formula $(C_5H_5M)_a(C_5H_5M')_bC_cB_nH_{n+2}$ where M and M′ are transition metals and $a = 1, 2, 3, \ldots$; $b = 0, 1, 2, 3, \ldots$; $c = 1$ or 2; and $a + b + c + n \leq 13$.

In addition each of these polyhedral expansion reactions has resulted in an abundance of interesting side products which have further broadened the scope of metalloborane chemistry. The direct formation of species such as $(C_5H_5M)_2C_2B_nH_{n+2}$, $C_5H_5M(C_2B_nH_{n+1})(C_2B_nH_{n+1})$, and $C_5H_5MC_2B_{n+1}H_{n+3}$ from $C_2B_nH_{n+2}$ in addition to the expected $C_5H_5MC_2B_nH_{n+2}$ gives some indication of the complexity of this reaction.

The polyhedral expansion of $C_2B_{10}H_{12}$ to form 13-vertex polyhedral complexes has already been reported[12,13] as have preliminary accounts of cobalt complexes derived from 1,6-$C_2B_8H_{10}$[9] and 1,7-$C_2B_6H_8$.[14] In this paper we describe the polyhedral expansion of 1,7-$C_2B_6H_8$, 4,5-$C_2B_7H_9$, 1,6-$C_2B_8H_{10}$, 1,10-$C_2B_8H_{10}$, and 2,3-$C_2B_9H_{11}$. In each case these carboranes were expanded with cobalt. In addition, 1,7-$C_2B_6H_8$ and 1,6-$C_2B_8H_{10}$ have been expanded with iron to form the first ferracarboranes of intermediate size.

The general procedure employed in the polyhedral expansion reaction involves the initial reduction of a closo carborane with sodium, sodium naphthalide, or sodium amalgam in tetrahydrofuran (THF) or sodium in liquid ammonia. Since each carborane was reduced in a characteristic manner, the exact reaction conditions were dependent upon the substrate used. Following reduction, the addition of excess NaC_5H_5 and MCl_2 resulted in metallocarborane formation. After air oxidation of the reaction mixture the various polyhedral expansion products were separated by liquid chromatography on silica gel. Variations in the reductant or the reaction temperature were found to influence the yield and nature of the side products. The primary products of the most representative reactions for each of the carboranes enumerated above are reported here.

1,7-$C_2B_6H_8$. The reduction of 1,7-$C_2B_6H_8$ was effected at −20° over a 3-day period with sodium metal in the presence of naphthalene. Addition of $CoCl_2$ and NaC_5H_5 produced a mixture of two metallocarboranes which were separated by column chromatography.[15]

$$1,7\text{-}C_2B_6H_8 \xrightarrow[C_{10}H_8]{2Na} \xrightarrow[CoCl_2]{NaC_5H_5} \underset{\text{I}}{C_5H_5CoC_2B_6H_8} + \underset{\text{II}}{(C_5H_5Co)_2C_2B_6H_8}$$

The dark red crystals isolated from the first fraction exhibited a cutoff in the mass spectrum at *m/e* 222 which corresponds to the $^{59}Co^{12}C_7{}^{11}B_6{}^1H_{13}{}^+$ ion. The elemental analysis was in agreement with the formulation $C_5H_5CoC_2B_6H_8$, I, and the reduction potential and electronic and infrared spectra, reported in the Experimental Section, were consistent with such a species. The 80.5-MHz ^{11}B nmr spectrum of I[16] (Table I) was comprised of six doublets of equal intensity consistent with an unsymmetrical structure in which all of the boron atoms occupy different environments. The 60-MHz ^1H nmr spectrum[17] consisted of a sharp singlet of relative area 5 at τ 4.94 assigned to the cyclopentadienyl protons and two broad resonances each of area 1, at τ 3.88 and 6.08, assigned to two types of polyhedral CH units. Assuming that the CoC_2B_6 framework of atoms in I constitutes a polyhedral structure grossly resembling the known $C_2B_7H_9$,[18,19]

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[6] J. N. Francis and M. F. Hawthorne, *Inorg. Chem.*, **10**, 863 (1971).

[7] C. J. Jones, J. N. Francis, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **94**, 8391 (1972).

[8] In general equations and formulas in this paper, M represents a transition metal. Formal oxidation states denoted in Roman numerals will always be enclosed in parentheses and are not to be confused with the Roman numerals used to identify the various metalloboranes discussed.

[9] W. J. Evans and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **93**, 3063 (1971).

[10] W. J. Evans and M. F. Hawthorne, *J. Chem. Soc., Chem. Commun.*, 611 (1972).

[11] W. J. Evans and M. F. Hawthorne, manuscript in preparation.

[12] G. B. Dunks, M. M. McKown, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **93**, 2541 (1971).

[13] D. F. Dustin, G. B. Dunks, and M. F. Hawthorne, *ibid.*, **95**, 1109 (1973).

[14] (a) G. B. Dunks, Ph.D. Dissertation, University of California, Riverside, Calif., 1970; (b) G. B. Dunks and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **92**, 7213 (1970).

[15] In this and following equations, products are listed in order of elution from silica gel with CH_2Cl_2–hexane.

[16] This spectrum as well as several other pertinent ^{11}B nmr spectra of the new compounds described will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-73-4565. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

[17] Except where the solvent is specifically stated, each ^1H nmr spectrum was determined in the same solvent as the corresponding ^{11}B nmr spectrum (Table I).

[18] T. F. Koetzle, F. E. Scarbrough, and W. N. Lipscomb, *Inorg. Chem.*, **7**, 1096 (1968).

Table I, 80.5-MHz ^{11}B Nmr Spectra

Compound	Solvent	Chemical shift[a] (rel intensity)
$C_5H_5CoC_2B_6H_8$, I	CH_3CN-d_3	−63.8 (1), −3.1 (1), +4.3 (1), +9.2 (1), +16.3 (1), +21.4 (1)
$(C_5H_5Co)_2C_2B_6H_8$, II	$CHCl_3$-d_1	−3.6 (2), +20.9 (1)
$[(C_6H_5)_4As][Co(C_2B_6H_8)_2]$, III	CH_3CN-d_3	−52.7 (1), +3.8 (1), +7.3 (1), +12.1 (1), +13.9 (1), +27.6 (1)
$C_5H_5FeC_2B_6H_8$, IV	CH_3CN-d_3	−1.2 (2), +10.4 (2), +13.5 (2)
$C_5H_5FeC_2B_6H_8$, V	CH_3CN-d_3	−16.9 (1), +5.8 (2), +16.0 (2), +31.2 (1)
$C_5H_5CoC_2B_7H_9$, VI	$CHCl_3$-d_1	−49.6 (1), +3.0 (1), +3.8 (1), +11.5 (1), +23.1 (1), +24.2 (1), +26.1 (1)
$C_5H_5CoC_2B_6H_8$, VII	CH_3CN-d_3	−20.4 (1), −8.5 (2), +12.2 (2), +14.6 (1)
$C_5H_5CoC_2B_8H_9(C_2B_8H_9)$, VIII	CH_2Cl_2	−9.8 (2), +5.9 (2), +7.9 (2), +12.2 (8), +18.8 (1), +20.6 (1)
$C_5H_5CoC_2B_8H_{10}$, IX	CH_2Cl_2	−10.6 (1), +8.1 (2), +20.7 (1)
$(C_5H_5Co)_2C_2B_8H_{10}$, X	$(CH_3)_2CO$-d_6	−4.7 (1), +4.3 (2), +13.3 (1)
$[Co(C_2B_8H_{10})_2]^-$, XI[b]	$(CH_3)_2CO$-d_6	−9.0 (1), +7.7 (2), +22.6 (1)
$C_5H_5FeC_2B_8H_{10}$, XII	$(CH_3)_2CO$-d_6	−1.5 (1), +19.0 (2), +25.5 (1)
$(C_5H_5Co)_2C_2B_8H_{10}$, XIII	$(CH_3)_2CO$-d_6	−12.0 (1), +4.0 (1), +6.0 (1), +18.5 (1)

[a] Ppm *vs.* $BF_3 \cdot O(C_2H_5)_2$; all signals doublets with $J_{B-H} = 140 \pm 20$ Hz. [b] Cobalticinium salt.

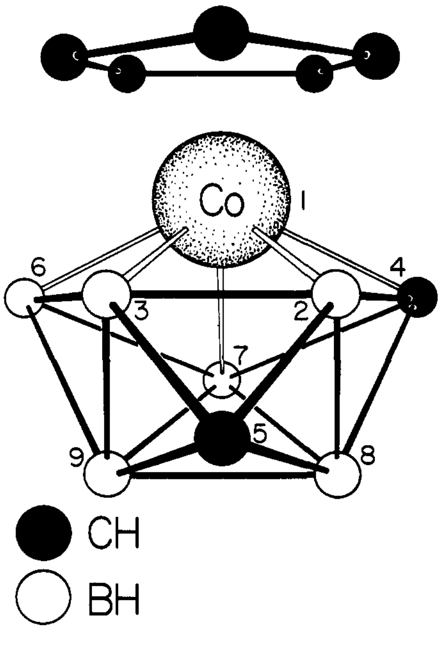

Figure 1. Proposed structure of $C_5H_5CoC_2B_6H_8$, I.

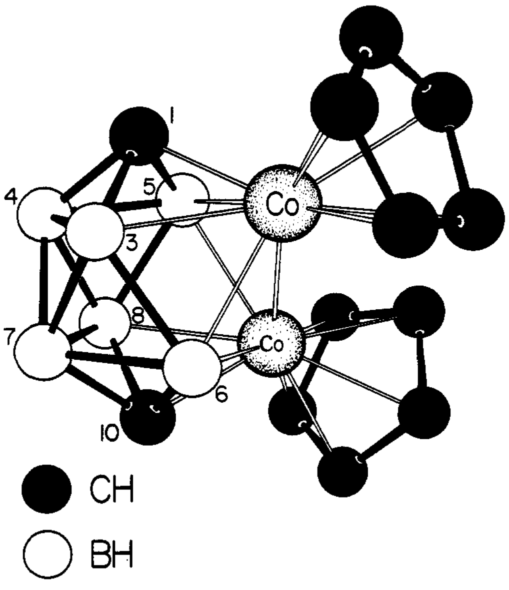

Figure 2. Structure of $(C_5H_5Co)_2C_2B_6H_8$, II.

i.e., a tricapped trigonal prism, a number of possible isomers exist. Since the carbon atoms in I are unlikely to occupy adjacent positions,[22] are nonequivalent, and "prefer" to occupy five-coordinate positions,[23] the structure shown in Figure 1 is proposed although we are quite aware that other possibilities exist. This particular structure is also consistent with an empirical observation that a closo metalloborane containing a low-coordinate boron atom adjacent to a metal has a resonance in the ^{11}B nmr spectrum at low field (*vide infra*).

The second metallocarborane produced by polyhedral expansion of 1,7-$C_2B_6H_8$ was the green species, II, characterized as $(C_5H_5Co)_2C_2B_6H_8$ by elemental analysis and by the mass spectral cutoff at *m/e* 346 for the molecular ion. The ^1H nmr data indicated a highly symmetrical structure containing equivalent cyclopentadienyl moieties and equivalent carborane CH protons with resonances at τ 4.92 and 1.38, respectively. The geometry of a bicapped square antiprism containing two equivalent sets of vertices, in this case the two carbon and two cobalt atoms, requires three additional sets of equivalent vertices be present also. Hence the six boron atoms must exist in three equivalent sets and coincidental overlap in the ^{11}B nmr spectrum (Table I) must be assumed. A likely structure containing nonadjacent cobalt atoms consistent with other known bimetallic systems was proposed, although other possibilities were not excluded.[14b] Preliminary X-ray diffraction results[24] indicate the species has the gross geometry previously proposed, but contains cobalt atoms in the *adjacent* positions 2 and 6 (Figure 2). The carbon atoms occupy the two available five-coordinate positions 1 and 10 and consequently no low-coordinate boron atoms adjacent to cobalt are present. This is consistent with the absence of low field resonances in the ^{11}B nmr spectrum (*vide supra*).

Polyhedral expansion of 1,7-$C_2B_6H_8$ in the absence of

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(19) X-Ray diffraction studies support the assumption that in a metallocarborane, *e.g.*, $C_5H_5MC_2B_nH_{n+2}$, the metal (M) occupies a vertex position in a polyhedral structure resembling a larger carborane, in this case $C_2B_{n+1}H_{n+3}$.[5,20,21]

(20) D. St. Clair, A. Zalkin, and D. Templeton, *Inorg. Chem.*, **11**, 377 (1972).

(21) M. R. Churchill and K. Gold, *J. Chem. Soc., Chem. Commun.*, 901 (1972).

(22) The migration of carbon atoms to form the thermodynamically less stable isomer containing adjacent carbon atoms has not been observed in metallocarborane synthesis.

(23) The known structures of $C_2B_6H_8$, $C_2B_7H_9$, and $C_2B_9H_{11}$ as well as the most stable structures of $C_2B_8H_{10}$ and $C_5H_5CoC_2B_7H_9$ contain carbon atoms in the five-coordinate positions.

(24) E. L. Hoel, C. E. Strouse, and M. F. Hawthorne, manuscript in preparation.

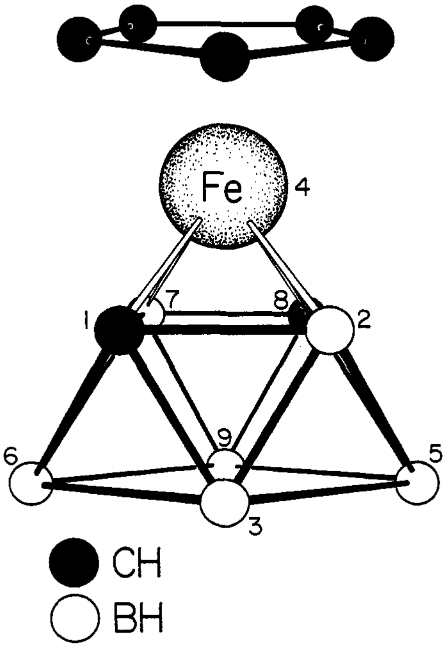

Figure 3. Proposed structure of $C_5H_5FeC_2B_6H_8$, IV.

NaC_5H_5 produced a metallocarborane comprised of two polyhedra which share the metal atom. The

$$1,7\text{-}C_2B_6H_8 \xrightarrow[C_{10}H_8]{2Na} \xrightarrow{CoCl_2} Co(C_2B_6H_8)_2^- \quad \text{III}$$

elemental analysis and equivalent weight of the anion III, precipitated as brown needles with $(C_6H_5)_4As^+$, were in agreement with the formulation $[(C_6H_5)_4As][Co(C_2B_6H_8)_2]$. Electrochemical and spectroscopic data include an ^{11}B nmr spectrum containing six nonequivalent doublets of equal area. In addition to the resonance of relative area 10 at τ 2.24 arising from the cation, two nonequivalent carborane CH resonances of relative area 1 were found in the ^1H nmr spectrum at τ 4.66 and 6.02. The gross structure of this commo metallocarborane is presumably that of two nine-vertex polyhedra sharing a common cobalt atom. The nmr data suggest that the two polyhedra are equivalent and are individually comprised of a CoC_2B_6 framework of atoms arranged unsymmetrically as in I.

Complexation of the $1,7\text{-}C_2B_6H_8$ reduction product with $FeCl_2$ in the presence of NaC_5H_5 also resulted in the formation of two new metallocarboranes of composition $C_5H_5FeC_2B_6H_8$ (IV and V).

$$1,7\text{-}C_2B_6H_8 \xrightarrow[C_{10}H_8]{2Na} \xrightarrow[NaC_5H_5]{FeCl_2} C_5H_5FeC_2B_6H_8 \quad \text{IV and V}$$

The red compound, IV, was formulated as $C_5H_5FeC_2B_6H_8$ based on the mass spectral cutoff at 219 for the molecular ion, and this was verified by high-resolution mass spectroscopy. The ^{11}B nmr spectrum[16] of the purple solution of IV formed by reduction to formal Fe(II)[8] with Na(Hg) consisted of three doublets of equal area (Table I). The ^1H nmr spectrum of this solution revealed a single broad area 2 resonance at τ 7.1 assigned to carborane CH and a sharp area 5 singlet at τ 6.45 assigned to the cyclopentadienyl protons. Within the expected gross geometry of a tricapped trigonal prism there exist only two structures which contain three pairs of equivalent boron atoms: iron at position 1 and carbon at 5 and 7, or iron at 4 and carbon at 1 and 8 positions, using the numbering system shown in Figure 1.[25] The first of these has nonequivalent carborane CH units, which is inconsistent with the ^1H nmr spectrum. Furthermore it has two low-coordinate boron atoms adjacent to Fe which should presumably provide a low field resonance in the ^{11}B nmr spectrum. This resonance was not observed. The second structure, Figure 3, is the only atomic arrangement within the framework of a trigonal tricapped prism consistent with the spectroscopic data. This structure, however, is particularly unusual, since the carbon atoms are not in the favored, five-coordinate positions and the iron atom is in a low-coordinate position previously unobserved in closo metallocarboranes.

The broad area 2 resonance of IV in the ^1H nmr spectrum was reexamined at 250 MHz to determine if indeed these protons were equivalent, but again a single resonance was observed. Further support for the proposed structure shown in Figure 3 was obtained from the ^{11}B nmr spectrum of the unreduced paramagnetic $C_5H_5Fe^{III}C_2B_6H_8$. Two resonances were observed: an area 2 resonance at +82.1 ppm ($W_{1/2}$ = 1600 Hz) relative to $BF_3 \cdot O(C_2H_5)_2$ and a sharper resonance of area 4 centered at +10.9 ppm ($W_{1/2}$ = 300 Hz). These data indicate that only two boron atoms strongly interact with the metal; *i.e.*, only two boron atoms reside in positions adjacent to the iron, which is additional evidence consistent with the proposed structure.[27] Crystallographic studies are presently in progress which will precisely determine the structure of this presumably unique new metallocarborane.

The second ferracarborane isolated from this $C_2B_6H_8$ expansion reaction, V, was characterized by its mass spectrum as an isomer of IV, and a high-resolution mass measurement confirmed the $C_5H_5FeC_2B_6H_8$ formulation. The 1:2:2:1 pattern of doublets in the ^{11}B nmr spectrum[16] of the reduced Fe(II) species contained no low field resonances (Table I). The ^1H nmr spectrum of V contained a single cyclopentadienyl resonance at τ 6.15 as well as equivalent carborane CH signals at τ 4.442. Assuming that the carbon atoms did not move together during the reaction the only isomer with the proper symmetry contains iron at position 1 and carbon at positions 4 and 6 (Figure 1), *i.e.*, $4,6\text{-}C_5H_5FeC_2B_6H_8$. The geometry and carbon atom positions in this species are identical with those proposed for $(CO)_3MnC_2B_6H_8$ prepared earlier.[4]

$4,5\text{-}C_2B_7H_9$. The polyhedral expansion reaction was applied to $4,5\text{-}C_2B_7H_9$ using $CoCl_2$ and NaC_5H_5 and resulted in three cobaltacarboranes.

$$4,5\text{-}C_2B_7H_9 \xrightarrow{Na} \xrightarrow[NaC_5H_5]{CoCl_2} \underset{\text{VI}}{C_5H_5CoC_2B_7H_9} + \underset{\text{VII}}{C_5H_5CoC_2B_6H_8} + \underset{\text{X}}{(C_5H_5Co)_2C_2B_8H_{10}}$$

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[25] The numbering system used here follows that proposed in the nomenclature rules for boron compounds.[26] Metallocarboranes will be treated as heteroboranes, as their structure[19] and chemistry[7,10] suggest. Heteroatoms with largest atomic number are given lowest numbers. Numbers preceding the formulas refer to carbon atom positions.

[26] *Inorg. Chem.*, 7, 1945 (1968).

[27] R. J. Wiersema and M. F. Hawthorne, manuscript in preparation.

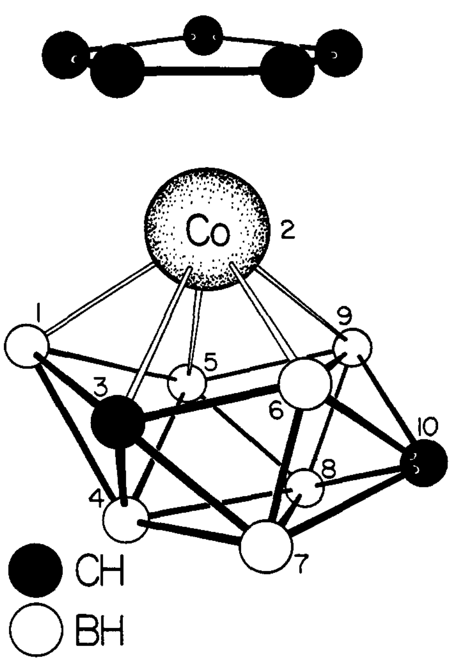

Figure 4. Possible structure of $C_5H_5CoC_2B_7H_9$, VI. Only one enantiomer is shown.

Intense color changes accompanied the reduction of this carborane at room temperature, and a reaction time of 1 week was necessary. The mass spectrum of VI exhibited a cutoff at 234 corresponding to the $^{11}B_7{}^{12}C_7{}^1H_{14}Co^+$ ion, and by thin-layer chromatography (tlc) VI appeared to be $1,10\text{-}C_5H_5CoC_2B_7H_9$.[3] Consistent with this formula was an exact mass measurement. Further characterization, however, indicated that VI was a new isomer of the $C_5H_5CoC_2B_7H_9$ series, bringing the number of known isomers to five.[3,7] Nonequivalent carborane CH resonances at τ 9.1 and 10.34 were found in the ^1H nmr spectrum in acetone-d_6 as well as seven unique boron resonances including a low field signal in the ^{11}B nmr spectrum[16] (Table I). Excluding enantiomers, 17 structural possibilities exist which have the necessary lack of symmetry characteristic of this new isomer. Of the two possible positions for cobalt in bicapped square antiprimatic geometry, the equatorial position, 2, appears favored over the lower coordinate apical position, 1, Figure 4. An X-ray diffraction study has confirmed this equatorial cobalt position in $Co(1,6\text{-}C_2B_7H_9)_2^-$,[20] and this assignment allows a five-coordinate boron atom to be adjacent to cobalt at position 1, consistent with the -49.6 ppm resonance found in the ^{11}B nmr spectrum. Assuming that the carbon atoms have not moved to adjacent positions, five possible structures remain for VI: 3,8-, 3,9-, 3,10-, 4,6-, and $6,8\text{-}C_5H_5CoC_2B_7H_9$. The ^{11}B nmr spectra of the series of five paramagnetic isomers $[C_5H_5Co^{II}C_2B_7H_9]^-$ were measured and found to be not as amenable to immediate analysis as the systems $C_5H_5MC_2B_6H_8$ or $C_5H_5MC_2B_8H_{10}$ (*vide infra*).[27] However, analysis of the data, while not entirely conclusive, indicates the structure of VI to be that shown in Figure 4, $3,10\text{-}C_5H_5CoC_2B_7H_9$.

Analysis of VII, the second main product of the polyhedral expansion of $4,5\text{-}C_2B_7H_9$, indicated it to be a new isomer of $C_5H_5CoC_2B_6H_8$, I. High-resolution mass spectroscopy substantiated the formula. The 1:2:2:1 pattern of doublets in the ^{11}B nmr spectrum of VII[16] was similar to that of V although the high field resonances overlapped (Table I). The ^1H nmr spectrum in acetone-d_6 contained a single carborane CH resonance at τ 3.37 and a cyclopentadienyl signal at τ 4.47. We propose that VII is the cobalt analog of V, *viz.*, $4,6\text{-}C_5H_5CoC_2B_6H_8$.

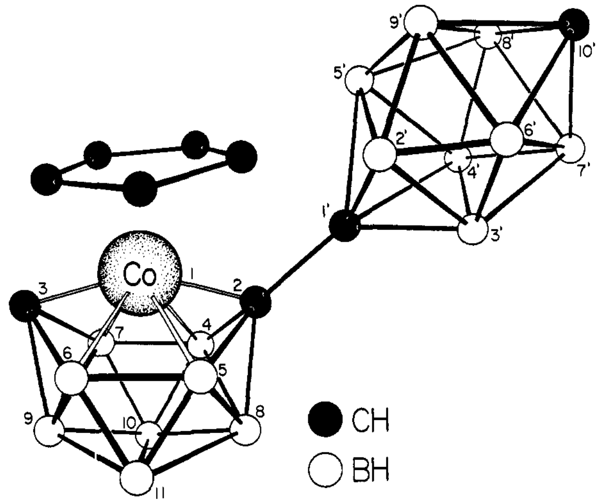

Figure 5. Proposed structure of $C_5H_5CoC_2B_8H_9(C_2B_8H_9)$, VIII.

A minor product isolated from this reaction was characterized by tlc, ^1H nmr, and infrared spectroscopy as the previously reported $2,3\text{-}C_5H_5CoC_2B_8H_{10}$.[9] The purity of the $4,5\text{-}C_2B_7H_9$ used for this reaction was verified by gas chromatography in order to ensure that no 1,6- or $1,10\text{-}C_2B_8H_{10}$ was present and hence it appears this larger metallocarborane was produced in the course of the reaction. This phenomenon has also been observed in the polyhedral expansion of $1,10\text{-}C_2B_8H_{10}$ (*vide infra*).

$1,6\text{-}C_2B_8H_{10}$. Reduction of $1,6\text{-}C_2B_8H_{10}$ can be accomplished with Na or $Na^+C_{10}H_8^-$ in THF at $-78°$, room temperature, or 66°. Complexation with NaC_5H_5 and $CoCl_2$ produces a variety of products which were separated by column and high-pressure liquid chromatography.

$$1,6\text{-}C_2B_8H_{10} \xrightarrow{2Na} \xrightarrow[NaC_5H_5]{CoCl_2} 1,6\text{-}C_5H_5CoC_2B_7H_9 + \underset{VIII}{C_5H_5CoC_2B_8H_9(C_2B_8H_9)} + \underset{IX}{C_5H_5CoC_2B_8H_{10}} + \underset{X}{(C_5H_5Co)_2C_2B_8H_{10}} + \underset{XI}{Co(C_2B_8H_{10})_2^-}$$

The initial product separated from the reaction mixture was characterized by tlc and ^1H and ^{11}B nmr as $1,6\text{-}C_5H_5CoC_2B_7H_9$.[3] Following the elution of this red band two purple bands with similar R_f values appeared. Purification of the first of these, VIII, was effected using high-pressure liquid chromatography.[28] The mass spectra cutoff at m/e 366 corresponded to the $^{11}B_{16}{}^{12}C_9{}^1H_{23}{}^{59}Co^+$ ion, and the intensities around the base peak at m/e 363 were consistent with the expected isotopic distribution for a $B_{16}C_9H_{23}Co$ species. Elemental analysis was also in agreement with this formulation. We propose for VIII the structure shown in Figure 5 based on the following data. The ^1H nmr of VIII in acetone-d_6 consists of a cyclopentadienyl singlet

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(28) W. J. Evans and M. F. Hawthorne, manuscript in preparation.

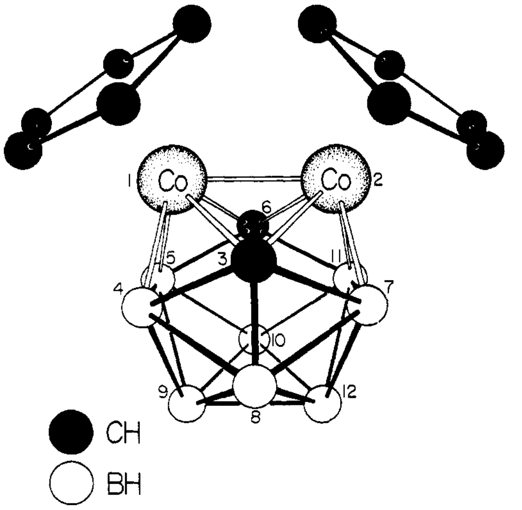

Figure 6. Possible structure of $(C_5H_5Co)_2C_2B_8H_{10}$, X.

and two carborane CH resonances in a 5:1:1 intensity ratio. The cyclopentadienyl singlet at τ 4.22 and the high field carborane CH at τ 3.42 are remarkably close to the τ 4.18 and 3.35 resonances of 2,3-$C_5H_5CoC_2B_8H_{10}$, IX, in acetone-d_6. The low field carborane CH resonance at τ 2.85 compares favorably with the CH resonance reported for 1,10-$C_2B_8H_{10}$[29] and several of its substituted derivatives.[30,31] Comparison of the ^{11}B nmr spectrum of VIII[16] (Table I) with a number of substituted $C_2B_8H_{10}$ derivatives indicates that the doublet at +12.2 ppm arises from a substituent $C_2B_8H_9$ group in VIII. 1-[π-$C_5H_5Fe(CO)_2$]-10-CH_3-1,10-$C_2B_8H_8$ and 1-[$Mn(CO)_5$]-10-CH_3-1,10-$C_2B_8H_8$ show one doublet in this region as does VIII, while other derivatives show closely overlapped doublets for the two sets of boron atoms.[31] Comparison of the ^{11}B nmr spectrum of IX[16] (Table I) to that of VIII is also informative. The low field doublet of area 2 in IX at −10.6 ppm compares favorably with the −9.8 ppm doublet for VIII. The area 4 doublet of IX at +8.1 ppm upon substitution in VIII becomes two doublets at +5.9 and +7.9 ppm. The area 2 doublet at +20.7 ppm in IX becomes the two area 1 doublets at +18.8 and +20.6 ppm in VIII. In further support of this structure are the very similar reduction potentials and electronic spectra of VIII and IX (see Experimental Section). The similarity of R_f values, reduction potentials and electronic, ^1H nmr, and ^{11}B nmr spectra for any given isomer of $C_5H_5CoC_2B_9H_{11}$ and its dimethyl substituted derivative is well established.[32] The similarity of these data in VIII and IX leads us to propose that the carbon atoms in VIII remain in the 2,3 positions as determined for IX (*vide infra*). The absence of low field resonances in the ^{11}B nmr further supports the assignment of the carbon atoms to the five-coordinate positions adjacent to cobalt.

The third metallocarborane isolated from the expansion of 1,6-$C_2B_8H_{10}$ was the predominant product of this reaction, the purple species, IX. The cutoff in the mass spectrum at *m/e* 246 for the molecular ion $^{11}B_8{}^{12}C_7{}^1H_{15}{}^{59}Co^+$ was consistent with the formulation $C_5H_5CoC_2B_8H_{10}$. The elemental analysis confirmed this formulation. A single area 5 cyclopentadienyl signal at τ 4.32 and an area 2 carborane CH resonance at τ 3.28 comprised the ^1H nmr spectrum in acetonitrile-d_3. The 1:2:1 pattern of doublets in the ^{11}B nmr spectrum[16] was consistent with a structure of C_{2v} symmetry in which the carbon atoms were at positions 2,3, 8,9, or 10,11. The paramagnetic ^{11}B nmr spectrum of the red reduced species, $[C_5H_5Co^{II}C_2B_8H_{10}]^-$, was examined to further verify carbon atom positions.[27] The spectrum consisted of two resonances of equal area at −13.2 ($W_{1/2}$ = 300 Hz) and +125 ppm ($W_{1/2}$ = 1900 Hz). The 1:1 ratio of resonances indicated that four boron atoms were strongly interacting with the cobalt, *i.e.*, adjacent to the metal, while four other boron atoms were not. If the carbon atoms were at either positions 8,9 or 10,11, a 3:1 ratio would be expected; hence assignment of the carbon atoms to positions 2 and 3 appears to be correct.

A fourth product isolated from this reaction was the green bimetallic species $(C_5H_5Co)_2C_2B_8H_{10}$, X. The characterization of this compound has already been reported as well as a more facile synthesis by direct polyhedral expansion of 2,3-$C_5H_5CoC_2B_8H_{10}$.[10] The 1:2:1 doublet pattern in the ^{11}B nmr spectrum (Table I) is consistent with several structures. Analysis of the ^{11}B nmr spectra of several other $C_2B_8H_{10}{}^{4-}$ species indicated the (1,7)-5,12-$(C_5H_5Co)_2C_2B_8H_{10}$ structure to be preferred although the (1,2)-3,6 isomer, Figure 6, was also put forth as a possibility involving the then unknown structural feature of adjacent cobalt atoms in the polyhedron. In light of the subsequent discovery of adjacent cobalt atoms in $(C_5H_5Co)_2C_2B_6H_8$, II,[24] the (1,2)-3,6 isomer is quite appealing and an X-ray diffraction study of X is in progress.

An additional species obtained from the 1,6-$C_2B_8H_{10}$ polyhedral expansion reaction was the anion $Co(C_2B_8H_{10})_2{}^-$, XI, isolated as the $(C_5H_5)_2Co^+$ salt. This species was identified by comparison with the cesium salt of XI prepared directly from 1,6-$C_2B_8H_{10}$ by polyhedral expansion in the absence of NaC_5H_5. Elemental analysis and an equivalent weight determination confirmed the formulation for $Cs[Co(C_2B_8H_{10})_2]$. The ^{11}B nmr spectrum of each salt, $Cs[Co(C_2B_8H_{10})_2]$ and $[(C_5H_5)_2Co][Co(C_2B_8H_{10})_2]$, contained a 1:2:1 doublet pattern similar to that of IX. The ^1H nmr spectrum of each exhibited a single carborane CH resonance at τ 4.6. The cobalticinium salt also exhibited a sharp resonance at τ 4.02 arising from the cyclopentadienyl protons of the cation. The structure of XI consists presumably of two equivalent 11-vertex polyhedra sharing a common cobalt atom. The similarity in spectra of XI and IX leads us to propose that the atomic arrangement within each polyhedron of XI is the same as in IX.

Complexation of the reduction product of 1,6-$C_2B_8H_{10}$ with $FeCl_2$ in the presence of $C_5H_5^-$ produced the desired ferracarborane, a red brown complex, XII, in 68–90% yield.

$$1,6\text{-}C_2B_8H_{10} \xrightarrow{2Na} \xrightarrow[NaC_5H_5]{FeCl_2} \underset{\text{XII}}{C_5H_5FeC_2B_8H_{10}}$$

The mass spectral cutoff at *m/e* 243 corresponded to

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[29] P. M. Garrett, J. C. Smart, G. S. Ditta, and M. F. Hawthorne, *Inorg. Chem.*, 8, 1907 (1969).

[30] D. A. Owen and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **91**, 6002 (1969).

[31] D. A. Owen, J. C. Smart, P. M. Garrett, and M. F. Hawthorne, *ibid.*, **93**, 1362 (1971).

[32] M. K. Kaloustian, R. J. Wiersema, and M. F. Hawthorne, *ibid.*, **94**, 6679 (1972).

the $^{11}B_8{}^{12}C_7{}^1H_{15}{}^{56}Fe^+$ ion, and elemental analysis supported the formula $C_5H_5FeC_2B_8H_{10}$. The ^1H nmr spectrum of the reduced species $[C_5H_5Fe^{II}C_2B_8H_{10}]^-$ in acetonitrile-d_3 consisted of an area 5 cyclopentadienyl resonance at τ 5.83 and a carborane CH resonance of area 2 at τ 4.45. The 1:2:1 pattern of doublets in the ^{11}B nmr spectrum was very similar to that of IX and contained no low field resonances. The paramagnetic nmr spectrum of XII was also similar to that for $[2,3\text{-}C_5H_5Co^{II}C_2B_8H_{10}]^-$ (*vide supra*), containing a resonance at -56.1 ($W_{1/2}$ = 820 Hz) and a broad resonance centered at $+257$ ($W_{1/2}$ = 10,650 Hz). Both resonances were of equal area, in agreement with IX, and the analogous $2,3\text{-}C_5H_5FeC_2B_8H_{10}$ structure is proposed.

1,10-$C_2B_8H_{10}$. The polyhedral expansion of 1,10-$C_2B_8H_{10}$ paralleled that of 1,6-$C_2B_8H_{10}$ for the most part, producing some identical products and several isomeric analogs.

$$1,10\text{-}C_2B_8H_{10} \xrightarrow{2Na} \xrightarrow[CoCl_2]{NaC_5H_5}$$

$$1,10\text{-}C_5H_5CoC_2B_7H_9 + 2,9\text{-}C_5H_5CoC_2B_9H_{11} + \underset{\text{XIII}}{(C_5H_5Co)_2C_2B_8H_{10}} +$$

$$\underset{\text{VIII}}{C_5H_5CoC_2B_8H_9(C_2B_8H_9)} + \underset{\text{IX}}{C_5H_5CoC_2B_8H_{10}} + \underset{\text{X}}{(C_5H_5Co)_2C_2B_8H_{10}}$$

The initial metallocarborane isolated was characterized by tlc as 1,10-$C_5H_5CoC_2B_7H_9$.[3] Further characterization by mass spectroscopy and ^1H nmr showed this to be a mixture of 1,10-$C_5H_5CoC_2B_7H_9$ and 2,9-$C_5H_5CoC_2B_9H_{11}$,[25,33] and the ^{11}B nmr spectra confirmed these assignments. Purification of these metallocarboranes by high-pressure liquid chromatography revealed that several additional compounds were present which could be isolated in small quantities.[28]

The next compound characterized from this reaction was a green compound, XIII. The mass spectral isotopic distribution was consistent with the formulation, $(C_5H_5Co)_2C_2B_8H_{10}$, as was the cutoff for the molecular ion at *m/e* 370. Elemental analysis and an exact mass determination confirmed this formula. Four doublets of equal area comprised the ^{11}B nmr spectrum. Only the cyclopentadienyl resonance was detectable at τ 4.63 in the ^1H nmr spectrum due to limited solubility of XIII. Four equivalent sets of boron atoms require equivalent carborane CH units, and three structures exist which possess the proper symmetry and nonadjacent carbon atoms: (1,2)-4,11-, (1,7)-4,11-, and (1,12)-2,8-$(C_5H_5Co)_2C_2B_8H_{10}$. We feel that the most likely structure of XIII is the (1,2)-4,11 isomer since its formation from 1,10-$C_2B_8H_{10}$ or 2,3-$C_5H_5CoC_2B_8H_{10}$ would involve a minimum amount of atomic rearrangement. This proposed structure shown in Figure 7 is the 12-vertex analog of the structure determined for $(C_5H_5Co)_2C_2B_6H_8$, II[24] (the (1,2)-5,7 enantiomer is pictured here to show this relationship more clearly).

Three other metallocarboranes produced in this reaction were identical with those synthesized from 1,6-$C_2B_8H_{10}$, *viz.*, $C_5H_5CoC_2B_8H_9(C_2B_8H_9)$, VIII; 2,3-$C_5H_5CoC_2B_8H_{10}$, IX; and $(C_5H_5Co)_2C_2B_8H_{10}$, X. The best yield of $C_5H_5CoC_2B_8H_{10}$ from the polyhedral expansion of 1,10-$C_2B_8H_{10}$ was obtained at room temperature, and was similar to that of 1,6-$C_2B_8H_{10}$ (*ca.* 44%).

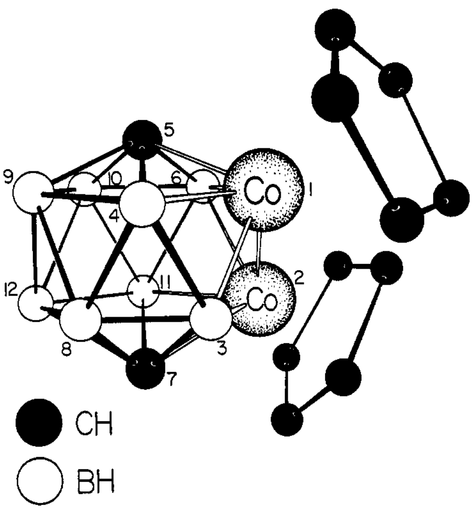

Figure 7. Possible structure of $(C_5H_5Co)_2C_2B_8H_{10}$, XIII.

2,3-$C_2B_9H_{11}$. Although all possible isomers of $C_5H_5CoC_2B_9H_{11}$ or its derivatives are now known[32] and an excellent preparative route to the 2,3 isomer exists,[34] the polyhedral expansion of 2,3-$C_2B_9H_{11}$ was carried out to further determine the generality of the polyhedral expansion method. The carborane reacted readily with 1 equiv of sodium; however, addition of $C_{10}H_8$ was necessary in order to obtain reaction with the second equivalent of metal. Complexation with NaC_5H_5 and $CoCl_2$ afforded the most complex mixture of metallocarboranes reported so far in polyhedral expansion. Two isomers of the desired $C_5H_5CoC_2B_9H_{11}$ were produced: the 2,4 and 2,9 isomers.[35] In addition, the following known metallocarboranes were isolated: 3,10-$C_5H_5CoC_2B_7H_9$, VI; 1,6-$C_5H_5CoC_2B_7H_9$;[3] 2,3-$C_5H_5CoC_2B_8H_{10}$, IX; and $(C_5H_5Co)_2C_2B_8H_{10}$, X; as well as the anion 7,9-$C_2B_9H_{12}^-$ [36] which was isolated as its cobalticinium salt.

Conclusion

Although we have not yet extended the polyhedral expansion reaction to all carboranes or all possible transition metals, it appears to be a general synthetic route to metallocarboranes. The specific metallocarborane formed is dependent upon the reduction conditions as well as the transition metal employed. Characterization of the anions formed as well as the elucidation of the reaction pathways which result with various transition metals remain to be studied. Although the specific mechanistic details of this reaction are not known, the application of this synthesis to a few carboranes has greatly broadened the scope of metallocarborane chemistry and indicated new synthetic goals for further research.

Experimental Section

Physical Measurements. Proton nmr spectra were measured using a Varian A-60D. The 250-MHz ^1H and 80.5-MHz ^{11}B nmr spectra were measured using an instrument designed and built by Professor F. A. L. Anet and his coworkers. Electrochemical data were obtained from an instrument which has been previously

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(33) This was numbered 1,12-$C_5H_5CoC_2B_9H_{11}$ in the original report.[32]

(34) C. J. Jones and M. F. Hawthorne, *Inorg. Chem.*, 12, 608 (1973).

(35) Previously numbered 1,7 and 1,12.[32]

(36) M. F. Hawthorne, D. C. Young, P. M. Garrett, D. A. Owen, S. G. Schwerin, F. N. Tebbe, and P. A. Wegner, *J. Amer. Chem. Soc.*, **90**, 862 (1968).

described.[37] Cyclic voltammetric data were measured in acetonitrile (0.1 *M* tetraethylammonium perchlorate) at a platinum button electrode. Redox potentials are reported as $E_{p/2}$ (V) *vs.* sce. Ultraviolet-visible spectra were measured in acetonitrile using either a Beckman DB or a Cary 14 spectrophotometer. Infrared spectra were determined as Nujol mulls using a Perkin-Elmer 137 sodium chloride spectrophotometer. Mass spectra were obtained using an Associated Electrical Industries MS-9 spectrometer.

Elemental analyses were carried out by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y.

Materials. Anhydrous sublimed ferric chloride, hydrogen reduced iron powder, naphthalene, and spectroquality acetonitrile were obtained from Matheson Coleman and Bell. Anhydrous $CoCl_2$ was prepared from $CoCl_2 \cdot 6H_2O$, purchased from Mallinckrodt Chemical Co., by heating under vacuum. Sodium was obtained from Allied Chemical Co., and sodium hydride, used as a 60% dispersion in mineral oil, was purchased from Metal Hydrides, Inc. Tetraphenylarsonium chloride was obtained from Aldrich Chemical Co. as was dicyclopentadiene which was converted to C_5H_6 immediately prior to use. Silica gel powder, 60–200 mesh, was obtained from J. T. Baker Chemical Co. for use in column chromatography. Preparative thick-layer chromatography was done on ChromAR Sheet 1000 purchased from Mallinckrodt Chemical Co. Hexane, methylene chloride, ethanol, and acetone were reagent grade. THF was freshly distilled from $LiAlH_4$ and kept under nitrogen. Literature methods were used to prepare 1,7-$C_2B_6H_8$,[38] 4,5-$C_2B_7H_9$,[38] 1,6-$C_2B_8H_{10}$,[39] 1,10-$C_2B_8H_{10}$,[40] and 2,3-$C_2B_9H_{11}$.[41] NaC_5H_5 was prepared as previously described.[13]

Cobalt Metallocarboranes from 1,7-$C_2B_6H_8$. Under a nitrogen atmosphere, sodium (1.0 g, 44 mmol) and naphthalene (0.4 g, 3.2 mmol) were placed in a 100-ml flask. THF (20 ml) was added, and the solution was stirred 1 hr. Addition of 1,7-dicarba-*closo*-octaborane(8) (1.9501 g, 20.1 mmol) by condensation into the flask cooled to −78° caused the dark green color of sodium naphthalide to immediately disappear. The flask was allowed to warm to −20° in a cold room and stirring was continued for 3 days. The amber solution which formed was syringed into a 500-ml three-neck flask containing 20 mmol of previously prepared NaC_5H_5 cooled to −50°. A slurry of finely ground anhydrous $CoCl_2$ (6.0 g, 46 mmol) in 50 ml of THF was added dropwise to the stirred solution. After addition was complete the flask was allowed to warm to room temperature slowly and stir for 15 hr. After a stream of oxygen was passed through the reaction mixture for 30 min, the brown solution was filtered into a 1-l. flask, 150 ml (dry volume) of silica gel was added, and the solvent was stripped using a rotary evaporator and a water aspirator. The last traces of solvent were removed under high vacuum. The solids were placed in a large Soxhlet thimble and extracted with 1 l. of hexane. The solvent was stripped to approximately 30 ml and the solution was passed through a 4 × 20 cm column of silica gel in hexane. Two bands were separated.

(a) $C_5H_5CoC_2B_6H_8$, I. The deep red solution comprising the first fraction was stripped to approximately 50 ml and placed in a flask attached to a sublimer. The solvent was evaporated, and dark red crystals were collected on the 0° cold finger. The yield was 0.1811 g (0.82 mmol, 4.1%), mp 61–64°. *Anal.* Calcd for $C_5H_5CoC_2B_6H_8$: B, 29.36; C, 38.06; H, 5.89; Co, 26.70. Found: B, 29.82; C, 39.07; H, 6.04; Co, 24.67. Uv-visible [λ_{max}, nm (log ϵ)]: 248 (4.38), 260 sh (4.14), 324 (3.70), 470 (2.33). Ir (cm^{-1}): 2910 vs, 2560 vs, 1460 vs, 1420 w, 1375 vs, 1145 m, 1115 m, 1095 s, 1060 w, 1015, m, 920 w, 860 w, 828 vs, 786 w, 755 w, 727 w. A reduction was observed at −1.09 V.

(b) $(C_5H_5Co)_2C_2B_6H_8$, II, Continued elution with hexane resulted in a second fraction from the above reaction. Recrystallization of this compound from hexane afforded 0.508 g (1.47 mmol, 7.3%) of green crystals, mp 236–238°. *Anal.* Calcd for $(C_5H_5Co)_2C_2B_6H_8$: B, 18.53; C, 41.76; H, 5.22; Co, 34.17. Found: B, 18.02; C, 42.45; H, 5.36; Co, 34.51. Uv-visible [λ_{max}, nm (log ϵ)]: 233 (4.38), 324 (4.39), 548 sh (2.64), 652 (2.88). Ir (cm^{-1}): 2900 vs, 2540 s, 1470 s, 1420 w, 1375 m, 1270 w, 1125 w, 1105 w, 1080 w, 1040 w, 1020 w, 925 m, 890 w, 870 m, 850 m, 840 s, 820 s, 790 w, 770 w. A reduction was observed at −1.07 V, an oxidation at +0.87 V.

$(C_6H_5)_4As[Co(C_2B_6H_8)_2]$, III, Mercury (80 g) and a magnetic stirring bar were placed in a 100-ml flask. Under an atmosphere of nitrogen, sodium (0.50 g, 22 mmol) was added in small pieces. The flask was cooled, and 15 ml of THF was added. The mixture was degassed, 1,7-$C_2B_6H_8$ (0.9987 g, 10.3 mmol) was added by condensation, and the reaction was stirred 3 days at −20°. A slurry of anhydrous cobaltous chloride (2.0176 g, 15.5 mmol) in 50 ml of dry tetrahydrofuran was added dropwise over a 2-hr period. The mixture was stirred at −30° for 1 additional hr and then allowed to warm to room temperature and stirred for 15 hr. The mixture was filtered through Celite and the solvent stripped using a rotary evaporator. The solid, dark residue was dissolved in 200 ml of absolute ethanol and added to a solution of tetraphenylarsonium chloride (3.0 g, 7.2 mmol) in 100 ml of absolute ethanol. After standing 15 min the solution was filtered into a 1-l. flask containing 150 ml of silica gel. The bulk of the solvent was stripped on a rotary evaporator, and the last traces of solvent were removed under high vacuum. The solids were placed in a large Soxhlet thimble and extracted using 1 l. of ethyl ether.

The resulting ether solution was condensed on a steam bath to approximately 400 ml and sufficient hexane was added to cause cloudiness. The solution was allowed to stand on a warming table (40°) until crystals formed. The yield of crude, dark brown crystals was 0.3420 g. The crude material was recrystallized from a dichloromethane–ether–hexane solution to yield 0.1278 g (3.9%) of long, dark brown needles. *Anal.* Calcd for $(C_6H_5)_4As[(C_2B_6H_8)_2Co]$: C, 52.86; B, 20.42; H, 5.66; As, 11.79; Co, 9.26. Found: C, 51.30; B, 20.62; H, 6.27; As, 12.28; Co, 9.25. The equivalent weight was determined by passing a solution of 31.8 mg of salt in approximately 30 ml of 1:1 acetonitrile-water through a 1 × 6 cm acid ion-exchange column. The eluent was titrated with 5.01 ml of 9.8×10^{-3} *M* sodium hydroxide solution (equiv wt calcd, 635.7; found, 647). Uv-visible [λ_{max}, mn (log ϵ)]: 260 (4.02), 266 (4.07), 273 (4.04), 386 (3.69), 456 sh (3.28), 583 sh (2.33). Ir (cm^{-1}): 2950 vs, 2540 vs, 1590 w, 1480 vs, 1380 vs, 1340 w, 1320 w, 1190 w, 1175 w, 1150 w, 1120 w, 1105 w, 1090 m, 1070 w, 1030 w, 1005 m, 946 w, 930 w, 918 w, 887 w, 838 w, 824 w, 794 w, 762 w, 748 s, 728 w, 690 s. An irreversible reduction was observed at −1.75 V, an irreversible oxidation at +0.69 V.

Iron Metallocarboranes from 1,7-$C_2B_6H_8$. Sodium naphthalide was used to reduce 1,7-$C_2B_6H_8$ (0.9695 g, 10.0 mmol) as described above in the preparation of $C_5H_5CoC_2B_6H_8$, I. The reduced carborane solution was added to a cooled solution of 30 mmol of freshly prepared NaC_5H_5. A gray slurry of $FeCl_2$ in THF prepared by reaction of iron powder (1.2 g, 20 mmol) and $FeCl_3$ (3.2 g, 20 mmol) in 100 ml of THF at reflux for 3 hr was added to the flask cooled to −30°. The flask was allowed to warm to room temperature and stirred overnight. After oxygen was bubbled through the solution for 30 min, it was filtered through Celite. Silica gel (150 ml) was added to the solution and the solvent removed. The remaining solids were placed in a Soxhlet thimble and extracted with 1 l. of hexane. The solution was evaporated to a small volume and placed on a 4 × 20 cm column of silica gel in hexane. Among the several components which were separated on the column, three main bands were collected and characterized. The first fraction consisted of a yellow band characterized by its infrared spectrum as ferrocene.

(a) $C_5H_5FeC_2B_6H_8$, IV. Next eluted was a red band which crystallized as the solvent was stripped by rotary evaporation. Recrystallization from hexane produced 0.228 g (1.05 mmol, 10.5%) of $C_5H_5FeC_2B_6H_8$, IV, mp 132–133°. High-resolution mass measurement: calcd for $^{11}B_6{}^{12}C_7{}^{1}H_{13}{}^{56}Fe^+$, 219.092497; found, 219.0927 ± 0.0003. Uv-visible [λ_{max}, nm (log ϵ)]: 226 (4.28), 294 (3.92), 344 sh (3.10), 460 (2.97), 670 (2.17). Ir (cm^{-1}): 2900 vs, 2520 s, 1470 s, 1420 m, 1375 s, 1130 m, 1070 m, 1020 w, 985 w, 930 w, 890 m, 850 m, 840 m, 815 w, 795 w. A reduction was observed at −0.58 V.

(b) $C_5H_5FeC_2B_6H_8$, V. Elution with hexane–dichloromethane (9:1 v/v) resulted in a brown fraction. $C_5H_5FeC_2B_6H_8$, V (0.170 g, 0.79 mmol, 7.9%), was recrystallized from hexane. High-resolution mass measurement calcd for $^{11}B_6{}^{12}C_7{}^{1}H_{13}{}^{66}Fe^+$, 219.092497; found 219.0925 ± 0.0003. Uv-visible [λ_{max}, nm (log ϵ)]: 228 (4.18), 284 (3.78), 346 (3.56), 464 (2.95). Ir (cm^{-1}): 2900 vs, 2520 s, 1460 s, 1430 m, 1370 s, 1140 m, 1070 w, 1040 m, 1020 m, 1010 m, 895 w, 880 w, 845 s, 795 m, 725 w. A reduction was observed at −0.40 V.

Cobalt Metallocarboranes from 4,5-$C_2B_7H_9$. 4,5-Dicarba-*closo*-nonaborane(9) (0.1088 g, 10 mmol) was dissolved in 80 ml of THF

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in a previously dried, nitrogen-flushed 500-ml, three-neck flask equipped with a nitrogen inlet and mechanical stirrer with a glass blade. Sodium (0.46 g, 20 mmol) was added to the stirred solution and within 15 min the solution was a deep golden color. This changed to dark green within 30 min and opaque blue within 60 min of sodium addition. After 1 week the reaction became translucent and purple. One hour after the reaction had become purple, an additional color change to red-orange or yellow-brown occurred with the concomitant disappearance of the last traces of sodium. Freshly prepared NaC_5H_5 (10 mmol) was added followed by a slurry of $CoCl_2$ (3.0 g, 23 mmol) in 50 ml of THF, and the reaction was stirred overnight. Silica gel (500 ml) was placed under high vacuum for 1 hr. Under nitrogen 30 ml of this silica gel was added to the reaction mixture and the solvent removed under high vacuum. The solvent free silica gel mixture was chromatographed under nitrogen on a column of deoxygenated silica gel in nitrogen saturated hexane.

(a) **$C_5H_5CoC_2B_7H_9$, VI,** A yellow band moving rapidly in hexane was first collected and the solvent stripped on a rotary evaporator. Sublimation of the residue produced 0.210 g (0.9 mmol, 9%) of $C_5H_5CoC_2B_7H_9$, VI, mp 57–58°. High-resolution mass measurement calcd for $^{11}B_7{}^{12}C_7{}^{1}H_{14}{}^{59}Co^+$, 234.107872; found, 234.1081 ± 0.0005. Uv-visible [λ_{max}, nm (log ϵ)]: 254 (4.02), 308 (3.57), 448 (2.23). Ir (cm^{-1}): 2910 vs, 2570 s, 1470 s, 1430 w, 1380 m, 1140 w, 1110 m, 1070 m, 1020 w, 975 w, 940 m, 920 m, 890 w, 860 w, 840 m, 800 w, 725 w. A reduction was observed at −1.15 V.

(b) **$C_5H_5CoC_2B_6H_8$, VII.** The second major band observed in the above reaction was a red-orange fraction eluted with hexane–CH_2Cl_2 (9:1 v/v). Recrystallized from hexane–CH_2Cl_2 was 0.260 g (1.17 mmol, 11.7%) of $C_5H_5CoC_2B_6H_8$, VII, mp 120–122°. High-resolution mass measurement calcd for $^{11}B_6{}^{12}C_7{}^{1}H_{13}{}^{59}Co^+$, 222.090740; found, 222.0908 ± 0.0004. Uv-visible [λ_{max}, nm (log ϵ)]: 250 (4.01), 274 sh (3.84), 350 (3.56), 460 (2.32). Ir (cm^{-1}): 2910 vs, 2540 s, 1470 s, 1415 m, 1380 m, 1320 w, 1270 w, 1190 w, 1100 m, 1080 w, 1035 m, 1010 m, 935 w, 850 m, 820 w, 805 m, 755 w, 740 w, 725 w. A reduction was observed at −0.84 V.

Cobalt Metallocarboranes from 1,6-$C_2B_6H_{10}$. 1,6-Dicarba-*closo*-decaborane(10) (1.1710 g, 9.7 mmol) was dissolved in 80 ml of THF in a previously dried, nitrogen flushed, 500-ml, three-neck flask equipped with a nitrogen inlet and mechanical stirrer with a glass blade. Sodium (0.45 g, 19.4 mmol) was added and within several hours the reaction became yellow. After stirring overnight the solution was once again colorless and no sodium was visible. Addition of NaC_5H_5 (40 mmol) and a THF slurry of $CoCl_2$ (7.0 g, 54 mmol) produced a greenish solution. After stirring overnight, air was bubbled through the reaction mixture for 30 min. The solution was poured onto 30 ml of silica gel and the solvent removed on a rotary evaporator. The solids were chromatographed on two 5 × 30 cm columns of silica gel in hexane. Five reaction products were separated.

(a) **1,6-$C_5H_5CoC_2B_7H_9$.** Initially a red-orange band was eluted with hexane. Isolated by sublimation from this fraction was 0.057 g (0.24 mmol, 2.5%) of 1,6-$C_5H_5CoC_2B_7H_9$[3] characterized by ^1H and ^{11}B nmr.

(b) **$C_5H_5CoC_2B_8H_9(C_2B_8H_9)$, VIII,** Next isolated from the above reaction was a purple band eluted with hexane–CH_2Cl_2 (9:1 v/v). The ^1H nmr spectrum of this species indicated the presence of another metallocarborane and purification was effected by high-pressure liquid chromatography.[28] Recrystallization from hexane–CH_2Cl_2 afforded 0.011 g (0.03 mmol, 0.3%) of $C_5H_5CoC_2B_8H_9(C_2B_8H_9)$, mp 179–180°. *Anal.* Calcd for $C_5H_5CoC_2B_8H_9(C_2B_8H_9)$: B, 47.62; C, 29.76; H, 6.38; Co, 16.22. Found: B, 47.58; C, 29.82; H, 6.54; Co, 16.68. Uv-visible [λ_{max}, nm (log ϵ)]: 235 (4.29), 274 sh (3.71), 358 (3.78), 448 (2.66), 578 (2.60). Ir (cm^{-1}): 2900 vs, 2560 s, 2540 s, 2520 s, 1470 s, 1420 m, 1370 s, 1140 w, 1120 m, 1070 w, 1020 w, 1005 w, 960 w, 935 w, 925 w, 895 w, 855 m, 840 m, 825 w, 780 w, 770 w, 720 w, 710 w. A reduction was observed at −0.75 V.

(c) **2,3-$C_5H_5CoC_2B_6H_{10}$, IX.** A second purple band from the above reaction was eluted with hexane–CH_2Cl_2 (8:2 v/v). Flocculent purple solids precipitated upon rotary evaporation of this fraction. Recrystallization from hexane–CH_2Cl_2 resulted in the isolation of 1.05 g (4.3 mmol, 44%) of 2,3-$C_5H_5CoC_2B_8H_{10}$, mp 297–300°. *Anal.* Calcd for $C_5H_5CoC_2B_8H_{10}$: B, 35.36; C, 34.37; H, 6.18; Co 24.09. Found: B, 36.33; C, 34.03; H, 5.95; Co, 23.20. Uv-visible [λ_{max}, nm (log ϵ)]: 230 sh (3.04), 277 (3.60), 352 (3.76), 442 (2.58), 572 (2.66). Ir (cm^{-1}): 2910 vs, 2570 s, 1470 s, 1430 m, 1370 s, 1110 s, 1085 w, 1075 w, 1015 w, 940 m, 900 w, 880 w, 855 m, 840 w, 830 m, 785 w, 770 w, 725 m, 715 m. A reduction was observed at −0.77 V.

(d) **$(C_5H_5Co)_2C_2B_8H_{10}$, X.** Following IX was a green band, X, which moved in hexane–CH_2Cl_2 (1:1 v/v). Preparative thick-layer chromatography in benzene effected the final purification of X which was recrystallized from CH_2Cl_2. $(C_5H_5Co)_2C_2B_8H_{10}$, mp 275–277° (0.115 g, 0.3 mmol), was isolated in 3.2% yield. *Anal.* Calcd for $(C_5H_5Co)_2C_2B_8H_{10}$: B, 23.46; C, 39.10; H, 5.47; Co, 31.97. Found: B, 23.40; C, 38.46; H, 5.51; Co, 31.15. Uv-visible [λ_{max}, nm (log ϵ)]: 233 (4.35), 265 (4.06), 308 (4.24), 415 sh (2.96), 610 (2.95). Ir (cm^{-1}): 2900 vs, 2500 s, 1450 s, 1410 m, 1360 s, 1250 w, 1105 w, 1070 m, 1010 m, 970 w, 940 w, 920 w, 870 w, 855 w, 840 m, 835 m, 725 m. A reduction was observed at −1.07 V, an oxidation at +1.06 V.

(e) **$(C_5H_5)_2Co[Co(C_2B_8H_{10})_2]$, XI.** A subsequent green band was eluted with CH_2Cl_2. Recrystallization from acetone–hexane produced 0.193 g (0.4 mmol, 4%) of XI, mp 310° dec.

$Cs[Co(C_2B_6H_{10})_2]$, Na (0.45 g, 19.8 mmol) and $C_{10}H_8$ (0.1, g 0.8 mmol) were added to 1,6-$C_2B_8H_{10}$ (1.1906 g, 9.9 mmol) in 80 ml of THF in a dried, nitrogen-flushed, 500-ml, three-neck flask. The solution was cooled to −78° and stirred overnight. $CoCl_2$ (9.5 g, 74 mmol) was added as a THF slurry and the stirring mixture was allowed to gradually warm to room temperature overnight. Silica gel was added and the solvent removed. The solids were placed on a 5 × 30 cm column of silica gel in hexane. A dark green band was eluted with hexane–CH_2Cl_2 (1:5 v/v). The solvent was removed and the residue dissolved in acetone. Following addition of CsCl in H_2O, slow evaporation produced green crystals. Repeated recrystallization from acetone–water resulted in 2.05 g (4.7 mmol, 48%) of $Cs[Co(C_2B_8H_{10})_2]$, mp 324° dec. *Anal.* Calcd for $Cs[Co(C_2B_8H_{10})_2]$: B, 39.96; C, 11.10; H, 4.62; Co, 13.61; Cs, 30.70. Found: B, 40.07; C, 11.19; H, 5.00; Co, 13.14; Cs, 29.71. The equivalent weight was determined by passing a solution of 0.062 g of the salt in approximately 30 ml of 1:1 CH_3CN-H_2O through a 1 × 10 cm acid ion-exchange column. The eluent was titrated with 3.87 ml of 0.0351 *M* sodium hydroxide solution (equiv wt: calcd, 433; found, 457). Uv-visible [λ_{max}, nm (log ϵ)]: 236 (4.45), 320 (4.21), 637 [broad, two overlapping unsymmetrical peaks] (2.19). Ir (cm^{-1}): 2910 vs, 2550 vs, 1470 m, 1370 m, 1130 m, 1110 s, 1060 m, 935 s, 920 m, 910 w, 895 w, 875 m, 840 m, 830 w, 790 m, 770 w, 735 m, 725 s, 695 w. A reduction was observed at −0.28 V, an oxidation at +1.27 V.

$C_5H_5FeC_2B_8H_{10}$ from 1,6-$C_2B_6H_{10}$. 1,6-$C_2B_8H_{10}$ (0.8865 g, 7.05 mmol) was reduced with sodium as described above. Freshly prepared NaC_5H_5 (35 mmol) and a gray slurry of $FeCl_2$ (82 mmol) in THF, prepared as previously described, were added, and the reaction mixture was stirred overnight. Air was bubbled through the reaction mixture for 30 min, 20 ml silica gel was added, and the solvent was removed. The solids were placed on a 5 × 30 cm silica gel column in hexane. A red-brown band was eluted with hexane–CH_2Cl_2 (8.5:1 v/v). $C_5H_5FeC_2B_8H_{10}$, mp 275–277° (1.17 g, 4.8 mmol, 68%), was recrystallized from hexane–CH_2Cl_2 as red-brown needles. *Anal.* Calcd for $C_5H_5FeC_2B_8H_{10}$: B, 35.81; C, 34.81; H, 6.26; Fe, 23.12. Found: B, 35.98; C, 34.78; H, 6.73; Fe, 23.52. Uv-visible [λ_{max}, nm (log ϵ)]: 232 (4.18), 285 (3.77), 348 (3.67), 460 (2.84), 513 (2.72). Ir (cm^{-1}): 2920 vs, 2560 s, 1470 s, 1430 w, 1370 m, 1120 m, 1070 w, 1015 w, 945 w, 930 w, 905 w, 885 w, 850 m, 835 m, 820 w, 775 w, 725 w, 710 m. A reduction was observed at −0.17 V.

Cobalt Metallocarboranes from 1,10-$C_2B_6H_{10}$. 1,10-Dicarba-*closo*-decaborane(10) (1.5077 g, 12.5 mmol) was reduced at room temperature in THF with Na (0.57 g, 25 mmol) and $C_{10}H_8$ (0.1 g, 0.8 mmol) using a procedure similar to that for 1,6-$C_2B_8H_{10}$. Within 6 hr all Na had disappeared and 50 mmol of NaC_5H_5 and 15 g (115 mmol) of $CoCl_2$ were added. After stirring overnight, air was bubbled through the mixture and 30 ml of silica gel was added. The solvent was removed and the solids were chromatographed on two 5 × 30 cm columns of silica gel in hexane. Gradual enrichment of the eluent with CH_2Cl_2 allowed the separation of six metallocarboranes formed from 1,10-$C_2B_8H_{10}$.

(a) **1,10-$C_5H_5CoC_2B_7H_9$,** Initially a yellow band was collected. Purification by high-pressure liquid chromatography and subsequent sublimation produced 0.117 g (0.5 mmol, 4%) of 1,10-$C_5H_5CoC_2B_7H_9$ identified by ^1H and ^{11}B nmr.

(b) **2,9-$C_5H_5CoC_2B_9H_{11}$,** A second component of the initially collected yellow band was purified by high-pressure liquid chromatography and characterized by ^1H and ^{11}B nmr as 2,9-$C_5H_5CoC_2B_9H_{11}$ (0.062 g, 0.25 mmol, 2%).

(c) **$(C_5H_5Co)_2C_2B_8H_{10}$, XIII,** A green band was subsequently eluted with hexane–CH_2Cl_2 (9:1 v/v). Green crystals, mp 334–335° (0.045 g, 0.12 mmol), were isolated in 1% yield. *Anal.* Calcd for

$(C_5H_5Co)_2C_2B_8H_{10}$: B, 23.46; C, 39.10; H, 5.47; Co, 31.97. Found: B, 26.31; C, 38.99; H, 5.65; Co. 28.89. Exact mass measurement calcd for $^{11}B_8{}^{12}C_{12}{}^{1}H_{20}{}^{59}Co_2{}^+$, 370.097305; found, 370.0985 ± 0.0014. Uv-visible [λ_{max}, nm (log ϵ)]: 230 (4.29), 315 (4.49), 426 (2.92), 598 (2.84). Ir (cm^{-1}): 2900 vs, 2560 s, 1460 s, 1420 w, 1370 s, 1130 w, 1120 w, 1110 w, 1050 m, 1020 w, 1010 w, 975 m, 930 w, 910 w, 870 w, 855 w, 835 s, 820 m, 755 w, 725 w. A reduction was observed at −1.32 V, an oxidation at +1.03 V.

(d) $C_5H_5CoC_2B_6H_9(C_2B_8H_9)$, VIII. Separated and isolated as described above was 0.182 g (0.5 mmol, 4%) of VIII.

(e) $C_5H_5CoC_2B_8H_{10}$, IX. Isolated as described above was 1.35 g (5.5 mmol, 44%) of IX.

(f) $(C_5H_5Co)_2C_2B_8H_{10}$, X. Isolated as described above was 9.2 mg (0.025 mmol, 0.2%) of X.

Cobalt Metallocarboranes from 2,3-$C_2B_9H_{11}$. 2,3-Dicarba-*closo*-undecaborane(11) (2.6 g, 19.6 mmol) was taken up in 80 ml of THF in a 500-ml flask identical with that used for 1,6-$C_2B_8H_{10}$, and Na (1.0 g, 40 mmol) was immediately added. The solution rapidly became yellow. After stirring overnight the solution was colorless and approximately half the Na had disappeared. $C_{10}H_8$ (0.2 g, 1.6 mmol) was added and the reaction continued for 3 days at which time no Na was visible. The reaction was cooled to 0°, and 60 mmol of NaC_5H_5 and 8.0 g (60 mmol) of $CoCl_2$ were added. After stirring overnight, air was bubbled through the reaction mixture, silica gel added, and the solvent removed. Two 5 × 30 cm columns of silica gel in hexane were used to separate the reaction mixture. The following products, listed in order of elution, were separated by techniques described above and characterized by tlc, ^1H nmr, and cyclic voltammetry: 3,10-$C_5H_5CoC_2B_7H_9$, VI (8 mg, 0.030 mmol, 0.15%); 2,9-$C_5H_5CoC_2B_9H_{11}$ (120 mg, 0.5 mmol, 2.5%); 1,6-$C_5H_5CoC_2B_7H_9$ (47 mg, 0.2 mmol, 1.0%); 2,4-$C_5H_5CoC_2B_9H_{11}$ (10 mg, 0.04 mmol, 0.2%); 2,3-$C_5H_5CoC_2B_8H_{10}$, IX (10 mg, 0.04 mmol, 0.2%); $(C_5H_5Co)_2C_2B_8H_{10}$, X (22 mg, 0.06 mmol, 0.3%); and $(C_5H_5)_2Co^+(7,9\text{-}C_2B_9H_{12})^-$ (19 mg, 0.06 mmol, 0.3%).

Acknowledgment. The authors wish to thank Dr. R. J. Wiersema for obtaining the 80.5-MHz ^{11}B and 250-MHz ^1H nmr spectra and the cyclic voltammetry data. This research was supported by the Office of Naval Research and the Army Research Office (Durham).

Organometallic Reactions of 1-Ethynyl-1,2-carborane

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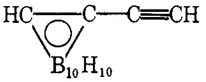
Received February 1, 1973

Abstract: Ethynylcarborane has been catalytically trimerized to 1,2,4-tris(1′-1′,2′-carboranyl)benzene in high yield. The latter species failed to undergo electrophilic substitution on the aromatic ring. A normal substitution product was obtained from the reaction between $Co_2(CO)_8$ and ethynylcarborane. The interaction of ethynylcarborane with *trans*-IrCl(CO)[P(C_6H_5)$_3$]$_2$ afforded a novel octahedral complex containing σ-2-carboranylacetylide and σ-*trans*-2-carboranylvinyl substituents. Copper(II)-catalyzed oxidative coupling produced 1,4-di(1′-1′,2′-carboranyl)butadiyne in good yield. The latter compound was resistant to addition reactions at the triple bonds.

The preparation of 1-ethynyl-1,2-carborane (I) was first reported by Dupont and Hawthorne in 1964.[1] These early investigations illustrated that reactions at the acetylenic CH bond with species such as Grignard reagents proceeded in a fashion similar to other substituted acetylenes. No additional studies on the chemical behavior of I have been reported, although its reactivity would be expected to be affected by its bulky, electron-withdrawing carboranyl substituent.



I

The recent development of an improved synthesis of I[2] has prompted a further study of its chemistry, and we wish to report its reactions with several transition metal species.

Results and Discussion

Catalytic Trimerization. Reaction of a benzene solution of I with a catalytic amount of the acetylene cyclotrimerization catalyst, bis(acrylonitrile)nickel(0),[3] followed by column chromatography, afforded an 85% yield of a product characterized as 1,2,4-tris(1′-1′,2′-carboranyl)benzene (II). No evidence was found for the production of the 1,3,5 isomer or linear polymers although some dark colored material, which was not investigated further, was found to adhere to the top of the chromatographic column.

Compound II exhibited a mass spectral cutoff at *m/e* 510, corresponding to the $^{11}B_{30}{}^{12}C_{12}{}^{1}H_{36}{}^+$ ion. An osmometric molecular weight determination in benzene solution (calcd, 506; found, 503) further confirmed the formulation. The infrared spectrum of II (Table I) exhibited a strong B–H stretching absorption at 2600 cm^{-1}, and the C≡C and ≡C—H vibrations of the starting material were absent. Very weak absorptions in the 2000–1650-cm^{-1} range, in which phenyl overtones commonly occur,[4] were also observed. The 80.5-MHz ^{11}B nmr spectrum of II (Table II) showed severe overlap of resonances and gave no structural information. The ultraviolet–visible spectrum of II is presented in Table III.

The structure of II was assigned on the basis of its ^1H nmr spectrum (Table IV). In deuterioacetone solution at 60 MHz, II exhibited a multiplet of relative

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(1) J. A. Dupont and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **86**, 1643 (1964); U. S. Patents 3,228,986 and 3,228,987 (1966).

(2) T. E. Paxson, K. P. Callahan, and M. F. Hawthorne, *Inorg. Chem.*, **12**, 708 (1973).

(3) G. N. Schrauzer, *J. Amer. Chem. Soc.*, **81**, 5310 (1959).

(4) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Wiley, New York, N. Y., 1958.