Registry No. 1-Methyl-2-tropenyl-*closo*-1,2-dicarbadodecaborane(10), 17116-44-8; 1-tropenyl-*closo*-1,2-dicarbadodecaborane(11), 50599-62-7; 1-tropenyl-*closo*-1,7-dicarbadodecaborane(11), 50599-63-8; 1,2-ditropenyl-*closo*-1,2-dicarbadodecaborane(10), 50599-64-9; 1,7-ditropenyl-*closo*-1,7-dicarbadodecaborane(10), 50599-65-0; 1-methyl-2-γ-tropenyl-*closo*-1,2-dicarbadodecaborane(10), 17203-65-5; 1-γ-tropenyl-*closo*-1,2-dicarbadodecaborane(11), 50599-66-1; 1-γ-tropenyl-*closo*-1,7-dicarbadodecaborane(11), 50599-67-2; 1,2-di-γ-tropenyl-*closo*-1,2-dicarbadodecaborane(10), 50599-68-3; 1,7-di-γ-tropenyl-*closo*-1,7-dicarbadodecaborane(10), 50599-69-4; 1-methyl-[7.12^2]-1,2-dicarbahemiousenium hexafluoroarsenate, 50600-65-2; 1-methyl-[7.12^2]-1,2-dicarbahemiousenium hexafluoroantimonate, 26837-93-4; 1-methyl-[7.12^2]-1,2-dicarbahemiousenium bromide, 26837-92-3; [7.12^1]-1,2-dicarbahemiousenium hexafluoroantimonate, 50790-60-8; [7.12^1]-1,7-dicarbahemiousenium hexafluoroarsenate, 50600-63-0; [$7.7.12^{1,7}$]-1,7-dicarbaousenium hexafluoroarsenate, 50600-67-4; [$7.7.12^{1,7}$]-1,7-dicarbaousenium hexachlorostannate, 50883-26-6; [$7.7.12^{1,7}$]-1,7-dicarbaousenium bromide, 50600-55-0; [$7.7.10^{2,x}$]ousene, 50639-83-3; potassium 1-methyl-*nido*-(3)-1,2-dicarbaundecaborate(11), 50639-76-4; trimethylammonium 1-methyl-*nido*-(3)-1,2-dicarbaundecaborate(11), 50639-77-5; 1-methyl-[$7.7.11^{x,y}$]-*nido*-(3)-1,2-dicarbaousenium fluoroborate, 50639-84-4; 1-methyl-[7.11^x]-*nido*-(3)-1,2-dicarbahemiousene, 50639-81-1; tropenyl methyl ether, 1714-38-1; 1-methyl-*closo*-1,2-dicarbadodecaborane(11), 16872-10-9; *closo*-1,2-dicarbadodecaborane(12), 16872-09-6; *closo*-1,7-dicarbadodecaborane(12), 16986-24-6; cesium [7.10^2]hemiousenide, 50639-80-0; tropenylium bromide, 5376-03-4; tropenylium fluoroborate, 27081-10-3.

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Polyhedral Expansion of Metallocarboranes

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New metallocarboranes of general formulas $(C_5H_5)_2Co_2C_2B_nH_{n+2}$ and $(C_5H_5)_3Co_3C_2B_nH_{n+2}$ can be directly prepared by the reduction of the closo metallocarboranes 2,1,6-$C_5H_5CoC_2B_7H_9$, 1,2,3-$C_5H_5CoC_2B_8H_{10}$, 1,2,4-$C_5H_5CoC_2B_8H_{10}$, and 3,1,2-$C_5H_5CoC_2B_9H_{11}$ with Na in the presence of naphthalene followed by addition of $CoCl_2$ and NaC_5H_5. The preparation, characterization, and proposed structures of these metallocarboranes are discussed.

The general reaction sequence involving the reduction of a carborane with subsequent or concomitant complexation with a transition metal to produce a monometallocarborane has been established.[1-7] The primary objective of this polyhedral expansion[2] reaction was the synthesis of a polyhedral monometallocarborane one vertex larger than the starting carborane

$$C_2B_nH_{n+2} \xrightarrow{2e^-} [C_2B_nH_{n+2}]^{2-} \xrightarrow[NaC_5H_5]{MCl_2} C_5H_5MC_2B_nH_{n+2}$$

and this was usually the principal product observed. The achievement of this goal was enhanced, however, by the simultaneous formation of a wealth of side products. Monometallic species including $C_5H_5MC_2B_{n+1}H_{n+3}$, $C_5H_5MC_2B_{n-1}H_{n+1}$, $C_5H_5MC_2B_nH_{n+1}(C_2B_nH_{n+1})$, and $C_5H_5MC_2B_nH_{n+1}(C_{10}H_7)$ were formed as well as several new bimetallic compounds, $(C_5H_5)_2M_2C_2B_nH_{n+2}$ where $n = 4, 5, 6,$ and 8. The isolation of these bimetallic species suggested that the polyhedral expansion reaction could be extended to metallocarboranes to provide not only an improved preparative route to known bimetallocarboranes but also a direct synthesis of new bimetallic species

$$C_5H_5MC_2B_nH_{n+2} \xrightarrow{3e^-} \xrightarrow[2.\ [O]]{1.\ M'Cl_2,\ NaC_5H_5} (C_5H_5)_2MM'C_2B_nH_{n+2}$$

We report here the results of the polyhedral expansion of 2,1,6-$C_5H_5CoC_2B_7H_9$,[8,10] 1,2,3-$C_5H_5CoC_2B_8H_{10}$,[2,11] 1,2,4-$C_5H_5CoC_2B_8H_{10}$,[12] and 3,1,2-$C_5H_5CoC_2B_9H_{11}$[13] to form *inter alia* the first eleven- and thirteen-vertex bimetallic metallocarboranes and the first trimetallic metallocarborane.[14]

General Procedure

Each metallocarborane was treated in tetrahydrofuran (THF) with 3 equiv of sodium metal in the presence of naphthalene. This may be formally viewed as a M(III) → M(II) reduction followed by an additional two-electron reduction to form an anionic nido metallocarborane species. While reduction times varied depending upon the metallocarborane, in each case the THF solution gradually darkened to near opacity with deposition of material on the sides of the reaction vessel. When the reduction was complete, excess NaC_5H_5 and $CoCl_2$ were added and the air-oxidized reaction mixture was chromatographed on silica gel. As in the polyhedral expansion of carboranes,[5] variations in reaction times and temperatures affected the yield and nature of the products. The primary products obtained from the most representative reactions for each metallocarborane enumerated above are reported here.

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(1) G. B. Dunks and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 92, 7213 (1970).

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(9) "I. U. P. A. C. Nomenclature of Inorganic Chemistry," Butterworths, London, 1970.

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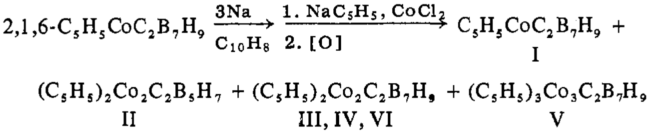
(14) W. J. Evans and M. F. Hawthorne, *J. Chem. Soc., Chem. Commun.*, 706 (1973).

$2,1,6\text{-}C_5H_5CoC_2B_7H_9$. The reduction of $2,1,6\text{-}C_5H_5CoC_2B_7H_9$[10] in THF was effected over an 8-hr period at room temperature. Addition of NaC_5H_5 and $CoCl_2$ produced a complex mixture of metallocarboranes which were separated by column chromatography



$$2,1,6\text{-}C_5H_5CoC_2B_7H_9 \xrightarrow[C_{10}H_8]{3Na} \xrightarrow[2.\ [O]]{1.\ NaC_5H_5,\ CoCl_2} \underset{I}{C_5H_5CoC_2B_7H_9} + \underset{II}{(C_5H_5)_2Co_2C_2B_5H_7} + \underset{III,\ IV,\ VI}{(C_5H_5)_2Co_2C_2B_7H_9} + \underset{V}{(C_5H_5)_3Co_3C_2B_7H_9}$$

The yellow product, I, initially separated by chromatography, exhibited a mass spectral cutoff at *m/e* 234 corresponding to the $^{11}B_7{}^{12}C_7{}^{1}H_{14}{}^{59}Co^+$ ion. Characterization by ^1H and ^{11}B nmr spectroscopy identified I as the same product obtained by the polyhedral expansion[5] of $4,5\text{-}C_2B_7H_9$, *viz.*, $3,2,10\text{-}C_5H_5CoC_2B_7H_9$.

The second metallocarborane isolated from this reaction, II, exhibited a cutoff in the mass spectrum at *m/e* 334 corresponding to the $^{11}B_5{}^{12}C_{12}{}^{1}H_{17}{}^{59}Co_2{}^+$ ion. The 80.5-MHz ^{11}B nmr (Table I) and ^1H nmr spectra of this red-brown species were consistent with those of $1,9,4,5\text{-}(C_5H_5)_2Co_2C_2B_5H_7$ prepared by the polyhedral expansion of $C_2B_5H_7$.[7] It is of interest to note that the line widths of the components of the doublet at −4.8 ppm ($W_{1/2} \approx 64$ Hz) are noticeably smaller than those of the +10.7-ppm resonance ($W_{1/2} \approx 96$ Hz) as would be expected for a structure containing two boron atoms between two carbon positions.[15]

The next species separated chromatographically was the red-brown III. A mass spectral cutoff at *m/e* 358 corresponding to the $^{11}B_7{}^{12}C_{12}{}^{1}H_{19}{}^{59}Co_2{}^+$ ion coupled with an exact mass measurement showed III to be the expected $(C_5H_5)_2Co_2C_2B_7H_9$. The ^{11}B nmr spectrum (Table I) exhibited a 2:2:2:1 pattern containing no low-field resonances. Two cyclopentadienyl signals of equal area were observed at τ 4.67 and 5.10 in the 251-MHz ^1H nmr spectrum in acetonitrile-d_3, as well as a single carborane CH resonance at τ 6.3. On the assumption that one of the cobalt atoms is in the high-coordinate position, 1 (Figure 1), the absence of low-field resonances in the ^{11}B nmr spectrum suggests that boron atoms are not in the low-coordinate positions 2 and 3, adjacent to the metal.[5,7] The only structure for III consistent with these ideas and containing equivalent carborane CH protons is that shown in Figure 1. The cyclic voltammograms and ^1H nmr, infrared, and electronic spectra of III and the other new metallocarboranes discussed in this paper are given in the Experimental Section.

The major product of this polyhedral expansion reaction was a second red-brown isomer of $(C_5H_5)_2CoC_2B_7H_9$, IV, isolated in 22% yield. Elemental analysis confirmed this composition. The nmr data of IV were similar to those of III: a 1:2:2:2 pattern in the ^{11}B nmr spectrum (Table I) containing no low-field signals and two cyclopentadienyl resonances in the ^1H nmr spectrum. Two carborane CH resonances were located in the 251-MHz ^1H nmr spectrum, however, including one at τ 1.72. Assuming that one cobalt atom resides in the high-coordinate position, only two structures are possible for IV which contain no low-coordinate boron atoms adjacent to cobalt. The structure $1,8,2,3\text{-}(C_5H_5)Co_2C_2B_7H_9$ is favored for IV over the other possibility, the 1,2,3,8 isomer, since carbon rather than cobalt is in the low-coordinate position.

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

Compd	Solvent	Chem shift[a] (rel intens)
$(C_5H_5)_2Co_2C_2B_5H_7$, II	$(CD_3)_2CO$	−118 (1), −4.8 (2), +10.7 (2)
$(C_5H_5)_2Co_2C_2B_7H_9$, III	$(CD_3)_2CO$	−30.1 (2), −15.9 (2), +4.1 (2), +21.2 (1)
$(C_5H_5)_2Co_2C_2B_7H_9$, IV	$CDCl_3$	−34.1 (1), −19.1 (2), 11.5 (2), 11.1 (2)
$(C_5H_5)_3Co_3C_2B_7H_9$, V	$CDCl_3$	−12.7 (2), −8.4 (2), +5.8 (2), +22.3 (1)
$(C_5H_5)_2Co_2C_2B_7H_9$, VI	$(CD_3)_2CO$	−15.1 (1), −6.4 (1), −2.8 (1), −1.2 (1), −0.4 (1), +0.8 (1), +17.9 (1)
$(C_5H_5)_2Co_2C_2B_8H_{10}$, IX	$(CD_3)_2CO$	−30 (1), −12.8 (1), −6.0 (1), −1.5 (1), +2.1 (1), +4.5 (2), +21.5 (1)
$(C_5H_5)_2Co_2C_2B_9H_{11}$, X	$(CD_3)_2CO$	−23.4 (2), −7.1 (4), −1.2 (3)
$(C_5H_5)_2Co_2C_2B_9H_{11}$, XI	$(CD_3)_2CO$	−17.5 (2), −13.1 (2), −7.5 (1), −2.4 (1), +1.6 (2), +5.6 (1)

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

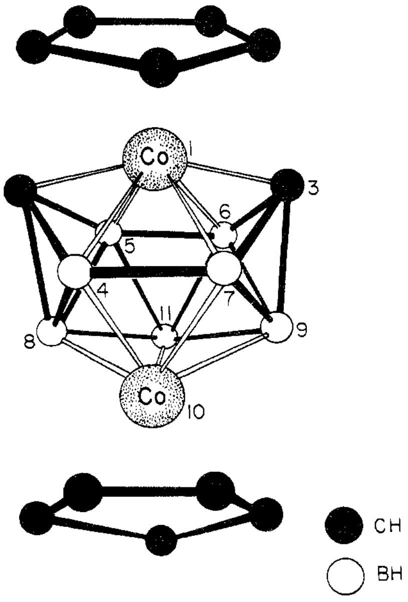


Figure 1. The proposed structure of $(C_5H_5)_2Co_2C_2B_7H_9$, III.

The fifth product isolated from this reaction was the green V. A cutoff in the mass spectrum was observed at *m/e* 482 corresponding to the $^{11}B_7{}^{12}C_{17}{}^{1}H_{24}{}^{59}Co_3{}^+$ ion. Elemental analysis established the identity of V as the trimetallic metallocarborane $(C_5H_5)_3Co_3C_2B_7H_9$. The ^{11}B nmr spectrum of V (Table I) contained four doublets of relative intensity 2:2:2:1. Two cyclopentadienyl signals were observed in the ^1H nmr spectrum in a 2:1 ratio. The skeletal structure of V is presumably an icosahedron in which the twelve vertices are comprised of three cobalt, two carbon, and seven boron atoms. Eliminating structures with adjacent carbon atoms,[5,7] eight icosahedral atomic arrangements were found to be consistent with the nmr data.

Additional evidence for the structure of V was obtained by observing its decomposition. In solution the green $(C_5H_5)_3Co_3C_2B_7H_9$, V, turned brown after several days. This color change also occurred on thick- and thin-layer silica gel chromatography paper, the reaction being accelerated by exposure to light. The brown product was isolated and characterized by tlc, and by its ^1H nmr and electronic spectra as $(C_5H_5)_2Co_2C_2B_7H_9$, IV. Loss of a cobalt vertex from the icosahedral V presumably forms a nido species which closes to the octadecahedral IV. Simple closure without extensive atomic rearrangement might be expected under these mild conditions; hence the structures IV and V may be closely related. The structure $2,3,5,1,7\text{-}(C_5H_5)_3Co_3C_2B_7H_9$ (Figure 2) is proposed for V since removal of a cobalt vertex at position 2 or 3

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[15] F. P. Boer, R. A. Hegstrom, M. D. Newton, J. A. Potenza, and W. N. Lipscomb, *J. Amer. Chem. Soc.*, 88, 5340 (1966).

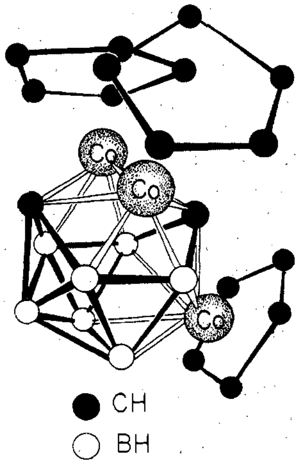

Figure 2. The proposed structure of $(C_5H_5)_3Co_3C_2B_7H_9$, V.

readily generates IV. This structural assignment is further substantiated by the observation of another decomposition reaction, described in the next section, in which identical geometries and similar reaction conditions are involved.

The remaining neutral product characterized from this reaction was the greenish species VI. Mass spectral data and elemental analysis identified VI as a third isomer of $(C_5H_5)_2Co_2C_2B_7H_9$. The absence of any low-field signals among the seven unique resonances in the ^{11}B nmr spectrum again favored a structure containing low-coordinate carbon atoms. The $1,4,2,3\text{-}(C_5H_5)_2Co_2C_2B_7H_9$ structure is proposed for VI since all other possibilities must contain at least one low-coordinate cobalt atom or one seven-coordinate boron atom.

The polyhedral expansion of $2,1,6\text{-}C_5H_5CoC_2B_7H_9$ was also carried out in THF at the reflux temperature. The major product formed was $3,2,10\text{-}C_5H_5CoC_2B_7H_9$,[5] I, and hence this proved to be a superior synthesis of I rather than a route to bimetallocarboranes. The three bimetallic species discussed above were also formed with $1,8,2,3\text{-}(C_5H_5)_2Co_2C_2B_7H_9$, IV, being the predominant isomer in this case. An additional side product formed under these conditions was identified spectroscopically as $1,4,6\text{-}C_5H_5CoC_2B_6H_8$.[5]

The Polyhedral Expansion of $1,2,3\text{-}C_5H_5CoC_2B_8H_{10}$. In comparison to the polyhedral expansion of $2,1,6\text{-}C_5H_5CoC_2B_7H_9$ the reaction involving $1,2,3\text{-}C_5H_5CoC_2B_8H_{10}$ was relatively clean

$$1,2,3\text{-}C_5H_5CoC_2B_8H_{10} \xrightarrow[C_{10}H_8]{3Na} \xrightarrow[CoCl_2]{NaC_5H_5} \underset{VII}{2,3,1,7\text{-}(C_5H_5)_2Co_2C_2B_8H_{10}} + \underset{VIII}{[Co(C_2B_8H_{10})_2]^-}$$

Both products, VII and VIII, were previously synthesized by the polyhedral expansion of $1,6\text{-}C_2B_8H_{10}$;[5] hence no new metallocarboranes were formed in significant yields from this reaction. The yield of $(C_5H_5)_2Co_2C_2B_8H_{10}$, VII, was increased nearly tenfold by using this direct method of synthesis, however.

The structure of VII has recently been shown by X-ray crystallography[16] to be $2,3,1,7\text{-}(C_5H_5)_2Co_2C_2B_8H_{10}$ in which the cobalt atoms occupy adjacent polyhedral vertices. This icosahedral species undergoes a decomposition to the octadecahedral $1,2,3\text{-}C_5H_5CoC_2B_8H_{10}$ similar to that described above for V. In acetone, acetonitrile, or CH_2Cl_2 solution over a period of months at room temperature or within 90 min in hexadecane at 200°, $1,2,3\text{-}C_5H_5CoC_2B_8H_{10}$ is formed from VII. The conversion of $2,3,1,7\text{-}(C_5H_5)_2Co_2C_2B_8H_{10}$ to $1,2,3\text{-}C_5H_5CoC_2B_8H_{10}$ involves little atomic rearrangement as proposed for the analogous conversion of $(C_5H_5)_3Co_3C_2B_7H_9$, V, to $(C_5H_5)_2Co_2C_2B_7H_9$, IV.

The other product of this polyhedral expansion reaction was the anionic commo metallocarborane VIII, isolated as the cobalticinium salt. This anion for which the structure $[1,1'\text{-}Co(2,3\text{-}C_2B_8H_{10})_2]^-$ was proposed,[5] has recently been shown to be a precursor to bimetallocarboranes by a new and direct synthetic method.[17]

The Polyhedral Expansion of $1,2,4\text{-}C_5H_5CoC_2B_8H_{10}$. Investigations of the chemistry of $1,2,4\text{-}C_5H_5CoC_2B_8H_{10}$ revealed that this metallocarborane readily formed substituted nido species which upon closure retained their substituent.[12,18] It might be expected therefore that such substituted species, both nido and closo, might be formed when the polyhedral expansion reaction was applied to $1,2,4\text{-}C_5H_5CoC_2B_8H_{10}$. Indeed this was the case. Among the many fractions separated chromatographically three main neutral products were present. Mass spectroscopy indicated that two of these were substituted and they were not further characterized. The third main product, IX, was identified as the desired $(C_5H_5)_2Co_2C_2B_8H_{10}$ by the cutoff and isotopic distribution in the parent peak envelope in the mass spectrum. The ^{11}B nmr spectrum (Table I) of IX contained seven resonances of relative intensity 1:1:1:1:1:2:1. Two cyclopentadienyl resonances were observed in the ^1H nmr spectrum, but the very limited solubility of IX precluded the location of carborane CH signals. Since there are no possible icosahedral structures containing two equivalent and six nonequivalent boron atoms, a totally asymmetric structure for IX is proposed. Of the sixteen possible structures for IX, the $3,4,1,2\text{-}(C_5H_5)_2Co_2C_2B_8H_{10}$ isomer appears likely since its formation from $1,2,4\text{-}C_5H_5CoC_2B_8H_{10}$ is analogous to the formation of $2,3,1,7\text{-}(C_5H_5)_2Co_2C_2B_8H_{10}$, VII, from $1,2,3\text{-}C_5H_5CoC_2B_8H_{10}$. This is shown in Figure 3. Other structures are also possible, however.

The Polyhedral Expansion of $3,1,2\text{-}C_5H_5CoC_2B_9H_{11}$. The synthesis of bimetallic metallocarboranes from $3,1,2\text{-}C_5H_5CoC_2B_9H_{11}$ could be accomplished at 0° or room temperature using $Na^+C_{10}H_8^-$ in THF or at −50° using Na in liquid ammonia

$$3,1,2\text{-}C_5H_5CoC_2B_9H_{11} \xrightarrow[C_{10}H_8]{3Na} \xrightarrow[CoCl_2]{NaC_5H_5} 2,1,7\text{-}C_5H_5CoC_2B_9H_{11} + \underset{X,\,XI}{(C_5H_5)_2Co_2C_2B_9H_{11}} + \underset{XII}{[Co(C_2B_9H_{11})_2]^-}$$

The two initial yellow fractions separated by chromatography were identified by ^1H and ^{11}B nmr spectroscopy as $2,1,7\text{-}C_5H_5CoC_2B_9H_{11}$ and unreacted $3,1,2\text{-}C_5H_5CoC_2B_9H_{11}$. The next product isolated was the green species X. The cutoff in the mass spectrum of X at *m/e* 382, corresponding to the $^{11}B_9{}^{12}C_{12}{}^1H_{21}{}^{59}Co_2{}^+$ ion, and the isotopic distribution in the parent peak envelope were consistent with the formula $(C_5H_5)_2Co_2C_2B_9H_{11}$. Elemental analysis confirmed this formulation. The ^{11}B nmr spectrum contained a 2:4:2:1 pattern and included no low-field resonances (Table I). A single cyclopentadienyl resonance was observed in the ^1H nmr spectrum, but no carborane signals were found due to the limited solu-

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(16) K. P. Callahan, A. L. Sims, C. E. Strouse, and M. F. Hawthorne, *Inorg. Chem.*, in press.

(17) W. J. Evans and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 96, 301 (1974).

(18) C. J. Jones, J. N. Francis, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 95, 7633 (1973).

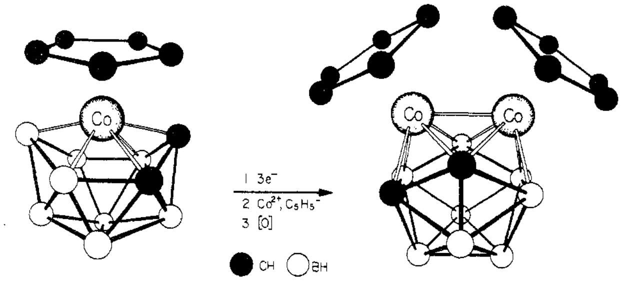

Figure 3. A possible structure of $(C_5H_5)_2Co_2C_2B_8H_{10}$, IX, formed from 1,2,4-$C_5H_5CoC_2B_8H_{10}$.

bility of X. A second isomer of $(C_5H_5)_2Co_2C_2B_9H_{11}$, the green species XI, was also formed in this reaction and could be separated from X by repeated thick-layer chromatography. An exact mass measurement verified the elemental composition of this isomer. A 2:2:1:1:2:1 pattern of doublets containing no low-field resonances was observed in the ^{11}B nmr spectrum of XI and two cyclopentadienyl signals of equal intensity were found in the ^1H nmr spectrum.

The assignment of structures to these isomers is complicated by the lack of crystallographic data. Only one thirteen-vertex polyhedral structure, 4,1,6-$C_5H_5CoC_2B_{10}H_{12}$, has been confirmed crystallographically and this particular metallocarborane is fluxional in solution.[3,14,19] The structure of the corresponding substituted nido carborane anion, $[C_2B_{10}H_{11}(C_6H_5)_2]^-$, has a different geometry, however.[20,21] While this may not be particularly surprising considering the preferred coordination numbers for boron, it may indicate that structures of supraicosahedral species are quite sensitive to the nature of the constituent framework atoms. Crystallographic studies of both X and XI are currently in progress.

The last product isolated from the polyhedral expansion of 3,1,2-$C_5H_5CoC_2B_9H_{11}$ was the cobalticinium salt of the commo species $[Co(C_2B_9H_{11})_2]^-$, XII. The ^1H and ^{11}B nmr spectra of this compound indicated that this was $[(C_5H_5)_2Co]$-[3,3′-$Co(1,2$-$C_2B_9H_{11})_2]$.

Conclusion

The polyhedral expansion reaction appears to be as generally applicable to metallocarboranes as it has been to carboranes. Indeed, the prediction[5] that this reaction would provide a basis for the rational synthesis of a large variety of metallocarboranes appears to be true. The existence of a general direct synthesis of bimetallocarboranes from monometallic precursors naturally provides a method of mixed-metal metallocarborane synthesis, and work in this area has already begun.[22] The synthesis of additional trimetallocarboranes by extending the polyhedral expansion reaction to bimetallic starting materials appears feasible although initial studies in this laboratory[23] suggest the specific bimetallic isomer utilized is a more important factor in this case. The use of the polyhedral expansion reaction to form polymetallocarboranes containing more than three transition metal vertices may also be possible. However, the decomposition reactions observed with 2,3,1,7-$(C_5H_5)_2Co_2C_2B_8H_{10}$, VII, and 2,3,5,1,7-$(C_5H_5)_3Co_3C_2B_7H_9$, V, clearly demonstrate that additional factors regarding stability are present in polymetallic species. Since some metallocarboranes containing adjacent cobalt atoms, notably 2,6,1,10-$(C_5H_5)_2Co_2C_2B_6H_8$[5,24] and 2,7,1,12-$(C_5H_5)_2Co_2C_2B_8H_{10}$,[5] do not revert to monometallic precursors in a similar manner,[25] factors such as carbon atom positions and geometry will probably be highly critical.

The applicability of the polyhedral expansion reaction to monometallocarboranes as well as carboranes appears to be another chemical manifestation of the similarity of the $C_5H_5Co^{2+}$ and BH^{2+} moieties.[26,27] How appropriate these electronic analogies are in polymetallocarboranes remains to be determined. The application of the polyhedral expansion reaction to metallocarboranes may well provide the synthetic means to make this determination possible.

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 described.[28] 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. 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. Dicyclopentadiene was obtained from Aldrich Chemical Co. and 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. THF was freshly distilled from $LiAlH_4$ and kept under nitrogen. Hexane and methylene chloride were reagent grade. Ammonia was obtained from Liquid Carbonic. Literature methods were used to prepare 2,1,6-$C_5H_5CoC_2B_7H_9$,[10] 1,2,3-$C_5H_5CoC_2B_8H_{10}$,[5] 1,2,4-$C_5H_5CoC_2B_8H_{10}$,[12] and 3,1,2-$C_5H_5CoC_2B_9H_{11}$.[29,30] Sodium cyclopentadienide was prepared in the following manner. Sodium hydride was placed in a 250-ml three-neck flask equipped with a nitrogen inlet and a magnetic stirring bar, washed with THF, and dispersed in 80 ml of THF. Freshly distilled cyclopentadiene was added slowly from a calibrated collection vessel through a nitrogen-flushed glass tube bent to a 120° angle. After stirring for 3 hr, the solution was decanted under nitrogen through another bent glass tube into the reaction flask containing the reduced metallocarborane.

Cobaltacarboranes from 2,1,6-$C_5H_5CoC_2B_7H_9$. 2,1,6-$C_5H_5CoC_2B_7H_9$ (1.2486 g, 5.35 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 (0.37 g, 16 mmol) and naphthalene (~0.2 g, 1.5 mmol) were added

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and the reaction mixture was stirred. Within 2 hr the reaction was dark brown. After 19 hr no sodium was visible. Freshly prepared NaC_5H_5 (30 mmol) was added followed by a slurry of $CoCl_2$ (6 g, 46 mmol) in THF and the reaction mixture was stirred 35 min. The nitrogen inlet was removed and the reaction mixture was stirred in air for 5 min. Silica gel (30-ml dry volume) was added to the solution and the solvent was removed on a rotary evaporator. The solids were chromatographed on a 5 × 40 cm column of silica gel (450-ml dry volume) in hexane. At least fourteen chromatographic fractions containing neutral products were observed but only the six major fractions were characterized. In addition, several faint chromatographic bands appeared to decompose during chromatography. Initially an orange band was eluted which decomposed upon exposure to air.

(a) $C_5H_5CoC_2B_7H_9$, I. A yellow band moving rapidly in hexane was collected and the solvent removed on a rotary evaporator. Sublimation of the residue produced 106 mg (0.45 mmol, 8.5%) of I.[5]

(b) $(C_5H_5)_2Co_2C_2B_5H_7$, II. Next eluted was an orange band. Recrystallized from CH_2Cl_2–hexane was 36 mg (0.11 mmol, 2%) of II.[7] A reduction was observed at −1.55 V; an oxidation, at +0.82 V.

(c) $(C_5H_5)_2Co_2C_2B_7H_9$, III. The next distinct band was red-brown and was eluted with CH_2Cl_2–hexane (2:8 v/v). Recrystallization from CH_2Cl_2–hexane resulted in red-brown needles of III, mp 219–220° (29 mg, 0.08 mmol, 1.5%). High resolution mass measurement: calcd for $^{11}B_7{}^{12}C_{12}{}^{1}H_{19}{}^{59}Co_2{}^+$, 358.0805; found, 358.0809 ± 0.0004. Nmr (CD_3CN): τ 4.67 (s, 5, C_5H_5), 5.10 (s, 5, C_5H_5), 6.3 (broad, 2, carborane CH). Uv–visible [λ_{max}, nm (log ϵ)]: 242 (4.44), 292 (4.30), 320 (4.19), 464 (3.30). Ir (cm^{-1}): 2900 vs, 2490 s, 1460 vs, 1420 m, 1375 s, 1340 w, 1260 m, 1120 m, 1090 m, 1060 w, 1030 m, 950 w, 940 m, 890 w, 840 m, 810 m, 805 m, 750 m, 725 w. A reduction was observed at −1.17 V; an oxidation, at +1.06 V.

(d) $(C_5H_5)_2Co_2C_2B_7H_9$, IV. After the elution of a faint greenish band following III, a dark brown band was collected. Red-brown needles, mp 265–266°, of IV were obtained by recrystallization of this fraction from CH_2Cl_2–hexane. A 420-mg amount (1.18 mmol, 22%) was collected. *Anal.* Calcd for $(C_5H_5)_2Co_2C_2B_7H_9$: B, 21.21; C, 40.39; H, 5.37; Co, 33.03. Found: B, 21.51; C, 40.27; H, 5.35; Co, 32.14. Nmr (CD_3CN): τ 4.61 (s, 5, C_5H_5), 4.90 (s, 5, C_5H_5), 1.72 (broad, 1, carborane CH), 3.58 (broad, 1, carborane CH). Uv–visible [λ_{max}, nm (log ϵ)]: 248 (4.60), 360 (4.02), 384 (4.06), 524 (3.30). Ir (cm^{-1}): 2880 vs, 2480 s, 1440 vs, 1420 m, 1370 s, 1260 w, 1100 m, 1080 m, 1040 w, 1010 m, 970 w, 920 w, 890 w, 880 w, 860 w, 830 m, 810 m, 775 m, 740 w, 725 m. A reduction was observed at −0.85 V; an oxidation, at +0.75 V.

(e) $(C_5H_5)_3Co_3C_2B_7H_9$, V. After the elution of a faint band following IV, a dark green band was eluted with hexane–CH_2Cl_2 (6:4 v/v). Dark green needles, mp 237–240° dec, of V were recrystallized from CH_2Cl_2 in 3% yield (77 mg, 0.16 mmol). *Anal.* Calcd for $(C_5H_5)_3Co_3C_2B_7H_9$: B, 15.74; C, 42.46; H, 5.03; Co, 36.77. Found: B, 16.19; C, 42.14; H, 5.36; Co, 36.76. Nmr [$(CD_3)_2CO$]: τ 4.36 (s, 10, C_5H_5), 5.22 (s, 5, C_5H_5). Uv–visible [λ_{max}, nm (log ϵ)]: 248 (4.40), 294 (4.55), 414 (3.38), 484 (3.12), 648 (3.36). Ir (cm^{-1}): 2880 vs, 2480 s, 1470 vs, 1420 m, 1370 s, 1300 w, 1260 w, 1160 w, 1120 w, 1100 w, 1070 w, 1030 w, 1020 m, 1000 w, 980 w, 935 w, 895 w, 860 m, 835 w, 820 m, 790 w, 740 w, 725 m. A reduction was observed at −0.87 V; an oxidation, at +0.65 V. Follow-up waves at −1.27 and +0.83 V were also observed and found to be dependent on scan rate.

(f) $(C_5H_5)_2Co_2C_2B_7H_9$, VI. One final neutral product was eluted in hexane–CH_2Cl_2 (1:1 v/v) as a greenish brown band. Recrystallization from CH_2Cl_2 allowed the isolation of 18 mg (0.05 mmol, 1%) of VI, mp 275–277°. *Anal.* Calcd for $(C_5H_5)_2Co_2C_2B_7H_9$: B, 21.21; C, 40.39; H, 5.37; Co, 33.03. Found: B, 21.34; C, 40.12; H, 5.45; Co, 32.63. Nmr [$(CD_3)_2CO$]: τ 4.50 (s, 5, C_5H_5), 4.75 (s, 5, C_5H_5). Uv–visible [λ_{max}, nm (log ϵ)]: 250 (4.59), 280 (4.48), 360 (3.86), 516 (2.89), 604 sh (2.68). Ir (cm^{-1}): 2880 vs, 2480 s, 1470 vs, 1420 m, 1370 s, 1120 w, 1080 m, 1060 m, 1040 w, 1010 m, 930 m, 910 w, 880 w, 860 m, 840 s, 830 w, 810 m, 775 w, 725 w, 710 w, 700 m. A reduction was observed at −0.87 V; an oxidation, at +0.87 V.

Cobaltacarboranes from 1,2,3-$C_5H_5CoC_2B_8H_{10}$. 1,2,3-$C_5H_5CoC_2B_8H_{10}$ (1.1551 g, 4.72 mmol) was dissolved in 80 ml of THF in a previously dried, nitrogen-flushed 500-ml three-neck flask equipped with a nitrogen inlet connected to a Liebig condenser and a mechanical stirrer with a glass blade. Sodium (0.33 g, 14.1 mg-atom) and naphthalene (~0.2 g, ~1.5 mmol) were added and the reaction mixture was heated to ~60°. Within hours the reaction turned red-brown and after stirring 24 hr no sodium was present. The mixture was cooled to room temperature and NaC_5H_5 (20 mmol) and a slurry of $CoCl_2$ (5 g, 39 mmol) in THF were added. After an additional 30 min at 60°, the reaction was cooled, air-oxygenated, and poured onto 30 ml of silica gel. The solvent was removed on a rotary evaporator and the solids were chromatographed on three 5 × 15 cm columns of silica gel (300-ml dry volume) in hexane.

(a) $C_5H_5CoC_2B_8H_{10}$. A purple band was eluted with hexane–CH_2Cl_2 (8:2 v/v). Recrystallized from hexane–CH_2Cl_2 was 0.6781 g (28 mmol, 59%) of 1,2,3-$C_5H_5CoC_2B_8H_{10}$.[5]

(b) $(C_5H_5)_2Co_2C_2B_8H_{10}$, VII. Following the elution of 1,2,3-$C_5H_5CoC_2B_8H_{10}$, a green band was separated in hexane–CH_2Cl_2 (1:1 v/v). Preparative thick-layer chromatography of VII in benzene allowed the isolation of 0.19 g [0.5 mmol, 11% (26% based on 1,2,3-$C_5H_5CoC_2B_8H_{10}$ consumed)].

(c) $[(C_5H_5)_2Co][Co(C_2B_8H_{10})_2]$, VIII. A subsequent green band was eluted with CH_2Cl_2. Recrystallized from acetone–hexane was 0.12 g [0.25 mmol, 11% (26% based on 1,2,3-$C_5H_5CoC_2B_8H_{10}$ consumed)] of VIII.

Cobaltacarboranes from 1,2,4-$C_5H_5CoC_2B_8H_{10}$. 1,2,4-$C_5H_5CoC_2B_8H_{10}$ (0.9664 g, 4 mmol) was dissolved in 80 ml of THF in a dried, nitrogen-flushed, three-neck, 500-ml flask. The mechanically stirred solution was cooled with an ice bath, and sodium (0.27 g, 12 mg-atom) and naphthalene (~0.2 g) were added. The solution became dark red and after 3 days most of the sodium was gone. Following addition of NaC_5H_5 (20 mmol) and $CoCl_2$ (7.0 g, 54 mmol), the reaction was stirred for 2 hr at 0°. The ice bath was then removed, and the reaction was stirred 1 additional hr and oxygenated for 5 min. The solution was poured onto silica gel (30 ml) and the THF was removed by rotary evaporation. The solids were chromatographed on a 5 × 40 cm column of silica gel in hexane. Several faint yellow and red bands were initially eluted and elution with hexane–CH_2Cl_2 (8:2 v/v) resulted in a dark blue-green fraction and a dark green fraction containing substituted metallocarboranes.

$(C_5H_5)_2Co_2C_2B_8H_{10}$, IX. Closely following the above two fractions was a greenish purple band. Preparative thick-layer chromatography in hexane–CH_2Cl_2 (1:1 v/v) effected the purification of 74 mg (0.2 mmol, 5%) of IX, mp 280–282°. High-resolution mass measurement: calcd for $^{11}B_8{}^{12}C_{12}{}^{1}H_{20}{}^{59}Co_2{}^+$, 370.097305; found, 370.0976 ± 0.0007. Nmr (CD_3CN): τ 4.50 (s, 5, C_5H_5), 4.68 (s, 5, C_5H_5). Uv–visible [λ_{max}, nm (log ϵ)]: 248 (4.1), 312 (4.1), 368 sh (3.6), 564 (2.9). Ir (cm^{-1}): 2900 vs, 2510 s, 1470 vs, 1420 m, 1375 s, 1150 w, 1110 w, 1100 m, 1030 w, 980 w, 895 w, 880 w, 870 w, 850 m, 820 m, 800 m, 740 w, 725 m.

Cobaltacarboranes from 3,1,2-$C_5H_5CoC_2B_9H_{11}$. 3,1,2-$C_5H_5CoC_2B_9H_{11}$ (1.0066 g, 3.9 mmol) was dissolved in 80 ml of THF in a dried, nitrogen-flushed three-neck, 500-ml flask. Sodium (0.27 g, 12 mg-atom) and naphthalene (~0.2 g, 1.5 mmol) were added and the reaction mixture was stirred. After 90 min the mixture was nearly black. After 30 hr nearly all the sodium was consumed and NaC_5H_5 (20 mmol) and a slurry of $CoCl_2$ (7 g, 54 mmol) in THF were added. After 40 min, the nitrogen inlet was removed and the reaction mixture was stirred in air for 5 min. The solution was poured onto silica gel (30 ml) and the THF was removed by rotary evaporation. The solids were chromatographed on a 5 × 40 cm column of silica gel in hexane. A faint yellow band was initially eluted with hexane but was not characterized.

(a) 2,1,7-$C_5H_5CoC_2B_9H_{11}$. Elution with hexane–CH_2Cl_2 (9:1 v/v) allowed the separation of 31 mg (0.12 mmol, 3%) of 2,1,7-$C_5H_5CoC_2B_9H_{11}$.

(b) 3,1,2-$C_5H_5CoC_2B_9H_{11}$. Elution with hexane–CH_2Cl_2 (8:2 v/v) allowed the recovery of 0.4198 g (1.6 mmol), 40%) of 3,1,2-$C_5H_5CoC_2B_9H_{11}$.

(c) $(C_5H_5)_2Co_2C_2B_9H_{11}$, X. Closely following the yellow fraction containing 1,2,3-$C_5H_5CoC_2B_9H_{11}$ was a green band containing two compounds with very similar R_f values, X and XI. Repeated thick-layer chromatography in hexane–CH_2Cl_2 (4:1 v/v) effected the purification of 55 mg (0.145 mmol, 6% based on 3,1,2-$C_5H_5CoC_2B_9H_{11}$ consumed) of X, mp 293–295°. *Anal.* Calcd for $(C_5H_5)_2Co_2C_2B_9H_{11}$: B, 25.57; C, 37.88; H, 5.56; Co, 30.98. Found: B, 25.60; C, 37.94; H, 5.67; Co, 30.36. Nmr [$(CD_3)_2CO$]: τ 4.58 (s, C_5H_5). Uv–visible [λ_{max}, nm (log ϵ)]: 260 (4.4), 292 (4.3), 408 (3.5), 608 (2.8). Ir (cm^{-1}): 2870 vs, 2480 s, 1460 vs, 1420 m, 1370 s, 1300 w, 1260 w, 1180 w, 1140 w, 1110 w, 1080 w, 1060 w, 1040 w, 1010 m, 1005 w, 975 m, 930 w, 880 w, 840 m, 820 m, 770 w, 735 w, 720 m.

(d) $(C_5H_5)_2Co_2C_2B_9H_{11}$, XI. Separated from X by repeated thick-layer chromatography was 10 mg (0.03 mmol, 1% based on 3,1,2-$C_5H_5CoC_2B_9H_{11}$ consumed) of XI, mp 286–288°. High-resolution mass measurement: calcd for $^{11}B_9{}^{12}C_{12}{}^{1}H_{21}{}^{59}Co_2$, 382.114437; found, 382.1148 ± 0.0008. Nmr [$(CD_3)_2CO$]: τ 4.59 (s, 5, C_5H_5), 4.89 (s, 5, C_5H_5). Uv–visible [λ_{max}, nm (log ϵ)]: 244 (4.31), 288 (4.16), 396 (3.43), 606 (2.73). Ir (cm^{-1}): 2850 vs, 2500 s, 1450 vs, 1420 m, 1320 s, 1190 w, 1170 w, 1140 m, 1110 m, 1080 m, 1060 m, 1040 w, 1020 m, 1010 m, 990 w, 970 m, 930 w, 880 w, 855 m, 835 m, 820 s, 805 w, 770 w, 720 w.

(e) **$[(C_5H_5)_2Co][Co(C_2B_9H_{11})_2]$, XII.** A dark yellow band was eluted with CH_2Cl_2. Recrystallization afforded 0.1863 g (0.35 mmol, 18%) of $[(C_5H_5)_2Co][Co(C_2B_9H_{11})_2]$.

Cobaltacarboranes from 3,1,2-$C_5H_5CoC_2B_9H_{11}$ using Na in NH_3(l). The polyhedral expansion of 3,1,2-$C_5H_5CoC_2B_9H_{11}$ was equally successful when the reduction was carried out with sodium in liquid ammonia; hence, a viable low-temperature method of polyhedral expansion is also available. 3,1,2-$C_5H_5CoC_2B_9H_{11}$ (1.369 g, 5.2 mmol) was placed in a previously dried, nitrogen-flushed, 500-ml, three-neck flask equipped with a nitrogen inlet and a magnetic stirring bar. The flask was cooled with a 2-propanol cold bath maintained at −50° by the periodic addition of Dry Ice. Ammonia (125 ml) was condensed into the flask and sodium (0.36 g, 15.6 mmol) was added turning the yellow solution a deep blue. After stirring for 4 hr the reaction mixture was very dark brown. Stirring was continued for 2 hr and NaC_5H_5 (78 mmol) in THF and a slurry of $CoCl_2$ (20 g) in THF were added. The reaction was gradually allowed to warm to room temperature over a 20-hr period. After air was bubbled through the reaction mixture for 45 min, the solution was poured onto silica gel and the solvents were removed by rotary evaporation. The solids were chromatographed on a column of silica gel (500 ml) in hexane. Several unstable yellow bands were initially eluted. Separated and isolated as described above were 0.1905 g (0.74 mmol, 14%) of 3,1,2-$C_5H_5CoC_2B_9H_{11}$, 95 mg (0.25 mmol, 5.5% based on starting material consumed) of $(C_5H_5)_2Co_2C_2B_9H_{11}$, X, and 32 mg (0.08 mmol, 2%) of $(C_5H_5)_2Co_2C_2B_9H_{11}$, XI.

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Registry No. I, 50803-36-6; II, 50803-43-5; III, 50803-44-6; IV, 50803-45-7; V, 50803-51-5; VI, 50803-46-8; VII, 50803-48-0; VIII, 39475-06-4; IX, 50803-47-9; (X–XI), 50639-82-2; XII, 50803-40-2; 2,1,7-$C_5H_5CoC_2B_9H_{11}$, 50803-38-8; 2,1,6-$C_5H_5CoC_2B_7H_9$, 50803-35-5; 1,2,3-$C_5H_5CoC_2B_8H_{10}$, 11072-15-4; 1,2,4-$C_5H_5CoC_2B_8H_{10}$, 50803-37-7; 3,1,2-$C_5H_5CoC_2B_9H_{11}$, 11056-78-3.

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Urea-Boron Trihalide Adducts. III. Mixed Boron Trihalide Adducts of Tetramethylurea and the Difluorobis(tetramethylurea)boron(III) Cation

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Under certain conditions the adduct tmu·BF_3 rearranges to give small amounts of the ionic adduct $(tmu)_2BF_2^+ \cdot BF_4^-$. Mixed boron trihalide adducts of tetramethylurea, tmu·BF_2Cl and tmu·$BFCl_2$, form readily from tmu·BF_3 and tmu·BCl_3 in solution. tmu·BF_2Cl is shown to be a convenient source of larger amounts of $(tmu)_2BF_2^+$, *via* nucleophilic attack of tmu on the tmu·BF_2Cl adduct with displacement of chloride ion. All of the mixed fluorochloroborate anions are also present in these solutions as a result of halogen redistribution reactions.

Introduction

We have recently investigated donor site and restricted rotation in BF_3 adducts of alkylureas.[1,2] In the course of studies of the BF_3 adduct of tetramethylurea (tmu), we observed the appearance of an additional species under certain conditions. We tentatively identified this as an ionic form of the adduct $(tmu)_2BF_2^+ \cdot BF_4^-$. Extension of our studies to halogen redistribution and the mixed boron trihalide adducts of tmu showed that the redistribution reactions were more complex than in the Me_2O, Me_3N, or Me_2S mixed boron trihalide adduct systems[3-5] and provided further evidence about the nature of the additional species which can exist in the tetramethylurea-boron trihalide adduct system. We now report a study of this system, giving evidence for the presence of the difluoroboron cation $(tmu)_2BF_2^+$ and various mixed tetrahaloborate anions,[6] as well as mixed boron trihalide adducts of tmu.

Experimental Section

Rigorous dryness was maintained in the synthesis of adducts and in the preparation of nmr samples.

Pure tmu·BF_3, which gave single ^1H and ^{19}F nmr peaks (δ 3.02 and 149.2 ppm, respectively) was prepared as described previously.[1] An excess of pure BF_3 was condensed onto a solution of tmu in dry, vacuum-distilled methylene chloride, followed by removal of solvent and drying of the residue.

A second method of preparing tmu·BF_3 was employed in which BF_3 was slowly added with constant stirring to liquid tmu, on the vacuum system. The temperature of the reaction mixture was maintained near room temperature with the aid of an ice bath. After uptake had ceased, the temperature was raised to 60° and the BF_3 pressure maintained at 0.5 atm until uptake was complete. Excess BF_3 was removed by pumping on the molten adduct at 80° with constant stirring for 1 hr. The adduct prepared by this method gave the same large ^1H and ^{19}F peaks and in addition small peaks, as described below, which are attributed to an ionic form of the adduct, $(tmu)_2BF_2^+ \cdot BF_4^-$.

Pure tmu·BCl_3 was prepared under anhydrous conditions on a vacuum line. An excess of pure BCl_3 was condensed onto a solution of tmu in dry, vacuum-distilled methylene chloride. The dried product was recrystallized from methylene chloride a total of three times to remove occluded BCl_3 and finally dried overnight under vacuum, mp 145.5–146.0°.

Mixed boron trihalide adducts readily formed in methylene chloride solutions of tmu·BF_3 and tmu·BCl_3. The tmu·BCl_3 adduct was only moderately soluble in methylene chloride but dissolved over a period of several minutes in the presence of tmu·BF_3.

The ^1H and ^{19}F nmr instrumentation has been described previously.[1] Boron-11 nmr spectra were obtained on a Varian

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