$\overline{\text{PMe}}_2)_2Mo(CO)_4$ have been presented. The pathway is now clear to explore the reactivity and properties of the heterobimetallic polar Rh-Mo bond[28] in **1**.

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Supplementary Material Available: Listing of structure factor amplitudes (10 pages). Ordering information is given on any current masthead page.

Intramolecular B-B Linkage between Polyhedral Cages in a *commo*-Metallacarborane. Synthesis and Structure of a Fluxional Metal-Boron Cluster, $[\eta^5\text{-}C_5(CH_3)_5]_2Co_3(CH_3)_4C_4B_8H_7$

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Abstract: The reaction of $Li^+C_5(CH_3)_5^-$, $CoCl_2$, and $Na^+(CH_3)_2C_2B_4H_5^-$ in cold THF forms primarily *closo*-1,2,3-$[\eta_5\text{-}C_5(CH_3)_5]Co(CH_3)_2C_2B_4H_4$ (I), the triple-decker complex 1,7,2,3-$[\eta^5\text{-}C_5(CH_3)_5]_2Co_2(CH_3)_2C_2B_3H_3$ (II), a structurally novel complex, $[\eta^5\text{-}C_5(CH_3)_5]_2Co_3(CH_3)_4C_4B_8H_7$ (III), and traces of other products in a combined isolated yield of ~50%. Complexes I and II are $C_5(CH_3)_5$ analogues of C_5H_5-substituted cobalta carboranes reported earlier, but III has no previous counterpart. An X-ray diffraction study of III disclosed a structure consisting of two identical $[\eta^5\text{-}C_5(CH_3)_5]Co(CH_3)_2C_2B_4H_3$ units face coordinated to a third cobalt atom, with a direct B-B bond [1.758 (5) Å] between the two ligands; the linked boron atoms have no terminal hydrogen atoms *in the solid-state structure*. The "extra" hydrogen atom was not directly located, but its general position was indicated by a 3.5° fold in the molecule which creates a larger interligand pocket on one side than on the other. In the crystal, the unique hydrogen is proposed to reside in the larger pocket (in the vicinity of the central cobalt atom), but ^{11}B and ^1H FT NMR and infrared evidence indicates that, *in solution, this hydrogen atom tautomerizes between equivalent terminal positions on the (formerly) linked boron atoms on the two ligands*, with cleavage of the B-B link. Possible mechanisms of formation and stereochemical implications of the structure and fluxional behavior of III are presented. The chemistry of complex I resembles that of its C_5H_5-substituted counterpart; thus, degradation of I in basic CH_3CN produces *nido*-1,2,3-$[\eta^5\text{-}C_5(CH_3)_5]Co(CH_3)_2C_2B_3H_5$ in 93% yield. Crystal data for III: space group $P\bar{1}$, $Z = 2$, $a = 8.555$ (2) Å, $b = 12.599$ (2) Å, $c = 16.268$ (9) Å, $\alpha = 102.76$ (4)°, $\beta = 92.71$ (3)°, $\gamma = 99.15$ (4)°, $V = 1682$ Å^3, $R = 0.073$ for the 3739 reflections for which $F_o^2 > 3\sigma(F_o^2)$.

The extraordinary richness of polyhedral borane chemistry is evident from the seemingly unlimited variety of structural features and bonding modes that have been found, with new ones continually being discovered. In addition to the many kinds of known polyhedral cage structures, numerous types of direct bonding *between* polyhedra have been established; indeed, ten distinguishable modes of interpolyhedral linkage *in established compounds* have been cited by Lipscomb[1] (if one also includes polyhedra connected by bridging atoms such as mercury, silicon, or tin, the list is even longer).

In this paper we describe a stereochemical phenomenon involving linked borane cages in which there are two aspects of interest: a novel solid-state molecular geometry and a curious form of fluxional behavior in solution which we believe implies reversible interpolyhedral boron-boron bond formation. These findings resulted from the serendipitous isolation of a byproduct in the preparation of the *closo*-carborane 1,2,3-$[\eta^5\text{-}C_5(CH_3)_5]Co(CH_3)_2C_2B_4H_4$. In the course of this routine synthesis (which was based on the earlier preparation[2] of the corresponding cyclopentadienyl species 1,2,3-$(\eta^5\text{-}C_5H_5)Co(CH_3)_2C_2B_4H_4$ from 2,3-$(CH_3)_2C_2B_4H_5^-$ ion, $CoCl_2$, and NaC_5H_5), the new compound $[\eta^5\text{-}C_5(CH_3)_5]_2Co_3(CH_3)_4C_4B_8H_7$ was obtained as a dark red, air-stable, crystalline solid and subsequently characterized by spectroscopic and X-ray diffraction techniques. We report here the structural investigation of this complex as well as the synthesis and characterization of other (η^5-pentamethylcyclopentadienyl)cobalt complexes isolated from this reaction.

Experimental Section

Materials. 2,3-Dimethyl-2,3-dicarbahexaborane(8), $(CH_3)_2C_2B_4H_6$, was prepared from B_5H_9, $(CH_3)_2C_2$, and $(C_2H_5)_3N$ as described elsewhere.[3] Pentamethylcyclopentadiene (Alfa) was used as received, and all other chemicals were reagent grade. Hygroscopic metal salts were dried at high temperature in vacuo, and tetrahydrofuran (THF) was rigorously dried over $LiAlH_4$ prior to use. *n*-Butyllithium was obtained from Alfa as a hexane solution and determined to be 1.8 M by the method of Silveira et al.[4] Sodium hydride (50% in mineral oil, Alfa) was washed with pentane prior to use. Column chromatography was conducted with silica gel 60 (Merck), and thin-layer chromatography (TLC) was performed on precoated plates of silica gel F-254 (Brinkmann Instruments, Inc.)

Instrumentation. ^{11}B (32 MHz) and ^1H (100 MHz) pulse Fourier Transform NMR spectra were recorded on a JEOL PS-100P spectrometer interfaced to a JEOL-Texas Instruments computer system. Broad-band heteronuclear decoupling was employed. ^1H NMR (90 MHz) spectra and some single-frequency homonuclear-decoupling ex-

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periments were performed on a Varian EM-390 NMR spectrometer. Unit-resolution EI mass spectra were obtained on a Hitachi Perkin-Elmer RMU-6E mass spectrometer. Unit resolution CI mass spectra were recorded on an A.E.I. MS-902 double-focusing instrument equipped with an SRI chemical ionization source. Infrared spectra were obtained on a Beckman IR-8 spectrometer. Preparative-scale high-pressure liquid chromatography (HPLC) was performed on a Waters Prep-500 instrument with prepacked silica gel columns and a refractive index detector.

Reaction of $Li^+C_5(CH_3)_5^-$, $Na^+(CH_3)_2C_2B_4H_5^-$, and $CoCl_2$. Under an atmosphere of dry nitrogen, pentamethylcyclopentadiene [$C_5(CH_3)_5H$, 1.20 g (8.8 mmol)] was dissolved in 10 mL of hexane (dried over molecular sieve) in a two-neck round-bottom flask in an ice bath. To this was added 4.2 mL of 1.8 M *n*-butyllithium in hexane (7.6 mmol) via a syringe over a period of 20 min, producing a lemon yellow slurry. This mixture was magnetically stirred and allowed to warm to 23 °C over a period of 3 h. The flask was then attached, under N_2, to a vacuum line below a tip-in side-arm flask (containing 5.8 mmol NaH, a medium glass frit, and Teflon stopcock). A tip-in side arm containing 1.541 g of dry $CoCl_2$ (11.9 mmol) was also connected to the flask containing the $C_5(CH_3)_5^-$ anion, after which the system was evacuated to remove the hexane. The stopcock was closed, 4.1 mmol of $(CH_3)_2C_2B_4H_6$ and 35 mL of THF were condensed onto the NaH in the upper tip-in flask at −196 °C, and the flask was allowed to warm to 23 °C over a period of 1 h, generating H_2. After being recooled to −196 °C to remove H_2, the reactor was again warmed to 23 °C. The $Na^+(CH_3)_2C_2B_4H_5^-$ solution was filtered onto the $Li^+C_5(CH_3)_5^-$ salt and quickly frozen at −196 °C. The $CoCl_2$ was added to the mixture, the solution was warmed to 0 °C (turning dark green) and then to 23 °C (turning dark brown) with gas evolution. The mixture was stirred in vacuo for 45 min, air was admitted to the system (with no apparent reaction), and stirring was continued for another 15 min. The THF was then partially removed by rotary evaporation to give a thick brown slurry. To this was added 50 mL of 0.5 M aqueous HCl, and the mixture was stirred for 20 min to give a chocolate brown suspension. This material was extracted three times with 50 mL of CH_2Cl_2 in a separatory funnel to form a brown organic phase and a light pink aqueous phase. The organic phase was rotary evaporated to a thick slurry, a small quantity of silica gel was added to form a transferable sludge, and the material was loaded onto a 14 × 2 cm silica gel column packed in hexane. The column was eluted with 50-mL portions of 0%, 10%, 20%, 30%, 40%, and 50% CH_2Cl_2 in hexane, then with 100 mL of CH_2Cl_2, and finally with 50 mL of acetone. A large red-brown band was eluted at 30–50% CH_2Cl_2 in hexane and further purified as described below. The more polar fractions were rotary evaporated to dryness and analyzed by TLC in 1:1 CH_2Cl_2/hexane. This gave an orange triple-decker complex, 1,7,2,3-[η^5-$C_5(CH_3)_5]_2Co_2(CH_3)_2C_2B_3H_3$ (II) (26 mg, 1.4% yield, R_f = 0.53, parent *m/e* 478), a trace of a second, brown isomer of that species (R_f = 0.80), and small quantities of other products that were not identified. The red-brown mixture (~1 g) was separated via preparative-scale HPLC with 20% CH_2Cl_2 in hexane, giving red and orange fractions whose retentions were 1.2 and 1.5 column volumes, respectively. Purification of these fractions via preparative HPLC gave orange 1,2,3-[η^5-$C_5(CH_3)_5]Co(CH_3)_2C_2B_4H_4$ (I) [540 mg (44% yield), R_f = 0.1 in hexane, HPLC retention = 7 column volumes in hexane, mp 192 °C, parent *m/e* 296] and red [η^5-$C_5(CH_3)_5]_2Co_3(CH_3)_4C_4B_8H_7$ (III) (R_f = 0.6 in hexane, HPLC retention = 2.4 column volumes in 5% CH_2Cl_2/hexane, parent *m/e* 650 (see below), mp >300 °C). The isolated yield of III was 30 mg (2.2%) following considerable loss of material due to its rapid decomposition on silica (it is otherwise stable in air). Indications are that III is actually formed in much higher yield in the reaction.

Degradation of *closo*-1,2,3-[η^5-$C_5(CH_3)_5]Co(CH_3)_2C_2B_4H_4$ (I) to *nido*-1,2,3-[η^5-$C_5(CH_3)_5]Co(CH_3)_2C_2B_3H_5$ (IV). A 382-mg (1.29 mmol) sample of I was dissolved in 15 mL of CH_3CN; 10 mL of 0.6 M NaOH was added and vigorously stirred. The reaction was monitored by spot TLC and after 2 days was terminated by extraction of the products with three 20-mL CH_2Cl_2 portions in a separatory funnel. The extracts were combined, rotary evaporated to dryness, and the yellow residue was loaded onto a 15 × 2 cm silica gel column packed in hexane. Elution with hexane gave yellow 1,2,3-[η^5-$C_5(CH_3)_5]Co(CH_3)_2C_2B_3H_5$ (IV) (224 mg, 93% yield, mp 190 °C, R_f = 0.6 in hexane), and elution with 1:1 CH_2Cl_2/hexane gave 130 mg of I. Compound IV, unlike its cyclopentadiene analogue (η^5-$C_5H_5)Co(CH_3)_2C_2B_3H_5$,[2] decomposes slowly (hours) on silica gel plates. Trace amounts of darker compounds were subsequently eluted but were not investigated further. The unit resolution mass spectrum of IV shows a high-mass cutoff at *m/e* 286 with facile hydrogen abstraction.

X-ray Structure Determination on [η^5-$C_5(CH_3)_5]_2Co_3(CH_3)_4C_4B_8H_7$ (III). Large single crystals of III were grown by slow evaporation at room temperature from the high-pressure LC eluant (20% CH_2Cl_2 in hexane.) A large crystal was cut in three sections, one of which was mounted on a glass fiber in an arbitrary orientation and examined by preliminary precession photographs which indicated acceptable crystal quality. Crystal data were as follows: $Co_3C_{28}B_8H_{49}$; mol wt 648.99; space group $P\bar{1}$, $Z = 2$; a = 8.555 (2), b = 12.599 (2), c = 16.268 (9) Å; α = 102.76 (4)°; β = 92.71 (3)°; γ = 99.15 (4)°; V = 1682 Å^3; μ (Mo Kα) = 15.4 cm^{-1}; ρ(calcd) = 1.281 g cm^{-3}. Crystal dimensions in mm from centroid: (001) 0.22, (00$\bar{1}$) 0.22, (100) 0.22, ($\bar{1}$00) 0.22, (011) 0.29, (0$\bar{1}\bar{1}$) 0.29, (01$\bar{1}$) 0.32, (0$\bar{1}$1) 0.32.

For this crystal the Enraf-Nonius program SEARCH was used to obtain 25 accurately centered reflections which were then used in the program INDEX to obtain an orientation matrix for data collection and to provide approximate cell dimensions. Refined cell dimensions and their estimated standard deviations were obtained from 28 accurately centered reflections.

The mosaicity of the crystal was examined by the ω scan technique and judged to be satisfactory. The absence of any indications of higher symmetry, together with chemical and spectroscopic information on the molecule, dictated the space group $P\bar{1}$; this was eventually confirmed by the successful solution and refinement of the structure.

Collection and Reduction of the Data. Diffraction data were collected at 295 K on an Enraf-Nonius four-circle CAD-4 diffractometer controlled by a PDP8/M computer with use of Mo Kα radiation from a highly oriented graphite-crystal monochrometer. The ω scan technique was used to record the intensities of all reflections for which 1.4° < 2θ < 46°. Scan widths were calculated from the formula SW = (A + B tan θ), where A is estimated from the mosaicity of the crystal and B compensates for the increase in the width of the peak due to Kα_1–Kα_2 splitting. The values of A and B were 0.60 and 0.35, respectively. The calculated scan angle was extended at each side by 25% for background determination (BG1 and BG2). The net count (NC) was then calculated as NC = TOT − 2(BG1 + BG2), where TOT is the estimated peak intensity. Reflection data were considered insignificant if intensities registered less than ten counts above background on a rapid prescan, such reflections being rejected automatically by the computer.

The intensities of four standard reflections, at 100 reflection intervals, showed no greater fluctuations during the data collection than those expected from Poisson statistics. The raw intensity data were corrected for Lorentz–polarization effects and then for absorption (minimum transmission factor 0.72, maximum 0.85), resulting in 4823 reflections for which 3739 had $F_o^2 > 3\sigma(F_o^2)$, where $\sigma(F_o^2)$ was estimated from counting statistics (p = 0.03).[5] Only these latter data were used in the final refinement of the structural parameters.

Solution and Refinement of the Structure. Full-matrix least-squares refinement was based on F, and the function minimized was $\sum w(|F_o| - |F_c|)^2$. The weights w were taken as $[2F_o/\sigma(F_o^2)]^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes. The atomic scattering factors for nonhydrogen atoms were taken from Cromer and Waber[6] and those for hydrogen from Stewart et al.[7] The effects of anomolous dispersion for all nonhydrogen atoms were included in F by using the values of Cromer and Ibers[8] for $\Delta f'$ and $\Delta f''$.

The positions of the three cobalt atoms were determined from a three-dimensional Patterson map calculated from all the intensity data. The intensity data were phased sufficiently well by these positional coordinates to permit location of the remaining nonhydrogen atoms from Fourier difference syntheses. Some positional disorder was observed in the $C_5(CH_3)_5$ rings, but the disordered positions could not be adequately established and in any case contributed little to the overall scattering. This disorder is unimportant in terms of the interesting structural features of the molecule and was therefore not pursued further. Anisotropic temperature factors were introduced for all the nonhydrogen atoms, and subsequent Fourier difference functions revealed terminal hydrogens on six of the eight boron atoms (see discussion below) and one hydrogen on each of the carboranyl methyl groups. The positions of the remaining hydrogens on each carboranyl methyl group and on several $C_5(CH_3)_5$ methyl groups (see last nine atoms in Table IV) were calculated, and all hydrogens were included in the refinement except during the last three cycles. There are no intermolecular contacts (nonhydrogen) less than 3.68 Å. The estimated standard deviation of unit weight was 4.7. The model converged with R = 0.073 and R_w = 0.091, where $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. A final Fourier difference map was featureless. Tables of the observed and calculated structure factors are available (see paragraph at end of paper on sup-

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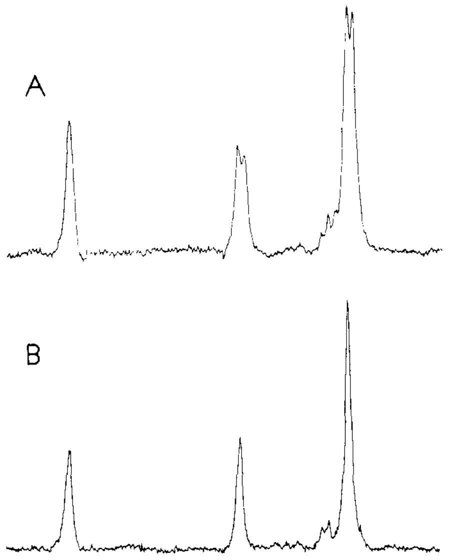

Figure 1. 64-MHz ^{11}B FT NMR spectra of $[\eta^5\text{-}C_5(CH_3)_5]_2Co_3(CH_3)_4C_4B_8H_7$ (III) in $(CD_3)_2CO$: A, proton coupled; B, proton decoupled. Width of spectra is approximately 9000 Hz.

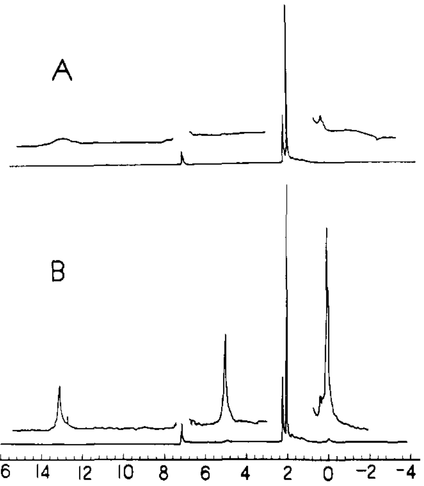

Figure 2. 100-MHz ^1H FT NMR spectra of III in C_6D_6, with chemical shift scale in ppm vs. $Me_4Si = 0$. Peak at δ 7.2 is C_6D_5H. A, ^{11}B coupled; B, ^{11}B decoupled. The 200-MHz ^1H spectra are similar.

plementary material). The computing system and programs are described elsewhere.[9]

Results and Discussion

Synthesis of (Pentamethylcyclopentadienyl)cobalt Metallacarboranes. The reaction of $C_5H_5^-$, 2,3-$(CH_3)_2C_2B_4H_5^-$, and $CoCl_2$ in THF, described several years ago,[2] produces mainly *closo*-1,2,3-$(\eta^5\text{-}C_5H_5)Co(CH_3)_2C_2B_4H_4$, an orange, air-stable pentagonal-bipyramidal species in which cobalt occupies one apex and the framework carbon atoms are in adjacent equatorial vertices. When the workup is conducted in 1 M aqueous HCl, the yield of this complex is 68%, and only minor amounts of other cobaltacarboranes [*closo*-1,7,2,3-$(\eta^5\text{-}C_5H_5)_2Co_2(CH_3)_2C_2B_3H_3$ and *nido*-1,2,3-$(\eta^5\text{-}C_5H_5)Co(CH_3)_2C_2B_3H_5$] are obtained; similar results have been obtained with the parent $C_2B_4H_7^-$ ion and the 2-$CH_3C_2B_4H_6^-$ derivative.[2]

In the present investigation, the analogous reaction was examined with $C_5(CH_3)_5^-$ ion, since recent work in our laboratory[10] has shown that cobaltaborane syntheses in which the $C_5(CH_3)_5^-$ ion is employed give notably different products from those obtained with $C_5H_5^-$.[11] Addition of $CoCl_2$ to a solution of $Li^+C_5(CH_3)_5^-$ and $Na^+[2,3\text{-}(CH_3)_2C_2B_4H_5^-]$ in cold THF followed by workup in air and treatment with aqueous HCl gave several products which were isolated by plate and column chromatography. Boron-11 and proton FT NMR data of the products are presented in Tables I and II and Figures 1 and 2, and infrared absorptions are listed in Table III. As expected, the major product (44% yield) was *closo*-1,2,3-$[\eta^5\text{-}C_5(CH_3)_5]Co(CH_3)_2C_2B_4H_4$ (I) an orange, air-stable solid (mp 192 °C), whose ^{11}B and ^1H FT NMR spectra closely resemble those of its C_5H_5-substituted counterpart.[2] Minor products included a triple-decker complex, *closo*-1,7,2,3-$[\eta^5\text{-}C_5(CH_3)_5]_2Co_2(CH_3)_2C_2B_3H_3$ (II), also characterized spectroscopically, and another (unidentified) isomer of that species. The cyclopentadienyl analogue of II, 1,7,2,3-$(\eta^5\text{-}C_5H_5)_2Co_2(CH_3)_2C_2B_3H_3$, has been described previously.[2]

Table I. 32.1-MHz ^{11}B FT NMR Data[a]

compd	chem shift, ppm[b] (*J*, Hz)	rel area [assignment]
$[C_5(CH_3)_5]Co(CH_3)_2C_2B_4H_4$ (I)	14.9 (146)	1 [B(5)]
	5.5 (136)	3 [B(4,6,7)]
1,7,2,3-$[C_5(CH_3)_5]_2Co_2(CH_3)_2$-$C_2B_3H_3$ (II)	52.0 (112)	1 [B(5)]
	12.3 (115)	2 [B(4,6)]
$[C_5(CH_3)_5]_2$-$Co_3(CH_3)_4C_4B_8H_7$ (III)[c]	92.9	1 [B(8,8′)]
	32.3 (120[d])	1 [B(5,5′)]
	−7.1 (150[d])	2 [B(4,4′,6,6′)]
$[C_5(CH_3)_5]Co(CH_3)_2C_2B_3H_5$ (IV)	10.5[e]	1 [B(5)]
	4.0[e]	2 [B(4,6)]

[a] Spectra obtained in $CDCl_3$ solution. [b] $BF_3\cdot O(C_2H_5)_2 = 0$, positive shifts downfield. [c] See text for discussion of assignments. [d] Extremely broad peaks; estimated *J* given. [e] Coupling to terminal and bridge protons was obscured by peak overlap.

Table II. 100.0-MHz ^1H FT NMR Data[a]

	chem shift, ppm[b]			
compd	$C_5(CH_3)_5$	CH_3	BH	rel area
I	1.50	1.88	4.33, 3.77	15, 6, 1, 3
II[c]	1.60	2.31	4.75 [H(5)], 2.77 [H(4,6)]	30, 6, 1, 2
III[d]	2.01	2.21	13.12 [H(8,8′)], 5.01 [H(5,5′)], 0.07 [H(4,4′,6,6′)]	30, 12, 1, 2, 4
IV	1.59	1.72	3.37 [H(4,6)], 2.96 [H(5)], −5.49 [H_{bridge}][e]	15, 6, 2, 1, 1

[a] C_6D_6 solution except where otherwise indicated. [b] Shifts referenced to $Si(CH_3)_4$. [c] In $CDCl_3$ solution. [d] See text for discussion of assignments. [e] Doublet of doublets; assigned to coupling of H_{bridge} to $H(4,5,6)_{terminal}$; $J_{HH} = 2.7$, 7.0 Hz.

Table III. IR absorptions (cm^{-1}, KBr pellets)

I	2965 m, 2910 m, 2870 m, 2520 s, 1450 m br, 1375 s, 1115 w, 1030 m, 865 m, 800 w, 725 m, 700 m, 620 w
II	2950 m, 2900 m, 2860 m, 2440 s, 1450 m br, 1375 s, 1075 w, 1020 s, 880 w, 810 s
III[a]	2950 m, 2900 m, 2830 m, 2400 s, 1470 m, 1440 m br, 1375 s, 1040 m, 1020 s, 930 s, 910 s, 820 s, 760 s, 720 s, 660 w
IV	2960 m, 2910 m, 2850 m, 2500 s, 1870 w, 1850 m, 1825 w, 1600 m, 1520 m, 1480 m, 1440 m, 1375 s, 1260 w, 1170 w, 1020 s, 1000 m, 985 m, 940 s, 880 m, 780 s, 735 m, 705 m, 700 m, 690 m

[a] A solution spectrum in $CHCl_3$ was virtually identical.

In contrast to the $C_5H_5^-$ reaction, no nido product (i.e., $[\eta^5\text{-}C_5(CH_3)_5]Co(CH_3)_2C_2B_3H_5$) was obtained; this was subsequently explained by the much higher resistance to cage degradation of compound I as compared to its C_5H_5 analogue.[2] Thus, *closo*-1,2,3-$(\eta^5\text{-}C_5H_5)Co(CH_3)_2C_2B_4H_4$ is converted in 80% yield to *nido*-$(\eta^5\text{-}C_5H_5)Co(CH_3)_2C_2B_3H_5$ in 2 h on treatment with strong base,[12] but *closo*-1,2,3-$[\eta^5\text{-}C_5(CH_3)_5Co(CH_3)_2C_2B_4H_4$ (I) required

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Table IV. Positional and Thermal Parameters and Their Estimated Standard Deviations for $[((CH_3)_5C_5)Co(CH_3)_2C_2B_4H_3]_2CoH$[a]

atom	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co(3)	0.2600 (1)	0.19891 (6)	0.15957 (5)	0.0448 (4)	0.0404 (4)	0.0426 (4)	0.0109 (3)	0.0163 (4)	0.0060 (3)
Co(7)	0.1275 (1)	0.07902 (7)	0.31271 (5)	0.0571 (5)	0.0502 (4)	0.0381 (4)	0.0189 (4)	0.0164 (4)	0.0102 (3)
Co(7′)	0.2042 (1)	0.46067 (7)	0.20812 (6)	0.0697 (5)	0.0336 (4)	0.0611 (5)	0.0062 (4)	0.0240 (4)	0.0025 (4)
C(1)	0.3637 (7)	0.0701 (5)	0.1716 (4)	0.055 (3)	0.057 (3)	0.049 (3)	0.024 (3)	0.021 (3)	0.013 (3)
C(M1)	0.5169 (9)	0.0385 (7)	0.1399 (5)	0.067 (4)	0.110 (5)	0.066 (4)	0.049 (3)	0.021 (4)	0.019 (4)
C(2)	0.2098 (7)	0.0310 (5)	0.1237 (4)	0.056 (3)	0.044 (3)	0.041 (3)	0.018 (3)	0.015 (3)	0.010 (2)
C(M2)	0.1854 (9)	−0.0459 (5)	0.0388 (4)	0.088 (5)	0.051 (3)	0.051 (4)	0.025 (3)	0.021 (4)	0.006 (3)
C(1′)	0.4096 (8)	0.3008 (5)	0.1073 (4)	0.060 (4)	0.048 (3)	0.074 (4)	0.004 (3)	0.035 (3)	0.014 (3)
C(M1′)	0.5674 (9)	0.2855 (7)	0.0706 (5)	0.069 (4)	0.085 (5)	0.091 (5)	0.009 (4)	0.046 (4)	0.007 (4)
C(2′)	0.2575 (8)	0.2692 (5)	0.0584 (4)	0.077 (4)	0.040 (3)	0.048 (3)	0.013 (3)	0.025 (3)	0.010 (3)
C(M2′)	0.2370 (10)	0.2201 (6)	−0.0355 (5)	0.105 (5)	0.058 (4)	0.054 (4)	0.021 (4)	0.025 (4)	0.013 (3)
C(P1)	0.0076 (11)	−0.0453 (7)	0.3595 (5)	0.102 (6)	0.084 (5)	0.063 (4)	−0.010 (5)	0.034 (4)	0.016 (4)
C(P2)	−0.0729 (9)	0.0388 (9)	0.3695 (5)	0.049 (4)	0.218 (7)	0.082 (4)	0.059 (4)	0.037 (3)	0.087 (4)
C(P3)	0.0385 (12)	0.1359 (6)	0.4235 (4)	0.255 (7)	0.061 (4)	0.080 (4)	0.080 (4)	0.128 (3)	0.036 (3)
C(P4)	0.1756 (11)	0.0857 (8)	0.4391 (4)	0.103 (6)	0.129 (7)	0.033 (3)	−0.013 (6)	0.006 (4)	0.021 (4)
C(P5)	0.1482 (10)	−0.0162 (7)	0.3998 (5)	0.105 (5)	0.104 (5)	0.063 (4)	0.041 (4)	0.041 (4)	0.044 (3)
C(P1′)	0.0341 (10)	0.5615 (6)	0.2156 (6)	0.084 (5)	0.038 (3)	0.111 (6)	0.011 (4)	0.020 (5)	0.004 (4)
C(P2′)	0.1636 (10)	0.6114 (6)	0.1862 (6)	0.109 (6)	0.039 (3)	0.094 (5)	0.017 (4)	0.028 (5)	0.013 (4)
C(P3′)	0.2946 (10)	0.6269 (6)	0.2464 (7)	0.065 (5)	0.030 (3)	0.175 (9)	0.000 (3)	0.026 (5)	−0.018 (5)
C(P4′)	0.2298 (12)	0.5796 (6)	0.3164 (5)	0.162 (7)	0.064 (4)	0.066 (5)	0.061 (4)	−0.023 (5)	−0.028 (4)
C(P5′)	0.0649 (10)	0.5418 (6)	0.2915 (5)	0.112 (6)	0.047 (4)	0.090 (5)	0.024 (4)	0.039 (5)	0.005 (4)
C(PM1)	−0.0616 (20)	−0.1655 (9)	0.3100 (8)	0.338 (15)	0.094 (7)	0.117 (7)	−0.073 (8)	0.110 (8)	−0.010 (6)
C(PM2)	−0.2262 (19)	0.0376 (24)	0.3360 (9)	0.134 (11)	1.503 (33)	0.286 (7)	0.199 (17)	0.108 (7)	0.600 (9)
C(PM3)	0.0110 (25)	0.2531 (11)	0.4606 (8)	0.862 (20)	0.159 (7)	0.217 (8)	0.278 (9)	0.365 (9)	0.116 (6)
C(PM4)	0.3284 (18)	0.1487 (19)	0.4902 (8)	0.172 (11)	0.513 (23)	0.079 (7)	−0.163 (12)	−0.040 (7)	0.100 (10)
C(PM5)	0.2782 (15)	−0.0894 (10)	0.4049 (8)	0.201 (9)	0.265 (7)	0.174 (7)	0.162 (6)	0.092 (7)	0.160 (5)
C(PM1′)	−0.1263 (16)	0.5369 (9)	0.1664 (10)	0.159 (9)	0.084 (7)	0.251 (15)	0.046 (6)	−0.072 (10)	−0.028 (8)
C(PM2′)	0.1723 (20)	0.6492 (8)	0.1027 (7)	0.360 (17)	0.102 (6)	0.110 (7)	0.108 (7)	0.066 (9)	0.055 (5)
C(PM3′)	0.4560 (16)	0.6809 (9)	0.2342 (15)	0.135 (8)	0.051 (6)	0.640 (29)	−0.030 (6)	0.172 (11)	−0.064 (11)
C(PM4′)	0.3286 (22)	0.5799 (11)	0.3955 (8)	0.440 (18)	0.164 (9)	0.118 (8)	0.173 (9)	−0.129 (10)	−0.057 (8)
C(PM5′)	−0.0583 (14)	0.4942 (8)	0.3462 (8)	0.209 (8)	0.077 (6)	0.202 (8)	0.044 (6)	0.147 (6)	0.032 (6)
B(4)	0.3426 (9)	0.1341 (6)	0.2657 (5)	0.055 (4)	0.066 (4)	0.045 (4)	0.025 (3)	0.005 (4)	0.007 (3)
B(5)	0.2260 (10)	−0.0077 (6)	0.2198 (5)	0.074 (5)	0.056 (4)	0.049 (4)	0.032 (3)	0.027 (4)	0.015 (3)
B(6)	0.0742 (9)	0.0659 (5)	0.1820 (4)	0.054 (4)	0.036 (3)	0.039 (3)	0.010 (3)	0.014 (3)	0.008 (3)
B(8)	0.1588 (9)	0.1978 (6)	0.2636 (5)	0.053 (4)	0.042 (3)	0.045 (4)	0.008 (3)	0.015 (3)	0.007 (3)
B(4′)	0.3913 (10)	0.3689 (7)	0.2007 (6)	0.049 (4)	0.050 (4)	0.072 (5)	−0.004 (4)	0.009 (4)	0.003 (4)
B(5′)	0.3094 (11)	0.4091 (7)	0.1048 (6)	0.091 (6)	0.049 (4)	0.070 (5)	0.013 (4)	0.042 (4)	0.013 (4)
B(6′)	0.1207 (10)	0.3137 (6)	0.1139 (5)	0.066 (5)	0.038 (3)	0.051 (4)	0.011 (3)	0.016 (4)	0.009 (3)
B(8′)	0.1851 (9)	0.3217 (5)	0.2292 (5)	0.054 (4)	0.036 (3)	0.050 (4)	0.010 (3)	0.019 (3)	0.004 (3)

atom	*x*	*y*	*z*	***B***, Å²	atom	*x*	*y*	*z*	***B***, Å²
H(M11)	0.521 (7)	−0.032 (5)	0.149 (4)	5 (2)	H(M23′)	0.123 (10)	0.186 (6)	−0.058 (5)	9 (2)
H(M12)	0.615 (8)	0.094 (6)	0.169 (5)	7 (2)	H(4′)	0.499 (9)	0.385 (6)	0.241 (5)	7 (2)
H(M13)	0.518 (8)	0.042 (5)	0.083 (5)	7 (2)	H(5′)	0.341 (7)	0.457 (5)	0.056 (4)	4 (1)
H(M21)	0.212 (7)	−0.097 (5)	0.035 (4)	5 (2)	H(6′)	−0.022 (7)	0.288 (5)	0.088 (4)	4 (1)
H(M22)	0.254 (8)	−0.012 (5)	0.007 (4)	6 (2)	H(21)	−0.260 (8)	0.098 (5)	0.350 (4)	6 (2)
H(M23)	0.071 (9)	−0.057 (6)	0.016 (5)	8 (2)	H(22)	−0.229 (7)	0.006 (5)	0.275 (4)	6 (2)
H(4)	0.452 (7)	0.167 (5)	0.309 (4)	4 (1)	H(23)	−0.293 (7)	−0.022 (5)	0.355 (4)	6 (2)
H(5)	0.239 (7)	−0.097 (4)	0.213 (3)	3 (1)	H(11′)	−0.138 (8)	0.523 (6)	0.088 (4)	7 (2)
H(6)	−0.055 (8)	0.047 (5)	0.146 (4)	6 (2)	H(12′)	−0.194 (8)	0.594 (6)	0.191 (5)	7 (2)
H(M11′)	0.651 (8)	0.267 (5)	0.115 (4)	6 (2)	H(13′)	−0.180 (9)	0.470 (6)	0.173 (5)	8 (2)
H(M12′)	0.610 (9)	0.350 (6)	0.056 (5)	7 (2)	H(31′)	0.516 (8)	0.646 (6)	0.219 (5)	7 (2)
H(M13′)	0.548 (8)	0.229 (6)	0.023 (5)	7 (2)	H(32′)	0.494 (9)	0.726 (6)	0.279 (5)	7 (2)
H(M21′)	0.306 (8)	0.170 (5)	−0.040 (4)	6 (2)	H(33′)	0.448 (10)	0.726 (6)	0.201 (5)	9 (2)
H(M22′)	0.271 (8)	0.273 (5)	−0.072 (4)	6 (2)					

[a] The form of the anisotropic thermal parameter is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

2 days for conversion to the yellow *nido*-$[\eta^5\text{-}C_5(CH_3)_5]Co(CH_3)_2C_2B_3H_5$ (IV) by concentrated NaOH (see Experimental Section).

Of principal interest, however, was the isolation of a new product characterized as $[\eta^5\text{-}C_5(CH_3)_5]_2Co_3(CH_3)_4C_4B_8H_7$ (III). This compound, a red air-stable solid which does not melt below 300 °C, has no detectable counterpart in the corresponding $C_5H_5^-$ reaction.[2] The compositional and structural peculiarities of III quickly became apparent, as described in the following section.

Structural Characterization of $[\eta^5\text{-}C_5(CH_3)_5]_2Co_3(CH_3)_4C_4B_8H_7$ (III). Both the electron-impact and chemical ionization (argon-water or isobutane) mass spectra of III exhibit a sharp parent cutoff at *m*/*e* 650, corresponding to $^{59}Co_3{}^{12}C_{28}{}^{11}B_8{}^{1}H_{49}{}^{+}$. The parent group profile in the CI spectra is closely consistent with the presence of eight boron atoms (subsequently confirmed by ^{11}B NMR and X-ray diffraction evidence), while the EI spectrum indicates substantial hydrogen loss. The molecular weight of 650 was puzzling since this implied only seven nonmethyl hydrogen atoms, one less than the number of borons. If the molecule consisted of two $[\eta^5\text{-}C_5(CH_3)_5]Co^{III}(CH_3)_2C_2B_4H_4{}^{2-}$ moieties complexed to a common Co^{3+} unit, an additional proton would be required for electroneutrality, corresponding to a composition of $([C_5(CH_3)_5]Co^{III}(CH_3)_2C_2B_4H_4)_2Co^{III}H$, mol wt 652; such a species would contain two 8-vertex $Co_2C_2B_4$ closo polyhedra, each having 18 skeletal electrons[13] in conformity with the skeletal electron-counting rules.[14] As noted, however, the molecule ac-

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(12) Miller, V. R.; Finster, D. C.; Grimes, R. N., unpublished observations.

(13) Based on a contribution[14] of two electrons from each BH and $[\eta^5\text{-}C_5(CH_3)_5]Co$ unit, three from each CCH_3 group, and two (per cage) from the central CoH group.

Table V. Bond Distances (Å) in $[C_5(CH_3)_5]_2Co_3(CH_3)_4C_4B_8H_7$ (III)

	unprimed[a]	primed[a]
Co(3)–C(1)	2.010 (3)	2.017 (3)
Co(3)–C(2)	2.035 (3)	2.034 (3)
Co(3)–B(4)	2.199 (4)	2.198 (4)
Co(3)–B(6)	2.223 (2)	2.237 (4)
Co(3)–B(8)	1.939 (3)	1.923 (3)
Co(7)–B(4)	2.101 (4)	2.111 (4)
Co(7)–B(5)	1.968 (4)	1.976 (4)
Co(7)–B(6)	2.119 (3)	2.124 (4)
Co(7)–B(8)	1.835 (3)	1.840 (3)
C(1)–C(2)	1.453 (4)	1.442 (5)
C(1)–B(4)	1.598 (5)	1.600 (5)
C(1)–B(5)	1.738 (5)	1.730 (6)
C(1)–C(M1)	1.511 (4)	1.525 (5)
C(2)–B(5)	1.743 (5)	1.733 (5)
C(2)–B(6)	1.588 (4)	1.607 (5)
C(2)–C(M2)	1.486 (4)	1.508 (5)
B(4)–B(5)	1.877 (6)	1.882 (7)
B(4)–B(8)	1.877 (5)	1.882 (5)
B(5)–B(6)	1.867 (5)	1.886 (6)
B(6)–B(8)	1.897 (5)	1.906 (5)
B(8)–B(8′)	1.758 (5)	
Co(7)–C(P1)	2.043 (4)	2.069 (4)
Co(7)–C(P2)	2.032 (4)	2.086 (4)
Co(7)–C(P3)	2.019 (3)	2.058 (3)
Co(7)–C(P4)	2.058 (4)	2.022 (4)
Co(7)–C(P5)	2.066 (4)	2.058 (4)
⟨Co(7)–C(P)⟩	2.044	2.059
C(P1)–C(P2)	1.339 (7)	1.346 (6)
C(P2)–C(P3)	1.500 (8)	1.413 (7)
C(P3)–C(P4)	1.455 (8)	1.488 (7)
C(P4)–C(P5)	1.280 (6)	1.424 (7)
C(P5)–C(P1)	1.300 (6)	1.335 (6)
⟨C(P)–C(P)⟩	1.375	1.401
C(P1)–C(PM1)	1.557 (7)	1.506 (7)
C(P2)–C(PM2)	1.393 (9)	1.536 (7)
C(P3)–C(PM3)	1.524 (7)	1.482 (7)
C(P4)–C(PM4)	1.520 (7)	1.505 (7)
C(P5)–C(PM5)	1.565 (7)	1.545 (7)
⟨C(P)–C(PM)⟩	1.512	1.515
B(4)–H(4)	1.115 (4)	1.069 (4)
B(5)–H(5)	1.128 (4)	1.113 (4)
B(6)–H(6)	1.192 (4)	1.238 (4)
⟨B–H⟩	1.145	1.140
⟨C–H⟩ (cage)	0.92	0.98
⟨C–H⟩ (ring)	0.94	0.94
Co(3)–Co(7)[b]	3.340 (1)	3.334 (1)
Co(7)–Co(7′)[b]	5.400 (1)	

[a] Reference is to the atom labels designated with and without primes. [b] Nonbonded distances.

Table VI. Selected Bond Angles (Deg) in III

	unprimed	primed
Cage Framework		
C(1)–Co(3)–C(2)	42.1 (1)	41.7 (1)
C(1)–Co(3)–B(4)	44.3 (1)	44.4 (1)
C(1)–Co(3)–C(1′)	108.7 (1)	
C(2)–Co(3)–B(6)	43.5 (1)	43.9 (1)
C(2)–Co(3)–C(2′)	111.8 (1)	
B(4)–Co(3)–B(8)	53.5 (1)	53.9 (2)
B(4)–Co(3)–B(4′)	98.4 (2)	
B(6)–Co(3)–B(8)	53.7 (1)	53.9 (2)
B(8)–Co(3)–B(8′)	54.2 (2)	
B(6)–Co(3)–B(6′)	103.7 (1)	
B(8)–Co(3)–B(8′)	54.2 (2)	
B(4)–Co(7)–B(5)	54.8 (2)	54.7 (2)
B(5)–Co(7)–B(6)	54.2 (2)	54.6 (2)
B(6)–Co(7)–B(8)	56.8 (1)	56.9 (2)
B(8)–Co(7)–B(4)	56.5 (2)	56.4 (2)
Co(3)–C(1)–C(2)	69.9 (2)	69.8 (2)
Co(3)–C(1)–B(4)	74.1 (2)	73.8 (2)
Co(3)–C(1)–C(M1)	129.8 (3)	130.0 (3)
C(2)–C(1)–B(5)	65.5 (2)	65.5 (3)
C(2)–C(1)–C(M1)	123.6 (3)	124.0 (3)
B(4)–C(1)–B(5)	68.3 (2)	68.7 (2)
B(4)–C(1)–C(M1)	125.4 (3)	124.9 (3)
B(5)–C(1)–C(M1)	126.1 (3)	126.2 (3)
Co(3)–C(2)–C(1)	68.0 (2)	68.5 (2)
Co(3)–C(2)–B(6)	74.6 (2)	74.8 (2)
Co(3)–C(2)–C(M2)	131.5 (2)	132.0 (2)
C(1)–C(2)–B(5)	65.2 (2)	65.3 (3)
C(1)–C(2)–C(M2)	123.8 (3)	123.7 (3)
B(5)–C(2)–B(6)	68.0 (2)	68.6 (2)
B(5)–C(2)–C(M2)	125.4 (3)	124.8 (3)
B(6)–C(2)–C(M2)	126.0 (3)	124.9 (3)
Co(3)–B(4)–Co(7)	101.9 (2)	101.4 (2)
Co(3)–B(4)–C(1)	61.5 (2)	61.8 (2)
Co(3)–B(4)–B(8)	56.1 (2)	55.6 (1)
Co(7)–B(4)–B(5)	59.0 (2)	59.0 (2)
Co(7)–B(4)–B(8)	54.6 (1)	54.5 (2)
C(1)–B(4)–B(5)	59.4 (2)	58.9 (2)
Co(7)–B(5)–B(4)	66.2 (2)	66.3 (2)
Co(7)–B(5)–B(6)	67.0 (2)	66.7 (2)
C(1)–B(5)–C(2)	49.3 (2)	49.2 (2)
C(1)–B(5)–B(4)	52.3 (2)	52.4 (2)
C(2)–B(5)–B(6)	52.1 (2)	52.5 (2)
Co(3)–B(6)–Co(7)	100.6 (1)	99.7 (2)
Co(3)–B(6)–C(2)	61.9 (2)	61.3 (2)
Co(7)–B(6)–B(5)	58.8 (2)	58.7 (2)
Co(7)–B(6)–B(8)	54.1 (1)	54.0 (1)
C(2)–B(6)–B(5)	60.0 (2)	58.9 (2)
Co(3)–B(8)–Co(7)	124.5 (2)	124.7 (2)
Co(3)–B(8)–B(4)	70.4 (2)	70.5 (2)
Co(3)–B(8)–B(6)	70.8 (2)	71.5 (2)
Co(3)–B(8)–B(8′)	62.5 (2)	
Co(3)–B(8′)–B(8)		63.4 (2)
Co(7)–B(8)–B(8′)	172.7 (3)	
Co(7)–B(8′)–B(8)		171.8 (3)
$C_5(CH_3)_5$ ligands		
C(P2)–C(P1)–C(P5)	111.9 (5)	112.7 (5)
C(P2)–C(P1)–C(PM1)	124.4 (7)	121.2 (6)
C(P5)–C(P1)–C(PM1)	123.6 (6)	126.0 (5)
C(P1)–C(P2)–C(P3)	105.3 (4)	108.6 (4)
C(P1)–C(P2)–C(PM2)	127.6 (1)	127.2 (6)
C(P3)–C(P2)–C(PM2)	127.2 (1)	124.2 (6)
C(P2)–C(P3)–C(P4)	101.3 (3)	105.1 (4)
C(P2)–C(P3)–C(PM3)	129.8 (10)	122.6 (8)
C(P4)–C(P3)–C(PM3)	128.6 (10)	132.4 (8)
C(P3)–C(P4)–C(P5)	109.2 (5)	105.3 (4)
C(P3)–C(P4)–C(PM4)	123.8 (8)	123.4 (8)
C(P5)–C(P4)–C(PM4)	127.0 (8)	131.3 (8)
C(P1)–C(P5)–C(P4)	112.3 (5)	108.2 (4)
C(P1)–C(P5)–C(PM5)	128.0 (6)	126.2 (6)
C(P4)–C(P5)–C(PM5)	119.7 (7)	125.4 (6)
⟨C(P)–C(P)–C(P)⟩	108.0	108.0
⟨C(P)–C(P)–C(PM)⟩	126.0	126.0

tually falls short of this "idealized" composition by two hydrogens and hence by two electrons. In addition, the 100- and 200-MHz ^1H FT NMR spectra exhibit no signal in the high-field region (ca. −5 to −20 ppm) expected for a Co-H proton. The ^{11}B and ^1H spectra do, however, indicate high symmetry.

So that structural ambiguities could be resolved, an X-ray diffraction study of III was undertaken. The molecular geometry (Figures 3–5 and Tables IV–VII) does indeed consist of two $[\eta^5\text{-}C_5(CH_3)_2]Co(CH_3)_2C_2B_4$ units fused to a common cobalt atom, but it also contains a striking and unexpected feature: the two polyhedral cages are directly linked by a boron–boron bond [1.758 (5) Å] which is shorter than any other B–B bond in the structure; moreover, *the two linked borons both lack terminal hydrogen atoms*. That the absence of terminal hydrogens on B(8) and B(8′) is real, and does not simply reflect a failure to locate these atoms from the X-ray data, is clear from the following evidence: (1) the terminal hydrogen atoms on all other boron atoms in the molecule were easily located from difference Fourier maps in early stages of refinement, yet none ever appeared on B(8) or B(8′), and (2) introduction of hydrogen atoms into various

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(14) (a) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1. (b) Rudolph, R. W. *Acc. Chem. Res.* **1976**, *9*, 446.

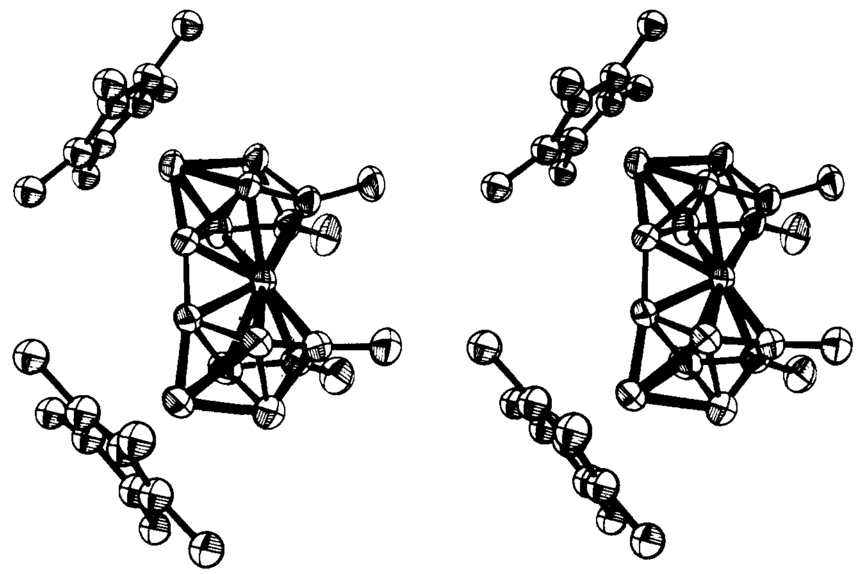

Figure 3. Stereoview of the molecular geometry of III with hydrogen atoms omitted. Cage atoms are shown as 50% thermal ellipsoids, but $C_5(CH_3)_5$ carbon atoms, which exhibit large thermal librations, are drawn as spheres of arbitrary radius. A terminal hydrogen atom is attached to each boron atom except B(8) and B(8′).

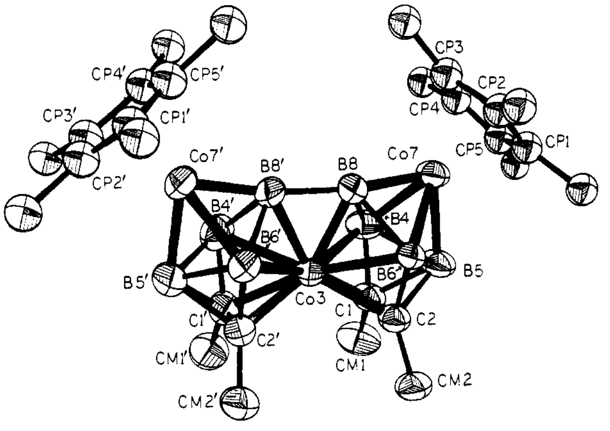

Figure 4. Numbering system in III.

calculated positions in the vicinity of B(8) and B(8′) failed to refine successfully and did not lower the *R* factor. In addition, the fact that B(8) and B(8′) are directly bonded correlates well with the absence of terminal hydrogens; if such hydrogens were present, there would be no discernible reason for the cages to form a B–B link.[15]

Table VII. Selected Molecular Planes in III

atom	dev (Å)	atom	dev (Å)
Plane 1: C(P1), C(P2), C(P3), C(P4), C(P5)			
$0.3776x + 0.4385y - 0.8156z + 5.5324 = 0$			
C(P1)	−0.0023	C(PM1)	−0.0552
C(P2)	−0.0031	C(PM2)	−0.0211
C(P3)	0.0071	C(PM3)	−0.1087
C(P4)	−0.0095	C(PM4)	0.0023
C(P5)	0.0078	C(PM5)	−0.0338
Co(7)	1.6774		
Plane 2: C(P1′), C(P2′), C(P3′), C(P4′), C(P5′)			
$0.3720x - 0.8150y - 0.4442z + 6.9330 = 0$			
C(P1′)	0.0047	C(PM1′)	−0.0261
C(P2′)	−0.0022	C(PM2′)	−0.0501
C(P3′)	−0.0009	C(PM3′)	−0.0240
C(P4′)	0.0034	C(PM4′)	−0.0553
C(P5′)	−0.0050	C(PM5′)	−0.1141
Co(7′)	1.6868		
Plane 3: C(1), C(2), B(4), B(6)			
$-0.0552x + 0.9537y - 0.2957z + 0.7427 = 0$			
C(1)	0.0005	Co(3)	1.6908
C(2)	−0.0005	C(M1)	−0.1981
B(4)	−0.0003	C(M2)	−0.2120
B(6)	0.0003		
Plane 4: C(1′), C(2′), B(4′), B(6′)			
$0.0354x + 0.9496y - 0.3115z - 2.7426 = 0$			
C(1′)	0.0052	Co(3)	−1.6880
C(2′)	−0.0052	C(M1′)	0.1828
B(4′)	−0.0030	C(M2′)	0.2140
B(6′)	0.0030		
Plane 5: Co(3), Co(7), B(5), B(8)			
$-0.8280x - 0.2063y - 0.5214z + 3.1074 = 0$			
Co(3)	−0.0030	B(5)	0.0024
Co(7)	−0.0042	B(8)	0.0048
Plane 6: Co(3), Co(7′), B(5′), B(8′)			
$-0.8307x - 0.1468y - 0.5371z + 3.0402 = 0$			
Co(3)	−0.0027	B(5′)	0.0022
Co(7′)	−0.0038	B(8′)	0.0043

planes	angle, deg	planes	angle, deg
1,2	81.64	4,6	90.09
3,4	5.28	5,6	3.53
3,5	89.82		

Given that the six borons B(4), B(5), B(6), B(4′), B(5′), and B(6′) each have a terminal hydrogen, there remained one hydrogen atom still to be located. This was clear from the mass spectroscopic

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(15) Previous X-ray diffraction studies of commo-metallacarboranes (with the possible exception of $(\eta^5\text{-}C_5H_5)CoFe(CH_3)_4C_4B_8H_8$, a special case discussed in the concluding section) disclose no instance of a direct B–B bond between ligands: (a) Lo, F. Y.; Strouse, C. E.; Callahan, K. P.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1975**, *97*, 428. (b) St. Clair, D.; Zalkin, A.; Templeton, D. H. *Inorg. Chem.* **1971**, *10*, 2587. (c) St. Clair, D.; Zalkin, A.; Templeton, D. H. *Ibid.* **1972**, *11*, 377. (d) Churchill, M. R.; Gold, K. *Ibid.* **1973**, *12*, 1157. (e) Zalkin, A.; Hopkins, T. E.; Templeton, D. H. *Ibid.* **1967**, *6*, 1911. (f) DeBoer, B. G.; Zalkin, A.; Templeton, D. H. *Ibid.* **1968**, *7*, 2288. (g) Churchill, M. R.; Gold, K. *Ibid.* **1971**, *10*, 1928. (h) St. Clair, D.; Zalkin, A.; Templeton, D. H. *Ibid.* **1969**, *8*, 2980. (i) Churchill, M. R.; Reis, A. H., Jr.; Francis, J. N.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1970**, *92*, 4993. (j) Hansen, F. V.; Hazell, R. G.; Hyatt, C.; Stucky, G. C. *Acta Chem. Scand.* **1973**, *27*, 1210. (k) St. Clair, D.; Zalkin, A.; Templeton, D. H. *J. Am. Chem. Soc.* **1970**, *92*, 1173. (l) Evrard, G.; Ricci, J. A., Jr.; Bernal, I.; Evans, W. J.; Dustin, D. F.; Hawthorne, M. *J. Chem. Soc., Chem. Commun.* **1974**, 234. (m) Churchill, M. R.; Gold, K. *J. Am. Chem. Soc.* **1970**, *92*, 1180. (n) Wing, R. M. *Ibid.* **1970**, *92*, 1187. (o) Wing, R. W. *Ibid.* **1967**, *89*, 5599. (p) Wing, R. M. *Ibid.* **1968**, *90*, 4828. (q) Todd, L. J.; Paul, I. C.; Little, J. L.; Welcker, P. S.; Peterson, C. R. *Ibid.* **1968**, *90*, 4489. (r) Pipal, J. R.; Maxwell, W. M.; Grimes, R. N. *Inorg. Chem.* **1978**, *17*, 1447. (s) Pipal, J. R.; Grimes, R. N. *Ibid.* **1979**, *18*, 263. (t) Creswick, M.; Bernal, I.; Evrard, G. *Cryst. Struct. Commun.* **1979**, *8*, 839. (u) Guggenberger, L. J. *J. Am. Chem. Soc.* **1972**, *94*, 114. (v) Colquhoun, H. M.; Greenough, T. J.; Wallbridge, M. G. H. *J. Chem. Soc., Chem. Commun.* **1976**, 1019. (w) Fronczek, F. R.; Halstead, G. W.; Raymond, K. W. *J. Am. Chem. Soc.* **1977**, *99*, 1769. (x) Davis, B. R.; Bernal, I.; Buttone, J.; Good, M. L. *Moessbauer Eff. Methodol.* **1973**, *8*, 127.

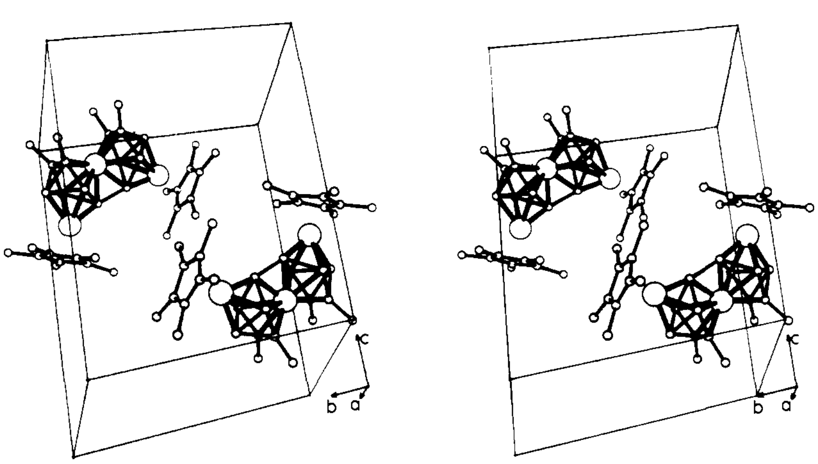

Figure 5. Unit cell packing in III.

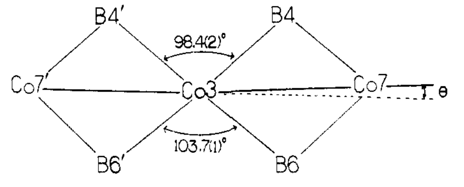

Figure 6. Schematic diagram showing the molecular "fold" distortion, viewed down an axis passing through Co(3) and the midpoint of the B(8)–B(8′) link. The angle θ between the Co(3)–Co(7) vector (solid line) and the extension of the Co(3)–Co(7′) vector (dotted line) is 3.5°.

evidence which dictated seven nonmethyl hydrogens, as noted above, and also from the diamagnetism of the molecule, which was confirmed by a magnetic susceptibility measurement at 4 K. (If no "extra" hydrogen atom were present, III would be an odd-electron, paramagnetic species (mol wt mw 649); this is clearly ruled out.) Although the seventh hydrogen was not directly found in the X-ray study, its approximate location was deduced from indirect evidence. An obvious possibility—a B–H–B bridge between the linked borons B(8) and B(8′)—is eliminated both from the X-ray data, which reveals no electron density attributable to a bridging atom, and from the absence of a B–H–B IR absorption (1500–2300 cm^{-1}) in both solid-state and solution spectra. However, the detailed structure of the heavy-atom framework yields an important clue.

The cobaltacarborane framework has virtual (not crystallographic) mirror symmetry with respect to a plane passing through the central cobalt and bisecting the B(8)–B(8′) vector; the two halves of the molecule (depicted by primed and nonprimed atoms, respectively, in Figure 4) are nearly identical, as shown by a comparison of corresponding bond distances and angles (Tables V and VI). However, the framework does *not* exhibit a mirror plane through the three cobalt atoms, and the idealized symmetry is C_s rather than C_{2v}. The molecule is, in fact, slightly "folded" on an axis passing through Co(3) and bisecting the B(8)–B(8′) vector (Figure 6). This can be seen in several ways: (1) the planes defined by Co(3)–B(8)–Co(7)–B(5) and by Co(3)–B(8′)–Co(7′)–B(5′) exhibit a small but significant dihedral angle of 3.5° (Table VII); (2) the C(1)–C(1′) nonbonded interligand distance is significantly shorter than C(2)–C(2′) [3.270 (5) vs. 3.370 (5) Å]; (3) bond lengths on one side of the "fold" [e.g., Co(3)–C(1), Co(3)–C(1′), Co(3)–B(4), Co(3)–B(4′), B(4)–B(8), B(4′)–B(8′)] are consistently shorter than their counterparts on the other side [e.g., Co(3)–C(2), Co(3)–C(2′), Co(3)–B(6), Co(3)–B(6′), B(6)–B(8), B(6′)–B(8′)]; (4) a similar effect is seen in a comparison of bond angles, e.g., B(4)–Co(3)–B(4′) is 98.4 (2)° while B(6)–Co(3)–B(6′) is 103.7 (1)° (Figure 6).

The molecular distortion can be explained by the presence of the "extra" hydrogen in the vicinity of atoms Co(3), B(6), B(8), B(6′), and B(8′), causing that side of the molecule to open slightly and producing the observed lengthening of the bonds directly involved. Precedent for such an effect is found in the *commo*-ferracarborane $[2,3\text{-}(CH_3)_2C_2B_4H_4]_2FeH_2$, where the "extra" hydrogens in the region of the metal atom evidently force the two carborane ligands to tilt toward each other in such a way that the methyl groups on different ligands are in close proximity.[15a] Whether, in the present case, the hydrogen atom occupies a fixed location in the Co(3)–B(6)–B(8)–B(6′)–B(8′) "pocket" cannot be determined; more probably, it is disordered over several positions in that region of the molecule, which would account for the failure to locate it crystallographically.

Other bond distances and angles in the molecule are within normal ranges for metallacarboranes, although comparison with other structures is limited by the fact that III is the first crystallographically characterized metallacarborane containing a "normal" 8-vertex closo cage (the only other structurally established 8-vertex metal–boron polyhedra are $(\eta^5\text{-}C_5H_5)CoFe(CH_3)_4C_4B_8H_8$, a hypercloso system,[16] and the metallaboranes $(\eta^5\text{-}C_5H_5)_4Co_4B_4H_4$[17] and $(\eta^5\text{-}C_5H_5)_4Ni_4B_4H_4$[18]). Although the framework carbon–carbon distance [1.448 (1) Å] is comparable to nido-carboranes in which localized C–C interaction is postulated,[19] the present value probably reflects primarily the intrinsic geometric properties of the 8-vertex cage.

The coordination of the $[\eta^5\text{-}C_5(CH_3)_5]Co$ moieties to B_4 faces is unusual and has mechanistic implications (discussed below).

Spectroscopic Studies of $[\eta^5\text{-}C_5(CH_3)_5]_2Co_3(CH_3)_4C_4B_8H_7$ (III) in Solution. The structure of III in the solid state, described above, is significantly different from its geometry in solution as revealed by ^{11}B and ^1H FT NMR spectra. The apparent symmetry on the NMR time scale is C_{2v}, with a single cage CH_3 environment and boron nuclei in a 4:2:2 pattern (Figures 1 and 2); in itself, this would not necessarily be inconsistent with the crystallographic structure since the deviation from C_{2v} symmetry produced by the "wedging" hydrogen might not be readily detectable by NMR techniques. More revealing, however, is the fact that both the 100- and the 200-MHz ^1H NMR spectra clearly reveal *seven terminal BH resonances* in a 4:2:1 ratio. With assignment of the area 4 signal to H(4), H(6), H(4′), and H(6′) and the area 2 peak to H(5) and H(5′), the remaining resonance must arise from the unique or "extra" proton. Its strongly deshielded location (13.12 ppm downfield from Me_4Si) rules out association with a metal atom, which would produce a substantial *upfield* shift, or a B–H–B bridge, whose presence would normally generate resonances in the 0 to −10 ppm region; rather, this proton must be associated *in solution* with B(8) and B(8′), which lack terminal hydrogens in the solid state. This assignment is further supported by heteronuclear single-frequency decoupling experiments that establish that the low-field ^1H resonance and the low-field ^{11}B signal arise

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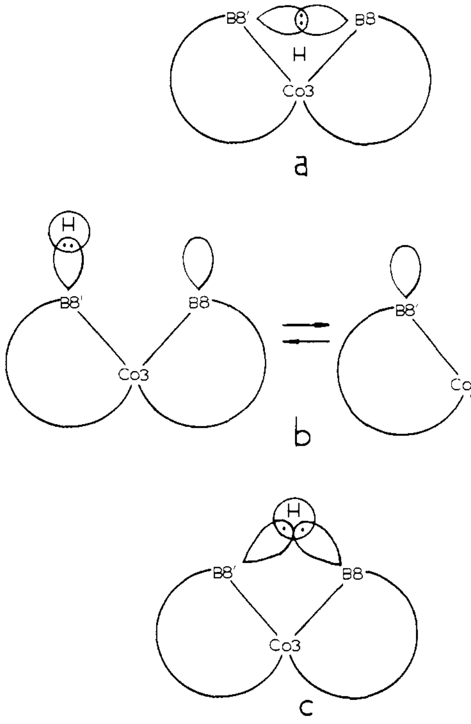

Figure 7. Sites for location of the unique hydrogen atom in III: (a) hydrogen in the vicinity of Co(3), with a direct bond between B(8) and B(8′) (solid-state structure); (b) tautomeric exchange between terminal positions on nonlinked B(8) and B(8′) (solution structure); (c) three-center B–H–B intercage bridge. This feature is apparently excluded in both solid state and solution as a *static* arrangement (see text); however, such a bridge may exist in solution as a transient during the tautomeric exchange shown in (b). Moreover, the "terminal" sites in (b) may in fact be quasibridging, with the hydrogen alternating between two energy minima in the vicinity of B(8) and B(8′).

from the same BH units, clearly B(8)–H and B(8′)–H. Moreover, the large downfield shift of the B(8), B(8′) resonances imply low-coordinate BH groups adjacent to cobalt.[20] Thus, it appears that *in solution the B(8)–B(8′) link is severed (Figure 7b) and the "extra" hydrogen tautomerizes between terminal positions on these two borons.* This hypothesis is strengthened by the observation that the H(8),H(8′) resonance remains a broad singlet even in the absence of ^{11}B decoupling (Figure 2); this is consistent with hydrogen exchange between B(8) and B(8′) at a rate comparable to the reciprocal of the coupling constant, effectively modulating J_{BH} (typically 150–180 Hz) to a smaller than normal value. In contrast, the remaining H–B proton resonances are visible only under ^{11}B decoupling (Figure 1), in the absence of which they are broad, unobservable quartets. Both the ^{1}H and ^{11}B spectra were essentially unchanged at −80 °C.

Assignment of the ^{11}B FT NMR peaks is straightforward (Table I). The area 2 peak at very low field δ (92.9 ppm) can be readily attributed to B(8) and B(8′), which in the absence of a mutual bond occupy low-coordinate vertices adjacent to two cobalt atoms, a situation that has previously been shown to produce extreme downfield shifts.[20] The very large line widths of the ^{11}B resonances (260–290 Hz), which nearly obscure the scalar coupling to the terminal protons, are a consequence of extremely fast relaxation of the ^{11}B nuclei. A null-time study utilizing a $180°-\tau-90°$ pulse sequence indicated a spin–lattice relaxation time of $\sim$1 ms, the downfield peak being the longest of the three. (For quadrupolar nuclei where $T_1 = T_2$, natural line width $= 1/\pi T_2 \simeq 1/\pi(0.001) \simeq 320$ Hz.)

In summary, the NMR data for compound III in THF solution are consistent with a fluxional molecule in which one hydrogen atom rapidly tautomerizes between equivalent terminal positions on B(8) and B(8′), which are probably not linked to each other in solution (Figure 7b). Other hydrogen atoms may conceivably tautomerize also but only on a time scale long relative to that of NMR. In the crystal, the "extra" hydrogen moves to a wedging location in the vicinity of the metal, thereby inducing linkage between B(8) and B(8′) which would otherwise be coordinatively unsaturated (Figure 7a).

Mechanism of Formation of III. A peculiarity of the structure of III is the location of Co(7) and Co(7′) in low-coordinate vertices adjacent only to boron atoms. The central cobalt, on the other hand, is coordinated to C_2B_3 faces on both carborane ligands. Since insertion of metals into nido-carboranes nealy always occurs at an open face containing carbon,[21] a plausible sequence for the formation of III would involve initial complexation of cobalt to two carborane anions to give a bis(carborane) complex such as $[(CH_3)_2C_2B_4H_4]_2Co^-$; inasmuch as that species[22] would have no open faces, subsequent attack of $[\eta^5\text{-}C_5(CH_3)_5]Co^{n+}$ units could well occur at equivalent B–B edges on the two C_2B_4 ligands. Indeed, the location of the latter two cobalts at vertices 7 and 7′ in III is highly reasonable on steric grounds, since interaction of the bulky $C_5(CH_3)_5$ ligands with each other and with the cage CH_3 groups is thereby minimized.

Elimination of hydrogen to give III, which has only seven nonmethyl hydrogen atoms, may take place via evolution of H_2 gas (an observed product of the overall reaction), but the driving force for such a process is not clear. One can speculate that the "normal", but unobserved, species $([\eta^5\text{-}C_5(CH_3)_5]Co(CH_3)_2C_2B_4H_4)_2CoH$, which would have terminal hydrogens on all boron atoms (and no intercage link) places H(8) and H(8′) so close together that the thermodynamic driving force for elimination of H_2 is supplied by the relief of H–H repulsion, augmented by the energy released in formation of a B(8)–B(8′) link. However, at present this is at best an educated guess.

Conclusions

The major consequence, insofar as products are concerned, of replacing $C_5H_5^-$ with $C_5(CH_3)_5^-$ in the reaction with $CoCl_2$ and $2,3\text{-}(CH_3)_2C_2B_4H_5^-$ ion is the formation of the structurally unique complex III, whose $C_5H_5^-$ analogue is unknown. Whether viewed in terms of isolated or actual yield in the reaction, the generation of III is mechanistically significant. The elimination of two hydrogen atoms from its (assumed) fully hydrogenated precursor is an oxidative process and results in linkage of the two ligands via a boron–boron bond. A process of this type may be a first step in the oxidative ligand fusion mechanism[23] whereby two ligands coordinated to a metal atom are combined into a single cage with expulsion of the metal. There is no evidence thus far that III itself can undergo fusion, but it is possible that linked-cage species similar to III may be intermediates in the conversions of $[(CH_3)_2C_2B_4H_4]_2CoH$ and $[(CH_3)_2C_2B_4H_4]_2FeH_2$ to $(CH_3)_4C_4B_8H_8$,[22–24] of $(\eta^5\text{-}C_5H_5)CoC_2B_3H_6^-$ to $(\eta^5\text{-}C_5H_5)_2Co_2C_4B_6H_{10}$,[25] and of $(\eta^5\text{-}C_5H_5)Co(CH_3)_2C_2B_3H_4^-$ to $(\eta^5\text{-}C_5H_5)_2Co_2(CH_3)_4C_4B_6H_6$.[25] If III is in fact structurally analogous to a typical intermediate in the oxidative fusion sequence, its own stability may be traceable to the bulky pentamethylcyclopentadienyl ligands, which could block the entry of an oxidant (i.e., O_2) to the metal center and thereby prevent completion of the fusion process. The possibility of electronic effects originating in the $C_5(CH_3)_5$ groups also exists.

Complex III is the first clear example of direct interligand B–B linkage in a *commo*-metallaborane or -metallacarborane, but the species $(\eta^5\text{-}C_5H_5)CoFe(CH_3)_4C_4B_8H_8$ is closely related. In that complex,[16] a BH unit is wedged between two 7-vertex closo cages

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[22] The protonated form, $[(CH_3)_2C_2B_4H_4]_2CoH$, has been characterized: Maxwell, W. M.; Miller, V. R.; Grimes, R. N. *J. Am. Chem. Soc.* **1976**, *98*, 4818.

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which are fused at a common iron vertex such that the unique BH caps a triangular Co–Fe–B face on one polyhedron and interacts weakly with the other. There are also several bis(dicarbollyl) transition-metal complexes in which the two $C_2B_9H_{10}$ ligands are bridged by HCS_2, CH_3CO_2,[26] or other[21,27] groups.

A fundamental question is whether the observed stereochemical behavior of III is a general phenomenon that is likely to be encountered in other *commo*-metallaboron complexes (either as isolable species or as reaction intermediates) or is, rather, a consequence of special circumstances associated with the peculiar electronic and steric properties of the $C_5(CH_3)_5^-$ ligand. Continuing studies in this area may help to resolve this issue.

Acknowledgment. This work was supported by the National Science Foundation, Grant No. CHE-79-09948, and the Office of Naval Research. We are indebted to Dr. Ralph E. Hurd of the Nicolet Magnetics Corp. and Mr. William Hutton of our department for the 200-MHz ^1H and 64-MHz ^{11}B NMR spectra and to Dr. Greig Sim for assistance in the magnetic susceptibility measurement.

Supplementary Material Available: Listing of observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

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Synthesis, Structure, and Reactions of $[Mo(SnCl_3)(CN\text{-}t\text{-}Bu)_6][(Ph_3B)_2CN]$, Containing a Potentially Useful New Anion for Crystallizations[1]

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Contribution from the Department of Chemistry, Columbia University, New York, New York 10027. Received August 18, 1980

Abstract: Stannous chloride reacts with yellow chlorohexakis(*tert*-butyl isocyanide)molybdenum(II) chloride to give the maroon complex $[Mo(SnCl_3)(CN\text{-}t\text{-}Bu)_6]^+$, in which insertion of tin into the Mo–Cl bond has formally occurred. Crystals suitable for X-ray analysis were obtained by using the "BBCN" anion, $[(Ph_3B)_2CN]^-$, which may be viewed as an analogue of the PPN cation, $[(Ph_3P)_2N]^+$. The seven-coordinate complex has crystallographically required C_s symmetry. Its geometry may be described as that of a C_s 4:3 piano stool or as that of a distorted capped octahedron with $SnCl_3^-$ as the capping ligand. The Mo–Sn bond length is 2.663 (1) Å, and the Mo–C distances vary from 2.071 (18) to 2.138 (8) Å. The C≡N group in the anion is disordered across a center of symmetry in the crystal lattice and has a bond length of 1.147 (12) Å. The sodium and tetramethylammonium salts of the BBCN anion have been synthesized. The compound $[Mo(SnCl_3)(CN\text{-}t\text{-}Bu)_6][(Ph_3B)_2CN]$ crystallizes in the orthorhombic system, space group *Pbcm*, with $a = 11.968$ (7) Å, $b = 23.012$ (6) Å, $c = 26.905$ (4) Å, and $Z = 4$. Reaction of $[Mo(SnCl_3)(CN\text{-}t\text{-}Bu)_6]^+$ with zinc in aqueous ethanol does not lead to reductive coupling of adjacent *tert*-butyl isocyanide ligands to form a coordinated *N,N'*-dialkyldiaminoacetylene, as in the reaction of zinc with other $[MoX(CN\text{-}t\text{-}Bu)_6]^+$ complexes. Instead, the $[Mo(CN\text{-}t\text{-}Bu)_7]^{2+}$ cation has been isolated from the reaction mixture as the tetraphenylborate salt.

Introduction

Seven-coordinate alkyl isocyanide (L) complexes of molybdenum(II), MoL_5X_2,[3] MoL_6X^+,[4,5] MoL_7^{2+} [5,6] (X = halide), have been known for several years. These stable compounds can be prepared by a variety of methods and most recently have been shown[7,8] to form in the reaction of quadruply bonded dimolybdenum(II) complexes with alkyl isocyanides (Figure 1). X-ray structural studies have revealed that the MoL_7^{2+} cations adopt various heptacoordinate geometries depending upon the anion and nature of the alkyl substituent.[6,7,9] In the isomorphous series of compounds $[MoL_6X]Y$, X = Y = Cl, Br, or I or X = CN and Y = PF_6, the cations all have capped trigonal prismatic structures.[4,5,9]

The reactions of the MoL_7^{2+} and MoL_6X^+ cations have been the subject of several investigations. Molecular orbital calculations[10] of seven-coordinate molecules suggested that d^4-capped trigonal prismatic complexes might experience ligand–ligand bonding interactions on the unique edge of the coordination polyhedron at the time that just such a reaction, the reductive coupling of adjacent isocyanides in $[MoI(CN\text{-}t\text{-}Bu)_6]I$ to form the novel acetylene complex $[MoI(CN\text{-}t\text{-}Bu)_4(t\text{-}BuHNCCNH\text{-}t\text{-}Bu)]I$, was reported.[11] Chemical[5] and kinetic[12] studies of the interconversion of the MoL_7^{2+} and MoL_6X^+ cations have also been carried out. Mixed phosphine–isocyanide complexes can be

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[1] Part 10 of a continuing series on higher coordinate cyanide and isocyanide complexes. For part 9, see ref 2.

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