Table I. Relative Concentration of Products during the Addition of $BF_3 \cdot O(C_2H_5)_2$ to $NaBH_4$

% $BF_3 \cdot O(C_2H_5)_2$ added[a]	Concentration,[b] M		
	BH_4^-	$B_3H_8^-$	$B_{11}H_{14}^-$
58.9	0.420[c]	0.383	0.000
80.1	0.406	0.636	0.011
92.9	0.318	0.751	0.015
109.0	0.121	0.812	0.031
112.0	0.056	0.724	0.027
118.5	0.000	0.714	0.048
131.0	0.000	0.396	0.104
138.0	0.000	0.264	0.146
157.0	0.000	0.000	0.221
182.0	0.000	0.000	0.225
208.0	0.000	0.000	0.231

[a] Stoichiometry based upon eq 2. [b] Determined in diglyme solution by ^{11}B NMR. [c] Apparently saturated.

Table II. Extended Heating of $B_3H_8^-$ Ion Formed in Situ

Aliquot	Time elapsed, h	$[B_3H_8]$, M
1	4.8	0.516
2	6.6[a]	0.840
3	21.8	0.728
4	31.0	0.784
5	46.2	0.798

[a] Stoichiometric amount of $BF_3 \cdot O(C_2H_5)_2$ added (eq 2).

Reaction Study Using ^{11}B NMR. Apparatus was assembled as shown in Figure 1 using a 1000 mL, four-neck flask. The fourth neck contained a tube which extended below the surface of the reaction mixture and equipped with a side inlet through which N_2 could be swept. This tube was stoppered except when aliquots were taken. The flask was charged with 500 mL of diglyme and 60 g (1.59 mol) of $NaBH_4$. The mixture was heated to 105 °C and a total of 250 mL (2.04 mol) of $BF_3 \cdot O(C_2H_5)_2$ was added at the rate of 30 mL/h. Aliquots (~2 mL) were withdrawn from the mixture and placed into screw cap vials and allowed to stand. When the reaction was complete, the supernatant in each vial was placed into an NMR tube and the spectrum measured. Each spectrum was calibrated, and peak areas were determined by comparison to the peak due to $B(OCH_3)_3$ contained in a capillary tube successively placed into each sample. The capillary had been previously calibrated against various known concentrations of purified $(C_2H_5)_4NB_3H_8$ in diglyme solution. The results are shown in Table I.

Extended Heating of $B_3H_8^-$ Ion Formed in Situ. Apparatus was assembled as shown in Figure 1 with a 500-mL, four-neck flask. The fourth neck contained a tube for the withdrawal of aliquots (vide supra). The flask was charged with 250 mL of diglyme and 30 g (0.79 mol) of $NaBH_4$. The mixture was heated to 105 °C and $BF_3 \cdot O(C_2H_5)_2$ (78 mL, 0.64 mol) was added in 6.6 h. Aliquots were withdrawn and analyzed by ^{11}B NMR as above. The results are shown in Table II.

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Registry No. $(C_2H_5)_4NB_{11}H_{14}$, 12555-78-1; $B_3H_8^-$, 12429-74-2; $NaBH_4$, 16940-66-2; $BF_3 \cdot O(C_2H_5)_2$, 109-63-7; $(C_2H_5)_4NB_3H_8$, 12555-74-7.

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The Chemistry of Beryllaboranes. Characterization and Reactions of Beryllium Bis(tetrahydroborate), $Be(BH_4)_2$, and Beryllium Bis(octahydrotriborate), $Be(B_3H_8)_2$

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Gas-phase ^{11}B and ^1H NMR spectra of $Be(BH_4)_2$ show that only one monomeric species is present. A linear B–Be–B framework is inferred, and the hydrogens of each tetrahydroborate undergo rapid local internal exchange. The preparation and characterization of beryllium bis(octahydrotriborate), $Be(B_3H_8)_2$, cyclopentadienylberyllium octahydrotriborate, $C_5H_5BeB_3H_8$, and methylberyllium octahydrotriborate, $(CH_3BeB_3H_8)_2$, are described. The $B_3H_8^-$ derivatives of beryllium exhibit a range of fluxional character as identified by variable-temperature NMR studies. The ^{11}B NMR spectrum of cyclopentadienylberyllium tetrahydroborate consists of a quintet of quartets indicating ^{11}B–H and ^{11}B–^9Be coupling, with the tetrahydroborate hydrogen atoms undergoing rapid intramolecular exchange. The reaction chemistry of BH_4^- and $B_3H_8^-$ derivatives of beryllium is discussed.

Introduction

The chemistry of beryllium–boron compounds, the beryllaboranes, has not been extensively studied. Several of the simple beryllaboranes, however, have been structurally characterized. For example, the structure of $C_5H_5BeBH_4$ is proposed, on the basis of electron diffraction[2] and infrared[3] data, to contain a η^5-cyclopentadienyl ring and a tetrahedral tetrahydroborate group attached to beryllium by two hydrogen bridges; infrared data[4] for $(CH_3BeBH_4)_2$ are consistent with a structure containing bridging methyl groups between the beryllium atoms and a terminal tetrahydroborate group attached to each beryllium with two bridging hydrogens.

The structural characterization of gas-phase, monomeric $Be(BH_4)_2$, however, has a controversial history, and its structure cannot be unequivocally defined. Electron diffraction data have been interpreted in terms of linear D_{2d},[5] triangular C_{2v},[6] and linear C_{3v} or D_{3d}[7] structures (Figure 1a, b, and c or d, respectively). Another such study[8] suggested the presence of two unidentified structures depending on the sample history. Vibrational data for $Be(BH_4)_2$ have been interpreted in terms of linear D_{2d},[9] triangular C_2,[10] and triangular C_{2v}[11] structures (Figure 1a, b, and e, respectively), as well as in terms of a

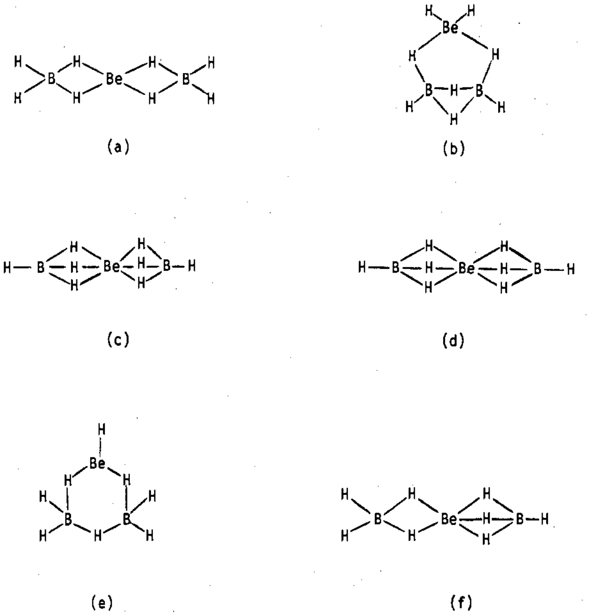


Figure 1. Possible structures for gas-phase $Be(BH_4)_2$.

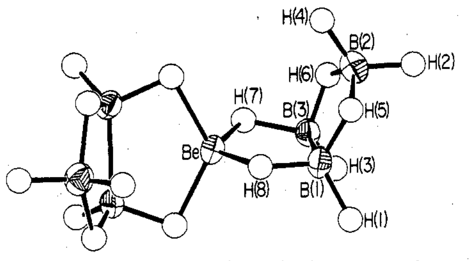


Figure 2. Molecular structure and numbering system for $Be(B_3H_8)_2$.

two-structure system[12] containing a C_{3v} structure and another structure with two bridge hydrogens between boron and beryllium. Mass spectral[11] and dipole moment[13] studies have also been presented in support of triangular structures (Figure 1b and e). Theoretical studies[14] have indicated that linear structures with two or three bridge hydrogens between beryllium and boron (Figure 1a, c, d, and f) are more favorable than other structures in Figure 1, but it was difficult to differentiate between the linear structures. A single-crystal X-ray structural study[15] has shown that solid $Be(BH_4)_2$ consists of a helical polymer with one terminal tetrahydroborate group attached to each beryllium by two bridge hydrogens. A bridging tetrahydroborate links adjacent beryllium atoms in the polymeric chain with two bridge hydrogens to each beryllium. The solid-state structure does not appear to have a direct bearing on the gas-phase structure.

We have previously reported the preparation[16] and structural characterization[17] of beryllium bis(octahydrotriborate), $Be(B_3H_8)_2$, the first example of a metal complex having two covalent $B_3H_8^-$ ligands. In $Be(B_3H_8)_2$ each $B_3H_8^-$ ligand is bonded to beryllium in a bidentate fashion by two hydrogen bridge bonds producing tetrahedral coordination about the beryllium atom (Figure 2). The NMR spectra of $Be(B_3H_8)_2$ suggest fluxional behavior on the NMR time scale above −30 °C.

We report here some chemical and spectroscopic studies of $Be(BH_4)_2$[18] and $Be(B_3H_8)_2$ and several of their derivatives.

Experimental Section

All manipulations were performed using standard high-vacuum techniques.[19] All beryllaborane species discussed here are expected to be very toxic, pyrophoric, air- and moisture-sensitive compounds. They appear to be thermally stable in vacuo for short periods at room temperature. The preparations of $Be(BH_4)_2$,[20] CsB_3H_8,[21] and $C_5H_5BeBH_4$[2] are described elsewhere. Sodium cyclopentadienide was prepared by reaction of freshly distilled C_5H_6 with sodium in dry liquid ammonia solution. The NaC_5H_5 was isolated by distilling off the ammonia under vacuum. Beryllium chloride was sublimed twice before use. Methylene chloride was distilled from 3-Å molecular sieves, and other solvents were distilled from lithium aluminum hydride. Other materials are from reagent grade commercial sources and were used without further purification.

Table I. Infrared Spectral Data for $Be(B_3H_8)_2$, $C_5H_5BeB_3H_8$, and $(CH_3BeB_3H_8)_2$, in cm^{-1} (±10)

$Be(B_3H_8)_2$	Gas phase (10-cm cell): 2570 vs, 2495 s, 2160 vs, 2050 m, sh, 1440 m, 1390 m, 1315 w, 1155 m, 1025 m, 990 m, 900 m, 845 s, 655 m, 595 m
$C_5H_5BeB_3H_8$	Solid film at −196 °C: 3100 w, 2545 m, 2470 m, 2190 w, 1640 s, br, 1440 m, 1170 m, 1130 m, 1090 w, 1020 m, 985 s, 900 s, 835 m, 800 m, sh, 790 m, 755 m, 680 w
$(CH_3BeB_3H_8)_2$	Solid film at −196 °C: 2940 w, 2550 vs, 2490 s, 2220 vs, 2150 s, sh, 1425 m, sh, 1390 m, 1340 m, 1260 s, 1155 m, 1040 s, 1015 m, 985 m, 890 s, 835 s, 780 m, 730 m, 690 m

Table II. ^{11}B NMR Data for $Be(B_3H_8)_2$, $C_5H_5BeB_3H_8$, and $(CH_3BeB_3H_8)_2$

Compd	Solvent	Temp, °C	Chem shift,[a] ppm ($J_{^{11}B-H}$, Hz)	
			B(1), B(3)	B(2)
$Be(B_3H_8)_2$	CD_2Cl_2	−31	−43.6 (132, 57)	−11.8 (122)
	CD_2Cl_2	23	−43.8 (74)	−11.7 (124)
$C_5H_5BeB_3H_8$	CD_2Cl_2	23	−25.5 (34)	
$(CH_3BeB_3H_8)_2$	CD_2Cl_2	−50	−42.4 (135, 59)	−12.1[b]
	CD_2Cl_2	23	−42.4 (123, 60)	−12.0 (117)
	C_6D_6	23	−42.2 (127, 56)	−11.5 (116)
	C_6D_6	37	−42.3 (78)	−11.8 (114)

[a] Chemical shifts downfield from $BF_3 \cdot O(C_2H_5)_2$ have positive signs.[22] [b] No coupling resolved.

Nuclear magnetic resonance spectra were obtained on a Bruker WH-270 (^1H, 270 MHz; ^{11}B, 86.7 MHz) and a Varian XL-100 (^1H, 100 MHz; ^{11}B, 32.1 MHz) spectrometer. Unless otherwise stated, spectra refer to those obtained on the Bruker instrument. A Nicolet BNC-12 computer and associated software programs were used with the Bruker for data collection and manipulation. The ^1H spectra on the Bruker were selectively ^{11}B decoupled using a Type B-FS100 frequency synthesizer, a B-BM1 broad-band modulator, and a B-LV80 selective power amplifier. To obtain gas-phase ^{11}B spectra, the boron probe was modified to eliminate borosilicate glass. A Varian XL-100 spectrometer interfaced to a Varian 620/L minicomputer was used to obtain 100-MHz ^1H NMR spectra or 32.1-MHz ^{11}B NMR spectra. For the gas-phase ^1H spectrum of $Be(BH_4)_2$ the FT mode was used with a gaseous Me_4Si-d_{12} lock (~600 Torr). Beryllium-decoupled ^1H spectra were obtained using a proton (C_6H_6) lock and irradiating at approximately 14.06 MHz. Infrared spectra were obtained on a Perkin-Elmer Model 700 spectrometer. A 10-cm cell with NaCl windows was used for gases. For low-temperature spectra the gases were condensed on a liquid nitrogen cooled Irtran-2 window supported in an evacuated cell having NaCl windows. To obtain IR spectra of $Be(BH_4)_2$ and $(CH_3BeBH_4)_2$, the NaCl salt plates for a gas-phase IR cell were coated with Plexiglas by pouring a dilute chloroform solution of Plexiglas onto the salt plate and allowing the chloroform to evaporate. Another NaCl salt plate was coated such that, when placed in the reference beam, it almost entirely canceled the Plexiglas absorptions in the spectrum. Mass spectra were obtained on an AEI MS-902 spectrometer.

Infrared, ^{11}B NMR, and ^1H NMR data for $Be(B_3H_8)_2$, $C_5H_5BeB_3H_8$, and $(CH_3BeB_3H_8)_2$ are listed in Tables I, II, and III, respectively.

Gas-phase NMR samples of $Be(BH_4)_2$ were prepared in 5-mm quartz NMR tubes for the Bruker spectra (^{11}B and ^1H) and a 12-mm Pyrex NMR tube for the Varian spectrum (^1H). The NMR tubes were pretreated with $Be(BH_4)_2$ to remove borane-reactive materials. Freshly distilled $Be(BH_4)_2$ was added to the NMR tube such that an excess of solid $Be(BH_4)_2$ would be present in the upper portion

Table III. ^1H NMR Data for $Be(B_3H_8)_2$, $C_5H_5BeB_3H_8$, and $(CH_3BeB_3H_8)_2$

			Chem shift,[a] ppm ($J_{^{11}B-H}$, Hz)				
Compd	Solvent	Temp, °C	H(1), H(3)	H(2) and/or H(4)	H(5) and H(6)	H(7) and/or H(8)	Other
$Be(B_3H_8)_2$	CD_2Cl_2	−31	1.00 (140)	2.14 (120)	−0.71 (~50)	−0.98 (~60) or −1.66 (~60)	
	CD_2Cl_2	23	~0.83[b]	2.19 (125)	⟵ ~−0.68 ⟶		
$C_5H_5BeB_3H_8$	C_7D_8	−75	⟵ 1.16[b] ⟶				5.59 or 5.08[c]
	C_7D_8	23	⟵ 0.46[b] ⟶				5.87 or 6.50[c]
$(CH_3BeB_3H_8)_2$	CD_2Cl_2	7	0.89 (131)	2.17[b]	~−0.7[b]	1.06 (~60)	0.13, −0.14, −0.39[d]
	CD_2Cl_2	22					0.11, −0.12, −0.34[d]
	CD_2Cl_2	40					−0.15[d]
	CD_2Cl_2	60					−0.10[d]

[a] Chemical shifts downfield from Me_4Si have positive signs. [b] No coupling resolved. [c] C_5H_5 hydrogens, $Be(C_5H_5)_2$ contamination prevents precise assignment. [d] CH_3 hydrogens.

of the tube. A high sample pressure ($\gtrsim$1 atm) is required to obtain gas-phase spectra with appropriately narrow lines. Since the vapor pressure of $Be(BH_4)_2$ is only 5 Torr at 25 °C, deuterated Me_4Si and/or argon were added such that the final pressure was 4–5 atm for 5-mm tubes and about 2 atm for the 12-mm tube.

The ^{11}B spectrum of gaseous $Be(BH_4)_2$ was obtained at ambient temperature (23 °C) by collecting 450 000 scans at 10 000-Hz spectral width with a repetition time of 0.1 s. Data collection took about 12 h. The ^1H NMR spectrum on the Bruker was obtained by collecting 82 812 scans at 4000-Hz spectral width with a repetition time of 0.512 s. No lock signal was used on the Bruker samples, and field drift was negligible during data collection.

The Varian ^1H spectrum was obtained in the FT mode using gaseous Me_4Si-d_{12} lock. A repetition time of 1.600 s was used to collect 1000 scans at 2048-Hz spectral width. The Bruker and Varian ^1H probes each exhibited a significant background signal, but the background was unique to each instrument.

Solution NMR spectra were obtained using freshly distilled $Be(BH_4)_2$ and solvents distilled from $LiAlH_4$ or 3-Å molecular sieves. Because of the extremely low solubility of $Be(BH_4)_2$, in noncoordinating solvents, undissolved $Be(BH_4)_2$ was always present. A tensimetric titration of $Be(BH_4)_2$ with benzene exhibited no sign of an inflection due to solvent–solute interaction.

Reactions of $Be(BH_4)_2$. Reaction of 0.0167 g (0.43 mmol) of $Be(BH_4)_2$ with 0.26 mmol of BCl_3 for 20 min at room temperature produced 0.21 mmol of B_2H_6 and a white nonvolatile solid, presumably $BeCl_2$. Excess $Be(BH_4)_2$ (0.27 mmol) and BCl_3 (0.11 mmol) were recovered. Reaction of 0.018 g (0.47 mmol) of $Be(BH_4)_2$ with 0.41 mmol of $(CH_3)_2BCl$ at room temperature produced 0.41 mmol of 1,1-$(CH_3)_2B_2H_4$. Excess $Be(BH_4)_2$ (0.18 mmol) was recovered.

Reaction of $Be(BH_4)_2$ with MB_3H_8 (M = Cs, $N(C_2H_5)_4$) produces $Be(B_3H_8)_2$ in small yields, but, in the case of M = $N(C_2H_5)_4$, production of $MBH_4 \cdot Be(BH_4)_2$ adducts[23] complicates the reaction.

The most unusual reaction of $Be(BH_4)_2$ is that with 1-ClB_5H_8 to produce $B_5H_{10}BeBH_4$, in which the beryllium atom is inserted into a basal position of a borane cage.[24]

Preparation of $(CH_3BeBH_4)_2$. Reaction of 0.086 g (2.2 mmol) of $Be(BH_4)_2$ with 1.3 mmol of $Zn(CH_3)_2$ for 1.5 h at room temperature produced a number of volatile solids. Fractionation of the products through a −30 °C trap and condensation in a −80 °C trap isolated 0.089 g (1.1 mmol) of $(CH_3BeBH_4)_2$, identified by NMR and IR data.[4a] Purification was not easy, which suggests that equilibria may exist between the zinc and/or beryllium by-products. When $Al_2(CH_3)_6$ was used in place of $Zn(CH_3)_2$, a solid and liquid were produced, apparently in equilibrium, and the desired $(CH_3BeBH_4)_2$, if produced, could not be isolated. No reaction was observed between $Sn(CH_3)_4$ and $Be(BH_4)_2$.

Preparation of $Be(B_3H_8)_2$. Approximately 15.6 mmol of $BeCl_2$ and 17.3 mmol of CsB_3H_8 were added to a 100-mL Pyrex reaction flask containing 4-mm glass beads, broken glass, and a Teflon-coated stirring bar. The material in the flask was stirred and heated at 60 °C with continuous evacuation for 3 days, the product being collected in a trap at −196 °C. The $Be(B_3H_8)_2$ was purified by distillation through a −45 °C trap and condensation in a −63 °C trap. The product, obtained in 75% yield, is a colorless, volatile liquid (vp = 15 Torr at 25 °C, mp −51 °C). Use of TlB_3H_8 in place of CsB_3H_8 resulted in lower yields. When $N(C_2H_5)_4B_3H_8$ was used, a higher temperature was required, and the low yields of $Be(B_3H_8)_2$ obtained were contaminated with B_6H_{10}, which could not be separated by distillation. The mass spectrum of $Be(B_3H_8)_2$ showed a parent ion at *m/e* 91 for $^9Be(^{11}B_3H_8)_2$. The most intense peak occurs at *m/e* 84 (84.1503 observed, 84.1499 calculated for $^9Be^{10}B^{11}B_5H_{10}$).

Preparation of $C_5H_5BeB_3H_8$. Reaction of 0.05 g (0.6 mmol) of $Be(B_3H_8)_2$ with 0.06 g (0.07 mmol) of NaC_5H_5 for several hours at room temperature produced a moderate yield of a low-volatility liquid, $C_5H_5BeB_3H_8$, which was isolated by condensation in a 0 °C trap. The mass spectrum of $C_5H_5BeB_3H_8$ showed no parent peak (*m/e* 115), but the p − 2 peak confirmed the presence of $C_5H_5BeB_3H_8$ (113.1262 observed, 113.1261 calculated for $^9Be^{11}B_3{}^{12}C_5{}^1H_{11}$).

Preparation of $(CH_3BeB_3H_8)_2$. Reaction of 0.30 mmol of $Be(B_3H_8)_2$ with 0.23 mmol of $Zn(CH_3)_2$ for 1 h at room temperature produces a moderate yield of a low-volatility solid, $(CH_3BeB_3H_8)_2$, which is isolated by condensation in a −22 °C trap. A more volatile product believed to be $CH_3ZnB_3H_8$ is condensed in a −50 °C trap. The $(CH_3BeB_3H_8)_2$ appears to be the product of the reactions of $(CH_3BeBH_4)_2$ with $Be(B_3H_8)_2$ and with CsB_3H_8, but these preparations are less convenient and have not been well characterized.

Reactions of $Be(B_3H_8)_2$. The reactions of $Be(B_3H_8)_2$ with NaC_5H_5 and $Zn(CH_3)_2$ are described above. Reaction of 2.76 mmol of $Be(B_3H_8)_2$ with 5.88 mmol of HCl for 3 h at room temperature produces 2.5 mmol of B_4H_{10} and 2.5 mmol of noncondensables (H_2). Addition of 0.82 mmol of $O(C_2H_5)_2$ to 0.14 mmol of $Be(B_3H_8)_2$ at −78 °C followed by removal of excess $O(C_2H_5)_2$ (0.55 mmol) leaves a product of 2.2:1 mole ratio of $O(C_2H_5)_2$ to $Be(B_3H_8)_2$. At 0 °C all materials are volatile. Lewis base complexes [$O(CH_3)_2$, $O(C_2H_5)_2$, $S(C_2H_5)_2$, NH_3] of $Be(B_3H_8)_2$ are unstable at room temperature, decomposing to resinous, intractable products. No reaction was observed in mixtures of $Be(B_3H_8)_2$ and acetylene or 1-butene, even after several days at room temperature.

Reaction of $Be(B_3H_8)_2$ with $Be(BH_4)_2$. Whenever $Be(B_3H_8)_2$ and $Be(BH_4)_2$ are mixed in an NMR tube, the resulting ^{11}B spectrum exhibits, in addition to the $Be(B_3H_8)_2$ resonances, a signal believed to be a nonet due to coupling of eight equivalent hydrogens ($\delta = -34.4$, $J = 36$ Hz). Attempts to characterize the species giving rise to this signal have been unsuccessful.

Results and Discussion

NMR Characterization of $Be(BH_4)_2$. The ^{11}B NMR spectra of $Be(BH_4)_2$ in benzene and methylene chloride solution consist of a single 1:4:6:4:1 quintet ($\delta = -35.8$ ppm[22] in C_6D_6, $J_{^{11}B-H} = 85$ Hz) which collapses to a singlet on ^1H decoupling. The solution ^1H NMR spectrum of $Be(BH_4)_2$ consists of a 1:1:1:1 quartet ($\delta = 0.39$ ppm, $J_{^{11}B-H} = 87$ Hz). No evidence of ^{11}B or ^1H coupling to ^9Be ($I = {}^3/_2$, 100% natural abundance) is observed. Coupling is observed between ^9Be and the BH_4^- hydrogen and boron nuclei in $C_5H_5BeBH_4$ (see below) and between ^9Be and the BH_4^- hydrogen nuclei in $B_5H_{10}BeBH_4$,[25] but no such couplings are observed for $(CH_3BeBH_4)_2$.[4a] The $Be(BH_4)_2$ quintet in the ^{11}B spectrum is sharpest at about 40 °C but broadens and apparently decreases in intensity at both higher and lower temperatures. At −20 °C essentially no signal remains, apparently due to low solubility.

The gas-phase ^{11}B and ^1H NMR spectra of the saturated vapor of $Be(BH_4)_2$, Figure 3, consist of a sharp quintet and a sharp quartet, respectively, similar to the solution spectra. A small amount of diborane (58.0 ppm downfield from

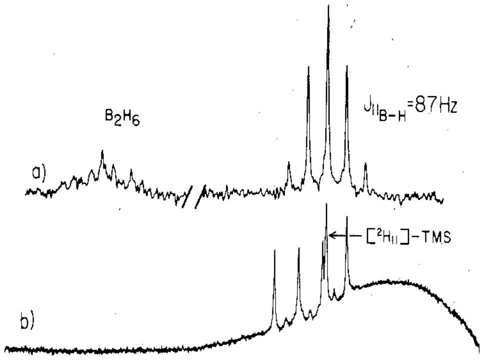


Figure 3. Gas-phase NMR spectra of $Be(BH_4)_2$: (a) ^{11}B (86.7 MHz); (b) ^1H (100 MHz).

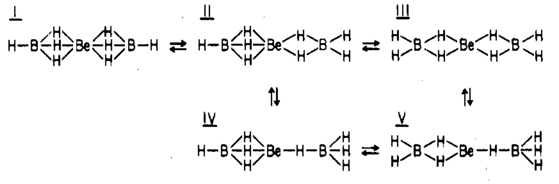


Figure 4. Proposed mechanism for configurational interchange in $Be(BH_4)_2$.

($Be(BH_4)_2$) accumulated during the course of ^{11}B data collection (>12 h). The gas-phase ^1H NMR spectra of $Be(BH_4)_2$ were recorded on two spectrometers, each of which exhibited unique probe background signals.

The gas-phase NMR spectra of $Be(BH_4)_2$ indicate that only one species is present in gaseous, monomeric[10,12] $Be(BH_4)_2$. That species contains apparently magnetically equivalent BH_4 groups in which the hydrogen atoms undergo raid exchange within each BH_4 group on the NMR time scale. Because coupling between boron or hydrogen nuclei and ^9Be is not observed, intermolecular exchange of BH_4^- groups cannot be ruled out, but likewise there is no evidence to suggest that it is occurring.

These gas-phase NMR spectra of $Be(BH_4)_2$ cannot be interpreted in support of the previously postulated triangular B–Be–B structures.[6,10,13] Recent infrared [12] and electron diffraction[7] data have been interpreted in terms of structures with three bridge hydrogens between beryllium and each boron. Two hydrogen bridges are observed for $(CH_3BeBH_4)_2$,[4] $C_5H_5BeBH_4$,[3] and crystalline $B_5H_{10}BeBH_4$.[24] Theoretical studies[14] have shown that small energy differences exist between linear structures with two or three hydrogen bridges and that these structures are lower in energy than the other possibilities suggested. The gas-phase structure of monomeric $Be(BH_4)_2$ is therefore postulated to contain a linear B–Be–B framework in which local configurational interchange of hydrogens results in rapid hydrogen exchange on the NMR time scale, as illustrated in Figure 4. Intramolecular exchange mechanisms, similar to that depicted in Figure 4, have been proposed[26] for covalent metal–tetrahydroborate complexes. The time scale of the NMR experiment does not allow distinction between the configurations presented in Figure 4 but suggests that more than one is involved in effecting the observed hydrogen exchange. The structural characterization of gas-phase $Be(BH_4)_2$ by experimental techniques other than NMR has been plagued with experimental problems and the possible presence of impurities. The time scale of these other techniques should provide information beyond that available to NMR but, at this stage, they have not been able to provide this additional information on an unequivocal basis.

The ^{11}B and ^1H NMR spectra of $Be(BH_4)_2$ in benzene or methylene chloride solution suggest that equivalent BH_4 groups are present which undergo rapid internal hydrogen exchange in a situation analogous to the gas-phase behavior. However, the possibility of solvent interaction with $Be(BH_4)_2$ may complicate the chemical system involved.

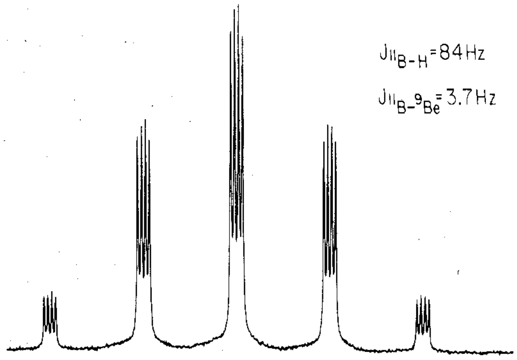


Figure 5. ^{11}B NMR spectrum of $C_5H_5BeBH_4$.

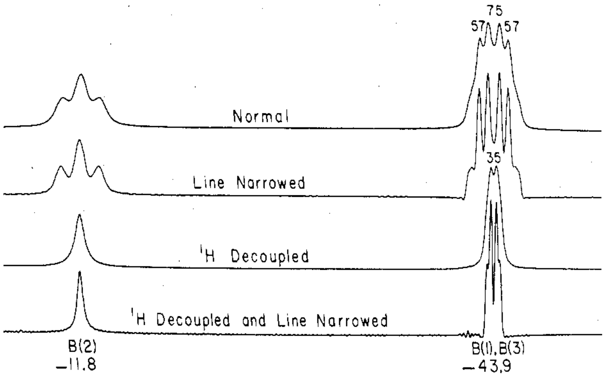


Figure 6. ^{11}B NMR spectra of $Be(B_3H_8)_2$ at −30 °C.

NMR Characterization of $C_5H_5BeBH_4$. A report of the ^1H NMR spectrum of $C_5H_5BeBH_4$[25] presented the first example of ^9Be–H coupling. The ^{11}B NMR spectrum of $C_5H_5BeBH_4$, Figure 5, indicates that coupling of beryllium to the boron nuclei in $C_5H_5BeBH_4$ is also observed ($J_{^9Be-^{11}B}$ = 3.7 Hz). The observed quintet of quartets indicates that rapid exchange of hydrogens takes place within the BH_4 group, but intermolelcular exchange of BH_4 groups is not observed.

The 100-MHz ^1H spectrum of $C_5H_5BeBH_4$ was ^9Be decoupled by irradiating at 14.059539 MHz. The quartet splitting due to ^9Be coupling is removed leaving a major quartet due to ^{11}B–H coupling (^{11}B: $I = {}^3/{}^2$, 80% natural abundance), as well as small resonances due to ^{10}B–H coupling (^{10}B: I = 3, 20% natural abundance).

The lines of the BH_4 resonances in the ^{11}B and ^1H spectra of $C_5H_5BeBH_4$ are exceedingly narrow (half-height width: ^{11}B, 1.5 Hz; ^1H, 2 Hz) for boron hydride species. The narrow lines suggest that the electric field gradient at the boron nucleus is effectively zero, in which case quadrapole broadening is removed. The chemical shift (−53.6 ppm) of the boron atom in $C_5H_5BeBH_4$ is unusually high for a tetrahydroborate species.

The ^9Be INDOR spectrum of $C_5H_5BeBH_4$ was generated on the Varian XL-100.[27] Although coupling is observed, the signal to noise ratio and line width did not allow resolution of the expected overlapping quintet of quartets.

NMR Characterization of $Be(B_3H_8)_2$. Below −30 °C $Be(B_3H_8)_2$ appears to be static on the NMR time scale. The 86.7-MHz ^{11}B NMR spectrum at −30 °C, Figure 6, consists of a triplet assigned to B(2) (see Figure 2 for the numbering convention used for $B_3H_8^-$ ligands), which indicates approximately equivalent coupling to the attached terminal hydrogens, and a broad uninterpretable resonance at −43.8 ppm assigned to B(1) and B(3). Upon ^1H decoupling the triplet collapses to a singlet and the −43.8-ppm resonance collapses to a broad doublet with shoulders on each side. The line-narrowed normal and ^1H-decoupled spectra shown in Figure 6 indicate a complex coupling or overlapping pattern.

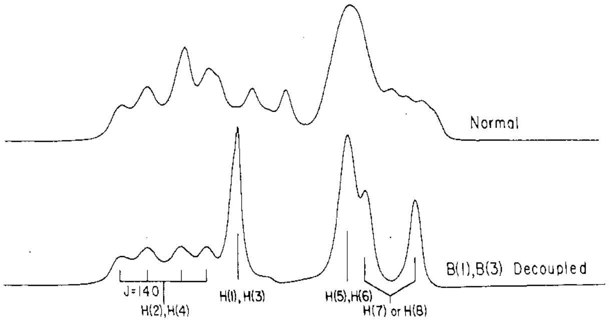


Figure 7. ^{1}H NMR spectra of $Be(B_3H_8)_2$ at −30 °C.

At −28 °C the ^{11}B NMR spectrum at 32.1 MHz shows a major doublet for the B(1), B(3) resonance, but a small hump is at the center of the doublet, and shoulders are evident on the outside of the resonance. The ^{1}H-decoupled spectrum exhibits a broad singlet for the B(1), B(3) resonance.

At −30 °C the ^{1}H NMR spectrum of $Be(B_3H_8)_2$ in CD_2Cl_2, Figure 7, suggests that the two terminal hydrogens on B(2) [H(2) and H(4)] are equivalent. However, in toluene solution their nonequivalence is apparent. The terminal hydrogens on B(1) and B(3) [H(1) and H(3)] exhibit the same chemical shift and coupling constants. The Be–H–B hydrogens, H(7) and H(8), are nonequivalent and show partially resolved coupling (~60 Hz) to B(1) and B(3), respectively. The B–H–B hydrogens, H(5) and H(6), exhibit the same chemical shift, and selective ^{11}B decoupling suggests that they are coupled more strongly to B(1) [or B(3)] than to B(2) (approximately 50 Hz vs. <40 Hz).

The ^{1}H and ^{11}B NMR spectra indicate that the $B_3H_8^-$ ligands of $Be(B_3H_8)_2$ are bonded to beryllium in a bidentate fashion. The ^{1}H-decoupled ^{11}B NMR spectrum and the change in appearance of the ^{11}B spectrum upon changing field strength indicate that B(1) and B(3) exhibit different chemical shifts, in agreement with the X-ray-determined C_2 symmetry for the static molecule. The difference in chemical shift is not exhibited by the B(1), B(3) borons in species containing a static bidentate $B_3H_8^-$ ligand in which B(1) and B(3) are symmetry equivalent.[28] The ^{1}H-decoupled ^{11}B spectrum suggests that a complex situation is present, possibly due to ^{11}B–^{11}B or ^{9}Be–^{11}B coupling. A precise interpretation of the ^{11}B NMR spectrum cannot be given as yet, but an approximation will be presented.

In the line-narrowed ^{11}B spectrum of $Be(B_3H_8)_2$ the splitting between alternate major lines is 140 Hz, similar to the boron–terminal hydrogen coupling constant observed in the ^{1}H spectrum. Thus, these lines suggest a major pattern of overlapping doublets. For the major overlapping doublet pattern to be observed, each member of the doublet probably contains an odd number of lines. A triplet due to approximately equivalent coupling of B(1) [or B(3)] to H(5) and H(8) [or H(6) and H(7)] would fulfill this requirement. All inner lines of the four triplets would overlap such that only the outer two intensity 1 lines of the four 1:2:1 triplets are observed. A 1:3:4:4:3:1 intensity ratio is expected which approximates that observed. The ^{1}H spectrum and ^{1}H-decoupled ^{11}B spectrum suggest, however, that this interpretation is not complete and that more complex couplings undoubtedly are present.

The ^{11}B NMR spectrum of $Be(B_3H_8)_2$ broadens between −10 and +10 °C, but at 23 °C another pattern, shown in Figure 8, becomes relatively sharp. The B(2) resonance remains a triplet, but the B(1), B(3) resonance can be resolved into a quartet with a coupling of 74 Hz by line narrowing. Each resonance collapses to a singlet upon ^{1}H decoupling. This suggests that B(1) and B(3) are approximately equivalent and the terminal and two bridge hydrogens around B(1) or B(3) are coupled approximately equivalently to the respective borons. The ^{1}H spectrum at 25 °C exhibits a broad quartet due to the terminal hydrogens on B(2) and a very broad hump due to the remaining hydrogens.

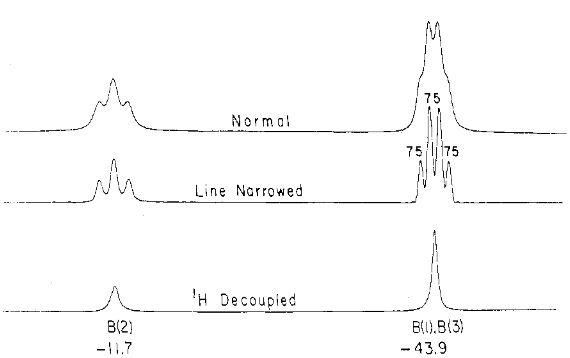


Figure 8. ^{11}B NMR spectra of $Be(B_3H_8)_2$ at 23 °C.

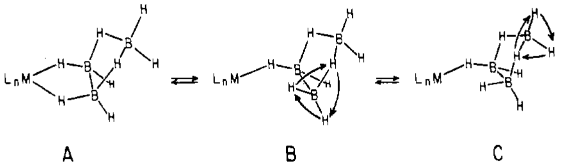


Figure 9. Proposed exchange mechanism for covalent metal–octahydrotriborate species.

A mechanism somewhat different from that previously postulated[29] is proposed in Figure 9 to explain hydrogen exchange in covalent metal–octahydrotriborate species. Opening of a metal–bridge hydrogen bond of A produces B. If this occurs in $Be(B_3H_8)_2$, B(1) and B(3) on the unaffected $B_3H_8^-$ ligand, Ln, can be approximately equivalent. The three hydrogens on the boron whose bridge hydrogen bond to beryllium has been broken can now exchange positions readily and become equivalent, as shown in B. This situation is consistent with the observed NMR behavior at 25 °C. Other Be–H_b bonds can be opened as well such that all boron atoms adjacent to beryllium become equivalent and exhibit equivalent coupling to the respective adjacent hydrogens.

At higher temperatures, above 60 °C, the ^{11}B spectrum of $Be(B_3H_8)_2$ broadens and begins to coalesce suggesting that at even higher temperatures the three boron atoms would be equivalent and couple equivalently to all eight hydrogens. All eight hydrogens are apparently undergoing rapid tautomerization at this higher temperature. This can be interpreted as participation of the terminal hydrogens on B(2) in the hydrogen exchange, as depicted in Figure 9C. Rapid internal hydrogen exchange also occurs in other metal–$B_3H_8^-$ complexes,[29] sometimes at very low temperatures (see $C_5H_5BeB_3H_8$ below).

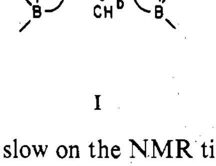
NMR Spectrum of $C_5H_5BeB_3H_8$. At room-temperature, the ^{11}B NMR spectrum of $C_5H_5BeB_3H_8$ consists of a nonet with seven of the nine lines resolved and shoulders visible for the two lines of lowest intensity. The ^{1}H spectrum consists of a broad resonance showing some fine structure due to B–H hydrogens (a decet with intensity ratio 1:3:6:10:12:12:10:6:3:1 is expected) and a sharp singlet due to equivalent C–H hydrogens. At −87 °C the coupling in the ^{11}B spectrum is no longer visible owing to thermal decoupling, but the resonance is essentially the same overall width as at room temperature. The line width of the B–H resonance in the ^{1}H spectrum decreases from 164 Hz at room temperature to 85 Hz at −75 °C. The C–H resonance remains a sharp singlet at −75 °C. These results indicate that the $B_3H_8^-$ moiety in $C_5H_5BeB_3H_8$ is undergoing rapid hydrogen tautomerism at room temperature as suggested for $Be(B_3H_8)_2$ (Figure 9) at higher temperatures. This tautomerism is rapid on the NMR time scale even at −87 °C. There is no evidence to suggest that (under static conditions) the $B_3H_8^-$ ligand would be other than a bidentate species as observed for most metal–$B_3H_8^-$ complexes.[28] All C–H hydrogens also remain equivalent on the NMR time scale, even at −75 °C, which suggests that the C_5H_5 ring is η^5 in this molecule as it is in $C_5H_5BeBH_4$.[2,3]

The nonet signal in the ^{11}B NMR spectrum of $C_5H_5BeB_3H_8$ is at an unusually low field (−24 ppm) for a $B_3H_8^-$ species, whereas the ^{11}B signal for $C_5H_5BeBH_4$ is at an unusually high field (−55 ppm) for a tetrahydroborate species. These shifts are tentatively ascribed to as yet undefined electronic effects of the η^5-C_5H_5 ring.

NMR Spectrum of $(CH_3BeB_3H_8)_2$. The room-temperature ^{11}B NMR spectrum of $(CH_3BeB_3H_8)_2$ consists of a low-field triplet assigned to B(2) and a broad high-field resonance due to B(1) and B(3). This indicates that the $B_3H_8^-$ ligand is static on the NMR time scale at room temperature and attached to beryllium in a bidentate fashion.[28] Upon ^1H decoupling, both signals collapse to singlets. The line-narrowed B(1), B(3) resonance appears to be a doublet of triplets with the doublet splitting 123 Hz due to terminal hydrogen coupling and the triplet splitting of 60 Hz due to approximately equal coupling to the adjacent bridge hydrogens.

The ^{11}B NMR spectrum of $(CH_3BeB_3H_8)_2$ at 37 °C exhibits the same B(1), B(3) resonance appearance as the corresponding $Be(B_3H_8)_2$ resonance at 25 °C, and the B(2) triplet remains intact. The B(1), B(3) signal can be resolved, by line narrowing, into a quartet with a coupling of 78 Hz. The intermediate-exchange situation for $B_3H_8^-$ ligands, as depicted in Figure 9B, is occurring in $(CH_3BeB_3H_8)_2$ at this temperature. At 70 °C only broad singlets are observed for the B(2) and the B(1), B(3) resonances, suggesting that, at even higher temperatures, rapid exchange of all hydrogen positions would be observed.

The B–H portion of the ^1H spectrum of $(CH_3BeB_3H_8)_2$ at room temperature is qualitatively the same as for the static ^1H spectrum of $Be(B_3H_8)_2$ except that the Be–H–B hydrogens appear to be equivalent in $(CH_3BeB_3H_8)_2$. The coupling of B(1) and B(3) to the Be–H–B hydrogens is larger than to the B–H–B hydrogens, but again this difference is not apparent in the ^{11}B spectrum. At 7 °C, the ^1H NMR spectrum of the methyl hydrogens consists of three resonances in an approximate ratio of 1:2:1 with separations as shown in Figure 10 and tabulated in Table III. At room temperature the methyl resonances are significantly broader than at 7 °C, but the 1:2:1 triplet-like character remains. Above room temperature these resonances broaden and finally collapse to a singlet at 60 °C as shown in Figure 10. These observations may be explained as follows. The structure of $(CH_3BeB_3H_8)$ was expected to be a methyl-bridged dimer analogous to that observed for $(CH_3BeBH_4)_2$, but since the $B_3H_8^-$ ligands are static on the NMR time scale, two geometric isomers are possible, depending on the relative orientation of the $B_3H_8^-$ ligands as depicted by I and II. If reorientation of the $B_3H_8^-$ ligands is slow on the NMR time scale yet rapid on the time scale of separation techniques, a statistical (1:1) mixture of I and II would be present. Thus, the ^1H NMR spectra would be expected to show three methyl resonances in a ratio 1:1:2, for methyl groups of types a, b, and c, respectively, in I and II. Nonequivalence of the $B_3H_8^-$ ligands is not observed because of their relatively large separation. At high temperature, the $B_3H_8^-$ ligands are reorienting at a rate which is rapid on the NMR time scale, and, therefore, the methyl groups appear equivalent. The behavior of $(CH_3BeB_3H_8)_2$ is similar to that of monomeric $(CH_3)_2AlB_3H_8$[29c] in which nonequivalent methyl groups are observed at low temperature due to the orientation of the $B_3H_8^-$ ligand, while at high temperature the methyl groups are equivalent on the NMR time scale. The equilibration of methyl groups in $(CH_3BeB_3H_8)_2$ occurs at about the same temperature as this necessary to produce the intermediate B_3H_8 ligand exchange situation depicted in Figure 9B. Cleavage of a Be–H_b bond either allows rapid rotation of the $B_3H_8^-$ ligand about the remaining bridge hydrogen bond or produces an intermediate in which the methyl groups are equivalent.



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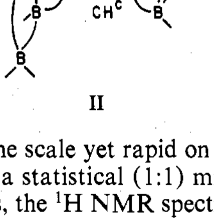

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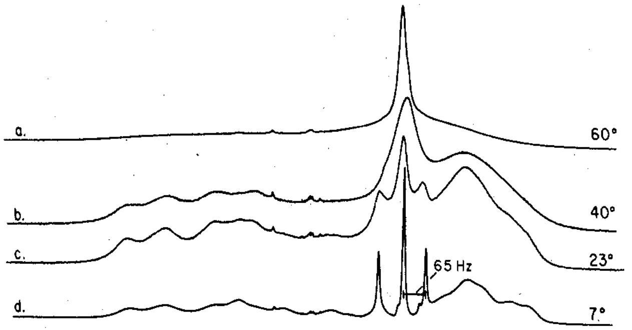

Figure 10. Variable-temperature ^1H NMR spectra of $(CH_3BeB_3H_8)_2$ in CD_2Cl_2.

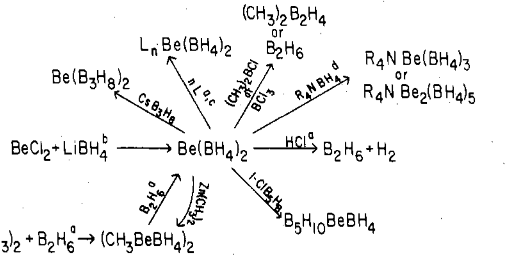

Figure 11. Summary of the reaction chemistry of $Be(BH_4)_2$. Superscripts: a, ref 30; b, ref 20; c, ref 31; d, ref 23.

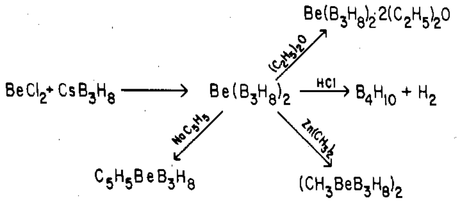

Figure 12. Summary of the reaction chemistry of $Be(B_3H_8)_2$.

Reactions of $Be(BH_4)_2$ and $Be(B_3H_8)_2$. The reaction chemistry of $Be(BH_4)_2$ and $Be(B_3H_8)_2$ is summarized in Figures 11 and 12. The results can be classified along three lines: (1) Lewis base coordination at the beryllium; (2) ligand-exchange reactions; and (3) reactions typical of BH_4^- or $B_3H_8^-$ species. The particularly novel reaction of $Be(BH_4)_2$ with 1-ClB_5H_8 to produce $B_5H_{10}BeBH_4$ has led to a new class of beryllaborane species.[24]

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Registry No. $Be(BH_4)_2$, 30374-53-9; $(CH_3BeBH_4)_2$, 30500-90-4; $Be(B_3H_8)_2$, 60669-75-2; $C_5H_5BeB_3H_8$, 66374-41-2; $(CH_3BeB_3H_8)_2$, 66374-42-3.

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Studies of 2-(η^5-C_5H_5)CoB_4H_8, a Cobaltaborane Analogue of B_5H_9

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The chemistry of the title compound was examined in the light of known reactions of its structural counterpart, pentaborane(9). Like B_5H_9, 2-(η^5-C_5H_5)CoB_4H_8 undergoes deprotonation with NaH at a bridging position, forming the $(C_5H_5)CoB_4H_7^-$ ion; the proton removed is adjacent to cobalt. Reaction of the anion with HCl regenerates the neutral metalloborane. Treatment of the anion with $CoCl_2$ and NaC_5H_5 produces the known cobaltaborane cluster 1,2-(η^5-C_5H_5)$_2Co_2B_4H_6$ in moderate yield with lesser amounts of tri- and tetracobalt metalloboron species, all of which are identical with products of the $B_5H_8^-$–$CoCl_2$–$C_5H_5^-$ reaction previously reported. The reaction of 2-(η^5-C_5H_5)CoB_4H_8 with C_2H_2 produces the known metallocarborane 1,2,3-(η^5-C_5H_5)$CoC_2B_3H_7$, a process formally analogous to the insertion of C_2H_2 into B_5H_9 to yield $C_2B_4H_8$. The reactions of 2-(η^5-C_5H_5)CoB_4H_8 with higher alkynes yield not only the corresponding metallocarboranes $(C_5H_5)CoRR'C_2B_3H_5$ but also in each case an "addition product" corresponding to $(C_5H_5)CoB_4H_8 \cdot RR'C_2$ whose structures were not determined. The latter species were shown to be intermediates in the formation of the metallocarboranes. The reaction of the title compound with $Fe(CO)_5$ under ultraviolet light gave in low yield a novel mixed-metal metalloborane cluster, 1,2,3-(η^5-C_5H_5)$_2Co_2(CO)_4FeB_3H_3$, whose proposed structure consists of an octahedral Co_2FeB_3 cage with all metal atoms on the same triangular face.

The family of known metalloborane[1] cage compounds is rapidly expanding as discoveries of new and structurally novel compounds continue to be reported.[2] Understandably, most of the effort in this area has concentrated on the preparation and characterization of new compounds; detailed studies of the chemical behavior of individual metalloboranes have been relatively rare. In the work to be described here, we have examined the chemistry of a particular species,[3] 2-(η^5-C_5H_5)CoB_4H_8, a red crystalline solid structurally analogous to B_5H_9 from which it is formally derived by replacement of a basal BH unit with (η^5-C_5H_5)Co. In addition to its inherent structural interest, this compound is well suited for detailed investigation in that it is chemically stable, can be handled in air, and is readily prepared in workable quantity from commercially available reagents. The synthesis[3] involves treatment of $B_5H_8^-$ ion with $CoCl_2$ and NaC_5H_5 in tetrahydrofuran (THF), giving a complex reaction in which (η^5-C_5H_5)CoB_4H_8 is the major cobaltaborane product accompanied by a number of other species having one to four cage cobalt atoms.

The close relationship of 2-(η^5-C_5H_5)CoB_4H_8 to B_5H_9 was the point of most immediate interest to us, and accordingly our first chemical studies were designed to compare the behavior of the complex with known reactions of pentaborane(9). The essential question to be examined was, "what are the chemical consequences of substituting (η^5-C_5H_5)Co for a BH unit in the B_5H_9 framework?" At the outset two facts had been established. The structure of (η^5-C_5H_5)CoB_4H_8, proposed[3a] from ^{11}B and ^{1}H NMR evidence and later confirmed by x-ray crystallographic analysis,[4] is that of a distorted square pyramid with the metal in a basal location and four bridging hydrogen atoms (two B–H–B and two Co–H–B) on the open face (Figure 1); the bond angles and distances are close to those in B_5H_9 save for the distortions created by the introduction of a transition-metal atom in place of a boron. Second, the cobaltaborane contrasts dramatically with B_5H_9 in air stability, the former hydrolyzing only very slowly over several weeks while the borane exhibits well-known pyrophoricity and forms explosive mixtures with oxygen (kinetic effects arising from the large volatility difference may be a

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