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Chemistry of 2-Berylla-*nido*-hexaborane(11) Compounds. Insertion of Beryllium into a Borane Cage

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A series of beryllaborane compounds has been prepared in which the beryllium atom occupies a basal position in a pentagonal-pyramidal borane cage. The compounds include $B_5H_{10}BeX$, where X = BH_4, B_5H_{10}, Cl, Br, CH_3, and C_5H_5. The majority of the chemistry observed involves substitution at the beryllium atom. The beryllium atom shows an unusual flexibility in coordination, and the bonding in several of these compounds cannot be interpreted using conventional valence bond concepts.

Introduction

Beryllaboranes have previously been limited to species in which beryllium and a borane ligand are linked by bridge hydrogen bonds. The solid-state structure of beryllium bis(tetrahydroborate),[1] $Be(BH_4)_2$, consists of a helical polymer in which terminal and bridging tetrahydroborate moieties are linked to beryllium by two bridge hydrogens. The gas-phase structure of $Be(BH_4)_2$ undoubtedly involves bridge hydrogen bonding between beryllium and boron.[2] In $(CH_3BeBH_4)_2$[3] and $C_5H_5BeBH_4$,[4] double-hydrogen bridges between beryllium and boron are proposed. In the solid state,[5] beryllium bis(octahydrotriborate) contains two $B_3H_8^-$ ligands attached to beryllium by two bridge hydrogen bonds. The only report of a direct beryllium–boron linkage is 3-BeL-1,2-$B_9C_2H_{11}$ (L = $N(CH_3)_3$ or $O(C_2H_5)_2$).[6]

The chemistry of a series of compounds in which beryllium occupies a borane cage position is described here. A preliminary report[7] of the structural characterization of one of these, 2-tetrahydroborato-2-berylla-*nido*-hexaborane(11), $B_5H_{10}BeBH_4$, has appeared. The structural characterization of $B_5H_{10}BeBH_4$ and a related compound, 2,2′-*commo*-bis(2-berylla-*nido*-hexaborane(11)), $B_5H_{10}BeB_5H_{10}$, is detailed elsewhere.[8] The structure of $B_5H_{10}BeBH_4$, Figure 1, is a distorted pentagonal-pyramidal cage with the beryllium atom occupying a basal position. Bridge hydrogen bonds link all adjacent basal atom positions, and one terminal hydrogen atom is attached to each cage boron. An approximately tetrahedral tetrahydroborate group is attached to the beryllium atom by two hydrogen bridges. The structure of $B_5H_{10}BeB_5H_{10}$ consists of two $B_5H_{10}Be$ fragments, similar to that of $B_5H_{10}BeBH_4$, linked at a common beryllium atom. The dihedral angle between the planes defined by the basal boron atoms of the two cages is 66°.

Experimental Section

All the beryllium-containing compounds employed in this investigation are undoubtedly very toxic, pyrophoric, and air- and moisture-sensitive materials. They were handled exclusively using high-vacuum techniques. Disposal procedures involved hydrolysis under nitrogen in a hood. The resulting Be^{2+}-containing solutions were then diluted to 10^{-4} M before disposal. As a further precaution, most preparations employed less than 2 mmol and in no case more than 10 mmol of a beryllium-containing reagent.

The preparations of $Be(BH_4)_2$,[9] 1-ClB_5H_8,[10] and CsB_3H_8[11] are described elsewhere. Sodium cyclopentadienide was prepared by reaction of freshly distilled C_5H_6 with sodium in ammonia solution. The product was isolated by distilling off the ammonia and drying under high vacuum. Other materials are from reagent grade commercial sources. Methylene chloride was distilled from 3-Å molecular sieves and other solvents were distilled from lithium aluminum hydride.

Nuclear magnetic resonance spectra were obtained on a Bruker WH-270 Fourier transform spectrometer at 270 MHz for ^1H spectra and 86.7 MHz for ^{11}B spectra. A Nicolet BNC-12 computer and associated Nicolet software packages were used for data collection and manipulation routines. Selective ^{11}B decoupling of ^1H spectra was accomplished using a Bruker Type B-FS 100 frequency synthesizer, a Bruker B-BM1 broad-band modulator, and a B-LV80 selective power amplifier to continuously irradiate the desired ^{11}B frequency. Beryllium-decoupled ^1H NMR spectra of $B_5H_{10}BeBH_4$ were obtained on a Varian XL-100 spectrometer in CW mode using a proton (CH_2Cl_2) lock using a decoupler frequency of 14.060023 MHz. Infrared spectra of gases, in a 10-cm cell with NaCl windows, and solids, condensed on an Irtran-2 window at −196 °C in an evacuated cell having NaCl windows, were obtained using a Perkin-Elmer Model 700 spectrometer. Mass spectra of $B_5H_{10}BeBr$ and $B_5H_{10}BeC_5H_5$ were obtained using an AEI MS 902 spectrometer. Attempts to obtain mass spectra of $B_5H_{10}BeBH_4$, $B_5H_{10}BeB_5H_{10}$, $B_5H_{10}BeCl$, and $B_5H_{10}BeCH_3$ were unsuccessful.

Table I. Infrared Frequencies of $B_5H_{10}BeX$ Compounds (X = BH_4, B_5H_{10}, Cl, Br, CH_3, C_5H_5), in cm^{-1} (±10)

$B_5H_{10}BeBH_4$ (gas phase): 2640 s, 2600 s, 2555 m, 2500 m, 2270 m, 2140 s, 1860 w, br, 1540 m, br, 1420 m, 1355 w, 1270 w, 1140 m, 1070 m, 930 w, 800 m

$B_5H_{10}BeB_5H_{10}$ (solid film): 2620 s, 2570 s, 2510 w, 2330 m, 2280 m, 1860 w, br, 1600 w, br, 1480 m, 1420 s, 1360 w, 1220 w, sh, 1180 m, 1140 w, 1070 m, 1050 m, 1000 m, 930 s, 910 m, sh, 810 w

$B_5H_{10}BeCl$ (gas phase): 2610 m, 2490 w, 2280 w, 1440 w, br, 1170 w, 1050 w, 900 w (B_5H_{11} contamination likely)

$B_5H_{10}BeBr$ (solid film): 2620 s, 2180 s, 2150 m, sh, 1870 w, 1580 w, 1510 m, 1450 s, 1440 s, 1320 s, 1060 s, 920 s, 870 w, 820 m, 810 m, 770 s

$B_5H_{10}BeMe$ (gas phase): 3000 w, 2640 s, 2600 s, 2250 s, 1880 w, br, 1580 w, 1520 m, 1440 m, 1280 m, 1220 s, 1070 m, 990 m, 940 m, 880 w

$B_5H_{10}BeC_5H_5$ (solid film): 3140 w, 2610 s, 2600 s, 2520 s, 2490 s, 2470 s, 1970 w, 1930 w, 1850 w, br, 1750 w, 1490 m, 1420 m, 1410 m, 1390 m, 1370 m, 1340 m, 1160 m, 1120 w, 1090 m, 1080 m, 1050 s, 1020 s, 970 s, 940 m, sh, 890 m, 850 w, 840 w, 790 w

Infrared, ^{11}B NMR, and ^1H NMR data for the subject compounds are listed in Tables I, II, and III, respectively.

Preparation of $B_5H_{10}BeBH_4$. $B_5H_{10}BeBH_4$ was prepared by the reaction of 0.114 g (2.95 mmol) of $Be(BH_4)_2$ with 0.180 g (1.84 mmol) of 1-ClB_5H_8 in a Pyrex reaction flask equipped with a Teflon stopcock, for 24–48 h at room temperature. The major products are B_2H_6, $B_5H_{10}BeBH_4$, and a white nonvolatile solid, assumed to be $BeCl_2$. When a 2.8:1 reactant mole ratio of $Be(BH_4)_2$:1-ClB_5H_8 was used, the mole ratio of starting 1-ClB_5H_8 to product B_2H_6 was 1:1. When a 0.9:1 mole ratio of $Be(BH_4)_2$:1-ClB_5H_8 was used, the mole ratio of starting $Be(BH_4)_2$ to product B_2H_6 was 3:2. Trap-to-trap distillation (pass −20 °C, stop in −50 °C) removed reaction by-products but not excess starting materials. Therefore, a slight (10%) excess of $Be(BH_4)_2$ was used, by-products were removed, and then the product mixture was treated with NaCl[12] or $(CH_3)_4NBH_4$[13] to remove excess $Be(BH_4)_2$. Final trap-to-trap distillation resulted in typically 60–80% yields based on moles of product per mole of 1-ClB_5H_8. $B_5H_{10}BeBH_4$ is a low-volatility liquid (vp 2 Torr at 25 °C, mp −22 °C). Samples of $B_5H_{10}BeBH_4$ and its derivatives appear to be thermally stable for short periods at room temperature in vacuo.

Preparation of $B_5H_{10}BeBr$. As described above, approximately 10 mmol of $B_5H_{10}BeBH_4$ was prepared but in pentane solvent. Without

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Table II. Room-Temperature ^{11}B NMR Data[a] for $B_5H_{10}BeX$ (X = BH_4, B_5H_{10}, Cl, Br, CH_3, C_5H_5)

Compd	Chemical shift[c] ($J_{^{11}B-H}$, Hz)			
	B(1)[b]	B(3), B(6)	B(4), B(5)	B(7)
$B_5H_{10}BeBH_4$	−53.5 (146)	−9.8 (135, 83)	+8.2 (164)	−33.4 (86)
$B_5H_{10}BeB_5H_{10}$	−54.6 (139)	−8.1 (127, 98)	+5.3 (159)	
$B_5H_{10}BeBr$	−54.0 (146)	−1.6 (138, 84)	+10.0 (161)	
$B_5H_{10}BeCl$	−54.5 (146)	−2.9 (138, 84)	+9.2 (164)	
$B_5H_{10}BeCH_3$	−54.6 (146)	−2.0 (138, 83)	+9.6 (161)	
$B_5H_{10}BeC_5H_5$	−64.0 (117)	−3.6 (117, 117)	−0.3 (156)	

[a] C_6D_6 or C_7D_8 solvent; chemical shifts in ppm from $BF_3{\cdot}O(C_2H_5)_2$. [b] See Figure 1 for numbering convention. [c] Downfield shifts are positive.

Table III. Room-Temperature ^1H NMR Data[a] for $B_5H_{10}BeX$ (X = BH_4, B_5H_{10}, Cl, Br, CH_3, C_5H_5)

Compd	Chemical shift ($J_{^{11}B-H}$, Hz)						
	H(1)[b]	H(3), H(6)	H(4), H(5)	H(7), H(11)	H(8), H(10)	H(9)	Other
$B_5H_{10}BeBH_4$	−0.25 (145)	2.25 (135)	3.40 (155)	1.21 (83)	−1.62	−2.58	1.23 (83)[d]
$B_5H_{10}BeB_5H_{10}$	−0.03 (140)	2.52 (130)[c]	3.53 (152)	2.36 (95)[c]	−1.28	−2.47	
$B_5H_{10}BeCl$	−0.37 (147)	2.26 (140)	3.38 (166)	0.89 (75)	−1.28	−2.34	
$B_5H_{10}BeBr$	−0.24 (147)	2.79 (140)	3.42 (164)	0.95 (70)	−1.05	−2.11	
$B_5H_{10}BeCH_3$	−0.20 (141)	2.77 (136)	3.54 (164)	0.82 (75)	−1.27	−2.13	0.30[e]
$B_5H_{10}BeC_5H_5$	−1.45 (115)	2.32 (115)	3.23 (156)	2.32 (115)	−1.09	−3.20	5.77[f]

[a] Solvent C_6D_6 or C_7D_8; chemical shift in ppm downfield from Me_4Si. [b] See Figure 1 for numbering convention. [c] Estimates; overlap of these resonances prevents accurate measurement of coupling constant. [d] BH_4 hydrogens, quartet. [e] CH_3 hydrogens, singlet. [f] C_5H_5 hydrogens, singlet.

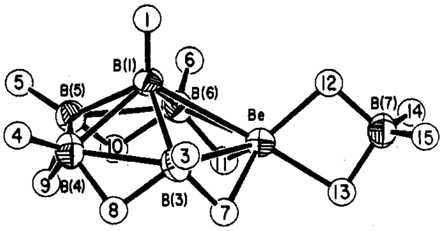


Figure 1. Static molecular structure and numbering scheme for $B_5H_{10}BeBH_4$.

separation of the reaction mixture, 17 mmol of HBr was condensed onto the frozen solution at −196 °C. The solution was warmed to −80 °C with stirring and vigorous gas evolution occurred. The $B_5H_{10}BeBr$ was isolated by trap-to-trap distillation (pass 0 °C, stop in −22 °C). The yield of $B_5H_{10}BeBr$, a low-volatility liquid (mp +13 °C), was 74%. The mass spectrum of $B_5H_{10}BeBr$ showed a parent peak at *m/e* 155 (155.0530 exptl, 155.0533 calcd for $^{11}B_5{}^1H_{10}{}^9Be^{81}Br$).

Preparation of $B_5H_{10}BeCl$. $B_5H_{10}BeCl$ is prepared in the same way as $B_5H_{10}BeBr$ by reaction of 6 mmol of HCl with 3 mmol of crude $B_5H_{10}BeBH_4$. The low-volatility liquid product was inconvenient to handle as vacuum distillation left a white deposit in the vacuum line. The compound was also isolated from the reaction of $Be(BH_4)_2$ with excess 1-ClB_5H_8 for several days.

Preparation of $B_5H_{10}BeB_5H_{10}$. No convenient, rational method of preparation of $B_5H_{10}BeB_5H_{10}$ has been found. The best preparation involves reaction of 0.13 g (0.84 mmol) of $B_5H_{10}BeBr$ with excess (0.20 g, 1.15 mmol) CsB_3H_8 at room temperature for several hours. Low yields (0.025 g or ~40% based on conservation of B_5H_{10}) of the low-volatility sublimable solid (mp 52 °C) are obtained by distilling all other volatile materials out of the reaction mixture and then trapping the $B_5H_{10}BeB_5H_{10}$ at −196 °C. A small amount of $Be(B_3H_8)_2$ is obtained as a by-product. $B_5H_{10}BeB_5H_{10}$ is also produced in low yields from reaction of $B_5H_{10}BeBr$ with KH and from reaction of $Be(BH_4)_2$ with excess 1-ClB_5H_8. The direct reaction of $B_5H_{10}BeBH_4$ with 1-ClB_5H_8 did not result in production of $B_5H_{10}BeB_5H_{10}$.

Preparation of $B_5H_{10}BeCH_3$. Reaction of 0.08 g (0.52 mmol) of $B_5H_{10}BeBr$ with 0.43 mmol of $Al_2(CH_3)_6$ for 1 h at room temperature produces $B_5H_{10}BeCH_3$, a volatile liquid which can be readily isolated by trap-to-trap distillation (pass −30 °C, stop in −50 °C). If $Zn(CH_3)_2$ is used in place of $Al_2(CH_3)_6$, the reaction is much faster and unidentified by-products make purification of $B_5H_{10}BeCH_3$ more difficult.

Preparation of $B_5H_{10}BeC_5H_5$. Reaction of 0.082 g (0.53 mmol) of $B_5H_{10}BeBr$ with 0.057 g (0.65 mmol) of NaC_5H_5 at room temperature for 8–10 h produces a low-volatility liquid (81% yield) which behaves much like $B_5H_{10}BeBr$. The product is identified by its NMR and mass spectra as $B_5H_{10}BeC_5H_5$. The mass spectrum shows a parent peak at *m/e* 139 (139.1768 exptl, 139.1761 calcd for $^9Be^{11}B_5{}^{12}C_5{}^1H_{15}$).

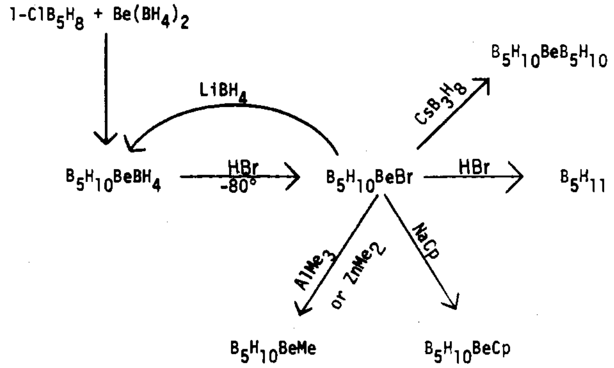


Figure 2. Summary of the reaction chemistry of $B_5H_{10}BeX$ compounds.

Reaction of $B_5H_{10}BeBr$ with $LiBH_4$. Reaction of a large excess of $LiBH_4$ with 0.022 g (0.15 mmol) of $B_5H_{10}BeBr$ at room temperature for about 1 h produced 0.0014 g (0.016 mmol) of $B_5H_{10}BeBH_4$ as well as small quantities of B_2H_6, B_4H_{10}, B_5H_9, and B_5H_{11}.

Reaction of $B_5H_{10}BeBr$ with HCl. Reaction of approximately 0.4 mmol of $B_5H_{10}BeBr$ with about 0.3 mmol of HCl at room temperature for several hours produced about a 10% yield of B_5H_{11}. The excess HCl was recovered and unreacted $B_5H_{10}BeBr$ was still present. A reaction using HBr instead of HCl behaved similarly.

Results

The reaction of $Be(BH_4)_2$ with 1-ClB_5H_8 results in the opening of the pentaborane(9) cage and the insertion of a beryllium atom into a basal position of the cage. The reaction, whose stoichiometry appears to be as shown in eq 1, is complex and a detailed mechanism cannot as yet be postulated.

$$3Be(BH_4)_2 + 2(1\text{-}ClB_5H_8) \rightarrow 2B_5H_{10}BeBH_4 + 2B_2H_6 + BeCl_2 \quad (1)$$

The observed chemistry of $B_5H_{10}Be$ species, shown schematically in Figure 2, is dominated by substitution at the beryllium atom. Treatment of $B_5H_{10}BeBH_4$ with HCl or HBr at −80 °C produces $B_5H_{10}BeCl$ or $B_5H_{10}BeBr$, respectively. The bromo derivative has been found to be the most convenient to prepare and has been used as the starting material in most reactions. The methyl or cyclopentadienyl derivatives have been prepared by the reaction of $B_5H_{10}BeBr$ with $Al_2(CH_3)_6$ or NaC_5H_5, respectively. Attempts to prepare the octa-

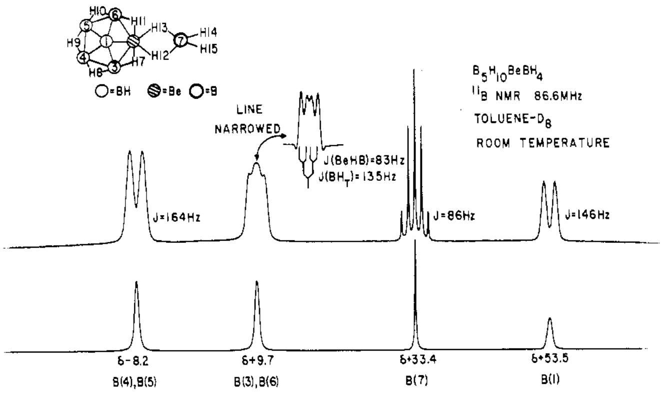


Figure 3. Room-temperature ^{11}B NMR spectrum of $B_5H_{10}BeBH_4$ (top—normal, bottom—^1H decoupled).

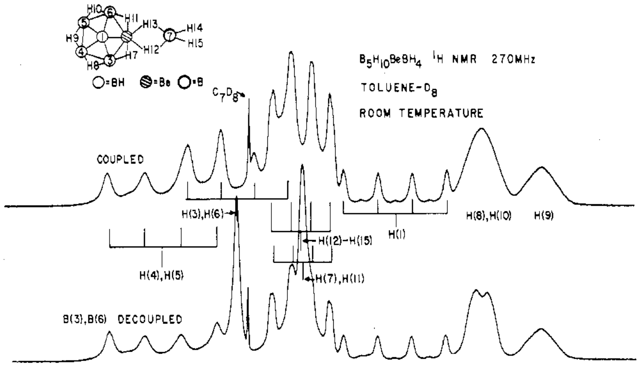


Figure 4. Room-temperature ^1H NMR spectrum of $B_5H_{10}BeBH_4$ (top—normal, bottom—B(3), B(6) decoupled).

hydrotriborate or hydride derivatives resulted in low yields of $B_5H_{10}BeB_5H_{10}$.

The structure of $B_5H_{10}BeBH_4$ indicates that the B_5H_{10} fragment bears a close resemblance to B_5H_{11}. Reaction of HCl or HBr with $B_5H_{10}BeBr$ at room temperature produces B_5H_{11} but the reaction is too slow to be of synthetic value.

The 86.7-MHz ^{11}B NMR spectrum of $B_5H_{10}BeBH_4$, Figure 3, is assigned as indicated. The broad, pseudotriplet resonance assigned to B(3) and B(6) can be resolved by line-narrowing techniques into a doublet of doublets. The quintet observed for B(7) indicates equivalent coupling to the tetrahydroborate hydrogens which are apparently undergoing rapid internal exchange on the NMR time scale. The low-temperature crystal structure of $B_5H_{10}BeBH_4$ (Figure 1) shows that the static structure has two bridge hydrogens between B(7) and Be. All resonances in the ^{11}B spectrum collapse to singlets upon ^1H decoupling.

By selective ^{11}B decoupling of the 270-MHz ^1H spectrum of $B_5H_{10}BeBH_4$, Figure 4, all terminal hydrogen resonances can be resolved as 1:1:1:1 quartets due to ^{11}B–H coupling. The B–H–B resonances are broad and unresolved but sharpen upon decoupling adjacent ^{11}B nuclei. The four equivalent tetrahydroborate hydrogens and the two Be–H–B hydrogens appear as quartets of doublets. The major quartet is due to ^{11}B–H coupling and the resonances collapse to poorly resolved doublets upon ^{11}B decoupling. The coupling constant between B(3) (or B(6)) and H(7) (or H(11)) is unusually large (83 Hz) for boron–bridge hydrogen coupling (typically <50 Hz).[14a]

Upon line narrowing in the B(3), B(6) decoupled ^1H spectrum of $B_5H_{10}BeBH_4$, the doublet splittings of the BH_4 and Be–H–B hydrogen resonances are observed as 16 and 8 Hz, respectively. This splitting is the result of ^9Be–H coupling (^9Be, $I = {}^3/_2$, 100% natural abundance) in a situation where quadrupole broadening produces a line shape that has the appearance of a doublet.[15] The presence of ^9Be–H coupling for the BH_4 hydrogens was confirmed by irradiating the 100-MHz ^1H spectrum of $B_5H_{10}BeBH_4$ at a frequency corresponding to ^9Be. The line width of each BH_4 quartet signal is significantly decreased (from 23 to 8 Hz) upon ^9Be decoupling. The observation of ^9Be–H coupling for these hydrogens proves that the proton exchange within the tetrahydroborate group occurs by an intramolecular mechanism. The only other compound in which ^9Be–H coupling has been observed is $C_5H_5BeBH_4$.[16]

The ^{11}B NMR spectra of the other $B_5H_{10}Be$ derivatives (except $B_5H_{10}BeC_5H_5$) are qualitatively very similar to that for the $B_5H_{10}Be$ fragment of $B_5H_{10}BeBH_4$. In each case the B(3), B(6) resonance is a pseudotriplet which can be resolved into a doublet of doublets by line narrowing. The ^{11}B spectrum of $B_5H_{10}BeC_5H_5$ is unique in that the B(3), B(6) resonance is a well-resolved triplet which suggests nearly equivalent coupling of B(3) and B(6) to the terminal and Be–H–B hydrogens on that boron. The chemical shift of the apical boron, B(1), in $B_5H_{10}BeC_5H_5$ is +64.0 ppm, whereas the B(1) resonances for the other three derivatives are +53.0 ± 2 ppm. This is one of the highest field ^{11}B resonances which has been observed for diamagnetic boron hydride compounds. The B(1)–H(1) coupling constant is also significantly smaller for $B_5H_{10}BeC_5H_5$ than for the other derivatives (115 Hz vs. ~140 Hz).

The ^1H spectra of all $B_5H_{10}Be$ derivatives are qualitatively the same as for the $B_5H_{10}Be$ portion of $B_5H_{10}BeBH_4$. In each case the Be–H–B proton resonance is a well-resolved quartet (except when overlapping other resonances). Coupling of Be–H–B protons to ^9Be has been observed only for $B_5H_{10}BeBH_4$ but ^9Be decoupling experiments have not been done for the other compounds. The ^1H NMR spectra of the methyl hydrogens in $B_5H_{10}BeCH_3$ and the cyclopentadienyl hydrogens in $B_5H_{10}BeC_5H_5$ show sharp singlets.

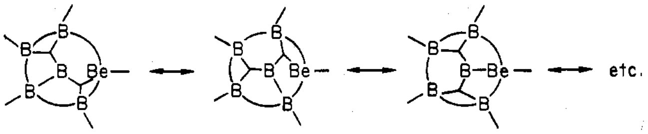
Variable-temperature NMR studies have shown that the quintet resonance observed for B(7) in the ^{11}B NMR of $B_5H_{10}BeBH_4$ is somewhat broadened at −87 °C. This broadening is probably due to thermal decoupling, and the tetrahydroborate hydrogens are still undergoing rapid internal exchange at this temperature. The basal boron resonances for all the $B_5H_{10}Be$ species also broaden at lower temperature due to thermal decoupling. However, the B(1) resonances remain unusually sharp at −50 to −87 °C indicating relatively long ^{11}B relaxation times even at low temperature. The static structure of $B_5H_{10}BeB_5H_{10}$[8] suggests that B(3) and B(3′) are not equivalent to B(6) and B(6′). Room-temperature ^{11}B and ^1H NMR spectra indicate equivalence in the groups of [B(3), B(3′), B(6), B(6′)], [H(3), H(3′), H(6), H(6′)], and [H(7), H(7′), H(11), H(11′)]. The equivalence at room temperature may be due to accidental overlap in a static structure or to fluxional behavior in the molecule. Variable-temperature ^1H spectra indicate equivalence of the above sets of hydrogens down to −75 °C. The −87 °C ^{11}B spectrum of $B_5H_{10}BeB_5H_{10}$ shows excessive broadening of the basal boron resonances but no features directly attributable to nonequivalence for [B(3), B(3′), B(6), B(6′)] are present. The ^1H spectrum of the C_5H_5 protons of $B_5H_{10}BeC_5H_5$ continues to show a sharp singlet down to −75 °C.

Discussion

The reaction of $Be(BH_4)_2$ with $1\text{-}ClB_5H_8$ results in a unique cage-opening process and insertion of a beryllium atom into a basal cage position. The stoichiometry of the reaction and nature of the reactants and products suggest that significant molecular rearrangement occurs during the reaction but no mechanism can be postulated at this time. Much of the reaction chemistry of the $B_5H_{10}Be$ species involves substitution at the beryllium atom. Interestingly, attempts to prepare the parent compound of the $B_5H_{10}Be$ species, $B_5H_{10}BeH$, have been unsuccessful, as have attempts to prepare the $B_3H_8^-$ derivative.

Structural characterization[8] of $B_5H_{10}BeBH_4$ and $B_5H_{10}BeB_5H_{10}$ shows that the beryllium atom indeed occupies a cage position in these species. The same situation is expected for all the $B_5H_{10}Be$ derivatives presented here. These are the first well-characterized compounds in which a Be–B linkage does not involve at least one bridge hydrogen. The $B_5H_{10}Be$ derivatives are of particular interest because of the environment of beryllium and the unusual bonding situations present.

For the derivatives $B_5H_{10}BeX$ with X = Cl, Br, or CH_3, the X substituent is expected to be bonded to beryllium by a single two-electron σ bond. Thus the Cl, Br, and CH_3 derivatives are isoelectronic with B_6H_{10} with the combination of a beryllium atom and a bridge hydrogen isoelectronic with a boron atom. The beryllium atom is in a bonding situation analogous to that found for many boron and carbon atoms in borane and carborane cages. A boron atom in this situation is thought to use three orbitals for cage bonding and one orbital for bonding external to the cage.[14] The *styx* bonding description as modified for beryllaboranes[8] describes the structures of the above $B_5H_{10}BeX$ species as 5210 formulations with several resonance forms (probably of unequal weight):



However, for $B_5H_{10}BeBH_4$, $B_5H_{10}BeB_5H_{10}$, and $B_5H_{10}BeC_5H_5$ (in which the cyclopentadienyl group is expected to be π bonded to beryllium), the beryllium atom is involved in a bonding situation external to the cage which has not been observed for cage boron or carbon atoms. Structural results[8] indicate that the tetrahydroborate ligand in $B_5H_{10}BeBH_4$ is attached to beryllium through the two bridge hydrogens which will require two bonding interactions. If the bonding of beryllium to the B_5H_{10} cage involves three interactions as noted above, then five bonding interactions are required by beryllium in $B_5H_{10}BeBH_4$ and six interactions are required for $B_5H_{10}BeB_5H_{10}$. If the cyclopentadienyl ring of $B_5H_{10}BeC_5H_5$ is truly a η^5 ligand, a total of six bonding interactions is required in this compound also. The *styx* formulation does not provide a reasonable respresentation of the bonding situation in $B_5H_{10}BeBH_4$ and $B_5H_{10}BeB_5H_{10}$.[8]

Bonding situations similar to those in $B_5H_{10}BeBH_4$, $B_5H_{10}BeB_5H_{10}$, and $B_5H_{10}BeC_5H_5$ exist in $Be(C_5H_5)_2$[17] and in triple-hydrogen-bridged structures of $Be(BH_4)_2$.[18] A theoretical study[17] of a $[\eta^5\text{-}Be(C_5H_5)_2]_2$ described the bonding using three-center beryllium–ring interactions with six localized molecular orbitals at the beryllium. The solid-state polymeric structure of $Be(BH_4)_2$[1] has been shown to contain a trigonal-prismatic array of six bridging hydrogens around the beryllium. The bonding has been described in terms of an ionic structure with H_4BBe^+ and BH_4^- ions.[19]

The beryllium-cage interactions in $B_5H_{10}BeBH_4$, $B_5H_{10}BeB_5H_{10}$, and $B_5H_{10}BeC_5H_5$ are not understood but these Be interactions may be related to those in $Be(C_5H_5)_2$ and $Be(BH_4)_2$. Perhaps theoretical studies of the charge distribution and bonding interactions will shed some light on this problem. Normal valence bond descriptions are clearly inadequate in this situation.

In a formal sense the $B_5H_{10}Be$ species can be thought of as containing a $B_5H_{10}^-$ ligand. The only report[20] of a $B_5H_{10}^-$ species is $(NH_3)_2BH_2^+B_5H_{10}^-$, produced by the reaction of B_6H_{12} with NH_3. Of the homologous series $B_2H_7^-$, $B_3H_8^-$, $B_4H_9^-$, $B_5H_{10}^-$, and $B_6H_{11}^-$, only $B_3H_8^-$ has shown an extensive metal coordination chemistry. The present series containing the $B_5H_{10}^-$ ligand suggests that this ligand may exhibit other interesting coordination chemistry. The ligand is expected to show tridentate character with one M–B and two M–H–B linkages between a metal and the boron cage.

It is interesting to speculate about the nature of $B_5H_{10}BeC_5H_5$ in light of the structures observed for $B_5H_{10}BeBH_4$ and $B_5H_{10}BeB_5H_{10}$. The ^{11}B and ^1H NMR spectra of $B_5H_{10}BeC_5H_5$ indicate that terminal and M–H–B bridge hydrogens on B(3) or B(6) are coupled approximately equivalently to B(3) or B(6). The chemical shift of B(1) and the coupling constant between B(1) and H(1) are significantly different than those for the other $B_5H_{10}Be$ species. These NMR results may suggest stronger Be–B(1) interaction and weaker Be–H_b and Be–B(3), B(6) interactions. However, other derivatives of beryllaboranes[16,21] have shown uncommon chemical shifts and spectra of an unusual nature, and the uniqueness of the NMR spectra may be due to the electronic effects of the C_5H_5 ring.

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Registry No. $B_5H_{10}BeBH_4$, 60923-64-0; $B_5H_{10}BeBr$, 65760-52-3; $B_5H_{10}BeCl$, 65760-51-2; $B_5H_{10}BeB_5H_{10}$, 65762-38-1; $B_5H_{10}BeCH_3$, 65859-18-9; $B_5H_{10}BeC_5H_5$, 65760-50-1; $Be(BH_4)_2$, 30374-53-9; 1-ClB_5H_8, 19469-13-7; $C_5B_3H_8$, 33220-36-9; $Al_2(CH_3)_6$, 15632-54-9.

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