Low-Temperature Crystal and Molecular Structures of 2-Tetrahydroborato-2-berylla-*nido*-hexaborane(11) and 2,2'-*commo*-Bis[2-berylla-*nido*-hexaborane(11)]

DONALD F. GAINES,* JERRY L. WALSH, and JOSEPH C. CALABRESE

The solid-state structure of 2-tetrahydroborato-2-berylla-*nido*-hexaborane(11), $B_5H_{10}BeBH_4$, was determined by x-ray diffraction to be a pentagonal-pyramidal cage in which one basal position is occupied by a beryllium atom. A terminal hydrogen is attached to each of the cage boron atoms, and bridge hydrogens link all adjacent basal atoms in the cage. The tetrahydroborate group is attached to the beryllium atom by two bridging hydrogen atoms. The compound forms crystals in the monoclinic space group $P2_1/n$ with unit cell parameters $a = 10.632$ (4) Å, $b = 8.337$ (2) Å, $c = 8.604$ (2) Å, $\beta = 98.09$ (3)°, $V = 754.9$ (4) Å³, and $Z = 4$ (−165 °C). The structure was solved by direct methods, and all atomic positions, including hydrogens, were refined anisotropically to $R_1 = 0.046$ and $R_2 = 0.051$ for 1274 independent $\theta-2\theta$ reflections collected at −165 °C. The solid-state structure of 2,2'-*commo*-bis[2-berylla-*nido*-hexaborane(11)], $B_5H_{10}BeB_5H_{10}$, consists of two pentagonal-pyramidal cages, very similar to that for $B_5H_{10}BeBH_4$, linked by a common beryllium atom. The dihedral angle between the basal plane of the two boron cages is 66°. The *m*-xylene solvent was incorporated into the crystal with $B_5H_{10}BeB_5H_{10}$ in a 1:1 ratio to give an orthorhombic crystal of the $P2_12_12_1$ space group with unit cell dimensions $a = 14.581$ (4) Å, $b = 8.898$ (2) Å, $c = 13.803$ (3) Å, $V = 1791.0$ (8) Å³, and $Z = 4$ (−135 °C). The structure was solved by direct methods and atomic positions were refined to $R_1 = 0.045$ and $R_2 = 0.061$ for 1092 independent $\theta-2\theta$ reflections.

Introduction

Investigation of the chemistry of beryllium bis(tetrahydroborate), $Be(BH_4)_2$, and other beryllaboranes has led to the production of several species in which a beryllium atom has been inserted into a pentaborane cage.[1] The reaction of 1-chloropentaborane(9) with $Be(BH_4)_2$ produces 2-tetrahydroborato-2-berylla-*nido*-hexaborane(11), $B_5H_{10}BeBH_4$, and 2,2'-*commo*-bis[2-berylla-*nido*-hexaborane(11)], $B_5H_{10}BeB_5H_{10}$. The nature of the structural and bonding interactions between the beryllium atom and the B_5H_{10} framework in $B_5H_{10}BeBH_4$ could not be unequivocally deduced from NMR, infrared, and mass spectra. A single-crystal x-ray study has shown that the Be atom clearly occupies a polyhedral vertex position in the base of a six-atom $B_5H_{10}Be$ pentagonal-pyramidal structure with a terminal BH_4 group attached to the Be atom. NMR spectra of a second low-yield product indicated the presence of a similar B_5H_{10} moiety and no other terminal group on the Be atom. On the basis of this lack of information it was postulated that two B_5H_{10} units were bound to a single Be atom in $B_5H_{10}BeB_5H_{10}$. Single-crystal x-ray studies were undertaken to confirm the identity of the postulated $B_5H_{10}BeB_5H_{10}$ and to discover the structural geometry and bonding interactions between the two B_5H_{10} borane fragments and the commo beryllium atom.

Experimental Section

Syntheses of $B_5H_{10}BeBH_4$ and $B_5H_{10}BeB_5H_{10}$ are described elsewhere.[1] X-ray samples were sealed in Pyrex capillaries on the vacuum line and the capillaries were then mounted on a Syntex $P\bar{1}$ four-circle computer-controlled diffractometer equipped with LT-1 low-temperature accessories.[2] Single crystals were grown in the capillaries on the diffractometer. Crystals of $B_5H_{10}BeBH_4$ were grown from the neat liquid. It was necessary, however, to grow crystals of $B_5H_{10}BeB_5H_{10}$ from *m*-xylene solution, the solvent being incorporated into the crystal in a 1:1 ratio. Absorption corrections were not obtained. Crystal symmetry and lattice parameters[2] for both structures were confirmed by partial rotation photographs along each reciprocal axis. Intensity data were collected using the $\theta-2\theta$ scan technique. Monitoring of two standard reflections indicated intensity stability throughout the data collection procedure. Experimental conditions and final results of the data collection routines are summarized in Table I.

The structures were solved using direct methods.[3,4] Atomic scattering factors[5] were used in the solution of the $B_5H_{10}BeBH_4$ structure. For $B_5H_{10}BeB_5H_{10}$ these scattering factors were used to

Table I. Crystallographic Data for $B_5H_{10}BeBH_4$ and $B_5H_{10}BeB_5H_{10} \cdot C_8H_{10}$

	$B_5H_{10}BeBH_4$	$B_5H_{10}Be-B_5H_{10} \cdot C_8H_{10}$
Mp, °C	−22	
Crystal growing temp, °C	−40	−37
Data collection temp, °C	−165	−135
Radiation (graphite monochromator)	Mo Kα	Cu Kα
Scan speed, deg/min	2–24	2–24
Bkgd:scan time	2:3	2:3
Range of 2θ, deg	3–60	3–115
Total reflections	2562	1574
Independent reflections	1558	1401
Independent obsd reflections	1274	1116
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$P2_12_12_1$
Equiv positions	$\pm(x, y, z)$	x, y, z
	$\pm(^1/_2 + x, ^1/_2 - y, ^1/_2 + z)$	$-x, ^1/_2 - y, ^1/_2 + z$
		$^1/_2 - x, ^1/_2 + y, -z$
		$^1/_2 + x, -y, ^1/_2 - z$
Systematic absences	$0k0$: k odd	$h00$: h odd
	$h0l$: $h + l$ odd	$0k0$: k odd
		$00l$: l odd
a, Å	10.632 (4)	14.581 (4)
b, Å	8.337 (2)	8.898 (2)
c, Å	8.604 (2)	13.803 (3)
β, deg	98.09 (3)	
V, Å³	1145 (1)	1791 (1)
Calcd density, g/cm³ $(T, °C)$	0.774 (−165)	0.903 (−135)
R_1	0.046	0.045
R_2	0.051	0.061

form molecular scattering factors for the *m*-xylene carbon atoms and for the boron atoms in the B_5H_{10} fragment. The first E-map synthesis for each structure located all nonhydrogen atoms. For $B_5H_{10}BeBH_4$ all hydrogen atoms were located by the usual Fourier and difference electron density maps. For the structure $B_5H_{10}BeB_5H_{10} \cdot C_8H_{10}$, a partial least-squares refinement of the positional parameters for the heavy atoms was necessary to locate most of the hydrogen atoms.

Full-matrix least-squares refinement of $B_5H_{10}BeBH_4$ with anisotropic beryllium and boron atoms and isotropic hydrogen atoms gave discrepancy values of $R_1 = 0.047$ and $R_2 = 0.054$. The data to parameter ratio (6.74) suggested that anisotropic refinement of

Table II. Atomic Coordinates and Anisotropic Temperature Parameters for $B_5H_{10}BeBH_4{}^a$

A. Atomic Coordinates (A) ($\times 10^4$)

Atom	x	y	z	Atom	x	y	z
Be	1772 (2)	8311 (2)	6579 (2)	H(6)	−300 (14)	7568 (19)	4431 (15)
B(1)	1781 (1)	8965 (2)	4304 (2)	H(7)	3207 (14)	7936 (19)	6582 (15)
B(3)	3268 (1)	8748 (2)	5536 (2)	H(8)	3796 (16)	7725 (21)	4787 (19)
B(4)	3057 (1)	8086 (2)	3561 (2)	H(9)	2657 (14)	6700 (20)	3235 (16)
B(5)	1542 (2)	7312 (2)	3070 (2)	H(10)	1017 (13)	6340 (19)	3901 (16)
B(6)	692 (1)	7435 (2)	4704 (2)	H(11)	991 (13)	6783 (16)	5893 (16)
B(7)	1455 (2)	9042 (2)	8601 (2)	H(12)	1374 (14)	9705 (19)	7410 (17)
H(1)	1473 (12)	10129 (20)	3893 (14)	H(13)	1731 (15)	7739 (19)	8234 (16)
H(3)	3907 (13)	9727 (21)	5831 (16)	H(14)	494 (14)	9047 (23)	9015 (20)
H(4)	3587 (15)	8548 (19)	2699 (18)	H(15)	2238 (15)	9590 (19)	9379 (19)
H(5)	1110 (14)	7337 (21)	1882 (16)				

B. Anisotropic Temperature Parameters^b ($\times 10^4$)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Be	44 (1)	59 (2)	62 (2)	−1 (1)	10 (1)	0 (2)
B(1)	41 (1)	63 (2)	62 (2)	11 (1)	10 (1)	8 (2)
B(3)	40 (1)	73 (2)	76 (2)	1 (1)	12 (1)	−5 (2)
B(4)	50 (1)	77 (2)	72 (2)	9 (1)	17 (1)	0 (2)
B(5)	51 (1)	96 (2)	58 (2)	9 (1)	6 (1)	−8 (2)
B(6)	40 (1)	81 (2)	70 (2)	−2 (1)	6 (1)	−13 (2)
B(7)	62 (1)	87 (2)	60 (2)	−10 (2)	16 (1)	−9 (2)
H(1)	34 (15)	102 (28)	37 (21)	−5 (17)	7 (14)	17 (20)
H(3)	48 (16)	117 (32)	102 (27)	−23 (19)	7 (17)	−3 (24)
H(4)	84 (19)	125 (32)	79 (26)	−21 (20)	36 (18)	−4 (24)
H(5)	58 (18)	176 (36)	53 (25)	26 (20)	−9 (17)	−54 (24)
H(6)	46 (17)	145 (32)	40 (22)	−5 (19)	7 (16)	−23 (21)
H(7)	53 (16)	124 (30)	19 (21)	2 (19)	−3 (15)	−18 (20)
H(8)	93 (21)	156 (36)	98 (28)	−17 (23)	10 (20)	−16 (27)
H(9)	70 (19)	141 (35)	69 (24)	−64 (21)	−1 (17)	−14 (24)
H(10)	41 (16)	112 (30)	90 (26)	0 (18)	−12 (16)	12 (23)
H(11)	58 (16)	47 (24)	76 (25)	7 (16)	7 (17)	−16 (21)
H(12)	68 (18)	119 (31)	76 (25)	10 (19)	21 (17)	−10 (24)
H(13)	70 (18)	102 (31)	64 (24)	−16 (19)	0 (17)	−10 (22)
H(14)	58 (18)	193 (39)	169 (33)	13 (22)	66 (20)	42 (28)
H(15)	69 (18)	114 (33)	114 (27)	−12 (21)	−29 (18)	−10 (25)

^{a} Standard deviations of the last significant figures are given in parentheses. ^{b} Anisotropic temperature parameters are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.
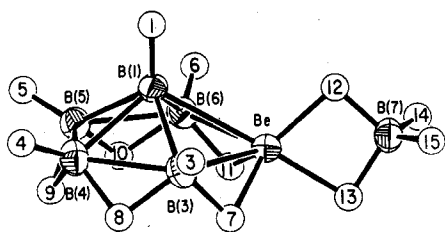

Figure 1. The static molecular structure of $B_5H_{10}BeBH_4$ showing 50% probability ellipsoids for nonhydrogen atoms. The hydrogen atoms are represented by spheres of 0.14-Å radius.

hydrogen atoms may be warranted. Upon doing so, R_1 was reduced to 0.046, R_2 to 0.051. The Hamilton R-value ratio test[6] suggests that the improvement from anisotropic refinement of the hydrogen atoms was significant at the 0.01 level.

Least-squares refinement of $B_5H_{10}BeB_5H_{10}$ was complicated by the disorder of the xylene methyl group hydrogens. Final refinement included anisotropic terms for carbon, boron, and beryllium atoms and isotropic terms for all ordered hydrogen atoms. Disordered xylene methyl hydrogens were included as fixed-atom contributions in idealized positions expected (1.00 Å) from a tetrahedral carbon adjacent to an aromatic ring.

The final parameters converged with $R_1 = 0.045$ and $R_2 = 0.061$. The absolute configuration of the acentric structure of $B_5H_{10}BeB_5H_{10}$ was not determined. Least-squares refinements were based on minimization of $\sum w_i(|F_o| - |F_c|)^2$, with weights equal to $1/\sigma(F_o)^2$. The estimated standard deviations in all bond lengths and angles were calculated from the full variance–covariance matrix obtained from the last least-squares refinement cycle. Difference maps were calculated for the two structures using the refined atomic positions and no features were present which suggested unusually large electron

Table III. Interatomic Distances for $B_5H_{10}BeBH_4$ (A)

Be–B(1)	2.033 (2)	Be–H(7)	1.557 (14)
Be–B(3)	1.967 (2)	Be–H(11)	1.589 (14)
Be–B(6)	1.983 (2)	Be–H(12)	1.458 (15)
Be–B(7)	1.917 (2)	Be–H(13)	1.508 (14)
B(1)–B(3)	1.784 (2)	B(3)–H(7)	1.135 (14)
B(1)–B(4)	1.741 (2)	B(3)–H(8)	1.249 (17)
B(1)–B(5)	1.736 (2)	B(4)–H(8)	1.260 (17)
B(1)–B(6)	1.788 (2)	B(4)–H(9)	1.250 (15)
B(3)–B(4)	1.771 (2)	B(5)–H(9)	1.280 (16)
B(4)–B(5)	1.732 (2)	B(5)–H(10)	1.262 (15)
B(5)–B(6)	1.777 (2)	B(6)–H(10)	1.223 (15)
B(1)–H(1)	1.069 (16)	B(6)–H(11)	1.163 (14)
B(3)–H(3)	1.070 (16)	B(7)–H(12)	1.156 (15)
B(4)–H(4)	1.064 (14)	B(7)–H(13)	1.180 (16)
B(5)–H(5)	1.060 (13)		
B(6)–H(6)	1.053 (14)		
B(7)–H(14)	1.129 (14)		
B(7)–H(15)	1.092 (16)		

density within bonding distance of the nonhydrogen atoms.

Results

$B_5H_{10}BeBH_4$. The static molecular structure of B_5H_{10}-$BeBH_4$ and the numbering system used are shown in Figure 1. The structure is a distorted pentagonal pyramid with the beryllium atom occupying a basal position in the cage. The beryllium–boron distances in the cage are longer than the boron–boron distances. An approximately tetrahedral tetrahydroborate group is attached to the beryllium atom by two hydrogen bridges. A terminal hydrogen atom is bonded to each cage boron atom and there are hydrogen atom bridges between all adjacent basal atoms in the cage.

Table IV. Intramolecular Angles for $B_5H_{10}BeBH_4$ (deg)[a]

X–X–X Angles		H–X–H and X–H–X Angles	
B(1)–Be–B(3)	53.0 (1)	H(7)–Be–H(11)	107.5 (8)
B(1)–Be–B(6)	52.8 (1)	H(7)–Be–H(12)	120.8 (8)
B(1)–Be–B(7)	144.4 (1)	H(7)–Be–H(13)	95.4 (8)
B(1)–Be–H(7)	85.3 (5)	H(11)–Be–H(12)	130.4 (8)
B(3)–Be–B(6)	96.3 (1)	H(11)–Be–H(13)	90.8 (8)
B(3)–Be–B(7)	127.7 (1)	H(12)–Be–H(13)	74.9 (8)
B(6)–Be–B(7)	134.4 (1)	H(12)–B(7)–H(13)	101.2 (10)
Be–B(1)–B(3)	61.6 (1)	H(12)–B(7)–H(14)	108.6 (12)
Be–B(1)–B(4)	110.5 (1)	H(12)–B(7)–H(15)	107.4 (11)
Be–B(1)–B(5)	110.8 (1)	H(13)–B(7)–H(14)	111.0 (13)
Be–B(1)–B(6)	62.1 (1)	H(13)–B(7)–H(15)	110.6 (11)
B(3)–B(1)–B(4)	60.3 (1)	H(14)–B(7)–H(15)	116.8 (13)
B(3)–B(1)–B(5)	108.9 (1)	Be–H(12)–B(7)	93.6 (10)
B(3)–B(1)–B(6)	110.9 (1)	Be–H(13)–B(7)	90.1 (10)
B(4)–B(1)–B(5)	59.7 (1)		
B(4)–B(1)–B(6)	109.2 (1)	**X–X–H Angles**	
B(5)–B(1)–B(6)	60.6 (1)		
Be–B(3)–B(1)	65.4 (1)	B(1)–Be–H(11)	86.0 (5)
Be–B(3)–B(4)	112.3 (1)	B(1)–Be–H(12)	107.4 (6)
B(1)–B(3)–B(4)	58.6 (1)	B(1)–Be–H(13)	176.8 (6)
B(1)–B(4)–B(3)	61.1 (1)	B(3)–Be–H(7)	35.2 (5)
B(1)–B(4)–B(5)	60.0 (1)	B(3)–Be–H(11)	113.1 (5)
B(3)–B(4)–B(5)	109.8 (1)	B(3)–Be–H(12)	112.7 (6)
B(1)–B(5)–B(4)	60.3 (1)	B(3)–Be–H(13)	128.5 (6)
B(1)–B(5)–B(6)	61.2 (1)	B(6)–Be–H(7)	112.5 (5)
B(4)–B(5)–B(6)	110.2 (1)	B(6)–Be–H(11)	35.9 (5)
Be–B(6)–B(1)	65.0 (1)	B(6)–Be–H(12)	121.2 (6)
Be–B(6)–B(5)	111.4 (1)	B(6)–Be–H(13)	124.1 (6)
B(1)–B(6)–B(5)	58.3 (1)	Be–B(7)–H(14)	124.7 (10)
		Be–B(7)–H(15)	118.3 (8)

[a] X = B or Be.

Table V. Distances (Å) of Atoms Out of Various Molecular Planes and Dihedral Angles (deg) between Various Planes for $B_5H_{10}BeBH_4$

Plane B(3), B(4), B(5), B(6)		Plane B(1), Be, B(7)	
Atoms out of plane	Dist	Atoms out of plane	Dist
B(1)	0.9025	B(3)	1.4122
B(3)	0.0003	B(4)	0.7126
B(4)	−0.0004	B(5)	−1.0098
B(5)	0.0004	B(6)	−1.5150
B(6)	−0.0003	H(1)	0.0622
Be	−0.0898	H(9)	−0.2642
B(7)	0.1174	H(12)	0.0105
H(14)	0.3321	H(13)	0.0573
H(15)	0.1135	H(14)	0.9256
		H(15)	−0.9614

Atoms defining plane 1	Atoms defining plane 2	Dihedral angle[a]
B(3), B(4), B(5), B(6)	B(3), B(6), Be	3.9
B(3), B(4), B(5), B(6)	Be, B(7), H(12), H(13)	83.5
B(3), B(4), B(5), B(6)	B(1), Be, B(7)	85.0
B(3), B(6), Be	Be, B(7), H(12), H(13)	83.4
Be, B(7), H(12), H(13)	B(7), H(14), H(15)	89.4

[a] Between planes 1 and 2.

Figure 2. A stereoview of $B_5H_{10}BeB_5H_{10}$ looking down the C_2 axis.

Figure 3. An end view showing the relative orientations of the two B_5 cages in $B_5H_{10}BeB_5H_{10}$.

The atomic coordinates and anisotropic thermal parameters are listed in Table II. Interatomic distances and intramolecular angles are listed in Tables III and IV, respectively. The crystal packing appears normal with no unusually short interatomic distances. The boron–boron distances (1.76 ± 0.03 Å) are typical of similar boron cage compounds such as B_5H_9,[7] B_5H_{11},[8] and B_6H_{10}.[9] The Be–B(7) distance (1.917 Å) is the shortest beryllium–boron distance in $B_5H_{10}BeBH_4$ and is the same as the Be–B distance for the terminal tetrahydroborate in solid polymeric $Be(BH_4)_2$.[10] Be–B(1), Be–B(3), and Be–B(6) distances are approximately the same as the Be–B distance for the bridging tetrahydroborate group in solid $Be(BH_4)_2$, with the Be–B(3) and Be–B(6) distances being slightly shorter than and nearly identical with the beryllium–adjacent boron atom distances in $Be(B_3H_8)_2$.[11] The beryllium–bridging hydrogen distances in $B_5H_{10}BeBH_4$ also compare favorably with like bridging hydrogen distances in $Be(BH_4)_2$ and $Be(B_3H_8)_2$. Considering the apical boron atom and the bridge hydrogens around beryllium, the coordination about beryllium approximates trigonal bipyramidal with a B(1)–Be–H(13) angle of 176° (Table IV) and B(1)–Be–H(7), B(1)–Be–H(11), and B(1)–Be–H(12) angles of 85.3, 86.0, and 107.4°, respectively.
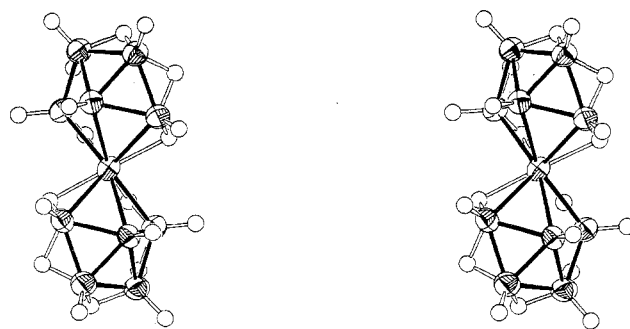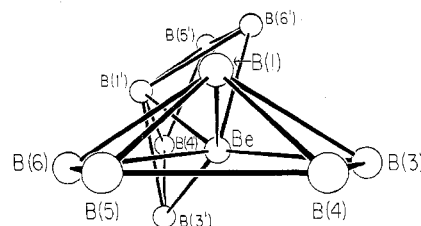
The beryllium atom is slightly below (0.09 Å) the plane of B(3), B(4), B(5), and B(6), and the tetrahydroborate boron is slightly above that plane (0.12 Å). The dihedral angles between various molecular planes are listed in Table V. Although there appears to be mirror-plane symmetry in the molecule, there is distortion from that symmetry as noted by comparing the B(3)–Be–B(7) angle with the B(6)–Be–B(7) angle (134° vs. 128°). The deviations of various atoms from the pseudomirror plane through B(1), Be, and B(7) support this contention (see H(9) and the pairs B(3), B(6) and B(4), B(5) in Table V).

In view of the interest in the structure of gaseous Be(BH$_4$)$_2$,[12] it is interesting to note that in solid $B_5H_{10}BeBH_4$, the tetrahydroborate boron atom, B(7), is bonded to the beryllium by two hydrogen bridge bonds. The tetrahydroborate group

is approximately tetrahedral with H–B–H angles close to 109° and the dihedral angle between planes defined by H(12), B(7), H(13) and H(14), B(7), H(15) about 89°. Nuclear magnetic resonance data for $B_5H_{10}BeBH_4$ in solution[1] indicate rapid internal exchange for the four tetrahydroborate hydrogens at room temperature.

$B_5H_{10}BeB_5H_{10}$. The $B_5H_{10}BeB_5H_{10}$ molecule consists of two pentagonal BeB_5 pyramids sharing a common beryllium atom. The dihedral angle between the basal planes of the two boron cages is 66°. One asymmetric unit in the crystal consists of one molecule each of $B_5H_{10}BeB_5H_{10}$ and C_8H_{10}. A stereoscopic projection of $B_5H_{10}BeB_5H_{10}$ looking down the approximate twofold axis in the molecule is shown in Figure 2. The numbering scheme is the same for the $B_5H_{10}Be$ fragment as in $B_5H_{10}BeBH_4$, the second BeB_5H_{10} cage having primed numbers. The relative orientation of the two cages is shown more clearly in Figure 3, looking through one of the $B_5H_{10}Be$ cages perpendicular to the B(4)–B(5) bond. A view of the unit

Table VI. Atomic Coordinates and Temperature Parameters for $B_5H_{10}BeB_5H_{10}\cdot C_8H_{10}$

A. Atomic Coordinates (Å) (×10⁴) and Isotropic Temperature Factors (Å²)

Atom	x	y	z	B_{iso}	Atom	x	y	z	B_{iso}
Be	4670 (4)	286 (5)	−5007 (4)		C(1)	2293 (3)	3309 (4)	1914 (3)	
B(1)	4938 (3)	1473 (5)	−6277 (3)		C(2)	2886 (3)	2332 (4)	1444 (3)	
B(3)	4320 (4)	−238 (5)	−6441 (3)		C(3)	2895 (3)	2192 (5)	442 (3)	
B(4)	5125 (4)	414 (6)	−7314 (3)		C(4)	2286 (4)	3060 (5)	−94 (3)	
B(5)	6047 (4)	1285 (6)	−6754 (3)		C(5)	1697 (4)	4036 (5)	354 (3)	
B(6)	5897 (3)	1198 (6)	−5480 (3)		C(6)	1694 (5)	4163 (5)	1359 (3)	
B(1')	4529 (3)	1255 (5)	−3661 (3)		C(7)	2298 (3)	3403 (6)	3007 (3)	
B(3')	4924 (4)	−646 (5)	−3668 (3)		C(8)	3544 (4)	1130 (6)	−51 (3)	
B(4')	4245 (3)	60 (5)	−2719 (3)		H(12)	3313 (22)	1722 (39)	1818 (23)	3.0 (5)
B(5')	3431 (4)	1332 (6)	−3164 (3)		H(13)	2255 (28)	3041 (50)	−802 (31)	5.7 (7)
B(6')	3559 (4)	1435 (6)	−4446 (3)		H(14)	1233 (29)	4549 (45)	−44 (26)	4.9 (7)
H(1)	4663 (21)	2590 (36)	−6344 (22)	2.8 (6)	H(15)	1332 (36)	4853 (63)	1685 (32)	8.0 (8)
H(3)	3610 (27)	−247 (42)	−6706 (22)	3.7 (6)	H(16)	2744	4198	321	5.0
H(4)	4878 (27)	696 (44)	−8052 (25)	4.7 (6)	H(17)	2486	2415	3282	5.0
H(5)	6392 (24)	2105 (42)	−7161 (25)	3.6 (6)	H(18)	1671	3675	3243	5.0
H(6)	6175 (25)	2182 (45)	−5017 (27)	4.2 (6)	H(16')	1856	2660	3278	5.0
H(7)	4487 (24)	−1156 (40)	−5832 (22)	3.3 (6)	H(17')	2929	3183	3251	5.0
H(8)	4835 (23)	−907 (39)	−7074 (23)	3.2 (6)	H(18')	2115	4442	3212	5.0
H(9)	6006 (25)	72 (43)	−7266 (23)	3.8 (7)	H(19)	3250	120	−119	5.0
H(10)	6497 (23)	723 (38)	−6093 (24)	3.5 (6)	H(20)	3708	1526	−706	5.0
H(11)	5855 (23)	82 (37)	−5107 (21)	2.5 (7)	H(21)	4116	1029	349	5.0
H(1')	4959 (23)	2147 (41)	−3499 (24)	3.3 (6)	H(19')	4133	1664	−198	5.0
H(3')	5618 (24)	−946 (34)	−3413 (21)	2.3 (5)	H(20')	3675	258	389	5.0
H(4')	4504 (25)	163 (45)	−1970 (24)	4.1 (5)	H(21')	3267	755	−666	5.0
H(5')	3138 (29)	2179 (49)	−2675 (31)	5.6 (6)					
H(6')	3390 (25)	2525 (43)	−4780 (25)	3.6 (6)					
H(7')	4660 (26)	−1241 (51)	−4322 (27)	5.1 (7)					
H(8')	4333 (27)	−1264 (45)	−3060 (24)	4.7 (5)					
H(9')	3378 (26)	96 (45)	−2800 (25)	4.4 (5)					
H(10')	2927 (26)	1086 (44)	−3868 (25)	4.6 (6)					
H(11')	3471 (25)	409 (38)	−4937 (23)	3.2 (6)					

B. Anisotropic Temperature Parameters^a (×10⁴)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Be	37 (2)	63 (4)	40 (2)	2 (3)	−5 (2)	−4 (3)	C(1)	48 (2)	106 (3)	47 (2)	−18 (2)	3 (1)	−8 (2)
B(1)	46 (2)	78 (4)	41 (2)	2 (2)	−1 (1)	5 (2)	C(2)	42 (2)	100 (3)	47 (1)	−6 (2)	4 (1)	0 (2)
B(3)	48 (2)	96 (4)	40 (2)	10 (3)	−2 (2)	−10 (3)	C(3)	60 (2)	92 (3)	49 (2)	−26 (2)	15 (2)	−7 (2)
B(4)	51 (2)	130 (5)	42 (2)	21 (3)	1 (2)	3 (3)	C(4)	75 (2)	122 (4)	49 (2)	−46 (3)	−4 (2)	10 (3)
B(5)	52 (2)	124 (5)	48 (2)	15 (3)	5 (2)	22 (3)	C(5)	58 (2)	112 (4)	73 (2)	−28 (2)	−20 (2)	14 (3)
B(6)	42 (2)	103 (4)	46 (2)	1 (3)	1 (2)	6 (3)	C(6)	46 (2)	105 (4)	71 (2)	−17 (2)	0 (2)	−4 (3)
B(1')	49 (2)	68 (3)	40 (2)	1 (2)	−4 (2)	−12 (2)	C(7)	60 (2)	187 (5)	51 (2)	−7 (3)	17 (2)	−23 (3)
B(3')	42 (2)	84 (4)	39 (2)	3 (2)	−5 (2)	2 (2)	C(8)	73 (2)	163 (5)	68 (2)	−28 (3)	26 (2)	−23 (3)
B(4')	48 (2)	101 (4)	42 (2)	1 (3)	−1 (2)	−2 (3)							
B(5')	56 (2)	103 (4)	41 (2)	−3 (3)	0 (2)	−9 (3)							
B(6')	48 (2)	92 (4)	41 (2)	2 (3)	−2 (2)	−2 (2)							

^{a} Anisotropic temperature factors are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.
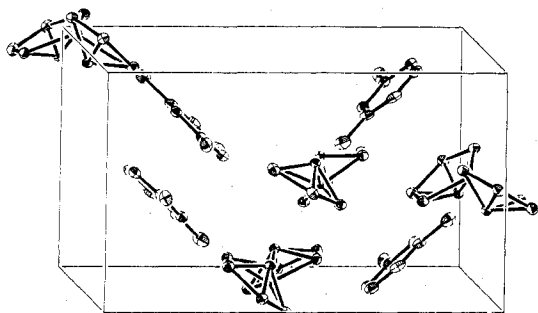
Figure 4. The unit-cell diagram for $B_5H_{10}BeB_5H_{10}\cdot C_8H_{10}$.

cell, showing the packing of the cocrystallized $B_5H_{10}BeB_5H_{10}$ and C_8H_{10} molecules, is shown in Figure 4.

The atomic coordinates and thermal parameters for $B_5H_{10}BeB_5H_{10}$ are listed in Table VI. Interatomic distances and intramolecular angles are listed in Tables VII and VIII, respectively. These distances and angles are very similar to those for $B_5H_{10}BeBH_4$ except as noted here. The beryllium–boron distances are slightly longer in $B_5H_{10}BeB_5H_{10}$ than in $B_5H_{10}BeBH_4$ and the beryllium–basal boron atom distances are the same as the beryllium–apical boron atom distances.

The beryllium–bridge hydrogen distances are significantly longer than in $B_5H_{10}BeBH_4$ (1.66–1.78 Å vs. 1.46–1.59 Å). In contrast to $B_5H_{10}BeBH_4$, the beryllium atom in B_5H_{10}-BeB_5H_{10} is slightly above the plane of the basal boron atoms for each cage, 0.13 and 0.18 Å for the unprimed and primed cages, respectively, with "above the plane" defined as in the same direction as the apical boron.

If the apical boron atoms and the hydrogen atoms bridging to beryllium are considered, the coordination of the beryllium in $B_5H_{10}BeB_5H_{10}$ seems to be approximately octahedral with H(11) and H(11') occupying axial positions. The H(11)–Be–H(11') angle is 176° and the H(11)–Be–H(7) and H(11)–Be–H(7') angles are close to 90° (92 and 86°). However, the B(1) and B(1') positions deviate significantly from idealized octahedral positions, with angles B(1)–Be–H(11), B(1)–Be–B(11'), and Be(1)–Be–H(1') equal to 79, 102, and 124°, respectively.

Discussion

The structures of $B_5H_{10}BeBH_4$ and $B_5H_{10}BeB_5H_{10}$ are unique from the standpoint of the structure of the resulting boron cage and of the environment of the beryllium atom.

The $B_5H_{10}Be$ species discussed here are prepared from 1-chloropentaborane(9) in a unique cage-opening–insertion

Table VII. Interatomic Distances for $B_5H_{10}BeB_5H_{10}\cdot C_8H_{10}$ (A)

$B_5H_{10}BeB_5H_{10}$

Be–B(1)	2.084 (7)	B(3)–B(4)	1.780 (7)
Be–B(3)	2.097 (7)	B(4)–B(5)	1.733 (8)
Be–B(6)	2.070 (7)	B(5)–B(6)	1.773 (6)
Be–B(1')	2.059 (6)	B(1')–B(3')	1.788 (6)
Be–B(3')	2.059 (6)	B(1')–B(4')	1.729 (6)
Be–B(6')	2.066 (7)	B(1')–B(5')	1.743 (7)
B(1)–B(3)	1.784 (6)	B(1')–B(6')	1.788 (7)
B(1)–B(4)	1.735 (6)	B(3')–B(4')	1.759 (6)
B(1)–B(5)	1.753 (7)	B(4')–B(5')	1.752 (7)
B(1)–B(6)	1.796 (6)	B(5')–B(6')	1.782 (6)
Be–H(7)	1.737 (33)	B(6)–H(10)	1.288 (34)
Be–H(11)	1.742 (34)	B(6)–H(11)	1.120 (32)
Be–H(7')	1.655 (42)	B(3')–H(7')	1.115 (39)
Be–H(11')	1.754 (37)	B(3')–H(8')	1.323 (37)
B(3)–H(7)	1.198 (33)	B(4')–H(8')	1.275 (38)
B(3)–H(8)	1.297 (32)	B(4')–H(9')	1.270 (37)
B(4)–H(8)	1.293 (33)	B(5')–H(9')	1.212 (39)
B(4)–H(9)	1.322 (36)	B(5')–H(10')	1.238 (34)
B(5)–H(9)	1.292 (36)	B(6')–H(10')	1.257 (37)
B(5)–H(10)	1.231 (32)	B(6')–H(11')	1.144 (33)
B(1)–H(1)	1.076 (32)	B(1')–H(1')	1.037 (35)
B(3)–H(3)	1.097 (37)	B(3')–H(3')	1.103 (33)
B(4)–H(4)	1.109 (34)	B(4')–H(4')	1.105 (33)
B(5)–H(5)	1.049 (36)	B(5')–H(5')	1.098 (43)
B(6)–H(6)	1.158 (38)	B(6')–H(6')	1.102 (38)

C_8H_{10}

C(1)–C(2)	1.388 (5)	C(4)–C(5)	1.369 (6)
C(1)–C(6)	1.388 (6)	C(5)–C(6)	1.391 (6)
C(1)–C(7)	1.511 (5)	C(2)–H(12)	0.974 (32)
C(2)–C(3)	1.389 (5)	C(4)–H(13)	0.978 (41)
C(3)–C(4)	1.390 (6)	C(5)–H(14)	0.984 (40)
C(3)–C(8)	1.501 (6)	C(6)–H(15)	0.927 (52)

Table VIII. Intramolecular Angles for $B_5H_{10}BeB_5H_{10}\cdot C_8H_{10}$ (deg)[a]

A. $B_5H_{10}BeB_5H_{10}$

X–X–X Angles

B(1)–Be–B(3)	50.5 (2)	B(1)–B(4)–B(5)	60.7 (3)
B(1)–Be–B(6)	51.2 (2)	B(3)–B(4)–B(5)	110.8 (3)
B(1)–Be–B(1')	124.5 (3)	B(1)–B(5)–B(4)	59.7 (3)
B(1)–Be–B(3')	157.8 (3)	B(1)–B(5)–B(6)	61.2 (3)
B(1)–Be–B(6')	102.2 (3)	Be–B(6)–B(1)	64.8 (3)
B(3)–Be–B(6)	90.0 (3)	Be–B(6)–B(5)	115.9 (4)
B(3)–Be–B(1')	157.0 (3)	B(1)–B(6)–B(5)	58.8 (3)
B(3)–Be–B(3')	143.3 (3)	Be–B(1')–B(3')	64.3 (2)
B(3)–Be–B(6')	105.8 (3)	Be–B(1')–B(4')	116.4 (3)
B(6)–Be–B(1')	102.0 (3)	Be–B(1')–B(5')	117.6 (3)
B(6)–Be–B(3')	106.6 (3)	Be–B(1')–B(6')	64.5 (2)
B(6)–Be–B(6')	127.0 (3)	B(3')–B(1')–B(4')	60.0 (3)
B(1')–Be–B(3')	51.5 (2)	B(3')–B(1')–B(5')	109.6 (3)
B(1')–Be–B(6')	51.4 (2)	B(3')–B(1')–B(6')	109.7 (3)
B(3')–Be–B(6')	90.2 (3)	B(4')–B(1')–B(5')	60.6 (3)
Be–B(1)–B(3)	65.1 (3)	B(4')–B(1')–B(6')	108.8 (4)
Be–B(1)–B(4)	116.6 (3)	B(5')–B(1')–B(6')	60.6 (3)
Be–B(1)–B(5)	116.1 (3)	Be–B(3')–B(1')	64.3 (2)
Be–B(1)–B(6)	64.0 (2)	Be–B(3')–B(4')	115.0 (3)
B(3)–B(1)–B(4)	60.8 (3)	B(1')–B(3')–B(4')	58.4 (3)
B(3)–B(1)–B(5)	109.7 (3)	B(1')–B(4')–B(3')	61.7 (2)
B(3)–B(1)–B(6)	110.8 (3)	B(1')–B(4')–B(5')	60.1 (3)
B(4)–B(1)–B(5)	59.6 (3)	B(3')–B(4')–B(5')	110.6 (3)
B(4)–B(1)–B(6)	108.0 (3)	B(1')–B(5')–B(4')	59.3 (3)
B(5)–B(1)–B(6)	59.9 (3)	B(1')–B(5')–B(6')	60.9 (3)
Be–B(3)–B(1)	64.4 (2)	B(4')–B(5')–B(6')	108.0 (4)
Be–B(3)–B(4)	113.9 (3)	Be–B(6')–B(1')	64.1 (3)
B(1)–B(3)–B(4)	58.3 (3)	Be–B(6')–B(5')	115.4 (3)
B(1)–B(4)–B(3)	61.0 (3)	B(1')–B(6')–B(5')	58.5 (3)

X–X–H Angles

B(1)–Be–H(7)	81.5 (11)	B(1')–Be–H(7)	152.4 (11)
B(1)–Be–H(11)	78.5 (11)	B(1')–Be–H(11)	102.4 (10)
B(1)–Be–H(7')	153.9 (14)	B(1')–Be–H(7')	80.1 (14)
B(1)–Be–H(11')	101.6 (11)	B(1')–Be–H(11')	79.9 (11)
B(3)–Be–H(7)	34.8 (11)	B(3')–Be–H(7)	108.6 (12)
B(3)–Be–H(11)	98.2 (10)	B(3')–Be–H(11)	81.4 (11)
B(3)–Be–H(7')	110.7 (14)	B(3')–Be–H(7')	32.7 (14)
B(3)–Be–H(11')	79.8 (11)	B(3')–Be–H(11')	98.9 (11)
B(6)–Be–H(7)	102.5 (11)	B(6')–Be–H(7)	119.4 (12)
B(6)–Be–H(11)	32.8 (11)	B(6')–Be–H(11)	149.2 (11)
B(6)–Be–H(7')	120.6 (14)	B(6')–Be–H(7')	100.7 (14)
B(6)–Be–H(11')	148.7 (11)	B(6')–Be–H(11')	33.6 (11)

H–X–H and X–H–X Angles

H(7)–Be–H(11)	91.3 (16)	H(6)–B(6)–H(11)	115.8 (23)
H(7)–Be–H(7')	76.5 (17)	H(3')–B(3')–H(7')	117.4 (27)
H(7)–Be–H(11')	85.9 (16)	H(6')–B(6')–H(11')	115.4 (23)
H(11)–Be–H(7')	88.2 (18)	Be–H(7)–B(3)	89.3 (20)
H(11)–Be–H(11')	177.2 (15)	Be–H(11)–B(6)	89.9 (21)
H(7')–Be–H(11')	90.6 (17)	Be–H(7')–B(3')	94.0 (29)
H(3)–B(3)–H(7)	114.9 (25)	Be–H(11')–B(6')	88.3 (22)

B. C_8H_{10}

C(2)–C(1)–C(6)	118.5 (4)	C(1)–C(6)–C(5)	120.3 (4)
C(2)–C(1)–C(7)	119.9 (4)	C(1)–C(2)–H(12)	120.0 (19)
C(6)–C(1)–C(7)	121.6 (4)	C(3)–C(2)–H(12)	118.2 (19)
C(1)–C(2)–C(3)	121.8 (4)	C(3)–C(4)–H(13)	123.5 (26)
C(2)–C(3)–C(4)	118.4 (4)	C(5)–C(4)–H(13)	115.7 (26)
C(2)–C(3)–C(8)	120.9 (4)	C(4)–C(5)–H(14)	118.2 (23)
C(4)–C(3)–C(8)	120.8 (4)	C(6)–C(5)–H(14)	121.1 (22)
C(3)–C(4)–C(5)	120.8 (4)	C(1)–C(6)–H(15)	116.9 (30)
C(4)–C(5)–C(6)	120.3 (5)	C(5)–C(6)–H(15)	122.7 (30)

[a] X = B or Be

process. The cage-opening process has separated the basal boron atoms in the parent pentaborane species from a bonding distance of 1.77 Å[7] to a nonbonding B(3)–B(6) distance for the $B_5H_{10}BeBH_4$ product of 2.93 Å. A comparison of interatomic distances for $B_5H_{10}BeBH_4$, $B_5H_{10}BeB_5H_{10}$, B_5H_9,[7] B_5H_{11},[8] and B_6H_{10}[9] is given in Table IX. The $B_5H_{10}Be$ species have the general geometric shape of B_6H_{10} except that a beryllium atom has been substituted for a boron atom and an extra bridge hydrogen atom is present in the $B_5H_{10}Be$ species. This completes the isoelectronic series of pentagonal-pyramidal carborane, borane, and beryllaborane species containing 0–5 bridge hydrogens ($C_4B_2H_6$, $C_3B_3H_7$, $C_2B_4H_8$, CB_5H_9, B_6H_{10}, and $B_5H_{10}BeBH_4$)[13] (only substituted species are known for the last member of the series). For $B_5H_{10}BeBH_4$ and $B_5H_{10}BeB_5H_{10}$, the beryllium atom is involved in an electron-deficient linkage external to the cage (BH4 in B_5H_{10}-BeBH4, another B_5H_{10} cage in $B_5H_{10}BeB_5H_{10}$). In fact, all unsubstituted beryllaboranes involve linkages of electron-deficient units at a common beryllium atom. This appears to be a property unique to beryllaborane species, as other first-row elements carbon and boron have not been observed to link electron-deficient boron cages at a single commo atom.

The borane which is most closely related to $B_5H_{10}Be$ is B_5H_{11} as the B_5H_{10} moiety corresponds closely to the structure of B_5H_{11} if the unique hydrogen on the apical boron of B_5H_{11} is omitted. In $B_5H_{10}BeBH_4$ and $B_5H_{10}BeB_5H_{10}$, the B(1)–B(3) and B(1)–B(6) distances are longer than the B(1)–B(4) and B(1)–B(5) distances, as is true for the corresponding boron distances in B_5H_{11}. The B(3)–H(7) and B(6)–H(11) distances (1.12–1.18 Å) are somewhat shorter than many boron–bridge hydrogen distances (about 1.2–1.4 Å) but are typical of boron–bridge hydrogen distances when the hydrogen bridges to a beryllium.[10,11] This shorter B–H bridge distance is close to a typical B–H terminal distance. That $B_5H_{10}Be$ moieties can be described as containing $B_5H_{10}^-$ character is suggested by the production of B_5H_{11} upon protonation of $B_5H_{10}BeBr$ with HBr or HCl.[1] Only one report of a $B_5H_{10}^-$ species,

$(NH_3)_2BH_2^+B_5H_{10}^-$,[14] has appeared and thus, $B_5H_{10}BeBH_4$ and $B_5H_{10}BeB_5H_{10}$ are the first well-characterized examples of metal complexes formally containing a $B_5H_{10}^-$ ligand.

The electron-counting procedures of Wade[15] can be used for $B_5H_{10}BeBH_4$ and $B_5H_{10}BeB_5H_{10}$ as with analogous boranes and carboranes. In each $B_5H_{10}Be$ fragment, each boron atom contributes one electron to terminal B–H bonding and two electrons to cage bonding. The beryllium atom contributes one electron to bonding external to the cage and one electron

Table IX. Comparison of $B_5H_{10}BeBH_4$, $B_5H_{10}BeB_5H_{10}$, B_5H_9, B_5H_{11}, and $B_6H_{10}{}^a$

$B_5H_{10}BeBH_4$		$B_5H_{10}BeB_5H_{10}$		$B_5H_9{}^b$		$B_5H_{11}{}^c$		$B_6H_{10}{}^d$	
Apical–Basal Boron Distance, A									
B(1)–B(3)	1.786	B(1)–B(3)	1.788	B(1)–B(2)	1.66	B(1)–B(2)	1.87	B(1)–B(2)	1.740
B(1)–B(4)	1.738	B(1)–B(3)	1.740			B(1)–B(3)	1.72	B(1)–B(3)	1.753
								B(1)–B(4)	1.795
Basal–Basal Boron Distances, A									
B(3)–B(4)	1.774	B(3)–B(4)	1.774	B(2)–B(3)	1.77	B(2)–B(3)	1.76	B(2)–B(3)	1.794
B(4)–B(5)	1.732	B(4)–B(5)	1.742			B(3)–B(4)	1.77	B(3)–B(4)	1.737
Be–B(3)	1.976	Be–B(3)	2.073					B(4)–B(5)	1.596
Angles within Basal Plane, Deg									
B(3)–B(4)–B(5)	110.0	B(3)–B(4)–B(5)	109.6	B(2)–B(3)–B(4)	90	B(2)–B(3)–B(4)	112		
Be–B(3)–B(4)	111.8	Be–B(3)–B(4)	115.1						
B(3)–Be–B(6)	96.3	B(3)–Be–B(6)	90.1						
H–B–H Angles, Deg									
H(3)–B(3)–H(7)	112	H(3)–B(3)–H(7)	116			H(2)–B(2)–H(6)	117		
B–H Distances, A									
B(1)–H(1)	1.069	B(1)–H(1)	1.057	B(1)–H(1)	1.21	B(1)–H(1)	1.14	B(1)–H(1)	1.25
B(3)–H(3)	1.062	B(3)–H(3)	1.115	B(2)–H(2)	1.20	B(2)–H(2)	1.10	B(2)–H(2)	1.28
B(4)–H(4)	1.062	B(4)–H(4)	1.090			B(3)–H(3)	1.09	B(3)–H(3)	1.18
B(3)–H(7)	1.149	B(3)–H(7)	1.145			B(2)–H(6)	1.16	B(4)–H(4)	1.14

^{a} Results are the average of approximately equivalent groups in the molecule. Boron atoms are labeled according to IUPAC rules. A terminal hydrogen is given the same number as the boron it is attached to and the endo hydrogen in the basal BH_2 group of B_5H_{11} is called H(6). ^{b} Reference 7. ^{c} Reference 8. ^{d} Reference 9.
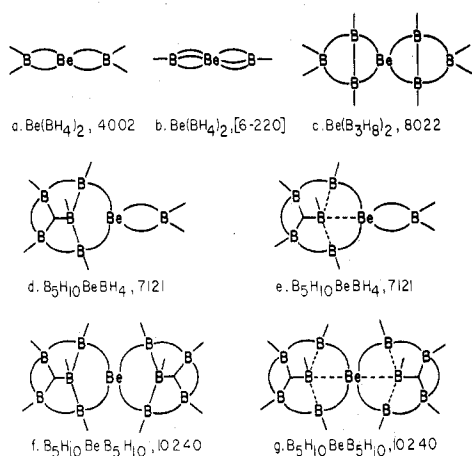

Figure 5. Some examples of *styx* type structures for beryllaboranes.

to cage bonding. With one electron from each bridge hydrogen involved in cage bonding, the total electron count for the cage is 16 or $n + 2$ electron pairs (n = number of vertices) as observed for *nido*-borane and -carborane species.

The description of the bonding about beryllium in B_5-$H_{10}BeBH_4$ and $B_5H_{10}BeB_5H_{10}$ presents some problems. Beryllium is commonly found in a tetrahedral environment which allows the bonding to be described using sp^3 hybrid orbitals from the beryllium. Although the precise coordination which should be defined for beryllium in $B_5H_{10}BeBH_4$ and $B_5H_{10}BeB_5H_{10}$ is not clear, it is apparently more complex than tetrahedral. As noted above, arguments can be made for approximate trigonal-bipyramidal and octahedral environments for beryllium in $B_5H_{10}BeBH_4$ and $B_5H_{10}BeB_5H_{10}$, respectively. If these are proper representations of the coordination of beryllium, it would seem that beryllium is somewhat orbitally deficient in these compounds.

The orbitally deficient character of $B_5H_{10}BeBH_4$ and $B_5H_{10}BeB_5H_{10}$ is exemplified by the application of the *styx* bonding description[16] used for boranes and carboranes. For neutral beryllaboranes $Be_uBe_vB_pH_{p+q+u}$ with u beryllium atoms, each having a single external two-electron bond, and v commo beryllium atoms, as in $Be(B_3H_8)_2$ or $B_5H_{10}BeBH_4$, the equations of balance are modified to account for the one less electron available from beryllium than from boron and

for the change in orbital distribution. The results are $s + x = q$, $s + t = p + 2u + 2v$, and $t + y = p + u/2 + v - q/2$. Several reasonable *styx* representations of known beryllaborane species are shown in Figure 5. The 4002 structure for doubly hydrogen bridged monomeric $Be(BH_4)_2$ (Figure 5a) and the 8022 structure for $Be(B_3H_8)_2$ (Figure 5c) are straightforward. However, the other species present a problem and may reflect the orbital deficiency of beryllium in these species. The triple-hydrogen-bridged $Be(BH_4)_2$ structure (Figure 5b), which is one of those supported by experimental evidence,[17] would require an unacceptable 6-220 formulation based on the number of bridge hydrogens. The structure of $B_5H_{10}BeBH_4$ dictates a 7121 *styx* formulation of which two possibilities exist (Figure 5d, e), neither of which are wholly acceptable. In Figure 5d, no bonding interaction is observed between B(1) and Be, contrary to observed results. In Figure 5e, resonance structures are required if no more than four bonding interactions to beryllium are allowed. Similar limitations apply in the case of $B_5H_{10}BeB_5H_{10}$ (Figure 5f, g).

Thus, conventional valence bond descriptions of beryllaboranes seem to be unacceptable. The unusual coordination around the beryllium may result from electrostatic interactions between the beryllium and the boron cage, analogous to the ionic character used to describe the interactions in solid $Be(BH_4)_2$.[10] A recent theoretical study of $(C_5H_5)_2Be^{18}$ with two η^5-C_5H_5 rings has been interpreted to indicate that three bonding interactions exist between beryllium and each C_5H_5 ring. Localized three center-bonding interactions were used to suggest a total of six localized molecular orbitals at the beryllium. The $B_5H_{10}BeB_5H_{10}$ structure seems to require six bonding interactions about beryllium as well, one to each apical boron and one to each basal boron–bridge hydrogen combination. Thus, the beryllium bonding interactions in these $B_5H_{10}Be$ species are unusual, if not unique, and a better theoretical understanding is desirable.

References and Notes

(1) D. F. Gaines and J. L. Walsh, *Inorg. Chem.*, preceding paper in this issue.
(2) R. A. Sparks et al., "PĪ Autodiffractometer Operations Manual", Syntex Analytical Instruments Division, Cupertino, Calif., 1970.
(3) MULTAN (G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr., Sect. B*, **26**, 274 (1974)).
(4) Computer programs used in the structural analysis were written by J.C.C. Plots were made using ORTEP (C. K. Johnson).
(5) For nonhydrogen atoms, the scattering factors of H. P. Hanson et al., *Acta Crystallogr.*, **17**, 1040 (1964), were used. For hydrogen atoms, scattering factors of R. F. Stewart et al., *J. Chem. Phys.*, **42**, 3175 (1965), were used.
(6) (a) W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965); (b) G. S. Pawley, *Acta Crystallogr., Sect. A*, **26**, 691 (1970).
(7) W. J. Dulmage and W. N. Lipscomb, *Acta Crystallogr.*, **5**, 260 (1952).
(8) L. R. Lavine and W. N. Lipscomb, *J. Chem. Phys.*, **22**, 614 (1954); E. Moore, Jr., R. E. Dickerson, and W. N. Lipscomb, *J. Chem. Phys.*, **27**, 209 (1957).

(9) F. L. Hirschfeld, K. Eriks, R. E. Dickerson, E. L. Lippert, Jr., and W. N. Lipscomb, *J. Chem. Phys.*, **28**, 56 (1958).
(10) D. S. Marynick and W. N. Lipscomb, *Inorg. Chem.*, **11**, 820 (1972).
(11) J. C. Calabrese, D. F. Gaines, S. J. Hildebrandt, and J. H. Morris, *J. Am. Chem. Soc.*, **98**, 5489 (1976).
(12) D. F. Gaines, J. L. Walsh, and D. F. Hillenbrand, *J. Chem. Soc., Chem. Commun.*, 224 (1977), and references therein.
(13) R. N. Grimes, "Carboranes", Academic Press, New York, N.Y., 1970.
(14) (a) G. J. Long and S. G. Shore, Abstracts, 164th National Meeting of the American Chemical Society, New York, N.Y., 1972, No. INOR 143; (b) G. J. Long, Ph.D. Thesis, The Ohio State University, Columbus, Ohio, 1973.
(15) K. Wade, *Chem. Br.*, **11**, 177 (1975).
(16) (a) E. L. Muetterties, Ed., "Boron Hydride Chemistry", Academic Press, New York, N.Y., 1975, p 88. (b) W. N. Lipscomb, *Acc. Chem. Res.*, **6**, 257 (1973).
(17) (a) J. W. Nibler, *J. Am. Chem. Soc.*, **94**, 3349 (1972); (b) G. Gundersen, L. Hedberg, and K. Hedberg, *J. Chem. Phys.*, **59**, 3777 (1973).
(18) D. S. Marynick, *J. Am. Chem. Soc.*, **99**, 1436 (1977).

Structural Studies of Coordination Compounds. A Joint NQR and X-Ray Investigation of Trialkylphosphine–Gallium Trichloride Adducts

JOHN C. CARTER, GÉRARD JUGIE,* RENÉE ENJALBERT, and JEAN GALY

The temperature dependence of the ^{35}Cl NQR spectra of trimethyl- and triethylphosphine–gallium trichloride adducts and the crystal structure of the trimethyl compound at 297 and 223 K are reported. The NQR data, which indicate that the phosphines are very good donors toward $GaCl_3$, are interpreted by means of the Townes and Daily treatment, and a simple vibrational analysis by computer curve fitting is described. The tendency toward equivalence of the three chlorines in the vicinity of 420 K is tentatively explained by conformational changes and the onset of hindered molecular rotation. The crystal structure of $(CH_3)_3P \cdot GaCl_3$ shows that the space group is $P2_1/m$ with $a = 7.630$ (7) Å, $b = 10.465$ (9) Å, $c = 6.510$ (9) Å, $\beta = 113.86$ (9)° at 297 K, and $Z = 2$. The structure is solved by standard methods based on two sets of reflections collected at 297 and 223 K with final agreement indexes of 6.3 and 3.8%. An unusual feature is that the molecules adopt an eclipsed rather than staggered conformation. Comparison of the unit cell parameters with those of analogous compounds reveals an unusually short b axis and small cell volume resulting from the rearrangement to a more compact structure. It is proposed that, within the series considered, molecular size influences the conformation adopted and hence the possibility of an energetically favorable contraction; a critical b-axis length is postulated above which rearrangement is possible.

Introduction

While conducting a systematic investigation of addition compounds of the type $R_nD \cdot ACl_3$, with $R = CH_3$ or C_2H_5, D = O, S, N, P, or As, and A = B, Al, or Ga, we have generally observed different line multiplicities for the ^{35}Cl nuclear quadrupole resonance spectra of the ethyl and methyl compounds.[1] Three signals of equal intensity are normally found for the ethyl adducts while the spectra of the methyl complexes usually consist of two lines, having intensities corresponding to a 2:1 ratio of inequivalent chlorine sites, which strongly indicates that a molecular plane of symmetry is a feature common to the structures of the latter compounds.

Previous x-ray diffraction studies of members of the series have been confined to the trimethylamine and trimethylphosphine adducts of boron trichloride[2,3] and trimethylamine–aluminium trichloride.[4] No crystal structure of a gallium analogue has been reported although gas-phase electron diffraction measurements on related compounds are known.[5] Broad-line NMR and NQR variable temperature data for trimethylamine boron trichloride have been explained by Gilson and Hart in terms of hindered molecular rotation.[6] Apparently this is in conflict with the published x-ray structure,[2] in which the atomic positions are well defined; however, the difficulty may possibly be resolved if the difference in time scale of the experiments is considered and a suitable rotational transition rate postulated.

For these reasons we decided that a joint study of other compounds in the series, by NQR and x-ray diffraction at several temperatures, would be of interest. Since, to our knowledge, no other crystal structure of a coordination compound involving the gallium–phosphorus bond has been reported, trimethylphosphine–gallium trichloride was chosen to be the subject of this investigation.

Experimental Section

Preparation of Samples. The trialkylphosphines were obtained by the action of phosphorus tribromide on the appropriate Grignard reagent.[7] Both adducts were prepared by the dropwise addition of a slight excess of the ligand, dissolved in dichloromethane, to a well-agitated solution containing 10 g of commercial (99.99%) gallium trichloride in the same solvent at 250 K under a strictly controlled dry argon atmosphere in a general purpose vacuum-line apparatus. After returning to ambient temperature overnight, the reaction mixture was filtered by means of a glass sinter, integral to the apparatus, and all volatile material was removed by vacuum. The triethyl adduct, which is moderately soluble in dichloromethane, was purified by recrystallization at room temperature with a gentle current of dry argon providing controlled evaporation of the solvent; this method has proved successful in producing samples of compounds, sensitive to atmospheric reagents, with the high bulk crystallinity desirable for NQR spectroscopy. No satisfactory solvent for trimethylphosphine–gallium trichloride was found but the initial reaction product was of sufficient crystallinity to permit the NQR determinations to be made without further treatment. A small quantity of this material