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Preparation and X-ray Structure of 2-Tetrahydroborato-2-berylla-nido-hexaborane(11): Insertion of Beryllium into a Borane Cage

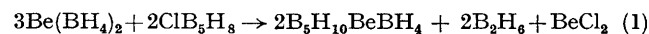
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Summary Reaction of beryllium borohydride with 1-chloropentaborane(9) results in insertion of a beryllium atom into the borane cage to give 2-tetrahydroborato-2-berylla-nido-hexaborane(11).

ALTHOUGH carbon, with atomic number one greater than boron, is known to form a wide variety of carbon-boron cage compounds, compounds with beryllium, with atomic number one less than boron, as part of the boron cage are virtually unknown.¹ Few beryllium-boranes of any kind are known.¹⁻⁴

Reaction of beryllium borohydride² with 1-chloropentaborane(9)⁵ at room temperature *in vacuo* produces a beryllium-borane cage compound, 2-tetrahydroborato-2-berylla-nido-hexaborane(11), $B_5H_{10}BeBH_4$. The product is most conveniently prepared using a slight excess of $Be(BH_4)_2$ and is purified by treating the reaction mixture with solid sodium chloride to remove the excess of $Be(BH_4)_2$, followed by high vacuum trap-to-trap distillation. The stoichiometry appears to be as in reaction (1). The product is



thermally stable at room temperature but is expected to be air- and moisture-sensitive; m.p. $-22^\circ C$; v.p. 2 Torr at $25^\circ C$.

The ^{11}B Fourier transform (F.T.) n.m.r. spectrum of $B_5H_{10}BeBH_4$ in $[^2H_8]$ toluene solution at 86.7 MHz consists of the following resonances (assignments have been made as indicated, chemical shifts are relative to $BF_3 \cdot Et_2O$): doublet at $\delta -8.2$ p.p.m. (J_{B-H} 163 Hz), B(4), B(5); pseudotriplet at $\delta +9.8$ p.p.m., B(3), B(6); quintet at δ

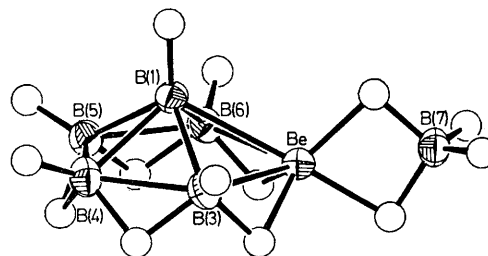


FIGURE. Static molecular structure of $B_5H_{10}BeBH_4$ showing 50% probability contours for the atomic vibration ellipsoids for nonhydrogen atoms. The hydrogen atoms are represented by spheres of 0.14 \AA radius.

+ 33.4 p.p.m. (J_{B-H} 85 Hz), B(7); doublet at $\delta +53.4$ p.p.m. (J_{B-H} 144 Hz), B(1). The pseudotriplet is resolved using line-narrowing techniques into a doublet of doublets interpreted as coupling of B(3) [or B(6)] to the terminal hydrogen

on B(3) [or B(6)] and to the bridge hydrogen between B(3) [or B(6)] and the beryllium atom [$J_{\text{B-H}}$ (terminal) 135 Hz, $J_{\text{B-H}}$ (bridge) 83 Hz]. The quintet resonance results from equivalent coupling of the four borohydride hydrogens to B(7) and indicates rapid exchange of these hydrogens on the n.m.r. time scale, as is observed for beryllium borohydride.⁶

The ¹H F.T. n.m.r. spectrum of B₅H₁₀BeBH₄ at 270 MHz shows three quartets for terminal hydrogens attached to B(1) (δ -0.25 p.p.m.), B(3) and B(6) (δ +2.25 p.p.m.), and B(4) and B(5) (δ +3.40 p.p.m.). In addition, one quartet (δ +1.24 p.p.m.) is observed for the borohydride hydrogens and another (δ +1.21 p.p.m.) for the bridging hydrogens between B(3) or B(6) and the beryllium atom. Two broad resonances of areas *ca.* 2:1 (δ -1.61 and -2.56 p.p.m.) correspond to the three remaining bridge hydrogens.

† *Crystal data*: B₅H₁₀BeBH₄, monoclinic, space group $P2_1/n$; $a = 10.632$, $b = 8.337$, $c = 8.604$ Å, $\beta = 98.09^\circ$; $Z = 4$; $U = 754.9$ Å³. A single crystal of B₅H₁₀BeBH₄ was grown in a sealed Pyrex capillary and mounted on a Syntex P1 automated diffractometer, and 2562 reflections were collected at -165 °C using Mo- K_α radiation. Data reduction yielded 1274 independent observed reflections. All atomic positions were refined anisotropically to $R_1 = 4.7$ and $R_2 = 5.5\%$.

The n.m.r. results indicated that a unique pentaborane (9) cage-opening reaction had occurred but did not define the bonding of the beryllium to the boron cage. Therefore, an X-ray structural determination was undertaken.⁷ The structure, shown in the Figure, consists of a pentagonal pyramid in which the beryllium occupies a basal atom position. Distances indicate the beryllium is bonded to B(1), B(3), B(6), and B(7) [Be-B(1) 2.03; Be-B(3) 1.97; Be-B(6) 1.98; Be-B(7) 1.92 Å]. The borohydride group is bonded to the beryllium atom by two bridging hydrogen atoms, similar to the borohydride groups in solid Be(BH₄)₂.⁸

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