Synthesis and Structure of New Aminopentaborane Derivatives

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The field of group V (15) heteroborane chemistry has been an active one for several years, though boron hydride clusters with boron directly bonded to nitrogen in a covalent, nondative sense remain scarce. Examples of the few known compounds include bridging amino groups in $(EtNH_2)B_8H_{11}(NHEt)$[1] and in *arachno*-$B_{10}H_{12}(N_3)(NH_2)$.[2] Paetzold et al. have also reported aza-*arachno*-heptaborane and diaza-*nido*-hexaborane structures,[3] the first nitrogen-containing borane clusters of intermediate size.

Our examination of nitrogen–borane cluster bond formation using intermediate-sized borane clusters has led to syntheses of several new compounds, including a double-nitrogen-bridged tetraborane(10), μ-$(Me_2N)_2B_4H_8$,[4] from $B_3H_8^-$ salts and Me_2NBBr_2, a C–N-bridged *arachno* pentaborane, $(Me_2NCH_2)B_5H_8$,[5] prepared from $B_5H_8^-$ salts and $(Me_2NCH_2)I$, and μ-(t-Bu(H)C=N)B_5H_8,[6] prepared by hydroboration of *tert*-butyl cyanide using pentaborane(9), B_5H_9. Here we report extensions of these investigations to reactions of selected secondary amines with 2-bromopentaborane(9), 2-BrB_5H_8, which produce the first terminally bonded amino derivative of a midsized borane cluster, 2-(bis(trimethylsilyl)amino)pentaborane(9), 2-$[(Me_3Si)_2N]B_5H_8$, and the first *hypho* derivative of pentaborane(11), 2,3-μ-(*tert*-butylamino)pentaborane(11), 2,3-μ-(t-BuNH)B_5H_{10}, which has been characterized by single-crystal X-ray analysis.

Hexamethyldisilazane reacts with 2-BrB_5H_8 in CH_2Cl_2 solution upon warming from −78 °C to room temperature to form 2-(bis(trimethylsilyl)amino)pentaborane(9), 2-$[(Me_3Si)_2N]B_5H_8$ (**1**), in ca. 52% yield. The other major boron-containing products are a μ-aminodiborane, pentaborane(9), $B_3H_7{\cdot}NH(SiMe_3)_2$, and several different borazines. These byproducts were identified by comparison of ^{11}B NMR spectra of the product mixture before fractionation procedures and of the residue in the reaction pot after fractionation (a spectrum consistent with a $B_3H_7{\cdot}L$ species) with published data.[7] We believe HBr is also a byproduct, although it has not yet been directly identified. If formed, the HBr probably reacts readily with other species in solution. Removal of HBr as it is formed, by either chemical or physical means, may greatly improve the yield of **1**.

Isolation of **1** from all except the borazines is accomplished via standard high-vacuum fractionation techniques,[8] but rigorous removal of all borazine requires painstaking distillation on a variable-temperature high-vacuum column. From such a distillation a sample of **1** contaminated with only a trace of a *hypho*-2,3-μ-aminopentaborane(11) may be isolated as a colorless air-sensitive liquid. 2-$[(Me_3Si)N]B_5H_8$ appears to be stable at room temperature both neat and in solution.

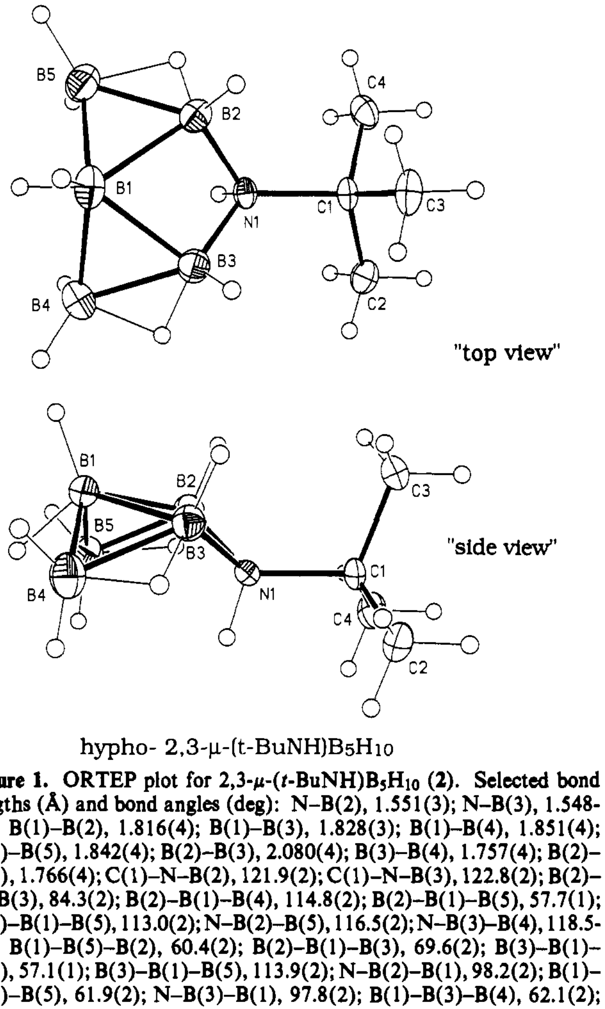

Figure 1. ORTEP plot for 2,3-μ-(t-BuNH)B_5H_{10} (**2**). Selected bond lengths (Å) and bond angles (deg): N-B(2), 1.551(3); N-B(3), 1.548(3); B(1)-B(2), 1.816(4); B(1)-B(3), 1.828(3); B(1)-B(4), 1.851(4); B(1)-B(5), 1.842(4); B(2)-B(3), 2.080(4); B(3)-B(4), 1.757(4); B(2)-B(5), 1.766(4); C(1)-N-B(2), 121.9(2); C(1)-N-B(3), 122.8(2); B(2)-N-B(3), 84.3(2); B(2)-B(1)-B(4), 114.8(2); B(2)-B(1)-B(5), 57.7(1); B(4)-B(1)-B(5), 113.0(2); N-B(2)-B(5), 116.5(2); N-B(3)-B(4), 118.5(2), B(1)-B(5)-B(2), 60.4(2); B(2)-B(1)-B(3), 69.6(2); B(3)-B(1)-B(4), 57.1(1); B(3)-B(1)-B(5), 113.9(2); N-B(2)-B(1), 98.2(2); B(1)-B(2)-B(5), 61.9(2); N-B(3)-B(1), 97.8(2); B(1)-B(3)-B(4), 62.1(2); B(1)-B(4)-B(3), 60.8(2).

The ^{11}B NMR spectrum of 2-(bis(trimethylsilyl)amino)pentaborane(9) consists of four resonances: a singlet at +15.22 ppm (B(2)), a doublet at −14.09 ppm (J = 147 Hz, B(3,5)), a doublet at −27.36 ppm (J = 155 Hz, B(4)), and a doublet at −52.51 ppm (J = 165 Hz, B(1)). Such a spectrum is consistent with a *nido* pentaborane cage substituted with a strong electron-withdrawing group at a basal position.[9] The downfield shift at the 2-position (relative to B_5H_9) accompanied by an upfield shift at the 4-position, a cross-cage or antipodal effect, has been the subject of several papers, mostly in reference to *closo* deltahedral clusters.[10]

The ^1H NMR spectrum of **1** shows a large singlet at +0.24 ppm corresponding to the trimethylsilyl groups on nitrogen, superimposed over part of a quartet centered at +0.85 ppm which corresponds to the apical B(1) hydrogen. The resonances due to the basal terminal protons at the equivalent 3,5-positions and the 4-position produce overlapping quartets centered at +2.35 ppm

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(B(3,5)–H) and +2.02 ppm (B(4)–H), respectively. A broad hump at −2.53 ppm corresponds to the three bridge protons. The electron impact mass spectrum of **1** shows a fragmentation pattern consistent with the proposed structure. The parent ion corresponding to the formula $^{12}C_6{}^1H_{26}{}^{11}B_4{}^{10}B^{14}N^{28}Si_2$ was observed at 222.211 amu (calculated: 222.209 amu).

The reaction of (*tert*-butylamino)trimethylsilane with $2\text{-}BrB_5H_8$ proceeds in CH_2Cl_2 solution upon warming from −78 °C to room temperature to form a 2-aminopentaborane similar to **1** and *hypho*-2,3-μ-(*tert*-butylamino)pentaborane(11), 2,3-μ-(*t*-BuNH)-B_5H_{10} (**2**). A ^{11}B NMR spectrum of the product mixture showed only small amounts of borazines and other unidentified boron-containing byproducts. The 2-aminopentaborane does not appear to be separable from **2** using standard high-vacuum techniques. However, unlike the 2-aminopentaborane, **2** does crystallize when distilled under high vacuum and thus may be separated physically. The X-ray structure of **2** is presented in Figure 1.[11]

The ^{11}B NMR spectrum of **2** consists of three resonances: a triplet at −9.03 ppm (J = 122 Hz, B(4,5)), a doublet of doublets at −17.79 ppm (J_1 = 134 Hz, J_2 = 45 Hz, B(2,3)), and a doublet of doublets at −58.59 ppm (J_1 = 136 Hz, J_2 = 46 Hz, B(1)). Two unique features are immediately apparent in this spectrum. First, the magnitude of the smaller (J_2) B–H couplings observed in both the B(2,3) and the B(1) signals is typical of that observed for a B–H(bridge) interaction, but such coupling is often not observed in intermediate-sized clusters. The smaller coupling in the basal resonances presumably arises from interaction with the bridge hydrogens shown in the figure; the coupling at the apex probably results from interaction with the endo hydrogen on B(1). Second, the extreme upfield shift of the B(1) resonance is evidence of an unusually high shielding magnetic environment. The ^1H NMR spectrum of **2** is consistent with the solid-state structure. The chemistries of **1** and **2** are being explored, as are the mechanisms of their formation and the effect of starting amine basicity on the product mixture.

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Supplementary Material Available: Spectra for compound **1** (^{11}B NMR, ^1H NMR, and mass) and compound **2** (^{11}B NMR) and, for the X-ray structure, tables of atomic positional parameters, interatomic distances and angles, thermal parameters, crystal data, and data collection and refinement parameters (10 pages). Ordering information is given on any current masthead page.

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(11) It has been brought to our attention by a reviewer that a *hypho* derivative of a dodecahedron may be indistinguishable from an *arachno* derivative of a pentagonal bipyramid. However, for the present discussion we are not considering nitrogen to be a cluster atom; therefore, electron-counting rules mandate naming the compound as a *hypho* structure.