Synthesis and Reactivity of New Aminopentaboranes

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Reactions of 2-XB_5H_8 (X = Br or Cl) with secondary or tertiary silylamines proceed with elimination of hydrogen halides and/or halosilanes and attachment of amino groups to the clusters. Reaction of 2-BrB_5H_8 with $(Me_3Si)_2NH$ produces 2-$[(Me_3Si)_2N]B_5H_8$ in 57% yield. Other bis(silyl)amines react analogously. With (*t*-Bu)(Me_3Si)NH, 2-BrB_5H_8 produces 2-$[(Me_3Si)$(*t*-Bu)$N]B_5H_8$ and *hypho*-2,3-μ-(*t*-BuNH)B_5H_{10}. (*t*-Bu)(Et_3Si)NH reacts analogously. Low temperature analysis of the (*t*-Bu)(Me_3Si)NH reaction in dichloromethane solution via ^{11}B NMR spectroscopy discloses a dual reaction pathway producing a 2-aminopentaborane and a proposed *arachno*-2,3-μ-(*t*-BuNH)B_5H_8 intermediate which subsequently reacts with boranes to form *hypho*-2,3-μ-(*t*-BuNH)B_5H_{10}. When the above reaction is carried out in B_5D_9 solution, normal *nido*-[(*t*-Bu)(Me_3Si)N]B_5H_8 and partially deuterated *hypho*-2,3-μ-(*t*-BuNH)B_5H_{10} is formed. Reaction of 2-$[(Me_3Si)_2N]B_5H_8$ with BCl_3 produces 2-$[(Me_3Si)_2N{\cdot}BCl_3]$-$B_5H_8$, and with (*t*-Bu)CN produces 2,3-μ-(*t*-BuCH═N)-2-$[(Me_3Si)_2N]B_5H_7$.

Introduction

Two general routes to incorporation of nitrogen containing moieties into boron hydride clusters have been reported. Cluster insertion processes, in which a nitrogen-containing moiety is incorporated into a preexisting cluster with the formation of boron−nitrogen bonds, have been employed in the formation of many larger nitrogen-containing boranes.[1] Cluster assembly reactions, in which a nitrogen-containing heteroborane is assembled from fragments that already contain boron−nitrogen bonds, have found application in the formation of several medium-sized nitrogen-containing heteroboranes, such as the diaza-*nido*-hexaboranes reported by Paetzold and co-workers.[2] Routes to new medium-sized nitrogen-containing heteroboranes *via* cluster modification and insertion processes have been of interest to us for some time.

We report herein the formation of amino nitrogen−boron linkages to pentaborane clusters by metathesis-driven reactions of halogenated pentaborane derivatives with silylamines. In all but one case, secondary silylamines are employed. The products of these reactions display interesting structural characteristics, NMR properties and reactivity. A study of the mechanism of the reaction between 2-BrB_5H_8 and (*t*-Bu)(Me_3Si)NH using variable temperature ^{11}B NMR spectroscopy has revealed identifiable intermediate species in solution.

Results and Discussion

Reactions of 2-halopentaboranes, 2-XB_5H_8 (where X= Br or Cl), with secondary or tertiary silyl amines (RR′NR″, where R = silyl, R′ = alkyl or silyl, and R″= H or alkyl) proceed with elimination of hydrogen halides and/or halosilanes and attachment of amino (NR_2; R = alkyl, silyl, or H) groups to the clusters. These products are the first amino derivatives of medium-sized boron hydrides. The position of amino substitution on the clusters and resulting cluster framework structures seem to depend on the identity of the substituents remaining on the nitrogen atom after reaction.

Synthesis and Characterization of 2-Aminopentaboranes. Hexamethyldisilazane, $(Me_3Si)_2NH$, reacts with 2-BrB_5H_8 in dichloromethane solution to form *nido*-2-(bis(trimethylsilyl)-amino)pentaborane(9), 2-$[(Me_3Si)_2N]B_5H_8$ **(1)**,[3] as represented in eq 1. A 57% yield of ca. 95% purity **1** (based on ^{11}B NMR)

$$2\text{-}BrB_5H_8 + (Me_3Si)_2NH \rightarrow 2\text{-}[(Me_3Si)_2N]B_5H_8 + HBr + \text{byproducts} \quad (1)$$

is isolated by distillation on the vacuum line. The other major boron-containing products are a μ-aminodiborane,[4] B_5H_9, an amine adduct of B_3H_7,[5] and at least two different borazines.[6] We believe HBr is also a product, although it has not been directly identified. The reaction of hexamethyldisilazane with 2-ClB_5H_8 proceeds similarly. Isolation of **1** from all of the byproducts except the borazines is easily accomplished by standard high-vacuum distillation, but rigorous removal of all borazines requires painstaking distillation on a variable-temperature high-vacuum column.[7] Compound **1**, a viscous, air-sensitive liquid, appears to be stable *in vacuo* both neat and in solution at room temperature. Thermolysis of **1** proceeds slowly at 75 °C and more rapidly at 100 °C to produce B_5H_9, H_2, and other unidentified byproducts.

The ^{11}B NMR spectrum of **1**, Table 1, is consistent with that expected for a nido pentaborane cage with an electron withdrawing group substituted at a basal position.[8] The downfield shift at the B(2) position (relative to B_5H_9) is accompanied by an upfield shift at the B(4) position, as is observed in several other pentaborane(9) derivatives with terminal basal substitution.[8,9] This cross-cage (antipodal) effect has been the subject of several prior reports.[10]

The ^{1}H NMR spectrum of **1** contains the expected resonances corresponding to the Me_3Si groups on N, terminal H on apical

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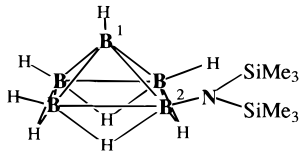
Table 1. ^{11}B NMR Chemical Shifts for 2-Aminopentaboranes, 2-RR′NB_5H_8 **(1**−**6)**

R/R′	B(1), ppm (doublet)	B(2), ppm (singlet)	B(3,5), ppm (doublet)	B(4), ppm (doublet)
Me_3Si/Me_3Si **(1)**	−52.51	+15.22	−14.09	−27.36
Me_2HSi/Me_2HSi **(2)**	−52.9	+14.3	−15.0	−27.3
(*i*-Bu)Me_2Si/(*i*-Bu)Me_2Si **(3)**	−53.4	+14.5	−14.7	−27.9
Me/Me_3Si **(4)**	−53.9	+18.3	−15.3	−28.0
t-Bu/Me_3Si **(5)**	−52.0	+17.8	−13.2	−26.4
t-Bu/Et_3Si **(6)**	−52.1	+16.4	−13.7	−26.7

and basal B atoms, and the bridge H's. (See figures in Supporting Information). A sketch of the NMR-determined structure of **1** is shown.



(**1**)

The electron impact mass spectrum of **1** shows the parent ion and a fragmentation pattern consistent with the proposed structure.

Synthesis of Other 2-Aminopentaboranes. The reaction of 2-BrB_5H_8 three other bis(silyl)amines was examined in a series of small-scale (NMR tube) pilot reactions. 2-BrB_5H_8 reacts with the bis(silyl)amines $(Me_2HSi)_2NH$, ((*i*-Bu)Me_2-$Si)_2NH$, and $(Me_3Si)_2NMe$ to produce 2-aminopentaboranes **(2**−**4**, respectively). These aminopentaboranes have been identified by comparison of their ^{11}B NMR spectra to that of the fully characterized **1**. The spectra are reported in Table 1. The reaction of ((*i*-Bu)$Me_2Si)_2NH$ with 2-BrB_5H_8 proceeds very slowly, probably for steric reasons. On the basis of the ^{11}B NMR spectrum of the main product, it appears that Me_3SiBr is eliminated in the reaction of $(Me_3Si)_2NMe$ with 2-BrB_5H_8, eq 2. Elimination of methane would produce **1** but the observed

$$2\text{-}BrB_5H_8 + (Me_3Si)_2NMe \rightarrow 2\text{-}[(Me)(Me_3Si)N]B_5H_8\ \mathbf{(4)} + Me_3SiBr + \text{byproducts} \quad (2)$$

spectrum displays slightly different chemical shifts, consistent with the formation of 2-[(Me)(Me_3Si)N]B_5H_8 **(4).**

The reactions of 2-BrB_5H_8 with the secondary amines (*t*-Bu)(Me_3Si)NH and (*t*-Bu)(Et_3Si)NH produce the 2-aminopentaboranes **5** and **6**, whose ^{11}B NMR spectra are reported in Table 1.

Synthesis and Characterization of *hypho*-2,3-μ-(*t*-BuNH)-B_5H_{10} (7). The reaction of (*t*-Bu)(Me_3Si)NH with 2-BrB_5H_8, in the presence of excess B_5H_9 in CH_2Cl_2 solution, proceeds upon warming from −78 °C to room temperature to form a 2-aminopentaborane, 2-[(*t*-Bu)(Me_3Si)N]B_5H_8 **(5)**, and *hypho*-2,3-μ-(*tert*-butylamino)pentaborane(11), 2,3-μ-(*t*-BuNH)B_5H_{10} **(7)**, the first *hypho* derivative of pentaborane(11). Pentaborane-(9) does not react with the starting materials directly, but acts as a B−H source, reacting with an intermediate in the production of **7** (eq 3). It appears that this intermediate reacts indiscriminatly with B−H bonds present in solution.

$$2\text{-}BrB_5H_8 + (t\text{-}Bu)(Me_3Si)NH \rightarrow 2\text{-}[(t\text{-}Bu)(Me_3Si)N]B_5H_8\ \mathbf{(5)} + HBr + Me_3SiBr + 2,3\text{-}\mu\text{-}(t\text{-}BuNH)B_5H_{10}\ \mathbf{(7)} + \text{byproducts} \quad (3)$$

(10) Felner, T. P.; Czech, P. T.; Fenske, R. F. *Inorg. Chem.* **1990**, *29*, 3103 and references therein.

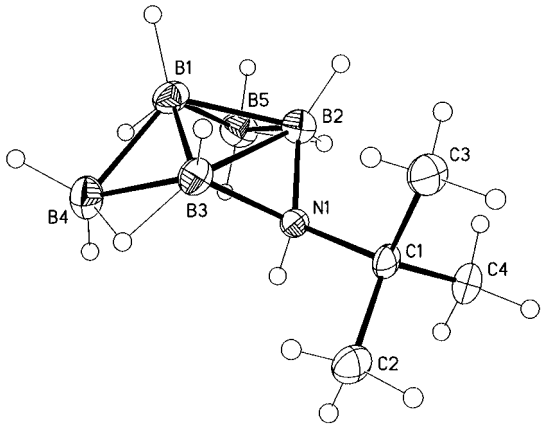


Figure 1. ORTEP plot of the solid state structure of 2,3-μ-(*t*-BuNH)-B_5H_{10} **(7)**. Reprinted with permission from ref 3. Copyright 1993 American Chemical Society.

An ^{11}B NMR spectrum of the product mixture showed only small amounts of borazines and other boron-containing byproducts. Compound **5** is not totally separable from **7** using standard high-vacuum techniques, but unlike **2**, **7** crystallizes when distilled under high vacuum and thus may be separated physically. Treatment of a mixture of **5** and **7** with methanol results in the destruction of **5**, while **7** reacts slowly or not at all. Compound **7** can then be separated from the methanolysis products by high-vacuum distillation in 23% yield, based on starting 2-BrB_5H_8. The stability of **7** in the presence of alcohols is quite unexpected for a medium-sized boron hydride, as most react vigorously, sometimes explosively, with alcohols and water. The origin of this stability is not yet understood. Compound **7** is quite stable in pure form and in solution and survives vaporization through a hot tube at 150 °C. The X-ray structure of **7** is shown in Figure 1. Selected bond distances and angles, atomic coordinates and crystallographic data are available elsewhere.[3]

The ^{11}B NMR spectrum of **7** 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 the coupling observed 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. However, such coupling is often not observed in intermediate-sized clusters. The smaller coupling at −17.79 ppm is assigned to interaction of the basal borons, B(2,3), with the bridge hydrogen atoms. Second, the smaller coupling at −58.59 ppm is assigned to interaction of the apical B(1) boron with the "endo" hydrogen on B(1). The magnitude of the coupling constant of this "endo" hydrogen may be a result of partial association with the basal boron atoms in the solution structure.

In an NMR tube experiment, the reaction of 2-BrB_5H_8 with (*t*-Bu)(Et_3Si)NH was shown to proceed in a fashion analogous to the reaction with (*t*-Bu)(Me_3Si)NH. Resonances in the ^{11}B NMR spectrum of the products of this reaction, in the presence

of excess amine, indicate a 2-aminopentaborane, presumably 2-[(Et_3Si)(*t*-Bu)N]B_5H_8 **(6)** and compound **7**.

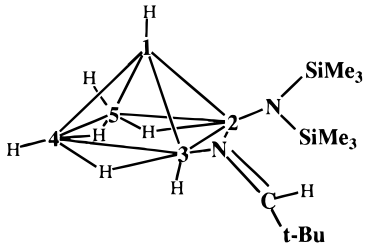
Reaction of 2-BrB_5H_8 with Diisopropylamine. The secondary amine (i-Pr)$_2$NH reacts with 2-BrB_5H_9 to give $B_{10}H_{14}$, identified on the basis of its ^{11}B NMR spectrum,[11] as the primary product. No 2-aminopentaborane or 2,3-μ-aminopentaborane species are isolated from the product mixture. Thus, the influence of the silyl groups in the reactions of silyl amines with 2-halopentaboranes appears to be mainly electronic, rather than steric, in nature. In the reaction of 2-BrB_5H_8 with diisopropylamine, $B_{10}H_{14}$ is believed to be formed by complex cluster decomposition and growth processes that are aided by the moderately strong Lewis base (i-Pr)$_2$NH.

Reactivity Studies of 2-[(Me_3Si)$_2$N]B_5H_8. Reactivity studies on compound **1** were undertaken to explore the effects of amino substitution on the pentaborane skeleton and to synthesize new nitrogen-containing boranes. The reactivity of **1** as an amine is demonstrated in the formation of a Lewis base adduct with BCl_3. The presence of the amino group on the base of the pentaborane cage is found to have a profound effect on the cluster's ability to hydroborate *t*-BuCN. In reactions of **1** with many reagents, cluster decomposition is observed.

Reaction of 2-[(Me_3Si)$_2$N]B_5H_8 with BCl_3. Reaction of BCl_3 with an excess of **1** appears to produce the amine−BCl_3 adduct 2-[(Me_3Si)$_2$N·BCl_3]B_5H_8 **(8)**, based on analysis of the ^{11}B NMR spectrum of the reaction mixture. This spectrum shows residual starting material **1** and a singlet at +36.05 ppm which presumably corresponds to a BCl_3 moiety coordinated through the nitrogen lone pair in **8**, a singlet at +4.58 ppm (B(2)), a doublet at −14.62 ppm (J = 155 Hz, B(3,5)), a doublet at −24.56 ppm (J = 155 Hz, B(4)), and a doublet at −52.73 ppm (J = 164 Hz, B(1). The ^{11}B NMR spectrum of the reaction after 2 h at room temperature showed resonances corresponding to the adduct, although they were of very low intensity. Thus, **1** appears to function as a relatively weak Lewis base. The assumption of weak nitrogen basicity is further supported by the failure of **1** to displace tetrahydrofuran from BH_3·THF in another NMR tube experiment. Still, the reaction of **1** with BCl_3 is relatively clean and proceeds to completion after 3 days, as evidenced by the disappearance of the resonance corresponding to BCl_3 in the ^{11}B NMR spectrum. It is possible that the extreme downfield shift of the nitrogen-substituted position in **1** results to a large degree from paramagnetic contributions of the type discussed by Fehlner and others.[10] It is interesting to note that the antipodal effect of the amino group is lessened upon adduct formation, as the resonance corresponding to the B(4) position across the cage from the amino group moves downfield by 2.8 ppm upon BCl_3 coordination.

Reaction of 2-[(Me_3Si)$_2$N]B_5H_8 with *t*-BuCN. Reaction of **(1)** with excess trimethylacetonitrile in diethyl ether produces an apparent hydroboration product 2,3-μ-(t-BuCH═N)-2-[(Me_3Si)$_2$N]B_5H_7 **(9)**. The structure proposed for **9** on the basis of 1-dimensional ^{11}B NMR and 2-dimensional ^{11}B−^{11}B COSY NMR spectroscopy is shown. The position of the *tert*-butyl group on the imine function is assumed, based on steric considerations, and the structure shown is one of two possible optical isomers that are indistinguishable by NMR.

Assignment of two of the ^{11}B NMR resonances of **9** is clear: the singlet appearing at +17.39 corresponds to the amino-substituted B(2), and the doublet at −43.84 ppm corresponds to the apical B(1). Assignment of the other three resonances is less straightforward. Analysis of the ^{11}B−^{11}B COSY spectrum (Supporting Information) shows that the only coupling of the



(9)

+17.39 ppm resonance in the COSY spectrum is to the apical resonance (−43.84 ppm) and to the resonance at −17.38 ppm. [In the hypothetical 3,4-μ-imino structure, the +17.39 ppm resonance would be coupled to two other basal resonances and to the apex]. Thus, the 2,3-imino structure appears to be correct, and the resonance at −17.38 ppm is assigned to the B(5) position on **9**. The resonance at −18.06 ppm is assigned to the B(4) position and the +1.09 ppm resonance is assigned to the B(3) position. Coupling between the N-bridged B(2) and B(3) positions is not observed. Although Spencer observed B−P coupling of phosphorous-bridged boron atoms,[12] similar coupling is unlikely in the case of bridging nitrogen, which has a substantial quadrupole moment. It is interesting to note that although the resonance corresponding to the amino-substituted boron in **9** exhibits a downfield chemical shift even more pronounced than in **1**, the effect of the amino group on the B(4) position appears to have been largely eliminated. Cluster symmetry appears to play an important role in the origin of this effect. In previous work in our group, trimethylacetonitrile reacted with unsubstituted pentaborane(9) to form an imino-bridged pentaborane similar to **9**, 2,3-μ-(*t*-BuHC═N)B_5H_8.[13] However, the yield was very low, ca. 2%. Though not isolated, the yield of the hydroboration product in the present case, based on ^{11}B NMR, is much higher. Thus, the amino group in **1** appears to activate the pentaborane cage for reaction with the nitrile.

Survey reactions of **1** with a variety of reagents were carried out in NMR tubes in a similar manner to the reaction with BCl_3. The products of these reactions were identified by comparison of their ^{11}B NMR spectra with published data. Reaction of **1** with diborane in methylene chloride solution was very slow but produced B_5H_9, a μ-aminodiborane,[5] and other minor products. Anhydrous HCl reacted with a tetrahydrofuran/diethyl ether solution of **1**, completely destroying the pentaborane framework; the identifiable boron-containing products appear to be either amine or ether adducts of $HBCl_2$[14] and H_2BCl.[15] Reaction of **1** with $AlMe_3$ in CH_2Cl_2 unexpectedly produced BMe_3[16] as the only boron-containing product.

Reaction Mechanism Studies. The reaction of 2-BrB_5H_8 with (*tert*-butylamino)trimethylsilane, (*t*-Bu)(Me_3Si)NH, has been carried out at low temperatures in the probe of an NMR spectrometer. The reagents were condensed into the NMR tube in an approximate ratio of 2 equiv of (*t*-Bu)(Me_3Si)NH to 1 equiv of 2-BrB_5H_8 with enough deuterated dichloromethane to give a suitable volume of solution. After quick mixing of the

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(13) Coons, D. E. Ph.D. Dissertation, University of Wisconsin−Madison, 1984. The ^{11}B NMR spectrum of 2,3-μ-(*t*-BuHC═N)B_5H_8 consists of overlapping doublets observed at −1.6 and −2.6 ppm which correspond to boron atoms in the 2 and 3 positions but cannot be further distinguished, a doublet at −14.1 ppm (J = 156 ppm, B(4,5)) and a doublet at −51.5 ppm (J = 161 Hz, B(1)).

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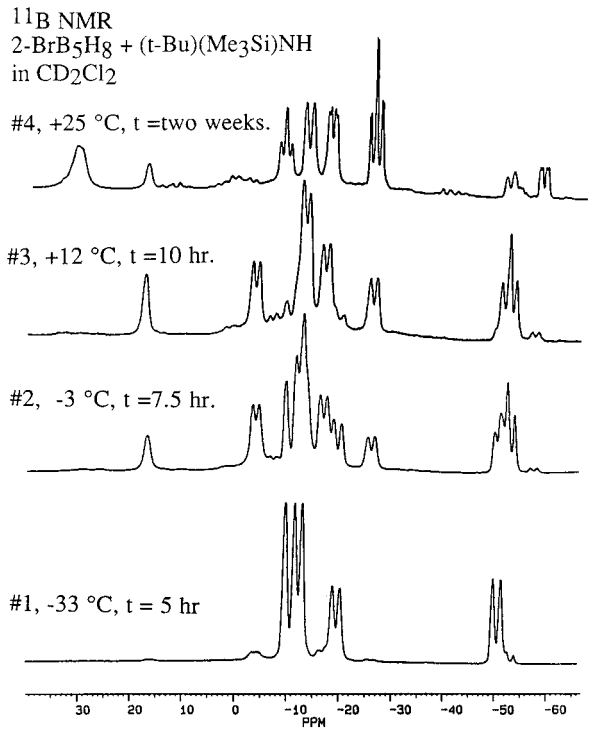


Figure 2. 115.15 MHz ^{11}B NMR spectra recorded during the in-probe reaction of 2-BrB_5H_8 with (*t*-Bu)(Me_3Si)NH in deuterated dichloromethane: spectrum 1, (bottom trace) recorded at −33 °C, 5 h after mixing the reagents; spectrum 2, recorded at −3 °C, 7.5 h after mixing the reagents; spectrum 3, recorded at +12 °C, 10 h after mixing the reagents; spectrum 4, (upper trace) recorded at +25 °C, several weeks after mixing the reagents. See the Discussion for a detailed description of these spectra.

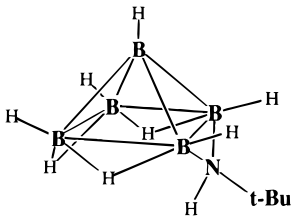
reagents, the NMR tube was cooled to −78 °C and inserted into the spectrometer probe, also at −78°C. After an initial ^{11}B NMR spectrum was recorded, a series of spectra were recorded as the probe was warmed in 15 °C steps to room temperature. A series of six ^{11}B NMR spectra were recorded during the course of the reaction. Figure 2 shows representative spectra. By analysis of these spectra, an intermediate species present in solution has been identified and the overall reaction has been found to proceed *via* dual reaction pathways.

Spectrum 1, Figure 2, recorded at −33 °C, 5 h after mixing of the reagents, is similar to that of the starting material, 2-BrB_5H_8.[17] Resonances arising from 2-BrB_5H_8 are at −10 (s, B(2)), −12.6 (d, B(3,5)), −19.8 (d, B(4)), and −50.9 ppm (d, B(1)). There is a small resonance just upfield of the apical resonance of 2-BrB_5H_8, and doublets have appeared at −4.1 ppm and about −17 ppm, partially overlapping the B(4) resonance of 2-BrB_5H_8. These resonances were determined to be mutually coupled in a ^{11}B−^{11}B COSY experiment, and are consistent with a substituted pentaborane(9) framework in which the substituent replaces a hydrogen atom in a bridging position between two boron atoms on a basal edge. Such a substitution is observed in the *arachno*-pentaborane μ-2,3-(Me_2P)B_5H_8.[18] The compound corresponding to these resonances (-4.1 ppm and about −17 ppm) is proposed to be a bridge-substituted *arachno*-aminopentaborane species. Also apparent in spectrum 1 are a (broadened) singlet at about +16 ppm and a broadened doublet at about −26.5 ppm; these resonances correspond to the *nido*-2-[(*t*-Bu)(Me_3Si)N]B_5H_8 **(5)** product. Though the resonances in spectrum 1 are broadened it is apparent that the solution contains significantly more of the proposed *arachno*-μ-aminopentaborane than the *nido*-2-aminopentaborane. This provides the first hint that these species are formed in separate processes.

Spectrum 2, Figure 2, was recorded at −3 °C, 7.5 h after mixing of the reagents. The spectrum shows an increasingly complex set of resonances due to the presence of significant amounts of three compounds in solution. The entire spectrum of **5** is now observed, with resonances at +16.9 (s, B(2)), −13.2 (d, B(3,5)), −26.4 (d, B(4)) and −51.9 ppm (d, B(1)). The proposed *arachno*-μ-aminopentaborane resonances have also increased in intensity, and a significant amount of 2-BrB_5H_8 is still present. Also appearing in spectrum 2 is the apical resonance of *hypho*-2,3-μ-(*t*-BuNH)B_5H_{10} **(7)**, a doublet of low intensity at about −58 ppm. At room temperature, this resonance appears as a doublet of doublets.[3]

Spectrum 3, Figure 2, recorded at +12 °C, 10 h after mixing the reagents, shows mainly **5** and the proposed *arachno*-2,3-μ-aminopentaborane, a small amount of **7**, and a minute quantity of 2-BrB_5H_8. The basal resonances of **7**, −9.03 and −17.79 ppm in a pure sample at room temperature,[3] remain mostly masked by larger resonances, and the apical resonance does not yet exhibit all of the coupling observed at room temperature.

Spectrum 4, Figure 2, was recorded after the sample had been at room temperature for several weeks, and thus is representative of the final product distribution. The most significant changes observed from spectrum 3 are the disappearance of the resonances associated with the proposed *arachno*-2,3-μ-aminopentaborane and their replacement by the resonances due to **(2)** at −8.8 ppm (d, B(4,5)), −17.8 ppm (dd, B(2,3)), and −58.6 ppm (dd, B(1)). The replacement of the proposed *arachno*-2,3-μ-aminopentaborane resonances by the resonances of **7** is a strong indication that the disappearing signals correspond to an intermediate in the formation of **7**. The probable formulation of the intermediate is *arachno*-2,3-μ-(*t*-BuNH)B_5H_8 **(10)**, whose expected structure is shown. The resonance due to B(4) in



(10)

compound **5** (d, −26.4 ppm) seems to exhibit a secondary coupling in spectrum 4.

In addition to the signals corresponding to **5** and **7**,the resonance at about +31 ppm (broad) probably corresponds to one or more borazines,[19] while the resonance at −25.9 ppm (triplet of doublets) is characteristic of a μ-aminodiborane, μ-(*t*-BuNH)B_2H_5.[20] These may be byproducts of the transformation of the proposed intermediate **10** into **7**.

Transformation of the proposed *arachno*-2,3-μ-(*t*-BuNH)-B_5H_8, (10), into *hypho*-2,3-μ-(*t*-BuNH)B_5H_{10} (7). The NMR evidence presented above suggests that **5** and **7** are formed by

(17) Tucker, P. M.; Onak, T.; Leach, J. B. *Inorg. Chem.* **1970**, *9*, 1430.
(18) Burg, A. B.; Heinen, H. *Inorg. Chem.* **1968**, *7*, 1021.
(19) Nöth, H.; Wrackmeyer, B. *Nuclear Magnetic Resonance Spectroscopy of Boron Compounds*; Springer-Verlag:New York, 1978.
(20) We observe a slightly different chemical shift for the ^{11}B NMR resonance of μ-(t-BuNH)B_2H_5 than the value of −23.6 ppm reported by Schwartz and Keller (Schwartz, L. D.; Keller, P. C. *J. Am. Chem. Soc.* **1972**, *94*, 3015). We have synthesized μ-(*t*-BuNH)B_2H_5 by reaction of *t*-$BuNH_2$ with BH_3·THF in refluxing THF and characterized the product by ^{1}H and ^{11}B NMR spectroscopy. The characteristic triplet of doublets in the ^{11}B NMR spectrum is observed at −26.1 ppm in THF.

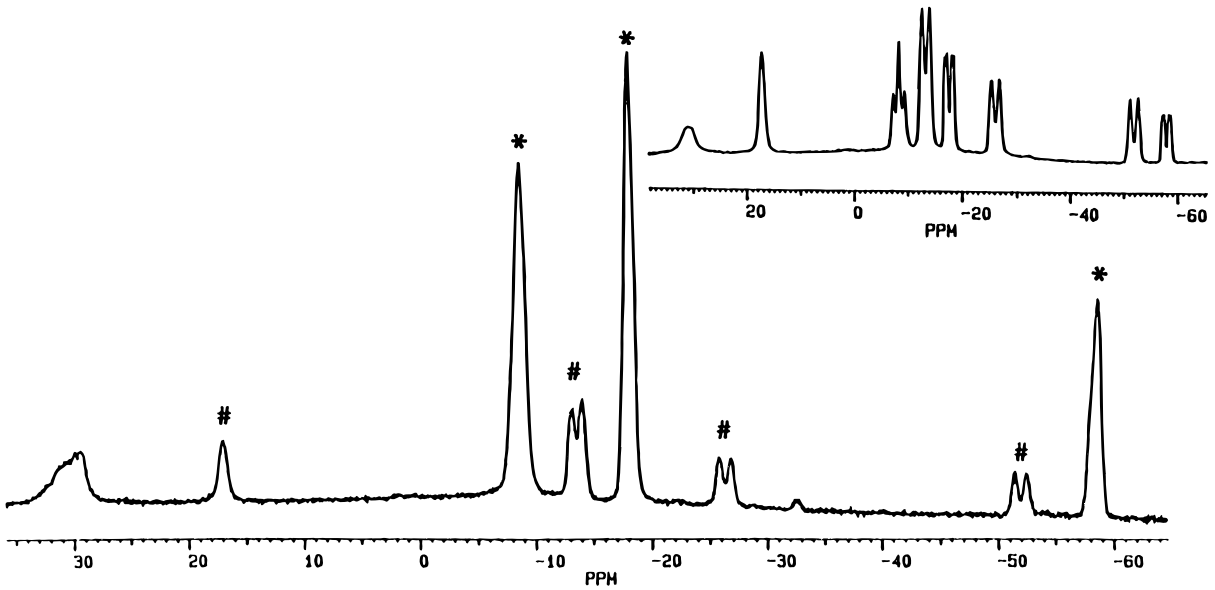


Figure 3. Lower trace: 160 MHz ^{11}B NMR spectrum in deuterated benzene of a fraction isolated from the product mixture from reaction of 2-BrB_5H_8 with (*t*-Bu)(Me_3Si)NH in B_5D_9. Resonances of 2,3-μ-(*t*-BuNH)$B_5D_nH_{10-n}$ are marked with *. Resonances of **(1)** are marked with #. Inset: 160 MHz ^{11}B NMR spectrum of a sample isolated under analogous conditions from the same reaction, run in dichloromethane in the absence of B_5D_9.

independent pathways in the reaction of 2-BrB_5H_8 with (*t*-Bu)(Me_3Si)NH, and that compound **10** is an intermediate in the formation of **7**. However, the question remains: how does the *arachno* compound **(10)**, with eight cluster-associated hydrogen atoms, incorporate two more hydrogen atoms (and thus two more cluster electrons) to form the *hypho* cluster **(7)**? That the dichloromethane solvent is not the hydrogen atom source is confirmed by the observation of isotopically normal products when the solvent was *deuterated* dichloromethane. The excess amine reagent is also unlikely to act as the hydrogen source. The added hydrogen in **7** most likely originates from B−H bonds in boron hydride species.

Isolation of *arachno*-2,3-μ-(*t*-BuNH)B_5H_8 (10) and Observed Decomposition to *hypho*-2,3-μ-(*t*-BuNH)B_5H_{10} (7). A sample of **10** has been isolated and shown to convert to **7** and other compounds. The reactants 2-BrB_5H_8 and (*t*-Bu)(Me_3Si)-NH were allowed to mix briefly at room temperature in a U-trap on the vacuum line; subsequently, the more volatile contents of the trap were evaporated. The residue remaining in the trap could be extracted using dichloromethane or diethyl ether. An ^{11}B NMR spectrum of a dichloromethane extract recorded minutes after extraction showed a 2:2:1 pattern of doublets corresponding to **10**: −3.4 (J = 140 Hz, B(2,3)), −16.9 (J = 155 Hz, B(4,5)) and −53.3 ppm (J = 153 Hz, B(1)), in addition to smaller resonances due to **5** and **7**. These three resonances have been determined by ^{11}B-^{11}B COSY NMR spectroscopy to be mutually coupled. The timewise progression of the ^{11}B NMR spectra reveals slow formation of **7**, as indicated by reduction in intensity of the resonances attributed to **10** and appearance of the resonances of **7** at −8.8, −17.8 (overlapping the resonance due to remaining **10**), and −58.6 ppm. Although the formation of **10** appears to proceed more slowly under these conditions than in the in-probe experiment described above, it is clear that **10** does react to form **7**. It is interesting to note that the small resonance at ca. +18 ppm, corresponding to B(2) in compound **(5)**, does not change significantly in intensity relative to the rest of the spectrum. This observation lends further credence to the assertion that **5** and **10** are formed by independent processes.

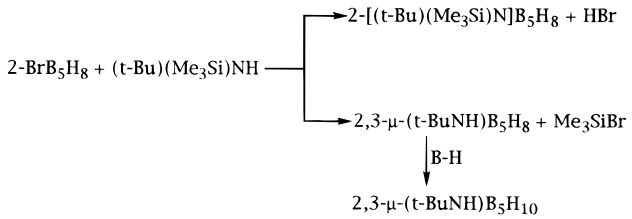
Given the initial composition of the sample, it is likely that the source of hydrogen atoms in the formation of **7** from **10** described above is **10** itself. After "donating" hydrogen to another molecule of **10** in the formation of **7**, the remnants of a donor molecule of **10** appear to decompose to μ-(*t*-BuNH)-B_2H_5, as evidenced by the appearance of the characteristic triplet of doublets at −25.9 ppm,[20] and other unidentified products.

Reaction of (*t*-Bu)(Me_3Si)NH with 2-BrB_5H_8 in Perdeuterated Pentaborane(9). The reaction of (*t*-Bu)(Me_3Si)NH with 2-BrB_5H_8, carried out in the presence of a large excess of perdeuterated pentaborane(9), confirms the hypothesis that **10** reacts with B−H bonds to form **7**. The perdeuterated pentaborane(9), B_5D_9, replaced methylene chloride as the solvent in the reaction; the other conditions, except for the scale of reaction, were similar to the synthetic procedure described elsewhere.[3] Distillation of the reaction products on the vacuum line yielded a mixture of two compounds. An ^{11}B NMR spectrum of this mixture is presented in Figure 3, while the inset spectrum in the upper right corner corresponds to a sample isolated under analogous conditions from the reaction run in dichloromethane solution. Three major differences between the lower spectrum and the inset spectrum are apparent. First, no B−H coupling is observed in the resonances of **7** in the lower spectrum, due to deuterium incorporation in the *hypho*-aminopentaborane produced in the presence of excess B_5D_9. Clearly, the intermediate **10** has reacted with B_5D_9 and incorporated deuterium atoms from B−D bonds. The lack of resolved B−H coupling in any of the resonances of **7** indicates scrambling of the deuterium atoms to all cluster positions.

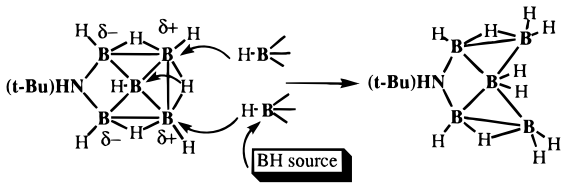
Second, the spectrum of **5** in the lower trace shows no evidence of deuteration in the formation of **5**. This is another indication that the reaction pathway to **5** is not related to that for **7** (or to that for **10**). The third difference between the lower and inset spectra is in the relative intensities of the resonances attributed to **7** and **5**. Comparison of the two spectra indicates that the ratio of **7** to **5** is far greater in the sample isolated from reaction in B_5D_9 than the sample from reaction in dichloromethane. This observation is logical, since the presence of a B−H (in this case, B−D) source other than the intermediate in the formation of **7**, or even **7** itself, would be expected to increase the yield of **7** significantly.

On the basis of the experiments described above, the dual reaction pathway shown in Scheme 1 is proposed for the reaction

Scheme 1



Scheme 2



of (*t*-Bu)(Me_3Si)NH with 2-BrB_5H_8. While it seems clear that **5** and **7** are formed by separate reaction pathways and that **10** is an intermediate, reacting with B−H bonds to give **7**, the *mechanism* of incorporation of hydrogen into **10** has yet to be ascertained. The presence of the *t*-BuNH moiety along one basal edge in the structure of **10** may create an accentuated electron deficiency at the opposite basal edge by electron withdrawal. A plausible partial mechanism for hydrogen incorporation and formation of **7** based on this possibility is shown in Scheme 2.

Experimental Section

Standard high vacuum techniques were employed.[7] Pentaborane-(9) was from laboratory stock. Preparation of 1-BrB_5H_8[21] and isomerization to 2-BrB_5H_8[22] were accomplished by slight modifications of published procedures: direct bromination of B_5H_9 was carried out over $AlBr_3$ rather than $AlCl_3$, generated *in situ* from Br_2 and aluminum foil, and isomerization of the resulting 1-BrB_5H_8 to 2-BrB_5H_8 was done in diethyl ether, rather than dimethyl ether solution. Preparation of 1-ClB_5H_8 and isomerization to 2-ClB_5H_8[23] were accomplished by published procedures. Methyl lithium (1.5 M solution in diethyl ether) and anhydrous HCl (1.0 M solution in diethyl ether) were purchased from Aldrich Chemical Co. and used as received. Hexamethyldisilazane, ($Me_3Si)_2NH$, purchased from Aldrich, and (*t*-Bu)(Me_3Si)NH, (*t*-Bu)(Et_3Si)NH, ($Me_2HSi)_2NH$, and ((*i*-Bu)$Me_2Si)_2NH$, purchased from Hüls Chemical Co., were used as received. Trimethylacetonitrile was purchased from Aldrich and distilled prior to use. BCl_3 (Matheson Chemical Co., technical grade) and trimethylaluminum (Ethyl Corp., Industrial Chemicals Division) were purified by distillation on the vacuum line. The small amount of diborane required was obtained from BH_3·THF (1.0 M solution in tetrahydrofuran, Aldrich Chemical Co.) by distillation on the vacuum line. Dichloromethane was dried and stored over P_2O_5, diethyl ether was dried and stored over Na/benzophenone, toluene was dried over CaH_2 and stored over Na/benzophenone, and deuterated benzene was dried and stored over Na/K. Hexanes were distilled from CaH_2. Solvents were stored in high vacuum flasks and distilled on the vacuum line immediately prior to use. Methanol from laboratory stock was used without drying or distillation. Proton NMR spectra were recorded at 500 MHz on a Brüker AM-500 spectrometer, while ^{11}B NMR spectra were recorded at 160.15 MHz on a Brüker AM-500 spectrometer or at 115.15 MHz on a Brüker AM-360 spectrometer. All reported ^{11}B NMR chemical shifts are relative to BF_3·OEt_2 = 0 ppm (external reference). The ^{11}B−^{11}B COSY spectra were recorded and analyzed by standard methods.[24] Electron-impact mass spectra were recorded on a Kratos MS-80 mass spectrometer operating at 70eV.

Synthesis of 2-[($Me_3Si)_2N$]B_5H_8 (5). In a typical experiment, 17.4 mmol of 2-BrB_5H_8 and 10 mL of dichloromethane were condensed at −196 °C into a 100 mL high vacuum reaction vessel equipped with an o-ring stopcock and a Teflon-coated stir bar. The vessel was allowed to warm to room temperature with stirring and then cooled to −196 °C. A layer of 23.49 mmol of hexamethyldisilazane (a 35% excess) was then condensed into the vessel above the frozen solution, followed by another layer of 7.5 mL dichloromethane. The contents of the reactor were warmed to −78 °C using a stirring dewar containing dry ice/ethanol. Stirring was continued overnight while the solution warmed gradually as the dry ice evaporated. After 11 h the dewar had warmed to −22 °C, but no visible sign of reaction was present. After 15 h, the temperature was +14 °C and the solution was quite cloudy. The reaction vessel was cooled to −196 °C and checked for noncondensable gas; only a trace was present. The vessel was then allowed to warm to ambient temperature and stir for an additional 8 h. Removal of the solvent and more volatile byproducts (including most of the μ-aminodiborane) was accomplished by fractionation through a −30 °C U-trap on the vacuum line. Everything passing the −30 °C trap was discarded. The low volatility material remaining in the reaction vessel consisted predominantly of an amine adduct of B_3H_7, as evidenced by its ^{11}B NMR spectrum. The material condensing at −30 °C was mostly **5**, contaminated with some borazines, as shown by ^{11}B NMR in deuterated benzene. Samples of **5** isolated in this manner were pure enough for reactivity studies, but rigorous removal of all borazine required distillation on a 3 ft variable temperature distillation column attached to the vacuum line.[21] In such a purification, the contents of the −30 °C U-trap were condensed into a U-trap at the bottom of the column. The column was then isolated from the rest of the vacuum line, and the temperature gradient was set so that the temperature at the top of the column was −47 °C and the temperature at bottom was −16 °C. Cooling was accomplished by boiling nitrogen out of a 50 L dewar through a cooling jacket around the column, from the top to the bottom. The N_2 flow rate and thus the temperature was controlled by adjusting the current in a heating element in the bottom of the dewar. Materials from the column were collected in a U-trap on the vacuum line held at −78 °C and checked for purity by ^{11}B NMR. 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).

Synthesis of *hypho*-2,3-μ-(*t*-BuNH)B_5H_{10} (7). The reaction procedure was similar to that employed in the reaction of 2-BrB_5H_8 and hexamethyldisilazane described above. In a typical experiment, a solution containing 9.93 mmol of 2-BrB_5H_8 in 10 mL of dichloromethane was prepared in a 100 mL high vacuum reactor equipped with a Teflon stopcock. A layer of 19.68 mmol of (*t*-Bu)(Me_3Si)NH (a 2:1 excess) was then condensed in a layer above the frozen solution at -196 °C, followed by a layer of 28 mmol of B_5H_9. The contents of the reactor were warmed to −78 °C and allowed to react with slow warming to room temperature overnight, as described above.

The contents of the flask after reaction were distilled on the vacuum line through a U-trap held at −51 °C. Materials passing this trap were discarded, and materials condensing were subsequently distilled through a tared, removable trap held at −30 °C. The materials condensing in the removable trap, 0.96 g of a mixture of **5** and **7**, were dissolved in 12 mL of hexanes and transferred to a 100 mL three-necked flask. One neck of the flask was connected to a mineral oil bubbler, a second neck was fitted with a stopper, and the third neck was fitted with a septum. Addition of methanol by syringe through the septum produced vigorous gas evolution. Addition was continued until no further gas evolution was observed, and then the flask was removed from the bubbler and attached to the vacuum line by an adapter. The flask was cooled to −196 °C and evacuated, and the contents were vacuum distilled through a tared, removable trap cooled to −22 °C for 5 h. The removable trap was then cooled to −78 °C and evacuation was continued for 48 h. In this fashion 0.31 g (2.28 mmol) of **7** were isolated in the removable trap.

Reaction of 2-BrB_5H_8 with (i-Pr)$_2$NH. The reaction was carried out in similar fashion to the other reactions of 2-BrB_5H_8 with amines. A standard 100 mL high vacuum reactor was charged with 2.5 mmol of 2-BrB_5H_8 and 2.5 mL of dichloromethane. After the mixture was warmed to room temperature to make a solution, the solution was cooled to −196 °C and 2.9 mmol of the amine were condensed in a layer

(21) Onak, T.; Dunks, G. B. *Inorg. Chem*. **1964**, *3*, 1060.
(22) Burg, A. B.; Sandhu, J. S. *J. Am. Chem. Soc*. **1965**, *87*, 3787.
(23) Gaines, D. F.; Martens, J. A. *Inorg. Chem.* **1968**, *7*, 704.
(24) Gaines, D. F.; Edvenson, G. M.; Hill, T. G.; Adams, B. R. *Inorg. Chem*. **1987**, *26*, 1813.

above the frozen solution, followed by a layer of 1 mL of dichloromethane. The reagents were then allowed to react with slow warming from −78 °C to room temperature and stirring in the usual fashion. An ^{11}B NMR spectrum of the product mixture, removed from the flask under nitrogen after reaction, showed $B_{10}H_{14}$ as the main product.

Reaction of 2-[(Me$_3$Si)$_2$N]B$_5$H$_8$ with Trimethylacetonitrile. A 100 mL high vacuum reactor was charged with 1 mmol of 2-[(Me$_3$Si)$_2$N]-B_5H_8. The aminopentaborane was dissolved by condensing 3 mL of diethyl ether into the reactor and warming it to room temperature. The solution was cooled to −196 °C and 2 mmol of trimethylacetonitrile was condensed in a layer above the frozen solution, followed by a layer of 1 mL of diethyl ether. The reactor was warmed to −78 °C and allowed to warm to room temperature slowly with stirring overnight. Stirring was continued at room temperature for 24 h, and then about 0.5 mL of the yellow solution was transferred to an NMR tube under nitrogen by syringe. An ^{11}B NMR spectrum of this solution indicated the presence of **9** and borazines, with a small amount of **1**. A third equivalent of the nitrile was condensed into the reactor at −196 °C and allowed to react under the same conditions as the first two equivalents. An NMR sample was prepared; the ^{11}B NMR spectrum indicated the presence of more **9** and borazines and only a trace of **1**.

Pyrolysis of 2-[(Me$_3$Si)$_2$N]B$_5$H$_8$ (1). A solution of **1** was made by condensing about 0.4 mL of neat, nearly pure **1** into a removable U-trap on the vacuum line under dynamic vacuum, followed by 3 mL of toluene. The U-trap was filled with N_2, and 0.4 mL of the solution was transferred to an NMR tube for assay. The remainder was transferred to a 12 mm o.d. Pyrex pyrolysis tube equipped with an o-ring Teflon stopcock and a Teflon coated stir bar. The tube was cooled to −196 °C and evacuated on the vacuum line. It was then immersed in an oil bath to within a few inches of the stopcock. The pyrolysis was begun and monitored by periodically removing the tube from the bath and connecting it to the vacuum line to check for noncondensable gas production, as well as filling it with N_2 and removing aliquots for ^{11}B NMR assay. After each check for gas and NMR assay, the tube was re-evacuated and placed back in the oil bath. Heating at 50 °C for 18.5 h produced no visible signs of reaction. Heating at 75 °C for 24 h produced a small amount of noncondensable gas and a pale yellow solution, but NMR assay showed that little decomposition of **1** had occurred. Heating for another 24 h at 100 °C resulted in a dark yellow solution and significantly more noncondensable gas. ^{11}B NMR assay of this solution showed that B_5H_9 is the main pyrolysis product of **1**.

NMR Tube Reactions. All NMR tube reactions of **1** were carried out in medium-walled tubes. Typically, a solution of **1** was either transferred *via* syringe into the NMR tube under N_2 or made by condensing **1** and the solvent into the tube attached to an adapter equipped with an o-ring stopcock on the vacuum line. In reaction with excess HCl, a solution of anhydrous HCl in diethyl ether was added to the solution of **(1)** *via* syringe under N_2 with the tube held at −78 °C. After a few minutes the −78 °C dewar was removed, and the tube was allowed to warm to room temperature. It was then cooled to −196 °C, evacuated and sealed off. In other NMR tube experiments, reagents were condensed in layers above frozen solutions of **1**, except for the case of attempted reaction with BH_3·THF, in which neat aminopentaborane was used. All tubes were sealed off while pumping on the contents dynamically at −196 °C and then allowed to warm to room temperature behind a protective shield.

In-Probe Reaction of (*t*-Bu)(Me$_3$Si)NH with 2-BrB$_5$H$_8$. A medium-walled NMR tube attached to an adapter allowing connection to the vacuum line was charged with 0.61 g (0.43 mmol) of 2-BrB_5H_8, approximately 0.4 mL of deuterated dichloromethane and 0.125 g (0.86 mmol) of (*t*-Bu)(Me$_3$Si)NH at −196 °C. The NMR tube was flame sealed under dynamic vacuum, and the contents were allowed to melt. When all of the material in the tube had melted, the tube was tipped back and forth twice to mix the reagents and then placed in a −78 °C bath for transport to the spectrometer. The tube was inserted into the probe of the spectrometer, precooled to −78 °C. The temperature adjustments and recording of spectra detailed in Table 2 were then carried out. Selected spectra are shown in Figure 2.

Table 2. Time and Temperature Data for the In-Probe Reaction of (*t*-Bu)(Me$_3$Si)NH with 2-BrB_5H_8

reaction time (nearest 15 min)	probe temp adjustments	spectra recorded
15 min		
2 h, 15 min	warmed to −63 °C	
3 h, 15 min	warmed to −48 °C	
4 h, 15 min	warmed to −33 °C	
5 h		spectrum 1
5 h, 15 min	warmed to −18 °C	
6 h, 45 min	warmed to −3 °C	
7 h, 30 min		spectrum 2
9 h, 30 min	warmed to +12 °C	
10 h		spectrum 3
11 h	warmed to +25 °C	
13 h		
(several weeks)		spectrum 4

Formation of *arachno*-2,3-μ-(*t*-BuNH)B$_5$H$_8$, (10). Isolation of **(10)** was accomplished by distillation of 3 mmol each of 2-BrB_5H_8 and (*t*-Bu)(Me$_3$Si)NH into a U-trap on the vacuum line containing ca. 2 mL of dichloromethane. The materials in the U-trap were allowed to stand for a few minutes at room temperature, and then the more volatile components in the trap were evaporated using a dynamic vacuum. A sample of the residual material in the trap was obtained by condensing dichloromethane into the trap, then filling the trap with nitrogen at room temperature, and removing the resulting solution *via* syringe.

Reaction of (*t*-Bu)(Me$_3$Si)NH with 2-BrB$_5$H$_8$ in B$_5$D$_9$. About 0.2 mmol of 2-BrB_5H_8 were condensed into a 10 mm o.d. reaction tube equipped with a Teflon-coated stir bar and a high-vacuum o-ring stopcock. Then 2.75 mL (ca. 25 mmol) of B_5D_9 were condensed into the tube and allowed to warm to room temperature with stirring to make a solution. About 0.4 mmol of the amine was then condensed into the reaction tube at −196 °C and allowed to run down onto the frozen solution. The contents of the tube were melted and then stirred at −48 °C for 6 h. Finally, the tube was allowed to warm slowly to room temperature while being stirred overnight. The reaction tube contained a slightly cloudy colorless solution 24 h after the initial mixing of the reagents. The reaction products were distilled on the vacuum line through a U-trap cooled to −22 °C. All materials passing this trap (including unreacted deuterated pentaborane) were discarded. The materials stopping in the −22 °C trap were condensed into an NMR tube attached to the vacuum line with approximately 0.5 mL of deuterated benzene. The tube was flame sealed, and a ^{11}B NMR spectrum was recorded, indicating the presence of isotopically normal **5** and (partially) deuterated **7**.

Supporting Information Available: Selected ^{11}B and ^{1}H NMR spectra for compounds **1**, **7**, **8**, **9**, and **10** (6 pages). Ordering information is given on any current masthead page.

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