$(Me_3Si)_2NP(Cl)CH_2SiMe_3$ used. Compound **11** was isolated by short-path distillation as a very viscous colorless liquid. Two redistillation were required to produce an analytically pure sample of **11**. ^{31}P NMR: δ 75.5.

[([Bis(trimethylsilyl)amino]-*tert*-butylboryl)amino][bis(trimethylsilyl)amino]chlorophosphine (12). A solution of the amide **5a** (30 mmol) in hexane (50 mL) was added to a stirred solution of $(Me_3Si)_2NPCl_2$[14] [30 mmol, freshly prepared from PCl_3 and $(Me_3Si)_2NLi$] in Et_2O (30 mL) at 0 °C. The mixture was allowed to warm to room temperature and was stirred overnight. Filtration and solvent removal left a partially solid residue, which was dissolved in a minimal amount of hexane. Cooling the solution to 0 °C produced **12** as a white crystalline solid, mp 65–67 °C. ^{31}P NMR: δ 151.2.

[([Bis(trimethylsilyl)amino]-*tert*-butylboryl)amino]phenylchlorophosphine (13). The same procedure described above for **6** was followed with 30-mmol quantities of **5a** and $PhPCl_2$ used. Compound **11** was isolated by short-path distillation as a high boiling, viscous liquid. ^{31}P NMR: δ 108.1.

[([Bis(trimethylsilyl)amino]-*tert*-butylboryl)amino]dichlorophosphine (14). By use of the same procedure as described above for **12**, a solution of the amide **5a** (30 mmol) in hexane (50 mL) was added to PCl_3 (2.6 mL, 30 mmol) in Et_2O (50 mL) at −78 °C. After being stirred overnight at room temperature, the mixture was filtered and freed of solvent and other volatile materials. At this point, the dichlorophosphine derivative **14** remained as a colorless liquid, which gave a satisfactory elemental analysis without any further purification. ^{31}P NMR: δ 166.0.

Mass Spectra. The new compounds prepared in this study gave reasonable mass spectral fragmentation patterns and correct molecular ion peaks. Typically, the following significant peaks were observed with relative intensities in the indicated ranges: M^+ (2%), $M^+ - CH_3$ (5–20%), $M^+ - C(CH_3)_3$ (30–100%), $M^+ - Si(CH_3)_3$ (5–20%).

Acknowledgment. The authors thank the Robert A. Welch Foundation and the Texas Christian University Research Fund for financial support of this research.

Registry No. 1, 89487-06-9; 2, 99748-65-9; 3, 99748-66-0; 4, 99748-67-1; 5, 99748-68-2; 5a, 99748-76-2; 6, 99748-69-3; 7, 99748-70-6; 8, 99748-71-7; 9, 99766-97-9; 10, 99748-72-8; 11, 99748-73-9; 12, 99748-77-3; 13, 99748-74-0; 14, 99748-75-1.

Contribution from the Department of Chemistry,
University of Wisconsin—Madison, Madison, Wisconsin 53706

Reactions of Boron Hydrides with the Iminium Salt $[Me_2NCH_2]I$. Synthesis and Characterization of 1-X-μ-$(Me_2NCH_2)B_5H_7$ (X = H, C_2H_5, Br), a New Class of Bridge-Substituted Pentaborane Derivatives

Donald F. Gaines* and Darrell E. Coons

Received June 14, 1985

Reactions of $[Me_2NCH_2]I$ (**1**) with salts of the $B_5H_8^-$, $1\text{-}(C_2H_5)B_5H_7^-$, and $1\text{-}BrB_5H_7^-$ anions produce the μ-((dimethylamino)-methyl)pentaborane derivatives μ-$(Me_2NCH_2)B_5H_8$, $1\text{-}(C_2H_5)\text{-}\mu\text{-}(Me_2NCH_2)B_5H_7$, and $1\text{-Br-}\mu\text{-}(Me_2NCH_2)B_5H_7$, respectively, in good yields. A structure for these compounds is proposed in which a bridging hydrogen atom of B_5H_9 has been replaced by a C–N two-atom bridge, the Me_2NCH_2 group. These clusters are analogues of the *arachno*-$B_5H_{10}^-$ anion, and there is no evidence of direct bonding between the Me_2NCH_2-bridged boron atoms. Reaction of **1** with $NaBH_4$ forms $Me_3N{\cdot}BH_3$, while reaction with $[Me_4N][B_3H_8]$ produces a variety of products including $Me_3N{\cdot}BH_3$, $Me_3N{\cdot}B_3H_7$, B_2H_6, and B_5H_9. Attack of **1** on B_5H_9 occurs slowly at 65 °C, forming $Me_3N{\cdot}BH_3$ and $Me_3N{\cdot}B_3H_7$.

Introduction

The organic chemistry of methyleneaminium (methaniminium) salts has been reviewed.[1] These species are powerful electrophiles, reacting with a wide range of nucleophiles through the methylene carbon, upon which the lowest unoccupied molecular orbital (of π symmetry) is primarily localized.[2] In valence bond terms the electrophilic nature of the methylene carbon results from the predominance of the resonance form in which the carbon atom bears the positive charge:

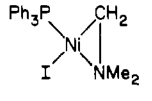
$$\overset{+}{N}{=}C \longleftrightarrow \overset{\cdot\cdot}{N}{-}\overset{+}{C}$$

The reactions of methyleneaminium salts with organic nucleophiles generally result in aminomethylation or, in some cases, hydride abstraction.

The organometallic chemistry of iminium salts has received considerable recent attention. The reactions of commercially available $[Me_2NCH_2]I$ (Eschenmoser's salt, **1**) illustrated in eq 1–3, are typical of the reactivity that has been observed for iminium salts with different types of organometallic complexes. Reactions of **1** with organometallic nucleophiles (eq 1) result in a metathesis giving η^1-aminomethyl complexes such as **2**.[3] Loss of carbon monoxide from **2** occurs on heating to give the η^2-aminomethyl complex **3** (eq 2).[3] Reactions of **1** with neutral complexes (eq 3) usually result in oxidative addition with spontaneous loss of ligands from the metal to give η^2-aminomethyl

$$Na[(\eta^5\text{-}C_5H_5)Mo(CO)_3] + \underset{\mathbf{1}}{[Me_2NCH_2]I} \longrightarrow \underset{\mathbf{2}}{(\eta^5\text{-}C_5H_5)(CO)_3MoCH_2NMe_2} + NaI \quad (1)$$

$$\mathbf{2} \xrightarrow{80\ ^\circ C} \underset{\mathbf{3}}{(\eta^5\text{-}C_5H_5)(CO)_2Mo(\eta^2\text{-}CH_2NMe_2)} + CO \quad (2)$$

$(Ph_3P)_3Ni$ + 1 ⟶  + $2Ph_3P$ (3)

4

---

[1] See, for example: Böhme, H.; Haake, M. *Adv. Org. Chem.* **1976**, *9*, 107–223 (Part 1).

[2] Kollman, P. A. *Adv. Org. Chem.* **1976**, *9*, 1–8 (Part 1).

[3] Fong, C. W.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1975**, 1100–1104.

[4] Barefield, E. K.; Carrier, A. M.; Sepelak, D. J.; Van Derver, D. G. *Organometallics* **1982**, *1*, 103–110.

0020-1669/86/1325-0364$01.50/0

Table I. ^{11}B and ^{1}H NMR Spectral Data for **5**–**7** in Benzene-d_6

^{11}B NMR[a]

	B(2–4)	B(1)
μ-$(Me_2NCH_2)B_5H_8$ (**5**)	+16.3 (112), +0.9 (156), −0.7 (117), −4.0 (156)	−47.4 (117)
1-(C_2H_5)-μ-$(Me_2NCH_2)B_5H_7$ (**6**)	+14.3 (88), +4.0 (151), −0.8 (112), −3.5 (154)	−36.3
1-Br-μ-$(Me_2NCH_2)B_5H_7$ (**7**)	+14.9 (93), +3.7 (*b*), +1.6 (*b*), −3.0 (151)	−31.8

^{1}H NMR[c]

	H(2–5)	Me_2N	CH_2	apex	H(6–8)
5	+3.84, +3.27, +3.03, +2.92	+2.20, +1.80	+2.15 (*b*), +1.21 (13)	H(1): +0.20 (136)	−0.60, −2.12
6	+3.80–+2.86	+2.12, +1.63	+2.06 (*b*), +1.75 (7)	$H(C_2H_5)$: +1.36, +1.06	−0.04, −1.76
7	+3.91–+2.89	+2.22, +1.67	+2.07 (17), +0.94 (13)		−0.01, −0.19, −1.49

[a] Values are chemical shifts in ppm measured relative to external $BF_3{\cdot}OEt_2$, 0 ppm. Values in parentheses are coupling constants in hertz measured directly from the observed peak separations. [b] These values could not be obtained due to overlapping resonances. [c] Values are chemical shifts in ppm measured relative to internal C_6D_5H, 7.15 ppm.

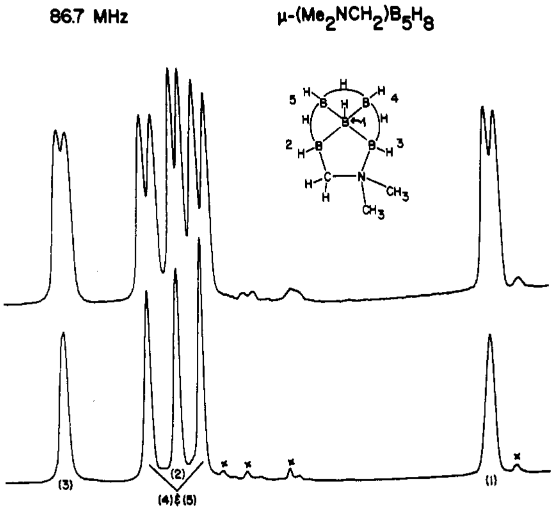


Figure 1. ^{11}B NMR spectra of μ-$(Me_2NCH_2)B_5H_8$ (**5**) in benzene-d_6. Proposed resonance assignments are given below the lower trace, which is the broad-band ^{1}H-decoupled spectrum (× = impurities).

complexes such as **4**, presumably via η^1-aminomethyl complexes.

Iminium salts react with hydride donors to give amines (eq 4).

$$[R_2NCR'_2]^+ + H^- \rightarrow R_2NCHR'_2 \qquad (4)$$

Tetrahydroborate (BH_4^-) salts are frequently used for this purpose, and this reaction is generally followed by hydrolysis and isolation of the free amine. We report here on the reactions of $[Me_2NCH_2]I$ with several boron hydrides and the discovery of a new class of bridge-substituted pentaborane derivatives.

Results and Discussion

In order to assess the reactivity of the iminium salt $[Me_2NCH_2]I$ (**1**) toward smaller boron hydride species, we have examined the reactions of **1** with sodium tetrahydroborate, $NaBH_4$, and tetramethylammonium octahydrotriborate, $[Me_4N][B_3H_8]$. The reaction of **1** with $NaBH_4$ occurs at ambient temperature when a mixture of the two powdered reactants is stirred. The reaction is much faster in diethyl ether solution. The trimethylamine–borane product (eq 5) can be thought of as the result

$$[Me_2NCH_2]I + NaBH_4 \rightarrow Me_3N{\cdot}BH_3 + NaI \qquad (5)$$

of hydroboration of the iminium C=N bond. As in the reaction of the BH_4^- anion with carbonyl compounds,[5] the proposed initial step involves interaction of a hydridic hydrogen of the BH_4^- anion with the relatively positive carbon atom. Alternatively, the formation of $Me_3N{\cdot}BH_3$ may occur in two steps: hydride abstraction from the BH_4^- anion by the iminium cation followed by complex formation between the intermediate species Me_3N and BH_3 (see below).

In the reaction of **1** with $[Me_4N][B_3H_8]$ in the solid state or in solution, the principal products are the trimethylamine complexes of BH_3 and B_3H_7. In addition, B_2H_6, B_4H_{10}, B_5H_9, and B_6H_{10} are observed. The presence of these boron hydride species in this reaction suggests that the iminium cation abstracts a hydride from the $B_3H_8^-$ anion, giving unstable B_3H_7, which can react with either Me_3N or another B_3H_7. Combination of intermediates B_3H_7 and BH_3 (from B_2H_6 or another B_3H_7) gives B_4H_{10},[6] which can react with Me_3N to give $Me_3N{\cdot}BH_3$ and $Me_3N{\cdot}B_3H_7$ (eq 6).[7]

$$B_4H_{10} + 2Me_3N \rightarrow Me_3N{\cdot}BH_3 + Me_3N{\cdot}B_3H_7 \qquad (6)$$

A reaction between **1** and B_5H_9 in diethyl ether occur at 65 °C, producing $Me_3N{\cdot}BH_3$, $Me_3N{\cdot}B_3H_7$, and other unidentified products over a period of several days.

The reaction of **1** with lithium and potassium salts of the $B_5H_8^-$ anion at −78 °C produces $Me_2NCH_2B_5H_8$ (**5**) (eq 7). The only

$$[Me_2NCH_2]I + M[B_5H_8] \rightarrow \underset{\mathbf{5}}{Me_2NCH_2B_5H_8} + MI \qquad (7)$$

side product observed in the ^{11}B NMR spectrum of the reaction mixture is a small amount of $Me_3N{\cdot}BH_3$. **5** is a colorless liquid melting between 10 and 15 °C. At 25 °C it has a vapor pressure of less than 1 torr and decomposes slowly, producing $Me_3N{\cdot}BH_3$.

The ^{11}B NMR spectrum of **5** (Figure 1 and Table I) consists of five doublets of equal area, indicating that all five boron atoms in the molecule are in different chemical environments and each bears one terminal hydrogen substituent. The complex ^{1}H NMR spectrum of **5** consists of many overlapping peaks from +4.81 to −2.12 ppm (Table I). The region from +4.81 to +2.80 ppm is made up of four overlapping quartets arising from the four terminal hydrogen atoms, which are attached to the basal boron atoms as determined with use of selective ^{11}B decoupling. The quartet arising from the apical, terminal hydrogen atom is located at +0.20 ppm. Two broad resonances arising from the bridging hydrogen atoms appear in a 2:1 ratio at −0.60 and −2.12 ppm. The methyl groups attached to the nitrogen atom give rise to sharp singlets at +2.20 and +1.80 ppm. The methylene hydrogens are also nonequivalent, giving rise to two resonances at +2.15 and +1.21 ppm. The +1.21 ppm resonance is a slightly broadened doublet (13 Hz), undoubtedly coupled to the geminal proton which appears at +2.15 ppm. The +2.15 ppm resonance fine structure is not resolved, as it overlaps with the +2.20 ppm methyl resonance.

The 1-ethyl and 1-bromo derivatives of **5** (**6** and **7**, respectively) are formed in analogous reactions between $[Me_2NCH_2]I$ and salts of the 1-$(C_2H_5)B_5H_7^-$ and 1-$BrB_5H_7^-$ anions. The ^{11}B and ^{1}H NMR spectra of **6** and **7** are similar to those of **5**. (Chemical shift and coupling constant data for these spectra are compiled in Table I.)

Structure and Bonding. A proposed structure for compounds **5**–**7** consistent with the NMR spectra is illustrated in Figure 2. In this structure, a bridging hydrogen atom of B_5H_9 has been replaced by a C–N two-atom bridge, the CH_2NMe_2 group, el-

---

(5) Brown, H. C. "Boranes in Organic Chemistry"; Cornell University Press: Ithaca, NY, 1972; Vol. 21, pp 1952–1957.

(6) Toft, M. A.; Leach, J. B.; Himpsl, F. L.; Shore, S. G. *Inorg. Chem.* **1982**, *21*, 1952–1957.

(7) Edwards, L. J.; Hough, W. V.; Ford, M. D. *Angew. Chem.* **1957**, *69*, 678.

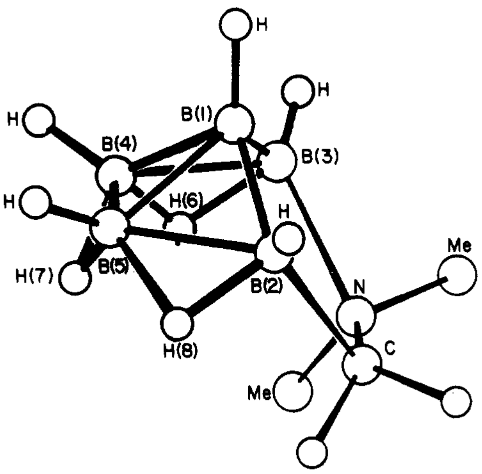
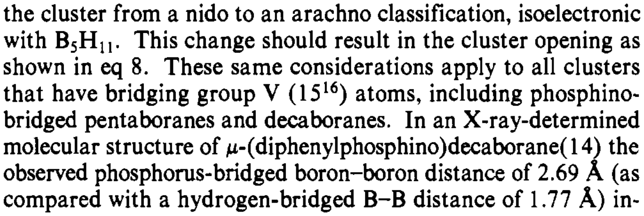


Figure 2. Proposed structure of μ-$(Me_2NCH_2)B_5H_8$ (**5**). Terminal hydrogens are numbered the same as the boron to which they are attached.

minating and direct bonding between Me_2NCH_2-bridged boron atoms. The Me_2NCH_2 group is most likely located well below the plane of the basal boron atoms, as observed for bridging H and $SiMe_3$ moieties.[8] Formation of these compounds probably occurs in two steps. First, attack of the $Me_2NCH_2^+$ carbon at the vacant bridge site of the $B_5H_8^-$ anion produces an intermediate containing a bridging carbon atom bonded to the B_5H_8 cage via a three-center, two-electron bond, analogous to the B–Si–B bond in μ-$(Me_3Si)B_5H_8$.[8] The proximity of the adjacent dimethylamino group lowers the stability of this intermediate. The amino group nitrogen lone-pair electrons compete favorably for an adjacent boron orbital to form a B–N coordinate bond with elimination of the B–C–B three-center, two-electron bond and formation of a conventional C–B σ bond as shown in eq 8.



(8)

Wade's rules for polyhedral electron-pair counting[9] indicate that the addition of a pair of electrons from the nitrogen changes the cluster from a nido to an arachno classification, isoelectronic with B_5H_{11}. This change should result in the cluster opening as shown in eq 8. These same considerations apply to all clusters that have bridging group V (15^{16}) atoms, including phosphino-bridged pentaboranes and decaboranes. In an X-ray-determined molecular structure of μ-(diphenylphosphino)decaborane(14) the observed phosphorus-bridged boron–boron distance of 2.69 Å (as compared with a hydrogen-bridged B–B distance of 1.77 Å) indicates that there is no direct bonding between these two boron atoms.[10] This compound is therefore best considered an arachno cluster, a formal analogue of $B_{10}H_{14}^{2-}$, in which the phosphorus-bridged edge is "electronically open" but is physically held together by the bridging atom. Likewise, it appears that μ-(phosphino)pentaboranes and compounds **5**–**7** are best considered as arachno clusters, formally derivatives of the $B_5H_{10}^-$ anion, in which the bridged B(2,3) edge is open to the limit allowed by the "bite" of the bridging group.

A further manifestation of the arachno nature of phosphino-bridged pentaborane derivatives occurs in their ^{11}B and ^1H NMR spectra. The observed boron–terminal hydrogen coupling constants for the bridged boron atoms B(2,3) are 105–114 Hz, about 30% less than the B(4,5)-H coupling constants of 156–164 Hz.[11] The BH_2 groups on the open face of B_5H_{11}, B(2,5), exhibit couplings of 132 and 127 Hz, some 20% less than the B(3,4)–H coupling of 160 Hz. In the ^{11}B NMR spectra of **5**–**7**, two of the four basal boron resonances exhibit B–H couplings ranging from 93 to 117 Hz, 25–38% less than the B(4,5)–H coupling of 151–156 Hz. These resonances are tentatively assigned to B(2,3) on this basis. In addition, the broadness of the resonance at lowest field may be due to a neighboring quadrupolar ^{14}N nucleus, so this resonance is tentatively assigned to the nitrogen-bonded B(3).

Experimental Section

Manipulations of volatile compounds were performed in a standard high-vacuum line. Other air-sensitive materials were handled in glovebags flushed with dry nitrogen. The ^{11}B and ^1H NMR spectra were obtained at 86.7 and 270.13 MHz, respectively, on a Bruker WP270SY spectrometer. Mass spectra were obtained with a KRATOS MS80 spectrometer.

Pentaborane(9) was from laboratory stock. 1-EtB_5H_8,[12] 1-BrB_5H_8,[13] and $[Me_4N][B_3H_8]$[14] were prepared by standard methods. Sodium borohydride (Alfa) was used as received. Boron trifluoride (Matheson, CP) and hydrogen chloride (Matheson, tech) were purified by repeated high-vacuum distillation through a −126 °C U-trap and condensation in a −196 °C U-trap. Potassium hydride, obtained from Alfa Products as a mineral oil dispersion, was washed with pentane to remove the oil. Methyllithium, obtained from Aldrich Chemical Co. as a 1.4 M solution in diethyl ether, was used as received; $[Me_2NCH_2]I$ (Eschenmoser's salt), obtained from Aldrich Chemical Co., was sublimed before use. Tetrahydrofuran, dimethyl ether, diethyl ether, and benzene-d_6 were dried over $LiAlH_4$ and were vacuum transferred directly into the vacuum line as needed.

Reaction of $[Me_2NCH_2]I$ with $NaBH_4$. Under N_2, a 50-mL round-bottom flask equipped with a greased stopcock was charged with 0.334 g of $NaBH_4$ (8.82 mmol), 0.807 g of $[Me_2NCH_2]I$ (4.36 mmol) a Teflon-coated stirring bar, and glass beads. The flask was attached to the vacuum line and evacuated, and then the contents were vigorously stirred at 25 °C with continuous evacuation, the volatile products condensing in a −196 °C U-trap. After 2 h a small amount of white solid was visible in the U-trap. An ^{11}B NMR spectrum of this solid in C_6D_6 showed a quartet at −7.2 ppm (J_{BH} = 98 Hz): $Me_3N{\cdot}BH_3$. Some smaller unidentified resonances were also present.

About 5 mL of Et_2O was vacuum distilled into the flask at −196 °C. The flask was then sealed, warmed to 25 °C, and stirred overnight. All volatile components were then distilled into a −196 °C U-trap. Fractional condensation using U-traps at −68 and −196 °C yielded 0.145 g (1.99 mmol) of $Me_3N{\cdot}BH_3$ in the −68 °C trap; yield 45.6% based on $[Me_2NCH_2]I$.

Reaction of $[Me_2NCH_2]I$ with $[Me_4N][B_3H_8]$. A 50-mL round-bottom flask equipped with a greased stopcock was charged with 0.662 g of $[Me_2NCH_2]I$ (3.58 mmol), 0.497 g of $[Me_4N][B_3H_8]$ (4.34 mmol), a Teflon-coated stirring bar, and glass beads. The flask was evacuated on the vacuum line, and then the contents were stirred at 25 °C with continuous evacuation, volatile products condensing in a −196 °C U-trap. After several minutes, liquid and solid were observed in the trap, both colorless. The ^{11}B NMR spectrum of this material in C_6D_6 showed a triplet of triplets at +17.1 ppm (B_2H_6), a quartet at −7.8 ppm ($Me_3N{\cdot}BH_3$), doublets at −14.0 and −53.6 ppm (4:1, B_5H_9), and resonances at +13.5 (doublet, probably a small amount of B_6H_{10}), −18.4 (multiplet, probably μ-$Me_2NB_2H_5$), and −42.1 ppm (doublet, probably B_4H_{10}).

About 5 mL of tetrahydrofuran was vacuum distilled into the flask at −196 °C. The flask was sealed and warmed to 25 °C, and the contents were stirred overnight. The volatile components were distilled into a −196 °C U-trap and then separated by fractional condensation using U-traps cooled to −63 and −196 °C. A 0.044-g amount of white solid condensed in the −63 °C trap. An ^{11}B NMR spectrum of this material in tetrahydrofuran revealed it to be a mixture of similar quantities of $Me_3N{\cdot}BH_3$ (δ −7.9) and $Me_3N{\cdot}B_3H_7$ (δ −18.4).

Reaction of $[Me_2NCH_2]I$ with B_5H_9. A 5 mm o.d., 3 mm i.d. NMR tube was charged with 0.142 g of $[Me_2NCH_2]I$ (0.77 mmol) under N_2. The tube was attached to the vacuum line and evacuated. A 0.4-mL

---

(8) Calabrese, J. C.; Dahl, L. F. *J. Am. Chem. Soc.* **1971**, *93*, 6042–6047.

(9) (a) Wade, K. *J. Chem. Soc., Chem. Commun.* **1971**, 792–793. (b) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1–66. (c) Rudolph, R. W. *Acc. Chem. Res.* **1976**, *9*, 446–452.

(10) Friedman, J. B.; Perry, S. L. *Inorg. Chem.* **1973**, *12*, 288–293.

(11) (a) Burg, A. B.; Heinen, H. *Inorg. Chem.* **1968**, *7*, 1021–1025. (b) Mishra, I. B.; Burg, A. B. *Inorg. Chem.* **1972**, *11*, 664–666.

(12) Ryschkewitch, G. E.; Harris, S. W.; Mezey, E. J.; Sisler, H. H.; Weilmuenster, E. A.; Garrett, A. B. *Inorg. Chem.* **1963**, *2*, 890–893.

(13) Burg, A. B.; Sandhu, J. S. *J. Am. Chem. Soc.* **1965**, *87*, 3787–3788.

(14) Dewkett, W. J.; Grace, M.; Beall, H. *Inorg. Synth.* **1974**, *15*, 115–118.

amount of Et_2O was vacuum distilled into the tube at −196 °C followed by 0.77 mmol of B_5H_9. The tube was flame sealed and warmed to 25 °C. After 24 h the ^{11}B NMR spectrum showed only B_5H_9. The bottom half of the tube was immersed in a 65 °C oil bath for 68 h. The ^{11}B NMR spectrum then showed B_5H_9, $Me_3N{\cdot}BH_3$, $Me_3N{\cdot}B_3H_7$, and several smaller unidentified resonances. When the sample was heated at 65 °C for an additional 5 days, the ^{11}B NMR spectrum still showed B_5H_9 and $Me_3N{\cdot}BH_3$ plus an increased amount of $Me_3N{\cdot}B_3H_7$ and a number of unidentified resonances.

Preparation of μ-(Me_2NCH_2)B_5H_8 (5). Typically a solution of 3.0 mmol of LiB_5H_8 was prepared in the usual manner[15] from MeLi and B_5H_9 in 4 mL of diethyl ether in a 50-mL round-bottom reactor equipped with an 3-mm Kontes O-ring stopcock. The reactor was cooled to −196 °C, and the CH_4 was removed by vacuum distillation. Dry N_2 was admitted to the flask, and under a stream of N_2, 0.570 g of [Me_2NCH_2]I (3.08 mmol) was added via a solid-addition tube with plunger. The flask was reevacuated, sealed, and warmed to −78 °C with stirring. After 1 h at −78 °C, the reaction was allowed to warm slowly to −10 °C over a period of 2 h. A ^{11}B NMR spectrum of the reaction solution exhibited the five doublets due to **5** (see Table I), plus smaller resonances attributed to B_5H_9 and $Me_3N{\cdot}BH_3$. The volatile contents of the flask were distilled into U-traps cooled to −63 and −196 °C in series. The ether and B_5H_9 condensed in the −196 °C trap while a white solid condensed in the −63 °C trap. The solid was further purified by fractional condensation in a −45 °C U-trap. The volatility of **5** is low, each distillation requiring several days to complete. The yield of purified **5** was 0.164 g (1.36 mmol), 45.3% based on LiB_5H_8. It is a colorless liquid, melting at 10–15 °C and decomposing quite slowly (days) at ambient temperature, giving $Me_3N{\cdot}BH_3$ and unidentified products. It can be crystallized from ether/pentane below 0 °C.

Preparation of 1-(C_2H_5)-μ-(Me_2NCH_2)B_5H_7 (6) and 1-Br-μ-(Me_2NCH_2)B_5H_7 (7). The 1-ethyl and 1-bromo derivatives of μ-(Me_2NCH_2)B_5H_8 were prepared in the same manner as the parent compound by starting with 1-(C_2H_5)B_5H_8 and 1-BrB_5H_8, respectively. These reactions are very clean, the only byproduct observed in the ^{11}B NMR spectra being $Me_3N{\cdot}BH_3$. 1-(C_2H_5)-μ-(Me_2NCH_2)B_5H_7, a colorless liquid of low volatility, was purified by fractional condensation in a −10 °C U-trap. 1-Br-μ-(Me_2NCH_2)B_5H_7, a colorless, crystalline solid, is more thermally stable than the parent or 1-ethyl derivatives and sublimes slowly at 50 °C (10^{-5} torr). Compounds **5**–**7** are very soluble in ethers, CH_2Cl_2, benzene, and toluene and very slightly soluble in aliphatic hydrocarbons.

Mass Spectra. Mass spectra for compounds **5**–**7** show strong parent envelopes and an envelope at $M^+ - 20$ (unassigned). **5** and **6** show strong $M^+ - 15$ and $M^+ - 30$ envelopes corresponding to loss of one and two methyl groups, respectively. The high-resolution mass spectra confirmed the molecular formula for each compound: calcd for $^{11}B_5{}^1H_{16}{}^{12}C_3{}^{14}N$ (**5**) 121.1748, found 121.1749; calcd for $^{11}B_5{}^1H_{20}{}^{12}C_5{}^{14}N$ (**6**) 149.2061, found 149.2062; calcd for $^{11}B_5{}^1H_{15}{}^{12}C_3{}^{79}Br$ (**7**) 199.0853, found 199.0853.

Acknowledgment. This research was supported in part by grants from the National Science Foundation.

Registry No. **5**, 99657-83-7; **6**, 99657-84-8; **7**, 99657-85-9; $Me_3N{\cdot}BH_3$, 75-22-9; $Me_3N{\cdot}B_3H_7$, 57808-48-7; B_2H_6, 19287-45-7; B_5H_9, 19624-22-7; B_6H_{10}, 23777-80-2; μ-$Me_2NB_2H_5$, 23273-02-1; B_4H_{10}, 18283-93-7; [Me_2NCH_2]I, 36627-00-6; $NaBH_4$, 16940-66-2; [Me_4N][B_3H_8], 12386-10-6; LiB_5H_8, 34370-18-8; 1-(C_2H_5)B_5H_8, 23753-61-9; 1-BrB_5H_8, 23753-67-5.

---

(15) Gaines, D. F.; Iorns, T. V. *J. Am. Chem. Soc.* **1967**, *89*, 3375–3376.

(16) The periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

Contribution from the Department of Chemistry,
The Ohio State University, Columbus, Ohio 43210

Pentaborane(9) as a Source for Higher Boron Hydride Systems. A New Synthesis of *nido*-5,6-$(CH_3)_2$-5,6-$C_2B_8H_{10}$

Steven H. Lawrence, Joseph R. Wermer, Simon K. Boocock, Michael A. Banks, Phillip C. Keller,[†] and Sheldon G. Shore*

Received August 29, 1985

Pentaborane(9), B_5H_9, is shown to be a useful source for the production of higher boron hydride systems. Investigation of the reaction of B_5H_9 with sodium hydride or potassium hydride in THF or glyme to produce the tetradecahydrononaborate(1−) anion, $[B_9H_{14}]^-$, is reported in detail, and evidence is given for reaction pathways. This anion is also obtained from the reaction of NaI with B_5H_9. When generated in situ from B_5H_9, $[B_9H_{14}]^-$ is an intermediate in the syntheses of a number of other higher boron hydride systems: $B_9H_{13}{\cdot}L$ ligand adducts, *n*-$B_{18}H_{22}$, $B_{10}H_{14}$, *nido*-5,6-$C_2B_8H_{12}$, and *nido*-5,6-$(CH_3)_2$-5,6-$C_2B_8H_{10}$. The synthesis of $B_{10}H_{14}$ reported here is an improved procedure over the earlier reported preparation from B_5H_9, and the preparations of *nido*-5,6-$(CH_3)_2$-5,6-$C_2B_8H_{10}$ and *nido*-5,6-$C_2B_8H_{12}$ are new syntheses.

Introduction

Earlier work from this laboratory showed that pentaborane(9) is a viable starting material for the synthesis of decaborane(14), $B_{10}H_{14}$.[1,2] Decaborane(14), in turn, has proved to be a useful starting point in the preparation of higher boron hydrides, carboranes, and metalla derivatives of these systems.[3] Because large stockpiles of B_5H_9 remain from the borane-based fuels program of the 1950s, this boron hydride is a potentially attractive starting material[4] for the syntheses of higher borane species. In this report we demonstrate the utility of B_5H_9 by showing that species such as $B_9H_{13}{\cdot}L$, *n*-$B_{18}H_{22}$, *nido*-5,6-$C_2B_8H_{12}$, and *nido*-5,6-$(CH_3)_2$-5,6-$C_2B_8H_{10}$ can be prepared in "one-pot" procedures using B_5H_9 as the starting material without the necessity of preparing $B_{10}H_{14}$. Nevertheless these procedures do not obviate other uses for $B_{10}H_{14}$. Accordingly we also report here a significantly improved procedure for the preparation of $B_{10}H_{14}$ from B_5H_9

All of the syntheses described in this report are based on the conversion of B_5H_9 to the tetradecahydrononaborate(1−) anion,[5] $[B_9H_{14}]^-$, an anion that has found use as a precursor in the syntheses of a number of boranes[1,2,6,7] and metallaboranes.[8-15] The

---

[†] Department of Chemistry, University of Arizona.

(1) Toft, M. A.; Leach, J. B.; Himpsl, F. L.; Shore, S. G. *Inorg. Chem.* **1982**, *21*, 1952.

(2) Leach, J. B.; Toft, M. A.; Himpsl, F. L.; Shore, S. G. *J. Am. Chem. Soc.* **1981**, *103*, 988.

(3) "Gmelin Handbuch der Anorganischen Chemie", 8th ed.; Springer-Verlag: New York, 1979; Vol 54, Borverbindungen, Teil 20.

(4) Pentaborane(9) is commercially available from Callery Chemical Co., Callery, PA.

(5) Benjamin, L. E.; Stafiej, S. F.; Takacs, E. A. *J. Am. Chem. Soc.* **1963**, *85*, 2674.

(6) Dobson, J.; Keller, P. C.; Schaeffer, R. *Inorg. Chem.* **1968**, *7*, 399.

(7) Dobson, J.; Keller, P. C.; Schaeffer, R. *J. Am. Chem. Soc.* **1965**, *87*, 3522.

(8) Kennedy, J. D. *Prog. Inorg. Chem.* **1984**, *32*, 519.

0020-1669/86/1325-0367$01.50/0