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.

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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.

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

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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

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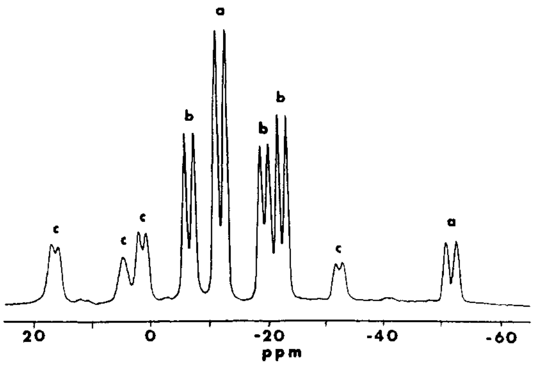

Figure 1. 96.3-MHz ^{11}B NMR spectrum of the reaction of $K[B_5H_8]$ with excess B_5H_9 in THF at 270 K: (a) B_5H_9; (b) $K[B_9H_{14}]$; (c) $K[B_6H_{11}]$.

most widely employed preparations of $[B_9H_{14}]^-$ rely upon base degradation of $B_{10}H_{14}$.[5,11,16] However, it has been known for some time that $[B_9H_{14}]^-$ is produced from the decomposition of $[B_5H_8]^-$.[17-20] More recently $[B_9H_{14}]^-$ has been obtained in better yields from the deprotonation of B_5H_9 in the presence of excess B_5H_9.[1,2,21] The latter reaction is utilized in a procedure reported by this laboratory for the conversion of B_5H_9 to $B_{10}H_{14}$.[1,2]

The increasing importance of $[B_9H_{14}]^-$ prompted us to study the conversion of B_5H_9 to $[B_9H_{14}]^-$ in greater detail and to determine the conditions that maximize the yield of $[B_9H_{14}]^-$. Specifically, we report here an analysis of the reaction between B_5H_9 and MH (M = Na, K) as a function of time and mole ratio of reactants. On the basis of the observed products, a sequence of reactions is provided that suggests the major pathways to the observed products. Additionally it has been of interest to demonstrate that other higher boron hydride systems can be obtained from $[B_9H_{14}]^-$ generated in situ without ever isolating this intermediate and without ever preparing $B_{10}H_{14}$, the generally employed starting material for such compounds.

Results and Discussion

I. Preparation of $[B_9H_{14}]^-$ from Deprotonation Reactions of B_5H_9. A. Reactions of B_5H_9 with NaH and with KH. Evidence for Reaction Pathways. Reacting B_5H_9 with alkali-metal hydride, KH or NaH, in THF or glyme produced the alkali-metal salt of $[B_9H_{14}]^-$. A detailed analysis of the reaction by ^{11}B NMR spectroscopy showed that the yield of $[B_9H_{14}]^-$ is optimized when the B_5H_9:NaH ratio is 1.8:1 (Reaction 1) rather than the 2:1 ratio

$$1.8B_5H_9 + MH \xrightarrow[\text{THF or glyme}]{12\text{–}18\ \text{h}} M[B_9H_{14}] + H_2 + \text{minor products} \qquad (1)$$

$$M = Na, K$$

employed earlier.[1] The reaction was followed by ^{11}B NMR spectroscopy as a function of mole ratio of reactants. Below a B_5H_9:NaH ratio of 1.8:1, all of the B_5H_9 was consumed. As the ratio was increased from 1:1 to the optimum ratio of 1.8:1, the yield of $[B_9H_{14}]^-$ was maximized and side reactions, which gave primarily $[B_{11}H_{14}]^-$, $[B_3H_8]^-$, $[BH_4]^-$, and B_2H_6 plus unidentified species, were minimized.

The major product $[B_9H_{14}]^-$ plus the minor species obtained under optimum conditions can be accounted for by the following series of reactions believed to be the primary pathways to these materials.

$$B_5H_9 + MH \rightarrow M[B_5H_8] + H_2 \qquad (2)$$

$$M[B_5H_8] + B_5H_9 \rightarrow M[B_9H_{14}] + {}^1/_2B_2H_6 \qquad (3)$$

$$M[B_5H_8] + {}^1/_2B_2H_6 \rightarrow M[B_6H_{11}] \qquad (4)$$

$$M[B_6H_{11}] \rightarrow M[B_6H_9] \rightarrow M[B_{11}H_{14}] + M[B_3H_8] \qquad (5)$$

$$M[B_5H_8] \rightarrow M[B_9H_{14}] + M[B_3H_8] + M[BH_4] \qquad (6)$$

$$M = Na, K$$

The initial deprotonation step (reaction 2) is well-known.[21-23] Reaction 3 is inferred from earlier work in this laboratory,[1,2] but had not previously been studied in detail. We examined at low temperature (250–270 K) the reaction of $K[B_5H_8]$ with an excess of B_5H_9 in THF and found that $[B_5H_8]^-$ was rapidly consumed, resulting in the formation of an unidentified intermediate species, which might be $[B_{10}H_{17}]^-$, which further decomposed to form $[B_9H_{14}]^-$. After 30 min at 270 K, the ^{11}B NMR spectrum (Figure 1) showed the presence of only B_5H_9, $K[B_9H_{14}]$, and $K[B_6H_{11}]$, thereby providing evidence for reactions 3 and 4. Any B_2H_6 liberated in reaction 3 would react with $[B_5H_8]^-$ to form $[B_6H_{11}]^-$ (reaction 4), a facile reaction.[24,25] The $[B_6H_{11}]^-$ anion has been shown to undergo thermal decomposition at room temperature (reaction 5), first to $[B_6H_9]^-$ and then to $[B_{11}H_{14}]^-$, $[B_3H_8]^-$, and a number of unidentified products.[20,25] Another potential but less significant source of $[B_{11}H_{14}]^-$ is the reaction of $[B_9H_{14}]^-$ with B_5H_9. A separate study in THF showed that these react to give $[B_{11}H_{14}]^-$ much more slowly than the rate of decomposition of $[B_6H_{11}]^-$ to form $[B_{11}H_{14}]^-$. The decomposition of $[B_5H_8]^-$ (reaction 6) results[17-20] in the formation of $[B_9H_{14}]^-$, $[B_3H_8]^-$, and $[BH_4]^-$. The presence of B_5H_9 in the system favors reaction 3 in preference to the decomposition of $[B_5H_8]^-$. As discussed in more detail below in section I.B., $[B_3H_8]^-$ and $[BH_4]^-$ also react with the starting material to form $[B_9H_{14}]^-$.

Another laboratory[17] reported a 90% yield of $[B_9H_{14}]^-$ based on the 32-MHz ^{11}B NMR spectrum of the reaction mixture from the reaction between equimolar amounts of B_5H_9 and NaH in glyme. However, only 60% yields of solid $[B_9H_{14}]^-$ salt could be isolated. High-field (96.3 and 160.4 MHz) ^{11}B NMR studies in this laboratory of the reaction between equimolar quantities of B_5H_9 and NaH showed the product to be contaminated with considerable quantities of the $[BH_4]^-$ and $[B_3H_8]^-$ anions. The method described here of reacting pentaborane(9) with sodium hydride in a 1.8:1 molar ratio in THF or glyme is superior because the yield of $[B_9H_{14}]^-$ is maximized, the production of side products is suppressed, and less sodium hydride is consumed per mole of $Na[B_9H_{14}]$ formed.

When $[B_9H_{14}]^-$ is employed as an intermediate for the preparation of other higher boron hydride systems, it can be used in situ without further purification for the cases cited here. If a tetraalkylammonium salt is desired, the alkali-metal halide generated from the metathesis reaction does not interfere with further syntheses. However, the alkali-metal and tetraalkylammonium salts of $[B_9H_{14}]^-$ can be isolated as free-flowing solids of approximately 90% and 75% purity, respectively, based on integrated ^{11}B NMR spectra.

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A similar reaction is the reaction of B_6H_{10} with $^1/_2$ equiv of KH in THF. This reaction produced $K[B_{11}H_{14}]$ in good yield, indicating a parallel reaction to reaction 3 in which $^1/_2$ equiv of B_2H_6 is evolved.

B. Preparation of $[B_9H_{14}]^-$. Variations in the Product Distribution with Time. Variations in the reaction mixture with time were followed by means of ^{11}B NMR spectroscopy for the reaction of B_5H_9 with NaH in a 2:1 mole ratio in THF at room temperature. Essentially the same results were obtained in glyme.

Rapid initial formation of $[B_9H_{14}]^-$ occurred. Within 20 min of the onset of reaction, boron-11 NMR spectral data showed that $[B_9H_{14}]^-$ was by far the predominant boron hydride in solution, accounting for well over 44% of the total boron in solution. The rate of $[B_9H_{14}]^-$ formation decreased steadily thereafter; it accounted for approximately 55% of the boron in solution after 2 h, 62% after 24 h, and 70% after 72 h of reaction.

Also noteworthy is the absence of evidence for the presence of $[B_5H_8]^-$, and the fact that barely discernible signals attributable to $[BH_4]^-$ were observed only in spectra recorded during the earliest stages of reaction, thus indicating the rapid reaction of both of these anions with B_5H_9 to form $[B_9H_{14}]^-$. While observed in all spectra, signals due to $[B_3H_8]^-$ indicated a solution concentration that was consistently much lower than that observed in our corresponding studies of the decomposition of $Na[B_5H_8]$ in THF, thus signifying the consumption of $[B_3H_8]^-$ at an appreciable rate. Pentaborane(9) has been found to react rapidly at room temperature with $[BH_4]^-$,[18,19] and more slowly with $[B_3H_8]^-$,[17] to produce $[B_9H_{14}]^-$. Since both $[BH_4]^-$ and $[B_3H_8]^-$ are decomposition products of $[B_5H_8]^-$, any B_5H_9 present in solution can react with them as they are formed.

As discussed above, $[B_{11}H_{14}]^-$ formation was also observed. One of the main factors affecting its ultimate concentration appeared to be the amount of B_5H_9 in solution, the concentration of which decreased slowly over several weeks as the concentration of $[B_{11}H_{14}]^-$ increased. In a spectrum recorded after 10 weeks, $[B_9H_{14}]^-$ and $[B_{11}H_{14}]^-$ accounted for over 90% of the boron in solution. The reactions discussed above were run at room temperature. Elevating the temperature to 46 °C resulted in a diminished yield of $[B_9H_{14}]^-$ and an increased amount of $[B_{11}H_{14}]^-$ in the reaction solutions.

The only other boron hydride identified in the ^{11}B NMR spectra was $BH_3\cdot THF$, which was formed in the early stages of reaction and was observed in reaction solutions after 10 weeks. In the corresponding studies involving glyme, $BH_3\cdot$glyme was not observed.

In another series of experiments B_5H_9, $[(CH_3)_4N]Cl$, and NaH were employed in the molar ratio of 1.8:1:1, according to eq 7.

$$1.8B_5H_9 + MH + [(CH_3)_4N]Cl \rightarrow [(CH_3)_4N][B_9H_{14}] + H_2 + MCl + \text{minor products} \quad (7)$$

$$M = Na, K$$

The results were in agreement with those in the experiment described above. After 72 h, approximately 70% of the starting B_5H_9 had been incorporated into $[B_9H_{14}]^-$ according to integrated ^{11}B NMR spectra. Although there was less $[B_{11}H_{14}]^-$ produced in this experiment than in that without tetraalkylammonium halide, other impurities were present in similar amounts. The presence of a tetraalkylammonium salt in the reaction mixture suppressed the formation of $[B_{11}H_{14}]^-$, which accounted for up to 5% of the boron content after 15 h in the absence of these salts.

In the course of this study, a number of signals were observed in the NMR spectrum, which could not be associated with any known boron hydride. Some were due to short-lived intermediates that only existed at low concentrations early in the reaction, e.g. broad singlets at 2.8, −4.2 and −42.3 ppm. More prominent and enduring, however, were signals at 6.2 (doublet, $J(^{11}B-^1H) = 132 \pm 3$ Hz) and −5.6 ppm (multiplicity undetermined, $J(^{11}B-^1H) \cong 29$ Hz) and two doublets of equal intensity at −36.9 ($J(^{11}B-^1H) = 140 \pm 2$ Hz) and −42.7 ppm ($J(^{11}B-^1H) = 140 \pm 1$ Hz). These signals were also reported by Savory and Wallbridge.[17] The two upfield doublets were particularly noteworthy, growing to their maximum size within the first 6 h of reaction and then slowly diminishing thereafter. Their parallel behavior suggests that they are associated with the same boron hydride species. Decomposition studies of $K[B_6H_{11}]$ in THF showed that these unknown species, along with $[B_{11}H_{14}]^-$ and $[B_3H_8]^-$, are the major products from $[B_6H_{11}]^-$ decomposition. This study thus provides further evidence for the reaction pathway proposed in section I.A.

Similar results were generally obtained in ^{11}B NMR spectroscopic studies using KH in place of NaH. Relative to the rate of formation of $Na[B_9H_{14}]$, formation of $K[B_9H_{14}]$ was somewhat slower in the earlier stages of the reaction, probably as a result of the very low solubility of $K[BH_4]$ in ether solvents. After 24 h, however, ^{11}B NMR spectra of the sodium and potassium systems were indistinguishable.

C. Reaction of B_5H_9 with NaI. The reaction of NaI with B_5H_9 in a 1:2 molar ratio in THF over a 7-day period, followed by ^{11}B NMR spectroscopy, gave products essentially identical with those from reactions between B_5H_9 and NaH or KH (2:1 mole ratio in THF or glyme). The same reaction took place in glyme over a 2–3-week period; $[(n\text{-}Bu)_4N]I$ and B_5H_9 also reacted in CH_2Cl_2 over a 5-week period to give the same products. These reactions are believed to proceed through the initial deprotonation of B_5H_9 by iodide ion (eq 8). The $[B_5H_8]^-$ formed in this manner, and

$$B_5H_9 + I^- \rightleftarrows [B_5H_8]^- + HI \quad (8)$$

its decomposition products, may then react with B_5H_9 as described previously. Any HI formed by this reaction could be consumed in a reaction involving the ring-opening polymerization of THF, since mass spectral data are consistent with the presence in product mixtures of significant quantities of oligomers of THF. Ring-opening and polymerization of THF by strong acids are well-known.[26-29]

II. Preparation of $B_9H_{13}\cdot L$ from B_5H_9. The $[B_9H_{14}]^-$ anion was converted to the neutral adduct $B_9H_{13}\cdot O(C_2H_5)_2$ by a previously reported procedure.[6] $B_9H_{13}SR_2$ and $B_9H_{13}PR_3$ adducts were obtained by ligand displacement[6,7,30,31] (reaction 9). Yields

$$L + B_9H_{13}\cdot O(C_2H_5)_2 \xrightarrow[\text{room temp}]{(C_2H_5)_2O} B_9H_{13}\cdot L + (C_2H_5)_2O \quad (9)$$

$$L = (CH_3)_2S,\ (C_2H_5)_2S,\ (n\text{-}C_4H_9)_2S,\ (t\text{-}C_4H_9)_2S,\ (C_6H_5)_2S,\ (C_6H_5)_3P$$

of $B_9H_{13}\cdot L$, 75–85% based upon B_5H_9, are at least as favorable as those obtained from reactions based upon $B_{10}H_{14}$.[30-33] However, in order to obtain these yields it was first necessary to remove an active boron hydride impurity from the crude $M[B_9H_{14}]$ resulting from reaction 1. This was accomplished by brief treatment of the crude $M[B_9H_{14}]$ salt with methanol, and removal of the trimethyl borate that was formed, by pumping under high vacuum.

III. A New Synthesis of *nido*-5,6-$(CH_3)_2$-5,6-$C_2B_8H_{10}$ and *nido*-5,6-$C_2B_8H_{12}$. The first *nido*-C_2B_8 carboranes were obtained by Schaeffer and co-workers[34-36] as a mixture of *nido*-5,6-$(CH_3)_2$-5,6-$C_2B_8H_{10}$ and *nido*-4,5-$(CH_3)_2$-4,5-$C_2B_7H_9$ from the reaction of B_8H_{12} with 2-butyne in diethyl ether. We found that *nido*-5,6-$(CH_3)_2$-5,6-$C_2B_8H_{10}$ is formed from the reaction of 2-butyne with $B_9H_{13}\cdot O(C_2H_5)_2$ in diethyl ether. The advantages of the present procedure are that $B_9H_{13}\cdot O(C_2H_5)_2$ is appreciably

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(32) Hermanek, S.; Plesek, J.; Stibr, B.; Hanousek, J. *Collect. Czech. Chem. Commun.* **1968**, *33*, 2177.

(33) $B_9H_{13}\cdot L$ adducts where L = $(CH_3)_2S$, $(C_2H_5)_2S$, and $(C_6H_5)_3P$ have been previously reported. See ref 30–32.

(34) Rietz, R. R.; Schaeffer, R. *J. Am. Chem. Soc.* **1971**, *93*, 1263.

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more stable and much easier to prepare than B_8H_{12}. Furthermore, the product was separated by simple vacuum-line fractionation techniques in contrast to the low-temperature column fractionation techniques[37] employed earlier. Product yields of 37% (based on the B_5H_9 starting material) have been obtained with this method. Best yields of the carborane were obtained from $B_9H_{13}\cdot O(C_2H_5)_2$, while only trace quantities were obtained from $B_9H_{13}\cdot S(CH_3)_2$ and no carborane was produced when $B_9H_{13}\cdot P(C_6H_5)_3$ was used. These results are consistent with earlier observations[38] and suggest that the active species in the carborane formation is B_9H_{13}, perhaps obtained through ligand dissociation of the adduct. Thus $B_9H_{13}\cdot L$ complexes having weak Lewis bases as ligands are favored for this synthesis.

Yields of carborane were maximized when the reactants were employed in a 4:1 ratio of butyne:$B_9H_{13}\cdot O(C_2H_5)_2$. This suggests that hydroboration is taking place, resulting in the loss of one boron atom from the nonaborane cage as shown in reaction 10. In the course of the reaction, it is believed that the BH_3 is displaced from $B_9H_{13}\cdot O(C_2H_5)_2$ and hydroborates the unreacted alkyne to give a trivinylborane. This hypothesis is supported by a singlet in the ^{11}B NMR spectrum of the reaction mixture at 66 ppm, indicating the presence of the trivinylborane $B(C(CH_3){=}C(H)(CH_3))_3$.[39,40] Additional evidence for the presence of the trivinylborane was the evolution of *cis*-2-butene from the reaction solution upon acidification with acetic acid. The alkene was isolated by using vacuum-line fractionation techniques and identified by its characteristic gas-phase IR spectrum.

$$B_9H_{13}\cdot O(C_2H_5)_2 + 4H_3CC{\equiv}CCH_3 \rightarrow 5,6\text{-}(CH_3)_2\text{-}5,6\text{-}C_2B_8H_{10} + (C_2H_5)_2O + B(C(CH_3){=}C(CH_3)(H))_3 \quad (10)$$

In a synthesis similar to that described above, we also obtained *nido*-5,6-$C_2B_8H_{12}$ from the reaction of $B_9H_{13}\cdot O(C_2H_5)_2$ with acetylene in diethyl ether. This carborane had been obtained earlier[34-36] from the reaction of B_8H_{12} with acetylene in diethyl ether. However, it could be separated only with great difficulty from $C_2B_7H_{11}$, another reaction product.[36] We have obtained and separated *nido*-5,6-$C_2B_8H_{12}$ in yields of 9% based on the B_5H_9 starting material and separated it from the reaction mixture by a simple vacuum-line fractionation.

IV. Conversion of B_5H_9 to *n*-$B_{18}H_{22}$. Pentaborane(9) was converted to octadecaborane(22), *n*-$B_{18}H_{22}$, in a "one-pot" synthesis from the sequence of reactions 1, 11, and 12. Reactions 11 and 12 have been previously reported.[6] Yields of 30–40% based on starting B_5H_9 are commonly obtained with this procedure.

$$Na[B_9H_{14}] + HCl \xrightarrow{n\text{-}Bu_2O} B_9H_{13}\cdot OBu_2 + H_2 \quad (11)$$

$$B_9H_{13}\cdot OBu_2 \xrightarrow{\Delta} n\text{-}B_{18}H_{22} + H_2 + n\text{-}Bu_2O \quad (12)$$

V. Improved Conversion of B_5H_9 to $B_{10}H_{14}$. Our earlier reported synthesis[1,2] of $B_{10}H_{14}$ from B_5H_9 (reactions 7, 13) has been improved. By using a B_5H_9:NaH:$[(CH_3)_4N]Cl$ ratio of 1.8:1:1, as detailed in section I.B., and by using glyme as a solvent instead of THF, $B_{10}H_{14}$ was obtained in yields of 55–60% based on the B_5H_9 starting material. Interestingly, the use of pure, freshly prepared $[(CH_3)_4N][B_9H_{14}]$ instead of the product prepared in situ resulted in lower yields (ca. 45%) of $B_{10}H_{14}$. Apparently the impurities in the reaction mixture enhance the production of $B_{10}H_{14}$. Additionally it was found that much lower sublimation temperatures can be used to recover the $B_{10}H_{14}$ from the reaction pot without significant losses in product yield. Sublimation (10^{-3} torr) for 5–8 h at 40–50 °C results in the isolation of a much purer product. Alternatively, instead of sublimation, decaborane(14) can be extracted from the final reaction mixture with hot *n*-butyl ether.

$$[Me_4N][B_9H_{14}] + BCl_3 \rightarrow [Me_4N][BCl_3H] + B_{10}H_{14} \quad (13)$$

Experimental Section

Methods. Materials were handled by using standard vacuum-line and inert-atmosphere techniques.[41]

Materials. Pentaborane(9) (Chemical Systems, Inc.) was used as received. KH (Alfa) and NaH (Metal Hydrides, Inc.) in mineral oil dispersions were washed repeatedly with dry pentane to remove the oil and then stored under dry, oxygen-free nitrogen; only metal hydrides with an activity greater than 90% were used (determined by reaction with methanol and measurement of the H_2 evolved). $[(CH_3)_4N]Cl$ (J. T. Baker), $[(n\text{-}Bu)_4N]I$ (Alfa) and NaI (J. T. Baker) were heated to 150 °C under dynamic vacuum and stored under dry nitrogen. Glyme (1,2-dimethoxyethane), *n*-butyl ether, ethyl ether, THF, and 1,4-dioxane were distilled from sodium benzophenone ketyl immediately prior to use. Methyl sulfide and ethyl sulfide (Aldrich) were stirred over and distilled from NaH prior to use. Phenyl sulfide, *tert*-butyl sulfide, and *n*-butyl sulfide (Aldrich) were used as received. Triphenylphosphine (Aldrich) was recrystallized from ethanol prior to use. 2-Butyne (Wiley Organics) was used as received. Acetylene (Matheson) was passed through a U-trap maintained at −111 °C to remove acetone.

Equipment. Boron-11 NMR spectra at 32.1, 96.3, and 160.4 MHz were obtained on Varian HA-100, Bruker WM-300, and GE/Nicolet NT-500 spectrometers, respectively. Chemical shifts for ^{11}B NMR spectra were referenced to $BF_3\cdot OEt_2$ (0.0 ppm), which was also the external standard employed. Mass spectra were recorded on an AEI MS-9 Spectrometer operated by Mr. C. R. Weisenberger, using heptacosafluorotributylamine as calibrant.

1. Preparation and Isolation of $[B_9H_{14}]^-$ Salts. (a) $[R_4N][B_9H_{14}]$ (R = Me, *n*-Bu). The following is a specific example of the general procedure employed for the preparation and isolation of tetraalkylammonium salts of $[B_9H_{14}]^-$ using either THF or glyme as the reaction medium. All preparations employed reactants in the mole ratio of 1.8:1:1 B_5H_9:MH:$[R_4N]X$ (M = Na, K; R, X = Me, Cl or *n*-Bu, I).

In a glovebox filled with dry, oxygen-free N_2, a 200-mL reaction vessel fitted with a 15-mm Fischer-Porter Solv-Seal joint was charged with a magnetic stirring bar, 502.4 mg of NaH (19.9 mmol [95% active]) and 2.186 g of $[(CH_3)_4N]Cl$ (19.9 mmol), after which it was attached to a vacuum extractor with a 500-mL receiving vessel. The reaction assembly was evacuated, and 20 mL of glyme was condensed into the reaction vessel at −196 °C, followed by the introduction at −196 °C of 39.5 mmol of B_5H_9, measured as a liquid at 0 °C where the density is 0.66 g/cm^3. *CAUTION! B_5H_9 is known to be spontaneously flammable and very toxic.*[42] Reaction was allowed to proceed at room temperature with stirring for 18 h, followed by the removal of H_2 (24.5 mmol) and then filtration to remove NaCl (1.152 g, 99%). Solvent and unreacted B_5H_9 were removed from the filtrate under vacuum to give 3.71 g of a light yellow, free-flowing solid; its ^{11}B NMR spectrum, recorded in glyme at 160.44 MHz, indicated that $[B_9H_{14}]^-$ accounted for approximately 75% of the boron present in solution.

(b) $M[B_9H_{14}]$ (M = Na, K). In the glovebox, 11.8 mmol of KH (95% active, 469 mg) was introduced into a 500-mL 15-mm Solv-Seal reaction vessel containing a magnetic spin-bar. This was then sealed with a 15-mm to ₮ 14/35 greased-joint stopcock adapter and removed from the glovebox.

On the vacuum line the reaction vessel was evacuated and cooled to −196 °C. Pentaborane(9) (20 mmol, 2.0 mL at 0 °C) and 12 mL of dry THF were distilled into the reaction flask.

The contents of the flask were allowed to thaw and come into contact with KH. Vigorous H_2 evolution ensured, but subsided after 15 min. The reaction mixture was stirred for 20 h at room temperature, during which time the color of the mixture gradually turned to a light yellow. The system was cooled to −196 °C, and evolved H_2 was measured (12.8 mmol).

THF and volatile boranes were removed by distillation into a removable −196 °C trap. Mild heating was used to ensure that all volatiles were distilled away, and then the reaction mixture was pumped on dynamically for 4 h under high vacuum to yield a yellow gum.

(c) Isolation of Solid $M[B_9H_{14}]$. Attempts to isolate $M[B_9H_{14}]$ (M = Na, K) by removing solvent under vacuum yielded only viscous oils. However, these could be obtained as free-flowing solids by precipitation from solution with dioxane or extraction from aqueous solutions with diethyl ether. The ether extraction method was adapted from a procedure for the preparation of $K[B_9H_{14}]$ from $B_{10}H_{14}$.[16]

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(37) Dobson, J.; Schaeffer, R. *Inorg. Chem.* **1970**, *9*, 2183.

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(39) Work in the laboratory has shown the B_2H_6 reacts with 6 equiv of 2-butyne in diethyl ether to produce a species that has a single peak at 65.2 ppm in the ^{11}B NMR spectrum.

(40) Hosmane, N. S., personal communication.

(41) Shriver, D. F. "The Manipulation of Air-Sensitive Compounds"; McGraw-Hill: New York, 1969.

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(c(i)) Isolation of K[B_9H_{14}] by Ether Extraction from Aqueous Solution. KH (5.73 mmol) and B_5H_9 (11.29 mmol) were reacted in 40 mL of THF as described above in section 1(b) to produce K[B_9H_{14}]. As much THF as possible was removed under vacuum, followed by the addition (in air) of a quantity of water sufficient to dissolve the material. The solution was transferred to a beaker, and 12 M HCl was added dropwise with stirring until the pH was approximately 2. After addition of 50 mL of peroxide-free Et_2O and 47 g of K_2CO_3, the mixture was stirred for 10 min and then placed into a separatory funnel and agitated. The ether and aqueous layers were collected separately, and the aqueous layer was extracted further with 3–30-mL portions of ether, which were then combined with the ether solution collected earlier. The ether was removed under vacuum, leaving an almost colorless, free-flowing solid product (560 mg) found by ^{11}B NMR spectroscopy (96.27 MHz, sample in THF) to be K[B_9H_{14}] of over 99% purity.

(c(ii)) Isolation of Na[B_9H_{14}] and K[B_9H_{14}] by Precipitation with Dioxane. In a 30-mL reaction vessel attached to an extractor assembly, B_5H_9 (6.29 mmol, measured as a gas) and NaH (79.7 mg, 3.15 mmol [95%]) were reacted in 3.15 mL of glyme for 48 h. After H_2 was removed, a large excess of dioxane was added and the mixture stirred for 12 h. The extractor assembly was inverted, and the light green, free-flowing solid precipitate was collected (1.21 g) and dried under vacuum. The ^{11}B NMR spectrum (160.44 MHz) of the product in glyme showed that $[B_9H_{14}]^-$ accounted for approximately 85% of the boron in solution. A similar procedure was used to isolate K[B_9H_{14}].

2. Boron NMR Spectroscopic Studies of the Deprotonation of B_5H_9 by Alkali-Metal Hydrides. Reactions between B_5H_9 and NaH (or KH) that were to be followed by ^{11}B NMR spectroscopy were carried out as follows: A reaction vessel (10-15 mL) with a 9-mm Solv-Seal joint and an NMR sample tube sealed to a sidearm of the neck of the vessel was charged with a magnetic stirring bar and 0.5 mmol of NaH (or KH), accurately weighed to the nearest 0.2 mg. The vessel was attached to a stopcock adapter and evacuated, and 1.0 mL of solvent (THF or glyme) was condensed into the vessel at −196 °C, followed by addition of the desired amount of B_5H_9 at −196 °C. The vessel was warmed to room temperature, and reaction was allowed to proceed for the desired period of time. The reaction solution was then tipped into the NMR sample tube and frozen at −196 °C, H_2 was pumped away, and the sample tube was flame-sealed and stored at −196 °C until used.

Boron-11 NMR studies involving the addition of tetraalkylammonium halides were carried out in the same manner; the alkali-metal halide precipitates formed in these reactions were allowed to settle prior to the decanting of the reaction solution into the NMR sample tube, which was then flame-sealed and stored at −196 °C until use.

3. Reaction of B_5H_9 with Iodide Salts. A 250-mL reaction vessel was charged with a magnetic stirring bar and 1.68 g of NaI (11.2 mmol), attached to a stopcock adapter, and evacuated. After the introduction of 15 mL of THF and 14.5 mmol of B_5H_9 into the reaction vessel at −196 °C, reaction was allowed to proceed at room temperature with stirring for 11 days. Recovery of volatiles gave 6.71 mmol of H_2, 0.17 mmol of B_2H_6, some unreacted B_5H_9, THF, and a liquid with a vapor pressure of less than 1 torr (25 °C), the mass spectrum of which suggested that it was an oligomer of THF. The material remaining in the reaction vessel was treated with 10 mL of 2-propanol and then with an excess of an aqueous solution of [Me_4N]Cl, and the resulting precipitate was recovered by filtration, washed with water, and dried under vacuum. The ^{11}B NMR spectrum (32.1 MHz) of the material in THF showed it to be a mixture of [Me_4N][B_9H_{14}] and [Me_4N][$B_{11}H_{14}$] in a molar ratio of approximately 3:1.

4. Preparation of $B_9H_{13}·O(C_2H_5)_2$ from K[B_9H_{14}]. In a procedure similar to that reported by Schaeffer and co-workers,[6] the product from section 1(b), was cooled to −196 °C. HCl (10 mmol, measured manometrically), followed by $(C_2H_5)_2O$, (20 mL) was distilled onto the K[B_9H_{14}]. The contents of the flask were allowed to warm slowly to room temperature. *CAUTION! To prevent pyrolytic self-decomposition it is recommended that the reaction be stirred at −78 °C for 5 min. Additional "quenching" with a −78 °C bath may be necessary to slow the reaction.* Immediate and vigrous H_2 evolution ensued, accompanied by the precipitation of KCl. The contents of the flask were frozen at −196 °C, and evolved H_2 was measured via a Oepler pump (found 9.3 mmol); the excess of HCl was pumped away from the reaction vessel at −78 °C. The reaction vessel was then attached to a 15-mm Solv-Seal extractor fitted with a 100-mL receiver flask. The reaction vessel was cooled to −196 °C and evacuated. After being warmed to room temperature, the $B_9H_{13}·O(C_2H_5)_2$ solution was filtered; KCl (0.7923 g) was collected on the frit and washed repeatedly with $(C_2H_5)_2O$ to remove traces of $B_9H_{13}·O(C_2H_5)_2$.

5. Preparation of $B_9H_{13}·SR_2$ Compounds from $B_9H_{13}·O(C_2H_5)_2$. Two different methods dependent upon the volatility of the ligand were used in the ether displacement procedure. (a) Volatile ligands were added by distillation of a known volume of material on the vacuum line. (b) Nonvolatile ligands were added to the reaction vessel via a side-arm tip-tube. Yields reported below are based on B_5H_9 starting material. To obtain these compounds as semicrystalline solids in good yield, it was first necessary to treat the K[B_9H_{14}] with CH_3OH to remove an active borane impurity before the $B_9H_{13}·O(C_2H_5)_2$ adduct was prepared (section 4 above). After preparation of K[B_9H_{14}] as described in section 1(b), the reaction vessel was then removed from the vacuum line and CH_3OH (5–6 mL) was added cautiously via the stopcock. Vigorous H_2 evolution ensued; after this had subsided, the volatiles were removed by pumping under a high vacuum. Mild heating was used to remove the last traces of solvent. The resultant product K[B_9H_{14}] was an off-white semicrystalline solid and was used in the synthesis of $B_9H_{13}·O(C_2H_5)_2$ and detailed above in section 4.

(a) L = $(CH_3)_2S$, $(C_2H_5)_2S$, and $(t\text{-}C_4H_9)_2S$. A 10-mmol sample of the volatile dialkyl sulfide, measured by volume, was distilled into the 100-mL receiver flask containing $B_9H_{13}·O(C_2H_5)_2$ at −196 °C. The contents of the vessel were allowed to thaw and were stirred for 2 h at room temperature. After this time the $(C_2H_5)_2O$ was removed by pumping under high vacuum, leaving the product as a white or off-white solid. In the event that the product was discolored it was made colorless by filtration in a second extraction from $(C_2H_5)_2O$/hexane (1:6). Yields: $(CH_3)_2S·B_9H_{13}$, 1,341 g, 78%; $(C_2H_5)_2S·B_9H_{13}$, 1.603 g, 80%; ((t-$C_4H_9)_2S·B_9H_{13}$, 2.179 g, 85%.

(b(i)) L = $(C_6H_5)_2S$. The initial filtration step to isolate $B_9H_{13}·O(C_2H_5)_2$ was performed by using a two-necked 100-mL receiver vessel. $(C_6H_5)_2S$ (10 mmol) was introduced into the flask via a side arm, under an N_2 atmosphere. After the mixture was stirred for 2 h, the $(C_2H_5)_2O$ and N_2 were removed under dynamic vacuum. This yielded off-white $B_9H_{13}·S(C_6H_5)_2$ as a solid in 80% yield.

(b(ii)) L = $P(C_6H_5)_3$. The initial filtration of $B_9H_{13}·O(C_2H_5)_2$ was performed by using a 100-mL two-necked receiver vessel, fitted with a side-arm tip-tube containing $P(C_6H_5)_3$ (10 mmol, 3.729 g). The $P(C_6H_5)_3$ was tipped into the receiver vessel, and after the mixture was stirred at room temperature for 2 h, removal of $(C_2H_5)_2O$ effected the isolation of pure-white $B_9H_{13}·P(C_6H_5)_3$, yield 3.057 g (82%).

(b(iii)) L = $(n\text{-}C_4H_9)_2S$. This ligand displacement reaction was performed as per $(C_6H_5)_2S·B_9H_{13}$ (section 5(b(i))). On removal of $(C_2H_5)_2O$, however, an off-white oil was obtained, which would not solidify on trituration with hexane. Therefore, the yield was estimated by performing a second displacement reaction of $(t\text{-}C_4H_9)_2S$ by $P(C_6H_5)_3$ in the manner described for in section 5(b(ii)); yield ($B_9H_{13}·P(C_6H_5)_3$) 2.98 g, 80%.

6. Synthesis of *nido*-5,6-$(CH_3)_2$-5,6-$C_2B_8H_{10}$. In a typical reaction NaH (6.0 mmol) was reacted with B_5H_9 (10.8 mmol) in 10 mL of THF to produce Na[B_9H_{14}] as described in section 1(b) of this report. The yellow gum was then converted to $B_9H_{10}·O(C_2H_5)_2$ as described in section 4; however, it was not necessary to remove KCl by filtration. The etheral solvent was pumped away, and freshly distilled ether was condensed into the reaction vessel at −196 °C. 2-Butyne (24.9 mmol), providing a 4.8:1 molar ratio of alkyne to adduct, was also condensed into the reaction vessel at −196 °C. The reaction mixture was slowly warmed to room temperature with stirring for 18–22 h. The initially clear, yellow solution mixture darkened to a deep red color in less than 2 h. The reaction mixture was then fractionated through U-traps maintained at −35, −78, and −196 °C for 24–28 h, leaving behind a red tar in the reaction vessel. 5,6-$(CH_3)_2$-5,6-$C_2B_8H_{10}$ (337 mg, 34% yield) was obtained in the −35 °C trap. This product was identified from its mass spectrum (exact mass calcd 152.199 650, found 152.2034) and from its boron-11 NMR spectrum.

In the procedure described above, 5,6-$(CH_3)_2C_2B_8H_{10}$ was obtained in a "one-pot" reaction with no prior purification of the $[B_9H_{14}]^-$ salt. A second experiment using pure $[B_9H_{14}]^-$ was carried out to determine if this would give an improved yield. A yield comparable to that indicated above was obtained.

7. Preparation of *nido*-5,6-$C_2B_8H_{12}$. NaH (11.8 mmol) and B_5H_9 (23.0 mmol) were allowed to react in 10–15 mL of THF in a 500-mL reaction vessel as described in section 4 above to form Na[B_9H_{14}]. After the volatiles had been pumped away, 10 mL of diethyl ether and 11.5 mmol of HCl were condensed into the vessel, which was cooled to −196 °C. The vessel was allowed to warm to room temperature, causing H_2 evolution. After 30 min, the reaction was complete. The vessel was cooled to −196 °C, and 11.0 mmol of evolved H_2 was measured in a Toepler system and pumped away. A 29.2-mmol sample of C_2H_2 was then condensed into the vessel. *CAUTION! Pure acetylene is shock sensitive and should be handled in shielded vessels.*[43] The reaction

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(43) "Prudent Practices for Handling Hazardous Chemicals"; National Research Council, National Academy Press: Washington, DC, 1981; p 89.

mixture was warmed to room temperature and stirred overnight in a shielded metal bomb. After 18 h, the reaction mixture was light beige in color. Volatile materials were fractionated through traps at −78, −111, and −196 °C; 6.0 mmol of C_2H_2 was recovered in the −196 °C trap. $(C_2H_5)_2O$ stopped in the −111 °C trap. The −78 °C trap contained 162 mg of *nido*-5,6-$C_2B_8H_{12}$ (9% based on B_5H_9 starting material), which was identified by its ^{11}B NMR[36] and mass spectra.

8. Conversion of B_5H_9 to *n*-$B_{18}H_{22}$. $Na[B_9H_{14}]$ was prepared from 8.30 mmol of NaH (199.3 mg) and 15.0 mmol of B_5H_9 reacting in 10 mL of dry glyme in a 500-mL reaction vessel according to the procedure described in section 1(b). By the use of a procedure reported by Dobson, Keller, and Schaeffer,[7] the $Na[B_9H_{14}]$ was first converted to $B_9H_{13}\cdot O(C_4H_9)_2$, which was then pyrolyzed to form *n*-$B_{18}H_{22}$; 316 mg of *n*-$B_{18}H_{22}$ (35% based on B_5H_9) was isolated.

9. Improved Preparation of $B_{10}H_{14}$ from B_5H_9. This preparation is similar to that reported earlier[1] except that the mole ratio of reactants is 1.8:1:1 B_5H_9:NaH:$[(CH_3)_4N]Cl$ (instead of 2:1:1) and glyme is used as the solvent. In this example, 372.4 mg of NaH (95% active, 14.74 mmol) and 26.3 mmol of B_5H_9 were used as starting material.

Isolation of the product can be achieved either by sublimation (method A) or extraction with *n*-butyl ether (method B).

Method A. The reaction flask was immersed in an oil bath heater, and the U-trap was cooled to 0 °C in an ice bath. While the reaction was pumped under dynamic vacuum (10^{-3} torr), the temperature of the oil bath was slowly raised to 45 °C and maintained there for 3 h. Most of the product sublimed in this step. The temperature was then raised to 110 °C over a period of 3 h. After cooling, the vessel was disassembled and the 938 mg (7.68 mmol) of slightly yellow decaborane(14) was scraped out. This represents a 58.4% conversion from B_5H_9.

Method B. If this method is used it is not necessary to attach the U-trap to the reaction vessel. After H_2 has been pumped away following reaction with BCl_3, 40 mL of dry *n*-butyl ether was added in the drybox. The vessel was again attached to the vacuum line, and the solvent was degassed. The flask was heated to 110 °C over a period of 3-4-h with an oil bath heater. The light yellow solution was filtered. A product yield of approximately 50% was estimated by comparison with ^{11}B NMR samples of standard concentrations.

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Registry No. B_5H_9, 19624-22-7; $[Me_4N][B_9H_{14}]$, 12545-93-6; $K[B_9H_{14}]$, 39296-28-1; $Na[B_9H_{14}]$, 70865-40-6; $[Me_4N][B_{11}H_{14}]$, 52619-67-7; $B_9H_{13}\cdot O(C_5H_5)_2$, 12545-41-4; $(CH_3)_2S\cdot B_9H_{13}$, 32357-02-1; $(C_5H_5)_2S\cdot B_9H_{13}$, 32356-99-3; $(t\text{-}C_4H_9)_2S\cdot B_9H_{13}$, 99686-00-7; $B_9H_{13}\cdot S(C_6H_5)_2$, 99666-93-0; $B_9H_{13}\cdot P(C_6H_5)_3$, 32235-80-6; $(n\text{-}C_4H_9)_2S\cdot B_9H_{13}$, 99666-94-1; 5,6-$(CH_3)_2$-5,6-$C_2B_8H_{10}$, 31566-09-3; $B_{10}H_{14}$, 17702-41-9; *nido*-5,6-$C_2B_8H_{12}$, 41655-26-9; *n*-$B_{18}H_{22}$, 21107-56-2.

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Methylpentaborane(11): A Mixture of Isomers

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Use of high-field-strength NMR, 500.1 MHz for ^{1}H and 160.4 MHz for ^{11}B, has shown that preparations previously considered to be 2-$CH_3B_5H_{10}$ and 3-$CH_3B_5H_{10}$ are identical equilibrium mixtures of the two isomers. Through assessment of relative values for areas under the ^{1}H(C–H) resonance curves, temperature-dependent equilibrium constants and the related thermochemical values have been determined for the isomerization process.

Two preparations have been reported for methylpentaborane(11), $CH_3B_5H_{10}$. The product from the exchange of pentaborane(11) and methyldiboranes was called the 2-methyl derivative[1] (I), and the product from the NH_3/H^+ process applied to methylhexaborane(12) was considered to be the 3-methyl isomer[2] (II). We can now show that the two preparations are very probably identical equilibrium mixtures of isomers having substituent locations at front corners (2 or 5) or back corners (3 or 4) of the trapezoidal-pyramidal base. This conclusion was not reached earlier because prior work[1-3] was handicapped by the necessity of using NMR spectrometers unequal to the task of fully resolving the spectra. In this work, it has been possible to measure spectra at 500.1 MHz for ^{1}H NMR and at 160.4 MHz for ^{11}B NMR with ^{1}H decoupling. Consequently the ^{11}B NMR spectra are found dispersed to the point of zero overlap, and the ^{1}H NMR spectra, though still displaying overlap, can be interpreted with much more certainty than before.

Results and Discussion

Preparations I and II were recognized to be identical when the two were found to have the same ^{11}B NMR spectra at 64 MHz. This is a remarkable result as one would scarcely expect that preparative pathways so different would yield the same product. One proceeds through a gas/liquid-phase molecular exchange reaction and the other via ionic intermediates. Confirmation that samples identical with the original preparation of II were being dealt with can be seen by comparison with ^{11}B NMR spectra taken at 32.1 MHz[2,2b] and at 160.4 MHz as seen in Table I. Even though the field strength is so much reduced, of the eight resonances seen at 160 MHz, six are seen almost identically at 32 MHz.

Table I. ^{11}B Magnetic Resonance Spectra of Methylpentaborane(11) Mixtures

this work[a]			ref 2a[b]		assignts[c] (this work)	
δ	*J*, Hz	rel area	δ	*J*, Hz	2-Me	3-Me
21.0	130	1	20.4		B(2) (d)	
19.4		2				B(3) (s)
8.5	125	3	8.78	122	B(5) (t)	B(5) (t)
1.8	126	2	0.9	103		B(2) (t)
−1.7	126	1			B(4) (d)	
−2.4	126	1	−2.4	127	B(3) (d)	
−8.7	166	2	−7.8	179		B(4) (d)
−52.3	149	3	−52.0	142	B(1) (d)	B(1) (d)

[a] At 160.4 MHz, −35 °C. [b] At 32 MHz. [c] Key: (d) doublet; (s) singlet; (t) triplet.

The ^{11}B NMR spectrum taken at 164.4 MHz shows the nature of the situation as can be seen in Figure 1 and Table I. It is apparent that the preparations are mixtures of 3-methylpentaborane(11) and 2-methylpentaborane(11). At −35 °C the proportions seen in the ^{1}H-decoupled spectrum are 2:1.

Ten resonances might be expected from a mixture of the two isomers, but since only eight can be seen in Figure 1, two peaks must be common to both. It is unlikely that atoms in different environments in the two isomers would have chemical shifts that are not resolved at the field strength employed; therefore, the common peaks must arise from similarly located boron atoms. The two peaks with relative area 3, a triplet at 8.5 ppm and a doublet at −52.3 ppm, are the ones shared. These have been

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