mium(VI)), no general pattern that would make chromium(V) a promising selective oxidant has emerged.

Registry No. I, 70132-29-5; $Na_2Cr_2O_7$, 10588-01-9; HO_2CCO_2H, 144-62-7; $CH_3CH(OH)CO_2H$, 50-21-5; $C_6H_5CH_2CH(OH)CO_2H$, 156-05-8; $HOCH_2CO_2H$, 79-14-1; $HO_2CCH(OH)CH(OH)CO_2H$, 526-83-0; $C_6H_5CH(OH)CO_2H$, 90-64-2; $C_6H_5C(CH_3)(OH)CO_2H$, 515-30-0; $OHCCO_2H$, 298-12-4; $CH_3C(O)CO_2H$, 127-17-3; $HO_2C(CH_2)_2C(O)CO_2H$, 328-50-7; $HO_2CCH_2C(O)CH_2CO_2H$, 542-05-2; PrOH, 71-23-8; *i*-PrOH, 67-63-0; $HO(CH_2)_2OH$, 107-21-1; $CH_3CH(OH)CH_2OH$, 57-55-6; $CH_3CH(OH)CH(OH)CH_3$, 513-85-9; HCHO, 50-00-0; CH_3CHO, 75-07-0; CH_3CH_2CHO, 123-38-6; $CH_3(CH_2)_2CHO$, 123-72-8; $(CH_3)_2C(OH)CO_2H$, 594-61-6; $CH_3CH_2C(CH_3)(OH)CO_2H$, 3739-30-8; $Et_2C(OH)CO_2H$, 3639-21-2; $CH_3CH(OH)CO_2H$, 50-21-5; cyclobutanol, 2919-23-5; cyclopentanol, 96-41-3; cyclohexanol, 108-93-0; pinacol, 76-09-5.

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Hydrogen Isotope Exchange between Boranes and Deuterated Aromatic Hydrocarbons: Evidence for Reversible Hydroboration of Benzene

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Pentaborane(9), B_5H_9, and diborane(6), B_2H_6, undergo hydrogen isotope exchange with deuterated aromatic hydrocarbons. Lewis acid catalyzed hydrogen isotope exchange occurs between benzene-d_6 and the apical hydrogen atom of B_5H_9 to form $1\text{-}DB_5H_8$ at ambient temperature. In uncatalyzed exchanges, B_5H_9 reacts with deuterated aromatic hydrocarbons to produce $1,2,3,4,5\text{-}D_5B_5H_4$ at +45 °C and B_5D_9 at +120 °C. This thermally induced hydrogen isotope exchange apparently occurs via a reversible hydroboration of the aromatic ring. Diborane undergoes a similar isotope exchange with benzene-d_6 under mild thermal conditions.

Introduction

Hydroboration was discovered in 1936 during a study of the reaction of diborane(6), B_2H_6, with various carbonyl-containing organic molecules.[2] The importance of the reaction grew with the discovery that, on addition of B_2H_6 to asymmetrically substituted olefins, anti-Markovnikov alcohol products were isolated after oxidative workup.[3] Subsequent investigations have established the applicability of hydroboration reductions for carbon–carbon and carbon–heteronuclear multiple bonds of many types. The development of new borane, borane anion, and borane–base adduct reagents has increased the selectivity of the reaction and widened its utility from regiospecific to stereospecific synthetic applications.

Hydroboration reactions involving higher boranes have also been known for many years. The hydroboration of ethylene at elevated temperatures by pentaborane(9), whose structure is shown in Figure 1, was the first reported synthesis of 2-ethylpentaborane (eq 1).[4] Another example is the addition of the $6\text{-}SB_9H_{11}$ thiaborane to olefins under mild conditions to produce high yields of $9\text{-(alkyl)-}6\text{-}SB_9H_{11}$ derivatives.[5] In addition, intramolecular hydroboration has been suggested as a likely mechanism for the rearrangement of $2\text{-(vinyl)}B_5H_8$ compounds to various derivatives of $2\text{-}CB_5H_9$.[6]

$$B_5H_9 + C_2H_4 \xrightarrow{150\ ^\circ C} 2\text{-}EtB_5H_8 \qquad (1)$$

As a part of our studies of pentaborane rearrangement mechanisms, we have recently explored various methods for labeling B_5H_9 with deuterium. In this paper we report the preparation of deuterium-labeled pentaboranes and diborane by deuterium–hydrogen exchange between the borane and deuterated aromatic hydrocarbons in the presence and absence of $AlCl_3$ catalyst. It appears that this hydrogen–deuterium exchange may be facilitated by reversible hydroboration of the aromatic ring by B_5H_9 and B_2H_6.

Table I. ^{11}B NMR Spectral Data (86.6 MHz)

compd	δ^a ($J_{BH}{}^b$) B(1)	B(2–5)
$1\text{-}DB_5H_8$	−53.4	−13.7 (166)
$1,2,3,4,5\text{-}D_5B_5H_4$	−53.4	−13.4
B_5D_9	−53.8	−14.1
B_5H_9	−53.4 (179)	−13.7 (162)

[a] All chemical shifts are referenced against $BF_3{\cdot}OEt_2$. [b] All coupling constants are in Hz.

Results

Lewis Acid Catalyzed Exchange between B_5H_9 and C_6D_6. Deuterium–hydrogen exchange between C_6D_6 and the apical terminal H(1) hydrogen of B_5H_9 occurs in the presence of $AlCl_3$, producing $1\text{-}DB_5H_8$ at ambient temperature (eq 2). The exchange is typically complete in 1 day. The recovery of the pentaborane is quantitative, and the extent of deuteration of the apical H(1) position is controlled by the C_6D_6:B_5H_9 reactant ratio. ^{11}B NMR data for $1\text{-}DB_5H_8$ are given in Table I. Insignificant quantities of label are incorporated into the basal terminal H(2–5) positions of B_5H_9 as indicated by the ^1H NMR spectrum and verified by the ^2H NMR spectrum of $1\text{-}DB_5H_8$ shown in Figure 2. Increasing the reaction temperature to +55 °C does not increase the amount of label in the basal terminal positions. The rate of apical deuteration varies for different pentaborane derivatives, and preliminary results indicate that the rate increases in the order $2\text{-}(Me_3Si)B_5H_8 < 2\text{-}ClB_5H_8 < B_5H_9 < 2\text{-}BrB_5H_8$. The rate of deuteration at the terminal H(2–5) positions is also affected by substitution on the pentaborane cage. For example, deuterium exchange at the H(4) and H(1) positions in $2\text{-}ClB_5H_8$ occurs at approximately the same rate.[7]

$$B_5H_9 + C_6D_6 \xrightarrow{AlCl_3} 1\text{-}DB_5H_8 + C_6D_5H \qquad (2)$$

Thermolysis of B_5H_9 and C_6D_6 or C_7D_8. Deuterium–hydrogen exchange between the terminal H(1–5) hydrogens of B_5H_9 and deuterated aromatic hydrocarbons can be observed at elevated

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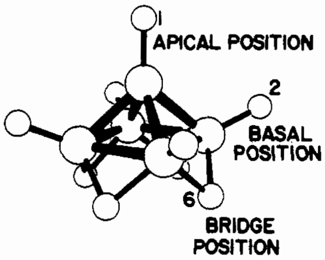

Figure 1. Structure of pentaborane(9), B_5H_9, showing the numbering of the hydrogen positions. The apex is labeled as the H(1) position, the basal terminal positions, H(2–5), are represented by H(2), and the bridge hydrogen positions, H(6–9), are represented by H(6).

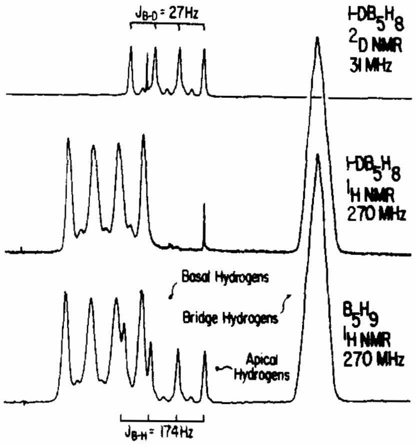

Figure 2. ^{1}H and ^{2}H NMR spectra (270 and 30.6 MHz, respectively) of 1-DB_5H_8 compared with the 270-MHz ^{1}H NMR spectrum of B_5H_9. B–^{1}H and B–^{2}H coupling constants are given in Tables II and III.

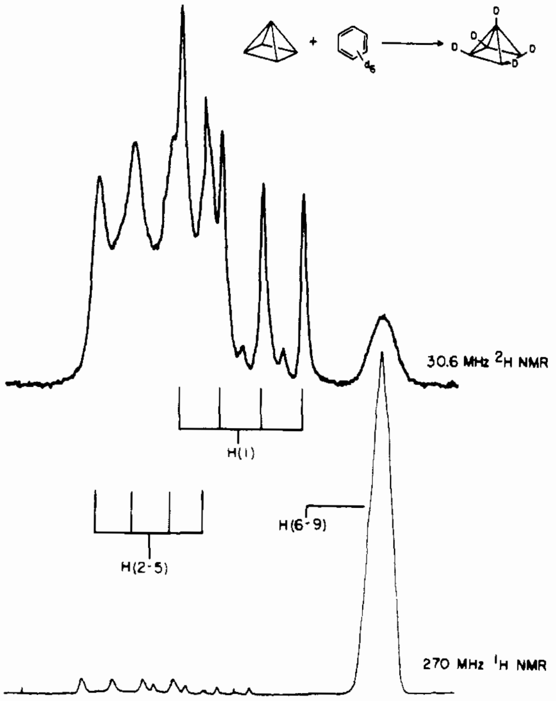

Figure 3. ^{1}H and ^{2}H NMR spectra (270 and 30.6 MHz, respectively) of 1,2,3,4,5-$D_5B_5H_4$. The boron–deuterium coupling constants for ^{2}H(1) and ^{2}H(2–5) are indicated on the figure. Numerical values are given in Table III.

temperatures. This exchange process has a threshold temperature of +45 °C, but reaction is quite slow. At 60 °C, exchange occurs more rapidly, requiring about 2 weeks to come to equilibrium. Recovery of pentaborane is nearly quantitative. The mass spectral data indicate an average of four deuterium atoms per pentaborane cage, and the ^{1}H and ^{2}H NMR data, shown in Figure 3, reveal that these deuterium labels are statistically distributed between the five terminal hydrogen positions of the cage. This deuterated pentaborane will be referred to as 1,2,3,4,5-$D_5B_5H_4$ to indicate all potential label positions. ^{11}B NMR spectral data are reported in Table I. Small quantities of C_6D_6 or C_7D_8 and C_6D_{12} impurities were detected in the product by IR and ^{2}H NMR spectroscopy.

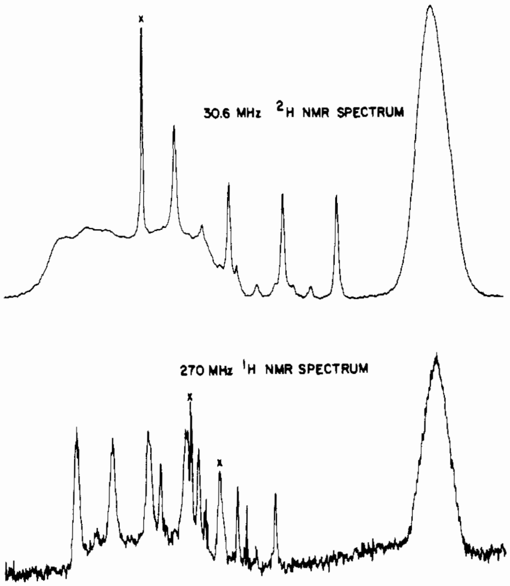

Figure 4. ^{1}H and ^{2}H NMR spectra (270 and 30.6 MHz, respectively) of B_5D_9. B–^{1}H and B–^{2}H coupling constants are reported in Tables II and III.

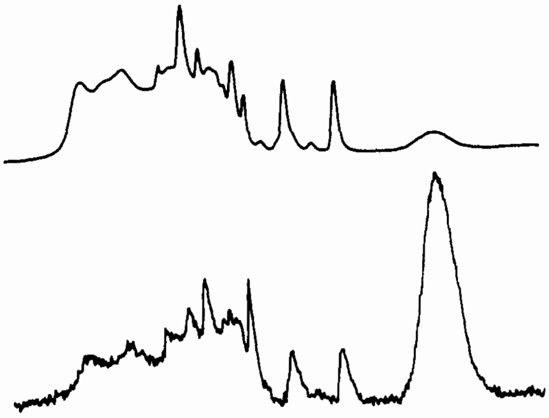

Figure 5. ^{2}H NMR spectra (30.6 MHz) showing the thermal rearrangement of 1,2,3,4,5-$D_5B_5H_4$ at 140 °C. The upper trace is before heating, and the lower trace is after heating.

Increased percentages of deuterium incorporation in the bridging H(6–9) positions are observed at higher temperatures. At 120 °C, polydeuterated pentaboranes are produced. Some residual hydrogen content can be observed by ^{1}H NMR, and the mass spectral data show a range of deuterated products having compositions in the range B_5D_9 to $B_5D_5H_4$. Inspection of the ^{1}H and ^{2}H spectra, shown in Figure 4, reveals that deuterium has migrated nearly statistically into all of the hydrogen positions of pentaborane. The ^{2}H NMR spectrum integration shows a deuterium ratio of apex:base:bridge deuterium positions of 1.0:4.4:3.0. These deuterated pentaboranes will be referred to as B_5D_9 in order to indicate all potential label positions. Recovery of pentaborane is about 75%. These elevated-temperature reactions produce significant thermal side reactions with polydeuterated decaborane as the major pyrolysis decomposition product.

NMR Study of the Thermolysis of 1,2,3,4,5-$D_5B_4H_4$ to Statistically Deuterium-Labeled Pentaborane(9). ^{2}H NMR data (Figure 5) have shown that deuterium atoms in terminal hydrogen positions move into the bridge hydrogen positions of pentaborane under thermal conditions in the absence of solvent. This reaction is quite slow at +105 °C but proceeds readily at +140 °C.

NMR Studies of the Thermolysis of (μ-D)B_5H_8 and B_5H_9 with Various Aromatic Hydrocarbons. The ^2H NMR data, obtained from the +160 °C thermolysis of (μ-D)B_5H_8 in solutions of benzene, toluene, and *p*-xylene, indicate that the deuterium migrates out of the bridge position and into the terminal hydrogen positions of B_5H_9 and then exchanges onto the aromatic ring. However, no deuterium is transferred to the alkyl groups of the aromatic derivatives. Relative rates of deuterium movement in the various solvents was not assessed due to experimental design limitations.

Hydrogen Isotope Exchange between B_2H_6 and C_6D_6. Hydrogen–deuterium exchange between B_2H_6 and C_6D_6 occurs under mild thermal conditions at +65 °C. The reaction is not quantitative, however, as significant amounts of B_2H_6 are converted to pentaborane and decaborane. The rate of deuteration is apparently dependent on BH_3 concentration, as heating the samples to achieve reasonable deuteration rates also speeds the production of higher boranes. The $AlCl_3$ catalyst causes no significant acceleration of the deuterium-exchange rate.

Discussion

Deuterium–Hydrogen Exchange in the Presence of $AlCl_3$. Pentaborane, like aromatic hydrocarbons, undergoes electrophilic substitution reactions to form 1-alkyl- and 1-halopentaborane derivatives (eq 3 and 4).[8,9] The synthesis of 1-DB_5H_8 was first

$$B_5H_9 + RX \xrightarrow{AlX_3} 1\text{-}RB_5H_8 + HX \qquad (3)$$

$$B_5H_9 + X_2 \xrightarrow{AlX_3} 1\text{-}XB_5H_8 + HX \qquad (4)$$

accomplished by deuterium–hydrogen exchange between DCl and B_5H_9 with an $AlCl_3$ catalyst (eq 5).[10] Mixtures of a deuterated

$$B_5H_9 + DCl \xrightarrow{AlCl_3} 1\text{-}DB_5H_8 + HCl \qquad (5)$$

and a nondeuterated aromatic hydrocarbon undergo hydrogen isotope exchange in the presence of Lewis acid catalysts.[11] The similar exchange between C_6D_6 and the H(1) position of pentaborane is consistent with the existing body of pseudoaromatic chemistry associated with the apex of B_5H_9.[12]

The mechanism of intermolecular hydrogen exchange in aromatic hydrocarbons remains ill-defined. Previous researchers argued that hydrogen halides were the deuterium carriers in the exchange process and added catalytic amounts of water to their reactions to ensure that some HX was present.[11c] Our experiments, in contrast, were performed under conditions that would exclude hydrogen halides. The $AlCl_3$ catalyst was sublimed in situ under vacuum and was left under dynamic vacuum at ambient temperature for several hours afterward. In addition, all reagents were dry and air was rigorously excluded from the reaction system. Only nondetectable trace quantities of hydrogen chloride could have been present in the reaction mixture.

While the apex of B_5H_9 is most susceptible to electrophilic attack, the chemistry of the other terminal H(2–5) positions is somewhat affected by the presence of Lewis acid catalysts. Detectable but insignificant deuterium incorporation into the terminal H(2–5) positions of pentaborane has been observed in the C_6D_6 exchange system, previously on thermolysis of B_5H_9 with SiD_4, and in hydrogen isotope exchange between B_5H_9 and DCl (eq 5).[10,13]

Deuterium–hydrogen exchange between B_5H_9 and C_6D_6 in the presence of $AlCl_3$ is an excellent route for the synthesis of 1-DB_5H_8. While care is required to separate the products of the benzene-d_6 exchange system, the isotopic purity of the deuterium source is far more easily controlled in C_6D_6 than in DCl. This reduces the number of exchanges necessary to obtain 1-DB_5H_8 of the desired isotopic content.

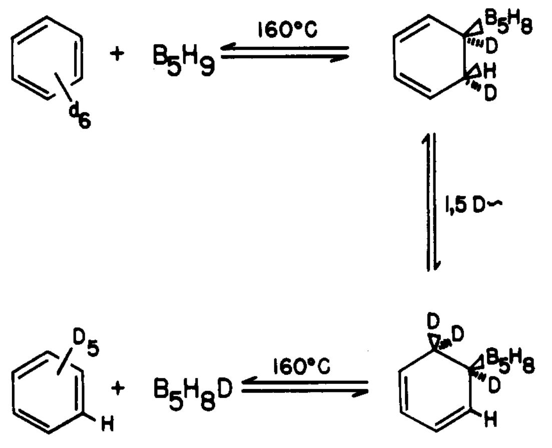

Figure 6. Proposed reversible hydroboration mechanism for uncatalyzed hydrogen isotope exchange between pentaborane(9) and benzene-d_6.

Uncatalyzed Isotope Exchange. Thermally induced isotopic exchange between B_5H_9 and deuterated aromatic hydrocarbons is a useful route for producing 1,2,3,4,5-$D_5B_5H_4$ and B_5D_9. 1,2,3,4,5-$D_5B_5H_4$ was produced previously through exchange between B_2D_6 and B_5H_9 at +80 °C.[14] The C_6D_6 exchange process offers the advantage of a readily available and more easily handled deuterium source. Although C_6D_6 and B_2D_6 exchanges both introduce deuterium label in the H(1–5) positions of B_5H_9, there is no obvious mechanistic connection between the reaction systems. B_5D_9 was previously made by repeated exchanges between B_5H_9 and D_2 over a chromia–alumina dehydrogenation catalyst.[15] The advantages of the high-temperature thermolysis over the previous system are that the higher deuterium atom density of C_6D_6 will allow the same deuterium content in the borane to be reached in fewer exchange cycles and that simpler equipment and reagents are required for the reaction.

The uncatalyzed exchange of hydrogen isotopes between deuterated aromatic hydrocarbons and B_5H_9 or B_2H_6 apparently represents a new class of hydrogen-exchange reactions in boranes. One possible route for this exchange is the production of a Lewis acid at elevated temperatures, which facilitates deuterium–hydrogen transfer in a process similar to the $AlCl_3$-catalyzed exchange between B_5H_9 and C_6D_6. This mechanism however would be specific for the apical hydrogen position, producing largely 1-DB_5H_8. It seems unlikely that this is the sole mechanism, as deuterium label is substantially introduced into the basal terminal hydrogen positions as well as the apical hydrogen position. In addition, $AlCl_3$ causes no significant increase in the deuterium-exchange rate for B_2H_6 and C_6D_6. It is not likely that this reaction is operating via a Lewis acid catalyzed exchange. A rationale also consistent with the observed data is a hydroboration of the aromatic ring by a B–H terminal bond followed by dehydroboration to form a B–D bond. After the syn-hydroboration of the aromatic ring, a 1,5-deuteride shift can produce a CD_2 group adjacent to the B_5H_8 moiety. Syn-dehydroboration from this intermediate will result in the formation of a B–D bond. This reversible hydroboration mechanism is illustrated in Figure 6.

While a hydroboration mechanism explains the exchange of deuterium label into the terminal hydrogen positions of pentaborane, it does not explain the movement of deuterium into the bridge hydrogen positions of B_5H_9 in the high-temperature (120 °C) total-immersion experiments. As was demonstrated in a separate experiment, solvent is not necessary for deuterium label

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Table II. ^{1}H NMR Spectral Data (270 MHz)

	δ^a ($J_{BH}{}^b$)		
compd (solvent)	H(1)	H(2-5)	H(6-9)
1-DB_5H_8 (CD_2Cl_2)		2.40 (164)	−2.69
1,2,3,4,5-$D_5B_5H_4$ (CD_2Cl_2)	0.44 (174)	2.34 (167)^c	−2.48
B_5D_9 (C_6D_6)	0.77 (174)^c	2.36 (166)^c	−2.71^c
B_5H_9 (C_6D_6)	0.89 (175)	2.37 (166)	−2.75

^{a} All chemical shifts are referenced against an external Me_4Si standard. ^{b} All coupling constants are in Hz. ^{c} Resonances appearing at these chemical shifts are due to trace quantities of residual proton nuclei.

Table III. ^{2}H NMR Spectral Data (30.6 MHz)

	δ^a ($J_{BH}{}^b$)		
compd	D(1)	D(2-5)	D(6-9)
1-DB_5H_8	0.43 (27)		
1,2,3,4,5-$D_5B_5H_4$	0.42 (27)	2.31 (23)	−2.52^c
B_5D_9	0.43 (27)	2.36 (22)	−2.56

^{a} All chemical shifts are referenced against an external C_6D_6 standard. ^{b} All coupling constants are in Hz. ^{c} This resonance represented a trace quantity of deuterium label in the bridge position of pentaborane.

movement from the terminal hydrogen positions into the bridge positions. Although the mechanism is unknown, this may be an intramolecular process that allows deuterium scrambling into the bridge positions of pentaborane under appropriate thermal conditions.

Experimental Section

All inert-atmosphere manipulations were performed in dry-nitrogen-filled glovebags and on standard high-vacuum lines.[16] All solvents were dried over $LiAlH_4$ prior to use. C_6D_6 and $CD_3C_6D_5$ were obtained from Stohler Isotope Chemicals. $AlCl_3$ was purified in situ by repeated sublimation. (μ-D)B_5H_8 was prepared by the standard method.[17]

The 86.6-MHz ^{11}B and 270-MHz ^{1}H NMR spectra were acquired on a Bruker WH-270 or an IBM WP-270 spectrometer at spectral field widths of 10000 and 6000 Hz, respectively. The 30.6-MHz ^{2}H NMR spectra were acquired on a JEOL FX-200 spectrometer with a 1000-Hz spectral width and a pulse repetition time of 50 s. Mass spectra were obtained at 70 eV on an AEI MS-9 instrument using a standard gas-inlet system. Infrared spectra were obtained on Perkin-Elmer 700 and Beckman 4250 spectrophotometers using 10-cm gas cells with NaCl windows.

Reaction of B_5H_9 and C_6D_6 in the Presence of $AlCl_3$. In a typical reaction, 0.03 g of finely gound $AlCl_3$ was placed into a 100-mL reaction vessel. A 1.0-mmol sample of B_5H_9 and 16.5 mmol of C_6D_6 were added in vacuo. The flask was sealed, warmed to room temperature, and allowed to stand for 1 day. It was then opened onto a high-vacuum line, and the contents were distilled through a −78 °C U-trap into a −196 °C U-trap. The material in the −196 °C U-trap was repeatedly distilled (six to eight times) through a −78 °C trap into a −196 °C trap until IR spectroscopy confirmed that it was free of C_6D_6. The 1-DB_5H_8 product was contaminated with minute quantities of C_6D_6 even after many purification steps. Cyclohexane-d_{12}, which is present in low levels in some C_6D_6 samples, was a more serious contaminant.[18] Pentaborane and cyclohexane have nearly identical volatilities at low temperature and consequently cannot be separated by vacuum-line distillation. Benzene-d_6 must be free of C_6D_{12} before it can be used in the preparation of 1-DB_5H_8. The material in the −196 °C U-trap was identified by ^{11}B, ^{1}H, and ^{2}H NMR spectroscopy (Tables I–III) and mass spectrometry as 1-DB_5H_8, yield 1.0 mmol (100%).

Thermolysis of B_5H_9 and C_6D_6 or C_7D_8. A. Synthesis of 1,2,3,4,5-$D_5B_5H_4$. In a typical reaction, 5.54 mmol of B_5H_9 and 2.4 g (28.6 mmol) of C_6D_6 were placed in a breaktip reaction tube of approximately 15-mL volume. The sealed tube was heated totally immersed in an oven at +60 °C for 2 weeks. The volume of the reaction vessel was crucial as too large a gas volume reduced the apparent exchange rate. Total immersion in the oven is also important, since this promotes uniform heating of the sample and prevents solvent reflux upon a cooler portion of the reaction vessel. After being heated, the reaction vessel was opened on a high-vacuum line and the volatiles were repeatedly fractionated through a −78 °C U-trap until IR spectroscopy showed the material in the adjacent −196 °C trap to be pure. A total of 5.51 mmol (99.5%) of the pentaborane was recovered. The product was analyzed by ^{1}H, ^{11}B, and ^{2}H NMR spectroscopy and mass spectrometry. The mass spectrum revealed an average of four deuterium atoms per pentaborane cage.

Experiments using other deuterated aromatic hydrocarbons, such as toluene-d_8, indicated that these solvents may be substituted for benzene-d_6 with no loss of reactivity. Reactions in C_7D_8 occurred at a lower temperature than those in C_6D_6. In a typical experiment, 0.93 mmol of B_5H_9 and 3.76 mmol of C_7D_8 were sealed in 5-mm-o.d. NMR tubes and heated at +45 °C totally immersed in an oven for 8 days. Exchange into the terminal positions was observed by ^{11}B and ^{1}H NMR spectroscopy.

B. Synthesis of B_5D_9. In a typical experiment, 63.15 mmol of C_6D_6 and 6.01 mmol of B_5H_9 were sealed in a 15-mL breaktip reaction vessel as described earlier. The vessel was heated at 117 °C totally immersed in an oven for 18 days. Yellow precipitates formed, which ^{11}B NMR showed to be polydeuterated decaborane. Volatile products were purified as before by repeated fractionation through a −78 °C U-trap until the contents of the adjacent −196 °C trap was pure by IR spectroscopy. A total of 4.64 mmol (77%) of the pentaborane was recovered. The product was analyzed by ^{1}H, ^{2}H, and ^{11}B NMR spectroscopy and mass spectrometry. The mass spectrum indicated a range of deuteration products from B_5D_9 to $B_5D_5H_4$, with an average of about seven deuterium atoms per molecule.

Thermolysis of 1,2,3,4,5-$D_5B_5H_4$. A 1.45-mmol sample of 1,2,3,4,5-$D_5B_5H_4$ was placed in a thick-walled 5-mm-o.d. NMR tube and sealed in vacuo. The tube was heated to +137 °C for 6 days. Yellow solids were observed, and 1.13 mmol of pentaborane was recovered (78% yield). The ^{2}H NMR spectrum of the sample is shown in Figure 5.

Thermolysis of (μ-D)B_5H_8 with Benzene, Toluene, and *p*-Xylene. Three NMR samples were prepared by transferring in vacuo 3.0 mmol of benzene, toluene, or *p*-xylene and 2.0 mmol of (μ-D)B_5H_8 into 5-mm medium-walled NMR tubes and sealing the tubes under high vacuum. The samples were placed in an oven that covered the bottom half of each tube. The oven was heated to +160 °C. The exchange of deuterium in the samples was monitored at intervals by ^{2}H NMR spectroscopy. After the first heating, the solutions developed a yellow tint that darkened with each subsequent heating. The ^{2}H NMR spectra of all three tubes indicated that the deuterium left the bridge position, moving slowly into the terminal hydrogen positions of the B_5H_9 molecule and exchanging onto the aromatic ring. In all three tubes (over the duration of the experiment), the concentration of deuterium in the terminal hydrogen positions of the pentaborane was greater than the concentration of the deuterium on the aromatic ring. Due to experimental design limitations, relative rates of deuterium movement in the various solvents were not assessed.

Reaction of B_2H_6 and C_6D_6. Into two 5-mm-o.d. NMR tubes, one empty and one containing a catalytic amount of $AlCl_3$, were transferred, in vacuo, 3.0 mmol of C_6D_6 and 0.3 mmol of B_2H_6. The samples were frozen, sealed under vacuum, and warmed to ambient temperature. The ^{11}B NMR spectra were monitored before and after the samples were heated half-immersed in an oil bath at +45 °C for 3 days, and no changes were observed. After the samples were heated to +65 °C for 3 days, the triplet of triplets coupling of the B_2H_6 resonance, which appears at +17.2 ppm, collapsed to a broad singlet in both spectra. New singlet resonances that are characteristic of polydeuterated pentaborane(9) and decaborane(14) also appeared.

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Registry No. 1-DB_5H_8, 63643-91-4; 1,2,3,4,5-$D_5B_5H_4$, 94706-80-6; B_5D_9, 24034-84-2; B_5H_9, 19624-22-7; B_2H_9, 19287-45-7; C_6D_6, 1076-43-3; C_7D_8, 2037-26-5; $AlCl_3$, 7446-70-0.

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(18) ^{2}H NMR spectral data: singlet at 1.27 ppm. IR spectral data: 2200, 2100 cm^{-1} strong (CD_2 stretch); 1260, 1190, 1020, 910 cm^{-1} weak.