volumetric vessel. When the O_2 uptake reached 1 mmol (ca. 2 min), the dark purple powder was filtered off and dried under vacuum. IR spectra were recorded on a Hitachi Model EPI-G3 spectrometer in KBr pellets (X = ClO_4^-; bands in cm^{-1}: 3310 (s), 3260 (s), 1621 (m), 1582 (s), 1505 (vs), 1102 (vs), 780 (s), 752 (s)).

Polarograms were recorded in EtOH–H_2O (1:1). The ESR spectra were taken on a JES FE 3X instrument and the UV–vis spectra on a Beckman ACTA MIV spectrophotometer. Mass spectra of the gas phase obtained from thermal decomposition of the purple μ-peroxo complex under N_2 were recorded on an AEI MS 902 instrument.

Kinetic measurements were performed in a stopped-flow device as well as on a Beckman ACTA MIV spectrophotometer, by monitoring the buildup of the μ-peroxo complex. Data from the two sources were in good agreement in the 440–750-nm range used. The average of three to give runs was used to estimate kinetic parameters for each individual composition, the reproduciblity being ±5%. All reactions were run at 25 °C in MeOH, up to a conversion of ca. 80%. The solubility of O_2 in MeOH was taken as in ref 19.

Registry No. $[(OPD)_2Co–O_2–Co(OPD)_2](ClO_4)_4$, 87012-56-4; $Co(OPD)_2^{2+}$, 49866-76-4.

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^2H NMR Spectral Studies of Intramolecular Rearrangements in Pentaborane(9)

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The rearrangement of various deuterium-labeled derivatives of pentaborane(9) in diethyl ether was studied by ^{11}B and ^2H NMR spectroscopy. Two distinct pathways for intramolecular exchange were identified at temperatures under 65 °C. One pathway allows movement from bridging positions to basal terminal positions, and a second higher energy pathway allows migration from basal terminal positions into the apex of the molecule. Exchange into and out of the apex of pentaborane appears to occur only when a substituent is one of the migrating groups. A mechanistic model for the isomerizations that conforms to the new data is suggested.

Introduction

Acid- and base-catalyzed intramolecular rearrangements are common in organic chemistry. Simple 1,2-hydride shifts and Wagner–Meerwein and Pinacole[1] rearrangements have been known for as long as 100 years. Many such acid-catalyzed rearrangements proceed via the formation of a carbonium ion and subsequent functional group migration. In cases where unfavorable orbital orientations preclude simple 1,2-shifts, intermolecular functional group transfer[2] and skeletal rearrangements[3] have been shown to operate in apparent intramolecular isomerizations. Base-catalyzed intramolecular rearrangements are historically more infrequent than acid-catalyzed reactions.[4] Consequently, the mechanisms involved in base-catalyzed rearrangements have been less exhaustively investigated.

The mechanism of isomerization of various pentaborane(9) derivatives by Lewis bases remains clouded despite the fact that the phenomenon was observed nearly 20 years ago. The first example of pentaborane rearrangement was the nearly quantitative production of 2-MeB_5H_8 from 1-MeB_5H_8 in the presence of lutidine (eq 1).[5]

$$1\text{-}MeB_5H_8 \xrightleftharpoons{2,6\text{-}Me_2(C_6H_3N)} 2\text{-}MeB_5H_8 \qquad (1)$$

Since this discovery, a wide variety of main group-substituted pentaboranes have been shown to isomerize in the presence of Lewis bases.[6] Among them are the bridge-silyl-substituted pentaboranes,[6a] which were the first compounds to demonstrate that all three positional isomers could be interconverted by Lewis base catalysts (eq 2). It was also

$$(\mu\text{-}Me_3Si)B_5H_8 \xrightarrow{Et_2O} 2\text{-}(Me_3Si)B_5H_8 \xrightleftharpoons{HMTA} 1\text{-}(Me_3Si)B_5H_8 \qquad (2)$$

determined that various derivatives could interact differently with a given Lewis base. For example, while 1-ClB_5H_8 rapidly forms 2-ClB_5H_8 in the presence of diethyl ether,[6b] only nitrogen bases (i.e., lutidine or HMTA) catalyze the conversion of 1-alkyl- to 2-alkylpentaboranes.[6c]

Early in the investigation of isomerization reactions, various mechanisms were proposed to explain the observed rearrangements. These explanations were largely derived by empirical means and attempted to deal with two major questions: What is the role of the Lewis base in isomerization, and what is the structure of the intermediate involved in the isomerization process?

Two proposals were developed for the role of the Lewis base in the isomerization of pentaborane derivatives. The first model proposed that isomerization proceeded by base deprotonation of the borane, followed by rearrangement of the borane anion, and subsequent reprotonation of the isomerized anion.[5,6d] A second proposal suggested that the base coordinated with the borane, causing sufficient distortion of the

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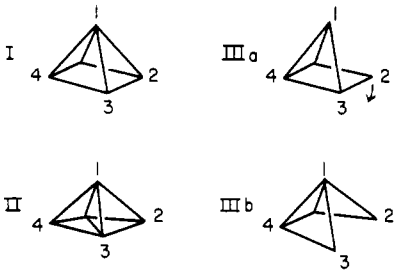

Figure 1. Suggested intermediates in pentaborane isomerization.

boron framework to produce skeletal rearrangement.[6e,g] One study confirmed that the rate-determining step in the diethyl ether catalyzed isomerization of monochloropentaboranes is first order in both ether and borane.[7] This result could be consistent with either of the proposed models.

More recent investigations have provided additional information about the role of the Lewis base in pentaborane isomerizations. A study of the isomerization of $(\mu\text{-D})B_5H_8$ determined that no intermolecular deuterium transfer occurred in the presence of THF.[6h] If deprotonation of the borane is one step in the isomerization process, then molecular rearrangement and recombination must occur very rapidly (i.e., before one of the ionic species can diffuse out of the solvent cage). Pentaborane is deprotonated at low temperature in ether solutions of lithium alkyls and sodium or potassium hydrides.[8] It has been determined that a bridging hydrogen atom is removed during deprotonation. Boron-11 NMR evidence has shown that intramolecular fluxionality in the deprotonated species is limited to tautomerism in the remaining three bridging hydrogen atoms.[8a] The same studies demonstrated that the 2-halopentaborane derivatives, which are known to be products of isomerization reactions, decompose when deprotonated by strong bases. In light of these observations, deprotonation appears to be a poor model for the behavior of the Lewis base in pentaborane rearrangements.

Suggested structures for intermediates in the isomerization process have been confined to a nido, a closo, and a "pseudoarachno" species (Figure 1; I, II, and IIIa).[6d,e,g] Structure I was suggested by some of the earlier investigators who proposed that the rearrangement might occur through a simple deprotonated species.[6d] The "pseudoarachno" structure (IIIa), which may be derived from *STYX* rules, implies that the Lewis base forms an adduct with the pentaborane, interrupting the bonding interaction between an apical and a basal boron atom.[6e] The coordinated boron atom then has two options: either to reassociate with the original apex boron atom, producing no net isomerization, or to associate with the cross-cage basal boron atom, forming the rearranged species. The closo structure (II) was the last intermediate suggested and has become tacitly accepted as the best proposal thus far.[6g] The model was based on the assertion that coordination by a Lewis base would lead to bond formation between two cross-cage boron atoms (i.e., a B(2) to B(4) bond). In the trigonal-bipyramidal intermediate thus formed, the scission of any boron–boron bond in the equatorial triangle would lead to the production of either the original isomer or a rearranged pentaborane product. This mechanism was developed as a rationale based on steric considerations for the preferential production of $2,3\text{-}Me_2B_5H_7$ over $2,4\text{-}Me_2B_5H_7$ in the isomerization of $1,2\text{-}Me_2B_5H_7$.[6g]

We conducted an empirical analysis of pentaborane(9) rearrangements several years ago, beginning from a different perspective than those of the previous researchers.[9] Our approach was based on the postulate that the structure of a Lewis base adduct intermediate in pentaborane isomerizations must be compatible with Wade's rules[10] and *STYX* rules[11] analyses. The addition of a base to pentaborane(9) adds one pair of skeletal bonding electrons and therefore predicts a progression from the nido starting material to an arachno intermediate. The analysis of the adduct by *STYX* rules leads to two possible structures for the intermediate: The first structure is a (3122) species, represented by IIIb, and the second is a (4031) species, represented by IIIa.

Structure IIIa has previously been suggested as an isomerization intermediate.[6e] Although IIIa is not strictly a correct *STYX* structure because it contains adjacent, nonbonded boron atoms, it has a structural precedent in $2,4\text{-}(\mu\text{-}CH_2)_2B_4H_8$. The major disadvantage of the mechanism based on structure IIIa is that it implies a one-step, complex migration of many of the hydrogen atoms in the molecule during any one isomerization event. Studies of the rearrangement of the $(\mu\text{-}Me_3Si)B_5H_8$[6a] and $(\mu\text{-D})B_5H_8$[6h] derivatives, however, have suggested that multistep processes with different activation energies may be involved.

While structure IIIb is a more acceptable *STYX* and Wade's rules model for a base adduct intermediate, it is not immediately obvious how this intermediate could lead to isomerization. One suggestion is that 1,2-alkyl and -hydrogen shifts may be facilitated by the opening of the molecule. A second proposal involves cage rearrangement: A diamond–square–diamond operation on either of the two diamonds in IIIb will interconvert the apical boron atom and one basal boron atom. This second model also accounts for the observation of multiple activation energies for the isomerization process.

Many of the problems associated with the understanding of the mechanism of isomerization of pentaborane derivatives arise from the proliferation of mechanistic models based on incomplete information. The development of improved synthetic routes to monodeuterated pentaboranes and the availability of high-field ^2H NMR instrumentation have made possible more detailed analyses of the movement of deuterium during the isomerization of various labeled pentaborane derivatives. In this paper we report the results of our ^{11}B and ^2H NMR studies of the isomerization of various monodeuterated pentaborane derivatives. We discuss the impact of these results on previous models of pentaborane rearrangement and propose a new mechanism that is consistent with current experimental information.

Experimental Section

Inert-atmosphere manipulations were performed in nitrogen-filled glovebags and standard high-vacuum systems.[12] Ether and benzene-d_6 were dried over $LiAlH_4$ before use. Phosphorus trichloride was distilled and transferred to a high-vacuum storage vessel prior to use. Aluminum trichloride was purified by repeated in situ sublimations. Deuterium oxide (99.8%), tri-*n*-butyltin deuteride, and *n*-butyllithium were used as received from Merck, Alfa, and Aldrich, respectively. $(\mu\text{-}Me_3Si)B_5H_8$ and $2\text{-}ClB_5H_8$ were prepared by literature methods.[6a,b] Deuterium chloride was prepared by the reaction of deuterium oxide and phosphorus trichloride in a 30-mL stainless-steel bomb.

All ^1H and ^{11}B NMR spectra were obtained on a Bruker WH-270 spectrometer at 270.071 and 86.653 MHz, respectively. The ^{11}B NMR spectra were acquired over a 10000-Hz spectral width, while ^1H NMR spectra were acquired over a 6000-Hz spectral width. The ^2H NMR

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Table I. ^{11}B NMR Chemical Shifts[a] and Coupling Constants[b]

	B(1)	B(2,5)		B(3,4)	
	δ	δ	J_{BH}	δ	J_{BH}
1-D(μ-Me_3Si)B_5H_7	−48.3	−8.56	151	−13.3	161

	B(1)	B(2)	B(3,5)		B(4)	
	δ	δ	δ	J_{BH}	δ	J_{BH}
1-D-2-(Me_3Si)B_5H_7	−50.4	−9.80	−10.6	(146)	−6.79	161
1-D-2-ClB_5H_7	−51.8	−0.79	−13.4	151	−23.3	151

	B(1)	B(2-5)	
	δ	δ	J_{BH}
1-(Me_3Si)B_5H_7D	−57.9	−12.8	151

[a] All chemical shifts, in ppm, referenced against an external BF_3·OEt_2 standard. [b] All coupling constants listed in Hz.

spectra were obtained on a JEOL FX-200 spectrometer with a 10-mm tunable broad-band probe at 30.6 MHz. All ^2H NMR spectra were acquired over a 1000-Hz spectral width, with a 50-s overall pulse repetition time and a 50° pulse angle (12 μs), and were referenced against an external C_6D_6 standard. The T_1 values of various ^2H nuclei were determined by an inversion recovery sequence with a 42-μs 180° pulse time. The τ values chosen for the studies were between 1 and 20 s. The T_1 data were reduced by using the T_1 calculation package in the FX-200 software.

Mass spectra were obtained on an AEI MS-9 instrument at 70 eV. Infrared spectra were obtained with a Beckman 4250 spectrophotometer using a 10-cm gas cell.

Preparation of Monodeuterated Pentaborane Derivatives. All of the three possible monodeueterated pentaborane isomers were prepared for our studies. The (μ-D)B_5H_8 isomer was prepared by the literature method.[6h] 1-DB_5H_8 was prepared by a previously unreported route.[13] A catalytic amount of $AlCl_3$ was transferred into a small glass reactor and was sublimed in situ. A 5.0-mmol sample of B_5H_9 and 15 mmol of C_6D_6 were condensed into the reactor at −196 °C. The reactor was sealed, warmed to room temperature, and allowed to stand for 1 day. The vessel was then opened onto a high-vacum line, and the contents were distilled through a −78 °C U-trap into a −196 °C U-trap. The material that stopped in the −196 °C U-trap was again distilled through a −78 °C U-trap into a −196 °C U-trap. This process was repeated until the 1-DB_5H_8 in the −196 °C U-trap was confirmed to be free of C_6D_6 by IR spectroscopy.

The 2-DB_5H_8 derivative, a previously unknown isomer, was prepared by a new method developed in our laboratories.[14] A 10.0-mmol sample of 2-ClB_5H_8 was condensed into a 100-mL round-bottom reactor equipped with a Viton-A O-ring stopcock and a Teflon-coated stir bar. The sample was frozen at −196 °C, the flask was vented to dry N_2 gas, and 2.5 mL of Bu_3SnD was added by syringe. The reactor was sealed, evacuated, and allowed to warm from −78 °C to room temperature over several hours. The reaction mixture was then distilled through a −63 °C and a −96 °C U-trap and was stopped in a −196 °C U-trap. The material isolated in the −96 °C U-trap was identified by ^{11}B and ^2H NMR spectroscopy as 2-DB_5H_8.

Preparation of 1-D(μ-Me_3Si)B_5H_7. The 1-D(μ-Me_3Si)B_5H_7 derivative was produced by a modification of the (μ-Me_3Si)B_5H_8 preparation.[14] A 20-mmol samle of 1-DB_5H_8, prepared as above, was deprotonated with *n*-BuLi in diethyl ether at −78 °C. A 20-mmol sample of Me_3SiCl was condensed into the reaction mixture at −196 °C. The contents of the reactor were allowed to warm to −30 °C. The products were distilled through a −22 °C U-trap into a −196 °C U-trap. The product isolated in the −22 °C U-trap was identified as 1-D-(μ-Me_3Si)B_5H_7 by ^{11}B, ^1H, and ^2H NMR (Tables I, II, and III) and mass spectroscopy for $^{11}B_5{}^1H_{16}{}^{12}C_3{}^2H^{28}Si$: *m/e* calculated, 137.1628; *m/e* observed, 137.1644. The ^1H and ^2H NMR spectra of the product indicated that 80% incorporation of ^2H had occurred in the D(1) position and a slight amount of ^2H incorporation had occurred in the D(3–5) positions of the 1-D(μ-Me_3Si)B_5H_7 product.

Preparation of 1-D-2-ClB_5H_7. The 1-D-2-ClB_5H_7 derivative was prepared in a modification of the original technique for producing 1-DB_5H_8.[6e] A 20-mmol sample of 2-ClB_5H_8 was condensed into a 1-L reactor containing a catalytic amount of presublimed $AlCl_3$. A 30-mmol sample of DCl was condensed into the vessel, which was then sealed and allowed to stand at ambient temperature for 1 day. The reactor was opened and the chloroborane derivative was recovered by distillation into a −63 °C U-trap, with the residual DCl being stopped in a −196 °C U-trap. The recovered 2-chloropentaborane was again treated with fresh DCl in the presence of $AlCl_3$. After isolation it was analyzed by ^{11}B, ^1H, and ^2H NMR (Tables I, II, and III) and mass spectroscopy for $^{11}B_5{}^1H_7{}^{35}Cl^2H$: *m/e* calculated, 99.0843; *m/e* observed, 99.0843. The ^{11}B NMR spectrum identified the product as 1-D-2-ClB_5H_7. The ^1H and ^2H NMR spectra disclosed that a 50.8% incorporation of deuterium had occurred in the D(1) position. Unfortunately, an approximately equivalent amount of deuterium was incorporated into the basal terminal D(3–5) positions. Most of this excess deuterium was concentrated in the D(4) position, across the cage from the chloro substituent.

Interaction of Monodeuteriopentaborane Isomers with Ether. A series of NMR samples of each monodeuteriopentaborane isomer were prepared to study the migration of deuterium atoms throughout the molecule in the presence of diethyl ether. All samples were prepared in 5-mm o.d. medium-walled NMR tubes. Into each tube were condensed 1.5 mmol of the deuterated pentaborane isomer and 4.5 mmol of diethyl ether. The samples were mixed by allowing them to thaw briefly at low temperature. The solutions were refrozen at −196 °C, and the tubes were sealed. Three individual tubes were prepared for each monodeuterated isomer.

After several hours at room temperature, no changes were observed in the ^2H NMR spectra of any of the isomers. When the samples were heated to 45 °C, however, changes were observed in the spectra of the μ- and 2-DB_5H_8 isomers over a period of several days. In the sample prepared with μ-DB_5H_8 a diminution in the intensity of the singlet resonance associated with bridge deuterium nuclei D(6–9) and a concurrent appearance of the quartet resonance associated with the basal terminal deuterium nuclei D(2–5) were observed. Similarly, in the 2-DB_5H_8 sample a loss of intensity in the D(2–5) resonance was accompanied by an increase in the intensity of the D(6–9) resonance. No changes were observed in the ^2H NMR spectra of the 1-DB_5H_8 samples after 15 h at 95 °C.

A relaxation time study on one of the 2-DB_5H_8 samples that had exchanged to near equilibrium disclosed that deuterium nuclei associated with pentaborane have extremely large T_1 values. For basal terminal deuterium nuclei D(2–5), T_1 is 3.60 s, while for bridge deuterium nuclei D(6–9), T_1 is greater than 9 s. The T_1 value of the apical terminal deuterium nucleus D(1) is close to that of D(2–5), but its exact value could not be accurately determined. Due to these large T_1 values, it was necessary to choose long pulse repetition times to ensure that integrable ^2H NMR spectra of pentaborane derivatives were acquired.

Interaction of (μ-Me_3Si)B_5H_8 and Ether. Two sets of NMR samples were prepared to study the interaction of (μ-Me_3Si)B_5H_8 and diethyl ether. In the first set, two samples containing a nondeuterated derivative were used to study the μ- to 2-position isomerization of the Me_3Si– group by ^{11}B NMR spectroscopy. A 0.40-mmol sample of (μ-Me_3Si)B_5H_8 was condensed into a 5-mm medium-walled NMR tube. The sample was frozen into the bottom of the tube, and 3.0 mmol of diethyl ether was condensed into the tube above the borane. The tube was sealed and stored at −196 °C until immediately before introduction into the spectrometer.

The progress of the isomerization reactions was followed for 6–9 h. ^{11}B NMR spectra were acquired with a 2.0-s pulse repetition time. Broad-band proton decoupling was employed during acquisition to resolve the apex B(1) boron resonances of the μ- and 2-Me_3Si isomers into distinct singlets. The quantity of each isomer present was determined by comparison of the relative intensities of the B(1) resonances.

A second set of samples were used to study the behavior of the apical terminal H(1) hydrogen atom during the μ- to 2-position isomerization of the Me_3Si group. The samples were prepared and treated in the same manner as those above, except that 1-D(μ-Me_3Si)B_5H_7 was substituted for the nondeuterated derivative. The progress of isomerization in the samples was observed by ^2H NMR spectroscopy.

Two changes in the NMR spectra of the deuterated samples occurred at room temperature. The first change was a reduction in the intensity of the D(1) quartet resonances associated with the 1-D(μ-Me_3Si)B_5H_7 isomer and the development of new D(1) quartet of equal

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Table II. ^{1}H NMR Chemical Shifts[a] and Coupling Constants[b]

	H(1)[b]		H(3,5)		H(4)		H(6,9)	H(7,8)
	δ	J_{BH}	δ	J_{BH}	δ	J_{BH}	δ	δ
1-D-2-ClB_5H_7	0.98	178.5	2.31	167.2	2.08	163.2	−0.96	−2.66

	H(2,3)		H(3,4)		H(9)	H(7,8)	Me_3Si
	δ	J_{BH}	δ	J_{BH}	δ	δ	δ
1-D(μ-Me_3Si)B_5H_7	2.43	(165.7)	2.43	(165.7)	−2.13	−2.62	0.47

[a] All chemical shifts referenced against a Me_4Si external standard. [b] All coupling constants listed in Hz.

Table III. ^{2}H NMR Chemical Shifts[a] and Coupling Constants[b]

	D(1)			D(1)	
	δ	J_{B-D}		δ	J_{B-D}
1-DB_5H_8	0.43	26.7	1-D-2-(Me_3Si)B_5H_7	0.56	26.5
1-D(μ-Me_3Si)B_5H_7	0.60	26.7	1-D-2-ClB_5H_7	−0.10	26.8

	D(2)			D(6)	
	δ	J_{B-D}		δ	J_{B-D}
2-DB_5H_8	2.26	24.2	(μ-D)B_5H_8	−2.75	...

[a] All chemical shifts referenced against an external C_6D_6 standard. [b] All coupling constants listed in Hz.

intensity at 0.4 ppm upfield from the original quartet. The second change appeared to be a slow migration of the weak basal terminal D(2) resonance (present in the 1-D(μ-Me_3Si)B_5H_7 starting material) into the bridge position. No significant loss of D(1) intensity was observed over the 12 h during which the first process occurred. The samples were monitored thereafter for up to 8 days by ^{11}B and ^{2}H NMR spectroscopy, and no additional changes in their spectra were noted during that period. The final product was identified as 1-D-2-(Me_3Si)B_5H_7 by its ^{11}B and ^{2}H NMR spectra (Tables I and III).

Further changes were observed in the spectra of the samples on heating to 65 °C for a period of days. The D(1) resonance diminished in intensity, and new resonances appeared in the regions associated with the D(2–5) and D(6–9) positions. This indicated that the apical terminal deuterium atom was exchanging into positions in the base of the molecule. The ^{11}B NMR spectrum (Table I) showed the concurrent appearance of a new doublet at −12.2 ppm and a singlet at −57.4 ppm. The chemical shifts of these resonances are characteristic of a 1-(trimethylsilyl)pentaborane derivative. Furthermore, the residual apical resonance of the 1-D-2-(Me_3Si)B_5H_7 retained its singlet character during the initial portion of the experiments. A comparison of the rate of appearance of the 1-silyl resonance and the rate of disappearance of the D(1) position resonance of the 1-D-2-(Me_3Si)B_5H_7 derivative confirmed that the two processes occur at the same rate. As the intensity of the 1-silyl isomer reonance neared its equilibrium value, the intensity of the D(1) resonance continued to decrease toward its own equilibrium value.

Interaction of 2-ClB_5H_8 and Diethyl Ether. Two sets of NMR samples were prepared to study the interaction of 2-ClB_5H_8 with diethyl ether.[15] The first set of samples were prepared and handled in the same manner as the (μ-Me_3Si)B_5H_8 samples had been previously, except that 2.4 mmol of 2-ClB_5H_8 were substituted for the silyl derivative. The samples were monitored by ^{11}B NMR spectroscopy and were near equilibrium after 13 h.

The second group of samples was identical with the original set except that 2.4 mmol of 1-D-2-ClB_5H_7 was substituted for the nondeuterated derivative. The samples were monitored by ^{2}H NMR spectroscopy with a 60-s pulse repetition time. Two processes were observed in the isomerization of the 1-D-2-ClB_5H_7. The first process scrambled the intensity of the basal terminal D(3–5) resonance, which had been present in the starting material, into resonances representing both the D(3–5) and the bridge D(6–9) positions. This exchange was completed within minutes. The second process, which reached equilibrium in 3–4 h, was the scrambling of the D(1) position resonance among all of the resonances in the ^{2}H NMR spectrum. The ^{11}B NMR spectrum of a sample after 4.5 h confirmed that the 1-chloropentaborane isomer had not reached its equilibrium concentration though exchange of the deuterium atoms out of the D(1) position of the 1-D-2-ClB_5H_8 starting material was complete.

(15) Data from the previous kinetic study of the isomerization of chloropentaboranes[6] was not used in this study. Higher concentrations of boranes were necessary to obtain ^{2}H NMR spectra within the required time period.

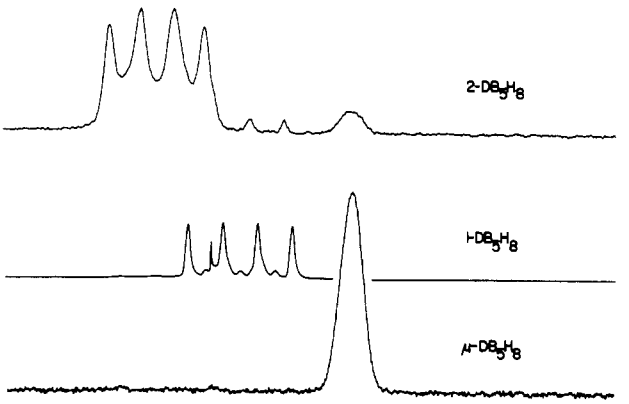


Figure 2. ^{2}H NMR spectra (30.6 MHz) of monodeuterated pentaborane(9).

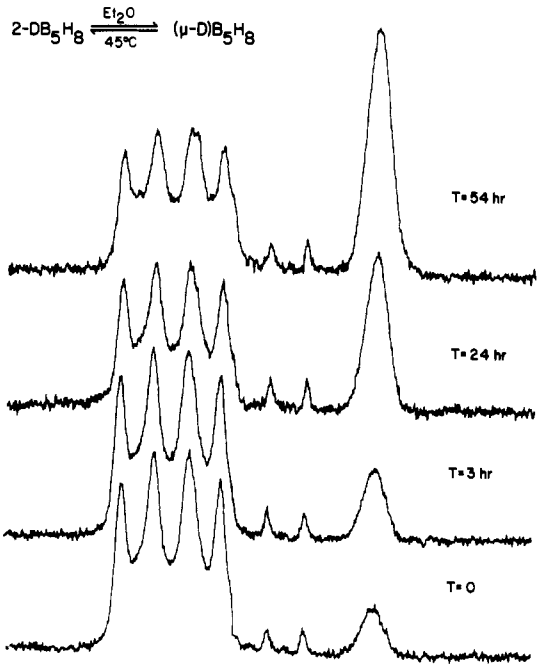


Figure 3. ^{2}H NMR spectra (30.6 MHz) of the isomerization of 2-DB_5H_8.

Results

Isomerization of the Monodeuteriopentaboranes. The ^{2}H NMR spectra of the three monodeuterated pentaborane isomers are shown in Figure 2. The ^{2}H NMR spectra of the μ-DB_5H_8 and 2-DB_5H_8 derivatives in diethyl ether clearly demonstrate the facile interconversion of the two isomers at 45 °C (Figure 3). The exchange reactions, as monitored by ^{2}H NMR spectroscopy, progressed identically and reached equilibrium in approximately 60 h (Figure 4). No significant positional isotope effect was observed in the final distribution

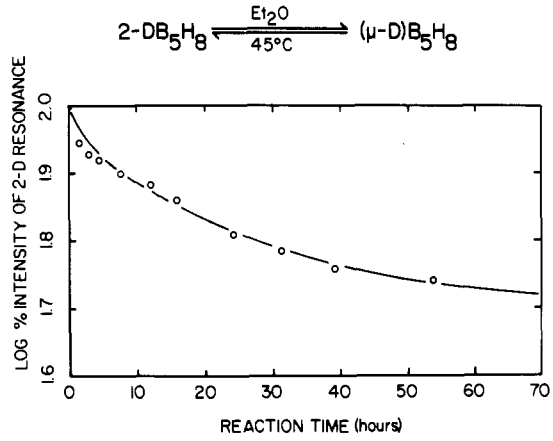


Figure 4. Rate of isomerization of $2\text{-}DB_5H_8$.

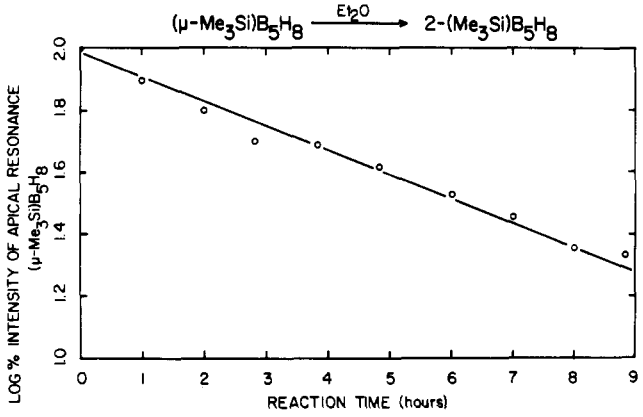
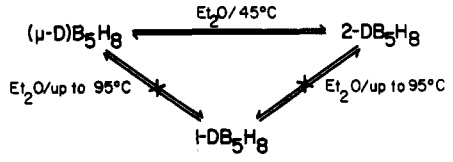


Figure 5. Rate of isomerization of $(\mu\text{-}Me_3Si)B_5H_8$.

Scheme I. Isomerization of Monodeuteriopentaborane(9) Derivatives



of the label. No movement of deuterium label into the apical terminal D(1) position was observed in either the $\mu\text{-}DB_5H_8$ or $2\text{-}DB_5H_8$ samples. The $1\text{-}DB_5H_8$ samples demonstrated that no measureable exchange occurred between the D(1) position and the basal terminal D(2–5) or bridge D(6–9) positions even after many hours at 95 °C. A complete description of the exchange routes for the monodeuterated pentaborane derivatives is shown in Scheme I.

The results of this study confirm much of the data obtained in previous investigations of the rearrangement of monodeuteriopentaborane isomers.[6e,h] The availability of new labeling procedures, better analytical tools, and the use of milder conditions allow for a more accurate analysis of the several exchange processes.[6e,h] The reversible isomerization of $\mu\text{-}DB_5H_8$ to $2\text{-}DB_5H_8$ in THF occurs at room temperature,[6h] a result consistent with our results in the weaker base diethyl ether at 45 °C. Complete scrambling of the label in $1\text{-}DB_5H_8$ occurred at room temperature in the presence of the much stronger base 2,6-dimethylpyridine.[6e] In addition, some intermolecular migration of the label was observed, but significant decomposition of the borane samples in the presence of the base renders the actual mechanism of intermolecular deuterium transfer unclear.[6e]

The most surprising information gained from our studies is the magnitude of the rate difference between the processes responsible for the interchange of hydrogen atoms in the base

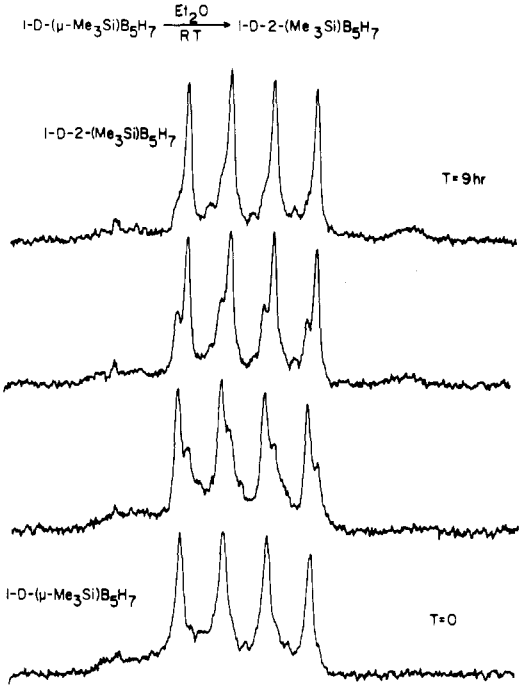


Figure 6. ^2H NMR spectra (30.6 MHz) of the isomerization of $1\text{-}D(\mu\text{-}Me_3Si)B_5H_7$.

of the pentaborane molecule and those responsible for the interchange of hydrogen atoms between the apex and the base of the molecule. In pentaborane, the rates of the two types of exchange may differ by 2 orders of magnitude or more. These results reinforce the supposition that the mechanisms leading to intramolecular rearrangement in pentaborane have two distinct rate-determining steps.

Isomerization of the Silylpentaborane Derivatives. The study of the isomerization of $1\text{-}D(\mu\text{-}Me_3Si)B_5H_7$ has provided important information concerning the behavior of apical terminal hydrogen atoms during the movement of substituents on the pentaborane cage. The rearrangement of the $(\mu\text{-}Me_3Si)B_5H_8$ isomer, monitored by ^{11}B NMR spectroscopy, followed a first-order rate law (Figure 5) and, as was previously reported,[6a] eventually produced pure $2\text{-}(Me_3Si)B_5H_8$ (eq 3).

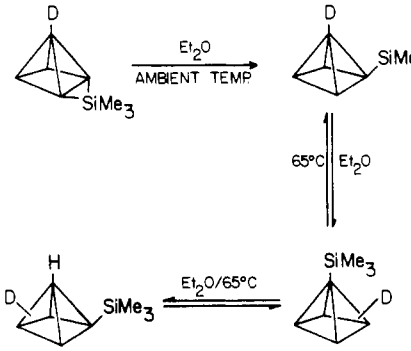
$$(\mu\text{-}Me_3Si)B_5H_8 \xrightarrow[\text{ambient temp}]{Et_2O} 2\text{-}(Me_3Si)B_5H_8 \quad (3)$$

When identically prepared samples of $1\text{-}D(\mu\text{-}Me_3Si)B_5H_7$ were monitored by ^2H NMR spectroscopy, the apical D(1) position resonance associated with the $1\text{-}D(\mu\text{-}Me_3Si)B_5H_7$ isomer was gradually replaced with a new quartet D(1) resonance associated with $1\text{-}D\text{-}2\text{-}(Me_2Si)B_5H_7$ (Figure 6). Significantly, no diminution in the intensity of the D(1) resonance was observed for several days after the completion of the μ- to 2-position isomerization of the Me_3Si group. These results indicate that the migration of the silyl group occurred without the involvement of any pathway that exchanges hydrogen out of the apex of the pentaborane framework (eq 4).

$$1\text{-}D(\mu\text{-}Me_3Si)B_5H_7 \xrightarrow[\text{ambient temp}]{Et_2O} 1\text{-}D\text{-}2\text{-}(Me_3Si)B_5H_7 \quad (4)$$

No evidence for further isomerization of the new $1\text{-}D\text{-}2\text{-}(Me_3Si)B_5H_7$ isomer was observed until the samples were heated. After 7 days at 65 °C, however, the ^{11}B NMR spectrum indicated that 50% conversion from the 2-trimethylsilyl isomer to a 1-trimethylsilyl isomer had occurred. In addition, an examination of the ^2H NMR spectrum of the sample revealed that only 50% of the original intensity from the D(1) resonance of the $1\text{-}D\text{-}2\text{-}(Me_3Si)B_5H_7$ derivative remained. Subsequent studies showed the deuterium label being displaced from the 1-position at the same rate as Me_3Si groups

Scheme II. Isomerization Pathways for 1-D(μ-Me_3Si)B_5H_7



moved into that position (Figure 7). It is evident that there is no viable independent route for the apical hydrogen atom to exchange with a hydrogen atom from the base of the molecule. The presence of the trimethylsilyl group lowers the activation energy for apex-to-base migration in the molecule in a manner that allows only that group to migrate efficiently into the apical position. A complete description of the isomerization pathways for 1-D(μ-Me_3Si)B_5H_7 is shown in Scheme II.

Isomerization of Monochloropentaboranes. The behavior of 2-ClB_5H_8 in diethyl ether has already been investigated in detail by ^{11}B NMR spectroscopy. Our studies of samples containing nondeuterated material were used only as a reference framework for the analysis of data obtained from samples containing 1-D-2-ClB_5H_7. Immediately upon warming, deuterium atoms that had been concentrated on the basal terminal D(3–5) positions of the starting material scrambled between the D(3–5) and the bridge D(6–9) positions. This rapid exchange of hydrogen atoms in the base of the 2-chloro derivative is consistent with behavior observed in pentaborane and the (trimethylsilyl)pentaborane derivative. A comparison of the 2- to 1-position isomerization of the chloro group and the rate of deuterium migration in 1-D-2-ClB_5H_7 yielded results strikingly different from those observed for 1-D-2-(Me_3Si)B_5H_7. While samples containing 2-ClB_5H_8 took over 13 h to reach an equilibrium concentration of 1-ClB_5H_8, deuterium atoms in the 1-position were statistically distributed throughout the molecule in approximately 4 h. This behavior may be caused by the presence of an energetically accessible pathway in the chlorinated pentaborane that allows the apical hydrogen atom to exchange with basal hydrogen atoms without concurrent migration of the chlorine atom. Another possible explanation, however, stems from the difference in equilibrium constants for the chloropentaborane and (trimethylsilyl)-pentaborane systems (eq 5 and 6). Because the 2- to 1-

$$2\text{-}ClB_5H_8 \xrightarrow{Et_2O} 1\text{-}ClB_5H_8 \qquad K_{eq} = 0.20 \qquad (5)$$

$$2\text{-}(Me_3Si)B_5H_8 \xrightarrow{Et_2O} 1\text{-}(Me_3Si)B_5H_8 \qquad K_{eq} = 4.0 \qquad (6)$$

position isomerizations are equilibrium reactions, some back-reaction of the 1-substituted product will occur before the system reaches equilibrium. This back-reaction will scramble protons into the apex of the 2-substituted material and, consequentially, the deuterium label in the 1-position will seem to disappear more rapidly than the 1-substituted product is formed. For the silylpentaboranes, the back-reaction is a much slower process and, therefore, significant differences between the quantity of deuterium label lost from the 1-position and the quantity of 1-silyl derivative formed are only observed after a long period of reaction. Back-reaction in the chloropentaborane systems, however, is a faster process, and the scrambling of protons into the apical position of the labeled material is observed early in the course of the reaction.

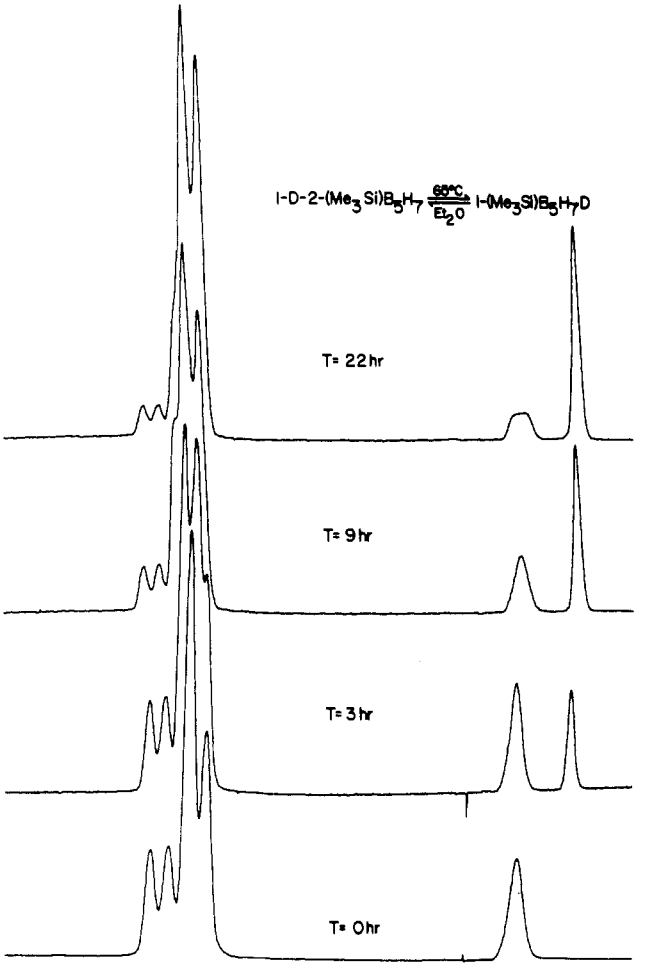


Figure 7. ^{11}B NMR spectra (86.6 MHz) of the isomerization of 1-D-2-(Me_3Si)B_5H_7.

Discussion

Our experiments have defined two distinct paths for Lewis base catalyzed hydrogen exchange in the pentaborane molecule. The first process is a relatively low-energy scrambling of basal terminal H(2-5) and bridge H(6–9) hydrogens. The second process is the higher energy exchange of hydrogen and substituents into the apical H(1) position. While it is unclear whether migration in the second process is distinct from the first, we have established that the H(2–5) to H(6–9) isomerization takes place under conditions where migration into the H(1) position is not observed. Two of the cases studied have demonstrated that interchanges of hydrogens in the H(1) position with those in the H(2–9) positions are extremely high-energy processes compared to other exchange routes available in the molecule. It should be noted that this may not be the case in all pentaborane derivatives. The possible existence of different exchange routes is emphasized by the complex results obtained in our study of 1-D-2-ClB_5H_7. Although the cases we studied have many similarities, the exact mechanisms of proton and substituent migration may be different for other pentaborane derivatives.

Our studies provide indirect information about the mechanism of apex-to-base hydrogen atom and functional group transfer. The possibility that various substituents can undergo 1,2-shifts between adjacent boron atoms via some bridging intermediate is certainly implicated by methyl group transfer in the base-catalyzed production of 4,5-$Me_2B_6H_8$.[16] It is disturbing, however, that in pentaborane isomerizations a wide variety of functional groups undergo facile 1- to 2-position

(16) Gaines, D. F.; Iorns, T. V. *J. Am. Chem. Soc.* **1970**, *92*, 4571–4574.

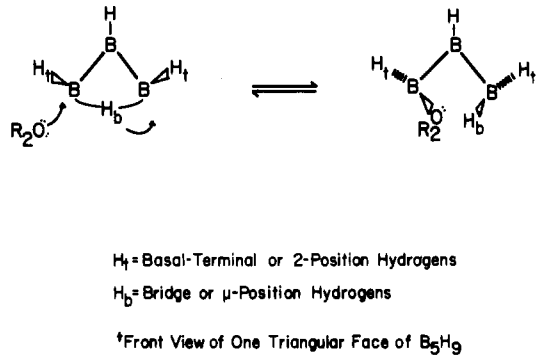
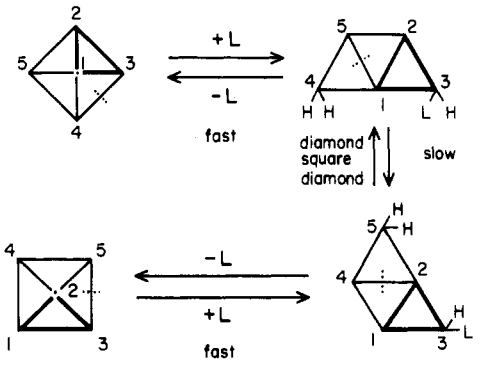


Figure 8. Formation of IIIb.

Scheme III. Diamond-Square-Diamond Model for B_5H_9 Rearrangement via an Arachno Complex



migrations, while hydrogen atoms appear to have comparatively high barriers to such movement. Were a simple 1,2-shift involved in the apex-to-base isomerization mechanism, one might expect hydrogen exchange under milder conditions. For this reason, it seems that cage rearrangement is the more likely pathway for 1- to 2-position functional group and hydrogen transfer.

The observation of two distinct exchange pathways associated with the pentaborane molecule eliminates several previously proposed mechanisms. Early proposals based on deprotonation or cage fragmentation[6d,f] are inappropriate models, as they are inconsistent with the rearrangement behavior observed under mild conditions.[6h] Mechanisms based on intermediate II are inconsistent with the skeletal-electron-counting requirements that we imposed earlier. In addition, intermediate II should provide facile exchange of hydrogen between the H(1) and H(2–5) positions in B_5H_9, which is not observed.

A mechanism can be developed involving arachno adduct IIIb, which explains the hydrogen exchange observed during pentaborane isomerizations. The interaction of a Lewis base with the pentaborane cage to give IIIb leaves an "open face" of three boron atoms in which one B–H–B interaction has been interrupted (Figure 8). Various proposals can be developed that will allow bridge-to-terminal hydrogen and functional group transfer across this open face.[17] The μ- to 2-position migration in IIIb represents the low-energy exchange pathway

(17) See supplementary material for this paper.

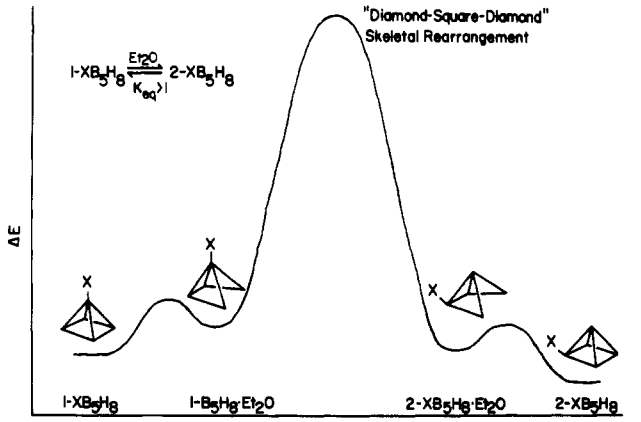


Figure 9. Proposed reaction-coordinate diagram for the rearrangement of 1-XB_5H_8 in diethyl ether.

in the molecule, and consequently, cage opening and closing may occur many times before sufficient energy is imparted to the complex to allow 1- to 2-position isomerization. Migration into the apical position of pentaborane may occur from IIIb either by 1,2-alkyl and -hydrogen shifts, as was discussed previously, or by skeletal rearrangement through a "diamond–square–diamond" mechanism,[18] outlined in Scheme III. The diamond–square–diamond interaction has been proposed as a useful model for some borane rearrangements.[18] Isomerization via this route implies that boron–hydrogen and boron–functional group units move intact into the apex of the molecule. Figure 9 shows a reaction-coordinate diagram for the mechanism proposed above.

The experimental data are also consistent with an exchange model combining intermediates IIIa and IIIb. Basal hydrogen exchange could occur via intermediate IIIb, as above. A higher energy process via intermediate IIIa could be invoked to provide for movement to and from the H(1) position by interchange of intact boron–hydrogen or boron–functional group units in a "base-swing" process. We currently favor the "base-swing" and "diamond–square–diamond" cluster rearrangements over the "1,2-shift" model for base–apex substituent interchange. Boron-labeling experiments in progress provide additional independent data regarding this point.

Acknowledgment. This research was supported in part by grants, including deparmental instrument grants, from the National Science Foundation.

Registry No. 1-D(μ-Me_3Si)B_5H_7, 86884-74-4; 1-D-2-(Me_3Si)B_5H_7, 86884-75-5; 1-D-2-ClB_5H_7, 86884-76-6; 1-(Me_3Si)B_5H_7D, 86884-77-7; 1-DB_5H_8, 63643-91-4; 2-DB_5H_8, 63643-93-6; (μ-D)B_5H_8, 16743-79-6; (μ-Me_3Si)B_5H_8, 19553-47-0; 2-(Me_3Si)B_5H_8, 22142-53-6; 2-ClB_5H_8, 19469-14-8; 1-ClB_5H_8, 19469-13-7; 1-(Me_3Si)B_5H_8, 28323-19-5.

Supplementary Material Available: A proposal for μ- to 2-position hydrogen migration in IIIb and Figure 10, showing the potential mechanism (1 page). Ordering information is given on any current masthead page.

(18) (a) Kaczmarczyk, A.; Dobrott, R.; Lipscomb, W. N. *Proc. Natl. Acad. Sci. U.S.A.* **1962**, 729–733. (b) Hoffmann, R.; Lipscomb, W. N. *Inorg. Chem.* **1963**, *2*, 231–232.