and mass spectral facilities, from the National Science Foundation.

Registry No. $(CO)_4MnB_3H_8$, 53801-97-1; $(CO)_4ReB_3H_8$, 53801-98-2; $(\eta^5\text{-}C_5H_5)(CO)FeB_3H_8$, 53802-00-9; $(H)(CO)_3FeB_3H_8$, 65452-41-7; $(\eta^5\text{-}C_5H_5)(CO)_2MoB_3H_8$, 65452-40-6; $(\eta^5\text{-}C_5H_5)(CO)_2WB_3H_8$, 65452-39-3; $(Ph_3P)(CO)_3MnB_3H_8$, 65452-38-2; $(Ph_2PCH_2CH_2PPh_2)(CO)_2MnB_3H_8$, 65452-37-1; $(PF_3)(CO)_3MnB_3H_8$, 65452-36-0; $(NH_3)(CO)_3MnB_3H_8$, 65452-35-9; $(CO)_4MnB_3H_7Cl$, 65452-34-8; $(CO)_4MnB_3H_7Br$, 65452-33-7; $(CO)_4MnB_3H_7I$, 65452-32-6; $(CH_3)_4NB_3H_8$, 12386-10-6; $C_5B_3H_8$, 33220-36-9; TlB_3H_8, 12447-30-2; $(CH_3)_2AlB_3H_8$, 12654-95-4; $(CH_3)_2GaB_3H_8$, 12654-96-5; $Mn(CO)_5Br$, 14516-54-2; $Mn(CO)_5I$, 14879-42-6; $Re(CO)_5Br$, 14220-21-4; $(\eta^5\text{-}C_5H_5)(CO)_2FeI$, 12078-28-3; $Fe(CO)_4Br_2$, 14878-20-7; $(\eta^5\text{-}C_5H_5)(CO)_3MoCl$, 12128-23-3; $(\eta^5\text{-}C_5H_5)(CO)_3WCl$, 12128-24-4; *trans*-$(Ph_3P)(CO)_4MnBr$, 65437-12-9; (diphos)-$(CO)_3MnBr$, 19195-72-3; $(CO)_3MnB_3H_8$, 53801-96-0.

Supplementary Material Available: ^1H NMR, ^{11}B NMR, and mass spectra of some neutral octahydrotriborate(1−) complexes of chromium-, manganese-, and iron-group metals (9 pages). Ordering information is given on any current masthead page.

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Kinetics of the Isomerization of 1-Chloro- and 2-Chloropentaborane(9) Using Diethyl Ether Catalyst

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The isomerization of 1-chloro- or 2-chloropentaborane(9), $1\text{-}ClB_5H_8$ or $2\text{-}ClB_5H_8$, with diethyl ether catalyst is approximately first order in ClB_5H_8 and in diethyl ether. For the reaction

$$1\text{-}ClB_5H_8 + Et_2O \underset{k'_{21}}{\overset{k'_{12}}{\rightleftharpoons}} 2\text{-}ClB_5H_8 + Et_2O$$

at 24.5 °C, 0.174 M $1\text{-}ClB_5H_8$, and 3.65 M Et_2O, the overall second-order rate constants are $k'_{12} = 2.72\ (3) \times 10^{-6}\ M^{-1}\ s^{-1}$, $k'_{21} = 0.48\ (1) \times 10^{-6}\ M^{-1}\ s^{-1}$, and $K_{eq}\ (=k'_{12}/k'_{21}) = 5.62$. The activation energy for the forward reaction is 14.6 (5) kcal. The data suggest that the isomerization occurs by a boron cage rearrangement mechanism involving an $Et_2O\text{–}ClB_5H_8$ complex rather than a mechanism involving B–Cl bond cleavage.

Introduction

The mechanism by which 1- and 2-substituted pentaboranes isomerize has not been well characterized experimentally. One mechanism which has been proposed for the isomerizations involves polyhedral rearrangement.[1] The square-pyramidal substituted pentaborane(9) has been proposed[1] to rearrange through a trigonal-bipyramidal intermediate which allows interconversion of apical and basal boron atoms and, thus, isomerization of 1- or 2-substituted species.

This stereochemical nonrigidity in polyhedral structures is an interesting and important aspect of inorganic chemistry. Mechanistic models[2] for interconversion of structures with diamond and square faces have been proposed to describe possible pathways for low-energy rearrangement of polyhedral species. Other polytopal rearrangement processes have been described[3] for polyhedral cage molecules and coordination complexes. The most favorable geometric arrangement of a five-vertex polyhedron[3,4] is, theoretically, a trigonal bipyramid but a tetragonal pyramid is only slightly less favorable. The atom movement required to interchange structures with these geometries is small, little more than bending or stretching motions in the molecules. Interchange of trigonal-bipyramidal and tetragonal-pyramidal geometries can be rapid with resulting interchange of all sites in the molecules. Such a mechanism, proposed by Berry,[5] is illustrated in Figure 1. The proposed rearrangement which occurs during isomerization of pentaborane(9) species[1] is closely related to that illustrated in Figure 1. However, the tetragonal pyramid is found to be

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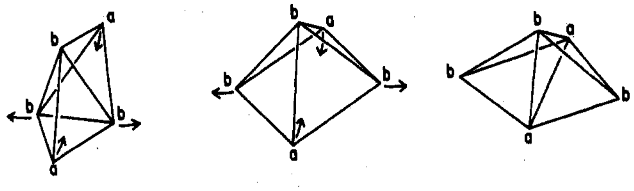

Figure 1. Proposed mechanism for the rearrangement of trigonal-bipyramidal species.

Table I. Longitudinal Relaxation Times, T_1, for Pentaborane Species

B_5H_9	T_1, ms	1-ClB_5H_8[a]	T_1, ms	2-ClB_5H_8[a]	T_1, ms
B(1)[a]	320	B(1)	77	B(1)	230
B(2)–B(5)[b]	63.6	B(2)–B(5)	31	B(2)	51
				B(3), B(5)	19
				B(4)	31

[a] Reference 8. [b] Reference 9.

Scheme I

$$1\text{-ClB}_5H_8 + Et_2O \rightleftarrows G$$
$$G \rightleftarrows 2\text{-ClB}_5H_8 + Et_2O$$
$$1\text{-ClB}_5H_8 \rightleftarrows 2\text{-ClB}_5H_8 \qquad (1)$$

the favored geometry of B_5H_9 and its derivatives, and a trigonal bipyramid is the geometry of the assumed intermediate.

In order to characterize the proposed rearrangement mechanism for pentaborane(9) derivatives in more detail, we have studied the kinetics of the isomerization of 1-chloro- to 2-chloropentaborane(9) using diethyl ether catalyst.

Experimental Section

1-Chloro- and 2-chloropentaborane(9) were prepared as described elsewhere.[6] All of the boranes employed in this study are toxic and spontaneously flammable and may be explosive under some conditions. Diethyl ether (Mallinckrodt) and toluene-d_8 (Aldrich) were distilled from lithium aluminum hydride and then treated with diborane to remove any borane-reactive impurities. Diethyl-d_{10} ether (Merck) was treated with diborane. Kinetic samples of chloropentaborane(9) and diethyl ether in toluene were prepared under high-vacuum conditions[7] by distilling the reagents into a 5-mm o.d. Pyrex NMR tube, which contained a constriction for flame sealing and was fused to an O-ring stopcock (Viton O-rings were used). The quantity of each reagent was determined by weighing the stopcock, NMR tube, and contents before and after the addition of each reagent. Finally, the NMR tube was flame sealed at the constriction. Total volume of the final solutions was determined by measuring the total liquid height in the tube and using a previously determined calibration curve. Concentration measurements were estimated to be within 1%. Except for weighing time during preparation, samples were held at −196 °C until the initiation of the experiment. Experimental temperatures and the estimated fluctuations were 0.0 ± 0.2, 24.5 ± 0.1, and 49 ± 1 °C. Typically less than 1% decomposition of chloropentaborane(9) materials occurred during the course of the experiment.

Periodic sample analysis, which normally took about 8 min, was done at ambient probe temperature (23 °C) on a Bruker WH-270 NMR spectrometer controlled by a Nicolet BNC-12 computer system. The longitudinal relaxation times (T_1) for B_5H_9, 1-ClB_5H_8, and 2-ClB_5H_8 (Table I) indicate that a scan repetition rate of about 1 s per pulse would be appropriate to allow complete relaxation of boron nuclei between pulses. The pulse sequence used was (1) 90° pulse (13 μs), (2) data collection (0.204 s), and (3) delay (0.796 s).[8] Five hundred pulses were collected using a 10 000-Hz spectral width. Spectra and integrals were plotted and integral heights were measured manually to give the desired peak area ratios. (This technique was found to give satisfactory results for samples of B_5H_9, 1-ClB_5H_8, and 2-ClB_5H_8 in the absence of diethyl ether.)

A model fitting the proposed isomerization mechanism is detailed in Scheme I with the overall reaction given in eq 1. According to Scheme I, pseudo-first-order conditions exist as long as an insignificant amount of diethyl ether exists in complexed form at a given time. In addition, an excess of diethyl ether was used which ensures pseudo-first-order conditions.

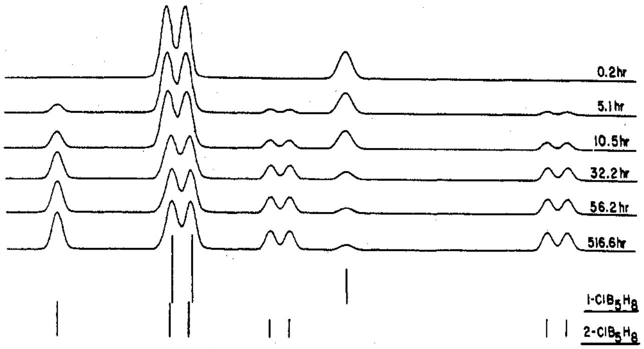

Figure 2. Typical ^{11}B NMR plots showing the isomerization of 1-ClB_5H_8 to 2-ClB_5H_8. Resonances due to each isomer are shown below.

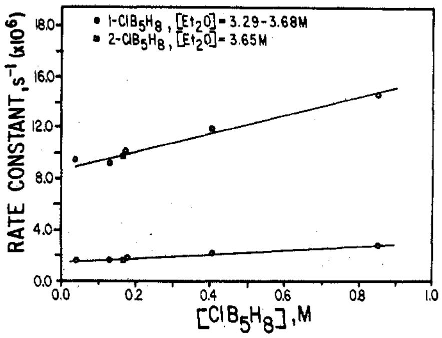

Figure 3. Dependence of pseudo-first-order rate constants on $[\text{ClB}_5H_8]$.

The mathematical expression which describes a first-order equilibrating system A ⇄ B with only A present at the start of the reaction is

$$A_t = \frac{k_r A_0}{k_f + k_r} + \frac{k_f A_0}{k_f + k_r} e^{-(k_f + k_r)t}$$

where t is time, A_t is [A] at time t, k_f is the overall forward rate constant, and k_r is the overall reverse rate constant. A nonlinear least-squares package[10] was used to fit the data to the model using k_f, k_r, and A_0 as variable parameters. Thermodynamic and activation parameters were determined by linear least-squares fitting of ln h vs. T^{-1}, where h is the equilibrium constant, k_f or k_r, respectively.

Results

A series of spectra depicting an equilibrating 1-ClB_5H_8–Et_2O system is shown in Figure 2. The observed pseudo-first-order rate constants determined for the model A ⇄ B are listed in Table II (k_{12} is the overall first-order rate constant for 1-ClB_5H_8 (+Et_2O) → 2-ClB_5H_8; k_{21} is the overall first-order rate constant for $2\text{-ClB}_5H_8 \rightarrow 1\text{-ClB}_5H_8$; $K_{eq} = k_{12}/k_{21}$). Both 1-chloro- and 2-chloropentaborane(9) were used as starting materials with the initial concentration of chloropentaborane (ClB_5H_8 is used to indicate 1-ClB_5H_8 and/or 2-ClB_5H_8) varying from 0.040 to 0.852 M and that of diethyl ether varying from 0.95 to 9.75 M. The temperature was 24.5 °C for the most part, but experiments at 0 and 49 °C were included in a variable-temperature study.

The isomerization reaction is approximately first order in ClB_5H_8. There is a slight increase in the pseudo-first-order rate constant as the ClB_5H_8 concentration, $[\text{ClB}_5H_8]$, increases (Figure 3). Plots of the pseudo-first-order rate constant vs. $[Et_2O]$ at approximately constant $[\text{ClB}_5H_8]$, Figure 4, indicate linear dependence on $[Et_2O]$. Thus the rate law for the overall reaction (eq 1) is

$$-d[1\text{-ClB}_5H_8]/dt = k'_{12}[Et_2O][1\text{-ClB}_5H_8] - k'_{21}[Et_2O][2\text{-ClB}_5H_8]$$

Table II. Pseudo-First-Order Rate Constants and Equilibrium Constants for the Isomerization of 1-ClB_5H_8 and 2-ClB_5H_8 with Et_2O^a

Trial no.	$[Et_2O]$, M	$A_0(e)$,^{b} M	$A_0(c)$,^{b} M	10^6k_{12}, M^{-1} s^{-1}	10^6k_{21}, M^{-1} s^{-1}	$K_{eq}{}^c$
			A. 1-ClB_5H_8 as Starting Chloropentaborane			
			Temperature 24.5 °C			
1	1.01	0.177	0.178 (3)	2.94 (6)	0.54 (3)	5.44 (4)
2	2.08	0.191	0.192 (2)	6.08 (6)	1.11 (2)	5.48 (2)
3	3.40	0.133	0.134 (1)	9.06 (8)	1.58 (3)	5.73 (2)
4	3.65	0.174	0.175 (2)	9.94 (11)	1.77 (4)	5.62 (2)
5	9.75	0.204	0.205 (2)	32.8 (3)	5.25 (11)	6.25 (2)
6	9.75	0.208	0.207 (2)	32.2 (6)	5.11 (13)	6.30 (3)
7	2.16	0.045	0.045 (1)	5.39 (17)	0.98 (7)	5.50 (8)
8	3.68	0.040	0.040 (2)	9.2 (4)	1.61 (14)	5.71 (10)
9	3.43	0.406	0.406 (7)	11.5 (2)	2.15 (8)	5.35 (4)
10	3.29	0.852	0.854 (27)	14.2 (5)	2.78 (20)	5.10 (8)
			Temperature 49 °C			
11	3.65	0.179	0.185 (2)	51.7 (6)	8.50 (2)	6.08 (4)
			Temperature 0 °C			
12	3.64	0.174	0.172 (4)	0.917 (19)	0.174 (7)	5.27 (4)
			B. 2-ClB_5H_8 as Starting Chloropentaborane			
			Temperature 24.5 °C			
13	0.95	0.173	0.173 (11)	2.75 (17)	0.50 (3)	5.50 (9)
14	3.65	0.171	0.170 (5)	9.5 (3)	1.65 (6)	5.76 (5)
15	4.87	0.155	0.155 (17)	12.4 (14)	2.2 (3)	5.64 (18)
16	9.75	0.213	0.212 (16)	27.8 (22)	4.4 (4)	6.32 (12)

[a] Numbers in parentheses following calculated values represent computed confidence limits.[9] [b] $A_0(e)$ is experimentally determined initial concentration; $A_0(c)$ is initial concentration calculated by least-squares procedure. [c] $K_{eq} = k_{12}/k_{21}$.

Table III. Activation and Thermodynamic Parameters for the Reaction 1-ClB_5H_8 $(+Et_2O) \rightleftharpoons 2\text{-ClB}_5H_8$ at 24.5 °C

Activation parameters	Thermodynamic parameters
$E_{act}(k_{12}) = 14.6$ (5) kcal/mol	$\Delta H = 0.52$ (3) kcal/mol
$E_{act}(k_{21}) = 14.1$ (6) kcal/mol	$\Delta S = 5.2$ (1) eu
	$\Delta G = -1.02$ (1) kcal/mol

where $k'_{12}[Et_2O] = k_{12}$ and $k'_{21}[Et_2O] = k_{21}$. Typically, values are $k' = 2.72\ (3) \times 10^{-6}\ M^{-1}\ s^{-1}$ and $k'_{21} = 0.48\ (1) \times 10^{-6}\ M^{-1}\ s^{-1}$ at 24.5 °C, $[1\text{-ClB}_5H_8] = 0.174$ M, and $[Et_2O] = 3.65$ M. The nonideality of the rate constants is reflected in a slight dependence of K_{eq} on $[ClB_5H_8]$ and $[Et_2O]$. Thermodynamic and activation parameters are given in Table III. There is a slight thermodynamic favorability of 2-ClB_5H_8 over 1-ClB_5H_8 under the conditions employed, as a statistical distribution would yield a K_{eq} value of 4.0 and the observed value is 5.62.

Discussion

The model in Scheme I describing the chemical processes occurring during the isomerization of 1-ClB_5H_8 or 2-ClB_5H_8 in the presence of Et_2O is consistent with the kinetic results. The first-order rate law dependence on $[ClB_5H_8]$ and $[Et_2O]$ suggests that the isomerization may occur through an activated complex containing one molecule of each compound. Any intermediates probably make up a small portion (<1%) of the total chloropentaborane present in the reaction as there is no evidence for intermediates in the NMR spectra.

The isomerization process is best described as (1) reversible formation of a $ClB_5H_8\text{–}Et_2O$ complex, (2) cage rearrangement which can reversibly interchange the initial apical and basal boron atoms, and (3) loss of complexing diethyl ether to give the final product. The first and third processes are known to occur readily for many borane–Lewis base systems.[11] Unfortunately, no direct evidence was obtained for the presence of such complexes in the systems studied. For the second step, the cage rearrangement process, it is difficult to distinguish kinetically between a process of cage rearrangement with maintenance of the B–Cl bond integrity and a process which involves a type of terminal substituent movement around a rigid cage.

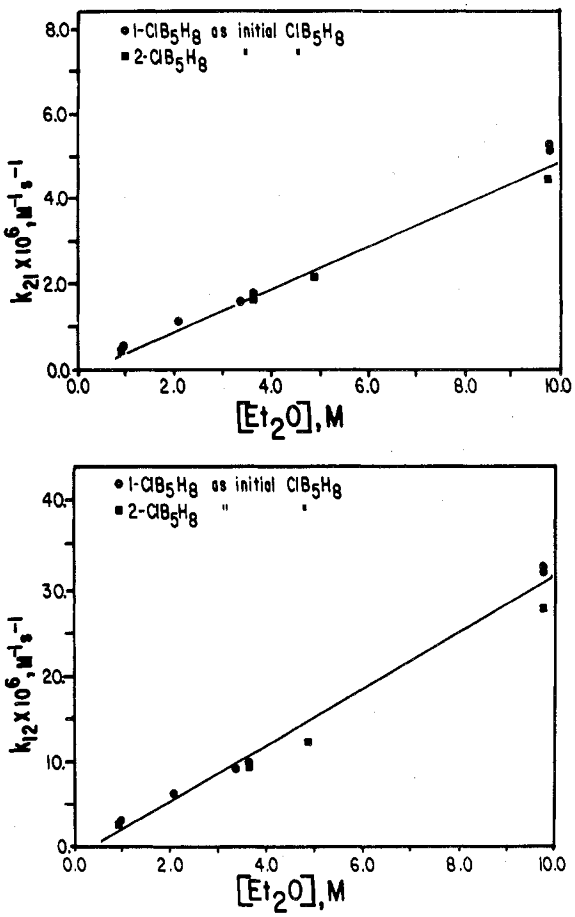

Figure 4. Dependence of pseudo-first-order rate constants on $[Et_2O]$.

A process involving outright B–Cl bond cleavage can be ruled out on the basis of the strength of the B–Cl bond (>100 kcal)[12] and the low activation energy for the overall isomerization process. A process involving terminal substituent movement which does not involve outright B–Cl bond cleavage

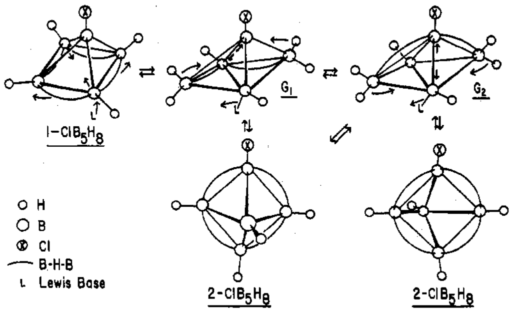

Figure 5. Proposed mechanism for the Lewis base catalyzed isomerization of 1-ClB_5H_8 or 2-ClB_5H_8. Arrows on G_1 or G_2 indicate atomic motion necessary to produce the 2-ClB_5H_8 product directly below it. Cleavage of other equatorial B–B bonds can generate all products indicated.

could occur by a lower energy pathway. One such possibility would be terminal substituent migration which might involve bridging moieties between apical and basal boron atoms. However, no such species have been observed to date and chlorine has not been observed to occupy bridging positions in boranes. Another possibility which may account for a low-energy isomerization process is one involving intermolecular substituent exchange. This is a process which has been observed for hydrogen atoms in pentaborane(9) above 145 °C.[13,14] However, there is no kinetic evidence for such a process occurring in the ClB_5H_8–Et_2O system.

The isomerization of chloropentaborane is therefore proposed to occur via a polytopal rearrangement process in which the B–Cl bond integrity is maintained and the rearrangement of the boron atom vertices in the cage results in effective apical–basal substituent interchange. A slight variation of a mechanism proposed earlier[1a] is illustrated in Figure 5 along with its relation to Scheme I. Lewis-base complexation of ClB_5H_8 at the favored basal position probably results in cleavage of one or more bridge hydrogen bonds. A decrease in one of the cross cage boron distances produces an approximately trigonal-bipyramidal intermediate. Adduct formation and rearrangement is shown as a concerted process though there is no direct experimental evidence on this point. Rearrangement of bridge and terminal hydrogens on the axial borons suggests that two nearly equivalent intermediates are possible, G_1 and G_2. Reopening of an equatorial–equatorial bond and loss of the Lewis base can result in a species in which the initially apical boron atom is in a basal position.

The entire process depicted in Figure 5 takes place with a minimal movement of heavy atoms as proposed for a Berry-type arrangement.[5] The major bond-cleavage processes involve the relatively weak bridge hydrogen bonds. The entire rearrangement process can take place by low-energy pathways consistent with the experimental results. In fact, the observed rearrangements for trigonal-bipyramidal complexes[15] have shown activation barriers in the range of 5–10 kcal/mol and the observed barrier for this ClB_5H_8–Et_2O system is at the lower end of the ranges predicted for other polyhedral cage species.[16] In previous studies in which mono- and diligand adducts of B_5H_9 have been prepared using amine or phosphine ligands, extensive rearrangement has occurred, in those cases characterized,[17] with the adducts not breaking up to re-form B_5H_9 on addition of hydrogen halides. These properties of strong-base adducts of B_5H_9 suggest a tenuous relationship at best to the very weak complex formed during the isomerizations described here.

Ideally, specific labeling of boron atoms in the pentaborane(9) cage could identify the process occurring during the isomerization of pentaborane(9) derivatives as a polytopal rearrangement of boron atoms or as a scrambling of terminal substituents. Unfortunately, synthesis of specifically boron-labeled pentaborane(9) species has not yet been accomplished. Kinetic studies of the rearrangement of other pentaborane(9) derivatives, including base and substituent effects, would be of interest. It might be expected that a mechanism involving Lewis-base attack at a site remote to the substituent, as proposed here, would exhibit smaller substituent effects than a mechanism involving some type of cleavage at or near the substituent–cage linkage. Still, a significant base effect would be expected. However, other substituted pentaborane(9) derivatives do not isomerize cleanly[13,18] and therefore do not appear amenable to kinetic characterization.

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Registry No. 1-ClB_5H_8, 19469-13-7; 2-ClB_5H_8, 19469-14-8; Et_2O, 60-29-7.

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