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Rearrangement of Mono- and Poly-*B*-methyl Derivatives of 2,4-*closo*-Dicarbaheptaborane, 2,4-$C_2B_5H_7$

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An equilibrium can be established between (*B*-CH_3)$_x$-2,4-$C_2B_5H_{7-x}$ (x = 1, 2, 3, or 4) isomers at 300 °C; and it is evident, after statistical corrections, that the methyl positional preference follows the order 3 > 1, 7 > 5, 6. The mechanism of isomer interconversions most likely does not involve substituent migration from boron to boron but instead either a dsd (diamond–square–diamond) or a triangle rotation cage rearrangement. Within presumed energy-preferred dsd conversions of one 2,4-cage isomer to another 2,4-cage isomer, the allowed equilibria for interconversion of *B*,*B*′-Me_2-2,4-$C_2B_5H_5$ isomers are 5,6-Me_2-2,4-$C_2B_5H_5$ ⇌ 1,5- ⇌ 3,5- ⇌ 1,7-; and 1,5- ⇌ 1,3-. In a carefully controlled thermal rearrangement of 5,6-$(CH_3)_2$-2,4-$C_2B_5H_5$, the 1,5-dimethyl isomer is observed to form prior to the production of the 1,3-, 3,5-, and 1,7-$(CH_3)_2$-2,4-$C_2B_5H_5$ isomers. Furthermore, the rate of 3,5-isomer production from the 1,5-isomer exceeds that of the 1,3-isomer formation from the 1,5-isomer although the 1,3-isomer is more stable. A significant increase in separation of *B*-Me groups in the transition state could account for the high rate of 1,5- to 3,5-Me_2-$C_2B_5H_5$ conversion. The methyl group positional preference trend observed in this thermal rearrangement study is exactly the opposite of that observed in the obviously kinetically controlled "electrophilic" methylation of the $C_2B_5H_7$ carborane, the latter reaction showing the following overall positional preference of boron methylation: 5, 6 > 1, 7 > 3. It is advanced that increased *B*-methyl positional stability, under equilibrium conditions, involves a simple electrostatic polarization model in which the methyl group is more effective in dispersing the charge when located on the more positively charged boron atoms.

Introduction

Most carborane skeletal rearrangements have involved the net movement of two cage carbon atoms to positions of increased mutual separation. Examples include the thermal conversion of 1,2-$C_2B_{10}H_{12}$ to 1,7-$C_2B_{10}H_{12}$ and then to 1,12-$C_2B_{10}H_{12}$[2] and of 1,6-$C_2B_8H_{10}$ to 1,10-$C_2B_8H_{10}$[3] and the rearrangement of 1,2-$C_2B_4H_6$ to 1,6-$C_2B_4H_6$.[4] In this regard it is not surprising that there have been no reports of the parent 2,4-$C_2B_5H_7$ rearrangement, for the two carbons in this cage carborane are already at maximum separation among the predicted stable[5] low-coordination equatorial sites. However, attachment of a group onto the 5-position of *closo*-2,4-$C_2B_5H_7$[6,7] allows for the possibility of observing rearrangement in this cage system without forcing the carbons to occupy positions in the D_{5h} structural framework of the product isomers other than the stable 2,4-positions.

Experimental Section

Nuclear Magnetic Resonance. Proton spectra were recorded on Varian A-60 and HA-100 spectrometers. The boron-11 spectra were obtained at 32.1 MHz by using the Varian HA-100 instrument. Boron-11-decoupled proton spectra at 100 MHz were observed while irradiation was done at 32.1 MHz by using a General Radio Model 1061 frequency synthesizer with power booster provided by an Electronic Navigation Industries Model 320L RD power amplifier. Proton-decoupled ^{11}B spectra at 32.1 MHz were observed while irradiation was done at 100 MHz by using the above-mentioned system. Boron-11-decoupled ^1H NMR spectra were also obtained by using a FT-Bruker WP-60 instrument equipped with a Fluka 6160B frequency synthesizer and the ENI-320L amplifier.

The boron-11 chemical shift data (Table I) are reported relative to boron trifluoride ethyl etherate and were obtained by using boron trichloride (δ = −46.8) as a secondary external standard. The proton chemical shifts are reported relative to internal tetramethylsilane (τ = 10.00). In addition to the proton data given in Table II, 3-CH_3-2,4-$C_2B_5H_6$ exhibited ^{11}B-decoupled proton resonances at τ = 6.00 (H–B(5,6)), 9.83 (H–B(1,7)), and 4.77 (H–C(2,4)); also $J(H_C–H_{B(5)}) \simeq 7$ Hz. For 1,5-$(CH_3)_2$-2,4-$C_2B_5H_5$, τ = 5.19 (H–B(3)), 6.13 (H–B(6)), 10.01 (H–B(7)), 4.61 (H–C(2)), and 4.85 (H–C(4)); $J(H_{C(2)}–H_{B(3)}) \simeq 6.5$ Hz. For 3,5-$(CH_3)_2$-2,4-$C_2B_5H_5$, τ = 5.28 (H–B(6)), 9.75 (H–B(1,7)), 4.8–5.0 (H–C(2)), and 5.14 (H–C(4)).

The gas-phase infrared spectra were recorded on a Beckman Acculab 3 spectrometer.

Mass spectra were recorded on a Varian CH-5 high-resolution mass spectrometer and GLC–MS data were gathered by using a Varian Mat 111 equipped with 10% Kel-F grease on a 60/80 mesh Chro-

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Table I. ^{11}B Chemical Shifts (ppm) of Me_x-2,4-$C_2B_5H_{7-x}$ Isomers[a]

compd	atom B(1)	B(3)	B(5)	B(6)	B(7)
1-CH_3-2,4-$C_2B_5H_6$	+11.6	−8.3 (183)	−4.0 (166)	−4.0 (166)	+27.1 (182)
	[+11.8]	[−8.3]	[−4.0]	[+4.0]	[+26.5]
3-CH_3-2,4-$C_2B_5H_6$	+20.7 (178)	−14.1	−4.0 (166)	−4.0 (166)	+20.7 (178)
	[+20.3]	[−13.9]	[−3.9]	[−3.9]	[+20.3]
5-$CH_3$2,4-$C_2B_5H_6$	+20.6 (176)	−6.8 (182)	−11.2	−2.7 (169)	+20.6 (176)
	[+20.6]	[−6.4]	[−11.2]	[−2.6]	[+20.6]
1,3-$(CH_3)_2$-2,4-$C_2B_5H_5$	*+12.0*	−14.0	−3.2 (167)	*−3.2* (167)	+27.1 (196)
	[+10.9]	[−15.0]	[−3.9]	[−3.9]	[+25.6]
1,5-$(CH_3)_2$-2,4-$C_2B_5H_5$	*+12.0*	−7.2 (176)	*−10.6*	*−3.2* (167)	*+27.1* (196)
	[+11.2]	[−7.5]	[−11.2]	[−2.6]	[+25.9]
1,7-$(CH_3)_2$-2,4-$C_2B_5H_5$	*+15.6 to +17.2*	?	?	?	*+15.6 to +17.2*
	[+17.1]	[−9.4]	[−4.0]	[−4.0]	[+17.1]
3,5-$(CH_3)_2$-2,4-$C_2B_5H_5$	*+20.4* (186)	−12.8	*−10.6*	*−1.4 to −3.2*	*+20.4* (186)
	[+19.7]	[−13.1]	[−11.1]	[−2.5]	[+19.7]
5,6-$(CH_3)_2$-2,4-$C_2B_5H_5$	*+20.4* (177)	−5.3 (177)	−9.6	−9.6	*+20.4* (177)
	[+20.0]	[−5.6]	[−9.8]	[−9.8]	[+20.0]
1,3,5-$(CH_3)_3$-2,4-$C_2B_5H_4$	+10.7	−13.9	−10.4	−3.2	+25.2 (176)
	[+10.3]	[−14.2]	[−11.1]	[−2.5]	[+25.0]
1,3,7-$(CH_3)_3$-2,4-$C_2B_5H_4$	*+16.9*	ca. −15.3	*−3.2*	*−3.2*	+16.9
	[+16.2]	[−16.1]	[−3.9]	[−3.9]	[+16.2]
1,5,6-$(CH_3)_3$-2,4-$C_2B_5H_4$	+10.5	−6.9 (173)	−9.6	−9.6	+25.2 (175)
	[+10.6]	[−6.7]	[−9.8]	[−9.8]	[+25.3]
1,5,7-$(CH_3)_3$-2,4-$C_2B_5H_4$	+16.9	*−10.4*	*−10.4*	*−3.2*	+16.9
	[+16.5]	[−8.6]	[−11.2]	[−2.6]	[+16.5]
3,5,6-$(CH_3)_3$-2,4-$C_2B_5H_4$	+19.2 (177)	*−13.9*	*−10.4*	*−10.4*	+19.2 (177)
	[+19.1]	[−12.3]	[−9.7]	[−9.7]	[+19.1]
1,3,5,6-$(CH_3)_4$-2,4-$C_2B_5H_3$	+12.6	*−11.2*	−9.3	−9.3	+25.4 (160)
	[+9.7]	[−13.4]	[−9.7]	[−9.7]	[+24.4]
1,3,5,7-$(CH_3)_4$-2,4-$C_2B_5H_3$	+17.7	*−11.2*	*−11.2*	*+0.9*	+17.7
	[+15.6]	[−15.3]	[−11.1]	[−2.5]	[+15.6]
1,5,6,7-$(CH_3)_4$-2,4-$C_2B_5H_3$	+16.0	−7.7 (180)	−9.8	−9.8	+16.0
	[+15.9]	[−7.8]	[−9.8]	[−9.8]	[+15.9]

[a] All *B*-H boron resonances observed as 1:1 doublets and the *B*-Me borons observed as singlets. Numbers in parentheses are spin-coupling values in Hz; chemical shifts in italics are obtained from resonances which overlap peaks of other isomers in the equilibrium mixture; question marks indicate that overlap with peaks of other isomers and weak intensity do not permit an assignment; chemical shifts in brackets are calculated from eq 1-3 in ref 7. Also, the NMR data for the monomethyl derivatives of $C_2B_5H_7$ are in reasonable agreement with those reported by R. N. Grimes, *J. Am. Chem. Soc.*, 88, 1895 (1966).

Table II. Proton NMR Data for Me_x-2,4-$C_2B_5H_{7-x}$ Compounds

compd	chem shift, τ: 1- and/or 7-methyl position	3-methyl position	5- and/or 6-methyl position
1-CH_3-$C_2B_5H_6$	10.472		
3-CH_3-		8.981	
5-CH_3-			9.252
1,3-$(CH_3)_2$-$C_2B_5H_5$	10.502	9.053	
1,5-$(CH_3)_2$-	10.476		9.318
1,7-$(CH_3)_2$-	10.568		
3,5-$(CH_3)_2$-		9.053	9.343
5,6-$(CH_3)_2$-			9.380
1,3,5-$(CH_3)_3$-$C_2B_5H_4$	10.476	9.097	9.361
1,3,7-$(CH_3)_3$-	10.545	9.097	
1,5,6-$(CH_3)_3$-	10.460		9.420
1,5,7-$(CH_3)_3$-	10.529		9.335
3,5,6-$(CH_3)_3$-		9.097	9.412
1,3,5,6-$(CH_3)_4$-$C_2B_5H_3$	10.462	9.142	9.442
1,3,5,7-$(CH_3)_4$-	10.512	9.142	9.372
1,5,6,7-$(CH_3)_4$-	10.512		9.439
1,3,5,6,7-$(CH_3)_5$-$C_2B_5H_2$	10.505	9.187	9.480

mosorb W 20 ft × $^1/_8$ in. column.

Materials. The starting materials were given to us by R. E. Williams, Chemical Systems Inc. Additional amounts of both 5-CH_3-2,4-$C_2B_5H_6$ and 5,6-$(CH_3)_2$-2,4-$C_2B_5H_5$ were prepared by a procedure similar to that described in the literature.[7] The carborane products from a reaction of a 1:1 ratio of 2,4-$C_2B_5H_7$ and CH_3Cl at 130 °C with a catalytic amount of $AlCl_3$ were separated by cold-column[8] distillation; 5-CH_3-2,4-$C_2B_5H_6$ was distilled between −80 and −75 °C, and 5,6-$(CH_3)_2$-2,4-$C_2B_5H_5$ was removed in the −75 to −60 °C fraction. The yields were 36% and 39%, respectively, on the basis of consumed carborane. The ^{1}H and ^{11}B NMR spectra of both 5-(CH_3)-2,4-$C_2B_5H_6$ and 5,6-$(CH_3)_2$-2,4-$C_2B_5H_5$ were in perfect agreement with a prior report.[7]

Rearrangement of $(CH_3)_xC_2B_5H_{7-x}$ (x = 1-4). 5-CH_3-2,4-$C_2B_5H_6$. A sample of 5-CH_3-2,4-$C_2B_5H_6$ (0.56 mmol) was sealed off in an NMR tube and heated to 300 °C over a 2-h period (note: temperatures much lower than 300 °C did not cause a significant rate of rearrangement, and additional time at 300 °C did not result in further significant change). The GLC–MS analysis exhibits only one slightly broadened GLC peak having the mass spectrum (P = m/e 100) of a monomethyl derivative[9] of $C_2B_5H_7$ with trace impurity evident at the tail end of the GLC peak. This impurity, P = m/e 114, is assigned to $(CH_3)_2$-2,4-$C_2B_5H_5$ (mixture of isomers) present as the 5,6-dimethyl isomer in the starting material. The ^{1}H NMR spectrum of equilibrium product mixture after 16 h of heating contained three *B*-methyl peaks at τ 9.00, 9.28, and 10.50 in an area ratio of 1.25:1.00:1.39. These data and the ^{11}B NMR spectrum were consistent with a mixture of 1-, 3-, and 5-CH_3-2,4-$C_2B_5H_6$ having the composition listed in column 2 of Table III.

3-CH_3-2,4-$C_2B_5H_6$. An NMR sample of 3-CH_3-2,4-$C_2B_5H_6$, when heated to 300 °C for 16 h, exhibited the same ^{1}H and ^{11}B NMR patterns as the equilibrium mixture of 1-, 3-, and 5-CH_3-2,4-$C_2B_5H_6$ as obtained above from the 300 °C heating of the 5-CH_3-2,4-$C_2B_5H_6$.

5,6-$(CH_3)_2$-2,4-$C_2B_5H_5$. 5,6-$(CH_3)_2$-2,4-$C_2B_5H_5$ (0.5 mmol) was sealed off in a 4 mm diameter, 15 cm long Pyrex tube. After the sample was heated at 250 °C for 3 h, a small change was detected in the ^{1}H NMR spectrum, revealing a minor quantity (<1%) of 1,5-$(CH_3)_2$-2,4-$C_2B_5H_5$. The sample temperature was then raised to 275 °C, stopping for NMR analysis at 21, 45, 113, and 185 h (see Figure 1). Additional rearrangement was observed at 300 °C for 5 h and at 320 °C for 17 h. Subsequently, a very minor change in composition was detected upon heating the sample 4.5 h at 360 °C, but an additional 6.5 h at this same temperature revealed no further rearrangement at which point it was assumed that the reaction had reached equilibrium. The composition of the mixture after each heating period (Tables III and IV) was determined by "best-fitting"

Table III. Rearrangement Data for Methyl Derivatives of 2,4-$C_2B_5H_7$

(1) compd	(2) % compn at equil (obsd)	(3) W^a	(4) $\Delta H_{exptl}{}^b$	(5) $\Delta H_{calcd}{}^c$	(6) % compn (theor derived from col 5)^d
1-CH_3-2,4-$C_2B_5H_6$	38.2 ± 0.5	2	667	667	38.2
3-	34.3 ± 0.5	1	0	0	34.3
5-	27.5 ± 0.5	2	1041	1041	27.5
1,3-$(CH_3)_2$-2,4-$C_2B_5H_5$	37.4 ± 2	2	0	0	32.5
1,5-	25.5 ± 1	4	1354	1041	28.4
1,7-	7.2 ± 1	1	1200	667	9.6
3,5-	24.9 ± 1	2	512	374	24.2
5,6-	5.0 ± 1	1	1659	1415	5.3
1,3,5-$(CH_3)_3$-2,4-$C_2B_5H_4$	62.3 ± 5	4	26	374	49.1
1,3,7-	15.9 ± 3	1	0	0	16.5
1,5,6-	5.1 ± 2	2	2302	1415	10.7
1,5,7-	8.1 ± 3	2	1720	1041	14.6
3,5,6-	8.6 ± 3	1	773	748	9.1
1,3,5,6-$(CH_3)_4$-2,4-$C_2B_5H_3$	37.6 ± 2	2	345	374	37.5
1,3,5,7-	50.9 ± 2	2	0	0	52.1
1,5,6,7-	11.5 ± 2	1	904	1041	10.4

[a] See text, eq 1. [b] See text, eq 1; ΔH is in calories; the isomer in each set with the lowest enthalpy is arbitrarily assigned a $\Delta H = 0$; the equilibrium temperatures are 300 °C for both the mono- and tetramethylcarborane equilibrium mixtures and 360 °C for both the di- and trimethylcarborane mixtures. [c] The di-, tri-, and tetramethyl ΔH values are calculated by adding the effects of each methyl substituent by using ΔH(1- or 7-substituted) = 667 cal and ΔH(5- or 6-substituted) = 1041 cal relative to the enthalpy of 3-substitution (see monomethyl ΔH values, column 4). The isomer within each series having the lowest enthalpy is arbitrarily assigned $\Delta H = 0$. [d] See text, eq 1.

Table IV. Rearrangement of 5,6-$(CH_3)_2$-2,4-$C_2B_5H_5$

		% of each B,B'-$(CH_3)_2$-2,4-$C_2B_5H_5$ isomer				
temp, °C	time, h	5,6	1,5	3,5	1,3	1,7
-	0	100	0	0	0	0
275	21	57 ± 1	42 ± 1	0 - 5	0	0
275	45	35.5 ± 2	53 ± 3	11.5 ± 0.5	0	0
275	113	17.3 ± 1	47.2 ± 2	24.8 ± 1	10.7 ± 0.5	0
275	185	15.3 ± 1	36.3 ± 2	33.3 ± 2	14.7 ± 1	0.4 ± 0.1
360	11	5 ± 0.25	25.5 ± 1	24.9 ± 1	37.4 ± 2	7.2 ± 0.4
275	*a*	4.3	22.6	27.5	39.1	6.5

[a] The data given above this line are experimentally obtained. The data shown on this line represent the theoretical equilibrium amounts of each isomer at 275 °C calculated from the 360 °C equilibrium data; see Table III.

the individual ^1H and ^{11}B NMR spectra with the available data in Tables I and II and the data given in the NMR section (see above) and in ref 7.

1,5,6-$(CH_3)_3$-2,4-$C_2B_5H_4$. A sample of 1,5,6-$(CH_3)_3$-2,4-$C_2B_5H_4$ (0.46 mmol) was sealed off in an NMR tube and heated at 300 °C over a 36-h period. Temperatures much lower than 300 °C did not cause a significant rate of rearrangement, and additional heating at 300 °C did not result in further change; however, the sample was then heated at 360 °C for 4 h to ensure that the rearrangement products had reached equilibrium. The ^{11}B and ^1H NMR patterns were consistent with the percent composition given in column 2 of Table III.

1,5,6,7-$(CH_3)_4$-2,4-$C_2B_5H_3$ (0.44 mmol) was sealed off in an NMR tube and heated at 300 °C over a 36-h period. Temperatures much lower than 300 °C did not cause a significant rate of rearrangement, and additional time at 300 °C did not result in further change. A GLC–MS analysis of the equilibrium mixture gave one slightly broad GLC peak in which a spot-check of the MS at four points along this GLC peak indicated that only $(CH_3)_4C_2B_5H_3$ was present in the mixture. Integration of both decoupled and undecoupled ^1H and ^{11}B NMR spectra provided data from which a percent composition of the isomers in the mixture was calculated (column 2, Table III).

Results and Discussion

At 300 °C 5-CH_3-*closo*-2,4-$C_2B_5H_6$ equilibrates with both the 1-CH_3-*closo*-2,4-$C_2B_5H_6$ and 3-CH_3-*closo*-2,4-$C_2B_5H_6$ isomers with the *B*-methyl group showing a positional preference 3 > 1, 7 > 5, 6 based on enthalpy considerations alone. Similar conditions are required to rearrange the di-, tri-, and tetramethyl derivatives of this same *closo*-2,4-dicarbaheptaborane. From the observed equilibrium distribution of isomers (B-$CH_3)_x$-2,4-$C_2B_5H_{7-x}$ (x = 2, 3, 4) in each category of x it is evident that the methyl positional preference in these polymethyl derivatives on this cage system also follows the order 3 > 1, 7 > 5, 6.

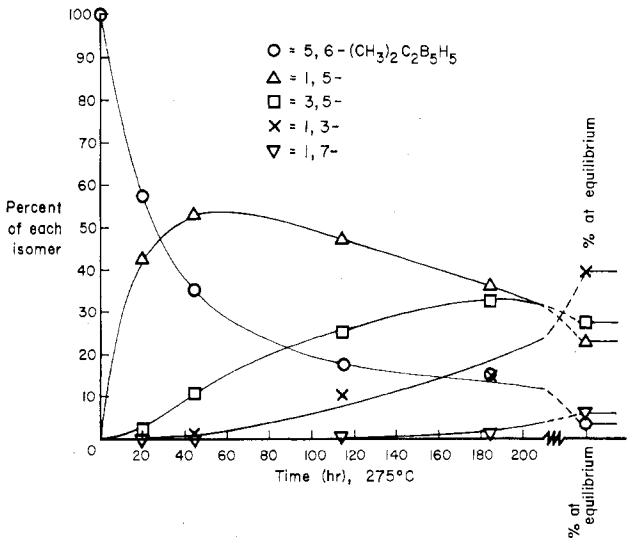


Figure 1. Composition–time diagram for the rearrangement of 5,6-$(CH_3)_2$-2,4-$C_2B_5H_5$.

Enthalpy differences among isomers can be easily obtained from the equilibrium data (column 2, Table III) upon attributing entropy differences to symmetry variations only. Thus if bond-entropy differences between closely related isomers are ignored, the following simple relationship applies:

$$\Delta H = -RT \ln K + T\Delta(-R \ln W) \quad (1)$$

$R \ln W$ is the molar entropy and W is the number of distinguishable conformations that a compound may assume (column 3, Table III).[10] If it is assumed that the enthalpy differences between isomers are solely a function of substituent position(s), then ΔH_{exptl} for the 1-, 3-, and 5-monomethyl

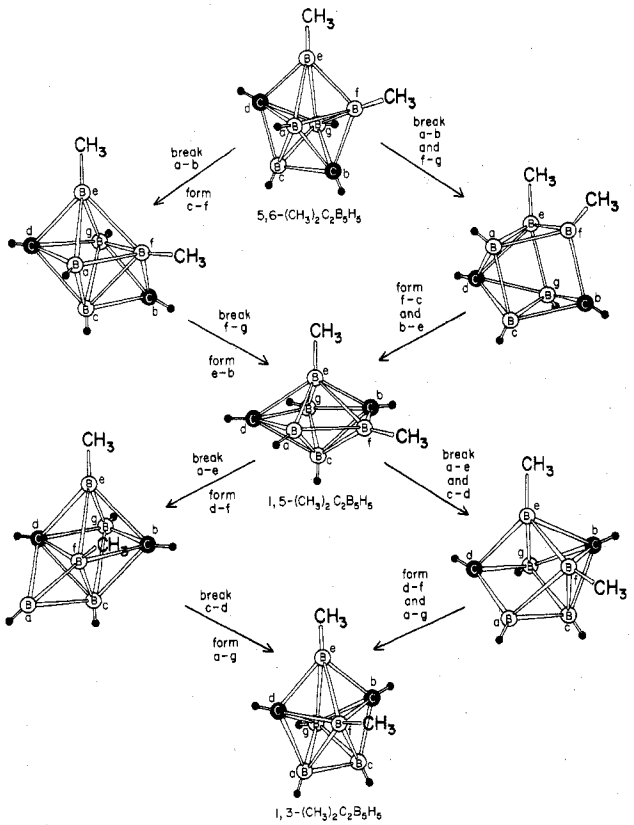
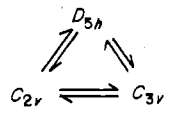


Figure 2. Mechanistic schemes, partial, for the dsd rearrangement of 5,6-$(CH_3)_2$-2,4-$C_2B_5H_5$.

isomers (column 4, Table III) can be employed to predict the relative enthalpies, ΔH_{calcd} (column 5), for the polymethyl isomer sets; e.g., ΔH_{calcd} (for the difference between the 5,6- and 1,3-dimethyl isomers) = 2(1041 cal) − 667 cal = 1415 cal. In turn, a theoretical percent isomer composition at equilibrium (column 6) is derived from these ΔH_{calcd} values. The agreement between the equilibrium percentages, observed (column 2) and calculated (column 6), for the polymethyl species is remarkably good upon considering errors in the measurements used to obtain the experimental values as well as the above assumptions concerning entropy factors and ΔH substituent additivity.

The mechanism of this rearrangement most likely does not involve substituent migration from boron to boron but instead a dsd cage rearrangement approximated by the stylized cycle for seven-vertex cage molecules.[11-17]

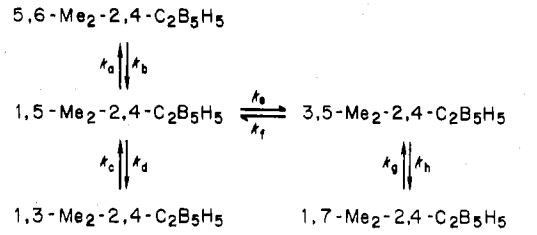


Pertinent mechanistic sequences for the rearrangement of 5,6-$(CH_3)_2$-2,4-$C_2B_5H_5$ are shown in Figure 2. The depicted intermediates (presumably not isolable) are based on seven-vertex cage geometries of idealized C_{3v} and C_{2v} symmetries. Strictly speaking, these symmetry assignments only apply when all vertices are occupied by the same type of atom or group, and the presence of two types of atoms, C and B, in the cage skeleton indicate that the actual intermediate(s) is (are) only indirectly related to the indicated symmetry categories. The mechanistic scheme given in Figure 2 is probably too strict a representation of the cage rearrangement; but it is highly likely that common to both the depicted and the actual mechanism are the specific bonds broken and formed, and it is just a matter of sorting out the sequence of these processes that decides the polyhedral structure(s) of the intermediate(s).

Table V. Rearrangement Possibilities for 5,6-Me_2-2,4-$C_2B_5H_5$

case	bonds broken	bonds formed	product
A	a–b, f–g	c–f, b–e	1,5-Me_2-2,4-$C_2B_5H_5$
B	a–c, b–g	c–f, b–d	4,7-Me_2-1,2-$C_2B_5H_5$
C	a–d, c–g	c–e, b–d	4,7-Me_2-1,2-$C_2B_5H_5$
D	a–e, d–g	c–e, f–d	1,5-Me_2-2,4-$C_2B_5H_5$
E	a–f, e–g	b–e, f–d	2,3-Me_2-1,7-$C_2B_5H_5$
F	a–b, c–g	c–f, b–d	4,7-Me_2-1,2-$C_2B_5H_5$
G	a–c, d–g	c–e, b–d	4,7-Me_2-1,2-$C_2B_5H_5$
H	a–d, e–g	c–e, f–d	1,5-Me_2-2,4-$C_2B_5H_5$
I	a–e, f–g	b–e, f–d	2,3-Me_2-1,7-$C_2B_5H_5$
J	a–f, b–g	c–f, b–e	1,5-Me_2-2,4-$C_2B_5H_5$

In both formal mechanisms shown in Figure 2, the first rearrangement step involves the breaking of bonds a–b and f–g and the formation of bonds c–f and b–e. Table V summarizes the rearrangement product expected when these and other bond pairs are broken and formed within the constraints of this general mechanistic picture. Only in the related bond-breaking and bond-forming cases A, D, H, and J are products obtained without cage carbons located at unfavorable high-coordination sites (apical 1 and/or 7 positions), and in each of these four instances 1,5-$(CH_3)_2$-2,4-$C_2B_5H_5$ is formed. No 3-substituted isomers are formed in this first stage of the rearrangement, but both 1,3- and 3,5-$(CH_3)_2$-2,4-$C_2B_5H_5$ can be produced by further application of this rearrangement scheme to the 1,5-$(CH_3)_2$-2,4-$C_2B_5H_5$ isomer. The net effect is to establish the equilibria shown in eq 2 within the presumed energy-preferred dsd conversions of one 2,4-cage isomer to another 2,4-cage isomer.



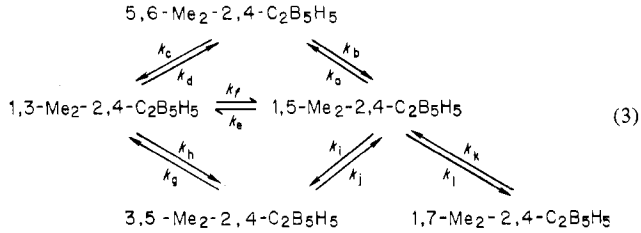
(2)

In a carefully controlled rearrangement of the 5,6-$(CH_3)_2$-2,4-$C_2B_5H_5$, we have obtained evidence that the 1,5-dimethyl isomer is indeed formed prior to the production of the 1,3-, 3,5-, and/or 1,7-$(CH_3)_2$-2,4-$C_2B_5H_5$ isomers. An inspection of the graph, Figure 1, also reveals that the rate of 3,5-isomer production, k_e, exceeds that of the 1,3-isomer, k_d, although the latter isomer is more stable. With the assumption of the reasonable unimolecular mechanistic pathway, Figure 2 and eq 2, a set of relative rates can be easily derived from both the observed equilibria (Table III) and the graphical data (Figure 1): relative values of $k_a/k_b/.../k_h$ (k_h normalized to 1.00) are 3.05/15.8/2.50/3.71/6.60/5.90/3.84/1.00, respectively. Because three isomers, 5,6, 1,3, and 3,5, are involved in direct equilibria (eq 2) with a common isomer, 1,5, it is interesting to compare 1,5-$(CH_3)_2$-2,4-$C_2B_5H_5$ structural rearrangement patterns with the corresponding relative rates. Possible dsd pair changes leading from the 1,5-isomer to dimethyl-2,4-dicarbaheptaboranes only follow: case I, breaking bond pairs c–f/b–e (Figure 2), ultimately leading to the 5,6-isomer; case II, breaking c–d/a–e en route to the 1,3-isomer; case III, breaking b–c/e–f en route to the 3,5-isomer; case IV, breaking a–c/d–e en route to an equilibrium with the enantiomer of the 1,5-isomer. The present study cannot give information on the rate of case IV interconversion of 1,5-enantiomers, but the relative rates of cases I, II, and III are those derived for k_a, k_d, and k_e which are 3.05, 3.71, and 6.60, respectively. Significant increase in separation of *B*-Me groups in the case III transition state could well account for k_e having the highest relative value among the three. More surprising

is the relative rate ratio $k_f/k_h = 5.90$ representing the conversion of the 3,5-isomer to the 1,5- and 1,7-isomers, respectively. An inspection of mechanistic models, Figure 2, indicates that serious steric interactions between *B*-methyl groups do not come into play in the 3,5- to 1,5-rearrangement until the final bond construction step and, of course, do not appear to be a problem during any aspect of the 3,5 to 1,7 conversion.

The apparent ease with which the 5,6-isomer rearranges to the 1,5 should be moderated by a statistical factor. Within the dsd mechanistic picture, there are four bond-breaking/bond-construction combinations by which the 5,6-isomer is converted to the 1,5-isomer. By comparison, each of the four bond-breaking/bond-construction combinations involved in the *dsd* rearrangement of 1,5-$(CH_3)_2$-2,4-$C_2B_5H_5$ results in four different products. Extending this kind of statistical weighting for each of the above relative rate constants yields another set which may prove useful for future mechanistic considerations. $k_a/k_b.../k_h$ (k_h normalized to 1.00) are 12.2/15.8/5.00/14.84/26.4/11.8/7.68/1.00, respectively.

A plausible alternative mechanism involves either a 120 and/or 240° rotation of a triangular face[17-21] of the pentagonal-bipyramidal framework. Possible equilibria within this mechanistic scheme are shown in eq 3. The derived rate



(3)

constants for the triangle-rotation mechanism are $k_a/k_b/.../k_l$ (k_l normalized to 1.0) are 2.5/12.4/~0/~0/2.1/1.4/~0/~0/2.5/2.4/3.5/1.0. It is noted that k_c, k_d, k_g, and k_h are very small and so the equilibria between the 1,3-isomer and both the 5,6- and 3,5-isomers can be ignored. Except for the equilibrium between the 1,7- and 1,5-isomers, the remaining pattern of equilibria, eq 3, resembles that derived from the dsd mechanism, eq 2.

In searching for a rationale for the methyl group positional preference trend observed in this thermal rearrangement study, it is to be noted that this trend is exactly the opposite of that observed in the obviously kinetically controlled "electrophilic" methylation of the $C_2B_5H_7$ carborane, the latter reaction[7] showing the overall positional preference of boron methylation: 5, 6 > 1, 7 > 3. It is not unexpected to find that the results of the electrophilic substitution reaction are consistent with the ground-state Mulliken charges (obtained from minimum basis-set Slater orbital SCF calculations)[22] assigned to the boron atoms of this cage, although the usual caution must be exercised in comparing ground and activated states. These MO calculations indicate that positive charge increases as B(5) < B(1) ≤ B(3). It is then advanced that increased *B*-methyl positional stability (found to be 3 > 1, 7 > 5, 6 in the present study under equilibrium conditions) involves a simple electrostatic polarization model[23] in which the methyl group is more effective in dispersing the charge when located on the more positively charged boron atoms.

Prior knowledge of ^{11}B and ^1H NMR trends[7,24] for certain $C_2B_5H_7$ methyl derivatives assisted in the resonance assignments of isomeric mixtures during the course of the present rearrangement studies. Additionally, we find that a sufficient resolution of the *B*-Me regions (τ 8–11) in the ^1H NMR is obtained upon ^{11}B decoupling to allow at least one resonance of each isomer within an isomer set to be clearly observed. Trends in the methyl chemical shift values that become evident for $(CH_3)_xC_2B_5H_{7-x}$, x = 2–5, are τ(1- and/or 7-methyl) = 10.463 + a(0.044) + b(−0.005) + c(−0.022), τ(3-methyl) = 8.962 + (a + 1 + c)(0.0452), and τ(5- and/or 6-methyl) = 9.203 + a(0.025) + b(0.035) + c(0.093), where a = number of groups in the 1, 7 positions (0, 1, or 2), b = number of groups in the 3 position (0 or 1), and c = number of groups in the 5, 6 positions (0, 1, or 2). The largest upfield shifts of methyl resonances were observed when both sites of either the 1,7- or the 5,6-position pairs were substituted. Additionally, a feature unique to compounds with a methyl group in only one of the two apical 1,7-positions is a coupling of this methyl group to the antipodal B(7)-attached hydrogen, giving a sharp doublet (upon ^{11}B decoupling) with J values falling between 0.34 and 0.52 Hz.

Except for the 1,7 region, δ = +10 to +30, of $C_2B_5H_7$, the ^{11}B NMR patterns of the $(B\text{-}CH_3)_x$-$C_2B_5H_{7-x}$ equilibrium mixture were more complicated and thus less useful than the ^1H patterns. However, many resonances could be unambiguously assigned (Table I), and the chemical shift values are in good agreement with calculated shifts derived from an earlier study.[7]

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Registry No. 1-CH_3-2,4-$C_2B_2H_6$, 23810-31-3; 3-CH_3-2,4-$C_2B_5H_6$, 23940-13-8; 5-CH_3-2,4-$C_2B_5H_6$, 23810-32-4; 1,3-$(CH_3)_2$-2,4-$C_2B_5H_5$, 71155-69-6; 1,5-$(CH_3)_2$-2,4-$C_2B_5H_5$, 68238-17-5; 1,7-$(CH_3)_2$-2,4-$C_2B_5H_5$, 23753-78-8; 3,5-$(CH_3)_2$-2,4-$C_2B_5H_5$, 68238-16-4; 5,6-$(CH_3)_2$-2,4-$C_2B_5H_5$, 58548-76-8; 1,3,5-$(CH_3)_3$-2,4-$C_2B_5H_4$, 71155-73-2; 1,3,7-$(CH_3)_3$-2,4-$C_2B_5H_4$, 71129-68-5; 1,5,6-$(CH_3)_3$-2,4-$C_2B_5H_4$, 58548-77-9; 1,5,7-$(CH_3)_3$-2,4-$C_2B_5H_4$, 71155-72-1; 3,5,6-$(CH_3)_3$-2,4-$C_2B_5H_4$, 71155-71-0; 1,3,5,6-$(CH_3)_4$-2,4-$C_2B_5H_3$, 71129-69-6; 1,3,5,7-$(CH_3)_4$-2,4-$C_2B_5H_3$, 71155-70-9; 1,5,6,7-$(CH_3)_4$-2,4-$C_2B_5H_3$, 58540-73-1; 1,3,5,6,7-$(CH_3)_5$-$C_2B_5H_2$, 18972-11-7.

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