Articles

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Substituent Effects on *closo*-2,4-$C_2B_5H_7$ Derivative Rearrangement Rates. Comparison of Rearrangement Pattern and Rate Constants of a Mixed Disubstituted Carborane, 5-CH_3-6-Cl-2,4-$C_2B_5H_5$, with Those of Monosubstituted 5-X-2,4-$C_2B_5H_6$ and Disubstituted 5,6-X_2-2,4-$C_2B_5H_5$ (X = CH_3, Cl): Mechanistic Implications and Isomer Stability Correlations

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The rearrangement of 5-CH_3-6-Cl-*closo*-2,4-$C_2B_5H_5$ to an equilibrium mixture of all eight *B*-CH_3-*B'*-Cl-*closo*-2,4-$C_2B_5H_5$ isomers is carried out at 295 °C. The first isomer produced is 1-CH_3-5-Cl-2,4-$C_2B_5H_5$ followed by 3-CH_3-5-Cl-2,4-$C_2B_5H_5$. The order of appearance of the other five isomers is as follows: 5-CH_3-1-Cl-2,4-$C_2B_5H_5$, 5-CH_3-3-Cl-2,4-$C_2B_5H_5$, 3-CH_3-1-Cl-2,4-$C_2B_5H_5$, 1-CH_3-3-Cl-2,4-$C_2B_5H_5$, 1-CH_3-7-Cl-2,4-$C_2B_5H_5$. Rearrangement rate comparisons to those of the related mono- and disubstituted compounds 5-X-*closo*-2,4-$C_2B_5H_6$ and 5,6-X_2-*closo*-2,4-$C_2B_5H_5$ (X = CH_3, Cl) indicate that (a) the presence of a second substituent accelerates the apparent rearrangement of the first substituent and (b) the effect of Cl in this regard is greater than that of CH_3. The rearrangement pattern for 5-CH_3-6-Cl-*closo*-2,4-$C_2B_5H_5$ rules out a triangle-face-rotation mechanism in which cage-carbon atoms stay in the low-coordination nonadjacent positions and is consistent with a "diamond-square-diamond" mechanism. The relative stabilities of the eight *B*-CH_3-*B'*-Cl-*closo*-2,4-$C_2B_5H_5$ isomers, after statistical weighting, are 1-CH_3-3-Cl- > 3-CH_3-5-Cl- > 3-CH_3-1-Cl- > 5-CH_3-3-Cl- ≥ 1-CH_3-5-Cl- > 5-CH_3-6-Cl- > 5-CH_3-1-Cl- > 1-CH_3-7-Cl-$C_2B_5H_5$. This order of observed isomer stabilities is forecast, with only minor departures, from additive substituent-positional effects.

Introduction

Thermal rearrangements of several *B*-X-*closo*-2,4-$C_2B_5H_6$ and *B,B'*-X_2-*closo*-2,4-$C_2B_5H_5$ (X = CH_3, Cl, Br, I) carboranes[1-5] have resulted in the formation of most all isomers of these systems and in certain instances provide the only route to some of the isomers. No rearrangement has previously been attempted on a mixed disubstituted carborane of the type *B*-X-*B'*-Y-*closo*-2,4-$C_2B_5H_5$ (X ≠ Y). Of interest is (a) the possibility of finding new mixed-substituent $C_2B_5H_7$ derivatives, (b) the correlation of *B*-X-*B'*-Y-*closo*-2,4-$C_2B_5H_5$ rearrangement rate patterns with the corresponding *B*-X- or *B*-Y-2,4-$C_2B_5H_6$ and *B,B'*-X_2- or *B,B'*-Y_2-closo-2,4-$C_2B_5H_5$ rearrangements, and (c) the correlation of mixed-substituent isomer stabilities (obtained from isomer equilibration) with the type and position of the individual substituents. In the present work we report the results of a study involving the *B*-CH_3-*B'*-Cl-*closo*-2,4-$C_2B_5H_5$ isomer system.

Experimental Section

Materials and Handling of Chemicals. 5-Cl-2,4-$C_2B_5H_6$, 5-CH_3-2,4-$C_2B_5H_6$, and 5,6-$(CH_3)_2$-2,4-$C_2B_5H_5$ were prepared according to literature procedures.[2-4,6-8] Aluminum chloride, obtained from Aldrich Chemical Corp., was freshly sublimed directly into the reaction vessel prior to use. All materials were handled by using conventional high-vacuum techniques.

Nuclear Magnetic Resonance. Boron-11 NMR spectra were obtained by using both Varian HA-100 CW (32.1 MHz) and Bruker WM-500 FT (160.44 MHz) spectrometers. Proton-decoupled boron spectra were also recorded at all carborane-derivative rearrangement time intervals (see below). By varying the delay times between radio-frequency pulses, we minimized saturation effects in the determination of rearrangement mixture isomer concentrations by NMR area integration measurements. Boron chemical shift data (Table I) were referenced relative to BF_3·OEt_2, δ = 0.00, with the parent 2,4-$C_2B_5H_7$ used as a secondary standard: δ(B(1,7)) = -21.73, $J(^{11}BH)$ = 180 Hz; δ(B(3)) = +7.02 $J(^{11}BH)$ = 183 Hz; δ(B(5,6)) = +3.83, $J(^{11}BH)$ = 170 Hz. Negative chemical shift values are upfield of the BF_3·OEt_2 resonance. Approximate chemical shift and coupling-constant errors for all dicarbaheptaboranes are as follows: ±0.02 ppm and ±3 Hz, for the cage 1-, 3-, and 7-positions of the carborane; ±0.06 ppm and ±10 Hz, for the cage 5- and 6-positions. Triple-resonance proton NMR spectra (60 MHz) were obtained on a Bruker WP-60 FT spectrometer equipped with a Fluke 6160B frequency synthesizer set at 19.255 MHz for decoupling boron-11 and a Fluke 6011A frequency synthesizer set at 6.447 MHz for decoupling boron-10; the frequency synthesizers were powered by ENI Model 320L RD amplifiers.

Synthesis of 5-CH_3-6-Cl-2,4-$C_2B_5H_5$. To a 50-mL reaction vessel equipped with an NMR tube (the inside of which was coated with a thin layer of $AlCl_3$) was added 5-Cl-2,4-$C_2B_5H_6$ (2.25 mmol) and CH_3Cl (3.6 mmol). The reaction vessel and its contents were heated at 126 °C for 21.0 h. Cold-column vacuum fractionation[9] of the product mixture yielded (a) a portion emerging from the column at -104 to -90 °C, which was largely carborane cleavage products, (b) a 0.24-mmol fraction distilling at -65 to -45 °C consisting of 18% 5-Cl-2,4-$C_2B_5H_6$, 6% 5-CH_3-6-Cl-2,4-$C_2B_5H_5$, 27% BCl_3, 21% $(Cl_2B)_2CH_2$, 2% CH_3BCl_2, and a remainder of a mixture of cage-cleavage products showing ^{11}B NMR singlets at δ = 16.9, 21.2, 26.2, 31.9, 41.6, 63.4, and 74.0, (c) a 0.60-mmol fraction (-45 to -39 °C) consisting of pure 5-CH_3-6-Cl-2,4-$C_2B_5H_5$,[10] (d) ca. 0.5 mmol (-39 to -29 °C), which consisted, on the basis of NMR analysis (Table I), of 29% 5-CH_3-6-Cl-2,4-$C_2B_5H_5$, 55% 1,5-$(CH_3)_2$-6-Cl-$C_2B_5H_4$, 8% 3,5-$(CH_3)_2$-6-Cl-$C_2B_5H_4$, and 8% 1,5,7-$(CH_3)_3$-6-Cl-$C_2B_5H_3$, (e) ca. 0.63 mmol (distilling from -29 °C to room temperature) containing a mixture of 1,5-$(CH_3)_2$-6-Cl-$C_2B_5H_4$, 3,5-$(CH_3)_2$-6-Cl-$C_2B_5H_4$, 1,3,5-$(CH_3)_3$-6-Cl-$C_2B_5H_3$, 1,5,7-$(CH_3)_3$-6-Cl-$C_2B_5H_3$, 1,3,5,7-$(CH_3)_4$-6-Cl-$C_2B_5H_2$, and compound(s) with a singlet at δ = 10.1 and doublets at δ = -23.9, -18.25, 1.7 ppm in the ^{11}B NMR spectrum. The overall yield of 5-CH_3-6-Cl-2,4-$C_2B_5H_5$ was ca. 34%.

5-CH_3-6-Cl-2,4-$C_2B_5H_5$ Rearrangement. A sample of 5-CH_3-6-Cl-2,4-$C_2B_5H_5$ (0.38 mmol), sealed in a 3-mm NMR tube, which was fitted at one end with a 3.5-mL glass bulb, was heated at 295 °C for a number of time intervals (Table II) up to a total of 51+ days; after each heating

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Table I. ^{11}B NMR Data for *B*-Methyl *B'*-Chloro Derivatives of 2,4-$C_2B_5H_7$[a]

compd	atom				
	B(1)	B(3)	B(5)	B(6)	B(7)
1-CH_3-3-Cl-	−8.76	15.51	3.50	3.50	−24.11 (183)
	[−8.49]	[16.07]	[3.50]	[3.50]	[−24.26]
1-CH_3-5-Cl-	−10.17	6.23 (185)	13.83[b]	1.62 (161)[b]	−25.74 (182)
	[−10.18]	[6.26]	[14.06]	[1.30]	[−25.95]
1-CH_3-7-Cl-	−23.20	9.50	3.50[b]	3.50[b]	−19.97
	[−23.20]	[9.29]	[3.60]	[3.60]	[−22.00]
3-CH_3-1-Cl-	−15.37	14.81	3.08	3.08	−31.59 (182)
	[−14.75]	[15.24]	[2.97]	[2.97]	[−31.72]
3-CH_3-5-Cl-	−18.82 (178)[b]	12.50	13.11[b]	0.30 (155)[b]	−18.82 (178)[b]
	[−18.70]	[12.21]	[13.43]	[0.67]	[−18.70]
5-CH_3-1-Cl-	−15.58	7.78 (194)[b]	10.86	1.71[b]	−32.27 (180)
	[−15.40]	[7.68]	[10.87]	[1.76]	[−32.37]
5-CH_3-3-Cl-	−17.74 (175)[b]	14.27	10.86	1.36 (170)[b]	−17.74 (175)[b]
	[−17.66]	[14.46]	[10.77]	[1.66]	[−17.66]
5-CH_3-6-Cl-	−19.63 (185)	3.68 (189)	8.52	12.02	−19.63 (185)
	[−19.35]	[4.65]	[8.57]	[12.22]	[−19.35]
1,5-$(CH_3)_2$-6-Cl-	−9.88	4.87 (182)[b]	8.47[b]	12.07[b]	−25.05 (182)
	[−9.48]	[5.76]	[8.83]	[12.48]	[−25.25]
3,5-$(CH_3)_2$-6-Cl-	−18.82 (186)	*b*	8[b]	*b*	−18.82 (186)
	[−18.00]	[11.71]	[8.20]	[11.85]	[−18.00]
1,3,5-$(CH_3)_3$-6-Cl-	−9.27	11.49[b]	7.99[b]	11.49[b]	−23.42 (176)
	[−8.13]	[12.82]	[8.46]	[12.11]	[−23.90]
1,5,7-$(CH_3)_3$-6-Cl-	−15.4	6.2 (177)	8[b]	12.53[b]	−15.4
	[−15.38]	[6.87]	[9.09]	[12.74]	[−15.31]
1,3,5,7-$(CH_3)_4$-6-Cl-	−14.46	*b*	*b*	*b*	−14.46
	[−14.03]	[13.93]	[8.72]	[12.37]	[−14.03]

[a] All B–H boron resonances are observed as 1:1 doublets and B-X (X = CH_3, Cl) borons are observed as singlets. Chemical shifts are in ppm relative to $\delta(BF_3{\cdot}OEt_2) = 0.00$, and negative values are upfield; numbers in parentheses are ^{11}B–H coupling constants, in Hz. All experimental data were obtained at 160.44 MHz; for uncertainties in values, see Experimental Section and footnote *b* below. Chemical shifts in brackets were calculated by assuming a substituent additivity effect (see text); the required *B*-chloro additivity data were obtained by subtracting the 2,4-$C_2B_5H_7$ chemical shifts (see Experimental Section) for the pertinent chemical shifts of the *B*-monochloro system in ref 4. The required additivity data for the *B*-methyl positions were obtained by subtracting the 2,4-$C_2B_5H_7$ chemical shifts from the following *B*-CH_3-2,4-$C_2B_5H_6$ 160.44 MHz ^{11}B NMR data: $\delta(B(1)) = -11.86$, $\delta(B(3)) = 8.13$, $\delta(B(5,6)) = 4.09$, $\delta(B(7)) = -27.63$ for 1-CH_3-2,4-$C_2B_5H_6$; $\delta(B(1,7)) = -20.38$, $\delta(B(3)) = 14.08$, $\delta(B(5,6)) = 3.46$ for 3-CH_3-2,4-$C_2B_5H_6$; $\delta(B(1,7)) = -21.03$, $\delta(B(3)) = 6.52$, $\delta(B(5)) = 11.36$, $\delta(B(6)) = 2.25$ for 5-CH_3-2,4-$C_2B_5H_6$. [b] Cannot be accurately determined due to peak overlap.

Table II. Kinetic Data for the Rearrangement of 5-CH_3-6-Cl-*closo*-2,4-$C_2B_5H_5$ at 295 °C

total heating time, h	% *B*-CH_3-*B'*-Cl-2,4-$C_2B_5H_5$ isomers[a]							
	5-CH_3-6-Cl-	1-CH_3-5-Cl-	3-CH_3-5-Cl-	5-CH_3-1-Cl-	5-CH_3-3-Cl-	3-CH_3-1-Cl-	1-CH_3-3-Cl-	1-CH_3-7-Cl-
0	100.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.5	56.7	35.9	6.6	0.8	0.0	0.0	0.0	0.0
1	37.8	48.9	12.0	1.3	0.0	0.0	0.0	0.0
2	24.3	48.9	24.5	2.3	0.0	0.0	0.0	0.0
4	16.4	44.6	35.3	1.7	1.6	0.4	0.0	0.0
8.5	13.5	42.3	37.7	2.9	2.5	0.7	0.4	0.0
21.5	13.4	39.7	35.9	3.5	4.3	2.1	1.1	0.0
45	13.7	37.2	31.9	3.6	8.4	3.1	1.6	0.5
93	11.9	29.8	26.6	7.1	11.0	5.9	6.3	1.4
189	8.3	24.6	22.4	6.3	10.9	10.1	14.1	3.3
284	8.6	23.1	18.3	5.7	11.7	12.0	18.7	1.9
524.5	7.2	21.8	18.3	7.5	9.1	12.0	21.8	2.3
595.5	7.5	21.5	16.1	7.7	9.4	13.3	21.7	2.8
927	7.2	20.8	17.0	7.2	9.5	13.2	23.1	2.0
1231	7.6	20.7	17.4	8.8	8.8	12.2	22.4	2.0

[a] Average estimated errors in concentration measurements: ±1.0%.

period, the sample was immediately cooled to room temperature (at ambient temperature the rearrangement was essentially quenched) and the percentage composition of isomers (Table II) was determined by boron-11 (160.44 MHz; both proton-coupled and proton-decoupled) and proton (^{11}B- and ^{10}B-decoupled) NMR analyses. The boron-11 NMR data are given in Table I. Partial proton NMR assignments are as follows: for CH_3, $\delta = -0.320$ for 1-CH_3-3-Cl-, −0.280 for 1-CH_3-5-Cl-, −0.534 for 1-CH_3-7-Cl-, 1.038 for 3-CH_3-1-Cl-, 0.965 for 3-CH_3-5-Cl-, 0.652 for 5-CH_3-6-Cl-2,4-$C_2B_5H_5$; for 7-HB, $\delta = 0.359$ for 1-CH_3-3-Cl-, 0.360 for 1-CH_3-5-Cl-; for 1,7-HB, $\delta = 0.598$ for both 3-CH_3-5-Cl- and 5-CH_3-6-Cl-2,4-$C_2B_5H_5$. The kinetic data are shown graphically in Figure 1. Small amounts (<2% each) of carborane species other than the eight methyl–chloro isomers were evident from the ^{11}B NMR at the end of the 1231-h heating period; these appear to be the three *B*-CH_3-2,4-$C_2B_5H_6$ isomers[3,6] and the following *B*-CH_3-*B'*,*B''*-Cl_2-2,4-$C_2B_5H_4$ species: 1-CH_3-3,5-Cl_2- [observed $\delta(B(7)) = -22.5$, calculated by assuming substituent additivity effects[2-4] = −22.6; obsd. $\delta(B(1)) = -7.4$, calcd −6.8], 3-CH_3-1,5-Cl_2- [obsd $\delta(B(7)) = -29.8$, calcd −30.0; obsd $\delta(B(1)) = -12.8$; calcd. −13.1], 5-CH_3-1,6-Cl_2- [obsd. $\delta(B(7)) = -30.7$, calcd −30.7; obsd $\delta(B(1)) = -13.9$; calcd −13.7], 5-CH_3-1,3-Cl_2- [obsd $\delta(B(7)) = -28.8$, calcd −29.0]. The quantities of the *B*-CH_3-*B'*-Cl-2,4-$C_2B_5H_5$ isomers cited for this heating period in Table I have been normalized to total 100% for all eight *B*-CH_3-*B'*-Cl- species.

Comparative Kinetic Study of 5-Cl-*closo*-2,4-$C_2B_5H_6$ and 5-CH_3-*closo*-2,4-$C_2B_5H_6$ Thermal Rearrangements. To a 3-mm NMR tube equipped with an "expansion" bulb (ca. 3 mL) were transferred 0.20 mmol each of 5-Cl-2,4-$C_2B_5H_6$ and 5-CH_3-2,4-$C_2B_5H_6$. The tube was heated at 295 °C for a number of intervals (Tables III and IV). After every heating period, the sample was allowed to cool to room temperature and subsequently subjected to both ^1H and ^{11}B NMR[2-4] analyses. The methyl regions in the proton NMR were heavily relied upon in determining the percentages of the monomethyl isomers, whereas the boron NMR was used to determine the monochloro isomer percentages as well as semiquantitatively confirm the monomethyl isomer ratio. The kinetic

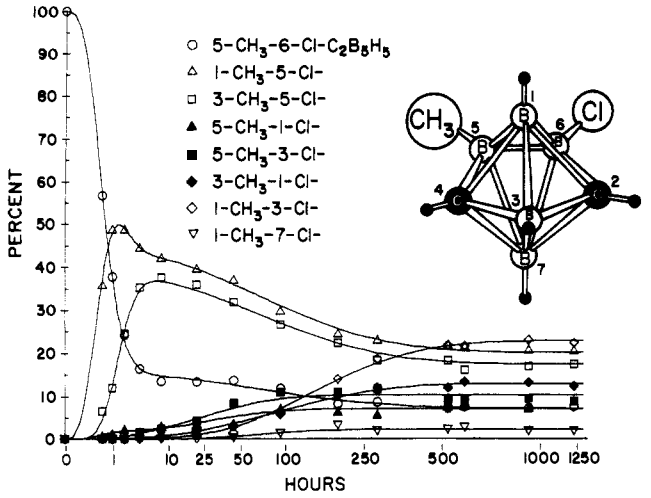

Figure 1. Data (○, △, □, ▲, ■, ◆, ◇, ▽) for the 295 °C rearrangement of 5-CH_3-6-Cl-2,4-$C_2B_5H_5$. Curves are fitted to data (Table II) by assuming a DSD mechanism (Figure 4); derived first-order rate constants (h^{-1}) are as follows: $k_1 = 0.433$, $k_2 = 1.22$, $k_3 = 3.19 \times 10^{-2}$, $k_4 = 3.14 \times 10^{-2}$, $k_5 = 3.58 \times 10^{-3}$, $k_6 = 2.28 \times 10^{-3}$, $k_7 = 1.92 \times 10^{-2}$, $k_8 = 5.89 \times 10^{-3}$, $k_{13} = 0.458$, $k_{14} = 0.530$, $k_{15} = 0.196$, $k_{16} = 0.286$, $k_{19} = 2.15 \times 10^{-2}$, $k_{20} = 4.87 \times 10^{-3}$; k_{9-12} and $k_{17,18}$ are assumed to be negligible (see text). $r^2 = 0.996$, indicating a very good fit of generated curves to data points. In order to plot the heating intervals in a reasonable fashion it was found expedient to make the division spacings along the horizontal axis follow the relationship: the distance along the axis is proportional to the cube root of the time.

Table III. Kinetic Data for the 295 °C Rearrangement of 5-Cl-*closo*-2,4,-$C_2B_5H_6$, Beginning with an Equimolar Mixture of 5-CH_3-*closo*-2,4-$C_2B_5H_6$ and 5-Cl-*closo*-2,4-$C_2B_5H_6$

total heating time, h	% *B*-Cl-*closo*-2,4-$C_2B_5H_6$ isomers[a]		
	5-Cl-$C_2B_5H_6$	1-Cl-$C_2B_5H_6$	3-Cl-$C_2B_5H_6$
0	100.0	0.0	0.0
23	94.2	4.0	1.8
46	88.6	7.1	4.3
92	80.2	11.3	8.5
197.83	71.9	11.3	16.8
337.83	56.0	17.2	26.8
414	50.7	17.4	31.9
1068.25	44.9	18.2	36.9
1712.25	38.3	20.0	41.7

[a] The percentages are cited in terms of total *B*-Cl-*closo*-2,4-$C_2B_5H_6$ normalized to 100.00%. To obtain actual percentages in the *B*-Cl-*closo*-2,4-$C_2B_5H_6$/*B*-CH_3-*closo*-2,4-$C_2B_5H_6$ mixture divide each of the above values by two. Average estimated errors in concentration measurements: ±1%.

data are shown graphically in Figure 2. At the end of the 1068.25-h heating period, trace amounts, <1% each, of most *B*-methyl-*B'*-chloro and *B,B'*-dichloro isomer species were detected (constituting a combined total of 3.8%). A 4.0% quantity of parent carborane, 2,4-$C_2B_5H_7$, was also observed in the sample at the end of the 1068.25-h heating period. The quantities of each of two *B*-X-2,4-$C_2B_5H_6$ (X = CH_3, Cl) sets of three isomers cited for all heating periods in Tables III and IV have been normalized to total 100% for each set.

Rearrangement of 5,6-$(CH_3)_2$-2,4-$C_2B_5H_5$ at 295 °C. A sample containing 87.7% 5,6-$(CH_3)_2$-2,4-$C_2B_5H_5$ and 12.3% 1,5-$(CH_3)_2$-2,4-$C_2B_5H_5$ was sealed in an NMR tube equipped with an attached 3-mL expansion bulb and heated at 295 °C for various increments of time. The composition of the mixture after each heating period (Table V) was determined by analyzing both the ^1H and ^{11}B NMR spectra.[2,5] Assuming a DSD mechanism[2] (see Discussion), eq 1, best-fit first-order rate constants

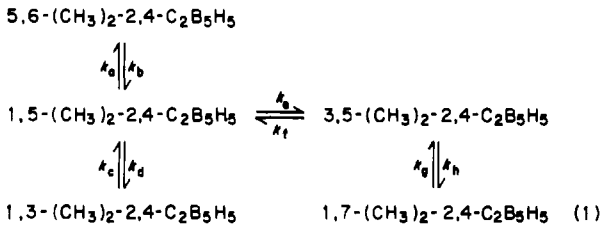

Table IV. Kinetic Data for the 295 °C Rearrangement of 5-CH_3-*closo*-2,4-$C_2B_5H_6$, Beginning with an Equimolar Mixture of 5-Cl-*closo*-2,4-$C_2B_5H_6$ and 5-CH_3-*closo*-2,4-$C_2B_5H_6$

total heating time, h	% *B*-CH_3-*closo*-2,4-$C_2B_5H_6$ isomers[a]		
	5-CH_3-$C_2B_5H_6$	1-CH_3-$C_2B_5H_6$	3-CH_3-$C_2B_5H_6$
0	97.3	2.7	0
23	82.7	14.5	2.8
46	70.7	24.3	5.0
92	54.1	32.4	13.5
197.83	39.5	34.6	25.9
337.83	30.1	34.6	35.3
414	26.2	36.8	37.0
823	23.5	33.3	43.2
1068.25	21.4	36.4	42.2
1712.25	22.8	34.3	42.9

[a] The percentages are cited in terms of total *B*-CH_3-*closo*-2,4-$C_2B_5H_6$ normalized to 100.00%. To obtain actual percentages in the *B*-CH_3-*closo*-2,4-$C_2B_5H_6$/*B*-Cl-*closo*-2,4-$C_2B_5H_6$ mixture divide each of the above values by two. Average estimated errors in concentration measurements: ±1%.

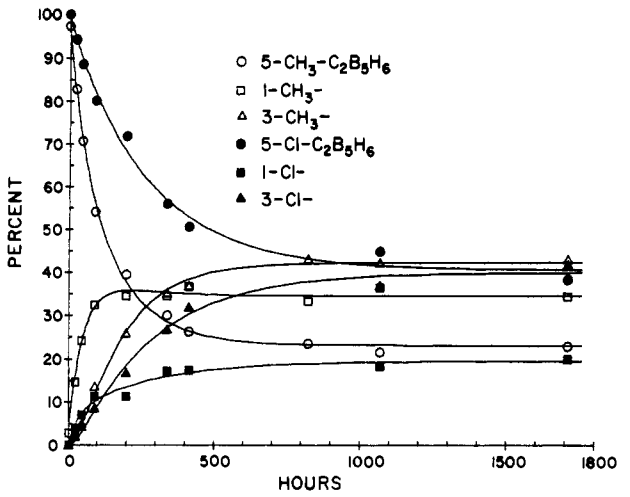

Figure 2. Data (○, □, △, ●, ■, ▲) for the 295 °C rearrangement of a 5-CH_3-2,4-$C_2B_5H_6$/5-Cl-2,4-$C_2B_5H_6$ mixture; curves are fitted to data (Tables III and IV) by assuming a DSD mechanism (eq 3). The percentage total in each of the two isomer sets has been normalized to 100%. First-order calculated rate constants (10^{-3} h^{-1}) are as follows: $k_a = 7.66$, $k_b = 5.11$, $k_c = 7.22$, $k_d = 5.90$ ($r^2 = 0.997$) for the *B*-CH_3-2,4-$C_2B_5H_6$ system; $k_a = 2.59$, $k_b = 5.39$, $k_c = 17.6$, $k_d = 8.58$ ($r^2 = 0.990$) for the *B*-Cl-2,4-$C_2B_5H_6$ system.

were calculated for the 5,6-$(CH_3)_2$-2,4-$C_2B_5H_5$ rearrangement from the data given in Table V. The derived rate constants (in 10^{-3} h^{-1}) are $k_a = 6.88$, $k_b = 62.9$, $k_c = 2.48$, $k_d = 4.20$, $k_e = 30.4$, $k_f = 28.7$, $k_g = 5.91$, and $k_h = 1.60$; a regression analysis, $r^2 = 0.98$, indicates good agreement between the data points and theoretical isomer percentages generated from use of the fitted rate constants. By extending the "best-fit" curves to "time-infinity" the equilibrium percentages for the five isomers are found to be as follow: 5,6-$(CH_3)_2$-2,4-$C_2B_5H_5$, 2.64%; 1,5-$(CH_3)_2$-2,4-$C_2B_5H_5$, 24.10%; 3,5-$(CH_3)_2$-2,4-$C_2B_5H_5$, 25.52%; 1,3-$(CH_3)_2$-2,4-$C_2B_5H_5$, 40.83%; 1,7-$(CH_3)_2$-2,4-$C_2B_5H_5$, 6.91%.

Kinetic Analyses. Best-fit first-order rate constants were calculated for *B*-CH_3-*B'*-Cl-2,4-$C_2B_5H_5$, *B*-X-2,4-$C_2B_5H_6$ (X = CH_3, Cl), and the 5,6-$(CH_3)_2$-2,4-$C_2B_5H_5$ rearrangements from the data given in Tables II–V, assuming a DSD mechanism (see Discussion and ref 2–4). The rate constants were determined by using a PROPHET network (Bolt, Beranek, and Newman, Inc.) computer program (DIFFEQ-FITDIFF) available through the National Institutes of Health. The best-fit rate constants were subsequently used to generate (by using the DIFFEQ-INTDIFF program) rate curves, Figures 1 and 2, for visual comparison to the measured data.

Results and Discussion

The 295 °C rearrangement of 5-CH_3-6-Cl-*closo*-2,4-$C_2B_5H_5$ to an equilibrium mixture of all eight *B*-CH_3-*B'*-Cl-*closo*-2,4-$C_2B_5H_5$ isomers leads to the following isomer equilibrium con-

Table V. Kinetic Data for the Rearrangement of 5,6-$(CH_3)_2$-*closo*-2,4-$C_2B_5H_5$ at 295 °C

total heating time, h	% *B,B'*-$(CH_3)_2$-2,4-$C_2B_5H_5$ isomers[a]				
	5,6-$(CH_3)_2$-	1,5-$(CH_3)_2$-	1,3-$(CH_3)_2$-	3,5-$(CH_3)_2$-	1,7-$(CH_3)_2$-
0	87.7	12.3	0	0	0
0.5	85.2	14.8	0	0	0
2.5	81.6	18.4	0	0	0
7.0	67.9	27.5	0	4.6	0
14.0	33.6	51.9	0	14.5	0
20.0	22.4	56.4	1.2	20.0	0
40.0	11.9	47.5	5.9	34.1	0.6
85.0	6.6	36.3	13.1	40.7	3.3
165	6.6	32.7	21.2	34.0	5.5
260	5.9	27.9	28.7	30.4	7.2
455	3.5	25.8	36.6	27.2	6.9
1005	3.2	24.1	38.8	27.1	6.8

[a] Average estimated errors in concentration measurements: ±1%.

Table VI. Rearrangement Equilibrium Data and Calculations for *B*-X- (X = CH_3, Cl), *B,B'*-$(CH_3)_2$-, and *B*-CH_3-*B'*-Cl- Derivatives of 2,4-$C_2B_5H_7$ (at 295 °C)

compd	% compn at equil (exptl)[a]	*W*[b]	ΔH_{exptl}[c]	ΔH_{calcd}[d]	% compn (theor derived from col 3 and 5 and eq 2)
1-CH_3-	34.6	2	4222	4222	34.6
3-CH_3-	42.3	1	0	0	42.3
5-CH_3-	23.1	2	6130	6130	23.1
1-Cl-	19.5	2	6665	6665	19.5
3-Cl-	40.0	1	0	0	40.0
5-Cl-	40.5	2	3213	3213	40.5
1,3-$(CH_3)_2$-	40.8	2	0	0	39.9
1,5-$(CH_3)_2$-	24.1	4	5761	6130	21.8
1,7-$(CH_3)_2$-	6.9	1	5121	4222	8.1
3,5-$(CH_3)_2$-	25.5	2	2222	1908	26.4
5,6-$(CH_3)_2$-	2.7	1	9552	8038	3.6
1-CH_3-3-Cl-	22.9	2	0	1009	18.4
1-CH_3-5-Cl-	20.1	4	3887	4222	18.7
1-CH_3-7-Cl-	2.3	2	10853	7674	4.5
3-CH_3-1-Cl-	12.8	2	2749	3452	11.0
3-CH_3-5-Cl-	17.4	2	1297	0	22.8
5-CH_3-1-Cl-	7.0	4	8870	9582	6.0
5-CH_3-3-Cl-	10.3	2	3774	2917	12.3
5-CH_3-6-Cl-	7.2	2	5464	6130	6.2

[a] The carborane isomer equilibrium concentrations, in each set, were derived from the relevant "best-fit" DSD rate constant ratios (obtained from the present study only; in contrast, see Table VII, footnote *a*); consult the text and Figures 1 and 2. These agree well with the data in Tables II–V at long rearrangement times when equilibration appears to have been reached. Estimated errors: ±1–1.5% for values in the 10–50% range; ±0.5–1.0% for values in the 5–10% range; ±0.3–0.4% for values in the 1–5% range. The equilibrium temperature is 568 K for all of the isomer sets. [b] *W* is related to the symmetry of the molecule and represents the number of ways a substituent (or substituents) may be placed on the molecule and still represent the same isomer; for a discussion of a related approach see: Benson, S. W. *Thermochemical Kinetics*; Wiley: New York, 1976; p 47. [c] See eq 2 in text and eq 1 in ref 2; all of the values derived from equilibria (column 2) as a result of the present study. ΔH is in joules; the isomer with the lowest enthalpy in each set is arbitrarily assigned $\Delta H = 0$. [d] The values for the monosubstituted compounds are necessarily assumed to be the same as in column 4. The dimethyl- and methylchlorocarborane isomer ΔH values are calculated by adding two appropriate (monomethyl and monochloro) positional ΔH values from column 4; the isomer in each set with the lowest calculated enthalpy is arbitrarily assigned $\Delta H = 0$.

centration order: 1-CH_3-3-Cl- > 1-CH_3-5-Cl- > 3-CH_3-5-Cl- > 3-CH_3-1-Cl- > 5-CH_3-3-Cl- > 5-CH_3-6-Cl- ≥ 5-CH_3-1-Cl- > 1-CH_3-7-Cl-$C_2B_5H_5$ (Figure 1 and Tables VI and VII; see footnote *a* in each of the two tables for the variation in approach between them). Statistical weighting of these quantities, which takes into account the multiplicity of equivalent isomers (e.g. "two" compounds, 1-CH_3-3-Cl- and 7-CH_3-3-Cl-, constitute the 1-CH_3-3-Cl- set, whereas "four" compounds, 1-CH_3-5-Cl-, 1-CH_3-6-Cl-, 7-CH_3-5-Cl-, and 7-CH_3-6-Cl-, comprise the 1-CH_3-5-Cl- set), gives a more meaningful order of the relative isomer stabililities: 1-

Table VII. Rearrangement Equilibrium Data and Calculations for *B*-X- (X = CH_3, Cl), *B,B'*-$(CH_3)_2$-, and *B*-CH_3-*B'*-Cl- Derivatives of 2,4-$C_2B_5H_7$

compd	% compn at equil (exptl)[a]	*W*[b]	ΔH_{exptl}[c]	ΔH_{calcd}[d]	% compn (theor derived from col 3 and 5 and eq 2)
1-CH_3-	37.9	2	3171	3171	37.9
3-CH_3-	37.1	1	0	0	37.1
5-CH_3-	25.0	2	5138	5138	25.0
1-Cl-	21.9	2	6473	6473	21.9
3-Cl-	39.0	1	0	0	39.0
5-Cl-	39.1	2	3519	3519	39.1
1,3-$(CH_3)_2$-	40.8	2	0	0	37.0
1,5-$(CH_3)_2$-	24.1	4	5761	5138	25.0
1,7-$(CH_3)_2$-	6.9	1	5121	3171	9.5
3,5-$(CH_3)_2$-	25.5	2	2222	1967	24.4
5,6-$(CH_3)_2$-	2.7	1	9552	7105	4.1
1-CH_3-3-Cl-	22.9	2	0	0	20.3
1-CH_3-5-Cl-	20.1	4	3887	3519	19.2
1-CH_3-7-Cl-	2.3	2	10853	6473	5.1
3-CH_3-1-Cl-	12.8	2	2749	3302	10.1
3-CH_3-5-Cl-	17.4	2	1297	348	18.8
5-CH_3-1-Cl-	7.0	4	8870	8440	6.8
5-CH_3-3-Cl-	10.3	2	3774	1967	13.4
5-CH_3-6-Cl-	7.2	2	5464	5486	6.3

[a] The carborane isomer equilibrium concentrations, in each set, were derived from the relevant DSD rate constant ratios; see text and Figure 1. The monochlorocarborane equilibrium concentrations were obtained from ref 4; the monomethyl concentrations were obtained from a DIFFEQ-FITDIFF (see Experimental Section) analysis of previous work.[3] For the dimethyl equilibrium concentrations, see the Experimental Section. Estimated errors: ±1–1.5% for values in the 10–40% range; ±0.5–1.0% for values in the 5–10% range; ±0.3–0.4% for values in the 1–5% range. The equilibrium temperature is 568 K for all of the isomer sets except for the *B*-Cl-2,4-$C_2B_5H_6$ isomer set,[4] which is 613 K. [b] *W* is related to the symmetry of the molecule and represents the number of ways a substitutent (or substituents) may be placed on the molecule and still represent the same isomer; for a discussion of a related approach see: Benson, S. W. *Thermochemical Kinetics*; Wiley: New York, 1976; p 47. [c] See eq 2 in text and eq 1 in ref 2. ΔH is in joules; the isomer with the lowest enthalpy in each set is arbitrarily assigned $\Delta H = 0$. [d] The values for the monosubstituted compounds are necessarily assumed to be the same as in column 4. The dimethyl- and methylchlorocarborane isomer ΔH values are calculated by adding two appropriate (monomethyl and monochloro) positional ΔH values from column 4; the isomer in each set with the lowest calculated enthalpy is arbitrarily assigned $\Delta H = 0$.

CH_3-3-Cl- > 3-CH_3-5-Cl- > 3-CH_3-1-Cl- > 5-CH_3-3-Cl- ≥ 1-CH_3-5-Cl- > 5-CH_3-6-Cl- > 5-CH_3-1-Cl- > 1-CH_3-7-Cl-$C_2B_5H_5$.

Among the monosubstituted compounds *B*-X-2,4-$C_2B_5H_6$ (X = CH_3, Cl) it has already been established that the 3-X- isomer is the most stable in each of the two sets;[2-4] so that if an additive "positional–substituent" effect is operating,[2,4,5] it is expected that one of the two 3-Cl-*B*-CH_3-, or two 3-CH_3-*B*-Cl-, isomers (among the eight *B*-CH_3-*B'*-Cl-*closo*-2,4-$C_2B_5H_5$ isomers) should be the most stable. When a methyl group is present on the B(3) boron,

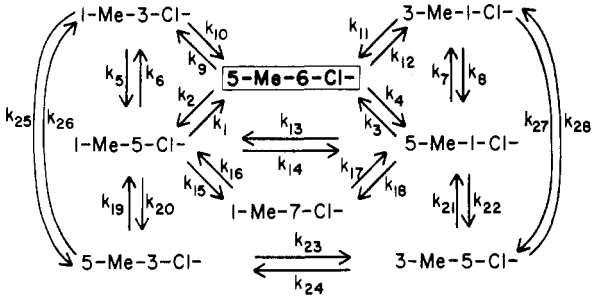

Figure 3. TFR-allowed pathways (with cage-carbon movement restrictions; see text) betwen B-CH_3-B'-Cl-*closo*-2,4-$C_2B_5H_5$ isomers.

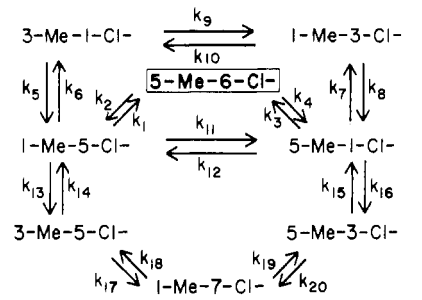

Figure 4. DSD-allowed pathways (with cage-carbon movement restrictions; see text) between B-CH_3-B'-Cl-*closo*-2,4-$C_2B_5H_5$ isomers.

the chlorine can only be placed on a 1- or 5-type boron; since chlorine in the B-Cl-2,4-$C_2B_5H_6$ series is predisposed to the position order 5- > 1- (vide infra and ref 4), it is anticipated that the 3-CH_3-5-Cl- isomer should be more stable than the 3-CH_3-1-Cl- isomer. This is found to be the case. Similarly, when a chlorine is present on B(3), the methyl group can then only be placed on a 1- or 5-type boron; upon noticing that the methyl group in the B-CH_3-2,4-$C_2B_5H_6$ isomer set prefers the position order 1- > 5-,[2,3] then 1-CH_3-3-Cl-2,4-$C_2B_5H_5$ is expected to be more stable than 5-CH_3-3-Cl-2,4-$C_2B_5H_5$. This is in agreement with experimental data gathered in the present study (Tables VI and VII).

The following question then logically arises: Is it possible to predict the relative stabilities of the entire B-CH_3-B'-Cl-*closo*-2,4-$C_2B_5H_5$ eight-isomer set solely on the basis of substituent–positional preferences in the appropriate monosubstituted series? A reasonable quantitative approach to this invokes an enthalpy additivity argument similar to that employed earlier.[2,4,5] In this approach enthalpy differences between B-X-2,4-$C_2B_5H_6$ isomers are derived, assuming that isomer entropy differences are attributed to symmetry variations only. The relationship used is

$$\Delta H = -RT(\ln K) + T\Delta(R(\ln W)) \qquad (2)$$

where $R(\ln W)$ is the molar entropy and W is the number of distinguishable configurations that a compound may assume.[11] If it is additionally assumed that the enthalpy differences between isomers are solely a function of substituent position, then relative ΔH values for the methylchlorocarborane isomers can then be deduced in a manner similar to that carried out earlier for disubstituted systems of the type B,B'-X_2-2,4-$C_2B_5H_5$.[2,4,5] This method is spelled out in footnote *d* of Tables VI and VII. A "theoretical" percent isomer composition for all eight B-CH_3-B'-Cl-closo-2,4-$C_2B_5H_5$ at equilibrium (column 6, Tables VI and VII) is subsequently derived from ΔH_{calcd} values. In general, the agreement between the observed equilibrium percentages (column 2) and the calculated percentages (column 6) is remarkably good, considering (a) realistic errors in equilibrium quantity measurements, and (b) the previously stated assumptions concerning entropy factors and ΔH additivity.

The first isomer produced during the course of the 5-CH_3-6-Cl-2,4-$C_2B_5H_5$ rearrangement is 1-CH_3-5-Cl-2,4-$C_2B_5H_5$, followed by the appearance of 3-CH_3-5-Cl-2,4-$C_2B_5H_5$. The order of appearance of the other five isomers are 5-CH_3-1-Cl-2,4-$C_2B_5H_5$, 5-CH_3-3-Cl-2,4-$C_2B_5H_5$, 3-CH_3-1-Cl-2,4-$C_2B_5H_5$, 1-CH_3-3-Cl-2,4-$C_2B_5H_5$, 1-CH_3-7-Cl-2,4-$C_2B_5H_5$ (Table II and Figure 1). This rearrangement pattern for 5-CH_3-6-Cl-*closo*-2,4-$C_2B_5H_5$ rules out a triangle-face-rotation (TFR) mechanism (Figure 3) in which cage-carbon atoms stay in low-coordination nonadjacent positions,[12,13] and is consistent with a "diamond–square-diamond" (DSD) mechanism,[2-4,12,14-17] Figures 4 and 5. If the TFR mechanism were operating, then the appearance of 5-CH_3-1-Cl-, and/or 5-CH_3-3-Cl-, and/or 3-CH_3-1-Cl-2,4-$C_2B_5H_5$ should precede that of 3-CH_3-5-Cl-2,4-$C_2B_5H_5$. This is clearly not observed (Table II and Figure 1). Elimination of this type of mechanism[11,12] for the B-CH_3-B'-Cl-*closo*-2,4-$C_2B_5H_5$ rearrangement is consistent with the mechanistic conclusions reached from each of the two monosubstituted, B-X-*closo*-2,4-$C_2B_5H_6$ (X = CH_3, Cl)[3,4] rearrangement results.

Table VIII. Unimolecular DSD Rate Constants at 295 °C

isomer conversion	k, h^{-1}	$k/(k_mS)$
5-CH_3-2,4-$C_2B_5H_6$ → 1-CH_3-2,4-$C_2B_5H_6$	0.0077[a]	
	0.0067[b]	
5-Cl-2,4-$C_2B_5H_6$ → 1-Cl-2,4-$C_2B_5H_6$	0.0026[a]	
5,6-$(CH_3)_2$-2,4-$C_2B_5H_5$ → 1,5-Me_2-2,4-$C_2B_5H_5$	0.063[c]	4.1–4.7[d]
5,6-Cl_2-2,4-$C_2B_5H_5$ → 1,5-Cl_2-2,4-$C_2B_5H_5$	1.0[e]	192[d]
5-CH_3-6-Cl-2,4-$C_2B_5H_5$ → 1-CH_3-5-Cl-$C_2B_5H_5$	1.22[a]	158–182[f]
5-CH_3-6-Cl-2,4-$C_2B_5H_5$ → 5-CH_3-1-Cl-$C_2B_5H_5$	0.031[g]	11[f]

[a] The present study. [b] See reference 3. [c] See Experimental Section; also, consult ref 2. [d] Values represent a comparison of the rate constant for the disubstituted compound with the corresponding rate constant of the related monosubstituted rearrangement. This was derived by dividing the rate constant in this row by both k_m and S, where k_m = the appropriate rate constant(s) cited just above for the related monosubstituted rearrangement and S = a symmetry term, which in this case is 2, because there are two equivalent substituents that can translocate in the disubstituted compound. [e] See ref 4. [f] The same as in footnote *d* with S = 1 being the only difference. [g] This represents a maximum value for k_4; it may be lower if other routes (e.g. k_{11} of Figure 4) to 5-CH_3-1-Cl-2,4-$C_2B_5H_5$ are significant (see text).

Best-fit rate constants for a DSD-driven B-CH_3-B'-Cl-*closo*-2,4-$C_2B_5H_5$ interconversion pattern (Figure 4) are given in Figure 1. This set of rate constants has been derived with the arbitrary assumption that the following k values are negligible: k_{9-12} and $k_{17,18}$. Careful examination of the DSD pattern (Figure 4) leads to the conclusion that a satisfactory evaluation of the rate constants is only possible for k_1 and k_2, i.e. the interconversion of the starting material, 5-CH_3-6-Cl-, with 1-CH_3-5-Cl-2,4-$C_2B_5H_5$. A maximum value for k_4 (the rate constant representing the conversion of 5-CH_3-6-Cl- to 5-CH_3-1-Cl-; see caption to Figure 1) can be derived by employing the above assumptions for k_{9-12} and $k_{17,18}$.

Rearrangement rate comparisons between monosubstituted and related disubstituted 2,4-$C_2B_5H_7$ compounds become possible once all pertinent systems are studied under the same conditions. Whereas the B-CH_3-2,4-$C_2B_5H_6$[3] and B,B'-Cl_2-2,4-$C_2B_5H_5$[4] rearrangements were previously carried out at 295 °C, the same temperature as used for the present B-CH_3-B'-Cl-*closo*-2,4-$C_2B_5H_5$ work, the B-Cl-2,4-$C_2B_5H_6$ rearrangements had previously been studied at 340 °C[4] and a B,B'-$(CH_3)_2$-2,4-$C_2B_5H_5$ rearrangement was carried out at 275 °C.[2] In order to draw a more direct comparison of these rearrangements, we conducted studies on the dimethyl system 5,6-$(CH_3)_2$-2,4-$C_2B_5H_5$ as well as on a 5-Cl-2,4-$C_2B_5H_6$/5-CH_3-2,4-$C_2B_5H_6$ mixture at 295 °C. The results for the 5-Cl-2,4-$C_2B_5H_6$/5-CH_3-2,4-$C_2B_5H_6$ mixture are seen in Tables III and IV and in Figure 2, and the results on the dimethyl

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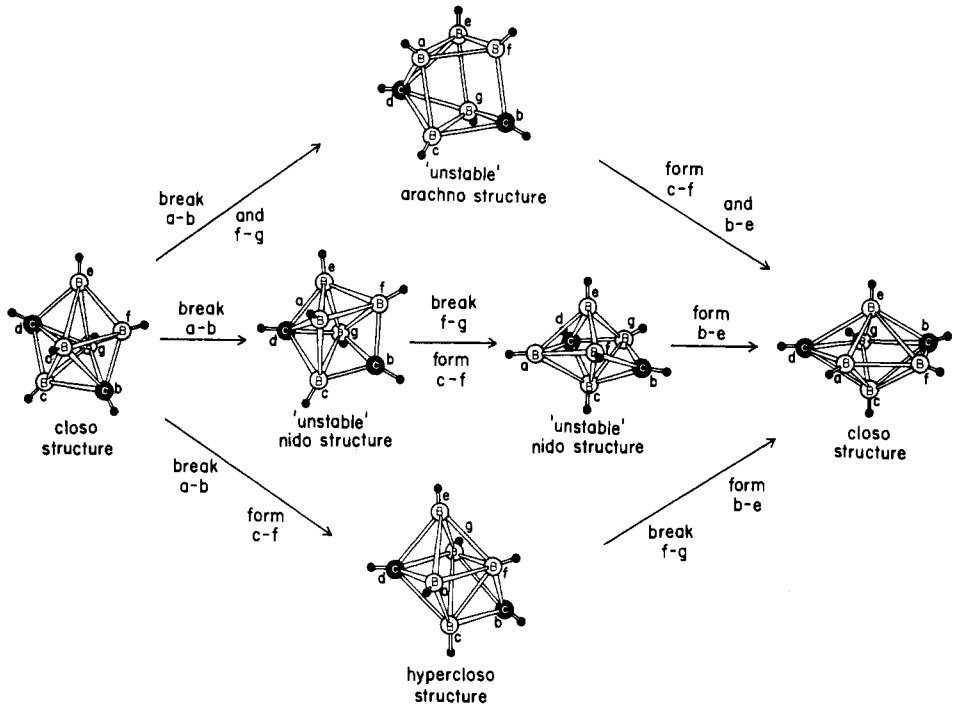

Figure 5. Three possible DSD mechanistic schemes for *closo*-2,4-$C_2B_5H_7$ interconversions.

system are given in Table V (also see Experimental Section). A comparison of the present 5-CH_3-2,4-$C_2B_5H_6$ rearrangement with that previously reported[3] shows that, within experimental error, the two are about the same.[18] The reasonable agreement between the two 295 °C monomethylcarborane rearrangements (past and present) raises the confidence that the presence of *B*-Cl-2,4-$C_2B_5H_6$ in the present methylcarborane study does not significantly affect the methylcarborane rearrangement rate(s), and vice versa. Derived rearrangement rate constant comparisons (Table VIII) among related mono- and disubstituted compounds, 5-X-*closo*-2,4-$C_2B_5H_6$, 5,6-X_2-*closo*-2,4-$C_2B_5H_5$ (X = CH_3, Cl), and 5-CH_3-6-Cl-*closo*-2,4-$C_2B_5H_5$ indicate that (a) the presence of a second substituent accelerates the apparent translocation of the first substituent (i.e., the nature of the "stationary" substituent is more critical in affecting the rearrangement rate than that of the "migrating" substituent) and (b) the effect of Cl in this regard is greater than that of CH_3. Quantitatively, the presence of a chlorine in the 6-position increases the conversion rate for the 5-X- (X = CH_3, Cl) to the 1-X- isomer by a factor of 158–192 whereas the presence of the methyl group in a 6-position (or 5-position) increases the conversion of 5-X- (or 6-X-) to the 1-X- isomer by a factor of only 4–11. Chlorine with its unshared pairs of electrons may well "back-bond" to the cage boron(s), thereby facilitating the formation of a partially "open" intermediate (or transition state) as proposed in the course of a DSD rearrangement (Figure 5). When the "stationary" substituent is CH_3, the much lower rate constants associated with the migrating group (in the disubstituted systems) may be attributed to the more moderate electron-donating nature and/or potential hyperconjugative character of the methyl group.

The activation energies for the interconversion of *B*-Cl-2,4-$C_2B_5H_6$ isomers can be estimated by applying the Arrhenius expression to the available DSD-derived rearrangement rate constants at different temperatures (295 °C, this study; 340 °C, ref 4). All four conversions in eq 3 are found to have E_{act} values in the vicinity of 180–200 kJ/mol (43–48 kcal/mol).

$$5\text{-X-2,4-}C_2B_5H_6 \underset{k_b}{\overset{k_a}{\rightleftharpoons}} 1\text{-X-2,4-}C_2B_5H_6 \underset{k_d}{\overset{k_c}{\rightleftharpoons}} 3\text{-X-2,4-}C_2B_5H_6 \quad (3)$$

Intermolecular chlorine exchange of the type mentioned earlier[4] occurs to a minor extent as the 5-CH_3-6-Cl-2,4-$C_2B_5H_5$ and the competitive 5-X-2,4-$C_2B_5H_6$ (X = CH_3, Cl) rearrangements approach equilibrium. At the "end" of the methylchlorocarborane rearrangement small amounts of dichloromethyl- and monomethylcarborane (chlorine-absent) isomers are observed, indicating that chlorine, and not methyl, has undergone intermolecular exchange. Similarly, in the competitive 5-CH_3-2,4-$C_2B_5H_6$/5-Cl-2,4-$C_2B_5H_6$ rearrangement carried out in a "single" container, no dimethyl products are found but there is evidence of some dichlorocarboranes (most likely a result of transfer of a chlorine between two monochlorocarborane molecules) and methylchlorocarboranes (most likely a result of chlorine transfer from a chlorocarborane to a monomethylcarborane) toward the completion of the rearrangement(s).

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Registry No. 5-Cl-$C_2B_2H_6$, 28347-92-4; 5-CH_3-6-Cl-$C_2B_5H_5$, 79550-11-1; 1-CH_3-5-Cl-$C_2B_5H_5$, 79568-29-9; 3-CH_3-5-Cl-$C_2B_5H_5$, 102648-58-8; 5-CH_3-1-Cl-$C_2B_5H_5$, 102614-50-6; 5-CH_3-3-Cl-$C_2B_5H_5$, 102630-00-2; 3-CH_3-1-Cl-$C_2B_5H_5$, 102614-51-7; 1-CH_3-3-Cl-$C_2B_5H_5$, 102614-52-8; 1-CH_3-7-Cl-$C_2B_5H_5$, 102630-01-3; 5-CH_3-$C_2B_5H_6$, 23810-32-4; 1-Cl-$C_2B_5H_6$, 28347-69-5; 3-Cl-$C_2B_5H_6$, 28347-93-5; 1-CH_3-$C_2B_5H_6$, 23810-31-3; 3-CH_3-$C_2B_5H_6$, 23940-13-8; 5,6-$(CH_3)_2$-$C_2B_5H_5$, 58548-76-8; 1,5-$(CH_3)_2$-$C_2B_5H_5$, 68238-17-5; 1,3-$(CH_3)_2$-$C_2B_5H_5$, 68297-89-2; 3,5-$(CH_3)_2$-$C_2B_5H_5$, 68238-16-4; 1,7-$(CH_3)_2$-$C_2B_5H_5$, 23753-78-8.

(18) Slight discrepancies of the presently obtained monomethyl rate constants at 295 °C with those obtained earlier might be ascribed to the fact that the previous rearrangements were carried out in NMR tubes lacking "expansion" bulbs. The additional volumes provided by the bulbs (present study) insure attainment of gas-phase equlibria, which inhibit nonvolatile product (e.g. coupled carboranes) formation. In the absence of bulbs, one or more isomers could participate in side reactions in the liquid phase (e.g. coupling). The 3-CH_3-2,4-$C_2B_5H_6$ isomer is particularly suspected to have undergone such reactions since its equilibrium percentage is less in the 3-CH_3-2,4-$C_2B_5H_6$ rearrangement than in the 5-CH_3-2,4-$C_2B_5H_6$ rearrangement.