binuclear complexes, $M_2(PAA)_2$. Under identical synthetic conditions, only the trinuclear Ni(II) is isolated. Crystallization of the Cu(II) and Zn(II) complexes from pyridine in air yields crystals of the pyridine adduct, $M_2(PAA)_2(py)_2$, in which the metals are bonded to four enolate oxygens, two terminal and two bridging, and one pyridine nitrogen in typical five-coordinate manner. The triketonate moieties in such complexes are very nearly planar as demonstrated in a number of structural studies.[16] Since there is some reason to believe that PAA^{2-} in $Ni_3(PAA)_2(OH)_2(CH_3OH)_4$ might be distorted from planarity, i.e. if the structure is similar to $[Ni(acac)_2]_3$, there is the possibility that such distortions account for the oxidizability of the ligands rather than the metal itself.

(16) See for example, ref 9 and 13.

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Registry No. H_2PAA, 66734-21-2; $Ni_3(PAA)_2(OH)_2(CH_3OH)_4$, 96504-41-5; $Ni_2(PAA)_2(OH)_2(py)_4$, 96532-46-6; $Ni_2(t\text{-}BHMA)_2(py)_4 \cdot py \cdot 3H_2O$, 96504-43-7.

Supplementary Material Available: Complete listing of hydrogen atom parameters, final positional and thermal parameters, and observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

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Kinetic Studies on the Rearrangements of *B*-Monochloro Derivatives of *closo*-2,4-$C_2B_5H_7$ and on the Rearrangement of 5,6-Cl_2-*closo*-2,4-$C_2B_5H_5$. Characterization of All *B*,*B*′-Cl_2-*closo*-2,4-$C_2B_5H_5$ Isomers

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The rearrangement patterns for two *B*-monochloro derivatives of *closo*-2,4-$C_2B_5H_7$ suggest that a triangular-face-rotation mechanism for such a reaction in this set of compounds is highly unlikely. The relative stabilities of the *B*,*B*′-dichloro derivatives of this cage carborane system have been determined from a rearrangement rate study on one of the isomers; a correlation of these *B*,*B*′-Cl_2-$C_2B_5H_5$ isomer stabilities with the results from the thermal equilibration of the *B*-monochloro set of isomers leads to the suggestion that, with the exception of the 1,3-Cl_2 isomer, a (substituent) positional additivity effect is operating. An electronic interaction through the cage between a Cl located in an apical position and a Cl located at the unique equatorial 3-position may account for the stability of the 1,3-Cl_2 isomer. All of the *B*,*B*′-Cl_2-*closo*-2,4-$C_2B_5H_5$ isomers are characterized for the first time. A slow side reaction observed during the rearrangement reactions involves intermolecular chlorine exchange; the rate of this halogen exchange is considerably reduced when the rearrangements are carried out at reduced pressures.

Introduction

Preparations of the monochloro-*closo*-dicarbaheptaborane isomer 5-Cl-*closo*-2,4-$C_2B_5H_6$[1] and the dichloro isomer 5,6-Cl_2-*closo*-2,4-$C_2B_5H_5$ are effected by the aluminum chloride catalyzed reactions of the parent *closo*-2,4-$C_2B_5H_7$ with varying quantities of Cl_2.[2,3] Presumed electrophilic halogen attack occurs predominantly at the electron-rich equatorial boron 5- and 6-positions[4] with only trace evidence of attack at the axial 1- (or symmetry-related 7-) position.[5] Both 1- and 3-Cl-$C_2B_5H_6$, as well as the 5-Cl isomer, can be obtained from a light-initiated reaction of $C_2B_5H_7$ with Cl_2,[2] but both the 1- and 3-Cl isomers are more reliably obtained in usable quantities from the thermal rearrangement of 5-Cl-$C_2B_5H_6$.[3] Subjecting the dichloro cage compound, 5,6-Cl_2-$C_2B_5H_5$, to thermal rearrangement conditions leads to a mixture of *B*,*B*′-Cl_2-isomers; however, difficulty in separating the various isomers along with lack of adequate NMR peak resolution made full identification and characterization of the various *B*,*B*′-dichloro isomers uncertain.[3]

In the present study we report a procedure used to characterize all of the *B*,*B*′-Cl_2-$C_2B_5H_5$ isomers; in addition, kinetic studies are carried out on one dichloro and two monochloro isomers.

Experimental Section

Nuclear Magnetic Resonance Spectroscopy. Boron-11 (160.44-MHz) and proton (60-MHz) NMR spectra were obtained on Bruker WM-500 FT and Bruker WP-60 spectrometers, respectively. For the rearrangement studies, proton-decoupled boron spectra were recorded at all time intervals cited in the tables; an occasional proton-coupled boron NMR spectrum was recorded for verifying peak assignments. Triple-resonance studies, observing the proton resonance, while decoupling both ^{11}B and ^{10}B resonances, were conducted with a modified WP-60 probe equipped to accept two decoupling channels; two frequency synthesizers (Fluke 6160B and General Radio 1062), each output modulated by a homemade pseudo-random-noise generator driving an Electronic Navigation Industries Model 320L power amplifier, were used to decouple the two boron isotopes. Delay times between pulses were varied during the course of measuring the spectra of several samples in order to verify the saturation effects were negligible in all *B*-chloro- and *B*,*B*′-dichlorocarborane spectra employed for the determination of the relative carborane concentrations in rearrangement mixtures. All ^{11}B chemical shift data are based on $\delta(BF_3 \cdot Et_2O)$ 0.00, with the parent 2,4-$C_2B_5H_7$ used as a secondary standard: δ(B(1,7)) −21.73 (J = 180 Hz), δ(B(3)) 7.02 (J = 184 Hz), δ(B(5,6)) 3.83 (J = 170 Hz). Negative chemical shift values are upfield of the $BF_3 \cdot Et_2O$ resonance. Approximate chemical shift and coupling constant errors for all dicarbaheptaboranes (parent and derivatives) are as follows: ±0.02 ppm and ±3 Hz for the cage 1-, 3-, and 7-positions of carborane; ±0.06 ppm and ±10 Hz, for the 5- and 6-positions.

(1) The compounds reported in the present work have been named, and numbered, by using previously accepted nomenclature rules. It is noted, however, that a new nomenclature scheme has been devised for cage polyboranes; e.g., 5-(chloro)hexahydro-2,4-dicarba[D_{5h}-(1$v^5$5$v^4$1v^5)-Δ^{10}-*closo*]heptaborane is recommended for 5-Cl-*closo*-2,4-$C_2B_5H_6$: (a) Casey, J. B.; Evans, W. J.; Powell, W. H. *Inorg. Chem.* **1983**, *22*, 2236–2245. (b) *Ibid.* **1983**, *22*, 2228–2235. (c) *Ibid.* **1981**, *20*, 3556–3561. (d) *Ibid.* **1981**, *20*, 1333–1341.

(2) Warren, R.; Paquin, D.; Onak, T.; Dunks, G.; Spielman, J. R. *Inorg. Chem.* **1970**, *9*, 2285–2287.

(3) Takimoto, C.; Siwapinyoyos, G.; Fuller, K.; Fung, A. P.; Liauw, L.; Jarvis, W.; Millhauser, G.; Onak, T. *Inorg. Chem.* **1980**, *19*, 107–110.

(4) Dixon, D. A.; Kleier, D. A.; Halgren, T. A.; Hall, J. H.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1977**, *99*, 6226–6237. A value for the group charge of B(3)H of 2,4-$C_2B_5H_7$ in this reference has been corrected to read +0.06.

(5) Siwapinyoyos, G.; Onak, T. *Inorg. Chem.* **1982**, *21*, 156–163.

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Table I. Kinetic Data for the Rearrangement of 3-Cl-2,4-$C_2B_5H_6$ at 340 °C

total heating time, h	% compn of *B*-Cl-*closo*-$C_2B_5H_6$[a]		
	3-Cl	1-Cl	5-Cl
0	92.6	7.4	0
1.0	83.3	16.0	0.7
2.0	78.2	21.8	0
3.5	72.6	26.0	1.4
6.5	61.6	30.8	7.6
8.0	57.5	30.1	12.4
9.5	55.1	27.8	17.1
12.0	53.6	26.9	19.5
15.0	51.0	26.6	22.4
21.0	48.3	24.7	27.0
31.0	45.7	22.7	31.6
53.0	40.9	22.0	37.1
77.5	39.1	21.7	39.2
101.5	38.6	21.6	39.8
173.5	37.9	21.9	40.2

[a] Estimated average error in concentration measurements ±1%.

Materials and Handling of Chemicals. Both 5-Cl-*closo*-2,4-$C_2B_5H_6$ and 5,6-Cl_2-*closo*-2,4-$C_2B_5H_5$ were synthesized by reaction of Cl_2 with the parent carborane in the presence of $AlCl_3$ as described earlier.[2,3,5] The 5,6-Cl_2-*closo*-2,4-$C_2B_5H_5$ was prepared in better yield by using a 2.5:1 ratio of Cl_2:$C_2B_5H_7$ starting materials, and instead of cold-column fractionation of the products, it was found that trap-to-trap vacuum separation, with traps at −20, −130, and −190 °C, gave pure 5,6-Cl_2-*closo*-2,4-$C_2B_5H_5$ in the −20 °C trap.

Repeated cold-column[6] fractionation of a mixture of 1- and 3-Cl-2,4-$C_2B_5H_6$[3] provided 0.38 mmol of a fraction (distilling in the region of −65 °C) containing 92.6% of the 3-Cl isomer and 7.4% of the 1-Cl isomer, as analyzed by both ^{11}B and proton NMR spectra. The gas-phase infrared spectrum of this fraction exhibited absorptions (in cm^{-1}) at 2620 (s), 1300 (s), 1270 (s), 1250 (w), 1120 (w, br), 1085 (m, br), 1045 (m), 1030 (w), 1015 (w), 940 (w), 900 (w), and 825 (m); the melting point was determined to be in the range −57 to −55 °C.

Kinetic Study of the 3-Cl-*closo*-2,4-$C_2B_5H_6$ Thermal Rearrangement. A sample (0.6 mmol) containing 3-Cl-2,4-$C_2B_5H_6$ (92.6%) and 1-Cl-2,4-$C_2B_5H_6$ (7.4%) was sealed in a 3-mm NMR tube equipped at one end with a ca. 3.5-mL glass bulb. The additional volume provided by the bulb inhibited side reactions (vide infra), including the formation of nonvolatile products, at the elevated temperatures used for the rearrangement. The sample was heated at 340 °C for a number of intervals (Table I); after each heating period the sample was immediately cooled to room temperature, and boron-11 (160.44-MHz; coupled and proton-decoupled) NMR analyses of the rearrangement products were made. The *B*-monochlorocarboranes were identified by the following peaks (J(B–H), in parentheses, in Hz): δ(B(1)) −16.10, δ(B(3)) 8.18 (188), δ(B(5,6)) 3.34 (174), δ(B(7)) −33.07 (187) for 1-Cl-2,4-$C_2B_5H_6$; δ(B(1,7)) −18.36 (182), δ(B(3)) 14.96, δ(B(5,6)) 3.24 (172) for 3-Cl-2,4-$C_2B_5H_6$; δ(B(1,7)) −20.05 (185), δ(B(3)) 5.15 (189), δ(B(5)) 13.80, δ(B(6)) 1.04 (176) for 5-Cl-2,4-$C_2B_5H_6$. No significant change in (relative) *B*-chloro isomer concentration was noted upon heating the sample longer than 100 h. However, detectable amounts of carborane side products were produced in small quantities toward the end of the rearrangement period; the percentage concentrations of all boron species at the 173.5-h interval, 340 °C, were as follows: $C_2B_5H_7$, 4.2%; 1-Cl-$C_2B_5H_6$, 21.2%; 3-Cl-$C_2B_5H_6$, 32.5%; 5-Cl-$C_2B_5H_6$, 36.1%; 1,3-Cl_2-$C_2B_5H_5$, 1.6%; 1,5-Cl_2-$C_2B_5H_5$, 1.3%; 3,5-Cl_2-$C_2B_5H_5$, 2.6%; 5,6-Cl_2-$C_2B_5H_5$, 0.5%. After the sample was heated for an additional 284 h, this time at 295 °C, the following percentage concentrations were found: $C_2B_5H_7$, 5.0%; 1-Cl-$C_2B_5H_6$, 18.1%; 3-Cl-$C_2B_5H_6$, 35.3%; 5-Cl-$C_2B_5H_6$, 36.9%; 1,3-Cl_2-$C_2B_5H_5$, 1.6%; 1,5-Cl_2-$C_2B_5H_5$, 1.0%; 3,5-Cl_2-$C_2B_5H_5$, 1.5%; 5,6-Cl_2-$C_2B_5H_5$, 0.6%. The percentage concentrations of the monochloro isomers cited in Table I have been normalized to total 100% for all *B*-Cl-2,4-$C_2B_5H_6$ compounds for each heating period.

Kinetic Study of the 5-Cl-*closo*-2,4-$C_2B_5H_6$ Thermal Rearrangement. In a manner similar to that described for the above rearrangement of 3-Cl-$C_2B_5H_6$, a sample of 5-Cl-$C_2B_5H_6$ was subjected to a temperature of 340 °C for a number of intervals (Table II); after each heating period the sample was immediately cooled to room temperature, and boron-11 (160.44-MHz; coupled and proton-decoupled) NMR analyses of the rearrangement products were made. Trace quantities of the parent 2,4-$C_2B_5H_7$, as well as some of its *B*,*B*′-dichloro derivatives, were noticed in the NMR spectrum of the *B*-Cl-2,4-$C_2B_5H_6$ mixture after the 12.5-h (at 340 °C) heating period (Table II). After the mixture was heated for a total of 36.25 h at 340 °C, the following carborane composition was observed: $C_2B_5H_7$, 7.9%; 1-Cl-$C_2B_5H_6$, 16.1%; 3-Cl-$C_2B_5H_6$, 33.0%; 5-Cl-$C_2B_5H_6$, 34.3%; 1,3-Cl_2-$C_2B_5H_5$, 2.2%; 1,5-Cl_2-$C_2B_5H_5$, 2.2%; 3,5-Cl_2-$C_2B_5H_5$, 3.9%; 5,6-Cl_2-$C_2B_5H_5$, 0.4%. The percentage concentrations of the monochloro isomers cited in Table II have been normalized to total 100% for all *B*-Cl-2,4-$C_2B_5H_6$ compounds for each heating period.

Table II. Kinetic Data for the Rearrangement of 5-Cl-2,4-$C_2B_5H_6$ at 340 °C

total heating time, h	% compn of *B*-Cl-*closo*-$C_2B_5H_6$[a]		
	5-Cl	1-Cl	3-Cl
0	100.0	0	0
2.0	85.8	10.2	4.0
4.5	68.7	16.0	15.3
12.5	52.8	18.6	28.6
20.0	46.3	19.7	34.0
36.25	41.1	19.3	39.6

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

Table III. Kinetic Data for the Rearrangement of 5,6-Cl_2-*closo*-2,4-$C_2B_5H_5$ at 295 °C

interval no.	total heating time, h	% compn of *B*,*B*′-Cl_2-*closo*-2,4-$C_2B_5H_5$[a]				
		5,6-Cl_2	1,5-Cl_2	3,5-Cl_2	1,3-Cl_2	1,7-Cl_2
1	0	100.0	0	0	0	0
2	0.5	62.6	24.8	12.6	0	0
3	1.0	43.7	30.7	25.6	0	0
4	2.0	20.7	32.3	47.0	0	0
5	4.0	13.6	29.6	56.8	0	0
6	7.0	12.0	30.8	55.5	1.7	0
7	11.0	14.2	30.8	51.5	2.6	0.9
8	19.0	12.5	30.2	52.9	3.8	0.6
9	30.5	11.5	29.2	52.5	6.1	0.7
10	61.0	11.2	25.7	50.8	10.9	1.4
11	100.0	11.8	23.9	43.9	18.8	1.6
12	157.25	9.5	23.7	41.1	24.6	1.1
13	264.0	8.7	24.4	40.2	25.9	0.8
14	505.5	7.4	22.8	42.3	26.4	1.1

[a] Average estimated error in concentration measurements ±1%; for concentrations less than 5%, estimated error ±0.5%.

Kinetic Study of the 5,6-Cl_2-*closo*-2,4-$C_2B_5H_5$ Thermal Rearrangement. Two samples (A and B) of pure 5,6-Cl_2-2,4-$C_2B_5H_5$ (approximately 0.5–0.6 mmol apiece; impurities assessed to be less than 0.2%) were each sealed into separate 3-mm NMR tubes similar to that described in the section above concerning the 3-Cl-*closo*-2,4-$C_2B_5H_6$ thermal rearrangement. The two NMR tubes, with samples, were heated at 295 °C for various intervals (Table III). After each heating period the rearrangement process was essentially quenched by cooling the sample immediately to room temperature, and ^{11}B NMR analysis (Table IV) of the dichlorocarborane rearrangement products was made. The data reported for interval numbers 1, 2, 4, 6, 8, 10, and 12 in Table III were obtained from sample A, and the data reported for interval numbers 1, 3, 5, 7, 9, 11, 13, and 14 were obtained from sample B. Other carborane species (3-Cl-2,4-$C_2B_5H_6$, 5-Cl-2,4-$C_2B_5H_6$, 1-Cl-2,4-$C_2B_5H_6$, and 1,3,5-Cl_3-2,4-$C_2B_5H_4$), besides the five *B*,*B*′-dichlorocarborane isomers, were detected as early as the end of 100 h of heating at 295 °C; therefore, the quantities of the *B*,*B*′-Cl_2-2,4-$C_2B_5H_5$ isomers cited for each heating period in Table III have been normalized to total 100% for all the dichloro species. By the time sample B had been heated at 295 °C for 505.5 h, peaks appeared (in addition to those of the dichloro isomers) in the ^{11}B NMR spectrum corresponding to resonances expected for the following compounds: 2,4-$C_2B_5H_7$ (2.2%), 5-Cl-2,4-$C_2B_5H_6$ (11.4%), 3-Cl-2,4-$C_2B_5H_6$ (7.9%), 1-Cl-2,4-$C_2B_5H_6$ (5.5%), 1,3,5-Cl_3-2,4-$C_2B_5H_4$ (12.8%), 1,5,6-Cl_3-2,4-$C_2B_5H_4$ (3.1%), 1,3,7-Cl_3-2,4-$C_2B_5H_4$ (1.3%), 3,5,6-Cl_3-2,4-$C_2B_5H_4$ (3.7%), 1,3,5,6-Cl_4-2,4-$C_2B_5H_3$ (1%), 1,3,5,6,7-Cl_5-2,4-$C_2B_5H_2$ (0.6%). The sample heated for 157.25 h (Table III) was transferred to a 100-mL glass reaction vessel, and the vessel was sealed and heated at 295 °C for an additional 832.5 h. Subsequently, the contents of the vessel were then transferred to a 3-mm NMR tube for NMR analysis. The ^{11}B NMR spectrum indicated that only chlorinated dicarbaheptaboranes were present, with a total of 87% attributed to equilibrated quantities of the five *B*,*B*′-Cl_2-2,4-$C_2B_5H_5$ isomers; the remaining compounds of the mixture were identified as 1-Cl-2,4-$C_2B_5H_6$

(6) Dobson, J.; Schaeffer, R. *Inorg. Chem.* **1970**, *9*, 2183–2184.

Table IV. ^{11}B NMR Data for *B,B'*-Cl_2-2,4-$C_2B_5H_5$ Isomers[a]

compd	atom				
	B(1)	B(3)	B(5)	B(6)	B(7)
1,3-Cl_2-2,4-$C_2B_5H_5$	−13.41	15.08	2.97 (173)	2.97 (173)	−29.63 (186)
	[−12.73]	[16.12]	[2.75]	[2.75]	[−29.70]
1,5-Cl_2-2,4-$C_2B_5H_5$	−14.75	6.45 (190)	12.89	0.69 (170)	−31.25 (192)
	[−14.42]	[6.31]	[13.31]	[0.55]	[−31.39]
1,7-Cl_2-2,4-$C_2B_5H_5$	−22.45 (185)	9.79 (184)	3.23 (172)	3.23 (172)	−22.45
	[−27.44]	[9.34]	[2.85]	[2.85]	[−27.44]
3,5-Cl_2-2,4-$C_2B_5H_5$	−17.10 (185)	12.58	12.31	−0.21 (170)	−17.10 (185)
	[−16.68]	[13.09]	[13.21]	[0.45]	[−16.68]
5,6-Cl_2-2,4-$C_2B_5H_5$	−18.71 (190)	1.83 (193)	10.16	10.16	−18.71 (190)
	[−18.37]	[3.28]	[11.01]	[11.01]	[−18.37]

[a] All B–H boron resonances are observed as 1:1 doublets and B–Cl borons as singlets. Chemical shifts are in ppm. Numbers in parentheses are spin-coupling values, in Hz, for ^{11}B–H. All experimental data were obtained at 160.44 MHz. Chemical shifts in brackets are calculated by assuming a substituent additivity effect (see text).

(1.9%), 3-Cl-2,4-$C_2B_5H_6$ (5.0%), 5-Cl-2,4-$C_2B_5H_6$ (2.9%) and 1,3,5-Cl_3-2,4-$C_2B_5H_4$ (3.6%).

Fractionation of *B,B'*-Cl_2-2,4-$C_2B_5H_5$ isomers. A sample of 5,6-Cl_2-2,4-$C_2B_5H_5$ (7.0 mmol), heated in a 1-L sealed glass flask at 290–310 °C for 24 h and subsequently at 360 °C for 4 h, was opened in a vacuum line and fractionated through a cold column.[6] Seven fractions were collected: fraction 1, passing a column-head temperature of −60 °C (0.15 mmol), contained a mixture of *B*-Cl-2,4-$C_2B_5H_6$ isomers (0.08 mmol) and 1,3-Cl_2-2,4-$C_2B_5H_5$ (0.07 mmol); fraction 2, passing −59 to −48 °C, contained pure 1,3-Cl_2-2,4-$C_2B_5H_5$ (1.1 mmol); fraction 3, passing −47 to −45 °C, contained 1,3-Cl_2-2,4-$C_2B_5H_5$ (0.88 mmol), 1,7-Cl_2-2,4-$C_2B_5H_5$ (0.04 mmol), 3,5-Cl_2-2,4-$C_2B_5H_5$ (0.08 mmol); fraction 4, passing −44 to −40 °C, contained 1,3-Cl_2-2,4-$C_2B_5H_5$ (0.02 mmol), 1,7-Cl_2-2,4-$C_2B_5H_5$ (0.05 mmol), and 3,5-Cl_2-2,4-$C_2B_5H_5$ (0.28 mmol); fraction 5, passing −39 to −38 °C, contained 1,3-Cl_2-2,4-$C_2B_5H_5$ (0.02 mmol), 1,5-Cl_2-2,4-$C_2B_5H_5$ (0.29 mmol), 1,7-Cl_2-2,4-$C_2B_5H_5$ (0.03 mmol), and 3,5-Cl_2-2,4-$C_2B_5H_5$ (0.20 mmol); fraction 6, passing −37 to −30 °C, contained 1,5-Cl_2-2,4-$C_2B_5H_5$ (1.08 mmol) and 3,5-Cl_2-2,4-$C_2B_5H_5$ (1.17 mmol); fraction 7, passing between −29 °C and ambient temperature, contained 1,5-Cl_2-2,4-$C_2B_5H_5$ (0.12 mmol), 3,5-Cl_2-2,4-$C_2B_5H_5$ (0.73 mmol), and 5,6-Cl_2-2,4-$C_2B_5H_5$ (0.64 mmol). The total quantities for each of the five *B,B'*-Cl_2-2,4-$C_2B_5H_5$ isomers (presumably present in the original mixture before separation) are as follows: 1,3-Cl_2, 2.09 mmol; 1,5-Cl_2, 1.49 mmol; 1,7-Cl_2, 0.12 mmol; 3,5-Cl_2, 2.46 mmol; 5,6-Cl_2, 0.64 mmol. Analyses of the separate fractions were carried out by both ^{11}B (Table IV) and proton NMR. For the proton NMR data of 1,3-, 3,5-, and 5,6-Cl_2-2,4-$C_2B_5H_5$ see ref 7. Proton NMR data for the remaining two isomers are as follows: for 1,5-Cl_2-2,4-$C_2B_5H_5$, δ 5.77 (H(2)), 4.91 (H(3)), 5.73 (H(4)), 4.00 (H(6)), 0.47 (H(7)); for 1,7-Cl_2-2,4-$C_2B_5H_5$, δ 6.35 (H(2,4)), 4.42 (H(5,6)).

Kinetic Analyses. Best-fit first-order rate constants were determined for the mono- and dichlorocarborane rearrangements from the data in Table I–III. These calculations were performed by using PROPHET computer programs (DIFFEQ, FITDIFF, INTDIFF) made available by the National Institutes of Health.

Results and Discussion

Thermal equilibration of 5-Cl-2,4-$C_2B_5H_6$ with the two other *B*-chloro isomers (1-Cl and 3-Cl) in this carborane system is nearly complete after 36 h at 340 °C (Table II). The relative amounts of each isomer observed under these conditions indicate that the 5-Cl isomer is the most stable of the three; however, a statistical correction that takes into account equivalent cage positions (i.e., in the parent carborane: 5-position = 6-position, 1-position = 7-position, but the 3-position is unique) leads to the cage positional preference of a *B*-Cl group: 3 > 5 > 1. The equilibrium isomer concentrations found from the rearrangement of the 3-Cl isomer, at 340 °C, confirm these conclusions.

Kinetic data for these rearrangements (Tables I and II, Figures 1 and 2) rule out a triangle-face-rotation (TFR) mechanism of the type considered earlier for a pentagonal-bipyramidal framework of atoms.[8-10] This type of TFR mechanism, in which the two cage carbon atoms are not allowed to move to adjacent or

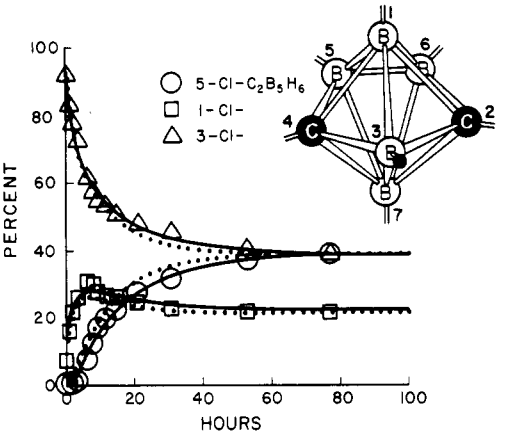

Figure 1. Data (○, △, □) for the 340 °C rearrangement of 3-Cl-2,4-$C_2B_5H_6$ initially containing 92.6% of the 3-Cl isomer and 7.4% of the 1-Cl isomer. Curves are fitted to data (Table I) by assuming a DSD mechanism (eq 2). The solid lines are obtained from curve fitting of these data only; rate constants (10^{-3} h^{-1}) are k_a = 43, k_b = 75, k_c = 245, and k_d = 142. The dotted lines represent the best fit to both 3-Cl-2,4-$C_2B_5H_6$ (this figure and Table I) and 5-Cl-2,4-$C_2B_5H_6$ (Figure 2, Table II) rearrangement data: rate constants (10^{-3} h^{-1}) are k_a = 61, k_b = 109, k_c = 282, and k_d = 158.

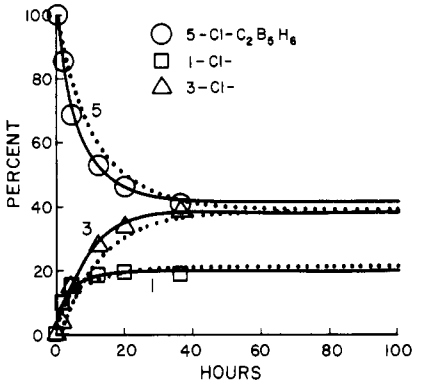

Figure 2. Data (○, △, □) for the 340 °C rearrangement of 5-Cl-2,4-$C_2B_5H_6$. Curves are fitted to data (Table II) by assuming a DSD mechanism (eq 2). The solid lines are obtained from curve fitting of these data only; rate constants (10^{-3} h^{-1}) are k_a = 103, k_b = 216, k_c = 383, and k_d = 198. The dotted lines represent the best fit to both 5-Cl-2,4-$C_2B_5H_6$ (this figure and Table II) and 3-Cl-2,4-$C_2B_5H_6$ (Figure 1, Table I) rearrangement data: rate constants (10^{-3} h^{-1}) are k_a = 61, k_b = 109, k_c = 282, and k_d = 158.

higher coordination positions, implies that the 5-Cl isomer, and not the 1-Cl isomer, must be initially formed from the 3-Cl isomer (eq 1). This consideration, *together with the observed equilibrium*

$$\text{3-Cl-2,4-}C_2B_5H_6 \rightleftharpoons \text{5-Cl-2,4-}C_2B_5H_6 \rightleftharpoons \text{1-Cl-2,4-}C_2B_5H_6 \quad (1)$$

isomer stability results, leads to the prediction (contrary to the

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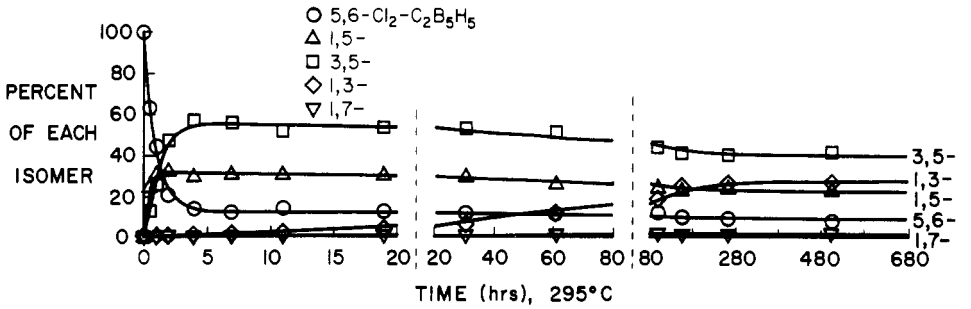


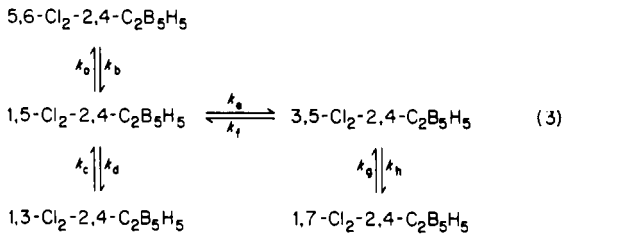
Figure 3. Data (O, Δ, □, ◇, ▽) for the 295 °C rearrangement of 5,6-Cl_2-2,4-$C_2B_5H_5$. Curves are fitted to data (Table III) by assuming a DSD mechanism (eq 2); derived rate constants (h^{-1}) are $k_a = 0.41$, $k_b = 1.0$, $k_c = 7.7 \times 10^{-3}$, $k_d = 9.4 \times 10^{-3}$, $k_e = 1.8$, $k_f = 1.0$, $k_g = 1.8 \times 10^{-2}$, and $k_h = 5.3 \times 10^{-4}$.

observations in the present study (Figure 1)) that the concentration of the 1-Cl isomer should never exceed that of the 5-Cl isomer during the course of the 3-Cl-2,4-$C_2B_5H_6$ rearrangement. The results of the present study bear a similarity to those found for the rearrangements of *B*-methyl derivatives of 2,4-$C_2B_5H_7$.[9] In addition to excluding this triangle-face-rotation rearrangement mechanism, the observed kinetic data for the *B*-CH_3-2,4-$C_2B_5H_6$ rearrangement study were found to be consistent with a DSD (diamond–square–diamond) mechanism in which the two cage carbon atoms are not allowed to move to adjacent, or higher coordination, positions.[9,11,12] Correspondingly, the kinetic data obtained in the present study for the rearrangements of both the 5- and the 3-chloro derivatives fit well to this DSD scheme; this mechanistic premise leads to the prediction that both the 5-Cl and 3-Cl isomers must produce the 1-Cl isomer before proceeding to give the third isomer in the respective rearrangements (eq 2).

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

Other reasonable mechanisms to be considered are as follows: (a) a 1,2-substituent (cage-) surface migration (SSM) mechanism,[10] which cannot be ruled out by the present study, but seems unlikely on the basis of arguments presented earlier;[9] (b) DSD and TFR mechanistic schemes that allow the separated 2,4-carbon cage atoms of the dicarbaheptaborane to decrease their mutual separation or to move to vertices of higher coordination. Such species are not observed in the course of the rearrangement and would necessarily have to be very short-lived intermediates. Category b mechanisms appear unattractive in that routes leading to intermediates with cage carbon atoms at either high-coordination axial sites or adjacent cage sites are expected to be energetically unfavorable[13] and thus to entail negligible rate constants when compared to routes (e.g. the DSD mechanism considered earlier[9,12] in eq 2) that can avoid these problems.

Rearrangement of the 5,6-Cl_2-*closo*-2,4-$C_2B_5H_5$ isomer to give a mixture of all five *B,B'*-Cl_2 isomers proceeds at a reasonable rate at 295 °C; the 1,5-Cl_2-2,4-$C_2B_5H_5$ isomer is produced initially (Table III, Figure 3), followed by the buildup of the 3,5-Cl_2-, the 1,3-Cl_2-, and finally the 1,7-Cl_2-2,4-$C_2B_5H_5$ isomer. In this respect, the composition vs. time diagram (Figure 3) vaguely resembles that observed for the rearrangement of 5,6-Me_2-2,4-$C_2B_5H_5$.[12] The major difference between the two rearrangement rate patterns is that in the dichloro system a rapid equilibration of the 1,5- and 3,5-Cl_2 isomers with the 5,6-Cl_2 isomer occurs, relative to the very slow production of 1,3-Cl_2-2,4-$C_2B_5H_5$, whereas in the dimethylcarborane rearrangement the 5,6-/1,5-/3,5-Me_2-2,4-$C_2B_5H_5$ interconversions occur only slightly faster than the 1,3-Me_2-2,4-$C_2B_5H_5$ buildup. If a DSD mechanism (in which cage carbon atoms are not allowed to move to adjacent, or higher coordination, positions) is assumed for the rearrangement of 5,6-Cl_2-2,4-$C_2B_5H_5$, the following reversible pathways can be derived:[12]



(3)

The rate contants are given in the caption of Figure 3.

After the *B,B'*-dichloro and the *B,B'*-dimethyl isomer groups are allowed to reach equilibrium it is also noticed that the relative isomer stabilities among each group are not the same: 3,5- > 1,3- > 1,5- > 5,6- > 1,7-Cl_2-2,4-$C_2B_5H_5$ vs. 1,3- > 3,5- > 1,5- > 1,7- > 5,6-Me_2-2,4-$C_2B_5H_5$. When statistically corrected (e.g. "four" compounds, 1,5-, 1,6-, 5,7-, and 6,7-Cl_2-2,4-$C_2B_5H_5$, make up the 1,5-Cl_2 isomer set, but there is only "one" 5,6-Cl_2-2,4-$C_2B_5H_5$, etc.), the isomer stability comparisons are as follows: 3,5- > 1,3- > 5,6- > 1,5- > 1,7-Cl_2-2,4-$C_2B_5H_5$ vs. 1,3- > 3,5- > 1,7- > 1,5- > 5,6-Me_2-2,4-$C_2B_5H_5$.

The stability trend in the *B,B'*-dimethylcarborane isomer group[12] was previously correlated with the (statistically corrected) monomethyl group positional preference 3 > 1 (or 7) > 5 (or 6),[9,12] and from this comparison it does not seem unreasonable to find the 1,3-dimethyl isomer the most stable, and the 5,6-dimethyl isomer the least stable, in the group of five *B,B'*-Me_2-2,4-$C_2B_5H_5$ isomers.[12] A similar consistency in relative isomer stabilities is found when one compares the statistically corrected *B*-monochloro positional preference, 3 > 5 > 1 (Tables I and II, Figures 1 and 2), with that of the *B,B'*-dichloro system (Table III, Figure 3). If a substituent positional "additivity" effect[12] is applied, it is reasoned that the 3,5-Cl_2 isomer should be the most stable and the 1,7-Cl_2 isomer the least stable of the *B,B'*-Cl_2-2,4-$C_2B_5H_5$ set, as is observed (Tables III and V, Figure 3); and in general, the stability order of all the *B,B'*-dichlorocarborane isomers is forecasted, without exception, from the application of this substituent positional "additivity" effect. The predicted isomer equilibrium concentrations (Table V, column 6) compare favorably with the observed percentages (column 2) although it appears the 1,3-Cl_2 isomer is found (experimentally) to be more stable, relative to all other *B,B'*-dichloro isomers, than predicted by this method. This could well reflect a substituent electronic interaction through the cage between the 1- and 3-positions, a situation that may not exist between any other two *B*-Cl positions.

Rearrangements of both the monochloro and the dichloro derivatives of *closo*-2,4-$C_2B_5H_7$ are accompanied by a slow chlorine exchange between cage molecules. As the *B*-monochlorocarborane rearrangements at 340 °C approach isomer equilibration, small quantities of the parent carborane, 2,4-$C_2B_5H_7$, are produced along with an equilibrium distribution of *B,B'*-dichlorocarborane isomers. Similarly, the thermal rearrangement of dichlorocarborane, after the starting 5,6-Cl_2-2,4-$C_2B_5H_5$ isomer has nearly reached 95%

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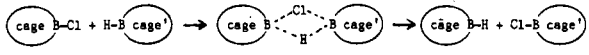
Table V. Rearrangement-Equilibrium Data and Calculations for *B*-Cl and *B,B'*-Cl_2 Derivatives of 2,4-$C_2B_5H_7$

(1) compd	(2) % compn at equil (exptl)[a]	(3) W[b]	(4) ΔH(exptl)[c]	(5) ΔH(calcd)[d]	(6) % compn (theor derived from col 3 and 5)
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-Cl_2	27.4	2	1810	2954	22.8
1,5-Cl_2	22.3	4	6056	6473	21.6
1,7-Cl_2	1.2	1	13309	9427	2.9
3.5-Cl_2	40.2	2	0	0	42.6
5,6-Cl_2	8.9	1	3847	3519	10.1

[a] Estimated errors: ±1–1.5% for 3-Cl, 5-Cl, 1,3-Cl_2-, and 3,5-Cl_2; ±0.5–1.0% for 1-Cl and 1,5-Cl_2; ±0.3–0.4% for 1,7-Cl_2 and 5,6-Cl_2. The equilibrium temperature is 613 K for the monochloro set and 568 K for the dichloro set of isomers. [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 1 in ref 12; ΔH is in joules, and the isomer with the lowest enthalpy in each set is arbitrarily assigned $\Delta H = 0$. [d] The dichlorocarborane isomer ΔH values are calculated by adding two appropriate monochloro positional ΔH values from column 4; the dichloro isomer with the lowest calculated enthalpy is arbitrarily assigned $\Delta H = 0$.

of its equilibrium quantity, produces trace amounts of *B*-monochloro and *B,B',B''*-trichloro derivatives of $C_2B_5H_7$. Heating this mixture for a considerably longer period of time produces substantial amounts of certain mono and trichloro derivatives as well as small quantities of 1,3,5,6-Cl_4-2,4-$C_2B_5H_3$, 1,3,5,6,7-Cl_5-2,4-$C_2B_5H_2$, and the parent $C_2B_5H_7$. As might be expected, the production of these halogen-exchanged side products are curtailed when the rearrangements are carried out at reduced pressures. In contrast to the above observations, no cage-to-cage substituent migration is detected during any stage of the *B*-monomethyl or the *B,B'*-dimethyldicarbaheptaborane rearrangements.[9,12] A speculative mechanism for Cl transfer between carborane polyhedra is



(4)

Chlorine, with its several pairs of "unshared" electrons, could more easily stabilize a bridging intermediate, such as shown in eq 4, than an alkyl group could. This bridging intermediate is not unlike that proposed for substituent exchange between monoboron compounds catalyzed by B–H-containing species;[14] but in the case of the substituted monoboron redistribution reactions an "empty" orbital on the trivalent boron starting material(s) should make a bridging intermediate more easily formed. No readily accessible "empty" boron orbitals are imagined for the carborane species in the ground state; however, at the elevated temperatures used in the present study, LUMO considerations for a perturbed carborane polyhedron may well be instructive in this regard.

The relationship between the *B*-monochlorocarborane volatilities (3-Cl > 1-Cl > 5-Cl) and the expected dipole moments (5-Cl > 1-Cl > 3-Cl) has been previously discussed;[3] and an extension of this relationship to the dichloro derivatives appears straightforward. The observed volatilities for the *B,B'*-Cl_2-*closo*-2,4-$C_2B_5H_5$ isomers are 1,3-Cl_2 > 1,7-Cl_2 ≥ 3,5-Cl_2 > 1,5-Cl_2 > 5,6-Cl_2. This is what might be expected upon a consideration of the combined influence of two chlorines in each isomer on the carborane dipole (note: on the basis of earlier dipole moment work on $C_2B_{10}H_{12}$ isomers,[15] the direction of the dipole in the parent $C_2B_5H_7$ is expected to lie along the axis passing through B(3) and bisecting the B(5)–B(6) bond, with the negative end of the dipole in the direction of the B(5)–B(6) bond).

The chemical shifts and coupling constants for all the *B,B'*-Cl_2-2,4-$C_2B_5H_5$ isomers are cited in Table IV. Calculated chemical shifts, assuming a substituent additivity effect, are also given; see ref 5, 12, and 16 for the approach used in obtaining the calculated shifts. With the exception of δ(exptl) – δ(calcd) for B(1,7) of the 1,7-Cl_2-2,4-$C_2B_5H_5$ isomer, the differences between the observed and calculated shifts are less than 1.5 ppm with an average difference of about 0.5 ppm. The rather large difference, almost 5 ppm, found between the experimental and calculated B(1,7) shifts of the 1,7-Cl_2 isomer represents a novel antipodal substituent effect. Antipodal NMR effects have been noticed for a number of *closo*-carboranes and are thought to be a reflection of unique cage electronic perturbations.[17] Antipodal chemical shift effects are also manifested by the significant upfield shifts (7–9 ppm) of the B(7) resonances of the 1-substituted carboranes 1,3- and 1,5-Cl_2-2,4-$C_2B_5H_5$ (Table IV).

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Registry No. 3-Cl-2,4-$C_2B_5H_6$, 28347-93-5; 1-Cl-2,4-$C_2B_5H_6$, 28347-69-5; 5-Cl-2,4-$C_2B_5H_6$, 28347-92-4; 2,4-$C_2B_5H_7$, 23940-01-4; 1,3-Cl_2-2,4-$C_2B_5H_5$, 71849-89-3; 1,5-Cl_2-2,4-$C_2B_5H_5$, 71849-88-2; 3,5-Cl_2-2,4-$C_2B_5H_5$, 71849-90-6; 5,6-Cl_2-2,4-$C_2B_5H_5$, 71849-86-0; 1,3,5-Cl_3-2,4-$C_2B_5H_4$, 96445-05-5; 1,5,6-Cl_3-2,4-$C_2B_5H_4$, 96445-06-6; 1,3,7-Cl_3-2,4-$C_2B_5H_4$, 96445-07-7; 3,5,6-Cl_3-2,4-$C_2B_5H_4$, 96445-08-8; 1,3,5,6-Cl_4-2,4-$C_2B_5H_3$, 96445-09-9; 1,3,5,6,7-Cl_5-2,4-$C_2B_5H_2$, 96445-10-2; 1,7-Cl_2-2,4-$C_2B_5H_5$, 71849-91-7.

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