The rigidity of the molecular array and the strong CS bond indicate that the double-bond formulation of the two canonical forms

$$R_2C{=}SF_4 \longleftrightarrow R_2\overset{-}{C}{-}\overset{+}{S}F_4$$

certainly has major importance, quite in contrast to normal ylides. However, there are many examples where $CH_2{=}SF_4$ does react as polar species in addition reactions.[12]

The chemistry of $CH_3CH{=}SF_4$ has not been investigated so far, except for its thermal decomposition at ambient temperature. The formation of $CH_3CH_2SF_5$ is a clear indication that HF is among the decomposition products since $CH_3CH{=}SF_5$ is expected to add HF rapidly, as does $CH_2{=}SF_4$, forming CH_3SF_5. The presence of CH_3CHF_2 may indicate some intermediate formation of methylcarbene.

Conclusion

The method of lithiation of a 1-bromo-1-pentafluorosulfonyl compound and its LiF elimination may be a general procedure for preparing $> C{=}SF_4$ species, as long as the carbon atom is alkyl substituted. The structure of the alkylidenesulfur tetrafluorides are probably all alike, as indicated by two known cases.

Registry No. $CH_3CH{=}SF_4$, 81553-81-3; $CH_3C{\equiv}COCH_3$, 13169-01-2; $CH_3C(SF_5){=}C(Cl)OCH_2CH_3$, 81535-06-0; $CH_3C{\equiv}COCH_2CH_3$, 14273-06-4; $CH_3CH(SF_5)COCl$, 81535-07-1; $CH_3CH(SF_5)COOH$, 81535-08-2; $CH_3CH(SF_5)COO^-Ag^+$, 81553-82-4; $CH_3CH(SF_5)Br$, 81535-09-3; $CH_3C(SF_5){=}C(Cl)OCH_3$, 81535-10-6; $SClF_5$, 13780-57-9.

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Rate Study on the Rearrangement of *B*-CH_3-*closo*-2,4-$C_2B_5H_6$ Isomers and Mechanistic Implications

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The rates of rearrangement of 5- and 3-CH_3-*closo*-2,4-$C_2B_5H_6$ at 295 °C to an equilibrium mixture of *B*-CH_3-*closo*-2,4-$C_2B_5H_6$ isomers were measured and correlated to possible mechanisms. Of two possible mechanistic routes (diamond–square–diamond, DSD, and triangle face rotation, TFR) the DSD pathway is in much better accord with the observed rate patterns than the TFR route.

Introduction

It has been previously reported that 5-CH_3-*closo*-2,4-$C_2B_5H_6$ slowly equilibrates with a mixture of *B*-CH_3-*closo*-2,4-$C_2B_5H_6$ isomers at 300 °C, with the *B*-methyl group showing a positional preference 3 > 1, 7 > 5, 6 based on enthalpy considerations alone.[1] A related set of equilibria and methyl group positional preferences were also established for B-polymethylated derivatives of 2,4-$C_2B_5H_7$. For the 5,6-$(CH_3)_2$-2,4-$C_2B_5H_5$ rearrangement a rate study was found to be consistent with two viable mechanisms, diamond–square–diamond (DSD)[2-8] and triangle face rotation (TFR).[8-12] In an attempt to differentiate between these two possible mechanistic pathways, we conducted a rearrangement rate study on two isomers of *B*-CH_3-*closo*-2,4-$C_2B_5H_6$.

Experimental Section

Materials and Handling of Chemicals. The parent *closo*-2,4-$C_2B_5H_7$ was obtained from Chemical Systems Inc., Irvine, CA. Methyl chloride (J. T. Baker) was used without further purification. Aluminum trichloride (Matheson Coleman and Bell) was freshly sublimed into the reaction vessel immediately prior to use. All materials were handled in conventional high-vacuum equipment or in a drybox under an atmosphere of dry nitrogen. Cold-column fractionation was effected with an apparatus similar to that described previously.[13]

Table I. ^1H NMR Data for 1-, 3-, and 5-CH_3-*closo*-2,4-$C_2B_5H_6$

compd	position	δ^a	$J(H-^{11}B)$/ Hz
1-CH_3-2,4-$C_2B_5H_6$	$CH_3B(1)$	−0.47	*b*
	HC(2,4)	5.58	
	HB(3)	4.94	190
	HB(5,6)	4.10	163
	HB(7)	−0.03	178
3-CH_3-2,4-$C_2B_5H_6$	HB(1,7)	0.18	176
	HC(2,4)	5.25	
	$CH_3B(3)$	1.02	
	HB(5,6)	4.03	168
5-CH_3-2,4-$C_2B_5H_6$	HB(1,7)	0.22	184
	HC(2)	5.36	
	HB(3)	4.87	190
	HC(4)	5.19	
	$CH_3B(5)$	0.75	*c*
	HB(6)	3.94	167

[a] Relative to internal $(CH_3)_4Si$. [b] An ill-defined pattern, $J \simeq 9$ Hz, was observed that may be due to $H_3CB(1)$ coupling. [c] An ill-defined pattern, $J \simeq 4$ Hz, was observed that is possibly due to $H_3CB(5)$ coupling.

Nuclear Magnetic Resonance. Proton NMR spectra, Table I, were recorded on a Bruker WM-500 instrument and on a FT-Bruker WP-60 equipped with a Fluke 6061 B frequency synthesizer operating at 19.255 MHz and a ENI-320 L amplifier. The boron-11 NMR spectra were obtained on a Varian HA-100 spectrometer operating at 32.1 MHz and on a Bruker WM-500 operating at 160.44 MHz. The proton-decoupled boron-11 NMR spectra at 32.1 MHz were obtained while irradiating at 100.08 MHz with a General Radio 1061 frequency synthesizer, an Electronic Navigation Industries 320 L power amplifier,

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(1) A. P. Fung and T. Onak, *J. Am. Chem. Soc.*, **99**, 5512 (1977); T. Onak, A. P. Fung, G. Siwapinyoyos, and J. B. Leach, *Inorg. Chem.*, **18**, 2878 (1979).
(2) W. N. Lipscomb, *Science (Washington, D.C.)*, **153**, 373 (1966).
(3) R. E. Williams, *Prog. Boron Chem.*, **2**, Chapter 2 (1970).
(4) E. L. Muetterties and L. J. Guggenberger, *J. Am. Chem. Soc.*, **96**, 1748 (1974).
(5) E. L. Muetterties and C. M. Wright, *Q. Rev., Chem. Soc.*, **21**, 109 (1967).
(6) E. L. Muetterties, *Rec. Chem. Prog.*, **31**, 51 (1970).
(7) E. L. Muetterties, "Boron Hydride Chemistry", Academic Press, New York, 1975, Chapter 1.
(8) E. L. Muetterties and W. H. Knoth, "Polyhedral Boranes", Marcel Dekker, New York, 1968, p 70.
(9) T. Onak, *Adv. Organomet. Chem.* **3**, 263 (1965); see p 334.
(10) H. D. Kaesz, R. Bau, H. A. Beall, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **89**, 4218 (1967).
(11) H. Hart and W. N. Lipscomb, *J. Am. Chem. Soc.*, **91**, 771 (1969).
(12) V. R. Miller and R. N. Grimes, *J. Am. Chem. Soc.*, **97**, 4213 (1975).
(13) J. Dobson and R. Schaeffer, *Inorg. Chem.*, **9**, 2183 (1970).

Table II. Kinetic Data for the Rearrangement of 5-CH_3-*closo*-2,4-$C_2B_5H_6$ at 295 °C

	percent composition		
time, h	5-CH_3-2,4-$C_2B_5H_6$	1-CH_3-2,4-$C_2B_5H_6$	3-CH_3-2,4-$C_2B_5H_6$
0	94.0	5.7	0.3
9	89.6	9.7	0.7
25	84.2	15.0	0.8
43.5	74.7	22.7	2.6
54.5	68.7	25.5	5.8
79	59.1	30.0	10.9
99	52.8	33.4	13.8
120	54.0	31.6	14.4
159.5	44.1	34.4	21.5
180	44.1	35.4	20.4
201.5	39.0	35.1	25.9
222	38.6	35.8	25.6
297	34.9	34.7	30.4
368	29.6	35.6	34.8
656	25.6	37.8	36.6

and a locally constructed broad-band unit.

Preparation of 5-CH_3-*closo*-2,4-$C_2B_5H_6$. With use of a modified literature procedure[14] 5-CH_3-2,4-$C_2B_5H_6$ was prepared from $C_2B_5H_7/CH_3Cl/AlCl_3$. Cold-column[13] fractionation of the product mixture gave 5-CH_3-2,4-$C_2B_5H_6$ emerging from the column between −75 and −60 °C.

Preparation of 3-CH_3-*closo*-2,4-$C_2B_5H_6$. A sample of 5-CH_3-2,4-$C_2B_5H_6$, 2.38 mmol, in a glass tube was heated at 295 °C for 200 h. Fractionation of the product mixture using a cold-column distillation technique[13] gave a mixture of 5- and 1-CH_3-2,4-$C_2B_5H_6$ (−90 to −70 °C) and a fraction (−70 °C on up), 0.6 mmol, containing 80% 3-CH_3-2,4-$C_2B_5H_6$ and 20% of a mixture of 5- and 1-CH_3-2,4-$C_2B_5H_6$. Refractionation of the latter fraction through the cold column afforded 0.33 mmol of $CH_3C_2B_5H_6$, which (by ^1H and ^{11}B NMR) was analyzed as 89.8% 3-CH_3-2,4-$C_2B_5H_6$, 4.9% 5-CH_3-2,4-$C_2B_5H_6$, and 5.2% 1-CH_3-2,4-$C_2B_5H_6$. The gas-phase infrared spectrum of this CH_3-$C_2B_5H_6$ sample exhibited absorption bands at 3090 (w), 3040 (w), 3010 (m), 2980 (m), 2925 (m), 2855 (w), 2620 (s), 1510 (w, br), 1395 (sh), 1380 (s), 1350 (s), 1290 (s), 1280 (s), 1155 (m, br), 1045 (s), 940 (m), 905 (m), and 835 (m) cm^{-1}.

Kinetic Study of the 5-CH_3-*closo*-2,4-$C_2B_5H_6$ Thermal Rearrangement. A 5-CH_3-2,4-$C_2B_5H_6$ sample (0.4 mmol) containing 5.7% 1-CH_3-2,4-$C_2B_5H_6$ and 0.3% 3-CH_3-2,4-$C_2B_5H_6$ was sealed in a 3-mm NMR tube and heated at 295 °C for a number of intervals (Table II). After each heating period the sample was immediately cooled to room temperature and ^1H (Table I) and ^{11}B NMR[1] analyses of the rearrangement products were made (Table II). Very little change in isomer concentrations was noted upon heating the sample longer than 400 h. Toward the termination of the rearrangement a minor side reaction, believed to involve cage coupling,[15,16] occurred. ^1H and ^{11}B analyses of the rearranged monomer products, when separated from the trace quantity of coupled products by cold-column distillation at the termination of the rearrangement (656 h) (Table II), gave excellent agreement with the monomer product percentages determined by NMR before the separation (Table II).

Kinetic Study of the 3-CH_3-*closo*-2,4-$C_2B_5H_6$ Thermal Rearrangement. A sample of 3-CH_3-2,4-$C_2B_5H_6$, containing 4.9% 5-CH_3-2,4-$C_2B_5H_6$ and 5.2% 1-CH_3-2,4-$C_2B_5H_6$, was subjected to thermal rearrangement at 295 °C in a manner similar to that described above. The results of ^1H and ^{11}B NMR analyses of the product mixture after each heating period are given in Table III.

Results and Discussion

The kinetic data (Table II) for the rearrangement of 5-CH_3-*closo*-2,4-$C_2B_5H_6$ (actually, 94% 5-CH_3, 5.7% 1-CH_3, and 0.3% 3-CH_3-$C_2B_5H_6$) at 295 °C to give, ultimately, an equilibrium mixture of B-CH_3-*closo*-2,4-$C_2B_5H_6$ isomers are presented graphically in Figure 1. The curves fitted to the data points in Figure 1 are derived by applying the following assumptions: (a) The mechanism of the reaction follows a first-order diamond–square–diamond (DSD) pathway[2-8] in which methyl group migration from boron to boron does not occur[1] (Figure 2). (b) DSD pathways involving the formation of intermediates having cage-carbon atoms at nonadjacent sites are considered energetically accessible;[1] however, routes that lead to intermediates with cage-carbon atoms at either axial or adjacent equatorial closo-cage sites are expected to be energetically very unfavorable[17] and would entail negligible rate constants as compared to routes that can avoid this problem. This results in a consideration of the following direct equilibria only:

Table III. Kinetic Data for the Rearrangement of 3-CH_3-*closo*-2,4-$C_2B_5H_6$ at 295 °C

	percent composition		
time, h	3-CH_3-2,4-$C_2B_5H_6$	5-CH_3-2,4-$C_2B_5H_6$	1-CH_3-2,4-$C_2B_5H_6$
0	89.9	4.9	5.2
14.8	86.2	3.2	10.6
46.5	77.6	5.3	17.1
71.9	69.2	9.2	21.6
99.7	62.4	10.5	27.1
132.3	57.8	12.6	29.6
148.2	57.6	12.8	29.6
178.8	52.7	17.7	29.6
195.9	52.0	16.8	31.2
229.2	48.0	19.7	32.3
252.1	44.9	19.9	35.2
286.1	43.6	22.2	34.2
322.9	41.2	23.8	35.0
359.3	39.8	23.7	36.5
393.0	40.4	23.6	36.0
438.8	38.1	25.0	36.9
511.0	37.6	24.5	37.9

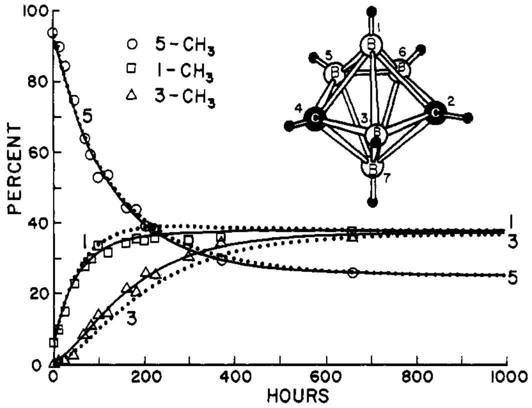

Figure 1. Data (○, □, △) for the 295 °C rearrangement of 5-CH_3-2,4-$C_2B_5H_6$ containing initially 5.7% 1-CH_3- and 0.3% 3-CH_3-2,4-$C_2B_5H_6$ and curves fitted to data with assumption of a DSD mechanism. The solid lines are obtained from best fitting this data only and are generated from eq 1 with use of (in 10^{-5} h^{-1}) k_a = 671, k_b = 444, k_c = 755, and k_d = 770. The dotted lines represent the best fit to *both* 5-CH_3-2,4-$C_2B_5H_6$ (this figure) and 3-CH_3-2,4-$C_2B_5H_6$ (Figure 5) rearrangement data where for eq 1 (in 10^{-5} h^{-1}) k_a = 670, k_b = 444, k_c = 503, and k_d = 513.

$$5\text{-}CH_3\text{-}2,4\text{-}C_2B_5H_6 \underset{k_b}{\overset{k_a}{\rightleftharpoons}} 1\text{-}CH_3\text{-}2,4\text{-}C_2B_5H_6 \underset{k_d}{\overset{k_c}{\rightleftharpoons}} 3\text{-}CH_3\text{-}2,4\text{-}C_2B_5H_6 \quad (1)$$

It is important to notice that in this DSD scheme no "direct" equilibrium exists between the 5- and the 3-methyl isomers. On this premise, first-order DSD rate constants calculated to

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[14] J. F. Ditter, E. B. Klusmann, R. E. Williams, and T. Onak, *Inorg. Chem.*, **15**, 1063 (1976).

[15] J. S. Plotkin and L. G. Sneddon, *J. Chem. Soc., Chem. Commun.*, 95 (1976).

[16] J. S. Plotkin, R. J. Astheimer, and L. G. Sneddon, *J. Am. Chem. Soc.*, **101**, 4155 (1979).

[17] M. J. S. Dewar and M. L. McKee, *Inorg. Chem.*, **19**, 2662 (1980); R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, **36**, 3489 (1962).

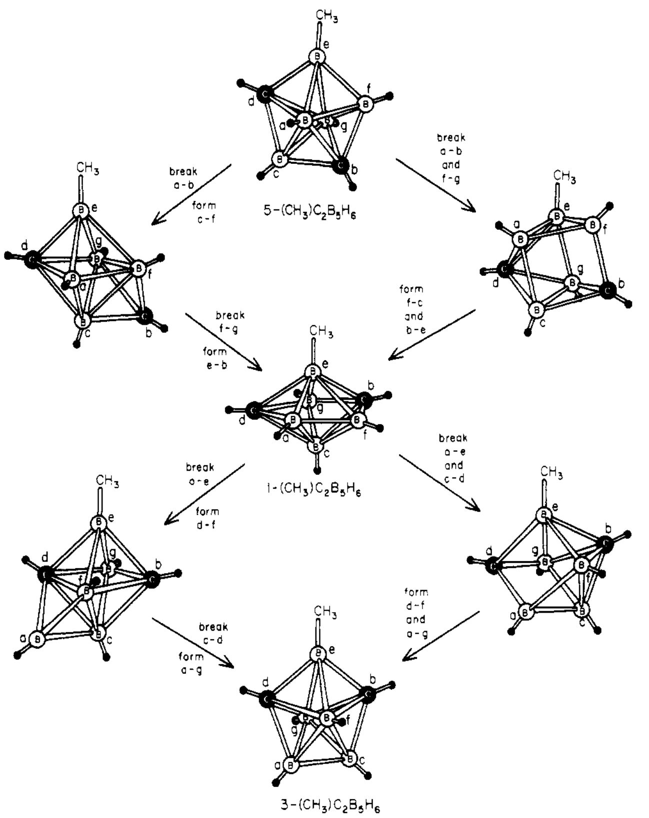


Figure 2. Plausible DSD pathways for the rearrangement of B-CH_3-2,4-$C_2B_5H_6$ isomers (center column of cage structures). Intermediate structures shown on the left side of figures represent "pseudo"-C_{3v} geometries whereas those on the right side of the figure represent "pseudo"-C_{2v} geometries.

"best fit" the rate data at 295 °C are found to be (in 10^{-5} h^{-1}) $k_a = 671$, $k_b = 444$, $k_c = 755$, and $k_d = 770$ (solid lines, Figure 1).

An alternative mechanism, triangle face rotation (TFR),[8-12] has been proposed to explain the rearrangement of several related cage compounds, and when invoked in the present instance, it is concluded that the following "direct" equilibria exist:

$$1\text{-CH}_3\text{-2,4-C}_2\text{B}_5\text{H}_6 \underset{k_b}{\overset{k_a}{\rightleftharpoons}} 5\text{-CH}_3\text{-2,4-C}_2\text{B}_5\text{H}_6 \underset{k_d}{\overset{k_c}{\rightleftharpoons}} 3\text{-CH}_3\text{-2,4-C}_5\text{B}_5\text{H}_6 \quad (2)$$

in which there is no "direct" equilibrium between the 1- and 3-methyl isomers (arriving at this conclusion assumes point b above). Derived first-order TFR rate constants that best fit the data (Figure 3) are found to be (in 10^{-5} h^{-1}) $k_a = 258$, $k_b = 390$, $k_c = 294$, and $k_d = 198$.

Although the TFR rate diagrams derived from the best fit rate constants do not correspond to the data points as well as the DSD curves (cf. Figures 1 (solid lines) and 3), the difference is not sufficient to rule out the TFR mechanism on this basis alone. It is possible, however, to predict from the DSD and TFR rate constants derived from the 5-CH_3-2,4-$C_2B_5H_6$ rearrangement that a rate study starting with one of the two other isomers, 1- and/or 3-CH_3-2,4-$C_2B_5H_6$, should discriminate between these two plausible mechanisms. The predicted rate profiles starting with 3-CH_3-2,4-$C_2B_5H_6$ (actually 89.9% 3-CH_3, 5.2% 1-CH_3, and 4.9% 5-CH_3) are given in Figure 4, and it is noticed that the DSD mechanism (solid lines) predicts a sharp rise of the 1-methyl isomer followed by a gradual increase of the 5-methyl isomer whereas the TFR mechanism (dotted lines) predicts, at the outset of the rearrangement, a faster initial rise in 5-methyl isomer concentrations as compared to those of the 1-methyl isomer. Application of the TFR mechanism (using the TFR rate constants derived from the 5-CH_3-2,4-$C_2B_5H_6$ rearrangement) also predicts (see Figure 4) that, when 3-CH_3-2,4-$C_2B_5H_6$ is rearranged, >95% of the equilibrium concentrations of the 1-CH_3 and 3-CH_3 isomers will *not* be established within a 1000-h heating period at 295 °C. Experimentally, we find (Figure 5) that the 3-methyl rearrangement rate profile agrees well with the pattern expected for the DSD mechanistic route and very poorly with the rate profile derived from a TFR route. This study consequently rules out a TFR mechanism of the type described above for B-CH_3-2,4-$C_2B_5H_6$ rearrangements.

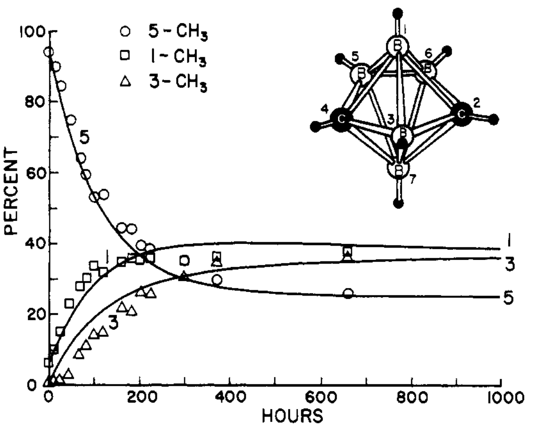


Figure 3. Data (○, □, △) for the 295 °C rearrangement of 5-CH_3-2,4-$C_2B_5H_6$ (containing initially 5.7% 1-CH_3- and 0.3% 3-CH_3-2,4-$C_2B_5H_6$) and curves fitted to data with assumption of a TFR mechanism. The curves are generated from eq 2 with use of the rate constants (in 10^{-5} h^{-1}) $k_a = 258$, $k_b = 390$, $k_c = 294$, and $k_d = 198$.

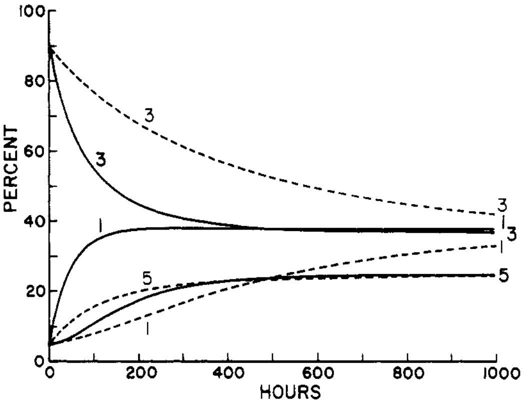


Figure 4. Predicted rate profiles for the 295 °C rearrangement of 3-CH_3-2,4-$C_2B_5H_6$ (containing initially 5.2% 1-CH_3- and 4.9% 5-CH_3-2,4-$C_2B_5H_6$). Solid lines indicate the percentage of each isomer, against time, based on the assumption of the DSD mechanism (eq 1) with the best fit rate constants (in 10^{-5} h^{-1}) obtained from the 5-CH_3-2,4-$C_2B_5H_6$ rearrangement data $k_a = 671$, $k_b = 444$, $k_c = 755$, and $k_d = 770$. Dashed lines indicate the percent of each isomer, against time, based on a TFR mechanism (eq 2) with the best fit rate constants (in 10^{-5} h^{-1}) obtained from the 5-CH_3-2,4-$C_2B_5H_6$ rearrangement data $k_a = 258$, $k_b = 390$, $k_c = 294$, and $k_d = 198$.

The DSD rate constants derived from the 3-CH_3-2,4-$C_2B_5H_6$ rearrangement (Figure 5) differ slightly from those obtained from the 5-CH_3-2,4-$C_2B_5H_6$ rearrangement (Figure 1) and are attributed to experimental error. Best fit DSD rate constants for both 5-CH_3- and 3-CH_3-$C_2B_5H_6$ rearrangement patterns are (in 10^{-5} h^{-1}) $k_a = 670$, $k_b = 444$, $k_c = 503$, and $k_d = 513$ (eq 1).

A more detailed analysis of the formal DSD mechanism, whether it proceeds via pseudo-C_{2v} or via C_{3v} intermediates[1,2] (Table IV), indicates four equivalent bond-breaking/bond-construction combinations (steps I–L) implicated in the rearrangement of 3-CH_3-2,4-$C_2B_5H_6$ to the 1-CH_3 isomer (k_d,

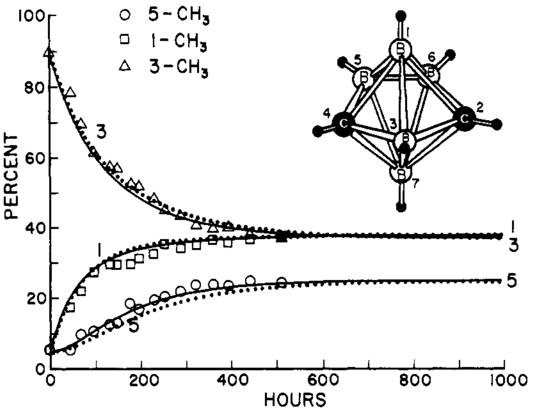
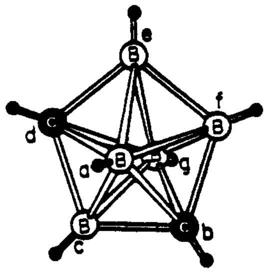


Figure 5. Data (○, □, △) for the 295 °C rearrangement of 3-CH_3-2,4-$C_2B_5H_6$ (containing initially 5.2% 1-CH_3- and 4.9% 5-CH_3-2,4-$C_2B_5H_6$) and curves fitted to data with assumption of a DSD mechanism. The solid lines are obtained from best fitting this data only and are generated from eq 1 with use of the rate constants (in 10^{-5} h^{-1}) $k_a = 990$, $k_b = 656$, $k_c = 540$, and $k_d = 550$. The dotted lines are best fitted to both 3-CH_3-2,4-$C_2B_5H_6$ (this figure) and 5-CH_3-2,4-$C_2B_5H_6$ (Figure 1) rearrangement data whereby, with use of eq 1, the rate constants are (in 10^{-5} h^{-1}) $k_a = 670$, $k_b = 444$, $k_c = 503$, and $k_d = 513$.

Table IV. Bond-Cleavage and Bond-Formation Steps Applying a DSD Rearrangement Mechanism to B-CH_3-2,4-$C_2B_5H_6$ Isomers



step	bonds broken	bonds formed	isomer
Starting with Substituent at "e" (5-CH_3-2,4-$C_2B_5H_6$)			
A	a–b, f–g	b–e, c–f	1-CH_3-2,4-$C_2B_5H_6$
B	a–f, b–g	b–e, c–f	1-CH_3-2,4-$C_2B_5H_6$
C	a–e, d–g	c–e, d–f	5-CH_3-2,4-$C_2B_5H_6$
D	a–d, e–g	c–e, d–f	5-CH_3-2,4-$C_2B_5H_6$
Starting with Substituent at "a" (1-CH_3-2,4-$C_2B_5H_6$)			
E	a–b, f–g	b–e, c–f	5-CH_3-2,4-$C_2B_5H_6$
F	a–f, b–g	b–e, c–f	3-CH_3-2,4-$C_2B_5H_6$
G	a–e, d–g	c–e, d–f	3-CH_3-2,4-$C_2B_5H_6$
H	a–d, e–g	c–e, d–f	5-CH_3-2,4-$C_2B_5H_6$
Starting with Substituent at "c" (3-CH_3-2,4-$C_2B_5H_6$)			
I	a–b, f–g	b–e, c–f	1-CH_3-2,4-$C_2B_5H_6$
J	a–f, b–g	b–e, c–f	1-CH_3-2,4-$C_2B_5H_6$
K	a–e, d–g	c–e, d–f	1-CH_3-2,4-$C_2B_5H_6$
L	a–d, e–g	c–e, d–f	1-CH_3-2,4-$C_2B_5H_6$

eq 1) whereas only two (equivalent) such bond-breaking/bond-construction combinations (A, B; E, H; F, G) are involved in each of the three other isomer transformations (k_{a-c}) in eq 1. Thus, applying a statistical weighting to each of the above best fit rate constants[18] yields (in 10^{-5} h^{-1}) $k_a = 335$, $k_b = 222$, $k_c = 252$, and $k_d = 128$. From these weighted k values, and consideration of the DSD bond-conversion steps outlined in Table IV, it may be estimated that cage C–B bond formation is favored when the pertinent boron has an attached methyl group whereas the opposite may well be true when considering B–B formation (i.e., an attached methyl group may destabilize a B–B bond in this cage system).

As mentioned above, earlier DSD mechanistic schemes, as applied to a rearrangement of a seven-atom closo system, suggest "C_{2v}" or "C_{3v}" intermediates (or transition states). The "C_{3v}" structure, a capped octahedron, can be viewed as a somewhat strained hypercloso framework in which there are no open (nontriangular, e.g., square, pentagonal, etc.) faces. The "C_{3v}" related structure (Figure 2) is formed from one DSD operation on the closo-D_{5h} framework. This is followed by a second DSD operation to convert the "C_{3v}" framework to another D_{5h} isomer (Figure 2). In contrast the "C_{2v}" related cage structure, formed from two simultaneous DSD operations, is essentially an unstable arachno seven-atom system (formally derived by uncapping two of the square faces of a nine-vertex closo tricapped trigonal prism). Rather than invoking the formation of either the hypercloso "C_{3v}" or arachno "C_{2v}" transition (or intermediate) structure, it seems more likely that the DSD rearrangement process involves the formation of only one square face (starting from the closo framework) followed by DSD closing of this face within the *same* time interval that the other square face is forming. Closing the second square face in the appropriate DSD fashion gives rise to rearranged product. The intermediate with only one square face can be considered a nido seven-atom system that is derived from a closo eight-atom cage by removing a *low*-coordination vertex atom. Such a nido species with only 16 cage electrons is expected to be more stable than the above arachno "C_{2v}" cage with the same number of cage electrons and is probably much less strained than the proposed capped-octahedral "C_{3v}" related intermediate containing a CB_3 tetrahedron.

Although the DSD mechanism is consistent with the rate data, it is possible that still other rearrangement routes could also explain the observed rate patterns. A mechanism that appears worthy of consideration is an "edge-twist" (ET), which may be implied from two studies[19,20] concerning $C_2B_4H_6$ structures. In the case of B-methyl derivatives of $C_2B_5H_7$ the application of 180° ET operations leads to the result that all three isomers are potentially in *direct* equilibrium with each other:

$$\begin{tikzcd} & \text{5-CH}_3\text{-2,4-C}_2\text{B}_5\text{H}_6 \arrow[dl, shift right, "k_a"'] \arrow[dr, shift left, "k_e"] & \\ \text{1-CH}_3\text{-} \arrow[ur, shift right, "k_b"'] \arrow[rr, shift left, "k_c"] & & \text{3-CH}_3\text{-} \arrow[ll, shift left, "k_d"] \arrow[ul, shift left, "k_f"] \end{tikzcd} \qquad (3)$$

The only manner in which this ET mechanism could agree with the observed rearrangement data (Figures 1 and 5), however, would entail small values of both k_e and k_f relative to all other rate constants. This is tantamount to the equilibrium conclusions (eq 1) reached from the DSD mechanism.

There is also the question of intramolecular methyl migration as a viable alternative to the observed rearrangement. If a methyl group migration mechanism were operational here, it is somewhat surprising that very close to the same minimum thermal conditions (295–300 °C) are required to cause observable rearrangement not only in the mono- and poly-B-methyldicarbaheptaborane derivatives[1] but also in the B-monochloro and B,B'-dichloro derivatives[21] as well. Should the B-methyl and B-chloro compounds all rearrange by the same general mechanism, the coincidence of rearrangement

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(18) This is performed in a manner analogous to a similar statistical weighting of rate constants on page 2882, lines 9–20, of T. Onak, A. P. Fung, G. Siwapinyoyos, and J. B. Leach, *Inorg. Chem.*, **18**, 2878 (1979); lines 19 and 20 of this reference should be corrected to read $k_a/k_b .../k_h$ (related to $k_h = 2.00$) are 12.2/15.8/5.00/14.84/26.4/11.8/3.84/2.00.

(19) M. J. S. Dewar and M. L. McKee, *J. Am. Chem. Soc.*, **99**, 5231 (1977).

(20) R. Camp, D. Marynick, G. Graham, and W. Lipscomb, *J. Am. Chem. Soc.*, **100**, 6781 (1978).

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

conditions suggests a cage fluxional process that need not be very dependent on the nature and number of substituents. By comparison, intramolecular substituent migration rates could well be expected to be considerably dependent on (a) some fraction of the B–X bond strengths (an expected ~55 kJ/mol difference for B–Cl vs. B–C),[22] (b) the number of such bonds (if the migration for polysubstituted compounds is concerted), and (c) steric influences in some instances (e.g., the tetramethyl derivative). Nevertheless, intramolecular substituent migration, although considered unlikely, cannot be entirely ruled out; but this problem probably cannot be settled until a $C_2B_5H_7$ molecule that is isotopically enriched at specific sites becomes a synthetic reality.

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Registry No. 5-CH_3-*closo*-2,4-$C_2B_5H_6$, 23810-32-4; 3-CH_3-*closo*-2,4-$C_2B_5H_6$, 23940-13-8; 1-CH_3-*closo*-2,4-$C_2B_5H_6$, 23810-31-3; *closo*-2,4-$C_2B_5H_7$, 20693-69-0.

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[22] K. Wade, "Electron Deficient Compounds", Thomas Nelson and Sons, London, 1971, p 62.

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Reduction Kinetics of Pentaamminecobalt(III) Complexes Containing 4,4'-Bipyridine and Related Ligands at Mercury, Platinum, and Gold Electrodes

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The electroreduction kinetics of pentamminecobalt(III) complexes containing 4,4'-bipyridine (BP), 1,2-bis(4-pyridyl)ethane, *trans*-1,2-bis(4-pyridyl)ethylene, pyridine, or pyrazine ligands were studied at mercury–, platinum–, and gold–aqueous interfaces in order to explore the ability of such nitrogen heterocycles to mediate electron transfer at metal surfaces. These reactivity patterns are compared with those for corresponding homogeneous reactions; the electrochemical reduction rates of the nitrogen-heterocycle-containing complexes were found to be considerably faster than expected from their outer-sphere homogeneous reactivities relative to the rates of $Co(NH_3)_5OH_2^{3+}$ and $Co(NH_3)_6^{3+}$ reduction. Likely causes of the apparent mediation of the heterogeneous reactions by the heterocyclic ligands are discussed. The primary factor appears to be the ability of these ligands to induce the adsorption of Co(III), as measured for $Co(NH_3)_5py^{3+}$ and $Co(NH_3)_5BP^{3+}$ at mercury electrodes by using chronocoulometry.

Introduction

We have recently been examining the electrochemical kinetics of various transition-metal complexes that engage in one-electron outer- and inner-sphere reactions at metal surfaces.[1-9] One aim of this work is to explore in a systematic manner the similarities and differences between the energetics of such simple redox reactions at metal electrodes and in homogeneous solution.[2,3,5,6,8,9] Our initial studies at the well-defined mercury–aqueous interface[1-4] have more recently been broadened to include a number of solid metals, particularly platinum, gold, and silver.[5,7] Methods have been developed for distinguishing between outer-sphere and some inner-sphere (ligand-bridged) reaction mechanisms at both mercury[1,10] and solid metal surfaces.[5] Large reactivity variations for some outer-sphere as well as anion-bridged pathways have been observed as the electrode material is altered,[5,7] illustrating the important influences that the electrode surface structure can exert upon the reaction energetics.

Although somewhat neglected by electrochemists, the reduction of pentaamminecobalt(III) complexes provides a valuable reactant class with which to explore structural factors in electrochemical kinetics, especially in view of the wealth of homogeneous kinetic information that has become available for such systems containing a wide variety of bridging ligands. We have found that the effect of systematic variations in the double-layer structure upon the outer-sphere reduction kinetics of $Co(NH_3)_5X$ complexes ($X = NH_3$, OH_2, F^-, OH^-) is uniformly in reasonable agreement with the predictions of the simple Gouy–Chapman–Stern–Frumkin (GCSF) model, both at mercury[2,11] and at solid electrodes.[5,7] Complexes containing adsorbing anionic ligands ($X = Cl^-$, Br^-, NCS^-, NO_3^-, etc.) are usually reduced via more facile ligand-bridged pathways,[2,5]

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[1] M. J. Weaver and T. L. Satterberg, *J. Phys. Chem.*, **81**, 1772 (1977).

[2] T. L. Satterberg and M. J. Weaver, *J. Phys. Chem.*, **82**, 1784 (1978).

[3] M. J. Weaver, *Inorg. Chem.*, **18**, 402 (1979).

[4] M. J. Weaver, *J. Phys. Chem.*, **83**, 1748 (1979).

[5] (a) K. L. Guyer, S. W. Barr, R. J. Cave, and M. J. Weaver, *Proc. Symp. Electrode Processes, 3rd*, 390 (1980); (b) K. L. Guyer and M. J. Weaver, submitted for publication; (c) S. W. Barr and M. J. Weaver, submitted for publication; (d) K. L. Guyer, S. W. Barr, and M. J. Weaver, *Proc. Symp. Electrocatalysis*, 377 (1982).

[6] M. J. Weaver, *J. Phys. Chem.*, **84**, 568 (1980).

[7] S. W. Barr, K. L. Guyer, and M. J. Weaver, *J. Electroanal. Chem. Interfacial Electrochem.*, **111**, 41 (1980).

[8] M. J. Weaver, P. D. Tyma, and S. M. Nettles, *J. Electroanal. Chem., Interfacial Electrochem.*, **114**, 53 (1980).

[9] M. J. Weaver, *Isr. J. Chem.*, **18**, 35 (1979).

[10] M. J. Weaver and F. C. Anson, *J. Am. Chem. Soc.*, **97**, 4403 (1975); *Inorg. Chem.*, **15**, 1871 (1976).

[11] M. J. Weaver, *J. Electroanal. Chem. Interfacial Electrochem.*, **93**, 321 (1978).