4×10^{-2} *M* Cr^{2+}, and 0.35 *M* $HClO_4$ was allowed to react for ~3 hr and then exposed to air to oxidize the excess chromium(II). The solution was then placed on a column (50 mm long and 10 mm in diameter) of Dowex 50W-X8 cation-exchange resin immersed in a cold bath at ~5°. The resin had been pretreated with dilute perchloric acid, water, 50% acetone, ethanol, and distilled water. The elution of chromium(III) product was carried out with decreasingly dilute solutions of a stock solution of 0.5 *M* $NaClO_4$ and 0.1 *M* $HClO_4$. A band with ion-exchange properties typical of a 2+ chromium(III) complex was eluted from the column with an eluent solution of about 50% dilution of the stock solution. The absorption spectrum of this product was recorded on a Cary Model 14 spectrophotometer. The total amount of chromium in this product was determined spectrophotometrically as chromate after oxidation with alkaline hydrogen peroxide.

Results

The total amount of chromium in the 2+ charged product from the ion-exchange experiment was equal to 96.5% of the initial $(NH_3)_5CrN_3^{2+}$. The maxima in the visible spectrum of this product are in good agreement with the values of 434 nm (ϵ 66.4 M^{-1} cm^{-1}) and 585 nm (ϵ 67.5 nm) reported by Swaddle and King[10] for $(H_2O)_5CrN_3^{2+}$. These results show that the reaction proceeds virtually completely by an inner-sphere mechanism with transfer of the azide ion ligand.

The kinetic results, which are summarized in Table I, are consistent with the rate law

TABLE I

KINETIC DATA FOR THE REDUCTION OF AZIDOPENTAAMMINECHROMIUM(III) BY CHROMIUM(II)

Temp, °C	$[H^+]$, *M*	$10^2[Cr^{2+}]$, *M*	$10^3[(NH_3)_5CrN_3^{2+}]$, *M*	10^2k_1,[a] M^{-1} sec^{-1}
15.0	0.20	6.06	1.172	0.842
24.8	0.20	6.36	0.614	1.82
	0.20	6.36	1.210	1.77
	0.20	3.18	1.266	1.78
	0.74	3.18	1.300	1.76
35.0	0.20	6.20	1.124	3.56
	0.20	6.06	1.085	3.55
	0.20	3.10	1.044	3.54
	0.74	3.10	1.196	3.47
44.0	0.20	3.03	1.134	6.60
	0.20	3.03	0.589	6.47
	0.74	3.03	1.124	6.47

[a] The temperature dependence of k_1 gives values for $\Delta H_1^{\ddagger}$ and $\Delta S_1^{\ddagger}$ of 12.4 ± 0.4 kcal mol^{-1} and −24.9 ± 1.3 cal mol^{-1} deg^{-1}, respectively. Errors are estimated standard errors, calculated from a least-squares best fit as described by P. D. Lark, *et al.*, "The Handling of Chemical Data," Pergamon Press, Oxford, 1968, p 148.

$$-\frac{d[(NH_3)_5CrN_3^{2+}]}{dt} = k_1[Cr^{2+}][(NH_3)_5CrN_3^{2+}] \qquad (1)$$

The activation enthalpy and entropy $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are given in Table II along with values for the chromium(II) reductions of other chromium(III) systems for comparison.

The data in Table II for $(NH_3)_5CrX^{2+}$ systems show that the reactivity order for varying X^- is $I^- > Br^- > Cl^- > N_3^- > F^-$. This is the same reactivity order observed for the analogous reaction of $(NH_3)_5CoX^{2+}$ complexes;[3,4] however the overall changes in reactivity are much greater in the chromium(III) system. This may simply be due to a greater spread in thermodynamic stability of the $(NH_3)_5CrX^{2+}$ systems, as is found in the $(H_2O)_5CrX^{2+}$ system. Unfortunately very few data on thermodynamic stability are available for the chromium(III)–ammine complexes. It may also be noted that the rate trends in the $(NH_3)_5CrX^{2+}$ system are largely due to changes in $\Delta H^{\ddagger}$. Values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are not available for the reduction of the cobalt(III) complexes.

TABLE II

KINETIC RESULTS FOR THE CHROMIUM(II) REDUCTION OF SOME CHROMIUM(III) COMPLEXES

Oxidant	k_1,[a] M^{-1} sec^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal mol^{-1} deg^{-1}
$(NH_3)_5CrF^{2+}$ [b]	2.7×10^{-4}	13.4	−30
$(NH_3)_5CrN_3^{2+}$ [c]	1.8×10^{-2}	12.4	−24.9
$(NH_3)_5CrCl^{2+}$ [b]	5.1×10^{-2}	11.1	−27[d]
$(NH_3)_5CrBr^{2+}$ [b]	0.32	8.5	−33
$(NH_3)_5CrI^{2+}$ [b]	5.5	...	...
$(H_2O)_5CrF^{2+}$ [e]	2.3×10^{-2}	13.7	−20
$(H_2O)_5CrCl^{2+}$ [f]	29	8.0	−25
$(H_2O)_5CrN_3^{2+}$ [g]	6.9	9.6	−22.8

[a] Values calculated at 25° and $I = 1.0$ unless otherwise stated. [b] Reference 2. [c] This work. [d] This value is incorrectly given as −23 in ref 2. [e] D. L. Ball and E. L. King, *J. Amer. Chem. Soc.*, **80,** 1091 (1958). [f] Values obtained by interpolation from results at $I = 0.2$ and 5.0 *M:* R. V. James and E. L. King, *Inorg. Chem.*, **9,** 1301 (1970). [g] R. Snellgrove and E. L. King, *ibid.*, **3,** 288 (1964).

Comparison of the $(NH_3)_5CrX^{2+}$ and $(H_2O)_5CrX$ complexes for $X^- = Cl^-$ and N_3^- indicates the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are more favorable by ~3 kcal mol^{-1} and 2 cal mol^{-1} deg^{-1} for the pentaaquo systems. However, this trend is not borne out for $X^- = F^-$, but the correlation is too limited as yet to know whether there is something unusual about the reduction of $(H_2O)_5CrF^{2+}$.[11] It may be noted that if the changes recorded above did hold for $(H_2O)_5CrF^{2+}$, then the calculated rate constant at 25° would be ~0.11 or five times greater than the observed value. Therefore the activation parameters cannot be explained by the intervention of some more favorable mechanism for $(H_2O)_5CrF^{2+}$. Qualitatively the differences in reactivity between the pentaaquo and pentaammine systems might be due to the lower ligand rearrangement energies in the aquo system as has been suggested by Pennington and Haim[12] and discussed with reference to chromium(III) by DeChant and Hunt.[13]

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(11) If this correlation holds approximately for $(H_2O)_5CrBr^{2+}$ and $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are estimated to be 5.5 kcal mol^{-1} and −30 cal mol^{-1} deg^{-1}, then the calculated rate constant at 0° is 63 M^{-1} sec^{-1}. The latter value is consistent with the lower limit of 60 M^{-1} sec^{-1} given by D. L. Ball and E. L. King, *J. Amer. Chem. Soc.*, **80,** 1091 (1958).

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Reactions of 1,6-Dicarba-*closo*-hexaborane(6)

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As an extension of our recent studies[2] of the carborane $2,4\text{-}C_2B_5H_7$, we have examined a few character-

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istic reactions of the next smaller homolog of the $C_2B_{n-2}H_n$ polyhedral series, 1,6-$C_2B_4H_6$. From nmr and mass spectroscopic evidence, this molecule has been assigned[3] an octahedral structure with nonadjacent carbon atoms, but no chemistry has been described other than deuterium exchange with deuteriodiborane.[3] Since the calculated ground-state charge distribution[4] places slight negative charge (0.050−) on each carbon atom and a small positive charge (0.025+) on each boron, the possibility of electrophilic attack at carbon, rather than boron, cage positions could not *a priori* be ruled out.

Lithiation and Alkylation.—The room-temperature reaction of 1,6-$C_2B_4H_6$ with excess *n*-butyllithium in an ether–hexane solvent mixture was extremely slow, in comparison with the corresponding treatment of 2,4-$C_2B_5H_7$[2] and of 1,2-$C_2B_{10}H_{12}$.[5–7] No precipitation was

$$HCB_4H_4CH + 2C_4H_9CLi \longrightarrow LiCB_4H_4CLi + 2C_4H_{10}$$

evident for several hours, and conversion to the dilithio compound was incomplete even after 24 hr. However, glpc analysis of the solution after 48 hr indicated no remaining unreacted carborane.

A suspension of the white dilithio carborane in ether reacted as expected with methyl iodide to produce the *C,C′*-dimethyl derivative, which was characterized from its ^{11}B and proton nmr spectra, mass spectra, and infrared spectra. Small quantities of unidentified carboranes of higher molecular weight were also obtained.

$$LiCB_4H_4CLi + 2CH_3I \longrightarrow CH_3CB_4H_4CCH_3 + 2LiI$$

Bromination.—The parent carborane reacted smoothly with excess bromine over $AlBr_3$ in carbon disulfide at 0°, producing only the *B*-bromo derivative in significant yield. Glpc analysis gave no evidence for any *C*-bromo or *B*-polybromo carboranes.

In order to effect bromine substitution at carbon, the *C,C′*-dilithio derivative was treated with an equimolar quantity of methyl iodide, and the presumed methyl lithio derivative was then brominated as in the scheme

$$LiCB_4H_4CLi + CH_3I \xrightarrow[-LiI]{(C_2H_5)_2O} CH_3CB_4H_4CLi \xrightarrow[-LiBr]{Br_2,\ (C_2H_5)_2O} CH_3CB_4H_4CBr$$

Gas chromatography of the volatile products at 100° unfortunately was accompanied by partial decomposition with formation of brownish black residues, but the expected methylbromo derivative was isolated in pure form and identified by mass spectroscopic analysis. In addition, 1,6-$(CH_3)_2$-1,6-$C_2B_4H_4$ was found, indicating that the monomethylation of $Li_2C_2B_4H_4$ is complicated by side reactions similar to those encountered[2] with the mono- and dilithio derivatives of 2,4-$C_2B_5H_7$.

Experimental Section

1,6-Dicarba-*closo*-hexaborane (6) was purified *via* preparative-scale glpc[2] from a mixture of the lower carboranes supplied by Chemical Systems, Inc. Reagent grade solvents were used except for *n*-pentane, which was washed with concentrated H_2SO_4 and acidic $KMnO_4$ solution and distilled from $LiAlH_4$ prior to use. Diethyl ether was distilled from $LiAlH_4$ immediately before using. *n*-Butyllithium in hexane (Alfa), CP grade aluminum powder (Baker), bromine (Baker), and methyl iodide (Baker) were used as received. All manipulations were carried out in a high-vacuum system.

Lithiation and Alkylation.—The parent carborane (0.62 mmol) was stirred with 1.88 mmol of *n*-butyllithium in a mixture of 1 ml of hexane and 2 ml of diethyl ether. After 2 hr there was no visible change in the clear yellow solution, but within 5 hr the solution had become slightly murky. After 48 hr very little solid was evident, but replacement of the solvent by pentane produced a gray precipitate which was filtered *in vacuo*, washed with 2 ml of pentane, and dried to a white solid on the filter. The solid dilithiocarborane was suspended in 2.1 ml of dry diethyl ether and 1.28 mmol of methyl iodide was added. After 6 hr at room temperature the solution was nearly clear, but the reaction was allowed to continue an additional 18 hr. Separation of the volatile materials by glpc gave only one major product, characterized as 1,6-$(CH_3)_2$-1,6-$C_2B_4H_4$ (0.13 mmol, corresponding to 21% of theory). The mass spectrum exhibits a high-mass cutoff at *m/e* 102, corresponding to the $^{12}C_4{}^{11}B_4H_{10}{}^+$ parent ion, while the gas-phase ir spectrum (30 mm) contains bands at 3070 (w), 3047 (w), 3017 (m), 2988 (m), 2948 (vs), 2887 (vs), 2650 (vvs), 1504 (w), 1485 (w), 1470 (s), 1451 (w), 1427 (w), 1385 (m), 1320 (m, b), 1146 (s), 976 (vs), and 917 cm^{-1} (vs). The 32.1-MHz ^{11}B nmr spectrum consists of one doublet at δ +14.5 ppm relative to boron trifluoride etherate (J = 181 Hz), confirming that all borons are equivalent and no B-substitution has occurred.[8]

Preparation of 2-Br-1,6-$C_2B_4H_5$.—A 3.0-mmol quantity of bromine was added to 1.00 g-atom of aluminum powder in 4.0 ml of carbon disulfide. After stirring 30 min, 1.00 mmol of 1,6-$C_2B_4H_6$ was condensed into the mixture at −196°. The solution was warmed to −10° for 0.5 hr, followed by stirring for 16 hr at 0°. Gas chromatography of the volatile contents gave unreacted carborane, solvent, and 2-Br-1,6-$C_2B_4H_5$ (0.05 mmol). Since no other volatile carborane products were obtained, the low yield of the bromo derivative is attributed to side reactions involving formation of nonvolatile polymeric carboranes.[2] Careful analysis of all fractions of the volatile materials gave no evidence of any other bromocarborane species. The mass spectrum of the 2-bromo derivative displays a cutoff at *m/e* 154, corresponding to the $^{81}Br^{12}C_2{}^{11}B_4{}^1H_5{}^+$ parent ion. The 32.1-MHz ^{11}B nmr spectrum exhibits a doublet of area 2 at δ +16.3 ppm (J = 193 Hz), a doublet of area 1 at δ +18.2 ppm (J = 205 Hz), and a singlet of area 1 at δ +27.7 ppm, assigned to the B(3,5)–H, B(4)–H, and B(2)–Br resonances, respectively. The 100-MHz proton nmr spectrum contains nearly superimposed B–H quartets centered at δ −2.17 ppm relative to tetramethylsilane (J = 195 Hz) and a sharp C–H singlet at −3.50 ppm. The gas-phase ir spectrum exhibits bands at 3123 (w), 2655 (vs), 1517 (m), 1337 (m), 1257 (vs), 1195 (vs), 1147 (vs), 1115 (sh), 1024 (vs), 937 (m), 867 (s), 740 (w), and 648 cm^{-1} (w).

Preparation of 1-CH_3-6-Br-1,6-$C_2B_4H_4$.—A 1.02-mmol quantity of 1,6-$C_2B_4H_6$ was lithiated with 2.35 mmol of *n*-butyllithium in ether–pentane and the resulting dilithiocarborane was washed and dried as described above. The latter compound was suspended in 3 ml of diethyl ether and 0.92 mmol of methyl iodide was added. After stirring 24 hr, a solution of 1.10 mmol of bromine in diethyl ether was added slowly in small portions; the first few portions were rapidly decolorized, but addition of the remaining bromine gave a red-orange color which persisted. The reaction mixture was stirred for 20 hr at room temperature, after which all volatile materials were distilled under high vacuum and analyzed by glpc. Other than solvent and traces of unidentified materials, the only components of the product mixture were 1,6-$(CH_3)_2$-1,6-$C_2B_4H_4$, identified from its glpc retention volume and mass spectrum (see above), $CH_3BrC_2B_4H_4$, and $CH_3IC_2B_4H_4$. The mass spectrum of the methylbromo derivative contains a sharp cutoff at *m/e* 168, corresponding to the ^{81}Br-$^{12}C_3{}^{11}B_4{}^1H_7{}^+$ parent ion, and the fragmentation pattern in the parent region is in good agreement with the pattern calculated for a species containing four boron, one bromine, and three carbon atoms in their natural isotopic abundances. The agreement was further improved when the ionization voltage was reduced to a

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low level (12 ev) in order to minimize hydrogen loss in the spectrometer. The methyliodo derivative, which undoubtedly resulted from iodination of $CH_3LiC_2B_4H_4$ by I_2 formed from LiI and Br_2, was identified from its mass spectroscopic cutoff at *m/e* 214, corresponding to the $^{127}I^{12}C_3{}^{11}B_4{}^1H_7{}^+$ parent ion, and its fragmentation pattern, which closely matches the profile calculated for the composition indicated.

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Activation Parameters for Substitution Kinetics of Methyl(aquo)bis(dimethylglyoximato)cobalt(III)

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Crumbliss and Wilmarth[1] (see also ref 2) have reported that the substitution kinetics of methyl(aquo)bis(dimethylglyoximato)cobalt(III) with various ligands are quite rapid compared to other bis(dimethylglyoximato)cobalt(III) complexes.[3-7] The rates were found to be as much as 10^5 times faster than the comparable reactions with a nitrite[3] ion in place of the methyl group showing that the methyl group exhibits a very large trans effect. Because of the interest in these compounds as models for vitamin B_{12}[8] and because of this large rate enhancement by the methyl group we wish to report the activation parameters of two of these reactions, the reactions with thiocyanate and with pyridine.

Experimental Section

Kinetic Measurements.—Chemicals used for kinetic measurements were reagent grade. Sodium thiocyanate was once recrystallized and the pyridine used was spectroquality grade (Matheson Coleman and Bell). Deionized water was used for preparation of solutions. Methyl(aquo)bis(dimethylglyoximato)cobalt(III) (abbreviated as $CH_3Co(DH)_2OH_2$) was prepared by the method of Schrauzer and Windgassen.[9]

The rate of ligand substitution was observed spectrophotometrically at 445 nm with a Beckman Model 260 kinetic system employing a stopped-flow apparatus. At this wavelength the molar extinction coefficient of the aquo derivative is 1430, of the pyridine derivative is 465, and of the thiocyanate derivative is 827.

Kinetic observations were carried out under pseudo-first-order kinetic conditions; *i.e.*, the concentration of NCS^- or pyridine was 50–100 times that of $CH_3Co(DH)_2OH_2$. The concentration of $CH_3Co(DH)_2OH_2$ was in the range 2.0×10^{-4} to 5.0×10^{-4} *M*. Solutions of $CH_3Co(DH)_2OH_2$ were rapidly mixed with solutions of pyridine or NCS^-. The temperature was maintained constant to within ±0.5° and was reproducible to within ±1°. Observed pseudo-first-order rate constants, k_{obsd}, were estimated directly from the slope of a plot of log (absorbance) *vs.* time stored on the instrument oscilloscope and the appropriate circuit constants. The total error in the rate constants, k_{obsd}, was estimated from the total absorbance change during the reaction to be 10%. Second-order rate constants, k_1, M^{-1} sec^{-1}, for pyridine substitution were obtained by the relationship $k_1 = k_{obsd}/[py]$. The standard deviation of values for k_1 was ±5% for several observations at three different pyridine concentrations. The rate constants for thiocyanate substitution were obtained from the slope and intercept of plots of k_{obsd} *vs.* $[NCS^-]$ for five concentrations of thiocyanate. The error in the rate constants was graphically estimated to be ±3%.

Formation Constants.—Equilibrium constants for the formation of methyl(pyridinato)bis(dimethylglyoximato)cobalt(III) were determined spectrophotometrically at 445 nm by a Cary recording spectrophotometer, Model 14, maintained at constant temperature with a circulating water bath. Equilibrium constants *K* were determined from linear plots of $(A - B)/B$ *vs.*

$$K = \frac{[CH_3Co^{III}(DH)_2py]}{[CH_3Co^{III}(DH)_2OH][py]}$$

[py], where *A* is the difference in absorption between $CH_3(DH)_2OH_2$ only and $CH_3Co(DH)_2OH_2$ in the presence of a 1000-fold excess of pyridine, and *B* is the difference in absorption between $CH_3Co(DH)_2OH_2$ only and $CH_3Co(DH)_2OH_2$ in the presence of an equilibrium pyridine concentration. The error in the equilibrium constants was estimated graphically to be ±5%.

Results and Discussion

The formation constants K_f, M^{-1}, for methyl(pyridinato)bis(dimethylglyoximato)cobalt(III) at various temperatures are presented in Table I. The standard enthalpy and entropy for the reaction were -5.1 ± 0.4 kcal mol^{-1} and -2 ± 1.5 eu, respectviely, as estimated from the slope and intercept of a plot of log K_f *vs.* $1/T$.

TABLE I
THERMODYNAMIC DATA FOR THE
$CH_3Co(DH)_2OH_2 + py \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} CH_3Co(DH)_2py$
EQUILIBRIUM IN WATER[a]

Temp, °C	$10^{-3}K_f$, M^{-1}	Temp, °C	$10^{-3}K_f$, M^{-1}	Temp, °C	$10^{-3}K_f$, M^{-1}
10	4.81[b]	30	1.58	40	1.12
20	1.90	35	1.24	45	0.96
25	1.66				

[a] The concentration of $CH_3Co(DH)_2OH_2$ was 2.0×10^{-4} *M* and the concentration of pyridine was in the range 2.0×10^{-3} to 1.6×10^{-2} *M*. ΔH^* and ΔS^* estimated from the slope and intercept of a plot of log K_f *vs.* $1/T$ were -5.1 ± 0.4 kcal mol^{-1} and -2 ± 1.5 eu, respectively. [b] Data of Crumbliss and Wilmarth[1] at unit ionic strength added for comparison.

For the substitution reaction

$$CH_3Co(DH)_2OH_2 + X \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} CH_3Co(DH)_2X + H_2O$$

the observed rate constants, k_{obsd}, are related to the individual rate constants by the relationship $k_{obsd} = k_1[X] + K_{-1}$. If $k_1[X] > k_{-1}$, then k_1 may be obtained from the relationship $k_1 = k_{obsd}/[X]$. Second-order rate constants for pyridine substitution were calculated by this method. However, for the thiocyanate reaction k_{-1} is not negligible compared to the value of $k_1(NCS^-)$. Therefore, k_1 and k_{-1} were estimated from the slope and intercept of a plot of k_{obsd} *vs.* $[NCS^-]$. The rate

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