was used to obtain $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, the activation enthalpy and entropy. The kinetic parameters are summarized in Table II along with other results for

TABLE II
SUMMARY OF KINETIC PARAMETERS FOR $Al(L)_6^{3+}$

L, ligand	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal deg^{-1} mol^{-1}	k(25°), sec^{-1}	L, ligand	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal deg^{-1} mol^{-1}	k(25°), sec^{-1}
H_2O	27.0	28.0	0.13	DMSO	20.0	5.6	0.34
TMP	20.8	8.3	0.36	DMF	17.7	−2.3	0.30

Al^{3+}. The results for $Al(DMF)_6^{3+}$ and $Al(DMSO)_6^{3+}$ were analyzed *via* eq 1. With the exception of $Al(H_2O)_6^{3+}$ the kinetic parameters show a remarkable consistency. Several factors may contribute to this result and it is not possible definitively to attribute this to a single effect.[10]

The excess line widths for $Al(TMP)_6^{3+}$ in TMP–nitromethane mixed solvents at 327.2°K are summarized in Table III. The excess line widths and

TABLE III
SUMMARY OF RESULTS FOR 0.10 *M* $Al(TMP)_6^{3+}$ IN TMP–NITROMETHANE MIXED SOLVENTS AT 327.2°K

Mole ratio of free TMP/bound TMP	$\Delta\nu_B - \Delta\nu_B^0$	τ_B, sec	$\Delta\nu_F - \Delta\nu_F^0$	τ_F, sec	P^a	P^b
0.58	3.1	0.103	6.0	0.053	0.37	0.34
2.02	3.3	0.097	1.7	0.187	0.67	0.66
6.36	3.3	0.097	0.6	0.53	0.86	0.85
13.98	3.1	0.103	0.2	1.6	0.93	0.94
25.04	3.3	0.097			0.96	

[a] Calculated from $\tau_F/(\tau_B + \tau_F)$. [b] Calculated from composition of solution.

therefore the mean lifetimes are independent of the composition of the solvent. $Al(TMP)_6^{3+}$ in pure nitromethane showed no evidence of exchange. Note particularly that the ratio of free to bound ligand varies by a factor of 43. The low range of the above ratio allows us definitively to conclude that the immediate environment of the complex, the second coordination sphere, must contain a significant amount of nitromethane. This strongly suggests that a truly dissociative mechanism (D mechanism) is involved rather than a dissociative interchange mechanism, I_d.[11]

The excess line width of the free ligand can also be used to obtain the exchange rate. An equation similar to eq 1 is applicable with τ_F equal to the mean lifetime of TMP in the bulk solution and the line widths appropriately redefined. In a pure solution of the ligand, with the concentration of complex typically utilized, $1/T_{2F}^0$ is always much greater than $1/\tau_F$ and therefore the exterior solvent peak does not show a significant increase in line width. However, in the mixed solvent the above limiting condition is not applicable and the mean lifetime in the bulk solution can be calculated. These results are summarized in Table III.

The probability, P, of a ligand molecule being in the bulk solution can be calculated *via* the equation[12] $P = \tau_F/(\tau_B + \tau_F)$. P may also be calculated from the composition of the solution. The values of P calculated by the above methods are in good agreement (Table III). Since the mean lifetime in the primary coordination sphere is independent of solvent composition, the mean lifetime of the bulk solvent TMP molecules must be dependent on the composition of the solvent.

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(11) C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, New York, N. Y., 1968.
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Kinetic Study of the Chromium(II) Reduction of Substituted Glycinatopentaamminecobalt(III) Ions

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Most of the carboxylatopentaamminecobalt(III) ions studied to date as oxidizing agents have been doubly charged cations. The rates of reduction of *N*-methyl-substituted glycinatopentaamminecobalt(III) ions by Cr(II) in aqueous acidic solution have been measured to determine the effect of an increase in positive charge on the kinetic behavior of carboxylatopentaamminecobalt(III) complexes. Also of interest is the possibility that steric crowding as alkyl substitution on the ammonium nitrogen increases may hinder adjacent carboxyl attack sufficiently to force a change in mechanism from inner- to outer-sphere reduction.

Experimental Section

All solutions were prepared from deionized water which had been distilled from an alkaline permanganate solution and redistilled twice. Nitrogen gas used to deoxygenate solutions for kinetic work was passed through chromous perchlorate gas-scrubbing towers to remove oxidizing impurities. Hexaaquochromium(III) perchlorate was prepared by reducing primary standard potassium dichromate with excess hydrogen peroxide and boiling the solution for several hours to destroy residual peroxide. Chromous solutions were prepared by reducing hexaaquochromium(III) perchlorate over amalgamated zinc under an atmosphere of nitrogen. Glycinatopentaamminecobalt(III) perchlorate salts were prepared by the method of Quagliano, *et al.*[1] Crystalline hydrated lithium perchlorate, pretreated with Cr(II) to remove oxidizing impurities, was kindly furnished by Dr. M. V. Olson. A solution of this salt was used to maintain the ionic strength of reaction mixtures at 1.0 during the determination of acid dependences. Reagent perchloric acid was used for this purpose in all of the runs reported in Table II. Dowex 50W-X2 analytical grade cation-exchange resin, furnished by Bio-Rad Laboratories, was cleaned by the method of Deutsch[2] and was used in the sodium form.

The hexaaquochromium(III) perchlorate stock solution was assayed by performing analyses for chromium, perchlorate, and free acid by methods previously described.[2] The lithium perchlorate solution was standardized by determining its total perchlorate concentration. Microanalyses (Table I) of pentaammine-

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(2) E. Deutsch and H. Taube, *Inorg. Chem.*, **7**, 1532 (1968).

TABLE I
ANALYTICAL DATA

Compound	Calcd, % C	H	N	Cl	Found, % C	H	N	Cl
$[(NH_3)_5CoOOCCH_2NH_3](ClO_4)_3$	4.6	3.9	16.2	20.6	4.7	3.9	16.1	19.7
$[(NH_3)_5CoOOCCH_2NH_2(CH_3)](ClO_4)_3$	6.78	4.17	15.81	20.00	6.79	4.32	17.13	19.84
$[(NH_3)_5CoOOCCH_2NH(CH_3)_2](ClO_4)_3$	8.81	4.43	15.41	19.49	8.71	4.27	15.74	19.41
$[(NH_3)_5CoOOCCH_2N(CH_3)_3](ClO_4)_3$	10.73	4.68	15.02	19.00	10.72	4.82	15.21	19.24

cobalt(III) complexes were performed by the Microanalytical Laboratory, Stanford University. Several recrystallizations did not improve the agreement between calculated and observed % N for the *N*-methylglycinato complex; the high result may reflect contamination of the cobalt salt with tetraamminecobalt(III) species.

To determine the amount of free glycine present among the products of the reduction of the glycinatopentaaminecobalt(III) ion by Cr(II), it was necessary to absorb the reaction mixture on an ion-exchange column to separate the organic molecule from colored metal ions. The complex (0.53 mmol) was reduced with an excess of Cr(II) in 0.1 *M* $HClO_4$, and the product mixture was added to a 23 × 2 cm cation-exchange column, stored at 5° to minimize aquation of the glycinatochromium(III) product. The effluent was collected until the first colored band, Co^{2+}, was about to be eluted by a 1 *M* $LiClO_4$, 0.1 *M* $HClO_4$ solution and then prepared for analysis by neutralizing strong acid with NaOH and diluting in a volumetric flask.

Glycine was determined spectrophotometrically by the method of Spies.[3] Matheson Coleman and Bell ammonia-free glycine was used in the preparation of standards.

Several trial runs were performed to test the assumption that free glycine is quantitatively recovered from the column before Co^{2+} is eluted. Solutions containing known amounts of $CoCl_2 \cdot 6H_2O$, $HClO_4$, and glycine were subjected to the same ion-exchange procedure as above; results of glycine analyses for these text mixtures indicated that a quantitative separation of glycine from Co^{2+} was achieved in each case.

The kinetics of the Cr(II) reduction of glycinatopentaamminecobalt(III) complexes was followed at 501 nm using a Cary 14 recording spectrophotometer. Chromous solution was injected with a syringe into a serum-capped 10-cm cell with quartz faces containing the cobalt complex and enough $HClO_4$–$LiClO_4$ to give a final ionic strength of 1.0. Absorbance measurements were recorded continuously while the cell rested submerged in a water-filled compartment with quartz windows which was continually supplied with fresh water from a constant temperature bath. Temperature variation was less than ±0.1°.

Pseudo-first-order conditions for Cr(II) were employed in all runs. Initial concentrations of chromous ion and of the cobalt complexes were approximately 0.100 and 0.001 *M*, respectively. Rate constants were evaluated from plots of log $(A_t - A_\infty)$ *vs.* time, where A_t and A_∞ are the absorbances at time t and after the reaction is complete, respectively.

Results and Discussion

Kinetic data for the reduction of glycinatopentaamminecobalt(III) ions by Cr(II) are summarized in Table II. Calculations were based on plots of log $(A_t - A_\infty)$ *vs.* time which were linear to at least 90% completion of the reaction. Experiments in which the initial chromous ion concentration was varied from 0.025 to 0.100 *M* verified that the observed second-order rate constants are not dependent on the reducing agent concentration. The data are consistent with the simple rate law

$$-d[Co(III)]/dt = k_1[Cr(II)][(NH_3)_5Co^{III}L^{3+}]$$

Activation parameters taken from Eyring plots are given in Table III and are compared with values found for other carboxylatopentaamminecobalt(III) ions. Estimated uncertainties in the activation parameters for the substituted glycinatopentaamminecobalt(III) ions are ±0.2 kcal/mol in $\Delta H^{\pm}$ and ±1 eu in $\Delta S^{\pm}$.

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TABLE II
KINETIC DATA FOR THE REDUCTION OF GLYCINATOPENTAAMMINECOBALT(III) IONS BY CHROMIUM(II)[a]

Ligand	*T*, °C	10^3k_1, M^{-1} sec^{-1} [b]
Glycine	14.8	3.8
	25.0	6.4
	34.4	9.0
	45.5	15.2
N-Methylglycine	15.5	2.8
	24.9	4.4
	34.4	6.8
	44.4	10.9
N,N-Dimethylglycine	15.3	2.3
	24.9	3.8
	34.7	6.0
	45.3	8.4
N,N,N-Trimethylglycine	14.9	0.97
	24.9	1.6
	34.2	2.4
	45.4	3.9

[a] μ = 1.0, $[H^+]$ = 0.55 *M*. [b] Each value the mean of at least two runs.

TABLE III
COMPARISON OF KINETIC DATA FOR THE REDUCTION OF CARBOXYLATOPENTAAMMINECOBALT(III) IONS BY CHROMIUM(II)

Ligand	k_1, M^{-1} sec^{-1} [a]	$\Delta H^{\pm}$, kcal/mol	$\Delta S^{\pm}$, eu	Ref
—OOCCH$_3$	0.35[b]	8.2	−33	4
—OOCC(CH$_3$)$_3$	0.007[b]	11.1	−31	4
—OOCCH$_2$Cl	0.012[b]	8.9	−33	4
—OOCCF$_3$	0.017[b,c]	9.3	−35	4
—OOCCH$_2$NH$_3^+$	0.064[d]	7.7	−38	This work
—OOCCH$_2$NH$_2$(CH$_3$)$^+$	0.044[d]	8.0	−38	This work
—OOCCH$_2$NH(CH$_3$)$_2^+$	0.038[d]	7.5	−40	This work
—OOCCH$_2$N(CH$_3$)$_3^+$	0.016[d]	7.7	−41	This work

[a] μ = 1.0, 25° unless otherwise stated. [b] $[H^+]$ = 0.1 *M*. [c] μ = 0.2. [d] $[H^+]$ = 0.55 *M*.

Five runs in the range 0.019 $M \leq [H^+] \leq$ 0.541 *M* showed that there is no hydrogen ion dependence of the rate of reduction of $(NH_3)_5Co^{III}gly^{3+}$ by Cr^{2+} (k_1 = 0.064 ± 0.001 M^{-1} sec^{-1}, 25°). This value is close to that reported by Kopple and Svatos[4] (k_1 = 0.06 M^{-1} sec^{-1}, 26°, μ = 1.0) but is in disagreement with Fraser's result[5] (k_1 = 0.53 M^{-1} sec^{-1}, 24°). Titration of the glycinato complex with NaOH gave an estimate of the ammonium pK_a as 8.5 (μ = 0.03). Protonation of this ion is thus essentially complete over the entire range of acid concentrations employed. The comparable pK_a of pure glycine[6] is 9.78; coordination to $(NH_3)_5Co^{III}$ thus lowers the pK_a about 1.3 units.

A maximum of 4% of the glycine in $(NH_3)_5Co^{III}gly^{3+}$ is released into solution upon reduction of the complex by Cr(II), confirming that chromous ion reacts with this ion predominantly by an inner-sphere mechanism. The similarity of activation parameters among all of the glycinatopentaamminecobalt(III) ions studied implies no change in the mechanism of reduction occurs

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(5) R. T. M. Fraser, *Inorg. Chem.*, **3**, 1561 (1964).
(6) B. B. Owen, *J. Amer. Chem. Soc.*, **56**, 24 (1934).

as methyl substitutions on the ammonium nitrogen are made. Attempts at isolating pure solutions of the glycinatochromium(III) product by ion exchange were frustrated by difficulties in achieving complete separation from hexaaquochromium(III).

Barrett[7] has found spectral evidence for the protonation of the acetatopentaamminecobalt(III) ion and attributes the decrease in its rate of chromous reduction as acidity increases to this effect. The absence of such an effect in the reduction of the glycinatopentaamminecobalt(III) ion is not surprising in light of a study of the aquation of this and other amino acid–pentaamminecobalt(III) complexes.[8] The rate constant for the aquation path first order in hydrogen ion concentration is considerably larger for L = acetate[9] than it is for L = glycine, *N*-methylglycine, or *N,N,N*-trimethylglycine; the electrostatic influence of the ammonium group is thought to hinder protonation of the coordinated carboxyl function.

Comparison of activation parameters for the Cr(II) reduction of the glycinato and acetato complexes shows that the slower reduction rate for the former complex may be attributed principally to an activation entropy value more negative by 5 eu. The qualitative difference in $\Delta S^{\pm}$ for the two reactions is consistent with expectations, as the activated complex for the chromous reduction of the glycinatopentaamminecobalt(III) ion must bear an extra positive charge. The factor of 4 decrease in room-temperature reduction rates from the glycinato to the *N,N,N*-trimethylglycinato complex is reflected in a difference of only 3 eu in $\Delta S^{\pm}$. Experiments with molecular models[7] have suggested that as long as at least one α hydrogen is present, a configuration can be found for which steric repulsions in the approach of chromous ion to acetatopentaamminecobalt(III) derivatives are not expected to differ significantly from one complex to the next.

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Photochemical Substitution Reactions of Substituted Group VI Metal Carbonyls

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During the early 1960's Strohmeier[1] published several papers on the photochemical substitution reactions of metal carbonyls and their derivatives. More recently there has been additional interest in the photolysis of group VI metal carbonyls.[2-7] Most of these studies have centered around the photolysis of the parent hexacarbonyls and the nature of the species $M(CO)_5$ generated in these reactions. We have reported the photochemical reaction of $Mo(CO)_5NHC_5H_{10}$ with ^{13}CO to produce $Mo(CO)_4(^{13}CO)NHC_5H_{10}$, preferentially labeled in the equatorial positions.[8]

In this paper we report an extension of our initial study into the photolysis of substituted metal carbonyls to include photochemical substitution reactions of $M(CO)_5L$ compounds with Lewis bases as well as ^{13}CO (eq 1), where M = Cr, Mo, or W; L = an amine or

$$M(CO)_5L + L' \xrightarrow{h\nu} M(CO)_4LL' + CO \qquad (1)$$

phosphine; and L′ = an amine, phosphine, or ^{13}CO. The preparation of new mixed (phosphine–amine)metal tetracarbonyl compounds by this procedure is described within.

Studies have been made of the dependence of the stereochemistries of the products and rates of the substitution process on the nature of the ligands L and L′ and the wavelength region of the irradiation source. Correlation of the photochemical substitution process with the electronic spectra of the $M(CO)_5L$ compounds has also been initiated.

Experimental Section

Preparation and Purification of Materials.—The starting materials, $M(CO)_5L$ compounds, were prepared by photolysis of the corresponding $M(CO)_6$ in the presence of the appropriate entering ligand L. Purification was affected by recrystallization from hexane or chloroform–methanol solvents. Infrared spectra in the carbonyl region and melting points were in agreement with published data. Tetrahydrofuran was refluxed and distilled over $LiAlH_4$ under dry nitrogen.

All photochemical reactions were carried out in a cylindrical quartz vessel fitted with an internal water condenser to maintain the solutions at about 25°. The reaction mixtures were stirred by means of a magnetic stirrer and were kept under a dry nitrogen atmosphere during the irradiation period. A 550-W Hanovia mercury lamp was positioned at a constant distance (approximately 10 in.) from the reaction vessel and was enclosed with a Pyrex filter sleeve when desired. This filter sleeve has the absorption characteristics indicated in Figure 1. The general method employed for preparative-scale reactions is outlined below specifically for *cis*-$W(CO)_4[P(C_6H_5)_3]NC_5H_5$.

Preparation of *cis*-$W(CO)_4[P(C_6H_5)_3]NC_5H_5$.—In a quartz reaction vessel 0.6 g (1.0 mmol) of $W(CO)_5P(C_6H_5)_3$ and 2.0 g (25 mmol) of pyridine in 20 ml of freshly distilled THF were irradiated under a nitrogen atmosphere for approximately 0.5 hr. An infrared spectrum of the resultant bright yellow solution revealed the presence of 70–80% *cis*-$W(CO)_4[P(C_6H_5)_3]NC_5H_5$ in addition to the starting material $W(CO)_5P(C_6H_5)_3$.

The solvent was removed at room temperature under vacuum to yield a bright yellow solid. This material was extracted with hexane to remove excess $W(CO)_5P(C_6H_5)_3$, *cis*-$W(CO)_4LL'$ compounds being generally much less soluble in hexane than $W(CO)_5L$ compounds. The remaining yellow residue was dissolved in chloroform, the solution was filtered, and an equal

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