understood as due to a 1-CH proton trans to CH_3 in the propenyl group. Hence the CH_3 and $C_2B_3H_4$ groups are cis to each other. The CH protons in the propenyl group gave spectra difficult to resolve, but the carborane CH protons showed as a sharp peak at τ 4.6, scarcely shifted from $C_2B_3H_5$ itself.

The observed alkyne addition to $C_2B_3H_5$ is an unusual type of hydroboration: the first such reaction in which a C=C bond is retained in the product. The process seems to be more effective for propyne than for acetylene, for a mixture of 1.15 mmol of $C_2B_3H_5$ with 4 mmol of C_2H_2, after 16 hr in a 40-ml tube at 165°, showed only 5% destruction of the carborane (without H_2 formation), yielding 0.02 mmol of a product which was trapped out at −95° under high vacuum. Its infrared spectrum showed C–H and B–H bonds, and the mass spectrum had a parent ion cutoff at *m/e* 88, corresponding to $C_2B_3H_4C_2H_3$. Another such cutoff peak, at 114, could be ascribed to $C_2B_3H_3(C_2H_3)_2$; but we have not succeeded in obtaining either product in yields high enough for characterization. On a larger scale, any such products obviously would be interesting to polymer chemistry.

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A Nuclear Magnetic Resonance Study of the Ligand-Exchange Kinetics of Hexakis(trimethyl phosphate)aluminum(III) Ion in Mixed Solvents

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Recently data have been reported for the ligand-exchange kinetics of octahedral transition metal complexes in mixed solvents. Results have been reported for $Ni(DMSO)_6^{2+}$ (DMSO = dimethyl sulfoxide) and $Co(DMSO)_6^{2+}$ in DMSO–nitromethane and DMSO–methylene chloride,[2] $Ni(DMF)_6^{2+}$ (DMF = *N,N*-dimethylformamide) in DMF–nitromethane,[3] and $Ni(3\text{-picO})_6^{2+}$ in nitromethane–acetone.[4] In all three studies, the kinetic exchange parameters were virtually independent of the composition of the solvent. Results of this type are of considerable aid in elucidating the mechanism of the reaction. Nitromethane appears to be the inert solvent of choice because it usually does not coordinate to the metal complex, a moderate number of metal complexes are soluble in this solvent, and it has a reasonable liquid range. To ascertain if this conclusion is applicable to other metal ions we wish to report data for $Al(TMP)_6^{3+}$ (TMP = trimethyl phosphate) in TMP–nitromethane mixed solvents. Previous studies for $Al(H_2O)_6^{3+}$,[5] $Al(DMSO)_6^{3+}$,[6] and $Al(DMF)_6^{3+}$ [7] in pure solutions of the ligand have been reported.

$Al(TMP)_6(ClO_4)_3$ was prepared as previously described.[8] *Anal.* Calcd for $Al(TMP)_6(ClO_4)_3$: C, 18.5; H, 4.7; Al, 2.3; Cl, 9.1; P, 15.9. Found: C, 18.5; H, 4.7; Al, 2.3; Cl, 9.1; P, 15.9. Karl Fisher analysis indicated less than 0.2% water. Nitromethane-d_3 was identical with that previously described.[2] Neither $Al(DMF)_6(ClO_4)_3$ nor $Al(DMSO)_6(ClO_4)_3$ is particularly soluble in nitromethane.

The proton nmr spectra were obtained on a Varian A-60 spectrometer equipped with a variable-temperature probe. The temperature was calculated by use of ethylene glycol either immediately before or after a spectrum was taken.

Infrared spectra were obtained on a Perkin-Elmer Model 521 spectrometer as Nujol mulls on CsI plates. The infrared spectra of TMP and $Al(TMP)_6(ClO_4)_3$ had P=O stretching frequencies at 1277 and 1248 cm^{-1}, respectively.[8] The low-energy shift is indicative of coordination through the phosphoryl group.[9]

The methyl resonance of TMP is a doublet due to coupling with the phosphorus nucleus. The methyl doublet of coordinated TMP occurs 0.33 ppm downfield from the free ligand. The coupling constants for coordinated and free ligand are 11.2 and 11.4 ± 0.1 Hz.

Coordination numbers (N) for $Al(TMP)_6^{3+}$ were obtained in CD_3NO_2–$CHCl_3$ (ethanol free), $N = 5.9 \pm 0.2$, and in the above solvent mixture with excess TMP, $N = 5.8 \pm 0.2$.

The exchange rates were measured in 0.10 and/or 0.13 *M* solutions of $Al(TMP)_6^{3+}$ in pure TMP and in nitromethane–TMP mixed solvents of various compositions. The excess line widths at half-height ($\Delta\nu_B - \Delta\nu_B^0$) of the coordinated ligand as a function of temperature in pure TMP are summarized in Table I.

TABLE I

TEMPERATURE DEPENDENCE OF THE EXCESS LINE WIDTH ($\Delta\nu_B - \Delta\nu_B^0$) OF $Al(TMP)_6^{3+}$ IN TMP

[Al^{3+}], *M*	Temp, °K (±0.2°K)	$\Delta\nu_B - \Delta\nu_B^0$ (±0.2)	Temp, °K (±0.2°K)	$\Delta\nu_B - \Delta\nu_B^0$ (±0.2)
0.13	329.4	4.1	324.5	2.5
	326.7	3.0	323.3	2.2
0.10	330.9	4.7	324.0	2.4
	329.4	4.3	320.2	1.6
	327.0	3.5		

The line width of the coordinated ligand was analyzed by using the equation

$$\pi\Delta\nu_B = 1/\tau_B + 1/T_{2B}^0 \qquad (1)$$

where τ_B is the mean lifetime of a TMP molecule in the coordination sphere, $\Delta\nu_B$ is the observed line width of the bound ligand, and $1/T_{2B}^0$ ($1/T_{2B}^0 = \pi\Delta\nu_B^0$) is the relaxation rate of a bound TMP molecule in the absence of chemical exchange. Transition-state theory

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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 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]

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

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 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]

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.

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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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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