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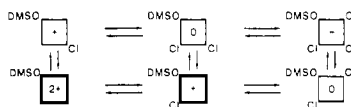
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Kinetics and Mechanism for Ligand Substitution Reactions of Square-Planar (Dimethyl sulfoxide)platinum(II) Complexes. Stability and Reactivity Correlations

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The 14 rate constants in the system (aqua ligands excluded)



have been determined at 25.0 °C and in 1.00 M perchloric acid medium using both stopped-flow and conventional spectrophotometry. The equilibrium constants have been obtained from the rate constants, and three of them, also from independent spectrophotometric equilibrium measurements. The overall stability constants for the complexes $\text{Pt}(\text{DMSO})\text{Cl}_j(\text{H}_2\text{O})_{3-j}$, $j = 1, 2, 3$, are $\beta_1 = (1.20 \pm 0.12) \times 10^6 \text{ M}^{-1}$, $\beta_2 = (3.2 \pm 1.1) \times 10^{10} \text{ M}^{-2}$, and $\beta_3 = (5.8 \pm 2.9) \times 10^{12} \text{ M}^{-3}$. Comparisons of thermodynamic and kinetic parameters for the reactions in this system with corresponding reactions of similar complexes have been used to distinguish between the cis and trans influence and the cis and trans effect for DMSO compared to other ligands. The cis and trans influences, obtained from comparisons of equilibrium constants, are related to energy differences between complexes in their ground states, while the cis and trans effects, obtained from comparisons of rate constants, are related to energy differences between transition states and ground states. A quantitative evaluation of these contributions to the reactivity gave the trans influence order $\text{H}_2\text{O} \approx \text{Cl}^- \approx \text{Br}^- < \text{C}_2\text{H}_4 \approx \text{DMSO} < \text{NH}_3$ (1:1:1:3:4:10) and the cis influence order $\text{DMSO} \approx \text{C}_2\text{H}_4 < \text{Br}^- \approx \text{Cl}^- \approx \text{H}_2\text{O} < \text{NH}_3$ (0.1:~0.3:1:1:1:~2). Thus, DMSO destabilizes trans chlorides by a factor of about 4 and stabilizes cis chlorides by a factor of about 10 compared to water. These thermodynamic influences are small compared to the (kinetic) trans effects, which are in the order $\text{H}_2\text{O} < \text{NH}_3 < \text{Cl}^- < \text{Br}^- < \text{DMSO} < \text{C}_2\text{H}_4$ (1:200:330:3000:2 $\times 10^6$:~ 10^{11}). The (kinetic) cis effects are generally much smaller than the trans effects and are approximately $\text{C}_2\text{H}_4 < \text{Br}^- \approx \text{Cl}^- < \text{NH}_3 \approx \text{H}_2\text{O} < \text{DMSO}$ (0.05:0.3:0.4:1:1:5). Thus, DMSO has an intermediate trans effect and a relatively large cis effect compared to other ligands. Activation parameters for some reactions have been determined. The variation of activation entropies indicates that the ionic charge of the substrate complex is also an important factor for the rates of halide anation reactions. It appears that both the stability and reactivity of simple square-planar complexes can be described by empirical relationships with a small number of parameters. The stability constant for $\text{Pt}(\text{DMSO})(\text{H}_2\text{O})_3^{2+}$ is at least 10^7 M^{-1} .

Introduction

In aqueous solution, dimethyl sulfoxide (DMSO) reacts with tetrachloroplatinate(II) forming a strong, sulfur-bonded 1:1 complex which can be prepared in the solid state as the potassium salt $\text{KPt}(\text{DMSO})\text{Cl}_3$.¹ Isotopic exchange studies have indicated that the exchange of the trans chloride in $\text{Pt}(\text{DMSO})\text{Cl}_3^-$ is "instantaneous" whereas the cis chlorides are exchanged slowly.² Hydrolysis products of the aqua complexes $\text{Pt}(\text{DMSO})(\text{H}_2\text{O})\text{Cl}_2$, *cis*- $\text{Pt}(\text{DMSO})(\text{H}_2\text{O})_2\text{Cl}^+$, and $\text{Pt}(\text{DMSO})(\text{H}_2\text{O})_3^{2+}$ have been prepared by equilibration of aqueous solutions of $\text{Pt}(\text{DMSO})\text{Cl}_3^-$ in the presence of excess silver(I) ion.³⁻⁵ Kukushkin⁶ has reviewed these investigations.

We here report a complete kinetic and equilibrium study of the platinum(II)-DMSO-chloro-aqua system. Comparisons of thermodynamic and kinetic parameters for the reactions in this system with corresponding reactions in the platinum(II)-chloro-aqua system studied previously⁷ and with reactions of other similar complexes, such as $\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3^-$, can be used to distinguish between the trans and cis influence and the trans and cis effect for DMSO compared to other

ligands. It also enables a quantitative evaluation of these contributions to the reactivity of the complexes.

Reaction Model and Rate Expressions

The kinetic scheme in Figure 1 (eq 1-7) is applicable. Rate constants for chloride anations are denoted k_n and for acid

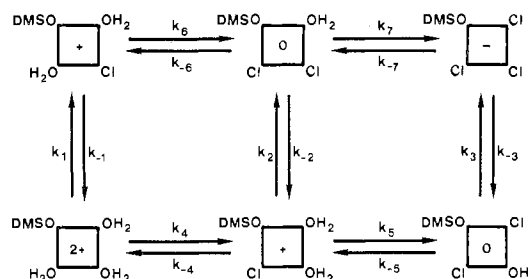


Figure 1. Reaction model. Rate constants for chloride anations are denoted k_n and for acid hydrolyses k_{-n} , $n = 1, 2, \dots, 7$. Vertical arrows denote very fast substitutions of ligands trans to DMSO and horizontal arrows comparatively slow reactions.

hydrolyses k_{-n} . The corresponding stability constants are defined by (8) and the respective equilibrium reactions will

$$K_n = k_n/k_{-n} \quad n = 1, 2, \dots, 7 \quad (8)$$

be referred to as reactions 1, 2, ..., 7 in the following text. Reactions 1, 2, and 3 which are denoted by vertical arrows in Figure 1 are fast substitutions of ligands trans to DMSO, which can be followed using the stopped-flow technique. They are kinetically separated from each other and from the other reactions in the system. The relaxation time τ_i for a concentration jump experiment on one of these reactions is described by eq 9, where $[Cl^-]$ is at least 10 times the total

$$1/\tau_i = k_{-i} + k_i[Cl^-] \quad i = 1, 2, 3 \quad (9)$$

concentration of platinum complexes (C_{Pt}) to give first-order kinetics. Reactions 4-7 are comparatively slow substitutions of ligands cis to DMSO, which can be followed by conventional or stopped-flow spectrophotometry. Reactions 1-3 can then be regarded as rapid equilibria, and the scheme in Figure 1 reduces to (10), where A_i ($i = 1, 2, 3$) denotes the equilibrium



mixtures formed by reactions 1-3. With C_i representing the total concentration of platinum for each of these equilibrium mixtures we arrive at eq 11, which can be explicitly solved (see

$$\frac{dC_1}{dt} = \frac{k_6[Cl^-]^2K_1 + k_4[Cl^-]}{1 + [Cl^-]K_1} C_1 - \frac{k_{-6}[Cl^-]K_2 + k_{-4}}{1 + [Cl^-]K_2} C_2 = k_{12}C_1 - k_{21}C_2 \quad (11a)$$

$$\frac{dC_3}{dt} = -\frac{k_7[Cl^-]^2K_2 + k_5[Cl^-]}{1 + [Cl^-]K_2} C_2 + \frac{k_{-7}[Cl^-]K_3 + k_{-5}}{1 + [Cl^-]K_3} C_3 = -k_{23}C_2 + k_{32}C_3 \quad (11b)$$

$$C_{Pt} = C_1 + C_2 + C_3 \quad (11c)$$

ref 8, p 175), giving the relaxation times

$$1/\tau_+ = 1/2(p + q) \quad (12)$$

$$1/\tau_- = 1/2(p - q) \quad (13)$$

where

$$p = k_{12} + k_{21} + k_{23} + k_{32} \quad (14)$$

and

$$q = \{p^2 - 4(k_{12}k_{23} + k_{21}k_{32} + k_{12}k_{32})\}^{1/2} \quad (15)$$

The experiments indicate that the scheme (10) can be further simplified to (16), so the relaxation time τ_- defined by (13)



for the reaction between A_1 and A_2 can be written

$$1/\tau_- = k_{12} + \frac{k_{21}k_{32}}{k_{23} + k_{32}} \quad (17)$$

where the k 's are defined by eq 11. For large concentrations of chloride (in practice for $[Cl^-] > 0.01$ M) the limiting value of $1/\tau_-$ defined by eq 17 will be

$$\lim_{[Cl^-] \rightarrow \infty} (1/\tau_-) = k_{-6} + k_4/K_1 + k_6[Cl^-] \quad (18)$$

Equation 17 can be further simplified to (19), since $k_{21} \ll k_{12}$

for $[Cl^-] > 10^{-4}$ M (cf. the values of k_6 , k_4 , k_{-6} , k_{-4} , K_1 , and K_2 given in Tables II and IV).

$$1/\tau_- = k_{12} = (k_6[Cl^-]^2K_1 + k_4[Cl^-]) / (1 + [Cl^-]K_1) \quad (19)$$

If reaction 16 is followed in the reverse direction ($A_1 \leftarrow A_2$), the forward reaction described by k_{12} being negligible, eq 17 can be simplified to (20).

$$\lim_{[Cl^-] \rightarrow 0} (1/\tau_-) = k_{-4} \quad (20)$$

Furthermore, the scheme (16) implies that the reaction between A_2 and A_3 can be studied without disturbance from the much slower process $A_1 \rightleftharpoons A_2$, so the relaxation time τ_+ defined by (12) for the reaction between A_2 and A_3 can be simplified to (21), where k_{23} and k_{32} are defined by eq 11b.

$$1/\tau_+ = k_{23} + k_{32} \quad (21)$$

For large concentrations of chloride (in practice for $[Cl^-] > 0.05$ M) eq 21 transforms to (22). If the reaction is followed

$$\lim_{[Cl^-] \rightarrow \infty} (1/\tau_+) = k_{-7} + k_5/K_2 + k_7[Cl^-] \quad (22)$$

in the reverse direction ($A_3 \leftarrow A_2$), the forward reaction being negligible, eq 21 can be simplified to (23).

$$\lim_{[Cl^-] \rightarrow 0} (1/\tau_+) = k_{-5} \quad (23)$$

Experimental Section

Chemicals and Solutions. $KPt(DMSO)Cl_3$ was prepared in aqueous solution according to Kukushkin et al.¹ by reaction of equivalent amounts of K_2PtCl_4 (Johnson and Matthey) and DMSO (BDH, freshly distilled under vacuum over calcium hydride). Anal. Calcd for $KPtC_2H_6OSCl_3$: Cl, 25.44; S, 7.66. Found: Cl, 25.39; S, 7.60.

Stock solutions of $Pt(DMSO)(H_2O)_3(ClO_4)_2$ were prepared by mixing 10.00 mmol $KPt(DMSO)Cl_3$ dissolved in 500 mL of 1.00 M $HClO_4$ (Baker p.a.) with 50.0 mmol of $AgNO_3$ (Merck p.a.) dissolved in 500 mL of 1.00 M $HClO_4$. After equilibration in the dark for 40 days at about 20 °C, the silver chloride precipitate was filtered off. Analysis showed that the precipitation of chloride was complete. The excess silver in the filtrate was precipitated as silver chloride by addition of a slight excess (20.40 mmol) of KCl (Merck p.a.). The solution was centrifuged, filtered, and diluted with 1.00 M $HClO_4$ to $C_{Pt} = 2 \times 10^{-5}$ M before use in the kinetics. One sample of the solution was analyzed for platinum by addition of excess (0.1 M) chloride and aging for 3 h at 25 °C. The spectrum for $Pt(DMSO)Cl_3^-$ reappeared quantitatively. Solutions of $Pt(DMSO)(H_2O)_3^{2+}$ prepared in this manner were stable for more than 1 year. No dissociation of DMSO takes place (vide infra).

Stock solutions of *cis*- $Pt(DMSO)(H_2O)_2Cl^+$ in 1.00 M perchloric acid were prepared by mixing 1.000 mmol of $KPt(DMSO)Cl_3$ dissolved in 50.0 mL of 1.00 M $HClO_4$ with 2.100 mmol of $AgNO_3$ dissolved in 50.0 mL of 1.00 M $HClO_4$. The solution was aged for 2 h at about 20 °C and the silver chloride precipitate filtered off. Analysis showed that 2.00 equiv of chloride per platinum was precipitated. The excess silver was precipitated by addition of 0.100 mmol of KCl , centrifugation, and filtration. The subsequent reaction 4 to $Pt(DMSO)(H_2O)_3^{2+}$ has a half-life of about 6 days and is therefore negligible. The solutions of $Pt(DMSO)(H_2O)_2Cl^+$ were always prepared immediately before use.

The solvent was 1.00 M perchloric acid in all experiments except for the kinetics for reactions 2 and 3 which were also studied in 0.0100 and 0.0050 M perchloric acid. According to Kukushkin and Strelin,³ pK_a for *trans*- $Pt(DMSO)(H_2O)Cl_2$ is about 5, pK_1 for *cis*- $Pt(DMSO)(H_2O)_2Cl^+$ about 3.5, and for $Pt(DMSO)(H_2O)_3^{2+}$ less than about 1. The latter value is probably too large because of polynuclear protolysis.³ We have checked that the observed rate constants for reaction 1 were independent of pH for $[H^+] \geq 0.05$ M. We therefore conclude that the hydrogen ion concentrations used in all cases were sufficiently large to suppress protolysis of the aqua complexes. Mercury(II) perchlorate solutions were prepared from HgO (Merck p.a.) and perchloric acid.

Apparatus. The modified Durrum-Gibson stopped-flow instrument was the same as used previously.⁹ Slow reactions were followed using

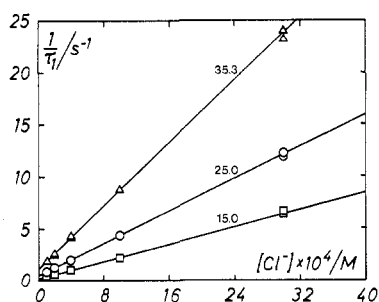


Figure 2. $1/\tau_1$ vs. $[\text{Cl}^-]$ for reaction 1 at 15.0 (\square), 25.0 (\circ), and 35.3 $^\circ\text{C}$ (Δ). The ionic strength was 1.00 M, C_{Pt} was 1.00×10^{-5} M, and the wavelength was 230 nm.

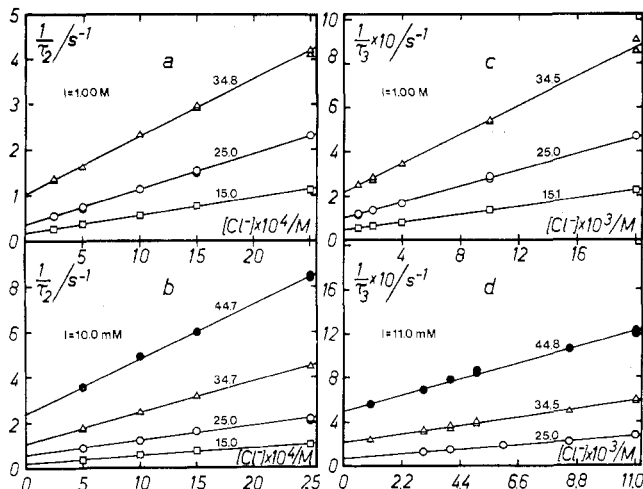


Figure 3. $1/\tau_2$ and $1/\tau_3$ vs. $[\text{Cl}^-]$ for reactions 2 and 3 at different ionic strengths I and temperatures. C_{Pt} was 5×10^{-5} M and the wavelength was 238 nm.

a Zeiss PMQ II spectrophotometer equipped with a thermostated cell holder (± 0.05 $^\circ\text{C}$) and a Kipp and Zonen recorder. Spectra were recorded using a Cary 15 instrument.

Kinetic Procedure. The relaxation experiments were started by mixing equal volumes of two solutions, M and L. The M solutions contained platinum complex and sometimes extra chloride. The L solutions were mixed from stock solutions of perchloric acid and hydrochloric acid and contained chloride in large enough concentrations to give $[\text{Cl}^-] \geq 10C_{\text{Pt}}$ in the kinetic runs, so that first-order kinetics were always obtained. The pseudo-first-order rate constants were calculated using a least-squares program from the transmittance vs. time curves from 10 equidistant observations between 0.5 and 2.5 half-lives. All reactions were kinetically separated from disturbing parallel or consecutive processes, so the wavelengths could be chosen only with the respect to give sufficiently large transmittance changes.

Reactions 1, 2, and 3. The relaxation times τ_i defined by eq 9 were measured by the stopped-flow method at 230 or 238 nm. Supplementary Tables X–XII give experimental details, and Figures 2 and 3 review the measurements. The M solution was pure $\text{Pt}(\text{DMSO})(\text{H}_2\text{O})_3^{2+}$ for reaction 1 and a freshly prepared (less than 3 h old) solution of $\text{cis-Pt}(\text{DMSO})(\text{H}_2\text{O})_2\text{Cl}^+$ for reaction 2. For reaction 3 an equilibrated solution of $\text{trans-Pt}(\text{DMSO})(\text{H}_2\text{O})\text{Cl}_2$ and $\text{Pt}(\text{DMSO})\text{Cl}_3^-$, containing extra chloride (2 mM) to give a mean ligand number at the start of the kinetics of about 2.3 (cf. Figure 5), was prepared from solid $\text{KPt}(\text{DMSO})\text{Cl}_3$. The concentration of $\text{cis-Pt}(\text{DMSO})(\text{H}_2\text{O})\text{Cl}_2$ in the latter solution is negligible, since the cis-trans equilibrium is displaced practically completely to the trans isomer (cf. Table III).

Reaction $A_1 \rightleftharpoons A_2$. The equilibrium mixture A_1 which is rapidly formed with the relaxation time τ_1 , when chloride is added to $\text{Pt}(\text{DMSO})(\text{H}_2\text{O})_3^{2+}$, reacts further with the relaxation time τ_+ defined by eq 17. A series of experiments, in which $\text{Pt}(\text{DMSO})(\text{H}_2\text{O})_3^{2+}$ solutions were mixed with HCl-HClO_4 solutions and the kinetics followed by conventional spectrophotometry at 230 nm, gave τ_+ for $1.25 \times 10^{-4} \leq [\text{Cl}^-] \leq 0.250$ M (cf. supplementary Table XIII and Figure 4).

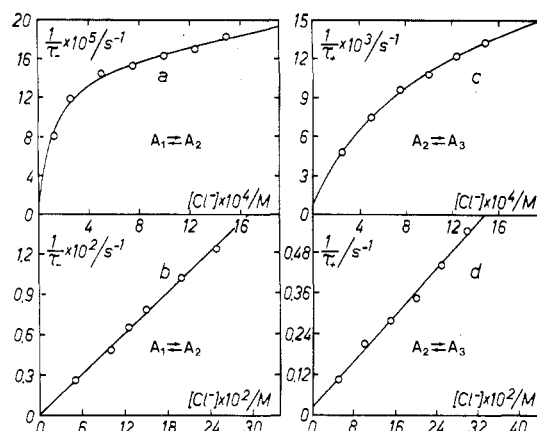


Figure 4. The relaxations $A_1 \rightleftharpoons A_2$ and $A_2 \rightleftharpoons A_3$: $1/\tau_+$ vs. $[\text{Cl}^-]$ according to eq 19 (a) and according to eq 18 (b); $1/\tau_+$ vs. $[\text{Cl}^-]$ according to eq 27 (c) and according to eq 22 (d). The full-drawn curves in (a) and (c) represent least-squares curve fittings of eq 19 and 27 to the experimental points, with k_4 (a) and k_5 , k_{-5} (c) as parameters.

Eight solutions (100 mL) in stoppered flasks containing 6.0 mM $\text{trans-Pt}(\text{DMSO})(\text{H}_2\text{O})\text{Cl}_2$ and 15.0 mM AgNO_3 dissolved in 1.00 M HClO_4 were thermostated at 25.00 ± 0.05 $^\circ\text{C}$. Within the first 2 h after mixing, reaction 5 is complete, and the slow reaction (4) described by k_{-4} of eq 20 can be followed. The solutions were filtered at different times, and the silver chloride precipitate was washed, dissolved in cyanide, and analyzed for silver by electrolysis. The following silver weights were obtained for different aging times (t/h , m/mg): 5.0, 129.3; 23.5, 138.0; 30.5, 142.7; 54.5, 156.1; 119.0, 180.2; 150.0, 181.4; 197.0, 192.0; 1152, 236.13. The final value represents 100% reaction. The rate was independent of silver ion concentration within the range of concentrations used.

Reaction $A_2 \rightleftharpoons A_3$. The equilibrium mixture A_2 which is rapidly generated with the relaxation time τ_2 when chloride is added to $\text{cis-Pt}(\text{DMSO})(\text{H}_2\text{O})_2\text{Cl}^+$ reacts further with the relaxation time τ_+ defined by eq 21. A series of experiments, in which freshly prepared $\text{cis-Pt}(\text{DMSO})(\text{H}_2\text{O})_2\text{Cl}^+$ solutions were mixed with HCl-HClO_4 solutions and the kinetics followed at 230 nm using both stopped-flow and conventional spectrophotometry, gave τ_+ for $2.5 \times 10^{-4} \leq [\text{Cl}^-] \leq 0.300$ M (cf. supplementary Table XIII and Figure 4).

Equilibrium Measurements. The stability constants K_1 , K_3 , and K_4 were determined by spectrophotometric equilibrium measurements at 25.0 ± 0.1 $^\circ\text{C}$ which are summarized in supplementary Table XIV. Each of the equilibria 1, 3, and 4 can be studied independently of all other reactions in the system, due to the differences in rates.

In the experiments for determination of K_1 and K_3 , chloride was present in excess of platinum, so the concentration of free chloride was approximately equal to the total concentration; $[\text{Cl}^-] = C_{\text{Cl}}$. K_1 was obtained from eq 24, where ΔA denotes the change of absorbance

$$1/\Delta A = 1/\Delta A' + (1/\Delta A')K_1^{-1}[\text{Cl}^-]^{-1} \quad (24)$$

at 230 nm and zero time for kinetic runs followed using the stopped-flow instrument after mixing $\text{Pt}(\text{DMSO})(\text{H}_2\text{O})_3^{2+}$ solutions with excess chloride. $\Delta A'$ is the corresponding quantity for complete conversion of $\text{Pt}(\text{DMSO})(\text{H}_2\text{O})_3^{2+}$ to $\text{trans-Pt}(\text{DMSO})(\text{H}_2\text{O})_2\text{Cl}^+$. $\Delta A'$ is not accessible experimentally, since the chloride concentrations required for a complete conversion will give too fast reactions compared to the dead time of the instrument. K_3 was obtained from the corresponding eq 25, where $\Delta A'$ denotes the difference in absorbance

$$1/\Delta A = 1/\Delta A' + (1/\Delta A')K_3[\text{Cl}^-] \quad (25)$$

at 238 nm between an equilibrated solution containing $\text{Pt}(\text{DMSO})\text{Cl}_3^-$ and $\text{trans-Pt}(\text{DMSO})(\text{H}_2\text{O})\text{Cl}_2$ and a solution which only contains $\text{Pt}(\text{DMSO})\text{Cl}_3^-$ of the same total concentration. $\Delta A'$ is the corresponding absorbance difference for complete conversion to $\text{trans-Pt}(\text{DMSO})(\text{H}_2\text{O})\text{Cl}_2$, which is not observable experimentally, because of formation of noticeable amounts of $\text{cis-Pt}(\text{DMSO})(\text{H}_2\text{O})_2\text{Cl}^+$ for $[\text{Cl}^-] < 1$ mM—cf. the distribution diagram in Figure 5.

In the experiments for determination of K_4 , the concentration of free chloride was varied by means of a Hg^{2+} , HgCl^+ , HgCl_2 chloride

Table I. Rate Constants with Standard Deviations^a

I/M		Constant				Method
Chloride Anations						
$10^{-3}k_1/M^{-1} s^{-1}$	1.00	2.08 ± 0.03 (15.0)	3.89 ± 0.03 (25.0)	7.6 ± 0.1 (35.0)		Linear regression, eq 9
$10^{-2}k_2/M^{-1} s^{-1}$	1.00	1.95 ± 0.04 (15.0)	3.90 ± 0.03 (25.0)	6.4 ± 0.1 (34.8)		
	0.010	3.54 ± 0.06 (15.0)	6.7 ± 0.2 (25.0)	13.8 ± 0.2 (34.8)	24.4 ± 0.4 (44.7)	
	0.005		7.1 ± 0.2 (25.0)			
$10^{-1}k_3/M^{-1} s^{-1}$	1.00	0.91 ± 0.01 (15.0)	1.82 ± 0.03 (25.0)	3.31 ± 0.06 (34.5)		
	0.011		1.88 ± 0.06 (25.0)	3.52 ± 0.09 (34.5)	6.7 ± 0.2 (44.8)	
$k_4/M^{-1} s^{-1}$	1.00		1.4 ± 0.2 (25.0)			Curve fitting, eq 19
$10^{-1}k_5/M^{-1} s^{-1}$	1.00		2.05 ± 0.04 (25.0)			Curve fitting, eq 27
$10^2k_6/M^{-1} s^{-1}$	1.00		5.0 ± 0.1 (25.0)			Linear regression, eq 18
$k_7/M^{-1} s^{-1}$	1.00		1.72 ± 0.07 (25.0)			Linear regression, eq 22
Acid Hydrolyses						
$10k_{-1}/s^{-1}$	1.00	1.7 ± 0.1 (15.0)	4.7 ± 0.1 (25.0)	11 ± 1 (34.8)		Linear regression, eq 9
$10k_{-2}/s^{-1}$	1.00	1.54 ± 0.06 (15.0)	3.39 ± 0.05 (25.0)	10.0 ± 0.2 (34.8)		
	0.010	1.86 ± 0.06 (15.0)	5.4 ± 0.2 (25.0)	10.6 ± 0.2 (34.8)	23.6 ± 0.4 (44.7)	
	0.005		5.2 ± 0.2 (25.0)			
$10k_{-3}/s^{-1}$	1.00	0.431 ± 0.005 (15.0)	0.981 ± 0.002 (25.0)	2.12 ± 0.03 (34.5)		
	0.011		0.69 ± 0.04 (25.0)	2.12 ± 0.04 (34.5)	5.00 ± 0.08 (44.8)	
$10^6k_{-4}/s^{-1}$	1.00		1.3 ± 0.1 (25.0)			Addition of Ag ⁺
	1.00		1.2 ± 0.2 (25.0)			k_4/K_4
$10^4k_{-5}/s^{-1}$	1.00		8.0 ± 0.8 (25.0)			Curve fitting, eq 27
	1.00		9.2 ± 0.1 (25.0)			Addition of Hg ²⁺ , ref 10
$10^7k_{-6}/s^{-1}$	1.00		3.3 ± 1			k_6K_1/K_2K_4
$10^4k_{-7}/s^{-1}$	1.00		4 ± 1 (25.0)			k_7K_2/K_3K_5
	~0.1		4.96 (25)			Isotopic exchange, ref 2

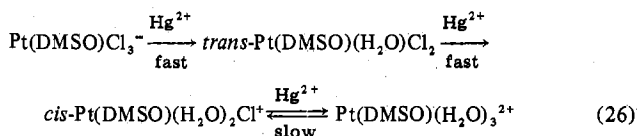
^a Notations as in Figure 1. The temperature (°C) is given within parentheses. The values refer to a perchloric acid medium of ionic strength and hydrogen ion concentration I .

Table II. Activation Enthalpies and Entropies at 25 °C^a

Reaction	Rate const	$\Delta H^\ddagger/kJ mol^{-1}$		$-\Delta S^\ddagger/J K^{-1} mol^{-1}$	
		$I = 1.00$ M	$I = 0.010$ M	$I = 1.00$ M	$I = 0.010$ M
Pt(DMSO)(H ₂ O) ₃ ²⁺ + Cl ⁻ → <i>trans</i> -Pt(DMSO)(H ₂ O) ₂ Cl ⁺ + H ₂ O	k_1	45 ± 1		26 ± 1	
<i>cis</i> -Pt(DMSO)(H ₂ O) ₂ Cl ⁺ + Cl ⁻ → <i>cis</i> -Pt(DMSO)(H ₂ O)Cl ₂ + H ₂ O	k_2	42 ± 1	48 ± 2	56 ± 4	29 ± 5
<i>trans</i> -Pt(DMSO)(H ₂ O)Cl ₂ + Cl ⁻ → Pt(DMSO)Cl ₃ ⁻ + H ₂ O	k_3	46 ± 1	48 ± 1	65 ± 2	60 ± 1
<i>trans</i> -Pt(DMSO)(H ₂ O) ₂ Cl ⁺ + H ₂ O → Pt(DMSO)(H ₂ O) ₃ ²⁺ + Cl ⁻	k_{-1}	66 ± 3		30 ± 11	
<i>cis</i> -Pt(DMSO)(H ₂ O)Cl ₂ + H ₂ O → <i>cis</i> -Pt(DMSO)(H ₂ O) ₂ Cl ⁺ + Cl ⁻	k_{-2}	67 ± 8	61 ± 3	28 ± 30	46 ± 9
Pt(DMSO)Cl ₃ ⁻ + H ₂ O → <i>trans</i> -Pt(DMSO)(H ₂ O)Cl ₂ + Cl ⁻	k_{-3}	58 ± 1	76 ± 6	70 ± 8	13 ± 18

^a Standard state of water: unit mole fraction. Standard state of complex and halide ligands: unit concentration, M.

buffer. The solutions contained excess mercury(II) perchlorate (1.250 < C_{Hg} < 15.00 mM) and 1.00 mM Pt(DMSO)Cl₃⁻. The following reactions take place:



Within 20 min the two fast reactions are complete, and the solution contains all platinum as *cis*-Pt(DMSO)(H₂O)₂Cl⁺. The subsequent slow reaction to Pt(DMSO)(H₂O)₃²⁺ requires about 30 days to go to completion. The differences in absorbance ΔA between solutions which contain all platinum as *cis*-Pt(DMSO)(H₂O)₂Cl⁺ and solutions which contain equilibrium mixtures of *cis*-Pt(DMSO)(H₂O)₂Cl⁺ and Pt(DMSO)(H₂O)₃²⁺ of the same total concentration were determined. The corresponding absorbance change for complete conversion to Pt(DMSO)(H₂O)₃²⁺ is $\Delta A'$. The measurements were performed at 280 and 285 nm, where the mercury(II) complexes have negligible absorptivity; cf. supplementary Table XIV.

Results

Reactions 1–3. Figures 2 and 3 review the results. The values of k_1 and k_{-1} defined by eq 9 and given in Table I were obtained by linear regression analysis. The activation parameters are given in Table II, and the values of the equilibrium constants calculated from eq 8 are given in Table III. Romeo et al.²⁹ have measured k_{-3} in 95% H₂O–5% MeOH from the kinetics of the reaction of Pt(DMSO)Cl₃⁻ with

cyclohexylamine. Their value (0.15 s⁻¹ at 30 °C) is in close agreement with our results in Table I.

Reaction A₁ ⇌ A₂. The plot in Figure 4b of $1/\tau_+$ vs. [Cl⁻] for large concentrations of chloride gives k_6 as the slope according to eq 18. The plot in Figure 4a shows $1/\tau_+$ vs. [Cl⁻] for small concentrations of chloride. The full-drawn curve represents a least-squares curve fitting of eq 19 to the experimental points. k_6 and K_1 were introduced as known parameters, and k_4 was varied to give the best fit. The values of k_6 and k_4 obtained from these experiments are given in Table I.

A first-order plot of $\ln(m_{eq} - m)$ vs. t for the experiments performed by addition of silver to the platinum solutions gave a straight line with slope k_{-4} according to eq 20. This k_{-4} value agrees excellently with that calculated using eq 8; cf. Table I.

Reaction A₂ ⇌ A₃. The plot in Figure 4d of $1/\tau_+$ vs. [Cl⁻] for large concentrations of chloride gives k_7 as the slope according to eq 22. Kukushkin et al.² have determined $k_{-7} = 4.96 \times 10^{-4} s^{-1}$ from isotopic-exchange experiments. It is obvious that the term $k_{-7}[Cl^-]K_3/(1 + [Cl^-]K_3)$ in the expression for k_{32} in eq 11b never amounts to more than 1% of the experimental values of $1/\tau_+$ for the concentrations used. $1/\tau_+$ from eq 21 can therefore be simplified to (27), where

$$1/\tau_+ = \frac{k_7K_2[Cl^-]^2 + k_5[Cl^-]}{1 + [Cl^-]K_2} + \frac{k_{-5}}{1 + [Cl^-]K_3} \quad (27)$$

Table III. Equilibrium Constants with Standard Deviations at 25 °C and in 1.00 M Perchloric Acid Medium^a

Constant		Method
$10^{-2}K_1/M^{-1}$	8.3 ± 0.3	k_1/k_{-1}
$10^{-2}K_2/M^{-1}$	8.3 ± 0.7	Eq 24
$10^{-2}K_3/M^{-1}$	1.15 ± 0.03	k_2/k_{-2}
$10^{-2}K_4/M^{-1}$	1.85 ± 0.07	k_3/k_{-3}
$10^{-2}K_5/M^{-1}$	1.91 ± 0.02	Eq 25
$10^{-6}K_6/M^{-1}$	1.1 ± 0.2	k_4/k_{-4}
$10^{-6}K_7/M^{-1}$	1.2 ± 0.1	Eq 31
$10^{-4}K_8/M^{-1}$	2.5 ± 0.3	k_5/k_{-5}
$10^{-5}K_9/M^{-1}$	1.5 ± 0.2	$K_1/(K_2K_4)$
$10^{-2}K_{10}/M^{-1}$	4.3 ± 0.6	$K_2/(K_3K_5)$
$[cis-Pt(DMSO)(H_2O)_2Cl^+]/[trans-Pt(DMSO)(H_2O)_2Cl^+]$	140 ± 20	K_4/K_1
$[trans-Pt(DMSO)(H_2O)Cl_2]/[cis-Pt(DMSO)(H_2O)Cl_2]$	22 ± 4	K_5/K_2
$10^{-6}K_{1,stab}/M^{-1}$	1.20 ± 0.12	$K_1 + K_4$
$10^{-4}K_{2,stab}/M^{-1}$	2.6 ± 0.7	$(K_2 + K_5)/(1 + K_2/K_4)$
$10^{-2}K_{3,stab}/M^{-1}$	1.83 ± 0.3	$K_3/(1 + K_3/K_7)$
$10^{-6}\beta_1/M^{-1}$	1.20 ± 0.12	$K_{1,stab}$
$10^{-10}\beta_2/M^{-2}$	3.2 ± 1.1	$K_{1,stab}K_{2,stab}$
$10^{-12}\beta_3/M^{-3}$	5.8 ± 2.9	$K_{1,stab}K_{2,stab}K_{3,stab}$

^a K_n , $n = 1, 2, \dots, 7$, defined by eq 8 and $K_{j,stab}$ and β_j , $j = 1, 2, 3$, by eq 32 and 33.

k_7 , K_2 , and K_3 are known. The full-drawn curve in Figure 4c has been calculated from eq 27 by variation of k_5 and k_{-5} to give the best least-squares fit to the experimental points. The values of k_7 , k_5 , and k_{-5} obtained from these experiments are given in Table I. The k_{-5} value agrees within experimental errors with the value $(9.2 \pm 0.1) \times 10^{-4} s^{-1}$ which can be calculated from catalysis experiments with Hg^{2+} and will be reported subsequently.¹⁰ Although k_5 and k_3 are almost equal, $1/\tau_3$ according to eq 9 is always at least 10 times larger than $1/\tau_4$ so the reaction model described by (10) is valid.

k_{-6} and k_{-7} . Twelve of the fourteen rate constants in the system can thus be determined by direct experiment. The remaining two constants k_{-6} and k_{-7} can be calculated from eq 8; cf. Table I. The agreement between the value of k_{-7} obtained in this way and Kukushkin's result of the isotopic-exchange experiments is satisfactory (Table I).

Equilibria. The values of K_1 and K_3 given in Table III were calculated from linear plots according to eq 24 and 25; cf. supplementary Table XIV. The values of $1/\Delta A'$ are obtained with good accuracy from the intercepts. The determination of K_4 is also summarized in the supplementary material. We define

$$f = [Pt(DMSO)(H_2O)_3^{2+}]/C_{Pt} = \Delta A/\Delta A' \quad (28)$$

The mean ligand number \bar{n}_{Hg} in the $Hg^{2+}-Cl^-$ system was obtained from (29) and the concentration of free chloride from

$$\bar{n}_{Hg} = (2 + f)C_{Pt}/C_{Hg} \quad (29)$$

(30), where the stability constants $\log(\beta_1/M^{-1}) = 6.72 \pm 0.02$

$$\bar{n}_{Hg} = (\beta_1[Cl^-] + 2\beta_2[Cl^-]^2)/(1 + \beta_1[Cl^-] + \beta_2[Cl^-]^2) \quad (30)$$

and $\log(\beta_2/M^{-2}) = 13.23 \pm 0.02$ have been determined by Ciavatta and Grimaldi¹¹ for 1.00 M perchlorate medium and 25.0 °C. The stability constant $K_4 = (1.2 \pm 0.2) \times 10^6 M^{-1}$ was then obtained from eq 31.

$$K_4 = (1 - f)/(f[Cl^-]) \quad (31)$$

All equilibrium constants are summarized in Table III. K_1 , K_2 , K_3 , K_4 , and K_5 were calculated from the rate constants according to eq 8. The agreement between these values of K_1 , K_3 , and K_4 and those obtained independently from the

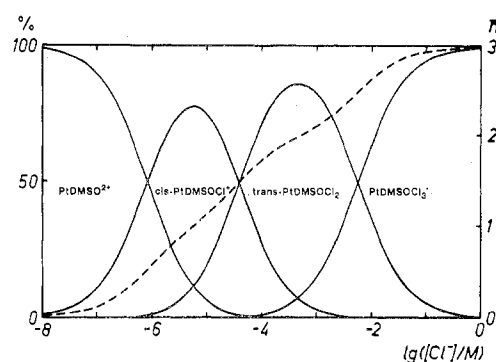


Figure 5. The mean ligand number \bar{n}_{Cl} (dashed) and the distribution of platinum vs. $\log [Cl^-]$ for 25.0 °C and 1.00 M perchloric acid medium calculated from the stability constants in Table III.

equilibrium measurements is good. The remaining two equilibrium constants K_6 and K_7 and the two constants for the cis-trans equilibria in the system were calculated from K_1 to K_5 as shown in Table III. Table III also contains the stepwise stability constants for the chloro complexes formed from $Pt(DMSO)(H_2O)_3^{2+}$ defined by (32) and the corresponding

$$K_{j,stab} = [Pt(DMSO)Cl_j(H_2O)_{3-j}^{2-j}]/[Pt(DMSO)Cl_{j-1}(H_2O)_{4-j}^{3-j}][Cl^-] \quad (j = 1, 2, 3) \quad (32)$$

overall stability constants β_j defined by (33) which can be

$$\beta_j = \prod_{k=1}^j K_{k,stab} \quad (33)$$

calculated from K_1 to K_5 . In (32), $[Pt(DMSO)Cl(H_2O)_2^+]$ and $[Pt(DMSO)Cl_2(H_2O)]$ stand for the equilibrium mixtures of the cis and trans isomers. Figure 5 shows the mean ligand number and the equilibrium distribution of the different complexes as functions of the concentration of free chloride.

Kukushkin et al.⁴⁻⁶ have reported values for the instability constants $1/K_{j,stab}$ of eq 32. Their values of $K_{2,stab}$ and $K_{3,stab}$ agree with ours within a factor of 2, whereas their $K_{1,stab}$ value differs by a factor of 15. The discrepancies are probably due to the different ionic media used and to the neglect of mononuclear protolysis of the aqua ligands in the neutral solutions used in ref 4 and 5.

Approximate values for the enthalpy changes for reactions 1-3 were obtained from the temperature dependence of K_1 , K_2 , and K_3 as -20 ± 4 , -25 ± 12 , and -11 ± 1 kJ mol⁻¹, respectively, for 1.00 M ionic strength.

Discussion

Stabilities. The equilibrium constants and rate constants for the DMSO complexes are compared with those for the platinum(II)-chloro-aqua complexes in Table IV. The ratios between the equilibrium constants indicate that substitution of water by DMSO causes a destabilization of chlorides in a trans position by a factor of about 4 and a stabilization of cis chlorides by a factor of about 10. We define this influence on the two pairs of ground states involved in each comparison as the relative trans influence (I_t) and cis influence (I_c) of DMSO compared to water. Table V shows analogous comparisons between H_2O and Cl , NH_3 , DMSO, and ethylene, which lead to the following approximate trans influence and cis influence orders (there is no difference between chloride and bromide¹²):

$$I_t \left\{ \begin{array}{l} H_2O \approx Cl^- \approx Br^- < C_2H_4 \approx DMSO < NH_3 \\ 1 : 1 : 1 : 3 : 4 : 10 \end{array} \right.$$

$$I_c \left\{ \begin{array}{l} DMSO \approx C_2H_4 < Br^- \approx Cl^- \approx H_2O < NH_3 \\ 0.1 : < 0.3 : 1 : 1 : 1 : \sim 1-2 \end{array} \right.$$

Table IV. Comparison of Acid Hydrolysis Equilibrium Constants, K , Rate Constants for Acid Hydrolyses, k_{-} , and Rate Constants for Halide Anions, k^a

Complex	K/M ; X:Cl			k-/s ⁻¹ ; X:Cl			k/s ⁻¹ M ⁻¹ ; X:H ₂ O		
	L:DMSO	L:H ₂ O	K _{DMSO} /K _{H₂O}	L:DMSO	L:H ₂ O	k _{-DMSO} /k _{-H₂O}	L:DMSO	L:H ₂ O	k _{DMSO} /k _{H₂O}
$\begin{matrix} L \\ \square \\ Cl \\ \square \\ X \end{matrix}$	5.3×10^{-3}	$2 \times 6.1 \times 10^{-4}$	4.3	0.10	2.8×10^{-8}	3.6×10^6	18.2	$\frac{1}{2} \times 4.6 \times 10^{-5}$	8×10^5
$\begin{matrix} L \\ \square \\ Cl \\ \square \\ X \end{matrix}$	8.7×10^{-4}	1.5×10^{-4}	5.8	0.34	$\frac{1}{2} \times 3 \times 10^{-7}$	2.2×10^6	390	$\frac{1}{2} \times 2 \times 10^{-3}$	4×10^5
$\begin{matrix} L \\ \square \\ Cl \\ \square \\ X \end{matrix}$	1.2×10^{-4}	$4 \times 1.2 \times 10^{-5}$	2.5	0.47	3.2×10^{-7}	1.4×10^6	3.9×10^3	$\frac{1}{4} \times 2.7 \times 10^{-2}$	6×10^5
$\begin{matrix} L \\ \square \\ Cl \\ \square \\ Cl \end{matrix}$	$\frac{1}{2} \times 3 \times 10^{-4}$	8.0×10^{-4}	0.20	$\frac{1}{2} \times 4 \times 10^{-4}$	$\frac{1}{2} \times 6 \times 10^{-5}$	6.7	1.7	$\frac{1}{2} \times 7.5 \times 10^{-2}$	45
$\begin{matrix} L \\ \square \\ Cl \\ \square \\ OH_2 \end{matrix}$	$2 \times 8 \times 10^{-6}$	1.5×10^{-4}	0.10	4×10^{-7}	$\frac{1}{2} \times 3 \times 10^{-7}$	3	$\frac{1}{2} \times 5 \times 10^{-2}$	$\frac{1}{2} \times 2 \times 10^{-3}$	25
$\begin{matrix} L \\ \square \\ Cl \\ \square \\ OH_2 \end{matrix}$	$\frac{1}{2} \times 4 \times 10^{-5}$	$\frac{1}{2} \times 2.2 \times 10^{-4}$	0.18	$\frac{1}{2} \times 8 \times 10^{-4}$	$\frac{1}{2} \times 1 \times 10^{-4}$	8	20.5	0.5	41
$\begin{matrix} L \\ \square \\ Cl \\ \square \\ OH_2 \end{matrix}$	$2 \times 9 \times 10^{-7}$	$4 \times 1.2 \times 10^{-5}$	0.04	1.3×10^{-6}	3.2×10^{-7}	4	$\frac{1}{2} \times 1.4$	$\frac{1}{4} \times 2.7 \times 10^{-2}$	100

^a The leaving ligand is X = Cl, H₂O in trans or cis position to the ligand L = DMSO, H₂O. The constants are valid at 25 °C and have been multiplied by their statistical factors. Values for L = H₂O are from ref 7, 13, and 14.

Table V. Equilibrium Constants, K , and Rate Constants, k , for Acid Hydrolysis of Chloride Ligands (Marked \odot) from Some Selected Substrates Having the Ionic Charge -1^c

Complex	K/M	k/s ⁻¹	Ref.
trans-substitution			
$\begin{matrix} H_2O \\ \square \\ Cl \\ \square \\ Cl \end{matrix}$	$2 \times 6 \times 10^{-4}$	2.8×10^{-8}	7
$\begin{matrix} Cl \\ \square \\ Cl \\ \square \\ OH_2 \end{matrix}$	8×10^{-4}	$\frac{1}{2} \times 6 \times 10^{-5} \times 0.4^a$	7
$\begin{matrix} DMSO \\ \square \\ Cl \\ \square \\ Cl \end{matrix}$	5.2×10^{-3}	0.10	this paper
$\begin{matrix} C_2H_4 \\ \square \\ Cl \\ \square \\ Cl \end{matrix}$	3×10^{-3}	$\sim 10^4$	15,17
$\begin{matrix} H_3N \\ \square \\ Cl \\ \square \\ Cl \end{matrix}$	1.4×10^{-2}	6×10^{-6}	18
cis-substitution			
$\begin{matrix} Cl \\ \square \\ OH_2 \\ \square \\ Cl \end{matrix}$	8×10^{-4}	$\frac{1}{2} \times 6 \times 10^{-5}$	7
$\begin{matrix} H_2O \\ \square \\ Cl \\ \square \\ Cl \end{matrix}$	$2 \times 6 \times 10^{-4}$	$2.8 \times 10^{-8} \times 330^b$	7
$\begin{matrix} Cl \\ \square \\ DMSO \\ \square \\ Cl \end{matrix}$	$\frac{1}{2} \times 2.3 \times 10^{-4}$	$\frac{1}{2} \times 4 \times 10^{-4}$	this paper
$\begin{matrix} Cl \\ \square \\ C_2H_4 \\ \square \\ Cl \end{matrix}$	$\frac{1}{2} \times 5 \times 10^{-4}$	$\frac{1}{2} \times 3 \times 10^{-6}$	16
$\begin{matrix} Cl \\ \square \\ NH_3 \\ \square \\ Cl \end{matrix}$	$\frac{1}{2} \times 5 \times 10^{-4}$	$\frac{1}{2} \times 5.6 \times 10^{-5}$	18

^a Corrected for the relative cis effect Cl/H₂O (cf. Table VI).

^b Corrected for the relative trans effect Cl/H₂O (cf. Table VI).

^c The constants are valid at 25 °C and have been multiplied by their statistical factors.

The relative values are summarized in Table VI.

The relative influence of DMSO and ethylene agrees qualitatively with previous findings.^{6,19,20} As a result of the influence of DMSO on the thermodynamic properties of the complexes, the isomers of Pt(DMSO)(H₂O)Cl₂ and Pt(DMSO)(H₂O)₂Cl⁺, which have H₂O trans to DMSO, are stabilized. Correction of the two cis-trans equilibrium constants in Table III for statistical factors, i.e., $\frac{1}{2}(K_4/K_1) = 70 \pm 10$ and $2(K_5/K_2) = 44 \pm 8$, shows that the stabilization is approximately the same in the two cases. The corresponding complexes Pt(C₂H₄)(H₂O)Cl₂ and Pt(NH₃)(H₂O)Cl₂ should have similar cis-trans distribution as proposed by Lokken and Martin.¹⁶ The thermodynamic influence is small, and no significant lengthening of the trans Pt-Cl bond has been observed in the solid state either for KPt(DMSO)Cl₃²¹ or for KPt(C₂H₄)Cl₃.²²

Reactivities. The kinetic effects are demonstrated by the comparisons between the rate constants in Tables IV and V. DMSO increases the rates for acid hydrolysis of trans chlorides by a factor of about 2×10^6 and of cis chlorides by a factor of about 5 compared to water. We define these effects on the

Table VI. Approximate Thermodynamic Trans and Cis Influence, I_t and I_c , and Kinetic Trans and Cis Effect, E_t and E_c , for Platinum Complexes, Estimated from the Constants in Tables IV and V

	H ₂ O	Cl	Br	NH ₃	DMSO	C ₂ H ₄
I_t	1	1	1	10	4	3
I_c	1	1	1	$\sim 1-2$	0.1	<0.3
E_t	1	330	3000	~ 200	2×10^6	$\sim 10^{11}$
E_c	1	0.4	0.3	1	5	5×10^{-2}

Table VII. Calculation of Cis and Trans Effects for Chloride Relative to Water from the Rate Constants in Table I and the Ionic Charge Factor $Q = 8 \pm 2$

	E_c	E_t	
$k_2 Q^{-1}/k_1 Q^{-2}$	0.77	$k_5 Q^{-1}/\frac{1}{2} k_4 Q^{-2}$	230
$k_3/k_2 Q^{-1}$	0.36	$k_7/\frac{1}{2} k_6 Q^{-1}$	540
$k_4 Q^{-1}/k_4 Q^{-2}$	0.28	$\frac{1}{2} k_{-5}/k_{-4}$	310
$k_7/k_5 Q^{-1}$	0.68	$\frac{1}{2} k_{-7}/k_{-5}$	~ 600
k_7/k_{-5}	0.50	$\frac{1}{2} k_{-7} E_c^{-1}/k_{-4}$	310
k_{-6}/k_{-4}	0.3	$k_7 E_c^{-1}/\frac{1}{2} k_4 Q^{-2}$	310
k_{-2}/k_{-1}	0.72	$\frac{1}{2} k_{-5}/k_{-6} E_c^{-1}$	~ 600
k_{-3}/k_{-2}	0.30	$k_5/\frac{1}{2} k_6 E_c^{-1}$	410
Mean	0.50 ± 0.2	370 ± 100	
Ref 7	0.33	300	

acid hydrolysis rate constants as the relative trans effect, E_t , and cis effect, E_c , of DMSO.

The variation of the acid hydrolysis rate constants shown in Table V together with the relative values Cl⁻/Br⁻ from a previous study¹² leads to the trans effect and cis effect orders

$$E_t \begin{cases} H_2O < NH_3 < Cl^- < Br^- < DMSO < C_2H_4 \\ 1 : 200 : 330 : 3 \times 10^3 : 2 \times 10^6 : \sim 10^{11} \end{cases}$$

$$E_c \begin{cases} C_2H_4 < Br^- \approx Cl^- < NH_3 \approx H_2O < DMSO \\ 0.05 : 0.3 : 0.4 : 1 : 1 : 5 \end{cases}$$

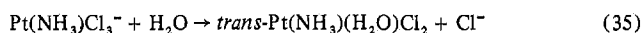
The relative values are given in Table VI. The hypothesis by Kukushkin et al.^{2,23} that ethylene and DMSO have similar trans effects can be discarded. They differ by a factor of at least 10^5 .

The relative kinetic effects defined in this manner appear to be additive and relatively constant properties for the reactions of these simple complexes. In Table VII, E_t and E_c for chloride have been calculated for the reactions of the DMSO complexes. The values agree within experimental errors with those used previously for the reactions of the Pt(II)-chloro-aqua^{7,9} and -chloro-bromo¹² complexes. Consequently, the seven acid hydrolysis rate constants in the present system can be described by the same empirical relationship (34) as used previously^{7,9,12} for the twelve acid

$$k_{-}/n = \kappa_{-} E_t E_{c1} E_{c2} \quad (34)$$

hydrolysis rate constants of the Pt(II)-chloro-aqua^{7,9} and -chloro-bromo¹² complexes. Here, $n = 1, 2,$ or 4 is a statistical factor, equal to the number of equivalent leaving halide ligands in the complex, and $\kappa_{-} = 3 \times 10^{-7} \text{ s}^{-1}$ is a rate constant, characteristic for the metal (Pt) and the incoming (H_2O) and leaving (Cl^-) ligands.⁹

As originally proposed by Martin et al.,²⁴ the relation (34) is also valid for acid hydrolysis of other chloro complexes containing the ligands in Table VI. For instance, the rate constant for



should be approximately $(3 \times 10^{-7}) \times 200 \times 0.4 \times 0.4 = 1 \times 10^{-5} \text{ s}^{-1}$ using the parameters in Table VI. The experimental value is $7 \times 10^{-6} \text{ s}^{-1}$.¹⁸

Halide anation rate constants for chloro- and bromo-aqua complexes of palladium and platinum can be described by a relation of the same type as (34).⁹ These rates also depend on the ionic charge of the complex (vide infra), which is accounted for by introduction of a charge factor, Q :⁹

$$k/m = \kappa E_t E_{c1} E_{c2} Q^q \quad (36)$$

m is a statistical factor, equal to the number of equivalent leaving aqua ligands, and $q = 2, 1, 0, -1$ is the ionic charge of the complex. $\kappa = 3 \times 10^{-4} \text{ s}^{-1} \text{ M}^{-1}$ is a rate constant, characteristic for the metal (Pt) and the entering (Cl) and leaving (H_2O) ligands.⁹ The charge factor Q is about 5 and the relative cis and trans effects are the same for acid hydrolyses as for halide anations for these simple complexes.⁹ This implies that it is possible to express the stability constants as functions only of $\kappa, \kappa_{-}, Q,$ and statistical factors, since E_t and E_c cancel in the division of eq 36 by eq 34:

$$K = k/k_{-} = m\kappa Q^q / (n\kappa_{-}) \quad (37)$$

The four stepwise stability constants of a square-planar complex system are thus given by eq 37 as

$$\begin{aligned} K_1 &= 4Q^2\kappa/\kappa_{-} \\ K_2 &= 3/2Q\kappa/\kappa_{-} \\ K_3 &= 2/3\kappa/\kappa_{-} \\ K_4 &= 1/4Q^{-1}\kappa/\kappa_{-} \end{aligned} \quad (38)$$

For the platinum(II) chloro complexes $\text{PtCl}_n(\text{H}_2\text{O})_{4-n}^{2-n}$ ($n = 0, 1, 2, 3, 4$) the above-mentioned values of $Q, \kappa,$ and κ_{-} give $K_1 = 1 \times 10^5 \text{ M}^{-1}, K_2 = 8 \times 10^3 \text{ M}^{-1}, K_3 = 7 \times 10^2 \text{ M}^{-1},$ and $K_4 = 50 \text{ M}^{-1}$. These constants agree satisfactorily with the experimental values^{7,14} of $8.5 \times 10^4, 1 \times 10^4, 1 \times 10^3,$ and 80 M^{-1} , respectively. The stability constants of the palladium(II) chloro and bromo complexes⁹ also conform to eq 38 if the appropriate κ values are used.

The simple equation (37) holds only when there is no difference in the ground state trans or cis influence between the ligands involved. This is the case for $\text{H}_2\text{O}, \text{Cl},$ and Br ; cf. Table VI. When there is also a thermodynamic influence on the ground states in addition to the kinetic effects, as for the DMSO complexes, the apparent cis and trans effects for forward and reverse reactions will of course no longer be equal. This is illustrated by Table IV, where $k_{\text{DMSO}}/k_{\text{H}_2\text{O}}$ is 2×10^6 (E_t) for acid hydrolyses but 6×10^5 for halide anations of trans ligands. There is an analogous difference for the cis ligands. In this case, the apparent trans effect and cis effect for the halide anations can be expressed as E_t/I_t and E_c/I_c , respectively; cf. Table IV. Equation 36 for the halide anation rate constants can then be generalized to (39), where $E_t, I_t, E_c,$ and

$$k/m = \kappa(E_t/I_t)(E_c/I_c)_1(E_c/I_c)_2Q^q \quad (39)$$

Table VIII. Stability Constants K_n of Eq 8 Calculated from Eq 40 Using $Q = 8, I_t(\text{DMSO}) = 4, I_c(\text{DMSO}) = 0.1, \kappa = 3 \times 10^{-4} \text{ s}^{-1} \text{ M}^{-1},$ and $\kappa_{-} = 3 \times 10^{-7} \text{ s}^{-1},$ Experimental Values from Table III Being Given for Comparison

Constant	K_n/M^{-1}	
	Calcd	Exptl
$K_1 = Q^2[I_t(\text{DMSO})^{-1}]\kappa/\kappa_{-}$	16×10^3	8×10^3
$K_2 = Q[I_t(\text{DMSO})^{-1}]\kappa/\kappa_{-}$	2×10^3	1.1×10^3
$K_3 = [I_t(\text{DMSO})^{-1}]\kappa/\kappa_{-}$	2×10^2	1.9×10^2
$K_4 = 2Q^2[I_c(\text{DMSO})^{-1}]\kappa/\kappa_{-}$	1.3×10^6	1.2×10^6
$K_5 = 1/2Q[I_c(\text{DMSO})^{-1}]\kappa/\kappa_{-}$	4×10^4	2.5×10^4
$K_6 = 2Q[I_c(\text{DMSO})^{-1}]\kappa/\kappa_{-}$	1.6×10^5	1.5×10^5
$K_7 = 1/2[I_c(\text{DMSO})^{-1}]\kappa/\kappa_{-}$	5×10^3	4×10^3

I_c are given in Table VI. Equation 39 with $\kappa = 3 \times 10^{-4} \text{ s}^{-1} \text{ M}^{-1}$ describes approximately both the seven halide anation rate constants in the Pt(II)-DMSO-chloro-aqua system and the halide anation rate constants for the simple chloro-aqua^{7,9} and mixed chloro-bromo complexes¹² of Pt(II), if the parameters in Table VI are used.

The stability constants K_1 to K_7 of eq 8 can be expressed as (40) which is a generalization of eq 37. The stability

$$K_n = k_n/k_{-n} = m\kappa I_t^{-1} I_{c1}^{-1} I_{c2}^{-1} Q^q / n\kappa_{-} \quad (40)$$

constants calculated from eq 40 agree satisfactorily with the experimental values; cf. Table VIII.

The charge factor Q is about 5 for the simple chloro- and bromo-aqua systems of Pt and Pd.⁹ Independent values can be calculated from the present equilibrium constants. For substitution trans to DMSO we obtain (cf. Table VIII)

$$Q = K_1/K_2 = 7$$

$$Q = K_2/K_3 = 6$$

and for substitution cis to DMSO

$$Q = 2K_6/(1/2K_7) = 9$$

$$Q = 1/2K_5/(1/2K_7) = 7$$

$$Q = 2K_4/(1/2K_5) = 10$$

A mean value of $Q = 8 \pm 2$ can be used to describe all the present results.

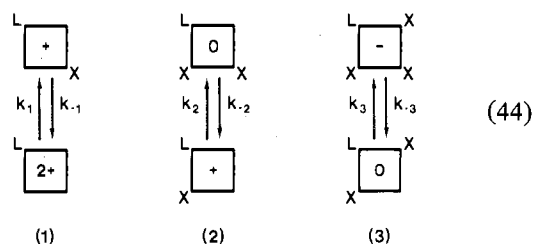
Equations 40, 36, and 39 imply that

$$K_2 = (K_1K_3)^{1/2} \quad (41)$$

$$k_2 = (k_1k_3)^{1/2} \quad (42)$$

$$k_{-2} = (k_{-1}k_{-3})^{1/2} \quad (43)$$

Table IX shows empirical tests of these relations for six different systems which can be described by (44), where the



aqua ligands have been omitted and $L = \text{DMSO}$ or $\text{H}_2\text{O}, X = \text{Cl}$ or Br and the metal is Pd or Pt. The experimental values in Table IX show that the relation (41) for the equilibrium constants is valid with good accuracy in all cases studied. The experimental values for the rate constants k_2 and k_{-2} , on the other hand, are always larger than $(k_1k_3)^{1/2}$ and $(k_{-1}k_{-3})^{1/2}$, respectively. The discrepancy is largest for bromide complexes of platinum where it amounts to a factor of nearly 10 and

Table IX. Rate Constants and Stability Constants Corrected for Statistical Factors for the Reactions (44)^f

	Pt, L = DMSO, X = Cl ^a	Pt, L = DMSO, X = Br ^b	Pt, L = H ₂ O, X = Cl ^c	Pt, L = H ₂ O, X = Br ^d	Pd, L = H ₂ O, X = Cl ^e	Pd, L = H ₂ O, X = Br ^e
<i>K</i> ₁ /M ⁻¹	3.0 × 10 ³	2 × 10 ⁴	2.3 × 10 ⁴	~2.4 × 10 ⁵	5.5 × 10 ³	2.8 × 10 ⁴
<i>K</i> ₂ /M ⁻¹	4.1 × 10 ²	1.3 × 10 ³	6.7 × 10 ³	3.1 × 10 ⁴	1.3 × 10 ³	1.3 × 10 ⁴
<i>K</i> ₃ /M ⁻¹	6.7 × 10 ¹	1.8 × 10 ²	8.3 × 10 ²	6.2 × 10 ³	4.0 × 10 ²	7.0 × 10 ³
(<i>K</i> ₁ <i>K</i> ₃) ^{1/2} /M ⁻¹	4.5 × 10 ²	1.9 × 10 ³	4.4 × 10 ³	~3.9 × 10 ⁴	1.5 × 10 ³	1.4 × 10 ⁴
<i>k</i> ₁ /s ⁻¹ M ⁻¹	4 × 10 ³	1.7 × 10 ⁴	6.8 × 10 ⁻³	4.8 × 10 ⁻²	4.6 × 10 ³	2.3 × 10 ⁴
<i>k</i> ₂ /s ⁻¹ M ⁻¹	4 × 10 ²	6 × 10 ³	1 × 10 ⁻³	1.5 × 10 ⁻²	2.5 × 10 ²	2 × 10 ³
<i>k</i> ₃ /s ⁻¹ M ⁻¹	2 × 10 ¹	54	2.3 × 10 ⁻⁵	9 × 10 ⁻⁵	1.1 × 10	4 × 10
(<i>k</i> ₁ <i>k</i> ₃) ^{1/2} /s ⁻¹ M ⁻¹	2.8 × 10 ²	9 × 10 ²	3.9 × 10 ⁻⁴	2 × 10 ⁻³	2.2 × 10 ²	9.6 × 10 ²
<i>k</i> ₋₁ /s ⁻¹	0.45	0.86	3 × 10 ⁻⁷	~8 × 10 ⁻⁷	8.3 × 10 ⁻¹	8.3 × 10 ⁻¹
<i>k</i> ₋₂ /s ⁻¹	0.35	1.5	1.5 × 10 ⁻⁷	2 × 10 ⁻⁶	2 × 10 ⁻¹	1.5 × 10 ⁻¹
<i>k</i> ₋₃ /s ⁻¹	0.10	0.10	2.8 × 10 ⁻⁸	1.4 × 10 ⁻⁸	2.7 × 10 ⁻²	6 × 10 ⁻³
(<i>k</i> ₋₁ <i>k</i> ₋₃) ^{1/2} /s ⁻¹	0.2	0.3	9 × 10 ⁻⁸	~1.1 × 10 ⁻⁷	1.5 × 10 ⁻¹	7 × 10 ⁻²

^a This paper. ^b Reference 10. ^c References 7 and 14. ^d References 14 and 25. ^e Reference 9. ^f Values printed in italics from eq 41-43.

smallest for chloride complexes of palladium. This acceleration of both the forward and reverse processes of reaction 2, compared to reactions 1 and 3, probably reflects some property of the transition state. An activated complex of approximately trigonal-bipyramidal structure, with the two cis ligands at the apices of the bipyramid, will be a much stronger dipole for reaction 2 than for reactions 1 and 3, since the two cis ligands are equal for reactions 1 and 3, whereas for reaction 2 one of them is a water molecule and the other a halide ion. Reaction 2 should, therefore, be accelerated in a polar solvent like water, due to a better solvation of the transition state.

The chloride anation rate constants *k*₁, *k*₂, and *k*₃ vary by a factor of about 200. It is apparent from Table II that the variation of Δ*H*[‡] for these reactions is very small; all values lie within 45 ± 3 kJ K⁻¹ mol⁻¹. The differences in rate are, therefore, mainly due to a variation of the activation entropy caused by differences in solvation between the reactant ions and the activated complexes. Reactions 1 and 2 both result in a lowering of the net charge which is partly opposed by the dipole character of the activated complex for reaction 2. For reaction 3, the net charge is approximately unchanged. This is in accordance with the observed change in the Δ*S*[‡] values of -26, -56, and -65 J K⁻¹ mol⁻¹ (cf. ref 8, pp 143-144). The values also agree with observed Δ*S*[‡] values for other square-planar substitutions. For instance, Δ*S*[‡] for the chloride anation of Pd(H₂O)₄²⁺ is -24 J K⁻¹ mol⁻¹,⁹ i.e., approximately the same as for reaction 1.

These results indicate that the rates of square-planar halide anation reactions depend on the ionic charge of the substrate complexes. It is therefore natural to introduce the charge factor *Q* in eq 36 when rate constants for such reactions are compared.

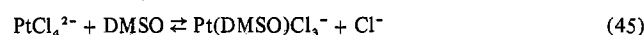
The acid hydrolysis rate constants *k*₋₁, *k*₋₂, and *k*₋₃ vary only by a factor of about 5. No definite conclusions can be drawn from the activation parameters in Table II. The variation of the chloride anation rate constants *k*₂ and *k*₃ with ionic strength agrees qualitatively with the Debye-Hückel relations for reactions between ions (cf. ref 8, pp 150-153). The variation of the acid hydrolysis rate constants *k*₋₃ and *k*₋₂ is consistent with ion-dipole and dipole-dipole interactions, respectively (cf. ref 8, pp 150-153).

To conclude, empirical relationships like (34), (36), (37), (39), and (40) are valuable, since a large amount of kinetic information can be summarized using a few parameters. Because these parameters approximately retain their numerical values for different complexes, the relations can also be used to predict approximate magnitudes both of rate constants and of equilibrium constants.

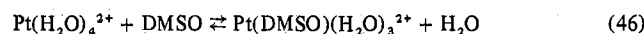
As an example, the chloride anation rate constant for *cis*-Pt(DMSO)₂(H₂O)₂²⁺ is predicted by eq 39 to be approximately 2 × (3 × 10⁻⁴) × (2 × 10⁶/4) × (5/0.1) × (1/1)

× 5² = 4 × 10⁵ s⁻¹ M⁻¹. Preliminary experiments²⁸ indicate a rate constant of about 2 × 10⁵ s⁻¹ M⁻¹.

Stability of Pt(DMSO)(H₂O)₃²⁺. Kukushkin and Kirillov²⁶ have shown that the reaction



is practically irreversible. Hence, its equilibrium constant *K'* is at least 10⁶. This gives an opportunity to estimate a lower limit for the stability constant *K*_{DMSO} for the process



from the known stability constants

$$\beta_{4\text{Cl}} = [\text{PtCl}_4^{2-}][\text{Pt}^{2+}]^{-1}[\text{Cl}^{-}]^{-4} = 10^{14} \text{ M}^{-4}$$

(from ref 14) and

$$\beta_3 = [\text{Pt}(\text{DMSO})\text{Cl}_3^{-}][\text{Pt}(\text{DMSO})_2^{2+}]^{-1}[\text{Cl}^{-}]^{-3} = 5.8 \times 10^{12} \text{ M}^{-3}$$

(from Table III). Thus, *K*_{DMSO} = *K'*/β_{4Cl}β₃⁻¹ > 10⁷ M⁻¹. Since the rate constant for formation of Pt(DMSO)(H₂O)₃²⁺ according to (46) is 8.4 × 10⁻⁵ s⁻¹ M⁻¹,²⁷ the half-life for dissociation of DMSO from Pt(DMSO)(H₂O)₃²⁺ must be at least 10³ years. It is worth noting that the corresponding palladium complex is much weaker, having a stability constant of only about 8 M⁻¹.²⁸

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Registry No. Pt(DMSO)Cl₃⁻, 31203-96-0; Pt(DMSO)(H₂O)₃²⁺, 25460-49-5.

Supplementary Material Available: Tables X-XIII describing the kinetic experiments and Table XIV summarizing the equilibrium measurements (5 pages). Ordering information is given on any current masthead page.

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Structural Isomerization of (Bis(trimethylsilyl)amino)phosphine Oxides

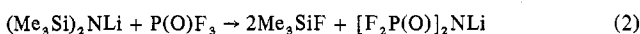
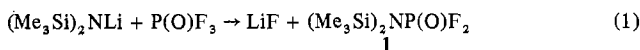
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The reactions of lithium bis(trimethylsilyl)amide with phosphoryl chlorides ClP(O)X_2 ($\text{X} = \text{F, Cl, Ph}$) result in the formation of the *N*-silylated phosphinimines $\text{Me}_3\text{SiN}=\text{PX}_2\text{OSiMe}_3$ rather than the isomeric phosphine oxides $(\text{Me}_3\text{Si})_2\text{NP(O)X}_2$. Stereochemical arguments and ^{13}C NMR data provide support for the assignment of the imine structure.

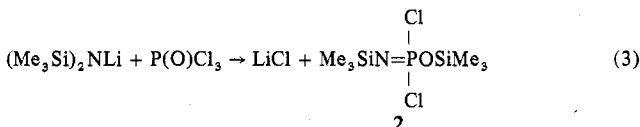
Introduction

The reactions of lithium bis(trimethylsilyl)amide with simple phosphorus halides have been the subject of several recent investigations and, in some cases, conflicting results have appeared. For example, although PF_3 and P(S)F_3 react with $\text{LiN}(\text{SiMe}_3)_2$ to produce the expected products $(\text{Me}_3\text{Si})_2\text{NPF}_2$ ^{1,2} and $(\text{Me}_3\text{Si})_2\text{NP(S)F}_2$,² PF_5 affords $(\text{Me}_3\text{Si})_2\text{NPF}_2\text{NSiMe}_3$ if the reaction is carried out in ether³ or $\text{LiN}(\text{PF}_4)_2$ if hexane is used as the solvent.² Even more inconsistent are the facts that Glemser et al.⁴ report (bis(trimethylsilyl)amino)difluorophosphine oxide (**1**) as the product of the reaction (eq 1) of P(O)F_3 with $\text{LiN}(\text{SiMe}_3)_2$ in ether solution, while Fluck⁵ has observed silicon-nitrogen bond cleavage under essentially the same conditions (eq 2).

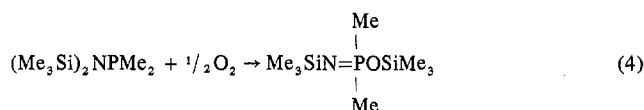


In still another study, Kling et al.² have obtained quantitative yields of $\text{LiN}[\text{P(O)F}_2]_2$ in hexane solution but mixtures of $\text{LiN}[\text{P(O)F}_2]_2$ and compound **1** in ether solution. However, these authors reported neither the yield of the phosphine oxide **1** nor its method of characterization.

Not only has there been difficulty in reproducing the synthesis of the (silylamino)phosphine oxide **1**, but the structural assignment of the compound may also be open to question. Thus, while the observation of two Me_3Si signals in the ^1H NMR spectrum of **1** is attributed to hindered *N*-*P* bond rotation, a comparable spectrum obtained on the chlorine analogue⁴ (eq 3) is cited as evidence for the rearranged



phosphinimine structure **2**. A similar structural isomerization (eq 4) has been recently observed in our laboratory for the *P*-dimethyl compound.⁶

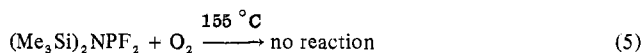


We report here an alternate synthetic route to compound **1** and an investigation of the generality of the phenomenon of Me_3Si migration from nitrogen to oxygen in compounds of this type.

Results and Discussion

In our hands, the reaction of P(O)F_3 with $\text{LiN}(\text{SiMe}_3)_2$ in ether solution produced only Me_3SiF and a nonvolatile, white solid, presumed to be $\text{LiN}[\text{P(O)F}_2]_2$, as reported by Fluck.⁵ No indication of the formation of **1** or any other liquid product was obtained. While this observation is not consistent with those of some other workers,^{2,4} it may simply reflect the sensitivity of such reactions to small changes in reaction conditions as we have encountered previously.⁶ Rather than attempt an exhaustive survey of this particular reaction, we chose to investigate other possible synthetic routes to compound **1**.

It was found to be impossible to prepare **1** by the direct oxidation (eq 5) of (bis(trimethylsilyl)amino)difluoro-



phosphine. Even when heated at reflux in an atmosphere of oxygen for several hours, the phosphine resisted oxidation. By comparison, the less sterically hindered compound Me_2NPF_2 can be oxidized under considerably milder conditions.⁷

Alternatively, when difluorophosphoryl chloride was allowed to react (eq 6) with an ether solution of $\text{LiN}(\text{SiMe}_3)_2$, the

$$(\text{Me}_3\text{Si})_2\text{NLi} + \text{ClP(O)F}_2 \rightarrow \text{LiCl} + (\text{Me}_3\text{Si})_2\text{NP(O)F}_2 \quad (6)$$

product obtained in 55% yield was a clear colorless liquid whose boiling point, infrared spectrum, and NMR (^1H and ^{19}F) spectra are identical with the data reported⁴ for $(\text{Me}_3\text{Si})_2\text{NP(O)F}_2$. This is taken as strong evidence that we have indeed prepared the same compound as the earlier workers.⁴ The reaction (eq 6) is quite reproducible, giving high