# The Ion-Pair Mechanism in Square Planar Substitution. Displacement of Dimethyl Sulfoxide from Chloro(dimethyl sulfoxide)(*N,N,N',N'*-tetramethyldiaminoethane)platinum(II) Salts by Halide Ions in Dichloromethane Solution

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Freshly prepared [Pt(Me$_4$en)(Me$_2$SO)Cl]Cl rapidly loses Me$_2$SO in the solid state to give [Pt(Me$_4$en)Cl$_2$]. This reaction also occurs in chloroform and dichloromethane solution. The kinetics are first-order with a rate constant ($10^4k_1$/s$^{-1}$ = 3.7 at 298 K, $\Delta H^{\ddagger}$ = 98 ± 2 kJ mol$^{-1}$, $\Delta S^{\ddagger}$ = 19 ± 5 J K$^{-1}$ mol$^{-1}$ in CH$_2$Cl$_2$) that is independent of the initial concentration of the complex and of added [Me$_2$SO]. Addition of small amounts of [AsPh$_4$]Cl causes the rate of displacement of dimethyl sulfoxide to increase, but further addition leads to a rate that is independent of the concentration of added nucleophile. Other anions replace the chloride at a rate that is too fast to measure and then replace the dimethyl sulfoxide. The kinetics are consistent with an interchange within ion aggregates. The limiting interchange rate constant depends only slightly on the nature of the entering halide, $10^4k_2$/s$^{-1}$ = 5.3, 4.3, and 11.6 for the entry of Cl$^-$, Br$^-$, and I$^-$, respectively, at 298 K in CH$_2$Cl$_2$, but it is not possible to separate the cis effects of the different halides from the nucleophilic discrimination of the substrate. Uncharged nucleophiles react either slowly or not at all in these weakly-polar solvents. Other salts of this cation are described, and the ion-association equilibria of the hexafluorophosphate and the tetraphenylborate have been investigated in dichloromethane. In aqueous and methanolic solution, [Pt(Me$_4$en)(Me$_2$SO)Cl]Cl remains unchanged for a long time even in the presence of a large excess of chloride ions, and in aqueous solution the coordinated chloride is replaced by other nucleophiles at a rate that is some 2 orders of magnitude slower than that in the reaction of the analogous diaminoethane complex. The dimethyl sulfoxide is not replaced. The molecular structure of [Pt(Me$_4$en)(Me$_2$SO)Cl]BPh$_4$ was determined by single-crystal X-ray diffraction analysis. White C$_{32}$H$_{42}$N$_2$BClOPtS crystallizes in the orthorhombic *Pcab* space group with *a* = 12.088 (4) Å, *b* = 22.738 (6) Å, *c* = 23.246 (9) Å, and *Z* = 8. There are no unusual steric interactions within the cation to account for the unusual lability of the dimethyl sulfoxide.

## Introduction

In 1970, when few people believed that Rosenberg's observation of the carcinostatic properties of *cis*-[Pt(NH$_3$)$_2$Cl$_2$] would have any medical consequences,[1] we started an extensive study, as part of a consortium funded by Rustenberg Platinum Mines, of the antitumor properties of complexes of the platinum group metals. Among other things we investigated the reaction between *cis*-[Pt(Me$_2$SO)$_2$Cl$_2$] and amines (am) as a general method for the formation of complexes of the type *cis*-[Pt(am)$_2$Cl$_2$].[2] The displacement of dimethyl sulfoxide from the intermediate species *cis*-[Pt(am)$_2$(Me$_2$SO)Cl]Cl frequently required drastic conditions, such as heating to 180 °C an oven, and was often accompanied by cis–trans isomerization, but we have recommended this method as a means of making analogous complexes with chelating diamines (L-L), [Pt(L-L)Cl$_2$], where the problem of isomerization does not arise.[3] Recently, this idea has been revived.[4,5] This inertness of a single dimethyl sulfoxide is not universal, and many years ago we were surprised to find that when *N,N,N',N'*-tetramethyldiaminoethane was reacted with *cis*-[Pt(Me$_2$SO)$_2$Cl$_2$] in methanol, the white [Pt(Me$_4$en)(Me$_2$SO)Cl]Cl intermediate could be precipitated and filtered off but rapidly lost dimethyl sulfoxide on the filter to give [Pt(Me$_4$en)Cl$_2$].[6] We have now isolated the cation as stable salts of noncoordinated anions, [PF$_6$]$^-$, [B(C$_6$H$_5$)$_4$]$^-$, and [ClO$_4$]$^-$, and in this paper we report the preparation and properties of these complexes, the structure of the cation, and the kinetics of the reactions in water, chloroform, and dichloromethane solutions.

## Experimental Section

**Preparations. Chloro(dimethyl sulfoxide)(*N,N,N',N'*-tetramethyldiaminoethane)platinum(II) Hexafluorophosphate.** A solution of the stoichiometric amount of *N,N,N',N'*-tetramethyldiaminoethane (0.464 g; 4 mmol) in methanol (50 cm$^3$) was added drop by drop to a suspension in methanol (100 cm$^3$) of *cis*-[Pt(Me$_2$SO)$_2$Cl$_2$] (1.69 g; 4 mmol), prepared by the method of Wayland.[3,7] When all the solid had dissolved, the solution was set aside overnight. Some yellow material that settled out was filtered off, and the filtrate was concentrated to a volume of 60 cm$^3$ and divided into four aliquots.

AgPF$_6$ (0.252 g; 1 mmol) was added to one of the aliquots, and the precipitated AgCl was filtered off and the filtrate concentrated to a volume of 5 cm$^3$. The required compound crystallized on cooling and was recrystallized from methanol.

Anal. Found: C, 16.9; H, 3.84; N, 4.74. Calcd for C$_8$H$_{22}$N$_2$ClF$_6$OPPtS: C, 16.86; H, 3.89; N, 4.92.

**The perchlorate salt** was obtained by adding LiClO$_4$ (0.106 g; 1 mmol) to another aliquot of the stock solution. After evaporation of most of the solvent, the complex separated on cooling as white crystals.

Anal. Found: C, 18.24; H, 4.12; N, 5.41. Calcd for C$_8$H$_{22}$N$_2$Cl$_2$O$_5$PtS: C, 18.33; H, 4.23; N, 5.34.

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**The tetraphenylborate salt** was obtained as a white precipitate on adding $NaB(C_6H_5)_4$ (0.34 g; 1 mmol) to one of the above aliquots. It was recrystallized from dichloromethane/diethyl ether.

Anal. Found: C, 51.7; H, 5.55; N, 3.67. Calcd for $C_{32}H_{42}N_2BClOPtS$: C, 51.7; H, 5.69; N, 3.76.

**Chloride Salt.** Provided the chloride salt is kept in methanolic solution, it is stable for a considerable time, and only after many weeks in the dark at room temperature do yellow crystals of $[Pt(Me_4en)Cl_2]$ start to separate. When excess diethyl ether is added to one of the above aliquots, a white solid is precipitated. This rapidly turns yellow, and the conversion to the dichloro complex is complete within a few hours. If redissolved in methanol, the chloride salt returns to its previous inertness.

**(Dimethyl sulfoxide)iodo(*N,N,N',N'*-tetramethyldiaminoethane)platinum(II) iodide** was prepared by adding KI to an aqueous solution of $[Pt(Me_4en)(Me_2SO)Cl]Cl$. The course of the reaction was followed spectrophotometrically, and when all of the substrate had been converted to product, the solvent was removed rapidly under reduced pressure. The pale-yellow solid was washed with small quantities of water, methanol, and diethyl ether and air dried. Because of its instability, it was not possible to obtain elemental analyses.

**Complexes of the type $[Pt(Me_4en)X_2]$ (X = Cl, Br, I, $N_3$, $NO_2$)** were obtained by mixing concentrated methanolic solutions of $[Pt(Me_4en)(Me_2SO)Cl]Cl$ (prepared as described above) with at least a 10-fold molar excess of the appropriate LiX (or NaX) dissolved in acetone or water.

Dichloromethane used in the kinetic runs was distilled from barium oxide under nitrogen and then redistilled through a 60-cm platinum spinning band column. Only the center cut was used.

**Microanalyses** were performed by Bernhardt Microanalytishes Laboratorium.

**Conductance data** were obtained using a Radiometer CDM3 conductivity bridge and an Ehrlenmeyer type cell with unplatinized electrodes. The cell constant (0.5693 $cm^{-1}$) was determined using standard aqueous solutions of potassium chloride. The temperature was held constant to ±0.01 °C in a thermostated bath.

**$^1H$ NMR measurements** were recorded at 80 MHz on a Bruker WP 80 spectrometer and at 300 MHz on a Varian Gemini 300 spectrometer. Chemical shifts are reported in parts per million downfield from $Me_4Si$.

**Infrared spectra** of Nujol mulls of the complexes between CsI or KBr windows were measured on a Perkin-Elmer Model FT-IR 1730 instrument.

**Structure Determination.** Suitable crystals of $[Pt(Me_4en)(Me_2SO)Cl][BPh_4]$ were grown by placing a filtered solution of the complex in dry $CH_2Cl_2$ in an open beaker in a vacuum desiccator that already contained an open beaker of diethyl ether. After 1–2 h crystals of the complex, some as long as 1 cm, had separated and were filtered off. A suitable crystal was mounted on a glass fiber with Araldite cement.

All geometric and intensity data were taken from these crystals using an automated four-circle diffractometer (Nicolet R3mV) equipped with a graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) source. Important crystallographic data are collected in Table I.

The lattice vectors were identified by application of the automatic indexing routine of the diffractometer to the positions of 27 reflections taken from a rotation photograph and centered by the diffractometer. The $\omega$–$2\theta$ technique was used to measure 6227 reflections in the range $5° < 2\theta < 50°$, of which 5625 were unique. Three standard reflections, remeasured every 97 scans, showed no significant loss of intensity during data collection. The data were corrected for Lorentz and polarization effects and empirically for absorption.

The 3094 unique data with $I \geq 1.5\sigma(I)$ were used in the structure solution and refinement in the space group *Pcab*. The structure was solved by direct methods. Alternating cycles of least-squares refinement and difference Fourier synthesis led to the complete solution of the structure. The asymmetric unit contains one cation and one tetraphenylborate anion. All of the non-hydrogen atoms were refined anisotropically. The hydrogens of the phenyl groups were idealized to trigonal planar positions with C–H = 0.96 Å ($U$ = 0.08Å$^2$), while the aliphatic hydrogens were idealized to tetrahedral positions with the same dimensions. The final least-squares cycle included 352 parameters for 3094 variables ($I \geq 2.5\sigma(I)$) with $R$ = 0.0535 and $R_w$ = 0.0658 and did not shift any parameter by more than 0.001 times its esd. The final difference Fourier contains a number of peaks of about 1.1 e Å$^{-3}$. A selection of bond lengths and angles is listed in Table II.

**Kinetics.** The reactions were carried out in a silica cell in the thermostated cell compartment of either a Cary 219 or a Perkin-Elmer Lambda 3 spectrophotometer, with a temperature accuracy of ±0.02 °C. The fastest reactions required the use of a rapid-scanning Hewlett-Packard Model 8452A spectrophotometer.

**Table I.** Crystallographic Data for $[Pt(Me_4en)(Me_2SO)Cl]BPh_4$

| | |
|---|---|
| formula | $C_{32}H_{42}N_2BClOPtS$ |
| fw | 744.17 |
| space group | *Pcab* |
| $a$, Z | 12.088 (4) |
| $b$/Å | 22.738 (6) |
| $c$/Å | 23.246 (9) |
| $\alpha$/deg | 90.0 |
| $\beta$/deg | 90.0 |
| $\gamma$/deg | 90.0 |
| $V$/Å$^3$ | 6389.05 |
| $Z$ | 8 |
| $F(000)$ | 2976.00 |
| $d_{calc}$/g cm$^{-3}$ | 1.55 |
| cryst size/mm | 0.60 × 0.16 × 0.06 |
| $\mu$(Mo K$\alpha$)/cm$^{-1}$ | 46.1 |
| data collcn instrument | Nicolet R3m/V |
| radiation (λ/Å) | Mo (0.710 73) |
| orientation reflcns: no.; range ($2\theta$)/deg | 27; $13.4 \leq 2\theta \leq 25.51$ |
| temp/°C | 19 |
| no. of unique data | 5625 |
| tot. no. with $I \geq 2.5\sigma(I)$ | 3094 |
| no. of params | 352 |
| $R^a$ | 0.0535 |
| $R_w{}^b$ | 0.0658 |
| weighting scheme | $w^{-1} = \sigma^2(F) + g(F)^2$ |
| $g$ | 0.017 389 |
| largest shift/esd in final cycle | 0.001 |
| largest peak/e Å$^{-3}$ | 1.2 |

$^a$ $R = \sum[|F_o| - |F_c|]/\sum|F_o|$. $^b$ $R_w = \sum[|F_o| - |F_c|]w^{1/2}/\sum|F_o|w^{1/2}$.

**Table II.** Important Bond Lengths/Å and Angles/deg in $[Pt(Me_4en)(Me_2SO)Cl][BPh_4]$

| | | | | | |
|---|---|---|---|---|---|
| Pt–N(1) | 2.082 (15) | Pt–N(2) | 2.067 (13) | Pt–S | 2.234 (4) |
| Pt–Cl | 2.296 (5) | C(1)–S | 1.795 (18) | C(2)–S | 1.809 (16) |
| S–O | 1.470 (12) | C(3)–N(1) | 1.525 (25) | C(4)–N(2) | 1.446 (21) |
| C(5)–N91) | 1.456 (25) | C(6)–N(2) | 1.455 (25) | C(7)–N(1) | 1.513 (31) |
| C(8)–N(2) | 1.468 (36) | C(7)–C(8) | 1.352 (44) | C(10)–B | 1.642 (22) |
| C(20)–B | 1.683 (23) | C(30)–B | 1.602 (24) | C(40)–B | 1.684 (22) |

| | | | |
|---|---|---|---|
| N(1)–Pt–N(2) | 85.4 (6) | N(1)–Pt–S | 174.9 (4) |
| N(2)–Pt–S | 95.6 (4) | N(1)–Pt–Cl | 90.6 (5) |
| N(2)–Pt–Cl | 175.1 (4) | S–Pt–Cl | 88.5 (2) |
| Pt–S–C(1) | 108.3 (6) | Pt–S–C(2) | 111.0 (5) |
| Pt–S–O | 118.7 (5) | C(1)–S–C(2) | 102.8 (8) |
| C(1)–S–O | 107.3 (8) | C(2)–S–O | 107.4 (7) |
| Pt–N(1)–C(3) | 110.0 (11) | Pt–N(1)–C(5) | 118.1 (12) |
| C(3)–N(1)–C(5) | 106.7 (14) | C(5)–N(1)–C(7) | 109.3 (17) |
| Pt–N(2)–C(4) | 115.0 (10) | Pt–N(2)–C(6) | 114.6 (11) |
| C(8)–C(7)–N(1) | 113.6 (21) | C(7)–C(8)–N(2) | 119.7 (22) |

For all studies of the reactions of the chloride salt, frresh samples of solid $[Pt(Me_4en)(Me_2SO)Cl]Cl$, prepared by adding diethyl ether to a methanolic solution of the complex, were separated rapidly, washed with ether, dried, and dissolved in the appropriate solvent. The reactions were followed by ultraviolet spectroscopy ([complex] = $10^{-3}$–$10^{-4}$ mol dm$^{-3}$), conductance changes ([complex] = $10^{-2}$–$10^{-3}$ mol dm$^{-3}$), and NMR ([complex] = >$10^{-3}$ mol dm$^{-3}$). The reactions with added nucleophile were followed in a similar fashion by ultraviolet spectroscopy and NMR and were initiated by adding prethermostated solutions of the nucleophile to solutions of the $PF_6^-$ salt of the complex in the same solvent. The kinetics of $Me_2SO$ displacement in acetone or dichloromethane solutions were also followed by monitoring the decrease of the height of the IR peak assigned to $\delta_{S-O}$ for coordinated $Me_2SO$ and the parallel increase in the height of the corresponding peak assigned to the free sulfoxide using solution cells with $BaF_2$ or KBr windows. It was also possible to use IR spectroscopy to follow the displacement of coordinated $Me_2SO$ in solid samples of the chloride salt.

## Results

The IR spectra of the salts $[Pt(Me_4en)(Me_2SO)Cl]X$ (X = $Cl^-$, $PF_6^-$, $ClO_4^-$, $BPh_4^-$) all show a sharp absorption assigned to the S=O stretch in the range 1110–1150 cm$^{-1}$, which indicates that the ligand is linked to Pt through sulfur. The UV spectra of solutions of the complexes with X = $Cl^-$, $PF_6^-$, and $ClO_4^-$ are virtually identical and are unaffected by changing the solvent from dichloromethane to methanol. The differences in the spectrum of the tetraphenylborate salt arise from absorptions

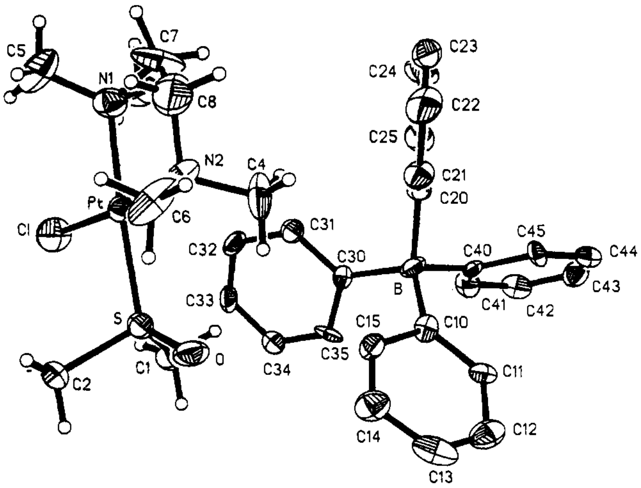

**Figure 1.** View of the asymmetric cell in [Pt(Me$_4$en)(Me$_2$SO)Cl][BPh$_4$].

due to the anion. Addition of excess chloride as [AsPh$_4$]Cl to a solution of the [BPh$_4$]$^-$ salt in dichloromethane does not change the spectrum initially.

The single-crystal, X-ray diffraction analysis of the tetraphenylborate salt shows that the structure of the cation (Figure 1) is typical for an Pt–S-bonded dimethyl sulfoxide complex. The coordination about the platinum in the cation is essentially square planar, with a small bisphenoidal distortion. The coordination shell contains the two nitrogens of the Me$_4$en ligand, the sulfur of the dimethyl sulfoxide, and the chlorine. The Pt–S bond length (2.234 ± 0.004 Å) lies within the range of the other values recorded, e.g., 2.174 (2) Å in [Pt(pyca)(Me$_2$SO)Cl] (pyca = pyridine-2-carboxylate, O trans to S),[8] 2.2186 (4) Å in *cis*-[Pt(Me$_2$SO)(NH$_3$)Cl$_2$],[9] 2.220 (4) Å in *trans*-[Pt(Me$_2$SO)(cyd)Cl] (cyd = cytidine),[10] and 2.244 Å in *cis*-[Pt(Me$_2$SO)$_2$Cl$_2$].[11] The coordination about the sulfur shows an interesting distortion from tetrahedral in that, while the two carbons and the oxygen occupy three of the tetrahedral sites with an angle (107.5°) only slightly less than that required, the platinum is bent away from the oxygen (Pt–S–O = 118.7°). This is also seen in [Pt(pyca)(Me$_2$SO)Cl] (117.2°)[8] and in a number of palladium complexes, although not always as marked as this.[12] No significance is attached to the apparent shortness of the C–C bond in the chelated amine [C(7)–C(8) = 1.352 (44) Å]. Models were tried that included disorder in the Me$_4$en ligand, but while they increased the number of parameters, they did not significantly improve the fit.

**Table III.** $^1$H NMR Data for [Pt(Me$_4$en)(Me$_2$SO)Cl]X Complexes in Various Solvents

| X | $\delta(-S(CH_3)_2)^a$ | $\delta(-N(CH_3)_2)^a$ | $\delta(-N(CH_2)_2N-)^a$ |
|---|---|---|---|
| $Cl^{-\,b}$ | 3.51 (23) | 3.28 (40), 2.98 (30) | 3.10 |
| $Cl^{-\,b}$ | 3.52 (23) | 3.28 (40), 2.98 (29) | 3.10 |
| $PF_6^{-\,b}$ | 3.49 (23) | 3.19 (40), 2.91 (30) | 3.03 |
| $ClO_4^{-\,b}$ | 3.46 (23) | 3.20 (40), 2.91 (30) | 3.03 |
| $BPh_4^{-\,b}$ | 3.34 (23) | 2.78 (40), 2.57 (30) | 2.16 |
| $Cl^{-\,d}$ | 3.57 (23) | 3.29 (40), 2.96 (30) | 3.21 |
| $PF_6^{-\,d}$ | 3.57 (23) | 3.29 (41), 2.96 (30) | 3.22 |
| $Cl^{-\,e}$ | 3.44 (23) | 3.04 (41), 2.75 (30) | 2.90 |
| $PF_6^{-\,e}$ | 3.47 (23) | 3.07 (40), 2.79 (30) | 2.93 |

[a] Chemical shifts in ppm relative to TMS. Coupling constants of $^1$H with $^{195}$Pt are given in parnetheses. [b] In CD$_2$Cl$_2$. [c] Obtained by adding [AsPh$_4$]Cl to a solution of [Pt(Me$_4$en)(Me$_2$SO)Cl]PF$_6$ in the ratio 2.5:1. [d] In (CD$_3$)$_2$CO. [e] In D$_2$O.

**Table IV.** Analysis of the Dependence of $\delta(CH_2)$ on Concentration ($C$) in Terms of Ion Association[a]

| $10^3C$/mol dm$^{-3}$ | $\delta$/ppm | $\alpha^b$ | $10^{-3}K_{IP}$/dm$^3$ mol$^{-1}$ | $10^4I$/mol dm$^{-3}$ | $10^{-3}K_{IP}{}^0$/dm$^3$ mol$^{-1}$ |
|---|---|---|---|---|---|
| 12.9 | 2.169 | 0.235 | 1.08 | 30.3 | 13.3 |
| 6.45 | 2.202 | 0.272 | 1.53 | 17.5 | 11.7 |
| 3.23 | 2.239 | 0.313 | 2.16 | 10.1 | 11.1 |
| 1.61 | 2.283 | 0.363 | 3.00 | 5.84 | 10.9 |
| 0.806 | 2.339 | 0.426 | 3.93 | 3.43 | 10.9 |
| 0.403 | 2.391 | 0.484 | 5.46 | 1.95 | 12.0 |
| 0.202 | 2.483 | 0.588 | 5.91 | 1.19 | 11.0 |
| 0.101 | 2.548 | 0.661 | 7.70 | 0.67 | 12.4 |
| 0.0252 | 2.710 | 0.843 | 8.77 | 0.21 | 11.6 |

[a] The correction to $I = 0$ is based on the relationship

$$\log K_{IP}{}^0 = \log K_{IP} - 2\left(\frac{-13.34\sqrt{I}}{1 + 6.26\sqrt{I}}\right)$$

[b] Using $\delta_{IP} = 1.96$ and $\delta_I = 2.85$.

The $^1$H NMR spectra of all the salts in CD$_2$Cl$_2$, (CD$_3$)$_2$CO, and D$_2$O are consistent with the solid-state structure and, apart from the BPh$_4^-$ salt, are similar (Table III). The peak at $\delta$ 3.48 ± 0.3 with $^{195}$Pt satellites is consistent with the methyl protons of a S-bonded dimethyl sulfoxide, and the chemical shifts of the methyl and methylene peaks of the diamine chelate are as expected for a planar four-coordinate complex. The spectrum of the tetraphenylborate salt is strongly concentration dependent, and while all proton chemical shifts are affected, those of the methylene protons of the Me$_4$en ligand are most concentration dependent. This would suggest that the orientation of the cation and anion within the ion pair resembles that found in the crystal, where a phenyl group is packed adjacent to the methylene groups of the diamine (Figure 1) and that the ring currents from a phenyl group in the anion are mainly responsible for the special behavior of the BPh$_4^-$ salt. A similar effect has been observed in dry methanol by Crociani et al.[13] This concentration dependence is shown in Table IV. Assuming that the observed chemical shift, $\delta$, is the weighted average of those of the free ion, $\delta_I$, and the ion pair, $\delta_{IP}$, it is possible to determine $\alpha$, the degree of dissociation of the ion pair

$$\alpha = \frac{\delta - \delta_{IP}}{\delta_I - \delta_{IP}}$$

and from this the equilibrium constant, $K_{IP}$. The value of $K_{IP}{}^0$

$$K_{IP} = \frac{(1 - \alpha)}{\alpha^2 C}$$

at zero ionic strength was calculated using the expression

$$\log K_{IP}{}^0 = \log K_{IP} - 2\left(\frac{-A\sqrt{\mu}}{1 + \text{å}B\sqrt{\mu}}\right)$$

with the Debye–Hückel coefficients $A$ and $B$, calculated for a solvent of dielectric constant = 8.89 at 298 K, equal to 13.34 and 1.00, respectively. å is the sum of the ionic radii, and it has been assumed that this is equal to the distance of closest approach of the ions in the crystal (B···Pt = 6.26 Å)). The values chosen for $\delta_I$ and $\delta_{IP}$ were those that gave the minimum root mean square deviation for a constant value of $K_{IP}{}^0$ consistent with a random distribution of the residuals. The values of $K_{IP}$ and $K_{IP}{}^0$ are also collected in Table IV.

The $^1$H NMR spectrum of the chloride in CD$_2$Cl$_2$ changes with time, the peaks due to the substrate decreasing while the peak at $\delta$ 2.56, assigned the free dimethyl sulfoxide, grows. Peaks at $\delta$ 2.93 and 2.76 assigned to N–C*H*$_3$ and N–C*H*$_2$–C of [Pt(Me$_4$en)Cl$_2$] also appear. The rate of this reaction compares well with that of the changes observed spectrophotometrically and discussed

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below, but precipitation of the product at the higher concentrations needed for the NMR studies precluded a proper kinetic analysis.

The variations with concentration of the conductance of solutions of the $PF_6^-$ and $BPh_4^-$ salts in dichloromethane at 25.0 °C were analyzed by the method of Shedlovsky and Fuoss[14] and also by the more recent D'Aprano and Fuoss equation,[15-17] where the best fit of conductance, $\Lambda$, to stoichiometric concentration, $c$, values was made by computer analysis using the relationships

$$\Lambda = \Lambda_0 - Sc^{1/2}\gamma^{1/2}$$

$$1 - \gamma = K_a^0(c\gamma)^2 f^2$$

where $c\gamma$ is the concentration of free ions, $S$ is the slope of the theoretical limiting tangent, and $f$ is the Debye–Hückel value of the activity coefficients (see above). A viscosity of 0.412 cP and dielectric constant of 8.89 were used in the calculations.

The Shedlovsky–Fuoss method yields values for $K_a^0$ (the ion-pair dissociation constant at zero ionic strength) of $1.47 \times 10^{-5}$ and $5.57 \times 10^{-5}$ mol dm$^{-3}$ for the $PF_6^-$ and $BPh_4^-$ salts respectively, with $\Lambda_0$ values of 147.7 and 106.7 $\Omega^{-1}$ cm$^2$ mol$^{-1}$ at 25.0 °C. Since $K_a^0 = (K_{IP}^0)^{-1}$, these correspond to values of $6.8 \times 10^4$ and $1.8 \times 10^4$ dm$^3$ mol$^{-1}$, respectively, for the ion-association constants, $K_{IP}^0$. The agreement between the values of the ion-association constants determined from the dependence of chemical shift and conductance of the $BPh_4^-$ salt on concentration is pleasing. The D'Aprano–Fuoss method, which requires more precision of the data, gave a value of $1.70 \times 10^{-5}$ mol dm$^3$ for $K_a^0$ for the $PF_6^-$ salt, with $\Lambda_0 = 138.5$ $\Omega^{-1}$ cm$^2$ mol$^{-1}$, but the analysis of the conductance of the $BPh_4^-$ salt did not converge. The conductance of a solution of a freshly precipitated sample of [Pt(Me$_4$en)(Me$_2$SO)Cl]Cl in $CH_2Cl_2$ decreases with time, but the change is slow enough for the extrapolation to the time of dissolution to be a reasonably reliable way of determining $\Lambda$. The concentration was determined by applying Beer's law to the UV spectrum also extrapolated to the time of discussion, using the spectrum of the stable $PF_6^-$ salt as a standard. This method required too much material to be used for a full evaluation of the ion-association constant. The extrapolated conductance of a fresh solution containing 0.0076 mol dm$^{-3}$ of the chloride salt at 25.0 °C was 4.22 $\Omega^{-1}$ cm$^2$ mol$^{-1}$, and this rose to 6.13 $\Omega^{-1}$ cm$^2$ mol$^{-1}$ for a more dilute solution (0.0015 mol dm$^{-3}$). The $PF_6^-$ salt has a conductance of 23.5 $\Omega^{-1}$ cm$^2$ mol$^{-1}$ at 0.00105 mol dm$^{-3}$, the highest concentration studied. In view of the greater mobility of the chloride anion, this indicates that the ion-association constant for the chloride ion pair will be significantly greater than that of the hexafluorophosphate salt. The conductance change follows a first-order rate law, and the rate constant corresponds well with those determined spectrophotometrically.

The spectrum of a chloroform or dichloromethane solution of a freshly prepared sample of [Pt(Me$_4$en)(Me$_2$SO)Cl]Cl changes slowly to that of [Pt(Me$_4$en)Cl$_2$], and at low enough concentration, there is no precipitation of product. The absorbance change is first-order, and the first-order rate constants, measured over a range of temperature, are collected in Table V.

**Table V.** Rate Data and Activation Parameters for the Reaction [Pt(Me$_4$en)(Me$_2$SO)Cl]Cl → [Pt(Me$_4$en)Cl$_2$] + Me$_2$SO[a]

| solvent | temp/K | [Me$_2$SO]/mol dm$^{-3}$ | $10^4k_{obs}$/s$^{-1}$ |
|---|---|---|---|
| $CHCl_3$[b] | 288.7 | | 0.228 |
| | 298.4 | | 0.932 |
| | 303.7 | | 1.82 |
| | 308.3 | | 3.40 |
| | 313.2 | | 6.40 |
| | 318.0 | | 10.3 |
| $CH_2Cl_2$[c] | 284.0 | | 0.456 |
| | 288.4 | | 0.868 |
| | 293.2 | | 1.86 |
| | 298.6 | | 3.70 |
| | 303.2 | | 6.80 |
| | 303.2 | 0.140 | 6.72 |
| | 303.2 | 0.280 | 6.87 |
| | 303.2 | 0.560 | 6.60 |
| | 303.2 | 1.12 | 6.50 |

[a] [Complex] within the range $2 \times 10^{-4}$ to $2 \times 10^{-3}$ mol dm$^{-3}$. [b] $\Delta H^\ddagger = 97 \pm 1$ kJ mol$^{-1}$, $\Delta S^\ddagger = 5 \pm 4$ J K$^{-1}$ mol$^{-1}$. [c] $\Delta H^\ddagger = 98 \pm 2$ kJ mol$^{-1}$, $\Delta S^\ddagger = 19 \pm 5$ J K$^{-1}$ mol$^{-1}$.

**Table VI.** Pseudo-First-Order Rate Constants for the Reaction [Pt(Me$_4$en)(Me$_2$SO)X]$^+$ + X$^-$ → [Pt(Me$_4$en)X$_2$] + Me$_2$SO[a]

| X | $10^3$[X$^-$]/mol dm$^{-3}$ | $10^3k_{obs}$/s$^{-1}$ | X | $10^3$[X$^-$]/mol dm$^{-3}$ | $10^3k_{obs}$/s$^{-1}$ |
|---|---|---|---|---|---|
| Cl[b] | 0.500 | 0.418 | Br[c] | 25.0 | 0.412 |
| | 1.00 | 0.502 | | 50.0 | 0.437 |
| | 10.0 | 0.521 | I[d] | 0.500 | 0.740 |
| | 25.0 | 0.522 | | 1.00 | 0.950 |
| | 50.0 | 0.531 | | 2.50 | 1.03 |
| Br[c] | 0.500 | 0.285 | | 5.00 | 1.11 |
| | 2.50 | 0.364 | | 10.0 | 1.13 |
| | 5.00 | 0.402 | | 25.0 | 1.13 |
| | 10.0 | 0.407 | | 50.0 | 1.13 |

[a] In dichloromethane at 25.0 °C, [complex] = $2.5 \times 10^{-4}$ mol dm$^{-3}$ (provided as [Pt(Me$_4$en)(Me$_2$SO)Cl][PF$_6$]). [b] As [Ph$_4$As]Cl. [c] As [Bu$_4$N]Br. [d] As [Bu$_4$N]I.

When a solution of [Pt(Me$_4$en)(Me$_2$SO)Cl]PF$_6$ in dichloromethane is treated with another [Ph$_4$As]Cl, yellow crystals of [Pt(Me$_4$en)Cl$_2$] soon separate. In dilute solution the spectrum changes slowly from that of the starting material to that of the dichloro product with first-order kinetics, and isosbestic points are maintained throughout. If [Bu$_4$N]Br or [Bu$_4$N]I is used, the corresponding dibromo and diiodo species are precipitated. Examination of the spectral changes that occur on mixing the reagents in dilute solution shows that an initial spectral change that is too fast to be followed kinetically with any of the techniques at our disposal is followed by a slow change with isosbestic points at 321 nm for the reaction with Br$^-$ and 302 and 319 nm for the reaction with I$^-$. In any run the slow change of absorbance follows first-order kinetics, and the rate constants are collected in Table VI.

The reaction with iodide has been studied in detail. The spectrum of the solution at the end of the fast reaction is identical to that of an authentic sample of [Pt(Me$_4$en)(Me$_2$SO)I]$^+$, and the rate constant for the reaction of freshly prepared [Pt(Me$_4$en)(Me$_2$SO)I]I with excess iodide in dichloromethane is identical to that measured in the reaction of the chloro complex with iodide under the same experimental conditions. This rules out the possibility that the fast spectral change is due to the formation of a five-coordinate species or an ion pair. The spectrum of a solution of [Pt(Me$_4$en)Cl$_2$] in $CH_2Cl_2$ is unaffected by the addition of a large excess of [Bu$_4$N]I, nor has it changed significantly 1 h later.

It is therefore concluded that the spectrophotometric changes correspond to the two-stage reaction sequence

$$[\mathrm{Pt(Me_4en)(Me_2SO)Cl}]\mathrm{PF_6} + \mathrm{MX} \xrightarrow{\text{fast}} [\mathrm{Pt(Me_4en)(Me_2SO)X}]\mathrm{PF_6} + \mathrm{MCl} \quad (1)$$

$$[\mathrm{Pt(Me_4en)(Me_2SO)X}]\mathrm{PF_6} + \mathrm{MX} \rightarrow [\mathrm{Pt(Me_4en)X_2}] + \mathrm{MPF_6} + \mathrm{Me_2SO} \quad (2)$$

and that the rate constants in Table VI are those of the second stage.

In aqueous solution, [Pt(Me$_4$en)(Me$_2$SO)Cl]PF$_6$ reacts with a range of nucleophiles but the only reaction observed is the replacement of the chloride by the nucleophile. The subsequent replacement of dimethyl sulfoxide is extremely slow under the

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**Table VII.** Pseudo-First-Order Rate Constants of the Reaction $[Pt(Me_4en)(Me_2SO)Cl]^+ + Y^{n-} \rightarrow [Pt(Me_4en)(Me_2SO)Y]^{(n-1)+} + Cl^-$ [a]

| Y | $10^3[Y^{n-}]$/mol dm$^{-3}$ | $10^3k_{obs}$/s$^{-1}$ | $10^3k_2$/dm$^3$ mol$^{-1}$ s$^{-1}$ |
|---|---|---|---|
| $Br^-$ | 25 | 0.013 | 0.543 ± 0.050 |
| | 50 | 0.023 | |
| | 100 | 0.053 | (53.4)[b] |
| $SC(NH_2)_2$ | 5 | 0.061 | 7.92 ± 0.20 |
| | 10 | 0.081 | |
| | 25 | 0.180 | (4480) |
| | 50 | 0.400 | |
| | 100 | 0.800 | |
| $I^-$ | 5 | 0.038 | 7.78 ± 0.10 |
| | 10 | 0.072 | |
| | 25 | 0.200 | (1540) |
| | 50 | 0.400 | |
| | 100 | 0.774 | |
| $SeCN^-$ | 5 | 0.51 | 97.7 ± 1.0 |
| | 10 | 1.10 | |
| | 25 | 2.51 | (26 100) |
| | 50 | 4.95 | |

[a] In water at 25.0 °C; $\mu = 0.10$ mol dm$^{-3}$ ($LiClO_4$). [b] Corresponding values of $k_2$ for the reaction of $[Pt(en)(Me_2SO)Cl]^+$ in parentheses.

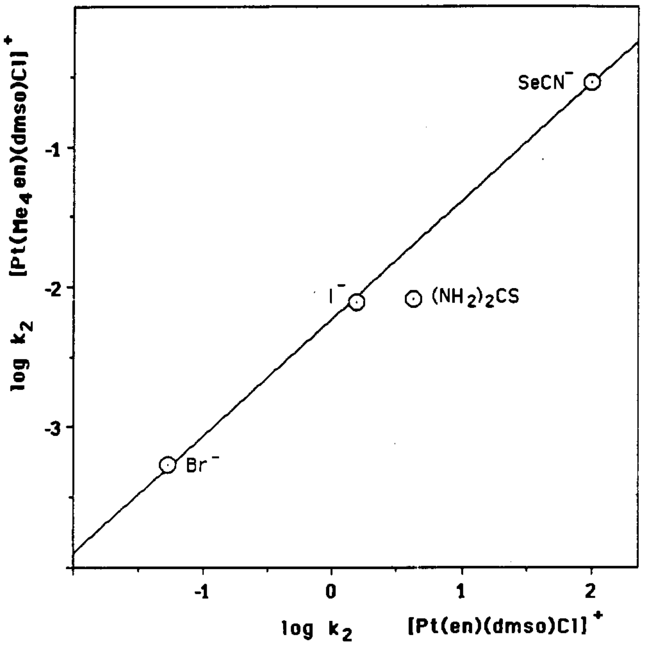

**Figure 2.** Plot of log $k_2$ for the reaction of anionic nucleophiles with $[Pt(Me_4en)(Me_2SO)Cl]^+$ versus the corresponding values for $[Pt(en)(Me_2SO)Cl]^+$ in aqueous solution at 25.0 °C ($I = 0.10$ mol dm$^{-3}$).

conditions used for these kinetic runs. The rate constants, which are collected in Table VII, are dependent upon the concentration of nucleophile, and the complex behaves like $[Pt(en)(Me_2SO)Cl]ClO_4$.[18]

## Discussion

In aqueous solution the behavior of $[Pt(Me_4en)(Me_2SO)Cl]PF_6$ closely resembles that of the analogous unsubstituted ethylenediamine species. The salt is fully dissociated, the chloride can be replaced by other nucleophiles, and the usual two-term rate law, $k_{obs} = k_1 + k_2[nu]$, is obeyed. A plot of log $k_2$ for the reaction of a particular nucleophile with $[Pt(Me_4en)(Me_2SO)Cl]^+$ against log $k_2$ for the same nucleophile reacting with $[Pt(en)(Me_2SO)Cl]^+$ is linear for the three anionic reagents, $Br^-$, $I^-$, and $SeCN^-$, with a slope of 0.83 (Figure 2), the diaminoethane complex being nearly 2 orders of magnitude more reactive than the tetramethylated analogue. The neutral nucleophile thiourea is less reactive than predicted by this relationship, in spite of the fact that the two studies were carried out at the same ionic strength (0.01 mol dm$^{-3}$).

When the solvent is changed to dichloromethane or chloroform, the chloride is replaced very rapidly by anionic reagents and the dimethyl sulfoxide is also substituted. This is not just a consequence of a massive rate acceleration accompanying the change in solvent because uncharged nucleophiles, even when they are strong nucleophiles such as thiourea and phosphines, react very slowly. There is no evidence, in these solvents, for the displacement of chloride by any of the neutral nucleophiles to give a thermodynamically unstable dicationic species, i.e.

$$[Pt(Me_4en)(Me_2SO)Cl]^+ + L \rightleftharpoons [Pt(Me_4en)(Me_2SO)(L)]^{2+} + Cl^- \quad (3)$$

$$[Pt(Me_4en)(Me_2SO)(L)]^{2+} + Cl^- \rightleftharpoons [Pt(Me_4en)(L)Cl]^+ + Me_2SO \quad (4)$$

where L = $^*Me_2SO$, py, thiourea, and $PR_3$, because this would certainly lead to some exchange of dimethyl sulfoxide and probably lead to a catalysis of the displacement of dimethyl sulfoxide by the strong nucleophiles.

The second stage of the reaction presents a pattern of behavior that has not been observed before. The reaction of the chloride salt in the absence of added nucleophile is particularly interesting. The displacement of dimethyl sulfoxide follows first-order kinetics under all circumstances even though the concentration of chloride is equal to that of unreacted complex, and the first-order rate constant is independent of the initial concentration of complex. The entropies of activation in $CHCl_3$ and $CH_2Cl_2$ are considerably greater than those observed in the usual associative substitution processes. In the presence of an excess of anionic nucleophile, the rate constants increase but eventually become independent of $[Y^-]$. The dependence of rate constant upon the nature of Y is small. However, the rate law, the entropies of activation, and the low discrimination are not the result of a change to dissociative activation since there is no exchange of dimethyl sulfoxide or mass-law retardation, nor is there any significant replacement of coordinated dimethyl sulfoxide by other neutral ligands, even those as strong as thiourea.

The behavior is consistent with an interchange reaction within preformed aggregates of some sort. The concentration dependence of the conductance of solutions of the cation with the noncoordinating anions $PF_6^-$ and $BPh_4^-$ in dichloromethane indicates, as might be expected in a solvent of low polarity, that there is extensive ion association and the concentration dependence of the chemical shift of the methylene protons in the $BPh_4^-$ salt is quantitatively consistent with this. The conductance of the chloride salt in dichloromethane indicates that, to the first approximation, the salt is fully associated at the concentrations used in the kinetic studies.

The distinction between an ion pair involving a four-coordinate planar cation and a five-coordinate complex is not always clear-cut, but in this case the spectral changes associated with the association are negligible and the interaction is observed when the anion does not have suitable donor sites. The association constants are of the magnitudes expected for the ions concerned in a solvent with a dielectric constant of 9. In the interaction between the dicationic $[Pt(diars)_2]^{2+}$ [diars = *o*-phenylenebis(dimethylarsine)] and iodide ions the spectral changes are enormous[19] and one would expect to find that the formation of a five-coordinate entity would lead to considerable spectral changes that depended upon the chemical nature of the anion. Apart from the $BPh_4^-$ ion pair, where the changes in the $^1H$ NMR spectrum indicate that some of the methylene protons of the $Me_4en$ group are strongly affected by the ring current of one of the

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phenyl groups of the anion suggesting that the orientation is similar to that found in the crystal, the location of the anion in the ion pair is not known.

At first sight, the observation that the reaction of the chloride salt is first-order and the rate constant is independent of the initial concentration is incompatible with the fact that addition of $[AsPh_4]Cl$ increases the rate still further. The new rate law takes the form

$$k_{obs} = \frac{k_1 + k_2K'[Ph_4AsCl]}{1 + K'[Ph_4AsCl]}$$

with $k_1 = 3.70 \times 10^{-4}\ s^{-1}$ (the value obtained for the chloride salt in the absence of any added nucleophile), $k_2 = 5.31 \times 10^{-4}\ s^{-1}$, and $K' = 1730\ dm^3\ mol^{-1}$ in $CH_2Cl_2$ at 298.6 K. Since the value of $K'$ is much less than that of the estimated ion-association constant of the chloride ion pair (the latter being large enough to ensure that the major part of the substrate is in the form of the ion pair even when no excess chloride is present), we must conclude that the equilibrium constant $K'$ relates to a different process. This cannot be an equilibrium involving the distribution of reagents between two ion pairs, e.g.

$$\{[Pt(Me_4en)(Me_2SO)Cl]^+\cdots[PF_6^-]\} + \{[Ph_4As]^+\cdots Cl^-\} = \{[Pt(Me_4en)(Me_2SO)Cl]^+\cdots Cl^-\} + \{[Ph_4As]^+\cdots[PF_6^-]\} \quad (5)$$

since this would require that $k_1$ in the above expression must be zero and the value of the limiting rate constant, $k_2$, must be the same as that of the rate constant in the absence of added chloride. A second equilibrium of the form

$$\{[Pt(Me_4en)(Me_2SO)Cl]+\cdots Cl^-\} + \{[Ph_4As]^+\cdots Cl^-\} = \{[Pt(Me_4en)(Me_2SO)Cl]^+\cdots 2Cl^-\}^- + [Ph_4As]^+ \quad (6)$$

is therefore required.

A similar analysis cannot be made for the reaction between the substrate and the other halides because the value for the rate constant for the interchange of the ion pair is not known. A three-parameter nonlinear fit is over parametrized, and although reasonable values can be obtained for the limiting rate constant, $k_2 = 4.3 \times 10^{-4}\ s^{-1}$ and $11.6 \times 10^{-4}\ s^{-1}$ for X = $Br^-$ and $I^-$, respectively, the ion-pair interchange rate constants ($k_1$) and ion-triplet association constants ($K'$) are strongly dependent on one another. Although the curves for the reactions with MBr and MI in Figure 3 are calculated on the assumption that the value of $k_2$ is approximately twice that of $k_1$ and are not intended to represent a proper analysis of the rate expression, the behavior cannot differ greatly from that of the chloride system; i.e., the equilibrium constant for the association of the second anion is nearly 2 orders of magnitude smaller than that for the association of the first. The difference between the three values of $k_2$ is small, spanning a factor of 2.5, and the unusual sequence, Br < Cl < I, is even more intriguing. However, it is not possible to separate the effect of changing the entering group from that of changing the cis ligand. Little is known about cis effects of halides in this type of system, and so it is not possible to say whether the apparently low nucleophilic discrimination within the aggregate is due to opposing cis effects and nucleophilicity effects (the unusual reactivity sequence might indicate this) or whether the nucleophilic discrimination is low and the reactivity differences reflect the consequence of changing the halide cis to the leaving group. We are examining ways of resolving this rather important question.

We suggest that the preassociation allows the anionic nucleophile to increase its effective concentration enormously (in much the same way as is found in small-ring formation reactions[20]) and that the uncharged nucleophiles are unable to take advantage of this. The greater interchange rate constant of the ion triplet is therefore, mainly, a statistical effect. The packing within the crystal of the chloride salt probably places the chloride in a very favorable position for replacing the dimethyl sulfoxide. The lack of reactivity of the neutral dihalo complexes with halide ions is probably due to the ion association of the halide salt used and the resulting low concentration of free halide ions.

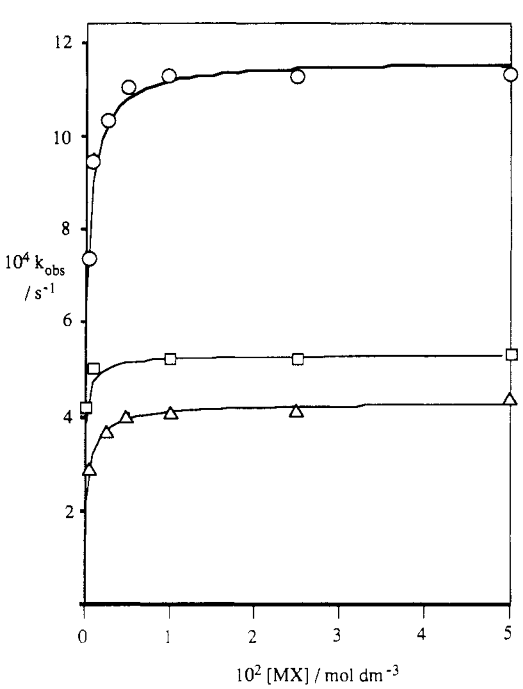

**Figure 3.** Plots of $k_{obs}$ versus [MX] for the reaction $[Pt(Me_4en)(Me_2SO)X]^+\cdots X^- + MX \rightarrow [Pt(Me_4en)Cl_2] + Me_2SO + MX$ in $CH_2Cl_2$ at 25.0 °C. Key: MX = $[Ph_4As]Cl$ (□), $[Bu_4N]Br$ (△), and $[Bu_4N]I$ (○). The curve for MX = $[Ph_4As]Cl$ is calculated for the parameters $k_1 = 3.7 \times 10^{-4}\ s^{-1}$, $k_2 = 5.3 \times 10^{-4}\ s^{-1}$, and $K' = 1730\ dm^3\ mol^{-1}$. The curves for MX = $[Bu_4N]Br$ and $[Bu_4N]I$ are calculated for $k_1 = 2 \times 10^{-4}$, $6 \times 10^{-4}\ s^{-1}$; $k_2 = 4.3 \times 10^{-4}$, $1.16 \times 10^{-3}\ s^{-1}$; and $K' = 1100$, $1200\ dm^3\ mol^{-1}$, respectively.

Cationic species such as $[M(Me_2S)_4]^{2+}$ (M = Pt, Pd) exchange their ligands rapidly in nitromethane ($\epsilon = 37.0$) even in the absence of coordinating anions,[21,22] but the labilities of these complexes are probably even larger in aqueous solution.[23] There are many neutral complexes that readily exchange neutral ligands in dichloromethane and similar solvents. For example the exchange of free and coordinated L in a large number of complexes of the type $[Pt(L)_2X_2]$ (L = $PR_3$, $AsR_3$; X = Cl, Br) is much more rapid in nonpolar solvents than it is in methanol and is accompanied by cis ⇌ trans isomerization. Although it was concluded that the solvent effects were consistent with direct exchange and a long enough lived five-coordinate intermediate to allow rearrangement, a very facile replacement of $Cl^-$ from $[Pt(Me_2S)_2Cl_2]$ by $Me_2S$, followed by a rapid reverse reaction (possibly analogous to the reactions discussed in this paper), is shown to take place in dichloromethane.[24] A sequence of substitutions, each of which takes place without rearrangement, involving ionic intermediates is therefore indicated. The kinetics and activation parameters are all consistent with the normal associative mode of activation.

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**Supplementary Material Available:** Tables of positional and thermal parameters and bond distances and angles (5 pages). Ordering information is given on any current masthead page.

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