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# Dissociative Substitution in Four-Coordinate Planar Platinum(II) Complexes. Kinetics of Sulfoxide Exchange and Displacement by Bidentate Ligands in the Reactions of *cis*-Diarylbis(dimethyl sulfoxide)platinum(II) in Chloroform and Benzene

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The kinetics of the exchange of dimethyl sulfoxide with *cis*-[Pt(C$_6$H$_5$)$_2$(Me$_2$SO)$_2$] in CDCl$_3$ have been followed by stopped-flow $^1$H NMR, and the rate law, rate = ($k_1$ + $k_2$[Me$_2$SO])[complex], has been established. At 300 K, $k_1$ = 7.9 × 10$^{-2}$ s$^{-1}$ and $k_2$ = 1.0 × 10$^{-1}$ M$^{-1}$ s$^{-1}$, the latter pathway making only a minor contribution that may be due to changes in the bulk solvent. The reaction *cis*-[Pt(Ph)$_2$(Me$_2$SO)$_2$] + bpy = [Pt(Ph)$_2$(bpy)] + 2Me$_2$SO takes place in a single observable step whose rate is determined by the displacement of the first sulfoxide, and the kinetic form is consistent with competition between Me$_2$SO and the chelate for a reactive intermediate. The reactions of the bis(sulfoxide) complex with 2,2'-bipyridyl, 1,10-phenanthroline, and 1,2-bis(diphenylphosphino)ethane have been studied spectrophotometrically in benzene. The sulfoxides are displaced, and the rate law −d[complex]/d$t$ = {$k_1k_3$[L−L]/($k_{-1}$[Me$_2$SO] + $k_3$[L−L]) + $k_2$[L−L]}[complex] is established. Only in the case where L−L = (diphenylphosphino)ethane does the $k_2$ pathway make any significant contribution. $k_1$ is independent of the nature of L−L, 1.8 × 10$^{-2}$ s$^{-1}$ at 303.2 K, $\Delta H_1^{*}$ = 15.3 ± 0.4 kcal mol$^{-1}$, and $\Delta S_1^{*}$ = −16 ± 2 cal K$^{-1}$ mol$^{-1}$, while $k_3/k_{-1}$ = 0.049 ± 0.007, 0.26 ± 0.01, and 5.6 ± 0.8 for bpy, phen, and dppe, respectively, at 303.2 K. For dppe, $k_2$ = 10 ± 0.7 M$^{-1}$ s$^{-1}$ at 303.2 K. The reactions of *cis*-[Pt(4-MeC$_6$H$_4$)$_2$(Me$_2$SO)$_2$] are similar. A dissociative mechanism with [Pt(R)$_2$(Me$_2$SO)] as reactive intermediate has been demonstrated in both solvents.

## Introduction

Sulfoxides are ambidentate ligands that can bind to metals through oxygen or sulfur. The normal mode of bonding to the soft Pt(II) is through sulfur except in some cases where the ligand is forced into a sterically crowded environment.[4,5] Symbiotic and antisymbiotic effects can also affect the choice of donor atoms.[6]

The reluctance of a single dimethyl sulfoxide to be displaced from Pt(II) in which there is little steric hindrance[7] makes it difficult to think of mono(sulfoxide) complexes as "labile solvento intermediates" and, yet, a nucleophile-independent, solvent-mediated pathway is indicated for substitution in dimethyl sulfoxide solutions.[8] In contrast, preparative[9] and kinetic[10,11] studies have revealed a very strong mutual labilizing power of two sulfoxides, even when cis to one another. It has been suggested that the general pattern of behavior of these reactions is consistent with a relative stabilization of the five-coordinate intermediate in the A reaction[11] rather than a mutual bond weakening in the substrate, and for this reason, it seemed particularly interesting to extend our studies to the displacement of Me$_2$SO from a bis(dimethyl sulfoxide) complex in which *trans* labilization in the ground state (as evidenced by long Pt–S bonds[12]) is important. For this reason, we have studied the reaction *cis*-[Pt(R)$_2$(Me$_2$SO)$_2$] + L–L → [Pt(R)$_2$(L–L)] + 2Me$_2$SO (R = C$_6$H$_5$, 4-MeC$_6$H$_4$; L–L = 2,2'-bipyridyl (bpy), 1,10-phenanthroline (phen), 1,2-bis(diphenylphosphino)ethane (dppe)), the chelating ligand being chosen to ensure the displacement of both sulfoxides and to avoid complications due to isomerization. A preliminary

communication has appeared.[13]

## Experimental Section

**Reagents.** *cis*-[Pt(C$_6$H$_5$)$_2$(Me$_2$SO)$_2$]. [Pt(COD)(C$_6$H$_5$)$_2$] (COD = cyclooctane-1,4-diene) (457 mg, 1 mmol), prepared by the method of Puddephat,[14] was dissolved in dimethyl sulfoxide (5 cm$^3$) and the solution warmed for 30 min at 80 °C. Evaporation of the solvent under reduced pressure left a pale yellow solid that was recrystallized, as white plates, from a dichloromethane–petroleum ether mixture. Anal. Calcd for C$_{16}$H$_{22}$O$_2$PtS$_2$: C, 38.0; H, 4.3. Found: C, 37.9; H, 4.3.

*cis*-[Pt(4-MeC$_6$H$_4$)$_2$(Me$_2$SO)$_2$] was prepared in a similar way from [Pt(COD)(4-MeC$_6$H$_4$)$_2$]. Anal. Calcd for C$_{18}$H$_{26}$O$_2$PtS$_2$: C, 40.5; H, 4.9. Found: C, 40.2; H, 4.8.

Complexes of the type [Pt(C$_6$H$_5$)$_2$(L–L)] (L–L = bpy (I), phen (II), dppe (III)) and [Pt(4-MeC$_6$H$_4$)$_2$(bpy)] (IV) were prepared by adding stoichiometric amounts of the appropriate chelate to a concentrated (0.1 mol dm$^{-3}$) solution of the bis(sulfoxide) complex in dichloromethane. Apart from the complex with dppe, which required the addition of diethyl ether before it would precipitate, all the complexes separated after the reagents were mixed. Anal. Calcd for C$_{22}$H$_{18}$N$_2$Pt (I): C, 52.3; H, 3.6. Found: C, 52.0; H, 3.5. Calcd for C$_{24}$H$_{18}$N$_2$Pt (II): C, 54.4; H, 3.4. Found: C, 54.2; H, 3.2. Calcd for C$_{38}$H$_{34}$P$_2$Pt (III): C, 61.1; H, 4.6. Found: C, 60.7; H, 4.8. Calcd for C$_{24}$H$_{22}$N$_2$Pt (IV): C, 54.0; H, 4.1. Found: C, 53.9; H, 4.1.

The spectroscopic properties of these complexes are identical with those previously described in the literature whether they were prepared by the addition of L–L to [Pt(COD)(R)$_2$][14] or [Pt(R)$_2$(Me$_2$SO)$_2$].[15,16]

1,10-Phenanthroline hydrate was dehydrated by heating under vacuum for 24 h at 80 °C; mp 117 °C.

Other compounds were the best available commercial materials, purified by recrystallization or distillation as necessary.

The $^1$H NMR spectra were recorded either on a Hitachi Perkin-Elmer R24A spectrometer using [$^2$H$_6$]benzene as solvent and tetramethylsilane as reference or, in the flow NMR experiments, with a Bruker WH90 spectrometer with CDCl$_3$ as solvent.

**Kinetics.** (a) $^1$H NMR Stopped-Flow Kinetics. The kinetics of the exchange between free and coordinated Me$_2$SO in CDCl$_3$ solutions of *cis*-[Pt(C$_6$H$_5$)$_2$(Me$_2$SO)$_2$] and [$^2$H$_6$]Me$_2$SO were studied at 300 K by a stopped-flow technique that has been described elsewhere.[17]

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The peak at $\delta$ 2.82, with $^{195}$Pt satellites $^3J_{^{195}Pt-^1H} = 14.7$ Hz, assigned to coordinated Me$_2$SO decreases with time when [$^2$H$_6$]Me$_2$SO is added to the solution and is replaced by another at $\delta$ 2.61 due to uncoordinated Me$_2$SO. After an initial delay of 0.8 s, spectra were measured at intervals of 2 s. The height of the central peak of the coordinated Me$_2$SO ($=C$) was measured and adjusted for the presence of the $^{195}$Pt satellites (33.8% abundance) with the relationship corrected height $= C + 33.8C/66.2 = 1.51C$. The height of the peak of the unco-ordinated Me$_2$SO ($=U$) needed no such correction. The fraction of exchange ($=Y$) is given by $Y = U/(U + 1.51C)$ and the first-order rate constant for the exchange of the label was obtained from the nonlinear regression analysis of the equation $Y = c_1 + c_2 \exp(-k_{exch}t)$, where $c_1$, $c_2$ and $k_{exch}$ are the unknown parameters.

A similar study was carried out on the reaction between *cis*-[Pt-(C$_6$H$_5$)$_2$(Me$_2$SO)$_2$] and bpy in CDCl$_3$ at 300 K. The relative heights of the peaks due to free and coordinated Me$_2$SO, with due correction for the $^{195}$Pt satellites of the coordinated ligands, were determined as before and used to determine the fraction of reaction, $F_r = U/(U + 1.51C)$ (since one act of reaction leads to the displacement of both coordinated sulfoxides).

**(b) Spectrophotometric Kinetics.** The rates of the substitution reactions of *cis*-[Pt(R)$_2$(Me$_2$SO)$_2$] in benzene solution were measured with a Cary 219 spectrophotometer or, at selected wavelengths, with a Beckmann DU spectrophotometer equipped with a Saitron 301 photometer and a Servogor S recording potentiometer. The solution of all the reagents except the complex was brought to the reaction temperature in a silica cell placed in the thermostated cell compartment of the spectrophotometer, and the reaction was started by adding a weighed amount of a finely powdered sample of the complex and shaking the solution rapidly. In certain cases, the reaction was started by mixing known volumes of prethermostated solutions of (i) the complex and (ii) the other reagents. In all cases a large excess of nucleophile with respect to the complex was used. When the ab-sorbance change followed a first-order rate law, the rate constants, $k_{obsd}$, were obtained, either from the slopes of the plots of $-\ln (A_\infty - A_t)$ against time, where $A_t$ and $A_\infty$ are the absorbances of the solution at time $t$ and at the end of the reaction, respectively, or, when $A_\infty$ could not be measured from a best nonlinear least-squares fit of the experimental $A$ vs. $t$ data to the expression $A_t = A_\infty + (A_0 - A_\infty) \exp(-k_{obsd}t)$, with $A_0$ (the absorbance at $t = 0$), $A_\infty$, and $k_{obsd}$ as parameters to be optimized.

## Results

A series of complexes of the type [Pt(R)$_2$(Me$_2$SO)$_2$], including those with R = C$_6$H$_5$ and 4-MeC$_6$H$_4$, has been prepared by Eaborn at al.[15,16] by reacting K$_2$PtCl$_4$ and Me$_3$SnR in dimethyl sulfoxide, and the members have been fully characterized analytically, chemically, and spectroscopically by infrared and $^1$H NMR. A cis configuration with Pt-S bonding was assigned. This has been confirmed, in the case of the diphenyl complex, by a single-crystal X-ray diffraction study[12] that shows that, in the solid state at least, the two sulfoxides, bound through sulfur to platinum, are cis to each other. The Pt-S distances (2.315 and 2.324 Å) are the longest reported bonds for sulfoxides bound to platinum, presumably because of the high trans influence of the phenyl groups.

The $^1$H NMR spectrum of [Pt(C$_6$H$_5$)$_2$(Me$_2$SO)$_2$] in [$^2$H$_6$]benzene has the same form as that reported in CDCl$_3$[16] and contains the expected resonances for the aryl protons together with a single peak at $\delta$ 2.3 (12 H) with $^{195}$Pt satellites ($^3J_{^{195}Pt-^1H} = 14$ Hz) due to the dimethyl sulfoxide protons. Since the methyl resonances of O-bonded Me$_2$SO are not expected to be significantly split by coupling with $^{195}$Pt, bonding through sulfur is confirmed in benzene solution and the low coupling constant is consistent with the presence of a strong trans influence ligand in the trans position, thereby indicating that the cis configuration is retained in benzene solution. The bis(4-methylphenyl) analogue in [$^2$H$_6$]benzene solution has a resonance at $\delta$ 2.1 (6 H), assigned to the tolyl methyl protons, and another at $\delta$ 2.3 (12 H) with $^{195}$Pt satellites

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**Table I.** Exchange between Free and Coordinated Me$_2$SO in *cis*-[Pt(C$_6$H$_5$)$_2$(Me$_2$SO)$_2$] in CDCl$_3$ at 300 K

| [[$^2$H$_6$]-Me$_2$SO]/ M | [complex]/ M | $k_{exch}$/ s$^{-1}$ | $10^3R_{exch}$/ M s$^{-1}$ | $k_{obsd}{}^a$/ s$^{-1}$ |
|---|---|---|---|---|
| 0.247 | 0.0091 | 0.055 | 0.93 | 0.102 |
| 0.427 | 0.0138 | 0.066 | 1.71 | 0.124 |
| 0.990 | 0.0195 | 0.093 | 3.49 | 0.179 |

$^a$ $k_{obsd} = 0.079 + 0.102$[Me$_2$SO] s$^{-1}$.

($^3J_{^{195}Pt-^1H} = 14$ Hz), assigned to the Me$_2$SO protons. Again, a cis, S-bonded arrangement is indicated.

**Exchange of *cis*-[Pt(C$_6$H$_5$)$_2$(Me$_2$SO)$_2$] Sulfoxides with [$^2$H$_6$]Me$_2$SO in CDCl$_3$.** When a solution of *cis*-[Pt(Ph)$_2$-(Me$_2$SO)$_2$] in CDCl$_3$ was mixed with a large molar excess of [$^2$H$_6$]Me$_2$SO in the stopped-flow $^1$H NMR spectrometer,[17] there is a steady decrease in the signal associated with the coordinated sulfoxide and a parallel and matching increase in the signal due to unbound Me$_2$SO, which is replaced in the complex by the deuterated ligand. The exchange, of course, follows a first-order rate law, and the first-order rate constant, $k_{exch}$, was obtained as described above. From the McKay equation, $R_{exch} = k_{exch}2ab(2a + b)^{-1}$ (where $R$ is the rate of the exchange process; $a$ the concentration of complex, the factor of 2 being required for two equivalent exchanging sulfoxides; and $b$ the concentration of free sulfoxide), the pseudo-first-order rate constants, $k_{obsd} = R_{exch}/a$, were cal-culated and are collected in Table I.

**Reaction between *cis*-[Pt(C$_6$H$_5$)$_2$(Me$_2$SO)$_2$] and 2,2'-Bi-pyridyl in CDCl$_3$.** When approximately equimolar solutions of *cis*-[Pt(Ph)$_2$(Me$_2$SO)$_2$] and 2,2'-bipyridyl in CDCl$_3$ are mixed, the part of the $^1$H NMR spectrum assigned to the Me$_2$SO protons changes from a triplet at $\delta$ 2.82 ($^3J_{^{195}Pt-^1H} = 14$ Hz), characteristic of the coordinated ligand with $^{195}$Pt coupling to a singlet at $\delta$ 2.61 characteristic of the free ligand. When excess bipyridyl is used, the signal due to the coordi-nated Me$_2$SO vanishes, but with a 2:1 excess of complex over bipyridyl the spectrum at the end of the reaction contains only signals due to the cis-bis starting material and free dimethyl sulfoxide. There is no evidence for the presence of significant amounts of any other species containing Me$_2$SO bound to platinum. In the stopped-flow experiments, the signal assigned to Me$_2$SO in *cis*-[Pt(Ph)$_2$(Me$_2$SO)$_2$] decreases while that assigned to free Me$_2$SO increases. There is no evidence for the buildup of any significant quantities of any intermediate, Me$_2$SO-containing, species. The sequence of spectra are in-distinguishable from those observed in the Me$_2$SO-exchange experiments. This contrasts with the results of an experiment in which equimolar amounts of 4-methylpyridine and *cis*-[Pt(Ph)$_2$(Me$_2$SO)$_2$] are mixed in CDCl$_3$ solution where the $^1$H NMR spectrum shows clearly, in addition to the $^{195}$Pt-coupled signal at $\delta$ 2.82 due to the Me$_2$SO in the substrate, a new peak at $\delta$ 2.72 with $^{195}$Pt satellites ($^3J_{^{195}Pt-^1H} = 14$ Hz) assigned to the mono(sulfoxide) complex.

The kinetics of the reaction were examined by using the time dependence of the fraction of reaction, $F_r$, which was deter-mined from the peak heights, corrected where necessary for splitting, in the way described above. The $F_r$ vs. time curves did not follow the simple exponential relationship expected for a first-order process, and because of the relative inaccuracy of the flow NMR technique, it was not possible to analyze the form explicitly but, as will be shown below, the data can be made to fit the rate expression that is consistent with the assigned mechanism.

**Spectrophotometric Kinetic Studies.** The reaction

$$\textit{cis-}[Pt(R)_2(Me_2SO)_2] + L\text{-}L \rightarrow$$
$$[Pt(R)_2(L\text{-}L)] + 2Me_2SO$$
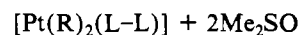
was studied. Although the $^1$H NMR stopped-flow technique

allows a clear demonstration of the absence of any detectable amounts of $Me_2SO$-containing intermediate species and a proper identification of reagents and products, it suffers from the disadvantage that relatively large concentrations of the complex must be used and so very high concentrations of L–L are needed to ensure that [L–L] does not change significantly during the reaction. Furthermore, it is not possible to work in the presence of sufficient $Me_2SO$ to control the mass law retardation and reduce the kinetics to a simple first-order form.

The visible/UV spectrophotometric technique requires far less complex for the study, concentrations of less than $10^{-4}$ M, allowing a sufficient excess of L–L and $Me_2SO$ to ensure first-order kinetics. Furthermore, the reaction can be slow enough to be followed by classical techniques.

The reactions of *cis*-$[Pt(R)_2(Me_2SO)_2]$ with bpy and phen in benzene solution were followed by repetitive scanning of the spectrum in the visible and near-UV part of the spectrum where the absorbance due to the substrate and other reagents is negligible. The reactions, carried out in the presence of at least a 10-fold excess of chelate over complex, went to completion, and the final spectrum was identical with that of an independently synthesized authentic sample of $[Pt(R)_2(L–L)]$. There was no indication from the spectra (or later from the kinetic analysis) of the presence of significant concentrations of any intermediate species, in agreement with the $^1H$ NMR experiments in $CDCl_3$, but the plots of ln $(A_\infty - A_t)$ against time ($A_t$ and $A_\infty$ are the absorbance at time $t$ and at the end of the reaction, respectively) were curved (as was the case in the NMR experiments). This was shown to be due to mass law retardation by the released sulfoxide and was most apparent at the lowest concentrations of L–L. By adding a sufficient excess of dimethyl sulfoxide to ensure that its concentration was sensibly constant throughout the reaction, the semilogarithmic plots were made linear and the negative slopes, = $k_{obsd}$, are collected in Table II.

The reactions with dppe were followed in a similar way, although the product did not absorb so strongly in the visible and the spectra were measured over the range 300–350 nm where the reagents also absorb. Values for the observed first-order rate constants are also collected in Table II.

### Discussion

The exchange of the coordinated $Me_2SO$ in *cis*-$[Pt(Ph)_2$-$(Me_2SO)_2]$ with free ligand in $CDCl_3$ takes place with a rate law of the form rate = $(k_1 + k_2[Me_2SO])[complex]$, with $k_1$ = 7.9 × $10^{-2}$ $s^{-1}$ and $k_2$ = 1.02 × $10^{-1}$ $M^{-1}$ $s^{-1}$ at 300 K. The sulfoxide-dependent contribution is relatively small, except at its highest concentrations, and it is not clear whether this is truly a second-order contribution or just a reflection of the changing character of the solvent.

The $^1H$ NMR experiments indicate quite clearly that, in $CDCl_3$, the reaction *cis*-$[Pt(Ph)_2(Me_2SO)_2]$ + bpy → $[Pt(Ph)_2(bpy)]$ + $2Me_2SO$ is seen as a single conversion of substrate to product, it being presumed that the act of ring closing is always fast compared to that of the displacement of the first sulfoxide. The release of dimethyl sulfoxide does not follow a first-order rate law under the experimental conditions used but approaches it as the concentration of bpy becomes very large compared to that of the complex. A proper kinetic analysis shows that the behavior is consistent with retardation by the released sulfoxide due to competition between it and bipyridyl for some reactive intermediate. From the rate law derived below, $-d[complex]/dt = (k_1k_3/k_{-1})$ × $[complex][bpy]/([Me_2SO] + k_3/k_{-1}[bpy])$, it can be shown that (Appendix) under non-first-order conditions [$\beta$ ln (1 – $F_r\alpha/\beta$) – $\alpha$ ln (1– $F_r$)] = $(\beta - \alpha)k_3/2k_{-1}[ln (1 - F_r) + k_1t]$, where $\alpha$ is the initial concentration of the complex and $\beta$ the initial concentration of bipyridine. However, we were unable to separate the variables in this expression. Plots of the
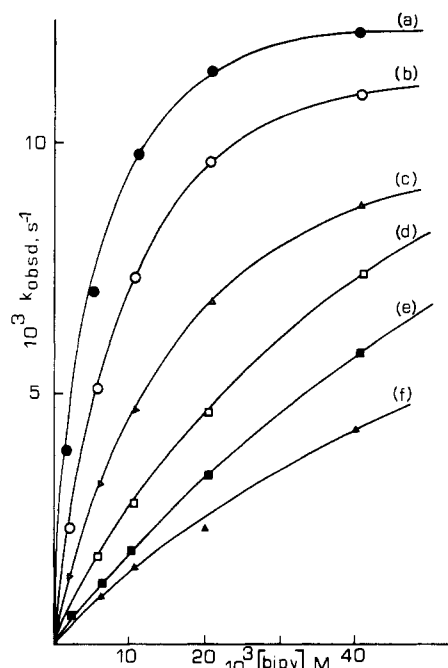


**Figure 1.** Dependence of the pseudo-first-order rate constants $k_{obsd}/s^{-1}$ on the concentration of the entering ligand for the reaction of *cis*-$[Pt(C_6H_5)_2(Me_2SO)_2]$ with bpy in benzene solution at 303.2 K at various $Me_2SO$ concentrations ([$Me_2SO$], M): (a) 0.00025; (b) 0.0005; (c) 0.001; (d) 0.002; (e) 0.003; (f) 0.004.

left-hand side against the portion of the right hand side in brackets, using trial values of $k_1$, gave reasonably good straight lines for a wide range of [bpy] and $k_1$ values. However, with the criterion that the ratio $k_3/k_{-1}$ should be independent of [complex] and [L–L], the best value of $k_1$ was 0.08 $s^{-1}$ and $k_3/k_{-1}$ = 0.06 ± 0.02. This is consistent with the assigned mechanism that requires that $k_1$ be independent of the nature of the entering group. Although, at the highest concentrations used, the departure from a simple first-order process was less marked, the high concentrations of complex needed for the NMR experiments made it impossible to achieve sufficiently high concentrations of added bipyridine and dimethyl sulfoxide to establish pseudo-first-order conditions.

The detailed kinetic study was carried out in benzene solution and followed spectrophotometrically. This enabled the concentration of complex to be drastically reduced, and the kinetics were studied under pseudo-first-order conditions. The reactions with bipyridine and phenanthroline exhibit typical saturation kinetics in that, at high [L–L], $k_{obsd}$ tends to become independent of [L–L]; this saturation is held back by increasing the concentration of $Me_2SO$ (Figure 1). At constant [$Me_2SO$], plots of $k_{obsd}^{-1}$ against [L–L]$^{-1}$ are linear with a finite intercept that is independent of [$Me_2SO$]. The slopes are proportional to [$Me_2SO$].

The general relationship, therefore, takes the form $k_{obsd}$ = $a[L–L]/([Me_2SO] + b[L–L])$. The reactions with dppe are considerably faster than those with nitrogen chelates, and instead of $k_{obsd}$ tending toward a limit as dppe increased, the plots became linear and independent of [$Me_2SO$] (Figure 2). When this limiting slope was taken as $c$ and $(k_{obsd} - c[dppe])^{-1}$ was plotted against [$Me_2SO$]/[dppe], a straight line was obtained, with the same intercept as was found for the reactions with the nitrogen chelates. This indicated that the higher rates observed with dppe came from an additional term that had a first-order dependence on [dppe].

A common rate law with $k_{obsd}$ = $a[L–L]/([Me_2SO]$ + $b[L–L]) + c[L–L]$ is indicated. The values of $k_{obsd}$, [$Me_2SO$], and [L–L] were fitted to this expression with a nonlinear least-squares curve-fitting program and the optimum values

**Table II.** Rate Constants for the Reactions $cis$-[Pt(R)$_2$(Me$_2$SO)$_2$] + L-L → [Pt(R)$_2$(L-L)] + 2Me$_2$SO in Benzene as Solvent

| $10^3$[Me$_2$SO]/M | $10^3$[L-L]/M | $10^3 k_{obsd}$/s$^{-1}$ | $10^3 k_{calcd}$/s$^{-1}$ | $10^3$[Me$_2$SO]/M | $10^3$[L-L]/M | $10^3 k_{obsd}$/s$^{-1}$ | $10^3 k_{calcd}$/s$^{-1}$ |
|---|---|---|---|---|---|---|---|
| | | | R = C$_6$H$_5$, L-L = bpy[a] | | | | |
| 0.25 | 5.0 | 2.41 | 2.44 | 0.25 | 25.0 | 5.55 | 5.59 |
| 0.25 | 10.0 | 3.87 | 3.77 | 0.25 | 50.0 | 6.62 | 6.67 |
| 0.25 | 15.0 | 4.42 | 4.60 | | | | |
| | | | R = C$_6$H$_5$, L-L = bpy[b] | | | | |
| 0.25 | 5.0 | 5.37 | 5.40 | 0.25 | 25.0 | 10.4 | 10.4 |
| 0.25 | 10.0 | 7.68 | 7.74 | 0.25 | 50.0 | 11.8 | 11.8 |
| 0.25 | 15.0 | 9.03 | 9.03 | | | | |
| | | | R = C$_6$H$_5$, L-L = bpy[c] | | | | |
| 0.25 | 2.0 | 3.78 | 3.94 | 1.00 | 20.0 | 6.72 | 6.93 |
| 0.25 | 6.0 | 6.91 | 7.56 | 1.00 | 40.0 | 8.48 | 9.27 |
| 0.25 | 10.0 | 9.49 | 9.27 | 2.00 | 2.0 | 0.66 | 0.65 |
| 0.25 | 20.0 | 11.4 | 11.1 | 2.00 | 6.0 | 1.77 | 1.79 |
| 0.25 | 40.0 | 11.9 | 12.4 | 2.00 | 10.0 | 2.73 | 2.75 |
| 0.50 | 2.0 | 2.03 | 2.29 | 2.00 | 20.0 | 4.37 | 4.60 |
| 0.50 | 6.0 | 5.00 | 5.18 | 2.00 | 40.0 | 7.23 | 6.92 |
| 0.50 | 10.0 | 7.25 | 6.92 | 3.00 | 2.0 | 0.47 | 0.44 |
| 0.50 | 20.0 | 9.37 | 9.27 | 3.00 | 6.0 | 1.26 | 1.25 |
| 0.50 | 40.0 | 10.7 | 11.1 | 3.00 | 10.0 | 1.86 | 1.96 |
| 0.75 | 2.0 | 1.52 | 1.62 | 3.00 | 20.0 | 3.30 | 3.44 |
| 0.75 | 6.0 | 3.89 | 3.94 | 3.00 | 40.0 | 5.60 | 5.53 |
| 0.75 | 10.0 | 5.29 | 5.53 | 4.00 | 6.0 | 0.94 | 0.96 |
| 0.75 | 20.0 | 7.94 | 7.93 | 4.00 | 10.0 | 1.52 | 1.53 |
| 0.75 | 40.0 | 9.38 | 10.1 | 4.00 | 20.0 | 2.11 | 2.75 |
| 1.00 | 2.0 | 1.26 | 1.25 | 4.00 | 40.0 | 4.18 | 4.60 |
| 1.00 | 6.0 | 3.10 | 3.18 | | | | |
| 1.00 | 10.0 | 4.60 | 4.60 | | | | |
| | | | R = C$_6$H$_5$, L-L = bpy[d] | | | | |
| 0.25 | 5.0 | 12.4 | 12.4 | 0.25 | 25.0 | 23.4 | 22.6 |
| 0.25 | 10.0 | 17.3 | 17.3 | 0.25 | 50.0 | 25.3 | 25.2 |
| 0.25 | 15.0 | 18.8 | 19.9 | | | | |
| | | | R = C$_6$H$_5$, L-L = bpy[e] | | | | |
| 0.25 | 5.0 | 20.2 | 20.0 | 0.25 | 25.0 | 35.2 | 36.3 |
| 0.25 | 10.0 | 26.4 | 27.8 | 0.25 | 50.0 | 43.1 | 40.4 |
| 0.25 | 15.0 | 32.0 | 31.9 | | | | |
| | | | R = C$_6$H$_5$, L-L = phen[c] | | | | |
| 0.50 | 0.50 | 4.66 | 4.12 | 1.00 | 0.50 | 2.21 | 2.30 |
| 0.50 | 0.75 | 5.96 | 5.61 | 1.00 | 1.00 | 4.25 | 4.12 |
| 0.50 | 1.00 | 7.63 | 6.84 | 1.00 | 2.50 | 9.17 | 7.88 |
| 0.50 | 2.50 | 10.5 | 11.3 | 1.00 | 5.00 | 11.1 | 11.3 |
| 0.50 | 5.00 | 15.9 | 14.4 | 1.00 | 10.0 | 14.1 | 14.4 |
| 0.50 | 7.50 | 16.7 | 15.9 | 3.00 | 0.50 | 0.75 | 0.83 |
| 0.75 | 0.75 | 3.98 | 4.12 | 3.00 | 1.00 | 1.37 | 1.59 |
| 0.75 | 1.50 | 7.23 | 6.84 | 3.00 | 2.50 | 3.38 | 3.56 |
| 0.75 | 3.00 | 9.44 | 10.2 | 3.00 | 5.00 | 5.45 | 6.04 |
| 0.75 | 5.00 | 11.9 | 12.6 | | | | |
| 0.75 | 7.50 | 13.7 | 14.4 | | | | |
| | | | R = C$_6$H$_5$, L-L = dppe[c] | | | | |
| 1.00 | 0.50 | 20.1 | 19.7 | 5.00 | 3.00 | 45.0 | 45.4 |
| 1.00 | 1.00 | 28.0 | 27.0 | 5.00 | 5.00 | 67.1 | 67.0 |
| 1.00 | 2.00 | 38.8 | 38.4 | 50.0 | 0.50 | 6.41 | 6.06 |
| 1.00 | 3.00 | 48.8 | 48.8 | 50.0 | 1.00 | 12.4 | 12.0 |
| 1.00 | 5.00 | 68.8 | 69.3 | 50.0 | 2.00 | 24.0 | 23.6 |
| 5.00 | 0.50 | 12.0 | 12.2 | 50.0 | 3.00 | 35.9 | 35.0 |
| 5.00 | 1.00 | 19.6 | 20.5 | 50.0 | 5.00 | 57.0 | 57.2 |
| 5.00 | 2.00 | 33.4 | 33.8 | | | | |
| | | | R = 4-MeC$_6$H$_4$, L-L = bpy[c] | | | | |
| 0.25 | 5.00 | 7.15 | 7.44 | 1.00 | 50.0 | 10.2 | 10.9 |
| 0.25 | 10.0 | 9.52 | 10.1 | 1.00 | 100.0 | 13.0 | 12.9 |
| 0.25 | 20.0 | 12.5 | 12.4 | 5.00 | 5.00 | 0.680 | 0.670 |
| 0.25 | 50.0 | 13.6 | 14.3 | 5.00 | 10.0 | 1.40 | 1.28 |
| 0.25 | 100.0 | 14.8 | 15.0 | 5.00 | 20.0 | 2.68 | 2.38 |
| 1.00 | 5.00 | 3.03 | 2.86 | 5.00 | 50.0 | 4.50 | 4.86 |
| 1.00 | 10.0 | 5.13 | 4.86 | 5.00 | 100.0 | 7.30 | 7.44 |
| 1.00 | 20.0 | 7.14 | 7.44 | | | | |

[a] 293.2 K. [b] 299.0 K. [c] 303.2 K. [d] 307.7 K. [e] 312.6 K.

of $a$, $b$, and $c$ obtained. The values of $c$ generated by this program for the bpy and phen data were zero within the error limits.

Rate laws with the above form are quite common in the substitution reactions of four-coordinate planar d$^8$ metal complexes,[18,19] but the first part (and the only part in the case of the reactions with bpy and phen) has been due, invariably,

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**Table III.** Derived Rate Constants for the Reaction
$cis$-[Pt(R)$_2$(Me$_2$SO)$_2$] + L-L → [Pt(R)$_2$(L-L)] + 2Me$_2$SO

| R | L-L | $10^2 k_1/s^{-1}$ | $k_3/k_{-1}$ | $k_2/$ $M^{-1} s^{-1}$ |
|---|---|---|---|---|
| C$_6$H$_5$ | Me$_2$SO$^{a,b}$ | 7.9 | | 0.102 |
| | bpy$^a$ | 8.0 ± 2.0 | 0.06 ± 0.02 | 0 |
| | bpy$^c$ | 0.83 ± 0.03 | 0.021 ± 0.002 | 0 |
| | bpy$^d$ | 1.36 ± 0.02 | 0.033 ± 0.003 | 0 |
| | bpy$^e$ | 1.40 ± 0.10 | 0.049 ± 0.007 | 0 |
| | bpy$^f$ | 2.84 ± 0.10 | 0.039 ± 0.003 | 0 |
| | bpy$^g$ | 4.56 ± 0.70 | 0.039 ± 0.004 | 0 |
| | phen$^e$ | 2.00 ± 0.03 | 0.26 ± 0.01 | 0 |
| | dppe$^e$ | 2.00 ± 0.01 | 5.60 ± 0.8 | 10.0 ± 0.7 |
| 4-MeC$_6$H$_4$ | bpy$^e$ | 1.59 ± 0.06 | 0.044 ± 0.001 | 0 |

$^a$ In CDCl$_3$ at 300 K by flow $^1$H NMR.  $^b$ Dimethyl sulfoxide exchange.  $^c$ In benzene at 293.2 K, spectrophotometrically.  $^d$ 299.0 K.  $^e$ 303.2 K.  $^f$ 307.7 K.  $^g$ 312.6 K, in benzene.

to the associatively activated solvent-mediated pathway. In poorly coordinating solvents such as chloroform and, especially, benzene it seems most unlikely that solvolysis could make such a major contribution. A dissociative mechanism (together with a parallel associative pathway in the case of dppe) would lead to the observed kinetics. Thus, for Scheme I, it can be shown, quite easily, that provided [Me$_2$SO] and [L-L] are held constant in any run, the kinetics will be first order with $k_{obsd}$ = $(k_1 k_3/k_{-1})$[L-L]/([Me$_2$SO] + $(k_3/k_{-1})$[L-L]) + $k_2$[L-L], which is of the form described above with $a = k_1 k_3/k_{-1}$, $b = k_3/k_{-1}$, and $c = k_2$. Values of $k_1$, $k_2$, and $k_3/k_{-1}$ for the reactions in benzene and CDCl$_3$ are collected in Table III.

An alternative scheme, which leads to the same rate law as the reactions of bpy and phen, involves a rapid and reversible (presumably bimolecular) displacement of one sulfoxide by one end of the chelate followed by a rate-determining ring closing. This is ruled out because the saturation kinetics is due to the partition of the material between two sulfoxide-containing species, and the $^1$H NMR experiments show this not to be so. Furthermore, it is difficult to visualize an alternative direct attack by dppe to give extra first-order dependence.

A requirement of the dissociative mechanism (and of the associatively activated solvolytic alternative) is that $k_1$ be independent of the nature of L-L and equal to the rate constant for solvent exchange. Such differences as are found in Table III are probably due to experimental error. On the other hand, the ratio $k_3/k_{-1}$ is strongly dependent on the nature of L-L, indicating that the first intermediate has a reasonable discriminating ability. The increase in the value of $k_1$ on changing from benzene to CDCl$_3$ (1.8 × 10$^{-2}$ to 7.9 × 10$^{-2}$ s$^{-1}$ at 300 K) is rather small to be accounted for in terms of the difference in the coordinating power of benzene and chloroform, and neither molecule, especially benzene, could be expected to exert the nucleophilic power required to give associatively activated rate constants of the observed magnitude. This is especially true if one consider that dppe, which as a phosphorus donor would be expected to be a very powerful nucleophile,[20] only has a rate constant of 10 M$^{-1}$ s$^{-1}$ in benzene. This is less than 4 orders of magnitude greater than $k_1$/[C$_6$H$_6$], which is the rate constant if there was bimolecular solvolysis. The difference between the values of $k_1$ obtained in C$_6$H$_6$ and CDCl$_3$ is much more likely to arise from the differing abilities of the two solvents to interact with the released Me$_2$SO. Calorimetric studies on the mixing of Me$_2$SO and CHCl$_3$ indicate a much stronger specific interaction than between Me$_2$SO and benzene.[21]

The experimental evidence therefore points unequivocally to a dissociative reaction, but in view of the evidence that supports the idea that the mutual labilization of cis sulfoxides arises from the phenomena associated with the relative stabilization of the five-coordinate intermediate of an A mechanism,[10,11] this demonstration of a D mechanism was quite unexpected. This is the first time that a facile dissociative mechanism has been observed in substitution reactions of four-coordinate planar d$^8$ metal complexes; all the previous attempts to induce a dissociative mode of activation, by means of bonding weakening[22] and/or steric hindrance,[23,28] generally served to reduce the nucleophilic discrimination of the substrate to a point where the substitution takes place by way of solvolysis. The activation remains associative. The dissociative mechanism for cis–trans isomerization of complexes of the type [Pt(PEt$_3$)$_2$RX] (R = aryl; X = halide)[29,32] can only be examined when the nucleophile is the same as the leaving group, since the associative pathway is still very much faster (except in the case of the extremely sterically hindered R = mesityl).

The dissociative mechanism is expected to be enhanced by extra electron release from the ligands. Thus, changing R from C$_6$H$_5$ to 4-CH$_3$C$_6$H$_4$ virtually doubled the rate of isomerization of $cis$-[Pt(PEt$_3$)$_2$(R)Cl],[30] but in the reactions of $cis$-[Pt-(R)$_2$(Me$_2$SO)$_2$], a similar change in the nature of R has led to no significant change in the magnitude of $k_1$. A possible explanation of this result, and indeed the promotion of a dissociative mechanism in this system, is that the ambidentate sulfoxide can function as a chelate, but the three-membered ring, while lowering the energy of the intermediate below that of a formally three-coordinate 14-electron species, is insufficiently stabilizing to allow such a species to be isolated and characterized. The electron deficiency is then partly (at least) satisfied by the oxygen, and the process therefore needs less inductive assistance from R.
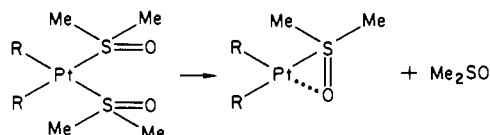


It might be claimed that, if this is so, a process of this sort does not really have a D mechanism since there is no intermediate of lower coordination number. It is a classical example of anchimeric assistance,[33] and it is almost necessary to define a new set of criteria if one wishes to assign an intimate mechanism, i.e., the mode of activation. There is a close parallel with the hydrolysis of 2-chloroethyl thioether (mustard gas), which is not catalyzed by OH$^-$ (lack of nucleophilic discrimination) and involves the formation of a cyclic sulfonium intermediate:
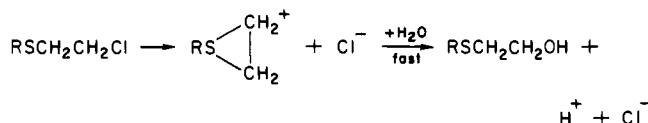
(20) Belluco, U.; Cattalini, L.; Basolo, F.; Pearson, R. G.; Turco, A. *J. Am. Chem. Soc.* **1965**, *87*, 241.
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(32) Van Eldik, R.; Palmer, D. A.; Kelm, H. *Inorg. Chem.* **1979**, *18*, 572.
(33) Capon, B. *Q. Rev., Chem. Soc.* **1964**, *18*, 45.
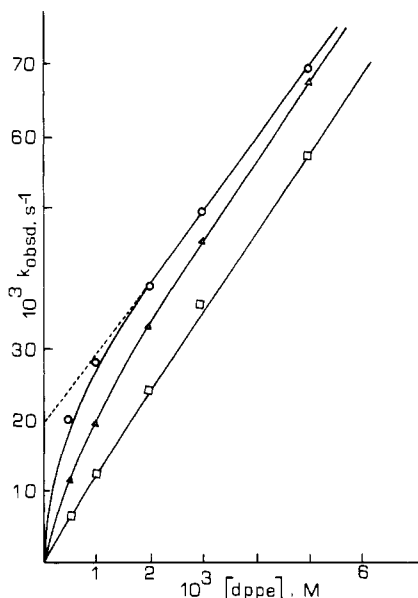
**Figure 2.** Effect of added $Me_2SO$ on the rates of reaction of *cis*-$[Pt(C_6H_5)_2(Me_2SO)_2]$ with dppe in benzene solution at 303.2 K ($[Me_2SO]$, M): O, 0.001; △, 0.005; □, 0.05.

**Scheme I**
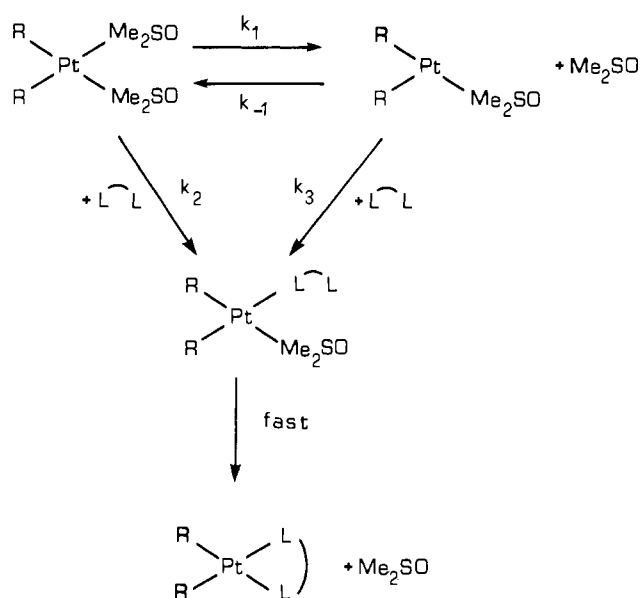


Ingold argues strongly against this being a dissociative mechanism on account of the $10^7$-fold rate enhancement and talks in terms of an internal equivalent of a bimolecular mechanism (i.e., associative activation).[34]

The temperature dependence of $k_1$ in the reaction of *cis*-$[Pt(Ph)_2(MeSO)_2]$ with bipyridyl gives $\Delta H^{\ddagger} = 15.3 \pm 0.4$ kcal $mol^{-1}$ and $\Delta S^{\ddagger} = -16 \pm 2$ cal $K^{-1}$ $mol^{-1}$. A simple-minded view (not unreasonable perhaps for reactions in the gas phase) is that a proper dissociative reaction, since the leaving group is very much loosened in the transition state, should have a positive $\Delta S^{\ddagger}$. However, Bennetto and Caldin[35,36] have argued that, even in a dissociatively activated process, solvation changes resulting from interaction of the leaving group with the solvent may make a major contribution to the energetics of the transition state and lead to a negative entropy of activation. The chelation of the remaining sulfoxide, which might

allow the transition state to be reached while there is still significant bonding between the leaving group and the platinum, and the loss of rotational entropy that ensues might both contribute to the reduction in the entropy of activation.

It is important to note that this explanation cannot be used to account for the mutual labilisation of *cis*-bis(sulfoxide) complexes of the type $[Pt(en)(Me_2SO)_2]^{2+}$ [11] and *cis*-$[PtCl_2(Me_2SO)_2]$,[10] the latter study being made in the noncoordinating solvent dimethoxyethane and finding no evidence for a nucleophile-independent term. These reactions are classically associative, since there is high nucleophilic discrimination. Clearly, the presence of a strong trans influence ligand is required. It would be interesting to know whether this has to be trans to the leaving group or to the remaining sulfoxide or to both. Observations by Eaborn et al.[16] suggest that, in the case of *cis*-$[PtPhCl(Me_2SO)_2]$, it is the sulfoxide trans to Ph that is exchanged, but there is no indication of the molecularity of the exchange process. Furthermore, it could be predicted that if this anchimeric assistance is important, other suitable ambidentate ligands such as $SO_3^{2-}$ (or even oxyanions such as $RCO_2^-$, $SO_4^{2-}$, or $PO_4^{3-}$ with a less strained four-membered ring) might generate the same behavior in appropriate complexes.

**Appendix**

For a reaction with rate law

$$-d[complex]/dt =$$
$$(k_1k_3/k_{-1})[complex][L-L]/([Me_2SO] + k_3/k_{-1}[L-L]) \quad (1)$$

at $t = 0$ let $[complex] = \alpha$, $[L-L] = \beta$, $[Me_2SO] = 0$, and at $t = t$ let $[complex] = (\alpha - x)$, and so $[L-L] = (\beta - x)$ and $[Me_2SO] = 2x$. Substituting in (1) gives

$$-d(\alpha - x)/dt = dx/dt =$$
$$(k_1k_3/k_{-1})(\alpha - x)(\beta - x)/(2x + k_3(\beta - x)/k_{-1}) \quad (2)$$

which can be rearranged to give

$$\frac{(A - 1)x + \beta}{(\alpha - x)(\beta - x)} \, dx = k_1 \, dt \quad (3)$$

where $A \doteq 2k_{-1}/k_3$, which on integration gives

$$-\ln(\alpha - x) + \frac{A}{\beta - \alpha}[\beta \ln(\beta - x) - \alpha \ln(\alpha - x)] =$$
$$k_1 t + C \quad (4)$$

at $t = 0$ and $x = 0$, so

$$-\ln \alpha + \frac{A}{\beta - \alpha}[\beta \ln \beta - \alpha \ln \alpha] = C \quad (5)$$

Substituting for $C$ in (4) gives

$$-\ln(1 - x/\alpha) +$$
$$\frac{A}{\beta - \alpha}[\beta \ln(1 - x/\beta) - \alpha \ln(1 - x/\alpha)] = k_1 t \quad (6)$$

which on writing $F_r$ for $x/\alpha$ and rearranging gives

$$\beta \ln(1 - F_r\alpha/\beta) - \alpha \ln(1 - F_r) =$$
$$\frac{\beta - \alpha}{A}[\ln(1 - F_r) + k_1 t] \quad (7)$$

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