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Kinetics of sulfoxide displacement by 2,2′-bipyridine in *cis*-diphenyl-, dimethyl- and dichloro-bis(dimethyl sulfoxide)platinum(II) in acetonitrile

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Abstract

The kinetics of the reaction *cis*-$[PtR_2(Me_2SO)_2] + bpy \rightarrow [PtR_2(bpy)] + 2Me_2SO$ ($R = CH_3, C_6H_6$; bpy = 2.2′-bipyridine) have been studied in the coordinating solvent acetonitrile, where sulfoxide complexes are in equilibrium with the solvento species *cis*-$[PtR_2(Me_2SO)(CH_3CN)]$. Rate data obey the relationship $k_{obs} = k_1k_3[L\text{-}L]/k'_{-1} + k_{-1}[Me_2SO] + k_3[L\text{-}L]$ which implies that both starting materials and their solvato counterparts in equilibrium generate, in a dissociative way, a common intermediate $[R_2Pt(Me_2SO)]$ at a similar rate. The relative efficiency of three different nucleophiles bpy, Me_2SO and CH_3CN in capturing the reactive species $[R_2Pt(Me_2SO)]$ shows that the latter maintains a reasonable discriminating ability also in CH_3CN. In contrast, *cis*-$[Pt(Me_2SO)Cl_2]$ does not undergo any solvolysis in CH_3CN and, in its reaction with chelating bpy, substitutes both sulfoxides in the usual associative mode of activation.

Introduction

For a long time [1], bis-sulfoxide complexes of platinum(II) have attracted much interest owing to the *trans* activating properties of the ligands and to their mutual labilization even when *cis* to one another in the coordination sphere of platinum(II). Such characteristics have been exploited in inorganic synthesis to prepare a series of monosubstituted and disubstituted amine complexes of formula *cis*- and *trans*-$[PtCl_2(Me_2SO)(am)]$ [2] and *cis*-$[PtCl(Me_2SO)(am)_2]Cl$. These latter compounds are easily formed from the reaction of *cis*-$[Pt(dmso)_2Cl_2]$ and amines since the removal of a chloride ion is preferred with respect to that of the second molecule of dimethyl sulfoxide that appears to be extremely difficult [3]. In the strictly similar organometallic complexes of formula *cis*-$[PtR_2(Me_2SO)_2]$, reported by Eaborn *et al.* at the beginning of the eighties [4], both sulfoxides can be easily removed by chelating imines or phosphines to yield compounds of the type *cis*-$[PtR_2L_2]$.

The mechanistic aspect of the reaction between *cis*-$[PtPh_2(Me_2SO)_2]$ and various chelating ligands has been studied in great detail [5]. It has been shown, for the first time and with undoubted evidence, that a dissociative mechanism is operating in a nucleophilic substitution to platinum(II). Following these results, we have undertaken the present study knowing that a *cis*-$[PtR_2(Me_2SO)_2]$ species, in the coordinating solvent acetonitrile at least, is in equilibrium with its solvent counterpart *cis*-$[PtR_2(Me_2SO)(CH_3CN)]$ [6]. This allows us to investigate in what extent a different group coordinated in *cis* position to Me_2SO affects the reactivity of the system.

Changes in the nature of the *trans* groups coordinated to the Me_2SO molecules have also been tested by studying the substitution of sulfoxides by chelating bpy in *cis*-dichloro-bis(dimethyl sulfoxide)platinum(II). The use of an imine as reagent, in contrast to what has been found for the amines, leads to the substitution of both molecules of sulfoxide.

Experimental

Materials

The complexes *cis*-$[PtMe_2(Me_2SO)_2]$ [4], *cis*-$[Pt(Ph_2(Me_2SO)_2]$ [4], *cis*-$[PtCl_2(Me_2SO)_2]$ [1] and $[PtCl_2(bpy)]$ [7] were prepared according to known procedures. $[PtCl_2(bpy)]$ was also obtained by mixing equimolar quantities of *cis*-$[Pt(dmso)_2Cl_2]$ and bpy in chloroform. The compound isolated was identical to that prepared following the procedure of ref. 7.

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Acetonitrile (Fluka, puriss. p.a.) and dimethyl sulfoxide (Fluka, purum) were stored in dark bottles over 4 Å molecular sieves. Acetonitrile-d_3 and dimethyl sulfoxide-d_6 were used without further purification.

IR spectra were recorded on a PE 1720 X FT-IR instrument, and ^1H NMR spectra on a Varian Gemini model 300 spectrometer.

Kinetics

All the reactions were started by mixing known volumes of prethermostated standard solutions of reagents in the thermostated compartment cell of a Perkin-Elmer Lambda 5 spectrophotometer and followed by repetitive scanning of the spectrum at suitable times in the visible region or at a fixed wavelength where the difference of absorbance was largest. The use of at least a 10-fold excess of nucleophile over complex ensured first-order kinetics in any run. The rate constants, k_{obs} (s^{-1}) were obtained either from the usual linear plots or from a non-linear least-squares fit of the experimental data to $At = A_\infty + (A_0 - A_\infty) \times \exp(-k_{obs}\, t)$ with A_0, A_∞ and k_{obs} as the parameters to be optimized (A_0 = absorbance after mixing of reagents; A_∞ = absorbance at completion of reaction.)

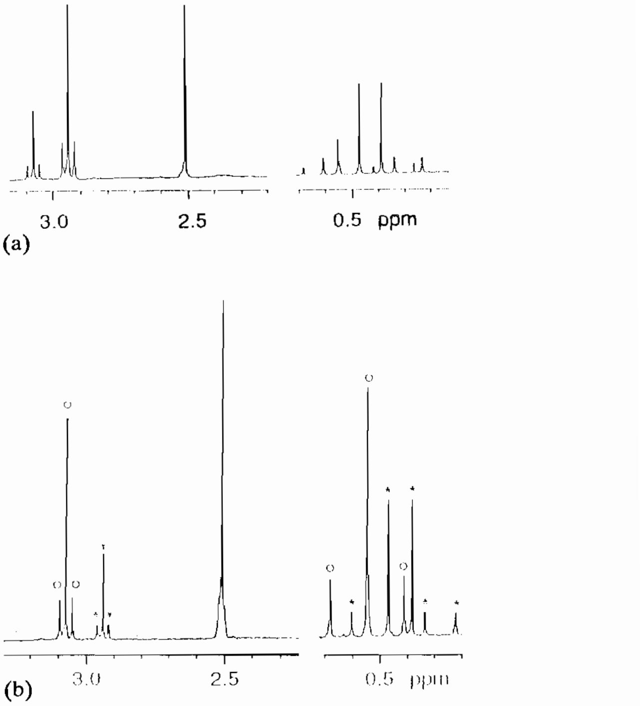


Fig. 1. (a) ^1H NMR spectrum of an equilibrium mixture of *cis*-$[PtMe_2(Me_2SO)_2]$ and *cis*-$[PtR_2(Me_2SO)(CD_3CN)]$; (b) spectrum of (a) after addition of ten-fold $[Me_2SO]$ excess over total platinum concentration; asterisks indicate signals of the solvated species, circles indicate signals of *cis*-$[PtMe_2(Me_2SO)_2]$.

Results

The UV spectrum of a sample of *cis*-$[PtR_2(Me_2SO)_2]$ in acetonitrile is remarkably different from that of the same substance recorded in dichloromethane. However, addition of free dimethyl sulfoxide to this solution produces changes in the UV spectrum and, when the concentration of sulfoxide is sufficiently large, the spectrum becomes coincident to that of *cis*-$[PtR_2(Me_2SO)_2]$ in CH_2Cl_2. Such a dmso-dependent equilibrium was measured spectrophotometrically for the complex *cis*-$[Pt(C_6H_5)_2(Me_2SO)_2]$ by the method of Sacconi *et al.* [8]. The absorbances measured at various concentrations of Me_2SO are reported in Table S1 (see 'Supplementary material'). The calculated equilibrium constant is 0.044 M at 25 °C.

The species in equilibrium are easily detected by ^1H NMR. Thus, the protonic spectrum of *cis*-$[PtMe_2(Me_2SO)_2]$ in CD_3CN (Fig. 1(a)) exhibits three groups of signals: the first one consists of two singlets partially splitted by ^{195}Pt, typical of S-coordinated dimethyl sulfoxide ($\delta = 3.07$ ppm, $^3J(Pt-H) = 13.5$ Hz; $\delta = 2.94$ ppm, $^3J(Pt-H) = 12.3$ Hz); another one corresponds to the resonance of uncoordinated Me_2SO; the last group of three signals ($\delta = 0.55$, $^2J(Pt-H) = 79.9$ Hz; $\delta = 0.47$ ppm, $^2J(Pt-H) = 79.9$ Hz; $\delta = 0.39$, $^2J(Pt-H) = 93.6$ Hz) is attributable to platinum coordinated methyl groups. The signals at 3.07 and 0.55 (intensity ratio 2:1) reproduce the spectral pattern of *cis*-$[PtMe_2(Me_2SO)_2]$ in CD_2Cl_2 showing that part of the starting material retains its identity in acetonitrile solution. The peak of coordinated dmso at 2.94 ppm has the same intensity of the free dmso resonance, as well as of the remaining methyl signals. These latter exhibit equal intensities but different coupling constants. Clearly, part of the starting material undergoes substitution of one molecule of sulfoxide with a molecule of solvent so leading to the splitting of the signal of the methyl groups. The signal at 0.47 ppm refers to the methyl group *trans* to Me_2SO in the solvated species. This is borne out by the fact that Me_2SO is known to possess a higher *trans* influence than that of a coordinated acetonitrile and, as a consequence, the methyl group *trans* to dmso exhibits a lower coupling constant. Furthermore, addition of free Me_2SO enhances the intensity of the signals corresponding to the species *cis*-$[PtMe_2(Me_2SO)_2]$ and diminishes that of the signals attributable to the solvent species (Fig. 1(b)). A similar pattern of behavior, at least in the coordinated Me_2SO region, is shown by *cis*-$[PtPh_2(Me_2SO)_2]$.

From these results, the equilibrium process can be formulated in the following way

$$cis\text{-}[PtR_2(Me_2SO)_2] + CH_3CN \rightleftharpoons cis\text{-}[PtR_2(Me_2SO)(CH_3CN)] + Me_2SO \quad (1)$$

From the integration ratios the values of the equilibrium constants calculated, at 25 °C, were $K=0.089$ M for R = Me and $K=0.053$ M for R = Ph, the latter being in good agreement with the value obtained by spectrophotometric measurements.

Addition of an equivalent quantity of bpy to an equilibrium mixture of *cis*-[PtMe$_2$(Me$_2$SO)$_2$] and *cis*-[PtMe$_2$(Me$_2$SO)(CH$_3$CN)] causes the disappearance of the ^{1}H NMR resonances of the coordinated sulfoxides together with those of the methyl signals; at the end, the only signal left due to methyl groups is that of the species [Pt(bpy)Me$_2$]. The same behaviour is observed when an equimolar quantity of bpy is added to an equilibrium mixture where *cis*-[PtMe$_2$(Me$_2$SO)$_2$] is in excess because of the presence of added free dmso.

The ^{1}H NMR spectrum of *cis*-[Pt(Me$_2$SO)$_2$Cl$_2$] in CD$_3$CN shows the expected resonance at $\delta=3.49$ ppm due to the methyl groups of the S-coordinated sulfoxides, with the two satellites due to the coupling with ^{195}Pt in the expected intensity ratio (1:4:1 intensities, ^3J(Pt–H) = 23.2 Hz). There is no significant solvolysis for the dichloro complex, as shown by the lack of any free dimethyl sulfoxide resonance.

The reactions of dimethyl-, diphenyl- and dichloro-bis(sulfoxido)platinum complexes with bpy, when monitored by means of UV–Vis spectroscopy in the region 350–500 nm, are consistent with a simple smooth conversion of the starting complex into a strongly absorbing product, the final spectra being identical with those of independently synthesized authentic samples of [Pt(bpy)Ph$_2$], [Pt(bpy)Me$_2$] and [Pt(bpy)Cl$_2$], respectively.

The values of rate constants, k_{obs}, are listed in Table S2 where they are compared with k_{calc} from the derived rate constants.

Discussion

The pattern of behavior observed for the reactions between *cis*-[PtMe$_2$(Me$_2$SO)$_2$] or *cis*-[PtPh$_2$(Me$_2$SO)$_2$] with 2,2′-bipyridine is closely similar to that already observed for the same reactions in non-coordinating solvents [5], while *cis*-[Pt(Me$_2$SO)$_2$Cl$_2$] seems to react with the diimine in a different way.

Thus, for the organometallic substrates the rate of displacement of sulfoxides by bpy is retarded by the addition of a free leaving group and, on increasing the amount of free dimethyl sulfoxide, the approach of the rate to a limiting value requires higher concentrations of reagents. As a result, by plotting the observed rate constants versus [bpy] at various Me$_2$SO concentrations a set of rectangular hyperboles is obtained.

In contrast, the substitution of the sulfoxides with bpy from *cis*-dichloro-bis(dimethyl sulfoxide)platinum(II) does not show any mass law retardation due to the added sulfoxide and the plot of the rate constants against the reagent concentrations is linear with no detectable intercept (Fig. 2).

For the organometallic substrates, the empirical rate law has the form

$$k_{\mathrm{obs}}=\frac{a[\mathrm{bpy}]}{b+c[\mathrm{Me_2SO}]+[\mathrm{bpy}]} \tag{2}$$

while, for the dichloro complex, the rate data follow the rate equation

$$k_{\mathrm{obs}}=k_2[\mathrm{bpy}]$$

typical of bimolecular processes which occur without a significant contribution of the solvent [9].

Reasonably, the substitution of sulfoxides in the dichloro complex is associatively activated, while the same reaction of the organometallic substrates may be correctly interpreted in terms of a dissociative mechanism, once the contribution of the solvento complex *cis*-[PtR$_2$(Me$_2$SO)(CH$_3$CN)] to the reactivity is taken into account, according to Scheme 1.

The reaction scheme assumes that the diorgano-bis(sulfoxide)platinum complex and its solvent counterpart in equilibrium lose a molecule of dimethyl sulfoxide and acetonitrile, respectively, to yield a reactive intermediate of reduced coordination number (a 14-electron species). The fate of this latter depends on the relative ability with which it undergoes the reentry of the leaving groups or the attack of the nitrogen

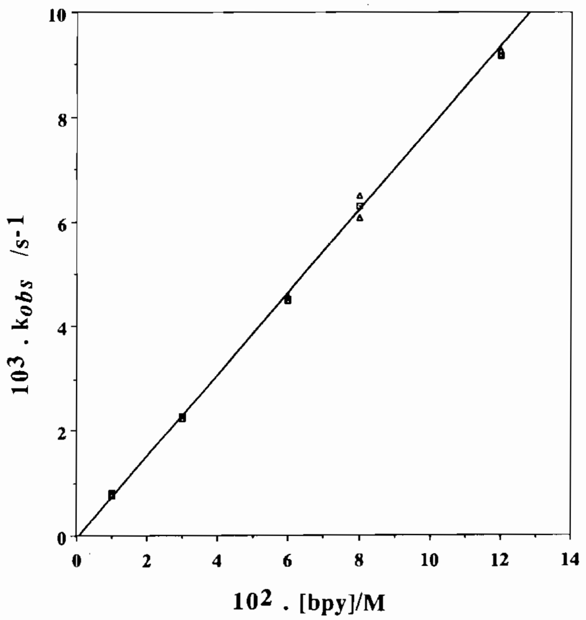
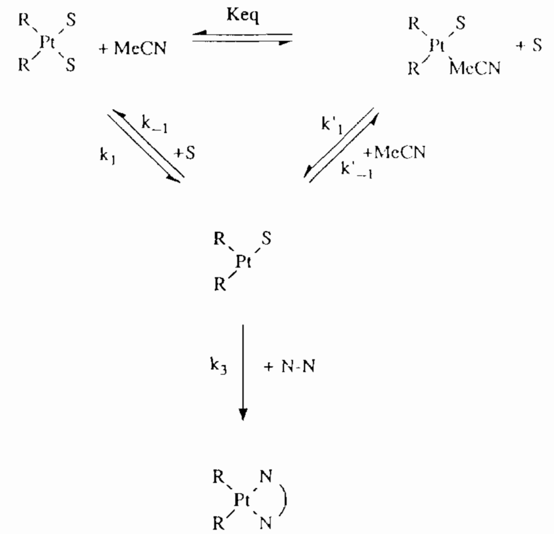


Fig. 2. [bpy] dependencies on the observed rate for the reaction *cis*-[Pt(Me$_2$SO)Cl$_2$] with bpy at 303.16 K. For each bpy concentration three k_{obs} were measured at [Me$_2$SO]] = 0.000, 0.001 and 0.250 M.



S = Me$_2$SO

R = CH$_3$ or C$_6$H$_5$

N-N = 2,2'-bipyridine

Scheme 1.

reagent to form the observed products. Applying the stationary state to the unsaturated [PtR$_2$(Me$_2$SO)] species, this reaction scheme leads to the following rate law

$$k_{\text{obs}}=\frac{(k_1[\text{Me}_2\text{SO}]+k'_1K_{\text{eq}})k_3[\text{bpy}]}{k'_{-1}+k_{-1}[\text{Me}_2\text{SO}]+k_3[\text{bpy}]}\times\frac{1}{K_{\text{eq}}+[\text{Me}_2\text{SO}]} \qquad (3)$$

which is somewhat different from the empirical expression (2) because of the presence of a first-order dependence on the [Me$_2$SO].

If we assume that k_1 is not significantly different from k'_1 or, in other words, that dissociation of Me$_2$SO from the starting complex or dissociation of acetonitrile from the solvent species occur at a similar rate, expression (3) is reduced to eqn. (4)

$$k_{\text{obs}}=\frac{k_1k_3[\text{bpy}]}{k'_{-1}+k_{-1}[\text{Me}_2\text{SO}]+k_3[\text{bpy}]} \qquad (4)$$

which is consistent with the empirical rate law.

The reciprocal of k_{obs} in such a simplified form, i.e.

$$(k_{\text{obs}})^{-1}=\frac{1}{k_1}+\frac{k'_{-1}+k_{-1}[\text{Me}_2\text{SO}]}{k_1k_3}[\text{bpy}]^{-1} \qquad (5)$$

shows a linear dependency of $k_{\text{obs}}{}^{-1}$ versus both [bpy]$^{-1}$ and [Me$_2$SO], as one can see in Fig. 3.

According to eqn. (5), the straight lines of $k_{\text{obs}}{}^{-1}$ versus [bpy]$^{-1}$ have a common intercept, independent of [Me$_2$SO], while in the lines of $k_{\text{obs}}{}^{-1}$ versus [Me$_2$SO] the intercepts are dependent on [bpy]$^{-1}$.

An easy analysis of intercepts and slopes in Fig. 3 allows us to relate the rate constants to the empirical parameters a, b and c by the expression $a=k_1$, $b=k'_{-1}/k_3$, $c=k_{-1}/k_3$.

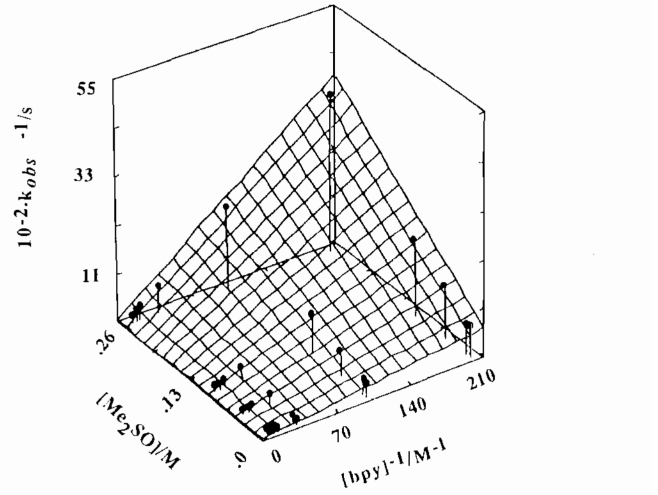


Fig. 3. Tridimensional view of the dependencies of $k_{\text{obs}}{}^{-1}$ on [Me$_2$SO] and [bpy]$^{-1}$ for the reactions: *cis*-[PtMe$_2$(Me$_2$SO)$_2$] + bpy → [Pt(bpy)Me$_2$] + 2Me$_2$SO.

In Table 1 the said rate constants are shown together with the corresponding ones obtained previously for the same bis-sulfoxide [5, 10] and the analogous bis-sulfide compounds [10, 11] in the poor coordinating solvent benzene.

We would like to point out that, for the system under study, the data in Table 1 were obtained using the assumption that both the bis-sulfoxide and the solvent species dissociate at a similar rate. Such an assumption implies that the leaving group does not play a significant role in the dissociation process. Accordingly, a comparison of the k_1 values for the reactions in acetonitrile with those already obtained for bis-sulfoxide and bis-sulfide species in benzene, shows very little differences on going from one to another species in both solvents. This is still in agreement with the results of a study of the reaction of bpy with a series of thioether complexes of formula *cis*-[PtR$_2$(R'$_2$S)$_2$] (R = phenyl; R' = an extended series of alkyl and aryl groups), where the rates of dissociation were found to depend very little on the nature and on the electronic properties of the substituted thioethers, except in a few cases in which steric hindrance becomes of overwhelming importance [12]. In other words, it seems that differences in either the leaving groups (Me$_2$SO, R$_2$S, MeCN) or *trans* activating groups (CH$_3$, C$_6$H$_5$, pMe-C$_6$H$_4$) so far examined play a role of secondary importance in the dissociative substitution of the above mentioned organometallic substrates.

The most significant feature of this work is the possibility for evaluating the relative efficiency with which three different nucleophiles bpy, Me$_2$SO and CH$_3$CN react with the three-coordinate intermediate [PtR$_2$(Me$_2$SO)] from the values of the competition ratios

Table 1. Derived rate constants for the reactions *cis*-$[PtR_2(Me_2SO)_2] + bpy \rightarrow [PtR_2(bpy)] + 2Me_2SO$ in acetonitrile and benzene at 303.16 K

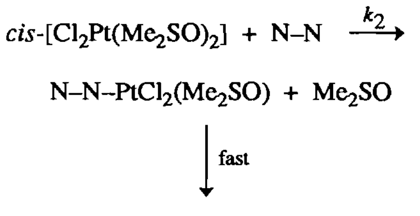
Complex	Solvent	k_1	k'_1	k_3/k_{-1}	k_3/k'_{-1}	k'_{-1}/k_{-1}
cis-$[PtPh_2(Me_2SO)_2]$[a]	acetonitrile	0.028	0.028	0.60	12.95	0.046
cis-$[PtMe_2(Me_2SO)_2]$[a]	acetonitrile	0.022	0.022	0.54	13.20	0.041
cis-$[Pt(p\text{-tolyl})_2(Me_2SO)_2]$[b]	benzene	0.0159		0.044		
cis-$[PtPh_2(Me_2SO)_2]$[b]	benzene	0.0140		0.049		
cis-$[PtMe_2(Me_2SO)_2]$[c]	benzene	0.0112		0.17		
cis-$[PtPh_2(Me_2S)_2]$[d]	benzene	0.0053		0.68		
cis-$[PtMe_2(Me_2S)_2]$[c]	benzene	0.0234		0.60		

[a]This work. [b]Data from ref. 5. [c]Data from ref. 10. [d]Data from ref. 11.

k_3/k_{-1}, k_3/k'_{-1}, k_{-1}/k'_{-1} (Table 1). Thus, the following sequence of nucleophilicity: $Me_2SO \sim bpy > MeCN$ is evidenced, indicating that the three-coordinate intermediate maintains a reasonable discriminating ability also in MeCN. This seems to be a specific property of three-coordinated species containing sulfoxide, while the corresponding thioethers exhibit a poor discriminating ability that is related to a shorter lifetime [5]. The stabilization of the three-coordinate $[PtR_2(Me_2SO)]$ species could be related to the tendency of the oxygen of the remaining coordinated sulfoxide to satisfy the electron deficiency on the metal by interacting partly at the vacant coordination site. The fact that Me_2SO and bpy in acetonitrile show a comparable efficiency in capturing the three-coordinate intermediate while in benzene the nitrogen chelate is much less reactive than Me_2SO could be explained by differences in the solvation properties of the two reagents. Indeed, calorimetric studies indicate that Me_2SO interacts more efficiently with polar solvents rather than with the apolar benzene [13].

Rate data for the reaction between *cis*-$[Pt(Me_2SO)_2Cl_2]$ and bpy obey the classical rate law for nucleophilic substitutions on square planar complexes. In this case, the slow step is the bimolecular attack of the chelating bpy leading to the substitution of the first molecule of dimethyl sulfoxide, while the subsequent ring closure is fast. This is a classical mechanism of chelation which can be represented by Scheme 2.

This is in agreement with previous findings for substitution of sulfoxides or sulfides in classical coordination compounds, that were found to occur through the normal associative mode of activation [14–16]. These kinetics on the strictly similar *cis*-$[PtR_2(Me_2SO)_2]$ and *cis*-$[Pt(Me_2SO)_2Cl_2]$ confirm the observation [10–12, 17] that on moving from classical Werner compounds to substrates with Pt–C σ-bonds there is a sharp changeover of mechanisms.



$$\begin{tikzcd} cis\text{-}[Cl_2Pt(Me_2SO)_2] + N\text{–}N \arrow[r, "k_2"] & {} \\ N\text{–}N\text{–}PtCl_2(Me_2SO) + Me_2SO \arrow[d, "fast"] \\ {[(N\text{–}N)PtCl_2] + Me_2SO} \end{tikzcd}$$

Scheme 2.

An analysis of the crystallographic data for *cis*-$[PtPh_2(Me_2SO)_2]$ [18] and *cis*-$[Pt(Me_2SO)_2Cl_2]$ [19] shows that, on going from the dichloro to diphenyl platinum complex, there is a remarkable lengthening (0.12 Å) of the Pt–S bond as the result of the strong σ-donor power of organic groups. This ground state destabilization could well be the possible origin for the different substitution pathway. However, as recently pointed out [20], other factors could play a significant role in promoting dissociative substitution in square planar systems and other studies are required before any statement can be made with confidence.

Supplementary material

Tables S1 and S2 are available from the authors on request.

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