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Dissociative Substitution in Four-Coordinate Planar Platinum(II) Complexes As Evidenced by Variable-Pressure High-Resolution Proton NMR Magnetization Transfer Experiments[1]

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Abstract: The ligand exchange rate constants for the reactions *cis*-$[PtR_2L_2] + 2{*}L \rightleftharpoons$ *cis*-$[PtR_2{*}L_2] + 2L$ have been determined in nonpolar solvents as a function of pressure, up to 200 MPa, by high-resolution ^1H NMR magnetization transfer experiments. The resulting volumes of activation, ΔV^{*}, for the exchange on the square-planar complexes *cis*-$[PtPh_2(Me_2S)_2]$ in benzene, *cis*-$[PtPh_2(Me_2SO)_2]$ in chloroform, and *cis*-$[PtMe_2(Me_2SO)_2]$ in benzene are respectively +4.7 ± 0.5, +5.5 ± 0.8, and +4.9 ± 0.5 $cm^3\ mol^{-1}$. These values of activation volume are strongly indicative of a dissociative mode of activation and are consistent with all the previous evidence coming from substitution reactions on the same substrates. Thus, the overall mechanistic picture can be taken as the first clear-cut evidence for the operation of a D mechanism involving a 3-coordinate 14-electron intermediate for simple ligand substitution on square-planar complexes. Since the pattern of behavior in ligand exchange or substitution reactions on classical strictly similar coordination compounds is fully consistent with an associative mode of activation, it must be concluded that the presence of a Pt–C bond produces a sharp changeover of reaction pathway.

The mechanistic picture for substitution reactions on square-planar complexes is well established[4] and involves a concurrent bimolecular attack by solvent and the nucleophile on the substrate with a considerable discrimination among different entering groups. The dissociative mode of activation is a rarity. The search for factors promoting the conversion of the normal associative mode of activation into a dissociative process has then attracted much attention.

The attempts to induce dissociation have utilized mainly two methods: one is to prevent bond formation by means of sterically hindered ligands, such as alkyl-substituted diethylenetriamine in the so called "pseudo-octahedral" complexes;[5] the other is to promote bond weakening at the leaving group, usually a halide ion, by making use of strong σ-donor trans activating ligands.[6] Complexes of the type *cis*- or *trans*-$[Pt(PEt_3)_2(R)Cl]$ (R = Ph, *o*-tolyl, or mesityl) meet both conditions.[7]

Increasing steric hindrance or extensive electron transfer from the trans activating group to the metal led to a common phenomenon, possibly for different reasons. In both cases the contribution of the reagent pathway is reduced to the point where the substitution takes place only by way of solvolysis. Anyway, this loss of discriminating ability of the substrate and the predominance of the solvolytic path falls short of providing direct evidence of a dissociative mechanism involving a three-coordinate intermediate. The simplest way of envisaging the enhanced importance of the solvent in the substitution is to consider it as the more favored nucleophile than any other. There is little doubt that the activation remains associative. Accordingly, an extensive series of measures of activation volumes of solvolysis reactions on a variety of alkyl-substituted diethylenetriamine complexes of palladium(II) and on *trans*-$[Pt(PEt_3)_2(\text{mesityl})Br]$ have been interpreted in terms of a basically associative mechanism.[8] A further evidence that steric hindrance on the ancillary ligands or on the entering group is not sufficient to prevent an associative mode of activation has been given by measures of water exchange and anation reactions under pressure for $[Pd(R_5dien)H_2O]^{2+}$ (R_5dien = 1,1,4,7,7-pentamethyl- and 1,1,4,7,7-pentaethyldiethylenetriamine).[2]

Recent studies on the kinetics of sulfoxide or thioether displacement by chelating ligands in the reactions of *cis*-$[PtR_2L_2]$ (R = Me or Ph, L = Me_2SO or RR′S) in apolar solvents[9] have provided the first clear-cut examples of a facile dissociative mechanism in substitution reactions of four-coordinate planar d^8 metal complexes. Thus, dissociation of S-bonded Me_2SO or sulfide and the intermediacy of an unsaturated 14-electron $[PtR_2L]$ three-coordinate species offers a more favorable path to substitution than a direct attack by the ligand on the four-coordinate substrate.

The reaction represented by eq 1, which involves exchange of neutral molecules with an uncharged substrate and where solvent electrostriction effects should contribute very little, is particularly interesting and suitable for the interpretation of volumes of activation as obtained from the pressure dependence of the exchange rates. For this reason we were prompted to carry out a detailed kinetic study of the pressure effect on the rates of ligand exchange

$$cis\text{-}[PtR_2L_2] + 2{*}L \overset{k_{ex}}{\rightleftharpoons} cis\text{-}[PtR_2{*}L_2] + 2L \qquad (1)$$

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(1) Part 41 of the series High Pressure NMR Kinetics. For part 40 see ref 2.

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on the complexes *cis*-$[PtPh_2(Me_2SO)_2]$, *cis*-$[PtPh_2(Me_2S)_2]$, and *cis*-$[PtMe_2(Me_2SO)_2]$. The results give further evidence for ligand dissociation as the dominant pathway for the exchange and lead to exclude any possible associative contribution.

Experimental Section

Materials. The complexes *cis*-$[PtMe_2(Me_2SO)_2]$,[10] *cis*-$[PtPh_2(Me_2S)_2]$,[9b] and *cis*-$[PtPh_2(Me_2SO)_2]$[9c] were prepared by methods reported elsewhere. Benzene (Fluka, puriss. p.a.), chloroform (Fluka, puriss. p.a.), dimethyl sulfide (Fluka, purum), and dimethyl sulfoxide (Fluka, purum) were stored in dark bottles over 4-Å molecular sieves. Benzene-d_6 (Ciba-Geigy, 99.5%) and chloroform-d (Ciba-Geigy 99.8%) were used without further purification. All samples were prepared by weight by adding the reagents directly to the solvent. Consequently, concentrations are given in terms of molality, m, in moles per kilogram of solvent.

NMR Measurements. The ambient pressure ^1H NMR spectra were recorded on a Bruker CXP-200 spectrometer, operating in the FT mode at 200 MHz, using a commercial thermostated probe unit. Temperature was found constant within ±0.2 K and was measured before and after spectral accumulation by substituting the sample with a Pt-100 Ω resistance.[11] The spectra were obtained with use of a pulse width of 4μs in the quadrature detection mode. We used 4K data points resulting from 1–40 scans accumulated over total spectral widths of 500–2000 Hz. ^1H NMR chemical shifts are referred to TMS and measured with respect to the nondeuterated solvent signal $CHCl_3$ or C_6D_5H, 7.27 and 7.40 ppm, respectively.

^1H NMR spectra at variable pressure were recorded using a Bruker AM-400 (CXP-200) spectrometer working at 400 MHz (200 MHz). The measurements were made up to 200 MPa using homebuilt high-pressure probes described elsewhere.[12,13] A built-in platinum resistor allows temperature measurement within an accuracy of ±1 K after all corrections.[14] By pumping thermostated synthetic oil through the bomb, the temperature was stabilized to ±0.2 K. The 90° pulse length varied from 35-50 μs (12-15 μs) due to pressure changes. We used a deuterium lock for field stabilization for the spectra recorded at 400 MHz.

The magnetization-transfer measurements were performed using the "inversion-recovery technique" as described in the literature.[15] Selective inversion of the free or bound solvent signal was achieved, using the so-called "1,-3,3,-1" pulse train.[16] After a variable time, t, a nonselective 90° pulse allows observation of the signals.

Results and Data Treatment

Magnetization Transfer. The dimethyl sulfoxide exchange rate on $[PtPh_2(Me_2SO)_2]$ (eq 1) has been studied previously[9b] by stopped-flow NMR, as a function of free Me_2SO concentration at 300 K in chloroform. However, this technique has not yet been adapted for variable-pressure work to obtain the mechanistically relevant activation volumes. The ^1H NMR spectra of this, and related complexes, show narrow signals for the bound and free solvent molecules over the accessible temperature domain. These reactions are therefore too slow to be studied quantitatively by NMR line-broadening technique with our home-built high-pressure probe-heads. However, magnetization transfer NMR is a useful technique to study exchange rates intermediate between those accessible by stopped-flow and line-broadening NMR.

In systems in which the longitudinal relaxation rate, $1/T_1$, is less than or equal to the exchange rate it is possible to deduce the exchange rate between two sites, by selectively inverting the signal of one site and monitoring the intensity of the signal of both sites as a function of time between the inversion and monitoring pulses. The return of the magnetization to equilibrium is then governed by both the $1/T_1$ of the exchanging species and the exchange rate between the sites.[17,18] In this work the two sites are that of the solvent molecules bound to the platinum complex and that of the free solvent molecules. A complication arises from the triplet-like structure of the bound signal. The two satellites correspond to the solvent bound to the platinum 195 isotope with spin $^1/_2$. Its total amount is 33.8% and the central line represents the 66.2% bound to Pt without spin. To perform fine selective inversion we need well-separated signals without strong scalar coupling. The chemical shifts, δ, of free and bound Me_2SO and the coupling constant, $J(^{195}Pt-^1H)$, of the solvent bound to Pt are respectively 2.05 ppm, 2.80 ppm, and 13.1 Hz for $[PtMe_2(Me_2SO)_2]$ in benzene and 2.61 ppm, 2.82 ppm, and 14.5 Hz for $[PtPh_2(Me_2SO)_2]$ in chloroform. In these two cases the solvent signals are more or less well separated compared to the $^{195}Pt-^1H$ coupling constant. For solutions of $[PtPh_2(Me_2S)_2]$ the δ of free and bound Me_2S and $J(^{195}Pt-^1H)$ are respectively 2.16 ppm, 2.14 ppm, and 23.5 Hz in chloroform and 1.98 ppm, 1.83 ppm, and 23.6 Hz in benzene. From these values it follows that it is impossible to perform magnetic transfer experiments to derive rate constants of the Me_2S exchange in chloroform for the last complex. Nevertheless, in benzene the experiment is feasible but only at high magnetic field. Figure 1 shows the ^1H NMR (400 MHz) magnetic transfer spectra obtained at 342 K and 162 MPa for this case.

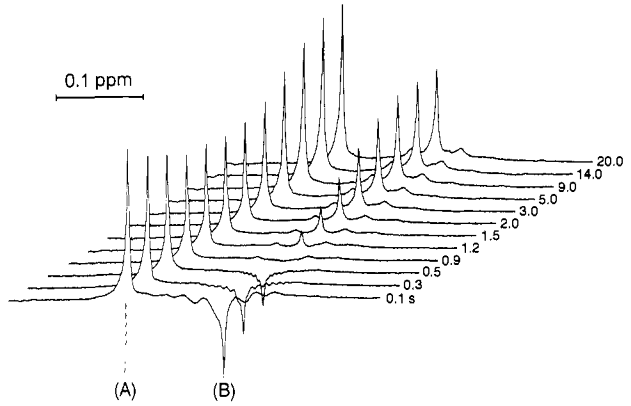

Figure 1. 400-MHz ^1H NMR spectra of a 0.1 m $[PtPh_2(Me_2S)_2]$ and 0.2 m Me_2S solution in C_6D_6 (25% C_6H_6) at 342 K and at 162 MPa as a function of the time interval t between the inversion pulse train and the observation pulse. The pulse sequence employed was the following: $(25.5°-D_1-67.5°-D_1-67.5°-D_1-25.5°-t-90°-D_2)$ where the delay D_1 = 11 ms, D_2 = 60 s, and the 90° pulse = 50 μs. Each spectrum was recorded over a sweep width of 500 Hz and required 1 scan. 4K data points were recorded. (A) Free Me_2S and (B) Me_2S bound to the platinum complex $J(Pt-H)$ = 24 Hz.

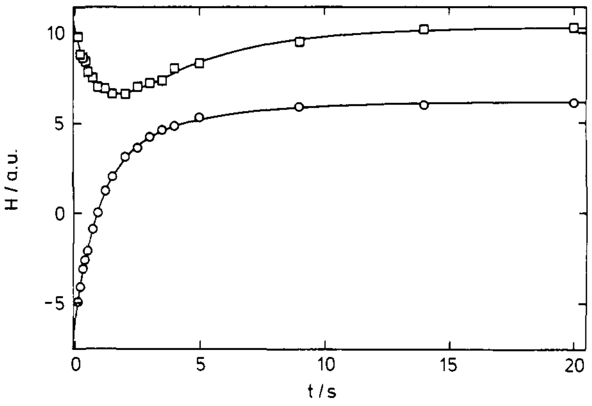

Figure 2. Calculated curve from the magnetization transfer experiment shown in Figure 1: (○) signal height of the central line from the Me_2S bound to Pt and (□) signal height of the free Me_2S. The lines are generated by the equations given in ref 17 and are fitted to the experimental values.

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Table I. Rate Constants, k_{ex}, for the Solvent Exchange Reaction on *cis*-$[PtR_2L_2]$ at Variable Pressure and at Different Temperatures Obtained from the 400-MHz ^1H NMR Magnetic Transfer Experiments[a]

P/MPa	k_{ex}/s^{-1}	P/MPa	k_{ex}/s^{-1}	P/MPa	k_{ex}/s^{-1}	P/MPa	k_{ex}/s^{-1}	P/MPa	k_{ex}/s^{-1}
0.1	0.48 ± 0.02	0.1	0.87 ± 0.10	0.1	0.99 ± 0.14[c]	0.1	0.94 ± 0.12[c]	0.1	0.53 ± 0.04
0.1	0.48 ± 0.03	0.1	0.93 ± 0.08	0.1	0.96 ± 0.14	0.1	1.09 ± 0.10	0.1	0.51 ± 0.04
27	0.42 ± 0.03	50	0.77 ± 0.05	25	0.88 ± 0.07	0.1	0.98 ± 0.11	0.1	0.51 ± 0.03
51	0.45 ± 0.02	101	0.70 ± 0.06	50	0.80 ± 0.08	50	0.90 ± 0.14	45	0.46 ± 0.02
73	0.40 ± 0.02	125	0.72 ± 0.07	75	0.69 ± 0.06	50	0.97 ± 0.10	71	0.41 ± 0.03
103	0.39 ± 0.02	151	0.65 ± 0.03	100	0.64 ± 0.09	75	0.86 ± 0.10	72	0.43 ± 0.02
122	0.40 ± 0.03	202	0.68 ± 0.04	125	0.68 ± 0.09	100	0.88 ± 0.11	87	0.41 ± 0.03
153	0.36 ± 0.03			150	0.71 ± 0.08	125	0.71 ± 0.09	105	0.40 ± 0.01
162	0.34 ± 0.01			175	0.70 ± 0.08	150	0.73 ± 0.16	137	0.40 ± 0.03
				200	0.63 ± 0.06	175	0.83 ± 0.15	139	0.39 ± 0.01
						200	0.60 ± 0.10	170	0.38 ± 0.02
								186	0.38 ± 0.02
								200	0.35 ± 0.05
0.12 m $[PtPh_2(Me_2S)_2]$ 0.25 m Me_2S[b] in C_6D_6 (25% C_6H_6) 342.1 K		0.22 m $[PtPh_2(Me_2S)_2]$ 0.35 m Me_2S[b] in C_6D_6 (25% C_6H_6) 348.0 K		0.020 m $[PtPh_2(Me_2SO)_2]$ 0.041 m Me_2SO in $CDCl_3$ (10% $CHCl_3$) 330.8 K		0.021 m $[PtPh_2(Me_2SO)_2]$ 0.039 m Me_2SO in $CDCl_3$ (10% $CHCl_3$) 331.1 K		0.035 m $[PtMe_2(Me_2SO)_2]$ 0.079 m Me_2SO in C_6D_6 (20% C_6H_6) 333.4 K	

[a] Reported errors represent one standard deviation. [b] Due to the high vapor pressure of Me_2S, the concentration of this compound was obtained by integration of the ^1H NMR signal. [c] Measurements performed at 200 MHz.

Table II. Derived NMR and Kinetic Parameters for the Variable-Pressure Studies of Ligand-Exchange Reaction on *cis*-$[PtR_2L_2]$[a]

	$[PtPh(Me_2S)_2]$	$[PtPh_2(Me_2SO)_2]$	$[PtMe_2(Me_2SO)_2]$
$\Delta V^{\ddagger}/cm^3\ mol^{-1}$	+4.7 ± 0.5	+5.5 ± 0.8	+4.9 ± 0.5
$(k_{ex})_0/s^{-1}$	0.47 ± 0.01[b] 0.88 ± 0.02[c]	0.91 ± 0.03[d] 1.01 ± 0.03[e]	0.50 ± 0.01[f]
$\Delta V^{\ddagger}(T_{1b})/cm^3\ mol^{-1}$	−7.6 ± 1.7	−8.1 ± 1.9	−10.1 ± 0.9
$(1/T_{1b})_0/s^{-1}$	0.33 ± 0.02[b] 0.20 ± 0.02[c]	0.78 ± 0.07[d] 0.56 ± 0.05[e]	0.22 ± 0.01[f]
$\Delta V^{\ddagger}(T_{1f})/cm^3\ mol^{-1}$	−17.8 ± 5.3	−10.0 ± 1.8	−6.9 ± 1.6
$(1/T_{1f})_0/s^{-1}$	0.05 ± 0.01[b] 0.13 ± 0.03[c]	0.20 ± 0.02[d] 0.25 ± 0.02[e]	0.10 ± 0.01[f]

[a] Reported errors represent one standard deviation. [b] 342.1 K. [c] 348.0 K. [d] 330.8 K. [e] 331.1 K. [f] 337.1 K.

The experimental magnetizations were obtained by direct measurements of the signal heights from the spectra and were fitted to the equations given by Led and Gesmar[17] using an iterative, nonlinear least-squares routine. The contribution of the satellites to the height of the central line and the ratio between the signal line widths were taken into account. Seven parameters were fitted: the final and initial signal heights of free and bound solvent, their spin-lattice relaxation rates ($1/T_{1f}$ and $1/T_{1b}$), and the exchange rate constant k_{ex}. An example of a fit is shown in Figure 2. The detailed results are given in the supplementary material and the k_{ex} values are summarized in Table I and Figure 3.

Variable Temperature. The first-order exchange rate constant k_{ex}^{298} and the activation parameters, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, were determined by an iterative linear least-squares-fitting procedure. The rate constants for the study of Me_2SO exchange on $[PtMe_2(Me_2SO)_2]$ as a function of temperature lead to the following: $k_{ex}^{298} = (1.12 \pm 0.15) \times 10^{-2}\ s^{-1}$, $\Delta H^{\ddagger} = 84.0 \pm 2.6$ kJ mol^{-1}, and $\Delta S^{\ddagger} = -0.5 \pm 7.8$ J K^{-1} mol^{-1} (Figure 3). These values are in agreement with the derived kinetic parameters $\Delta H^{\ddagger} = 84.9 \pm 0.8$ kJ mol^{-1} and $\Delta S^{\ddagger} = -2.9 \pm 3.3$ J K^{-1} mol^{-1} obtained by Romeo and colleagues[9d] using a ligand-substitution technique.

Variable Pressure. The pressure dependence of ln (Q) (Q = k_{ex}, $1/T_{1b}$, or $1/T_{1f}$, respectively) can be described by the linear equation

$$\ln(Q) = \ln(Q)_0 - P\Delta V^{\ddagger}_Q/RT \qquad (2)$$

$\Delta V^{\ddagger}_Q$ is the activation volume and the $(Q)_0$ value is the rate constant at zero pressure, for the corresponding process. By fitting eq 2 to experimental data in Figure 4 we obtain the results reported in Table II. The values for the longitudinal relaxation rates show that the proton spin belonging to a bound solvent molecule always relaxes faster than one sitting on a bulk molecule. This can be explained by a longer correlation time, τ_c, for the reorientation of these particles due to its binding to the larger complex. All activation volumes for the longitudinal relaxation times are in the range of −7 to −10 cm^3 mol^{-1} and do not differ very much if we take into account the errors. The negative value for the activation volumes arises from an increase in relaxation rates under pressure and reflects the increasing viscosity under pressurization leading to longer correlation times.

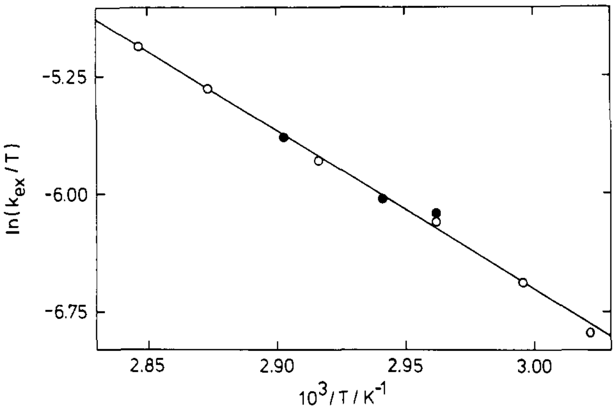

Figure 3. Plot of ln (k_{ex}/T) data vs reciprocal temperature for ligand-exchange reaction between $[PtMe_2(Me_2SO)_2]$ and free Me_2SO in benzene: (○) 0.050 m $[PtMe_2(Me_2SO)_2]$ and 0.109 m Me_2SO in C_6D_6 (10% C_6H_6); (●) 0.085 m $[PtMe_2(Me_2SO)_2]$ and 0.273 m Me_2SO in C_6D_6 (25% C_6H_6).

Discussion

The reactions of *cis*-$[PtR_2L_2]$ (R = Ph or Me, L = Me_2S or Me_2SO) with nitrogen chelating ligands such as 2,2'-bipyridine in inert solvents have been explained[9] by a stepwise mechanism involving dissociation of the starting complex to yield a coordinatively unsaturated 14-electron $[PtR_2L]$ intermediate followed by attachment of the ligand to form an open-ring species. There

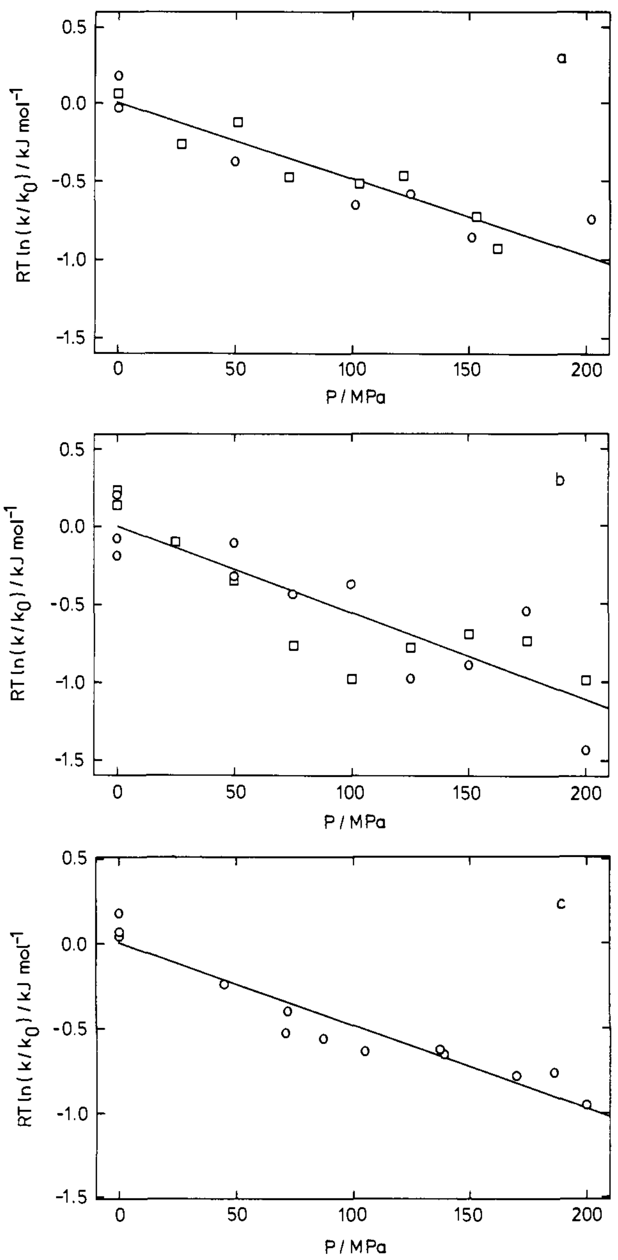

Figure 4. Plot of $RT \ln (k_{ex}/(k_{ex})_0)$ vs pressure for the ligand-exchange reaction between (a) $[PtPh_2(Me_2S)_2]$ and free Me_2S at 342.1 K (□) and 348.0 K (○); (b) $[PtPh_2(Me_2SO)_2]$ and free Me_2SO at 330.8 K (□) and 331.1 K (○); and (c) $[PtMe_2(Me_2SO)_2]$ and free Me_2SO at 337.1 K.

follows fast ring closing to yield the observed products. Stronger nucleophiles such as chelating phosphines can also use a parallel associatively activated pathway. However, in the case of the *cis*-$[PtPh_2(Me_2SO)_2]$ complex the unsaturated intermediate shows a significant nucleophilic discrimination ability.

The assessment of the mechanism has been made essentially on the basis of (i) the saturation kinetics observed on plotting the rate constants against the concentration of the entering ligand, as a result of mass-law retardation produced by the leaving thioether or sulfoxide, (ii) the independence of the rate of dissociation of the nature of entering group, (iii) the identity of the rate of dissociation with the rate of solvent exchange, at least in the case of exchange between free and coordinated Me_2SO in *cis*-$[PtPh_2(Me_2SO)_2]$, (iv) the sign and the magnitude of the entropy of activation always being low and even positive, except for the case of *cis*-$[PtPh_2(Me_2SO)_2]$. The solvent was assumed to be insufficiently coordinating to give an associatively activated contribution.

A requirement of the dissociative mechanism is that the rate of substitution be independent of the nature of the entering group and equal to the rate constant for the solvent exchange. This has been proven already to be the case for the kinetics of exchange between free and coordinated Me_2SO in $CDCl_3$ solutions of $[PtPh_2(Me_2SO)_2]$ and $[^2H_6]Me_2SO$ studied by ^1H NMR stopped-flow technique.[9b] The sulfoxide-dependent contribution was found to be negligible. This pattern of behavior is confirmed in the kinetics of sulfoxide exchange on $[PtMe_2(Me_2SO)_2]$ (Figure 3).

The advantages of using variable-pressure high-resolution proton NMR magnetization transfer experiments have been illustrated above and the greater reliability of the volume of activation data with respect to that of entropy of activation is widely recognized. It seems useful to add here that the symmetrical exchange system (eq 1) offers the additional advantage of avoiding the buildup in solution of unwanted species, whose presence in line of principle is always possible in substitution reactions, even though already excluded for the reactions cited on the basis of ^1H NMR and other spectral evidences. The values of volume of activation listed in Table II for *cis*-$[PtPh_2(Me_2S)_2]$ ($\Delta V^{\ddagger} = +4.7 \pm 0.5$ cm^3 mol^{-1}), *cis*-$[PtPh_2(Me_2SO)_2]$ ($\Delta V^{\ddagger} = +5.5 \pm 0.8$ cm^3 mol^{-1}), and *cis*-$[PtMe_2(Me_2SO)_2]$ ($\Delta V^{\ddagger} = +4.9 \pm 0.5$ cm^3 mol^{-1}) are supportive and implement all previous experimental evidence arising from substitution kinetics and are conclusive of a dissociative mode of activation. It should be kept in mind that the use of volumes of activation in the context of a solvent exchange reaction is of primary importance as a mechanistic tool.[19] Indeed, in the exchange the solvational part due to electrostriction or to other volume changes of the molecules of the surrounding diluent solvent can be assumed to be constant throughout the reaction ($\Delta V^{\ddagger}_{solv} = 0$) and the measured volume of activation represents only the change in volume ($\Delta V^{\ddagger}_{intr}$) due to changes in bond lengths and angles. Since 14-electron ML_3 or ML_2X species are known to avoid the most symmetrical high-spin trigonal-planar geometry in favor of a T-shaped geometry of much lower energy,[20] we do not expect significant contributions by changes in bond lengths between the central metal and the nonexchanging ligands.

Once that the mechanistic picture is reasonably clear and it is consistent with all the experimental evidence at hand, the main question that begs an answer is what factors are promoting the facile dissociation of these complexes. The similarities of their labilities as well as of the associated volumes of activation suggest that the main factor promoting dissociation is the strong σ-donor power of the Pt–C bond, which lengths and weakens the trans Pt–S bond. A comparison of the few existing structural data in literature for related *cis*-$[PtCl_2L_2]$ and *cis*-$[PtPh_2L_2]$ (L = S-bonded Me_2SO or R_2S)[21] indicates that when Cl is replaced by Ph as the trans-activating group the Pt–S(thioether) or the Pt–S(sulfoxide) bond distances are lengthened by at least 0.1 Å. Changes from Ph to Me, while obviously increasing the disposibility of the substrate to the bimolecular attack,[9d] do not greatly affect the ease with which the dissociative activation takes place. This suggests that steric hindrance from the phenyl ring or stabilization of the three-coordinate intermediate by interaction between the ortho hydrogens and the metal plays little, if any, part in promoting dissociation. Likewise, a comparison of the kinetic behavior and of the volumes of activation of thioether and sulfoxide compounds

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Table III. Selected Exchange Rate Constants and Activation Parameters for Solvent and Ligand Exchange Reaction on Square-Planar Pd^{2+} and Pt^{2+}

complex	solvent	$k_{ex}^{298\,a}$	$\Delta H^{\ddagger}$/ kJ mol^{-1}	$\Delta S^{\ddagger}$/ J K^{-1} mol^{-1}	$\Delta V^{\ddagger}$/ cm^3 mol^{-1}	mechanism	ref
$[Pd(H_2O)_4]^{2+}$	water	$10^{b,i}$	49	-60^{i}	−2.2 (324 K)	I_a, A	22
$[Pd(dien)H_2O]^{2+}$	water	93^{b}	38	−80	−2.8 (296 K)	I_a, A	23
$[Pd(Me_5dien)H_2O]^{2+}$	water	3.4^{b}	62	−27	−7.2 (320, 323 K)	I_a, A	2
$[Pd(Et_5dien)H_2O]^{2+}$	water	$5.3 \times 10^{-2\,b}$	63	−58	−7.7 (369 K)	I_a, A	2
trans-$[Pd(Me_2S)_2Cl_2]$	C_6H_5CN	197^{b}	38	−73	−5.9 (300 K)^{d}	I_a, A	24
$[Pt(H_2O)_4]^{2+}$	water	$7.1 \times 10^{-6\,b}$	90	−43	−4.6 (297 K)	I_a, A	25
$[Pt(Me_2SO)_2(Me_2SO)_2]^{2+\,e}$	CH_3NO_2	$3.2 \times 10^{3\,b}$	33	−62	−2.5 (265 K)	I_a, A	26
$[Pt(Me_2SO)_2(Me_2SO)_2]^{2+\,f}$	CH_3NO_2	2^{b}	47	−74	−5 (360 K)	I_a, A	26
cis-$[PtPh_2(Me_2S)_2]$	benzene	$0.21^{c,g}$	101^{g}	$+42^{g}$	+4.7 (342, 348 K)	D	this work
cis-$[PtPh_2(Me_2SO)_2]$	benzene	$1.24^{c,g}$	64^{g}	-67^{g}	+5.5 (331 K)^{h}	D	this work
cis-$[PtMe_2(Me_2S)_2]$	benzene	$1.38^{c,g}$	90^{g}	$+21^{g}$		D	
cis-$[PtMe_2(Me_2SO)_2]$	benzene	$0.60^{c,g}$	85^{g}	-3^{g}			
	benzene	1.12^{c}	84	−1	+4.9 (337 K)	D	this work

[a] All values refer to the exchange of one particular solvent molecule. [b] In m^{-1} s^{-1}. [c] In s^{-1}. [d] Intrinsic $\Delta V^{\ddagger}$ in a hypothetical nonsolvating solvent.[24] [e] O-Bonded exchange. [f] S-Bonded exchange. [g] Obtained indirectly from substitution reaction studies of L with bidentated ligands.[9] [h] In $CHCl_3$. [i] The rate constant and $\Delta S^{\ddagger}$ in ref 26 are for the exchange of one of the four-coordinated water molecules, and not for a particular water molecule.

argues against the possibility that a significant contributory factor in promoting dissociation could be the tendency for the oxygen of the remaining sulfoxide to satisfy the electron deficiency in the three-coordinate $[PtR_2(Me_2SO)]$ intermediate by interacting partly at the vacant coordination site. Even though the anchimeric assistance by this oxygen atom does not reach the point of being seen as an internally, associatively activated, substitution, the loss of rotational entropy which ensues could well be reflected in the low value of the entropy of activation $\Delta S^{\ddagger} = -67$ J K^{-1} mol^{-1} for dissociation of *cis*-$[PtPh_2(Me_2SO)_2]$ (see Table III). This is a particular case in which $\Delta V^{\ddagger}$ and $\Delta S^{\ddagger}$ exhibit opposite signs and it is a reminder that an unquestioning use of activation data to determine the molecularity of the reactions is dangerous and can be misleading. A further indication that such an interaction between the oxygen and the metal in $[PtR_2(Me_2SO)]$ exists is given by the fact that this unsaturated species, unlike $[PtR_2(Me_2S)]$, has a lifetime long enough to discriminate among different nucleophiles.[9]

Table III lists available kinetic data for solvent and ligand exchange reactions on square-planar complexes. The values of volumes of activation derived from the pressure effect on the rates have been used as a mechanistic tool to assign the mode of activation (column 7), according to the current therminology.[4] Apart from the details of the intimate mechanism we see that classical coordination compounds undergo substitution through a normal associative mode of activation; on the contrary, compounds with a metal–carbon bond are shown to react through a dissociative pathway. Although the examples reported are very few and hardly can be assumed as a sure indication of a trend, one is led to wonder to what extent the well-known mechanistic patterns for substitutions on square-planar complexes apply to organometallic compounds. In this context it is also worth pointing out that the complexes *cis*-$[PtCl_2(Me_2S)_2]$,[27] *cis*-$[PtCl_2(Me_2SO)_2]$,[28] and $[Pt(en)(Me_2SO)_2]^{2+}$ [29] (en = 1,2-diamminoethane) were shown to undergo substitution by way of the normal associative mode of activation. In particular, the presence of two sulfoxides in cis position plays a significant role in the stabilization of a five-coordinate intermediate.[24] If we restrict the comparison to the kinetic behavior of *cis*-$[PtCl_2L_2]$ and *cis*-$[PtR_2L_2]$ (R = Me, Ph; L = Me_2S or Me_2SO) it is possible to see that moving from chloride to alkyl or aryl, the extensive electron density transfer associated with the presence of a Pt–C bond produces a sharp changeover of reaction pathways. Whether the phenomenon is related only to ground-state destabilization (lengthening and weakening of the Pt–S bond distance) or even to a change of electron density at the metal center remains to be clarified.

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Registry No. *cis*-$[PtMe_2(Me_2SO)_2]$, 70423-98-2; *cis*-$[PtPh_2(Me_2S)_2]$, 64827-20-9; *cis*-$[PtPh_2(Me_2SO)_2]$, 70423-99-3.

Supplementary Material Available: Listings of kinetic and NMR relaxation rates as a function of temperature (Table SI) and pressure (Tables SII–SIV) and Figures S1 and S2 representing the pressure dependence of the normalized longitudinal relaxation rate of the free and bound solvent ^1H NMR signals (6 pages). Ordering information is given on any current masthead page.

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