to signals associated with four types of O-*i*-Pr ligands, a signal at $\delta = 9.87$ (relative to Me_4Si), of integral intensity 1 H, assignable to the imido proton. (3) The IR spectrum shows a band at 3375 cm^{-1} assignable to ν(N–H). In these respects the new compound is notably different from $W_3(\mu_3\text{-}O)(O\text{-}i\text{-}Pr)_{10}$, and we are confident in our affirmation of this as the first imido-capped triangulo tungsten cluster. This new cluster is an alkoxy analogue of $Fe_3(\mu\text{-}NH)(CO)_{10}$.[8]

Further studies are in progress.

Acknowledgment. We thank the Department of Energy, Office of Basic Research, Chemical Sciences Division, and the Wrubel Computing Center for support of this work.

Note Added in Proof. Synthesis of the ^{15}N-labeled compound $W_3(\mu_3\text{-}^{15}NH)(O\text{-}i\text{-}Pr)_{10}$ has allowed characterization of the imido capping ligand by ^{15}N NMR spectroscopy: $\delta(^{15}NH) = 250.3$ relative to NH_3; $^1J_{^{15}N-^1H} = 79.3$ Hz and $^1J_{^{183}W-^{15}N} = 23.3$ Hz.

Supplementary Material Available: Listings of atomic coordinates and thermal parameters (4 pages). Ordering information is given on any current masthead page.

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Articles

Contribution from the Istituto di Chimica Generale ed Inorganica, Università di Venezia, Venice, Italy, and Christopher Ingold Laboratories, University College London, London WC1H 0AJ, England

Preparation of Chloro-Bridged Dimers and Trans Complexes of Platinum(II) Containing Alkyl Sulfoxides and the Kinetics of the Trans–Cis Isomerization of Dichlorobis(sulfoxide)platinum(II) in Dichloromethane

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Chloro-bridged complexes of the type $[Pt_2L_2(\mu\text{-}Cl)_2Cl_2]$ (L = dimethyl sulfoxide and diethyl sulfoxide) have been prepared and characterized by IR and ^{1}H NMR spectroscopy. *trans*-$[Pt(L)_2Cl_2]$ complexes have been synthesized by a bridge-splitting reaction of the binuclear complexes with the appropriate sulfoxide. The kinetics of their isomerization to the cis form in dichloromethane is reported and interpreted in terms of an associative mechanism.

Introduction

Complexes of sulfoxides with transition-metal ions have received much attention in recent years, especially with respect to their structures and reactivity.[3] These ligands are generally coordinated to platinum(II) and palladium(II) through sulfur, as might be expected from the HSAB principle,[4] the oxygen only activing as donor when the ligands are forced into a sterically crowded environment. Most complexes of the type $[M(L)_2X_2]$ (X = halogen, L = sulfoxide) have the trans configuration when M = Pd, whereas the cis configuration is preferred when M = Pt except with very sterically demanding ligands such as diisoamyl sulfoxide.[5] More recently, *trans*-$[Pt(n\text{-}Pr_2SO)_2Cl_2]$, isolated as an intermediate in the reaction of $[PtCl_4]^{2-}$ with di-*n*-propyl sulfoxide, was shown to isomerize to the cis form in the subsequent reaction. This sequence is consistent with the high trans effect of sulfoxide.[6] Attempts to prepare directly and isolate the *trans*-$[Pt(L)_2Cl_2]$ complexes by the method that was successful for the *n*-Pr_2SO complex invariably produced the cis species when L = Me_2SO and Et_2SO as did the method proposed by Braddock and Tobe[7] (reaction between $K_2[PtCl_4]$ and a fivefold excess of Me_2SO, poured into ether to precipitate the trans isomer before it could isomerize to the cis species). Chloroform solutions enriched with the trans isomer have been obtained by photoisomerization of the stable cis species.[8]

In this paper we report the preparation and isolation of the *trans*-$[Pt(Me_2SO)_2Cl_2]$ and *trans*-$[Pt(Et_2SO)_2Cl_2]$ complexes from the new dimers $[Pt_2(Me_2SO)_2Cl_4]$ and $[Pt_2(Et_2SO)_2Cl_4]$ and report the kinetics of their isomerization in dichloromethane.

Experimental Section

Dimethyl sulfoxide, diethyl sulfide, and di-*n*-propyl sulfoxide were purchased from Aldrich Chemical Co., Inc., vacuum distilled, and stored under vacuum over Linde 4A molecular sieves. Diethyl sulfoxide was prepared from Et_2S by the literature method.[9] Dichloromethane was purified by a standard method,[10] and all other chemicals were reagent grade.

Preparations. *cis*-$[Pt(Me_2SO)_2Cl_2]$, *cis*-$[Pt(Et_2SO)_2Cl_2]$, and *trans*-$[Pt(n\text{-}Pr_2SO)_2Cl_2]$ were prepared by published methods[8] and characterized by elemental analyses and infrared spectra.

Bis(μ-chloro)bis[chloro(dimethyl sulfoxide)platinum(II)]. A mixture of *cis*-$[Pt(Me_2SO)_2Cl_2]$ (0.5 g, 1.2 mmol), platinum(II) chloride (0.34 g, 1.3 mmol) and naphthalene (1 g) was finely ground in a mortar and transferred to a boiling tube. The mixture was heated in an oil bath at 165 °C for 30 min with continuous stirring. After the mixture was cooled, it was again ground in a mortar, transferred to a sintered-glass filter, and washed with several 5-cm^3 portions of light petroleum ether (bp 40–70 °C) to remove the naphthalene. The brown-orange residue was dissolved in dichloromethane (200 cm^3), a small amount of charcoal was added, and the solution was filtered through paper. The filtrate was concentrated to 50 cm^3 in a rotary evaporator, and light petroleum ether (50 cm^3) was added to precipitate a fine yellow-orange solid, which was filtered off, washed twice with petroleum ether, and air-dried; yield 60%. Anal. Calcd for $C_4H_{12}Cl_4O_2Pt_2S_2$: C, 6.98; H, 1.76; Cl, 20.6. Found: C, 7.2; H, 1.71; Cl, 20.6.

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[1] Università di Venezia.

[2] University College London.

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Table I. IR Data of Complexes

complex	ν_{S-O}, cm^{-1}	peaks in range 500-250 cm^{-1} ^{a,b}
$[Pt_2(Me_2SO)_2Cl_4]$	1155	450 (10), 380 (9), *370* (10), 315 (5), 290 (8), 264 (8)
$[Pt_2(Et_2SO)_2Cl_4]$	1155	475 (5), 430 (8), *365* (10), *290* (8), 270 (7)
trans-$[Pt(Me_2SO)_2Cl_2]$	1130	415 (9), 380 (8), *355* (10), 320 (4), 275 (5)
trans-$[Pt(Et_2SO)_2Cl_2]$	1140	470 (6), 410 (10), *360* (10), 345 (5), 275 (7)

[a] ν_{Pt-Cl} in italics. [b] The values in parentheses are the approximate intensities of the peaks relative to an arbitrary value of 10 for the intensity of the highest frequency peak assigned to ν_{Pt-Cl}.

Table II. ^1H NMR Data of Complexes in CD_2Cl_2 Solution

complex	δ_{CH_3}	$\delta_{CH_2}{}^a$	$^3J_{^{195}Pt-^1H}$, Hz
$[Pt(Me_2SO)_2Cl_4]$	3.47		27
trans-$[Pt(Me_2SO)_2Cl_2]$	3.29		22
cis-$[Pt(Me_2SO)_2Cl_2]$	3.48		23
$[Pt_2(Et_2SO)_2Cl_4]$	1.63	3.45	
trans-$[Pt(Et_2SO)_2Cl_2]$	1.55	3.55	
cis-$[Pt(Et_2SO)_2Cl_2]$	1.53	3.60	

[a] The reported values refer to the baricenter of the complex methylene multiplet; the ^{195}Pt-H spin coupling was not determined.

Bis(μ-chloro)bis[chloro(diethyl sulfoxide)platinum(II)] was prepared in a similar way; yield 60%. Anal. Calcd for $C_8H_{20}Cl_4O_2Pt_2S_2$: C, 12.9; H, 2.71; Cl, 19.1. Found: C, 12.8; H, 2.73; Cl, 19.1.

***trans*-Dichlorobis(dimethyl sulfoxide)platinum(II).** To a solution of $[Pt_2(Me_2SO)_2Cl_4]$ (0.2 g, 0.3 mmol) in dichloromethane (5 cm^3) was added with stirring one of dimethyl sulfoxide (0.5 g, 0.6 mmol) in dichloromethane (1 cm^3). The solution changed immediately from yellow-orange to pale yellow, and soon a yellow precipitate started to separate. The mixture was cooled in ice and the solid filtered off, washed twice with ice-cold CH_2Cl_2 (2 cm^3) and diethyl ether (10 cm^3), and air-dried; yield 90%. Anal. Calcd for $C_4H_{12}Cl_2O_2PtS_2$: C, 11.4; H, 2.86; Cl, 16.8. Found: C, 11.4; H, 2.86; Cl, 16.8.

***trans*-Dichlorobis(diethyl sulfoxide)platinum(II).** A solution of diethyl sulfoxide (0.06 g, 0.6 mmol) in CH_2Cl_2 (0.5 cm^3) was added to a solution of $[Pt_2(Et_2SO)_2Cl_4]$ (0.2 g, 0.3 mmol) in CH_2Cl_2 (1 cm^3) with stirring. The mixture was cooled in an ice bath and diethyl ether (10 cm^3) added to precipitate a yellow solid, which was filtered off, washed with diethyl ether, and air-dried; yield 70%. Anal. Calcd for $C_8H_{20}Cl_2O_2PtS_2$: Calcd for C, 20.1; H, 4.21; Cl, 14.8. Found: C, 20.1; H, 4.15; Cl, 14.8.

The infrared data are reported in Table I and ^1H NMR data in CD_2Cl_2 in Table II. Infrared spectra of Nujol mulls between KBr or polyethylene (below 400 cm^{-1}) plates were recorded with a Perkin-Elmer 683 spectrometer. ^1H NMR spectra of CD_2Cl_2 solutions, with $SiMe_4$ as internal standard, were recorded on a Varian EM 390 or FT 80A spectrometer. Electronic spectra were recorded with a Cary 219 spectrometer.

Photoirradiation Experiments. Dichloromethane solutions of *cis*-$[Pt(Me_2SO)_2Cl_2]$ and *cis*-$[Pt(Et_2SO)_2Cl_2]$ (10^{-3} mol dm^{-3}) were irradiated in a 0.1 cm light path quartz cell for 30 min with a 150-W Leitz XBO-150 xenon lamp, the light being filtered through a Pyrex filter. The electronic spectrum was recorded immediately after irradiation.

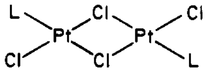
Kinetics. The approach to equilibrium of the isomerization process was slow enough to be followed spectrophotometrically by repeatedly scanning the spectrum over the range 230-400 nm at suitable times. Preliminary experiments showed that the method produced no photochemical effect upon the rate. Pseudo-first-order rate constants (k_{obsd}) were calculated, either from the slopes of the linear plots of ln ($A_t - A_\infty$) against time, where A_t and A_∞ are the absorbances at time t and after at least 6 half-lives, respectively, or from a nonlinear least-squares fit of the experimental data to $A_t = A_\infty + (A_0 - A_\infty) \exp(-k_{obsd}t)$ with A_0, A_∞, and k_{obsd} as the parameters to be optimized (A_0 is the absorbance immediately after mixing the reagents). The rate constants (which are independent of the method used for their calculation) are listed in Table III.

Table III. First-Order Rate Constants, k_{obsd}, for the Reaction *trans*-$[PtL_2Cl_2] \rightleftharpoons$ *cis*-$[PtL_2Cl_2]$ in Dichloromethane Solution

L	temp, °C	$10^2[L]$, mol dm^{-3}	$10^4 k_{obsd}$, s^{-1}
Me_2SO	10.8	1.42	0.685 ± 0.002
		2.12	1.034 ± 0.003
		4.19	2.062 ± 0.006
		6.85	3.289 ± 0.012
	20.0	1.42	1.293 ± 0.004
		2.81	2.485 ± 0.011
		4.19	3.796 ± 0.016
		6.87	6.108 ± 0.022
	25.0	0.0991	0.1410 ± 0.0004
		0.204	0.316 ± 0.001
		0.593	0.817 ± 0.002
		1.54	1.963 ± 0.005
		1.96	2.474 ± 0.011
		3.97	5.098 ± 0.022
		4.94	6.741 ± 0.041
		5.32	6.886 ± 0.035
		6.34	8.386 ± 0.068
	30.7	1.42	2.906 ± 0.007
		2.81	5.414 ± 0.019
		4.19	8.117 ± 0.026
		6.85	13.79 ± 0.02
Et_2SO	25.0	15.0	0.236 ± 0.001
		26.5	0.463 ± 0.002
		40.1	0.676 ± 0.004
		52.0	0.937 ± 0.004

Results and Discussion

Platinum(II) complexes of empirical formula $[Pt(L)Cl_2]$ (L = Me_2SO and Et_2SO) were readily obtained by the general method of Chatt and Venanzi[11] from *cis*-$[Pt(L)_2Cl_2]$ and $PtCl_2$ as orange solids soluble in chlorinated solvents such as dichloromethane and chloroform. They have been assigned a chloro-bridged trans binuclear structure (I) on the basis of the following evidence:



I

(i) The S-O stretching frequency is consistent with S-bonded sulfoxide and not with a bridging sulfoxide.[3]

(ii) Three regions of Pt-Cl stretching frequencies, consistent with a symmetrical trans chloride-bridged dimer, are observed, terminal ν_{Pt-Cl} in the range 365-340 cm^{-1} and two bridging ν_{Pt-Cl} at 335-310 and 295-250 cm^{-1}.[12,13]

(iii) The bridge-splitting reaction of the two dimers with the corresponding sulfoxide leads exclusively, initially, to the monomeric $[Pt(L)_2Cl_2]$ species. These, in contrast to the almost white cis isomers, are yellow solids, and the assignment of the trans configuration is of key importance in this work. There is only one peak that can be assigned to ν_{Pt-Cl} in the far-infrared spectrum at 355 and 360 cm^{-1} for the Me_2SO and Et_2SO complexes, respectively. This comes at a higher frequency than those found in the cis isomer, 334 and 309 cm^{-1} for Me_2SO and 339 and 332 cm^{-1} for the Et_2SO complex. A single S-O stretching peak is also consistent with the assignment of a trans configuration.

The absorption spectrum of *cis*-$[Pt(Me_2SO)_2Cl_2]$ in CH_2Cl_2 (Figure 1a) is compared with that of a freshly prepared solution of the product of the bridge-splitting reaction (presumed to be the trans isomer) (Figure 1b) at the same concentration. The latter is characterized by a band at 258 nm with $\epsilon_{max} = 1.15 \times 10^4$ dm^3 mol^{-1} cm^{-1}, while the cis isomer has its peak at 265 nm ($\epsilon_{max} = 3.8 \times 10^3$ dm^3 mol^{-1} cm^{-1}). The spectra of the diethyl sulfoxide complexes are related in a similar way (262 nm, 1.34×10^4 dm^3 mol^{-1} cm^{-1} for the trans isomer and 266 nm, 4.5×10^3 dm^3 mol^{-1} cm^{-1} for the cis isomer) as indeed are those for the *cis*- and *trans*-$[Pt(n\text{-}Pr_2SO)_2Cl_2]$ isomers prepared by the method of Wayland et al.[8] These authors provided NMR evidence to show that irradiation of $CDCl_3$ solutions of *cis*-$[Pt(L)_2Cl_2]$ leads to

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(13) Adams, D. M.; Chandler, P. J. *Chem. Commun.* **1966**, 69.

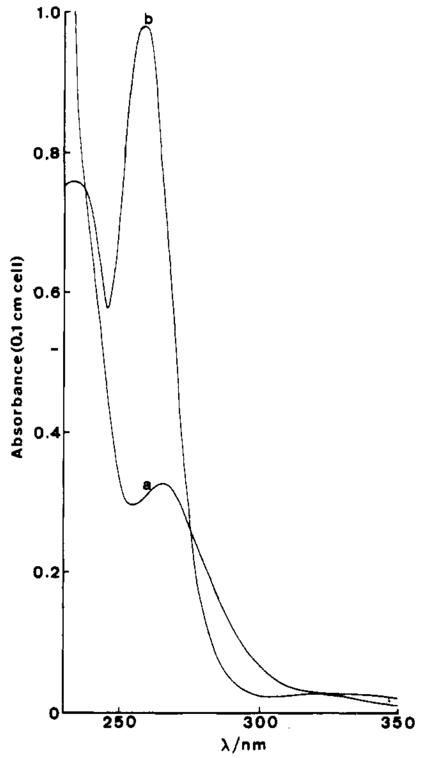

Figure 1. Absorption spectra of 8.55 × 10^{-4} mol dm^{-3} solutions of *cis*-[$Pt(Me_2SO)_2Cl_2$] (a) and *trans*-[$Pt(Me_2SO)_2Cl_2$] (b) in dichloromethane.

enrichment of the trans isomer (L = Me_2SO and Et_2SO), and we find that the electronic spectra of the irradiated solutions are identical with those of the complexes to which we have assigned a trans configuration. The ^1H NMR data are in close agreement with those of Wayland et al.[8]

Isomerization Kinetics of *trans*-[$Pt(L)_2Cl_2$] (L = Me_2SO, Et_2SO). The trans complexes isomerize in CH_2 Cl_2 solution to an equilibrium cis–trans mixture; the electronic and ^1H NMR spectra of the equilibrated solution indicate that, in the case of the Me_2SO complex, the equilibrium lies entirely in favor of the cis isomer while, in the case where L = Et_2SO, [trans]/[cis] = 0.2 at equilibrium.

Once it had been demonstrated that the technique produced no photochemical effect, it was possible to follow the isomerization spectrophotometrically. This allows a study at concentrations of complex much lower than those employed by Wayland, who followed the process by ^1H NMR spectroscopy. The spectrum of a 10^{-3} mol dm^{-3} solution of *trans*-[$Pt(Me_2SO)_2Cl_2$] in CH_2Cl_2 slowly changes to that of the cis isomer over a period of 3 days. The isomerization is slower in more dilute solutions. Isosbestic points are observed at 238, 275, and 320 nm throughout the process, indicating either that only two absorbing species (the trans and the cis isomers) are present or that one equilibrium mixture of constant relative composition is changing to the cis isomer. Under these experimental conditions, the plot of ln ($A_g - A_\infty$) for *trans*-[$Pt(Me_2SO)_2Cl_2$] was not linear but the slope decreased with time. No such departures were observed in the trans–cis isomerizations of the [$Pt(Et_2SO)_2Cl_2$] and [$Pt(n\text{-}Pr_2SO)_2Cl_2$] complexes, where good first-order plots were obtained throughout,[8] but there the concentration of complex (0.14 mol dm^{-3}) was very much greater.

The ^1H NMR spectrum of a 10^{-3} mol dm^{-3} solution of *trans*-[$Pt(Me_2SO)_2Cl_2$] in CD_2Cl_2 (Figure 2) shows, in addition to the signal at δ 3.29, with ^{195}Pt satellites, a small peak at δ 2.46 identical with that for Me_2SO in this solvent. This indicates that there is a partial loss of Me_2SO from the trans isomer with the formation of either the solvato species or the chloro-bridged dimer. In view of the poor coordinating properties of the solvent and the fact that *trans*-[$Pd(sulfoxide)_2Cl_2$] has been shown to be in equilibrium with the chloro-bridged dimer in chloroform,[14] dimerization appears to be more plausible but we have no evidence in the ^1H NMR spectrum for the presence of the dimer (δ 3.47). We will refer to this as the "dissociation equilibrium". It is suggested that the free Me_2SO catalyzes the isomerization of the remaining undissociated trans complex by the normal sulfoxide-catalyzed route discussed below and, as the reaction proceeds, the formation of the cis isomer, which does not undergo any "dissociation" of this sort, will reduce the concentration of the free sulfoxide. The decrease in the concentration of the catalyst will account for the departure from first-order kinetics. The lengthening of the half-life of the reaction when the initial concentration of complex is reduced can also be explained by "dissociation" to give free sulfoxide.

Figure 2. ^1H NMR spectra of a 10^{-3} mol dm^{-3} solution of *trans*-[$Pt(Me_2SO)_2Cl_2$] in CD_2Cl_2.

Table IV. Second-Order Rate Constants (k_2) and Activation Parameters for the Reaction *trans*-[PtL_2Cl_2] ⇌ *cis*-[PtL_2Cl_2] in Dichloromethane Solution

L	temp, °C	10^2k_2, mol^{-1} dm^3 s^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal K^{-1} mol^{-1}
Me_2SO	10.8	0.479 ± 0.006	11.4 ± 0.6	−29 ± 2
	20.0	0.889 ± 0.011		
	25.0	1.32 ± 0.02		
	30.7	2.03 ± 0.03		
Et_2SO	25.0	0.0185 ± 0.0007		

Addition of excess dimethyl sulfoxide has two effects. It shifts the "dissociation equilibrium" toward *trans*-[$Pt(Me_2SO)_2Cl_2$], and it increases the rate constant for the approach to the cis–trans equilibrium. The rate law becomes pseudo first order when the amount of ligand coming from the dissociation of the complex is negligible compared to that added. Good first-order plots are obtained when [complex] = 10^{-3} mol dm^{-3} when [Me_2SO] > 2 × 10^{-3} mol dm^{-3}. When [complex] = 10^{-4} mol dm^{-3}, [Me_2SO] must be greater than 10^{-3} mol dm^{-3}. The values of k_{obsd} are tabulated as a function of $[Me_2SO]_0$ and temperature in Table III. Plots of k_{obsd} against $[Me_2SO]_0$ are linear with intercepts smaller than or equal to their standard deviation, i.e. $k_{obsd} = k_2[\text{complex}][Me_2SO]_0$. Values of k_2 are collected in Table IV.

Under conditions where the dissociative equilibrium does not contribute toward the distribution of the substrate and the concentration of the catalyst, the isomerization can be represented by

$$trans\text{-}[Pt(Me_2SO)_2Cl_2] \underset{k_r}{\overset{k_f}{\rightleftharpoons}} cis\text{-}[Pt(Me_2SO)_2Cl_2]$$

which, if the forward and reverse reactions are catalyzed by Me_2SO, will have the rate law $k_{obsd} = (k_f + k_r)[Me_2SO]_0$ so that $k_2 = k_f + k_r$. In the case of the Me_2SO complex, where equilibrium lies almost completely on the side of the cis isomer, $k_2 \approx k_f$. To take account of the "dissociation equilibrium" at low [Me_2SO], it would be necessary to know whether the process was solvolysis or dimerization. In principle, a detailed analysis of the kinetics would allow us to make a distinction, but at the moment, this is beyond our reach. The activation parameters, ΔH^* and ΔS^*, were calculated by fitting the k_2, T data to the Eyring

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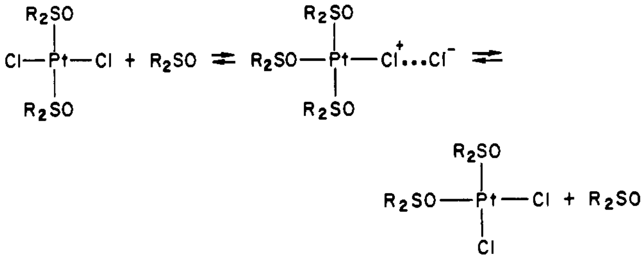
(14) Kitching, W.; Moore, C. J.; Doddrell, D. *Inorg. Chem.* **1970**, *3*, 541.

Scheme I



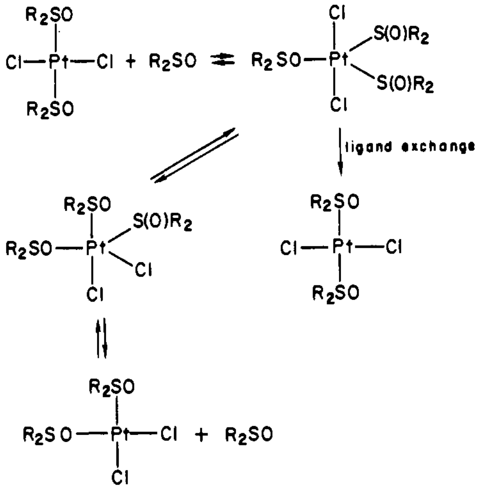
equation in the exponential form $k_2 = (kT/h)e^{-\Delta H^{\ddagger}/RT\cdot\Delta S^{\ddagger}/R}$ by a nonlinear least-squares analysis (each value of k_2 being weighted as $1/\sigma_{k_2}{}^2$).

trans-$[Pt(Et_2SO)_2Cl_2]$ does not appear to release any significant amount of Et_2SO in Cd_2Cl_2 solution, but otherwise the isomerization kinetics are identical with those of the corresponding Me_2SO complex in the presence of excess ligand. The values of k_{obsd} for the various Et_2SO concentrations are collected in Table III, and the slope of the plot of k_{obsd} vs. $[Et_2SO]$ is reported in Table IV. The 100-fold decrease in k_2 as a result of replacing methyl by ethyl is fully consistent with steric hindrance in an associately activated process, as is the large negative $\Delta S^{\ddagger}$ (−29 cal K^{-1} mol^{-1}) found in the case of the Me_2SO complex. Wayland et al.[8] did not report the isomerization of the Me_2SO complex, but the change from L = Et_2SO to *n*-Pr_2SO in *trans*-$[Pt(L)_2Cl_2]$ also leads to a decrease in k_f, but by less than a factor of 2. The rate constant for the reverse reaction, however, changes in the opposite direction.

It is probably dangerous to make too close a comparison between the behavior of the system at high concentration with little or no excess sulfoxide and that where the complex is at low concentration and the sulfoxide in excess. Even if the mechanism involves the same combination of reaction steps, the derived rate constants (one first order and the other second order) will not necessarily relate directly to one another. There is indication that, in the Wayland studies, the rate starts to increase with sufficient added sulfoxide but precipitation prevented a kinetic study. Preliminary studies in dilute CD_2Cl_2 solutions show that exchange of free Me_2SO with both *cis*- and *trans*-$[Pt(Me_2SO)_2Cl_2]$ is much faster than the isomerization, but until a flow NMR experiment can be carried out, the kinetics of the stereoretentive exchange cannot be examined.

The rate law does not distinguish between a mechanism involving a sequence of stereoretentive displacements, e.g. Scheme I, and the pseudorotation of a five-coordinate species that lives long enough and is able to undergo this type of rearrangement, e.g. Scheme II. This is one of a number of pseudorotation mechanisms that are possible, but it will be noted that a single Berry twist, which simultaneously exchanges a pair of axial and equatorial ligands, will not be sufficient, and a sequence of such twists, or else an alternative twist, is needed to exchange the single axial–equatorial pair. Fluxional five-coordinate intermediates have been invoked to account for the mutual labilization of a pair of cis sulfoxides[15] and the Me_2SO-catalyzed isomerization of Pt(II) complexes containing amino acid chelates.[16]

Scheme II



At first sight, the sulfoxide system bears a considerable resemblance to the corresponding phosphine system, *cis*- and *trans*-$[Pt(PR_3)_2Cl_2]$, even to the extent that the position of equilibrium lies far toward the cis isomer in the case where R = Me and mainly toward the *cis* isomer when R = Et, and the second-order rate constant for the isomerization is much reduced when R is changed from Me to Et.[17] There has been much discussion about the mechanism of the catalyzed isomerization of *cis*- and *trans*-$[Pt(PR_3)_2Cl_2]$, and the pros and cons of the successive stereoretentive displacement mechanism and the alternative pseudorotation of a five-coordinate intermediate have been evaluated in a recent review.[18] However, Roulet[17] has found no evidence for the formation of five-coordinate phosphine species such as $[Pt(PMe_3)_3Cl_2]$ in the $[Pt(PMe_3)_2Cl_2]$ + PMe_3 system in CD_2Cl_2 and has shown that the ionic species $[Pt(PMe_3)_3Cl]Cl$ and $[Pt(PMe_3)_4Cl]Cl$ can exist in a solvent of such low polarity and favors the successive displacement mechanism. Similar studies have not yet been made in the Me_2SO system. $[Pt(Me_2SO)_3Cl]^+$ has not yet been described, and $[Pt(Me_2SO)_4]^{2+}$ is unstable in the presence of chloride. Furthermore, it has two S-bonded and two O-bonded ligands as cis pairs, whereas the phosphines do not possess any ambidenticity. The preparation of $[Pt(Me_2SO)_4](ClO_4)_2$ is more complicated than indicated in the literature.[8,19] Addition of 2 equiv of anhydrous $AgClO_4$ to a solution of *cis*-$[Pt(Me_2SO)_2Cl_2]$ in Me_2SO does not give the desired product immediately. Only half the expected amount of AgCl is precipitated, and a repeated cycle of treatment is necessary before all the chloride has been removed and the desired product can be crystallized.[20] This suggests that a monochloro species can have some stability.

However, in the absence of the analogous preparative chemistry we would prefer not to choose between these mechanisms.

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Registry No. $Pt_2(Me_2SO)_2Cl_4$, 89632-81-5; $Pt_2(Et_2SO)_2Cl_4$, 89632-80-4; *trans*-$[Pt(Me_2SO)_2Cl_2]$, 25794-47-2; *trans*-$[Pt(Et_2SO)_2Cl_2]$, 66767-30-4; *cis*-$[Pt(Me_2SO)_2Cl_2]$, 22840-91-1; *cis*-$[Pt(Et_2SO)_2Cl_2]$, 22840-92-2.

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