step 2 above and compete for the porphyrin nitrogens with the univalent silver. Electrochemical investigation currently in progress might resolve this.

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Registry No. $Ag^{II}TPPSNa_4$, 66810-80-8; $Ag^{III}TPPSNa_3$, 66810-81-9; nitric acid, 7697-37-2.

References and Notes

(1) (a) Presented in part at the First Chemical Congress of the North American Continent, Mexico City, Mexico, 1975. (b) Peripheral charges of the porphyrin species are omitted for clarity.
(2) F. A. Cotton and G. Wilkinson in "Advanced Inorganic Chemistry", 3rd ed, Wiley, New York, N.Y., 1972, p 1049.
(3) H. N. Po, *Coord. Chem. Rev.*, **20**, 171 (1976).
(4) J. N. Phillips in "Comprehensive Biochemistry", M. Florkin and E. H. Stotz, Ed., Elsevier, Amsterdam, 1963.
(5) U. Eisner and M. J. C. Harding, *J. Chem. Soc.*, 4089 (1974).
(6) P. Hambright in "Porphyrins and Metalloporphyrins", K. M. Smith, Ed., Elsevier, Amsterdam, 1975, p 233.
(7) A. Adler, F. R. Longo, J. D. Finarelli, J. Goldmacher, J. Assour, and L. Korsakoff, *J. Org. Chem.*, **32**, 476 (1967).
(8) M. Krishnamurthy, *Inorg. Chim. Acta*, **25**, 215 (1977).
(9) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).
(10) The absorption spectral characteristics of monomeric species are listed as follows [species: λ_{max} in nm, molar extinction coefficient at λ_{max} in M^{-1} cm^{-1}]: H_2TPPS: 413, 6.0×10^5; 515, 1.70×10^4; 551, 7.12×10^3; 579, 6.50×10^3; 632, 3.50×10^3; H_4TPPS^{2+}: 433, 5.10×10^5; 545, 2.90×10^3; 593, 1.09×10^4; 644, 4.83×10^4; $Ag^{II}TPPS$: 422, 4.57×10^5; 540, 1.45×10^4; $Ag^{III}TPPS$: 421, 2.55×10^5; 537, 1.20×10^4.
(11) M. Krishnamurthy, J. R. Sutter, and P. Hambright, *J. Chem. Soc., Chem. Commun.*, 13 (1975).
(12) E. L. King, *J. Chem. Educ.*, **51**, 186 (1974).
(13) R. F. Pasternack, L. Francesconi, D. Raff, and E. Spiro, *Inorg. Chem.*, **12**, 2606 (1973).
(14) M. Krishnamurthy, unpublished results.
(15) K. M. Kadish, D. G. Davis, and J. H. Fuhrhop, *Angew. Chem., Int. Ed. Engl.*, **11**, 1014 (1972).
(16) A. A. Noyes, J. L. Hoard, and K. S. Pitzer, *J. Am. Chem. Soc.*, **57**, 1221 (1935).
(17) A. A. Noyes, C. D. Coryell, F. Stitt, and A. Kossiakoff, *J. Am. Chem. Soc.*, **59**, 1316 (1937).
(18) J. B. Kirwin, F. D. Peat, P. J. Proll, and L. H. Sutcliffe, *J. Phys. Chem.*, **67**, 1617 (1963).
(19) G. A. Rechnitz and S. B. Zamochnick, *Talanta*, **11**, 713, 1645 (1964); **12**, 479 (1965).
(20) H. N. Po, J. H. Swinehart, and T. L. Allen, *Inorg. Chem.*, **7**, 244 (1968).
(21) A. Viste, D. A. Holm, P. L. Wang, and G. D. Veith, *Inorg. Chem.*, **10**, 631 (1971).
(22) D. Mauzerall, *Ann. N. Y. Acad. Sci.*, **206**, 483 (1973).
(23) J. J. Katz and T. R. Janson, *Ann. N.Y. Acad. Sci.*, **206**, 579 (1973).
(24) D. Mauzerall and G. Feher, *Biochim. Biophys. Acta*, **79**, 430 (1964).

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Thermal and Photochemical Cis–Trans Isomerization of PtL_2Cl_2 (L = Dialkyl Sulfoxide) Complexes. Kinetics and Mechanisms for Thermal Isomerization

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trans-Pt(n-$Pr_2SO)_2Cl_2$, where n-Pr_2SO = di-n-propyl sulfoxide, has been isolated as a solid kinetic product where the cis form is the thermodynamically stable species. Photolyzing deuteriochloroform solutions containing predominantly cis isomers of $Pt(Me_2SO)_2Cl_2$, $Pt(Et_2SO)_2Cl_2$, and Pt(n-$P_2SO)_2Cl_2$, where Me_2SO = dimethyl sulfoxide and Et_2SO = diethyl sulfoxide, results in enrichment of the trans isomer. The three trans complexes thermally isomerize in solution to cis–trans equilibrium mixtures. The forward, k_f, and reverse, k_r, rate constants have been determined by NMR for the first-order kinetic process

$$\textit{trans}\text{-Pt(L)}_2\text{Cl}_2 \underset{k_r}{\overset{k_f}{\rightleftarrows}} \textit{cis}\text{-Pt(L)}_2\text{Cl}_2$$

where L = Et_2SO or n-Pr_2SO. Temperature dependence of the rate constants suggest the trans isomer is enthalpy favored and the cis isomer entropy favored. Free-ligand additions to isomerizing *trans*-Pt(n-$Pr_2SO)_2Cl_2$ solutions have permitted several mechanisms to be proposed for the isomerization. The interchange in $Pt(L)_2Cl_2$ solutions of Me_2SO for Et_2SO, and i-Am_2SO, where i-Am_2SO = diisoamyl sulfoxide, has been followed by proton NMR. These interchanges occur with retention of geometric configuration. The intermediate $Pt(Me_2SO)(L)Cl_2$ complexes and the thermal isomerization of these intermediates are described.

Introduction

Cis–trans isomerization of platinum(II) and palladium(II) complexes has received increasing attention in recent years. Earlier reports of the thermal[1–4] and photochemical[5–8] interconversions of the cis–trans isomers of $Pt(L)_2X_2$, where L = various phosphorus, nitrogen, and sulfur donor ligands and X = halogen, have been succeeded by more recent studies which focus on the mechanism of isomerization since this phenomenon is pertinent to the broader topic of square-planar substitution reactions. Two hypotheses have emerged which account for the isomerization of platinum(II) phosphine complexes where isomeric equilibrium occurs in the presence of free catalyzing phosphine ligand, L. The first involves an association of L to give a distorted five-coordinate intermediate $[L_3PtX_2]$ which undergoes fluxional change interconverting axial and equatorial ligands resulting in isomerization.[9] The second, which has found wider support, involves a consecutive displacement process in which an ionic intermediate $[Pt(L)_3X^+]X^-$ is formed which then takes up a halide ion to form the new isomer.[10–15] In the case of uncatalyzed isomerization of similar platinum complexes, where no free ligand is present, the process is believed to proceed by a dissociative mechanism in which the rate-determining step is the breaking of the Pt–X bond.[16,17]

We previously reported a series of complexes of the form $Pt(L)_2Cl_2$ where L = dialkyl sulfoxide.[18] Sulfoxide ligands

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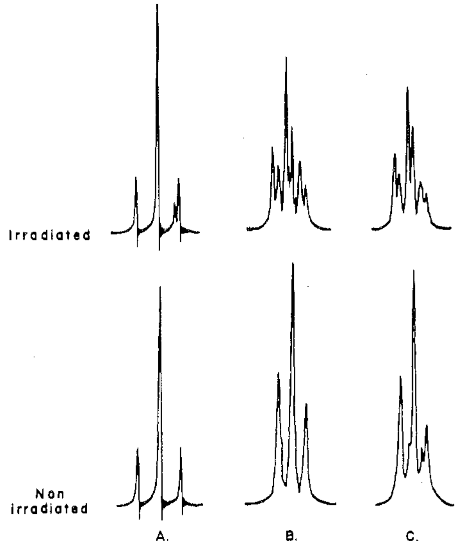

Figure 1. NMR in the terminal methyl resonance region of deuteriochloroform solutions before and after photoirradiation: (A) Pt(Me$_2$SO)$_2$Cl$_2$; (B) Pt(Et$_i$SO)$_2$Cl$_2$; (C) Pt(n-Pr$_2$SO)$_2$Cl$_2$.

can coordinate to metal ions via either the sulfur or the oxygen donor site. The cis sulfur-bonded structure was indicated by infrared studies for the dimethyl sulfoxide (Me$_2$SO),[19] diethyl sulfoxide (Et$_2$SO),[20] and di-*n*-propyl sulfoxide (n-Pr$_2$SO) complexes. The most sterically demanding ligand, diisoamyl sulfoxide (i-Am$_2$SO), produced a trans complex, Pt(i-Am$_2$SO)$_2$Cl$_2$. Subsequent to those studies we prepared *trans*-Pt(n-Pr$_2$SO)$_2$Cl$_2$ and found that it spontaneously thermally isomerizes to a cis–trans equilibrium mixture in deuteriochloroform solution. Solutions of the predominantly cis isomer of Pt(L)$_2$Cl$_2$, where L = Me$_2$SO, Et$_2$SO, and n-Pr$_2$SO, have also been ennriched in the trans isomer by photoisomerization. Tobe et al. have recently observed that *trans*-Pt(Me$_2$SO)(L)Cl$_2$ complexes, where L = amine, can also be prepared.[21]

We report here a study of the kinetics of uncatalyzed trans–cis isomerization of Pt(L)$_2$Cl$_2$ complexes, where L = n-Pr$_2$SO and Et$_2$SO, in deuteriochloroform solution. Two multistep mechanisms are proposed which include respectively three- and four-coordinate intermediates which undergo geometric conversion to enable isomerization. Ligand interchange reactions involving substitution of Me$_2$SO in *cis*-Pt(Et$_2$SO)$_2$Cl$_2$, *trans*-Pt(n-Pr$_2$SO)$_2$Cl$_2$, and *trans*-Pt(i-Am$_2$SO)$_2$ have been qualitatively examined to gain insight into reactivity patterns of the geometric isomers. These reactions are found consistent with the well-known tendency in square-planar substitutions for retention of geometric configuration.

Results and Discussion

***trans*- and *cis*-Pt(n-Pr$_2$SO)$_2$Cl$_2$.** Our previous study of Pt(n-Pr$_2$SO)$_2$Cl$_2$ reported the cis isomer which has two bands in both the ν_{M-Cl} (357, 343 cm^{-1}) and ν_{S-O} (1136, 1117 cm^{-1}) regions.[18] The cis complex was prepared by reacting excess n-Pr$_2$SO with K$_2$PtCl$_4$ in aqueous solution for several hours and collecting the precipitate and recrystallizing from a mixed n-Pr$_2$SO–chloroform solvent. We have now observed that the precipitate which forms during the first 5 min in this reaction has the stoichiometry Pt(n-Pr$_2$SO)$_2$Cl$_2$ but only single IR bands in the ν_{M-Cl} (355 cm^{-1}) and ν_{S-O} (1135 cm^{-1}) regions and a proton NMR methyl resonance triplet pattern (δ = 1.333, 1.217, 1.097) different from that of *cis*-Pt(n-Pr$_2$SO)$_2$Cl$_2$ (δ = 1.297, 1.183, 1.077). This complex is assigned as *trans*-Pt(n-Pr$_2$SO)$_2$Cl$_2$. It is found to isomerize in a chloroform or benzene solution to an equilibrium mixture of the two geometric isomers. Initial formation of the trans isomer is apparently a manifestation of the kinetic trans effect for sulfur-bonded sulfoxides. (The cis complex is slightly more thermodynamically stable than the trans complex at laboratory temperatures).

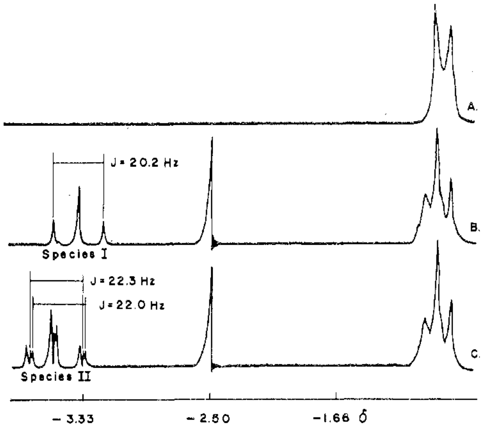

Figure 2. NMR of deuteriochloroform solution of Pt(i-Am$_2$SO)$_2$Cl$_2$: (A) before addition of Me$_2$SO; (B) 2 min after addition of Me$_2$SO; (C) 5 min after addition of Me$_2$SO.

Photoirradiation of a chloroform solution of the cis isomer at 0 °C with light of wavelength 300–500 nm results in the enhancement of the NMR spectrum of the trans isomer and a corresponding decrease in the spectrum of the cis isomer (Figure 1). There is no evidence for the formation of free n-Pr$_2$SO ligand in this process. This photolytic method has previously been used to interconvert geometric isomers of Pt(L)$_2$Cl$_2$ complexes containing phosphorus and nitrogen donors.[5–8] Photoisomerization presumably occurs through an excited state with near-tetrahedral symmetry which decays to either the cis or the trans isomer. Solutions enriched in the trans isomer can thus be prepared directly from the isolated solid trans isomer or photogenerated. The trans isomer is thermodynamically less stable than the cis isomer at ambient laboratory temperatures and converts to an equilibrium mixture of both isomers.

***trans*- and *cis*-Pt(Et$_2$SO)$_2$Cl$_2$ and Pt(Me$_2$SO)$_2$Cl$_2$.** Attempts to directly prepare and isolate the trans isomers of Pt(Et$_2$SO)$_2$Cl$_2$ and Pt(Me$_2$SO)$_2$Cl$_2$ by the method successful for Pt(n-Pr$_2$SO)Cl$_2$ invariably produced the cis species. Equilibrium mixtures of cis and trans isomers occur in solution, but the cis isomer predominates. The cis isomers have been previously described and characterized.[19,20] Photoirradiation of a solution of *cis*-Pt(Et$_2$SO)$_2$Cl$_2$ results in the appearance of proton NMR resonances which can be associated with approximately 70% trans and 30% cis isomers in a manner similar to the case of the Pt(n-Pr$_2$SO)$_2$Cl$_2$ system (Figure 1). The NMR spectrum for the trans complex decays with time with equivalent enhancement of the cis spectrum. No uncoordinated Et$_2$SO is observed in this process. Irradiation of cis Pt(Me$_2$SO)$_2$Cl$_2$ results in appearance of a small new NMR peak at δ = 3.383. In analogy with the behavior of Pt(n-Pr$_2$SO)$_2$Cl$_2$ and Pt(Et$_2$SO)$_2$Cl$_2$ this photochemically generated species is tentatively assigned as *trans*-Pt(Me$_2$SO)$_2$Cl$_2$. Tobe and co-workers have observed this trans complex but have not yet described its properties.[22] We find that the proposed complex *trans*-Pt(Me$_2$SO)$_2$Cl$_2$ converts with time to the virtually pure cis complex in solution.

Ligand Interchange Studies. As a means of gaining insight into the substitution of trans and cis sulfoxide complexes, the interchange of Me$_2$SO for other alkyl sulfoxide ligands (Et$_2$SO, n-Pr$_2$SO, i-Am$_2$SO) has been qualitatively examined. Ligand interchange was followed by proton NMR of the entering Me$_2$SO and the displayed alkyl sulfoxide.

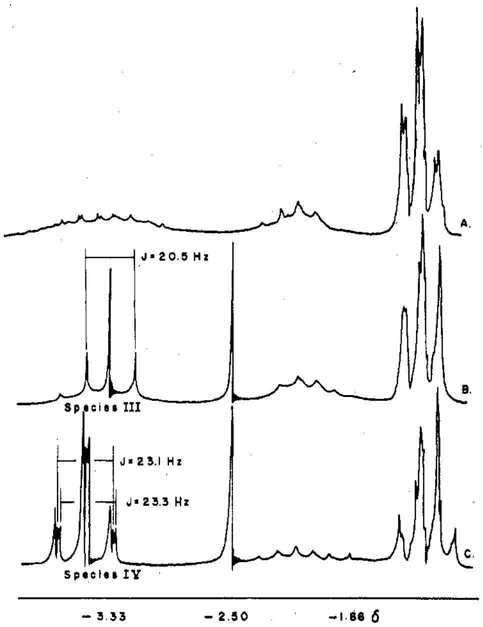

Figure 3. NMR of deuteriochloroform solution of cis–trans mixtures of $Pt(n\text{-}Pr_2SO)_2Cl_2$: (A) before addition of Me_2SO; (B) 2 min after addition of Me_2SO; (C) 5 min after addition of Me_2SO.

Addition of Me_2SO to 0.1000 M *trans*-$Pt(i\text{-}Am_2SO)_2Cl_2$ resulted in the rapid appearance of a coordinated Me_2SO species (I) ($\delta = -3.383$, $J(^{195}Pt\text{–}H) = 20.2$ Hz) and an equivalent amount of free *i*-Am_2SO (Figure 2). The resonance position and ^{195}Pt–H coupling constant for species I are closely related to those of *trans*-$Pt(Me_2SO)_2Cl_2$ ($\delta = -3.383$, $J = 20.2$ Hz). Species I decays to a second species (II) which has NMR parameters ($\delta = -3.525$, 3.510, $J = 22.3$, 22.0 Hz) similar to those of *cis*-$Pt(Me_2SO)_2Cl_2$ ($\delta = -3.547$, $J = 23.5$ Hz). Species II subsequently reacts with excess Me_2SO to form authentic *cis*-$Pt(Me_2SO)_2Cl_2$ (Figure 2). Species I and II are reasonably assigned to the mixed-ligand complexes *trans*- and *cis*-$Pt(Me_2SO)(i\text{-}Am_2SO)Cl_2$, respectively.

Addition of excess amounts of Me_2SO to a 0.1000 M cis–trans mixture of $Pt(n\text{-}Pr_2SO)_2Cl_2$ resulted in selective disappearance of the trans isomer and appearance of a new species (III) with NMR parameters ($\delta = -3.375$, $J = 20.5$ Hz) associated with trans-coordinated Me_2SO (Figure 3). Species III subsequently decays to species IV, which has NMR parameters ($\delta = -3.510$, -3.498, $J = 23.1$, 23.3 Hz) associated with cis-coordinated Me_2SO. Further additions of Me_2SO converts species IV into *cis*-$Pt(Me_2SO)_2Cl_2$. Starting with 0.1000 M *cis*-$Pt(Me_2SO)_2Cl_2$ and adding *n*-Pr_2SO results in the slow formation of species IV which is then converted to *cis*-$Pt(n\text{-}Pr_2SO)_2Cl_2$ by excess *n*-Pr_2SO. Species III and IV are assigned to the mixed-ligand complexes *trans*- and *cis*-$Pt(Me_2SO)(n\text{-}Pr_2SO)Cl_2$, respectively. Similar ligand interchange reactions are observed for *cis*-$Pt(Et_2SO)_2Cl_2$ and the photogenerated trans isomer.

In these ligand-interchange reactions, the trans isomers are found to react much faster than the cis isomers. Reactions of both trans and cis isomers occur with apparent retention of the geometric configuration. Trans complexes thus react to form trans mixed-ligand complexes as the initial products which then thermally isomerize to the more stable cis isomers. Cis complexes react to produce cis products without observation of trans species. The later observation does not prove the stereochemical integrity of the cis complex reactions because the trans-to-cis isomerization is faster than the sulfoxide ligand-interchange reaction for the cis complexes. The splittings of the methyl (Me_2SO) resonances in *cis*-$Pt(Me_2SO)(n\text{-}Pr_2SO)Cl_2$ and *cis*-$Pt(Me_2SO)(i\text{-}Am_2SO)Cl_2$ apparently arise from interference of the propyl and isoamyl groups with Me_2SO rotation about the Pt–S bond in the cis geometry. The respective trans isomers show singlet resonances as would be expected for free rotation of the Me_2SO groups. However, rotation is apparently permitted in the cis geometry by the smaller ethyl sulfoxide, for the Me_2SO resonance appears as a singlet in *cis*-$Pt(Me_2SO)(Et_2SO)Cl_2$.

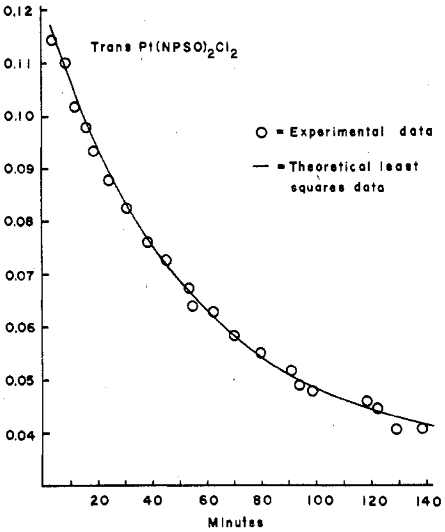

Figure 4. Concentration of *trans*-$Pt(n\text{-}Pr_2SO)_2Cl_2$ plotted as a function of time (initial concentration 0.1366 M).

Kinetics for Cis–Trans Thermal Isomerization of $Pt(Et_2SO)_2Cl_2$ and $Pt(n\text{-}Pr_2SO)_2Cl_2$. Cis–trans thermal isomerization for $Pt(Et_2SO)_2Cl_2$ and $Pt(n\text{-}Pr_2SO)_2Cl_2$ can be conveniently studied by following the time dependence of the proton NMR spectra in deuteriochloroform. The methyl resonances in these complexes were selected for observation because of the simplicity of the spectra in that region. The trans-to-cis isomerization for $Pt(n\text{-}Pr_2SO)_2Cl_2$ was studied on solutions prepared from the solid trans isomer and from solutions enriched in trans species by photoisomerization. Kinetic results from both procedures compared favorably. Kinetic studies on $Pt(Et_2SO)_2Cl_2$ were obtained on solutions photoenriched with the trans isomer. The isomerization is found to follow simple first-order kinetics for opposing reactions approaching equilibrium

$$A \underset{k_r}{\overset{k_f}{\rightleftharpoons}} B$$

$$-d[A]/dt = k_f[A] - k_r[B] \tag{1}$$

$$\ln\left(\frac{k_f[A] - k_r[B]}{k_f[A_0] - k_r[B_0]}\right) = -(k_f + k_r)t \tag{2}$$

$$[A] = \frac{(k_f[A_0] - k_r[B_0])e^{-(k_f+k_r)t} + k_r([A_0] + [B_0])}{k_f + k_r} \tag{3}$$

Representative experimental data and the theoretical least-squares line fitting eq 3 are found in Figure 4. Results of the kinetic studies appear in Table I. The ratio of k_f to k_r gives the equilibrium constant K ([B]/[A]) for the trans ⇄ cis isomerization reactions. Equilibrium constants measured directly from the NMR intensities at equilibrium are in satisfactory agreement with the values obtained from kinetics (Table I).

Mechanisms for Cis–Trans Isomerization. Intramolecular thermal isomerization is very unlikely due to the high energy expected for the transition state. Dissociative or medium-assisted interchange mechanisms are more likely. In order to test several possible mechanisms for trans–cis isomerization,

Table I. Kinetic Data for the Isomerization

$$\mathit{trans}\text{-Pt(L)}_2\text{Cl}_2 \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \mathit{cis}\text{-Pt(L)}_2\text{Cl}_2$$

concn, M	temp, °C	k_f, min^{-1}	k_r, min^{-1}	k_{eq}
		$\text{Pt(Et}_2\text{SO)}_2\text{Cl}_2$		
0.1386	41.0	0.02252 ± 0.00068	0.00311 ± 0.00044	7.23
0.1390	30.5	0.00758 ± 0.00011	0.00128 ± 0.00008	5.91[a]
0.1406	13.0	0.00149 ± 0.00006	0.00052 ± 0.00007	2.86
		$\text{Pt(}n\text{-Pr}_2\text{SO)}_2\text{Cl}_2$		
0.1582	53.0	0.04719 ± 0.00570	0.00981 ± 0.00288	4.81
0.1366	41.0	0.01427 ± 0.00038	0.00507 ± 0.00040	2.81[b]
0.1427	26.5	0.00321 ± 0.00005	0.00210 ± 0.00007	1.52

[a] k_{eq} directly measured from NMR intensities at equilibrium is 5.3 ± 0.7 (30.5 °C). [b] k_{eq} directly measured from NMR intensities at equilibrium is 2.5 ± 0.4 (41.0 °C).

the effect of excess n-Pr$_2$SO on the isomerization kinetics was examined. Small additions of n-Pr$_2$SO to solutions enriched to *trans*-Pt(n-Pr$_2$SO)$_2$Cl$_2$ resulted in depressing the rate of trans–cis isomerization. Near-linear plots of $1/k_f$ and $1/k_r$ vs. the concentration of added n-Pr$_2$SO occur in the concentration region up to stoichiometric equivalent of added ligand. Larger quantities of n-Pr$_2$SO caused an apparent rate increase; however, noticeable precipitation occurred which prohibited a meaningful analysis of this data. The intercepts for $1/k_f$ and $1/k_r$ vs. [L] occur at the values determined for k_f and k_r in the absence of excess ligand. The pertinent kinetic observations that must be accommodated by an appropriate isomerization mechanism are as follows: (1) first-order kinetics must approach an equilibrium and (2) a plot of $1/k_f$ and $1/k_r$ vs. the concentration of excess ligand must be linear.

A pure dissociative mechanism which gives an intermediate that is not stereochemically distinct (i.e., a geometric isomer) and which subsequently adds a ligand to form the cis or trans complex is unacceptable.

$$\mathit{trans}\text{-Pt(L)}_2\text{Cl}_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{Pt(L)Cl}_2 + \text{L} \qquad (\text{L} = n\text{-Pr}_2\text{SO})$$

$$\text{Pt(L)Cl}_2 + \text{L} \underset{k_4}{\overset{k_3}{\rightleftharpoons}} \mathit{cis}\text{-Pt(L)}_2\text{Cl}_2$$

This pure dissociative mechanism has the proper first-order kinetics; however, this mechanism predicts that the isomerization is independent of excess n-Pr$_2$SO (L):

$$\frac{-\text{d}[\mathit{trans}\text{-Pt(L)}_2\text{Cl}_2]}{\text{d}t} = \frac{k_1k_3[\mathit{trans}\text{-Pt(L)}_2\text{Cl}_2] - k_2k_4[\mathit{cis}\text{-Pt(L)}_2\text{Cl}_2]}{k_2 + k_3}$$

Similarly, an intramolecular isomerization has kinetics which are independent of excess n-Pr$_2$SO and is thus inconsistent with the observations.

$$\mathit{trans}\text{-Pt(L)}_2\text{Cl}_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathit{cis}\text{-Pt(L)}_2\text{Cl}_2$$

$$\frac{-\text{d}[\mathit{trans}\text{-Pt(L)}_2\text{Cl}_2]}{\text{d}t} = k_1[\mathit{trans}\text{-Pt(L)}_2\text{Cl}_2] - k_2[\mathit{cis}\text{-Pt(L)}_2\text{Cl}_2]$$

Mechanisms that properly accommodate the kinetic data involve the initial loss of a ligand to produce an intermediate that has stereochemical integrity (i.e., a geometric isomer). The next step or series of steps involves the rapid geometric isomerization of the intermediate. The final step involves the recombination of the ligand with the isomerized intermediate to form the isomerized product. The most likely mechanism in our option is the four-step process shown by eq 4–7 (solv

$$\mathit{trans}\text{-Pt(L)}_2\text{Cl}_2 + \text{solv} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathit{trans}\text{-Pt(L)(solv)Cl}_2 + \text{L} \tag{4}$$

$$\mathit{trans}\text{-Pt(L)(solv)Cl}_2 \underset{k_4}{\overset{k_3}{\rightleftharpoons}} \text{Pt(L)Cl}_2 + \text{solv} \tag{5}$$

$$\text{Pt(L)Cl}_2 + \text{solv} \underset{k_6}{\overset{k_5}{\rightleftharpoons}} \mathit{cis}\text{-Pt(L)(solv)Cl}_2 \tag{6}$$

$$\mathit{cis}\text{-Pt(L)(solv)Cl}_2 + \text{L} \underset{k_8}{\overset{k_7}{\rightleftharpoons}} \mathit{cis}\text{-Pt(L)}_2\text{Cl}_2 + \text{solv} \tag{7}$$

= solvent). The rate expression for this mechanism is of the form

$$\frac{-\text{d}[\mathit{trans}\text{-Pt(L)}_2\text{Cl}_2]}{\text{d}t} = k_f[\mathit{trans}\text{-Pt(L)}_2\text{Cl}_2] - k_r[\mathit{cis}\text{-Pt(L)}_2\text{Cl}_2]$$

where

$$k_f = \frac{k_1k_3k_5k_7}{(k_2k_4k_6 + k_3k_5k_7) + (k_2k_4k_7 + k_2k_5k_7)[\text{L}]}$$

and

$$k_r = \frac{k_2k_4k_6k_8}{(k_2k_4k_6 + k_3k_5k_7) + (k_2k_4k_7 + k_2k_5k_7)[\text{L}]}$$

The important kinetic properties associated with this mechanism are that $k_f/k_r = k_{eq} = [\mathit{cis}\text{-Pt(L)}_2\text{Cl}_2]_{eq}/[\mathit{trans}\text{-Pt(L)}_2\text{Cl}_2]_{eq}$ and a plot of $1/k_f$ vs. [L] is linear with the intercept corresponding to $1/k$ ([L] = 0) which agree with the experimental observations. This mechanism is essentially a dissociative type, but as L dissociates, interactions with the medium cause retention of the geometric configuration in the first intermediate. The dissociation from the square complex of one ligand is plausible considering competative π bonding or mutual trans labilization of the sulfoxides. In the second step (eq 5) the stereochemically distinct intermediate then loses the solvent molecule, forming a three-coordinate intermediate. This then relaxes to a trans structure without memory of the original stereochemical configuration. In the final step, the sulfoxide ligand displaces the coordinated solvent molecule. Such a three-coordinate "cis-like" or "trans-like" platinum(II) species has recently been suggested by Romeo for the mechanism of the cis–trans isomerization of Pt(PEt$_3$)$_2$(L)Br, where L is an aryl ligand.[16,17] Three-coordinate intermediates are also invoked elsewhere in the mechanisms of several other types of platinum(II) reactions.[24–30]

A second acceptable mechanism would involve three steps (eq 8–10) where a solvent molecule (solv) would displace one

$$\mathit{trans}\text{-Pt(L)}_2\text{Cl}_2 + \text{solv} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathit{trans}\text{-Pt(L)(solv)Cl}_2 + \text{L} \tag{8}$$

$$\mathit{trans}\text{-Pt(L)(solv)Cl}_2 \underset{k_4}{\overset{k_3}{\rightleftharpoons}} \mathit{cis}\text{-Pt(L)(solv)Cl}_2 \tag{9}$$

$$\mathit{cis}\text{-Pt(L)(solv)Cl}_2 + \text{L} \underset{k_6}{\overset{k_5}{\rightleftharpoons}} \mathit{cis}\text{-Pt(L)}_2\text{Cl}_2 + \text{solv} \tag{10}$$

sulfoxide ligand in the first step, the intermediate formed would isomerize to the cis configuration in the second step, and the coordinated solvent molecule would be displaced by sulfoxide

Table II. Thermodynamic Data for the Isomerization

$$trans\text{-}Pt(L)_2Cl_2 \underset{\text{rev}}{\overset{\text{fwd}}{\rightleftharpoons}} cis\text{-}Pt(L)_2Cl_2$$

	$Pt(Et_2SO)_2Cl_2$	$Pt(n\text{-}Pr_2SO)_2Cl_2$
$\Delta H_{fwd}^{\ddagger}$, kcal	16.8 ± 1.5	18.8 ± 2.5
$\Delta H_{rev}^{\ddagger}$, kcal	10.5 ± 2.9	10.6 ± 3.1
ΔH°, kcal	6.3 ± 4.4	8.2 ± 5.6
$\Delta S_{fwd}^{\ddagger}$, eu	−13.1 ± 5.1	−6.7 ± 8.0
$\Delta S_{rev}^{\ddagger}$, eu	−36.3 ± 9.7	−35.2 ± 9.8
ΔS°, eu	23.2 ± 14.8	28.5 ± 17.8

in the final step to give the cis complex. The rate expression for this mechanism is the same form as before:

$$\frac{-\mathrm{d}[trans\text{-}Pt(L)_2Cl_2]}{\mathrm{d}t} = k_f[trans\text{-}Pt(L)_2Cl_2] - k_r[cis\text{-}Pt(L)_2Cl_2]$$

where

$$k_f = \frac{k_1k_3k_5}{(k_2k_4 + k_3k_5) + k_2k_5[L]}$$

and

$$k_r = \frac{k_2k_4k_6}{(k_2k_4 + k_3k_5) + k_2k_5[L]}$$

Table II indicates that the trans isomers of both propyl and ethyl complexes are enthalpy favored with the former of slightly greater value. Steric considerations of the cis vs. trans isomers and propyl vs. ethyl groups make these data plausible. The entropy preference of the cis isomer for both complexes is more difficult to explain, considering the expectation of greater solvation in the more polar cis isomer and the decreased freedom of internal ligand motions relative to the trans form. The more open trans structure must permit more effective interactions with the environment. The preponderance of cis isomer in solution at ambient laboratory temperatures is apparently the result of this entropy effect. The results of this study support a dissociative type of mechanism in the uncatalyzed isomerization of $Pt(L)_2Cl_2$, where L = alkyl sulfoxide. Both three- and four-coordinate intermediate structures are consistent with the results. The ligand interchange of Me_2SO in certain $Pt(L)_2Cl_2$ complexes is consistent with the well-known tendency for retention of configuration in square complexes.

Experimental Section

Materials. Dimethyl sulfoxide (Me_2SO) and di-*n*-propyl sulfoxide (n-Pr_2SO) were obtained from Aldrich Chemical Co., Inc. Both were dried over 4A Linde molecular sieves and vacuum distilled. Ethyl sulfide was obtained from Phillips Petroleum, Inc. Deuteriochloroform, $CDCl_3$, spectral grade, was obtained from Thompson Packard, Inc. Chloroform and sodium periodate were ACS reagent grade and were obtained from Fisher Scientific Co. Diethyl sulfoxide (Et_2SO) was prepared by the sodium periodate oxidation of diethyl sulfide. The sulfoxide was extracted into chloroform, isolated, and vacuum distilled. All sulfoxide ligands were stored over molecular sieve until used. Potassium tetrachloroplatinate was obtained from Englehard Industries.

Preparation of *cis*-$Pt(Me_2SO)_2Cl_2$, *cis*-$Pt(Et_2SO)_2Cl_2$, and *cis*-$Pt(n\text{-}Pr_2SO)_2Cl_2$. The sulfoxide ligand (0.009 mol) was added with stirring to an aqueous solution of K_2PtCl_4 (0.0029 mol) in 10 mL of water. The mixture was stirred at room temperature for 12 h. The yellow crystals which formed were washed with water, ethanol, and ether and were dried in vacuo for 5 h.

Preparation of *trans*-$Pt(n\text{-}Pr_2SO)_2Cl_2$. The reactant mixture was prepared in the same manner as that for the cis isomer. After sulfoxide addition of the K_2PtCl_4 solution and vigorous stirring for only 4 min a fine yellow precipitate of the trans isomer formed. This was filtered immediately and dried in vacuo for 2 h. The filtrate of the solution yielded the cis isomer when allowed to stand at room temperature for several hours.

Chemical Analysis. All complexes were analyzed by Galbraith Laboratories, Knoxville, Tenn.

Instrumenation. Infrared spectra were obtained as Nujol mulls of the solids using sodium chloride plates or polyethylene discs. The spectrum from 4000 to 600 cm^{-1} was recorded using a Perkin-Elmer 421 or 225 spectrophotometer. The spectrum was calibrated against a polyethylene standard.

Proton NMR spectra were recorded on Varian HA-60 and HA-100 spectrometers.

The kinetic experiments were conducted using the HA-60 spectrometer with samples in conventional thin-walled tubes. The temperature was determined using methanol or ethylene glycol samples. Probe temperature was checked before and after each kinetic experiment.

Photolysis Procedure. Deuteriochloroform solutions of *cis*-$Pt(Et_2SO)_2Cl_2$ were irradiated directly in the NMR tube for 2 h at 0 °C with a 450-W high-pressure mercury lamp (Hanovia No. 679A-36). Light of wavelength greater than 300 nm was employed through use of Pyrex filter. After irradiation, the sample was held at 0 °C in an ice bath to retard the thermal isomerization which is virtually stopped at this temperature.

Preparation of Samples. Solutions of 0.1400 M concentration were prepared for the kinetic studies by weighing samples of $Pt(L)_2Cl_2$ (L = Et_2SO, n-Pr_2SO) and dissolving in purified deuteriochloroform. Solutions enriched in *trans*-$Pt(n\text{-}Pr_2SO)_2Cl_2$ were prepared from the solid trans isomer and from photoisomerization of the predominantly cis isomer in solution. Solutions enriched in the *trans*-$Pt(Et_2SO)_2Cl_2$ isomer could only be prepared by photoisomerization of the cis complex in solution. Concentrations of the cis and trans isomers were monitored by the methyl proton NMR intensity for both the Et_2SO and n-Pr_2SO complexes. Kinetic studies were performed by following the disappearance of the trans isomer and appearance of the cis isomer. The isomerization reaction was followed for a minimum of 5 half-lives. The isomerization reaction follows first-order kinetics:

$$\frac{-\mathrm{d}[trans\text{-}Pt(L)_2Cl_2]}{\mathrm{d}t} = k_f[trans\text{-}Pt(L)_2Cl_2] - k_r[cis\text{-}Pt(L)_2Cl_2]$$

The ratio of k_f/k_r was used to determine the equilibrium constant K for the reaction *trans*-$Pt(L)_2Cl_2 \rightleftarrows$ *cis*-$Pt(L)_2Cl_2$. The K values were also directly measured from the NMR peak intensities after 7 half-lives. The kinetic data were analyzed for k_f and k_r by least-squares curve fitting[31] of the experimental data to the theoretical integrated form for the first-order process

$$\frac{-\mathrm{d}[A]}{\mathrm{d}t} = k_f[A] - k_r[B]$$

$$[A] = \frac{k_f[A_0] - k_r[B_0]e^{-(k_1+k_2)t} + k_r([A_0] - [B_0])}{k_f + k_r}$$

The k_f and k_r values were similarly obtained on solutions containing excess n-Pr_2SO ligand.

Registry No. *trans*-$Pt(Me_2SO)_2Cl_2$, 25794-47-2; *trans*-$Pt(Et_2SO)_2Cl_2$, 66767-30-4; *trans*-$Pt(n\text{-}Pr_2SO)_2Cl_2$, 40211-39-0; *trans*-$Pt(i\text{-}Am_2SO)_2Cl_2$, 36992-83-3; *cis*-$Pt(Me_2SO)_2Cl_2$, 22840-91-1; *cis*-$Pt(Et_2SO)_2Cl_2$, 22840-92-2; *cis*-$Pt(n\text{-}Pr_2SO)_2Cl_2$, 36992-80-0; *trans*-$Pt(Me_2SO)(i\text{-}Am_2SO)Cl_2$, 66719-27-5; *cis*-$Pt(Me_2SO)(i\text{-}Am_2SO)Cl_2$, 66767-31-5; *trans*-$Pt(Me_2SO(n\text{-}Pr_2SO)Cl_2$, 66719-28-6; *cis*-$Pt(Me_2SO)(n\text{-}Pr_2SO)Cl_2$, 66767-32-6.

References and Notes

(1) E. G. Cox, H. Saenger, and W. Wardlaw, *J. Chem. Soc.*, 182 (1934).
(2) G. B. Kauffman and D. O. Cowan, *Inorg. Synth.*, **6**, 211 (1960); **7**, 239 (1963).
(3) L. M. Volshtein and I. O. Volodina, *Zh. Neorg. Khim.*, **7**, 2685 (1962).
(4) J. Chatt and R. G. Wilkins, *J. Chem. Soc.*, 273, 4300 (1952); 70, (1953); 525 (1956).
(5) I. Lifschitz and W. Froentjes, *Z. Anorg. Allg. Chem.*, **233**, 1 (1937).
(6) P. Haake and T. A. Hylton, *J. Am. Chem. Soc.*, **84**, 3774 (1962).
(7) V. Balzani, V. Carassiti, L. Moggi, and F. Scandola, *Inorg. Chem.*, **4**, 1243 (1965).
(8) S. H. Mastin and P. Haake, *Chem. Commun.*, 202 (1970).

(9) P. Haake and R. M. Pfeiffer, *J. Am. Chem. Soc.*, **92**, 4996, 5243 (1970); *Chem. Commun.*, 1330 (1969).
(10) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", 2nd ed, Wiley, New York, N.Y., 1967.
(11) C. H. Langford and H. B. Gray, "Ligand Substitution Processes", W. A. Benjamin, New York, N.Y., 1966.
(12) L. Cattalini, *MTP Int. Rev. Sci.*: *Inorg. Chem.*, *Ser. One*, 9 (1972).
(13) D. G. Cooper and J. Powell, *J. Am. Chem. Soc*, **95**, 1102 (1973).
(14) W. J. Louw, *J. Chem. Soc.*, *Chem. Commun.*, 353 (1974).
(15) J. Powell and D. G. Cooper, *J. Chem. Soc.*, *Chem. Commun.*, 749 (1974).
(16) R. Romeo, D. Minniti, and M. Trozzi, *Inorg. Chem.*, 1134 (1976).
(17) G. Faraone, V. Ricevuto, R. Romeo, and M. Trozzi, *J. Chem. Soc. A*, 1877 (1971).
(18) J. H. Price, A. N. Williamson, R. F. Schramm, and B. B. Wayland, *Inorg. Chem.*, **11**, 1280 (1972).
(19) F. A. Cotton, R. Francis, and W. D. Horrocks, Jr., *J. Phys. Chem.*, **64**, 1534 (1960).
(20) W. Kitching, C. J. Moore, and D. Doddrell, *Inorg. Chem.*, **9**, 541 (1970).
(21) M. L. Tobe, personal communication.
(22) P. D. Braddock, R. Romeo, and M. L. Tobe, *Inorg. Chem.*, **13**, 1170 (1974).
(23) S. W. Benson, "The Foundations of Chemical Kinetics", McGraw-Hill, New York, N.Y., 1960, p 27.
(24) G. M. Whitesides, J. F. Gaash, and E. R. Sdedronsky, *J. Am. Chem. Soc.*, **94**, 5258 (1972).
(25) H. C. Clark, C. Jablonski, J. Halpern, A. Mantovani, and T. A. Weil, *Inorg. Chem.*, **13**, 1541 (1974).
(26) H. C. Clark and R. C. R. Jablonski, *Inorg. Chem.*, **13**, 2213 (1974).
(27) H. C. Clark and C. S. Wong, *J. Am. Chem. Soc.*, **96**, 7214 (1974).
(28) C. J. Wilson, M. Green, and R. J. Mawby, *J. Chem. Soc.*, *Dalton Trans.*, 1293 (1974).
(29) M. Kubota, R. K. Rothcock, and J. Geibel, *J. Chem. Soc.*, *Dalton Trans.*, 1267 (1973).
(30) R. W. Glyde and R. J. Mawby, *Inorg. Chem.*, **10**, 854 (1971).
(31) The program was written by R. H. Moore and R. K. Ziegler of Los Alamos Scientific Laboratory. It was revised by Professor James P. Birk, now at Arizona State University. Computations were conducted at the IBM 360 computer facility at the University of Pennsylvania.

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Comparative Photochemistry of Carbon Monoxide Labilization from Macrocyclic Iron(II) Complexes

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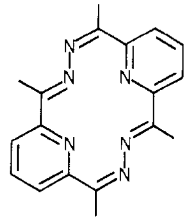
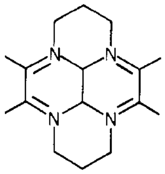
The comparative photochemistry of Fe(TIM)XY and Fe($C_{18}H_{18}N_6$)XY complexes (TIM and $C_{18}H_{18}N_6$ are planar quadridentate macrocyclic diimine ligands, and X and Y are acetonitrile, carbon monoxide, chloride, and bromide) is reported. The quantum yield for CO loss from the mixed-ligand acetonitrile–carbon monoxide complexes is 0.60 when the macrocycle is TIM and 0.49 when the macrocycle is $C_{18}H_{18}N_6$. The quantum yield for CO loss from the mixed-ligand halo–carbon monoxide complexes is 0.76 when the macrocycle is TIM but less than 10^{-2} when the macrocycle is $C_{18}H_{18}N_6$. These results strongly support an interpretation based on reactivity from ligand field excited states. The interpretation of the reactivity and the ligand which is labilized is discussed.

Six-coordinate low-spin d^6 complexes of iron(II) with the planar quadridentate macrocyclic ligand TIM (TIM = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene) and a variety of axial ligands including carbon monoxide are photoactive.[1] The primary photochemical reaction is axial ligand loss with quantum yields ranging from 0.8 for $[Fe(TIM)(CH_3CN)CO]^{2+}$ to less than 10^{-4} for $[Fe(TIM)(imid)_2]^{2+}$.[1] The electronic absorption spectra of the complexes are dominated by a charge-transfer transition from the degenerate d_{xz} and d_{yz} orbitals on the iron to the π-antibonding orbitals on TIM. The energy of this metal to ligand charge transfer (MTLCT) is sensitive to the axial ligands and ranges from 22 000 cm^{-1} when the ligands are carbon monoxides to 14 300 cm^{-1} when they are ammonias.[1,2] As the axial ligands are varied from good π acceptors to poor π acceptors, the d_{xz} and d_{yz} orbitals rise in energy and the MTLCT energy correspondingly decreases.

The trends in the photoreactivities for the iron(II)–TIM complexes could be interpreted in terms of either ligand field reactivity or charge-transfer excited-state reactivity.[1] According to the former interpretation, the reactivity is caused by the bonding changes upon populating a d–d excited state[3] and the low reactivity occurs when a photoinactive charge-transfer excited state is lower in energy than the d–d states. According to the latter interpretation, the iron is formally oxidized in the MTLCT excited state resulting in decreased π back-bonding and labilization of carbonyl ligands but increased σ donation and stabilization of strong σ donor and anionic ligands.

In order to differentiate between the two explanations of the photoreactivity, iron(II) complexes of the macrocyclic ligand $C_{18}H_{18}N_6$ were chosen for study.[4] Because its delocalization is greater than that of TIM, its MTLCT bands are lower in energy than those of analogous TIM complexes. This lowering could cause the MTLCT state which is higher in energy than a ligand field state in TIM to drop lower in energy than the ligand field state in the $C_{18}H_{18}N_6$ complex. If the photoreactivity were substantially diminished, the ligand field interpretation would be favored. If the reactivity were essentially unchanged, the charge transfer state interpretation would be favored. We report here the comparative photochemical studies of TIM and $C_{18}H_{18}N_6$ complexes of iron(II).


$C_{18}H_{18}N_6$


TIM

Experimental Section

Synthesis. [Fe(TIM)Cl](PF$_6$) and [Fe(TIM)Cl(CO)](PF$_6$) were synthesized according to the method of Fey.[5]

[Fe($C_{18}H_{18}N_6$)CH$_3$CN(CO)](PF$_6$)$_2$ was prepared according to the method of Goedken et al.[4] Satisfactory elemental analyses were obtained for the above compounds.

[Fe($C_{18}H_{18}N_6$)Br(CO)](PF$_6$) was prepared by modification of the method of Goedken et al.[4] The procedure reported for the chloro analogue was followed with one variation: a higher concentration of NH_4PF_6 was required to induce crystallization. The best yields were obtained with 0.2 g of NH_4PF_6 dissolved in 2 mL of methanol for each 0.5 g of precursor complex. Samples prepared in this manner

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