Kinetics of Displacement of Dimethyl Sulfide from cis- and trans-Dichlorobis(dimethyl sulfide)platinum(II) by Heterocyclic Amines in 1,2-Dimethoxyethane

LUCIANO CANOVESE,[1] LUCIO CATTALINI,*[1] GIAMPAOLO MARANGONI,[1] GIANNI MICHELON,[1]
and MARTIN L. TOBE[2]

Second-order rate constants for the reactions cis- or trans-[Pt(Me$_2$S)$_2$Cl$_2$] + am → cis- or trans-[Pt(Me$_2$S)(am)Cl$_2$] + Me$_2$S (am = pyridine, 4-methylpyridine, 3,4-dimethylpyridine, 3,5-dimethylpyridine, 3-methylpyridine, 2,4-dimethylpyridine, 2-methylpyridine, 4-cyanopyridine, m-diazine, p-diazine) in 1,2-dimethoxyethane at 25 °C are reported. The trans complexes are some 2.5 times more reactive than the cis isomers, but the dependence of the second-order rate constant on the amine basicity is the same in both cases: log k_2 = 0.18pK_a(amH$^+$) + c. The results are compared with published data for the opening of a bis(thioether) chelate and with those for the analogous sulfoxide complexes. It is concluded that the bond breaking transition state contributes much less to the overall reactivity of the thioether complexes than it does to the reactivity of the corresponding sulfoxide species.

Introduction

As part of a program investigating the role of sulfur donors in the substitution reactions of 4-coordinate planar d^8 metal complexes, we have shown that the displacement of Me$_2$SO (Me$_2$SO = dimethyl sulfoxide) from cis-[Pt(Me$_2$SO)$_2$Cl$_2$] by amines in 1,2-dimethoxyethane is some 2 orders of magnitude faster than the opening of chelate ring in the corresponding reactions of complexes with a chelating disulfoxide [Pt(pse)Cl$_2$] (pse = rac- or meso-1,2-bis(phenylsulfinyl)ethane).[3,4] The corresponding reactions of the analogous thioether complexes had not been studied although it was known that the displacement of i-Pr$_2$S from trans-[Pt(i-Pr$_2$S)Cl$_2$] by amines in 1,2-dimethoxyethane[5] was somewhat slower than the corresponding ring opening reaction of [Pt(pte)Cl$_2$] (pte = 1,2-bis(phenylthio)ethane).[6] This suggested that there might be a significant difference between the sulfoxide and the thioether systems since it would be predicted that the cis bis(thioether) complex would be even less labile than the trans isomer because S-donor ligands have greater trans-labilizing effects than chloride. On the other hand, the steric hindrance arising from the bulky i-Pr$_2$S ligands might possibly be the dominant cause of the low reactivity of these complexes. In order to resolve these uncertainties and to allow a direct comparison, we decided to examine the reactions of the corresponding cis- and trans-[Pt(Me$_2$S)$_2$Cl$_2$] with amines in 1,2-dimethoxyethane, and the results are reported in this paper.

Experimental Section

Materials. cis- and trans-Dichlorobis(dimethyl sulfide)platinum(II) were prepared by the method of Cox et al.[7] Dimethyl sulfide (1.6 mL, 30.4 mM) was added with stirring to 4.0 g (9.6 mM) of K$_2$PtCl$_4$ in 60 mL of water. A pink and a yellow product which precipitated together within a few hours were filtered off and dried over P$_2$O$_5$. The solid mixture was treated with CHCl$_3$ in which the two isomers are soluble so that they are separated from the pink [Pt(Me$_2$S)$_4$]-[PtCl$_4$]. The solution was passed through a silica column and, on eluting with CHCl$_3$, the trans isomer is the first to be removed and thus could be separated from the cis isomer.

cis-[Pt(Me$_2$S)(py)Cl$_2$], cis-[Pt(Me$_2$S)(4-Mepy)Cl$_2$], trans-[Pt-(Me$_2$S)(py)Cl$_2$], and trans-[Pt(Me$_2$S)(4-Mepy)Cl$_2$] were all obtained by reacting the cis- and trans-bis(dimethyl sulfide) isomers, respectively, with a tenfold excess of pyridine (or 4-Mepy) in 1,2-dimethoxyethane at 25 °C and stopping the reaction at the appropriate time as suggested by the kinetic measurements, by evaporating the solvent and volatile reagent rapidly under vacuum. The products were

recognized through their IR spectra in KBr pellets or Nujol mulls, measured with a Perkin-Elmer 621 spectrophotometer, and showing the characteristic absorption bands of the coordinated dimethyl sulfide and pyridine, as well as the ν_{Pt-Cl} peaks which are diagnostic of the cis and trans configurations.

The liquid amines were purified by distillation in a stream of nitrogen at reduced pressure over KOH pellets. The solid ones were recrystallized from 1,2-dimethoxyethane/hexane solutions. The solvent, 1,2-dimethoxyethane, was refluxed with LiAlH$_4$ and then distilled before use from potassium in the presence of benzophenone.

Kinetics. Reactions were started by mixing known volumes of freshly prepared solutions of the desired complex and heterocyclic base that had been brought to the reaction temperature separately and were followed in the thermostated cell of a Cary 219 spectrophotometer by measuring the change in the absorbance at a fixed wavelength, in the range 400–280 nm, depending on the amine used. All the kinetics were carried out in the presence of a sufficient excess of amine to ensure pseudo-first-order conditions and complete conversion of the substrate. The pseudo-first-order rate constants were calculated in the usual way from the values of the absorbance at different times with the use of a nonlinear regression. The second-order rate constants were then obtained with a linear least-squares program.

Results and Discussion

In the reactions between trans-[Pt(Me$_2$S)$_2$Cl$_2$] and heterocyclic amines in 1,2-dimethoxyethane at 25 °C and in the range of concentrations used (5 × 10^{-3} < [am] < 10^{-1} M, [complex] 10^{-4} M), there is a spectroscopic change consistent with a single-stage reaction, and, where compared, the final spectrum is identical with that of an authentic sample of trans-[Pt(Me$_2$S)(am)Cl$_2$]. The reactions of the cis-[Pt-(Me$_2$S)$_2$Cl$_2$] complex are complicated by its tendency to isomerize to the more stable trans isomer. This contrasts to the cis dimethyl sulfoxide complex where the cis isomer is generally the stable form and the trans species undergoes isomerization.[8] The reactions with the unhindered amines are sufficiently rapid for the parallel isomerization not to interfere, but it prevents a study of the rate constants for the

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(2) University College, London.
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Table I. Second-Order Rate Constants for the Reactions:[a]

$$trans\text{-}[Pt(Me_2S)_2Cl_2] + am \rightarrow$$
$$trans\text{-}[Pt(Me_2S)(am)Cl_2] + Me_2S \quad (A)$$

$$cis\text{-}[Pt(Me_2S)Cl_2] + am \rightarrow$$
$$cis\text{-}[Pt(Me_2S)(am)Cl_2] + Me_2S \quad (B)$$

am	pK_a of amH$^+$	$10^3 k_2$(A), M^{-1} s^{-1}	$10^3 k_2$(B), M^{-1} s^{-1}	$10^3 k_2$,[c] M^{-1} s^{-1}
4-methylpyridine	6.02	99 ± 3	43 ± 1	14.7
pyridine	5.17	59 ± 1.3	26 ± 2	11.5
4-cyanopyridine	1.84	18.3 ± 0.2	7.71 ± 0.06	
pyrimidine[b]	1.30	20 ± 1		
pyrazine[b]	0.65	20.5 ± 0.3	8.2 ± 0.2	
3,4-dimethylpyridine	6.44	106 ± 3		16.6
3,5-dimethylpyridine	6.34	77 ± 4		15.9
3-methylpyridine	5.68	69.1 ± 0.6		13.3
2,4-dimethylpyridine	6.99	1.14 ± 0.04		0.48
2-methylpyridine	6.10	0.62 ± 0.03		0.32

[a] In 1,2-dimethoxyethane at 25 °C. [b] Without statistical correction. [c] k_2 values for the ring opening reaction of the chelated dithioether complex, [Pt(dte)Cl$_2$] under the same experimental conditions, taken from ref 6.

entry of the hindered amines. The spectrum of the reaction mixture at the end of the substitution is virtually identical with that of an authentic sample of *cis*-[Pt(Me$_2$S)(am)Cl$_2$], and therefore we assume that, as in the case of the trans isomer and in the case of the analogous cis species with dimethyl sulfoxide, the reaction is the displacement of the sulfur donor by the entering amine. Moreover, on repeating the experiment on a preparative scale (see Experimental Section) *cis*-[Pt(Me$_2$S)(am)Cl$_2$] can be isolated, and the cis structure is confirmed by the IR spectra.

The spectrophotometric changes therefore correspond clearly to the reactions shown in eq 1. The kinetic data can be

$$cis\text{- or } trans\text{-}[Pt(Me_2S)_2Cl_2] + am \rightarrow$$
$$cis\text{- or } trans\text{-}[Pt(Me_2S)(am)Cl_2] + Me_2S \quad (1)$$

analyzed in the usual way[3,4] to obtain the first-order rate constants, k_{obsd}. Plots of k_{obsd} against [am] are linear and pass through the origin. The slopes, obtained by an unweighted linear least-squares analysis of the data, are collected in Table I, together with the corresponding k_2 values for the ring opening reaction of the chelated dithioether complex [Pt(dte)Cl$_2$] under the same experimental conditions. The absence of an intercept, corresponding to a solvolytic pathway, is usual for reactions in this noncoordinating solvent.

The plots of log k_2 against the pK_a (in water at 25 °C) of amH$^+$ are shown in Figure 1. In order to apply a statistical correction, we cut in half the rate constants for the bifunctional diazines, pyrazine, and pyrimidine, in order to make a proper comparison with the monofunctional pyridines. There is a linear relationship between the log k_2 and the pK_a of the entering amine for nucleophiles with the same extent of steric hindrance. As in the case of the *cis*-bis(dimethyl sulfoxide) complex and of the chelated disulfoxide complex, there is a small but nevertheless significant retardation from a methyl group in the position meta to the donor nitrogen. The best fit (least-squares) lines for unhindered amines entering the cis and trans complexes are essentially parallel (slopes, $\alpha = 0.18$ ± 0.01 and 0.18 ± 0.02, respectively). The lines for the data for the unhindered amines and the 2-methyl-substituted amines reacting with the trans complex have a vertical separation $\Delta = 0.96$.

The difference in the rate constants for the reactions of the cis and trans isomers with a particular amine is not very large, the ratio k_{trans}/k_{cis} lying within the range 2.3–2.5. In view of the fact that the trans effect of SMe$_2$ is considerably greater than that of chloride,[9] this similarity of reactivity is surprising.
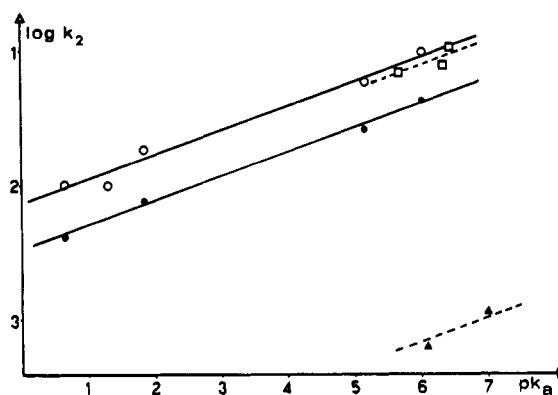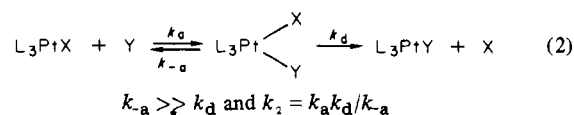

Figure 1. log k_2 against pK_a of amH$^+$ of the entering amines for the reactions *trans*-[Pt(Me$_2$S)$_2$Cl$_2$] + am → *trans*-[Pt(Me$_2$S)(am)Cl$_2$] + Me$_2$S (lines through empty symbols), and *cis*-[Pt(Me$_2$S)$_2$Cl$_2$] + am → *cis*-[Pt(Me$_2$S)(am)Cl$_2$] + Me$_2$S (line through full symbol): (O, ●) para-substituted pyridines and diazines; (□) meta-substituted pyridines; (△) ortho-substituted pyridines.

Electronic cis effects in compounds of the type [Pt(L)(en)Cl]$^+$ (en = ethylenediamine) do not appear to be large, especially for the entry of poor nucleophiles, and cannot provide the compensation needed.[10] The results suggest either that a further effect involving mutual labilization of cis thioethers must also be invoked or that quantitative scales for trans and cis effect cannot be transferred from one type of reaction to another.

The reactions of *trans*-[Pt(Me$_2$S)$_2$Cl$_2$] can be compared to those of the corresponding *i*-Pr$_2$S complex already reported.[5] The latter is less reactive: for example, k_2 for the reaction with pyridine is 5.3×10^{-3} M^{-1} s^{-1} (c.f. 5.9×10^{-2} M^{-1} s^{-1} for the Me$_2$S complex) and the amine discriminating ability is somewhat less ($\alpha = 0.14$ compared to 0.18), but, most significantly, the steric retardation parameter is considerably greater, $\Delta = 2.48$ compared to 0.96, which strongly suggests that the main reactivity differences arise from the greater bulkiness of *i*-Pr$_2$S.

The comparison of the data for the *cis*-[Pt(Me$_2$S)$_2$Cl$_2$] and [Pt(dte)Cl$_2$] systems confirm, as suspected, that the difference between the rate constants for the ring-opening reaction and those for the displacement of the analogous monodentate are very much less than those involving the analogous sulfoxide complexes, the monodentate reaction with pyridine being only about twice as fast as the chelates reaction, compared to a factor of 10^2 in the case of the sulfoxide, i.e., there is little or no chelate effect associated with ring opening in the former case.

It was suggested that the major cause of the relatively low reactivity of the sulfoxide chelate arise from the importance of the bond-breaking transition state, i.e., if we represent the substitution as an A-type process with a 5-coordinate intermediate, eq 2. The strain in the chelating ring resulting from

$$L_3PtX + Y \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} L_3Pt\overset{X}{\underset{Y}{\diagdown}} \overset{k_d}{\longrightarrow} L_3PtY + X \quad (2)$$

$$k_{-a} \gg k_d \text{ and } k_2 = k_a k_d / k_{-a}$$

bond stretching to form the transition state would result in a much lower value for k_d in the opening of a chelate ring than in the displacement of a monodentate ligand. This is reflected in the observed values for k_2. A parallel consequence of such

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an intimate mechanism is that k_2 will also include k_{-a}, which must be sensitive to the basicity of the entering amine since this process involves the breaking of the Pt–N bond. This is also found in the reactions of the sulfoxide system, where α = 0.41 and 0.58 for the bis(dimethyl sulfoxide) and the -pse complexes, respectively. On going to the thioether analogues, the absence of the large differences between the labilities of a bis monodentate and a chelate system suggests that the bond-breaking part of the intimate mechanism is less important and that the system has moved in the direction where $k_d >$ k_{-a} and $k_2 = k_a$. This would require that k_2 was not sensitive to differences in the bond-breaking rate constants and also far less sensitive to amine basicity (smaller α). This is indeed what has been observed (α = 0.18 and 0.14 for the bis(dimethyl sulfide) and -pte complexes, respectively).

Registry No. *trans*-[Pt(Me₂S)₂Cl₂], 17457-51-1; *cis*-[Pt-(Me₂S)₂Cl₂], 17836-09-8; 4-methylpyridine, 108-89-4; pyridine, 110-86-1; 4-cyanopyridine, 100-48-1; pyrimidine, 289-95-2; pyrazine, 290-37-9; 3,4-dimethylpyridine, 583-58-4; 3,5-dimethylpyridine, 591-22-0; 3-methylpyridine, 108-99-6; 2,4-dimethylpyridine, 108-47-4; 2-methylpyridine, 109-06-8.

Supplementary Material Available: Listings of first-order rate constants (3 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
Tulane University, New Orleans, Louisiana 70118

Kinetic Studies of Ligand Substitution Reactions and General-Base Catalysis in Amine-Ligand Exchange Processes for Group 6B Metal Carbonyl Amine Derivatives. Kinetic and Spectroscopic Evidence for Hydrogen-Bonded Intermediates

DONALD J. DARENSBOURG* and JOHN A. EWEN

The decomposition and ligand substitution reactions of group 6B metal pentacarbonyl piperidine derivatives with phosphines have been studied. The reactions are catalyzed by the Lewis bases OP(n-C₄H₉)₃ and tetrahydrofuran (THF). It is concluded that the results are best accounted for in terms of hydrogen-bonded intermediates in the general-base catalysis with the mechanism for catalysis being closely analogous to a dissociative interchange (I_d) pathway. The intermediates have been observed and characterized by infrared spectroscopy.

Introduction

The kinetics of amine substitution reactions for group 6B metal pentacarbonyl amine derivatives with phosphorus donor ligands (eq 1) have been shown to obey the empirical rate law
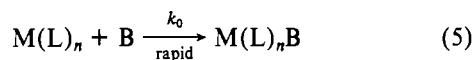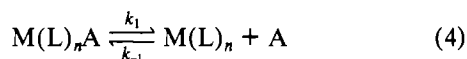
$$M(CO)_5(\text{amine}) + PR_3 \rightarrow M(CO)_5PR_3 + \text{amine} \quad (1)$$
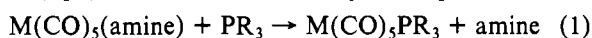
given by eq 2.[1-4] This corresponds to the rate constant expression in eq 3 upon integration.

$$\text{rate} = (k_1 + k_2[PR_3])[M(CO)_5(\text{amine})] \quad (2)$$
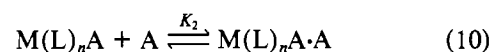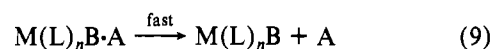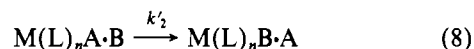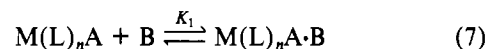
$$k_{obsd} = k_1 + k_2[PR_3] \quad (3)$$

It is generally accepted that the first-order term (k_1 in eq 2) represents a purely dissociative (D) mechanism. The proposed dissociative (D) mechanism giving rise to k_1 is given by eq 4 and 5. The rate constant expression is given by eq 6, which reduces to $k_{obsd} = k_1$ for the condition that is usually satisfied, $k_{-1}[A] \ll k_0[B]$.[5]

$$M(L)_nA \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} M(L)_n + A \quad (4)$$

$$M(L)_n + B \xrightarrow[\text{rapid}]{k_0} M(L)_nB \quad (5)$$

$$k_{obsd} = \frac{k_1 k_0[B]}{k_{-1}[A] + k_0[B]} \quad (6)$$

Mechanisms that have been postulated to accommodate the rate data presume a concurrent bimolecular pathway (k_2 in eq 2), which could involve either attack by PR₃ (at the metal center or at a carbonyl carbon atom) resulting in displacement of the amine ligand to form M(CO)₅PR₃ or a rapid associative–dissociative equilibrium occurring by an unknown process followed by a rate-determining dissociative step.[4] This latter mechanism (a dissociative interchange or I_d substitution pathway[6]) proceeding to completion (eq 7–10) obeys the rate constant expressions provided in eq 11 and 12. If $K_2[A] \ll$

$$M(L)_nA + B \overset{K_1}{\rightleftharpoons} M(L)_nA \cdot B \quad (7)$$

$$M(L)_nA \cdot B \xrightarrow{k'_2} M(L)_nB \cdot A \quad (8)$$

$$M(L)_nB \cdot A \xrightarrow{\text{fast}} M(L)_nB + A \quad (9)$$

$$M(L)_nA + A \overset{K_2}{\rightleftharpoons} M(L)_nA \cdot A \quad (10)$$

$$k_{obsd} = \frac{k'_2 K_1[B]}{1 + K_1[B] + K_2[A]} \quad (11)$$

$$\frac{1}{k_{obsd}} = \frac{1}{k'_2} + \frac{1 + K_2[A]}{k'_2 K_1[B]} \quad (12)$$

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(5) Reactions are carried out generally under conditions where the concentration of the incoming ligand (B) exceeds that of the leaving ligand (A). Values of the rate constants k_{-1} and k_0 are expected to be of comparable magnitude; for an example, see ref 4.
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