been characterized. Six-coordinated acyls of the type $IrCl_2[C(O)R](CO)L_2$ are quite stable, though they can be decarbonylated by heating in an open system where carbon monoxide is lost. The reverse process, CO insertion, occurs at mild temperatures and low pressures of CO or in the presence of added nucleophiles.[40-42] Insertion of olefins into iridium-hydrogen bonds has also been observed under mild conditions.[43]

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Registry No. *trans*-$[IrCl(CO)(PMe_3)_2]$, 21209-86-9; $IrCl(CO)(PMe_3)_2 \cdot I_2$, 75112-06-0; $IrCl(CO)(PMe_3)_2 \cdot CH_3C(O)I$, 75125-15-4; $IrCl(CO)(PMe_3)_2 \cdot HI$, 75112-07-1; $IrCl(CO)(PMe_3)_2 \cdot CH_3I$, 74524-96-2; $IrCl(CO)(PMe_3)_2 \cdot C_2H_5I$, 74511-76-5; $IrCl(CO)(PMe_3)_2 \cdot n\text{-}C_3H_7I$, 75112-08-2; $IrCl(CO)(PMe_3)_2 \cdot i\text{-}C_3H_7I$, 74511-77-6; $IrCl(CO)(PMe_3)_2 \cdot C_6H_5CH_2I$, 75112-09-3; $IrCl(CO)(PMe_3)_2 \cdot C_6H_5C(O)I$, 75112-10-6; I_2, 7553-56-2; HI, 10034-85-2; CH_3I, 74-88-4; C_2H_5I, 75-03-6; $1\text{-}C_3H_7I$, 107-08-4; $2\text{-}C_3H_7I$, 75-30-9; $C_6H_5CH_2I$, 620-05-3; $CH_3C(O)I$, 507-02-8; $C_6H_5C(O)I$, 618-38-2; $CH_3C(O)Cl$, 75-36-5.

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Contribution from the Istituto di Chimica Generale ed Inorganica, Università di Venezia, Venezia, Italy, the Laboratorio di Chimica e Tecnologia dei Radioelementi, CNR, Padova, Italy, and the Chemistry Department, University College, London, England

Nucleophilic Displacement of the Chelating Bis(sulfoxide) from *cis*-[*meso*-1,2-Bis(phenylsulfinyl)ethane]dichloroplatinum(II) and *cis*-[*rac*-1,2-Bis(phenylsulfinyl)ethane]dichloroplatinum(II)

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The kinetics of ring opening, by amines in 1,2-dimethoxyethane, have been measured for two bis(sulfoxide)-platinum(II) isomers. The results make possible a discussion of the differences between the two isomers, in comparison with other platinum(II) complexes, in terms of absolute reactivity, nucleophilic discrimination, and steric retardation effects.

Introduction

Kinetic studies of the closing and opening of chelate rings in 4-coordinated square-planar d^8 complexes as a means of investigating the chelate effect in systems that undergo associatively activated substitution have become of increasing interest in recent years. Much of the work has been done with chelating polyamines[2] where control of the process can be obtained by a suitable choice of pH and is therefore restricted to aqueous solutions. The other studies in this area were, until now, restricted to ring opening and subsequent displacement of chelating bis(thioethers)[3] and bis(selenoethers)[4] by amines in dimethoxyethane solutions.

We have recently synthesized and characterized[5] meso and racemic isomers of [1,2-bis(phenylsulfinyl)ethane]dichloroplatinum(II), whose structures are shown in Figure 1, and now wish to report the kinetics of the displacement of the chelating bis(sulfoxides) from platinum in order (a) to compare the behavior of sulfoxides with thioethers and (b) to examine the extent to which the reactivity depends upon the isomeric form.

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Experimental Section

Materials. [*meso*-1,2-Bis(phenylsulfinyl)ethane]dichloroplatinum(II) and [*rac*-1,2-bis(phenylsulfinyl)ethane]dichloroplatinum(II) were prepared and purified by previously reported methods.[5] The amines, with the exception of 4-chloropyridine, were purified by distillation over KOH pellets at reduced pressure under an atmosphere of nitrogen. 4-Chloropyridine, which decomposes by this treatment, was obtained from the hydrochloride which was dissolved in water and treated with an excess of Na_2CO_3. The amine was extracted with diethyl ether, the extract dried over Na_2SO_4, and the pure amine separated by distillation under a reduced pressure of nitrogen. 1,2-Dimethoxyethane was first refluxed over $LiAlH_4$ and distilled under nitrogen and subsequently distilled over potassium in the presence of benzophenone.

Kinetics. The reactions were started by mixing known prethermostated volumes of freshly prepared, nearly saturated, and filtered solutions of the complex and solutions of the amine in the thermostated cell of a Cary 17-D spectrophotometer and followed by periodically scanning the spectrum over the range 400-280 nm and/or measuring the decrease of absorbance at 320 nm as a function of time. The temperature was monitored by a precision microthermocouple, which was inserted in the reaction cell.

All kinetics were carried out in the presence of a sufficient excess of amine to ensure pseudo-first-order kinetics in the separable stages of the reaction.

Results and Discussion

The spectrophotometric changes, in all cases, are consistent with two, well-separated, processes. The first stage is characterized by a well-defined isosbestic point at about 355 nm (the actual wavelength depending upon the entering amine) and a marked decrease in the absorbance in the range 300-350

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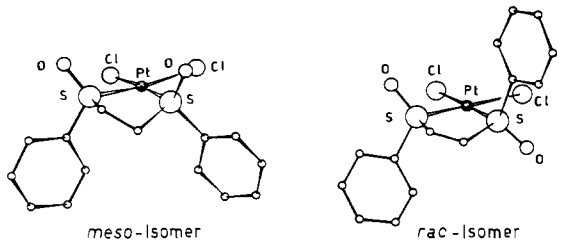


Figure 1. Clinographic projections of the structures of the isomers *cis*-[*meso*-1,2-bis(phenylsulfinyl)ethane]dichloroplatinum(II) and *cis*-[*rac*-1,2-bis(phenylsulfinyl)ethane]dichloroplatinum(II).

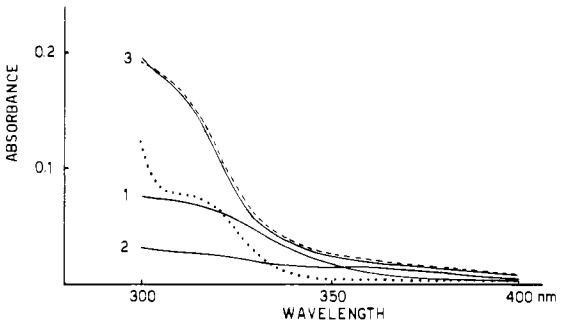
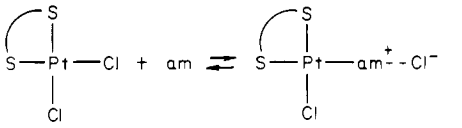


Figure 2. Electronic spectra (5.5×10^{-5} M in 1,2-dimethoxyethane, 25 °C): 1, *cis*-[*rac*-1,2-bis(phenylsulfinyl)ethane]dichloroplatinum(II); 2, intermediate at the end of the first stage of the reaction between complex 1 and pyridine; 3, intermediate at the end of the second stage; ···, *trans*-$[Pt(py)_2Cl_2]$; ---, *cis*-$[Pt(py)_2Cl_2]$.

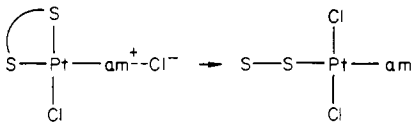
nm, and this is followed by a much slower change which is characterized by an increase in absorbance (Figure 2).

Since the major interest lies in the first step, the second stage was only followed to completion in the case where the entering nucleophile is pyridine. There the final spectrum corresponds closely to that of a freshly prepared solution of an authentic sample of *cis*-$[Pt(py)_2Cl_2]$ in dimethoxyethane, as reported in Figure 2. The spectrum of *trans*-$[Pt(py)_2Cl_2]$, measured under identical conditions, is also shown for comparison. The cis–trans isomerization of *cis*-$[Pt(py)_2Cl_2]$ does not occur to any significant extent during the time taken by the second stage of the reaction even in the presence of the largest concentration of pyridine used.

It is therefore concluded that the two stages of the reaction being studied are (1) the opening of the chelate ring and (2) the displacement of the monodentate bis(sulfoxide). [Note: A mechanism in which chloride is the initial leaving group (stage 1) should not be discarded without further consideration. In the nonpolar solvent dimethoxyethane, it is unlikely that


(1)

the ion-pair product will separate and the effective concentration of chloride would be high and its entry could lead to the opening of the chelate ring. In view of the higher translabilizing effect of chloride as compared to that of amine, one would expect the chloride to return to give the trans isomer with the monodentate sulfoxide (stage 2). A second dis-


(2)

placement of chloride by amine would lead to the formation

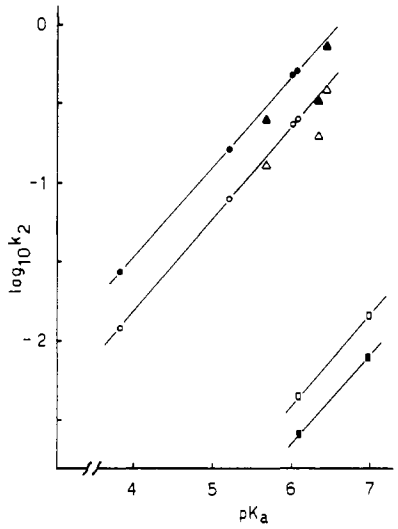
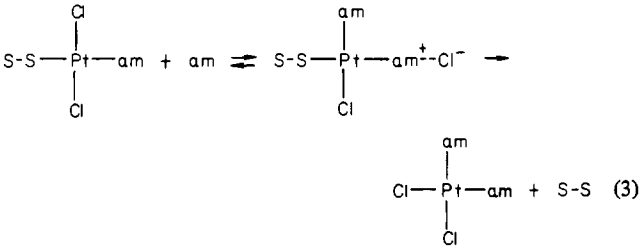


Figure 3. Plot of log k_2 against pK_a of the entering amines for the reactions of *cis*-[*rac*-1,2-bis(phenylsulfinyl)ethane]dichloroplatinum(II) isomer (lines through full symbols) and *cis*-[*meso*-1,2-bis(phenylsulfinyl)ethane]dichloroplatinum(II) isomer (lines through empty symbols): (●, ○) para-substituted pyridines; (▲, △) meta-substituted pyridines; (■, □) ortho-substituted pyridines.

of a cis-diamino species and, finally, to the observed product (stage 3).


(3)

This mechanism would require that the intermediate is the *trans*-dichloro–amine–sulfoxide complex. A comparison of the spectra of the intermediate with those of *cis*- and *trans*-$[Pt(Me_2SO)(py)Cl_2]$ shows that it is the cis isomer, and therefore this alternative mechanism can be ruled out.]

The first-order rate constants, k_{obsd}, obtained in this way and listed in Table I obey the relationship $k_{obsd} = k_2[am]$. The values of k_2 obtained from a linear least-squares analysis of the k_{obsd} vs. [am] plot are collected in Table II. In every case the intercept was zero, within the error limits of the analysis. The absence of a solvolytic (k_1) term is not surprising in view of the poor coordinating ability of the solvent toward platinum(II) and is indeed a characteristic of all substitution reactions carried out in this solvent.[3,4,6] In the case of the reaction with pyridine the studies were made over a range of temperatures and the plot of ln (k_2/T) against $1/T$ was linear. The observed values for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are also included in Table II. The plots of log k_2 against the pK_a of amH$^+$ (measured in water at 25 °C, $\mu = 0$) are shown in Figure 3. The validity of these pK_a values as a measure of relative nucleophilicity has been discussed previously,[7] and it is possible to discuss the relationship in Figure 3 in terms of (a) substrate reactivity, (b) substrate discrimination of amines offering similar steric hindrance but different basicity, and (c) substrate response to steric hindrance.

It has been observed on many previous occasions that ortho methyl substitution in heterocyclic amines can lead to considerable retardation of the substitution in square-planar complexes and that the linear free energy relationship between

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Table I. First-Order Rate Constants, k_{obsd}, for the Reactions of Meso and Racemic Platinum(II) Isomers with Amines (am) in 1,2-Dimethoxyethane[a]

10^2[am], M	$10^4 k_{obsd}$, s^{-1}	10^2[am], M	$10^4 k_{obsd}$, s^{-1}
Meso Isomer, 15 °C, am = py			
26.82	91.3	11.00	36.7
25.34	80.5	8.04	24.5
21.45	70.6	7.60	22.8
13.40	43.9	2.68	9.66
12.66	41.7		
Racemic Isomer, 15 °C, am = py			
21.45	145.8	10.72	71.5
19.10	132.6	6.44	43.3
15.00	101.2	2.14	14.8
12.66	88.5	1.34	6.43
11.00	78.0		
Meso Isomer, 25 °C, am = py			
16.48	137.5	2.35	17.5
12.66	102.0	1.17	8.83
10.08	80.3	0.58	4.40
4.71	36.5		
Racemic Isomer, 25 °C, am = py			
16.48	268.0	6.28	104.0
12.66	213.3	4.71	72.5
12.66	208.3	2.35	36.5
12.56	207.5	1.17	20.0
9.42	156.2	1.17	18.3
Meso Isomer, 34.5 °C, am = py			
26.82	373.0	12.66	176.5
25.34	346.3	11.00	151.7
21.46	280.2	8.45	116.5
18.77	241.5	8.04	112.0
17.70	244.0	2.53	37.5
13.41	170.5	1.27	17.0
12.66	180.3		
Racemic Isomer, 34.5 °C, am = py			
16.48	461.0	6.26	167.5
12.66	355.2	4.71	131.4
9.42	268.5	2.26	61.3
Meso Isomer, 25 °C, am = 4-Cl(py)			
49.44	59.6	16.48	16.9
34.61	41.0	9.89	12.8
24.72	28.3	4.94	6.0
Racemic Isomer, 25 °C, am = 4-Cl(py)			
49.44	147.2	16.48	39.3
34.61	93.8	9.89	25.2
24.72	65.8	4.94	15.0
Meso Isomer, 25 °C, am = 4-Me(py)			
18.59	425.5	5.03	112.3
14.87	334.0	1.86	43.5
9.29	218.2	0.93	22.5
5.58	129.0		
Racemic Isomer, 25 °C, am = 4-Me(py)			
18.59	814.0	5.03	224.5
14.87	654.2	2.51	112.0
9.29	447.5	1.86	84.5
5.58	265.0		
Meso Isomer, 25 °C, am = 4-Et(py)			
16.90	410.0	5.07	130.5
11.83	290.5	3.38	78.7
8.45	210.2	1.69	43.2
Racemic Isomer, 25 °C, am = 4-Et(py)			
16.90	855.5	5.07	260.6
11.83	495.5	3.38	170.4
8.45	435.0	1.69	87.0
Meso Isomer, 25 °C, am = 3-Me(py)			
7.46	94.0	3.73	46.2
5.22	69.7	2.24	28.1
5.22	68.0	0.74	8.92
3.73	47.2	0.37	4.67
Racemic Isomer, 25 °C, am = 3-Me(py)			
7.46	184.2	3.73	89.0
7.46	184.2	2.24	54.6
5.22	128.0	0.74	18.5
Meso Isomer, 25 °C, am = 3,4-Me_2(py)			
5.74	240.0	1.72	66.2
4.02	164.5	1.15	48.0
2.87	119.5	0.57	22.5
Racemic Isomer, 25 °C, am = 3,4-Me_2(py)			
5.74	433.2	1.72	123.0
4.02	302.0	1.15	83.2
2.87	210.5	0.57	22.5
Meso Isomer, 25 °C, am = 3,5-Me_2(py)			
6.30	126.0	1.89	40.0
6.30	121.5	0.63	12.2
5.04	99.5	0.31	6.25
3.15	62.2		
Racemic Isomer, 25 °C, am = 3,5-Me_2(py)			
9.96	320.5	3.15	105.0
6.30	215.0	1.89	60.8
5.04	165.2	0.63	20.0
4.98	161.5		
Meso Isomer, 25 °C, am = 2-Me(py)			
86.7	37.8	20.0	8.50
86.7	37.0	10.0	4.23
60.7	26.7	8.7	3.75
43.3	18.9		
Racemic Isomer, 25 °C, am = 2-Me(py)			
86.7	22.5	12.0	2.90
86.7	22.5	10.0	2.41
70.0	18.2	8.7	2.13
43.3	11.2	5.0	1.30
Meso Isomer, 25 °C, am = 2,4-Me_2(py)			
68.0	101.5	34.0	50.5
61.2	90.3	20.4	24.3
47.6	76.0	6.80	9.40
Racemic Isomer, 25 °C, am = 2,4-Me_2(py)			
68.0	53.8	34.0	26.8
61.2	48.0	20.4	16.1
47.6	38.4	6.80	4.95

[a] The concentrations of the complexes were always in the range 10^{-4}–5×10^{-5} M.

log k_2 and pK_a of amH^+ only applies for amines with the same extent of ortho methylation.[8] For this reason the amines have been separated into those with and without an ortho methyl substituent. However, in this case, there is not only a large ortho effect but also a measurable retardation for meta methyl substitution, the decrease in reactivity being even more marked when there is double meta substitution as in the case of 3,5-dimethylpyridine. This has previously been noted in the reactions of $[Pt(dien)Br]^+$[9] with amines and in the amine-catalyzed cis–trans isomerization of $[Pd(am)_2Cl_2]$.[10]

Taking the data for the 4-substituted pyridines only, we find that there is a linear free energy relationship between log k_2 and pK_a for both isomers. The slopes are reported in Table III. The rate constants for the 2-methyl-substituted pyridines fall far from this line, and, bearing in mind that only two data points per isomer are available, we still report the slopes, α, of the lines joining them in Table III. The steric retardation parameter, Δ, which is the vertical separation of the lines for

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(10) L. Cattalini and M. Martelli, *J. Am. Chem. Soc.*, **91**, 312 (1969).

Table II. Values of k_2 and Activation Parameters for the Reactions of Meso and Racemic Platinum(II) Isomers with Amines in 1,2-Dimethoxyethane from Linear Least Squares[a]

amine	pK_a	k_2, M^{-1} s^{-1} 15.0 °C	25.0 °C	34.5 °C	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
		cis-[*meso*-1,2-Bis(phenylsulfinyl)ethane]dichloroplatinum(II)				
pyridine	5.17	$(3.32 \pm 0.15) \times 10^{-2}$	$(7.82 \pm 0.32) \times 10^{-2}$	$(13.66 \pm 0.68) \times 10^{-2}$	12.3 ± 1	−22 ± 4
4-chloropyridine	3.84		$(11.78 \pm 0.81) \times 10^{-3}$			
4-methylpyridine	6.02		$(23.04 \pm 0.48) \times 10^{-2}$			
4-ethylpyridine	6.08		$(24.69 \pm 0.82) \times 10^{-2}$			
3-methylpyridine	5.68		$(12.63 \pm 0.39) \times 10^{-2}$			
3,4-dimethylpyridine	6.44		$(40.56 \pm 1.35) \times 10^{-2}$			
3,5-dimethylpyridine	6.34		$(19.87 \pm 0.58) \times 10^{-2}$			
2-methylpyridine	6.10		$(43.13 \pm 0.63) \times 10^{-4}$			
2,4-dimethylpyridine	6.99		$(143.6 \pm 12.7) \times 10^{-4}$			
		cis-[*rac*-1,2-Bis(phenylsulfinyl)ethane]dichloroplatinum(II)				
pyridine	5.17	$(6.87 \pm 0.15) \times 10^{-2}$	$(16.20 \pm 0.59) \times 10^{-2}$	$(27.68 \pm 0.59) \times 10^{-2}$	12.0 ± 0.8	−22 ± 3
4-chloropyridine	3.84		$(27.18 \pm 2.26) \times 10^{-3}$			
4-methylpyridine	6.02		$(47.02 \pm 3.61) \times 10^{-2}$			
4-ethylpyridine	6.08		$(50.95 \pm 0.51) \times 10^{-2}$			
3-methylpyridine	5.68		$(24.50 \pm 0.31) \times 10^{-2}$			
3,4-dimethylpyridine	6.44		$(73.02 \pm 1.56) \times 10^{-2}$			
3,5-dimethylpyridine	6.34		$(32.67 \pm 0.76) \times 10^{-2}$			
2-methylpyridine	6.10		$(25.51 \pm 0.74) \times 10^{-4}$			
2,4-dimethylpyridine	6.99		$(78.15 \pm 2.37) \times 10^{-4}$			

[a] The concentrations of the complexes were always in the range 10^{-4}–5×10^{-5} M.

Table III. Discrimination (α) and Steric Retardation (Δ) Parameters for the Reactions of Meso and Racemic Platinum(II) Isomers with Amines Compared with Data Available for Some Other Planar Complexes[a]

substrate[e]	solvent	leaving group	α	Δ
meso isomer	$(CH_3OCH_2)_2$	*b*	0.58	1.8
racemic isomer	$(CH_3OCH_2)_2$	*b*	0.58	2.31
Pt(S-S)Cl_2	$(CH_3OCH_2)_2$	*c*	0.14	1.6
trans-[Pt(*i*-$Pr_2S)_2Cl_2$]	$(CH_3OCH_2)_2$	*i*-Pr_2S	0.13	2.3
trans-[Pt(py)$_2Cl_2$]	CH_3OH	Cl^-	0.05	
[Pt(bpy)Cl_2]	CH_3OH	Cl^-	0.06	0.96
[Pd(S-S)Cl_2]	$(CH_3OCH_2)_2$	*c*	0.22	2.4
trans-[Pd(*i*-$Pr_2S)_2Cl_2$]	$(CH_3OCH_2)_2$	*i*-Pr_2S	0.13	2.3
[Pd(dien)X]$^+$	H_2O	X^-[d]	0.01	1.6
[$AuCl_4$]$^-$	CH_3OH	Cl^-	0.15	0.95
[$AuCl_4$]$^-$	CH_3COCH_3	Cl^-	0.15	0.95
[Au(phen)Cl_2]$^+$	CH_3COCH_3	Cl^-	0.22	1.2
[Au(5-NO_2-phen)Cl_2]$^+$	CH_3COCH_3	Cl^-	0.89	1.2
[Au(bpy)Cl_2]$^+$	CH_3COCH_3	Cl^-	0.46	1.2

[a] L. Cattalini, "Inorganic Reaction Mechanisms"; Wiley, New York, 1970, and references therein. [b] Present paper. [c] The data refer to the opening of the chelate ring S-S. [d] $X^- = I^-$, SCN^-, N_3^-, NO_2^-. [e] Abbreviations: S-S = $PhSCH_2CH_2SPh$; py = pyridine; bpy = 2,2′-bipyridyl; phen = *o*-phenanthroline; dien = $(H_2NCH_2CH_2)_2NH$.

the unhindered and 2-methyl-substituted pyridines at the pK_a of pyridine, is also reported in Table III for each of the isomers.

The difference in the behavior of the two isomers is of considerable interest. In the reactions with the unhindered pyridines, the racemic (*RR*, *SS*) form is about twice as reactive as the meso (*RS*) isomer. The nucleophilic discrimination between pyridines (α) does not differ significantly between the two isomers, nor do the entropies and enthalpies of activation for the reactions with pyridine itself (Table II). However, the reactivity order is reversed in the reactions with 2-methyl-substituted pyridines, the meso form now being more reactive than the racemic; once again, the slopes, α, are indistinguishable. This behavior must clearly arise from the difference in the steric hindrance presented to substitution.

In the case of the racemic isomer, the steric retardation parameter ($\Delta = 2.31$) is one of the largest encountered so far in the substitution reactions of platinum(II) (see Table III). The two sides of the platinum in this isomer offer the entering group the same amount of hindrance, whereas in the meso form the nucleophile can choose between the side blocked by the two phenyl groups and that blocked by two oxygens. It also suggests that, in the rate-determining 5-coordinate transition state, the bond with the leaving sulfur is still well formed; i.e., the bond-making transition state is the most important. This is also consistent with the high (for Pt(II) at least) positive value of α. It is of interest to note that the small, but nevertheless significant, steric retardation arising from 3-methyl substituents is more marked in the case of the racemic isomer.

The fact that the values of α for the two isomers are essentially equal in all cases suggests that, electronically, the two chelating bis(sulfoxides) are equivalent and therefore the reactivity differences are entirely steric in origin. This is further demonstrated by the fact that the rate constants for the second stage of the displacement of the bis(sulfoxide) are almost the same for the racemic and meso isomers (10.6×10^{-5} and 9.43×10^{-5} M^{-1} s^{-1}, respectively).

It is instructive to compare the behavior of the chelating bis(sulfoxides) with that of the corresponding bis(thioether), $PhSCH_2CH_2SPh$, whose displacement from platinum(II) has been studied under the same experimental conditions.[3] Only one form of the bis(thioether) complex is known, and it is not clear whether this is a single isomeric species or a dynamic equilibrium between the meso and racemic forms. One might estimate from published data relating to NMR coalescence temperatures and activation parameters[11] that the rate of inversion of the sulfur will be fast compared to the rate of substitution reactions that we are studying. The absence of any complication in the kinetic form at any single amine concentration indicates clearly that a noninterconvertible mixture of isomers is not involved.

Taking the reaction with pyridine as a standard, we find that both bis(sulfoxide) isomers are more reactive than the bis(thioether) complex; $k_2 = 7.82 \times 10^{-2}$, 16.2×10^{-2} M^{-1} s^{-1} as compared to 1.15×10^{-2} M^{-1} s^{-1}. The slope, α, is also

(11) (a) P. Haake and P. C. Turley, *J. Am. Chem. Soc.*, **89**, 4611 (1967); (b) R. J. Cross, I. G. Dalgleish, G. J. Smith, and R. Wardle, *J. Chem. Soc., Dalton Trans.*, 992 (1972); (c) R. J. Cross, G. J. Smith, and R. Wardle, *Inorg. Nucl. Chem. Lett.*, **7**, 191 (1971); (d) R. J. Cross, T. H. Green, R. Keat, and J. F. Peterson, *ibid.*, **11**, 145 (1975); (e) F. R. Hartley, S. G. Murray, W. Levason, H. E. Soutter, and C. A. McAuliffe, *Inorg. Chim. Acta*, **35**, 265 (1979).

considerably larger for the sulfoxide system (0.58) than it is for the thioether (0.14). This is the largest value of α so far observed in the reactions of platinum(II) complexes with heterocyclic amines, now covering the range $\sim 0 < \alpha < 0.58$, and is surpassed only by the value of 0.89 observed[12] in the displacement of Cl^- from cationic $[Au(5\text{-}NO_2\text{-}1,10\text{-}phen)Cl_2]^+$. It is clear now that the statement made many years ago[6] that the rate of nucleophilic substitution at platinum(II) is essentially independent of the basicity of the entering amine is no longer valid.

These results are consistent with the observation that the cis effect of a thioether is less than that of a sulfoxide and is characterized by a lower nucleophilic discrimination ability.[13]

The steric retardation effect is higher in the sulfoxide system, especially in the case of the racemic form of the ligand (Δ = 2.31, 1.8 as compared to 1.6 for the thioether complex), and it is worth noting that the retardation resulting from meta substitution is only apparent in the sulfoxide system. The higher discrimination (α) and larger Δ suggest strongly that bond making is more important in the sulfoxide system than in the thioether system.

In any comparison of the absolute reactivity of the bis(thioether) and bis(sulfoxide) complexes, we must take account of the difference in the leaving ability of the two types of donor. The most obvious difference between the displacement of the bis(sulfoxide) and the bis(thioether) is that in the former case ring opening is much faster than the subsequent loss of the monodentate ligand, whereas the loss of the monodentate thioether is fast compared to ring opening which becomes the rate-determining stage. On the basis that a second stage less than 5 times faster than ring opening could cause noticeable departure from a simple first-order kinetic rate law, it can be assumed that the k_2 for the loss of the monodentate thioether is greater than 5×10^{-2} M^{-1} s^{-1}. This is some 500 times faster than the observable displacement of the monodentate bis(sulfoxide) and therefore might be considered to be a measure of the *minimum* difference in the leaving-group effect of the two donor species.

The ring-opening rate constants, on the other hand, differ by a factor of 1 order of magnitude only, in spite of the fact that the cis effect of a single thioether is less than that of the corresponding sulfoxide. It is clear therefore that, in this case, leaving-group effects and electronic cis effects cannot alone account for the observed behavior. It is known, for example, from preparative chemistry, that one of the two sulfoxide ligands in *cis*-$[Pt(Me_2SO)_2Cl_2]$ is readily replaced by amines,[14] while a single Me_2SO cannot readily be replaced in aqueous solution. Wayland, in his study of the thermal isomerization of $Pt(R_2SO)_2Cl_2$ has shown[15] that the labilities of cis and trans pairs of sulfoxides are of similar magnitude in spite of the large difference in the trans effect of Cl and R_2SO. Furthermore, it has been shown that for a sterically hindered sulfoxide *i*-Pr_2SO the trans isomer is obtained in the preparative reaction ($PtCl_4^{2-} + R_2SO$), whereas the stable product of the analogous reaction with Me_2SO is the cis isomer,[14] the trans isomer appearing as an unstable intermediate that can be isolated only under certain conditions.[16] All of these observations indicate that mutual steric repulsion may play a very important part in promoting the unusual lability of a cis pair of sulfoxides and indeed may be as important as the mutual trans effect of sulfoxides. This problem is now being examined in depth and will be reported elsewhere.

Finally it is worth noting that in this aprotic, nonpolar solvent, the chloride which is under the moderate trans effect of the sulfoxide, and is generally considered to be a much more labile ligand, is retained in the product while the neutral ligand is lost (see note in Results and Discussion).

Preliminary experiments in methanol show that iodide and thiocyanate displace the chloride, and the ratio of the reactivity of the two isomers is as found here for their reactions with unhindered amines. On the other hand basic nucleophiles, e.g., N_3^-, CH_3O^-, and RNH_2, lead to a general decomposition of the substrate. This is another example of the way in which the ligand displaced from a complex can be determined by the solvent and the entering nucleophile.

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Registry No. [*meso*-1,2-Bis(phenylsulfinyl)ethane]dichloroplatinum(II), 41233-57-2; [*rac*-1,2-bis(phenylsulfinyl)ethane]dichloroplatinum(II), 41276-66-8; py, 110-86-1; 4-Cl(py), 626-61-9; 4-Me(py), 108-89-4; 4-Et(py), 536-75-4; 3-Me(py), 108-99-6; 3,4-Me_2(py), 583-58-4; 3,5-Me_2(py), 591-22-0; 2-Me(py), 109-06-8; 2,4-Me_2(py), 108-47-4; *cis*-$[Pt(py)_2Cl_2]$, 15227-42-6; *trans*-$[Pt(py)_2Cl_2]$, 14024-97-6.

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Bonding in the Syn and Anti Isomers of Di-μ-sulfido-bis(sulfido(1,2-dimercaptoethanato)molybdate(V)) Anions

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The electronic structure and bonding interactions in the syn, anti, and closed isomers of $[Mo_2S_4(S_2C_2H_4)_2]^{2-}$ are examined and compared through extended Hückel and Fenske–Hall molecular orbital calculations. A molybdenum–molybdenum bonding interaction is found to account for the diamagnetism of the complexes and to be important in determining the relative stability of the isomers. The predicted stabilities are syn > closed > anti.

Current interest in molybdenum enzymes and in molybdenum desulfurization catalysts has stimulated research on the coordination chemistry of sulfur-rich molybdenum complexes. One particularly stable class of compounds is di-μ-sulfido-

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