Electronic and Steric Effects in the Dissociative Displacement of Thioethers from Mixed Phenyl(thioether)platinum(II) Complexes

Giuseppe Alibrandi, Domenico Minniti,* Luigi Monsù Scolaro, and Raffaello Romeo*

Received August 17, 1988

A series of compounds of the type *cis*-[PtPh$_2$L$_2$], where L encompasses a wide range of thioethers of different steric and electron-donating characteristics, have been prepared and characterized. Most of these monomeric compounds exist in solution in equilibrium with the sulfur-bridged dimer [Pt$_2$Ph$_4$(μ-L)$_2$] and the free thioether. Addition of small amounts of ligand in solution allows the stabilization of the monomeric form. Kinetic studies of the displacement of the thioethers with 2,2'-bipyridine (bpy) to yield [PtPh$_2$(bpy)] in CH$_2$Cl$_2$ at 298.16 K, carried out in the presence of sufficient excess of [L] and [bpy] to ensure pseudo-first-order conditions, showed that the reactions follow a bivariate nonlinear rate law $k_{obsd} = a[bpy]/(b[L] + [bpy]) + c[bpy]$, which has the same form as that of similar systems for which a dissociative mechanism has been proposed. The reactivity decreases linearly with increasing σ-donor ability of the leaving thioether, with bulky substituents on sulfur playing an accelerating role. The relative sensitivities of the dissociative and associative processes to the inductive effects of the leaving group are compared and related to the degree of lengthening and weakening of the bond with the metal produced by the trans-activating group.

Introduction

Four-coordinate square-planar complexes of d^8 transition-metal ions easily undergo the addition of a fifth ligand to form five-coordinate species either as discrete compounds or as reaction intermediates.[1] This has led in the past to the firm belief that 16-electron coordination or organometallic compounds react only via an 18-electron intermediate by an associative mechanism. Notwithstanding, the number of fundamental processes in which the existence of three-coordinate d^8 intermediates (i.e., 14-electron compounds) is involved is rapidly growing, especially in platinum(II) chemistry. Indeed, such species offer a favorable reaction route for geometrical isomerizations,[2] insertion of carbon monoxide across a platinum–alkyl bond (or alkyl migration from the metal to carbon monoxide),[3] insertion of olefins across the Pt–H bond[4] or β-elimination from alkyl complexes,[5] reductive elimination of ethane from dimethyl compounds,[6] and methyl for halogen exchange in the reaction of *cis*-[PtMe$_2$(Me$_2$S)$_2$] with *cis*- or *trans*-[PtCl$_2$(Me$_2$S)$_2$] to give *trans*-[PtMeCl(Me$_2$S)$_2$].[7]

Recently we showed that easy ligand dissociation from *cis*-[PtR$_2$L$_2$] (R = Me or Ph, L = Me$_2$SO or Me$_2$S)[8] to yield a coordinatively unsaturated 14-electron [PtR$_2$L] species was the dominant pathway in ligand substitution by nitrogen chelating ligands in inert solvents. The facile dissociation is thought to derive essentially from the strong σ-donor power of the trans group, which lengthens and weakens the Pt–S bond. The unsaturated intermediate showed a significant nucleophilic discrimination ability. Stronger nucleophiles can also use a parallel associatively activated pathway.

In this study we were interested in searching for a correlation between the lability of the substrate and the nature of the leaving group. This theme is strictly related to the chemistry of transition-metal complexes containing weak donor ligands and to their role as potentially reactive intermediates in homogeneous catalytic processes or as starting materials for the synthesis of organometallic or coordination compounds.[9]

Thus, we prepared a series of complexes of the type *cis*-[PtPh$_2$L$_2$], where L encompasses a wide range of thioethers of different steric and electron-donating characteristics, and have carried out a detailed kinetic study of the reaction

$$cis\text{-}[PtPh_2L_2] + bpy \rightarrow [PtPh_2(bpy)] + 2L \qquad (1)$$

Besides confirming the dissociative mechanism, these results provide a means of ascertaining the relative importance of the steric and electronic properties of the alkyl substituents on the sulfur atom in governing the lability of the coordinated thioethers.

Experimental Section

Preparation of Complexes. *cis*-[PtPh$_2$(Me$_2$S)$_2$][8c] and [Pt$_2$Ph$_4$(μ-SEt$_2$)$_2$][10] were prepared by methods reported elsewhere. *cis*-[PtPh$_2$L$_2$] (L = diethyl sulfide (Et$_2$S), di-*n*-propyl sulfide (*n*-Pr$_2$S), diisopropyl sulfide (*i*-Pr$_2$S), di-*n*-butyl sulfide (*n*-Bu$_2$S), methyl ethyl sulfide (MeEtS), dibenzyl sulfide (Bz$_2$S), methyl benzyl sulfide (MeBzS), methyl phenyl sulfide (MePhS), and diethyl selenide (Et$_2$Se)) are new compounds and were prepared by using essentially the following procedure. A weighed amount of [Pt$_2$Ph$_4$(μ-SEt$_2$)$_2$] was dissolved in an excess of liquid thioether at room temperature. After a few hours, the excess of reagent was evaporated and the residue was crystallized from petroleum ether. In the case of diisopropyl sulfide, the reaction was much slower and required a further treatment with the reagent to go to completion. The reaction with dibenzyl sulfide was carried out in dichloromethane by reacting the dimeric starting material with a stoichiometric amount of reagent. After evaporation of the solvent, the reaction product was extracted from the residue with dichloromethane and crystallized after addition of petroleum ether in a 1:10 ratio. The final compound incorporates a molecule of solvent of crystallization. All complexes react with 2,2'-bipyridine (bpy) to yield [Pt(Ph)$_2$(bpy)], whose synthesis has been reported elsewhere.[11]

(1) Basolo, F.; Pearson, R. G. *Mechanisms of Inorganic Reactions*; John Wiley: New York, 1968. Wilkins, R. G. *The Study of Kinetics and Mechanisms of Reactions of Transition Metal Complexes*; Allyn and Bacon: Boston, MA, 1974. Langford, C. H.; Gray, H. B. *Ligand Substitution Processes*; W. A. Benjamin: New York, 1965. Tobe, M. L. *Inorganic Reaction Mechanisms*; Nelson: London, 1972. Atwood, J. D. *Inorganic and Organometallic Reaction Mechanisms*; Brooks/Cole Publishing Co.: Monterey, CA, 1985.
(2) Alibrandi, G.; Minniti, D.; Monsù Scolaro, L.; Romeo, R. *Inorg. Chem.* **1988,** *27,* 318 and references therein.
(3) Wilson, C. J.; Green, M.; Mawby, R. J. *J. Chem. Soc., Dalton Trans.* **1974,** 1293. Kubota, M.; Rothcock, R. K.; Geibel *Ibid.* **1973,** 1267. Glyde, R. W.; Mawby, R. J. *Inorg. Chem.* **1971,** *10,* 854.
(4) Clark, H. C.; Wong, C. S. *J. Am. Chem. Soc.* **1974,** *96,* 7214 and references therein. Thorn, D. L.; Hoffmann, R. *J. Am. Chem. Soc.* **1978,** *100,* 2079.
(5) Whitesides, G. M. *Pure Appl. Chem.* **1981,** *53,* 287. Yamamoto, A.; Yamamoto, T.; Komiya, S.; Ozawa, F. *Ibid.* **1984,** *56,* 1621. McCarthy, T. J.; Nuzzo, R. G.; Whitesides, G. M. *J. Am. Chem. Soc.* **1981,** *103,* 3396. Whitesides, G. M.; Gaash, J. F.; Sdedronsky, E. R. *J. Am. Chem. Soc.* **1972,** *94,* 5258. Nuzzo, R. G.; McCarthy, T. J.; Whitesides, G. M. *Ibid.* **1981,** *103,* 3404. Foley, P.; Di Cosimo, R.; Whitesides, G. M. *Ibid.* **1980,** *102,* 6713. Komiya, S.; Morimoto, Y.; Yamamoto, A.; Yamamoto, T. *Organometallics* **1982,** *1,* 1528.
(6) Komiya, S.; Albright, T. A.; Hoffmann, R.; Kochi, J. K. *J. Am. Chem. Soc.* **1976,** *98,* 7255. Tatsumi, K.; Hoffmann, R.; Yamamoto, A.; Stille, J. *Bull. Chem. Soc. Jpn.* **1981,** *54,* 1857.
(7) Scott, J. D.; Puddephatt, R. J. *Organometallics* **1983,** *2,* 1643.
(8) Lanza, S.; Minniti, D.; Romeo, R.; Moore, P.; Sachinidis, J.; Tobe, M. L. *J. Chem. Soc., Chem. Commun.* **1984,** 542. Lanza, S.; Minniti, D.; Moore, P.; Sachinidis, J.; Tobe, M. L. *Inorg. Chem.* **1984,** *23,* 4428. Alibrandi, G.; Bruno, G.; Lanza, S.; Minniti, D.; Romeo, R.; Tobe, M. L. *Ibid.* **1987,** *26,* 185. Minniti, D.; Alibrandi, G.; Tobe, M. L.; Romeo, R. *Ibid.* **1987,** *26,* 3956.
(9) Davies, J. A.; Hartley, F. R. *Chem. Rev.* **1981,** *81,* 79. Hartley, F. R.; Davies, J. A. *Rev. Inorg. Chem.* **1982,** *4,* 27.
(10) Steele, B. R.; Vrieze, K. *Transition Met. Chem. (Weinheim, Ger.)* **1977,** *2,* 140.

Table I. Analytical and ^{1}H NMR Data for Mixed Phenyl–Thioether *cis*-[PtPh$_2$L$_2$] Complexes

complex	% C[a]	% H[a]	% S[a]	δ(PtPh)[b,c]	δ(ligand)[b,c]	^3J(PtSCH)
[PtPh$_2$(Me$_2$S)$_2$]	40.5 (40.6)	4.7 (4.6)	13.4 (13.5)	6.8 (m), 7.4 (m)	2.09 (s)	23.6
[Pt$_2$Ph$_4$(μ-SEt$_2$)$_2$]	43.8 (43.7)	4.7 (4.6)	7.2 (7.3)	6.9 (m), 7.3 (m)	1.81 (t), 2.50 (m)	
[PtPh$_2$(Et$_2$S)$_2$]	45.3 (45.4)	5.8 (5.7)	12.2 (12.1)	6.7 (m), 7.2 (m)	1.32 (t), 2.53 (m)	
[PtPh$_2$(MeEtS)$_2$]	43.1 (43.1)	5.1 (5.2)	12.9 (12.8)	6.8 (m), 7.3 (m)	2.06 (s), 1.28 (t), 2.47 (q)	25.9
[PtPh$_2$(n-Pr$_2$S)$_2$]	49.0 (49.2)	6.4 (6.5)	11.1 (11.0)			
[PtPh$_2$(i-Pr$_2$S)$_2$]	48.6 (49.2)	6.4 (6.5)	10.8 (11.0)			
[PtPh$_2$(n-Bu$_2$S)$_2$]	52.3 (52.4)	7.1 (7.2)	10.1 (10.0)			
[PtPh$_2$(Bz$_2$S)$_2$]·CH$_2$Cl$_2$	57.9 (57.1)	4.8 (4.7)	7.8 (7.4)	6.9 (m), 7.4 (m)	7.2 (s), 3.33 (s)	17.8
[PtPh$_2$(MeBzS)$_2$]	53.7 (53.7)	4.8 (4.8)	10.2 (10.2)	6.9 (m), 7.4 (m)	7.3 (s), 1.79 (s), 3.48 (s)	23.3; 16.3
[PtPh$_2$(MePhS)$_2$]	52.3 (52.3)	4.4 (4.4)	10.8 (10.7)	7.0 (m), 7.4 (m)	7.3 (s), 2.15 (s)	24.2
[PtPh$_2$(Et$_2$Se)$_2$]	38.8 (38.6)	4.9 (4.8)		7.0 (m), 7.7 (m)	1.04 (t), 2.20 (m)	

[a]Theoretical values are given in parentheses. [b]In CDCl$_3$ as solvent; chemical shifts relative to tetramethylsilane. [c]s = singlet, t = triplet, q = quartet, m = multiplet.

The compounds were characterized by using elemental analysis, infrared spectroscopy, ^{1}H NMR spectroscopy, and, where relevant, ^{13}C NMR spectroscopy. The thioethers used were commercial products purified by recrystallization or distillation where necessary.

Infrared spectra were recorded as Nujol mulls on a Perkin-Elmer 783 spectrometer; ^{1}H and ^{13}C NMR spectra were recorded on a Bruker WP 80 spectrometer using CDCl$_3$ as solvent and tetramethylsilane as standard.

Kinetics. Slower reactions were started by mixing known volumes of prethermostated standard solutions of reagents in the thermostated (± 0.05 °C) cell compartment of a Cary 219 or a Perkin-Elmer Lambda 5 spectrophotometer and followed by repetitive scanning of the spectrum at suitable times in the visible and near-UV region or at a fixed wavelength, where the difference of absorbance was largest. The reactions of the diisopropyl sulfide and of the methyl phenyl sulfide complexes required the use of a HI-TECH SF3 stopped-flow spectrophotometer. The use of at least a 10-fold excess of nucleophile over complex ensured first-order kinetics in any run. The rate constants k_{obsd}, s^{-1}, were obtained either from a graph 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 = absorbance after mixing of reagents; A_∞ = absorbance at completion of reaction).

Results

Steele and Vrieze[10] have shown that the reaction of *cis*-[PtCl$_2$L$_2$] (L = dialkyl sulfide) with an excess of aryllithium yields binuclear diarylplatinum(II) compounds of the type [Pt$_2$R$_4$L$_2$] (R = aryl), with the thioether bridging the two metal centers through the sulfur atom. We were interested in the synthesis of the corresponding monomeric species *cis*-[PtR$_2$L$_2$], and a useful synthetic route has been the facile reaction of dimeric sulfide-bridged [PtPh$_4$(μ-SEt$_2$)$_2$] with an excess of ligand L (L = Me$_2$S, Et$_2$S, *n*-Pr$_2$S, *i*-Pr$_2$S, *n*-Bu$_2$S, MeEtS, Bz$_2$S, MeBzS, MePhS, Et$_2$Se). With the most sterically hindered reagents, the reaction occurs less readily, and in these cases the product has been separated from some unreacted starting material by taking advantage of the very low solubility of the latter in petroleum ether. With some reagents, such as for *sec*-Bu$_2$S, the reaction does not occur, and upon repeated treatment only unreacted material was recovered from the reaction mixture. The elemental analysis (Table I) indicates that the solid compounds have been separated in the monomeric form.

Whereas the preparation of the complexes *cis*-[PtPh$_2$L$_2$] and their isolation as crystals are straightforward, most of them in solution undergo dissociation according to the equilibrium

$$2[PtPh_2L_2] \rightleftharpoons [Pt_2Ph_4L_2] + 2L \qquad (2)$$
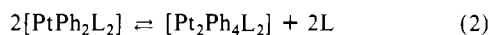
A ready indication of such an equilibrium is given by the complexity of the ^{1}H NMR spectrum and by the presence of signals due to the free ligand. A proper ^{1}H NMR analysis can be performed when the proton resonances of the free ligand, of the ligand coordinated in the monomeric species, and of the bridging ligand in the dimeric species are well separated, as for L = Et$_2$S. In this case, a triplet at $\delta = 1.25$ (6 H) is due to the methyl protons of the free diethyl sulfide, a peak at $\delta = 1.32$ (12 H) is due to those of the ligand in [PtPh$_2$(Et$_2$S)$_2$], and a peak at $\delta = 1.81$ (12 H)

is due to the methyl protons of the ligand in [PtPh$_4$(μ-SEt$_2$)$_2$]. Even when the analysis is not so straightforward, from the intensity of the peaks of the free ligand it is possible to have an indication of the extent of decomposition, which appears to be very low for L = Me$_2$S, MeEtS, Bz$_2$S, MePhS, and Et$_2$Se and zero in the case of MeBzS. The dissociation is dependent on the nature of the solvent, since *cis*-[PtPh$_2$(Me$_2$Se)$_2$] is dissociated in CDCl$_3$ and very stable in benzene. For the thioethers containing branched or longer chain alkyl substituents, such as *n*-propyl, isopropyl, or *n*-butyl, the ^{1}H NMR analysis becomes much more difficult because of the multiplicity and superposition of the peaks for the three species in equilibrium.

As already shown by Scott and Puddephatt[7] for the related *cis*-[PtMe$_2$(Me$_2$S)$_2$] complex, an equilibrium such as that in eq 2 can be easily shifted toward the monomeric species by adding a sufficient excess of thioether (at least 10 times greater than the concentration of complex). The bridge-splitting reaction of L on the binuclear complex is rapid, and the ^{1}H NMR spectrum of the mixture changes immediately to a simpler spectrum with separate signals for *cis*-[PtPh$_2$L$_2$] and L. This allows the assignment of the resonances reported in Table I. The methylene protons in *cis*-[PtPh$_2$(Bz$_2$S)$_2$] and the methyl protons in the corresponding complexes containing Me$_2$S, MePhS, MeBzS, and MeEtS give single peaks with two ^{195}Pt satellites (see last column of Table I). Such simple first-order spectra are expected only if inversion at the sulfur is rapid and the protons are equivalent,[12] and they are consistent with the view that the inversion is a function of the M–S bond strength and that it is aided by a strong σ-bond-weakening trans ligand such as Ph$^-$.[13] The low values of the coupling constants with ^{195}Pt, in the cases in which these can be determined accurately, indicate that the cis stereochemistry of the solid [PtPh$_2$L$_2$] compounds is maintained in solution. The absence of line broadening indicated that ligand exchange is slow with respect to the NMR time scale under these conditions.

The ^{13}C NMR spectra give further information about the equilibrium in eq 2. The peaks due to the carbons of the aliphatic chain of the substituents on the sulfur atom do not appear particularly diagnostic with respect to the number of species present in solution, while it is possible to assign different resonances to the carbons directly bonded to the metal (C$_1$) and to those in ortho (C$_2$), meta (C$_3$), and para (C$_4$) positions on the aromatic ring for the monomeric and the dimeric species. Once again, the addition of a sufficient excess of ligand is required to simplify the spectrum and to assign by comparison the resonances reported in Table II (Figure 1).

When equimolar solutions of the [PtPh$_2$L$_2$] complex and of the chelating 2,2'-bipyridine nucleophile are mixed, the signals assigned to the protons of the coordinated ligand vanish, and only peaks due to the free ligand L and to the [PtPh$_2$(bpy)] product are seen in the ^{1}H NMR spectrum. The same pattern of behavior is observed in the presence of excess free ligand, indicating that the

(11) Chaudhury, N.; Puddephatt, R. J. *J. Organomet. Chem.* **1975**, *84*, 105.

(12) Abel, E. W.; Bush, R. P.; Hopton, F. J.; Jenkins, C. R. *J. Chem. Soc., Chem. Commun.* **1966**, 58. Haake, P.; Cronin Turley, P. *J. Am. Chem. Soc.* **1967**, *89*, 4611; 4617.

(13) Cross, R. J.; Dalgleish, I. G.; Smith, G. J.; Wardle, R. *J. Chem. Soc., Dalton Trans.* **1972**, 992.

Table II. $^{13}C\{^{1}H\}$ NMR Data for Some Monomer and Dimer Phenyl Complexes of Platinum(II) with Thioether Ligands[a]

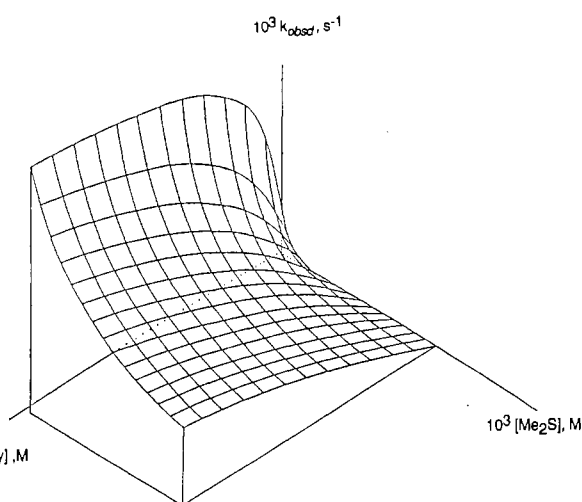| complex	$\delta(C_1)$	$\delta(C_2)$ $(J(PtC_2))$	$\delta(C_3)$ $(J(PtC_3))$	$\delta(C_4)$ $(J(PtC_4))$	$\delta(C_\alpha)$	$\delta(C_\beta)$	$\delta(C_\gamma)$	$\delta(C_\delta)$	$\delta(C'\alpha)$
[PtPh$_2$(Me$_2$S)$_2$]	152.8	136.5 (36.6)	127.0	122.0 (14.6)					20.4
[Pt$_2$Ph$_4$(μ-SEt$_2$)$_2$]	147.8	134.4 (39.7)	127.5 (83.1)	122.8 (14.7)	29.1	12.4 (13.2)			
[PtPh$_2$(Et$_2$S)$_2$]	150.2	136.2 (36.3)	126.9 (82.6)	121.6 (13.9)	27.9	13.1 (16.9)			
[Pt$_2$Ph$_4$(μ-SPr$_2$)$_2$]	147.0	134.6	127.4 (83.8)	122.8 (18)	36.3	21.7 (15.4)	13.5		
[PtPh$_2$(n-Pr$_2$S)$_2$]	150.1	136.3 (36.8)	126.9 (83.1)	121.5 (15.4)	36.3	21.7 (15.4)	13.5		
[Pt$_2$Ph$_4$(μ-SBu$_2$)$_2$]	147.4	134.5 (38.2)	127.4 (83.8)	122.8 (14.7)	34.2	30.4 (14.6)	22.1	13.7	
[PtPh$_2$(n-Bu$_2$S)$_2$]	150.3	136.3 (36.8)	126.9 (82.4)	121.6 (14.7)	34.2	30.4 (14.6)	22.1	13.7	
[PtPh$_2$(MeBzS)$_2$]	149.2	136.5 (34.8)	127.2 (82)	122 (14)	40.6				16.9
[PtPh$_2$(MePhS)$_2$]	147.7	136.7 (37.8)	127.0 (84)	122					21.2
[Pt$_2$Ph$_4$(μ-SMeEt)$_2$]		134.6	127.4	123.0	30.3	12.9			17.4
[PtPh$_2$(MeEtS)$_2$]		136.4 (36.0)	126.8 (83)	121.6 (14)	30.3	12.9			17.4
[PtPh$_2$(SeEt$_2$)$_2$][b]	151.0	137.7 (36.9)	128.3 (83.9)	123.0	22.1	14.9			

[a] Recorded in CDCl$_3$ as solvent; chemical shifts (δ) in ppm relative to TMS. Coupling constants of ^{13}C with ^{195}Pt in Hz are given in parentheses. C_1 is carbon directly bonded to Pt. C_2, C_3, and C_4 are ortho, meta, and para, respectively. C_α, C_β, C_γ, and C_δ, are alkyl carbons, C_α being that bonded to sulfur. $C'\alpha$ is a methyl carbon bonded to sulfur. [b] In [$^2H_8$]toluene.
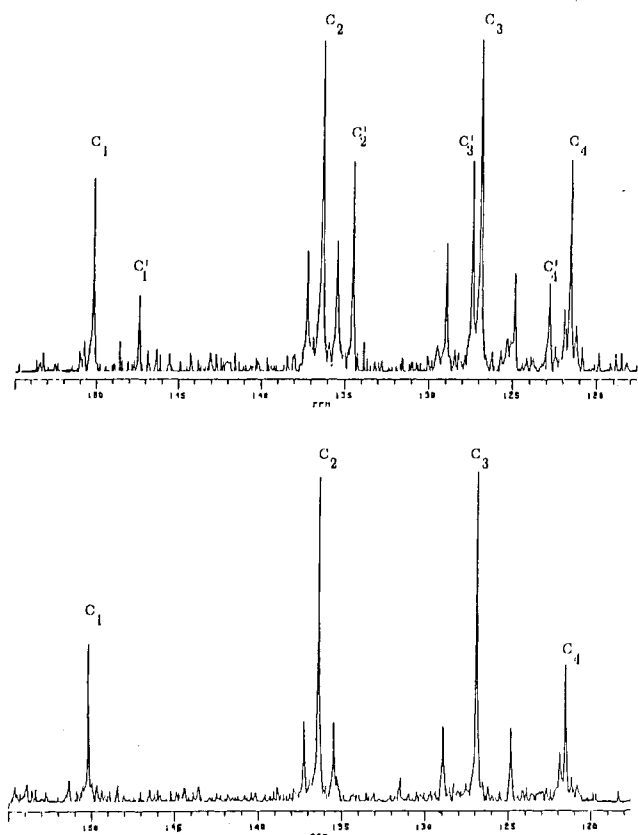
Figure 1. Expanded ^{13}C NMR spectra (20.15 MHz) in the phenyl region of (above) an equilibrium mixture of [Pt$_2$Ph$_4$(μ-SBu$_2$)$_2$], cis-[PtPh$_2$(n-Bu$_2$S)$_2$], and free n-Bu$_2$S and (below) cis-[PtPh$_2$(n-Bu$_2$S)$_2$] in the presence of an excess of n-Bu$_2$S. C_1 is the carbon directly bonded to Pt in the monomer; C_2, C_3, and C_4 are ortho, meta, and para, respectively. C'_1, C'_2, C'_3, and C'_4 are the corresponding carbons of the dimer.

substitution reaction goes to completion. There is no evidence for the buildup in solution of any other intermediate species containing thioether coordinated to the metal. This was confirmed by an abstract factor analysis of the spectral changes in the visible region,[14] which is consistent with a simple smooth conversion of the colorless substrate into a strongly absorbing product, the final spectrum being identical with that of an independently synthesized authentic sample of [PtPh$_2$(bpy)]. The kinetic study was carried out in CH$_2$Cl$_2$ and followed spectrophotometrically. The reactions were carried out under first-order conditions, in the presence of a sufficient and known excess of ligand L and of the entering

(14) Uguagliati, P.; Benedetti, A.; Enzo, S.; Schiffini, L. *Comput. Chem.* **1984**, *8*, 161. Sandrini, P. L.; Mantovani, A.; Crociani, B.; Uguagliati, P. *Inorg. Chim. Acta* **1981**, *51*, 71. Malinowski, E. R.; Hovery, D. G. *Factor Analysis in Chemistry*; Wiley-Interscience: New York, 1980; pp 159–161.

Figure 2. 3-D representation of the [Me$_2$S] and [bpy] dependencies for the reaction of cis-[PtPh$_2$(Me$_2$S)$_2$] with bpy at 298.16 K.

2,2'-bipyridine. The values of the rate constants, k_{obsd}, are available as supplementary material (Table SI), where they are compared with k_{calcd} from the derived rate constants.

Discussion

As found previously for similar cis-[PtR$_2$L$_2$] (R = Me, Ph; L = Me$_2$SO, Me$_2$S) systems,[8] the displacement of thioethers from cis-[PtPh$_2$(L)$_2$] by the nitrogen chelating ligand 2,2'-bipyridine (eq 1) is retarded by the free leaving group, and the addition of this latter in solution offers the double advantage of stabilizing the monomeric species and of maintaining the concentration of L constant throughout the reaction. Under these circumstances the usual semilogarithmic plots were perfectly linear and the values of k_{obsd} could be obtained either from their slopes or by nonlinear regression analysis of the spectral changes. At a constant concentration of sulfide, a curvilinear dependence on the concentration of the entering 2,2'-bipyridine is observed, which levels off to a limiting value at high nucleophile concentration. A global 3-D representation of the [L] and [bpy] dependencies is given in Figure 2 for the kinetic data of substitution reactions of cis-[PtPh$_2$-(Me$_2$S)$_2$] in dichloromethane at 298.16 K.

All of the rate data appear to fit the bivariate nonlinear rate law

$$k_{obsd} = a[bpy]/(b[L] + [bpy]) + c[bpy]$$

In most of the cases the process is dominated by the first term of the expression, the contribution of $c[bpy]$ to the rate being negligible. For L = Et$_2$S the contribution of this second term is so little that it could not be assessed. The values of k_{obsd}, [bpy], and [L] were fitted to this expression by using a nonlinear least-squares curve-fitting program, and the best values of the constants a, b, and c were obtained together with their standard deviations.

Table III. Derived Rate Constants for the Reaction cis-[PtPh$_2$L$_2$] + bpy → [PtPh$_2$(bpy)] + 2L in Dichloromethane at 298.16 K

complex	$10^2 k_1/\text{s}^{-1}$	k_3/k_{-1}	$k_2/\text{M}^{-1}\text{s}^{-1}$
[PtPh$_2$(Me$_2$S)$_2$]	0.528 ± 0.01	0.246 ± 0.02	0.0023 ± 0.002
[PtPh$_2$(Et$_2$S)$_2$]	0.378 ± 0.007	0.467 ± 0.05	0.00
[PtPh$_2$(MeEtS)$_2$]	0.432 ± 0.008	0.332 ± 0.02	0.0064 ± 0.002
[PtPh$_2$(n-Pr$_2$S)$_2$]	0.356 ± 0.01	0.590 ± 0.1	0.0065 ± 0.003
[PtPh$_2$(i-Pr$_2$S)$_2$]	19.0 ± 0.1	3.74 ± 0.2	0.43 ± 0.3
[PtPh$_2$(n-Bu$_2$S)$_2$]	0.272 ± 0.01	0.602 ± 0.1	0.0017 ± 0.002
[PtPh$_2$(Bz$_2$S)$_2$]	1.25 ± 0.02	0.318 ± 0.01	0.0042 ± 0.003
[PtPh$_2$(MeBzS)$_2$]	0.542 ± 0.02	0.333 ± 0.04	0.006 ± 0.002
[PtPh$_2$(MePhS)$_2$]	17.6 ± 0.2	0.484 ± 0.04	0.94 ± 0.2
[PtPh$_2$(Et$_2$Se)$_2$]	0.601 ± 0.01	0.270 ± 0.02	0.012 ± 0.002

All of these results can be explained by a stepwise mechanism involving dissociation of the starting complex to yield a 14-electron [PtPh$_2$L] intermediate followed by the attachment of bpy to form an open-ring sulfide species, also formed by a parallel associative attack of bpy on cis-[PtPh$_2$L$_2$]. There follows a fast ring closing to yield the observed products.
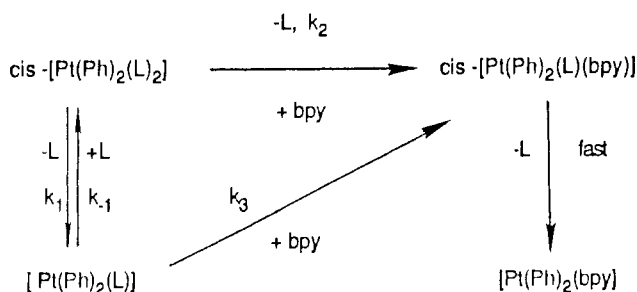
The rate constants are related to the empirical parameters a, b, and c by the expressions $a = k_1$, $b = k_{-1}/k_3$, and $c = k_2$. Values of these rate constants are collected in Table III.

The general pattern of behavior is much the same as that found in our previous studies on strictly similar systems,[8] where the easy dissociation of thioethers or sulfoxides was shown to be due to the strong σ-donor power of the trans Pt–C bond. The assessment of the mechanism in that case has been made essentially on the basis of (i) the mass-law retardation produced by the leaving group, (ii) the independence of the dissociation constant k_1 of the nature of the entering group, (iii) the identity of k_1 with the rate of exchange between coordinated and uncoordinated thioethers or sulfoxides, and (iv) the positive values of the activation entropy as a result of the effect of the temperature on k_1. The solvent is considered to be insufficiently coordinating to give associatively activated rate constants of the observed magnitude. Alternative reaction schemes, involving fast and reversible attack of the chelating ligand on the complex followed by slow release of the sulfide, lead to different forms of the rate law; furthermore, under saturation conditions, such mechanisms imply the formation of considerable amounts of a chelate sulfide species and its presence has not been detected in solution either by ^{1}H NMR spectra or by abstract factor analysis of spectral changes during kinetic runs.

The choice of the nitrogen chelating ligand 2,2'-bipyridine as reagent has been dictated by the need to avoid complications due to possible isomerizations and to limit the associative pathway that becomes dominant in the case of more powerful nucleophiles such as phosphines. The rate data in Table III confirm that the k_2 pathway makes a negligible, if any, contribution to the overall rate, even at the higher nucleophile concentrations. Under these circumstances, it is not possible to search for any correlation between the bimolecular process and the lability of the thioethers. No particular trend is observed along the series of examined complexes in the competition ratio k_3/k_{-1}, which measures the efficiency with which bpy captures the highly reactive three-coordinate intermediate in competition with the leaving sulfide, except for the bulky diisopropyl sulfide, which seems to experience some difficulty in reentering the coordination sphere of the metal.

The dissociation constants k_1 measure the rates at which the thioethers leave the coordination sphere of the metal and can be related to the steric and electronic properties of the leaving group.
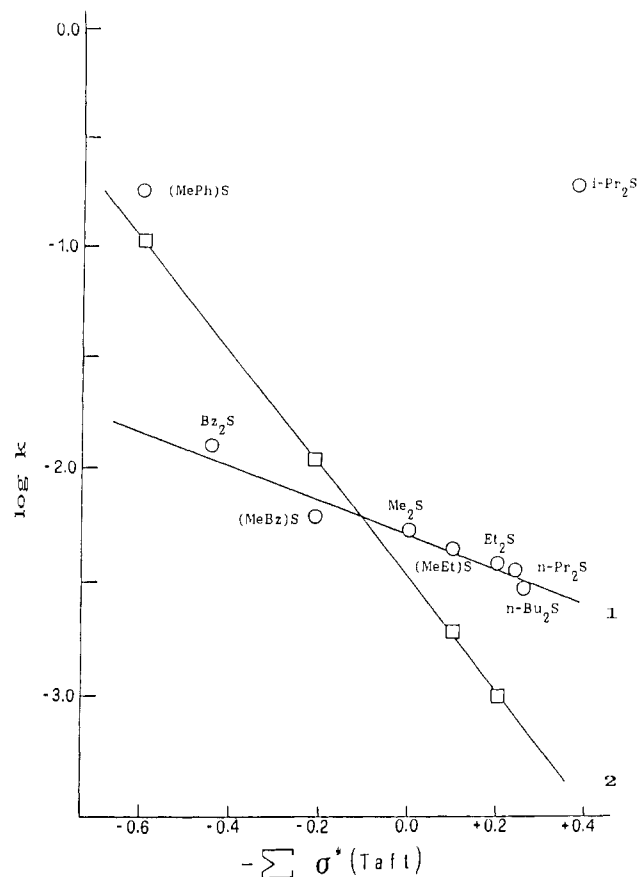
Figure 3. Correlation between lability of thioethers and polar effects of substituents on sulfur, as expressed by the sum of the σ^* values (1) in the dissociation of cis-[PtPh$_2$L$_2$] complexes in CH$_2$Cl$_2$ [log (k_1 (s^{-1}))] and (2) in the bimolecular attack of Cl$^-$ on [Pt(bpy)Cl(L)]$^+$ in MeOH [log (k_2 (M^{-1} s^{-1}))] from ref 22.

Setting apart the data for the complexes with methyl phenyl sulfide and diisopropyl sulfide, it is possible to see that the rates decrease with the increasing electron-donating ability of the substituents, following the sequence of lability Bz$_2$S > MeBzS > Me$_2$S > MeEtS > Et$_2$S > n-Pr$_2$S > n-Bu$_2$S. The overall difference of reactivity is not large, being a factor of 5 between the first and the last members of the series. The value of k_1 for [PtPh$_2$(Et$_2$Se)$_2$] is still in this range of reactivity. Figure 3 shows that these rate data are correlated by a linear free energy relationship of the type $\log k_1 = m\sum\sigma^*$ where $\sum\sigma^*$ is the sum of the Taft σ^* values,[15] which, with some caution,[16,17] are still regarded as good parameters for the inductive effects of the radicals bonded to the sulfur atom, and where m represents the sensitivity of the process to these electronic effects ($m = -0.76$, $R = -0.945$, by linear regression analysis). These facts are consistent with the view that, in the absence of steric effects, the lability of the sulfide is dictated by the amount of electron density transmitted by the substituents to the sulfur and finally by the Pt–S bond strength.

A sharp increase of reactivity with large positive deviations from the plot in Figure 3 is observed when L = i-Pr$_2$S or MePhS. Molecular models show that the branched alkyl groups or phenyl groups directly bonded to sulfur induce a significant amount of steric congestion in the ground state, favoring dissociation. These results can be related to the experimental difficulty in synthesizing cis-[PtPh$_2$(sec-Bu$_2$S)$_2$]. Thus, it is possible to conclude that the dissociation of these mixed phenyl–thioether complexes depends on a combination of steric and polar effects, with the former playing a predominant role.
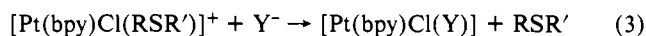
(15) Taft, R. W. *Steric Effects in Organic Chemistry*; Newman, M. S., Ed.; John Wiley: New York, 1956.

(16) MacPhee, J. A.; Dubois, J. E. *Tetrahedron Lett.* **1976**, 2471; **1978**, 2225.

(17) Charton, M. *J. Am. Chem. Soc.* **1977**, *99*, 5687.

Thioethers have been widely used in reactions with platinum(II) complexes for systematic studies of the way in which the nucleophilicity of the ligands depends on the nature of the organic groups attached to the donor atom (S). When the steric effect is held constant, as in the reactions of [Pt(pyridine)$_2$Cl$_2$] with 4,4'-substituted diphenyl sulfides,[18] a marked dependence of nucleophilicity upon the inductive effect is observed. The same effect is seen in the reactions of [Pt(bpy)(C)X][19] (C and X are anionic ligands, X being the one that is displaced), while detailed studies on [Pd(dien)(H$_2$O)]$^{2+}$ [20] and [Pt(dien)Br]$^+$ [21] (dien = 1,5-diamino-3-azapentane) have revealed the importance of steric effects as compared to inductive effects. This duality of behavior has been utilized to gain information about the intimate mechanism that implies asynchronysm in the formation of the new bond and the breaking of the old one and the presence of two maxima separated by a minimum (corresponding to a transient five-coordinate intermediate) in the energy profile. The interpretation for the cases in which the rate is sensitive to substituent effects was that, in contrast with the most obvious conclusion, the second maximum (bond breaking) is the rate-determining transition state.[21]

Comparatively very few studies have been reported on the displacement of thioethers coordinated to platinum(II) complexes, perhaps because of the difficulty in synthesizing the starting materials. Cattalini et al.[22] have studied the reaction

$$[\text{Pt(bpy)Cl(RSR')}]^+ + Y^- \rightarrow [\text{Pt(bpy)Cl(Y)}] + RSR' \qquad (3)$$

Y = Cl$^-$, Br$^-$, I$^-$; RSR' = Et$_2$S, MeEtS, MePhS, MeBzS

There is a decrease of reactivity, expressed in terms of log k_2 (second-order rate constant), as the σ-donor ability of the thioethers, measured in terms of $\sum\sigma^*$, increases. The plot of the rate data for Cl$^-$ as entering group reported in Figure 3 is a straight line with $m = -2.51$ and $R = -0.999$, and the comparison of the two plots indicates, rather unexpectedly, that an associative process, with the second maximum in the reaction profile of higher energy (an A mechanism, according to the terminology of Langford and Gray[1]), is by far more sensitive to the effect of the nature of the leaving group than a dissociative process (D mechanism).

The first conclusion to be drawn is that the extent to which the nature of the leaving group affects the reactivity of a process cannot be used as the only guide to assess the nature of the mode of activation. Indeed, an associative process in which the dissociation of the five-coordinate intermediate is rate determining appears to be more dependent on the nature of the leaving group than the dissociation of a four-coordinate square-planar complex into a three-coordinate intermediate. In such an asynchronous mechanism (see Figure 4a) the leaving group is thought to remain as firmly bonded in the five-coordinate intermediate as it was in the original square-planar complex, and if there is a considerable amount of bond breaking in reaching the transition state, this is reflected in a great sensitivity of the process to leaving group effects
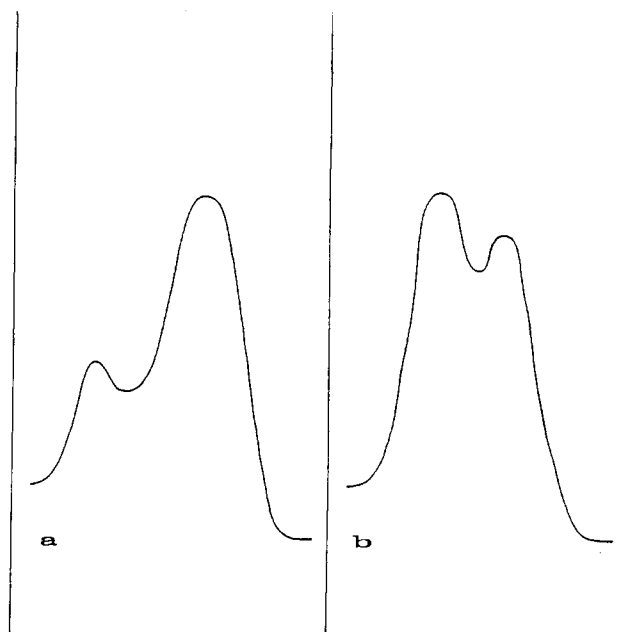
(18) Gaylor, J. R.; Senoff, C. V. *Can. J. Chem.* **1971,** *49,* 2390.
(19) Cattalini, L.; Martelli, M.; Kirschner, G. *Inorg. Chem.* **1968,** *7,* 1488.
(20) Jones, T. E.; Cole, J. R.; Nusser, B. J. *Inorg. Chem.* **1978,** *17,* 3680.
(21) Bonivento, M.; Canovese, L.; Cattalini, L.; Marangoni, G.; Michelon, G.; Tobe, M. L. *Inorg. Chem.* **1983,** *22,* 802.
(22) Cattalini, L.; Marangoni, G.; Degetto, S.; Brunelli, M. *Inorg. Chem.* **1971,** *10,* 1545.

Figure 4. Energy profiles for (a) reaction 3 and (b) reaction 1.

as found for reaction 3. In contrast, if the bond is partially broken in the ground state, little help is needed to break it fully in a D transition state. This is a further reminder that an unquestioning use of LFER relationships of this sort to determine the molecularity of substitution reactions is dangerous and can be misleading.

The low discrimination of reactivity observed within the series of substrates examined suggests that the differences in the bond strength between the metal and the various leaving groups in the ground state are very little. It would be interesting at this stage to be able to make a comparison of structural data within a series of closely related platinum–thioether compounds. A survey of the little diffraction data in the literature suggests that only under the strong trans-activating influence of the phenyl group is the platinum–thioether bond greatly lengthened and weakened (Alibrandi et al.[8]). Under these circumstances, electronic effects arising from changes in the nature of the thioethers within the series of cis-[PtPh$_2$L$_2$] complexes are expected to produce small effects on the Pt–S bond and consequently to play a minor role in the lability of thioethers.