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Dissociative Substitution in Four-Coordinate Planar Platinum(II) Complexes. 2. Crystal Structure of *cis*-Diphenylbis(dimethyl sulfide)platinum(II) and Kinetics of Thioether Displacement by Bidentate Ligands in Benzene

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A single-crystal X-ray diffraction study has confirmed the cis geometry of $[Pt(C_6H_5)_2((CH_3)_2S)_2]$. $C_{16}H_{22}S_2Pt$ (M_r 473.56) crystallizes in the space group $P2_1/n$ with cell constants of $a = 14.026$ (2) Å, $b = 10.186$ (1) Å, $c = 11.902$ (1) Å, $\alpha = 90°$, $\beta = 96.88$ (3)°, $\gamma = 90°$, $V = 1688.2$ Å^3, and $d = 1.86$ g cm^{-3} calculated for $Z = 4$. The phenyl groups exert a marked trans influence, the Pt–S bonds (2.370 (2) and 2.389 (2) Å) being among the longest reported for a Pt(II) complex with a tetrahedral sulfur donor. The kinetics of the reaction *cis*-$[Pt(Ph)_2(Me_2S)_2]$ + L-L → $[Pt(Ph)_2(L\text{-}L)]$ + $2Me_2S$ (L-L = 2,2′-bipyridine, 2,2′-bipyrimidine, 1,10-phenanthroline, 1,2-bis(diphenylphosphino)ethane, 1,3-bis(diphenylphosphino)propane, 1,2-bis(phenylthio)ethane) have been followed spectrophotometrically in benzene in the presence of a sufficient excess of L-L and Me_2S to ensure pseudo-first-order kinetics. The first-order rate constant obeys the relationship $k_{obsd} = k_1[\text{L-L}]\{(k_{-1}[Me_2S]/k_3) + [\text{L-L}]\}^{-1} + k_2[\text{L-L}]$, which is of the same form as that for the analogous reactions of the *cis*-$[Pt(Ph)_2(Me_2SO)_2]$ complex for which a similar dissociative mechanism together with an associative pathway for the entry of P and S donor ligands has been proposed. The data for the bis(sulfoxide) complex have been extended, and the two substrates are compared. It is concluded that the dissociative mechanism is a consequence of the trans influence of the two cis phenyl groups and not the result of internal substitution by the oxygen of the sulfoxide. The three-coordinate intermediate formed by loss of Me_2S is significantly less discriminating than that derived from the bis(sulfoxide) complex.

Introduction

There is a great deal of interest in the preparative chemistry of transition-metal complexes, especially those of platinum and palladium, containing weak donor ligands, such as nitriles, dialkyl sulfides, sulfoxides, olefins or, more generally, coordinated solvent molecules.[1-4] Part of this interest lies in the fact that these species, because of the enhanced reactivity due to the labile metal–ligand interaction, are useful starting materials for the facile synthesis of organometallic and coordination compounds. In addition, there is an inherent interest in their role as potentially reactive intermediates in homogeneous catalytic processes, where coordinative unsaturation by the metal is thought to be a prerequisite for the occurrence of the process. Comparatively, very few kinetic studies have been performed in this field.

We have been interested in the study of the lability of sulfur-bonded dimethyl sulfoxide in some platinum(II) substrates. While a single Me_2SO, as in $[Pt(dien)Me_2SO]^{2+}$ (dien = 1,5-diamino-3-azapentane),[5] is reasonably inert, it is easily displaced in the presence of another Me_2SO coordinated as in $[Pt(en)(Me_2SO)_2]^{2+}$ (en = 1,2-diaminoethane).[6] This strong mutual labilization of two sulfoxides even when cis, which had already been seen in other bis(sulfoxide)platinum(II) complexes,[7,8] was thought to be due to a peculiar stabilization of the five-coordinate intermediate in an A-type reaction, rather than to unusual nonbonding interactions or steric repulsions in the ground state. When the study was extended to the kinetics of sulfoxide exchange and displacement by bidentate ligands in *cis*-$[Pt(Ph)_2(Me_2SO)_2]$ in inert solvents, we found unequivocal experimental evidence for Me_2SO dissociation as dominant step in the substitution.[9] This was the first clear-cut example of a facile dissociative mechanism in substitution reactions of square-planar d^8 complexes. Whether the promotion of a dissociative pathway was due only to ground-state destabilization through the σ-donor trans influence of the aryl groups as seen in the Pt–S bond lengthening, or was assisted by stabilization of the coordinatively unsaturated 14-electron $[Pt(Ph)_2Me_2SO]$ intermediate through electron donation to the metal by the oxygen of the remaining Me_2SO molecule, remained to be clarified.

Thus we compare in this paper the kinetic behavior of *cis*-$[Pt(Ph)_2(Me_2SO)_2]$ with that of the thioether analogue *cis*-$[Pt(Ph)_2(Me_2S)_2]$, where only inductive effects from the phenyl groups are expected to operate. To measure the extent of these effects and to search for any correlation between structure and kinetic behavior, we have grown single crystals of this compound and determined its structure by X-ray analysis.

Experimental Section

(A) Complexes. *cis*-$[Pt(Ph)_2(Me_2S)_2]$. *cis*-$[Pt(Ph)_2(Me_2SO)_2]$ (505 mg, 1 mmol) prepared by the method already described,[9] was dissolved in dimethyl sulfide (10 mL). Addition of *n*-hexane to the solution led to the precipitation of the required compound as white crystals (440 mg), which did not require further recrystallization. Anal. Calcd for $C_{16}H_{22}S_2Pt$: C, 40.6; H, 4.6; S, 13.5. Found: C, 40.5; H, 4.7; S, 13.4.

***cis*-$[Pt(Ph)_2(L\text{-}L)]$.** The synthesis of compounds of this type has been already described in the literature. The diolefin complex $[Pt(Ph)_2(COD)]$ is reacted with 2,2′-bipyridyl (bpy)[10] or *cis*-$[Pt(Ph)_2(Me_2SO)_2]$ with 1,10-phenanthroline (phen),[9] 1,2-bis(diphenylphosphino)ethane (dppe),[4] and 2,2′-bipyrimidine (bpym).[11,12] The thioether is readily displaced from *cis*-$[Pt(Ph)_2(Me_2S)_2]$ by L-L to yield $[Pt(Ph)_2(L\text{-}L)]$, irrespective of the bonding strength of the ligand. In a typical preparative procedure, stoichiometric amounts of the appropriate chelate were added to a concentrated (0.1 mol dm^{-3}) solution of *cis*-$[Pt(Ph)_2(Me_2S)_2]$ in dichloromethane. In those cases in which the product did not precipitate immediately, the solution was set aside for 0.5 h and then treated with diethyl ether or petroleum ether. Compounds with L-L = bpy, phen, dppe, and bpym were prepared together with the new species with 1,3-bis(diphenylphosphino)propane (dppp) and 1,2-bis(phenylthio)ethane (dpte). All the complexes were characterized through elemental analyses, and IR, ^1H NMR, and electronic spectra.

1,2-Bis(phenylthio)ethane was prepared according to the literature method.[13] 1,10-Phenanthroline hydrate was dehydrated by heating

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Table I. Single-Crystal X-ray Crystallographic Analysis

A. Crystal Parameters	
formula	$C_{16}H_{22}S_2Pt$ (M_r 473.56)
color	white transparent
cryst size, mm	0.12 × 0.18 × 0.15
cryst syst	monoclinic
space group	$P2_1/n$
temp, K	295 (1)
cell dimens	
a, Å	14.026 (2)
b, Å	10.186 (1)
c, Å	11.902 (1)
α, deg	90
β, deg	96.88 (3)
γ, deg	90
V, Å^3	1688.2
Z (molecules/cell)	4
d_{calcd}, g cm^{-3}	1.86
radiation	Mo Kα (λ = 0.71069 Å)
μ(Mo Kα), cm^{-1}	86.2
orientation reflcns: no.; range (2θ), deg	20; 15–30
scan method	$\omega-\theta$
data collcn range (2θ), deg	3, 50
B. Refinement Parameters	
total no. of reflcns collcd	4100
no. with $F_o^2 > 3\sigma(F_o^2)$	2580
% decay of stds	>2
std reflcns	$40\bar{6}$, $\bar{2}\bar{5}4$, $\bar{4}\bar{2}6$
data collcd	$\pm h,+k,+l$
R_{int}, F	0.012
no. of params refined	186
R^a	0.028
R_w^a	0.031
largest shift/esd, final cycle	0.005
largest peak final difference map, e/Å^3	0.87

$^a R = [\sum|F_o| - |F_c|]/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

under vacuum for 24 h at 80 °C; mp 117 °C. Other compounds were the best available commercial materials, purified by recrystallization or distillation as necessary.

Infrared spectra were recorded as Nujol mulls on a Perkin-Elmer 783 spectrometer; ^1H NMR spectra were recorded at 80 MHz on a Bruker WP 80 spectrometer with [$^2H_6$]benzene or $CDCl_3$ as solvent and tetramethylsilane as reference.

(B) X-ray Data Collection and Structure Refinement. Diffraction data were collected on a Siemens-Stoe four-circle diffractometer by using graphite-monochromated Mo Kα (λ = 0.71069 Å) radiation. Accurate unit -cell dimensions and crystal orientation matrices were obtained from least-squares refinement of 2θ, ω, χ, and ψ values of 20 strong reflections in the range 15° < 2θ < 34°.

Crystallographic data and other pertinent information are summarized in Table I. Lorentz and polarization corrections were applied to the intensity data. An absorption correction was also applied to the data with use of an empirical method based on ψ scans (ψ = 0–360° every 10°) for χ values near 90°. Seven sets of ψ-scan curves were used with maximum, minimum, and average relative transmission values of 1.00, 0.56, and 0.78, respectively.

The structure was solved by using standard Patterson methods, successive least-squares refinements, and difference Fourier maps. All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were included in the scattering model in calculated idealized positions (d(C-H) = 0.96 Å) with a common thermal parameter.

Of 3800 independent reflections, measured with an ω/θ scan technique in the range $3 < 2\theta < 50$, 2580 having $I > 3\sigma(I)$ were used to refine 186 parameters to final residuals of R = 0.028 and R_w = 0.031.

The weighting scheme used in the last refinement cycles was $w = 1.3117/(\sigma^2(F_o) + 0.000513F_o^2)$.

The anomalous dispersion terms[14] for Pt and S atoms were taken into account in the refinement. Atomic scattering factors for all non-hydrogen atoms were taken from ref 15 and those for hydrogen atoms from ref 16.

Table II. Fractional Coordinates (×10^4) for Non-Hydrogen Atoms

atom	x/a	y/b	z/c
Pt	1560 (1)	2184 (1)	2767 (1)
S(1)	3178 (1)	1954 (2)	2412 (1)
S(2)	2069 (1)	1808 (2)	4729 (2)
C(1)	155 (5)	2390 (7)	3011 (6)
C(2)	−382 (6)	1312 (8)	3339 (7)
C(3)	−1319 (6)	1423 (10)	3515 (7)
C(4)	−1762 (6)	2602 (10)	3421 (7)
C(5)	−1266 (6)	3685 (9)	3106 (7)
C(6)	−316 (5)	3550 (8)	2911 (6)
C(7)	1118 (5)	2444 (7)	1113 (6)
C(8)	875 (5)	1408 (8)	365 (6)
C(9)	640 (5)	1620 (10)	−786 (7)
C(10)	645 (5)	2847 (10)	−1230 (6)
C(11)	869 (6)	3887 (9)	−523 (7)
C(12)	1087 (5)	3680 (7)	612 (6)
C(13)	3507 (6)	3448 (8)	1765 (8)
C(14)	3243 (6)	835 (9)	1264 (7)
C(15)	3150 (8)	2703 (10)	5177 (7)
C(16)	1269 (8)	2645 (12)	5565 (7)

Table III. Bond Lengths (Å), Interbond Angles (deg), and Torsion Angles (deg)

Lengths

Pt–S(1)	2.370 (2)	Pt–S(2)	2.389 (2)
Pt–C(1)	2.036 (7)	Pt–C(7)	2.010 (7)
S(1)–C(13)	1.790 (8)	S(2)–C(15)	1.795 (10)
S(1)–C(14)	1.791 (8)	S(2)–C(16)	1.800 (10)
C(1)–C(2)	1.413 (10)	C(7)–C(8)	1.396 (10)
C(2)–C(3)	1.360 (11)	C(8)–C(9)	1.387 (11)
C(3)–C(4)	1.351 (13)	C(9)–C(10)	1.357 (13)
C(4)–C(5)	1.379 (13)	C(10)–C(11)	1.366 (12)
C(5)–C(6)	1.386 (10)	C(11)–C(12)	1.365 (10)
C(6)–C(1)	1.352 (11)	C(12)–C(7)	1.391 (10)

Angles

S(1)–Pt–S(2)	88.7 (1)	C(7)–Pt–C(1)	86.3 (3)
S(1)–Pt–C(7)	91.6 (2)	S(2)–Pt–C(1)	93.4 (2)
S(1)–Pt–C(1)	177.9 (2)	S(2)–Pt–C(7)	178.3 (2)
Pt–S(1)–C(13)	107.1 (3)	Pt–S(2)–C(15)	110.6 (3)
C(14)–S(1)–C(13)	100.0 (4)	C(15)–S(2)–C(16)	98.9 (4)
Pt–S(1)–C(14)	109.6 (3)	Pt–S(2)–C(16)	109.3 (3)
C(13)–S1–C(14)	100.0 (4)	C(15)–S2–C(16)	98.9 (5)
Pt–C(1)–C(2)	121.1 (6)	Pt–C(7)–C(8)	123.2 (5)
Pt–C(1)–C(6)	123.3 (6)	Pt–C(7)–C(12)	121.9 (5)
C(1)–C(2)–C(3)	122.4 (8)	C(7)–C(8)–C(9)	121.5 (8)
C(2)–C(3)–C(4)	120.2 (8)	C(8)–C(9)–C(10)	121.1 (8)
C(3)–C(4)–C(5)	119.5 (7)	C(9)–C(10)–C(11)	119.0 (7)
C(4)–C(5)–C(6)	119.5 (8)	C(10)–C(11)–C(12)	119.9 (8)
C(5)–C(6)–C(1)	122.8 (8)	C(11)–C(12)–C(7)	123.7 (7)
C(6)–C(1)–C(2)	115.5 (7)	C(12)–C(7)–C(8)	114.7 (6)

Torsion Angles

C(7)–Pt–S(1)–C(14)	−47.5 (4)
C(7)–Pt–S(1)–C(13)	60.0 (4)
C(1)–Pt–S(2)–C(15)	−136.9 (4)
C(1)–Pt–S(2)–C(16)	−29.0 (4)
S(1)–Pt–C(7)–C(8)	87.4 (6)
S(2)–Pt–C(1)–C(2)	−68.1 (6)

All calculations were performed with the SHELX76[17] and PARST[18] sets of programs on the IBM 4341 computer of the Centro di Calcolo dell'-Università di Messina. The refined structure was plotted with use of the ORTEP program (Figure 1). Hydrogen coordinates, anisotropic temperature factors, and calculated and observed structure factors are available as supplementary material (Tables SI–SIII). Non-hydrogen coordinates are shown in Table II. Interatomic distances and their standard deviations, bond angles and esd's, and relevant torsion angles are given in Table III. Some least-squares planes and distances of atoms to the plane are listed in Table IV.

(C) Kinetics. The kinetics of the substitution reactions of *cis*-[Pt(Ph)$_2$(Me$_2$S)$_2$] in benzene solution were carried out in a silica cell in the thermostated cell compartment of a double-beam Perkin-Elmer Lambda

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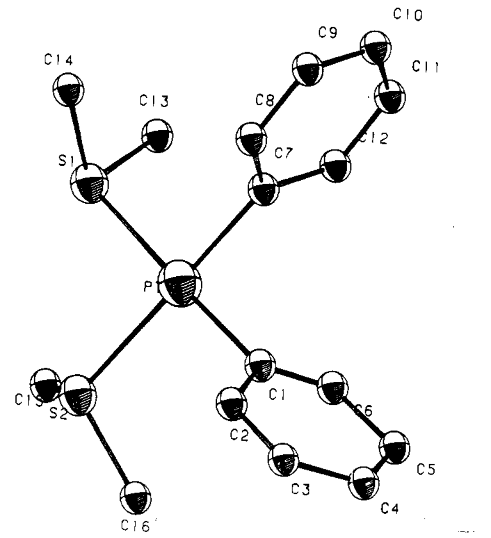

Figure 1. ORTEP drawing of the [Pt(Ph)$_2$(Me$_2$S)$_2$] molecule.

Table IV. Least-Squares Planes[a]

Plane 1: S(1)–S(2)–C(7)–C(1)–Pt
$-0.1228X - 0.9829Y - 0.1369Z = -2.8522$
[S(1), −0.0001; S(2), 0.0036; C(7), 0.0520; C(1), −0.0012; Pt, −0.0020; C(13), −1.4585; C(14), 1.275; C(15), −1.1434; C(16), −0.8168]

Plane 2: C(1)–C(2)–C(3)–C(4)–C(5)–C(6)
$-0.1824X - 0.1968Y - 0.9633Z = -3.8697$

Plane 3: C(7)–C(8)–C(9)–C(10)–C(11)–C(12)
$0.9864X - 0.0992Y - 0.1309Z = 0.9610$

Angles (deg) between Planes

1–2	69.7 (2)	1–3	90.3 (2)	2–3	92.0 (4)

[a] Deviations of relevant atoms from the plane (Å) are given in square brackets.

5 or a Cary 219 spectrophotometer, with the temperature held constant to within ±0.05 °C. A solution of all the reagents except the complex was brought to the reaction temperature, and the reaction was started by adding a weighed amount of a finely powdered sample of the complex and shaking the solution rapidly. In all cases at least a 10-fold excess of nucleophile with respect to the complex was used. The rate constants k_{obsd} were obtained either from the slopes of the plots of $-\ln (A_\infty - A_t)$ against time (A_t and A_∞ are the absorbances of the solution at time t and at the end of the reaction, respectively) or from a nonlinear least-squares fit of the experimental A vs. t data to the expression $A_t = A_\infty + (A_0 - A_\infty) \exp(-k_{obsd}\ t)$, with A_0 (the absorbance a $t = 0$), A_∞, and k_{obsd} as parameters to be optimized. Activation parameters were derived from a nonlinear fit of k/T vs. T data according to the Eyring equation.

Results

The synthesis of mixed thioether–σ-carbon ligand platinum(II) complexes by reaction of dihalo complexes with aryllithium compounds has been already reported.[19,20] When both halides are displaced, dimeric [Pt$_2$Ph$_4$(μ-SR$_2$)$_2$] or a mixture of dimeric and monomeric [Pt(Ph)$_2$(R$_2$S)$_2$] species can be formed, depending on the geometry of the starting dihalo complex and the experimental conditions. Monomeric species can also be obtained by bridge splitting reactions of R$_2$S on binuclear complexes. Our method of synthesizing *cis*-[Pt(Ph)$_2$(Me$_2$S)$_2$], as described above, taking advantage of the lability of Me$_2$SO in the starting bis(sulfoxide) compound, is more convenient.

(A) Description of the Structure. The single-crystal X-ray diffraction analysis shows, as expected, that the two thioethers are cis to each other. As shown in Figure 1, the structure of *cis*-[Pt(Ph)$_2$(Me$_2$S)$_2$] is made up of discrete molecules separated by ordinary van der Waals distances. The coordination around the Pt atom is square planar. The least-squares plane through the five atoms of the coordination sphere (Table IV) indicates that this portion of the molecule slightly deviates from planarity. As is evident from the C–Pt–S–C torsion angles (Table III), the Me$_2$S molecules adopt a different orientation with respect to the coordination plane; the phenyl rings are tilted from the coordination plane by 69.7 (2) and 90.3 (2)°, being rotated by 92.0 (4)° to each other. The Pt–S–C and C–S–C angles (109–100°) leave no doubt that both sulfur atoms are in an approximate tetrahedral environment, as those of the corresponding bis(sulfoxide) complex.[21] The C–C ring and S–C distances do not differ significantly from the expected values (mean 1.38 and 1.794 Å). No significant difference is found in the Pt–C bond lengths (2.036 (7) and 2.010 (7) Å), which are in the range of values found for these distances in other aryl complexes of platinum(II).[22] The observed Pt–S distances of 2.370 (2) and 2.389 (2) Å differ slightly, the longer being adjacent to the ring that is tilted towards the Me$_2$S molecule, and are significantly longer than the sum of the single-bond radii (2.35 Å). To our knowledge, these Pt–S bond distances are the longest that have been recorded so far for platinum(II) complexes with coordinated tetrahedral sulfur atoms.

(B) Behavior in Solution. The ^{1}H NMR spectrum of pure *cis*-[Pt(Ph)$_2$(Me$_2$S)$_2$] in CDCl$_3$ contains the expected resonances of the phenyl groups together with a single peak at δ 2.09 (12 H) with ^{195}Pt satellites ($^3J_{^{195}\mathrm{Pt}-^1\mathrm{H}}$ = 23.6 Hz) due to coordinated dimethyl sulfide protons. This low value of the coupling constant leaves no doubt that the cis stereochemistry seen in the solid state is maintained in solution, with a dimethyl sulfide trans to each phenyl group. There is also evidence for some dissociation of the compound according to the equilibrium

$$2[\mathrm{Pt(Ph)_2(Me_2S)_2}] \rightleftarrows [\mathrm{Pt_2(Ph)_4(\mu\text{-}SMe_2)_2}] + 2\mathrm{Me_2S} \quad (1)$$

in the presence of a single peak at δ 2.14 due to free Me$_2$S in an intensity ratio of 1:14 with respect to the coordinated molecule and a multiplet with a main resonance at δ 2.73, which could be due to the bridging Me$_2$S ligands in the binuclear species.[23] No attempts have been made to investigate the system further since, upon addition of small amounts of Me$_2$S in solution, only the NMR signals due to *cis*-[Pt(Ph)$_2$(Me$_2$S)$_2$] and Me$_2$S are seen in the spectrum. Thus the presence of an excess of Me$_2$S during the kinetic runs ensures the stability of the starting material. An equilibrium such as that in eq 1 has been already described by Puddephatt[24] for the related *cis*-[Pt(Me)$_2$(Me$_2$S)$_2$] complex, which, unlike the phenyl derivative, cannot be isolated as pure compound and can be obtained only in solution by adding a sufficient amount of Me$_2$S to the binuclear [Pt$_2$Me$_4$(μ-SMe$_2$)$_2$] species. *cis*-[Pt(Ph)$_2$(Me$_2$S)$_2$] exhibits the same behavior in [^{2}H$_6$]benzene, where the peak due to coordinated Me$_2$S can be found at δ 1.60 with definite satellites due to coupling with ^{195}Pt ($^3J_{^{195}\mathrm{Pt}-^1\mathrm{H}}$ = 23.6 Hz).

When approximately equimolar solutions of complex and of the chelate L-L ligands in [^{2}H$_6$]benzene are mixed, the signal at δ 1.60 assigned to coordinated Me$_2$S protons vanishes, changing from a triplet to a singlet at δ 1.74 characteristic of the free ligand. The other signals in the NMR spectrum are due to the reaction product [Pt(Ph)$_2$(L-L)], and there is no evidence for the buildup in solution of any other species containing Me$_2$S coordinated to the metal. When an excess of complex over the ligand L-L is used, NMR signals due to *cis*-[Pt(Ph)$_2$(Me$_2$S)$_2$], *cis*-[Pt(Ph)$_2$(L-L)], and free Me$_2$S are observed.

The spectral properties of the [Pt(Ph)$_2$(L-L)] products do not deserve particular comment except those of the complexes in which L-L = 2,2′-bipyrimidine and 1,2-bis(phenylthio)ethane, which, for reasons of solubility, need to be measured in [^{2}H$_1$]chloroform

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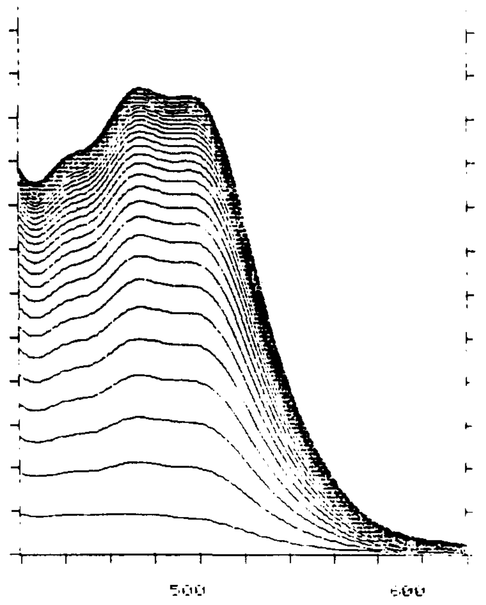

Figure 2. Spectral changes observed during the displacement of Me_2S from *cis*-$[Pt(Ph)_2(Me_2S)_2]$ by 2,2′-bipyrimidine in benzene at 303.2 K: [bpym] = 0.005 M; $[Me_2S]$ = 0.0025 M; rate of scanning, 40 s.

solution. Bipyrimidine can function as a bidentate ligand on a single metal to form mononuclear species or as a bridging ligand between two metal centres to give binuclear species. Compounds of the type $[Pt(Ph)_2(bpym)]$ and $[Pt_2(Ph)_4(\mu\text{-}bpym)]$ have been prepared and fully characterized through elemental analyses and IR, NMR, and electronic spectra.[12] The ^1H NMR resonances of the product that is formed from the reaction of *cis*-$[Pt(Ph)_2(Me_2S)_2]$ with bpym are perfectly in line with those reported for the mononuclear $[Pt(Ph)_2(bpym)]$ species. The same conclusion can be drawn from the electronic spectra of the reaction (Figure 2).

The ^1H NMR spectrum of $[Pt(Ph)_2(PhSC_2H_4SPh)]$ at room temperature, apart from the resonances of the phenyl protons, shows a 1:4:1 triplet at δ 3.00 ($^3J_{^{195}Pt-^1H}$ = 17 Hz) due to the protons of the bridging carbon atoms. Such a simple first-order spectrum is expected only if inversion at sulfur is rapid and the methylene protons are equivalent.[25]

(C) Spectrophotometric Kinetic Studies. The rates of the reaction

$$cis\text{-}[Pt(Ph)_2(Me_2S)_2] + L\text{-}L \rightarrow [Pt(Ph)_2(L\text{-}L)] + 2Me_2S \quad (2)$$

in benzene solution were followed by repetitive scanning in the visible and near-UV regions of the spectrum. The reactions, carried out in the presence of at least a 10-fold excess of chelate and a 20-fold excess of Me_2S over complex, went to completion, the final spectrum being identical with that of an independently synthesized authentic sample of $[Pt(Ph)_2(L\text{-}L)]$. The reactions with bpy, bpym, and phen were followed in the wavelength range 400–600 nm, where the absorbance due to the substrate is negligible. Abstract factor analysis[26] of the spectral changes like those in Figure 2 has shown the presence of only one absorbing species in solution, viz. the chelate product. Thus there is no indication of the presence of significant amounts of any intermediate species. As was found in the study of the bis(sulfoxide) complex,[9] mass-law retardation by the released sulfide produced significant deviations from linearity in the plots of ln $(A_\infty - A_t)$ against time, especially at the lowest concentrations of L-L. By adding at least a 20-fold excess of Me_2S with respect to the complex the concentration of sulfide remains constant throughout the reaction and the rate constants k_{obsd} (s^{-1}) can be obtained precisely from the slope of these linear semilogarithimic plots. The reactions with dpte, dppe, and dppp were followed in a similar way, in the wavelength range 300–400 nm where the reagents also absorb.

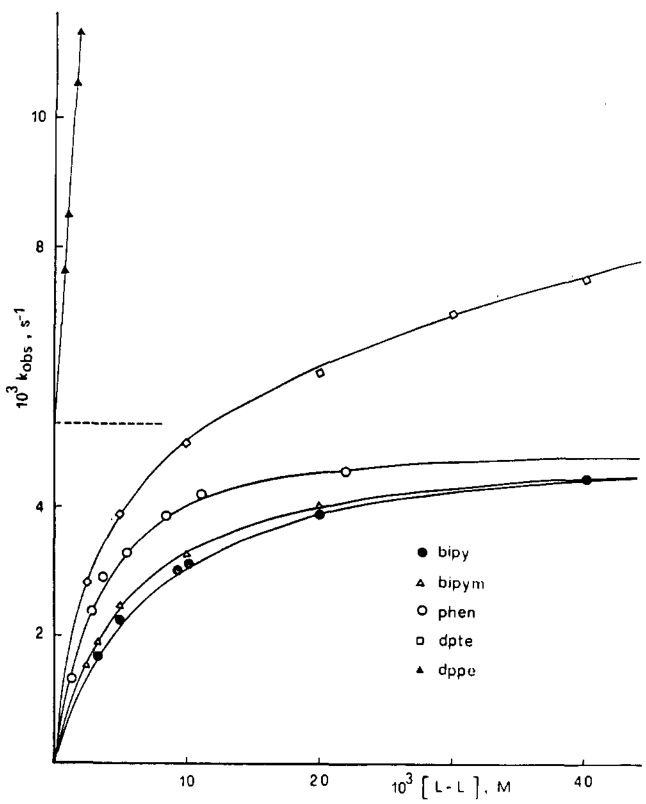

Figure 3. Dependence of the pseudo-first-order rate constants k_{obsd} (s^{-1}) on the concentration of the entering ligand for the reaction of *cis*-$[Pt(Ph)_2(Me_2S)_2]$ with various reagents at 303.2 K in benzene solution. $[Me_2S]$ = 0.005 M.

The values of the pseudo-first-order rate constants observed (k_{obsd}/s^{-1}) and calculated (k_{calcd}/s^{-1}) for the reactions of *cis*-$[Pt(Ph)_2(Me_2S)_2]$ are available as supplementary material (Table SIV). The reactions of *cis*-$[Pt(Ph)_2(Me_2SO)_2]$ with bpym, dpte, and dppp were also studied in order to extend the previously reported data and to make a proper comparison with the kinetic behavior of the bis(sulfide)species. The kinetics were followed essentially by the procedure described above, and the values of k_{obsd} (s^{-1}) and of k_{calcd} (s^{-1}) are available as supplementary material (Table SV).

Discussion

The kinetic study was carried out in benzene and followed spectrophotometrically. The electronic and ^1H NMR evidence clearly indicates that the changes that are observed and kinetically analyzed correspond to the reaction 2. The conversion of the substrate into the product is seen as a single process, the act of ring closing being much faster than the displacement of the first sulfide. The reactions with the nitrogen chelates bpy, bpym, and phen exhibit typical saturation kinetics in that, at high concentrations of ligand, the rate constants become independent of [L-L] (see Figure 3). Thus, for any nitrogen chelate, the dependence of the rate constant on [L-L], at various concentrations of added Me_2S, is described by a series of curves whose curvature is less marked and whose "saturation" is more held back as the concentration of sulfide increases. Plots of k_{obsd}^{-1} against $[L\text{-}L]^{-1}$, at constant $[Me_2S]$, gave a family of straight lines with a finite intercept, independent of $[Me_2S]$, and slopes proportional to $[Me_2S]$.

The form of the rate law that can be derived

$$k_{obsd} = a[L\text{-}L]/(b[Me_2S] + [L\text{-}L]) \quad (3)$$

is identical with that already found for the reactions of *cis*-$[Pt(Ph)_2(Me_2SO)_2]$ with bpy and phen and is still valid for the reaction of this substrate with bpym. When *cis*-$[Pt(Ph)_2(Me_2S)_2]$ reacts with chelates having sulfur and phosphorus donor atoms,

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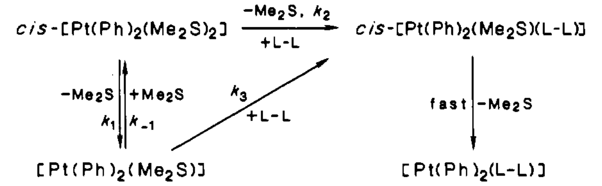
Table V. Derived Rate Constants for the Reactions *cis*-$[Pt(Ph)_2(X)_2]$ + L-L → $[Pt(Ph)_2(L\text{-}L)]$ + 2X in Benzene as Solvent

	X = Me_2S			X = Me_2SO		
L-L	$10^2k_1/s^{-1}$	k_3/k_{-1}	$k_2/(mol^{-1}\ dm^3\ s^{-1})$	$10^2k_1/s^{-1}$	k_3/k_{-1}	$k_2/(mol^{-1}\ dm^3\ s^{-1})$
bpy[a]	0.064 ± 0.003	0.70 ± 0.1	0			
bpy[b]	0.13 ± 0.01	0.68 ± 0.01	0	0.83 ± 0.03	0.021 ± 0.002	0[e]
bpy[c]	0.29 ± 0.01	0.65 ± 0.03	0	1.36 ± 0.02	0.033 ± 0.003	0[e]
bpy[d]	0.53 ± 0.01	0.68 ± 0.05	0	1.40 ± 0.10	0.049 ± 0.007	0[e]
bpym[d]	0.51 ± 0.02	0.92 ± 0.05	0	2.30 ± 0.02	0.092 ± 0.001	0.122 ± 0.001
phen[d]	0.53 ± 0.01	1.43 ± 0.1	0	2.00 ± 0.03	0.26 ± 0.01	0[e]
dpte[d]	0.60 ± 0.01	1.65 ± 0.23	0.052 ± 0.001	2.50 ± 0.01	0.21 ± 0.01	0.263 ± 0.002
dppe[d]	0.47 ± 0.01	0.89 ± 0.01	3.87 ± 0.01	2.00 ± 0.01	5.60 ± 0.8	10.0 ± 0.7[e]
dppp[d]	0.59 ± 0.01	0.77 ± 0.01	2.64 ± 0.01	1.90 ± 0.01	1.71 ± 0.01	9.32 ± 0.01

[a] At 288.2 K. [b] At 293.2 K. [c] At 298.2 K. [d] At 303.2 K. [e] From ref 9.

Scheme I



especially with dppe and dppp, the rates are significantly faster thn those with the nitrogen chelates, and the k_{obsd} vs. [L-L] curves tend to become linear and independent of $[Me_2S]$ as [L-L] increases. It can be easily shown by a graphical analysis that the higher rates and the departure from saturation kinetics for these ligands arise from an additional term that has a first-order dependence on [L-L]. Thus, a common rate law is derived with

$$k_{obsd} = a[\text{L-L}]/(b[Me_2S] + [\text{L-L}]) + c[\text{L-L}] \quad (4)$$

The best values of the constants *a*, *b*, and *c*, together with their standard deviations, were obtained by multiple nonlinear regression of k_{obsd} vs. [L-L] and $[Me_2S]$ dependencies. Again, the reactions of the bis(sulfoxide) complex with dpte and dppp fit eq 4.

All this evidence can be accommodated by reaction Scheme I, which implies the dissociative loss of Me_2S from the substrate in the k_1 path to yield a 3-coordinate 14-electron intermediate. This can be trapped either by the reentry of Me_2S in the k_{-1} path or by the competitive attachment of L-L via k_3 to form an open-ring sulfide species, also formed by a parallel associative attack of L-L on the starting complex (k_2 path). There follows a fast ring closing to yield the observed products. For this reaction sequence, assuming that [L-L] and $[SMe_2]$ are large compared to [complex], the observed first-order rate constant is given by the relationship

$$k_{obsd} = k_1[\text{L-L}]/((k_{-1}/k_3)[Me_2S] + [\text{L-L}]) + k_2[\text{L-L}]$$

which is of the form described in eq 4, with $a = k_1$, $b = k_{-1}/k_3$ and $c = k_2$. Values of k_1, k_2 and k_3/k_{-1} for the reactions of *cis*-$[Pt(Ph)_2(SMe_2)_2]$ and *cis*-$[Pt(Ph)_2(Me_2SO)_2]$ are collected in Table V.

An alternative reaction scheme, involving fast and reversible attack of one end of the chelate on the substrate followed by slow ring closing, leads to a rate law similar to that which is operative in the case of the nitrogen chelates (eq 3) but does not account for the additional term *c*[L-L], which appears in the more general form of the rate law (eq 4). Furthermore such a mechanism requires that under forcing conditions ([L-L] >> $[Me_2S]$) a considerable amount of the starting complex would be rapidly transformed into the monodentate sulfide species, and its presence has not been detected in solution either by ^1H NMR spectra or by abstract factor analysis of spectral changes during kinetic runs.

Associative attack by the solvent in the k_1 path and competition between the leaving sulfide and the entering chelate for a solvento intermediate would also lead to a rate law of the above form, which indeed has been occasionally found in some substitution reactions of square-planar d^8 complexes.[27] However, it seems most unlikely that solvolysis can make a significant contribution in a poor coordinating solvent such as benzene. For most of the reagents studied the reaction takes place exclusively through the nucleophile independent pathway, and this path still makes a major contribution to the overall process in the reactions of powerful nucleophiles such as the phosphine ligands dppe and dpp.

As expected for a dissociative mechanism, the value of k_1 is constant and independent of the nature of L-L, being centered at (0.54 ± 0.05) × 10^{-2} s^{-1} at 30 °C. The temperature dependence of k_1 in the reaction of *cis*-$[Pt(Ph)_2(Me_2S)_2]$ with bipyridyl gives $\Delta H^‡ = 100.7 \pm 2.9$ kJ mol^{-1} and $\Delta S^‡ = +42 \pm 8$ J mol^{-1} K^{-1}. These values of the activation parameters, especially the positive entropy of activation, are perfectly in keeping with the assumption of a dissociative loss of Me_2S from the substrate in the rate-determining step. There are a number of examples of substitution reactions of square-planar platinum(II) complexes where the rate of substitution is completely controlled by solvolysis.[28] There, for various reasons, e.g. steric hindrance of the substrate and/or reagents, metal–ligand bond weakening, and high solvent nucleophilicity, the contribution from the reagent-dependent pathway can become too small to be noticed. In all these cases the activation remains associative, as indicated by low enthalpies and largely negative entropies of activation and, in some cases, by negative volumes of activation.[29]

In searching for reasons for the easy promotion of a dissociative mechanism in this organometallic substrate, it should be realized that a thioether does not offer any particular anomaly with respect to the normal associative mode of activation in its role as entering, leaving, or trans-activating group in classical coordination compounds of platinum(II). Reactivity is dominated by its σ-donor ability in the displacement of anionic ligands from *trans*-$[PtCl_2(py)_2]$[30] or from [Pt(bpy)XY] complexes[31] as well as its lability in the reverse reaction,[32] while Me_2S is reported to exert a modest trans effect that is smaller than that of sulfoxides, arsines, or phosphines in the reactions of $[Pt(L)Cl_3]^-$ complexes with amines.[27-33]

The facile dissociation of *cis*-$[Pt(Ph)_2(Me_2S)_2]$ derives essentially from the strong σ-donor power of the phenyl group, which lengths and weakens the platinum–thioether bond. The average value of the Pt–S bond distance calculated from the diffraction data (Table III) is 2.379 (10) Å. There are few structural data in the literature for related platinum–thioether compounds.[1] Perhaps the most comparable structure is that of *cis*-$[PtCl_2(S(4\text{-}ClC_6H_4)_2)_2]$[34] where the mean Pt–S distance is 2.285 (7) Å. Thus when Cl is replaced with Ph as the trans-activating group the Pt–S(thioether) bond distance is lengthened by 0.1 Å, which is essentially the same amount as is found for the Pt–S(sulfoxide) distance when the values for *cis*-$[PtCl_2(Me_2SO)_2]$[35] (Pt–S =

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2.236(2) Å) and for *cis*-$[Pt(Ph)_2(Me_2SO)_2]$[21] (Pt–S = 2.319 (2) Å) are compared. At this stage is worth noting that both *cis*-$[PtCl_2(Me_2SO)_2]$[8b] an *cis*-$[PtCl_2(Me_2S)_2]$[36] undergo substitution through the normal associative pathway, even though the bis(sulfoxide) complex exhibits an enhanced reactivity due to the mutual labilization of a pair of sulfoxides.

In the solid state the phenyl rings of *cis*-$[Pt(Ph)_2(Me_2S)_2]$ are tilted from the coordination plane by 69.7 (2) and 90.3 (2)°. This circumstance might suggest that steric hindrance from the ligands could be a contributory factor in preventing the approach of bulky chelates to the metal. In fact there are indications that such a steric hindrance plays a negligible role, since Puddephatt[24] has shown that easy dissociation of Me_2S from *cis*-$[PtMe_2(Me_2S)_2]$ is a preliminary step in the latter's reaction with *cis*- or *trans*-$[PtCl_2(Me_2S)_2]$ to give *trans*-$[PtClMe(Me_2S)_2]$ as the sole product. An analysis of the kinetic data gave a value of $k_1 = 9 \times 10^{-3}$ s^{-1} at 20 °C in chloroform.

The most relevant feature of this work is the clear demonstration that easy ligand dissociation from *cis*-$[Pt(Ph)_2(Me_2S)_2]$ to form coordinatively unsaturated 14-electron $[Pt(Ph)_2(Me_2S)]$ as the intermediate species, offers a favorable route to the substitution. This competes with the bimolecular pathway of the most powerful nucleophiles and is dominant in the reactions with the nitrogen chelates. Thus the kinetic behavior is strictly similar to that already found for *cis*-$[Pt(Ph)_2(Me_2SO)_2]$[9] although some relevant differences between the two substrates must be pointed out. The bis(sulfide) and the bis(sulfoxide) complexes have comparable reactivity but differ markedly in their activation parameters. For *cis*-$[Pt(Ph)_2(Me_2SO)_2]$ $k_1(30\ °C) = (2.01 \pm 0.4) \times 10^{-2}$ s^{-1}, $\Delta H^{\ddagger} = 64 \pm 2$ kJ mol^{-1}, and $\Delta S^{\ddagger} = -67 \pm 8$ J K^{-1} mol^{-1}. Since in neither case does the process involve charge separation, it seems most unlikely that the observed differences can be the consequence of different specific interactions between the apolar solvent and the neutral Me_2S and Me_2SO ligands or the uncharged reaction intermediates. It is reasonable to think that much of the negative entropy of activation in the case of the sulfoxide complex stems from the loss of rotational entropy through interaction between the oxygen and the metal in the 14-electron $[Pt(Ph)_2(Me_2SO)]$ intermediate. Strong support for this hypothesis comes from the values of the competition ratios k_3/k_{-1} for the two compounds in Table V. These ratios measure the efficiency of a nucleophile in capturing the proposed 3-coordinate intermediate in competition with the reentry of the leaving group. Data in Table V show that the rate of reassociation of $[Pt(Ph)_2(Me_2S)]$ with Me_2S is comparable to that of reaction with L-L. The ratio k_3/k_{-1} does not exhibit any particular trend and remains nearly constant along the series of nucleophiles examined. This lack of discrimination strongly supports the view that the transient sulfide intermediate must possess a very high reactivity. By way of contrast the $[Pt(Ph)_2(Me_2SO)]$ intermediate appears to have a lifetime long enough to discriminate among different nucleophiles. The phosphine ligands are much more effective in capturing $[Pt(Ph)_2(Me_2SO)]$ than the dithioether or the phenanthroline, which show comparable reactivity, while the efficiency of bpym and bpy is still lower. The entire difference of reactivity encompasses 2 orders of magnitude. Within the limited range of nucleophiles studied, the nucleophilic discrimination of the 3-coordinate sulfoxide intermediate seems to resemble that of 4-coordinate substrates.

Three-coordinate d^8 species (i.e., 14-electron compounds) are highly interesting from a structural viewpoint and because of their relevant catalytic potential. Since their first appearance in the mechanism of spontaneous isomerization of *cis*-$[Pt(PEt_3)_2(aryl)X]$ complexes,[37] such species have been implicated in a number of fundamental processes of d^8 transition-metal complexes. MO calculations provide theoretical support for the configurational stability of T-shaped 3-coordinate species and the energetic scheme for their conversion.[38] The formation of such species offers a favorable reaction route for the insertion of olefins into the Pt–H bond,[39] the conversion of methyl carbonyls into acetyl derivatives,[40] and, in the reverse reaction, the migration of the alkyl group from carbon monoxide.[41] They are also implicated in the reactions of CO with *cis*- and *trans*-dialkylbis(phosphino)palladium(II) complexes,[42] the spontaneous isomerization and the reductive elimination of ethane from $[AuMe_3L]$[38a] or $[PdMe_2L_2]$,[38b] the β-elimination from symmetrical[43] and unsymmetrical[44] dialkyldiphosphino platinum(II) complexes, the β-elimination from $[Pt(CH_2CMe_3)_2L_2]$,[45] and in the thermal decomposition of metallocyclopentanes $[M(CH_2)_4L_2]$.[46] All of these reactions involve dissociation of the ligand L as a prerequisite for the occurrence of the process. Most of these reactions concern compounds with M–C σ bonds, and one is led to wonder to what extent the well-established mechanistic patterns of d^8 transition-metal compounds apply to organometallic species. In this context the changeover of reaction pathways observed in substitution reactions of *cis*-$[PtCl_2X_2]$ and *cis*-$[Pt(Ph)_2X_2]$ (X = Me_2S and Me_2SO) is extremely relevant. While the chemistry of 3-coordinate 14-electron species is becoming a new, fascinating field of research, particular attention must be paid to the role of ancillary ligands in assisting their formation and stabilization.

Acknowledgment. Financial support for the present work from the Italian Ministry of Education is gratefully acknowledged.

Registry No. bpy, 366-18-7; phen, 66-71-7; dppe, 1663-45-2; bpym, 34671-83-5; dppp, 6737-42-4; dpte, 622-20-8; *cis*-$[Pt(Ph)_2(Me_2S)_2]$, 64827-20-9; *cis*-$[Pt(Ph)_2(Me_2SO)_2]$, 70423-99-3; $[Pt(Ph)_2(dppp)]$, 105597-79-3; $[Pt(Ph)_2(dpte)]$, 105597-80-6; Me_2S, 75-18-3.

Supplementary Material Available: Tables of hydrogen atom coordinates (Table SI), anisotropic thermal parameters (Table SII), and primary kinetic data (k_{obsd}/s^{-1} and k_{calcd}/s^{-1}) (Tables SIV and SV) (10 pages); a table of calculated and observed structure factors (Table SIII) (16 pages). Ordering information is given on any current masthead page.

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