Rates of Dimethyl Sulfoxide Exchange in Monoalkyl Cationic Platinum(II) Complexes Containing Nitrogen Bidentate Ligands. A Proton NMR Study

Raffaello Romeo,* Luigi Monsù Scolaro, Nicola Nastasi, and Giuseppe Arena

Dipartimento di Chimica Inorganica, Analitica e Chimica Fisica and Istituto Chimica Tecnologia dei Prodotti Naturali (ITCPN-CNR) Sezione di Messina, Università di Messina, Salita Sperone 31, Vill. S. Agata, 98166 Messina, Italy

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A series of monoalkyl square-planar complexes of the type $[Pt(N\text{-}N)(CH_3)(Me_2SO)]PF_6$ (**1**−**14**), where N-N represents chelating diamines or diimines of widely different steric and electronic characteristics, was synthesized, and the complexes were fully characterized as solids and in solution. The substrates were tailored to offer only one site of exchange to a neutral molecule, i.e. Me_2SO, in a noncoordinating solvent. No evidence for fluxionality of the N-N ligands was found, except for the case of complex **11** formed by 2,9-dimethyl-1,10-phenanthroline. In solution this complex is fluxional with the phenanthroline oscillating between nonequivalent bidentate modes by a mechanism which involves rupture of the metal−nitrogen bond and rapid interconversion of two coordinatively unsaturated T-shaped 14-electron three-coordinate molecular fragments. Rates of this fluxion were measured by NMR spectroscopy from the exchange effects on the ^1H signals of the methyl and aromatic hydrogens. The $\Delta G^{\ddagger}$ value for the fluxion is 49.6 ± 4 kJ mol^{-1}. Dimethyl sulfoxide exchange with all the complexes has been studied as a function of ligand concentration by ^1H NMR line-broadening, isotopic labeling, and magnetization transfer experiments with deuterated acetone as the solvent. Second-order rate constants were obtained from linear plots of k_{obs} *vs* $[Me_2SO]$ and activation parameters were obtained from exchange experiments carried out at different temperatures. Second-order kinetics and negative entropies of activation indicate an associative mechanism. The lability of dimethyl sulfoxide in the complexes depends in a rather unexpected and spectacular way upon the nature of the coordinate N-N ligands, the difference in reactivity between the first (N-N = *N*,*N*,*N*′,*N*′-tetramethyl-1,2-diaminoethane, $k_2^{298} = (1.15 \pm 0.1) \times 10^{-6}$ mol^{-1} s^{-1}) and the last (N-N = 2,9-dimethyl-1,10-phenanthroline, $k_2^{298} = (3.81 \pm 0.005) \times 10^4$ mol^{-1} s^{-1}) members of the series being greater than 10 orders of magnitude, as a result of a well-known phenomenon of steric retardation (for the first complex) and an unprecedented case of steric acceleration (for the last complex). Other factors of primary importance in controlling the reactivity are (i) the presence of an extensive π system on the ligand N-N, (ii) the ease with which this π system interacts with nonbonding d electrons of the metal, and (iii) the flexibility and ease of elongation of the chelate bite distance. The basicity plays a somewhat minor role, except in the restricted range of the same class of compounds such as substituted phenanthrolines.

Introduction

Neutral and cationic square planar complexes of general structure $[M(N\text{-}N)(CH_3)X]$ (M = Pd(II); N-N = bidentate nitrogen ligand; X = Cl^-, $CF_3SO_3^-$, MeCN) are known to be good catalysts for the homogeneous copolymerization of olefins with carbon monoxide.[1,2] A key step in the mechanism of the alternating insertion of CO and alkenes is the removal of the coordinated X group from the coordination sphere of the metal promoted by the steric and electronic characteristics of the "spectator" N-N ligands. Compounds of platinum(II) of the same type are less useful as catalysts, altough interesting reactions with alkenes, alkynes, and 1,2- and 1,3-dienes have been reported.[3]

Another theme of great chemical interest comes from the ease with which dimethyl sulfoxide can be displaced from square planar platinum(II) complexes.[4,5] Cationic complexes of the type $[Pt(diam)(Me_2SO)Cl]Cl$ are easily formed by reaction of diamines with *cis*-$[PtCl_2(Me_2SO)_2]$ and have proved to be useful intermediates in the synthesis of neutral antitumor complexes with the general formula $[Pt(diam)Cl_2]$.[6,7] The labilization of the bound sulfoxide is a crucial step in the synthetic procedure.

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Recently, this class of cationic complexes was found to exhibit by itself chemiotherapeutic activity,[8] offering the advantage of being more soluble in water than the neutral complexes. Here again the role of the sulfoxide as leaving group is of overriding importance in order to obtain some insight into the mechanism of antitumor activity.

In searching for a correlation between the lability of substrates and the nature of the ancillary ligands, we thought it of interest to carry out a kinetic study of the exchange reaction

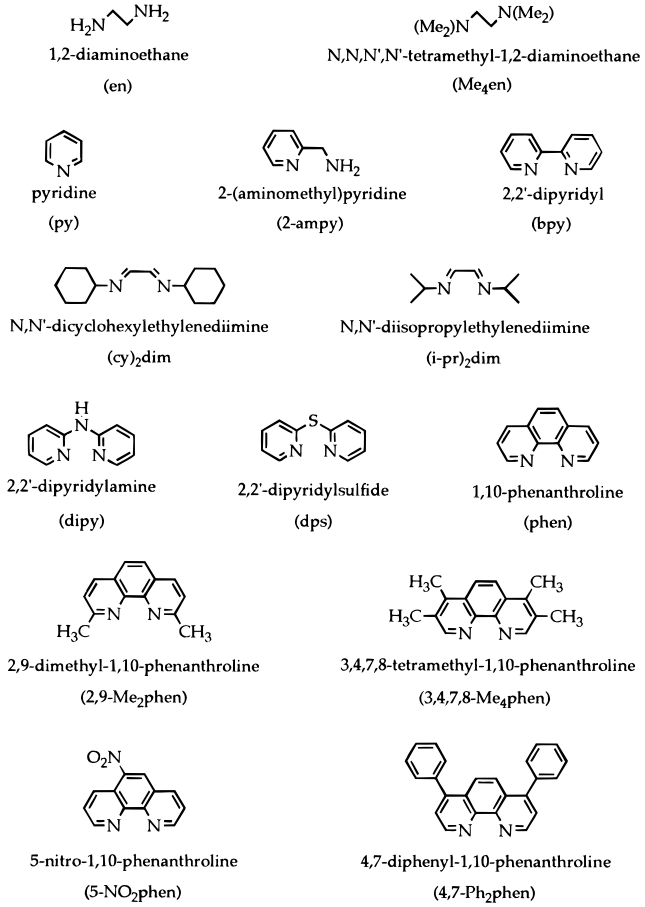
$$[Pt(N\text{-}N)(CH_3)(Me_2SO)]^+ + Me_2SO^* \rightarrow [Pt(N\text{-}N)(CH_3)(Me_2SO)^*]^+ + Me_2SO \quad (1)$$

where N-N represents a series of chelating diamines or diimines of widely different steric and electronic properties. Kinetic studies of solvent exchange on square planar complexes are scarce.[9] The systems studied so far include $[Pd(H_2O)_4]^{2+}$,[10] $[Pt(H_2O)_4]^{2+}$,[11] non-aqueous tetrasolvates $[PdS_4]^{2+}$ (S = DMA, DMF, MeCN, MeNC, Me_2S, Et_2S),[12] $[Pd(NH_3)_4]^{2+}$,[13] $[Pt(MeCN)_4]^{2+}$,[12] $[Pd(CN)_4]^{2-}$,[14] $[Pt(CN)_4]^{2-}$,[14] $[Pt(Me_2S)_4]^{2+}$,[15] $[Pt(1,4\text{-dithiane})_2]^{2+}$,[15] $[Pd(dien)(H_2O)]^{2+}$,[16] $[Pd(Et_4dien)(H_2O)]^{2+}$,[16] *trans*-$[Pd(Me_2S)_2Cl_2]$,[17] $[Pt(Me_2SO)_2(Me_2SO)_2]^{2+}$,[18] and the organometallic complexes *cis*-$[PtR_2(Me_2S)_2]$[19] and *cis*-$[PtR_2(Me_2SO)_2]$[19] (R = alkyls and aryls). Associative[10−18] and dissociative pathways[19] for the exchange have been demonstrated.

In the complexes of this study the presence of a methyl group ensures that only the sulfoxide can undergo the substitution process and provides an array of donor atoms strictly similar to that of the palladium catalysts.[1,2] The organometallic complexes were synthesized and fully characterized as solids and in solution. The range of reactivity was so large as to require the use of various NMR techniques, including isotopic labeling, magnetization transfer, and line broadening, taking advantage of the relatively large difference of chemical shift between the proton signals of coordinated and free sulfoxide.

The overall structure−reactivity relationship for these complexes is presented. The results are discussed within the framework of an associative mechanism and provide direct evidence for the great importance of the steric and electronic properties of the ancillary N-N ligands in governing the lability of the substrates. The difference in reactivity between the first and the last members of the series is greater than 10 orders of magnitude. This enormous variation of lability of the sulfoxide will be discussed in connection with some factors affecting the energy of a 5-coordinate transition state or intermediate such as (i) the presence of an extensive π system on the ligand N-N, (ii) the ease with which this π system interacts with nonbonding d electrons of the metal, (iii) the flexibility of the N-N ligand, and (iv) the relative importance of steric repulsions in the square planar and in the trigonal bipyramidal configurations.

Chart 1



Experimental Section

Materials. Solvents used in the synthetic procedures were distilled under nitrogen from appropriate drying agents (diethyl ether from sodium benzophenone; dichloromethane from barium oxide; dimethyl sulfoxide, at a low pressure, from CaH_2, after preliminary filtration through an alumina column) and then stored in dried, N_2-filled flasks over activated 4 Å molecular sieves. Acetone-d_6 and dimethyl sulfoxide-d_6 were used as received from Aldrich Chemical Co.

Pyridine (py), ethylenediamine (en), and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (Me_4en) were purified by distillation from KOH at normal pressure. *N*,*N*′-dicyclohexylethylenediimine (cy_2dim), and *N*,*N*′-diisopropylethylenediimine (pr^i_2dim), were synthesised and purified according to literature methods.[20]

All the other reagents were the highest grade commercially available and were used as received or were purified by distillation or crystallization when needed. Ligand abbreviations are given in Chart 1.

Synthesis of Complexes. All the complexes were synthesized under a dry oxygen-free nitrogen atmosphere using standard Schlenk-tube techniques. The reaction products are air stable and therefore they were handled without particular precautions.

***trans*-[Pt(Me$_2$SO)$_2$(CH$_3$)Cl]** was prepared according to a published method,[21] and was crystallized several times from dichloromethane/diethyl ether mixtures.

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[Pt(en)(Me$_2$SO)(CH$_3$)]PF$_6$ (1). A solution of ethylenediamine (15 mg, 0.25 mmol) in methanol (2 mL) was added drop by drop under stirring to a solution of *trans*-[Pt(Me$_2$SO)$_2$(CH$_3$)Cl] (80.4 mg, 0.2 mmol) in methanol (3 mL). After completion of the reaction, KPF$_6$ (46 mg; 0.25 mmol) was added and the solution set aside for 2 h. A white solid began to precipitate and the precipitation was completed by adding diethyl ether and cooling to −30 °C. IR: ν(S═O) 1110 cm^{-1}. ^{1}H NMR (CD$_3$OD/acetone-d_6, 1:1, v:v): δ 5.25 (s, broad, 2H), 4.28 (s, broad, 2H), 3.28 (s, $^3J_{PtH}$ = 33 Hz, 6H), 3.09 (m, 2H), 3.03 (m, 2H), 0.32 (s, $^2J_{PtH}$ = 76.5 Hz, 3H). Anal. Calcd for C$_5$H$_{17}$F$_6$N$_2$OPSPt: H 3.47; C, 12.17; N, 5.68. Found: H, 3.59; C, 12.01; N, 5.72.

The hexafluorophosphate salts of the complexes with the ligands Me$_4$en, py, and 2-ampy were prepared by following essentially the same procedure used for complex **1**. The solid compounds separated out in a good yield from the reaction mixture on adding diethyl ether and cooling.

[Pt(Me$_4$en)(Me$_2$SO)(CH$_3$)]PF$_6$ (2). IR: ν(S═O) 1128 cm^{-1}. ^{1}H NMR (D$_2$O): δ 3.30 (s, $^3J_{PtH}$ = 36.3 Hz, 6H), 2.90 (m, 2H), 2.80 (s, $^3J_{PtH}$ = 16.5 Hz, 6H), 2.74 (m, 2H), 2.67 (s, $^3J_{PtH}$ = 44 Hz, 6H), 0.26 (s, $^2J_{PtH}$ = 72.6 Hz, 3H). Anal. Calcd for C$_9$H$_{25}$F$_6$N$_2$OPSPt: H, 4.59; C, 19.68; N, 5.10. Found: H, 4.71; C, 19.62; N, 5.00.

***cis*-[Pt(py)$_2$(Me$_2$SO)(CH$_3$)]PF$_6$ (3).** ^{1}H NMR (acetone-d_6): δ 8.95 (d, $^3J_{PtH}$ unresolvable, 2H), 8.74 (d, $^3J_{PtH}$ = 41.8 Hz, 2H), 8.07 (m, 2H), 7.63 (m, 4H), 3.41 (s, $^3J_{PtH}$ = 34.1 Hz, 6H), 0.72 (s, 3H, $^2J_{PtH}$ = 75.9 Hz, 3H).

[Pt(2-ampy)(Me$_2$SO)(CH$_3$)]PF$_6$ (4). Two isomers with a relative ratio 2:1. *Pyridyl trans to Me$_2$SO*. IR: ν(S═O) 1128 cm^{-1}. ^{1}H NMR (CD$_3$OD): δ 8.69 (d, $^3J_{PtH}$ = 41.4 Hz, 1H), 8.16 (t, 1H), 7.77 (d, 1H), 7.56 (t, 1H), 4.43 (s, $^3J_{PtH}$ unresolvable, 2H), 3.44 (s, $^3J_{PtH}$ = 35.1 Hz, 6H), 0.60 (s, $^2J_{PtH}$ = 75.1 Hz, 3H). *Pyridyl cis to Me$_2$SO*. IR: ν(S═O) 1110 cm^{-1}. ^{1}H NMR (CD$_3$OD): δ 9.39 (d, $^3J_{PtH}$ = 20.0 Hz, 1H), 8.08 (t, 1H), 7.71 (d, 1H), 7.50 (t, 1H), 4.41 (s, $^3J_{PtH}$ unresolvable, 2H), 3.42 (s, $^3J_{PtH}$ = 34.4 Hz, 6H), 0.60 (s, $^2J_{PtH}$ = 75.1 Hz, 3H).

[Pt(cy$_2$dim)(Me$_2$SO)(CH$_3$)]PF$_6$ (5). A weighed amount of *trans*-[Pt(Me$_2$SO)$_2$(CH$_3$)Cl] (0.201 g, 0.5 mmol) was reacted in dimethyl sulfoxide (2 mL) with AgPF$_6$ (135 mg; 0.53 mmol). After the mixture was stirred for a few hours, AgCl was filtered off and 0.115 g (0.52 mmol) of dicyclohexylethylenediimine (cy$_2$dim) were added to the solution. The color turned from pale yellow to orange. The solution was set aside overnight, some additional solid silver chloride that settled out was separated by centrifugation, and the excess solvent was evaporated under reduced pressure (0.1 mmHg, 70 °C). The solid residue was dissolved in dichloromethane, the solution was filtered on a cellulose column to remove residual AgCl, and the orange product separated out on adding diethyl ether and cooling at −30 °C. IR: ν(S═O) 1135 cm^{-1}. ^{1}H NMR (acetone-d_6): δ 9.00 (s, $^3J_{PtH}$ = 47.7 Hz, 1H), 8.91 (s, $^3J_{PtH}$ = 85.2 Hz, 1H), 4.52 (s, $^3J_{PtH}$ = 18.8 Hz, 1H), 3.96 (s, $^3J_{PtH}$ = 21 Hz, 1H), 3.55 (s, $^3J_{PtH}$ = 35.1 Hz, 6H), 2.14 (m, 4 H), 1.89 (m, 4 H), 1.72 (m, 2 H), from 1.62 to 1.09 (m, 10H), 0.92 (s, $^2J_{PtH}$ = 73.8 Hz, 3H). Anal. Calcd for C$_{17}$H$_{33}$F$_6$N$_2$OPSPt: H, 5.09; C, 31.24; N, 4.29. Found: H, 5.05; C, 31.00; N, 4.36.

All the other hexafluorophosphate salts with the dinitrogen ligands pr$^i_2$dim, bpy, dipy, dps, phen, Me$_2$phen, Me$_4$phen, NO$_2$phen, and Ph$_2$-phen were prepared in satisfactory yields by following essentially the same procedure used for complex **5**.

[Pt(pr$^i_2$dim)(Me$_2$SO)(CH$_3$)]PF$_6$ (6). IR: ν(S═O) 1128 cm^{-1}. ^{1}H NMR (acetone-d_6): δ 9.10 (s, $^3J_{PtH}$ = 46.7 Hz, 1H), 9.00 (s, $^3J_{PtH}$ = 84.7 Hz, 1H), 4.94 (m, 1H), 4.45 (m, 1H), 3.56 (s, $^3J_{PtH}$ = 35.2 Hz, 6H), 1.46 (d, 6H), 1.38 (d, $^3J_{HH}$ = 6.0 Hz, 6H), 0.95 (s, $^3J_{PtH}$ = 73.1 Hz, 3H). Anal. Calcd for C$_{11}$H$_{25}$F$_6$N$_2$OPSPt: H, 4.39; C, 23.04; N, 4.89. Found: H, 4.33; C, 22.93; N, 4.78.

[Pt(bpy)(Me$_2$SO)(CH$_3$)]PF$_6$ (7). IR: ν(S═O) 1128 cm^{-1}. ^{1}H NMR (acetone-d_6): δ 9.85 (dd, $^3J_{PtH}$ = 19.8 Hz, 1H), 9.08 (dd, $^3J_{PtH}$ = 45.1 Hz, 1H), 8.76 (m, 2H), 8.56 (m, 2H), 8.02 (m, 2H), 3.69 (s, $^3J_{PtH}$ = 36.3 Hz, 6H), 0.92 (s, $^2J_{PtH}$ = 72.6 Hz, 3H). Anal. Calcd for C$_{13}$H$_{17}$-F$_6$N$_2$OPSPt: H, 2.91; C, 26.49; N, 4.75. Found: H, 3.10; C, 26.53; N, 4.86.

[Pt(dipy)(Me$_2$SO)(CH$_3$)]PF$_6$ (8). IR: ν(S═O) 1130 cm^{-1}. ^{1}H NMR (acetone-d_6): δ 9.99 (s, 1H), 8.76 (dd, $^3J_{PtH}$ = 17 Hz, 1H), 8.43 (dd, $^3J_{PtH}$ = 46.5 Hz, 1H), 8.08 (m, 2H), 7.55 (t, 2H), 7.38 (t, 1H), 7.29 (t, 1H), 3.51 (s, $^3J_{PtH}$ = 36.3 Hz, 6H), 0.68 (s, $^2J_{PtH}$ = 73.7 Hz, 3H). Anal. Calcd for C$_{13}$H$_{18}$F$_6$N$_3$OPSPt: H, 3.00; C, 25.83; N, 6.95. Found: H, 3.10; C, 25.89; N, 7.10.

[Pt(dps)(Me$_2$SO)(CH$_3$)]PF$_6$ (9). IR: ν(S═O) 1129 cm^{-1}. ^{1}H NMR (acetone-d_6): δ 8.99 (d, $^3J_{PtH}$ = 19.8 Hz, 1H), 8.79 (d, $^3J_{PtH}$ = 45.9 Hz, 1H), 8.25 (m, 2H), 8.17 (m, 2H), 7.82 (m, 1H), 7.71 (m, 1H), 3.60 (s, $^3J_{PtH}$ = 35.8 Hz, 3H), 3.49 (s, $^3J_{PtH}$ = 35.8 Hz, 3H), 0.84 (s, $^2J_{PtH}$ = 75.6 Hz, 3H). Anal. Calcd for C$_{13}$H$_{17}$F$_6$N$_2$OPS$_2$Pt: H, 2.76; C, 25.13; N, 4.51. Found: H, 2.83; C, 25.02; N, 4.63. FABMS: *m/e* 475.9 [M$^+$]$^+$.

[Pt(phen)(Me$_2$SO)(CH$_3$)]PF$_6$ (10). IR: ν(S═O) 1123 cm^{-1}. ^{1}H NMR (acetone-d_6): δ 10.15 (dd, $^3J_{PtH}$ = 16.5 Hz, 1H), 9.46 (dd, $^3J_{PtH}$ = 44.5 Hz, 1H), 9.16 (dd, 1H), 9.09 (dd, 1H), 8.39 (m, 2H), 8.35 (dd, 1H), 8.31 (dd, 1H), 3.75 (s, $^3J_{PtH}$ = 36.8 Hz, 6H), 1.12 (s, $^2J_{PtH}$ = 73.7 Hz, 3H). Anal. Calcd for C$_{15}$H$_{17}$F$_6$N$_2$OPSPt: H, 2.79; C, 29.37; N, 4.57. Found: H, 2.82; C, 29.41; N, 4.63.

[Pt(Me$_2$phen)(Me$_2$SO)(CH$_3$)]PF$_6$ (11). ^{1}H NMR (acetone-d_6): δ 8.82 (d, 2H), 8.20 (s, 2H), 8.04 (d, $^4J_{PtH}$ = 6.6 Hz, 2H), 3.57 (s, $^3J_{PtH}$ = 36.3 Hz, 6H), 3.10 (s, $^4J_{PtH}$ = 4.8 Hz, 6H), 1.00 (s, $^2J_{PtH}$ = 78.6 Hz, 3H). Anal. Calcd for C$_{17}$H$_{21}$F$_6$N$_2$OPSPt: H, 3.30; C, 31.83; N, 4.37. Found: H, 3.32; C, 31.90; N, 4.52.

[Pt(Me$_4$phen)(Me$_2$SO)(CH$_3$)]PF$_6$ (12). IR: ν(S═O) 1126 cm^{-1}. ^{1}H NMR (acetone-d_6): δ 9.91 (s, $^3J_{PtH}$ unresolvable, 1H), 9.09 (s, $^3J_{PtH}$ = 46.2 Hz, 1H), 8.48 (2H), 3.72 (s, $^3J_{PtH}$ = 37.4 Hz, 6H), 2.96 (s, 3H), 2.87 (s, 3H), 2.74 (s, 3H), 2.68 (s, 3H), 1.04 (s, $^2J_{PtH}$ = 72.6 Hz, 3H). Anal. Calcd for C$_{19}$H$_{25}$F$_6$N$_2$OPSPt: H, 3.76; C, 34.08; N, 4.18. Found: H, 3.70; C, 34.15; N, 4.09.

[Pt(NO$_2$phen)(Me$_2$SO)(CH$_3$)]PF$_6$ (13). IR: ν(S═O) 1131 cm^{-1}. ^{1}H NMR analysis (acetone-d_6) revealed the presence of two geometrical isomers in an equimolar ratio: δ 10.34 (m, 2H), from 9.68 to 9.36 (m, 8H), 8.52 (m, 4H), 3.77 (s, $^3J_{PtH}$ = 37.2 Hz, 12H), 1.17(s, $^2J_{PtH}$ = 73.8 Hz, 3H), 1.15 (s, $^2J_{PtH}$ = 73.7 Hz, 3H). Anal. Calcd for C$_{15}$H$_{16}$F$_6$N$_3$O$_3$-PSPt: H, 2.45; C, 27.36; N, 6.38. Found: H, 2.35; C, 27.49; N, 6.42.

[Pt(Ph$_2$phen)(Me$_2$SO)(CH$_3$)]PF$_6$ (14). IR: ν(S═O) 1123 cm^{-1}. ^{1}H NMR (acetone-d_6): δ 10.24 (d, $^3J_{PtH}$ = 19 Hz, 1H), 9.52 (d, $^3J_{PtH}$ = 45.6 Hz, $^3J_{HH}$ = 5.8 Hz, 1H), 7.71 (m, 14H), 3.78 (s, $^3J_{PtH}$ = 36.3 Hz, 6H), 1.16 (s, $^2J_{PtH}$ = 73.7 Hz, 3H). Anal. Calcd for C$_{27}$H$_{25}$F$_6$N$_2$-OPSPt: H, 3.29; C, 42.36; N, 3.66. Found: H, 3.37; C, 42.45; N, 3.72.

Instrumentation and Measurements. Infrared spectra were recorded as Nujol mulls in the range 4000−200 cm^{-1} using CsI disks on a Perkin Elmer FT-IR Model 1730 spectrometer. ^{1}H NMR spectra were obtained on a Bruker AMX R-300 spectrometer equipped with a broad-band probe operating at 300.13 MHz. ^{1}H chemical shifts are measured relative to the residual solvent peak and are reported in δ units downfield from Me$_4$Si. The temperature within the probe was checked using the methanol or ethylene glycol method.[22] Fast atom bombardment mass spectrometry (FABMS) was performed in a glycerol matrix with a Kratos instrument equipped with a standard FAB source. Microanalysis were performed by Analytical Laboratories, Engelskirchen. The activation parameters $\Delta H^‡$ and $\Delta S^‡$ were calculated by linear regression analysis of Eyring plots.

Results

Synthesis and Characterization of Complexes. The complex *trans*-[PtMeCl(Me$_2$SO)$_2$] is a useful synthon to synthesize square planar platinum(II) organometallic compounds containing the molecular fragments [Pt(Me)(Me$_2$SO)] or [PtMeX] (X = halide ions).[23] As shown in the reaction scheme, two different procedures were applied to the synthesis of the [Pt(N-N)Me-(Me$_2$SO)]PF$_6$ complexes, depending on the nature of the dinitrogen ligand N-N and on the lability of the coordinated Me$_2$SO in the ensuing product. When N-N is a diamine, pyridine or a mixed aminopyridine, as for compounds **1**−**4**, the reaction of the precursor in methanol with a slight excess of the chelating ligand leads to the easy formation of [Pt(N-N)-

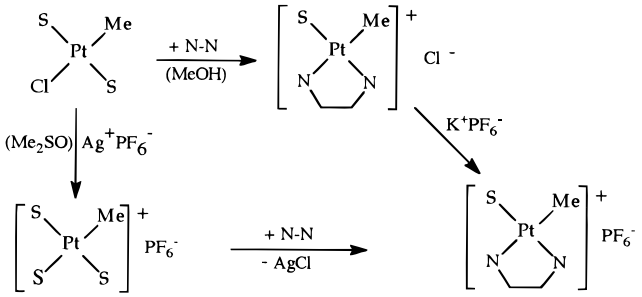
(22) Van Geet, A. L. *Anal. Chem.* **1968**, *40*, 2227. Van Geet, A. L. *Anal. Chem.* **1970**, 42, 679.
(23) Romeo, R.; Monsù Scolaro, L., submitted for publication.

Table 1. Selected ^{1}H NMR Data for [Pt(N-N)Me(Me_2SO)] PF_6 Complexes[a]

	N-N	$\delta(CH_3Pt)$	$\delta(Me_2SO)$	δ(H aliphatics)	δ(H aromatics)
1	en[b]	0.32 (76.5)	3.28 (33.0)		
2	Me_4en[c]	0.26 (72.6)	3.30 (36.3)	2.80 (16.5); 2.67 (44.0)	
3	py	0.72 (75.9)	3.41 (34.1)		8.95; 8.74 (41.8)
4a	*trans*-2-ampy[d,f]	0.60 (75.1)	3.44 (35.1)	4.43	8.69 (41.4)
4b	*cis*-2-ampy[e,f]	0.60 (75.1)	3.42 (34.4)	4.41	9.39 (20.0)
5	cy_2dim	0.92 (73.8)	3.55 (35.1)	4.52 (18.8); 3.96 (21.0)	9.00 (47.7); 8.91 (85.2)
6	pr^i_2dim	0.95 (73.1)	3.56 (35.2)	1.46; 1.38	9.10 (46.7); 9.00 (84.7)
7	bpy	0.92 (72.6)	3.69 (36.3)		9.85 (19.8); 9.08 (45.1)
8	dipy	0.68 (73.7)	3.51 (36.3)		8.76 (17.0); 8.43 (46.5)
9	dps	0.84 (75.6)	3.60 (35.8) 3.49 (35.8)	3.49 (35.8)	8.99 (19.8); 8.79 (45.9)
10	phen	1.12 (73.7)	3.75 (36.8)		10.15 (16.5); 9.46 (44.5)
11	Me_2phen	1.00 (78.6)	3.57 (36.3)	3.10 (4.8)[g]	
12	Me_4phen	1.04 (72.6)	3.72 (37.4)	2.96; 2.87; 2.74; 2.68	9.91; 9.09 (46.2)
13	NO_2phen	1.17 (73.8) 1.15 (73.7)	3.77 (37.2)		10.34
14	Ph_2phen	1.16 (73.7)	3.78 (36.3)		10.24 (19.0); 9.52 (45.6)

[a] Resonances in ppm from TMS at 298 K; solvent = acetone-d_6, unless noted otherwise; $^2J_{PtH}$ in Hz for $PtCH_3$ and $^3J_{PtH}$ in Hz for $Pt(CH_3)_2SO$, for the aliphatic and the aromatic protons are given in parentheses. [b] Solvent = 1:1 $CD_3OD/(CD_3)_2CO$ v:v. [c] Solvent = D_2O. [d] py trans to Me_2SO. [e] py cis to Me_2SO. [f] Solvent = CD_3OD. [g] $^4J_{PtH}$ in Hz.

Me(Me_2SO)]Cl, which can be isolated directly as chloride salts or as hexafluorophosphate salts on adding KPF_6.



With all the phenanthrolines and diimines (compounds **5**−**14**), it is necessary first to add $AgPF_6$ to the solution of *trans*-[PtMeCl($Me_2SO)_2$] in dimethyl sulfoxide, followed by the addition of the proper chelating ligand. A slight excess of the latter serves to shift the equilibrium toward complete precipitation of AgCl. In the presence of chloride ion the only product is [Pt(N-N)MeCl].

All the complexes were fully characterized by elemental analyses, IR and ^{1}H NMR spectroscopy. A collection of selected spectroscopic data for the various complexes is reported in Table 1. The presence of a strong peak at 1125 ± 7 cm^{-1}, which is assigned to the S=O stretch, is taken to indicate bonding through sulfur, since this is shifted to higher frequency than the corresponding vibration in the free ligand.[24] All the ^{1}H NMR spectra, with the exception of that for the complex (**11**) containing the Me_2phen ligand (*see below*), are consistent with the proposed structures showing the pattern of an S-bound sulfoxide (δ in the range 3.30−3.80 ppm), of a methyl group directly coordinated to the metal (δ in the range 0.15−1.20 ppm), and of a chelate ligand coordinated to an asymmetric platinum metal center. As an example, the complex (**6**) containing pr^i_2dim as chelating ligand displays two distinct resonances in the low field region at δ 9.10 and 9.00 due to the imino protons of the diimine ligand, as well as two easily distinguishable isopropyl groups in the aliphatic region. The assignment of the iminic protons was facilitated by the presence of largely different coupling constants with the isotopically abundant ^{195}Pt (33%, $I = {}^1/_2$). The most downfield shifted signal at δ 9.10 ppm (1H) shows two satellite peaks due to ^{195}Pt coupling (47.6 Hz) and it is attributable to the iminic proton trans with respect to the strong activating methyl group.[25] The corresponding proton trans to Me_2SO (at δ 9.00 ppm) exhibits a much higher coupling constant (84.7 Hz). The coordinated Me_2SO gives a singlet at δ 3.56 with a $^3J_{PtH}$ = 35.2 Hz consistent with the retention of the S-bonded mode. The methyl group gives a singlet at δ 0.95 ppm with $^2J_{PtH}$ = 73.1 Hz, a value in the range of similar cationic species. The ^{1}H NMR spectra of the complexes with the ligands 2-ampy (**4**) and NO_2-phen (**13**) clearly show the presence of the two possible isomers. In the case of complex **4**, the presence of markedly different coupling constants with ^{195}Pt for the ortho proton on the pyridine ring is particularly diagnostic for assigning the two species indicated in Table 1 as **4a** (pyridine trans to S-bonded Me_2SO) and **4b** (pyridine in the cis position), respectively. On the contrary, a close inspection of the spectrum for the mixture relative to complex **13** does not allow a definitive assignment to be made.

The ^{1}H NMR spectrum of the complex [Pt(dps)(CH_3)(Me_2-SO)]$^+$ is of interest in that two methyl resonances are observed at δ 3.60 and at δ 3.49, each with ^{195}Pt satellites. A molecular model shows that the six-membered ring formed by coordination of the two nitrogens of the ligand assumes conformations in which the sulfur atom lies well outside of the square planar coordination plane. The dimethyl sulfoxide ligand becomes therefore prochiral, and the two methyl groups are diastereotopic. The same pattern of behavior is expected for the complex containing dipy, the only difference with the dps complex being the presence of an out-of-plane nitrogen atom instead of the sulfur atom. Contrary to these expectations, only one methyl signal is observed for the compound **8** at δ 3.51 ($^3J_{PtH}$ = 36.3 Hz). If we exclude that such a single signal is the result of a perfect coincidence of resonances of two diastereotopic methyls, it must be concluded that the secondary nitrogen of the coordinated dipy ring moves rapidly from one side of the coordination plane to the other with a rate that is fast in the NMR time scale and faster than that of the dps ring. The reasons for this are unclear. The suspicion of a possible oxidation "*in situ*" of the sulfide to sulfoxide with an increased rigidity of the ring, was ruled out by the results of the elemental analysis and the FAB MS spectrum carried out on the complex recovered from the NMR measurements. One reviewer sug-

(24) Davies, J. A. *Adv. Inorg. Chem. Radiochem.* **1981**, *24*, 115.

(25) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335.

gested the possibility of (partial) deprotonation and aromatization of the 2.2′-dipyridylamine ligand and another the formation of five-coordinate species, but both hypotheses are not in keeping with the NMR spectral evidence.

Flipping of the 2,9-Dimethyl-1,10-phenanthroline Ligand. As for all the other compounds the coordinated phenanthroline in compound **11** should result in the halves of the molecule being inequivalent. In fact, at 298 K, the two methyls and the aromatic proton pairs H_3 and H_8, H_4 and H_7, and H_5 and H_6 are chemically equivalent, indicating a fast site exchange of the two nitrogen atoms of the Me_2phen ligand. As the temperature is lowered below 230 K, the signals of the phenanthroline ligand start to decoalesce and at 200 K the NMR spectrum shows two singlets, one for each methyl, four doublets, one for H_3, H_8, H_4, and H_7 protons, and an AB system for H_5 and H_6 protons, as expected as a result of the asymmetry of a firmly bonded bidentate phenanthroline. Both the methyl protons and the aromatic protons of the substituted phenanthroline were used for the line-shape analysis of the spectra. The exchange rates were calculated using the computer program DNMR 5,[26] and the computer-calculated spectra were visually compared to the experimental spectra. The results of the two sets of data agreed well. Values of $\Delta H^{\ddagger} = 44.8 \pm 2$ kJ mol^{-1}, $\Delta S^{\ddagger} = -20 \pm 8$ J K^{-1} mol^{-1} and $\Delta G^{\ddagger} = 49.6 \pm 4$ (kJ mol^{-1}), at the coalescence temperature, were derived from a linear regression analysis of the Eyring plot. The aromatic region of the ^{1}H NMR spectra of compound **11**, taken at different temperatures, is shown in Figure 1.

Kinetics of Sulfoxide Exchange. The exchange of sulfoxide for the various complexes takes place according to the reaction scheme in (1) with no evidence throughout of ring opening or of other concurrent processes, except for the case of Me_2phen (compound **11**) discussed above. The exchange rates have been measured by ^{1}H NMR using different experimental methods according to the rate of the process.

(i) Isotopic Exchange. In the case of slowly exchanging systems, the kinetic runs were performed by adding with a microsyringe a known volume of dimethyl sulfoxide-d_6 on a prethermostated solution of weighted [Pt(N-N)Me(Me_2SO)]PF_6 complex and acetone-d_6. At least a 5-fold excess of Me_2SO-d_6 over complex was ensured in any run. All concentrations are expressed in moles per kilogram of solvent (m = mol kg^{-1}). The isotopic exchange was followed by monitoring the increase in intensity of the proton NMR signal of free Me_2SO at δ 2.60 and the matching decrease of the signal of the sulfoxide coordinated to the metal (values of the chemical shifts and of the ^{195}Pt coupling constants for the various complexes are reported in the third column of Table 1). The spectra were recorded at appropriate intervals of time (Figure 2). The mole fraction $F = [Me_2SO]_f/([Me_2SO]_f + [Me_2SO]_b)$ of the free nondeuterated dimethyl sulfoxide was obtained by integration of the signals, and the first-order rate constants k_{exch} (s^{-1}) for the exchange of the label were obtained from a nonlinear least-squares fit of the experimental data to $F = c_1 + c_2 \exp(-k_{exch}t)$, with c_1, c_2, and k_{exch} as the parameters to be optimized. A similar analysis can be performed by using the mole fraction of the nondeuterated bound dimethyl sulfoxide. An example of a fit is shown in Figure S2. From the McKay equation, $R_{exch} = k_{exch}\, ab(a + b)^{-1}$ (where R_{exch} is the rate of the exchange process, a the concentration of complex, and b the concentration of free sulfoxide) the pseudo-first-order rate constants, $k_{obsd} = R_{exch}/a$, were calculated and are collected in Table 2. The exchange is first-order with respect to free ligand and the linear plots of k_{obs} *vs* [Me_2SO] pass through the origin. The exchange

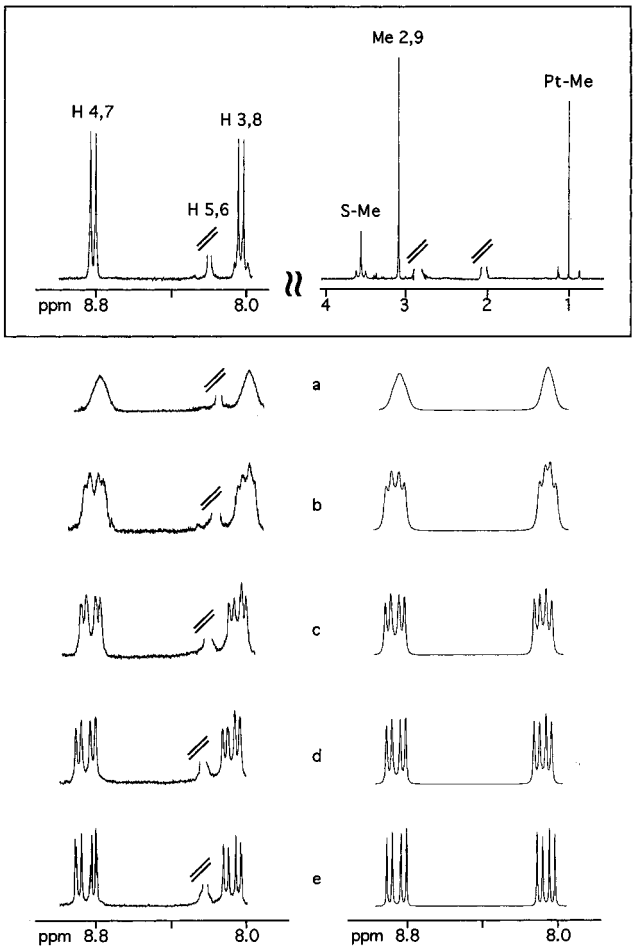


Figure 1. Upper plot (in the frame): ^{1}H NMR spectrum of the complex [Pt(Me_2phen)(CH_3)(Me_2SO)]PF_6 in acetone-d_6 at 298 K. Intensities are given in arbitrary units and in different scales for the aromatic and the aliphatic regions of the spectrum. Lower plot: experimental (on the left) and simulated NMR spectra (on the right) of the signals of the phenanthroline aromatic protons. The temperatures and the "best-fit" rate constants for the fluxional motion of the nitrogen ligand are as follows: (a) T = 238 K, k_{obs}, s^{-1} = 58; (b) T = 228 K, k_{obs}, s^{-1} = 23; (c) T = 223 K, k_{obs}, s^{-1} = 12; (d) T = 218 K, k_{obs}, s^{-1} = 7; (e) T = 208 K, k_{obs}, s^{-1} = 2.

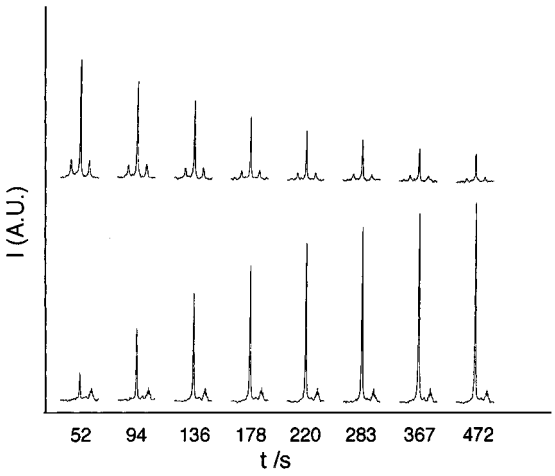


Figure 2. 300-MHz spectra of a 0.008 m [Pt(Me_4phen)(CH_3)(Me_2SO)]$^+$and 0.292 m $(CD_3)_2$SO solution in deuterated acetone at 298 K as a function of time. Upper plot: coordinated Me_2SO (δ = 3.72 ppm, $^3J_{PtH}$ = 37.4 Hz). Lower plot: free Me_2SO (δ = 2.56 ppm).

therefore follows the rate law $k_{obs} = k_2[Me_2SO]$. The values of k_2, obtained from a linear regression analysis of the rate law, are collected in Table 2.

(26) Stephenson, D. S.; Binsch, G. *QCPE* 1978. *11*, 365.

Table 2. Pseudo-First-Order Rate Constants k_{obs}, as a Function of Concentration of Free Me_2SO, and Second-Order Rate Constants, k_2, for Me_2SO Exchange on $[Pt(N\text{-}N)(CH_3)(Me_2SO)]PF_6$ Complexes in Acetone-d_6[a]

	N-N	$[Me_2SO]$[b]	10^3k_{obs}[c]	k_2[d]		N-N	$[Me_2SO]$[b]	10^3k_{obs}[c]	k_2[d]
1	en	0.571	0.00548		**8**	dipy	0.124	6.55	
		0.974	0.00936				0.244	12.9	
		1.50	0.0143	$(9.49 \pm 0.05) \times 10^{-6}$			0.410	21.6	0.053 ± 0.002
2	Me_4en	0.500	0.00055		**14**	Ph_2phen	0.0400	4.44	
		1.00	0.00112				0.0713	7.10	
		1.53	0.00174	$(1.15 \pm 0.01) \times 10^{-6}$			0.142	14.8	0.10 ± 0.01
4a	2-ampy	0.100	0.354		**7**	bpy	0.0150	2.21	
		0.188	0.706				0.0311	4.91	
		0.373	1.32	$(3.5 \pm 0.3) \times 10^{-3}$			0.0453	7.00	0.16 ± 0.01
9	dps	0.100	0.840		**10**	phen	0.0352	6.62	
		0.251	2.22				0.0708	13.0	
		0.496	4.93	$(1.0 \pm 0.1) \times 10^{-2}$			0.142	26.3	0.180 ± 0.04
3	py	0.090	1.44		**13**	NO_2phen	0.040	13.5	
		0.196	3.20				0.080	25.7	
		0.400	6.34	$(1.6 \pm 0.1) \times 10^{-2}$			0.119	39.9	0.33 ± 0.04
12	Me_4phen	0.145	3.65		**5**	cy_2dim[e]			0.920
		0.292	7.49						
		0.410	10.7	$(2.66 \pm 0.05) \times 10^{-2}$	**6**	$pr^i{}_2$dim[f]			0.79 ± 0.06
					11	Me_2phen[g]			38100

[a] At 298 K. [b] *m*. [c] s^{-1}. [d] m^{-1} s^{-1}. [e] From Eyring plots (data in Table 3). [f] From magnetization transfer experiments (data in Table 3). [g] From line broadening experiments.

Table 3. Temperature Dependence of Observed k_{obs}, and Second-Order Rate Constants, k_2, for Me_2SO Exchange with $[Pt(cy_2dim)(CH_3)(Me_2SO)]PF_6$ (**5**) and $[Pt(i\text{-}pr_2dim)(CH_3)(Me_2SO)]PF_6$ (**6**) Complexes in Acetone-d_6

compound **5**				compound **6**			
T/K	$[Me_2SO]$[a]	10^3k_{obs}[b]	10^2k_2[c]	*T*/K	$[Me_2SO]$[a]	10^3k_{obs}[b]	10^2k_2[c]
238[d]	0.0452	0.386		248[d]	0.054	0.762	
	0.081	0.697			0.100	1.39	
	0.151	1.29	0.85 ± 0.01		0.150	2.10	1.39 ± 0.03
248[d]	0.0382	0.710		258[d]	0.033	1.55	
	0.0767	1.38			0.0697	3.26	
	0.151	2.76	1.82 ± 0.05		0.158	7.41	4.69 ± 0.02
258[d]	0.0383	1.76		268[d]	0.033	2.87	
	0.0.697	3.49			0.0752	6.50	
	0.158	7.33	4.6 ± 0.4		0.155	13.4	8.65 ± 0.01
268[d]	0.045	4.31		298[e]	0.169	136	
	0.082	7.86			0.316	242	
	0.150	14.3	9.4 ± 0.2		0.497	395	79 ± 6
313[e]	0.110	295					
	0.226	583					
	0.333	878	261 ± 12				

[a] *m*. [b] s^{-1}. [c] m^{-1} s^{-1}. [d] From isotopic exchange experiments. [e] From magnetization transfer experiments.

(ii) Magnetization Transfer. The rate constants for the moderately fast exchanging complexes **5** and **6** at the highest temperatures were measured by applying a magnetization transfer technique as proposed by Forsen and Hoffman.[27] The two sites are those of free and bound Me_2SO. For both complexes the two signals are well-separated without scalar coupling, and no complications arise from the triplet-like structure of the bound signal. In a typical procedure the resonance of the free Me_2SO was completely saturated by selective decoupling pulses of variable length. The experimental heights of the bound Me_2SO peak, corrected for the contribution of the ^{195}Pt satellites (33% abundance), were fitted by linear regression analysis to eq 2, where $M_0{}^A$, $M_t{}^A$, and $M_\infty{}^A$ are the

$$(M_t{}^A - M_\infty{}^A) = M_0{}^A \tau_{1A}/\tau_A \exp(-t/\tau_{1A}) \qquad (2)$$

experimental intensities before saturation, at the time *t*, and after a prolonged saturation, respectively. τ_{1A} is correlated to τ_A (the lifetime of the observed site) and T_{1A} (spin-lattice relaxation time) by eqs 3 and 4.

The variable-temperature rate constants including data obtained from isotopic exchange and from magnetization transfer

$$M_\infty{}^A = M_0{}^A(\tau_{1A}/T_{1A}) \qquad (3)$$

$$1/\tau_{1A} = 1/\tau_A + 1/T_{1A} \qquad (4)$$

experiments in Table 3 were fitted to the Eyring equation, leading to $k_2{}^{298} = 0.920$ m^{-1} s^{-1}, $\Delta H^\ddagger = 45.5 \pm 3$ kJ mol^{-1} and $\Delta S^\ddagger = -93 \pm 9$ J K^{-1} mol^{-1} for the $[Pt(cy_2dim)(CH_3)(Me_2SO)]^+$ complex (**5**) and to $k_2{}^{298} = 0.79 \pm 0.06$ m^{-1} s^{-1}, $\Delta H^\ddagger = 46.2 \pm 4$ kJ mol^{-1} and $\Delta S^\ddagger = -91 \pm 10$ J K^{-1} mol^{-1} for the $[Pt(pr^i{}_2dim)(CH_3)(Me_2SO)]^+$ complex (**6**).

(iii) Line-Broadening Analysis. The rate of sulfoxide exchange with the $[Pt(Me_2phen)(CH_3)(Me_2SO)]^+$ complex was measured in the slow-exchange region from the width of the NMR signals at half-height using eq 5 where τ_a is the residence

$$1/\tau_a = \pi(\omega_A - \omega^o{}_A) \qquad (5)$$

time in site A and ω_A and $\omega^o{}_A$ are the linewidths in the presence and in the absence of exchange, respectively.[28] The latter was measured at low temperature, where the reaction is frozen on

(27) Forsèn, S.; Hoffman, R. A. *J. Chem. Phys.* **1963**, *39*, 2892.

(28) Becker, E. D. *High Resolution NMR. Theory and Chemical Applications*; Academic Press: New York, 1980; pp 240−245.

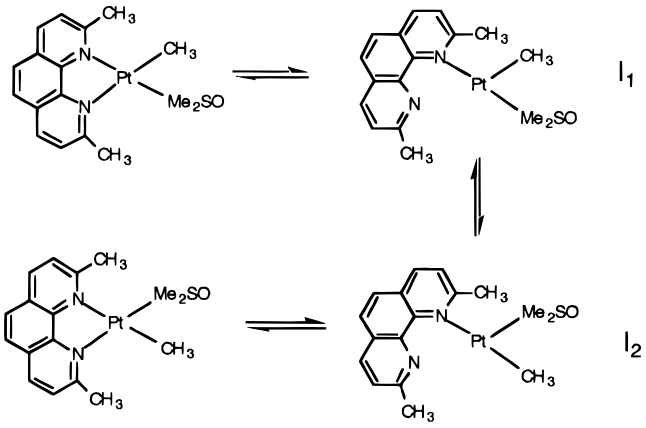
the NMR time scale. The experimental linewidths were corrected by subtracting the line width of TMS to minimize the effect of instrumental line-broadening. Values of observed, k_{obs}, and second-order rate constants, k_2, for the exchange, at various temperatures and dimethysulfoxide concentrations, are given as Supporting Information (Table S1).

Discussion

The reaction of *trans*-[Pt(CH_3)Cl(Me_2SO)$_2$] with an extended series of nitrogen N-N bidentate ligands, carried out according to the procedures described above, afforded a series of new cationic complexes of general formula [Pt(N-N)(CH_3)(Me_2SO)]$^+$, that have been fully characterized analytically, chemically, and spectroscopically by infrared and ^{1}H NMR. The assignment of the ^{1}H NMR spectra was facilitated by the presence of coupling constants associated with the isotopically abundant ^{195}Pt and the data in Table 1 are consistent with the pattern of a S-bound sulfoxide, a methyl group directly coordinated to the metal and a chelate ligand coordinated to an asymmetric platinum metal center. The complexes formed by the asymmetric ligands 2-ampy and NO_2phen showed the presence of the two expected isomers that could be definitely identified as compounds **4a** and **4b** only in the case of the mixed aminopyridine ligand. The prochirality showed by the dimethyl sulfoxide of the complex containing dps has been interpreted as an indication that the sulfur of the pyridyl sulfide does not move rapidly from one side to the other of the coordination plane.

A significant feature of the ^{1}H NMR spectra of the Me_2phen complex is that, at ambient temperature, the halves of the ligand show coincident signals that separate out into different sets of signals only when the temperature is lowered (see Figure 1). Fast exchange of the two nitrogen atoms at a single coordination site (flipping) has been previously investigated for platinum complexes of the type *cis*-[Pt(PR_3)$_2$Cl(N-N)] and the fluxional process found to be strongly dependent on the orientation of the lone pairs of the chelate.[29] Complexes containing monocoordinate 2,9-dimethyl-1,10-phenanthroline of the type *cis*- and *trans*-[Pt(Me_2phen)X_2(PPh_3)] (X = Cl, Br, and I),[30] *trans*-[Pt(Me_2phen)XL_2][30] (L = PPh_3 and PBu^n_3) and [Pt(Me_2phen)-X_2L] (L = CO, PPh_3, Me_2SO, Me_2S, nitrosobenzene, pyridine, amine)[31] were recently shown to exhibit the same fluxional motion. The $\Delta G^{\ddagger}$ values for the fluxion were measured and found to be strongly dependent upon the nature of the trans activating group (for a phosphine in position trans to the phenanthroline only an upper limit of 25 kJ mol^{-1} could be estimated for the exchange process) and upon the covalent radius of the halide ion. The mechanism for the exchange of the donor atoms of a monocoordinated Me_2-phen at a single coordination site requires the formation of a five-coordinated transition state in which both ends of the phenanthroline are coordinated to the metal. Ring closure on [Pt(Me_2phen)X_2L] yields fairly stable trigonal-bypiramidal five-coordinate compounds only in the case of L = alkenes[32] or alkynes.[3c]

The complex [Pt(Me_2phen)(CH_3)(Me_2SO)]$^+$, in contrast with those mentioned above, has only two coordination sites occupied in the asymmetric molecular fragment [Pt(CH_3)(Me_2SO)] opposite to the half of the molecule which contains the coordination positions accessible to the two nitrogens of the chelate ligand. Thus, any conceivable mechanism for the flipping of the phenanthroline does not need to take into account the presence or the role of additional ligands L and therefore the system appears to be by far simpler than those described in previous studies.[29,30] We cannot rigorously exclude pathways which involve five-coordinate complexes promoted by nucleophilic attack by the solvent, by traces of free ligand, or even by weak coordination of hexafluorophosphate. However, a simple reaction scheme which accounts for all experimental findings is the following one



which involves rupture of the metal-nitrogen bond and formation of the coordinatively unsaturated T-shaped 14-electron three coordinate species $\mathbf{I}_1$ that rapidly interconverts into its $\mathbf{I}_2$ counterpart. Thereby, ring closure follows. The mechanism is reminiscent of that proposed to account for the apparent rotation of a π-allyl group relative to nitrogen ligands on palladium, which involves a monocoordinate chelating ligand on tricoordinated palladium.[33,34] This is obviously a simplified reaction scheme that does not account for the role of the solvent as a potential nucleophile in promoting ring rupture or in trapping the coordination sites of the highly unstable $\mathbf{I}_1$ and $\mathbf{I}_2$ three-coordinate intermediates after the opening of the ring. There is no reasonable doubt that the driving force for ring opening is a specific steric interaction of the *ortho* substituents of the chelated ligand with the other *cis* atoms in the square planar coordination plane, nicely evidenced in some molecular structures of platinum(II) containing chelated 2,9-dimethyl-1,-10-phenanthroline such as those of [Pt(Me_2phen)X_2] (X = Br and I)[31] in which a major distortion from the square-planar geometry is indicated by the dihedral angle between the plane of the chelating moiety (N−C−C−N) and the plane of coordination (X−Pt−X). The fast interconversion of the two T-shaped platinum cations intermediates I_1 and I_2 containing monodentate phen is accounted for by the low-energy barrier indicated by theoretical calculations for the fluxionality of coordinatively unsaturated three-coordinate species of this type.[35] It is now widely accepted that the formation of such 3-coordinate

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14-electron compounds offers a favourable reaction route to a number of fundamental processes as an alternative to the participation of 4- and 5-coordinate species.[36] Among them, the uncatalyzed cis to trans isomerization of complexes of the type *cis*-[$Pt(PEt_3)_2(R)X$] (R = alkyl or aryl groups; X = halide ion),[37] β-hydride elimination from dialkyl-[38] and monoalkyldiphosphinoplatinum(II)[39] complexes, olefin insertion into a Pt−H bond,[39a] reductive elimination of hydrogen from a three-coordinate $PtLH_2$ (L = phosphine) fragment,[40] some symmetrization reactions,[41] and nucleophilic substitutions.[19,42] The fluxional motion of the phenanthroline seen in this study for the complex $[Pt(Me_2phen)(CH_3)(Me_2SO)]^+$ can be safely added to the previous list. Moreover, it suggests the possibility for the flipping to occur also in other [Pt(Me2phen)XY] molecules and that for the $[Pt(Me_2phen)X_2]$ species it is not seen only because of the symmetry of the molecule. A detailed investigation of this aspect of the problem is underway.

At temperatures below 210 K the Me_2phen NMR signals show two singlets, one for each methyl, and separated signals for the aromatic protons, as a consequence of the freezing of the flipping of the ligand. When a stoichiometric amount of Me_2SO is added to a solution of the complex $[Pt(Me_2phen)(CH_3)(Me_2SO)]^+$ at this temperature, the NMR signals of bound and free dimethyl sulfoxide are broad and the broadening increases with increasing the temperature or sulfoxide concentration. The dependence of the rate constant upon [Me_2SO] and the temperature (in the range 250−300 K) was determined from the width of the NMR signals by using eq 5. The second-order rate law of eq 6 was assumed for this exchange reaction.

$$k_{obs} = k_2[Me_2SO] \qquad (6)$$

The second-order rate constants k_2 were fitted to the Eyring equation leading to $k_2^{298} = 38.1 \times 10^3\ m^{-1}\ s^{-1}$, $\Delta H^{\ddagger} = 13.5 \pm 0.8$ kJ mol^{-1} and $\Delta S^{\ddagger} = -112 \pm 3$ JK^{-1} mol^{-1}.

The systematic kinetics of the slow reactions, studied at different Me_2SO concentrations, were followed by isotopic exchange. During the exchange there was no indication of a loss of asymmetry in the NMR signals of the two halves of the coordinated bidentate N-N ligand. The dependence of the pseudo-first-order rate constants, listed in Table 2, is described by a family of straight lines with a zero intecept (Figure S3) and obeys eq 6. Linear regression analysis of these plots gave the values of k_2, the second-order rate constants for the bimolecular attack of Me_2SO on the substrate. Thus, the exchange is perfectly in keeping with an associative mode of activation, with no evidence of a significant contribution to the reactivity of a concurrent solvolytic pathway. This is supported by the low enthalpies of activation and the negative entropies of activation found for the complexes **5** and **6** (see Results section).

Steric Effects. The experimental findings indicate that the exchange is dominated by the direct attack of the nucleophile on the metal. The lability of the sulfur-bonded Me_2SO in the $[Pt(N\text{-}N)(CH_3)(Me_2SO)]^+$ complexes appears to be profoundly affected by the nature and the characteristics of the coordinated N-N ligand, the difference of reactivity between the first and the last members of the series being greater than 10 orders of magnitude (for complexes **2** and **11** the values of k_2 are $1.15 \times 10^{-6}\ m^{-1}\ s^{-1}$ and $38.1 \times 10^3\ m^{-1}\ s^{-1}$, respectively). The circumstance that **2** and **11** are formed by the most sterically demanding ligands Me_4en and Me_2phen, calls for a careful analysis of the specificity of steric effects. A significant feature is that steric bulk due to alkyl substituents at the nitrogens of the chelated diamine or in positions 2 and 9 of the phenanthroline, affects the lability of the corresponding complexes in opposite directions. For **2** a decrease of rate of 10 times is observed with respect to **1**, the complex formed by unsubstituted ethylenediamine, in agreement with similar results obtained in a study of the solvolysis of alkyl-substituted ethylenediamine platinum(II) complexes[43] and in a number of other studies of steric retardation on square planar complexes.[44] The interpretation is straightforward. The moderate decrease of rate can be ascribed to the additional difficulty of the nucleophile in approaching the metal center and in forming the new bond or, in other words, to a fairly modest destabilization of the 5-coordinate transition state. In contrast, the substrate containing Me_2phen exchanges the coordinated Me_2SO at a rate that is 5 orders of magnitude higher than that of **10**, the complex containing unsubstituted phen ($k_2 = 0.18\ m^{-1}\ s^{-1}$) or even of **12** and **14**, complexes with alkyl substituents ($k_2 = 0.026\ m^{-1}\ s^{-1}$) or aryl substituents ($k_2 = 0.10\ m^{-1}\ s^{-1}$) on the phenanthroline in positions different from 2,9.

This pattern of behavior finds its origin in the specific relevant nonbonding repulsions by the methyl groups in positions 2,9 with the two cis groups in the square-planar configuration, as seen in the congestion and distortion of the molecular structures of the $[Pt(Me_2phen)X_2]$ complexes.[31] There is significant steric relief when the metal adds a fifth ligand in the formation of a 5-coordinate trigonal-bypiramidal structure, where the phenanthroline occupies two positions of the equatorial plane. The molecular structures of a number of 5-coordinated complexes containing Me_2phen show[32] that, in this new position, the ligand is completely planar with the carbon atoms of the methyl groups far away from short range steric repulsions. In conclusion, observed consequences of the great steric destabilization of the square planar configuration are (i) a fluxional motion of the ligand (flipping), (ii) the easy uptake of an additional ligand (expecially olefins or alkynes)[45] yielding fairly stable 5-coordinate species, and (iii) a marked acceleration of the rate of ligand exchange.

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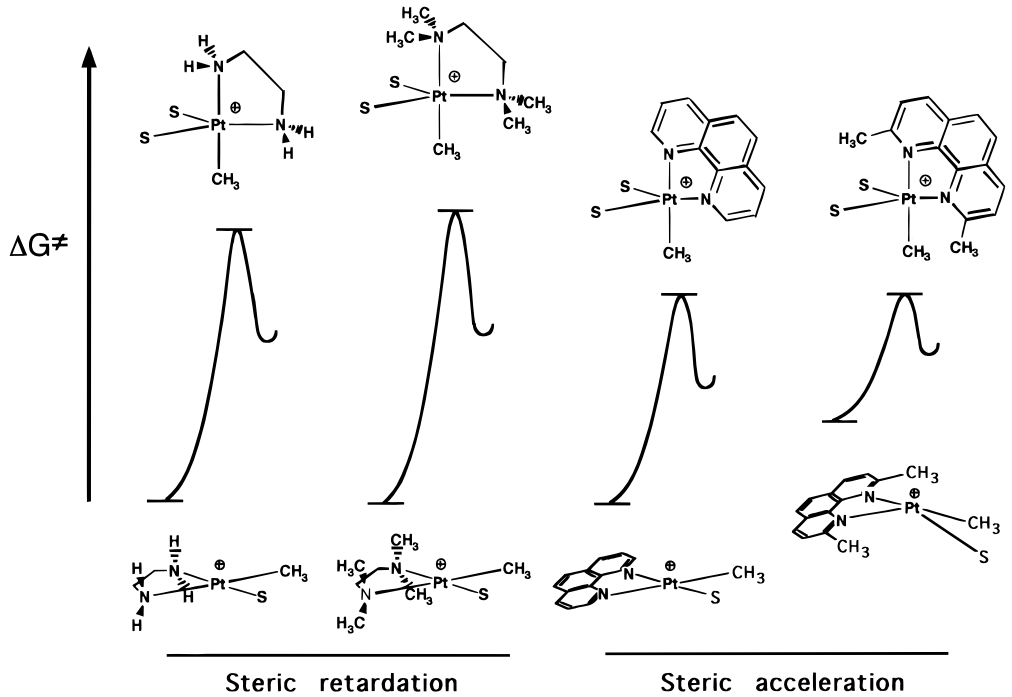

Figure 3. Relative changes of the free energy $\Delta G^{\ddagger}$, calculated from the rate constants in Table 2, on going from the square planar ground state to the trigonal bypiramidal transition state. The first two illustrate a case of steric retardation, as result of nonbonding interactions at the transition state; the last two refer to a rare example of steric acceleration in a bimolecular substitution.

A qualitative view of the different ways in which steric effects come into play can be seen in Figure 3, based on the reasonable assumption that the relative energies of the square-planar complexes **1**, **2**, and **10** as well as those of the trigonal bypiramidal transition states **10** and **11** are not greatly different. On going from **1** to **2** we observe a classic case of steric retardation in bimolecular processes, due to steric congestion at the 5-coordinate transition state;[46] the passage from **10** to **11** offers an unprecedented example of steric acceleration, as a result of steric destabilization of the square-planar ground state.

Electronic Effects. We will refer to the lability of complexes **7** and **14** as a term of comparison to examine changes of reactivity due primarily to electronic effects. Diimines, such as 2,2′-bipyridyl and phenanthroline, exert a considerable labilizing effect when compared to saturated nitrogen donors such as ethylendiamine, so that the displacement of the neutral ligand from $[Pt(N\text{-}N)(Me_2SO)(CH_3)]^+$ (N-N = bpy or phen) is at least 4 orders of magnitude faster than from $[Pt(en)(Me_2SO)(CH_3)]^+$. This is not a new phenomenon[5c,47,48] and it can be ascribed to the planarity of the imine ligands and to their ability to act as π acceptors and stabilize intermediates of higher coordination number. An increased electrophilicity of the metal, besides the increase of reactivity, leads also to a significant increase of the nucleophilic discrimination ability of the substrate.[47,48] It is of interest to note that in the complex *cis*-$[Pt(py)_2(Me_2SO)(CH_3)]^+$, which has the same array of donor atoms around the metal as for bpy and phen, but a different orientation of the pyridine aromatic rings, the reactivity is significantly less (2 orders of magnitude) than that of **7** and **14**. Thus, back-donation from filled d orbitals on the metal to empty antibonding orbitals of the ligands appears to be somewhat reduced, although there is a wide range of kinetic,[49] spectroscopic,[50] and structural[51] evidence in favor of a tendency of pyridine for π-bonding interactions.

Much of the reduction of reactivity of complexes containing 2,2′-dipyridylamine and 2,2′-dipyridyl sulfide is due to the fact that the bidentate ligands are no longer α-diimines. The introduction of a spacer group between the pyridine rings, such as the sulfur atom for dps, has little effect on the reactivity which remains comparable to that of the pyridine complex, whereas comparison of the rates of **8** and **9** suggests that to a certain extent NH is more effective than the sulfur in assisting sulfoxide exchange.

The mixed ligand 2-(aminomethyl)pyridine is coordinated to the metal through a sp^3 amine nitrogen and a sp^2 imine nitrogen. The rate of exchange in Table 2 ($k_2 = 3.5 \times 10^{-3}\ m^{-1}\ s^{-1}$) refers to the isomer **4a** that contains the pyridyl moiety trans to the leaving sulfoxide. The reactivity appears to be somewhat lower than that of the pyridine complex but still more than 100

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times higher than that of the ethylenediamine complex having two saturated nitrogen atoms. It is therefore confirmed that the nature of the trans-activating group and its π bonding ability play a major role in controlling the rates of bimolecular exchange.

Further evidence for a relationship between the lability of Me_2SO and the electrophilicity of the reaction center, as dictated by the extent of displacement of charge by the spectator ligands, is given by the dependence of the reactivity of complexes of substituted phenanthrolines upon their basicity. Setting apart the highly hindered Me_2phen discussed previously, and taking into account only data points for phenanthrolines in which the substituents are in positions far away from the reaction center with little if any possibility of steric interactions, one finds a linear relationship between the pK_a of the phenanthrolines, taken as a measure of their electron donicity, and the logarithms of rates constants for ligand exchange, according to the equation $\log k_2 = 0.663 - 0.341$ pK_a (four data points, $R = 0.931$, from linear regression analysis). The correlation is very much improved (three data points, $R = 0.997$) if the point for the phen complex, which lies above the line determined by the remainder of the data, is excluded from the analysis. As can be seen from the slope of the plot, the sensitivity of the reaction rates to the electron density brought about by substituents on the phenanthroline is significant (on going from the least basic NO_2phen, p$K_a = 3.23$, to the most basic Me_4phen, p$K_a = 6.35$, the reactivity is decreased by a factor of 10) but still modest in comparison to the overall change of reactivity observed for the entire set of ligands examined.

The reactivity shown by the complexes containing flexible diimine ligands such as cy_2dim and pr^i_2dim, despite their strong tendency to transfer electron density to the metal,[52] appears to be somewhat greater than that of complexes with the more rigid and less basic bpy and phen. All these ligands, on coordinating to the metal in a square planar configuration, form five-membered rings, whose rigidity varies significantly on going from the completely rigid phen to bpy, which can undergo some rotation around the C(2)−C(2′) bond axis, to cy_2dim and pr^i_2dim that possess a higher flexibility around the N−C−C−N bond chain. No previous kinetic studies can be found on these systems or information on the extent to which such ligands favor electron delocalization from platinum. However, the results of this study seem to suggest that the ease with which both the backbone and the bite angle[53] of these molecules can be distorted on going from the square planar to the trigonal bypiramidal configuration does play a significant role in controlling the substitution rate.

In conclusion, the overall structure-reactivity relationship for these complexes having the same array of donor atoms around the metal, has been rationalized on the basis of an interplay of electronic and steric effects. It is worth of interest to note that a fine tuning of the properties of the "spectator" ligands can lead to platinum(II) substrates of very high reactivity, comparable or even by far greater (as for the Me_2phen complex) to that of similar palladium(II) species.[47] A study to ascertain whether these highly reactive Pt(II) compounds possess catalytic properties is underway.

Acknowledgment. We wish to thank Dr. B. E. Mann for helpful discussions and the CNR and MURST for financial support. Thanks are due also to the reviewers for helpful suggestions.

Supporting Information Available: Table S1, reporting the dependence of dimethyl sulfoxide exchange rates, k_{obs} (s^{-1}), of **11** upon the temperature and [Me_2SO], Figure S2, a typical kinetic plot for isotopic labeling experiment, and Figure S3, an overall plot of the dependence of k_{obs} (s^{-1}) on [Me_2SO] for isotopic labeling experiments on various complexes (3 pages). Ordering information is given in any current masthead page.

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