Fluxional Behavior of the Dinitrogen Ligand 2,9-Dimethyl-1,10-phenanthroline in Cationic Methyl Platinum(II) Complexes

Raffaello Romeo,*,† Lucia Fenech,† Luigi Monsù Scolaro,†,‡ Alberto Albinati,§ Alceo Macchioni,|| and Cristiano Zuccaccia||

Dipartimento di Chimica Inorganica, Chimica Analitica e Chimica Fisica and Istituto di Chimica e Tecnologia dei Prodotti Naturali (ICTPN−CNR), Sezione di Messina, Università di Messina, Salita Sperone 31, Vill. S. Agata, 98166 Messina, Italy, INFM Unità di Messina, Messina, Italy, Istituto di Chimica Farmaceutica e Tossicologica, Università di Milano, Milano, Italy, and Dipartimento di Chimica, Università di Perugia, Perugia, Italy

Received December 13, 2000

The ionic methylplatinum(II) complexes [Pt(Me)(L)(dmphen)]X (dmphen = 2,9-dimethyl-1,10-phenanthroline, L = Me_2SO, X = PF_6^- **1a**, BF_4^- **1b**, $CF_3SO_3^-$ **1c**, ClO_4^- **1d**, $B(C_6H_5)_4^-$ **1e**, $[B(3,5\text{-}(CF_3)_2C_6H_3)_4]^-$ **1f**; L = *n*-Bu_2SO, X = $CF_3SO_3^-$ **1g**; L = PPh_3, X = PF_6^- **2a**, BF_4^- **2b**, $CF_3SO_3^-$ **2c**, ClO_4^- **2d**, $B(C_6H_5)_4^-$ **2e**, $[B(3,5\text{-}(CF_3)_2C_6H_3)_4]^-$ **2f**; X = $CF_3SO_3^-$, L = $CyNH_2$ **3a**, *i*-$PrNH_2$ **3b**, 2,6-Me_2py **3c**, $EtNH_2$ **3d**, $AsPh_3$ **3e**, dimethylthiourea (Me_2th) **3f** and the uncharged [Pt(Me)(X)(dmphen)] (X = SCN^- **4a**, $SeCN^-$ **4b**) complexes have been synthesized and fully characterized. In chloroform, as well as in acetone or methanol, complexes **1a**−**1g**, **2a**−**2h** (X = Cl^- **g**, NO_2^- **h**, formed "in situ"), and **3e** show dynamic behavior due to the oscillation of the symmetric chelating ligand dmphen between nonequivalent bidentate modes. All the other compounds feature a static structure in solution. The crystal structure of **2a** shows a tetrahedral distortion of the square planar coordination geometry, a loss of planarity of the dmphen ligand, and, most notably, a rotation of the dmphen moiety, around the N1−N2 vector, to form a dihedral angle of 42.64(8)° with the mean coordination plane. The hexafluorophosphate ion lies on the side of the phenanthroline ligand. The interionic structures of **2a**, **2b**, and **2f** were investigated in $CDCl_3$ at low temperature by ^{1}H-NOESY and ^{19}F{^{1}H}-HOESY NMR spectroscopies. Whereas PF_6^- (**2a**) and BF_4^- (**2b**) show strong contacts with the cation $[Pt(Me)(PPh_3)(dmphen)]^+$, being located preferentially on the side of the phenanthroline ligand, the $[B(3,5\text{-}(CF_3)_2C_6H_3)_4]^-$ (**2f**) ion does not form a tight ion pair. The dynamic process was studied by variable-temperature NMR spectroscopy for **1a**−**1f** and **2a**−**2h** in $CDCl_3$. The activation energies $\Delta G^{\ddagger}_{298}$ for the sulfoxide complexes **1a**−**1f** are lower than those of the corresponding phosphine complexes **2a**−**2f** by ≈10 kJ mol^{-1}. The nature of the counteranion exerts a tangible influence on the fluxionality of dmphen in both series of complexes **1** and **2**. The sequence of energies observed for **2a**−**2h** encompasses an overall difference of about 16 kJ mol^{-1}, increasing in the order $Cl^- \approx NO_2^- \ll CF_3SO_3^- < ClO_4^- < B(C_6H_5)_4^- < BF_4^- \approx PF_6^- < B(3,5\text{-}(CF_3)_2C_6H_3)_4^-$. Acetone and methanol have an accelerating effect on the flipping. Concentration-dependent measurements, carried out in $CDCl_3$ for **2a** with *n*-Bu_4NPF_6 and the ligands dmphen, *n*-Bu_2SO, *sec*-Bu_2SO, and *sec*-Bu_2S showed that the rate of the fluxional motion is unaffected by added *n*-Bu_4NPF_6, whereas in the other cases this increases linearly with increasing ligand concentration, according to a pattern of behavior typical of substitution reactions. Dissociative and associative mechanisms can be envisaged for the observed process of flipping. Dissociation can be prevalent within the ion pair formed by a "noncoordinating" anion with the metallic cationic complex in chloroform. Among the possible associative mechanisms, promoted by polar solvents or by relatively strong nucleophiles, a consecutive displacement mechanism is preferred to intramolecular rearrangements of five-coordinate intermediates.

Introduction

The bidentate nitrogen ligand 2,9-dimethyl-1,10-phenanthroline (dmphen, hereafter), when binding to platinum(II) in a square-planar coordinative environment, is severely distorted because of the steric hindrance of the methyl substituents of dmphen that are in proximity to the other groups coordinated to the metal. This distortion can be easily described by the dihedral angle that the plane of the chelating moiety forms with the coordination plane.[1] Observed consequences of this strong steric congestion in the square coordination plane are (i) easy addition of a fifth group to form five-coordinate species, where steric congestion is relieved,[1a,2] (ii) steric acceleration of the

* To whom correspondence should be addressed. Telephone: +39-090-391984. FAX: +39-090-393756. E-mail: Raf.Romeo@chem.unime.it.
† Università di Messina.
‡ INFM Unità di Messina.
§ Università di Milano.
|| Università di Perugia.

(1) (a) Fanizzi, F. P.; Intini, F. P.; Maresca, L.; Natile, G.; Lanfranchi, M.; Tiripicchio, A. *J. Chem. Soc., Dalton Trans.* **1991**, 1007. (b) De Felice, V.; Albano, V. G.; Castellari, C.; Cucciolito, M. E.; De Renzi, A. *J. Organomet. Chem.* **1991**, *403*, 269. (c) Milani, B.; Alessio, E.; Mestroni, G.; Sommazzi, A.; Garbassi, F.; Zangrando, E.; Bresciani-Pahor, N.; Randaccio, L. *J. Chem. Soc. Dalton Trans.* **1994**, 1903. (d) Clark, R. J. H.; Fanizzi, F. P.; Natile, G.; Pacifico, C.; van Rooyen, C. G.; Tocher, D. A. *Inorg. Chim. Acta* **1995**, *235*, 205. (e) Cucciolito, M. E.; De Renzi, A.; Giordano, F.; Ruffo, F. *Organometallics* **1995**, *14*, 5410.

10.1021/ic0014080 CCC: $20.00
Published on Web 05/30/2001

substitutional rate of exchanging ligands,[3] and (iii) fluxional motion of the dinitrogen ligand between two different exchanging sites.[4] The direct uptake of a ligand L by $[PtX_2(dmphen)]$ (X = halide ion) to yield five-coordinate trigonal bipyramidal $[PtX_2(dmphen)L]$ species is favored when L is a strong π-acceptor (e.g., an alkene or alkyne).[5] The dinitrogen ligand lies, together with the ligand L, in the trigonal plane, forming a flat unconstrained five-membered ring,[1a,2] even though a rare case for axial−equatorial N−N coordination for dmphen has been reported.[6] When L is a C, P, S, or N donor atom (CO, PPh_3, SMe_2, $SOMe_2$, ONPh), the phenanthroline switches from a doubly to a singly binding mode.[1d,7] The resulting open-ring square-planar $[PtX_2(dmphen)L]$ addition products are characterized by a fluxional motion of the monocoordinate phenanthroline that renders the two halves of dmphen equivalent in the NMR time scale.[4] The activation energy for this flipping was found to decrease by increasing the labilizing effect of the trans ligand.[1d,4]

In a recent kinetic study of sulfoxide exchange in monoalkyl cationic platinum(II) complexes of the type $[Pt(Me)(Me_2SO)(N-N)]PF_6$, containg nitrogen N−N bidentate ligands widely different in steric and electronic characteristics, we found that the substrate containing dmphen exchanges the coordinated Me_2SO at a rate that is 5 orders of magnitude greater than that of the complex containing unsubstituted phenanthroline.[3] In addition, only dmphen, among the various N−N ligands examined, was characterized by a fast exchange between nonequivalent bidentate modes in acetone solution. Both acceleration of ligand exchange and flipping of dmphen have a common origin in the great steric destabilization of the square-planar configuration and in the stability of the five-coordinate transition state, which is in contrast to the widely accepted idea that an increase of steric hindrance favors a lower coordination number. The mechanism proposed for the dmphen flipping involves (i) initial dissociation of the metal−nitrogen bond, (ii) fast interconversion between two three-coordinate T-shaped intermediates containing monocoordinated dmphen, and (iii) final ring closure. The dissociative mechanism was proposed on the basis of the parallelism between the fluxional process and the dissociative uncatalyzed isomerization of monoalkylbisphosphine platinum(II) complexes[8] or the apparent rotation of a π-allyl group relative to nitrogen ligands on palladium.[9,10] It was necessary to assume that the solvent and the hexafluorophosphate ion are too weakly coordinating to promote a nucleophilic attack and reaction pathways via five-coordinate species.

The monoalkyl cationic complexes $[Pt(Me)(dmphen)(L)]^+$ synthesized in this work, compared to the $[PtX_2(dmphen)(L)]$ complexes discussed above, offer the great advantage of having a definite geometrical configuration (square planar), no ambiguity in the coordination number (four- or five-coordinate) or in the four-coordinate geometry (cis or trans), nor external groups that may be potential nucleophiles (the open arm of dmphen). The structural properties of the complex $[Pt(Me)(dmphen)(PPh_3)]PF_6$ have been determined in the solid state and in chloroform solution, where the cation shows strong contacts with the anion. The dynamic exchange process of the dinitrogen ligand on the cation $[Pt(Me)(dmphen)(PPh_3)]^+$ was investigated by variable-temperature NMR spectroscopy in $CDCl_3$, as a function of the nature of the counteranion, of the solvent, or of added nucleophiles. The experimental results are consistent with a mechanism involving two different pathways, dissociative and associative. Which will prevail depends on a delicate balance between the structural features of the complexes in solution and the action of potential nucleophiles.

Experimental Section

General Procedures and Chemicals. All syntheses were performed under a dry, oxygen-free nitrogen atmosphere using standard Schlenk-tube techniques, and the products were worked up in air. Solvents (from Aldrich) used in the synthetic procedures were distilled under nitrogen from appropriate drying agents (diethyl ether from sodium benzophenone ketyl, dichloromethane from barium oxide, dimethyl sulfoxide, at low pressure, from CaH_2, after preliminary filtration through an alumina column) and then stored in N_2-filled flasks over activated 4-Å molecular sieves. Chloroform-*d* (D, 99.96%, Cambridge Isotope Laboratories) was dried standing for many days over CaH_2, distilled under nitrogen over activated magnesium sulfate and sodium carbonate, and then stored over activated 4-Å molecular sieves. Acetone-d_6 (D, 99.96%) and methanol-d_4 (D, 99.96%) were used as received from CIL. K_2PtCl_4 (Strem) was purified by dissolving it in water and filtering. The salt $Na[B(3,5\text{-}(CF_3)_2C_6H_3)_4]$ was prepared according to a published method[12] and was used to prepare the analogous potassium salt by ion exchange (KPF_6) over a Dowex 50W(50×8−100) resin, which was preliminarily washed with water and activated with HCl. The amines were purchased from Aldrich and distilled over KOH under reduced pressure. Triphenylphosphine (Strem) was crystallized from ethanol.

Instrumentation. Infrared spectra were recorded as Nujol mulls using CsI disks on a Perkin-Elmer FT-IR Model 1730 spectrophotometer. One- and two-dimensional ^1H, ^{13}C, ^{31}P and ^{19}F NMR spectra were measured on Bruker DPX 200, AMX R-300, and DRX 400 spectrometers. Referencing is relative to TMS (^1H and ^{13}C), 85% H_3PO_4 (^{31}P), and CCl_3F (^{19}F). NMR samples were prepared by dissolving about 10 mg of compound in 0.5 mL of $CDCl_3$, acetone-d_6, or methanol-d_4. Two-dimensional ^1H-NOESY and $^{19}F\{^1H\}$-HOESY spectra were recorded with a mixing time of 500−800 ms. The temperature within the probe was measured using the methanol or ethylene glycol method.[13] UV/vis electronic spectra were recorded on a Cary 219 or a Hewlett-Packard HP 8452 A diode array spectrophotometer. Microanalyses were performed by Redox Analytical Laboratories, Milan, Italy.

Synthesis of Complexes. The complex *trans*-$[PtCl(Me)(Me_2SO)_2]$ was prepared according to Eaborn et al.[14] and was purified by several crystallizations from dichloromethane/diethyl ether mixtures. The

(2) (a) Albano, V. G.; Ferrara, M. L.; Monari, M.; Panunzi, A.; Ruffo, F. *Inorg. Chim. Acta* **1999**, *285*, 70. (b) De Felice, V.; Ferrara, M. L.; Giordano, F.; Ruffo, F. *Gazz. Chim. Ital.* **1994**, *124*, 117. (c) Giordano, F.; Ruffo, F.; Saporito, A.; Panunzi, A. *Inorg. Chim. Acta* **1997**, *264*, 231.(d) Fanizzi, F. P.; Natile, G.; Lanfranchi, M.; Tiripicchio, A.; Pacchioni, G. *Inorg. Chim. Acta* **1998**, *275*, 500. (e) Albano, V. G.; Castellari, C.; Monari, M.; De Felice, V.; Panunzi, A.; Ruffo, F. *Organometallics* **1996**, *15*, 4012. (f) Albano, V. G.; Castellari, C.; Monari, M.; De Felice, V.; Panunzi, A.; Ruffo, F. *Organometallics* **1992**, *11*, 3665.

(3) Romeo, R.; Monsù Scolaro, L.; Nastasi, N.; Arena, G. *Inorg. Chem.* **1996**, *35*, 5087.

(4) Fanizzi, F. P.; Lanfranchi, M.; Natile, G.; Tiripicchio, A. *Inorg. Chem.* **1994**, *33*, 3331.

(5) (a) Albano, V. G.; Natile, G.; Panunzi, A. *Coord. Chem. Rev.* **1994**, 133, 67. (b) Maresca L.; Natile, G. *Comments Inorg. Chem.* **1993**, *14*, 349.

(6) Albano, V. G.; Monari, M.; Orabona, I.; Ruffo, F.; Vitagliano, A. *Inorg. Chim. Acta* **1997**, *265*, 35−46.

(7) (a) Fanizzi, F. P.; Maresca L.; Natile, G.; Lanfranchi, M.; Tiripicchio, A.; Pacchioni, G. *J. Chem. Soc., Chem. Commun.* **1992**, 333.

(8) Romeo, R.; Alibrandi, G. *Inorg. Chem*. **1997**, *36*, 4822 and references therein.

(9) Albinati, A.; Kunz, R. W.; Ammann, C. J.; Pregosin, P. S. *Organometallics* **1991**, *10*, 1800.

(10) Gogoll, A.; Ornebro, J.; Grennberg, H.; Bakwall, J. E. *J. Am. Chem. Soc.* **1994**, *116*, 3631.

(11) (a) Riddik, J. A.; Burger, W. B.; Sakano, T. K. *Organic solvent*, 4th ed.; Weissenberger, A., Ed.; Wiley: New York, 1986.

(12) Brookhart, M.; Grant B.; Volpe, A. F., Jr. *Organometallics* **1992**, *11*, 3920.

(13) (a) Van Geet, A. L. *Anal. Chem*. **1968**, *40*, 2227. (b)Van Geet, A. L. *Anal. Chem*. **1970**, *42*, 679.

(14) Eaborn, C.; Kundu, K.; Pidcock, A. *J. Chem. Soc., Dalton Trans.* **1981**, 933.

complexes [PtMe(dmphen)(Me_2SO)]X (X^- = PF_6, **1a**; BF_4, **1b**; CF_3SO_3, **1c**; ClO_4, **1d**) were prepared according to the following procedure. On adding a weighed amount of dmphen (0.125 g, 0.57 mmol) to a methanol solution (50 mL) of *trans*-[PtCl(Me)(Me_2SO)$_2$] (0.232 g, 0.57 mmol), a yellow precipitate of [PtMe(dmphen)Cl] is immediately formed, which is dissolved by adding slowly under stirring a methanol solution of the stoichiometric amount of AgX ($AgPF_6$ for **1a**; $AgBF_4$ for **1b**; $AgCF_3SO_3$ for **1c**; $AgClO_4$ for **1d**). AgCl was filtered off and the excess solvent was evaporated under reduced pressure, the residue was dissolved in dichloromethane, the solution was filtered on a cellulose column to remove residual AgCl, and the products were separated out on adding diethyl ether and cooling.

[Pt(Me)(dmphen)(Me_2SO)]PF_6, 1a. IR: ν(S═O) 1127 cm^{-1}. ^{1}H NMR ($CDCl_3$, T = 295 K): δ 8.51 (s, br, 2H, $H_{4,7}$), 7.97 (s, 2H, $H_{5,6}$), 7.80 (s, br, 2H, $H_{3,8}$), 3.45 (s, $^3J_{PtH}$ = 35.5 Hz, 6H, S−CH_3), 3.07 (s, 6H, $Me_{A,B}$), 0.94 (s, $^2J_{PtH}$ = 76.1 Hz, 3H, Pt−CH_3). Anal. Calcd for $PtC_{17}H_{21}F_6N_2OPS$: C, 31.83; H, 3.30; N, 4.37. Found: C, 31.90; H, 3.35; N, 4.52.

[Pt(Me)(dmphen)(Me_2SO)]BF_4, 1b. ^{1}H NMR ($CDCl_3$, T = 295 K): δ 8.53 (d, $^3J_{HH}$ = 8.4 Hz, 2H, $H_{4,7}$), 7.98 (s, 2H, $H_{5,6}$), 7.81 (d, $^3J_{HH}$ = 8.4 Hz, 2H, $H_{3,8}$), 3.45 (s, $^3J_{PtH}$ = 35.5 Hz, 6H, S−CH_3), 3.06 (s, 6H, $Me_{A,B}$), 0.93 (s, $^2J_{PtH}$ = 76.4 Hz, 3H, Pt−CH_3).

[Pt(Me)(dmphen)(Me_2SO)]CF_3SO_3, 1c. ^{1}H NMR ($CDCl_3$, T = 295 K): δ 8.56 (d, $^3J_{HH}$ = 8.4 Hz, 2H, $H_{4,7}$), 8.00 (s, 2H, $H_{5,6}$), 7.82 (d, $^3J_{HH}$ = 8.4 Hz, 2H, $H_{3,8}$), 3.48 (s, $^3J_{PtH}$ = 35.5 Hz, 6H, S−CH_3), 3.06 (s, 6H, $Me_{A,B}$), 0.94 (s, $^2J_{PtH}$ = 76.9 Hz, 3H, Pt−CH_3).

[Pt(Me)(dmphen)(Me_2SO)]ClO_4, 1d. ^{1}H NMR ($CDCl_3$, T = 295 K): δ 8.56 (d, $^3J_{HH}$ = 8.4 Hz, 2H, $H_{4,7}$), 7.98 (s, 2H, $H_{5,6}$), 7.81 (d, $^3J_{HH}$ = 8.4 Hz, 2H, $H_{3,8}$), 3.43 (s, $^3J_{PtH}$ = 35.5 Hz, 6H, S−CH_3), 3.08 (s, 6H, $Me_{A,B}$), 0.93 (s, $^2J_{PtH}$ = 76.5 Hz, 3H, Pt−CH_3).

The compounds **1e** and **1f** were prepared by adding to a methanolic solution of **1a** concentrated solutions of $NaB(C_6H_5)_4$ and Na[B(3,5-$(CF_3)_2C_6H_3)_4$], respectively.

[Pt(Me)(dmphen)(Me_2SO)]$B(C_6H_5)_4$, 1e. ^{1}H NMR ($CDCl_3$, T = 295 K): δ 8.11 (s, br, 2H, $H_{4,7}$), 7.94 (s, br, 2H, $H_{5,6}$), 7.63 (s, br, 2H, $H_{3,8}$), 7.40−7.51 (m, 8H, *o*-*H*), 6.98 (t, $^3J_{HH}$ = 7.5 Hz, 8H, *m*-*H*), 6.81 (t, $^3J_{HH}$ = 7.5 Hz, 4H, *p*-*H*), 2.87 (s, $^3J_{PtH}$ = 34.2 Hz, 6H, S−CH_3), 2.85 (s, br, 6H, $Me_{A,B}$), 0.67 (s, $^2J_{PtH}$ = 76.1 Hz, 3H, Pt−CH_3).

[Pt(Me)(dmphen)(Me_2SO)][B(3,5-$(CF_3)_2C_6H_3)_4$], 1f. ^{1}H NMR ($CDCl_3$, T = 298 K): δ 8.34 (d, $^3J_{HH}$ = 8.8 Hz, 2H, $H_{4,7}$), 7.82 (s, br, 2H, $H_{5,6}$), 7.70 (s, br, 8H, *o*-*H*), 7.65 (buried under *m*-H, $H_{3,8}$), 7.48 (s, 4H, *p*-*H*), 3.32 (s, $^3J_{PtH}$ = 36.3 Hz, 6H, S−CH_3), 2.95 (s, br, 6H, $Me_{A,B}$), 0.77 (s, $^2J_{PtH}$ = 76.8 Hz, 3H, Pt−CH_3).

[Pt(Me)(dmphen)(*n*-Bu_2SO)]CF_3SO_3, 1g. This compound was synthesized by adding di-*n*-butyl sulfoxide to a dichoromethane solution of **1c** in a 1:3 ratio, evaporating most of the solvent and cooling to −30 °C. ^{1}H NMR ($CDCl_3$, T = 298 K): δ 8.62 (d, $^3J_{HH}$ = 8.8 Hz, 2H, $H_{4,7}$), 8.05 (s, 2H, $H_{5,6}$), 7.84 (d, $^3J_{HH}$ = 8.8 Hz, 2H, $H_{3,8}$), 3.41 (t, 4H, CH_2–S), 3.02 (s, 6H, $Me_{A,B}$), 1.92 (m, 4H), 1.50 (m, 4H), 0.91 (t, 6H, CH_3–CH_2), 0.79 (s, $^2J_{PtH}$ = 76.2 Hz, 3H, Pt−CH_3). Anal. Calcd for $PtC_{24}H_{33}F_3N_2O_4S_2$: C, 39.50; H, 4.56; N, 3.84. Found: C, 38.96; H, 4.28; N, 3.88.

Complexes of the type [Pt(Me)(dmphen)(PPh_3)]X (X = PF_6^-, 2a; BF_4^-, 2b; $CF_3SO_3^-$, 2c; ClO_4^-, 2d) were prepared by Me_2SO for triphenylphosphine substitution from compounds **1a**, **1b**, **1c,** and **1d**, respectively. In a typical procedure a dichloromethane solution (20 mL) of triphenylphosphine (0.078 g, 0.3 mmol) was added drop by drop under stirring to a solution (20 mL) of **1a** (0.192 g, 0.3 mmol). Evaporation of most of the solvent, addition of diethyl ether, and cooling to −30 °C, led to the separation of a powdery solid.

[Pt(Me)(dmphen)(PPh_3)]PF_6, 2a. ^{1}H NMR ($CDCl_3$, T = 260 K): δ 8.64 (d, $^3J_{HH}$ = 8.4 Hz, 1H, H_4), 8.46 (d, $^3J_{HH}$ = 8.4 Hz, 1H, H_7), 8.04 (AB system, $^3J_{HH}$ = 8.9 Hz, H_5), 8.01 (AB system, $^3J_{HH}$ = 8.9 Hz, H_6), 7.90 (dd, $^3J_{HH}$ = 8.4 Hz, $^5J_{PH}$ = 1.5 Hz, 1H, H_3), 7.54 (dd, $^3J_{PH}$ = 10.5 Hz; $^3J_{HH}$ = 8.3 Hz, *o*-H), 7.54 (buried under *o*-H, *p*-H), 7.41 (ddd, $^3J_{HH}$ = 8.3 Hz; $^3J_{HH}$ = 6.9 Hz; $^4J_{PH}$ = 2.4 Hz, *m*-H), 7.29 (d, $^3J_{HH}$ = 8.4 Hz, 1H, H_8), 3.08 (s, 3H, Me_A), 1.95 (s, 3H, Me_B), 0.73 (d, $^3J_{PH}$ = 4.1 Hz; $^2J_{PtH}$ = 66.9 Hz, 3H, Pt−CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 260 K): δ 163.61 (s, C_2), 163.15 (s, C_9), 147.40 (d, $^4J_{PC}$ = 1.6 Hz, $C_{4'}$), 146.62 (s, $C_{6'}$), 139.87 (s, C_4), 139.12 (s, C_7), 134.81 (d, $^2J_{PC}$ = 10.8 Hz, *o*-C), 132.12 (d, $^4J_{PC}$ = 2.3 Hz, *p*-C), 129.25 (d, $^3J_{PC}$ = 11.1 Hz, *m*-C), 128.76 (d, $^3J_{PC}$ = 1.5 Hz, C_{10}), 128.47 (s, $C_{10'}$), 127.52 (d, $^4J_{PC}$ = 3.8 Hz, C_3), 127.17 (s, C_6), 126.81 (s, C_5), 126.76 (s, C_8). ^{31}P{^{1}H} NMR ($CDCl_3$, 260 K): δ 15.52 (s, $^1J_{PtP}$ = 4565 Hz, PPh_3), −143.14 (sept, $^1J_{PF}$ = 714 Hz, PF_6^-). ^{19}F NMR ($CDCl_3$, 260 K): δ −73.71 (d, $^1J_{FP}$ = 713 Hz).

[Pt(Me)(dmphen)(PPh_3)]BF_4, 2b. ^{1}H NMR ($CDCl_3$, T = 260 K): δ 8.70 (d, $^3J_{HH}$ = 8.4 Hz, 1H, H_4), 8.51 (d, $^3J_{HH}$ = 8.4 Hz, 1H, H_7), 8.08 (AB system, $^3J_{HH}$ = 8.8 Hz, H_5), 8.05 (AB system, $^3J_{HH}$ = 8.9 Hz, H_6), 7.93 (dd, $^3J_{HH}$ =8.4 Hz, $^5J_{PH}$ = 1.5 Hz, 1H, H_3), 7.53 (dd, $^3J_{PH}$ = 10.5 Hz; $^3J_{HH}$ = 8.3 Hz, *o*-H), 7.53 (buried under *o*-H, *p*-H), 7.41 (ddd, $^3J_{HH}$ = 8.3 Hz; $^3J_{HH}$ = 6.9 Hz; $^4J_{PH}$ = 2.4 Hz, *m*-H), 7.29 (d, $^3J_{HH}$ = 8.4 Hz, 1H, H_8), 3.08 (s, 3H, Me_A), 1.95 (s, 3H, Me_B), 0.73 (d, $^3J_{PH}$ = 4.1 Hz; $^2J_{PtH}$ = 66.9 Hz, 3H, Pt−CH_3).^{31}P{^{1}H} NMR ($CDCl_3$): δ 14.50 (s, $^1J_{PtP}$ = 4581 Hz, PPh_3), ^{19}F{^{1}H} NMR: δ −153.76 (br, $^{10}BF_4^-$), −153.81 (q, $^1J_{BF}$ = 1.0 Hz, $^{11}BF_4^-$).

[Pt(Me)(dmphen)(PPh_3)]CF_3SO_3, 2c. ^{1}H NMR ($CDCl_3$, T = 295 K): δ 8.60 (d, br, 2H, $H_{4,7}$), 8.08 (s, 2H, $H_{5,6}$), 7.89 (s, br, 1H, H_3), 7.62−7.48 (m, 9H, *o*-*H*, *p*-*H*), 7.47−7.37 (m, 6H, *m*-*H*), 7.29 (buried under $CDCl_3$, H_8), 3.09 (s, br, 3H, Me_A), 1.99 (s, br, 3H, Me_B), 0.75 (d, $^3J_{PH}$ = 4.2 Hz, $^2J_{PtH}$ = 73.6 Hz, 3H, Pt−CH_3). ^{31}P NMR ($CDCl_3$) δ: 14.5 ($^1J_{PtP}$ = 4580.0 Hz). Anal. Calcd for $PtC_{34}H_{30}N_2F_3O_3PS$: C, 49.22; H, 3.64; N, 3.38. Found: C, 48.86; H, 3.55; N, 3.40.

[Pt(Me)(dmphen)(PPh_3)]ClO_4, 2d. ^{1}H NMR ($CDCl_3$, T = 295 K): δ 8.67 (s, br, 1H, H_4), 8.52 (s, br, 1H, H_7), 8.07 (s, 2H, $H_{5,6}$), 7.90 (s, br, 1H, H_3), 7.62−7.48 (m, 9H, *o*-*H*, *p*-*H*), 7.45−7.35 (m, 6H, *m*-*H*), 7.29 (buried under $CDCl_3$, H_8), 3.08 (s, br, 3H, Me_A), 1.99 (s, br, 3H, Me_B), 0.75 (d, $^3J_{PH}$ = 4.2 Hz , $^2J_{PtH}$ = 72.7 Hz, 3H, Pt−CH_3). ^{31}P NMR ($CDCl_3$) δ: 14.5 (s, $^1J_{PtP}$ = 4577.6 Hz).

[Pt(Me)(dmphen)(PPh_3)]$B(C_6H_5)_4$, 2e. Obtained from **2a** and $NaB(C_6H_5)_4$ following essentially the same procedure described for the synthesis of **1e**. ^{1}H NMR ($CDCl_3$, T = 296 K): δ 8.11 (d, $^3J_{HH}$ = 8.1 Hz, 1H, H_4), 7.87 (d, $^3J_{HH}$ = 8.1 Hz, 1H, H_7), 7.62 (AB system, $^3J_{HH}$ = 8.5 Hz, 2H, $H_{5,6}$), 7.56−7.34 (m, 25H), 7.02−6.97 (m, 8H); 6.87−6.81 (m, 4H), 2.95 (s, 3H, Me_A), 1.85 (s, 3H, Me_B), 0.72 (d, $^2J_{PtH}$ = 73.6 Hz, $^3J_{PH}$ = 4.2 Hz, 3H, Pt−CH_3). ^{31}P NMR ($CDCl_3$): δ 14.5 (s, $^1J_{PtP}$ = 4575.3 Hz).

[Pt(Me)(dmphen)(PPh_3)] [B(3,5-$(CF_3)_2C_6H_3)_4$], 2f. A concentrated methanol solution of K[B(3,5-$(CF_3)_2C_6H_3)_4$] was added under stirring to a solution (5 mL) of **2a** (0.05 g, 0.06 mmol). The solid KPF_6 was filtered off, and the solid was obtained by evaporation of the residual solvent. ^{1}H NMR ($CDCl_3$, T = 260 K): δ 8.33 (d, $^3J_{HH}$ = 8.3 Hz, 1H, H_4), 8.16 (d, $^3J_{HH}$ = 8.4 Hz, 1H, H_7), 7.76 (AB system, $^3J_{HH}$ = 8.9 Hz, H_5), 7.74 (AB system, $^3J_{HH}$ = 8.9 Hz, H_6), 7.74 (m, *o*-*H*′), 7.69 (dd, $^3J_{HH}$ =8.5 Hz, $^5J_{PH}$ = 1.3 Hz, 1H, H_3), 7.53 (dd, $^3J_{PH}$= 10.5 Hz; $^3J_{HH}$ = 8.3 Hz, *o*-H), 7.53 (buried under *o*-H, *p*-H), 7.49 (br, *p*-*H*′), 7.39 (ddd, $^3J_{HH}$ = 8.3 Hz; $^3J_{HH}$ = 6.9 Hz; $^4J_{PH}$ = 2.4 Hz, *m*-*H*), 7.10 (d, $^3J_{HH}$ = 8.4 Hz, 1H, H_8), 3.03 (s, 3H, Me_A), 1.91 (s, 3H, Me_B), 0.75 (d, $^3J_{PH}$ = 4.1 Hz; $^2J_{PtH}$ = 66.9 Hz, 3H, Pt−CH_3).^{31}P{^{1}H} NMR ($CDCl_3$): δ 14.50 (s, $^1J_{PtP}$ = 4587 Hz, PPh_3), ^{19}F{^{1}H} NMR: δ −62.65 (s).[15]

[Pt(Me)(dmphen)(PPh_3)]Cl, 2g. Prepared by reacting in a NMR tube a solution of **2a** with the stoichiometric amount of $AsPh_4Cl$. The salt $AsPh_4PF_6$ separated out as a solid from the solution that, besides the compound **2g**, revealed the presence of small amounts of *cis*- and *trans*-[Pt(Me)Cl_2(PPh_3)] together with some free dmphen. ^{1}H NMR ($CDCl_3$, T = 295 K): δ 8.52 (d, br, 2H, $H_{4,7}$), 8.13 (s, 2H, $H_{5,6}$), 7.73−7.27 (m, 17H), 2.58 (s, br, 6H, $Me_{A,B}$), 0.75 (d, $^2J_{PtH}$ = 72.7 Hz, $^3J_{PH}$ = 4.2 Hz, 3H, Pt−CH_3).

[Pt(Me)(dmphen)(PPh_3)]NO_2, 2h. Prepared as described above for **2g** using $AsPh_4NO_2$ as reagent. ^{1}H NMR ($CDCl_3$, T = 295 K): δ 8.46 (d, br, 2H, $H_{4,7}$), 7.97 (s, 2H, $H_{5,6}$), 7.75−7.27 (m, 17H), 2.62 (s, br, 6H, $Me_{A,B}$), 0.76 (d, $^2J_{PtH}$ = 72.7 Hz, $^3J_{PH}$ = 4.2 Hz, 3H, Pt−CH_3).

Complexes of the type [Pt(Me)(dmphen)(L)]CF_3SO_3 (L = cyclohexylamine, $CyNH_2$, **3a**; isopropylamine, *i*-$PrNH_2$, **3b**; 2,6-dimethylpyridine, 2,6-Me_2py, **3c**; ethylamine, $EtNH_2$, **3d**; triphenylarsine, $AsPh_3$, **3e**; *N*,*N*′-dimethylthiourea, Me_2th, **3f**) and [Pt(Me)X(dmphen)] (X = SCN^-, **4a**; $SeCN^-$, **4b**) were prepared by reacting **1c** in dichloromethane with a slight excess of the appropriate reagent. The solid compounds were obtained after evaporation of most of the solvent, addition of diethyl ether, and cooling to −30 °C.

(15) The prime (′) refers to the aromatic protons of B(3,5-$(CF_3)_2C_6H_3)_4^-$.

[Pt(Me)(dmphen)(CyNH$_2$)]CF$_3$SO$_3$, 3a. ^{1}H NMR (acetone-d_6, T = 295 K): δ 8.81 (d, $^3J_{HH}$ = 8.4 Hz, 1H, H_4), 8.75 (d, $^3J_{HH}$ = 8.4 Hz, 1H, H_7), 8.15 (s, 2H, $H_{5,6}$), 8.00 (d, $^3J_{HH}$ = 8.4 Hz, 1H, H_3), 7.94 (d, $^3J_{HH}$ = 8.4 Hz, 1H, H_8), 4.90 (s, br, 2H, NH_2), 3.10 (s, 3H, CH_3), 3.00 (s, $^4J_{PtH}$ = 7 Hz, 3H, CH_3), 2.83 (s, br, 1H, CH), 2.28 (m, br, 2H, CH_2), 1.70 (m, br, 2H, CH_2), 1.60−1.10 (m, br, 6H, CH_2), 1.12 (s, $^2J_{PtH}$ = 80.2 Hz, 3H, CH_3–Pt). Anal. Calcd for PtC$_{22}$H$_{28}$F$_3$N$_3$O$_3$S: C, 39.64; H, 4.23; N, 6.30. Found: C, 39.73; H, 4.29; N, 6.19.

[Pt(Me)(dmphen)(*i*-PrNH$_2$)]CF$_3$SO$_3$, 3b. ^{1}H NMR (CDCl$_3$, T = 295 K): δ 8.43 (d, $^3J_{HH}$ = 8.4 Hz, 1H, H_4), 8.39 (d, $^3J_{HH}$ = 8.4 Hz, 1H, H_7), 7.85 (AB system, $^3J_{HH}$ = 8.8 Hz, 2H, $H_{5,6}$), 7.79 (d, $^3J_{HH}$ = 8.4 Hz, 1H, H_3), 7.64 (d, $^3J_{HH}$ = 8.4 Hz, 1H, H_8), 4.52 (s, br, 2H, NH_2), 3.19 (m, 1H, CH−N), 3.08 (s, 3H, CH_3), 2.97 (s, 3H, CH_3), 1.38 (d, $^3J_{HH}$ = 6.5 Hz, 6H, CH_3–CH), 1.09 (s, $^2J_{PtH}$ = 77.1 Hz, 3H, CH_3–Pt). Anal. Calcd for PtC$_{19}$H$_{24}$F$_3$N$_3$O$_3$S: C, 36.42; H, 3.86; N, 6.71. Found: C, 35.93; H, 4.10; N, 6.74.

[Pt(Me)(dmphen)(2,6-Me$_2$py)]CF$_3$SO$_3$, 3c. ^{1}H NMR (CDCl$_3$, T = 298 K): δ 8.63 (d, $^3J_{HH}$ = 8.4 Hz, 1H, H_4), 8.58 (d, $^3J_{HH}$ = 8.4 Hz, 1H, H_7), 8.02 (AB system, $^3J_{HH}$ = 8.7 Hz, $H_{5,6}$), 7.8 (m, 3H), 7.37 (d, $^3J_{HH}$ = 7.7 Hz, 2H, *m*-*H* py), 3.11 (s, 3H, CH_3), 3.01 (s, 6H, CH_3−py), 1.93 (s, 3H, CH_3), 0.86 (s, $^2J_{PtH}$ = 80.5 Hz, 3H, CH_3–Pt). Anal. Calcd for PtC$_{23}$H$_{24}$F$_3$N$_3$O$_3$S: C, 40.95; H, 3.59; N, 6.23. Found: C, 40.93; H, 3.52; N, 6.22.

[Pt(Me)(dmphen)(EtNH$_2$)]CF$_3$SO$_3$, 3d. ^{1}H NMR (acetone-d_6, T = 295 K): δ 8.81 (d, $^3J_{HH}$ = 8.4 Hz, 1H, H_4), 8.76 (d, $^3J_{HH}$ = 8.4 Hz, 1H, H_7), 8.15 (s, 2H, $H_{5,6}$), 8.02 ($^3J_{HH}$ = 8.4 Hz, 1H, H_3), 7.99 (d, $^3J_{HH}$ = 8.4 Hz, 1H, H_8), 5.10 (br-s, 2H, NH$_2$), 3.16 (s, 3H, CH_3), 3.00 (s, 3H, CH_3), 2.98 (m, 2H, CH_2) 1.09 (t, $^3J_{HH}$ = 6.7 Hz, 3H, CH_3–CH$_2$), 1.03 (s, $^2J_{PtH}$ = 81.2 Hz, 3H, CH_3–Pt).

[Pt(Me)(dmphen)(AsPh$_3$)]CF$_3$SO$_3$, 3e. ^{1}H NMR (CDCl$_3$, T = 298 K): δ 8.63 (s, br, 2H, $H_{4,7}$), 8.10 (s, 2H, $H_{5,6}$), 7.90 (s, br, 1H, H_3), 7.55−7.53 (m, 9H, *o*-*H*, *p*-*H*), 7.50−7.40 (m, 6H, *m*-*H*), 7.29 (br, H_8), 3.09 (s, br, 3H, Me_A), 2.06 (s, br, 3H, Me_B), 0.81 (s, $^2J_{PtH}$ = 74.4 Hz, 3H, CH_3–Pt). Anal. Calcd for PtAsC$_{34}$H$_{30}$F$_3$N$_2$O$_3$S: C, 46.74; H, 3.46; N, 3.21. Found: C, 46.08; H, 3.46; N, 3.18.

[Pt(Me)(dmphen)(Me$_2$th)]CF$_3$SO$_3$, 3f. ^{1}H NMR (CDCl$_3$, T = 298 K): δ 8.46 (d, $^3J_{HH}$ = 8.3 Hz, 1H, H_4), 8.41 (d, $^3J_{HH}$ = 8.3 Hz, 1H, H_7), 7.93 (br-s, 1H, NH), 7.90 (AB, $^3J_{HH}$ = 8.7 Hz, 2H, $H_{5,6}$), 7.75 (d, $^3J_{HH}$ = 8.3 Hz, 1H, H_3), 7.72 (d, $^3J_{HH}$ = 8.3 Hz, 1H, H_8),7.30 (br-s, 1H, NH), 3.19 (s, br, 3H, CH_3–N), 3.09 (s, 3H, CH_3), 3.05 (s, 3H, CH_3), 2.92 (s, br, 3H, CH_3–N), 1.18 (s, $^2J_{PtH}$ = 80.1 Hz, 3H, CH_3–Pt). Anal. Calcd for PtC$_{19}$H$_{23}$F$_3$N$_4$O$_3$S$_2$: C, 33.98; H, 3.45; N, 8.34. Found: C, 33.91; H, 3.38; N, 8.05.

[Pt(Me)(SCN)(dmphen)], 4a. Obtained by reacting stoichiometric amounts of **1c** and *n*-Bu$_4$NSCN in dichloromethane. ^{1}H NMR (CDCl$_3$, T = 298 K): δ 8.38 (d, $^3J_{HH}$ = 8.4 Hz, 1H, H_4), 8.36 (d, $^3J_{HH}$ = 8.4 Hz, 1H, H_7), 7.82 (AB system, $^3J_{HH}$ = 8.7 Hz, 2H, $H_{5,6}$), 7.72 (d, $^3J_{HH}$ = 8.4 Hz, 1H, H_3), 7.62 (d, $^3J_{HH}$ = 8.3 Hz, 1H, H_8), 3.13 (s, 3H, CH_3), 2.99 (s, 3H, CH_3), 1.31 (s, $^2J_{PtH}$ = 87.7 Hz, 3H, CH_3–Pt). Anal. Calcd for PtC$_{16}$H$_{15}$N$_3$S: C, 40.33; H, 3.17; N, 8.82. Found: C, 40.58; H, 3.30; N, 8.27.

[Pt(Me)(SeCN)(dmphen)], 4b. A solution of KSeCN (0.014 g, 0.1 mmol) in methanol (10 mL) was added drop by drop to a solution of **1c** (0.065 g, 0.1 mmol) in methanol (10 mL). After complete evaporation of the solvent, the brown solid compound was dissolved in CH_2Cl_2, the solution was filtered through a Celite column, then concentrated, added with diethyl ether, and cooled at −30 °C to yield a brown solid of **4b**. ^{1}H NMR (CDCl$_3$, T = 298 K): δ 8.37 (d, $^3J_{HH}$ = 8.4 Hz, 2H, $H_{4,7}$), 7.83 (AB system, $^3J_{HH}$ = 8.7 Hz, 2H, $H_{5,6}$), 7.71 (d, $^3J_{HH}$ = 8.4 Hz, 1H, H_3), 7.69 (d, $^3J_{HH}$ = 8.4 Hz, 1H, H_8), 3.39 (s, 3H, CH_3), 3.09 (s, 3H, CH_3), 1.34 (s, $^2J_{PtH}$ = 81.5 Hz, 3H, CH_3–Pt). Anal. Calcd for PtC$_{16}$H$_{15}$N$_3$Se: C, 36.72; H, 2.89; N, 8.03. Found: C, 36.71; H, 2.83; N, 8.00.

X-ray Data Collection and Structure Refinement. Air-stable, pale yellow crystals of [Pt(Me) (dmphen)(PPh$_3$)]PF$_6$ (**2a**) were obtained by slow diffusion of cyclohexane into a concentrated dichloromethane solution of the complex. For the data collection, a prismatic single crystal was mounted on a Bruker SMART CCD diffractometer. The crystals are triclinic and the space group, assumed to be $P\bar{1}$, was confirmed by the successful solution and refinement of the structure. Using an ω scan in steps of 0.3°, 2450 frames were collected, with counting time of 20 s. The cell constants were refined, at the end of the data collection, using 11 860 reflections, with the data reduction software SAINT.[16] The intensities were corrected for Lorentz and polarization factors[16] and empirically for absorption using the SADABS program.[17] Selected crystallographic and other relevant data are listed in Table 1 and in Supporting Information Table SI3. The standard deviations on intensities were calculated in term of statistics alone, while those on F_o^2 were calculated as shown in Table 1. The structure was solved by direct and Fourier methods and refined by full matrix least squares,[18] minimizing the function $[\sum w(F_o^2 - (1/k)F_c^2)^2]$. During the refinement anisotropic displacement parameters were used for all atoms, except the hydrogens that were treated isotropically. No extinction correction was deemed necessary. Upon convergence (see Supporting Information Table SI3) the final difference Fourier map showed no significant features. The hydrogen atoms, in their calculated positions, (C−H = 0.96 (Å), B(H) = 1.5B(C$_{bonded}$) (Å^2)), were included in the refinement using a riding model. All calculations were carried out by using the PC version of the SHELX-97 programs.[18] The scattering factors used, corrected for the real and imaginary parts of the anomalous dispersion, were taken from the literature.[19]

Table 1. Experimental Data for the X-ray Diffraction Study of the Complex [PtMe(dmphen)(PPh$_3$)]PF$_6$, **2a**

compound	[**2a**]
formula	$C_{33}H_{30}F_6N_2P_2Pt$
mol wt	825.62
data coll. T, K	293
diffractometer	SMART CCD
cryst syst	triclinic
space group(no.)	$P\bar{1}$ (2)
a, Å	9.4205 (6)
b, Å	9.9922 (7)
c, Å	17.5951 (12)
α, deg	79.918 (1)
β, deg	75.151 (1)
γ, deg	81.961 (1)
V, Å^3	1568.4 (3)
Z	2
ρ(calcd), g cm^{-3}	1.748
μ, cm^{-1}	46.38
radiation	Mo Kα (graphite monochromated, λ = 0.710 73 Å)
θ range, deg	2.08 < θ < 25.00
no. independent data	5491
no. obsd refl (n_o) $[\|F_o\|^2 > 2.0\sigma(\|F\|^2)]$	4679
transmission coeff	0.6948−1.0000
no. of param refined (n_v)	397
R^a (obsd refl)	0.0184
$R^2_w{}^b$ (obsd refl)	0.0446
GOF^c	0.541

^{a} $R = \sum(|F_o - (1/k)F_c|)/\sum|F_o|$. ^{b} $R^2_w = [\sum w(F_o^2 - (1/k)F_c^2)^2/\sum w|F_o^2|^2]$. ^{c} GOF $= [\sum_w(F_o^2 - (1/k)F_c^2)^2/(n_o - n_v)]^{1/2}$.

Variable-Temperature NMR Experiments. In a typical experiment, approximately 6 mg of the complex was dissolved in the appropriate deuterated solvent. When required, the appropriate amount of a nucleophile was added. The ^{1}H NMR spectrum was recorded over a temperature range depending on the rate of the fluxional motion (from 213 to 313 K for complexes **1a**−**1g** in CDCl$_3$; from 240 to 343 K for complexes **2a**−**2h**; from 194 to 341 K for **2a** in acetone-d_6 and methanol-d_4. Either the aromatic protons (for complexes **1a**−**1g**) or the methyl protons (for complexes **2a**−**2h**) of the phenanthroline were monitored and used for the line-shape analysis of the spectra. The exchange rates were calculated using the computer program gNMR

(16) SAINT: SAX Area Detector Integration; Siemens Analytical Instrumentation, 1996.
(17) Sheldrick, G. M. SADABS, Universität Göttingen. To be published.
(18) Sheldrick, G. M. SHELX-97. Structure Solution and Refinement Package; Universität Göttingen, 1997.
(19) *International Tables for X-ray Crystallography*; Wilson, A. J. C., Ed.; Kluwer Academic Publisher: Dordrecht, The Netherlands, 1992; Vol. C.

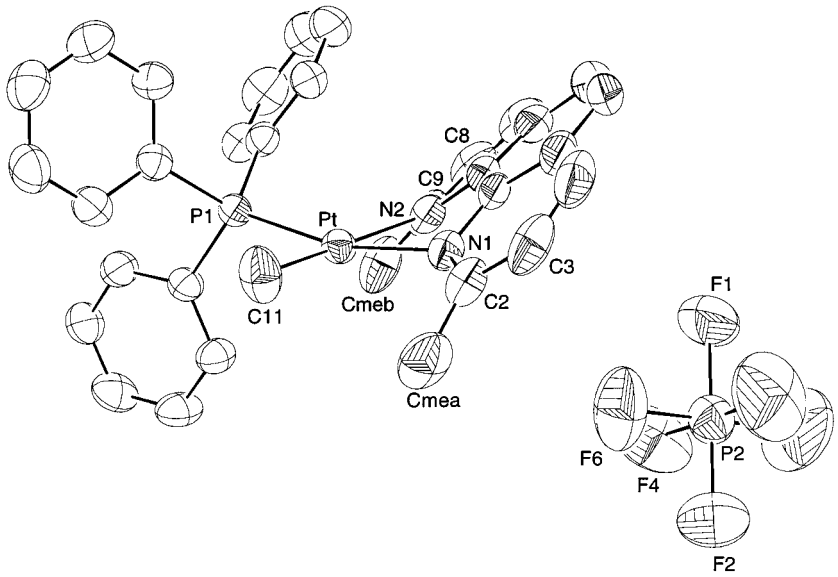


Figure 1. Molecular structure of complex **2a**.

4.0.[20] The activation parameters $\Delta G^{\ddagger}$(at 298 K), $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ were derived from a linear regression analysis of the Eyring plots.

Results

Synthesis. We have already reported on the use of the complex *trans*- [Pt(Me)Cl(Me_2SO)$_2$] as a useful synthon for the formation of cationic complexes of the type [Pt(Me)(N−N)(Me_2SO)]$^+$ (N−N = a wide series of diamines and diimines).[3] To synthesize different salts of the same cation [Pt(Me)(dmphen)(Me_2SO)]$^+$, the published procedure was slightly changed involving the preliminary synthesis of the neutral complex [Pt(Me)Cl(dmphen)] in methanol and the subsequent chloride abstraction by the appropriate silver salt in the presence of small amounts of dimethyl sulfoxide. Salts of low solubility, such as compounds **1e** and **1f**, were prepared directly from the hexafluorophosphate salt **1a** by addition of concentrated solutions of $NaB(C_6H_5)_4$ and $Na[B(3,5\text{-}(CF_3)_2C_6H_3)_4]$, respectively. All the other complexes **2a**−**2h**, **3a**−**3f**, and **4a** and **4b**, were prepared according to the substitution reaction

$$[Pt(Me)(dmphen)(Me_2SO)]X + L \rightleftharpoons [Pt(Me)(dmphen)(L)]X + Me_2SO \quad (1)$$

taking advantage of the extreme lability of the coordinated sulfoxide molecule.

X-ray Structure of 2a. An ORTEP view of compound **2a** is given in Figure 1, while selected bond distances and angles are listed in Table 2. The crystal structure consists of discrete cationic [PtMe(dmphen)(PPh_3)]$^+$ units and hexafluorophosphate anions held together by Coulombic interactions. The packing shows that each PF_6^- moiety mainly interacts with one of the two symmetry-related cations present in the cell, possibly reflecting the existence of ion pairs (see Figure SI1). The shortest distances between a fluorine atom of PF_6^- and one ring of the phenanthroline ligand (e.g., F1 and the N1-containing ring in Figure 1) are in the range 3.1−3.8 Å, while the remaining packing separations are >4.2−4.5 Å. The immediate coordination sphere of the metal consists of two nitrogen donors of the dmphen ligand (with a bite angle of 76.4(1)°), the phosphorus of the triphenylphosphine, and the carbon of the methyl group. The Pt−C and Pt−P bond lengths (2.052(4) and 2.23(8) Å, respectively) are in the expected range of values.[21] The Pt−N2 distance (2.162(3) Å), for the nitrogen trans to the strong σ-donor Pt−C bond, and the Pt−N1 distance (2.152(3) Å), for the nitrogen trans to phosphorus, are equal and in the upper range of separations reported for platinum(II) complexes where only electronic effects are present. In the related complex [Pt(Me)(phen)(Me_2SO)]PF_6,[22] where the 1,10-phenanthroline ligand is planar and coordinates to the Pt atom with a bite angle of 79.3(2)°, the Pt−N2 and Pt−N1 separations (2.135(4) and 2.075(4) Å, respectively) are significantly shorter than those in **2a**. Even shorter Pt−N bonds have been reported for dmphen Pt(II) complexes containing trans activating groups weaker than the methyl or the phosphine ligands, as in [Pt(dmphen)Cl_2][1a] (Pt−(N1) 2.045(8) and Pt−(N2) 2.046(12) Å), in [Pt(dmphen)Br_2][1d] (Pt−(N1) 2.058(9), Pt−(N2) 2.049(7) Å), in [Pt(dmphen)I_2][1d] (Pt−(N1) 2.082(8), Pt−(N2) 2.062(8) Å), or in [PtI_2(2,9-

Table 2. Selected Bond Distances (Å) and Angles (deg) for Compound **2a**

Bond Distances	
Pt−C11	2.052 (4)
Pt−N1	2.152 (3)
Pt−N2	2.162 (3)
Pt−P1	2.233 (8)
Angles	
C11−Pt−N1	95.5 (1)
C11−Pt−N2	171.4 (1)
N1−Pt−N2	76.4 (1)
C11−Pt−P1	86.2 (1)
N1−Pt−P1	165.13 (7)
N2−Pt−P1	100.92 (7)
Dihedral Angles	
C10′−C6′−C6−C5−C4′−C10 ∧ N1−C2−C3−C4−C4′	9.6 (2)
C10′−C6′−C6−C5−C4′−C10 ∧ N2−C9−C8−C7−C6′−C10′	8.7 (2)
C10′−C6′−C6−C5−C4′−C10 ∧ N1−Pt−N2	33.2 (2)
dmphen[a] ∧ Pt−C11−N1−N2−P1	42.64 (8)

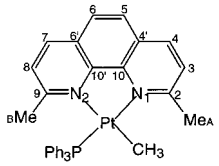
[a] dmphen refers to the lsq-plane defined by the atoms of the phenanthroline moiety.

(20) gNMR 4.0; Cherwell Science: Oxford.

(21) Cambridge Structural Data Base (1992−1997); Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, England.

(22) Bruno, G.; Nicolò, F.; Scopelliti, R.; Arena, G. *Acta Crystallogr., Sect. C: Struct. Crystallogr. Cryst. Chem.* **1996**, *C52*, 827.

Scheme 1. Structural Formula of Complex **2a** with the Atomic Numbering Scheme



Me_2-4,7-Ph_2phen)][23] (Pt−(N1) 2.09(2), Pt−(N2) 2.07(2) Å). Moreover, compound **2a** shows severe steric distortions in the coordination geometry and in the phenanthroline ligand as also found in the above-mentioned compounds and in analogous dmphen complexes of palladium(II), such as [PdMe(Cl)-(dmphen)],[1b] [PdPh(Cl)(dmphen)],[1e] and [Pd($MeCO_2$)$_2$(dmphen)].[1c] Indeed we observe, as a consequence of the steric congestion caused by the two methyl substituents on the dinitrogen ligand (i) a tetrahedral distortion of the square planar coordination geometry, with the Pt atom 0.14 Å away from the lsq-plane defined by N1, N2, Pt, C11, P1 atoms; (ii) a loss of planarity of the dmphen ligand, which assumes a lenslike conformation with dihedral angles, between the mean planes defined by the six atoms of the three rings, of 9.6(2)° and 8.7(2)°, respectively (see Table 2); and (iii) most notably, a rotation of the dmphen moiety, around the N1−N2 vector, to form a dihedral angle of 42.64(8)° with the mean coordination plane defined by Pt, N1, N2, P1, C11 atoms.

Solution Structure. At room temperature the ^{1}H NMR spectra of the compounds **1a**−**1g**, **2a**−**2h**, and **3e** exhibit the expected resonances (given in the Experimental Section) of the ligands Me_2SO (**1a**−**1f**), *n*-Bu_2SO (**1g**), PPh_3 (**2a**−**2h**), and $AsPh_3$ (**3e**) and of a methyl group directly coordinated to the metal. However, the methyl groups and the aromatic proton pairs H_3 and H_8, H_4 and H_7, H_5 and H_6 of the phennanthroline ligand are chemically equivalent, indicating a fast site exchange of the two nitrogen atoms of the dmphen ligand. In contrast, the appearance of the ^{1}H NMR spectra of the complexes, where L = $CyNH_2$ (**3a**), *i*-$PrNH_2$ (**3b**), 2,6-Me_2py (**3c**), $EtNH_2$ (**3d**), Me_2th (**3f**), SCN^- (**4a**), and $SeCN^-$ (**4b**), is consistent with the expected static structure up to 340 K in chloroform-*d* solution and up to 330 K in methanol-d_4.

The characterization of compounds **2a**, **2b**, and **2f** was carried out in chloroform-*d* at low temperature. At 260 K the fluxional motion is slow in the chemical shift time scale but is still fast in the longitudinal relaxation time scale, as demonstrated by the presence of exchange cross-peaks between protons of the two halves of the phenanthroline ligand in the ^{1}H-NOESY spectrum.[24] Only at 220 K does it become slow even compared to the longitudinal relaxation process. The experiments based on scalar couplings (^{1}H-COSY, ^{1}H{^{13}C}-COSY, and ^{1}H{^{13}C}-COSY long range) were performed at 260 K, while those based on the dipolar couplings (^{1}H-NOESY and ^{19}F{^{1}H}-HOESY) were obtained both at 260 and 220 K. All the proton and carbon resonances of compound **2a** were assigned starting from the ^{1}H resonance of the Me group directly bonded to the platinum. This latter shows a contact with Me_A in the ^{1}H-NOESY spectrum. From Me_A and Me_B it is possible to assign the protons belonging to the phenanthroline following either the scalar or dipolar connectivity. The carbon resonances were assigned by the ^{1}H{^{13}C}-COSY spectra.

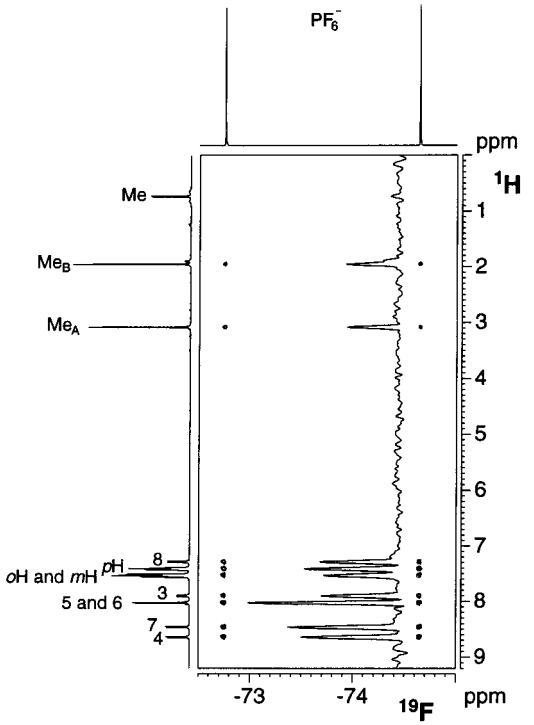


Figure 2. Section of the ^{19}F{^{1}H}-HOESY NMR spectrum of complex **2a** recorded at 376.63 MHz in chloroform-*d* (260 K) showing the contacts between PF_6^- and all the protons of the cation except those of Me. The one-dimensional trace relative to the PF_6^- column is reported on the right of the spectrum.

The interionic structure of complexes **2a**, **2b**, and **2f** was investigated at low temperature in chloroform-*d*. We have previously shown[25] that, if intimate ion pairs are predominant in solution, detailed information about the average position of the counterion with respect to the cation can be obtained, by detecting interionic dipolar contacts in the ^{1}H-NOESY or ^{19}F{^{1}H}-HOESY NMR spectra. Chloroform, with a dielectric constant of 4.81 (at 20 °C), is a good solvent for studying the interionic structure, and we can reasonably assume that complexes with "classical" counterions are exclusively present as intimate ion pairs (at the concentration values used to detect the NMR spectra). ^{19}F{^{1}H}-HOESY spectra of complexes **2a** and **2b** recorded at 260 K (see Figure 2) show intense cross-peaks between the fluorine atoms of the counterion and all the aromatic protons (even if the contacts with the aromatic protons of PPh_3 are weaker, especially considering the higher number of equivalent protons; see Figure 2). There are also contacts with Me_A and Me_B, even if their intensity is lower than the others. No contact is observed with the methyl group directly bonded to the platinum. A ^{19}F{^{1}H}-HOESY spectrum recorded at 220 K for complex **2a** gave similar results.

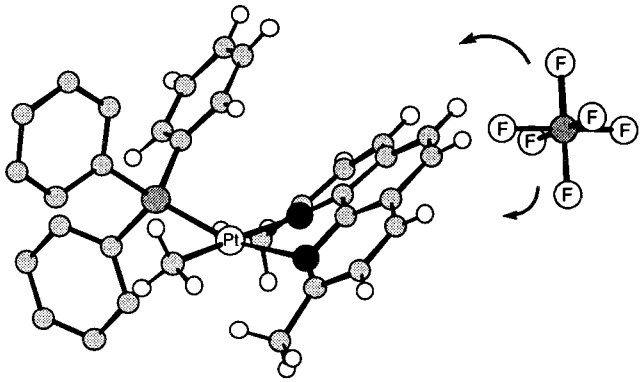
The average interionic structure that can be deduced from the above results is shown in Scheme 2: the counterion stays on the side of the phenanthroline ligand, in agreement with the solid-state structure. In contrast to the planar "nonhindered" phenanthroline or bipyridine ligands studied previously,[25c] in the present case the positions above and below the coordination

(23) Fanizzi, F. P.; Natile, G.; Lanfranchi, M.; Tiripicchio, A.; Laschi, F.; Zanello, P. *Inorg. Chem.* **1996**, *35*, 3173.

(24) Neuhaus, D.; Williamson, M. *The Nuclear Overhauser Effect in Structural and Conformational Analysis*; VCH Publishers: New York, 1989.

(25) (a) Zuccaccia, C.; Bellachioma, G.; Cardaci, G.; Macchioni, A. *Organometallics* **1999**, *18*, 1 and references therein. (b) Romeo, R.; Nastasi, N.; Monsù Scolaro, L.; Plutino, M. R.; Albinati, A.; Macchioni, A. *Inorg. Chem.* **1998**, *37*, 5460. (c) Macchioni, A.; Bellachioma, G.; Cardaci, G.; Travaglia, M.; Zuccaccia, C.; Milani, B.; Corso, G.; Zangrando, E.; Mestroni, G.; Carfagna, C.; Formica, M. *Organometallics* **1999**, *18*, 3061. (d) Zuccaccia, C.; Macchioni, A.; Orabona, I.; Ruffo, F. *Organometallics* **1999**, *18*, 4367.

Scheme 2. Balls and Sticks Schematization of the Ion-Pair Solution Structure of **2a**[a]



[a] The structural parameters for the two ionic moieties are obtained from X-ray data. Arrows are reported for the counterion to indicate that PF_6^- preferentially lies "under" the phenanthroline, away from the phosphine, but it can move up and down the phenanthroline moiety.

plane are different. The counterion prefers a location below the aromatic rings of the phenanthrolinic ligand but the situation is not static and PF_6^- still has the possibility to oscillate up and down interacting weakly with the phosphine protons. The $^{19}F\{^1H\}$-HOESY spectrum of complex **2f**, recorded at 260 K, shows only intramolecular contacts within the B(3,5-$(CF_3)_2C_6H_3)_4^-$ anion between the fluorine atoms of the substituent CF_3 groups and the *o*-H′ and *p*-H′. The absence of interionic contacts indicates that in chloroform the compound is not appreciably present as an intimate ion pair, in line with the well-known noncoordinating properties of this counteranion.

Dynamic Behavior of Complexes 1a−1f, 2a−2h. The above-mentioned dynamic process in the cationic [Pt(Me)-(dmphen)(L)]$^+$ species **1**−**4** was investigated as a function of the nature of the ligand L, of the solvent, of the addition of nucleophiles, and, eventually, in the temperature range 213−343 K, in $CDCl_3$ as a function of the nature of the counteranion. The passage from slow to fast exchange was followed either through the ^1H NMR spectral changes of the aromatic proton pairs H_4–H_7 and H_3–H_8 (for sulfoxide complexes **1**) or (see Figure 3) from those of the dmphen methyl groups (for phosphine complexes **2**). The rate constants for the flipping of complexes **1a**−**1f** and **2a**−**2h** at different temperatures were determined by a full line-shape analysis (Supporting Information Table S1). The activation parameters for the fluxional process were derived from Eyring plots and are listed in Table 3. The $\Delta G^‡$ values for **2g** and **2h** are based on a single temperature measurement at 298 K. The entropy changes, $\Delta S^‡$, range in magnitude from −62 to 20 J K^{-1} mol^{-1}, but these values are not considered to provide any real insight into the nature of the fluxional process because of their extreme sensitivity to systematic errors associated with the line-shape analysis. The activation energies $\Delta G^‡$(298 K) are more meaningful.[26]

The fastest fluxional motion is exhibited by **2a** in methanol-d_4 and the slowest by **2f** in chloroform-*d*. Compounds characterized by activation energies $\Delta G^‡_{298}$ higher than 70 kJ mol^{-1} and showing ^1H NMR spectra at room temperature in agreement with a static structure in solution were considered inert from the fluxional viewpoint. The validity of such an assumption was confirmed by two-dimensional EXSY spectra and by magnetization transfer experiments. A detailed investigation using dynamic NMR techniques, on a more extended series of cationic

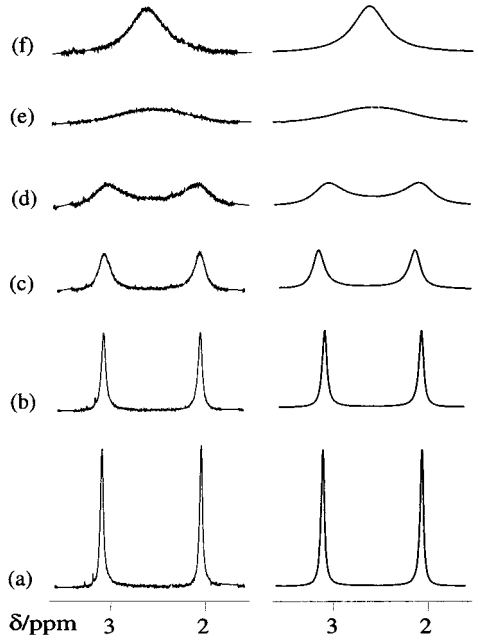


Figure 3. Variable-temperature ^1H NMR spectra of the phenanthroline methyl protons of the complex **2d** recorded at 300.13 MHz in $CDCl_3$ (on the left). Simulated spectra are on the right. The temperatures (K) and the rate constants (s^{-1}) for the fluxional motion of the nitrogen ligand are as follows: (a) $T = 295$, $k_f = 30$; (b) $T = 300$, $k_f = 48$; (c) $T = 311$, $k_f = 131$; (d) $T = 322$, $k_f = 344$; (e) $T = 333$, $k_f = 875$; (f) $T = 343$, $k_f = 1650$.

[Pt(Me)(dmphen)(L)]$^+$ species, is currently underway in our laboratory. However, it may be safely assumed that compounds where L = sulfoxide, phosphine, or arsine are fluxional, whereas those containing an amine, pyridine, thiourea, or negatively charged ions such as SCN^- or $SeCN^-$ are fluxionally inert. A quantitative estimation of the ligand influence on the rate of the fluxional process, at least as far as dimethyl sulfoxide and triphenylphosphine complexes are concerned, can be made by comparing the $\Delta G^‡_{298}$ values in $CDCl_3$ for pairs of complexes differing only in the nature of the ligand L, as for **1a**−**2a**, **1c**−**2c**, and so on. Substitution of Me_2SO for PPh_3 leads to a mean statistical increase of the $\Delta G^‡_{298}$ value of 9.4 ± 2 kJ mol^{-1} and to a significant decrease of the fluxional motion.

Data in Table 3 reveal that the nature of the counteranion has a tangible influence on the fluxionality of dmphen in both series of complexes **1** and **2**. The sequence of energies observed in the series **2a**−**2h** increases in the order $Cl^- \approx NO_2^- \ll CF_3SO_3^- < ClO_4^- < B(C_6H_5)_4^- < BF_4^- \approx PF_6^- <$ B(3,5-$(CF_3)_2C_6H_3)_4^-$, reflecting to some extent the nucleophilic ability of these anions. Leaving aside the $\Delta G^‡$ values for Cl^- and NO_2^-, which appear to be by far the lowest, the energy difference between the fastest system ($CF_3SO_3^-$) and the slowest [B(3,5-$(CF_3)_2C_6H_3)_4^-$] is less than 10 kJ mol^{-1}. In contrast to the clear-cut influence of the nature of the anion on the rate of flipping of dmphen in the cation, no anion concentration effect on the rate was observed. Thus, the rate of flipping of **2a** at 298 K in $CDCl_3$ remained unchanged at a value of $k_f = 20 \pm 1$ s^{-1} upon addition of *n*-Bu_4NPF_6 up to 0.048 *m* (see data in Table SI2).

The effect of polar solvents is to lower the $\Delta G^‡_{298}$ value for the fluxional process. The magnitude of this effect is remarkable. Changing the solvent from $CDCl_3$ to acetone-d_6 resulted in a much lower value of the coalescence temperature T_c for **1a** and **2a** and in a reduction of about 10 kJ mol^{-1} of the $\Delta G^‡_{298}$ value. When the more nucleophilic solvent CD_3OD was used, a further decrease of 10 kJ mol^{-1} of the $\Delta G^‡_{298}$ value was observed for **2a**, making such a system the fastest among those studied.

(26) Sandström, J. *Dynamic NMR Spectroscopy*; Academic Press: London, 1982. ISBN 0-12-618620.

Table 3. Ligand, Solvent, and Counterion Effects on the Rates of Fluxional Motion of the Ligand 2,9-Dimethyl-1,10-phenanthroline in the Cationic Complexes $[PtMe(dmphen)(L)]^+$

no.	ligand	counterion	solvent	$\Delta G^{\ddagger a}$	$\Delta H^{\ddagger b}$	$\Delta S^{\ddagger c}$
1a	Me_2SO	PF_6^-	$CDCl_3$	59.1	63.9 ± 2	16 ± 7
1a	Me_2SO	PF_6^-	$(CD_3)_2CO$	50.8	44.6 ± 1	-21 ± 4
1c	Me_2SO	$CF_3SO_3^-$	$CDCl_3$	49.4	53.9 ± 1	15 ± 5
1e	Me_2SO	$B(C_6H_5)_4^-$	$CDCl_3$	58.5	54.0 ± 2	-15 ± 6
1f	Me_2SO	$B(3,5\text{-}(CF_3)_2C_6H_3)_4^-$	$CDCl_3$	61.1	58.4 ± 2	-9 ± 7
2a	$P(C_6H_5)_3$	PF_6^-	$CDCl_3$	66.5	48.0 ± 1	-62 ± 2
2a	$P(C_6H_5)_3$	PF_6^-	$(CD_3)_2CO$	56.6	39.9 ± 2	-56 ± 7
2a	$P(C_6H_5)_3$	PF_6^-	CD_3OD	46.5	34.6 ± 1	-40 ± 4
2b	$P(C_6H_5)_3$	BF_4^-	$CDCl_3$	66.7	56.6 ± 1	-34 ± 5
2c	$P(C_6H_5)_3$	$CF_3SO_3^-$	$CDCl_3$	61.6	64.0 ± 1	8 ± 1
2d	$P(C_6H_5)_3$	ClO_4^-	$CDCl_3$	63.8	69.8 ± 6	20 ± 2
2e	$P(C_6H_5)_3$	$B(C_6H_5)_4^-$	$CDCl_3$	65.7	47.2 ± 2	-62 ± 6
2f	$P(C_6H_5)_3$	$B(3,5\text{-}(CF_3)_2C_6H_3)_4^-$	$CDCl_3$	70.2	63.4 ± 2	-23 ± 5
2g	$P(C_6H_5)_3$	Cl^-	$CDCl_3$	52.8		
2h	$P(C_6H_5)_3$	NO_2^-	$CDCl_3$	53.5		

[a] kJ mol^{-1} at 298 K. [b] kJ mol^{-1}. [c] J K^{-1} mol^{-1}.

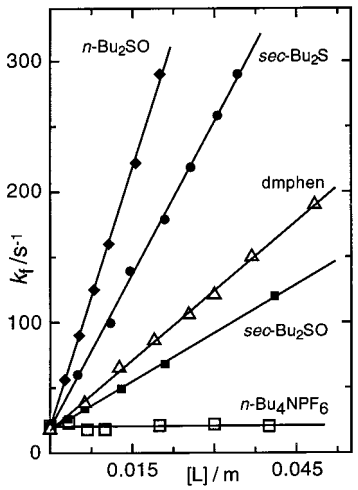


Figure 4. Dependence of the rate constant for the flipping of **2a** at 298 K in $CDCl_3$ on the concentration of added ligands.

The recognition of an accelerating effect on the fluxionality by nucleophilic solvents led us to investigate the effect of added ligands on the rearrangement. The results are collected in Supporting Information Table SI2 and are partially illustrated in Figure 4. Addition of dmphen to the complex **2a** at 298 K in $CDCl_3$ caused an extra line broadening of the signals of the Me substituents of the coordinated dinitrogen ligand. No intermolecular exchange was observed, since the signals of the noncoordinated nitrogen ligand remained sharp. The rate k_f, measured on the methyl signals, increased linearly with increasing concentration of dmphen. Concentration-dependent measurements, carried out with the ligands *n*-Bu_2SO, *sec*-Bu_2SO, and *sec*-Bu_2S, exhibited a behavior similar to that described above for dmphen. The addition of a ligand has the effect of increasing the fluxionality rate, and no intermolecular exchange occurs. The rate constants k_f (see Table SI2), when plotted against the concentration of added ligand L, give straight lines with a common intercept (Figure 4), indicating that the two-term rate eq 2 is obeyed.

$$k_f = k_{ip} + k_2[L] \qquad (2)$$

The values of k_{ip} (s^{-1}) and k_2 (m^{-1} s^{-1}) from linear regression analysis of the dependence of k_f on [L] are listed in Table 4, together with their standard deviations. The concentration-independent rate constant k_{ip} measures the rate of dmphen flipping within the ion pair $[PtMe(dmphen)(PPh_3)]^+PF_6^-$, while the second-order rate constant k_2 measures the capacity of noncoordinated ligand to accelerate such fluxionality.

Table 4. Stereoelectronic Parameters for S-Donor Ligands and Rate Constants Derived from the Ligand Concentration Dependence of the dmphen Flipping in the Complex $[PtMe(dmphen)(PPh_3)]PF_6$ (**2a**)[a]

ligand	k_{ip}, s^{-1}	k_2, m^{-1} s^{-1}	$\chi^{b,c}$	$\theta^{b,d}$
n-Bu_4NPF_6	20 ± 1	16 ± 56		
dmphen	17 ± 1	3560 ± 50		
n-Bu_2SO	20 ± 2	13260 ± 190	3.50	91
sec-Bu_2SO	18 ± 1	2470 ± 32	3.44	107
sec-Bu_2S	19 ± 3	7850 ± 120	3.44	107

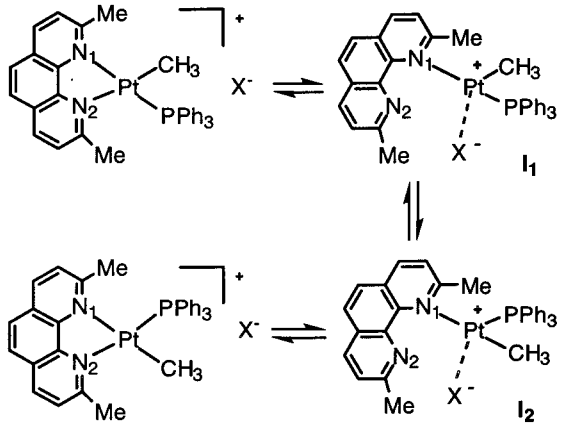
[a] At 298 K in $CDCl_3$. [b] Fractional values calculated from the phosphorus(III) values (see Tracey, A. A.; Eriks, K.; Prock, A.; Giering, W. P. *Organometallics* **1990**, *9*, 1399). [c] χ values (cm^{-1}) were taken from: Bartik, T.; Himmler, T.; Schulte, H. G.; Seevogel, K. *J. Organomet. Chem.* **1984**, *272*, 29. [d] Cone angles θ (deg) were taken from: White, D.; Coville, N. J. *Adv. Organomet. Chem.* **1994**, *36*, 95.

Discussion

Although the present reaction is a rearrangement between identical species, the process features an isomerization and, as for this latter topological change, a variety of mechanisms are conceivable.[27,28] Therefore, we must address the question of whether the fluxional motion of the dinitrogen ligand occurs (i) directly on the square-planar cationic complex, (ii) via a dissociative process in which one arm of N−N ligand dissociates, followed by isomerization of the tricoordinated T-shaped species thus formed, (iii) via a sequence of consecutive associative substitution steps, or (iv) via a pseudorotation or turnstile mechanism on a five-coordinate intermediate. The first mechanism can be removed from consideration since (1) orbital symmetry arguments suggest that the barrier to thermal distortion of the square-planar structure toward a tetrahedral transition state would be very high[29] and (2) counteranions, solvents, or added ligands should not have a marked effect on the fluxional motion, in contrast with the observed behavior (see data in Table 3). Such an intramolecular twist rotation pathway is accessible to photochemical activation, as for $[Pt(C_6H_5)Cl(PEt_3)_2]$[30] or $[PtCl_2(Me_2SO)_2]$,[31] or in a rare case in which the molecule has

(27) Anderson, G. K.; Cross, R. J. *J. Chem. Soc. Rev.* **1980**, *9*, 185.
(28) Romeo, R. *Comments Inorg. Chem.* **1990**, *11*, 21−57.
(29) Whitesides, T. W. *J. Am. Chem. Soc.* **1969**, *91*, 2395.
(30) Costanzo, L. L.; Giuffrida, S.; Romeo, R. *Inorg. Chim. Acta* **1980**, *38*, 31.

Scheme 3. Dissociative Mechanism Involving Cationic T-Shaped Three-Coordinate Intermediates with Monocoordination of the Bidentate Ligand and Ionic Interaction with the Counteranion X^-



already a strong tetrahedral distortion in the ground state, as reported recently for the fluxional behavior of *cis*-bis(silyl)bis(phosphine)platinum(II).[32] A dissociative mechanism, such as that illustrated in Scheme 3, which involves initial dissociation of one Pt−N bond, isomerization of the T-shaped intermediate, and remaking of the Pt−N bond, has been proposed by Pregosin et al.[9] and Backvall and Gogoll[10] for the dynamic behavior of bidentate nitrogen ligands in some (π-allyl)palladium(II) complexes and by Vrieze et al.[33] for the fluxionality of [Pd(N−N)(C(=NR)Me)Cl] complexes, and it is strongly reminiscent of the mechanism of uncatalyzed isomerization of $[Pt(PEt_3)_2(R)X]$ or $[Pt(PEt_3)_2(R)(S)]^+$ complexes.[8]

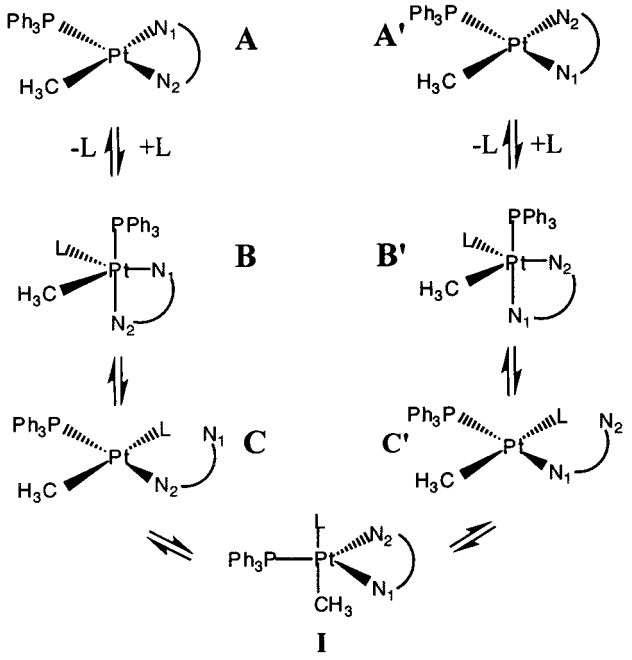
On discussing the possible occurrence of a dissociative process, it is necessary to focus on the strong differences of nucleophilic power among the counterions and the solvents examined. Thus, the behavior of Cl^- and NO_2^- must differ from that of the other "classical-noncoordinating" anions such as $CF_3SO_3^-$, ClO_4^-, $B(C_6H_5)_4^-$, BF_4^-, PF_6^-, and $B(3,5\text{-}(CF_3)_2C_6H_3)_4^-$. The addition of stoichiometric amounts of $AsPh_4Cl$ or $AsPh_4NO_2$ to a chloroform solution of **2a** to yield **2g** and **2h** "in situ" is accompanied by a partial dechelation of dmphen. A small excess of reagent leads to complete removal of dmphen instead of the formation of **2g** and **2h**. This is a strong and conclusive indication that the low energy value found for the fluxional motion of **2g** and **2h** (Table 3) is due to ligand (Cl^- and NO_2^-) promoted associative process. Free dmphen concurs to the accelerating effect. In contrast, the NMR interionic characterization of **2f** has shown that the noncoordinating properties of $B(3,5\text{-}(CF_3)_2C_6H_3)_4^-$ are such to even prevent the formation of an ion pair, and chloroform successfully competes with the anion in staying close to the cationic fragment. Intimate ion pairs are formed by **2a** and **2b**, with a preferential location of the anions around the phenanthroline ligand, but addition of a significant excess of *n*-Bu_4NPF_6 in solution (see Table SI2) does not affect the rate of fluxional motion of dmphen in **2a**. Therefore, we are inclined to think that a dissociative process occurs in chloroform not only for **2f**, the compound characterized by the least coordinating anion, but also for **2a**−**2e**, within the intimate ion pairs formed between the anion and the cationic complex. Along the sequence $B(3,5\text{-}(CF_3)_2C_6H_3)_4^-$, PF_6^-, BF_4^-, $B(C_6H_5)_4^-$, ClO_4^-, $CF_3SO_3^-$, the change of counterion produces a moderate acceleration effect which is somewhat stronger for ClO_4^- and $CF_3SO_3^-$. This acceleration could well be a consequence of the stabilization of the three-coordinate cation (see Scheme 3) forming part of an intimate ion pair in a cage of solvent. Easy dissociation of an arm of the bidentate nitrogen ligand is supported by the long Pt−N1 and Pt−N2 separations exhibited by **2a** (see Table 1). Within this mechanistic framework the sign of $\Delta S^\ddagger$ is not easily predictable, and this is a further warning about an indiscriminate use of the activation data in Table 3.[34]

Changing the solvent from $CDCl_3$ to acetone-d_6 resulted in a significant decrease of $\Delta G^\ddagger$ for **2a** from 66.5 to 56.6 kJ mol^{-1}, and when the more nucleophilic solvent CD_3OD was used, $\Delta G^\ddagger$ was further reduced to 46.5 kJ mol^{-1} (Table 3). In this latter dissociating solvent, where separated solvated ions will be produced, the compounds **2a**−**2h** show the same rate of flipping, at the same temperature, irrespective of differences in the nature of the counterion. These results appear to be consistent with an associative mechanism in which the solvent promotes the dmphen rearrangement acting as a weak nucleophile.

The addition of external ligands to **2a** in chloroform solution must be carried out with care. With the most nucleophilic ligands, such as phosphines or halide ions, displacement of dmphen occurs. In contrast, dmphen, *n*-Bu_2SO, *sec*-Bu_2SO, or *sec*-Bu_2S accelerate the fluxionality of dmphen in **2a** without promoting any detectable exchange between free and coordinated ligands. The dependence of the flipping rates k_f (listed in Table SI2) upon the nature and the concentration of added ligands is described by a family of straight lines with a common intercept (Figure 4). The contribution of the reagent-independent term is small but detectable. According to these rate data (k_2, in Table 4), the catalytic efficiency of the added ligands on the rearrangement decreases in the order *n*-Bu_2SO > *sec*-Bu_2S > dmphen > *sec*-Bu_2SO, while for *n*-Bu_4NPF_6 it is zero. Thus, we observe a significant nucleophilic discrimination ability as a result of differences in the nature of the donor atom and of the steric and electronic characteristics of the ligands. A sulfide (*sec*-Bu_2S) is more reactive than a sulfoxide (*sec*-Bu_2SO) having comparable basicity and size whereas, within the sulfoxide pair, *n*-Bu_2SO is more reactive than the sterically hindered analogue *sec*-Bu_2SO. This pattern of behavior is typical of associative substitution reactions of square-planar platinum(II) complexes.[35] Thus, the most likely mechanism that can be envisaged for the flipping is made up by a sequence of nucleophilic substitution reactions which takes place with complete retention of configuration (see Scheme 4). The mechanism involves (i) bimolecular attacks of the nucleophile to form five-coordinate intermediates (A→B and A′→B′), (ii) dissociation of one arm of the bidentate ligand (B→C and B′→C′) to afford two different complexes (C and C′) in which dmphen is η^1-coordinated, (iii) inter-

(31) Price, J. H.; Birk, J. P.; Wayland, B. B. *Inorg. Chem.* **1978**, *17*, 22.
(32) (a) Tsuji, Y.; Nishiyama, K.; Hori, S.-Y.; Ebihara, M.; Kawamura, T. *Organometallics* **1998**, *17*, 507. (b) Obora, Y.; Tsuji, Y.; Nishiyama, K.; Ebihara, M.; Kawamura, T. *J. Am. Chem. Soc.* **1996**, *118*, 10922.
(33) Delis, J. G. P.; Aubel, P. G.; Vrieze, K.; van Leuwen, P. W. N. M.; Veldman, N.; Spek, A. L.; van Neer, F. J. R. *Organometallics* **1997**, *16*, 2948.
(34) Since the reaction rates for all the anions (less and more coordinating) follow the trend of their coordinating power (see Strauss, S. H. *Chem. Rev.*, **1993**, *93*, 927 and references therein), a referee has suggested that a single associative mechanism could explain the behavior of all nucleophiles. If this is true, the sequence of free energies in Table 3 ($Cl^- \approx NO_2^- \ll CF_3SO_3^- < ClO_4^- < B(C_6H_5)_4^- < PF_6^- \approx BF_4^- < B(3,5\text{-}(CF_3)_2C_6H_3)_4^-$) can be assumed as a quantitative measure of the relative nucleophilicity and coordinating ability of the anions.
(35) (a) Tobe, M. L. In *Comprehensive Coordination Chemistry*; Wilkinson, G.; Gillard, R. D.; McCleverty, J. A., Eds.; Pergamon Press: Oxford, UK, 1987; Vol. 1, Chapter 7, pp 311−329. (b) Tobe, M. L.; Burgess, J. *Inorganic Reaction Mechanisms*; Addison-Wesley Longman: Essex, England, 1999; Chapter 3, pp 70−112.

Scheme 4. Sequence of Associative Substitution Reaction Steps Leading to the Exchange of the Bidentate Modes of the Phenanthroline Ligand



conversion of the two η^1-coordinated complexes via formation of a common five-coordinate chelated intermediate I, and (iv) ring closure and elimination of the catalyst L (C→A and C′→A′). This mechanism is somewhat reminescent of that proposed for the fluxionality of 2,2′-bipyridine in [Pd(η^1,η^2-C_8H_{12}OMe)(bipy)]$^+X^-$,[25c] and for the geometrical isomerization of *cis*-[Pd(am)$_2$Cl$_2$],[36] of *cis*- and *trans*-[Pt(Me$_2$S)$_2$Cl$_2$],[37] of *trans*-[Pt(Me$_2$SO)$_2$Cl$_2$],[38] and of *cis*-[Pt(PR$_3$)$_2$Cl$_2$][39] catalyzed by free amine, am, Me$_2$S, Me$_2$SO, and PR$_3$, respectively. In the present case the methyl group and PPh$_3$ remain firmly bonded to the metal and the easy Pt−N1 and Pt−N2 bond breaking is the combined result of their high trans effect and trans influence, as well as of the steric congestion at the square-planar configuration. This successive displacement mechanism could well account also for the dynamic exchange process occurring in chloroform for the **2a**−**2f** complexes, in the absence of added nucleophiles (if one emphasizes the disposability of these complexes to add a fifth ligand and the possibility of weakly coordinating counteranions or of CDCl$_3$ to act as nucleophiles).

The available evidence indicates that on substituting PPh$_3$ with an amine, with a pyridine, with thiourea, or with SCN$^-$ and SeCN$^-$ ions the dynamic of dmphen is interrupted. The reasons for the static structure of these derivatives perhaps lie in the fact that dmphen Pt(II) complexes containing trans activating groups weaker than phosphine would be characterized by significantly shorter Pt−N separations (average 2.16 Å). Given that the fluxionality of dmphen is connected to its lability and to the facility of Pt−N bond breaking, the operation of an alternative intramolecular rearrangement from a five-coordinate intermediate, formed in sufficient concentration with sufficient lifetime to undergo a Berry pseudorotation or a "turnstile" mechanism,[40] seems very unlikely.

Concluding Remarks. The fluxional behavior in solution of [Pt(Me)(L)(dmphen)]$^+X^-$ complexes is strongly affected by the nature of the coordinated ligand L and, when L = PPh$_3$, by the coordinating properties of the solvent, of the counterions X$^-$, and of nucleophiles added in solution. The high trans effect and trans influence of the methyl and phosphine groups, together with the remarkable steric congestion at the coordination plane in **2a**, favor either a facile dissociation of a Pt−N bond or the addition of a fifth group. The first process can be prevalent within the ion pairs formed by "noncoordinating" anions with the cationic complex. Specific interionic dipolar interactions, such as those detected in the $^{19}F\{^1H\}$-HOESY NMR spectra for the four-coordinate [Pt(Me)(PPh$_3$)(dmphen)]$^+X^-$ (X = PF$_6^-$ and BF$_4^-$) complexes, could well stabilize a three-coordinate T-shaped intermediate formed upon Pt−N dissociation and explain the counterion effect on the fluxionality. Among the possible associative mechanisms promoted by polar solvents or by relatively strong nucleophiles, a consecutive stepwise displacement mechanism is to be preferred to intramolecular rearrangements of five-coordinate intermediates. Although the experimental findings do not prove or disprove the operation of either mechanism, nonetheless the strict similarity of the former with the traditional substitution mechanism is in the present case attractive.

Acknowledgment. We are grateful to the Ministero dell' Università e della Ricerca Scientifica e Tecnologica (MURST), Programmi di Ricerca Scientifica di Rilevante Interesse Nazionale, Cofinanziamento 2000−2002, to the Messina, Perugia, and Milano Universities and CNR for funding this work.

Supporting Information Available: Tables giving the temperature dependence of the rate constants (k_f/s^{-1}) for the dynamic behavior of compounds **1a**−**1f** and **2a**−**2h**, the catalytic effect of nucleophiles on the fluxionality of **2a**, and complete crystallographic data, bond distances, bond angles, anisotropic thermal parameters, and hydrogen coordinates of **2a**, Ortep figure of the unit cell content. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0014080

(36) Cattalini, L.; Martelli, M. *J. Am. Chem. Soc.* **1969**, *91*, 312.
(37) Roulet, R.; Barbey, C. *Helv. Chim. Acta* **1973**, *56*, 2179.
(38) Annibale, G.; Bonivento, M.; Canovese, L.; Cattalini, L.; Michelon, G.; Tobe, M. L. *Inorg. Chem.* **1985**, *24*, 797.
(39) Favez, R.; Roulet, R.; Pinkerton, A. A.; Schwatzenbach, D. *Inorg. Chem.* **1980**, *19*, 1356.
(40) (a) Ugi, I.; Marquarding, D.; Klusacek, H.; Gillespie, P. *Acc. Chem. Res.* **1971**, *4*, 288. (b) Casares, J. A.; Espinet, P. *Inorg. Chem.* **1997**, *36*, 5428. (c) Stockland, R. A., Jr; Anderson, G. K. *Organometallics* **1998**, *17*, 4694.