Articles

To What Extent Can Cyclometalation Promote Associative or Dissociative Ligand Substitution at Platinum(II) Complexes? A Combined Kinetic and Theoretical Approach

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The ligand exchange rate constants for the reactions $[Pt(bph)(SR_2)_2] + 2*SR_2 \rightarrow [Pt(bph)(*SR_2)_2] + 2SR_2$ (bph = 2,2′-biphenyl dianion; R = Me and Et) and cis-$[PtPh_2(SMe_2)_2] + 2*SMe_2 \rightarrow cis$-$[PtPh_2(*SMe_2)_2] + 2SMe_2$ have been determined in $CDCl_3$ as a function of ligand concentration and temperature, by ^1H NMR isotopic labeling and magnetization transfer experiments. The rates of exchange show no dependence on ligand concentration and the kinetics are characterized by largely positive entropies of activation. The kinetics of displacement of the thioethers from $[Pt(bph)(SR_2)_2]$ with the dinitrogen ligands 2,2′-bipyridine and 1,10-phenanthroline (N−N) to yield $[Pt(bph)(N−N)]$, carried out in the presence of sufficient excess of thioether and N−N to ensure pseudo-first-order conditions, follow a nonlinear rate law $k_{obsd} = a[N−N]/(b[SR_2] + [N−N])$. The general pattern of behavior indicates that the rate-determining step for substitution is the dissociation of a thioether ligand and the formation of a three-coordinated $[Pt(bph)(SR_2)]$ intermediate. The value of the parameter a, which measures the rate of ligand dissociation, is constant and independent of the nature of N−N, and it is in reasonable agreement with the value of the rate of ligand exchange at the same temperature. Theoretical ab initio calculations were performed for both $[Pt(bph)(SMe_2)_2]$ and cis-$[PtPh_2(SMe_2)_2]$, and for their three-coordinated derivatives upon the loss of one SMe_2 ligand. The latter optimize in a T-shaped structure. Calculations were performed in the HF approximation (LANL2DZ basis set) and refined by introducing the correlation terms (Becke3LYP model). The activation enthalpies from the optimized vacuum-phase geometries are 52.3 and 72.2 kJ mol^{-1} compared to the experimental values in $CDCl_3$ solution, 80 ± 1 and 93 ± 1 kJ mol^{-1} for $[Pt(bph)(SMe_2)_2]$ and cis-$[PtPh_2(SMe_2)_2]$, respectively. The electrostatic potential maps of both parent compounds show a remarkable concentration of negative charge over the platinum atom which exerts a repulsion force on an axially incoming nucleophile. On the other hand, the strength of the organic carbanions trans to the leaving group and the stabilization of the T-shaped intermediate in the singlet ground state may also rationalize the preference for the dissociative mechanism. All of the kinetic and theoretical data support the latter hypothesis and indicate, in particular, that dissociation from the complex containing the planar 2,2′-biphenyl dianion is easier than from its analogue with single aryl ligands. Electron back-donation from filled d orbitals of the metal to empty π^* of the in-plane cyclometalated rings is weak or absent and is not operative in promoting an associative mode of activation.

Introduction

The potential catalytic activity of square-planar complexes of d^8 metals is related to the possible dissociation of one ligand and to the stability of the derived 14-electron species. The coordinatively and electronically unsaturated metal could then accept and activate molecular fragments.[1] Recently, ligand dissociation has been recognized as the initial step of many fundamental processes involving square-planar organometallic complexes.[2] The most recent studies refer to thermal decomposition of alkyl compounds,[3] insertion of olefins into the M−H bond,[4] reductive elimination,[5] geometrical isomerization,[6] reactions of electrophilic attack at the metal−carbon bond,[7] exchange reactions,[8] and fluxional motions of coordinated ligands.[9]

For a long time, simple ligand-substitution reactions have

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(1) (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. C. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987. (b) Yamamoto, A. *Organotransition Metal Chemistry*; Wiley & Sons: New York, 1986. (c) James, B. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Chapter 51. (d) Parshall, G. W. *Homogeneous Catalysis*; Wiley-Interscience: New York, 1980.

(2) Romeo, R. *Comments Inorg. Chem.* **1990**, *11*, 21−57.

(3) (a) Brainard, R. L.; Whitesides, G. M. *Organometallics* **1985**, *4*, 1550. (b) Brainard, R. L.; Miller, M. T.; Whitesides, G. M. *Organometallics* **1986**, *5*, 1481. (c) McCarthy, T. J.; Nuzzo, R. J.; Whitesides, G. M. *J. Am. Chem. Soc.* **1981**, *103*, 3396. (d) Whitesides, G. M.; Gaash, J. F.; Sdedronsky, E. R. *J. Am. Chem. Soc.* **1972**, *94*, 5258. (e) Nuzzo, R. G.; McCarthy, T. J.; Whitesides, G. M. *J. Am. Chem. Soc.* **1981**, *103*, 3404. (f) Foley, P.; Di Cosimo, R.; Whitesides, G. M. *J. Am. Chem. Soc.* **1980**, *102*, 6713. (g) Komiya, S.; Morimoto, Y.; Yamamoto, A.; Yamamoto, T. *Organometallics* **1982**, *1*, 1528. For general reviews of β-elimination reactions, see (a) Cross, R. J. In *The*

been interpreted in terms of an associative process, which implies the formation of 18e five-coordinated intermediates.[10] Conversely, the dissociative mechanism has been considered just as a hypothesis without a concrete confirmation. The first clear-cut evidence for a dissociative mechanism has been provided by studies of ligand exchange or ligand substitution on organometallic substrates of the type cis-[PtR$_2$L$_2$] (R = Ph or Me; L = thioethers or dimethyl sulfoxide).[11] The underpinnings of the observed changeover are a combination of ground-state destabilization (lengthening of the Pt−S bond), increase of electron density at the metal preventing the approach of nucleophiles, and stabilization of the coordinatively unsaturated three-coordinated intermediate.[12] The activation mode becomes again associative for cis-[PtR$_2$(CO)L], because of the strong π electron withdraw by the CO ligand. Moreover, a low-lying LUMO, π-delocalized over the Pt−C−O atoms, can favor the nucleophilic attack.[12] Also, it has become evident that the substrate does not necessarily carry one or more Pt−C bonds to dissociate. In fact, an appropriate set of strong σ-donor groups can favor sufficient accumulation of electron density at the metal and stabilize the 14e intermediate. This is the case for the

complex cis-[Pt(SiMePh$_2$)$_2$(PMe$_2$Ph)$_2$], which shows a partial tetrahedral distortion.[13]

With the goal of tuning the metal electrophilicity to induce a changeover of reaction pathways for substitution, we planned to understand better the role of ancillary ligands characterized by geometric constraints (planarity) as well as by π-delocalization. The structural features and reactivities of the corresponding substrates can be compared with those of complexes having the same set of donor atoms but less-constrained arrangements of the ligands. A class of compounds with potential interest for us is that of the cyclometalated derivatives. Recent kinetic studies of nucleophilic substitution on the cyclometalated platinum(II) complexes [Pt(N−N−C)Cl] (N−N−CH = 6-(1-methylbenzyl)-2,2′-bipyridine)[14] and [Pt(N−C)(N)(H$_2$O)] (N−CH = N,N-dimethylbenzylamine, N = pySO$_3$-3)[15] and on the complex cation [Pt(N−C−N)(H$_2$O)]$^+$ (N−CH−N = 2,6-bis((dimethylamino)methyl)phenyl)[16] have shown that the activation mode is associative in nature. The considerable acceleration in rate observed for the substitution of the aqua ligand in the latter orthoplatinated complexes has led to different interpretations. In particular, an important question is whether there is a significant contribution of back-donation into the empty π^* orbitals of the in-plane aryl ligand, thereby increasing the electrophilicity of the metal center and assisting the nucleophilic attack,[15,16] or if the accelerated rate is simply the result of the well-known strong trans labilizing effect of the Pt−C bond.[17] In platinum(II) complexes containing the 2,2′-biphenyl dianion (bph^{2-}) the aryl groups lie approximately in plane with the complex, and photochemical studies[18] showed an effective electron density transfer from filled d orbitals of the metal into empty π^* orbitals of the cyclometalated ligand. In any case, the point at which the π-electron back-donation could determine the changeover from a dissociative to an associative mechanism remains undetermined.

In this paper we report on comparative kinetic studies we have carried out on the complexes cis-[PtPh$_2$(SMe$_2$)$_2$] and [Pt(bph)(SMe$_2$)$_2$]. The first compound, in which the two monodentate σ-bonded aryl rings are almost perpendicular to the plane of the complex, is known to exchange the thioethers with a dissociative mechanism.[11c,e] Kinetic data, ab initio calculations performed for the ground and the transition states, and an analysis of the molecular electrostatic potentials concur to indicate that cyclometalation and planarity of the aromatic rings do not induce a changeover of the dissociative mechanism but, rather, cause a considerable acceleration of the dissociation rate.

Chemistry of the Metal−Carbon Bond; Hartley, F. R., Patai, S., Eds.; Wiley: New York, 1985; Vol. 2, Chapter 8. (b) Whitesides, G. M. *Pure Appl. Chem.* **1981**, *53*, 287. (c) Yamamoto, A.; Yamamoto, T.; Komiya, S.; Ozawa, F. *Pure Appl. Chem.* **1984**, *56*, 1621.

(4) (a) Romeo, R.; Alibrandi, G.; Monsù Scolaro, L. *Inorg. Chem.* **1993**, *32*, 4688. (b) Coussens, B. B.; Buda, F.; Oevering, H.; Meier, R. J. *Organometallics* **1998**, *17*, 795. (c) Romeo, R.; Uguagliati, P.; Belluco, U. *J. Mol. Catal.* **1975/1976**, *1*, 325−366. (d) Alibrandi, G.; Cusumano, M.; Minniti, D.; Monsù Scolaro, L.; Romeo, R. *Inorg. Chem.* **1989**, *28*, 342. (e) Thorn, D. L.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 2079.

(5) (a) Gillie, A.; Stille, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 4933. (b) Loar, M.; Stille, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 4174. (c) Moravskiy, A.; Stille, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 4182. (d) Paonessa, R. S.; Trogler, W. C. *J. Am. Chem. Soc.* **1982**, *104*, 3529.

(6) (a) Romeo, R.; Alibrandi, G. *Inorg. Chem.* **1997**, *36*, 4822 and references therein. (b) Minniti, D. *Inorg. Chem.* **1994**, *33*, 2631. (c) Casado, A. L.; Casares, J. A.; Espinet, P. *Inorg. Chem.* **1998**, *37*, 4154.

(7) (a) Romeo, R.; Plutino, M. R.; Elding, L. I. *Inorg. Chem.* **1997**, *36*, 5909. (b) Romeo, R.; Minniti, D.; Lanza, S.; Uguagliati, P.; Belluco, U. *Inorg. Chem.* **1978**, *17*, 2813.

(8) Scott, J. D.; Puddephatt, R. *Organometallics* **1983**, *2*, 1643 and references therein.

(9) (a) Casares, J. A.; Coco, S.; Espinet, P.; Lin, Y. S. *Organometallics* **1995**, *14*, 3058. (b) Romeo, R.; Monsù Scolaro, L.; Nastasi, N.; Arena, G. *Inorg. Chem.* **1996**, *35*, 5087. (c) Rotondo, E.; Giordano, G.; Minniti, D. *J. Chem. Soc., Dalton Trans.* **1996**, 253. (d) Gelling, A.; Orrell, K. G.; Osborne, A. G.; Sik, V. *J. Chem. Soc., Dalton Trans.* **1998**, 937.

(10) (a) Tobe, M. L.; Burgess, J. *Inorganic Reaction Mechanisms*; Addison-Wesley Longman: Essex, England, 1999. (b) Wilkins, R. G. *Kinetics and Mechanisms of Reactions of Transition Metal Complexes*; VCH: Weinheim, Germany, 1991. (c) Tobe, M. L. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon Press: Oxford, U.K., 1987; Vol. 1, pp 311−329. (d) Atwood, J. D. *Inorganic Organometallic Reaction Mechanisms*; Brook/Cole: Monterey, CA, 1985. (e) Basolo, F.; Pearson, R. G. *Mechanisms of Inorganic Reactions*; Wiley: New York, 1968. (f) Langford, C. H.; Gray, H. B. *Ligand Substitution Processes*; W. A. Benjamin: New York, 1965. (g) Basolo, F. *Coord. Chem. Rev.* **1996**, *154*, 151.

(11) (a) Lanza, S.; Minniti, D.; Moore, P.; Sachinidis, J.; Romeo, R.; Tobe, M. L. *Inorg. Chem.* **1984**, *23*, 4428. (b) Lanza, S.; Minniti, D.; Romeo, R.; Moore, P.; Sachinidis, J.; Tobe, M. L. *J. Chem. Soc., Chem. Commun.* **1984**, 542. (c) Alibrandi, G.; Bruno, G.; Lanza, S.; Minniti, D.; Romeo, R.; Tobe, M. L. *Inorg. Chem.* **1987**, *26*, 185. (d) Minniti, D.; Alibrandi, G.; Tobe, M. L.; Romeo, R. *Inorg. Chem.* **1987**, *26*, 3956. (e) Frey, U.; Helm, L.; Merbach, A. E.; Romeo, R. *J. Am. Chem. Soc.* **1989**, *111*, 8161. (f) Alibrandi, D.; Minniti, D.; Monsù Scolaro, L.; Romeo, R. *Inorg. Chem.* **1989**, *28*, 1939.

(12) Romeo, R.; Grassi, A.; Monsù Scolaro, L. *Inorg. Chem.* **1992**, *31*, 4383.

(13) Wendt, O. F. Platinum(II) and Palladium(II) Complexes with Group 14 and 15 Donor Ligands: Synthesis, Structure and Substitution Mechanisms, Ph.D. Thesis, Lund University, Sweden, 1997.

(14) Romeo, R.; Plutino, M. R.; Monsù Scolaro, L.; Stoccoro, S. *Inorg. Chim. Acta* **1997**, *265*, 225.

(15) (a) Schmülling, M.; Ryabov, A. D.; van Eldik, R. *J. Chem. Soc., Chem. Commun.* **1992**, 1609. (b) Schmülling, M.; Ryabov, A. D.; van Eldik, R. *J. Chem. Soc., Dalton Trans.* **1994**, 1257.

(16) Schmülling, M.; Grove, D. M.; van Koten, G.; van Eldik, R.; Veldman, N.; Spek, A. L. *Organometallics* **1996**, *15*, 1384.

(17) (a) Elding, L. I.; Romeo, R. *J. Chem. Soc., Dalton Trans.* **1996**, 1471. (b) Wendt, O. F.; Oskarsson, A.; Leipold, J. G.; Elding, L. I. *Inorg. Chem.* **1997**, *36*, 4514.

(18) (a) Cornioley-Deuschel, C.; von Zelewsky, A. *Inorg. Chem.* **1987**, *26*, 3354. (b) Chen, Y. H.; Merkert, J. W.; Murtaza, Z.; Woods, C.; Rillema, D. P. *Inorg. Chim. Acta* **1995**, *240*, 41. (c) Blanton, C. B.; Murtaza, Z.; Shaver, R. J.; Rillema, D. P. *Inorg. Chem.* **1992**, *31*, 3230. (d) Blanton, C. B.; Rillema, D. P. *Inorg. Chim. Acta* **1990**, *168*, 145. (e) Zheng, G. Y.; Rillema, D. P. *Inorg. Chem.* **1998**, *37*, 1392.

Experimental Section

General Procedures and Chemicals. All syntheses were performed under a dry, oxygen-free nitrogen atmosphere using standard Schlenk-tube techniques. Spectrophotometrical-grade dichloromethane (Aldrich Chemical Co.) was distilled over barium oxide before use in the kinetic runs. Diethyl ether, tetrahydrofuran, and toluene were distilled from sodium benzophenone ketyl and stored in N_2-filled flasks over activated 4-Å molecular sieves. Benzene-d_6 (99.5+%), chloroform-d (99.8+%), and dimethyl sulfide-d_6 (99.9+%) were used as received from Aldrich. All of the other reagents were of the highest-purity grade commercially available and were used without further purification. Microanalyses were performed by Redox Analytical Laboratories, Milan, Italy.

Instrumentation. ^1H and ^{13}C NMR spectra were obtained on a Bruker AMX R-300 spectrometer equipped with a broad-band probe operating at 300.13 and 75.46 MHz, respectively (δ (ppm) downfield relative to Me$_4$Si, J (Hz)). The temperature within the probe was measured using the methanol or ethylene glycol method.[19] The spectrophotometric kinetics were carried out with a rapid-scanning Hewlett-Packard model 8452 A spectrophotometer or, at a selected wavelength, with a Perkin-Elmer Lambda 5 spectrophotometer, interfaced with a microcomputer for data collection and equipped with a cell compartment thermostated by a Perkin-Elmer Peltier temperature programmer (PTP). The temperature accuracy was ±0.05 °C. Rate constants were evaluated using the SCIENTIST software package.[20]

Synthesis of Complexes. The dinuclear complex [Pt(bph)(SEt$_2$)]$_2$ (**4**)[18a] (bph = 2,2'-biphenyl dianion) and the monomeric complex *cis*-[PtPh$_2$(SMe$_2$)]$_2$ (**1**)[11c] were prepared following published procedures. The purity and identity of the complexes were checked by elemental analyses and by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy.

[Pt(bph)(SMe$_2$)$_2$] (2). A solid sample of **4** (200 mg, 0.23 mmol) was added to liquid dimethyl sulfide (3 mL, 41 mmol). The suspension was stirred for 2 h, until the formation of a pale yellow solid was observed. Addition of 1 mL of *n*-hexane led to the precipitation of the required compound, which was separated by filtration, washed several times with 1 mL portions of *n*-hexane, and dried under vacuum in a desiccator to give 92 mg of **2** (yield 42%). ^1H NMR (CDCl$_3$), in the presence of excess of SMe$_2$ (in a 20:1 ratio with respect to **2**): δ 7.49 (dd, $^3J_{HH} = 7.7$ Hz, $^4J_{HH} = 1.1$ Hz, $^3J_{PtH} = 57.7$ Hz, 2H, H_3); 7.36 (dd, $^3J_{HH} = 7.7$ Hz, $^4J_{HH} = 1.7$ Hz, $^4J_{PtH} = 13.2$ Hz, 2H, H_6); 7.00 (ddd, $^3J_{av} = 7.2$ Hz, $^4J_{HH} = 1.1$ Hz, 2H, H_5); 6.90 (ddd, $^3J_{av} = 7.4$ Hz, $^4J_{HH} = 1.7$ Hz, $^4J_{PtH} = 14.0$ Hz, 2H, H_4); 2.63 (s, $^3J_{PtH} = 20.9$ Hz, 12H, S–CH_3). ^{13}C NMR (CDCl$_3$): δ 155.9 ($J_{PtC} = 139$ Hz); 149.5 ($J_{PtC} = 1141$ Hz); 133.0 ($J_{PtC} = 48$ Hz); 125.6 ($J_{PtC} = 61$ Hz); 125.1 ($J_{PtC} = 7$ Hz); 120.1 ($J_{PtC} = 63$ Hz); 21.1 ($J_{PtC} = 7$ Hz). Chloroform-d solutions of **2** show signals belonging to the dinuclear species [Pt(bph)(SMe$_2$)]$_2$ (**5**) ^1H NMR (CDCl$_3$): δ 7.34 (dd, $^3J_{HH} = 7.4$ Hz, $^4J_{HH} = 1.7$ Hz, 2H, H_6); 7.04 (ddd, $^3J_{av} = 7.4$ Hz, $^4J_{HH} = 1.7$ Hz, 2H, H_5); 6.97 (dd, $^3J_{HH} = 7.4$ Hz, $^4J_{HH} = 1.9$ Hz, 2H, H_3); 6.92 (ddd, $^3J_{av} = 7.4$ Hz, $^4J_{HH} = 1.1$ Hz, 2H, H_4); 3.48 (s, $^3J_{PtH} = 18.1$ Hz, 6H, S–CH_3).

[Pt(bph)(SEt$_2$)$_2$] (3) was prepared in situ, at the desired concentration, by the bridge-splitting reaction of **4** with an excess of SEt$_2$ in chloroform-d (NMR experiments) or in dichloromethane and spectrophotometric-grade (s.g.) toluene (UV–vis measurements). In a typical procedure a 20-fold excess of SEt$_2$ (0.056 mmol) was added to a solution of 2.5 mg (0.0028 mmol) of **4** in 0.5 mL of CDCl$_3$ contained in a 5-mm NMR tube. ^1H NMR (CDCl$_3$): δ 7.53 (dd, $^3J_{HH} = 7.3$ Hz, $^4J_{HH} = 1.1$ Hz, $^3J_{PtH} = 59.4$ Hz, 2H, H_3); 7.35 (dd, $^3J_{HH} = 7.5$ Hz, $^4J_{HH} = 1.4$ Hz, $^4J_{PtH} = 13.9$ Hz, 2H, H_6); 7.00 (ddd, $^3J_{av} = 7.4$ Hz, $^4J_{HH} = 1.1$ Hz, 2H, H_5); 6.89 (ddd, $^3J_{av} = 7.4$ Hz, $^4J_{HH} = 1.4$ Hz, $^4J_{PtH} = 14.0$ Hz, 2H, H_4); 3.07 (q, $^3J_{HH} = 7.4$ Hz, $^3J_{PtH} = 15.6$ Hz, 8H, S–CH_2–CH$_3$); 1.40 (t, $^3J_{HH} = 7.4$ Hz, 12H, S–CH$_2$–CH_3). ^{13}C NMR (CDCl$_3$): δ 156.0 ($J_{PtC} = 140$ Hz), 150.7 ($J_{PtC} = 1152$ Hz); 133.3 ($J_{PtC} = 49$ Hz); 125.5 ($J_{PtC} = 62$ Hz); 124.8 ($J_{PtC} = 8$ Hz); 119.9 ($J_{PtC} = 64$ Hz); 29.6 ($J_{PtC} = 5$ Hz); 13.8 ($J_{PtC} = 16$ Hz).

[Pt(bph)(bpy)] (6). This complex was prepared by a synthetic route different from that reported in the literature.[18a] Thus, [Pt(bph)(SMe$_2$)$_2$]

(50 mg, 0.106 mmol) dissolved in toluene (2 mL) was reacted with a toluene solution of 2,2'-bipyridine (bpy) (32.8 mg, 0.21 mmol). After the mixture was stirred for 1 h at 40 °C, addition of *n*-hexane to the red solution led to the precipitation of **6**. ^1H NMR (CDCl$_3$): δ 9.62 (d, br, $^3J_{HH} = 5.7$ Hz, $^3J_{PtH} = 17.0$ Hz, 2H, $H_{6'}$); 8.13 (ddd, $^3J_{av} = 7.3$ Hz, $^4J_{HH} = 2.0$ Hz, 2H, $H_{4'}$); 8.09 (dd, $^3J_{HH} = 7.8$ Hz, $^4J_{HH} = 1.6$, 2H, $H_{3'}$); 7.62 (ddd, $^3J_{HH} = 7.1, 5.6$ Hz, $^4J_{HH} = 1.5$ Hz, 2H, $H_{5'}$); 7.44 (d, $^3J_{HH} = 7.2$ Hz, $^4J_{HH} = 1.5$ Hz, $^3J_{PtH} = 53.8$ Hz, 2H, H_3); 7.39 (dd, $^3J_{HH} = 7.0$ Hz, $^4J_{HH} = 1.4$ Hz, $^4J_{PtH} = 15.6$ Hz, 2H, H_6); 7.01 (ddd, $^3J_{av} = 7.4$ Hz, $^4J_{HH} = 1.4$ Hz, 2H, H_5); 6.95 (ddd, $^3J_{av} = 7.4$ Hz, $^4J_{HH} = 1.4$ Hz, 2H, H_4). ^{13}C NMR (CDCl$_3$): δ 157.1 ($J_{PtC} = 130$ Hz); 156.2; 150.3 ($J_{PtC} = 34$ Hz); 145.9 ($J_{PtC} = 956$ Hz); 137.1; 132.8 ($J_{PtC} = 42$ Hz); 126.6 ($J_{PtC} = 21$ Hz); 124.9 ($J_{PtC} = 61$ Hz); 124.1 ($J_{PtC} = 66$ Hz); 122.8 ($J_{PtC} = 10$ Hz); 119.6 ($J_{PtC} = 62$ Hz).

[Pt(bph)(phen)] (7). A solution of 1,10-phenanthroline (phen) (22.7 mg, 0.126 mmol) in toluene (2 mL) was added dropwise to a solution of **4** (50 mg, 0.057 mmol) in toluene (4 mL) under continuous stirring. After the orange reaction mixture was refluxed for 1 h, the complex separated out as a solid upon adding *n*-hexane (1:1, v:v) and cooling at −35 °C. Anal. Calcd for C$_{24}$H$_{16}$N$_2$Pt: H, 3.06; C, 54.65; N, 5.31. Found: H, 3.08; C, 53.69; N, 5.18. ^1H NMR (CDCl$_3$): δ 9.95 (d, br, $^3J_{HH} = 5.5$ Hz, $^3J_{PtH} = 17.1$ Hz, 2H, $H_{2',9'}$); 8.61 (ddd, $^3J_{av} = 8.1$ Hz, $^4J_{HH} = 1.3$ Hz, 2H, $H_{4',7'}$); 7.97 (d, $^4J_{HH} = 1.2$ Hz, 2H, $H_{5',6'}$); 7.94 (dd, $^3J_{HH} = 5.5, 8.1$ Hz, 2H, $H_{3',8'}$); 7.53 (dd, $^3J_{HH} = 7.3$ Hz, $^4J_{HH} = 1.2$ Hz, $^3J_{PtH} = 49.1$ Hz, 2H, H_3); 7.40 (d, $^3J_{HH} = 7.1$ Hz, $^4J_{HH} = 1.2$ Hz, $^4J_{PtH} = 11.3$ Hz, 2H, H_6); 7.02 (ddd, $^3J_{av} = 7.4$ Hz, $^4J_{HH} = 1.2$ Hz, 2H, H_5); 6.97 (ddd, $^3J_{av} = 7.2$ Hz, $^4J_{HH} = 1.2$ Hz, 2H, H_4). ^{13}C NMR (CDCl$_3$): δ 157.3; 150.1 ($J_{PtC} = 34$ Hz); 147.3; 145.7; 136.5; 132.9 ($J_{PtC} = 39$ Hz); 130.4; 127.3; 125.4 ($J_{PtC} = 20$ Hz); 124.8 ($J_{PtC} = 61$ Hz); 124.0 ($J_{PtC} = 8$ Hz); 119.6 ($J_{PtC} = 62$ Hz). Electronic spectrum (CH$_2$Cl$_2$): λ_{max} (10^3 cm^{-1}) = 43.1 (ϵ = 32 100 M^{-1} cm^{-1}), 38.1 (34 500), 36.5 (31 500), 31.8 (8930), 29.4 (5630), 27.8 (3910), 22.7 (5340).

Computational Details. Theoretical calculations were performed on the square-planar four-coordinated *cis*-[PtPh$_2$(SMe$_2$)$_2$] (**1**) and [Pt-(bph)(SMe$_2$)$_2$] (**2**) complexes, for the T-shaped residues *cis*-[PtPh$_2$-(SMe$_2$)] (**1'**) and [Pt(bph)(SMe$_2$)] (**2'**), and for the isolated SMe$_2$ molecule by using the ab initio effective *core potential* technique. All calculations were performed using the Gaussian 94 package.[21] All geometries were optimized at the restricted Hartree−Fock (RHF) level with electronic correlation terms. All calculations were performed using the LANL2DZ atomic basis set, in which a Dunning−Huzinaga full double-ζ (D95)[22] expansion is introduced for the first row atomic orbitals. For atoms from Na to Bi the core electrons were fitted to an effective core potential (*pseudo-potential* model), while the valence electrons are described with a double-ζ basis (3s3p3d).[23] The basis set for H consisted of three Gaussian contractions from which the most diffuse component was split off to form a double-ζ basis. The electronic correlation terms were introduced using a hybrid method, which includes a mixture of Hartree−Fock (exchange terms) and DFT (Becke3LYP[24] functional for exchange-correlation terms).

The molecular electrostatic potential (MEP) analysis was obtained by using the standard procedure.[25] All calculations were performed on a Digital AlphaStation 500 computer.

Results

The preparation of the dinuclear complex [Pt(bph)(SEt$_2$)]$_2$ (**4**) has been reported by Cornioley-Deuschel and von Zelewsky.[18a]

(19) (a) Van Geet, A. L. *Anal. Chem.* **1968**, *40*, 2227. (b) Van Geet, A. L. *Anal. Chem.* **1970**, *42*, 679.
(20) SCIENTIST, Version 2.0; Micro Math Scientific Software: Salt Lake City, UT.

(21) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*; Gaussian, Inc.: Pittsburgh, PA, 1995.
(22) Dunning, T. H.; Hay, P. J. In *Modern Theoretical Chemistry*; Schaefer, H. F., III, Ed.; Plenum: New York, 1976; pp 1−28.
(23) (a) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270. (b) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 284.
(24) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
(25) Carbo, R.; Martin, M. *Int. J. Quantum Chem.* **1975**, *9*, 235.

The ^{1}H NMR spectrum contains the expected resonances of the diphenyl dianion together with a quartet at δ 3.85 and a triplet at 1.78 ppm due to the bridging Et_2S ligands. As for the related $[PtMe_2(SMe_2)]_2$[26] and $[PtPh_2(SMe_2)]_2$[11c] complexes, there is evidence of a monomer−dimer equilibrium

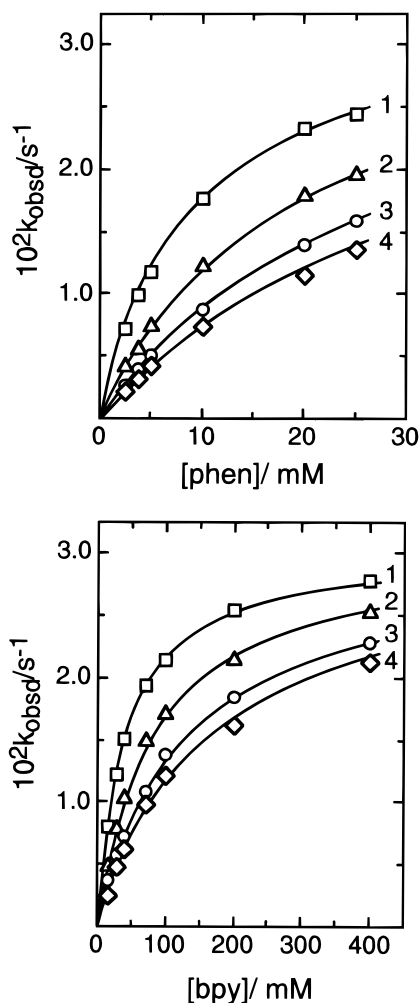$$2[Pt(bph)(SEt_2)_2] \leftrightarrow [Pt(bph)(\mu\text{-}SEt_2)]_2 + 2SEt_2 \quad (1)$$

which can be shifted toward the monomeric species [Pt(bph)-$(SEt_2)_2$] (**3**) by addition of an excess of thioether (SEt_2). The proton resonances of the coordinated diethyl sulfides in **3** show an upfield shift relative to the bridging ligands in **4**, and the electronic spectrum in toluene exhibits a band at 29.6×10^3 cm^{-1} compared to the band at 29.4×10^3 cm^{-1} for **4** which has been attributed to a Pt → bph metal-to-ligand charge transfer (MLCT) transition.[18a] The complex **3** cannot be isolated as a pure compound and it can be obtained only in solution by adding a sufficient excess of SEt_2 to **4**. Unlike the diethyl sulfide derivative, the monomeric species [Pt(bph)(SMe_2)_2] (**2**) ($\delta = $ 2.63 ppm, $^3J_{PtH} = 20.9$ Hz, S−CH$_3$, in CDCl$_3$, $\lambda = 29.7 \times 10^3$ cm^{-1}, in toluene) was obtained as a solid by the bridge splitting reaction of SMe_2 on **4**, as described above. This pure compound is in equilibrium with a dimeric species and, therefore, the presence of an excess of free SMe_2 was necessary during the kinetic runs to ensure the stability of the starting material.

The monomeric complex [Pt(bph)(SMe_2)_2] (**2**) is a useful synthon, as is the dinuclear compound **4**,[18] for synthesizing square-planar platinum(II) organometallic compounds containing the 2,2′-biphenyl dianion metal moiety. When reacting with a bidentate ligand N−N (bpy or phen), thioethers are readily displaced to yield [Pt(bph)(N−N)] compounds. The absorption features of the complex containing 1,10-phenanthroline appear to be similar to those of the 2,2′-bypyridine complex and, by analogy to previous transition assignment for [Pt(bph)(bpy)],[18a] and for dialkyl or diaryl *cis*-[PtR_2(N−N)] (R = methyl, aryl; N−N = di-imine) compounds,[27] the strong absorption band in the visible region (22.7×10^3 cm^{-1}, $\epsilon = 5340$ M^{-1} cm^{-1}) can be assigned to a metal-to-ligand (N−N) charge transfer transition.

Kinetics of Thioether Substitution. The substitution reactions of thioethers SR_2 (R = methyl, ethyl) from [Pt(bph)(SR_2)_2] by the dinitrogen ligands N−N (bpy or phen), according to eq 2, were carried out at 298.2 ± 0.05 K in a silica cell located in

$$[Pt(bph)(SR_2)_2] + N\text{-}N \rightarrow [Pt(bph)(N\text{-}N)] + 2SR_2 \quad (2)$$

the thermostated cell compartment of the spectrophotometer, using dichloromethane or toluene as the solvent. The kinetics were followed by repetitive scanning of the spectrum at suitable times in the wavelength range 350−550 nm, where the absorbance of the starting thioether complex is negligible and the absorbance of the di-imine product is strong (Pt → (N−N) MLCT band). The reactions, carried out in the presence of at least a 10-fold excess of chelate and a 20-fold excess of SR_2 over the complex, went to completion, with the final spectra being identical to those of authentic samples of [Pt(bph)(N−N)]. Abstract factor analysis of the spectral changes[28] confirmed that the di-imine-containing product is the only absorbing species

(26) Scott, J. D.; Puddephatt, R. J. *Organometallics* **1983**, *2*, 1643.
(27) Chaudury, N.; Puddephatt, R. J. *J. Organomet. Chem* **1975**, *84*, 105.
(28) (a) Uguagliati, P.; Benedetti, A.; Enzo, S.; Schiffini, L. *Comput. Chem.* **1984**, *8*, 161−168. (b) Sandrini, P. L.; Mantovani, A.; Crociani, B.; Uguagliati, P. *Inorg. Chim. Acta* **1981**, *51*, 71−80. (c) Malinowski, E. R.; Howery, D. G. *Factor Analysis in Chemistry*; Wiley-Interscience: New York, 1980; pp 159−161.

Figure 1. Saturation kinetics for the reaction ([Pt(bph)(SEt_2)_2] + N−N → [Pt(bph)(N−N)] + 2 SEt_2) carried out in the presence of different amounts of entering ligand and of free sulfide (increasing in the range 10−70 mmol from 1 to 4). Upper plot, N−N = 1,10-phenanthroline; lower plot, N−N = 2,2′-bipyridine.

in solution, and there was no indication of the presence of significant amounts of any intermediate species. Thus, the conversion of the substrate into the product is seen as a single step, the rate of ring closure being much faster than the rate of displacement of the first thioether. All reactions obeyed a first-order rate law until well over 90% conversion. Rate constants k_{obsd} (s^{-1}) were obtained from nonlinear least-squares fits of the experimental data to $A_t = A_\infty + (A_0 - A_\infty) \exp(-k_{obsd}t)$ with A_0, A_∞, and k_{obsd} as the parameters to be optimized ($A_0 = $ absorbance after mixing of reagents, $A_\infty = $ absorbance at completion of reaction). The pseudo-first-order rate constants k_{obsd} for reaction 1 are reported in Supporting Information Tables S1 and S2 for a range of N−N and R_2S concentrations at 298.2 K.
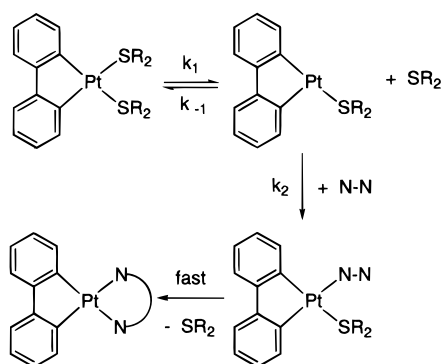
The pseudo-first-order rate constants, k_{obsd}, when plotted against the concentration of the chelating ligand, at a constant concentration of sulfide, give a curvilinear dependence, which levels off to a limiting value at high nucleophile concentration. A representation of the N−N and SEt_2 dependencies for the kinetic data of [Pt(bph)(SEt_2)_2] is given in Figure 1 (upper plot, N−N = phen; lower plot, N−N = bpy) and displays the typical saturation profiles whose curvature decreases as the concentration of free sulfide increases. The pattern of behavior is strictly similar to that found in our previous studies on *cis*-[PtPh_2-(SMe_2)_2][11c] and other dialkyl and diaryl systems,[11,12] where the

Scheme 1

Table 1. Rate Constants at 298 K Derived from the Kinetic Analysis of Nucleophilic Substitution Reactions

no.	complex	solvent	N−N	$10^2 k_1/s^{-1}$	(k_{-1}/k_2)
2	$[Pt(bph)(SMe_2)_2]$	toluene	bpy	10.7 ± 0.3	10.4 ± 1
		toluene	phen	12.0 ± 0.3	1.8 ± 0.1
3	$[Pt(bph)(SEt_2)_2]$	toluene	bpy	3.02 ± 0.08	2.15 ± 0.15
		toluene	phen	3.32 ± 0.12	0.70 ± 0.05
		CH_2Cl_2	bpy	10.1 ± 0.6	10.7 ± 2.0

easy dissociation of thioethers or sulfoxides was shown to be the rate-determining step of the substitution. The same dissociative mechanism (Scheme 1) applies here which involves (i) dissociative loss of SR_2 from the substrate (k_1 path) to yield a three-coordinated 14-electron intermediate, (ii) competition for it between the reentry of SR_2 (via k_{-1}) and the attack of the chelating ligand (via k_2) to form an open-ring species, and (iii) final fast ring-closure to yield the observed products.

The rate data were fitted to the following equation:

$$k_{obsd} = k_1[N-N]/\{(k_{-1}/k_2)[SR_2] + [N-N]\} \qquad (3)$$

The best values of the rate constant k_1 and of the competition ratio k_{-1}/k_2, together with their standard deviations, were obtained by a multiple nonlinear regression of k_{obsd} vs [N−N] and [SR_2], and are reported in Table 1.

Kinetics of Thioether Exchange. The kinetics of ligand exchange reactions

$$[PtL_2(SR_2)_2] + 2*SR_2 \rightarrow [PtL_2(*SR_2)_2] + 2SR_2 \qquad (4)$$

were investigated by ^1H NMR magnetization transfer experiments for L = 1/2 (bph), SR_2 = SMe_2 or SEt_2, and by ^1H NMR isotopic exchange experiments for L = Ph, SR_2 = SMe_2, according to the rate of the process.

(i) Magnetization Transfer. The rate constants for the moderately fast exchange of the species SR_2 (R = Me, Et) between the two nonequivalent sites, S_{bound} and S_{free}, in the cyclometalated complexes $[Pt(bph)(SR_2)_2]$, were determined by magnetization transfer experiments, as described by Forsèn and Hoffman.[29] In a typical experiment, the resonance of the free site, S_{free}, was completely saturated through a selective rf pulse, while the resonance of S_{bound} was monitored as a function of the variable irradiation time. For both sulfides the condition of a good separation of the free and the bound signals was fulfilled, thereby allowing for saturation of the free signals without perturbing the magnetization of the bound signals.[30] The integrals of S_{bound} (M_b) were fitted by linear regression analysis to eq 5

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

$$\ln[(M_b)_t - (M_b)_\infty] = -\ln(M_b)_0(\tau_{1b}/\tau_b) + t/\tau_{1b} \qquad (5)$$

where $(M_b)_0$, $(M_b)_t$, and $(M_b)_\infty$ are the integrals of the peak before saturation, at the time t, and after a prolonged saturation, respectively. τ_{1b} is correlated to T_{1b}, the spin−lattice relaxation time, and to τ_b, the lifetime of the observed site, by eqs 6 and 7.

$$(M_b)_\infty = (M_b)_0(\tau_{1b}/T_{1b}) \qquad (6)$$

$$1/\tau_{1b} = 1/\tau_b + 1/T_{1b} \qquad (7)$$

The pseudo-first-order constants were calculated as $k_{exch} = 2\tau_b^{-1}$, taking into account the fact that the exchange involves two equivalent sites. All of the rates of ligand exchange were independent of the concentration of free sulfide. The rate constants, at different temperatures, from magnetization transfer experiments (in Supporting Information Tables S4 and S5) were fitted to the Eyring equation (Supporting Information Figure S1) leading to the activation parameters reported in Table 2.

(ii) Isotopic Exchange. In the case of the slowly exchanging complex *cis*-$[PtPh_2(SMe_2)_2]$, the thioether exchange rates were obtained by isotopic exchange. A known volume of dimethyl sulfide-d_6 was added, with a microsyringe, into a 5-mm NMR tube containing a prethermostated solution of *cis*-$[PtPh_2(SMe_2)_2]$ in chloroform-d. A 7-fold excess of dimethyl sulfide-d_6 over the complex was ensured in every run. The rate of exchange was monitored through the increase in intensity of the signal at δ 2.12 ppm relative to the free SMe_2 and the matching decrease of the signal at 2.09 ppm for the bound SMe_2. The molar fraction of free SMe_2, $F_f = [SMe_2]_f/([SMe_2]_f + [SMe_2]_b)$, was obtained by integration of both signals. The exchange of the label follows a first-order rate law, and the first-order rate constant, $k_{exch}(s^{-1})$, was obtained from the nonlinear regression analysis of the equation $F_f = c_1 + c_2 \exp(-k_{exch}t)$ with c_1, c_2, and k_{exch} as the parameters to be optimized. A similar analysis was performed on the molar fraction of the nondeuterated bound dimethyl sulfide. From the McKay equation, $R_{exch} = 2k_{exch}ab(2a + b)^{-1}$ (where R_{exch} is the rate of the exchange process, a is the concentration of complex, the factor of 2 is required for two equivalent exchanging sulfides, and b is the concentration of free sulfide), the pseudo-first-order rate constants, R_{exch}/a, were calculated, and their values are reported in Supporting Information Table S3. The exchange rate constants were independent of the free dimethyl sulfide concentration. The variable-temperature rate constants were fitted to the Eyring equation and the derived activation parameters are reported in Table 2.

Theoretical Calculations

Table 3 reports selected energetic and structural parameters computed for the minimum-energy conformations of the square-planar compounds *cis*-$[PtPh_2(SMe_2)_2]$ (**1**) and $[Pt(bph)(SMe_2)_2]$ (**2**), of their three-coordinated derivatives (**1′** and **2′**), and of the isolated molecule SMe_2. No attempt was made to determine the transition state for the reaction, nor was any made to define

(30) The pulse sequence can be summarized as the following: $[(D_1-P_{DEC}-V_T-P_1-AQ)N_S]N_E$, with D_1 = relaxation delay, 20 s; P_{DEC} = decoupler power, 50 dB, used to saturate S_{free}; V_T = variable irradiation time, different for each of the different N_E experiments; P_1 = pulse at 40.9°, 4 μs; AQ = acquisition time, 0.9 s; and N_S = number of scans. As far as the SEt_2 is concerned, the scalar coupling of the CH_2-CH_3 system gives rise to a quadruplet signal at 3.06 ppm for the bound group, S_{bound}, and 2.58 ppm for the free sulfide, S_{free}, that has been saturated using cycles (C) of selective irradiation for each of the four peaks, with an overall irradiation time $V_T = C*V_T'$ and $C = 4n$.

Table 2. Rates and Activation Parameters for Ligand Exchange Reactions[a]

no.	complex	ligand	$10^2 k_{exc}$[b]	$\Delta H^{\ddagger}$[c]	$\Delta S^{\ddagger}$[d]
1	*cis*-[PtPh$_2$(SMe$_2$)$_2$][e]	SMe$_2$	0.713 ± 0.003	93 ± 1	26 ± 3
2	[Pt(bph)(SMe$_2$)$_2$][f]	SMe$_2$	106 ± 2	80 ± 1	24 ± 4
3	[Pt(bph)(SEt$_2$)$_2$][f]	SEt$_2$	8.38 ± 0.03	86 ± 2	23 ± 8

[a] In CDCl$_3$. [b] Values of the exchange rate (s^{-1}), calculated at 298.2 K. [c] In kJ mol^{-1}. [d] In JK^{-1} mol^{-1}. [e] From isotopic exchange experiments. [f] From ^{1}H NMR magnetization transfer experiments.

any reaction coordinate. High-level computation to prove the existence of a three-coordinated transition state has been avoided on the basis of the following assumptions: (i) the activation mode is exclusively dissociative, and (ii) the energy of the transition states is comparable to that of the optimized T-shaped structures of the three-coordinated [PtPh$_2$(SMe$_2$)] and [Pt(bph)-(SMe$_2$)] reaction intermediates. Although an upright disposition of the residual dimethyl sulfide molecule could favor the saturation of the metal in a trigonal planar geometry (the orthogonal p$_\pi$ orbital of the ligand would act as a donor toward the empty in-plane d$_\pi$ hybrid of metal), such a major rearrangement does not seem mandatory. This is in line with several examples which show the stability of 14e T-shaped species.[31] Moreover, a trigonal planar geometry and its possible implications for a high-spin state are most reasonably avoided by a metal such as platinum coordinated by strong σ-donor ligands such as carbanions. The optimization of the three-coordinated species to a T-shaped geometry suggests that dissociation can occur simply through a least motion pathway with progressive elongation of one M−S linkage. We do not expect significant energy contributions to ligand dissociation by changes in bond lengths and angles between the central metal and the non-exchanging ligands. Because the restrictions introduced to the computation are the same for both [PtPh$_2$(SMe$_2$)] and [Pt(bph)-(SMe$_2$)], the results of the theoretical calculations would be at least coherent with the kinetic results and in agreement with the difference of reactivity observed between the two systems.

Figure 2 summarizes the main data for the optimized geometries of **1** and **2** and of their dissociation derivatives, obtained from the RHF calculation, together with the values of the calculated activation enthalpies. Although the bonding between the metal and the carbo ligands is fairly well reproduced with respect to available experimental data in terms of both distances and angles, the Pt−S bond lengths appear to be overestimated. In fact, the values of 2.612 Å for **1** and 2.636 Å for **2** are ca. 0.2 Å longer than those found in the X-ray diffraction study of **1** (2.401 Å).[11c] Such a difference is fairly common for the type of computation adopted and is most probably due to the *pseudo-potential* technique which indicates a relevant overlap between the core orbitals of the Pt and S atoms.[23] As mentioned above, other structural details indicate good reliability of the results; thus, the sulfur atoms are in a tetrahedral environment and the phenyl rings are almost perpendicular to the coordination plane. In **1′** the three-coordinated fragment exhibits a slight widening of the angle between the two aromatic rings that here adopt a butterfly-like conformation. All of the bond distances remain almost unchanged with respect to the starting four-coordinated species.

(31) (a) Komyia, S.; Albright, T. A.; Hoffmann, R.; Kochi, J. K. *J. Am. Chem. Soc.* **1976**, *98*, 7255. (b) Thorn, D. L.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 2079. (c) Tatsumi, K.; Hoffmann, R.; Yamamoto, A.; Stille, J. K. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1857. (d) Carr, N.; Dunne, B. J.; Orpen, G. A.; Spencer, J. L. *J. Chem. Soc., Chem. Commun.* **1988**, 926. (e) Mole, L.; Spencer, J. L.; Carr, N.; Orpen, A. G. *Organometallics* **1991**, *10*, 49.

Importantly, the energy calculated for dissociation of SMe$_2$ from **1** (difference between the total energy of the complex and the sum of the separated fragments) is relatively low (ca. 72.2 kJ mol^{-1}). Such a value is consistent with a feasible thermal decomposition of the starting compound.

The main structural characteristics of compound **2** are associated with the geometrical constraint imposed by the biphenyl group. In particular, as found in some X-ray structures,[18d] the C−Pt−C bite angle (81.4°) is much smaller than that in **1** (88.5°) and the Pt−S bond distance appears preferentially longer (∼0.02 Å), given the clear-cut artifact of major elongation noted above. All of the other bond distances (Pt−C, C−C, and S−C) are comparable to those of **1**. The increase of energy associated with SMe$_2$ dissociation is 52.3 kJ mol^{-1}. On formation of the three-coordinated species, the C−Pt−C bite angle (81.3°) remains unchanged and, as a result of the rigidity of the chelate bite, the C−Pt−S angle is widened with respect to that of the four-coordinate (from 100° to 108°). The Pt−S bond distance of the residual thioether is shortened (from 2.636 to 2.580 Å), in agreement with the idea that a decrease of the coordination number should cause a general strengthening of the residual bonds to the metal.

In Figure 3 the molecular electrostatic potentials (MEPs) for the same species are plotted. For **1** and **2** the electrostatic potential (EP) is calculated on a plane parallel to the main coordination plane, shifted by 2.5 Å; for the transition states, the plane of the calculated EP is 2.5 Å over the molecular fragments on the side of the vacant site. The colored areas represent the values of the EPs in electrostatic units (e.u.), starting from +10 (red areas) and going to −10 (blue areas). The map of each molecule shows a highly negative area (about −10 e.u.) over the platinum atom and a highly positive one (about +10 e.u.) over the SMe$_2$ groups. Largely negative values of EP are displayed over the biphenyl fragment of [Pt(bph)-(SMe$_2$)$_2$], thus showing clearly the delocalization of the π electron cloud over the two rings. Obviously, in *cis*-[PtPh$_2$-(SMe$_2$)$_2$], the analogous area lies orthogonal, while the map shown is positive in correspondence to the hydrogen atoms. The EP planes appear somewhat different for both of the three-coordinated molecules as positive and neutral areas appear around the metal atom.

Discussion

The assessment of the dissociative mechanism for organometallic substrates of the type *cis*-[PtR$_2$L$_2$] (R = Ph or Me; L = thioethers or dimethyl sulfoxide)[11] has been made essentially on the basis of (i) the saturation profile observed on plotting the rate constants against the concentration of the entering ligand, as a result of mass-law retardation produced by the leaving group, (ii) the independence of the dissociation rate on the nature of the entering group, (iii) the identity of the rate of dissociation with the rate of solvent exchange, (iv), the sign and the magnitude of the entropy of activation always being positive, and (v) positive values of the volume of activation. For example, a variable-pressure study on compound **1**, assumed in this work as paradigmatic of a dissociative behavior, has already led to a positive volume of activation $\Delta V^{\ddagger} = +4.7 \pm 0.5$ cm^3 mol^{-1} in toluene.[11e] The solvents used were insufficiently coordinating to give an associatively activated contribution. The kinetic pattern of behavior of the compounds **2** and **3**, as we will see in detail below, perfectly satisfies points i−iv and, therefore, the experimental kinetic evidence points unequivocally to a dissociative mode of activation for the cyclometalated compounds examined.
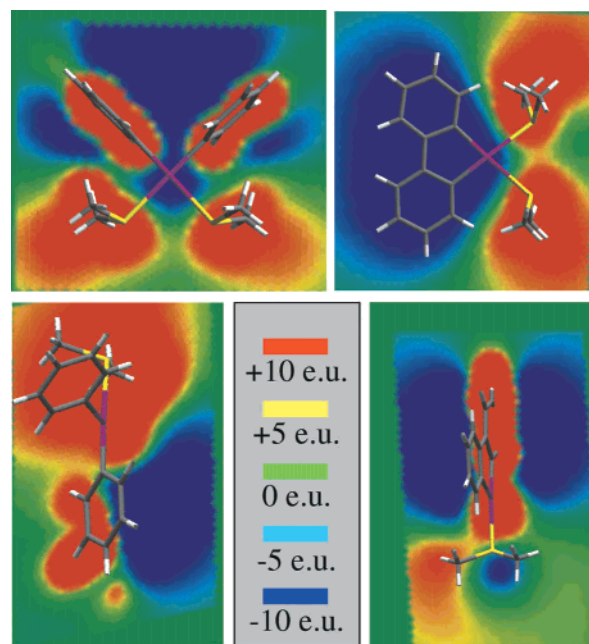
Table 3. Calculated Energies and Some Structural Parameters for Four-Coordinated Square-Planar Complexes and for the Corresponding Three-Coordinated T-Shaped Molecular Fragments

no.	molecule	$E_{HF+corr}{}^a$	μ^b	$\Delta E_{HF+corr}{}^c$	$d_{k2/k1}{}^d$	Pt−S^e	ΔE^f
1	[PtPh$_2$(SMe$_2$)$_2$]	−762.24372	4.00	72.2	3063	2.612	0.1864
1′	[PtPh$_2$(SMe$_2$)]	−672.30509	5.00				
2	[Pt(bph)(SMe$_2$)$_2$]	−761.04512	5.57	52.3		2.636	0.1512
2′	[Pt(bph)(SMe$_2$)]	−671.11407	5.37				
	SMe$_2$	−89.91115					

^{a} Given in au, with geometry optimization; basis set LANL2DZ + Becker3LY. ^{b} In Debye units. ^{c} Energy difference in kJ mol^{-1} between (**1′** + SMe$_2$) and **1** and (**2′** + SMe$_2$) and **2**, respectively. ^{d} Ratio of the calculated rate constants for ligand dissociation in compounds **2** and **1** (see text). ^{e} In Å. ^{f} Energy difference HOMO−LUMO, in au.
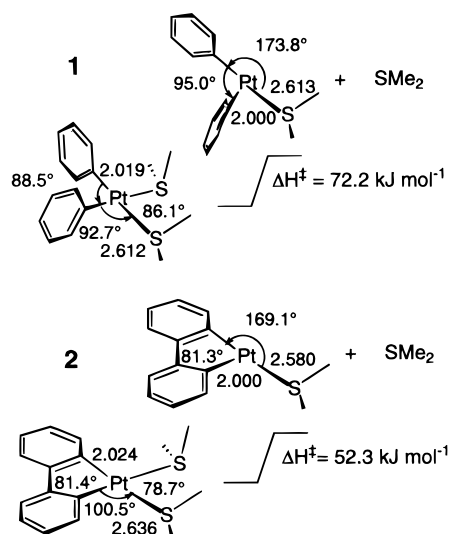
Figure 2. Optimized geometries for starting square-planar complexes and T-shaped molecular fragments formed upon ligand (SMe$_2$) dissociation. Bond lengths are given in angstroms and bond angles are given in degrees.

Figure 3. MEP maps of the four-coordinate square-planar sulfide compounds *cis*-[PtPh$_2$(SMe$_2$)$_2$] and [Pt(bph)(SMe$_2$)$_2$] and of the corresponding three-coordinated T-shaped species. Colored areas represent the values of the EP in e.u. (electrostatic units), starting from +10 (red areas) and going to −10 (blue areas).

The reactions of **2** and **3** with the nitrogen-chelating ligands 2,2′-bipyridine and 1,10-phenanthroline are retarded by the addition of small amounts of free thioether and, according to eq 3, exhibit typical saturation kinetics (see Figure 1). The dependence of the rate constant on [N−N], at various concentrations of added thioether, is described by a series of curves whose curvature depends on the concentration of free sulfide. The values of k_1, which, according to reaction Scheme 1, refers to the rate of dissociation of the first thioether, are constant and independent of the nature of the entering ligand, being centered at $(11.4 \pm 0.9) \times 10^{-2}$ s^{-1} and at $(3.17 \pm 0.2) \times 10^{-2}$ s^{-1} for compounds for **2** and **3**, respectively, in toluene at 298 K. The reactivity appears to be sensitive to the electron-donating ability of the substituents on the sulfur atom of the leaving thioether, decreasing by a factor of 4 on going from compound **2** (dimethyl sulfide) to **3** (diethyl sulfide). These findings are consistent with the view that the lability of the sulfide is dictated by the amount of electron density transmitted by the substituents to the sulfur and, finally, by the Pt−S bond strength. Accordingly, along the series of compounds of the type *cis*-[PtPh$_2$L$_2$], where L encompasses a wide range of thioethers of different electron-donating characteristics, the reactivity was found to decrease linearly with increasing σ-donor ability of the leaving thioether.[11f] The polarity of the solvent also slightly affects the reactivity. The value of k_1 for **3** increases from $(3.02 \pm 0.08) \times 10^{-2}$ s^{-1} in toluene to $(10.1 \pm 0.6) \times 10^{-2}$ s^{-1} in dichloromethane at 298 K, indicating a somewhat greater

stabilization of the transition state, formed by the [Pt(bph)(SEt$_2$)] and SEt$_2$ moieties, with respect to the initial state [Pt(bph)-(SEt$_2$)$_2$].

Exchange of the coordinated SR$_2$ thioethers in the compounds **1, 2,** and **3** with free ligand in CDCl$_3$, at 298 K, takes place with a rate law of the form $rate = k_{exch}$[complex], with $k_{exch} = 0.713 \times 10^{-2}$ s^{-1}, $k_{exch} = 106 \times 10^{-2}$ s^{-1}, and $k_{exch} = 8.38 \times 10^{-2}$ s^{-1}, respectively (Table 2). There is no thioether-dependent contribution, even at the highest thioether concentrations. As required by the dissociative mechanism, the rate constants for solvent exchange (k_{exch}) are equal to the dissociation rates (k_1) obtained from substitution reactions. For [Pt(bph)(SEt$_2$)$_2$] the exchange rate $(8.38 \pm 0.03) \times 10^{-2}$ s^{-1} in CDCl$_3$ is almost identical to the value of $k_1 = (10.1 \pm 0.6) \times 10^{-2}$ s^{-1} in CH$_2$Cl$_2$. Such differences as those found in comparing the other data in Table 1 (in toluene) with those in Table 2 (in deuterated chloroform) can be accounted for in terms of the difference in the solvating powers of toluene and chloroform.

The temperature dependence of k_{exch} in the reaction of solvent exchange of the compounds **1, 2,** and **3** (see Figure S1) gives $\Delta S^\ddagger = 26 \pm 3$ J K^{-1} mol^{-1}, $\Delta S^\ddagger = 24 \pm 4$ J K^{-1} mol^{-1}, and $\Delta S^\ddagger = 23 \pm 8$ J K^{-1} mol^{-1}, respectively (Table 2). As expected for dissociatively activated processes, the entropy of activation is positive. The differences in rates are accounted for by the

differences in the enthalpies of activation that decrease in the order $\Delta H^{\ddagger} = 93 \pm 1$ kJ mol^{-1} for compound **1**, $\Delta H^{\ddagger} = 86 \pm 2$ kJ mol^{-1} for **3**, and $\Delta H^{\ddagger} = 80 \pm 1$ kJ mol^{-1} for **2**.

A conclusion of this work is that cyclometalation does not cause a changeover of mechanism. In other words, π back-bonding from the metal to the in-plane aryl rings does not come into play. In particular, there is no appreciable change of the electrophilic character of the platinum(II) center with respect to complex **1**, at least not at the extent shown when carbon monoxide is introduced as ancillary ligand in *cis*-[PtPh$_2$(CO)-(SEt$_2$)].[12] Most importantly, it is confirmed that a ligand set of two cis σ-bonded carbon atoms and two sulfur atoms induces dissociation of one of the sulfured ligands, no matter whether the carbon atom comes from an alkyl, an aryl, or a metalated aryl ligand.

The kinetic data indicate that, contrary to initial expectations, SMe$_2$ dissociation is much easier from the cyclometalated [Pt-(bph)(SMe$_2$)$_2$] (**2**) complex than from *cis*-[PtPh$_2$(SMe$_2$)$_2$] (**1**). Because the two processes are almost isoentropic, the difference of 2 orders of magnitude in the rate of ligand dissociation is entirely attributable to the difference in the enthalpies of activation of ca. 13 kJ mol^{-1} (Table 2). The greater reactivity of **2** with respect to **1** is confirmed by the theoretical calculations which indicate a lowering of ca. 20 kJ mol^{-1} in the energy necessary for SMe$_2$ dissociation. The calculated difference in the enthalpy of activation is higher than the difference derived from the kinetics. However, the requirement that gas-phase results, despite the restrictions introduced in the theoretical model, would give a simple relationship to the liquid-phase results seems to be completely fulfilled. Perhaps significantly, the easier dissociation of SMe$_2$ is implicit in the slightly longer (hence weaker) Pt−S bonds in **2** as indicated by the calculations (compare again in Figure 2 the different Pt−S values of 2.612 Å for **1** and 2.636 Å for compound **2**).

Additional factors have to be taken into account in comparing gas-phase and liquid-phase results. From data in Table 3 it appears that on going from the four- to three-coordinated species, there is a decrease of polarity for the cyclometalated compound **2** and an increase in polarity for **1**. As a consequence, dissociation of **1** should be favored in the liquid phase with respect to **2** and, therefore, we expect that in solution the ratio $k_{(bph)}/k_{(Ph2)} = 3060$ should decrease to approach that derived from the experimental exchange rates $k_{(bph)}/k_{(Ph2)} = 140$. Also, the calculated HOMO−LUMO energy differences of the two compounds are in agreement with the higher lability of compound **2** with respect to **1**, if one considers that the first step of the dissociative mechanism most likely involves excitement of the substrate from the ground to the first excited state. The lower HOMO−LUMO energy difference in **2** (0.15 au) with respect to **1** (0.19 au) is consistent with the higher dissociation rate of **2**.

In comparing associative mechanisms to dissociative mechanisms, the accessibility of the metal atom in the axial position is a relevant point. The EP map in Figure 3 confirms that a significant negative potential must be overcome in order to form a five-coordinated species. Also, Lin and Hall, in their theoretical study of the trans effect in square-planar platinum(II) substitution reactions,[32] have re-marked the barrier constituted by the filled d orbitals above and below the coordination plane. We are inclined to think that in the present case the level of the electronic barrier is such to prevent the entrance of the attacking nucleophile. The lone pair of the nucleophile does not find a

Scheme 2

$k_{exch} = 0.016$ M^{-1}s^{-1}

$k_{exch} = 0.16$ M^{-1}s^{-1}

$k_{exch} = 0.08$ M^{-1}s^{-1}
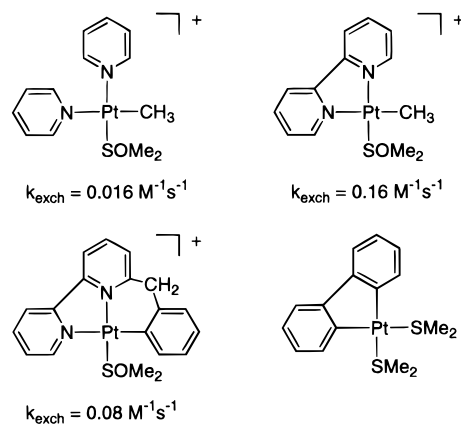
channel through which to approach the metal, and the concerted associative process of nucleophilic attack and displacement of the outgoing ligand does not come into play. A comparison of the present EP maps of **1** and **2** with those of comparable systems containing ligands other than carbanions (e.g., chloride ions)[12] provides useful evidence that in the latter systems the nucleophilic agent can still approach the metal atom through a moderately positive channel. A possible way to stabilize a five-coordinated adduct is the usage of strong π-acceptor ligands such as carbon monoxide. In *cis*-[PtPh$_2$(CO)(SEt$_2$)], the effect is not only that of a significant π back-donation which reduces the electron density at the metal, but also, p$_z$ becomes more susceptible to the nucleophilic attack as it mixes with the CO π^* level (the LUMO is delocalized over the Pt, C, and O atoms and is lowered in energy).[12] In the present case we have enough evidence to show that the ancillary ligands, which are potentially electron-withdrawing through their delocalized π system, have little relevance. Under these circumstances, dissociation becomes the energetically preferred pathway for substitution. The complete loss of the leaving group with its lone pair produces a three-coordinated intermediate in which the total concentration of charge density around the platinum atom (Figure 3) is largely decreased. Strong σ-donation from the carbanions confers sufficient thermodynamic stability to the T-shaped molecule.

The results of this work seem to suggest that the process of relief of electron density from the metal through π-bonding by ancillary ligands and the creation of a positive area around the metal atom are crucial in favoring the approach of the lone pair of a nucleophile to the metal. The different response of ligands to such a requirement is exemplified by the pattern of behavior of the complexes shown in Scheme 2. A planar di-imine, such as 2,2′-bipyridyl, exerts a considerable labilizing effect when compared to single pyridines or to saturated nitrogen donors such as ethylenediamine, so that the rate of sulfoxide exchange in the complex cation [Pt(bpy)(CH$_3$)(Me$_2$SO)]$^+$ is 10-fold faster than in [Pt(py)$_2$(CH$_3$)(Me$_2$SO)]$^+$ and 4 orders of magnitude faster than in [Pt(en)(CH$_3$)(Me$_2$SO)]$^+$.[33] Second-order kinetics and negative entropies of activation indicate an associative mechanism. Factors of primary importance in controlling the reactivity and the mode of activation are the presence of an extensive π system on the chelating ligand N−N and the ease with which this π system interacts with nonbonding d electrons of the metal. The introduction of a cyclometalated in-plane aryl ring, separated from the bpy moiety by a spacer methylene group, as for [Pt(bpy$^{\beta}$H)(Me$_2$SO)]$^+$ (bpy$^{\beta}$H = 6-(1-benzyl)-2,2′-

(32) Lin, Z.; Hall, M. B. *Inorg. Chem.* **1991**, *30*, 646.

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

bipyridyl), has little effect on the reactivity, and the mode of activation remains associative.[34] In contrast, compound **2**, which contains two strong σ-donor carbon atoms coordinated to the metal in the planar Pt(bph) moiety, reacts with a dissociative mechanism. HOMO, LUMO, and two virtual MO (UMO) of compound **1** and **2** are reported in Supporting Information Figures S2 and S3. It can be seen that HOMO and LUMO are not pure orbitals, i.e., they are orbitals mixing atomic orbitals of the metal with π orbitals of the rings. Pure π^* of rings, suitable for π back-bonding, are present only for **1**, at rather high energy. This is a further indication that back-donation from filled d orbitals of the metal to empty antibonding orbitals of the cylometalated ligand is somehow prevented, and it is not effective in removing the excess of electron density brought about at the metal through the σ-bonding framework.

Conclusions

Complexes containing ligands with the same array of donor atoms *cis*-[Pt(C,C)(S,S)] around the metal but different potential π-bonding properties undergo substitution of one sulfur ligand through the same dissociative mechanism. The lability of the compounds is dominated by the Pt—S bond strength. Contrary to previous claims for specific roles of the cyclometalation and of the in-plane disposition of single aryl ligands in increasing the electrophilicity of the platinum atom through π-back-bonding, there is a clear demonstration that this is not the case. Thus, the associative mode of activation for substitution reactions is not favored. Most significantly, the complexes [Pt-(bph)(SR$_2$)$_2$], which combine cyclometalation and a favorable in-plane disposition of the aryl groups, show reaction trends which differ substantially from those of other species carrying ligands such as CO or chelating di-imines. The crossing of the negative electrostatic potential which surrounds the 16-electron

square-planar substrate by the nucleophile seems to be a prerequisite to starting the associative mode of activation. When the lone pair of the entering ligand does not find a positive electrostatic channel to pursue, dissociation takes over as an energetically favored reaction pathway. Factors which concur in promoting dissociation are as follows: (i) bond weakening at the leaving group due to the trans influence of strong σ-donors (in the present cases, the organic carbanions which form a strong Pt—C σ-bond), and (ii) the stabilization by the remaining set of three in-plane ligands of a three-coordinated 14-electron intermediate without changing the singlet ground state. These favorable factors do not apply in the presence of other carbon σ-donors, such as CO, which exhibit major π-acceptor capabilities. By relieving the excess of electron density at the metal they not only destabilize the 14-electron three-coordinated intermediate but facilitate the addition of the axially incoming nucleophile. Evidently, the cyclometalated 2,2′-biphenyl dianion either does not possess, or cannot exert, a similar behavior despite its presumed π-acceptor capabilities.

Supporting Information Available: Figures S1, S2, and S3 reporting Eyring plots for ligand exchange reactions, HOMO, LUMO, and two virtual MO (UMO) of compounds **1** and **2**, respectively; Tables S1 and S2 giving pseudo-first-order rate constants (k_{obsd}/s^{-1}) for nucleophilic substitution on compounds **2** and **3**, respectively; Tables S3, S4, and S5 reporting the temperature and the ligand concentration dependence of the rates of ligand exchange (k_{exch}/s^{-1}) for compounds **1**, **2**, and **3**, respectively. This material is available free of charge via the Internet at http://pubs.acs.org.

(34) Romeo, R., et al. manuscript in preparation, 2000.

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