Role of Cyclometalation in Controlling the Rates of Ligand Substitution at Platinum(II) Complexes

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The rates of chloride for triphenylphosphine substitution have been measured in dichloromethane for a series of cyclometalated [Pt(N−N−C)Cl] complexes containing a number of terdentate N−N−C anionic ligands, derived from deprotonated alkyl-, phenyl-, and benzyl-6-substituted 2,2′-bipyridines. These rates have been compared with those of the corresponding [Pt(N−N)(C)Cl] (N−N = 2,2′-bipyridine; C = CH_3 or C_6H_5) complexes having the same set of donor atoms but less constrained arrangements of the ligands. The reactions of the cyclometalated compounds occur as a single-stage conversion from the substrate to the ionic pair [Pt(N−N−C)(PPh_3)]Cl products. There is no evidence by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy for the formation of other Pt(II) species or of concurrent ring-opening processes. In contrast, in the monoalkyl- or monoaryl-2,2′-bipyridine complexes, chloride substitution is followed by subsequent slower processes which involve the detachment of one arm of the chelated 2,2′-bipyridine, fast *cis* to *trans* isomerization of the *cis*-[Pt(PPh_3)$_2$(η^1-bipy)(R)]$^+$ transient intermediate, and, eventually, the release of free bipy, yielding *trans*-[Pt(PPh_3)$_2$(R)Cl] (R = Me or Ph). All reactions are first-order with respect to complex and phosphine concentration, obeying the simple rate law $k_{obsd} = k_2[PPh_3]$. The values of the second-order rate constant k_2 do not seem particularly sensitive to the nature of the bonded organic moiety (alkyl or aryl), to its structure (cyclometalated or not), to the size of the ring, or to the number of alkyl substituents on it. The effects are those foreseen on the basis of an associative mode of activation. The only exception to this pattern of behavior is constituted by the complex [Pt(bipy$^\phi$-H)Cl] (bipy$^\phi$ = 6-phenyl-2,2′-bipyridine), which features a significant rate enhancement with respect to the analogue [Pt(bipy)(Ph)Cl] complex. The results of this work, together with those of a previous paper, suggest that there is not a specific role of cyclometalation in controlling the reactivity, unless an in-plane aryl ring becomes part of the π-acceptor system of the chelated 2,2′-bipyridine, behaving as a cyclometalated analogue of the nitrogen terdentate 2,2′:6′,2″-terpyridine.

Introduction

Kinetic studies of substitution reactions on square planar platinum(II) complexes have shown that the lability of these compounds can be nicely tuned through changes in the electronic or steric properties of the ancillary ligands. Ligands such as carbon monoxide,[1] α,α′-diimines,[2,3] and 2,2′:6′,2″-terpyridine[4] can favor the addition of a fifth ligand and the stabilization of a five-coordinate transition state through electron back-donation from filled d orbitals of the metal to empty π*-orbitals of the ligand. Carbon σ-donor ligands (e.g., alkyl or aryl groups)[5] can enhance the lability of a *trans*-positioned X group (kinetic *trans* effect)[6] in a rather different way, through a strong electron σ-donation along the C−Pt−X bond axis. Generally, changes of lability do not imply changes in the mode of activation, which remains associative in nature. The introduction of a carbon−metal bond is not a sufficient condition to promote dissociative pathways. On the contrary, if the organic moiety possesses π-acceptor properties, the lability can be very high with an associative mechanism, as in the case of solvent exchange in the cationic complex [Pt(CH_3CN)$_4$]$^{2+}$ [7] or olefin exchange at chloro ethene complexes.[8] In this respect it is worth mentioning that the presence of olefins as ligands is fundamental for the isolation of stable five-coordinate platinum(II) complexes.[9] Therefore, if the control of the reactivity of Pt(II) complexes can be achieved rather easily, tuning steric or electronic

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properties of the ligands, the promotion of dissociative pathways is still a very difficult task. We are currently investigating the reasons which induce a changeover in the mechanism of substitution. So far, the only well-documented examples of dissociative ligand exchange and substitution refer to the reactions of complexes of the type *cis*-[PtR_2S_2] (R= Me or Ph; S = thioethers or Me_2SO).[1,10] Recently we extended these studies to the complexes [Pt(bph)(SR_2)$_2$], where the 2,2′-biphenyl dianion (bph^{2-}), a cyclometalating analogue of 2,2′-bipyridine, combines cyclometalation and a favorable in-plane disposition of the aryl rings.[11] Contrary to expectation, kinetic and theoretical results indicated that thioether dissociation is much easier than in the diaryl analogue *cis*-[$PtPh_2(SR_2)_2$]. Electron back-donation from filled d orbitals of the metal to empty π*-orbitals of the in-plane cyclometalated rings is weak or absent and is not operative in promoting an associative mode of activation. These results are quite surprising in view of the structural similarity between platinum(II) complexes containing cyclometalating and polypyridine ligands, especially as far as photochemical and photophysical properties are concerned,[12] and strongly suggest investigating in detail the role of cyclometalation in controlling the reactivity. Systematic studies of the substitution ligand lability of these compounds are quite few[13,14] and have led to different interpretations. In particular, an important question is whether the considerable acceleration in rate observed for the substitution of the aqua ligand in the complexes [Pt(N−C)(N)(H_2O)] (N−CH = *N*,*N*-dimethylbenzylamine, N = $pySO_3$-3)[14a,b] and [Pt(N−C−N)(H_2O)]$^{+}$ [14c] (N−CH−N = 2,6-bis((dimethylamino)methyl)phenyl) stems from a significant contribution of back-donation into the empty π*-orbitals of the in-plane aryl ligand or if it is simply the result of the well-known strong *trans*-labilizing effect of the Pt−C bond.[15]

In this paper we have carried out kinetic studies on cyclometalated compounds of the type [Pt(N−N−C)Cl], containing a number of terdentate N−N−C anionic ligands derived from deprotonated alkyl-, phenyl-, or benzyl-6-substituted 2,2′-bipyridines of different structural properties. The aim of this work is to investigate the sensitivity of the rate of chloride for phosphine substitution to the nature of the organic bonded moiety (alkyl or aryl), its size, its orientation with respect to the coordination plane, and the number and position of alkyl substituents on the ring. The lability of the chloride in the cyclometalated complexes does not differ markedly from that measured for [Pt(N−N)(C)Cl] (N−N = 2,2′-bipyridine; C = Me or Ph) complexes having the same set of donor atoms but less constrained arrangements of the ligands. The results of this study, together with those of a previous investigation,[11] would suggest that there is not a specific role of cyclometalation in controlling the substitution lability.

Experimental Section

General Procedures. All solvents were purchased from Aldrich Chemical Co. The solvents employed in the synthetic procedures were distilled before use over appropriated drying agents under an oxygen-free nitrogen atmosphere. Spectrophotometric grade dichloromethane, used in the kinetic runs, was freshly distilled and degassed by several freezing−pumping cycles and stored in Schlenk tubes. Methanol was distilled from magnesium methoxide. Chloroform-*d* (99.8+%) and methanol-d_4 (99.8+%) were used as received. All the other reagents were the highest purity grade commercially available and were used without further purification. All manipulations in the synthesis of the complexes were carried out under a dry oxygen-free N_2 atmosphere using standard Schlenk-line techniques.

Synthesis of Complexes. [Pt(terpy)Cl]Cl was prepared according to the method reported by Lippard et al.[16] The alkyl- and aryl-2,2′-bipyridine complexes [Pt(bipy)(R)(Cl)] (R = methyl (**1**)[17] and phenyl (**4**)) were prepared following a previously described general method[18] which affords easily and in a quantitative yield compounds of the type [Pt(N−N)(R)Cl] containing nitrogen ligands.

[Pt(bipy)(Me)(Cl)] (1). The complex *trans*-[$Pt(Me_2SO)_2$(Me)Cl] was prepared according to Eaborn et al.[19] and purified by several crystallizations from dichloromethane/diethyl ether mixtures. A sample of this complex (0.05 g, 0.125 mmol) was dissolved in the minimum amount of CH_2Cl_2 (10 mL) and reacted under stirring with a solution of bipy (0.021 g, 0.133 mmol) in dichloromethane (5 mL). After a few hours, most of the solvent was evaporated under vacuum and the solution added with diethyl ether (1/1, v/v) and cooled at −35 °C, to afford the pure yellow solid in greater than 90% yield. ^{1}H NMR ($CDCl_3$): δ 9.64 (d, $^3J_{PtH}$ = 16.2 Hz, $^3J_{HH}$ = 5.9 Hz, 1H, $H_{6'}$); 9.22 (d, $^3J_{PtH}$ = 59.6 Hz, $^3J_{HH}$ = 5.8 Hz, 1H, H_6); 8.17 (ddd, $^3J_{av}$ = 8.0 Hz, $^4J_{HH}$ = 1.5 Hz, 1H, H_4); 8.11 (ddd, $^3J_{av}$ = 8.0 Hz, $^4J_{HH}$ = 1.5 Hz, 1H, $H_{4'}$); 8.02 (m, 2H, H_3+ $H_{3'}$); 7.64 (ddd, $^3J_{HH}$ = 5.9, 7.4 Hz, $^4J_{HH}$ = 1.5 Hz, 1H, $H_{5'}$); 7.47 (ddd, $^3J_{HH}$ = 5.9, 7.4 Hz, $^4J_{HH}$ = 1.5 Hz, 1H, H_5); 1.22 (s, $^2J_{PtH}$ = 77.9 Hz, 3H, CH_3Pt).

[Pt(bipy)(Ph)(Cl)] (4). The complex was obtained from the reaction of 2,2′-bipyridine with *trans*-[Pt(Ph)(Cl)($Me_2SO)_2$][19] following the same procedure described above. ^{1}H NMR ($CDCl_3$): δ 9.68 (d, $^3J_{PtH}$ = 12.9 Hz, $^3J_{HH}$ = 5.2 Hz, 1H, $H_{6'}$); 8.72 (d, $^3J_{PtH}$ = 59.1 Hz, $^3J_{HH}$ = 5.8 Hz, 1H, H_6); 8.13 (m, 2H, $H_{4'}$ + H_4); 8.07 (dd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.4 Hz, 1H, $H_{3'}$); 8.02 (dd, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 1.1 Hz, 1H, H_3); 7.69 (ddd, $^3J_{HH}$ = 5.5, 7.4 Hz, $^4J_{HH}$ = 1.7 Hz, 1H, $H_{5'}$); 7.47 (dd, $^3J_{PtH}$ = 36.8 Hz, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.4 Hz, 2H, $H_{2'',6''}$); 7.31 (ddd, $^3J_{HH}$ = 5.8, 7.4 Hz, $^4J_{HH}$ = 1.7 Hz, 1H, H_5); 7.12 (ddd, $^3J_{av}$ = 7.4 Hz, $^4J_{HH}$ = 1.4 Hz, 2H, $H_{3'',5''}$); 6.99 (ddd, J_{av} = 7.4 Hz, $^4J_{HH}$ = 1.4 Hz, 1H, $H_{4''}$).

Cyclometalated complexes [Pt(N−N−C)Cl] [N−N−CH = 6-*tert*-butyl-2,2′-bipyridine, bipy^t (**2**);[20] 6-neopentyl-2,2′-bipyridine, bipy^n (**3**);[21] 6-phenyl-2,2′-bipyridine, bipy$^\phi$ (**5**);[22] 6-benzyl-2,2′-bipyridine, bipy$^\beta$ (**6**);[23] 6-(α-methyl)benzyl-2,2′-bipyridine, bipy$^{\alpha Me}$ (**7**);[24] and 6-(α,α-

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dimethyl)benzyl-2,2′-bipyridine, bipy^c (**9**)][23] were prepared following published methods. The purity and identity of the complexes were checked by elemental analyses and ^{1}H NMR spectroscopy.

[Pt(bipy$^{\alpha Et}$-H)Cl] (bipy$^{\alpha Et}$ = 6-(1-ethylbenzyl)-2,2′-bipyridine) (8). A 0.274 g (1 mmol) sample of racemic bipy$^{\alpha Et}$ and 3.5 mL of HCl (2 M) were added to a solution of $K_2[PtCl_4]$ (0.415 g, 1 mmol) in water (30 mL). The mixture was heated on a water bath until the solution was colorless and then cooled to afford a yellow-orange precipitate which was filtered off, washed successively with water, ethanol, and diethyl ether, and recrystallized from CH_2Cl_2/Et_2O, yield 64%, mp 273−274 °C. Anal. Calcd for $C_{19}H_{17}N_2PtCl$: C, 45.28; H, 3.4; N, 5.56. Found: C, 44.73; H, 3.55; N, 5.36. MS-FAB (*m*/*z*): 504 $[M + H]^+$. ^{1}H NMR ($CDCl_3$): δ 9.69 (d, $^3J_{PtH}$ = 15.4 Hz, $^3J_{HH}$ = 5.5 Hz, 1H, $H_{6'}$); 8.09 (d, $^3J_{PtH}$ = 48.4 Hz, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 1.6 Hz, 1H, $H_{6''}$); 8.05 (m, 1H, $H_{4'}$); 7.95 (m, 2H, $H_4 + H_{3'}$); 7.83 (d, 1H, H_3); 7.63 (dd, 1H, $H_{5'}$); 7.45 (d, 1H, H_5); 7.04 (m, 3H, $H_{4''} + H_{3''} + H_{5''}$); 3.99 (t, $^3J_{HH}$ = 7.4 Hz, 1H, C*H*−CH$_2$−); 2.44, 2.34 (m, 2H, CH−C*H*$_2$−CH$_3$); 0.803 (t, $^3J_{HH}$ = 7.4 Hz, 3H, −CH$_2$−C*H*$_3$).

The phosphine complexes [Pt(bipy)(PPh$_3$)(R)]Cl (**10**, **13**) and [Pt(N−N−C)(PPh$_3$)]Cl (**11**, **12**, **14**−**18**) were prepared in situ by reacting in an NMR tube weighted amounts of complexes **1**−**9** dissolved in $CDCl_3$ with the stoichiometric amount of PPh$_3$. A detailed collection of ^{1}H and ^{31}P{^{1}H} NMR resonances of the neutral chloride complexes **1**−**9** and of the corresponding phosphine derivatives **10**−**18** is reported as Supporting Information Table S1 together with the assignment (**10** is the corresponding PPh$_3$ complex of **1**, **11** of **2**, and so on).

[Pt(bipy)(Me$_2$SO)Me]CF$_3$SO$_3$ (19). $AgCF_3SO_3$ (0.137 g, 0.53 mmol) and the complex *trans*-[Pt(Me$_2$SO)$_2$(Me)(Cl)] (0.200 g, 0.5 mmol) were reacted in dimethyl sulfoxide (4 mL). After a few hours of stirring, AgCl was filtered off and 0.080 g of 2,2′-bipyridine was added to the solution. The yellow solution was filtered on cellulose powder to remove traces of residue AgCl, and the excess solvent was evaporated under reduced pressure (0.1 mmHg, 70 °C). The solid yellow residue was washed several times with ether, and recrystallized from a dichloromethane/ether (1/1, v/v) mixture with a yield of 80%. ^{1}H NMR ($CDCl_3$): δ 9.74 (dd, $^3J_{PtH}$ = 14.3 Hz, $^3J_{HH}$ = 6.0 Hz, $^4J_{HH}$ = 1.7 Hz, 1H, $H_{6'}$); 8.86 (dd, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 1.1 Hz, 1H, H_3); 8.83 (d, $^3J_{PtH}$ = 46.2 Hz, $^3J_{HH}$ = 5.5 Hz, 1H, H_6); 8.77 (d, $^3J_{HH}$ = 8.2 Hz, 1H, $H_{3'}$); 8.45 (ddd, $^3J_{av}$ = 8.0 Hz, $^4J_{HH}$ = 1.1 Hz, 1H, H_4); 8.34 (ddd, $^3J_{av}$ = 8.0 Hz, $^4J_{HH}$ = 1.1 Hz, 1H, $H_{4'}$); 7.80 (ddd, $^3J_{HH}$ = 5.5, 7.7 Hz, $^4J_{HH}$ = 1.7 Hz, 1H, H_5); 7.71 (ddd, $^3J_{HH}$ = 6.0, 8.2 Hz, $^4J_{HH}$ = 1.7 Hz, 1H, $H_{5'}$); 3.57 (s, $^3J_{PtH}$ = 35.7 Hz, 6H, C*H*$_3$S); 0.87 (s, $^2J_{PtH}$ = 71.5 Hz, 3H, C*H*$_3$Pt).

[Pt(bipy)(PPh$_3$)Me]CF$_3$SO$_3$ (20). Triphenylphosphine (0.049 g, 0.19 mmol) in 20 mL of dichloromethane was added dropwise to a solution of the complex **19** (0.100 g, 0.17 mmol) dissolved in CH_2Cl_2 (20 mL). Rotary-vacuum concentration, addition of ether (1/1, v/v), and cooling at −35 °C yielded a pure white solid in 90% yield. ^{1}H NMR ($CDCl_3$): δ 8.93 (d, $^3J_{PtH}$ = 37.7 Hz, 2H, $H_3 + H_6$); 0.78 (s, $^2J_{PtH}$ = 70.4 Hz, $^3J_{PH}$ = 3.3 Hz, 3H, C*H*$_3$Pt). ^{31}P{^{1}H} NMR: δ 19.7 ($^1J_{PtP}$ = 4355 Hz).

[Pt(bipy)(Me$_2$SO)(Ph)]CF$_3$SO$_3$ (21). In a fashion identical to the preparation of **19** the compound was obtained in 85% yield by reaction of bipy and *trans*-[Pt(Me$_2$SO)$_2$(Ph)(Cl)]. ^{1}H NMR ($CDCl_3$): δ 9.67 (d, $^3J_{HH}$ = 5.5 Hz, 1H, $H_{6'}$); 8.82 (m, 2H, $H_3 + H_{3'}$); 8.35 (m, 2H, $H_4 + H_{4'}$); 7.75 (dd, $^3J_{HH}$ = 5.5, 8.2 Hz, 1H, $H_{5'}$); 7.59 (dd, $^3J_{PtH}$ = 51.6 Hz, $^3J_{HH}$ = 5.5 Hz, 1H, H_6); 7.44 (d, br, $^3J_{PtH}$ = 36.2 Hz, $^3J_{HH}$ = 6.0 Hz, 2H, $H_{2'', 6''}$); 7.39 (d, $^3J_{HH}$ = 6.0, 8.2 Hz, 1H, H_5); 7.23 (m, br, 3H, $H_{3'', 5''} + H_{4''}$); 3.28 (s, $^3J_{PtH}$ = 35.7 Hz, 6H, C*H*$_3$S).

[Pt(bipy)(PPh$_3$)(Ph)]CF$_3$SO$_3$ (22). In a fashion identical to the preparation of **20** the compound was obtained by reacting stoichiometric amounts of **21** and PPh$_3$. ^{1}H NMR ($CDCl_3$): δ 7.78 (d, $^3J_{PtH}$ = 40.6 Hz, $^3J_{HH}$ = 5.5 Hz, 1H, H_6). ^{31}P{^{1}H} NMR: δ 17.1 ($^1J_{PtP}$ = 4299 Hz).

Instrumentation and Measurements. ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded on a BRUKER AMX-R 300 spectrometer equipped with a broad-band probe operating at 300.13 and 121.49 MHz, respectively. ^{1}H chemical shifts were measured relative to the residual solvent peak and are reported in δ units downfield from $SiMe_4$. ^{31}P{^{1}H} chemical shifts, in parts per million, are given relative to external phosphoric acid. The temperature within the probe was checked using the methanol or ethylene glycol method.[25] The resonances were assigned by performing selective decoupling experiments of the signals. Stopped-flow kinetic runs were recorded on an HP8452A spectrophotometer equipped with a Hi-Tech SFA-20 Rapid Kinetic Accessory; for $t_{1/2}$ < 5 s an Applied Photophysics Bio Sequential SX-17 MX stopped-flow ASVD spectrophotometer was used.

Kinetics. The chloride for phosphine substitution reactions were followed by stopped-flow spectrophotometry under pseudo-first-order conditions. Initial concentrations of starting complex were in the range 0.05−0.1 mM, and pseudo-first-order conditions were achieved by having the ligand in at least 10-fold excess. Rate constants were evaluated with the SCIENTIST software package[26] by fitting the absorbance/time data to the exponential function $A_t = A_{00} + (A_0 - A_{00}) \exp(-k_{obsd}\, t)$. Rate constants are reported as average values from five to seven kinetic runs.

Results

We have already reported the use of the complex *trans*-[Pt(Me$_2$SO)$_2$(Me)Cl] as a useful synthon to introduce the moieties {PtMe} and {PtMeCl}.[18] The method was applied successfully to the formation of the cationic complexes [Pt(N−N−N)(Me)]Cl (N−N−N = 2,2′:6′,2″-terpyridine and 1,5-diamino-3-azapentane (dien))[27] and [Pt(N−N)(Me$_2$SO) (Me)]PF$_6$ (N−N = a wide series of diamines and diimines),[3] to the synthesis of *cis*-(Me,am) and *trans*-(Me,am) [Pt(Me$_2$SO)(am)(Me)Cl] (am = monodentate nitrogen ligands),[28] and as a new route to [Pt(1,10-phenanthroline)(Me)Cl].[18] The complex [Pt(Me$_2$SO)$_2$(Ph)Cl] behaves likewise.[29] Thus, the addition of the equimolar amount of 2,2′-bipyridine to a dichloromethane solution of [Pt(Me$_2$SO)$_2$(Me)Cl] led to the rapid substitution of both sulfoxide ligands, yielding compound **1** in a pure crystalline form and in an almost quantitative yield. In a similar fashion compound **4** was formed starting from [Pt(Me$_2$SO)$_2$(Ph)Cl], prepared according to ref 19. When the reaction is carried out in dimethyl sulfoxide as the solvent and in the presence of a silver salt ($AgCF_3SO_3$), the sulfoxide-containing compounds [Pt(bipy)(Me$_2$SO)(R)]CF_3SO_3 (R = Me or Ph) are obtained in high yield (ca. 80%).

The synthesis and the spectroscopic properties of cyclometalated platinum(II) [Pt(N−N−C)Cl] complexes, containing 6-alkyl-2,2′-bipyridine (**2**, **3**),[20,21] 6-benzyl-2,2′-bipyridine (**6**, **7**, **9**),[23,24] and 6-phenyl-2,2′-bipyridine (**5**) ligands,[22] have been described in detail elsewhere. Compound **8**, where N−N−C is the deprotonated form of 6-(α-ethyl)benzyl-2,2′-bipyridine, is new and was prepared as reported in the Experimental Section.

NMR Measurements. The most evident feature in the ^{1}H NMR spectra of [Pt(bipy)(R)Cl] compounds (Table 1) is the signal of the $H_{6'}$ proton of the pyridine ring in a position *trans* to the carbon atom (at about δ 9.6 ppm, $^3J_{PtH}$ = 16.2 and 12.9 Hz for **1** and **4**, respectively) which can be distinguished from that of the H_6 proton *trans* to chloride ($^3J_{PtH}$ = 59.6 and 59.1 Hz for **1** and **4**, respectively) on the basis of the magnitude observed for the $^3J_{PtH}$ coupling constant. On substituting the

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Table 1. Relevant Proton and $^{31}P\{^1H\}$ NMR Data[a]

compd no.	CH_3	CH_2	CH	H_6	$H_{6'}$	$H_{6''}$	^{31}P
1	1.22 (77.9)			9.22 (59.6)	9.64 (16.2)		
10	0.76 (70.3)			8.90 (35.5)	7.58		19.8 [4346]
2	1.46 (10.4)	2.86 (84.4)			9.25 (14.3)		
11	1.34	2.13 (68.2)			7.51		20.6 [4078]
3	1.11	2.45 (87.4)			9.60 (13.2)		
		2.84					
12	0.86	1.59 (65.4)			7.59 (13.2)		22.6 [4444]
		2.90					
4				8.72 (59.1)	9.68 (12.9)	7.47 (36.8)	
13				7.76 (39.9)	7.00	7.03 (45.1)	17.2 [4288]
5					9.07 (12.6)	7.75 (44.0)	
14					6.45 (13.1)	6.40 (53.3)	25.8 [4098]*b*
6		4.35 (9.3)			9.63 (14.8)	8.07 (41.8)	
15		4.38 (8.8)			7.64	6.77 (55.0)	20.4 [4374]
7	1.87		4.39		9.71 (15.4)	8.11 (46.2)	
16	2.07		4.44		7.66	6.87 (58.2)	20.6 [4408]
8	0.803	2.44, 2.34	3.99		9.69 (15.4)	8.09 (48.4)	
17	0.847	2.72, 2.37	4.05		7.70	6.92 (57.2)	20.0 [4417]
9	2.16				9.70 (15.4)		
18	2.24				7.65	6.93 (54.9)	21.1 [4453]

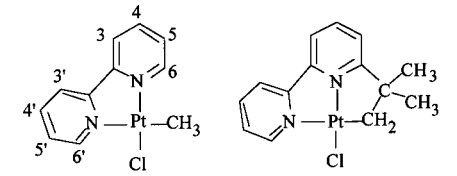
[a] Chemical shifts in parts per million from internal $SiMe_4$ and external H_3PO_4, room temperature, coupling constants in hertz; J_{PtH} in parentheses, J_{PtP} in square brackets, $CDCl_3$ as solvent. The assignment follows the numeration pattern shown in Chart 1. [b] At 273 K.

chloride ion with PPh_3, as for compounds **10** and **13**, the signal of the $H_{6'}$ proton experiences a marked upfield shift (e.g., δ = 7.58 ppm, **10**; 7.00 ppm, **13**) due to the anisotropic shielding by the adjacent aromatic rings.

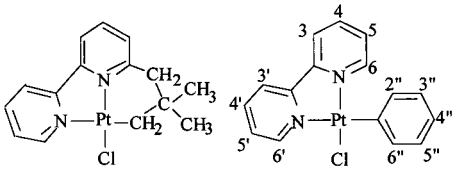
The ^1H NMR spectra of the cyclometalated compounds are in agreement with the formulation proposed in Chart 1. The complexes are characterized by the presence of [5,6]- or [5,5]-ring systems, arising from the coordination of the metal to the two nitrogen atoms and to a linking methyl or *o*-phenyl carbon. As for compounds **1** and **4**, the average value of the ^1H NMR signal of the $H_{6'}$ proton (Table 1) is found at $\delta = 9.52 \pm 0.2$ ppm with a coupling to the ^{195}Pt nucleus $^3J_{PtH} = 14.4 \pm 1$ Hz and moves to higher frequencies ($\delta = 7.46 \pm 0.5$ ppm) as a result of the substitution of the chloride ion with triphenylphosphine. The six-membered cyclometalated rings derived from the 6-benzyl-2,2′-bipyridine ligands adopt a boat conformation in the solid state,[30−32] but in solution, at room temperature, they exhibit a fluxional motion between two boatlike conformations as shown by the equivalence of the two protons of the methylene group in compounds **6** and **15** and of the two methyl groups in compounds **9** and **18**. The ^1H NMR spectra of the complexes [Pt(bipy$^{\alpha Et}$)Cl] (**8**) and [Pt(bipy$^{\alpha Et}$)(PPh_3)]Cl (**17**) are of interest in that two resonances are observed for the diastereotopic methylene protons of the ethyl substituent, due to the presence of the chiral α carbon.

The $^{31}P\{^1H\}$ NMR spectra of the cationic phosphine [Pt(N−N−C)(PPh_3)]Cl derivatives show a singlet signal with an average value centered at $\delta = 20.9 \pm 2$ ppm. The values of the $^1J_{PtP}$ coupling constants are in a range typical for a phosphorus atom *trans* to a pyridine nitrogen donor atom,[33] and setting apart the rogue values for complexes **11** and **14**, they encompass a range of 165 Hz with $^1J_{PtP} = 4390 \pm 60$ Hz. The large deviations from this value for compound **11** ($^1J_{PtP} = 4078$ Hz) and for compound **14** ($^1J_{PtP} = 4098$ Hz) could be associated with stereoelectronic effects arising from the smaller five-

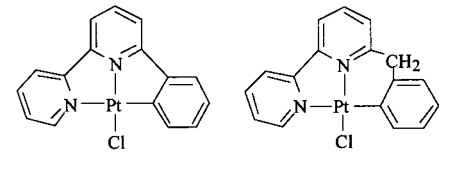
Chart 1. Structural Formulas of the Complexes



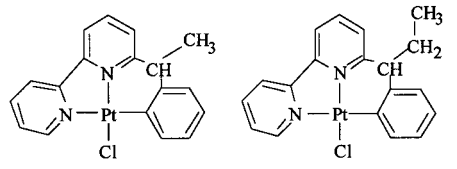
[**1**] [Pt(bipy)MeCl] [**2**] [Pt(bipy^t-H)Cl]



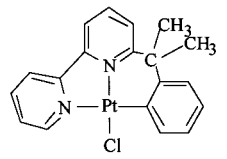
[**3**] [Pt(bipy^n-H)Cl] [**4**] [Pt(bipy)(Ph)Cl]



[**5**] [Pt(bipy$^\phi$-H)Cl] [**6**] [Pt(bipy$^\beta$-H)Cl]



[**7**] [Pt(bipy$^{\alpha Me}$-H)Cl] [**8**] [Pt(bipy$^{\alpha Et}$-H)Cl]



[**9**] [Pt(bipy^c-H)Cl]

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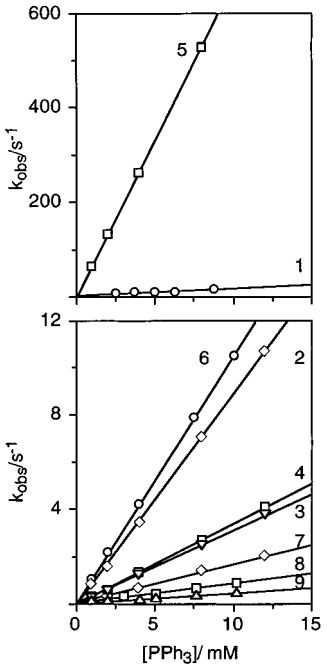

Figure 1. Dependence of the pseudo-first-order rate constants (k_{obsd}) on phosphine concentration for the chloride substitution from cyclometalated [Pt(N−N−C)Cl] and uncyclometalated [Pt(N−N)(C)Cl] complexes (in dichloromethane, at 298.2 K). Numbers refer to the compounds as listed in Chart 1.

membered cyclometalated rings, but this hypothesis deserves confirmation.

Substitution Reactions. The substitution of chloride for triphenylphosphine from the cyclometalated complexes [Pt(N−N−C)Cl] (N−N−CH = bipy^t (**2**), bipy^n (**3**), bipy$^\phi$ (**5**), bipy$^\beta$ (**6**); bipy$^{\alpha Me}$ (**7**), bipy$^{\alpha Et}$ (**8**), bipy^c (**9**)) takes place in a single step according to the reaction

$$[Pt(N-N-C)Cl] + PPh_3 \rightarrow [Pt(N-N-C)(PPh_3)]Cl \quad (1)$$

The fused [5,5]- and [5,6]-ring systems are robust, and there is no evidence of ring opening or of other concurrent processes. The ^{1}H and the ^{31}P{^{1}H} NMR spectra taken after completion of the reactions showed that the process under study was indeed the simple replacement of chloride with a phosphine.

The spectral changes of reaction 1 occur in the near-visible region between 500 and 320 nm and are associated mainly with the disappearance of the starting complex. The systematic kinetics of these reactions were studied at different ligand concentrations and required the use of stopped-flow techniques. At the concentrations of phosphine used, the reactions went to completion and excellent fits were obtained from the regression analysis of the absorbance vs time data. The dependence of the pseudo-first-order rate constants (Table S2, in the Supporting Information) is described by a family of straight lines (Figure 1) and obeys eq 2.

$$k_{obs} = k_1 + k_2[PPh_3] \quad (2)$$

The contribution of the reagent-independent term k_1 is negligible (k_1 refers to a solvolytic path, and k_2 is the second-order rate constant for the bimolecular attack of PPh_3 on the substrate). The absence of a k_1 term indicates that the poor nucleophile dichloromethane, as expected, cannot provide a solvolytic pathway to the products, but also proves the absence of a possible parallel dissociative pathway. The values of k_2, from linear regression analysis of the dependence of k_{obs} on [PPh_3], are listed in Table 2, together with their standard deviations.

Table 2. Second-Order Rate Constants of Chloride for Triphenylphosphine Substitution on Cyclometalated [Pt(N−N−C)Cl] (**2**, **3**, **5**−**9**) and Uncyclometalated [Pt(N−N)(C)Cl] (**1**, **4**) Complexes[a]

complex	k_2, M^{-1} s^{-1}	complex	k_2, M^{-1} s^{-1}	complex	k_2, M^{-1} s^{-1}
1	1854 ± 37	**4**	343 ± 3	**7**	166 ± 1
2	903 ± 18	**5**	65610 ± 267	**8**	85 ± 2
3	311 ± 5	**6**	1046 ± 6	**9**	45.5 ± 0.9

[a] By spectrophotometric kinetic runs carried out in dichloromethane at T = 298.16 K.

Ring-Opening Reactions. Under the same experimental conditions adopted for the cyclometalated complexes, the compounds **1**, **4**, and [Pt(terpy)Cl], after the first fast chloride for phosphine substitution, undergo dechelation in a series of subsequent slower steps. In fact, the addition of a slight excess of phosphine to **1** leads to the formation of *trans*-[Pt(PPh_3)$_2$(Me)Cl][34] and free 2,2′-bipyridine. Similar results were obtained for the phenyl derivative **4**, with formation of *trans*-[Pt(PPh_3)$_2$(Ph)Cl].[35] To shed some light on the sequence of dechelation steps on the cationic complex, avoiding any possible interference by chloride ion, we synthesized compounds **20** and **22** containing the weakly coordinating $CF_3SO_3^-$ counteranion. Addition of the stoichiometric amount of phosphine to **20** in $CDCl_3$ at 220 K led to the formation of *trans*-[Pt(PPh_3)$_2$(η^1-bipy)(Me)]CF_3SO_3.[36] On adding further small amounts of phosphine, the monodentate nitrogen ligand was easily displaced, yielding [Pt(PPh_3)$_3$(Me)]CF_3SO_3 (^{1}H NMR: δ 0.30 (m, $^2J_{PtH}$ = 56.0 Hz, 3H, CH_3Pt). ^{31}P{^{1}H} NMR: δ 29.1 ($^1J_{PtP}$ = 2929 Hz); 20.8 ($^1J_{PtP}$ = 1915 Hz; $^2J_{PP}$ = 20 Hz)). Any attempt to reveal the presence of the transient *cis*-[Pt(PPh_3)$_2$(η^1-bipy)(Me)]CF_3SO_3 complex, containing 2,2′-bipyridine bound in an η^1-mode, was unsuccessful. This is probably due to the fact that its conversion into the most thermodynamically stable *trans* isomer is very fast. The mechanism of geometrical isomerization of organometallic diphosphine complexes of the type [Pt(PEt_3)$_2$(Me)X] (X = halide ion) has been studied in great detail and proved to be dissociative in nature in protic solvents.[37] However, these species are relatively stable in nonpolar solvents as well as their cationic [Pt(PEt_3)$_2$(Me)(am)]X derivatives. Most likely, the fast geometrical conversion of the transient *cis*-[Pt(PPh_3)$_2$(η^1-bipy)(Me)]$^+$ could be associated with a fast exchange between the free and the bound ends of the nitrogen chelating ligand. This hypothesis is currently checked in our laboratory. On reacting [Pt(bipy)(Me_2SO)(Me)]CF_3SO_3 (**19**) with a chelating phosphine (1,2-diphosphinoethane, dppe), it is possible to isolate easily the [Pt(dppe)(η^1-bipy)(Me)]CF_3SO_3 complex, a stable chelated analogue of the transient bisphosphine intermediate. Its NMR spectrum features the proton pattern of bound η^1-2,2′-bipyridine and of the methyl group and two ^{31}P resonances at δ 36.3 ($^1J_{PtPa}$ = 4078 Hz) and 49.4 ($^1J_{PtPb}$ = 1838 Hz; P_a, phosphorus atom

(34) ^{1}H NMR ($CDCl_3$): δ 7.73 (m, 12H, $H_{o,o'}$(P)); 7.41 (m, br, 12H, $H_{m,m'}$(P)); 7.39 (m, br, 6H, H_p(P)); −0.08 (m, $^2J_{PtH}$ = 78.6 Hz, 3H, CH_3-Pt). ^{31}P{^{1}H} NMR: δ 29.8 ($^1J_{PtP}$ = 3150 Hz).

(35) ^{1}H NMR ($CDCl_3$): δ 7.53 (d, $^3J_{HH}$ = 6.2 Hz, 12H, $H_{o,o'}$(P)); 7.34 (m, $^3J_{av}$ = 6.9 Hz, 6H, H_p(P)); 7.25 (m, $^3J_{av}$ = 6.9 Hz, 12H, $H_{m,m'}$(P)); 6.67 (d, $^3J_{PtH}$ = 55.0 Hz, $^3J_{HH}$ = 7.4 Hz, 2H, $H_{2'',6''}$); 6.29 (dd, $^3J_{av}$ = 8.0 Hz, 1H, $H_{4''}$); 6.12 (dd, $^3J_{av}$ = 7.6 Hz, 2H, $H_{3'',5''}$). ^{31}P{^{1}H} NMR: δ 25.0 ($^1J_{PtP}$ = 3151 Hz).

(36) ^{1}H NMR ($CDCl_3$): δ 8.39 (s, br, 2H); 7.72 (s, br, 2H); 7.50−7.15 (m, br, 32H); 7.08 (s, br, 2H); 0.17 (s, br, $^2J_{PtH}$ = 68.4 Hz, 3H, CH_3-Pt).^{31}P{^{1}H} NMR: δ 27.0 ($^1J_{PtP}$ = 3209 Hz).

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trans to the pyridyl nitrogen; P_b, phosphorus atom *trans* to the methyl group).

The same procedure of a stepwise addition of phosphine applied to [Pt(terpy)Cl]Cl in $CDCl_3/CD_3OD$ (1/4, v/v) revealed the presence of only one relatively stable open-ring species in solution, [Pt(η^2-terpy)(PPh_3)$_2$]Cl_2 ($^{31}P\{^1H\}$ NMR: δ 18.8 ($^1J_{PtPa}$ = 3701 Hz), 7.30 ($^1J_{PtPb}$ = 3286 Hz; $^2J_{PP}$ = 19 Hz)), in agreement with other cases in which terpy coordinates in a bidentate fashion.[38,39] Complete dechelation yields [Pt(PPh_3)$_3$-Cl]Cl ($^{31}P\{^1H\}$ NMR: δ 27.3 (d, $^1J_{PtP}$ = 2450 Hz), 16.8 (t, $^1J_{PtP}$ = 3643 Hz; $^2J_{PP}$ = 19 Hz)) and free terpyridine ligand.

Discussion

In keeping with the usual pattern of behavior for square planar platinum(II) complexes,[40] the chloride for phosphine substitution from cyclometalated [Pt(N−N−C)Cl] complexes takes place with an associative mode of activation. The process is entirely dominated by the direct attack of the nucleophile on the substrate, and the values of the second-order rate constants k_2, collected in Table 2, offer an interesting structure−reactivity relationship. Before this set of rate data is examined in detail, it is of interest to focus on some attractive features emerging from the comparison between the behavior exhibited by the cyclometalated compounds and that of the other compounds investigated. Interestingly, upon nucleophilic attack, the terdentate N−N−C donor skeleton remains firmly bound to the metal center and the chloride ion is the only labile group undergoing substitution. Thus, the fused [5,5]- and [5,6]-ring systems formed by the cyclometalated N−N−C ligands are better stabilizing than the [5,5] N−N−N ring system formed by the terdentate terpy ligand. The latter, as described above, is easily removed from the metal in a series of consecutive substitution steps. We can exclude, however, that the anionic character of the N−N−C must be held responsible for its stability because the strictly similar set of (N−N)(C) ligands, in which the donor carbon atom is not contained in an intramolecular coordination system, is by far less stable. In fact, in compounds **1** and **4**, chloride substitution by phosphine is followed by subsequent substitution steps which involve the detachment of one arm of 2,2′-bipyridine, fast geometrical *cis* to *trans* isomerization of the transient species in which the bidentate ligand is coordinated in a monodentate fashion, and, eventually, the complete removal of the chelating nitrogen ligand. Since the carbon atom of [Pt(N−N−C)Cl] (as well as that of [Pt(N−N)(C)Cl]) is hardly removed from the coordination sphere upon nucleophilic attack, it puts an anchoring effect into action which avoids the detachment of the bipyridine molecular fragment.

The cation [Pt(terpy)Cl]$^+$ is characterized by extensive planarity and π-acceptor properties of the terdentate nitrogen ligand. We find that the rate of chloride substitution by PPh_3 in dichloromethane is too fast to be followed, even with stopped-flow techniques ($k_2 \geq 10^5$ M^{-1} s^{-1}). The extreme lability of the chloride in this complex is not surprising, since previous kinetic studies with nucleophiles weaker than PPh_3, in methanol, showed a rate enhancement of 5-6 orders of magnitude with respect to the complex containing 1,5-diamino-3-azapentane (dien) as chelating ligand.[4a] The origin of this rate enhancement lies in the noticeable π-acceptor capability of the terpy ligand. By relieving the excess of electron density at the metal, the polypyridine facilitates the addition of the incoming nucleophile and the stabilization of a 18-electron five-coordinate transition state. A marked increase of reactivity was observed also on going from an a diamine to an α,α′-diimine,[3] and it again reflects the increase of electrophilicity of the reaction center as the ability to transfer electron density to the ancillary ligands increases. Following this reasoning, the decreased reactivity of the [Pt-(N−N−C)Cl] complexes with respect to [Pt(N−N−N)Cl]$^+$ (N−N−N = terpy), except for [Pt(bipy$^\phi$-H)Cl] as we will see below, is a combined effect of a partial loss of aromaticity of the terdentate ligand, due to the formation of a cyclometalated ring, and of a specific *cis* effect of the carbon atom. Electron donation by the strong σ-donor carbon group can favor a sufficient accumulation of electron density at the metal to compensate the π-electron withdrawal by the bipyridyl moiety.

Factors of primary importance in controlling the reactivity and the mode of activation of complexes containing a planar α,α′-diimine, such as 2,2′-bipyridine, are the presence of an extensive π-system on the chelating ligand and the ease with which this π-system interacts with the nonbonding d electrons of the metal. The sequence of rate data in Table 2 strongly suggests that the introduction of a cyclometalated ring has little effect on these factors and on the reactivity. Setting apart the case of [Pt(bipy$^\phi$-H)Cl], the lability of the chloride appears to be affected very little by changes in the nature and in the structural properties of the coordinated N−N−C or (N−N)(C) ligands, the difference of reactivity between the first and the last members of the series in Table 2 being less than 2 orders of magnitude (for complexes **1** and **9** the values of k_2 are 1850 and 45 M^{-1} s^{-1}, respectively).

On going from [Pt(bipy)(CH_3)Cl] (**1**) to [Pt(bipy^t-H)Cl] (**2**) the second-order rate constant (k_2 = 1850 M^{-1} s^{-1}) is reduced by half (k_2 = 903 M^{-1} s^{-1}) and becomes 6 times slower for [Pt(bipy^n-H)Cl] (**3**) (k_2 = 311 M^{-1} s^{-1}). Thus, the closure of an alkyl chain to form a five- or six-membered ring does not cause a great difference of reactivity with respect to compound **1**. Both the size of the ring and the position of the two methyl substituents on the aliphatic chain play little if any role in controlling the reactivity. The increase of steric hindrance by the methyl substituents is brought about at the periphery of the coordination plane, and it does not significantly affect the rate of attack of the reagent on the metal.

The reactivity of [Pt(bipy)(Ph)Cl] (**4**), in which the phenyl ring lies perpendicular to the square coordination plane, is 6 times smaller than that of [Pt(bipy)(CH_3)Cl] (**1**) (k_2 = 343 M^{-1} s^{-1}). The magnitude of the *trans* and *cis* effect of the methyl and phenyl groups being comparable, the moderate decrease of rate is steric in nature, and it can be ascribed to the additional difficulty of the nucleophile in approaching the metal center and in forming the new bond. Similar results were obtained for substitution reactions on *trans*-[Pt(PEt_3)$_2$(R)Cl][41] and in the protonolysis of alkylarylplatinum(II) complexes.[42]

As pointed out by Constable et al.[43] the ligand 6-phenyl-2,2′-bipyridine behaves as a true cyclometalating analogue of 2,2′:6′,2″-terpyridine. The molecular structure of the cation [Pt-

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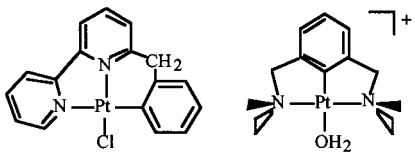
(bipy$^{\phi}$-H)(MeCN)]$^+$ shows strict similarities with the structure of terpy complex cations such as [Pt(terpy)Cl]$^+$,[44,45] [Pt(terpy)-(CH_2NO_2)]$^+$,[46] and [Pt(terpy)(CH_3)]$^+$,[47] as far as planarity and bond lengths and angles are concerned. Likewise, this cation forms discrete dimeric units held together by stacking interactions between the aromatic ligands. Most importantly, the equivalence between the pyridyl and the phenyl rings is notable. In the compound [Pt(bipy$^{\phi}$-H)Cl] (**5**) the lability of the chloride ion is very high ($k_2 = 65 \times 10^3$ M^{-1} s^{-1}), almost 2 orders of magnitude higher than that of compound **4**, and this sharp increase of reactivity finds its origin in the aromaticity of the cyclometalated 6-phenyl-2,2′-bipyridine ligand, comparable to or not much less than that of 2,2′:6′,2″-terpyridine. Only in this particular case, the in-plane phenyl ring concurs to the electron withdrawal from filled d orbitals of the metal to empty π^* of the terdentate ligand.

Further evidence for a relationship between the lability of chloride and the aromaticity of the terdentate ligand is given by the fact that the introduction of a spacer group in the cyclometalated ring, as for the benzyl derivatives, produces a sharp decrease in rate with respect to compound **5**. The compound [Pt(bipy$^{\beta}$-H)Cl] ($k_2 = 1046$ M^{-1} s^{-1}) reacts at a rate comparable to that of [Pt(bipy)(CH_3)Cl], and the rate is still reduced as a result of methyl ([Pt(bipy$^{\alpha Me}$-H)Cl], $k_2 = 166$ M^{-1} s^{-1}), ethyl ([Pt(bipy$^{\alpha Et}$-H)Cl], $k_2 = 85$ M^{-1} s^{-1}), and dimethyl ([Pt(bipy^{c}-H)Cl], $k_2 = 45$ M^{-1} s^{-1}) substitution on the methylene carbon. Since the six-membered cycle adopts a boat conformation, the substituent alkyl groups are directed toward the metal atom and their proximity to the reaction center is at the origin of the steric retardation.

Finally, it is of interest to compare briefly the behavior of platinum(II) complexes with N−N−C and N−C−N anionic ligands, at least as far as the lability of the fourth coordinated group is concerned. Both the cyclometalated compounds **1** and **2** exhibit high reactivity. The results of this study show that



1

2

the relief of electron density from the metal through π-bonding by the planar diimine is crucial in controlling the reactivity and activation mode of compound **1**. The introduction of a cyclometalated in-plane aryl ring, separated through a spacer methylene group from the bipy moiety, hardly affects the rate of chloride substitution. This fact rules out any effective back-donation toward the aromatic π^*-orbitals in the 18-e five-coordinated transition state. In principle, some flow of electron density from the metal to the in-plane aryl ring of **2** cannot be excluded. However, all the kinetic evidence[11,15] and the comparison with similar noncyclometalated organometallic systems suggest that the presence of the strong *trans*-labilizing platinum−carbon σ bond is the main, if not the only, factor responsible for the high lability of H_2O in compound **2**.

Conclusions

The lability of chloride in platinum(II) [Pt(N−N−C)Cl] complexes, containing terdentate N−N−C anionic ligands derived from deprotonated 6-substituted 2,2′-bipyridines, depends very little on the various factors which characterize a cyclometalated ring, such as its size, the nature of the Pt−C bond (whether metalation comes from phenyl or alkyl C−H activation), and the number of substituents on the ring. The main factor controlling the reactivity is the electrophilicity of the metal, as dictated by the strong π-electron withdrawal of the 2,2′-bipyridine fragment. There is not a specific role of cyclometalation in increasing the reactivity, as shown by the comparison with the lability of chloride in the [Pt(N−N)(C)-Cl] (C = CH_3 or C_6H_5) complexes having the same set of donor atoms but less constrained arrangements of the ligands. The only exception to this pattern of behavior is constituted by the complex [Pt(bipy$^{\phi}$-H)Cl], which experiences a significant rate enhancement with respect to [Pt(bipy)(Ph)Cl]. In the latter the in-plane phenyl ring of the 6-phenyl-2,2′-bipyridine ligand becomes part of an extensive π-acceptor system, like that of the nitrogen terdentate 2,2′:6′,2″-terpyridine. The 2,2′-biphenyl dianion (bph^{2-}) ligand, which is a cyclometalating analogue of 2,2′-bipyridine, behaves in a completely different way. In the complexes [Pt(bph)(SR_2)$_2$], back-donation into the empty π^*-orbitals of the in-plane aryl rings does not come into play, and the mechanism of ligand exchange is dissociative.

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Supporting Information Available: Tables listing resonances of compounds **1**−**18** and observed pseudo-first-order rate constants (k_{obsd}/s^{-1}) for nucleophilic substitution on compounds **1**−**9** as a function of [PPh_3]. This material is available free of charge via the Internet at http://pubs.acs.org.

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