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THE REACTIVITY OF CATIONIC PLATINUM (II) COMPLEXES CONTAINING THE TRIDENTATE LIGAND BIS(2-PYRIDYLMETHYL)SULPHIDE

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Abstract—The kinetics of the displacement of coordinated nitrogen donor bases (L) by chloride from complexes of the type $[Pt(NSN)(L)]^{2+}$ [NSN = bis(2-pyridylmethyl) sulphide; L = a series of pyridines, isoquinoline and NH_3] as well as chloride substitution from the substrate $[Pt(NSN)Cl]^+$ by Br^- and I^- have been studied in methanol at 25°C and constant ionic strength and compared with those of the corresponding platinum(II) complexes containing the 2,6-bis(methylsulphanylmethyl)pyridine tridentate ligand. The two-term rate law usually found in substitutions at square-planar platinum(II) complexes is obeyed. Both the first and second-order rate constants for the displacement of L decrease as the basicity of the leaving group increases. π interactions between coordinated pyridines and the metal centre are suggested by comparison of their lability with that of ammonia as well as with that of *para*-substituted pyridines with enhanced π system. Steric hindrance on the leaving base also significantly decreases the reactivity.

We recently reported kinetic data dealing with the reversible displacement of nitrogen donor bases L (L = a number of pyridines and some heterocyclic and aromatic amines) by chloride from both the mono-cationic[1] $[Pt(S\text{-}S)(L)Cl]^+$ and the bis-cationic[2] $[Pt(SNS)(L)]^{2+}$ complexes [S-S = 1,2-bis (phenylsulphanyl)ethane; SNS = 1,2-bis (methylsulphanylmethyl)pyridine] in MeOH at 25°C. In both cases, the kinetic behaviour accorded with a reaction profile involving a transition state in which the Pt—Cl bond is almost completely formed, whereas the Pt—N bond is significantly weakened. The lability of isosteric pyridines was found to be linearly dependent upon their basicity and evidence has been presented for a significant contribution of π interactions between the filled *d* orbitals of the metal and the empty antibonding orbitals of the heterocyclic ring.

Moreover, whereas the normal reactivity sequence, $MeOH < py < Br^- < I^-$, has been found for the displacement of chloride from substrates having nitrogen *trans* to the leaving chloride,[2,3] the enhancement of the relative nucleophilicity[4] of the neutral reagents pyridine and solvent as compared to that of anionic entering groups towards the $[Pt(S\text{-}S)Cl_2]$ substrate was tentatively attributed to the presence of a sulphur atom *trans* to the leaving group in the ground state.[1]

On developing a systematic study about these subjects we have now synthesized both the mono-cationic $[Pt(NSN)Cl]^+$ and the derived series of bis-cationic $[Pt(NSN)L]^{2+}$ species (NSN = the tridentate ligand bis(2-pyridylmethyl)sulphide in which the S donor atom lies in *trans* position with respect to the displaceable monodentate ligand, Cl or L; L = pyridines, isoquinoline and ammonia) and have measured the rate of chloride displacement by the solvent (methanol) and some anionic nucleophiles from the former as well as the rate of substitution of L by chloride from the latter series.

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EXPERIMENTAL

Reagents

Platinum(II) chloride, $PtCl_2$, was obtained from Janssen Chimica. Pure reagent-grade LiBr, $[NEt_4]I$, $[NBu^n_4][ClO_4]$, $[NBu^n_4]Cl$, $LiClO_4$, (Fluka and Aldrich) were dried over P_2O_5 in a vacuum desiccator and used without further purification. Nitrogen bases were recrystallized or distilled before use. Anhydrous CH_3OH was obtained by distillation over $(CH_3O)_2Mg$, but traces of water did not appear to have any appreciable effect upon reactions.

Instruments

IR spectra (4000–500 cm^{-1}, KBr disks; 600–50 cm^{-1}, polyethylene pellets) were recorded on a Nicolet Magna FT IR 750 spectrometer. Electronic spectra and kinetic measurements were obtained on a Perkin–Elmer Lambda 16 spectrophotometer. ^1H NMR spectra were taken on a Bruker AC 200 F spectrometer. Conductivity measurements were carried out with a CDM 83 Radiometer Copenhagen conductivity meter and a CDC 334 immersion cell. Elemental analyses were performed by the Microanalytical Laboratory of the University of Padua.

Kinetics

Reactions were initiated by adding a 0.015 mol dm^{-3} dimethylformamide solution (2–20 μl) of the substrate complex, $[Pt(NSN)Cl]^+$ or $[Pt(NSN)(L)]^{2+}$, to a methanol solution (3 cm^3) of the appropriate reagent previously brought to the reaction temperature (25°C) in a thermostatted cell in the spectrophotometer. The concentration of the entering group was always large enough to provide pseudo-first-order conditions. In the case of the displacement of L from $[Pt(NSN)(L)]^{2+}$ the reactions were followed in the presence of 1×10^{-2} mol dm^{-3} $HClO_4$ to ensure protonation of the released nitrogen base L. After preliminary repetitive scan experiments in the range 240–360 nm to search for isosbestic points and spectral changes, the kinetics were studied by measuring the changing absorbance at suitable wavelengths as a function of time. Pseudo-first-order rate constants (k_{obs}, s^{-1}) were obtained either from the gradients of plots of $\log(D_t - D_\infty)$ vs time or from a non-linear least-squares fit of experimental data to $D_t = D_\infty + (D_0 - D_\infty)\exp(-k_{obs}t)$ with D_0, D_∞ and k_{obs} the parameters to be optimized (D_0 = absorbance after mixing of reactants, D_∞ = absorbance at completion of reaction).

Preparation of bis(2-pyridylmethyl)sulphide (NSN).

This compound was prepared according to a published method[5] (Found: C, 66.5; H, 5.8; N, 12.8; S, 14.6. Calc. for $C_{12}H_{12}N_2S$: C, 66.6; H, 5.6; N, 13.0; S, 14.8%). ^1H NMR (δ, 200 MHz, solvent $CDCl_3$, standard $SiMe_4$) 8.47 [2H, dm, $J = 4.9$ Hz], 7.55 [2H, td, $J = 7.6$ and 1.8 Hz], 7.29 [2H, dm, $J = 7.8$ Hz], 7.07 [2H, ddd, $J = 7.6$, 4.9 and 1.2 Hz], 3.76 [4H, s].

Preparation of complexes

Chloro[bis(2-pyridylmethyl)sulphide]platinum (II) perchlorate, $[Pt(NSN)Cl]ClO_4$. To $[Pt(PhCN)_2Cl_2]$[6] (1.416 g, 3 mmol) dissolved in a minimum amount of dichloromethane was added dropwise a solution of NSN (0.648 g, 3 mmol) in dichloromethane (10 cm^3). The mixture was refluxed for 2 h, during which time the yellow $[Pt(NSN)Cl]Cl$ gradually precipitated. The crude product (1.2 g, 83%) was filtered off, dried under reduced pressure and crystallized as perchlorate from a concentrated boiling aqueous solution containing excess $LiClO_4$, slowly cooled at room temperature.

Bromo[bis(2-pyridylmethyl)sulphide]platinum (II)perchlorate, $[Pt(NSN)Br]ClO_4$; *iodo[bis(2-pyridylmethyl)sulphide]platinum(II)perchlorate*, $Pt(NSN)I]ClO_4$. Stoichiometric amounts of either LiBr or $[NEt_4]I$ were added under stirring to warm (70°C) aqueous solutions (30 cm^3) of $[Pt(NSN)Cl]ClO_4$ (0.137 g, 0.25 mmol). After few minutes of reaction, addition of an excess of solid $LiClO_4$ and slow cooling of the solutions at room temperature resulted in the formation of the crystalline products, which were filtered off, washed with cold water and dried *in vacuo*.

$[Pt(NSN)(L)](ClO_4)_2$. The complexes $[Pt(NSN)(L)](ClO_4)_2$ (L = pyridine, 4-chloropyridine, 4-methylpyridine, 4-aminopyridine, 4-acetylpyridine, isonicotinic acid, methyl-isonicotinate, 2-methylpyridine, 2,4-dimethylpyridine, isoquinoline, NH_3) were prepared as follows. Stoichiometric amounts of L were added to warm and concentrated aqueous solutions of $[Pt(NSN)Cl](ClO_4)$ (0.273 g, 0.5 mmol, 20 cm^3) and the resultant mixtures were stirred at 70–80°C for 15 min. After the addition of an excess of solid $LiClO_4$ (0.5 g), the crystalline products were slowly precipitated when the solutions were cooled at room temperature. These were filtered off, washed with cold water (4–5 cm^3) and dried *in vacuo*.

Analytical and some physico-chemical data for the complexes are collected in Table 1.

Table 1. Analytical and physical data for the complexes

Complex	Analysis[a](%) C	H	N	S	Colour	M.p. (°C)	UV-VIS λ max[b] (nm) (ε/dm^{3}mol^{-1}cm^{-1})	λ_M[c] (Ω^{-1}cm^{2}mol^{-1})
[Pt(NSN)Cl]ClO$_4$[d]	26.6	2.0	4.7	6.2	Cream	>230	277 (9200)	58
	(26.4)	(2.2)	(5.1)	(5.9)			280 (sh)	
[Pt(NSN)Br]ClO$_4$[e]	24.4	2.2	4.9		Pale yellow	238–240	269 (7700)	61
	(24.4)	(2.0)	(4.7)				278 (sh)	
[Pt(NSN)I]ClO$_4$[f]	22.8	2.0	4.5		Yellow	229–231	280 (sh)	70
	(22.6)	(1.9)	(4.4)					
[Pt(NSN)(4-COOHpy)](ClO$_4$)$_2$	29.2	2.1	5.3	4.3	Cream	215 dec	264 (17300)	116
	(29.5)	(2.3)	(5.7)	(4.4)			270 (sh)	
[Pt(NSN)(4-COOCH$_3$py)](ClO$_4$)$_2$	31.0	2.4	5.4	4.2	Cream	225–227	265 (15800)	154
	(30.5)	(2.6)	(5.6)	(4.3)			270 (sh)	
[Pt(NSN)(4-COCH$_3$py)](ClO$_4$)$_2$	31.3	2.4	5.2	4.5	Cream	223–224	264 (15600)	136
	(31.2)	(2.6)	(5.7)	(4.4)				
[Pt(NSN)(4-Clpy)](ClO$_4$)$_2$	28.1	2.3	5.8	4.2	Pale yellow	227	263 (12200)	132
	(28.2)	(2.2)	(5.8)	(4.4)			268 (12200)	
[Pt(NSN)(py)](ClO$_4$)$_2$	30.1	2.3	5.7	4.9	Cream	216–218	260 (13500)	131
	(29.6)	(2.5)	(6.1)	(4.6)			263 (sh)	
[Pt(NSN)(isoquinoline)](ClO$_4$)$_2$	34.7	2.6	5.7	4.0	Cream	190–192	265 (18800)	133
	(34.1)	(2.6)	(5.7)	(4.3)			318 (5400)	
							330 (4200)	
[Pt(NSN)(2-Mepy)](ClO$_4$)$_2$	30.6	2.5	5.9	4.4	Cream	204–206	264 (16100)	135
	(30.7)	(2.7)	(6.0)	(4.6)			270 (sh)	
[Pt(NSN)(4-Mepy)](ClO$_4$)$_2$	31.0	2.6	5.9	4.6	Cream	207 dec	257 (14200)	126
	(30.7)	(2.7)	(6.0)	(4.6)			263 (14100)	
[Pt(NSN)(2,4-Me$_2$py)](ClO$_4$)$_2$	31.9	2.9	5.8	4.3	Cream	192–194	262 (15800)	131
	(31.8)	(2.9)	(5.9)	(4.5)			268 (sh)	
[Pt(NSN)(4-NH$_2$py)](ClO$_4$)$_2$	28.7	2.4	7.6	4.4	White	211–213	264 (31000)	125
	(29.0)	(2.6)	(8.0)	(4.5)				
[Pt(NSN)(NH$_3$)](ClO$_4$)$_2$	23.4	2.3	6.4	5.0	Cream	250 dec	269 (11500)	122
	(23.0)	(2.4)	(6.7)	(5.1)				

[a] Calculated values in parentheses.

[b] In methanol.

[c] In dimethylformamide.

[d] ν(Pt—Cl) = 320 cm^{-1}; ^{1}H NMR (δ, 200 MHz, solvent D$_2$O, reference: solvent peak) 8.67 [2H, dm, J = 6.0 Hz], 7.89 [2H, td, J = 7.9 and 1.5 Hz], 7.51 [2H, dm, J = 7.9 Hz], 7.22 [2H, ddd, J = 7.6, 6.0, 1.6 Hz]. Methylene protons undergo fast exchange with the solvent.

[e] ν(Pt—Br) = 216 cm^{-1}.

[f] ν(Pt—I) = 172 cm^{-1}.

RESULTS AND DISCUSSION

Freshly prepared methanol solutions of $[Pt(NSN)Cl]ClO_4$ follow Beer's law and their UV spectra do not change in the presence of added HCl. The molar conductivity of a 1×10^{-3} mol dm^{-3} solution in dimethylformamide (58 Ω^{-1} cm^2 mol^{-1}) is typical of a 1 : 1 electrolyte.[7]

When a neutral or acidic ($HClO_4$) methanol solution of the chloro complex is allowed to react with Br^- or I^- under pseudo-first order conditions, the UV spectrum changes with time in a mono-exponential fashion to those of the independently prepared bromo and iodo species, respectively, with well maintained isosbestic points. The observed rate constants, k_{obs}, measured at $\mu = 0.5$ mol dm^{-3} ($LiClO_4$), are linearly related to the nucleophile concentration according to the expression $k_{obs} = k_1 + k_2[Y^-]$ (Y = Br, I), where, as usual,[8] k_1 refers to the nucleophilic attack of the solvent and k_2 to the direct bimolecular attack of the entering anion. The value of k_1 is (4.7 ± 0.2) 10^{-3} s^{-1} in the reactions with Br^- whereas it could not be extimated with accuracy in the reactions with I^-, it being too small as compared to the second-order contribution. k_{obs}, k_1 and k_2 values are summarized in Table 2 together with the k_2° values extrapolated at $\mu = 0$ according to the Debye–Huckel relationship.[1,9]

Kinetic measurements on $[Pt(NSN)Cl]^+$ have been carried out also with hydroxide ion as nucleophile in the range of concentrations 2×10^{-3} to 1×10^{-2} at $\mu = 0.1$ mol dm^{-3} ($LiClO_4$). In this case the addition of the reagent to the solution of the substrate gives rise to an immediate change in the UV spectrum, followed by a slow mono-exponential decay with a rate constant of 4.5 ± 0.2 s^{-1}, practically independent from $[OH^-]$ and very similar, within the limit of experimental error, to that measured for the solvolytic pathway of the mono-cationic chloro complex in the reaction with Br^-. The final reaction product was not isolated, but it seems reasonable to attribute the immediate spectral change to a partial deprotonation of the chelating ligand, with formation of a neutral [Pt(NSN-H)Cl] species, as suggested by the ^{1}H NMR spectrum of $[Pt(NSN)Cl]^+$ in D_2O, where fast H/D exchange of the methylene protons of the coordinated tridentate ligand takes place. Therefore, the observed kinetic is likely to be due to the solvolytic attack at the original chloro complex, the neutral mono-deprotonated species in equilibrium being expected to provide a less electrophilic reaction centre than the cationic one.

The fact that $[Pt(NSN)Cl]^+$ can undergo deprotonation in basic solutions accounts for the failure to synthesize the bis-cationic species with L = piperidine. In order to obtain the substrates containing pyridines, addition of excess perchlorate was essential to precipitate the bis-cationic derivatives.

The second order rate constants for the reactions of the chloro substrate with bromide and iodide ions enabled us to calculate, from the known values[10] of n°_{Pt} for I^- (5.46) and Br^- (4.18), the nucleophilic discrimination factor for $[Pt(NSN)Cl]^+$,

$$s = \{\log[k_2^\circ(I)] - \log[k_2^\circ(Br)]\}/[n^\circ_{Pt}(I) - n^\circ_{Pt}(Br)] = 1.18$$

which can be compared with the values obtained with the substrates $[Pt(S\text{-}S)Cl_2]$ ($s = 1.27$)[1] and $[Pt(SNS)Cl]^+$ ($s = 1.47$)[2] under the same experimental conditions. The increase of the discrimination parameter on going from the neutral

Table 2. Rate constants for the reactions $[Pt(NSN)Cl]^+ + Y^- \rightarrow [Pt(NSN)(Y)]^+ + Cl^-$, ($Y^- = Br^-, I^-$) in methanol at 25°C ($\mu = 0.5$ mol dm^{-3}, $LiClO_4$; 2×10^{-3} mol dm^{-3} $HClO_4$)

$10^4[Br^-]$ (mol dm^{-3})	$10^3 k_{obs}$[a] (s^{-1})	$10^4[I^-]$ (mol dm^{-3})	$10^3 k_{obs}$[a] (s^{-1})
5	6.3	1.25	22.1
10	8.3	2.50	36.5
20	11.2	3.75	52.0
30	15.1	5.00	64.0
50	21.7	6.25	76.9

$k_1(Br) = (4.7 \pm 0.2) \times 10^{-3}$ s^{-1}

$k_2(Br) = 3.41 \pm 0.07$ dm^3 mol^{-1} s^{-1}; $k_2(I) = 110 \pm 3$ dm^3 mol^{-1}s^{-1}

$k_2^\circ(Br) = 65$ dm^{3}mol^{-1}s^{-1} $k_2^\circ(I) = 2110$ dm^{3}mol^{-1}s^{-1}

[a] Errors on individual k_{obs} determinations are in the range $\pm 5\%$.

$[Pt(S\text{-}S)Cl_2]$ to the mono-cationic $[Pt(SNS)Cl]^+$ complex is easily related to the increase of electrophilicity of the reaction centre due to the different total charge. However, the small decrease of s from 1.27 to 1.18 on going from $[Pt(S\text{-}S)Cl_2]$ to $[Pt(NSN)Cl]^+$ indicates that the nature of the non-participating ligands can be even more important than the total charge in determining the electrophilicity. Large changes in the s values due to the nature of the non-participating ligands are reported in the literature.[11] It seems therefore that the presence of two good σ nitrogen donors *cis* to the leaving group in $[Pt(NSN)Cl]^+$ can balance the change of the total charge as compared to $[Pt(S\text{-}S)Cl_2]$.

The difference in the discrimination ability of the three substrates is accompanied by a consistent change in the reactivity. The value of $k^\circ_2(Br) = 7.24 \times 10^{-3}$ dm^3 mol^{-1} s^{-1} for the neutral substrate $[Pt(S\text{-}S)Cl_2]$ increases to 0.87 and 65 dm^3 mol^{-1} s^{-1} for the cationic complexes $[Pt(SNS)Cl]^+$ and $[Pt(NSN)Cl]^+$, respectively. Even though S instead of N is *trans* to the leaving chloride, the first increase is likely to be due principally to the different charge of the substrates; the second increase can be attributed mainly to the *trans* effect of sulphur which is larger than that of nitrogen. The same conclusion can be drawn by comparing the $k^\circ_2(I)$ values for the three complexes, 3.04×10^{-1}, 67 and 2110 dm^3 mol^{-1} s^{-1}, respectively.

The comparison of the solvolytic rate constants, k_1, for the three substrates appears to confirm the hypothesis that the entry of neutral molecules, as compared to the anionic nucleophiles, is accelerated more than expected from the n°_{Pt} relationship in the case of complexes with a sulphur atom *trans* to the leaving group.[1] In fact, the relatively large $k_1 = 7.9 \times 10^{-4}$ s^{-1} in the case of the neutral substrate $[Pt(S\text{-}S)Cl_2]$, decreases to a value $<10^{-6}$ s^{-1} with $[Pt(SNS)Cl]^+$, in spite of the different charge, and increases again on going to $[Pt(NSN)Cl]^+$ to 4.7×10^{-3} s^{-1}.

Unfortunately, it was not possible to measure the second order rate constants for the entry of the nitrogen bases on $[Pt(NSN)Cl]^+$. The strong absorbance of the aromatic nucleophiles at the required concentrations precluded any spectrophotometric determinations. Spectrophotometric attempts to follow the reaction with less absorbing aliphatic amines, such as morpholine, ammonia and piperidine, show an immediate spectral change similar to that observed in the reactions with hydroxide ion, and complicate kinetic behaviours reasonably arising from deprotonation of the chelating ligand. Also, conductivity experiments did not allow measurement of second-order rate constants. The conductivity of a solution of 1×10^{-3} mol dm^{-3} $[Pt(NSN)Cl]^+$ and 0.1 mol dm^{-3} 4-$COCH_3$py, a base poor enough not to undergo extensive protonation in methanol, increases to a final value which indicates that the reaction has proceeded by only 5%. Kinetic measurements with entering pyridines of higher basicity could not be followed, due to the high conductivity of the solutions containing the required excess of nucleophile.

Freshly prepared methanol solutions of the bis-cationic species $[Pt(NSN)L]^{2+}$ (L = pyridines, isoquinoline and ammonia) follow the Beer's law, whereas in the presence of free OH^- an immediate change in the UV spectrum accompanied by intensification of the colour is observed, which can again be attributed to an acid–base equilibrium involving the methylene protons. The chemical characteristics and kinetic behaviour of the conjugate bases will be the subject of a further study.

On reacting the substrates $[Pt(NSN)(L)]^{2+}$ in acidic methanol (1×10^{-2} mol dm^{-3} $HClO_4$) with chloride ion, the displacement of L is in all cases complete, leading to the formation of $[Pt(NSN)Cl]^+$ and the free base, more or less protonated according to its basicity. In every case the rate is linearly dependent upon $[Cl^-]$ according to the expression $k_{obs} = k_1 + k_2[Cl^-]$. The k_{obs} values are reported in Table 3, whereas the specific rate constants k_1 and k_2, which have the usual meaning and depend upon the nature of the substrate, are summarized in Table 4, together with the k°_2 values, extrapolated at $\mu = 0$ to make possible comparison with rate constants relative to reactions at complexes of different charge.

On comparing the rate of the displacement of pyridine, assumed typical for a leaving nitrogen base, from $[Pt(S\text{-}S)Cl(py)]^+$ ($k^\circ_2 = 7.81 \times 10^{-2}$)[1] with those from $[Pt(SNS)(py)]^{2+}$ ($k^\circ_2 = 1.48$)[2] and $[Pt(NSN)(py)]^{2+}$ ($k^\circ_2 = 1439$), the same conclusions derived for the entry of bromide and iodide on the mono-cationic $[Pt(NSN)Cl]^+$ can be reached. The first increase is likely to be due to the different charge of the substrates, the second can be mainly attributed to the *trans* effect of sulphur, larger than that of nitrogen.

A plot of log k°_2 vs the basicity (pK_a) of the leaving nitrogen donor is reported in Fig. 1. A linear decrease of the reactivity with increasing basicity of the displaceable ligands can be easily recognized as far as the isosteric 4-Cl-, 4-H-, 4-Me- and 4-H_2N-pyridine are concerned. The slope of this line ($\alpha = -0.53 \pm 0.01$) is comparable with the slopes measured for the displacement of the same pyridines (L) from the cationic substrates $[Pt(S\text{-}S)(L)Cl]^+$ ($\alpha = -0.56$) and $[Pt(SNS)(L)]^{2+}$ ($\alpha = -0.45$), showing that the nature of the non-

Table 3. First-order rate constants, k_{obs}, for the reaction $[Pt(NSN)(L)]^{2+} + Cl^- \rightarrow [Pt(NSN)Cl]^+ + L$ in methanol at 25°C [$\mu = 0.1$ mol dm^{-3} $[NBu^n_4][ClO_4]$]; 0.01 mol dm^{-3} $HClO_4$]

L	$10^4[Cl^-]$ (mol dm^{-3})	10^2k_{obs}[a] (s^{-1})
Isonicotinic acid	1	12.0
	2	13.1
	3	14.5
	4	15.2
	6	17.7
Methylisonicotinate	2	10.2
	3	11.7
	4	12.9
	6	15.9
	8	18.7
	12	24.4
	16	31.0
4-Acetylpyridine	1.0	9.9
	1.5	10.1
	2.0	10.4
	3.0	12.0
	4.0	12.5
	6.0	14.3
4-Chloropyridine	1	9.9
	2	11.7
	3	14.2
	4	15.1
	5	17.3
	6	19.5
Pyridine	2	3.40
	4	4.03
	6	4.78
	8	5.46
	10	6.01
	12	7.01
Isoquinoline	2	0.56
	4	0.88
	6	1.22
	8	1.58
	12	2.06
2-Methylpyridine	2	0.217
	4	0.253
	6	0.303
	8	0.339
	10	0.383
	12	0.433
4-Methylpyridine	2	1.04
	4	1.35
	6	1.64
	8	1.71
	10	2.07
	12	2.39
	16	2.95
2,4-Dimethylpyridine	2	0.150
	4	0.170
	6	0.188
	8	0.212
	10	0.220
	12	0.242
4-Aminopyridine	2	0.0150
	4	0.0220
	8	0.0330
	12	0.0406
	16	0.0610
Ammonia	4	0.0473
	8	0.0800
	12	0.1014
	16	0.1310
	20	0.1640

[a] Errors on individual k_{obs} determinations are in the range ±5%.

participating ligands influences the reactivity much more than the relative lability. The similar response to the leaving group basicity again suggests that also in this case the main energy required to form the transition state is attributable to the weakening of the Pt—N bond.

Ammonia, as compared to the above mentioned pyridines, is more labile than expected according to its basicity (Fig. 1). This can be due either to a different change in solvation on going from the ground to the transition state, and/or to the fact that pyridines are stabilized to some extent in the ground state by π-back donation.[2,12,13] As previously pointed out,[2] π contributions emerge also by examining the behaviour of a group of pyridines having a π system larger than that of the previous ones, i.e. 4-$COCH_3$-, 4-COOH- and 4-COOMe-pyridine, but still comparable as far as steric hindrance is concerned. They are all less reactive than predicted on the basis of their basicity. A sig-

Table 4. First- and second order rate constants[a] for the reaction $[Pt(NSN)(L)]^{2+} + Cl^- \rightarrow [Pt(NSN)Cl]^+ + L$ in methanol at 25°C; $\mu = 0.1$ mol dm^{-3}, $[NBu^n{}_4][ClO_4]$; 0.01 mol dm^{-3} $HClO_4$

L	10^3k_1 (s^{-1})	k_2 ($dm^3\ mol^{-1}\ s^{-1}$)	k_2° ($dm^3\ mol^{-1}\ s^{-1}$)	pK_a of LH^+
Isonicotinic acid	109 ± 2	113 ± 5	4646	3.26
Methyl isonicotinate	71 ± 2	147 ± 2	6044	3.26
4-Acetylpyridine	89 ± 2	92 ± 6	3783	3.52
4-Chloroyridine	80 ± 3	188 ± 9	7731	3.84
Pyridine	26 ± 1	35 ± 1	1439	5.25
Isoquinoline	2.9 ± 0.5	15.2 ± 0.8	625	5.36
2-Methylpyridine	1.71 ± 0.04	2.15 ± 0.05	88	5.94
4-Methylpyridine	7.7 ± 0.6	13.4 ± 0.6	551	6.02
2,4-Dimethylpyridine	1.34 ± 0.03	0.91 ± 0.04	37	6.99
4-Aminopyridine	0.08 ± 0.03	0.31 ± 0.03	13	9.11
Ammonia	0.19 ± 0.04	0.71 ± 0.03	29	9.85[b]

[a] Determined by weighted linear regression of k_{obs} values vs nucleophile concentration.
[b] pK_a value corrected according to Ref. 15.

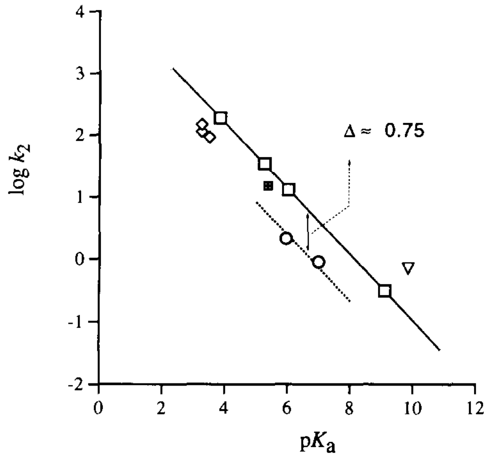

Fig. 1. Log k_2 for the reaction $[Pt(NSN)(L)]^{2+} + Cl^- \rightarrow [Pt(NSN)Cl]^+ + L$ plotted against pK_a of LH^+: □ 4-chloropyridine, pyridine, 4-methylpyridine and 4-aminopyridine; ◇ isonicotinic acid, methyl isonicotinate and 4-acetylpyridine; ⊞ isoquinoline; ○ 2-methylpyridine and 2,4-dimethylpyridine; ▽ ammonia.

nificative retardation is also observed for leaving isoquinoline which, although not directly comparable, has a more extended π system than pyridines.

The presence in the bis-cationic substrates of sterically hindered pyridines having a methyl group in the *ortho* position reduces significantly the reactivity, giving rise to a steric retardation parameter $\Delta = 0.75$.[14] This Δ value, relatively larger than those previously reported for the systems $[Pt(S\text{-}S)Cl(L)]^+$ ($\Delta = 0.6$)[1] and $[Pt(SNS)(L)]^{+2}$ ($\Delta = 0.57$)[2] can be easily explained by considering that in this case the *ortho* hydrogens of the two *cis* pyridine moieties of the chelating ligand are forced to lie in the coordination plane, thus interfering with the free rotation of the monodentate *ortho*-methyl pyridines around the Pt—N bond.

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14. Δ can be regarded as the steric effect due to the introduction of a methyl group *ortho* to the nitrogen in the entering pyridine without any interference from the basicity change that might arise from the presence of the substituent.
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