

Reactivity of Neutral Nitrogen Donors in Planar d⁸ Metal Complexes. Part 2.¹ The System [2,6-Bis(methylsulfanyl-methyl)pyridine]chloroplatinum(II) with Pyridines and Amines in Methanol. Effect of Basicity, π-Acceptor Capacity and Steric Hindrance†

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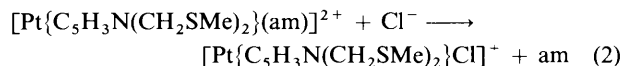
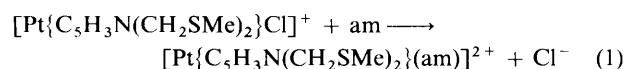
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The kinetics of the forward and reverse steps of the process $[\text{Pt}\{\text{C}_5\text{H}_3\text{N}(\text{CH}_2\text{SMe})_2\}\text{Cl}]^+ + \text{am} \rightleftharpoons [\text{Pt}\{\text{C}_5\text{H}_3\text{N}(\text{CH}_2\text{SMe})_2\}(\text{am})]^{2+} + \text{Cl}^-$ [C₅H₃N(CH₂SMe)₂ = 2,6-bis(methylsulfanyl-methyl)pyridine; am = one of a number of pyridines and some heterocyclic and aromatic amines covering a wide range of basicity] has been studied in methanol at 25 °C. Both forward and reverse reactions obey the usual two-term rate law observed in square-planar substitution. The second-order rate constants for the forward reactions, k_2' , show only a slight dependence upon the basicity of the entering am, and steric hindrance markedly decreases the reactivity. The second-order rate constants for the reverse reactions, k_2'' , are very sensitive to the nature of the leaving group and plots of $\log k_2''$ against the $\text{p}K_a$ of the conjugate acids of unhindered pyridines with different π systems are linear with a slope of -0.45. A comparison among the different pyridines and sp³ nitrogen donor bases indicates an appreciable π contribution to the stability of the Pt-N(sp²) bond. The equilibrium constants for the reactions have been determined in a number of cases from the ratio of the rate constants and a plot of $\log K$ against the $\text{p}K_a$ is linear with a slope of 0.66. The results are compared with data from the literature.

As part of a systematic study of the nucleophilicity and lability of neutral nitrogen-donor bases towards planar four-coordinate complexes, and the relationships between reactivity and proton basicity, we recently reported data concerning the reversible displacement of chloride from the neutral substrate $[\text{Pt}(\text{PhSCH}_2\text{CH}_2\text{SPh})\text{Cl}_2]$ by pyridines, quinolines and morpholine, in methanol at 25 °C.¹ The results showed a small dependence of the reactivity upon the basicity of the entering nitrogen donor and a relatively large influence of the basicity of the co-ordinate base upon its lability, which were interpreted in terms of a reaction profile with a transition state containing a well formed Pt-Cl and a weak Pt-N bond.

Anomalies in the reactivity of pyridine and solvent, the nucleophilicity of which was greater than expected on the basis of the n°_{Pt} scale² as compared to those of anionic entering groups (Br⁻, I⁻), have also been observed and attributed to the presence of a sulfur atom *trans* to the leaving group in the ground state. The same type of anomaly has previously been reported with the anionic substrates $[\text{Pt}(\text{dmsO})\text{Cl}_3]^-$ (dmsO = dimethyl sulfoxide)³ and $[\text{Pt}(\text{Me}_2\text{S})\text{Cl}_3]^-$,⁴ whereas the normal reactivity sequence, *i.e.* MeOH < pyridine < Br⁻ < I⁻, has been observed in a number of complexes having nitrogen *trans* to the leaving chloride.⁵

We have now measured the rate of chloride displacement by pyridines and some heterocyclic and aromatic amines (am) from the cationic substrate $[\text{Pt}\{\text{C}_5\text{H}_3\text{N}(\text{CH}_2\text{SMe})_2\}\text{Cl}]^+$ [C₅H₃N(CH₂SMe)₂ = 2,6-bis(methylsulfanyl-methyl)pyridine], according to the forward and reverse reactions (1) and (2) in



methanol at 25 °C. Besides a charge variation with respect to $[\text{Pt}(\text{PhSCH}_2\text{CH}_2\text{SPh})\text{Cl}_2]$, the partner *trans* to the leaving group is a nitrogen atom instead of a thioether sulfur.

The substitution of chloride by bromide and iodide from $[\text{Pt}\{\text{C}_5\text{H}_3\text{N}(\text{CH}_2\text{SMe})_2\}\text{Cl}]^+$ is also reported.

Experimental

Materials.—All the reagents used were pure reagent-grade products, dried, recrystallized or distilled before use when necessary. Anhydrous MeOH was obtained by distillation over Mg(OMe)₂, but traces of water did not appear to have any appreciable effect upon the reactions.

Instruments.—Physicochemical measurements (IR, UV/VIS, ¹H NMR and conductivity) were performed with the instruments previously described.¹

Preparations.—Both 1,2-bis(methylsulfanyl-methyl)pyridine and $[\text{Pt}\{\text{C}_5\text{H}_3\text{N}(\text{CH}_2\text{SMe})_2\}\text{Cl}]\text{ClO}_4$ were prepared according to published methods.^{5,6}

The complexes $[\text{Pt}\{\text{C}_5\text{H}_3\text{N}(\text{CH}_2\text{SMe})_2\}(\text{am})][\text{ClO}_4]_2$ (am = pyridine, 4-chloro-, 4-methyl-, 4-cyano-, 4-amino-, 4-acetyl-, 2-methyl- or 2,4-dimethyl-pyridine, isonicotinic acid, aniline, morpholine or piperidine) were prepared as follows. Stoichiometric amounts of am were added to warm and concentrated aqueous solutions of $[\text{Pt}\{\text{C}_5\text{H}_3\text{N}(\text{CH}_2\text{SMe})_2\}\text{Cl}]\text{ClO}_4$ (0.264 g, 0.5 mmol, 20 cm³) and the resultant mixtures stirred at 70–80 °C for 15 min. After addition of an excess of solid LiClO₄ (0.5 g), crystalline products were slowly precipitated on cooling the solutions at room temperature. These were filtered off, washed with cold water (4–5 cm³) and dried *in vacuo*.

† Supplementary data available (No. SUP 57038, 4 pp.): Tables of observed first-order rate constants. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Analytical and some physicochemical data for the complexes are collected in Table 1.

Kinetics.—The reactions were followed spectrophotometrically under pseudo-first-order conditions as previously described.¹

Results

Examination of the spectral changes with time in the range 240–340 nm and the close similarity of the spectra at the end of the reactions with those of authentic samples of the expected

reaction products taken under the same experimental conditions demonstrate that the reactions that have been studied kinetically involve either the displacement of co-ordinated chloride or nitrogen bases, according to equations (1) and (2) respectively. The kinetics of the reverse processes (2) was studied at constant ionic strength ($I = 0.1 \text{ mol dm}^{-3}$, $[\text{NBu}^n_4]\text{ClO}_4$). The observed rate constants, k_{obs} , obey the usual relationship $k_{\text{obs}} = k_1 + k_2[\text{nucleophile}]$.⁷ The k_1 terms, namely k_1^f and k_1^r for the forward and reverse processes respectively, are quite small (10^{-5} – 10^{-7} s^{-1}) and contribute little to the reactions. The second-order rate constants k_2^f and k_2^r are summarized in Table 2, together with the corresponding k_2^0

Table 1 Analytical and physical data for the complexes

Complex ^a	Analysis ^b (%)				Colour	M.p./°C	UV/VIS $\lambda_{\text{max}}^c/\text{nm}$ ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$)	$\Lambda_{\text{M}}^d/\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$
	C	H	N	S				
$[\text{Pt}\{\text{C}_5\text{H}_3\text{N}(\text{CH}_2\text{SMe})_2\}\text{Cl}]\text{ClO}_4^e$	20.2 (20.4)	2.45 (2.50)	2.35 (2.65)	—	Pale yellow	182	285 (6700) 280 (sh)	63
$[\text{Pt}\{\text{C}_5\text{H}_3\text{N}(\text{CH}_2\text{SMe})_2\}(\text{NC}_5\text{H}_4\text{R})][\text{ClO}_4]_2$ R = 4-NH ₂	24.7 (24.5)	2.65 (2.80)	5.85 (6.10)	9.95 (9.35)	Ochre	230 (decomp.)	264 (28 200) 284 (sh)	141
4-CN	26.0 (25.8)	2.30 (2.45)	5.75 (6.00)	10.1 (9.20)	Cream	230 (decomp.)	265 (16 400)	146
4-Cl	24.1 (23.8)	2.30 (2.40)	3.85 (3.95)	10.0 (9.05)	Ochre	225 (decomp.)	269 (16 100) 264 (sh)	143
2-Me	26.6 (26.2)	2.75 (2.95)	3.95 (4.10)	10.4 (9.35)	Yellow	232	265 (12 500) 273 (sh)	147
4-Me	26.2 (26.2)	2.70 (2.95)	4.00 (4.10)	9.40 (9.35)	Yellow	235 (decomp.)	259 (11 200) 264 (sh)	145
4-COMe	27.1 (26.9)	2.60 (2.80)	3.85 (3.90)	9.20 (9.00)	Yellow	231	262 (16 600)	146
4-CO ₂ H	24.6 (25.1)	2.50 (2.50)	3.75 (3.90)	9.00 (8.95)	Yellow	233	262 (16 200)	135
$[\text{Pt}\{\text{C}_5\text{H}_3\text{N}(\text{CH}_2\text{SMe})_2\}(\text{NC}_5\text{H}_3\text{Me}_2-2,4)][\text{ClO}_4]_2$	27.4 (27.4)	3.00 (3.15)	3.80 (4.00)	9.90 (9.15)	Cream	238 (decomp.)	263 (12 000) 269 (sh)	145
$[\text{Pt}\{\text{C}_5\text{H}_3\text{N}(\text{CH}_2\text{SMe})_2\}(\text{pip})][\text{ClO}_4]_2$	24.2 (24.8)	3.40 (3.55)	4.05 (4.15)	9.60 (9.45)	Cream	211	264 (10 350)	147
$[\text{Pt}\{\text{C}_5\text{H}_3\text{N}(\text{CH}_2\text{SMe})_2\}(\text{morph})][\text{ClO}_4]_2$	23.1 (22.9)	3.30 (3.25)	4.15 (4.10)	9.70 (9.40)	Yellow	203	264 (9 550)	131
$[\text{Pt}\{\text{C}_5\text{H}_3\text{N}(\text{CH}_2\text{SMe})_2\}(\text{C}_6\text{H}_5\text{NH}_2)][\text{ClO}_4]_2$	26.4 (26.2)	3.05 (2.95)	4.25 (4.10)	9.60 (9.35)	Cream	222	262 (11 300)	136
$[\text{Pt}\{\text{C}_5\text{H}_3\text{N}(\text{CH}_2\text{SMe})_2\}(\text{py})][\text{ClO}_4]_2$	25.2 (25.0)	2.50 (2.70)	4.15 (4.15)	10.5 (9.55)	Cream	271	260 (12 900) 267 (sh)	127

^a pip = Piperidine, morph = morpholine, py = pyridine. ^b Calculated values in parentheses. ^c In methanol. ^d In dimethylformamide. ^e Cl 13.6 (13.4)%.

Table 2 First- and second-order rate constants^a and equilibrium constants for the reaction $[\text{Pt}\{\text{C}_5\text{H}_3\text{N}(\text{CH}_2\text{SMe})_2\}\text{Cl}]^+ + \text{am} \xrightleftharpoons[k_1^r + k_2^r[\text{Cl}^-]]{k_1^f + k_2^f[\text{am}]}$ $[\text{Pt}\{\text{C}_5\text{H}_3\text{N}(\text{CH}_2\text{SMe})_2\}(\text{am})]^{2+} + \text{Cl}^-$ in methanol at 25 °C; $I = 0.1 \text{ mol dm}^{-3}$, $[\text{NBu}^n_4]\text{ClO}_4$

am	λ/nm	Isosbestic point	Used for calculations ^b	$10^3 k_2^f/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$10^3 k_2^r/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$10^3 k_2^0/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$K = k_2^f/k_2^r$	$10^2 K^0 = k_2^f/k_2^0$	$\text{p}K_a^c$
4-Cyanopyridine	297		(264)		501 ± 8	20 598			1.90
4-Chloropyridine	279		300 (258)	4.5 ± 0.1	126 ± 1	5 180	0.0357 ± 0.0008	0.087	3.84
4-Chloropyridine ^d					$1\,170 \pm 40$	5 329			3.84
Pyridine	277		305 (260)	9.7 ± 0.1	36 ± 2	1 480	0.27 ± 0.02	0.655	5.17
4-Methylpyridine	278		300 (258)	14.3 ± 0.1	14.1 ± 0.3	580	1.01 ± 0.02	2.465	6.03
4-Aminopyridine	248		300 (262)	53 ± 1	0.52 ± 0.02	21	102 ± 4	252.4	9.12
2-Methylpyridine	278		300 (264)	0.498 ± 0.007	3.25 ± 0.06	134	0.153 ± 0.004	0.371	5.94
2,4-Dimethylpyridine	277		300 (262)	0.756 ± 0.004	1.70 ± 0.05	70	0.44 ± 0.01	1.080	6.99
4-Acetylpyridine ^e	283		(254)	4.9 ± 0.2	82 ± 2	3 371	0.060 ± 0.003	0.145	3.51
Isonicotinic acid	282		(254)		103 ± 2	4 235			3.26
Aniline ^e	278		(262)	7.7 ± 0.3	280 ± 10	11 512	0.027 ± 0.001	0.067	4.6 (5.07)
Morpholine ^e	275		260 (260)	28.9 ± 0.4	15.6 ± 0.2	641	1.85 ± 0.03	0.045	8.33 (8.63)
Piperidine	275		260 (260)	60 ± 2	0.98 ± 0.05	40	61 ± 4	150	11.1 (11.4)

^a Determined by weighted linear regression of k_{obs} values vs. nucleophile concentration. ^b For the forward reactions and in parentheses for the reverse reactions. ^c $\text{p}K_a$ values of the conjugated acids Ham^+ in water at 25 °C⁸ and, in parentheses, $\text{p}K_a$ values corrected according to ref. 9. ^d $I = 0.01 \text{ mol dm}^{-3}$, $[\text{NBu}^n_4]\text{ClO}_4$. ^e Conductivity measurements for the forward reaction.

values extrapolated to zero ionic strength according to the Debye-Huckel relationship previously discussed,^{1,10} and the derived equilibrium constants $K = k_2^f/k_2^r$ and $K^0 = k_2^f/k_2^{0,r}$. The effectiveness of the extrapolation to zero ionic strength was confirmed on measuring the substitution of co-ordinated 4-chloropyridine by chloride at two sufficiently different values of ionic strength, *i.e.* 0.1 and 0.01 mol dm⁻³, which gives $k_2^{0,r}$ values in close agreement, 5.18 and 5.33 dm³ mol⁻¹ s⁻¹ respectively.

The kinetics of displacement of chloride by bromide and iodide from [Pt{C₅H₃N(CH₂SMe)₂}Cl]ClO₄ was followed at $I = 0.1$ mol dm⁻³ ([NBuⁿ]₄ClO₄), under the same experimental conditions. Plots of k_{obs} vs. [nucleophile] are linear with small intercepts (k_1). The rate constants k_{obs} , k_2 and k_2^0 are reported in Table 3.

Tables of observed first-order rate constants, k_{obs} , have been deposited as SUP No. 57038.

Discussion

Both the starting substrate [Pt{C₅H₃N(CH₂SMe)₂}Cl]⁺ and the substituted products [Pt{C₅H₃N(CH₂SMe)₂}am]²⁺ can exist in two isomeric forms depending on the projection of the sulfur methyl groups on the same side (*meso* isomer) or different sides (*DL* isomer) of the co-ordination plane.

In spite of the fact that the chelate ligand in both the chloro and pyridine derivatives has the *DL* conformation in the solid state,¹¹ ¹H NMR spectra taken soon after dissolution of the crystalline solids in CD₃OD at room temperature show that both isomers are present. At 296 K the chloro complex displays two sharp, symmetric and equally intense SMe singlets at δ 2.817 and 2.787 respectively ($\Delta\nu = 6.05$ Hz), both with $J_{\text{Pt-H}} = 46.5$ Hz, whereas the very slightly soluble pyridine derivative shows two unequally intense SMe singlets (integrals ratio = 0.39) at about δ 2.76 and 2.71 ($\Delta\nu = 10$ Hz) with not well resolved platinum satellites. The SMe resonances of both complexes broaden on raising the temperature, but coalescence temperatures, from which the relative rates of inversion at sulfur can be deduced,¹² cannot be reached in this solvent.

On measuring the ¹H NMR spectra of both [Pt{C₅H₃N(CH₂SMe)₂}Cl]⁺ and [Pt{C₅H₃N(CH₂SMe)₂}py]²⁺ (py = pyridine) in D₂O, in which the compounds are more soluble than in CD₃OD, coalescence can be observed. At 296 K the two symmetric sharp SMe singlets of the two equally populated isomers of the chloro species fall at δ 2.556 and 2.632 respectively ($\Delta\nu = 15.2$ Hz), both with $J_{\text{Pt-H}} = 45.5$ Hz, and coalesce at 372 K. The analogous resonances of the pyridine derivative (integrals ratio = 0.40) fall at δ 2.700 and 2.655 ($\Delta\nu = 9.04$ Hz), both with $J_{\text{Pt-H}} = 51.5$ Hz, and coalesce at 368 K. According to the equation $k = \pi\Delta\nu/\sqrt{2}$,¹³ the rate of sulfur inversion at the coalescence temperature for the chloro species can be estimated to be *ca.* 33 s⁻¹.

Assuming that the rate of inversion does not change significantly in the two solvents, the presence of a well maintained isosbestic point in all the strictly monoexponential kinetic runs for both the forward (1) and reverse (2) reactions

Table 3 Rate constants for the reactions [Pt{C₅H₃N(CH₂SMe)₂}Cl]⁺ + X⁻ → [Pt{C₅H₃N(CH₂SMe)₂}X]⁺ + Cl⁻ (X⁻ = Br⁻ or I⁻) in methanol at 25 °C ($I = 0.1$ mol dm⁻³, [NBuⁿ]₄ClO₄)

[Br ⁻]/ mol dm ⁻³	10 ⁴ k _{obs} / s ⁻¹	[I ⁻]/ mol dm ⁻³	10 ² k _{obs} / s ⁻¹
0.001	2.00 ± 0.09	0.001	0.97 ± 0.01
0.003	4.12 ± 0.05	0.002	2.09 ± 0.06
0.005	7.26 ± 0.08	0.003	3.13 ± 0.09
0.007	9.74 ± 0.08	0.004	4.1 ± 0.2
0.01	14.1 ± 0.6	0.005	5.21 ± 0.09

$k_2(\text{Br}^-) = 0.136 \pm 0.004$ dm³ mol⁻¹ s⁻¹, $k_2(\text{I}^-) = 10.5 \pm 0.1$ dm³ mol⁻¹ s⁻¹, $k_2^0(\text{Br}^-) = 0.87$ dm³ mol⁻¹ s⁻¹, $k_2^0(\text{I}^-) = 67.3$ dm³ mol⁻¹ s⁻¹

strongly indicates that the substitutions proceed by slow transformations of rapidly interconverting mixtures of isomers, as already suggested for other sulfur chelate platinum(II) complexes,¹⁴ the substitution process always being slower than sulfur inversion under our experimental conditions.

A comparison of the reactivity of the cationic [Pt{C₅H₃N(CH₂SMe)₂}Cl]⁺ and the neutral species [Pt(PhSCH₂CH₂SPh)Cl₂]⁰,¹ as measured by the corresponding $k_2^f(\text{py})$ values, shows it to be smaller for the former than for the latter [$k_2^f(\text{py}) = 0.0097$ and 0.283 dm³ mol⁻¹ s⁻¹] in spite of the positive charge of [Pt{C₅H₃N(CH₂SMe)₂}Cl]⁺, as a consequence of the lower *trans*-labilizing effect of the nitrogen atom of the chelating moiety compared to that of the thioether sulfur atom.

The 'anomalous' reactivity sequence MeOH ($k_1 = 0.82 \times 10^{-3}$ s⁻¹) < Br⁻ ($k_2 = 7.22 \times 10^{-3}$ dm³ mol⁻¹ s⁻¹) < py ($k_2 = 0.283$ dm³ mol⁻¹ s⁻¹) < I⁻ ($k_2 = 0.304$ dm³ mol⁻¹ s⁻¹) reported for the chloride displacement from the substrate [Pt(PhSCH₂CH₂SPh)Cl₂] had been tentatively related to the presence of a thioether sulfur atom *trans* to the leaving group.¹ In the present case, where a nitrogen donor is *trans* to the leaving chloride, the usual sequence in accordance with the n_{Pt}° scale² is obeyed, as previously found for the reactions with the same nucleophiles in water at 25 °C.⁵ The actual values, extrapolated at zero ionic strength, are MeOH ($k_1 \approx 10^{-6}$ s⁻¹) < py ($k_2 = 9.7 \times 10^{-3}$ dm³ mol⁻¹ s⁻¹) < Br⁻ ($k_2 = 0.87$ dm³ mol⁻¹ s⁻¹) < I⁻ ($k_2 = 67.3$ dm³ mol⁻¹ s⁻¹). However, whereas the nucleophilicities of water and methanol are comparable and that of pyridine is about an order of magnitude larger in water than in methanol [$k_2^0(\text{py})^{\text{H}_2\text{O}}/k_2^0(\text{py})^{\text{MeOH}} = 11.7$], the same ratio is smaller and reversed for the entry of bromide (0.77) and iodide (0.38). This fact is likely to reflect the change in solvation of neutral and anionic ligands when free or bonded in the corresponding transition states in the two solvents and seems to confirm that general solvation effects with anionic reagents are small in substitution reactions at platinum(II) complexes.¹⁵ It implies, for instance, that the solvation of a free iodide ion is not very different from that of the partially co-ordinated ion in the transition state, as already pointed out.¹⁶ Since, on the contrary, solvent effects seem to play a role for neutral nucleophiles, particular care is needed on applying the n_{Pt}° scale to charged and neutral nucleophiles in different solvents.

The specific second-order rate constants k_2^f (Table 2) obey the linear free-energy relationship $\log k_2^f = \alpha \text{p}K_a + \text{constant}$, with $\alpha = 0.15 \pm 0.01$ (Fig. 1), as far as pyridine and the isosteric 4-substituted pyridines (4-chloro-, 4-methyl-, 4-amino- and 4-acetyl-pyridine) are concerned as well as aniline, morpholine

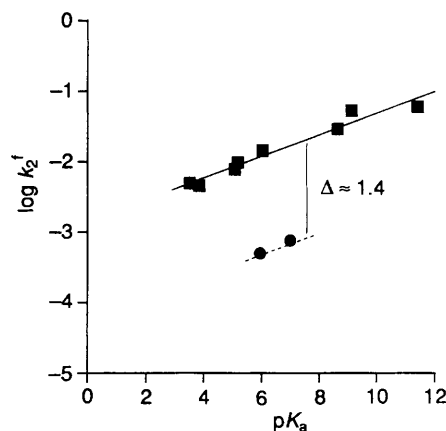


Fig. 1 Plots of $\log k_2^f$ for the reaction [Pt{C₅H₃N(CH₂SMe)₂}Cl]⁺ + am → [Pt{C₅H₃N(CH₂SMe)₂}am]²⁺ + Cl⁻ against $\text{p}K_a$ of Ham⁺: (■), 4-acetyl- and 4-chloro-pyridine, pyridine, 4-methyl- and 4-amino-pyridine, aniline, morpholine and piperidine; (●), 2-methyl- and 2,4-dimethyl-pyridine

and piperidine for which the pK_a values have been corrected to take into account the different number of hydrogens in the corresponding acid forms.⁹ The kinetics with 4-acetylpyridine has been measured by conductivity, due to the large absorption of the excess ligand required in the suitable spectrophotometric range and its k_2^r value is that expected from its pK_a value. Unfortunately, it was not possible to measure the nucleophilicity of isonicotinic acid owing to its zwitterionic nature as well as that of 4-cyanopyridine, the substitution not going to completion even in the presence of a large excess of nucleophile.

The slope (α), 0.15, indicates the usual small dependence of the reactivity upon the basicity of the entering nitrogen base, but it is relatively large compared to the values measured in neutral platinum(II) complexes, *i.e.* 0.036 for $[\text{Pt}(\text{PhSCH}_2\text{CH}_2\text{SPh})\text{Cl}_2]$,¹ 0.06 for $[\text{Pt}(\text{bipy})\text{Cl}_2]$ (bipy = 2,2'-bipyridine),¹⁷ and 0.05 for $[\text{Pt}\{\text{Ph}(\text{Me})\text{NN}=\text{C}(\text{Me})\text{C}(\text{Me})=\text{NN}(\text{Me})\text{Ph}\}\text{Cl}_2]$,¹⁸ in accord with the observation that the ability of a substrate to discriminate among entering nucleophiles increases with the electrophilicity of the reaction centre.¹⁹

The substrates can also be compared as far as steric retardation effects are concerned. Steric hindrance, usually measured using 2-methylpyridines as nucleophiles,¹ is expressed by the value of $\Delta \approx 1.4$ for the $[\text{Pt}\{\text{C}_5\text{H}_3\text{N}(\text{CH}_2\text{SMe})_2\}\text{Cl}]^+$ substrate* (Fig. 1), which is comparable with the value of $\Delta \approx 1.6$ measured for the neutral $[\text{Pt}(\text{PhSCH}_2\text{CH}_2\text{SPh})\text{Cl}_2]$. It therefore appears that the limitation to free rotation around the Pt-N(am) bond in the trigonal-bipyramidal transition state, due to the presence of two thioether sulfur atoms in the apical position, is not very different from that arising from the presence of a single sulfur atom and a chloride ligand. These two Δ values are both considerably larger than the value of $\Delta \approx 1.0$ for the reaction of $[\text{Pt}(\text{bipy})\text{Cl}_2]$ ¹⁷ where a nitrogen atom and a chloride occupy the apical positions.

As far as the reverse reactions (2) are concerned, the reacting species can be divided into groups depending on the nature of the leaving am. The plots of $\log k_2^r$ vs. pK_a of the leaving am are shown in Fig. 2.

The first group includes the complexes with 4-chloropyridine, pyridine, 4-methylpyridine and 4-aminopyridine, for which the linear relationship $\log k_2^r = -(0.45 \pm 0.01) pK_a + \text{constant}$ is obeyed.

The reactivity of the pyridine complex $[\text{Pt}\{\text{C}_5\text{H}_3\text{N}(\text{CH}_2\text{SMe})_2(\text{py})\}]^{2+}$ at $I = 0 \text{ mol dm}^{-3}$ ($k_2^0 = 1.48 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) compared with that of the mono-cationic $[\text{Pt}(\text{PhSCH}_2\text{CH}_2\text{SPh})(\text{py})\text{Cl}]^+$ ($k_2^0 = 0.078 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) indicates that the nucleophilic attack of chloride occurs more easily at the former than the latter. The response of reactivity upon basicity of the leaving group does not differ greatly from that of the $[\text{Pt}(\text{PhSCH}_2\text{CH}_2\text{SPh})(\text{am})\text{Cl}]^+$ substrates ($\alpha = -0.56$), the difference indicating a minor role of the nature of the leaving group in determining their relative lability.

As already discussed in Part 1,¹ the relatively large dependence of reactivity upon the basicity of the nitrogen donors in the reverse as compared to the forward reactions allows us to postulate also in the present case an associative asynchronous displacement mechanism with a transition state in which the nitrogen ligand is partially bonded to the metal, and the Pt-Cl bond is almost completely formed.

Attempts to measure the displacement of pyridine by chloride in water show that, even in the presence of excess acid to provide complete protonation of the free base, no reaction occurs, whereas the entry of pyridine on the chloro complex⁵ has $k_2 = 0.114 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The absence of reactivity of $[\text{Pt}\{\text{C}_5\text{H}_3\text{N}(\text{CH}_2\text{SMe})_2(\text{py})\}]^{2+}$ must therefore be related to the role of the different solvation of the reacting species in the two

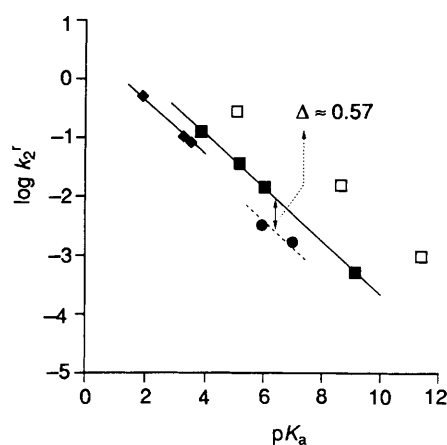


Fig. 2 Plots of $\log k_2^r$ for the reaction $[\text{Pt}\{\text{C}_5\text{H}_3\text{N}(\text{CH}_2\text{SMe})_2(\text{am})\}]^{2+} + \text{Cl}^- \longrightarrow [\text{Pt}\{\text{C}_5\text{H}_3\text{N}(\text{CH}_2\text{SMe})_2\}\text{Cl}]^+ + \text{am}$ against pK_a of H^+ am: (□), aniline, morpholine and piperidine; (■), 4-chloropyridine, pyridine, 4-methyl- and 4-amino-pyridine; (◆), 4-cyanopyridine, isonicotinic acid and 4-acetylpyridine; (●), 2-methyl- and 2,4-dimethylpyridine

solvents, and particularly to better solvent assistance in the transition state to pyridine in methanol than in water. It is interesting that solvation/desolvation has been proved not to influence the energetics of the halogen exchange reaction $[\text{Pt}(\text{PhSCH}_2\text{CH}_2\text{SPh})\text{X}_2] + \text{Y}^- \rightleftharpoons [\text{Pt}(\text{PhSCH}_2\text{CH}_2\text{SPh})\text{XY}] + \text{X}^-$ (X, Y = Cl, Br or I), in which, however, anionic nucleophiles are involved and the system moves along the reaction profile without changing the total charge.¹⁶

The lability of the pyridines from the first group of substrates is considerably lower than that of the sp^3 co-ordinated aniline, morpholine and piperidine (Fig. 2), strongly suggesting that, in addition to possible solvation effects, the Pt-N bond in the case of the pyridine derivatives may be reinforced by π bonding. The possibility for sp^2 nitrogen moieties to present π contribution in the Pt-N bond has been reported in a discussion of the IR and Raman spectra of platinum(II)-pyridine species²⁰ and in a structural study on platinum(II)-Schiff base complexes.²¹ The lower lability could be due, in principle, either to π back-donation from the filled orbitals of the metal to the antibonding orbitals of the ligand, leading to a relative stabilization of the ground state, or from repulsion between the π electrons of both metal and ligand which would increase the relative energy level of the transition state. However, a π repulsion effect would lead to a lower reactivity of these pyridines in the reaction of chloride displacement, compared to the sp^3 nitrogen donor bases of the first group. In spite of the fact that any effect would be minimized by the weakness of the Pt-N bond in the transition state, their reactivity responds to pK_a variations in the same way.

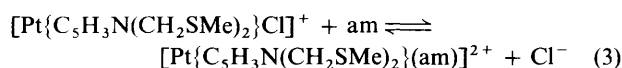
Another group includes the substrates with 4-cyanopyridine, 4-acetylpyridine and isonicotinic acid as the leaving groups. Compared with the first group these substrates show a small but significant decrease in reactivity corresponding to a difference of about 2 kJ mol^{-1} between the free activation energies of the reacting systems, which cannot be attributed to steric factors. The nature of the substituents in the 4 position is unlikely to change the solvation of the co-ordinated ligand significantly, but influences both the σ and π charge distribution in the ligand. For the former no difference has been found with all the other bases, the response to proton basicity being practically the same [$\log k_2^r = -(0.49 \pm 0.01) pK_a + \text{constant}$]. Such an increase in the free energy of activation must therefore be attributed to differences in the π interaction with the metal. Preliminary data dealing with a comparison of the lability of pyridines and thiazoles co-ordinated to platinum(II) substrates²² show that an almost equal response to proton basicity is accompanied by a remarkable difference in reactivity, again suggesting a significant role of π bonding in the

* 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.

interaction of platinum(II) with aromatic nitrogen heterocycles. Further investigations are in progress to examine the presence of anomalies in the ground state and to check the behaviour of these peculiar ligands in other platinum(II) systems.

The final group is formed by the hindered substrates containing 2-methylpyridine and 2,4-dimethylpyridine. The steric factor $\Delta \approx 0.57$ is nearly the same as that found in $[\text{Pt}(\text{PhSCH}_2\text{CH}_2\text{SPh})(\text{am})\text{Cl}]^+$ ($\Delta \approx 0.6$),¹ as already observed for the forward reactions. The steric retardation effect in the reverse reactions therefore confirms that the presence of two sulfur atoms or a sulfur and a chloride in the axial positions of the trigonal-bipyramidal transition state leads to a comparable amount of steric hindrance. The actual value of Δ , smaller for the reverse (0.57) than for the forward reaction (1.4), can be expected as a consequence of a partial compensation of steric hindrance in the ground and transition states for the nitrogen base displacement processes.

The ratio between the second-order rate constants for the forward and reverse reactions gives the corresponding equilibrium constants for the systems (3) and the actual values of K



at $I = 0.1 \text{ mol dm}^{-3}$ and K^0 at zero ionic strength are reported in Table 2.

The plot of $\log K^0$ versus $\text{p}K_a$ is linear for the group of pyridines formed by pyridine, 4-chloro-, 4-methyl- and 4-amino-pyridine and the free-energy relationship $\log K^0 = (0.66 \pm 0.01) \text{p}K_a + \text{constant}$ can be derived. As expected the corresponding value for 4-acetylpyridine is out of line indicating a greater stability of this species compared to the others, whereas the values for the hindered pyridines are relatively lower.

The dependence of the stability of the complexes upon the basicity of pyridines is higher (0.66) for the present bis-cationic substrates than that (0.58) measured with the mono-cationic substrates in the systems $[\text{Pt}(\text{PhSCH}_2\text{CH}_2\text{SPh})\text{Cl}_2] + \text{am} \rightleftharpoons [\text{Pt}(\text{PhSCH}_2\text{CH}_2\text{SPh})(\text{am})\text{Cl}]^+ + \text{Cl}^-$. However, the actual values of the equilibrium constants are lower than those found in the previous case. Such a difference, apart from the possible interference of the two *cis* sulfur donors compared to a single sulfur and a chloride, may reflect a greater tendency of Cl^- to neutralize the positive charge in the bis-cationic than in mono-cationic substrate.

Acknowledgements

We thank the Italian Ministry of University and Consiglio

Nazionale delle Ricerche (Rome) for financial support, Dr. S. Antoniutti for ^1H NMR measurements and Miss Tatiana Bobbo for technical assistance.

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Received 8th April 1994; Paper 4/02104E