Reactivity of Neutral Nitrogen Donors in Planar d^8 Metal Complexes. Part 1. The System [1,2-Bis(phenylsulfanyl)ethane]dichloroplatinum(II) with Pyridines in Methanol. Effect of Basicity and Steric Hindrance

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The kinetics of the forward and reverse steps of the process $[Pt(PhSCH_2CH_2SPh)Cl_2] + am \rightleftharpoons [Pt(PhSCH_2CH_2SPh)(am)Cl]^+ + Cl^-$ (am = one of a number of pyridines and other heterocyclic nitrogen bases 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^f, show only a slight dependence upon the nature of the entering pyridine, and steric hindrance due to the presence of one or two methyl groups in α position to the nitrogen markedly decreases the reactivity. The first- and second-order rate constants for the reverse reaction are very sensitive to the basicity of the leaving group and a plot of log k_2^r against the pK_a of the conjugate acids of unhindered pyridines is linear with a slope of −0.56. Steric retardation for monosubstituted α-methylpyridines is relatively small. The equilibrium constants for these reactions have been determined from the ratio of the rate constants and a plot of log K against the pK_a of the unhindered pyridines is linear with a slope of 0.58. The results are compared with data from the literature and discussed in terms of the reaction profile.

Neutral nitrogen donors (am) have seldom been investigated as nucleophiles towards planar four-co-ordinate d^8 metal complexes.[1] As far as platinum(II) substrates are concerned there are indications that proton basicity, as measured by the pK_a values of the donors, plays a minor role in determining the relative nucleophilicity, the major differences among reaction rates arising from steric retardation effects. However, there are cases[2,3] in which the reactivity increases linearly with the basicity of isosteric entering groups and others[4,5] where aromatic nitrogen donors, like pyridines, behave differently from aliphatic and/or alicyclic donors.

Less attention has been paid to the study of the relationship between the basicity and the substitution lability of co-ordinated nitrogen donors mainly because of the general inertness of the Pt–N bond toward substitution.[6] No systematic studies have been carried out, to our knowledge, to correlate this information to the charge of the substrate or to the nature of the non-participating ligands.

As studies on the role of basicity and steric effects in this type of reaction can provide a useful tool to understand the intimate asynchronous mechanism of substitution, we decided to make a systematic study of this aspect of ligand-substitution reactions. In this paper we report the kinetics of the forward and reverse steps of the process (1) in methanol at 25 °C and discuss the results in terms of both electronic and steric effects.

$$[Pt(PhSCH_2CH_2SPh)Cl_2] + am \rightleftharpoons [Pt(PhSCH_2CH_2SPh)(am)Cl]^+ + Cl^- \quad (1)$$

Experimental

Materials.—Platinum(II) chloride was obtained from Janssen Chimica. Pure reagent-grade $[NBu^n_4][ClO_4]$, $[NBu^n_4]Cl$ and $AgNO_3$ (Fluka and Aldrich) were dried over P_2O_5 in a vacuum desiccator and used without further purification. The pyridines and the other nitrogen donors were recrystallized or distilled before use when necessary.

Instruments.—Infrared spectra (4000–400 cm^{-1}, KBr discs; 400–200 cm^{-1}, polyethylene pellets) were recorded on a Perkin-Elmer 683 spectrophotometer. Electronic spectra were obtained and kinetic measurements made on a personal-computer-controlled Perkin-Elmer Lambda 16 spectrophotometer. Proton NMR spectra were recorded on a Bruker AC 200 F spectrometer and referred to tetramethylsilane. 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.

Preparation of 1,2-*Bis(phenylsulfanyl)ethane.*—This compound was prepared according to a published method[7] and its purity confirmed by elemental analysis, IR, UV/VIS and ^{1}H NMR spectra.

Preparation of Complexes.—Bis(benzonitrile)dichloroplatinum(II), $[Pt(PhCN)_2Cl_2]$, and $[Pt(PhSCH_2CH_2SPh)Cl_2]$ were prepared as reported.[8,9]

[1,2-*Bis(phenylsulfanyl)ethane*]*chloro(pyridine)platinum*(II) *nitrate*, $[Pt(PhSCH_2CH_2SPh)(py)Cl]NO_3$. Silver nitrate (0.170 g, 1 mmol) was added to a warm solution (60 °C) of $[Pt(PhSCH_2CH_2SPh)Cl_2]$ (0.512 g, 1 mmol) in dimethylformamide (dmf) (25 cm^3) and the mixture stirred in the dark for 30 min. The AgCl formed was filtered off and the solution treated with pyridine (0.079 g, 1 mmol) and stirred at 80 °C for 10 min. After cooling at room temperature, the crude product precipitated with diethyl ether was filtered off, washed twice with diethyl ether and dried under reduced pressure. Yield 0.42 g (70%).

All the other complexes of the type $[Pt(PhSCH_2CH_2SPh)(R\text{-}py)Cl]NO_3$ (R = 4-chloro, 2-methyl, 4-methyl, 2,4-dimethyl or 4-cyano) were prepared similarly.

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

Kinetics.—The reactions were followed (*a*) spectrophotometrically and/or (*b*) conductometrically.

Table 1 Analytical and physical data for the complexes

Complex	Analysis[a] (%) C	H	N	S	Colour	M.p. (°C)	Λ_M[b]/ Ω^{-1} cm^2 mol^{-1}	IR $\tilde{\nu}$(Pt–Cl)/cm^{-1}
$[Pt(PhSCH_2CH_2SPh)Cl_2]$[c]	32.8 (32.8)	2.75 (2.75)	—	12.1 (12.5)	Yellow	> 230	—	335, 320
$[Pt(PhSCH_2CH_2SPh)(NC_5H_4R)Cl]NO_3$								
R = H	35.6 (36.9)	3.20 (3.10)	4.75 (4.55)	—	Pale yellow	> 230	68	335
4-Cl[d]	33.0 (35.0)	2.80 (2.80)	4.15 (4.30)	—	Deep yellow	> 230	69	335
2-Me	36.4 (38.0)	3.40 (3.35)	4.45 (4.45)	9.60 (10.1)	Pale yellow	> 230	70	335
4-Me	37.1 (38.0)	3.45 (3.35)	4.70 (4.45)	9.45 (10.1)	Cream	> 230	71	335
2,4-Me$_2$	38.5 (39.0)	3.60 (3.60)	4.20 (4.35)	10.0 (9.95)	Cream	> 230	66	335
4-CN	36.8 (37.3)	3.00 (2.80)	7.00 (6.55)	9.30 (9.95)	Pale yellow	> 230	75	330

[a] Calculated values in parentheses. [b] In methanol at 25 °C. [c] ^{1}H NMR [$(CD_3)_2SO$, reference $SiMe_4$]: δ 3.14 (s, 4 H) and 7.30–8.09 (m, 10 H). [c] Cl 13.9 (13.8)%. [d] Cl 10.5 (10.9)%.

(*a*) *Spectrophotometric changes*. Reactions were initiated by adding a 0.05 mol dm^{-3} dmf solution (5–20 μl) of the substrate complex, $[Pt(PhSCH_2CH_2SPh)Cl_2]$ or $[Pt(PhSCH_2CH_2SPh)(am)Cl]^+$, to a methanolic solution (3 cm^3) of the appropriate reagent, the nitrogen donor or chloride ion respectively, 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. After preliminary repetitive scan experiments in the range 280–360 nm to search for isosbestic points and spectral changes, the kinetics was 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 $\log(A_t - A_\infty)$ *vs.* time or from a non-linear least-squares fit of experimental data by $A_t = A_\infty + (A_0 - A_\infty)\exp(-k_{obs}t)$ with A_0, A_∞ and k_{obs} as the parameters to be optimized (A_0 = absorbance after mixing of reactants, A_∞ = absorbance at completion of reaction).

(*b*) *Conductivity changes*. Reactions were initiated by adding a 0.05 mol dm^{-3} dmf solution (60 μl) of the substrate complex $[Pt(PhSCH_2CH_2SPh)Cl_2]$ to a methanolic solution (10 cm^3) of the appropriate nitrogen-donor reagent in the thermostatted cell of the conductivity meter (25 °C), under the pseudo-first-order conditions. The conductivity, initially nearly zero, increased with time, and the change followed a first-order rate law. Rate constants (k_{obs}/s^{-1}) were obtained either from the gradients of plots of $\log(\Lambda_t - \Lambda_\infty)$ *vs.* time or from a non-linear least-squares fit of experimental data to $\Lambda_t = \Lambda_\infty + (\Lambda_0 - \Lambda_\infty)\exp(-k_{obs}t)$ with Λ_0, Λ_∞ and k_{obs} as the parameters to be optimized (Λ_0 = conductivity after mixing of reactants, Λ_∞ = conductivity at completion of reaction).

Results

Kinetics of Displacement of Chloride by Nitrogen Donors from $[Pt(PhSCH_2CH_2SPh)Cl_2]$.—The spectrophotometric changes observed in repetitive scanning of the spectrum of the reaction mixture are characteristic of a single chemical stage, with well maintained isosbestic points. Careful examination of the spectral changes (subsequent changes have never been observed) which occur after the reagents are mixed and the close similarity of the spectra at the end of the reaction with those of authentic samples of the expected reaction product demonstrate that all the reactions that have been studied kinetically involve the displacement of co-ordinated chloride by the nitrogen base. The rate constants were determined in the usual way from the change in absorbance as a function of time at a convenient wavelength within the region 310–330 nm. The products of some substitution reactions were not independently synthesised and characterized, but the general similarity of the spectral changes indicated that the same type of reaction was being observed. When am = 4-aminopyridine, morpholine, quinoline, 2-methylquinoline, 2,6-dimethylpyridine or 2,4,6-trimethylpyridine, the reactions were studied kinetically from the change in conductivity as a function of time and in any case the conductivity values at the end of reaction (Λ_∞) were typical of 1 : 1 electrolytes in methanol. The reactions with 4-methylpyridine were followed with both methods and the measured rate constants are in close agreement. All the reactions were studied in the presence of a sufficient excess of nucleophile over the substrate to provide pseudo-first-order conditions and the observed rate constants, k_{obs}, collected in Table 2, obey the general relationship $k_{obs} = k_1^f + k_2^f[am]$, which is usual for nucleophilic substitution at planar four-co-ordinate d^8 metal complexes.[10] The spectral intervals used, the isosbestic points characteristic of the stage, the conditions of measurements as well as the values of k_1^f and k_2^f are summarized in Table 4.

Kinetics of Displacement of Nitrogen Donors by Chloride from $[Pt(PhSCH_2CH_2SPh)(am)Cl]^+$.—In all the reactions with an excess of chloride ion the spectrophotometric changes are characteristic of a single chemical stage, with the same isosbestic points as those observed for the reverse reactions. The spectra at the end of the reaction coincide with those of authentic samples of the expected products $[Pt(PhSCH_2CH_2SPh)Cl_2]$ + Ham$^+$ at the same concentration, so that the displacement of co-ordinated nitrogen donor by chloride is assured. This confirms that the presence of the S-bonded thioether chelate ligand provides sufficient *trans*-labilizing power for it to be possible to observe the displacement of the *trans* N-donor by a rather poor nucleophile like chloride. The reactions were studied in the presence of 0.01 mol dm^{-3} $HClO_4$ at constant ionic strength (I = 0.1 mol dm^{-3}, $[NBu^n{}_4][ClO_4]$). Preliminary experiments had shown that, at constant chloride concentration, the rate of reaction was independent of the concentration of acid over the range 0.005–0.020 mol dm^{-3}. The acid serves simply to protonate the released am and to prevent the reverse reaction. The observed rate constants, k_{obs}, collected in Table 3, obey the general relationship $k_{obs} = k_1^r + k_2^r[Cl]$, where k_1^r and k_2^r have the usual meaning and their values at I = 0.1 mol dm^{-3} are reported in Table 4 together with the corresponding values $k^0{}_2{}^r$ extrapolated to zero ionic strength. The extrapolation to zero ionic strength uses the Debye–Huckel relationship, $\log k^0{}_2{}^r$ =

Table 2 First-order rate constants, k_{obs}, for the reaction $[Pt(PhSCH_2CH_2SPh)Cl_2] + am \longrightarrow [Pt(PhSCH_2CH_2SPh)(am)Cl]^+ + Cl^-$ in methanol at 25 °C

am	[am]/mol dm^{-3}	$10^3k_{obs}/s^{-1}$
4-Aminopyridine *	0.0035	2.48 ± 0.03
	0.0050	3.25 ± 0.05
	0.0075	4.32 ± 0.06
	0.0100	5.40 ± 0.07
	0.0125	6.53 ± 0.08
	0.0150	7.78 ± 0.06
	0.0200	10.04 ± 0.05
	0.0250	12.25 ± 0.07
4-Cyanopyridine	0.0035	3.10 ± 0.09
	0.0050	3.57 ± 0.06
	0.0065	4.02 ± 0.07
	0.0080	4.2 ± 0.1
	0.0095	4.70 ± 0.07
	0.0120	5.32 ± 0.05
	0.0150	6.1 ± 0.2
	0.0200	7.4 ± 0.1
Pyridine	0.003	1.68 ± 0.02
	0.005	2.24 ± 0.03
	0.007	2.82 ± 0.02
	0.010	3.60 ± 0.02
	0.012	4.18 ± 0.03
	0.015	5.12 ± 0.02
	0.018	5.95 ± 0.04
	0.020	6.44 ± 0.05
Morpholine *	0.0035	3.66 ± 0.06
	0.0050	4.46 ± 0.09
	0.0075	5.32 ± 0.02
	0.0100	6.16 ± 0.05
	0.0125	7.2 ± 0.3
	0.0150	8.15 ± 0.04
	0.0200	10.1 ± 0.1
	0.0250	12.3 ± 0.1
Quinoline *	0.025	1.25 ± 0.02
	0.050	1.61 ± 0.01
	0.100	2.22 ± 0.01
	0.150	2.97 ± 0.03
	0.200	3.53 ± 0.04
	0.250	4.21 ± 0.05
	0.300	4.87 ± 0.04
2-Methylpyridine	0.055	1.40 ± 0.03
	0.103	1.70 ± 0.04
	0.153	2.22 ± 0.03
	0.256	3.0 ± 0.1
	0.358	3.89 ± 0.04
	0.511	5.1 ± 0.1
	0.652	6.4 ± 0.2
2,4-Dimethylpyridine	0.012	1.06 ± 0.02
	0.050	1.50 ± 0.04
	0.080	1.78 ± 0.04
	0.100	2.0 ± 0.1
	0.125	2.23 ± 0.05
	0.150	2.52 ± 0.4
	0.200	3.06 ± 0.2
3-Methylpyridine	0.0015	1.52 ± 0.05
	0.0030	2.04 ± 0.02
	0.0045	2.62 ± 0.03
	0.0060	3.26 ± 0.02
	0.0075	3.80 ± 0.03
	0.0090	4.42 ± 0.03
	0.0105	4.91 ± 0.02
	0.0120	5.45 ± 0.04
4-Methylpyridine *	0.003	2.02 ± 0.07
	0.004	2.28 ± 0.05
	0.007	3.32 ± 0.05
	0.010	4.43 ± 0.04
	0.015	6.12 ± 0.05
	0.020	7.8 ± 0.1
	0.025	9.45 ± 0.04
4-Methylpyridine	0.003	1.99 ± 0.04
	0.004	2.24 ± 0.02
	0.006	2.96 ± 0.03
	0.007	3.21 ± 0.02
	0.009	3.99 ± 0.01
	0.010	4.40 ± 0.03
	0.015	5.99 ± 0.04
	0.020	7.68 ± 0.05
	0.025	9.38 ± 0.03
2-Methylquinoline *	0.05	1.06 ± 0.03
	0.20	1.1 ± 0.1
	0.50	1.2 ± 0.1
	0.75	1.25 ± 0.07
	1.00	1.31 ± 0.02
	1.25	1.39 ± 0.04
	1.50	1.48 ± 0.04
	2.00	1.6 ± 0.1
	3.00	1.88 ± 0.05
2,6-Dimethylpyridine *	0.05	1.03 ± 0.03
	0.10	1.06 ± 0.04
	0.20	1.1 ± 0.1
	0.40	1.25 ± 0.02
	0.60	1.35 ± 0.04
	0.80	1.47 ± 0.02
	1.00	1.57 ± 0.02
2,4,6-Trimethylpyridine *	0.05	1.38 ± 0.03
	0.10	1.41 ± 0.02
	0.30	1.51 ± 0.01
	0.50	1.67 ± 0.02
	1.30	2.18 ± 0.04
	1.80	2.59 ± 0.05
	2.40	2.93 ± 0.07
	3.00	3.22 ± 0.08

* Conductivity measurements.

$\log k_2{}^r - 2\alpha Z_aZ_bI^{\frac{1}{2}}/(1 + \beta I^{\frac{1}{2}})$ with $Z_a = +1$, $Z_b = -1$, $\alpha = 1.90$ and $\beta = 1.55$ (estimated from the relative permittivity of methanol at 25 °C).[11] The rate of processes between the neutral platinum(II) substrates and the nitrogen donor is not influenced by primary salt effects, whereas that of the reverse reactions between the cationic species and chloride ion depends upon ionic strength. As a consequence, also the equilibrium constants, K, depend upon ionic strength and in Table 4 are reported the values $K = k_2{}^f/k_2{}^r$ and $K^0 = k_2{}^f/k^0{}_2{}^r$ determined from the ratios of the second-order rate constants for the forward and reverse reactions.

Discussion

The complex $[Pt(PhSCH_2CH_2SPh)Cl_2]$ can exist in two isomeric forms, depending on the projection of the SPh groups on the same (*meso* isomer) or different sides (DL isomer) of the chelate ring. In the present case, as well as in the previous work

Table 3 First-order rate constants, k_{obs}, for the reaction $[Pt(PhSCH_2CH_2SPh)(am)Cl]^+ + Cl^- \longrightarrow [Pt(PhSCH_2CH_2SPh)Cl_2] + am$ in methanol at 25 °C (I = 0.1 mol dm^{-3}, $[NBu^n{}_4][ClO_4]$; 0.01 mol dm^{-3} $HClO_4$)

am	$[Cl^-]$/mol dm^{-3}	10^3k_{obs}/s^{-1}	am	$[Cl^-]$/mol dm^{-3}	10^3k_{obs}/s^{-1}
4-Cyanopyridine	0.003	4.26 ± 0.04	4-Methylpyridine	0.005	0.047 ± 0.003
	0.004	5.01 ± 0.05		0.010	0.077 ± 0.001
	0.006	6.92 ± 0.05		0.015	0.101 ± 0.003
	0.008	8.56 ± 0.08		0.020	0.120 ± 0.001
	0.010	10.50 ± 0.02		0.030	0.173 ± 0.001
	0.015	14.8 ± 0.1		0.040	0.220 ± 0.002
	0.020	19.3 ± 0.2		0.050	0.273 ± 0.001
	0.025	23.9 ± 0.1			
4-Chloropyridine	0.005	0.95 ± 0.03	2-Methylpyridine	0.02	0.023 ± 0.001
	0.010	1.50 ± 0.02		0.04	0.043 ± 0.001
	0.015	2.08 ± 0.02		0.05	0.056 ± 0.006
	0.020	2.61 ± 0.02		0.07	0.073 ± 0.005
	0.030	3.84 ± 0.03		0.09	0.095 ± 0.007
	0.040	4.95 ± 0.04		0.10	0.105 ± 0.001
	0.050	6.10 ± 0.06			
Pyridine	0.010	0.17 ± 0.02	2,4-Dimethylpyridine	0.02	0.0068 ± 0.0005
	0.010	0.19 ± 0.03		0.04	0.0181 ± 0.0003
	0.020	0.28 ± 0.02		0.06	0.0244 ± 0.0006
	0.025	0.35 ± 0.01		0.08	0.0348 ± 0.0004
	0.030	0.40 ± 0.01		0.10	0.0372 ± 0.0002
	0.030	0.41 ± 0.01			
	0.050	0.66 ± 0.03			
	0.070	0.91 ± 0.01			

in which all the mutual interconversions of the $[Pt(PhSCH_2CH_2SPh)X(Y)]$ species (X, Y = Cl, Br or I) were examined,[9] the solid-state structure of crystalline $[Pt(PhSCH_2CH_2SPh)Cl_2]$, obtained on slow cooling at room temperature of a hot dmf–water solution of the crude product shows it to be the DL isomer.[12]

All the reaction mixtures used for the present kinetic study were prepared by dissolving the crystalline product in dmf at room temperature and, considering the rather high temperature for sulfur inversion of platinum(II) complexes of this type,[13] any isomerization process appears unlikely. Accordingly, the ^1H NMR spectrum of crystalline $[Pt(PhSCH_2CH_2SPh)Cl_2]$ in $(CD_3)_2SO$ solution indicates the presence of the DL isomer only and the kinetics of chloride substitution obeys a single monoexponential rate law.

The only reaction occurring between nitrogen donors and $[Pt(PhSCH_2CH_2SPh)Cl_2]$ in methanol at 25 °C is the displacement of a chloride ligand. It is known[9] that, under the same experimental conditions, the substrate undergoes chloride displacement upon reaction with anionic nucleophiles like Br^- and I^-. However, with a number of pyridines in 1,2-dimethoxyethane at the same temperature, ring opening followed by substitution of the chelating sulfur ligand occurs[14] instead of chloride substitution, showing that the nature of the solvent plays an important role in determiming the course of the reaction.

The chloride displacement reactions (2) obey the two-term

$$[Pt(PhSCH_2CH_2SPh)Cl_2] + am \longrightarrow [Pt(PhSCH_2CH_2SPh)(am)Cl]^+ + Cl^- \quad (2)$$

rate equation, $k_{obs} = k_1{}^f + k_2{}^f[am]$, usually found in substitutions at platinum(II) complexes. The $k_1{}^f$ term, referring to the pathway in which the rate-determining step is nucleophilic attack of the solvent followed by rapid entry of am into the solvento-complex,[1] is obviously independent of the nature of the amine so that $k_1{}^f$ is the same [(0.97 ± 0.06) × 10^{-3} s^{-1}] in all the reactions within the limit of experimental errors. This value is also comparable to that determined for replacement of chloride by bromide and iodide ions, under the same experimental conditions.[9] The only exception amongst pyridines is represented by the reaction with 4-cyanopyridine, having a relatively higher $k_1{}^f$ value [(2.24 ± 0.05) × 10^{-3} s^{-1}]. This can probably be related to the low basicity of 4-cyanopyridine so that its reactivity towards the solvento-intermediate is decreased, as found in other cases with entering groups of low nucleophilicity.[5]

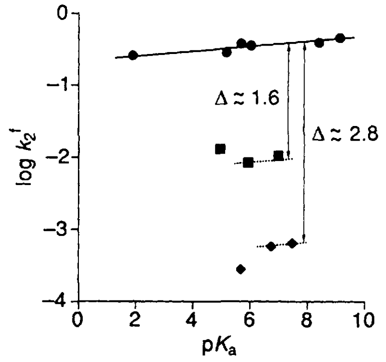

Fig. 1 Plots of log $k_2{}^f$ for the reaction $[Pt(PhSCH_2CH_2SPh)Cl_2] + am \longrightarrow [Pt(PhSCH_2CH_2SPh)(am)Cl]^+ + Cl^-$ against pK_a of Ham^+: (●), morpholine, pyridine and *para*-substituted pyridines; (■), quinoline, 2-methyl- and 2,4-dimethyl-pyridine; (◆), 2-methylquinoline, 2,6-dimethyl- and 2,4,6-trimethyl-pyridine

The $k_2{}^f$ values depend both on the electronic and steric features of the nucleophile, as expected for an associative process. A plot of log $k_2{}^f$ *vs.* the basicity of am, as usually measured by the pK_a values of the conjugate acids Ham^+ in water at 25 °C,[15] allows the nucleophiles to be separated into three groups (Fig. 1). The first group is formed by the five isosteric *para*-substituted pyridines, covering a pK_a range from 1.9 to 9.11. The entry of these nucleophiles obeys a linear-free-energy relationship of the type (3) with α = 0.035 ± 0.009

$$\log k_2{}^f = \alpha(pK_a) + \text{constant} \quad (3)$$

which measures the ability of the substrate to discriminate among entering nitrogen donors of different basicity having the same form of hindrance.[6] Also morpholine, the steric requirements of which are not very different from that of

Table 4 First- and second-order rate constants[a] and equilibrium constants for the reaction $[\mathrm{Pt(PhSCH_2CH_2SPh)Cl_2}] + \mathrm{am} \underset{k_1^r + k_2^r[\mathrm{Cl^-}]}{\overset{k_1^f + k_2^f[\mathrm{am}]}{\rightleftharpoons}} [\mathrm{Pt(PhSCH_2CH_2SPh)(am)Cl}]^+ + \mathrm{Cl^-}$ in methanol at 25 °C

am	λ/nm		$10^3k_1^f$/ $\mathrm{s^{-1}}$	$10^3k_2^f$/ $\mathrm{dm^3\ mol^{-1}\ s^{-1}}$	$10^3k_1^{r\,b}$/ $\mathrm{s^{-1}}$	$10^3k_2^{r\,b}$/ $\mathrm{dm^3\ mol^{-1}\ s^{-1}}$	$10^3k^0{}_2^r$/ $\mathrm{dm^3\ mol^{-1}\ s^{-1}}$	$K = k_2^f/k_2^r$	$K^0 = k_2^f/k^0{}_2^r$	$\mathrm{p}K_a$ of $\mathrm{Ham^+}$
	Isosbestic point	Used for calculations								
4-Cyanopyridine	322	310	2.24 ± 0.05	257 ± 4	1.55 ± 0.07	887 ± 7	5680	0.289 ± 0.005	0.045	1.90
4-Chloropyridine	310	320			0.36 ± 0.02	115 ± 1	737			3.84
Pyridine	309	330	0.82 ± 0.03	283 ± 3	0.047 ± 0.008	12.2 ± 0.2	78.1	23.2 ± 0.5	3.62	5.17
3-Methylpyridine	309	320	0.94 ± 0.03	379 ± 4						5.68
4-Methylpyridine[c]			0.97 ± 0.03	341 ± 2						6.03
4-Methylpyridine	308	320	0.93 ± 0.03	338 ± 3	0.024 ± 0.002	4.94 ± 0.07	31.6	68 ± 1	10.7	6.03
4-Aminopyridine[c]			0.91 ± 0.04	454 ± 3						9.11
Morpholine[c]			2.32 ± 0.08	393 ± 6						8.33
Quinoline[c]			0.94 ± 0.03	13.1 ± 0.1						4.95
2-Methylpyridine	311	320	0.90 ± 0.04	8.4 ± 0.1	0.003 ± 0.001	1.02 ± 0.02	6.53	8.2 ± 0.5	1.29	5.94
2,4-Dimethylpyridine	311	320	0.95 ± 0.02	10.4 ± 0.2	0.001 ± 0.003	0.39 ± 0.04	2.50	27 ± 3	4.16	6.99
2-Methylquinoline[c]			1.05 ± 0.01	0.278 ± 0.004						5.69
2,6-Dimethylpyridine[c]			1.00 ± 0.01	0.58 ± 0.01						6.75
2,4,6-Trimethylpyridine[c]	308	320	1.35 ± 0.02	0.65 ± 0.02						7.48

[a] Determined by weighted linear regression of k_{obs} values *vs.* nucleophile concentration. [b] $I = 0.1\ \mathrm{mol\ dm^{-3}}$, $[\mathrm{NBu^n{}_4}][\mathrm{ClO_4}]$; $0.01\ \mathrm{mol\ dm^{-3}}\ \mathrm{HClO_4}$. [c] Conductivity measurements for the forward reactions.

pyridine, can be considered to belong to this group, at least to a first approximation, and it seems that in these processes π-back donation from the filled d orbitals of the metal to antibonding orbitals of the aromatic ring of pyridine, even if theoretically possible, does not contribute significantly to bond formation.

As found in other planar four-co-ordinate systems,[6] a second group is formed by pyridines having a methyl group *ortho* to the nitrogen (2-methyl- and 2,4-dimethylpyridine in the present case), to which quinoline may be also added, at least to a first approximation. The steric retardation, typical for associative processes, can be measured by the value of $\Delta \approx 1.6$ (Fig. 1). Pyridines with two *o*-methyl substituents (2,6-dimethyl- and 2,4,6-trimethylpyridine and possibly 2-methylquinoline) form the third group with steric retardation $\Delta \approx 2.8$ with respect to unhindered 4-substituted pyridines (Fig. 1).

The parameters α and Δ, together with the rate of entry of pyridine [k_2^f(py) = 0.283 dm^3 mol^{-1} s^{-1}], which can be assumed as the typical nucleophile for this class of reagents, characterize the system of reactions considered.

The entry of pyridine (and solvent) can be compared with the substitution of chloride by Br$^-$ and I$^-$ (k_2 = 7.22 × 10^{-3} and 0.304 dm^3 mol^{-1} s^{-1} respectively) measured under the same experimental conditions.[9] Whereas the n^0_{Pt} nucleophilicity scale[16] would lead to a reactivity sequence I$^-$ > Br$^-$ ≫ pyridine > MeOH, the results show that the k_2^f value for pyridine is comparable to that of iodide (0.283 and 0.304 dm^3 mol^{-1} s^{-1} respectively) and also the solvent, MeOH, is more reactive as expected (k_1^f = 9.7 × 10^{-4} s^{-1}). Such an anomaly, already reported for substrates containing ligands of high *trans* effect,[17] seems to be related to the presence of a thioether sulfur atom *trans* to the leaving group, and it has been observed also with the parent compound [Pt(MeSCH$_2$CH$_2$SMe)Cl$_2$],[18] whereas it is not present with substrates like [Pt(en)(Me$_2$S)Cl]$^+$ (en = ethane-1,2-diamine)[19] and [2,6- bis(methylsulfanylmethyl)-pyridine]chloroplatinum(II) cations,[20] having one or two thioether sulfur atoms *cis* to the leaving group. However, it would be necessary to extend this type of study over a much wider range of nucleophiles before any firm conclusions could be drawn.

The substrate [Pt(bipy)Cl$_2$] (bipy = 2,2′-bipyridine) reacts with amines with k_2(py) = 0.0115 dm^3 mol^{-1} s^{-1}, α = 0.06 and Δ = 1.0.[2] The relatively larger reactivity of the present compound containing the chelating thioether can be probably attributed to a combination of a (*trans* + *cis*)-labilizing effect of the sulfur donors, expected to be somewhat larger than that of nitrogen donors, as found for the reactions of the same substrates with ionic nucleophiles.[9] The discrimination ability of [Pt(PhSCH$_2$CH$_2$SPh)Cl$_2$] is less than that of [Pt(bipy)Cl$_2$], suggesting a lower electrophilicity of the former reaction centre as compared to the latter. Both values (0.035 and 0.06) however are relatively low as compared to data for other reaction centres [*e.g.* for cationic gold(III) substrates values of α up to 0.89 have been reported],[21] indicating again that proton basicity plays a minor role in determining the reactivity of these processes.

Another substrate which has been studied under the same experimental conditions is the neutral N,N′ chelate complex [Pt{Ph(Me)NN=C(Me)C(Me)=NN(Me)Ph}Cl$_2$],[3] for which k_2(py) = 0.73 dm^3 mol^{-1} s^{-1} and α = 0.05. The relatively large reactivity was attributed to hydrogen-bonding assistance to the leaving chloride in the transition state, and the ability to discriminate among different amines is very small indeed.

A different behaviour has been reported for the anionic substrate [Pt(dmso)Cl$_3$]$^-$ reacting with nitrogen donors (am) to form the neutral complexes *trans*-[Pt(dmso)(am)Cl$_2$] (dmso = dimethyl sulfoxide).[4] In this case the reactivity is relatively high, as expected for the moderate *trans*-labilizing effect of dmso, and steric retardation effects have not been studied, but a discrimination factor of about 0.13 can be evaluated for primary and secondary amines, whereas the reactivity of pyridines seems to decrease slightly on increasing their proton basicity. Similar trends have been observed with the anionic substrate [Pt(Me$_2$S)Cl$_3$]$^-$.[5] This anomalous behaviour may perhaps be due to some π interaction between the filled d metal orbitals and the antibonding orbitals of the aromatic ligands, as a consequence of the negative charge of the trigonal-bipyramidal transition state and/or the simultaneous presence of π-bonded sulfur in the trigonal plane. The role of the total charge in this class of processes is known to be important in gold(III) substitution reactions,[21] but not enough data are available for platinum(II) complexes.

It has been already mentioned that when the solvent is 1,2-dimethoxyethane the substrate [Pt(PhSCH$_2$CH$_2$SPh)Cl$_2$], on reacting with pyridines, undergoes ring opening instead of chloride substitution and the corresponding parameters are α = 0.14 and Δ = 1.6.[14] In both cases in the trigonal-bipyramidal transition state an S, Cl pair of ligands will lie in the trigonal plane, together with the entering nitrogen donor, am. The different course of the reaction seems then to be controlled by the solvation of the leaving group in the transition state, methanol thus leading to chloride substitution and dimethoxyethane to ring opening.

The steric retardation due to the interaction between the *o*-methyl group(s) in the pyridine ring and the axial non-participating ligands in the trigonal-bipyramidal transition state is much the same in the two processes. On the contrary, the reactivity is nearly two orders of magnitude smaller for ring opening than for chloride substitution and the discrimination among the entering amines somewhat larger. This seems to suggest that, when the reagents are allowed to react in methanol, a relatively small degree of bond formation between the metal and the incoming nitrogen is required to form the transition state and to promote the release of solvated chloride ion in methanol. In 1,2-dimethoxyethane, however, the interaction with the solvent is less efficient in assisting a leaving chloride, the Pt–N bond is more substantially formed and ring opening occurs.

Bearing in mind that the forward and reverse reactions must proceed along the same reaction profile, a kinetic study of the reverse processes can provide further information on the transition state. The data reported in Table 4 for the kinetics of the processes (4) show that the rate of substitution decreases on

$$[\mathrm{Pt(PhSCH_2CH_2SPh)(am)Cl}]^+ + \mathrm{Cl}^- \longrightarrow [\mathrm{Pt(PhSCH_2CH_2SPh)Cl_2}] + \mathrm{am} \quad (4)$$

increasing basicity of the displaceable pyridine. This is clearly evident for the second-order rate constants k_2^r, but also observable for the first-order rate constants k_1^r relative to the solvolytic processes.

A plot of log k_2^r *vs.* pK_a is linear (Fig. 2) for unhindered pyridines, with a slope of −0.56 ± 0.04. Steric retardation for monosubstituted 2-methylpyridines is relatively small ($\Delta \approx 0.6$), whereas the reactivity of substrates containing disubstituted 2,6-dimethylpyridines is too small to allow a proper measure. It may be pointed out that, if steric retardation due to hindrance of the entering nucleophiles is obvious and expected in associative processes, the same is not necessarily true when the hindrance lies with the displaceable ligand. The presence of sterically hindered groups in the substrate can shield to some extent the approach of the nucleophile and, in a limiting case, prevent the associative second-order process ('pseudo-octahedral complexes').[22] On the contrary, in dissociative processes, steric acceleration can be expected.[10]

However, since steric destabilization can affect the energy levels of both the ground and transition states, a certain amount of mutual compensation can be expected, so that the steric effects in the displacement of pyridines should be less than in their entry. A limiting case of the complete absence of steric effects has been reported for the displacement of pyridines (L) from the gold(III) substrates [AuLCl$_3$].[23]

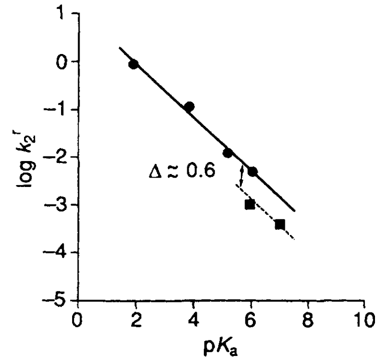

Fig. 2 Plots of log k_2^r for the reaction $[Pt(PhSCH_2CH_2SPh)(am)Cl]^+ + Cl^- \longrightarrow [Pt(PhSCH_2CH_2SPh)Cl_2] + am$ against pK_a of Ham^+: (●), pyridine and *para*-substituted pyridines; (■), 2-methyl- and 2,4-dimethyl-pyridine

In the present case the relatively large dependence of substitution lability upon ligand basicity suggests that the formation of the transition state requires a considerable change in the Pt–N bond, confirming therefore the observation reported above that the transition state can be described as a structure containing a well formed Pt–Cl and a weak Pt–N bond.

In the reactions[4] (5) the reactivity is smaller than that for

$$trans\text{-}[Pt(dmso)(am)Cl_2] + Cl^- \longrightarrow [Pt(dmso)Cl_3]^- + am \quad (5)$$

the systems reported here (second-order rate constants for the displacement of pyridine being 1.96×10^{-4} and 1.22×10^{-2} dm^3 mol^{-1} s^{-1} respectively) thus indicating that the *trans*-labilizing effect of dmso combined with the *cis* effect of chloride is not as efficient as the (*trans* + *cis*)-labilizing effect of the two sulfur atoms (bearing in mind that the different charge of the substrates can also play a role). The dependence of the reactivity upon the basicity of the leaving group is however surprisingly similar (−0.55 *vs.* −0.56). Data for the displacement of different pyridines from *trans*-$[Pt(Me_2S)(am)Cl_2]$ by chloride are unfortunately not available.

It is finally to be noted that in the case of 4-cyanopyridine the equilibrium constant at $I = 0.1$ mol dm^{-3} is less than 1 which may also be related to the anomaly in the k_1 value reported above.

The linear-free-energy relationship between log K for the equilibria (1) and the pK_a of the unhindered pyridines, log $K = 0.58(pK_a)$ + constant, provides a clear example of the influence of the σ-donor ability of the heterocyclic bases upon the stability of these platinum(II) complexes.

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