Nucleophilic Displacement of Halides from Monocationic Platinum(II) Complexes containing Neutral Tridentate Chelating Ligands with Sulfur and Nitrogen Donors: Kinetics and Equilibria

Bruno Pitteri,* Giampaolo Marangoni, Lucio Cattalini and Tatiana Bobbo
Dipartimento di Chimica, Università di Venezia, Calle Larga S. Marta 2137, 30123–Venezia, Italy

Kinetic and equilibrium measurements on the displacement of halides from the substrates $[Pt(L)X]^+$ [L = diethylenetriamine, 2,6-bis(methylsulfanylmethyl)pyridine, bis(2-pyridylmethyl) sulfide or 2,2′:6′,2″-terpyridine, X = Cl, Br or I] with the nucleophiles Cl^-, Br^- and I^- have been carried out in methanol at 25 °C and constant ionic strength. The results are discussed in terms of the relative stability of the planar ground and five-co-ordinate transition states. The significant differences in kinetic behaviour along the series are related to the presence of π-interacting pyridine rings as well as to the nature of the donor atoms *trans* and *cis* to the replaceable halogen. The equilibrium parameters, the leaving-group effect and the intimate mechanism are also discussed and compared with literature data.

In a recent paper[1] we reported some kinetic results showing that aromatic nitrogen donors are capable of significant π-bonding interactions with Pt^{II} when acting as leaving groups in nucleophilic substitution reactions. In order to gain further evidence on the nature of these Pt–N bonds and quantitative information on the kinetic and thermodynamic behaviour of comparable systems, we decided to study the reactions (1)

$$[Pt(L)X]^+ + Y^- \rightleftharpoons [Pt(L)Y]^+ + X^- \qquad (1)$$

{X = Cl, Br or I; Y = Cl, Br or I; L = diethylenetriamine$[NH(CH_2CH_2NH_2)_2]$,2,6-bis(methylsulfanylmethyl)pyridine $[NC_5H_3(CH_2SMe)_2]$, bis(2-pyridylmethyl) sulfide $[(NC_5H_4CH_2)_2S]$ or 2,2′:6′,2″-terpyridine (terpy)} in which L is a tridentate ligand containing zero, one, two and three pyridine rings, forced by chelation to lie in the square-planar co-ordination plane[2–4] and thus favouring the interaction of the empty π aromatic orbitals with the filled d_{xz} and d_{yz} orbitals of the metal. The approach employed was that previously used for kinetic and equilibrium measurements on the displacement of halides from the neutral platinum(II) substrates $[Pt(PhSCH_2CH_2SPh)X(Y)]$ $[PhSCH_2CH_2SPh$ = 1,2-bis(phenylsulfanyl)ethane; X, Y = Cl, Br or I],[5] which allows comparison of the relative stability of the ground and transition states.

Experimental

Instruments.—Infrared spectra (4000–250 cm^{-1}, KBr discs; 250–150 cm^{-1}, polyethylene pellets) were recorded on a Nicolet Magna FT IR 750 spectrophotometer. Electronic spectra, kinetics and equilibria were measured with a Perkin-Elmer Lambda 16 spectrophotometer. Proton 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.

Materials.—Platinum(II) chloride, diethylenetriamine, and 2,2′:6′,2″-terpyridine were obtained from Janssen Chimica and Aldrich. Pure reagent-grade $LiClO_4$, LiBr, LiCl, LiI and NaO_3SMe (Fluka and Aldrich) were dried over P_2O_5 in a vacuum desiccator and used without further purification. The other reagents were of AR quality and 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.

2,6-Bis(methylsulfanylmethyl)pyridine and bis(2-pyridylmethyl) sulfide were prepared according to published methods[6,7] and their purity confirmed by elemental analysis, UV/VIS and ^1H NMR spectra.

Preparation of the Complexes.—The complexes $[Pt\{NC_5H_3(CH_2SMe)_2\}X]ClO_4$ (X = Cl, Br or I); and $[Pt\{(NC_5H_4CH_2)_2S\}X]ClO_4$ (X = Cl, Br or I) were prepared as reported previously and their purity monitored by elemental analysis, IR, UV/VIS and ^1H NMR spectra and conductivity measurements.[6,8]

Chloro(diethylenetriamine)platinum(II) *perchlorate*, $[Pt\{NH(CH_2CH_2NH_2)_2\}Cl]ClO_4$. This compound was obtained from a concentrated boiling aqueous solution of $[Pt\{NH(CH_2CH_2NH_2)_2\}Cl]Cl$ (prepared as reported[9]) containing an excess of $LiClO_4$, slowly cooled at room temperature. Yield = 80% (Found: C, 11.1; H, 3.10; Cl, 16.0; N, 9.60. $C_4H_{13}Cl_2N_3O_4Pt$ requires C, 11.1; H, 3.05; Cl, 16.4; N, 9.70%).

Bromo- and iodo-(diethylenetriamine)platinum(II) *perchlorate*, $[Pt\{NH(CH_2CH_2NH_2)_2\}X]ClO_4$ (X = Br *or* I). Stoichiometric amounts of either LiBr or LiI were added under stirring to warm and concentrated aqueous solutions of $[Pt\{NH(CH_2CH_2NH_2)_2\}Cl]Cl$. After 30 min 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 products, which were filtered off, washed with acetone, diethyl ether and dried *in vacuo*. Yield = 90% (Found: C, 10.0; H, 2.70; N, 8.70. $C_4H_{13}BrClN_3O_4Pt$ requires C, 10.1; H, 2.75; N, 8.80%). Yield = 75% (Found: C, 9.30; H, 2.40; N, 8.15. $C_4H_{13}ClIN_3O_4Pt$ requires C, 9.15; H, 2.50; N, 8.00%).

Chloro(2,2′:6′,2″-terpyridine)platinum(II) *chloride dihydrate*, $[Pt(terpy)Cl]Cl{\cdot}2H_2O$. This compound was prepared as previously reported.[9] The chloro-, bromo- and iodo-derivatives were obtained as perchlorates following the same procedure used for the synthesis of the diethylenetriamine derivatives. Yield = 70% (Found: C, 32.1; H, 2.05; Cl, 12.3; N, 7.30. $C_{15}H_{11}Cl_2N_3O_4Pt$ requires C, 32.0; H, 1.95; Cl, 12.6; N, 7.45%). Yield = 80% (Found: C, 30.0; H, 1.90; N, 6.90. $C_{15}H_{11}BrClN_3O_4Pt$ requires C, 29.7; H, 1.85; N, 6.90%). Yield = 90% (Found: C, 27.9; H, 1.70; N, 6.55. $C_{15}H_{11}ClIN_3O_4Pt$ requires C, 27.5; H, 1.70; N, 6.40%).

The purity of the new complexes was also monitored by IR, UV/VIS and conductivity measurements.

Kinetics.—The reactions were followed spectrophotometrically by measuring the changing absorbance at suitable wavelengths as a function of time and were initiated by adding 1–60 μl of a 0.004 mol dm^{-3} dimethylformamide solution of the substrate to a methanolic solution (3 cm^3) of the appropriate nucleophile (Cl^-, Br^- or I^-) 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. All the reactions were measured at constant ionic strength $I = 0.5$ mol dm^{-3} ($LiClO_4$) or, in the case of terpyridine complexes, at $I = 0.1$ mol dm^{-3} (NaO_3SMe). The kinetics of the substrates $[Pt\{(NC_5H_4CH_2)_2S\}X]^+$ (X = Cl, Br or I) was studied in acidic methanol solution ($I = 0.5$ mol dm^{-3}, $LiClO_4$; 2×10^{-3} mol dm^{-3} $HClO_4$) to prevent possible deprotonation of the chelate ligand.[8] 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 by $D_t = D_\infty + (D_0 - D_\infty)\exp(-k_{obs}t)$ with D_0, D_∞ and k_{obs} as the parameters to be optimized (D_0 = absorbance after mixing of reactants, D_∞ = absorbance at completion of reaction). Rate constants were accurate within 5%.

Results

In all the reactions of $[Pt(L)X]^+$ (X = Cl, Br or I) with an excess of halide ion, Y^- (Y = Cl, Br or I), the spectrum of the reaction mixture evolves with time in a first-order fashion from that of the starting substrate to that of the substituted product, often with well maintained isosbestic points. The observed rate constants, k_{obs}, obey the general relationship[10] $k_{obs} = k_1 + k_2[Y^-]$ (Table 1). Attention has been focused on the second-order rate constants, k_2, which can be measured with accuracy. The k_1 values are generally much less precise and a direct determination would require the use of much poorer nucleophiles, *e.g.* OH^-.

In the case of the forward reaction of the system [equation (2)] where the chloride concentrations required to ensure

$$[Pt\{(NC_5H_4CH_2)_2S\}I]^+ + Cl^- \rightleftharpoons [Pt\{(NC_5H_4CH_2)_2S\}Cl]^+ + I^- \quad (2)$$

pseudo-first-order conditions and to shift completely the equilibrium to the right are so large that the reactions are too fast to be followed, the second-order rate constant $k_{2I/Cl}$ was calculated from the rate of approach to equilibrium in the presence of iodide ion ($[I^-]$ = constant = 2×10^{-4} mol dm^{-3}, $[I^-] \gg$ [complex]). The customary expression $D_t = D_\infty + (D_0 - D_\infty)\exp(-k_{obs}t)$ was used, where D_∞ becomes the absorbance of the equilibrium mixture and k_{obs} takes the form $k_{obs} = k_{2I/Cl}[Cl^-] + k_{2Cl/I}[I^-]$. The linear regression of k_{obs} *vs.* $[Cl^-]$ for such an equation gives $k_{2I/Cl}$ as the slope and $k_{2Cl/I}[I^-]$ as the intercept of the resulting straight line. The ratio intercept/$[I^-]$ = 105 ± 5 dm^3 mol^{-1} s^{-1} is in good agreement with the second-order rate constant of the reverse reaction, $k_{2Cl/I}$ = 110 ± 3 dm^3 mol^{-1} s^{-1}, obtained in the usual way.

The values of k_2 for all the reactions are summarized in Table 2 together with the $k^0{}_2$ values, *i.e.* the second-order rate constants extrapolated to zero ionic strength according to the Debye–Hückel relationship previously discussed,[1,11,12] and the corresponding values of the free energy of activation, $\Delta G^‡$. The effectiveness of the long extrapolation to zero ionic strength, already tested on the substitution of co-ordinated 4-chloropyridine by chloride from $[Pt\{NC_5H_3(CH_2SMe)_2\}(NC_5H_4Cl\text{-}4)]^{2+}$ at $I = 0.1$ and 0.01 mol dm^{-3},[1] has been confirmed by measuring the rate of displacement of co-ordinated Cl by Br^- from the complex $[Pt\{NC_5H_3(CH_2SMe)_2\}Cl]^+$ at two sufficiently different values of the ionic strength, *i.e.* 0.5 ($LiClO_4$, $k^0{}_2$ = 0.806 dm^3 mol^{-1} s^{-1}) and 0.1 mol dm^{-3} ($[NBu^n{}_4]ClO_4$, $k^0{}_2$ = 0.87 dm^3 mol^{-1} s^{-1}).[1] Moreover, the reaction rate is largely independent of the nature of the salt used to keep constant the ionic strength. The second-order rate constants for the same reaction carried out at $I = 0.1$ mol dm^{-3} with either NaO_3SNa or $[NBu^n{}_4]ClO_4$[1] are 0.140 ± 0.003 and 0.136 ± 0.004 dm^3 mol^{-1} s^{-1} respectively. The extrapolated $k^0{}_2$ values relative to the reactions of halide substitution from the $[Pt(terpy)X]^+$ substrates, almost insoluble in any perchlorate medium ($I = 0.1$ mol dm^{-3}, NaO_3SMe), are therefore directly comparable to the $k^0{}_2$ values relative to the reactions of the other substrates.

Discussion

The second-order rate constants, $k^0{}_2$ (Table 2), for the reactions (1) together with the leaving-group effects and the discrimination parameters $s = \log[k^0{}_{2(Y_1)}/k^0{}_{2(Y_2)}]/[n^0{}_{Pt(Y_1)} - n^0{}_{Pt(Y_2)}]$ (the corresponding nucleophilicity index n^0 Pt being 5.46, 4.18 and 3.04 for iodide, bromide and chloride ions respectively)[13] which give a measure of the ability of each substrate to discriminate among the entering nucleophiles (Table 3), reveal significant trends and differences.

Reactivity.—The largest difference in the kinetic behaviour arising from the different natures of the tridentate chelating ligands is not due, as might be expected, to the progressive substitution of nitrogen with sulfur donors, but to the presence or absence of aromatic pyridine rings. The second-order rate constants ($k^0{}_2$) for the reactions of the substrates $[Pt(terpy)X]^+$, in which the tridentate ligand provides three aromatic pyridine rings in the co-ordination plane, are from five to six orders of magnitude larger than those of the corresponding $[Pt\{NH(CH_2CH_2NH_2)_2\}X]^+$ complexes in which all the nitrogen donors have sp^3 hybridization.

The substrates $[Pt(terpy)X]^+$ and $[Pt\{(NC_5H_4CH_2)_2S\}X]^+$, both having the same nitrogen-donor groups *cis* to the leaving X, show quite comparable reactivities, thus indicating that the *trans*-labilizing effect of a coplanar pyridine ring is almost the same as that of the thioether sulfur atom. It may be pointed out that the 'normal' *trans*-effect sequence of monodentate pyridines σ bonded to platinum(II) is considerably smaller than that of thioethers and comparable to that of sp^3 nitrogen donors, *i.e.* ammonia and aliphatic amines.[10] This 'anomalous' *trans* effect can be ascribed to the peculiar co-ordination geometry of the aromatic pyridine ring leading to a relative increase of the electrophilicity of the reaction centre, as a consequence of π delocalization of electron density.

The same conclusion can be reached by comparing the reactivity of the $[Pt(terpy)X]^+$ with that of the $[Pt\{NC_5H_3(CH_2SMe)_2\}X]^+$ substrates. In this case the donor ligand *trans* to the leaving group is the same, and the variation of the *cis* partners from coplanar pyridine groups to the CH_2SMe moieties results in a decrease in reactivity of about two to three orders of magnitude.

A straightforward comparison between the $[Pt\{(NC_5H_4CH_2)_2S\}X]^+$ and $[Pt\{NC_5H_3(CH_2SMe)_2\}X]^+$ complexes is more difficult since (*i*) both the *trans* and *cis* partners are changed and (*ii*) the σ-donor ability of the sulfur atom is known to be considerably affected by the nature of the radicals bonded to it.[14,15] However, the higher reactivity (two to three orders of magnitude) of $[Pt\{(NC_5H_4CH_2)_2S\}X]^+$ is in accordance with the role of two coplanar *cis*-pyridine rings capable of delocalizing negative charge away from the reaction centre.

Table 1 First-order rate constants, k_{obs}, for the reactions of the nucleophiles Y^- displacing X from the substrate $[Pt(L)X]^+$ in methanol at 25 °C [I = 0.5 mol dm^{-3} ($LiClO_4$)]

X	Y	$[Y^-]$/mol dm^{-3}	$10^3 k_{obs}$/s^{-1}	X	Y	$[Y^-]$/mol dm^{-3}	$10^3 k_{obs}$/s^{-1}
(*a*) L = $NH(CH_2CH_2NH_2)_2$							
Cl	Br	0.050	0.011 0	Br	I	0.01	0.042
		0.125	0.027 0			0.03	0.092
		0.300	0.028 0			0.05	0.136
		0.400	0.038 5			0.07	0.196
		0.500	0.050 0			0.10	0.271
Cl	I	0.010	0.026 6	I	Cl	0.1	0.012 0
		0.025	0.074 7			0.2	0.014 0
		0.050	0.136 9			0.3	0.015 0
		0.070	0.186 0			0.4	0.018 0
		0.100	0.273 0			0.5	0.020 2
Br	Cl	0.1	0.006 8	I	Br	0.04	0.020 3
		0.2	0.009 3			0.12	0.026 5
		0.3	0.011 7			0.20	0.029 9
		0.4	0.014 2			0.30	0.036 3
		0.5	0.017 0			0.40	0.040 2
(*b*) L = $NC_5H_3(CH_2SMe)_2$							
Cl	Br	0.01	0.76	Br	I	0.000 5	5.5
		0.02	1.10			0.001 0	11.6
		0.03	1.69			0.002 0	18.8
		0.04	1.94			0.003 0	25.0
		0.05	2.42			0.004 0	30.8
						0.005 0	37.0
Cl	I	0.000 5	2.61	I	Cl	0.1	0.75
		0.001 0	5.08			0.2	1.47
		0.002 0	9.90			0.3	2.70
		0.003 0	15.00			0.4	3.50
		0.004 0	19.10			0.5	4.90
Br	Cl	0.05	0.31	I	Br	0.01	1.43
		0.10	0.60			0.02	2.74
		0.20	1.18			0.03	3.70
		0.30	1.91			0.05	6.57
		0.40	2.22			0.07	8.01
		0.50	2.65			0.10	11.70
(*c*) L = $(NC_5H_4CH_2)_2S$, 2 mmol dm^{-3} $HClO_4$							
Cl[a]	Br	0.05	6.3	Br	I	0.01	46
		0.10	8.3			0.02	65
		0.20	11.2			0.03	92
		0.30	15.1			0.04	114
		0.50	21.7			0.05	133
Cl[a]	I	0.012 5	22.1	I	[b]Cl	0.1	29
		0.025 0	36.5			0.2	35
		0.037 5	52.0			0.3	43
		0.050 0	64.0			0.5	62
		0.062 5	76.9			0.6	69
Br	Cl	0.05	12.6			0.7	75
		0.10	13.5			0.8	81
		0.20	14.1	I	Br	0.05	64
		0.30	15.6			0.10	79
		0.50	18.0			0.15	102
						0.20	140
						0.30	210
						0.40	282
						0.70	394
(*d*) L = terpy, I = 0.1 mol dm^{-3} NaO_3SMe							
Cl	Br	0.005	0.89	Br	I	0.005	46
		0.010	1.48			0.010	73
		0.015	1.71			0.015	85
		0.020	2.20			0.020	113
		0.030	2.96			0.025	130
Cl	I	0.006 25	16.3	I	Cl	0.005	4.7
		0.012 50	32.1			0.010	6.4
		0.018 75	48.0			0.015	9.3
		0.031 25	89.0			0.020	10.7
		0.037 50	110.1			0.030	13.0

Table 1 (*continued*)

X	Y	$[Y^-]$/mol dm^{-3}	$10^3\ k_{obs}/s^{-1}$	X	Y	$[Y^-]$/mol dm^{-3}	$10^3\ k_{obs}/s^{-1}$
Br	Cl	0.010 0	1.92	I	Br	0.006 25	62
		0.015 0	2.13			0.012 50	73
		0.020 0	2.25			0.018 75	84
		0.030 0	2.36			0.025 00	95
		0.040 0	2.72			0.031 25	106
		0.050 0	2.99				

[a] Data taken from ref. 8. [b] In the presence of 2×10^{-4} mol dm^{-3} I^-; $[I^-] \gg [Pt\{(NC_5H_4CH_2)_2S\}I]^+$.

Table 2 Specific second-order rate constants[a] for the displacement of X from the substrates $[Pt(L)X]^+$ by the nucleophile Y^- in methanol at 25 °C and free energy of activation $\Delta G^\ddagger$

		λ/nm				
X	Y	Isosbestic point	Used	$10^2\ k_2$/dm^3 mol^{-1} s^{-1}	$10^2\ k^0{}_2$/dm^3 mol^{-1} s^{-1}	$\Delta G^\ddagger$/kJ mol^{-1}
L = $NH(CH_2CH_2NH_2)_2$[b]						
Cl[c]	Cl				0.005 2	97.5
Cl	Br	277	300	0.007 ± 0.001	0.134	89.4
Cl	I	283	310	0.268 ± 0.006	5.14	72.7
Br	Cl	277	300	0.002 45 ± 0.000 01	0.047	92.0
Br[c]	Br				0.42	86.6
Br	I	—	310	0.256 ± 0.006	4.91	80.5
I	Cl	283	310	0.002 ± 0.000 2	0.038	92.5
I	Br	—	310	0.005 5 ± 0.000 3	0.106	90.0
I[c]	I				0.335	87.1
L = $NC_5H_3(CH_2SMe)_2$[b]						
Cl[c]	Cl				1.19	
Cl	Br	292	280	4.2 ± 0.3	80.6	84.0
Cl	I	265, 296	320	480 ± 10	9 207	73.6
Br	Cl	292	280	0.53 ± 0.03	10.17	61.8
Br[c]	Br				296	78.7
Br	I	267, 299	320	680 ± 30	13 040	70.3
I	Cl	265, 296	282	1.03 ± 0.06	19.76	60.95
I	Br	267, 299	320	11.3 ± 0.4	216.8	77.0
I[c]	I				3 192	71.1
						64.4
L = $(NC_5H_4CH_2)_2S$[d]						
Cl[c]	Cl				296.5	70.3
Cl	Br		280	341 ± 7	6 541.2	62.7
Cl	I	265, 293	250	11 000 ± 300	211 000	54.05
Br	Cl	272, 300	280	118 ± 7	2 263.5	65.3
Br[c]	Br	265, 293			26 742	59.2
Br	I		250	22 300 ± 800	427 800	52.3
I	Cl	285, 297	250	780 ± 30[e]	14 960	60.6
I	Br	272, 300	250	5 400 ± 300	103 600	55.8
I[c]	I	285, 297			907 670	50.4
L = terpy[f]						
Cl[c]	Cl				206	71.2
Cl	Br	283, 334, 345, 354	340	810 ± 50	5 190	63.2
Cl	I	286, 327, 337	344	30 300 ± 1 100	194 144	54.3
Br	Cl	283, 334, 345, 354	340	250 ± 20	1 603	66.15
Br[c]	Br				17 834	60.2
Br	I	287, 328, 339, 352	336	41 600 ± 2 600	266 700	53.5
I	Cl	286, 327, 337	344	3 400 ± 400	21 784	59.7
I	Br	287, 328, 339, 352	336	17 600 ± 100	112 763	55.6
I[c]	I				714 014	51.0

[a] Determined by weighted linear regression of k_{obs} values *vs.* nucleophile concentration. [b] $I = 0.5$ mol dm^{-3} ($LiClO_4$) [c] Calculated values. [d] $I = 0.5$ mol dm^{-3} ($LiClO_4$), 2×10^{-3} mol dm^{-3} $HClO_4$. [e] Slope of the function $k_{obs} = k_{2I/Cl}[Cl^-] + k_{2Cl/I}[I^-]$ with $[I^-] = 2 \times 10^{-4}$ mol dm^{-3} $\gg$ [complex]. [f] $I = 0.1$ mol dm^{-3} (NaO_3SMe).

Nucleophilic Discrimination Factors.—The comparison of the ability of the various substrates to discriminate among the entering groups is also of interest, even if attention has to be paid to the fact that the nucleophilic discrimination parameter *s* has been obtained, for each substrate, with just two entering nucleophiles. Two significant features emerge upon examining the data in Table 3.

First the discrimination decreases on moving from the chloro to the bromo and iodo species for all series of substrates $[Pt(L)X]^+$, indicating an increasing role of the nature of the

Table 3 Nucleophilic discrimination factors, *s*, for the substrates $[Pt(L)X]^+$

	L			
X	$NH(CH_2CH_2NH_2)_2$	$NC_5H_3(CH_2SMe)_2$	$N(C_5H_4CH_2)_2S$	terpy
Cl	1.24	1.61	1.18	1.23
Br	0.83	1.28	0.94	0.92
I	0.39	0.91	0.74	0.63

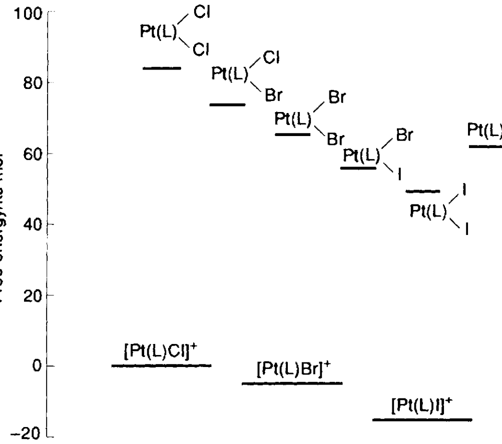

Fig. 1 Relative free-energy levels for ground and transition states of the species $[Pt\{NC_5H_3(CH_2SMe)_2\}X]^+$ and $[Pt\{NC_5H_3(CH_2SMe)_2\}X, Y]^‡$ where that of $[Pt\{NC_5H_3(CH_2SMe)_2\}Cl]^+$ is taken as zero

leaving halide in determining the energy of the transition states. Systems are well known in which the discriminating ability of the substrates does not change with the nature of the leaving group. For instance in the reactions of the neutral complexes $[Pt(bipy)(NO_2)X]$ (bipy = 2,2′-bipyridine) with various nucleophiles[16] the values of *s* are the same, within the limit of experimental errors, for X = NO_2, N_3, Cl, Br or I, the sequence of substitution lability being I > Br > Cl > NO_2 > N_3. The same is true for the complexes *trans*-$[Pt(pip)_2(NO_2)X]$ (pip = piperidine),[17,18] with the lability sequence Br > Cl > NO_2 > N_3. The independence of the discrimination upon the nature of the leaving group was assumed as an indication of an almost complete asynchronicity of the mechanism of substitution (S_N2 lim.), and we may therefore conclude that the substitution mechanism is less asynchronous for cationic than for the neutral platinum(II) complexes. The asynchronicity of the present cationic species seems therefore intermediate between that of neutral platinum(II) and that of neutral gold(III) substrates.[19]

Secondly, the values of *s* depend considerably upon the nature of L, but their changes with the nature of X are more significant for L = $NH(CH_2CH_2NH_2)_2$ (almost three times) than for the other substrates (almost twice). In other words, the discriminating ability of the $[Pt\{NH(CH_2CH_2NH_2)_2\}X]^+$ substrates is much more determined by the nature of X than in the other complexes in which the similarity of the L ligands reduces the differences.

Leaving-group Effect.—In order to compare how the relative lability of the co-ordinated halides depends upon the nature of the tridentate ligand and the entering nucleophile, the reactivities of all the substrates, relative to that of the chloro species taken as unity, are summarized in Table 4. In the systems with L = $NH(CH_2CH_2NH_2)_2$ and $NC_5H_3(CH_2SMe)_2$ the lability of the halides is quite comparable and the sequence depends upon the nature of the entering nucleophile. Minor solvation effects may be responsible for such small differences. In the case of L = $(NC_5H_4CH_2)_2S$ and terpy the difference in the lability of the leaving group is more pronounced and the observed sequence is always I > Br > Cl, suggesting that the lability pattern is modified by the presence of aromatic nitrogen donors in the chelating ring. It is however confirmed, as already observed in other platinum(II) complexes,[5] that the reactivity is largely dominated by the nature of the entering group.

Table 4 Relative substitution lability of halides, $k^0{}_2(X)/k^0{}_2(Cl)$, for the reactions $[Pt(L)X]^+ + Y^- \rightarrow [Pt(L)Y]^+ + X^-$ in methanol at 25 °C

L	Y	X
$NH(CH_2CH_2NH_2)_2$	Cl	Br (9.0) > I (7.3) > Cl (1.0)
	Br	Br (3.1) > Cl (1.0) ≈ I (0.8)
	I	Cl (1.0) ≈ Br (0.96) > I (0.06)
$NC_5H_3(CH_2SMe)_2$	Cl	I (16.6) > Br (8.5) > Cl (1.0)
	Br	Br (3.7) > I (2.7) > Cl (1.0)
	I	Br (1.4) ≈ Cl (1.0) > I (0.35)
$(NC_5H_4CH_2)S$	Cl	I (50) > Br (7.6) > Cl (1.0)
	Br	I (16) > Br (4.1) > Cl (1.0)
	I	I (4.3) > Br (2.0) > Cl (1.0)
terpy	Cl	I (106) > Br (7.8) > Cl (1.0)
	Br	I (22) > Br (3.4) > Cl (1.0)
	I	I (3.7) > Br (1.4) > Cl (1.0)

Transition States.—In studies of the dependence of the reactivity sequence upon the total charge of the substrate[6,20,21] it has been demonstrated that halide ions follow closely the relationship $\log k^0{}_2 = s(n^0Pt) + \text{constant}$. It is then possible to extrapolate from the second-order rate constants for the entry of two halogens the rate of entry of the third one, *i.e.* estimate a value of the rate constants for the exchange reactions (3). The

$$[Pt(L)X]^+ + {}^*X^- \rightleftharpoons [Pt(L){}^*X]^+ + X^- \quad (3)$$

calculated second-order rate constants, $k^0{}_2$, for X = Cl, Br or I are also reported in Table 2.

The relative free-energy levels of the transition states (always taking that of the planar chloro species as zero) together with those of the ground states are summarized in Table 5, whereas in Fig. 1 are they schematically exemplified in the case of the systems $[Pt\{NC_5H_3(CH_2SMe)_2\}X]^+ + Y^-$. In the transition states the bonds are not completely formed and therefore a direct comparison between four-co-ordinated ground and five-co-ordinated transition states is meaningless. However, it may be noted that the difference in the free energy between the $[Pt(L)Cl,Cl]^‡$ and $[Pt(L)I,I]^‡$ transition states is comparable and larger than twice the difference between the $[Pt(L)Cl]^+$ and $[Pt(L)I]^+$ ground states, suggesting that the polarizability of the anions is more important in determining the relative energy of the five-co-ordinated transition states than that of the four-co-ordinated ground states.

Ground States, Equilibrium Constants, Relative Stability.—The ratio of the second-order rate constants for the reversible processes (1) provides a measure of the equilibrium constants and therefore of the corresponding free-energy changes ($-\Delta G^{\circ} = RT\ln K$) (Table 6), which can be used to estimate the relative stability of the bromo- and iodo as compared to the chloro-species. The sum of the ΔG° values relative to the transformation of the chloro- to the bromo- and of the bromo-

Table 5 Relative free-energy levels ($\Delta G^\ddagger$) of the transition states $[Pt(L)X(Y)]^\ddagger$ and relative stabilization energy levels (ΔG° of the ground states $[Pt(L)X]^+$ (chloro-complexes taken as zero)

		$\Delta G^\ddagger$/kJ mol^{-1}			
X	Y	L = $NH(CH_2CH_2NH_2)_2$	$NC_5H_3(CH_2SMe)_2$	$N(C_5H_4CH_2)_2S$	terpy
Cl	Cl	97.5	84.0	70.3	71.2
Cl	Br	89.4	73.6	62.7	63.2
Cl	I	72.7	61.8	54.05	54.3
Br	Br	84.0	65.2	56.6	57.3
Br	I	77.9	55.9	49.7	50.6
I	I	75.0	49.2	43.8	45.5
		ΔG°/kJ mol^{-1}			
X					
Cl		0	0	0	0
Br		−2.6	−5.1	−2.6	−2.9
I		−12.1	−15.2	−6.6	−5.5

Table 6 Equilibrium constants for the systems $[Pt(L)X]^+ + Y^- \rightleftharpoons [Pt(L)Y]^+ + X^-$ in methanol at 25 °C

L	X	Y	K	$-\Delta G^\circ$/kJ mol^{-1}
$NH(CH_2CH_2NH_2)_2$	Cl	Br	2.9 ± 0.4	2.6 ± 0.3
	Br	I	46 ± 3	9.5 ± 0.2
	I	Cl	0.0075 ± 0.0008	−12.1 ± 0.3
$NC_5H_3(CH_2SMe)_2$	Cl	Br	7.9 ± 0.7	5.1 ± 0.2
	Br	I	60 ± 3	10.2 ± 0.1
	I	Cl	0.0021 ± 0.0001	−15.2 ± 0.1
$N(C_5H_4CH_2)_2S$	Cl	Br	2.9 ± 0.2	2.6 ± 0.2
	Br	I	4.1 ± 0.3	3.5 ± 0.2
	I	Cl	0.071 ± 0.003	−6.6 ± 0.1
terpy	Cl	Br	3.2 ± 0.3	2.9 ± 0.2
	Br	I	2.4 ± 0.1	2.2 ± 0.1
	I	Cl	0.11 ± 0.01	−5.5 ± 0.2

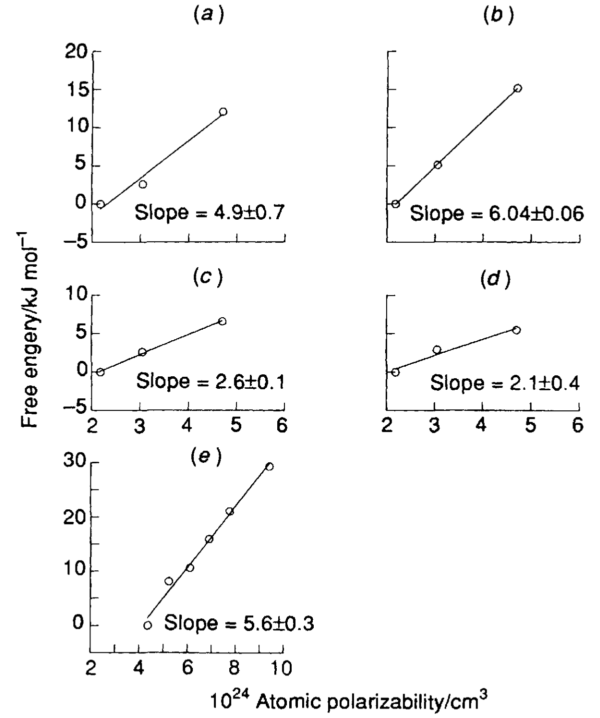

Fig. 2 Plots of the relative stabilization free energies for the species $[Pt(L)X]^+$ [L = dien (*a*), $NC_5H_3(CH_2SMe)_2$ (*b*), $(NC_5H_4CH_2)_2S$ (*c*) or terpy (*d*); X = Cl, Br or I] and $[Pt(PhSCH_2CH_2SPh)X,Y]^+$ (X, Y = Cl, Br or I) (*e*) against the atomic polarizabilities of X and Y; chloro species taken as zero

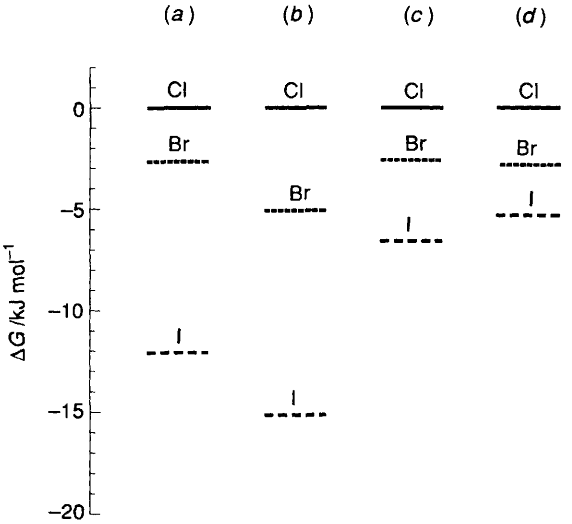

Fig. 3 Relative free-energy levels for the ground states of the species $[Pt(L)X]^+$. L = dien (*a*); $NC_5H_3(CH_2SMe)_2$ (*b*), $(NC_5H_4CH_2)_2S$ (*c*) or terpy (*d*); X = Cl, Br or I; chloro species taken as zero

to the iodo-species is in close agreement, in the limit of experimental errors, with ΔG° measured for the direct transformation of the chloro- to the iodo-species.

The stability of platinum(II) complexes is known to be determined by a number of different factors, including polarizability, σ-donor ability and π-back bonding. However, as far as halide ions are concerned, both the σ basicity and π-back donation are almost negligible. It is therefore of interest to observe that the relative stabilization free energies for the species $[Pt(L)X]^+$ are linearly related to the atomic polarizabilities of the halogens (Cl, 2.18×10^{-24}; Br, 3.05×10^{-24}; I, 4.7×10^{-24} cm^3)[22] (Fig.2). The same linear relationship can be observed for the complexes $[Pt(PhSCH_2CH_2SPh)X(Y)]$,[5] on plotting the relative stabilization free energies *vs.* the sum of the polarizabilities of the two halogens bonded to the metal.

It is not surprising that in all cases the relative stability of the halogeno-species increases with the polarizability of X, platinum(II) being a typical 'soft' Lewis acid. It may however be noted (Fig. 3) that the differences in stability depend upon the nature of L, being larger for $[Pt\{NC_5H_3(CH_2SMe)_2\}X]^+$ (15.2 kJ mol^{-1}) and $[Pt\{NH(CH_2CH_2NH_2)_2\}X]^+$ (12.1 kJ mol^{-1}) than for $[Pt\{(NC_5H_4CH_2)_2S\}X]^+$ and $[Pt(terpy)X]^+$ (6.6 and 5.5 kJ mol^{-1} respectively). In addition, the values for the latter systems are quite comparable and smaller than the former ones. This fact can be related, in our opinion, to the structural features of the substrates. In the systems having two pyridine groups *cis* to the halogen in the co-ordination plane, two *ortho*-hydrogens interfere with the co-ordination site of X and can therefore reduce to some extent the relative stability of the iodo-as compared to the chloro-species.

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