Nucleophilic Displacement of Halides from Dihalogenoplatinum(II) Complexes containing a Chelating Thioether. Kinetics and Equilibria

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Kinetic and equilibrium measurements on the displacement of halides from the substrates [Pt(PhSCH$_2$CH$_2$SPh)X(Y)] (X, Y = Cl, Cl; Cl, Br; Br, Br; Br, I; I, I; Cl, I) with the nucleophiles Cl$^-$, Br$^-$ and I$^-$ have been carried out in methanol at 25 °C, *I* = 0.5 mol dm^{-3} (LiClO$_4$). The results are discussed in terms of the relative stability of the planar ground and five-co-ordinate transition states, and the lability and kinetic *cis* effects of co-ordinated halides are compared. All substrates appear to be characterized by a sort of stereoelectronic hindrance leading to retardation effects, mainly in the second-order substitution pathway.

The reactivity of the platinum(II) complex [Pt(PhSCH$_2$CH$_2$SPh)Cl$_2$] was investigated several years ago by measuring the rate of displacement of the chelating ligand by neutral nitrogen donors in 1,2-dimethoxyethane.[1] Recently we observed that in methanol, under the same experimental conditions, anionic nucleophiles displace chloride instead of the chelate from [Pt(PhSCH$_2$CH$_2$SPh)Cl$_2$], as well as bromide and iodide from the corresponding dibromo and diiodo species. As the reactivity and spectral features of the [Pt(PhSCH$_2$CH$_2$SPh)X$_2$] complexes (X = Cl, Br or I) allow a spectrophotometric study of the consecutive displacement of both X groups, we decided to examine kinetically all the mutual interconversions of the [Pt(PhSCH$_2$CH$_2$SPh)X(Y)] species (X, Y = Cl, Br or I), *i.e.* dichloro, dibromo, diiodo, chlorobromo, chloroiodo and bromoiodo, in order to compare the lability and *cis* effect of co-ordinated Cl, Br, I under the *trans* + *cis* effect of thioether sulfur and evaluate both the relative thermodynamic stability of the planar four-co-ordinate species and the energetics of the corresponding five-co-ordinate transition states.

Experimental

Materials.—Platinum(II) chloride, PtCl$_2$, was obtained from Janssen Chimica. Pure reagent-grade LiClO$_4$, LiBr, LiCl, NEt$_4$I and AgNO$_3$ (Fluka and Aldrich) were dried over P$_2$O$_5$ in a vacuum desiccator and used without further purification. The other reagents were of AR quality and recrystallized or distilled before use when necessary.

Instruments.—Infrared spectra (4000–250 cm^{-1}, KBr discs; 250–150 cm^{-1}, polyethylene pellets) were recorded on Perkin-Elmer 683 and 180 spectrophotometers respectively. Electronic spectra, kinetics and equilibria were measured with a Perkin-Elmer Lambda 5 spectrophotometer. Proton NMR spectra were recorded on a Bruker AC 200 F spectrometer. Elemental analyses were performed by the Microanalytical Laboratory of the University of Padua.

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

Preparation of Complexes.—Bis(benzonitrile)dichloroplatinum(II), [Pt(PhCN)$_2$Cl$_2$], was prepared as reported.[3]

[1,2-*Bis(phenylthio)ethane*]*dichloroplatinum*(II), [Pt(PhSCH$_2$CH$_2$SPh)Cl$_2$] **1**. A solution of PhSCH$_2$CH$_2$SPh (0.739 g, 3 mmol) in dichloromethane (20 cm^3) was added dropwise with stirring to a solution of [Pt(PhCN)$_2$Cl$_2$] (1.417 g, 3 mmol) dissolved in the minimum volume of dichloromethane (25 cm^3). The resulting mixture was refluxed for 2 h, during which time the pale yellow complex **1** precipitated. The product was filtered off, washed with the minimum amount of cold methanol, twice with diethyl ether, and dried under reduced pressure. Yield = 1.306 g (85%). Well formed crystals were obtained on slowly cooling at room temperature a hot dimethylformamide (dmf) solution of **1** to which a small amount of hot water was added until cloudiness appeared.

[1,2-*Bis(phenylthio)ethane*]*dibromoplatinum*(II), [Pt(PhSCH$_2$CH$_2$SPh)Br$_2$] **2**. A solution of LiBr (2.605 g, 30 mmol) in methanol (30 cm^3) was slowly added to a hot suspension of complex **1** (0.512 g, 1 mmol) in the same solvent (30 cm^3). The colour changed rapidly from pale yellow to deep yellow and warm dmf (10 cm^3) was added until complete dissolution. On slow cooling of the resulting solution to room temperature, well formed yellow crystals of **2** separated, which were filtered off, washed with the minimum amount of cold methanol, twice with diethyl ether and dried under reduced pressure. Yield = 0.421 g (70%).

[1,2-*Bis(phenylthio)ethane*]*diiodoplatinum*(II), [Pt(PhSCH$_2$CH$_2$SPh)I$_2$] **3**. Orange crystals of complex **3** were obtained in the same way as for **2** starting from **1** (1 mmol) and using NEt$_4$I instead of LiBr. Yield = 0.528 g (75%).

[1,2-*Bis(phenylthio)ethane*]*bromochloroplatinum*(II), [Pt(PhSCH$_2$CH$_2$SPh)Cl(Br)] **4**. Silver nitrate (0.170 g, 1 mmol) was added to a warm solution (60 °C) of complex **1** (0.512 g, 1 mmol) in dmf (25 cm^3) and the mixture was stirred in the dark for 30 min. The AgCl formed was filtered off and the solution treated with LiBr (0.087 g, 1 mmol) and stirred at 80 °C for 10 min. The well formed yellow crystals of **4** obtained on slowly cooling at room temperature the dmf solution, to which hot water was added until incipient cloudiness, were filtered off, washed with the minimum amount of cold methanol, twice with diethyl ether and dried under reduced pressure. Yield = 0.306 g (55%).

[1,2-*Bis(phenylthio)ethane*]*chloroiodo- and -bromoiodo-platinum*(II) [Pt(PhSCH$_2$CH$_2$SPh)Cl(I)] **5** *and* [Pt(PhSCH$_2$CH$_2$SPh)Br(I)] **6**. Crystalline complexes **5** and **6** were obtained in the same way as for **4** starting from **1** or **2** (1 mmol) and NEt$_4$I (1 mmol). Yields = 0.362 (60) and 0.369 g (57%) respectively.

Table 1 Analytical and physical data for the complexes

Complex	Analysis[a] (%) C	H	S	Colour	M.p./°C	UV/VIS λ_{max}[b]/nm (ε/dm^3 mol^{-1} cm^{-1})	IR bands below 400 cm^{-1}
1 $[Pt(PhSCH_2CH_2SPh)Cl_2]$[c]	32.8 (32.8)	2.75 (2.75)	12.1 (12.5)	Pale yellow	> 230	318 (900) 370 (217)	335, 320
2 $[Pt(PhSCH_2CH_2SPh)Br_2]$[d]	28.0 (28.0)	2.30 (2.35)	10.2 (10.7)	Lemon yellow	> 230	338 (1085) 316 (sh)	238, 212
3 $[Pt(PhSCH_2CH_2SPh)I_2]$[e]	23.95 (24.2)	1.85 (2.05)	8.90 (9.20)	Deep orange	> 230	325 (770) 393 (2653)	188, 164
4 $[Pt(PhSCH_2CH_2SPh)Cl(Br)]$	29.2 (30.2)	2.35 (2.55)	10.8 (11.5)	Yellow	> 230	330 (960)	328, 240
5 $[Pt(PhSCH_2CH_2SPh)Cl(I)]$	26.5 (27.85)	2.15 (2.35)	10.4 (10.6)	Orange	> 230	388 (1395)	318, 188, 166
6 $[Pt(PhSCH_2CH_2SPh)Br(I)]$	25.8 (25.9)	2.05 (2.20)	9.60 (9.90)	Orange	> 230	316 (sh) 382 (1519)	210, 167

[a] Calculated values in parentheses. [b] In methanol. [c] Cl 13.9 (13.8)%. [d] Br 26.0 (26.6)%. [e] I 36.4 (36.5)%.

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

Kinetics.—The reactions were initiated by adding a 0.05 mol dm^{-3} dmf solution (20 μl) of the substrate complex to a methanolic solution (3 cm^3) of the appropriate nucleophile (Cl^-, Br^-, 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. After preliminary repetitive scan experiments in the range 280–400 nm to search for isosbestic points and spectral changes, the kinetics were studied by measuring the changing absorbance at suitable wavelengths as a function of time. All the reactions were measured at constant ionic strength $I = 0.5$ mol dm^{-3} ($LiClO_4$). Pseudo-first-order rate constants (k_{obs}/s^{-1}) were obtained either from the gradients of plots of $\log(D_t - D_\infty)$ *vs.* time or from a non-linear least-squares fit of experimental data to $D_t = D_\infty + (D_0 - D_\infty)\exp(-k_{obs}t)$ with D_0, D_∞ and k_{obs} as the parameters to be optimized (D_0 = absorbance after mixing of reactants, D_∞ = absorbance at completion of reaction).

Equilibria.—Equilibria (1) and (2) (Y = Br or Cl) were

$$[Pt(PhSCH_2CH_2SPh)I_2] + Y^- \overset{K_1}{\rightleftharpoons} [Pt(PhSCH_2CH_2SPh)I(Y)] + I^- \quad (1)$$

$$[Pt(PhSCH_2CH_2SPh)I(Y)] + Y^- \overset{K_2}{\rightleftharpoons} [Pt(PhSCH_2CH_2SPh)Y_2] + I^- \quad (2)$$

resolved. A series of spectra (280–400 nm) of equilibrated solutions of the complex (at the same initial concentration) and the nucleophile at various concentrations were measured and calculations carried out at the most convenient wavelength (392 nm) for the analysis.

The equilibrium constants K_1 and K_2 were determined by a non-linear fitting of absorbance (D) data to the concentrations of Y^- according to equations (3)–(6) where $[Y^-]_0 \gg$

$$K_1 = [Pt(PhSCH_2CH_2SPh)I(Y)][I^-]/[Pt(PhSCH_2CH_2SPh)I_2][Y^-]_0 \quad (3)$$

$$K_2 = [Pt(PhSCH_2CH_2SPh)Y_2][I^-]/[Pt(PhSCH_2CH_2SPh)I(Y)][Y^-]_0 \quad (4)$$

$$[Pt(PhSCH_2CH_2SPh)I_2]_0 = [Pt(PhSCH_2CH_2SPh)I_2] + [Pt(PhSCH_2CH_2SPh)I(Y)] + [Pt(PhSCH_2CH_2SPh)Y_2] \quad (5)$$

$$[I^-] = [Pt(PhSCH_2CH_2SPh)I(Y)] + 2[Pt(PhSCH_2CH_2SPh)Y_2] \quad (6)$$

$[Pt(PhSCH_2CH_2SPh)I_2]_0$ and $D = \varepsilon_{PtI_2}[Pt(PhSCH_2CH_2SPh)I_2] + \varepsilon_{PtIY}[Pt(PhSCH_2CH_2SPh)I(Y)] + \varepsilon_{PtY_2}[Pt(PhSCH_2CH_2SPh)Y_2]$, where ε_{PtI_2}, ε_{PtIY} and ε_{PtY_2} are the molar absorption coefficients of the corresponding complexes; $[Y^-]_0$ and $[Pt(PhSCH_2CH_2SPh)I_2]_0$ are initial concentrations and $[Pt(PhSCH_2CH_2SPh)I_2]$, $[Pt(PhSCH_2CH_2SPh)I(Y)]$ and $[Pt(PhSCH_2CH_2SPh)Y_2]$ the equilibrium concentrations of the complexes. The optimized parameters were K_1 and K_2, and ε_{PtI_2}, ε_{PtIY} and ε_{PtY_2} were determined independently. During each iterative cycle of refinement[4] the concentrations of all species involved were determined by solving the equilibria and mass-balance equations system at the current parameter values by means of a Newton System Solver based on the LU decomposition/back substitution scheme.[5]

Results

In all the reactions of $[Pt(PhSCH_2CH_2SPh)X_2]$ (X = Cl or Br) with an excess of halide ion Y^- (Y = Cl, Br or I) the spectrophotometric changes observed upon repetitive scanning of the spectrum of the reaction mixture are characteristics of two consecutive processes, with well maintained isosbestic points. Careful examination of the spectral changes occurring after the reagents are mixed and the close similarity of the spectra at the end of the reactions with those of authentic samples of the expected reaction product demonstrate that all the reactions that have been studied kinetically involve consecutive double displacement of co-ordinated halides by the nucleophile Y^-. This observation has been independently confirmed in some cases in which it was possible to measure directly the single-stage reactions starting from the intermediate species, $[Pt(PhSCH_2CH_2SPh)Z(X)]$ (Z being the non-participating ligand *cis* to the leaving group). All the reactions were studied in the presence of a sufficient excess of Y^- to provide pseudo-first-order conditions and the observed rate constants, k_{obs} (Table 2), obey the general relationship $k_{obs} = k_1 + k_2[Y^-]$, which is usual for nucleophilic substitution at planar four-co-ordinate d^8 metal complexes.[6] The k_1 term refers to the solvolytic pathway, involving the entry of solvent as nucleophile, and k_2 is the second-order rate constant for direct attack of the nucleophile at the substrate. The isosbestic points characteristic of the stage, the conditions of measurements, the values of k_1 and k_2 as well as those of the relative free energy of activation, $\Delta G^\ddagger$, are summarized in Table 3. The uncertainties quoted are the usual standard errors of estimation. More realistic errors, taking into account the Student *t* test and the appropriate degrees of freedom, are likely to be much larger. This would

Table 2 First-order rate constants, k_{obs}, for the reactions of the nucleophiles Y^- displacing X from the substrate $[Pt(PhSCH_2CH_2SPh)Z(X)]$ in methanol at 25 °C [I = 0.5 mol dm^{-3} ($LiClO_4$)][a]

Z	X	Y	$[Y^-]$/ mol dm^{-3}	10^3k_{obs}/ s^{-1}
[b]Cl	Cl	Br	0.05	1.17
			0.10	1.53
			0.15	1.85
			0.25	2.60
			0.35	3.35
			0.50	4.40
[d]Cl	Br	Cl	0.05	0.27
			0.15	0.29
			0.25	0.33
			0.40	0.37
			0.50	0.39
[c]Cl	Br	Cl	0.05	0.34
			0.15	0.36
			0.25	0.39
			0.40	0.43
			0.50	0.47
[d]Br	Cl	Br	0.10	0.72
			0.15	0.85
			0.25	1.17
			0.35	1.47
			0.50	1.91
[c]Br	Cl	Br	0.05	0.40
			0.10	0.52
			0.15	0.56
			0.25	0.94
			0.35	1.21
			0.50	1.51
[b]Br	Br	Cl	0.05	0.96
			0.05	1.01
			0.10	1.04
			0.15	1.17
			0.15	1.11
			0.20	1.17
			0.25	1.27
			0.25	1.25
			0.30	1.25
			0.40	1.33
			0.40	1.31
			0.50	1.57
			0.50	1.54
[b]Br	Br	I	0.004	1.85
			0.006	2.14
			0.008	2.98
			0.010	3.41
			0.014	4.60
			0.020	6.22
[c]I	Br	I	0.003	0.51
			0.006	0.81
			0.009	1.12
			0.012	1.42
			0.015	1.71
			0.020	2.15
[b]I	I	Br	0.05	0.33
			0.10	0.46
			0.20	0.79
			0.30	1.21
			0.40	1.59
			0.50	1.89
[b]Cl	Cl	I	0.003	1.83
			0.006	2.71
			0.009	3.65
			0.012	4.57
			0.015	5.47
			0.020	6.99
[c]I	Cl	I	0.003	0.42
			0.006	0.72
			0.009	1.04
			0.012	1.20
			0.015	1.49
			0.020	1.96
[b]I	I	Cl	0.1	0.33
			0.2	0.35
			0.3	0.38
			0.4	0.45
			0.5	0.48
[d]I	Cl	Br	0.05	0.70
			0.10	0.97
			0.15	1.18
			0.20	1.48
			0.30	2.10
[d]I	Br	Cl	0.10	0.39
			0.20	0.45
			0.30	0.51
			0.35	0.53
			0.40	0.58
			0.45	0.57

[a] Rate constants were accurate within 5%. [b] Measured as first-stage of reaction on starting from the substrate $[Pt(PhSCH_2CH_2SPh)X_2]$. [c] Measured as second stage of reaction on starting from the substrate $[Pt(PhSCH_2CH_2SPh)X_2]$. [d] Measured on starting from the intermediate $[Pt(PhSCH_2CH_2SPh)Z(X)]$.

account for the apparent discrepancies between k_1 values pertaining to the same substrate.

In the case of the reactions of $[Pt(PhSCH_2CH_2SPh)I_2]$ with Cl^- and Br^-, in spite of the large excess of entering nucleophile, only the first stages go to completion. Therefore, the second-order rate constants for the displacement of chloride from the $[Pt(PhSCH_2CH_2SPh)I(Cl)]$ and bromide from the $[Pt(PhSCH_2CH_2SPh)I(Br)]$ intermediate, by Cl^- and Br^- respectively, have been evaluated from the independently measured equilibrium constants and the second-order rate constants of the reverse processes, as reported in Table 3.

The equilibrium constants K for the systems studied (Scheme 1) always refer to the displacement of a lighter halogen by a heavier one. Some values were determined, as described in the Experimental section, from direct equilibrium measurements, others from the ratios of the second-order rate constants for the forward and reverse reactions. For the systems (7) it was

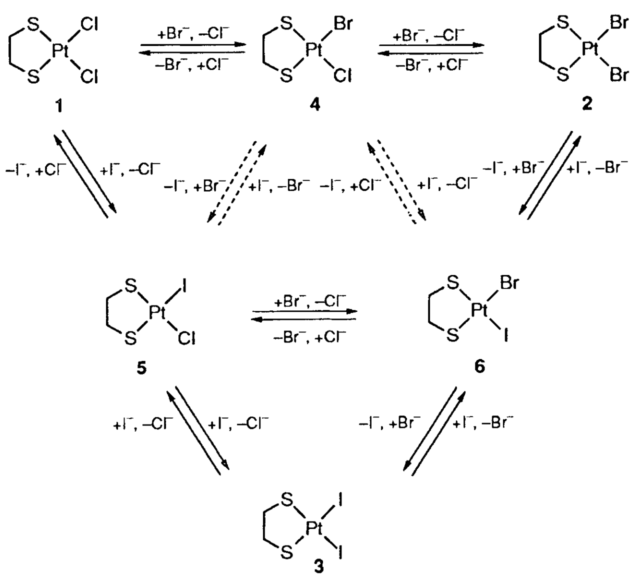
$$[Pt(PhSCH_2CH_2SPh)I(X)] + I^- \rightleftharpoons [Pt(PhSCH_2CH_2SPh)I_2] + X^- \quad (X = Cl \text{ or } Br) \qquad (7)$$

possible to apply both methods and the independently

Table 3 First- and second-order rate constants[a] for the displacement of X from the substrates [Pt(PhSCH$_2$CH$_2$SPh)Z(X)] by the nucleophile Y$^-$ in methanol at 25 °C [I = 0.5 mol dm^{-3} (LiClO$_4$)] and the free energy of activation $\Delta G^{\ddagger}$

Z	X	Y	λ/nm Isosbestic point	Used for calculations	10^4k_1/s^{-1}	10^3k_2/dm^3 mol^{-1} s^{-1}	$\Delta G^{\ddagger}$/kJ mol^{-1}
Cl	Cl	Br	309	295	7.9 ± 0.2	7.24 ± 0.07[b]	85.4
Cl	Br	Cl	309	295	2.55 ± 0.05	0.28 ± 0.02[c]	93.5
Cl	Br	Cl	309	295	3.20 ± 0.05	0.29 ± 0.02[b]	93.4
Br	Cl	Br	295	309	4.1 ± 0.1	3.00 ± 0.03[c]	87.6
Br	Cl	Br	295	309	2.5 ± 0.4	2.6 ± 0.1[b]	87.9
Br	Br	Cl	295	309	9.5 ± 0.3	1.1 ± 0.1[b]	90.0
Br	Br	I	348	374	6 ± 1	281 ± 9[b]	76.3
Br	I	Br	—	—	—	2.9 ± 0.2[d]	87.7
I	Br	I	374	348	2.3 ± 0.2	97 ± 2[b]	78.9
I	I	Br	374	348	1.2 ± 0.3	3.6 ± 0.1[b]	87.1
I	I	Br	—	—	—	3.6 ± 0.3[d]	87.1
Cl	Cl	I	314	369	9.1 ± 0.1	304 ± 1[b]	76.1
Cl	I	Cl	—	—	—	0.51 ± 0.02[d]	92.0
I	Cl	I	369	314	1.8 ± 0.4	89 ± 3[b]	79.2
I	I	Cl	369	314	2.8 ± 0.1	0.40 ± 0.05[b]	92.6
I	I	Cl	—	—	—	0.36 ± 0.02[d]	92.8
I	Cl	Br		348	3.9 ± 0.4	5.6 ± 0.2[c]	86.0
I	Br	Cl		314	3.4 ± 0.2	0.55 ± 0.05[c]	91.8

[a] Determined by weighted linear regression of k_{obs} values *vs.* nucleophile concentration. [b] Measured as first or second stage of reaction on starting from the substrate [Pt(PhSCH$_2$CH$_2$SPh)X$_2$]. [c] Measured on starting from the intermediate [Pt(PhSCH$_2$CH$_2$SPh)Z(X)]. [d] Calculated from the equilibrium constant and the second-order rate constant of the reverse reaction.



Scheme 1. Substitution reactions and equilibria in the systems [Pt(PhSCH$_2$CH$_2$SPh)Z(X)] + Y$^-$ in methanol at 25 °C [I = 0.5 mol dm^{-3} (LiClO$_4$)]

measured K values are in good agreement within the limit of the experimental errors. When the substrate [Pt(PhSCH$_2$CH$_2$SPh)Cl(Br)] is allowed to react with an excess of iodide two stages can again be observed, but the isosbestic point in the second stage is not well maintained, this suggesting that the displacements of both chloride and bromide occur during the first stage, thus providing a mixture of [Pt(PhSCH$_2$CH$_2$SPh)Cl(I)] and [Pt(PhSCH$_2$CH$_2$SPh)Br(I)] both leading to the final diiodo species with comparable rates, as independently measured. Therefore, the equilibrium constants for the reactions (8) and (9) have been calculated as a combination of the other related equilibrium constants and are also reported in Table 4.

$$[\text{Pt}(\text{PhSCH}_2\text{CH}_2\text{SPh})\text{Cl}(\text{Br})] + \text{I}^- \rightleftharpoons [\text{Pt}(\text{PhSCH}_2\text{CH}_2\text{SPh})\text{Cl}(\text{I})] + \text{Br}^- \quad (8)$$

Table 4 Equilibrium constants for the systems [Pt(PhSCH$_2$CH$_2$SPh)Z(X)] + Y$^-$ $\rightleftharpoons$ [Pt(PhSCH$_2$CH$_2$SPh)Z(Y)] + X$^-$ in methanol at 25 °C [I = 0.5 mol dm^{-3} (LiClO$_4$)]

Z	X	Y	K	$-\Delta G^{\circ}$/kJ mol^{-1}
Cl	Cl	Br	26 ± 2[a,b]	8.1
Cl	Cl	Br	25 ± 2[a,c]	8.0
Br	Cl	Br	2.7 ± 0.2[a,d]	2.5
Br	Cl	Br	2.4 ± 0.2[a,e]	2.2
Br	Br	I	98 ± 5[f]	11.4
I	Br	I	27 ± 2[f]	8.2
I	Br	I	26.9 ± 0.9[a]	8.2
Cl	Cl	I	599 ± 18[f]	15.9
I	Cl	I	247 ± 10[f]	13.7
I	Cl	I	222 ± 29[a]	13.4
I	Cl	Br	10 ± 1[a]	5.7
Br	Cl	I	265 ± 24[g]	13.8
Cl	Br	I	23 ± 2[h]	7.8

[a] Determined as the ratio of the second-order rate constants for the forward, k_2^{f}, and reverse, k_2^{r}, reactions. [b] k_2^{r} relative to the reaction of the intermediate [Pt(PhSCH$_2$CH$_2$SPh)Cl(Br)] + Cl$^-$. [c] k_2^{r} relative to the second stage of the reaction [Pt(PhSCH$_2$CH$_2$SPh)Br$_2$] + Cl$^-$. [d] k_2^{f} relative to the reaction of the intermediate [Pt(PhSCH$_2$CH$_2$SPh)Br(Cl)] + Br$^-$. [e] k_2^{f} relative to the second stage of the reaction [Pt(PhSCH$_2$CH$_2$SPh)Cl$_2$] + Br$^-$. [f] Determined from equilibrium measurements. [g] $K_{42}K_{26}$ (Scheme 1). [h] K_{15}/K_{14} (Scheme 1).

$$[\text{Pt}(\text{PhSCH}_2\text{CH}_2\text{SPh})\text{Cl}(\text{Br})] + \text{I}^- \rightleftharpoons [\text{Pt}(\text{PhSCH}_2\text{CH}_2\text{SPh})\text{Br}(\text{I})] + \text{Cl}^- \quad (9)$$

Discussion

The equilibrium constants for reaction (10) as well as the

$$[\text{Pt}(\text{PhSCH}_2\text{CH}_2\text{SPh})\text{Z}(\text{X})] + \text{Y}^- \rightleftharpoons [\text{Pt}(\text{PhSCH}_2\text{CH}_2\text{SPh})\text{Z}(\text{Y})] + \text{X}^- \quad (10)$$

corresponding free-energy changes ($-\Delta G^{\circ} = RT \ln K$) are reported in Table 4.

It has been known for several years that the rate constants for halide substitution at platinum(II) complexes do not change considerably on going from protic to dipolar aprotic solvents.[7-10] This means that the driving force for the

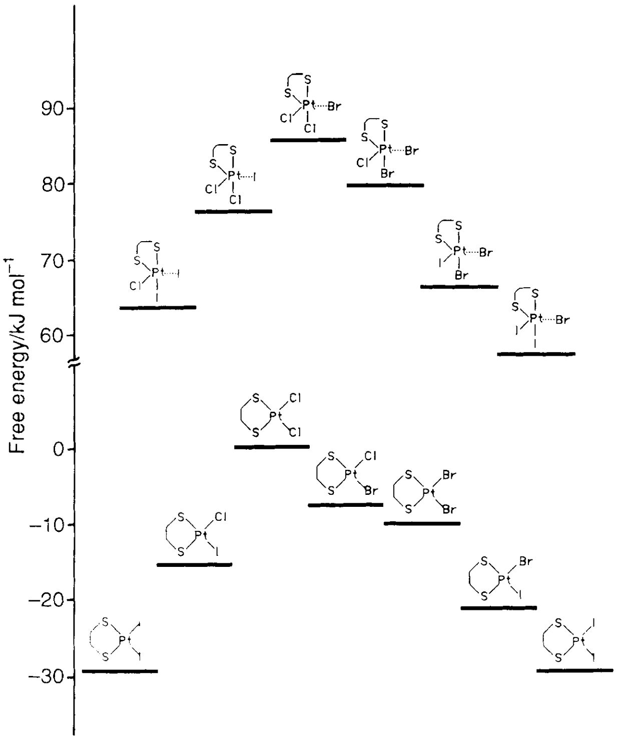


Fig. 1 Relative energy levels for ground and transition states; [Pt(PhSCH$_2$CH$_2$SPh)Cl$_2$] taken as zero

substitution reactions is controlled by the changes in the nature of platinum–halide bonds, whereas solvation–desolvation contributions from the anion involved are well balanced by the solvent interactions with the platinum–halide groups. Based on this assumption, it is then possible to compare the relative energy levels of the ground and transition states with respect to [Pt(PhSCH$_2$CH$_2$SPh)Cl$_2$] taken as zero, as shown in Fig. 1. It can be observed, as expected, that the relative stability of the complexes [Pt(PhSCH$_2$CH$_2$SPh)Z(X)] increases with the atomic weight of the halogens Z and X, platinum(II) being a typically 'soft' or 'class b' metal centre. The diiodo complex [Pt(PhSCH$_2$CH$_2$SPh)I$_2$] is 19.6 kJ mol^{-1} more stable than the dibromo species [Pt(PhSCH$_2$CH$_2$SPh)Br$_2$], which is somewhat 10.4 kJ mol^{-1} more stable than the dichloro species [Pt(PhSCH$_2$CH$_2$SPh)Cl$_2$]. The sum of the ΔG° values (-30.0 kJ mol^{-1}) is in close agreement with the total ΔG° variation of -29.4 kJ mol^{-1} measured through the direct transformation of the dichloro into the diiodo species. (The sum of the ΔG° values for any cyclic interchange must obviously be zero.)

The free-energy change for the replacement of chloride by bromide in the mixed-halide iodo species [Pt(PhSCH$_2$CH$_2$SPh)I(Cl)] ($-\Delta G^\circ = 5.7$ kJ mol^{-1}) is not very different from that relative to the same replacement in the dichloro species [Pt(PhSCH$_2$CH$_2$SPh)Cl$_2$] ($-\Delta G^\circ = 8.0$ kJ mol^{-1}), indicating a relatively small *cis* influence in these complexes. However any further speculation in this direction would require a much wider range of experimental data.

The energy levels of the transition states (Fig. 1) can also be compared. In this case, however, one must bear in mind that the degree of bond making and breaking in the transition state is unknown, the nucleophilic substitution of these d^8 systems being a typically asynchronous process.[11] If we assume, as a first approximation, that at least the bonds between the metal and the *cis* groups, which are not involved in the substitution and occupy the axial positions in the trigonal-bipyramidal transition state, remain totally formed, some further comments can be made. The substitution of an axial chloride with iodide in the transition state increases the stability by 12.8 kJ mol^{-1}, to be compared with 15.9 kJ mol^{-1} for the corresponding substitution in the square-planar configuration. In the same way, the substitution of an axial chloride with bromide increases the stability by 5.7 kJ mol^{-1} in the former case and 8.0 kJ mol^{-1} in the latter. One may conclude, not surprisingly, that the replacement of a ligand is energetically more relevant in the four- than in a five-ligand system.

The data in Table 4 indicate that the same conclusion can be roughly applied to the ligands lying in the trigonal plane, where the replacement of a bromide or a chloride with iodide stabilizes the transition state by 9.3 and 13.7 kJ mol^{-1} respectively.

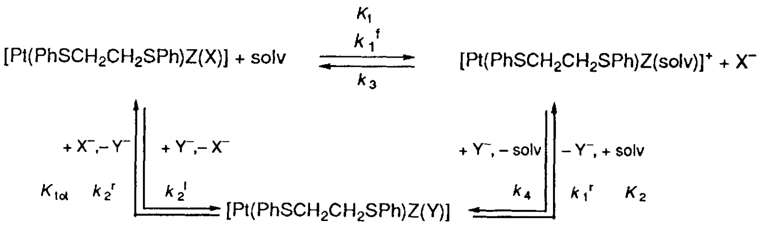
As far as the second-order rate constants for the displacement of chloride from [Pt(PhSCH$_2$CH$_2$SPh)Cl$_2$] are concerned, they can be compared with those obtained, under the same experimental conditions, with the substrate [Pt(bipy)Cl$_2$] containing the chelating nitrogen donor 2,2′-bipyridine.[12] The rates are not very different in the two systems, in spite of the *trans* + *cis* labilizing effect of the sulfur donor, expected to be higher than that of the nitrogen donor.[11] On going from the N–N to the S–S system the second-order rate constant for the displacement of chloride with iodide increases only from 4.5×10^{-2} to 30.4×10^{-2} dm^3 mol^{-1} s^{-1}. This may be due to a some stereoelectronic hindrance arising from the phenyl group and the lone pair of electrons which are present at each sulfur donor atom, providing some distribution of negative charge above and below the co-ordination plane larger than in [Pt(bipy)Cl$_2$] where all atoms lie in the co-ordination plane.

As expected,[13] steric retardation is much less important in the solvolytic reaction pathway. On going from the N–N to the S–S system the k_1 values increase from 3.8×10^{-5} to almost 10^{-3} s^{-1}, in accordance with a S–S > N–N *trans* + *cis* effect. The relevance of the k_1 as compared to the k_2[Y$^-$] contribution to the measured rate constant is such that in the extreme case of the substrate [Pt(PhSCH$_2$CH$_2$SPh)Cl(Br)] reacting with [Cl$^-$] = 0.05 mol dm^{-3}, 95% of the substitution occurs through the solvolytic pathway. Of course, this observation becomes evident when Y$^-$ is a relatively poor nucleophile, like chloride ion.

The second-order rate constants (Table 3) show that in any case the reactivity of these systems is largely controlled by the nature of the incoming nucleophile Y$^-$, as expected for associative processes, and according to the sequence I$^-$ > Br$^-$ > Cl$^-$, typical of substitutions at platinum(II) substrates. (The corresponding nucleophilicity index, n^0Pt, is 5.46, 4.18 and 3.04 for iodide, bromide and chloride ions respectively.[14])

A *cis*-labilizing effect of the non-participating ligand Z may also be evaluated and can be shown to be small and dependent upon the nature of Y$^-$. A comparison of the reactions of [Pt(PhSCH$_2$CH$_2$SPh)Br$_2$] and [Pt(PhSCH$_2$CH$_2$SPh)I(Br)] with iodide ($k_2 = 28.1 \times 10^{-2}$ and 9.7×10^{-2} dm^3 mol^{-1} s^{-1} respectively) suggests a *cis*-labilizing effect Br > I. However, if one takes into account a statistical correction due to the presence of two replaceable bromides in the first substrate, the difference is much reduced (14×10^{-2} to 9.7×10^{-2}).

It is also possible to compare systems differing only in the nature of the leaving group, in order to obtain indications about the relative lability of the halogens. The substitution of X by iodide in [Pt(PhSCH$_2$CH$_2$SPh)I(X)] ($k_2 = 8.9 \times 10^{-2}$ and 9.7×10^{-2} dm^3 mol^{-1} s^{-1} for X = Cl and Br respectively) indicate the same lability for the two halogens, within the limit of experimental errors. Since the reactions of [Pt(PhSCH$_2$CH$_2$SPh)Cl(Br)] and [Pt(PhSCH$_2$CH$_2$SPh)Cl(I)] with chloride ($k_2 = 2.8 \times 10^{-4}$ and 5.1×10^{-4} dm^3 mol^{-1} s^{-1} respectively) lead to a lability sequence I > Br, a more general sequence I > Br ≈ Cl can be derived. However the differences are quite small, the reactivity being largely dominated by the nature of the entering group. Analogous results with small differences within the sequence are reported in the literature for the lability of halogens in cationic substrates [Pt(dien)X]$^+$ (dien = 1,5-diamino-3-azapentane; X = Cl, Br or I)[15] as well as for the neutral systems [Pt(bipy)(NO$_2$)X][16] (X = Cl, Br or I) reacting



Scheme 2

Table 5 Nucleophilic discrimination factors, *s*, for the [Pt(PhSCH$_2$-CH$_2$SPh)Z(X)] complexes

	Nucleophile		
Complex	a	b	*s*
[Pt(PhSCH$_2$CH$_2$SPh)Cl$_2$]	Br	I	1.27
[Pt(PhSCH$_2$CH$_2$SPh)Br$_2$]	Cl	I	0.99
[Pt(PhSCH$_2$CH$_2$SPh)I$_2$]	Br	Cl	0.84
[Pt(PhSCH$_2$CH$_2$SPh)I(Cl)]	Br	I	0.94
[Pt(PhSCH$_2$CH$_2$SPh)I(Br)]	Cl	I	0.93

with anionic nucleophiles and seems to be relatively general, the only reported exception being the [Pt(dien)X]$^+$ substrates[17] reacting with pyridine, where chloride has been quoted to be approximately two times more labile than bromide and three times than iodide.

The ability of a substrate to discriminate among various nucleophiles is usually numerically expressed by the slope of the straight line obtained by plotting log k_2 *vs.* the nucleophilicity, n^0Pt, of the reagent.[11] In the present case, this cannot be done properly, since just two nucleophiles have been studied for each substrate. However a rough estimate of the discrimination is possible in terms of $s = \log\{[k_2(\mathrm{a})/k_2(\mathrm{b})]/[n^0\mathrm{Pt(a)} - n^0\mathrm{Pt(b)}]\}$, a and b being the two nucleophiles examined. The results, summarized in Table 5, suggest that the nucleophilic discrimination factors are related to some extent to the electronegativity of the ligands. The presence of the more electronegative halogens seems to lead to an enhancement of the electrophilicity of the reaction centre and then to a relatively large ability to discriminate among the entering nucleophiles. However, this interpretation needs to be supported by further measurements with a wider range of nucleophiles.

Finally, a combination of the first- and second-order rate constants can provide some information on the ability of the monocationic intermediate solvento species, [Pt(PhSCH$_2$-CH$_2$SPh)Z(solv)]$^+$ (solv = solvent), to discriminate among the entering nucleophiles. From the general reaction Scheme 2 attention can be drawn to the fact that $K_{\mathrm{tot}} = K_1K_2$, *i.e.* $k_2{}^{\mathrm{f}}/k_2{}^{\mathrm{r}} = (k_1{}^{\mathrm{f}}/k_3)(k_4/k_1{}^{\mathrm{r}})$ where $k_4/k_3 = K_{\mathrm{tot}}(k_1{}^{\mathrm{r}}/k_1{}^{\mathrm{f}})$ and that the ratio $[\log(k_4/k_3)]/[n^0\mathrm{Pt(Y)} - n^0\mathrm{Pt(X)}] = s$ is a measure of the nucleophilic discrimination factor for the cationic intermediate. This type of calculation can be done for each equilibrium, when the first- and second-order kinetic constants are available. The results show that the solvento complexes, in spite of being monocationic species, exhibit nucleophilic discrimination factors less than 1, in the range 0.7–0.9. In our opinion this could be related to the fact that the small oxygen atom acting as donor localizes negative charge near to the reaction centre better than do the halogens.

Acknowledgements

We thank the Italian Ministry of University and Consiglio Nazionale delle Ricerche (Rome) for financial support and Miss Tatiana Bobbo for technical assistance.

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Received 21*st July* 1993; *Paper* 3/04306A