The *cis*-Effect of Anionic Ligands in Nucleophilic Substitution Reactions on Planar Platinum(II) Complexes.
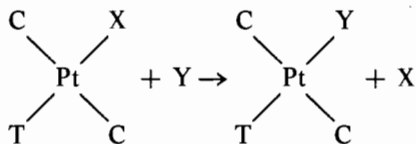
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The kinetics of replacement of chloride in the complexes of the type [Pt(bipy)(C)Cl], *where C is an anionic ligand, by various nucleophiles, have been studied in MeOH at 25°C. The nature of the ligand C, which is* cis *to the leaving chloride, has an appreciable influence upon the intrinsic reactivity and upon the nucleophilic discrimination factor. The nature of this* cis *effect is discussed.*

Introduction

The ligand displacement reactions of planar platinum(II) complexes have been quite extensively studied from a kinetic point of view in the last few years[1] and some generalizations have been made. The general rate law for the process,

$$
\begin{array}{ccc}
C \quad X & & C \quad Y \\
\diagdown \diagup & & \diagdown \diagup \\
Pt \quad + Y \rightarrow & & Pt \quad + X \\
\diagup \diagdown & & \diagup \diagdown \\
T \quad C & & T \quad C
\end{array}
$$

(where X and Y are the leaving and entering groups respectively, and C and T are the ligands *cis* and *trans* to X in the starting complex) is rate = $(k_1 + k_2[Y])$[complex]. The first and second order rate constants are both associated with bimolecular processes, the k_1 arising from the solvolytic path of the reaction.

It has been shown[2,3] that the entering ligands Y can be arranged in a quantitative sequence of relative reactivity by assuming, as a standard, their reactivity with *trans*-[Pt(py)$_2$Cl$_2$]. This is expressed as an index of nucleophilicity (n_{Pt}) which is a property of each entering group Y, and can be applied to Pt(II) complexes quite generally, by using the equation:

$$\log_{10}k_2 = s(n_{Pt}) + \log_{10}k_S \qquad (1)$$

where s (nucleophilic discrimination factor) and $\log_{10}k_S$ (intrisic reactivity) are two parameters that depend upon the nature of the complex. However, biphilic reagents such as NO$_2^-$, SeCN$^-$ and thiourea do not follow equation (1) and their relative reactivity depents also upon the charge and nature of the substrate.[3] The deviations from equation (1) can be useful in discussing the influence of π interactions during the formation of the transition state.

The n_{Pt} sequence was first applied[2] to non-electrolyte complexes of the type *trans*-[Pt(C)$_2$Cl$_2$], and the values obtained for the parameters s and $\log_{10}k_S$ were related to the influence of the neutral ligands C, *cis* to the leaving chloride, upon the reaction rates.

Equation (1) was also applied to series of Pt(II) complexes having different leaving groups[4,5,6] and it was pointed out that, other factors being equal, change of X produces a significant change in the intrinsic reactivity, but not in the nucleophilic discrimination factor.

Such observations were discussed in terms of a small effect of the nature of the leaving group upon the extent of the formation of the new bond in the transition state and were also related to the possible existence of labile five coordinated reaction intermediates.

There have not been until now, any systematic studies upon the effect on the kinetics of anionic ligands that are *cis* to the leaving group. Therefore we would like to report, in this paper, the data for the replacement of the coordinated chloride in the complexes [Pt(bipy)(C)Cl] (C=NCS, NO$_2$, N$_3$, Cl) by MeOH, NO$_2^-$, N$_3^-$, I$^-$ CNS$^-$ and thiourea, in methanol at 25°C. Chloride ion is the leaving group in all the cases, in spite of the different *trans*-effect of the ligands C, because of the very small lability of the chelating aromatic ligand.

Experimental Section

Materials. The complexes [Pt(bipy)(NO$_2$)Cl] and [Pt(bipy)Cl$_2$] were prepared according to the methods reported in the literature.[6] The complexes with C=N$_3$ and NCS were obtained by treating the dichloro complex with less than one equivalent of AgNO$_3$, in dimethyl-

(1) For a review on the argument: C. H. Langford and H. B. Gray, «Ligand Substitution Processes», W. A. Benjamin Inc., New York, N. Y., (1965), Chapter 2 and references therein.
(2) U. Belluco, L. Cattalini, F. Basolo, R. G. Pearson and A. Turco, *J. Am. Chem. Soc.*, 87, 241 (1965).
More recently eq. (1) has been modified in order to have the values of n_{Pt} dimensionless (U. Belluco, *Coordination Chemistry Reviews*, 1, 111 (1966). It does not affect the arguments discussed here.
(3) L. Cattalini, A. Orio, M. Nicolini, *J. Am. Chem. Soc.*, 88, 5734 (1966).

(4) U. Belluco, M. Graziani, M. Nicolini, P. Rigo, *Inorg. Chem.*, 6, 721 (1967).
(5) U. Belluco, R. Ettorre, F. Basolo, R. G. Pearson, A. Turco, *Inorg. Chem.*, 5, 591 (1966).
(6) L. Cattalini and M. Martelli, *Gazz. Chim. It.*, 97, 488 (1967).

formamide at 50°C for 20 mins. The AgCl formed was separated by centrifugation from the cooled solution. Dilution with water caused the precipitation of the unreacted dichloro complex, which was then separated by filtration. On adding an equivalent amount of NaN$_3$ (or KSCN) to the solution, the products were obtained as precipitates, which were washed with water and dried in vacuum over P$_2$O$_5$. The analytical data relative to all the complexes studied are summarized in Table I. The various reagents were all pure commercial samples. The methanol was dried by distillation over Mg(OCH$_3$)$_2$.

Kinetics. The complexes obey Beer's Law and are stable in methanol solution. The kinetics were followed in the way previously described[6] from the change in optical density with the time in the U.V. region of the spectrum, by using a double beam recording spectrophotometer Optica CF4. In all the experiments the concentration of the complex was less than $3 \times 10^{-5} M$ and that of the entering group was always sufficiently greater, in order to provide first-order conditions, and avoid complication from the reverse reaction. The values of the pseudo-first order rate constants, k_{obs}, determined in each experiment are reported in Table II.

Table I. Analytical Data for the Complexes of the type [Pt(bipy) (C)Cl]

cis group, C	Pt% calcd.	found.	N% calcd.	found.	C% calcd.	found.	H% calcd.	found.
SCN	43.8	44.2	9.43	9.35	29.6	29.1	1.81	1.86
N$_3$	45.5	45.2	16.3	15.9	28.0	28.1	1.88	1.87
Cl	46.2	46.8	6.63	6.53	28.5	28.8	1.91	1.94
NO$_2$	45.1	44.9	9.71	9.8	27.7	27.5	1.86	1.90

Table II. First order rate constants (k_{obs}) for the replacement of the coordinated chloride in the complexes [Pt(bipy)(C)Cl], in MeOH at 25°C

Complex	Reagent, $10^4 \times$ concn. (mole/l)		$10^4 \times k_{obs}$, sec^{-1}
[Pt(bipy)(NCS)Cl]	NO$_2^-$	300	1.0
»	»	600	1.7
»	»	1,000	2.7
»	»	1,300	3.5
»	N$_3^-$	50	1.15
»	»	150	2.8
»	»	250	4.5
»	»	500	8.5
»	I$^-$	5	35
»	»	20	140
»	»	30	210
»	»	50	350
»	CNS$^-$	1	13
»	»	2.4	30.6
»	»	5	64
»	»	7	90
»	Thiourea	1	75
»	»	2	150
»	»	4	300
»	»	5	370
[Pt(bipy)Cl$_2$]	NO$_2^-$	100	0.36
»	»	500	0.43
»	»	1,000	0.50
»	N$_3^-$	16.1	0.45
»	»	100	0.58
»	»	500	1.30
»	»	1,300	2.95
»	I$^-$	47	2.81
»	»	500	22.5
»	»	1,000	44.5
»	»	1,270	56.5
»	CNS$^-$	71	4.5
»	»	142	9.5
»	»	500	34.5
»	»	700	48.0
»	Thiourea	20	19
»	»	40	34
»	»	60	48
»	»	100	96
[Pt(bipy)(N$_3$)Cl]	NO$_2^-$	200	0.22
»	»	700	0.38
»	»	1,300	0.56
»	N$_3^-$	100	0.32
»	»	500	1.10
»	»	800	1.64
»	»	1,000	2.00
»	I$^-$	100	5.0
»	»	450	22.5
»	»	600	30.0
»	»	800	40.0
»	CNS$^-$	20.3	2.0
»	»	350	35
»	»	600	60
»	Thiourea	5	8
»	»	18.3	28.1
»	»	47.2	75.5

Results and Discussion

The specific rate constants, k_1 and k_2, determined for each substrate and entering group are collected in Table III, together with data previously reported[6] for the complex [Pt(bipy)(NO$_2$)Cl]). In Fig. 1 the values

Table III. Specific rate constants k_2 ($M^{-1} \times$ sec^{-1}) for the replacement of coordinated chloride in the complexes of the type [Pt(bipy)(C)Cl], in methanol at 25°C

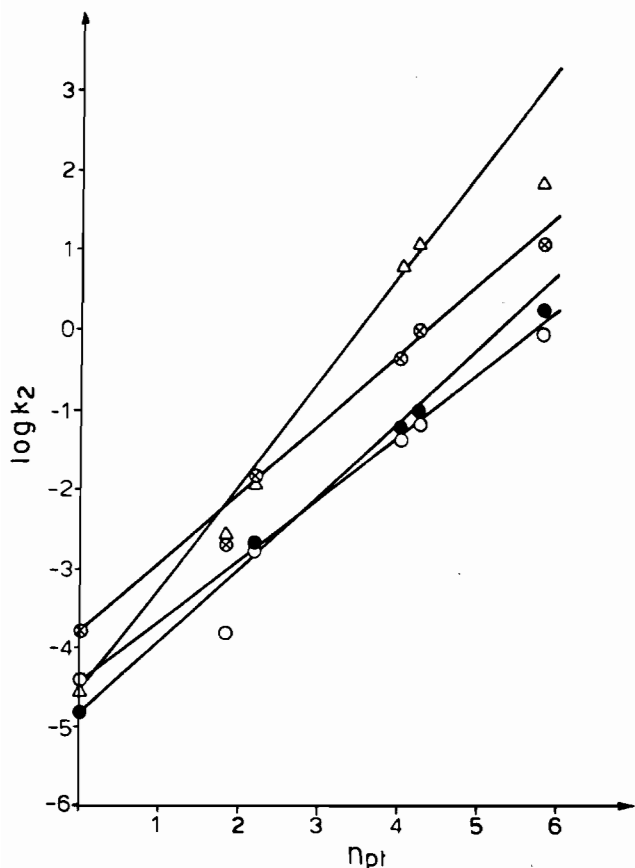| Entering group, Y	C=Cl	C=NO$_2$ [a]	C=N$_3$	C=NCS
MeOH [b]	3.8×10^{-5}	1.6×10^{-4}	1.6×10^{-5}	3.0×10^{-5}
NO$_2^-$	1.5×10^{-4}	2.0×10^{-3}	3.1×10^{-4}	2.4×10^{-3}
N$_3^-$	1.9×10^{-3}	1.6×10^{-2}	1.84×10^{-3}	1.65×10^{-2}
I$^-$	4.5×10^{-2}	4.45×10^{-1}	5.0×10^{-2}	6.9
CNS$^-$	7.0×10^{-2}	1.0	1.0×10^{-1}	12.85
Tu	9.4×10^{-1}	11.6	1.6	75.0

[a] Data from ref. 6. [b] Data of k_1, sec^{-1}.

Figure 1. Plot of $\log_{10}k_2$ vs the nucleophilicity index n_{Pt} for the various substrates, of the type [Pt (bipy) (C) Cl]. C = SCN = △; C = N₃ = ●; C = Cl = ○; C = NO₂ = ⊗.

of $\log_{10}k_2$ are plotted against the index of relative nucleophilicity, n_{Pt}. It appears quite clearly than equation (1) can apply to each complex, as far as non biphilic reagents are concerned; but, as expected, NO_2^- and thiourea do not lie on the straight lines. The values of intrinsic reactivity ($\log_{10}k_s$, intercepts in Fig. 1) and of nucleophilic discrimination factors (s, slopes in Fig. 1) are summarized in Table IV, together with the

Table IV. Substrate parameters and deviations Δ (Tu) for the complexes [Pt(bipy)(C)Cl] in MeOH at 25°C

Complex	s	$\log_{10}k_s$	Δ (Tu)
[Pt(bipy)Cl₂]	0.75	— 4.45	— 0.10
[Pt(bipy)(NO₂)Cl]	0.87	— 3.80	— 0.15
[Pt(bipy)(N₃)Cl]	0.95	— 4.80	— 0.30
[Pt(bipy)(NCS)Cl]	1.3	— 4.60	— 1.20

deviations for thiourea, Δ (Tu), expressed as the differencies between the experimental value of $\log_{10}k_2$ and the value obtained by interpolation from s, $\log_{10}k_s$ and n_{Pt}:[3,6]

$$\Delta \text{ (Tu)} = \log_{10}k_2 \text{ (exp)} - \log_{10}k_2 \text{ (calc)}$$

We prefer to discuss the deviations for thiourea rather than those for NO_2^- since the values of Δ (Tu) appear to be more sensitive to the nature of the substrate.

It has been recently found that the nature of the leaving group has a strong influence upon the intrinsic reactivity, but does not affect, to any considerable extent, the value of s.[4,5,6] However, the data in Table IV show that the nature of the cis ligand affects both the parameters, s and $\log_{10}k_s$. This behaviour corresponds to that observed when neutral ligands are cis to the leaving chloride, in the series trans-[Pt(C)₂Cl₂]², but the fact that in trans-[Pt(C)₂Cl₂] a large value of s is associated with a small value of $\log_{10}k_s$ (and viceversa) is no longer observed and no simple relationship between the two parameters can be found.

In the complexes of the series trans-[Pt(C)₂Cl₂] the larger values of s were obtained for substrates where the neutral ligands C were able to interact in a π fashion with the metal, so that a delocalization of negative charge from the reaction center to the ligands could occur during the formation of the transition state. In our opinion it is noteworthy that, in the present case (Table IV), large values of s parallel large negative values of Δ (Tu). In fact, if a relatively great nucleophilic discrimination factor is observed, it can be related with a relatively smaller localization of negative charge on the reaction center, as was previously sugggested,² and consequently the biphilicity of thiourea will become less important in decreasing the free energy of activation, owing to the reduced extent of π interactions. The deviations are more evident for thiourea than for NO_2^-, probably because the greater nucleophilicity of thiourea corresponds to a greater degree of bond-making in the transition state. Incidentally, the values of Δ (Tu) can only be compared to each other, since the absolute values are related to the index n_{Pt} for thiourea, i.e. to its particular behaviour towards the standard substrate trans-[Pt(py)₂Cl₂].

The value of s increases for the various cis ligands, according to the sequence:

$$SCN (1.3) > N_3 (0.95) > NO_2 (0.87) > Cl (0.75$$
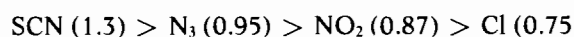
and it might be significant that this sequence corresponds to that of n_{Pt}, i.e. of relative nucleophilicity towards Pt(II) complexes:[2]

$$Tu (5.78) > SCN^- (4.26) > I^- (4.02) > N_3^- (2.19) >$$
$$NO_2^- (1.81) > Cl^- (1.65)$$
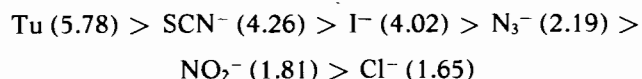
and also to the qualitative sequence of trans-effect. If the presence of a soft ligand, either as entering group, or cis or trans to the leaving group, can contribute through its micropolarizability to a better distribution of charge in the transition state, the correspondence of these sequences might be not fortuitous.

Finally, a comparison can be made for the reactions of thiourea with the complexes [Pt(bipy)(NO₂)₂] and [Pt(bipy)(NO₂)Cl]. In the first case[6] the deviation Δ (Tu) is strongly positive (+0.80) as expected since two biphilic ligands are both present in the plane of the trigonal bipyramid which is the transition state for

these processes.[1]   In the second case the value of Δ(Tu) is negative (—0.15) and in the sequence of *cis* effect the group NO_2 does not exibit any particular behaviour. The overall behaviour agrees closely with the suggestion[1] that, because of the different possibility of π interactions for ligands in the trigonal plane and those axial to it, *cis* ligands cannot be as helpful as *trans* ligands in lowering the free energy of activation by metal→ligand π bonding.