Coordination Chemistry Reviews
Elsevier Publishing Company, Amsterdam
Printed in the Netherlands.

DISPLACEMENTS ON SOME Pt(II) SQUARE-PLANAR COMPLEXES IN PROTIC AND DIPOLAR APROTIC SOLVENTS

UMBERTO BELLUCO*

Istituto di Chimica Generale, Università di Padova (Italy)

An extensive study of mono-halide displacement of some platinum(II) square-planar complexes of the type *trans*-$[PtL_2Cl_2]$ has been made with various nucleophiles in methanol[1]. The rates of the reactions follow the two terms rate law given by equation (1):

$$\text{Rate} = k_1[\text{complex}] + k_2[\text{complex}][\text{Y}] \tag{1}$$

k_2 is a second order rate constant for the nucleophile Y; k_1 is a measure of the pseudo first-order rate constant for the reaction in which the solvent is the nucleophile[1–3]. A set of nucleophilic reactivity constants, n^0_{Pt}, is defined for these reagents by selecting *trans*-$[Pt(py)_2Cl_2]$ in methanol at 30 °C as a standard. The values of

TABLE I

VALUES OF NUCLEOPHILIC REACTIVITY CONSTANTS, $n_{Pt}{}^0$, DEFINED FOR VARIOUS REAGENTS Y BY SELECTING *trans*-$[Pt(py)_2Cl_2]$ IN CH_3OH AT 30 °C AS A STANDARD SUBSTRATE

Entering group, Y	$n_{Pt}{}^0 = \log (k_2/k_2{}^0)_0$
CH_3OH	0
CH_3O^-	<2.4
Cl^-	3.04
NH_3	3.06
C_5H_5N	3.13
NO_2^-	3.22
N_3^-	3.58
NH_2OH	3.85
N_2H_4	3.86
C_6H_5SH	4.14
Br^-	4.18
I^-	5.42
SCN^-	5.65
$SO_3{}^{2-}$	5.79
$SeCN^-$	7.10
$C_6H_5S^-$	7.17
Thiourea	7.17
$S_2O_3{}^{2-}$	7.34

---

* Centro Chimica Radiazioni e Radioelementi – C.N.R.

n_{Pt}° are equal to $\log (k_2/k_2^{\circ})_0$. Other platinum(II) complexes are found to obey the linear free energy relationship:

$$\log k_2 = s n_{Pt}^{\circ} + \log k_2^{\circ} \qquad (2)$$

The values of the first order rate constants, k_1 $\sec^{-1}$, for the reaction of solvent as a nucleophilic reagent have been divided by the "concentration" of methanol to convert them to second order[3b] rate constants, k_2^0 $M^{-1}\sec^{-1}$. In the relationship (2), s is a nucleophilic discrimination factor (N.D.F.) and $\log k_2^{\circ}$ is a measure of the intrinsic reactivity of each complex referring to the reaction in which the methanol is the entering group. Complexes with a low intrinsic reactivity have a large value of N.D.F. and complexes which are highly reactive show little discrimination. Strong π-bonding ligands, in the *cis* position, produce low values of k_2^0 but large values of discrimination (Table II).

TABLE II

NUCLEOPHILIC DISCRIMINATION FACTORS AND INTRINSIC REACTIVITIES, LOG k_2°, FOR SEVERAL PLATINUM(II) COMPLEXES IN METHANOL*

Complex	*Intrinsic reactivity, log* k_2°	*Nucleophilic discrimination factors*
trans-$[Pt(PEt_3)_2Cl_2]$	-8.82	1.43
trans-$[Pt(AsEt_3)_2Cl_2]$	-7.49	1.25
trans-$[Pt(pip)(PEt_3)Cl_2]$	-7.35	1.15
trans-$[Pt(SeEt_2)_2Cl_2]$	-6.13	1.05
trans-$[Pt(pip)_2Cl_2]$	-5.82	0.91
trans-$[Pt(S(s\text{-}Bu)_2)_2Cl_2]$	-5.74	0.57
$[Pt(en)Cl_2]$**	—	0.64
$[Pt(dien)Br]^{+}$**	—	0.75
$[Pt(dien)Cl]^{+}$**	—	0.65
$[Pt(dien)H_2O]^{2+}$**	—	0.44

* For the survey of these data see ref. 1 and references therein.

** Data in water. Data for *trans*-$[PtL_2Cl_2]$ are at 30 °C. Data for *trans*-$[Pt(S(s\text{-}Bu)_2)_2Cl_2]$ at 55 °C.

Fig. 1 shows that the reactivity of poor nucleophiles (solvent, Cl^-, Br^-, NO_2^-, N_3^-) is higher in *trans*-$[Pt(pip)_2Cl_2]$ than in *trans*-$[Pt(PEt_3)_2Cl_2]$. With good nucleophiles (I^-, SCN^-, $SeCN^-$ and thiourea), the phosphine-complex exhibits a reactivity which becomes comparable to that of the piperidine-complex. This kinetic behaviour might be rationalized by considering the features which generally promote strong interaction in a generalized acid–base reaction.

It is known that the softness of the central atom in a complex compound depends, among other factors, on the associated ligands[4,5]. Soft ligands coordinated can confer softness to a metal ion. Thus, the complex $Co(NH_3)_5F^{2+}$ is more stable than $Co(NH_3)_5I^{2+}$, but the reverse stability order is found for $Co(CN)_5X^{3-}$. In complexes of the type $[ML_2XY]$ of d^8 metal ions, one finds that the compounds $[ML_2XR]$ ($M = Ni^{II}$, Pd^{II}, Pt^{II}; $X = Cl$, Br, I; $R = H$, CH_3, C_6H_5) are

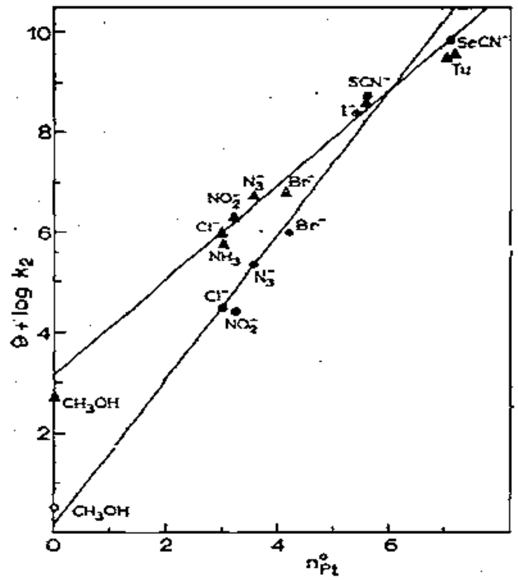

Fig. 1. Correlation between the rates of reaction of Pt^{II} complexes in methanol at 30 °C with the standard *trans*-[Pt(pyridine)$_2$Cl$_2$] for different entering groups: *trans*-[Pt(PEt$_3$)$_2$Cl$_2$] ●; *trans*-[Pt(piperidine)$_2$Cl$_2$] ▲.

stable when L is a soft ligand such as PR_3, whereas, the corresponding complexes with L = amines (hard ligands) are not known[6]. This "symbiosis" of soft ligands CN^-, CO, R^-, R_3P, I^- in stable complexes was pointed out by Jørgensen and it reveals the tendency of "soft ligands to flock together"[4].

Considering the kinetics of platinum(II) complexes, it can be noted that in going from hard to soft entering groups, the reaction becomes relatively easier with the phosphine-complex than with the piperidine-complex. This is probably due to the lower softness induced on the metal ion by the uncharged ligands in the last case. Of course, the electrophilic–nucleophilic interaction in the transition state for substitution reactions is a generalized acid–base reaction.

The working hypothesis that soft ligands L cooperate to stabilize the transition state in reactions of *trans*-[PtL$_2$Cl$_2$] with soft nucleophiles, suggests that the order of softness of the coordinated platinum atom should parallel the order of increasing nucleophilic discrimination. Thus, for these systems, the softness of the metal ion in the *trans*-[PtL$_2$Cl$_2$] follows the order:

$$L = PEt_3 > AsEt_3 > SeEt_2 > \text{pyridine} > \text{piperidine}.$$

The linear free energy relationship is obeyed also for the reactions in ethanol and in *tert*-butanol. In these solvents the difference in the nucleophilic discriminations is in accordance with the different solvation of the anions. The reactivity order parallels the polarizability order of the nucleophiles, *i.e.*, the softness order.

The assumption of course is made that the transition state structure is the same in different solvents.

Most of platinum(II) kinetics refer to reactions in hydroxylic solvents such as alcohols and water[1,3,7]. In dipolar aprotic solvents the only data available deal with the chloride exchange[8] of *trans*-$[Pt(py)_2Cl_2]$.

Many factors have been recognized to influence the nucleophilic reactivity towards different electrophilic centers. Two factors seem to be generally predominant: the energy required to remove the fraction of electron from Y^- in solution and the energy corresponding to the fraction of desolvation at transition state[9–14]. However, no attempts have been made to evaluate the contribution of the solvation to the reactivity of the entering groups reacting with soft center, such as Pt^{II}. Thus, mono-halide displacements on some *trans*-$[PtL_2Cl_2]$ complexes have been studied also in dipolar aprotic solvents. The kinetic data relative to the *trans*-$[Pt(PEt_3)_2Cl_2]$ in different solvents are summarized in Table III.

TABLE III

NUCLEOPHILIC DISCRIMINATION FACTORS FOR *trans*-$[PtL_2Cl_2]$ IN DIFFERENT SOLVENTS. THE VALUES IN ACETONE AND IN DIMETHYLSULFOXIDE ARE CALCULATED BY USING THE KINETIC DATA OF FIVE ENTERING GROUPS AT 25 °C.*

Solvent	*L = PEt₃*	*L = piperidine*
Methanol**	1.43	0.91
Acetone	1.04	0.78
Dimethylsulfoxide	1.05	0.61

* U. BELLUCO, M. MARTELLI AND A. ORIO, *Inorg. Chem.*, 5 (1966).
** Data at 30 °C.

The rate constants for the bimolecular reactions of free anions, k_2 $M^{-1}sec^{-1}$, in acetone were estimated by Acree's analysis which ascribes different reactivities to free and paired ions. The validity of this treatment is supported by the fact that the calculated k_2 value for a given anion is independent of the nature of the cation[15–17].

Data in Table III show that the reactivity order of free ions is the same in protic and dipolar aprotic solvents and it parallels the polarizability order. The reactivity is about the same in the two classes of solvents and the only difference is that the nucleophilic discrimination factor is greater in protic than in aprotic solvents, in accordance with the usual solvation of the entering groups. In principle, the solvent can affect the nucleophilic reactivity by means of the reagent solvation[14,18,19] and by the interaction platinum–solvent in the rate-determining step[8]. Solvation of the leaving group appears to be of small importance (to be discussed later). In the case of the *trans*-$[Pt(PEt_3)_2Cl_2]$, the presence of the two uncharged strong π-bonding ligands probably reduces the interaction of platinum(II) with dipolar solvents. Thus, the different reactivities found for the two complexes in going from methanol to acetone can be rationalized mainly on the basis of different solvation energies of the entering groups.

The general conclusion which can be drawn by examining these data is that in the reactions at soft centers, such as Pt^{II}, the solvation of the entering group becomes of relatively small importance when compared with the contribution of polarizability to the reactivity of the nucleophile.

It is of interest to note that in S_N2 reactions of some saturated carbon substrates, the nucleophilic order in protic solvents is: $I^- > Br^- > Cl^-$ but it is reversed in acetone[20] or dimethylformamide[19]. Moreover, with respect to some reactions of Pt^{II}, *e.g.* S_N2 reactions of methyl chloride with halide ions, there is also a larger shift of reactivity (about 100-fold) as the solvent is changed from water to acetone[21]. This kinetic behaviour was rationalized in terms of ion solvation. Thus, in protic solvents, the chloride ion, owing to its larger solvation, reacts slower than iodide ion. In dipolar aprotic solvents the reactivity order observed is expected because of the smaller solvation of Cl^- in respect to I^-. In most of these systems, "solvation is one of the most important factors controlling nucleophilicity, and hence the two factors affecting nucleophilic order cannot be separated"[14].

In order to investigate the effect of the solvent on the leaving group in Pt^{II} reactions, kinetics of *trans*-$[Pt(PEt_3)_2X(R)]$ (R = phenyl or substituted phenyl groups and X = Cl, Br, I, N_3, NO_2) with iodide ion and with thiourea have been studied in methanol and in dimethylsulfoxide[22].

TABLE IV

RELATIVE REACTIVITY RATIOS $(k_2^{Pt-X}/k_2^{Pt-Cl})_{Y=Tu}$ AT 30 °C FOR THE REACTION: *trans*-$[Pt(PEt_3)_2X\ (m\text{-}FC_6H_4)] + Tu \rightarrow$ *trans*-$[Pt(PEt_3)_2Tu\ (m\text{-}FC_6H_4)]^+ + X^-$

Complex	$(k_2^{Pt-X}/k_2^{Pt-Cl})_{Y=Tu}$	
	in *CH₃OH*	*in* *DMSO*
trans-$[Pt(PEt_3)_2Cl\ (C_6H_5)]$	1	1
trans-$[Pt(PEt_3)_2Br\ (C_6H_5)]$	0.7	0.6
trans-$[Pt(PEt_3)_2Cl\ (m\text{-}FC_6H_4)]$	1	1
trans-$[Pt(PEt_3)_2N_3\ (m\text{-}FC_6H_4)]$	0.36	0.31
trans-$[Pt(PEt_3)_2NO_2\ (m\text{-}FC_6H_4)]$	0.0037	0.0044
trans-$[Pt(PEt_3)_2I\ (m\text{-}FC_6H_4)]$	0.43	—

The rate data in Table IV show that in both the solvents the relative ease of replacement of the leaving groups in these complexes follows the order: Cl ~ Br ~ I $\lesssim$ N_3 > NO_2. This is the same order as that found for the $[Pt(dien)X]^+$ species reacting in water with a variety of entering groups[23,24]. Therefore, no relationship exists between the reactivity order of the nucleophiles towards Pt^{II} and the ease of displacement of the same ligands as replaceable groups. Furthermore, the ease of replacement is approximatively the same for all the X groups except for NO_2, (the biphilic character of which can probably make the Pt-leaving group bond stronger). The mobilities of the displaced groups compared with chloride (selected as a standard) are about the same in methanol and in dimethylsulfoxide. That is to say, the reactivity ratios

$$\left(\frac{k_2^{\mathrm{Pt-X}}}{k_2^{\mathrm{Pt-Cl}}}\right)_{\mathrm{Y\,=\,Thiourea}}$$

are independent of the nature of the solvent. The solvation of the leaving group is therefore not a kinetically important step and this suggests that probably charge separation at the transition state is not very large.

Consequently, one can conclude that, at least with halide displacements in $\mathrm{Pt^{II}}$ complexes, bond formation at the transition state is the predominant factor. It is therefore likely, that these reactions proceed *via* formation of an unstable five-coordinated intermediate, in which bond-making is rate-determining step and the Pt–Y bond may be still partially ionic. It may be pointed out that stable five-coordinated $\mathrm{Pt^{II}}$ complexes are now well known[25,26]. Moreover, $\mathrm{Pt^{II}}$ reactions are generally accompanied by relatively low values of activation enthalpies and by rather large negative entropies, in agreement with an increase in bonding in the transition state[24]. Work is presently in progress to investigate whether this conclusion is of general validity: Can it be applied to complexes of low intrinsic reactivity or to complexes which react with poor nucleophiles?

Halide-displacement reactions with *trans*-$[\mathrm{Pt(PEt_3)_2Cl(R)}]$ (R = methyl and phenyl groups) and various entering groups have been investigated in methanol and in dimethylsulfoxide[27]. The nuclephilic discriminations in methanol are: $\mathrm{NDF^{R=Cl}} = 1.43$; $\mathrm{NDF^{R=C_6H_5}} = 0.84$; $\mathrm{NDF^{R=CH_3}} = 0.74$. The rate data for the reactions of the complexes *trans*-$[\mathrm{Pt(PEt_3)_2Cl(R)}]$ (with R = Cl, $\mathrm{C_6H_5}$, substituted phenyl groups or $\mathrm{CH_3}$) in methanol indicate that the *trans*-effect order of R varies by changing the nature of the entering group. Thus, by using the k_2 values as a measure of the *trans*-effect, the *trans*-effect order is methyl > phenyl > chloride when a poor nucleophile is the entering group *e.g.* $\mathrm{NO_2^-}$ and $\mathrm{Br^-}$; whereas, with good entering groups, such as $\mathrm{I^-}$ or Tu, the order is methyl > chloride > phenyl. In order to render the *trans*-effect order independent of the nature of the entering group, the influence of a group R in displacements on *trans*-$[\mathrm{Pt(PEt_3)_2Cl(R)}]$ can be conveniently expressed in terms of inverse of the nucleophilic discrimination factor. Following this criterion, the relative influence of R is Cl = 1; phenyl = 1.7; methyl = 1.93.

Returning to the reactions of *trans*-$[\mathrm{PtL_2Cl_2}]$ complexes with L = $\mathrm{PEt_3}$ or piperidine, data in Table II show that the influence of the chloride as *trans*-group is higher in the piperidine-complex (1/NDF = 1.1) than in phosphine-complex (1/NDF = 0.7). That is to say, the influence of a Cl group in nucleophilic displacements on *trans*-$[\mathrm{PtL_2Cl_2}]$ is larger when the *cis* group L is not π-bonding ligand.

Finally, we have recently found that in some complexes of the type *trans*-$\mathrm{Pt(pip)_2(NO_2)X}$ (X = Cl, Br, $\mathrm{N_3}$, $\mathrm{NO_2}$) the leaving group X has little effect upon the discrimination power of the platinum, whereas the reactivity depends significantly on the nature of the leaving group. This differs to some extent from the observations made with the Au^{III} complexes[28].

Part of the work here discussed has been done at Northwestern University with Professors F. Basolo and R. G. Pearson and in Padova with Professor A. Turco. The work was supported by the Italian Consiglio Nazionale delle Ricerche (C.N.R. – Roma).

REFERENCES

1 U. Belluco, L. Cattalini, F. Basolo, R. G. Pearson and A. Turco, *J. Am. Chem. Soc.*, 87 (1965) 241.
2 H. B. Gray and R. J. Olcott, *Inorg. Chem.*, 1 (1962) 481.
3 a) F. Basolo and R. G. Pearson, *Progr. Inorg. Chem.*, 4 (1962) 381; b) R. J. Mawby, F. Basolo, R. G. Pearson, *J. Am. Chem. Soc.*, 86 (1964) 3994.
4 C. K. Jørgensen, *Inorg. Chem.*, 3 (1964) 1201, and references therein.
5 R. G. Yalman, *Inorg. Chem.*, 1 (1962) 16.
6 J. Chatt and B. L. Shaw, *J. Chem. Soc.*, (1959) 705, 4020.
7 H. B. Gray, *J. Am. Chem. Soc.*, 84 (1962) 1548.
8 R. G. Pearson, H. B. Gray and F. Basolo, *J. Am. Chem. Soc.*, 82 (1960) 787.
9 J. O. Edwards and R. G. Pearson, *J. Am. Chem. Soc.*, 84 (1962) 16.
10 R. G. Pearson, *J. Am. Chem. Soc.*, 85 (1963) 3533.
11 J. F. Bunnett, *Ann. Rev. Phys. Chem.*, (1963) 271.
12 C. A. Bunton, *Nucleophilic Substitution at a Saturated Carbon Atom*, Elsevier, Amsterdam, 1963.
13 E. S. Gould, *Mechanism and Structure in Organic Chemistry*, Ed. Holt, New York, 1959, p. 260.
14 R. F. Hudson, *Chimia*, 16 (1962) 173.
15 H. C. Robertson and S. F. Acree, *J. Am. Chem. Soc.*, 37 (1915) 1902.
16 J. H. Shroder and S. F. Acree, *J, Chem. Soc.*, (1914) 2582.
17 E. K. Marshal and S. F. Acree, *J. Phys. Chem.*, 19 (1915) 589.
18 A. J. Parker, *Quart. Rev.*, 16 (1962) 163.
19 W. M. Weaver and S. D. Hutchison, *J. Am. Chem. Soc.*, 86 (1964) 261.
20 S. Winstein, L. G. Savedoff, S. Smith, I. D. R. Stevens and J. S. Gall, *Tetrahedron Letters*, 9 (1960) 24.
21 A. J. Parker, *J. Chem. Soc.*, (1961) 1328.
22 U. Belluco, P. Rigo, M. Graziani and R. Ettorre, *Inorg. Chem.*, 5 (1966).
23 F. Basolo, H. B. Gray and R. G. Pearson, *J. Am. Chem. Soc.*, 82 (1960) 4200.
24 U. Belluco, R. Ettorre, F. Basolo, R. G. Pearson and A. Turco, *Inorg. Chem.*, 5 (1966).
25 U. Belluco, L. Cattalini, F. Basolo, R. G. Pearson and A. Turco, *Inorg. Chem.*, 4 (1965) 25.
26 L. M. Venanzi, *Angew. Chem. Intern. Ed. Engl.*, 3 (1964) 453 for a review; R. O. Cramer, R. V. Lindsey, Jr., C. T. Prewitt and V. G. Stolberg, *J. Am. Chem. Soc.*, 87 (1965) 658; P. C. Westland, *J. Chem. Soc.*, (1965) 3060, 5371; F. G. Mann, *Chem. Ind.*, (1965) 944; C. M. Harris, R. S. Nyholm and D. J. Philips, *J. Chem. Soc.*, (1963) 4379; J. W. Collier, F. G. Mann, D. G. Watson and H. R. Watson, *J. Chem. Soc.*, (1964) 1803.
27 U. Belluco, M. Graziani and P. Rigo, *Inorg. Chem.*, 5 (1966).
28 L. Cattalini and M. L. Tobe, *Inorg. Chem.*, 5 (1966).