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Influence of the Entering Group on the *trans* Effect in Some Platinum(II) Complexes

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The rates of substitution reactions of Pt(II) square-planar complexes of the type *trans*-$[Pt(P(C_2H_5)_3)_2ClR]$ (R = CH_3 or C_6H_5) with different nucleophiles have been measured in methanol. The *trans* effect order of R groups depends on the nature of the entering group Y^-. The suggestion is made that the *trans* effect of a given R group can be defined in terms of an inverse correlation with the nucleophilic discrimination factor, whereby the *trans* effect becomes independent of the nature of the entering group.

Introduction

Kinetic studies of the reactions in ethanol solution between pyridine and several alkyl and aryl compounds of the type *trans*-$[Pt(P(C_2H_5)_3)_2ClR]$ have been reported. The relative rates of attainment of equilibrium were discussed in terms of both electrostatic (polarization) and π-bonding theories of the *trans* effect.[1,2]

In the present work the reactions of *trans*-$[Pt(P(C_2H_5)_3)_2ClR]$ have been carried out by using strong nucleophiles in order to force the reactions to go to completion. Thus, it was possible to estimate the second-order rate constants.

The object was to study the dependence of the *trans* effect of R on the nature of the entering group in nucleophilic displacements.

Experimental Section

Materials.—The complexes *trans*-$[Pt(P(C_2H_5)_3)_2ClR]$ (R = CH_3 or C_6H_5) were prepared and characterized by the methods reported in the literature.[3]

Absolute methanol was dried and purified by distillation after refluxing over $Mg(OCH_3)_2$.

Conductivity Measurements.—For these measurements a conductivity bridge has been used with the cell thermostated at 30°.

Results

Kinetics.—The reactions with lithium, sodium, or *n*-tetrabutylammonium salts of NO_2^-, N_3^-, Br^-, I^-, and thiourea were followed by measuring the changes in absorbance in the ultraviolet region, using a Beckman DK-2A or an Optica CF-4 recording apparatus, with a cell compartment thermostated at the desired temperature. The details of experimental procedure have been given in a separate paper.[4]

The reactions were carried out in methanol by using an excess of reagent (10^{-3}–10^{-1} M) with respect to the complex ($\sim 10^{-4}$ M) in order to provide pseudo-first-order conditions and to force the reactions to go to completion. In most cases the reagent concentration was varied by at least a factor of ten, and measurements were made at six different reagent concentrations. In some runs the ionic strength was changed by adding $LiNO_3$, and the rate constants were practically unaffected. Data have been reported in the table filed with the American Documentation Institute (see footnote *a* of Table II). The variation of the pseudo-first-order rate constants, k_{obsd} (sec^{-1}), with the initial reagent concentration was consistent with the two-term rate law

$$k_{obsd} = k_1 + k_2[Y^-]$$

where k_1 (sec^{-1}) is the rate constant for the solvent path and k_2 (M^{-1} sec^{-1}) is for the direct reagent path.[5] The reactions were carried out at at least two different temperatures.

The rate constants and the activation parameters for the reactions in methanol are summarized in Tables I and II. The error in ΔH^* is ±1 kcal/mole, estimated, and in ΔS^* it is ±2 eu/mole.

Discussion

Nucleophilic discrimination factors for the two Pt(II) complexes examined are reported in Table III. These values were estimated using the least-square analysis on the linear free energy relationship

$$\log k_2 = sn^\circ_{Pt} + \log k_2^\circ$$

s is a nucleophilic discrimination factor and $\log k_2^\circ$ is the intrinsic reactivity of the complex for the reaction in which the solvent is the incoming group; k_2° is the second-order rate constant for the solvent path. The nucleophilic reactivity constants, n°_{Pt}, are defined as $\log (k_2/k_2^\circ)_0$ for substitution reactions of various Y ligands with *trans*-$[Pt(py)_2Cl_2]$ in methanol at 30°.[6]

As shown in Table III, the solvent rate constants for the methyl and phenyl complexes are predicted to be considerably smaller than the values experimentally found. It is likely that, in addition to the solvent path, some other process, such as a bond cleavage by a dissociation path, is responsible for the increased reactivity. It is worth noting that in the case of $[Pt(dien)H_2O]^{2+}$ (dien = diethylenetriamine) reacting with Cl^- and NO_2^-, a reagent-independent rate was found, although

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[1] F. Basolo, J. Chatt, B. H. Gray, R. G. Pearson, and B. L. Shaw, *J. Chem. Soc.*, 2207 (1961).

[2] F. Basolo and R. G. Pearson, *Progr. Inorg. Chem.*, **4**, 388 (1962).

[3] J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 705, 4020 (1959).

[4] U. Belluco, P. Rigo, M. Graziani, and R. Ettorre, *Inorg. Chem.*, **5**, 1125 (1966).

[5] H. B. Gray and R. J. Olcott, *ibid.*, **1**, 481 (1962).

[6] (a) U. Belluco, L. Cattalini, F. Basolo, R. G. Pearson, and A. Turco, *J. Am. Chem. Soc.*, **87**, 241 (1965); (b) U. Belluco, "Coordination Chemistry Review," Elsevier Publishing Co., New York, N. Y., 1966.

TABLE I

RATES OF MONOHALIDE DISPLACEMENTS (VALUES OF 10^2k_2, M^{-1} SEC^{-1}) ON SOME Pt(II) COMPLEXES WITH VARIOUS NUCLEOPHILES IN METHANOL AT 30°

Nucleophile, Y^-	*trans*-$[Pt(P(C_2H_5)_3)_2ClCH_3]$	*trans*-$[Pt(P(C_2H_5)_3)_2ClC_6H_5]$	*trans*-$[Pt(P(C_2H_5)_3)_2Cl_2]$[a]
CH_3OH[b]	4×10^{-2}	0.85×10^{-2}	
NO_2^-	1.6	0.45	0.0027
N_3^-	7	0.8	0.02
Br^-	11.6	1.8	0.093
I^-	40	6.0	23.6
Thiourea	≥ 1500	630	Very fast

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

TABLE II[a]

ACTIVATION PARAMETERS FOR REACTIONS IN METHANOL

$$trans\text{-}[Pt(P(C_2H_5)_3)_2ClR] + Y^- \longrightarrow trans\text{-}[Pt(P(C_2H_5)_3)_2YR] + Cl^-$$

Nucleophile, Y^-	Examined temp, °C	ΔH^*, kcal/mole			ΔS^*, eu/mole		
		R = C_6H_5	R = CH_3	R = Cl	R = C_6H_5	R = CH_3	R = Cl
Br^-	20, 30	16.5	14	...	−12	−16	...
N_3^-	20, 30	17	15.5	15.5	−11	−13	−24
I^-	20, 25, 30	12	12	...	−24	−21	...
Thiourea	20, 25, 30	7.5	...	...	−30	...	...
CH_3OH[b]	20, 30	12	12	...	−36	−31	...

[a] Supplementary material (specific kinetic data used to estimate values in this table) has been deposited as Document No. 8854 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. 20540. A copy may be secured by citing the document number and by remitting \$1.25 for photoprints or \$1.25 for 35-mm microfilm. Advance payment is required. Make checks payable to: Chief, Photoduplication Service, Library of Congress. [b] Activation parameters for the reagent-independent path; the ΔS^* values are for the second-order rate constant, $k_2°$ (M^{-1} sec^{-1}).

TABLE III

NUCLEOPHILIC DISCRIMINATION AND INTRINSIC REACTIVITY OF *trans*-$[Pt(P(C_2H_5)_3)_2ClR]$ IN METHANOL

Ligand R	Nucleophilic discrimination factor	Intrinsic reactivity,[c] log $k_2°$	
Methyl	0.74	−4.13	(−2.43)[b]
Phenyl	0.84	−5.27	(−3.27)[b]
Chloride	1.43[a]	−8.82	...

[a] Value from ref 6. [b] Experimental data. [c] $k_2°$ is equal to k_1 divided by the "concentration" of methanol (see ref 6b).

the principal mechanism responsible for the observed rates is a bimolecular reaction with the reagent. Indeed, totally second-order rates are expected if a bimolecular reaction with the solvent is assumed to determine the k_1 value.[5] Due to a larger electron transfer from R^- toward platinum than from Cl^-,[1,3] the hypothesis of an additional path independent of the solvent would agree with a considerable ionic character of the Pt–Cl bond in the *trans*-$[Pt(P(C_2H_5)_3)_2ClR]$ complexes.[7] In the case of the ethylenetrichloroplatinite ion, appreciable ionic dissociation in aqueous 0.2 *N* perchloric acid was observed. The dissociation of one chloride ion is practically complete in a 10^{-3} *M* solution of $C_2H_4PtCl_3^-$, and the equilibrium is established within a few minutes.[8]

Conductance measurements were made, to look for evidence of ionic species in solutions of methyl and phenyl complexes. The very low conductivity values found indicate that these compounds are nonelectrolytes in methanol. However, a dissociation path contributing to the k_1 value cannot be excluded. Competition experiments in the presence of chloride ion cannot distinguish between solvolytic and dissociative paths, since it is likely that the two intermediates are kinetically undistinguishable owing to their high and comparable reactivity.[9] Thus, the nucleophilic discrimination factors listed in Table III have been estimated regardless of the solvent rate constants.

Rate data in Table I indicate that the *trans* effect order of ligands R depends on the nature of the entering groups.

Thus, by using the values of k_2 as a measure, the *trans* effect order is: $CH_3 > C_6H_5 > Cl$ for the reactions with the nucleophiles Br^-, N_3^-, and NO_2^-. On the other hand, a different *trans* effect order is found by comparing the rate constants k_2 (M^{-1} sec^{-1}) for the reactions with good nucleophiles (*e.g.*, iodide), the order being: $CH_3 > Cl > C_6H_5$.

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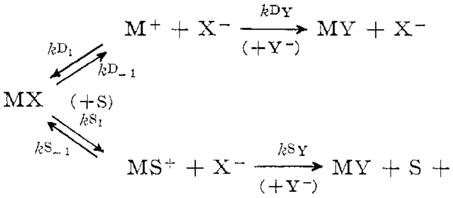
(7) P. G. Owston, J. M. Partridge, and J. M. Rowe, *Acta Cryst.*, **13**, 246 (1960).

(8) J. Leden and J. Chatt, *J. Chem. Soc.*, 2936 (1955).

(9) The general equations related to the reaction path independent of the nucleophile (*i.e.*, k_1) can be expressed as



$$M^+ + X^- \xrightarrow[(+Y^-)]{k^D_Y} MY + X^-$$
$$MX \underset{k^D_{-1}}{\overset{k^D_1}{\rightleftharpoons}} M^+ + X^-$$
$$MX \underset{k^S_{-1}}{\overset{k^S_1}{\rightleftharpoons}} (+S)\ MS^+ + X^-$$
$$MS^+ + X^- \xrightarrow[(+Y^-)]{k^S_Y} MY + S + X^-$$

The notations are the following: MX is the initial complex; $k^D{}_1$ and $k^D{}_{-1}$ are related to the dissociative path; $k^S{}_1$ and $k^S{}_{-1}$ are related to the solvolytic process. It is reasonable to assume that the displacements on MY by X^- or by the solvent S are negligible, due to the fact that the reagents Y^- are poor as leaving groups. Since the concentrations of the species M^+ and MS^+ are always small, we can apply a stationary-state treatment. Thus, in terms of the pseudo-first-order rate constant

$$(k_1)_{obsd} = \frac{k^D{}_1}{1 + \dfrac{k^D{}_{-1}[X^-]}{k^D{}_Y[Y^-]}} + \frac{k^S{}_1[S]}{1 + \dfrac{k^S{}_{-1}[X^-]}{k^S{}_Y[Y^-]}}$$

The decrease in $(k_1)_{obsd}$ on increasing the concentration of the added X^- does not permit distinction between solvolytic and dissociative paths, since their related terms both depend on the concentration of X^-.

In order to avoid the dependence of the *trans* effect on the entering group, it is suggested to define the *trans* effect of R in displacements on *trans*-[Pt(P(C_2H_5)$_3$)$_2$ClR] in terms of the inverse of the nucleophilic discrimination factor. Following this criterion, the *trans* effect order is: methyl = 1.93; phenyl = 1.7; chloride = 1 (selected as a standard). This is the same order found for the reactions of these complexes with the poor nucleophile pyridine (py)[1] in which the relative rates are k_{py} (R = CH_3) = 200, k_{py} (R = C_6H_5) = 30, k_{py} (R = Cl) = 1.

The high *trans* effect of the methide can be accounted mainly for its large polarizability. The *trans* activation of the phenyl group has been already attributed almost entirely to an inductive effect.[1] On the other hand, it is worth noting that aryl ligands seem to form π bonds to the platinum[8,10] and this may accelerate the *trans* substitution by stabilizing *via* π bonding the distorted trigonal bipyramidal transition state.

The rather small activation enthalpies and the relatively large negative entropies (Table II) seem to be a feature of Pt(II) complex reactions.[11] This is probably due to the fact that formation of the transition state is accompained by a net increase of bonding.[12]

Acknowledgments.—This work was supported by the Italian Consiglio Nazionale delle Ricerche (CNR, Rome).

[10] G. A. Parshall, *J. Am. Chem. Soc.*, **86**, 5367 (1964).

[11] W. H. Baddley and F. Basolo, *Inorg. Chem.*, **3**, 1087 (1964).

[12] U. Belluco, R. Ettorre, F. Basolo, R. G. Pearson, and A. Turco, *ibid.*, **5**, 591 (1966).

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Solvent Effect on the Leaving Group in Displacements on *trans*-[Pt(P(C_2H_5)$_3$)$_2$XR]

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Kinetic data of substitutions with iodide and thiourea on *trans*-[Pt(P(C_2H_5)$_3$)$_2$XR] complexes with different leaving groups X^- in methanol and in dimethyl sulfoxide are reported. In both solvents the ease of replacement of the leaving group varies with changes in X^- in the order: $Cl^- \sim Br^- \sim I^- \overset{\sim}{>} N_3^- \gg NO_2^-$. The reactivity of a complex (Pt–X) relative to the chloride complex (Pt–Cl), *i.e.*, k_2^{Pt-X}/k_2^{Pt-Cl}, with thiourea as entering group, is found to be constant, regardless of the nature of the solvent. These results are discussed in terms of predominant bond formation between the Pt(II) center and the entering group in the transition state of the rate-determining step.

Introduction

In a previous paper kinetic data of monohalide displacements on *trans*-[Pt(P(C_2H_5)$_3$)$_2$Cl$_2$] in protic and dipolar aprotic solvents have been reported.[1] The reactivity order parallels the polarizability order of the entering groups, regardless of the nature of the solvent. In displacements at a soft center, such as Pt(II), the reagent solvation exerts a secondary role. No data, however, are available concerning the solvent effect on the leaving group X^- of Pt(II) complexes.

In the present work, investigations have been extended to the reactions of *trans*-[Pt(P(C_2H_5)$_3$)$_2$XR], where R is an alkyl or aryl group and X^- is Cl^-, Br^- I^-, N_3^-, or NO_2^-, with iodide ion and thiourea in methanol and in dimethyl sulfoxide. The object was, first, to investigate the leaving group solvation and, second, to see if a correlation exists between kinetic data and nmr shielding parameters of ^{19}F in *trans*-[Pt(P(C_2H_5)$_3$)$_2$R(*m*- or *p*-FC$_6$H$_4$)] recently reported by Parshall.[2]

Experimental Section

Materials.—The platinum(II) complexes of the type *trans*-[Pt(P(C_2H_5)$_3$)$_2$ClR] were prepared by the procedures reported in the literature.[2,3] The complexes *trans*-[Pt(P(C_2H_5)$_3$)$_2$XR] (with X^- = Br^-, I^-, N_3^-, NO_2^-) were prepared by simple metathetical reactions of the chloro compound. Each complex was characterized by means of elemental analysis.

Absolute methanol was dried and purified by distillation after refluxing over Mg(OCH$_3$)$_2$; dimethyl sulfoxide (DMSO) was fractionated under reduced pressure in nitrogen atmosphere. All other materials used were reagent grade.

Kinetics.—The reactions were followed spectrophotometrically by measuring changes in optical density in the ultraviolet region; 1-cm quartz cells were used. Either a Beckman DK-2A or an Optica CF-4R recording apparatus with appropriate attachments to maintain the reaction mixture at constant temperature was used. The spectral changes during the reactions were recorded and, in those cases where the substrate and product have the same extinction coefficients at some wavelength in the ultraviolet region, the spectra showed well-defined isosbestic points. Beer's law was obeyed for starting materials in the solvents examined. The reference cell in each case contained the reagent blank. In the case of relatively fast reactions, an Optica CF-4R spectrophotometer was used and the chart drive on the attached recorder was started at the moment of mixing. The absorbance at a selected wavelength was recorded against time.

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[1] U. Belluco, M. Martelli, and A. Orio, *Inorg. Chem.*, **5**, 582 (1966).

[2] G. W. Parshall, *J. Am. Chem. Soc.*, **86**, 5367 (1964).

[3] J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 4020 (1949).