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]

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(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: $Cl^- \sim Br^- \sim I^- \gtrsim N_3^- \gg NO_2^-$. 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$(C_2H_5)_3)_2Cl_2$] 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_6H_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).

The kinetic runs were carried out with an excess of reagent. Pseudo-first-order rate constants, k_{obsd}, were obtained graphically by means of a usual first-order plot. The substrate concentration in the reaction mixture was about $5 \times 10^{-4}\ M$, and the reagent concentrations varied from about 5×10^{-3} to $10^{-1}\ M$.

The rates of the reactions investigated follow the two-term rate law

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

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.[4]

The reactions go to completion, as shown by the identical final spectra obtained for runs carried out by changing the concentration of a given entering group. In some reactions, isosbestic points were observed between the substrate and the substituted product.

For each system, at least six different concentrations of reagent were examined. Because of the large contribution of k_1 to k_{obsd}, the slopes of the plots of k_{obsd} *vs.* the initial concentration of the reagent could not be determined with sufficient accuracy to calculate activation parameters. However, it can be noted that in Pt(II) reactions high k_2 values parallel low values of ΔH_2^*.[5]

For the same reason, poor nucleophiles could not be used in these reactions.

The effect of ionic strength is small, judging from the results obtained at various ionic strengths for the reaction of *trans*-[Pt(P(C_2H_5)$_3$)$_2$Cl(C_6H_5)] with I^-.

Results and Discussion

In Tables I and II the rate data for the reactions of *trans*-[Pt(P(C_2H_5)$_3$)$_2$XR], where R = CH_3, C_6H_5, *m*-FC_6H_4, or *p*-FC_6H_4 and X^- = Cl^-, Br^-, I^-, N_3^-, or NO_2^-, with iodide ion and thiourea in methanol and in dimethyl sulfoxide at 30° are summarized.

The data in Table I show that the ease of replacement of the leaving group in *trans*-[Pt(P(C_2H_5)$_3$)$_2$XR] for changes in X^- varies in the order $Cl^- \sim Br^- \sim I^- \gtrsim N_3^- \gg NO_2^-$, either in methanol or in dimethyl sulfoxide. This is the same order found for the planar [Pt(diethylenetriamine)X]$^+$ complexes reacting with different reagents in water.[5] It appears that no relationship exists between the reactivity order of the entering groups toward Pt(II) and the ease of replacement of the same ligands as leaving groups. The group mobility is approximately the same, regardless of the nature of X^-, except for NO_2^-, probably because of its biphilic character. It is reasonable to assume that the more difficult replacement of NO_2^- does not arise from its influence on bond formation in the transition state. In fact, in the cases in which such an influence is operating, one must expect that, apart from the steric factors, the presence of a coordinated π-bonding ligand facilitates the bond formation by withdrawing *via* π the excess of electron density due to the addition of the nucleophile.[6] Thus, the Pt–X bond strength increases, and therefore the bond breaking becomes rate determining.[5]

Table I

Rate Constants, k_2, for Reactions in Methanol and in Dimethyl Sulfoxide at 30°

trans-[Pt(P(C_2H_5)$_3$)$_2$XR] + Y^- → *trans*-[Pt(P(C_2H_5)$_3$)$_2$YR] + X^-

Nucleophile, Y^-	10^2k_2, M^{-1} sec^{-1} Solvent CH_3OH	Solvent DMSO	k_2^{Pt-X}/k_2^{Pt-Cl}, Y = Tu CH_3OH	DMSO
trans-[Pt(P(C_2H_5)$_3$)$_2$Cl(CH_3)]				
Solvent	$4 \times 10^{-2\,a}$	0.2×10^{-2}		
I^-	40[a]	...		
Tu	≥1500[a]	140		
trans-[Pt(P(C_2H_5)$_3$)$_2$Br(CH_3)]				
Solvent	5×10^{-2}			
I^-	26			
Tu	≥1500			
trans-[Pt(P(C_2H_5)$_3$)$_2$Cl(C_6H_5)]				
Solvent	$0.8 \times 10^{-2\,a}$	0.02×10^{-2}		
I^-	6[a]	...		
Tu	630[a]	57	1	1
trans-[Pt(P(C_2H_5)$_3$)$_2$Br(C_6H_5)]				
Solvent	0.7×10^{-2}	0.1×10^{-2}		
I^-	8	...		
Tu	450	34	0.7	0.6
trans-[Pt(P(C_2H_5)$_3$)$_2$Cl(*m*-FC_6H_4)]				
Solvent	0.4×10^{-2}	0.02×10^{-2}		
I^-	3.2	...		
Tu	395	30.6	1	1
trans-[Pt(P(C_2H_5)$_3$)$_2$I(*m*-FC_6H_4)]				
Solvent	...			
Tu	170		0.43	
trans-[Pt(P(C_2H_5)$_3$)$_2$$N_3$(*m*-$FC_6H_4$)]				
Solvent	0.07×10^{-2}	...		
I^-	5.1			
Tu	143	9.5	0.36	0.31
trans-[Pt(P(C_2H_5)$_3$)$_2$$NO_2$(*m*-$FC_6H_4$)]				
Solvent	0.01×10^{-2}	0.001×10^{-2}		
I^-	0.14	...		
Tu	1.48	0.134	0.0037	0.0044

[a] Data from U. Belluco, M. Graziani, and P. Rigo, *Inorg. Chem.*, **5**, 1123 (1966). Data for the solvent: k_1 in sec^{-1}.

Table II[a]

Rate Constants, k_2, for Reactions in Methanol and in Dimethyl Sulfoxide at 30°

trans-[Pt(P(C_2H_5)$_3$)$_2$ClR] + Y^- →
trans-[Pt(P(C_2H_5)$_3$)$_2$YR] + Cl^-

Ligand, R	Nucleophile, Y^-	10^2k_2, M^{-1} sec^{-1} Solvent CH_3OH	Solvent DMSO	$k_2^{CH_3OH}/k_2^{DMSO}$ Y = Tu	$k_2^{Tu}/k_2^{I^-}$ in CH_3OH
C_6H_5	Solvent[b]	0.8×10^{-2}	0.02×10^{-2}		
	I^-	6	...		
	Tu	630	57	11	105
p-FC_6H_4	Solvent	0.5×10^{-2}	0.02×10^{-2}		
	I^-	4.6	...		
	Tu	590	40	14.5	128
m-FC_6H_4	Solvent	0.4×10^{-2}	0.02×10^{-2}		
	I^-	3.2	...		
	Tu	395	30.6	13	123

[a] Supplementary material (specific kinetic data used to estimate values in this table) has been deposited as Document No. 8855 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] Data for the solvent: k_1 in sec^{-1}.

In the substitutions of halogenopentaamminecobalt(III) complexes with hydroxide ion in water, the ease of replacement of the leaving group follows the order F < Cl < Br or I.[7] This pattern has been found also in S_N2 reactions of carbon-saturated compounds. These features were rationalized in terms of bond forma-

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[4] H. B. Gray, *J. Am. Chem. Soc.*, **84**, 1548 (1962).

[5] F. Basolo and R. G. Pearson, *Progr. Inorg. Chem.*, **4**, 388 (1962); see also U. Belluco, R. Ettorre, F. Basolo, R. G. Pearson, and A. Turco, *Inorg. Chem.*, **5**, 591 (1966).

[6] U. Belluco, L. Cattalini, F. Basolo, R. G. Pearson, and A. Turco, *ibid.*, **4**, 525 (1965).

[7] S. C. Chan, K. J. Hui, J. Miller, and W. S. Tsang, *J. Chem. Soc.*, 3207 (1965), and references therein.

tion synchronous with the departure of the displaced group, with a single transition state involving a change from sp^3 to sp^2p hybridization.[8]

In the examined Pt(II) complexes, the ease of replacement of a leaving group relative to chloride (selected as a standard)[9] is about the same in methanol or in dimethyl sulfoxide. That is to say, the reactivity ratios $k_2^{\text{Pt-X}}/k_2^{\text{Pt-Cl}}$ with thiourea as entering group are independent of the solvent. This circumstance indicates that the solvation of the leaving group is not a kinetically significant step. Furthermore, considering the different solvations of the incipient X^- and Cl^- ions in going from a hard to a soft solvent,[10] this suggests that probably the charge separation in the transition state is not very large. Of course, the activated complex structure is assumed to be the same in these solvents.

The conclusion that the solvation of the leaving group has a secondary importance is in agreement with the failure of HCl to show any large increase in rate compared to chloride ion for the radiochloride exchange of *trans*-$[Pt(py)_2Cl_2]$.[11]

These reactions probably proceed *via* an intermediate two-step mechanism which resembles that of bimolecular substitutions at an aromatic carbon atom.[12] It is likely, therefore, that, at least with halides as leaving groups, the rate-determining step is the formation of an unstable five-coordinate intermediate in which the Pt–Y bond still has a partially ionic character.[5] Stable five-coordinated platinum(II) complexes have already been prepared.[13]

The data in Table II show that in the complexes of the type *trans*-$[Pt(P(C_2H_5)_3)_2ClR]$, with R = C_6H_5, *m*-FC_6H_4, or *p*-FC_6H_4, the nature of R does not appreciably affect either k_2 values or the nucleophilic discriminations $k_2^{\text{Tu}}/k_2^{\text{I}^-}$. Moreover, it has already been reported that *para* substituents X in complexes of the type *trans*-$[Pt(P(C_2H_5)_3)_2Cl(p\text{-}XC_6H_4)]$, where X = H, C_6H_5, CH_3O, or Cl, hardly affect the rate of displacement of chloride ion.[14] Both the donor properties (weakening the *trans* metal–ligand bond by polarization of the platinum atom) and π-acceptor capacity (either by stabilizing the transition state[5] or by attracting electrons of the d_{xz} orbital of the platinum and thus opening a position for the nucleophilic attack[15]) can account for the influence of the *trans*-aryl groups on the substitution reactions.

Parshall[2] has recently reported a criterion for discriminating between the two electronic factors which can contribute to the *trans* effect in displacements on Pt(II) complexes. Thus, by measuring the ^{19}F shielding parameters of the *m*- and *p*-fluorophenyl complexes *trans*-$[Pt(P(C_2H_5)_3)_2R(\text{fluorophenyl})]$, a sequence of σ-donor character and an order of π-bonding capacity of some anionic ligands have been reported. In these complexes both π interaction and σ-donor character depend significantly on the nature of the aryl groups R. Since the rates of chloride displacements on *trans*-$[Pt(P(C_2H_5)_3)_2ClR]$ are not sensitive to the changes of R and therefore do not follow either the order of the donor ability or the π-bonding capacity order of these ligands, it is reasonable to assume that both these electronic mechanisms affect the Pt(II) substitution reactions.[16]

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

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[8] C. A. Bunton, "Nucleophilic Substitution at Saturated Carbon Atom," Elsevier Publishing Co., New York, N. Y., 1963, p 87.

[9] This relative mobility has been called the group replacement factor or G.R.F.; see A. R. Bolto, J. Miller, and V. A. Williams, *J. Chem. Soc.*, 2926 (1955).

[10] J. Miller and A. J. Parker, *J. Am. Chem. Soc.*, **83**, 117 (1961); see also A. J. Parker, *Quart. Rev.* (London), **16**, 163 (1962).

[11] R. G. Pearson, H. B. Gray, and F. Basolo, *J. Am. Chem. Soc.*, **82**, 787 (1960).

[12] See J. F. Bunnett, *Quart. Rev.* (London), **12**, 1 (1958), for a review; E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston, New York, N. Y., 1964, p 452; J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., London, 1962, p 384; A. Streitwieser, *Chem. Rev.*, **56**, 571 (1956); H. B. Gray, Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965, p 102.

[13] See L. M. Venanzi, *Angew. Chem. Intern. Ed. Engl.*, **3**, 453 (1964), for a recent review; R. O. Cramer, R. V. Lindsey, Jr., C. T. Prewitt, and V. G. Stobberg, *J. Am. Chem. Soc.*, **87**, 658 (1965); C. M. Harris, R. S. Nyholm, and D. J. Philips, *J. Chem. Soc.*, 4379 (1963); C. M. Harris and R. S. Nyholm, *ibid.*, 63 (1957); F. G. Mann, *Chem. Ind.* (London), 944 (1965); A. D. Westland, *J. Chem. Soc.*, 3060 (1965).

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

[15] I. B. Bersuker, *Russ. J. Inorg. Chem.*, **9**, 18 (1964).

[16] It must be pointed out, however, that the parameters of Parshall do not permit any prediction about the Pt–ligand π interaction in the transition state of the substitution reaction.