Steric Effects in Substitution Reactions of *cis*- and *trans*-Arylchlorobis(triethylphosphine)platinum(II) Complexes: New Kinetic Data for the Approach to the Problem of Transition-state Geometry

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The rate of displacement of Cl^- ion in the complexes *trans*- and *cis*-$[Pt(PEt_3)_2(R)Cl]$ (R = Ph, *o*-MeC_6H_4, and 2,4,6-$Me_3C_6H_2$) with CN^- has been studied in propan-2-ol containing 6% water. Analysis of the relative reactivity of the two sets of isomers gives some indication of the configuration of the transition state. It is shown that literature data concerning reactions of the same systems with pyridine (py) in ethanolic solution are incorrect. The *trans*-complexes do not undergo bimolecular attack and the *cis*-complexes spontaneously isomerize to the *trans*-form before or during their reaction with py.

THERE are many indications [1,2] that addition of a fifth ligand to the metal ion in the activation process of nucleophilic-substitution reactions of platinum(II) square-planar complexes should favour a trigonal-bipyramidal transition state with the *trans*-ligand, the entering and leaving groups in the trigonal plane, and the two ex-*cis*-ligands in apical positions. Compelling support for this seems to arise from widely reported data concerning displacement of chloride ion by pyridine (py) in the complexes *cis*- and *trans*-$[Pt(PEt_3)_2(R)Cl]$ (R = Ph, *o*-MeC_6H_4, and 2,4,6-$Me_3C_6H_2$). According to the expected form of trigonal bipyramid, the original work [3] pointed out that the effect of blocking potential co-ordination positions on the metal ion with methyl groups of the aromatic ring is much more marked when R is *cis* to the leaving group. The alternative square-pyramidal structure should not be sensitive to changes in position of the ligand R in the original square-planar complex. We made a detailed kinetic study of the same reactions in methanol [4] showing that py does not attack the *trans*-complexes directly and that *cis*-$[Pt(PEt_3)_2(o\text{-}MeC_6H_4)Cl]$ changes spontaneously into its *trans*-isomer in protic solvents.[5] These facts indicated the necessity of re-examining the reactivity of these systems in the solvent used in the original work and has led to new data for the approach to the problem of transition-state geometry.

EXPERIMENTAL

The complexes *cis*- and *trans*-$[Pt(PEt_3)_2(R)Cl]$ (R = Ph, *o*-MeC_6H_4, and 2,4,6-$Me_3C_6H_2$) were prepared by published methods [3,6] and characterized through their u.v. and i.r. spectra, elemental analysis, and molecular weights in benzene solution. Commercial pyridine (py) was purified by distillation over KOH in a nitrogen atmosphere. All other salts were reagent grade. The solvents ethanol and propan-2-ol were purified by distillation after heating under reflux over magnesium metal.

Kinetics.—Slow reactions were followed spectrophotometrically in the u.v. region by using either an Optica CF recording spectrophotometer or a Beckmann D.U. apparatus. Known volumes of solutions of the complex and nucleophile were brought separately to the desired temperature and then mixed in a thermostatted cell in the spectrophotometer. Spectral changes during reactions of the complexes with CN^- ion showed well defined isosbestic points indicating that the only absorbing species were the starting complex and final product. All reactions were carried out in the presence of a large excess of nucleophile and values of pseudo-first-order rate constants k_{obs} (s^{-1}) were obtained graphically from gradients of plots of log ($A_\infty - A_t$) against time, where A_t and A_∞ are optical densities of the reaction mixture at time t and after 8—10 half-lives respectively, at the most suitable wavelength. Faster reactions of the complexes *cis*-$[Pt(PEt_3)_2(Ph)Cl]$ and -$[Pt(PEt_3)_2(o\text{-}MeC_6H_4)Cl]$ were followed with the stopped-flow method using a Durrum–Gibson spectrophotometer. Electrical signals from the photomultiplier tube were displayed on the scale of a Tektronix type 564 oscilloscope against a time base and recorded on Polaroid film. Transmittance values were converted to optical densities and analysed according to the usual semilogarithmic plots.

RESULTS

Reaction of the Complexes trans-$[Pt(PEt_3)_2(R)Cl]$ (R = Ph, o-MeC_6H_4, *and* 2,4,6-$Me_3C_6H_2$) *with Pyridine*.—We have already shown [4] that displacement of chloride ion by pyridine (py) from the species *trans*-$[Pt(PEt_3)_2(R)Cl]$ (R = Ph, *o*-MeC_6H_4, and 2,4,6-$Me_3C_6H_2$) in methanol can be represented by equations (1) and (2) (S = solvent

$$trans\text{-}[Pt(PEt_3)_2(R)Cl] + S \underset{k_2}{\overset{k_1}{\rightleftharpoons}} trans\text{-}[Pt(PEt_3)_2(R)S]^+ + Cl^- \quad (1)$$

$$trans\text{-}[Pt(PEt_3)_2(R)S]^+ + py \underset{k_4}{\overset{k_3}{\rightleftharpoons}} trans\text{-}[Pt(PEt_3)_2R(py)]^+ + S \quad (2)$$

molecule). The same mechanism has been suggested for reaction with a series of amines of various basicity and steric hindrance.[7] Because of competition between py and chloride ion for the transient solvent intermediate

[1] F. Basolo and R. G. Pearson, 'Mechanism of Inorganic Reactions,' John Wiley and Sons Inc., New York, 1967.
[2] C. H. Langford and H. B. Gray, 'Ligand Substitution Processes,' W. A. Benjamin Inc., New York, 1965, ch. 2.
[3] F. Basolo, J. Chatt, H. B. Gray, R. G. Pearson, and B. L. Shaw, *J. Chem. Soc.*, 1961, 2207.
[4] V. Ricevuto, R. Romeo, and M. Trozzi, *J.C.S. Dalton*, 1972, 1857.
[5] G. Faraone, V. Ricevuto, R. Romeo, and M. Trozzi, *J. Chem. Soc.* (*A*), 1971, 1877.
[6] J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1959, 4020.
[7] V. Ricevuto, R. Romeo, and M. Trozzi, *J.C.S. Dalton*, 1974, 927.

species *trans*-$[Pt(PEt_3)_2(R)S]^+$, a rate dependence on [py] is apparent. Under pseudo-first-order conditions for $[Cl^-]$ and [py], values of the rate constant k_{obs} conform to expression (3).

$$k_{obs} = \frac{k_1[py] + (k_4k_2/k_3[Cl^-])}{(k_2/k_3[Cl^-]) + [py]} \quad (3)$$

Table 1 gives rate data for reaction (4), selected as a test of the validity of the indicated mechanism in the

$$trans\text{-}[Pt(PEt_3)_2(o\text{-}MeC_6H_4)Cl] + py \overset{K}{\rightleftharpoons} trans\text{-}[Pt(PEt_3)_2(o\text{-}MeC_6H_4)py]^+ + Cl^- \quad (4)$$

solvent used in the early work of Basolo *et al.*[3] All the rate constants which appear in expression (3) have been calculated according to the method illustrated in previous

TABLE 1

Rate of approach to equilibrium for reaction of the complex *trans*-$[Pt(PEt_3)_2(o\text{-}MeC_6H_4)Cl]$ with pyridine in the presence of 0·005M-LiCl in ethanol at 30 °C

[py]/M	$10^4k_{obs}/s^{-1}$	10^4k_{calc} [a]$/s^{-1}$
0·04	1·04	1·03
0·08	1·33	1·34
0·10	1·48	1·49
0·20	2·23	2·21
0·30	2·88	2·88
0·40	3·53	3·48
0·60	4·54	4·56
0·80	5·46	5·48

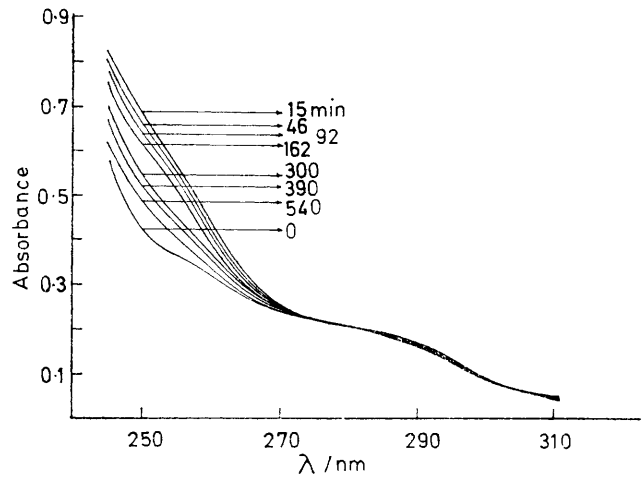
[a] Obtained by introducing in the relation (3) values of the kinetic parameters.

papers.[4,7] In ethanol at 30 °C, values of the solvolysis rate constants k_1 and k_4 are $1·78 \times 10^{-3}$ and $7·03 \times 10^{-5}$ s^{-1}, respectively. The value of the ratio $k_2 : k_3$ is 412 : 1 and represents the efficiency of chloride ion in competing with py for the intermediate. The value of 0·061 for the equilibrium constant of reaction (4) was obtained by introducing the calculated kinetic parameters into the expression $K = k_1k_2/k_3k_4$. The consistency of rate and equilibrium data was checked spectrophotometrically by measuring optical densities of mixtures of complex, LiCl, and py at equilibrium. Analysis of the absorption data, by means of a least-squares program on an IBM 1130 computer using the relation already reported,[4] gave a value of 0·058 for K which is in reasonable agreement with that calculated from the kinetic parameters.

Spontaneous Isomerization of the Complexes cis-$[Pt(PEt_3)_2(R)Cl]$ (R = Ph, o-MeC_6H_4, *and* 2,4,6-$Me_3C_6H_2$).—The species *cis*-$[Pt(PEt_3)_2(R)Cl]$ (R = Ph, *o*-MeC_6H_4, and 2,4,6-$Me_3C_6H_2$) start to change spontaneously into the *trans*-isomers as soon as the solid compounds are dissolved in protic solvents. The Figure shows spectral changes associated with *cis–trans*-isomerization of the complex *cis*-$[Pt(PEt_3)_2(2,4,6\text{-}Me_3C_6H_2)Br]$ in ethanol at 30 °C. The isomeric equilibrium largely favours the *trans*-form and conversion of the *cis*-isomer, taking place with a half-life of 5 h, is much faster than the reported reaction with pyridine[1] ($t_{1/2}$ = 192 h with [py] = 0·0062M at 25 °C). Likewise the complexes *cis*-$[Pt(PEt_3)_2(Ph)Cl]$ and -$[Pt(PEt_3)_2(o\text{-}MeC_6H_4)Cl]$[5] isomerize with $t_{1/2}$ = 56 and 150 min respectively under the same experimental conditions.

In view of the fact that reaction of *trans*-$[Pt(PEt_3)_2(R)Cl]$ species with py does not involve bimolecular attack of the entering group on Pt^{II} so that the transition state does not contain py and chloride at the same time and, in addition, because the rate at which the complexes *cis*-$[Pt(PEt_4)_2(R)Cl]$ isomerize into the *trans*-species is too close to rates of substitution with py, it is clear that data reported in the early work[3] and extensively quoted in many books and reviews[8] are meaningless.

Reactions of the Complexes cis- *and* trans-$[Pt(PEt_3)_2(R)Cl]$ (R = Ph, o-MeC_6H_4, *and* 2,4,6-$Me_3C_6H_2$) *with* CN^-.—We



U.v. spectra changes in *cis–trans*-isomerization of the complex *cis*-$[Pt(PEt_3)_2(2,4,6\text{-}Me_3C_6H_2)Br]$ in ethanol at 30 °C. [Complex] = $5·0 \times 10^{-5}$M

studied the displacement rate of Cl^- ion in the species *cis*- and *trans*-$[Pt(PEt_3)_2(R)Cl]$ (R = Ph, *o*-MeC_6H_4, and 2,4,6-$Me_3C_6H_2$) with CN^- in propan-2-ol containing 6% water. The choice of incoming group was limited by the need to ensure bimolecular reaction. As pointed out above, displacement of Cl^- ion from *trans*-isomers by simple nucleophiles such as Br^-, N_3^-, I^-, *etc.*[9,10] is completely controlled by the solvent and only biphilic reagents (CN^-, $SeCN^-$, and thiourea) exhibit a definite second-order contribution. The same trend seems to be exhibited by the *cis*-complexes, judging from cases where precautions were adopted in order to prevent isomerization taking place. In fact no k_2 term has yet been found[5] in substitution reactions of the complex *cis*-$[Pt(PEt_3)_2(o\text{-}MeC_6H_4)Cl]$ with I^- ion in methanol, and a large contribution of k_1 to k_{obs} accompanies displacement of Br^- from *cis*-$[Pt(PEt_3)_2(2,4,6\text{-}Me_3C_6H_2)Br]$ by SCN^- in ethanol. The present solvent system was chosen because preliminary tests ascertained that *cis*–

[8] F. Basolo, *Adv. Chem. Series*, 1965, **49**, 81; R. Heslop and P. L. Robinson, 'Inorganic Chemistry: A guide to Advanced Study,' 3rd edn., Elsevier, 1967; D. Benson, 'Mechanisms of Inorganic Reactions in Solution: An Introduction,' 1968, McGraw-Hill, London; L. Cattalini, 'Inorganic Reaction Mechanisms,' ed. J. O. Edwards, Wiley, New York, 1970, vol. 13; 'Reaction Mechanisms in Inorganic Chemistry,' ed. M. L. Tobe, M.T.P. International Review of Science, Series 1, vol. 9, Butterworths, London, 1972; 'Inorganic Reaction Mechanisms,' Nelson, London, 1972; A. Peloso, 'Kinetics of Nickel, Palladium, and Platinum Complexes,' *Co-ordination Chem. Rev.*, 1973, **10**, 123—181; F. R. Hartley, 'The Chemistry of Platinum and Palladium,' Applied Science Pub., London, 1973.

[9] G. Faraone, V. Ricevuto, R. Romeo, and M. Trozzi, *Inorg. Chem.*, 1969, **8**, 2207.

[10] G. Faraone, V. Ricevuto, R. Romeo, and M. Trozzi, *Inorg. Chem.*, 1970, **9**, 1525.

trans-isomerization either does not take place in it or else is much slower than the substitution process.

All the complexes underwent substitution according to the usual two-term rate expression, $k_{obs} = k_1 + k_2[Y]$ ($Y = CN^-$ or SCN^-). The constant k_2 was obtained from gradients of linear plots of k_{obs} against [Y] and the k_1 contribution was almost negligible, except in the reaction of the complex *cis*-[Pt(PEt$_3$)$_2$(2,4,6-Me$_3$C$_6$H$_2$)Br] with SCN^- ion. Arrhenius plots of log k_2 against $1/T$ were linear in the range of temperature examined and values of the activation enthalpies $\Delta H^{\ddagger}$ were calculated from the best least-squares straight line.

DISCUSSION

Analysis of the kinetic data (Table 2) shows that in every case an increase in steric hindrance of the complex causes a decrease in reaction rate. The sequence of relative reactivity (Table 3) is a measure of the congestion and destabilization of the transition state produced by *o*-Me substitution in the aromatic ring, as compared with the ground state. It can be shown, using molecular models, that in the *trans*-series methyl groups hinder rotation of the phenyl ring around the Pt–C bond through interference with the bulky phosphine ligands. The steric strain does not greatly change whether these groups are *cis* to the group R in a square-planar ground state or occupy the apical position in a trigonal-bipyramidal transition state. According to Cattalini [11] no steric retardation can be expected 'if the bond between the metal and the *trans*-partner does not greatly change in going from the ground to the transition state,' as is shown in displacement [12] of hindered and unhindered pyridine ligands (am) from the complexes [AuCl$_3$(am)] by Cl^- ion.

Nevertheless steric retardation is by no means negligible in reactions of the complexes *trans*-[Pt(PEt$_3$)$_2$-(R)Cl] with CN^- ion, as shown by the sequence of relative reactivity (1 : 21 : 809) in Table 3, which is in reasonable agreement with that found [9] in methanol (1 : 27 : 425). Comparison with rate data concerning other entering groups such as MeOH (1 : 5 : 22) [4] or SC(NH$_2$)$_2$ (1 : 13 : 126) [9] suggests that the effect of increasing steric hindrance on the *trans*-ligand by the methyl groups is additive. The variation of the relative reactivity seems to depend on the nature of the entering group and could be related to the extent to which the new bond alters the distribution of the other ligands around the central metal atom in the transition state. Steric retardation is particularly marked when the group R is *cis* to the leaving Cl^-. This result substantially agrees with the original suggestion that an aromatic ring in an apical position in an approximate trigonal-bipyramidal structure, with substituted methyl groups extending just into the trigonal plane, destabilizes the transition state much more than if the group was in the equatorial plane. The strain produced by two *o*-Me groups is not additive. Molecular models show

TABLE 2

Second-order rate constants, k_2, and activation parameters for displacement of Cl^- by CN^- ion from the complexes *cis*- and *trans*-[Pt(PEt$_3$)$_2$(R)Cl] (R = Ph, *o*-MeC$_6$H$_4$, and 2,4,6-Me$_3$C$_6$H$_2$) in propan-2-ol–water (6%)

Complex	t / °C	k_2 [a] / l mol^{-1} s^{-1}	$\Delta H^{\ddagger}$ / kcal mol^{-1}	$\Delta S^{\ddagger}$ / cal K^{-1} mol^{-1}
trans-[Pt(PEt$_3$)$_2$(Ph)Cl]	10	15·20		
	20	23·50	6·46 ± 0·07	−30·3 ± 0·2
	30	34·80		
trans-[Pt(PEt$_3$)$_2$(*o*-MeC$_6$H$_4$)Cl]	15	0·40		
	30	0·90	7·67 ± 0·67	−33·5 ± 2·2
	45	1·56		
trans-[Pt(PEt$_3$)$_2$(2,4,6-Me$_3$C$_6$H$_2$)Cl]	20	0·021		
	30	0·043	12·44 ± 0·18	−23·8 ± 0·6
	45	0·122		
cis-[Pt(PEt$_3$)$_2$(Ph)Cl]	20	14,800		
	30	21,400	6·13 ± 0·14	−18·6 ± 0·5
	40	31,000		
cis-[Pt(PEt$_3$)$_2$(*o*-MeC$_6$H$_4$)Cl]	20	1,620		
	30	2,460	6·75 ± 0·01	−20·9 ± 0·04
	40	3,630		
cis-[Pt(PEt$_3$)$_2$(2,4,6-Me$_3$C$_6$H$_2$)Br]	30	0·312		
	37·5	0·520	11·42 ± 0·4	−23·3 ± 1·4
	45	0·800		
cis-[Pt(PEt$_3$)$_2$(2,4,6-Me$_3$C$_6$H$_2$)Br] [b]	30	0·66 × 10^{-3}		
	35	1·05 × 10^{-3}	18·06 ± 0·47	−13·6 ± 1·5
	40	1·80 × 10^{-3}		
	45	2·80 × 10^{-3}		

[a] Determined over at least six different nucleophile concentrations. [b] The entering group was SCN^-.

TABLE 3

Steric effects in the substitution reactions: [Pt(PEt$_3$)$_2$-(R)Cl] + CN^- $\longrightarrow$ [Pt(PEt$_3$)$_2$(R)CN] + Cl^-

	Relative rates	
R	R *trans* to Cl	R *cis* to Cl
2,4,6-Me$_3$C$_6$H$_2$	1	1 [a]
o-MeC$_6$H$_4$	21	7 900
Ph	809	68 600

[a] The complex is *cis*-[Pt(PEt$_3$)$_2$(2,4,6-Me$_3$C$_6$H$_2$)Br].

[11] L. Cattalini, M. Nicolini, and A. Orio, *Inorg. Chem.*, 1966, **5**, 1674.

[12] L. Cattalini and M. L. Tobe, *Inorg. Chem.*, 1966, **6**, 1145.

that there is by far greater congestion and destabilization of the transition state by the two such groups of the 2,4,6-$Me_3C_6H_2$ ligand than by the single group of the *o*-MeC_6H_4 ligand. This is reflected in the kinetics which show that the change from Ph to *o*-MeC_6H_4 only causes a ten-fold reduction in k_2, whereas on going from *o*-MeC_6H_4 to 2,4,6-$Me_3C_6H_2$ the reduction is nearly 10^4 fold. Unfortunately is not possible to draw further conclusions about the congestion of the five-co-ordinate transition state by comparing activation data of the *cis*- and *trans*-isomers (Table 2). Indeed the value of the activation enthalpy $\Delta H^{\ddagger}$ depends either on steric or electronic factors and the two systems differ in the nature of the *trans*-activating group. It is probable that in the *cis*-complexes electronic π-interaction of filled *d* orbitals of the metal with suitable empty orbitals of CN^- and PEt_3 groups in the plane largely compensates for the strain of the methyl groups of the aromatic ring in the apical position. Supporting this is the rate retardation and large increase in activation enthalpy (7 kcal mol^{-1}) * when CN^- is replaced by SCN^- ion as entering group.

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* 1 cal = 4·184 J.