Mechanism of the Substitution of Chloride in *trans*-[Pt(PEt$_3$)$_2$(R)Cl] by Pyridine: Kinetic Evidence for a Reaction Intermediate

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The rate of displacement of Cl$^-$ in *trans*-[Pt(PEt$_3$)$_2$(R)Cl] (R = phenyl, *o*-tolyl, and mesityl) by pyridine has been studied in the presence of LiCl (0·005M) in methanol at 30 °C. The pseudo-first-order rate constants for approach to equilibrium (k_{obs}) conform to the equation (i) where k_1 and k_4 represent the solvolytic rates of generation of an

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

intermediate from *trans*-[Pt(PEt$_3$)$_2$(R)Cl] and *trans*-[Pt(PEt$_3$)$_2$(R)(py)]$^+$ respectively, and k_2/k_3 represents the relative efficiency of Cl$^-$ compared with pyridine in competing for the reactive intermediate, *trans*-[Pt(PEt$_3$)$_2$(R)-(MeOH)]$^+$. k_3 Has been measured directly from the kinetics of the reaction of *trans*-[Pt(PEt$_3$)$_2$(R)NO$_3$] with pyridine, so that it is possible to calculate all the rate constants which appear in the expression for k_{obs}. The consistency of the rate and equilibrium data has been checked by comparing the values of the equilibrium constants calculated from kinetic parameters with those obtained by means of direct spectrophotometric and conductance methods. The effect of increasing steric hindrance in the substrate upon the reactivity of simple nucleophiles is discussed.

MANY studies of steric effects in the substitution reactions of low-spin d^8 square-planar complexes have been undertaken to provide evidence for the associative nature of the activation process.[1,2] Steric hindrance can be introduced in the reacting system either by using bulky ligands co-ordinated to the metal[3-7] or hindered entering reagents such as the substituted heterocyclic amines.[8-12] Basolo *et al.*[3] measured the rates of attainment of the equilibrium (1), (R = phenyl, *o*-tolyl, and

$$[\text{Pt(PEt}_3)_2\text{(R)Cl}] + \text{py} \rightleftharpoons [\text{Pt(PEt}_3)_2\text{(R)(py)}]^+ + \text{Cl}^- \qquad (1)$$

mesityl) in ethanol solution and showed that *ortho*-substitution on the phenyl ligands led to a decrease in reactivity. Steric retardation was shown to be much greater when ligand R was *cis* to the leaving chloride and this was interpreted as direct evidence for an approximate trigonal-bipyramidal transition state.

We have made a detailed study of the kinetics of the displacement of chloride from *trans*-[Pt(PEt$_3$)$_2$(R)Cl] with a range of nucleophiles in methanol solution[13,14] and have pointed out that either the increase of electron density induced on the platinum atom by the strong σ-donor R$^-$ ligands or the steric shielding of the reaction centre by the methyl groups markedly hinder the attack by reagents whose nucleophilicity depends mainly upon the polarizability of the donor atom.[15] The reaction with nucleophiles such as Br$^-$, I$^-$, PhS$^-$, and S$_2$O$_3^{2-}$ obeys the rate law: $-\text{d[Complex]/d}t = k_1\text{[Complex]}$ and only strong biphilic reagents[16] (CN$^-$, SeCN$^-$, thiourea) which can stabilize the five-co-ordinate transition state by means of π-interactions with the filled $5d$ orbitals of the metal exhibit a definite additional second-order contribution (the same value of k_1 is found in every case). However, the reaction with the weak and non-biphilic reagent pyridine [equation (1)] has been reported to obey the two-term rate law $k_{obs} = k_1' + k_2[\text{py}]$,[3] where the first-order rate constant, k_1', is considerably smaller than k_1 obtained under similar conditions for the stronger reagents. We have therefore made a detailed study of the kinetics of the pyridine reaction; a preliminary report has appeared.[17]

EXPERIMENTAL

The complexes used: *trans*-[Pt(PEt$_3$)$_2$(Ph)NO$_3$]; *trans*-[Pt(PEt$_3$)$_2$(Ph)Cl]; *trans*-[Pt(PEt$_3$)$_2$(*o*-tolyl)NO$_3$]; *trans*-[Pt(PEt$_3$)$_2$(*o*-tolyl)(py)]NO$_3$; *trans*-[Pt(PEt$_3$)$_2$(*o*-tolyl)Cl]; *trans*-[Pt(PEt$_3$)$_2$(mesityl)NO$_3$]; and *trans*-[Pt(PEt$_3$)$_2$-(mesityl)Cl] (PEt$_3$ = triethylphosphine) are all known and were prepared by the methods reported.[3,18] The purity was established through the u.v. and i.r. spectra and the elemental analysis of carbon, hydrogen, and phosphorus. Methanol was purified by distillation after refluxing over Mg(OMe)$_2$ to remove water. The solvent was redistilled over tribromobenzoic acid to remove basic impurities.[19] Commercial pyridine was purified by distillation over KOH

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[16] R. G. Pearson, H. B. Gray, and F. Basolo, *J. Amer. Chem. Soc.*, 1960, **82**, 787.

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[19] H. Lund and J. Bjerrum, *Ber.*, 1931, 210.

pellets. Conductances were measured by means of a Jones conductivity bridge.

Kinetics.—Known volumes of methanol solutions of the substrate and reagent were brought separately to 30 °C and mixed in the thermostatted cell of a spectrophotometer. The instruments used were either a Beckman DU or a double-beam Optica CF 4R recording apparatus. The reactions were followed by measuring the changing optical density of the reaction mixture in the u.v. region at selected wavelengths where the difference between the absorption of the starting complex and that of the final product was largest. All the reactions were carried out with the reagents in sufficient excess of the complex to provide pseudo-first-order conditions. The values of the rate constants, k_{obs}/s^{-1} were obtained graphically by means of the usual first-order plots. Some reactions were repeated several times under the same conditions and the reproducibility was better than ±4%.

RESULTS AND DISCUSSION

Basolo *et al.*[3] followed the rate of the reversible reaction (1) by measuring the change in conductance of the reaction mixture. Using the same technique we obtained for all the three complexes plots as that shown in Figure 1 (the reaction occurs in the presence of a large excess of reagent and a first-order treatment to the conductance data is applied). The shape of the plot does not allow us to calculate the rate constant of the process. Moreover the conductometric method appears unsuitable in following these reactions, proof of this coming from the observation that the species *cis*-[Pt(PEt$_3$)$_2$(*o*-tolyl)Cl] converts spontaneously into its *trans*-form in ethanol solution [20] with a rate comparable with that found conductometrically for the reaction of this same species with pyridine.[3]

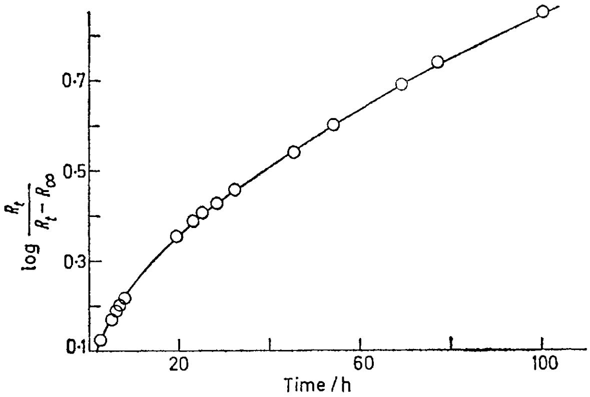

FIGURE 1 Attempted first-order plot of the reaction of *trans*-[Pt(PEt$_3$)$_2$(mesityl)Cl] with pyridine in methanol at 30 °C. [Complex] = 2·0 × 10^{-4}M; [pyridine] = 0·0125M. R_t and R_∞ are the electrical resistances of the solution at time t and at equilibrium

Since the position of equilibrium under the conditions of Figure 1 is forced *ca.* 90% of the way to the right-hand side the observed curvature cannot be due to the fact that the reverse process is not first order. We suggest that the cause of the regular decrease in rate is a mass-law retardation arising out of an effective competition for an intermediate between the incoming pyridine and the leaving chloride. By addition of a 20-fold excess of LiCl with respect to the complex the concentration of chloride remains essentially constant during the reaction and the deviations from a pseudo-first-order approach to equilibrium disappear. The position of equilibrium is, of course, shifted to the left. It is now necessary to follow the reaction spectrophotometrically and the rate of approach to equilibrium is characterized by a first-order rate constant k_{obs}/s^{-1} which can be obtained precisely from the slope of the now linear plots of log $(D_t - D_\infty)$ against time. (D_t and D_∞ are the absorbances of the solution at time t and after a time long enough for the system to reach equilibrium, respectively.)

TABLE 1

Rates of attainment of equilibrium between pyridine and the complexes *trans*-[Pt(PEt$_3$)$_2$(R)Cl] in presence of 0·005M-LiCl in methanol at 30 °C (R = Ph, *o*-tolyl, and mesityl). The reactions were followed spectrophotometrically and in any run the concentration of the complex was 2·5 × 10^{-4}M

[Pyridine]/M	$10^4k_{obs}/s^{-1}$	$10^4k_{calc}/s^{-1}$
R = Mesityl		
0·06	0·063	0·062
0·08	0·075	0·074
0·10	0·087	0·085
0·20	0·147	0·144
0·30	0·203	0·200
0·40	0·272	0·254
0·50	0·315	0·308
0·60	0·364	0·359
0·80	0·452	0·458
R = *o*-tolyl		
0·030	0·400	0·392
0·040	0·464	0·408
0·060	0·657	0·657
0·080	0·836	0·830
0·10	0·999	1·000
0·20	1·802	1·810
0·30	2·604	2·573
0·40	3·336	3·278
0·50	3·945	3·935
0·60	4·583	4·550
R = phenyl		
0·006	1·11	1·10
0·008	1·29	1·28
0·010	1·47	1·45
0·020	2·42	2·32
0·040	4·04	4·01
0·060	5·58	5·63
0·080	7·02	7·19
0·100	8·98	8·69
0·200	16·72	15·38
0·300	24·91	20·99
0·400	36·57	25·77
0·500	44·74	29·88

The values of the pseudo-first-order rate constants of approach to equilibrium k_{obs}/s^{-1} for the reactions of the complexes *trans*-[Pt(PEt$_3$)$_2$(R)Cl] with pyridine in presence of 0·005M-LiCl are reported in Table 1.

Figure 2 shows the dependence of k_{obs}/s^{-1} on the concentration of pyridine when R is the mesityl group. Analogous behaviour is found with the complexes where

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[20] G. Faraone, V. Ricevuto, R. Romeo, and M. Trozzi, *J. Chem. Soc.* (*A*), 1971, 1877.

R is *o*-tolyl or phenyl. The curvature indicates that the simple two-term rate law is not operating and that the dependence of rate on the concentration of pyridine does not arise from a bimolecular attack of pyridine on the chloro-substrate.

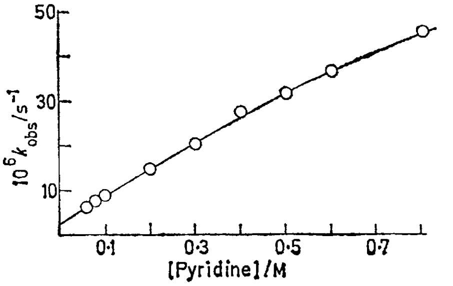

FIGURE 2 Dependence of k_{obs} on reagent concentration for reactions of *trans*-$[Pt(PEt_3)_2(mesityl)Cl]$ with pyridine in methanol at 30 °C

The dependence of the rate on the concentration of pyridine can be accounted for by reactions (2) and (3),

$$\textit{trans}\text{-}[Pt(PEt_3)_2(R)Cl] + MeOH \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \textit{trans}\text{-}[Pt(PEt_3)_2(R)(MeOH)]^+ + Cl^- \quad (2)$$

$$\textit{trans}\text{-}[Pt(PEt_3)_2(R)MeOH]^+ + py \underset{k_4}{\overset{k_3}{\rightleftharpoons}} \textit{trans}\text{-}[Pt(PEt_3)_2(R)(py)]^+ + MeOH \quad (3)$$

where $[Pt(PEt_3)_2(R)(MeOH)]^+$ is postulated as an intermediate species generated from $[Pt(PEt_3)_2(R)Cl]$ or $[Pt(PEt_3)_2(R)py)]^+$ with characteristic rate constants k_1 and k_4. The reactive intermediate should have a long enough life-time for it to distinguish between various nucleophiles and the ratio of rate constants $k_2 : k_3$ should then be a measure of the efficiency of chloride compared with pyridine in competing for the intermediate.

Under pseudo-first-order conditions, where $[Cl^-]$ and [py] remain constant in any run, a steady-state treatment, it being assumed that the concentration of $[Pt(PEt_3)_2(R)(MeOH)]^+$ remains small, leads to the relationship (4). Analogous expressions have been

$$k_{obs} = \frac{k_1[py] + k_4k_2/k_3[Cl^-]}{k_2/k_3[Cl^-] + [py]} \quad (4)$$

used by Haim *et al.*[21-26] in the study of substitution reactions of cobalt(III) cyanide complexes and by Robb *et al.*[27] in the study of anation of the $Rh(Cl)_5(H_2O)^{2-}$ anion.

The intercept on the ordinate in Figure 2 gives k_4, the rate constant for the solvolysis of *trans*-$[Pt(PEt_3)_2(R)(py)]^+$. Equation (4) can be rewritten as (5), a form

$$1/(k_{obs} - k_4) = 1/(k_1 - k_4) + k_2[Cl^-]/k_3(k_1 - k_4)[py] \quad (5)$$

which allows us to obtain k_1 from the intercept and k_2/k_3 from the ratio of slope to intercept of plots of $1/(k_{obs} - k_4)$ against $[Cl^-]$/py].

For all the three complexes, linear plots of $1/(k_{obs} - k_4)$ against $[Cl^-]/[py]$ were obtained in the range of pyridine concentration examined (Figure 3 shows only the points at high reagent concentration so as to make the curves focus on the region near the intercept). The intercepts and slopes of these plots were obtained by the least-squares method and used to derive values for k_1 and k_2/k_3 which are collected in Table 2 together with the values of the other kinetic parameters.

The k_1 term represents the rate constant for the generation of the intermediate from *trans*-$[Pt(PEt_3)_2(R)Cl]$ and is in close agreement with the value obtained from the kinetics of the reactions of these substrates with highly polarizable nucleophiles (Br^-, I^-, *etc.*). These nucleophiles are much more effective than pyridine in the competition with chloride for the solvated intermediate and the reaction is irreversible so that the k_2 and k_4 terms can be ignored and equation (4) reduces to $k_{obs} = k_1$. Competition experiments provide additional evidence that the suggested intermediate reacts much more rapidly with iodide than with pyridine. By adding a small amount of I^- to the solution (only 1% of the concentration of pyridine) the conversion of the species

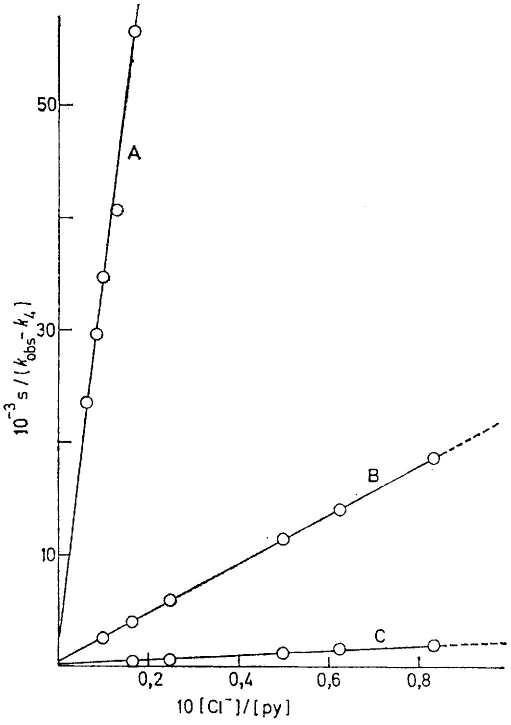

FIGURE 3 Plot of $1/(k_{obs} - k_4)$ against $[Cl^-]/[py]$ at 30 °C; A, R = mesityl; B, R = *o*-tolyl; C, R = Ph

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trans-$[\mathrm{Pt(PEt_3)_2(R)Cl}]$ into *trans*-$[\mathrm{Pt(PEt_3)_2(R)I}]$ is complete and it occurs at a rate equal to k_1.

The discrepancy between the two values of k_1 for the complex *trans*-$[\mathrm{Pt(PEt_3)_2(Ph)Cl}]$ is even larger if the least-squares analysis is extended to the data for concentrations of pyridine above 0·2M. This can be seen effectively in Table 1 by comparing the experimental values of k_{obs} with those calculated using the rate constants in Table 2. Marked discrepancies appear when the phenyl substrate reacts with pyridine in concentration $>$0·2M, while the agreement for the other two complexes is good over the entire concentration range. It is suggested that the anomalous behaviour of this unhindered complex may be due to the appearance of a direct bimolecular attack by pyridine at high concentrations. In this regard it is noteworthy that a k_2 term for the reactions of this substrate with the smaller strong nucleophiles $\mathrm{NO_2^-}$, $\mathrm{Br^-}$, $\mathrm{N_3^-}$, and $\mathrm{I^-}$ has been found.[28]

TABLE 2

Kinetic parameters for the reactions (2) and (3) at 30 °C and $\mu = 0{\cdot}005$M

Complex	10^3k_1 [a]/s^{-1}	10^5k_4/s^{-1}	k_2/k_3	k_3/l mol^{-1} s^{-1}	k_2/l mol^{-1} s^{-1}
trans-$[\mathrm{Pt(PEt_3)_2(Ph)Cl}]$	8·50 [b]	5·70	188	7·416	1394
trans-$[\mathrm{Pt(PEt_3)_2}(o\text{-tolyl})\mathrm{Cl}]$	2·29 [c]	1·20	497	1·866	927
trans-$[\mathrm{Pt(PEt_3)_2(mesityl)Cl}]$	0·40 [d]	0·26	1309	0·341	446

[a] The values of k_1 are those obtained in the reactions of these substrates with strong nucleophiles and are the mean of a very large number of k_{obs} values. The values of k_1 found in this work are: $0{\cdot}44 \times 10^{-3}$ s^{-1}; $2{\cdot}00 \times 10^{-3}$ s^{-1}; and $1{\cdot}03 \times 10^{-2}$ s^{-1} for R = mesityl, *o*-tolyl, and phenyl respectively. [b] Ref. 28. [c] Ref. 14. [d] Ref. 13.

The equilibrium constants K for the reversible overall reaction (1) can be obtained by using the kinetic parameters of the reactions (2) and (3) and the relationship $K = k_1k_3/k_2k_4$. They have also been measured directly by conductance and spectrophotometric measurements. In the former technique, $5{\cdot}0 \times 10^{-4}$M solutions of *trans*-$[\mathrm{Pt(PEt_3)_2(R)Cl}]$ in methanol were allowed to reach equilibrium with various concentrations of pyridine at 30 °C and the apparent molar conductivity (λ_{M}) was measured. The molar conductivies of *trans*-$[\mathrm{Pt(PEt_3)_2(R)Cl}]$ and *trans*-$[\mathrm{Pt(PEt_3)_2(R)py}]^+\mathrm{Cl}^-$ (λ^0_{M}) were determined directly or estimated as shown in Table 3. The equilibrium constant was determined by using the expression (6) where $[\mathrm{py}]^0$ and $[\mathrm{Complex}]^0$ are the analytical

$$K = \frac{x^2}{([\mathrm{py}]^0 - x)([\mathrm{Complex}]^0 - x)} \qquad (6)$$

concentrations of pyridine and chloro-complex respectively, and x is the product $\lambda_{\mathrm{M}}/\lambda^0_{\mathrm{M}}[\mathrm{Complex}]^0$.

TABLE 3

Molar conductivity [a] of some platinum(II) complexes in methanol at 30 °C

Complex	Λ/Ω^{-1} cm^{-1} l mol^{-1}
trans-$[\mathrm{Pt(PEt_3)_2(mesityl)Cl}]$	0·67
trans-$[\mathrm{Pt(PEt_3)_2(mesityl)NO_3}]$	72·35
trans-$[\mathrm{Pt(PEt_3)_2(mesityl)(py)}]\mathrm{NO_3}$	91·28 [b]
trans-$[\mathrm{Pt(PEt_3)_2(mesityl)(py)}]\mathrm{Cl}$	81·52
trans-$[\mathrm{Pt(PEt_3)_2}(o\text{-tolyl})\mathrm{Cl}]$	1·13
trans-$[\mathrm{Pt(PEt_3)_2}(o\text{-tolyl})\mathrm{NO_3}]$	71·03
trans-$[\mathrm{Pt(PEt_3)_2}(o\text{-tolyl})\mathrm{(py)}]\mathrm{NO_3}$	91·03
trans-$[\mathrm{Pt(PEt_3)_2}(o\text{-tolyl})\mathrm{(py)}]\mathrm{Cl}$	81·27
trans-$[\mathrm{Pt(PEt_3)_2(Ph)Cl}]$	2·83
trans-$[\mathrm{Pt(PEt_3)_2(Ph)NO_3}]$	76·83
trans-$[\mathrm{Pt(PEt_3)_2(Ph)(py)}]\mathrm{NO_3}$	94·83 [b]
trans-$[\mathrm{Pt(PEt_3)_2(Ph)(py)}]\mathrm{Cl}$	85·07

[a] The values of the molar conductivity for the complexes listed were obtained by measuring the conductance of methanol solutions, $5{\cdot}0 \times 10^{-4}$M in complex, at 30 °C. Care was taken in purifying the solvent and the compounds. [b] These values were obtained by measuring the conductance of methanolic solutions of *trans*-$[\mathrm{Pt(PEt_3)_2(R)NO_3}]$ ($5{\cdot}0 \times 10^{-4}$M) to which pyridine (0·0125M) had been added. The data for the chloro-derivative were calculated after correction for the relative ionic mobility of $\mathrm{Cl^-}$ and $\mathrm{NO_3^-}$ anions in methanol solutions (Conway, 'Electrochimical Data,' Elsevier Publishing Company, New York, 1952, p. 162).

The equilibrium constants K were also determined from the optical densities between 285 and 315 nm of methanol solutions $2{\cdot}5 \times 10^{-4}$M in *trans*-$[\mathrm{Pt(PEt_3)_2(R)Cl}]$, 0·005M in LiCl, and with pyridine at various concentrations, that were allowed to reach equilibrium. The absorption data were analysed by means of equation (7),

$$K = \frac{(D - D^0_{\mathrm{Pt-Cl}})[\mathrm{Cl^-}]}{(D^0_{\mathrm{Pt-py}} - D)[\mathrm{py}]} \qquad (7)$$

where D is the optical density of the reaction mixture at equilibrium and $D^0_{\mathrm{Pt-Cl}}$ and $D^0_{\mathrm{Pt-py}}$ are the optical densities of *trans*-$[\mathrm{Pt(PEt_3)_2(R)Cl}]$ and *trans*-$[\mathrm{Pt(PEt_3)_2(R)(py)}]$ solutions respectively at the same total concentration of $\mathrm{Pt^{II}}$ of the solution under examination. The results obtained for the three complexes are collected in Table 4. The agreement between the values of K determined from the kinetic parameters and the values obtained by conductance and spectrophotometric methods is good.

Reactivity of the Intermediates trans-$[\mathrm{Pt(PEt_3)_2(R)(MeOH)}]^+$.—Preliminary tests, such as molecular-weight and molar-conductivity determination (Table 3) have shown that the complexes *trans*-$[\mathrm{Pt(PEt_3)_2(R)NO_3}]$ largely dissociate in methanol solution probably giving rise to the same species *trans*-$[\mathrm{Pt(PEt_3)_2(R)(MeOH)}]^+$ that have been invoked as intermediates in reactions (2) and (3). Consequently, by following the rates of the reactions of a methanol solution originally containing *trans*-$[\mathrm{Pt(PEt_3)_2(R)NO_3}]$, with pyridine, it is possible to obtain a direct measure of the rate constant k_3 for the bimolecular attack of pyridine upon the reaction intermediate. Further it is possible to verify whether the solvo-complex is reactive enough to be an intermedate in the reaction of the chloro-complex. Results are in Table 6.

The plots of k_{obs} against [py] are all linear and pass

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[28] U. Belluco, M. Graziani, and P. Rigo, *Inorg. Chem.*, 1966, **5**, 1123.

TABLE 4

Equilibrium constants for reaction (1) in methanol at 30 °C $[Pt^{II}] = 2{\cdot}5 \times 10^{-4}$M

$10[Cl^-]/[py]$	D	K	λ/nm	ε_{Pt-Cl} *	ε_{Pt-py}
R = mesityl					
0·125	0·398	0·136	300	684	1675
0·833	0·245	0·106	305	405	1433
0·625	0·261	0·102	305	405	1433
0·500	0·275	0·104	305	405	1433
0·250	0·333	0·091	305	405	1433
0·166	0·326	0·116	305	405	1433
0·125	0·335	0·125	305	405	1433
0·125	0·281	0·136	310	250	1204
0·125	0·220	0·125	315	150	953
R = *o*-tolyl					
6·250	0·435	0·352	290	1385	2371
5·000	0·459	0·421	290	1385	2371
2·500	0·499	0·407	290	1385	2371
1·666	0·519	0·390	290	1385	2371
1·250	0·535	0·408	290	1385	2371
6·250	0·297	0·334	295	906	1716
5·000	0·317	0·404	295	906	1716
1·666	0·370	0·405	295	906	1716
R = Ph					
8·333	0·528	0·805	285	1512	2733
6·250	0·552	0·828	285	1512	2733
5·000	0·566	0·802	285	1512	2733
8·333	0·453	0·819	290	1350	2282
6·250	0·469	0·810	290	1350	2282
5·000	0·482	0·816	290	1350	2282
8·333	0·339	0·757	295	1105	1632
6·250	0·348	0·747	295	1105	1632

* The molar extinction coefficients ε_{Pt-Cl} for the complexes *trans*-$[Pt(PEt_3)_2(R)Cl]$ were obtained by verifying the validity of Beer's law in the range of examined concentration. The values of ε_{Pt-py} of pyridino-compounds were obtained by mixing a solution of nitrato-complex with an excess of pyridine, allowing reaction to go to completion, and measuring the absorption against a blank containing pyridine at the same concentration as the solution under investigation. The completeness of the reaction was checked by verifying the identity of the final spectra and the conductance data of solutions at various reagent concentrations.

through the origin and the absence of a solvolytic path is certainly an indication that the process under consideration is really the bimolecular attack of pyridine on the methanol intermediate. The values of k_3/l mol^{-1} s^{-1} can be obtained from the slopes of these plots and can be used in combination with the known k_2/k_3 to calculate the rate constants k_2/l mol^{-1} s^{-1} which are too large to be measured directly by the experimental method.

TABLE 5

Comparison of equilibrium constants K obtained by various methods for the reversible reaction of *trans*-$[Pt(PEt_3)_2(R)Cl]$ with pyridine in methanol at 30 °C

	A	B	C
R = Ph	0·793	0·816	0·796
R = *o*-tolyl	0·384	0·382	0·390
R = mesityl	0·118	0·111	0·115

Equilibrium constants K obtained from (A) kinetic parameters, (B), a conductance method, and (C), a spectrophotometric method.

It can be seen from Tables 2 and 5 that k_2/k_3 increases and the value of the equilibrium constant decreases on going from the phenyl to the mesityl complex. Some consideration of the influence of steric effects on the substitution rates can be derived from the analysis of the relative reactivity of various reagents (Table 7) towards these substrates. It appears that the increasing steric hindrance makes it more difficult for the incoming group to approach the complex and to form the transition state. The same sequence of relative reactivity 22 : 5 : 1 is found for the entry of the solvent in the chloro- and pyridino-compounds and in the bimolecular reaction of the methanol intermediate with pyridine. Even though the relative reactivity values may depend on the bulkiness of the incoming nucleophiles, the observed sequence may be seen as a rough measure of the shielding that opposes the approach of the nucleophile, varying from no blocking by phenyl to blocking above and below the plane of the complex by mesityl. The rate constant for the entry of chloride into the methanol intermediate does not appear to be very sensitive to the extent of steric hindrance in the substrate. This may be due

TABLE 6

Pseudo-first-order rate constants k_{obs}/s^{-1} for the reaction of the methanolic intermediate *trans*-$[Pt(PEt_3)_2(R)(MeOH)]^+$ with pyridine in methanol at 30 °C. The concentration of the starting nitrate complex was $2{\cdot}5 \times 10^{-4}$M

Complex	10^3[py]/M	$10^3k_{obs}/s^{-1}$	10^3[py]/M	$10^3k_{obs}/s^{-1}$
trans-$[Pt(PEt_3)_2(mesityl)NO_3]$	1·0	0·38	7·5	2·61
	2·5	0·82	10·0	3·75
	5·0	1·81	15·0	5·20
			50·0	17·10
trans-$[Pt(PEt_3)_2(o\text{-tolyl})NO_3]$	1·0	1·92	5·0	9·26
	1·25	2·34	7·5	14·00
	2·50	4·88	10·0	18·79
trans-$[Pt(PEt_3)_2(Ph)NO_3]$	1·0	8·00	4·0	30·58
	1·5	11·68	5·0	37·77
	3·0	23·64	6·0	45·05

TABLE 7

Effect of increasing steric hindrance on the rates of substitution reactions of *trans*-$[Pt(PEt_3)_2(R)X]$ with various reagents

Complex	Reagent	R = Mesityl	R = *o*-tolyl	R = Ph
trans-$[Pt(PEt_3)_2(R)Cl]$	MeOH	1	5·72	21·25
trans-$[Pt(PEt_3)_2(R)(py)]$	MeOH	1	4·61	21·9
trans-$[Pt(PEt_3)_2(R)(MeOH)]$	py	1	5·47	21·7
	Cl^-	1	2·08	3·12

either to the small size of the chloride ion or to the fact that in the competition process it may be found in a favourable position for a re-entry in the co-ordination sphere of the metal.

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