Kinetics and Mechanism of Replacement of Chloride Ion in *trans*-Chloro-(*o*-tolyl)bis(triethylphosphine)platinum(II) by Substituted Pyridine Compounds: Influence of the Basicity and Steric Hindrance of the Pyridines on their Reactivity towards the Reaction Intermediate

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Rates of reversible reactions between the complex *trans*-[$Pt(PEt_3)_2$(*o*-tolyl)Cl] and various substituted pyridine compounds has been studied in methanol at 30 °C. The strong rate dependence on the incoming group arises from competition between the incoming pyridine and leaving chloride ion for the reaction intermediate which incorporates one molecule of solvent. The efficiency of the reagent in capturing the intermediate species and the position of the equilibrium of the overall reversible reaction do not depend on the change in σ-donor ability of the pyridine compound but only on its size and steric hindrance.

KINETIC study of the reaction of the complexes *trans*-[$Pt(PEt_3)_2$(R)Cl] (R = *o*-tolyl and mesityl) with various nucleophiles in methanol solution [1,2] has shown that displacement of the chloride ion does not take place according to the usual pattern of behaviour of platinum(II) complexes.[3] Both steric and electronic factors combine to prevent direct bimolecular attack by non-biphilic reagents on these substrates which have *ortho*-substituted phenyl ligands. The rate of the process is not dependent on the nature of the entering group or its concentration and, as for the 'pseudo-octahedral complexes,'[4] the solvent dominates the substitution process. In the case where pyridine is used as reactant a strong rate dependence on the incoming group is found which can be explained by competition between the incoming pyridine and leaving chloride for the reaction intermediate.[5] From the rate data it is possible to calculate the efficiency of pyridine in capturing the intermediate in competition with chloride ion. In this paper these studies have been extended to reactions of the complex *trans*-[$Pt(PEt_3)_2$(*o*-tolyl)Cl] with various substituted pyridine compounds with the aim of elucidating the mechanistic features of these processes and the factors affecting the reactivity of the pyridines towards the reaction intermediate.

EXPERIMENTAL

The complex *trans*-[$Pt(PEt_3)_2$(*o*-tolyl)Cl] was prepared by the published method [6] and identified by elemental analysis and its i.r. spectrum. The commercial pyridine compounds were purified by fractional distillation over KOH in a nitrogen atmosphere. Methanol was purified by distillation after heating under reflux over $Mg(OMe)_2$.

The reactions were followed spectrophotometrically by measuring changes in optical density with time, using an Optica CF4R double-beam recording spectrophotometer or a Beckman D.U. instrument. The reactions were initiated by mixing known volumes of standard solutions of the reactants in the thermostatted cell compartment of the spectrophotometer. In all cases the concentration of the complex was $2{\cdot}5 \times 10^{-4}$M and the incoming ligand was in sufficient excess to provide pseudo-first-order conditions. The concentration of Cl^- was kept constant at 0·005M by adding LiCl to the reaction mixture.

RESULTS AND DISCUSSION

All reactions were followed in methanol at 30 °C. By adding to the reaction mixture sufficient excess of LiCl over the starting complex (20 : 1) the concentration of free Cl^- does not considerably change during the reversible processes (1) and both forward and reverse paths

$$\textit{trans}\text{-}[Pt(PEt_3)_2(o\text{-tolyl})Cl] + am \rightleftharpoons \textit{trans}\text{-}[Pt(PEt_3)_2(o\text{-tolyl})(am)]^+ + Cl^- \quad (1)$$

follow pseudo-first-order kinetics. Values of pseudo-first-order rate constants for the approach to equilibrium, k_{obs}, are shown in Table 1 and were obtained from gradients of linear plots of log $(A_t - A_\infty)$ against time. (A_t and A_∞ are optical densities of the reaction mixture at time t and at equilibrium respectively, at wavelengths where the difference in optical density between the starting material and reaction products was largest.) The reproducibility of the k_{obs} values was better than $\pm 5{\cdot}0\%$.

It has been shown [5] that displacement of Cl^- from the species *trans*-[$Pt(PEt_3)_2$(R)Cl] does not take place through bimolecular attack by the nucleophile. The rate dependence on the incoming group can be explained on the basis of equations (2) and (3). The intermediate

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

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

complex *trans*-[$Pt(PEt_3)_2$(*o*-tolyl)(MeOH)]$^+$ arises from solvolysis of the initial chloro-complex and of the pyridine derivative with rate constants k_1 and k_4, respectively. The ratio $k_2 : k_3$ measures the efficiency of

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chloride ion in capturing the intermediate in competition with the pyridine compound. Both forward and reverse processes contribute to the approach to equilibrium of the overall reversible reactions (1).

TABLE 1

Rates of approach to equilibrium for the reaction between the complex *trans*-[Pt(PEt$_3$)$_2$(*o*-tolyl)Cl] and various pyridine compounds in the presence of 0·005M-LiCl in methanol at 30 °C

	[am]/M	$10^4k_{obs}/s^{-1}$	10^4k_{calc} [a]$/s^{-1}$
3-Chloropyridine	0·03	5·13	5·09
	0·06	5·40	5·38
	0·10	5·68	5·75
	0·20	6·79	6·61
	0·40	8·88	8·10
	0·60	10·8	9·34
	0·80	12·4	10·4
	1·00	14·7	11·3
Pyridine [b]	0·008	0·196	0·194
	0·010	0·213	0·212
	0·020	0·305	0·303
	0·030	0·400	0·393
	0·040	0·464	0·482
	0·060	0·657	0·659
	0·080	0·836	0·832
	0·100	0·999	1·00
	0·200	1·80	1·82
	0·300	2·60	2·58
	0·400	3·34	3·28
	0·500	3·94	3·94
	0·600	4·58	4·56
3-Methylpyridine	0·03	0·322	0·322
	0·06	0·532	0·536
	0·10	0·850	0·822
	0·20	1·53	1·50
	0·40	2·75	2·73
	0·60	3·98	3·84
	0·80	4·66	4·82
	1·00	5·48	5·71
4-Methylpyridine	0·03	0·400	0·383
	0·06	0·612	0·645
	0·10	0·964	0·987
	0·20	1·69	1·79
	0·40	3·23	3·25
	0·60	4·74	4·51
	0·80	5·80	5·62
	1·00	6·73	6·60
3,5-Dimethylpyridine	0·03	0·336	0·336
	0·06	0·546	0·540
	0·10	0·800	0·805
	0·20	1·44	1·44
	0·40	2·51	2·61
	0·60	3·71	3·66
	0·80	4·82	4·61
	1·00	5·39	5·46
3,4-Dimethylpyridine	0·03	0·397	0·383
	0·06	0·600	0·634
	0·10	0·926	0·962
	0·20	1·64	1·73
	0·40	3·05	3·12
	0·60	4·50	4·34
	0·80	5·61	5·42
	1·00	6·67	6·38
2-Methylpyridine	0·20	0·022	0·022
	0·40	0·034	0·033
	0·60	0·046	0·045
	0·80	0·054	0·056
2,4-Dimethylpyridine	0·10	0·036	0·036
	0·20	0·052	0·053
	0·40	0·092	0·089
	0·60	0·128	0·124
	0·80	0·159	0·159
	1·00	0·186	0·194

[a] Obtained by introducing in relation (4) the kinetic parameters in Table 2. [b] Data from ref. 5.

If [am] and [Cl$^-$] remain constant in any experiment, by applying the principle of the stationary state to the intermediate species *trans*-[Pt(PEt$_3$)$_2$(*o*-tolyl)(MeOH)]$^+$ the full rate expression for the reactions (1) is as in (4).

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

According to this expression plots of k_{obs} against [am] should be curved, the measure of the curvature depending on either the concentration of the pyridine compound or its nucleophilic power. If $k_2/k_3[\mathrm{Cl}^-] \gg [\mathrm{am}]$ the expression (4) reduces to $k_{obs} = k' + k''[\mathrm{am}]$, which has the same form, but a completely different meaning, to that usually found in substitution reactions of platinum(II) complexes. All examined pyridine compounds conform to equation (4). Values of k_4 were obtained from intercepts of plots of the pseudo-first-order rate constant, k_{obs}, against the reactant concentration. Relation (4) can be rewritten as (5), which enables

$$\frac{1}{k_{obs} - k_4} = \frac{1}{k_1 - k_4} + \frac{k_2/k_3}{k_1 - k_4} \cdot \frac{[\mathrm{Cl}^-]}{[\mathrm{am}]} \tag{5}$$

calculation of k_1 (from the intercept) and k_2/k_3 (from the ratio of the gradient to the intercept) from straight lines obtained by plotting $(k_{obs} - k_4)^{-1}$ against $[\mathrm{Cl}^-]/[\mathrm{am}]$. The rate constant k_1 is $2{\cdot}29 \times 10^{-3}$ s^{-1} for the complex *trans*-[Pt(PEt$_3$)$_2$(*o*-tolyl)Cl] in methanol at 30 °C. This value was obtained [2] from reactions of the chloro-complex with highly nucleophilic reagents (Br$^-$, I$^-$, *etc.*) which, because of their scavenger effect on the intermediate, reduce equation (4) to the simple form $k_{obs} = k_1$. Plots of $1/(k_{obs} - k_4)$ against $[\mathrm{Cl}^-]/[\mathrm{am}]$ were linear with intercepts corresponding to $1/k_1$. Indeed, except for 3-chloropyridine, k_4 values for the pyridine compounds are all much lower than k_1 (Table 2) and cannot influence the value of $1/(k_1 - k_4)$. By using the k_1 value thus obtained and relation (4) values of k_4 and of the ratio $k_2 : k_3$ were recalculated by means of a non-linear least-squares program on an I.B.M. 1130 computer. The calculations were made by assuming that the same experimental uncertainty in the value of k_{obs} should arise in any kinetic run. Table 2 shows values of the

TABLE 2

Kinetic parameters and equilibrium constants, obtained spectrophotometrically (K') and from the kinetic parameters (K), for reaction of the complex *trans*-[Pt(PEt$_3$)$_2$(*o*-tolyl)Cl] with various substituted pyridine compounds in methanol at 30 °C and I = 0·005M

Reactant	pK_a	$10^5k_4/s^{-1}$	$10^3k_3 : k_2$	K	K'
3-Chloropyridine	2·84	48·00	2·79	0·013	
Pyridine	5·17	1·21	2·01	0·38	0·43
3-Methylpyridine	5·68	1·02	1·64	0·37	0·38
4-Methylpyridine	6·02	1·14	1·99	0·40	
3,5-Dimethylpyridine	6·34	1·29	1·53	0·27	0·29
3,4-Dimethylpyridine	6·50	1·28	1·89	0·34	
2-Methylpyridine	6·10	0·11	0·0122	0·025	0·027
2,4-Dimethylpyridine	6·99	0·18	0·0387	0·049	

Standard deviations in both the kinetic parameters and equilibrium constants is ±5·00%.

kinetic parameters of reactions (1) obtained graphically and refined on the computer.

TABLE 3

Absorption data for reactions (1) in methanol at 30 °C and $I = 0{\cdot}005\text{M}$

Reactant	λ/nm	[Cl⁻]/[am]	A_∞
Pyridine	290 [a]	0·500	0·459
		0·250	0·499
		0·166	0·519
		0·125	0·535
	295 [b]	0·500	0·317
		0·332	0·337
		0·166	0·370
		0·083	0·393
3-Methylpyridine	295 [c]	0·332	0·352
		0·166	0·390
		0·083	0·421
		0·050	0·433
3,5-Dimethylpyridine	310 [d]	0·500	0·143
		0·332	0·158
		0·166	0·180
		0·083	0·196
2-Methylpyridine	300 [e]	0·0250	0·462
		0·0125	0·486
		0·0083	0·499
		0·0062	0·506

A_∞ = Absorbance of reaction mixture at equilibrium; $\varepsilon_{\text{Pt-Cl}}$ and $\varepsilon_{\text{Pt-am}}$ are molar absorption coefficients of the chloro-complex and of the pyridine derivative respectively, and $[\text{Pt}^{\text{II}}]$ is the total concentration of platinum(II) in solution.

[a] $\varepsilon_{\text{Pt-Cl}}$ 1 385, $\varepsilon_{\text{Pt-am}}$ 2 371 l mol⁻¹ cm⁻¹; $[\text{Pt}^{\text{II}}] = 2{\cdot}5 \times 10^{-4}\text{M}$. [b] $\varepsilon_{\text{Pt-Cl}}$ 906, $\varepsilon_{\text{Pt-am}}$ 1 716 l mol⁻¹ cm⁻¹; $[\text{Pt}^{\text{II}}] = 2{\cdot}5 \times 10^{-4}\text{M}$. [c] $\varepsilon_{\text{Pt-Cl}}$ 906, $\varepsilon_{\text{Pt-am}}$ 1 830 l mol⁻¹ cm⁻¹; $[\text{Pt}^{\text{II}}] = 2{\cdot}5 \times 10^{-4}\text{M}$. [d] $\varepsilon_{\text{Pt-Cl}}$ 188, $\varepsilon_{\text{Pt-am}}$ 444 l mol⁻¹ cm⁻¹; $[\text{Pt}^{\text{II}}] = 5{\cdot}0 \times 10^{-4}\text{M}$. [e] $\varepsilon_{\text{Pt-Cl}}$ 512 l mol cm⁻¹, $[\text{Pt}^{\text{II}}] = 7{\cdot}5 \times 10^{-4}\text{M}$.

Values of the equilibrium constants K for reactions (1) were calculated from the relation $K = k_1k_3/k_2k_4$ and some of these were checked spectrophotometrically by allowing mixtures of complex, LiCl, and pyridine compound to reach equilibrium and measuring the optical density of the solution at wavelengths in the range 285—315 nm. The absorption data (Table 3) were analysed as before [5] and the data collected in Table 2 show that there is reasonable agreement between values of the equilibrium constants obtained spectrophotometrically and those calculated by means of the kinetic parameters. Even though the basicity of the entering group plays a negligible part compared to the polarisability of the donor atom in determining the rate of attack on polarisable reaction sites such as d^8 metal ions, free-energy relations of the type $\log k_2 = \text{constant} + s \,.\, \text{p}K_\text{a}$ obtain [7] for amines having the same form of steric hindrance. (Values of $\text{p}K_\text{a}$ are a relative index of the proton basicity of the reactant and s is a nucleophilic discrimination factor.) The nucleophilic power of the various reactants in the studied reactions is displayed during the competition process and can be measured by the value of the ratio $k_2 : k_3$ (Table 2). For heterocyclic amines substituted in positions 3, 4, and 5, values of the ratio $k_2 : k_3$ do not differ greatly. The transient *trans*-$[\text{Pt}(\text{PEt}_3)_2(o\text{-tolyl})(\text{MeOH})]^+$ does not even exhibit the small sensitivity to changes in the σ-donor ability of the incoming amine found [8] for the complex *trans*-$[\text{Pt}(\text{py})_2\text{Cl}_2]$ and its total charge does not seem directly related to the electrophilicity of the reaction centre. In any case the intermediate has a lifetime long enough to discriminate between the various reagents. Indeed the reactivity of 2-methylpyridine and 2,4-dimethylpyridine is much lower (*ca.* 100 times) than that of the other substituted pyridine compounds, a consequence of steric hindrance produced by the methyl group near the nitrogen atom.

The steric retardation (*ortho*-effect) is much greater than that found for other substrates of Pt^{II}, Pd^{II}, and Au^{III} and may be related to the presence above the square plane of the intermediate complex of another methyl group from the aromatic ring co-ordinated to the central metal atom. Judging from the k_4 values, the role played by the *ortho*-methyl group of the pyridine compound as leaving group in decreasing the solvolysis rate of the pyridine complexes appears to be less important. This could mean that strains caused by the *ortho*-methyl group in the ground and transition states are not very different. Because the values of K are mainly determined by those of the rate constants k_3, the position of equilibrium in reactions (1) is not controlled by basicity but by the size and structure of the incoming pyridine compound.

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