The Kinetics of the Displacement, by Chloride, of Heterocyclic Nitrogen Bases (am) from *trans*-$[PtL(am)Cl_2]$ (L = C_2H_4, CO, or PMe_3); The Effect of Steric Hindrance in the Leaving Group on the *trans* Effect of L

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The kinetics of the reaction, *trans*-$[PtL(am)Cl_2] + Cl^- \xrightarrow{H^+} [PtLCl_3]^- + Ham^+$ (L = C_2H_4, CO, or PMe_3; am = pyridine, 2-methylpyridine, 2,6-dimethylpyridine, or 2,4,6-trimethylpyridine) have been studied in 5% aqueous methanol at 25.0 °C. Only the ethene complexes show a significant dependence on $[Cl^-]$ and this is much reduced on *o*-methyl substitution in the leaving pyridine. In all cases the reactivity is greatly decreased by steric hindrance in the leaving group. The results are discussed in terms of a general destabilisation of the transition state due to steric crowding, together with a specific effect arising from restrictions on the orientation of the ethene molecule in the transition state.

In recent years we have been examining, systematically, the way in which the nature of a neutral ligand, L, affects the rates and equilibrium constants associated with reaction (1),

$$[PtLCl_3]^- + am \rightleftharpoons trans\text{-}[PtL(am)Cl_2] + Cl^- \qquad (1)$$

where am is one of a variety of amines or heterocyclic nitrogen bases and L = Me_2SO,[1] Me_2S,[2] Et_2S,[3] PMe_3,[4] PEt_3,[4] $PBu^n{}_3$,[4] PPh_3,[4] $P(OMe)_3$,[4] or $AsEt_3$.[4] Steric effects are minimised in these systems and the rates of the forward reaction were found to be sensitive to the basicity of am, although not in a systematic fashion. Indeed, the second-order rate constants for the entry of the heterocyclic bases decreased as the basicity increased. The displacement of the co-ordinated bases by chloride was very sensitive to their basicity; however, the chloride-dependent pathway frequently made only a small contribution to the total rate of reaction. This was especially true where L = PR_3 (R = Me, Et, Bu^n, Ph, or OMe). Attempts to discuss the problem in terms of σ (ground-state weakening, *trans* influence) and π (transition-state strengthening) effects required studies of complexes where L = CO and C_2H_4, but the displacement of chloride from their trichloroplatinum(II) complexes was too fast for the techniques at our disposal. Elding and Gröning[5] state in a footnote that the observed rate constant for the displacement of Cl^- from $[Pt(C_2H_4)Cl_3]^-$ is *ca.* 10^5 s^{-1} at 25 °C. In spite of the enormous interest in the reactivity of complexes containing CO and C_2H_4, much of the work relating to ligand exchange in these systems is based on n.m.r. studies and rarely quotes rate constants, the reactions being either too fast or too slow for the n.m.r. time-scale.[6] The exchange of substituted pyridines (R-py) in equation (2) indicated that steric hindrance from *ortho*

$$trans\text{-}[Pt(C_2H_4)(R\text{-}py)Cl_2] + R\text{-}py^* \rightleftharpoons trans\text{-}[Pt(C_2H_4)(R\text{-}py^*)Cl_2] + R\text{-}py \qquad (2)$$

substitution in the pyridine reduced the rate of exchange enormously so that, whereas the signals for free and co-ordinated pyridine coalesced even at the lowest temperatures studied, the analogous 2,6-dimethylpyridine (2,6Me_2-py) and 2,4,6-trimethylpyridine (2,4,6Me_3-py) complexes showed two sharp and separate signals for free and bound base with no tendency for them to broaden or coalesce, even at the highest temperatures studied.[7,8]

With this in mind we set out to examine the displacement of am from *trans*-$[PtL(am)Cl_2]$ (L = C_2H_4, CO, or PMe_3) by chloride in the presence of acid in the hope that, with sufficient steric hindrance, the rates would come within the range of the techniques at our disposal and we could add the two strong *trans*-effect ligands to our list and to see whether, when L is a potentially strong π acceptor, a different pattern of behaviour is observed. The results are presented in this paper.

Experimental

Preparations.—Potassium trichloro(ethene)platinate(II) was prepared by the method of Chock *et al.*[9] The complexes *trans*-$[Pt(C_2H_4)(am)Cl_2]$ [am = py, 2-methylpyridine (2Me-py), or 2,4,6Me_3-py] were prepared by adding the appropriate heterocyclic base dissolved in a small amount of water (methanol in the case of 2,4,6Me_3-py), to an aqueous solution of $K[Pt(C_2H_4)Cl_3]$. The product formed immediately and was filtered off and recrystallised from chloroform–pentane, according to the method of Schmidt and Orchin.[10] The analytical data (Table 1), i.r. and ^{1}H n.m.r. spectra are consistent with their formulation. Tetra-n-butylammonium trichloro(carbonyl)platinate(II) was prepared by the method of Orchin and co-workers.[11]

The complexes *trans*-$[Pt(CO)(am)Cl_2]$ (am = 2Me-py or py) were prepared by the method of Clement and Orchin[12] which involved bubbling CO through a solution of the corresponding C_2H_4 complex in carefully dried $CHCl_3$ or CH_2Cl_2. After several minutes, the solution was concentrated and pentane was added to precipitate the complex which was then recrystallised from CH_2Cl_2–pentane. The complex with 2,4,6-Me_3-py could not be prepared in this way. When CO was passed through a solution of the appropriate ethene complex there was general decomposition with the deposition of metallic platinum. Direct reaction between $[Pt(CO)Cl_3]^-$ and 2,4,6Me_3-py led to general decomposition on the preparative scale and a study of the equilibrium between these two species in dilute methanolic solution indicated a complicated sequence of reactions which was not the simple displacement of the *trans* chloride by 2,4,6Me_3-py. We did not have the

Table 1. Analytical data *(%)

Complex	Empirical formula	C	H	N
[Pt(C_2H_4)(2,4,6Me_3-py)Cl_2]	$C_{10}H_{15}Cl_2NPt$	29.0 (28.9)	3.65 (3.65)	3.40 (3.35)
[Pt(C_2H_4)(2Me-py)Cl_2]	$C_9H_{13}Cl_2NPt$	25.0 (24.8)	2.80 (2.85)	3.55 (3.60)
[Pt(C_2H_4)(py)Cl_2]	$C_8H_{11}Cl_2NPt$	22.6 (22.5)	2.40 (2.45)	3.70 (3.75)
[NBu^n_4][Pt(CO)Cl_3]	$C_{17}H_{36}Cl_3NOPt$	35.7 (35.7)	6.25 (6.35)	2.45 (2.45)
[Pt(CO)(2Me-py)Cl_2]	$C_7H_7Cl_2NOPt$	21.8 (21.7)	1.85 (1.80)	3.55 (3.60)
[Pt(CO)(py)Cl_2]	$C_6H_5Cl_2NOPt$	19.4 (19.3)	1.35 (1.35)	3.65 (3.75)
[Pt(PMe_3)(2,4,6Me_3-py)Cl_2]	$C_{17}H_{20}Cl_2NPPt$	28.3 (28.5)	4.25 (4.35)	2.95 (3.00)
[Pt(PMe_3)(2Me-py)Cl_2]	$C_{16}H_{18}Cl_2NPPt$	24.9 (24.8)	3.75 (3.70)	2.35 (3.20)

* Calculated values are in parentheses.

autoclave facilities to prepare the dimer [$Pt_2(CO)_2Cl_4$] in order to investigate bridge cleavage with 2,4,6Me_3-py.

The complexes *trans*-[Pt(PMe_3)(am)Cl_2] (am = 2,4,6Me_3-py or 2Me-py) were prepared by adding stoicheiometric amounts of the appropriate base to dichloromethane solutions of the dimer, [$Pt_2(\mu\text{-}Cl)_2Cl_2(PMe_3)_2$] (prepared by the method of Goodfellow and Venanzi [13]). The solution was filtered, the volume reduced at low pressure, and the required complex precipitated by adding diethyl ether. Analyses are given in Table 1.

Standard solutions of the [Pt(PMe_3)Cl_3]$^-$ anion were generally prepared by dissolving a known amount of the dimer in a concentrated methanolic solution of LiCl.

Infrared and electronic spectra of the complexes were in close agreement with those already published for *trans*-[PtL(am)Cl_2].[14-17] The ^{1}H n.m.r. spectra recorded in CD_2Cl_2 and CD_3OD were quite similar for all the complexes examined, and were consistent with their formulation as *trans*-[PtL(am)-Cl_2] species. No significant change therefore accompanied their dissolution.

Kinetics.—Reactions were initiated by mixing equal volumes of freshly prepared, pre-thermostatted solutions of the complex in dry methanol and the nucleophile in acidified 10% aqueous methanol and were followed spectrophotometrically at a suitable single wavelength. For half-lives longer than 20 s, the reaction was studied with a Perkin-Elmer 554 spectrophotometer. Faster reactions were followed using a Hi-Tech stopped-flow spectrophotometer. I.r. spectra of the complexes in CsCl discs were measured with a Perkin-Elmer 225 spectrometer and ^{1}H n.m.r. spectra were measured with a Varian XL 200 FT spectrometer.

Results

Addition of an acidified solution of lithium chloride in methanol to a solution of *trans*-[PtL(am)Cl_2] in methanol leads to a smooth single-stage spectral change, the rate of which depends upon the nature of L and am, to a product whose spectrum is identical to that of an equimolar mixture of [PtLCl_3]$^-$ and Ham$^+$ measured under the same conditions of [Cl^-] and [H^+]. The kinetics were studied in the presence of excess LiCl to ensure that [Cl^-] remained constant during any run. Preliminary experiments to examine the effect of [H^+] on the kinetics indicated no change in rate when the concentration was varied between 5×10^{-3} and 5×10^{-2} mol dm^{-3} and the higher concentration was maintained in all subsequent runs. Preliminary experiments also showed that the rate was insensitive to ionic strength and so no attempt was made to hold this constant during the runs. The change in absorbance followed a first-order rate law and the first-order rate constants were obtained from a non-linear regression program to fit the expression $A_t = A_\infty - (A_\infty - A_0)\exp(-k_{obs.}t)$ (with A_t, the absorbance at time t, and the time, t, as variables) using the Gauss–Newton algorithm to optimise the three parameters A_0, A_∞, and $k_{obs.}$. The random distribution of the residuals confirmed that the absorbance change did, indeed, obey a first-order rate law. The values of $k_{obs.}$ are collected in Table 2. For the *trans*-[Pt(PMe_3)(am)Cl_2] complexes $k_{obs.}$ was effectively independent of [Cl^-], but for the others the rate constants obeyed the usual two-term rate law, $k_{obs.} = k_1 + k_2[Cl^-]$. Values of k_1 and k_2, obtained from a weighted linear least-squares analysis, are also included in Table 2.

Discussion

It is now possible, using reaction (3), to extend the *trans* effect

$$trans\text{-}[PtL(am)Cl_2] + Cl^- \xrightarrow{H^+} [PtLCl_3]^- + Ham^+ \quad (3)$$

sequence from L = Me_2S to L = C_2H_4. Qualitatively, the sequence appears as expected, $R_2S < R_2SO < PR_3 < P(OR)_3 < CO < C_2H_4$; however, quantitatively it presents a number of intriguing problems.

The ratio k_2/k_1, which has been used as a measure of the ability of the substrate to discriminate between nucleophiles, changes quite dramatically from L = C_2H_4 (300), through CO (2.4), to PMe_3 (0.04). The ratio for L = Me_2SO is 1.8 [1] and it is estimated to be 1.0 for Me_2S.[2] This is in accord with the idea that the greater the importance of the lowering of the energy of the transition state towards the *trans* effect, the greater will be the observed nucleophilic discrimination. It was predicted that a large *trans* effect, coupled with a small *trans* influence should be associated with high nucleophilic discrimination, whereas a large *trans* effect coupled with a large *trans* influence should be associated with a low nucleophilic discrimination.[4] In the case of L = C_2H_4 and PMe_3 this appears to be borne out by the results, but the relatively small discrimination ratio found for CO came as a surprise in view of the belief that its high *trans* effect arose from its ability to act as a π acceptor. If the relative lengths of the Pt–Cl bonds *cis* and *trans* to CO in the complex *trans*-[Pt(CO)Cl_3]$^-$ are used as a criterion of *trans* influence, it might be concluded that the *trans* influence of CO is no greater than that of Cl.[18] However, it has been properly pointed out that π acceptance by a *trans* ligand may also affect the bond length,[19] the length of the Pt–Cl bond decreasing as the extent of the metal–ligand π-bonding increases. Criteria based on n.m.r. coupling constants, on the other hand, quantify the *trans* influence in terms of the extent to which the Pt 6*s* orbital is involved in the binding of the platinum to the probe nucleus and are sensitive only to σ interactions. Appleton and Bennett,[20] on the basis of ^2J(Pt–P) coupling constants obtained from the ^{31}P n.m.r. spectrum of the phosphorus *trans* to the ligand being exam-

Table 2. Rate constants for the reaction (3)[a]

L	am	λ/nm	$10^3[Cl^-]$/mol dm^{-3}	$k_{obs.}$/s^{-1}
C_2H_4	py	310	5.0	175[b]
			7.0	212[b]
			10.0	250[b]
			12.0	330[b]
			16.0	400[b]
		$k^1 = 68 \pm 14$ s^{-1}, $k_2 = 20\,300 \pm 1\,100$ dm^3 mol^{-1} s^{-1}		
C_2H_4	2Me-py	310	5.0	51[b]
			10.0	67[b]
			20.0	99[b]
			30.0	120[b]
			40.0	150[b]
			50.0	170[b]
		$k_1 = 47 \pm 2$ s^{-1}, $k_2 = 2\,450 \pm 90$ dm^3 mol^{-1} s^{-1}		
C_2H_4	2,4,6Me$_3$-py	289	5.0	0.0146[c]
			10.0	0.0155[c]
			30.0	0.0170[c]
			50.0	0.0178[c]
			80.0	0.0199[c]
			100	0.0201[c]
			500	0.0383[c]
			1 000	0.059[c]
		$k_1 = (1.56 \pm 0.03) \times 10^{-2}$ s^{-1}, $k_2 = (4.4 \pm 0.01) \times 10^{-2}$ dm^3 mol^{-1} s^{-1}		
C_2H_4	2,6Me$_2$-py	340	10.0	0.045[c]
			20.0	0.044[c]
			50.0	0.049[c]
			100	0.053[c]
			250	0.073[c]
			500	0.101[c]
		$k_1 = 0.042 \pm 0.001$ s^{-1}, $k_2 = 0.117 \pm 0.001$ dm^3 mol^{-1} s^{-1}		
CO	py	286	10.0	1.28
			20.0	1.27
			50.0	1.31
			100	1.38
			200	2.06
			500	2.64
		$k_1 = 1.21 \pm 0.05$ s^{-1}, $k_2 = 2.9 \pm 0.1$ dm^3 mol^{-1} s^{-1}		
CO	2Me-py	320	10	0.0258
			30	0.0274
			60	0.0302
			80	0.0328
			100	0.0347
			300	0.0523
			600	0.0807
			800	0.101
			1 000	0.129
		$k_1 = (2.47 \pm 0.03) \times 10^{-2}$ s^{-1}, $k_2 = (9.43 \pm 0.06) \times 10^{-2}$ dm^3 mol^{-1} s^{-1}		
[d] PMe$_3$	py	$k_1 = (1.54 \pm 0.09) \times 10^{-2}$ s^{-1}, $k_2 = (5.8 \pm 1.8) \times 10^{-4}$ dm^3 mol^{-1} s^{-1}		
PMe$_3$	2Me-py	315	10	7.6×10^{-4}
			20	7.7×10^{-4}
			30	7.5×10^{-4}
			50	7.6×10^{-4}
			100	7.7×10^{-4}
			250	7.6×10^{-4}
			500	7.6×10^{-4}
		$k_1 = (7.6 \pm 0.03) \times 10^{-4}$ s^{-1}		
[e] PMe$_3$	2Me-py	315	20	3.7×10^{-4}
			50	4.4×10^{-4}
			100	4.3×10^{-4}
			500	4.0×10^{-4}
		$k_1 = (4.1 \pm 0.2) \times 10^{-4}$ s^{-1}		
[f] PMe$_3$	2Me-py	315	20	2.5×10^{-3}
			50	2.4×10^{-3}
			100	2.5×10^{-3}
			500	2.3×10^{-3}
		$k_1 = (2.4 \pm 0.1) \times 10^{-3}$ s^{-1}, $\Delta H^\ddagger = 13 \pm 2$ kcal mol^{-1}, $\Delta S^\ddagger = -27 \pm 7$ cal K^{-1} mol^{-1}		
PMe$_3$	2,4,6Me$_3$-py	315	20	4.7×10^{-6}
			100	4.6×10^{-6}
			500	4.5×10^{-6}
		$k_1 = (4.6 \pm 0.05) \times 10^{-6}$ s^{-1}		

[a] In 5% aqueous methanol at 25.0 °C; $[H^+] = 5 \times 10^{-2}$, [complex] $= 5 \times 10^{-4}$ mol dm^{-3}; ionic strength variable. [b] ±5%. [c] ±1%. [d] Data taken from ref. 4 (30 °C). [e] At 20.0 °C. [f] At 40.0 °C; cal = 4.184 J.

ined, suggest that CO has a σ *trans* influence that lies somewhere between that of PPh$_3$ and AsPh$_3$ and they also are critical of the bond length criterion when applied to the *trans* influence of ligands with potential π-acceptor character. This would account for the unexpectedly low discrimination factor. We conclude, therefore, that the high *trans* effect of carbon monoxide has less contribution from its role as a π acceptor and a greater contribution from its σ-donor capacity than has hitherto been recognised.

The effect of introducing *o*-methyl substituents in the pyridine leaving-group also underlines major differences in the *trans* effects of C_2H_4 and CO. On going from pyridine to 2-methylpyridine there is no major effect upon $k_{obs.}$ for the reaction of the C_2H_4 complex. However, this proves to be due to the relative insensitivity of k_1 to this change; k_2 is strongly affected and the ratio k_2/k_1 decreases from 300 to 52. With the analogous change in the CO complex there is a 50-fold decrease in the general reactivity but the ratio k_2/k_1 hardly changes (2.4 to 3.8). The placing of a second methyl group in the *ortho* position of the leaving group has a very profound effect upon the reactivity of the ethene complex: k_1 is reduced by a factor of 3×10^3, while k_2 is reduced by a factor of 6×10^4. As a consequence, the ratio k_2/k_1 is reduced to 2.9, similar to that found for the CO complexes already examined. The fact that the 2,6-dimethylpyridine and 2,4,6-trimethylpyridine complexes have very similar reactivities suggests that this is a steric and not an electronic effect. Our inability, in spite of much effort, to prepare *trans*-[Pt(CO)(2,4,6Me$_3$-py)Cl$_2$] prevents us from seeing the effect of the second *ortho* substitution here. A comparable study of the steric effects on the *trans* effect of PMe$_3$ is prevented by the fact that the contribution from the pathway involving $k_2[Cl^-]$, barely measurable in the pyridine complex, is too small to be measured in the others and so the effect of *o*-methyl substitution on the ratio k_2/k_1 cannot be determined but it has clearly reduced it. The extent of the retardation of the solvolytic pathway (k_1) lies between that observed for the C_2H_4 and the CO complexes when a single *o*-methyl substituent is introduced, and less than that found for the C_2H_4 complex when the second *o*-methyl group is introduced.

The first is a general effect that might be expected from the non-bonded repulsions in the transition state involving all ligands adjacent to the heterocyclic base. This is the first time such an effect has been independently demonstrated in square-planar substitution although it has always been assumed that the very marked reduction in the rate of amine exchange in these complexes involved a contribution from the leaving-group effect as well as the entering-group effect.[6-8] It is of interest to note that this type of steric hindrance is absent when similar hindered amines are displaced from $[Au(am)Cl_3]$ in the presence of HCl.[21] On the other hand, this type of steric hindrance is very common when the amine is an entering group,[22] and when *ortho*-substituted phenyl is co-ordinated *cis* to the leaving group.[23] In the former case, rate reduction by factors between 10 and 100 per *ortho* substituent is usual; in more crowded substrates it can be greater.[24] In the reactions of *cis*-$[Pt(PEt_3)_2(R)Cl]$, the reduction in the first-order rate constant can be in the order of 80 000 : 200 : 1 on going from R = phenyl, through *o*-tolyl, to mesityl. The second steric effect applies specifically, in this work, to the ethene complexes, where the bulky groups will prevent the ethene from orienting itself in the transition state to function effectively as a π acceptor. It has been suggested that, in the $[Pt(C_2H_4)Cl_3]^-$ ion, the amount of π metal-to-ligand back donation is small [25] and that the barrier to rotation is mainly due to steric repulsion between the ethene and the *cis* chlorines, a conclusion reached at much the same time by Hoffmann and co-workers.[26] Since this will reduce the ability of the ethene to assist the formation of the bond with the incoming group, it will manifest itself in the reduction of the nucleophilic discrimination and hence in the reduction of the ratio k_2/k_1. Carbon monoxide, being a cylindrical π acceptor, would not be affected in the same way by bulky substituents in the adjacent ligands.

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