Conversion of Methyl Carbonyl Complexes of Platinum(II) into Acetyl Derivatives: A Kinetic Study

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Study of the reactions $[Pt(CO)(PPh_3)(I)Me] + L' \longrightarrow [Pt(PPh_3)(L')I(COMe)]$ [L' = $AsPh_3$, $As(p\text{-}MeC_6H_4)_3$, $AsMe(o\text{-}MeC_6H_4)_2$, and $SbPh_3$] indicates that the first, and largely rate-controlling, step involves neither the incoming ligand nor the solvent, in sharp contrast to related reactions of alkyl carbonyl complexes of other metals and to the normal pattern of ligand-substitution reactions of platinum(II) complexes. This step is thought to involve formation of the intermediate $[Pt(PPh_3)I(COMe)]$, which then reacts rapidly with the ligand L'. The apparent change in kinetic behaviour when one or more phenyl groups in the phosphine ligand of the starting material are replaced by *o*-tolyl groups is believed to be due to a large drop in the rate constant for reaction of the intermediate with ligand L', arising from crowding caused by the *o*-tolyl substituents.

SOME time ago, we reported[1] that kinetic data for reaction (1) ($L = L' = AsPh_3$, $X = Cl$, and $R = Et$)

$$[Pt(CO)L(X)R] + L' \longrightarrow [PtL(L')X(COR)] \quad (1)$$

indicated that the step which was mainly rate-determining involved neither the incoming ligand L' nor the solvent. The proposed mechanism for the reaction [equations (2) and (3)] differs radically from that characteristic

$$[Pt(CO)L(X)R] \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [PtL(X)(COR)] \quad (2)$$

$$[PtL(X)(COR)] + L' \xrightarrow{k_3} [PtL(L')X(COR)] \quad (3)$$

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[1] R. W. Glyde and R. J. Mawby, *Inorg. Chem.*, 1971, **10**, 854.

of ligand-substitution reactions of planar four-co-ordinate complexes of platinum(II), in which the incoming ligand or the solvent attacks the complex to give a five-co-ordinate transition state or intermediate [2] {an exception to this general rule is isomerization of the complex *cis*-$[Pt(PEt_3)_2Cl(o\text{-}MeC_6H_4)]$ which, it has been suggested, proceeds *via* a three-co-ordinate intermediate [3]}. It is also unlike the mechanism observed for similar reactions of several other complexes, such as $[Mn(CO)_5R]$, $[(cp)Fe(CO)_2R]$, and $[(cp)Mo(CO)_3R]$ (R = alkyl, cp = η-cyclopentadienyl) [4]: in these cases combination of alkyl and carbonyl ligands occurs only with the assistance of an incoming solvent molecule or ligand.

Since, for reasons given earlier,[1] only the one reaction could be studied, we were unable to check on two points vital to the proposed mechanism: (*a*) whether the value for the rate constant k_1 for a given complex [Pt(CO)L(X)R] was independent of the nature of the incoming ligand L′; and (*b*) whether its value increased with increasing bulkiness of the ligand L, as would be expected if a three-co-ordinate intermediate [PtL(X)(COR)] is formed. Following our recent report [5] of a two-step route to new complexes of the type [Pt(CO)L(X)R], we now describe experiments on these complexes designed to deal with these points.

RESULTS AND DISCUSSION

Independence of the Nature of the Incoming Ligand.—The complex $[Pt(CO)(PPh_3)(I)Me]$ reacts with ligands L′ = $AsPh_3$, $SbPh_3$, $As(p\text{-}MeC_6H_4)_3$, and $AsMe(o\text{-}MeC_6H_4)_2$ in accordance with equation (4). Details of

$$[Pt(CO)(PPh_3)(I)Me] + L' \longrightarrow [Pt(PPh_3)(L')I(COMe)] \quad (4)$$

the characterization and probable stereochemistry of the complexes have been given in an earlier paper; [5] the reactions are essentially quantitative. The kinetics of the reactions in tetrahydrofuran (thf) solution were studied at three different temperatures, using concentrations of the ligand L′ at least 10 times greater than that of the platinum complex so that the ligand concentration could be regarded as constant throughout the run. The reactions were found to be first order in platinum complex concentration, and the pseudo-first-order rate constants (k_{obs}) are listed in Table 1. It can be seen that the values increase with ligand concentration, but that the increase is not linear.

Assuming that the concentration of the intermediate is small and effectively constant, the mechanism outlined by equations (2) and (3) leads to expression (5).

$$k_{obs} = k_1k_3[L']/(k_2 + k_3[L'])$$

$$\text{or} \qquad k_{obs}^{-1} = (k_2/k_1k_3)[L']^{-1} + k_1^{-1} \qquad (5)$$

It follows that the data are only compatible with the mechanism if plots of k_{obs}^{-1} against $[L']^{-1}$ are linear, and if all plots for a given temperature have the same intercept at $[L']^{-1} = 0$, regardless of the nature of the incoming ligand L′. Plots for reactions with all four ligands at 297·5 K are collected in the Figure. The points lie on fairly good straight lines and the variation in intercept (and hence in the value of k_1) is small. Values for k_1 at other temperatures, obtained from similar plots, are collected in Table 3. The activation parameters derived from these data for the k_1 step are $\Delta H^\ddagger = 18{\cdot}3 \pm 0{\cdot}3$ kcal mol^{-1} and $\Delta S^\ddagger = -10{\cdot}3 \pm 1{\cdot}1$ cal K^{-1} mol^{-1}.* Also included in Table 3 are values for k_1 for reaction of the complex $[Pt(CO)(PPh_3)(I)Me]$ with $AsPh_3$ in chlorobenzene and cyclohexanone, similarly derived from data given in Table 2. It can be seen that there is little variation in the value of k_1 with change in either dielectric constant or co-ordinating ability of the solvent. Thus the results are compatible with the mechanism given in equations (2) and (3), and there is no evidence to suggest that the solvent plays an important role in the k_1 step.

The gradients of the plots of k_{obs}^{-1} against $[L']^{-1}$ allow values to be obtained for the ratio $k_2 : k_3$. Since k_2 is independent of the nature of the incoming ligand, the

TABLE 1

Observed rate constants for reaction of the complex $[Pt(CO)(PPh_3)(I)Me]$ with ligands L′ in tetrahydrofuran

T/K	L′	[L′]/mol dm^{-3}	10^4k_{obs}/s^{-1}
287·6	$AsPh_3$	0·133	1·7
		0·307	2·5
		0·495	3·2
	$As(p\text{-}MeC_6H_4)_3$	0·133	2·9
		0·207	3·1
		0·287	3·5
	$AsMe(o\text{-}MeC_6H_4)_2$	0·134	3·4
		0·210	3·6
		0·384	3·9
	$SbPh_3$	0·135	2·5
		0·310	3·3
		0·502	3·6
297·5	$AsPh_3$	0·133	4·8
		0·211	6·4
		0·383	8·5
		0·495	9·2
	$As(p\text{-}MeC_6H_4)_3$	0·133	7·9
		0·212	9·9
		0·272	10·0
		0·384	11·1
	$AsMe(o\text{-}MeC_6H_4)_2$	0·134	6·2
		0·211	8·3
		0·384	9·9
		0·494	10·7
	$SbPh_3$	0·135	7·5
		0·214	9·4
		0·389	11·6
		0·502	11·8
308·0	$AsPh_3$	0·133	11·3
		0·211	15·3
		0·384	22·8
	$As(p\text{-}MeC_6H_4)_3$	0·133	21·0
		0·207	23·8
		0·287	26·5
	$AsMe(o\text{-}MeC_6H_4)_2$	0·134	17·1
		0·211	21·1
		0·384	26·6
	$SbPh_3$	0·135	20·2
		0·310	28·3
		0·502	31·3

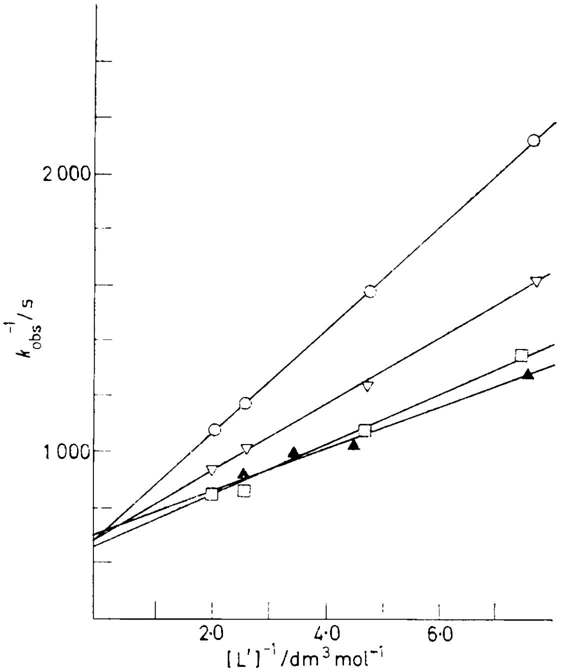
* 1 cal = 4·184 J.

[2] C. H. Langford and H. B. Gray, 'Ligand Substitution Processes,' Benjamin, New York, 1965, ch. 2.

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

[4] A. Wojcicki, *Adv. Organometallic Chem.*, 1973, **11**, 87.

[5] C. J. Wilson, M. Green, and R. J. Mawby, *J.C.S. Dalton*, 1974, 421.



Plots of k_{obs}^{-1} against $[L']^{-1}$ for reactions of the complex [Pt(CO)-(PPh$_3$)(I)Me] with ligands L′ in tetrahydrofuran at 297·5 K: (▲), L′ = As(p-MeC$_6$H$_4$)$_3$; (▽), AsMe(o-MeC$_6$H$_4$)$_2$; (○), AsPh$_3$; and (□), SbPh$_3$

TABLE 2

Observed rate constants for reaction of the complex [Pt(CO)(PPh$_3$)(I)Me] with AsPh$_3$ in different solvents

T/K	Solvent	[AsPh$_3$]/mol dm^{-3}	10^4k_{obs}/s^{-1}
283·0	Chlorobenzene	0·133	2·3
		0·211	2·5
		0·383	2·7
		0·495	2·7
	Cyclohexanone	0·133	1·35
		0·211	1·52
		0·383	1·77
		0·495	1·80
297·5	Chlorobenzene	0·133	10·6
		0·211	12·3
		0·384	13·4
		0·495	14·0
	Cyclohexanone	0·132	6·7
		0·211	8·0
		0·383	9·5
		0·495	9·9

TABLE 3

Calculated values for k_1 for reactions of the complex [Pt(CO)(PPh$_3$)(I)Me] with ligands L′

Solvent	T/K	L′	10^4k_1/s^{-1}
Tetrahydrofuran	287·6	AsPh$_3$	4·5
		As(p-MeC$_6$H$_4$)$_3$	4·1
		AsMe(o-MeC$_6$H$_4$)$_2$	4·3
		SbPh$_3$	4·3
	297·5	AsPh$_3$	15·0
		As(p-MeC$_6$H$_4$)$_3$	14·3
		AsMe(o-MeC$_6$H$_4$)$_2$	15·3
		SbPh$_3$	15·4
	308·0	AsPh$_3$	39·2
		As(p-MeC$_6$H$_4$)$_3$	35·1
		AsMe(o-MeC$_6$H$_4$)$_2$	37·7
		SbPh$_3$	39·7
Chlorobenzene	283·0	AsPh$_3$	3·0
	297·5	AsPh$_3$	15·8
Cyclohexanone	283·0	AsPh$_3$	2·0
	297·5	AsPh$_3$	12·2

values can be used as a measure of the relative magnitudes of k_3, the rate constant for attack on the intermediate by the ligand L′; the order is AsPh$_3$ < AsMe(o-MeC$_6$H$_4$)$_2$ < SbPh$_3$ < As(p-MeC$_6$H$_4$)$_3$. The electronic effect of methyl substituents on the nucleophilicity of the donor atom is shown by the presence at the top of the list of As(p-MeC$_6$H$_4$)$_3$, while the intermediate position for AsMe(o-MeC$_6$H$_4$)$_2$ reflects the balance between favourable electronic and unfavourable steric factors.

(b) *Effect of Increasing the Bulkiness of the Ligand* L.—All three complexes [Pt(CO)L(I)Me] [L = PPh$_3$, PPh$_2$(o-MeC$_6$H$_4$), or PPh(o-MeC$_6$H$_4$)$_2$] react with AsPh$_3$ in thf to give [PtL(AsPh$_3$)I(COMe)]; reactants and products have been fully characterized.[5] At low temperature and high concentration of AsPh$_3$ all the reactions go essentially to completion, but with higher temperature and lower concentration reactions of the complexes [Pt(CO)-{PPh$_2$(o-MeC$_6$H$_4$)}(I)Me] and [Pt(CO){PPh(o-MeC$_6$H$_4$)$_2$}-(I)Me] come to equilibrium. By using fairly high ligand concentrations and discarding data from the later portion of the reactions, it was possible to calculate rate constants based on the assumption that the reactions did go to completion; these are given in Table 4. (Rate constants for approach to equilibrium were also calculated but have not been included since in most cases they differ little from those for completion and are not particularly informative.)

TABLE 4

Observed rate constants (calculated for completion) for reaction of complexes [Pt(CO)L(I)Me] with AsPh$_3$ in tetrahydrofuran

T/K	L	[AsPh$_3$]/mol dm^{-3}	10^4k_{obs}/s^{-1}
297·5	PPh$_2$(o-MeC$_6$H$_4$)	0·184	1·94
		0·211	2·43
		0·384	4·45
		0·500	5·94
	PPh(o-MeC$_6$H$_4$)$_2$	0·133	0·38
		0·211	0·64
		0·384	1·06
		0·494	1·42
307·8	PPh$_2$(o-MeC$_6$H$_4$)	0·184	4·96
		0·211	5·40
		0·384	10·3
		0·495	13·1
318·0	PPh$_2$(o-MeC$_6$H$_4$)	0·184	9·19
		0·211	11·7
		0·495	25·6
	PPh(o-MeC$_6$H$_4$)$_2$	0·133	1·69
		0·211	2·74
		0·384	4·58
		0·495	6·12
325·1	PPh(o-MeC$_6$H$_4$)$_2$	0·133	3·33
		0·211	4·85
		0·384	8·67
		0·495	11·4

Plots of observed rate constant against [AsPh$_3$] for reactions of the complexes containing the more bulky phosphorus ligands show the reactions to be first order in [AsPh$_3$] over the range of concentration which could be used. At first sight this suggests an associative mechanism for the reactions, but since (see earlier) the less-crowded complex [Pt(CO)(PPh$_3$)(I)Me] does not react in this way one would hardly expect the more-crowded ones to do so. The true explanation appears to be that the same mechanism [equations (2) and (3)] applies, but that under the conditions used equation (5) can be simplified to (6), because $k_3[L']$ is much smaller

$$k_{obs} = (k_1k_3/k_2)[L'] \qquad (6)$$

than k_2. The sharp decrease in the value of the ratio $k_3 : k_2$ when the ligand L in [Pt(CO)L(I)Me] is changed from PPh_3 to $PPh_{3-n}(o\text{-}MeC_6H_4)_n$ ($n = 1$ or 2) is presumably due to a drop in k_3 caused by the unfavourable steric interaction between the phosphorus ligand in the intermediate [PtL(I)(COMe)] and the incoming $AsPh_3$ ligand, since there is no reason to expect a rise in the value of k_2. In the circumstances, it is not possible to extract values for k_1 from the data, which give only the combination k_1k_3/k_2, and hence we cannot determine whether introduction of a more bulky ligand L into the complex [Pt(CO)L(I)Me] actually increases the value of k_1.

EXPERIMENTAL

Details of the preparation and characterization of the starting materials and products were given previously.[5] The choice of ligands L in the complexes [Pt(CO)L(I)Me] was limited by the preparative method, which was unsuccessful for other ligands tried, and the range of incoming ligands L′ employed in the kinetic study was restricted by the fact that in many cases the desired reaction was accompanied by competing carbonyl-substitution reactions. The ligands $AsPh_3$ and $SbPh_3$ were recrystallized twice from dichloromethane–ethanol, as was $As(p\text{-}MeC_6H_4)_3$ obtained from $AsCl_3$ and $(p\text{-}MeC_6H_4)MgBr$. The ligand $AsMe(o\text{-}MeC_6H_4)_2$ was prepared from AsI_2Me and $(o\text{-}MeC_6H_4)MgBr$, and purified by distillation under reduced pressure. Solvent-purification procedures were described previously.[6]

The reactions studied were carried out under a nitrogen atmosphere using concentrations of platinum complex in the region of $1{\cdot}5 \times 10^{-2}$ mol dm^{-3}. Rate constants were calculated from the rate of disappearance of the C–O stretching band in the i.r. spectra of the complexes [Pt(CO)-L(I)Me]. In several cases values were checked by measuring the rate of appearance of the corresponding (acetyl) band in the products [PtL(L′)I(COMe)]; the two methods gave results which agreed well with one another. Both types of band obeyed the Lambert–Beer law over the range of concentrations used. Rate constants were reproducible to 3%, while least-mean-squares analysis of data from individual runs showed the error in calculating a particular rate constant to be less than 1%.

We thank the S.R.C. for a maintenance grant (to C. J. W.).

[4/042 *Received*, 10*th January*, 1974]

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[6] R. W. Glyde and R. J. Mawby, *Inorg. Chim. Acta*, 1970, **4**, 331.