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Kinetics of Carbonyl Insertion in a Platinum(II) Complex

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Kinetic data are reported for the reaction $Pt(CO)ClC_2H_5(As(C_6H_5)_3) + As(C_6H_5)_3 \rightarrow Pt(COC_2H_5)Cl(As(C_6H_5)_3)_2$ and are shown to be compatible with a two-step mechanism. The step which is mainly rate determining involves combination of ethyl and carbonyl ligands to form a propionyl group and is not assisted by either the solvent or the incoming nucleophile. This is in complete contrast to the normal mechanism for substitution reactions of platinum(II) complexes.

Introduction

In a recent paper,[1] we have shown that carbonyl insertion reactions of octahedral iridium(III) complexes of the type

$$Ir(CO)_2Cl_2RL + L \longrightarrow Ir(CO)(COR)Cl_2L_2 \qquad (1)$$

(where R is an alkyl group and L is a neutral ligand with an arsenic donor atom) take place by a two-step mechanism. The first step involves a rate-determining combination of alkyl and carbonyl ligand to give an acyl intermediate, while the second involves attack on this intermediate by the incoming nucleophile.

$$Ir(CO)_2Cl_2RL \overset{\text{slow}}{\rightleftharpoons} Ir(CO)(COR)Cl_2L \xrightarrow[+L]{\text{fast}} Ir(CO)(COR)Cl_2L_2 \qquad (2)$$

This mechanism, which involves a rate-determining rearrangement which is unassisted by either the solvent or the incoming ligand, differs basically from those proposed for carbonyl insertion reactions in other complexes.[2-6]

This paper describes a study of similar reactions involving square-planar platinum(II) complexes. The reactions chosen for study were those of complexes $Pt(CO)ClC_2H_5L$ (where L is a neutral ligand), whose existence was implied by Lodewijk and Wright[7] in a paper describing the preparation and reactions of the complex $[Pt(CO)ClC_2H_5]_2$. The reason for the choice of platinum(II) was that substitution reactions of complexes of this metal ion inevitably involve participation in the rate-determining step by either the incoming ligand or the solvent.[8] We wished to see whether carbonyl insertion reactions on platinum(II) would follow this pattern or follow the pattern set by carbonyl insertion reactions on iridium(III).

Experimental Section

All reactions, including the kinetic studies, were carried out under nitrogen.

Solvents and Ligands.—Purification of many of the solvents used, and of triphenylarsine, was described in a previous paper.[1] Diethyl ketone was dried over Na_2SO_4 and fractionally distilled. This process was then repeated, and the solvent was stored over Na_2SO_4. Nitrobenzene (Analar grade) was dried over P_2O_5 and fractionally distilled at reduced pressure. The process was repeated and the solvent was stored over P_2O_5. All solvents used for kinetic studies were distilled again shortly before use.

Complexes.—$[Pt(CO)ClC_2H_5]_2$ was prepared by the method described by Lodewijk and Wright.[7]

$Pt(CO)ClC_2H_5(As(C_6H_5)_3)$.—A solution of $As(C_6H_5)_3$ (0.2 g) in petroleum ether (bp 40–60°, 30 ml) was added slowly to $[Pt(CO)ClC_2H_5]_2$ (0.2 g) in petroleum ether (20 ml), giving a mass of crystals. This was separated from the solution, dissolved in the minimum of benzene at 50°, filtered, and treated with petroleum ether (bp 100–120°). The resulting solution was slowly concentrated under reduced pressure, giving yellow crystals which were recrystallized from CH_2Cl_2–petroleum ether (bp 100–120°); yield 90%. *Anal.* Calcd for $C_{21}H_{20}OClAsPt$: C, 42.4; H, 3.4. Found: C, 42.4; H, 3.5. Nmr spectrum in $CDCl_3$ solution: τ 2.6 ($As(C_6\mathit{H}_5)_3$, complex), 7.66 ($Pt\mathit{CH}_2CH_3$, quartet), 8.53 ($PtCH_2\mathit{CH}_3$, triplet). Side bands due to coupling with ^{195}Pt gave J_{Pt-CH_2} as 74 Hz. Ir spectrum in CH_2Cl_2 solution: terminal C–O stretching frequency, 2075 cm^{-1}.

$Pt(COC_2H_5)Cl(As(C_6H_5)_3)_2$.—The complex $Pt(CO)ClC_2H_5(As(C_6H_5)_3)$ (0.2 g) and $As(C_6H_5)_3$ (0.6 g) were dissolved in CH_2Cl_2 (20 ml). After 48 hr at room temperature, petroleum ether (bp 100–120°) was added. Slow evaporation of the solvent under nitrogen gave yellow crystals of the product, which were well washed with petroleum ether (bp 40–60°) and recrystallized from CH_2Cl_2–petroleum ether (bp 100–120°); yield 90%. *Anal.* Calcd for $C_{39}H_{35}OClAs_2Pt$: C, 52.0; H, 3.9. Found: C, 51.9; H, 3.9. Nmr spectrum in $CDCl_3$ solution: τ 2.5 ($As(C_6\mathit{H}_5)_3$, complex), 8.35 ($PtCO\mathit{CH}_2CH_3$, quartet), 10.9 ($PtCOCH_2\mathit{CH}_3$, triplet). No coupling was observed between ^{195}Pt and the protons of the acyl group. Ir spectrum in CH_2Cl_2 solution: acyl C–O stretching frequency, 1655 cm^{-1}.

Kinetic Studies.—The methods used were those described in a previous paper.[1] Reactions were followed by infrared spectroscopy, rate constants being calculated from the rate of disappearance of the C–O stretching band in $Pt(CO)ClC_2H_5(As(C_6H_5)_3)$ and checked using the rate of appearance of the corresponding band in the product $Pt(COC_2H_5)Cl(As(C_6H_5)_3)_2$. The bands used obeyed the Lambert–Beer law over the range of concentrations used. Rate constants were reproducible to 5%, while least-mean-squares analysis of the data from individual runs showed the error in calculating a particular rate constant to be less than 1%. Errors in activation parameters were estimated to be ±2 kcal mol^{-1} for $\Delta H^{\ddagger}$ and ±6 eu for $\Delta S^{\ddagger}$.

Results

The reaction of $Pt(CO)ClC_2H_5(As(C_6H_5)_3)$ with $As(C_6H_5)_3$ proceeded quantitatively in accordance with eq 3, where $L = L' = As(C_6H_5)_3$. We have, as yet,

$$Pt(CO)ClC_2H_5L + L' \longrightarrow Pt(COC_2H_5)ClLL' \qquad (3)$$

been unable to find any other combination of ligands L

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

[2] F. Calderazzo and F. A. Cotton, *Inorg. Chem.*, **1**, 30 (1962).

[3] R. J. Mawby, F. Basolo, and R. G. Pearson, *J. Amer. Chem. Soc.*, **86**, 3994 (1964).

[4] I. S. Butler, F. Basolo, and R. G. Pearson, *Inorg. Chem.*, **6**, 2074 (1967).

[5] P. J. Craig and M. Green, *J. Chem. Soc. A*, 1978 (1968).

[6] M. Green, R. I. Hancock, and D. C. Wood, *ibid.*, *A*, 2718 (1968).

[7] E. Lodewijk and D. Wright, *ibid.*, *A*, 119 (1968).

[8] G. Faraone, V. Ricevuto, R. Romeo, and M. Trozzi, *Inorg. Chem.*, **9**, 1525 (1970), and references therein.

and L′ which gives the same reaction free of side reactions or other complications.

All kinetic studies were carried out using concentrations of $As(C_6H_5)_3$ at least 10 times greater than that of $Pt(CO)ClC_2H_5(As(C_6H_5)_3)$, which was about 0.0135 *M*. Reactions were uniformly first order with respect to the platinum complex. Observed rate constants for the reaction in tetrahydrofuran and chlorobenzene at various temperatures are listed in Table I, while rate constants in a variety of other solvents at 40° are listed in Table II.

TABLE I

OBSERVED RATE CONSTANTS IN TETRAHYDROFURAN AND CHLOROBENZENE

THF[a]			Chlorobenzene[b]		
Temp, °C	$[As(C_6H_5)_3]$, *M*	10^5k_{obsd}, sec^{-1}	Temp, °C	$[As(C_6H_5)_3]$, *M*	10^5k_{obsd}, sec^{-1}
30.2	0.141	15.5	20.6	0.141	7.7
	0.193	15.7		0.194	7.8
	0.320	16.0		0.318	7.9
	0.444	16.7		0.445	8.0
40.0	0.129	47.6	30.3	0.141	24.6
	0.191	48.3		0.193	24.8
	0.315	48.5		0.318	24.7
	0.438	48.8		0.443	25.1
50.2	0.141	110	40.0	0.129	71.7
	0.194	121		0.190	71.9
	0.319	133		0.315	73.4
	0.443	140		0.438	75.0

[a] Dielectric constant 7.7 at 25°.[1] [b] Dielectric constant 5.6 at 25°.[1]

TABLE II

OBSERVED RATE CONSTANTS IN SEVERAL SOLVENTS AT 40°

Solvent	Dielectric constant	$[As(C_6H_5)_3]$, *M*	10^5k_{obsd}, sec^{-1}
Diethyl ketone	17.0 (20°)[a]	0.140	61.1
		0.193	61.3
		0.318	63.9
		0.443	64.3
Cyclohexanone	18.3 (20°)[b]	0.141	70.7
		0.193	72.9
		0.318	77.9
		0.443	77.3
Nitrobenzene	34.8 (25°)[a]	0.141	113
		0.193	114
		0.318	113
		0.443	114
1,2-Dichloroethane	10.4 (25°)[b]	0.136	140
		0.193	141
		0.318	138
		0.442	138

[a] J. A. Riddick and E. E. Toops, Ed., "Technique of Organic Chemistry," Vol. VII, 2nd ed, Interscience, New York, N. Y., 1955. [b] Reference 1.

Discussion

The results listed in Tables I and II show that the rate of reaction is independent of $As(C_6H_5)_3$ concentration, over the range of concentrations studied, in the solvents 1,2-dichloroethane and nitrobenzene, but varies with ligand concentration to a small extent in the remaining four solvents used. This variation is in some cases so small as to be within the experimental error involved in determining individual rate constants.

By analogy with other carbonyl insertion reactions which have been studied,[1-6] there would appear to be three possible mechanisms for reaction 3. Mechanism A involves a solvent-assisted rearrangement to form the acyl group, followed by rapid displacement of solvent by $As(C_6H_5)_3$. Mechanism B is again a two-step pro-

$$Pt(CO)ClC_2H_5(As(C_6H_5)_3) + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Pt(COC_2H_5)Cl(As(C_6H_5)_3)S \xrightarrow[As(C_6H_5)_3]{k_2} Pt(COC_2H_5)Cl(As(C_6H_5)_3)_2 \quad (A)$$

cess but without any solvent assistance in the first step.

$$Pt(CO)ClC_2H_5(As(C_6H_5)_3) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Pt(COC_2H_5)Cl(As(C_6H_5)_3) \xrightarrow[As(C_6H_5)_3]{k_2} Pt(COC_2H_5)Cl(As(C_6H_5)_3)_2 \quad (B)$$

Mechanism C is a one-step process, involving simultaneous rearrangement to form the acyl group and nucleophilic attack by $As(C_6H_5)_3$.

$$Pt(CO)ClC_2H_5(As(C_6H_5)_3) + As(C_6H_5)_3 \xrightarrow{k_3} Pt(COC_2H_5)Cl(As(C_6H_5)_3)_2 \quad (C)$$

Mechanisms A and B, using the steady-state approximation for the concentration of the intermediate, both lead to the following expression for the dependence of observed rate constant on ligand concentration

$$k_{obsd} = \frac{k_1k_2[L]}{k_{-1} + k_2[L]} \qquad (4)$$

where [L] represents the concentration of $As(C_6H_5)_3$. When $k_2[L]$ is much greater than k_{-1}, eq 4 can be simplified to give

$$k_{obsd} = k_1 \qquad (5)$$

This accords with the independence of ligand concentration shown by the observed rate constants for the reaction in 1,2-dichloroethane and nitrobenzene.

The dependence of the observed rate constant on ligand concentration which is observed in the remaining four solvents could be caused in either of two ways. The first possibility is that, in the range of ligand concentrations which it was feasible to use, $k_2[L]$ is not large enough compared to k_{-1} to make the simplification of eq 4 to eq 5 valid. The second possibility is that the simplification is valid but that a certain proportion of the reaction goes by mechanism C. The observed rate constant would then obey the expression

$$k_{obsd} = k_1 + k_3[L] \qquad (6)$$

Theoretically, it is possible to decide which of these explanations is correct on the basis of the precise nature of the dependence of observed rate constant on ligand concentration. If the first explanation is correct, one should obtain linear plots of $1/k_{obsd}$ against $1/[L]$ (this can be demonstrated by inversion of eq 4), while the second explanation requires linear plots of k_{obsd} against [L].

In practice, the variation in observed rate constant is so small that it is impossible, in most cases, to distinguish between the two possibilities. In the case where the variation is largest, however (in tetrahydrofuran at 50.2°), the reciprocal plot (Figure 1) is a good straight line, while a plot of k_{obsd} against [L] is not. Accordingly, in all cases where the observed rate constant increases with increasing ligand concentration, a value of k_1, the true constant for the rate-determining step, has been obtained by plotting $1/k_{obsd}$ against $1/[L]$ and extrapolating to a $1/[L]$ value of zero. The values of k_1 obtained are listed, together with activation parameters derived from them, in Table III.

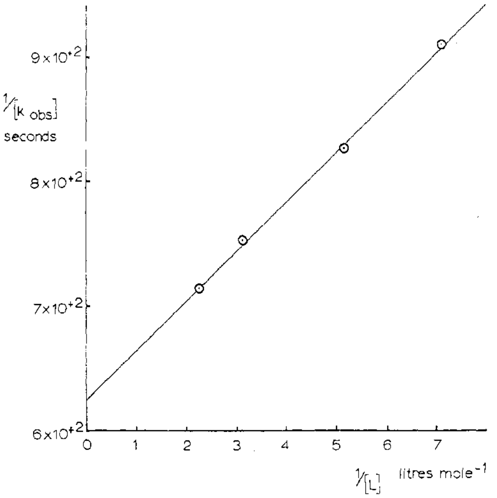

Figure 1.—Plot of $1/k_{obsd}$ *vs.* $1/[L]$ for the reaction in tetrahydrofuran at 50.2°.

Having ruled out any significant contribution by mechanism C to the reaction, a choice must be made between A and B, both of which fit the kinetic data. Mechanism A implies that coordination of the solvent is involved in the rate-determining step, and it would therefore be expected that the value of k_1 would increase markedly with increasing coordinating ability of the solvent. The fact that the value of k_1 actually decreases with increasing coordinating ability of the solvent therefore rules out mechanism A. This conclusion is supported by the small values for the entropy of activation for the reaction (Table III), compared with the large negative values (−20 to −30 eu) typical for carbonyl insertion reactions[3-6] which involve considerable solvent assistance in the rate-determining step.

TABLE III

CALCULATED VALUES OF k_1 AND ACTIVATION PARAMETERS

Solvent	Dielectric constant[a]	Temp, °C	10^5k_1, sec^{-1}
Chlorobenzene	5.6	40.0	75.7
Tetrahydrofuran	7.7	40.0	49.2
1,2-Dichloroethane	10.4	40.0	140
Diethyl ketone	17.0	40.0	66.0
Cyclohexanone	18.3	40.0	82.0
Nitrobenzene	34.8	40.0	114
Chlorobenzene[b]	5.6	20.6	8.1
		30.3	25.1
Tetrahydrofuran[c]	7.7	30.2	16.9
		50.2	160

[a] For details, see Tables I and II. [b] Activation parameters: $\Delta H^{\ddagger} = 19.4$ kcal mol^{-1}, $\Delta S^{\ddagger} = -8.0$ eu. [c] Activation parameters: $\Delta H^{\ddagger} = 21.4$ kcal mol^{-1}, $\Delta S^{\ddagger} = -6.0$ eu.

We conclude that the correct mechanism for reaction 3 is mechanism B, namely, that previously shown to be correct for carbonyl insertion reactions of *octahedral* complexes of the neighboring element, iridium.[1] This conclusion is supported by the similarity in the variation of k_1 with solvent and in activation parameters, between the two systems. Such a mechanism is in sharp contrast to the mechanisms of all substitution reactions of platinum(II) complexes which have been investigated.[8]

The fact that there is no involvement of either the entering ligand or the solvent in the rate-determining step of reaction 3 is remarkable in view of the presence of vacant coordination sites on the platinum throughout the reaction. Any suggestion that there is rapid and complete association of $As(C_6H_5)_3$ to the starting material prior to the rate-determining step is ruled out by the absence of any immediate change in infrared, visible, or nmr spectra of solutions of $Pt(CO)ClC_2H_5(As(C_6H_5)_3)$ on adding $As(C_6H_5)_3$.

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