

Carbonyl Insertion Reactions in Iridium(III) Complexes. I. A Kinetic Study

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Received February 18, 1970

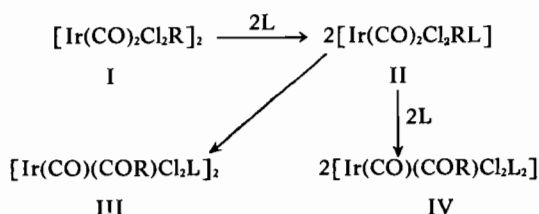
The kinetics of the carbonyl insertion reactions:



are reported for $\text{R} = \text{Me}$, $\text{L} = \text{L}' = \text{AsPh}_3$; $\text{R} = \text{Et}$, $\text{L} = \text{L}' = \text{AsPh}_3$, $\text{R} = \text{Et}$, $\text{L} = \text{L}' = \text{AsMe}_2\text{Ph}$; $\text{R} = \text{Et}$, $\text{L} = \text{AsMe}_2\text{Ph}$, $\text{L}' = \text{AsPh}_3$. The reactions are first order in iridium complex and independent of the nature and concentration of the ligand. Activation parameters and solvent effects suggest a substantially different mechanism from that postulated for other carbonyl insertion reactions.

Introduction

Shaw and Singleton¹ have prepared iridium(III) complexes of the type $[\text{Ir}(\text{CO})_2\text{Cl}_2\text{R}]_2$ ($\text{R} = \text{Me}$, Et , Pr^i , Ph). The complexes I react with Lewis bases (L) to give compounds $[\text{Ir}(\text{CO})_2\text{Cl}_2\text{RL}]$, $[\text{Ir}(\text{CO})(\text{COR})\text{Cl}_2\text{L}]_2$ or $[\text{Ir}(\text{CO})(\text{COR})\text{Cl}_2\text{L}_2]$, depending on the nature and concentration of the ligand L .¹ We have found that these three types of product are formed via the routes shown below.



We have isolated complexes of type II from the reactions of I ($\text{R} = \text{Et}$) with the ligands $\text{L} = \text{P}(\text{OPh})_3$, AsPh_3 and AsMe_2Ph . These complexes dimerize in solution to give the acyl complexes III, and react with excess ligand L to give complexes of type IV. The reactions $\text{II} \rightarrow \text{III}$ and $\text{II} \rightarrow \text{IV}$ proceed very rapidly at room temperature for complexes where L is a ligand with a phosphorus donor atom, but with arsenic ligands the reactions are slower, and are amenable to kinetic study by static methods.

We report here the results of a kinetic study on the carbonyl insertion reactions $\text{II} \rightarrow \text{IV}$, where $\text{R} = \text{Me}$, Et , and with the ligands AsPh_3 and AsMe_2Ph .

Experimental Section

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

Solvents. Chlorobenzene was purified by the method of McAlpine and Smyth.² Cyclohexanone was dried over anhydrous sodium sulphate and fractionally distilled twice. 1,2-Dichloroethane was washed with dilute sodium hydroxide solution, then with water, dried over calcium chloride and fractionally distilled. All three solvents were distilled shortly before use for kinetic studies. Tetrahydrofuran was dried over sodium, and kept over sodium and benzophenone, from which it was distilled before use.

Ligands. AsMe_2Ph was prepared from Me_2AsI and PhMgBr and then distilled under vacuum. For kinetic studies, it was redistilled before use. AsPh_3 , obtained from B.D.H., was recrystallized twice from $\text{CH}_2\text{Cl}_2/\text{EtOH}$.

Preparations of Complexes. $[\text{Ir}(\text{CO})_2\text{Cl}_2\text{Me}]_2$ and $[\text{Ir}(\text{CO})_2\text{Cl}_2\text{Et}]_2$ were prepared as described by Shaw and Singleton.¹ $[\text{Ir}(\text{CO})_2\text{Cl}_2\text{Et}(\text{AsPh}_3)]$. AsPh_3 (0.18 g) in petroleum ether (100–120°C, 10 ml), was added to $[\text{Ir}(\text{CO})_2\text{Cl}_2\text{Et}]_2$ (0.2 g) in CH_2Cl_2 (5 ml).

Evaporation of the solvent gave yellow crystals which were recrystallized from $\text{CH}_2\text{Cl}_2/\text{petroleum ether}$.

$[\text{Ir}(\text{CO})_2\text{Cl}_2\text{Me}(\text{AsPh}_3)]$ and $[\text{Ir}(\text{CO})_2\text{Cl}_2\text{Et}(\text{AsMe}_2\text{Ph})]$ were prepared in the same way.

$[\text{Ir}(\text{CO})(\text{COEt})\text{Cl}_2(\text{AsMe}_2\text{Ph})_2]$. $[\text{Ir}(\text{CO})_2\text{Cl}_2\text{Et}(\text{AsMe}_2\text{Ph})]$ (0.2 g) and AsMe_2Ph (0.7 g) were allowed to react in CH_2Cl_2 (10 ml) at 40°C until the C–O stretching band of the starting material at about 2120 cm^{-1} had disappeared (ca. 4 hr). Yellow crystals were obtained on adding petroleum ether and removing the CH_2Cl_2 by evaporation. These were recrystallized from $\text{CH}_2\text{Cl}_2/\text{petroleum ether}$.

$[\text{Ir}(\text{CO})(\text{COMe})\text{Cl}_2(\text{AsPh}_3)_2]$ and $[\text{Ir}(\text{CO})(\text{COEt})\text{Cl}_2(\text{AsPh}_3)_2]$ were prepared similarly, but longer reaction times were needed.

$[\text{Ir}(\text{CO})(\text{COEt})\text{Cl}_2(\text{AsMe}_2\text{Ph})(\text{AsPh}_3)]$ was prepared in the same way from $[\text{Ir}(\text{CO})_2\text{Cl}_2\text{Et}(\text{AsMe}_2\text{Ph})]$ and AsPh_3 .

$[\text{Ir}(\text{CO})_2\text{Cl}_2\text{Et}(\text{P}^i\text{OPh}_3)]$. P^iOPh_3 (0.18 g) in petroleum ether (10 ml) was treated, at -60°C , with

(1) B. L. Shaw and E. Singleton, *J. Chem. Soc. (A)*, 1683 (1967).

(2) K. B. McAlpine and C. P. Smyth, *J. Chem. Phys.*, 3, 55 (1935).

Table I. Analytical Data and I.R. Carbonyl Stretching Frequencies

	M.P. (°C)	Analysis				$\nu(\text{CO})$ terminal cm^{-1}	$\nu(\text{CO})$ acyl cm^{-1}
		Found		Calcd.			
		%C	%H	%C	%H		
$[\text{Ir}(\text{CO})_2\text{Cl}_2\text{EtAsPh}_3]$	135-7	40.2	3.0	40.3	3.0	2122, 2070	—
$[\text{Ir}(\text{CO})_2\text{Cl}_2\text{EtAsMe}_2\text{Ph}]$	180-2	26.8	3.0	27.2	3.0	2118, 2067	—
$[\text{Ir}(\text{CO})_2\text{Cl}_2\text{EtP}(\text{OPh})_3]$	165-7	—	—	40.1	3.1	2127, 2085	—
$[\text{Ir}(\text{CO})_2\text{Cl}_2\text{MeAsPh}_3]$	265-7	40.7	3.0	39.4	2.8	2120, 2070	—
$[\text{Ir}(\text{CO})(\text{COEt})\text{Cl}_2(\text{AsPh}_3)_2]$	238-40	49.6	3.7	50.0	3.7	2055	1646
$[\text{Ir}(\text{CO})(\text{COEt})\text{Cl}_2(\text{AsMe}_2\text{Ph})_2]$	111-4	33.6	3.7	33.7	3.8	2052	1645
$[\text{Ir}(\text{CO})(\text{COEt})\text{Cl}_2\text{AsMe}_2\text{Ph} \cdot \text{AsPh}_3]$	178-80	43.1	3.7	43.0	3.7	2056	1643
$[\text{Ir}(\text{CO})(\text{COMe})\text{Cl}_2(\text{AsPh}_3)_2]$	281-3	49.4	3.5	49.5	3.5	2062	1635

$[\text{Ir}(\text{CO})_2\text{Cl}_2\text{Et}]_2$ (0.2 g) in CH_2Cl_2 (0.5 ml). The product was precipitated immediately in crystalline form. Rapid dimerization of the complex in solution (II \rightarrow III in the scheme above) prevented purification, and hence the analytical data were poor. The formulation of the complex as $[\text{Ir}(\text{CO})_2\text{Cl}_2\text{Et}(\text{P}\{\text{OPh}\}_3)]$ is supported by its infra-red spectrum (Table I), which is similar to those of complexes known to be of the type $[\text{Ir}(\text{CO})_2\text{Cl}_2\text{EtL}]$.

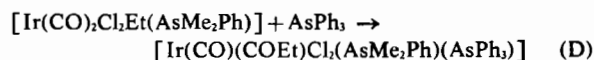
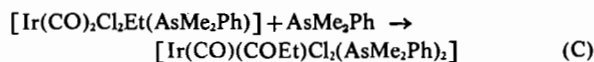
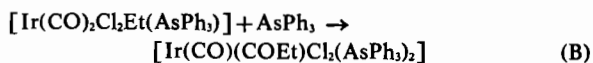
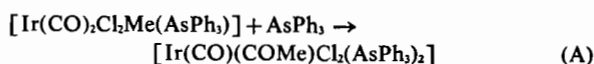
Analytical data and carbonyl stretching frequencies for the complexes are listed in Table I.

Kinetic Studies. In a typical experiment, the complex $[\text{Ir}(\text{CO})_2\text{Cl}_2\text{RL}]$, dissolved in the minimum volume of solvent, was added to a thermostatted solution of the ligand in the reaction flask. Samples were removed by syringe through a rubber serum cap, and transferred to a KBr infra-red cell (0.2 mm). The reaction was monitored by following the rate of disappearance of the high frequency carbonyl band (ca. 2120 cm^{-1}) of $[\text{Ir}(\text{CO})_2\text{Cl}_2\text{RL}]$, using a Perkin-Elmer 257 infra-red spectrophotometer. All the complexes obeyed the Lambert-Beer law in this region. All reactions went to completion and yielded good linear plots of $\log_{10}(A_t - A_\infty)$ versus time, where A_t is the absorbance at time t , for at least two and a half half-lives. Initial complex concentrations were ca. 0.01 M; ligand concentrations were at least ten times greater.

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%. In several cases the reaction was also monitored by measuring the rate of appearance of the acyl C—O stretching band (ca. 1640 cm^{-1}) of the product. Rate constants obtained by the two methods were in reasonable agreement with one another. Errors in activation parameters were estimated to be $\pm 1 \text{ Kcal.mole}^{-1}$ for ΔH^* and $\pm 2 \text{ e.u.}$ for ΔS^* .

Results

The reactions studied will be referred to as (A), (B), (C), and (D), as shown below.



The reaction of $[\text{Ir}(\text{CO})_2\text{Cl}_2\text{Et}(\text{AsPh}_3)]$ with AsMe_2Ph was also studied, but merely resulted in rapid ligand interchange to give $[\text{Ir}(\text{CO})_2\text{Cl}_2\text{Et}(\text{AsMe}_2\text{Ph})]$, followed by reactions (C) and (D).

All four reactions were found to be first order in iridium complex. The observed first order rate constants in chlorobenzene at 40°C are listed in Table II. The lack of dependence of reaction rate on ligand concentration shown by the data in Table II is general for all the conditions used, and to save space a rate constant for a single ligand concentration is given in subsequent tables. Rate constants for other concentrations may be taken to be, within experimental error, identical to the value quoted.

The data in Table II also demonstrates that the reaction rate is independent of the nature of the entering ligand, since reactions (C) and (D) proceed at the same rate. This was also found to be true in other solvents: in tetrahydrofuran at 40°C the rate constant for reaction (C) was $24.0 \times 10^{-5} \text{ sec}^{-1}$, while that for (D) was $23.8 \times 10^{-5} \text{ sec}^{-1}$. The dependence of reaction rate on the solvent used is illustrated by the data given for reaction (B) in Table III. The reaction product was the same in all solvents used, and in no case was there any secondary reaction with the solvent.

Typical data used to calculate activation parameters are listed in Table IV, although in each case a number of runs (of which only one is listed) were made with varying ligand concentrations, and an average rate constant was used to calculate the activation parameters. The activation parameters for reactions (A), (B), and (D) are listed in Table V.

Discussion

Kinetic studies on so-called «insertion» reactions, which involve the combination of a carbonyl group and an alkyl group (both bound to a transition metal) to give an acyl group, have been reported for complexes such as $\text{Mn}(\text{CO})_5\text{Me}$,^{3,4,5} $\pi\text{-C}_3\text{H}_5\text{Fe}(\text{CO})_2\text{Me}$,⁶

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

(4) F. Calderazzo and F. A. Cotton, *Inorg. Chem.*, **1**, 30 (1962).

Table II. Rate Constants for Reactions (A), (B), (C) and (D) in Chlorobenzene at 40°C

Reaction	Complex	Ligand	Ligand Concentration (M)	10 ⁵ k _{obs} (sec ⁻¹)
A	[Ir(CO) ₂ Cl ₂ Me(AsPh ₃)]	AsPh ₃	0.122	1.7
			0.222	1.6
B	[Ir(CO) ₂ Cl ₂ Et(AsPh ₃)]	AsPh ₃	0.122	10.6
			0.248	11.0
			0.371	11.0
			0.489	10.9
			0.119	36.9
C	[Ir(CO) ₂ Cl ₂ Et(AsMe ₂ Ph)]	AsMe ₂ Ph	0.230	37.2
			0.393	37.8
			0.484	37.7
			0.122	37.9
D	[Ir(CO) ₂ Cl ₂ Et(AsMe ₂ Ph)]	AsPh ₃	0.248	37.9
			0.371	38.7
			0.491	38.8
			0.122	37.9

Table III. Rate Constants for Reaction (B) in Various Solvents at 40°C

Solvent	Dielectric Constant	AsPh ₃ Concentration (M)	10 ⁵ k _{obs} (sec ⁻¹)
Chlorobenzene	5.6 (25°C) ^a	0.248	11.0
Cyclohexanone	18.3 (20°C) ^a	0.246	4.2
1,2-Dichloroethane	10.4 (25°C) ^a	0.245	15.0
Tetrahydrofuran	7.7 (25°C) ^b	0.248	5.8

^a «Technique of Organic Chemistry», Interscience, New York, 1955, Vol. VII. ^b Reference 3.

Table IV. Rate Constants for Reactions (A), (B), and (D) at Various Temperatures^a

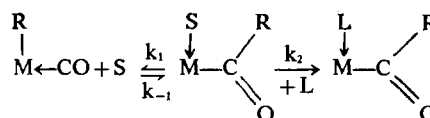
Reaction	Solvent	Temperature (C°)	10 ⁵ k _{obs} (sec ⁻¹)
A	Chlorobenzene	40.0	1.6
		49.8	5.1
		60.2	16.0
		70.0	44.8
B	Chlorobenzene	40.0	11.0
		49.9	34.0
		59.6	96.0
	Tetrahydrofuran	30.0	1.4
		40.0	5.8
		50.0	18.8
D	Chlorobenzene	30.3	12.1
		40.0	37.9
		49.8	110.0
	Tetrahydrofuran	30.2	6.9
		40.0	24.4
		49.2	64.5

^a Ligand concentration 0.248 M except for the first reaction listed (0.222 M).

Table V. Activation Parameters for Reactions (A), (B) and (D)

Reaction	Solvent	ΔH* (kcal.mole ⁻¹)	ΔS* (e.u.)
A	Chlorobenzene	23.0	-6.7
	Tetrahydrofuran	25.0	+1.8
B	Chlorobenzene	22.5	-5.0
	Tetrahydrofuran	25.0	+1.8
D	Chlorobenzene	21.4	-5.9
	Tetrahydrofuran	22.7	-4.7

and π-C₅H₅Mo(CO)₃R.^{6,7,8} The data obtained, particularly the large negative entropies of activation and the marked effect of solvent on reaction rate, have led to the proposal that most of these reactions proceed by the solvent-assisted mechanism shown below, where S represents the solvent.



Two pieces of evidence show that this mechanism cannot be correct for the iridium(III) complexes. Firstly, Table III shows that changes in solvent over a fairly wide range of dielectric constants have very little effect on reaction rate: control experiments on Mn(CO)₅Me in the same solvents produced a much greater variation in reaction rate. The data in Table III suggest that the reaction proceeds more slowly in coordinating solvents than in non-coordinating solvents, which is the reverse of the trend expected for a solvent-assisted mechanism.

Secondly, Table V shows that the values for the entropy of activation are small, compared with values of -20 to -30 e.u. found for systems where a solvent-assisted mechanism has been proposed. This also suggests that the solvent plays no major part in the reaction.

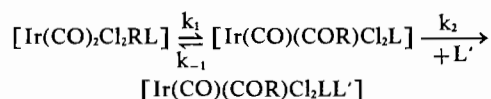
(5) M. Green, R. I. Hancock and D. C. Wood, *J. Chem. Soc. (A)*, 2718 (1968).

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

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

(8) P. J. Craig and M. Green, *J. Chem. Soc. (A)*, 157 (1969).

A mechanism, consistent with these facts and with the lack of dependence of reaction rate on ligand concentration, is shown below.

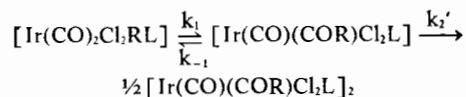


where $k_2 \gg k_{-1} \gg k_1$ under the conditions used. The rate determining step involves the combination of alkyl ligand and carbonyl ligand to give an acyl ligand, producing an intermediate, $[\text{Ir}(\text{CO})(\text{COR})\text{Cl}_2\text{L}]$, of coordination number five. The rearrangement to form the acyl group is *not* solvent-assisted, although it is possible that solvent could be loosely coordinated to the intermediate once it is formed.

The noticeable difference in rate between the reactions of $[\text{Ir}(\text{CO})_2\text{Cl}_2\text{Me}(\text{AsPh}_3)]$ and $[\text{Ir}(\text{CO})_2\text{Cl}_2\text{Et}(\text{AsPh}_3)]$ probably results from a decrease in the Ir-alkyl bond strength. Craig and Green⁷ have reported a similar effect for the corresponding complexes $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{R}$. In agreement with this, there is

a drop in ΔH^* when the two reactions are compared in chlorobenzene, although the difference between the two values is probably too small to be trusted.

In conclusion, it is interesting to note that this « unassisted » rearrangement to form the five-coordinate acyl intermediate is probably also the first step in the dimerization reaction:



Attempts to obtain kinetic data to confirm this point were unfortunately frustrated by the insolubility of the products.

Acknowledgments. We are most grateful to Esso Petroleum Co. for a grant to R.W.G., and to Johnson, Matthey and Co. for a loan of iridium compounds. We would also like to thank Dr. B. L. Shaw for information, prior to publication, on the preparation of the iridium(III) alkyl complexes.