Kinetics and Mechanism of the Formation and Isomerization of some Propionyl Complexes of Iridium(III)

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Reactions of the complex $[Ir(CO)_2Cl_2Et]_2$ with phosphorus ligands [L = PMe_2Ph, $PMePh_2$, $P(OMe)_3$, $P(OMe)_2Ph$, and $P(OMe)Ph_2$] yield complexes $[Ir(CO)L_2Cl_2(COEt)]$ which subsequently rearrange in solution to a more stable isomeric form. The rearrangement is inhibited by the presence of free ligand L and kinetic data support a mechanism in which a five-co-ordinate intermediate (formed by loss of L from the less stable isomer) rearranges to a second intermediate. The latter then recombines with L to produce the more stable isomer. The reason for the exclusive formation of the less stable isomer of $[Ir(CO)L_2Cl_2(COEt)]$ from $[Ir(CO)_2Cl_2Et]_2$ is discussed in the context of the findings for the rearrangement reaction and a mechanism is proposed which is based on the large *trans*-effect of the propionyl ligand.

REACTIONS of the complex $[Ir(CO)_2Cl_2Et]_2$ with ligands L containing arsenic donor atoms, using a 1 : 4 molar ratio of the reactants, yield propionyl complexes of the type $[Ir(CO)L_2Cl_2(COEt)]$. Kinetic studies [1] indicate the following reaction sequence:

$$[Ir(CO)_2Cl_2Et]_2 + 2L \xrightarrow{\text{fast}} 2[Ir(CO)_2LCl_2Et]$$

$$[Ir(CO)_2LCl_2Et] \xrightarrow{\text{slow}} [Ir(CO)LCl_2(COEt)] \xrightarrow[+L]{\text{fast}} [Ir(CO)L_2Cl_2(COEt)] \quad (1)$$

An important feature of these reactions is that subsequent rearrangement of the products, $[Ir(CO)L_2Cl_2(COEt)]$ [isomer (A)], to a different isomer [(B)] is observed.[2] This paper discusses the stereochemistry and mechanism of the rearrangement and the light which they throw on the reasons for the formation of isomer (A), rather than the more stable isomer (B), in sequence (1).

For complexes with arsenic ligands L, other than $AsMe_2Ph$, study of the isomerization is complicated by the fact that the rate constants for isomerization of the complexes are similar in magnitude to those for their formation. In order to avoid this difficulty, we studied the reactions of the analogous complexes with ligands L containing phosphorus donor atoms. We found that $[Ir(CO)_2Cl_2Et]_2$ reacts rapidly with the ligands [L = PMe_2Ph, $PMePh_2$, $P(OMe)_3$, $P(OMe)_2Ph$, and $P(OMe)Ph_2$] to yield complexes $[Ir(CO)L_2Cl_2(COEt)]$ in one isomeric form [(A)], and that in all cases these then rearrange at a slower rate to another form [(B)]. [The reaction with PMe_2Ph has been reported by Shaw and Singleton [3] who did not observe the rearrangement, which presumably occurred during the isolation of the product since the compound they characterized was, in our terminology, the (B) isomer.]

RESULTS AND DISCUSSION

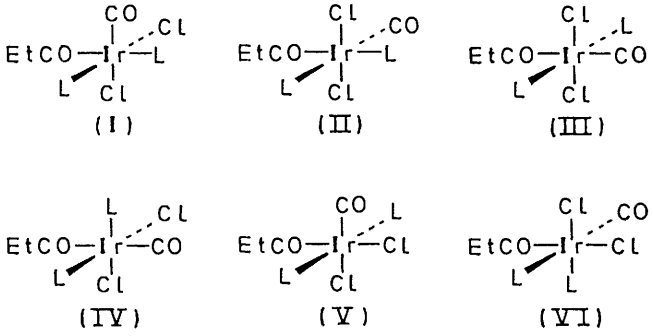
Stereochemistry of the (A) Isomers of $[Ir(CO)L_2Cl_2(COEt)]$.—Assuming that the arrangement of ligands around the iridium atom in these complexes is basically octahedral, six different structures are possible (ex-

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

[2] R. W. Glyde and R. J. Mawby, *Inorg. Chim. Acta*, 1971, **5**, 317.

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

cluding the possibilities for optical isomerism). For reasons described earlier,[2] structure (I) can be assigned



to the (A) isomers of the complexes with arsenic ligands, with the incoming ligand in the last step of sequence (1) *trans* to the propionyl group, and the n.m.r. spectra (Table 1) of the (A) isomers of the complexes with phosphorus ligands indicate that they have the same structure. Thus (i) the number of resonances for the methyl protons in the ligands L indicates that in every case the two molecules of L are in different environments. [The observation of a single resonance for the methyl groups in the $P(OMe)_3$ ligands of the (A) isomer of $[Ir(CO)\{P(OMe)_3\}_2Cl_2(COEt)]$ is due to an accidental superimposition of resonances (see below).] (ii) The spectra of the (A) isomers with L = PMe_2Ph and $P(OMe)_2Ph$ exhibit separate resonances for the individual

TABLE 1

N.m.r. data [a] for the (A) and (B) isomers of $[Ir(CO)L_2Cl_2(COEt)]$ complexes

		δ/p.p.m.		
L	Isomer	CH_2CH_3	CH_2CH_3	CH_3 in L
PMe_2Ph	(A)	3·25(q)	0·90(t)	1·80(d), 1·79(d), 1·55(d), 1·49(d)
$PMePh_2$	(A)	3·05(q)	0·55(t)	2·15(d), 1·73(d)
$P(OMe)_3$	(A)	3·32(q)	0·94(t)	3·85(d)
$P(OMe)_2Ph$	(A)	3·12(q)	0·81(t)	3·82(d), 3·72(d),[b] 3·61(d)
$P(OMe)Ph_2$	(A)	*ca.* 3·4 [c]	0·80(t)	3·40(d), 3·33(d)
PMe_2Ph	(B)	1·81(q)	0·13(t)	2·11(t), 2·03(t)
$PMePh_2$	(B)	1·10(q)	−0·18(t)	2·50(t)
$P(OMe)_3$	(B)	2·83(q)	0·83(t)	3·92(t)
$P(OMe)_2Ph$	(B)	2·20(q)	0·20(t)	3·99(t), 3·89(t)
$P(OMe)Ph_2$	(B)	2·05(q)	0·18(t)	3·70(t)
$AsMe_2Ph$	(B)	*ca.* 2·0 [c]	0·13(t)	1·99(s), 1·93(s)
$AsMePh_2$	(B)	1·52(q)	−0·08(t)	2·30(s)

[a] Excluding resonances due to phenyl protons. Integrations were correct in all cases. s = Singlet, d = doublet, t = triplet, q = quartet. Chemical shifts are accurate to within δ ±0·02. All spectra were recorded on $CDCl_3$ solutions of the complexes, using TMS as an internal standard. Spectra of the (A) isomers of complexes with arsenic ligands are given in ref. 2. [b] The accidental superimposition of two doublets at δ 3·72 p.p.m. is lost at higher temperatures as a result of slight chemical-shift changes. [c] Resonance partly obscured by ligand methyl proton resonances.

methyl groups in each of the two phosphorus ligands, indicating that neither Ir–L bond lies in a plane of symmetry through the $[Ir(CO)L_2Cl_2(COEt)]$ molecule. (iii) The spectra indicate that one of the two Ir–L bonds is extremely labile [as would be expected for structure (I) in view of the powerful *trans*-effect of the propionyl ligand [4]]. For example, the two methyl resonances due to one of the $P(OMe)_2Ph$ ligands in the (A) isomer of $[Ir(CO)\{P(OMe)_2Ph\}_2Cl_2(COEt)]$ broaden markedly between 306 and 348 K, whereas the resonances due to the other ligand remain sharp, implying that one of the two ligands is exchanging rapidly between the free and co-ordinated states while the other is not. When the n.m.r. spectrum of the (A) isomer of $[Ir(CO)\{P(OMe)Ph_2\}_2Cl_2(COEt)]$ is run in the presence of free $P(OMe)Ph_2$ ligand, the methyl resonances of the free ligand and *one* of the co-ordinated ligands broaden with rising temperature, while the resonance due to the other co-ordinated ligand remains sharp. Similar effects are observed when the spectra of the (A) isomers of the other complexes are recorded in the presence of free ligand, and in each case the implication is that one of the co-ordinated ligands is exchanging rapidly with the free ligand.* (At 298 K the spectrum of the (A) isomer of $[Ir(CO)\{P(OMe)_3\}_2Cl_2(COEt)]$ in the presence of free $P(OMe)_3$ consists of two sharp doublets due to free and co-ordinated ligand respectively. At 340 K the resonance due to the free ligand has collapsed, while a reasonably sharp doublet of reduced area remains in the co-ordinated ligand position, confirming that the resonance in this position in the low-temperature spectrum is an accidental superimposition of the resonances due to the labile and non-labile co-ordinated ligands.)

All the changes in spectra are reversed on cooling. It was not possible to demonstrate the coalescence of free and co-ordinated ligand resonances since, at the required temperatures, rearrangement to the (B) isomers is rapid.

Stereochemistry of the (B) *Isomers of* $[Ir(CO)L_2Cl_2(COEt)]$.—The n.m.r. spectra of these complexes (Table 1) indicate that the two ligands L occupy equivalent positions, but that the Ir–L bonds do not lie in a plane of symmetry through the $[Ir(CO)L_2Cl_2(COEt)]$ molecule. In addition, the observation (for complexes with phosphorus ligands) of ' virtual coupling ' between the two ligands L indicates that they are mutually '*trans*'.[5] Only structure (V) fulfils all these requirements. In contrast to the situation for the (A) isomers, there is no indication that the ligands L in the (B) isomers undergo rapid exchange between the co-ordinated and free states.

Kinetics and Mechanism of the Rearrangement.—The mechanism for the rearrangement could be either intra- or inter-molecular. In view of the known lability (see earlier) of the Ir–L bond *trans* to the propionyl group in the (A) isomer, a likely first step in an intermolecular rearrangement would be the breaking of this bond. The intermediate resulting from this step could then react

* Details of this work have been omitted but may be obtained from the authors.

[4] A. J. Deeming and B. L. Shaw, *J. Chem. Soc.* (*A*), 1969, 1128.
[5] J. M. Jenkins and B. L. Shaw, *Proc. Chem. Soc.*, 1963, 279.

with L to give the (B) isomer directly [equation (2)]

$$(A) \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{intermediate} + L \xrightarrow{k_3} (B) \qquad (2)$$

or could rearrange (presumably intramolecularly) to a second intermediate, which then reacts with L to give the (B) isomer as in (3).

$$(A) \underset{k_4}{\overset{k_3}{\rightleftharpoons}} \text{first intermediate} + L \underset{k_7}{\overset{k_6}{\rightleftharpoons}} \text{second intermediate} + L \xrightarrow{k_8} (B) \qquad (3)$$

Using a steady-state treatment, (2) leads to the rate expression (4)

$$-\frac{d[(A)]}{dt} = \frac{k_1 k_3 [(A)]}{k_2 + k_3} \qquad (4)$$

while (3) gives:

$$-\frac{d[(A)]}{dt} = \frac{k_4 k_6 k_8 [(A)]}{k_5 k_7 + k_6 k_8 + k_5 k_8 [L]} \qquad (5)$$

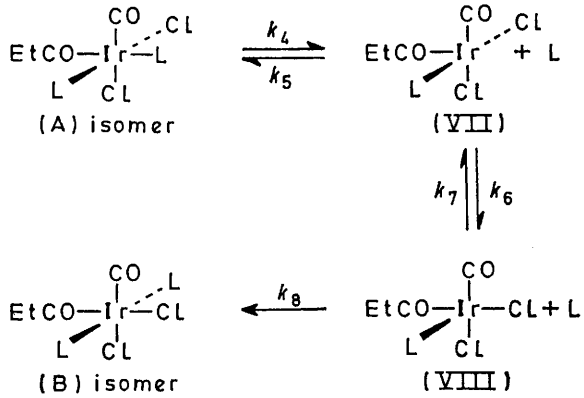
Rate constants for rearrangement of (A) isomers in the presence of varying concentrations of free ligand L are given in Table 2 and show that the rearrangement is inhibited by L, thus ruling out an intramolecular mechanism and intermolecular mechanism (2). Mechanism (3), however, is seen to be compatible with this finding. Expression (5) leads to equation (6) for the

$$k_{obs} = \frac{k_4 k_6 k_8}{k_5 k_7 + k_6 k_8 + k_5 k_8 [L]} \qquad (6)$$

observed rate constant which on inversion yields:

$$\frac{1}{k_{obs}} = \text{constant} + \frac{k_5}{k_4 k_6} [L] \qquad (7)$$

Plots of $1/k_{obs}$ against [L] are indeed linear, as equation (7) requires, to within the limits of accuracy imposed by the uncertainty in the values for the observed rate constants. Our results are therefore consistent with mechanism (3). The stereochemistry of the rearrangement, based on the assumption of an approximately square-pyramidal shape for the intermediates (although there are, of course, other possible stereochemistries), is shown below.



Relevance of the Isomerization Mechanism to the Mechanism of Formation of the (A) Isomers.—The first step in the isomerization is the formation of the first intermediate (VII) from the (A) isomer. This is the exact reverse of the *last* step in the formation of the (A) isomer in the reaction sequence (1). That the (A) isomer is obtained stereospecifically in the formation reaction implies one of two things: either (i) that the mechanism of formation from $[Ir(CO)_2LCl_2Et]$ leads specifically to (VII) and this reacts with the ligand L to give the (A) isomer before it can rearrange to the (perhaps more stable) second intermediate (VIII); or (ii) that the mechanism of formation does not give (VII) specifically but leads to an equilibrium mixture of (VII) and (VIII). On this basis, the exclusive formation of the (A) isomer must be attributed to the greater stability (and hence much higher concentration) of intermediate (VII) in which the vacant co-ordination site is *trans* to the most

TABLE 2

Observed rate constants for rearrangement of the $[Ir(CO)L_2Cl_2(COEt)]$ complexes

Solvent	T/K	Complex	Free ligand concentration [a] / mol l^{-1}	$10^4 k_{obs}$ [b] / s^{-1}
$CDCl_3$	306·5	$[Ir(CO)\{PMe_2Ph\}_2Cl_2(COEt)]$		1·76
		$[Ir(CO)\{PMePh_2\}_2Cl_2(COEt)]$		4·09
		$[Ir(CO)\{P(OMe)Ph_2\}_2Cl_2(COEt)]$		1·11
		$[Ir(CO)\{AsMe_2Ph\}_2Cl_2(COEt)]$		0·073
PhCl	306·5	$[Ir(CO)\{PMe_2Ph\}_2Cl_2(COEt)]$		1·90
		$[Ir(CO)\{PMePh_2\}_2Cl_2(COEt)]$		3·10
			0·190	1·16
			0·320	0·88
			0·465	0·65
	313·0	$[Ir(CO)\{P(OMe)Ph_2\}_2Cl_2(COEt)]$		3·08
			0·220	2·10
			0·320	1·82
	343·0	$[Ir(CO)\{P(OMe)_2Ph\}_2Cl_2(COEt)]$		7·60
			0·250	3·52
			0·325	3·12
			0·475	2·53

[a] Initial concentrations of (A) isomer were varied between 0·2 and 0·4 mol l^{-1}; rate constants were found to be independent of the concentration used. [b] Values accurate to within 5% (at worst).

strongly *trans*-directing ligand, the propionyl group. This is a slightly unusual version of the ' kinetic *trans*-effect,' the implication being that the incoming ligand is forced to occupy the site *trans* to the most strongly *trans*-directing ligand already present, even though this leads to an unstable isomer of the product. Although we have no evidence which would allow a choice between these two explanations, we are inclined to believe that the *trans*-effect explanation is the correct one and note that recent results obtained on a slightly different system by Kubota and Blake appear to fit into the same pattern.[6]

EXPERIMENTAL

All preparative and kinetic work was carried out under nitrogen, using pure oxygen-free solvents. Analytical data for the complexes prepared are given in Table 3.

The complexes $[Ir(CO)\{PMe_2Ph\}_2(COEt)Cl_2]$ and $[Ir(CO)\{P(OMe)Ph_2\}_2(COEt)Cl_2]$ were prepared similarly, using slightly longer reaction times.

Complexes with arsenic ligands: Details of the preparation of these complexes have been given previously.[1,2]

Kinetic Studies.—The rearrangement of (A) isomers to (B) isomers is accompanied by marked changes in n.m.r. spectra (Table 1), but the corresponding changes in visible and u.v. spectra, and in i.r. spectra in the C–O stretching region (Table 3) are negligible. Kinetic data were therefore obtained by n.m.r. spectroscopy, relative concentrations of the (A) and (B) isomers being measured at intervals during the reaction by integration of the resonances due to the methyl protons in the propionyl group. Spectra were recorded on a Perkin-Elmer R10 spectrometer fitted with a variable-temperature probe attachment. Initially, reactions were studied in $CDCl_3$ solution, but the observation that some of the phosphorus ligands used react with $CDCl_3$ prompted a change in solvent to chlorobenzene.

TABLE 3

Analytical data and i.r. spectra for the $[Ir(CO)L_2Cl_2(COEt)]$ complexes

			Found (%)			Calc. (%)			ν_{C-O} (terminal)	ν_{O-O} (acyl)
L	Isomer	M.p.(*T*/K)	C	H	Cl	C	H	Cl	cm^{-1}	cm^{-1}
PMe_2Ph	(B)	436—438	38·7	4·35	11·4	38·45	4·35	11·35	2060	1638
$PMePh_2$	(B)	448—450	47·9	4·05	9·6	48·15	4·15	9·45	2067	1640
$P(OMe)_3$	(A)	384—385	20·4	3·8	11·75	20·15	3·9	11·9	2086	1642
$P(OMe)_3$	(B)	408—410	19·85	3·85	12·0	20·15	3·9	11·9	2084	1650
$P(OMe)_2Ph$	(A)	374—376	34·85	3·9	10·15	34·9	3·95	10·3	2086	1647
$P(OMe)_2Ph$	(B)	394—395	35·1	3·85	10·2	34·9	3·95	10·3	2085	1650
$P(OMe)Ph_2$	(B)	325—326	45·85	3·95	9·2	46·15	4·0	9·1	2080	1646

Preparation of $[Ir(CO)L_2Cl_2(COEt)]$ *Complexes.*—$[Ir(CO)\{P(OMe)_2Ph\}_2Cl_2(COEt)]$, *isomer* (*A*). This was obtained from the reaction of the complex $[Ir(CO)_2Cl_2Et]_2$ (0·35 g) [3] with $P(OMe)_2Ph$ (0·34 g) in chloroform at room temperature. Addition of light petroleum (b.p. 373—393 K) and concentration of the solution under a nitrogen stream gave white crystals of the product (yield 65%).

Isomer (*B*). The same reactants were heated in chloroform at 323 K for several hours. The subsequent isolation procedure, which yielded white crystals, was the same as that for isomer (A) (yield 70%).

$[Ir(CO)\{P(OMe)_3\}_2Cl_2(COEt)]$, *isomers* (*A*) *and* (*B*). These were obtained by methods similar to those used for the complexes with $P(OMe)_2Ph$.

$[Ir(CO)\{PMePh_2\}_2Cl_2(COEt)]$, $[Ir(CO)\{PMe_2Ph\}_2Cl_2(COEt)]$, *and* $[Ir(CO)\{P(OMe)Ph_2\}_2Cl_2(COEt)]$, *isomer* (*A*). These were observed in solution by n.m.r. spectroscopy during the reactions between the complex $[Ir(CO)_2Cl_2Et]_2$ and the appropriate phosphorus ligands, using a 1 : 4 molar ratio of the reactants, in $CDCl_3$ solution. None could be isolated in a pure state because of the fairly rapid rearrangement to the (B) isomer.

Isomer (*B*). The complex $[Ir(CO)\{PMePh_2\}_2Cl_2(COEt)]$ was obtained from the reaction of the complex $[Ir(CO)_2Cl_2Et]_2$ (0·35 g) with $PMePh_2$ (0·40 g) in chloroform at 308 K for several hours. The isolation procedure, which produced white crystals, was similar to that for the complexes mentioned above (yield 68%).

The rearrangements were all first order in (A) isomer, good straight lines being obtained for at least two half-lives on plotting $\log_{10}$ [% (A) isomer] against time. The most significant source of uncertainty in the rate constants quoted in Table 2 arises from the integration values which were found to be reproducible to within 5% at worst.

No kinetic data are given for the rearrangement of the complex $[Ir(CO)\{P(OMe)_3\}_2Cl_2(COEt)]$ because the appropriate resonances in the spectra of the (A) and (B) isomers overlap. It was, however, clear that the rate of rearrangement of this complex is slower than that of any of the other complexes with phosphorus ligands at the temperatures used. Accurate data for the rearrangement of the complex $[Ir(CO)\{PMe_2Ph\}_2Cl_2(COEt)]$ could not be obtained in the presence of free PMe_2Ph ligand because of overlap between the resonance due to the methyl protons in the free ligand and that due to the methyl protons of the propionyl group in the (A) isomer. At a semi-quantitative level, it was evident that the rate of rearrangement decreases with increasing concentration of free PMe_2Ph ligand.

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[2/1770 *Received*, 28*th July*, 1972]

[6] M. Kubota and D. M. Blake, *J. Amer. Chem. Soc.*, 1971, **93**, 1368.