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*Contribution from the Department of Chemistry,
The University of York, Heslington, York YO1 5DD, United Kingdom*

Carbonyl Insertion Reactions in Iridium(III) Complexes. II.[1] Mechanism and Stereochemistry

R. W. Glyde and R. J. Mawby

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A study of the stereochemistry of the 'carbonyl insertion' reactions:

$$[IrCl_2Et(CO)_2L]+L'\rightarrow[IrCl_2(COEt)(CO)LL']$$

shows that the rate-determining step involves the combination of ethyl and carbonyl ligands to give a five-coordinate intermediate, probably of square-pyramidal geometry, with the propionyl group in the apical position. The combination is a symmetrical process for which the two terms 'carbonyl insertion' and 'alkyl migration' are equally misleading.

Subsequent attack by the incoming ligand L' occurs at the vacant octahedral coordination site trans *to the propionyl group. That the stereochemistry of the products is a direct result of the mechanism of the reactions is shown by the subsequent rearrangement of the products to a more thermodynamically stable isomer.*

Introduction

Iridium(III) complexes $[IrCl_2R(CO)_2L]$, where R is an alkyl group and L is a ligand with an arsenic donor atom, undergo 'carbonyl insertion' reactions with similar ligands L′ to give products $[IrCl_2(COR)(CO)LL']$.[1] The reaction rate, for a given complex and temperature, is independent of the nature and concentration of the entering ligand L′, and varies little from solvent to solvent. There is in fact a slight decrease in rate with increasing coordinating ability of the solvent. The entropies of activation for these reactions are small, ranging from +2 to –7 e.u.

This clearly rules out a solvent-assisted alkyl migration mechanism of the type which has been proposed for other 'carbonyl insertion' reactions where there is marked sensitivity of the reaction rate to the solvent used, and entropies of activation are large and negative (typically –20 to –30 e.u.).[2]

This paper reports a detailed study of the stereochemistry of the 'carbonyl insertion' reactions of these iridium(III) complexes, and draws conclusions about the reaction mechanism from the findings. The particular reactions chosen for study were the following:

$$[IrCl_2Et(CO)_2L]+L'\rightarrow[IrCl_2(COEt)(CO)LL'] \quad (1)$$

where

(a) L = L′ = $AsMe_2Ph$;

(b) L = L′ = $AsMePh_2$;

(c) L = $AsMe_2Ph$, L′ = $AsMePh_2$.

Experimental Section

The preparations of $[IrCl_2Et(CO)_2(AsMe_2Ph)]$ and isomer A of $[IrCl_2(COEt)(CO)(AsMe_2Ph)_2]$ have been described in a previous paper.[1] In the preparations reported below, the petroleum ether used had a 100-120°C boiling range, except where otherwise stated. All reactions were performed under a nitrogen atmosphere.

$[IrCl_2Et(CO)_2(AsMePh_2)]$. A solution of $[IrCl_2Et(CO)_2]_2$[3] (0.2 g) in CH_2Cl_2 (5 ml) was treated with $AsMePh_2$ (0.15 g) in petroleum ether (10 ml). Removal of CH_2Cl_2 by evaporation caused precipitation of the product as yellow crystals which could be recrystallized from CH_2Cl_2/petroleum ether. M.P. 158-60°.

Analysis: Found C, 34.7; H, 3.1%. $C_{17}H_{18}IrO_2Cl_2As$ requires C, 34.5; H, 3.1%.

$[IrCl_2(COEt)(CO)(AsMe_2Ph)_2]$, *isomer B*. A solution of isomer A[1] in 1,2–dichloroethane was allowed to stand for 1 week at room temperature. Addition of petroleum ether and evaporation under nitrogen gave crystals of isomer B, which were recrystallized from CH_2Cl_2/petroleum ether. M.P. 127-9°C.

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[1] Part I: R. W. Glyde and R. J. Mawby, *Inorg. Chim. Acta*, *4*, 331 (1970).
[2] See references listed in Part I.
[3] B. L. Shaw and E. Singleton, *J. Chem. Soc.* (A), 1683 (1967).

Analysis: Found C, 33.5; H, 3.8%. $C_{20}H_{27}IrO_2Cl_2As_2$ requires C, 33.7; H, 3.8%.

[$IrCl_2(COEt)(CO)(AsMePh_2)_2$], *isomer A*. This was observed, by N.M.R. spectroscopy, in $CDCl_3$ solution during the reaction of [$IrCl_2Et(CO)_2(AsMePh_2)$] with $AsMePh_2$. Isolation was impossible owing to the accompanying rearrangement to isomer B. The same applies to isomer A of [$IrCl_2(COEt)(CO)(AsMe_2Ph)(AsMePh_2)$], which was observed in $CDCl_3$ solution during the reaction of [$IrCl_2Et(CO)_2(AsMe_2Ph)$] with $AsMePh_2$.

[$IrCl_2(COEt)(CO)(AsMePh_2)_2$], *isomer B*. A solution of [$IrCl_2Et(CO)(AsMePh_2)$] (0.25 g) in CH_2Cl_2 (10 ml) was treated with $AsMePh_2$ (0.2 g) and allowed to stand at room temperature for 2 days. Petroleum ether was then added and the CH_2Cl_2 removed by slow evaporation. The product, which was precipitated in crystalline form, could be recrystallized from CH_2Cl_2/petroleum ether. M.P. 176-8°C.
Analysis: Found C, 43.1; H, 3.7%. $C_{30}H_{31}IrO_2Cl_2As_2$ requires C, 43.1; H, 3.7%.

[$IrCl_2(COEt)(CO)(AsMe_2Ph)(AsMePh_2)$], *isomer B*. This was prepared, in the same way as the previous compound, from [$IrCl_2Et(CO)_2(AsMe_2Ph)$] (0.3 g) and $AsMePh_2$ (0.2 g), but with 1,2-dichloroethane instead of CH_2Cl_2. Precipitation of the product in crystalline form could only be achieved at –60°C. The yellow crystals were separated from the mother liquor and washed with petroleum ether (boiling range 40-60°C) at –60°C, before being dried under vacuum at –20°C. The crystals melted at *ca.* 0°C.
Analysis: Found C, 38.8; H, 4.3%. $C_{25}H_{29}IrO_2Cl_2As_2$ requires C, 38.8; H, 3.8%.

[$IrCl_2(COEt)(CO)(AsMe_2Ph)]_2$. This was slowly precipitated in crystalline form from a solution of [$IrCl_2Et(CO)_2(AsMe_2Ph)$] (0.25 g) in CH_2Cl_2 (4 ml) and petroleum ether (4 ml) over a period of 4 days. The crystals were removed by filtration, washed with petroleum ether (40-60°C) and dried under vacuum. M.P. 141-3°C.
Analysis: Found C, 27.1; H, 3.2%. $C_{24}H_{32}Ir_2O_4Cl_4As_2$ requires C, 27.2; H, 3.0%.

All N.M.R. studies were performed in $CDCl_3$ solution on a Perkin-Elmer R10 spectrometer with variable temperature attachment. The values given in the Table are on the τ scale, and were measured relative to tetramethylsilane as internal standard.

Results and Discussion

On the basis of the kinetic data,[1] the rate-controlling step in the reactions shown in equation (1) involves neither the entering ligand nor the solvent. It therefore seems clear that this step consists of the combination of ethyl and carbonyl ligands to give a propionyl group.

$$[IrCl_2Et(CO)_2L] \rightarrow [IrCl_2(COEt)(CO)L] \qquad (2)$$

The stereochemistry of the product[$IrCl_2(COEt)(CO)LL'$] relative to that of the original complex, will depend on the mechanism by which ethyl and carbonyl ligands combine, and on the subsequent direction of attack by L′ on the intermediate. Thus the stereochemistry of starting materials and products can provide vital evidence about the reaction mechanism.

Virtually all six-coordinate complexes of iridium(III), including[4] the closely related complex [$IrCl_2Me(CO)_2]_2$, are basically octahedral in shape, and we assume that this is true of the complexes described in this paper.

Stereochemistry of the Starting Materials, [$IrCl_2Et(CO)_2L$]. Six forms of the complexes [$IrCl_2Et(CO)_2L$] are theoretically possible (exluding optical, rather than geometrical, isomers). These are labelled I to VI in Figure 1. The infra-red spectra of these complexes contain two strong bands in the C–O stretching region (see Table). The positions and relative intensities of the two bands are almost exactly the same for [$IrCl_2Et(CO)_2(AsMe_2Ph)$] as for [$IrCl_2Et(CO)_2(AsMePh_2)$], suggesting that both have the same stereochemistry. The fact that in each compound the two bands are of similar intensity is compatible only with a *cis*-arrangement of the two carbonyl groups (structures I, III, IV, V), since a *trans*-isomer would exhibit either a single band or two bands of very different intensities. The N.M.R. spectrum of [$IrCl_2Et(CO)_2(AsMe_2Ph)$] (see Table I) contains only one resonance for the two methyl groups in the $AsMe_2Ph$ ligand. This is *not* due to rapid exchange of $AsMe_2Ph$ between the coordinated and free states, since separate sharp resonances for free and coordinated $AsMe_2Ph$ can be seen when this ligand is added to a solution of [$IrCl_2Et(CO)_2(AsMe_2Ph)$] in $CDCl_3$. We therefore conclude that the Ir–As bond lies in a plane of symmetry through the molecule, since the two methyl groups would otherwise be inequivalent.[5] Hence the compounds [$IrCl_2Et(CO)_2L$] must have structure I or structure IV.

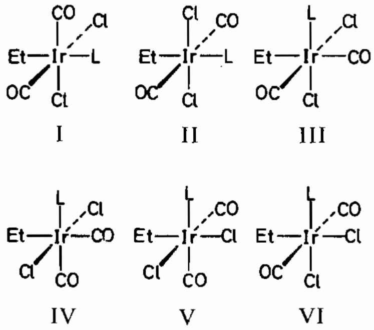

Figure 1. Possible arrangements of ligands in octahedral complexes [$IrCl_2Et(CO)_2L$].

It should, in theory, be possible to choose between these structures on the basis of Ir–Cl stretching frequencies. In practice, lack of data on comparable

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[4] N. A. Bailey, C. J. Jones, B. L. Shaw and E. Singleton, *Chem. Comm.*, 1051 (1967).
[5] A. J. Deeming and B. L. Shaw, *J. Chem. Soc.* (A), 1128 (1969), and references therein.

Table I. N.M.R. spectra[a] and C—O stretching frequencies in the infra-red spectra of iridium(III) complexes.

Complex	ν(C—O)cm.$^{-1}$	τ(CH_2CH$_3$)	τ(CH$_2$$CH_3$)	τ(As—CH_3)
[IrCl$_2$Et(CO)$_2$(AsMe$_2$Ph)]	2118, 2067[b]	7.21 (q,2)	8.08 (t,3)	8.00 (1,6)
[IrCl$_2$Et(CO)$_2$(AsMePh$_2$)]	2117, 2066[b]	7.39 (q,2)	8.23 (t,3)	7.95 (s,3)
[IrCl$_2$(COEt)(CO)(AsMe$_2$Ph)$_2$], isomer A	2052, 1645[b]	6.67 (q,2)	9.06 (t,3)	8.26 (s,3); 8.41[c] (s,3) 8.46 (s,3); 8.55[c] (s,3)
[IrCl$_2$(COEt)(CO)(AsMePh$_2$)$_2$], isomer A	not recorded	6.70 (q,2)	9.08 (t,3)	8.09[c] (s,3); 8.48 (s,3)
[IrCl$_2$(COEt)(CO)(AsMe$_2$Ph)(AsMePh$_2$)], isomer A	not recorded	6.74 (q,2)	9.08 (t,3)	8.17[c] (s,3) 8.37 (s,3); 8.61 (s,3)
[IrCl$_2$(COEt)(CO)(AsMe$_2$Ph)]$_2$	2060, 1666[d]	e	e	e

[a] Multiplicities and integration values are given in parentheses: q=quartet; t=triplet; s=singlet. Phenyl resonances are not recorded. [b] In CH$_2$Cl$_2$ solution. [c] The appearance of this band alters with temperature: see text. [d] In nujol mull [e] Too insoluble to allow a spectrum to be recorded.

complexes and the presence in the same part of the spectrum of bands due to Ir—As stretching modes make such a distinction impossible. There are, however, good grounds for preferring structure I to structure IV. The complexes [IrCl$_2$R(CO)$_2$L], where R= alkyl, are obtained instantaneously and in excellent yield on adding the ligand L to the dimeric species [IrCl$_2$R(CO)$_2$]$_2$.[1] The stereochemistry of these dimeric complexes is known[4] (Figure 2), and the crystal structure of the complex [IrCl$_2$Me(CO)$_2$]$_2$ shows that the bridging Ir—Cl bond *trans* to the alkyl group is longer (and presumably weaker) than that *trans* to the carbonyl group. Hence it is natural to expect this bond to break, so that the ligand L occupies the position *trans* to the alkyl group, as in structure I. In contrast, there is no obvious relationship between the stereochemistry of structure IV and that of the dimeric complexes [IrCl$_2$R(CO)$_2$]$_2$.

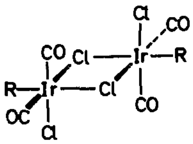

Figure 2. Structure of complexes [IrCl$_2$R(CO)$_2$]$_2$ (see reference 4).

We have also found[1] that the Ir—L bond in complexes [IrCl$_2$Et(CO)$_2$L] is labile. Ligand interchange occurs when either the complex with L=AsPh$_3$ or that with L=AsMePh$_2$ is treated with AsMe$_2$Ph. It is well known that the lability of the bond to a ligand in an octahedral iridium(III) complex is strongly dependent on the ligand in the *trans*-position, and little affected by the ligands in *cis*-positions.[6] In these complexes, alkyl ligands are known to exert a very strong *trans*-labilizing influence:[7] hence the finding that the Ir—L bond is labile lends further support to the proposed structure, I.

Stereochemistry of the Products, [IrCl$_2$(COEt)(CO)LL′]. In each of the reactions listed at the end of the introduction, the product [IrCl$_2$(COEt)(CO)LL′] is obtained in one isomeric form (isomer A), which subsequently rearranges to a more thermodynamically stable form (isomer B). Isolation and full characterization of an A isomer is only possible for [IrCl$_2$(COEt)(CO)(AsMe$_2$Ph)$_2$], since the A isomers of the other two complexes rearrange to B isomer at rates not much less than their rates of formation from [IrCl$_2$Et(CO)$_2$L] and L′. Analytical data for the B isomers are given in the experimental section.

There are six possible structures for the A isomers of [IrCl$_2$(COEt)(CO)(AsMe$_2$Ph)$_2$] and [IrCl$_2$(COEt)(CO)(AsMePh$_2$)$_2$]. These are labelled VII to XII in Figure 3. At 30°C, the N.M.R. spectrum of the former compound exhibits separate resonances for each of the four methyl groups in the two AsMe$_2$Ph ligands. This establishes that the two ligands are in different environments, and that neither As—Ir bond lies in a plane of symmetry through the molecule. Only structures VII and XII meet these requirements.

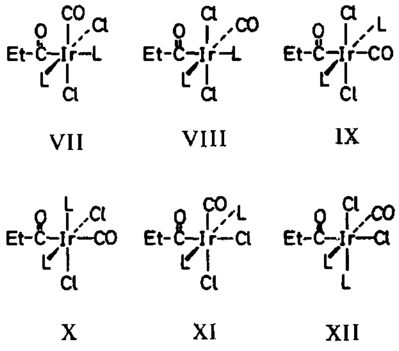

Figure 3. Possible arrangements of ligands in octahedral complexes [IrCl$_2$(COEt)(CO)L$_2$].

The N.M.R. spectrum of this compound varies with temperature. As the temperature is raised to 50°C, two of the four methyl resonances for the AsMe$_2$Ph ligands broaden and then collapse, while the rest of the spectrum remains unaltered. On cooling, the spectrum returns to its original form. The implication is that one of the two arsenic ligands is in rapid exchange between complex and solution, while the other is not.

$$[\mathrm{IrCl_2(COEt)(CO)(AsMe_2Ph)_2}] \rightleftharpoons [\mathrm{IrCl_2(COEt)(CO)(AsMe_2Ph)}] + \mathrm{AsMe_2Ph} \qquad (3)$$

The fact that the rest of the spectrum is unaffected

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(6) J. M. Jenkins and B. L. Shaw, *J. Chem. Soc.*, 6789 (1965).
(7) B. L. Shaw and A. C. Smithies, *J. Chem. Soc.* (A), 1047 (1967).

by the change in temperature indicates that the posiion of this rapid equilibrium is far over to the left. Evidence from other workers[5] on iridium(III) complexes shows that—of the ligands present in this complex—the acyl group possesses much the largest *trans*-labilizing effect, indicating that in isomer A of [$IrCl_2(COEt)(CO)(AsMe_2Ph)_2$] one of the two $AsMe_2Ph$ ligands is *trans* to the acyl group. This demonstrates that the correct structure for this compound is VII.

Isomer A of the complex [$IrCl_2(COEt)(CO)(AsMePh_2)_2$] can be assigned the same structure as isomer A of [$IrCl_2(COEt)(CO)(AsMe_2Ph)_2$] for the following reasons. (i) The N.M.R. spectra of the protons in the acyl groups of the two compounds are closely similar. (ii) The N.M.R. spectrum of isomer A of [$IrCl_2(COEt)(CO)(AsMePh_2)_2$] shows that the two $AsMePh_2$ ligands are in different environments, as would be expected for structure VII. (iii) Whereas a solution containing isomer A of [$IrCl_2(COEt)(CO)(AsMePh_2)_2$] and free $AsMePh_2$ at −5°C exhibits three sharp resonances for the methyl groups on the arsenic ligands, one for each of the coordinated ligands and one for the free ligand, raising the temperature causes the resonance of *one* of the coordinated ligands and the resonance of the free ligand to broaden and then coalesce. At 35°C, a single broad resonance is observed for the two, and this sharpens with further increase in temperature. These changes are reversed on cooling. The rest of the spectrum remains unaltered over the whole temperature range. This pattern of behaviour is so similar to that for isomer A of [$IrCl_2(COEt)(CO)(AsMe_2Ph)_2$] that we are forced to conclude that *both* compounds have structure VII.

One important question about the structure of the A isomers remains to be answered. Since the two arsenic ligands are in different environments, it is important to know which of the two is the ligand L, present in the starting material, and which is the entering ligand L′. This question was resolved by a study of the N.M.R. spectrum of isomer A of the compound [$IrCl_2(COEt)(CO)(AsMe_2Ph)(AsMePh_2)$], obtained from the reaction of [$IrCl_2Et(CO)_2(AsMe_2Ph)$] with $AsMePh_2$. At 10°C, the spectrum of this compound exhibits two sharp resonances for the methyl groups in the $AsMe_2Ph$ ligand, and one for the methyl group in $AsMePh_2$. When the temperature is raised, it is the resonance due to $AsMePh_2$ which broadens and then collapses, while the resonances due to $AsMe_2Ph$ are unaffected. The change in spectrum is reversed on cooling. This indicates that it is the incoming ligand, $AsMePh_2$, which occupies the positions *trans* to the acyl group.

(The B isomers of these compounds, whose stereochemistry is not of direct relevance to the present paper, will be shown, in a subsequent paper on the mechanism of the rearrangement of A isomers to B isomers, to have structure XI in Figure 3.)

It is therefore established that the stereochemistry of these 'carbonyl insertion' reactions is as shown in Figure 4. As indicated in this Figure, the intermediate could be either trigonal bipyramidal[8] or square pyramidal in shape. Although the choice between the two is not a crucial one from a mechanistic point of view, we prefer to formulate the intermediate as a square pyramid for two reasons. Firstly, it is difficult to see why attack on a trigonal bipyramidal intermediate should lead specifically to one isomer (which is not even the most thermodynamically stable isomer) of the product [$IrCl_2(COEt)(CO)LL'$], when there appear to be three equivalent directions of attack. With a square pyramidal intermediate there is only one possible direction of attack. Secondly, in the rapid exchange of L′ between complex and solution, the ligand L retains its identity. If the intermediate involved in the exchange (equation (3)), which is the same species as the intermediate in the carbonyl insertion reaction, has trigonal bipyramidal geometry, it is surprising that the positions of L and L′ are never reversed during the exchange process. If the intermediate has square pyramidal geometry, one would not expect L and L′ to change places during the exchange process.

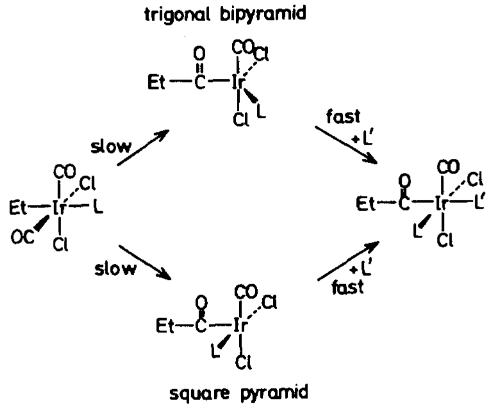

Figure 4. Stereochemistry of the 'carbonyl insertion' reactions.

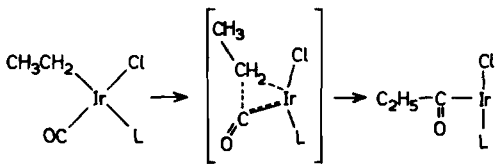

Figure 5. Stereochemistry of the rate-determining step.

Figure 5 shows the stereochemistry of the rate-determining step of the 'carbonyl insertion' reactions. A pair of mutually *trans* ligands which play no direct part in the reaction are omitted for simplicity. Clearly, this step should be described neither as carbonyl insertion nor as alkyl migration, since it involves a concerted movement of alkyl and carbonyl ligands, accompanied by a widening of the Cl–Ir–L bond angle. This conclusion applies even if one assumes a trigonal bipyramidal shape for the intermediate.

The complex [$IrCl_2Et(CO)_2(AsMe_2Ph)$] undergoes a 'carbonyl insertion' reaction in solution even if a ligand L′ is not added. The product of the reaction has the empirical formula [$IrCl_2(COEt)(CO)(AsMe_2Ph)$]$_n$, and—by analogy with similar complexes pre-

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(8) D. M. Blake and M. Kubota, *J. Am. Chem. Soc.*, *92*, 2578 (1970).

viously prepared with phosphorus ligands[3]—is probably dimeric with two bridging chlorine atoms. This cannot be verified by physical means owing to the insolubility of the compound in common solvents. It is possible to visualize this reaction as involving the combination of two square pyramidal $[IrCl_2(COEt)(CO)(AsMe_2Ph)]$ intermediates, with a chloride ligand on one iridium atom acting as the incoming ligand for the other, as shown in Figure 6. Again, a pair of mutually *trans*-ligands is omitted on each iridium atom.

The dimeric complex $[IrCl_2(COEt)(CO)(AsMe_2Ph)]_2$ reacts with $AsMe_2Ph$ to produce isomer A of $[IrCl_2(COEt)(CO)(AsMe_2Ph)_2]$ rather than the thermodynamically more stable isomer B. This is what one would expect on the basis of the structure shown for $[IrCl_2(COEt)(CO)(AsMe_2Ph)]_2$ in Figure 6, since one would expect the Ir–Cl bonds *trans* to the labilizing acyl groups to be broken preferentially in the reaction with $AsMe_2Ph$.

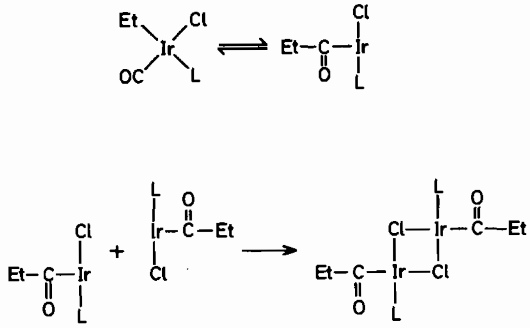

Figure 6. A possible mechanism for the 'dimerization' of $[IrCl_2Et(CO)_2L]$.

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