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ADDITION OF ACETIC FORMIC ANHYDRIDE TO
trans-[IrCl(CO)(PMe₂Ph)₂]; ANION-,
 INCLUDING HYDRIDO-, TRANSFER REACTIONS

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SUMMARY

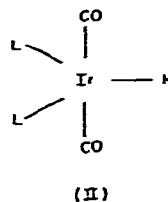
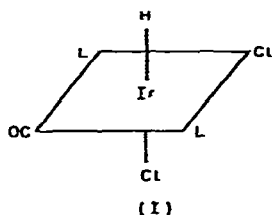
Addition of acetic formic anhydride to trans-[IrCl(CO)(PMe₂Ph)₂] leads, via a series of intermolecular anion (hydrido, formato and chloro) ligand exchange reactions, to the formation of the cis-dihydrido, trans-tertiary-phosphino complex [IrClH₂(CO)(PMe₂Ph)₂].

INTRODUCTION

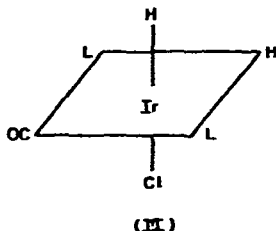
Although a number of transition metals are known to give anionic complexes containing a formyl group^{1,2} there is only one report of a neutral transition metal-formyl complex³. The possible importance of this type of complex as an intermediate in the catalytic reduction of carbon monoxide with hydrogen^{4,5}, coupled with the observation that carboxylic acid anhydrides, R(CO)O(CO)R, readily add to square-planar iridium(I) complexes of the type trans-[IrCl(CO)L₂] (L = tertiary phosphine) to give acyl-carboxylate complexes of the type [IrCl{(CO)R}O(CO)R(CO)L₂] (R = CH₃, CF₃ or C₂F₅)⁶, prompted us to investigate the reaction between acetic formic anhydride and trans-[IrCl(CO)(PMe₂Ph)₂].

RESULTS AND DISCUSSION

Addition of two equivalents of acetic formic anhydride to a solution of trans-[IrCl(CO)L₂] (L = PMe₂Ph or PPh₃) in benzene resulted in a rapid (ca. 15 min at 25 °C) bleaching of the yellow solution. The ¹H NMR spectrum of the resulting mixture indicated the formation, in equal amounts, of (I) and (II)* (L = PMe₂Ph, or PPh₃), together with



acetic anhydride.† The expected product, *i.e.* [IrCl{(CO)H}{O(CO)CH₃}(CO)L₂] or [IrCl{O(CO)H}{(CO)CH₃}.CO)L₂], resulting from "simple" oxidative addition of the mixed anhydride, was not observed. At this stage of the reaction only half the acetic formic anhydride originally added had been consumed. When the mixture was allowed to stand for ca. 30 h at ambient temperature (I) and (II) disappeared with simultaneous formation of (III), (L = PMe₂Ph or PPh₃). The second equivalent of



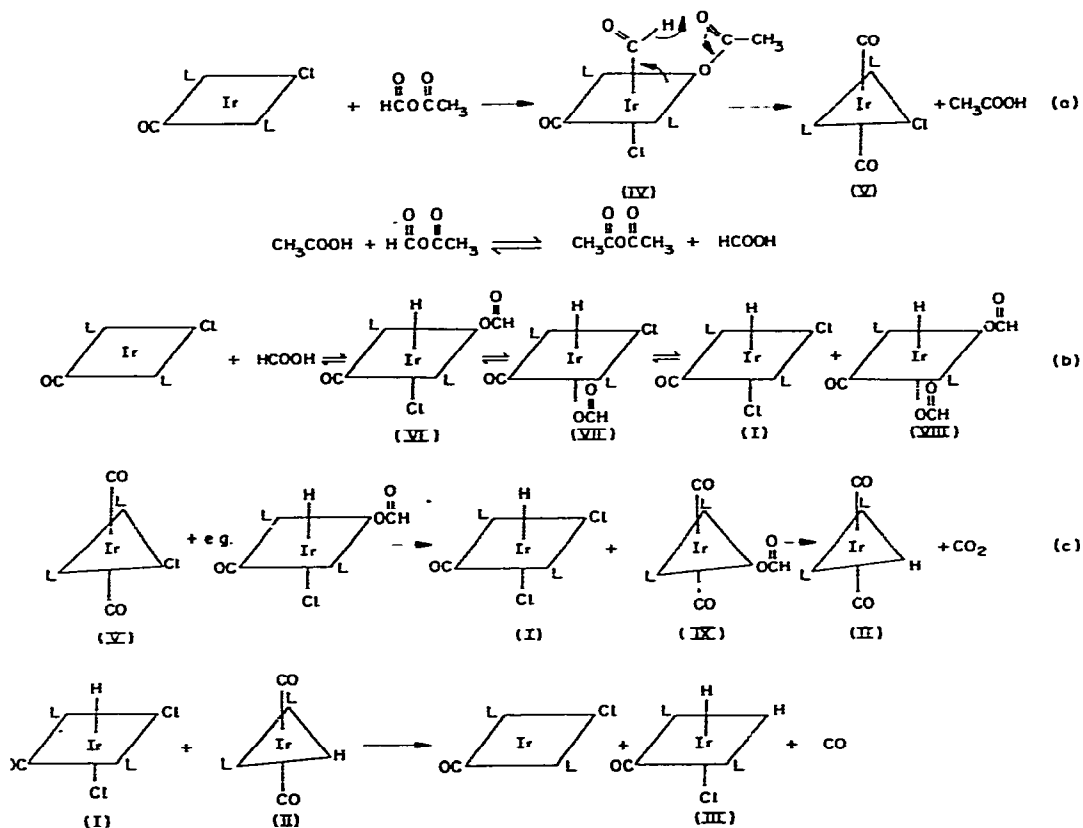
* For a full discussion of the structure of five-coordinate iridium(I) species of this type see ref.7.

† In some cases the hydrido resonances in the ¹H NMR spectrum of this mixture were broadened, possibly indicating exchange with a third species present in solution. However, the phenomenon, which proved to be sample- and solvent-dependent, was irreproducible, and was not investigated further.

of formic acetic anhydride was consumed and a further amount of acetic anhydride produced. Allowing the mixture to stand for a further 30 h resulted in no further change. At no stage was a metal-formyl species detected. The NMR parameters for (I) and (III), (L = PMe₂Ph or PPh₃), have previously been reported^{8,9}, & have those for (II) with L = PPh₃⁷. Compound (II) with L = PMe₂Ph - which can also be prepared by passing carbon monoxide through a solution of [IrH₅(PMe₂Ph)₂] in benzene - gives rise to a triplet at $\delta = -1.10$ ppm ($^2J(^{31}\text{P-H}) = 30$ Hz) assigned to hydrido hydrogen and a double doublet at $\delta = 1.43$ ppm [$^2J(^{31}\text{P-H}) + ^4J(^{31}\text{P-H}) = 8$ Hz; $^4J(\text{H-H}) = 0.6$ Hz] due to the methyl hydrogens of the tertiary phosphine ligand. The small coupling of 0.6 Hz was shown by double-resonance techniques to be due to coupling between methyl-group hydrogens and the hydrido hydrogen. Deeming and Shaw¹⁰ observed an analogous tertiary phosphine-methyl-hydrido coupling of 1 Hz in [IrHCl(CO)(PMe₂Ph)₃].

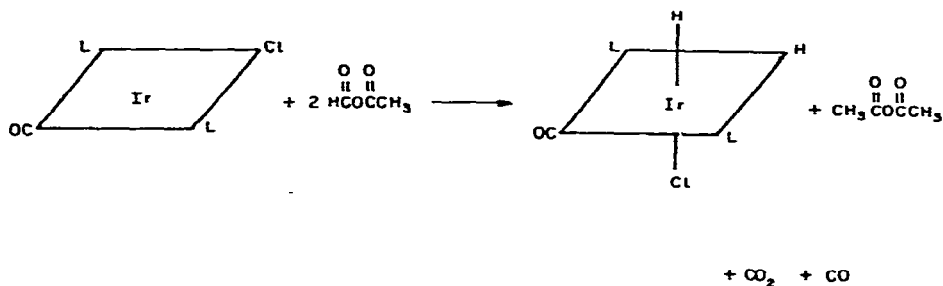
The formation of these, at first sight, unexpected, products can be rationalized on the basis of the sequence of reactions shown in the Scheme. By analogy with the behaviour previously observed⁶ for the trans-[IrCl(CO)(PPh₃)₂]/R(CO)O(CO)R (R = CH₃, CF₃ or C₂F₅) system we suggest that the initial interaction involves oxidative addition of the formic acetic anhydride to trans-[IrCl(CO)L₂] (L = PMe₂Ph or PPh₃), to give a formyl acetato iridium(III) complex of type (IV) (L = PMe₂Ph or PPh₃). This species then rapidly undergoes an internal rearrangement, eliminating acetic acid and forming the dicarbonyl species (V) (L = PMe₂Ph or PPh₃), sequence (a). The acetic acid so formed reacts with the excess formic acetic anhydride giving acetic anhydride and formic acid. The latter immediately adds to any unreacted trans-[IrCl(CO)L₂][†] to give, as previously described¹¹, the four hydrido species (VI), (VII), (I) and (VIII), sequence (b). At this stage we propose an anionic ligand

 † This species may also be formed by loss of CO from the dicarbonyl species (V). Such species, with L = PPh₃, have been shown to readily lose CO⁷.

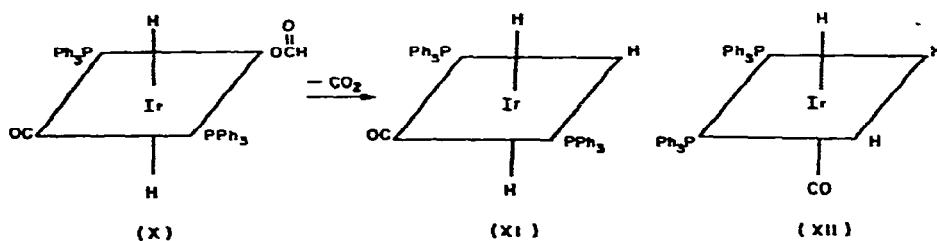


SCHEME

exchange reaction between species (V), ($L = \text{PMe}_2\text{Ph}$, or PPh_3) and one of the formato-containing complexes formed in sequence (b), resulting in a chloro/formato exchange and giving rise to one of the initially observed reaction products viz. (I) ($L = \text{PMe}_2\text{Ph}$ or PPh_3) and the five-coordinate dicarbonyl-formato complex (IX). The latter complex undergoes dicarboxylation to yield the second initially observed product, viz. (II) ($L = \text{PMe}_2\text{Ph}$ or PPh_3), sequence (c). A hydrido/chloro exchange between (I) and (II), possibly preceded by carbon-monoxide dissociation, completes the sequence and leads to the final reaction product (III) ($L = \text{PMe}_2\text{Ph}$ or PPh_3), sequence (d); the trans- $[\text{IrCl}(\text{CO})\text{L}_2]$ formed re-enters the sequence via (a). Thus the overall reaction may be summarized as:



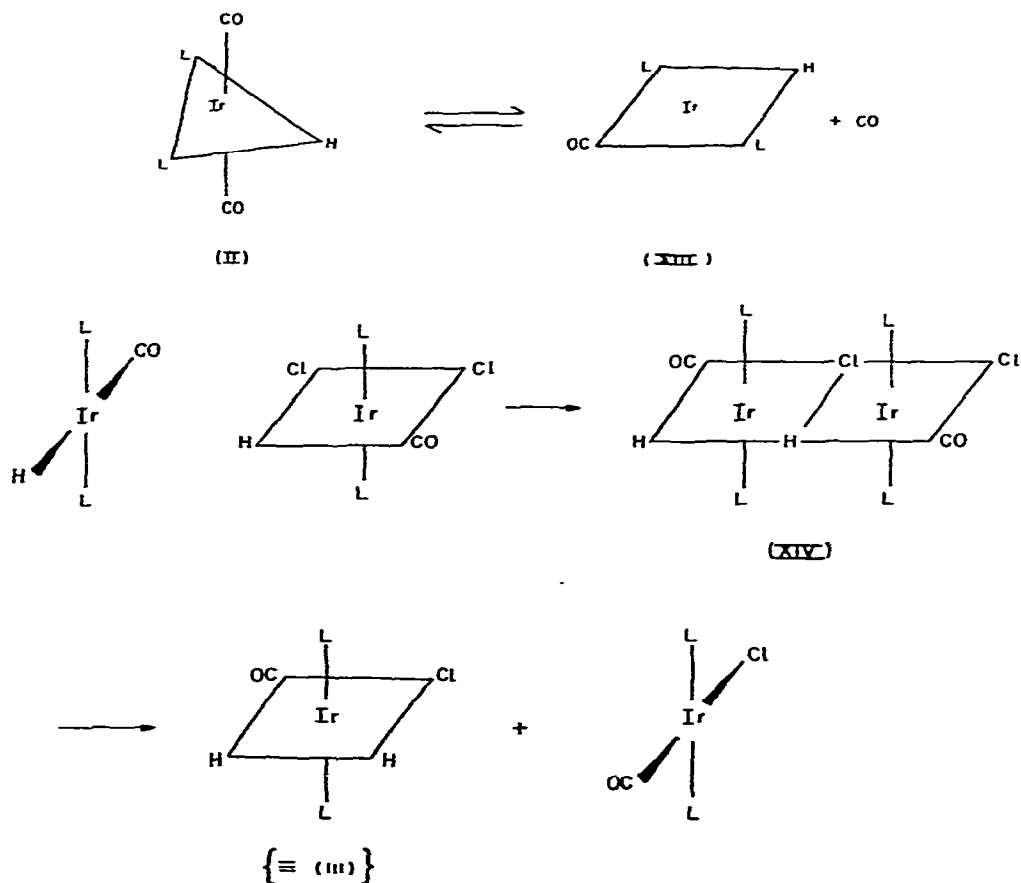
As discussed above, there is a good precedent⁶ for the initial oxidative addition reaction proposed in reaction (a) and we have previously shown that reaction (b) readily occurs¹¹. We have demonstrated the feasibility of reaction (c) using independently synthesised starting materials. Thus addition of (V) ($L = \text{PPh}_3$)⁺ to the mixture obtained by adding HCOOH to trans- $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$ resulted in the rapid (ca. 5 min at 20 °C) formation of equal amounts of (I) and (II) ($L = \text{PPh}_3$). In addition to (I) and (II) ($L = \text{PPh}_3$), a third hydrido species, thought to be the dihydrido-formato complex (X), was formed. On standing in solution this compound underwent decarboxylation to give a mixture of the trihydrido species (XI) and (XII)¹¹.



The feasibility of reaction (d), which is in essence a hydrido transfer, was demonstrated using a 1/1 mixture of (I) and (II) ($L = \text{PMe}_2\text{Ph}$).

 † Triphenylphosphine was used as with this ligand product (V) ($L = \text{PPh}_3$) can be readily isolated as a stable crystalline compound⁷.

We observed a smooth (ca. 48 h at 20 °C) conversion to trans-[IrCl(CO)(PMe₂Ph)₂] and the dihydrido species (III) (L = PMe₂Ph), with evolution of carbon monoxide. We have not investigated the detailed mechanism of this hydrido-transfer reaction; however, the sequence shown overleaf would appear, by analogy with known systems, to be feasible. Although species of type (XIII) are not known, carbon monoxide dissociation from the chloro analogue of (II) is well established⁷. Dimeric iridium compounds containing bridging hydride ligands are well known¹² and we have previously demonstrated¹³ the intermediary of hydrido-bridged species in related intermetallic hydrido-transfer reactions.



L = PMe₂Ph or PPh₃

CONCLUSIONS

Although the original goal of this work, *viz* the isolation of a neutral transition-metal-formyl complex, was not achieved, the complexity of the resulting reaction sequence, as set forth in the Scheme, is, we believe, of some significance in the general field of organometallic chemistry. There has been a tendency to attempt to explain many reactions involving transition-metal complexes, especially in the area of homogeneous catalysis, as single-site, or at least single-metal reactions. In other words, a reactant once bound to a given metal remains with that metal throughout a given reaction sequence, any changes the reactant undergoes during the course of the sequence occurring at that metal. It is becoming increasingly clear that, at least in solution, many "stable" transition-metal complexes are "labile". Thus, intermetallic transfer of metal-bound alkyl¹⁴⁻¹⁹, hydrido^{12,13,20}, carboxylate¹¹, halogen^{18,21}, carbonyl²¹ and tertiary-phosphine²¹⁻²³ ligands is now established. The system reported here demonstrates the occurrence of two such reactions, *viz.* halogen and hydrido transfer, in the, at first sight, simple system $\text{trans-}[\text{IrCl}(\text{CO})(\text{PMe}_2\text{Ph})_2] / \text{H}(\text{CO})\text{O}(\text{CO})\text{CH}_3$. We would suggest that the occurrence of ligand redistribution reactions is more common in organo-transition-metal chemistry than has previously been recognized and may well play an important role in homogeneous, transition-metal-catalysed reactions.

EXPERIMENTAL

All operations with air-sensitive materials were performed in an argon atmosphere.

$[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$ was obtained commercially. The compounds $[\text{IrCl}(\text{CO})(\text{PMe}_2\text{Ph})_2]$ ⁸, $[\text{IrHCl}_2(\text{CO})(\text{PMe}_2\text{Ph})_2]$ ⁸, $[\text{IrCl}(\text{CO})_2(\text{PPh}_3)_2]$ ² and acetic formic anhydride²⁵ were prepared according to published methods. The $[\text{IrH}(\text{CO})_2(\text{PMe}_2\text{Ph})_2]$ complex was prepared by the procedure reported in ref.26.

¹H NMR spectra were recorded in deuterobenzene using a Bruker WH 90 instrument.

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