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Preliminary communication

THE ISOLATION OF INTERMEDIATES IN THE OXIDATIVE ADDITION OF THE HYDROGEN HALIDES TO SOME IRIDIUM(I) SPECIES

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Summary

The cationic complexes [Ir(cod)($PMePh_2$)$_2$] A (I, A = PF_6 or BF_4; cod = 1,5-cyclooctadiene) react with HX (X = Cl, Br, I) to give [IrHX(cod)L_2] A (II). In two cases (X = I, Br) an intermediate, [IrX(cod)L_2] (III), was isolated from the reaction mixtures. Complexes of type III are also formed by the action of X^- (X = Cl, Br and I) on I; they react in turn with HA to give II. [Ir(cod)(PMe_2Ph)$_3$] A react with HX to give II (L = PMe_2Ph).

The mechanisms of oxidative addition reactions are the subject of much current interest [1,2]. From kinetic evidence, Louw [2] has suggested that the oxidative addition of hydrochloric acid in methanol to some iridium(I) species proceeds by addition of halide ion followed by protonation.

We now report the isolation of intermediates in the oxidative addition of the hydrogen halides to [Ir(cod)($PMePh_2$)$_2$] A [3] (I, A = PF_6 or BF_4). The red complexes I, in methanol suspension or dichloromethane solution, react rapidly with gaseous HX or the concentrated aqueous acids to give [IrHX(cod)L_2] A (II)*. When the reaction is performed in methanol at 0°C with a stoichiometric quantity of aqueous HX (X = Br or I), a further product [IrX(cod)L_2] (III) can be isolated from the reaction mixture in addition to complex II. The neutral light yellow products III precipitate on the addition of acetone to the reaction mixture; they can be recrystallised from CH_2Cl_2/Et_2O. The more soluble white ionic derivatives II remain in solution, but can be isolated by removal of the solvent under reduced pressure. The yield of III is greater where

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* Louw [2b] independently discovered this reaction and, for X = Cl, studied its kinetics. We obtained 80—95% yields of all the complexes described, except where stated. Satisfactory analytical data were obtained in all cases.

X = I (50%) than where X = Br (5%). These intermediates, III, in acetone, methanol or chloroform react with an excess of HA (A = PF_6 or BF_4) to give the complexes II, of identical stereochemistry to that observed in the direct addition.

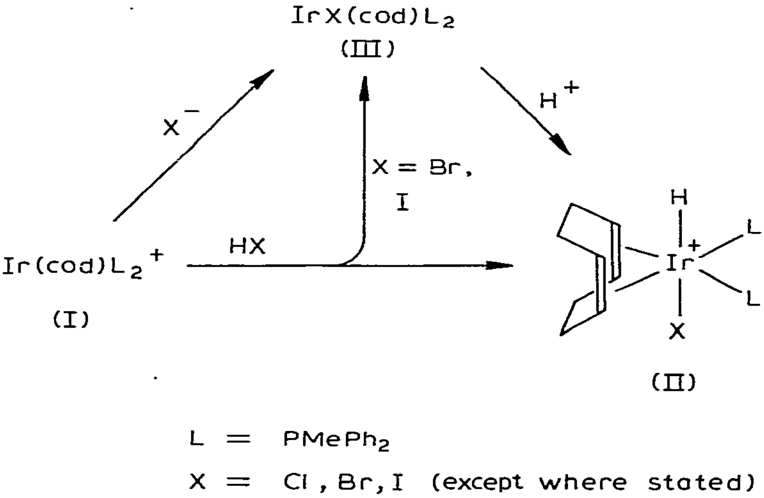
The cationic complexes $[Ir(cod)L_2]A$ (I) also react with KBr or KI in aqueous acetone to give the neutral intermediates III of identical IR and NMR spectral characteristics to those formed as by-products in the oxidative addition reactions. The action of LiCl on I in aqueous acetone gives the isolable complex $[IrCl(cod)L_2]$, which in turn reacts with HA to give the oxidative addition product II (X = Cl). Complexes II and III can be recovered unchanged from methanol/acetone.

The stereochemistry of the complexes II (see Scheme 1) follows from their ^1H NMR spectrum in $CDCl_3$ at 35°C. Only one doublet PMe resonance ($^2J(P—H)$ 10 Hz) is observed at δ 2.0 ppm (relative to TMS), indicating the presence of equivalent *cis*-$PMePh_2$ ligands. A hydridic resonance at δ —13 ppm (X = I) to δ —14.8 ppm (X = Cl) shows coupling ($^2J(P—H)$ (*cis*) 16 Hz) to two equivalent phosphorus nuclei. Finally, the (cod)-vinyl resonances take the form of two broad peaks due to the absence of a plane of symmetry bisecting the (cod) C=C bonds and the metal centre [4]. Finally, the position of the Ir—H stretching frequency in the IR spectrum of complexes II (2210—2250 cm^{-1}) is consistent with the presence of a halide ligand *trans* to H [5].

The 5-coordinate complexes III were fluxional on the NMR time scale at 35°C and showed only one broad (cod)-vinyl resonance at δ 4.8—4.9 ppm and one PMe resonance at δ 1.8—1.9 ppm. The form of the PMe resonance in these complexes, two sharp peaks flanking an unresolved central resonance, indicates virtual coupling of an intermediate type, and is consistent with an equatorial—equatorial or an axial—equatorial IrL_2 arrangement [6]. The related complex $[IrCl(cod)(PPh_3)_2]$ [7] is also fluxional in the same way.

The white complex $[Ir(cod)(PMe_2Ph)_3]A$ (IV) also reacts with HX under the same conditions to give complexes of type II (L = PMe_2Ph). The PMR

SCHEME 1



spectra of these complexes are very similar to those of their $PMePh_2$ analogues,

$$\underset{(IV)}{[Ir(cod)(PMe_2Ph)_3]^+} + 2HX \rightarrow \underset{(II)}{[IrHX(cod)(PMe_2Ph)_2]^+} + [HPMe_2Ph]X$$

except for the presence of a pair of PMe doublet resonances (e.g., at δ 1.75 and 1.95 ppm with ^2J(P—H) 10 Hz for II, X = Cl, L = PMe_2Ph), consistent with the diastereotopy of the PMe groups expected on the basis of the stereochemistry for II shown in Scheme 1. No intermediates were isolated in this case, nor did halide ion react with IV in methanol in the absence of acid.

Complexes I and IV can be recovered unchanged from dilute ethanolic HF or KF solutions, presumably because the fluoride ion is insufficiently nucleophilic to effect substitution.

Since complexes I are unaffected by the non-coordinating acids HA, but react readily with the halide anions X^- and the halogen acids HX, the course of the oxidative addition of HX, at least in polar solvents, seems clear: halide ion addition takes place first and is followed by protonation [2]. We have demonstrated each step independently for the first time and in two cases have isolated the intermediates from the reaction mixtures themselves.

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