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THE ISOLATION OF INTERMEDIATES IN HYDROGEN HALIDE ADDITIONS TO SOME IRIDIUM COMPLEXES *

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Summary

The complexes $[Ir(cod)L_n]PF_6$ (I, L = PPh_3, $PMePh_2$; n = 2. L = PMe_2Ph; n = 3) react with HX to give $[IrHX(cod)L_2]PF_6$ (II, L = $PMePh_2$ or PMe_2Ph) or $[IrHX_2(cod)(PPh_3)]$ (III). The intermediates $[IrX(cod)L_2]$ have, in two cases (L = $PMePh_2$, X = I, Br), been directly isolated from the reaction mixtures at 0°C, and are also formed from I with KX (L = PPh_3, X = Cl; L = $PMePh_2$, X = Cl, Br, I); these intermediates protonate to give II (L = $PMePh_2$), or an equimolar mixture of III and I (L = PPh_3, X = Cl). Surprisingly, I_2 reacts with I in MeOH to give III (L = PPh_3). The stereochemistries of II and III were determined by ^1H NMR and especially by new methods using ^{13}C NMR spectroscopy. The complexes I exhibit a Lewis acid reactivity pattern.

Introduction

Many examples of the reaction of the hydrogen halides with electron-rich transition metal complexes are known [1—3]. The metal can undergo oxidative addition, protonation, or reaction at a ligand. Oxidative addition of the hydrogen halides seems generally to be either concerted or ionic. Up to 1977, whenever the ionic mechanism had been examined in detail it had been found to proceed by protonation followed by halide substitution [3]. This order of addition is appropriate for an electron rich metal, having Lewis base character.

Recently we found evidence that led us to believe that the addition of hydrogen to $[Ir(cod)L_2]PF_6$(I) is not oxidative, but reductive in character [4]. For example, electron-donor ligands inhibit this addition, rather than, as is normally

* Dedicated to Joseph Chatt on the occasion of his 65th birthday.

found [5], promote it. The metal appears to show Lewis acid character, tending to attract electron density to itself in its reaction, rather than, as is normal for a metal center capable of 'oxidative' addition, dispersing electron density in its reactions.

We now find that in the addition of HX to I, the first step is not protonation, which would be characteristic of a Lewis base. Instead, halide addition is the first step of the reaction; this behaviour may be characteristic of this class of metal centre, capable of (so-called) "oxidative" addition but resistant to oxidation. We have discussed elsewhere [4] other examples of the resistance of the complexes I to oxidation, such as their failure to react with O_2, $CHCl_3$, or EtI.

We have also discussed [4b] alternative ways of systematising such reactions, which avoid the presumption of oxidative character, implied in the term "oxidative" addition.

As suggested above, the complexes I show their Lewis acid character by the mechanism they adopt for HX addition: X^- addition, followed by protonation, the reverse of the usual order. We were able to isolate intermediates from the reaction mixtures themselves, and demonstrate each step of the reaction separately. Louw [6] had come to the same mechanistic conclusions from kinetic evidence, both for these complexes and for their neutral counterparts [IrCl(cod)L]. The Lewis acid character of the cationic complexes is therefore not simply a manifestation of their overall positive charge.

Results and discussion

The formation of the HX adducts

The complexes $[Ir(cod)L_n]PF_6$ (Ia: L = PMe_2Ph, n = 3; Ib: L = $PMePh_2$, n = 2; Ic: L = PPh_3, n = 2) in methanol suspension, CH_2Cl_2 solution, or in the solid state, readily react with molecular HX (X = Cl, Br, I) or with the concentrated aqueous acids. In the case of Ia and Ib, the products are $[IrHX(cod)L_2]PF_6$ (X = Cl, Br, I; IIa: L = PMe_2Ph; IIb: L = $PMePh_2$).

$$[Ir(cod)L_n]PF_6 + (n-1)HX \longrightarrow \left[\begin{array}{c} H \\ | \\ L \diagup Ir \diagdown L \\ | \\ X \end{array}\right] PF_6 + (n-2)[LH]X \qquad (1)$$

(I) — Structure A (II)

(X = Cl, Br, I; a: L = PMe_2Ph, n = 3; b: L = $PMePh_2$, n = 2)

In the case of Ic, they are $[IrHX_2(cod)(PPh_3)]$ (III, X = Cl, Br, I). In the cases of Ia and Ic, the corresponding tertiary phosphonium hydrochloride is also formed.

$$[Ir(cod)L_2]PF_6 + 2HX \longrightarrow \left[\begin{array}{c} H \\ | \\ L \diagup Ir \diagdown X \\ | \\ X \end{array}\right] PF_6 + (LH)X \qquad (2)$$

(Ic) — Structure C (III)

(L = PPh_3, X = Cl, Br, I)

The compounds III were first prepared by Haszeldine et al. [7] by the addition of HX to [IrX(cod)L]; compounds IIb were made independently by Louw and by ourselves by the same method (eq. 2); and complexes IIa are new.

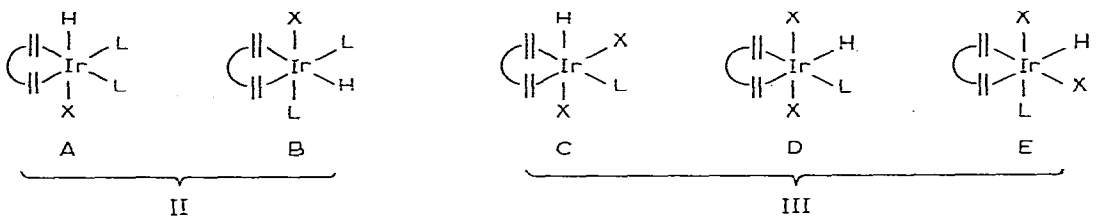
We never observed the complexes $[IrHX_2(cod)(PMePh_2)]$, described by Louw [6] and formed by eq. 2 (L = $PMePh_2$); our reaction conditions were somewhat milder.

All the complexes were characterised by microanalysis, by ^1H and ^{13}C NMR, and by IR spectroscopy (Table 1).

The stereochemistries of the HX adducts

We were interested to determine the stereochemistry of complexes II and III unambiguously, because of our interest in the insertion reactions of metal hydrides into C=C bonds. We had found that when the M(C=C)H system of the dihydridodiolefin complex cations $[IrH_2(cod)L_2]^+$ was coplanar, rapid insertion of the metal hydride into the C=C bond take place [4]. The stereochemistries which had been proposed for II and III (see eqs. 1—2) contained coplanar M(C=C)H systems, yet the complexes were moderately thermally stable, although they decomposed slowly even in the solid state.

The available evidence, essentially based on the splitting pattern of the hydridic resonance in the ^1H NMR spectra of II,III was consistent with structures A and C, but did not rule out structure B for II and structures D and E for III.



In the case of complexes III, for example, doublet hydridic resonances, having coupling constants (J(P,H) 7 Hz) characteristic of a *cis* arrangement of H and L, had always been observed [6,7]. Only structures C, D and E are therefore possible. To proceed, we first need to be able to distinguish between isomers having L *cis* or *trans* to a (cod)vinylic group; previous studies had not resolved this question.

We have recently found an unambiguous way of determining this stereochemistry by ^{13}C NMR spectroscopy, which we have now applied with uniform success to several series of (cod) complexes both of iridium(I) and iridium(III) [8,9].

Fortunately, the (cod)vinylic resonances in the ^{13}C NMR spectra occur at chemical shifts (56—110 ppm) that are generally quite free of interfering resonances which might otherwise complicate the assignments.

The vinylic carbon nuclei of a (cod) ligand show greater coupling to *trans*- than to *cis*-L groups (L = PR_3). The *cis* coupling is not normally observed, and the *trans* coupling is normally in the range ^2J(P,C, *trans*) = 10—21 Hz. The ^{13}C NMR data (Table 1) for complexes III unambiguously characterise them as adopting a structure in which L is *trans* to (cod). This result rules out structure E.

To distinguish between structures C and D we used the fact that D possesses a plane of symmetry through the metal and bisecting the (C=C) bonds of the

(Continued on p. 208)

TABLE 1

COLOURS, YIELDS, IR AND NMR DATA FOR THE COMPLEXES

Compound	Colour	Yield (%)	ν(IrH) [a] (cm^{-1})	PMR data [b] (ppm)			^{13}C NMR data [c] (ppm)		Refs.
				(cod)vinyl [d]	IrH	PMe	(cod)vinyl	(cod)allyl	
$[IrHCl_2(cod)(PPh_3)]$	yellow	85	2250	3.8, 5.4, 3.6, 5.2	−12.8 d(7)	—	102.8, d(18); 78.8; 100.2, d(10); 72.2	38.9, 28.3, 28.3, 27.9	7
$[IrHCl(cod)(PMePh_2)_2]PF_6$	white	63	2210	4.3, 4.8	−14.8 t(16)	2.0, d(10)	99.0, c; 96.3, c	32.9, 28.8	7
$[IrHCl(cod)(PMe_2Ph)_2]PF_6$	white	55	2200	4.9, 4.2	−16.2 t(16)	1.75, 1.95, d(10)	—	—	
$[IrHBr_2(cod)(PPh_3)]$ [e]	yellow	80	2250	3.8, 5.5 3.5, 5.2	−12.5 d(7)	—	101.8, d(20); 79; 100.2, d(12); 72	39.0, 31.0, 29.3, 27.5	7
$[IrHBr(cod)(PMePh_2)_2]PF_6$	white	65	2250	4.8, 4.3	−14.2, t(16)	2.0, d(10)	—	—	6
$[IrHBr(cod)(PMe_2Ph)_2]PF_6$	white	75	2200	4.5, 4.9	−15.5 t(16)	1.7, 1.95, d(10)	97.4, c; 95.1, c	32.6, 29.9	
$[IrHI_2(cod)(PPh_3)]$	yellow	80	2240	4.0, 5.6, 3.7, 5.3	−11.8 d(7)	—	97.2, d(12); 79.6; 94.8, d(18); 71.6	38.0, 35.0, 29.9, 27.1	7

$[IrHI(cod)(PMePh_2)_2]PF_6$	white	45	2230	4.8, 4.3	−13.0, t(16)	2.0, d(10)	—		6
$[IrHI(cod)(PMe_2Ph)_2]PF_6$	yellow	65	2200	4.8, 4.3	−13.0 t(16)	2.0 2.2, d(10)	—		
$[IrCl(cod)(PPh_3)_2]$ [f,g]	yellow-orange	85	—	3.9	—		—	—	12
$[IrCl(cod)(PMePh_2)_2]$ [g]	yellow	75	—	3.4	—	1.6, d(10) [h]	—	—	
$[IrBr(cod)(PPh_3)_x]$ [g,h]	yellow-orange	60	—	3.9	—	—	—	—	
$[IrBr(cod)(PMePh_2)_2]$ [g]	yellow	70	—	3.4	—	1.6, d(10) [j]	—	—	
$[IrI(cod)(PPh_3)_x]$ [f,g,h]	yellow-orange	75	—	4.0	—	—	—	—	
$[IrI(cod)(PMePh_2)_2]$ [g]	yellow	75	—	3.4	—	1.6, d(10) [j]	—	—	

[a] In IR spectrum (Nujol null). [b] In $CDCl_3$ at 30°C (the (cod)vinyl resonances, in particular, were not resolved properly at 100 MHz). Resonances reported as position (δ, ppm), multiplicity (d, doublet; t, triplet), coupling constant (Hz) in parenthesis. [c] In CH_2Cl_2 at 25°C (external D_2O lock) (δ, ppm). [d] Broad resonances $\omega(1/2) \approx 10$ Hz; [e] Crystallised with 1 mol of CH_2Cl_2. [f] Non-conductors in CH_2Cl_2. [g] Fluxional at 20°C (see text). [h] These complexes were never obtained completely pure (see text) x was in the range 1.8—2.1 (microanalysis). [j] A virtually coupled system of the intermediate type (see text). Separation of outer peaks reported.

(cod) ligand; C does not have this symmetry element. We have found, in these situations, that the number of (cod)vinylic resonances in the PMR spectrum, preferably recorded at 270 MHz (see Table 1, note b), and in the proton-decoupled ^{13}C NMR are characteristic of the symmetry of the molecules [4,8,9]. The fact that four separate resonances are observed for these CH groups, in both the PMR and ^{13}C NMR spectra, indicates that there is no plane of symmetry in the molecule, ruling out structure D. The same symmetry relationships are also evident in the ^{13}C NMR resonances of the allylic carbons: four resonances can be clearly distinguished in the region of 25—35 ppm in every case but one (Table 1).

The bis-phosphine substituted complexes II had shown [6] a triplet resonance (^2J(P,H *cis*) 16 Hz) for the hydride ligands. This left structures A and B as possibilities.

The ^{13}C NMR spectrum shows that the molecule possesses a plane of symmetry, since only two vinylic (and only two allylic) resonances ever appear. These complexes (II), therefore, must adopt structure A.

A complex coupling pattern appears for the (cod)vinylic carbons (Fig. 1), apparently due to coupling to both *cis*- and *trans*-L groups. We have only observed this when there are two L groups *trans* to (cod), as for example, in $[Ir(cod)L_2]PF_6$ [9]. Further work is in progress in this area.

A number of other indications confirm this assignment. (i) The PMe resonances in the PMR spectrum of II, for example, are characteristic of equivalent *cis*- (structure A) rather than inequivalent *trans*-groups (structure B). In the case of IIb (L = $PMePh_2$), this resonance is a doublet, but in the case of IIa (L = PMe_2Ph), two doublets arise from the diastereotopic methyl groups of the L ligands. This diastereotopy is itself due to the absence of a plane of symmetry containing the IrP_2 system. (ii) Our previous work [4,8,9] leads us to expect that the chemical shift of the (cod)vinyl PMR resonances should depend on the nature of the *trans*-ligand (see Table 2). The observed shifts (δ 4.2—4.9 ppm) suggest the *trans*-ligand is a tertiary phosphine (structure A). (iii) Chatt [10] showed that the position of ν(Ir—H) absorptions in the IR spectrum depend on the nature of the *trans*-ligand (Table 2). The position of these absorptions for II (2200—2250 cm^{-1}) suggest H is *trans* to X rather than to L or (cod).

Since the M(C=C)H systems in these complexes are coplanar, we examined the possibility of inducing the metal to transfer the coordinated HX to the olefin. We have not yet succeeded, but further experiments are in progress.

TABLE 2

SPECTROSCOPIC DATA FOR 1,5-CYCLOOCTADIENE AND HYDRIDO COMPLEXES OF IRIDIUM

L	δ(CH) [a]	ν(IrH) [b]
Cl, Br, I	2.6—4.0	2160—2250
PR_3	4.2—5.5	2000—2100
H	5.8—6.6	1740—1790
cod	4.1—4.2	2060—2200

[a] Of (cod) vinyl group *trans* to L (ppm) in PMR spectrum. [b] Of IrH vibration in the IR spectrum (cm^{-1}) where H is *trans* to L. Data from refs. 4,8 and 10.

The isolation of intermediates in the addition of HX

When the addition of HI to $[Ir(cod)(PMePh_2)_2]PF_6$ (Ib) is carried out at 0°C in MeOH, an intermediate, IVb, was formed in addition to the usual HI adduct (IIb). IIb is quite soluble in acetone, but IVb is not, so that we were able to achieve almost complete separation of these complexes. Each complex, which was formed in approximately equal quantities, was recrystallized from Me_2CO/MeOH (IIb) or CH_2Cl_2/MeOH (IVb).

We found that this intermediate was $[IrX(cod)(PMePh_2)_2]$ (IVb, X = I), both by microanalysis and PMR spectroscopy (see experimental) and by comparison with a sample of IVb prepared directly from Ib and KI in MeOH (see below). A similar intermediate (IVb, X = Br) was isolated in about 5% yield from the analogous reaction with HBr, or almost quantitatively from KBr and Ib. The chloro-analogue (IVb, X = Cl) could not be isolated from the reaction mixture during HCl addition, but was isolated by the direct reaction of Ib with LiCl. All these complexes are fluxional on the NMR timescale at 35°C and show 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, two sharp peaks flanking an unresolved central resonance, indicates "virtual" coupling of an intermediate type and is consistent with an equatorial—equatorial or, less likely, an axial—equatorial IrL_2 arrangement [11].

These intermediates, when treated with HPF_6 in MeOH, $CHCl_3$ or CH_2Cl_2, gave the HX adducts IIb identical to those formed in the direct reaction.

$$\underset{\text{(IVb)}}{[IrX(cod)L_2]} + HPF_6 \rightarrow \underset{\text{(IIb)}}{[IrHX(cod)L_2]PF_6} \qquad (3)$$

(L = $PMePh_2$; X = Cl, Br, I)

The complexes I do not react with HPF_6 in methanol, nor do they react with HF or KF, since the anions in these cases are insufficiently nucleophilic to effect substitution and the complexes themselves are insufficiently basic to protonate.

Where L is PPh_3, $[IrHX(cod)L_2]PF_6$ (IIc) is never obtained by the action of HX on $[Ir(cod)L_2]PF_6$ (Ic); only $[IrHX_2(cod)L]$ (III) is ever formed, even at low temperature. We therefore tried to obtain IIc (L = PPh_3) by an indirect route. Ic was treated with LiCl to give $[IrCl(cod)(PPh_3)_2]$ (IVc) [12] as a yellow crystalline solid. Treatment of this complex with HPF_6, even at —60°C led to a disproportionation reaction (eq. 4), which gives only III and Ic.

$$2\underset{\text{(IVc)}}{[IrCl(cod)(PPh_3)_2]} + HPF_6 \xrightarrow{-60°C} \underset{\text{(III)}}{[IrHCl_2(cod)PPh_3]} + \underset{\text{(Ic)}}{[Ir(cod)(PPh_3)_2]PF_6} + PPh_3 \qquad (4)$$

All the complexes $[IrX(cod)L_2]$ (IV), especially where L is PPh_3, tended to lose one L on recrystallisation to give a mixture of IV and [IrX(cod)L] (V) [8]. For this reason we were never able to purify IVc, where X = Br or I.

[IrCl(cod)L] (V, L = PPh_3 or $PMePh_2$) [8] did not react at all with HPF_6, nor could an anionic complex of the type $[IrCl_2(cod)L]^-$ be isolated from IV or V with LiCl in acetone or THF.

No intermediates were isolated in the reactions of $[Ir(cod)(PMe_2Ph)_3]PF_6$ (Ia) with HX. Attempts to substitute Ia with X^- failed, as did attempts to protonate the complex with non-coordinating acids.

Addition of I_2 to complex Ic

In more recent studies on the additions of the halogens to complexes of the type Ic (L = PPh_3), we have found an additional, and highly unusual, synthetic route to III via the addition of I_2 to complex Ia. This reaction, in CH_2Cl_2, or in the solid state (see experimental), gives the hydrogen iodide adduct in good yield (75%).

$$\underset{\text{(Ic)}}{[Ir(cod)(PPh_3)_2]^+} \xrightarrow[\substack{CH_2Cl_2 \text{ or} \\ \text{no solvent}}]{I_2} \underset{\text{(IIIc)}}{[IrHI_2(cod)(PPh_3)]} \qquad (5)$$

Possibly, the halogen hydrolyses with adventitious water, the HOI so formed being reduced to HI by PPh_3. Whatever the mechanism (upon which we are currently working), it is striking that a complex capable of oxidative addition should prefer to form the less oxidised HI adduct III, when it would have been expected to form the more oxidised, and as yet unknown, I_2 adduct, $[IrI_3(cod)(PPh_3)]$.

This seems to be another example of the unusual resistance to oxidation exhibited by complex I. These iridium cations show a Lewis acid reactivity pattern both in their reactions with HX (by adding X^- before protonation) and with I_2 (by forming the less oxidised HI adduct in preference to an I_2 adduct). That is, they tend to attract electron density, rather than disperse it, in their reactions. This is unusual among low-valent complexes capable of oxidative addition. These cations may, in this repect, constitute a new and useful class of metal complex, for example, as catalysts [4] resistant to oxidizing poisons.

Conclusions

The kinetic studies of Louw [6] first suggested that halide ion attack preceded protonation in HX addition to I and V. We have now isolated the intermediate (X = I, Br) from the reaction mixtures themselves and demonstrated each individual step separately (X = Cl, Br, I) for HX addition to $[Ir(cod)(PMePh_2)_2]PF_6$ (Ib). Since $[IrCl(cod)L_2]$ (IVb) protonates while [IrCl(cod)L] (Vb) and $[Ir(cod)L_2]PF_6$ (Ib) do not, we believe IVb is the true intermediate in these systems. Louw [6] found that the kinetic parameters of these reactions are invariant upon addition of radical trap such as hydroquinone, which tends to exclude a radical pathway.

A similar mechanism probably also obtains for HX (X = Cl, Br, I) addition to $[Ir(cod)(bipy)]^+$ (bipy=2,2′-bipyridyl) to give $[IrHX(cod)(bipy]^+$, since the same adduct is also obtained from $HClO_4$ and [IrX(cod)(bipy)] [13].

Experimental

The starting materials were synthesised, as previously described [8]. NMR spectra were recorded on Brucker 270 MHz, or Perkin—Elmer R32 90 MHz

instruments (PMR) or on a Varian CFT 20 MHz instrument (^{13}C NMR). Operations involving these complexes need not be carried out with the rigorous exclusion of air, however, inert atmosphere techniques were used. For NMR data, see Table 1.

Formation of hydridodihalo(cyclooctadiene)(triphenylphosphine)iridium (I) Hexafluorophosphates (III). $[Ir(cod)(PPh_3)_2]PF_6$ (100 mg) was treated, in methanol or acetone (5 ml), with a few drops of concentrated hydrohalic acid (HX: X = Cl, Br, I) or, in CH_2Cl_2 (5 ml), with gaseous HX. The solvent was removed in vacuo and the product recrystallised from acetone/methanol, or CH_2Cl_2/Et_2O. The products were identical to those described in ref. 7.

Formation of hydridohalo(cyclooctadiene)bis(methyldiphenylphosphine)-iridium(I) hexafluorophosphates (IIb). Method A. $[Ir(cod)(PMePh_2)_2]PF_6$ (100 mg), in methanol (10 ml) suspension, was treated with a few drops of the pure concentrated hydrohalic acids. The colorless products separated from the mixtures, and were recrystallised from acetone/methanol. They were identical to the products described in ref. 6.

Method B. $[IrX(cod)(PMePh_2)_2]$ (100 mg), in methanol, was treated with a few drops of concentrated aqueous HPF_6. The products, isolated as above, and in similar yield (X = Cl, 65%; X = Br, 70%; X = I, 50%), proved to be rigorously identical (IR, PMR and ^{13}C NMR and analysis) to the products obtained by Method A.

Halo(cyclooctadiene)bis(methyldiphenylphosphine)iridium(I) (IVb). Method A, described above for IIb, was used, except that the reaction was performed at 0° C. The crude product was extracted with acetone, which preferentially dissolved IV. The complexes were recrystallised from acetone/methanol. Yields: X = I, 50%; X = Br, 5%; X = Cl, product not formed.

Method B. $[Ir(cod)(PMePh_2)_2]PF_6$ (100 mg) was treated with KX (50 mg) in methanol (3 ml) for 2 h. The yellow precipitates were collected, washed with water and recrystallised from dichloromethane/ether. (Found (calcd.)) X = I: C, 49.32 (49.33); H, 4.4 (4.6); I, 15.1 (15.3); X = Br: C, 51.0 (52.3); H, 5.0 (4.9); Br, 10.2 (10.2); X = Cl: C, 55.2 (55.5); H, 5.0 (5.2); Cl, 4.1 (4.8)%).

Hydridohalo(cyclooctadiene)bis(dimethylphenylphosphine)iridium(I) hexafluorphosphates (IIa). $[Ir(cod)(PMe_2Ph)_3]PF_6$ (100 mg) was treated with hydrohalic acid as in the preparation of IIb above. The complexes separated and were recrystallised from CH_2Cl_2/Et_2O, or, better, from acetone/methanol in the presence of a little NH_4PF_6. (Found (calcd.) X = Cl: C, 38.3 (38.2); H, 4.6 (4.7); Cl, 4.7 (4.7). X = Br: C, 35.7 (36.9); H, 4.2 (4.4); Br, 10.5 (10.0). X = I: C, 33.8 (33.9); H, 4.1 (4.1); I, 14.8 (14.9)%.)

Halo(cyclooctadiene)bis(triphenylphosphine)iridium(I) (IVc). $[Ir(cod)(PPh_3)_2]PF_6$ (100 mg) was treated with KCl in methanol (3 ml) as for IVb (Method B). The crude product was obtained as for IVb, after washing with water. IVc (X = Cl), so obtained, was identified from PMR [12] and microanalysis. (Found (calcd.) X = Cl: C, 61.2 (61.4); H, 4.7 (4.9); Cl, 4.0 (4.1)%.)

The preparations of the complexes IVc (X = Br, I) were also attempted by an analogous method using KX, but these were never obtained pure (see text). The microanalyses were not reproducible from sample to sample but usually corresponded to $[IrX(cod)(PPh_3)_x]$ $(1.8 < x < 2.1)$ for the crude product.

Protonation of IVb—IVc. These reactions were performed in an NMR tube, in

acetone-d_6 or chloroform-d and the products identified by PMR spectroscopy. For IVb (L = $PMePh_2$) they were also carried out on a preparative scale (100 mg) in methanol. The products so formed (yields: 80%) were rigorously identical to the same products (IIb) formed by the direct addition of HX (eq. 1).

Addition of I_2 to complex Ic. $[Ir(cod)(PPh_3)_2]PF_6$ (Ic, 100 mg) was treated with an equivalent of I_2 either in CH_2Cl_2 or in the absence of solvent. Neither the solvent nor the flask were rigorously dried, although the CH_2Cl_2 was distilled from CaH_2. The complexes were isolated with ether and recrystallised from dichloromethane/ether to give III, rigorously identical (PMR, ^{13}C NMR, analysis) to that obtained above (Yield: 75%).

Observation of protonation reactions

These reactions (e.g., eq. 3) were performed in an NMR tube and followed by PMR spectroscopy. CD_2Cl_2 was a convenient solvent, to which a small drop (0.1 ml) of concentrated aqueous HPF_6 was added. In selected cases (e.g., IIb, Method A and eq. 4) the protonations were also performed on a preparative scale and the products isolated by standard methods. These products proved to be identical (IR, NMR, analysis) to authentic samples prepared by other routes.

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