Journal of Organometallic Chemistry, 168 (1979) 183—195

DIHYDRIDOIRIDIUM DIOLEFIN COMPLEXES AS INTERMEDIATES IN HOMOGENEOUS HYDROGENATION

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(Received August 25th, 1978)

Summary

Two isomeric series of dihydrido-diolefin complex cations, *cis*- and *cis,trans*-$[IrH_2(cod)L_2]PF_6$ (cod = 1,5-cyclooctadiene; L = tertiary phosphine) have been observed directly by PMR spectroscopy and in some cases have been isolated as crystalline solids. They are prepared by H_2 addition to a diolefin complex (unsaturated route) or by diolefin addition to a hydrido complex (hydride route), respectively. These complexes appear to be important intermediates in the catalytic hydrogenation of (cod) by the catalysts $[Ir(cod)L_2]PF_6$. The *cis*- isomers transfer hydrogen to the coordinated (cod) much more rapidly than the *cis, trans* isomers; the hydrogen transfer to the olefin seems to require a coplanar M(C=C)H system. H_2 addition to $[Ir(cod)_2]^+$ at —80° C gives $[IrH_2(cod)_2]^+$; electron-withdrawing substituents therefore do not deactivate the metal center with respect to oxidative addition.

Although dihydrido-olefin complexes have been considered [1,2] as intermediates in the homogeneous hydrogenation of olefins, until our own preliminary report [3] none had been directly observed or isolated. Further examples have, however, recently been described [4].

Two routes can be envisioned for the formation of such dihydrido-olefin complexes in the catalytic cycles of homogeneous hydrogenation reactions catalysed by $[RhCl(PPh_3)_3]$ or similar compounds. One, the "hydride" route (a), involves the attack of an olefin on a dihydrido complex, the other, the "unsaturated" route (b), involves the attack of H_2 on a metal—olefin complex [5] (see eq. 1).

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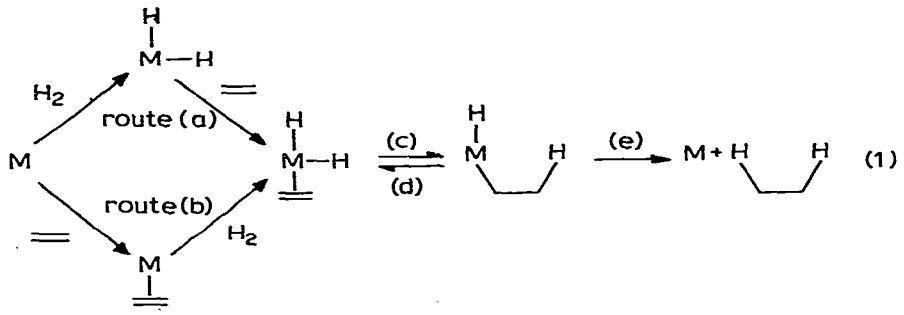


It has been generally held that an olefin, as an electron-withdrawing substituent, should deactivate a metal centre for the "oxidative" addition of hydrogen and the hydride route has therefore been widely proposed as the major mechanistic path for many catalysts of the "dihydride" type [1,5].

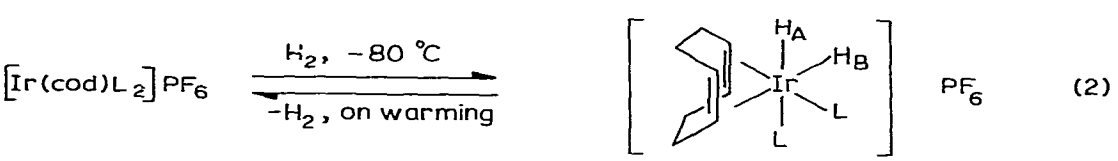
Olefin complexes have been used as hydrogenation catalysts [6] but no adducts formed by direct hydrogen addition to these complexes have ever been observed.

We now report the preparation and, in some cases, the isolation of a number of dihydrido-diolefin complexes synthesised by both the hydride and the unsaturated route. In the catalytic hydrogenation of (cod) by $[Ir(cod)L_2]PF_6$ (L = a variety of neutral ligands such as: PR_3, 1/2(cod)), these dihydrido-diolefin complexes also appear to be intermediates in the reaction.

Results and discussion

The cations cis-$[IrH_2(cod)L_2]^+$

The complex $[Ir(cod)(PMePh_2)_2]PF_6$ (Ia) [6a], in a non-coordinating solvent such as CH_2Cl_2 at 0°C, is the precursor for a highly active hydrogenation catalyst [3,7] which rapidly hydrogenates even tri- and tetra-substituted olefins. The red solution of Ia becomes colorless on admission of hydrogen and the catalyst quickly becomes active for hydrogenation. If the hydrogen is pumped away within the first minute of the experiment the red color of the initial solution is partially restored. More concentrated solutions in an NMR tube behave in the same way: hydrogen is bubbled through a CD_2Cl_2 solution of Ia at 0°C to form the colorless intermediate and nitrogen is bubbled through to sweep out the H_2 and largely restore the red color and the PMR spectrum of the precursor Ia. At −80°C the colorless intermediate is stable for several hours even in air and its PMR spectrum at this temperature unambiguously characterises it as the *cis*-cation (IIa).



(I) (II)

(L = $PMePh_2$ (a); PPh_3 (b); $\frac{1}{2}$dpe (c); $PBu\text{-}n_3$ (d); $\frac{1}{2}$diop (e); $\frac{1}{2}$cod (f); dpe = 1,2-bis(diphenylphosphino)-ethane; diop = L-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane).

On warming in the absence of excess hydrogen, hydrogen is lost and the parent complex is recovered in high yield; some of the iridium complex (ca. 5%) is hydrogenated to give cyclooctane, HPF_6, and $[Ir_2H_5(PMePh_2)_4]PF_6$ [7,8]. If hydrogen is bubbled through the solution of IIa as it is warmed to room temperature, the iridium complex is completely hydrogenated.

A number of analogous complexes of type I also give H_2 adducts at —80° C in CD_2Cl_2 (see eq. 2).

In the PMR spectrum (see Table 1) of IIa—e two sets of metal hydride resonances can be distinguished: one, due to H_A, is coupled to one *trans* {^2J(P—H) = 85—90 Hz} and one *cis* phosphorus nucleus {^2J(P'—H) = 15—20 Hz}; another, due to H_B, is coupled to two inequivalent *cis* phosphorus nuclei {^2J(P—H) ≈ ^2J(P'—H) = 15—20 Hz}. In addition, four peaks due to the four magnetically inequivalent (cod) vinyl protons at δ(ppm) 3.3—5.8 are seen. In the case of the $PMePh_2$ complex IIa, two doublets are observed for the phosphine methyl resonances corresponding to two inequivalent *cis* phosphine ligands.

The complex IIa can be isolated as a white solid by addition of Et_2O at —80° C; it decomposes at about 0° C on warming.

Deprotonation of IIa with, for example, NEt_3 did not occur although the neutral monohydride, IIIa, is known [6b]. This complex (IIIa) can be protonated to give IIa with HPF_6 at —40° C in CD_2Cl_2.

$$\underset{\text{(IIa)}}{\textit{cis}\text{-}[IrH_2(cod)(PMePh_2)_2]PF_6} \underset{HPF_6}{\overset{NEt_3}{\rightleftharpoons}} \underset{\text{(IIIa)}}{[IrH(cod)(PMePh_2)_2]} \qquad (3)$$

$[Ir(cod)(dpe)]PF_6$ (Ic) takes up H_2 at —80° C in CH_2Cl_2 and a white solid can be isolated from the solution in 60% yield by addition of diethyl ether. The IR spectrum of this complex, the stablest of the *cis* dihydrido-olefin complexes (IIc), shows two (Ir—H) bands at 2010 and 2060 cm^{-1}, as expected for *cis* ligands. IIc neither loses H_2 nor transfers it to coordinated (cod) at 0° C; hydrogen transfer does, however, take place at 25° C (see below). Consequently, Ic is activated to give a hydrogenation catalyst at 25° C but not at 0° C [7].

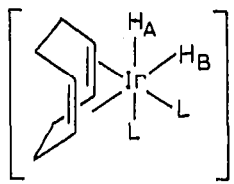
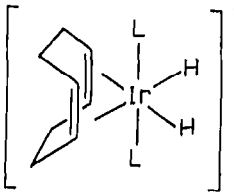
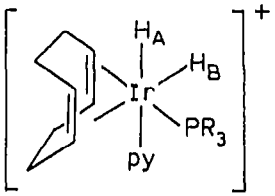
$[Ir(cod)(diop)]PF_6$ adds hydrogen readily, but the product shows only one set of hydride PMR resonances rather than the two sets that would have been expected if the two possible diastereomers of IIe had been formed, and were distinguishable.

$[Ir(cod)_2]PF_6$ (If) takes up H_2 at —80° C to give IIf. The solution shows a singlet hydride PMR resonance, as expected for equivalent hydrogens, and, once again, four distinct (cod) vinyl resonances, as expected for the *cis* stereochemistry. This remarkable reaction shows that electron-withdrawing ligands, such as olefins, need not deactivate the metal center towards H_2 addition.

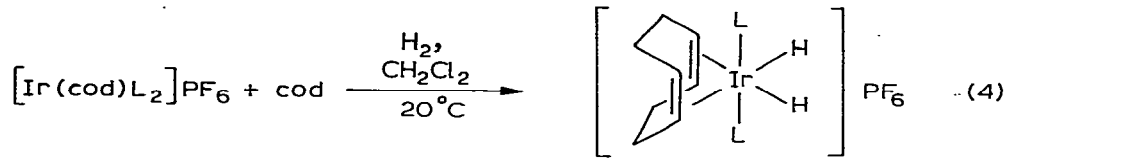
The cations cis,trans-$[IrH_2(cod)L_2]^+$

We were interested to discover whether $[IrH_2(cod)L_2]PF_6$ is an intermediate in the catalytic hydrogenation of (cod) by $[Ir(cod)L_2]PF_6$ (I). A CH_2Cl_2 solution of (cod) and Ia at 20° C was treated with H_2. The PMR spectrum of the mixture showed that an isomer of II, namely *cis,trans*-$[IrH_2(cod)(PMePh_2)_2]PF_6$ (IVa) was rapidly formed in solution. The complex Ib gave an analogous product, IVb.

TABLE 1. PMR DATA FOR THE DIHYDRIDO-DIOLEFIN COMPLEXES

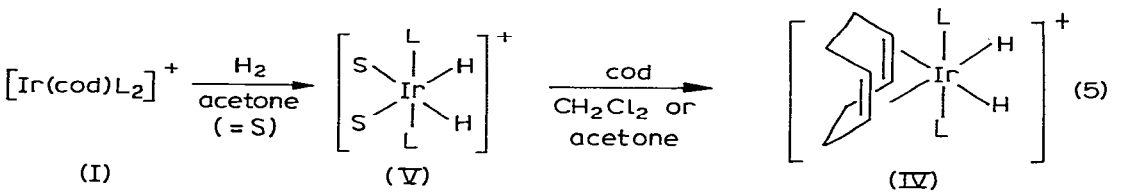
$[IrH_2(cod)L_2]PF_6$ or $[IrH_2(cod)L(py)]PF_6$ [a]		PMR data [b] δ(ppm)			
Configurations	L	Hydride	(cod)vinyl [c]		Other resonances
	$PMePh_2$ [d] IIa	−9.76, dd (20, 90), H_A −13.72, t (16), H_B	3.40 4.60	3.92 5.27	1.9, d and 2.2, d (9), MeP; 6.8–7.9, c, Ph
	PPh_3 [d] IIb	−9.69, dd (20, 85), H_A −12.63, dd (15, 20), H_B	3.29 4.29	3.55 5.81	6.7–7.8, c, Ph
	½(dpe) [d] IIc	−9.83, dd (16, 90), H_A −13.19, t (18), H_B	3.44 4.76	3.71 5.39	0.8–3.3, c, CH_2; 7.0–8.0, c, Ph
	$Pbu\text{-}n_3$ IId	−10.98, dd (20, 85), H_A −14.20, t (20), H_B	3.81 4.60	4.18 4.92	0.7–3.0, c, nBu
	½(diop) IIe	−9.55, dd (20, 90), H_A −14.05, t (18), H_B	3.71 4.71	4.02 5.50	1.05–2.4, c, CH, CH_2 and CH_3; 6.9–7.9, c, Ph
	½(cod) IIf	−14.8, s	3.30 4.44	3.44 5.08	
	$PMePh_2$ [d] IVa	−13.6, t (20)	4.10		2.5, t (7) [e], PMe; 7.3–7.8, c, Ph
	PPh_3 IVb	−13.3, t (15)	4.21		7.4–7.7, c, Ph
	PCy_3 VIIa	−18.0, d (19), H_A −12.7, d (20), H_B	4.45 4.90		0.8–2.5, c, Cy; 7.1–8.0 and 8.7–8.9, c, Ar
	(P-i-Pr_3 VIIb	−18.0, d (18), H_A −12.4, d (20), H_B	4.31 5.0	4.50	0.95–2.5, c, i-Pr; 7.2–8.1 and 8.7–8.9, c, Ar

[a] dpe = 1,2-bis(diphenylphosphino)ethane; diop = L-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane. [b] In CD_2Cl_2 at −80° C. Resonances reported as follows: position (δ), multiplicity (coupling constant in Hz), assignment. s = singlet, d = doublet, dd = doublet of doublets, t = triplet, c = complex resonance, Ar = aromatic group. In all cases satisfactory integrals were obtained. All compounds have a complex resonance at 1.8–2.6 δ assigned to the (cod)CH_2 protons. [c] Broad unresolved resonance(s) $\{\omega(1/2) \sim 10$ Hz$\}$. In complexes II and VII four (cod)vinyl resonances are expected as each proton is magnetically distinct; in most cases all these resonances can be distinguished. [d] These complexes were isolated as crystalline solids. [e] $|^2J(PH) + {}^4J(P'H)|$ since this is a virtually coupled system.



In the case of IVa, the pure white crystalline solid can be isolated by the addition of Et_2O at —80°C. This solid loses H_2 rapidly to give Ia only on heating above 85°C.

Dihydrido-diolefin complexes are also formed by the addition of the diolefin to a hydrido complex. The solvated cation $[IrH_2(S)_2L_2]^+$ (V, S = acetone, ethanol; L = $PMePh_2$, PPh_3) [6a] reacts readily with (cod) in acetone or in CH_2Cl_2 to give the same *cis,trans*-dihydrido-diolefin complexes, IV. This reaction may be followed in an NMR tube by mixing V and an equivalent of (cod) in CD_2Cl_2 at —80°C and raising the temperature. Between —40 and —30°C the free (cod) replaces the coordinated acetone and their PMR signals are smoothly and completely replaced by signals due to coordinated (cod) and free acetone. The hy-



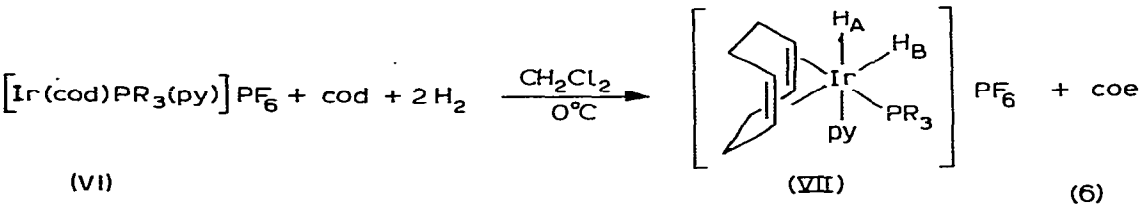
dride resonances of IV also completely replace those of V over the same temperature range.

The PMR spectra of the complexes IV (see Table 1) are much simpler than those of the *cis* isomer II. The main features are: a triplet hydride resonance due to coupling with two *cis* phosphorus nuclei (^2J(P—H) ~ 16 Hz); a single broad (cod) vinyl resonance; and, for the $PMePh_2$ complex, a triplet PMe resonance characteristic [9] of a *trans* arrangement of these ligands. The complexes Ic, Ie, If, having chelating ligands L, never gave analogous complexes of type IV.

We have not found any evidence for a direct interconversion of either of the complexes II and IV under any conditions other than by the reactions of eqs. 2 and 4 (see also Scheme 2).

The cations cis-$[IrH_2(cod)(PR_3)py]^+$

The complexes $[Ir(cod)(PR_3)py]PF_6$ (VI, PR_3 = PCy_3, P-i-Pr_3), which appear to be the most active hydrogenation catalysts yet described, particularly for tri- and tetra-substituted olefins [7], react with H_2 at 0°C in CH_2Cl_2 in the presence of excess (cod) to give the *cis*-dihydrido-diolefin complexes VII. Their stereochemistry is as shown in eq. 6; this follows from their PMR spectra at —80°C listed in Table 1, in particular. Only *cis* phosphorus—hydride coupling constants are observed for each of the inequivalent hydrido ligands and inequivalence of the (cod) vinyl protons is also observed. None of the three other possible isomers could give this spectrum.



(VI) (VII) (6)

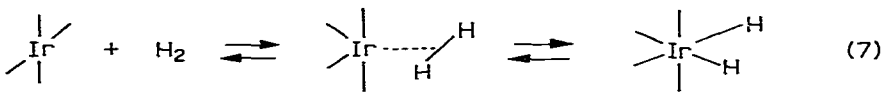
(coe = cyclooctene; R = Cy, a; i-Pr, b)

The assignment of H_A and H_B resonances in these complexes (see Table 1) is based on the observation by Chatt [10] that the hydridic chemical shifts in a wide variety of hydridoiridium(III) complexes depends on the nature of the *trans* ligand. Where the *trans* ligand is (cod) we find chemical shifts of −11.9 to −14.8 δ in the complexes II and IV. This suggests that the doublets between −12 and −13 δ in VII can be assigned to H_B. We have recently prepared a number of iridium(III) hydrido complexes having pyridine *trans* to hydride [11]; hydride chemical shifts around −19 δ are typical, suggesting the assignment of the remaining doublets at −18 δ to H_A. Both sets of hydride resonances arise from the same complex since they disappear together on raising the temperature to ca. 0°C.

We have no evidence that VII is formed in the direct activation of H_2 by VI in the absence of excess (cod) such as probably occurs when VI is used as a hydrogenation catalyst, in spite of many efforts to observe intermediates formed in this reaction at temperatures from −80 to +20°C. Possibly, a different and more labile isomer of VII is formed in this case.

Properties of the dihydrido complexes

The dihydrido complexes (II) formed by direct addition of H_2 to $[Ir(cod)L_2]PF_6$ (I) have a stereochemistry consistent with the concerted attack of H_2 from one side of the square plane of the complex, as discussed by Vaska [12] (cf. eqs. 2 and 7).



(7)

The *cis,trans* complexes IV, however, cannot be formed directly from I, but only from a precursor containing an as yet unknown *trans*-chelating (cod) ligand; we believe they are in fact always formed by (cod) addition to a hydrido complex (see below).

The stability of IV towards concerted loss of H_2 is probably also the result of stereochemical constraints which prevent the (cod) ligand from spanning the incipient *trans* ligand sites in the transition state for H_2 loss (eq. 7).

Table 2 lists the temperatures at which the dihydrido-diolefin complexes lose hydrogen, both in solution and in the solid state, in the absence of excess hydrogen. These figures give a measure of the stability of the hydride involved and the affinity of the parent complex for hydrogen.

The following analogous complexes failed to give observable adducts with H_2 under the conditions of eqs. 2 and 4: $[Rh(cod)_2]PF_6$, $[Rh(cod)(PPh_3)_2]PF_6$,

TABLE 2

THERMAL STABILITIES OF THE DIHYDRIDO COMPLEXES

Complex [a]		Temperature [b] (°C)	
		Solid	Solution
cis,trans-[IrH_2(cod)L_2]PF_6	IVa, b	85 [c]	45 [d]
cis-[IrH_2(cod)(dpe)]PF_6	IIc	40	20 [d]
cis-[IrH_2(cod)L(py)]PF_6	VIIa, b	—	0
cis-[IrH_2(cod)L_2]PF_6	IIa, b, d, e	0 [e]	−20
cis-[IrH_2(cod)$_2$]PF_6	IIf	—	−40

[a] cod = 1,5-cyclooctadiene; dpe = 1,2-diphenylphosphinoethane; the nature of L is indicated by the letters which follow the roman numerals in each case (please refer to Table 1 or eq. 2). [b] Approximate temperature of rapid $\{t(1/2) \approx 5\ s\}$ H_2 loss in air and in the absence of excess H_2, in the solid state or in solution. [c] To give [Ir(cod)L_2]PF_6 and only ca. 5% of $[Ir_2H_5L_4]PF_6$. [d] Considerable hydrogenation of coordinated (cod) takes place (ca. 30%) in these decomposition reactions. [e] L = PPh_3, $PMePh_2$.

[Rh(cod)(P-i-Pr_3)py]PF_6, [M(cod)py_2]PF_6, (M = Rh, Ir; py = pyridine), although all but the bis-pyridine complexes are hydrogenation catalysts [7] for olefins at 20°C in CH_2Cl_2. Rhodium complexes are generally more reluctant to form adducts with H_2 than iridium complexes [12,13] but the deactivating effect of pyridine (see also Table 2), a relatively donor ligand, was unexpected. The chloride ion, again strongly donor, also deactivates the metal center; the complexes [IrCl(cod)L] (L = PPh_3 or py) fail to add hydrogen at −80°C.

The nature of the hydrogen addition process

Donor ligands normally favor H_2 addition to a metal center [1,5,12]. This behaviour is consistent with the metal acting as a Lewis base, and with an addition having oxidative character.

In our case, in contrast, donor ligands inhibit H_2 addition (e.g., the donor ligands Cl^- and pyridine in [IrCl(cod)L] and [Ir(cod)py_2]$^+$), while acceptor ligands do not seem to affect it (e.g., $[Ir(cod)_2]^+$, containing only the relatively electron-withdrawing (cod) ligands, readily adds H_2). It is possible that these iridium cations behave more as Lewis acids than Lewis bases. If this is so, H_2 addition to these systems may be less oxidative than is commonly the case, and may even be reductive in character. Recently, we found a further example of Lewis acid behavior for Ia, which fails to react with H^+, but adds hydrogen halide (X ≠ F) by X^- addition, followed by protonation [14,15].

The hydrogenation of (cod) by [Ir(cod)L_2]PF_6

The reaction of eq. 4 above constitutes a homogeneous hydrogenation of free (cod) with [Ir(cod)L_2]PF_6 (I) as catalyst. The hydrogen absorption curve at 20°C (see Fig. 1) shows that for Ia this proceeds in stages. For Ib the absorption curve is similar.

Over a few seconds, the red color of the starting complex fades to give a colorless solution of IIa; the characteristic high field PMR resonances of this complex can be observed at −80°C in an aliquot of the sample. The hydrogenation solution continues to absorb hydrogen rapidly (35 mol H_2 {mol Ir}$^{-1}h^{-1}$ when 1 mol H_2 {mol Ir}$^{-1}$ has been absorbed {see Experimental}) but the rate

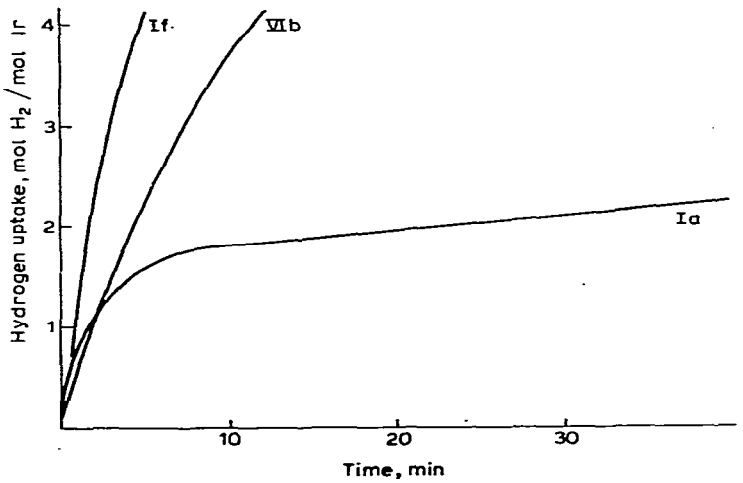


Fig. 1. Hydrogen uptake curves for the hydrogenation of free (cod) by the complexes $[Ir(cod)_2]PF_6$ (If); $[Ir(cod)(Pi\text{-}Pr_3)(py)]PF_6$ (VIb); and $[Ir(cod)(PMePh_2)_2]PF_6$ (Ia), in CH_2Cl_2 solution at 20°C in a constant-volume apparatus (see Experimental). The incipient curvature of the plots for If and VIb is a result of the limited quantity of H_2 {ca. 6 mol(mol Ir)$^{-1}$ }available in these experiments.

progressively slows as IIa is converted into IVa by the reaction of eq. 4, until after 8 min only IVa is present, as shown by the high-field PMR spectrum of an aliquot of the sample at —80°C, and the hydrogenation rate falls to 0.9 mol H_2-{mol Ir}$^{-1}h^{-1}$. The major product of the hydrogenation was cyclooctene, but some cyclooctane and 1,3-cyclooctadiene were also formed (see Experimental).

These results are consistent with the observation that IIa decomposed very much faster ($t\{1/2\} \approx 30$ s) than IVa ($t\{1/2\} \approx 30$ min) in PMR studies under H_2 in CD_2Cl_2 at 0°C, to give, in each case, $[Ir_2H_5L_4]PF_6$.

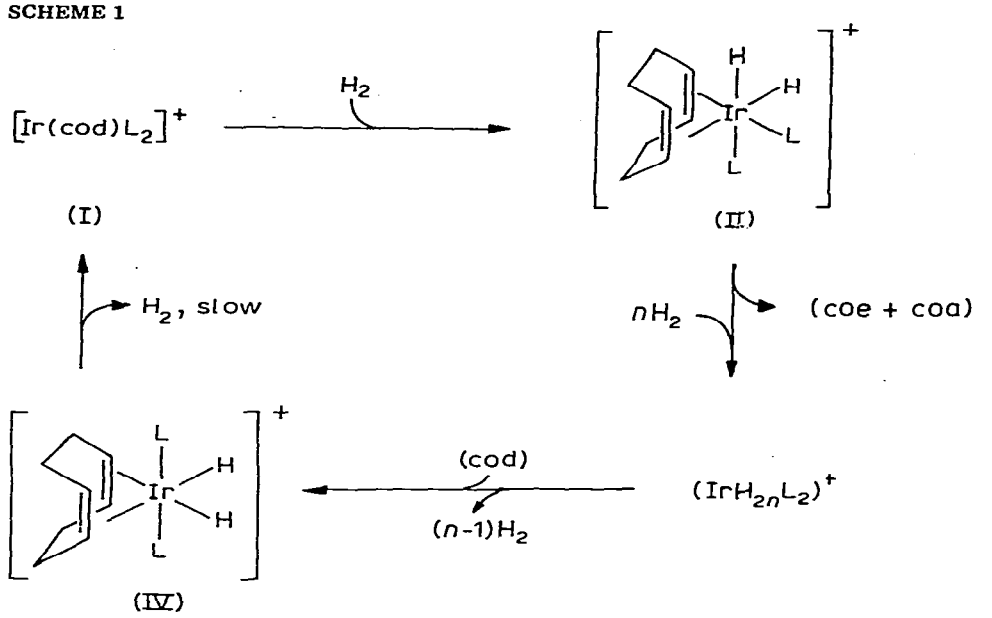
In contrast, $[Ir(cod)_2]PF_6$ (IIf) and $[Ir(cod)P\text{-}i\text{-}Pr_3(py)PF_6$ (VIb) rapidly and steadily hydrogenate (cod) under the same conditions (Fig. 1; rates: IIf, 60 mol{mol Ir}$^{-1}h^{-1}$; VIb, 25 mol{mol Ir}$^{-1}h^{-1}$), and only show the intermediates *cis*-$[IrH_2(cod)_2]PF_6$ (IIf) and *cis*-$[IrH_2(cod)P\text{-}i\text{-}Pr_3(py)]^+$ (VIIb) by PMR spectroscopy at —80°C.

It is likely that the rate-limiting step in the hydrogenation is the insertion of the coordinated (cod) into the M—H bond, since only the dihydrido-diolefin complexes, and not, for example, alkyl-hydrido complexes, were ever observed in these solutions.

These observations suggest that those complexes (IIa, IIf and VIIb) containing a coplanar M(C=C)H grouping more readily undergo the olefin insertion reaction than does the complex (IVa) which contains a *cis*- but non-coplanar M(C=C)H arrangement. Similar suggestions have been made for olefin insertion [16a], nucleophilic addition to coordinated olefin [16b] and for the β-elimination reaction [16c], the inverse of olefin insertion. We have now been able to test these ideas, as applied to olefin insertion, in an isomeric series of dihydrido-diolefin complexes, for the first time.

The slow hydrogenation of (cod) by *cis,trans*-$[IrH_2(cod)L_2]^+$ (IV) may be due to a slow transfer of hydrogen to (cod) within IV itself. More likely, a slow loss of hydrogen from IV gives I, which can take up H_2 to give the *cis*-dihydride II

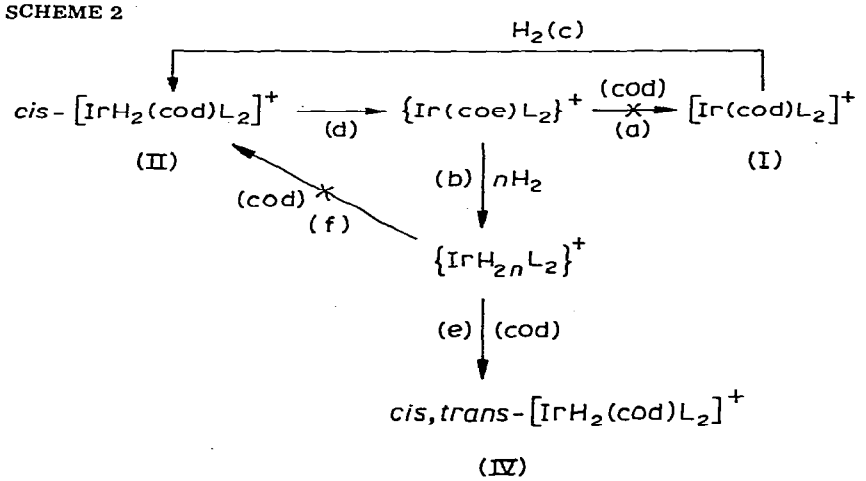
SCHEME 1



(L = $PMePh_2$, a; PPh_3, b. $n = 2$ or 3.
coe = cyclooctene; coa = cyclooctane)

(Scheme 1). II would then rapidly transfer hydrogen to the coordinated (cod) to give the *cis,trans* isomer, IV. Consistent with the latter route is the fact that IIa and IVa give the same organic products of (cod) hydrogenation (see Experimental). Scheme 1 shows the hydrogenation of cyclooctadiene by $[Ir(cod)L_2]^+$.

SCHEME 2



(L = $PMePh_2$ or PPh_3)

All species shown have been observed directly except $(IrH_{2n}L_2)^+$.

After complex II has transferred its hydrogen to the cod ligand, it seems to add H_2, rather than (cod) (Scheme 2). If the reaction proceeded to a significant extent via the latter pathway (a), more hydrogen would be absorbed (via steps a, c, d, b, and e) in the first 8 min of the hydrogenation of Fig. 1 than is observed. After this time, formation of IV is complete. The reaction must therefore go largely, or exclusively, via steps d, b, and e. Similarly, the addition of (cod) to the resulting intermediate seems to give predominantly IV (step e), and not II (step f), since, once again, more hydrogen absorbtion would be expected if II were formed. While we still lack direct evidence for step (e), we have already shown (eq. 5) that IV is the exclusive product of the addition of (cod) to the related hydride $[IrH_2(solvent)_2L_2]^+$ (V). It seems likely, therefore, that in the catalytic system, the hydride mechanism (b, then e) predominates. The initial activation of the catalyst (step c), in contrast, can be considered as an example of the unsaturated pathway. The formation of *cis,trans*-$[IrH_2(cod)L_2]^+$ in the hydrogenation of (cod) by the complexes I is shown in Scheme 2.

Some of these results have appeared in two previous notes [3,17].

Conclusion

We have shown that dihydrido-olefin complexes can be stable enough to be isolated. They appear to be intermediates in the catalytic hydrogenation of (cod) by $[Ir(cod)L_2]PF_6$ (I), and can even be detected in the catalytic solutions themselves. The "hydride" and "unsaturated" routes to these complexes have each been observed directly. Our studies of the reactivity of these complexes suggest that M(C=C)H coplanarity is required for olefin insertion into the M—H bond. In contrast to previous results on other systems, electron-withdrawing ligands do not seem to inhibit H_2 addition to the complexes I, which constitutes the "unsaturated" route to the dihydrido-olefin complexes.

Experimental

The precursor iridium [6,18,19] and rhodium [6,20] complexes were prepared by standard Schlenk tube techniques under nitrogen. Other reagents were obtained from Fluka AG or, in the case of PCy_3, prepared by M. Claude Frajerman, whom we thank, from CyMgBr and PCl_3 [21]. Hydrogen was supplied by Air Liquide.

NMR spectra were measured on Perkin—Elmer R 12B (35°C) and Bruker H-90 (—80°C) instruments. Microanalyses were performed by the Service de Microanalyses, C.N.R.S., Gif-sur-Yvette. Product analyses were made by GLC on a Perkin—Elmer F11 instrument with a Carbowax 20M, 3.5 m column at 90°C using decalin as internal standard.

The observation of the cations cis-$[IrH_2(cod)L_2]^+$ (II)

Hydrogen was bubbled (ca. 5 ml min^{-1}) through a red solution of $[Ir(cod)L_2]PF_6$ (40 mg, I; L = $PMePh_2$, PPh_3, 1/2 dpe, $PBu\text{-}n_3$, 1/2 diop, 1/2 cod) in CD_2Cl_2 (0.4 ml) at —80°C in a PMR tube by means of a glass capillary or, better, a stainless steel tube. After 2 min the colorless sample was transferred to

the NMR spectrometer at a probe temperature of —80°C. The spectra recorded are listed in Table 1. These spectra were unaffected by the addition of NEt_3 (0.1 ml). Where L = PPh_3 (IIb) addition of diethyl ether at —80°C gave a white solid which was filtered cold. This solid became red on heating to room temperature and the IR spectrum of the red solid confirmed its identity as Ib. Where L_2 = dpe (IIc) a white microcrystalline solid was isolated in the same way. The PMR spectrum of this solid in CD_2Cl_2 at —80°C was as listed in Table 1 and the IR data were as follows: ν(Ir—H) = 2010 and 2060 cm^{-1} (medium—weak); other peaks similar to Ic. The solid decomposed over several days even under N_2 at —30°C.

The protonation of the complex [IrH(cod)(PMePh$_2$)$_2$] (IIIa)

[IrH(cod)($PMePh_2$)$_2$] (40 mg) in CD_2Cl_2 (0.4 ml) at —40°C reacted with aqueous HPF_6 (60%, 0.05 ml) in an NMR tube to give a solution having a PMR spectrum at —80°C identical to that observed for IIa above. No *cis,trans* isomer was observed.

The observation of the cations cis,trans-[IrH$_2$(cod)L$_2$]$^+$ (IV)

Method A. Hydrogen was bubbled as described above into the red solutions of [Ir(cod)L_2]PF_6 (40 mg, L = $PMePh_2$, PPh_3) and (cod) (0.05 ml) in CD_2Cl_2 (0.4 ml) at 20°C in an NMR tube. After 5 min the spectra listed in Table 1 were obtained from the colorless samples.

Method B. [$IrH_2(Me_2CO)_2L_2$]PF_6 (35 mg, L = $PMePh_2$, PPh_3) in CD_2Cl_2 (0.4 ml) at —80°C in an NMR tube was treated with (cod) (10 μl). On warming to —30°C the peaks of the starting compounds were replaced by the peaks of the corresponding *cis,trans*-[IrH_2(cod)L_2]$^+$ cations and that of free Me_2CO.

cis,trans-Dihydrido(η-cyclooctadiene)bis(methyldiphenylphosphine)iridium-(III) hexafluorophosphate (IVa)

A red solution of [Ir(cod)($PMePh_2$)$_2$]PF_6 (150 mg) in CH_2Cl_2 (2 ml) containing (cod) (0.3 ml) was stirred under H_2 for 60 min. To the resulting colorless solution, cooled to —80°C, was added Et_2O. Fine white microcrystals of the dichloromethane (determined by PMR in $CDCl_3$) solvate separated and were filtered, washed with Et_2O and dried in air. Yield 100 mg (60%). Anal.: Found: C, 45.5; H, 4.7. $C_{34}H_{38}F_6P_3Ir \cdot 2/3CH_2Cl_2$ calcd.: C, 45.3; H, 4.6%. IR data: ν(Ir—H) = 2170 cm^{-1} (medium—weak).

The observation of the cations cis-[IrH$_2$(cod)(PR$_3$)py]$^+$ (VII)

A yellow solution of [Ir(cod)(PR_3)py]PF_6 (40 mg, R = Cy, i-Pr) in CD_2Cl_2 (0.4 ml) containing (cod) (20 μl) at 0°C in an NMR tube was treated with H_2 as above. After 5 min, the colorless sample was cooled to —80°C and the spectra listed in Table 1 were obtained.

The hydrogenation experiments

The hydrogenation experiments were carried out in a closed vessel of total volume 58.8 ml, equipped with a magnetic stirrer, a vacuum tap, and a capillary manometer. The CH_2Cl_2 (1 ml) solution of the complex (0.17 mmol) and (cod) (0.3 ml) to be studied was degassed by two freeze-thaw cycles in vacuo. The

solution was brought to 20°C with a thermostatted water bath and CH_2Cl_2-saturated H_2 admitted until the pressure indicated by the manometer was ca. 70 cmHg. After 3 min, to allow for equilibrium to be established, vigorous stirring of the solution led to a rapid decolorization of the sample and corresponding H_2 uptake (ca. 0.85 mol H_2 {mol Ir}$^{-1}$, theor.: 1.0 mol H_2 {mol Ir}$^{-1}$, see below).

The hydrogenation of Ia was followed for 60 min, during which time the product ratios (cyclooctene, 75%; cyclooctane, 15%; 1,3-cyclooctadiene, 10%) varied little (±3%). These products were determined from GLC peak areas for a sample obtained by quenching the reaction mixture at −80°C and precipitating the metal complexes with pentane. The ratio and identities of the metal hydrido complexes were determined from the PMR spectrum (high-field region only) of an aliquot of the reaction mixture, transferred to an NMR tube at −80°C with a steel catheter.

The hydrogen uptake curves were repeatable (±10%). They showed that at any time only ca. 85% of the hydrogen had been absorbed compared to what was required by the products formed: coe and coa, as measured by GLC; and isomers of $[IrH_2(cod)L_2]^+$, assuming that iridium is only present in this form in the catalytic solutions. It is possible that under the dynamic conditions of the catalytic experiment, some of the iridium was present in the form of colorless complexes other than isomers of $[IrH_2(cod)L_2]^+$($[Ir(cod)(coe)L_2]^+$ or some cluster complex) which were not observed in the static PMR experiments. Alternatively, hydrogen dissolved in the CH_2Cl_2 at the moment of quenching may have continued to be transferred to the olefin substrate before the sample was completely quenched. Despite continuous and strenuous efforts we have not yet been able to refine our experimental technique to obtain a better measure of the hydrogenation rate due to IIa. We were, however, able to show that it is very much faster than that due to IVa. We have therefore considered that the rate of hydrogen uptake at the point in the plot of Fig. 1 where 1 mol H_2-(mol Ir)$^{-1}$ has been absorbed (to account for the initial formation of $[IrH_2$-$(cod)L_2]^+$), corresponds to a lower limit for the rate of hydrogen transfer to coordinated (cod) by IIa, and that the slope of the linear portion of the plot corresponds to the hydrogenation rate for IVa. The following rates are ob-obtained: IIa, 35 mol H_2(mol Ir)$^{-1}h^{-1}$; IVa, 0.9 mol H_2(mol Ir)$^{-1}h^{-1}$. We believe, therefore, that IIa hydrogenates (cod) at least 40 times faster than does IVa.

All the hydrogenation solutions, except those derived from If and VIa and b, were colorless or pale yellow when stirred under H_2 and the corresponding hydrido complexes were apparently present in solution even at 20°C in these experiments. In these cases on stopping the stirrer the color of the precursor complexes Ia—c returned as the dissolved hydrogen was exhausted from the CH_2Cl_2. A thin layer at the surface of the solutions remained colorless, presumably due to the diffusion of H_2 into the solutions. Solutions derived from IVa and b became very pale yellow on cooling to 0°C, but solutions derived from If retained the red color of the precursor complex even at this temperature.

Acknowledgements

We thank the Compagnie des Métaux Précieux for a loan of iridium, and Mr. B. Septe for help in obtaining the NMR spectra.

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