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CATIONIC IRIDIUM DIOLEFIN COMPLEXES AS ALKENE HYDROGENATION CATALYSTS AND THE ISOLATION OF SOME RELATED HYDRIDO COMPLEXES

ROBERT H. CRABTREE *, HUGH FELKIN and GEORGE E. MORRIS **

Institut de Chimie des Substances Naturelles, C.N.R.S., 91190 Gif-sur-Yvette (France)

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Summary

In non-coordinating solvents, such as CH_2Cl_2, the complexes $[Ir(cod)L_2]PF_6$ (I) and $[Ir(cod)L(py)]PF_6$ (II) (cod = 1,5-cyclooctadiene; py = pyridine, L = tertiary phosphine) are very active homogeneous hydrogenation catalysts for alkenes. When the alkene has been consumed, or, in certain cases, only partially consumed, the catalyst is irreversibly deactivated; the metal-containing product from I is $[Ir_2(\mu\text{-}H)_3H_2L_4]PF_6$ (III). With HCl, III gives $[Ir_2(\mu\text{-}Cl)_2(\mu\text{-}H)H_2L_4]PF_6$. The catalyst system from I gives the isolable complexes $[IrH_5L_2]$ with NEt_3, while that from II gives these complexes in the presence of NEt_3 and an excess of L.

Introduction

Osborn [1] showed that in coordinating solvents such as acetone, ethanol or THF, the complexes $[M(cod)L_2]ClO_4$ (M = Rh or Ir; cod = 1,5-cyclooctadiene; L = tertiary phosphine) [1,2] react with hydrogen to give the isolable complexes $[MH_2L_2S_2]ClO_4$ ***. These are active hydrogenation catalysts for alkenes and, in some cases, selective catalysts for the reduction of alkynes or alkadienes to alkenes [3]. The iridium complexes were found to be less effective catalysts [4] than the rhodium analogues, and attention was therefore concentrated on the rhodium systems [2,3].

We found that the use of non-coordinating solvents [5] enhanced the catalytic activity of the rhodium complexes and we isolated a new series of catalytically active complexes of the type $[M(cod)L(py)]PF_6$ (M = Rh, Ir; py = pyridine) [5c,6]. We therefore decided to examine the catalytic activity of $[Ir(cod)L_2]PF_6$

* To whom correspondence should be sent at his present address: Sterling Chemistry Laboratory, Yale University, 225 Prospect Street, New Haven, Conn. 06520 (U.S.A.).

** Present address: Inorganic Chemistry Laboratory, South Parks Road, Oxford, OX1 3QR (Great Britain).

*** S = solvent.

(I) and [Ir(cod)L(py)]PF_6 (II) for alkene hydrogenation in non-coordinating solvents such as CH_2Cl_2. We have briefly reported some of our results [5b].

Results and discussion

The red complexes [Ir(cod)L_2]PF_6 (Ia: L = $PMePh_2$, Ib: L = PPh_3) dissolve readily in CH_2Cl_2 at 0°C. In the presence of a suitable substrate alkene, these solutions decolourise upon admission of H_2, and become highly active catalysts for alkene hydrogenation. Figure 1 shows some typical hydrogen absorption curves for Ia with a variety of substrates. The rates of reduction are considerably greater, particularly with the more highly substituted alkenes, than those observed, under comparable conditions, with [$RhCl(PPh_3)_3$] [7] or other similar systems [8]. Some comparative rates are listed in Table 1. The iridium catalysts show much smaller rate differences between mono-, di-, tri- and tetrasubstituted alkenes than do other homogeneous hydrogenation systems [3,7,8,]. The selectivity is greater, however, when two different alkenes are reduced together rather than separately (see Table 1, note d).

The reductions of 1-methylcyclohexene and 2,3-dimethyl-2-butene do not proceed to 100% under the conditions of Fig. 1 but only to 94.5% and 20%, respectively. At this point the colour of the solution becomes yellow and the catallyst is irreversibly deactivated. For 1-hexene and cyclohexene this deactivation also occurs, but only after all the substrate has been consumed. The metal complex formed in this process, the novel dimer [$Ir_2(\mu\text{-}H)_3H_2L_4$]$PF_6$ (III), was studied in detail only where L = PPh_3 (IIIb).

$$2[Ir(cod)L_2]PF_6 + 7H_2 \rightarrow [Ir_2(\mu\text{-}H)_3H_2L_4]PF_6 + HPF_6 + 2\ \text{cyclooctane} \qquad (1)$$

(I) (III)

(a: L = $PMePh_2$; b: L = PPh_3)

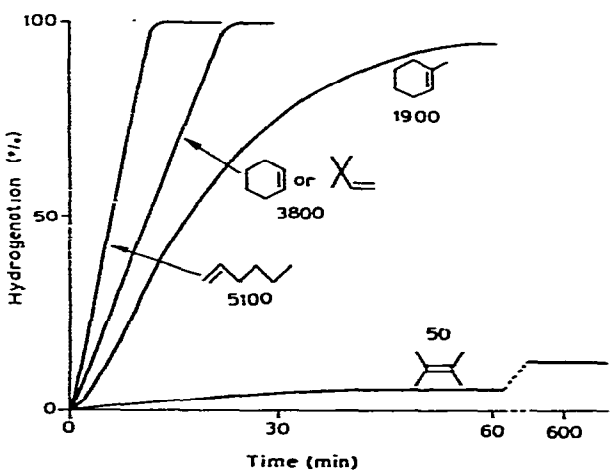


Fig. 1. Hydrogen absorption curves for the reduction of a variety of alkenes (0.5 *M*) in CH_2Cl_2 at 0°C catalysed by [Ir(cod)$(PMePh_2)_2$]PF_6 (Ia, 0.5 m*M*) in the constant-pressure apparatus ($p(H_2)$ 620 mmHg). The figures refer to the maximum rates observed expressed in mol H_2 (mol Ir)$^{-1}$ h^{-1}.

TABLE 1

COMPARATIVE RATES OF REDUCTION OF CYCLOHEXENE AND 1-METHYLCYCLOHEXENE BY A NUMBER OF CATALYSTS

Catalyst	Cyclohexene			1-Methylcyclohexene		
	Max. rate [a]	Extent of hydrogenation [b] (%)	Time [c] (min)	Max. rate [a]	Extent of hydrogenation [b] (%)	Time [c] (min)
[Ir(cod)(PMePh$_2$)$_2$]PF$_6$ [d] (Ia)	3700	100	22	1900	94	60
[Ir(cod)P-i-Pr$_3$(py)]PF$_6$ [d] (IIa)	4500	99.5	15	3800	35	15
[Ir(cod)(dpe)]PF$_6$ [e] (Ic)	1300	100	85	640	72	120
[Ir(cod)(PMe$_2$Ph)$_3$]PF$_6$ [f] (Vb)	1200	100	80	370	65	150
[RhCl(PPh$_3$)$_3$] [g]	700	100	120	12	100	9000

[a] The maximum rate observed during the reduction expressed in mol. H_2 absorbed per mol catalyst per h in the constant-pressure apparatus (see experimental). Catalyst: 0.5 m*M* in CH_2Cl_2 at 0°C Substrate: 0.5 *M*, $p(H_2)$ 600 mmHg, except where stated. [b] The extent of reduction of the substrate when deactivation occurs determined by GLC. [c] After which no further hydrogen is absorbed. [d] In the reduction of a mixture of cyclohexene (0.5 *M*) and 1-methylcyclohexene (0.5 *M*) under the same conditions, the maximum rates observed were 4200 (Ia) and 4800 (IIa), respectively. After absorption of half the hydrogen required for total reduction, the proportions of cyclohexane and methylcyclohexane in the products were 23/1 (Ia) and 5/1 (IIa), respectively. [e] At 20°C, induction time 15 min, $p(H_2)$ 400 mmHg. [f] At 20°C, induction time 15 min, $p(H_2)$ 400 mmHg, catalyst 1 m*M*. [g] In C_6H_6 at 25°C (our measurements).

The orange complexes [Ir(cod)L(py)]PF$_6$ (IIa: L = P-i-Pr$_3$; IIb: L = PPh$_3$; IIc: L = PCy$_3$) readily dissolve in CH_2Cl_2 at 0°C to give, under hydrogen and in the presence of a suitable substrate, light yellow catalytically active solutions. Figure 2 shows some typical absorption curves for IIa with a variety of alkenes. The results are broadly similar to those observed for complexes I. The phenomenon of deactivation occurs in exactly the same way, but the iridium-containing products have not yet been characterised.

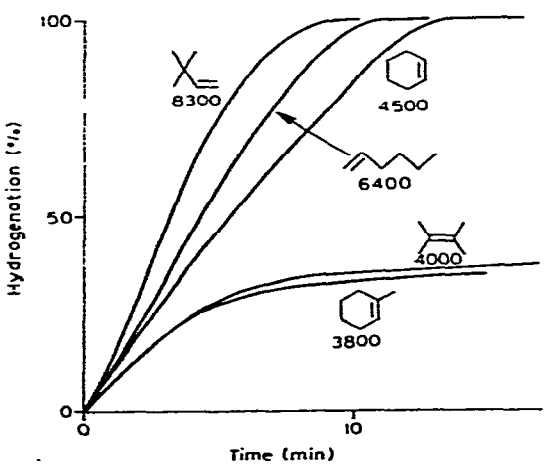


Fig. 2. Hydrogen absorption curves for the reduction of a variety of alkenes (0.5 *M*) in CH_2Cl_2 at 0°C catalysed by [Ir(cod)P-i-Pr$_3$(py)]PF$_6$ (IIa, 0.5 m*M*) in the constant-pressure apparatus ($p(H_2)$ 620 mmHg). The figure below each substrate refers to the maximum rate observed expressed in mol H_2 (mol Ir)$^{-1}$ h^{-1}.

We have been unable to find conditions in which the catalysts I and II are not deactivated at all; nevertheless, complete reduction even of tetra-substituted olefins can be achieved. The hydrogenation of 2,3-dimethyl-2-butene (0.5 *M*) in CH_2Cl_2 with IIa, for example, proceeds to completion with five consecutive additions of equal portions of catalyst every ten minutes. Each portion, after dilution in the reaction mixture gives an 0.5 m*M* solution of catalyst and each is equivalent to the whole amount used in the experiments shown in Fig. 2. Only ca. 50% reduction is observed if all five portions of catalyst are added at once.

In contrast to Osborn's system [1—3], where the coordinating solvent stabilises the iridium catalyst to give $[MH_2L_2S_2]^+$ (S = solvent), under our conditions, only the substrate alkene can stabilise the catalyst by coordination, and when it is all consumed (or, where the substrate olefin is a poor ligand, before it is all consumed) the catalyst deactivates. The higher catalyst activity obtained in a non-coordinating solvent is therefore obtained only at the cost of lower catalyst stability. Our systems are also sensitive to a number of functional groups: amines totally deactivate the catalysts by deprotonation and ketones, alcohols and carboxylic acids partially or totally deactivate them, presumably by coordination; ester groups, chlorinated solvents, and even molecular oxygen do not appear to affect them, however. Table 2 shows the effect of a number of solvents and cosolvents on the catalytic activity of IIa for 1-methylcyclohexene reduction. It is interesting to note that even $CHCl_3$ performs satisfactorily as a solvent. In contrast, $[RhCl(PPh_3)_3]$ is inactive in chlorinated solvents [7] and they have therefore been relatively little used for homogeneous hydrogenation. 1,1-Dichloroethylene and carbon tetrachloride fail to dissolve the catalyst precursors I and II, even under hydrogen.

The catalyst solutions of Ia and Ib were deactivated by NEt_3, and a white solid, $[IrH_5L_2]$ [9], precipitated from the mixture. In the case of IIa—IIc $[IrH_5L_2]$ also precipitated but only in the presence of an excess of L.

TABLE 2

RATE AND EXTENT OF HYDROGENATION OF 1-METHYLCYCLOHEXENE BY [Ir(cod)P-i-Pr$_3$(py)]PF_6 (IIa) WITH VARIOUS SOLVENTS AND COSOLVENTS AT 20°C

Solvent [a]	Cosolvent [a]	Rate [b]	Extent [c] (%)	Time [d] (min)
$CHCl_3$	—	1300	20	12
CH_2ClCH_2Cl	—	1300	35	20
CH_2Cl_2	—	1500	60	25
CH_2Cl_2	EtOAc	1300	55	120
CH_2Cl_2	Me_2CO	800	80	30
CH_2Cl_2	EtOH	150	5	—
CH_2Cl_2	MeCN	0	0	—
CH_2Cl_2	NEt_3 [e]	0	0	—

[a] 15 ml of solvent with 1 ml of cosolvent added (EtOH, 1.5 ml; NEt_3, 0.1 ml). [b] The maximum rate observed during the reduction expressed in mol H_2 absorbed per mol Ir per h. Catalyst: 2 m*M*. Substrate: 0.6 *M*. In the constant volume apparatus (see experimental). [c] Extent of reduction of substrate when deactivation occurs determined by GLC. [d] Time after which no further hydrogen is absorbed. [e] Deprotonation probably occurs in this case since addition of P-i-Pr$_3$ (1 mol equiv.) gives the isolable $[IrH_5(P\text{-}i\text{-}Pr_3)_2]$ (see text).

$$[Ir(cod)(PPh_3)_2]PF_6 + NEt_3 + 5H_2 \rightarrow [IrH_5(PPh_3)_2] + NEt_3HPF_6 + \text{cyclooctane}$$
(Ib)

$$[Ir(cod)(PCy_3)(py)]PF_6 + NEt_3 + PCy_3 + 5H_2 \rightarrow$$
(IIb)

$$[IrH_5(PCy_3)_2] + NEt_3)_2] + NEt_3HPF_6 + \text{cyclooctane}$$

Alkene isomerisation is a complicating side-reaction for the catalysts derived both from I and from II. Table 3 shows the proportions of the organic products present after the half-hydrogenation of 1-hexene. As can be seen considerable quantities of *trans*-2-hexene are present, as well as some of the *cis*-isomer.

$[Ir(cod)(dpe)]PF_6$ (dpe = 1,2-bis[diphenylphosphino]ethane) (Ic) is not a a catalyst at 0°C in CH_2Cl_2. It only absorbs 1 mol of hydrogen per mol of Ic and the product, *cis*-$[IrH_2(cod)(dpe)]PF_6$ (IV) may be isolated as a cream-coloured solid at −80°C. Complex IV fails to transfer coordinated hydrogen to the coordinated (cod) at 0°C in CH_2Cl_2, but does so slowly at 20°C [10] and Ic is a catalyst only at the higher temperature, but with an induction time of about 15 min. $[Ir(cod)(py)_2]PF_6$ (Id) is not a catalyst at all, and does not appear to react with H_2 under any conditions. $[Ir(cod)\{P(OMe)_3\}_3]PF_6$ (Va) does not react with H_2 and is not a catalyst, presumably because the trimethylphosphite ligands are strongly bound and do not dissociate in solution; such a dissociation would be required if H_2 is to add to the metal since Va is an 18-electron compound [11]. $[Ir(cod)(PMe_2Ph)_3]PF_6$ (Vb) does give an active catalyst at 20°C in CH_2Cl_2 but only after an induction period of 30 min. The relatively more basic PMe_2Ph ligand is clearly much more labile when coordinated to electron-rich iridium, than is the more π-accepting $P(OMe)_3$. Indeed, we have independent evidence of the lability of PMe_2Ph in Vb, since this complex exchanges readily with $[Ir(cod)(py)_2]PF_6$ (Id) in CH_2Cl_2 at room temperature to give complexes of type II. Since Vb is unaffected by pyridine, but Id is rapidly substituted by PMe_2Ph, dissociation of this ligand from Ib must be the first step of the exchange reaction [6]. The presence of extra phosphine ligand in Vb does not prevent the catalyst from deactivating as do Ia—Ic: the product, a yellow oil, is probably a complex of type

TABLE 3

HYDROGENATION AND ISOMERISATION OF 1-HEXENE BY $[Ir(cod)(PMePh_2)_2]PF_6$ (Ia) AND $[Ir(cod)P\text{-}i\text{-}Pr_3(py)]PF_6$ (IIa) IN CH_2Cl_2 AT 0°C

Catalyst [a]	Time [b] (min)	Products (%) [c]			
		Hexane	1-Hexene	2-Hexene	
				cis	*trans*
$[Ir(cod)(PMePh_2)_2]PF_6$ (Ia)	6	54	9	7	30
$[Ir(cod)P\text{-}i\text{-}Pr_3(py)]PF_6$ (IIa)	4	57	8	6	29

[a] 0.5 m*M* in CH_2Cl_2 at 0°C, substrate 0.5 *M*, $p(H_2)$ 600 mmHg, in the constant-pressure apparatus (see experimental). [b] Time when the hydrogenation was stopped by evacuating the apparatus and distilling an aliquot of the reaction mixture for GLC. [c] Determined by GLC.

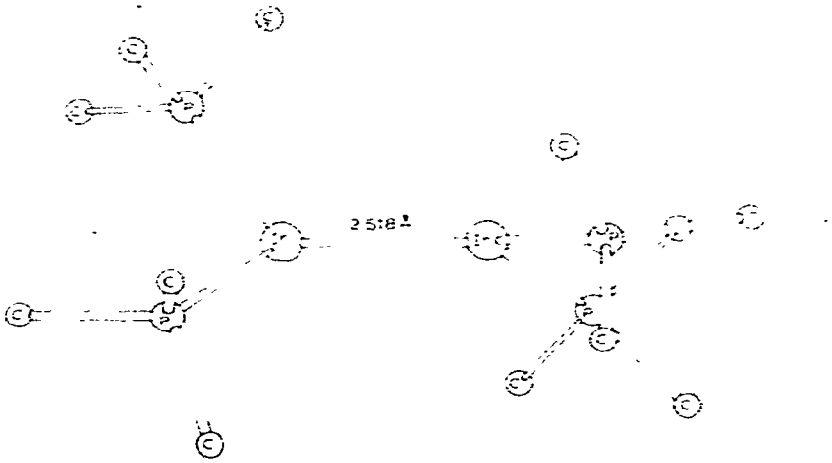


Fig. 3. The partial X-ray crystal structure of the cation $[Ir_2H_5(PPh_3)_4]^+$ in IIIb. Only the iridium, phosphorus, and carbon atoms directly bound to phosphorus were located due to disorder in the crystal.

III from its IR and NMR spectrum; free PMe_2Ph is also formed. Table 1 summarises the results obtained for the reduction of cyclohexene and 1-methylcyclohexene with the different types of catalyst we have discussed.

The complexes $[Ir_2(\mu\text{-}H)_3H_2L_4]PF_6$ (IIIa: L = $PMePh_2$ IIIb: L = PPh_3) were isolated from the catalytic solutions only in very small quantities. The pure complex IIIb was best prepared on a larger scale in CH_2Cl_2 or toluene by reaction of Ib with hydrogen. The HPF_6 also formed (eq. 1) was neutralised with NEt_3 at the end of the reaction, as III readily reacts with acids (see below). The total hydrogen absorption was determined as 6.5 mol H_2/Ir and 0.95 mol cyclooctane/Ir was detected in the products, in good agreement with eq. 1. The crystal structure of complex IIIb was determined by X-ray crystallography and has been reported [12]. Disorder in the crystal allowed the determination only of the atomic positions of iridium, phosphorus and those carbons directly bound to phosphorus. The structure of the cation is shown in Fig. 3. The stereochemistry around phosphorus is normal, precluding *ortho*-metallation. The hydrogen atoms bound to iridium were assigned from the PMR spectrum at −80°C in deuterioacetone. A doublet at δ −6.9 ppm with ^2J(P—H)(*trans*) 90 Hz was assigned to H_A (Fig. 4) which is *trans* to one phosphorus nucleus. A triplet at δ −8.4 ppm with ^2J(P—H)(*trans*) 65 Hz was assigned to H_B which is *trans* to two phosphorus nuclei. Finally a broad resonance at δ −23.9 ppm was assigned to the terminal hydrogens, H_C, which are *cis* to two phosphorus nuclei. The width of this peak is of the order of normal ^2J(P—H)(*cis*) coupling constants ~20 Hz [13]. The coupling constants for the bridging hydrogens are about half the values normally found for mononuclear complexes (120—180 Hz [13]). This must be related to the unusual bonding situation of these bridging hydrides.

The ^{31}P NMR spectrum at −80°C confirms these results: two rather broad resonances of equal intensity are observed for P_A and P_B at δ +15.3 ppm and δ +18.5 ppm (ext. H_3PO_4). At room temperature, the H_A and H_B and P_A and P_B re-

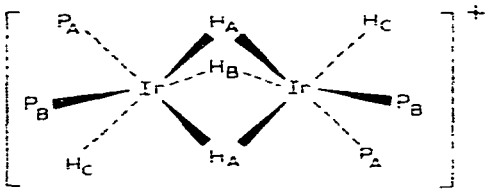


Fig. 4. The structure of the dimeric cation $[Ir_2H_5(PPh_3)_4]^+$ in IIIb, showing the location of the bridging hydrogen atoms.

sonances coalesce to give a broad signal; this is probably due to rotational fluxionality of one end of the molecule with respect to the other around the threefold axis, which could rapidly exchange these nuclei on the NMR time scale.

The IR spectrum of IIIb shows only terminal Ir—H stretching frequencies at 2200 cm^{-1} (1555 cm^{-1} in the deuteriated analogue) but none that can be assigned to the bridging hydrides. This may be associated with the total positive charge on the complex which can reduce the intensities of metal—hydride stretching frequencies [14]; alternatively, these vibrations may be hidden under other ligand vibrations.

The reaction of Ia, Ic, and Vb in CH_2Cl_2 with hydrogen gave yellow oils; each had a band between 2100 and 2200 cm^{-1} in the IR spectrum and in some cases also had broad resonances near δ —8 and —25 ppm in the PMR spectrum at 20°C. These complexes are therefore probably of type III.

In our initial report of IIIb [12] we assigned a triple metal—metal bond to this complex in line with similar assignments in analogous complexes [15]. It has been pointed out to us [16] that an alternative bonding scheme can be envisioned in which only six electrons, rather than twelve as in our original model, are engaged in $M(\mu\text{—}H)_3M$ bonding. That is to say there are three 3-centre, 2-electron bridge bonds and no additional M—M bonding; this would be similar to the bonding in B_2H_6. The short iridium—iridium distance (2.52 Å) would then result from the geometrical requirements of the MH_3M system rather than any direct M—M bonding. Indeed, if we take 1.6 Å [17] as a typical Ir—H bond distance, and arrange an $[L_3IrH_3IrL_3]$ system so that the metal atoms share an oxtahedral face, then from geometrical considerations alone, we calculate an Ir—Ir distance of 2.5 Å (but see also ref. 18). This bonding model (Fig. 4) is the simpler of the two and probably better represents this and similar H-bridged systems and has recently been discussed [18] in detail.

When it is formed from Ib, IIIb is accompanied by HPF_6 (eq. 1). If the resulting acid solution is left at ambient temperature for some hours it becomes orange-red. A red solid is isolated from acetone/ethanol which has a strong band at 2300 cm^{-1} in the IR spectrum and a broad single resonance at δ —20.4 ppm and a triplet resonance (coupling constant 65 Hz) at δ —8 ppm in the PMR spectrum in CD_2Cl_2 at 20°C. The same complex is formed from $[IrH_5(PPh_3)_2]$ and HPF_6 in CH_2Cl_2. This complex may be the fluoro analogue of VI (see below), but good analyses were never obtained.

The reaction of HCl with IIIb gave a single readily isolable product $[Ir_2(\mu\text{-}Cl)_2(\mu\text{-}H)H_2(PPh_3)_4]PF_4$ (VI). Only those hydrogens *trans* to hydride were replaced by chloride, in line with the known high *trans* effect of hydride [19]. The PMR

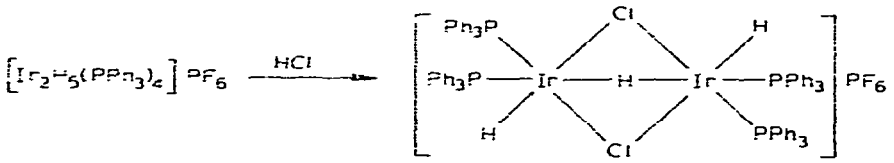
TABLE 4

COLOURS, YIELDS AND SOME IR AND NMR SPECTRAL DATA FOR THE NEW COMPLEXES

Complex	Colour	Yield (%)	ν(In—H) (cm^{-1}) [a]	Hydride resonances ^1H NMR [b]	
				Terminal	Bridging
$[IrH_5(PCy_3)_2]$ [c]	White	70	1945vs	−10.6, t, 11	—
$[Ir_2(\mu\text{-}H)_3H_2(PMePh_2)_4]PF_6$ [d] (IIIa)	Yellow	30	2150m	−21.0, (br)	−7.2, (br)
$[Ir_2(\mu\text{-}H)_3H_2(PPh_3)_4]PF_6$ [e] (IIIb)	Yellow	65	2200m	−23.9, (br)	−8.4, t, 65 −6.9, d, 90
$[Ir_2(\mu\text{-}Cl)_2(\mu\text{-}H)H_2(PPh_3)_4]PF_6$ [c] (VI)	Yellow	95	2300m	−23.3, dd, 16 and 20	−11.9, tt, 10 and 62

[a] Nujol. [b] Reported as: position (δ, ppm), multiplicity, coupling constants (Hz.); d = doublet, t = triplet, (br) = broad single resonance. [c] PMR in CD_2Cl_2 at 20°C. [d] PMR in acetone-d_6 at 20°C. [e] PMR in acetone-d_6 at −80°C.

spectrum at 20°C in CD_2Cl_2 shows a triplet of triplets at δ −11.9 ppm for the unique hydrogen, due to coupling of two *trans*- and two *cis*-phosphorus nuclei, and a doublet of doublets at δ −23.3 ppm for the terminal hydrogens,



due to coupling with two inequivalent *cis*-phosphorus nuclei. This complex is apparently not fluxional on the PMR timescale at 20°C. Table 4 lists the yields, colours, and spectral data for the new complexes.

Conclusion

We wished to design a catalyst system in which active sites are created by irreversible loss of a ligand in a non-coordinating solvent. The use of complexes I and II in CH_2Cl_2 fulfils these conditions. The resulting solutions, as far as we are aware, are the most highly active homogeneous hydrogenation catalysts yet described, and rapidly reduce even tri- and tetra-substituted alkenes. They readily undergo deactivation in the absence of substrate, or with a substrate which is an insufficiently good ligand. They are also very sensitive to a variety of functional groups. The active intermediates are probably of the form $[IrH_{2n}(alkene)_{(3-n)}L_2]^+$ (n = 0—3) of which we have isolated a number of examples such as $[IrH_2(cod)L_2]PF_6$ [10]. It is interesting to contrast these results with those of Osborn [4], where the same or similar complexes in coordinating solvents had much lower activities, but the active catalysts themselves, the isolable solvates $[IrH_2(solvent)_2L_2]^+$, were stable. These results show the critical role of the solvent in homogeneous catalysis.

Experimental

The complexes I [1,2,6], II [6] and V [20] were prepared by literature methods. NMR spectra were measured on a Perkin—Elmer R12B instrument. Reagents

were obtained from Fluka AG and used as received except for the olefins which were deperoxidised by passage through grade I Alumina (Merck) and the chlorinated solvents which were distilled from CaH_2 under nitrogen immediately before use. Hydrogen (Carboxyque Française 'S') and deuterium (Air Liquide) were used as received. Product analyses were made by GLC on a Perkin—Elmer F11 instrument with a β,β-oxidipropionitrile 20% on Chromosorb W 80/100 1.6 m column or, for the alicyclic compounds, a Silicone SE 30 20% on Chromosorb W HMDS, 3 m column.

The hydrogenation experiments

The hydrogenations were performed in one or other of two sets of apparatus: (1) The constant volume apparatus consisted of a 250 ml flask equipped with a magnetic stirrer, a mercury manometer, a hydrogen inlet (via a bubbler), and a connection to a vacuum line and (2) the constant pressure apparatus, designed and built by Dr. G. Giordano, whom we thank, consisted of a reservoir of hydrogen (1 litre) at 1—2 atmospheres pressure, a manometer with electrical contacts, and a reaction flask supplied with hydrogen by an electric tap, which was operated by the manometer contacts when the pressure in the reaction flask fell 2 mm below atmospheric. The total pressure $\{p(CH_2Cl_2) + p(H_2)\}$ in the reaction flask was therefore always atmospheric (±2 mm) and the course of the reaction was followed by observing the pressure changes in the high-pressure side of the apparatus using a mercury-filled U-tube as a manometer. Mention is made where appropriate which apparatus was used. In either case, the solutions (total volume 16 ml) were made up under nitrogen and degassed by two freeze-thaw cycles in vacuo. The reactions were apparently only marginally affected by the presence of air, or of peroxides in the substrate, or by the use of technical grade CH_2Cl_2. The system was allowed to equilibrate for 3 min at the required temperature after admission of hydrogen. Hydrogen absorbtion started as soon as stirring was begun, except in those cases where an induction period was observed (see Table 1). The activities of the various catalysts are expressed in mol H_2 absorbed (mol Ir)$^{-1}$ h^{-1}. The extent of hydrogenation was determined by GLC (directly from the peak areas). The hydrogenations using $[RhCl(PPh_3)_3]$ were performed in the same way, except that the solid catalyst was added to the frozen degassed solution under nitrogen, and the vessel immediately isolated, evacuated, warmed to 25°C, equilibrated, then filled with hydrogen.

Pentahydridobis(tertiary phosphine)iridium(V)

Method A. $[Ir(cod)(PPh_3)_2]PF_6$ (Ib, 485 mg, 0.46 mmol) in CH_2Cl_2 (20 ml) and NEt_3 (500 mg, 4.4 mmol) at 0°C absorbed ca. 4 mol of hydrogen per mol of complex and a white precipitate separated over 60 min. Cyclooctane (0.98 mol. equiv.) as well as a trace of cyclooctene were detected in the products (PMR and GLC). The white solid was filtered, washed with ether and dried in vacuo. Yield 85%. The identity of the product was confirmed by comparison of its IR spectrum with that reported for $[IrH_5(PPh_3)_2]$ [9].

Method B. $[Ir(cod)L(py)]PF_6$ (II, L = PCy_3 or P-i-Pr_3, 0.5 mmol) in CH_2Cl_2 (20 ml) and NEt_3 (500 mg) containing L (0.6 mmol) was treated with hydrogen for 60 min. The white solids were isolated with ether and recrystallised from CH_2Cl_2/Et_2O. L = PCy_3 (yield 80%) (Found C, 57.1; H, 9.5. $C_{36}H_{71}IrP_2$ calcd.:

C, 57.0; H, 9.4%). L = $P(i\text{-}Pr)_3$ (yield 70%) the identity of the product was confirmed by comparison of its IR and NMR spectra with those reported for $[IrH_5(P\text{-}i\text{-}Pr_3)_2]$ [9].

Tri-μ-hydridodihydridotetrakis(triphenylphosphine)diiridium(III) hexafluorophosphate

Method A. $[Ir(cod)(PPh_3)_2]PF_6$ (Ib, 750 mg, 0.71 mmol) in CH_2Cl_2 (10 ml) and toluene (200 mg) at 0°C was treated with H_2 (1 atm) for 40 min. To the yellow solution was added NEt_3 (0.3 ml) (white fumes) and then hexane (5 ml). Evaporation of the solvents in vacuo gives a yellow oil which was washed with ether and pumped in vacuo for 5 min. The residue was extracted with acetone (3 ml), ethanol (3 ml) added and the volume of the mixture was halved under reduced pressure to give yellow crystals of the product (yield 350 mg, 65%). Found: C, 54.6; H, 4.1; Cl, 0. $C_{72}H_{65}F_6P_5Ir$ calcd.: C, 53.7; H, 4.4; Cl, 0%. The hydrogen-absorption curve for an identical reaction, carried out in the constant volume (100 ml) apparatus showed that 3.25 mol-equiv. of hydrogen were absorbed per mole of Ib over 12 min (3.5 expected from eq. 1). 0.95 mol-equiv. of cyclooctane was also detected by PMR spectroscopy of the reaction mixture using the toluene as internal reference.

The methyldiphenylphosphine analogue was prepared in the same way but could not be isoalted other than as an oil.

Di-μ-chloro-μ-hydridodihydridotetrakis(triphenylphosphine)diiridium(III) hexafluorophosphate

$[Ir_2H_5(PPh_3)_4]PF_6$ (IIIb, 335 mg) in suspension in acetone (15 ml) was shaken with concentrated HCl (1 ml) for 2 min. A yellow solution was formed, ethanol (20 ml) added and the volume of the mixture was halved under reduced pressure. The resulting pale yellow solid was filtered and recrystallised from acetone/ethanol to give the product (350 mg, 95%). Found: C, 52.5; H, 3.9; Cl, 5.5. $C_{72}H_{63}Cl_2F_6P_5Ir_2$ calcd.: C, 52,3; H, 3.8; Cl, 4.3%.

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