INFLUENCE OF DIFFERENT LIGANDS IN HOMOGENEOUS HYDROGENATION USING IRIDIUM COMPLEXES WITH THIOETHER LIGANDS

JAUME SOLÉ, CARLES BO, CARMEN CLAVER* and AURORA RUIZ

Departament de Quimica, Universitat de Barcelona, Plaça Imperial Tarraco, 1, 43005 Tarragona (Spain)

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Summary

Dichloromethane solutions of mono- and dinuclear diolefin and carbonyl iridium(I) and dihydridoiridium(III) complexes containing thioether or dithioether ligands, and mixed complexes with PR_3 (R = Me, p-MePh, p-ClPh, OMe, OPh) have been used as catalyst precursors in the hydrogenation of olefins at 25 °C and 1 atm of H₂. The effect of the different ligands on the catalytic activity has been studied. Theoretical calculations using EHT method have been performed.

Introduction

In the 1970s, Crabtree and col. showed that dichloromethane solutions of cationic diolefinic iridium(I) complexes $[Ir(diolefin)(PR_3)_2]^+$, in the presence of an olefin constitute hydrogenation catalysts of unprecedented activity for iridium(I) complexes [1].

The catalytic activity, mechanism and application on different substrates of cationic $[Ir(diolefin)L_2]^+$ complexes with different P- or N-donor ligands have been studied [1, 2]. Recently, interesting results on the stereoselective and directed homogeneous hydrogenation of different organic substrates using $[Ir(COD)(PCy_3)(Py)]^+$ (COD = 1,5-cyclooctadiene) and [Ir(NBD) $(Ph_2P(CH_2)_4PPh_2)]BF_4$ (NBD = 2,5-norbornadiene) [3, 4] precursors have been reported. Hydridoiridium(III) complexes prepared *in situ* show highly selective catalytic activity for the hydrogenation of α,β -unsaturated ketones [5]. Not many other different types of iridium complexes have been used. In the case of related cationic complexes containing sulphur ligands, the catalytic activity in homogeneous hydrogenation has been scarcely studied.

It is known that rhodium(III) complexes containing SEt_2 are active in homogeneous hydrogenation [6], and the dinuclear thiolate bridged compounds $[Rh_2(\mu-SR)_2(CO)_2L_2]$ and $[Rh_2(\mu-SR)_2(L)_4]$ $(L=P(OR')_3)$, were found to be active catalysts for the same reaction [7]. Recently, we have

^{*}Author to whom correspondence should be addressed.

reported the hydrogenation of 1-heptene using $[M(diolefin) (SPR_3)_2]^+$ (M = Rh, Ir; diolefin = COD, NBD; R = Ph, Me) [8].

In this work mono- and dinuclear diolefin and carbonyl iridium(I) and dihydridoiridium(III) cationic complexes, containing thioether and dithioether ligands, previously reported [9–13], have been used as catalysts precursors in homogeneous hydrogenation at 25 °C and 1 atm of hydrogen. The effect of the different ligands in the catalytic activity has been studied. Furthermore, with the aim of obtaining additional information about the behaviour of such precursors, quantum chemical calculations using EHT method have been performed [14].

Results and discussion

Catalyst precursors

TABLE 1

We have previously described the preparation and properties of the complexes used in this work as catalyst precursors: $[Ir(COD)L_2]ClO_4$, L: tetrahydrothiophene (tht); $[(COD)Ir(\mu-L)_2Ir(COD)](ClO_4)_2$, L: tht, SMe₂ (dms) [9]; $[Ir(COD)(tht)(PPh_3)]ClO_4$ [10]; $[(CO)_2Ir\{\mu-(L-L)\}_2Ir(CO)_2]$ (ClO₄)₂, L-L: Bu^tS(CH₂)₂SBu^t (tmdto) [11]; $[(CO)_2(PPh_3)Ir\{\mu(L-L)\}Ir(PPh_3)(CO)_2]$ (ClO₄)₂ [12]; $[Ir(H)_2(COD)(PPh_3)L]ClO_4$, L: tht, dms, SEt₂ (des) and $[(COD)(H_2)(PPh_3)Ir(\mu-tmdto)Ir(PPh_3)(H_2)(COD)](ClO_4)_2$ [13].

Furthermore, in this work we report (Table 1) a series of mixed complexes $[Ir(COD)(tht)(PR_3)]ClO_4$ (R = Me, *p*-MePh, *p*-ClPh, OMe, OPh) which have been prepared in the same manner as $[Ir(COD)(tht)(PPh_3)]ClO_4$ [10], in order to study the influence of the different PR₃ on the catalytic activity of this type of compound.

Dichloromethane solutions of all these compounds containing 1-heptene (1:100 molar ratio) react with hydrogen at 25 °C and atmospheric pressure to

PR ₃	Elemental and (found (calc) (dysis (%))	Conductivity data	Melting Point (°C)
	c	Н	Λ _M -	
P(CH ₃) ₃	30.8 (31.9)	5.1 (5.3)	108	138-143
P(OCH ₃) ₃	27.6 (29.4)	4.7 (4.4)	132	108-111
$P(OC_6H_5)_3$	43.7 (45.1)	4.4 (4.4)	110	116-119
$P(p-Cl(C_6H_4))_3$	41.3 (42.2)	3.9 (3.7)	112	132-135
$P(p-Me(C_6H_4))_3$	50.0 (50.0)	5.4 (5.2)	130	146-149

Analytical results, conductivity data and melting points for the $[Ir(COD)(tht)(PR_3)]ClO_4$ complexes

^aMeasured in acetone solution $(\Omega^{-1} \operatorname{cm}^2 \operatorname{mol}^{-1})$.

TABLE 2

Hydrogenation of 1-heptene^a

Catalyst precursor	Reaction time (min)	Heptane (%)	1-Heptene (%)	t-3-Heptene (%)	c-2-Heptene (%)
[Ir(COD)(tht) ₂]ClO ₄	447	70.7	9.1	9.1	11.1
$[Ir(COD)(\mu-tht)]_2(ClO_4)_2$	486	55.2	11.7	22.4	10.6
$[Ir(COD)(\mu-dms)]_2(ClO_4)_2$	353	37.9	14.7	32.9	15.0

^aReaction conditions: [1-heptene]: [Ir] = 100:1, $p(H_2) = 1$ atm, T = 25 °C, solvent = 15 ml CH₂Cl₂.

form species which catalyze the homogeneous hydrogenation of this substrate.

Diolefin complexes

Table 2 and Fig. 1 show the results for the catalytic hydrogenation of 1-heptene using dichloromethane solutions of $[Ir(COD)(tht)_2]ClO_4$ and $[(COD)Ir(\mu-L)_2Ir(COD)](ClO_4)_2$ (L = tht, dms) [9] as catalyst precursors. Isomerization was observed in all cases and the mononuclear $[Ir(COD)(tht)_2]ClO_4$ complex provides more hydrogenated product (70% in 450 min) than the dinuclear complex $[COD)Ir(\mu-tht)_2Ir(COD)](ClO_4)_2$, which leads to more isomerization in *trans*-3-heptene. The conversion in heptane is very slow for the times presented in Table 2.

$[Ir(COD)(tht)(PR_3)]ClO_4$ complexes

We have used a series of $[Ir(COD)(tht)(PR_3)]ClO_4$ complexes $(PR_3 = P(C_6H_5)_3, P(p-CH_3(C_6H_4))_3, P(p-Cl(C_6H_4))_3, P(CH_3)_3, P(OCH_3)_3$ and $P(OC_6H_5)_3)$ with a double objective: to study the dependence of their



Fig. 1. Catalytic hydrogenation of 1-heptene using: $[Ir(COD)(tht)_2]ClO_4 (\Delta)$, $[Ir(COD)(\mu-tht)]_2(ClO_4)_2 (\bigcirc)$ and $[Ir(COD)(\mu-dms)]_2(ClO_4)_2 (\Box)$.

Catalyst precursor	Reaction time (min)	Heptane (%)	1-Heptene (%)	and/or	<i>t-</i> 3-Heptene (%)	c-2-Heptene (%)
[Ir(COD)(tht)(P(CH ₃) ₃)]ClO ₄	301	10.8		26.2		52.4
[Ir(COD)(tht)(P(C ₆ H ₅) ₃)]ClO ₄	303	72.5	9.7		13.7	4.1
$[Ir(COD)(tht)(P(C_6H_5)_3)_2]ClO_4$	14	100.0	0.0		0.0	0.0
$Ir(COD)(tht)_2(P(C_6H_5)_3)]ClO_4$	302	94.7	2.0		2.9	1.0
$Ir(COD)(tht)(P(p-Me(C_6H_4))_3)]ClO_4$	453	59.8	16.1		19.6	4.3
$Ir(COD)(tht)(P(p-Cl(C_{B}H_{4}))_{3})]ClO_{4}$	344	24.9	31.0		39.0	5.2
[Ir(COD)(tht)(P(OCH ₃) ₃)]ClO ₄	402	16.6	24.2		25.5	13.2
[Ir(COD)(tht)(P(OC ₆ H ₅) ₃)]ClO ₄	431	27.4	26.9		35.9	9.8

Hydrogenation of 1-heptene^{*}

^aReactions conditions: [1-heptene]: [Ir] = 100: 1, $p(H_2) = 1$ atm, T = 25 °C, solvent = 15 ml CH₂Cl₂.

catalytic activity on the different phosphine ligands and to compare these activities with that of $[Ir(COD)(tht)_2]ClO_4$.

Table 3 summarizes the results of the hydrogenation of 1-heptene using these mixed complexes as catalyst precursors. As shown in Fig. 2 the catalytic activity decreases in the order: $P(C_6H_5)_3 > P(p-CH_3(C_6H_4))_3 >$ $P(OC_6H_5)_3 \approx P(p-Cl(C_6H_4))_3 > P(OCH_3)_3 > P(CH_3)_3$ and depends not only on the σ -donor/ π -acceptor properties of the phosphorus ligands.

From the Tolman's cone angle data [15], which give a rough measure of the relative size, the steric constraint imposed by the phosphorus ligands is seen to lie in the order: $P(C_6H_5)_3 \approx P(p-CH_3(C_6H_4))_3 \approx P(p-Cl(C_6H_4))_3 > P(OC_6H_5)_3 > P(OCH_3)_3 > P(OCH_3)_3$.

Their basicities, which reflect electronic effects, lie in the order: $P(CH_3)_3 > P(p-CH_3(C_6H_4))_3 > P(C_6H_5)_3 > P(p-Cl(C_6H_4))_3 > P(OCH_3)_3 > P(OCH_3)_3 > P(OC_6H_5)_3.$



Fig. 2. Catalytic hydrogenation of 1-heptene using: $[Ir(COD)(tht)(PR_3)]ClO_4$ (PR₃ = P(C₆H₅)₃ (+), P((*p*-CH₃(C₆H₄))₃ (\triangle), P(OC₆H₅)₃ (\bigcirc), P(*p*-Cl(C₆H₄))₃ (\diamondsuit), P(OCH₃)₃ (\blacktriangle) and P(CH₃)₃) (\Box).

TABLE 3

x	Y	Q	[x, ,co]+
$\frac{S(CH_3)_2}{S(CH_3)_2}$	$\frac{S(CH_3)_2}{P(CH_3)_3}$	0.028 0.059 0.145	. Ir Y CO

TABLE 4

Electronic charge on iridium atom by EHT method

The hydrogenation induced by these mixed complexes follows neither series, and thus is probably determined by a combination of both steric and electronic factors. The data in Table 3, however, indicate that for ligands which are equal in size, hydrogenation is favoured by ligands which are more basic.

On the other hand, the $[Ir(COD)(tht)(PPh_3)]ClO_4$ complex is more active as precursor catalyst in the hydrogenation of 1-heptene than the $[Ir(COD)(tht)_2]ClO_4$ complex. This result is consistent with the previously reported increase in activity with more basic phosphine ligands [2a] and is probably due to the increase in electronic density at the metal center. Table 4 shows the electronic charge on the metal center calculated by the EHT method when sulphide ligands are substituted by the more basic $P(CH_3)_3$ phosphine ligands^{*}.

Hydrogenation experiments with the five-coordinate $[Ir(COD)(tht)PPh_3)_2]ClO_4$ and $[Ir(COD)(tht)_2(PPh_3)]ClO_4$ complexes [10] have also been carried out under the same conditions (Table 3). The $[Ir(COD)(tht)(PPh_3)_2]ClO_4$ complex provides more hydrogenation product and is more active than the corresponding $[Ir(COD)(PPh_3)_2]ClO_4$ [2a]. When the $[Ir(COD)(tht)_2(PPh_3)]ClO_4$ complex is used as a hydrogenation precursor, the activity is lower than in the case of $[Ir(COD)(PPh_3)_2]ClO_4$ complex, but the same selectivity is obtained.

Carbonyl Ir(I) and dihydride Ir(III) related complexes

When the dinuclear tetracarbonyl $[(CO)_2Ir(\mu-tmdto)_2Ir(CO)_2](CIO_4)_2$ complex [11] was used, no hydrogenation or isomerization was observed. However, when the mixed carbonyl phosphine dinuclear $[(CO)_2(PPh_3)Ir(\mu-tmdto)Ir(PPh_3)(CO)_2](CIO_4)_2$ complex [12] was used as precursor, slight hydrogenation of 1-heptene was obtained together with isomerized products (Table 5).

On the other hand, we have previously reported [13] the preparation of dihydride Ir(III) complexes containing thioether and dithioether ligands, and it seemed interesting to use these dihydride complexes in the hydrogenation

^{*}The calculations were of the Extended Hückel type and weighted $H_{ij}s$ were used with the standard value of K = 1.75. Idealized geometry for the square-planar complexes were assumed. The geometric parameters were (distances in Å, angles in degrees): Ir—C = 1.85, Ir—S = 2.4, Ir—P = 2.3, C—O = 1.22, P—C = 1.83, S—C = 1.82, C—H = 1.06, Ir—P—C = 116.0, Ir—S—C = 109.5. The ionization potentials and the coefficients and exponents for each atom were taken as follows: Ir[16], S[17], P[18], H, C, O, [14].

Hydrogenation	of 1-h	eptene ^a
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Catalyst precursor	Reaction time (min)	Heptane (%)	1-Heptene (%)	and/or	t-3-Heptene (%)	c-2-heptene (%)
$[Ir(CO)_2(COD)(tht)]ClO_4$	300	6.2		60.5		33.3
$Ir(CO)_2 I(\mu-undu)_2^{-1}$ $Ir(CO)_2 [(CIO_4)_2$ $[(CO)_2 (PPh_2) Ir(\mu-tmdt_2)_2^{-1}]$	330	0.		100.0		0.
$\frac{\text{Ir}(\text{PPh}_3)(\text{CO})_2](\text{ClO}_4)_2}{\text{Ir}(\text{PPh}_3)(\text{CO})_2](\text{ClO}_4)_2}$	300	11.4		75.7		12.9

^aReactions conditions: [1-heptene]: [Ir] = 100:1, $p(H_2) = 1$ atm, T = 25 °C, solvent = 15 ml CH₂Cl₂.

reaction. However the complexes showed very low hydrogenation activity, and only in the case of the dinuclear complex $[(H)_2(COD)(PPh_3)Ir(\mu-tmdto)Ir(PPh_3)(COD)(H)_2](ClO_4)_2$ was a significant amount of hydrogenated product obtained ($\approx 60\%$) (Table 6). The isomerization of 1-heptene predominates over the hydrogenation process when the $[Ir(H)_2(COD)(PPh_3)L]ClO_4$ (L = tht, dms, des) were used as catalyst precursors, and *trans*-3-heptene is the major product (Fig. 3).

Cyclohexene hydrogenation

Experiments in cyclohexene hydrogenation were carried out under the same conditions as 1-heptene hydrogenation (atmospheric pressure, 25 °C) using mixed $[Ir(COD)(tht)L]ClO_4$ complexes $(L = P(CH_3)_3, P(C_6H_5)_3, P(p-Me(C_6H_4)_3), [Ir(COD)(tht)_2(P(C_6H_5)_3)]$ and $[Ir(COD)(tht)(P(C_6H_5)_3)_2]ClO_4$ (Table 7).

According to the results obtained in the 1-heptene hydrogenation, $[Ir(COD)(tht)(P(C_6H_5)_3]ClO_4$ shows the best activity in the $[Ir(COD)(tht)(PR_3)]ClO_4$ series, and the five-coordinate $[Ir(COD)(tht)(P(C_6H_5)_3)_2]ClO_4$ achieves more than 90% conversion, al-

TABLE	6
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Hydrogenation	of 1-heptene ^a
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Catalyst precursor	Reaction time (min)	Heptane (%)	1-Heptene (%)	t-3-Heptene (%)	c-2-Heptene (%)
[Ir(H) ₂ (COD)(PPh ₃)(tht)]ClO ₄	400	10.1	27.0	62.9	0.0
[Ir(H) ₂ (COD)(PPh ₃)(des)]ClO ₄	360	12.9	27.6	47.8	1.7
$[Ir(H)_2(COD)(PPh_3)(dms)]ClO_4$ $[(H)_2(COD)(PPh_3)Ir(\mu-tmdto)]$	380	23.0	35.5	40.2	1.5
$Ir(PPh_3)(COD)(H)_2](ClO_4)_2$	333	59.7	16.1	19.9	4.2

^aReactions conditions: [1-heptene]: [Ir] = 100:1, $p(H_2) = 1$ atm, T = 25 °C, solvent = 15 ml CH₂Cl₂.



Fig. 3. Catalytic hydrogenation of 1-heptene using: $[Ir(H)_2(COD)(PPh_3)(tht)]ClO_4$ (\triangle), $[Ir(H)_2(COD)(PPh_3)(des)]ClO_4$ (\bigcirc), $[Ir(H)_2(COD)(PPh_3)(des)]ClO_4$ (\square) and $[(H)_2(COD)(PPh_3)Ir(\mu-tmdto)Ir(PPh_3)(COD)(H)_2](ClO_4)_2$ (\diamondsuit).

though the rate is lower than with the $[Ir(COD)(PPh_3)_2]ClO_4$ complex (Table 7).

Experimental

All reactions were carried out at room temperature under nitrogen atmosphere using Schlenk techniques. All the solvents were distilled and deoxygenated before use. The C and H analyses were carried out on a Perkin-Elmer 240B microanalyzer. Conductivities were measured in ca. 2×10^{-3} M acetone solutions with a Philips PW9509 conductimeter. Melting points were determinated with a Buchi 510 apparatus.

The starting materials were prepared as previously reported [19]. $IrCl_3 x H_2O$ was obtained from Johnson Matthey, phosphine and thioether ligands were purchased from Aldrich and Strem.

TABLE 7

Hydrogenation of cyclohexene^a

Catalyst precursor	Reaction time (min)	Cyclohexane (%)	Cyclohexene (%)
[Ir(COD)(tht)(P(CH ₃) ₃)]ClO ₄	57	0.0	100.0
$[Ir(COD)(tht)(P(C_6H_5)_3)]ClO_4$	407	60.3	39.7
$[Ir(COD)(tht)(P(C_6H_5)_3)_2]ClO_4$	140	91.5	8.5
$[Ir(COD)(tht)_{2}(P(C_{g}H_{5})_{3})]ClO_{4}$	402	13.6	86.4
$[Ir(COD)(tht)(P(p-Me(C_6H_4)_3))]ClO_4$	266	3.0	97.0
$[Ir(COD)(P(C_6H_5)_3)_2]ClO_4$	72	99.7	0.3

^aReactions conditions: [cyclohexene]:[Ir] = 100:1, $p(H_2) = 1$ atm, T = 25 °C, solvent = 15 ml CH₂Cl₂.

Catalytic activity experiments were performed in a conventional hydrogenation apparatus. The order of introduction of reactants into the hydrogenation flask was: 0.03 mmol catalyst precursor, 3 mmol substrate in 15 ml dichloromethane freshly distilled and dried and finally, hydrogen. The mixture was stirred in a thermostatted bath at 25 °C. The hydrogenation products were identified by analysis with a Hewlett-Packard 5840A chromatograph. The peak areas were obtained with a Hewlett-Packard 5840A computing integrator.

Caution: Mechanical handling and heating of perchlorate salts represent a potential danger. However we have never experienced an explosion with the present compounds.

Preparation of $[Ir(COD)(tht)(PR_3)]ClO_4$ complexes

The compounds $[Ir(COD)(tht)(PR_3)]ClO_4$ (R = Me, p-MePh, p-ClPh, OMe, OPh) were prepared by adding a stoichiometric amount (0.08 mmol) of the appropriate ligand PR₃ to a dichloromethane solution of $[Ir(COD)(tht)_2]ClO_4$ (0.08 mmol) prepared *in situ*. The yellow solutions became orange immediately. The products were precipitated as orange solids by addition of diethyl ether, filtered, washed with diethyl ether and vacuum dried.

Conclusions

The studied iridium(I) complexes with thioether and dithioether ligands behave as active precursors in the homogeneous hydrogenation of olefins. except in the case of the $[(CO)_{2}Ir{\mu (Bu^{t}S(CH_{2})_{2}SBu^{t})_{2}Ir(CO)_{2}](ClO_{4})_{2}$ complex. In general, olefin isomerization is observed and in some cases is the major process. Mononuclear $[Ir(COD)(tht)_2]ClO_4$ complex is more active in the hydrogenation of 1heptene than the corresponding dinuclear $[(COD)Ir(\mu-tht)_2Ir(COD)](ClO_4)_2$ complex.

The presence of PR₃ ligands enhances the catalytic activity. In the case of the mixed complexes $[Ir(COD)(tht)(PR_3)]ClO_4$ (PR₃ = P(C₆H₅)₃, P(p-CH₃(C₆H₄))₃, P(OC₆H₅)₃, P(p-Cl(C₆H₄))₃ P(OCH₃)₃ and P(CH₃)₃) the activity is determined by a combination of both steric and electronic effects.

The dihydridoiridium(III) complexes are not active hydrogenation precursors, however they act as active isomerization precursors. Cyclohexene is hydrogenated to cyclohexane (90%) using $[Ir(COD)(tht)(P(C_6H_5)_3)_2]ClO_4$ 90at 25 °C and 1 atm H₂.

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