

# Ir<sub>4</sub> cluster-based selective catalytic hydrogenation of 1,5-cyclooctadiene

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## Abstract

The iridium clusters [Ir<sub>4</sub>(CO)<sub>11</sub>PPh<sub>2</sub>H], [Ir<sub>4</sub>(CO)<sub>8</sub>(μ<sub>3</sub>-η<sup>2</sup>-HCCPh)(μ-PPh<sub>2</sub>)<sub>2</sub>], [Ir<sub>4</sub>(CO)<sub>9</sub>(μ<sub>3</sub>-η<sup>3</sup>-Ph<sub>2</sub>PC(H)CPh)(μ-PPh<sub>2</sub>)] and [Ir<sub>4</sub>(CO)<sub>12</sub>] were investigated as catalyst precursors for the selective hydrogenation of 1,5-cyclooctadiene (1,5-COD). The results showed that these clusters have a special catalytic behaviour producing high activity (average TON 2816) and high selectivity for the monohydrogenated product cyclooctene (COE) and the isomerisation products 1,3-COD and 1,4-COD, with almost complete suppression of the total hydrogenation reaction to cyclooctane (COA). When other iridium based catalyst precursors were used, however, e.g. Vaska's compound [IrClCO(PPh<sub>3</sub>)<sub>2</sub>], the dinuclear [Ir<sub>2</sub>Cl<sub>2</sub>(COE)<sub>4</sub>] and a heterogeneous catalyst composed of Ir metal supported on activated carbon, formation of the fully hydrogenated product COA was observed instead. The participation of the Ir<sub>4</sub> clusters in the catalytic reaction rather than cluster fragments or highly dispersed Ir metallic particles is supported by experiments of light scattering of the cluster solutions after the reaction, addition of metallic Hg and filtration in celite followed by reuse of the solution and the celite for catalytic reactions. Reactions with cyclooctene, cyclohexene and 1,3-COD showed that the mononuclear precursor [IrClCO(PPh<sub>3</sub>)<sub>2</sub>] completely hydrogenates these substrates whereas all Ir<sub>4</sub> clusters exhibit very low activities. Based on experiments with Shapley's compound, [Ir<sub>4</sub>(CO)<sub>5</sub>(C<sub>8</sub>H<sub>12</sub>)<sub>2</sub>(C<sub>8</sub>H<sub>10</sub>)], and literature results, an "anchor-type" interaction between 1,5-COD and the Ir<sub>4</sub> species is proposed, in which one double bond anchors the 1,5-COD molecule for the activation of the other double bond in a Ir<sub>4</sub>-diolefin η<sup>2</sup>-η<sup>2</sup>-COD type activated species, which can lead to hydrogenation or isomerisation. © 2004 Elsevier B.V. All rights reserved.

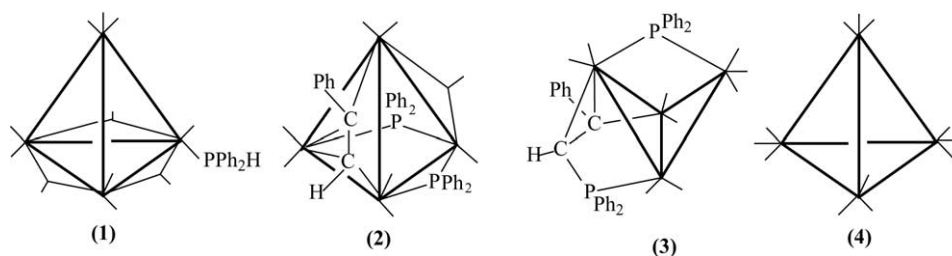
**Keywords:** Cluster catalysis; Selective hydrogenation; Iridium clusters

## 1. Introduction

The development of transition metal cluster chemistry was strongly stimulated by the considerable potential of such species as catalysts and as models for catalytic metallic surfaces [1–3]. The possibility of multi-site interactions between the substrate molecule and the cluster profoundly influence their subsequent reactivity [4,5] and can facilitate the activation and transformation of the substrate in catalytic processes. Small molecules such as alkenes, alkynes, CO, and H<sub>2</sub> can be activated on metal clusters in far

more complex ways than those afforded by a single metal centre, [6–13] which enables organic transformations not possible by mononuclear homogeneous catalysts [14–18]. Several convincing examples of cluster-catalysed reactions have been reported in the literature [19]. For instance, [Ru<sub>3</sub>(CO)<sub>12-n</sub>L<sub>n</sub>] (n = 0–3 and L = phosphines) [20–26] and [Os<sub>3</sub>(CO)<sub>10</sub>(μ-H)(μ-OSi≡)] [27–29] have been used for olefin hydrogenation, isomerisation and hydroformylation, [H<sub>4</sub>Ru<sub>4</sub>(CO)<sub>12</sub>], as a selective catalyst for alkene hydroformylation using CO [30], [H<sub>4</sub>Ru<sub>4</sub>(CO)<sub>10-n</sub>(L<sub>2</sub>)<sub>n</sub>] (n = 0 or 2 and L<sub>2</sub> = chiral bidentate phosphine) [31–34], for asymmetric isomerisation [35], hydroformylation [36] as well as homogeneous asymmetric hydrogenation of carboxylic acids [37]; [Pd<sub>4</sub>(dppm)<sub>4</sub>(H<sub>2</sub>)<sub>2</sub>]<sup>2+</sup> has been investigated

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Scheme 1.

for the homogeneous hydrogenation of alkynes [38] and finally  $[\text{H}_2\text{Pt}_3\text{Ru}_6(\text{CO})_{20}(\mu_3\text{-C}_2\text{Ph}_2)]$ , has been used for the hydrogenation of diphenylacetylene to *trans*-stilbene [39,40]. In contrast very few examples using iridium clusters have been reported in the literature, most probably due to the low solubility of the well known  $[\text{Ir}_4(\text{CO})_{12}]$  [41–43].

We report herein the first example of the use of  $\text{Ir}_4$  soluble clusters as catalyst precursors for the highly selective hydrogenation of 1,5-cyclooctadiene (1,5-COD) to cyclooctene (COE) [44].

The following  $\text{Ir}_4$  clusters were used as catalysts or catalyst precursors:  $[\text{Ir}_4(\text{CO})_{11}\text{PPh}_2\text{H}]$  (**1**) [45],  $[\text{Ir}_4(\text{CO})_8(\mu_3\text{-}\eta^2\text{-HCCPh})(\mu\text{-PPh}_2)_2]$  (**2**) [46],  $[\text{Ir}_4(\text{CO})_9(\mu_3\text{-}\eta^3\text{-Ph}_2\text{PC(H)CPh})(\mu\text{-PPh}_2)]$  (**3**) [47] and  $[\text{Ir}_4(\text{CO})_{12}]$  (**4**) (Scheme 1).

Several features of the selected iridium clusters are important from the point of view of catalysis, viz. (i) Ir being a third-row transition metal exhibits stronger metal–metal bonds than the metals of the first and second transition series, and therefore produces more robust clusters, (ii) the presence of multidentate ligands based on P donors to hold the metal frame together [48,49] and (iii) the high solubility of these clusters in different organic solvents. Compounds **2** and **3** are synthesised from **1**, via  $[\text{H}\text{Ir}_4(\text{CO})_{10}(\mu\text{-PPh}_2)]$  [50], which has proven itself a far better entry into iridium cluster chemistry than **4**, due to its solubility in common organic solvents and high lability associated to the presence of the phosphido bridging ligand, which also retains the integrity of the cluster when metal–metal bonds are broken. Although it does not react with alkynes and alkenes [51], phosphines containing unsaturated fragments, such as  $\text{Ph}_2\text{PC}\equiv\text{CPh}$ , interact further with this cluster to yield  $\mu_4\text{-}\eta^3\text{-Ph}_2\text{PCCPh}$  containing species and products resulting from P–C bond activation, e.g. cluster **2** [47,52–54], further hydrometallation [46], such as cluster **3** or P–C bond formation [55,56].

## 2. Experimental

### 2.1. Materials

The following iridium compounds were prepared by literature methods and their purity was assessed by thin-layer chromatography (TLC) and/or IR spectroscopy:  $[\text{Ir}_4(\text{CO})_{11}\text{PPh}_2\text{H}]$  (**1**),  $[\text{Ir}_4(\text{CO})_8(\mu_3\text{-}\eta^2\text{-HCCPh})(\mu\text{-PPh}_2)_2]$  (**2**)

$[\text{Ir}_4(\text{CO})_9(\mu_3\text{-}\eta^3\text{-Ph}_2\text{PC(H)CPh})(\mu\text{-PPh}_2)]$  (**3**),  $[\text{IrClCO}(\text{PPh}_3)_2]$  (**5**) [57] and  $[\text{Ir}_2\text{Cl}_2(\text{COE})_4]$  (**6**) [58].  $[\text{Ir}_4(\text{CO})_{12}]$  (**4**) (Strem Chemicals),  $\text{H}_2$  (99,99% White Martins) and 1,5-cyclooctadiene (Aldrich) were used as received. The catalyst Ir metal supported on activated carbon (Aldrich-Norit,  $780\text{ m}^2\text{ g}^{-1}$ ) was prepared by impregnation of **1** in  $\text{CH}_2\text{Cl}_2$ , drying under vacuum, followed by thermal decomposition under  $\text{H}_2$  at  $10\text{ }^\circ\text{C min}^{-1}$  up to  $600\text{ }^\circ\text{C}$  for 2 h and characterised by TG and XRD. Solvents were distilled from the appropriate drying agent under nitrogen prior to use. The separation and purification of the reaction products were carried out in air by preparative TLC (2 mm thick glass-backed silica plates,  $20\text{ cm} \times 20\text{ cm}$ , prepared from silica gel GF 254, Fluka) and the compounds were extracted from silica with  $\text{CH}_2\text{Cl}_2$ .

### 2.2. Spectroscopic studies

Infrared spectra were measured using a Perkin-Elmer Spectrum GX FT-IR.  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra were recorded on Bruker Advance DXR 400 and DXP 200 spectrometers. Mass spectra were obtained on a Hewlett-Packard MSD 5890/series II instrument operating at 70 eV. Thermogravimetric analyses were performed on a Shimadzu TG 50 H ( $\text{N}_2$   $100\text{ mL min}^{-1}$ ,  $25\text{ }^\circ\text{C} - 750\text{ }^\circ\text{C}$ ,  $10\text{ min}^{-1}$ , 9 mg). XRD were recorded on a Rigaku-Geigerflex Cu  $\text{K}\alpha$ .

### 2.3. Catalytic experiments and analysis of the products

In a typical reaction, a 100 mL Parr autoclave was loaded with 0.01 mmol of the catalyst and 40 mL of a benzene solution of 1,5-COD ( $0.4\text{ mol L}^{-1}$ ). The reaction vessel was closed, purged with hydrogen and pressurized at 20 atm. The  $\text{H}_2$  pressure was kept constant throughout the reaction by a continuous  $\text{H}_2$  feeding system. The reaction mixture was continuously stirred with a magnetic stirrer (300 rpm) and heated at  $110\text{ }^\circ\text{C}$ . When the reaction mixture reached the desired temperature the first sample was removed (time zero), samples were taken every hour. After 4 h reaction and a cooling period of ca. 1 h, the reaction vessel was depressurized and opened. The reaction products were identified by GC-MS and quantified in a Shimadzu 17A GC instrument fitted with a Carbowax 20 M capillary column and a flame ionisation detector. Isomerisation reaction and the hydrogenation of other olefins such as cyclohexene and cyclooctene were carried out

using the same procedure described for the hydrogenation of 1,5-COD.

#### 2.4. Characterisation of the iridium species after the catalytic reactions

The homogeneous reaction mixture was transferred to a 50 mL round bottom flask and the solvent was evaporated under vacuum affording a brown oil. The oil was dissolved in  $\text{CH}_2\text{Cl}_2$  (2 mL) and purified by TLC ( $\text{CH}_2\text{Cl}_2$ /hexane, 1:4 as eluent). The resulting dark brown compound was analysed by  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR and IR spectroscopy. IR ( $\nu_{\text{CO}}$  benzene): 2077 s, 2068 mbr, 2035 m and 2016 m,  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 25 °C):  $\delta$  6.21–5.00 (m), 4.8–3.9 (m) and 3.0–1.3 (m). No signal was observed in the  $^{31}\text{P}\{^1\text{H}\}$  NMR, indicating that the phosphorus ligands were lost during the hydrogenation reactions. It should be noted that the same brown oil was isolated from all the other hydrogenation reaction mixtures containing iridium cluster catalyst precursors.

### 3. Results and discussion

#### 3.1. Effect of the catalyst precursor

The hydrogenation reaction of 1,5-cyclooctadiene (1,5-COD) results in the formation of four products: 1,4-

cyclooctadiene (1,4-COD) and 1,3-cyclooctadiene (1,3-COD) due to isomerisation, cyclooctene (COE) from the selective hydrogenation and cyclooctane (COA) from the complete hydrogenation.

The following iridium compounds were used as catalyst precursors: clusters  $[\text{Ir}_4(\text{CO})_{11}\text{PPh}_2\text{H}]$  (**1**),  $[\text{Ir}_4(\text{CO})_8(\mu_3\text{-}\eta^2\text{-HCCPh})(\mu\text{-PPh}_2)_2]$ , (**2**)  $[\text{Ir}_4(\text{CO})_9(\mu_3\text{-}\eta^3\text{-Ph}_2\text{PC}(\text{H})\text{CPh})(\mu\text{-PPh}_2)]$  (**3**)  $[\text{Ir}_4(\text{CO})_{12}]$  (**4**) the mono and dinuclear complexes  $[\text{IrClCO}(\text{PPh}_3)_2]$  (**5**) and  $[\text{Ir}_2\text{Cl}_2(\text{COE})_4]$  (**6**), and the heterogeneous catalyst  $\text{Ir}^0$  supported on activated carbon. The conversion and product selectivities obtained for the reactions in the presence of these different iridium precursors are shown in Table 1.

Hydrogenation using the Vaska's complex **5** precursor showed high activity converting the 1,5-COD completely to its total hydrogenation product COA with 97% selectivity (Fig. 1a). The high 1,5-COD conversion observed at 0 min reaction time occurs during the heating period. Complex **6** is also very active, converting completely the 1,5-COD to COA as the major product, in 62% yield, and to the monohydrogenated product COE in only 32% yield.

From Fig. 1a and b it can be seen that COE is formed in the beginning of the reaction, but is further hydrogenated to COA. For the reaction of **6**, hydrogenation of COE to COA takes place significantly after 60 min. This is probably due to the low concentration of 1,5-COD after 60 min reaction time (90% conversion) favouring the hydrogenation of the monoolefin COE present in the reaction mixture. In the pres-

Table 1

Conversion and selectivities obtained for the hydrogenation of 1,5-COD in the presence of different Ir precursors<sup>a</sup>

Precursor	Conversion (%)	Selectivities (%)			
		COA	COE	1,4-COD	1,3-COD
$[\text{Ir}_4(\text{CO})_{11}\text{PPh}_2\text{H}]$ ( <b>1</b> ) (150 °C)	100	4	67	6	23
$[\text{Ir}_4(\text{CO})_{11}\text{PPh}_2\text{H}]$ ( <b>1</b> )	44	2	47	33	18
$[\text{Ir}_4(\text{CO})_{11}\text{PPh}_2\text{H}]$ ( <b>1</b> ) (80 °C)	6	6	23	57	14
$[\text{Ir}_4(\text{CO})_8(\mu_3\text{-}\eta^2\text{-HCCPh})(\mu\text{-PPh}_2)_2]$ ( <b>2</b> )	40	8	43	31	18
$[\text{Ir}_4(\text{CO})_9(\mu_3\text{-}\eta^3\text{-Ph}_2\text{PC}(\text{H})\text{CPh})(\mu\text{-PPh}_2)]$ ( <b>3</b> )	38	7	37	35	21
$[\text{Ir}_4(\text{CO})_{12}]$ ( <b>4</b> )	40	22	57	9	12
$[\text{IrClCO}(\text{PPh}_3)_2]$ ( <b>5</b> )	100	99	0	0	1
$[\text{Ir}_2\text{Cl}_2(\text{COE})_4]$ ( <b>6</b> )	100	62	32	1	5
$\text{Ir}^0/\text{AC}$	100	100	0	0	0

<sup>a</sup> Reaction conditions: [catalyst] = 0.01 mmol of Ir atoms,  $1.6 \times 10^{-2}$  mmol of 1,5-COD, 40 mL benzene, 110 °C and 20 atm of  $\text{H}_2$  for 240 min.

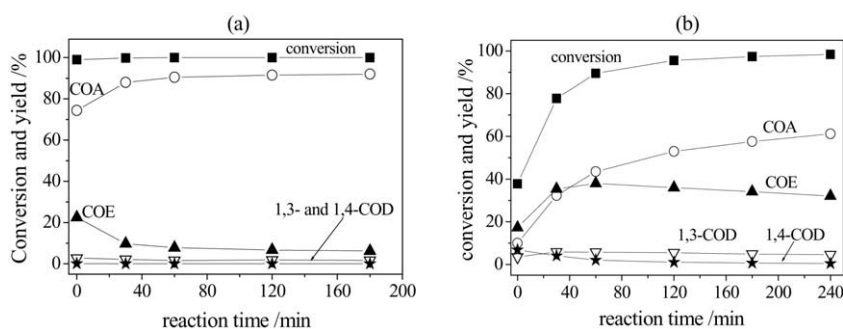


Fig. 1. 1,5-COD conversion and product yields in the catalytic hydrogenation in the presence of:  $[\text{IrClCO}(\text{PPh}_3)_2]$  (**5**) (a) and  $[\text{Ir}_2\text{Cl}_2(\text{COE})_4]$  (**6**) (b) as catalyst precursors (110 °C, 20 atm  $\text{H}_2$ ).

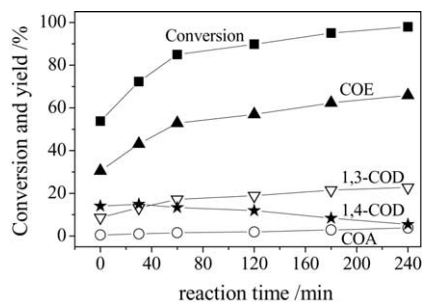


Fig. 2. Hydrogenation of 1,5-COD in the presence of  $[\text{Ir}_4(\text{CO})_{11}\text{PPh}_2\text{H}]$  (**1**) ( $150^\circ\text{C}$ , 20 atm  $\text{H}_2$ ).

ence of these catalyst precursors COE will always be completely converted to COA at longer reaction times. These results suggest a non-selective competitive process.

In contrast, tetranuclear iridium clusters catalyst precursors produced completely different results for the hydrogenation of 1,5-COD. For example, the reaction in the presence of precursor **1**, at  $150^\circ\text{C}$ , also resulted in complete conversion of 1,5-COD but with remarkable selectivity for the monohydrogenated product COE (Fig. 2). It is worth noting that even after 240 min, when all the 1,5-COD has been converted, no significant hydrogenation of COE was observed, in spite of its high concentration. Another interesting feature of this catalyst is its high activity for isomerisation: even under relatively high  $\text{H}_2$  pressure, it produces 1,3- and 1,4-COD with 23 and 6% selectivity, respectively (Table 1); this isomerisation reaction was investigated under  $\text{N}_2$  atmosphere, producing 1,3- and 1,4-COD with 40 and 60% selectivity, respectively, although with very low conversion of 1,5-COD (7%). It can also be observed from Fig. 2 that from 60 min on 1,4-COD is consumed, likely to produce COE via hydrogenation or isomerisation to 1,3-COD whose concentration apparently slightly increases during the reaction.

At lower temperatures, e.g.  $110^\circ\text{C}$ , **1** is still active with 1,5-COD conversion of 44% after 240 min reaction. The main reaction product is the monohydrogenated COE with no significant COA formed. On the other hand, high isomerisation activity is observed producing selectivities for the 1,4- and 1,3-COD of 33 and 18%, respectively (Table 1). It is interesting to observe that at this temperature the 1,4-COD isomer is formed preferentially, compared to 1,3-COD, which is the main isomer formed at  $150^\circ\text{C}$ . These results might indicate that the 1,4- isomer is kinetically favoured and is formed as a primary product. At higher temperatures the 1,4-isomer is further isomerised to the 1,3-, which is the thermodynamically favoured COD isomer [59–63].

Following the results obtained from these reactions other  $\text{Ir}_4$  clusters compounds, viz.  $[\text{Ir}_4(\text{CO})_8(\mu_3\text{-}\eta^2\text{-HCCPh})(\mu\text{-PPh}_2)_2]$  (**2**),  $[\text{Ir}_4(\text{CO})_9(\mu_3\text{-}\eta^3\text{-Ph}_2\text{PC}(\text{H})\text{CPh})(\mu\text{-PPh}_2)]$  (**3**) and  $[\text{Ir}_4(\text{CO})_{12}]$  (**4**), were tested as catalysts for the hydrogenation reaction of 1,5-COD (benzene  $110^\circ\text{C}$ , 20 atm  $\text{H}_2$ , 240 min reaction). These clusters were selected with the aim to investigate the effect of the presence of bridging ligands

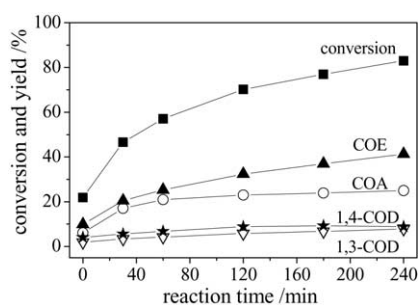


Fig. 3. Hydrogenation of 1,5-COD with the precursor  $[\text{Ir}_4(\text{CO})_{12}]$  (**4**) ( $110^\circ\text{C}$ , 20 atm  $\text{H}_2$ ).

and different polyhedral arrangements on the conversion and selectivity for the 1,5-COD hydrogenation reaction.

The results obtained for the reactions with **2** were very similar to those shown by **1**, under the same conditions, with high activity (40% conversion) and 43% selectivity for the monohydrogenated product and low formation of COA. Likewise, significant isomerisation activity was observed with 31 and 18% selectivities for the 1,4- and 1,3-COD, respectively (Table 1). The hydrogenation reaction of 1,5-COD was also investigated in the presence of  $[\text{Ir}_4(\text{CO})_9(\mu_3\text{-}\eta^3\text{-Ph}_2\text{PC}(\text{H})\text{CPh})(\mu\text{-PPh}_2)]$  (**3**), which has a butterfly type structure (Scheme 1). It is noteworthy that the results are similar to the other tetranuclear iridium clusters with a slight increase in the selectivity for the isomerisation products.

Precursor  $[\text{Ir}_4(\text{CO})_{12}]$  (**4**) also shows similar catalytic results compared to other  $\text{Ir}_4$  clusters, although in the beginning of the reaction a different behaviour is observed (Fig. 3). This cluster also produces COE with 57% selectivity after 240 min reaction. However, in the first 30 min the catalyst is not selective, producing COE and the undesirable COA in 44 and 37% selectivities, respectively. After 30 min reaction the system becomes very selective to COE and no more COA is produced. These results seem to indicate that the insoluble precursor **4** is transformed into a selective catalytic species in the first minutes of the reaction. This precursor has a lower activity for isomerisation when compared with other iridium clusters (Table 1) producing **9** and 21% selectivities for 1,4- and 1,3-COD, respectively, after 240 min reaction.

### 3.2. Kinetic investigation

Kinetic treatment of the data obtained at  $110^\circ\text{C}$  suggests a first-order dependence of the reaction rate on the 1,5-COD concentration (Fig. 4). The rate constants of ca.  $1.2 \times 10^{-3} \text{ min}^{-1}$  for the reactions with clusters **2** and **3** as catalytic precursors are significantly lower than the constants obtained when clusters **1** and **4** were employed as catalysts, ca.  $2.0 \times 10^{-3} \text{ min}^{-1}$  (Table 2).

These results suggest that interaction of the less hindered clusters **1** and **4** with 1,5-COD to form the active catalytic species is relatively easy, whereas for the phosphorus bridg-

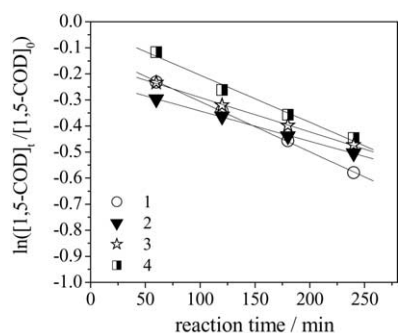


Fig. 4. Arrhenius plot for the reaction of 1,5-COD in the presence of different catalyst precursors. [catalyst] = 0.01 mmol of Ir atoms,  $1.6 \times 10^{-2}$  mmol of 1,5-COD, 40 mL benzene, 110 °C and 20 atm H<sub>2</sub> for 240 min.

Table 2

First order reaction rate constants and TON (turnover number) for the hydrogenation of 1,5-COD in the presence of different catalytic precursors at 110 °C and 20 atm H<sub>2</sub>

Catalyst precursor	$k$ (min <sup>-1</sup> )	TON
[Ir <sub>4</sub> (CO) <sub>11</sub> PPh <sub>2</sub> H] ( <b>1</b> )	0.0020	2816
[Ir <sub>4</sub> (CO) <sub>8</sub> (μ <sub>3</sub> -η <sup>2</sup> -HCCPh)(μ-PPh <sub>2</sub> ) <sub>2</sub> ] ( <b>2</b> )	0.0012	2560
[Ir <sub>4</sub> (CO) <sub>9</sub> (μ <sub>3</sub> -η <sup>3</sup> -Ph <sub>2</sub> PC(H)CPh)(μ-PPh <sub>2</sub> ) <sub>2</sub> ] ( <b>3</b> )	0.0013	2432
[Ir <sub>4</sub> (CO) <sub>12</sub> ] <sup>a</sup> ( <b>4</b> )	0.0018	2440

<sup>a</sup> Reaction rate constant between 30 and 240 min reaction.

ing ligand containing species **2** and **3** formation of the catalytic species is slower, leading to a slower reaction with the substrate 1,5-COD. Nevertheless, considering the selectivity of this hydrogenation reaction, it is probable that all different Ir<sub>4</sub> precursors are converted into similar catalytic species under the reaction conditions, and the P-ligands do not interfere significantly in the catalytic cycle. Catalytic turnover numbers of 2816, 2560, 2432, 2440, and for **1**, **2**, **3**, **4**, and, respectively, at 110 °C, are much larger when compared with other olefin hydrogenation reactions using Os, Ru, Rh, Ni and Pt clusters as catalysts [64]. For example, catalytic hydrogenation of 1,5-COD occurred in the presence of [Pt<sub>2</sub>Mo<sub>2</sub>Cp<sub>2</sub>(CO)<sub>6</sub>(PEt<sub>3</sub>)<sub>2</sub>] [65], under similar conditions, with a turnover number of ca. 580 and formation of 1,3-COD as the predominant isomerisation product.

To determine the temperature dependence of the hydrogenation of 1,5-COD in the presence of the catalyst precursor **1** the reaction was carried out at 80 °C, 110 °C and 150 °C (Table 1). The constant rates obtained for these three temperatures were  $3.0 \times 10^{-4}$ ,  $2.0 \times 10^{-3}$  and  $1.1 \times 10^{-2}$  min<sup>-1</sup>, respectively. These data expressed by means of the Arrhenius equation ( $\ln k = \ln A - E_a/RT$ ) yield an activation energy of ca. 65 kJ mol<sup>-1</sup> for this reaction. The reaction carried out at 80 °C exhibited low activity, only 6% conversion after 240 min, producing mainly the 1,4-COD isomer rather than the hydrogenation product. This result suggests that under these conditions activation of 1,5-COD is more facile than that of H<sub>2</sub>, which is likely the limiting step in the hydrogenation reaction.

Table 3

Hydrogenation of cyclooctene, cyclohexene and 1,3-COD in the presence of [Ir<sub>4</sub>(CO)<sub>11</sub>PPh<sub>2</sub>H] (**1**) and [IrClCO(PPh<sub>3</sub>)<sub>2</sub>] (**5**) at 110 °C and 20 atm H<sub>2</sub>

Catalyst precursor	Conversion of the olefins (%)		
	Cyclooctene	Cyclohexene	1,3-COD
[Ir <sub>4</sub> (CO) <sub>11</sub> PPh <sub>2</sub> H] ( <b>1</b> )	12	2	13
[IrClCO(PPh <sub>3</sub> ) <sub>2</sub> ] ( <b>5</b> )	100	100	100

### 3.3. Hydrogenation of monoolefins and 1,3-COD

The hydrogenation of the monoolefins cyclooctene, cyclohexene and of 1,3-COD in the presence of [Ir<sub>4</sub>(CO)<sub>11</sub>PPh<sub>2</sub>H] (**1**) and [IrClCO(PPh<sub>3</sub>)<sub>2</sub>] (**5**) was also investigated (Table 3). Whereas precursor **5** completely hydrogenated all the olefins studied, under the same reaction conditions, precursor **1** produced very low conversions of 12, 2 and 13%, for the olefins cyclooctene, cyclohexene and 1,3-COD, respectively.

These results suggest that a special interaction of the Ir<sub>4</sub> clusters with the diolefin 1,5-COD might take place, which would lead to the observed selective hydrogenation. In this way, after hydrogenation of 1,5-COD, the monoolefin COE is not further hydrogenated, resulting in high selectivity for monohydrogenation.

The relative position of the double bonds seems important as 1,5-COD shows a much higher reactivity towards the Ir<sub>4</sub> cluster **1** and much better selectivity compared to the 1,3-isomer. The hydrogenation of 1,3-COD produces preferably the total hydrogenated product COA with 67% selectivity and 33% of COE with no 1,4-COD isomer detected during the reaction.

### 3.4. Isomerisation reaction

The isomerisation of 1,5-COD yielding 1,4-COD and 1,3-COD was investigated in the presence of **1**. The reaction was carried out at 110 °C under N<sub>2</sub>. Isomers 1,3-COD and 1,4-COD were produced with 40 and 60% selectivities, respectively, although with a low conversion of 7% after 240 min reaction. Under these conditions, an isomerisation mechanism based on the displacement of hydrogen via a π-allylic intermediate might be operative. On the other hand, under H<sub>2</sub> atmosphere, an alternative pathway might be proposed for the isomerisation reaction, via addition-elimination of a hydride [59].

Although, these two mechanisms might take place in a single Ir atom, a multisite interaction of 1,5-COD with the cluster structure might also take place and could play an important role during the isomerisation reaction. Furthermore, it has to be considered that in the absence of hydrogen different active catalytic species might be present in the reaction medium.

### 3.5. Verification of the catalysis by clusters

Clusters frequently fragment in solution producing mononuclear metal complexes or aggregate to form high nu-

clarity clusters, even producing in some cases metal particles, which may be responsible for the catalytic activity [66]. For this reason it is important to establish the true nature of the catalyst in the reaction and to determine the active species. Several criteria have been discussed in the literature [5,67], which can be used as evidences for cluster catalysis. These criteria were used for the reactions of 1,5-COD with the different Ir<sub>4</sub> clusters.

### 3.5.1. Tests for heterogeneous catalysis

Several tests were carried out to investigate whether the catalysis occurred via heterogeneous metal particles generated in situ from cluster decomposition.

- (i) Direct examination of all catalysts solutions by light scattering under a strong light beam [68] did not evidence metal particles. However, it is important to bear in mind that this approach allows the ready detection of fairly large metal particles, and it is quite easy to miss small metal particles [69–71].
- (ii) The catalytic hydrogenation reactions with all Ir<sub>4</sub> clusters were carried out for 4 h, cooled, and the mixtures, filtered over celite, under Ar atmosphere. The filtrates and celite were used as catalysts for the hydrogenation reactions under the same conditions of the initial reaction (4 h, 110 °C and 20 atm of H<sub>2</sub>) [72]. The hydrogenation reactions with the filtered solutions exhibited an average conversion (40%), which was slightly lower than that of the initial reaction (ca. 44%), whereas the reaction carried out with the celite as catalyst showed a 7% conversion, which could well be related to some Ir<sub>4</sub> cluster adsorbed or retained on the celite surface.
- (iii) Another approach to identify catalysis by metal particles highly dispersed in the reaction medium involves addition of metallic mercury to amalgamate any metal particles [73], reducing or eliminating the catalytic activity of the dispersed metal. The results from the reactions carried out in the presence and absence of Hg<sup>0</sup> showed similar conversions and product selectivities (Fig. 5). These results are in agreement with the previous tests, suggesting a homogeneous catalytic process.

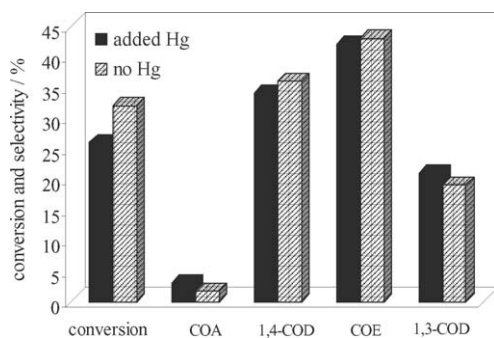


Fig. 5. Conversion and selectivity of the products formed during the reactions carried out in the presence and absence of Hg<sup>0</sup>, using 1 as the catalyst precursor (110 °C, 240 min, 20 atm H<sub>2</sub>).

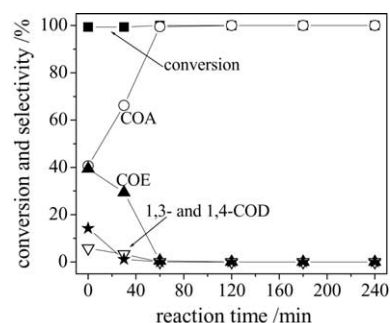


Fig. 6. Conversion of 1,5-COD and product selectivities in the presence of Ir<sup>0</sup>/AC at 110 °C and 20 atm H<sub>2</sub>.

- (iv) A reaction catalysed by a supported metallic Ir catalyst, Ir<sup>0</sup>/AC, was also carried out for comparison with the homogeneous catalyses. This is another approach to rule out the existence of heterogeneous reaction [74]. The Ir<sup>0</sup>/AC was very active for the hydrogenation reaction of 1,5-COD, leading to total conversion of the substrate at the beginning of the reaction, producing exclusively the total hydrogenated product COA (Fig. 6). This result is completely different from that shown by the Ir<sub>4</sub> clusters catalysed reactions.

### 3.5.2. Tests for lower nuclearity complexes being the catalytically active species

One of the most difficult aspects of cluster catalysis is to establish that the catalysis is not taking place on mononuclear fragments. A first indication that the cluster is acting as the catalytic species is that the product selectivities obtained using a cluster catalyst should be different from those obtained using mononuclear catalyst precursors. In this work the results obtained using low nuclearity compounds, [IrCICO(PPh<sub>3</sub>)<sub>2</sub>] (5) and [Ir<sub>2</sub>Cl<sub>2</sub>(COE)<sub>4</sub>] (6) showed completely different results compared to the Ir<sub>4</sub> clusters, with much higher activity and producing preferentially the total hydrogenation product COA (Table 1). On the other hand, the reactions using Ir<sub>4</sub> clusters showed lower conversion of ca. 40%, producing selectively the monohydrogenated product COE and higher activity for isomerisation.

## 4. Concentration

Variation of the hydrogenation rates with the cluster concentration can be used to investigate the nature of the catalytic species [67]. The catalytic hydrogenation of 1,5-COD using [Ir<sub>4</sub>(CO)<sub>9</sub>(μ<sub>3</sub>-η<sup>3</sup>-Ph<sub>2</sub>PC(H)CPh)(μ-PPh<sub>2</sub>)] (3) as a catalytic precursor was investigated using cluster concentrations between 0.05 (3 mg of cluster) up to 0.5 mmol L<sup>-1</sup> (30 mg of cluster) (Fig. 7). The influence of different concentrations on the conversion and product selectivities was mainly observed for the isomerisation reactions, which produce 1,3-COD and 1,4-COD. However, in all different cluster concen-

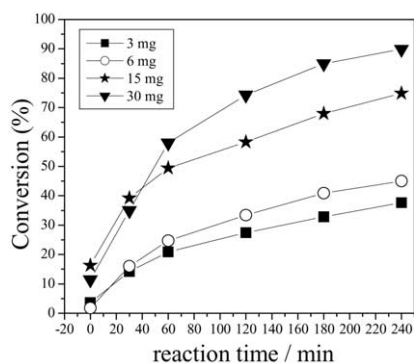


Fig. 7. Conversion and product selectivities for the hydrogenation of 1,5-COD in the presence of different concentrations of  $[\text{Ir}_4(\text{CO})_9(\mu_3\text{-}\eta^3\text{-Ph}_2\text{PC(H)CPh})(\mu\text{-PPh}_2)]$  (**3**) at 110 °C for 240 min.

trations COE was the main product and no significant change in the COA concentration was observed.

#### 4.1. Mechanistic considerations

The data presented in this work, showed that the catalytic behaviour of  $\text{Ir}_4$  clusters is completely different from that of the mono and dinuclear catalysts  $[\text{IrClCO}(\text{PPh}_3)_2]$  (**5**),  $[\text{Ir}_2\text{Cl}_2(\text{COE})_4]$  (**6**) and from the heterogeneous  $\text{Ir}^0/\text{AC}$ . The  $\text{Ir}_4$  clusters showed lower activity with high selectivity to the monohydrogenated product, COE, and to the isomerisation. Another relevant point for the reaction mechanism is that the  $\text{Ir}_4$  clusters cannot hydrogenate efficiently monoolefins, such as cyclooctene and cyclohexene, whereas the mononuclear Vaska's compound  $[\text{IrClCO}(\text{PPh}_3)_2]$  (**5**) is very efficient.

From the obtained data a simple sequence of reactions can be given which will differ for the different iridium precursors used (Fig. 8).

The mono and dinuclear iridium compounds (**5** and **6**) seem to promote all the pathways shown in Fig. 8, that lead to the formation of COA as a primary and a secondary products. All hydrogenation pathways are favoured under the re-

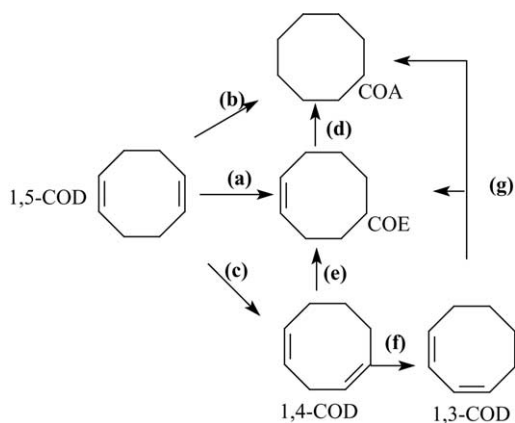


Fig. 8. Reaction pathways during the hydrogenation of 1,5-COD with the Ir catalysts.

action conditions, and no significant amounts of isomers are observed. On the other hand, the  $\text{Ir}_4$  cluster precursors (**1–4**) seem to be selective in taking the reaction through paths (a) and (c) mainly. Considering the very low selectivity observed for COA, no reaction seems to take place via paths (b) and (d). Isomerisation paths (c) and (f) are also important in the reactions catalysed by  $\text{Ir}_4$  clusters. However, hydrogenation of the isomers, via (e) and (g) paths, is not as favoured as path (a).

These results suggest that the  $\text{Ir}_4$  clusters interact in a special way with 1,5-COD leading to its selective hydrogenation to produce COE. Once the monoolefin COE is formed it cannot be further hydrogenated. The relative position of the two double bonds seems to be important to activate the substrate, as the  $\text{Ir}_4$  clusters are much more efficient to hydrogenate 1,5-COD than isomers 1,3- and 1,4-COD.

It is well known that Vaska's compound form stable  $\eta^2$ -complexes with monoolefins [75–77]. On the other hand, monoolefin  $\eta^2$ -complexes of  $\text{Ir}_4$  clusters are unstable, some even at low temperature [78,79]. Moreover,  $\text{Ir}_4$  clusters can readily produce stable  $\eta^4$ -complexes [75]. These observations are in agreement with the results obtained for the catalytic hydrogenation reactions using  $\text{Ir}_4$  clusters, which cannot activate and hydrogenate monoolefins.

Of interest to our catalytic studies is the work of Shapley et al. [80,81], who obtained the complex  $[\text{Ir}_4(\text{CO})_5(\text{C}_8\text{H}_{12})_2(\text{C}_8\text{H}_{10})]$  as a stable orange-brown solid, in high yields, from the direct reaction of  $[\text{Ir}_4(\text{CO})_{12}]$  with 1,5-COD. The facile preparation of this closo- $\text{Ir}_4\text{C}_2$  compound illustrates the ability of  $\text{Ir}_4$  clusters in complexing and even activating the C–H bond of 1,5-COD. However this stable species presumably results from the oxidative addition of one COD and reductive elimination of  $\text{H}_2$  and therefore would not be formed under the hydrogenation reaction conditions. Clusters containing three or more COD ligands coordinated via the double bonds could well be the active catalytic species.

In an attempt to investigate the formation of a Shapley-like intermediate during the hydrogenation, two procedures were used: (i) characterization of the iridium species after the reaction and (ii) use of Shapley's compound as catalyst precursor. After the reactions with precursors **1–4** the volatiles were evaporated under vacuum and the residues, purified by TLC. The resulting dark brown compounds were analysed by  $^1\text{H}$  NMR and IR spectroscopy that evidenced formation of the same species in all cases. The IR spectra in benzene clearly showed the presence of terminal carbonyl ligands ( $\nu_{\text{CO}}$  2077 s, 2068 mbr, 2035 m and 2016 m,  $\text{cm}^{-1}$ ), whereas the indication that 1,5-COD was coordinated to a metal cluster was obtained from the  $^1\text{H}$  NMR spectra ( $\text{CDCl}_3$ , 25 °C) that showed signals at  $\delta$  6.21–5.00 (m), 4.8–3.9 (m) and 3.0–1.3 (m), suggesting a complexed  $\text{C}_8$  ligand as observed by Shapley [80]. No signal was observed in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra, indicating that the phosphorus ligands were lost during the hydrogenation reactions.

The catalytic reaction using Shapley's compound  $[\text{Ir}_4(\text{CO})_5(\text{C}_8\text{H}_{12})_2(\text{C}_8\text{H}_{10})]$  as precursor was carried out under the same conditions and showed conversion of ca. 40% and selectivity for COE of 43%, which are very similar to those obtained for the other  $\text{Ir}_4$  clusters. The  $\text{Ir}_4$ -diolefin  $\eta^2$ - $\eta^2$ -COD interaction would explain two important features observed in this work: (i) only diolefines, especially 1,5-COD, which can efficiently interact with the  $\text{Ir}_4$  clusters would be hydrogenated, since formation of this intermediate with monoolefins (cyclohexene and cyclooctene) would be impossible and with 1,3-COD, far more difficult, leading to poor hydrogenation activity; (ii) the isomerisation of 1,5-COD to 1,4- and 1,3-COD, observed in our experiments, must go through a C–H bond activation analogous to that observed in the Shapley's compound [80].

It seems that a general feature of these  $\text{Ir}_4$ -diolefin  $\eta^2$ - $\eta^2$ -COD intermediates is the "anchor-type" interaction of both 1,5-COD double bonds with one Ir atom, which allows the activation and hydrogenation of one of this bonds by the cluster. For this reason monoolefins cannot be efficiently hydrogenated. This "anchor-type" interaction was previously proposed for the reaction of  $\text{Ir}_4$  clusters with  $\text{Ph}_2\text{PC}\equiv\text{CPh}$  [12,46,47,54,55] in which the phosphorus moiety coordinates to a Ir atom allowing the triple bond to be activated by the cluster. Significantly non-modified acetylenes, such as  $\text{HC}\equiv\text{CPh}$ , do not form stable complexes with  $\text{Ir}_4$  clusters [51].

## 5. Conclusion

The results presented herein suggest that  $\text{Ir}_4$  clusters interact in a unique way with diolefins to produce selective catalytic hydrogenation. As the first double bond is hydrogenated, cyclooctene immediately dissociates from the cluster and cannot re-coordinate to be further hydrogenated, which results in high selectivity for the monohydrogenation product. In contrast, mono- and dinuclear Ir precursors hydrogenate both mono and diolefins.

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