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The cyclooctadiene ligand in $[IrCl(COD)]_2$ is hydrogenated under transfer hydrogenation conditions: A study in the presence of PPh_3 and a strong base in isopropanol

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The interaction of $[IrCl(COD)]_2$ with PPh_3 in isopropanol has been investigated for various P/Ir ratios, in the absence or presence of a strong base (KO*t*Bu), at room temperature and at reflux. At room temperature, PPh_3 adds to the metal center to yield $[IrCl(COD)(PPh_3)]$ and additional PPh_3 only undergoes rapid degenerative ligand exchange. Subsequent addition of KO*t*Bu affords $[IrH(COD)(PPh_3)_2]$ as the main compound, even for high P/Ir ratios, although very minor amounts of products having a "$HIr(PPh_3)_3$" core are also generated. Warming to the solvent reflux temperature results in a rapid (<1 h) and quantitative COD removal from the system as hydrogenated products (54.4% of cyclooctene plus 32.2% of cyclooctane according to a quantitative GC analysis) and in the eventual generation of $[IrH_3(PPh_3)_3]$. The latter is observed as a mixture of the *fac* and *mer* isomers in solvent-dependent proportions. Other minor products, one of which is suggested to be *mer-cis*-$[IrH_2(OiPr)(PPh_3)_3]$ by the NMR characterization, are also generated. These results show that, contrary to certain previously published assumptions, systems of this kind are unlikely to function via a COD-containing active species in transfer hydrogenation catalysis conducted in hot isopropanol in the presence of a strong base.

1. Introduction

Transfer hydrogenation is a catalyzed process that allows unsaturated compounds such as aldehydes, ketones and imines to be reduced by a hydrogen donor DH_2, which is transformed to a by-product D, typically isopropanol giving acetone or formic acid giving CO_2 [1–7]. Hence, it performs the same transformations as hydrogenation but, relative to the latter, presents the main advantage of removing the hazards associated to the use of the gaseous and flammable H_2. However, because of the smaller thermodynamic driving force relative to hydrogenation, harsher conditions - namely higher temperatures - are generally required. Catalysts used to accelerate this reaction span from Lewis acids, which operate through the Meerwein-Ponndorf-Verley mechanism, to unsaturated transition metal hydrides that are able to promote a coordination/insertion mechanism, to transition metal complexes with π-loaded ligands such as amido functions able to operate via an outer-sphere (the so-called Noyori-Morris) mechanism [8,9]. Many transition metal complexes are able to promote both hydrogenation and transfer hydrogenation and a strong base is generally required in both cases to achieve high activity.

Rhodium and iridium complexes obtained from $[MX(COD)]_2$ (M = Rh, Ir; X = Cl, OMe) in the presence of various ligands have received considerable attention as pre-catalysts for transfer hydrogenation [10–54]. The nature of the active species and the mechanism have been discussed in several experimental and computational contributions [14,40,55–62]. It seems that a different mechanism may be adopted depending on the nature of the metal and of the supporting ligand. For instance, working with a computational model of the $[RhCl(COD)]_2$/chiral diamine pre-catalysts used in the Lemaire group, Delbecq et al. find that only the outer sphere mechanism is able to account for the observed enantioselectivity of the reaction [57,58]. Oro et al., on the other hand, conclude that systems generated from [Ir(μ-OMe)(diene)]/PR_3 function through a coordination/insertion mechanism [60].

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One crucial question is whether the diene ligand in the precatalyst remains coordinated to the metal in the catalytically active species or whether it is displaced, either as such or in a hydrogenated form. It seems clear that COD is removed under hydrogenation conditions (*i.e.* under H_2), but whether this occurs under transfer hydrogenation conditions (particularly in warm isopropanol) does not bring consensus. It has been shown that certain systems differing only by the nature of the diene have different activity. For instance, Lemaire et al. have shown that the activity trend at room temperature of the $[RhCl(diene)]_2$/diamine/KO*t*Bu/*i*PrOH system as the diene is changed goes as COD > norbonadiene > hexadiene > $(ethylene)_2$ [55]. Similarly, the iridium system $[IrCl(diene)]_2$/aminosulfide/HCOOH/NEt_3 has shown activities in the order COD >> $(COE)_2$ at 60 °C. These observation have led the authors to propose that the diene or alkene remains metal bonded in the active species [18]. On the basis of these reports, the above-mentioned computational investigations on Rh- and Ir-catalyzed transfer hydrogenation cycles were carried out on COD-containing systems, or models thereof [55–60].

However, evidence for COD release from iridium complexes under transfer hydrogenation conditions has been gathered since quite some time ago. Kvintovics et al. have shown that, in the presence of 2 equivalents of the chelating diphosphinite (2*R*,4*R*)-2,4-bis(diphenylphosphinoxy)pentane (BDPOP) and 10 equivalents of NaOMe, complex $[IrCl(COD)]_2$ loses COD within 60 min in isopropanol at room temperature to yield cyclooctene as the only detected product (no free COD and no cyclooctane) [13]. Spogliarich et al. have reported that the activation of $[Ir(COD)P_2]^+$ (P_2 = chiral diphosphine: chiraphos, prophos or diop) in refluxing *i*PrOH yields COD-free compounds with brigding hydrides [63], analogous to the $[Ir_2(\mu\text{-}H)_3H_2L_4]^+$ complexes previously reported by Crabtree et al. [64], even without adding a strong base to the system. In a much more recent contribution, Jiménez et al. have shown that, in isopropanol at 80 °C and in the presence of KOH, the transfer hydrogenation catalytic activity of $[Ir(COD)\{\kappa C\text{-}Me(o\text{-}pyCH_2)Im\}_2]^+$ is identical to that of separately synthesized $[IrH_2\{\kappa C,\kappa N\text{-}Me(o\text{-}pyCH_2)Im\}_2]^+$ where COD is not present, while a GC/MS analysis during catalysis with the COD derivative shows the presence of cyclooctene [61]. Finally, Oro et al. have recently show that addition of sodium isopropoxide to $[(COD)Ir\{\kappa^3 PCP\text{-}1,3\text{-}(Ph_2PCH_2CH_2)\text{-}2\text{-}CH_2Im\}]^+PF_6^-$ affords free COD upon heating to 80 °C [65]. It should also be underlined that certain Rh and Ir complexes are known to be active catalysts for the transfer hydrogenation from alcohols to olefins [66–70].

In this contribution, we report our investigations of the reaction between $[IrCl(COD)]_2$ and PPh_3 under a variety of conditions, including those typical of catalytic transfer hydrogenation. Indeed, in work by the Oro's group, complex $[IrH(COD)(PPh_3)_2]$, which is accessible directly from $[IrCl(COD)]_2$ and PPh_3 in the presence of base, was proven an efficient precatalyst for the transfer hydrogenation of cyclohexanone (62% conversion in 24 h in isopropanol at 60 °C with a 1% catalyst loading) [71]. However, a detailed investigation of the high-temperature activation has not been previously reported for this system to the best of our knowledge. We will show here that the COD ligand is hydrogenated and removed from the metal upon warming. Our investigation has retraced a few already well established transformations, but has also brought to the surface a few unexpected and surprising results.

2. Experimental

2.1. General

All reactions were carried out under an argon atmosphere using standard Schlenk techniques. Isopropanol was carefully dried by distillation on calcium hydride and kept over 4 Å molecular sieves under argon before use. All commercially available chemicals ($[IrCl(COD)]_2$, 99%, Strem Chemicals; PPh_3, 99%, Aldrich; NaOMe, 99%, Aldrich) were used as received. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded with Bruker Avance 400, Bruker Avance III 400 and Bruker Avance 500 FT-NMR spectrometers. The resonances were calibrated relative to the residual solvent peaks and are reported with positive values downfield from TMS. For all characterized compounds, the peak assignments in the ^1H and ^{13}C NMR spectra were based on COSY, HSQC and HMBC 2D experiments. Gas chromatographic analyses were carried out with a Supelco SPB-20 column (40 °C for 10 min then heating 3 °C/min up to new isotherm at 120 °C): cyclooctene (11.6 min); cyclooctane (13.1 min); cyclooctadiene (13.6 min).

2.2. Reaction of $[Ir(\mu\text{-}Cl)(COD)]_2$ and PPh_3 in isopropanol in the presence of KOtBu at room temperature: generation of $[Ir(COD)H(PPh_3)_2]$

PPh_3 (78 mg, 0.297 mmol) was added to an isopropanol solution (10 mL) of $[Ir(\mu\text{-}Cl)(COD)]_2$ (50 mg, 0.074 mmol) and the solution was stirred at room temperature for 3 h. Potassium *tert*-butoxide (83 mg, 0.74 mmol) was then added to the mixture and stirred at room temperature for 5 min. The white precipitate was removed by filtration and the filtrate was concentrated under reduced pressure. Yield: 96 mg (78%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.79–7.10 (m, 30H, Ph), 3.81 (br, 2H, COD), 3.47 (br, 2H, COD), 1.83 (br, 4H, COD), 1.54 (br, 4H, COD),-13.77 (t, 1H, Ir-H, J_{PH} = 22 Hz). ^{31}P $\{^1H\}$ NMR (400 MHz, $CDCl_3$): δ 7.5. ^{13}C NMR (400 MHz, $CDCl_3$): δ 139.7 (Ph-*ipso*, m with virtual coupling), 133.4 (Ph-*ortho*, virtual t, J_{PC} = 5.8 Hz), 128.1 (Ph-*para*, s), 127.3 (Ph-*meta*, virtual t, J_{PC} = 4.4 Hz), 79.3 (CH COD, s), 47.7 (CH COD, m with virtual coupling), 34.7 (CH_2 COD, s), 31.4 (CH_2 COD, s).

2.3. Reaction of $[Ir(\mu\text{-}Cl)(COD)]_2$ and PPh_3 in isopropanol in the presence of KOtBu at the reflux temperature: generation of fac-$[IrH_3(PPh_3)_3]$

PPh_3 (72 mg, 0.274 mmol) was added to an isopropanol solution (10 mL) of $[Ir(\mu\text{-}Cl)(COD)]_2$ (30 mg, 0.045 mmol) and the solution was stirred at room temperature for 3 h. Potassium *tert*-butoxide (50 mg, 0.446 mmol) was added to the mixture and refluxed for 3 h, with NMR monitoring (see Results and Discussion). The yellow solution became colorless with generation of a white solid. The precipitate was filtered off and the filtrate was concentrated to dryness under reduced pressure. Yield: 70 mg (80%, based on iridium). ^1H NMR (400 MHz, $CDCl_3$): δ 7.64–6.82 (m, 45H, Ph),-12.25 (AA'A″XX'X″, 3H). ^{31}P $\{^1H\}$ NMR ($CDCl_3$, 400 MHz): δ 9.3 (s). Colorless crystals suitable for X-ray diffraction were obtained as a $CDCl_3$ solvate from the NMR solution upon standing.

In a separate experiment, the same procedure was repeated using $[Ir(\mu\text{-}Cl)(COD)]_2$ (80 mg, 0.119 mmol), PPh_3 (124 mg, 0.473 mmol), KO*t*Bu (132 mg, 1.18 mmol) and mesilylene (10 mg) as an internal standard in 7 mL of *i*PrOH. After 3 h of heating at 85 °C, gas-chromatographic analysis of the solution revealed the generation of cyclooctene (54.4%) and cyclooctane (32.2%), while a peak at the elution time expected for cyclooctadiene was not observed.

2.4. X-ray structural analysis

A single crystal of *fac*-$[IrH_3(PPh_3)_3]\cdot CDCl_3$ was mounted under inert perfluoropolyether at the tip of glass fiber and cooled in the cryostream of a Bruker APEXII diffractometer fitted with a Mo microfocus source. The structure was solved by direct methods (SHELXt) [72] and refined by least-squares procedures on F^2 using SHELXL-97 [73]. All H atoms attached to carbon were introduced in calculation in idealised positions and treated as riding models. The Ir atom as well as the C atom of the chloroform solvate are located on a 3-fold axis and then only a third of the whole molecule defines the asymmetric unit. The search for the H hydride in the region where it could be expected gave one peak which could be attributed to the hydride. This H was freely refined isotropically and gave satisfactory results. The drawing of the molecules was realised with the help of ORTEP32 [74,75]. Crystal data and refinement parameters are shown in Table 1.

3. Results and discussion

The interaction between $[IrCl(COD)]_2$ and PPh_3, at various P/Ir ratios, in isopropanol solution was investigated sequentially under three different conditions. First, the phosphine ligand was added to the complex at room temperature in the absence of a base. Then, a strong base was added at room temperature. Finally, the resulting solution was warmed up to the reflux temperature.

The addition of phosphines to $[IrCl(COD)]_2$ is a well known process, leading to different products depending on stoichiometry, solvent and ligand denticity (monodentate L, bidentate L_2): neutral 4-coordinate [IrCl(COD)L], neutral 5-coordinate $[IrCl(COD)L_2]$, ionic $[Ir(COD)L_2]^+Cl^-$ or $[Ir(COD)L_2]^+[IrCl_2(COD)]^-$. Addition of 1 equiv of PPh_3 per Ir atom yields a solution of $[IrCl(COD)(PPh_3)]$, as previously described [76]. We have only been able to find ^1H NMR characterization for this compound in the literature [77,78]. We observe the phosphine resonance in the $^{31}P\{^1H\}$ NMR spectrum at δ 21.7. When the amount of PPh_3 was raised to 2 equiv per Ir, only one broad resonance was observed at an average position between those of $[IrCl(COD)(PPh_3)]$ and free PPh_3, indicating rapid self-exchange between free and coordinated ligand (Equation (1), Fig. 1). This shows that the formation of a 5-coordinate bis-triphenylphosphine adduct is not favorable.

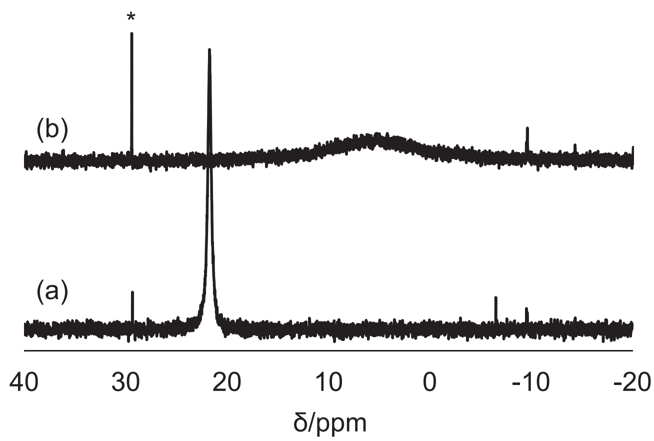


Fig. 1. $^{31}P\{^1H\}$ NMR spectra of the $[IrCl(COD)]_2 + PPh_3$ reaction in isopropanol (aliquot evaporated to dryness and residue redissolved in $CDCl_3$). (a) P/Ir ratio = 1. (b) P/Ir ratio = 2. The starred resonance (δ 29.3) is due to a small amount of Ph_3PO impurity.

$$[IrCl(COD)(PPh_3)] + PPh_3 \rightleftarrows PPh_3 + [IrCl(COD)(PPh_3)] \quad (1)$$

Subsequent addition of a strong base (NaOMe or KOtBu) to the solution having a P/Ir ratio of 2 led to the generation of the known $[IrH(COD)(PPh_3)_2]$ [79–81]. This compound was also previously obtained from $[Ir(OMe)(COD)]_2$ and PPh_3, or from $[Ir(COD)(PPh_3)_2]^+$ and KOH/MeOH, or from $[IrCl(COD)]_2/PPh_3$/KOH/MeOH [71], all of these procedures generating the hydride by β-H elimination from the methoxide ligand in the putative $[Ir(OMe)(COD)(PPh_3)_2]$ intermediate. In the present case, even though $tBuO^-$ has no available β-H, it can abstract a proton from the isopropanol solvent and lead to an isopropoxide intermediate than can β-H eliminate an acetone molecule. Replacement of chloride with hydride in the coordination sphere allows coordination of a second PPh_3 ligand (Equation (2)).

$$[IrCl(COD)(PPh_3)] + PPh_3 + Me_2CHO^- \rightarrow [IrH(COD)(PPh_3)_2] + Me_2C = O + Cl^- \quad (2)$$

The NMR (^1H, ^{31}P) properties of the product of Equation (2) (^1H triplet at δ -13.77 with J_{HP} = 21.9 Hz, collapsing to a singlet upon broadband P decoupling; $^{31}P\{^1H\}$ singlet at δ 7.5, see Fig. 1S) match those previously reported for $[IrH(COD)(PPh_3)_2]$ [71,82]. The ^{13}C NMR spectrum appears to be reported here for the first time. All phenyl groups are equivalent on the NMR timescale. The CH and CH_2 groups of the COD ligand give two resonances each, consistent with mirror symmetry. Their assignment was confirmed by a DEPT135 ^{13}C NMR experiment (see Fig. 2). The structure of this compound has not been elucidated, but it can reasonably be assumed identical to those of the structurally characterized analogues with the bidentate diphosphines L_2 = N(*sec*-Bu)$(CH_2CH_2PPh_2)_2$ [83] and HC(*o*-anisyl)(*o*-C_6H_4P*i*$Pr_2)_2$ [84], namely trigonal bipyramidal with the H ligand and one of the two COD double bonds placed in the axial position, thus rendering the two P atoms equivalent and the two COD double bonds inequivalent, in agreement with the NMR evidence. A particular feature of this spectrum is that the resonances of the phenyl *ipso*, *ortho* and *meta* atoms, as well as that of the COD equatorial C atoms, which show coupling to the P nuclei, are virtual triplets rather than doublets, consistent with a strong homonuclear P-P coupling (see excerpts in Fig. 2).

Table 1
Crystal data and structure refinement for *fac*-$[IrH_3(PPh_3)_3]$.

Identification code	$[IrH_3(PPh_3)_3]$
Empirical formula	C_{54} H_{48} Ir P_3, CH Cl_3
Formula weight	1101.40
Temperature, K	173(2)
Wavelength, Å	0.71073
Crystal system	Trigonal
Space group	R 3 c
a, Å	12.7235(8)
c, Å	51.890(3)
α,°	90.0
β,°	90.0
γ,°	120.0
Volume, $Å^3$	7274.9(10)
Z	6
Density (calc), Mg/m^3	1.507
Abs. coefficient, mm^{-1}	3.054
F(000)	3306
Crystal size, mm^3	0.270 × 0.240 × 0.100
Theta range,°	2.43 to 36.30
Reflections collected	158090
Indpt reflections (R_{int})	7821 (0.0391)
Completeness, %	99.9
Absorption correction	Multi-scan
Max./min. transmission	0.748/0.618
Refinement method	F^2
Data/restraints/parameters	7821/1/190
Goodness-of-fit on F^2	1.18
R1, wR2 [I > 2σ(I)]	0.0200, 0.0399
R1, wR2 (all data)	0.0292, 0.0434
Flack's parameter	0.000(2)
Residual density, e.$Å^{-3}$	0.912/-0.435

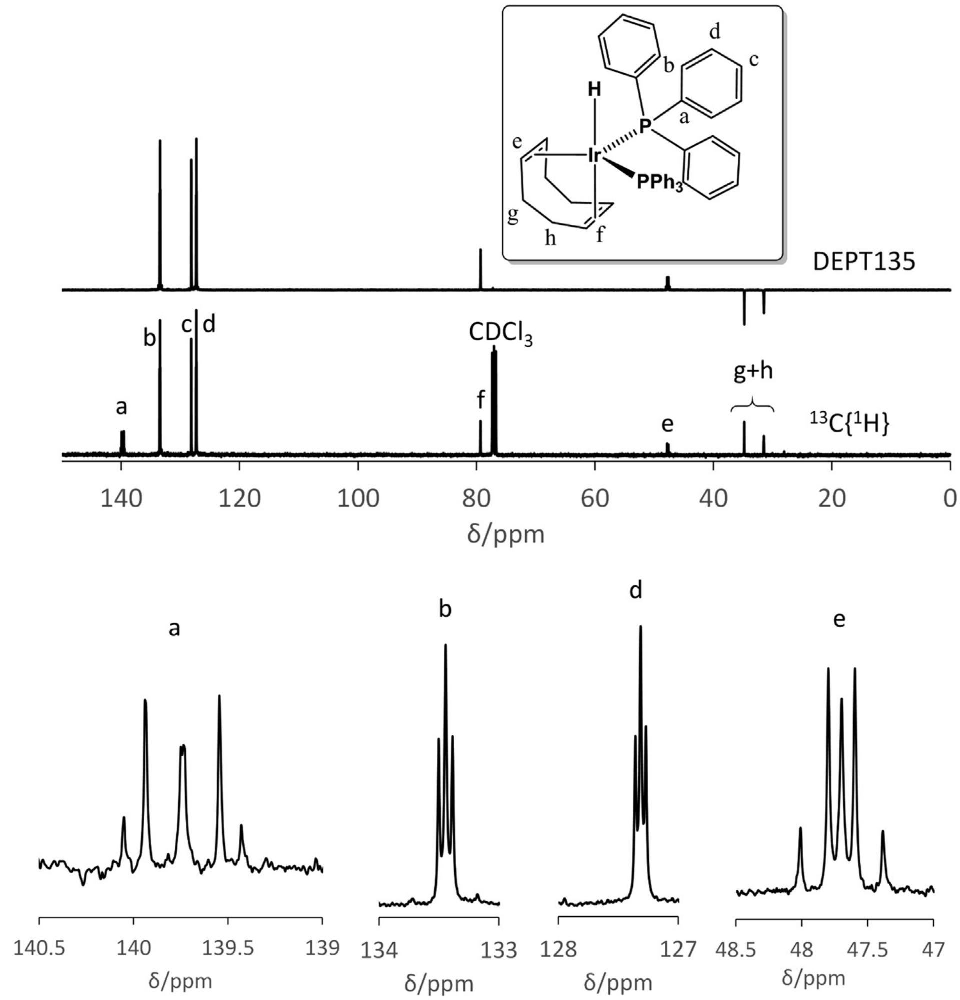


Fig. 2. $^{13}C\{^1H\}$ and DEPT135 NMR spectra of $[IrH(COD)(PPh_3)_2]$, with expanded excerpts for the C atoms exhibiting virtual coupling to the two P atoms.

The reaction yielding $[IrH(COD)(PPh_3)_2]$ (Equation (2)) also yields a minor by-product characterized by a ^1H quartet resonance at δ -10.73 (J_{HP} = 21.8 Hz) and a ^{31}P resonance at δ 14.3 (see Fig. 1S). Mutual coupling of these two resonances was confirmed by a H-P HMQC NMR experiment. This pattern is consistent with the presence of only one type of hydride and three equivalent PPh_3 ligands. The simplest possibility is $[IrH(PPh_3)_3]$, analogous to the Rh complex known as Wilkinson's catalyst, which has apparently never been described. This product could result from the replacement of COD by a third PPh_3 equivalent. Having a 16-electron configuration, this compound would be expected to adopt a square planar geometry with inequivalent *cis* and *trans* phosphine ligand, but an average spectrum could result from hydride positional scrambling in the fast kinetic regime. On the other hand, an isomeric *ortho*-metallated complex, $[IrH_2(PPh_3)_2(\kappa^2{:}C,P\text{-}2\text{-}C_6H_4PPh_2)]$, has been reported [85] and could also be consistent with the observed spectrum under the hypothesis of fluxional behavior, but the ^1H NMR properties reported for that compound (quartet at δ -7.7 with J_{PH} = 15 Hz) are different than those observed here.

When the experiment was repeated with a P/Ir ratio of 10, the major Ir product was still $[IrH(COD)(PPh_3)_2]$ and the above described by-product remained visible at low intensity (see Fig. 2S), but an additional by-product (also very minor) also appeared. This is characterized by a ^1H hydride resonance at δ -11.64, characteristic of coupling with one *trans* P atom (large doublet coupling of ca. 280 Hz) and two *cis* P atoms (smaller triplet coupling of ca. 20 Hz). This pattern is also indicative of a $[IrH(PPh_3)_3]$ stoichiometry, though this time not fluxional, compatible with an octahedral Ir^{III} product having two additional X-type ligands. Efforts at further elucidating the nature of this product were not made. The $^{31}P\{^1H\}$ NMR spectrum confirmed the presence of $[IrH(COD)(PPh_3)_2]$ as the major product and of the minor δ 14.3 by-product (Fig. 2S), while the excess free PPh_3 gave a broad resonance centered at ca. δ -3, showing dynamic exchange with one of the minor by-products. The ^1H spectrum of this mixture recorded in THF-d_8 solution showed the same products in the same relative proportion.

Warming the solution obtained as in Equation (2) to the reflux temperature initially leads to the rapid disappearance of the $[IrH(COD)(PPh_3)_2]$ complex. It is still the main compound after 10 min but it is completely consumed after 1 h. Several products are initially generated, as shown by ^1H (hydride region) and $^{31}P\{^1H\}$ NMR spectroscopy (Fig. 3), but continued reflux led to the decrease of the unknown intermediates and the accumulation of three products **I**, **II** and **III**, of which **I** is dominant (relative ratio = ca. 81:4:15 according to the hydride resonances integration) when the spectrum is recorded in $CDCl_3$. However, the spectrum of the same product mixture recorded in THF-d_8 shows compounds **I** and **II** in approximately equimolar amounts (ca. 47:53), while **III** was absent and other minor unidentified products are present (Fig. 3S). Products **I** and **II** have been identified respectively as *fac*- and *mer*-$[IrH_3(PPh_3)_3]$. Curiously, whereas both complexes have been known since the early 60's [86–91] and reported several times, including

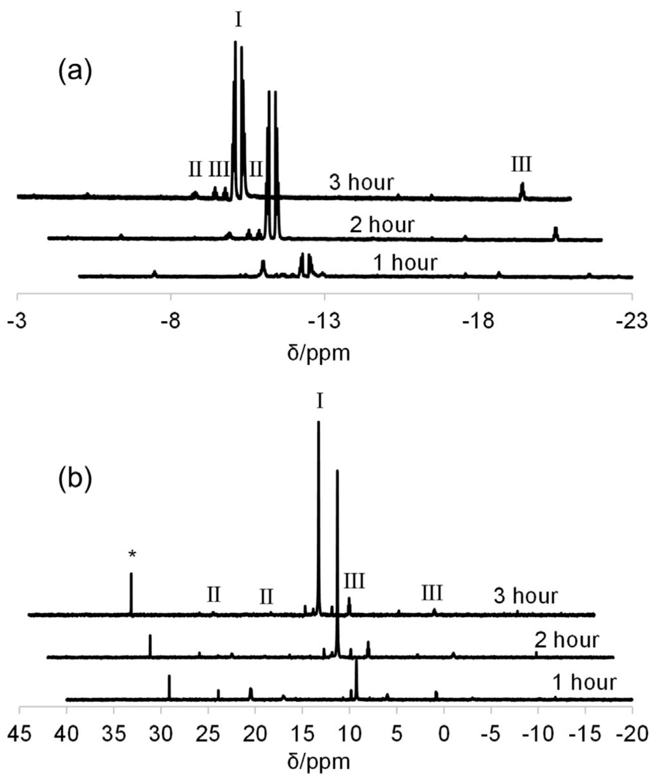


Fig. 3. Monitoring by ^{1}H NMR in the hydride region (a) and $^{31}P\{^{1}H\}$ (b) of the reaction between $[IrCl(COD)]_2$, PPh_3 (4 equiv) and excess NaOMe in boiling iPrOH. The spectra were taken from dried aliquots redissolved in $CDCl_3$. The starred resonance is assigned to the Ph_3PO impurity.

in more recent contributions [92–94], their NMR spectral properties have not been thoroughly described. The *fac* isomer is characterized by a complex 6-line pattern centered at δ -12.2 in the ^{1}H NMR spectrum for the AA′A″XX′X″ system. This feature has been well described and simulated in a previous contribution [93]. However, we find that the ^{31}P resonance is located at δ 9.3 (see Fig. 3) and not at the previously reported value of 30.05 [93], as confirmed by the ^{1}H-^{31}P HMQC (Fig. 4S in $CDCl_3$ and Fig. 5S in THF-d_8).

For the *mer* isomer, the ^{31}P properties have apparently never been reported and only a variable temperature ^{1}H NMR spectrum in $CDCl_3$ has been previously described [85]. The better resolved ^{1}H NMR spectrum in THF-d_8 solution, in which the relative proportion of this isomer is significant, reveals the expected pattern of an A_2BX_2Y spin system (A,B = H; X,Y = P) for the hydride resonances: δ_A -10.86 (2H, broad quartet, J_{HP} = 16 Hz, due to degeneracy of the couplings to the 2P_X and 1P_Y nuclei) and δ_B -12.30 (1H, broad dt, J_{HPY} = 116 Hz; J_{HPX} = 21 Hz), which sharpen at 243 K to reveal additional HH coupling (see Fig. 6S). The $^{1}H\{^{31}P\}$ spectrum at 243 K collapses these two hydride resonances into a doublet and a triplet (J_{HH} = 3.5 Hz) and the ^{1}H COSY (Fig. 5S) further confirms their mutual coupling. These properties agree with and complete those previously reported in $CDCl_3$ [85]. The corresponding $^{31}P\{^{1}H\}$ resonances are found at δ_X -21.3 (2P, doublet) and δ_Y 17.1 (1P, triplet) with J_{PP} = 15 Hz (mutual coupling confirmed by ^{31}P COSY) and the coupling to the above-described hydride ^{1}H resonances was confirmed by HMQC (Fig. 5S).

Product **III** shows an $ABXY_2$ spin system. The spectral properties, shown in detail in Fig. 4, are very similar but not identical to those described for *mer*-$[IrClH_2(PPh_3)_3]$ [95]. Notably, although the chemical shifts of the hydride resonances in the ^{1}H spectrum and of the phosphines in the ^{31}P spectrum and the HH and HP coupling constants are very close to those reported for this compound, the PP coupling (14.4 Hz) is about half that reported for the chloro derivative (26 Hz). It seems likely, therefore, that the complex corresponds to *mer*-$[IrXH_2(PPh_3)_3]$, where X is an alkoxide ligand originating from the base or from the solvent. Its formation can be

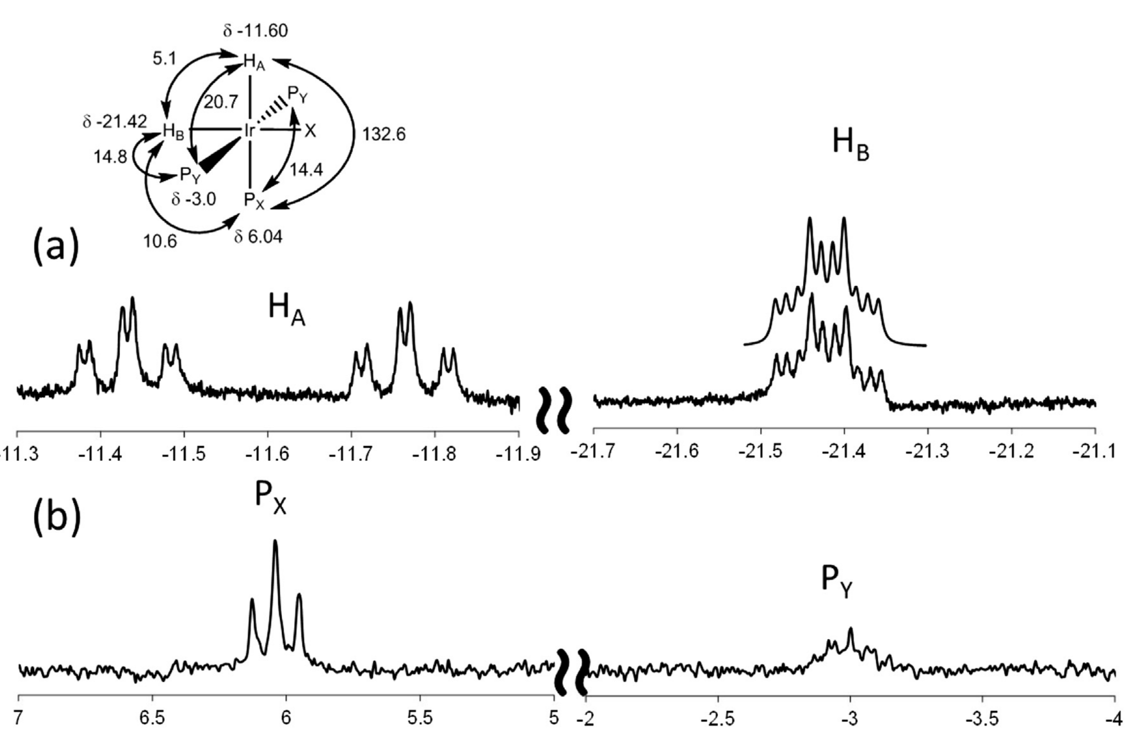


Fig. 4. ^{1}H (a) and $^{31}P\{^{1}H\}$ (b) NMR properties of the minor product **III** resulting from the reaction between $[IrCl(COD)]_2$, PPh_4 (4 equiv) and excess NaOMe in boiling iPrOH. The upper trace for the H_B resonance is the simulated spectrum using the parameters indicated in the molecular diagram (in Hz units).

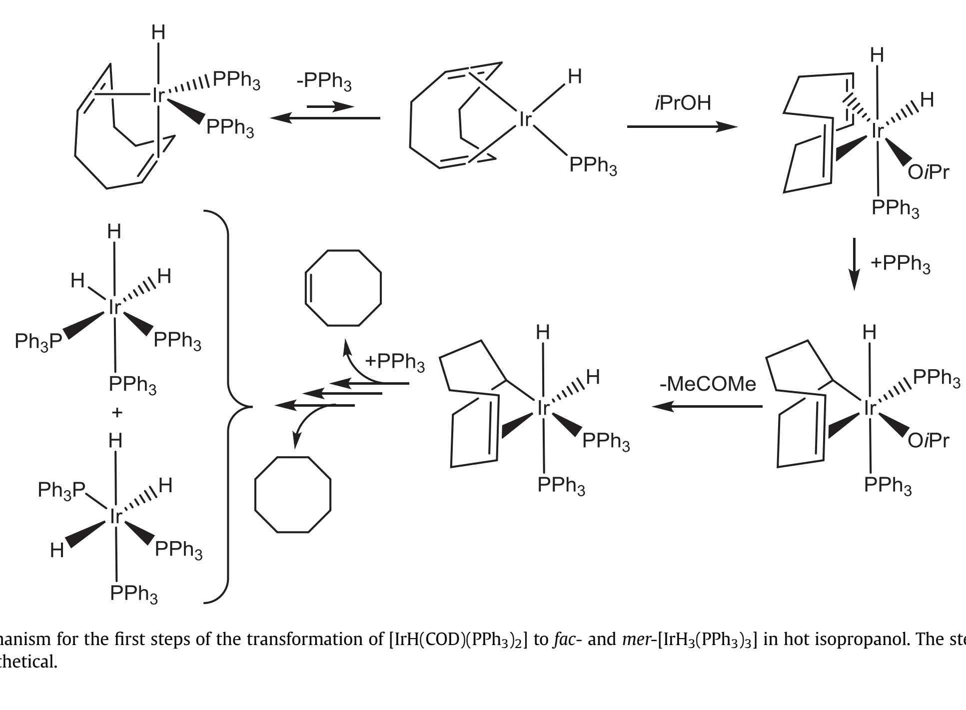
formally seen as an alcohol oxidative addition to [IrH(PPh_3)$_3$]. It is notable that the characteristic resonances of the previously described [94,96] anionic hydrides complexes [IrH_2(PPh_3)$_3$]$^-$ and [IrH_4(PPh_3)$_4$]$^-$ are absent. The correlation between the ^{1}H and ^{31}P resonances is confirmed by the HMQC experiment in $CDCl_3$ (Fig. 4S).

The generation of COD-free products upon heating [IrH(-COD)(PPh_3)$_2$] in the presence of base raises the question of the fate of COD. The NMR evidence that [IrH(PPh_3)$_3$] is generated at room temperature, even though in minor amounts (*vide supra*), suggests the ability of PPh_3 to displace COD. The observed isomeric [IrH_3(PPh_3)$_3$] products may result from subsequent transformations of this intermediate, for instance by oxidative addition of *i*PrOH to yield *mer*-[Ir(O*i*Pr)H_2(PPh_3)$_3$], which is one of the proposed products, followed by β-H elimination with the generation of acetone, while the expelled COD may remain unaltered. Alternatively, thermal activation of the [IrH(COD)(PPh_3)$_2$] complex may lead to hydride ligand migration to the COD ligand, followed by further alcohol activation and transfer hydrogenation of COD, which would eventually be eliminated as hydrogenated products. A quantitative gas-chromatographic analysis of the isopropanol solution revealed the generation of cyclooctene (54.4%) and cyclooctane (32.2%), while cyclooctadiene was not detected. Thus, it appears that transfer hydrogenation of the COD ligand is required to accomplish the transformation.

Another surprising feature of the above reaction is the generation of tris-PPh_3 complexes from a mixture where the PPh_3/Ir ratio is only 2. Nevertheless, the ^{1}H and ^{31}P spectra (Fig. 3 and Fig. 3S) do not show any other major phosphorus-containing product nor additional hydride resonances accounting for 1/3 of the missing Ir sample. This indicates that the formation of the [IrH_3(PPh_3)$_3$] isomers must be accompanied by the generation of one (or more) iridium by-product that contains neither PPh_3 nor hydride, for instance [Ir(μ-O*i*Pr)(COD)]$_2$. Repeating the same reaction with 3 equivalents of PPh_3 per Ir atom led to formation of the same observed products but, interestingly, the transformation was much slower: complex [IrH(COD)(PPh_3)$_2$] was still present in large amounts (ca. 40%) after 3 h of reflux, whereas it was totally consumed in less than 1 h when using a P/Ir ratio of 2. This indicates a determining role of PPh_3 dissociation for triggering the reaction. We therefore propose that the reaction mechanistically involves the initial steps shown in Scheme 1.

The COD hydrogenation and elimination from the metal coordination sphere in basic isopropanol, in the absence of H_2, is in line with the previous work already mentioned in the introduction on related systems with diphospine, diphosphinite and pyridine-functionalized N-heterocyclic carbene ligands [13,61,63]. However, whereas those previous contributions only indicated the formation of cyclooctene, we also find that a considerable amount of cyclooctane is generated in this case. A possible reason for the more extensive COD hydrogenation before expulsion in the present case is that the supporting PPh_3 ligand, through its lower binding ability and/or lack of chelate effect, dissociates more easily from the metal center allowing more isopropanol to oxidatively add and to transfer hydrogen atoms to the organic ligand before this can be expelled. However, more mechanistic work is needed before firmly rationalizing this observation. At any rate, the results described here clearly demonstrate that the previously reported transfer hydrogenation processes catalyzed by [IrCl(COD)]$_2$/phosphine ligand/strong base in isopropanol at high temperature likely generate active species that are devoid of the COD ligand. In the presence of PPh_3 [71], whether the active catalyst is one or both of the isomeric [IrH_3(PPh_3)$_3$] complexes or whether these are themselves precursors of the real catalyst is not yet quite clear. These compounds, in our hands, appear quite stable under the conditions used for transfer hydrogenation (prolonged reflux in isopropanol in the presence of strong base). However, it cannot be excluded that they generate irreversibly minor amounts of a very active catalyst or that the catalysis is promoted, when less than 3 equivalents of PPh_3 per Ir atom are used, by the other H- and PPh_3-free compounds that are generated by the thermal activation. It has been reported that compound [IrH_3(PPh_3)$_3$] (undefined isomer), catalyzes the transfer hydrogenation of aldehydes by formic acid [97].

It is also worthy to compare the presently described behavior with that of complex [IrCl(COD)(PS)], where (PS) is the bidentate ferrocenyl phosphine-thioether CpFe[1,2-C_5H_3(PPh_2)(CH_2S*t*Bu)] ligand, which was suggested on the basis of DFT calculations to generate the tetrahydrido complex [IrH_4(PS)]$^-$, isoelectronic with the above-mentioned [IrH_4(PPh_3)$_4$]$^-$, in basic isopropanol during the catalyzed hydrogenation of acetophenone [98]. However, in the



Scheme 1. Proposed mechanism for the first steps of the transformation of [IrH(COD)(PPh_3)$_2$] to *fac*- and *mer*-[IrH_3(PPh_3)$_3$] in hot isopropanol. The stereochemical assignment to the intermediates is hypothetical.

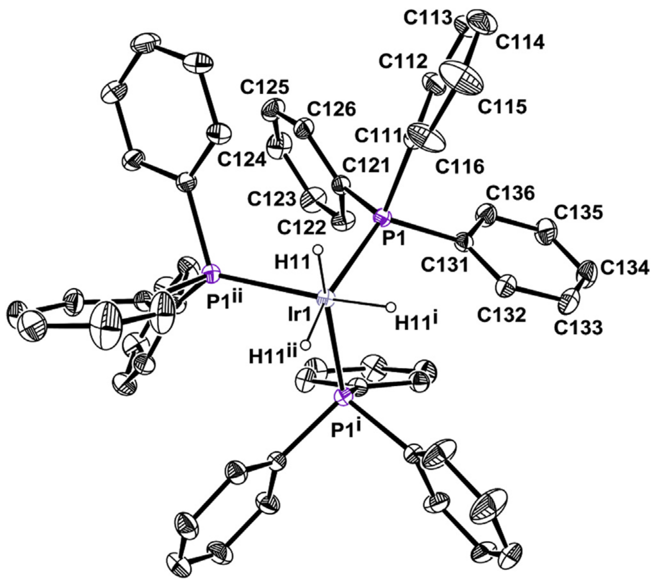


Fig. 5. ORTEP view of *fac*-$[IrH_3(PPh_3)_3]$. Relevant structural parameters: Ir-P, 2.3296(5); Ir-H, 1.39(5) Å; P-Ir-P^{i}, 103.021(16); H-Ir-P, 89.7(19); H-Ir-P^{i}, 84(2); H-Ir-P^{ii}, 164(2)°. Symmetry codes: (i) 1-y, x-y, z; (ii) -x + y, 1-x, z.

present case the activation and COD removal occurs without the use of H_2. The generation of the neutral $[IrH_3(PPh_3)_3]$ isomers, instead of $[IrH_4(PPh_3)_4]^-$, may be related to the greater basicity of two PPh_3 ligands relative to the (PS) ligand.

Crystallization of the product mixture of the $[IrCl(COD)]_2/PPh_3/$KO*t*Bu reaction in refluxing isopropanol from $CDCl_3$ afforded single crystals of the major *fac*-$[IrH_3(PPh_3)_3]$ product. A diffraction study has confirmed the molecular geometry (see Fig. 5). The molecule sits on a crystallographic threefold axis. Only the *mer* isomer was previously structurally characterized [99]. Other structurally characterized $[IrH_3L_3]$ molecules with phosphorus donor L ligands have been described with both the *mer* (for instance with $L_3 = PhP(CH_2CH_2CH_2PCy_2)_2$ [100] or $(PMe_2Ph)(PiPr_3)_2$ [101]) and the *fac* geometry (with $L = PMePh_2$ [102] or $L_3 = N(CH_2CH_2PPh_2)_3$ [103]). With respect to the closest structure of the *fac*-$[IrH_3(PMePh_2)_3]$ complex, the Ir-H distance (1.39(5) Å) is much shorter (cf. 1.627(4) Å) while the Ir-P distance (2.3296(5) Å) is slightly longer (cf. 2.314(2) Å), but the X-ray measurement is known to underestimate the metal-H distances, while the structure of *fac*-$[IrH_3(PMePh_2)_3]$ was more precisely determined by neutron diffraction [102]. In the structure of the isomeric *mer*-$[IrH_3(PPh_3)_3]$, also determined by X-ray diffraction, the Ir-H distances were rather unprecisely determined as 1.58(25), 1.62(28) and 1.59(26) Å, while the Ir-P distances are 2.347(3) Å for the unique P atom *trans* to H and 2.287(3) and 2.285(3) Å for the two P atoms *trans* to each other. The tendency for the Ir-P bonds to be lengthened by the *trans* influence of the H ligand is clear and the results for the two *mer* and *fac* isomers are consistent in this respect.

4. Conclusions

The main contribution of the present work is the unambiguous demonstration that the $[IrCl(COD)]_2/PPh_3/$KO*t*Bu precatalyst for transfer hydrogenation in isopropanol loses the COD ligand in a hydrogenated form (mixture of cycloctene and cyclooctane) when thermally activated. Thus, previous assumptions that this catalytic system, as well as related ones with other monodentate phosphine (and probably also bidentate diphosphines), operate by COD-containing active species must be discarded. This investigation arrives at the same conclusion as that of Jiménez et al. based on a systems with a pyridine-functionalized N-heterocyclic carbene as ligand [61]. It is of interest to verify whether this phenomenon is specific to those ligands or general for Ir-based precatalysts used as transfer hydrogenation precatalysts. It is also pertinent to ask the same question about the related Rh systems, at least those requiring high temperatures to achieve significant activity.

Along the present study, we have also completed the NMR spectroscopic characterization of compound $[IrH(COD)(PPh_3)_2]$ with the $^{13}C\{^1H\}$ spectrum, we have presented for the first time a full ^1H and $^{31}P\{^1H\}$ NMR characterization of compound *mer*-$[IrH_3(PPh_3)_3]$ and the X-ray structure of compound *fac*-$[IrH_3(PPh_3)_3]$, we have corrected a literature misassignment of the ^{31}P NMR resonance for the latter compound, and we have evidenced a few additional by-products formed by thermal activation of the above mentioned precatalyst system. The slowdown of the thermal activation in the presence of additional PPh_3 shows that PPh_3 dissociation from $[IrH(COD)(PPh_3)_2]$ is a prerequisite for the transformations leading to hydrogenation and elimination of the COD ligand.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2016.10.009.

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