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Room-temperature C–H activation of the phosphino-ketone $Ph_2PCH_2C(O)Ph$ leading to an iridium(III) complex with a hybrid phosphino-enolate ligand

Xianghao Liu, Mélanie Boucher, Pierre de Frémont, Pierre Braunstein *

Laboratoire de chimie de coordination, Institut de chimie, UMR 7177 CNRS, université de Strasbourg, 4, rue Blaise-Pascal, CS 90032, 67081 Strasbourg cedex, France

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ABSTRACT

The reaction of $[Ir(cod)(\mu\text{-}Cl)]_2$ (cod = 1,5-cyclooctadiene) with 2 equiv of the ketophosphine $Ph_2PCH_2C(O)Ph$ in the presence of $TlPF_6$ afforded the hydrido, phosphino-enolate Ir(III) complex $[IrH(cod)\{Ph_2PCH\cdots C(\cdots O)Ph,\kappa P,\kappa O\}\{Ph_2PCH_2C(O)Ph,\kappa P\}]PF_6$ (**4**), which results from the room temperature activation of a C–H bond from the PCH_2 moiety. The distorted octahedral coordination environment around the metal centre in **4** contains the cod ligand, the P atom of the monodentate ketophosphine and the P,O donor atoms of a chelating phosphino-enolate ligand acting as a 3-electron donor. The hydride ligand was located on the difference Fourier map obtained by single-crystal X-ray diffraction studies and is *trans* to the enolate oxygen and *cis* to the two, mutually *cis* P atoms. The reaction of this complex with NaH in THF led to the isolation of the Ir(I) complex $[Ir(cod)\{Ph_2PCH\cdots C(\cdots O)Ph,\kappa P,\kappa O\}\{Ph_2PCH_2C(O)Ph,\kappa P\}]$ (**5**). The penta-coordination environment around the metal centre in **5** includes the cod ligand, one 3-electron donor P,O chelating phosphino-enolate ligand and a P-bound $Ph_2PCH_2C(O)Ph$ ligand containing an uncoordinated ketone function. The structures of $\mathbf{4}\cdot CH_2Cl_2$ and $\mathbf{5}\cdot C_7H_8$ have been determined by X-ray diffraction analysis.

1. Introduction

By virtue of the variability of their chemically different donor groups, hybrid ligands provide excellent opportunities to study the chemoselective coordination of multifunctional ligands to metals centres and to fine-tune the stereo-electronic properties of their metal complexes. This can lead to improved reactivity and catalytic properties of their metal complexes in solution [1]. For these reasons, we and others became recently interested in the synthesis and coordination chemistry of a specific family of such ligands, which possess phosphorus and *N*-heterocyclic carbene (NHC) donor moieties, two ubiquitous functionalities in coordination/organometallic chemistry, possibly associated with a carbon-donor function in a pincer-type system [2–4]. A transition metal of particular significance is iridium because of the unique catalytic properties of its complexes in alkane C-H activation [5]. Transfer dehydrogenation of cyclooctane (coa) has been achieved using PCP [6] and POCOP [7] iridium pincer complexes, and these systems have since served as benchmarks for this reaction (Scheme 1).

* Corresponding author.
E-mail address: braunstein@unistra.fr (P. Braunstein).

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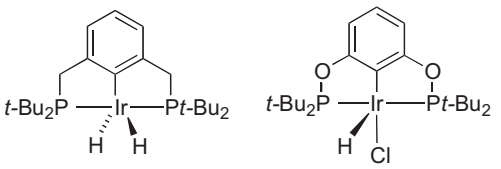
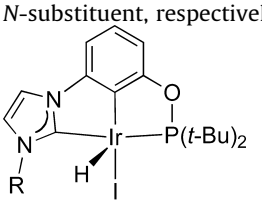


Kaska, Jensen *et al.* Brookhart *et al.*

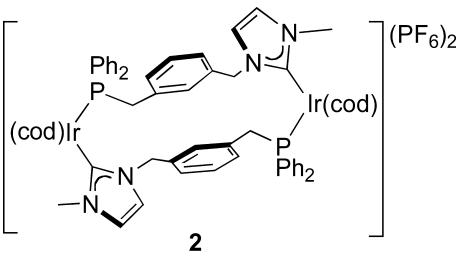
Scheme 1. PCP [6] and POCOP [7] iridium pincer complexes used in catalytic transfer dehydrogenation of cyclooctane.

We recently reported the synthesis of Ir(I) pincer-type complexes involving phosphorus and NHC donors, [IrH(I)(PO-NHC,$\kappa P,\kappa C,\kappa C_{NHC}$)^{Me}] (**1a**) and [IrH(I)(PO-NHC,$\kappa P,\kappa C,\kappa C_{NHC}$)$^{n\text{-}Bu}$] (**1b**), with a Me or *n*-Bu group as *N*-substituent, respectively [4].



1a R = Me
1b R = *n*-Bu

We found that slight differences in the nature of the spacers between the donor atoms may be sufficient to bring about major modifications in the structures of the corresponding metal complexes. Thus, with related NHC,P hybrid ligands, dinuclear Ir(I) complexes were obtained, also from the corresponding imidazolium salt, in which two such ligands behave as bridges rather than chelates, as in, e.g., the dicationic complex [Ir(cod)(μ-P-NHC,$\kappa P,\kappa C_{NHC}$)]$_2$[PF$_6$]$_2$ (**2**) (cod = 1,5-cyclooctadiene) [4].



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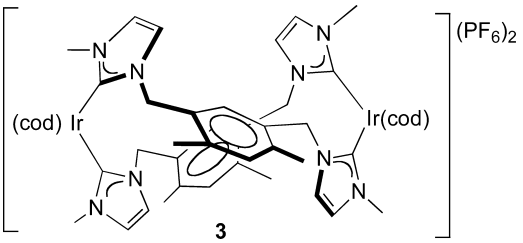
2. Results and discussion

It is highly desirable to perform the activation of alkanes by soluble transition-metal species in the absence of any competing solvent and this requires sufficient solubility of the precatalyst in the neat alkane. With the objective to prepare a neutral iridium complex that would have a better solubility in coa, and thus facilitate the activation of its C-H bonds, we envisaged replacing the neutral cod ligand of complex **2** with an anionic P,O-chelating phosphino-enolate ligand since we have previously observed that their Rh(I)/Ir(I) complexes catalysed the transfer dehydrogenation of coa [8]. The Ir(III) dihydride complex [Ir(cod)(H)$_2${Ph$_2$PCH...C(...O)Ph,$\kappa P,\kappa O$}] was moderately stable in toluene solution [8]. In general, phosphino-enolate functionalities can be readily generated under basic conditions from a β-ketophosphine ligand, such as Ph$_2$PCH$_2$C(O)Ph, coordinated or not [9]. We thus added a THF solution of Ph$_2$PCH$_2$C(O)Ph to the dicationic complex **2** in the presence of a base (NaH) but we did not succeed in displacing selectively the cod ligand from the iridium centre. For comparison, we performed the same experiment with the related, dicationic complex **3** which contains two bis-NHC bridging ligands and displays a "figure 8" conformation [10].



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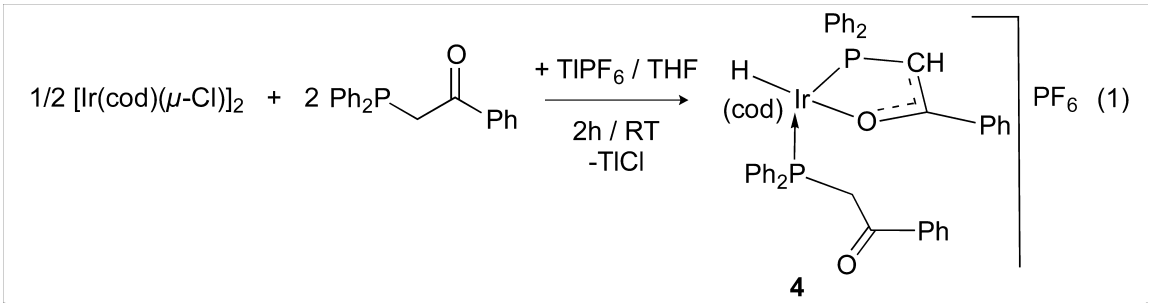
Unfortunately, this experiment was also unsuccessful. This led us to examine, for comparison, the reactivity of [Ir(cod)(μ-Cl)]$_2$ with this β-ketophosphine with the objective to deprotonate the latter and form a chelating phosphino-enolate. First, TlPF$_6$ was added to a THF solution of [Ir(cod)(μ-Cl)]$_2$, in order to abstract the chloride from the metal centre and render the latter more electrophilic, and then two equivalents of Ph$_2$PCH$_2$C(O)Ph and NaH in slight excess were added (see Experimental Section). Analysis by ^{31}P{^{1}H} NMR spectroscopy indicated the presence of different species, which turned out difficult to separate and purify. Clearly, no selective displacement of the cod ligand from [Ir(cod)(μ-Cl)]$_2$ occurs in the presence of Ph$_2$PCH$_2$C(O)Ph or its corresponding phosphine-enolate. In one instance however, a few yellow/orange crystals of a product could be isolated and characterized by X-ray diffraction as [Ir(cod){Ph$_2$PCH...C(...O)Ph,$\kappa P,\kappa O$}{Ph$_2$PCH$_2$C(O)Ph,κP}] (**5**) (see below).

Because of the difficulties encountered in trying to reproduce these results, we decided to operate in two consecutive steps and isolate the intermediate product(s): first by preparing a cationic β-ketophosphine Ir(I) complex by using a chloride abstractor and secondly by reacting this complex with a base, usually a facile reaction because of the increased acidity of the PCH$_2$ protons upon phosphorus coordination to a metal [9]. Targeting a cationic, square-planar complex of the type [Ir{Ph$_2$PCH$_2$C(O)Ph,$\kappa P,\kappa O$}{Ph$_2$PCH$_2$C(O)Ph,κP}(THF)]$^+$ or [Ir{Ph$_2$PCH$_2$C(O)Ph,$\kappa P,\kappa O$}$_2$]$^+$, we reacted [Ir(cod)(μ-Cl)]$_2$ with 2 equivalents of Ph$_2$PCH$_2$C(O)Ph in the presence of TlPF$_6$ at room temperature (equation 1), although it is often observed that the displacement by phosphines of the cod ligand from [Ir(cod)(μ-Cl)]$_2$ requires harsher experimental conditions or tridentate ligands (*e.g.*, $C_{NHC}CC_{NHC}$ pincers) [11].



The $^{31}P\{^{1}H\}$ NMR spectrum of the isolated product (see Experimental section) confirmed the presence of the PF_6 anion (δ −144.6 ppm) and contained two doublets, at δ 16.2 and –1.3 ppm, with $^{2}J(P,P) = 16.6$ Hz. This is consistent with the presence of two chemically different P atoms in a mutually *cis*-position. A 2D NMR experiment (HMQC $^{1}H/^{31}P$) established that the more downfield-shifted resonance (16.2 ppm) corresponded to the P atom belonging to the chelating ligand. The ^{1}H NMR spectrum contained resonances at δ 2.49 and 4.61 ppm corresponding to an ABX spin system (A = B = H, X = P) for the two diastereotopic protons of a PCH_2 group ($^{2}J(H,H) = 16.6$ Hz, $^{2}J(P,H) = 10.9$ and 6.8 Hz, respectively). A doublet at δ 5.91 ppm integrating for one proton is typical of the resonance for the enolate proton of a P,O-coordinated $Ph_2PCH{\cdots}C(\underline{\cdots}O)Ph$ group, with a $^{2}J(H,P)$ coupling of 4.6 Hz [8]. Accordingly, the $^{1}H\{^{31}P\}$ NMR spectrum showed only one singlet for this proton. Furthermore, the ^{1}H NMR spectrum revealed the unexpected presence of a triplet resonance at δ −16.65 ppm ($^{2}J(P,H) = 9.0$ Hz), corresponding to a hydride coupled to two P nuclei in a *cis*-position (the triplet pattern formally corresponds to overlapping doublets of doublets since the two P nuclei are chemically different). The IR absorptions at 1672 and 1510 cm^{-1} also suggested the presence of an uncoordinated ketone group of $Ph_2PCH_2C(O)Ph$ and of an *O*-coordinated enolate function in a P,O-chelating $Ph_2PCH{\cdots}C(\underline{\cdots}O)Ph$ system, respectively [12]. Furthermore, the $^{13}C\{^{1}H\}$ NMR data also confirmed the presence of two types of C–O carbons with resonances at 192.6 and 186.5 ppm for the uncoordinated ketone group and the *O*-coordinated enolate function, respectively. The former resonance is very close to that of the free ketophosphine ligand (196.9 ppm) [9].

Fortunately, plate-like colourless single crystals of this complex were obtained by slow diffusion of octane into a CH_2Cl_2 solution at room temperature. The X-ray diffraction analysis of **4**·CH_2Cl_2 allowed to confirm the interpretation based on spectroscopic data and to establish its formula as $[IrH(cod)\{Ph_2PCH{\cdots}C(\underline{\cdots}O)Ph,\kappa P,\kappa O\}\{Ph_2PCH_2C(O)Ph,\kappa P\}]PF_6$ (**4**) (Fig. 1).

The distorted octahedral coordination environment around the metal centre contains the cod ligand, the P atom of a monodentate ketophosphine and a P,O chelate acting as a 3-electron donor. The hydride ligand was located on the difference Fourier map and is *trans* to the enolate oxygen and *cis* to the two, mutually *cis* P atoms. As expected, the C-O bond length of the ketone group (O1–C14 1.219(9) Å) Å is shorter than that in the enolate moiety

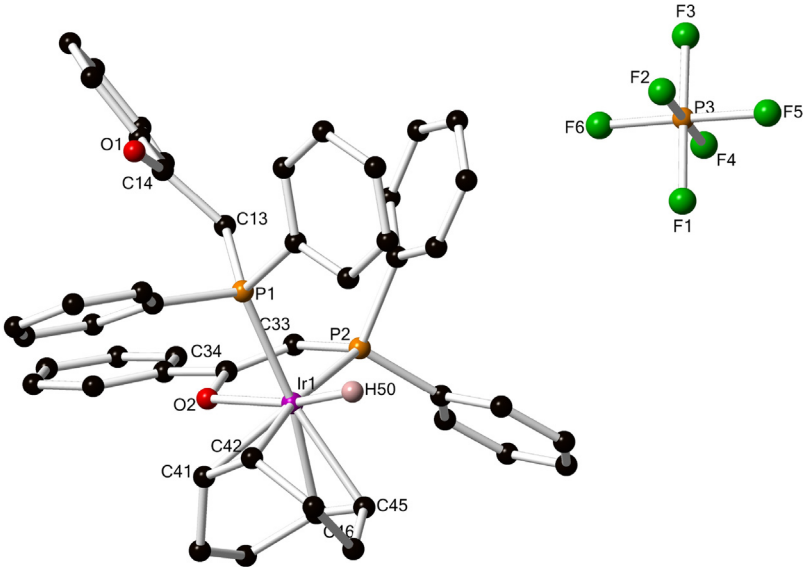
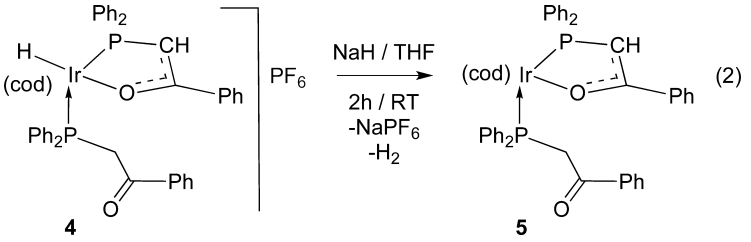


Fig. 1. (Colour online.) View of the structure of the Ir(III) complex $[IrH(cod)\{Ph_2PCH{\cdots}C(\underline{\cdots}O)Ph,\kappa P,\kappa O\}\{Ph_2PCH_2C(O)Ph,\kappa P\}]PF_6$ (**4**) in **4**·CH_2Cl_2. Selected bond lengths [Å] and angles (deg): Ir–P1 2.362(2), Ir–P2 2.302(2), Ir–O2 2.152(5), Ir–H50 1.49(7), P1–C13 1.843(7), C13–C14 1.521(10), C14–C15 1.486(10), O1–C14 1.219(9), P2–C33 1.757(8), C33–C34 1.345(10), O2–C34 1.332(8); P1–Ir–P2 93.82(6), O2–Ir–P1 85.55(14).

(O2–C34 1.332(8) Å) whereas the reverse applies to the corresponding C–C distances, of 1.521(10) Å for C13–C14 and 1.345(10) Å for C33–C34. The P–CH_2 bond length is slightly longer (P1–C13 1.843(7) Å) than that of the P–CH bond (P2–C33 1.757(8) Å). All these metrical data are consistent with values reported for related complexes containing chelating phosphino-enolates or P-bound ketophosphines, respectively [8,9].

Having established the nature of the Ir(III) hydride complex **4**, we can now interpret the reaction of equation (1) as having involved splitting of the chloride bridges of the precursor and formal oxidative-addition of a C–H bond of one of the two ketophosphine ligands introduced, resulting in the formation of a metal-hydride and an enolate moiety. Whether this oxidative-addition resulted from direct interaction between the P–CH_2 unit and the Ir(I) centre or from the transient P,O chelation of the minor, tautomeric enol form of the ligand, $Ph_2PCH{=}C(OH)Ph$ [9,13], cannot be stated at this stage.

Since our original objective was to prepare a neutral iridium(I) complex, we then reacted isolated **4** with NaH in THF for 2 h at room temperature (equation 2). The $^{31}P\{^1H\}$ NMR spectrum of the yellow product **5** (see Experimental section) confirmed the absence of PF_6^- and contained two doublets, at δ −3.5 and 14.3 ppm with $^2J(P,P) = 21.5$ Hz.



(2)

Considering the data for **4** and literature values, the doublet at 14.3 ppm was assigned to the phosphorus of a chelating $Ph_2PCH{\cdots}C(\cdots O)Ph$ ligand and that at -3.5 ppm to a P-bound $Ph_2PCH_2C(O)Ph$ ligand. For comparison, the $^{31}P\{^1H\}$ NMR singlet resonance of the Ir(III) complex $[Ir(cod)(H)_2\{Ph_2PCH{\cdots}C(\cdots O)Ph,\kappa P,\kappa O\}]$ was observed at 27.6 ppm [8]. The ^1H NMR spectrum of **5**, recorded at 203 K for a better resolution, indicated the disappearance of the hydride resonance and the presence of two PCH_2 protons at 2.61 and 3.61 ppm (ABX spin system (A = B = H, X = P), partly overlapping with cod signals, with $^2J(H,H) = 14.2$ Hz and $^2J(P,H) = 6.4$ Hz) and of one PCH proton corresponding to the chelating $Ph_2PCH{\cdots}C(\cdots O)Ph$ ligand at 5.68 ppm. Consistently, the $^{13}C\{^1H\}$ NMR data included resonances at 31.2 ppm (s, PCH_2) and 83.6 ppm (d, PCH, $^1J(P,C) = 57.7$ Hz). The IR data confirmed the presence of both a ketone group (1670 cm^{-1}, $\nu(C=O)$) and of an enolate moiety (1525 cm^{-1}, $[\nu(C{\cdots}O) + \nu(C{\cdots}C)]$) [9a].

This complex was identical to the single crystals of **5**·C_7H_8 obtained from the one-pot experiment (see above) by slow vapour diffusion of Et_2O into a d_8-toluene solution of the complex in a NMR tube. The X-ray diffraction study established the nature of the complex as $[Ir(cod)\{Ph_2PCH{\cdots}C(\cdots O)Ph,\kappa P,\kappa O\}\{Ph_2PCH_2C(O)Ph,\kappa P\}]$ (**5**) (Fig. 2).

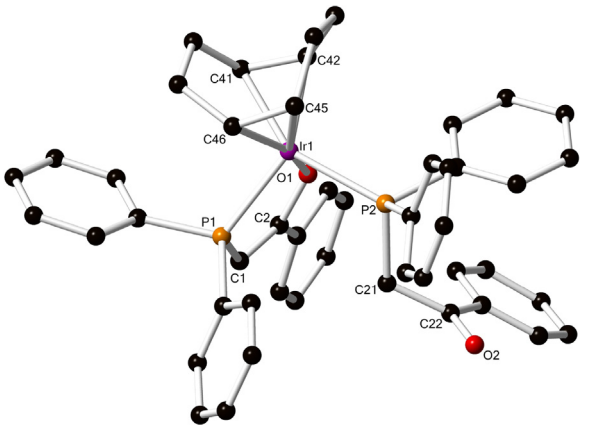


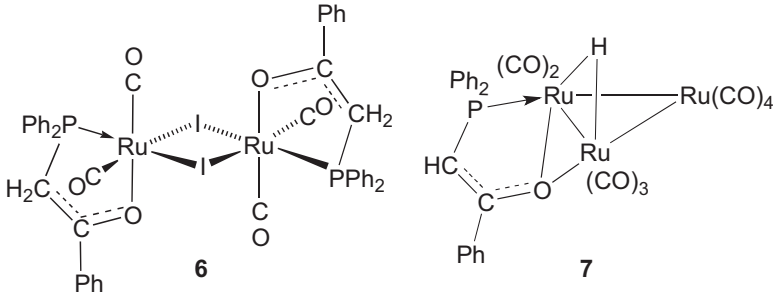
Fig. 2. (Colour online.) View of the structure of the Ir(I) complex $[Ir(cod)\{Ph_2PCH{\cdots}C(\cdots O)Ph,\kappa P,\kappa O\}\{Ph_2PCH_2C(O)Ph,\kappa P\}]$ (**5**) in **5**·C_7H_8. Hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles (deg): Ir1–P1 2.324(2), Ir1–P2 2.380(2), Ir1–O1 2.104(4), C1–C2 1.331(8), C21–C22 1.513(9), O1–C2 1.347(7), O2–C22 1.220(7); P1–Ir1–P2 100.21(6), P1–Ir1–O1 81.74(11), P2–Ir1–O1 84.85(12).

The penta-coordination environment around the metal centre includes the cod ligand, one P,O chelating ligand acting as a 3-electron donor (O1–C2 1.347(7) Å), and a P–bound ligand containing an uncoordinated ketone function (O2–C22 1.220(7) Å). The C21–C22 bond (1.513(9) Å) is longer than C1–C2 (1.331(8) Å), which is consistent with a neutral phosphine ligand and the presence of two hydrogen atoms on C21, in α position to P2. These values are similar to those in **4** for similar bonds and are typical for chelating phosphino-enolates or P-bound ketophosphines, respectively [8,9].

The reaction of **4** with NaH has thus led to the formation of H_2 (not evidenced), of $NaPF_6$ and of the Ir(I) complex **5**. Although the latter had been isolated once as a result of an *in situ* experiment where $[Ir(cod)(\mu\text{-}Cl)]_2$ was reacted with $TlPF_6$, the ketophosphine and NaH in THF, the sequential approach described above is much more satisfactory in terms of yields and of understanding the nature of the reaction intermediates.

3. Conclusion

It was found more difficult than anticipated to cleanly displace the Ir-coordinated cod ligand in complexes **2** and **3** by a chelating phosphine-enolate ligand. The reaction of $[Ir(cod)(\mu\text{-}Cl)]_2$ with 2 equivalents of the ketophosphine $Ph_2PCH_2C(O)Ph$ in the presence of $TlPF_6$ afforded the octahedral phosphino-enolate Ir(III) hydrido complex **4** as



Scheme 2. Previous examples of C-H activation of $Ph_2PCH_2C(O)Ph$ by Ru complexes [14,15] were less facile than reported in this work with Ir.

a result of the room temperature activation of a C-H bond from the PCH_2 moiety (equation 1). The subsequent reaction of **4** with NaH in THF did not lead to the deprotonation of the P-coordinated ketophosphine but to the removal of the hydride ligand, which resulted in the formation of the pentacoordinated Ir(I) complex **5** (equation 2). The structure of both **4** and **5** was established by X-ray diffraction. It is interesting to compare the facile C-H bond activation reaction observed here with observations made previously with Ru complexes (Scheme 2). Only modest yields of the dinuclear, phosphine-enolate complex **6** were obtained when a CH_2Cl_2 solution of $[Ru_3(CO)_{10}\{Ph_2PCH_2C(O)Ph\}_2]$ was left standing for 1 week [14]. It required refluxing THF to convert $[Ru_3(CO)_{11}\{Ph_2PCH_2C(O)Ph\}]$ in the phosphine-enolate Ru_3 cluster **7** [15].

It is also interesting to note that an oxidation of the metal centre somewhat related to that observed here during the formation of **4** was observed during attempts to deprotonate a Co(II) complex of the same ketophosphine ligand, $[CoCl_2\{Ph_2PCH_2C(O)Ph,\kappa P,\kappa O\}_2]$. Instead, the *fac*- and *mer*-isomers of the octahedral Co(III) complex $[Co\{Ph_2PCH\cdots C(\cdots O)Ph,\kappa P,\kappa O\}_3]$ were isolated [16]. The possible occurrence of such transformations should be remembered when studying the reactivity or catalytic properties of metal complexes bearing $Ph_2PCH_2C(O)Ph$ or related ligands since the corresponding phosphino-enolate ligand is known to play a key role in SHOP-type Ni(II) catalysts for ethylene oligomerization [17].

4. Experimental

General considerations: all reactions were performed under a dry argon atmosphere using standard Schlenk techniques. All solvents were distilled under argon from the appropriate drying agents and stored under argon. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AVANCE 300, 400 or 600 spectrometers and internally referenced using the residual proton solvent (^1H), solvent resonance (^{13}C) or externally (^{31}P) using H_3PO_4, with downfield shifts reported as positive. All NMR spectra were measured at 298 K, unless otherwise specified. Elemental analyses were performed by the "Service de microanalyses", Université de Strasbourg. Electrospray mass spectra (ESI-MS) were recorded on a microTOF (Bruker Daltonics, Bremen, Germany) instrument using acetonitrile as solvent, nitrogen as drying agent and nebulising gas.

4.1. Synthesis of *[IrH(cod){Ph$_2$PCH…C(…O)Ph,κP,κO}{Ph$_2$PCH$_2$C(O)Ph,κP}]PF$_6$* (4)

To a solution of $[Ir(cod)(\mu\text{-}Cl)]_2$ (0.5 equiv, 0.202 g, 0.301 mmol) in THF (20 mL) was added 1 equiv of $TlPF_6$ (0.210 g, 0.601 mmol) at room temperature. The solution was stirred for 30 min, then 2 equiv of $Ph_2PCH_2C(O)Ph$ (0.365 g, 1.20 mmol) was added at room temperature and the reaction mixture was stirred for 1 h, its colour changed from red to orange and a white precipitate formed. After stirring was maintained for 1 h, volatiles were evaporated and the residue was dissolved in CH_2Cl_2. The orange solution was filtered with a cannula equipped with a filter cap and then concentrated. Addition of hexane to the CH_2Cl_2 solution led to precipitation of a white product (in case this precipitate is slightly coloured, washing with 1 mL cold THF will afford a white solid). After filtration, the solid was washed with hexane and dried under vacuum. Yield: 0.232 g, 0.220 mmol, 73%. ^1H NMR (400 MHz, CD_2Cl_2): δ −16.65 (t, 1H, Ir–H, ^2J(P,H) = 9.0 Hz), 1.77–1.91 (m, 2H, $CH_{2\ COD}$), 2.31–2.38 (m, 1H, CH_{COD}), 2.49 (dd, 1H, PC*H*H, ^2J(P,H) = 10.9 Hz, ^2J(H,H) = 16.6 Hz), 2.54–2.64 (m, 2H, $CH_{2\ COD}$), 2.66–2.76 (m, 1H, CH_{COD}), 2.99–3.09 (m, 1H, CH_{COD}), 3.33–3.39 (m, 1H, CH_{COD}), 4.26–4.31 (m, 1H, CH_{COD}), 4.45–4.54 (m, 2H, $CH_{2\ COD}$), 4.61 (dd, 1H, PCH*H*, ^2J(P,H) = 6.8 Hz, ^2J(H,H) = 16.6 Hz), 5.15 (b, 1H, CH_{COD}), 5.91(d, 1H, CH_{enol}, ^2J(P,H) = 4.6 Hz), 6.97–8.39 (m, 30H, CH_{Ar}). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 24.6 (s, $CH_{2\ COD}$), 27.7 (s, $CH_{2\ COD}$), 28.8 (d, PCH_2, ^1J(P,C) = 30 Hz), 30.7 (s, $CH_{2\ COD}$), 37.5 (s, $CH_{2\ COD}$), 72.8 (d, PCH_{enol}, ^1J(P,C) = 73 Hz), 93.3 (d, CH_{COD}, ^2J(P,C) = 12 Hz), 96.4 (d, CH_{COD}, ^2J(P,C) = 9 Hz), 97.0 (d, CH_{COD}, ^2J(P,C) = 9 Hz), 101.6 (d, CH_{COD}, ^2J(P,C) = 12 Hz), 125.4–136.6 (CH_{Ar}), 186.5 (d, C_{enol}(O)Ph, ^2J(P,C) = 15 Hz), 192.6 (d, C(O)Ph, ^2J(P,C) = 10 Hz). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): δ −144.6 (sept., ^1J(PF) = 711 Hz, PF_6), 16.2 (d, PCH, ^2J(P,P) = 16.6 Hz), −1.3 (d, PCH_2, ^2J(P,P) = 16.6 Hz). Anal. calcd for $C_{48}H_{46}IrF_6O_2P_3$: C, 54.70; H, 4.40. Found: C, 54.6; H, 4.51. MS (ESI): *m/z* 909.27 $[M–PF_6]^+$. IR (selected): 1672 (ν(C = O), 1510 cm^{-1} (ν(C…O) + ν(C…C)).

4.2. Synthesis of *[Ir(cod){Ph$_2$PCH…C(…O)Ph,κP,κO}{Ph$_2$PCH$_2$C(O)Ph,κP}]* (5)

To a suspension of **4** (1 equiv, 0.100 g, 0.095 mmol) in THF (10 mL) was added excess NaH (5 equiv, 0.011 g, 0.46 mmol) at room temperature. The solution was stirred

for 2 h and the solvent was removed under reduced pressure. The yellow residue was dissolved in toluene (5 mL) and the solution was filtered *via* cannula to remove $NaPF_6$. The orange solution was evaporated under reduced pressure and the yellow residue was washed with a little cold acetone to obtain the product as a yellow powder. Yield: 0.061 g, 0.067 mmol, 70%. ^{1}H NMR (600 MHz, CD_2Cl_2, 203 K): δ 0.88 (b, 3H, CH_2 $_{COD}$), 1.65 (b, 2H, CH_2 $_{COD}$), 1.77 (m, 2H, CH_2 $_{COD}$), 2.25 (b, 1H, CH_2 $_{COD}$), 2.43 (b, 1H, CH_{COD}), 2.61 (dd, 1H, PCH*H*, ^2J(P,H) = 6.4 Hz, ^2J(H,H) = 14.2 Hz), 3.02 (b, 1H, CH $_{COD}$), 3.23 (b, 1H, CH_{COD}), 3.61 (dd, 1H, PCH*H*, ^2J(P,H) = 6.4 Hz, ^2J(H,H) = 14.2 Hz), 3.70 (b, 1H, CH_{COD}), 5.68 (s, 1H, PCH_{enol}), 5.75–7.99 (m, 30H, CH_{Ar}). ^{13}C{^{1}H} NMR (150 MHz, CD_2Cl_2, 203 K): δ 26.4 (s, CH_2 $_{COD}$), 29.3 (s, CH_2 $_{COD}$), 31.2 (s, PCH_2), 33.99 (s, CH_2 $_{COD}$), 36.3 (d, CH_2 $_{COD}$, ^1J(P,C) = 6.3 Hz), 57.4 (d, CH_{COD}, ^1J(P,C) = 32.7 Hz), 59.4 (s, CH_{COD}), 61.2 (s, CH_{COD}), 61.4 (d, CH_{COD}, ^1J(P,C) = 6.6 Hz), 83.6 (d, CH_{enol}, ^1J(P,C) = 57.7 Hz), 126.9–142.3 (m, C_{Ar}), 181.7 (d, C_{enol}(O)Ph, ^1J(P,C) = 26.4 Hz), 196.3 (d, *C*(O)Ph, ^1J(P,C) = 11 Hz). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2): δ 14.3 (d, PCH, ^2J(P,P) = 21.5 Hz), –3.5 (d, PCH_2, ^2J(P,P) = 21.5 Hz). Anal. calcd for $C_{48}H_{45}IrO_2P_2$: C, 63.49; H, 5.00. Found: C, 63.05; H, 4.83. MS (ESI): *m/z* 605.17 [*M*–L]$^+$, 799.16 [*M*–COD]$^+$, 909.27 [*M*–PF_6]$^+$. IR (selected): 1670 (ν(C = O)), 1525 cm^{-1} ((ν(C...O) + ν(C...C)).

4.3. Reaction of [Ir(cod)(μ-Cl)]$_2$ with $Ph_2PCH_2C(O)Ph$ and NaH and in situ synthesis of [Ir(cod){Ph_2PCH...C(...O)Ph, κP,κO}{$Ph_2PCH_2C(O)Ph$,κP}] (**5**)

Freshly distilled THF (5 mL) was added to a Schlenk tube containing [Ir(cod)(μ-Cl)]$_2$ (0.034 g, 0.051 mmol) and $TlPF_6$ (0.035 g, 0.10 mmol). The mixture was stirred at room temperature for 3 h until a white solid precipitated (TlCl). The suspension was filtered and $Ph_2PCH_2C(O)Ph$ (0.061 g, 0.20 mmol) and NaH (60% dispersion in oil, 0.009 g, 0.22 mmol) were added to the filtrate under an argon flow. When no more gas was formed (H_2), the mixture was further stirred at room temperature for 30 min. After filtration, the ^{31}P{^{1}H} NMR spectrum of the solution contained two major doublets at 1.30 and 27.9 ppm (^2J(P,P) = 9.0 Hz) (unidentified complex, most likely containing a Ph_2PCH...C(...O)Ph and a $Ph_2PCH_2C(O)Ph$ ligand in mutually cis position) and resonances corresponding to complexes **4** and **5** (estimated NMR yields: 80%, 10% and 10%, respectively). Addition of Et_2O (10 mL) to this solution precipitated an orange solid. A few single crystals of **5**·C_7H_8 suitable for X-ray diffraction studies were obtained by slow vapour diffusion of Et_2O into a toluene solution of the complex in a NMR tube. ^{31}P{^{1}H} NMR (d_8-toluene) for **5**: δ –3.55 (d), 14.32 (d, ^2J(PP) = 23.1 Hz).

4.4. X-ray data collection and structure refinement for 4·CH_2Cl_2 and 5·C_7H_8

Suitable crystals for the X-ray analysis were obtained as described above. The intensity data were collected at 173(2) K on a Kappa CCD diffractometer (graphite monochromated Mo Kα radiation, λ = 0.71073 Å). Crystallographic and experimental details for the structures are summarized in Table 1. The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures (based on F^2, SHELXL-97) [18] with anisotropic thermal parameters for all the non-hydrogen atoms.

Table 1
X-ray data collection and structure refinement parameters.

Compound reference	**4**·CH_2Cl_2	**5**·C_7H_8
Chemical formula	$C_{49}H_{48}Cl_2F_6IrO_2P_3$	$C_{48}H_{45}IrO_2P_2$•C_7H_8
CCDC ref	1,023,389	852,592
Formula Mass	1138.88	1000.11
Crystal system	Orthorhombic	Monoclinic
Space Group	*Pbca*	*C*2/*c*
a/Å	18.0680 (2)	43.3764 (18)
b/Å	19.9530 (4)	10.0952 (3)
c/Å	25.3600 (5)	22.0750 (8)
β/°	90.00	105.089 (2)
Unit cell volume/Å^3	9142.6 (3)	9333.2 (6)
Temperature/K	173 (2)	173 (2)
Z	8	8
Absorption coefficient, μ/mm^{-1}	3.207	2.970
No. of reflections measured	81661	16722
No. of independent reflections	8894	10212
R_{int}	0.1581	0.0646
Final R_1 values ($I > 2\sigma(I)$)	0.0772	0.0509
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.0968	0.0979
Final R_1 values (all data)	0.1119	0.1239
Final $wR(F^2)$ values (all data)	0.1040	0.1148
Goodness of fit on F^2	1.233	0.928

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Appendix A. Supplementary data

CCDC 852592 and 1023389 contain the supplementary crystallographic data for this paper that can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif and in the online version, at http://dx.doi.org/10.1016/j.crci.2015.03.014. *Supporting Information:* Electronic supplementary information (ESI) available contains the cif files of compounds **4**·CH_2Cl_2 and **5**·C_7H_8.

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