

New hydridoirida- β -diketones derived from 8-quinoline-carbaldehyde and *o*-(diphenylphosphino)benzaldehyde†

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Received 3rd February 2009, Accepted 19th March 2009

First published as an Advance Article on the web 6th April 2009

DOI: 10.1039/b902232e

8-Quinoline-carbaldehyde (C_9H_6NCHO) reacts in methanol with $[IrCl(Cod)]_2$ (Cod = 1,5-cyclooctadiene) to give the acylhydrido complex $[IrHCl(C_9H_6NCO)(Cod)]$ (**1**) or with $[IrHCl\{PPh_2(o-C_6H_4CO)\}(Cod)]$ to afford the hydridoirida- β -diketone complex $[IrHCl\{PPh_2(o-C_6H_4CO)\}(C_9H_6NCO)H]$ (**2**). Complex **2** reacts with silver perchlorate in the presence of pyridine to afford the cationic $[IrH\{PPh_2(o-C_6H_4CO)\}(C_9H_6NCO)H(py)]ClO_4$ (**3**), which in solution transforms slowly into the cationic dinuclear complex $[Ir\{\mu-PPh_2(o-C_6H_4CO)\}(C_9H_6NCO)(py)]_2(ClO_4)_2$ (**4**) with two acylphosphine chelate-bridging ligands. The reaction of **2** with $AgClO_4$ in the presence of carbon monoxide affords $[IrH\{PPh_2(o-C_6H_4CO)\}(C_9H_6NCO)H(CO)]ClO_4$ (**5**), which in solution is in equilibrium with the deprotonated diacylhydrido complex $[IrH\{PPh_2(o-C_6H_4CO)\}(C_9H_6NCO)(CO)]$ (**6**). The reaction of **2** with Et_3OPF_6 results in the formation of $[[IrH\{PPh_2(o-C_6H_4CO)\}(C_9H_6NCO)H]_2(\mu-Cl)]PF_6$ (**7**), containing a cationic dinuclear species with a single chlorine atom bridging two hydridoirida- β -diketone fragments. The reaction of **2** with $[Rh(OMe)(Cod)]_2$ affords the hydridoirida- β -diketonaterhodium(I) complex $[IrHCl\{\mu-PPh_2(o-C_6H_4CO)\}(\mu-C_9H_6NCO)Rh(Cod)]$ (**8**), which isomerizes to the thermodynamically stable isomer $[IrCl\{PPh_2(o-C_6H_4CO)\}(\mu-H)(\mu-C_9H_6NCO)Rh(Cod)]$ (**9**). The catalytic activity of these complexes in the hydrogen transfer from isopropanol to cyclohexanone has been tested. The X-ray diffraction structures of complexes **2**, **4** and **9** are reported.

Introduction

Metalla- β -diketones can be considered as acylhydroxycarbene complexes stabilized by an intramolecular hydrogen bond between the acyl and the hydroxycarbene moieties. Hydroxycarbene complexes have received considerable attention as they have been proposed as important intermediates in CO reduction reactions or in alkene hydrocarbonylation reactions to produce alcohols.¹ The protonation of diacylmetalate anions afforded the first reported saturated metalla- β -diketones $[M\{(COR)(COR')H\}L_x]$, which proved appropriate to form heterobinuclear metal complexes of metalla- β -diketonates with two bridging acyl ligands, and also metalla- β -ketoimines. These complexes were also reported to promote the carbon–carbon bond formation between the acyl carbon bonds.² Unsaturated 16e platina- β -diketones, $[Pt_2(\mu-Cl)_2\{(COR)_2H\}_2]$, obtained by the reaction of hexachloroplatinic acid with alkynes, have been reported to afford a variety of complexes such as platina- β -diketonates of platina- β -diketones analogous to platinum blue compounds; complexes containing enamide–amide type ligands; or dinuclear platinum(II) complexes with bridging μ -acyl(hydroxycarbene) ligands.³ The first hydridoirida- β -diketone

$[IrHCl\{PPh_2(o-C_6H_4CO)\}_2H]$ was prepared by the reaction of $[IrHCl\{PPh_2(o-C_6H_4CO)\}(Cod)]$ (Cod = 1,5-cyclooctadiene) with $PPh_2(o-C_6H_4CHO)$ in methanol.⁴ Hydridoirida- β -diketones may undergo deprotonation reactions to afford neutral mononuclear diacylhydridoiridium(III) derivatives $[IrH\{PPh_2(o-C_6H_4CO)\}_2L]$; dinuclear acyl bridged hydrido iridium(III) complexes such as $[Ir_2H_2\{PPh_2(o-C_6H_4CO)\}_2\{\mu-PPh_2(o-C_6H_4CO)\}_2]$, $[Ir_2H\{\mu-PPh_2(o-C_6H_4CO)\}_3\{PPh_2(o-C_6H_4CO)\}]^+$ or $[Ir_2(\mu-H)\{\mu-PPh_2(o-C_6H_4CO)\}_2\{PPh_2(o-C_6H_4CO)\}_2]^+$ species and also heterodinuclear rhodium(I) hydridoirida- β -diketonate derivatives.^{5–7} 8-Quinoline-carbaldehyde (C_9H_6NCHO) is well known to promote the chelate-assisted oxidative addition of the aldehyde to rhodium(I) derivatives to produce stable saturated and unsaturated rhodium(III) acyl hydrides;⁸ the insertion of olefins into the Rh–H bond followed by the formation of new C–C bonds to afford ketones;^{9–11} and the oxidative addition of aldehyde followed by loss of H_2 .¹²

We report now on the reactions of iridium complexes with C_9H_6NCHO that allow the preparation of new mixed hydridoirida- β -diketones containing N-acyl and P-acyl fragments. The deprotonation reactions to afford new homo- or heterodinuclear complexes with acylphosphine chelate-bridging ligands, acylquinoline chelate-bridging ligands and/or hydrido bridges depending on the reaction conditions and the catalytic activity in transfer hydrogenation of ketones are also reported.

Results and discussion

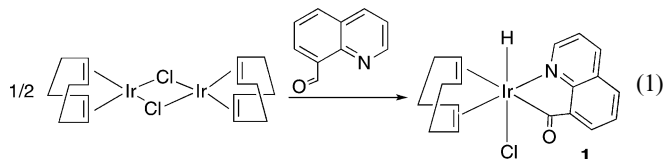
$[IrCl(Cod)]_2$ reacts with C_9H_6NCHO in benzene or in methanol at room temperature, to undergo the chelate-assisted oxidative

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† CCDC reference numbers 718373 (**2**), 718374 (**4**) and 718375 (**9**). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b902232e

addition of the aldehyde thus affording the acylquinolinehydrido complex $[\text{IrHCl}(\text{C}_9\text{H}_6\text{NCO})(\text{Cod})]$ (**1**) (see equation 1) identified on account of the spectroscopic and analytical data. The ^1H NMR spectrum contains four resonances due to the coordinated diolefin in the 5.6–4.5 ppm range and a singlet in the high field region, at -15.66 ppm, due to a hydride *trans* to chloride or to nitrogen.^{4,5,13} This chemical shift is similar to that reported for the related $[\text{IrHCl}\{\text{PPh}_2(o\text{-C}_6\text{H}_4\text{CO})\}(\text{Cod})]$ (δ -16.12 ppm) containing chloride and lacking nitrogen,¹⁴ therefore we propose that the hydride lies *trans* to chloride. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum shows a singlet at 207 ppm, in the range expected for acyl iridium complexes, and the resonances due to the coordinated diolefin.



Attempts to prepare irida- β -diketones using **1** as starting material proved unsuccessful. Complex **1** is insoluble in MeOH and its attempted reaction with *o*-(diphenylphosphine)benzaldehyde or with 8-quinoline-carbaldehyde in $\text{CH}_2\text{Cl}_2/\text{MeOH}$ gave only complex mixtures of compounds. At variance, the acylphosphine-hydrido complex $[\text{IrHCl}\{\text{PPh}_2(o\text{-C}_6\text{H}_4\text{CO})\}(\text{Cod})]$ reacted with $\text{C}_9\text{H}_6\text{NCHO}$ (Scheme 1), with displacement of cyclooctadiene, to afford the hydrido-irida- β -diketone derivative $[\text{IrHCl}\{\text{PPh}_2(o\text{-C}_6\text{H}_4\text{CO})\}(\text{C}_9\text{H}_6\text{NCOH})]$ (**2**) that may be described as a hydroxycarbene complex with an intramolecular hydrogen bridge to an acyl ligand, *i.e.* the resonance form of the canonical structures **2a** and **2b**. The IR spectrum shows a sharp absorption at 2160 cm^{-1} due to $\nu(\text{Ir-H})$ and two $\nu(\text{C=O})$ bands at 1620 and 1591 cm^{-1} due to coordinated terminal acyls.^{9,14} The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows a singlet at 19.9 ppm and the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum contains two doublets at 252.6 and 247.1 ppm, in the range expected for acyl(hydroxycarbene)iridium complexes.^{4,15} The large $^2J(\text{P,C})$ of 111 Hz indicates that the resonance at lower field corresponds to the acylquinoline moiety with the acyl group *trans* to the phosphorus atom of the acylphosphine fragment. The resonance of the acylphosphine moiety appears as a doublet due to coupling with the phosphorus atom of the metallocycle ($^2J(\text{P,C}) = 5$ Hz). The ^1H NMR spectrum shows a hydride resonance in the high field region, at -17.18 ppm, as a doublet due to $^2J(\text{P,H})$ of 15.0 Hz that agrees with the hydride being *cis* to the phosphine and a sharp low field singlet at 21.32 ppm that supports the presence of a fairly strong O–H–O hydrogen bond,² and the existence of a irida- β -diketone containing a formally tetradentate PCCN ligand. Because the formation of hydrido-irida- β -diketones requires both acyl groups and the donor atoms being coplanar,⁵ we believe that complex **2** has the structure depicted in Scheme 1. When the preparation of **2** was performed in CD_3OD , the isolated product

also contained the O–H–O fragment. No exchange with deuterium was observed because the precipitation of **2** occurred immediately. This observation shows that the aldehyde originates the O–H–O moiety; most likely *via* oxidative addition to the acylhydrido Ir(III) complex, followed by Ir-to-O proton transfer.

An X-ray diffraction study on **2** confirms the spectroscopic findings. The molecular structure is shown in Fig. 1, and selected bond distances and angles are listed in Table 1. The crystal structure consists of discrete $[\text{IrHCl}\{\text{PPh}_2(o\text{-C}_6\text{H}_4\text{CO})\}(\text{C}_9\text{H}_6\text{NCOH})]$ molecules and chloroform solvent held together by normal van der Waals forces. The geometry about the metal atom is distorted octahedral with four positions occupied by the two bidentate ligands bonded between them by a hydrogen bond, and the other two positions occupied by the hydride and the chloride ligands mutually *trans*. The bond distances in the Ir–C–O fragments show some differences. In the acylquinolinic fragment, the $\text{Ir1-C1} = 1.998(9)\text{ \AA}$ and the $\text{C1-O1} = 1.25(1)\text{ \AA}$ distances agree with those reported for other irida- β -diketones.^{4,5} In the acylphosphine fragment, the shorter $\text{Ir1-C11} = 1.941(9)\text{ \AA}$ distance is close to the normal region for localized Ir–C double bonds,¹⁶ and the $\text{C11-O2} = 1.31(1)\text{ \AA}$ distance is elongated with respect to the acylquinolinic fragment. These features point to a higher contribution from the canonical structure **2a** to the resonance form. The $\text{O1}\cdots\text{O2}$ distance, $2.447(11)\text{ \AA}$, is in accordance with a strong hydrogen bridge bond in mononuclear complexes,^{2,4} and the O1-H2-O2 angle, 164.9° , is consistent with a nearly linear $\text{O}\cdots\text{H}\cdots\text{O}$ bridge. The dihedral angle between the best least-squares planes for the Ir, C11, C12, C17, P1 and for the C12, C13, C14, C15, C16, C17 atoms is $3.9(2)^\circ$ and the dihedral angle

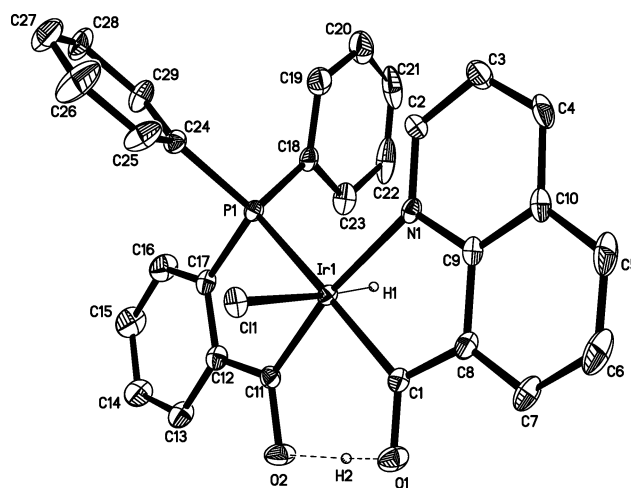
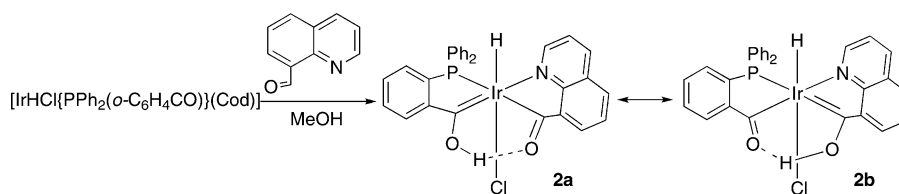


Fig. 1 ORTEP view of complex **2** showing the atomic numbering (30% probability ellipsoids) and the intramolecular hydrogen bond. The hydrogen atoms except two have been omitted for clarity.



Scheme 1

Table 1 Selected bond lengths (Å) and angles (deg) for **2**, **4** and **9**

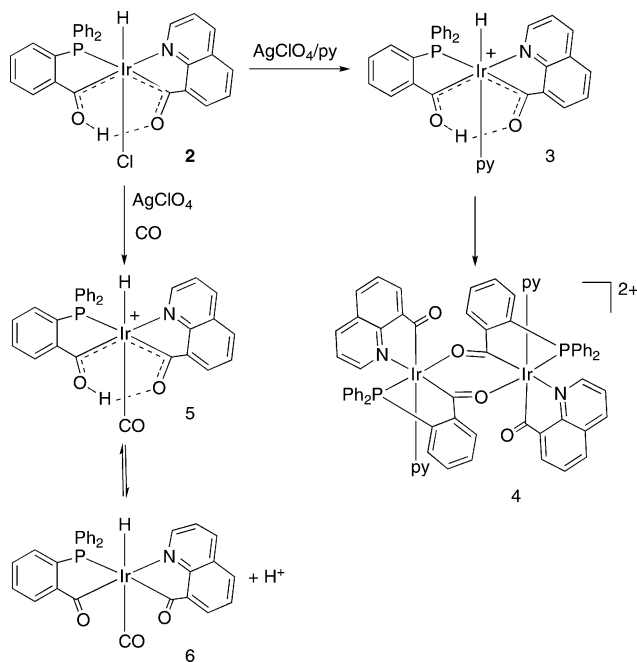
2		4		9	
Ir–P1	2.355(2)	Ir1–P1	2.229(4)	Ir–P1	2.348(4)
Ir–N1	2.158(8)	Ir1–N1	2.23(1)	Ir–N1	2.06(2)
Ir–Cl	2.488(2)	Ir1–O1	2.13(1)	Ir–Cl1	2.499(5)
Ir–C11	1.941(9)	Ir1–C1	1.95(1)	Ir–C1	1.92(1)
Ir–C1	1.998(9)	Ir1–C20	1.90(2)	Ir–C20	1.90(2)
Ir–H1	1.70	Ir1–N2	2.24(1)	Ir–H1	2.04
C11–O2	1.31(1)	C1–O1A	1.26(1)	C1–O1	1.25(2)
C1–O1	1.25(1)	C20–O2	1.23(2)	C20–O2	1.32(2)
O1–H2	1.14	Ir1–Ir1A	3.929(1)	Ir–Rh	2.883(2)
O2–H2	1.34				
O1–O2	2.46(1)				
C1–Ir–C11	92.1(4)	C20–Ir1–C1	86.3(7)	C20–Ir–C1	89.0(7)
C11–Ir–P1	83.4(3)	C1–Ir1–P1	85.6(4)	C1–Ir–P1	85.7(5)
C11–Ir–N1	171.2(3)	C1–Ir1–N1	168.5(5)	C1–Ir–N1	89.7(6)
C11–Ir–Cl	95.7(3)	C1–Ir1–O1	97.9(4)	C1–Ir–Cl1	177.2(5)
C11–Ir–H1	81.9	C1–Ir1–N2	93.7(5)	C1–Ir–H1	104.0
C1–Ir–P1	173.3(3)	C20–Ir1–P1	93.2(5)	C20–Ir–P1	174.1(5)
P1–Ir–N1	103.7(2)	P1–Ir1–N1	93.5(3)	P1–Ir–N1	104.1(4)
P1–Ir–Cl	102.0(1)	P1–Ir1–O1	176.1(3)	P1–Ir–Cl1	92.0(2)
P1–Ir–H1	71.9	P1–Ir1–N2	96.9(3)	P1–Ir–H1	89.9
C1–Ir–N1	80.3(3)	C20–Ir1–N1	82.2(5)	C20–Ir–N1	78.5(8)
N1–Ir–Cl	87.9(2)	N1–Ir1–O1	83.4(4)	N1–Ir–Cl1	89.4(4)
N1–Ir–H1	95.3	N1–Ir1–N2	97.8(4)	N1–Ir–H1	161.2
C1–Ir–Cl	83.5(3)	C20–Ir1–O1	89.7(6)	C20–Ir–Cl1	93.3(5)
C1–Ir–H1	102.6	C20–Ir1–N2	169.8(6)	C20–Ir–H1	88.8
Cl–Ir–H1	173.6	O1–Ir1–N2	81.2(4)	Cl1–Ir–H1	77.4
O1–H2–O2	164.8	O1A–C1–Ir1	130.6(9)	O2–C20–Ir	129(2)
		Ir1–O1–C1A	130.5(8)		
				C30–Rh–C31	36.6(8)
				C34–Rh–C35	36.9(8)
				H1–Rh–O2	99.7
				O2–Rh–C30	164.9(8)
				O2–Rh–C31	158.5(8)
				O2–Rh–C34	87.8(8)
				O2–Rh–C35	91.4(9)
				H1–Rh–C30	75.9
				H1–Rh–C31	88.1
				H1–Rh–C34	172.5
				H1–Rh–C35	141.1
				Ir–H1–Rh	100.9
				C20–O2–Rh	98(1)

(A) $-x + 1, -y + 2, -z + 1$.

between the best least-squares Ir, C1, C8, C9, N1 plane and the quinolinic plane is $2.2(2)^\circ$.

Complex **2** reacts with pyridine in the presence of silver perchlorate, which eliminates the chloride as AgCl, to afford the cationic hydrido-irida- β -diketone derivative $[\text{IrH}(\{\text{PPh}_2(o\text{-C}_6\text{H}_4\text{CO})\}(\text{C}_9\text{H}_6\text{NCO})\text{H})(\text{py})]\text{ClO}_4$ (**3**), shown in Scheme 2, as confirmed by IR, NMR and conductivity measurements. The spectroscopic data of **3** are similar to those of complex **2** (see experimental). In order to obtain single crystals of **3**, we allowed the slow diffusion of diethyl ether onto chloroform solutions of **2**. Brownish crystals were certainly obtained but the X-ray diffraction study revealed the corresponding crystals to be the cationic dinuclear complex with two acylphosphine chelate-bridging ligands $[\text{Ir}\{\mu\text{-PPh}_2(o\text{-C}_6\text{H}_4\text{CO})\}(\text{C}_9\text{H}_6\text{NCO})(\text{py})]_2(\text{ClO}_4)_2$ (**4**) (see Scheme 2). By dissolution of **3** in chloroform the rather insoluble complex **4** could be prepared in a slow reaction and was further characterized by IR and elemental analysis. Its insolubility in common solvents precluded any NMR measurement. The presence of strong absorptions at 1645 and 1512 cm^{-1} in the IR spectrum indicates terminal and bridging acyl groups respectively.^{7,17} The transformation of **3** into **4** may well occur by hydrogen loss, though we were unable to detect any H_2 formation. Evolution of H_2 has been detected in the oxidative addition of the aldehyde in $\text{C}_9\text{H}_6\text{NCHO}$ to $[\text{RhCl}(\text{CO})_2]_2$ followed by intermolecular reductive elimination of H_2 ,¹² and in the reaction of $[\text{RhCl}\{\text{PPh}_2(o\text{-C}_6\text{H}_4\text{CO})\}\{\text{PPh}_2(o\text{-C}_6\text{H}_4\text{CHO})\}(\text{py})]$ to afford diacyl derivatives, proposed to occur via a hydrido hydroxycarbene intermediate.¹⁸

Complex **4** consists of dinuclear cations and perchlorate anions packed within normal van der Waals distances. The compound

**Scheme 2**

crystallizes with two molecules of methanol per dimer, hydrogen-bonded to perchlorate anions. The middle point of the dimeric cations lies on an inversion centre. For this reason the asymmetric unit corresponds to half of the dimer, a perchlorate anion and a methanol molecule. Fig. 2 shows a PLUTO view of the dinuclear

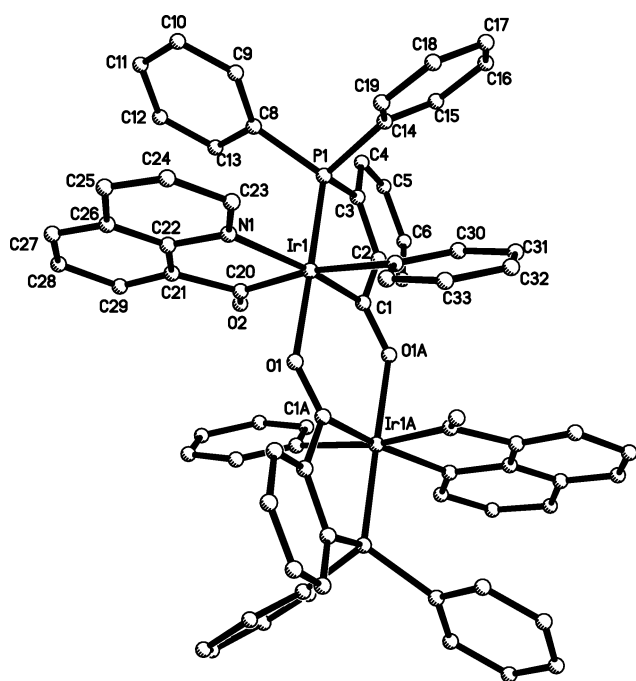


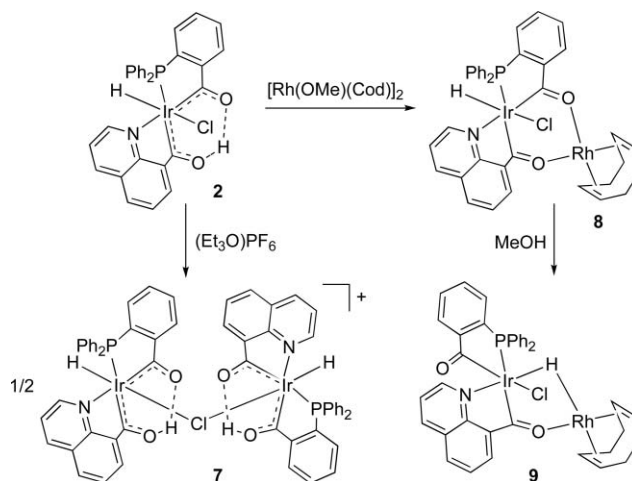
Fig. 2 PLUTO view of the complex cation in compound **4** showing the atomic numbering. The hydrogen atoms and the label of some C atoms have been omitted for clarity. (A) $-x + 1, -y + 2, -z + 1$.

cation with the labeling scheme of the asymmetric unit. Selected bond distances and angles are listed in Table 1. The Ir atoms are bonded to two bridging-chelating acyl-phosphine groups with a head-to-tail arrangement of the bridging acyls, a transoid disposition of the phosphine groups binding to opposite faces of the complex and also a transoid disposition of the quinolinic groups. The geometry around each iridium atom is pseudo-octahedral with the quinolinic nitrogens *trans* to the carbon atoms of the bridging acyl groups and the phosphorus atoms *trans* to the oxygen atoms of the bridging acyl groups. We thus observe that the disappearance of the acylhydroxycarbene character when **3** transforms into **4**, comprises losing the coplanarity of the acyl groups, the phosphorus and the nitrogen atoms, likely to be present in **3**. As in other iridium complexes containing bridging and terminal acyl groups,^{6,7} the Ir–C and the C–O distances of the bridging and terminal groups are equal, indicating low carbenoid character in the bridging groups.¹⁹ The Ir1–P1 bond distance is considerably shorter than the corresponding distance in **2**, presumably because of the presence in **4** of an oxygen atom, with weaker structural *trans* influence, in the *trans* position. The six-membered ring Ir1, C1, O1A, Ir1A, C1A, O1 adopts an almost planar conformation with a maximum deviation of 0.051(9) for the C1 atom and a Ir1...Ir1' distance of 3.929(1) Å ruling out any interaction between the metal centers.

Complex **2** also reacts with carbon monoxide in the presence of silver perchlorate, to afford the cationic derivative $[\text{IrH}(\{\text{PPh}_2(o\text{-C}_6\text{H}_4\text{CO})\}(\text{C}_9\text{H}_6\text{NCO})\text{H})(\text{CO})]\text{ClO}_4$ (**5**) shown in Scheme 2, as confirmed by IR, conductivity and NMR measurements. At room temperature, the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum shows two resonances in the low field region, at 252.6 {d, $^2J(\text{P,C}) = 85$ Hz} and 236.0 {d, $^2J(\text{P,C}) = 5$ Hz} ppm, and the resonance due to the carbonyl group at the expected higher field (170.0 {s} ppm).²⁰ The resonance

of the hydride, *trans* to CO, appears at -7.32 ppm as a doublet due to coupling with a *cis* phosphorus atom ($^2J(\text{P,H}) = 15.4$ Hz). The O–H–O resonance at low field is extremely broad at room temperature, sharpens on lowering the temperature and by -40°C becomes a sharp singlet at 21.94 ppm. Because neither the hydride resonance nor the ^{31}P NMR signal is modified on changing the temperature we believe that the fluxionality of **5** can be due to a deprotonation/protonation equilibrium or to a rapid exchange of the hydrogen atom between the oxygen atoms of both ligands, inhibited at low temperature. The deprotonated form, a neutral diacylhydrido species, can be obtained by addition of triethylamine to **5**, which gives $[\text{IrH}\{\text{PPh}_2(o\text{-C}_6\text{H}_4\text{CO})\}(\text{C}_9\text{H}_6\text{NCO})(\text{CO})]$ **6**, shown in Scheme 2. The hydride, the phosphine and also the carbonyl resonances for **6** appear at lower fields than in the cationic species, **5**. In line with the disappearance of the acyl(hydroxycarbene) character, the acyl resonances at 222.8 and 206.8 ppm in **6** appear at higher field than in **5**.

The reaction of **2** with halide scavengers such as $(\text{Et}_3\text{O})\text{PF}_6$ results in the abstraction of only half of the chlorine atoms in the starting material and the formation of compound $[\text{IrH}\{\{\text{PPh}_2(o\text{-C}_6\text{H}_4\text{CO})\}(\text{C}_9\text{H}_6\text{NCO})\text{H}\}_2(\mu\text{-Cl})]\text{PF}_6$ (**7**) containing a cationic dinuclear species with a single chlorine atom bridging two hydrido-irida- β -diketone fragments (see Scheme 3) as ascertained by spectroscopic measurements. Most likely, partial abstraction of chlorine from **2** affords the transient formation of unstable five-coordinated $[\text{IrH}\{\{\text{PPh}_2(o\text{-C}_6\text{H}_4\text{CO})\}(\text{C}_9\text{H}_6\text{NCO})\text{H}\}]^+$ species that may coordinate to the chlorine atom of still unreacted **2**, thus affording **7**. In acetone solution **7** behaves as 1:1 electrolyte and the FAB spectrum shows the $[\text{M}]^+$ peak at 1315 indicating the formation of a dinuclear species. The IR spectrum contains the $\nu(\text{C}=\text{O})$ absorption at 1619 cm^{-1} , showing that the acyl groups are terminal. The NMR spectra of **7** show two sets of resonances. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum contains two singlets at 25.6 and 24.5 ppm, in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum resonances due to the acyl(hydroxycarbene) groups are observed, two doublets at 252.7 ($^2J(\text{P,C}) = 111$ Hz) and 250.1 ($^2J(\text{P,C}) = 102$ Hz) ppm and two singlets at 250.1 and 245.4 ppm. The ^1H NMR spectrum shows two close doublets ($^2J(\text{P,H}) = 13.7$ Hz) in the high field region, at -20.29 and -20.41 ppm and two close singlets in the low field region at 20.77 and 20.29 ppm respectively. Such a pattern is



Scheme 3

consistent with the nonequivalence of two fragments, connected through the chlorine bridge, each containing a hydrido-irida- β -diketone similar to that present in **2**.

The structure depicted for **7** in Scheme 3, with the phosphorus atoms in a transoid fashion, is proposed because of similarity with complex **4**, which shows this disposition, though a structure with the phosphorus atoms in a cisoid fashion cannot be excluded. Our attempts to obtain single crystals to perform an X-ray diffraction study proved unsuccessful due to decomposition of the sample. In contrast to the related $[[\text{IrH}(\{\text{PPh}_2(o\text{-C}_6\text{H}_4\text{CO})\}_2\text{H})_2(\mu\text{-Cl})]\text{PF}_6$,⁶ complex **7** shows sharp resonances at room temperature excluding a fluxional behavior. This feature can be attributed to hindered rotation around the Ir–Cl bonds and/or hindered variation of the Ir–Cl–Ir angle, indicating a higher rigidity of the complex containing hydrogen-bonded acyl-quinoline and acyl-phosphine metallacycles.

As shown in Scheme 3 the reaction of **2** with transition metal complexes having basic ligands such as $[\text{Rh}(\text{OMe})(\text{Cod})]_2$ leads to the deprotonation of the acyl(hydroxycarbene) fragment by the methoxy group of the rhodium(I) complex to afford the dinuclear mixed-metal hydrido-irida- β -diketonaterhodum complex $[\text{IrHCl}\{\mu\text{-PPh}_2(o\text{-C}_6\text{H}_4\text{CO})\}(\mu\text{-C}_9\text{H}_6\text{NCO})\text{Rh}(\text{Cod})]$ (**8**), containing an iridium(III) and a rhodium(I) fragment. The FAB spectrum shows the $[\text{M} - \text{H}]^+$ peak at 885 required for the dinuclear mixed-metal species and in the corresponding IR spectrum only a strong absorption due to the bridging acyl groups at 1513 cm^{-1} is observed. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum contains a singlet at 14.7 ppm and the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum contains two close doublets at *ca.* 75 ppm due to non-equivalent olefinic groups bonded to the rhodium atom. The ^1H NMR spectrum contains a broad resonance at 4.23 ppm due to the olefinic groups bonded to the rhodium atom and a doublet at -18.19 ppm due to the iridium-bonded hydride *cis* to the phosphorus atom ($^2J(\text{P},\text{H}) = 17.9\text{ Hz}$). The chemical shift value can be consistent with the hydride being *trans* to chloride as in the starting material, **2**.

The hydrido-irida- β -diketonaterhodum(I) complex **8** isomerizes readily to complex $[\text{IrCl}\{\text{PPh}_2(o\text{-C}_6\text{H}_4\text{CO})\}(\mu\text{-H})(\mu\text{-C}_9\text{H}_6\text{NCO})\text{Rh}(\text{Cod})]$ (**9**), containing hydrido and acyl bridging groups (see Scheme 3). In the IR spectrum absorptions due to terminal and bridging acyl groups are observed. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum confirms the presence of a bridging acyl group with the carbon atom *trans* to phosphorus at $239.5\{\text{d}, ^2J(\text{P},\text{C}) = 102\text{ Hz}\}$ ppm, thus belonging to the quinolinic fragment, and of a terminal acyl group at 206.8 (s) ppm belonging to the phosphinic fragment. At variance with **4**, in complex **9** the acylquinoline fragment is preferred as a bridging group. The ^1H NMR spectrum contains two broad resonances due to the olefinic groups bonded to the rhodium atom, and the hydride resonance is a triplet at -20.40 ppm due to the hydride being *cis* to the phosphorus atom and bonded to the rhodium atom with equal $^2J(\text{P},\text{H})$ and $^1J(\text{Rh},\text{H})$ coupling constants of 18.0 Hz. The magnitude of these coupling constants is similar to that of the related heterodinuclear complex $[\text{RhIr}(\text{C}_2\text{Ph})(\text{CO})_2(\mu\text{-H})(\mu\text{-C}_2\text{Ph})(\text{dppm})_2]^+$, 12.0 and 12.7 Hz respectively, for which a stronger interaction of the hydrido ligand with Ir than with Rh has been suggested.²¹ We thus observe that the substitution of the proton in complex **2** by rhodium, to afford the hydrido-irida- β -diketonate species, is kinetically favored and that the species containing a bridging hydrido ligand is the thermodynamically

favored isomer. It thus appears that in this Rh/Ir heterodinuclear case the hydrido is more suitable than the acyl group to behave as a bridging ligand. Taking into consideration the spectroscopic data alone, two structures are possible for **9** that differ in the atom *trans* to the hydride being chlorine or nitrogen. Were the hydride *trans* to chlorine, the coplanarity of the acyl groups, the phosphorus and the nitrogen atoms around the iridium atom would be maintained, while for the derivative containing hydride *trans* to nitrogen this coplanarity would be lost.

We were able to grow crystals of **9** suitable for X-ray diffraction and the corresponding study was undertaken. The crystal consists in a heterodinuclear compound, which crystallizes with one solvent molecule of chloroform. The molecular structure of **9** is shown in Fig. 3 and selected bond distances and angles are listed in Table 1. The molecule can be described as a square-planar rhodium(I) fragment and a pseudo-octahedral iridium(III) moiety bonded by a hydride and an acyl group. The rhodium atom has a normal square-planar geometry with the COD ligand in an orthogonal disposition and the Rh–O and Rh–C distances in the expected ranges. The hydride bonded to the iridium atom is *trans* to the quinolinic nitrogen so that the coplanarity of the acyl groups, the phosphorus and the nitrogen atoms, present in **8**, is lost. The Ir–C distances and also the C–O distances in **9** are equivalent indicating low carbenoid character in the bridging group. The value of the Rh–Ir distance, $2.883(2)\text{ \AA}$ compares well with the corresponding distances found in other $\text{Ir}(\mu\text{-H})\text{Rh}$ complexes, for which the existence of M–M interactions have been suggested.²² For instance, in the compound $[(\text{PEt}_3)_2\text{Rh}(\mu\text{-H})(\mu\text{-Cl})\text{IrH}_2(\text{PEt}_3)_2]$,^{22d} the Ir–Rh separation amounts to $2.898(1)\text{ \AA}$ and in the complex $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\text{PMe}_3)(\mu_2\text{-H})(\mu_3\text{-S})\{\text{Rh}(\text{cod})\}\{\text{RhCl}(\text{cod})\}]$,^{22e} the corresponding distance is $2.8278(8)\text{ \AA}$. The M–H–M complexes are frequently considered as σ complexes of an M–H bond and the formation of such a three-centre bonding implies the presence of M–M bonding.²³ From this point of view, the IrHRh moiety can be interpreted as forming a three-centre-two-electron bond with a significant Rh–Ir bonding interaction. The presence of a hydrido

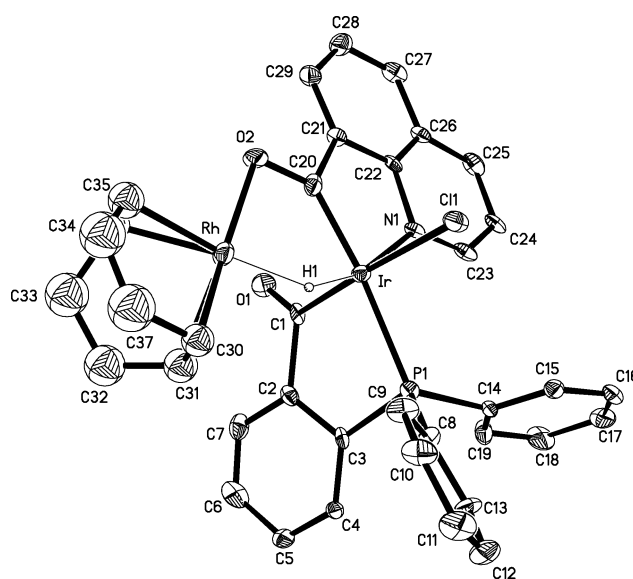


Fig. 3 ORTEP view of complex **9** showing the atomic numbering (30% probability ellipsoids). The hydrogen atoms except one have been omitted for clarity.

Table 2 Transfer hydrogenation of cyclohexanone^a

Pre-catalyst	Conversion (%) ^b	TOF ^c
1	72	270
2	92	270
7	93	392
8	40	95
9	70	217

^a Reaction conditions: 0.1 M substrate in ⁱPrOH (40 cm³); with 0.5 mol% pre-catalyst loading at 83 °C. [KOH]/[pre-catalyst] 10:1. ^b Reaction time: 120 min. ^c Calculated after 10 min and expressed in mol of product/(mol of pre-catalyst × h).

and an acyl as bridging groups in **9** instead of two acyl bridges as in **4** also has an influence on the geometry of the metallocycle Ir, H1, Rh, O2, C20 that presents a distorted boat conformation. The dihedral angles between the Ir, C20, H1 or the Rh, O2, H1 plane and the O2, C20, H1 plane are 12.3(7) or 41.1(8)° respectively. A search of the Cambridge Crystallographic Data Base failed to locate a structurally characterized example of a Rh/Ir μ -acyl μ -hydrido complex.

It is well known that metal hydrides are active catalysts in the transfer hydrogenation of ketones.²⁴ Recently it has been reported that the iridium(III) complex [IrH₂Cl{(ⁱPr₂PC₂H₄)₂NH}] containing mutually *cis* N–H and Ir–H functionalities serves as a convenient precursor to the catalytically active compounds [IrH₂{(ⁱPr₂PC₂H₄)₂N}] and [IrH₃{(ⁱPr₂PC₂H₄)₂N}], which are very effective for the transfer hydrogenation of ketones under base-free conditions.²⁵ The catalytic activity of complexes **1**, **2**, **7**, **8** and **9** was investigated in the transfer hydrogenation of cyclohexanone in ⁱPrOH, which required the presence of a strong base in order to promote the catalytic reaction to occur. Conversion was monitored by GC during the reaction and the results obtained are listed in Table 2, with selected data depicted in Fig. 4. From the transfer hydrogenation data it is apparent that complexes **1** and **2** show initially similar catalytic activity, though complex **1** undergoes deactivation before reaching a 50% conversion. This result indicates that the presence of a phosphine-acyl chelate and a quinoline-acyl chelate makes the corresponding complex more useful for these transfer hydrogenation reactions. To verify this

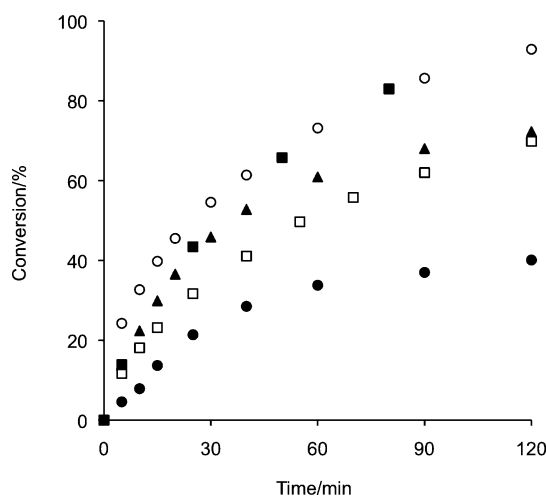


Fig. 4 Hydrogen transfer from ⁱPrOH to cyclohexanone using complexes **1** (▲), **2** (■), **7** (○), **8** (●) and **9** (□) as catalyst precursors.

assumption we have tested the catalytic activity of the related [IrHCl{PPh₂(*o*-C₆H₄CO)}₂H}] containing two phosphine-acyl chelates, which shows very poor activity. Initially, the observed TOF is 65 and only a 24% conversion is reached after 2h reaction. The most active complex is the dinuclear derivative **7**, which after 2h reaction gives similar results to those obtained with **2**. The heterodinuclear complex **8** shows low activity, which is enhanced in complex **9**, containing a hydrido bridge between the metal atoms, though it undergoes fast deactivation.

Conclusions

New mono- and dinuclear hydrido-irida- β -diketones derived from 8-quinoline-carbaldehyde and *o*-(diphenylphosphino)-benzaldehyde, with carbenoid character in the acyl groups bonded to iridium, have been prepared. Mononuclear [IrH{(PPh₂(*o*-C₆H₄CO))(C₉H₆NCO)H}L]ⁿ⁺ species can be deprotonated to afford new mononuclear diacylhydrido-iridium(III) derivatives, dinuclear Ir(III) complexes with acyl-phosphine chelating-bridging groups or heterodinuclear Ir(III)/Rh(I) complexes containing acyl-quinoline chelating-bridging groups. The kinetically favoured hydrido-irida- β -diketonaterrhodium(I) complex, isomerizes to the thermodynamically μ -acyl- μ -hydrido-iridium(III)rhodium(I) favoured species. The chlorine containing hydrido-irida- β -diketones can be used as pre-catalysts in the transfer hydrogenation of ketones.

Experimental

General procedures

The preparation of the metal complexes was carried out at room temperature under nitrogen by standard Schlenk techniques. [IrCl(Cod)]₂, [IrHCl{PPh₂(*o*-C₆H₄CO)}(Cod)], 8-quinoline-carbaldehyde and [Rh(OMe)(Cod)]₂ were prepared as previously reported.^{14,26} Microanalysis were carried out with a Leco CHNS-932 microanalyzer. Conductivities were measured in acetone solution with a Metrohm 712 conductimeter. IR spectra were recorded with a Nicolet FTIR 510 spectrophotometer in the range 4000–400 cm⁻¹ using KBr pellets. NMR spectra were recorded with Bruker Avance DPX 300 or Bruker Avance 500 spectrometers, ¹H and ¹³C{¹H} (TMS internal standard) and ³¹P{¹H} (H₃PO₄ external standard) spectra were measured from CDCl₃, CD₂Cl₂ or acetone-*d*₆ solutions. Mass spectra were recorded on a VG Autospec, by liquid secondary ion (LSI) MS using nitrobenzyl alcohol as matrix and a caesium gun (Universidad de Zaragoza).

[IrHCl(C₉H₆NCO)(Cod)] (**1**)

To a benzene solution of [IrCl(Cod)]₂ (0.149 mmol) was added C₉H₆NCHO (0.298 mmol) whereupon a yellow precipitate was formed that was filtered, washed with benzene and vacuum dried. Yield: 75%. IR (cm⁻¹): 2232(w), ν (IrH); 1641(s), ν (C=O). ¹H NMR (CDCl₃): δ –15.66 (s, 1H, H_{Ir}); 8.74 (d, 1H, ³J(H₃,H₂) 5.0 Hz, H₂); 8.54 (d, 1H, ³J(H₃,H₄) 8.3 Hz, H₄); 8.21 (d, 1H, ³J(H₆,H₇) 7.4 Hz, H₇); 8.03 (d, 1H, ³J(H₆,H₅) 8.3 Hz, H₅); 7.71 (dd, 1H, ³J(H₅,H₆) 8.3 Hz, ³J(H₇,H₆) 7.4 Hz, H₆); 7.58 (dd, 1H, ³J(H₂,H₃) 5.0 Hz, ³J(H₄,H₃) 8.3 Hz, H₃); 5.59 (m, 1H, =CH); 5.30 (m, 1H, =CH); 4.69 (m, 1H, =CH); 4.59 (m, 1H, =CH). ¹³C{¹H} NMR (CDCl₃):

δ 206.7 (C=O); 151.0 (C2); 148.4 (C9); 139.0 (C8); 139.0 (C7); 130.4 (C5); 129.5 (C6); 128.9 (C10); 125.5 (C4); 122.8 (C3); 107.3 (C=C); 103.1 (C=C); 74.8 (C=C). FAB MS: calcd. for $C_{18}H_{19}ClNOIr$: 493; observed: 492 $[M-H]^+$. Anal. calc. for $C_{18}H_{19}ClNOIr$: C, 43.85; H, 3.88; N, 2.84; found: C, 43.59; H, 3.67; N 2.88%.

$[IrHCl\{PPh_2(o-C_6H_4CO)\}(C_9H_6NCO)H](2)$

To a MeOH suspension of $[IrHCl\{PPh_2(o-C_6H_4CO)\}(Cod)]$ (0.160 mmol) was added C_9H_6NCHO (0.160 mmol). After 4 h an orange precipitate was formed that was filtered, washed with MeOH and vacuum dried. Yield: 50%. IR (cm^{-1}): 2160(s), $\nu(Ir-H)$; 1620(s), 1591(s) $\nu(C=O)$. 1H NMR ($CDCl_3$): δ -17.18 (d, 1H, $^2J(P,H)$ 15.0 Hz, HIr); 21.32 (s, 1H, OH). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 19.9 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 252.6 (d, $^2J(P,C)$ = 111 Hz, $N-C=O$); 247.1 (d, $^2J(P,C)$ = 5 Hz, $P-C=O$). FAB MS: calcd. for $C_{29}H_{22}ClNO_2PIr$: 675; observed: 675 $[M]^+$. Anal. calc. for $C_{29}H_{22}ClNO_2PIr$: C, 51.59; H, 3.28; N, 2.07; found: C, 51.80; H, 3.34; N, 2.15%.

$[IrH\{PPh_2(o-C_6H_4CO)\}(C_9H_6NCO)H(py)]ClO_4(3)$

To a dichloromethane solution of **2** (0.074 mmol) was added a stoichiometric amount of pyridine (0.074 mmol) in the presence of $AgClO_4$ (0.149 mmol). Stirring for 1 h at room temperature followed by filtration of the silver salts and evaporation of the solvent gave a yellow solid that was washed with diethyl ether and vacuum-dried. Yield: 66%. IR (cm^{-1}): 2148(w), $\nu(Ir-H)$; 1633(s, br), $\nu(C=O)$. Λ_M ($ohm^{-1} cm^2 mol^{-1}$): 145. 1H NMR ($CDCl_3$): δ -16.98 (d, 1H, $^2J(P,H)$ = 14.6 Hz, HIr); 21.72 (s, 1H, OH). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 31.3 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 256.5 (d, $^2J(P,C)$ = 102 Hz, $N-C=O$); 246.0 (d, $^2J(P,C)$ = 3 Hz, $P-C=O$). FAB MS: calcd for $C_{34}H_{27}N_2O_2PIr$: 719; observed: 719 $[M]^+$. Anal. calc. for $C_{34}H_{27}ClN_2O_2PIr \times CH_2Cl_2$: C, 46.55; H, 3.24; N, 3.10; found: C, 46.64; H, 3.00; N, 3.10.

$[Ir\{\mu-PPh_2(o-C_6H_4CO)\}(C_9H_6NCO)(py)]_2(ClO_4)_2(4)$

A chloroform solution of **3** (100 mg, 0.122 mmol) was stirred overnight to give a brownish solid that was filtered off, washed with chloroform and vacuum dried. Yield: 45%. IR (cm^{-1}): 1645(m), $\nu(C=O)_i$; 1512(m), $\nu(C=O)_b$. Anal. calc. for $C_{68}H_{50}Cl_2N_4O_{12}P_2Ir_2 \times 0.5CHCl_3$: C, 48.62; H, 3.01; N, 3.31; found: C, 48.69; H, 3.02; N, 3.43.

$[IrH\{PPh_2(o-C_6H_4CO)\}(C_9H_6NCO)H(CO)]ClO_4(5)$

Carbon monoxide at room temperature was bubbled for 1 h through a dichloromethane solution of complex **2** (0.148 mmol) in the presence of $AgClO_4$ (0.296 mmol). After filtration of the silver salts, the addition of diethyl ether to the solution gave a yellow precipitate that was filtered off, washed with diethyl ether and vacuum-dried. Yield: 87%. IR (cm^{-1}): 2119(s), $\nu(Ir-H)$; 2048(s), $\nu(C=O)$; 1633(s, br), $\nu(C=O)$. Λ_M ($ohm^{-1} cm^2 mol^{-1}$): 144. 1H NMR ($CDCl_3$, 233 K): δ -7.25 (d, 1H, $^2J(P,H)$ = 15.4 Hz, IrH); 21.94 (s, OH). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 233 K): δ 18.1 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K): δ 252.6 (d, $^2J(P,C)$ = 85 Hz, $N-C=O$); 236.0 (d, $^2J(P,C)$ = 5 Hz, $P-C=O$); 170.0 (s, $C=O$). FAB MS: calcd for $C_{30}H_{22}NO_3PIr$: 668; observed: 668 $[M]^+$. Anal. calc. for

$C_{30}H_{22}ClNO_7PIr$: C, 46.97; H, 2.89; N, 1.83; found: C, 46.96; H, 3.12; N, 1.60.

$[IrH\{PPh_2(o-C_6H_4CO)\}(C_9H_6NCO)(CO)](6)$

To a dichloromethane solution of complex **5** (0.065 mmol) was added a slight excess of triethylamine (0.074 mmol). After stirring for 30 min at room temperature, the solution was washed three times with distilled water and dried over magnesium sulfate. Filtration, followed by evaporation of the solvent gave a yellow solid that was vacuum-dried. Yield: 49%. IR (cm^{-1}): 2067(s), $\nu(Ir-H)$; 1976(m), $\nu(C=O)$; 1658(s), 1641(s), $\nu(C=O)$. 1H NMR ($CDCl_3$): δ -6.45 (d, 1H, $^2J(P,H)$ = 20.6 Hz, IrH). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 21.5 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 222.8 (d, $^2J(P,C)$ = 91 Hz, $N-C=O$); 206.8 (s, $P-C=O$); 175.7 (d, $^2J(P,C)$ = 4 Hz, $C=O$). Anal. calc. for $C_{30}H_{21}NO_3PIr \times 0.5 CH_2Cl_2$: C, 51.66; H, 3.13; N, 1.98; found: C, 51.92; H, 3.17; N, 1.93.

$[IrH\{PPh_2(o-C_6H_4CO)\}(C_9H_6NCO)H]_2(\mu-Cl)PF_6(7)$

To a dichloromethane solution of **2** (55 mg, 0.082 mmol) was added $(Et_3O)PF_6$ (10 mg, 0.040 mmol). After stirring for 60 min the addition of diethyl ether to the solution gave a yellow precipitate that was filtered off, washed with diethyl ether and vacuum dried. Yield: 87%. IR (KBr, cm^{-1}): 2185(m), $\nu(Ir-H)$; 1619(s, br), $\nu(C=O)$. Λ_M ($ohm^{-1} cm^2 mol^{-1}$): 104. 1H NMR ($CDCl_3$): δ -20.29 (d, $^2J(P,H)$ = 13.7 Hz, 1 H, HIr); -20.41 (d, $^2J(P,H)$ = 13.7 Hz, 1 H, HIr); 20.29 (s, 1 H, OH). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 25.6 (s), 24.5 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 252.7 (d, $^2J(P,C)$ = 111 Hz, $N-C=O$); 250.11 (d, $^2J(P,C)$ = 102 Hz, $N-C=O$); 250.13 (s, $P-C=O$); 245.4 (s, $P-C=O$). FAB MS: calcd. for $C_{58}H_{44}ClN_2O_4P_2Ir_2$: 1315; observed: 1315 $[M]^+$. Anal. calc. for $C_{58}H_{44}ClF_6N_2O_4P_2Ir_2 \times 0.5 CH_2Cl_2$: C, 46.77; H, 3.02; N, 1.87; found: C, 46.67; H, 2.70; N, 1.93%.

$[IrHCl\{\mu-PPh_2(o-C_6H_4CO)\}(\mu-C_9H_6NCO)Rh(Cod)](8)$

To a dichloromethane solution of **2** (50 mg, 0.074 mmol) was added $[Rh(OMe)(Cod)]_2$ (18 mg, 0.037 mmol). Stirring during 5 min and evaporation of the solvent gave an orange solid. Yield: 76%. IR (cm^{-1}): 2140(m), $\nu(Ir-H)$; 1513(s), $\nu(C=O)_b$. 1H NMR (acetone- d_6): δ -18.19 (d, 1H, $^2J(P,H)$ = 17.9 Hz, HIr); 4.23 (s, 4H, =CH), 2.64 (m, 4H, CH_2), 1.87 (m, 4H, CH_2). $^{31}P\{^1H\}$ NMR (acetone- d_6): δ 18.6 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 77.1 (d, $^1J(Rh,C)$ = 15 Hz, =CH), 77.0 (d, $^1J(Rh,C)$ = 15 Hz, =CH), 30.5 (s, CH_2), 30.4 (s, CH_2). FAB MS: calcd for $C_{37}H_{33}ClIrRhNO_2Prh$: 885; observed: 884 $[M-H]^+$. Anal. calc. for $C_{37}H_{33}ClIrRhNO_2Prh \times 0.5 CH_2Cl_2$: C, 48.60; H, 3.59; N, 1.51. Found: C, 48.83; H, 3.31; N, 1.63.

$[IrCl\{PPh_2(o-C_6H_4CO)\}(\mu-H)(\mu-C_9H_6NCO)Rh(Cod)](9)$

To a dichloromethane solution of **2** (50 mg, 0.074 mmol) was added $[Rh(OMe)(Cod)]_2$ (18 mg, 0.037 mmol). Stirring during 5 min and evaporation of the solvent gave an orange solid, which was suspended in MeOH and stirred for 1 h to give an orange solid that was decanted. Yield: 84%. IR (cm^{-1}): 1600(s), $\nu(C=O)$; 1514(s), $\nu(C=O)_b$. 1H NMR ($CDCl_3$): δ -20.40 (t, 1H, $^2J(P,H)_{cis}$ = $^1J(Rh,H)$ = 18.0 Hz, $IrHRh$); 4.51 (s, 2H, =CH), 3.90 (s, 2H, =CH), 2.17 (m, 4H, CH_2), 1.78 (m, 4H, CH_2). $^{31}P\{^1H\}$ NMR

Table 3 Crystal data and refinement data for **2**, **4** and **9**

Crystal data	2	4	9
Identification code	CCDC 718373	CCDC 718374	CCDC 718375
empirical formula	[C ₂₉ H ₂₂ Cl ₁ N ₁ O ₂ P ₁ Ir] CHCl ₃	[C ₆₈ H ₅₀ N ₄ O ₄ P ₂ Ir ₂]2ClO ₄ ·2CH ₃ OH·3CHCl ₃	[C ₃₇ H ₃₃ Cl ₁ N ₁ O ₂ P ₁ IrRh] CHCl ₃
formula wt	794.46	2054.55	1004.54
crystal sys.	Triclinic	Monoclinic	Monoclinic
space group	<i>P</i> (-1)	<i>P</i> 2(1)/ <i>c</i>	<i>P</i> 2(1)/ <i>c</i>
<i>a</i> /Å	8.885(3)	14.339(1)	10.441(1)
<i>b</i> /Å	11.159(3)	24.166(2)	16.999(2)
<i>c</i> /Å	15.768(5)	16.452(2)	21.716(2)
α /°	75.022(5)	—	—
β /°	86.646(5)	119.119(2)	101.344(2)
γ /°	74.942(5)	—	—
<i>V</i> /Å ³	1458.4(7)	4980.3(8)	3779.1(7)
<i>Z</i>	2	2	4
<i>D_c</i> /g cm ⁻³	1.809	1.37	1.766
μ (Mo-K α)/mm ⁻¹	5.028	3.048	4.314
<i>F</i> (000)	772	2020	1960
θ range/°	1.34 to 25.00	1.63 to 25.00	1.53 to 25.00
index ranges	-10, -13, -18 to 10, 12, 14	-16, -26, -19 to 17, 28, 13	-12, -20, -25 to 12, 19, 25
reflections collected	7427	26051	28672
unique reflections [<i>R</i> (int)]	5035 [<i>R</i> (int) = 0.0465]	86451 [<i>R</i> (int) = 0.0882]	6650 [<i>R</i> (int) = 0.2130]
completeness to θ	98.0%	98.6%	99.9%
data/restraints/params	5035/0/332	8645/1/325	6650/0/374
<i>R</i> 1 (reflns obsd) [<i>I</i> > 2 σ (<i>I</i>)] ^a	0.0492 (4125)	0.0651 (3332)	0.0596 (2317)
<i>wR</i> 2 (all data) ^b	0.1323	0.1897	0.1726
Largest diff. peak and hole/e Å ⁻³	2.655 and -2.226	1.232 and -0.973	1.384 and -1.231

^a $R1 = \sum \|F_o| - |F_c| / \sum |F_o|$. ^b $wR2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}$.

(CDCl₃): δ 14.7 (s). ¹³C{¹H} NMR (CD₂Cl₂): δ 239.5 (d, ²*J*(P,C) = 102 Hz, N=C=O_b), 206.8 (s, P=C=O_i), 80.2 (d, ¹*J*(Rh,C) = 13 Hz, =CH), 79.9 (d, ¹*J*(Rh,C) = 12 Hz, =CH), 31.8 (s, CH₂), 30.2 (s, CH₂). FAB MS: calcd for C₃₇H₃₃ClIrNO₂PRh: 885; observed: 884 [M - H]⁺. Anal. calc. for C₃₇H₃₃ClIrNO₂PRh × 0.5 CH₂Cl₂: C, 48.60; H, 3.59; N, 1.51. Found: C, 48.20; H, 3.45; N, 1.65.

Catalytic reactions

The transfer hydrogenation reactions were carried out under nitrogen in refluxing isopropanol with magnetic stirring. The equipment consisted of a 100 ml round bottom flask, fitted with a condenser and provided with a septum cap. The catalysts were prepared by adding 0.2 mmol of potassium hydroxide in 10 ml of isopropanol to solutions (30 ml) of 0.02 mmol of the catalyst. The resulting solutions were heated to 83 °C and 4 mmol of the substrate were injected. The analysis of the catalytic reactions were carried out with a Shimadzu GC-14A chromatograph, connected to a Shimadzu C-R6A calculation integrator.

X-ray structure determination of **2**, **4** and **9**

Suitable crystals for X-ray experiments were obtained by slow diffusion of diethyl ether onto chloroform solutions. Data were collected on a Bruker Smart CCD diffractometer, using graphite-monochromated Mo-K α (λ = 0.71073 Å) radiation, operating at 50 kV and 25 mA. In all cases the data were collected over a hemisphere of the reciprocal space by combination of three exposure sets. Each frame exposure time was of 20 s covering 0.3° in θ , except for **4**, for which different exposure times were used in different data collection, and the best results correspond to 10 s.

The cell parameters were determined and refined by a least-squares fit of all reflections collected. The first 100 frames were recollected at the end of the data collection to monitor crystal decay and no appreciable decay was observed, except for **4**, which gave 20% decay in the intensities of standard reflections. An empirical absorption correction has been performed for compounds **2** and **4**. A summary of the fundamental crystal and refinement data is given in Table 3. The structures were solved by Patterson methods and conventional Fourier techniques and refined by full-matrix least-squares calculations on *F*² (SHELXS-97).²⁷ Anisotropic parameters were used in the last cycle of refinement with exceptions for compounds **4** and **9**. For **4** some phenyl rings have been refined isotropically as riding group and the perchlorate group was not refined. In the last cycles of refinement residual electronic density was found partially assigned to a solvent molecule of CH₃OH, which was included with a common C–O distance restraint and not refined. The rest of residual diffuse electronic density could not be properly modelled. Therefore the SQUEEZE program, a part of the PLATON²⁸ package of crystallographic software, was used to calculate the solvent disordered area and to remove its contribution to the overall intensity data. An improvement was observed in all refinement parameters and residuals when this procedure is applied. The number of electrons in the solvent region corresponds to three disordered chloroform molecules per dimer molecule in the crystal. In compound **9** the cyclooctadiene group and the chloroform solvent molecules have been refined isotropically. The hydrogen atoms were included in their calculated positions and refined riding on their respective carbon atoms with the thermal parameters related to the bonded atom except for the metal hydride and the enolic hydrogen for **2** and the metal hydride for **9**, which were located in a final Fourier difference synthesis and

included with fixed isotropic factors and coordinates. The final R and R_w are shown in Table 3. The first largest residual peaks in the final difference map are near to the Cl atoms of the CHCl_3 group for **2** and **9**, for **4** in the vicinity to the metal atom.

Acknowledgements

Financial support by UPV, Diputación Foral de Guipuzcoa and MICINN (CTQ2008–2967/BQU) are gratefully acknowledged.

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