N–H and C–H Bond Activations of an Isoindoline Promoted by Iridium- and Osmium-Polyhydride Complexes: A Noninnocent Bridge Ligand for Acceptorless and Base-Free Dehydrogenation of Secondary Alcohols

María L. Buil, Miguel A. Esteruelas, Susana Izquierdo, Antonio I. Nicasio, Enrique Oñate*

Departamento de Química Inorgánica, Instituto de Síntesis Química y Catálisis Homogénea
(ISQCH), Centro de Innovación en Química Avanzada (ORFEO-CINQA), Universidad de
Zaragoza-CSIC, 50009 Zaragoza, Spain

ABSTRACT: The elusive C–H bond activation of an organic fragment contained in many biological active molecules and the use of the resulting noninnocent ligand in bimetallic catalysis applied on acceptorless and base-free dehydrogenation of secondary alcohols has been performed by using the polyhydrides IrH₅(P^{*i*}Pr₃)₂ (**1**) and OsH₆(P^{*i*}Pr₃)₂ (**2**). Complex **1** activates the N–H bond of 1,3-bis(6'-methylpyridyl-2'-imino)isoindoline (HBMepHI) to give the mononuclear complex IrH₂{ κ^2 -N_{py},N_{imine}(BMePHI)}(P^{*i*}Pr₃)₂ (**3**). Both **1** and **2** activate the C(sp²)–H bond at position 4 of the core isoindoline of the BMePHI ligand of **3**. Reactions lead to

the homo-binuclear complex $(P^iPr_3)_2H_2Ir\{\mu-(\kappa^2-N_{py},N_{imine}-BMePI-\kappa^2-N_{imine},C^4_{iso})\}IrH_2(P^iPr_3)_2$ (**4**) and the hetero-binuclear compound $(P^iPr_3)_2H_2Ir\{\mu-(\kappa^2-N_{py},N_{imine}-BMePI-\kappa^2-N_{imine},C^4_{iso})\}OsH_3(P^iPr_3)_2$ (**5**), respectively. The metallated carbon atom of **4** and **5** has a marked nucleophilic character. Thus, it adds the proton of alcohols to afford the respective cations $[(P^iPr_3)_2H_2Ir\{\mu-(\kappa^2-N_{py},N_{imine}-BMePHI-\kappa^2-N_{py},N_{imine})\}IrH_2(P^iPr_3)_2]^+$ (**6**) and $[(P^iPr_3)_2H_2Ir\{\mu-(\kappa^2-N_{py},N_{imine}-BMePHI-\kappa^2-N_{py},N_{imine})\}OsH_3(P^iPr_3)_2]^+$ (**7**), and the corresponding alkoxide. The mononuclear complex **3** and the binuclear compounds **4** and **5** are efficient catalysts for the acceptorless and base-free dehydrogenation of secondary alcohols. The binuclear complexes **4** and **5** are significantly more active than **3**. The catalytic synergism is consequence of the mutual electronic influence of the metals through the bridge. X-Ray diffraction analysis data of the structures of **3**, **4**, and **5** and the reactivity of **4** and **5** support a noninnocent character of the bridge ligand.

INTRODUCTION

Metal-mediated C–H bond activations are organometallic reactions of general interest,¹ by their relevance in the selective functionalization of organic fragments, which are present in molecules of practical usefulness.² The isoindoline skeleton is a part of a large variety of biologically active synthetic compounds, which have a wide range of applications in medicine.³ However, the activation of its C(sp²)–H bonds using transition metal complexes is difficult of carrying out, generally because the receptor organic compound also contains a high number of heteroatoms with free electrons, which block to the metal by means of their coordination. We here show a strategy that allows to activate the C–H bond at position 4 of the core isoindoline of 1,3-bis(6'-

methylpyridyl-2'-imino)isoindoline (HBMePHI) in spite of the presence of four coordinating nitrogen atoms. This compound exists as an equilibrium mixture of three tautomers (Scheme 1).

Scheme 1. Equilibrium between the HBMePHI tautomers.

We are interested in the development of catalysts for the dehydrogenation of alcohols, as a part of a research program focused on σ -bond activation reactions.⁴ The transition metal-mediated acceptorless alcohol dehydrogenation (eq 1) is an atom economical access for the preparation of carbonyl compounds, which displays a triple environmental interest because of it offers a green oxidation procedure of synthesis, minimizing waste formation, is a promising approach to the production of hydrogen from biomass, and provides a direct connection with the research on hydrogen-storage and -transport in organic liquids.⁵

This oxidation reaction is generally endothermic at room temperature. Thus, it is usually performed in open systems because the hydrogen elimination acts as driving force of the process. Metal-alkoxide species, which evolve by β -hydrogen elimination to afford hydride compounds, are key intermediates of the catalysis. They generally result from the deprotonation of the alcohol and subsequent coordination of the resulting alkoxide to the metal center. As a

consequence, strong basic media are necessary for the working of many catalysts.⁶ Ligands establish the thermal stability of the catalysts and govern the electron density of the metal ions and the accessible space for performing the reactions. There is also a class of ligands, which further possess some basic sites able to abstract a proton from the alcohol.⁷ These noninnocent ligands are highly desirable, since their use prevents the addition of strong bases to the reaction. In the search for new base-free catalytic systems, we explored the reactivity of the isoindoline HBMePHI with the hydride complexes $\text{OsH}_6(\text{P}^i\text{Pr}_3)_2$ and $\text{OsH}(\text{OH})(\text{CO})(\text{P}^i\text{Pr}_3)_2$, three years ago. This study led us to the complexes $\text{OsH}_3\{\kappa^2\text{-}N_{\text{py}},N_{\text{imine}}(\text{BMePHI})\}(\text{P}^i\text{Pr}_3)_2$ and $\text{OsH}\{\kappa^2\text{-}N_{\text{py}},N_{\text{imine}}(\text{BMePHI})\}(\text{CO})(\text{P}^i\text{Pr}_3)_2$, which are efficient catalysts for the acceptorless and base-free dehydrogenation of secondary alcohols. A noticeable feature of them is the unusual $\kappa^2\text{-}N_{\text{py}},N_{\text{imine}}$ coordination of the BMePHI anion to the metal center. This mode is common to other osmium fragments and provides the most stable Os-BMePHI compounds. Because it vacates three basic nitrogen atoms, the mononuclear species bearing the BMePHI ligand coordinated in this fashion can be employed to generate homoleptic and heteroleptic binuclear compounds, where the polydentate ligand acts as $\mu\text{-(}\kappa^2\text{-}N_{\text{py}},N_{\text{imine}}\text{)}_2$ -bridge. Frontier orbitals and electrochemical studies showed that the metal fragments behave independently and in a sequential manner.⁸

Osmium catalysts are comparatively less used than those of iridium.⁹ The unusual coordination of the BMePHI ligand in the above mentioned osmium compounds, prompted us to confirm it in related iridium-hydride catalysts. In addition, we wished to investigate the influence of a second metal-hydride fragment on the activity of the catalytic system, a subject scarcely studied for the acceptorless alcohols dehydrogenation.^{4,10} We reasoned that, although metal fragments behave independently, their coordination spheres should be modified during the catalysis and therefore each fragment would act as a metalloligand of variable electron density of the other one. Two

questions were of our interest: should the blockage of the free nitrogen atoms require the use of an external base? Do metals undergo catalytic synergism? In the answer process, we discovered the C–H bond activation of the core isoindoline of the BMePHI ligand and the behavior of the resulting bridge as a noninnocent ligand in the catalysis. This paper reports the elusive C–H bond activation of an organic fragment contained in many biological active molecules and its use as noninnocent ligand in bimetallic catalysis applied on acceptorless and base-free alcohol dehydrogenation reactions.

RESULTS AND DISCUSSION

C–H Bond Activation of the Core Isoindoline of HBMePHI. The d^4 -iridium-pentahydride $\text{IrH}_5(\text{P}^i\text{Pr}_3)_2$ (**1**) activates the N–H bond of the isoindoline HBMePHI, in agreement with the d^2 -osmium-hexahydride $\text{OsH}_6(\text{P}^i\text{Pr}_3)_2$ (**2**) and with the ability demonstrated by the polyhydrides of platinum group metals for activating σ -bonds.¹¹ Treatment of 2-propanol solutions of the pentahydride **1** with 1.1 equiv of the organic compound, under reflux, for 4h produces the release of two hydrogen molecules and the formation of the iridium (III) derivative $\text{IrH}_2\{\kappa^2\text{-}N_{\text{py}},N_{\text{imine}}(\text{BMePHI})\}(\text{P}^i\text{Pr}_3)_2$ (**3**), which was isolated as an orange solid in 86% yield, according to Scheme 2.

Scheme 2. Formation of **3**.

Complex **3** was characterized by X-ray diffraction analysis. The structure (Figure 1) proves that the (κ^2 - N_{py} , N_{imine})-coordination of the anion BMePHI is also the preferred one for an $[\text{IrH}_2(\text{P}^i\text{Pr}_3)_2]^+$ metal fragment. The coordination polyhedron around the iridium atom can be described as a distorted octahedron, with the phosphines disposed mutually *trans* ($\text{P}(1)\text{--Ir--P}(2) = 164.67(3)^\circ$). The perpendicular plane is formed by the chelating BMePHI ligand, which acts with a $\text{N}(1)\text{--Ir--N}(2)$ bite angle of $60.03(10)^\circ$, and the hydrides. The iridium-pyridine bond length ($\text{Ir--N}(1) = 2.206(3) \text{ \AA}$) is about $0.02 \text{ \AA}$ shorter than the iridium-imine distance ($\text{Ir--N}(2) = 2.229(3) \text{ \AA}$). The comparison of the bond lengths between the coordinated and free imine-pyridine moieties (Table 1) reveals that the coordinated moiety delocalizes electron density between the atom C(6) of the pyridine and the atom N(3) of the five-membered ring of the core isoindoline; i. e., the resonance forms **a^I-c^I** shown in Scheme 3, which fit with the deprotonation and coordination of the respective tautomers collected in Scheme 1, should be taken into account to describe the bonding between the metal center and the BMePHI ligand. According to this, a shortening of the bonds C(6)–N(2) and C(7)–N(3) with regard to the bonds C(15)–N(4) and C(14)–N(3) ($1.388(4)$ versus $1.411(4) \text{ \AA}$ and $1.350(4)$ versus $1.386(4) \text{ \AA}$, respectively) is observed. In contrast, the C(7)–N(2) bond ($1.322(4) \text{ \AA}$) lengthens about $0.03 \text{ \AA}$ with regard to C(14)–N(4) ($1.289(4) \text{ \AA}$) and between 0.02 and $0.05 \text{ \AA}$ with regard to those reported for imine ligands coordinated $\kappa^1\text{-N}$.¹² In agreement with the presence of inequivalent hydrides in the complex, its ^1H NMR spectrum, in dichloromethane- d_2 , at room temperature shows two hydride resonances at -24.22 and -26.35 ppm, which appear as doublets of triplets with a H–H coupling constant of 8.2 Hz and H–P coupling constants of 17.3 and 16.6 Hz , respectively. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum displays a singlet at 27.2 ppm, as expected for equivalent phosphines.

Figure 1. Molecular diagram of complex **3** (50% probability ellipsoids). Hydrogen atoms (except the hydrides) are omitted for clarity. Selected angles (deg): P(1)–Ir–P(2) = 164.67(3), N(1)–Ir–N(2) = 60.03(10).

Table 1. Selected bond lengths (Å) for complexes **3-6**.

	3	4^a	5^b	6^a
Ir(1)–N(1)	2.206(3)	2.161(10)	2.181(3)	2.207(3)
Ir(1)–N(2)	2.229(3)	2.229(10)	2.220(3)	2.223(3)
M–N(4)	-	2.268(9)	2.267(3)	2.219(3)
M–C(12)	-	2.137(14)	2.134(4)	-
Ir(2)–N(5)	-	-	-	2.211(3)
C(6)–N(2)	1.388(4)	1.408(15)	1.395(5)	1.405(4)
C(7)–N(2)	1.322(4)	1.298(15)	1.331(5)	1.314(4)
C(7)–N(3)	1.350(4)	1.390(15)	1.359(5)	1.356(4)
C(14)–N(3)	1.386(4)	1.397(13)	1.378(5)	1.367(4)
C(14)–N(4)	1.289(4)	1.280(14)	1.314(5)	1.309(4)

C(15)–N(4) 1.411(4) 1.400(14) 1.420(5) 1.400(4)

^a M = Ir(2). ^b M = Os(1).

Scheme 3. Main Resonance Forms to Describe the Metal-Polydentate Ligand Bonding Situation in Complexes **3-6**.

The κ^2 - N_{py},N_{imine} coordination for ligands of the class 1,3-bis(2-pyridylimino)isoindolate (BPHI) has been elusive so far, in the iridium chemistry. In this context, we note that the dicarbonyl derivative $\text{Ir}(\text{acac})(\text{CO})_2$ reacts with HBPHI molecules to form $\text{Ir}\{\kappa^3-(N_{py},N_{iso},N_{py})_{mer}-(\text{BPHI})\}(\text{CO})_2$ complexes. However, the reactions fail with those bearing a substituent at the 6-pyridyl positions.¹³ Related bis(ethylene) derivatives, $\text{Ir}\{\kappa^3-(N_{py},N_{iso},N_{py})_{mer}-(\text{BPHI})\}(\text{C}_2\text{H}_4)_2$, are also known. In contrast to ethylene, 1,5-cyclooctadiene affords square-planar species, $\text{Ir}\{\kappa^2-N_{iso},N_{py}-(\text{BPHI})\}(\eta^4-\text{C}_8\text{H}_{12})$, with a chelate (N_{iso},N_{py})-coordination fashion of the polydentate ligand.¹⁴ The latter has been also observed with $\text{Ir}(\eta^5-\text{C}_5\text{Me}_5)\text{X}$ ($\text{X} = \text{Cl}, \text{I}, \text{N}_3, \text{CH}_3\text{CN}$) metal fragments, whereas $\text{Ir}(\eta^5-\text{C}_5\text{Me}_5)(\text{PPh}_3)$ coordinates BMePHI in a κ^2 - N_{imine},N_{iso} form. A few iridium (III) cations bearing a $\kappa^3-(N_{py},N_{iso},N_{py})_{fac}$ coordination of the BPHI ligand have been recently characterized.¹⁵

Having confirmed that the κ^2 - N_{py},N_{imine} coordination of BMePHI to the $[\text{IrH}_2(\text{P}^i\text{Pr}_3)_2]^+$ metal fragment is also the preferred one, the reactions of **3** with **1** and **2** were subsequently studied, according with our initial aim. Both polyhydrides behave similarly promoting the elusive activation of the $\text{C}(\text{sp}^2)\text{--H}$ bond at position 4 of the core isoindoline of the BMePHI ligand (Scheme 4). Treatment of toluene solutions of **3** with 1.0 equiv of **1** under refluxing leads to the homo-binuclear complex $(\text{P}^i\text{Pr}_3)_2\text{H}_2\text{Ir}\{\mu-(\kappa^2-N_{py},N_{imine}\text{-BMePI-}\kappa^2-N_{imine},\text{C}^4_{iso})\}\text{IrH}_2(\text{P}^i\text{Pr}_3)_2$ (**4**) along with the release of two hydrogen molecules. Under the same experimental conditions, the reaction of **3** with the osmium-hexahydride **2** gives the hetero-binuclear compound $(\text{P}^i\text{Pr}_3)_2\text{H}_2\text{Ir}\{\mu-(\kappa^2-N_{py},N_{imine}\text{-BMePI-}\kappa^2-N_{imine},\text{C}^4_{iso})\}\text{OsH}_3(\text{P}^i\text{Pr}_3)_2$ (**5**) and two hydrogen molecules. Both reactions are spectroscopically quantitative; nevertheless, products were isolated in moderated yields, 42% and 46%, as dark red and dark purple solids, respectively, after the work up process. Complexes **4** and **5** were characterized by X-ray diffraction analysis.

Scheme 4. Formation of **4** and **5**.

Figure 2 shows a view of complex **4**. The structure proves its binuclear nature and the C–H bond activation of the isoindoline moiety of the BMePHI ligand, which gives rise to a $\mu-(\kappa^2-N_{py}, N_{imine}-BMePI-\kappa^2-N_{imine}, C^4_{iso})$ formally dianionic bridge. Both iridium centers display an octahedral environment with *trans* phosphines ($P(2)-Ir(1)-P(1) = 159.77(12)^\circ$ and $P(3)-Ir(2)-P(4) = 165.73(13)^\circ$). The coordination around the atom Ir(1) resembles that of **3** with iridium-imine and iridium-pyridine distances of 2.229(10) (Ir(1)–N(2)) and 2.161(10) (Ir(1)–N(1)) Å, respectively, which are statistically identical to those of **3** (Table 1). The atoms C(12) and N(4) of the bridge and the metal center Ir(2) form a five-membered heterometallacycle, which displays a C(12)–Ir(2)–N(4) angle of $79.4(4)^\circ$ and Ir(2)–C(12) and Ir(2)–N(4) bond lengths of 2.137(14) and 2.268(9) Å, respectively. The former compares well with those reported for related heterometallacycles,¹⁶ whereas the second one is similar to the iridium-imine distance Ir(1)–N(2). The C–H bond activation of the BMePHI ligand and its consequent coordination to a second metal fragment reduce the contribution of binuclear resonance forms analogous to **b^I** and **c^I** to the

$\kappa^2\text{-}N_{\text{py}}, N_{\text{imine}}$ coordination, proving the influence of second metal fragment on the electronic environment of that initially coordinated and supporting the idea that the phenomena does not necessarily require the direct interaction between the metal centers. Thus, in contrast to **3**, the imine bond lengths (C(7)–N(2) and C(14)–N(4)) are statistically identical (1.298(15) and 1.280(14) Å) and similar to those reported for a coordinated group of this class.¹² The same, it is observed for the C(7)–N(3) and C(14)–N(3) distances (1.390(15) and 1.397(13) Å) in the five-membered ring of the isoindoline and in the imine-pyridine bond lengths C(15)–N(4) and C(6)–N(2) (1.400(14) and 1.408(15) Å). The ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra, in benzene- d_6 , at room temperature reflect the asymmetry of the metal fragments. According to this, the ^1H NMR spectrum contains four higher field resonances between –12.90 and –25.60 ppm, corresponding to the inequivalent hydrides, whereas the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum displays two singlets at 27.0 and 32.5 ppm. The resonance due to the metallated carbon atom C(12) appears at 169.6 ppm, as a triplet with a C–P coupling constant of 8.0 Hz, in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum.

Figure 2. Molecular diagram of complex **4** (50% probability ellipsoids). Hydrogen atoms (except the hydrides) are omitted for clarity. Selected angles (deg): P(2)–Ir(1)–P(1) = 159.77(12), P(4)–Ir(2)–P(3) = 165.73(13), C(12)–Ir(2)–N(4) = 79.4(4), N(1)–Ir(1)–N(2) = 60.4(4).

The structure of the hetero-binuclear complex **5** (Figure 3) shows interesting differences with regard to that of **4**, which are a consequence of the different electronic nature of the central ion of the second fragment, d^6 for **4** and d^4 for **5**. Thus, in this case, only the environment around the iridium center is octahedral with *trans* phosphines (P(3)–Ir–P(4) = 162.77(4)°). It resembles to that of **3** with iridium-imine and iridium-pyridine distances of 2.220(3) (Ir–N(2)) and 2.181(3) (Ir–N(1)) Å, respectively. The coordination geometry around the d^4 -osmium center can be described as a distorted pentagonal bipyramid with axial phosphines (P(1)–Os(1)–P(2) = 170.06(3)°). At the base, the coordination of the atoms C(12) and N(4) of the bridge to the metal gives rise to a five-membered ring, which displays a C(12)–Os–N(4) angle of 77.93(13)°. The Os–C(12) distance of 2.134(4) Å compares well with those reported for other five-membered osmacycles.¹⁷ The comparison of the main bond lengths along the bridge between **3**, **4**, and **5** (Table 1) evidences the different electronic nature of the d^6 -IrH₂(P^{*i*}Pr₃)₂ and d^4 -OsH₃(P^{*i*}Pr₃)₂ metal fragments. In contrast to d^6 -IrH₂(P^{*i*}Pr₃)₂, fragment d^4 -OsH₃(P^{*i*}Pr₃)₂ does not prevent binuclear resonances forms related to **b^I** and **c^I** (**b^{III}** and **c^{III}** in Scheme 3), although their contribution to the κ^2 -N_{py},N_{imine} coordination of the BMePI ligand to the iridium center of **5** is lower than the contribution of **b^I** and **c^I** to the coordination of the BMePHI group to the metal center of **3**, because of the osmium fragment provides a fourth resonance form **d^{III}**. According to this, the distances in the bond sequence C(6)–N(2), C(7)–N(2), and C(7)–N(3) of 1.395(5), 1.331(5), and 1.359(5) Å are slightly longer than the respective parameters of **3** and significantly

shorter than the same parameters in **4**. In agreement with a significant contribution of the resonance form **d^{III}** to the bonding situation in the bridge of **5**, it should be noted that the imine distance C(14)–N(4), related to the part of the ligand coordinated to the osmium fragment, of 1.314(5) Å is longer than analogous parameter of **4**, while the bond length C(14)–N(3) in the five-membered ring of the isoindoline of 1.378(5) Å is shorter than the related distance in the homo-binuclear compound. The ¹H and ³¹P{¹H} NMR spectra in benzene-*d*₆ are consistent with the presence in the complex of two different metal-hydride fragments. Thus, in the ¹H NMR spectrum, the OsH₃-resonances display the typical pattern for a cyclometallated OsH₃(XY)(P^{*i*}Pr₃)₂ species,¹⁸ between –7 and –15 ppm, along with two doublets (²J_{H–H} = 8.0 Hz) of triplets at –24.35 (²J_{H–P} = 17.5 Hz) and –25.57 (²J_{H–P} = 16.6 Hz) ppm corresponding to the hydride ligands of the iridium moiety, whereas the ³¹P{¹H} NMR spectrum contains two singlets at 27.2 and 26.3 ppm; one for each group of equivalent phosphines. The resonance due to metallated carbon atom C(12) appears at 180.8 ppm, as a triplet with a C–P coupling constant of 7.1 Hz, in the ¹³C{¹H} NMR spectrum.

Figure 3. Molecular diagram of complex **5** (50% probability ellipsoids). Hydrogen atoms (except the hydrides) are omitted for clarity. Selected angles (deg): P(2)–Os(1)–P(1) = 170.06(3), C(12)–Os(1)–N(4) = 77.93(13), P(4)–Ir(1)–P(3) = 162.77(4), N(1)–Ir(1)–N(2) = 60.06(11).

The metallated carbon atom of **4** and **5** has a marked nucleophilic character, which is revealed by its ability to deprotonate alcohols. The stirring of methanol solutions of both compounds, for 1h, at room temperature quantitatively affords the binuclear cations $[(P^iPr_3)_2H_2Ir\{\mu-(\kappa^2-N_{py},N_{imine}-BMePHI-\kappa^2-N_{py},N_{imine})\}IrH_2(P^iPr_3)_2]^+$ (**6**) and $[(P^iPr_3)_2H_2Ir\{\mu-(\kappa^2-N_{py},N_{imine}-BMePHI-\kappa^2-N_{py},N_{imine})\}OsH_3(P^iPr_3)_2]^+$ (**7**), bearing a $\mu-(\kappa^2-N_{py},N_{imine})_2$ -BMePHI-bridge, and the anion methoxide, according to the 1H and $^{31}P\{^1H\}$ NMR spectra of the solutions. The reactions can be rationalized as the addition of the O–H bond of the solvent to the C–M bond of the isoindoline metallated compounds, to give the methoxy intermediates **A** (Ir) and **B** (Os), followed by the displacement of the coordinated alkoxide group by the free pyridine moiety of the bridge (Scheme 5). Reactions shown in Scheme 5 agree well with the behavior recently observed for the

rollover complex $\text{IrH}_2\{\kappa^2\text{-C,N-[C}_5\text{H}_3\text{N-py]}\}(\text{P}^i\text{Pr}_3)_2$, with a cyclometallated 2,2'-bipyridine ligand, which undergoes demetallation in methanol to afford the cation $[\text{IrH}_2\{\kappa^2\text{-N,N-(bipy)}\}(\text{P}^i\text{Pr}_3)_2]^+$, with the usual 2,2'-bipyridine ligand, and the anion $[\text{MeO}]^-$, as a result of the addition of the O–H bond of the alcohol to the Ir–C bond of the metallated species.¹⁹

Scheme 5. Formation of **6** and **7**.

The addition of NaBF_4 to the methanol solutions of **6** and **7** allows the isolation of the corresponding BF_4 -salts. Thus, the homo-binuclear cation was characterized by X-ray diffraction analysis. The structure (Figure 4) proves the demetallation of the aromatic six-membered ring of the core isoindoline of the BMePI ligand and the $\mu\text{-(}\kappa^2\text{-N}_{\text{py}},\text{N}_{\text{imine}}\text{)}_2$ -coordination of the resulting BMePHI anion. The geometry around the iridium atoms resembles that of **3** with P(1)–Ir(1)–P(2) and P(3)–Ir(2)–P(4) angles of $164.12(3)^\circ$ and $162.89(3)^\circ$, respectively. The bond lengths in each half are similar (Table 1), the iridium-pyridine distances of 2.207(3) (Ir(1)–N(1)) and 2.211(3) (Ir(2)–N(5)) Å are statistically identical as well as the iridium-imine ones of 2.223(3) (Ir(1)–N(2)) and 2.219(3) (Ir(2)–N(4)) Å. In the bridge, the same is observed between the exocyclic distances C(7)–N(2) and C(14)–N(4) (1.314(4) and 1.309(4) Å) and between the endocyclic

bond lengths C(7)–N(3) and C(14)–N(3) (1.356(4) and 1.367(4) Å). These values, intermediate between those expected for single and double N–C bonds, indicate significant electron delocalization between the imine nitrogen atoms N(2) and N(4) and suggest that the nucleophilicity of bridge is distributed between them (see resonance forms **a1**^{IV} and **a2**^{IV} in Scheme 3). The equivalence of the metal fragments in **6** is also revealed by the ¹H and ³¹P{¹H} NMR spectra in dichloromethane-*d*₂. Thus, the ¹H NMR spectrum shows two doublets (²*J*_{H–H} = 8.3 Hz) of triplets at –24.41 (²*J*_{H–P} = 17.0 Hz) and –26.43 (²*J*_{H–P} = 16.6 Hz) ppm due to the inequivalent hydride ligands of both iridium-moieties, whereas the ³¹P{¹H} NMR spectrum exhibits a singlet at 27.7 ppm for the four phosphines. In contrast to **6**, the ¹H and ³¹P{¹H} NMR spectra of **7** resemble those of **5**. In the ¹H NMR spectrum, the OsH₃-resonances display the pattern expected for an OsH₃(XY)(P^{*i*}Pr₃)₂ species, between –10.5 and –14.0 ppm, along with two doublets (²*J*_{H–H} = 8.3 Hz) of triplets at –24.40 (²*J*_{H–P} = 17.0 Hz) and –26.47 (²*J*_{H–P} = 16.6 Hz) ppm due to the IrH₂-unit, whereas the ³¹P{¹H} NMR spectrum contains two singlets at 27.8 and 20.7 ppm; one for each half.

Figure 4. Molecular diagram of cation **6** (50% probability ellipsoids). Hydrogen atoms (except the hydrides) are omitted for clarity. Selected angles (deg): P(2)–Ir(1)–P(1) = 164.12(3), P(4)–Ir(2)–P(3) = 162.89(3), N(1)–Ir(1)–N(2) = 60.20(9), N(5)–Ir(2)–N(4) = 60.12(10).

Compounds bearing bridge BPHI ligands are very scarce and, as far as we know, unknown for the iridium chemistry. In addition to the previously mentioned binuclear osmium compounds, Li, Yang, Zhang, and co-workers have suggested that the intermediate of the reaction of $\text{Lu}(\text{CH}_2\text{SiMe}_3)_3(\text{thf})_2$ with HBPHI, to give $\text{Lu}\{\kappa^3\text{-mer-(BPHI)}\}(\text{CH}_2\text{SiMe}_3)_2$, is a binuclear species also bearing a $\mu\text{-(}N_{\text{py}},N_{\text{imine}}\text{)}_2\text{-BMePHI}$ ligand.²⁰ Baird and co-workers have observed that HBPHI displaces an acetate group from $\text{Mo}_2(\text{OAc})_4$ to give $\text{Mo}_2(\text{OAc})_3(\text{BPHI})$, with the anion BPHI bound to one molybdenum by an imine nitrogen and to the other molybdenum by the isoindoline nitrogen and a pyridine.²¹ Bröring and co-workers have reported that one of the pyridyl groups of HBMePHI undergoes palladium-promoted 1,3-hydrogen shift, from C to N, to afford $\text{Pd}(\kappa^3\text{-}N_{\text{py}},N_{\text{iso}},C_{\text{Hpy}})\text{-pincer}$ derivatives, which add a second palladium to the free pyridyl-imine moiety.²²

Acceptorless and Base-Free Dehydrogenation of Secondary Alcohols. The mononuclear complex **3** and the binuclear compounds **4** and **5** are efficient catalysts for the acceptorless and base-free dehydrogenation of the above-mentioned hydrogen donors. The reactions were performed in toluene, at 100 °C, using a substrate concentration of 0.255 M and catalyst concentrations of 1.8×10^{-2} (**3**) or 9.0×10^{-3} (**4** and **5**) M; i. e., 7% mol of metal in all the cases. Table 2 collects the alcohols studied and the yield of carbonyl compound formed as a function of the catalyst, after 24 h. The previously reported conversions obtained with the mononuclear osmium catalyst $\text{OsH}_3\{\kappa^2\text{-}N_{\text{py}},N_{\text{imine}}(\text{BMePHI})\}(\text{P}^i\text{Pr}_3)_2$ are also included by comparative purposes.⁸

Table 2. Metal-promoted acceptorless and base-free dehydrogenation of secondary alcohols.^a

Catalyst
3	50	47	50	26	25
4	77	68	73	32	-
5	77	84	82	51	65
OsH₃{κ²-<i>N</i>_{py},<i>N</i>_{imine}(BMePHI)}(P^{<i>i</i>}Pr₃)₂	61 ^b	60 ^b	76 ^b	34 ^b	37 ^b

^aConditions: Complex **3** (0.018 mmol) or **4** or **5** (0.009 mmol); substrate (0.255 mmol); toluene (1 mL); heated at 100°C for 24 h. Conversions were calculated from the relative peak area integrations of the reactant and product in the GC spectra. ^bData were obtained from the previous work.⁸

Complex **3** dehydrogenates 1-phenylethanol and related alcohols with a substituent at the phenyl group to give molecular hydrogen and the corresponding ketone in about 50% yield. The replacement of the aromatic moiety by an alkyl group hampers the dehydrogenation. Thus, 2-octanol and 1-cyclohexylethanol are dehydrogenated worse, about 25 %. The same trend was observed with the osmium catalyst OsH₃{κ²-*N*_{py},*N*_{imine}(BMePHI)}(P^{*i*}Pr₃)₂ (60-76% *versus* 34-37 %), although the latter displays a significantly higher activity. On the basis of the resonance forms **b**^I and **c**^I shown in Scheme 3, the dehydrogenation can be rationalized according to the Scheme 6. The addition of the O–H bond of the alcohols to the bond Ir–N(2) or Ir–N(1) of **3** should give an alkoxide intermediate **C**, bearing the tautomer **b** or **c** of HBMePHI κ¹-N coordinated. Then, the subsequent β-hydrogen elimination on the alkoxide group could afford the ketone and the trihydride species **D**, which should release molecular hydrogen and regenerates the catalyst by means of the N–H bond activation of the coordinated tautomer.

Scheme 6. Proposed catalytic cycle for acceptorless and base-free dehydrogenation of secondary alcohols promoted by **3**.

Iridium catalysts for acceptorless and base-free dehydrogenation of secondary alcohols are scarce. Fujita, Yamaguchi, and coworkers have prepared half-sandwich-Iridium (III) complexes bearing 5- and 4,5-substituted 2-pyridonate ligands²³ or a chelating bidentate ligand that comprises NHC and α -hydroxypyridine moieties,^{7f} which exhibited high activity in toluene or aqueous media, respectively. Albrecht, Diéguez, and coworkers have reported compounds based on a triazolylidene-Iridium (III) scaffold, which also display high efficiency, particularly when the metal center is stabilized by chelating benzoxazole and thiazole substituents.²⁴ Martín-Matute's group has compared families of half-sandwich-Iridium (III) complexes bearing a bifunctional NHC ligand, amine- or hydroxy-functionalized, with those stabilized by a non-bifunctional NHC ligand; the results show the benefits of including a hemilabile alcohol-alkoxide moiety in the catalyst structure, rather than an amine-amide functionality or a spectator

ligand.^{7g} We have prepared a N,N,N-pincer osmaligand, which stabilizes an efficient iridium catalyst precursor.⁴

The binuclear complexes **4** and **5** are also more efficient in the dehydrogenation of 1-arylethanols than in the oxidation of aliphatic secondary alcohols. The Ir-Ir binuclear catalyst is significantly more active than **3**. Its efficiency is similar to that of the mononuclear osmium catalyst. The hetero-binuclear Ir-Os compound **5** is even more active. The increase of activity of the binuclear compounds with regard to the individual fragments indicates a noticeable catalytic synergism between the metals. Although they are separated, they communicate through the bridge as previously was demonstrated. Thus, the catalysis takes place in an independent manner in each metal center. The catalytic synergism is consequence of the increase of the efficiency of each metal center by action of its colleague of catalyst. According to Scheme 6, the bridge is a noninnocent ligand through the nitrogen atoms coordinated to the initial iridium center and is a noninnocent ligand through the metallated carbon atom of the isoindoline moiety due to the possibility of coordination-decoordination of this carbon, as demonstrated the reactions shown in Scheme 5. Scheme 7 rationalizes the dehydrogenation process through both metals for the hetero-binuclear complex **5**. The elemental steps on the initial iridium center are the same as in the mononuclear complex **3** whereas, according to Scheme 5, alkoxide intermediates **E** related to **A** and **B** should be the key for the dehydrogenation via the second metal. The β -hydrogen elimination on the alkoxide group should lead to the hydride **F** and the ketone. Thus, a new C-H bond activation of the position 4 of the isoindoline could close the cycle and releases molecular hydrogen. In addition, it should be pointed out that the addition of a second metal-hydride fragment to **3** does not block its relevant nucleophilic centers and therefore the addition of an external base is not necessary for the bimetallic catalysis.

Scheme 7. Proposed catalytic cycle for acceptorless and base-free dehydrogenation of secondary alcohols promoted by **5**.

CONCLUDING REMARKS

This study has revealed that the sequential treatment of HBMePHI with two equiv of the pentahydride **1** or with one equiv of the latter and other of the hexahydride **2** produces in a sequential manner the activations of the bonds N–H and C–H at position 4 of the core isoindoline of the organic molecule, to give the homo-binuclear complex **4** or the hetero-binuclear compound **5**, via the mononuclear iridium intermediate **3**. The bonding of the second metal fragment to the intermediate **3** modifies the electronic structure of the polydentate N–donor

ligand, which produces a noticeable perturbation on the electron density around the initial iridium center. As a consequence of the mutual electronic influence between the metals, through the bridge, catalytic synergism between them in the acceptorless and base-free dehydrogenation of secondary alcohols is observed. X-Ray diffraction analysis data of the structures of **3**, **4**, and **5** and reactivity results on **4** and **5** support a noninnocent character of the bridge ligand, since its donor atoms have a direct participation in the formation of the metal-alkoxides bonds, key for the catalysis, and in the release of molecular hydrogen.

In summary, a metal-mediated elusive C–H bond activation of the core isoindoline of a polynitrogenated organic molecule has been discovered, which generates a noninnocent bridge ligand, responsible of catalytic synergism between the bonded metals, in the acceptorless and base-free dehydrogenation of secondary alcohols.

EXPERIMENTAL SECTION

All reactions were carried out with rigorous exclusion of air using Schlenk-tube techniques. Solvents were obtained oxygen- and water-free from an MBraun solvent purification apparatus. ^1H , $^{31}\text{P}\{^1\text{H}\}$, and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded on either a Bruker ARX 300 MHz, Bruker Avance 300 MHz or Bruker Avance 400 MHz instruments. Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks (^1H , $^1\text{H}\{^{31}\text{P}\}$, $^{13}\text{C}\{^1\text{H}\}$) or external standard ($^{31}\text{P}\{^1\text{H}\}$ to 85% H_3PO_4). Coupling constants J and N ($N = J_{\text{H-P}} + J_{\text{H-P'}}$ for ^1H ; $N = J_{\text{C-P}} + J_{\text{C-P'}}$ for ^{13}C) are given in hertz. C, H and N analyses were carried out in a PerkinElmer 2400 CHNS/O analyzer. High-resolution electrospray mass spectra (HRMS) were acquired using a MicroTOF-Q hybrid quadrupole time-of-flight spectrometer (Bruker Daltonics, Bremen,

Germany). $\text{IrH}_5(\text{P}^i\text{Pr}_3)_2$ (**1**),²⁵ $\text{OsH}_6(\text{P}^i\text{Pr}_3)_2$ (**2**),²⁶ and 1,3-bis(6'-methylpyridyl-2'-imino)isoindoline (HBMePHI)²⁷ were prepared according to the published methods.

Preparation of $\text{IrH}_2\{\kappa^2\text{-N}_{\text{py}},\text{N}_{\text{imine}}(\text{BMePHI})\}(\text{P}^i\text{Pr}_3)_2$ (3**).** A solution of **1** (0.150 g, 0.290 mmol) in 2-propanol (5 mL) was treated with HBMePHI (0.104 g, 0.319 mmol), for 4 h, under reflux. The resulting dark-orange solution was evaporated to dryness. The residue was treated with diethyl ether (3 x 3 mL, 273 K), to afford an orange solid, which was dried *in vacuo*. Yield: 209 mg (86%). Orange crystals suitable for X-ray diffraction analysis were obtained from slow diffusion of pentane in a concentrated solution of the solid in toluene. Anal. Calcd. for $\text{C}_{38}\text{H}_{60}\text{IrN}_5\text{P}_2$: C, 54.26; H, 7.19; N, 8.33. Found: C, 54.30; H, 7.22; N, 8.22. HRMS (electrospray, m/z): Calcd. for $\text{C}_{38}\text{H}_{61}\text{IrN}_5\text{P}_2$ $[\text{M} + \text{H}]^+$: 842.4037, found: 842.4028. ^1H NMR (400.13 MHz, CD_2Cl_2 , 298 K): δ 8.80 (d, $^3J_{\text{H-H}} = 7.3$, 1 H, CH_{arom}), 8.43 (d, $^3J_{\text{H-H}} = 7.6$, 1 H, CH_{arom}), 7.87 (d, $^3J_{\text{H-H}} = 7.3$, 1 H, CH_{arom}), 7.55 (dd, $^3J_{\text{H-H}} = 7.6$ and 7.6, 1 H, CH_{arom}), 7.53 (dd, $^3J_{\text{H-H}} = 7.6$ and 7.6, 1 H, CH_{arom}), 7.44 (dd, $^3J_{\text{H-H}} = 7.3$ and 7.3, 1 H, CH_{arom}), 7.43 (d, $^3J_{\text{H-H}} = 7.6$, 1 H, CH_{arom}), 7.35 (dd, $^3J_{\text{H-H}} = 7.3$ and 7.3, 1 H, CH_{arom}), 6.82 (d, $^3J_{\text{H-H}} = 7.6$, 1 H, CH_{arom}), 6.78 (d, $^3J_{\text{H-H}} = 7.6$, 1 H, CH_{arom}), 2.51 (s, 3 H, py-CH_3), 2.39 (s, 3 H, py-CH_3), 2.18 (m, 6 H, $\text{PCH}(\text{CH}_3)_2$), 1.06 (dvt, $^3J_{\text{H-H}} = 6.9$, $N = 13.0$, 18 H, $\text{PCH}(\text{CH}_3)_2$), 1.01 (dvt, $^3J_{\text{H-H}} = 6.9$, $N = 13.0$, 18 H, $\text{PCH}(\text{CH}_3)_2$), -24.22 (td, $^2J_{\text{H-P}} = 17.3$, $^2J_{\text{H-H}} = 8.2$, 1 H, Ir-H), -26.35 (td, $^2J_{\text{H-P}} = 16.6$, $^2J_{\text{H-H}} = 8.2$, 1 H, Ir-H). $^{31}\text{P}\{^1\text{H}\}$ NMR (161.98 MHz, CD_2Cl_2 , 298 K): δ 27.2 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.62 MHz, CD_2Cl_2 , 298 K): δ 171.2, 169.4, 167.4, 163.7, 157.4, 155.7, 141.7, 140.6 (all s, C_{arom}), 137.9, 136.8, 129.8, 128.7, 123.1, 121.4, 117.4, 117.2, 116.8, 116.1 (all s, CH_{arom}), 27.4 (vt, $^1J_{\text{C-P}} = 26.9$, $\text{PCH}(\text{CH}_3)_2$), 24.7, 24.6 (both s, py-CH_3), 20.0, 19.7 (both s, $\text{PCH}(\text{CH}_3)_2$).

Preparation of $(\text{P}^i\text{Pr}_3)_2\text{H}_2\text{Ir}\{\mu\text{-(}\kappa^2\text{-N}_{\text{py}},\text{N}_{\text{imine}}\text{-BMePI-}\kappa^2\text{-N}_{\text{imine}},\text{C}^4_{\text{iso}})\}\text{IrH}_2(\text{P}^i\text{Pr}_3)_2$ (4**).** A solution of **3** (0.100 g, 0.119 mmol) in toluene was treated with **1** (0.062 g, 0.119 mmol), for 16

h, under reflux. After this time, volatiles were removed *in vacuo*. Then, pentane (3 x 5 mL, 273 K) was added and the resulting solution was filtered through Celite. The filtrate was evaporated to dryness. The residue was treated with cold acetone (3 x 3 mL, 243 K) to afford a dark red solid, which was dried under vacuum. Yield: 68 mg (42%). Red crystals suitable for X-ray diffraction analysis were obtained by crystallization from a concentrated solution of the solid in acetone. Anal. Calcd. for $C_{56}H_{103}Ir_2N_5P_4$: C, 49.65; H, 7.66; N, 5.17. Found: C, 49.62; H, 7.67; N, 4.88. HRMS (electrospray, m/z): Calcd. for $C_{56}H_{104}N_5P_4Ir_2$ $[M + H]^+$: 1354.6474; found: 1354.6510. 1H NMR (300.13 MHz, C_6D_6 , 298 K): δ 9.14 (d, $^3J_{H-H} = 8.1$, 1 H, CH_{arom}), 8.43 (d, $^3J_{H-H} = 7.1$, 1 H, CH_{arom}), 8.31 (d, $^3J_{H-H} = 7.1$, 1 H, CH_{arom}), 8.04 (d, $^3J_{H-H} = 8.1$, 1 H, CH_{arom}), 7.30 (dd, $^3J_{H-H} = 7.1$ and 7.1, 1 H, CH_{arom}), 7.25 (dd, $^3J_{H-H} = 7.5$ and 7.5, 1 H, CH_{arom}), 7.23 (dd, $^3J_{H-H} = 8.1$ and 8.1, 1 H, CH_{arom}), 6.54 (d, $^3J_{H-H} = 7.5$, 1 H, CH_{arom}), 6.29 (d, $^3J_{H-H} = 7.5$, 1 H, CH_{arom}), 2.51 (s, 3 H, py- CH_3), 2.45 (m, 6 H, $PCH(CH_3)_2$), 2.18 (s, 3 H, py- CH_3), 2.13 (m, 6 H, $PCH(CH_3)_2$), 1.27 (dvt, $^3J_{H-H} = 6.4$, $N = 12.5$, 18 H, $PCH(CH_3)_2$), 1.24 (dvt, $^3J_{H-H} = 6.4$, $N = 12.5$, 18 H, $PCH(CH_3)_2$), 1.04 (dvt, $^3J_{H-H} = 6.9$, $N = 13.1$, 18 H, $PCH(CH_3)_2$), 0.96 (dvt, $^3J_{H-H} = 6.9$, $N = 13.1$, 18 H, $PCH(CH_3)_2$), -12.94 (td, $^2J_{H-P} = 19.6$, $^2J_{H-H} = 5.9$, 1 H, Ir-H), -24.33 (td, $^2J_{H-P} = 17.6$, $^2J_{H-H} = 8.1$, 1 H, Ir-H), -25.48 (td, $^2J_{H-P} = 17.4$, $^2J_{H-H} = 5.9$, 1 H, Ir-H), -25.55 (td, $^2J_{H-P} = 16.5$, $^2J_{H-H} = 8.1$, 1 H, Ir-H). $^{31}P\{^1H\}$ NMR (121.49 MHz, C_6D_6 , 298 K): δ 32.5 (s), 27.0 (s). $^{13}C\{^1H\}$ NMR (75.48 MHz, C_6D_6 , 298 K): δ 185.0, 179.2, 169.9 (all s, C_{arom}), 169.6 (t, $^2J_{C-P} = 8.0$, Ir- C_{iso}), 163.6, 160.9, 156.7, 154.8 (all s, C_{arom}), 144.4, 137.5 (both s, CH_{arom}), 135.9 (s, C_{arom}), 135.5, 127.1, 118.6, 117.8, 117.6, 116.3, 114.1 (all s, CH_{arom}), 27.2 (vt, $N = 13.3$, $PCH(CH_3)_2$), 26.5 (vt, $N = 13.1$, $PCH(CH_3)_2$), 24.5 (s, py- CH_3), 24.4 (s, py- CH_3), 20.8, 20.3, 20.2, 19.7 (all s, $PCH(CH_3)_2$).

Preparation of $(\text{P}^i\text{Pr}_3)_2\text{H}_2\text{Ir}\{\mu-(\kappa^2\text{-}N_{\text{py}},N_{\text{imine}}\text{-BMePI-}\kappa^2\text{-}N_{\text{imine}},C^4_{\text{iso}})\}\text{OsH}_3(\text{P}^i\text{Pr}_3)_2$ (5). A solution of **3** (0.200 g, 0.238 mmol) in toluene was treated with **2** (0.122 g, 0.238 mmol), for 4 h, under reflux. After this time, volatiles were removed *in vacuo*. Then, cold pentane (10 mL, 273 K) was added and the resulting solution was filtered through Celite. The filtrate was evaporated to dryness. The residue was treated with cold acetone (3 x 3 mL, 273 K) to afford a dark purple solid, which was dried under vacuum. Yield: 150 mg (46%). Purple crystals suitable for X-ray diffraction analysis were obtained from a concentrated solution of the solid in acetone at $-20\text{ }^\circ\text{C}$. Anal. Calcd. for $\text{C}_{56}\text{H}_{104}\text{N}_5\text{P}_4\text{IrOs}$: C, 49.68; H, 7.74; N, 5.17. found: C, 49.39; H, 8.08; N, 4.93. HRMS (electrospray, m/z): Calcd. for $\text{C}_{56}\text{H}_{105}\text{N}_5\text{P}_4\text{IrOs}$ $[\text{M} + \text{H}]^+$: 1356.6567; found: 1356.6603. ^1H NMR (300.13 MHz, C_6D_6 , 298 K): δ 9.01 (d, $^3J_{\text{H-H}} = 8.2$, 1 H, CH_{arom}), 8.57 (d, $^3J_{\text{H-H}} = 7.1$, 1 H, CH_{arom}), 8.23 (d, $^3J_{\text{H-H}} = 7.1$, 1 H, CH_{arom}), 7.96 (d, $^3J_{\text{H-H}} = 8.2$, 1 H, CH_{arom}), 7.21 (m, 3 H, CH_{arom}), 6.55 (d, $^3J_{\text{H-H}} = 7.4$, 1 H, CH_{arom}), 6.25 ($^3J_{\text{H-H}} = 7.4$, 1 H, CH_{arom}), 2.52 (s, 3 H, py-CH_3), 2.36 (m, 6 H, $\text{PCH}(\text{CH}_3)_2$), 2.16 (s, 3 H, py-CH_3), 2.13 (m, 6 H, $\text{PCH}(\text{CH}_3)_2$), 1.26 (dvt, $^3J_{\text{H-H}} = 6.7$, $N = 12.6$, 18 H, $\text{PCH}(\text{CH}_3)_2$), 1.23 (dvt, $^3J_{\text{H-H}} = 6.7$, $N = 12.6$, 18 H, $\text{PCH}(\text{CH}_3)_2$), 1.03 (dvt, $^3J_{\text{H-H}} = 6.6$, $N = 13.0$, 18 H, $\text{PCH}(\text{CH}_3)_2$), 0.96 (dvt, $^3J_{\text{H-H}} = 6.6$, $N = 13.0$, 18 H, $\text{PCH}(\text{CH}_3)_2$), -8.76 (br, 2 H, Os-H), -13.66 (br, 1 H, Os-H), -24.35 (td, $^2J_{\text{H-P}} = 17.5$, $^2J_{\text{H-H}} = 8.0$, 1 H, Ir-H), -25.57 (td, $^2J_{\text{H-P}} = 16.6$, $^2J_{\text{H-H}} = 8.0$, 1 H, Ir-H). $T_{1(\text{min})}$ (ms, Os-H, 300.13 MHz, toluene- d_8 , 243 K): 40 (-8.75 ppm), 48 (-13.63 ppm). $T_{1(\text{min})}$ (ms, Ir-H, 300.13 MHz, toluene- d_8 , 253 K): 132 (-24.29 ppm), 206 (-25.47 ppm). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.49 MHz, C_6D_6 , 298 K): δ 27.2 (s), 26.3 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, C_6D_6 , 298 K): δ 183.3, 180.8 (t, $^2J_{\text{C-P}} = 7.1$, Os- C_{iso}), 179.1, 169.7, 164.3, 156.6, 156.5, 154.8 (all s, C_{arom}), 145.2, 137.4 (both s, CH_{arom}), 136.0 (s, C_{arom}), 135.3, 128.3, 118.3, 118.2, 117.4, 116.2, 113.1 (all s, CH_{arom}), 27.6 (vt, $N = 11.0$,

PCH(CH₃)₂), 27.2 (vt, *N* = 13.4, PCH(CH₃)₂), 24.4, 24.4 (both s, py-CH₃), 20.6, 20.6, 20.2, 19.7 (all s, PCH(CH₃)₂).

Preparation of [(PⁱPr₃)₂H₂Ir{μ-κ²-*N*_{py},*N*_{imine}-BMePHI-κ²-*N*_{py},*N*_{imine}-(PⁱPr₃)₂IrH₂}]BF₄ ([6]BF₄). Salt NaBF₄ (0.009 g, 0.077 mmol) was added to a solution of **4** (0.100 g, 0.074 mmol) in methanol (6 mL). After 1 h, at room temperature, volatiles were removed *in vacuo*. The resulting residue was dissolved in dichloromethane (10 mL) and filtered through Celite. The solvent was removed under vacuum and the residue was treated with cold diethyl ether (3 x 3 mL, 273 K) to afford a red solid which was dried *in vacuo*. Yield: 56 mg (51%). Red crystals suitable for X-ray diffraction analysis were obtained from slow diffusion of pentane in a concentrated solution of the solid in dichloromethane. Anal. Calcd. for C₅₆H₁₀₄Ir₂N₅P₄BF₄: C, 46.62; H, 7.27; N, 4.85. Found: C, 46.58; H, 7.38; N, 4.79. HRMS (electrospray, *m/z*): Calcd. for C₅₆H₁₀₄Ir₂N₅P₄ [M]⁺: 1354.6474, found: 1354.6474. ¹H NMR (300.13 MHz, CD₂Cl₂, 298 K): δ 8.90 (dd, ³*J*_{H-H} = 5.5 and 3.1, 2 H, CH_{arom}), 8.36 (d, ³*J*_{H-H} = 7.9, 2 H, CH_{arom}), 7.81 (dd, ³*J*_{H-H} = 7.9 and 7.9, 2 H, CH_{arom}), 7.44 (dd, ³*J*_{H-H} = 5.5 and 3.1, 2 H, CH_{arom}), 7.06 (d, ³*J*_{H-H} = 7.9, 2 H, CH_{arom}), 2.46 (s, 6 H, py-CH₃), 2.18 (m, 12 H, PCH(CH₃)₂), 1.06 (dvt, ³*J*_{H-H} = 6.8, *N* = 13.3, 36 H, PCH(CH₃)₂), 1.00 (dvt, *N* = 13.3, ³*J*_{H-H} = 6.8, 36 H, PCH(CH₃)₂), -24.41 (td, ²*J*_{H-P} = 17.0, ²*J*_{H-H} = 8.3, 2 H, Ir-H), -26.43 (td, ²*J*_{H-P} = 16.6, ²*J*_{H-H} = 8.3, 2 H, Ir-H). ³¹P{¹H} NMR (121.49 MHz, CD₂Cl₂, 298 K): δ 27.7 (s). ¹³C{¹H} NMR (75.48 MHz, CD₂Cl₂, 298 K): δ 168.5, 167.6, 157.1, 139.7, (all s, C_{arom}), 138.5, 130.3, 124.2, 120.7, 117.0 (all s, CH_{arom}), 27.4 (vt, *N* = 13.5, PCH(CH₃)₂), 24.7 (s, py-CH₃), 20.0, 19.6 (both s, PCH(CH₃)₂).

Preparation of [(PⁱPr₃)₂H₂Ir{μ-κ²-*N*_{py},*N*_{imine}-BMePHI-κ²-*N*_{py},*N*_{imine}-(PⁱPr₃)₂OsH₃}]BF₄ ([7]BF₄). Salt NaBF₄ (0.009 g, 0.077 mmol) was added to a dark purple solution of **5** (0.100 g, 0.073 mmol) in methanol (6 mL). After 1 h, at room temperature, the solvent was removed under

vacuum and the resulting residue was treated with dichloromethane (10 mL) and filtered through Celite. The filtrate was evaporated to dryness. The residue was treated with pentane (2 x 3 mL, 233 K) to afford a purple solid that was dried under vacuum. Yield: 20 mg (19%). Anal. Calcd. for $C_{56}H_{105}BF_4IrOsN_5P_4$: C, 46.66; H, 7.34; N, 4.86. Found: C, 46.64; H, 7.25; N, 4.64. HRMS (electrospray, m/z): Calcd. for $C_{56}H_{105}IrN_5OsP_4 [M]^+$: 1356.6567, found: 1356.6548. 1H NMR (300.13 MHz, CD_2Cl_2 , 298 K): δ 9.13 (d, $^3J_{H-H} = 6.8$, 1 H, CH_{arom}), 8.96 (d, $^3J_{H-H} = 6.8$, 1 H, CH_{arom}), 8.47 (d, $^3J_{H-H} = 8.4$, 1 H, CH_{arom}), 8.33 (d, $^3J_{H-H} = 8.4$, 1 H, CH_{arom}), 7.79 (dd, $^3J_{H-H} = 8.0$, 8.0, 1 H, CH_{arom}), 7.72 (dd, $^3J_{H-H} = 8.0$, 8.0, 1 H, CH_{arom}), 7.49 (m, 2 H, CH_{arom}), 7.08 (d, $^3J_{H-H} = 7.6$, 1 H, CH_{arom}), 7.06 (d, $^3J_{H-H} = 7.6$, 1 H, CH_{arom}), 2.57 (s, 3 H, py- CH_3), 2.46 (s, 3 H, py- CH_3), 2.18 (m, 6 H, PCH(CH_3) $_2$), 2.06 (m, 6 H, PCH(CH_3) $_2$), 1.10–0.93 (m, 72 H, PCH(CH_3) $_2$), –12.19 (br t, $^2J_{H-P} = 8.0$, 3 H, Os–H), –24.40 (td, $^2J_{H-P} = 17.0$, $^2J_{H-H} = 8.3$, 1 H, Ir–H), –26.47 (td, $^2J_{H-P} = 16.6$, $^2J_{H-H} = 8.3$, 1 H, Ir–H). 1H NMR (300.13 MHz, CD_2Cl_2 , 183 K): δ –10.75 (br, 1 H, Os–H), –12.10 (br, 1 H, Os–H), –13.78 (br, 1 H, Os–H), –24.24 (br, 1 H, Ir–H), –26.41 (br, 1 H, Ir–H). $T_{1(min)}$ (ms, Os–H, 300.13 MHz, CD_2Cl_2 , 213 K): 40 (–11.31 ppm), 41 (–13.77 ppm). $T_{1(min)}$ (ms, Ir–H, 300.13 MHz, CD_2Cl_2 , 233 K): 144 (–24.26 ppm), 189 (–26.41 ppm). $^{31}P\{^1H\}$ NMR (121.49 MHz, CD_2Cl_2 , 298 K): δ 27.8 (s), 20.7 (s). $^{13}C\{^1H\}$ NMR (75.48 MHz, CD_2Cl_2 , 298 K): δ 168.5, 167.6, 167.0, 164.9, 157.3, 156.1, 140.0, 139.1 (all s, C_{arom}), 138.5, 137.7, 130.3, 130.1, 124.4, 123.6, 121.7, 120.6, 116.6, 116.4 (all s, CH_{arom}), 28.5 (vt, $N = 12.0$, PCH(CH_3) $_2$), 27.4 (vt, $N = 13.5$, PCH(CH_3) $_2$), 25.0 (s, py- CH_3), 24.8 (s, py- CH_3), 20.1, 20.0, 19.9, 19.6 (all s, PCH(CH_3) $_2$).

General Procedure for the Ir-Catalyzed Dehydrogenation Reactions of Alcohols

A solution of the catalyst (**3**, 0.018 mmol, **4** or **5**, 0.009 mmol) and the corresponding substrate (0.255 mmol) in toluene (1 mL) was placed in a Schlenk flask equipped with a condenser under

argon atmosphere. The mixture was stirred at 100 °C for 24 h. After this time the solution was cooled at room temperature, and the progress of the reaction was monitored by GC (Agilent 6890N gas chromatograph with a flame ionization detector, using an Agilent 19091N-133 polyethylene glycol column (30 m × 250 µm × 0.25 µm thickness)). The oven conditions used are as follows: 80 °C (hold 5 min) to 200 °C at 15°C/min (hold 7 min).

ASSOCIATED CONTENT

Supporting Information.

The Supporting Information is available free of charge on the ACS Publications website.

Structural analysis and NMR spectra of complexes **3**, **4**, **5**, **6** and **7** (PDF)

CCDC 1999586-1999589 (**4**, **5**, **6** and **3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Author

*E-mail: maester@unizar.es.

ORCID

María L. Buil: 0000-0002-3284-1053

Miguel A. Esteruelas: 0000-0002-4829-7590

Susana Izquierdo: 0000-0002-6608-1910

Antonio I. Nicasio: 0000-0002-2268-4920

Enrique Oñate: 0000-0003-2094-719X

Notes

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