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# 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

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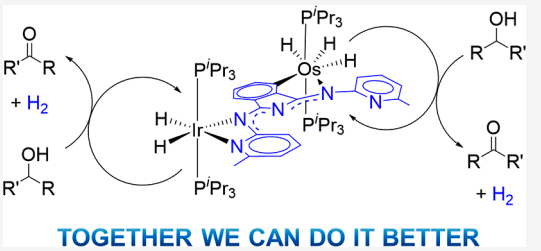
**ABSTRACT:** The elusive C−H bond activation of an organic fragment contained in many biologically active molecules and the use of the resulting noninnocent ligand in bimetallic catalysis applied to the acceptorless and base-free dehydrogenation of secondary alcohols has been performed by using the polyhydrides $IrH_5(P^iPr_3)_2$ (**1**) and $OsH_6(P^iPr_3)_2$ (**2**). Complex **1** activates the N−H bond of 1,3-bis(6′-methylpyridyl-2′-imino)isoindoline (HBMePHI) to give the mononuclear complex $IrH_2\{\kappa^2\text{-}N_{py},N_{imine}(BMePHI)\}(P^iPr_3)_2$ (**3**). Both **1** and **2** activate the C($sp^2$)−H bond at position 4 of the core isoindoline of the BMePHI ligand of **3**. The reactions lead to the homobinuclear complex $(P^iPr_3)_2H_2Ir\{\mu\text{-}(\kappa^2\text{-}N_{py},N_{imine}\text{-BMePI-}\kappa^2\text{-}N_{imine},C^4_{iso})\}IrH_2(P^iPr_3)_2$ (**4**) and the heterobinuclear compound $(P^iPr_3)_2H_2Ir\{\mu\text{-}(\kappa^2\text{-}N_{py},N_{imine}\text{-BMePI-}\kappa^2\text{-}N_{imine},C^4_{iso})\}OsH_3(P^iPr_3)_2$ (**5**), respectively. The metalated carbon atom of **4** and **5** has a marked nucleophilic character. Thus, it adds the proton of alcohols to afford the respective cations $[(P^iPr_3)_2H_2Ir\{\mu\text{-}(\kappa^2\text{-}N_{py},N_{imine}\text{-BMePHI-}\kappa^2\text{-}N_{py},N_{imine})\}IrH_2(P^iPr_3)_2]^+$ (**6**) and $[(P^iPr_3)_2H_2Ir\{\mu\text{-}(\kappa^2\text{-}N_{py},N_{imine}\text{-BMePHI-}\kappa^2\text{-}N_{py},N_{imine})\}OsH_3(P^iPr_3)_2]^+$ (**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 a consequence of the mutual electronic influence of the metals through the bridge. X-ray diffraction analysis data of the structures of **3**−**5** and the reactivity of **4** and **5** support a noninnocent character of the bridging ligand.

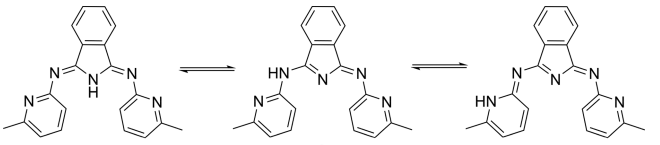


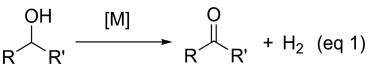

## INTRODUCTION

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($sp^2$)−H bonds using transition-metal complexes is difficult to carry out, generally because the receptor organic compound also contains a high number of heteroatoms with free electrons, which block access to the metal by means of their coordination. Here we show a strategy that allows activation of 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).

We are interested in the development of catalysts for the dehydrogenation of alcohols, as a part of a research program focused on $\sigma$-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]

**Scheme 1. Equilibrium among the HBMePHI Tautomers**




(eq 1)

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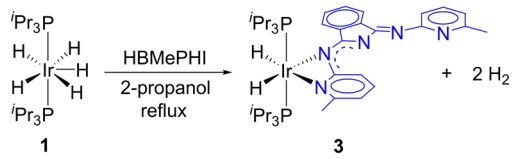
This oxidation reaction is generally endothermic at room temperature. Thus, it is usually performed in open systems because the hydrogen elimination acts as a driving force of the process. Metal-alkoxide species, which evolve by $\beta$-hydrogen elimination to afford hydride compounds, are key intermediates 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, strongly basic media are necessary for the operation 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 that 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, three years ago we explored the reactivity of the isoindoline HBMePHI with the hydride complexes $OsH_6(P^iPr_3)_2$ and $OsH(OH)(CO)(P^iPr_3)_2$. This study led us to the complexes $OsH_3\{\kappa^2\text{-}N_{py},N_{imine}(BMePHI)\}(P^iPr_3)_2$ and $OsH\{\kappa^2\text{-}N_{py},N_{imine}(BMePHI)\}(CO)(P^iPr_3)_2$, which are efficient catalysts for the acceptorless and base-free dehydrogenation of secondary alcohols. Their noticeable feature is the unusual $\kappa^2\text{-}N_{py},N_{imine}$ 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 a $\mu\text{-}(\kappa^2\text{-}N_{py},N_{imine})_2$ bridge. Frontier orbitals and electrochemical studies showed that the metal fragments behave independently 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 aforementioned 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 acceptorless alcohol 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 attracted our interest. Should the blockage of the free nitrogen atoms require the use of an external base? Do metals undergo catalytic synergism? In the process of answering this, 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 biologically active molecules and its use as a noninnocent ligand in bimetallic catalysis applied to 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 $IrH_5(P^iPr_3)_2$ (**1**) activates the N−H bond of the isoindoline HBMePHI, in agreement with the $d^2$ osmium-hexahydride $OsH_6(P^iPr_3)_2$ (**2**) and with the ability demonstrated by the polyhydrides of platinum group metals for activating $\sigma$ bonds.[11] Treatment of 2-propanol solutions of the pentahydride **1** with 1.1 equiv of the organic compound, under reflux, for 4 h produces the release of two hydrogen molecules and the formation of the iridium(III) derivative $IrH_2\{\kappa^2\text{-}N_{py},N_{imine}(BMePHI)\}(P^iPr_3)_2$ (**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 $\kappa^2\text{-}N_{py},N_{imine}$ coordination of the anion BMePHI is also the preferred one for an $[IrH_2(P^iPr_3)_2]^+$ metal fragment. The coordination polyhedron around the iridium atom can be described as a distorted octahedron, with the phosphines disposed mutually *trans* (P(1)−Ir−P(2) = 164.67(3)°). The perpendicular plane is formed by the chelating BMePHI ligand, which acts with a N(1)−Ir−N(2) bite angle of 60.03(10)°, and the hydrides. The iridium−pyridine bond length (Ir−N(1) = 2.206(3) Å) is about 0.02 Å shorter than the iridium−imine distance (Ir−N(2) = 2.229(3) Å). A 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 $\mathbf{a^I}$−$\mathbf{c^I}$ 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) Å and 1.350(4) versus 1.386(4) Å, respectively) is observed. In contrast, the C(7)−N(2) bond (1.322(4) Å) lengthens about 0.03 Å with regard to C(14)−N(4) (1.289(4) Å) and between 0.02 and 0.05 Å with regard to those reported for imine ligands with $\kappa^1\text{-}N$ coordination.[12] In agreement with the presence of inequivalent hydrides in the complex, its $^1$H 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 $^{31}P\{^1H\}$ NMR spectrum displays a singlet at 27.2 ppm, as expected for equivalent phosphines.

The $\kappa^2\text{-}N_{py},N_{imine}$ coordination for ligands of the class 1,3-bis(2-pyridylimino)isoindolate (BPHI) has been elusive so far, in iridium chemistry. In this context, we note that the dicarbonyl derivative $Ir(acac)(CO)_2$ reacts with HBPHI molecules to form $Ir\{\kappa^3\text{-}(N_{py},N_{iso},N_{py})_{mer}\text{-}(BPHI)\}(CO)_2$ complexes. However, the reactions fail with those bearing a substituent at the 6-pyridyl position.[13] Related bis(ethylene) derivatives, $Ir\{\kappa^3\text{-}(N_{py},N_{iso},N_{py})_{mer}\text{-}(BPHI)\}(C_2H_4)_2$, are also known. In contrast to ethylene, 1,5-cyclooctadiene affords square-planar species, $Ir\{\kappa^2\text{-}N_{iso},N_{py}\text{-}(BPHI)\}(\eta^4\text{-}C_8H_{12})$, with a chelate $N_{iso},N_{py}$-coordination fashion of the polydentate ligand.[14] The latter has been also observed with $Ir(\eta^5\text{-}C_5Me_5)X$ (X = Cl, I, $N_3$, $CH_3CN$) metal fragments, whereas $Ir(\eta^5\text{-}$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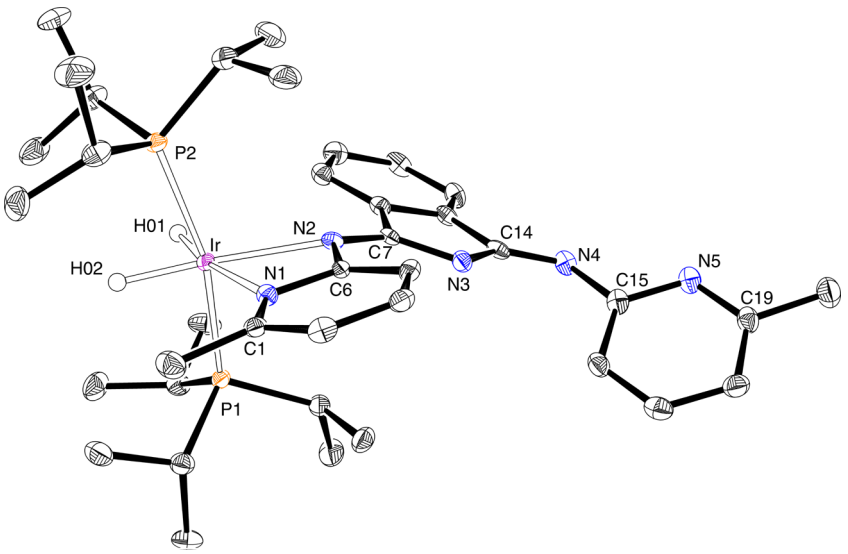


**Figure 1.** Molecular diagram of complex **3** (50% probability ellipsoids). Hydrogen atoms (except the hydrides) are omitted for clarity. Selected angles (deg): P(1)−Ir−P(2) = 164.67(3), N(1)−Ir−N(2) = 60.03(10).

**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).

$C_5Me_5$)($PPh_3$) coordinates BMePHI in a $\kappa^2$-$N_{imine}$,$N_{iso}$ 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 $\kappa^2$-$N_{py}$,$N_{imine}$ coordination of BMePHI to the $[IrH_2(P^iPr_3)_2]^+$ metal fragment is also the preferred one, we subsequently studied the reactions of **3** with **1** and **2**, in accord with our initial aim. Both polyhydrides behave similarly, promoting the elusive activation of the C(sp$^2$)−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 reflux leads to the homobinuclear 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**) along with the release of two hydrogen molecules. Under the same experimental conditions, the reaction of **3** with the osmium-hexahydride **2** gives the heterobinuclear 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**) and two hydrogen molecules. Both reactions are spectroscopically quantitative; nevertheless, products were isolated in moderate yields, 42% and 46%, as dark red and dark purple solids, respectively, after the workup process. Complexes **4** and **5** were characterized by X-ray diffraction analysis.

Figure 2 gives 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 the formally dianionic bridge $\mu$-($\kappa^2$-$N_{py}$,$N_{imine}$-BMePI-$\kappa^2$-$N_{imine}$,$C^4_{iso}$). Both iridium centers display an octahedral environment with *trans* phosphines (P(2)−Ir(1)−P(1) = 159.77(12)° and P(3)−Ir(2)−P(4) = 165.73(13)°). The coordination around the atom Ir(1) resembles that of **3** with iridium−imine and iridium−pyridine distances of 2.229(10) Å (Ir(1)−N(2)) and 2.161(10) Å (Ir(1)−N(1)), respectively, which are statistically identical with 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)° and Ir(2)−C(12) and Ir(2)−N(4) bond lengths of 2.137(14) and 2.268(9) Å, respectively. The former distance compares well with those reported for related heterometallacycles,[16] whereas the latter 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 $\mathbf{b}^I$ and $\mathbf{c}^I$ to $\kappa^2$-$N_{py}$,$N_{imine}$ coordination, proving the influence of a second metal fragment on the electronic environment of that initially coordinated and supporting the idea that the phenomenon 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 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 $^1$H and $^{31}$P{$^1$H} NMR spectra, in benzene-$d_6$, at room temperature reflect the asymmetry of the metal fragments. According to this, the $^1$H NMR spectrum contains four higher field resonances between −12.90 and −25.60 ppm, corresponding to the inequivalent hydrides, whereas the $^{31}$P{$^1$H} NMR spectrum displays two singlets at 27.0 and 32.5 ppm. The resonance due to the metalated carbon atom C(12) appears at 169.6 ppm, as a triplet with a C−P coupling constant of 8.0 Hz, in the $^{13}$C{$^1$H} NMR spectrum.

The structure of the heterobinuclear complex **5** (Figure 3) shows interesting differences with regard to that of **4**, which are


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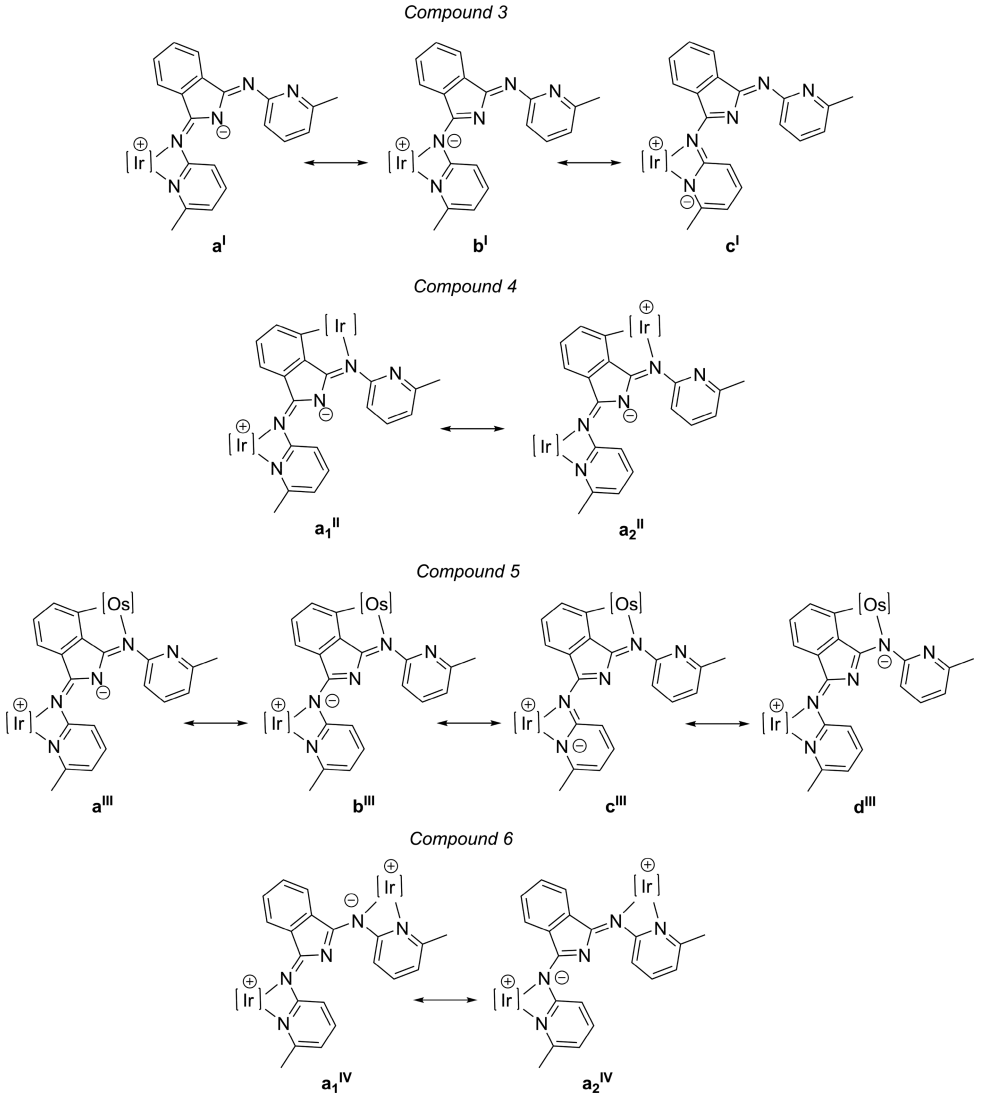
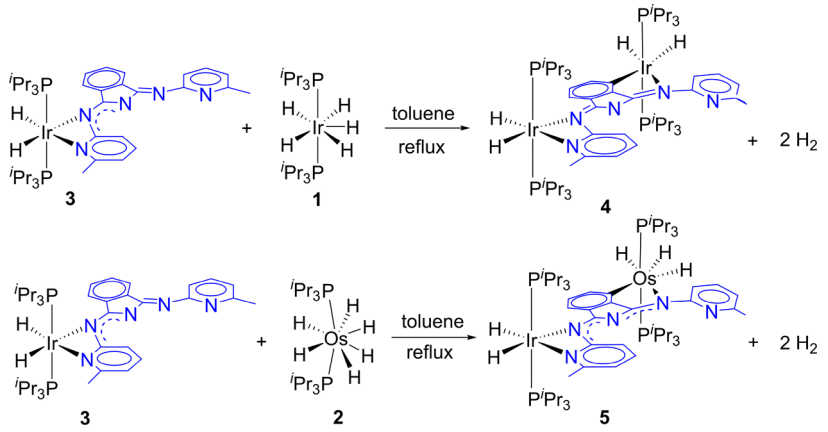
**Scheme 3. Main Resonance Forms to Describe the Metal−Polydentate Ligand Bonding Situation in Complexes 3−6**




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




a consequence of the different electronic natures 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 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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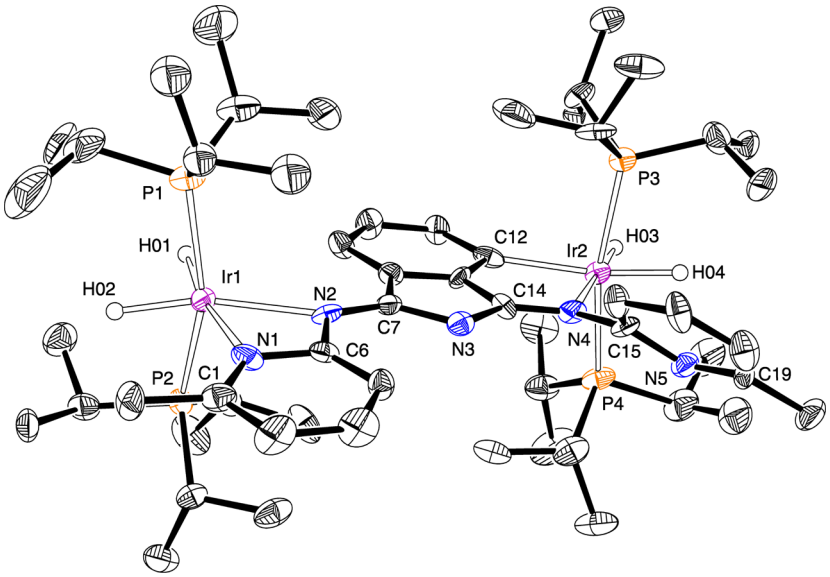


**Figure 2.** Molecular diagram of complex **4** (50% probability ellipsoids). Hydrogen atoms (except the hydrides) are omitted for clarity. Selected angles (deg): P(2)−Ir(1)−P(1) = 159.77(12), P(4)−Ir(2)−P(3) = 165.73(13), C(12)−Ir(2)−N(4) = 79.4(4), N(1)−Ir(1)−N(2) = 60.4(4).

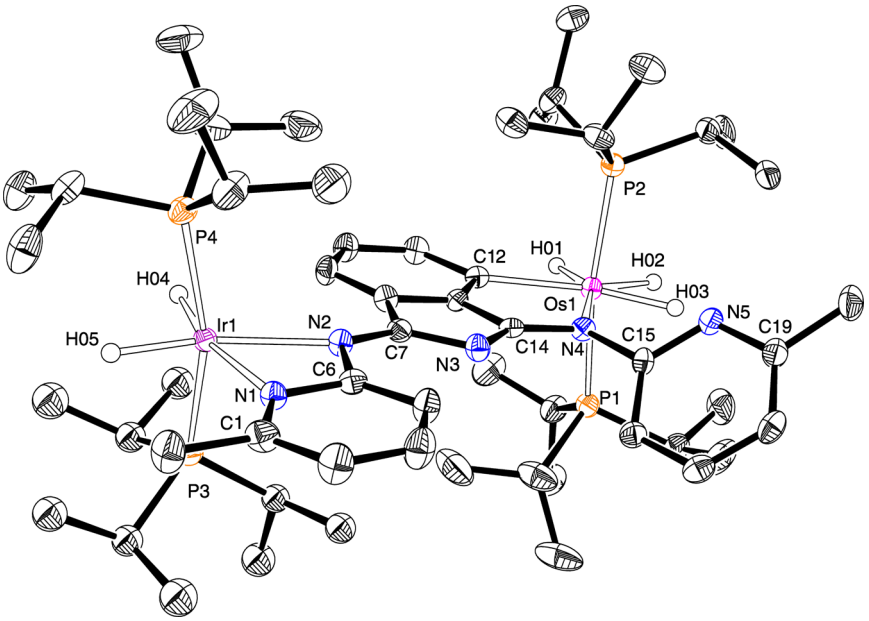


**Figure 3.** Molecular diagram of complex **5** (50% probability ellipsoids). Hydrogen atoms (except the hydrides) are omitted for clarity. Selected angles (deg): P(2)−Os(1)−P(1) = 170.06(3), C(12)−Os(1)−N(4) = 77.93(13), P(4)−Ir(1)−P(3) = 162.77(4), N(1)−Ir(1)−N(2) = 60.06(11).

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 among **3**−**5** (Table 1) evidence the different electronic natures of the $d^6$ $IrH_2(P^iPr_3)_2$ and $d^4$ $OsH_3(P^iPr_3)_2$ metal fragments. In contrast to $d^6$ $IrH_2(P^iPr_3)_2$, the fragment $d^4$ $OsH_3(P^iPr_3)_2$ does not prevent binuclear resonances forms related to $\mathbf{b}^{\mathbf{I}}$ and $\mathbf{c}^{\mathbf{I}}$ ($\mathbf{b}^{\mathbf{III}}$ and $\mathbf{c}^{\mathbf{III}}$ in Scheme 3), although their contribution to the $\kappa^2$-$N_{py}$,$N_{imine}$ coordination of the BMePI ligand to the iridium center of **5** is lower than the contribution of $\mathbf{b}^{\mathbf{I}}$ and $\mathbf{c}^{\mathbf{I}}$ to the coordination of the BMePHI group to the metal center of **3**, because the osmium fragment provides the fourth resonance form $\mathbf{d}^{\mathbf{III}}$. 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 $\mathbf{d}^{\mathbf{III}}$ 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 the 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 homobinuclear compound. The $^1H$ and $^{31}P\{^1H\}$ 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 $OsH_3$


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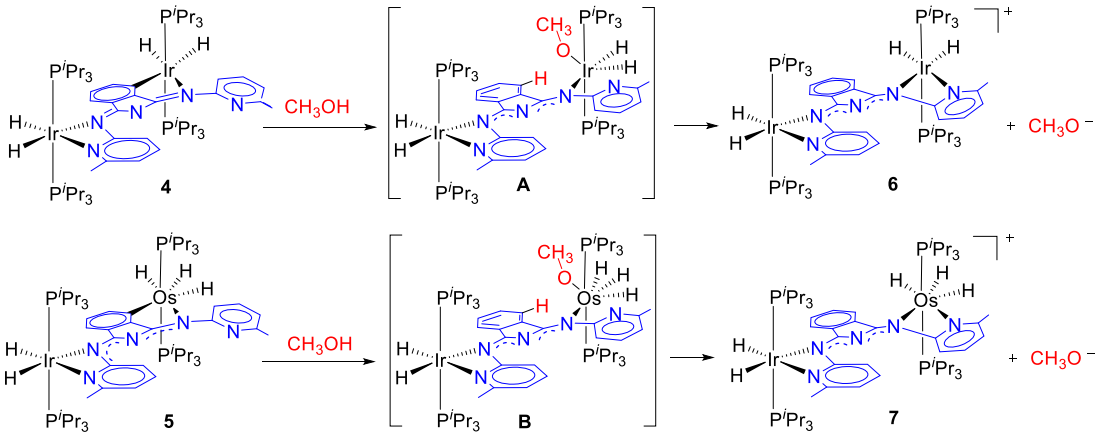
**Scheme 5. Formation of 6 and 7**



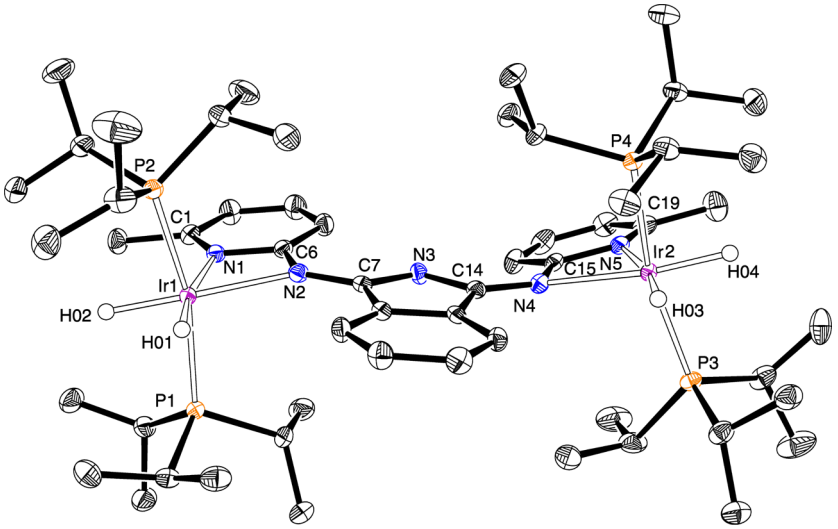




**Figure 4.** Molecular diagram of cation **6** (50% probability ellipsoids). Hydrogen atoms (except the hydrides) are omitted for clarity. Selected angles (deg): P(2)−Ir(1)−P(1) = 164.12(3), P(4)−Ir(2)−P(3) = 162.89(3), N(1)−Ir(1)−N(2) = 60.20(9), N(5)−Ir(2)−N(4) = 60.12(10).

resonances display the typical pattern for a cyclometalated $OsH_3(XY)(P^iPr_3)_2$ 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 $^{31}P\{^1H\}$ NMR spectrum contains two singlets at 27.2 and 26.3 ppm, one for each group of equivalent phosphines. The resonance due to the metalated carbon atom C(12) appears at 180.8 ppm, as a triplet with a C−P coupling constant of 7.1 Hz, in the $^{13}C\{^1H\}$ NMR spectrum.

The metalated 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 1 h, at room temperature quantitatively affords the binuclear cations $[(P^iPr_3)_2H_2Ir\{\mu\text{-}(\kappa^2\text{-}N_{py},N_{imine}\text{-}BMePHI\text{-}\kappa^2\text{-}N_{py},N_{imine})\}IrH_2(P^iPr_3)_2]^+$ (**6**) and $[(P^iPr_3)_2H_2Ir\{\mu\text{-}(\kappa^2\text{-}N_{py},N_{imine}\text{-}BMePHI\text{-}\kappa^2\text{-}N_{py},N_{imine})\}OsH_3(P^iPr_3)_2]^+$ (**7**), bearing a $\mu\text{-}(\kappa^2\text{-}N_{py}\text{-}N_{imine})_2$-BMePHI bridge and the methoxide anion, 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-metalated 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). The reactions shown in Scheme 5 agree well with the behavior recently observed for the *rollover* complex $IrH_2\{\kappa^2\text{-}C,N\text{-}[C_5H_3N\text{-}py]\}(P^iPr_3)_2$, with a cyclometalated 2,2′-bipyridine ligand, which undergoes demetalation in methanol to afford the cation $[IrH_2\{\kappa^2\text{-}N,N\text{-}(bipy)\}(P^iPr_3)_2]^+$, with the usual 2,2′-bipyridine ligand, and the anion $[MeO]^-$, as a result of the addition of the O−H bond of the alcohol to the Ir−C bond of the metalated species.[19]

The addition of $NaBF_4$ to methanol solutions of **6** and **7** allows the isolation of the corresponding $BF_4$ salts. Thus, the homobinuclear cation was characterized by X-ray diffraction analysis. The structure (Figure 4) proves the demetalation of the aromatic six-membered ring of the core isoindoline of the BMePI ligand and the $\mu\text{-}(\kappa^2\text{-}N_{py},N_{imine})_2$ 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) and 162.89(3)°, respectively. The bond lengths in each half are similar (Table 1); the iridium−pyridine distances of 2.207(3) (Ir(1)−N(1)) Å and 2.211(3) (Ir(2)−N(5)) Å are statistically identical as well as the iridium−imine distances of 2.223(3) (Ir(1)−N(2)) Å 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


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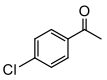
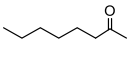
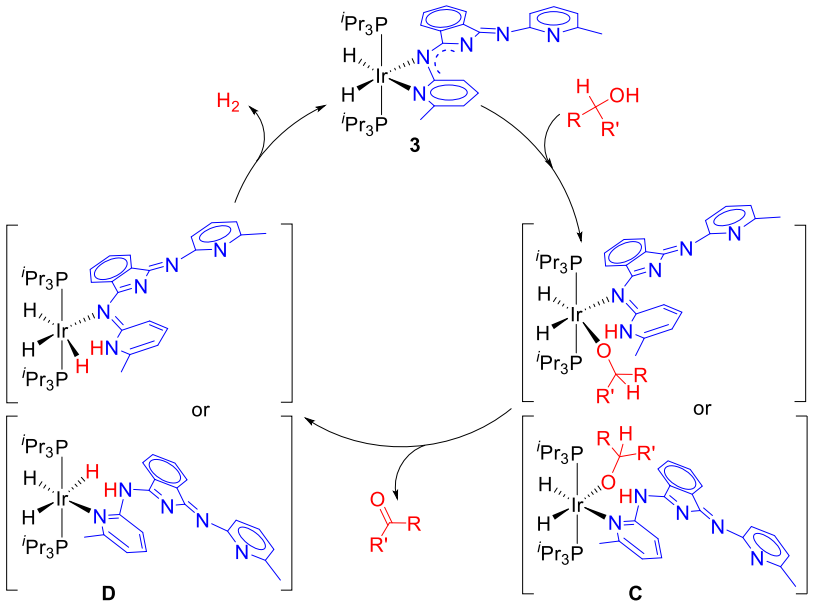
**Table 2. Metal-Promoted Acceptorless and Base-Free Dehydrogenation of Secondary Alcohols[a]**

| Catalyst |  |  |  |  |  |
|---|---|---|---|---|---|
| **3** | 50 | 47 | 50 | 26 | 25 |
| **4** | 77 | 68 | 73 | 32 | - |
| **5** | 77 | 84 | 82 | 51 | 65 |
| $OsH_3\{\kappa^2\text{-}N_{py},N_{imine}(BMePHI)\}(P^iPr_3)_2$ | 61[b] | 60[b] | 76[b] | 34[b] | 37[b] |

[a]Conditions: 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. [b]Data were obtained from a previous work.[8]

**Scheme 6. Proposed Catalytic Cycle for Acceptorless and Base-Free Dehydrogenation of Secondary Alcohols Promoted by 3**




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 the bridge is distributed between them (see resonance forms $\mathbf{a_1}^{IV}$ and $\mathbf{a_2}^{IV}$ in Scheme 3). The equivalence of the metal fragments in **6** is also revealed by the $^1H$ and $^{31}P\{^1H\}$ NMR spectra in dichloromethane-$d_2$. Thus, the $^1H$ NMR spectrum shows two doublets ($^2J_{H-H}$ = 8.3 Hz) of triplets at −24.41 ($^2J_{H-P}$ = 17.0 Hz) ppm and −26.43 ($^2J_{H-P}$ = 16.6 Hz) ppm due to the inequivalent hydride ligands of both iridium moieties, whereas the $^{31}P\{^1H\}$ NMR spectrum exhibits a singlet at 27.7 ppm for the four phosphines. In contrast to **6**, the $^1H$ and $^{31}P\{^1H\}$ NMR spectra of **7** resemble those of **5**. In the $^1H$ NMR spectrum, the $OsH_3$ resonances display the pattern expected for an $OsH_3(XY)(P^iPr_3)_2$ species, between −10.5 and −14.0 ppm, along with two doublets ($^2J_{H-H}$ = 8.3 Hz) of triplets at −24.40 ($^2J_{H-P}$ = 17.0 Hz) and −26.47 ($^2J_{H-P}$ = 16.6 Hz) ppm due to the $IrH_2$ unit, whereas the $^{31}P\{^1H\}$ NMR spectrum contains two singlets at 27.8 and 20.7 ppm, one for each half.

Compounds bearing bridging 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 $Lu(CH_2SiMe_3)_3(thf)_2$ with HBPHI, to give $Lu\{\kappa^3\text{-}mer\text{-}(BPHI)\}(CH_2SiMe_3)_2$, is a binuclear species also bearing a $\mu\text{-}(N_{py},N_{imine})_2$-BMePHI ligand.[20] Baird and co-workers have observed that HBPHI displaces an acetate group from $Mo_2(OAc)_4$ to give $Mo_2(OAc)_3(BPHI)$, 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 a palladium-promoted 1,3-hydrogen shift, from C to N, to afford $Pd(\kappa^3\text{-}N_{py},N_{iso},C_{Hpy})$-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 aforementioned hydrogen donors. The reactions were performed in toluene, at 100 °C, using a substrate concentration of 0.255 M and a catalyst concentration of $1.8 \times 10^{-2}$ (**3**) or $9.0 \times 10^{-3}$ (**4** and **5**) M: i.e., 7 mol % of the metal in all 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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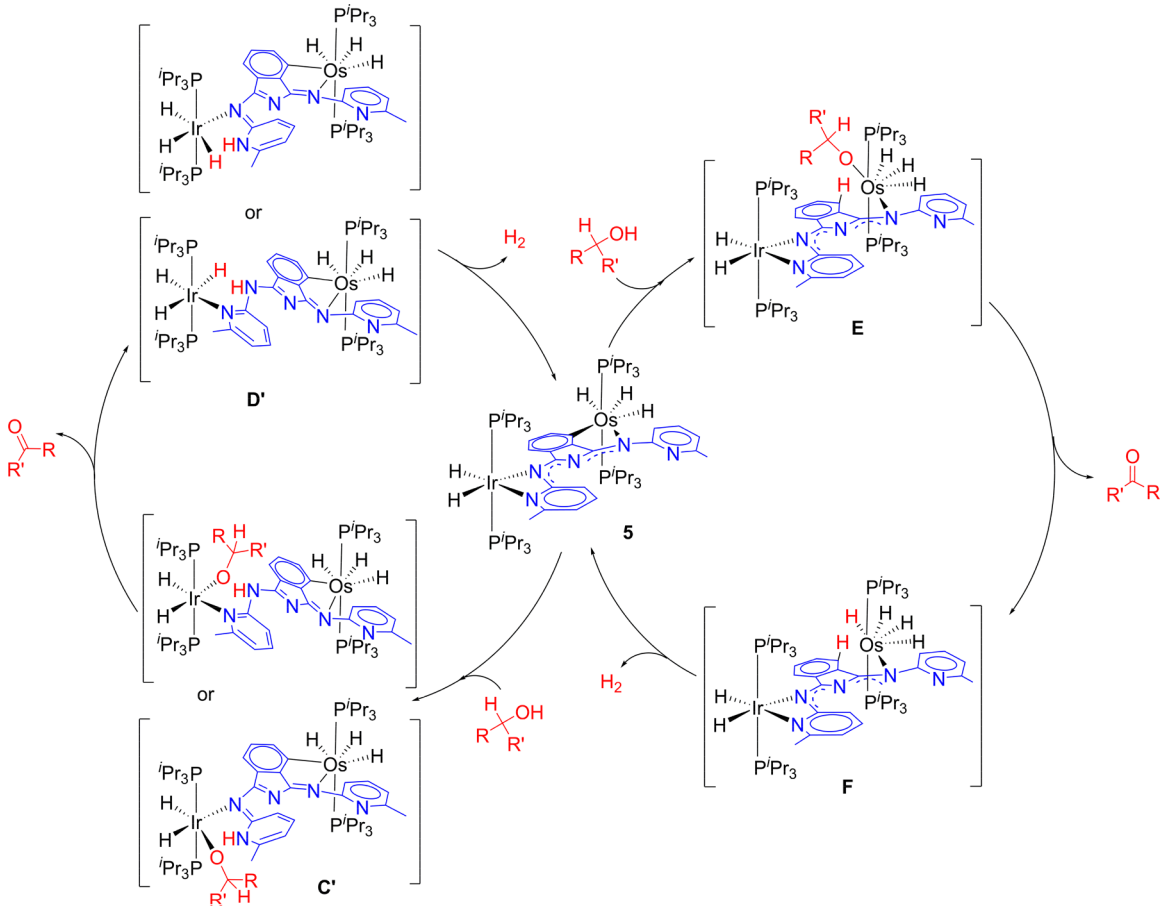
**Scheme 7. Proposed Catalytic Cycle for Acceptorless and Base-Free Dehydrogenation of Secondary Alcohols Promoted by 5**



mononuclear osmium catalyst $OsH_3\{\kappa^2\text{-}N_{py},N_{imine}(BMePHI)\}(P^iPr_3)_2$ are also included for comparison.[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 less dehydrogenated, about 25%. The same trend was observed with the osmium catalyst $OsH_3\{\kappa^2\text{-}N_{py},N_{imine}(BMePHI)\}(P^iPr_3)_2$ (60−76% versus 34−37%), although the latter displays a significantly higher activity. On the basis of the resonance forms $\mathbf{b}^{\mathbf{I}}$ and $\mathbf{c}^{\mathbf{I}}$ shown in Scheme 3, the dehydrogenation can be rationalized according to 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 the alkoxide intermediate **C**, bearing the tautomer **b** or **c** of HBMePHI with $\kappa^1$-*N* coordination. Then, the subsequent $\beta$-hydrogen elimination on the alkoxide group could afford the ketone and the trihydride species **D**, which should release molecular hydrogen and regenerate the catalyst by means of the N−H bond activation of the coordinated tautomer.

Iridium catalysts for acceptorless and base-free dehydrogenation of secondary alcohols are scarce. Fujita, Yamaguchi, and co-workers have prepared half-sandwich iridium(III) complexes bearing 5- and 4,5-substituted 2-pyridonate ligands[23] or a chelating bidentate ligand that comprises NHC and $\alpha$-hydroxypyridine moieties,[7f] which exhibited high activity in toluene and aqueous media, respectively. Albrecht, Diéguez, and co-workers 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, with amine or hydroxy functionalization, with those stabilized by a NHC ligand that is not bifunctional; 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 an N,N,N-pincer osma ligand, 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 heterobinuclear Ir-Os compound **5** is even more active. The increase in 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 was previously demonstrated. Thus, the catalysis takes places in an independent manner in each metal center. The catalytic synergism is a consequence of the increase in the efficiency of each metal center by the action of its catalyst colleague. 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 metalated carbon atom of the isoindoline moiety due to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the possibility of coordination−decoordination of this carbon, as demonstrated by the reactions shown in Scheme 5. Scheme 7 rationalizes the dehydrogenation process through both metals for the heterobinuclear complex **5**. The elemental steps on the initial iridium center are the same as in the mononuclear complex **3**, whereas according to Scheme 7 alkoxide intermediates **E** related to **A** and **B** should be the key for the dehydrogenation via the second metal. The $\beta$-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 release 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.

## CONCLUDING REMARKS

This study has revealed that the sequential treatment of HBMePHI with 2 equiv of the pentahydride **1** or with 1 equiv of the latter and 1 equiv 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 homobinuclear complex **4** or the heterobinuclear 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 of 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**−**5** and reactivity results on **4** and **5** support a noninnocent character of the bridging ligand, since its donor atoms have a direct participation in the formation of the metal−alkoxide bonds, key for the catalysis, and in the release of molecular hydrogen.

In summary, an elusive metal-mediated C−H bond activation of the core isoindoline of a polynitrogenated organic molecule has been discovered, which generates a noninnocent bridge ligand, responsible for 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. $^{1}$H, $^{31}$P{$^{1}$H}, and $^{13}$C{$^{1}$H} NMR spectra were recorded on a Bruker ARX 300 MHz, Bruker Avance 300 MHz, or Bruker Avance 400 MHz instrument. Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks ($^{1}$H, $^{1}$H{$^{31}$P}, $^{13}$C{$^{1}$H}) or an external standard ($^{31}$P{$^{1}$H} to 85% $H_3PO_4$). Coupling constants $J$ and $N$ ($N = J_{H-P} + J_{H-P'}$ for $^{1}$H; $N = J_{C-P} + J_{C-P'}$ for $^{13}$C) are given in hertz. C, H, and N analyses were carried out with 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). $IrH_5(P^iPr_3)_2$ (**1**),[25] $OsH_6(P^iPr_3)_2$ (**2**),[26] and 1,3-bis(6′-methylpyridyl-2′-imino)-isoindoline (HBMePHI)[27] were prepared according to the published methods.

**Preparation of $IrH_2\{\kappa^2$-$N_{py}$,$N_{imine}$(BMePHI)$\}(P^iPr_3)_2$ (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 × 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 $C_{38}H_{60}IrN_5P_2$: 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 $C_{38}H_{61}IrN_5P_2$ $[M + H]^+$ 842.4037, found 842.4028. $^{1}$H NMR (400.13 MHz, $CD_2Cl_2$, 298 K): $\delta$ 8.80 (d, $^{3}J_{H-H}$ = 7.3, 1 H, $CH_{arom}$), 8.43 (d, $^{3}J_{H-H}$ = 7.6, 1 H, $CH_{arom}$), 7.87 (d, $^{3}J_{H-H}$ = 7.3, 1 H, $CH_{arom}$), 7.55 (dd, $^{3}J_{H-H}$ = 7.6 and 7.6, 1 H, $CH_{arom}$), 7.53 (dd, $^{3}J_{H-H}$ = 7.6 and 7.6, 1 H, $CH_{arom}$), 7.44 (dd, $^{3}J_{H-H}$ = 7.3 and 7.3, 1 H, $CH_{arom}$), 7.43 (d, $^{3}J_{H-H}$ = 7.6, 1 H, $CH_{arom}$), 7.35 (dd, $^{3}J_{H-H}$ = 7.3 and 7.3, 1 H, $CH_{arom}$), 6.82 (d, $^{3}J_{H-H}$ = 7.6, 1 H, $CH_{arom}$), 6.78 (d, $^{3}J_{H-H}$ = 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, PC*H*$(CH_3)_2$), 1.06 (dvt, $^{3}J_{H-H}$ = 6.9, $N$ = 13.0, 18 H, PCH$(CH_3)_2$), 1.01 (dvt, $^{3}J_{H-H}$ = 6.9, $N$ = 13.0, 18 H, PCH$(CH_3)_2$), −24.22 (td, $^{2}J_{H-P}$ = 17.3, $^{2}J_{H-H}$ = 8.2, 1 H, Ir−H), −26.35 (td, $^{2}J_{H-P}$ = 16.6, $^{2}J_{H-H}$ = 8.2, 1 H, Ir−H). $^{31}$P{$^{1}$H} NMR (161.98 MHz, $CD_2Cl_2$, 298 K): $\delta$ 27.2 (s). $^{13}$C{$^{1}$H} NMR (100.62 MHz, $CD_2Cl_2$, 298 K): $\delta$ 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, $^{1}J_{C-P}$ = 26.9, PCH$(CH_3)_2$), 24.7, 24.6 (both s, py-$CH_3$), 20.0, 19.7 (both s, PCH$(CH_3)_2$).

**Preparation of $(P^iPr_3)_2H_2Ir\{\mu$-$(\kappa^2$-$N_{py}$,$N_{imine}$-BMePI-$\kappa^2$-$N_{imine}$,$C^4_{iso}\}IrH_2(P^iPr_3)_2$ (4).** 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, the volatiles were removed *in vacuo*. Then, pentane (3 × 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 × 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. $^{1}$H NMR (300.13 MHz, $C_6D_6$, 298 K): $\delta$ 9.14 (d, $^{3}J_{H-H}$ = 8.1, 1 H, $CH_{arom}$), 8.43 (d, $^{3}J_{H-H}$ = 7.1, 1 H, $CH_{arom}$), 8.31 (d, $^{3}J_{H-H}$ = 7.1, 1 H, $CH_{arom}$), 8.04 (d, $^{3}J_{H-H}$ = 8.1, 1 H, $CH_{arom}$), 7.30 (dd, $^{3}J_{H-H}$ = 7.1 and 7.1, 1 H, $CH_{arom}$), 7.25 (dd, $^{3}J_{H-H}$ = 7.5 and 7.5, 1 H, $CH_{arom}$), 7.23 (dd, $^{3}J_{H-H}$ = 8.1 and 8.1, 1 H, $CH_{arom}$), 6.54 (d, $^{3}J_{H-H}$ = 7.5, 1 H, $CH_{arom}$), 6.29 (d, $^{3}J_{H-H}$ = 7.5, 1 H, $CH_{arom}$), 2.51 (s, 3 H, py-$CH_3$), 2.45 (m, 6 H, PC*H*$(CH_3)_2$), 2.18 (s, 3 H, py-$CH_3$), 2.13 (m, 6 H, PC*H*$(CH_3)_2$), 1.27 (dvt, $^{3}J_{H-H}$ = 6.4, $N$ = 12.5, 18 H, PCH$(CH_3)_2$), 1.24 (dvt, $^{3}J_{H-H}$ = 6.4, $N$ = 12.5, 18 H, PCH$(CH_3)_2$), 1.04 (dvt, $^{3}J_{H-H}$ = 6.9, $N$ = 13.1, 18 H, PCH$(CH_3)_2$), 0.96 (dvt, $^{3}J_{H-H}$ = 6.9, $N$ = 13.1, 18 H, PCH$(CH_3)_2$), −12.94 (td, $^{2}J_{H-P}$ = 19.6, $^{2}J_{H-H}$ = 5.9, 1 H, Ir−H), −24.33 (td, $^{2}J_{H-P}$ = 17.6, $^{2}J_{H-H}$ = 8.1, 1 H, Ir−H), −25.48 (td, $^{2}J_{H-P}$ = 17.4, $^{2}J_{H-H}$ = 5.9, 1 H, Ir−H), −25.55 (td, $^{2}J_{H-P}$ = 16.5, $^{2}J_{H-H}$ = 8.1, 1 H, Ir−H). $^{31}$P{$^{1}$H} NMR (121.49 MHz, $C_6D_6$, 298 K): $\delta$ 32.5 (s), 27.0 (s). $^{13}$C{$^{1}$H} NMR (75.48 MHz, $C_6D_6$, 298 K): $\delta$ 185.0, 179.2, 169.9 (all s, $C_{arom}$), 169.6 (t, $^{2}J_{C-P}$ = 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 $(P^iPr_3)_2H_2Ir\{\mu$-$(\kappa^2$-$N_{py}$,$N_{imine}$-BMePI-$\kappa^2$-$N_{imine}$,$C^4_{iso}\}OsH_3(P^iPr_3)_2$ (5).** 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, the 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 × 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 °C. Anal. Calcd for $C_{56}H_{104}N_5P_4IrOs$: C, 49.68; H, 7.74; N, 5.17. found: C, 49.39; H, 8.08; N, 4.93. HRMS (electrospray, $m/z$): calcd


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for $C_{56}H_{105}N_5P_4IrOs$ $[M + H]^+$ 1356.6567, found 1356.6603. $^1H$ NMR (300.13 MHz, $C_6D_6$, 298 K): $\delta$ 9.01 (d, $^3J_{H-H}$ = 8.2, 1 H, $CH_{arom}$), 8.57 (d, $^3J_{H-H}$ = 7.1, 1 H, $CH_{arom}$), 8.23 (d, $^3J_{H-H}$ = 7.1, 1 H, $CH_{arom}$), 7.96 (d, $^3J_{H-H}$ = 8.2, 1 H, $CH_{arom}$), 7.21 (m, 3 H, $CH_{arom}$), 6.55 (d, $^3J_{H-H}$ = 7.4, 1 H, $CH_{arom}$), 6.25 ($^3J_{H-H}$ = 7.4, 1 H, $CH_{arom}$), 2.52 (s, 3 H, py-$CH_3$), 2.36 (m, 6 H, PC*H*$(CH_3)_2$), 2.16 (s, 3 H, py-$CH_3$), 2.13 (m, 6 H, PC*H*$(CH_3)_2$), 1.26 (dvt, $^3J_{H-H}$ = 6.7, *N* = 12.6, 18 H, PCH$(CH_3)_2$), 1.23 (dvt, $^3J_{H-H}$ = 6.7, *N* = 12.6, 18 H, PCH$(CH_3)_2$) 1.03 (dvt, $^3J_{H-H}$ = 6.6, *N* = 13.0, 18 H, PCH$(CH_3)_2$), 0.96 (dvt, $^3J_{H-H}$ = 6.6, *N* = 13.0, 18 H, PCH$(CH_3)_2$), −8.76 (br, 2 H, Os−H), −13.66 (br, 1 H, Os−H), −24.35 (td, $^2J_{H-P}$ = 17.5, $^2J_{H-H}$ = 8.0, 1 H, Ir−H), −25.57 (td, $^2J_{H-P}$ = 16.6, $^2J_{H-H}$ = 8.0, 1 H, Ir−H). $T_1$(min) (ms, Os−H, 300.13 MHz, toluene-$d_8$, 243 K): 40 (−8.75 ppm), 48 (− 13.63 ppm). $T_1$(min) (ms, Ir−H, 300.13 MHz, toluene-$d_8$, 253 K): 132 (−24.29 ppm), 206 (−25.47 ppm). $^{31}P\{^1H\}$ NMR (121.49 MHz, $C_6D_6$, 298 K): $\delta$ 27.2 (s), 26.3 (s). $^{13}C\{^1H\}$ NMR (75.5 MHz, $C_6D_6$, 298 K): $\delta$ 183.3, 180.8 (t, $^2J_{C-P}$ = 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$(CH_3)_2$), 27.2 (vt, *N* = 13.4, PC*H*$(CH_3)_2$), 24.4, 24.4 (both s, py-$CH_3$), 20.6, 20.6, 20.2, 19.7 (all s, PCH$(CH_3)_2$).

**Preparation of [($P^iPr_3$)$_2$$H_2$Ir{$\mu$-($\kappa^2$-$N_{py}$,$N_{imine}$-BMePHI-$\kappa^2$-$N_{py}$,$N_{imine}$)}Ir$H_2$($P^iPr_3$)$_2$]$BF_4$ ([6]$BF_4$).** The salt $NaBF_4$ (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, the 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 × 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 $C_{56}H_{104}Ir_2N_5P_4BF_4$: 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 $C_{56}H_{104}Ir_2N_5P_4$ $[M]^+$ 1354.6474, found 1354.6474. $^1H$ NMR (300.13 MHz, $CD_2Cl_2$, 298 K): $\delta$ 8.90 (dd, $^3J_{H-H}$ = 5.5 and 3.1, 2 H, $CH_{arom}$), 8.36 (d, $^3J_{H-H}$ = 7.9, 2 H, $CH_{arom}$), 7.81 (dd, $^3J_{H-H}$ = 7.9 and 7.9, 2 H, $CH_{arom}$), 7.44 (dd, $^3J_{H-H}$ = 5.5 and 3.1, 2 H, $CH_{arom}$), 7.06 (d, $^3J_{H-H}$ = 7.9, 2 H, $CH_{arom}$), 2.46 (s, 6 H, py-$CH_3$), 2.18 (m, 12 H, PC*H*$(CH_3)_2$), 1.06 (dvt, $^3J_{H-H}$ = 6.8, *N* = 13.3, 36 H, PCH$(CH_3)_2$), 1.00 (dvt, *N* = 13.3, $^3J_{H-H}$ = 6.8, 36 H, PCH$(CH_3)_2$), −24.41 (td, $^2J_{H-P}$ = 17.0, $^2J_{H-H}$ = 8.3, 2 H, Ir−H), −26.43 (td, $^2J_{H-P}$ = 16.6, $^2J_{H-H}$ = 8.3, 2 H, Ir−H). $^{31}P\{^1H\}$ NMR (121.49 MHz, $CD_2Cl_2$, 298 K): $\delta$ 27.7 (s). $^{13}C\{^1H\}$ NMR (75.48 MHz, $CD_2Cl_2$, 298 K): $\delta$ 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$(CH_3)_2$), 24.7 (s, py-$CH_3$), 20.0, 19.6 (both s, PCH$(CH_3)_2$).

**Preparation of [($P^iPr_3$)$_2$$H_2$Ir{$\mu$-($\kappa^2$-$N_{py}$,$N_{imine}$-BMePHI-$\kappa^2$-$N_{py}$,$N_{imine}$)}Os$H_3$($P^iPr_3$)$_2$]$BF_4$ ([7]$BF_4$).** The salt $NaBF_4$ (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 × 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): $\delta$ 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, PC*H*$(CH_3)_2$), 2.06 (m, 6 H, PC*H*$(CH_3)_2$), 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): $\delta$ −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): $\delta$ 27.8 (s), 20.7 (s). $^{13}C\{^1H\}$ NMR (75.48 MHz, $CD_2Cl_2$, 298 K): $\delta$ 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 an argon atmosphere. The mixture was stirred at 100 °C for 24 h. After this time the solution was cooled to 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 $\mu$m × 0.25 $\mu$m 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 at https://pubs.acs.org/doi/10.1021/acs.organomet.0c00316.

Structural analysis and NMR spectra of complexes **3**−**7** (PDF)

### Accession Codes

CCDC 1999586−1999589 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.

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### Notes

The authors declare no competing financial interest.

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