Base-Free and Acceptorless Dehydrogenation of Alcohols Catalyzed by an Iridium Complex Stabilized by a N,N,N-Osmaligand

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Supporting Information Placeholder

ABSTRACT: The preparation of a N,N,N-osmaligand, its coordination to iridium to afford an efficient catalyst precursor, and the catalytic activity of the latter in dehydrogenation reactions of hydrogen carriers based on alcohols are reported. Complex $\text{OsH}_2\text{Cl}_2(\text{P}^i\text{Pr}_3)_2$ (**1**) reacts with 3-(2-pyridyl)pyrazol to give the osmium(II) complex **2H**, which contains an acidic hydrogen atom. Deprotonation of the latter by the bridging methoxy groups of the dimer $[\text{Ir}(\mu\text{-OMe})(\eta^4\text{-COD})]_2$ (COD = 1,5-cyclooctadiene) leads to $\text{Ir}(\text{2})(\eta^4\text{-COD})$ (**3**), where the osmaligand **2** has a free-nitrogen atom. Iridium complex **3** catalyzes the dehydrogenation of secondary and primary alcohols to ketones and aldehydes or esters, respectively, and the dehydrogenation of diols to lactones. Cyclooctatriene is detected during the catalysis by GC-MS, suggesting that the true catalyst of the reactions is a dihydride $\text{IrH}_2(\text{2})$ -species with the osmaligand **2** acting as N,N,N-pincer. The presence of a phenyl group in the substrates favors the catalytic processes. The dehydrogenative homocoupling of primary alcohols to esters appears to take place via the transitory formation of hemiacetals.

INTRODUCTION

Metalloligands are coordination complexes, including organometallic species, bearing binding groups which can coordinate to other metal center.¹ The presence of the metallic core in the metalloligand allows a wide variety of dispositions for its donor atoms. This enlarges the range of geometries that can be stabilized around of the new metal center. Furthermore, as a consequence of the presence of empty and full *d* orbitals in the metal, the metalloligands generally possess variable electronic character, which is transmitted through the donor groups.² This property has given rise to significant enhancements in catalytic activity of some metal centers in notable reactions.³ Ferrocene compounds containing donor substituents are most probably the best known ligands of this class. The ferrocene moiety provides specific geometries and opens the door to the control of reactivity at the additional metal center due to the possibility of switching the redox state of the iron center.⁴

Metalloligands are having a notable influence in modern organic synthesis by stabilizing a wide range of homogeneous catalysts for cross-coupling, hydrogenation, allylic substitution, hydroformylation, cyclopropanation, among other reactions of relevance.⁵ However, the metalloligand strategy has been scarcely applied to the acceptorless alcohol dehydrogenation,⁶ which is an oxidant-free atom-economical approach for the transformation of these molecules to carbonyl compounds and has great interest in connection with the hydrogen production from biomass and the storage-transport of hydrogen in organic liquids.⁷

Acceptorless alcohol dehydrogenation is generally an endothermic reaction at room temperature. Nevertheless, the equilibrium can be driven by removal the generated molecular hydrogen. High temperatures and strong basic media are often

employed to promote the catalysis.⁸ The base is in principle able to deprotonate the alcohol. The resulting alkoxide then binds to the metal to generate a hydride by β -hydrogen elimination. Some ligands are described as noninnocent, giving rise to bifunctional complexes which can be engaged in deprotonation-protonation steps, and avoid the use of additional bases.⁹ The basic center of the ligands can reside in an atom bonded to the metal center (first coordination sphere) or in a remote position. Recent studies of Dub, Gordon, and coworkers,¹⁰ and Gusev¹¹ call into question the noninnocent character of these ligands and therefore the bifunctional role of the catalysts. Their results reveal that the ligands are involved in the catalysis via the stabilization of some transition states through hydrogen bonding interactions and not via a reversible proton transfer.

π -Conjugated azolate ligands are particularly efficient in the transmission of information between distant metal centers.^{3,5b,12} Taking into account this background, we have designed a strongly basic tridentate *N*-donor metalloligand bearing an osmium(II) core, based on the 3-(2-pyridyl)pyrazolate moiety, in the search of a novel class of catalysts for the acceptorless and base-free alcohol dehydrogenation. In this paper, we report the preparation of a novel osmaligand and its coordination to iridium, which generates an efficient catalyst for the acceptorless and base-free dehydrogenation of secondary and primary alcohols as well as diols.

RESULT AND DISCUSSION

Preparation of the Osmaligand and its Coordination to Iridium: Synthesis of the Catalytic Precursor. Complex $\text{OsH}_2\text{Cl}_2(\text{P}^i\text{Pr}_3)_2$ (**1**) has been one of the cornerstones in the development of the modern osmium chemistry due to its abil-

ity to act as starting compound in the preparation of a wide variety of complexes.¹³ In the light of these precedents, we decided to use it in order to prepare our osmaligand. Treatment of toluene solutions of **1** with 3.3 equiv of 3-(2-pyridyl)pyrazol (3-py-pzH), in the presence of (piperidinomethyl)polystyrene, for 5.5 h, under reflux lead to **2H** (eq 1), which was isolated as a dark green solid in 52% yield. The most noticeable spectroscopic features of this species, in benzene-*d*₆, at room temperature are a broad signal at 17.60 ppm, in the ¹H NMR spectrum, corresponding to the NH-nitrogen atom and a singlet at -2.2 ppm, in the ³¹P{¹H} NMR spectrum, due to the coordinated phosphine. In contrast to **1**, the *d*²-hexahydride complex OsH₆(P^{*i*}Pr₃)₂ reacts with 3-py-pzH to give the osmium(IV)-trihydride derivative OsH₃{κ²-*N,N*-(3-py-pz)}(P^{*i*}Pr₃)₂.¹⁴

Complex **2H** can be deprotonated by the bridging methoxy groups of the dimer [Ir(μ-OMe)(η⁴-COD)]₂ (COD = 1,5-cyclooctadiene). The deprotonation produces the coordination of two free nitrogen atoms of the metalloligand to iridium. Thus, the addition of 0.5 equiv of this dimer to acetone solutions of **2H** affords the heterobimetallic derivative **3** (eq 2), which was isolated as a dark brown solid in 78% yield.

Complex **3** was characterized by X-ray diffraction analysis. Figure 1 shows a view of the molecule. The structure proves the formation of the osmaligand and its coordination to the Ir(η⁴-COD) moiety. The metalloligand can be rationalized as an octahedral osmium(II) complex containing a triisopropylphosphine ligand and three different 3-(2-pyridyl)pyrazolate groups; chelate, chelate-bridge, and bridge. The phosphine ligand is disposed *trans* to the pyridyl group of the chelate ligand (P(1)-Os-N(9) = 174.3(2)°), whereas the pz-ring is located *trans* to the pz-ring of the chelate-bridge ligand (N(7)-Os-N(4) = 166.5(3)°). The pyridyl group of the latter lies *trans* to the bridging ligand (N(6)-Os-N(2) = 164.1(3)°). This geometry disposes three nitrogen atoms with free electron pairs, the pyrazolic N(1) and N(5) and pyridinic N(3), which can act as a pincer. Nevertheless, the metalloligand only coordinates the pyrazolic N(1) and N(5) atoms to the Ir(η⁴-COD) moiety (N(1)-Ir-N(5) = 89.5(3)°) to form a square-planar iridium(I) species, in agreement with the high stability of the *d*⁸-

compounds of this geometry. If M(1) is the midpoint of the coordinated C(25)-C(26) double bond and M(2) is the midpoint of the related C(29)-C(30) bond, the N(1)-Ir-M(2) and N(5)-Ir-M(1) angles are 175.0° and 173.3°, respectively. The 1,5-cyclooctadiene ligand takes its customary “tub” conformation. The coordinated bonds have lengths of 1.426(15) (C(25)-C(26)) and 1.392(15) (C(29)-C(30)) Å, which are longer than the C-C double bonds in the free diene (1.34 Å),¹⁵ in accordance with the usual Chatt-Dewar-Duncanson model. In agreement with the lack of symmetry of the molecule, the ¹H NMR spectrum in benzene-*d*₆ at room temperature and in toluene-*d*₈ at -50°C displays four olefinic C(sp²)-H resonances. Two of them appear together at about 3.4 ppm, while the other two resonances are observed at about 4.7 and 2.8 ppm. Consistently, the ¹³C{¹H} NMR spectrum in fluorobenzene at -30°C shows four singlets at 69.0, 66.8, 66.2, and 57.6 ppm for the C(sp²) carbon atoms of the diene. The separation between the iridium atom and the core of the metalloligand is long, 3.9317(6) Å.

Figure 1. Molecular diagram of complex **3** (50% probability ellipsoids). All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Os-P(1) = 2.326(3), Os-N(2) = 2.132(8), Os-N(4) = 2.048(9), Os-N(6) = 2.083(8), Os-N(7) = 2.075(9), Os-N(9) = 2.157(8), Ir-N(1) = 2.131(8), Ir-N(5) = 2.079(9), C(25)-C(26) = 1.426(15), C(29)-C(30) = 1.392(15); P(1)-Os-N(9) = 174.3(2), N(4)-Os-N(6) = 77.9(3), N(7)-Os-N(9) = 77.4(3), N(1)-Ir-N(5) = 89.5(3), N(1)-Ir-M(2) = 175.0, N(5)-Ir-M(1) = 173.3, M(1)-Ir-M(2) = 86.4.

Dehydrogenation of Secondary and Primary Alcohols and Diols. Complex **3** is a catalyst precursor for the base-free and acceptorless dehydrogenation of the above mentioned hydrogen donors. As expected the rate of the reaction increases as the precursor concentration increases (see Figure S1), reaching an optimal equilibrium between conversion and time required when the catalyst loading was 5% mol. Thus, the reactions were performed in toluene at 100 °C, using a substrate concentration of 0.19 M and a 5% mol of iridium complex.

Table 1 collects the studied secondary alcohols and the yields of their dehydrogenation reactions to the corresponding ketones (eq 3), after 18 h. 1-Phenylethanol (run 1) and related alcohols with a substituent at the phenyl groups (runs 2-6) are efficiently dehydrogenated into the ketones with yields between 63% and 95%. Under the same conditions, the iridium complex Ir{κ²-*N,N*-[3-py-pz]}(η⁴-COD)¹⁶ affords 15% of acetophenone, demonstrating that the metalloligand **2** is more

efficient than the 3-(2-pyridyl)pyrazolate ligand from a catalytic point of view. Chloride and methyl substituents at the *para* position have little influence in the amount of formed ketone (runs 2 and 3), while methoxy clearly favors the dehydrogenation. Jones and co-workers have conversely observed that, in the presence of nickel(II) precursors supported by tris(3,5-dimethylpyrazolyl)borate and 2-hydroxyquinolines, *para*-substituted 1-phenylethanol alcohols bearing electron-donating groups react much more slowly than those with electron-withdrawing substituents.¹⁷ In the presence of **3**, the substituent of the phenyl group influences the dehydrogenation when is close to the alcohol function, decreasing the amount of formed ketone. The same trend has been observed for the dehydrogenations of methyl-substituted 1-phenylethanol alcohols catalyzed by the osmium precursor $\text{OsH}_3\{\kappa^2\text{-}N_{\text{py}}, N_{\text{imine}}^-\text{(BMPI)}\}(\text{P}^i\text{Pr}_3)_2$ (BMPI = 1,3-bis(6'-methyl-2'-pyridylimino)isoindolate).¹⁸ The increase of the steric hindrance in the vicinity of the OH group certainly hinders the dehydrogenation. Thus, diphenylmethanol (run 7) is dehydrogenated with the same efficiency (61%) as 1-(*o*-tolyl)ethanol (63%; run 6); i.e., worse than 1-phenylethanol (78%). For the trihydride-Os-BMPI precursor, however, the adverse impact resulting from the increase of the steric hindrance in the proximity of the functional group is compensated for the higher stability of benzophenone with regard to acetophenone. Thus, in contrast to **3**, it oxidizes 1-diphenylmethanol better than 1-phenylethanol (77% versus 60%).¹⁸ Alcohols with two alkyl groups, such as 2-octanol and 1-cyclohexylethanol (runs 8 and 9) are dehydrogenated worse than diphenylmethanol. 2-Octanone and cyclohexyl methyl ketone are obtained in 40% and 50% yield, respectively. Complex **3** also dehydrogenates functionalized alcohols. 1-(4-Pyridyl)ethanol (run 10), 1-(3-pyridyl)ethanol (run 11), and 1-(2-furyl)ethanol (run 12) are transformed into the corresponding ketones and molecular hydrogen in 31%, 45%, and 56% yield, respectively. The increase in the amount of produced hydrogen as the heteroatom of the heterocycle approaches to the alcohol function agrees well with that observed for the iron precursor $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{CO})_2$ in the presence of NaH; while 2-pyridylmethanol derivatives are efficiently dehydrogenated, 4-pyridylmethanol and 3-pyridylmethanol do not undergo oxidation under the same conditions.^{8e}

Table 1. Acceptorless and Base-Free Dehydrogenation of Secondary Alcohols Catalyzed by **3^a**

Run	Substrate	Product	Yield (%) ^b
1			78
2			81
3			71
4			95

5			77
6			63
7			61
8			50
9			40
10			31
11			45
12			56

^a Conditions: Complex **3** (0.0093 mmol); substrate (0.19 mmol); toluene (1 mL) heated at 100 °C for 18 h. ^b Conversions were calculated from the relative peak area integrations of the reactant and product in the GC spectra.

Dehydrogenation of primary alcohols is more challenging than the dehydrogenation of secondary alcohols, since the aldehydes resulting from the former can generate inactive carbonyl complexes.¹⁹ Alternatively to aldehydes, these alcohols form esters as a consequence of a dehydrogenative homocoupling.²⁰ Complex **3** promotes both processes: the dehydrogenation to aldehydes (eq 4) and the dehydrogenative homocoupling to yield esters (eq 5). The reactions were performed under the same conditions as those used for promoting the dehydrogenation of secondary alcohols. Table 2 collects the studied alcohols, the percentage of alcohol dehydrogenated after 18 h, the formed oxidized products, and the percentages of alcohol transformed into each one of them; i.e., the percentage of molecular hydrogen generated according to eqs 4 and 5. Benzyl alcohol (run 1) and related alcohols with a substituent at the phenyl group (runs 2-7) are efficiently dehydrogenated in 86%-97%. The products resulting from the oxidation show a marked dependence upon the substituents. Electron donating groups at *para* position favor the dehydrogenation according to eq 4 and therefore the formation of aldehydes. However, electron withdrawing substituents benefit the generation of esters; i.e., the dehydrogenation through eq 5. There is a decreasing linear relationship between the percentage of alcohol

Table 2. Acceptorless and Base-Free Dehydrogenation of Primary Alcohols Catalyzed by **3**^a

Run	Substrate	Dehydrogenated alcohol (%) ^b	Alcohol transformed into			
			Aldehyde (%) ^b		Ester (%) ^b	
1		91		76		15
2		95		17		78
3		97		62		35
4		91		88		3
5		87		82		5
6		86		70		16
7		56		48		8
8		26		6		20
9		45		11		34
10		42		34		8
11		36		28		6

^a Conditions: Complex **3** (0.0093 mmol); substrate (0.19 mmol); toluene (1 mL) heated at 100 °C for 18 h. ^b Calculated by ¹H NMR spectroscopy.

transformed into aldehyde according to eq 4 and the Hammett σ_p values of the substituent,²¹ which is consistent with the increasing linear relationship between the percentage of alcohol transformed into ester according to eq 5 and the above mentioned values (Figure 2).

The position of the substituent mainly influences the amount of generated molecular hydrogen (runs 5-7), decreasing as the substituent approaches to the alcohol function, i.e., $p \approx m > o$ (runs 5 $\approx$ 6 > 7). Cyclohexylmethanol (run 8) and 1-octanol (run 9) are also dehydrogenated, although in lower extension (26% and 45%, respectively). In these cases, the correspond-

ing ester is the main oxidation product. In contrast, 2-furanylmethanol (run 10) and 3-pyridylmethanol (run 11) are dehydrogenated in 42% and 36%, respectively, mainly generating the aldehyde.

Figure 2. Percentages of alcohol transformed into aldehyde (green ■) and ester (red ●) as a function of the Hammett σ_p values for the dehydrogenation of *p*-substituted benzyl alcohols.

Complex **3** also dehydrogenates diols to lactones. The presence of a phenyl group in the substrate favors the process as has been shown for secondary and primary alcohols in Tables 1 and 2. Thus, 1,2-phenylenedimethanol gives 1-isobenzofuranone and molecular hydrogen in quantitative yield, after 18 h (eq 6), while 1,5-pentanediol affords tetrahydro-2*H*-pyran-2-one in 35% yield under the same conditions and the same time (eq 7). This class of reaction is of particular interest, since functionalized lactones are ubiquitous frameworks in a variety of biologically active natural products. Several catalysts have been developed for the reaction in the presence of hydrogen acceptors.^{20a,22} Catalysts working in the presence of bases are also known,²² while efficient systems under base-free and acceptorless conditions are more rare.^{20b,24}

Cyclooctatriene is detected during the catalysis by GC-MS. This suggests the formation of a dihydride-iridium(III) species stabilized by a pincer-N,N,N-osmaligand. Pincer complexes active in acceptorless dehydrogenation of alcohols are known.²⁵ This (N,N,N)IrH₂ species (**A**) should be the result of the dehydrogenation of the coordinated diene of **3** and of the coordination of the free nitrogen atom to the iridium center (Scheme 1) and can be viewed as a N,N,N-counterpart of the known dihydride (PCP)IrH₂ complexes, which promote the acceptorless dehydrogenation of alkanes.²⁶ Complex **A** would promote the dehydrogenation of the alcohols through the cycle shown in Scheme 1. The addition of the O-H bond of the alcohols to one of the Ir-H bonds of **A** should give the hydride-dihydrogen intermediate **B** containing an alkoxy ligand.

The addition could involve only one alcohol molecule or a dimer formed via O-H...O hydrogen bond. Previous relevant DFT mechanistic studies have revealed that *proton shuttle* type transition states, involving a molecule of alcohol as a *proton bridge*, significantly decrease the activation energy of the O-H rupture.²⁷ Once complex **B** is formed, the dissociation of the coordinated hydrogen molecule should lead to the hydride-alkoxide **C**. Then, this intermediate could undergo a β -hydrogen elimination reaction of the alkoxide group to afford the corresponding ketone or aldehyde and to regenerate **A**.

Scheme 1. Proposed catalytic cycle for the dehydrogenation of secondary alcohols.

Esters, as alternative products to aldehydes in the dehydrogenation of primary alcohols, seem to be a result of the transitory formation of hemiacetals. These compounds can be generated by means of the reaction of intermediate **B** with a molecule of aldehyde previously formed, according to eq 8. The carbon atom of the carbonyl group of the aldehyde removes the coordinated alkoxide group, whereas the oxygen atom abstracts the proton of the dihydrogen ligand. In agreement with this, it should be mentioned that, in a consistent manner with Figure 2, the natural bond orbital charge (b3lyp(GD3)-311G**) on the carbon atom of the carbonyl group of the aldehyde increases as the Hammett σ_p value also increases (See Table S1) and that the protic character of the coordinated hydrogen molecule is a well known property of these ligands.²⁸ Once the hemiacetal and **A** are formed, the latter can dehydrogenate to the ester as to any other alcohol.

CONCLUDING REMARKS

This study has revealed that the reaction of the known complex $\text{OsH}_2\text{Cl}_2(\text{P}^i\text{Pr}_3)_2$ with 3-(2-pyridyl)pyrazol gives rise to an osmium(II) compound, which can act as a N,N-bidentate or N,N,N-pincer osmaligand by deprotonation. Thus, its coordination to iridium has allowed us to stabilize an efficient catalyst precursor for base-free and acceptorless dehydrogenation of secondary and primary alcohols and diols, which leads to ketones, aldehydes or esters, and lactones, respectively. The presence of a phenyl group in the substrates favors the reactions. The products of the dehydrogenation of benzyl alcohols bearing a substituent at the phenyl group shows a marked dependence upon the Hammett σ_p value of the substituent, which is consistent with the transitory formation of hemiacetals in the dehydrogenative homocoupling to generate esters.

In conclusion, a novel osmaligand, which allows to stabilize catalysts for base-free and acceptorless dehydrogenation of alcohols and diols has been discovered.

EXPERIMENTAL SECTION

General Information. The reactions were carried out under moisture- and oxygen-free atmosphere using dried solvents and Schlenk-tube techniques. Instrumental methods, X-ray information, and DFT computational details are given in the Supporting Information. In the NMR spectra, chemical shifts (expressed in parts per million) are referenced to residual solvent peaks (^1H , $^{13}\text{C}\{^1\text{H}\}$) or external H_3PO_4 (^{31}P) and coupling constants (J) are given in hertz. $\text{OsH}_2\text{Cl}_2(\text{P}^i\text{Pr}_3)_2$ ²⁹ and $[\text{Ir}(\mu\text{-OMe})(\eta^4\text{-COD})]_2$ ³⁰ were prepared by previously published methods.

Reaction of $\text{OsCl}_2\text{H}_2(\text{P}^i\text{Pr}_3)_2$ (1**) with 3-(2-pyridyl)pyrazol: Preparation of **2H**.** A solution of **1** (200 mg, 0.343 mmol) in toluene (10 mL) was treated with 3-(2-pyridyl)pyrazol (164.2 mg, 1.131

mmol) and (piperidinomethyl)polystyrene (323 mg, 1.131 mmol). The resulting mixture was refluxed for 5.5 h, getting a dark green solution. After cooling at room temperature the solution was filtered evaporated to dryness, affording a dark green residue. Further purification was carried out by silica gel (230-400 mesh, eluted previously with a 20% solution of NEt_3 in pentane) column chromatography using a 1:1 mixture of pentane and CH_2Cl_2 , followed by precipitation in pentane, giving a dark green solid. Yield: 140 mg (52%). Anal. calcd. for $\text{C}_{33}\text{H}_{40}\text{N}_9\text{OsP}$: C, 50.56; H, 5.14; N, 16.08; found: C, 50.30; H, 4.86; N, 16.37. HRMS (electrospray, m/z) calcd for $\text{C}_{33}\text{H}_{39}\text{N}_9\text{NaOsP}$ [$\text{M-H}+\text{Na}$]⁺: 807.2574; found: 807.2576. ^1H NMR (300 MHz, C_6D_6 , 298 K): δ 17.60 (br, 1H, N-H), 8.47 (d, $J_{\text{H-H}} = 4.1$, 1H, py), 8.41 (d, $J_{\text{H-H}} = 2.1$, 1H, pz), 8.35 (d, $J_{\text{H-H}} = 2.1$, 1H, pz), 7.97 (d, $J_{\text{H-H}} = 5.7$, 1H, py), 7.13 (d, $J_{\text{H-H}} = 1.8$, 1H, pz), 7.00-6.89 (m, 5H, 1H pz and 4H py), 6.83 (d, $J_{\text{H-H}} = 1.8$, 1H, pz), 6.72 (d, $J_{\text{H-H}} = 5.6$, 1H, py), 6.44 (dd, $J_{\text{H-H}} = 7.7$, $J_{\text{H-H}} = 0.8$, 1H, py), 6.37 (t, $J_{\text{H-H}} = 7.7$, 1H, py), 6.29 (t, $J_{\text{H-H}} = 7.7$, 1H, py), 6.17 (d, $J_{\text{H-H}} = 2.1$, 1H, pz), 5.80 (m, 1H, py), 5.61 (1H, $J_{\text{H-H}} = 6.5$, 1H, py), 2.83 (m, 3H, $\text{PCH}(\text{CH}_3)_2$), 1.11 (dd, $J_{\text{H-H}} = 6.9$, $J_{\text{H-P}} = 7.5$, 9H, $\text{PCH}(\text{CH}_3)_2$), 1.07 (dd, $J_{\text{H-H}} = 7.2$, $J_{\text{H-P}} = 7.5$, 9H, $\text{PCH}(\text{CH}_3)_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.47 MHz, C_6D_6 , 298 K): δ 161.8 (s, C), 158.2 (s, C), 154.4 (s, CH py), 151.6 (s, C), 150.6 (s, C), 150.3 (s, CH py), 148.3 (s, C), 147.4, 144.5, 144.0 (s, C), 140.3, 137.8, 136.3, 135.0, 132.3, 122.2, 120.2, 119.9, 119.5, 117.3, 109.9, 104.3 (all s, CH py and pz), 26.5 (d, $J_{\text{C-P}} = 24.1$, $\text{PCH}(\text{CH}_3)_2$), 20.0 (s, $\text{PCH}(\text{CH}_3)_2$). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.49 MHz, C_6D_6 , 298 K): δ -2.2.

Reaction of **2H with $[\text{Ir}(\mu\text{-OMe})(\eta^4\text{-COD})]_2$: Preparation of **3**.** A solution of **2H** (140 mg, 0.18 mmol) in acetone (5 mL) was treated with $[\text{Ir}(\mu\text{-OMe})(\eta^4\text{-COD})]_2$ (59 mg, 0.09 mmol) and the resulting mixture was stirred at room temperature for 18 hours. After this time, the dark brown solution was evaporated to dryness to afford a dark-brown residue. Methanol was added to afford a dark-brown solid, which was washed with methanol (2 x 1 mL) and dried in vacuo. Yield: 150 mg (78%). Anal. calcd. for $\text{C}_{41}\text{H}_{51}\text{IrN}_9\text{OsP}$: C, 45.46; H, 4.74; N, 11.63; found: C, 45.24; H, 4.43; N, 11.92. HRMS (electrospray, m/z) calcd for $\text{C}_{41}\text{H}_{51}\text{IrN}_9\text{OsP}$ [M]⁺: 1085.3248; found: 1085.3276. IR (cm^{-1}): $\nu(\text{C}=\text{N})$, $\nu(\text{C}=\text{C})$ 1603 (m), 1586 (m). ^1H NMR (300 MHz, C_6D_6 , 298 K): δ 8.73 (d, $J_{\text{H-H}} = 7.8$, 1H, py), 8.52 (m, 1H, pz), 8.32 (d, $J_{\text{H-H}} = 1.9$, 1H, pz), 7.90 (d, $J_{\text{H-H}} = 6$, 1H, py), 7.75 (d, $J_{\text{H-H}} = 2.7$, 1H, pz), 7.34 (td, $J_{\text{H-H}} = 6.0$, $J_{\text{H-H}} = 1.9$, 1H, py), 7.05 (d, $J_{\text{H-H}} = 2.1$, 1H, pz), 6.85-6.63 (m, 5H, 2H pz and 3H py), 6.56 (d, $J_{\text{H-H}} = 1.8$, 1H, py), 6.49 (d, $J_{\text{H-H}} = 6$, 1H, py), 6.40-6.26 (m, 2H, py), 5.85-5.73 (m, 2H, py), 4.67 (br, 1H, =CH COD), 3.71 (m, 3H, $\text{PCH}(\text{CH}_3)_2$), 3.5 (br, 2H, =CH COD), 2.80 (br, 1H, =CH COD), 2.28 (m, 3H, CH_2 COD), 1.95 (br, 2H, CH_2 COD), 1.46 (m, 3H, CH_2 COD), 1.30 (dd, $J_{\text{H-H}} = 7.2$, $J_{\text{H-P}} = 12.0$, 9H, $\text{PCH}(\text{CH}_3)_2$), 1.21 (dd, $J_{\text{H-H}} = 7.2$, $J_{\text{H-P}} = 11.7$, 9H, $\text{PCH}(\text{CH}_3)_2$). ^1H NMR (300 MHz, C_7D_8 , 223 K, olefinic protons): δ 4.7 (br, 1H, =CH), 3.4 (br, 2H, =CH), 2.8 (br, 1H, =CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.47 MHz, C_6D_6 , 298 K): δ 160.9 (s, C), 157.2 (s, C), 156.9 (s, C), 154.7 (s, CH py), 154.6 (s, C), 153.0 (s, C), 150.3 (s, C), 149.5, 149.0, 146.8, 140.1, 136.0, 135.1, 134.7, 130.4, 122.8, 120.9, 120.4, 118.1, 118.1, 116.5, 108.5, 105.3, 104.7 (all s, CH py and pz), 32.9 (s, CH_2 , COD), 29.4 (s, CH_2 , COD), 27.5 (d, $J_{\text{C-P}} = 23.4$, $\text{PCH}(\text{CH}_3)_2$), 20.9, 20.1 (both s, $\text{PCH}(\text{CH}_3)_2$). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.49 MHz, C_6D_6 , 298 K): δ -4.0.

General procedure for the catalytic dehydrogenations. A solution of complex **3** (0.0093 mmol) and the corresponding alcohol (0.19 mmol) in toluene (1 mL) was placed in a Schlenk flask equipped with

a condenser and an oil bubbler. The reaction mixture was heated at 100 °C for 18 h. After this time the solution was cooled to room temperature, and the extent of the reaction was determined by different methods depending on the nature of the alcohol. Reactions were run in duplicate.

For secondary alcohols the extent of the conversion to ketones was determined by GC on an Agilent Technologies 6890N gas chromatograph with a flame ionization detector, using a HP-Innowax column (25 m x 0.2 mm, with 0.4 µm film thickness). The oven conditions used are as follows: 80 °C (hold 5 min) to 200 °C at 15 °C/min (hold 7 min), except for diphenylmethanol (150 °C (hold 5 min) to 240 °C at 15 °C/min (hold 13 min)). The identity of the ketones was confirmed by comparison of their retention times with those of pure products, as well as by GC-MS analyses. In the case of primary alcohols and diols, the crude solution was evaporated under reduced pressure to obtain an oil. Then, 0.187 mmol (20 µL) of 1,1,2,2-tetrachloroethane was added as an internal standard, and the mixture was dissolved in CDCl₃ and analyzed by ¹H NMR spectroscopy. The formed aldehydes, esters and lactones were characterized by ¹H NMR spectroscopy.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications web site:

General information, crystallographic data, computational details, and NMR spectra (pdf).

Cartesian coordinates of the optimized structures (XYZ).

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interests

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