Mer-, Fac-, and Bidentate-Coordination of an Alkyl-POP Ligand in the Chemistry of Nonclassical Osmium-Hydrides

Miguel A. Esteruelas, Cristina García-Yebra, Jaime Martín, and 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

Nonclassical and classical osmium polyhydrides containing the diphosphine 9,9-dimethyl-4,5-bis(diisopropylphosphino)xanthene ($\text{xant}(\text{P}^i\text{Pr}_2)_2$), coordinated $\kappa^3\text{-mer}$, $\kappa^3\text{-fac}$, and $\kappa^2\text{-P,P}$, have been isolated during the cyclic formation of H_2 by means of the sequential addition of H^+ and H^- or H^- and H^+ to the classical trihydride $\text{OsH}_3\text{Cl}\{\text{xant}(\text{P}^i\text{Pr}_2)_2\}$ (**1**). This complex adds H^+ to form the compressed dihydride-dihydrogen $[\text{OsCl}(\text{H}\cdots\text{H})(\eta^2\text{-H}_2)\{\text{xant}(\text{P}^i\text{Pr}_2)_2\}]^+$ (**2**). Under argon, cation **2** losses H_2 and the resulting unsaturated fragment dimerizes to give $[(\text{Os}(\text{H}\cdots\text{H})\{\text{xant}(\text{P}^i\text{Pr}_2)_2\})_2(\mu\text{-Cl})_2]^{2+}$ (**3**). During the transformation the phosphine changes its coordination mode from *mer* to *fac*. The benzofuran counterpart of **1**, $\text{OsH}_3\text{Cl}\{\text{dbf}(\text{P}^i\text{Pr}_2)_2\}$ (**4**)

(dbf(P^iPr_2)₂ = 4,6-bis(diisopropylphosphino)dibenzofuran), also adds H^+ to afford the benzofuran counterpart of **2**, $[OsCl(H\cdots H)(\eta^2-H_2)\{xant(P^iPr_2)_2\}]^+$ (**5**), which in contrast to the latter is stable and does not dimerize. Acetonitrile breaks the chloride bridge of **3** to form the dihydrogen $[OsCl(\eta^2-H_2)(CH_3CN)\{xant(P^iPr_2)_2\}]^+$ (**6**), regenerating the *mer* coordination of the diphosphine. The hydride ion also breaks the chloride bridge of **3**. The addition of KH to **3** leads to **1**, closing a cycle for the formation of H_2 . Complex **1** reacts with a second hydride ion to give $OsH_4\{xant(P^iPr_2)_2\}$ (**7**) as consequence of the displacement of the chloride. Similarly to the latter, the oxygen atom of the *mer*-coordinate diphosphine of **7** has tendency to be displaced by the hydride ion. Thus the addition of KH to **7** yields $[OsH_5\{xant(P^iPr_2)_2\}]^-$ (**8**), containing a κ^2 -P,P-diphosphine. Complex **8** is easily protonated to afford $OsH_6\{xant(P^iPr_2)_2\}$ (**9**), which releases H_2 to regenerate **7**, closing a second cycle for the formation of molecular hydrogen.

INTRODUCTION

The chemical behavior of a transition metal complex is determined by the central ion and by the ligands forming its coordination sphere. The groups surrounding the core govern the available electron density of the metal ion and the accessible space for performing the reactions. In some cases, the ligands also cooperate with the metal by means of a direct participation in the chemical transformations.¹ There are other ligands that change their properties during the reactions. This group includes ligands that modify their electronic donor ability while are adapted to the reaction medium by means of reversible transformations² and ligands that change their coordination mode to meet with the requirements of each stage of a multi-step process.

Hemilabile groups are the simplest class of ligands with the latter behavior. The reversible coordination-decoordination of the hemilabile donor atom allows the stabilization of highly reactive metal centers, which has a significant influence in the catalytic behavior of the complexes.³ Tridentate anionic PCP-diphosphines are situated in the opposite position. Although their *mer*-coordination allows them to stabilize complexes with unusual reactivity,⁴ the stability and rigidity of the pincer diminishes the adaptability of these ligands to the requirement of the sequential processes. In the search for more versatile diphosphines that could act as κ^3 -*fac* and bidentate groups, in addition to κ^3 -*mer*, flexible POP ethers have been also employed.⁵ Thus, Weller and co-workers have demonstrated that 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (xantphos) has the ability of changing its coordination fashion in several relevant rhodium- and iridium-mediated processes,⁶ such as the hydroacylation⁷ and carbothiolation⁸ of alkenes and alkynes and the dehydrocoupling of amineboranes.⁹

Transition metal polyhydrides are compounds having enough hydrogen atoms bonded to the metal center of a L_nM fragment to form at least two different types of ligands.¹⁰ These ligands are generally classified in four types depending upon the separation between the coordinated hydrogens: Kubas type dihydrogens (0.8 – 1.0 Å), elongated dihydrogens (1.0 – 1.3 Å), compressed dihydrides (1.3 – 1.6 Å), and classical hydrides (> 1.6 Å).^{10,11} Polyhydrides of the platinum group metals offer new exciting conceptual challenges and the possibility of interacting with different fields,¹⁰ including the conversion and storage of regenerative energy.¹² In this respect, osmium polyhydrides are of particular interest. In addition to promote the dehydrocoupling of amineboranes,¹³ their ability to activate C-H, N-H, and C-N bonds of a wide range of organic molecules, including 2-azetidinones¹⁴ and nucleobases¹⁵, allow them to interact with organic synthetic chemistry,¹⁶ drugs design,^{14a} and material science.¹⁷ Although the

chemistry of the osmium polyhydrides is rich, the complexes of this type with pincer ligands are a noticeable exception,¹⁰ being reduced to a few complexes with PNP,¹⁸ P(olefin)P¹⁹ and P(Csp³)P²⁰ ligands. Recently, we have reported that the reactions of complexes OsCl₂{xant(PⁱPr₂)₂}(κ-S-DMSO) (xant(PⁱPr₂)₂ = 9,9-dimethyl-4,5-bis(diisopropylphosphino)xanthene) and OsCl₂{dbf(PⁱPr₂)₂}(κ-S-DMSO) (dbf(PⁱPr₂)₂ = 4,6-bis(diisopropylphosphino)dibenzofuran) with molecular hydrogen, in the presence of Et₃N, lead to the classical trihydride derivatives OsH₃Cl{xant(PⁱPr₂)₂}²¹ and OsH₃Cl{dbf(PⁱPr₂)₂}^{16d} containing a pincer POP-ligand. Our interest in determining the influence of the different coordination modes of flexible pincer ligands on the nature of the H-donor ligands of Osmium polyhydrides prompted us to study the protonation of the hydride ion, kinetically controlled by OsH₃Cl{xant(PⁱPr₂)₂}. The kinetically controlled formation of molecular hydrogen by the exothermic neutralization of the hydride ion is a process of great interest in connection with the storage of hydrogen in solid materials, which would become a safe and efficient way to store energy for both stationary and mobile applications.²²

This paper shows that the ligand 9,9-dimethyl-4,5-bis(diisopropylphosphino)xanthene changes its coordination mode to stabilize Kubas type dihydrogens, elongated dihydrogens, compressed dihydrides, and classical hydrides, which act as intermediates to generate molecular hydrogen from H⁺ and H⁻, in the presence of osmium polyhydrides. In addition, it proves that the *mer* coordination favors nonclassical interactions between the coordinated hydrogen atoms, with regard to the *fac* and bidentate coordination modes.

RESULTS AND DISCUSSION

Scheme 1 summarizes the procedures used to generate molecular hydrogen starting from the classical trihydride $\text{OsH}_3\text{Cl}\{\text{xant}(\text{P}^i\text{Pr}_2)_2\}$ (**1**). The *route a* involves the sequential addition of H^+ and H^- whereas the *route b* involves the opposite addition.

Scheme 1. Formation of H_2 by sequential addition of H^+ and H^- or H^- and H^+ to $\text{OsH}_3\text{Cl}\{\text{xant}(\text{P}^i\text{Pr}_2)_2\}$ (**1**) in two related cycles.

Complex **1** adds a proton in agreement with the Lewis base character of the saturated polyhydrides. Under hydrogen atmosphere, the addition of 1.0 equiv of $\text{HBF}_4 \cdot \text{OEt}_2$ to **1** in dichloromethane- d_2 leads to the cation $[\text{OsCl}(\text{H}\cdots\text{H})(\eta^2\text{-H}_2)\{\text{xant}(\text{P}^i\text{Pr}_2)_2\}]^+$ (**2**). The presence of four hydrogen atoms bonded to the metal center is supported by the ^1H NMR spectrum of the resulting solution, which contains a broad signal at -10.71 ppm with an integrated intensity of 4. According to the existence of nonclassical interactions between the coordinated hydrogen atoms, this resonance exhibits a 400 MHz $T_1(\text{min})$ value of 40 ± 2 ms at 203 K. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows a singlet at 62.6 ppm. DFT calculations (energies calculated at the B3LYP(GD3)//6-31G(d,p)/SDD level with the Gaussian 09 program²³) reveal that there are two compressed dihydride-dihydrogen structures differing by $3.0 \text{ kcal}\cdot\text{mol}^{-1}$ (ΔG , 1 atm, 298.15 K): **2a** and **2b**. Figure 1 shows a view of these DFT-optimized structures. In both cases, the

diphosphine is *mer*-coordinated with P(1)-Os-P(2), O-Os-P(1), and O-Os-P(2) angles of 160.2°, 80.0°, and 80.2° for **2a** and 165.5°, 82.6°, and 82.4° for **2b**. The most stable structure **2a** shows the dihydrogen ligand (1.029 Å) at the perpendicular plane to the P-Os-P direction, *trans* disposed to the chloride, whereas the compressed dihydride (1.427 Å) lies *trans* to the oxygen atom of the diphosphine, almost parallel to the P-Os-P direction. In **2b**, the dihydrogen (1.091 Å) and the compressed dihydride (1.358 Å) ligands exchange their positions.

Figure 1 DFT optimized structures of **2a** and **2b**. Hydrogen atoms (except hydrides) are omitted for clarity. Selected bond lengths (Å) and angles (°): for **2a** Os-O = 2.307, Os-P(1) = 2.381, Os-P(2) = 2.384, Os-Cl = 2.438, H(1)-H(2) = 1.427, H(3)-H(4) = 1.029, O-Os-P(1) = 80.0, O-Os-P(2) = 80.2, P(1)-Os-P(2) = 160.2; for **2b** Os-O = 2.224, Os-P(1) = 2.390, Os-P(2) = 2.391, Os-Cl = 2.474, H(1)-H(2) = 1.091, H(3)-H(4) = 1.358, O-Os-P(1) = 82.6, O-Os-P(2) = 82.4, P(1)-Os-P(2) = 165.5.

The lability of the dihydrogen ligand in **2** suggests that it is of the Kubas type even though the separation between the two hydrogen atoms lies at the border between a Kubas-type dihydrogen and an elongated dihydrogen. Thus, complex **2** can be kept in dichloromethane, under hydrogen atmosphere, at room temperature, for a few hours. However, under argon, it loses the dihydrogen ligand to afford the dimer $[(\text{Os}(\text{H}\cdots\text{H})\{\text{xant}(\text{P}^i\text{Pr}_2)_2\})_2(\mu\text{-Cl})_2]^{2+}$ (**3**) which was

isolated as its yellow BF_4 -salt in 95% yield and characterized by X-ray diffraction analysis.²⁴

The structure (Figure 2) shows a change in the coordination mode of the diphosphine, which now coordinates in a κ^3 -*fac* fashion with O-Os-P(1), O-Os-P(2) and P(1)-Os-P(2) angles of $80.45(9)^\circ$, $82.32(9)^\circ$ and $107.72(5)^\circ$, respectively. The coordinated hydrogen atoms, separated by $1.36(6)$ (Å), lie *trans* to the oxygen atoms of the diphosphines forming a compressed dihydride.

The nonclassical nature of the OsH_2 -units was confirmed by the ^1H NMR spectrum in dichloromethane- d_2 , which shows a triplet ($^2J_{\text{H-P}} = 14.5$ Hz) at -9.53 ppm. In agreement with the H-H separation found by X-ray- diffraction analysis, this resonance exhibits a 400 MHz $T_1(\text{min})$ value of 63 ± 3 ms, at 243 K, and a $J_{\text{H-D}}$ value of 7 Hz which fit with H-H separations of 1.35 Å and 1.32 Å, respectively.²⁵ The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows a signal at 42.9 ppm.

Figure 2 ORTEP diagram of complex **3** with 50% probability ellipsoids. The counteranions, solvent molecules, and hydrogen atoms (except hydrides) are omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): Os-O = $2.156(3)$, Os-P(1) = $2.316(1)$, Os-P(2) = $2.295(1)$, H(1)-H(2) = $1.36(6)$, O-Os-centroid H(1)-H(2) = 169.65 , O-Os-P(1) = $80.45(9)$; O-Os-P(2) = $82.32(9)$, P(1)-Os-P(2) = $107.72(5)$.

The *fac*-coordination of the diphosphine in **3** is a determinant factor for the stabilization of the dimeric structure with regard to **2**, which is related to the flexibility of the xanthene group. In fact, the most rigid benzofuran stabilizes the OsH₄-species and prevents the formation of a counterpart dimer of **3**. Thus, under argon, the addition of 1.0 equiv of HBF₄·OEt₂ to OsH₃Cl{dbf(P^{*i*}Pr₂)₂} (**4**) in dichloromethane leads to the compressed dihydride-dihydrogen [OsCl(H···H)(η²-H₂){dbf(P^{*i*}Pr₂)₂}]BF₄ (**5**), which was isolated as a pale yellow solid in 85% yield (eq. 1). In contrast to **2**, this 4,6-bis(diisopropylphosphino)dibenzofuran counterpart is moderately stable under argon, in the solid state, and in dichloromethane and does not release molecular hydrogen to dimerize. Complex **5** was characterized by X-ray diffraction analysis. Its structure (Figure 3) is in full agreement with the optimized structure of the most stable isomer of **2**. As in the latter, the diphosphine is *mer*-coordinated with O-Os-P(1), O-Os-P(2) and P(1)-Os-P(2) angles of 78.66(9)°, 78.72(9)° and 157.23(4)° respectively. The dihydrogen ligand (H(3)-H(4) = 1.06(5) Å (X-ray), 0.976 Å (DFT)) lies at the perpendicular plane to the P-Os-P direction, *trans*-disposed to the chloride; and the compressed dihydride (1.10(7) Å (X-ray), 1.387 Å (DFT)) is situated *trans* to the oxygen atom of the diphosphine, almost parallel to the P-Os-P direction. In the ¹H NMR spectrum in dichloromethane-*d*₂, the OsH₄-unit displays a broad signal at -10.60 ppm, which exhibits a 400 MHz *T*₁(min) value of 40 ± 2 ms at 203 K, in agreement with **2**. The ³¹P{¹H} NMR spectrum contains a singlet at 65.3 ppm.

Figure 3. ORTEP diagram of complex **5** with 50% probability ellipsoids. The counteranions, solvent molecules, and hydrogen atoms (except hydrides) are omitted for clarity. Selected bond lengths (Å) and angles (°): Os-O = 2.092(3), Os-P(1) = 2.400(1), Os-P(2) = 2.403(1), H(3)-H(4) = 1.06(5), H(1)-H(2) = 1.10(7), Os-Cl = 2.415(1), O-Os-centroid H(1)-H(2) = 171.37, Cl-Os-centroid H(3)-H(4) = 178.09, O-Os-P(1) = 78.66(9), O-Os-P(2) = 78.72(9), P(1)-Os-P(2) = 157.23(4).

The coordination changes from κ^3 -*mer* to κ^3 -*fac* of the diphosphine is a requirement for the coordinative saturation of the metal center on the $[\text{OsClH}_2\{\text{xant}(\text{P}^i\text{Pr}_2)\}]^+$ fragment resulting from the dissociation of molecular hydrogen from **2**, since the steric hindrance experienced by the isopropyl substituents of the *mer*-coordinated diphosphines of two unsaturated fragments appears to prevent the dimerization. However, the coordination κ^3 -*mer* is clearly favored over the κ^3 -*fac*, when the metal center of a mononuclear complex is saturated. As a proof of concept, it should be mentioned that the chloride bridges of **3** are broken in acetonitrile to form the saturated dihydrogen complex $[\text{OsCl}(\eta^2\text{-H}_2)(\text{CH}_3\text{CN})\{\text{xant}(\text{P}^i\text{Pr}_2)_2\}]\text{BF}_4$ (**6**), which contains a κ^3 -*mer* coordinated diphosphine. This compound was isolated as a white solid, in almost quantitative yield, and characterized by X-ray diffraction analysis. The structure²⁶ (Figure 4) proves the *mer*-

coordination ($\text{O-Os-P(1)} = 83.08(6)^\circ$, $83.13(7)^\circ$; $\text{P(1)-Os-P(1)} = 165.85(13)^\circ$, $165.81(14)^\circ$) of the diphosphine. The dihydrogen ligand ($1.02(6) \text{ \AA}$ (X-ray), $0.985 \text{ \AA}$ (DFT)), which is almost parallel to the P-Os-P direction, lies *trans* to the chloride. In the ^1H NMR spectrum, in dichloromethane- d_2 , the coordinated hydrogen molecule displays a triplet ($^2J_{\text{H-P}} = 6 \text{ Hz}$) at -9.86 ppm. As expected for its Kubas type dihydrogen nature, this resonance exhibits a 300 MHz $T_1(\text{min})$ value of $21 \pm 1 \text{ ms}$, at 203 K, whereas the H-D coupling constant in the partially deuterated species is 20 Hz. These values allow to calculate H-H separations of $0.94 \text{ \AA}$ and $1.09 \text{ \AA}$, respectively,²⁵ which agree well with that obtained by X-ray diffraction analysis. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows a singlet at 27.2 ppm.

Figure 4. ORTEP diagram for one of the two molecules in the symmetry unit of complex **6** with 50% probability ellipsoids. The counteranions, solvent molecules, and hydrogen atoms (except hydrides) are omitted for clarity. Selected bond lengths ($\text{\AA}$) and angles ($^\circ$): $\text{Os-O} = 2.131(9)$, $\text{Os-P(1)} = 2.338(3)$, $\text{Os-Cl} = 2.441(4)$, $\text{Os-N} = 2.024(16)$, $\text{H(1)-H(2)} = 1.02(6)$, $\text{Cl-Os-centroid H(1)-H(2)} = 174.96$, $\text{O-Os-P(1)} = 83.08(6)$, $\text{P(1)-Os-P(1)} = 165.85(13)$.

The hydride ion also breaks the chloride bridges of **3**. The addition of KH to the tetrahydrofuran solutions of the dimer regenerates **1**, closing a cycle for the formation of molecular hydrogen by reaction of H^+ and H^- on the osmium center of **1** (*route a* in **Scheme 1**).

The hydride ion displaces the chloride ligand of **1** to afford the tetrahydride derivative $\text{OsH}_4\{\text{xant}(\text{P}^i\text{Pr}_2)_2\}$ (**7**). The classical nature of the coordinated hydrogen atoms of this previously reported compound was confirmed by X-ray diffraction analysis and DFT calculations.²¹ Similarly to chloride, the oxygen atom of the *mer*-coordinate diphosphine of the latter has tendency to be displaced by the hydride ion. The addition of KH to **7** in tetrahydrofuran leads to the anionic pentahydride $[\text{OsH}_5\{\text{xant}(\text{P}^i\text{Pr}_2)_2\}]^-$ (**8**), containing a κ^2 -P,P-bidentate diphosphine. In the presence of the crown ether 18-crown-6, yellow crystals of the $[\text{K}(\text{18-crown-6})]^+$ -salt were obtained in 66% yield. The X-ray diffraction structure (Figure 5) proves the bidentate coordination of the diphosphine, which acts with a P-Os-P bite angle of $109.46(3)^\circ$. The coordination polyhedron around the osmium atom can be idealized as a pentagonal bipyramid with the hydride H(5) and the P(1) atom of the diphosphine in axial positions ($\text{P}(1)\text{-Os-H}(5) = 165.6(16)^\circ$), whereas the P(2) atom and the remaining hydrides lie in the equatorial plane. The disposition of the phosphorous atoms is certainly enforced by the bidentate character of the diphosphine. In contrast to **8**, the related anion $[\text{OsH}_5(\text{P}^i\text{Pr}_3)_2]^-$ contains both monodentated phosphines at the axial positions of the bipyramid.²⁷ The structure also shows three hydrides pointing towards the potassium cation, which is slightly out of the plane of the crown ether. The ion pair is helped together through electrostatic interactions, enhanced by the ionic nature of cation and anion. In tetrahydrofuran the hydride ligands, as well as the phosphorous atoms of the diphosphine, rapidly exchange their positions even at 183 K. In agreement with this, the ^1H NMR spectrum shows a broad signal at -12.46 ppm, whereas the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum contains a singlet at 20.6 ppm. The classical hydride character of the coordinated hydrogen atoms is strongly supported by the 400MHz $T_1(\text{min})$ of the hydride resonance, 248 ms, at 208 K.

Figure 5. ORTEP diagram of complex **8** with 50% probability ellipsoids. The solvent molecules, and hydrogen atoms (except hydrides) are omitted for clarity. Selected bond lengths (Å) and angles (°): Os-O = 3.496(3), Os-P(1) = 2.309(1), Os-P(2) = 2.322(1), Os-K = 3.624(1), P(1)-Os-P(2) = 109.46(3), P(1)-Os-H(5) = 165.6(16).

Complex **8** is a strong Brønsted base which is even protonated by traces of water. The protonation leads to the hexahydride $\text{OsH}_6\{\text{xant}(\text{P}^i\text{Pr}_2)_2\}$ (**9**), also containing a P,P-bidentate diphosphine with the P atoms at a B site of the BAAB trapezoidal planes, which define its dodecaedral structure.^{21, 28} Complex **9** releases molecular hydrogen and coordinates the oxygen atom to regenerate the tetrahydride **7**, closing a second cycle for the formation of molecular hydrogen by reaction of H^- with H^+ on the metal center of the tetrahydride **7** (**route b** in **Scheme 1**).

CONCLUDING REMARKS

This study reveals that osmium-polyhydrides stabilized by the POP-pincer ligand 9,9-dimethyl-4,5-bis(diisopropylphosphine)xanthene sequentially add H^+ and H^- or H^- and H^+ to generate molecular hydrogen in a cyclic manner. During the process the diphosphine changes its coordination mode from $\kappa^3\text{-mer}$ to $\kappa^3\text{-fac}$ and $\kappa^2\text{-P,P-bidentate}$, depending upon the electronic

and steric requirements of the involved intermediates, to form both polyhydrides with nonclassical interactions and classical polyhydrides. The nonclassical interactions are favored by the tridentate coordination, in particular by the *mer*-disposition, whereas the classical polyhydrides are usual when the diphosphine is bidentate. The flexibility of the central xanthene group is a determinant factor for the behavior of the diphosphine.

EXPERIMENTAL SECTION

General Information. All reactions were carried out under argon with rigorous exclusion of air using Schlenk tube or glovebox techniques. Solvents were dried by the usual procedures and distilled under argon prior to use or obtained oxygen- and water-free from an MBraun solvent purification apparatus. The starting materials $[\text{OsH}_3\text{Cl}\{\text{xant}(\text{P}^i\text{Pr}_2)_2\}]$ (**1**),²¹ $[\text{OsH}_3\text{Cl}\{\text{dbf}(\text{P}^i\text{Pr}_2)_2\}]$ (**4**)^{16d} and $[\text{OsH}_4\{\text{xant}(\text{P}^i\text{Pr}_2)_2\}]$ (**7**)²¹ were prepared according to published methods. ^1H , $^{31}\text{P}\{^1\text{H}\}$, and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded on either a Bruker 300 ARX, Bruker Avance 300 MHz or a Bruker Avance 400 MHz instrument. 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 ($^{31}\text{P}\{^1\text{H}\}$). Coupling constants, J and N ($N = J_{\text{PH}} + J_{\text{P}^i\text{H}}$ for ^1H ; $N = J_{\text{PC}} + J_{\text{P}^i\text{C}}$ for ^{13}C) are given in hertz. Spectral assignments were achieved by ^1H - ^1H COSY, $^1\text{H}\{^{31}\text{P}\}$, ^{13}C APT, ^1H - ^{13}C HSQC and ^1H - ^{13}C HMBC experiments. Infrared spectra were recorded on a Perkin-Elmer Spectrum One or Perkin-Elmer Spectrum 100 FT-IR spectrometer, equipped with an ATR accessory, as neat solids. C, H, and N analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyzer. High-resolution electrospray mass spectra were acquired using a MicroTOF-Q hybrid quadrupole time-of-flight spectrometer (Bruker Daltonics, Bremen, Germany).

Formation of $[\text{OsCl}(\text{H}\cdots\text{H})(\eta^2\text{-H}_2)\{\text{xant}(\text{P}^i\text{Pr}_2)_2\}]\text{BF}_4$ (2**).** A solution of $[\text{OsH}_3\text{Cl}\{\text{xant}(\text{P}^i\text{Pr}_2)_2\}]$ (**1**) (50 mg; 0.073 mmol) in dichloromethane- d_2 (0.6 mL) was placed in a

screw-top NMR tube under H₂ atmosphere, and HBF₄·OEt₂ (11 µL; 0.081 mmol) was added. NMR spectra of the reaction solution showed immediate and quantitative formation of **2**. All attempts to isolate the new species were unsuccessful due to easy loss of hydrogen to form the dinuclear complex **3**.

HRMS (*electrospray*, *m/z*): calcd. for C₂₇H₄₄ClOOSp₂ [M]⁺: 673.2158, found: 673.2155. ¹H NMR (400 MHz, CD₂Cl₂, 233K): δ 7.76 (d, ³J_{HH} = 7.5, 2H, CH-arom), 7.67 (m, 2H, CH-arom), 7.53 (dd, ³J_{HH} = 7.6, ³J_{HH} = 7.5, 2H, CH-arom), 3.09 (m, 2H, PCH(CH₃)₂), 2.79 (m, 2H, PCH(CH₃)₂), 1.81 (s, 3H, C(CH₃)₂), 1.60 (dvt, *N* = 16.4, ³J_{HH} = 7.0, 6H, PCH(CH₃)₂), 1.56 (s, 3H, C(CH₃)₂), 1.45 (dvt, *N* = 18.4, ³J_{HH} = 7.6, 6H, PCH(CH₃)₂), 1.30 (dvt, *N* = 18.1, ³J_{HH} = 7.1, 6H, PCH(CH₃)₂), 0.75 (dvt, *N* = 17.2, ³J_{HH} = 7.1, 6H, PCH(CH₃)₂), -10.71 (br, 4H, OsH). ¹³C{¹H}-APT NMR (100.62 MHz, CD₂Cl₂, 233K): δ 155.4 (vt, *N* = 12.5, C-arom), 132.4 (vt, *N* = 5.9, C-arom), 132.0 (s, CH-arom), 131.9 (s, CH-arom), 127.7 (vt, *N* = 6.2, CH-arom), 119.8 (vt, *N* = 39.4, C-arom), 35.0 (s, C(CH₃)₂), 34.0 (s, C(CH₃)₂), 30.3 (s, C(CH₃)₂), 26.6 (vt, *N* = 33.1, PCH(CH₃)₂), 26.0 (vt, *N* = 35.4, PCH(CH₃)₂), 22.1 (s, PCH(CH₃)₂), 19.8 (s, PCH(CH₃)₂), 19.2 (s, PCH(CH₃)₂), 18.3 (s, PCH(CH₃)₂). ³¹P{¹H} NMR (161.98 MHz, CD₂Cl₂, 233K): δ 62.6 (s, POP). *T*_{1(min)} (ms, OsH, 400MHz, CD₂Cl₂, 203K): 40 ± 2 (-10.64 ppm).

Synthesis of [(Os(H···H){xant(P^{*i*}Pr₂)₂)₂(μ-Cl)₂][BF₄]₂ (3**).** HBF₄·OEt₂ (37 µL; 0.272 mmol) was added to a solution of [OsH₃Cl{xant(P^{*i*}Pr₂)₂}] (**1**) (130 mg; 0.194 mmol) in dichloromethane (5 ml). After stirring for 1 hour, the solvent was evaporated and the residue was treated with cold pentane (2 x 1 ml) to afford a pale yellow solid which was dried overnight under reduced pressure. Yield: 113 mg (95%). Yellow crystals suitable for X-ray diffraction were obtained by vapor diffusion of pentane into a CH₂Cl₂ solution. Anal. Calcd. for C₅₄H₈₄B₂Cl₂F₈O₂Os₂P₄: C, 42.84; H, 5.59. Found: C, 42.60; H, 5.82. IR (ATR, cm⁻¹): ν(BF) 1050 (s). ¹H NMR (500 MHz,

CD₂Cl₂, 293K): δ 7.83 (m, 4H, CH-arom), 7.55 (m, 8H, CH-arom), 2.58 (m, 4H, PCH(CH₃)₂), 2.11 (s, 3H, C(CH₃)₂), 2.08 (s, 3H, C(CH₃)₂), 1.99 (m, 4H, PCH(CH₃)₂), 1.24 (dd, $^3J_{HP}$ = 17.5, $^3J_{HH}$ = 7.0, 12H, PCH(CH₃)₂), 1.12 (dd, $^3J_{HP}$ = 17.0, $^3J_{HH}$ = 7.0, 12H, PCH(CH₃)₂), 1.02 (dd, $^3J_{HP}$ = 17.0, $^3J_{HH}$ = 7.3, 12H, PCH(CH₃)₂), 0.85 (dd, $^3J_{HP}$ = 15.1, $^3J_{HH}$ = 6.9, 12H, PCH(CH₃)₂), -9.53 (t, $^2J_{HP}$ = 14.5, 4H, OsH). ¹³C {¹H} NMR-APT (75.47 MHz, CD₂Cl₂, 293K): δ 159.7 (d, $^2J_{CP}$ = 8.7, C-arom), 137.8 (d, $^3J_{CP}$ = 4.6, C-arom), 130.9, 130.1 (both s, CH-arom), 128.3 (d, $^2J_{CP}$ = 6.1, CH-arom), 120.1 (d, $^1J_{CP}$ = 40.7, C-arom), 38.5 (s, C(CH₃)₂), 32.2 (s, C(CH₃)₂), 32.0 (d, $^1J_{CP}$ = 33.8, PCH(CH₃)₂), 25.0 (d, $^1J_{CP}$ = 36.3, PCH(CH₃)₂), 23.3 (s, C(CH₃)₂), 22.1 (s, PCH(CH₃)₂), 21.4 (s, PCH(CH₃)₂), 19.0 (s, PCH(CH₃)₂), 18.4 (d, $^2J_{CP}$ = 4.2, PCH(CH₃)₂). ³¹P {¹H} NMR (202.46 MHz, CD₂Cl₂, 293K): δ 42.9 (br, POP). $T_{1(\min)}$ (ms, OsH, 400MHz, CD₂Cl₂, 243K): 63 $\pm$ 3 (-9.53 ppm).

Determination of the J_{H-D} value for complex 3. A solution of DBF₄·D₂O was prepared by stirring HBF₄ (1 ml) and D₂O (1 ml) for 1 hour. Then, a solution of [OsH₃Cl{xant(PⁱPr₂)₂}] (**1**) (45 mg, 0.067 mmol) was placed in an NMR tube and treated with the freshly prepared solution of DBF₄ in D₂O (22 μ l; 0.080 mmol). After 24 hours, the ¹H{³¹P} NMR spectrum of the reaction mixture showed a triplet (J_{H-D} = 7.0 Hz), at -9.53 ppm, corresponding to the deuterated isotopomer of complex **3**.

Synthesis of [OsCl(H $\cdots$ H)(η^2 -H₂){dbf(PⁱPr₂)₂}]BF₄ (5**).** HBF₄·OEt₂ (14 μ L; 0.103 mmol) was added to a solution of [OsH₃Cl{dbf(PⁱPr₂)₂}] (**4**) (60 mg, 0.095 mmol) in dichloromethane (3 mL). After stirring for 15 min, at room temperature, the solvent was evaporated under reduced pressure and cold pentane (1 mL) was added to afford a pale yellow solid which was washed once with cold pentane (3 mL) and dried overnight under vacuum. Yield: 58 mg (85%). In order to confirm the structure of the cation, crystals suitable for X-ray diffraction analysis were

obtained by slow diffusion of pentane into a dichloromethane solution of complex

[OsCl(H $\cdots$ H)(η^2 -H₂){dbf(P^{*i*}Pr₂)₂}] [OTf]. Anal. Calcd. for C₂₄H₃₈BClF₄OOsP₂: C, 40.20; H, 5.34. Found: C, 39.99; H, 5.43. HRMS (*electrospray*, *m/z*): calcd. for C₂₄H₃₇OOsP₂ [M-HCl]⁺: 595.1930, found: 595.1935. IR (ATR, cm⁻¹): ν (B-F) 1049 (m). ¹H NMR (300 MHz, CD₂Cl₂, 293K): δ 8.25 (d, ³J_{HH} = 7.7, 2H, CH-arom), 8.00 (m, 2H, CH-arom), 7.77 (dd, ³J_{HH} = 7.7, ³J_{HH} = 7.6, 2H, CH-arom), 3.27 (m, 2H, PCH(CH₃)₂), 2.89 (m, 2H, PCH(CH₃)₂), 1.75 (dvt, *N* = 16.2, ³J_{HH} = 7.3, 6H, PCH(CH₃)₂), 1.57 (dvt, *N* = 19.9, ³J_{HH} = 7.5, 6H, PCH(CH₃)₂), 1.39 (dvt, *N* = 19.0, ³J_{HH} = 6.9, 6H, PCH(CH₃)₂), 0.91 (dvt, *N* = 18.1, ³J_{HH} = 7.0, 6H, PCH(CH₃)₂), -10.60 (br, 4H, OsH). ¹³C{¹H}-APT NMR (75.47 MHz, CD₂Cl₂, 293K): δ 161.0 (vt, *N* = 13.1, C-arom), 131.1 (s, CH-arom), 128.7 (vt, *N* = 5.4, CH-arom), 127.8 (s, CH-arom), 123.8 (vt, *N* = 6.5, C-arom), 115.0 (vt, *N* = 37.6, C-arom), 25.8 (vt, *N* = 30.7, PCH(CH₃)₂), 25.2 (vt, *N* = 29.3, PCH(CH₃)₂), 22.2 (s, PCH(CH₃)₂), 20.9 (vt, *N* = 4.5, PCH(CH₃)₂), 20.2 (s, PCH(CH₃)₂), 18.0 (s, PCH(CH₃)₂). ³¹P{¹H} NMR (121.49 MHz, CD₂Cl₂, 293K): δ 65.3 (s, POP). *T*_{1(min)} (ms, OsH, 400MHz, CD₂Cl₂, 203K): 40 $\pm$ 2 (-10.60 ppm).

Synthesis of [OsCl(η^2 -H₂)(CH₃CN){xant(P^{*i*}Pr₂)₂}] [BF₄] (6): [(Os(H $\cdots$ H){xant(P^{*i*}Pr₂)₂})₂(μ -Cl)₂][BF₄]₂ (3) (100 mg; 0.066 mmol) was dissolved in CH₃CN (3 mL) and stirred for 30 min after which the solvent was evaporated. The residue was precipitated with cold pentane (2 x 1 ml) to afford a white solid which was dried overnight under reduced pressure. Yield: 93 mg (99 %). Colorless crystals suitable for X-ray diffraction were obtained by vapor diffusion of pentane into a CH₂Cl₂ solution. Anal. Calcd. for C₂₉H₄₅BClF₄NOOsP₂: C, 43.64; H, 5.68; N, 1.76. Found: C, 43.26; H, 5.72; N, 1.79. IR (ATR, cm⁻¹): ν (C-N) 2288 cm⁻¹; ν (BF) 1048 (s). ¹H NMR (300 MHz, CD₂Cl₂, 293K): δ 7.64 (m, 2H, CH-arom), 7.57 (dd, ³J_{HH} = 7.6, ⁴J_{HH} = 1.3, 2H, CH-arom), 7.40 (dd, ³J_{HH} = 7.6, ³J_{HH} = 7.5, 2H, CH-arom), 3.32 (m, 2H, PCH(CH₃)₂), 2.86 (m,

2H, PCH(CH₃)₂), 2.77 (s, 3H, CH₃CN), 1.65 (dvt, $N = 15.1$, $^3J_{\text{HH}} = 7.2$, 6H, PCH(CH₃)₂), 1.61 (s, 3H, C(CH₃)₂), 1.59 (s, 3H, C(CH₃)₂), 1.54 (dvt, $N = 16.9$, $^3J_{\text{HH}} = 7.5$, 6H, PCH(CH₃)₂), 1.42 (dvt, $N = 17.2$, $^3J_{\text{HH}} = 6.9$, 6H, PCH(CH₃)₂), 0.94 (dvt, $N = 16.4$, $^3J_{\text{HH}} = 6.1$, 6H, PCH(CH₃)₂), -9.86 (t, $^2J_{\text{HP}} = 6.0$, 2H, OsH). ¹³C {¹H} NMR-APT (75.47 MHz, CD₂Cl₂, 293K): δ 158.2 (vt, $N = 11.6$, C-arom), 132.4 (vt, $N = 6.0$, C-arom), 132.1 (s, CH-arom), 131.2 (s, CH-arom), 127.3 (vt, $N = 6.3$, CH-arom), 124.4 (s, CH₃CN), 123.7 (vt, $N = 38.4$, C-arom), 34.2 (s, C(CH₃)₂) 34.1 (s, C(CH₃)₂), 33.1 (s, C(CH₃)₂), 28.0 (vt, $N = 28.1$, PCH(CH₃)₂), 27.9 (vt, $N = 32.0$, PCH(CH₃)₂), 21.8 (s, PCH(CH₃)₂), 19.8 (vt, $N = 5.9$, PCH(CH₃)₂), 19.8 (s, PCH(CH₃)₂), 18.7 (s, PCH(CH₃)₂), 4.2 (s, CH₃CN). ³¹P {¹H} NMR (121.49 MHz, CD₂Cl₂, 293K): δ 27.2 (s, POP). $T_{1(\text{min})}$ (ms, OsH, 300 MHz, CD₂Cl₂, 203K): 21 ± 1 (-10.51 ppm).

Determination of the J_{HD} value for complex 6. DOTf (3 μL ; 0.034 mmol) was added to a solution of [OsH₃Cl{xant(P^{*i*}Pr)₂}] (**1**) (23 mg; 0.034 mmol) in CD₂Cl₂ (0.5 mL). Then, CH₃CN (2 μL ; 0.038 mmol) was added. The ¹H{³¹P} NMR spectrum of this solution showed a triplet ($J_{\text{HD}} = 20$ Hz) at -9.87 ppm, corresponding to the deuterated isotopomer.

Synthesis of [K(18-crown-6)][OsH₅{xant(P^{*i*}Pr)₂}] (8**):** To a THF (0.6 mL) solution of [OsH₄{xant(P^{*i*}Pr)₂}] (**7**) (40 mg, 0.063 mmol) were added KH (8 mg, 0.200 mmol) and 18-crown-6 (50 mg, 0.190 mmol). The reaction mixture was heated at 70 °C for 14 h and then filtered while hot. The filtrate was cooled at room temperature to afford yellow crystals, which were isolated after removal of the supernatant by decantation, and dried overnight under reduced pressure. Yield: 39 mg (66%). Complex **8** can be recrystallized by slow vapor diffusion of pentane into a solution of the compound in THF. Anal. Calcd. for C₃₉H₆₉KO₇OsP₂·C, 49.77; H, 7.39. Found: C, 50.17; H, 7.65. HRMS (*electrospray*, m/z): calcd. for C₂₇H₄₄OOsP₂ [M-H]⁺: 638.2478, found: 638.2479. ¹H NMR (400.13 MHz, THF-*d*₈, 293K): 7.19 (d, $^3J_{\text{HH}} = 7.5$, 2H, CH-

arom), 7.13 (m, 2H, CH-arom) 6.89 (dd, $^3J_{\text{HH}} = 7.5$, $^3J_{\text{HH}} = 7.5$, 2H, CH-arom), 3.51 (s, 24H, CH₂-18-crown-6), 2.18 (m, 4H, PCH(CH₃)₂), 1.53 (s, 6H, C(CH₃)₂), 1.16 (dvt, $^3J_{\text{HH}} = 7.0$, $N = 13.0$, 12H, PCH(CH₃)₂), 1.13 (dvt, $N = 11.9$, $^3J_{\text{HH}} = 6.5$, 12H, PCH(CH₃)₂), -12.46 (br, 5H, OsH). ¹³C{¹H} NMR-APT (100.62 MHz, THF-*d*₈, 343K): δ 158.0 (vt, $N = 8.0$, C-arom), 135.0 (s, C-arom), 132.2 (m, C-arom), 127.6 (s, CH-arom), 121.7 (s, CH-arom), 120.0 (s, CH-arom), 70.5 (s, CH₂-18-crown-6), 36.0 (s, C(CH₃)₂), 29.2 (d, $^1J_{\text{CP}} = 27.1$, PCH(CH₃)₂), 26.6 (s, C(CH₃)₂), 20.9 (vt, $N = 4.6$, PCH(CH₃)₂), 19.1 (s, PCH(CH₃)₂). ³¹P{¹H} NMR (161.98 MHz, THF-*d*₈, 293K): δ 20.6 (s, POP).

Reaction of [(Os(H···H){xant(P^{*i*}Pr₂)₂)₂(μ-Cl)₂][BF₄]₂ (3) with KH:

[(Os(H···H){xant(P^{*i*}Pr₂)₂)₂(μ-Cl)₂][BF₄]₂ (3) (100 mg, 0.066 mmol) and KH (6 mg, 0.15 mmol) were placed in a schlenk tube and THF (5 mL) was added to form a suspension. The reaction mixture was stirred and monitored by NMR showing complete conversion into [OsH₃Cl{xant(P^{*i*}Pr₂)₂}] (1) after 1 h.

Computational details and Cartesian coordinates of 2, 5 and 6: All calculations were performed at the DFT level using the B3LYP functional²⁹ supplemented with the Grimme's dispersion correction D3³⁰ as implemented in Gaussian09²³. Os atom was described by means of an effective core potential SDD for the inner electron³¹ and its associated double- ζ basis set for the outer ones, complemented with a set of f-polarization functions.³² The 6-31G** basis set was used for the H, C, O, N, Cl and P atoms.³³ All minima were verified to have no negative frequencies. All geometries were fully optimized in vacuo.

Structural Analysis of Complexes 3, 5, 6 and 8. X-ray data were collected on a Bruker Smart APEX CCD (5, 6, and 8) and a Smart APEX CCD DUO (3) diffractometers using graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Data were collected over the complete sphere

and were corrected for absorption by using a multiscan method applied with the SADABS program. The structures were solved by Patterson or direct methods and refined by full-matrix least squares on F^2 with SHELXL97, including isotropic and subsequently anisotropic displacement parameters. The hydrogen atoms were observed in the least Fourier Maps or calculated, and refined freely or using a restricted riding model.

However, the hydride ligands were observed in the difference fourier maps but does not refined properly, therefore the osmium-hydride distance was fixed in the refinement (1.59 Å, CCDC). Complex **8** is twined by pseudomerohedry. The structure simulates orthorhombic but was properly refined in the monoclinic symmetry system with beta approximately 90° and refined with the twin law 1 0 0 0 -1 0 0 0 -1 plus one BASF parameter of ≈ 0.5 . Due to the difficulty of the refinement restrictions in the displacement parameters were used. In the four structures there are anions and crystallization molecules observed disordered and refined with different moieties, restrained geometry and isotropic thermal parameters.

Crystal data for **3**: $C_{54}H_{84}Cl_2O_2Os_2P_4$, $2(BF_4)$, CH_2Cl_2 , M_w 1598.94, irregular block, yellow (0.19 x 0.12 x 0.08), monoclinic, space group P21/c, a : 12.9473(15) Å, b : 20.565(2) Å, c : 12.0926(14) Å, β : 93.005(2)°, V = 3215.4(6) Å³, Z = 2, Z' = 0.5, D_{calc} : 1.651 g cm⁻³, $F(000)$: 1588, T = 100(2) K, μ 4.275 mm⁻¹. 41253 measured reflections (2θ : 3-58°, ω scans 0.3°), 8442 unique (R_{int} = 0.0411); min./max. transm. factors 0.633/0.862. Final agreement factors were R^1 = 0.0394 (6950 observed reflections, $I > 2\sigma(I)$) and wR^2 = 0.1061; data/restraints/parameters 8442/35/379; GoF = 0.949. Largest peak and hole: 2.66 (close to osmium atoms) and -1.705 e/Å³.

Crystal data for **5**: $C_{24}H_{38}ClO_2OsP_2$, CF_3O_3S , CHF_3O_3S , M_w 929.28, irregular block, colorless (0.19 x 0.14 x 0.08), monoclinic, space group Cc, a : 16.2471(10) Å, b : 21.4146(13) Å, c :

10.2694(6) Å, β : 104.6620(10)°, V = 3456.6(4) Å³, Z = 4, Z' = 1. D_{calc} : 1.786 g cm⁻³, $F(000)$: 1840, T = 100(2) K, μ 4.053 mm⁻¹. 19163 measured reflections (2θ : 3-58°, ω scans 0.3°), 7949 unique (R_{int} = 0.0320); min./max. transm. factors 0.687/0.862. Final agreement factors were R^1 = 0.0277 (7384 observed reflections, $I > 2\sigma(I)$) and wR^2 = 0.0555; data/restraints/parameters 7949/6/ 428; GoF = 1.022. Largest peak and hole: 0.827 and -0.846 e/ Å³.

Crystal data for **6**: C₂₉H₄₅ClNOOsP₂, BF₄, C₄H₁₀O, M_W 872.18, irregular block, colorless (0.15 x 0.10 x 0.07), monoclinic, space group P2₁/m, a : 11.843(3) Å, b : 22.139(5) Å, c : 14.179(3) Å, β : 89.988(3)°, V = 3717.4(14) Å³, Z = 4, Z' = 1, D_{calc} : 1.558 g cm⁻³, $F(000)$: 1760, T = 100(2) K, μ 3.638 mm⁻¹. 32991 measured reflections (2θ : 3-58°, ω scans 0.3°), 7908 unique (R_{int} = 0.0876); min./max. transm. factors 0.590/0.862. Final agreement factors were R^1 = 0.0521 (5862 observed reflections, $I > 2\sigma(I)$) and wR^2 = 0.1289; data/restraints/parameters 7908/256/417; GoF = 1.135. Largest peak and hole: 1.785 (close to osmium atoms) and -1.406 e/ Å³.

Crystal data for **8**: C₂₇H₄₅OOsP₂, C₁₂H₂₄KO₆, 0.5(C₄H₈O), 0.5(C₅H₁₂), M_W 1013.31, irregular block, yellow (0.25 x 0.06 x 0.06), monoclinic, space group P2₁/n, a : 17.0875(9) Å, b : 15.2536(8) Å, c : 19.5724(10) Å, β : 109.6270(10)°, V = 4805.1(4) Å³, Z = 4, Z' = 1, D_{calc} : 1.401 g cm⁻³, $F(000)$: 2100, T = 100(2) K, μ 2.852 mm⁻¹. 82792 measured reflections (2θ : 3-58°, ω scans 0.3°), 11705 unique (R_{int} = 0.0583); min./max. transm. factors 0.679/ 0.862. Final agreement factors were R^1 = 0.0386 (9412 observed reflections, $I > 2\sigma(I)$) and wR^2 = 0.0946; data/restraints/parameters 11705/17/510; GoF = 1.032. Largest peak and hole: 2.348 (close to osmium atoms) and -1.381 e/ Å³.

ASSOCIATED CONTENT

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

·Crystallographic details for **3**, **5**, **6** and **8** (CIF).

Theoretical complexes coordinates (XYZ).

AUTHOR INFORMATION

Corresponding Author

*E-mail: maester@unizar.es.

Author Contributions

The manuscript was written through contributions of all authors.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

(Financial support from the MINECO of Spain (Projects CTQ2014-52799-P and CTQ2014-51912-REDC), Gobierno de Aragón (E35), FEDER, and the European Social Fund is acknowledged.

REFERENCES

(1) (a) Noyori, R.; Ohkuma, T. Asymmetric Catalysis by Architectural and Functional Molecular Engineering: Practical Chemo- and Stereoselective Hydrogenation of Ketones. *Angew. Chem., Int. Ed.* **2001**, *40*, 40-73. (b) Clapham, S. E.; Hadzovic, A.; Morris, R. H. Mechanisms of the H₂-Hydrogenation and Transfer Hydrogenation of Polar Bonds Catalyzed by Ruthenium Hydride Complexes. *Coord. Chem. Rev.* **2004**, *248*, 2201-2237. (c) Conley, B. L.; Pennington-Boggio, M. K.; Boz, E.; Williams, T. J. Discovery, Applications, and Catalytic

Mechanisms of Shvo's Catalyst. *Chem. Rev.* **2010**, *110*, 2294-2312. (d) Gunanathan, C.; Milstein, D. Metal-Ligand Cooperation by Aromatization-Deaomatization: A New Paradigm in Bond Activation and "Green" Catalysis. *Acc. Chem. Res.* **2011**, *44*, 588-602. (e) Bajo, S.; Esteruelas, M. A.; López, A. M.; Oñate, E. Osmium-Acyl Decarbonylation Promoted by Tp-Mediated Allenylidene Abstraction: A New Role of the Tp Ligand. *Organometallics* **2014**, *33*, 4057-4066. (f) Bolaño, T.; Esteruelas, M. A.; Gay, M. P.; Oñate, E.; Pastor, I. M.; Yus, M. An Acyl-NHC Osmium Cooperative System: Coordination of Small Molecules and Heterolytic B-H and O-H Bond Activation. *Organometallics* **2015**, *34*, 3902-3908.

(2) (a) Periana, R. A.; Taube, D. J.; Gamble, S.; Taube, H.; Satoh, T.; Fujii, H. Platinum Catalysts for the High-Yield Oxidation of Methane to a Methanol Derivative. *Science* **1998**, *280*, 560-564. (b) Hashiguchi, B. G.; Young, K. J. H.; Yousufuddin, M.; Goddard, W. A.; Periana, R. A. Acceleration of Nucleophilic CH Activation by Strongly Basic Solvents. *J. Am. Chem. Soc.* **2010**, *132*, 12542-12545. (c) Crabtree, R. H. Creating Ligands with Multiple Personalities. *Science* **2010**, *330*, 455-456. (d) Kaim, W. Manifestations of Noninnocent Ligand Behavior. *Inorg. Chem.* **2011**, *50*, 9752-9765.

(3) (a) Braunstein, P.; Naud, F. Hemilability of Hybrid Ligands and the Coordination Chemistry of Oxazoline-Based Systems. *Angew. Chem., Int. Ed.* **2001**, *40*, 680-699. (b) Angell, S. E.; Rogers, C. W.; Zhang, Y.; Wolf, M. O.; Jones, W. E. Hemilabile Coordination Complexes for Sensing Applications. *Coord. Chem. Rev.* **2006**, *250*, 1829-1841. (c) Braunstein, P. Bonding and Organic and Inorganic Reactivity of Metal-Coordinated Phosphinoenolates and Related Functional Phosphine-Derived Anions. *Chem. Rev.* **2006**, *106*, 134-159. (d) Weng, Z. Q.; Teo, S. H.; Hor, T. S. A. Metal Unsaturation and Ligand Hemilability in Suzuki Coupling. *Acc. Chem. Res.* **2007**, *40*, 676-684. (e) Zhang, W. H.; Chien, S. W.; Hor, T. S. A. Recent Advances in Metal

Catalysts with Hybrid Ligands. *Coord. Chem. Rev.* **2011**, *255*, 1991-2024. (f) Annibale, V. T.; Song, D. T. Multidentate Actor Ligands as Versatile Platforms for Small Molecule Activation and Catalysis. *RSC Adv.* **2013**, *3*, 11432-11449.

(4) (a) van der Boom, M. E.; Milstein, D. Cyclometalated Phosphine-Based Pincer Complexes: Mechanistic Insight in Catalysis, Coordination, and Bond Activation. *Chem. Rev.* **2003**, *103*, 1759-1792. (b) Choi, J.; MacArthur, A. H. R.; Brookhart, M.; Goldman, A. S. Dehydrogenation and Related Reactions Catalyzed by Iridium Pincer Complexes. *Chem. Rev.* **2011**, *111*, 1761-1779. (c) Haibach, M. C.; Kundu, S.; Brookhart, M.; Goldman, A. S. Alkane Metathesis by Tandem Alkane-Dehydrogenation-Olefin-Metathesis Catalysis and Related Chemistry. *Acc. Chem. Res.* **2012**, *45*, 947-958. (d) Kumar, A.; Zhou, T.; Emge, T. J.; Mironov, O.; Saxton, R. J.; Krogh-Jespersen, K.; Goldman, A. S. Dehydrogenation of *n*-Alkanes by Solid-Phase Molecular Pincer-Iridium Catalysts. High Yields of α -Olefin Product. *J. Am. Chem. Soc.* **2015**, *137*, 9894-9911.

(5) (a) Boone, M. P.; Brown, C. C.; Ancelet, T. A.; Stephan, D. W. Interconversion of Ruthenium-O(CH₂CH₂PCy₂)₂ Alkylidene and Alkylidyne Hydride Complexes. *Organometallics* **2010**, *29*, 4369-4374. (b) Lumbroso, A.; Koschker, P.; Vautravers, N. R.; Breit, B. Redox-Neutral Atom-Economic Rhodium-Catalyzed Coupling of Terminal Alkynes with Carboxylic Acids Toward Branched Allylic Esters. *J. Am. Chem. Soc.* **2011**, *133*, 2386-2389. (c) Pawley, R. J.; Huertos, M. A.; Lloyd-Jones, G. C.; Weller, A. S.; Willis, M. C. Intermolecular Alkyne Hydroacylation. Mechanistic Insight from the Isolation of the Vinyl Intermediate that Precedes Reductive Elimination. *Organometallics* **2012**, *31*, 5650-5659. (d) Esteruelas, M. A.; Oliván, M.; Vélez, A. Xantphos-Type Complexes of Group 9: Rhodium versus Iridium. *Inorg. Chem.* **2013**, *52*, 5339-5349. (e) Esteruelas, M. A.; Oliván, M.; Vélez, A. POP-Pincer Silyl Complexes of

Group 9: Rhodium versus Iridium. *Inorg. Chem.* **2013**, *52*, 12108-12119. (f) Esteruelas, M. A.; Oliván, M.; Vélez, A. Conclusive Evidence on the Mechanism of the Rhodium-Mediated Decyanative Borylation. *J. Am. Chem. Soc.* **2015**, *137*, 12321-12329. (g) Esteruelas, M. A.; Nolis, P.; Oliván, M.; Oñate, E.; Vallribera, A.; Vélez, A. Ammonia Borane Dehydrogenation Promoted by a Pincer-Square-Planar Rhodium(I) Monohydride: A Stepwise Hydrogen Transfer from the Substrate to the Catalyst. *Inorg. Chem.* **2016**, *55*, 7176-7181.

(6) (a) Pontiggia, A. J.; Chaplin, A. B.; Weller, A. S. Cationic Iridium Complexes of the Xantphos Ligand. Flexible Coordination Modes and the Isolation of the Hydride Insertion Product with an Alkene. *J. Organomet. Chem.* **2011**, *696*, 2870-2876. (b) Dallanegra, R.; Chaplin, A. B.; Weller, A. S. Rhodium Cyclopentyl Phosphine Complexes of Wide-Bite-Angle Ligands DPEphos and Xantphos. *Organometallics* **2012**, *31*, 2720-2728.

(7) Pawley, R. J.; Moxham, G. L.; Dallanegra, R.; Chaplin, A. B.; Brayshaw, S. K.; Weller, A. S.; Willis, M. C. Controlling Selectivity in Intermolecular Alkene or Aldehyde Hydroacylation Reactions Catalyzed by $\{\text{Rh}(\text{L}_2)\}^+$ Fragments. *Organometallics* **2010**, *29*, 1717-1728.

(8) Ren, P.; Pike, S. D.; Pernik, I.; Weller, A. S.; Willis, M. C. Rh-POP Pincer Xantphos Complexes for C-S and C-H Activation. Implications for Carbothiolation Catalysis. *Organometallics* **2015**, *34*, 711-723.

(9) Johnson, H. C.; Leitao, E. M.; Whitten, G. R.; Manners, I.; Lloyd-Jones, G. C.; Weller, A. S. Mechanistic Studies of the Dehydrocoupling and Dehydropolymerization of Amine-Boranes Using a $[\text{Rh}(\text{Xantphos})]^+$ Catalyst. *J. Am. Chem. Soc.* **2014**, *136*, 9078-9093.

(10) Esteruelas, M. A.; López, A. M.; Oliván, M. Polyhydrides of Platinum Group Metals: Nonclassical Interactions and σ -Bond Activation Reactions. *Chem. Rev.* **2016**, *116*, 8770-8847.

- (11) Crabtree, R. H. Dihydrogen Complexation. *Chem. Rev.* **2016**, *116*, 8750-8769.
- (12) (a) Rossin, A.; Peruzzini, M. Ammonia-Borane and Amine-Borane Dehydrogenation Mediated by Complex Metal Hydrides. *Chem. Rev.* **2016**, *116*, 8848-8872. (b) Bhunya, S.; Malakar, T.; Ganguly, G.; Paul, A. Combining Protons and Hydrides by Homogeneous Catalysis for Controlling the Release of Hydrogen from Ammonia-Borane: Present Status and Challenges. *ACS Catal.* **2016**, *6*, 7907-7934.
- (13) (a) Esteruelas, M. A.; Fernández, I.; López, A. M.; Mora, M.; Oñate, E. Osmium-Promoted Dehydrogenation of Amine-Boranes and B-H Bond Activation of the Resulting Amino-Boranes. *Organometallics* **2014**, *33*, 1104-1107. (b) Esteruelas, M. A.; López, A. M.; Mora, M.; Oñate, E. Ammonia-Borane Dehydrogenation Promoted by an Osmium Dihydride Complex: Kinetics and Mechanism. *ACS Catal.* **2015**, *5*, 187-191.
- (14) (a) Casarrubios, L.; Esteruelas, M. A.; Larramona, C.; Muntaner, J. G.; Oliván, M.; Oñate, E.; Sierra, M. A. Chelated Assisted Metal-Mediated N-H Bond Activation of β -Lactams: Preparation of Irida-, Rhoda-, Osma-, and Ruthenatrinems. *Organometallics* **2014**, *33*, 1820-1833. (b) Casarrubios, L.; Esteruelas, M. A.; Larramona, C.; Lledós, A.; Muntaner, J. G.; Oñate, E.; Ortuño, M. A.; Sierra, M. A. Mechanistic Insight into the Facilitation of β -Lactam Fragmentation through Metal Assistance. *Chem. Eur. J.* **2015**, *21*, 16781-16785. (c) Casarrubios, L.; Esteruelas, M. A.; Larramona, C.; Muntaner, J. G.; Oñate, E.; Sierra, M. A. 2-Azetidinones as Precursors of Pincer Ligands: Preparation, Structure, and Spectroscopic Properties of CC'N-Osmium Complexes. *Inorg. Chem.* **2015**, *54*, 10998-11006.
- (15) (a) Esteruelas, M. A.; García-Raboso, J.; Oliván, M.; Oñate, E. N-H and N-C Bond Activation of Pyrimidinic Nucleobases and Nucleosides Promoted by an Osmium Polyhydride.

Inorg. Chem. **2012**, *51*, 5975-5984. (b) Esteruelas, M. A.; García-Raboso, J.; Oliván, M.

Reactions of an Osmium-Hexahydride Complex with Cytosine, Deoxycytidine, and Cytidine:

The Importance of the Minor Tautomers. *Inorg. Chem.* **2012**, *51*, 9522-9528.α

(16) (a) Esteruelas, M. A.; Herrero, J.; López, A. M.; Oliván, M. Alkyne-Coupling Reactions Catalyzed by OsHCl(CO)(PⁱPr₃) in the Presence of Diethylamine. *Organometallics* **2001**, *20*,

3202-3205. (b) Barrio, P.; Esteruelas, M. A.; Oñate, E. Reactions of a Hexahydride-Osmium

Complex with Aldehydes: Double C-H_α Activation-Decarbonylation and Single C-H_α

Activation-Hydroxylation Tandem Processes and Catalytic Tishchenko Reactions.

Organometallics **2004**, *23*, 1340-1348. (c) Esteruelas, M. A.; Masamunt, A. B.; Oliván, M.;

Oñate, E.; Valencia, M. Aromatic Diosmatricyclic Nitrogen-Containing Compounds. *J. Am.*

Chem. Soc. **2008**, *130*, 11612-11613. (d) Esteruelas, M. A.; Honczek, N.; Oliván, M.; Oñate, E.;

Valencia, M. Direct Access to POP-Type Osmium(II) and Osmium(IV) Complexes: Osmium a Promising Alternative to Ruthenium for the Synthesis of Imines from Alcohols and Amines.

Organometallics **2011**, *30*, 2468-2471.

(17) (a) Crespo, O.; Eguillor, B.; Esteruelas, M. A.; Fernández, I.; García-Raboso, J.; Gómez-Gallego, M.; Martín-Ortiz, M.; Oliván, M.; Sierra, M. A. Synthesis and Characterisation of [6]-Azaosmahelicenes: the First d⁴-Heterometallahelicenes. *Chem. Commun.* **2012**, *48*, 5328-5330.

(b) Alabau, R. G.; Eguillor, B.; Esler, J.; Esteruelas, M. A.; Oliván, M.; Oñate, E.; Tsai, J. Y.;

Xia, C. J. CCC-Pincer-NHC Osmium Complexes: New Types of Blue-Green Emissive Neutral Compounds for Organic Light-Emitting Devices (OLEDs). *Organometallics* **2014**, *33*, 5582-

5596. (c) Eguillor, B.; Esteruelas, M. A.; Fernández, I.; Gómez-Gallego, M.; Lledós, A.; Martín-Ortiz, M.; Oliván, M.; Oñate, E.; Sierra, M. A. Azole Assisted C-H Bond Activation Promoted

by an Osmium-Polyhydride: Discerning between N and NH. *Organometallics* **2015**, *34*, 1898-1910.

(18) Bertoli, M.; Chouale, A.; Gusev, D. G.; Lough, A. J.; Major, Q.; Moore, B. PNP Pincer Osmium Polyhydrides for Catalytic Dehydrogenation of Primary Alcohols. *Dalton Trans.* **2011**, *40*, 8941-8949.

(19) Liu, S. H.; Huang, X.; Lin, Z. Y.; Lau, C. P.; Jia, G. C. Synthesis and Characterization of Dihydrogen(olefin)osmium Complexes with (E)-Ph₂P(CH₂)₂CH=CH(CH₂)₂PPh₂. *Eur. J. Inorg. Chem.* **2002**, 1697-1702.

(20) Kuznetsov, V. F.; Gusev, D. G. Chiral Hydride and Dihydrogen Pincer-Type Complexes of Osmium. *Organometallics* **2007**, *26*, 5661-5666.

(21) Alós, J.; Bolaño, T.; Esteruelas, M. A.; Oliván, M.; Oñate, E.; Valencia, M. POP-Pincer Osmium-Polyhydrides: Head-to-Head (Z)-Dimerization of Terminal Alkynes. *Inorg. Chem.* **2013**, *52*, 6199-6213.

(22) (a) Kong, V. C. Y.; Foulkes, F. R.; Kirk, D. W.; Hinatsu, J. T. Development of Hydrogen Storage for Fuel Cell Generators. I: Hydrogen Generation Using Hydrolysis Hydrides. *Int. J. Hydrogen. Energ.* **1999**, *24*, 665-675. (b) Kong, V. C. Y.; Kirk, D. W.; Foulkes, F. R.; Hinatsu, J. T. Development of Hydrogen Storage for Fuel Cell Generators II: Utilization of Calcium Hydride and Lithium Hydride. *Int. J. Hydrogen. Energ.* **2003**, *28*, 205-214. (c) Dincer, I. Green Methods for Hydrogen Production. *Int. J. Hydrogen. Energ.* **2012**, *37*, 1954-1971. (d) Dincer, I.; Acar, C. Review and Evaluation of Hydrogen Production Methods for Better Sustainability. *Int. J. Hydrogen. Energ.* **2015**, *40*, 11094-11111.

(23) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09, Revision B.01*; Gaussian, Inc.: Wallingford, CT, **2009**.

(24) In addition to reference 21, for osmium complexes previously described with this diphosphine see: (a) Asensio, G.; Cuenca, A. B.; Esteruelas, M. A.; Medio-Simón, M.; Oliván, M.; Valencia, M. Osmium(III) Complexes with POP Pincer Ligands: Preparation from Commercially Available $\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$ and Their X-ray Structures. *Inorg. Chem.* **2010**, *49*, 8665-8667. (b) Alós, J.; Bolaño, T.; Esteruelas, M. A.; Oliván, M.; Oñate, E.; Valencia, M. POP-Pincer Ruthenium Complexes: d^6 Counterparts of Osmium d^4 Species. *Inorg. Chem.* **2014**, *53*, 1195-1209. (c) Alós, J.; Esteruelas, M. A.; Oliván, M.; Oñate, E.; Puylaert, P. C-H Bond Activation Reactions in Ketones and Aldehydes Promoted by POP-Pincer Osmium and Ruthenium Complexes. *Organometallics* **2015**, *34*, 4908-4921.

(25) $d_{\text{H-H}} = 5.815 (T_{\text{I (min)}/\nu})^{1/6}$ and $d_{\text{H-H}} = 1.44-0.0168 (J_{\text{H-D}})$. Morris, R. H. Dihydrogen, Dihydride and in Between: NMR and Structural Properties of Iron Group Complexes. *Coord. Chem. Rev.* **2008**, 252, 2381-2394.

(26) The structure has two chemically equivalent but crystallographically independent molecules in the symmetry unit.

(27) (a) Gusev, D. G.; Lough, A. J.; Morris, R. H. New Polyhydride Anions and Proton-Hydride Hydrogen Bonding in their Ion Pairs. X-ray Crystal Structure Determinations of $\text{Q}[\text{mer-Os}(\text{H})_3(\text{CO})(\text{P}^i\text{Pr}_3)_2]$, $\text{Q} = [\text{K}(18\text{-crown-6})]$ and $\text{Q} = [\text{K}(1\text{-aza-18-crown-6})]$. *J. Am. Chem. Soc.* **1998**, 120, 13138-13147. (b) Abdur-Rashid, K.; Gusev, D. G.; Lough, A. J.; Morris, R. H. Intermolecular Proton-Hydride Bonding in Ion Pairs: Synthesis and Structural Properties of $[\text{K}(\text{Q})][\text{MH}_5((\text{P}^i\text{Pr}_3)_2)]$ ($\text{M} = \text{Os, Ru}$; $\text{Q} = 18\text{-crown-6, 1-aza-18-crown-6, 1,10-diaza-18-crown-6}$). *Organometallics* **2000**, 19, 834-843.

(28) (a) Howard, J. A. K.; Johnson, O.; Koetzle, T. F.; Spencer, J. L. Crystal and Molecular Structure of Bis(diisopropylphenylphosphine)hexahydridoosmium, $[\text{OsH}_6(\text{PC}_{12}\text{H}_{19})_2]$: Single-Crystal Neutron Diffraction Study at 20 K. *Inorg. Chem.* **1987**, 26, 2930-2933. (b) Buil, M. L.; Cardo, J. J. F.; Esteruelas, M. A.; Fernández, I.; Oñate, E. An Entry to Stable Mixed Phosphine-Osmium-NHC Polyhydrides. *Inorg. Chem.* **2016**, 55, 5062-5070.

(29) (a) Lee, C. T.; Yang, W. T.; Parr, R. G. Development of the Colle-Salvetti Correlation-Energy Formula into a Functional of the Electron-Density. *Phys Rev B* **1988**, 37, 785-789. (b) Becke, A. D. A New Mixing of Hartree-Fock and Local Density-Functional Theories. *J. Chem. Phys.* **1993**, 98, 1372-1377. (c) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. Ab-Initio Calculation of Vibrational Absorption and Circular-Dichroism Spectra Using Density-

Functional Force-Fields. *J. Phys. Chem.* **1994**, *98*, 11623-11627. (1) Alós, J.; Bolaño, T.; Esteruelas, M. A.; Oliván, M.; Oñate, E.; Valencia, M. POP-Pincer Osmium-Polyhydrides: Head-to-Head (Z)-Dimerization of Terminal Alkynes. *Inorg. Chem.* 2013, *52*, 6199-6213.

(30) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A Consistent and Accurate *ab initio* Parametrization of Density Functional Dispersion Correction (DFT-D) for the 94 Elements H-Pu. *J. Chem. Phys.* **2010**, *132*.

(31) Andrae, D.; Haussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. Energy-Adjusted Abinitio Pseudopotentials for the 2nd and 3rd Row Transition-Elements. *Theoretica Chimica Acta* **1990**, *77*, 123-141.

(32) Ehlers, A. W.; Bohme, M.; Dapprich, S.; Gobbi, A.; Hollwarth, A.; Jonas, V.; Kohler, K. F.; Stegmann, R.; Veldkamp, A.; Frenking, G. A Set of F-Polarization Functions for Pseudo-Potential Basis-Sets of the Transition-Metals Sc-Cu, Y-Ag and La-Au. *Chem. Phys. Lett.* **1993**, *208*, 111-114.

(33) (a) Hehre, W. J.; Ditchfield, R.; Pople, J. A. Self-Consistent Molecular-Orbital Methods. XII. Further Extensions of Gaussian-Type Basis Sets for Use in Molecular-Orbital Studies of Organic-Molecules. *J. Chem. Phys.* **1972**, *56*, 2257-2261. (b) Francel, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; Defrees, D. J.; Pople, J. A. Self-Consistent Molecular-Orbital Methods .23. A Polarization-Type Basis Set for 2nd-Row Elements. *J. Chem. Phys.* **1982**, *77*, 3654-3665.

TABLE OF CONTENTS SYNOPSIS

New dihydrogen-, compressed dihydride-, and classical hydride-osmium compounds containing the diphosphine 9,9-dimethyl-4,5-bis(diisopropylphosphino)xanthene, coordinated κ^3 -*mer*, κ^3 -*fac*, and κ^2 -P,P, have been isolated during the cyclic formation of H₂ by means of the sequential addition of H⁺ and H⁻ or H⁻ and H⁺ to the classical trihydride OsH₃Cl{xant(P^{*i*}Pr₂)₂}.