Osmium(II)–bis(Dihydrogen) Complexes Containing C_{aryl},C_{NHC}–Chelate Ligands: Preparation, Bonding Situation, and Acidity.

Tamara Bolaño,[†] Miguel A. Esteruelas,*[,†] Israel Fernández,[‡] Enrique Oñate,[†] Adrián Palacios,[†] Jui-Yi Tsai,[√] and Chuanjun Xia[√]

†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

‡Departamento de Química Orgánica, Facultad de Ciencias Químicas, Centro de Innovación en Química Avanzada (ORFEO – CINQA), Universidad Complutense de Madrid, 28040 Madrid, Spain

√Universal Display Corporation, 375 Phillips Boulevard, Ewing, New Jersey 08618, United States

Supporting Information Placeholder

ABSTRACT: The hexahydride complex $OsH_6(P^iPr_3)_2$ (**1**) reacts with the BF_4-salts of 1-phenyl-3-methyl-1-*H*-benzimidazolium, 1-phenyl-3-methyl-1-*H*-5,6-dimethyl-benzimidazolium, and 1-phenyl-3-methyl-1-*H*-imidazolium to give the respective trihydride-osmium(IV) derivatives $OsH_3(\kappa^2\text{-}C_{aryl},C_{NHC})(P^iPr_3)_2$ (**2**–**4**). The protonation of these compounds with $HBF_4{\cdot}OEt_2$ produces the reduction of the metal center and the formation of the bis(dihydrogen)-osmium(II) complexes $[Os(\kappa^2\text{-}C_{aryl},C_{NHC})(\eta^2\text{-}H_2)_2(P^iPr_3)_2]BF_4$ (**5**–**7**). DFT calculations using AIM and NBO methods reveal that the Os–NHC bond of the Os-chelate link tolerates a significant π-backdonation from a doubly occupied d_π(Os) atomic orbital to the p_z atomic orbital of the carbene carbon atom. The π-accepting capacity of the NHC unit of the C_{aryl},C_{NHC}-chelate ligand, which is higher than those of the coordinated aryl group and phosphine ligands, enhances the electrophilicity of the metal center activating one of the coordinated hydrogen molecules of **5**–**7** towards the heterolysis. As a result, these compounds are strong Brønsted acid with pK_a^{water} values between 2.5 and 2.8. In acetonitrile the hydrogen molecules of **5** and **6** are displaced by the solvent, the resulting bis(solvento) compounds $[Os(\kappa^2\text{-}C_{aryl},C_{NHC})(CH_3CN)_2(P^iPr_3)_2]BF_4$ (**8**, **9**) react with acetylacetonate (acac) and *cis*-1,2-bis(diphenylsphosphino)ethylene (bdppe) to give $Os(\kappa^2\text{-}C_{aryl},C_{NHC})$(acac)(bdppe) (**10**, **11**) as a mixture of the two possible isomers, namely with P *trans* to the aryl group or to the NHC moiety.

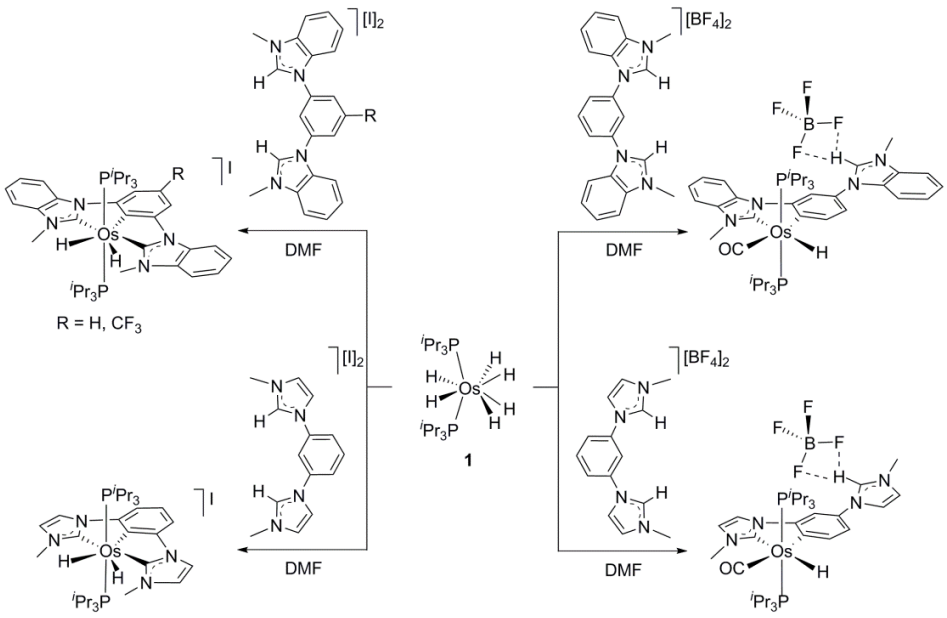
INTRODUCTION

N-Heterocyclic carbenes (NHCs) are singlet carbenes containing two π-electron donating amido substituents, which considerably increase the energy of the vacant p_z orbital at the carbon atom and therefore the σ-p_π gap. As a consequence, they bind to transition metals through σ donation, being the π-backbonding negligible.[1] This initial view is being however reconsidered. Recent studies suggest that the nature of the metal–NHC bond has greater complexity.[2] It has been found a remarkable π-backbonding in complexes with electron rich metal centers, in particular for those based on third row metals, whereas electron poor metal centers undergo NHC → M π-donation. This ability of the NHC-ligands to tune the electron density of the metallic core has made them powerful tools in homogeneous catalysis,[3] organometallic synthesis[4] and material science.[5]

The hydrogen molecule is vital in catalytic hydrogenation of unsaturated organic substrates[6] and the most efficient and clean energy carrier.[7] Its coordination to the unsaturated core of a transition metal complex affords dihydrogen derivatives, $M(\eta^2\text{-}H_2)$, which are determining species for its activation[8] and for its release from hydrogen bearers, such as amineboranes, in the metal promoted dehydrocoupling of these molecules.[9] Dihydrogen complexes stabilized with NHC-ligands are scarce,[10] in part due to the trend shown for these groups to release imidazolium salts.[11] The $M(\eta^2\text{-}H_2)$ interaction involves σ-donation from the σ-orbital of the coordinated H–H bond to empty orbitals of the metal and π-backbonding from the metal to the $\sigma^*(H_2)$ orbital. Thus, nucleophilic metal center; *i.e.*, having strongly donor ligands, 5d metals, and neutral charge; enhance the π-backbonding resulting in the oxidative addition of the H–H bond to the metal center to yield dihydride derivatives. On the other hand, electron-withdrawing ligands, 3d metals, and positive charge; *i.e.*, electrophilic metal centers; increase the σ-donation to the metal stabilizing the molecular hydrogen binding, which is promoted towards heterolysis.[12] The stability and chemical properties of the metal-dihydrogen interaction are further very sensitive to the position of the co-ligands in the metal coordination sphere.[13] As a result, complexes containing two coordinated hydrogen molecules are rare,[13a,14] in particular in the absence of hydride ligands, which exert an stabilizing *cis*-effect.[9a,15]

The hexahydride complex $OsH_6(P^iPr_3)$ has proven to activate σ bonds of a wide range of organic molecules,[16] in particular substrates containing a heteroatom binding site.[17] In agreement with this, it promotes the direct metalation of N-alkyl and N-arylimidazolium salts to give osmium-

Scheme 1

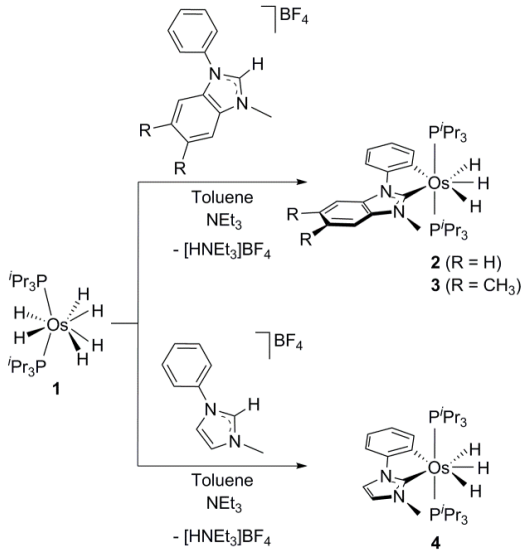


polyhydride derivatives containing neutral monodentated or chelate NHC ligands with normal or abnormal coordination modes depending upon the bulkiness of the N-substituents.[18] Recently, we have used this synthetic strategy to prepare novel homoleptic $Os(C_{NHC}C_{aryl}C_{NHC})_2$ and novel heteroleptic $Os(C_{NHC}C_{aryl}C_{NHC})(C_{NHC'}C_{aryl}C_{NHC'})$ and $Os(C_{NHC}C_{aryl}C_{NHC})(C_{NHC}C_{aryl'}C_{NHC})$ pincer complexes, which have shown to be new types of blue-green emissive additives for organic light-emitting devices.[19] The coordination of each anionic pincer implies the C–H bond activation of the central aryl group, in addition to the direct metalation of the benzimidazolium or imidazolium groups of the corresponding salts. During the study of the coordination process, we observed that, interestingly, the position of the activated aryl C–H bond depends upon the counteranion of the used salt (Scheme 1). Tetrafluoroborate favors the C–H bond activation at the 6-position, which presents the second NHC metalation to afford a *C,C'*-chelate zwiterionic salt. On the other hand, iodide favors the activation at the 2-position allowing the direct metalation of the second $C_{benzimidazolium}$ or $C_{imidazolium}$ moiety and therefore the pincer formation. Herein, we show that tetrafluoroborate salts of N-phenylbenzimidazolium and N-phenylimidazolium cations generate anionic C_{aryl},C_{NHC}-chelate ligands able of accepting that π-backbonding at the NHC moiety, which sufficiently increases the electrophilicity of the metal centers allowing the coordination of two hydrogen molecules; *i.e.*, the stabilization of bis(dihydrogen) derivatives.

RESULTS AND DISCUSSION

Metalation of the salts. The hexahydride complex $OsH_6(P^iPr_3)_2$ (**1**) promotes the N_2C–H bond activation of N-phenylbenzimidazolium and N-phenylimidazolium BF_4-salts and the *ortho*-C–H bond activation of the phenyl substituent. For each salt, at least one of the processes is a heterolysis,[20] being the resulting proton intermolecularly captured by the polyhydride, which subsequently releases 1.5 equiv of molecular hydrogen and dimerizes to afford the cation $[\{OsH_2(P^iPr_3)_2\}_2(\mu\text{-}H_3)]^+$.[16e] As a consequence, the treatment of **1** with 2.0 equiv of the BF_4-salts of 1-phenyl-3-methyl-1-*H*-benzimidazolium, 1-phenyl-3-methyl-1-*H*-5,6-dimethylbenzimidazolium, and 1-phenyl-3-methyl-1-*H*-imidazolium under reflux gives rise to mixtures of the trihydride-osmium(IV) $OsH_3(\kappa^2\text{-}C_{aryl},C_{NHC})(P^iPr_3)_2$ complexes **2**–**4** along with the polyhydride dimer $[\{OsH_2(P^iPr_3)_2\}_2(\mu\text{-}H_3)]^+$. The addition of triethylamine to the initial reaction mixture prevents the intermolecular protonation of **1**. Thus, in the presence of 1.1 equiv of the amine, the trihydrides are exclusively and quantitatively formed and isolated as white solids in high yield (74–86%) according to Scheme 2.

Scheme 2



Complexes **2** and **4** were characterized by X-ray diffraction analysis. The structures prove the double metalation of the salts to form anionic C_{aryl},C_{NHC}-chelate ligands. Figure 1 shows a drawing of **2**. The geometry around the osmium atom can be rationalized as a distorted pentagonal bipyramid with the phosphine ligands occupying axial positions (P(1)–Os–P(2) = 165.17(2)º). The metal coordination sphere is completed by the chelate group, which acts with a bite angle of 75.67(9)º, and the hydride ligands. The separation between H(01) and H(02) is 1.69(3) Å whereas H(02) and H(03) are separated by 1.74(3) Å. The Os–C(1) bond length of 2.069(2) Å agrees well with those reported for Os-NHC compounds with normal coordination of the NHC unit,[18,21] whereas the Os–C(6) distance of 2.140(2) Å compares well with the Os–aryl bond lengths found in other five-membered osmacycles resulting from orthometalation reactions.[17,22] The structure of **4** (Figure 2) resembles that of **2** with the orthometalated phenylimidazolidene group occupying the positions of the orthometalated phenylimidazolidene ligand and P(1)–Os–P(2) and C(1)–Os–C(6) angles of 166.01(2)º and 75.60(10)º, respectively. The Os–C(1) and Os–C(6) distances of 2.076(3) Å and 2.150(3) Å are statistically identical to those of **2**. In this compound, the separations between the hydride ligands H(01) and H(02) and H(02) and H(03) are 1.78(3) Å and 1.55(4) Å, respectively.

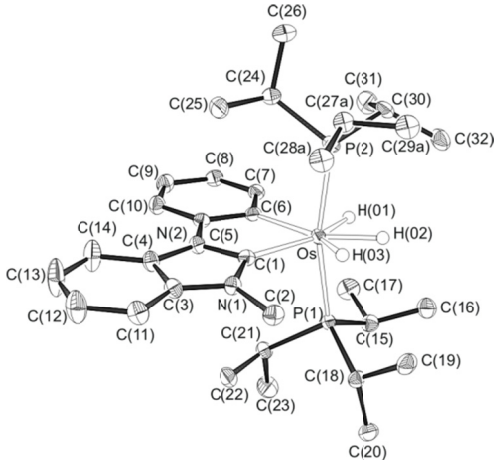


Figure 1. ORTEP diagram of complex **2** (50% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Os–C(1) = 2.069(2), Os–C(6) = 2.140(2), Os–P(1) = 2.3434(7), Os–P(2) = 2.3539(7), C(1)–Os–C(6) = 75.67(9), P(1)–Os–P(2) = 165.17(2).

The ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectra of **2**–**4** are consistent with the structures shown in Figures 1 and 2. The hydride ligands display two broad resonances at about –8 and –10 ppm, in a 1:2 intensity ratio, in the ^{1}H NMR spectra, in dichloromethane-d_2, between 293 and 183 K. On the base of NOE experiments, the lower field resonance has been assigned to the hydride ligand *cisoid* to the metalated phenyl carbon atom whereas the higher field resonance is consistent with a fast position exchange process involving the other two inequivalent hydrides. In agreement with the classical nature of the ligands, 400 MHz T_1 min values between 102 and 181 ms were found for these resonances. As expected for equivalent phosphines, the ^{31}P{^{1}H} NMR spectra shows a singlet at about 25 ppm. In the ^{13}C{^{1}H} NMR spectra in benzene-d_6, at room temperature, the most noticeable feature is the presence of the metalated carbon resonances, which appear between 190 and 206 ppm for the NHC unit and at about 158 ppm for the aryl group, as triplets with C–P coupling constants between 5 and 6 Hz.

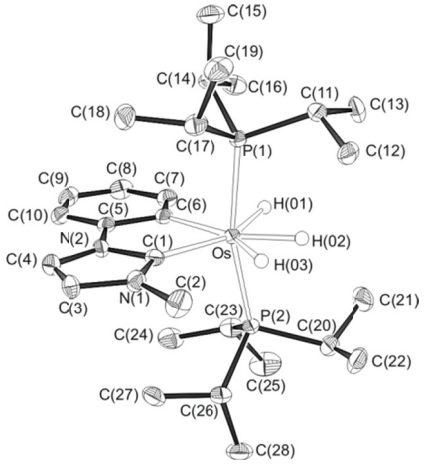
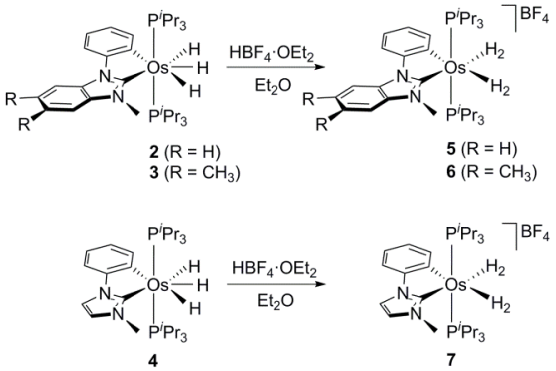


Figure 2. ORTEP diagram of complex **4** (50% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Os–C(1) = 2.076(3), Os–C(6) = 2.150(3), Os–P(1) = 2.3437(7), Os–P(2) = 2.3424(7), C(1)–Os–C(6) = 75.60 (10), P(1)–Os–P(2) = 166.01(2).

Bis(Dihydrogen) Complexes. The metal center of the trihydride-osmium(IV) complexes **2**–**4** undergoes reduction by protonation. Thus, the addition of 1.2 equiv of $HBF_4 \cdot OEt_2$ to diethyl ether solutions of these compounds, at room temperature, affords the corresponding bis(dihydrogen)-osmium(II) salts **5**–**7** (Scheme 3), which were isolated as white solids in high yield (83–85%).

Complex **6** was characterized by X-ray diffraction analysis. Figure 3 (left) shows an ORTEP drawing of the cation of the salt. The structure proves the reduction of the metal center. Thus, the coordination polyhedron around the osmium atom is the expected octahedron for a saturated d^6-species, with *trans*-phosphines (P(1)–Os–P(2) = 164.99(2)º). The perpendicular plane is formed by the chelated ligand, which acts with a C(1)–Os–C(6) bite angle of 77.30(8)º, and the coordinated

Scheme 3



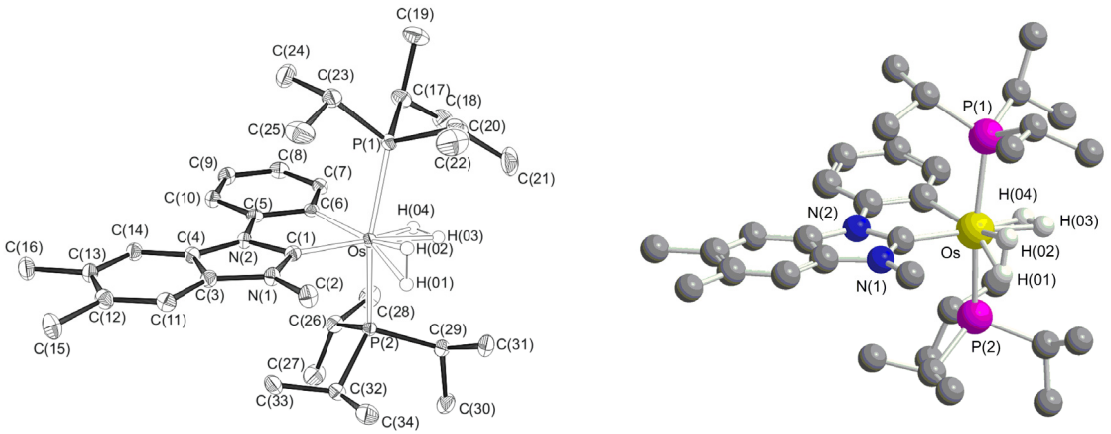


Figure 3. ORTEP diagram of complex **6** (50% probability ellipsoids) (left). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Os–C(1) = 2.055(2), Os–C(6) = 2.121(2), Os–P(1) = 2.3964(6), Os–P(2) = 2.4021(6), H(01)–H(02) = 0.89(4), H(03)–H(04) = 0.91(4), C(1)–Os–C(6) = 77.30 (8), P(1)–Os–P(2) = 164.99(2). DFT optimized structure of complex **6** (right). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): H(01)–H(02) = 0.971, H(03)–H(04) = 0.951.

hydrogen molecules. That situated *trans* to the aryl group (H(01)–H(02)) is disposed almost parallel to the P–Os–P direction with the hydrogen atoms separated by 0.89(4) Å, whereas that in *trans* position with regard to the NHC unit (H(03)–H(04)) lies in the plane of the *C,C'*-chelate ligand, perpendicular to the P–Os–P direction, with the hydrogen atoms separated by 0.91(4) Å. The Os–C(1) and Os–C(6) bond lengths of 2.055(2) Å and 2.121(2) Å, respectively, compare well with those found in **2** and **4**. Like in the trihydride derivatives, the Os–C(NHC) distance is about 0.07 Å shorter than the Os–aryl bond length. The DFT optimized structure shown in Figure 3 (right) confirms the non-classical interaction between the hydrogen atoms bonded to the metal center (H(01)–H(02) = 0.971 Å; H(03)–H(04) = 0.951 Å).

The ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectra of **5**–**7**, in dichloromethane-d_2, are consistent with the structure shown in Figure 3. In the ^{1}H NMR spectra, the most noticeable resonance is that due to the coordinated hydrogen molecules, which appears at about –7 ppm and displays 400 MHz T_1(min) values between 12 ± 2 ms and 14 ± 1 ms. They strongly support the non-classical interaction between the hydrogen atoms coordinated to the metal center, also in solution. In agreement with equivalent phosphines the ^{31}P{^{1}H} NMR spectra contain a singlet between 15 and 17 ppm. The ^{13}C{^{1}H} NMR spectra show the metalated carbon resonances of the chelate ligand between 173 and 189 ppm for the NHC unit and about 147 ppm for the aryl group.

The behavior of **2**–**4** is markedly different from that described for the previously reported family of trihydride osmium(IV) complexes $OsH_3(\kappa^2\text{-}C,X)(P^iPr_3)_2$ (X = O, N),[23] where the anionic *C,X*-chelate group prevents the reduction of the metal center. Thus, in contrast to **2**–**4**, they react with HBF_4, releasing molecular hydrogen, to afford unsaturated dihydride-osmium(IV) species, which are stabilized by coordination of weak Lewis bases, such as acetone or water, or halides. In order to understand the surprising stability of **5**–**7**, which can be isolated and characterized and do not dissociate molecular hydrogen under argon or release the reduced chelate ligand, we analyzed the bonding situation in **6** by means of DFT calculations, at the BP86-D3/def2-SVP level. In particular, the nature of the osmium-carbon interactions was investigated by using the Atoms In Molecules (AIM) and Natural Bonds Orbital (NBO) methods.

Figure 4 shows the contour line diagrams of the Laplacian distribution $\nabla^2\rho(r)$ in the perpendicular plane to the P–Os–P direction. As expected, according to the AIM method, complex **6** is a five-membered metalacycle species possessing two Os–C bond critical points (BCP) and one $OsNC_3$ ring critical point (RCP). Furthermore the Os–C(aryl) bond as well the Os–C(NHC) bond clearly exhibit an area of charge concentration ($\nabla^2\rho(r) < 0$, solid lines) at the carbon ends with the shape of a droplet-like appendix directed towards the osmium atom,

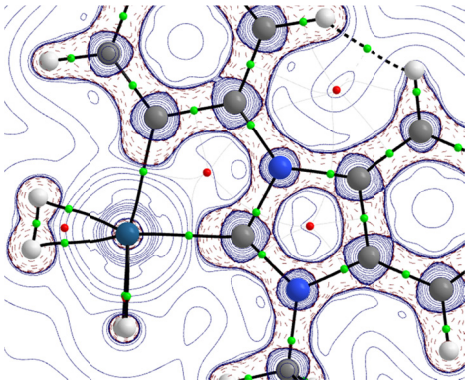


Figure 4. Contour line diagrams $\nabla^2\rho(r)$ for complex **6** C(aryl)−Os−C(NHC) in the plane. Dashed lines indicate areas of charge concentration ($\nabla^2\rho(r) < 0$) while solid lines show areas of charge depletion ($\nabla^2\rho(r) > 0$). The solid lines connecting the atomic nuclei are the bond paths while the small green and red spheres indicate the corresponding bond critical points and ring critical points, respectively. The solid lines separating the atomic basins indicate the zero-flux surfaces crossing the molecular plane.

therefore indicating a closed-shell donor-acceptor bond. In this sense, the situation resembles that for related osmacycles which are characterized by a σ(C–Os) bond established by donation of the in-plane lone-pair of the carbon atom to a vacant *d* atomic orbital of the transition metal.[17e]

The computed ellipticities (ε_c) at both Os–C bond critical points, which can be used as a measure of the double-bond character of a bond,[24] suggest that the π-contribution at the Os–C(NHC) bond is significantly higher than at the Os–C(aryl) bond (ε_c = 0.183 versus 0.029, respectively). A similar conclusion can be derived from the corresponding computed Wiberg Bond Indices (WBI = 0.81 versus 0.68 a.u.). Indeed, the second-order perturbation theory (SOPT) of the NBO method locates a stabilizing two-electron delocalization from a doubly-occupied d_π(Os) atomic orbital to the p_z atomic orbital at the carbene carbon (Figure 5). The computed associated SOPT stabilizing energy is quite significant ($\Delta E^{(2)}$ = –40.6 kcal·mol^{-1}) and, as expected, much higher than the d_π(Os) → π^*(C=C) delocalization involving the phenyl group ($\Delta E^{(2)}$ = –6.6 kcal·mol^{-1}). As a consequence, the electronic occupation of the p_z atomic orbital at the carbene carbon atom is remarkable (0.85e) and higher than that computed for the free NHC ligand (0.64e). It can be therefore concluded that the Os–C(NHC) bond has a significant π-backdonation, which enhances the electrophilicity of the metal center.

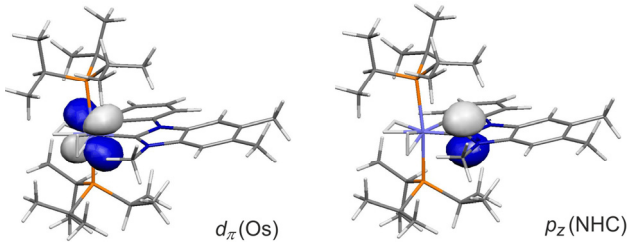


Figure 5. Computed Natural Bond Orbitals involved in the stabilizing d_π(Os) → p_z(NHC) two-electron delocalization in complex **6**.

The Os–C links influence the coordination of the hydrogen molecules to the metal center. As a consequence of the remarkable π-backdonation to the carbene carbon atom, the backdonation of the osmium atom to the hydrogen molecule *trans* disposed to the NHC unit decreases. Indeed, the SOPT method indicates that the π-backdonation from the doubly occupied $d\pi$(Os) orbital to the σ^*(H$_2$) molecular orbital of this molecule is lower ($\Delta E^{(2)}$ = –30.9 kcal·mol^{-1}) than that to the σ^*(H$_2$) molecular orbital corresponding to the hydrogen molecule trans disposed to the phenyl group ($\Delta E^{(2)}$ = –35.0 kcal·mol^{-1}).

It should be further mentioned that there are also significant differences between the Os–C(NHC) and Os–P bonds because is argued too many times that both types of bonds resemble. The Wiberg Bond Indices indicate that the Os–C(NHC) bond is stronger than the Os–P bond (0.81 versus 0.69) due to the π-acceptor capacity of the p_z orbital at the metalated carbon atom of the NHC unit, which has not counterpart at the phosphine. The computed ellipticities follow the same trend: Whereas a value of 0.183 was computed for the Os–C(NHC) bond, a much lower value of 0.040 was computed for the Os–P bond.

Deprotonation and Substitution of the Coordinated Hydrogen Molecules. The electrophility of the metal center of the dihydrogen derivatives **5**–**7** activates one of the coordinated hydrogen molecule of these compounds toward the heterolysis. As a consequence, complexes **5**–**7** are strong Brønsted acids. In acetone, at room temperature, they are in equilibrium with their respective trihydride precursors **2**–**4**. At 25 ºC, values of 2.4×10^{-5} (**5** and **6**) and 1.1×10^{-5} (**7**) for the dissociation equilibrium constants (K_{eq}) were determined by ^{31}P{^{1}H} NMR spectroscopy, which yield p$K_a^{acetone}$ values of 3.5 (**5** and **6**) and 3.8 (**7**). In order to compare the acidity of these complexes with that of species soluble in water, pK_a^{water} values of 2.5 (**5** and **6**) and 2.8 (**7**) were calculated by means of eq 1.[25] They reveal that the acidity of the dihydrogen complexes **5**–**7** is similar to the acidity of the phosphoric acid (p$K_{a_1}^{water}$ = 2.15)[26] and organic compounds such as bromoacetic acid (pK_a^{water} = 2.69) or chloroacetic acid (pK_a^{water} = 2.85).[27]

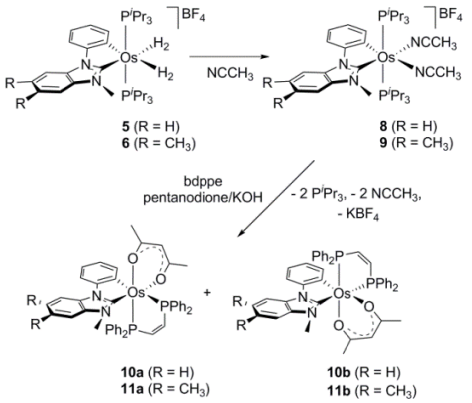
$$pK_a^{water}\{\mathbf{5}, \mathbf{6}, \mathbf{7}\} = pK_{eq}\{\mathbf{5}, \mathbf{6}, \mathbf{7}\} + pK_a^{water}\{[(CH_3)_2COH]^+\} \quad (1)$$

The heterolysis of one of the coordinated hydrogen molecules of the bis(dihydrogen) derivatives to afford the trihydrides **2**–**4** should be viewed as the last stage in the direct metalation process of the phenylbenzimidazolium and phenylimidazolium salts, which can be rationalized as follows: on an unsaturated dihydride species, generated by loss of two hydrogen molecules from **1**, the initial coordination of an *ortho*-CH bond of the phenyl substituent of the salts could promote its homolytic cleavage and the concerted NCHN-proton transfer from the NHCH$^+$ unit to one of the hydride ligands, to generate **5**–**7**, in a manner that resembles the ammoniaborane dehydrogenation on the unsaturated dihydrides $IrH_2(POCOP^{tBu})$[9a,c] (POCOP^{tBu} = κ^3-*P,C,P*-(OP^{t}Bu$_2$)$_2$C$_6$H$_3$) and $OsH_2(CO)(P^iPr_3)_2$.[28] The final transfer of the accepted proton to an external base should lead to **2**–**4**.

The hydrogen molecule is a weak Lewis base. Thus, it is displaced from the metal coordination sphere by good coordinating ligands which are also conjugated bases of very strong Brønsted acids. In contrast to acetone, acetonitrile substitutes the coordinated hydrogen molecules of **5** and **6**. As a consequence, the stirring of acetonitrile solutions of the dihydrogen complexes, under argon, at room temperature, for 20 h leads to the bis(solvento) derivatives **8** and **9**, which were isolated as green solids in 85% and 89% yield, respectively (Scheme 4).

Complex **9** was characterized by X-ray diffraction analysis. The structure has two cations and two anions chemically equivalent but crystallographically independent in the asymmetric unit. Figure 6 shows a view of one of these cations. The coordination polyhedron around the osmium atom can be rationalized as a distorted octahedron with *trans*-phosphines (P(1)–Os–P(2) = 173.49(3)º and 175.15(3)º). The chelate ligand (C(1)–Os–C(6) = 78.06(12)º and 78.66(12)º) and the acetonitrile molecules lie in the perpendicular plane. The Os–C(1) bond lengths of 2.014(3) and 2.004(3) Å as well as the Os–C(6) distances of 2.074(3) and 2.071(3) Å compare well with those of **2**, **4**, and **6** although they are now slightly shorter.

Scheme 4



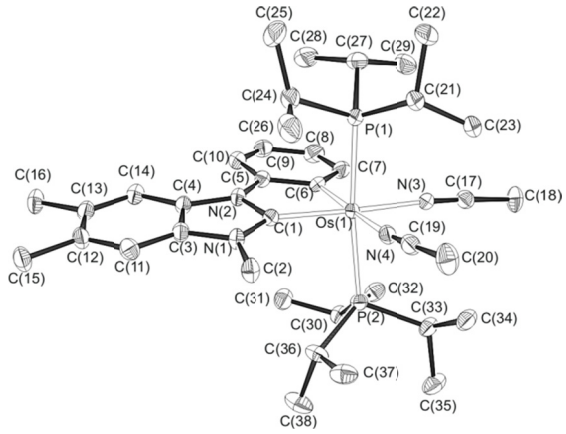


Figure 6. ORTEP diagram of complex **9** (50% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Os–C(1) = 2.014(3), 2.003(3), Os–C(6) = 2.074(3), 2.071(3), Os–P(1) = 2.4208(8), 2.4324(8), Os–P(2) = 2.4172(8), 2.4160(8), Os–N(3) = 2.078(3), 2.069(2), Os–N(4) = 2.092(3), 2.092(2), C(1)-Os–C(6) = 78.08(12), 78.67 (12), P(1)–Os–P(2) = 173.49(3), 173.15(3).

The ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectra of **8** and **9**, in dichloromethane-d_2, at room temperature are consistent with the structure shown in Figure 6. In agreement with the presence of two inequivalent acetonitrile ligands in the complexes, each ^{1}H NMR spectrum contains two acetonitrile methyl resonances at about 2.7 ppm whereas each ^{13}C{^{1}H} NMR spectrum shows two CN resonances between 123 and 125 ppm and two methyl signals at 5.4 and 5.3 ppm, along with the resonances due to the metalated carbon atoms of the chelate ligand at about 187 ppm (NCN) and at 147 ppm (C_{Ph}). As expected, the equivalent phosphines display a singlet at about 10 ppm in the ^{31}P{^{1}H} NMR spectra.

Acetonitrile and phosphine ligands of **8** and **9** can be replaced by *cis*-1,2-bis(diphenylphosphino)ethylene (bdppe) and acetylacetonate (acac) in a one-pot synthesis procedure, to afford novel complexes containing three different chelate ligands, *C,C*-, *P,P*-, and *O,O*-donor. Treatment of tetrahydrofuran solutions of **8** and **9** with 1.0 equiv of diphosphine and 2.0 equiv of pentane-2,4-dione, in the presence of 2.0 equiv of potassium hydroxide, at 50 ºC, for 5 h gives rise in a quantitative manner to a 1:1 mixture of the two possible isomers (namely, P *trans* to aryl (**a**) or P *trans* to NHC (**b**)) of **10** and **11** (Scheme 4). The isomers were separated by using their different solubility in pentane, isolated in moderated yield, and fully characterized including the X-ray diffraction analysis of **10a** and **11b**. Views of their octahedral structures are shown in Figures 7 and 8. Bond lengths and angles are in the expected ranges and do not need further comments. The ^{1}H NMR spectra contain the characteristic signal of the three types of ligands. In agreement with inequivalent PPh_2-groups, the ^{31}P{^{1}H} NMR spectra contain AB spin systems between 27 and 43 ppm for isomers **a** and between 30 and 49 ppm for isomers **b**. Chemical shifts and C–P coupling constants for the resonances corresponding to the metalated carbon atoms of the *C,C*-chelate ligands in the ^{13}C{^{1}H} NMR spectra are consistent with the stereochemistry of each isomer (see experimental section).

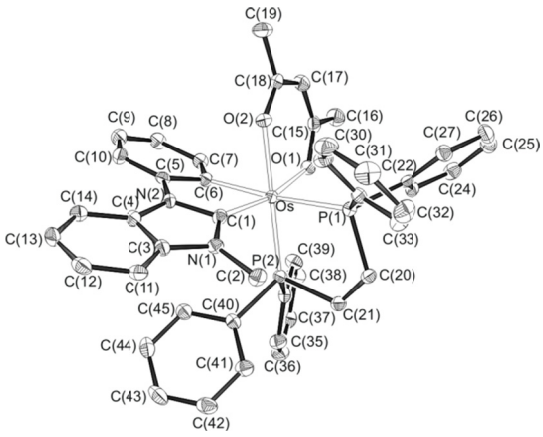


Figure 7. ORTEP diagram of complex **10a** (50% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Os–C(1) = 1.998(3), Os–C(6) = 2.100(3), Os–P(1) = 2.3251(9), Os–P(2) = 2.227(9), Os–O(1) = 2.136(2), Os–O(2) = 2.150(2), C(1)–Os–C(6) = 78.63(14), O(1)–Os–O(2) = 86.20(9), P(1)–Os–P(2) = 83.65(3).

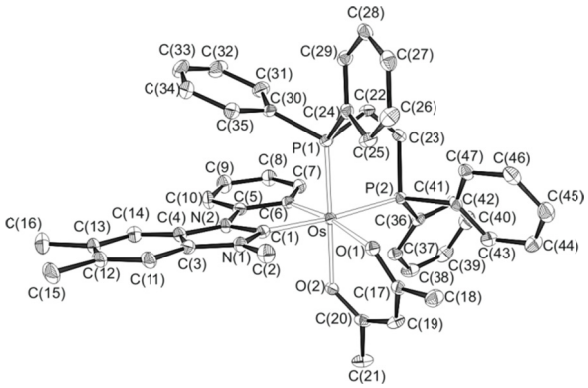


Figure 8. ORTEP diagram of complex **11b** (50% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Os–C(1) = 2.048(3), Os–C(6) = 2.065(3), Os–P(1) = 2.2271(7), Os–P(2) = 2.3155(7), Os–O(1) = 2.1780(19), Os–O(2) = 2.1500(18), C(1)–Os–C(6) = 78.23(11), O(1)–Os–O(2) = 84.58(7), P(1)–Os–P(2) = 83.24(2).

CONCLUDING REMARKS

The hexahydride complex $OsH_6(P^iPr_3)_2$ promotes the direct metalation of N-phenylbenzimidazolium and N-phenylimidazolium salts to afford trihydride-osmium(IV) derivatives, containing anionic C_{aryl},C_{NHC}-chelate ligands. The metal center of these compounds undergoes reduction by protonation leading to bis(dihydrogen) derivatives. AIM and NBO methods reveal that the Os–C(NHC) bond of the Os-chelate link tolerates a significant π-backdonation from a doubly-occupied d_π(Os) atomic orbital to the p_z atomic orbital at the carbene carbon atom, which enhances the electrophilicity of the metal center. Thus, one of the coordinated hydrogen molecules of the bis(dihydrogen) complexes is activated towards heterolysis. As a consequence the dihydrogen complexes behave as strong Brønsted acids with pK_a^{water} values between 2.5 and 2.8. In the presence of good coordinating ligands, which are also conjugated bases of very strong Brønsted acids, the hydrogen molecules are displaced by the ligands.

In conclusion, NHC's are very useful ligands to stabilize non-classical H–H interactions due to their significant π-accepting capacity, which is higher than those of the aryl groups and alkylphosphine ligands.

EXPERIMENTAL SECTION

All reactions were carried out with rigorous exclusion of air using Schlenk-tube techniques. Acetonitrile, methanol, and 2-propanol were dried and distilled under argon. Other solvents were obtained oxygen- and water-free from an MBraun solvent purification apparatus. NMR spectra were recorded on a Varian Gemini 2000, a Bruker ARX 300 MHz, a Bruker Avance 300 MHz, or a 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 external standard (^{31}P{^{1}H} to 85% H_3PO_4 and ^{11}B to $BF_3{\cdot}OEt_2$). Coupling constants J and N ($N = J(PH) + J(P'H)$ for ^{1}H and $N = J(PC) + J(P'C)$ for ^{13}C{^{1}H}) are given in hertz. Attenuated total reflection infrared spectra (ATR-IR) of solid samples were run on a Perkin-Elmer Spectrum 100 FT-IR spectrometer. C, H, and N analyses were carried out in a Perkin-Elmer 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). Triethylamine and pentane-2,4-dione (Hacac) were purchased from commercial sources and vacuum distilled. All other reagents were purchased from commercial sources and used as received. $OsH_6(P^iPr_3)_2$ was prepared according to the published method.[29] 1-phenyl-3-methyl-1-*H*-benzimidazolium iodide (HL_1I) was made with similar procedure to the reported by Hollis and co-workers for 1,3-bis(*N*-benzimidazolyl)benzene.[30] 1-phenyl-3-methyl-1-*H*-5,6-dimethyl-benzimidazolium iodine (HL_2I) and 1-phenyl-3-methyl-1-*H*-imidazolium iodine (HL_3I) were provided by UDC. Note: *C* is referred to *ortho*-metalated phenyl carbon atom (C_{Ph}); *C′* is referred to *N*-heterocyclic carbene carbon atom (NCN).

Preparation of 1-phenyl-3-methyl-1-*H*-benzimidazolium iodide (HL_1I). *Step 1:* Benzimidazole (3.500 g, 0.030 mol), K_2CO_3 (4.100 g, 0.030 mol), CuO (0.310 g, 0.004 mol) and bromobenzene (2.6 mL, 0.025 mol) were dissolved in dimethylsulfoxide (15 mL) and the mixture was stirred at 150 ºC for 48 hours. Upon cooling to room temperature, dichloromethane (100 mL) was added and the resulting mixture was filtered through activated basic alumina (30 g). The alumina was washed with a 1:10 mixture of 2-propanol/dichloromethane (20 mL) and the filtrate was concentrated to dryness. Addition of diethyl ether (5 mL) to the resulting brownish residue caused the appearance of a white solid, which was washed with additional portions of diethyl ether (4 x 3 mL) and dried *in vacuo*. The obtained white powder was identified by ^{1}H NMR as *N*-phenylbenzimidazole. Yield: 4.650 g (81%). *Step 2:* A mixture of *N*-phenylbenzimidazole (4.650 g, 0.024 mol), iodomethane (7.5 mL, 0.120 mol) and acetonitrile (30 mL) was stirred under reflux for 4 hours. The solution was cooled at room temperature with appearance of a yellowish precipitate. After removing volatiles under vacuum, the resulting solid was washed with a 2:1 mixture of diethyl ether/methanol (3 x 15 mL) and dried *in vacuo*. The obtained white powder was identified by ^{1}H NMR as 1-phenyl-3-methyl-1-*H*-benzimidazolium iodide. Yield: 6.920 g (86%).

Preparation of 1-phenyl-3-methyl-1-*H*-benzimidazolium tetrafluoroborate (HL_1BF_4). 1-phenyl-3-methyl-1-*H*-benzimidazolium iodide (HL_1I; 1.000 g, 2.975 mmol) and $AgBF_4$ (0.579 g, 2.975 mmol) were dissolved in acetonitrile (15 mL) in the absence of light. The resulting suspension was stirred protected from light at room temperature for 2 h before evaporating solvent under vacuum. Dichloromethane (15 mL) was added and the solution was filtered through Celite to remove AgI. The Celite was washed with dichloromethane (2 x 5 mL) and the filtrate was concentrated to dryness. Addition of diethyl ether (5 mL) to the residue resulted in the formation of a white solid, which was washed with additional portions of diethyl ether (2 x 4 mL) and dried *in vacuo*. Yield: 0.813 g (92%).

Preparation of 1-phenyl-3-methyl-1-*H*-5,6-dimethyl-benzimidazolium tetrafluoroborate (HL_2BF_4). HL_2BF_4 was prepared as described for HL_1BF_4, starting from HL_2I (1.000 g, 2.740 mmol) and $AgBF_4$ (0.535 g, 0.003 mmol). A white solid was obtained. Yield: 0.780 g (87%).

Preparation of 1-phenyl-3-methyl-1-*H*-imidazolium tetrafluoroborate (HL_3BF_4). HL_3BF_4 was prepared as described for HL_1BF_4, starting from HL_3I (0.250 g, 0.874 mmol) and $AgBF_4$ (0.179 g, 0.917 mmol). A white solid was obtained. Yield: 0.200 g (93%).

Preparation of $OsH_3(C,C'\text{-}L_1)(P^iPr_3)_2$ (2). HL_1BF_4 (0.229 g, 0.774 mmol) was added to a solution of $OsH_6(P^iPr_3)_2$ (**1**; 0.400 g, 0.774 mmol) in toluene (40 mL) and the resulting suspension was treated with triethylamine (0.119 mL, 0.860 mmol). The mixture was stirred for 4 hours under reflux. After cooling to room temperature, the resulting amber solution was filtered through Celite and the filtrate was concentrated to ca. 1 mL. Subsequent addition of methanol (8 mL) at 195 K caused the formation of a white precipitate, which was washed with additional portions of methanol (3 x 4 mL) at 195 K and dried *in vacuo*. Yield: 0.426 g (76%). X-ray quality crystals were grown by layering a solution of complex **2** in toluene with methanol. Anal. Calcd. for $C_{32}H_{56}N_2OsP_2$: C 53.31%; H 7.83%; N 3.89%. Found: C 53.01%; H 8.14%; N 3.91%. HRMS (electrospray, m/z): Calcd. for $C_{32}H_{51}N_2OsP_2$ $[M - 5\ H]^+$: 719.3295. Found: 719.3281. IR (cm^{-1}): ν(Os–H) 2044 (m). ^{1}H NMR (400 MHz, C_6D_6, 293 K): δ 8.66 (d, $^3J_{H-H}$ = 7.2, 1 H, CH_{Ph}), 8.0–7.8 (m, 2 H, CH_{Ph} and CH_{bzim}), 7.24 (ddd, $^3J_{H-H}$ = 7.2, $^3J_{H-H}$ = 7.2, $^4J_{H-H}$ = 1.0, 1 H, CH_{Ph}), 7.10 (ddd, $^3J_{H-H}$ = 7.2, $^3J_{H-H}$ = 7.2, $^4J_{H-H}$ = 1.0, 1 H, CH_{Ph}), 7.1–6.9 (m, 2 H, CH_{bzim}), 6.91 (m, 1 H, CH_{bzim}), 3.92 (s, 3 H, NCH_3), 1.79 (m, 6 H, PCH), 0.96 (dvt, N = 12.5, $^3J_{H-H}$ = 6.9, 18 H, PCH(CH_3)$_2$), 0.83 (dvt, N = 12.5, $^3J_{H-H}$ = 6.9, 18 H, PCH(CH_3)$_2$), –8.18 (br, 1 H, OsH), –9.94 (br, 2 H, OsH). ^{31}P{^{1}H} NMR (162.0 MHz, C_6D_6, 293 K): δ 25.7 (s). ^{13}C{^{1}H}-APT NMR, HMBC and HSQC (100.5 MHz, C_6D_6, 293 K): δ 206.3 (t, $^2J_{C-P}$ = 5.4, NCN), 157.9 (t, $^2J_{C-P}$ = 6.7, OsC_{Ph}), 148.9 (s, NC_{Ph}), 148.0 (s, CH_{Ph}), 137.5 and 133.6 (both s, C_{bzim}), 124.3 (s, CH_{Ph}), 122.1 (s, CH_{bzim}), 121.3 (s, CH_{bzim}), 119.8 (s, CH_{Ph}), 112.5 (s, CH_{bzim}), 110.4 (s, CH_{Ph}), 109.1 (s, CH_{bzim}), 36.6 (s, NCH_3), 27.9 (vt, N = 25.0, PCH), 19.9 and 19.8 (both s, PCH(CH_3)$_2$). $T_{1(min)}$ (ms, OsH, 400 MHz, CD_2Cl_2, 211 K): 141 ± 14 (–8.66 ppm); 102 ± 10 (–10.27 ppm).

Preparation of $OsH_3(C,C'\text{-}L_2)(P^iPr_3)_2$ (3). Complex **3** was prepared as described for **2**, starting from $OsH_6(P^iPr_3)_2$ (**1**; 0.400 g, 0.774 mmol), HL_2BF_4 (0.251 g, 0.774 mmol), and Et_3N (0.120 mL, 0.860 mmol). A white solid was obtained. Yield: 0.491 g (84%). Anal. Calcd. for $C_{34}H_{60}N_2OsP_2{\cdot}(CH_3OH)$: C 53.82%; H 8.26%; N 3.59%. Found: C 53.99%; H 8.51%; N 3.67%. HRMS (electrospray, m/z): Calcd. for $C_{34}H_{55}N_2OsP_2$ $[M - H]^+$: 745.3452; Found: 745.3460. IR (cm^{-1}): ν(Os–H) 2049 (m), ν(Os–H) 2027 (m). ^{1}H NMR (400 MHz, C_6D_6, 293 K): δ 8.67 (d, $^3J_{H-H}$ = 7.5, 1 H, CH_{Ph}), 8.02 (dd, $^3J_{H-H}$ = 7.5, $^4J_{H-H}$ = 0.8, 1 H, CH_{Ph}), 7.88 (s, 1 H, CH_{bzim}), 7.24 (ddd, $^3J_{H-H}$ = 7.5, $^3J_{H-H}$ = 7.5, $^4J_{H-H}$ = 1.1, 1 H, CH_{Ph}), 7.10 (ddd, $^3J_{H-H}$ = 7.5, $^3J_{H-H}$ =

7.5, $^4J_{H–H}$ = 0.8, 1 H, CH_{Ph}), 6.80 (s, 1 H, CH_{bzim}), 3.96 (s, 3 H, NCH_3), 2.13 and 2.12 (both s, each 3 H, CH_{3bzim}), 1.84 (m, 6 H, PCH), 0.99 (dvt, *N* = 12.5, $^3J_{H–H}$ = 6.9, 18 H, PCH(CH_3)$_2$), 0.87 (dvt, *N* = 12.5, $^3J_{H–H}$ = 6.9, 18 H, PCH(CH_3)$_2$), –8.21 (br, 1 H, OsH), –9.96 (br, 2 H, OsH). $^{31}P\{^1H\}$ NMR (162.0 MHz, C_6D_6, 293 K): δ 25.6 (s). $^{13}C\{^1H\}$-APT NMR, HMBC and HSQC (100.5 MHz, C_6D_6, 293 K): δ 204.9 (t, $^2J_{C–P}$ = 5.6, NCN), 157.7 (t, $^2J_{C–P}$ = 6.7, OsC_{Ph}), 149.2 (s, NC_{Ph}), 148.0 (s, CH_{Ph}), 136.2, 132.2, 130.3, and 129.6 (all s, C_{bzim}), 124.2, 119.8, and 112.3 (all s, CH_{Ph}), 111.6 and 110.2 (s, CH_{bzim}), 36.8 (s, NCH_3), 28.1 (vt, *N* = 24.8, PCH), 20.2 and 20.1 (both s, CH_{3bzim}), 20.0 and 19.8 (both s, PCH(CH_3)$_2$). $T_{1(min)}$ (ms, OsH, 400 MHz, CD_2Cl_2, 208 K): 181 ± 18 (–8.68 ppm); 128 ± 13 (–10.31 ppm).

Preparation of OsH$_3$(*C,C'*-L$_3$)(P^{i}Pr$_3$)$_2$ (4). Complex **4** was prepared as described for **2**, starting from $OsH_6(P^iPr_3)_2$ (**1**; 0.420 g, 0.813 mmol), HL_3BF_4 (0.200 g, 0.813 mmol), and Et_3N (0.114 mL, 0.813 mmol). A white solid was obtained. Yield: 0.456 g (74%). A crystal suitable for an X-ray diffraction study was obtained from a concentrated solution of **4** in methanol. Anal. Calcd. for $C_{28}H_{54}N_2OsP_2$: C 50.13%; H 8.11%; N 4.18%. Found: C 49.81%; H 7.70%; N 4.03%. HRMS (electrospray, m/z): Calcd. for $C_{28}H_{49}N_2OsP_2$ [M – 5 H]$^+$: 667.2981; Found: 667.3129. IR (cm^{-1}): ν(Os–H) 2020 (m), ν(Os–H) 2005 (m). ^1H NMR (400 MHz, C_6D_6, 293 K): δ 8.67 (d, $^3J_{H–H}$ = 7.2, 1 H, CH_{Ph}), 7.2–7.1 (m, 4 H, CH_{Ph} and CH_{im}), 6.39 (s, 1 H, CH_{im}), 3.67 (s, 3 H, NCH_3), 1.92 (m, 6 H, PCH), 1.13 (dvt, *N* = 12.4, $^3J_{H–H}$ = 6.4, 18 H, PCH(CH_3)$_2$), 1.00 (dvt, *N* = 12.4, $^3J_{H–H}$ = 6.4, 18 H, PCH(CH_3)$_2$), –8.41 (br, 1 H, OsH), –10.27 (br, 2 H, OsH). $^{31}P\{^1H\}$ NMR (162.0 MHz, C_6D_6, 293 K): δ 25.0 (s). $^{13}C\{^1H\}$-APT NMR, HMBC and HSQC (100.5 MHz, C_6D_6, 293 K): δ 190.0 (t, $^2J_{C–P}$ = 6.1, NCN), 158.1 (t, $^2J_{C–P}$ = 6.7, OsC_{Ph}), 148.0 (s, CH_{Ph}), 147.2 (s, NC_{Ph}), 124.6 (s, CH_{Ph}), 120.0 (s, CH_{im}), 119.4 (s, CH_{Ph}), 114.3 (s, CH_{im}), 110.3 (s, CH_{Ph}), 36.3 (s, NCH_3), 28.0 (vt, *N* = 24.3, PCH), 20.1 and 20.0 (both s, PCH(CH_3)$_2$). $T_{1(min)}$ (ms, OsH, 400 MHz, CD_2Cl_2, 203 K): 137 ± 13 (–9.01 ppm); 109 ± 13 (–10.76 ppm).

Preparation of [Os(*C,C'*-L$_1$)(η^2-H$_2$)$_2$(P^{i}Pr$_3$)$_2$]BF$_4$ (5). A colorless solution of **2** (0.353 g, 0.490 mmol) in diethyl ether (15 mL) was treated with $HBF_4{\cdot}OEt_2$ (0.087 mL, 0.539 mmol). The mixture was let to react at room temperature for 20 minutes before stirring at low temperature (195 K) for 4 hours. During this time, the formation of a white solid was observed. This solid was isolated by decantation, washed with diethyl ether (3 x 3 mL), and dried *in vacuo*. Yield: 0.403 g (83%). Anal. Calcd. for $C_{32}H_{57}BF_4N_2OsP_2$: C 47.52%; H 7.01%; N 3.35%. Found: C 47.37%; H 6.87%; N 3.42%. HRMS (electrospray, m/z): Calcd. for $C_{32}H_{51}N_2OsP_2$ [M – 6 H]$^+$: 717.3138; Found: 717.3309. IR (cm^{-1}): ν(B–F) 1034 (br, vs). ^1H NMR (300 MHz, CD_2Cl_2, 223 K): δ 8.10 (m, 1 H, CH_{bzim}), 7.98 (d, $^3J_{H–H}$ = 7.6, 1 H, CH_{Ph}), 7.90 (d, $^3J_{H–H}$ = 7.6, 1 H, CH_{Ph}), 7.54 (m, 1 H, CH_{bzim}), 7.5–7.4 (m, 2 H, CH_{bzim}), 7.30 (dd, $^3J_{H–H}$ = 7.6, $^3J_{H–H}$ = 7.6, 1 H, CH_{Ph}), 7.01 (dd, $^3J_{H–H}$ = 7.6, $^3J_{H–H}$ = 7.6, 1 H, CH_{Ph}), 3.96 (s, 3 H, NCH_3), 1.80 (m, 6 H, PCH), 0.86 (dvt, *N* = 13.7, $^3J_{H–H}$ = 6.8, 18 H, PCH(CH_3)$_2$), 0.81 (dvt, *N* = 13.1, $^3J_{H–H}$ = 6.5, 18 H, PCH(CH_3)$_2$), –6.74 (br, 4 H, OsH). $^{31}P\{^1H\}$ NMR (121.0 MHz, CD_2Cl_2, 293 K): δ 14.9 (s). $^{19}F\{^1H\}$ NMR (282.4 MHz, CD_2Cl_2, 293 K): δ –153.3 (br).$^{13}C\{^1H\}$-APT NMR, HMBC and HSQC (75.5 MHz, CD_2Cl_2, 223 K): δ 188.6 (t, $^2J_{C–P}$ = 5.6, NCN), 148.2 (br, OsC_{Ph}), 144.8 (s, CH_{Ph}), 135.2 and 131.2 (both s, C_{bzim}), 126.0 and 124.4 (both s, CH_{Ph}), 123.9 and 123.5 (s, C_{bzim}), 113.8 (s, CH_{Ph}), 111.5 and 111.0 (s, CH_{bzim}), 36.6 (s, NCH_3), 25.4 (vt, *N* = 13.9, PCH), 19.3 and 18.7 (both s, PCH(CH_3)$_2$). Note: NC_{Ph} signal missing presumably due to coincidental overlap. $T_{1(min)}$ (ms, OsH, 400 MHz, CD_2Cl_2, 193 K): 12.0 ± 2 (–6.83 ppm).

Preparation of [Os(*C,C'*-L$_2$)(η^2-H$_2$)$_2$(P^{i}Pr$_3$)$_2$]BF$_4$ (6). Complex **6** was prepared as described for **5**, starting from **3** (0.100 g, 0.134 mmol) and $HBF_4{\cdot}OEt_2$ (0.020 mL, 0.147 mmol). A white solid was obtained. Yield: 0.098 g (88%). X-ray quality crystals were grown by layering a solution of complex **6** in dicloromethane with pentane. Anal. Calcd. for $C_{34}H_{61}BF_4N_2OsP_2$: C 48.80%; H 7.35%; N 3.35%. Found: C 48.65%; H 7.51%; N 3.14%. HRMS (electrospray, m/z): Calcd. for $C_{34}H_{55}N_2OsP_2$ [M – 6 H]$^+$: 745.3583; Found: 745.3452. IR (cm^{-1}): ν(B–F) 1048 (vs), ν(B–F) 1034 (vs). ^1H NMR (300 MHz, CD_2Cl_2, 223 K): δ 7.98 (d, $^3J_{H–H}$ = 7.5, 1 H, CH_{Ph}), 7.89 (d, $^3J_{H–H}$ = 7.5, 1 H, CH_{Ph}), 7.85 (s, 1 H, CH_{bzim}), 7.4–7.2 (m, 2 H, CH_{bzim} and CH_{Ph}), 7.00 (dd, $^3J_{H–H}$ = 7.5, $^3J_{H–H}$ = 7.5, 1 H, CH_{Ph}), 3.90 (s, 3 H, NCH_3), 2.42 and 2.38 (both s, each 3 H, CH_{3bzim}), 1.80 (m, 6 H, PCH), 0.99 (dvt, *N* = 14.0, $^3J_{H–H}$ = 7.0, 18 H, PCH(CH_3)$_2$), 0.78 (dvt, *N* = 14.0, $^3J_{H–H}$ = 7.0, 18 H, PCH(CH_3)$_2$), –6.78 (br, 4 H, OsH). $^{31}P\{^1H\}$ NMR (121.0 MHz, CD_2Cl_2, 293 K): δ 15.2 (s). $^{19}F\{^1H\}$ NMR (282.4 MHz, CD_2Cl_2, 293 K): δ –153.3 (br). $^{13}C\{^1H\}$-APT NMR, HMBC and HSQC (75.5 MHz, CD_2Cl_2, 223 K): δ 187.0 (t, $^2J_{C–P}$ = 7.7, NCN), 148.6 (t, $^2J_{C–P}$ = 1.6, OsC_{Ph}), 145.1 (s, CH_{Ph}), 134.0, 133.5, 133.2, and 129.8 (all s, CH_{bzim}), 126.1, 125.0, and 114.1 (all s, CH_{Ph}), 112.3 and 111.4 (both s, CH_{bzim}), 36.7 (s, NCH_3) 25.8 (vt, *N* = 27.8, PCH), 20.7 and 20.4 (both s, CH_{3bzim}), 19.6 and 18.9 (s, PCH(CH_3)$_2$). Note: NC_{Ph} signal missing presumably due to coincidental overlap. $T_{1(min)}$ (ms, OsH, 400 MHz, CD_2Cl_2, 193 K): 14 ± 1 (–6.79 ppm).

Preparation of [Os(*C,C'*-L$_3$)(η^2-H$_2$)$_2$(P^{i}Pr$_3$)$_2$]BF$_4$ (7). Complex **7** was prepared as described for **5**, starting from **4** (0.150 g, 0.224 mmol) and $HBF_4{\cdot}OEt_2$ (0.034 mL, 0.246 mmol). A white solid was obtained. Yield: 0.151 g (89%). Anal. Calcd. for $C_{28}H_{55}BF_4N_2OsP_2$: C 44.33%; H 7.31%; N 3.69%. Found: C 44.13%; H 7.23%; N 3.84%. HRMS (electrospray, m/z): Calcd. for $C_{28}H_{49}N_2OsP_2$ [M – 6 H]$^+$: 667.2981; Found: 667.3005. IR (cm^{-1}): ν(B–F) 1050 (vs); ν(B–F) 1031 (vs). ^1H NMR (300 MHz, CD_2Cl_2, 223 K): δ 7.89 (d, $^3J_{H–H}$ = 7.7, 1 H, CH_{Ph}), 7.57 (s, 1 H, CH_{im}), 7.27 (s, 1 H, CH_{im}), 7.25 (d, $J_{H–H}$ = 7.7, 1 H, CH_{Ph}), 7.15 (dd, $^3J_{H–H}$ = 7.2, $^3J_{H–H}$ = 7.2, 1 H, CH_{Ph}), 6.96 (dd, $^3J_{H–H}$ = 7.2, $^3J_{H–H}$ = 7.2, 1 H, CH_{Ph}), 3.75 (s, 3 H, NCH_3), 1.81 (m, 6 H, PCH), 0.89 (dvt, *N* = 13.8, $^3J_{H–H}$ = 6.9, 18 H, PCH(CH_3)$_2$), 0.80 (dvt, *N* = 12.8, $^3J_{H–H}$ = 6.5, 18 H, PCH(CH_3)$_2$), –7.22 (br, 4 H, OsH). $^{31}P\{^1H\}$ NMR (121.0 MHz, CD_2Cl_2, 293 K): δ 16.4 (s). $^{19}F\{^1H\}$ NMR (282.4 MHz, CD_2Cl_2, 293 K): δ –153.6 (br). $^{13}C\{^1H\}$-APT NMR, HMBC and HSQC (75.5 MHz, C_6D_6, 223 K): δ 173.3 (t, $^2J_{C–P}$ = 6.6, NCN), 146.7 (t, $^2J_{C–P}$ = 1.9, OsC_{Ph}), 144.9 (s, CH_{Ph}), 138.4 (t, $^3J_{C–P}$ = 10.2, NC_{Ph}), 126.4 and 124.6 (both s, CH_{Ph}), 123.2 and 115.6 (both s, CH_{im}), 112.3 (s, CH_{Ph}), 39.2 (s, NCH_3), 25.5 (vt, *N* = 28.1, PCH), 19.6 and 18.8 (both s, PCH(CH_3)$_2$). $T_{1(min)}$ (ms, OsH, 400 MHz, CD_2Cl_2, 203 K): 13 ± 2 (–7.24 ppm).

Preparation of [Os(*C,C'*-L$_1$)(NCCH$_3$)$_2$(P^{i}Pr$_3$)$_2$]BF$_4$ (8). A pale amber solution of **5** (0.315 g, 0.376 mmol) in acetonitrile (20 mL) was stirred at room temperature under a flow of argon for approximately 20 hours. After filtration through Celite, the greenish-yellow solution was concentrated to dryness. Addition of diethyl ether (8 mL) to the residue at 195 K resulted in the formation of a green solid, which was washed with additional portions of diethyl ether (2 x 4 mL) and dried *in vacuo*. Yield: 0.292 g (85%). Anal. Calcd. for $C_{36}H_{59}BF_4N_4OsP_2$: C 48.76; H 6.71; N 6.32. Found: C 48.31; H 6.88; N 6.21. HRMS (electrospray, m/z): Calcd. for $C_{32}H_{51}N_2OsP_2$ [M – 2 H – 2(NCCH$_3$)]$^+$: 717.3138; Found: 717.3351. IR (cm^{-1}): ν(C≡N) 2253 (w), ν(B–F) 1049 (vs), ν(B–F) 1029 (vs). ^1H NMR (400 MHz, CD_2Cl_2, 293 K): δ 7.96 (m, 1 H, CH_{bzim}), 7.80 (d, $^3J_{H–H}$ = 7.3, 1 H, CH_{Ph}), 7.64 (d, $^3J_{H–H}$ = 7.3, 1 H, CH_{Ph}), 7.34 (m, 1 H, CH_{bzim}), 7.4–7.2 (m, 2 H, CH_{bzim}), 6.93 (dd, $^3J_{H–H}$ = 7.3, $^3J_{H–H}$ = 7.3, 1 H, CH_{Ph}), 6.84 (dd, $^3J_{H–H}$ = 7.3, $^3J_{H–H}$ = 7.3, 1 H, CH_{Ph}), 4.07 (s, 3 H, NCH_3), 2.74 and 2.69 (both s, each 3 H, $NCCH_3$), 2.2–2.0 (m, 6 H, PCH), 0.94 (dvt, *N* = 12.6, $^3J_{H–H}$ = 6.8, 18H, PCH(CH_3)$_2$), 0.89 (dvt, *N* = 12.6, $^3J_{H–H}$ = 6.8, 18 H, PCH(CH_3)$_2$). $^{31}P\{^1H\}$ NMR (121.0 MHz, CD_2Cl_2, 293 K): δ –10.2 (s). $^{19}F\{^1H\}$ NMR (162.0 MHz, CD_2Cl_2, 293 K): δ –153.3 (br). $^{13}C\{^1H\}$-APT NMR, HMBC and HSQC (100.5 MHz, CD_2Cl_2, 293 K): δ 188.2 (t, $^2J_{C–P}$ = 7.6, NCN), 151.4 (s, NC_{Ph}), 146.6 (t, $^2J_{C–P}$ = 7.7, OsC_{Ph}), 139.4 (s, CH_{Ph}), 137.5 and 133.4 (both s, C_{bzim}), 124.8 and 123.6 (both s, $NCCH_3$), 123.4 (br, CH_{Ph} and CH_{bzim}), 122.4 (s, CH_{bzim}), 120.6 and 112.1 (both s, CH_{Ph}), 110.4 and 109.6 (both s, CH_{bzim}), 35.2 (s, NCH_3), 25.1 (vt, *N* = 22.4, PCH), 19.6 and 19.5 (both s, PCH(CH_3)$_2$), 5.4 and 5.3 (both s, $NCCH_3$).

Preparation of [Os(*C,C'*-L$_2$)(NCCH$_3$)$_2$(P^{i}Pr$_3$)$_2$]BF$_4$ (9). Compound **9** was prepared as described for **8**, starting from **6** (0.422 g, 0.504 mmol) with exception that the acetonitrile solution was concentrated to ca. 1 mL before the addition of diethyl ether (8 mL). A pale green solid was obtained. Yield: 0.411 g (89%). X-ray quality crystals were grown by layering a solution of complex **9** in dichloromethane with pentane. Anal. Calcd. for $C_{38}H_{63}BF_4N_4OsP_2$: C 49.89; H 6.94; N 6.12.

Found: C 49.85; H 6.95; N 5.99. HRMS (electrospray, m/z): Calcd. for $C_{34}H_{55}N_2OsP_2$ [M – 2 H – 2 $(NCCH_3)$]$^+$: 745.3452; Found: 745.3489. IR (cm^{-1}): ν(C≡N) 2245 (w); ν(B–F) 1054 (vs), ν(B–F) 1036 (vs), ν(B–F) 1025 (vs). ^{1}H NMR (400 MHz, CD_2Cl_2, 293 K): δ 7.77 (d, $^3J_{H–H}$ = 7.3, 1 H, CH_{Ph}), 7.74 (s, 1 H, CH_{bzim}), 7.62 (d, $^3J_{H–H}$ = 7.3, 1 H, CH_{Ph}), 7.1 (s, 1 H, CH_{bzim}), 6.91 (dd, $^3J_{H–H}$ = 7.3, $^3J_{H–H}$ = 7.3, 1 H, CH_{Ph}), 6.81 (dd, $^3J_{H–H}$ = 7.3, $^3J_{H–H}$ = 7.3, 1 H, CH_{Ph}), 4.02 (s, 3 H, NCH_3), 2.73 and 2.69 (both s, each 3 H, NCCH_3), 2.43 and 2.39 (both s, each 3 H, CH_{3bzim}), 2.1 (m, 6 H, PCH), 0.93 (dvt, N = 12.8, $^3J_{H–H}$ = 6.5, 18 H, PCH(CH_3)$_2$), 0.89 (dvt, N = 12.8, $^3J_{H–H}$ = 6.5, 18 H, PCH(CH_3)$_2$). ^{31}P{^{1}H} NMR (121.0 MHz, CD_2Cl_2, 293 K): δ –10.1 (s). ^{19}F{^{1}H} NMR (162.0 MHz, CD_2Cl_2, 293 K): δ –148.2 (br). ^{13}C{^{1}H}-APT NMR, HMBC and HSQC (75.5 MHz, CD_2Cl_2, 293 K): δ 186.4 (t, $^2J_{C–P}$ = 7.7, NCN), 151.6 (s, NC_{Ph}), 146.6 (t, $^2J_{C–P}$ = 7.7, OsC_{Ph}), 139.3 (s, CH_{Ph}), 136.0, 132.1, 131.8, and 131.3 (all s, C_{bzim}), 124.5 and 123.4 (both s, NCCH_3), 123.1, 120.5, and 111.9 (all s, CH_{Ph}), 111.3 and 110.3 (both s, CH_{bzim}), 35.1 (s, NCH_3), 25.0 (vt, N = 22.4, PCH), 20.6 and 20.4 (both s, CH_{3bzim}), 19.5 and 19.4 (both s, PCH(CH_3)$_2$), 5.4 and 5.3 (both s, NCCH_3).

Preparation of Os(*C,C′*-L$_1$)(*O,O′*-acac)(*P,P′*-bdppe) (10). Potassium hydroxide (2.200 mL, 0.259 M in methanol, 0.570 mmol) was added to a solution of **8** (0.300 g, 0.338 mmol), *cis*-1,2-bis(diphenylphosphino)ethylene (bdppe; 0.134 g, 0.338 mmol), and pentane-2,4-dione (Hacac; 0.058 mL, 0.580 mmol) in THF (15 mL). After the reaction mixture was stirred at 323 K for 5 hours, volatiles were removed under vacuum. Dichloromethane (12 mL) was added and the resulting suspension was filtered through Celite. The filtrate was concentrated to dryness and pentane (15 mL) was added to afford a yellow solid corresponding to **10a**, which was washed with more pentane (10 x 15 mL) and dried *in vacuo*. The pentane solution previously obtained was filtrated through Celite and the filtrate concentrated to dryness to yield an orange solid corresponding to **10b**, which was purified by chromatography (silicagel 230-400 mesh and pentane/methylene chloride 1:1 as eluent).

Experimental data for Os(*C,C′*-L$_1$)(*O,O′*-acac)(*P,P′*-bdppe) (10a): Yield: 0.104 g (35%). X-ray quality crystals were grown by layering a solution of complex **10a** in dichloromethane with pentane. Anal. Calcd. for $C_{45}H_{40}N_2O_2OsP_2$: C 60.53; H 4.51; N 3.14. Found: C 60.92; H 4.56; N 2.75. HRMS (electrospray, m/z): Calcd. for $C_{45}H_{40}N_2O_2OsP_2$ [M]$^+$: 894.2177; Found: 894.2379. IR (cm^{-1}): ν(CO) 1580 (m), ν(CO) 1518 (m). ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ 8.2–6.4 (m, 30 H, 22 CH_{bdppe}, 4 CH_{bzim}, and 4 CH_{Ph}), 4.73 (s, 1 H, CH_{acac}), 2.64 (s, 3 H, NCH_3), 1.50 and 1.24 (both s, each 3 H, CH_{3acac}). ^{31}P{^{1}H} NMR (121.0 MHz, CD_2Cl_2, 293 K): δ 42.7 (d, $^2J_{P–P}$ = 18.5, bdppe), 26.5 (d, $^2J_{P–P}$ = 18.5, bdppe). ^{13}C{^{1}H}-APT NMR, HMBC and HSQC (75.5 MHz, CD_2Cl_2, 293 K): δ 189.6 (dd, $^2J_{C–P}$ = 9.5, $^2J_{C–P}$ = 1.6, NCN), 182.7 and 181.2 (both s, CO), 164.6 (dd, $^2J_{C–P}$ = 85.4, $^2J_{C–P}$ = 7.0, OsC_{Ph}), 154.6 (dd, $^1J_{C–P}$ = 45.5, $^2J_{C–P}$ = 32.5, $CH_{ethylene\text{-}bdppe}$), 151.0 (d, $^3J_{C–P}$ = 6.7, NC_{Ph}), 150.6 (dd, $^1J_{C–P}$ = 35.9, $^2J_{C–P}$ = 21.8, $CH_{ethylene\text{-}bdppe}$), 139.3 (d, $^1J_{C–P}$ = 33.1, $C_{Ph\text{-}bdppe}$), 138.7 (dd, $^1J_{C–P}$ = 57.2, $^3J_{C–P}$ = 2.6, $C_{Ph\text{-}bdppe}$), 137.9 (dd, $^1J_{C–P}$ = 30.6, $^3J_{C–P}$ = 1.5, $C_{Ph\text{-}bdppe}$), 137.3 (s, C_{bzim}), 137.3 (d, $^1J_{C–P}$ = 42.8, $C_{Ph\text{-}bdppe}$), 135.4 (s, CH_{Ph}), 134.3 (d, $J_{C–P}$ = 10.4, $CH_{Ph\text{-}bdppe}$), 133.6 (s, C_{bzim}), 132.7 (d, $J_{C–P}$ = 10.0, $CH_{Ph\text{-}bdppe}$), 130.5 (d, $J_{C–P}$ = 1.7, $CH_{Ph\text{-}bdppe}$), 129.6 (d, $J_{C–P}$ = 9.3, $CH_{Ph\text{-}bdppe}$), 129.6 (s, $CH_{Ph\text{-}bdppe}$), 129.0 (d, $J_{C–P}$ = 9.0, $CH_{Ph\text{-}bdppe}$), 128.3 (d, $J_{C–P}$ = 2.0, $CH_{Ph\text{-}bdppe}$), 128.2 (d, $J_{C–P}$ = 0.6, $CH_{Ph\text{-}bdppe}$), 128.0 (d, $J_{P\text{-}C}$ = 9.6, $CH_{Ph\text{-}bdppe}$), 127.8 (d, $J_{C–P}$ = 7.9, $CH_{Ph\text{-}bdppe}$), 127.5 (d, $J_{C–P}$ = 9.7, $CH_{Ph\text{-}bdppe}$), 123.1 (d, $J_{C–P}$ = 4.9, CH_{Ph}), 121.9 (s, CH_{Ph}), 121.7 and 120.9 (both s, CH_{bzim}), 112.2 (d, $^4J_{C–P}$ = 2.6, CH_{Ph}), 109.6 and 108.2 (both s, CH_{bzim}), 101.2 (s, CH_{acac}), 34.9 (d, $^4J_{C–P}$ = 4.7, NCH_3), 27.7 (s, CH_{3acac}).

Experimental data for Os(*C,C′*-L$_1$)(*O,O′*-acac)(*P,P′*-bdppe) (10b): Yield: 0.074 g (25%). Anal. Calcd. for $C_{45}H_{40}N_2O_2OsP_2$: C 60.53; H 4.51; N 3.14. Found: C 60.58; H 4.70; N 2.95. HRMS (electrospray, m/z): Calcd. for $C_{45}H_{40}N_2O_2OsP_2$ [M]$^+$: 894.2177; Found: 894.2208. IR (cm^{-1}): ν(CO) 1578 (m), ν(CO) 1512 (m). ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ 8.12 (m, 2 H, $CH_{Ph\text{-}bdppe}$), 7.92 (m, 2 H, $CH_{Ph\text{-}bdppe}$), 7.9–7.0 (m, 15 H, 2 $CH_{ethylene\text{-}bdppe}$, 9 $CH_{Ph\text{-}bdppe}$, and 4 CH_{bzim}), 7.0–6.9 (m, 1 H, CH_{Ph}), 6.89 (m, 2 H, $CH_{Ph\text{-}bdppe}$), 6.75 (m, 1 H, $CH_{Ph\text{-}bdppe}$), 6.7–6.6 (m, 1 H, CH_{Ph}), 6.5–6.4 (m, 1 H, CH_{Ph}), 6.34 (m, 2 H, $CH_{Ph\text{-}bdppe}$), 6.3–6.1 (m, 1 H, CH_{Ph}), 6.06 (m, 2 H, $CH_{Ph\text{-}bdppe}$), 5.04 (s, 1 H, CH_{acac}), 3.92 (s, 3 H, NCH_3), 1.60 and 1.20 (both s, each 3 H, CH_{3acac}). ^{31}P{^{1}H} NMR (121.0 MHz, CD_2Cl_2, 293 K): δ 48.4 (d, $^2J_{P–P}$ = 10.9, bdppe), 30.6 (d, $^2J_{P–P}$ = 10.9, bdppe). ^{13}C{^{1}H}-APT NMR, HMBC and HSQC (75.5 MHz, CD_2Cl_2, 293 K): δ 196.8 (dd, $^2J_{C–P}$ = 104.1, $^2J_{C–P}$ = 8.7, NCN), 184.2 and 183.4 (both s, CO), 153.8 (dd, $^1J_{C–P}$ = 45.9, $^2J_{C–P}$ = 28.4, $CH_{ethylene\text{-}bdppe}$), 152.6 (d, $^3J_{C–P}$ = 2.2, NC_{Ph}), 147.7 (dd, $^1J_{C–P}$ = 41.9, $^2J_{C–P}$ = 23.4, $CH_{ethylene\text{-}bdppe}$), 145.4 (dd, $^2J_{C–P}$ = 8.3, $^2J_{C–P}$ = 4.3, OsC_{Ph}), 144.4 (d, $J_{C–P}$ = 6.3, CH_{Ph}), 140.9 (d, $^1J_{C–P}$ = 42.6, $C_{Ph\text{-}bdppe}$), 139.2 (d, $^1J_{C–P}$ = 35.3, $C_{Ph\text{-}bdppe}$), 137.8, (d, $^1J_{C–P}$ = 35.3, $C_{Ph\text{-}bdppe}$), 137 (m, C_{bzim}), 136.2 (d, $J_{C–P}$ = 11.2, $CH_{Ph\text{-}bdppe}$), 135.2 (dd, $^1J_{C–P}$ = 34.3, $^3J_{C–P}$ = 2.4, $C_{Ph\text{-}bdppe}$), 135.1 (d, $J_{C–P}$ = 11.0, $CH_{Ph\text{-}bdppe}$), 133.8 (d, $J_{C–P}$ = 2.3 C_{bzim}), 132.6 (d, $J_{C–P}$ = 10.4, $CH_{Ph\text{-}bdppe}$), 130.5 (d, $J_{C–P}$ = 1.6, $C_{Ph\text{-}bdppe}$), 130–129 (m, $CH_{Ph\text{-}bdppe}$), 128.6 (d, $J_{C–P}$ = 9.1, $CH_{Ph\text{-}bdppe}$), 128.2 (s, $CH_{Ph\text{-}bdppe}$), 127.8 (d, $J_{C–P}$ = 9.5, $CH_{Ph\text{-}bdppe}$), 127.8 (d, $J_{C–P}$ = 8.1, $CH_{Ph\text{-}bdppe}$), 127.4 (d, $J_{C–P}$ = 2.0, $CH_{Ph\text{-}bdppe}$), 126.9 (d, $J_{C–P}$ = 9.7, $CH_{Ph\text{-}bdppe}$), 122.8 (s, CH_{bzim}), 122.7 (s, CH_{Ph}), 121.7 (s, CH_{bzim}), 118.9 (s, CH_{Ph}), 111.6 (s, CH_{Ph}), 111.0 and 109.5 (both s, CH_{bzim}), 101.9 (s, CH_{acac}), 32.1 (s, NCH_3), 28.1 (d, $^4J_{C–P}$ = 4.2, CH_{3acac}), 27.6 (s, CH_{3acac}).

Preparation of Os(*C,C′*-L$_2$)(*O,O′*-acac)(*P,P′*-bdppe) (11). Compound **11** was prepared in a similar way as **10**, starting from **9** (0.600 g, 0.656 mmol), *cis*-1,2-bis(diphenylphosphino)ethylene (bdppe; 0.260 g, 0.657 mmol), pentane-2,4-dione (Hacac; 0.115 mL, 1.120 mmol), potassium hydroxide (4.300 mL, 0.259 M in methanol, 1.114 mmol) and THF (24 mL). After the reaction mixture was stirred at 323 K for 3 hours, volatiles were removed under vacuum. Dichloromethane (25 mL) was added and the resulting suspension was filtered through Celite. The filtrate was concentrated to dryness and pentane (20 mL) was added to afford a yellow solid corresponding to **11a**, which was washed with further pentane (9 x 20 mL) and dried *in vacuo*. The pentane solution previously obtained was filtrated through Celite and the filtrate concentrated to dryness to yield an orange solid corresponding to **11b**, which was purified by chromatography (silicagel 230-400 mesh and pentane/methylene chloride 1:1 as eluent).

Experimental data for Os(*C,C′*-L$_2$)(*O,O′*-acac)(*P,P′*-bdppe) (11a): Yield: 0.245 g (41%). Anal. Calcd. for $C_{47}H_{44}N_2O_2OsP_2$: C 61.29; H 4.81; N 3.04. Found: C 61.77; H 5.00; N 2.83. HRMS (electrospray, m/z): Calcd. for $C_{47}H_{44}N_2O_2OsP_2$ [M]$^+$: 922.2506; Found: 922.2491. IR (cm^{-1}): ν(CO) 1581 (m), ν(CO) 1520 (m). ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ 8.2–6.3 (m, 28 H, 22 $CH_{Ph\text{-}bdppe}$, 2 CH_{bzim}, 4 CH_{Ph}), 4.75 (s, 1 H, CH_{acac}), 2.57 (s, 3 H, NCH_3), 2.35 and 2.22 (both s, each 3 H, CH_{3bzim}), 1.50 and 1.23 (both s, each 3 H, CH_{3acac}). ^{31}P{^{1}H} NMR (121.0 MHz, CD_2Cl_2, 293 K): δ 42.7 (d, $^2J_{P–P}$ = 18.1. bdppe), 26.6 (d. $^2J_{P-P}$ = 18.1, bdppe). ^{13}C{^{1}H}-APT NMR, HMBC and HSQC (75.5 MHz, CD_2Cl_2, 293 K): δ 188.2 (dd, $^2J_{C–P}$ = 10.1, $^2J_{C–P}$ = 1.5, NCN), 182.7 and 181.2 (both s, CO), 164.8 (dd, $^2J_{C–P}$ = 85.5, $^2J_{C–P}$ = 6.9, OsC_{Ph}), 154.8 (dd, $^1J_{C–P}$ = 45.3, $^2J_{C–P}$ =32.7, $CH_{ethylene\text{-}bdppe}$), 151.3 (d, $^3J_{C–P}$ = 2.2, NC_{Ph}), 150.6 (dd, $^1J_{C–P}$ = 35.9, $^2J_{C–P}$ = 21.9, $CH_{ethylene\text{-}bdppe}$), 139.5 (d, $^1J_{C–P}$ = 32.8, $C_{Ph\text{-}bdppe}$), 139.0 (dd, $^1J_{C–P}$ = 57.2, $^3J_{C–P}$ = 2.5, $C_{Ph\text{-}bdppe}$), 138.1 (dd, $^1J_{C–P}$ = 30.3, $^3J_{C–P}$ =1.5, $C_{Ph\text{-}bdppe}$), 137.6 (d, $^1J_{C–P}$ = 42.8, $C_{Ph\text{-}bdppe}$), 135.8 (s, C_{bzim}), 135.5 (s, CH_{Ph}), 134.3 (d, $J_{C–P}$ = 10.4, $CH_{Ph\text{-}bdppe}$), 132.7 (d, $J_{C–P}$ = 10.0, $CH_{Ph\text{-}bdppe}$), 132.2 (s, C_{bzim}), 130.4 (d, $J_{C–P}$ = 1.4, $CH_{Ph\text{-}bdppe}$), 130.1 (s, C_{bzim}), 129.8 (d, $J_{C–P}$ = 9.7, $CH_{Ph\text{-}bdppe}$), 129.5 (d, $J_{C–P}$ = 1.9, $CH_{Ph\text{-}bdppe}$), 129.4 (s, C_{bzim}), 129.0 (d, $J_{C–P}$ = 9.1, $CH_{Ph\text{-}bdppe}$), 128.4 (d, $J_{C–P}$ = 2.0, $CH_{Ph\text{-}bdppe}$), 128.1 (d, $J_{C–P}$ =1.0, $CH_{Ph\text{-}bdppe}$), 128.0 (d, $J_{C–P}$ = 10.0, $CH_{Ph\text{-}bdppe}$), 127.9 (d, $J_{C–P}$ = 8.3, $CH_{Ph\text{-}bdppe}$), 127.6 (s, $J_{C–P}$ = 9.7, $CH_{Ph\text{-}bdppe}$), 122.8 (d, $J_{C–P}$ = 5.0, CH_{Ph}), 121.8 (s, CH_{Ph}), 112.0 (d, $J_{C–P}$ =2.6, CH_{Ph}), 110.8 and 109.1 (both s, CH_{bzim}), 101.1 (s, CH_{acac}), 34.8 (d, $^4J_{C–P}$ = 5.0, NCH_3), 27.7 and 27.6 (both s, CH_{3acac}), 20.5 and 20.2 (both s, CH_{3bzim}).

Experimental data for Os(*C,C′*-L$_2$)(*O,O′*-acac)(*P,P′*-bdppe) (11b): Yield: 0.154 g (25%). X-ray quality crystals were grown by layering a solution of complex **11b** in dichloromethane with pentane. Anal. Calcd. for $C_{47}H_{44}O_2OsN_2P_2$: C 61.29; H 4.81; N 3.04. Found: C 61.08; H 4.70; N 2.95. HRMS (electrospray, m/z): Calcd. for $C_{47}H_{44}O_2OsN_2P_2$ [M]$^+$: 922.2506; Found: 922.2491. IR (cm^{-1}): ν(CO) 1581 (m), ν(CO) 1515 (m). ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ 8.11 (m, 2 H, $CH_{Ph\text{-}bdppe}$), 7.91 (m, 2 H, $CH_{Ph\text{-}bdppe}$), 7.73 (ddd, $^2J_{H–P}$ = 46.8, $^3J_{H–P}$ = 8.7 Hz, $^3J_{H–H}$ =8.7 Hz, 1 H, $CH_{ethylene\text{-}bdppe}$), 7.6–7.0 (m,

12 H, 1 $CH_{ethylene\text{-}bdppe}$, 9 $CH_{Ph\text{-}bdppe}$, and 2 CH_{bzim}), 6.96 (d, $^3J_{H-H}$ = 7.4, 1 H, CH_{Ph}), 6.89 (m, 2 H, $CH_{Ph\text{-}bdppe}$), 6.76 (m, 1 H, $CH_{Ph\text{-}bdppe}$), 6.62 (d, $^3J_{H-H}$ = 7.4, 1 H, CH_{Ph}), 6.45 (dd, $^3J_{H-H}$ = 7.4, $^3J_{H-H}$ = 7.4, 1 H, CH_{Ph}), 6.36 (m, 2 H, $CH_{Ph\text{-}bdppe}$), 6.15 (dd, $^3J_{H-H}$ = 7.4, $^3J_{H-H}$ = 7.4, 1 H, CH_{Ph}), 6.07 (m, 2 H, $CH_{Ph\text{-}bdppe}$), 5.02 (s, 1 H, CH_{acac}), 3.87 (s, 3 H, NCH_3), 2.40 and 2.36 (both s, each 3 H, CH_{3bzim}), 1.59 and 1.19 (both s, each 3 H, CH_{3acac}). $^{31}P\{^1H\}$ NMR (121. 0 MHz, CD_2Cl_2, 293 K): δ 48.5 (d, $^2J_{P-P}$ = 10.9, bdppe), 30.7 (d, $^2J_{P-P}$ = 10.9, bdppe). $^{13}C\{^1H\}$-APT NMR, HMBC and HSQC (75.5 MHz, CD_2Cl_2, 293 K): δ 195.6 (dd, $^2J_{C-P}$ = 103.6, $^2J_{P-C}$ = 7.7, NCN), 184.1 and 183.3 (both s, CO), 153.8 (dd, $^1J_{C-P}$ = 45.7, $^2J_{C-P}$ = 28.5, $CH_{ethylene\text{-}bdppe}$), 152.8 (d, $^3J_{C-P}$ = 1.9, NC_{Ph}), 147.8 (dd, $^1J_{C-P}$ = 41.7, $^2J_{C-P}$ = 23.2, $CH_{ethylene\text{-}bdppe}$), 145.2 (dd, $^2J_{C-P}$ = 7.2, $^2J_{C-P}$ = 3.5, OsC_{Ph}), 144.4 (d, J_{C-P} = 6.2, CH_{Ph}), 141.1 (d, $^1J_{C-P}$ = 42.5, $C_{Ph\text{-}bdppe}$), 139.4 (d, $^1J_{C-P}$ = 35.0, $C_{Ph\text{-}bdppe}$), 137.1, 136.4 and 133.5 (all s, C_{bzim} and 2 $C_{Ph\text{-}bdppe}$), 136.2 (d, J_{C-P} = 11.2, $CH_{Ph\text{-}bdppe}$), 135.1 (d, J_{C-P} = 10.9, $CH_{Ph\text{-}bdppe}$), 132.6 (d, J_{C-P} = 10.3, $CH_{Ph\text{-}bdppe}$), 132.3 (d, J_{C-P} = 2.4, C_{bzim}), 131.4 and 130.5 (both s, C_{bzim}), 130.4 (d, J_{C-P} = 1.6, $CH_{Ph\text{-}bdppe}$), 129.7 (d, J_{C-P} = 9.1, $CH_{Ph\text{-}bdppe}$), 129.6 (d, J_{C-P} = 0.6, $CH_{Ph\text{-}bdppe}$), 128.6 (d, J_{C-P} = 9.0, $CH_{Ph\text{-}bdppe}$), 128.2 (s, $CH_{Ph\text{-}bdppe}$), 127.8 (d, J_{C-P} = 9.4, $CH_{Ph\text{-}bdppe}$), 127.7 (d, J_{C-P} = 8.1, $CH_{Ph\text{-}bdppe}$), 127.3 (s, $CH_{Ph\text{-}bdppe}$), 126.9 (d, J_{C-P} = 9.6, $CH_{Ph\text{-}bdppe}$), 122.4 and 118.8 (both s, CH_{Ph}), 111.9 (s, CH_{bzim}), 111.4 (s, CH_{Ph}), 110.2 (s, CH_{bzim}), 101.9 (s, CH_{acac}), 32.0 (s, NCH_3), 28.0 (d, $^4J_{C-P}$ = 3.9, CH_{3acac}), 27.6 (s, CH_{3acac}), 20.7 and 20.5 (both s, CH_{3bzim}).

Determination of pK_a's of Complexes 5, 6 and 7. Three NMR tubes were charged with three 0.036 M solutions of **5**, **6**, and **7** in $(CH_3)_2CO$ (0.5 mL), respectively. The evolution of these acetone solutions was monitored by $^{31}P\{^1H\}$ NMR spectroscopy. The pK_a's values were determined by measuring the appearance of **2**–**4** and disappearance of **5**–**7**, by means phosphorus integrable experiments, until the equilibria were reached (*i.e.*; after ~30 hours at room temperature in the three cases), see Figures S1–S3. The concentration values in the equilibria were found to be 3.27×10^{-2} / 3.27×10^{-3} mol·L^{-1} (**5** / **2** and **6** / **3**) and 3.36×10^{-2} / 2.26×10^{-3} mol·L^{-1} (**7** / **4**).

Structural Analysis of Complexes 2, 4, 6, 9, 10a, and 11b. X-ray data were collected for the complexes on a Bruker Smart APEX and APEX DUO CCD diffractometers equipped with a normal focus, 2.4 kW sealed tube source (Mo radiation, λ = 0.71073 Å) operating at 50 kV and 30 mA. Data were collected over the complete sphere. Each frame exposure time was 10 (**2, 4, 6, 11b**) or 20 (**9** and **10a**) s covering 0.3° in ω. Data were corrected for absorption by using a multiscan method applied with the SADABS program.[31] The structures were solved by Patterson or direct methods and refined by full-matrix least squares on F^2 with SHELXL97,[32] including isotropic and subsequently anisotropic displacement parameters. The hydrogen atoms (except hydrides) were calculated, and refined using a restricted riding model. Hydrogens bonded to metal atoms were observed but some of them refined too close to metals, so a restricted refinement model was used for them in **2** and **4** (Os–H 1.59(1) Å), however were refined freely in **6**. The disordered groups or disordered solvent molecules were refined with isotropic displacement parameters and restrained geometries.

Crystal data for ***2***: $C_{32}H_{56}N_2OsP_2$, M_W 720.93, colourless, irregular block (0.25 x 0.18 x 0.10), monoclinic $P2_1/c$, *a*: 9.4244(18) Å, *b*: 18.294(4) Å, *c*: 19.003(4) Å, *β*: 99.266(3)°, *V* = 3233.6(11) Å^3, *Z* = 4, *Z'* = 1, D_{calc}: 1.481 g cm^{-3}, F(000): 1472, T = 100(2) K, μ 4.065 mm^{-1}. 21934 measured reflections (2θ: 3-58°, ω scans 0.3°), 7819 unique (R_{int} = 0.0237); min./max. transm. Factors 0.694/0.862. Final agreement factors were R^1 = 0.0221 (6759 observed reflections, I > 2σ(I)) and wR^2 = 0.0522; data/restraints/parameters 7819/3/352; GoF = 1.040. Largest peak and hole 1.388 (close to osmium atom) and -0.721 e/ Å^3.

Crystal data for ***4***: $C_{28}H_{54}N_2OsP_2$, M_W 670.87, colourless, irregular block (0.16 x 0.08 x 0.08), triclinic, space group P-1, *a*: 9.0462(4) Å, *b*: 11.6082(5) Å, *c*: 14.7453(7) Å, *α*: 79.6040(10)° , *β*: 89.3470(10)°, *γ*: 79.0970(10)°, *V* = 1495.08(12) Å^3, *Z* = 2, *Z'* = 1, D_{calc}: 1.490 g cm^{-3}, F(000): 684, T = 100(2) K, μ 4.390 mm^{-1}. 18182 measured reflections (2θ: 3-58°, ω scans 0.3°), 6940 unique (R_{int} = 0.0232); min./max. transm. Factors 0.749/0.862. Final agreement factors were R^1 = 0.0209 (6553 observed reflections, I > 2σ(I)) and wR^2 = 0.0467; data/restraints/parameters 6940/3/320; GoF = 1.042. Largest peak and hole 1.049 (close to osmium atom) and -0.548 e/ Å^3.

Crystal data for ***6***: $C_{34}H_{61}N_2OsP_2$ x BF_4 x CH_2Cl_2, M_W 921.72, colourless, irregular block (0.19 x 0.18 x 0.13), monoclinic, space group $P2_1/n$, *a*: 11.5135(5) Å, *b*: 29.8770(12) Å, *c*: 12.1210(5) Å, *β*: 108.3010(10)°, *V* = 3958.6(3) Å^3, *Z* = 4, *Z'* = 1, D_{calc}: 1.547 g cm^{-3}, F(000): 1872, T = 100(2) K, μ 3.483 mm^{-1}. 47899 measured reflections (2θ: 3-58°, ω scans 0.3°), 9571 unique (R_{int} = 0.0288); min./max. transm. Factors 0.727/0.842. Final agreement factors were R^1 = 0.0215 (8560 observed reflections, I > 2σ(I)) and wR^2 = 0.0506; data/restraints/parameters 9571/0/451; GoF = 1.043. Largest peak and hole 1.776 (close to osmium atom) and -0.540 e/ Å^3.

Crystal data for ***9***: $C_{38}H_{63}N_4OsP_2$ x BF_4 x CH_2Cl_2, M_W 999.80, colourless, irregular block (0.15 x 0.15 x 0.09), monoclinic, space group $P2_1/c$, *a*: 19.3809(14) Å, *b*: 34.928(3) Å, *c*: 13.0448(10) Å, *β*: 91.9010(10)°, *V* = 8825.7(11) Å^3, *Z* = 8, *Z'* = 2, D_{calc}: 1.505 g cm^{-3}, F(000): 4064, T = 100(2) K, μ 3.132 mm^{-1}. 89026 measured reflections (2θ: 3-58°, ω scans 0.3°), 21261 unique (R_{int} = 0.0358); min./max. transm. Factors 0.709/0.842. Final agreement factors were R^1 = 0.0305 (18648 observed reflections, I > 2σ(I)) and wR^2 = 0.0649; data/restraints/parameters 21261/48/1025; GoF = 1.080. Largest peak and hole 1.401 (close to osmium atom) and -0.869 e/ Å^3.

Crystal data for ***10a***: $C_{45}H_{40}N_2O_2OsP_2$, M_W 892.93, yellow, irregular block (0.13 x 0.03 x 0.03), monoclinic, space group $P2_1/n$, *a*: 10.0601(4) Å, *b*: 18.5522(8) Å, *c*: 19.7318(9) Å, *β*: 90.4110(10)°, *V* = 3682.6(3) Å^3, *Z* = 4, *Z'* = 1, D_{calc}: 1.611 g cm^{-3}, F(000): 1784, T = 100(2) K, μ 3.592 mm^{-1}. 44276 measured reflections (2θ: 3-58°, ω scans 0.3°), 8865 unique (R_{int} = 0.0501); min./max. transm. Factors 0.741/0.842. Final agreement factors were R^1 = 0.0336 (7623 observed reflections, I > 2σ(I)) and wR^2 = 0.0597; data/restraints/parameters 8865/0/478; GoF = 1.108. Largest peak and hole 0.822 (close to osmium atom) and -1.092 e/ Å^3.

Crystal data for ***11b***: $C_{47}H_{44}N_2O_2OsP_2$ x CH_2Cl_2, M_W 1005.91, orange, irregular block (0.18 x 0.11 x 0.08), triclinic, space group $P\bar{1}$, *a*: 10.6224(4) Å, *b*: 11.0347(4) Å, *c*: 19.3266(8) Å, *α*: 90.1500(10)°, *β*: 101.1980(10)°, *γ*: 102.7440(10)°, *V* = 2165.05(14) Å^3, *Z* = 2, *Z'* = 1, D_{calc}: 1.543 g cm^{-3}, F(000): 1008, T = 100(2) K, μ 3.183 mm^{-1}. 20277 measured reflections (2θ: 3-50°, ω scans 0.3°), 9961 unique (R_{int} = 0.0225); min./max. transm. Factors 0.733/0.862. Final agreement factors were R^1 = 0.0254 (9283 observed reflections, I > 2σ(I)) and wR^2 = 0.0587; data/restraints/parameters 9961/0/519; GoF = 1.055. Largest peak and hole 1.394 (close to osmium atom) and -1.074 e/ Å^3.

Computational Details. Geometry optimization of complex **6** was performed without symmetry constraints using the Gaussian09[33] suite of programs at the BP86[34]/def2-SVP[35] level of theory using the D3 dispersion correction suggested by Grimme et al.[36] This level is denoted BP86-D3/def2-SVP. Complex **6** was characterized by frequency calculations, and has positive definite Hessian matrices thus confirming that the computed structure is a minimum on the potential energy surface.

Donor-acceptor interactions and Wiberg Bond Indices have been computed using the natural bond orbital (NBO) method.[37] The energies associated with these two-electron interactions have been computed according to the following equation:

$$\Delta E^{(2)}_{\phi\phi^*} = -n_\phi \frac{\langle \phi^* | \hat{F} | \phi \rangle^2}{\varepsilon_{\phi^*} - \varepsilon_\phi}$$

where $\hat{F}$ is the DFT equivalent of the Fock operator and ϕ and ϕ^* are two filled and unfilled Natural Bond Orbitals having ε_ϕ and ε_{ϕ^*} energies, respectively; n_ϕ stands for the occupation number of the filled orbital.

All AIM results described in this work correspond to calculations performed at the BP86-D3/6-31+G(d)/WTBS (for Os) level on the optimized geometry obtained at the BP86-D3/def2-SVP level. The WTBS (well-tempered basis sets)[38] have been recommended for AIM calculations involving transition metals.[39] The topology of the electron density was conducted using the AIMAll program package.[40]

ASSOCIATED CONTENT

Supporting Information

$^{31}P\{^{1}H\}$ NMR spectra utilized for the determination of pK_a's of complexes **5**, **6** and **7**, full reference 32, cartesian coordinates and total energy of complex **6**, CIFs for **2**, **4**, **6**, **9**, **10a**, and **11b**. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail for M. A. E.: maester@unizar.es

Author Contributions

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 interest.

ACKNOWLEDGMENT

Financial support from the Spanish MINECO (Projects CTQ2011-23459, CTQ2013-44303-P, the Red de Excelencia Consolider (CTQ2014-51912-REDC), the DGA (E35), the European Social Fund (FSE) and FEDER, and Universal Display Corporation is acknowledged. T. B. thanks the Spanish MINECO for funding through the Juan de la Cierva programme.

REFERENCES

(1) Bourissou, D.; Guerret, O.; Gabbaï, F. P.; Bertrand, G. *Chem. Rev*. **2000**, *100*, 39.

(2) (a) Frenking, G.; Solà, M.; Vyboishchikov, S. F. *J. Organomet. Chem*. **2005**, *690*, 6178. (b) Díez-González, S.; Nolan, S. P. *Coord. Chem. Rev.* **2007**, *251*, 874. (c) Jacobsen, H.; Correa, A.; Poater, A.; Costabile, C.; Cavallo, L. *Coord. Chem. Rev.* **2009**, *253*, 687. (d) Nelson, D. J.; Nolan, S. P. *Chem. Soc. Rev.* **2013**, *42*, 6723.

(3) (a) Herrmann, W. A. *Angew. Chem. Int. Ed.* **2002**, *41*, 1290. (b) Peris, E.; Crabtree, R. H. *Coord. Chem. Rev.* **2004**, *248*, 2239. (c) *N-Heterocyclic Carbenes in Synthesis*; Nolan, S. P. Ed., Wiley-VCH: Weinheim, **2006**. (d) Kantchev, E. A. B.; O'Brien, C. J.; Organ, M. G. *Angew. Chem. Int. Ed*. **2007**, *46*, 2768. (e) Marion, N.; Nolan, S. P. *Acc. Chem. Rev*. **2008**, *41*, 1440. (f) Diez-Gonzalez, S.; Marion, N.; Nolan, S. P. *Chem. Rev.* **2009**, *109*, 3612. (g) Samojłowicz, C.; Bieniecki, M.; Grela, K. *Chem. Rev*. **2009**, *109*, 3708.

(4) Crudden, C. M.; Allen, D. P. *Coord. Chem. Rev*. **2004**, *248*, 2247. (b) Pugh, D.; Danopoulos, A. A. *Coord. Chem. Rev*. **2007**, *251*, 610. (c) Corborán, R.; Mas-Marzá, E.; Peris, E. *Eur. J. Inorg. Chem*. **2009**, 1700. (d) de Frémont, P.; Marion, N.; Nolan, S. P. *Coord. Chem. Rev*. **2009**, *253*, 862. (e) Poyatos, M.; Mata, J. A.; Peris, E. *Chem. Rev.* **2009**, *109*, 3677. (f) Schuster, O.; Yang, L.; Raubenheimer, H. G.: Albrecht, M. *Chem. Rev*. **2009**, *109*, 3445. (g) Clavier, H.; Nolan, S. P. *Chem. Commun.* **2010**, *46*, 841.

(5) (a) Mercs, L.; Albrecht, M. *Chem. Soc. Rev*. **2010**, *39*, 1903. (b) Visbal, R.; Gimeno, M. C. *Chem. Soc. Rev*. **2014**, *43*, 3551.

(6) (a) Chaloner, P. A.; Esteruelas, M. A.; Joó, F.; Oro, L. A. *Homogeneous Hydrogenation; Kluwer Academic Publisher*; Dordrecht, The Netherlands, **1994**. (b) Esteruelas, M. A.; Oro, L.A. *Chem. Rev.* **1998**, *98*, 577.

(7) *The Hydrogen Economy: Opportunities, Costs, Barriers and RgD Needs*; National Academic Press; Washington, D. C., **2004**.

(8) (a) Jessap, P. G.; Morris, R. H. *Coord. Chem. Rev*. **1992**, *121*, 155. (b) Kubas, G. J. *Chem. Rev.* **2007**, *107*, 4152. (c) Morris, R. H. *Coord. Chem. Rev*. **2008**, *252*, 2381. (d) Kubas, G. J. *J. Organomet. Chem.* **2009**, *694*, 2648. (e) Kubas, G. J. *J. Organomet. Chem.* **2014**, *751*, 33.

(9) (a) Paul, A.; Musgrave, C. B. *Angew, Chem. Int. Ed.* **2007**, *46*, 8153. (b) Waterman, R. *Chem. Soc. Rev*. **2013**, *42*, 5629. (c) John, A. St.; Goldberg, K. I.; Heinekey, D. M. *Top Organomet. Chem.* **2013**, *40*, 271. (d) Marziale, A. N.; Friedrich, A.; Klopsch, I.; Drees, M.; Celinski, V. R.; Schmedt auf der Günne, J.; Schneider, S. *J. Am. Chem. Soc.* **2013**, *135*, 13342. (e) Butera, V.; Russo, N.; Sicilia, E. *ACS Catal*. **2014**, *4*, 1104.

(10) (a) Giunta, D.: Hölscher, M.; Lehmann, C. W.; Mynott, R.; Wirtz, C.; Leitner, W. *Adv. Synth. Catal.* **2003**, *345*, 1139. (b) Chatwin, S. L.; Davidson, M. G.; Doherty, C.; Donald, S. M.; Jazzar, R. F. R.; Macgregor, S. A.; McIntyre, G. J.; Mahon, M. F.; Whittlesey, M. K. *Organometallics* **2006**, *25*, 99. (c) Burling, S.; Häller, L. J. L.; Mas-Marzá, E.; Moreno, A.; Mcgregor, S. A.; Mahon, M. F.; Pregosin, P. S.; Whittlesey, M. K. *Chem. Eur. J.* **2009**, *15*, 10912. (d) Dobereiner, G. E.; Nova, A.; Schley, N. D.; Hazari, N.; Miller, S. J.; Eisenstein, O.; Crabtree, R. H. *J. Am. Chem. Soc.* **2011**, *133*, 7547. (e) Schultz, K. M.; Goldberg, K. I.; Gusev, D. G.; Heinekey, D. M. *Organometallics* **2011**, *30*, 1429.

(11) (a) Nielsen, D. J.; Magill, A. M.; Yates, B. I.; Carell, K. J.; Skelton, B. W.; White, A. H. *Chem. Commun*. **2002**, 2500. (b) Clement, N. D.; Carell, K. J. *Angew. Chem. Int. Ed.* **2004**, *43*, 3845. (c) Bacciu, D.; Cavell, K. J.; Fallis, I. A.; Ooi, L. *Angew. Chem. Int. Ed.* **2005**, *44*, 5282. (d) Graham, D. C.; Cavell, K. J.; Yates, B. F. *Dalton Trans.* **2005**, 1093. (e) Graham, D. C.; Cavell, K. J.; Yates, B. F. *Dalton Trans* **2006**, 1768.

(12) Kubas, G. J. *Metal Dihydrogen and σ-Bond Complexes: Structure, Theory and Reactivity*; Kluwer: New York, **2001**.

(13) (a) Webster, C. E.; Gross, C. L.; Young, D. M.; Girolami, G. S.; Schultz, A. J.; Hall, M. B.; Eckert, J. *J. Am. Chem. Soc.* **2005**, *127*, 15091. (b) Baya, M.; Esteruelas, M.A.; Oliván, M.; Oñate, E. *Inorg. Chem*. **2009**, *48*, 2677.

(14) (a) Goff, S. E.; Nolan, T. F.; George, M. W.; Poliakoff, M. *Organometallics* **1998**, *17*, 2730. (b) Gusev, D. G.; Dolgushin, F. M.; Antipin, M. Y. *Organometallics*, **2001**, 20, 1001. (c) Castro-Rodrigo, R.; Esteruelas, M. A.; López, A. M.; Oliván, M.; Oñate, E. *Organometallics* **2007**, *26*, 4498. (d) Jimenez-Tenorio, M.; Puerta, M. C. Valerga, P.; Moncho, S.; Ujaque, G.; Lledós, A. *Inorg. Chem.* **2010**, *49*, 6035.

(15) (a) Crabtree, R. H.; Lavin, M.; Bonneviot, *J. Am. Chem. Soc*. **1986**, *108*, 4032. (b) Arliguie, T.; Chaudret, B.; Morris, R. H.; Sella, A. *Inorg. Chem*. **1988**, *27*, 598. (c) Moreno, B.; Sabo-Etienne, S.; Chaudret, B. *J. Chem. Soc*. **1994**, *116*, 2635. (d) Smith, K.-T.; Tilset, M.; Kuhlman, R.; Caulton, K. G. *J. Am. Chem. Soc*, **1995**, *117*, 9473. (e) Moreno, B.; Sabo-Etienne, S.; Chaudret, B.; Rodriguez, A.; Jalon, F.; Trofimenko, S. *J. Am. Chem. Soc.* **1995**, *117*, 7441. (f) Sabo-Etienne, S.; Chaudret, B. *Coord. Chem. Rev*. **1998**, 178-180, 381. (g) Abdur-Rashid, K.; Gusev D. G.; Lough, A. J.; Morris, R. H. *Organometallics* **2000**, *19*, 1652. (h) Borowski, A. F.; Donnadieu, B.; Daran, J.-C.; Sabo-Etienne, S.; Chaudret, B. *Chem. Commun*, **2000**, 543. (i) Wang, X.; Andrews L. *J. Phys. Chem. A* **2003**, *107*, 570. (j) Grellier, M.; Vendier, L.; Chaudret, B.; Albinati, A.; Rizzato, S.; Mason, S.; Sabo-Etienne, *J. Am. Chem. Soc*. **2005**, *127*, 17592. (k) Ingleson, M. J.; Brayshaw, S. K.; Mahon, M. F.; Ruggiero, G. D.; Weller, A. J. *Inorg. Chem*. **2005**, *44*, 3162. (l) Shima, T.; Namura, K.; Kameo, H.; Kakuta, S.; Suzuki, H. *Organometallics* **2010**, *29*, 337. (m) Namura, K.; Kakuta, S.; Suzuki, H. *Organometallics* **2010**, *29*, 4305.

(16) (a) Barrio, P.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2004**, *23*, 1340. (b) Esteruelas, M. A.; Masamunt, A. B.; Oliván, M.; Oñate, E.; Valencia, M. *J. Am. Chem. Soc*. **2008**, *130*, 11612. (c) Esteruelas, M. A.; Forcén, E.; Oliván, M.; Oñate, E. *Organometallics* **2008**, *27*, 6188. (d) Eguillor B.; Esteruelas, M. A.; García-Raboso, J.; Oliván.; Oñate, E. *Organometallics* **2009**, *28*, 3700. (e) Buil, M. L.; Esteruelas, M. A.; Garcés, K.; García-Raboso, J.; Oliván, M. *Organometallics* **2009**, *28*, 4606. (f) Esteruelas, M. A.; García-Raboso, J.; Oliván, M. *Organometallics* **2011**, *30*, 3844. (g) Esteruelas, M. A.; García-Raboso, J.; Oliván, M. *Inorg. Chem.* **2012**, *51*, 5975. (h) Esteruelas, M. A.; García-Raboso, J.; Oliván, M. *Inorg. Chem*. **2012**, *51*, 9522. (i) Casarrubios, L.; Esteruelas, M. A.; Larramona, C.; Muntaner, J. G.; Oliván, M.; Oñate, E.; Sierra, M. A. *Organometallics* **2014**, *33*, 1820.

(17) (a) Barrio, P.; Castarlenas, R.; Esteruelas, M. A.; Lledós, A.; Maseras, F.; Oñate, E.; Tomàs, J. *Organometallics* **2001**, *20*, 442. (b) Barrio, P.; Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *Organometa-*

llics **2001**, *20*, 2635. (c) Barrio, P.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2004**, *23*, 3627. (d) Baya, M.; Eguillor, B.; Esteruelas, M. A.; Lledós, A.; Oliván, M.; Oñate, E. *Organometallics* **2007**, *26*, 5140. (e) Esteruelas, M. A.; Fernández, I.; Herrera, A.; Martín-Ortiz, M.; Martínez-Álvarez, R.; Oliván, M.; Oñate, E.; Sierra, M. A.; Valencia, M. *Organometallics* **2010**, *29*, 976. (f) Crespo, O.; Eguillor, B.; Esteruelas, M. A.; Fernández, I.; García-Raboso, J.; Gómez-Gallego, M.; Martín-Ortiz, M.; Oliván, M.; Sierra, M. A. *Chem. Commun.* **2012**, *48*, 5328. (g) Esteruelas, M. A.; Fernández, I.; Gómez-Gallego, M.; Martín-Ortiz, M.; Molina, P.; Oliván, M.; Otón, F.; Sierra, M. A.; Valencia, M. *Dalton Trans.* **2013**, *42*, 3597.

(18) (a) Baya, M.; Eguillor, B.; Esteruelas, M. A.; Oliván, M.; Oñate, E. *Organometallics* **2007**, *26*, 6556. (b) Eguillor, B.; Esteruelas, M. A.; Oliván, M.; Puerta, M. *Organometallics* **2008**, *27*, 445. (c) Eguillor, B.; Esteruelas, M. A.; García-Raboso, J.; Oliván, M.; Oñate, E.; Pastor, I. M.; Peñafiel, I.; Yus, M. *Organometallics* **2011**, *30*, 1658.

(19) Alabau, R. G.; Eguillor, B.; Esler, J.; Esteruelas, M. A.; Oliván, M.; Oñate, E.; Tsai, J.-T.; Xia, C. *Organometallics* **2014**, *33*, 5582.

(20) Webb, J. R.; Bolaño, T.; Gunnoe, T. B. *ChemSusChem* **2011**, *4*, 37.

(21) See for example: (a) Castarlenas, R.; Esteruelas, M. A.; Lalrempuia, R.; Oliván, M.; Oñate, E. *Organometallics* **2008**, *27*, 795. (b) Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2008**, *27*, 3240. (c) Bolaño, T.; Buil, M. L.; Esteruelas, M. A.; Izquierdo, S.; Lalrempuia, R.; Oliván, M.; Oñate, E. *Organometallics* **2010**, *29*, 4517. (d) Buil, M. L.; Cadierno, V.; Esteruelas M. A.; Gimeno, J.; Herrero, J.; Izquierdo, S.; Oñate, E. *Organometallics* **2012**, *31*, 6861. (e) Buil, M. L.; Esteruelas, M. A.; Fernández, I.; Izquierdo, S.; Oñate, E. *Organometallics* **2013**, *32*, 2744. (f) Buil, M. L.; Cardo, J. J. F.; Esteruelas, M. A.; Fernández, I.; Oñate, E. *Organometallics* **2014**, *33*, 2689.

(22) See for example: (a) Esteruelas, M. A.; Gutiérrez-Puebla; E.; López, A. M.; Oñate, E.; Tolosa, J. I. *Organometallics* **2000**, *19*, 275. (b) Baya, M.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2001**, *20*, 4875. (c) Esteruelas, M. A.; González, A. I.; López, A. M.; Oñate, E. *Organometallics* **2003**, *22*, 414. (d) Esteruelas, M. A.; Hernández, Y. A.; López, A. M.; Oliván, M.; Oñate, E. *Organometallics* **2005**, *24*, 5989. (e) Cerón-Camacho, R.; Morales-Morales, D.; Hernández, S.; Le Lagadec, R.; Ryabov, A. D. *Inorg. Chem.* **2008**, *47*, 4988.

(23) Barea, G.; Esteruelas, M. A.; Lledós, A.; López, A. M.; Oñate, E.; Tolosa, J. I. *Organometallics* **1998**, *17*, 4065. (b) Barrio, P.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2002**, *21*, 2491. (c) Barrio, P.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2003**, *22*, 2472. (d) Barrio, P.; Esteruelas, M. A.; Lledós, A.; Oñate, E.; Tomàs, J. *Organometallics* **2004**, *23*, 3008.

(24) (a) Vyboishchikov, S. F.; Frenking, G. *Chem. Eur. J.* **1998**, *4*, 1428. (b) Matta, C. F.; Hernández-Trujillo, J. *J. Phys. Chem. A* **2003**, *107*, 7496.

(25) pK_a^{water} $\{[(CH_3)_2COH]^+\}$ = –2.16. See: McClelland, R. A.; Reynolds, W. F. *Can. J. Chem.* **1976**, *54*, 718.

(26) Petrucci, R.; Herring, F.; Madera, J. *General chemistry: Principles and modern applications*, 10th Ed.; Pearson Education: Canada, **2011**.

(27) Anslyn, E. V.; Dougherty, D. A. *Modern Physical Organic Chemistry*; University Science, **2005**.

(28) Esteruelas, M. A.; López, A. M.; Mora, M.; Oñate, E. *ACS Catal.* **2015**, *5*, 187.

(29) Aracama, M.; Esteruelas, M. A.; Lahoz, F. J.; López, J. A.; Meyer, U.; Oro, L. A.; Werner, H. *Inorg. Chem.* **1991**, *30*, 288

(30) Huckaba, A. J.; Hollis, T. K.; Howell, T. O.; Valle, H. U.; Wu, Y. *Organometallics* **2013**, *32*, 63.

(31) Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33. SADABS: Area-detector absorption correction; Bruker- AXS, Madison, WI, 1996.

(32) SHELXTL Package v. 6.14; Bruker-AXS, Madison, WI, 2000. Sheldrick, G. M. *Acta Cryst.* **2008**, *A64*, 112-122.

(33) Frisch, M. J., et al. *Gaussian 09, Revision D.01*; Gaussian, Inc., Wallingford, CT, 2009.

(34) Zhao, Y.; Schultz, N. E.; Truhlar, D. G. *J. Chem. Theory Comput.* **2006**, *2*, 364.

(35) Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys*. **2005**, *7*, 3297.

(36) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys*. **2010**, *132*, 154104.

(37) a) Foster, J. P.; Weinhold, F. *J. Am. Chem. Soc*. **1980**, *102*, 7211; b) Reed, A. E.; Weinhold, F. *J. Chem. Phys*. **1985**, *83*, 1736; c) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys*. **1985**, *83*, 735; d) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev*. **1988**, *88*, 899.

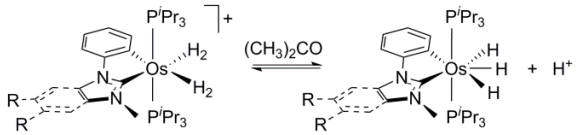
(38) a) Huzinaga, S.; Miguel, B. *Chem. Phys. Lett*. **1990**, *175*, 289; b) Huzinaga, S.; Klobukowski, M. *Chem. Phys. Lett*. **1993**, *212*, 260.

(39) (a) Cabeza, J. A.; Maelen van der, J. F.; García-Granda, S. *Organometallics* **2009**, *28*, 3666. (b) Fernández, I.; Logan, N.; Lavigne, G. *Organometallics* **2012**, *31*, 1155.

(40) Keith, T. A. AIMAll, 2010, http://tkgristmill.com.

"For Table of Contents Only"

Osmium(II)–bis(Dihydrogen) Complexes Containing C_{aryl},C_{NHC}–Chelate Ligands: Preparation, Bonding Situation, and Acidity.



R = H, CH_3

pK_a ^{acetone} = 3.5 - 3.8