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

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ABSTRACT: The hexahydride complex OsH$_6$(PPr$_3$)$_2$ (1) reacts with the BF$_4$-salts of 1-phenyl-3-methyl-1-H-imidazolium, 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$_4$(trans-$C_{aryl},C_{NHC}$)(PPr$_3$)$_2$ (2–4). The protonation of these compounds with HBF$_4$·OEt$_2$ produces the reduction of the metal center and the formation of the bis(dihydrogen)-osmium(II) complexes [Os(μ-$C_{aryl},C_{NHC}$)(η$_2$-H$_2$)$_2$(PPr$_3$)$_2$]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 $p_{π}$ 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 Bronsted 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(μ-$C_{aryl},C_{NHC}$)(CH$_3$CN)$_2$(PPr$_3$)$_2$]BF$_4$ (8, 9) react with acetylacetonate (acac) and cis-1,2-bis(diphenylphosphino)ethylen (bdppe) to give Os(μ-$C_{aryl},C_{NHC}$)(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 carbene (NHCs) are singlet carbenes containing two π-electron donating amido substituents, which considerably increase the energy of the vacant $p_{π}$ orbital at the carbon atom and therefore the σ-$p_{σ}$ gap. As a consequence, they bind to transition metals through π donation, being the π-backbonding negligible. This initial view is being however reconsidered. Recent studies suggest that the nature of the metal–NHC bond has greater complexity. 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. All this ability of the NHC-ligands to tune the electron density of the metallic core has made them powerful tools in homogeneous catalysis, organometallic synthesis and material science.

The hydrogen molecule is vital in catalytic hydrogenation of unsaturated organic substrates in the most efficient and clean energy carrier. Its coordination to the unsaturated core of a transition metal complex affords dihydrogen derivatives, M(μ-H$_2$)$_2$, which are determining species for its activation and for its release from hydrogen bearers, such as amineboranes, in the metal promoted dehydrocoupling of these molecules. Dihydrogen complexes stabilized with NHC-ligands are scarce in part due to the trend shown for these groups to release imidazolium salts. The M(μ-$H_2$)$_2$ 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 σ*(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. The stability and chemical properties of the metal-dihydride interaction are further very sensitive to the position of the cationic ligands in the metal coordination sphere. As a result, complexes containing two coordinated hydrogen molecules are rare, in particular in the absence of hydride ligands, which exert an stabilizing cis-effect.

The hexahydride complex OsH$_6$(PPr$_3$)$_2$ has proven to activate σ bonds of a wide range of organic molecules, in particular substrates containing a heterotatom binding site. In agreement with this, it promotes the direct metatation of N-alkyl and N-arylimidazolium salts to give osmium-
polyhydride derivatives containing neutral monodentated or chelate NHC ligands with normal or abnormal coordination modes depending upon the bulkiness of the N-substituents.\textsuperscript{18} Recently, we have used this synthetic strategy to prepare novel homoletic Os(C\textsubscript{NHC}C\textsubscript{aryl}C\textsubscript{NHC})\textsubscript{2} and novel heteroleptic Os(C\textsubscript{NHC}C\textsubscript{aryl}C\textsubscript{NHC})(C\textsubscript{NHC}C\textsubscript{aryl}C\textsubscript{NHC}) pincer complexes, which have shown to be new types of blue-green emissive additives for organic light-emitting devices.\textsuperscript{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 counterion of the used salt (Scheme 1). Tetrafluoroborate favors the C–H bond activation at the 6-position, which presents the second NHC metatation to afford the C,C'-chelate zwiterionic salt. On the other hand, iodide favors the activation at the 2-position allowing the direct metalation of the second Cbenzimidazolium 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\textsubscript{aryl},C\textsubscript{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

Metatation of the salts. The hexahydride complex OsH\textsubscript{6}(P\textsubscript{iPr}\textsubscript{3})\textsubscript{2} (1) promotes the N,C–H bond activation of N-phenylbenzimidazolium and N-phenylimidazolium BF\textsubscript{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,\textsuperscript{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\textsubscript{2}(P\textsubscript{iPr}\textsubscript{3})\textsubscript{2})(\mu-H\textsubscript{3})]\textsuperscript{16+}. As a consequence, the treatment of 1 with 2.0 equiv of the BF\textsubscript{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\textsubscript{3}(\mu-2-C\textsubscript{aryl},C\textsubscript{NHC})(P\textsubscript{iPr}\textsubscript{3})\textsubscript{2} complexes 2–4 along with the polyhydride dimer [(OsH\textsubscript{2}(P\textsubscript{iPr}\textsubscript{3})\textsubscript{2})(\mu-H\textsubscript{3})]\textsuperscript{16+}. 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.

\begin{scheme}
\centering
\includegraphics[width=\textwidth]{scheme1}
\caption{Scheme 1}
\end{scheme}

\begin{scheme}
\centering
\includegraphics[width=\textwidth]{scheme2}
\caption{Scheme 2}
\end{scheme}
Complexes 2 and 4 were characterized by X-ray diffraction analysis. The structures prove the double metatlation of the salts to form anionic $C_{\text{NHC}}$-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–$P(2) = 165.17(2)^\circ$). The metal coordination sphere is completed by the chelate group, which acts with a bite angle of $75.67(9)^\circ$, 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, 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. 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)$^\circ$ and 75.60(10)$^\circ$, 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.

The $^1H$, $^{31}P$($^1H$), and $^{13}$C($^1H$) 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 $^1H$ 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 $^{31}P$($^1H$) NMR spectra shows a singlet at about 25 ppm. In the $^{13}$C($^1H$) NMR spectra in benzene-$d_6$, at room temperature, the most noticeable feature is the presence of the metalated 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](image2.png)

**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) = 2.069(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).

**Bis(Dihydrogen) Complexes.** The metal center of the trihydrido-osmium(IV) complexes 2–4 undergoes reduction by protonation. Thus, the addition of 1.2 equiv of HBF$_4$·OE$_2$ 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$^8$-species, with transphosphines (P(1)–Os–P(2) = 164.99(2)$^\circ$). The perpendicular plane is formed by the chelated ligand, which acts with a C(1)–Os–C(6) bite angle of 77.30(8)$^\circ$, and the coordinated

### Scheme 3

![Scheme 3](image3.png)

**Scheme 3**

2 (R = H) 3 (R = CH$_3$) 5 (R = H) 6 (R = CH$_3$)
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 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$_x$(X$^2$-C,Y)(PPr$_3$)$_2$ ($X = O$, N), where the anionic C,X-chelate ligand 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 $V^2_{p}(r)$ in the perpendicular plane to the P–Os–P direction. As expected, according to the AIM method, complex 6 is a five-membered metalacyle species possessing two Os–C bond critical points (BCP) and one OsNC$_2$ ring critical point (RCP). Furthermore the Os–C(aryl) bond as well the Os–C(NHC) bond clearly exhibit an area of charge concentration ($V^2_{p}(r) < 0$, solid lines) at the carbon end with the shape of a droplet-like appendix directed towards the osmium atom.

![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.](image1)

![Figure 4. Contour line diagrams $V^2_{p}(r)$ for complex 6 C(aryl)–Os–C(NHC) in the plane. Dashed lines indicate areas of charge concentration ($V^2_{p}(r) < 0$) while solid lines show areas of charge depletion ($V^2_{p}(r) > 0$). 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.](image2)
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 stabilized 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) 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 σ-contribution at the Os–C(NHC) bond is significantly higher than at the Os–C(aryl) bond (ε = 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 (Os) atomic orbital to the p (H) atomic orbital at the carbene carbon (Figure 5). The computed associated SOPT stabilizing energy is quite significant (ΔESOPT = −40.6 kcal mol−1) and, as expected, much higher than the d (Os) → π^* (C=C) delocalization involving the phenyl group (ΔEσ = −6.6 kcal mol−1). As a consequence, the electronic occupation of the p (H) 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 σ-backdonation, which enhances the electrophilicity of the metal center.

Figure 5. Computed Natural Bond Orbitals involved in the stabilizing d (Os) → p (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 σ-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 σ-backdonation from the doubly occupied π (Os) orbital to the σ^* (H2) molecular orbital of this molecule is lower (ΔEσ = −30.9 kcal mol−1) than that to the σ^* (H2) molecular orbital corresponding to the hydrogen molecule trans disposed to the phenyl group (ΔEσ = −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 (H) 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 electrophilicity 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 3.5×10^−5 (5 and 6) and 1.1×10^−5 (7) for the dissociation equilibrium constants (Kd) were determined by 31P(1) NMR spectroscopy, which yield pK_a values of 2.5 (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 values of 2.5 (5) and 2.8 (7) were calculated by means of eq 1. They reveal that the acidity of the dihydrogen complexes 5–7 is similar to the acidity of the phosphoric acid (pK_a = 2.15) and organic compounds such as bromoacetic acid (pK_a = 2.69) or chloroacetic acid (pK_a = 2.85).

\[
pK_a = pK_{eq} + pK_{water}^{-1} \quad \text{(1)}
\]

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 dihydrogen 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 coordinated hydrogen molecules, to generate 5–7, in a manner that resembles the ammoniaborane dehydrogenation on the unsaturated dihydrides IrH2(POCOPtBu)2 (POCOPtBu = κ^2-P,C,P(OPtBu)3,C(H)) and OsH2(CO)(PPr3)2. 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 stirred 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(3)º and 78.66(3)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.
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 (NCH) and at 147 ppm ($^1$CN). 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 acetylacetone (acac) in a one-pot synthesis procedure, to afford novel complexes containing three different chelate ligands, $C,C_2$, $P,P_2$, and $O,O$-donor. Treatment of tetrahydrofuran solutions of 8 and 9 with 1.0 equiv of diphenylphosphino and 2.0 equiv of pentane-2,4-dione, in the presence of 2.0 equiv of potassium hydroxide, at 50 °C, for 5 h gives rise in a quantita-

tive 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).
CONCLUDING REMARKS
The hexahydride complex OsH₆(PPr₃)₂ promotes the direct metalation of N-phenylbenzimidazolium and N-phenylbenzimidazolium salts to afford trihydride-osmium(IV) derivatives, containing anionic C₆H₄N₃O⁺-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 σ-backdonation from a doubly-occupied d₉(Os) atomic orbital to the pₓ 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 Bronsted acids with pKₐ values between 2.5 and 2.8. In the presence of good coordinating ligands, which are also conjugated bases of very strong Bronsted 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 σ-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 a MBraun solvent purification apparatus. NMR spectra were recorded on a Varian Gemini 2000, a Bruker ARX 300, and a Bruker ARX 400 MHz instrument. Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks (H, 1H[CDCl₃], 3,00 ppm) or external standard 39P (H, 85% H₃PO₄ and 11B to BF₃·OEt₂). Coupling constants J and N (J = 2JPH + JHP) for 1H and N = 2JPC + JPC for 13C(1H) 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. OsH₆(PPr₃)₂ was prepared according to the published method. 1-phenyl-3-methyl-1-H-benzimidazolium iodide (HL₁I) was made with similar procedure to the reported by Hollis and co-workers. X-ray quality crystals were obtained by layering a solution of complex HL₁I; 0.400 g, 0.774 mmol) and AgBF₄ (0.535 g, 0.003 mmol) in toluene (40 mL) and washed with additional portions of metatholic ethanol (2 x 4 mL) and dried. A white solid was obtained. Yield: 0.780 g (87%).

Preparation of 1-phenyl-3-methyl-1-H-benzimidazolium tetrafluoroborate (HL₂BF₄). HL₂BF₄ was prepared as described for HL₂BF₄, starting from HL₁I (1.000 g, 2.974 mmol) and AgBF₄ (0.535 g, 0.003 mmol). A white solid was obtained. Yield: 0.200 g (93%).

Preparation of 1-phenyl-3-methyl-1-H-benzimidazolium tetrafluoroborate (HL₃BF₄). HL₃BF₄ was prepared as described for HL₂BF₄, starting from HL₁I (0.290 g, 0.874 mmol) and AgBF₄ (0.179 g, 0.917 mmol). A white solid was obtained. Yield: 0.426 g (76%). X-ray quality crystals were grown by layering a solution of complex 2 in toluene with methanol. Anal. Calc. for C₂₃H₂₃BF₄O₃P: C 53.15%; H 7.31%. Found: C 53.01%; H 8.14%. IR (cm⁻¹): ν(OH) 3414 (m), ν(As-H) 206.3 (t, 1H, OsH), 2044 (d, J = 7.2, 2H, CH₂, 293 K). 1H NMR (400 MHz, C₆D₆, 293 K): δ = 0.86 (t, J = 7.2, 2H, 1H, Cbzim), 8.0–8.7 (m, 2H, CH₃), and 7.2–6.9 (m, 9H, CH₃). 13C(1H) NMR (100 MHz, C₆D₆, 293 K): 141 ± 14 (–8.66 ppm); 102 ± 10 (–10.27 ppm). 13C(13C) NMR (100 MHz, C₆D₆, 293 K): 40 (Os–H) 2044 (m). 1H NMR (400 MHz, C₆D₆, 293 K): δ = 0.86 (t, J = 7.2, 2H, 1H, Cbzim), 8.0–8.7 (m, 2H, CH₃), and 7.2–6.9 (m, 9H, CH₃). 13C(1H) NMR (100 MHz, C₆D₆, 293 K): 141 ± 14 (–8.66 ppm); 102 ± 10 (–10.27 ppm). 13C(13C) NMR (100 MHz, C₆D₆, 293 K): 40 (Os–H) 2044 (m).
Preparation of Os(H(C=C=C)(Ph)2)(PPr3)2 [BF4] (6). A pale amber solution of 5 (0.353 g, 0.490 mmol) in diethyl ether (15 mL) was treated with HBF4·OEt2 (0.087 mL, 0.539 mmol). The mixture was left 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. Calcld. for C68H128N2OsP2·3BF4·8Et2O: C 58.95; H 8.55; N 4.60%. Found: C 58.76; H 8.58; N 4.56%.

Preparation of [Os(C=C-C)(η2-H2)(PPr3)]2[BF4] (7). A colorless solution of 2 (0.353 g, 0.490 mmol) in diethyl ether (15 mL) was treated with HBF4·OEt2 (0.087 mL, 0.539 mmol). The mixture was left 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. Calcld. for C68H128N2OsP2·3BF4·8Et2O: C 58.95; H 8.55; N 4.60%. Found: C 58.76; H 8.58; N 4.56%.
Experimental data for Os(10a-L1)(O2O(acac))(P,P'-bdppe) (10a). Potassium hydroxide (2.200 mL, 0.259 M in methanol, 0.570 mmol) was added to a solution of complex 10a in dichloromethane 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 × 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).

Preparation of Os(10b-L1)(O2O(acac))(P,P'-bdppe) (11b). Compound 11b was prepared in a similar way as 10, starting from 9 (0.600 g, 0.636 mmol), cis-1,2-bis(diphenylphosphino)ethane (bdppe; 0.134 g, 0.338 mmol), and pentane-2,4-dione (Hacac; 0.570 g, 0.0580 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 yield a pale yellow solid corresponding to 11b, which was washed with pentane (9 × 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).
12 H, 1 CHethylene-bdppe, 9 CHPh-bdppe, and 2 CHbzim), 6.96 (d, JH–H = 7.4, 1 H, CH2), 6.89 (m, 2 H, CH2-bdppe), 6.67 (m, 1 H, CH4-bdppe), 6.62 (d, JH–H = 7.4, 1 H, CH2), 6.45 (dd, JH–H = 7.4, JH–H = 7.4, 1 H, CH2), 6.36 (m, 2 H, CH2-bdppe), 6.15 (dd, JH–H = 7.4, JH–H = 7.4, 1 H, CH2), 6.07 (m, 2 H, CH2-bdppe), 5.02 (s, 1 H, CH3), 3.87 (s, 3 H, NCH3), 2.40 and 2.36 (both s, each 3 H, CH3), 1.59 and 1.19 (both s, each 3 H, CH3). 31P{1H} NMR (121.0 MHz, CD2Cl2, 293 K): δ 48.5 (d, JH–H = 10.9, bdppe, 307 (d, JH–H = 10.9, bdppe). 

Crystal data for C45H40N2O2OsP2, MW 892.93, yellow, irregular block (0.13 x 0.03 x 0.03), monoclinic, space group P21/n, a = 10.8696(4) Å, b = 16.1852(4) Å, c = 15.3418(3) Å, β = 99.5982(10)°, V = 3252.6(11) Å3, Z = 4, Dcalc: 1.543 g cm−3, F(000) = 832 (o), T = 100(2) K, μ = 8.671 mm−1, 12987 measured reflections (2519 unique, 0.0357%; 7240 unique reflections, 0.0296%; wR2 = 0.0587; data/restraints/parameters 8586/0/478; GoF = 1.108. 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 suite of programs at the B3LYP/def2-SVP level of theory using the D3 dispersion correction suggested by Grimme et al.28 This level is denoted B3P86-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 Viberg Bond Indices have been computed using the natural bond orbital (NBO) method.29 The energies associated with these two-electro interactions have been computed according to the following equation: 

\[ \Delta E_{\rho\sigma} = -n_\rho \left( \langle \sigma | \hat{F} | \rho \rangle \right) \hat{F} \] 

where \( \hat{F} \) is the DFT equivalent of the Fock operator and \( \rho \) and \( \sigma \) are two filled and unfilled Natural Bond Orbitals having \( e_\rho \) and \( e_\sigma \) energies, respectively; \( n_\rho \) 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)/WB97X-D level of theory on the optimized geometry obtained at the BP86-D3/def2-SVP level. The WB97X-D level of theory is shown to provide excellent agreement with experiment for a wide range of properties. The topology of the electron density was conducted using the AIMAll program package.30
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Osmium(II)-bis(Dihydrogen) Complexes Containing $C_{aryl}, C_{NHC}$—Chelate Ligands: Preparation, Bonding Situation, and Acidity.

\[
\begin{align*}
\text{R} & = \text{H}, \text{CH}_3 \\
\text{pK}_a \text{ (observed)} & = 3.5 - 3.8
\end{align*}
\]