An Entry to Stable Mixed Phosphine-Osmium-NHC Polyhydrides

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ABSTRACT: An entry to mixed phosphine-osmium-NHC polyhydride complexes is described, starting from the five-coordinate hydrido-alkylidyne compounds $[\text{OsHCl}(\equiv\text{CPh})(\text{IPr})(\text{PR}_3)]\text{OTf}$ ($\text{IPr} = 1,3\text{-bis}(2,6\text{-disopropylphenyl})\text{imidazolyliene}$. $\text{OTf} = \text{CF}_3\text{SO}_3$, $\text{PR}_3 = \text{P}^i\text{Pr}_3$ (**1**), PPh_3 (**2**)). The experimental procedure involves the borylation of the Os-C triple bond of **1** and **2** with NaBH_4 and the subsequent alcoholysis of the borylation products $\text{OsH}_2\text{Cl}(\eta^2\text{-H-BCH}_2\text{Ph})(\text{IPr})(\text{PR}_3)$ ($\text{PR}_3 = \text{P}^i\text{Pr}_3$ (**3**), PPh_3 (**4**)) or $\text{OsH}_2(\eta^2\text{-H}_2\text{BCH}_2\text{Ph})(\text{IPr})(\text{P}^i\text{Pr}_3)$ (**5**). Stirring of **3** in 2-propanol affords the five coordinate chloride-trihydride $\text{OsH}_3\text{Cl}(\text{IPr})(\text{P}^i\text{Pr}_3)_2$ (**6**), which reacts with NaBH_4 to give $\text{OsH}_3(\kappa^2\text{-H}_2\text{BH}_2)(\text{IPr})(\text{P}^i\text{Pr}_3)$ (**7**). This trihydride-tetrahydrideborate derivative and its PPh_3 -counterpart $\text{OsH}_3(\kappa^2\text{-H}_2\text{BH}_2)(\text{IPr})(\text{PPh}_3)$ (**8**) can be also obtained in a one-pot procedure, starting from **1** and **2** and using methanol at -60°C instead of 2-propanol as alcoholysis agent. The bonding situation in **7** and **8**, analyzed by DFT calculations using AIM and NBO methods, resembles that found in B_2H_6 and contrasts with the bonding situation in the bis- σ -borane derivative **5**. Stirring of **7** and **8** in 2-propanol leads to the corresponding d^2 -hexahydride derivatives $\text{OsH}_6(\text{IPr})(\text{PR}_3)$ ($\text{PR}_3 = \text{P}^i\text{Pr}_3$ (**9**), PPh_3 (**10**)), which reduce the $\text{C}\equiv\text{N}$ triple bond of benzonitrile and promote the subsequent chelate-assisted *ortho*-CH bond activation of the resulting phenylmethanimine, to form the trihydride compounds $\text{OsH}_3\{\kappa^2\text{-N,C-(NH=CH-C}_6\text{H}_4)\}(\text{IPr})(\text{PR}_3)_2$ ($\text{PR}_3 = \text{P}^i\text{Pr}_3$ (**11**), PPh_3 (**12**)), containing an stabilized orthometalated aldimine.

INTRODUCTION

The chemistry of polyhydride complexes of platinum group metals is a field under permanent development. Unlike other more mature areas, it offers new exciting conceptual challenges and at the same time the possibility of interacting with different fields, including conversion and storage of regenerative energy,¹ functionalization of hydrocarbons,² drugs design,³ or the preparation of new types of compounds with notable applications in material science.⁴ This versatility is a consequence of the ability of these compounds to activate a wide range of σ -bonds. In this respect, osmium is a privileged element because of its centered position in the periodic table at the third row.

The M-H bond is among the strongest metal-ligand bonds.⁵ Despite of its strength, the hydride ligand shows a great mobility.⁶ In agreement with this, polyhydrides complexes undergo combined movements of the hydrogen atom bound to the metal center. These position exchanges are thermally activated and take place with activation barriers which are lower than those involved in the movements of the heavy ligands defining the skeleton of the polyhydrides.⁷

Mass, basicity, geometry, rigidity and size of the co-ligands are factors that determine the geometry of the skeleton and the reactivity of the polyhydrides. According to the nature of the co-ligands, the polyhydrides of platinum group metals can be classified⁸ into bis(phosphine) compounds, complexes with tripodal phosphines, half-sandwich derivatives, complexes with trispyrazolylborate and related groups, and species with

pincer ligands. Although the N-heterocyclic carbenes (NHCs) have proven to be excellent ligands in coordination chemistry⁹ and promising results during the past few years underline a great potential of their transition metal complexes in catalysis¹⁰ and several fields of material science,¹¹ polyhydride complexes of platinum group metals with NHC ligands in their skeleton are extremely rare. Most of them are bis(phosphine)¹² or half-sandwich¹³ derivatives that contain an additional NHC ligand. Only in a few cases the NHC ligand is a fundamental element of the structure of the polyhydride. Macgregor, Pregosin, Whittlesey and co-workers have reported that the tetrakis(NHC) cation $[\text{RuH}(\text{IMe}_4)_4]^+$ coordinates H_2 to afford the *trans*-hydride-dihydrogen $[\text{RuH}(\eta^2\text{-H}_2)(\text{IMe}_4)_4]^+$ ($\text{IMe}_4 = 1,3,4,5\text{-tetramethylimidazol-2-ylidene}$).¹⁴ Conejero, Lledós, and co-workers have shown that the cationic species $[\text{Pt}(\text{NHC}')(\text{NHC})]^+$ ($\text{NHC} = 1,3\text{-bis}(2,6\text{-diisopropylphenyl})\text{imidazole-2-ylidene}$ (IPr); $1,3\text{-dimethyl-4,5-dimethylimidazol-2-ylidene}$ (IMes^*)), containing a cyclometalated NHC ligand (NHC'), undergo hydrogenolysis to afford the monohydrides $[\text{PtH}(\text{NHC})_2]^+$ in equilibrium with the *trans*-hydride-dihydrogen derivatives $[\text{PtH}(\eta^2\text{-H}_2)(\text{NHC})_2]^+$.¹⁵ Leitner and co-workers have observed that 1,3-dimethylimidazol-2-ylidene (IMes) displaces phosphine of $\text{RuH}_2(\eta^2\text{-H}_2)_2(\text{PCy}_3)_2$ to give the mixed phosphine-NHC dihydride-bis(dihydrogen) $\text{RuH}_2(\eta^2\text{-H}_2)_2(\text{IMes})(\text{PCy}_3)$. The double substitution to form the bis(NHC) counterpart $\text{RuH}_2(\eta^2\text{-H}_2)_2(\text{IMes})_2$ only occurs in very small amount.¹⁶ Some dihydrides have been also known.¹⁷

The preparation of mixed or heterolytic complexes with different ligands of similar characteristics but complementary properties, such as phosphine-metal-NHC, is challenging because of their strong tendency to undergo distribution reactions.¹⁸ During our catalytic studies on osmium-promoted C-C and C-heteroatom coupling reactions,¹⁹ we observed that the NHC-complex $[(\eta^6\text{-}p\text{-cymene})\text{OsCl}(\equiv\text{CHPh})(\text{IPr})]\text{OTf}$ ($\text{OTf} = \text{CF}_3\text{SO}_3$) easily loses the arene.²⁰ The resulting metal fragment can be trapped with phosphines to form the five-coordinate derivatives $[\text{OsHCl}(\equiv\text{CPh})(\text{IPr})(\text{PR}_3)]\text{OTf}$ ($\text{PR}_3 = \text{P}^i\text{Pr}_3$ (**1**), PPh_3 (**2**)),²¹ which allows us to develop new chemistry. Thus, borylation reactions of the metal-carbon triple bond have been recently achieved without affecting the $\text{R}_3\text{P-Os-IPr}$ skeleton. The reactions afforded both borinium, $\text{OsH}_2\text{Cl}(\eta^2\text{-H-BCH}_2\text{Ph})(\text{IPr})(\text{PR}_3)$ ($\text{PR}_3 = \text{P}^i\text{Pr}_3$ (**3**), PPh_3 (**4**)),²² and bis- σ -borane, $\text{OsH}_2(\eta^2;\eta^2\text{-H}_2\text{BCH}_2\text{Ph})(\text{IPr})(\text{P}^i\text{Pr}_3)$ (**5**), derivatives (Scheme 1). In the search for mixed $\text{R}_3\text{P-Os-NHC}$ polyhydrides, we have now carried out the borylation reactions under alcoholysis conditions, in view of the oxophilic character of both boron ligands.

This paper shows the first entry to $\text{R}_3\text{P-Os-NHC}$ polyhydrides complexes, which are relevant from a conceptual point of view because they demonstrate that it is possible to stabilize polyhydrides with a mixed L-M-L' skeleton, when the L and L' ligands have complementary properties, and are useful because they can be used as starting materials for the preparation of other hydride derivatives.

Scheme 1

RESULTS AND DISCUSSION

1. Formation of a six-coordinate chloro-trihydride-osmium(IV) complex. Previous EDA-NOCV calculations have revealed that the main contribution to the interaction between the borinium ligand of **3** and the square pyramidal metal fragment is the electrostatic term, which contributes about 57% to the total interaction energy.²² As a result, the osmium-borinium bond has a high degree of polarization, which is consistent with the high electronegativity of the osmium atom and suggests a significant positive partial charge on the ligand.²⁴ In agreement with this, the borinium group undergoes alcoholysis. In 2-propanol under reflux, the addition of the O-H bond of the alcohol to the Os-B bond of **3** affords the red, six-coordinate, chloride-trihydride-

osmium(IV) complex $\text{OsH}_3\text{Cl}(\text{IPr})(\text{P}^i\text{Pr}_3)$ (**6**) in quantitative yield, after 4 h (eq 1).

Complex **6** has been characterized by X-ray diffraction analysis. Figure 1 shows a view of the molecular geometry. The structure has essentially C_s symmetry with the phosphine and NHC ligands *trans* disposed ($\text{C}(1)\text{-Os-P} = 171.41(15)^\circ$) and the chloride, the metal center, and the hydrides lying in the perpendicular plane to the $\text{C}(1)\text{-Os-P}$ direction. The most noticeable feature of the complex is the $\text{H}(01)\text{-Os-H}(02)$ and $\text{H}(02)\text{-Os-H}(03)$ angles of $73(3)^\circ$, which markedly deviate from 90° . The structure resembles those of the bis(phosphine) derivatives $\text{OsH}_3\text{X}(\text{PR}_3)_2$ ($\text{PR}_3 = \text{P}^i\text{Bu}_2\text{Me}$; $\text{X} = \text{Cl}$, $\text{PR}_3 = \text{P}^i\text{Pr}_3$; $\text{X} = \text{Cl}$, Br , I),²⁵ $\text{OsH}_3(\text{OR}_F)(\text{P}^i\text{Pr}_3)_2$ ($\text{OR}_F = \text{OCH}_2\text{CF}_3$, $\text{OCH}(\text{CF}_3)_2$),²⁶ $\text{OsH}_3(\text{OPh})(\text{P}^i\text{Pr}_3)_2$ ²⁷ and $\text{OsH}(\text{Bcat})_2\text{Cl}(\text{P}^i\text{Pr}_3)_2$.²⁸ The octahedral geometry is not favorable for these compounds. They undergo distortion that destabilizes one orbital from the t_{2g} set and simultaneously stabilizes the occupied ones to be diamagnetic. The distortion partially cancels the electron deficiency at the metal, which receives additional electron density from the π -donor group.²⁵⁻²⁸

Figure 1. Molecular diagram of **6**. Selected bond lengths ($\text{\AA}$) and angles ($^\circ$): $\text{Os-Cl} = 2.4245(16)$, $\text{Os-P} = 2.3310(13)$, $\text{Os-C}(1) = 2.068(5)$; $\text{C}(1)\text{-Os-P} = 171.41(15)$, $\text{H}(01)\text{-Os-Cl} = 125(2)$, $\text{H}(03)\text{-Os-Cl} = 90(2)$, $\text{H}(01)\text{-Os-H}(02) = 73(3)$, $\text{H}(02)\text{-Os-H}(03) = 73(3)$. Displacement ellipsoids are given at the 50% probability level.

The ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **6** in toluene- d_8 are consistent with the structure shown in Figure 1. Thus, the hydride ligands display an AB_2 spin system in the $^1\text{H}\{^{31}\text{P}\}$ NMR spectrum. The AB_2 pattern, δ_A -15.16 and δ_B -21.17 is distinguished by the magnitude of the J_{AB} value of 290 Hz at -90°C , which supports quantum exchange coupling. At room temperature, the resonance corresponding to the metalated carbene carbon atom appears at 170.0 ppm, as a doublet with a C-P coupling constant of 74 Hz, in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum. At the same temperature, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows a singlet at 47.7 ppm.

2. Trihydride-tetrahydridoborate-osmium(IV) and hexahydride-osmium(VI) complexes. Treatment of a tetrahydrofuran solution of **6** with 1.5 equiv of NaBH₄, at -40°C, for 15 min produces the replacement of the chloride ligand by the tetrahydridoborate group, to afford the trihydride-tetrahydridoborate-osmium(IV) derivative OsH₃(κ²-H₂BH₂)(IPr)(P^{*i*}Pr₃) (**7**) which was isolated as a yellow solid in 44% yield (eq 2); i.e., 20% with regard to the hydride-alkylidyne **1**. Complex **7** and its triphenylphosphine counterpart OsH₃(κ²-H₂BH₂)(IPr)(PPh₃) (**8**) can be also obtained in a one-pot synthesis procedure, starting from the respective hydride-alkylidyne complexes **1** and **2**, when methanol instead 2-propanol is used at -60°C as alcoholysis agent of the borinium intermediates **3** and **4**. Under these conditions, both yellow trihydride-tetrahydridoborate derivatives were isolated in about 30% global yield (eq 3). Complexes **7** and **8** are notable because constitute the first mixed R₃P-M-NHC tetrahydrideborate compounds in the osmium chemistry. The known tetrahydrideborate complexes of this element are limited to bis(phosphine) species. They include the osmium(II) derivatives OsH(κ²-H₂BH₂)(CO)(PR₃)₂ (PR₃ = P^{*i*}Pr₃, P^{*t*}BuMe)²⁹ and Os(BR₂)(κ²-H₂BH₂)(CO)(P^{*i*}Pr₃)₂ (BR₂ = Bcat, Bpin)³⁰ and the osmium(IV) compounds OsH₃(κ²-H₂BH₂)(PR₃)₂ (PR₃ = P^{*i*}Pr₃³¹, P^{*i*}Pr₂Ph, PCy₃)³², which have been prepared by replacement of [Cl]⁻ by [BH₄]⁻,^{29,31} substitution of HB(OR)₂ by BH₃ from coordinated dihydridoborate groups,³⁰ and addition of BH₃ to unsaturated hydride compounds.³²

The formation of **7** and **8** was confirmed by means of the X-ray structure of **8** (Figure 2), which proves the κ²-coordination of the tetrahydridoborate group. The geometry around the osmium atom can be rationalized as a distorted pentagonal bipyramid with the phosphine and the NHC ligands occupying axial positions (P(1)-Os-C(1)) = 174.13(12)°. The metal coordination sphere is completed with the hydride ligands and both boron bridging hydrogen atoms in the equatorial plane.

Figure 2. Molecular diagram of **8**. Selected bond lengths (Å) and angles (deg): Os-B = 2.305(5), Os-H(04) = 1.71(5), B-H(07) = 1.01(3); P(1)-Os-C(1) = 174.13(12), H(06)-B-H(07) = 114(4), H(05)-Os-H(01) = 96(2), H(04)-B-H(05) = 89(3), H(01)-Os-H(02) = 59(2), H(02)-Os-H(03) = 48(2). Displacement ellipsoids are given at the 50% probability level.

The bonding situation in the tetrahydrideborate complexes was analyzed by means of DFT calculations at the BP86/def2-SVP level, using the Atoms in Molecules (AIM) and Natural Bond Orbital (NBO) methods. Figure 3a shows the Laplacian distribution for **8** in the Os-H-B plane. This compound is characterized by the AIM method as a four-membered cyclic species possessing two Os-H and two B-H bond critical points associated with one OsH₂B ring critical point. This particular topology, where the bond paths are inwardly curved, strongly resembles the situation found in B₂H₆ (Figure 3b). Thus, the computed electron densities (ρ) and ellipticities (ε) at the B-H bond critical points in **8** and diborane are consistent at the same level of theory: ρ = 0.16 eÅ⁻³ and ε = 0.08 (**8**) versus ρ = 0.17 eÅ⁻³ and ε = 0.04 (B₂H₆) for the terminal B-H bonds, and ρ = 0.12 eÅ⁻³ and ε = 0.04 (**8**) versus ρ = 0.12 eÅ⁻³ and ε = 0.03 (B₂H₆) for the bridging bonds. The computed NBO-charge at the boron atom of -0.35 e nicely agrees with its tetrahedral hybridization: sp^{2.6} calculated at the terminal B-H bond and sp^{3.6} calculated at the bridging B-H-Os bond. There is no Os-B ring critical point nor a bond path. This situation sharply contrasts with that found for bis-σ-borane **5**, which is clearly characterized by the occurrence of an Os-B ring critical point by the AIM method.²³ This difference is the result of a much stronger Os-B interaction in the latter as compared to **8**, which is clearly reflected in the corresponding Wiberg bond indices, 1.02 for **5** versus 0.39 for **8**.

Figure 3. Contour line diagrams $\nabla^2\rho(r)$ for complex $\text{OsH}_3(\kappa^2\text{-H}_2\text{BH}_2)(\text{IPr})(\text{PPh}_3)$ in the Os-H-B plane (a) and for B_2H_6 in the B-H-B plane (b). The solid lines connecting the atomic nuclei are the bond paths while the small green and red spheres indicate the corresponding bond critical and ring critical points, respectively.

The ^1H NMR spectra of **7** and **8** in toluene- d_8 are temperature dependent. Figure 4 shows the $^1\text{H}\{^{11}\text{B}\}$ NMR spectrum of **7** as a function of the temperature. At 233 K, the spectra of both compounds show four signals for the $\text{OsH}_3(\kappa^2\text{-H}_2\text{BH}_2)$ moiety, with a 1:1:2:3 intensity ratio, at 7.82 and 7.68 (H_t and H'_t), -6.41 (H_p) and -12.74 (H_a and H_b) ppm for **7** and at 7.81 (H_t and H'_t), -5.73 (H_p), and -11.53 (H_a and H_b) ppm for **8**. The resonances due to the boron-bridging hydrogen atoms, H_p , and the hydride ligands, H_a and H_b , coalesce at about 318 K for **7** and at about 333 K for **8**. This behavior is consistent with the existence of two intramolecular position exchange processes thermally activated (Scheme 2). The process of a lower energy barrier, involving the hydride ligands, is characteristic for $\text{OsH}_3\text{L}_2(\text{P}'\text{Pr}_3)_2$ species and seems to take place via dihydrogen intermediates,³ whereas that of higher activation energy corresponds to the position exchange between the hydride ligands and the boron-bridging hydrogen atoms, has an activation energy of about 14 kcal mol⁻¹, and seems to occur very likely through seven-coordinate tetrahydride- σ -borane intermediates.^{31b,33} In contrast to the ^1H NMR spectra, the $^{13}\text{C}\{^1\text{H}\}$, $^{31}\text{P}\{^1\text{H}\}$ and $^{11}\text{B}\{^1\text{H}\}$ NMR spectra are temperature invariant between 193 K and 338 K. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra, the most noticeable feature is the resonance due to the metalated carbene carbon atom, which appears at 184.6 ppm for **7** and at 182.5 for **8** as a doublet with a C-P coupling constant of 87.0 Hz for **7** and of 91.5 Hz for **8**. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra show a singlet at 40.9 ppm for **7** and at 24.7 ppm for **8**,

whereas the $^{11}\text{B}\{^1\text{H}\}$ spectra contain a broad signal at 17.8 ppm for **7** and at 19.4 ppm for **8**.

Figure 4 Low- (δ , 8.4-7.4) and high-field region of the $^1\text{H}\{^{11}\text{B}\}$ NMR spectrum of **7** as a function of temperature.

Scheme 2

Nucleophiles abstract BH_3 from a coordinated tetrahydrideborate group, in particular when the rupture of an M-H-B bridge takes place.³⁴ In agreement with this, complexes **7** and **8** are unstable in 2-propanol. Because the $\text{OsH}_4(\text{IPr})(\text{PR}_3)$ species

resulting from the extraction dehydrogenate alcohols, at room temperature, the stirring of 2-propanol solutions of these compounds for 4 h gives rise to the quantitative formation of the hexahydride derivatives $\text{OsH}_6(\text{IPr})(\text{PR}_3)$ ($\text{PR}_3 = \text{P}^i\text{Pr}_3$ (**9**), PPh_3 (**10**)). These compounds were isolated as white solids (eq 4). In accordance with the presence of six-hydride ligands in the complexes, their ^1H NMR spectra, in benzene- d_6 , at room temperature show a doublet ($^2J_{\text{H-P}} \approx 10$ Hz), at -8.81 ppm for **9** and at -7.37 ppm for **10**, which displays an integration intensity of 6. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra contain a singlet, at 56.5 ppm for **9** and at 25.5 ppm for **10**, which is split into a septet under off-resonance conditions. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra, the metalated carbene carbon atom displays a doublet at 177.5 ppm for **9** and at 176.5 ppm for **10** with a C-P coupling constants of 56.6 Hz and 63.5 Hz, respectively.

A few d^2 -hexahydride derivatives are known for osmium in the iron triade. Although recently an example containing the disphosphine 9,9-dimethyl-4,5-bis(diisopropylphosphine)xanthane ($\text{xant}(\text{P}^i\text{Pr}_2)_2$) has been reported,³⁵ they are generally stabilized with two monodentate phosphine co-ligands.^{32,36} In contrast to ruthenium, the OsH_6 -species are classical polyhydrides. This fact has been confirmed by means of the neutron diffraction structure of $\text{OsH}_6(\text{P}^i\text{Pr}_2\text{Ph})_2$. The geometry of the inner coordination sphere can be described as a dodecahedron defined by two orthogonal BAAB trapezoidal planes, with the heavy atoms at the B sites of one of them.³⁷ Complex **9** and **10** are the first mixed $\text{R}_3\text{P-M-NHC}$ members of this family of compounds.

3. Reduction and C-H bond activation of benzonitrile. The hexahydride complexes **9** and **10** promote the reduction of the $\text{C}\equiv\text{N}$ triple bond of benzonitrile and the subsequent chelate-assisted *ortho*-CH bond activation of the resulting imine. Thus, the treatment of toluene solutions of these compounds with 1.1 equiv of the nitrile, under reflux, for 10 h leads to the trihydride derivatives $\text{OsH}_3\{\kappa^2\text{-N,C-(NH=CH-C}_6\text{H}_4)\}(\text{IPr})(\text{PR}_3)$ ($\text{PR}_3 = \text{P}^i\text{Pr}_3$ (**11**), PPh_3 (**12**)), containing an stabilized *ortho*-metalated phenylmethanimine. Complexes **11** and **12** were isolated as orange solids in about 75% yield (eq 5).

$\text{PR}_3 = \text{P}^i\text{Pr}_3$ (**7**, **9**), PPh_3 (**8**, **10**)

Complex **11** was characterized by X-ray diffraction analysis. Figure 5 shows a view of the structure, which proves the stabilization of the aldimine. The complex presents a pentagonal-bipyramidal geometry with the phosphine and the NHC ligands in axial positions ($\text{P(1)-Os-C(8)} = 166.68(9)^\circ$), whereas the three hydride ligands and the chelated group ($\text{N(1)-Os-C(8)} = 74.13(12)^\circ$) lie in the equatorial plane. The five-membered ring formed by the *ortho*-metalated imine and

the osmium atom is almost planar. The Os-N(1) bond length of 2.118(3) and the Os-C(1) distance of 2.126(3) are typical for Os-N and Os-C_{aryl} single bonds and are in agreement with those previously reported for other osmium complexes containing *ortho*-metalated imines.³⁸

Figure 5. Molecular diagram of **11**. Selected bond lengths (Å) and angles (deg): $\text{Os-N(1)} = 2.118(3)$, $\text{Os-C(1)} = 2.126(3)$; $\text{P(1)-Os-C(8)} = 166.68(9)^\circ$, $\text{N(1)-Os-C(8)} = 74.13(12)^\circ$.

The ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **11** and **12**, in toluene- d_8 , are consistent with the structure shown in Figure 5. In agreement with the presence of three inequivalent hydrides ligand in these compounds, the ^1H NMR spectra in the high field region, at 223 K, show three resonances at -6.68, -9.37, and -9.61 ppm for **11** and at -5.79, -8.72, and at -8.96 ppm for **12**. In the low field region of the spectra, the most noticeable feature is the NH signal, which appears at 9.33 ppm for **11** and at 8.76 ppm for **12**. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra, the resonance corresponding to the metalated phenyl carbon atom appears at 191.8 ppm for **11** and at 188.7 ppm for **12** as a doublet with a C-P coupling constant of 6.7 Hz for **11** and of 9.2 Hz for **12**, whereas the signal due to the metalated carbene carbon atom is observed at 175.1 ppm for **11** and at 175.5 ppm for **12** also as a doublet but with a C-P coupling constant of 78.9 Hz for **11** and of 94.8 Hz for **12**. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra contain a singlet at 19.7 ppm for **11** and at 21.8 ppm for **12**.

Concluding Remarks

This study has revealed that the borolation of the metal-carbon triple bond of phosphine-osmium-NHC, five coordinate, hydride-alkylidyne complexes with the tetrahydrideborate anion under alcoholysis conditions, is the way to access polyhydrides stabilized by phosphine-osmium-NHC skeletons. Thus, the first compounds of four different types of mixed polyhydrides are reported: $\text{OsH}_3\text{Cl}(\text{NHC})(\text{PR}_3)$, $\text{OsH}_3(\kappa^2\text{-H}_2\text{BH}_2)(\text{NHC})(\text{PR}_3)$, $\text{OsH}_6(\text{NHC})(\text{PR}_3)$, and $\text{OsH}_3(\text{XY})(\text{NHC})(\text{PR}_3)$.

Arrangements to form the homoleptic species have not been observed in any case, despite relatively drastic experimental conditions, such as 2-propanol or toluene under reflux, have been used in some occasions. The mutually *trans* disposition of the heavy co-ligands and the small size of the hydrides, which prevent ligand dissociation process, disfavor the ligand exchange from a kinetic point of view. Furthermore, the complementary properties of phosphines and NHC ligands, mainly

σ -donor the first ones and quite π -acceptor the latter,^{12c} stabilize the skeleton of the polyhydride.

Because the previous developed procedure to prepare the five-coordinate hydride-alkylidene starting compounds is compatible with a wide range of phosphines and NHC ligands, this entry should allow the preparation of polyhydrides with a wide range of skeletons of this type. Furthermore, as the nature of the interactions between the hydrogen atoms coordinated to the metal center and those of the latter with the hydrogens depend upon the electronic properties of the heavy co-ligands, a very fine turning of the characteristic of the hydrides should be achieved by combining different phosphine and NHC groups at the skeleton. So, the use of these skeletons should allow a better control of the polyhydride properties.

In conclusion, an entry to the first families of stable mixed phosphine-osmium-NHC polyhydrides is described. Given the potential of the osmium polyhydrides and the subtle govern of the electron density of the metal center of the polyhydride that can be performed through the combination of ligands, a promising chemistry should be expected for this type of compounds.

EXPERIMENTAL SECTION

All reactions were carried out with rigorous exclusion of air using Schlenck-tube techniques. Solvents were dried by standard procedures and distilled under argon prior to use. The starting materials [OsHCl($\equiv$ CPh)(IPr)(P^{*i*}Pr₃)]OTf (P₃ = P^{*i*}Pr₃, (**1**), PPh₃ (**2**)) were prepared by the published method.⁹¹ ¹H, ¹³C{¹H}, ³¹P{¹H} and ¹¹B{¹H} NMR Spectra were recorded on 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 (¹H, ¹³C{¹H}) or external H₃PO₄ (³¹P{¹H}) and BF₃·Et₂O (¹¹B{¹H}). Coupling constants *J* 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 O Analyses were carried out with a Perkin-Elmer 2400 CHNS/O analyzer. High-resolution electrospray mass spectra were acquired using a MicroTOF-Q hybrid quadrupole time-of-fly spectrometer (Bruker Daltonics, Bremen, Germany).

Computational details.

Geometry optimizations without symmetry constraints for compounds **8** and B₂H₆ were carried out with the Gaussian 09³⁹ suite of programs using the BP86⁴⁰ functional in combination with the def2-SVP⁴¹ basis set for all atoms. The osmium atom was calculated with a quasi-relativistic effective core potential.⁴² The BP86/def2-SVP level was selected because it was previously used to study the bonding situation of related complexes having Os–B interactions.^{22–23,28} Stationary points were characterized by calculating the Hessian matrix analytically to confirm that all species are minima on the potential energy surface.

Wiberg Bond Indices (WBI) were computed using the Natural Bond Orbital (NBO) method.⁴³ All AIM results described in this work correspond to calculations performed at the BP86/6-31+G(d)/WTBS(for Os) level on the optimized geometries obtained at the BP86/def2-SVP level. The WTBS (well-tempered basis sets)⁴⁴ have been recommended for AIM calculations involving transition metals.⁴⁵ The topology of the electron density was conducted using the AIMAll program package.⁴⁶

Preparation of OsH₃Cl(IPr)(P^{*i*}Pr₃) (6**).** A yellow solution of OsH₂Cl(η^2 -H-BCH₂Ph)(IPr)(P^{*i*}Pr₃) (**3**) (100 mg, 0.114 mmol) in 10 mL of 2-propanol was stirred for 4 h at 110 °C. The resulting red solution was evaporated to dryness to afford a red solid. Yield 84mg (95%). ¹H NMR (300 MHz, C₆D₆, 298K): δ 7.30–7.19 (6H, Ph), 6.63 (s, 2H, NCH), 3.3 (hpt, ³*J*_{H-H} = 6.8, 4H, CHCH₃), 1.94 (m, 3H, PCH), 1.54, 1.11 (both d, ³*J*_{H-H} = 6.8, 12H, CHCH₃), 0.90 (dd, ³*J*_{H-H} = 12.6, ³*J*_{H-P} = 7.1, 18H, PCHCH₃), -19.53 (s wide, 3H, OsH). ¹H{³¹P} NMR

(300 MHz, C₆D₆, 183K): δ_A = -15.16, δ_B = -21.17 (AB₂ pattern, *J*_{AB} = 290, OsH₃). ³¹P{¹H} NMR (121.4 MHz, C₆D₆, 298 K): δ 47.7 (s). ¹³C{¹H}-APT NMR (75.4 MHz, C₆D₆, 298 K): δ 170.0 (d, ²*J*_{C-P} = 74, OsC) 147.0, 136.9, 126.9, 123.6 (all s, Ph), 122.6 (s, NCH), 28.9 (s, CHCH₃) 26.6 (d, ¹*J*_{C-P} = 22.4, PCH), 25.9, 22.6 (both s, CHCH₃), 20.3 (s, PCHCH₃).

Preparation of OsH₃(η^2 -H₂BH₂)(IPr)(P^{*i*}Pr₃) (7**). Method A:** A red solution of OsH₃Cl(IPr)(P^{*i*}Pr₃) (**6**) (88.4 mg, 0.114 mmol) in 5 mL of THF was treated with Na[BH₄] (6.5 mg, 0.171 mmol). The mixture was stirred for 15 minutes at -40 °C, and the resulting dark red solution was evaporated to dryness. The residue was treated with 10 mL of toluene and the mixture was filtered through Celite. The solution was then evaporated to dryness. The residue was washed with cold pentane (2 x 1 mL) to afford a yellow solid which was dried in vacuo. Yield: 37.5 mg (44%). **Method B:** An orange solution of [OsHCl($\equiv$ CPh)(IPr)(P^{*i*}Pr₃)]OTf (**2**) (200 mg, 0.197 mmol) in 9.5 mL of THF was treated with Na[BH₄] (111.7 mg, 2.96 mmol) in the presence of 0.5 mL of methanol. The mixture was stirred for 10 minutes at -60 °C. The resulting dark red solution was evaporated to dryness. The residue was treated with 10 mL of toluene and the suspension was filtered through Celite. The solution was then evaporated to dryness. The residue was washed with cold pentane (2 x 1 mL) to give a yellow solid which was dried in vacuo. Yield: 55.3 mg (37%). Anal. Calcd for C₃₆H₆₄N₂OsP: C, 57.12; H, 8.52; N, 3.70. Found: C, 56.80; H, 8.21; N, 3.39. IR (cm⁻¹): ν (BH) 2418 and 2437; ν (OsH) 2098 and 2152 cm⁻¹. ¹H NMR (300 MHz, C₆D₆, 298K): δ 7.75 (s wide, 2H, BH₄ + BH'), 7.30–7.20 (6H, Ph), 6.67 (s, 2H, NCH), 3.13 (hpt, ³*J*_{H-H} = 6.8, 4H, CHCH₃), 1.73 (m, 3H, PCH), 1.48, 1.10 (both d, ³*J*_{H-H} = 6.8, 24H, CHCH₃), 0.91 (dd, ³*J*_{H-H} = 12.4, ³*J*_{H-P} = 7.1, 18H, PCHCH₃), -6.43 (s wide, 2H, BH₄Os), -12.75 (s wide, 3H, OsH_a + OsH_b). ¹H NMR (400 MHz, C₇D₈, 233K): δ 7.82 (s, 1H, BH'), δ 7.68 (s, 1H, BH'), -6.41 (s wide, 2H, BH₄Os), -12.74 (s wide, 3H, OsH_a + OsH_b). ³¹P{¹H} NMR (121.4 MHz, C₆D₆, 298 K): δ 40.9 (s). ¹¹B NMR (96.2MHz, C₆D₆, 298 K): δ 17.8. ¹³C{¹H}-APT NMR (75.4 MHz, C₆D₆, 298 K): δ 184.6 (d, ²*J*_{C-P} = 87.0, OsC), 146.8, 139.0, 129.7, 124.0 (all s, Ph), 122.6 (s, NCH), 29.1 (s, CHCH₃), 26.7 (d, ¹*J*_{C-P} = 22.8, PCHCH₃), 26.1 (s, CHCH₃), 22.5 (s, PCHCH₃), 20.6 (s, CHCH₃).

Preparation of OsH₃(η^2 -H₂BH₂)(IPr)(PPh₃) (8**).** An orange solution of [OsHCl($\equiv$ CPh)(IPr)(PPh₃)]OTf (**2**) (150 mg, 0.134 mmol) in 9.5 mL of THF was treated with Na[BH₄] (75.98 mg, 2.01 mmol) in the presence of 0.5 mL of methanol. The mixture was stirred for 10 minutes at -60 °C. The resulting dark red solution was evaporated to dryness. The residue was treated with 10 mL of toluene and the suspension was filtered through Celite. The solution was then evaporated to dryness. The residue was washed with cold pentane (4 x 2 mL) to give a yellow solid which was dried in vacuo. Yield: 34.4 mg (30%). Anal. Calcd for C₄₅H₅₈N₂OsP: C, 62.92; H, 6.81; N, 3.26. Found: C, 62.71; H, 6.47; N, 3.02. HRMS (electrospray, *m/z*): C₄₅H₅₁N₂OsP [M - 7H]: 853.3502, found: 853.3569. IR (Nujol, cm⁻¹): ν (BH) 2435 and 2332; ν (OsH) 2120 and 2024 cm⁻¹. ¹H NMR (300 MHz, C₆D₆, 298K): δ 7.50–7.41 (5H, PPh), 7.27, 7.24, 7.13 (all d, ³*J*_{H-H} = 7.7, 6H, Ph), 7.00–6.90 (10H, PPh), 6.64 (s, 2H, NCH), 3.11 (hpt, ³*J*_{H-H} = 6.8, 4H, CHCH₃), 1.37, 1.07 (both d, ³*J*_{H-H} = 6.8, 24H, CHCH₃), -5.73 (s wide, 2H, BH₄Os), -11.53 (s wide, 3H, OsH_a + OsH_b). ¹H NMR (400 MHz, C₇D₈, 243K): δ 7.81 (wide, 2H, BH₄ + BH'), -5.73 (s wide, 2H, BH₄Os), -11.53 (d, ²*J*_{H-P} = 12.0 Hz, 3H, OsH_a + OsH_b). ³¹P{¹H} NMR (121.4 MHz, C₆D₆, 298 K): δ 24.7 (s). ¹¹B NMR (96.2MHz, C₆D₆, 298 K): δ 19.4. ¹³C{¹H}-APT NMR, HSQC and HMBC (75.4 MHz, C₆D₆, 298 K): δ 182.5 (d, ²*J*_{C-P} = 91.5, OsC), 146.6 (s, Ph), 140.8 (d, ¹*J*_{C-P} = 42.9, C_{ipso}-PPh), 138.7 (s, Ph), 134.6 (d, *J*_{C-P} = 11.3, PPh), 129.9 (s, Ph), 128.8 (d, *J*_{C-P} = 1.9, PPh), 127.5 (d, *J*_{C-P} = 9.2, PPh), 124.2 (s, Ph), 122.8 (s, NCH), 29.2 (s, CHCH₃), 26.1, 22.4 (both s, CHCH₃).

Preparation of OsH₆(IPr)(P^{*i*}Pr₃) (9**).** A yellow solution of OsH₃(η^2 -H₂BH₂)(IPr)(P^{*i*}Pr₃) (**7**) (100 mg, 0.132 mmol) in 5 mL of 2-propanol was stirred for 4 h at room temperature, and the resulting red solution was evaporated to dryness. The residue was washed with cold pentane (2 x 1 mL) obtaining a white solid which was dried in vacuo. Yield: 43.58 mg (44%). Anal. Calcd for C₃₆H₆₄N₂OsP: C, 58.03; H, 8.52; N, 3.76. Found: C, 57.68; H, 8.24; N, 3.61. HRMS (electrospray, *m/z*): C₃₈H₆₃N₃OsP [M - 4H+CH₃CN]: 784.4362.

Found: 784.4371. IR (cm⁻¹): ν(OsH) 1882 and 1972 cm⁻¹. ¹H NMR (400 MHz, C₆D₆, 298K): δ 7.24-7.07 (6H, Ph), 6.53 (s, 2H, NCH), 2.88 (hpt, ³J_{H-H} = 6.8, 4H, CHCH₃), 1.49 (d, ³J_{H-H} = 6.8, 12H, CHCH₃), 1.40 (m, 3H, PCH), 1.06 (d, ³J_{H-H} = 6.8, 12H, CHCH₃), 0.78 (dd, ³J_{H-H} = 13.4, ³J_{H-P} = 7.0, 18H, PCHCH₃), -8.81 (d, ²J_{H-P} = 9.7, 6H, OsH). ³¹P{¹H} NMR (161.9 MHz, C₆D₆, 298 K): δ 56.5. ¹³C{¹H}-APT NMR (75.4 MHz, C₆D₆, 298 K): δ 177.5 (d, ²J_{C-P} = 56.6, OsC), 146.7, 140.6, 129.5, 124.3 (all s, Ph), 121.6 (s, NCH), 29.3 (s, CHCH₃), 28.6 (d, ¹J_{C-P} = 28.7, PCHCH₃), 25.4 (s, CHCH₃), 23.0 (s, PCHCH₃), 20.6 (s, CHCH₃).

Preparation of OsH₆(IPr)(PPh₃) (10). A yellow solution of OsH₃(η²-H₂BH₂)(IPr)(PPh₃) (**8**) (100 mg, 0.116 mmol) in 5 mL of 2-propanol was stirred for 4 h at room temperature. The resulting red solution was dried in vacuo. The residue was washed with cold pentane (2 x 1 mL) to give a white solid which was dried in vacuo. Yield: 76 mg (50%). Anal. Calcd for C₄₅H₅₈N₂OsP: C, 63.72; H, 6.89; N, 3.30. Found: C, 63.51; H, 6.72; N, 3.06. HRMS (electrospray, m/z): C₄₇H₅₇N₂OsP [M - 4H+CH₃CN]: 886.3903, found: 886.3904. IR (cm⁻¹): ν(OsH) 1868 and 1944 cm⁻¹. ¹H NMR (300 MHz, C₆D₆, 298K): δ 7.55-7.49 (5H, PPh), 7.33, 7.30, 7.19 (all d, ²J_{H-H} = 7.6, 6H, Ph), 6.99-6.88 (10H, PPh), 6.61 (s, 2H, NCH), 2.90 (hpt, ²J_{H-H} = 6.8, 4H, CHCH₃), 1.40, 1.10 (both d, ²J_{H-H} = 6.8, 24H, CHCH₃), -7.37 (d, ²J_{H-P} = 9.8, 6H, OsH). ³¹P{¹H} NMR (121.4 MHz, C₆D₆, 298 K): δ 25.5 (s). ¹³C{¹H}-APT NMR (75.4 MHz, C₆D₆, 298 K): δ 176.5 (d, ²J_{C-P} = 63.5, OsC), 146.7 (s, Ph), 142.0 (d, ²J_{C-P} = 50.3, C_{ipso}-PPh), 140.3 (s, Ph), 134.4 (d, ²J_{C-P} = 11.6, PPh), 129.6 (s, Ph), 128.8 (s, PPh), 127.5 (d, ²J_{C-P} = 9.9, PPh), 124.5 (s, Ph), 121.7 (s, NCH), 29.3 (s, CHCH₃), 25.4, 22.9 (both s, CHCH₃).

Preparation of OsH₃{κ²-N-C-(NH=CHC₆H₄)}(IPr)(P^tPr₃) (11). A pale yellow solution of OsH₆(IPr)(P^tPr₃) (**9**) (100 mg, 0.134 mmol) in 5 mL of toluene was treated with benzonitrile (15 μL, 0.147 mmol). The mixture was stirred for 1 h at reflux, and the resulting red solution was evaporated to dryness. The residue was washed with 2 mL of cold methanol obtaining an orange solid which was dried in vacuo. Yield: 83.2 mg (73%). Anal. Calcd for C₄₃H₆₆N₃OsP: C, 61.03; H, 7.86; N, 4.7. Found: C, 60.66; H, 7.76; N, 4.90. HRMS (electrospray m/z): C₄₃H₆₅N₃OsP: 846.4528. Found: 846.4570. IR (cm⁻¹): ν(NH) 3378 cm⁻¹, ν(OsH) 2103 and 1931 cm⁻¹. ¹H NMR (300 MHz, C₆D₆, 298K): δ 9.43 (br, 1H, NH), 8.36 (d, ³J_{H-H} = 7.3, 1H, CHPh), 7.48, 7.39 (both dd, ³J_{H-H} = 7.3, ⁴J_{H-H} = 1.6, 2H, OsPh), 7.31 (t, ³J_{H-H} = 7.7, 2H, Ph), 7.22, 7.14 (both dd, ³J_{H-H} = 7.7, ⁴J_{H-H} = 1.6, 4H, Ph), 6.93, 6.86 (both td, ³J_{H-H} = 7.3, ⁴J_{H-H} = 1.6, 2H, OsPh), 6.41 (s, 2H, NCH), 3.36, 2.65 (both hpt, ³J_{H-H} = 6.8, 4H, CHCH₃), 1.53, (d, ³J_{H-H} = 6.8, 6H, CHCH₃), 1.5 (hpt, ²J_{H-P} = 7.2, 3H, PCHCH₃), 1.18, 1.07, 1.00 (all d, ³J_{H-H} = 6.8, 18H, CHCH₃), 0.84, 0.74 (both dd, ³J_{H-H} = 12.1, ³J_{H-P} = 7.2, 18H, PCHCH₃), -6.77 (br, 1H, OsH), -9.46 (br, 2H, OsH). ¹H NMR (400 MHz, C₇D₈, 223K): δ 89.33 (ddd, ³J_{H-P} = 9.3, ³J_{H-H} = 5.0, ³J_{H-H} = 5.0, 1H, NH), -6.68 (ddd, ²J_{H-P} = 10.4, ²J_{H-H} = 5.0, ³J_{H-H} = 5.0, 1H, OsH), -9.37 (vt, ²J_{H-P} = 13.2, ²J_{H-H} = 13.2, 1H, OsH), -9.61 (ddd, ²J_{H-P} = 26.2, ²J_{H-H} = 13.2, ²J_{H-H} = 5.0, 1H, OsH). ³¹P NMR (161.9 MHz, C₆D₆, 298 K): δ 19.7. ¹³C{¹H}-APT NMR, HSQC and HMBC (75.4 MHz, C₆D₆, 298 K): δ 191.8 (d, ²J_{C-P} = 6.7, C_{ipso}-OsPh), 175.1 (d, ²J_{C-P} = 78.9, OsC), 169.6 (s, OsPh), 147.4, 147.0 (both s, Ph), 146.9 (s, CHPh), 144.9 (s, OsPh), 140.3, 129.1 (both s, Ph), 128.8, 127.6 (both s, OsPh), 123.9, 123.4 (both s, Ph), 122.4 (s, NCH), 118.0 (s, OsPh), 29.2, 29.1 (both s, CHCH₃), 27.5, (d, ¹J_{C-P} = 21.5, PCHCH₃), 26.2, 26.9, 22.7, 22.5 (all s, CHCH₃), 20.0 (d, ²J_{C-P} = 17.5, PCHCH₃).

Preparation of OsH₃{κ²-N-C-(NH=CHC₆H₄)}(IPr)(PPh₃) (12). A pale yellow solution of OsH₆(IPr)(PPh₃) (**10**) (100 mg, 0.118 mmol) in 5 mL of toluene was treated with benzonitrile (13.2 μL, 0.130 mmol). The mixture was stirred for 1 h at reflux, and the resulting red solution was evaporated to dryness. The residue was washed with 2 mL of cold methanol obtaining an orange solid which was dried in vacuo. Yield: 82.8 mg (74%). Anal. Calcd for C₅₂H₆₀N₃OsP: C, 65.86; H, 6.38; N, 4.43. Found: C, 65.68; H, 6.39; N, 4.48. HRMS (electrospray m/z): C₅₂H₅₉N₃OsP: 948.406. Found: 948.412. IR (cm⁻¹): ν(OsH) 2114 and 1977 cm⁻¹, ν(NH) 3373 cm⁻¹. ¹H NMR (300 MHz, C₆D₆, 298K): δ 9.04 (br, 1H, NH), 7.99 (d, ³J_{H-H} = 7.5, 1H, CHPh), 7.54-7.48 (4H, OsPh), 7.53-7.50 (5H, PPh), 7.42, 7.33 (both d, ³J_{H-H} = 7.7, 4H, Ph), 7.10-7.02 (10H, PPh), 7.03, 6.80 (both t, ³J_{H-H}

= 7.2, 2H, Ph), 6.70 (s, 2H, NCH), 3.46, 2.95 (both hpt, ³J_{H-H} = 6.8, 4H, CHCH₃), 1.63, 1.31, 1.28, 1.22 (all d, ³J_{H-H} = 6.7, 24H, CHCH₃), -6.02 (br, 1H, OsH), -8.59 (br, 2H, OsH). ¹H NMR (400 MHz, C₇D₈, 223K): δ 8.76 (ddd, ³J_{H-P} = 9.6, ³J_{H-H} = 4.3, ³J_{H-H} = 4.3, 1H, NH), -5.79 (ddd, ²J_{H-P} = 14.6, ²J_{H-H} = 4.3, ³J_{H-H} = 4.3, 1H, OsH), -8.72 (vt, ²J_{H-P} = 11.8, ²J_{H-H} = 11.8, 1H, OsH), -8.96 (ddd, ²J_{H-P} = 23.5, ²J_{H-H} = 11.8, ²J_{H-H} = 4.3, 1H, OsH). ³¹P NMR (161.9 MHz, C₆D₆, 298 K): δ 21.8. ¹³C{¹H}-APT NMR, HSQC and HMBC (75.4 MHz, C₆D₆, 298 K): δ 188.7 (d, ²J_{C-P} = 9.2, C_{ipso}-OsPh), 175.5 (d, ²J_{C-P} = 94.8, OsC), 147.2, 147.3 (both s, Ph), 146.7 (s, CHPh), 144.9 (s, OsPh), 140.1 (s, Ph), 138.5 (d, ¹J_{C-P} = 41.6, C_{ipso}-PPh), 134.3 (d, ²J_{C-P} = 10.6, PPh), 129.2, 128.5, 128.2, 128.1 (all s, OsPh), 127.1 (d, ²J_{C-P} = 8.9, PPh), 123.9, 123.6 (both s, Ph), 122.4 (s, NCH), 118.2 (s, Ph), 29.3, 29.2 (both s, CHCH₃), 26.1, 25.9, 22.6, 22.3 (both s, CHCH₃).

Structural Analysis of Complexes 6, 8, and 11. X-ray data were collected for the complexes on a Bruker Smart APEX or APEX Duo diffractometers equipped with a normal focus, 2.4 kW sealed tube source (Mo radiation, λ = 0.71073 Å) operating at 50 kV and 40 mA (**8**) or 30 mA (**6** and **11**). Data were collected over the complete sphere. Each frame exposure time was 10 s covering 0.3° in ω. Data were corrected for absorption by using a multiscan method applied with the SADABS program.⁴⁷ The structures were solved by Patterson or direct methods and refined by full-matrix least squares on F² with SHELXL97,⁴⁸ including isotropic and subsequently anisotropic displacement parameters. The hydrogen atoms (except hydrides) were observed in the least Fourier Maps or calculated, and refined freely or using a restricted riding model. Hydrides were observed in the last cycles of refinement and refined too close to metals, so a restricted refinement model was used.

Crystal data for **6**: C₃₆H₆₀ClN₂OsP, M_w 777.48, red, irregular block (0.17 x 0.14 x 0.14), orthorhombic, space group P2₁2₁1, *a*: 12.8306(7) Å, *b*: 14.7159(8) Å, *c*: 20.3680(11) Å, *V* = 3845.8(4) Å³, *Z* = 4, *Z'* = 1, D_{calc}: 1.343 g cm⁻³, F(000): 1592, T = 100(2) K, μ 3.451 mm⁻¹. 34023 measured reflections (2θ: 3-58°, ω scans 0.3°), 9201 unique (R_{int} = 0.0398); min./max. transm. Factors 0.699/0.862. Final agreement factors were R¹ = 0.0390 (8683 observed reflections, I > 2σ(I)) and wR² = 0.0910; Flack parameter 0.002(8); data/restraints/parameters 9201/3/395; GoF = 1.077. Largest peak and hole 3.967 (close to osmium atom) and -1.114 e/Å³.

Crystal data for **8**: C₄₅H₅₈BN₂OsP, M_w 858.91, yellow, irregular block (0.19 x 0.16 x 0.12), monoclinic, space group C2/c, *a*: 21.4514(17) Å, *b*: 10.3031(8) Å, *c*: 38.022(3) Å, β: 100.2510(10)°, *V* = 8269.4(11) Å³, *Z* = 8, *Z'* = 1, D_{calc}: 1.380 g cm⁻³, F(000): 3504, T = 100(2) K, μ 3.155 mm⁻¹. 48295 measured reflections (2θ: 3-58°, ω scans 0.3°), 9839 unique (R_{int} = 0.0610); min./max. transm. Factors 0.714/0.862. Final agreement factors were R¹ = 0.0399 (7899 observed reflections, I > 2σ(I)) and wR² = 0.0878; data/restraints/parameters 9839/7/482; GoF = 1.022. Largest peak and hole 1.421 (close to osmium atom) and -1.178 e/Å³.

Crystal data for **11**: C₄₃H₆₆N₃OsP, M_w 846.16, red, irregular block (0.23 x 0.12 x 0.01), monoclinic, space group P2₁/n, *a*: 10.8632(19) Å, *b*: 20.893(4) Å, *c*: 18.388(3) Å, β: 92.917(3)°, *V* = 4168.0(13) Å³, *Z* = 4, *Z'* = 1, D_{calc}: 1.348 g cm⁻³, F(000): 1744, T = 173(2) K, μ 3.129 mm⁻¹. 66798 measured reflections (2θ: 3-58°, ω scans 0.3°), 11045 unique (R_{int} = 0.0528); min./max. transm. Factors 0.714/0.862. Final agreement factors were R¹ = 0.0312 (8563 observed reflections, I > 2σ(I)) and wR² = 0.0792; data/restraints/parameters 11045/3/459; GoF = 1.025. Largest peak and hole 1.869 and -0.470 e/Å³.

ASSOCIATED CONTENT

Supporting Information

Cartesian coordinates and energies of all species discussed in the text, and CIF crystallography data for compounds **6**, **8**, and **11**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

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SYNOPSIS.

The borylation of the metal-carbon triple bond of the phosphine-osmium-NHC, five coordinate, hydride-alkylidyne complexes $[\text{OsHCl}(\equiv\text{CPh})(\text{IPr})(\text{PR}_3)]\text{OTf}$ ($\text{PR}_3 = \text{P}^i\text{Pr}_3, \text{PPh}_3$) with the tetrahydridoborate anion under alcoholysis conditions is the key to access polyhydrides stabilized by phosphine-osmium-NHC basements. Thus, the first compounds of four different types of mixed polyhydrides are reported, including : $\text{OsH}_3\text{Cl}(\text{NHC})(\text{P}^i\text{Pr}_3)$, $\text{OsH}_3(\kappa^2\text{-H}_2\text{BH}_2)(\text{NHC})(\text{PR}_3)$, $\text{OsH}_6(\text{NHC})(\text{PR}_3)$, and $\text{OsH}_3(\text{XY})(\text{NHC})(\text{PR}_3)$.