

Hydroboration and Hydrogenation of an Osmium-Carbon triple Bond: A Bis- σ -Borane in the Osmium Chemistry

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ABSTRACT: Complex $[\text{OsHCl}(\equiv\text{CPh})(\text{IPr})(\text{P}^i\text{Pr}_3)]\text{OTf}$ (**1**; $\text{IPr} = 1,3\text{-bis}(2,6\text{-diisopropylphenyl})\text{imidazolyldiene}$, $\text{OTf} = \text{CF}_3\text{SO}_3$) replaces the chloride ligand by a hydroxo group to give $[\text{OsH}(\text{OH})(\equiv\text{CPh})(\text{IPr})(\text{P}^i\text{Pr}_3)]\text{OTf}$ (**2**), which undergoes hydroboration and hydrogenation of its metal-carbon triple bond. The hydroboration products depend upon the used reagent. Treatment of **2** with $\text{Na}[\text{BH}_4]$ leads to the bis- σ -borane complex $\text{OsH}_2(\eta^2, \eta^2\text{-H}_2\text{BCH}_2\text{Ph})(\text{IPr})(\text{P}^i\text{Pr}_3)$ (**3**), whereas pinacolborane (HBPin) affords the arene compound $[\text{Os}(\eta^6\text{-C}_6\text{H}_5\text{CH}_2\text{Bpin})\text{H}(\text{IPr})(\text{P}^i\text{Pr}_3)]\text{OTf}$ (**4**). The hydrogenation of the triple bond of **2** occurs under 4 atm of H_2 and yields the toluene derivative $[\text{Os}(\eta^6\text{-C}_6\text{H}_5\text{CH}_3)\text{H}(\text{IPr})(\text{P}^i\text{Pr}_3)]\text{OTf}$ (**5**).

Isolobality¹ often relates organometallics to organic functionalities. Hydroboration² and related processes, such as hydrogenation,³ of carbon-carbon multiple bonds are powerful tools in organic synthesis. Analogous reactions with the organometallic counterparts, where a unit of the multiple carbon-carbon bond has been replaced by a transition metal and its associated ligands, are also known and represent a relevant group of transformations with exceptional possibilities in organometallic chemistry. However, in contrast to the purely organic processes, they have received scarce attention.⁴ This is due in a part to their high complexity which is associated not only with the variety of transition metal and metal ions but also with the wide range of known co-ligands. These Lewis bases subtly govern the electron density of the metal center. Thus, they determine the behavior of a particular complex,⁵ although they do not participate directly in its reactions.

It is well established that the first step for the cleavage of a σ -bond is its coordination to an unsaturated transition metal compound to form a σ -complex. Thus, σ -B-H species are considered the key intermediates in the metal promoted B-H bond cleavage and have been therefore prepared by direct coordination to the metal center.⁶ In contrast to the large number of dihydrogen derivatives and silane compounds, which have been studied, few examples of B-H complexes have been isolated and characterized, in particular those having most electrophilic B-alkyl moieties⁷ and third row metals such as osmium.⁸ In this communication, we demonstrate that σ -derivatives of the type $\text{Os}(\eta^2, \eta^2\text{-H}_2\text{Balkyl})$ can be prepared by hydroboration of Os-alkylidene complexes, when the co-ligands of the starting compound and the hydroboration reagent are appropriately selected.

Hydride ligands of cationic complexes show protic character.⁹ Thus, they generally undergo deprotonation.¹⁰ In agreement with this, the hydride-alkylidyne cations $[\text{Os}(\eta^5\text{-C}_5\text{H}_5)\text{H}(\equiv\text{CPh})(\text{PR}_3)]^+$ react with Brønsted bases to afford the corresponding neutral derivatives $\text{Os}(\eta^5\text{-C}_5\text{H}_5)(\equiv\text{CPh})(\text{PR}_3)$

($\text{PR}_3 = \text{P}^i\text{Pr}_3$,¹¹ $\text{P}^i\text{Pr}_2[\text{C}(\text{CH}_3)=\text{CH}_2]$ ¹²). The five-coordinate hydride-alkylidyne derivative $[\text{OsHCl}(\equiv\text{CPh})(\text{IPr})(\text{P}^i\text{Pr}_3)]\text{OTf}$ (**1**; $\text{IPr} = 1,3\text{-bis}(2,6\text{-diisopropylphenyl})\text{imidazolyldiene}$, $\text{OTf} = \text{CF}_3\text{SO}_3$)¹³ does not follow the general trend in spite of that square-planar neutral complexes of the type $\text{Os}(\text{X})(\text{Y})\text{L}_2$ are well known since several years ago.¹⁴ In contrast to the cyclopentadienyl compounds, its hydride ligand is not removed from the metal coordination sphere in the presence of strong Brønsted bases. Instead of it, the replacement of the chloride ligand by a hydroxo group takes place as a result from the treatment of water suspensions of **1** with 2.0 equiv of NaOH, at room temperature (eq 1). The resulting $[\text{OsH}(\text{OH})(\equiv\text{CPh})(\text{IPr})(\text{P}^i\text{Pr}_3)]\text{OTf}$ (**2**) was isolated as a yellow solid in 89% yield and characterized by X-ray diffraction analysis.

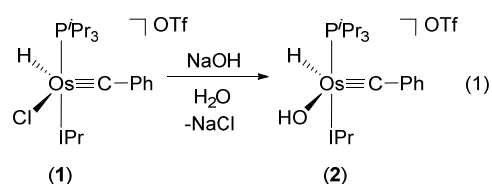


Figure 1 shows a view of the cation. The geometry around the osmium atom can be rationalized as a distorted trigonal bipyramid with the phosphine and NHC ligands in apical positions ($\text{P}(1)\text{-Os-C}(8) = 164.5(16)^\circ$) and inequivalent angles of $144.7(2)^\circ$ ($\text{C}(1)\text{-Os-O}(1)$), $83(2)^\circ$ ($\text{C}(1)\text{-Os-H}(01)$) and $132(2)^\circ$ ($\text{O}(1)\text{-Os-H}(01)$) within the Y-shaped equatorial plane. The $\text{Os-C}(1)$ bond length of $1.705(6)$ Å supports the osmium-carbon triple bond formulation,¹⁵ whereas the $\text{Os-O}(1)$ distance of $2.049(5)$ Å suggests some multiple-bond character for the osmium-oxygen bond.¹⁶ The π -donation from the oxygen atom into the metal is also supported by the $\text{Os-O}(1)\text{-H}(1)$ angle of $125(5)^\circ$. The most noticeable resonances of the ^1H NMR spectrum, in dichloromethane- d_2 , at room temperature are those due to the hydride and hydroxo ligands, which ap-

pear at -12.00 and 5.48 ppm, respectively. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, the signal corresponding to the C(sp) alkyldi-
nyne atom is observed at 275.9 ppm. In accordance with the *trans* disposition of the phosphine and NHC ligands, the meta-
lated carbon atom of the latter displays a doublet with a C-P
coupling constant of 85.4 Hz at 184.3 ppm.

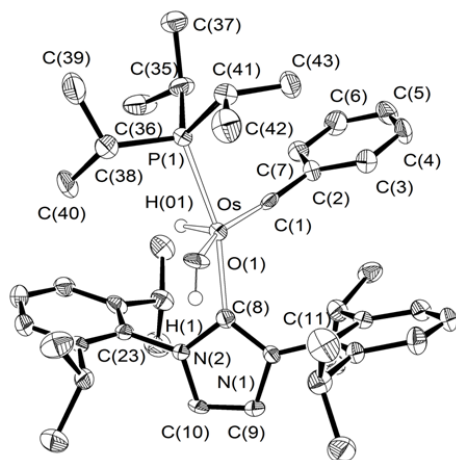
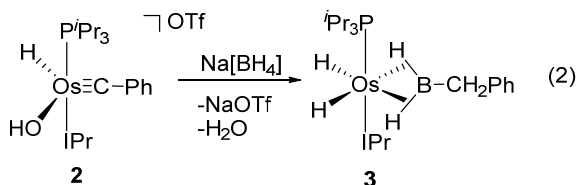


Figure 1. Molecular diagram of **2**. Selected bond lengths (Å) and angles (deg): Os-O(1) = 2.049(5), Os-C(1) = 1.705(6), Os-H(01) = 1.578(10); P(1)-Os-C(8) = 164.5(16), C(1)-Os-O(1) = 144.7(2), O(1)-Os-H(01) = 132(2), Os-O(1)-H(1) = 125(5), C(1)-Os-H(01) = 83(2). Displacement ellipsoids are given at the 50% probability level.

Treatment of toluene solutions of **2** with 15 equiv of $\text{Na}[\text{BH}_4]$ in the presence of methanol (6% in volume), for 30 min, at room temperature leads to the formation of the alkylborane derivative $\text{OsH}_2(\eta^2, \eta^2\text{-H}_2\text{BCH}_2\text{Ph})(\text{IPr})(\text{P}^i\text{Pr}_3)$ (**3**), which was isolated as a yellow solid in 51% yield (eq 2)



Complex **3**, which is the first bis-σ-borane in the osmium chemistry, was also characterized by X-ray diffraction analysis. The structure (Figure 2) proves the replacement of the hydroxo group of **2** by a hydride and the hydroboration of the metal-carbon triple bond to form the alkylborane, which is bonded to the metal center in a symmetrical manner through both B-H bonds. Thus, the coordination around the osmium atom can be rationalized as a distorted octahedron with the phosphine and NHC ligands *transoid* disposed (P-Os-C(8) = 155.80(8)°). The coordinated alkylborane features a nearly linear linkage with an Os-B-C(1) angle of 176.6(3)°. The separation between the metal center and the boron atom is 1.913(4) Å, whereas the angles around the boron atom are 122.5(18)° (H(01)-B-C(1)), 128.2(16)° (H(02)-B-C(1)) and 106(2)° (H(01)-B-H(02)) in agreement with its sp^2 -hybridization. Moreover, the computed hybridizations of the boron atom in the B-H and B-C bonds are $\text{sp}^{2.30}$ and $\text{sp}^{1.65}$, respectively, much higher than the respective values computed for the previously reported borinium complex $\text{OsH}_2\text{Cl}(\eta^2\text{-H}_2\text{BCH}_2\text{Ph})(\text{IPr})(\text{P}^i\text{Pr}_3)^{41}$ of $\text{sp}^{1.58}$ and $\text{sp}^{1.39}$.

The ^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{31}\text{P}\{^1\text{H}\}$, and $^{11}\text{B}\{^1\text{H}\}$ NMR spectra, in benzene- d_6 , at room temperature are consistent with the struc-

ture shown in figure 2. The ^1H NMR spectrum in the high field region exhibits the expected set of two signals in a 1:1 ratio: at -8.26 ppm a broad resonance that sharpens upon boron decoupling, and thus assigned to the hydrogen atoms attached to boron, and at -9.40 ppm a doublet ($J_{\text{H-P}} = 28.4$ Hz) that becomes singlet upon phosphorous decoupling corresponding to the terminal hydrides. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, the most noticeable resonance is a doublet ($J_{\text{C-P}} = 63.8$ Hz) at 189.1 ppm due to the NHC carbon atom C(8). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum displays a sharp singlet at 58.4 ppm, whereas the $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum shows a broad resonance at 81 ppm.

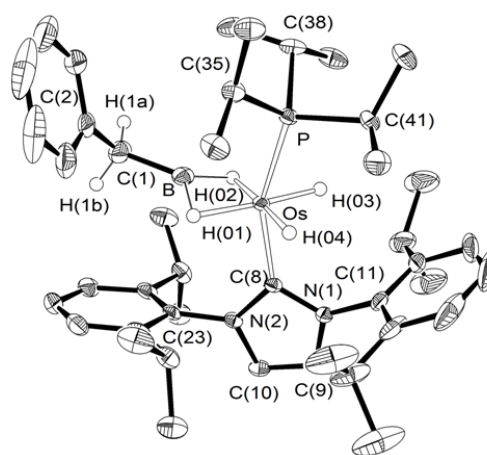


Figure 2. Molecular diagram of **3**. Selected bond lengths (Å) and angles (deg): Os-B = 1.913(4), Os-H(01) = 1.62(4), Os-H(02) = 1.58(4), Os-H(03) = 1.50(3), Os-H(04) = 1.46(4), B-H(02) = 1.44(4), B-H(01) = 1.32(4); Os-B-C(1) = 176.6(3), P-Os-C(8) = 155.80(8), H(02)-B-C(1) = 128.2(16), H(01)-B-C(1) = 122.5(18), H(01)-B-H(02) = 106(2), H(03)-Os-H(04) = 91.9(19), H(02)-Os-H(01) = 88(2). Displacement ellipsoids are given at the 50% probability level.

The bonding situation in **3** was studied by means of Density Functional Theory (DFT) calculations at the BP86/def2-SVP level.¹⁷ From the molecular orbitals depicted in Figure 3, it becomes clear that the interaction between the neutral $\text{OsH}_2(\text{IPr})(\text{P}^i\text{Pr}_3)$ and $\text{H}_2\text{BCH}_2\text{Ph}$ fragments consists of two main contributions namely the σ- and π- components represented by HOMO-1 and HOMO-2, respectively. The nature of both contributions to the bonding has been analyzed in detail with the help of the Natural Bond Orbital (NBO) method.

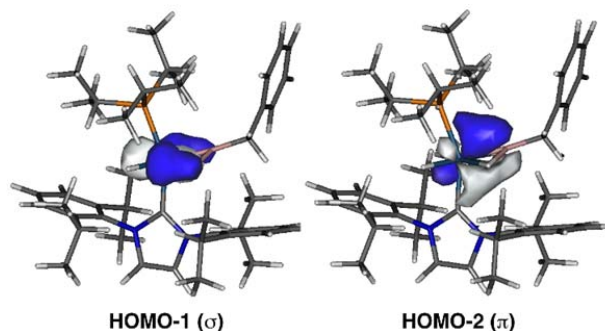


Figure 3. Molecular orbitals computed for compound **3** (isosurface value of 0.05 au).

The Second-Order Perturbation Theory (SOPT) of the NBO method describes the σ-bonding as the result of two significant

donor-acceptor interactions from both doubly-occupied σ -(BH) orbitals into an unoccupied osmium orbital whose associated SOPT energies, $\Delta E^{(2)}$, are -257.0 and -279.0 kcal·mol⁻¹. As a consequence, the computed electron population of the σ -(BH) orbitals are markedly lower than in the free benzylborane (1.62 e versus 1.99 e). The π -contribution is the result of a remarkable π -backdonation ($\Delta E^{(2)} = -71.4$ kcal·mol⁻¹) from a d_π atomic orbital of the osmium to the vacant p_z atomic orbital of the boron. Consequently, the computed electron population at the latter atomic orbital is clearly higher than in the free borane (0.84 e versus 0.08 e). This π -backdonation is even higher than in the borinium derivative $\text{OsH}_2\text{Cl}(\eta^2\text{-H-BCH}_2\text{Ph})(\text{IPr})(\text{P}^t\text{Pr}_3)$ ($\Delta E^{(2)} = -55.8$ kcal·mol⁻¹), which features a genuine Os-B covalent bond.⁴¹ As a result, the computed Os-B Wiberg bond indices for both species are comparable (1.02 versus 1.17) despite the rather different bonding situations.

The NBO study has been complemented with the analysis of the topology of the electron density through the Atoms in Molecules (AIM) method. The Laplacian in the Os-H-B plane exhibits a significant Os-B interaction as revealed by the occurrence of a bond critical point (BCP) located between the transition metal and the boron atom, which is associated with a bond path running between both atoms (Figure 4). However, no Os-H(B) bond critical points or bond paths were observed. This appears to be a direct consequence of the strong Os \rightarrow B π -backdonation^{7e} which gives rise to the buildup of electron-density (0.13 e bohr⁻³) in this direction, resulting in the formation of the Os-B BCP and the rupture of the fragile Os-H (1,2) bond paths. A similar situation has been described in the cationic complex $[\text{Cp}^*(\text{P}^t\text{Pr}_3)\text{Ru}(\eta^2, \eta^2\text{-H}_2\text{BMes})]^+ \text{X}^-$ and $\text{RuHX}(\eta^2, \eta^2\text{-H}_2\text{BNMe}_2)(\text{P}^t\text{Pr}_3)_2$ (X = H, Cl).¹⁸

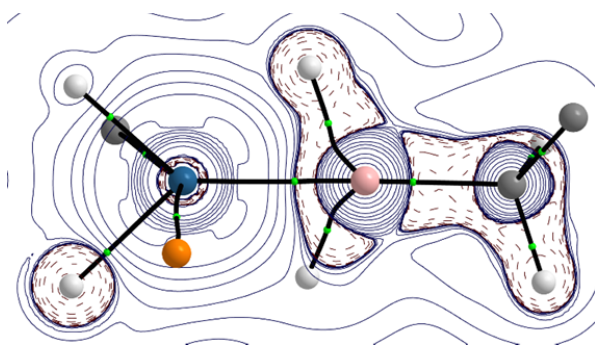
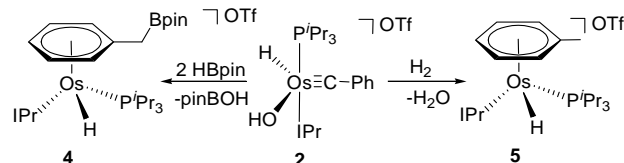


Figure 4. Contour line diagrams $\nabla^2\rho(r)$ for complex **3** in the Os-H-B. Dashed lines indicate areas of charge concentration ($\nabla^2\rho(r) < 0$) while solid lines show areas of charge depletion ($\nabla^2\rho(r) > 0$). The solid lines connecting the atomic nuclei are the bond paths while the small green spheres indicate the corresponding bond critical points.

The replacement of the chloride ligand of **1** by a hydroxo group has certainly a noticeable influence on the nature of the hydroboration product. Thus, in contrast to **2**, the reaction of its precursor **1** with $\text{Na}[\text{BH}_4]$ affords the borinium derivative $\text{OsH}_2\text{Cl}(\eta^2\text{-H-BCH}_2\text{Ph})(\text{IPr})(\text{P}^t\text{Pr}_3)$.⁴¹ Not only the co-ligands of the alkylidyne complex determine the hydroboration products but also the hydroboration reagent. Opposing $\text{Na}[\text{BH}_4]$, pinacolborane hydroborates the osmium-carbon triple bond of **2** to form a benzylpinacolborane, which coordinates to the osmium atom through the aromatic ring (Scheme 1). Thus, the treatment of tetrahydrofuran solutions of the hydroxo com-

plex with 2.0 equiv of the boron hydride, at room temperature, leads to $[\text{Os}(\eta^6\text{-C}_6\text{H}_5\text{CH}_2\text{Bpin})\text{H}(\text{IPr})(\text{P}^t\text{Pr}_3)]\text{OTf}$ (**4**). The hydroboration reaction is supported by the $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of the obtained solid, in dichloromethane- d_2 , at room temperature that shows a broad singlet at 31.8 ppm. In the ^1H NMR spectrum, the most noticeable signals are a doublet ($J_{\text{H-P}} = 41.0$ Hz) at -11.06 ppm, corresponding to the hydride ligand, and an AB spin system centered at 2.21 ppm and defined by $\Delta\nu$ 58.7 Hz and $J_{\text{AB}} = 16.0$ Hz, due to the CH_2B substituent of the arene. In agreement with the η^6 coordination of the benzylic aromatic ring, the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum contains six aromatic resonances between 102.8 and 79.4 ppm. As expected for the *cis* disposition of the phosphine and NHC ligands, the metalated carbon atom of the latter displays a doublet with a C-P coupling constant of 9.8 Hz, at 160.4 ppm.

Scheme 1



The hydroboration reaction with pinacolborane is extremely sensitive to the dampness of the solvents and the presence of OH groups in the waste pinBOH and/or in the glassware. As a consequence, in agreement with the boron oxophilicity, the boron hydride undergoes hydrolysis. The generated molecular hydrogen reduces the osmium-carbon triple bond to generate the toluene derivative $[\text{Os}(\eta^6\text{-C}_6\text{H}_5\text{CH}_3)\text{H}(\text{IPr})(\text{P}^t\text{Pr}_3)]\text{OTf}$ (**5**), which contaminates the formation of **4**. The hydrogenation of the osmium-carbon triple bond was confirmed by stirring a dichloromethane solution of the hydroxo complex under 4 atm of molecular hydrogen, for 14 h, at 50°C. Under these conditions, complex **5** was obtained as a red solid in 75% yield (Scheme 1) and characterized by X-ray diffraction analysis.

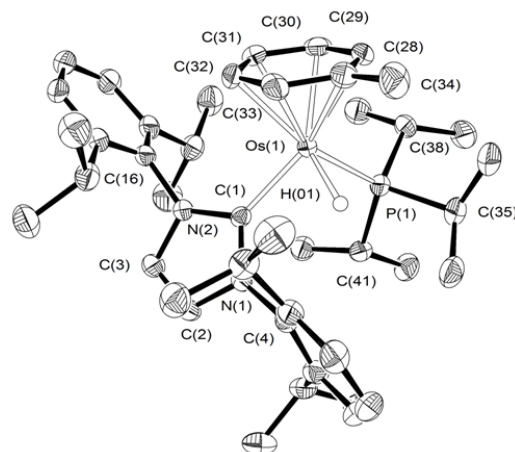


Figure 5. Molecular diagram of **2**. Selected bond lengths (Å) and angles (deg):¹⁹ Os(1)-P(1) = 2.3642(12), 2.3692(11), Os(1)-C(1) = 2.080(4), 2.080(4), Os(1)-H(01) = 1.64(4), 1.46(4); C(1)-Os(1)-P(1) = 96.80(12), 97.24(12), C(1)-Os(1)-H(01) = 81.1(15), 84.5(17), P(1)-Os(1)-H(01) = 79.4(16), 78.7(17). Displacement ellipsoids are given at the 50% probability level.

The structure (Figure 5)¹⁹ proves the reduction of the triple bond and the formation of toluene, which coordinates to the metal center in its typical η^6 -fashion. Thus, the geometry

around the osmium atom is close to octahedral, with the arene occupying three sites of a face and the monodentated groups in the opposed one. The latter undergoes a strong distortion resulting from the mutual *cis* disposition of the phosphine and NHC ligands, which experience a large steric hindrance, and the small size of the hydride. Thus, the angles C(1)-Os-P(1) (96.80(12)°, 97.24(12)°), C(1)-Os-H(01) (81.1(15)°, 84.5(17)°), and P(1)-Os-H(01) (79.4(16)°, 78.7(17)°) strongly deviate from the ideal value of 90°. The NMR spectra of the red solid, in dichloromethane- d_2 , at room temperature are consistent with Figure 5. The hydride ligand displays a doublet (J_{H-P} = 41 Hz) at -11.02 ppm in the 1H NMR spectrum, whereas the toluene methyl resonance is observed at 2.42 ppm as a singlet. In agreement with **4**, the $^{13}C\{^1H\}$ NMR spectrum shows at 160.5 ppm a doublet with a C-P coupling constant of 9.8 Hz for the metalated IPr carbon atom.

In conclusion, the hydroboration and hydrogenation of metal-carbon triple bonds of unsaturated transition metal complexes are reactions of utility in organometallic synthesis, in spite of their complexity. As a proof of concept, in this communication, we show the preparation of the first bis- σ -borane complex in the osmium chemistry and novel mixed R_3P -Os-NHC arene derivatives. The complexity of the processes is a consequence of the dependence of the reaction products on both the co-ligands of the starting complex and the nature of the reagents.

ASSOCIATED CONTENT

Supporting information

Experimental and computational details, NMR spectra, a text file of all computed molecule Cartesian coordinates in a format for convenient visualization, and CIF crystallography data for **2**, **3**, and **5** are available free of charge via the Internet at <http://pubs.acs.org>.

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- (19) The structure has two cations and two anions chemically equivalent but crystallographically independent in the asymmetric unit. Figure 5 shows a view of one of the cations.

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