Reactions of an Osmium-Elongated Dihydrogen Complex with Terminal Alkynes: Formation of Novel Bifunctional Compounds with Amphoteric Nature

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The trihydride complex $Os H_3\{C_6H_4C(O)CH_3\}(P^iPr_3)_2$ (**1**) reacts with $HBF_4 \cdot H_2O$ to give the elongated dihydrogen derivative $[Os\{C_6H_4C(O)CH_3\}(\eta^2\text{-}H_2)(H_2O)(P^iPr_3)_2]BF_4$ (**2**), with a separation between the hydrogen atoms of the elongated dihydrogen of 1.35 Å. The addition of acetone oxime to dichloromethane solutions of **2** produces the substitution of the water ligand by the oxime and the formation of $Os\{C_6H_4C(O)CH_3\}(\eta^2\text{-}H_2)\{N(OH)=C(CH_3)_2\}(P^iPr_3)_2]BF_4$ (**3**), which shows a hydrogen−hydrogen distance of 1.34 Å. Complex **3** reacts with phenylacetylene, cyclohexylacetylene, and *tert*-butylacetylene to give acetophenone and the oximate-carbyne derivatives $[OsH\{\kappa\text{-}N,\kappa\text{-}O[ON=C(CH_3)_2]\}(\equiv CCH_2R)(P^iPr_3)_2]BF_4$ (R = Ph (**4**), Cy (**5**), ^{t}Bu (**6**)). The structure of **4** has been determined by X-ray diffraction analysis. The distribution of ligands around the osmium atom can be described as a distorted trigonal bipyramid with apical phosphines and inequivalent angles within the Y-shaped equatorial plane. Complexes **4**−**6** have amphoteric nature, reacting with both KOH and $HBF_4 \cdot Et_2O$. The reactions with KOH afford the vinylidene derivatives $OsH\{\kappa\text{-}N,\kappa\text{-}O[ON=C(CH_3)_2]\}(=C=CHR)(P^iPr_3)_2$ (R = Ph (**7**), Cy (**8**), ^{t}Bu (**9**)), whereas the reactions with $HBF_4 \cdot Et_2O$ give the fluoro-oxime compounds $[OsH\{F\text{---}HON=C(CH_3)_2\}(\equiv CCH_2R)(P^iPr_3)_2]BF_4$ (R = Ph (**10**), Cy (**11**), ^{t}Bu (**12**)). The structures of **7** and **11** have been determined by X-ray diffraction analysis. The distribution of ligands around the osmium atom of **7** is like that of **4**, whereas the geometry around the metallic center of **11** can be rationalized as a distorted octahedron with the phosphine ligands in *trans* positions. Complexes **10**, **11**, and **12** contain a strong intramolecular F- - -H hydrogen bond between the fluorine and the OH-hydrogen atom of the oxime in the solid state and in dichloromethane solution (J_{H-F} = 67.5 (**10**), 68.1 (**11**), and 68.7 (**12**) Hz). The formation of **4**−**12** is also discussed, on the basis of deuterium label experiments.

Introduction

Hydrides are one of the best anchors to nail unsaturated organic molecules in transition metal compounds. Thus, ruthenium and osmium polyhydride complexes have shown to be useful templates to carbon−carbon and carbon−heteroatom coupling reactions.[1] The presence of more than one hydrogen atom bonded to the metallic center allows the access of several organic molecules into the metal. This facilitates different types of coupling reactions and the generation of organic fragments with a rich organic chemistry.[2]

The capacity of the osmium-dihydride complexes to afford C−C coupling reactions has been little-studied.[3] This is mainly due to the fact that the reactivity of this type of species toward alkynes, HC≡CR, is difficult to rationalize, which hinders the design a priori of the steps to obtain a particular ligand or molecule and even to know the most useful dihydride for the process.

At first glance, one would think that the nature of the obtained product from the reactions of osmium-dihydrides with alkynes depends on the nature of the substituent (R) of the alkyne. For instance, the seven-coordinate osmium(IV) dihydride cation $[OsH_2(\kappa^2\text{-}O_2CCH_3)(H_2O)(P^iPr_3)_2]^+$ reacts with phenylacetylene to give the metallocyclopropene derivative $[OsH(\kappa^2\text{-}O_2CCH_3)\{C(Ph)CH_2\}(P^iPr_3)_2]^+$, while under the same conditions *tert*-butylacetylene and (trimethylsilyl)acetylene afford hydride-carbyne compounds

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(1) Esteruelas, M. A.; López, A. M. Ruthenium- and Osmium-hydride compounds containing triisopropylphosphine as precursors for carbon−carbon and carbon−carbon-heteroatom coupling reactions. *Recent Advances in Hydride Chemistry*; Elsevier: Amsterdam 2001; Chapter 7, pp 189−284.

(2) See for example: (a) Esteruelas, M. A.; Lahoz, F. J.; López, A. M.; Oñate, E.; Oro, L. A. *Organometallics* **1994**, *13*, 1669. (b) Buil, M. L.; Esteruelas, M. A.; López, A. M.; Oñate, E. *Organometallics* **1997**, *16*, 3169. (c) Bohanna, C.; Callejas, B.; Edwards, A. J.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A.; Ruiz, N.; Valero, C. *Organometallics* **1998**, *17*, 373. (d) Bohanna, C.; Buil, M. L.; Esteruelas, M. A.; Oñate, E.; Valero, C. *Organometallics* **1999**, *18*, 5176. (e) Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2001**, *20*, 2294.

(3) Esteruelas, M. A.; García-Yebra, C.; Oliván, M.; Oñate, E.; Tajada, M. A. *Organometallics* **2000**, *19*, 5098.

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of formula $[OsH(\kappa^2\text{-}O_2CCH_3)(\equiv C-CH_2R)(P^iPr_3)_2]^+$,[4] and mixtures of both types of compounds has been found in reactions with alkynols.[5] However, the nature of the $Os-H_2$ interaction also seems to have a significant influence. Thus, the six-coordinate osmium(IV) dihydride $OsH_2Cl_2(P^iPr_3)_2$ reacts with phenylacetylene, cyclohexylacetylene, 1-(trimethylsilyl)-1,4-pentadiyne, and (trimethylsilyl)acetylene to give the hydride-carbyne derivatives $OsHCl_2(\equiv CCH_2R)(P^iPr_3)_2$,[6,7] related to the above-mentioned cationic carbyne species, while the reaction of the elongated dihydrogen derivative $OsCl_2(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2$ with phenylacetylene affords the carbene $OsCl_2(=CHCH_2Ph)(CO)(P^iPr_3)_2$.[8]

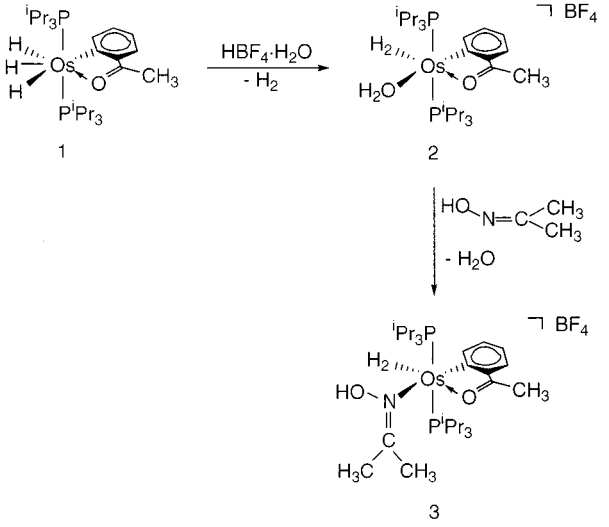
It has been recently shown that the hexahydride $OsH_6(P^iPr_3)_2$ activates *ortho*-CH bonds of aromatic[9] and cycloalkyl[10] ketones and *ortho*-CF bonds[9] of aromatic ketones to give the trihydride derivatives $\overline{OsH_3\{C_6H_4C(O)R\}}(P^iPr_3)_2$ (X = H, F) and $\overline{OsH_3\{C_6H_8C(O)CH_3\}}(P^iPr_3)_2$. We have now observed that complex $\overline{OsH_3\{C_6H_4C(O)CH_3\}}(P^iPr_3)_2$ is a useful precursor to prepare the elongated dihydrogen compound $[\overline{Os\{C_6H_4C(O)CH_3\}}(\eta^2\text{-}H_2)\{N(OH)=C(CH_3)_2\}(P^iPr_3)_2]^+$. Our interest in the use of osmium complexes containing two hydrogen atoms bonded to the metallic center as templates to carbon−carbon coupling reactions, and therefore our interest in learning to rationalize the reactivity of this type of derivatives toward alkynes, prompted us to study the reactions of $[\overline{Os\{C_6H_4C(O)CH_3\}}(\eta^2\text{-}H_2)\{N(OH)=C(CH_3)_2\}(P^iPr_3)_2]^+$ with these organic molecules.

This paper reports the preparation and characterization of the elongated dihydrogen complex $[\overline{Os\{C_6H_4C(O)CH_3\}}(\eta^2\text{-}H_2)\{N(OH)=C(CH_3)_2\}(P^iPr_3)_2]^+$, its reactions with terminal alkynes, and the reactions of the resulting oximate-carbyne derivatives with KOH and HBF_4.

Results and Discussion

1. Preparation of $[\overline{Os\{C_6H_4C(O)CH_3\}}(\eta^2\text{-}H_2)\{N(OH)=C(CH_3)_2\}(P^iPr_3)_2]BF_4$. This complex has been prepared according to the reaction sequence shown in Scheme 1. Treatment at room temperature of the trihydride $\overline{OsH_3\{C_6H_4C(O)CH_3\}}(P^iPr_3)_2$ (**1**) in diethyl ether−methanol (10:1) with 1.4 equiv of $HBF_4\cdot H_2O$ affords the cationic elongated dihydrogen intermediate $[\overline{Os\{C_6H_4C(O)CH_3\}}(\eta^2\text{-}H_2)(H_2O)(P^iPr_3)_2]BF_4$ (**2**), as a result of the protonation of one of the hydride

Scheme 1



ligands of **1** and the coordination of the water molecule. The subsequent addition of acetone oxime to dichloromethane solutions of **2** produces the substitution of the water ligand by the oxime and the formation of $[\overline{Os\{C_6H_4C(O)CH_3\}}(\eta^2\text{-}H_2)\{N(OH)=C(CH_3)_2\}(P^iPr_3)_2]BF_4$ (**3**).

Complex **2** was isolated as an orange solid in 89% yield. The presence of the water ligand in this compound is strongly supported by its IR and ^1H NMR spectra. The IR spectrum in KBr shows a strong ν(OH) band at 3418 cm^{-1}, whereas the ^1H NMR spectrum in dichloromethane-d_2 contains a broad singlet at 3.72 ppm, characteristic for a coordinated water molecule. In the high-field region of the spectrum, the hydrogen atoms bonded to the metal display a triplet at −7.87 ppm with a H−P coupling constant of 10.5 Hz. A variable-temperature 300 MHz T_1 study of this peak shows a slight broadening of the signal, as a result of the decrease of T_2 with decreasing temperature,[11] and gives a T_1(min) of 48 ± 2 ms at 193 K. This T_1(min) value corresponds to a hydrogen−hydrogen distance of 1.07 (fast spinning) or 1.35 (slow spinning) Å.[12]

The treatment of **2** with methanol-d_4−water-d_2 yields the partially deuterated derivative $[\overline{Os\{C_6H_4C(O)CH_3\}}(\eta^2\text{-}HD)(D_2O)(P^iPr_3)_2]BF_4$, which has a H−D coupling constant of 4.2 Hz. According to eq 1,[13] this value allows the calculation of a separation between the hydrogen atoms of 1.35 Å. The hydrogen−hydrogen distance in **2** agrees well with those found in the osmium complexes $OsCl_2(\eta^2\text{-}H_2)(Hpz)(P^iPr_3)_2$ (1.27 Å),[14] $OsCl_2(\eta^2\text{-}H_2)(NH=CPh_2)(P^iPr_3)_2$ (1.24 Å),[15] and $\overline{OsX\{NH=C(Ph)C_6H_4\}}(P^iPr_3)_2$ (X = Cl, Br, I; 1.31 Å)[16] and lies at about the

(4) Buil, M. L.; Eisenstein, O.; Esteruelas, M. A.; García-Yebra, C.; Gutiérrez-Puebla, E.; Oliván, M.; Oñate, E.; Ruiz, N.; Tajada, M. A. *Organometallics* **1999**, *18*, 4949.

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(6) Espuelas, J.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A.; Ruiz, N. *J. Am. Chem. Soc.* **1993**, *115*, 4683.

(7) Complexes $OsHCl_2(\equiv CCH_2R)(P^iPr_3)_2$ (R = Ph, CH_3) have been also obtained from the reactions of $OsH_2Cl_2(P^iPr_3)_2$ with styrene and propene, respectively. See: Spivak, G. J.; Coalter, J. N.; Oliván, M.; Eisenstein, O.; Caulton, K. G. *Organometallics* **1998**, *17*, 999.

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

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(14) Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A.; Oñate, E.; Ruiz, N. *Inorg. Chem.* **1994**, *33*, 787.

(15) Barea, G., Esteruelas, M. A.; Lledós, A.; López, A. M.; Tolosa, J. I. *Inorg. Chem.* **1998**, *37*, 5033.

center of the reported range (1.0−1.5 Å) for the elongated dihydrogen derivatives.[17]

$$d(\mathrm{H-H}) = -0.0167J(\mathrm{H-D}) + 1.42 \qquad (1)$$

The structure shown for **2** in Scheme 1 is proposed on the basis of a NOE experiment and the $^{31}P\{^1H\}$ NMR spectrum. The irradiation of the elongated dihydrogen resonance gave an increase of 9% in the resonance corresponding to the aromatic hydrogen atom disposed *ortho* with regard to the Os−aryl bond, in accordance with the mutually *cis* disposition of the Os−H_2 and Os−aryl bonds. In agreement with the mutually *trans* disposition of the phosphine ligands, the $^{31}P\{^1H\}$ NMR spectrum of **2** shows a singlet at 14.8 ppm.

Complex **3** was isolated in 86% yield, also as an orange solid. In the IR spectrum in KBr the most noticeable feature is a ν(OH) band at 3368 cm^{-1}, corresponding to the oxime ligand. In the ^1H NMR spectrum in dichloromethane-d_2, this ligand displays three singlets at 11.24 (OH) and 2.42 and 2.32 (CH_3) ppm, whereas the elongated dihydrogen gives rise to a triplet at −8.85 ppm with a H−P coupling constant of 10.8 Hz. In this case, the variable-temperature 300 MHz T_1 study of the elongated dihydrogen resonance gives a T_1(min) of 43 ± 1 ms at 203 K, which corresponds to a hydrogen−hydrogen distance of 1.05 (fast spinning) or 1.33 (slow spinning) Å.[12] The treatment of **3** with methanol-d_4 affords the partially deuterated derivative [Os{$C_6H_4C(O)CH_3$}(η^2-HD){N(OD)=$C(CH_3)_2$}(P^iPr_3)$_2$]-BF_4, which has a H−D coupling constant of 4.6 Hz. According to eq 1, this value yields a hydrogen−hydrogen separation of 1.34 Å, which agrees well with that found in **2**. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 6.25 ppm.

2. Reactions of [Os{$C_6H_4C(O)CH_3$}(η^2-H_2){N(OH)=$C(CH_3)_2$}(P^iPr_3)$_2$]BF_4 with Alkynes. The addition at room temperature of 1.2 equiv of phenylacetylene, cyclohexylacetylene, and *tert*-butylacetylene to dichloromethane solutions of the elongated dihydrogen complex **3** produces the release of acetophenone and the formation of the hydride-oximate-carbyne complexes [OsH{κ-*N*,κ-*O*[ON=$C(CH_3)_2$]}(≡CCH_2R)(P^iPr_3)$_2$]BF_4 (R = Ph (**4**), Cy (**5**), ^{t}Bu (**6**)), according to eq 2.

Complexes **4**−**6** were isolated as lilac (**4**) or white (**5** and **6**) solids in high yield (about 70%) and characterized by MS, elemental analysis, IR, and ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy. Complex **4** was further characterized by an X-ray crystallographic study. A view of the molecular geometry of the cation of this complex is shown in Figure 1. Selected bond distances and angles are listed in Table 1.

At first glance, if one considers that the oximate ligand occupies two sites in the coordination sphere of the metal, the geometry around the osmium atom of **4** could be described as a very distorted octahedron with the two phosphorus atoms of the phosphine ligands disposed in opposite positions (P(1)−Os−P(2) = 168.13(7)°), and the perpendicular plane formed by the oximate (acting with a bite angle of 37.89(19)°),[18] the hydride

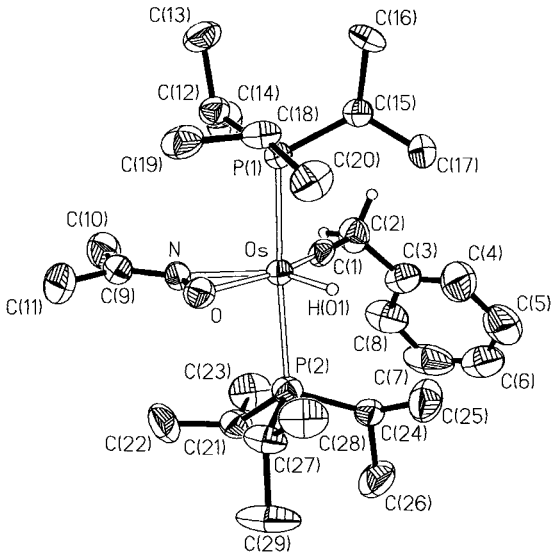
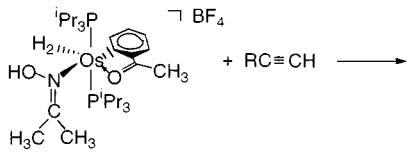


Figure 1. Molecular diagram of the cation of complex [OsH{κ-*N*,κ-*O*[ON=$C(CH_3)_2$]}(≡CCH_2Ph)(P^iPr_3)$_2$]BF_4 (**4**).

trans disposed to the nitrogen atom (N−Os−H(01) = 131(2)°), and the carbyne ligand *trans* disposed to the



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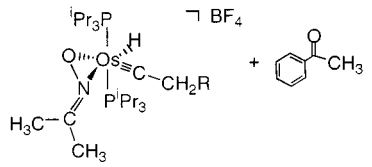

(2)

R = Ph (**4**), Cy (**5**), ^{t}Bu (**6**)

oxygen atom (C(1)−Os−O = 164.9(3)°). However, since the bite angle of the oximate ligand is very small, it appears to be more reasonable to describe the oximate group as a monodentate three-electron donor ligand. In this way, the structure of **4** can be rationalized as a distorted trigonal bipyramid with apical phosphines and inequivalent angles within the Y-shaped equatorial plane (H(01)−Os−M = 111(2)°, H(01)−Os−C(1) =

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(17) Kubas, G. J.; *Metal Dihydrogen and σ-Bond Complexes*; Kluwer Academic/Plenum Publishers: New York, 2001.

(18) Similar values have been found in other oximate compounds. See for example: (a) Dickman, M. H.; Doedens, R. J. *Inorg. Chem.* **1982**, *21*, 682. (b) Porter, L. C.; Doedens, R. J. *Acta Crystallogr., Sect. C* **1985**, *41*, 838. (c) Jaitner, P.; Huber, W.; Gieren, A.; Betz, H. *J. Organomet. Chem.* **1986**, *311*, 379. (d) Pizzotti, M.; Porta, F.; Cenini, S.; Demartin, F.; Masciocchi, N. *J. Organomet. Chem.* **1987**, *330*, 265. (e) Stella, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Dalton Trans.* **1988**, 545. (f) Sharp, P. R.; Hoard, D. W.; Barnes, C. L. *J. Am. Chem. Soc.* **1990**, *112*, 2024. (g) Hoard, D. W.; Sharp, P. R. *Inorg. Chem.* **1993**, *32*, 612. (h) Ang, H. G.; Kwik, W. L.; Ong, K. K. *J. Fluorine Chem.* **1993**, *60*, 43. (i) Vogel, S.; Huttner, G.; Zsolnai, L.; Emmerich, C. Z. *Naturforsch., B* **1993**, *48*, 353. (j) Werner, H.; Daniel, T.; Knaup, W.; Nürnberg, O. *J. Organomet. Chem.* **1993**, *462*, 309. (k) Skoop, S. J.; Campbell, J. P.; Gladfelter, W. L. *Organometallics* **1994**, *13*, 4137. (l) Kukushkin, V. Y.; Tudela, D.; Pombeiro, A. J. L. *Coord. Chem. Rev.* **1996**, *156*, 333. (m) Skoog, S. J.; Gladfelter, W. L. *J. Am. Chem. Soc.* **1997**, *119*, 11049. (n) Castarlenas, R.; Esteruelas, M. A.; Gutiérrez-Puebla, E.; Jean, Y.; Lledós, A.; Martín, M.; Tomàs, J. *Organometallics* **1999**, *18*, 4296. (o) Kukushkin, V. Y.; Pombeiro, A. J. L. *Coord. Chem. Rev.* **1999**, *181*, 147.

Table 1. Selected Bond Distances (Å) and Angles (deg) for the Complex [OsH{κ-*N*,κ-*O*[ON=C(CH$_3$)$_2$]}(≡CCH$_2$Ph)(P^{i}Pr$_3$)$_2$]BF$_4$ (4)

Os−P(1)	2.419(2)	O−N	1.368(7)
Os−P(2)	2.417(2)	N−C(9)	1.266(9)
Os−O	2.148(5)	C(1)−C(2)	1.489(10)
Os−N	2.057(6)	C(2)−C(3)	1.504(11)
Os−C(1)	1.708(8)		
Os−H(01)	1.44(5)		
P(1)−Os−P(2)	168.14(7)	Os−N−C(9)	160.7(6)
P(1)−Os−O	88.36(14)	Os−O−N	67.4(3)
P(1)−Os−N	89.72(16)	O−N−C(9)	124.3(7)
P(1)−Os−C(1)	91.0(2)	N−C(9)−C(10)	119.7(8)
P(1)−Os−H(01)	92(2)	N−C(9)−C(11)	121.0(8)
P(2)−Os−O	86.08(14)	Os−C(1)−C(2)	178.3(6)
P(2)−Os−N	92.30(16)	C(1)−C(2)−C(3)	115.8(7)
P(2)−Os−C(1)	97.1(2)		
P(2)−Os−H(01)	78(2)		
O−Os−N	37.89(19)		
O−Os−C(1)	164.9(3)		
O−Os−H(01)	93(2)		
N−Os−C(1)	127.0(3)		
N−Os−H(01)	131(2)		
C(1)−Os−H(01)	102(2)		

102(2)°, and C(1)−Os−M = 146.4(3)°).[19] This structure is broad, similar to those of the neutral hydride-vinylidene complexes MHCl(=C=CHR)(P^{i}Pr$_3$)$_2$ (M = Ru, Os)[20] and cationic azavinylidene-carbyne compounds [OsCl{=N=C(CH$_3$)$_2$}(≡CCH$_2$R)(P^{i}Pr$_3$)$_2$]$^+$.[21] The Os−C(1) bond length of 1.708(8) Å is fully consistent with an Os−C(1) triple bond formulation.[22]

The IR and ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra of **4**−**6** are consistent with the structure shown in Figure 1. The IR spectra in KBr contain a ν(Os−H) band between 2160 and 2119 cm^{-1}, along with the absorption due to the [BF$_4$]$^-$ anion with T_d symmetry centered at about 1050 cm^{-1}, in agreement with the salt character of the complexes. The ^{1}H NMR spectra show the hydride resonance as a triplet at about −6.5 ppm with a H−P coupling constant of about 17 Hz. The ^{13}C{^{1}H} NMR spectra contain the characteristic Os≡C resonance of the carbyne ligands, which appears as a triplet at about 285 ppm, with a C−P coupling constant of about 9 Hz. The ^{31}P{^{1}H} NMR spectra show a singlet between 35 and 38 ppm.

From a mechanistic point of view, it should be mentioned that complex **3** reacts with deuterated-phenylacetylene, PhC≡CD, to give acetophenone and the partially deuterated carbyne derivative **4-d$_1$**, containing 0.5 deuterium atom at the hydride position (δ_{Os-D}, −6.2) and 0.25 deuterium atom at the C_β atom of the carbyne (δ_{C-D2}, 2.89). The other 0.25 deuterium atom of the starting alkyne is missing in the reaction medium, whereas deuterium is not observed at the ketone positions. The absence of deuterium at acetophenone suggests that this molecule is released from the osmium center before the activation of the alkyne. The release of the ketone could be a result of the hydrogen transfer from the oxygen atom of the oxime to the metalated-aryl carbon atom. This process should afford an oximate intermediate, which should give **4**−**6** in a similar way to the reactions of the previously mentioned dihydride-acetate [OsH$_2$(κ^2-O$_2$CCH$_3$)(H$_2$O)(P^{i}Pr$_3$)]$^+$ with *tert*-butylacetylene and (trimethylsilyl)-acetylene.[4] Alternatively, the release of the ketone could be a consequence of the migration of a hydrogen atom of the elongated dihydrogen to the metalated-aryl carbon atom. This hydrogen transfer should afford the unsaturated hydride-oxime species [OsH(η^2-HC≡CR){N(OH)=C(CH$_3$)$_2$}(P^{i}Pr$_3$)$_2$]$^+$, which could give **4**−**6** (vide infra).

In the presence of 4.0 equiv of methanol-d_4,[23] the reaction of the complex [Os{C$_6$H$_4$C(O)CH$_3$}(η^2-H$_2$){N(OD)=C(CH$_3$)$_2$}(P^{i}Pr$_3$)$_2$]BF$_4$ (**3-d$_1$**), containing a deuterium at the oxygen atom of the oxime, with phenylacetylene affords the hydride-carbyne [OsH{κ-*N*,κ-*O*[ON=C(CH$_3$)$_2$]}(≡CCD$_2$Ph)(P^{i}Pr$_3$)$_2$]BF$_4$ (**4-d$_2$**). Complex **4-d$_2$** contains two deuteriums at the C_β atom of the carbyne; deuterium at the free ketone positions was not observed. This clearly indicates that the hydrogen transfer from the oxime to the ketone does not take place.

Schemes 2−5 show three possible routes for the formation of **4**−**6**, starting from the intermediate [OsH(η^2-HC≡CR){N(OH)=C(CH$_3$)$_2$}(P^{i}Pr$_3$)$_2$]$^+$.

According to the route a (Scheme 2), the formation of the hydride-carbyne complexes should involve the initial insertion of the alkyne into the Os−H bond of [OsH(η^2-HC≡CR){N(OH)=C(CH$_3$)$_2$}(P^{i}Pr$_3$)$_2$]$^+$ to give unsaturated alkenyl species, which should evolve into hydride-vinylidene intermediates by α-elimination. With some exceptions,[24] this has been previously considered the most favored pathway to obtain hydride-vinylidene complexes from hydride starting materials and terminal alkynes.[20b,25] The migration of the OH proton from the oxime to the C_β atom of the vinylidene should afford **4**−**6**.

Route b (Scheme 3) is similar to route a. The main difference between them is the formation of the hydride-vinylidene intermediates, which, in this case, involves the 1,2-hydrogen shift over the carbon−carbon triple bond of the η^2-coordinated alkyne.

According to route c (Scheme 4), the initial step should be the formation of dihydrogen-alkynyl species, which could evolve by a dissociative two-step (elimination−addition) mechanism into the same hydrido-vinylidenes as those obtained via routes a and b. A related H$^+$-

(19) M = midpoint of the N−O bond.

(20) (a) Oliván, M.; Eisenstein, O.; Caulton, K. G. *Organometallics* **1997**, *16*, 2227. (b) Oliván, M.; Clot, E.; Eisenstein, O.; Caulton, K. G. *Organometallics* **1998**, *17*, 3091. (c) Esteruelas, M. A.; Oro, L. A. *Adv. Organomet. Chem.* **2001**, *47*, 1.

(21) Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2001**, *20*, 3283.

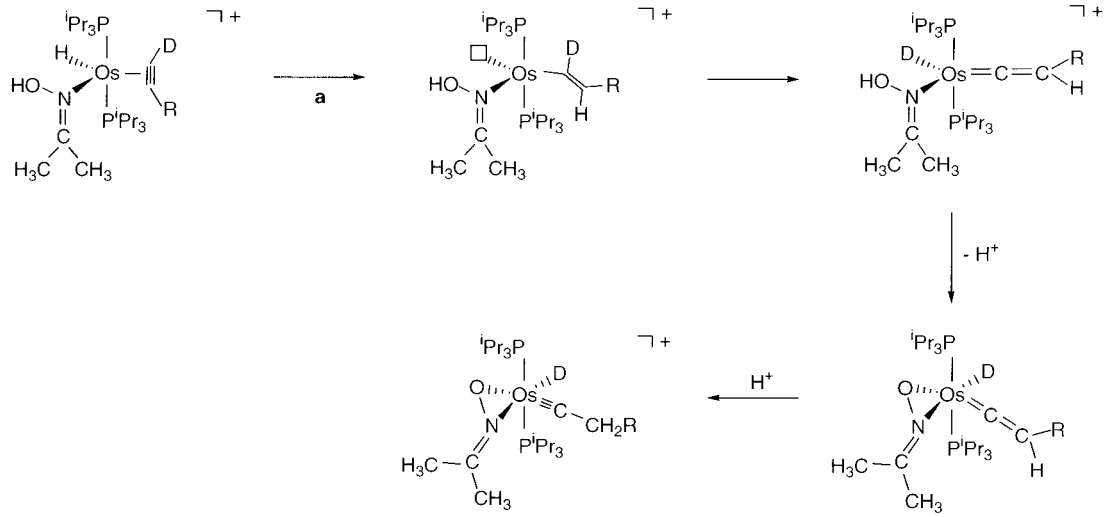
(22) Schubert, U. *Carbyne Complexes*; Verlagsgesellschaft mbH: Weinheim, Germany, 1998; pp 40−58.

(23) The reaction was carried out in the presence of methanol-d_4 because complex **3-d$_1$** undergoes D/H exchange with traces of water contained in the reaction medium, at a rate faster than the rate of the reaction of **3-d$_1$** with phenylacetylene.

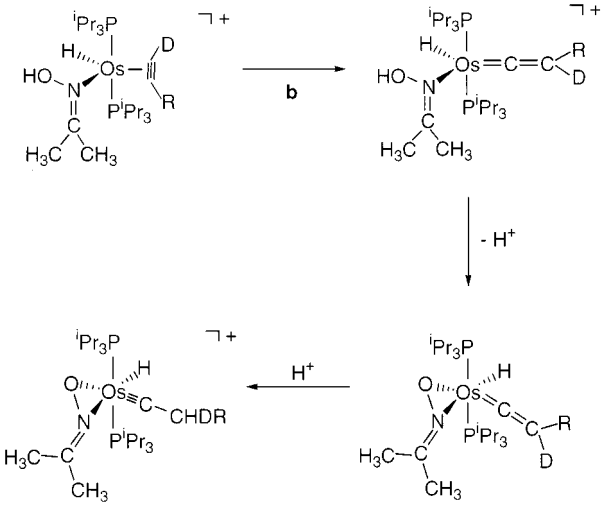
(24) (a) Esteruelas, M. A.; Oro, L. A.; Valero, C. *Organometallics* **1995**, *14*, 3596. (b) Crochet, P.; Esteruelas, M. A.; López, M. A.; Martínez, M.-P.; Oliván, M.; Oñate, E.; Ruiz, N. *Organometallics* **1998**, *17*, 4500.

(25) (a) van Asselt, A.; Burger, B. J.; Gibson, V. C.; Bercaw, J. E. *J. Am. Chem. Soc.* **1986**, *108*, 5347. (b) Dziallas, M.; Werner, H. *J. Organomet. Chem.* **1987**, *333*, C29. (c) Beckhaus, R.; Thiele, K.-H.; Ströhl, D. *J. Organomet. Chem.* **1989**, *369*, 43. (d) Bell, T. W.; Haddleton, D. M.; McCamley, A.; Partridge, M. G.; Perutz, R. N.; Willner, H. *J. Am. Chem. Soc.* **1990**, *112*, 9212. (e) Gibson, V. C.; Parkin, G.; Bercaw, J. E. *Organometallics* **1991**, *10*, 220. (f) Beckhaus, R. *J. Chem. Soc., Dalton Trans.* **1997**, 1991. (g) Luinstra, G. A.; Teuben, J. H. *Organometallics* **1992**, *11*, 1793. (h) Beckhaus, R. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 687. (i) Alvarado, Y.; Boutry, O.; Gutiérrez, E.; Monge, A.; Nicasio, M. C.; Poveda, M. L.; Pérez, P. J.; Ruíz, C.; Bianchini, C.; Carmona, E. *Chem. Eur. J.* **1997**, *3*, 860.

Scheme 2



Scheme 3



dissociation has been shown to be the key to the alkyne-vinylidene transformation by 1,3-hydrogen shift in half-sandwich ruthenium and osmium systems.[26] The last step of the reaction shown in eq 2 should be the hydrogen transfer from the oxime into the C_β atom of the vinylidene, as in routes a and b.

An alternative to route c is route d (Scheme 5), which involves oximate-dihydrogen-vinylidene species formed by migration of the OH proton of the oxime to the C_β atom of the alkynyl group of $[Os(C{\equiv}CR)(\eta^2\text{-}H_2)\{N(OH){=}C(CH_3)_2\}(P^iPr_3)_2]^+$. In this case, the formation of **4**−**6** should be a result of an elimination−addition process involving the dihydrogen and vinylidene ligands. A similar attack has been proposed to the formation of $OsHCl_2(\equiv CCH_2R)(P^iPr_3)_2$ from $OsH_2Cl_2(P^iPr_3)_2$ and terminal alkynes.[6]

If the reactions shown in eq 2 occur through route a, one should expect one deuterium atom in the hydride position of the product resulting from the reaction of **3** with deuterated phenylacetylene. However, if the reactions take place through route b, the deuterium should be located at the C_β atom of the carbyne ligand. As it has been previously mentioned, the distribution of deuterium atoms in the resulting product from the reaction of **3** with deuterated phenylacetylene is 0.5 deuterium atom at the hydride position and 0.25 deuterium atom at the C_β atom of the carbyne ligand. So, on the basis of this result routes a and b must be rejected.

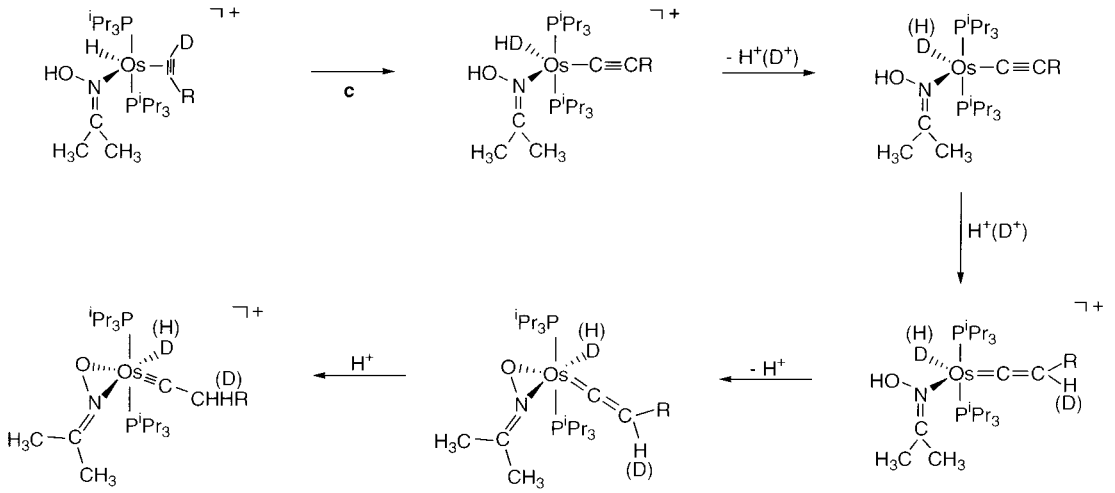
The presence of 0.5 deuterium atom at the hydride position of the product resulting from the reaction of **3** with deuterated phenylacetylene can be easily explained assuming that the reactions shown in eq 2 take place through route c or d. The formation of η^2-HD species during the activation of the deuterated alkyne and the subsequent dissociation of one of these atoms allows 0.5 deuterium atom at the hydride position of the resulting hydride complex, according to the statistics. Furthermore, the implication of two dissociation−addition steps of $H^+(D^+)$ for the formation of the carbyne ligand explains well the presence of an amount of deuterium at the C_β atom of the carbyne, which depends on the reaction medium. In this context, in should be noted that in the absence of H/D exchange with the reaction medium, 0.5 deuterium at the C_β atom of the carbyne ligand should be expected for the reaction of **3** with deuterated phenylacetylene and one deuterium should be expected for the reaction of **3-d$_1$** with phenylacetylene, in the presence of 4.0 equiv of methanol-d_4. The presence of two deuteriums at the C_β atom of the carbyne ligand of the product of this later reaction agrees well not only with a H/D exchange process between the organometallic species and the reaction medium but also with the higher strength of the alkyl−D bond in comparison with the alkyl−H bond.[27]

Routes c and d involve the same two dissociation−addition processes, and the difference between them is the order of these steps. For route c, the first dissocia-

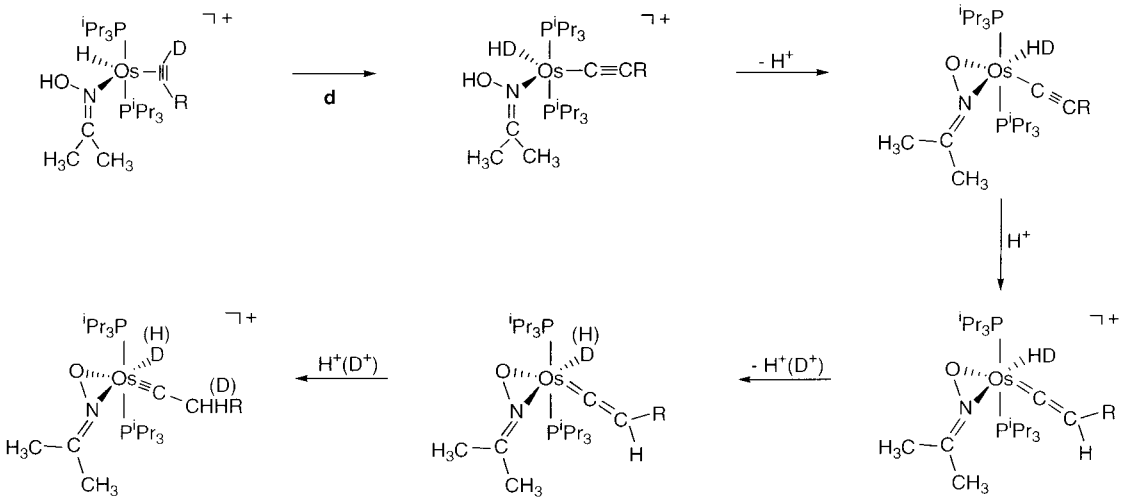
(26) (a) de los Ríos, I.; Jimenez-Tenorio, M.; Puerta, M. C.; Valerga, P. *J. Am. Chem. Soc.* **1997**, *119*, 6529. (b) Bustelo, E.; Jiménez-Tenorio, M.; Puerta, M. C.; Valerga, P. *Organometallics* **1999**, *18*, 950. (c) Bustelo, E.; Jiménez-Tenorio, M.; Puerta, M. C.; Valerga, P. *Organometallics* **1999**, *18*, 4563. (d) Puerta, M. C.; Valerga, P. *Coord. Chem. Rev.* **1999**, *193*, 3−195, 977. (e) Baya, M.; Crochet, P.; Esteruelas, M. A.; Gutiérrez-Puebla, E.; López, A. M.; Modrego, J.; Oñate, E.; Vela, N. *Organometallics* **2000**, *19*, 2585. (f) Bustelo, E.; Jiménez-Tenorio, M.; Puerta, M. C.; Valerga, P. *Eur. J. Inorg. Chem.* **2001**, 2391. (g) Baya, M.; Crochet, P.; Esteruelas, M. A.; López, A. M.; Modrego, J.; Oñate, E. *Organometallics* **2001**, *20*, 4291.

(27) Connors, K. A. Chemical Kinetics. *The Study of Reaction Rates in Solution*; VCH Publisher: New York, 1990.

Scheme 4

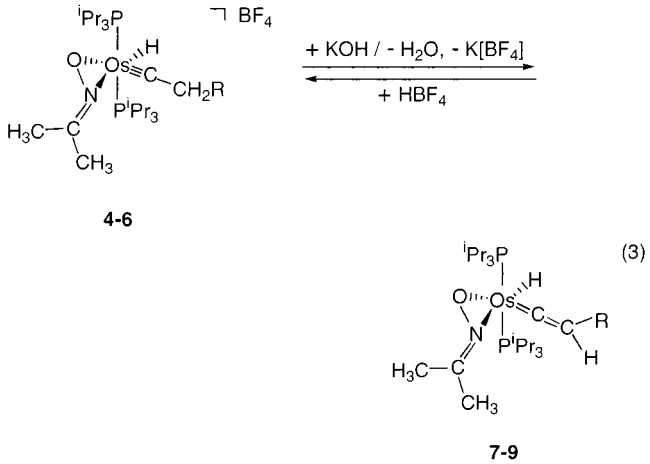


Scheme 5



tion−addition process involves the dihydrogen ligand, while the dissociation of the HO proton of the oxime is the first step of route d. Complex **3-d$_1$** does not exchange the deuterium atom at the oxime with the hydrogen atoms of the elongated dihydrogen ligand at a rate comparable with the rate of the reactions shown in eq 2. However, the H/D exchange between the oxime of **3** and methanol-d_4 is very fast. These observation agree well with the fact that complex **3-d$_1$** can be selectively prepared by treatment of **3** with methanol-d_4 during a short period of time (less than 10 min). The selective formation of **3-d$_1$**, starting from **3** and methanol-d_4, suggests that, for these systems, the dissociation of the proton from a coordinated oxime is meaningfully faster than the dissociation of a proton from a dihydrogen ligand. So, route d, involving the dissociation of the HO proton of the oxime before the dissociation of the dihydrogen, appears to be the most reasonable pathway for the formation of **4**−**6** according to eq 2.

3. Reactions of [OsH{κ-*N*,κ-*O*[ON=C(CH$_3$)$_2$]}(≡CCH$_2$R)(P^{i}Pr$_3$)$_2$]BF$_4$ with KOH. In agreement with the participation of hydride-oximate-vinylidene species as intermediates in the formation of **4**−**6**, the treatment of methanol solutions of these complexes with 2.0 equiv of KOH affords the derivatives OsH{κ-*N*,κ-*O*[ON=C(CH$_3$)$_2$]}(=C=CHR)(P^{i}Pr$_3$)$_2$ (R = Ph (**7**), Cy (**8**), ^{t}Bu (**9**)). The reactions are reversible; thus the addition of 1.0 equiv of HBF$_4$·Et$_2$O to dichloromethane solutions of **7**−**9** regenerates **4**−**6** (eq 3).



4-6

7-9

R = Ph (**4**, **7**), Cy (**5**, **8**), ^{t}Bu (**6**,**9**)

(3)

The protonation of the C$_\beta$ atom of the vinylidene ligands of **7**−**9** is fast, reversible, and selective and occurs without detectable participation of the metal. Thus, the addition of 1.0 equiv of DBF$_4$·D$_2$O to dichlo-

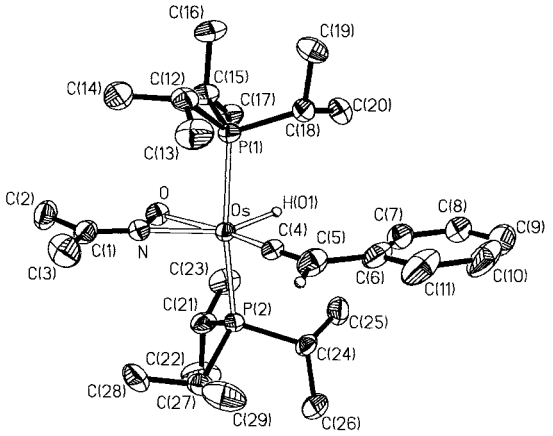


Figure 2. Molecular diagram of complex OsH{κ-*N*,κ-*O*[ON=C(CH$_3$)$_2$]}(=C=CHPh)(P^{i}Pr$_3$)$_2$ (**7**).

Table 2. Selected Bond Distances (Å) and Angles (deg) for the Complex OsH{κ-*N*,κ-*O*[ON=C(CH$_3$)$_2$]}(=C=CHPh)(P^{i}Pr$_3$)$_2$ (7)

Os−P(1)	2.3692(13)	O−N	1.351(5)
Os−P(2)	2.3656(13)	N−C(1)	1.285(7)
Os−O	2.216(4)	C(4)−C(5)	1.350(8)
Os−N	2.062(4)	C(5)−C(6)	1.465(9)
Os−C(4)	1.787(5)		
Os−H(01)	1.57(7)		
P(1)−Os−P(2)	168.91(5)	Os−O−N	65.5(2)
P(1)−Os−O	88.84(10)	Os−N−C(1)	160.4(4)
P(1)−Os−N	92.27(12)	O−N−C(1)	121.4(5)
P(1)−Os−C(4)	91.25(16)	N−C(1)−C(2)	121.0(5)
P(1)−Os−H(01)	78(2)	N−C(1)−C(3)	118.4(5)
P(2)−Os−O	91.39(10)	Os−C(4)−C(5)	178.0(5)
P(2)−Os−N	94.52(12)	C(4)−C(5)−C(6)	123.4(6)
P(2)−Os−C(4)	90.87(16)		
P(2)−Os−H(01)	91(2)		
O−Os−N	36.58(15)		
O−Os−C(4)	167.7(2)		
O−Os−H(01)	102(2)		
N−Os−C(4)	131.2(2)		
N−Os−H(01)	138(2)		
C(4)−Os−H(01)	90(2)		

romethane solutions of **4** gives instantly the corresponding carbyne derivative, containing 1.7 deuterium atoms at the C$_\beta$ atom of the carbyne, while deuterium at the hydride position is not observed.

Figure 2 shows a view of the molecular geometry of **7**. Selected bond distances and angles are listed in Table 2. Assuming that the oximate group acts as a monodentated three-electron donor ligand, the structure of **7** can be rationalized as a distorted trigonal bipyramid with apical phosphines (P(1)−Os−P(2) = 168.91(5)°) and inequivalent angles within the Y-shaped equatorial plane (H(01)−Os−M = 119(3)°, H(01)−Os−C(4) = 90(3)°, and C(4)−Os−M = 150.2(2)°).[19] This distribution of ligands around of the metal agrees well with that found in **4**, and it is similar to that calculated for the chlorohydride-vinylidene RuHCl(=C=CH$_2$)(PH$_3$)$_2$ (H−Ru−Cl = 128.71°, H−Ru−C$_\alpha$ = 84.78°, C$_\alpha$−Ru−Cl = 146.52°).[20a] It has been argued that the preference for a Y structure in this type of vinylidene complexes is originated by the presence of the vinylidene ligand, which is a potent π acceptor in the CR$_2$ plane but a weak π donor in the orthogonal plane. The donating property of π_{CC} disfavors a *trans* relationship of the three-electron donor and vinylidene ligands since this maximizes the overlaps between the occupied orbitals of the metal and the two

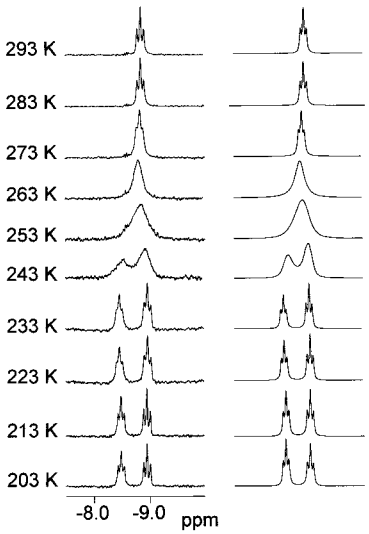


Figure 3. Left: Variable-temperature ^{1}H NMR spectra (300 MHz) in C$_7$D$_8$ in the high-field region of OsH{κ-*N*,κ-*O*[ON=C(CH$_3$)$_2$]}(=C=CH^{t}Bu)(P^{i}Pr$_3$)$_2$ (**9**). Right: Simulated spectra for the rotational process.

ligands. However, two stabilizing interactions occur when the CR$_2$ group lies in the H−M−(three-electron ligand) plane.[20]

The vinylidene ligand is bound to the metal in a nearly linear fashion with an Os−C(4)−C(5) angle of 178.0(5)°. The Os−C(4) (1.787(5) Å) and C(4)−C(5) (1.350(8) Å) bond lengths compare well with those found in other osmium-vinylidene complexes[28] and support the vinylidene formulation.

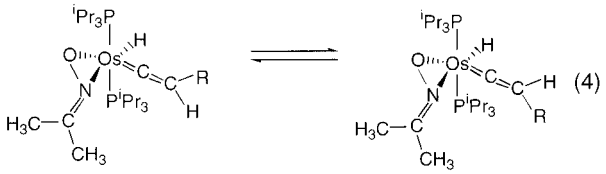
In the IR spectra of **7**−**9**, the most noticeable absorption is that corresponding to the ν(Os−H) vibration, which appears between 2110 and 2080 cm^{-1}. At room temperature, the ^{1}H NMR spectra show the resonance corresponding to the =CHR proton of the vinylidene ligands, which appears between 0.5 and 0.9 ppm. The hydride resonance is observed between −8.0 and −8.7 ppm. At the same temperature, in the ^{13}C{^{1}H} NMR spectra, the C$_\alpha$ atom of the vinylidene ligands gives rise between 287 and 284 ppm to a triplet with a C−P coupling constant between 10.2 and 8.3 Hz, whereas the C$_\beta$ atom displays a singlet between 109 and 115 ppm. The ^{31}P{^{1}H} NMR spectra show a singlet between 20 and 24 ppm.

The ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra of these compounds are temperature-dependent. Figure 3 shows the hydride region of the ^{1}H NMR spectrum of **9** as a function of the temperature. The spectra of **7** and **8** are similar. At low temperature, the spectra contain two hydride resonances. On raising the temperature, they coalesce, until finally only one resonance is observed. This behavior can be understood as the result of the equilibrium between the two possible rotational isomers of **7**−**9** (eq 4). The ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectra at low temperature also support the presence of both dispositions of the vinylidenes in solution (see Experimental Section).

For **7** and **9** the equilibrium constants were measured in the range from −70 to 40 °C. The temperature dependence of the equilibria provides the values

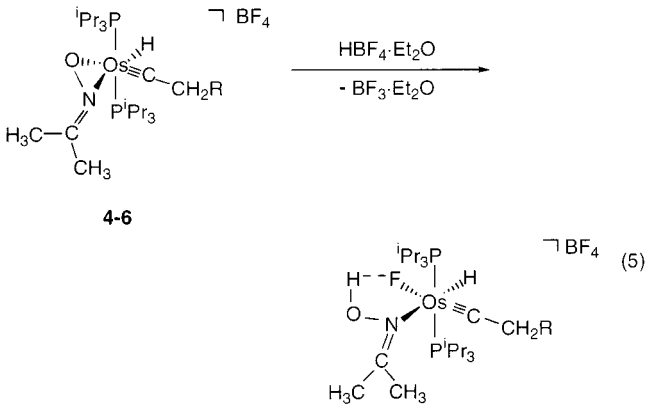
(28) Castarlenas, R.; Esteruelas, M. A.; Gutiérrez-Puebla, E.; Oñate, E. *Organometallics* **2001**, *20*, 1545.

$\Delta H° = 0.9 \pm 0.2$ kcal·mol^{-1} and $\Delta S° = 3.7 \pm 0.9$ cal·mol^{-1}·K^{-1} for **7** and $\Delta H° = 0.9 \pm 0.2$ kcal·mol^{-1} and $\Delta S° = 4.1 \pm 1.2$ cal·mol^{-1}·K^{-1} for **9**. The obtained values indicate that, for both cases, the rotational isomers have a similar thermodynamic stability, as at first glance could be expected from the proposed structures.



Line shape analysis of the hydride resonances of **7** and **9** allows the calculation of the rate constants for the rotation process. The activation parameters obtained from the corresponding Eyring analysis are $\Delta H^{\ddagger} = 11.3 \pm 0.6$ kcal·mol^{-1} and $\Delta S^{\ddagger} = -4.7 \pm 1.8$ cal·mol^{-1}·K^{-1} for **7** and $\Delta H^{\ddagger} = 12.9 \pm 0.5$ kcal·mol^{-1} and $\Delta S^{\ddagger} = 4.3 \pm 1.2$ cal·mol^{-1}·K^{-1} for **9**. The values of the activation entropy, near zero, are consistent with a rotational process, whereas the values of the activation enthalpy agree well with the reported one for the chloro-derivative OsHCl(=C=CHPh)(P^{i}Pr$_3$)$_2$ (11.2 ± 0.2 kcal·mol^{-1})[29] and the calculated rotational barrier for OsHCl(=C=CHPh)(PH$_3$)$_2$ (8.2 kcal·mol^{-1}).[30]

4. Reactions of [OsH{κ-*N*,κ-*O*[ON=C(CH$_3$)$_2$]}(≡CCH$_2$R)(P^{i}Pr$_3$)$_2$]BF$_4$ with HBF$_4$. The hydride-oximate-carbyne complexes **4**−**6** are difunctional compounds, which show amphoteric nature reacting not only with Brönsted bases but also with Brönsted acids. Thus, in addition to the reactions shown in eq 3, these compounds undergo the attack of HBF$_4$. Treatment at room temperature of dichloromethane solutions of **4**−**6** with 1.2 equiv of HBF$_4$·Et$_2$O leads to the instant formation of the fluoro-oxime derivatives [OsH{F---HON=C(CH$_3$)$_2$}(≡CCH$_2$R)(P^{i}Pr$_3$)$_2$]BF$_4$ (R = Ph (**10**), Cy (**11**), ^{t}Bu (**12**)), according to eq 5.



Although there is experimental evidence suggesting that the fluoro complexes are stable when π-back-bonding ligands are also present in the coordination sphere of the metal, the chemistry of these compounds is relatively unexplored.[31] To date, only a few osmium-fluoride organometallic compounds have been reported, between them the derivatives OsF(CO)$_2$(N=NPh)(PPh$_3$)$_2$,[32] [OsF$_2$(CO)$_3$]$_4$,[33] OsF(COF)(CO)$_2$(PPh$_3$)$_2$,[34] and OsF$_2$(CO)$_2$(PR$_3$)$_2$ (PR$_3$ = PPh$_3$, PCy$_3$).[35] In general, fluoro-carbyne complexes are very rare;[36] as far as we know, the only fluoro-osmium-carbyne compound previously described is the derivative [OsHF(≡CCH$_2$Ph)(Hpz)(P^{i}Pr$_3$)$_2$]BF$_4$.[37]

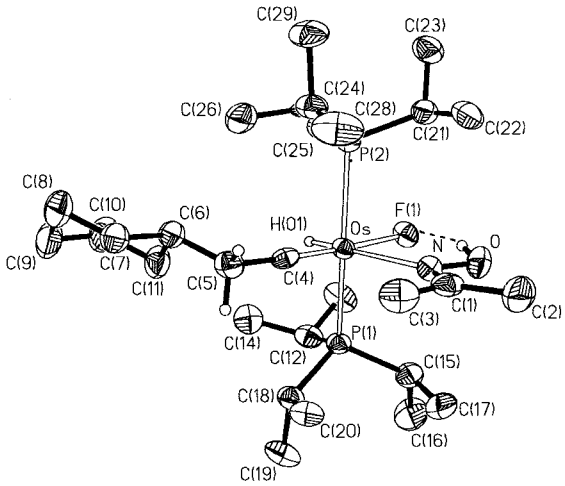


Figure 4. Molecular diagram of the cation of complex [OsH{F---HOH=C(CH$_3$)$_2$}(≡CCH$_2$Cy)(P^{i}Pr$_3$)$_2$]BF$_4$ (**11**).

Complexes **10**−**12** were isolated as lilac (**10**) or white (**11** and **12**) solids in high yield (between 60 and 90%) and characterized by MS, elemental analysis, IR, and ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopy. Complex **11** was further characterized by an X-ray crystallographic study. A view of the molecular geometry of the cation of **11** is shown in Figure 4. Selected bond distances and angles are listed in Table 3.

The geometry around the osmium atom can be rationalized as a distorted octahedron with the two phosphorus atoms of the triisopropylphosphine ligands in *trans* positions (P(1)−Os−P(2) = 161.91(4)°). The perpendicular plane is formed by the hydride and carbyne ligands, the oxime group *trans* disposed to the hydride (H(01)−Os−N = 162.3(16)°), and the fluoride atom *trans* disposed to the carbyne (C(4)−Os−F(1) = 175.74(15)°). The carbyne formulation is supported by the Os−C(4)−C(5) angle (176.4(4)°). The very short Os−C(4) distance is fully consistent with an osmium−carbon

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Table 3. Selected Bond Distances (Å) and Angles (deg) for the Complex [OsH{F---HO(N=C(CH$_3$)$_2$}(≡CCH$_2$Cy)(P^{i}Pr$_3$)$_2$]BF$_4$ (11)

Os−P(1)	2.4272(12)	O−N	1.399(4)
Os−P(2)	2.4198(12)	N−C(1)	1.279(4)
Os−F(1)	2.085(2)	C(4)−C(5)	1.476(6)
Os−N	2.252(4)	C(5)−C(6)	1.528(6)
Os−C(4)	1.694(4)		
Os−H(01)	1.22(4)		
P(1)−Os−P(2)	161.91(4)	Os−N−O	111.7(3)
P(1)−Os−F(1)	83.39(7)	Os−N−C(1)	136.9(3)
P(1)−Os−N	94.52(10)	O−N−C(1)	111.4(4)
P(1)−Os−C(4)	97.12(13)	N−C(1)−C(2)	120.3(5)
P(1)−Os−H(01)	77.2(16)	N−C(1)−C(3)	120.9(4)
P(2)−Os−F(1)	83.83(7)	Os−C(4)−C(5)	176.4(4)
P(2)−Os−N	95.38(9)	C(4)−C(5)−C(6)	115.7(4)
P(2)−Os−C(4)	94.70(14)		
P(2)−Os−H(01)	89.0(16)		
F(1)−Os−N	78.35(11)		
F(1)−Os−C(4)	175.74(15)		
F(1)−Os−H(01)	85.1(15)		
N−Os−C(4)	105.80(16)		
N−Os−H(01)	162.3(16)		
C(4)−Os−H(01)	90.9(15)		

triple bond,[22] whereas the Os−C(4)−C(5) angle clearly indicates the sp hybridization of C(4).

The Os−F(1) bond length (2.085(2) Å) is statistically identical with the Os−F distance in the previously mentioned complex [OsHF(≡CCH$_2$Ph)(Hpz)(P^{i}Pr$_3$)$_2$]BF$_4$ (2.087(2) Å),[37] where a F- - -H−N hydrogen bonding has been proposed to exist, and about 0.05 Å longer than the Os−F distances found in the dicarbonyl compounds OsF$_2$(CO)$_2$(PCy$_3$)$_2$ (2.023(4) and 2.022(4) Å) and OsF$_2$(CO)$_2$(PPh$_3$)$_2$ (2.023(5) Å).[35] Interestingly, the F(1)−Os−N angle (78.35(11)°) largely deviates from the ideal value of 90°, indicating an approach of the oxime group to the fluorine atom, which is also shown by the separation between the fluorine and oxygen atoms (2.464(4) Å). Although the hydrogen atom of the oxime group does not refine, at 173 K, it was located at 1.75 Å from the fluorine atom in the difference Fourier maps. This separation is shorter than the sum of the van der Waals radii of hydrogen and fluorine [r_{vdW}(H) = 1.20, r_{vdW}(F) = 1.47 Å][38] and suggests an intramolecular F- - -H hydrogen bond, as a result of the interaction of the electronegative fluorine with the acidic OH hydrogen of the oxime.

Of great importance in biological and organic chemistry,[39] the hydrogen bonding is presently attracting considerable interest in the chemistry of transition metals.[28,37,40]

The F- - -H hydrogen bond in **10**−**12** is also supported by the IR spectra of these compounds. In contrast to the IR spectrum of **3**, which shows a narrow ν(O−H) band at 3368 cm^{-1}, the IR spectra of **10**−**12** contain a broad ν(O−H) absorption centered between 3220 and 3186 cm^{-1}, thus shifted more than 140 cm^{-1} to lower wavenumbers if compared with that of **3**. In addition, it should be mentioned that the IR spectra of **10**−**12** show, at about 1050 cm^{-1}, the absorption of the [BF$_4$]$^-$ anion with T_d symmetry. This is in agreement with the salt character of these compounds and indicates that any fluorine atom of the [BF$_4$]$^-$ anion is not involved in an intermolecular F- - -H hydrogen bond with the OH hydrogen of the oxime.

The F- - -H hydrogen bond gives rise to a five-membered Os-F---H-O-N ring, which is stable in dichloromethane at room temperature. Thus, at this temperature, ^{1}H NMR spectra of **10**−**12** in dichloromethane-d_2 show at about 12 ppm a doublet with a H−F coupling constant of about 68 Hz, corresponding to the OH proton of the oxime ligand. This value is higher than that found in the complex IrH(bq-NH$_2$)F(PPh$_3$)$_2$ (52 Hz, at 193 K),[40h] where a F- - -H distance of 1.560 Å has been calculated by DFT theoretical studies,[40k] and suggests that the F- - -H hydrogen bond in **10**−**12** is stronger than that in the iridium derivative.

The addition of acetone to the dichloromethane solutions of **10**−**12** produces the release of HF and the regeneration of the oximate complexes **4**−**6**, suggesting that the presence of the F- - -H hydrogen bond stabilizes the Os−F bond in **10**−**12**. In this context, it should be noted that acetone can compete with the fluorine by the OH proton of the oxime.

The ^{1}H NMR spectra of **10** and **12** also support the presence of the carbyne and hydride ligands. The CH$_2$ hydrogen atoms of the carbynes display a broad singlet between 1.50 and 2.90 ppm, whereas the hydride ligand gives rise to a double triplet at about −7 ppm with H−F and H−P coupling constants of about 7 and 17 Hz, respectively. The ^{19}F, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR agree well with the ^{1}H NMR spectra and with the molecular diagram shown in Figure 4. The ^{19}F NMR spectra contain a double triplet of doublets between −260 and −266 ppm with a F−P coupling constant of about 38.5 Hz. In agreement with the ^{19}F NMR spectra, the ^{31}P{^{1}H} NMR spectra show a doublet between 37 and 33 ppm. In the ^{13}C{^{1}H} NMR spectra, the most noticeable resonance is that due to the C$_\alpha$ atom of the carbyne ligands, which appears as a double triplet between 277 and 285 ppm with C−F and C−P coupling constants of about 110 and 8 Hz, respectively. The C$_\beta$ atom of the carbyne ligands gives rise to a doublet between 57 and 66 ppm with a C−F coupling constant of about 12 Hz.

The formation of **10**−**12** can be rationalized as an addition−displacement two-step process. Initially, the oxygen atom of the oximate group adds the proton of HBF$_4$ to afford an unsaturated oxime intermediate where the metallic center is a Lewis acid stronger than BF$_3$. Thus, in the subsequent step, the metal of this intermediate displaces to BF$_3$ from F$^-$. The addition of the proton to the oximate ligand of **4**−**6**, as the addition of H$^+$ to vinylidene ligands **7**−**9**, is fast and selective and occurs without detectable participation of the metal. In agreement with this, we have observed that the

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addition of 1.0 equiv of $DBF_4 \cdot D_2O$ to dichloromethane solutions of **4** gives $[OsH\{F\text{---}DON{=}C(CH_3)_2\}](\equiv CCH_2Ph)(P^iPr_3)_2]BF_4$ (**10-d$_1$**), containing 1.0 deuterium atom at the oxygen of the oxime. Deuterium at the hydride position was not observed.[41]

The presence of a deuterium at the oxygen atom of the oxime of **10-d$_1$** is strongly supported by the ^2H NMR spectrum of this compound at room temperature, which shows at 11.90 ppm a doublet with a D−F coupling constant of 10 Hz. The value of this coupling constant agrees well with the expected one according to the gyromagnetic ratio of the involved nuclei[42] and suggests that the strength of the F- - -D deuterium bond is similar to that of the F- - -H hydrogen bond.

Concluding Remarks

This paper shows, once more, that the chemistry of the osmium compounds containing two hydrogen atoms bonded to the metallic center is fascinating and cannot be easily rationalized. Not only each osmium-dihydride complex but also each osmium-elongated dihydrogen derivative has a particular behavior in the presence of alkynes. In contrast to $OsCl_2(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2$, which affords carbene compounds, complex $[Os\{C_6H_4C(O)CH_3\}(\eta^2\text{-}H_2)\{N(OH){=}C(CH_3)_2\}(P^iPr_3)_2]BF_4$ gives carbyne derivatives.

In the presence of phenylacetylene, cyclohexylacetylene, and *tert*-butylacetylene the oxime-elongated dihydrogen complex eliminates acetophenone and the resulting unsaturated monohydride intermediate gives rise to $[OsH\{\kappa\text{-}N,\kappa\text{-}O[ON{=}C(CH_3)_2]\}(\equiv CCH_2R)(P^iPr_3)_2]BF_4$ (R = Ph, Cy, ^{t}Bu). The transformation of alkyne-carbyne appears to occur via alkynyl species involving two dissociation−addition processes, where the oxime ligand plays a main role.

Complexes $[OsH\{\kappa\text{-}N,\kappa\text{-}O[ON{=}C(CH_3)_2]\}(\equiv CCH_2R)(P^iPr_3)_2]BF_4$ are a novel type of bifunctional organometallic derivatives, which have amphoteric nature reacting with both KOH and HBF_4. The reactions with KOH afford the neutral vinylidene derivatives $OsH\{\kappa\text{-}N,\kappa\text{-}O[ON{=}C(CH_3)_2]\}(=C{=}CHR)(P^iPr_3)_2$, as a result of the deprotonation of the CH_2 group of the carbyne ligands. The reactions with HBF_4 give the fluoro-oxime complexes $[OsH\{F\text{---}HON{=}C(CH_3)_2\}(\equiv CCH_2R)(P^iPr_3)_2]BF_4$, where a strong F- - -H hydrogen bond between the fluorine and the OH proton of the oxime appears to stabilize the Os−F bond.

In conclusion the elongated dihydrogen complex $[Os\{C_6H_4C(O)CH_3\}(\eta^2\text{-}H_2)\{N(OH){=}C(CH_3)_2\}(P^iPr_3)_2]BF_4$ reacts with terminal alkynes to give the bifunctional organometallic compounds $[OsH\{\kappa\text{-}N,\kappa\text{-}O[ON{=}C(CH_3)_2]\}(\equiv CCH_2R)(P^iPr_3)_2]BF_4$, which are electrophiles at the CH_2 group of the carbyne ligands and nucleophiles at the oxygen atom of the oximate group.

Experimental Section

All reactions were carried out with rigorous exclusion of air using Schlenk-tube techniques. Solvents were dried by the usual procedures and distilled under argon prior to use. The starting material $OsH_3\{C_6H_4C(O)CH_3\}(P^iPr_3)_2$ (**1**)[9] and $DBF_4 \cdot D_2O$ were prepared by the published methods.

Synthesis of $(CH_3)_2C{=}NOD$. $(CH_3)_2C{=}NOH$ was dissolved in methanol-d_4 and stirred for 20 h. Removal of the solvent and addition of pentane afforded $(CH_3)_2C{=}NOD$ as a white solid.

NMR spectra were recorded on a Varian UNITY, a Varian Geminy 2000, and a Bruker ARX 300 MHz instrument. ^1H (300 MHz) and ^{13}C (75.42 MHz) NMR chemical shifts were referenced to TMS by using known shifts of residual proton or carbon signals in the solvents. ^{31}P (121.42 MHz) NMR were measured relative to external 85% phosphoric acid. MS data were recorded on a VG Austospec double-focusing mass spectrometer operating in the positive mode; ions were produced with the Cs^+ gun at ca. kV, and 3-nitrobenzyl alcohol (NBA) was used in the matrix.

Kinetic Analysis. The equilibrium constants $K = k_1/k_{-1}$ of the two rotamers of **7** and **9** were calculated by ^1H NMR spectroscopy in toluene-d_8. At temperatures below the coalescence point, the ratio was calculated by integration of the hydride signals corresponding to the two rotamers and above the coalescence temperature by measuring the chemical shift of the exchange-averaged hydride resonance. A least-squares fit of the values of ln K vs $1/T$ gave the thermodynamic magnitudes $\Delta H°$ and $\Delta S°$ involved in this equilibrium. Error analysis assumed a 10% error in the value of the equilibrium constant and 1 K in the temperature. Errors were computed by standard error propagation formulas for least-squares fitting.[43]

Complete line-shape analyses of the ^1H NMR spectra of the complexes **7** and **9** were achieved using the program gNMR (Cherwell Scientific Publishing Limited). The rate constants for various temperatures were obtained by fitting calculated to experimental spectra by full line shape iterations. The transverse relaxation time, T_2, was estimated at the lowest interval of temperatures using the resonances corresponding to the hydride ligands. The activation parameters $\Delta H^‡$ and $\Delta S^‡$ were calculated by least-squares fit of $\ln(k_1/T)$ vs $1/T$ (Eyring equation). Error analysis assumed a 10% error in the rate constant and 1 K in the temperature. Errors were computed by published methods.[44]

Preparation of $[Os\{C_6H_4C(O)CH_3\}(\eta^2\text{-}H_2)(H_2O)(P^iPr_3)_2]BF_4$ (2). A red solution of **1** (100 mg, 0.136 mmol) in a mixture of 10 mL of diethyl ether and 1 mL of methanol was treated with $HBF_4 \cdot H_2O$ (23.3 μL, 0.190 mmol) and stirred for 30 min at room temperature and then was evaporated to dryness. Subsequent addition of diethyl ether (5 mL) caused the precipitation of an orange solid, which was washed with further portions of diethyl ether and dried in vacuo. Yield: 103.6 mg (89%). Anal. Calcd for $C_{26}H_{53}BF_4O_2OsP_2$: C 42.39; H 7.25. Found: C 42.63; H 7.65. IR (KBr, cm^{-1}): ν(OH) 3418 (br), ν(OsH) 2184 (s), ν(CO) 1592 (s), ν(BF) 1050 (br). ^1H NMR (300 MHz, CD_2Cl_2, 293 K): δ 7.66 (br d, J_{H-H} = 6.6 Hz, 1H, Ph), 7.53 (br d, J_{H-H} = 6.6 Hz, 1H, Ph), 6.93 and 6.87 (both vtd, J_{H-H} = 6.6 Hz, J_{H-H} = 1.2 Hz, 1H, Ph), 3.72 (br, 2H, H_2O), 3.01 (s, 3H, CH_3), 1.99 (m, 6H, PC*H*), 1.17 and 0.97 (both dvt, N = 13.2 Hz, J_{H-H} = 6.9 Hz, 18H, PCHC*H*$_3$), −7.87 (t, J_{P-H} = 10.5 Hz, 2H, OsH). $^{31}P\{^1H\}$ NMR (121.42 MHz, CD_2Cl_2, 293 K): δ 14.8 (s). ^{19}F NMR (282.33 MHz, CD_2Cl_2, 293 K): δ −155.2 (s). $^{13}C\{^1H\}$ NMR (75.42 MHz, CD_2Cl_2, 293 K): δ 209.7 (s, C=O), 177.8 (br, Os−C), 143.3 (s, C_{ipso}Ph), 145.7, 137.2, 134.7, and 122.1 (all s, Ph), 26.7 (vt, N = 24.6 Hz, P*C*H), 25.8 (s, *C*H$_3$), 21.2 and 20.8 (both s, PCH*C*H$_3$). MS (FAB$^+$): m/z 650 (M^+ − H). $T_{1(min)}$ (ms, OsH_2, 300 MHz, CD_2Cl_2, 193 K): 48 ± 2 (−7.87 ppm, 2H).

(41) The partial deuteration of the CH_2 group of the carbyne is observed after several hours.

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[Os{$C_6H_4C(O)CH_3$}(η^2-HD)(D_2O)(P^iPr_3)$_2$]BF_4 was obtained from **2** in $CD_3OD{\cdot}D_2O$ (2:0.1 mL) for 2 days. ^{1}H NMR (300 MHz, CD_3OD, 293 K): δ −7.78 (tt(1:1:1), J_{H-P} = 10.5 Hz, J_{H-D} = 4.2 Hz, 1H, OsH).

Preparation of [Os{$C_6H_4C(O)CH_3$}(η^2-H_2){N(OH)=C(CH_3)$_2$}(P^iPr_3)$_2$]BF_4 (3). An orange solution of **2** (100 mg, 0.136 mmol) in 12 mL of dichloromethane was treated with acetone oxime (10.9 mg, 0.149 mmol) and stirred for 45 min at room temperature and then was filtered through Celite and evaporated to dryness. Subsequent addition of diethyl ether (5 mL) caused the precipitation of an orange solid, which was washed with further portions of diethyl ether and dried in vacuo. Yield: 80.0 mg (86%). Anal. Calcd for $C_{29}H_{58}BF_4NO_2OsP_2$: C 43.99; H 7.38; N 1.77. Found: C 43.54; H 7.33; N 1.92. IR (KBr, cm^{-1}): ν(OH) 3368 (s), ν(OsH) 2186 (s), ν(CO) 1592 (s), ν(CN) 1559 (s), ν(BF) 1050 (br). ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ 11.24 (s, 1H, OH), 7.91 (br d, J_{H-H} = 7.2 Hz, 1H, Ph), 7.89 (dd, J_{H-H} = 7.2 Hz, J_{H-H} = 1.8 Hz, 1H, Ph), 7.12 and 7.07 (both vtd, J_{H-H} = 7.2 Hz, J_{H-H} = 1.8 Hz, 1H, Ph), 3.12 (t, J_{P-H} = 1.5 Hz, 3H, C(O)CH_3), 2.42 and 2.32 (both s, 3H, NCCH_3), 1.79 (m, 6H, PC*H*), 1.14 and 0.94 (both dvt, *N* = 13.2 Hz, J_{H-H} = 7.2 Hz, 18H, PCHCH_3), −8.85 (t, J_{P-H} = 10.8 Hz, 2H, OsH). ^{31}P{^{1}H} NMR (121.42 MHz, CD_2Cl_2, 293 K): δ 6.25 (s). ^{19}F NMR (282.33 MHz, CD_2Cl_2, 293 K): δ −155.4 (s). ^{13}C{^{1}H} NMR (75.42 MHz, CD_2Cl_2, 293 K): δ 210.1 (s, C=O), 181.9 (t, J_{P-C} = 5.9 Hz, Os−C), 166.9 (s, N=C), 142.2 (s, C_{ipso}Ph), 145.1, 136.2, 134.8 and 121.8 (all s, Ph), 28.1 (s, C(O)-*C*H_3), 25.7 (vt, *N* = 24.9 Hz, P*C*H), 24.5 (s, NC*C*H_3), 19.6 and 19.1 (both s, PCH*C*H_3), 18.3 (s, NC*C*H_3). MS (FAB$^+$): *m*/*z* 704 (M$^+$ − 2H). $T_{1(min)}$ (ms, OsH_2, 300 MHz, CD_2Cl_2, 203 K): 43 ± 1 (−8.87 ppm, 2H).

[Os{$C_6H_4C(O)CH_3$}(η^2-HD){N(OD)=C(CH_3)$_2$}(P^iPr_3)$_2$]BF_4 was obtained from **3** stirred in CD_3OD 1 day, the solvent was removed, and then diethyl ether caused the precipitation of an orange solid. ^{1}H NMR (300 MHz, CD_3OD, 293 K): δ −9.09 (tt(1:1:1), J_{H-P} = 10.8 Hz, J_{H-D} = 4.6 Hz, 1H, OsH).

Preparation of [Os{$C_6H_4C(O)CH_3$}(η^2-H_2){N(OD)=C(CH_3)$_2$}(P^iPr_3)$_2$]BF_4 (3-d_1). To solutions of **2** (20 mg, 0.027 mmol) in 0.5 mL of CD_2Cl_2 (^{1}H NMR) or CH_2Cl_2 (^{2}H NMR) in NMR tubes was added the stoichiometric amount of acetone oxime-d_1, DON=C(CH_3)$_2$ (2 mg, 0.027 mmol). After 10 min the ^{1}H NMR spectrum indicates the quantitative formation of **3-d_1**. ^{2}H NMR (46.03 MHz, CH_2Cl_2, 293 K): δ 11.2 (br, 1D, OD).

Preparation of [OsH{κ-*N*,κ-*O*[ON=C(CH_3)$_2$]}(≡CCH_2Ph)(P^iPr_3)$_2$]BF_4 (4). An orange solution of **3** (100 mg, 0.126 mmol) in 12 mL of dichloromethane was treated with phenylacetylene (17 μL, 0.151 mmol) and stirred for 20 min at room temperature and then was filtered through Celite and evaporated to dryness. Subsequent addition of dichloromethane (0.5 mL) and diethyl ether (5 mL) caused the precipitation of a lilac solid, which was washed with further portions of diethyl ether and dried in vacuo. Yield: 66.4 mg (65%). Anal. Calcd for $C_{29}H_{56}BF_4NO_2OsP_2$: C 45.02; H 7.30; N 1.81. Found: C 45.07; H 7.41; N 1.92. IR (KBr, cm^{-1}): ν(OsH) 2119 (m), ν(CN) 1578 (s), ν(BF) 1050 (br). ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ 7.4−7.2 (m, 5H, Ph), 2.89 (s, 2H, Os≡CCH_2), 2.26 (s, 3H, NCCH_3), 2.22 (m, 6H, PC*H*), 2.18 (s, 3H, NCCH_3), 1.25 (dvt, *N* = 14.4 Hz, J_{H-H} = 7.2 Hz, 36H, PCHCH_3), −6.32 (t, J_{P-H} = 17.1 Hz, 1H, OsH). ^{31}P{^{1}H} NMR (121.42 MHz, CD_2Cl_2, 293 K): δ 37.16 (s). ^{19}F NMR (282.33 MHz, CD_2Cl_2, 293 K): δ −155.3 (s). ^{13}C{^{1}H} NMR (75.42 MHz, CD_2Cl_2, 293 K, plus dept): δ 282.6 (t, J_{C-P} = 9.1 Hz, Os≡C), 147.6 (s, N=C), 128.6 (s, C_{ipso}-Ph), 129.6, 129.3, and 128.7 (all s, Ph), 58.6 (s, Os≡C*C*H_2), 25.4 (vt, *N* = 27.2 Hz, P*C*H), 22.3 (s, NC*C*H_3), 19.5 and 19.1 (both s, PCH*C*H_3), 19.0 (s, NC*C*H_3). MS (FAB$^+$): *m*/*z* 668 (M$^+$).

Preparation of [OsH{κ-*N*,κ-*O*[ON=C(CH_3)$_2$]}(≡CCH_2Ph)(P^iPr_3)$_2$]BF_4 Partially Deuterated (4-d_1). Solutions of **3** (25 mg, 0.031 mmol) in 0.5 mL of CD_2Cl_2 (^{1}H NMR) or CH_2Cl_2 (^{2}H NMR) in NMR tubes were treated with the stoichiometric amount of phenylacetylene-d_1, PhC≡CD (3.5 μL, 0.031 mmol). After 10 min the ^{1}H NMR spectrum indicates the quantitative formation of **4-d_1**. ^{2}H NMR (46.03 MHz, CH_2Cl_2, 293 K): δ 2.89 (br, 0.25D, CHDPh), −6.2 (br, 0.5D, OsD).

Preparation of [OsH{κ-*N*,κ-*O*[ON=C(CH_3)$_2$]}(≡CCD_2Ph)(P^iPr_3)$_2$]BF_4 (4-d_2). To solutions of **2** (20 mg, 0.027 mmol) and acetone oxime-d_1 (2 mg, 0.027 mmol) in 0.5 mL of CD_2Cl_2 (^{1}H NMR) or CH_2Cl_2 (^{2}H NMR) in NMR tubes were added 4 equiv of methanol-d_4 (5 μL) and 1 equiv of phenylacetylene (3 μL). After 10 min the ^{1}H NMR spectrum indicates the quantitative formation of **4-d_2**. ^{2}H NMR (46.03 MHz, CH_2Cl_2, 293 K): δ 2.89 (br, 2D, CD_2Ph).

Preparation of [OsH{κ-*N*,κ-*O*[ON=C(CH_3)$_2$]}(≡CCH_2Cy)(P^iPr_3)$_2$]BF_4 (5). This complex was prepared as described for **4** starting from 100 mg (0.126 mmol) of **3** and cyclohexylacetylene (19.5 μL, 0.151 mmol). A white solid was obtained. Yield: 69.0 mg (68%). Anal. Calcd for $C_{29}H_{62}BF_4NOOsP_2$: C 44.67; H 8.01; N 1.80. Found: C 45.01; H 7.84; N 2.01. IR (KBr, cm^{-1}): ν(OsH) 2160 (m), ν(CN) 1631 (s), ν(BF) 1050 (br). ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ 3.5−0.9 (m, 11H, Cy), 2.33 (m, 6H, PC*H*), 2.26 and 2.13 (both s, 3H, NCCH_3), 1.59 (br, 2H, Os≡CCH_2), 1.33 and 1.31 (both dvt, *N* = 13.5 Hz, J_{H-H} = 6.9 Hz, 18H, PCHCH_3), −6.75 (t, J_{P-H} = 17.4 Hz, 1H, OsH). ^{31}P{^{1}H} NMR (121.42 MHz, CD_2Cl_2, 293 K): δ 37.05 (s). ^{19}F NMR (282.33 MHz, CD_2Cl_2, 293 K): δ −155.3 (s). ^{13}C{^{1}H} NMR (75.42 MHz, CD_2Cl_2, 293 K, plus dept): δ 287.5 (t, J_{C-P} = 8.7 Hz, Os≡C), 147.5 (s, N=C), 59.9 (s, Os≡C*C*H_2), 35.1, 33.4, and 25.8 (all s, secondary carbon atoms of the cyclohexyl group), 33.5 (s, primary carbon atom of the cyclohexyl group), 25.4 (vt, *N* = 27.2 Hz, P*C*H), 22.3 (s, NC*C*H_3), 19.6 and 19.2 (both s, PCH*C*H_3), 18.8 (s, NC*C*H_3). MS (FAB$^+$): *m*/*z* 694 (M$^+$).

Preparation of [OsH{κ-*N*,κ-*O*[ON=C(CH_3)$_2$]}(≡CCH_2-*t*Bu)(P^iPr_3)$_2$]BF_4 (6). This complex was prepared as described for **4** starting from 210 mg (0.265 mmol) of **3** and 3,3-dimethyl-1-butyne (39 μL, 0.318 mmol). A white solid was obtained. Yield: 153.0 mg (76%). Anal. Calcd for $C_{27}H_{60}BF_4NOOsP_2$: C 43.03; H 8.02; N 1.86. Found: C 43.37; H 7.77; N 2.23. IR (KBr, cm^{-1}): ν(OsH) 2140 (m), ν(CN) 1631 (s), ν(BF) 1050 (br). ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ 2.37 (m, 6H, PC*H*), 2.30 and 2.19 (both s, 3H, NCCH_3), 1.57 (br, 2H, Os≡CCH_2), 1.33 and 1.32 (both dvt, *N* = 14.4 Hz, J_{H-H} = 7.5 Hz, 18H, PCHCH_3), 1.14 (s, 9H, C(CH_3)$_3$), −6.31 (t, J_{P-H} = 18.0 Hz, 1H, OsH). ^{31}P{^{1}H} NMR (121.42 MHz, CD_2Cl_2, 293 K): δ 35.27 (s). ^{19}F NMR (282.33 MHz, CD_2Cl_2, 293 K): δ −155.4 (s). ^{13}C{^{1}H} NMR (75.42 MHz, CD_2Cl_2, 293 K): δ 288.0 (t, J_{C-P} = 8.3 Hz, Os≡C), 147.4 (s, N=C), 66.0 (s, Os≡C*C*H_2), 31.4 (s, *C*(CH_3)$_3$), 30.2 (s, C(*C*H_3)$_3$), 25.2 (vt, *N* = 26.7 Hz, P*C*H), 22.3 (s, NC*C*H_3), 19.4 (s, PCH*C*H_3), 19.1 (s, NC*C*H_3). MS (FAB$^+$): *m*/*z* 668 (M$^+$).

Preparation of OsH{κ-*N*,κ-*O*[ON=C(CH_3)$_2$]}(=C=CH-Ph)(P^iPr_3)$_2$ (7). A lilac solution of **4** (135 mg, 0.174 mmol) in 12 mL of methanol was treated with a solution of KOH in methanol (1.8 mL, 0.348 mmol, 0.1888 N) and stirred for 10 min at room temperature, then the solvent was removed and toluene was added to filter the ionic salts. The resulting solution was dried in vacuo, and methanol was added to afford a yellow solid, which was washed with methanol at −78 °C and dried in vacuo. Yield: 90.0 mg (75%). Anal. Calcd for $C_{29}H_{55}NOOsP_2$: C 50.78; H 8.08; N 2.04. Found: C 51.22; H 7.94; N 1.92. IR (KBr, cm^{-1}): ν(OsH) 2107 (m), ν(CN) 1627 (s). ^{1}H NMR (300 MHz, C_6D_6, 293 K): δ 7.46 (d, J_{H-H} = 7.2 Hz, 2H, H_{orto}Ph), 7.38 (t, J_{H-H} = 7.2 Hz, 2H, H_{meta}Ph), 6.94 (t, J_{H-H} = 7.2 Hz, 1H, H_{para}Ph), 2.48 (m, 6H, PC*H*), 2.09 (s, 6H, NC(CH_3)$_2$), 1.35 and 1.30 (both dvt, *N* = 13.2 Hz, J_{H-H} = 6.9 Hz, 18H, PCHCH_3), 0.53 (br, Os=C=CH), −8.18 (br, 1H, OsH). ^{31}P{^{1}H} NMR (121.42 MHz, C_6D_6, 293 K): δ 23.81 (s). ^{13}C{^{1}H} NMR (75.42 MHz, C_6D_6, 293 K, plus dept): δ 286.9 (t, J_{C-P} = 10.2 Hz, Os=C), 140.4 (s, N=C), 134.5 (s, C_{ipso}Ph), 128.4 (s, C_{para}Ph), 123.1 and 121.7 (both s, Ph), 109.4 (s, Os=C=*C*HPh), 24.8 (vt, *N* = 24.0 Hz, P*C*H), 22.6 (s, NC*C*H_3), 20.4 and 19.8

(both s, PCH*C*H$_3$), 18.4 (s, NC*C*H$_3$). ^{1}H NMR (300 MHz, C_7D_8, 233 K): δ 7.5−6.8 (m, 10H, Ph), 2.56 and 2.50 (both s, 3H, NCCH$_3$), 2.30 (m, 6H, PC*H*), 1.96 (s, 6H, NC(CH$_3$)$_2$), 1.81 (s, 6H, PCH), 1.2−1.1 (m, 72H, PCHC*H*$_3$), 0.32 and 0.30 (both br s, Os=C=CH), −7.97 and −8.70 (both t, J_{P-H} = 16.6 Hz, 1H, OsH). ^{31}P{^{1}H} NMR (121.42 MHz, C_7D_8, 233 K): δ 23.8 and 23.0 (both s). ^{13}C{^{1}H} NMR (75.42 MHz, C_7D_8, 233 K): δ_286.3 (t, J_{C-P} = 9.8 Hz, Os=C), 285.7 (t, J_{C-P} = 8.3 Hz, Os=C), 140.1 and 140.0 (both s, N=C), 134.6 and 133.7 (both s, C_{ipso}Ph), 122.8, 122.1, 121.4, and 121.3 (all s, Ph), 108.8 and 108.2 (both s, Os=C=*C*HPh), 25.1 (vt, *N* = 23.5 Hz, P*C*H), 23.8 (vt, *N* = 22.6 Hz, P*C*H), 22.7 (s, NC*C*H$_3$), 20.2, 19.5, and 19.4 (all s, PCH*C*H$_3$), 18.3, 18.0, and 16.6 (all s, NC*C*H$_3$). MS (FAB$^+$): *m*/*z* 687 (M$^+$).

The protonation of complex **7** (15 mg, 0.022 mmol) in 0.5 mL of CD_2Cl_2 (^{1}H NMR) or CH_2Cl_2 (^{2}H NMR) in NMR tubes with the stoichiometric amount of DBF_4·D_2O (3 μL, 0.022 mmol) gives the complex [OsH{κ-*N*,κ-*O*[ON=C(CH$_3$)$_2$]}(≡CCH$_2$Ph)(P^{i}Pr$_3$)$_2$]BF$_4$ with the $C_\beta H_2$ group partially deuterated. After 10 min the ^{1}H NMR spectrum indicates that the protonation is quantitative. ^{2}H NMR (46.03 MHz, CH_2Cl_2, 293 K): δ 2.89 (br, 1.7D, CD_2Ph).

Preparation of OsH{κ-*N*,κ-*O*[ON=C(CH$_3$)$_2$]}(=C=CH-Cy)(P^{i}Pr$_3$)$_2$ (8). This complex was prepared as described for **7** starting from **5** (83 mg, 0.106 mmol) and a solution of KOH in methanol (1.1 mL, 0.212 mmol, 0.1888 N). A brown oil was obtained. Yield: 30.0 mg (41%). IR (Nujol, cm^{-1}): ν(OsH) 2091 (m), ν(CN) 1631 (s). ^{1}H NMR (300 MHz, C_6D_6, 293 K, plus hetcor): δ 2.65 (m, 6H, PC*H*), 2.6−0.9 (m, 11H, Cy), 2.10 and 1.98 (both s, 3H, NC(CH$_3$)$_2$), 1.42 and 1.36 (both dvt, *N* = 12.9 Hz, J_{H-H} = 6.6 Hz, 18H, PCHC*H*$_3$), 0.98 (s, 1H, Os=C=CH), −8.49 (t, J_{H-P} = 17.4 Hz, 1H, OsH). ^{31}P{^{1}H} NMR (121.42 MHz, C_6D_6, 293 K): δ 22.26 (s). ^{13}C{^{1}H} NMR (75.42 MHz, C_6D_6, 293 K, plus dept): δ 284.7 (t, J_{C-P} = 9.8 Hz, Os=C), 138.7 (s, N=C), 110.0 (s, Os=C=*C*HCy), 30.0 (s, primary carbon atom of the cyclohexyl group), 38.4, 27.3, and 26.8 (all s, secondary carbon atoms of the cyclohexyl group), 24.4 (vt, *N* = 23.3 Hz, P*C*H), 22.3 (s, NC*C*H$_3$), 20.1 and 19.8 (both s, PCH*C*H$_3$), 18.1 (s, NC*C*H$_3$). MS (FAB$^+$): *m*/*z* 694 (M$^+$ + H).

Preparation of OsH{κ-*N*,κ-*O*[ON=C(CH$_3$)$_2$]}(=C=CH-^{t}Bu)(P^{i}Pr$_3$)$_2$ (9). This complex was prepared as described for **7** starting from **6** (210 mg, 0.279 mmol) and a solution of KOH in methanol (2.9 mL, 0.558 mmol, 0.1888 N). A yellow solid was obtained. Yield: 90.0 mg (48%). Anal. Calcd for $C_{27}H_{59}NOOsP_2$: C 48.70; H 8.93; N 2.10. Found: C 48.35; H 8.67; N 2.28. IR (KBr, cm^{-1}): ν(OsH) 2080 (m), ν(CN) 1628 (s). ^{1}H NMR (300 MHz, C_6D_6, 293 K, plus hetcor): δ 2.67 (m, 6H, PC*H*), 2.11 and 2.01 (both s, 3H, NCCH$_3$), 1.43 (dvt, *N* = 12.7 Hz, J_{H-H} = 6.6 Hz, 18H, PCHC*H*$_3$), 1.41 (s, 9H, C(CH$_3$)$_3$), 1.34 (dvt, *N* = 12.7 Hz, J_{H-H} = 6.6 Hz, 18H, PCHC*H*$_3$), 0.71 (s, 1H, Os=C=CH), −8.70 (t, J_{H-P} = 17.3 Hz, 1H, OsH). ^{31}P{^{1}H} NMR (121.42 MHz, C_6D_6, 293 K): δ 20.65 (s). ^{13}C{^{1}H} NMR (75.42 MHz, C_6D_6, 293 K, plus apt): δ 284.1 (t, J_{C-P} = 8.3 Hz, Os=C), 139.1 (s, N=C), 115.9 (s, Os=C=*C*H^{t}Bu), 33.7 (s, C(*C*H$_3$)$_3$), 24.6 (s, *C*(CH$_3$)$_3$), 24.4 (vt, *N* = 23.0 Hz, P*C*H), 22.4 (s, NC*C*H$_3$), 20.3 and 19.9 (both s, PCH*C*H$_3$), 18.4 (s, NC*C*H$_3$). ^{1}H NMR (300 MHz, C_7D_8, 218 K): δ 2.55 and 2.47 (both m, 6H, PC*H*), 2.00 (s, 6H, NC(CH$_3$)$_2$), 1.94 and 1.79 (both s, 3H, NCCH$_3$), 1.39 (s, 9H, C(CH$_3$)$_3$) 1.4−1.1 (m, 72H, PCHC*H*$_3$), 1.2 (s, 9H, C(CH$_3$)$_3$), 1.41 (s, 9H, C(CH$_3$)$_3$), 0.71 and 0.66 (both s, 1H, Os=C=CH), −8.49 (t, J_{H-P} = 16.5 Hz, 1H, OsH), −8.96 (t, J_{H-P} = 18.0 Hz, 1H, OsH). ^{31}P{^{1}H} NMR (121.42 MHz, C_7D_8, 218 K): δ 21.5 and 18.4 (both s). ^{13}C{^{1}H} NMR (75.42 MHz, C_7D_8, 218 K): δ 284.2 (t, J_{C-P} = 10.5 Hz, Os=C), 283.6 (t, J_{C-P} = 7.9 Hz, Os=C),139.3 and 139.1 (both s, N=C), 116.2 and 114.5 (both s, Os=C=*C*H^{t}Bu), 33.8 and 33.5 (both s, C(*C*H$_3$)$_3$), 24.9 and 24.6 (both s, *C*(CH$_3$)$_3$), 24.4 and 23.9 (both vt, *N* = 26.3 Hz, P*C*H), 22.9 and 22.5 (both s, NC*C*H$_3$), 20.3, 19.6, and 19.1 (all s, PCH*C*H$_3$), 18.3 and 17.9 (both s, NC*C*H$_3$). MS (FAB$^+$): *m*/*z* 668 (M$^+$ + H).

Preparation of [OsH{F---HON=C(CH$_3$)$_2$}(≡CCH$_2$Ph)(P^{i}Pr$_3$)$_2$]BF$_4$ (10). A lilac solution of **4** (142 mg, 0.183 mmol) in 12 mL of dichloromethane was treated with HBF_4·Et_2O (30 μL, 0.220 mmol) and stirred for 2.5 h at room temperature and then was filtered through Celite and evaporated to dryness. Subsequent addition of dichloromethane (0.5 mL) and diethyl ether (5 mL) caused the precipitation of a lilac solid, which was washed with further portions of diethyl ether and dried in vacuo. Yield: 90 mg (62%). Anal. Calcd for $C_{27}H_{61}BF_5NOOsP_2$: C 41.91; H 7.95; N 1.81. Found: C 41.57; H 7.78; N 2.0. IR (KBr, cm^{-1}): ν(OH) 3210 (br), ν(OsH) 2174 (m), ν(CN) 1580 (s), ν(BF) 1050 (br). ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ 11.59 (d, J_{F-H} = 67.5 Hz, 1H, OH), 7.4−7.1 (m, 5H, Ph), 2.88 (br, 2H, Os≡CC*H*$_2$), 2.49 and 2.32 (both s, 3H, NCCH$_3$), 2.31 (m, 6H, PC*H*), 1.29 and 1.25 (both dvt, *N* = 14.4 Hz, J_{H-H} = 7.2 Hz, 18H, PCHC*H*$_3$), −6.66 (td, J_{P-H} = 16.5 Hz, J_{F-H} = 6.9 Hz, 1H, OsH). ^{31}P{^{1}H} NMR (121.42 MHz, CD_2Cl_2, 293 K): δ 36.62 (d, J_{F-P} = 39.0 Hz). ^{19}F NMR (282.33 MHz, CD_2Cl_2, 293 K): δ −263.9 (dtd, J_{F-H} = 67.5 Hz, J_{F-P} = 39.0 Hz, J_{F-H} = 6.9 Hz, OsF), −154.6 (s, BF_4). ^{13}C{^{1}H} NMR (75.42 MHz, CD_2Cl_2, 293 K, plus dept): δ 277.9 (dt, J_{C-F} = 109.5 Hz, J_{C-P} = 9.2 Hz, Os≡C), 163.3 (s, N=C), 129.9 and 129.6 (both s, Ph), 129.1 (s, C_{para}Ph), 127.4 (s, C_{ipso}Ph), 57.9 (d, J_{C-F} = 11.5 Hz, Os≡*C*CH$_2$), 26.0 (s, NC*C*H$_3$), 25.4 (vt, *N* = 26.2 Hz, P*C*H), 19.8 (s, NC*C*H$_3$), 19.1 and 18.7 (both s, PCH*C*H$_3$). MS (FAB$^+$): *m*/*z* 689 (M$^+$ − F).

Preparation of [OsH{F---DON=C(CH$_3$)$_2$}(≡CCH$_2$Ph)(P^{i}Pr$_3$)$_2$]BF$_4$ (10-d$_1$). To solutions of **4** (15 mg, 0.019 mmol) in 0.5 mL of CD_2Cl_2 (^{1}H NMR) or CH_2Cl_2 (^{2}H NMR) in NMR tubes was added the stoichiometric amount of DBF_4·D_2O (2.5 mL, 0.019 mmol). After 10 min the ^{1}H NMR spectrum indicates the quantitative formation of **10-d$_1$**. ^{2}H NMR (46.03 MHz, CH_2Cl_2, 293 K): δ 11.90 (d, J_{D-F} = 10 Hz, OD).

Preparation of [OsH{F---HON=C(CH$_3$)$_2$}(≡CCH$_2$Cy)(P^{i}Pr$_3$)$_2$]BF$_4$ (11). This complex was prepared as described for **10** starting from 116 mg (0.148 mmol) of **5** and HBF_4·Et_2O (24 μL, 0.178 mmol). A white solid was obtained. Yield: 102 mg (86%). Anal. Calcd for $C_{29}H_{63}BF_5NOOsP_2$: C 43.55; H 7.94; N 1.75. Found: C 43.08; H 7.81; N 1.96. IR (KBr, cm^{-1}): ν(OH) 3186 (br), ν(OsH) 2183 (m), ν(CN) 1654 (s), ν(BF) 1050 (br). ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ 11.68 (d, J_{F-H} = 68.1 Hz, 1H, OH), 3.5−0.9 (m, 11H, Cy), 2.47 (m, 6H, PC*H*), 2.43 and 2.32 (both s, 3H, NCCH$_3$), 1.54 (br, 2H, Os≡CC*H*$_2$), 1.35 and 1.34 (both dvt, *N* = 14.2 Hz, J_{H-H} = 7.0 Hz, 18H, PCHC*H*$_3$), −6.98 (td, J_{P-H} = 17.1 Hz, J_{F-H} = 6.6 Hz, 1H, OsH). ^{31}P{^{1}H} NMR (121.42 MHz, CD_2Cl_2, 293 K): δ 35.90 (d, J_{F-P} = 38.1 Hz). ^{19}F NMR (282.33 MHz, CD_2Cl_2, 293 K): δ −265.9 (dtd, J_{F-H} = 68.1 Hz, J_{F-P} = 38.1 Hz, J_{F-H} = 6.6 Hz, OsF), −155.2 (s, BF_4). ^{13}C{^{1}H} NMR (75.42 MHz, CD_2Cl_2, 293 K, plus dept): δ 283.9 (dt, J_{C-F} = 109.1 Hz, J_{C-P} = 8.7 Hz, Os≡C), 163.3 (s, N=C), 59.3 (d, J_{C-F} = 10.6 Hz, Os≡*C*CH$_2$), 35.2 (s, primary carbon atom of the cyclohexyl group), 33.6, 25.8, and 25.6 (all s, secondary carbon atoms of the cyclohexyl group), 25.6 (vt, *N* = 24.4 Hz, P*C*H), 25.4 and 19.9 (both s, NC*C*H$_3$), 19.3 and 18.7 (both s, PCH*C*H$_3$). MS (FAB$^+$): *m*/*z* 694 (M$^+$ − HF).

Preparation of [OsH{F---HON=C(CH$_3$)$_2$}(≡CCH$_2$^{t}Bu)(P^{i}Pr$_3$)$_2$]BF$_4$ (12). This complex was prepared as described for **10** starting from 115 mg (0.152 mmol) of **6** and HBF_4·Et_2O (25 μL, 0.183 mmol). A white solid was obtained.Yield: 55.9 mg (66%). Anal. Calcd for $C_{27}H_{61}BF_5NOOsP_2$: C 41.91; H 7.95; N 1.81. Found: C 41.57; H 7.78; N 2.00. IR (KBr, cm^{-1}): ν(OH) 3218 (br), ν(OsH) 2176 (m), ν(CN) 1578 (s), ν(BF) 1050 (br). ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ 11.64 (d, J_{F-H} = 68.7 Hz, 1H, OH), 2.48 (m, 6H, PC*H*), 2.45 and 2.32 (both s, 3H, NCCH$_3$), 1.69 (br, 2H, Os≡CCH$_2$), 1.35 (dvt, *N* = 14.1 Hz, J_{H-H} = 7.0 Hz, 36H, PCHC*H*$_3$), 1.04 (s, 9H, C(CH$_3$)$_3$), −7.07 (td, J_{P-H} = 18.0 Hz, J_{F-H} = 6.6 Hz, 1H, OsH). ^{31}P{^{1}H} NMR (121.42 MHz, CD_2Cl_2, 293 K): δ 33.97 (d, J_{F-P} = 39.0 Hz). ^{19}F NMR

Table 4. Crystallographic Data and Structure Refinement for $[OsH\{\kappa\text{-}N,\kappa\text{-}O[ON{=}C(CH_3)_2]\}(\equiv CCH_2Ph)(P^iPr_3)_2]BF_4$ (4), $OsH\{\kappa\text{-}N,\kappa\text{-}O[ON{=}C(CH_3)_2]\}(=C{=}CHPh)(P^iPr_3)_2$ (7), and $[OsH\{F\text{---}HON{=}C(CH_3)_2\}(\equiv CCH_2Cy)(P^iPr_3)_2]BF_4$ (11)

	4	**7**	**11**
formula	$C_{29}H_{56}BF_4NOOsP_2$	$C_{29}H_{55}NOOsP_2$	$C_{29}H_{63}BF_5NOOsP_2$
M	773.70	685.88	799.75
space group	monoclinic, $P2_1/c$	triclinic, $P\bar{1}$	monoclinic, $C2/c$
a, Å	11.539(2)	10.385(2)	19.6481(11)
b, Å	11.930(2)	10.9978(19)	12.8849(11)
c, Å	25.261(4)	13.967(3)	28.644(2)
α, deg	90	97.471(4)	90
β, deg	96.029(3)	95.572(4)	91.301(2)
γ, deg	90	93.851(3)	90
V, Å^3	3458.2(9)	1569.1(5)	7249.7(9)
Z	4	2	8
ρ_{calc}, g cm^{-3}	1.486	1.452	1.465
T, K	296.0(2)	173.0(2)	173.0(2)
μ, mm^{-1}	3.823	4.186	3.654
2θ range data collect, deg	4−56	4−56	4−56
index ranges	h: −15, 14; k: −15, 15; l: −32, 33	h: −13, 13; k: −14, 14; l: −18, 18	h: −26, 20; k: −17, 17; l: −38, 38
no. of measd reflns	28 542	19 579	28 069
no. of data/params/restraints	8299/357/3	7496/329/0	8715/388/0
$R(F)$ $[F^2 > 2\sigma(F^2)]$[a]	0.0536	0.0468	0.0356
$wR(F^2)$ [all data][b]	0.0964[c]	0.1110[c]	0.0573[c]
S [all data][d]	0.794	0.956	0.773

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR(F^2) = (\sum[w(F_o^2 - F_c^2)^2/\sum[w(F_o^2)^2])^{1/2}$. [c] $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ with $P = (F_o^2 + 2F_c^2)/3$; $a = 0.0198$ and $b = 0$ for **4**, and $a = 0.0613$ and $b = 0$ for **7**, and a = 0.0107 and $b = 0$ for **11**. [d] $S = [\sum(F_o^2 - F_c^2)^2]/(n - p)$, n = number of reflections, p = number of parameters.

(282.33 MHz, CD_2Cl_2, 293 K): δ −261.1 (dtd, $J_{F-H} = 68.7$ Hz, $J_{F-P} = 39.0$ Hz, $J_{F-H} = 6.6$ Hz, OsF), −155.3 (s, BF_4). $^{13}C\{^1H\}$ NMR (75.42 MHz, CD_2Cl_2, 253 K): δ 284.1 (dt, $J_{C-F} = 111.6$ Hz, $J_{C-P} = 7.5$ Hz, Os≡C), 163.0 (s, N=C), 65.2 (d, $J_{C-F} = 9.6$ Hz, Os≡C*C*H_2), 32.3 (s, *C*$(CH_3)_3$), 30.0 (s, C(*C*$H_3)_3$), 25.2 (vt, $N = 25.1$ Hz, P*C*H), 25.1 and 20.1 (both s, NC*C*H_3), 19.3 and 18.5 (both s, PCH*C*H_3). MS (FAB$^+$): m/z 668 (M^+ − HF).

X-ray Structure Analysis of Complexes 4, 7, and 11. A summary of crystal data and refinement parameters for **4**, **7**, and **11** is given in Table 4. Suitable crystals for X-ray diffraction were obtained by slow diffusion of diethyl ether into a saturated solution of **4** and **11** in CH_2Cl_2, or methanol into a saturated solution of **7** in toluene. Diffraction data were recorded at room temperature (**4**) or 173(2) K (**7** and **11**) on a Bruker Smart Apex diffractometer with a CCD area detector, using graphite-monocromated Mo Kα radiation ($\lambda = 0.71073$ Å) operating at 50 kV, 35 mA for **4** and **11** or 50 kV, 40 mA for **7**. Frames of data were collected over a hemisphere for **4** and **11** or over the complete sphere for **7** with scan widths of 0.3° in ω and exposure times of 10 s/frame.

Data were corrected for absorption with the SADABS routine, based on the method of Blessing,[45] integrated in the Bruker SAINT program.[46] The structures were solved by the Patterson method (SHELXS97[47]) and difference Fourier techniques and refined by full-matrix least-squares on F^2 (SHELXL97[47]) first with isotropic and then with anisotropic displacement parameters for the non-hydrogen atoms of non-disordered groups. Organic hydrogen atoms were introduced in calculated positions or located in a difference Fourier map and refined riding on the corresponding carbon atoms. Hydride ligands were refined as free isotropic atoms. Scattering factors corrected for anomalous dispersion were as implemented in the refinement program.

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Supporting Information Available: Tables of positional and displacement parameters, crystallographic data, and bond lengths and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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