Reactions of Elongated Dihydrogen-Osmium Complexes Containing Orthometalated Ketones with Alkynes: Hydride-Vinylidene-π-Alkyne versus Hydride-Osmacyclopropene

Pilar Barrio, Miguel A. Esteruelas,* and Enrique Oñate

Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC, 50009 Zaragoza, Spain

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The trihydride complex $OsH_3\{C_6F_4C(O)CH_3\}(P^iPr_3)_2$ (**1**) reacts with $HBF_4{\cdot}H_2O$ to give the elongated dihydrogen derivative $[Os\{C_6F_4C(O)CH_3\}(\eta^2\text{-}H_2)(H_2O)(P^iPr_3)_2]BF_4$ (**2**), with a separation between the hydrogen atoms of the elongated dihydrogen of about 1.3 Å. Under one atmosphere of acetylene, complex **2** and the related $[Os\{C_6H_4C(O)CH_3\}(\eta^2\text{-}H_2)(H_2O)(P^iPr_3)_2]BF_4$ (**3**) afford the hydride-vinylidene-π-alkyne derivative $[OsH(=C=CH_2)(\eta^2\text{-}HC\equiv CH)(P^iPr_3)_2]BF_4$ (**4**), with the alkyne acting as a four-electron donor ligand. Complex **4** reacts with methylmagnesium chloride and acetone oxime. The first reaction gives the allyl derivative $OsH(\eta^3\text{-}C_3H_5)(=C=CH_2)(P^iPr_3)_2$ (**5**), whereas the second one affords the oximate-carbyne $[OsH\{\kappa\text{-}N,\kappa\text{-}O[ON=C(CH_3)_2]\}(\equiv CCH_3)(P^iPr_3)_2]BF_4$ (**6**). Similarly to acetylene, cyclohexylacetylene reacts with **2** and **3** to give $[OsH(=C=CHCy)(\eta^2\text{-}HC\equiv CCy)(P^iPr_3)_2]BF_4$ (**7**), which in solution at room temperature decomposes to a mixture of unidentified products. Complexes **2** and **3** also react with phenylacetylene. The reactions lead to complex mixtures of products containing $[OsH(=C=CHPh)(\eta^2\text{-}HC\equiv CPh)(P^iPr_3)_2]BF_4$ (**8**) and $[OsH\{C_6X_4C(O)CH_3\}\{C(Ph)CH_2\}(P^iPr_3)_2]BF_4$ (X = F (**9**), H (**11**)), as main components. In solution at room temperature, complex **8** evolves into the diphenylbutadiene derivative $[OsH(\eta^4\text{-}C_4H_4Ph_2)\{[\eta^2\text{-}CH_2=C(CH_3)]P^iPr_2\}(P^iPr_2{}^nPr)]BF_4$ (**10**). Complex **11** reacts with acetophenone to afford $[OsH\{C_6H_4C(O)CH_3\}_2(P^iPr_3)_2]BF_4$ (**12**). The X-ray structures of **4**, **9**, and **10** are also reported.

Introduction

The 1984 Kubas report of the molecular hydrogen complex[1] has revived the interest in the organometallic chemistry of the transition-metal hydride complexes, during the last years.[2] Within this field, the reactions with terminal alkynes have played a predominant role.[3] Until 1993, the observed products were in general alkenyl derivatives, resulting of the addition of the M−H bond to the C−C triple bond of the alkyne.[4]

In 1993, we observed that, in contrast to the general trend, the dihydride-dichloro complex $OsH_2Cl_2(P^iPr_3)_2$ reacts with terminal alkynes to afford hydride-carbyne derivatives of the type $OsHCl_2(\equiv CCH_2R)(P^iPr_3)_2$.[5] It was proposed that the reason for this unusual finding was the tendency shown by the starting dihydride to form dihydrogen complexes.[6] In subsequent years, we have shown that the reactions of transition-metal hydride complexes with terminal alkynes can afford a wide range of organometallic compounds. The nature of the products depends on all the factors related to the

* Corresponding author. E-mail: maester@posta.unizar.es. Fax: 34 976761187.

(1) Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, H. J. *J. Am. Chem. Soc.* **1984**, *106*, 451.

(2) (a) Kubas, G. J. *Metal Dihydrogen and σ-Bond Complexes*; Kluwer Academic/Plenum Publishers: New York, 2001. (b) Peruzzini, M.; Poli, R. *Recent Advances in Hydride Chemistry*; Elsevier: Amsterdam, 2001.

(3) See for example: (a) Grünwald, C.; Gevert, O.; Wolf, J.; González-Herrero, P.; Werner, H. *Organometallics* **1996**, *15*, 1960. (b) Wilhelm, T. E.; Belderrain, T. R.; Brown, S. N.; Grubbs, R. H. *Organometallics* **1997**, *16*, 3867. (c) Wolf, J.; Stüer, W.; Grünwald, C.; Gevert, O.; Laubender, M.; Werner, H. *Eur. J. Inorg. Chem.* **1998**, 1827. (d) Wolf, J.; Stüer, W.; Grünwald, C.; Werner, H.; Schwab, P.; Schulz, M. *Angew. Chem., Int. Ed.* **1998**, *37*, 1124. (e) Stüer, W.; Wolf, J.; Werner, H.; Schwab, P.; Schulz, M. *Angew. Chem., Int. Ed.* **1998**, *37*, 3421. (f) Huang, D.; Oliván, M.; Huffman, J. C.; Eisenstein, O.; Caulton, K. G. *Organometallics* **1998**, *17*, 4700. (g) Yasuda, T.; Fukuoka, A.; Hirano, M.; Komiya, S. *Chem. Lett.* **1998**, 29. (h) Lough, A. J.; Morris, R. H.; Ricciuto, L.; Schleis, T. *Inorg. Chim. Acta* **1998**, *270*, 238. (i) Xia, H. P.; Yeung, R. C. Y.; Jia, G. *Organometallics* **1998**, *17*, 4762. (j) Werner, H.; Jung, S.; Weberndörfer, B.; Wolf, J. *Eur. J. Inorg. Chem.* **1999**, 951. (k) Mulford, D. R.; Clark, J. R.; Schweiger, S. W.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1999**, *18*, 4448. (l) Yi, C. S.; Lee, D. W.; Chen, Y. *Organometallics* **1999**, *18*, 2043. (m) Tsai, Y.-C.; Diaconescu, P. L.; Cummins, C. C. *Organometallics* **2000**, *19*, 5260. (n) Wen, T. B.; Zhou, Z. Y.; Lau, C.-P.; Jia, G. *Organometallics* **2000**, *19*, 3466. (o) Yang, S. Y.; Wen, T. B.; Jia, G.; Lin, Z. *Organometallics* **2000**, *19*, 5477. (p) Yao, J.; Wong, W. T.; Jia, G. *J. Organomet. Chem.* **2000**, *598*, 228. (q) Cabeza, J. A.; Grepioni, F.; Llamazares, A.; Riera, V.; Trivedi, R. *Eur. J. Inorg. Chem.* **2000**, 1693. (r) Albertin, G.; Antoniutti, S.; Bordignon, E.; Pegoraro, M. *J. Chem. Soc., Dalton Trans.* **2000**, 3575. (s) Ara, I.; Berenguer, J. R.; Eguizábal, E.; Forniés, J.; Gómez, J.; Lalinde, E.; Sáez-Rocher, J. M. *Organometallics* **2000**, *19*, 4385. (t) Trebbe, R.; Schager, F.; Goddard, R.; Pörschke, K.-R. *Organometallics* **2000**, *19*, 521. (u) Cabeza, J. A.; Grepioni, F.; Moreno, M.; Riera, V. *Organometallics* **2000**, *19*, 5424. (v) Selmeczy, A. D.; Jones, W. D. *Inorg. Chim. Acta* **2000**, *300−302*, 138. (w) Marchenko, A. V.; Gérard, H.; Eisenstein, O.; Caulton, K. G. *New J. Chem.* **2001**, *25*, 1244. (x) O'Connor, J. M.; Closson, A.; Hiibner, K.; Merwin, R.; Gantzel, P.; Roddick, D. M. *Organometallics* **2001**, *20*, 3710. (y) Esteruelas, M. A.; Herrero, J.; López, A. M.; Oliván, M. *Organometallics* **2001**, *20*, 3202. (z) Rourke, J. P.; Stringer, G.; Chow, P.; Deeth, R. J.; Yufit, D. S.; Howard, J. A. K.; Marder, T. B. *Organometallics* **2002**, *21*, 429.

(4) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*; J. Wiley and Sons: New York, 1988; Chapter 7, pp 142−162.

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

(6) (a) Esteruelas, M. A.; Oro, L. A.; Ruiz, N. *Inorg. Chem.* **1993**, *32*, 3793. (b) Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A.; Oñate, E.; Ruiz, N. *Inorg. Chem.* **1994**, *33*, 787. (c) Barea, G.; Esteruelas, M. A.; Lledós, A.; López, A. M.; Tolosa, J. I. *Inorg. Chem.* **1998**, *37*, 5033.

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electronic structure of the starting material and even on the electronic nature of the substituent, R, of the alkyne.[7]

The electronic structure of the starting material has a marked influence on the interactions within the M−H_2 units. The character of the dihydride, elongated dihydrogen, or dihydrogen seems to determine the nature of the product. For example, in contrast to the dihydride $OsH_2Cl_2(P^iPr_3)_2$, the elongated dihydrogen $OsCl_2(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2$ reacts with terminal alkynes to give carbene derivatives of the type $OsCl_2(=CHCH_2R)(CO)(P^iPr_3)_2$,[8] while the reaction of the ruthenium dihydrogen complex $[Ru(\eta^5\text{-}C_5H_5)(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2]^+$ with 1,1-diphenyl-2-propyn-1-ol affords the allenylidene $[Ru(\eta^5\text{-}C_5H_5)(=C=C=CPh_2)(CO)(P^iPr_3)]^+$ via a hydroxyvinylidene intermediate.[9]

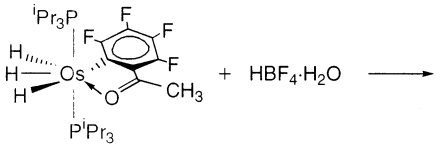
The character of the MH_2 units is not the sole factor determining the nature of the products. We have recently reported that, in contrast to $OsCl_2(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2$, the cationic elongated dihydrogen $[Os\{C_6H_4C(O)CH_3\}(\eta^2\text{-}H_2)\{N(OH)=C(CH_3)_2\}(P^iPr_3)_2]^+$ reacts with terminal alkynes to give the hydride-carbyne derivatives $[OsH\{\kappa\text{-}N,\kappa\text{-}O[ON=C(CH_3)_2]\}(\equiv CCH_2R)(P^iPr_3)_2]^+$, related to those obtained with $OsH_2Cl_2(P^iPr_3)_2$. Deuterium labeling experiments indicate that these reactions involve the initial elimination of acetophenone. The transformation alkyne-carbyne occurs, via a hydride-π-alkyne intermediate, in two dissociation−addition processes, where the oxime plays a main role.[10]

Osmium-hydride complexes have shown to be useful templates to carbon−carbon and carbon−heteroatom coupling reactions.[11] In the absence of oxime, the elimination of the ketone should provide a highly unsaturated system, which could coordinate several alkyne molecules, the first step for their subsequent coupling. Our interest in the use of osmium complexes as templates to carbon−carbon and carbon−heteroatom coupling reactions prompted us to eliminate the interference of the oxime, and our interest in learning to rationalize the reactivity of the hydride complex toward alkynes prompted us to investigate the behavior of the water complex $Os\{C_6H_4C(O)CH_3\}(\eta^2\text{-}H_2)(H_2O)(P^iPr_3)_2]BF_4$ in the presence of acetylene, cyclohexylacetylene, and phenylacetylene. Furthermore, to know the influence of the substituents of the metalated phenyl ring of the ketone on the stability of the starting complex and the resulting products, we have prepared the related elongated dihydrogen complex $[Os\{C_6F_4C(O)CH_3\}(\eta^2\text{-}H_2)(H_2O)(P^iPr_3)_2]BF_4$, and we have studied its reactivity toward the above-mentioned alkynes.

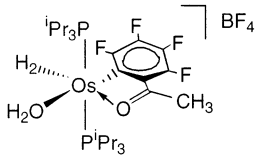
In this paper, we show (i) new reactions, (ii) the preparation and characterization of new organometallic compounds, (iii) the influence of the steric hindrance of the substituent, R, of the alkyne on the stability of the obtained complexes, and (iv) the characterization of some of the decomposition products from the latter species.

Results and Discussion

1. Preparation and Characterization of $[Os\{C_6F_4C(O)CH_3\}(\eta^2\text{-}H_2)(H_2O)(P^iPr_3)_2]BF_4$. Treatment at room temperature of the trihydride $OsH_3\{C_6F_4C(O)CH_3\}(P^iPr_3)_2$ (**1**) in dichloromethane with 1.2 equiv of $HBF_4{\cdot}H_2O$ affords the cationic elongated dihydrogen derivative $Os\{C_6F_4C(O)CH_3\}(\eta^2\text{-}H_2)(H_2O)(P^iPr_3)_2]BF_4$ (**2**), as a result of the protonation of one of the hydride ligands of **1** and the coordination of the water molecule. Complex **2** was isolated as an orange solid in 82% yield, according to eq 1.



(**1**)



(1)

(**2**)

The presence of the water ligand in **2** is strongly supported by its IR and ^1H NMR spectra. The IR spectrum in KBr shows a strong ν(OH) band at 3362 cm^{-1}, whereas the ^1H NMR spectrum in dichloromethane-d_2 contains a broad singlet at 4.38 ppm, characteristic of a coordinated water molecule. In the high-field region of the spectrum, the hydrogen atoms bonded to the metal display a triplet at −6.63 ppm with a H−P coupling constant of 8.4 Hz. A variable-temperature 300 MHz T_1 study of this peak gives a T_1(min) of 40 ± 1 ms at 213 K. The treatment of **2** with methanol-

(7) (a) Espuelas, J.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A.; Valero, C. *Organometallics* **1993**, *12*, 663. (b) Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A.; Zeier, B. *Organometallics* **1994**, *13*, 1662. (c) Esteruelas, M. A.; Oro, L. A.; Ruiz, N. *Organometallics* **1994**, *13*, 1507. (d) Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A.; Zeier, B. *Organometallics* **1994**, *13*, 4258. (e) Esteruelas, M. A.; Oro, L. A.; Valero, C. *Organometallics* **1995**, *14*, 3596. (f) Esteruelas, M. A.; Oliván, M.; Oro, L. A. *Organometallics* **1996**, *15*, 814. (g) Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A.; Rodriguez, L. *Organometallics* **1996**, *15*, 3670. (h) Bourgault, M.; Castillo, A.; Esteruelas, M. A.; Oñate, E.; Ruiz, N. *Organometallics* **1997**, *16*, 636. (i) Edwards, A. J.; Elipe, S.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A.; Valero, C. *Organometallics* **1997**, *16*, 3828. (j) Buil, M. L.; Elipe, S.; Esteruelas, M. A.; Oñate, E.; Peinado, E.; Ruiz, N. *Organometallics* **1997**, *16*, 5748. (k) Bohanna, C.; Callejas, B.; Edwards, A. J.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A.; Ruiz, N.; Valero, C. *Organometallics* **1998**, *17*, 373. (l) Crochet, P.; Esteruelas, M. A.; López, A. M.; Martínez, M.-P.; Oliván, M.; Oñate, E.; Ruiz, N. *Organometallics* **1998**, *17*, 4500. (m) Buil, M. L.; Eisenstein, O.; Esteruelas, M. A.; García-Yebra, C.; Gutiérrez-Puebla, E.; Oliván, M.; Oñate, E.; Ruiz, M.; Tajada, M. A. *Organometallics* **1999**, *18*, 4949. (n) Buil, M. L.; Esteruelas, M. A. *Organometallics* **1999**, *18*, 1798. (o) Esteruelas, M. A.; García-Yebra, C.; Oliván, M.; Oñate, E.; Tajada, M. A. *Organometallics* **2000**, *19*, 5098. (p) Buil, M. L.; Esteruelas, M. A.; García-Yebra, C.; Gutiérrez-Puebla, E.; Oliván, M. *Organometallics* **2000**, *19*, 2184. (q) Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2000**, *19*, 5454. (r) Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2001**, *20*, 3283.

(8) Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A.; Valero, C.; Zeier, B. *J. Am. Chem. Soc.* **1995**, *117*, 7935.

(9) Esteruelas, M. A.; Gómez, A. V.; Lahoz, F. J.; López, A. M.; Oñate, E.; Oro, L. A. *Organometallics* **1996**, *15*, 3423.

(10) Barrio, P.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2002**, *21*, 2491.

(11) Esteruelas, M. A.; López, A. M. Ruthenium- and Osmium-hydride compounds containing triisopropylphosphine as precursor for carbon−carbon and carbon-heteroatom coupling reactions. *Recent Advances in Hydride Chemistry*; Elsevier: Amsterdam, 2001; Chapter 7, pp 189−248.

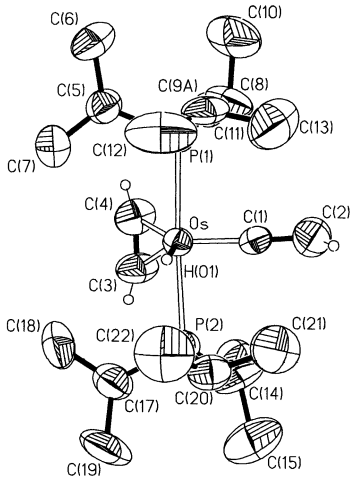
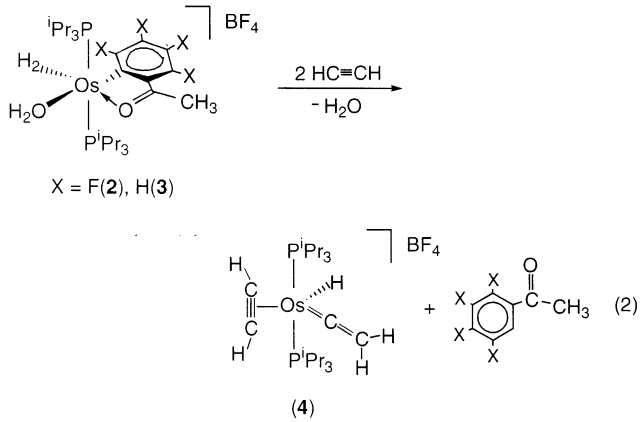


Figure 1. Molecular diagram of the cation of complex $[OsH(=C=CH_2)(\eta^2\text{-}HC\equiv CH)(P^iPr_3)_2]BF_4$ (**4**).

d_4−water-d_2 yields the partially deuterated derivative $[Os\{C_6F_4C(O)CH_3\}(\eta^2\text{-}HD)(D_2O)(P^iPr_3)_2]BF_4$, which has a H−D coupling constant of 3.3 Hz. The T_1(min) and J(H−D) values suggest that the separation between the hydrogen atoms of the dihydrogen ligand is about 1.3 Å.[12]

2. Reactions of $[Os\{C_6X_4C(O)CH_3\}(\eta^2\text{-}H_2)(H_2O)(P^iPr_3)_2]BF_4$ (X = F, H) with Acetylene and Cyclohexylacetylene. In dichloromethane, under 1 atm of acetylene, complexes **2** and $[Os\{C_6H_4C(O)CH_3\}(\eta^2\text{-}H_2)(H_2O)(P^iPr_3)_2]BF_4$ (**3**) eliminate the corresponding ketones. The resulting unsaturated metallic fragment coordinates two acetylene molecules to afford the hydride-vinylidene-π-alkyne derivative $[OsH(=C=CH_2)(\eta^2\text{-}HC\equiv CH)(P^iPr_3)_2]BF_4$ (**4**), which was isolated as a yellow solid in about 70% yield, according to eq 2.



Complex **4** is notable, not only because it is an isolated rare example of a five-coordinate cationic hydride-vinylidene compound but also because, as far as we know, species containing at the same time hydride, vinylidene, and π-acetylene ligands are not known. Figure 1 shows a view of the molecular geometry of the cation of **4**. Selected bond distances and angles are listed in Table 1.

Table 1. Selected Bond Distances (Å) and Angles (deg) for the Complex $[OsH(=C=CH_2)(\eta^2\text{-}C_2H_2)(P^iPr_3)_2]BF_4$ (4)

Os−P(1)	2.398(2)	C(1)−C(2)	1.320(13)
Os−P(2)	2.400(2)	C(3)−C(4)	1.230(12)
Os−C(1)	1.774(8)		
Os−C(3)	2.022(10)		
Os−C(4)	2.035(10)		
P(1)−Os−P(2)	155.39(7)	C(1)−Os−M[a]	124.3(4)
P(1)−Os−C(1)	87.8(2)	C(1)−Os−H(01)	95.0(18)
P(1)−Os−M[a]	101.2(3)	M−Os−H(01)[a]	139(2)
P(1)−Os−H(01)	90.3(19)	Os−C(1)−C(2)	169.7(9)
P(2)−Os−C(1)	87.7(2)	Os−C(3)−C(4)	72.9(7)
P(2)−Os−M[a]	101.3(3)	Os−C(4)−C(3)	71.8(7)
P(2)−Os−H(01)	66.0(19)		

[a] M is the midpoint of the C(3)−C(4) bond.

The geometry around the osmium atom can be described as a distorted trigonal bipyramid with apical phosphines (P(1)−Os−P(2) = 155.39(7)°) and inequivalent angles within the Y-shaped equatorial plane (H(01)−Os−M = 139(2)°, H(01)−Os−C(1) = 95.0(14)°, and C(1)−Os−M = 124.3(4)°).[13] The strong deviation of the P(1)−Os−P(2) angle from the ideal value of 180° is most probably a result of the large steric hindrance that occurs between the phosphines and the alkyne. The acetylene lies parallel to the phosphorus−phosphorus vector; the angle between the P(1)−P(2) and C(3)−C(4) vectors is 0.9°.

The alkyne coordinates to the osmium atom in a symmetrical fashion with statistically identical Os−C bond lengths of 2.022(10) Å (Os−C(3)) and 2.035(10) Å (Os−C(4)). The coordination does not produce any significant disturbance on the carbon−carbon triple bond. The C(3)−C(4) distance (1.230(12) Å) is statistically identical with the carbon−carbon distance determined for the free acetylene (1.212 Å) by electron diffraction.[14]

It has been shown that for five-coordinate complexes an X ligand with σ-donating and good π-acceptor capabilities favors a square-pyramidal structure with the X ligand *trans* to the empty site. In contrast, an X ligand with σ- and π-donating capabilities stabilizes the trigonal bipyramid, with the X ligand in the foot of the Y.[15]

At first glance, the chemical bonding in transition-metal alkyne complexes can be described in a way similar to that for transition-metal alkene compounds. The bonding is considered to arise from donor−acceptor interactions between the alkyne ligand and the transition metal (**a** and **b** in Figure 2). So, in principle, one should expect for **4** a square-pyramidal arrangement of ligands around the osmium atom, in contrast of that observed in Figure 1.

A major difference between alkene and alkyne complexes is that the alkyne ligand has a second occupied π orbital orthogonal to the MC_2 plane ($\pi_\perp$) which, in some cases, engages in the transition-metal−alkyne bonding (**c** in Figure 2). In that case, the alkyne is a

(12) (a) Earl, K. A.; Jia, G.; Maltby, P. A.; Morris, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 3027. (b) Desrosiers, P. J.; Cai, L.; Lin, Z.; Richards, R.; Halpen, J. *J. Am. Chem. Soc.* **1991**, *113*, 4173. (c) Jessop, P. G.; Morris, R. H. *Coord. Chem. Rev.* **1992**, *121*, 155. (d) Maltby, P. A.; Schlaf, M.; Steinbeck, M.; Lough, A. J.; Morris, R. H.; Klooster, W. T.; Koetzle, T. F.; Srivastava, R. C. *J. Am. Chem. Soc.* **1996**, *118*, 5396.

(13) M = midpoint of the C(3)−C(4) bond.

(14) Simonetta, M.; Gavezzotti, A. In *The Chemistry of the Carbon−Carbon Triple Bond*; Patai, S., Ed.; Wiley and Sons: Chichester, 1978; Chapter 1.

(15) Riehl, J.-F.; Jean, Y.; Eisenstein, O.; Pélissier, M. *Organometallics* **1992**, *11*, 729.

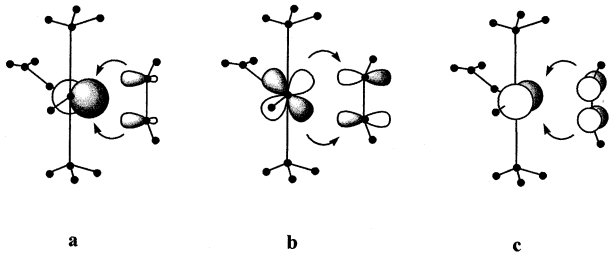


Figure 2. Schematic representation of the donative (**a** and **c**) and back-donative (**b**) interactions for metal−alkyne bonding in complex **4**.

four-electron-donor ligand by means of its $\pi_{\parallel}$ and $\pi_{\perp}$ orbitals; that is, in some cases the alkyne acts as σ- and π-donor. The structure shown in Figure 1 suggests that **4** is one of these cases.

The alkyne acts as an electron acceptor by means of its π^* orbitals, as is supported by the IR spectra of **4** in KBr showing a ν(C≡C) band at 1882 cm^{-1}. The $\pi_{\perp}^*$ orbital is, however, of local a_2 symmetry (within the C_{2v} group), which prevents it from significant interaction with the filled d metal orbital. The only significant interaction involves the acceptor orbital lying in the MC_2 plane ($\pi_{\parallel}^*$ of local b_1 symmetry).[16]

The chemistry of four-electron-donating alkynes has been centered at early transition metals, mainly molybdenum and tungsten. A wide variety of six-coordinate Mo(II) and W(II) complexes with four-electron-donor alkynes have been synthesized.[17] Four-coordinate d^6 complexes of the types ML(alkyne)$_3$[18] and ML$_2$(alkyne)$_2$[19] have been also reported. In contrast, five-coordinate d^6 monoalkyne complexes with the general formula ML$_4$(alkyne)[20] are very scarce. Recently, we have prepared the osmium-cyclopentadienyl derivatives [Os(η^5-C$_5$H$_5$)(η^2-HC≡CR)(P^{i}Pr$_3$)]PF$_6$ (R = C(OH)Ph$_2$, C(OH)Me$_2$).[16]

In the ^{1}H NMR spectrum of **4** in dichloromethane-d_2 at room temperature, the resonance corresponding to the protons of the alkyne appears at 10.17 ppm as the AA′ part of an AA′XX′ spin system. The chemical shift of this resonance agrees well with those found for the cyclopentadienyl complexes [Os(η^5-C$_5$H$_5$)(η^2-HC≡CR)(P^{i}Pr$_3$)]PF$_6$ (δ, 9.43 (R = C(OH)Ph$_2$) and δ, 9.17 (R = C(OH)Me$_2$)), where the alkynes also act as four-electron-donor ligands. These resonances appear strongly shifted toward lower field with respect to the HC≡ resonances observed for the two-electron-donor alkynes of the complexes Os(η^5-C$_5$H$_5$)Cl(η^2-HC≡CR)(P^{i}Pr$_3$) (δ, 4.32 (C(OH)Ph$_2$) and δ, 3.72 (C(OH)Me$_2$)).[16] A similar relationship is observed between ^{13}C{^{1}H} NMR spectra of these compounds. For **4** the acetylenic resonance is observed at 137.3 ppm, in agreement with the chemical shifts observed for the cationic cyclopentadienyl complexes (δ, 179.0 and 182.8 (≡CR) and δ, 146.0 and 143.3 (≡CH)). They are strongly shifted toward lower field with respect to those found for the neutral cyclopentadienyl derivatives (δ, 82.2 and 69.1 (≡CR) and δ, 57.5 and 49.6 (≡CH)).

The vinylidene ligand is bound to the metal in the usual manner, with the CH_2 unit lying in the equatorial plane. A slight bending in the Os−C(1)−C(2) moiety is present (Os−C(1)−C(2) = 169.7(9)°). The Os−C(1) (1.774(8) Å) and C(1)−C(2) (1.320(13) Å) bond lengths compare well with those found in other osmium-vinylidene complexes[21] and support the vinylidene formulation.

The trigonal bipyramid geometry of **4** agrees well with that found in the oximate-vinylidene complex OsH{κ-*N*,κ-*O*[ON=C(CH$_3$)$_2$]}(=C=CHPh)(P^{i}Pr$_3$)$_2$[10] and the calculated one for RuHCl(=C=CH$_2$)(PH$_3$)$_2$.[22] To explain this finding, it has been argued that the vinylidenes are also weak π-donor ligands in the orthogonal plane to the CR_2 plane. The donating properties of π_{CC} disfavor a *trans* relationship of the π-donor and vinylidene ligands since this maximizes the overlaps between the occupied orbitals of the metal and the two ligands.[22,23]

In the ^{1}H NMR spectrum of **4**, the protons of the vinylidene display only one resonance at 1.70 ppm, which appears as a triplet with a H−P coupling constant of 4.5 Hz. The resonance is temperature-invariant between 298 and 193 K. This suggests that the vinylidene rotation is rapid on the NMR time scale. In this context, it should be mentioned that Caulton and co-workers have calculated an electronic barrier of 4.6 kcal·mol^{-1} for the vinylidene rotation in RuHCl(=C=CH$_2$)(PH$_3$)$_2$.[22] In the ^{13}C{^{1}H} NMR spectrum, the characteristic resonances of the vinylidene ligand are observed at 283.6 (C_α) and 90.3 (C_β) ppm. Both resonances appear as a triplet with C−P coupling constants of 14.8 and 6.0 Hz, respectively.

The presence of a hydride ligand in **4** is strongly supported by the IR and ^{1}H NMR spectra. In addition to the ν(C≡C) band, the IR spectrum contains a ν(Os−H) absorption at 2161 cm^{-1} along with that due to the [BF$_4$]$^-$ anion with T_d symmetry, centered at about 1050 cm^{-1}, in agreement with the salt character of the complex. In the high-field region, the ^{1}H NMR spectrum contains a triplet at −3.58 ppm with a H−P coupling constant of 22.9 Hz. The ^{31}P{^{1}H} NMR spectrum contains a singlet at 30.8 ppm.

Complex **4** reacts with methylmagnesium chloride and acetone oxime (Scheme 1). Treatment at room temperature of **4** in tetrahydrofuran with 1.2 equiv of

(16) Carbó, J. J.; Crochet, P.; Esteruelas, M. A.; Jean, Y.; Lledós, A.; López, A. M.; Oñate, E. *Organometallics* **2002**, *21*, 305.

(17) See for example: (a) Templeton, J. L. *Adv. Organomet. Chem.* **1989**, *29*, 1. (b) Baker, P. K. *Adv. Organomet. Chem.* **1996**, *40*, 45. (c) Frohnapfel, D. S.; Reinartz, S.; White, P. S.; Templeton, J. L. *Organometallics* **1998**, *17*, 3759. (d) Frohnapfel, D. S.; Enriquez, A. E.; Templeton, J. L. *Organometallics* **2000**, *19*, 221.

(18) See for example: (a) Tate, D. P.; Augl, J. M. *J. Am. Chem. Soc.* **1963**, *85*, 2174. (b) Wink, D. J.; Creagan, T. *Organometallics* **1990**, *9*, 328. (c) Szymánska-Buzar, T.; Glowiak, T. *J. Organomet. Chem.* **1994**, *467*, 223. (d) Yeh, W.-Y.; Ting, C.-S. *Organometallics* **1995**, *14*, 1417. (e) Mealli, C.; Masi, D.; Galindo, A.; Pastor, A. *J. Organomet. Chem.* **1998**, *569*, 21.

(19) See for example: (a) Dötz, K. H.; Mühlemeier, J. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 929. (b) Salt, J. E.; Girolami, G. S.; Wilkinson, G.; Motevalli, M.; Thornton-Pett, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1985**, 685. (c) Wink, D. J.; Fox, J. R.; Cooper, N. J. *J. Am. Chem. Soc.* **1985**, *107*, 5012.

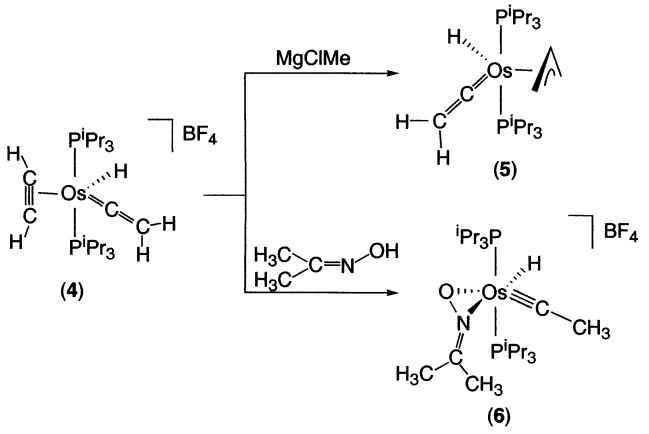
(20) (a) Wink, D. J.; Creagan, B. T. *J. Am. Chem. Soc.* **1990**, *112*, 8585. (b) Pearson, J.; Cooke, J.; Takats, J.; Jordan, R. B. *J. Am. Chem. Soc.* **1998**, *120*, 1434. (c) Mao, T.; Zhang, Z.; Washington, J.; Takats, J.; Jordan, R. B. *Organometallics* **1999**, *18*, 2331. (d) Ishino, H.; Kuwata, S.; Ishii, Y.; Hidai, M. *Organometallics* **2001**, *20*, 13.

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

(22) Oliván, M.; Eisenstein, O.; Caulton, K. G. *Organometallics* **1997**, *16*, 2227.

(23) (a) Poulton, J. T.; Sigalas, M. P.; Folting, K.; Streib, W. E.; Eisenstein, O.; Caulton, K. G. *Inorg. Chem.* **1994**, *33*, 1476. (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, and references in therein.

Scheme 1



MeMgCl leads to the allyl derivative $OsH(\eta^3\text{-}C_3H_5)(=C=CH_2)(P^iPr_3)_2$ (**5**), whereas the addition of 2.4 equiv of acetone oxime to the dichloromethane solutions of **4** affords oximate-carbyne compound $[OsH\{\kappa\text{-}N,\kappa\text{-}O[ON=C(CH_3)_2]\}(\equiv CCH_3)(P^iPr_3)_2]BF_4$ (**6**).

Complex **5** was isolated as a red oil in 91% yield. Formally, it is the result of the addition of a methyl group to the four-electron alkyne ligand. This addition should afford an alkenyl intermediate, which could isomerize into the allyl, via a π-allene species.[24]

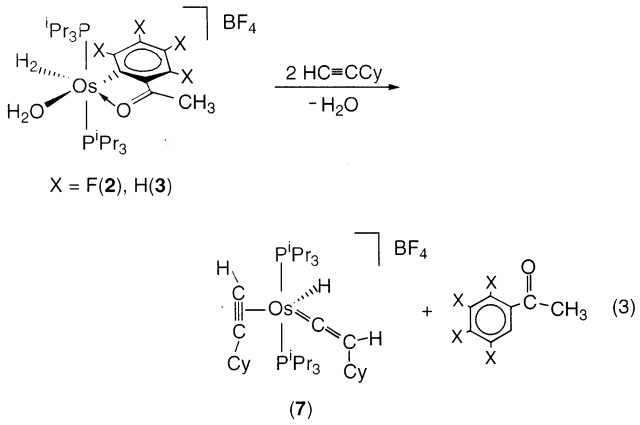
The presence of an allyl ligand in **5** is strongly supported by the ^1H and $^{13}C\{^1H\}$ NMR spectra of this compound. In the ^1H NMR spectrum in benzene-d_6, the allyl ligand gives rise to five resonances at 4.92 (CH), 3.01 (H_{syn}), 2.89 (H_{anti}), 2.16 (H_{syn}), and 1.46 (H_{anti}) ppm, with $H-H_{syn}$ and $H-H_{anti}$ coupling constants of 6.9 and 10.2 Hz, respectively. The resonance corresponding to the hydride ligand appears at −9.33 ppm, as a double doublet of doublets with H−P coupling constants of 24.6 and 17.1 Hz and a $H-H_{anti}$ coupling constant smaller than 1.0 Hz. In the $^{13}C\{^1H\}$ NMR spectrum the allyl ligand displays three resonances at 90.3 (CH), 29.1 and 23.3 (CH_2) ppm. The latter is observed as a doublet with a C−P coupling constant of 2.8 Hz, while the other two resonances appear as singlets. The resonance corresponding to the C_α atom of the vinylidene ligand is observed at 292.4 ppm, as a double doublet with both C−P coupling constants of 14.7 Hz, whereas the resonance due to the C_β atom appears at 92.4 ppm, also as a double doublet but with both C−P coupling constants of 4.1 Hz. In agreement with the structure shown in Scheme 1, the $^{31}P\{^1H\}$ NMR spectrum shows an AB spin system centered at 9.4 ppm and defined by $\Delta\nu = 948$ Hz and $J_{A-B} = 249$ Hz.

The related carbonyl complexes $MH(\eta^3\text{-}C_3H_5)(CO)(P^iPr_3)_2$ (M = Os,[25] Ru[26]) have been previously prepared, by reaction of the corresponding hydride-chloro-carbonyl compounds $MHCl(CO)(P^iPr_3)_2$ with allylmagnesium bromide. The previously mentioned spectroscopic data agree well with those reported for these compounds.

Complex **6** was isolated as a brown oil in 90% yield. Its formation involves the addition of the proton of the oxime to the C_β atom of the vinylidene and the displacement of the π-alkyne by the resulting oximate group. It is another member of the $[OsH\{\kappa\text{-}N,\kappa\text{-}O[ON=C(CH_3)_2]\}(\equiv CCH_2R)(P^iPr_3)_2]BF_4$ series. In a manner similar to these compounds, it can also be prepared, in high yield (about 80%), by reaction of the oxime elongated dihydrogen complex $[Os\{C_6H_4C(O)CH_3\}(\eta^2\text{-}H_2)\{N(OH)=C(CH_3)_2\}(P^iPr_3)_2]BF_4$ with acetylene or alternatively with trimethylsilylacetylene.

The most noticeable feature in the ^1H NMR spectrum of **6** in dichloromethane-d_2 is the presence of three singlets in the low-field region of the spectrum, at 2.25 and 2.18 ($N=C(CH_3)_2$) and 1.41 (CCH_3) ppm. The resonance corresponding to the hydride ligand appears at −6.81 ppm, as a triplet with a H−P coupling constant of 17.1 Hz. In the $^{13}C\{^1H\}$ NMR spectrum, the carbyne ligand gives rise to a triplet at 283.8 ($J_{C-P} = 9.4$ Hz) ppm corresponding to the C_α atom and a singlet at 40.2 ppm due to the C_β atom. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 37.2 ppm.

At 233 K, cyclohexylacetylene reacts in a manner similar to acetylene. At this temperature, the addition of 2.0 equiv of the alkyne to the dichloromethane solution of **2** or **3** affords the hydride-vinylidene-π-alkyne complex $[OsH(=C=CHCy)(\eta^2\text{-}HC\equiv CCy)(P^iPr_3)_2]BF_4$ (**7**) and the corresponding ketone. Complex **7** was isolated as a brown oil in about 55% yield, according to eq 3.



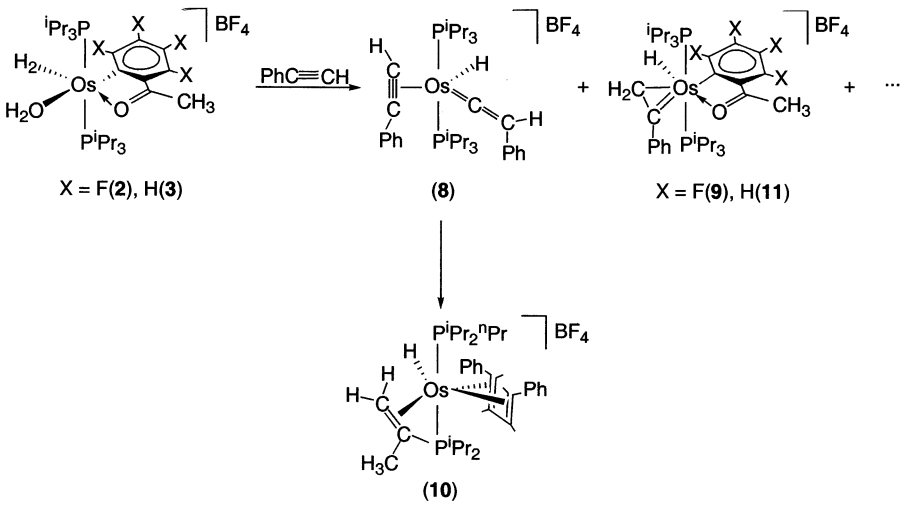
(3)

The ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra of **7** indicate that the structure of **7** is like that of **4** and that the π-alkyne also acts as a four-electron-donor ligand. In agreement with the ^1H NMR spectrum of **4**, the ^1H NMR spectrum of **7** in dichloromethane-d_2 at 233 K shows the resonance corresponding to the ≡CH proton of the alkyne at 10.26 ppm, as a doublet with a H−P coupling constant of 27.6 ppm. The resonance due to the =CH proton of the vinylidene appears at 2.41 ppm, as a double doublet of doublets with a H−H coupling constant of 7.8 Hz and both H−P coupling constants of 4.5 Hz.[27] In the high-field region, the spectrum contains the hydride resonance, which is observed at −4.64 ppm, as a double doublet with H−P coupling constants of 29.3 and 23.6 Hz. In the $^{13}C\{^1H\}$ NMR spectrum, the resonances due to the C(sp) atoms of the alkyne appear

(24) Buil, M. L.; Esteruelas, M. A.; López, A. M.; Oñate, E. *Organometallics* **1997**, *16*, 3169.
(25) Schlünken, C.; Werner, H. *J. Organomet. Chem.* **1993**, *454*, 243.
(26) Bohanna, C.; Esteruelas, M. A.; Herrero, J.; López, A. M.; Oro, L. A. *J. Organomet. Chem.* **1995**, *498*, 199.

(27) The resonance is temperature-invariant between 25 and −80 °C, suggesting that also in this case the vinylidene rotation is rapid on the NMR time scale.

Scheme 2



at 161.5 (CCy) and 139.3 (≡CH) ppm. The first of them is observed as a broad signal, while the second one appears as a double doublet with C−P coupling constants of 11.7 and 4.9 Hz. The vinylidene ligand displays a double doublet ($J_{C-P} = J_{C-P'} = 15.1$ Hz) at 283.3 (C_α) and a broad signal at 111.7 (C_β) ppm. The $^{31}P\{^1H\}$ NMR spectrum shows an AB spin system centered at 31.0 ppm, defined by $\Delta\nu = 342$ Hz and $J_{A-B} = 129$ Hz.

The stability of **7** is much less than the stability of **4**. In solution, complex **7** decomposes to a mixture of unidentified products. At room temperature, the decomposition is complete after 20 min. The low stability of **7** is consistent with the parallel disposition of the carbon−carbon triple bond of the alkyne with regard to the P−Os−P direction, which imposes a high steric hindrance between the substituent of the alkyne and the isopropyl groups of the phosphines.

3. Reactions of [Os{$C_6X_4C(O)CH_3$}(η^2-H_2)(H_2O)(P^iPr_3)$_2$]BF_4 (X = F, H) with Phenylacetylene. At room temperature, the addition of 1.0 equiv of phenylacetylene to an NMR tube containing a dichloromethane-d_2 solution of **2** leads to a complex mixture (Scheme 2). After 10 min, the main components of the mixture are the hydride-vinylidene-π-alkyne complex [OsH(=C=CHPh)(η^2-HC≡CPh)(P^iPr_3)$_2$]BF_4 (**8**, about 27%) and the hydride-metallacyclopropene compound **9** (about 45%). At this temperature complex **8** evolves into the 1,4-diphenylbutadiene derivative [OsH(η^4-$C_4H_4Ph_2$){[η^2-CH_2=C(CH_3)]P^iPr_2}($P^iPr_2{}^nPr$)]BF_4 (**10**), while **9** decomposes to unidentified products. After 3 h, the main component of the new mixture is **10** (about 25%), according to the $^{31}P\{^1H\}$ NMR spectrum.

When the reaction is carried out in a Schlenk tube, after 10 min, the hydride-metallacyclopropene complex **9** can be isolated from the mixture, by concentration of the solution and subsequent addition of diethyl ether. By this procedure, complex **9** was obtained as a green solid in 35% yield. Interestingly, at room temperature, the solutions of **9** in dichloromethane-d_2 are stable for several days. This suggests that the above-mentioned decomposition of **9** is a consequence of its reaction with any of the minor components of the mixture.

The spectroscopic data of **8** agree well with those of **4** and **7**. In the ^1H NMR spectrum, the ≡CH proton of the alkyne gives rise to a doublet at 10.61 ppm, with a H−P coupling constant of 25.8 Hz, whereas the resonance due to the =CH proton of the vinylidene ligand is observed at 3.77 ppm as a double doublet with both H−P coupling constants of 4.5 Hz.[27] The hydride resonance appears at −3.14 ppm as a double doublet with H−P coupling constants of 27.0 and 23.1 Hz. In the $^{13}C\{^1H\}$ NMR spectrum, the resonances due to the C(sp) atoms of the alkyne are observed at 152.6 (CPh) and 139.4 (CH) ppm, as double doublets with C−P coupling constants of 7.5 and 5.3 and 9.5 and 4.1 Hz, respectively. The resonance corresponding to the C_α atom of the vinylidene appears at 290.5 ppm, as a double doublet with both C−P constants of 15.1 Hz, whereas the resonance due to the C_β atom is observed at 110.6 ppm, also as a double doublet but with both C−P constants of 5.6 Hz. The $^{31}P\{^1H\}$ NMR spectrum shows an AB spin system centered at 29.6 ppm and defined by $\Delta\nu = 170$ Hz and $J_{A-B} = 126$ Hz.

Figure 3 shows a view of the structure of the cation of **9**. Selected bond distances and angles are listed in Table 2. The coordination geometry around the osmium atom can be rationalized as a distorted pentagonal bipyramid with the two phosphorus atoms of the tri-

Table 2. Selected Bond Distances (Å) and Angles (deg) for [OsH{$C_6F_4C(O)CH_3$}{C(Ph)CH_2}(P^iPr_3)$_2$]BF_4 (9)

Os−P(1)	2.445(6)	Os−C(10)	1.929(12)
Os−P(2)	2.434(7)	O−C(7)	1.231(15)
Os−O	2.153(6)	C(6)−C(7)	1.419(18)
Os−C(1)	2.16(2)	C(9)−C(10)	1.336(19)
Os−C(9)	2.114(16)		
P(1)−Os−P(2)	168.49(13)	O−Os−H(01)	166(3)
P(1)−Os−O	89.9(2)	C(1)−Os−C(9)	158.0(3)
P(1)−Os−C(1)	86.6(6)	C(1)−Os−C(10)	163.5(5)
P(1)−Os−C(9)	86.1(5)	C(1)−Os−H(01)	93(4)
P(1)−Os−C(10)	95.3(3)	C(9)−Os−C(10)	38.2(5)
P(1)−Os−H(01)	83(4)	C(10)−Os−H(01)	104(3)
P(2)−Os−O	99.9(2)	Os−C(1)−C(6)	111.6(12)
P(2)−Os−C(1)	90.0(6)	Os−O−C(7)	120.0(8)
P(2)−Os−C(9)	93.1(5)	O−C(7)−C(6)	116.6(13)
P(2)−Os−C(10)	91.1(3)	C(1)−C(6)−C(7)	116.2(14)
P(2)−Os−H(01)	86(4)	Os−C(9)−C(10)	63.4(8)
O−Os−C(1)	74.8(5)	Os−C(10)−C(9)	78.4(8)
O−Os−C(9)	125.8(5)	C(9)−C(10)−C(11)	133.4(13)
O−Os−C(10)	88.8(4)		

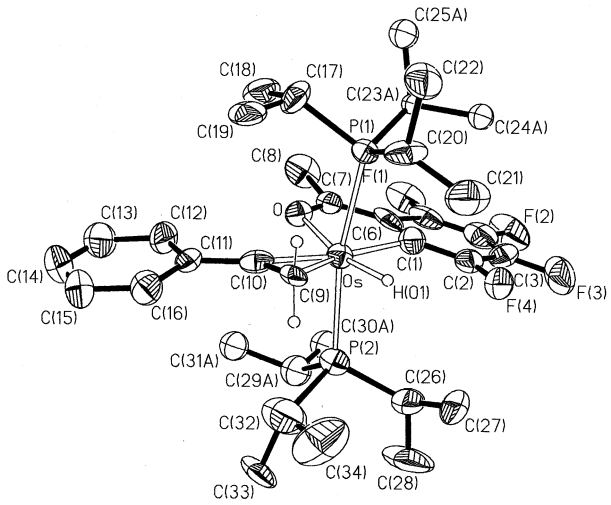


Figure 3. Molecular diagram of the cation of complex $[OsH\{C_6F_4C(O)CH_3\}\{C(Ph)CH_2\}(P^iPr_3)_2]BF_4$ (**9**).

isopropylphosphine ligands occupying *trans* positions (P(1)−Os−P(2) = 168.49(13)°). The osmium coordination sphere is completed by the metalated ketone, which acts with a bite angle O−Os−C(1) of 74.8(5)°, the hydride ligand, and the atoms C(9) and C(10), which are coordinated to the osmium atom to form a three-membered ring (C(10)−Os−C(9) = 38.2(5)°).

The M−C bond to the monosubstituted carbon (C(10)) is substantially shorter than the M−C bond to the disubstituted carbon (C(9)). Thus, the Os−C(10) bond length (1.929(12) Å) is statistically identical with the Os−C double-bond distance found in the carbene complex $OsCl_2(=CHCH_2Ph)(CO)(P^iPr_3)_2$ (1.887(9) Å),[8] while the Os−C(9) bond length (2.114(16) Å) agrees well with the values previously reported for Os−C(alkyl) distances (mean value 2.16(5) Å).[28] The C(9)−C(10) distance is 1.336(19) Å. Similar values have been reported for the related complex $[OsH(\kappa^2\text{-}O_2CCH_3)\{C(Ph)CH_2\}(P^iPr_3)_2]BF_4$, which has been prepared by reaction of phenylacetylene with the dihydride complex $[OsH_2(\kappa^2\text{-}O_2CCH_3)(H_2O)(P^iPr_3)_2]BF_4$.[7m]

In agreement with the Os−C(10) carbene and Os−C(9) alkyl formulation, the resonances due to C(10) and C(9) atoms appear in the $^{13}C\{^1H\}$ NMR spectrum at 272.9 and 4.2 ppm, respectively. In the ^1H NMR spectrum the most noticeable resonances are those corresponding to the Os−CH_2 and Os−H hydrogen atoms, which are observed at 1.91 and −7.72 ppm. The first of them appears as a triplet with a H−P constant of 8.5 Hz, while the second one is observed as a double triplet by spin coupling with the phosphorus nuclei of the phosphines (J_{H-P} = 17.2 Hz) and the fluorine F(4) of the metalated ketone (J_{H-F} = 10.6 Hz). The presence of a hydride ligand in **9** is also supported by its IR spectrum in KBr, which shows a ν(Os−H) band at 2210 cm^{-1}. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 3.7 ppm.

Metallacyclopropene compounds have been limited to early transition metals, mainly Mo,[29] W,[30] and Re.[31] In general they have been prepared by external nucleophilic attack on coordinated alkyne ligands.[17a] Osmacyclopropene complexes are rare. In addition to $[OsH(\kappa^2\text{-}O_2CCH_3)\{C(Ph)CH_2\}(P^iPr_3)_2]BF_4$, we have reported that the reactions of the dihydride $[OsH_2(\kappa^2\text{-}O_2CCH_3)(H_2O)(P^iPr_3)_2]BF_4$ with alkynols lead to hydride-hydroxyosmacyclopropene derivatives of the type $[OsH(\kappa^2\text{-}O_2CCH_3)\{C[C(OH)RR']CH_2\}(P^iPr_3)_2]BF_4$, which are unstable and in solution evolve into the corresponding cyclic hydroxycarbene complexes $[Os(\kappa^2\text{-}O_2CCH_3)\{C(Me)C(OH)RR'\}(P^iPr_3)_2]BF_4$.[7p] Harman and co-workers have shown that the electrophilic extraction of the methoxy group of the coordinated olefin in the complex $[Os\{\eta^2\text{-}CH_2{=}C(OMe)CH_3\}(NH_3)_5](OTf)_2$ affords the osmacyclopropene $[Os\{C(CH_3)CH_2\}(NH_3)_5](OTf)_3$.[32]

(28) Allen, F. H.; Kennard, O. 3D Search and Research Using the Cambridge Structural Database. *Chem. Des. Automation News* **1993**, *8* (1), 1, 31−37.

(29) (a) Davidson, J. L.; Murray, I. E. P.; Preston, P. N.; Russo, M. V.; Manojlović-Muir, L.; Muir, K. W. *J. Chem. Soc., Chem. Commun.* **1981**, 1059. (b) Green, M.; Norman, N. C.; Orpen, A. G. *J. Am. Chem. Soc.* **1981**, *103*, 1267. (c) Allen, S. R.; Green, M.; Orpen, A. G.; Williams, I. D. *J. Chem. Soc., Chem. Commun.* **1982**, 826. (d) Allen, S. R.; Baker, P. K.; Barnes, S. G.; Bottrill, M.; Green, M.; Orpen, A. G.; Williams, I. D.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1983**, 927. (e) Davidson, J. L.; Wilson, W. F.; Manojlović-Muir, L.; Muir, K. W. *J. Organomet. Chem.* **1983**, *254*, C6. (f) Davidson, J. L.; Murray, I. E. P.; Preston, P. N.; Russo, M. V. *J. Chem. Soc., Dalton Trans.* **1983**, 1783. (g) Allen, S. R.; Beevor, R. G.; Green, M.; Norman, N. C.; Orpen, A. G.; Williams, I. D. *J. Chem. Soc., Dalton Trans.* **1985**, 435. (h) Feher, F. J.; Green, M.; Rodrigues, R. A. *J. Chem. Soc., Chem. Commun.* **1987**, 1206. (i) Allen, S. R.; Beevor, R. G.; Green, M.; Orpen, A. G., Paddick, K. E.; Williams, I. D. *J. Chem. Soc., Dalton Trans.* **1987**, 591. (j) Conole, G. C.; Green, M.; McPartlin, M.; Reeve, C.; Woolhouse, C. M. *J. Chem. Soc., Chem. Commun.* **1988**, 1310. (k) Clegg, W.; Green, M.; Hall, C. A.; Hockless, D. C. R.; Norman, N. C.; Woolhouse, C. M. *J. Chem. Soc., Chem. Commun.* **1990**, 1330. (l) Gamble, A. S.; White, P. S.; Templeton, J. L. *Organometallics* **1991**, *10*, 693. (m) Agh-Atabay, N. M.; Canoira, L. J.; Carlton, L.; Davidson, J. L. *J. Chem. Soc., Dalton Trans.* **1991**, 1175. (n) Carfagna, C.; Deeth, R. J.; Green, M.; Mahon, M. F.; McInnes, J. M.; Pellegrini, S.; Woolhouse, C. B. *J. Chem. Soc., Dalton Trans.* **1995**, 3975. (o) Kiplinger, J. L.; Richmond, T. G. *Polyhedron* **1997**, *16*, 409. (p) Guillemot, G.; Solari, E.; Scopelliti, R.; Floriani, C. *Organometallics* **2001**, *20*, 2446.

(30) (a) Davidson, J. L.; Shiralian, M.; Manojlovic-Muir, L.; Muir, K. W. *J. Chem. Soc., Chem. Commun.* **1979**, 30. (b) Davidson, J. L.; Vasapollo, G.; Manojlović-Muir, L.; Muir, K. W. *J. Chem. Soc., Chem. Commun.* **1982**, 1025. (c) Carlton, L.; Davidson, J. L.; Miller, J. C.; Muir, K. W. *J. Chem. Soc., Chem. Commun.* **1984**, 11. (d) Davidson, J. L.; Shiralian, M.; Manojlović-Muir, L.; Muir, K. W. *J. Chem. Soc., Dalton Trans.* **1984**, 2167. (e) Carlton, L.; Davidson, J. L.; Ewing, P.; Manojlović-Muir, L.; Muir, K. W. *J. Chem. Soc., Chem. Commun.* **1985**, 1474. (f) Carlton, L.; Davidson, J. L. *J. Chem. Soc., Dalton Trans.* **1987**, 895. (g) Gamble, A. S.; Birdwhistell, K. R.; Templeton, J. L. *J. Am. Chem. Soc.* **1990**, *112*, 1818. (h) Silva, C. J., Giner, J. L.; Djerassi, C. *J. Am. Chem. Soc.* **1992**, *114*, 295. (i) Feng, S. G.; Templeton, J. L. *Organometallics* **1992**, *11*, 2168. (j) Kiplinger, J. L.; King, M. A.; Arif, A. M.; Richmond, T. G. *Organometallics* **1993**, *12*, 3382. (k) Mayr, A.; Asaro, M. F.; Glines, T. J.; Van Engen, D.; Tripp, G. M. *J. Am. Chem. Soc.* **1993**, *115*, 8187. (l) Lee, T.-Y.; Mayr, A. *J. Am. Chem. Soc.* **1994**, *116*, 10300. (m) Kiplinger, J. L.; King, M. A.; Fechtenkötter, A.; Arif, A. M.; Richmond, T. G. *Organometallics* **1996**, *15*, 5292. (n) Kiplinger, J. L.; Richmond, T. G.; Arif, A. M.; Dücker-Benfer, C.; van Eldik, R. *Organometallics* **1996**, *15*, 1545. (o) Giannini, L.; Guillemot, G.; Solari, E.; Floriani, C.; Re, N.; Chiesi-Villa, A.; Rizzoli, C. *J. Am. Chem. Soc.* **1999**, *121*, 2797. (p) Legzdins, P.; Lumb, S. A.; Rettig, S. J. *Organometallics* **1999**, *18*, 3128. (q) Frohnapfel, D. S.; White, P. S.; Templeton, J. L. *Organometallics* **2000**, *19*, 1497. (r) Guillemot, G.; Solari, E.; Floriani, C.; Re, N.; Rizzoli, C. *Organometallics* **2000**, *19*, 5218.

(31) (a) Pombeiro, A. J. L.; Hughes, D. L.; Richards, R. L.; Silvestre, J.; Hoffmann, R. *J. Chem. Soc., Chem. Commun.* **1986**, 1125. (b) Carfagna, C.; Carr, N.; Deeth, R. J.; Dossett, S. J.; Green, M.; Mahon, M. F.; Vaughan, C. *J. Chem. Soc., Dalton Trans.* **1996**, 415. (c) Casey, C. P.; Brady, J. T. *Organometallics* **1998**, *17*, 4620. (d) Casey, C. P.; Brady, J. T.; Boller, T. M.; Weinhold, F.; Hayashi, R. K. *J. Am. Chem. Soc.* **1998**, *120*, 12500. (e) Casey, C. P.; Chung, S. *Inorg. Chim. Acta* **2002**, *334*, 283.

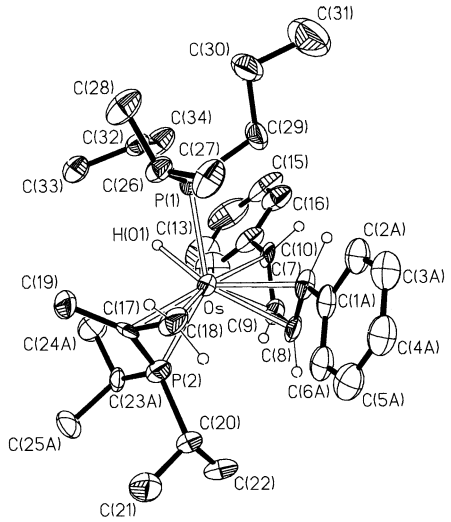


Figure 4. Molecular diagram of the cation of complex $[OsH(\eta^4\text{-}C_4H_4Ph_2)\{[\eta^2\text{-}CH_2{=}C(CH_3)]P^iPr_2\}(P^iPr_2{}^nPr)]BF_4$ (**10**).

Table 3. Selected Bond Distances (Å) and Angles (deg) for $[OsH(\eta^4\text{-}C_4H_4Ph_2)\{[\eta^2\text{-}CH_2{=}C(CH_3)]P^iPr_2\}(P^iPr_2{}^nPr)]BF_4$ (10)[a]

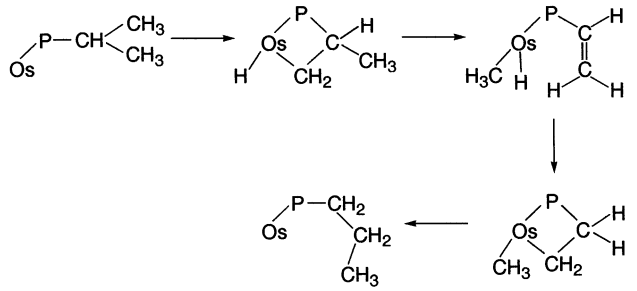
Os−P(1)	2.425(2)	C(8)−C(9)	1.437(10)
Os−P(2)	2.312(2)	C(9)−C(10)	1.390(11)
Os−C(7)	2.385(7)	C(17)−C(18)	1.426(14)
Os−C(8)	2.209(7)	P(1)−C(29)	1.855(8)
Os−C(9)	2.165(7)	C(29)−C(39)	1.538(12)
Os−C(10)	2.288(7)	C(30)−C(31)	1.554(14)
Os−C(17)	2.271(10)	P(2)−C(17)	1.780(13)
Os−C(18)	2.222(9)	C(17)−C(19)	1.498(12)
C(7)−C(8)	1.382(10)		
P(1)−Os−P(2)	141.52(8)	M(1)−Os−H(01)	149.0(2)
P(1)−Os−M(1)	105.5(2)	M(2)−Os−M(3)	155.4(3)
P(1)−Os−M(2)	106.7(2)	M(2)−Os−H(01)	94.7(2)
P(1)−Os−M(3)	96.8(3)	M(3)−Os−H(01)	102.3(3)
P(1)−Os−H(01)	63.2	C(7)−C(8)−C(9)	118.1(7)
P(2)−Os−M(1)	107.5(2)	C(8)−C(9)−C(10)	118.4(7)
P(2)−Os−M(2)	105.1(2)	C(9)−C(10)−C(11)	118.6(7)
P(2)−Os−M(3)	56.8(3)	P(1)−C(29)−C(30)	117.2(6)
P(2)−Os−H(01)	93.2	C(29)−C(30)−C(31)	107.8(8)
M(1)−Os−M(2)	58.1(3)	P(2)−C(17)−C(18)	108.7(7)
M(1)−Os−M(3)	108.4(4)	P(2)−C(17)−C(19)	126.6(9)
		C(18)−C(17)−C(19)	124.5(11)

[a] M(1), M(2), and M(3) are the midpoints of the C(7)−C(8), C(9)−C(10), and C(17)−C(18) bonds.

A few crystals of **10** suitable for an X-ray diffraction study were obtained by slow diffusion of diethyl ether into the dichloromethane-d_2 solution containing the mixture resulting from the addition of phenylacetylene to **2**. Figure 4 shows a view of the structure of the cation of this compound. Selected bond distances and angles are collected in Table 3.

The structure proves the formation of the diphenylbutadiene ligand, which is coordinated to the osmium atom as a *cis*-diene with *E*-stereochemistry at both carbon−carbon double bonds. This ligand is the result of the reductive condensation of the vinylidene and π-alkyne ligands of **8**. The reductor is one of the triisopropylphosphines, which undergoes dehydrogenation of one of the isopropyl groups, to afford a monoisopropenylphosphine. As far as we know, this tandem process involving the dimerization of an alkyne plus the reduction of the resulting dimer, by hydrogen transfer from an alkane,[33] has no precedents.

Scheme 3



Although the dehydrogenation of coordinated cycloalkylphosphines is a well-known process,[34] the dehydrogenation of acyclic alkylphosphines to give α-vinylphosphines is rare. We have previously reported that complex $OsH_2Cl_2(P^iPr_3)_2$ reacts with 2.0 equiv of 1,5-cyclooctadiene and 2,5-norbornadiene to give 1.0 equiv of the corresponding monoolefin and the isopropenylphosphine derivatives $OsCl_2(\eta^4\text{-diolefin})\{\eta^2\text{-}[CH_2{=}C(CH_3)]P^iPr_2\}$ (diolefin = COD, NBD).[35] Transition-metal complexes containing $R_2PC(R'){=}CH_2$ ligands are relatively scarce. These groups act as a monodentate ligand,[36] a bridge to two metal centers,[37] and a chelating ligand.[38] Complex **10** is a rare example of the latter type of compounds in osmium chemistry.

It should be noted that the formation of **10** involves, in addition to the previously metioned dimerization−reduction tandem, the carbon skeletal isomerization of one of the isopropyl groups of the other phosphine, which is converted into a *n*-propylbis(isopropyl)phosphine ligand. This isomerization should involve the initial C−H activation of a methyl group of the isomerized isopropyl, followed by the β-alkyl elimination of the other one. Thus, the process can be rationalized according to Scheme 3.

The C−C cleavage via β-alkyl elimination has been observed rarely. It has become recognized as an impor-

(32) Chen, H.; Harman, W. D. *J. Am. Chem. Soc.* **1996**, *118*, 5672.

(33) (a) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245. (b) Burk, M. J.; Crabtree, R. H. *J. Am. Chem. Soc.* **1987**, *109*, 8025. (c) Aoki, T.; Crabtree, R. H. *Organometallics* **1993**, *12*, 294. (d) Chaloner, P. A.; Esteruelas, M. A.; Joó, F.; Oro, L. A. *Homogeneous Hydrogenation*; Kluwer Academic Publisher: Dordrecht, 1994; Chapter 2. (e) Jensen, C. M. *Chem. Commun.* **1999**, 2443. (f) Morales-Morales, D.; Lee, D. W.; Wang, Z.; Jensen, C. M. *Organometallics* **2001**, *20*, 1144.

(34) See for example: (a) Hietkamp, S.; Stufkens, D. J.; Vrieze, K. *J. Organomet. Chem.* **1978**, *152*, 347. (b) Arliguie, T.; Chaudret, B.; Jalon, F.; Lahoz, F. J. *J. Chem. Soc., Chem. Commun.* **1988**, 998. (c) Campion, B. K.; Heyn, R. H.; Tilley, T. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **1993**, *115*, 5527. (d) Christ, M. L.; Sabo-Etienne, S.; Chaudret, B. *Organometallics* **1995**, *14*, 1082.

(35) Edwards, A. J.; Esteruelas, M. A.; Lahoz, F. J.; López, A. M.; Oñate, E.; Oro, L. A.; Tolosa, J. I. *Organometallics* **1997**, *16*, 1316.

(36) See for example: (a) Holt, M. S.; Nelson, J. H.; Alcock, N. W. *Inorg. Chem.* **1986**, *25*, 2288. (b) Rahn, J. A.; Holt, M. S.; O'Neil-Jonhson, M.; Nelson, J. H. *Inorg. Chem.* **1988**, *27*, 1316. (c) Rahn, J. A.; Delian, A.; Nelson, J. H. *Inorg. Chem.* **1989**, *28*, 215. (d) Rahn, J. A.; Holt, M. S.; Gray, G. A.; Alcock, N. W.; Nelson, J. H. *Inorg. Chem.* **1989**, *28*, 217. (e) Bhaduri, D.; Nelson, J. H.; Day, C. L.; Jacobson, R. A.; Solujić, L.; Milosavljević, E. B. *Organometallics* **1992**, *11*, 4069. (f) Adams, H.; Bailey, N. A.; Blenkiron, P.; Morris, M. J. *J. Organomet. Chem.* **1993**, *460*, 73. (g) Knox, S. A. R.; Morton, D. A. V.; Orpen, A. G.; Turner, M. L. *Inorg. Chim. Acta* **1994**, *220*, 201.

(37) See for example: (a) Wilson, W. L.; Nelson, J. H.; Alcock, N. W. *Organometallics* **1990**, *9*, 1699. (b) Hogarth, G. *J. Organomet. Chem.* **1991**, *407*, 91. (c) Doyle, M. J.; Duckworth, T. J.; Manojlović-Muir, L.; Mays, M. J.; Raithby, P. R.; Robertson, F. J. *J. Chem. Soc., Dalton Trans.* **1992**, 2703. (d) Acum, G. A.; Mays, M. J.; Raithby, P. R.; Solan, G. A. *J. Organomet. Chem.* **1996**, *508*, 137.

(38) (a) Mercier, F.; Hugel-Le Goff, C.; Ricard, L.; Mathey, F. *J. Organomet. Chem.* **1990**, *389*, 389. (b) Mathey, F. *J. Organomet. Chem.* **1990**, *400*, 149. (c) Ji, H.; Nelson, J. H.; DeCian, A.; Fischer, J.; Solujić, L.; Milosavljević, E. B. *Organometallics* **1992**, *11*, 401.

Table 4. Crystal Data and Data Collection and Refinement for 4, 9, and 10

	4	9	10
Crystal Data			
formula	$C_{22}H_{47}BF_4OsP_2$	$C_{34}H_{53}BF_8OOsP_2$	$C_{34}H_{55}BF_4OsP_2$
molecular wt	650.55	892.71	802.73
color and habit	red irregular block	red irregular block	yellow irregular block
symmetry, space group	monoclinic, $P2_1/c$	monoclinic, Cc	monoclinic, $C2/c$
a, Å	14.1849(12)	19.9856(14)	29.790(6)
b, Å	15.4206(12)	9.0906(7)	11.407(3)
c, Å	13.6054(11)	22.3226(16)	22.239(6)
α, deg	90	90	90
β, deg	105.361(2)	114.839(1)	111.561(9)
γ, deg	90	90	90
V, Å^3	2869.7(4)	3680.4(5)	7029(3)
Z	4	4	8
D_{calc}, g cm^{-3}	1.506	1.611	1.517
Data Collection and Refinement			
diffractometer		Bruker Smart APEX	
λ(Mo Kα), Å		0.71073	
monochromator		graphite oriented	
scan type		ω scans	
μ, mm^{-1}	4.588	3.619	3.763
2θ, range deg	3, 57	3, 57	3, 57
temp, K	296	173	100
no. of data collected	26 364	11 905	33 394
no. of unique data	6924 (R_{int} = 0.1078)	5980 (R_{int} = 0.0736)	8241 (R_{int} = 0.0717)
no. of params/restraints	394/27	435/110	491/294
R_1[a] [$F^2 > 2\sigma(F^2)$]	0.0488	0.0495	0.0587
wR_2[b] [all data]	0.0896	0.1149	0.1251
S[c] [all data]	0.806	0.931	1.005

[a] $R_1(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2(F^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. [c] Goof = $S = \{\sum[F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$, where n is the number of reflections, and p is the number of refined parameters.

tant chain-termination step in early transition-metal-based, model Ziegler−Natta, polymerization systems.[39] In late transition-metal systems there are also some reports in which β-alkyl elimination has been proposed.[35, 40]

The coordination geometry around the osmium atom of **10** can be rationalized as being derived from a highly distorted octahedron with the phosphorus atoms of the phosphines occupying pseudo-*trans* positions (P(1)−Os−P(2) = 141.52(8)°), at opposite sides of an ideal coordination plane defined by the hydride disposed *trans* to the midpoint of the C(8)−C(7) double bond (M(1)) of the diene (H(01)−M−M(1) = 149.0(2)°) and the midpoint of the C(17)−C(18) double bond (M(3)) of the isopropenyl group disposed *trans* to the midpoint (M(2)) of the other carbon−carbon double bond (C(9)−C(10)) of the diene (M(2)−Os−M(3) = 155.4(3)°). The distortion of the ideal octahedron appears to be a consequence of the bite angles of the diene (M(1)−Os−M(2) = 58.1(3)°) and the isopropenylphosphine (P(2)−Os−M(3) = 56.8(3)°).

The olefinic bond of the isopropenylphosphine ligand coordinates to the osmium atom in an asymmetrical fashion, with Os−C distances of 2.222(9) Å (Os−C(18)) and 2.271(10) Å (Os−C(17)). These bond lengths agree well with those found in other osmium-olefin complexes (between 2.13 and 2.28 Å).[7i,35,41] Similarly, the olefinic bond distance C(17)−C(18) (1.426(14) Å) is within the range reported for transition-metal olefin complexes (between 1.340 and 1.445 Å).[42] The P(2)−C(17) distance (1.780(13) Å) is about 0.05 Å shorter than the P(2)−C(20) (1.834(8) Å) bond length. In accordance with the sp^2 hybridization for C(17), the angles P(2)−C(17)−C(18), P(2)−C(17)−C(19), and C(18)−C(17)−C(19) are 108.7(7)°, 126.6(9)°, and 124.5(11)°, respectively.

The coordination of both double bonds of the diene is also asymmetrical. The Os−C(terminal) distances (Os−C(10) = 2.288(7) Å and Os−C(7) = 2.385(7) Å) are significantly longer than the Os−C(central) bond lengths (Os−C(9) = 2.165(7) Å and Os−C(8) = 2.209(7) Å). On

(39) See for example: (a) Watson, P. L.; Roe, D. C. *J. Am. Chem. Soc.* **1982**, *104*, 6471. (b) Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* **1985**, *18*, 51. (c) Bunel, E.; Burger, B. J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 976. (d) Bercaw, J. E. *Pure Appl. Chem.* **1990**, *62*, 1151. (e) Eshuis, J. J. W.; Tan, Y. Y.; Teuben, J. H.; Renkema, J. *J. Mol. Catal.* **1990**, *62*, 277. (f) Kesti, M. R.; Waymouth, R. M. *J. Am. Chem. Soc.* **1992**, *114*, 3565. (g) Eshuis, J. J. W.; Tan, Y. Y.; Meetsma, A.; Teuben, J. H.; Renkema, J.; Evens, G. G. *Organometallics* **1992**, *11*, 362. (h) Resconi, L.; Piemontesi, F.; Franciscono, G.; Abis, L.; Fiorani, T. *J. Am. Chem. Soc.* **1992**, *114*, 1025. (i) Yang, X.; Jia, L.; Marks, T. J. *J. Am. Chem. Soc.* **1993**, *115*, 3392. (j) Hajela, S.; Bercaw, J. E. *Organometallics* **1994**, *13*, 1147. (k) Sini, G.; Macgregor, S. A.; Eisenstein, O.; Teuben, J. H. *Organometallics* **1994**, *13*, 9. (l) Guo, Z.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1994**, *13*, 1424. (m) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143. (n) Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1996**, 255. (o) Horton, A. D. *Organometallics* **1996**, *15*, 2675. (p) Etienne, M.; Mathieu, R.; Donnadieu, B. *J. Am. Chem. Soc.* **1997**, *119*, 3218. (q) Corradi, M. M.; Jiménez Pindado, G.; Sarsfield, M. J.; Thornton-Pett, M.; Bochmann, M. *Organometallics* **2000**, *19*, 1150.

(40) See for example: (a) Flood, T. C.; Statler, J. A. *Organometallics* **1984**, *3*, 1795. (b) Flood, T. C.; Bitler, S. P. *J. Am. Chem. Soc.* **1984**, *106*, 6076. (c) Thomsons, S. K.; Young, G. B. *Organometallics* **1989**, *8*, 2068. (d) Hartwig, J. F.; Bergman, R. G.; Andersen, R. A. *Organometallics* **1991**, *10*, 3344. (e) Ermer, S. P.; Struck, G. E.; Bitler, S. P.; Richards, R.; Bau, R.; Flood, T. C. *Organometallics* **1993**, *12*, 2634. (f) Ankianiec, B. C.; Christou, V.; Hardy, D. T.; Thompson, S. K.; Young, G. B. *J. Am. Chem. Soc.* **1994**, *116*, 9963. (g) McNeill, K.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1995**, *117*, 3625. (h) Bharadwaj, S. S.; Schimdt, L. D. *J. Catal.* **1995**, *155*, 403.

(41) (a) Johnson, T. J.; Albinati, A.; Koetzle, T. F.; Ricci, J.; Eisenstein, O.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **1994**, *33*, 4966. (b) Esteruelas, M. A.; García-Yebra, C.; Oliván, M.; Oñate, E. *Organometallics* **2000**, *19*, 3260. (c) Baya, M.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2002**, *21*, 5681.

(42) Allen, F. H.; Davies, J. E.; Galloy, J. J.; Johnson, O.; Kennard, O.; Macrae, C. F.; Mitchell, E. M.; Mitchell, G. F.; Smith, J. M.; Watson, D. G. *J. Chem. Inf. Comput. Sci.* **1991**, *31*, 187.

the other hand, both C(terminal)−C(central) distances (C(7)−C(8) = 1.382(10) Å and C(9)−C(10) = 1.390(11) Å) are shorter than the C(central)−C(central) bond length (C(8)−C(9) = 1.437(10) Å). These structural parameters strongly support a η^4-π-coordination of the diene, which is characteristic of the vast majority of middle and late transition-metal diene complexes.[43] In agreement with the η^4-π-coordination, the dihedral angle between the C(7)−Os−C(10) and C(7)−C(8)−C(9)−C(10) planes (θ) is 80.0(4)° and the Δd and Δl parameters[44] have values of 0.15 and −0.05 Å, respectively.

The coordination fashion of the butadiene in **10** differs from that observed in the osmium(0) complex Os(η^4-C_4H_5Ph)(CO)(P^iPr_3)$_2$, where on the basis of the θ, Δd, and Δl parameters, a coordination intermediate between the resonance forms η^4-π and σ^2-π has been proposed.[45]

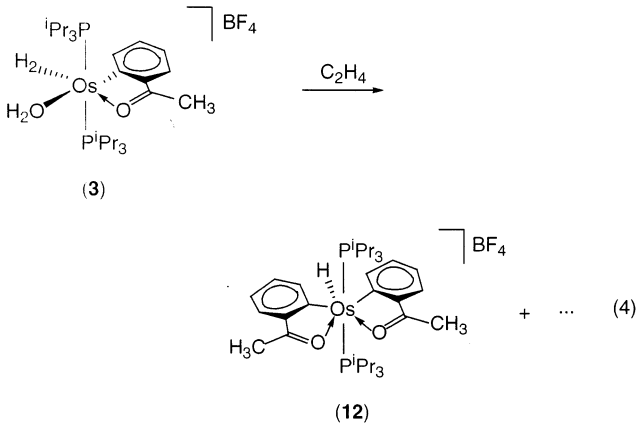
In the ^{1}H NMR spectrum of **10**, the most noticeable resonances are those corresponding to the =CH protons of the butadiene ligand, which are observed at 5.68, 5.23, 3.90, and 2.07 ppm. In the high-field region, the spectrum shows the hydride resonance, which appears at −12.98 ppm, as a double doublet with H−P coupling constants of 30.8 and 16.4 Hz. In the $^{13}C\{^1H\}$ NMR spectrum, the resonances corresponding to the =CH-carbon atoms of the butadiene are observed at 72.9, 71.0, 63.8, and 60.3 ppm, whereas the resonances due to the C(sp^2)-carbon atoms of isopropenyl group of the isopropenylphosphine ligand appear at 58.1 and 45.9 ppm. The $^{31}P\{^1H\}$ NMR spectrum contains two doublets at 1.4 and −11.0 ppm, with a P−P coupling constant of 117 Hz, in agreement with the mutually pseudo-*trans* disposition of the phosphines.

At room temperature, the addition of 1.0 equiv of phenylacetylene to an NMR tube containing a dichloromethane-d_2 solution of **3** leads, after 10 min, to a mixture of **8** (about 40%), the hydride-metallacyclopropene **11** (about 20%), and other unidentified products (Scheme 2).

The presence of **11** in the mixture is strongly supported by the ^{1}H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra. The ^{1}H NMR spectrum shows the resonance due to the CH_2-protons of the metallacyclopropene ligand at 1.62 ppm, as a triplet with a H−P coupling constant of 9.0 Hz. The hydride resonance is observed at −8.66 ppm, also as a triplet but with a H−P coupling constant of 19.3 Hz. In the $^{13}C\{^1H\}$ NMR spectrum the carbon atoms of the three-membered ring give rise to singlets at 268.9 (CPh) and 6.1 (CH_2) ppm. A singlet at 4.2 ppm in the $^{31}P\{^1H\}$ NMR spectrum is also characteristic of **11**.

The mixture is unstable, as that starting from **2**, and evolves. Complex **8** affords **10**. However, there are marked differences in behavior between **9** and **11**. In contrast to **9**, complex **11** reacts with the free ketone, present in the reaction medium, to give $[OsH\{\overline{C_6H_4C(O)CH_3}\}_2(P^iPr_3)_2]BF_4$ (**12**). After 6 h, the main components of the new mixture are **10** (about 35%) and **12** (about 20%).

Complex **12** was prepared as a pure analyzed solid by stirring of a dichloromethane solution of **3** under 1 atm of ethylene, at room temperature, for 15 min (eq 4). By this procedure, complex **12** was isolated in about 44% yield.



The structure proposed for **12** is strongly supported by its ^{1}H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra. In agreement with a highly symmetrical distribution of ligands around the osmium atom, the ^{1}H NMR spectrum shows aromatic resonances corresponding to only one type of phenyl group between 8.54 and 7.21 ppm, only one ketone-methyl resonance at 3.10 ppm, and only one resonance for the methyl groups of the triisopropylphosphine ligands at 0.84 ppm. In the high-field region, the spectrum contains the hydride resonance, which appears at −4.50 ppm as a triplet with a H−P coupling constant of 9.9 Hz. The position of this ligand, between the orthometalated phenyl groups, was inferred on the basis of a NOE experiment. The saturation of the hydride resonance increases the intensity of the phenyl resonance corresponding to the hydrogen atoms disposed *ortho* to the metal (42.6%), while the ketone-methyl resonance does not show any NOE effect. The $^{13}C\{^1H\}$ NMR spectrum also shows resonances corresponding to only one type of metalated ketone (for more details see Experimental Section). The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at −7.3 ppm, in accordance with the mutually *trans* disposition of the phosphine ligands.

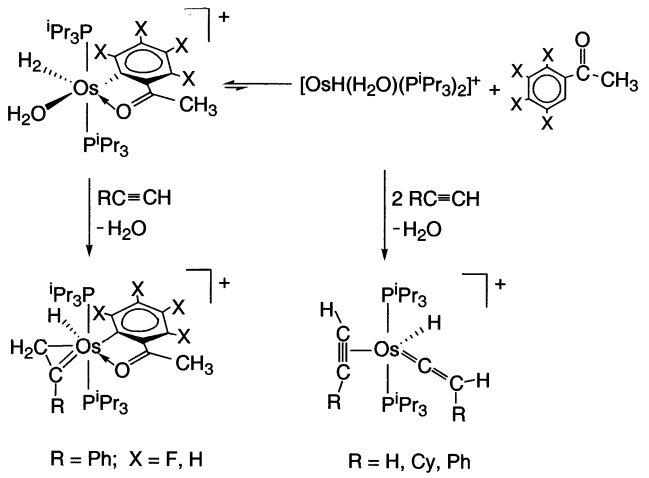
4. Hydride-Vinylidene-π-Alkyne Complexes versus Hydride-Metallacyclopropene Compounds. The formation of **4**, **7**−**9**, and **11** can be rationalized according to Scheme 4. In a manner similar to the oxime elongated dihydrogen complex $[Os\{\overline{C_6H_4C(O)CH_3}\}(\eta^2\text{-}H_2)\{N(OH)=C(CH_3)_2\}(P^iPr_3)_2]BF_4$,[10] in solution, complexes **2** and **3** release the ketone ligand as a consequence of the migration of a hydrogen atom of the elongated dihydrogen to the metalated-aryl carbon atom. This release affords the equilibrium between **2** (or **3**) and spectroscopically undetected concentrations of a highly unsaturated monohydride. The monohydride reacts with the alkynes to give the hydride-vinylidene-π-alkyne derivatives (**4**, **7**, and **8**), while the reactions of **2** and **3** with the alkynes lead to the hydride-

(43) Yasuda, H.; Nakamura, A. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 723.

(44) Δd = {*d*[Os−C(10)] + *d*[Os−C(7)]}/2 − {*d*[Os−C(9)] + *d*[Os−C(8)]}/2 and Δl = {*d*[C(10)−C(9)] + *d*[C(7)−C(8)]}/2 − *d*[C(8)−C(9)]. See ref 46.

(45) Bohanna, C.; Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A.; Sola, E. *Organometallics* **1995**, *14*, 4825.

Scheme 4



osmacyclopropene derivatives (**9** and **11**), in a way similar to the dihydride $[OsH_2(\kappa^2\text{-}O_2CCH_3)(H_2O)(P^iPr_3)_2]BF_4$.[7m]

Acetylene and cyclohexylacetylene favor the selective formation of hydride-vinylidene-π-alkyne complexes. However, phenylacetylene gives rise to a mixture of both types of compounds. In agreement with this, it has been shown that the presence of a phenyl substituent imposes an increase of the stability of the metallacyclopropene unit, by conjugation of the phenyl π orbitals with the π orbital of the Os=C-carbon atom.[7m]

In addition, it should be noted that the concentration of hydride-osmacyclopropene in the mixture starting from **2** is higher than that starting from **3**. This suggests that the presence of fluorine substituents in the metalated ketone stabilizes the five-membered osmium-ketone ring.

Concluding Remarks

This study has revealed that the reactions of the elongated dihydrogen complexes $[Os\{C_6X_4C(O)CH_3\}(\eta^2\text{-}H_2)(H_2O)(P^iPr_3)_2]BF_4$ (X = F, H) with terminal alkynes, RC≡CH, give rise in a competitive manner to hydride-vinylidene-π-alkyne compounds $[OsH(=C=CHR)(\eta^2\text{-}HC\equiv CR)(P^iPr_3)_2]BF_4$ and hydride-osmacyclopropene species $[OsH\{C_6X_4C(O)CH_3\}\{C(R)CH_2\}(P^iPr_3)_2]BF_4$. The preferred formation of one of the two types of compounds depends on the substituent R of the alkyne. When the substituent is hydrogen or alkyl, hydride-vinylidene-π-alkyne complexes are exclusively formed, while when the substituent is phenyl, a mixture of both types of derivatives is obtained.

With the exception of $[OsH(=C=CH_2)(\eta^2\text{-}HC\equiv CH)(P^iPr_3)_2]BF_4$, which is a suitable starting material to obtain other interesting organometallic compounds such as $OsH(\eta^3\text{-}C_3H_5)(=C=CH_2)(P^iPr_3)_2$ and $[OsH\{\kappa\text{-}N,\kappa\text{-}O[ON=C(CH_3)_2]\}(\equiv CCH_3)(P^iPr_3)_2]BF_4$, the hydride-vinylidene-π-alkyne complexes are unstable in solution. Complex $[OsH(=C=CHCy)(\eta^2\text{-}HC\equiv CCy)(P^iPr_3)_2]BF_4$ decomposes to unidentified products, while $[OsH(=C=CHPh)(\eta^2\text{-}HC\equiv CPh)(P^iPr_3)_2]BF_4$ evolves into the diphenylbutadiene derivative $[OsH(\eta^4\text{-}C_4H_4Ph_2)\{[\eta^2\text{-}CH_2=C(CH_3)]P^iPr_2\}(P^iPr_2{}^nPr)]BF_4$. The formation of this diolefin complex involves the dimerization of the alkyne together with the reduction of the resulting dimer, by hydrogen transfer from an isopropyl group of one of the phosphines, which is dehydrogenated to afford a mono-isopropenylphosphine ligand. One of the isopropyl groups of the other phosphine undergoes a carbon skeletal isomerization into *n*-propyl.

In contrast to $[OsH(=C=CHR)(\eta^2\text{-}HC\equiv CR)(P^iPr_3)_2]BF_4$ (R = Cy, Ph), the hydride-osmacyclopropene compounds are stable in solution. However, in the presence of acetophenone, complex $[OsH\{C_6H_4C(O)CH_3\}\{C(Ph)CH_2\}(P^iPr_3)_2]BF_4$ affords $[OsH\{C_6H_4C(O)CH_3\}_2(P^iPr_3)_2]BF_4$.

In conclusion, the stabilization of elongated dihydrogen complexes containing metal−σ-carbon bonds allows access to highly unsaturated monohydride intermediates, which can coordinate several alkyne molecules and, under particular conditions, subsequently couple them.

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 materials $OsH_3\{C_6F_4C(O)CH_3\}(P^iPr_3)_2$ (**1**),[46] $[Os\{C_6H_4C(O)CH_3\}(\eta^2\text{-}H_2)(H_2O)(P^iPr_3)_2]BF_4$ (**3**), and $[Os\{C_6H_4C(O)CH_3\}(\eta^2\text{-}H_2)\{N(OH)=C(CH_3)_2\}(P^iPr_3)_2]BF_4$[10] were prepared by the published methods.

^1H, ^{19}F, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra were recorded on either a Varian Unity 300, a Varian Gemini 2000, or a Bruker AXR 300 MHz instrument. Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks (^1H, $^{13}C\{^1H\}$), external H_3PO_4 ($^{31}P\{^1H\}$), or external $CFCl_3$ (^{19}F). Coupling constants, J and N ($N = J_{P-H} + J_{P'-H}$ for ^1H and $N = J_{P-C} + J_{P'-C}$ for $^{13}C\{^1H\}$) are given in hertz. Infrared spectra were run on a Perkin-Elmer 1730 spectrometer as solids (KBr pellet or Nujol mull). C, H, and N analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyzer. Mass spectral analyses were performed with a VG Austospec instrument. In FAB^+ mode, ions were produced with the standard Cs^+ gun at ca. 30 kV, and 3-nitrobenzyl alcohol (NBA) was used in the matrix.

Preparation of $[Os\{C_6F_4C(O)CH_3\}(\eta^2\text{-}H_2)(H_2O)(P^iPr_3)_2]BF_4$ (2). A red solution of **1** (100.0 mg, 0.142 mmol) in 12 mL of dichloromethane was treated with $HBF_4{\cdot}H_2O$ (21 μL, 0.170 mmol) and stirred for 30 min at room temperature. The resulting solution was filtered through Celite and concentrated under vacuum. The 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: 94.1 mg (82%). Anal. Calcd for $C_{26}H_{49}BF_8O_2OsP_2$: C 38.62; H 6.11. Found: C 38.45; H 6.27. IR (KBr, cm^{-1}): ν(OH) 3362 (s), ν(OsH) 2195 (m), ν(CO) 1641 (s), ν(BF) 1050 (br). ^1H NMR (300 MHz, CD_2Cl_2, 293K): δ 4.38 (br, 2H, H_2O), 3.09 (dt, $J_{H-F} = 4.8$ Hz, $J_{H-P} = 1.8$ Hz, 3H, CH_3), 1.88 (m, 6H, PC*H*), 1.05 and 0.91 (both dvt, $N = 13.5$ Hz, $J_{H-H} = 6.6$ Hz, 18H, PCHCH_3), −6.63 (t, $J_{P-H} = 8.4$ Hz, 2H, OsH). $^{31}P\{^1H\}$ NMR (121.42 MHz, CD_2Cl_2, 293 K): δ 14.5 (s). ^{19}F NMR (282.33 MHz, CD_2Cl_2, 293 K): δ −114.6, −136.6, −146.9 and −168.4 (all m, Ph), −153.1 (br s, BF_4). $^{13}C\{^1H\}$ NMR (75.42 MHz, CD_2Cl_2, 293 K): δ 204.8 (s, C=O), 158.2 (dm, $J_{C-F} =$ 35.0 Hz, Os−C), 152−124 (all m, Ph), 28.6 (d, $J_{C-F} = 8.7$ Hz,

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

CH_3), 24.6 (vt, N = 25.3 Hz, P*C*H), 19.1 and 19.0 (both s, PCH*C*H_3). MS (FAB$^+$): m/z 722 ($M^+ - H$). $T_{1(min)}$ (ms, OsH_2, 300 MHz, CD_2Cl_2, 213 K): 40 ± 1 (−6.63 ppm, 2H).

[Os{$C_6F_4C(O)CH_3$}(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 −6.52 (tt(1:1:1), J_{H-P} = 8.4 Hz, J_{H-D} = 3.3 Hz, 1H, OsH).

Preparation of [OsH(=C=CH_2)(η^2-HC≡CH)(P^iPr_3)$_2$]BF_4 (4). An orange solution of **2** (110.0 mg, 0.136 mmol) (*method a*) or **3** (100.0 mg, 0.136 mmol) (*method b*) in 12 mL of dichloromethane was stirred under an acetylene atmosphere for 10 min at room temperature. The resulting solution was filtered through Celite and concentrated in vacuo. The subsequent addition of diethyl ether (5 mL) caused the precipitation of a yellow solid, which was washed with further portions of diethyl ether and dried in vacuo. Yield: 60.1 mg (68%), *method a*; 63.1 mg (71%), *method b*. Anal. Calcd for $C_{22}H_{47}BF_4OsP_2$: C 40.61; H 7.28. Found: C 40.77; H 7.38. IR (KBr, cm^{-1}): ν(OsH) 2161 (m), ν(C≡C) 1882 (m), ν(BF) 1050 (br). ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ 10.17 (part AA′ of a AA′XX′ spin system, AA′ = H_2C_2 and XX′ = (P^iPr_3)$_2$), 3.01 (m, 6H, PC*H*), 1.70 (t, J_{P-H} = 4.5 Hz, 2H, =CH_2), 1.34 and 1.17 (both dvt, N = 14.9 Hz, J_{H-H} = 7.3 Hz, 18H, PCHCH_3), −3.58 (t, J_{P-H} = 22.9 Hz, 1H, OsH). ^{31}P{^{1}H} NMR (121.42 MHz, CD_2Cl_2, 293 K): δ 30.8 (s). ^{19}F NMR (282.33 MHz, CD_2Cl_2, 293 K): δ −155.1 (br s). ^{13}C{^{1}H} NMR (75.42 MHz, CD_2Cl_2, 293 K): δ 283.6 (t, J_{P-C} = 14.8 Hz, Os=C), 137.3 (dd, J_{P-C} = 7.3 Hz, J_{P-C} = 3.2 Hz, H_2C_2), 90.3 (t, J_{P-C} = 6.0 Hz, =CH_2), 25.0 (vt, N = 29.9 Hz, P*C*H), 20.2 and 19.3 (both s, PCH*C*H_3). MS (FAB$^+$): m/z 566 (M^+ + H).

Preparation of OsH(η^3-C_3H_5)(=C=CH_2)(P^iPr_3)$_2$ (5). A yellow solution of **4** (101.0 mg, 0.155 mmol) in 9 mL of tetrahydrofuran was treated with a solution of CH_3MgCl in tetrahydrofuran (62 μL, 0.186 mmol, 3 M) and stirred for 25 min at 213 K. Then the solvent was removed and pentane was added to filter the ionic salts. The resulting solution was dried in vacuo. A red oil was obtained. Yield: 82.1 mg (91%). IR (KBr, cm^{-1}): ν(OsH) 2020 (m). ^{1}H NMR (300 MHz, C_6D_6, 293 K, plus COSY): δ 4.92 (m, 1H, CH_{allyl}), 3.01 (m, 1H, C$_a$$H_{syn}$), 2.89 (m, 1H, C$_a$$H_{anti}$), 2.63 and 2.37 (both m, 3H, PC*H*), 2.16 (m, 1H, C$_b$$H_{syn}$), 1.46 (m, 1H, C$_b$$H_{anti}$), 1.31 (dd, J_{P-H} = 12.0 Hz, J_{H-H} = 7.2 Hz, 9H, PCCH_3), 1.2 (this peak is hidden under the P^iPr_3 signals, Os=C=CH_2), 1.18 (m, 18H, PCCH_3), 1.05 (dd, J_{P-H} = 12.0 Hz, J_{H-H} = 7.2 Hz, 9H, PCCH_3), −9.33 (ddd, J_{P-H} = 24.6 Hz, $J_{P'-H}$ = 17.1 Hz, $J_{H-Hanti}$ <1 Hz, 1H, OsH). ^{1}H{^{31}P} NMR (300 MHz, C_6D_6, 293 K, allyl group): δ 4.94 (tt, $J_{H-Hanti}$ = 10.2 Hz, J_{H-Hsyn} = 6.9 Hz, 1H, C*H*), 3.01 (dd, J_{H-Hsyn} = 6.9 Hz, $J_{Hsyn-Hsyn}$ = 3.0 Hz, 1H, C$_a$$H_{syn}$), 2.89 (d, J_{H-H} = 10.2 Hz, 1H, C$_a$$H_{anti}$), 2.16 (dd, J_{H-Hsyn} = 6.9 Hz, $J_{Hsyn-Hsyn}$ = 3.0 Hz, 1H, C$_b$$H_{syn}$), 1.46 (dd, J_{H-H} = 10.2 Hz, $J_{H(OsH)-Hanti}$ <1 Hz, 1H, C$_b$$H_{anti}$). ^{31}P{^{1}H} NMR (121.42 MHz, C_6D_6, 293 K): AB spin system: δ 9.4, $\Delta\nu$ = 948 Hz, J_{A-B} = 249 Hz. ^{13}C{^{1}H} NMR (75.42 MHz, C_6D_6, 293 K, plus HETCOR): δ 292.4 (dd, J_{P-C} = $J_{P'-C}$ = 14.7 Hz, Os=*C*), 92.4 (dd, J_{P-C} = $J_{P'-C}$ = 4.1 Hz, Os=C=*C*H_2), 90.3 (s, *C*H_{allyl}), 29.1 (s, *C*$_b$$H_{2allyl}$), 26.3 (dd, J_{P-C} = 23.1, $J_{P'-C}$ = 1.8 Hz, P*C*H), 25.8 (dd, J_{P-C} = 21.1 Hz, $J_{P'-C}$ = 1.3 Hz, P*C*H), 23.3 (d, J_{P-C} = 2.8 Hz, *C*$_a$$H_{2allyl}$), 20.8, 20.5, 20.2, and 19.9 (all s, PCH*C*H_3).

Preparation of [OsH{κ-*N*,κ-*O*[ON=C(CH_3)$_2$]}(≡CCH_3)(P^iPr_3)$_2$]BF_4 (6). This complex was prepared by three methods. *Method a*: a yellow solution of **4** (100.0 mg, 0.154 mmol) in 12 mL of dichloromethane was treated with acetone oxime (27.5 mg, 0.376 mmol) and stirred for 1 h at room temperature and then was filtered through Celite and evaporated to dryness. A brown oil was obtained, which was washed with diethyl ether and dried in vacuo. *Method b*: an orange solution of [Os{$C_6H_4C(O)CH_3$}(η^2-H_2){N(OH)=C(CH_3)$_2$}(P^iPr_3)$_2$]BF_4 (100.2 mg, 0.126 mmol) in 12 mL of dichloromethane was stirred under an acetylene atmosphere for 1 h at room temperature and then was filtered through Celite and evaporated to dryness. A brown oil was obtained, which was washed with diethyl ether and dried in vacuo. *Method c*: an orange solution of [(Os{C_6H_4CO)CH_3}(η^2-H_2){N(OH)=C(CH_3)$_2$}-(P^iPr_3)$_2$]BF_4 (182.1 mg, 0.230 mmol) in 12 mL of dichloromethane was treated with trimethylsilylacetylene (34 μL, 0.276 mmol) and stirred for 45 min at room temperature and then was filtered through Celite and evaporated to dryness. A brown oil was obtained, which was washed with diethyl ether and dried in vacuo. Yield: 96.2 mg (90%), *method a*; 70.5 mg (80%), *method b*; 138.8 mg (86%), *method c*. IR (KBr, cm^{-1}): ν(OsH) 2120 (m), ν(CN) 1643 (s), ν(BF) 1050 (br). ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ 2.33 (m, 6H, PC*H*), 2.25 and 2.18 (both s, 3H, NCCH_3), 1.41 (s, 3H, Os≡CCH_3), 1.31 and 1.29 (both dvt, N = 14.4 Hz, J_{H-H} = 7.2 Hz, 18H, PCHCH_3), −6.81 (t, J_{P-H} = 17.1 Hz, 1H, OsH). ^{31}P{^{1}H} NMR (121.42 MHz, CD_2Cl_2, 293 K): δ 37.3 (s). ^{19}F NMR (282.33 MHz, CD_2Cl_2, 293 K): δ −156.3 (br s). ^{13}C{^{1}H} NMR (75.42 MHz, CD_2Cl_2, 293 K): δ 283.8 (t, J_{C-P} = 9.4 Hz, Os≡C), 147.2 (s, N=C), 40.2 (s, Os≡*C*CH_3), 25.1 (vt, N = 27.2 Hz, P*C*H), 22.1 (s, NC*C*H_3), 19.6 (s, PCH*C*H_3), 19.2 (s, NC*C*H_3), 18.8 (s, PCH*C*H_3). MS (FAB$^+$): m/z 612 (M^+).

Preparation of [OsH(=C=CHCy)(η^2-HC≡CCy)(P^iPr_3)$_2$]BF_4 (7). An orange solution of **2** (100.0 mg, 0.124 mmol) (*method a*) or **3** (89.1 mg, 0.121 mmol) (*method b*) in 12 mL of dichloromethane was treated with cyclohexylacetylene (35 μL, 0.273 mmol, *method a*; or 34 μL, 0.266 mmol, *method b*) and stirred for 20 min at 233 K. The resulting solution was concentrated in vacuo. The additon of diethyl ether led to a brown oil, which was washed with diethyl ether and dried in vacuo. Yield: 54.2 mg (55%), *method a*; 54.5 mg (54%), *method b*. IR (Nujol, cm^{-1}): ν(OsH) 2116 (m), ν(C≡C) 1895 (m), ν(BF) 1050 (br). ^{1}H NMR (300 MHz, CD_2Cl_2, 233 K, plus HMQC): δ 10.26 (d, J_{P-H} = 27.6 Hz, 1H, ≡CH), 3.68 and 3.40 (both m, 1H, Cy), 3.00 and 2.93 (both m, 3H, PCH), 2.41 (ddd, $J_{H-H(CHCy)}$ = 7.8 Hz, J_{P-H} = $J_{P'-C}$ = 4.5 Hz, 1H, =CH), 2.0−0.8 (m, 20H, =CCy and ≡CCy), 1.5−1.0 (m, 36H, PCCH_3), −4.64 (dd, J_{P-H} = 29.3 Hz, $J_{P'-H}$ = 23.6 Hz, 1H, OsH). ^{31}P{^{1}H} NMR (121.42 MHz, CD_2Cl_2, 233 K): AB spin system: δ 31.0, $\Delta\nu$ = 342 Hz, J_{A-B} = 129 Hz. ^{19}F NMR (282.33 MHz, CD_2Cl_2, 233 K): δ −155.2 (br s). ^{13}C{^{1}H} NMR (75.42 MHz, CD_2Cl_2, 233 K, plus APT): δ 282.3 (dd, J_{P-C} = $J_{P'-C}$ = 15.1 Hz, Os=C), 161.5 (br s, ≡*C*Cy), 139.3 (dd, J_{P-C} = 11.7 Hz, $J_{P'-C}$ = 4.9 Hz, ≡*C*H), 111.7 (br s, =*C*H), 45.0 (s, *C*H_{Cy}), 34.8, 34.6, 26.0, 25.6, and 25.5 (all s, secundary carbon atoms of cyclohexyl groups), 31.3 (s, *C*H_{Cy}), 23.5 (d, J_{P-C} = 28.4 Hz, P*C*H), 20.1, 18.7, 18.6, and 17.2 (all s, PCH*C*H_3). MS (FAB$^+$): m/z 729 (M^+).

Reaction of [Os{$C_6F_4C(O)CH_3$}(η^2-H_2)(H_2O)(P^iPr_3)$_2$]BF_4 with Phenylacetylene. To a solution of **2** (20.0 mg, 0.025 mmol) in 0.5 mL of CD_2Cl_2 at 298 K in an NMR tube was added the stoichiometric amount of phenylacetylene (3 μL, 0.027 mmol). After 10 min the ^{1}H NMR spectrum indicated the formation of [OsH(=C=CHPh)(η^2-HC≡CPh)(P^iPr_3)$_2$]BF_4 (**8**) in a 27% yield and [Os{$C_6F_4C(O)CH_3$}{C(Ph)CH_2}(P^iPr_3)$_2$]BF_4 (**9**) in a 45% yield. After 3 h the ^{1}H NMR spectrum showed that the main component in the mixture was [OsH(η^4-C_4H_4-Ph_2){[η^2-CH_2=C(CH_3)]P^iPr_2}($P^iPr_2{}^nPr$)]BF_4 (**10**) (about 25%).

The metallacyclopropene complex **9** was isolated by following this procedure: an orange solution of **2** (100.0 mg, 0.124 mmol) in 12 mL of dichloromethane was treated with phenylacetylene (14 μL, 0.124 mmol) and stirred for 10 min at room temperature and then was filtered through Celite and concentrated to ca. 1 mL. Subsequent addition of diethyl ether caused the precipitation of a green solid, which was washed with further portions of diethyl ether and dried in vacuo. Yield: 31.7 mg (35%).

Data for [OsH(=C=CHPh)(η^2-HC≡CPh)(P^iPr_3)$_2$]BF_4 (8). IR (Nujol, cm^{-1}): ν(OsH) 2158 (m), ν(C≡C) 1910 (m), ν(BF) 1060 (br). ^{1}H NMR (300 MHz, CD_2Cl_2, 233 K): δ 10.61 (d, J_{P-H}

= 25.8 Hz, 1H, ≡CH), 7.50 (t, J_{H-H} = 7.5 Hz, 2H, *m*-Ph), 7.41 (t, J_{H-H} = 7.5 Hz, 1H, *p*-Ph), 7.18 (t, J_{H-H} = 7.5 Hz, 2H, *m*-Ph), 7.12 (d, J_{H-H} = 7.5 Hz, 2H, *o*-Ph), 6.95 (t, J_{H-H} = 7.5 Hz, 1H, *p*-Ph), 6.53 (d, J_{H-H} = 7.5 Hz, 2H, *o*-Ph), 3.77 (dd, J_{P-H} = $J_{P'-H}$ = 4.5 Hz, 1H, =CH), 3.00 and 2.46 (both m, 3H, PCH_3), 1.34 (dd, J_{P-H} = 13.2 Hz, J_{H-H} = 6.6 Hz, 9H, $PCCH_3$), 1.77 (m, 18H, $PCCH_3$), 1.05 (dd, J_{P-H} = 13.2 Hz, J_{H-H} = 6.6 Hz, 9H, $PCCH_3$), −3.14 (dd, J_{P-H} = 27.0 Hz, $J_{P'-H}$ = 23.1 Hz, 1H, OsH). $^{31}P\{^1H\}$ NMR (121.42 MHz, CD_2Cl_2, 233 K): AB spin system: δ 29.6, $\Delta\nu$ = 170 Hz, J_{A-B} = 126 Hz. ^{19}F NMR (282.33 MHz, CD_2Cl_2, 233 K): δ −154.6 (br s). $^{13}C\{^1H\}$ NMR (75.42 MHz, CD_2Cl_2, 233 K): δ 290.5 (dd, J_{P-C} = $J_{P'-C}$ = 15.1 Hz, Os=C), 152.6 (dd, J_{P-C} = 7.5 Hz, $J_{P'-C}$ = 5.3 Hz, ≡*C*Ph), 139.4 (dd, $J_{P'-C}$ = 9.5 Hz, J_{P-C} = 4.1 Hz, ≡*C*H), 129.5, 129.2, 129.0, 126.4, 126.3, and 125.6 (all s, aromatic carbon atoms), 110.6 (dd, J_{P-C} = $J_{P'-C}$ = 5.6, Os=C=*C*), 27.8 (d, J_{P-C} = 25.1 Hz, P*C*H), 21.2, 20.7, 19.3, and 19.1 (all s, PCH*C*H_3). MS (FAB^+): *m*/*z* 717 (M^+).

Data for [OsH{$C_6F_4C(O)CH_3$}{C(Ph)CH_2}(P^iPr_3)$_2$]BF_4 (9). Anal. Calcd for $C_{34}H_{53}BF_8OOsP_2$: C 45.74; H 5.98. Found: C 45.43; H 5.91. IR (KBr, cm^{-1}): ν(OsH) 2210 (m), ν(CO) 1629 (s), ν(BF) 1060 (br). ^1H NMR (300 MHz, CD_2Cl_2, 293 K): δ 10.02 (br, 1H, Ph), 8.22 (t, J_{H-H} = 7.5 Hz, 1H, Ph), 7.71 (br, 1H, Ph), 7.39 (t, J_{H-H} = 7.5 Hz, 1H, Ph), 7.24 (d, J_{H-H} = 7.5 Hz, 1H, Ph), 3.26 (d, J_{H-F} = 5.4 Hz, 3H, CH_3), 1.91 (t, J_{H-P} = 8.5 Hz, 2H, $OsCH_2$), 1.70 (m, 6H, P*CH*), 0.99 and 0.93 (both dvt, *N* = 13.9 Hz, J_{H-H} = 6.9 Hz, 18H, PCH*C*H_3), −7.72 (td, J_{H-P} = 17.2 Hz, J_{H-F} = 10.6 Hz, 1H, OsH). ^1H NMR (300 MHz, CD_2Cl_2, 233 K, aromatic region): δ 10.05 (d, J_{H-H} = 7.5 Hz, 1H, Ph), 8.19 (t, J_{H-H} = 7.5 Hz, 1H, Ph), 8.06 (d, J_{H-H} = 7.5 Hz, 1H, Ph), 7.73 (t, J_{H-H} = 7.5 Hz, 1H, Ph), 7.58 (t, J_{H-H} = 7.5 Hz, 1H, Ph); there are no significant changes in the other signals. $^{31}P\{^1H\}$ NMR (121.42 MHz, CD_2Cl_2, 293 K): δ 3.7 (s). ^{19}F NMR (282.33 MHz, CD_2Cl_2, 293 K): δ −96.1, −132.4, −143.5, and −158.0 (all m, Ph) −155.1 (br s, BF_4). $^{13}C\{^1H\}$ NMR (75.42 MHz, CD_2Cl_2, 233 K): δ 272.9 (s, Os=C), 211.3 (s, C=O), 166.2 (dm, J_{C-F} = 46.8 Hz, Os−C), 152−125 (all m, $OsPh_F$), 144.6 (s, C_{ipso}Ph), 135.8, 134.3, 133.3, 131.7, and 131.5 (all s, Ph), 30.8 (d, J_{C-F} = 9.2 Hz, *C*H_3), 26.3 (vt, *N* = 25.5 Hz, P*C*H), 19.1 (s, PCH*C*H_3), 4.2 (s, Os−CH_2). MS (FAB^+): *m*/*z* 807 (M^+).

Data for [OsH(η^4-$C_4H_4Ph_2$){[η^2-CH_2=C(CH_3)]P^iPr_2}-($P^iPr_2{}^nPr$)]BF_4 (10). ^1H NMR (300 MHz, CD_2Cl_2, 298 K): δ 7.6−7.0 (m, 10H, Ph), 5.68, 5.23, and 3.90 (all m, 1H, =CH butadiene group), 3.2−0.5 (m, CH, CH_2, and CH_3 of the phosphine groups), 2.07 (m, 1H, =CH butadiene group), −12.98 (dd, J_{H-P} = 30.8 Hz, $J_{H-P'}$ = 16.4 Hz, 1H, OsH). $^{31}P\{^1H\}$ NMR (121.42 MHz, CD_2Cl_2, 298 K): δ 1.4 and −11.0 (both d, J_{P-P} = 117 Hz). ^{19}F NMR (282.33 MHz, CD_2Cl_2, 298 K): δ −154.5 (br s). $^{13}C\{^1H\}$ NMR (75.42 MHz, CD_2Cl_2, 298 K): δ 131−125 (aromatic carbon atoms), 72.9, 71.0, 63.8, and 60.3 (CH carbon atoms of butadiene group), 58.1 (d, J_{C-P} = 11 Hz, PC=), 45.9 (d, J_{C-P} = 2 Hz, PC=*C*H_2), 33−16 (aliphatic carbon atoms of P^iPr and P^nPr groups). MS (FAB^+): *m*/*z* 635 (M^+ − Ph − 5H).

Reaction of [Os{$C_6H_4C(O)CH_3$}(η^2-H_2)(H_2O)(P^iPr_3)$_2$]BF_4 with Phenylacetylene. To solutions of **3** (20.0 mg, 0.027 mmol) in 0.5 mL of CD_2Cl_2 at 298 K in an NMR tube was added the stoichiometric amount of phenylacetylene (3 μL, 0.027 mmol). After 10 min the ^1H NMR spectrum indicated the formation of [OsH(=C=CHPh)(η^2-HC≡CPh)(P^iPr_3)$_2$]BF_4 (**8**) in a 40% yield and [OsH{$C_6H_4C(O)CH_3$}{C(Ph)CH_2}(P^iPr_3)$_2$]BF_4 (**11**) in a 20% yield. After 6 h the ^1H NMR spectrum showed that the main components in the mixture were [OsH(η^4-C_4H_4-Ph_2){[η^2-CH_2=C(CH_3)]P^iPr_2}($P^iPr_2{}^nPr$)]BF_4 (**10**) in a 35% yield and [OsH{$C_6H_4C(O)CH_3$}$_2$(P^iPr_3)$_2$]BF_4 (**12**) in a 20% yield.

The complex **12** was isolated by following this procedure: an orange solution of **3** (110.0 mg, 0.149 mmol) in 12 mL of dichloromethane was stirred under an ethylene atmosphere for 15 min at room temperature. The resulting solution was filtered through Celite and evaporated to dryness. The subsequent addition of dichloromethane (0.5 mL) and 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: 55.2 mg (44%).

Data for [OsH{$C_6H_4C(O)CH_3$}{C(Ph)CH_2}(P^iPr_3)$_2$]BF_4 (11). IR (KBr, cm^{-1}): ν(OsH) 2113 (m), ν(CO) 1628 (s), ν(BF) 1060 (br). ^1H NMR (300 MHz, CD_2Cl_2, 233 K): δ 10.20 (d, J_{H-H} = 7.5 Hz, 1H, Ph), 8.14 (t, J_{H-H} = 7.5 Hz, 1H, Ph), 8.07 (d, J_{H-H} = 7.5 Hz, 1H, Ph), 7.70 (t, J_{H-H} = 7.5 Hz, 1H, Ph), 7.61 (t, J_{H-H} = 7.5 Hz, 1H, Ph), 7.6−6.9 (m, 4H, Os−Ph), 3.12 (s, 3H, CH_3), 1.62 (t, J_{H-P} = 9.0 Hz, 2H, $OsCH_2$), 1.52 (m, 6H, P*CH*), 1.3−0.8 (m, 36H, PCH*C*H_3), −8.66 (t, J_{H-P} = 19.3 Hz, 1H, OsH). $^{31}P\{^1H\}$ NMR (121.42 MHz, CD_2Cl_2, 233 K): δ 4.2 (s). ^{19}F NMR (282.33 MHz, CD_2Cl_2, 233 K): δ −154.5 (br s). $^{13}C\{^1H\}$ NMR (75.42 MHz, CD_2Cl_2, 233 K): δ 268.9 (s, Os=C), 215.2 (s, C=O), 189.6 (t, J_{C-P} = 11.3 Hz, Os−C), 146−125 (all s, aromatic carbon atoms), 26.3 (vt, *N* = 24.4 Hz, P*C*H), 25.8 (s, *C*H_3), 19.8 (s, PCH*C*H_3), 6.1 (s, Os−CH_2). MS (FAB^+): *m*/*z* 735 (M^+).

Data for [OsH{$C_6H_4C(O)CH_3$}$_2$(P^iPr_3)$_2$]BF_4 (12). Anal. Calcd for $C_{34}H_{57}BF_4O_2OsP_2$: C 48.80; H 6.87. Found: C 48.49; H 6.64. IR (KBr, cm^{-1}): ν(OsH) 2020 (m), ν(CO) 1589 (s), ν(BF) 1060 (br). ^1H NMR (300 MHz, CD_2Cl_2, 293 K): δ 8.54 (d, J_{H-H} = 7.8 Hz, 2H, Ph), 7.88 (dd, J_{H-H} = 7.8 Hz, J_{H-H} = 1.5 Hz, 2H, Ph), 7.31 (vtd, J_{H-H} = 7.8 Hz, J_{H-H} = 1.5 Hz, 2H, Ph), 7.21 (vt, J_{H-H} = 7.8 Hz, 2H, Ph), 3.10 (t, J_{P-H} = 1.5 Hz, 6H, CH_3), 1.47 (m, 6H, P*CH*), 0.84 (dvt, *N* = 13.3 Hz, J_{H-H} = 6.6 Hz, 36H, PCH*C*H_3), −4.50 (t, J_{P-H} = 9.9 Hz, 1H, OsH). $^{31}P\{^1H\}$ NMR (121.42 MHz, CD_2Cl_2, 293 K): δ −7.3 (s). ^{19}F NMR (282.33 MHz, CD_2Cl_2, 293 K): δ −155.1 (br s). $^{13}C\{^1H\}$ NMR (75.42 MHz, CD_2Cl_2, 293 K): δ 211.4 (s, C=O), 173.6 (t, J_{P-C} = 6.9 Hz, Os−C), 144.7 (s, C_{ipso}), 147.7, 136.3, 134.0, and 123.7 (all s, Ph), 24.9 (s, *C*H_3), 23.2 (vt, *N* = 23.4 Hz, P*C*H), 18.9 (s, PCH*C*H_3). MS (FAB^+): *m*/*z* 751 (M^+).

Structural Analysis of Complexes 4, 9, and 10. X-ray data were collected for all complexes on a Bruker Smart APEX CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube source (molybdenum radiation, λ = 0.71073 Å) operating at 50 kV and 40 mA. Data were collected over the hemisphere or the complete sphere by a combination of three or four sets. Each frame exposure time was 10−30 s covering 0.3° in ω. Data were corrected for absorption by using a multiscan method applied with the SADABS[47] program. The structures for all compounds were solved by the Patterson method. Refinement, by full-matrix least squares on F^2 with SHELXL97,[48] was similar for all complexes, including isotropic and subsequently anisotropic displacement parameters. In the last cycles of anisotropic refinement, the shape and size of some thermal ellipsoids suggest the presence of disorder in some ligands in the three molecules. In **4**, the BF_4 anion was refined in two sites with a common B atom (occupancies 0.57(1) and 0.43(1), respectively). Two methyls (C9A−C9B, C16A−C16B) of the triisopropylphosphine ligands were refined in two positions (0.5−0.5). These groups were refined with an isotropic model and restrained geometry. In **9**, two isopropyls were observed also disordered. These groups were refined isotropically with restrained geometries with occupancies of 0.75(8) (C23A, C24A, C25A); 0.25(8) (C23B, C24B, C25B); 0.58(5) (C29A, C30A, C31A); and 0.42(5) (C29B, C30B, C31B). In **10**, the anion was observed disordered over two positions (0.52(2) and 0.48(2)) as result of a rotation over a B−F bond. A phenyl group was observed split in two sites with occupan-

(47) Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33−38. *SADABS*, Area-detector absorption correction; Bruker-AXS: Madison, WI, 1996.
(48) *SHELXTL* Package v. 6.10; Bruker-AXS: Madison, WI, 2000. Sheldrick, G. M. *SHELXS-86* and *SHELXL-97*; University of Göttingen: Göttingen, Germany, 1997.

cies of 0.67(2) (C1A to C6A) and 0.33 (2) (C1B to C6B) and an isopropyl refined in two positions, 0.57(1) (C23A−C24A−C25A) and 0.43(1) (C23B−C24B−C25B). In this case an anisotropic refinement was performed with restrained geometry.

The hydrogen atoms for nondisordered groups were observed or calculated and refined freely by using a restricted riding model. Hydride ligands were located but they do not refine appropriately, and fixed positions or fixed Os−H distances were used. All the highest electronic residuals were observed in close proximity of the Os centers and make no chemical sense.

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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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