One-Pot Dehydrogenative Addition of Isopropyl to Alkynes Promoted by Osmium: Formation of γ-(η^3-Allyl)-α-Alkenylphosphine Derivatives Starting from a Dihydride−Dihydrogen−Triisopropylphosphine Complex

Miguel A. Esteruelas,* Yohar A. Hernández, Ana M. López,* Montserrat Oliván, and Enrique Oñate

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

Received January 3, 2007

The dihydride−dihydrogen complex $[OsH_2(\eta^5\text{-}C_5H_5)(\eta^2\text{-}H_2)(P^iPr_3)]BF_4$ (**1**) reacts in acetone with 1-phenyl-1-propyne and 2-butyne to give the γ-(η^3-allyl)-α-alkenylphosphine derivatives $[OsH(\eta^5\text{-}C_5H_5)\{\kappa^4\text{-}(P,C,C,C)\text{-}CH_2C[CH_2C(=CH_2)P^iPr_2]CHR\}]BF_4$ (R = Ph (**2**), CH_3 (**3**)), by means of one-pot tandem processes of four reactions. The stable intermediates have been isolated and characterized. In acetone, complex **1** dissociates H_2 and coordinates the solvent to afford $[OsH_2(\eta^5\text{-}C_5H_5)(\kappa^1\text{-}OCMe_2)(P^iPr_3)]BF_4$ (**4**), which reacts with a molecule of 1-phenyl-1-propyne or 2-butyne to form $[OsH(\eta^5\text{-}C_5H_5)(\eta^3\text{-}CH_2\text{-}CHCHR)(P^iPr_3)]BF_4$ (R = Ph (**5**), CH_3 (**6**)), containing the CHR group *cisoid* disposed to the phosphine and the R substituent *anti* to C_{meso}. In dichloromethane, complexes **5** and **6** evolve to the thermodynamic isomers **7** and **8**, containing the CHR group *cisoid* disposed to the hydride and the R substituent *syn* to C_{meso}. The reactions of **5** and **6** with a second molecule of the respective alkyne lead to the corresponding *Z*-olefin and $[Os(\eta^5\text{-}C_5H_5)\{\eta^2\text{-}(Z)\text{-}CH(CH_3)=CHR\}\{\kappa^3\text{-}(P,C,C)\text{-}[CH_2=C(CH_3)]P^iPr_2\}]BF_4$ (R = Ph (**9**), CH_3 (**10**)). The isopropenyl group of the phosphine of **9** and **10** undergoes coupling with a third alkyne molecule to give **2** and **3**.

Introduction

C−H bond activation[1] and C−C bond formation[2] mediated by transition metal complexes are types of reactions of great importance due to their connection with the functionalization of hydrocarbons.[3] Those involving alkenes are promising regarding synthetic applications.[4] In contrast to C(sp^2)−H bonds, functionalization of a C(sp^3)−H bond remains difficult.[5] Thus, the alkane dehydrogenation has been used as the most reasonable first step in order to perform alkane transformations.[6] Although the process is thermodynamically unfavorable, the equilibrium is shifted to the right by adding a hydrogen acceptor.[7] Alkane dehydrogenation requires C(sp^3)−H bond activation, which is facilitated by effecting substrate precoordination using a donor functionality in the organic molecule.[8]

The hemilability of hybrid ligands is an important property in homogeneous catalysis and to prepare molecular-based sensors and materials.[9] This prompted us to initiate a research program dedicated to the functionalization of trialkylphosphines. Thus, as a part of our work with half-sandwich transition metal compounds,[10] we have recently converted one of the triisopro-

* Corresponding authors. E-mail: maester@unizar.es; amlopez@unizar.es.

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10.1021/om070004d CCC: $37.00
Publication on Web 03/27/2007

pylphosphine ligands of $Os(\eta^5\text{-}C_5H_5)Cl(P^iPr_3)_2$[11,10b] into a hemilabile isopropenyldi(isopropyl)phosphine, to afford $Os(\eta^5\text{-}C_5H_5)Cl\{\kappa^3\text{-}(P,C,C)\text{-}[CH_2{=}C(CH_3)]P^iPr_2\}$, in a three-step procedure involving oxidative addition of molecular hydrogen, reaction of the resulting dihydride with diphenylacetylene to give $Os(\eta^5\text{-}C_5H_5)Cl(\eta^2\text{-}PhC{\equiv}CPh)(P^iPr_3)$, and reduction of the coordinated alkyne by hydrogen transfer from an isopropyl substituent of triisopropylphosphine that is dehydrogenated.[12] In subsequent stages, we have also transformed the isopropenyldi(isopropyl)phosphine into α-allylphosphines by reaction with diazoalkanes via [2+2] cycloaddition reactions,[13] iminophosphines by insertion of the C≡N bond of benzonitriles into a $C(sp^2)-H$ bond,[14] dihydronaphthyldi(isopropyl)phosphine by a novel cyclization with phenylacetylene,[15] and dienylphosphines by ene-type reactions between the isopropenyl group and the C≡C bond of alkynes.[16]

Modern chemistry demands synthetic strategies that are respectful to the environment, avoiding workup steps, such as chromatographic purification, extraction, recrystallization, etc., in order to reduce the use of reagents and solvents. Thus, the combination of several reactions to form sequences that take place in a sort of domino or consecutive process is significant and of general interest.[17] These sequential transformations should afford a *one-pot tandem reaction*, which should lead to a simple, elegant, efficient, and highly selective formation of a novel compound.

Transition metal hydride complexes, in particular those with nonclassical interaction between the hydrogen atoms bonded to the metal, have a versatile reactivity with organic molecules.[18] They promote the reduction of C−C and C−heteroatom multiple bonds;[19] the activation of C−C,[20] C(sp)−H,[21] $C(sp^2)-H$,[22] $C(sp^2)-$halogen,[23] and $C(sp^3)-H$[24] bonds, including alkyl dehydrogenation;[25] and the formation of C−C[26] and C−heteroatom[27] bonds. The presence of more than one hydrogen at the metallic center allows the access of several organic molecules to the metal. This facilitates different types of

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coupling reactions and the generation of organic fragments with a rich chemistry.[28]

As part of the work of our group on the chemistry of osmium−polyhydride and −dihydrogen complexes,[29] we have recently reported the preparation and characterization of the dihydride−dihydrogen compound $[OsH_2(\eta^5\text{-}C_5H_5)(\eta^2\text{-}H_2)(P^i\text{-}Pr_3)]BF_4$, which promotes the selective C═C reduction and selective C−H bond activation of α,β-unsaturated ketones.[30] Now, we have found that this compound is also able to promote the dehydrogenative coupling between an isopropyl group of the phosphine and alkynes, to afford novel γ-(η^3-allyl)-α-alkenylphosphine derivatives by means of one-pot tandem processes of four reactions.

This paper shows the synthesis and characterization of unprecedented $[OsH(\eta^5\text{-}C_5H_5)\{\kappa^4\text{-}(P,C,C,C)\text{-}CH_2C[CH_2C(=CH_2)\text{-}P^iPr_2]CHR\}]BF_4$ compounds and the four reactions forming the tandem process, including the characterization of the three intermediate species and some of their isomers.

Results and Discussion

1. Preparation and Characterization of $[OsH(\eta^5\text{-}C_5H_5)\{\kappa^4\text{-}(P,C,C,C)\text{-}CH_2C[CH_2C(=CH_2)P^iPr_2]CHR\}]BF_4$. Treatment of acetone solutions of the dihydride−dihydrogen complex $[OsH_2(\eta^5\text{-}C_5H_5)(\eta^2\text{-}H_2)(P^iPr_3)]BF_4$ (**1**) with alkynes, such as 1-phenyl-1-propyne (5.2 equiv) and 2-butyne (9.6 equiv), for 12 h at 50 °C produces the release of a hydrogen molecule, the reduction of 2.0 equiv of alkyne into the corresponding *Z*-olefin, and the formation of the γ-(η^3-allyl)-α-alkenylphosphine derivatives $[OsH(\eta^5\text{-}C_5H_5)\{\kappa^4\text{-}(P,C,C,C)\text{-}CH_2C[CH_2C(=CH_2)P^iPr_2]\text{-}CHR\}]BF_4$ (R = Ph (**2**), CH_3 (**3**)), which are isolated as white solids in 91% (**2**) and 86% (**3**) yield (eq 1).

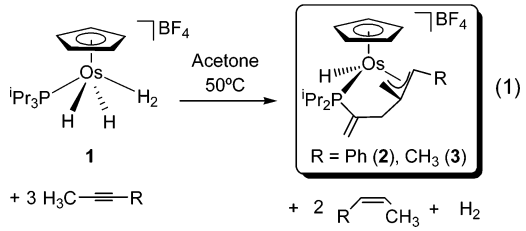

Figure 1 shows a view of the geometry of the cation of **2**. The structure proves the dehydrogenative coupling between an isopropyl group of triisopropylphosphine and an alkyne molecule to afford a novel η^3-allyl−(C(16)−C(15)−C(17))−alkenyl−(C(12)−C(13))−phosphine ligand. The coordination

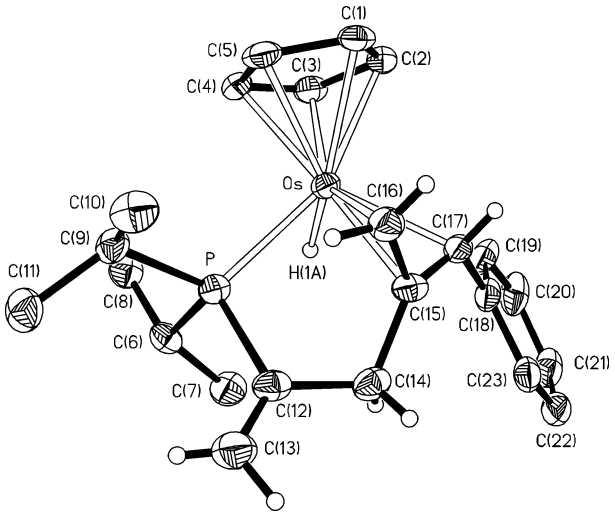

Figure 1. Molecular diagram of the cation of **2**. Selected bond lengths (Å) and angles (deg): Os−P 2.3115(11), Os−C(15) 2.153(4), Os−C(16) 2.181(5), Os−C(17) 2.223(4), C(12)−C(13) 1.317(6), C(12)−C(14) 1.499(6), C(14)−C(15) 1.505(6), C(15)−C(16) 1.403(6), C(15)−C(17) 1.413(6), $Cp_{centroid}$−Os−P 126.9, $Cp_{centroid}$−Os−H(1A) 115.0, $Cp_{centroid}$−Os−C(15) 147.4, $Cp_{centroid}$−Os−C(16) 119.7, $Cp_{centroid}$−Os−C(17) 121.5, C(15)−Os−H(1A) 89.1(18), C(16)−Os−H(1A) 124.7(18), C(17)−Os−H(1A) 80.5(18), P−Os−H(1A) 69.0(17), P−Os−C(15) 81.04(12), P−Os−C(16) 84.55(14), P−Os−C(17) 111.53(12), C(16)−Os−C(17) 65.01(17), C(16)−C(15)−C(17) 114.4(4).

around the osmium atom can be described as a four-legged piano-stool geometry, where the allyl unit of the phosphine occupies two *cisoid* positions with a C(16)−Os−C(17) angle of 65.01(17)°. The most noticeable features of the allyl moiety are the *cisoid* disposition of the substituted C(17) atom with regard to the hydride ligand, the *syn* disposition of the phenyl group with regard to the *meso* carbon atom, and the *endo* coordination. The latter is the preferred structural form in d^4-$M(\eta^5\text{-}C_5R_5)L_2(\eta^3\text{-allyl})$ complexes (L ≠ CO),[31] and it has been found in $[OsH(\eta^5\text{-}C_5H_5)(\eta^3\text{-}CH_2CHCHPh)(P^iPr_3)]BF_4$ (**7** in Scheme 1, *vide infra*),[32] $Os(\eta^5\text{-}C_5Me_5)X_2(\eta^3\text{-allyl})$ (X = Br, Me, H),[33] $Ru(\eta^5\text{-}C_5H_5)X_2(\eta^3\text{-allyl})$ (X = Cl, Br),[34] $Ru(\eta^5\text{-}C_5H_5)Cl_2(\eta^3\text{-}C_4H_4OMe)$,[35] $Ru(\eta^5\text{-}C_5Me_5)(CH_2Cl)Cl(\eta^3\text{-}C_3H_5)$,[36] $Ru(\eta^5\text{-}C_5H_5)(R)Br(\eta^3\text{-}C_3H_5)$ (R = CH_3, CH_2SiMe_3),[37] and $[Ru(\eta^5\text{-}C_5Me_5)(amidinate)(\eta^3\text{-}C_3H_5)]^+$.[38] When L = CO, both the *exo* and *endo* structural forms have comparable stability.[39] The disposition of the C_3 skeleton with regard to the metal center is asymmetric. The separation between the central carbon atom,

(28) See for example: (a) Buil, M. L.; Esteruelas, M. A.; López, A. M.; Oñate, E. *Organometallics* **1997**, *16*, 3169. (b) Albéniz, M. J.; Buil, M. L.; Esteruelas, M. A.; López, A. M. *J. Organomet. Chem.* **1997**, *545*−*546*, 495. (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) Esteruelas, M. A.; García-Yebra, C.; Oliván, M.; Oñate, E.; Tajada, M. A. *Organometallics* **2000**, *19*, 5098. (f) Bolaño, T.; Castarlenas, R.; Esteruelas, M. A.; Modrego, F. J.; Oñate, E. *J. Am. Chem. Soc.* **2005**, *127*, 11184. (g) Bolaño, T.; Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *J. Am. Chem. Soc.* **2006**, *128*, 3965.

(29) For some recent examples see: (a) Baya, M.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2001**, *20*, 4875. (b) Esteruelas, M. A.; Lledós, A.; Martín, M.; Maseras, F.; Osés, R.; Ruiz, N.; Tomàs, J. *Organometallics* **2001**, *20*, 5297. (c) Esteruelas, M. A.; García-Yebra, C.; Oliván, M.; Oñate, E.; Tajada, M. A. *Organometallics* **2002**, *21*, 1311. (d) Esteruelas, M. A.; Lledós, A.; Maresca, O.; Oliván, M.; Oñate, E.; Tajada, M. A. *Organometallics* **2004**, *23*, 1453. (e) Barrio, P.; Esteruelas, M. A.; Lledós, A.; Oñate, E.; Tomàs, J. *Organometallics* **2004**, *23*, 3008. (f) Eguillor, B.; Esteruelas, M. A.; Oliván, M. *Organometallics* **2006**, *25*, 4691.

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(32) Esteruelas, M. A.; González, A. I.; López, A. M.; Oliván, M.; Oñate, E. *Organometallics* **2006**, *25*, 693.

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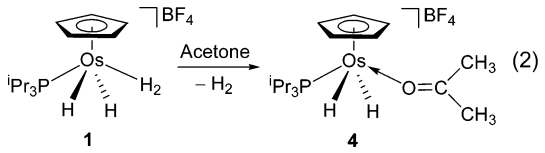
C(15), and the metal (2.153(4) Å) is shorter than the separation between the metal and the terminal carbon atoms C(16) (2.181(5) Å) and C(17) (2.223(4) Å). The carbon−carbon distances within the allylic skeleton are 1.403(6) Å for C(15)−C(16) and 1.413(6) Å for C(15)−C(17). The angle C(16)−C(15)−C(17) is 114.4(4)°. The Os−P bond length and the P−Os−C(15) angle reflect the peculiarities of the phosphine ligand. The Os−P distance of 2.3115(11) Å is about 0.06 Å shorter than the separation between the metal and the triisopropylphosphine ligand in **7**, whereas the P−Os−C(15) angle, 81.04(12)°, is about 12° smaller than the related one in the same compound.[32] The presence of the α-alkenyl group in the ligand is supported by the C(12)−C(13) bond length of 1.317(6) Å.

In agreement with the structure shown in Figure 1, the ^{1}H NMR spectrum of **2** in dichloromethane-d_2 at 20 °C shows three allylic resonances at 5.26 (CHPh) and 4.46 and 4.06 (CH_2) ppm. The C(sp^3)H_2 and C(sp^2)H_2-alkenyl protons give rise to ABX (X = ^{31}P) spin systems defined by δ_A 2.22, δ_B 4.47, J_{A-B} = 15.9 Hz, J_{A-X} = 2.0 Hz, and J_{B-X} = 30.9 Hz; and δ_A 5.66, δ_B 6.16, J_{A-B} = 2.5 Hz, J_{A-X} = 12.7 Hz, and J_{B-X} = 29.6 Hz, respectively. In the high-field region, the hydride displays a doublet at −16.37 ppm. The value of the H−P coupling constant of 32.8 Hz is consistent with the *cisoid* disposition of the hydride ligand and the phosphorus atom of the phosphine.[32,40] In the ^{13}C{^{1}H} NMR spectrum, the resonances corresponding to the allyl carbon atoms are observed at 91.7 (J_{C-P} = 3 Hz, C(15)), 52.2 (J_{C-P} = 2 Hz, C(17)), and 33.4 (C(16)) ppm, whereas those due to C(12), C(13), and C(14) appear at 146.8 (J_{C-P} = 41 Hz), 128.5, and 44.3 (J_{C-P} = 18 Hz) ppm, respectively. The ^{31}P{^{1}H} NMR spectrum contains a singlet at 42.3 ppm.

The ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra of **3** agree well with those of **2**. In the ^{1}H NMR spectrum the allylic resonances appear at 3.81 (CHMe) and 3.86 and 3.73 (CH_2) ppm, whereas the ABX (X = ^{31}P) spin systems corresponding to the C(sp^3)H_2 and C(sp^2)H_2-alkenyl protons of the phosphine are defined by δ_A 2.13, δ_B 4.37, J_{A-B} = 15.9 Hz, J_{A-X} = 2.1 Hz, and J_{B-X} = 31.5 Hz (C(sp^3)H), and δ_A 5.60, δ_B 6.08, J_{A-B} = 2.5 Hz, J_{A-X} = 12.8 Hz, and J_{B-X} = 29.6 Hz (C(sp^2)H-alkenyl). The resonance due to the hydride ligand is observed at −16.27 ppm as a doublet with a H−P coupling constant of 33.0 Hz. In the ^{13}C{^{1}H} NMR spectrum the allylic resonances appear at 95.0 (J_{C-P} = 3 Hz, C_{meso}), 46.4 (J_{C-P} = 3 Hz, CH), and 30.1 (CH_2) ppm, whereas those due to the alkenyl group are observed at 146.5 (J_{C-P} = 41 Hz, PC) and 127.5 (CH_2) ppm, and those corresponding to the C(sp^3)H_2 atom at 43.5 (J_{C-P} = 19 Hz) ppm. In the ^{31}P{^{1}H} NMR spectrum a singlet at 42.1 ppm is also characteristic of **3**.

The formation of **2** and **3** involves, in addition to the dehydrogenative coupling, the dissociation of the dihydrogen ligand of **1** and the reduction of two alkyne molecules. Thus, the reactions shown in eq 1 can be rationalized as one-pot tandem processes of four steps: (i) dissociation of a hydrogen molecule from **1**, (ii) reduction of an alkyne molecule by the resulting dihydride, (iii) reduction of a second molecule of alkyne by hydrogen transfer from an isopropyl substituent of triisopropylphosphine, which is dehydrogenated, and (iv) coupling between the resulting isopropenyl substituent of the phosphine and a third alkyne molecule.

2. Dissociation of Molecular Hydrogen. A characteristic of the dihydrogen ligand is its high tendency to undergo dissociation from the metallic center. In accordance with this, complex **1** releases a hydrogen molecule. The resulting unsaturated species is stabilized by coordination of acetone. Thus, at room temperature, the stirring of acetone solutions of **1** under a slight flow of argon for 1 h affords the dihydride−osmium(IV) solvate complex [$OsH_2(\eta^5$-$C_5H_5)(\kappa^1$-$OCMe_2)(P^iPr_3)$]BF_4 (**4**), which is isolated as a beige solid in 89% yield, according to eq 2.



The weakening of the C−O double bond of the solvent as a consequence of the coordination of the oxygen atom to the metal center is revealed by the IR spectrum of **4** in Nujol, which shows the ν(CO) band at 1650 cm^{-1}, shifted 65 cm^{-1} to lower wavenumbers if compared with the free molecule. The effect of the coordination of the oxygen atom is also evident in the ^{13}C{^{1}H} NMR spectrum,[41] where the carbonyl resonance is observed at 229.5 ppm, shifted 23.5 ppm to lower field with regard to the resonance of the free acetone. As expected for the *transoid* disposition of the hydride ligands, the ^{1}H NMR spectrum contains only one high-field resonance. It appears as a doublet at −7.72 ppm with a H−P coupling constant of 32.8 Hz. The ^{31}P{^{1}H} NMR spectrum shows a singlet at 41.3 ppm, which under off-resonance conditions is split into a triplet, as a result of the P−H coupling with two hydride ligands.

Because complex **1** is saturated, the dissociation of molecular hydrogen is necessary to activate the osmium atom. The formation of **4** suggests that the function of the reaction solvent is to stabilize the resulting highly reactive electrophilic metal center, until the first alkyne molecule replaces the solvent molecule to be reduced.

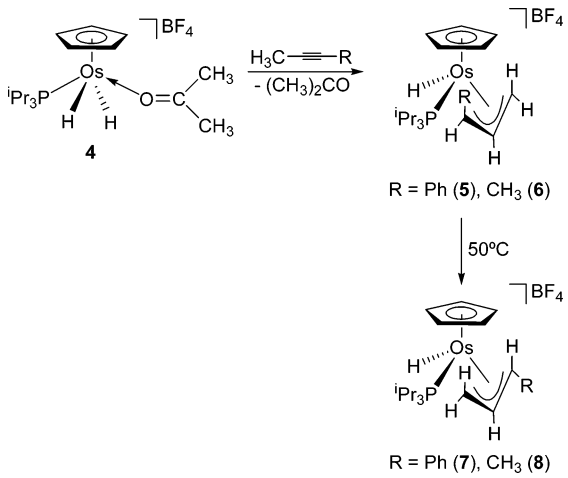
3. Reduction of the First Alkyne Molecule. At room temperature, the treatment of dichloromethane solutions of the dihydride−solvate complex **4** with 1.0 equiv of alkynes, such as 1-phenyl-1-propyne and 2-butyne, produces the release of the acetone molecule from the metal center and the reduction of the alkynes to afford the hydride−allyl−osmium(IV) complexes [$OsH(\eta^5$-$C_5H_5)(\eta^3$-$CH_2CHCHR)(P^iPr_3)$]BF_4 (R = Ph (**5**), CH_3 (**6**)), which are isolated as white solids in 85% (**5**) and 77% (**6**) yield, according to Scheme 1.

Figure 2 shows a view of the geometry of the cation of **5**. The distribution of ligands around the osmium atom can be described as a four-legged piano-stool geometry, where the allyl ligand occupies two *cisoid* positions with a C(1)−Os−C(3) angle of 66.44(14)°. The allyl group coordinates to the metal center in the *endo* form, with the substituted C(1) atom *cisoid* disposed to the phosphine ligand and the phenyl group in *anti* position with regard to the *meso* carbon atom C(2). Like in **2**, the coordination of the C_3 skeleton is asymmetric. The separation between the central carbon atom and the metal (2.163(4) Å) is shorter than the separation between the metal and the terminal carbon atoms C(1) (2.241(4) Å) and C(3) (2.197(4) Å). The carbon−carbon distances within the allylic skeleton are 1.418-

(40) See for example: (a) Esteruelas, M. A.; Gutiérrez-Puebla, E.; López, A. M.; Oñate, E.; Tolosa, J. I. *Organometallics* **2000**, *19*, 275. (b) Baya, M.; Crochet, P.; Esteruelas, M. A.; Gutiérrez-Puebla, E.; López, A. M.; Modrego, J.; Oñate, E.; Vela, N. *Organometallics* **2000**, *19*, 2585. (c) Esteruelas, M. A.; López, A. M.; Tolosa, J. I.; Vela, N. *Organometallics* **2000**, *19*, 4650. (d) Baya, M.; Crochet, P.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2001**, *20*, 240. (e) Baya, M.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2001**, *20*, 4875. (f) Esteruelas, M. A.; González, A. I.; López, A. M.; Oñate, E. *Organometallics* **2003**, *22*, 414.

(41) (a) Esteruelas, M. A.; Gómez, A. V.; Lahoz, F. J.; López, A. M.; Oñate, E, Oro, L. A. *Organometallics* **1996**, *15*, 3423. (b) Bohanna, C.; Esteruelas, M. A.; Gómez, A. V.; López, A. M.; Martínez, M.-P. *Organometallics* **1997**, *16*, 4464.

Scheme 1



(5) Å for C(1)−C(2) and 1.393(5) Å for C(2)−C(3). The angle C(1)−C(2)−C(3) is 119.8(4)°. As expected, the Os−P bond length of 2.3809(9) Å and the P−Os−C(2) angle of 88.06(10)° are longer and greater, respectively, than the related parameters in **2**, about 0.07 Å and 7°.

In agreement with the presence of a hydride ligand in **5**, its ^{1}H NMR spectrum in dichloromethane-d_2 shows at −15.91 ppm a doublet with a H−P coupling constant of 33.7 Hz. The resonance due to the CHPh−allyl proton appears at 5.84 ppm. The value of the H−H_{meso} coupling constant of 6.9 Hz is consistent with the *syn* disposition of this proton with regard to H_{meso}.[32] The resonance corresponding to the latter is observed at 3.66 ppm, whereas those due to the CH_2 protons appear at 4.16 and 4.12 ppm. As expected for the *cisoid* disposition of the CH_2 group of the allyl and the hydride ligand, the NOESY spectrum shows cross signals between the respective resonances. In the ^{13}C{^{1}H} NMR spectrum, the resonances corresponding to the allyl carbon atoms are observed at 72.5 (C(2)), 48.0 (C(1)), and 29.5 (C(3)) ppm. The ^{31}P{^{1}H} NMR spectrum contains a singlet at 15.5 ppm.

The ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra of **6** agree well

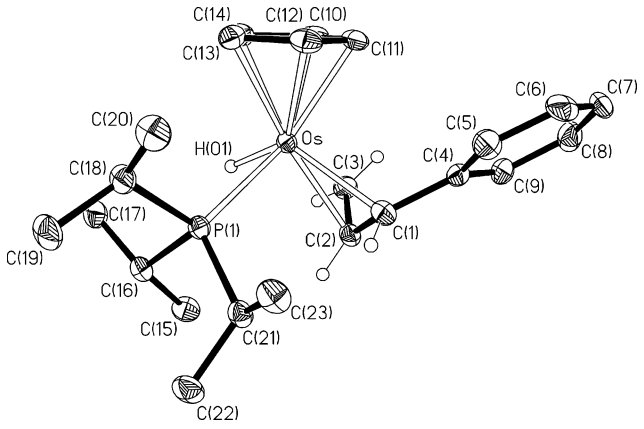
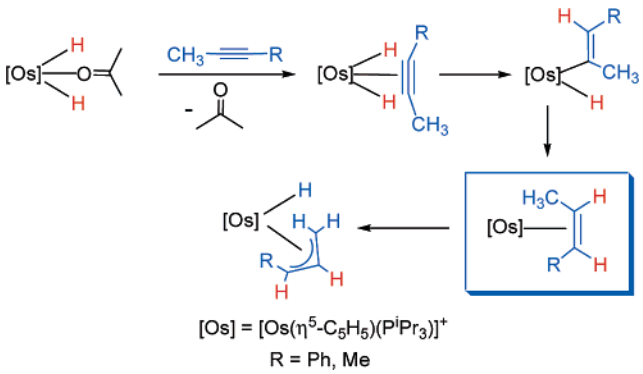


Figure 2. Molecular diagram of the cation of complex **5**. Selected bond lengths (Å) and angles (deg): Os−P(1) 2.3809(9), Os−C(1) 2.241(4), Os−C(2) 2.163(4), Os−C(3) 2.197(4), C(1)−C(2) 1.418(5), C(2)−C(3) 1.393(5), $Cp_{centroid}$−Os−P(1) 127.2, $Cp_{centroid}$−Os−H(01) 110.9, $Cp_{centroid}$−Os−C(1) 121.2, $Cp_{centroid}$−Os−C(2) 143.3, $Cp_{centroid}$−Os−C(3) 116.5, C(1)−Os−C(3) 66.44(14), P(1)−Os−H(01) 70.9(11), P(1)−Os−C(1) 91.06(9), P(1)−Os−C(2) 88.06(10), P(1)−Os−C(3) 114.46(10), C(1)−Os−H(01) 124.2(12), C(2)−Os−H(01) 88.1(11), C(3)−Os−H(01) 74.1(11), C(1)−C(2)−C(3) 119.8(4).

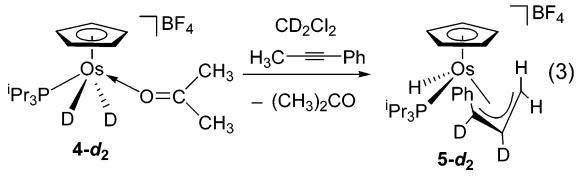
Scheme 2



with those of **5**. In the ^{1}H NMR spectrum, the hydride resonance appears at −15.90 (J_{H-P} = 33.4 Hz) ppm, whereas those due to the allylic protons are observed at 4.36 ($J_{H-Hmeso}$ = 6.0 Hz, CHMe), 3.63 (H_{meso}), and 3.81 and 3.58 (CH_2) ppm. Like for **5**, the NOESY spectrum contains cross signals between the hydride and the CH_2 resonances. The ^{13}C{^{1}H} NMR spectrum shows the allylic resonances at 75.5 (C_{meso}), 42.5 (CHMe), and 25.7 (CH_2) ppm. A singlet at 16.0 ppm in the ^{31}P{^{1}H} NMR spectrum is also characteristic of **6**.

The formation of **5** and **6** can be rationalized according to Scheme 2. The solvent molecule of **4** is displaced by the alkynes, which are reduced. The C(sp^3)−H bond activation of the methyl substituent of the resulting olefins affords the hydride−allyl species. The higher stability of the M(η^3-allyl) bond with regard to an M−aryl bond could be the driving force for the activation of the methyl substituent instead of the phenyl group, when the starting alkyne is 1-phenyl-1-propyne.[40f,42]

In agreement with Scheme 2, we have also observed that the reaction of $[OsD_2(\eta^5\text{-}C_5H_5)(\kappa^1\text{-}OCMe_2)(P^iPr_3)]BF_4$ (**4-*d*$_2$**) with 1.2 equiv of 1-phenyl-1propyne in dichloromethane-d_2 at room temperature leads to $[OsH(\eta^5\text{-}C_5H_5)(\eta^3\text{-}CH_2CDCDPh)(P^iPr_3)]BF_4$ (**5-*d*$_2$**) with the deuterium atoms mutually *syn* disposed (eq 3). The formation of this product is supported by its ^{1}H and ^{2}H NMR spectra. The first of them shows the absence of resonances at 5.84 and 3.66 ppm, while the second one contains two signals at 5.85 and 3.70 ppm.



The *cisoid* disposition of the CHR group of the allyl ligands and the phosphine in **5** and **6** is unfavorable with regard to that with the CHR group *cisoid* to the hydride, probably as a consequence of the steric hindrance experienced between the substituent of the allyls and the isopropyl groups of the phosphine. Thus, complexes **5** and **6** isomerize into the previously reported derivatives **7**[32] and **8**, respectively (Scheme 1). It is noteworthy that the position change of the substituted carbon atom is accompanied by an *anti*−*syn* rearrangement of the substituent. In an NMR tube at 50 °C using dichloromethane-d_2 as solvent, the transformation from **5** to **7** is quantitative after 24 h, while the quantitative formation of **8** from **6** occurs after

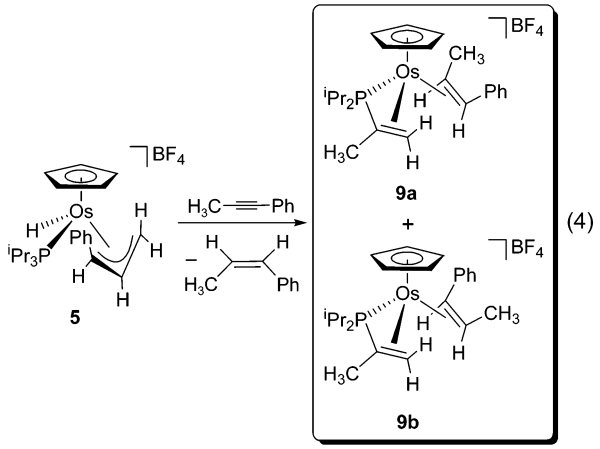
(42) Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A.; Valero, C.; Zeier, B. *J. Am. Chem. Soc.* **1995**, *117*, 7935.

15 min. The most likely mechanism for these isomerizations involves a $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ pathway.[32,43]

Complex **8** is isolated as a white solid in 81% yield. In the ^{1}H NMR spectrum, the hydride resonance appears at −15.60 ppm, as a doublet with a H−P coupling constant of 33.1 Hz, whereas those due to the allylic protons are observed at 3.95 ($J_{H-Hmeso}$ = 8.5 Hz, CHMe), 3.47 (H_{meso}), and 3.06 and 2.70 (CH_2) ppm. In contrast to **6**, the NOESY spectrum shows cross signals between the allylic−CHMe and hydride resonances. In the $^{13}C\{^1H\}$ NMR spectrum, the resonances due to the carbon atoms of the C_3 skeleton of the allyl appear at 79.4 (C_{meso}), 51.9 (CHMe), and 20.4 (CH_2) ppm. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 15.0 ppm.

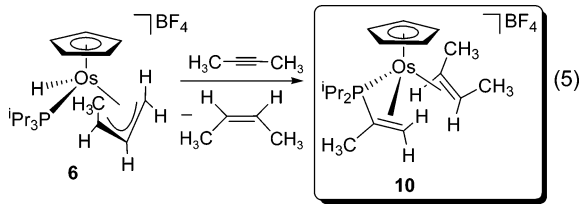
4. Reduction of the Second Alkyne Molecule. Complexes **5** and **6** react with a second molecule of alkyne to give the corresponding *Z*-olefin and isopropenyldi(isopropyl)phosphine−*Z*-olefin−osmium(II) derivatives.

Treatment at room temperature of acetone solutions of **5** with 1.2 equiv of 1-phenyl-1-propyne leads to (*Z*)-methylstyrene and $[Os(\eta^5\text{-}C_5H_5)\{\eta^2\text{-}(Z)\text{-}CH(CH_3)=CHPh\}\{\kappa^3\text{-}(P,C,C)\text{-}[CH_2=C(CH_3)]P^iPr_2\}]BF_4$ (**9**), which is isolated as a white solid in 72% yield. According to the ^{1}H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra of the solid, the complex is a 1.5:1 mixture of the isomers **a** and **b** shown in eq 4. They result from the chirality of the osmium atom and the prochirality of the olefin.[44]



In accordance with the presence of both isomers in solution, the ^{1}H NMR spectrum in dichloromethane-d_2 shows two ABX (X = ^{31}P) spin systems for the CH_2 group of the isopropenyl substituent of the phosphine, which are defined by δ_A 3.67, δ_B 3.87, J_{A-B} = 2.2 Hz, J_{A-X} = 32.2 Hz, and J_{B-X} = 8.4 Hz (**9a**), and δ_A 3.45, δ_B 3.74, J_{A-B} = 2.2 Hz, J_{A-X} = 32.5 Hz, and J_{B-X} = 8.8 Hz (**9b**). For **9a**, the olefinic resonances of the coordinated (*Z*)-methylstyrene are observed at 2.70 (CHPh) and 2.40 (CHMe) ppm, with a H−H coupling constant of 9.2 Hz. For **9b**, the CHPh resonance appears at 3.61 ppm with a H−H coupling constant of 8.8 Hz, while the CHMe resonance is masked by the signal corresponding to PCH and CH_3 protons (1.80−1.40 ppm). In the $^{13}C\{^1H\}$ NMR spectrum the resonances due to the C(sp^2) atoms of the isopropenyl group of the phosphine appear at 63.6 (PC) and 28.6 (CH_2) ppm (**9a**) and 63.1 (PC) and (30.6) (CH_2) ppm (**9b**), whereas those corresponding to the C(sp^2) atoms of methylstyrene are observed at 44.0 (CHPh) and 31.5 (CHMe) ppm (**9a**) and 41.3 (CHPh) and 25.8 (CHMe) ppm (**9b**), in agreement with those found for other π-olefin−osmium complexes.[12,25,44,45] The $^{31}P\{^1H\}$ NMR spectrum contains two singlets at −3.3 (**9a**) and −7.0 (**9b**) ppm.

Treatment at room temperature of acetone solutions of **6** with 2.1 equiv of 2-butyne produces *cis*-2-butene and $[Os(\eta^5\text{-}C_5H_5)\{\eta^2\text{-}(Z)\text{-}CH(CH_3)=CHCH_3\}\{\kappa^3\text{-}(P,C,C)\text{-}[CH_2=C(CH_3)]P^iPr_2\}]BF_4$ (**10**), which is isolated as a white solid in 56% yield according to eq 5.



The ^{1}H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra of **10** are consistent with those of **9**. In the ^{1}H NMR spectrum, the CH_2 group of the isopropenyl group of the phosphine displays an ABX (X = ^{31}P) spin system defined by δ_A 3.31, δ_B 3.55, J_{A-B} < 1 Hz, J_{A-X} = 32.7 Hz, and J_{B-X} = 8.3 Hz, whereas the olefinic protons of the coordinated 2-butene give rise to multiplets at 2.77 ppm and between 2.30 and 2.10 ppm. The latter appears masked with the PCH resonances. In the $^{13}C\{^1H\}$ NMR spectrum, the resonances due to the C(sp^2) atoms of the isopropenyl group of the phosphine are observed at 62.2 (PC) and 28.9 (CH_2) ppm, whereas those corresponding to the C(sp^2) atoms of the coordinated 2-butene appear at 25.4 and 20.4 ppm. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at −2.8 ppm.

The formation of (*Z*)-methylstyrene and *cis*-2-butene from the reactions of **5** and **6** with 1-phenyl-1-propyne and 2-butyne, respectively, suggests that in solution these complexes are in equilibrium with nondetectable concentrations of the corresponding π-olefin intermediates $[Os(\eta^5\text{-}C_5H_5)\{(Z)\text{-}CH(CH_3)=CHR\}(P^iPr_3)]^+$ (Scheme 2). Thus, the formation of **9** and **10** can be rationalized according to Scheme 3. The displacement of the olefins from these intermediates should give π-alkyne species, which could lead to the observed products by intramolecular hydrogen transfer from an isopropyl group of the phosphine, which is dehydrogenated, to the coordinated triple bond of the alkynes, which is reduced.

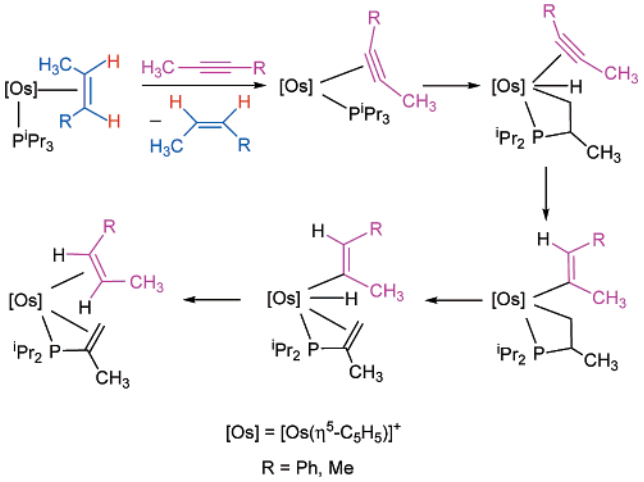
5. Coupling between the Isopropenyl Substituent of the Phosphine and the Third Alkyne Molecule. Treatment in NMR tubes of dichloromethane-d_2 solutions of **9** and **10** with 1-phenyl-1-propyne (1.2 equiv) and 2-butyne (2.1 equiv), at 50 °C, affords complexes **2** and **3**, respectively, in quantitative yield. The formation of these compounds can be rationalized as ene-type reations between the isopropenyl substituent of the phosphine ligand of the starting complexes and the alkynes.[16] It is generally believed that they proceed via metallacyclopentene intermediates.[2d] The selectivity in the formation of the obtained

(43) (a) Faller, J. W.; Thomsen, M. E.; Mattina, M. J. *J. Am. Chem. Soc.* **1971**, *93*, 2642. (b) Faller, J. W.; Tully, M. T. *J. Am. Chem. Soc.* **1972**, *94*, 2676. (c) Ward, Y. D.; Villanueva, L. A.; Allred, G. D.; Payne, S. C.; Semones, M. A.; Liebeskind, L. S. *Organometallics* **1995**, *14*, 4132. (d) Villanueva, L. A.; Ward, Y. D.; Lachicotte, R.; Liebeskind, L. S. *Organometallics* **1996**, *15*, 4190. (e) Abrams, M. B.; Yoder, J. C.; Loeber, C.; Day, M. W.; Bercaw, J. E. *Organometallics* **1999**, *18*, 1389.

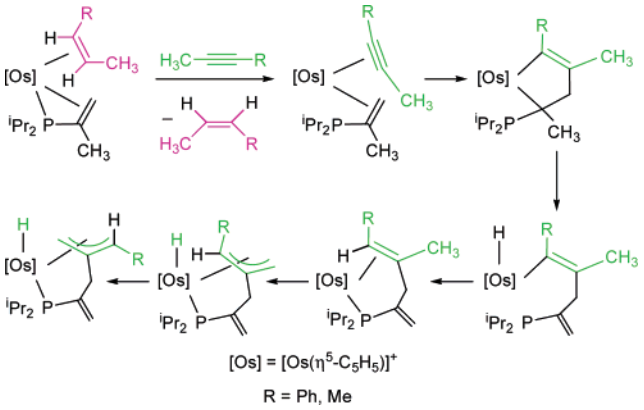
(44) Baya, M.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2002**, *21*, 5681.

(45) See for example: (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) Edwards, A. J.; Elipe, S.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A.; Valero, C. *Organometallics* **1997**, *16*, 3828. (c) Crochet, P.; Esteruelas, M. A.; Gutiérrez-Puebla, E. *Organometallics* **1998**, *17*, 3141. (d) Buil, M. L.; Esteruelas, M. A.; García-Yebra, C.; Gutiérrez-Puebla, E.; Oliván, M. *Organometallics* **2000**, *19*, 2184. (e) Esteruelas, M. A.; García-Yebra, C.; Oliván, M. Oñate, E. *Organometallics* **2000**, *19*, 3260. (f) Esteruelas, M. A.; García-Yebra, C.; Oliván, M.; Oñate, E. *Inorg. Chem.* **2006**, *45*, 10162.

Scheme 3



Scheme 4



products, resulting from the high regioselectivity of the couplings, is in agreement with this.

Scheme 4 summarizes the elemental steps that could lead to **2** and **3**. The displacement of the coordinated *Z*-olefins by the alkynes should give the key species, π-olefin−π-alkyne. Thus, the oxidative coupling of these unsaturated ligands could afford the osmacyclopentene intermediates. It should be noted that although four (R = Ph) or two (R = CH_3) stereoisomers are feasible, only those with the smallest steric hindrance between the initial organic moieties must be formed. The osmacyclopentenes could evolve by a hydrogen β-elimination reaction on the methyl substituent at the $C_\alpha(sp^3)$ atom of the metallacycles. The β-elimination reaction should lead to hydride−alkenyl intermediates, which should generate unsaturated dienylphosphine species by reductive elimination of olefin. The subsequent $C(sp^3)H$ bond activation of the methyl substituent of the coordinated carbon−carbon double bond of the dienylphosphines should initially lead to isomers of **2** and **3** with the CHR group of the allyl moieties *cisoid* disposed to the phosphorus atom and the R group in *anti* position with regard to C_{meso}. The isomerization of the allyl moieties should finally give **2** and **3**.

The groups of Gimeno[46] and Kirchner[47] have recently reported interesting couplings between alkenylphosphines and alkynes or alkynols promoted by ruthenium.

Concluding Remarks

This study reveals that the dihydride−dihydrogen complex $[OsH_2(\eta^5\text{-}C_5H_5)(\eta^2\text{-}H_2)(P^iPr_3)]BF_4$ reacts with alkynes to afford unprecedented derivatives $[OsH(\eta^5\text{-}C_5H_5)\{\kappa^4\text{-}(P,C,C,C)\text{-}CH_2C[CH_2C(=CH_2)P^iPr_2]CHR\}]BF_4$ as a result of the transformation of the alkylphosphine into novel γ-(η^3-allyl)-α-alkenylphosphine ligands, by means of unprecedented one-pot tandem processes of four reactions.

The first reaction involves the dissociation of a dihydrogen ligand from the osmium atom of the starting compound and the stabilization of the resulting unsaturated dihydride with a solvent molecule, acetone, to form $[OsH_2(\eta^5\text{-}C_5H_5)(\kappa^1\text{-}OCMe_2)(P^iPr_3)]BF_4$. During the second one, the displacement of the acetone molecule by an alkyne and the subsequent reduction of the hydrocarbon to give $[OsH(\eta^5\text{-}C_5H_5)\{\eta^3\text{-}CH_2CHCHR\}(P^iPr_3)]BF_4$ take place. The third reaction generates isopropenyldi(isopropyl)phosphine−π-olefin species, $[Os(\eta^5\text{-}C_5H_5)\{\eta^2\text{-}(Z)\text{-}CH(CH_3)=CHR\}\{\kappa^3\text{-}(P,C,C)\text{-}[CH_2=C(CH_3)]P^iPr_2\}]BF_4$, as a consequence of the elimination of *Z*-olefin from the allyl intermediate, and a hydrogen transfer from an isopropyl substituent of triisopropylphosphine to a second alkyne molecule. In the fourth reaction a third alkyne molecule displaces the coordinated olefin from the osmium atom, and it is coupled with the isopropenyl group of the α-alkenylphosphine, to afford the γ-(η^3-allyl)-α-alkenylphosphine derivatives through an ene-type reaction via an osmacyclopentene intermediate.

In conclusion, in this paper we report a novel type of phosphine ligands, unprecedented transition metal complexes, and an unprecedented one-pot tandem process involving $C(sp^3)$−H bond activation and C−C bond formation reactions. We have achieved this starting from a dihydride−dihydrogen derivative.

Experimental Section

General Methods and Instrumentation. All reactions were carried out under argon with rigorous exclusion of air using Schlenk-tube or glovebox techniques. Solvents were dried by the usual procedures and distilled under argon prior to use. The starting materials **1** and **1-*d*$_4$** were prepared by the published method.[30] ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra were recorded on either a Varian Gemini 2000, a Bruker ARX 300, a Bruker Avance 300 MHz, or a Bruker Avance 400 MHz instrument. Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks (^1H, $^{13}C\{^1H\}$) or external H_3PO_4 ($^{31}P\{^1H\}$). Coupling constants, *J*, are given in hertz. Spectral assignments were achieved by $^1H-^1H$ COSY and NOESY, $^1H\{^{31}P\}$, ^{13}C APT, $^1H-^{13}C$ HSQC, and $^1H-^{13}C$ HMBC experiments. Infrared spectra were run on a Perkin-Elmer Spectrum One spectrometer (Nujol mulls on polyethylene sheets). C and H analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyzer. GC-MS experiments were run on an Agilent 5973 mass selective detector interfaced to an Agilent 6890 series gas chromatograph system. Samples were injected into a 30 m × 250 μm HP-5MS 5% phenyl methyl siloxane column with a film thickness of 0.25 μm.

Preparation of $[OsH(\eta^5\text{-}C_5H_5)\{\kappa^4\text{-}(P,C,C,C)\text{-}CH_2C[CH_2C(=CH_2)P^iPr_2]CHPh\}]BF_4$ (2). An orange solution of **1** (117 mg, 0.23 mmol) in 4 mL of acetone was treated with 1-phenyl-1-propyne (150 μL, 1.19 mmol). The solution was allowed to react for 12 h

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(47) (a) Slugovc, C.; Mereiter, K.; Schmid, R.; Kirchner, K. *J. Am. Chem. Soc.* **1998**, *120*, 6175. (b) Slugovc, C.; Mereiter, K.; Schmid, R.; Kirchner, K. *Organometallics* **1999**, *18*, 1011.

at 50 °C. After that, the solution was concentrated to ca. 1 mL under reduced pressure. The addition of diethyl ether (10 mL) caused the formation of a white solid, which was separated by decantation, washed with diethyl ether (3 × 5 mL), and dried in vacuo. Yield: 129 mg (91%). GC-MS and ^{1}H NMR analysis of the mother liquor showed the presence of 1-phenyl-1-propyne and (*Z*)-methylstyrene. Anal. Calcd for $C_{23}H_{32}BF_4OsP$: C, 44.81; H, 5.23. Found: C, 44.53; H, 5.17. IR (Nujol, cm^{-1}): ν(OsH) 2127 (m). ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ 7.33−7.12 (m, 5H, Ph), 6.16 (dd, J_{H-P} = 29.6, J_{H-H} = 2.5, 1H, PC═C*H*$_{trans\ to\ P}$), 5.66 (dd, J_{H-P} = 12.7, J_{H-H} = 2.5, 1H, PC═C*H*$_{cis\ to\ P}$), 5.26 (d, J_{H-P} = 5.7, 1H, C*H*Ph), 5.21 (s, 5H, C_5H_5), 4.47 (dd, J_{H-P} = 30.9, J_{H-H} = 15.9, 1H, -CH_2-), 4.46 (s, 1H, H_{syn}), 4.06 (s, 1H, H_{anti}), 2.54 (m, 1H, PCH), 2.22 (br dd, J_{H-H} = 15.9, J_{H-P} = 2.0, 1H, −CH_2−), 2.04 (m, 1H, PCH), 1.43 (dd, J_{H-P} = 16.2, J_{H-H} = 7.1, 3H, PCHC*H*$_3$), 1.35 (dd, J_{H-P} = 16.8, J_{H-H} = 7.2, 3H, PCHC*H*$_3$), 1.05 (dd, J_{H-P} = 16.4, J_{H-H} = 6.9, 3H, PCHC*H*$_3$), 1.04 (dd, J_{H-P} = 17.4, J_{H-H} = 6.8, 3H, PCHC*H*$_3$), −16.37 (d, J_{H-P} = 32.8, 1H, Os−H). ^{31}P{^{1}H} NMR (121.49 MHz, CD_2Cl_2, 298 K): δ 42.3 (s). ^{13}C{^{1}H} NMR (75.48 MHz, CD_2Cl_2, 298 K): δ 146.8 (d, J_{C-P} = 41, P−C═), 142.6 (d, J_{C-P} = 2, C_{ipso}Ph), 129.6 (s, Ph), 128.5 (s, PC═*C*H$_2$), 127.5 and 127.3 (both s, Ph), 91.7 (d, J_{C-P} = 3, Os−C_{meso}), 86.6 (s, C_5H_5), 52.2 (d, J_{C-P} = 2, CHPh), 44.3 (d, J_{C-P} = 18, −CH_2−), 33.4 (s, OsCH_2), 31.8 (d, J_{C-P} = 40, PCH), 27.2 (d, J_{C-P} = 29, PCH), 19.5, 18.9, and 18.6 (all s, PCH*C*H$_3$), 17.7 (d, J_{C-P} = 2, PCH*C*H$_3$).

Preparation of [OsH(η^5-C_5H_5){κ^4-(*P,C,C,C*)-$CH_2C[CH_2C(═CH_2)P^iPr_2]CHCH_3$}]$BF_4$ (3). This complex was prepared as described for **2**, starting from 129 mg (0.26 mmol) of **1** and 2-butyne (200 μL, 2.50 mmol). A white solid was obtained. Yield: 121 mg (86%). Anal. Calcd for $C_{18}H_{30}BF_4OsP$: C, 38.99; H, 5.45. Found: C, 38.74; H, 5.21. IR (Nujol, cm^{-1}): ν(OsH) 2125 (m). ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ 6.08 (dd, J_{H-P} = 29.6, J_{H-H} = 2.5, 1H, PC═C*H*$_{trans\ to\ P}$), 5.60 (dd, J_{H-P} = 12.8, J_{H-H} = 2.5, 1H, PC═C*H*$_{cis\ to\ P}$), 5.56 (s, 5H, C_5H_5), 4.37 (dd, J_{H-P} = 31.5, J_{H-H} = 15.9, 1H, −CH_2−), 3.86 (s, 1H, H_{syn}), 3.81 (dq, J_{H-P} = 6.3, J_{H-HMe} = 6.3, 1H, C*H*CH$_3$), 3.73 (s, 1H, H_{anti}), 2.42 (m, 1H, PCH), 2.13 (br dd, J_{H-H} = 15.9, J_{H-P} = 2.1, 1H, −CH_2−), 1.97 (m, 1H, PCH), 1.51 (d, J_{H-H} = 6.3, 3H, CHC*H*$_3$), 1.22 (dd, J_{H-P} = 15.9, J_{H-H} = 7.1, 6H, PCHC*H*$_3$), 1.02 (dd, J_{H-P} = 16.0, J_{H-H} = 6.9, 3H, PCHC*H*$_3$), 1.01 (dd, J_{H-P} = 17.8, J_{H-H} = 6.9, 3H, PCHC*H*$_3$), −16.27 (d, J_{H-P} = 33.0, 1H, Os−H). ^{31}P{^{1}H} NMR (121.49 MHz, CD_2Cl_2, 298 K): δ 42.1 (s). ^{13}C{^{1}H} NMR (75.48 MHz, CD_2Cl_2, 298 K): δ 146.5 (d, J_{C-P} = 41, P−C═), 127.5 (s, PC═*C*H$_2$), 95.0 (d, J_{C-P} = 3, Os−C_{meso}), 85.1 (s, C_5H_5), 46.4 (d, J_{C-P} = 3, *C*HCH$_3$), 43.5 (d, J_{C-P} = 19, −CH_2−), 31.4 (d, J_{C-P} = 40, PCH), 30.1 (s, OsCH_2), 27.3 (d, J_{C-P} = 29, PCH), 20.9 (s, CH*C*H$_3$), 18.7, 18.6, and 18.1 (all s, PCH*C*H$_3$), 17.6, (d, J_{C-P} = 2, PCH*C*H$_3$).

Dissociation of Molecular Hydrogen: Formation of [OsH_2(η^5-C_5H_5){κ^1-$OC(CH_3)_2$}(P^iPr_3)]BF_4 (4). A Schlenk flask was charged with **1** (150 mg, 0.30 mmol). Acetone (5 mL) was added, and the solution was stirred at room temperature for 1 h under a slight flow of argon. The solution was concentrated to ca. 1 mL under reduced pressure. The addition of diethyl ether (10 mL) caused the formation of a beige solid, which was separated by decantation, washed with diethyl ether (3 × 3 mL), and dried in vacuo. Yield: 148 mg (89%). Anal. Calcd for $C_{17}H_{34}BF_4OOsP$: C, 36.30; H, 6.09. Found: C, 36.27; H, 5.97. IR (Nujol, cm^{-1}): ν(OsH) 2104 (m), 2057 (m), ν(CO) 1650 (s). ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ 5.48 (s, 5H, C_5H_5), 2.32 (s, 6H, CH_3), 2.17 (m, 3H, PCH), 1.22 (dd, J_{H-P} = 14.8, J_{H-H} = 7.1, 18H, PCHC*H*$_3$), −7.72 (d, J_{H-P} = 32.8, 2H, OsH). ^{31}P{^{1}H} NMR (121.49 MHz, CD_2Cl_2, 293 K): δ 41.3 (s, t in off-resonance). ^{13}C{^{1}H} NMR (75.48 MHz, CD_2Cl_2, 293 K): δ 229.5 (s, CO), 78.6 (d, J_{CP} = 2, C_5H_5), 32.5 (s, CH_3), 28.7 (d, J_{CP} = 34, P*C*HCH$_3$), 19.5 (d, J_{CP} = 2, PCH*C*H$_3$).

Reaction of 4 with 1-Phenyl-1-propyne: Formation of [OsH(η^5-C_5H_5)(η^3-$CH_2CHCHPh$)(P^iPr_3)]BF_4 (5). An orange solution of **4** (104 mg, 0.19 mmol) in 4 mL of dichloromethane was treated with 1-phenyl-1-propyne (25 μL, 0.20 mmol). The solution was allowed to react for 15 min at room temperature, and then, it was concentrated to ca. 1 mL under reduced pressure. The addition of diethyl ether (10 mL) caused the formation of a white solid, which was separated by decantation, washed with diethyl ether (3 × 5 mL), and dried in vacuo. Yield: 98 mg (85%). Anal. Calcd for $C_{23}H_{36}BF_4OsP$: C, 44.52; H, 5.85. Found: C, 44.45; H, 6.04. IR (Nujol, cm^{-1}): ν(OsH) 2126 (m). ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ 7.34 − 7.10 (m, 5H, Ph), 5.84 (dd, $J_{H-Hmeso}$ = 6.9, J_{H-P} = 6.0, 1H, C*H*Ph), 5.16 (s, 5H, C_5H_5), 4.16 (dd, $J_{H-Hmeso}$ = 6.9, J_{gem} = 1.5, 1H, H_{syn}), 4.12 (dd, $J_{H-Hmeso}$ = 10.8, J_{gem} = 1.5, 1H, H_{anti}), 3.66 (dddd, J_{H-P} = 3.8, $J_{H-Hanti}$ = 10.8, J_{H-Hsyn} = 6.9, $J_{H-Hsyn'}$ = 6.9, 1H, H_{meso}), 2.27 (m, 3H, PCH), 1.34 (dd, J_{H-P} = 14.2, J_{H-H} = 7.2, 9H, PCHC*H*$_3$), 1.26 (dd, J_{H-P} = 14.6, J_{H-H} = 7.2, 9H, PCHC*H*$_3$), −15.91 (d, J_{H-P} = 33.7, 1H, Os−H). The NOESY spectrum shows cross signals between each one of the resonances of the CH_2 group (4.16 and 4.12 ppm) and the hydride ligand (−15.91 ppm), among others. ^{31}P{^{1}H} NMR (121.49 MHz, CD_2Cl_2, 298 K): δ 15.5 (s). ^{13}C{^{1}H} NMR (75.48 MHz, CD_2Cl_2, 298 K): δ 142.4 (s, C_{ipso}Ph), 129.4, 127.4, and 127.2 (all s, Ph), 87.8 (s, C_5H_5), 72.5 (s, C_{meso}), 48.0 (d, J_{C-P} = 3, *C*HPh), 29.5 (d, J_{C-P} = 2, CH_2), 28.4 (d, J_{C-P} = 30, PCH), 19.9 (d, J_{C-P} = 3, PCH*C*H$_3$), 19.8 (d, J_{C-P} = 2, PCH*C*H$_3$).

Reaction of 4-d_2 with 1-Phenyl-1-propyne: Formation of [OsH(η^5-C_5H_5){η^3-$CH_2CDCDPh$}(P^iPr_3)]BF_4 (5-d_2). Two NMR tubes were charged with **1**-d_4 (30 mg, 0.06 mmol) and acetone (0.5 mL). The resulting solutions were left for 15 min at room temperature under a slight argon flow, and the solvent was removed in vacuo. Then, dichloromethane-d_2 (0.5 mL) and 1-phenyl-1-propyne (7.0 μL, 0.06 mmol) were added to the first tube, while dichloromethane (0.5 mL) and 1-phenyl-1-propyne (7.0 μL, 0.06 mmol) were added to the second one. ^{1}H and ^{2}H NMR were recorded immediately. The ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K) data were identical to those reported for **5** with the exception of the absence of the resonances at 5.84 and 3.66 ppm and broadening of the signals at 4.16 and 4.12 ppm. ^{2}H NMR (61.42 MHz, CH_2Cl_2, 293 K): δ 5.85 (br, CDPh), 3. 70 (br, D_{meso}).

Preparation of BPh_4 Salt of 5. An orange solution of **5** (150 mg, 0.24 mmol) in 10 mL of dichloromethane was treated with $NaBPh_4$ (166 mg, 0.49 mmol). After 2 h, the solution was filtered through Celite and concentrated to ca. 1 mL. The addition of 10 mL of diethyl ether caused the precipitation of a white solid, which was separated by decantation and dried in vacuo. Yield: 163 mg (79%). The ^{31}P and ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K) data were identical to those reported for **5** except the additional ^{1}H signals of BPh_4^-.

Reaction of 4 with 2-Butyne: Formation of [OsH(η^5-C_5H_5)-{η^3-$CH_2CHCHCH_3$}(P^iPr_3)]BF_4 (6). This complex was prepared as described for **5** starting from 100 mg (0.18 mmol) of **4** and 2-butyne (30 μL, 0.38 mmol), but the solution was allowed to react for 2 h at room temperature. A white solid was obtained. Yield: 76 mg (77%). Anal. Calcd for $C_{18}H_{34}BF_4OsP$: C, 38.71; H, 6.14. Found: C, 38.58; H, 5.86. IR (Nujol, cm^{-1}): ν(OsH) 2127 (m). ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ 5.55 (s, 5H, C_5H_5), 4.36 (dq, J_{H-HMe} = 6.4, J_{H-Hm} = 6.0, 1H, C*H*CH$_3$), 3.81 (d, J_{H-Hm} = 5.8, 1H, H_{syn}), 3.63 (m, 1H, H_{meso}), 3.58 (dd, J_{H-Hm} = 9.9, J_{H-P} = 2.3, 1H, H_{anti}), 2.20 (m, 3H, PCH), 1.43 (d, J_{H-H} = 6.4, 3H, CHC*H*$_3$), 1.25 (dd, J_{H-P} = 14.2, J_{H-H} = 7.2, 9H, PCHC*H*$_3$), 1.19 (dd, J_{H-P} = 14.5, J_{H-H} = 7.1, 9H, PCHC*H*$_3$), −15.90 (d, J_{H-P} = 33.4, 1H, Os−H). The NOESY spectrum shows cross signals between each one of the resonances of the CH_2 group (3.81 and 3.58 ppm) and the hydride ligand (−15.90 ppm), among others. ^{31}P{^{1}H} NMR (161.98 MHz, CD_2Cl_2, 298 K): δ 16.0 (s). ^{13}C-{^{1}H} NMR (100.63 MHz, CD_2Cl_2, 253 K): δ 86.2 (s, C_5H_5), 75.5

(s, C_{meso}), 42.5 (d, $J_{C-P} = 3$, *C*HCH$_3$), 28.3 (d, $J_{C-P} = 30$, PCH), 25.7 (d, $J_{C-P} = 2$, CH$_2$), 19.8 (d, $J_{C-P} = 2$, PCH*C*H$_3$), 19.7 (d, $J_{C-P} = 2$, PCH*C*H$_3$), 19.6 (s, CH*C*H$_3$).

Isomerization of 5 into 7. An NMR tube was charged with **5** (30 mg, 0.05 mmol) and 0.5 mL of dichloromethane-d_2, and the sample was heated at 50 °C and monitored by NMR periodically. ^{31}P{^{1}H} and ^{1}H NMR spectra indicated a quantitative conversion in 24 h. The spectroscopic data were identical to those previously reported for **7**.[32]

Isomerization of 6 into 8. An orange solution of **6** (120 mg, 0.22 mmol) in 2 mL of dichloromethane was stirred at 50 °C for 15 min. The solution was concentrated to ca. 0.5 mL under reduced pressure. The addition of diethyl ether (5 mL) caused the formation of a white solid, which was separated by decantation, washed with diethyl ether (3 × 3 mL), and dried in vacuo. Yield: 97 mg (81%). Anal. Calcd for $C_{18}H_{34}BF_4OsP$: C, 38.71; H, 6.14. Found: C, 38.42; H, 5.92. IR (Nujol, cm^{-1}): ν(OsH) 2135 (m). ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ 5.61 (s, 5H, C_5H_5), 3.95 (ddq, J_{H-Hm} = 8.5, J_{H-HMe} = 5.8, J_{H-P} = 2.6, 1H, C*H*CH$_3$), 3.47 (dddd, J_{H-Ha} = 9.0, $J_{H-Ha'}$ = 8.5, J_{H-Hsyn} = 5.8, J_{H-P} = 4.5, 1H, H_{meso}), 3.06 (ddd, J_{H-Hm} = 5.8, J_{H-P} = 5.8, J_{H-Hgem} = 1.5, 1H, H_{syn}), 2.70 (d, J_{H-Hm} = 9.0, 1H, H_{anti}), 2.19 (m, 3H, PCH), 2.01 (d, J_{H-H} = 5.8, 3H, CHC*H*$_3$), 1.24 (dd, J_{H-P} = 14.4, J_{H-H} = 7.4, 9H, PCHC*H*$_3$), 1.21 (dd, J_{H-P} = 14.4, J_{H-H} = 7.3, 9H, PCHC*H*$_3$), −15.60 (d, J_{H-P} = 35.1, 1H, Os−H). The NOESY spectrum shows a cross-peak between the signals at 3.95 and −15.60 ppm, among others. ^{31}P-{^{1}H} NMR (121.49 MHz, CD_2Cl_2, 298 K): δ 15.0 (s). ^{13}C{^{1}H} NMR (75.48 MHz, CD_2Cl_2, 253 K): δ 85.4 (s, C_5H_5), 79.4 (s, C_{meso}), 51.9 (d, J_{C-P} = 2, *C*HCH$_3$), 28.1 (d, J_{C-P} = 30, PCH), 24.0 (s, CH*C*H$_3$), 20.4 (d, J_{C-P} = 3, CH$_2$), 20.0 and 19.9 (both d, J_{C-P} = 2, PCH*C*H$_3$).

Reaction of 5 with 1-Phenyl-1-propyne: Formation of [Os(η^5-C$_5$H$_5$){η^2-(*Z*)-CH(CH$_3$)=CHPh}{κ^3-(*P*,*C*,*C*)-[CH$_2$=C(CH$_3$)]-P^{i}Pr$_2$}]BF$_4$ (9a and 9b). An orange solution of **5** (150 mg, 0.24 mmol) in 2 mL of acetone was treated with 1-phenyl-1-propyne (35 μL, 0.28 mmol). After 12 h at room temperature, a white solid appeared. The mixture was cooled to −70 °C in a dry ice/2-propanol bath, and then, the solid was separated by decantation, washed with acetone (3 × 1 mL), and dried in vacuo. The NMR spectra showed the presence of **9a** and **9b** in a molar ratio 1.5:1. Yield of the mixture: 108 mg (72%). GC-MS analysis of the mother liquor showed the presence of (*Z*)-methylstyrene. Anal. Calcd for $C_{23}H_{34}BF_4OsP$: C, 44.66; H, 5.54. Found: C, 44.58; H, 5.31. Spectroscopic data for **9a**: ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ 7.35−7.10 (5H, Ph), 5.07 (s, 5H, C_5H_5), 3.87 (dd, J_{H-P} = 8.4, J_{H-H} = 2.2, 1H, PC=CH$_{cis\ to\ P}$), 3.67 (dd, J_{H-P} = 32.2, J_{H-H} = 2.2, 1H, PC=CH$_{trans\ to\ P}$), 2.77 (m, 1H, PCH), 2.70 (d, J_{H-H} = 9.2, 1H, =C*H*Ph), 2.40 (m, 1H, =C*H*CH$_3$), 2.08 (d, J_{H-H} = 7.2, 3H, CH$_3$), 1.80−1.40 (16 H, PCH and CH$_3$ groups). The NOESY spectrum shows a cross-peak between the =C*H*Ph olefinic resonance (2.70 ppm) and one of the resonances of the CH$_2$ group of the isopropenyl substituent (3.67 ppm, PC=CH$_{trans\ to\ P}$). ^{31}P{^{1}H} NMR (161.98 MHz, CD_2Cl_2, 298 K): δ −3.3 (s). ^{13}C{^{1}H} NMR (100.63 MHz, CD_2Cl_2, 298 K): δ 145.4 (s, C_{ipso}Ph), 130.7, 128.7, and 127.8 (all s, Ph), 88.2 (s, C_5H_5), 63.6 (d, J_{C-P} = 21, P−C=), 44.0 (s, =*C*HPh), 31.5 (d, J_{C-P} = 3, =*C*HCH$_3$), 30.4 (d, J_{C-P} = 31, PCH), 28.6 (d, J_{C-P} = 7, =CH$_2$), 25.9 (s, CH$_3$), 23.5 (d, J_{C-P} = 30, PCH), 22.3 and 20.5 (both s, CH$_3$), 20.4 (d, J_{C-P} = 6, CH$_3$), 18.7 (s, CH$_3$), 10.0 (d, J_{C-P} = 4, CH$_3$). Spectroscopic data for **9b**: ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ 7.35−7.10 (5H, Ph), 5.22 (s, 5H, C_5H_5), 3.74 (dd, J_{H-P} = 8.8, J_{H-H} = 2.2, 1H, PC=CH$_{cis\ to\ P}$), 3.61 (dd, J_{H-P} = 8.8, J_{H-H} = 8.8, 1H, =C*H*Ph), 3.45 (dd, J_{H-P} = 32.5, J_{H-H} = 2.2, 1H, PC=CH$_{trans\ to\ P}$), 2.77 (m, 1H, PCH), 1.80−1.40 (20 H, PCH, =C*H*CH$_3$ and CH$_3$ groups). The NOESY spectrum shows a cross-peak between a signal centered at 1.61 ppm (=C*H*CH$_3$) and one of the resonances of the CH$_2$ group of the isopropenyl substituent (3.45 ppm, PC=CH$_{trans\ to\ P}$). ^{31}P{^{1}H} NMR (161.98 MHz, CD_2Cl_2, 298 K): δ −7.0 (s). ^{13}C{^{1}H} NMR (100.63 MHz, CD_2Cl_2, 298 K): δ 141.8 (s, C_{ipso}Ph), 128.5, 126.4, and 126.1 (all s, Ph), 87.0 (s, C_5H_5), 63.1 (d, J_{C-P} = 21, P−C=), 41.3 (d, J_{C-P} = 3, =*C*HPh), 36.8 (d, J_{C-P} = 3, CH$_3$), 30.6 (d, J_{C-P} = 7, =CH$_2$), 30.4 (d, J_{C-P} = 31, PCH), 25.8 (d, J_{C-P} = 6, =*C*HCH$_3$), 24.3 (d, J_{C-P} = 29, PCH), 22.8 (s, CH$_3$), 20.9 (d, J_{C-P} = 7, CH$_3$), 20.5 (s, CH$_3$), 19.1 (d, J_{C-P} = 1, CH$_3$), 10.2 (d, J_{C-P} = 3, CH$_3$).

Table 1. Crystal Data and Data Collection and Refinement for 2 and 5

	2	**5**
Crystal Data		
formula	$C_{23}H_{32}BF_4OsP$	$C_{47}H_{56}BOsP$
molecular wt	616.47	852.90
color and habit	orange, prism	colorless, plate
size, mm	0.20,0.14,0.12	0.12,0.10,0.02
symmetry, space group	triclinic, $P\bar{1}$	triclinic, $P\bar{1}$
a, Å	7.9073(12)	11.2407(16)
b, Å	11.2735(17)	12.5147(18)
c, Å	13.256(2)	13.4682(19)
α, deg	98.094(2)	87.048(2)
β, deg	93.655(2)	89.732(2)
γ, deg	104.019(2)	87.597(2)
V, Å^3	1129.1(3)	1890.4(5)
Z	2	2
D_{calc}, g cm^{-3}	1.813	1.498
Data Collection and Refinement		
diffractometer	Bruker Smart APEX	
λ(Mo Kα), Å	0.71073	
monochromator	graphite oriented	
scan type	*ω* scans	
μ, mm^{-1}	5.758	3.448
2*θ*, range, deg	3, 57	3, 58
temp, K	100.0(2)	100.0(2)
no. of data collected	14 145	23 924
no. of unique data	5412 (R_{int} = 0.0339)	9077 (R_{int} = 0.0388)
no. of params/restraints	307/1	475/1
R_1[a] [$F^2 > 2\sigma(F^2)$]	0.0280	0.0315
wR_2[b] [all data]	0.0557	0.0534
S[c] [all data]	0.910	0.854

[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.

Reaction of 6 with 2-Butyne: Formation of [Os(η^5-C$_5$H$_5$)-{η^2-(*Z*)-CH(CH$_3$)=CHCH$_3$}{κ^3-(*P*,*C*,*C*)-[CH$_2$=C(CH$_3$)]P^{i}Pr$_2$}]-BF$_4$ (10). This complex was prepared as described for the isomeric mixture of **9a** and **9b** starting from 200 mg (0.36 mmol) of **6** and 2-butyne (60 μL, 0.77 mmol). A white solid was obtained. Yield: 112 mg (56%). Anal. Calcd for $C_{18}H_{32}BF_4OsP$: C, 38.85; H, 5.80. Found: C, 38.62; H, 5.88. ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ 5.32 (s, 5H, C_5H_5), 3.55 (d, J_{H-P} = 8.3, 1H, PC=CH$_{cis\ to\ P}$), 3.31 (d, J_{H-P} = 32.7, 1H, PC=CH$_{trans\ to\ P}$), 2.77 (m, 1H, =C*H*CH$_3$), 2.30−2.10 (2H, PCH and =C*H*CH$_3$), 1.74−1.37 (22H, PCH and CH$_3$ groups). ^{31}P{^{1}H} NMR (161.98 MHz, CD_2Cl_2, 298 K): δ −2.8 (s). ^{13}C{^{1}H} NMR (100.63 MHz, CD_2Cl_2, 298 K): δ 85.8 (s, C_5H_5), 62.2 (d, J_{C-P} = 21, PC=), 38.9 (s, CH$_3$), 34.1 (d, J_{C-P} = 3, CH$_3$), 29.8 (d, J_{C-P} = 31, PCH), 28.9 (d, J_{C-P} = 7, =CH$_2$), 25.4 (d, J_{C-P} = 7, =*C*HCH$_3$), 23.2 (d, J_{C-P} = 30, PCH), 20.6 (d, J_{C-P} = 3, CH$_3$), 20.4 (d, J_{C-P} = 6, =*C*HCH$_3$), 19.5, 18.7, and 18.5 (all s, CH$_3$), 9.5 (d, J_{C-P} = 4, CH$_3$).

Reaction of 9a and 9b with 1-Phenyl-1-propyne. Formation of [OsH(η^5-C$_5$H$_5$){κ^4-(*P*,*C*,*C*,*C*)-CH$_2$C[CH$_2$C(=CH$_2$)P^{i}Pr$_2$]CHPh}]-BF$_4$ (2). An NMR tube containing an orange solution of **9a** and **9b** (50 mg, 0.08 mmol) in 0.5 mL of dichloromethane-d_2 was treated with 1-phenyl-1-propyne (12 μL, 0.10 mmol). The sample was heated at 50 °C and monitored by NMR periodically. ^{31}P{^{1}H} and ^{1}H NMR spectra indicated a quantitative conversion to **2** in 3 h.

Reaction of 10 with 2-Butyne. Formation of [OsH(η^5-C$_5$H$_5$)-{κ^4-(*P*,*C*,*C*,*C*)-CH$_2$C[CH$_2$C(=CH$_2$)P^{i}Pr$_2$]CHCH$_3$}]BF$_4$ (3). An

NMR tube containing an orange solution of **10** (50 mg, 0.09 mmol) in 0.5 mL of dichloromethane-d_2 was treated with 2-butyne (15 μL, 0.19 mmol). The sample was heated at 50 °C and monitored by NMR periodically. $^{31}P\{^1H\}$ and ^1H NMR spectra indicated a quantitative conversion to **3** in 4 h.

Structural Analysis of Complexes 2 and 5. Crystals suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether into a concentrated solution of **2** in dichloromethane and by slow diffusion of diethyl ether into a concentrated solution of the BPh_4 salt of **5** in dichloromethane. X-ray data for both complexes were collected on a Bruker Smart APEX CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube source (Mo radiation, $\lambda = 0.71073$ Å) operating at 50 kV and 30 mA. Data were collected over the complete sphere by a combination of four sets. Each frame exposure time was 10 s covering 0.3° in ω. Data were corrected for absorption by using a multiscan method applied with the SADABS program.[48] The structures of both compounds were solved by the Patterson method. Refinement, by full-matrix least-squares on F^2 with SHELXL97,[49] was similar for both complexes, including isotropic and subsequently anisotropic displacement parameters. The high quality and extended range of diffraction data allowed location of the hydride ligands in **2** and **5** in the difference Fourier maps. However, we observed short Os−H distances due to the well-known behavior of the X-ray experiments that usually show shorter M−H distances than those based on neutron diffraction, a radiation much more appropriate for the precise localization of lighter elements. Unfortunately, none of them supported a free refinement of these atoms, and a restrained geometry was used in the last cycles of refinement. Hydrogen atoms (except those corresponding to the allylic carbon atoms, which were observed in the difference Fourier maps and refined as free isotropic atoms) were included in calculated positions and refined riding on their respective carbon atoms with the thermal parameter related to the bonded atoms. All the highest electronic residuals were observed in the close proximity of the Os centers and make no chemical sense. Crystal data and details of the data collection and refinement are given in Table 1.

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Acknowledgment. Financial support from the MEC of Spain (Project CTQ2005-00656) and Diputación General de Aragón (E35) is acknowledged. Y.A.H. thanks the Spanish MEC for his grant.

Supporting Information Available: CIF files giving positional and displacement parameters, crystallographic data, and bond lengths and angles of compounds **2** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM070004D