Synthesis and Characterization of Hydride−Alkynyl, Allenylidene, Carbyne, and Functionalized-Alkynyl Complexes Containing the $[Os(\eta^5\text{-}C_5H_5)(P^iPr_3)_2]^+$ Fragment: The Complex $[Os(\eta^5\text{-}C_5H_5)(C{=}C{=}CPh_2)(P^iPr_3)_2]PF_6$, a New Type of Allenylidene Derivative from the Reactivity Point of View

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Received February 14, 2000

Complex $Os(\eta^5\text{-}C_5H_5)Cl(P^iPr_3)_2$ (**1**) reacts with equimolecular mixtures of $TlPF_6$ and alkynes such as phenylacetylene and cyclohexylacetylene to give $[OsH(\eta^5\text{-}C_5H_5)(C{\equiv}CR)(P^iPr_3)_2]PF_6$ (R = Ph (**2**), Cy (**3**)). The structure of **2** in the solid state has been determined by X-ray diffraction analysis. The distribution of ligands around the metallic center can be described as a four-legged piano-stool geometry with the hydride and alkynyl ligands mutually *transoid*. The reaction of **1** with 2-phenyl-3-butyn-2-ol and $TlPF_6$ leads to $[OsH(\eta^5\text{-}C_5H_5)\{C{\equiv}CC(OH)MePh\}(P^iPr_3)_2]PF_6$ (**4**), which evolves into the hydride−enynyl complex $[OsH(\eta^5\text{-}C_5H_5)\{C{\equiv}CC(Ph){=}CH_2\}(P^iPr_3)_2]PF_6$ (**5**) in solution of chloroform. Treatment of **1** with 1,1-diphenyl-2-propyn-1-ol and $TlPF_6$ affords $[OsH(\eta^5\text{-}C_5H_5)\{C{\equiv}CC(OH)Ph_2\}(P^iPr_3)_2]PF_6$ (**6**), which reacts with KOH in methanol to give the neutral compound $Os(\eta^5\text{-}C_5H_5)\{C{\equiv}CC(OH)Ph_2\}(P^iPr_3)_2$ (**7**) by extraction of the hydride ligand. The addition of 1 equiv of HPF_6 to the solutions of **7** leads to the allenylidene, $[Os(\eta^5\text{-}C_5H_5)(C{=}C{=}CPh_2)(P^iPr_3)_2]PF_6$ (**8**), which affords the dicationic carbyne derivative $[Os(\eta^5\text{-}C_5H_5)(CCH{=}CPh_2)(P^iPr_3)_2](PF_6)_2$ (**9**) by reaction with HPF_6. The structure of **9** in the solid state has been also determined by X-ray diffraction analysis. In this case, the geometry around the osmium center is close to octahedral with the triisopropylphosphine ligands mutually *cis* disposed (P−Os−P = 105.12(8)°). Complex **8** also reacts with nucleophilic reagents; the reaction with CH_3Li gives $Os(\eta^5\text{-}C_5H_5)\{C{\equiv}CC(CH_3)Ph_2\}(P^iPr_3)_2$ (**10**), whereas the reactions with acetone and methanol solutions of KOH afford $Os(\eta^5\text{-}C_5H_5)\{C{\equiv}CC[CH_2C(O)CH_3]Ph_2\}(P^iPr_3)_2$ (**11**) and $Os(\eta^5\text{-}C_5H_5)\{C{\equiv}CC(OCH_3)Ph_2\}(P^iPr_3)_2$ (**12**), respectively. To understand the chemical behavior of **8**, EHT−MO calculations on the model compounds $Os(\eta^5\text{-}C_5H_5)Cl(C{=}C{=}CH_2)(PH_3)$ (**13**) and $[Os(\eta^5\text{-}C_5H_5)(C{=}C{=}CH_2)L(PH_3)]^+$ (L = PH_3 (**14**), CO (**15**)) have been also carried out. The results suggest that the behavior of **8** as nucleophile is a consequence of the high electron density of the allenylidene ligand, while the behavior as γ-electrophile is due to its cationic nature. In addition, we have determined by ab initio calculations the energies of stabilization by protonation of **13**−**15** with a naked proton. In the three cases the formation of the corresponding carbyne derivatives $[Os(\eta^5\text{-}C_5H_5)Cl(CCH{=}CH_2)(PH_3)]^+$ (**16**; 267 kcal·mol^{-1}), $[Os(\eta^5\text{-}C_5H_5)(CCH{=}CH_2)(PH_3)_2]^{2+}$ (**17**; 180 kcal·mol^{-1}), and $[Os(\eta^5\text{-}C_5H_5)(CCH{=}CH_2)(CO)(PH_3)]^{2+}$ (**18**; 157 kcal·mol^{-1}) involves a stabilization of the system.

Introduction

Diarylallenylidene complexes of the iron triad have attracted a great deal of attention in recent years as a new type of organometallic intermediate that may have unusual reactivity in stoichiometric[1] and catalytic processes.[2]

Since the beginning, the dehydration of hydroxyvinylidene has been proposed as the reasonable previous step to allenylidene. This reaction implicates the coordination of the carbon−carbon triple bond of propargyl alcohols $HC{\equiv}CC(OH)R_2$, followed by tautomerization.[3]

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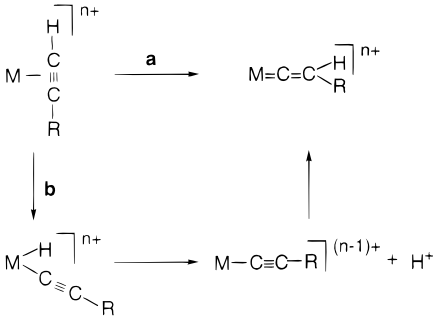
10.1021/om000141+ CCC: $19.00
Publication on Web 05/31/2000

Scheme 1



R = C(OH)R'$_2$, alkyl, aryl; n = 0, 1

The isomerization of the coordinate π-alkynes into vinylidenes has been shown to occur by two alternative pathways (**a** and **b** in Scheme 1), either intramolecular 1,2-hydrogen migration or via hydride−alkynyl species.[4] Pathway **b** is enhanced by basic metallic fragments, which favor the H−C(sp) activation of the alkyne.[5] Once the hydride−alkynyl intermediates are formed, the hydride dissociates as a proton, yielding alkynyl species. Protonation of these intermediates at the C_β atom affords the vinylidene derivatives. As a consequence of the common ion effect, the addition of strong acids inhibits the isomerization through pathway **b**.[5,6]

The reactivity of the C_3-organic unit of the allenylidene ligand of diarylallenylidene complexes of the iron triad strongly depends on the particular metallic fragment stabilizing the unsaturated ligand. Thus, according to the behaviors reported to the present, the compounds can be classified into three groups.

(i) Nucleophiles. The most representative example of this type is the neutral osmium(II) complex Os(η^5-C_5H_5)Cl(C=C=CPh_2)(P^{i}Pr$_3$). The C_3-organic unit of this compound does not react with water, alcohols, phosphines, amines, or strongly nucleophilic reagents. However, it adds HBF_4 and dimethyl acetylenedicarboxylate to give [Os(η^5-C_5H_5)Cl(CCH=CPh_2)(P^{i}Pr$_3$)]BF_4 and Os(η^5-C_5H_5)Cl{C=C(CO_2Me)C(CO_2Me)=C=CPh_2}(P^{i}Pr$_3$), respectively.[7]

(ii) γ-Electrophiles. The diarylallenylidene ligands show this behavior when they are bonded to cationic metallic fragments such as [RuCl(dppm)$_2$]$^+$ (dppm = $Ph_2PCH_2PPh_2$),[8] [Ru(η^5-C_5R_5)(PR′$_3$)$_2$]$^+$ (R = H, Me), [Ru(η^5-C_9H_7)L_2]$^+$ (L_2 = 2 PR_3, diphosphine),[10] [RuCl{N(CH_2CH_2PPh_2)$_3$}]$^+$,[11] or [Os{C[C(O)OCH_3]=CH_2}(CO)(P^{i}Pr$_3$)$_2$]$^+$.[12] In such cases, the diarylallenylidene moieties do not undergo intermolecular addition of weakly nucleophilic reagents (water, alcohols, amines, etc.), and the reactions with strong nucleophiles such as methoxide, alkyl, and acetylide lead to functionalized alkynyl compounds as a result of the regioselective addition of the reagents at the Cγ atom of the diarylallenylidene group.

(iii) α-Electrophiles. The best known complex of this type is the derivative [Ru(η^5-C_5H_5)(C=C=CPh_2)(CO)(P^{i}Pr$_3$)]$^+$.[13] The reactivity of the C_3-organic unit of this compound is characterized by its strong trend to add RXH molecules at the C_α−C_β double bond, to afford cationic complexes of the type Ru{C(XR)CH=CPh_2}. The diphenylallenylidene ligand stabilized by the metallic fragments [Ru(η^5-$C_9H_4Me_3$)(CO)(PPh_3)]$^+$ [14] and [Ru(η^6-$C_6H_4X_2$)Cl(PMe_3)]$^+$ (X = H, Me)[15] shows similar behavior.

As a part of our study on the chemical properties of the six-coordinate osmium(IV) complex OsH_2Cl_2(P^{i}Pr$_3$)$_2$, we have recently reported the synthesis of the half-sandwich derivative Os(η^5-C_5H_5)Cl(P^{i}Pr$_3$)$_2$.[16] Despite the high kinetic stability of the $OsCpL_3$ compounds,[17] this complex is a labile starting material for the development of new cyclopentadienyl−osmium chemistry.[7,18] As a continuation of our work in this field, we now show that the complex Os(η^5-C_5H_5)Cl(P^{i}Pr$_3$)$_2$ allows the prepara-

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tion of the first hydride−alkynyl derivatives of osmium(IV), and the allenylidene complex $[Os(\eta^5\text{-}C_5H_5)(C{=}C{=}CPh_2)(P^iPr_3)_2]PF_6$, which is of interest not only because the osmium allenylidene compounds are very rare[19] but also because the chemical properties of this new complex are intermediate between those previously mentioned for nucleophilic and γ-electrophilic diarylallenylidene derivatives. In addition, we report the analysis of the electronic structures of the model complexes $Os(\eta^5\text{-}C_5H_5)Cl(C{=}C{=}CH_2)(PH_3)$ and $[Os(\eta^5\text{-}C_5H_5)(C{=}C{=}CH_2)L(PH_3)]^+$ (L = PH_3, CO), to understand why the cation $[Os(\eta^5\text{-}C_5H_5)(C{=}C{=}CPh_2)(P^iPr_3)_2]^+$ has a different behavior from the previously reported allenylidene compounds.

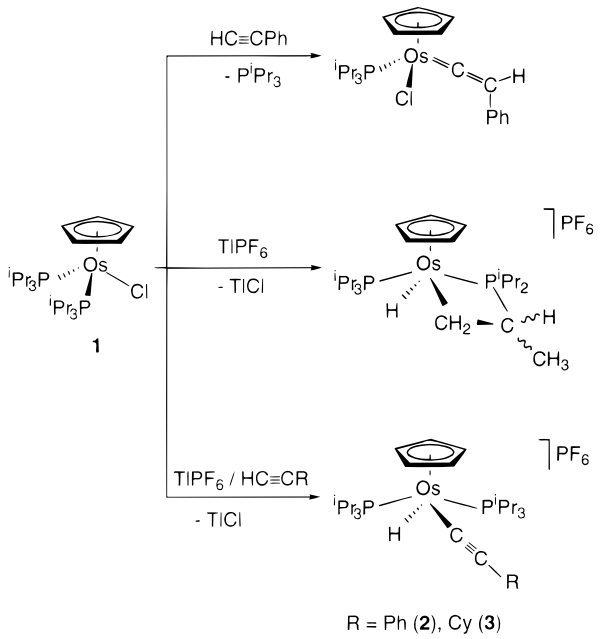
Results and Discussion

1. Synthesis and Characterization of $[OsH(\eta^5\text{-}C_5H_5)(C{\equiv}CR)(P^iPr_3)_2]PF_6$ (R = Ph, Cy). In pentane and toluene, complex $Os(\eta^5\text{-}C_5H_5)Cl(P^iPr_3)_2$ (**1**) reacts with phenylacetylene to give the vinylidene derivative $Os(\eta^5\text{-}C_5H_5)Cl(C{=}CHPh)(P^iPr_3)$ via the π-alkyne intermediate $Os(\eta^5\text{-}C_5H_5)Cl(\eta^2\text{-}HC{\equiv}CPh)(P^iPr_3)$. On the other hand, in polar solvents or in the presence of $TlPF_6$ the splitting of the Os−Cl bond of **1** is favored, and the resulting $[Os(\eta^5\text{-}C_5H_5)(P^iPr_3)_2]^+$ metallic fragment is capable of activating a methyl C−H bond of a triisopropylphosphine to give $[OsH(\eta^5\text{-}C_5H_5)\{CH_2CH(CH_3)P^iPr_2\}(P^iPr_3)]^+$.[16]

In contrast to the above-mentioned reactions, the combined treatment of **1** with alkynes, such as phenylacetylene or cyclohexylacetylene, and $TlPF_6$ in a 1:15 acetone/dichloromethane mixture as solvent leads to the hydride−alkynyl−osmium(IV) complexes $[OsH(\eta^5\text{-}C_5H_5)(C{\equiv}CR)(P^iPr_3)_2]PF_6$ (R = Ph (**2**), Cy (**3**)), as a result of the H−C(sp) oxidative addition of the alkynes to the $[Os(\eta^5\text{-}C_5H_5)(P^iPr_3)_2]^+$ metallic fragment (Scheme 2). Evidence for the participation of π-alkyne intermediates during the formation process of **2** and **3** was not found.

The ruthenium complex $Ru(\eta^5\text{-}C_5Me_5)Cl(dippe)$ (dippe = $^iPr_2PCH_2CH_2P^iPr_2$) reacts with terminal alkynes in the presence of $NaBPh_4$ to give vinylidene derivatives via hydride−alkynyl−ruthenium(IV) intermediates related to **2** and **3**, whereas, under the same conditions, the formation of the analogous vinylidene complexes containing the $[Ru(\eta^5\text{-}C_5H_5)(dippe)]^+$ unit proceeds through π-alkyne intermediates. To rationalize these observations, it has been argued that the pathways **a** and **b** of Scheme 1 are competitive, and the choice of either **a** or **b** is determined by the electron density of the metallic fragment.[5] At first glance, the formation of **2** and **3** is in agreement with this. The intrinsically higher basicity of the osmium atom in comparison with ruthenium[21] could explain why the metallic fragment $[Os(\eta^5\text{-}C_5H_5)(P^iPr_3)_2]^+$ favors the H−C(sp) oxidative addition, while the $[Ru(\eta^5\text{-}C_5H_5)(dippe)]^+$ unit gives rise to the formation of vinylidene derivatives by intramolecular 1,2-hydrogen shift. However, it should be noted

Scheme 2



that, in the presence of phenylacetylene, the metallic fragment $Os(\eta^5\text{-}C_5H_5)Cl(P^iPr_3)$, which reacts with HX (X = H, SiR_3, GeR_3, SnR_3, Cl) molecules to give $OsH(\eta^5\text{-}C_5H_5)XCl(P^iPr_3)$,[18c] shows the same behavior as $[Ru(\eta^5\text{-}C_5H_5)(dippe)]^+$. Furthermore, in contrast to the above-mentioned hydride−alkynyl−ruthenium(IV) species stabilized by the $[Ru(\eta^5\text{-}C_5Me_5)(dippe)]^+$ unit, complexes **2** and **3** do not rearrange to either vinylidene or π-alkyne isomers in the solid state or in solution.

The reasons for the *anomalous* behavior of the metallic fragment $[Os(\eta^5\text{-}C_5H_5)(P^iPr_3)_2]^+$ may be (i) the electrophilic power of the hydride ligands of **2** and **3** is significantly weaker than that of $[RuH(\eta^5\text{-}C_5Me_5)(C{\equiv}CR)(dippe)]^+$, and (ii) the formation of hydride−alkynyl species also takes place by an intermolecular process without previous coordination of the carbon−carbon triple bond of the alkyne.[22] The noncoordination of alkynes to $[Os(\eta^5\text{-}C_5H_5)(P^iPr_3)_2]^+$ could explain why this fragment does not form vinylidene derivatives, while the unit $Os(\eta^5\text{-}C_5H_5)Cl(P^iPr_3)$ affords $Os(\eta^5\text{-}C_5H_5)Cl(C{=}CHPh)(P^iPr_3)$.[23]

From an electronic point of view, the fragments $[Os(\eta^5\text{-}C_5H_5)(P^iPr_3)_2]^+$ and $Os(\eta^5\text{-}C_5H_5)Cl(P^iPr_3)$ are not significantly different (vide infra). Thus, the different behavior should be steric in origen. The approach of an alkyne to an $Os(\eta^5\text{-}C_5H_5)L_2$ metallic fragment can be parallel to the L−L vector or alternatively perpendicular, and the first approach requires more space around the metallic center than the second one. Furthermore, the parallel approach could give rise to either the coordination of the carbon−carbon triple bond or the H−C(sp) activation, while the perpendicular approach should give rise only to the H−C(sp) activation.

Two triisopropylphosphine groups generate a larger steric hindrance than the chloride and the phosphine

(19) The osmium−allenylidene complexes previously reported are $Os(\eta^5\text{-}C_5H_5)X(C{=}C{=}CPh_2)(P^iPr_3)$ (X = Cl, I),[7] $[Os\{C[C(O)OCH_3]{=}CH_2\}(C{=}C{=}CPh_2)(CO)(P^iPr_3)_2]BF$,[12] $[Os(\eta^5\text{-}C_9H_7)(C{=}C{=}CPh_2)(PPh_3)_2]PF_6$,[10b] and $[(PPh_3)_2(\eta^5\text{-}C_5H_5)Os{=}C{=}C{=}CHC{\equiv}C{-}Os(\eta^5\text{-}C_5H_5)(PPh_3)_2]^+$.[20]

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(23) Attempts to obtain **2** and **3** by reaction of $[OsH(\eta^5\text{-}C_5H_5)\{CH_2CH(CH_3)P^iPr_2\}(P^iPr_3)]^+$ with the corresponding alkyne were unsuccessful.

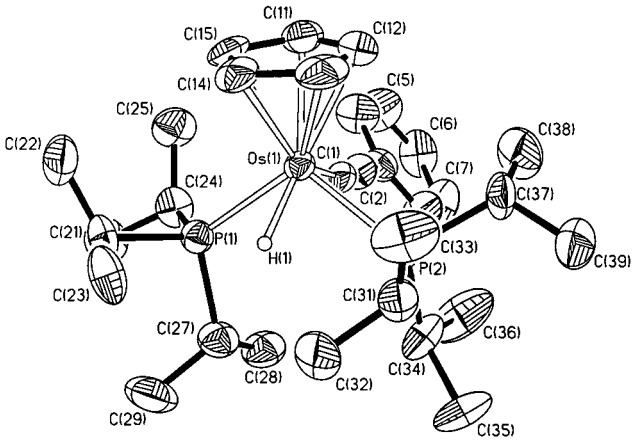


Figure 1. Molecular diagram of the cation of **2**, $[OsH(\eta^5\text{-}C_5H_5)(C{\equiv}CPh)(P^iPr_3)_2]^+$.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for the Complex $[OsH(\eta^5\text{-}C_5H_5)(C{\equiv}CPh)(P^iPr_3)_2]PF_6$ (2)

Os(1)−P(1)	2.397(3)	Os(1)−C(15)	2.291(10)
Os(1)−P(2)	2.387(3)	Os(1)−H(1)	1.64(15)
Os(1)−C(1)	2.044(12)	C(1)−C(2)	1.20(2)
Os(1)−C(11)	2.283(11)	C(2)−C(3)	1.43(2)
Os(1)−C(12)	2.238(12)	C(3)−C(4)	1.37(2)
Os(1)−C(13)	2.225(11)	C(3)−C(8)	1.39(2)
Os(1)−C(14)	2.233(10)		
P(1)−Os(1)−P(2)	111.87(9)	G(1)[a]−Os(1)−C(1)	114.0(6)
P(1)−Os(1)−G(1)[a]	123.1(5)	G(1)[a]−Os(1)−H(1)	124.0(5)
P(1)−Os(1)−C(1)	82.1(3)	C(1)−Os(1)−H(1)	121.0(5)
P(1)−Os(1)−H(1)	61.0(5)	Os(1)−C(1)−C(2)	168.5(9)
P(2)−Os(1)−G(1)[a]	122.7(5)	C(1)−C(2)−C(3)	178.4(12)
P(2)−Os(1)−C(1)	82.1(3)	C(2)−C(3)−C(4)	120.4(11)
P(2)−Os(1)−H(1)	69.0(4)	C(2)−C(3)−C(8)	121.3(12)

[a] G(1) is the midpoint of the C(10)−C(14) Cp ligand.

ligands. So, the formation of **2** and **3** can be rationalized assuming the perpendicular approaches of phenylacetylene and cyclohexylacetylene to the P−P vector of $[Os(\eta^5\text{-}C_5H_5)(P^iPr_3)_2]^+$. The parallel approach should give rise to π-alkyne species related to $Os(\eta^5\text{-}C_5H_5)Cl(\eta^2\text{-}HC{\equiv}CPh)(P^iPr_3)$, which is formed from $Os(\eta^5\text{-}C_5H_5)Cl(P^iPr_3)$ by a parallel approach of the alkyne to the P−Cl vector.

According to that previously mentioned, for $M(\eta^5\text{-}C_5R_5)L_2$ (M = Ru, Os) systems, the alkyne−vinylidene isomerization seems to be determined by the capacity of the metallic fragment to coordinate the alkyne and/or by the electrophilic power of the hydride ligand, when the isomerization proceeds through hyride−alkynyl intermediates.

The stereochemistry of **2** and **3** is strongly supported by their ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra and was confirmed by an X-ray diffraction study on a single crystal of **2**. A view of the molecular geometry is shown in Figure 1. The hydride ligand H(1) was located in the difference Fourier maps and refined as an isotropic atom together with the rest of the non-hydrogen atoms of the structure, giving an Os−H(1) distance of 1.64(15) Å.

The distribution of ligands around the osmium atom of **2** can be described as a four-legged piano-stool geometry with the hydride ligand *transoid* to the alkynyl group (C(1)−Os(1)−H(1) = 121(5)°) and *cisoid* to both phosphines, which are mutually *transoid* (P(1)−Os(1)−P(2) = 111.87(9)°). The Os(1)−C(1) bond length of 2.044(12) Å is consistent with a single bond from Os(IV) to a C(sp) atom and indicates a low degree of metal-to-ligand back-bonding.[24] The C(1)−C(2) distance and the Os(1)−C(1)−C(2) and C(1)−C(2)−C(3) angles are 1.20(2) Å, 168.5(9)°, and 178.4(12)°, respectively. Similar values have been found in other terminal alkynyl complexes.[25]

In agreement with the presence of the alkynyl ligand in **2**, its IR spectrum in Nujol shows a band at 2112 cm^{-1}, corresponding to the $\nu(C{\equiv}C)$ vibration. The presence of the hydride ligand is supported by the ^1H NMR spectrum of **2** in chloroform-*d*. It contains a triplet at −13.21 ppm, with an H−P coupling constant of 35.7 Hz,[26] which is consistent with the structure shown in Figure 1. In the $^{13}C\{^1H\}$ NMR spectrum the resonances corresponding to the C_α and C_β atoms of the alkynyl ligand appear as triplets at 57.2 and 118.0 ppm, with C−P coupling constants of 24.7 and 2.5 Hz, respectively. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 6.7 ppm, which under off-resonance conditions is split into a doublet as a consequence of the spin-coupling with the hydride ligand.

The spectroscopic data of **3** agree well with those of **2**. In the IR spectrum of **3** the $\nu(C{\equiv}C)$ band is observed at 2108 cm^{-1}. The ^1H NMR spectrum in dichloromethane-d_2 shows the hydride resonance as a triplet at −13.50 ppm, with an H−P coupling constant of 36.3 Hz. In the $^{13}C\{^1H\}$ NMR spectrum the resonances corresponding to the C(sp) atoms appear as triplets at 121.4 (C_β) and 36.4 (C_α) ppm, with C−P coupling constants of 2.5 and 24.9 Hz, respectively. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 5.6 ppm, which under off-resonance conditions is split into a doublet by spin-coupling with the hydride ligand.

2. Synthesis and Characterization of $[OsH(\eta^5\text{-}C_5H_5)\{C{\equiv}CC(OH)MePh\}(P^iPr_3)_2]PF_6$ and $[OsH(\eta^5\text{-}C_5H_5)\{C{\equiv}CC(Ph){=}CH_2\}(P^iPr_3)_2]PF_6$. Treatment of **1** with $TlPF_6$ and 2-phenyl-3-butyn-2-ol, under the same conditions as those previously mentioned for the formation of **2** and **3**, leads to the hydride−hydroxyalkynyl derivative $[OsH(\eta^5\text{-}C_5H_5)\{C{\equiv}CC(OH)MePh\}(P^iPr_3)_2]PF_6$ (**4**), as a result of the oxidative addition of the H−C(sp) bond of the alkynol to the $[Os(\eta^5\text{-}C_5H_5)(P^iPr_3)_2]^+$ metallic fragment. At room temperature, in solution of chloroform, complex **4** is unstable and evolves in quantitative yield after 6 h into the hydride−enynyl complex $[OsH(\eta^5\text{-}C_5H_5)\{C{\equiv}CC(Ph){=}CH_2\}(P^iPr_3)_2]PF_6$ (**5**) by dehydration of the hydroxyalkynyl ligand of **4** (Scheme 3). Similarly to **2** and **3**, complex **5** is stable and does not evolve into the corresponding alkenylvinylidene in the solid state or in solution.

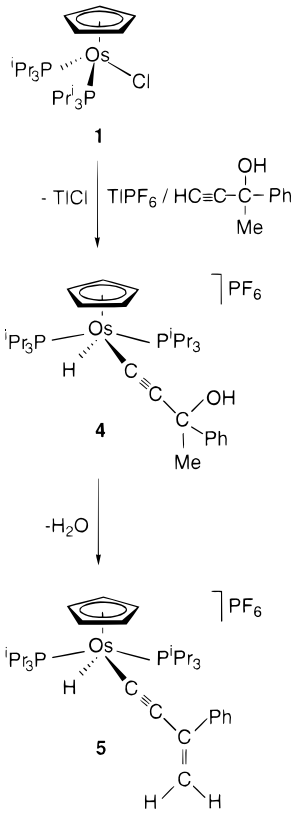
The chemical behaviors of the osmium fragment $[Os(\eta^5\text{-}C_5H_5)(P^iPr_3)_2]^+$ and related ruthenium fragments are

(24) Nast, R. *Coord. Chem. Rev.* **1982**, *47*, 89.

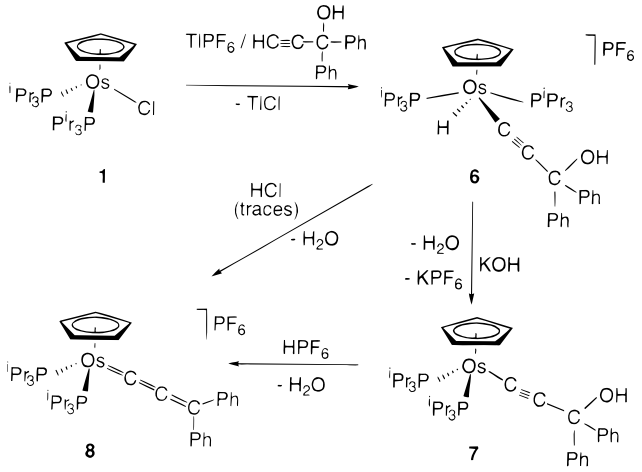
(25) See for example: (a) Fernández, M. J.; Esteruelas, M. A.; Covarrubias, M.; Oro, L. A.; Apreda, M.-C.; Foces-Foces, C.; Cano, F. H. *Organometallics* **1989**, *8*, 1158. (b) Echavarren, A. M.; López, J.; Santos, A.; Romero, A.; Hermoso, J. A.; Vegas, A. *Organometallics* **1991**, *10*, 2371. (c) Santos, A.; López, J.; Matas, L.; Ros, J.; Galán, A.; Echavarren, A. M. *Organometallics* **1993**, *12*, 4215. (d) Espuelas, J.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A.; Valero, C. *Organometallics* **1993**, *12*, 663. (e) Esteruelas, M. A.; Lahoz, F. J.; López, A. M.; Oñate, E.; Oro, L. A.; Valero, C. *Organometallics* **1995**, *14*, 2496.

(26) This is a typical value for four-legged piano-stool geometries with hydride and phosphine ligands mutually *cisoid*. See for example refs 18c and 18d, and (a) Rottink, M. K.; Angelici, R. J. *J. Am. Chem. Soc.* **1993**, *115*, 7267. (b) Wanandi, P. W.; Tilley, T. D. *Organometallics* **1997**, *16*, 4299.

Scheme 3



Scheme 4



different not only in the presence of phenylacetylene and cyclohexylacetylene but also in the presence of 2-phenyl-3-butyn-2-ol. Thus, at 0 °C the complex Ru(η^5-C_5Me_5)-Cl(PEt_3)$_2$ reacts with the latter alkynol and $NaBPh_4$ in methanol to give [RuH(η^5-C_5Me_5){C≡CC(OH)MePh}-(PEt_3)$_2$]BPh_4. In contrast to **4**, this compound evolves in the solid state and in solution into the hydroxyvinylidene [Ru(η^5-C_5Me_5){C=CHC(OH)MePh}(PEt_3)$_2$]BPh_4, which subsequently affords an isomeric mixture of allenylidene and alkenylvinylidene derivatives. A spontaneous dehydration of the hydroxyalkynyl ligand previous to the isomerization is not observed. The formation of the hydride−enynyl complex [RuH(η^5-C_5Me_5){C≡CC-(Ph)=CH_2}(PEt_3)$_2$]BPh_4 related to **5** requires the passing of a dichloromethane solution of the hydride−hydroxyalkynyl compound through acidic alumina. Similarly to its starting material, and in contrast to **5**, this hydride−enynyl complex spontaneously evolves into the corresponding alkenylvinylidene compound, which affords the thermodynamically more stable allenylidene isomer.[6b] These differences in behavior are due to the less electrophilic power of the hydride ligands of **4** and **5** in comparison with those of the related compounds containing the [Ru(η^5-C_5Me_5)(PEt_3)$_2$]$^+$ unit.

Complexes **4** and **5** were isolated as white solids in 58% (**4**) and 86% (**5**) yield and characterized by MS, elemental analysis, and IR and ^{1}H, ^{13}C{^{1}H}, and ^{31}P-{^{1}H} NMR spectroscopy.

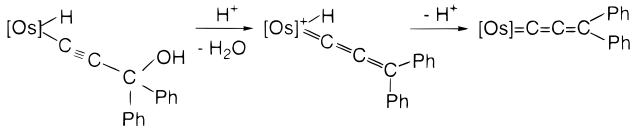
In agreement with the presence of the hydroxyalkynyl ligand in **4**, the IR spectrum of this compound in Nujol shows bands at 3605 and 2113 cm^{-1}, corresponding to the ν(O−H) and ν(C≡C) vibrations, respectively. In the ^{1}H NMR spectrum in dichloromethane-d_2, the most noticeable resonances of the hydroxyalkynyl ligand are two singlets at 2.16 and 1.74 ppm due to the OH proton and to the methyl group. In addition, the spectrum contains a double doublet at −13.40 ppm, with H−P coupling constants of 35.7 Hz, which supports the presence of the hydride ligand. In the ^{13}C{^{1}H} NMR spectrum the resonances due to the C_α and C_β atoms of the hydroxyalkynyl ligand appear as double doublets at 48.1 (C_α) and 120.7 (C_β) ppm, with C−P coupling constants of 23.7 (C_α) and 2.5 (C_β) Hz. The ^{31}P{^{1}H} NMR spectrum reveals the asymmetry of the hydroxyalkynyl group, which gives rise to inequivalent phosphines. Thus, the spectrum shows an AB system characterized by the parameters δ_A 7.0, δ_B 6.6, and J(AB) = 23.5 Hz. Under off-resonance conditions a double AB system is observed, as a consequence of the spin-coupling with the hydride ligand.

In the IR spectrum of **5** in Nujol the most noticeable feature is the absence of any ν(O−H) band. The ν(C≡C) and ν(Os−H) vibrations are observed at 2113 and 2035 cm^{-1}, respectively. In the ^{1}H NMR spectrum in chloroform-d, the =CH_2 protons of the enynyl ligand give rise to singlets at 5.38 and 5.00 ppm, whereas the resonance of the hydride ligand appears as a triplet at −13.30 ppm, with an H−P coupling constant of 36.5 Hz. The ^{13}C{^{1}H} NMR spectrum shows three triplets at 133.1, 118.0, and 59.2 ppm, with C−P coupling constants of 2.0, 3.1, and 24.3 Hz, corresponding to the =CPh, C_β, and C_α atoms of the enynyl ligand. The resonance of the =CH_2 atom appears at 117.3 ppm as a singlet. The ^{31}P{^{1}H} NMR spectrum contains a singlet at 6.9 ppm, which under off-resonance conditions is split into a doublet by spin-coupling with the hydride ligand.

3. Synthesis and Characterization of [Os(η^5-C_5H_5)(C=C=CPh_2)(P^iPr_3)$_2$]PF_6. Treatment, at room temperature, of 1:15 acetone/dichloromethane suspensions of $TlPF_6$ and 1.52 equiv of 1,1-diphenyl-2-propyn-1-ol with 1 equiv of **1** leads, after 2 min, to the hydride−hydroxyalkynyl−osmium(IV) derivative [OsH(η^5-C_5H_5)-{C≡CC(OH)Ph_2}(P^iPr_3)$_2$]PF_6 (**6**), as a result of the oxidative addition of the H−C(sp) bond of the alkynol to the unsaturated metallic fragment [Os(η^5-C_5H_5)-(P^iPr_3)$_2$]$^+$ (Scheme 4). This compound was isolated as a white solid in 76% yield.

In agreement with the null tendency of this type of systems to isomerize into hydroxyvinylidene derivatives, complex **6** is stable in the solid state and in solution. Even the metallic center can be deprotonated without

Scheme 5



[Os] = [Os(η^5-C_5H_5)(P^iPr_3)$_2$]$^+$

affecting the alkynyl unit. Thus, the addition of 2.7 equiv of KOH to methanol solutions of **6** affords the neutral hydroxyalkynyl compound Os(η^5-C_5H_5){C≡CC(OH)Ph_2}(P^iPr_3)$_2$ (**7**), as a white solid in 73% yield.

Complex **7** reacts with 1 equiv of HPF_6 to give the allenylidene derivative [Os(η^5-C_5H_5)(C=C=CPh_2)(P^iPr_3)$_2$]-PF_6 (**8**), as a result of the protonation of the −OH group of the hydroxyalkynyl ligand of **7** (Scheme 4). This complex can be also obtained in a one-pot synthesis by warming of **6** in chloroform under reflux for 6 h. It was isolated as a green solid in 89% yield. Although, it is well-known that the formation of allenylidene complexes starting from hydride−hydroxyalkynyl compounds proceeds via hydroxyvinylidene intermediates,[1a] the null tendency of **2**, **3**, **4**, and **5** to isomerize into the corresponding hydroxyvinylidene species suggests that in this case the dehydration process is catalyzed by traces of HCl, which are generated from the solvent during the warming process. In agreement with this, the addition of some drops of a HCl toluene solution to **6** in dichloromethane produces the instantaneous formation of **8**.

The formation of **8** can be rationalized according to Scheme 5. The acid could protonate the −OH group of the hydroxyalkynyl ligand of **6** to give a dicationic hydride−allenylidene intermediate, which should dissociate the protic hydride ligand.

The participation of this intermediate in the formation of **8** agrees well with previous observations.[27] The square-planar complexes OsCl(NO)(PR_3)$_2$ (PR_3 = P^iPr_3, P^iPr_2Ph) react with 1,1-diphenyl-2-propyn-1-ol to afford the six-coordinate hydride−hydroxyalkynyl−osmium(II) derivatives OsHCl{C≡CC(OH)Ph_2}(NO)(PR_3)$_2$, which similarly to **6** are inert with regard to isomerization to hydroxyvinylidenes. However, they react with chloride-containing acidic alumina to give the η^1-allenylosmium(II) compounds Os(CH=C=CPh_2)Cl_2(NO)(PR_3)$_2$, as a result of the migratory insertion of the hydride ligand into the C_α atom of the allenylidene group of hydride−allenylidene intermediates. The different behavior of these intermediates and that shown in Scheme 5 could be related to the dicationic nature of the latter, which should impose a higher electrophilic character to the hydride ligand hindering its attack at the C_α atom of the allenylidene group. In this context, it should be mentioned that EHT-MO calculations on transition metal allenylidene complexes indicate that the C_α atom of the allenylidene ligand is also an electrophilic center.[10b,13b,28]

Complexes **6**−**8** were characterized by MS, elemental analysis, and IR and ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopy. The IR spectrum of **6** in Nujol shows the ν(O−H) and the ν(C≡C) absorptions at 3543 and 2116 cm^{-1}, respectively. In the ^{1}H NMR spectrum in chloroform-*d*, the most noticeable resonances are a singlet at 2.30 ppm, corresponding to the −OH proton, and in the high-field region a triplet at −13.40 ppm, which confirms the presence of the hydride ligand. The H−P coupling constant of 35.7 Hz agrees well with those found in **2**−**5** and supports the geometry proposed in Scheme 4. The resonances corresponding to the C_α, C_β, and C_γ atoms of the alkynyl ligand appear in the ^{13}C{^{1}H} NMR spectrum at 53.3, 118.4, and 75.6 ppm, respectively. The first of them is observed as a triplet with a C−P coupling constant of 23 Hz, whereas the others are observed as singlets. The ^{31}P{^{1}H} NMR spectrum contains a singlet at 7.2 ppm, which under off-resonance conditions is split into a doublet by spin-coupling with the hydride ligand.

The IR spectrum of **7** in Nujol contains ν(O−H) and ν(C≡C) absorptions at 3532 and 2115 cm^{-1}, respectively. The ^{1}H NMR spectrum in benzene-d_6 shows the −OH resonance as a singlet at 2.62 ppm. In the ^{13}C{^{1}H} NMR spectrum, the most noticeable features are the chemical shift and the C−P coupling constant of the resonance corresponding to the C_α atom of the hydroxyalkynyl ligand. This resonance is found at 85.9 ppm, shifted 32.6 ppm to lower field in comparison with that of **6**, whereas the C−P coupling constant (17.5 Hz) is 5.5 Hz smaller than that in **6**. The phosphine ligand in the ^{31}P{^{1}H} NMR spectrum gives rise to a singlet at 4.7 ppm.

In agreement with the presence of the allenylidene ligand in **8**, the IR spectrum in Nujol of this compound shows the characteristic ν(C=C=C) band for this type of ligand at 1896 cm^{-1}, and the ^{13}C{^{1}H} NMR spectrum contains a triplet at 255.4 ppm with a C−P coupling constant of 13.8 Hz, which was assigned to the C_α atom, and two singlets at 229.8 and 148.4 ppm, corresponding to the C_β and C_γ atoms, respectively. The chemical shift of the resonance corresponding to the C_α atom and the frequency observed for the ν(C=C=C) band lie between those found for the complexes Os(η^5-C_5H_5)Cl(C=C=CPh_2)(P^iPr_3) (238.5 ppm and 1874 cm^{-1})[7] and [Ru(η^5-C_5Me_5)(C=C=CPh_2)(PEt_3)$_2$]$^+$ (293.1 ppm and 1907 cm^{-1}).[6b]

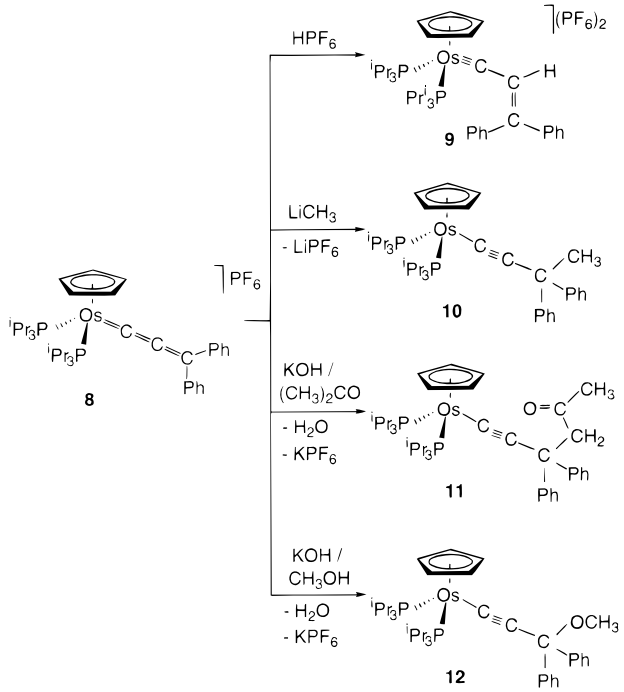
4. Reactivity of [Os(η^5-C_5H_5)(C=C=CPh_2)(P^iPr_3)$_2$]-PF_6. The investigations aimed at elucidating the reactivity of the allenylidene complex **8** are summarized in Scheme 6. This complex shows not only spectroscopic properties intermediate between the neutral osmium compound Os(η^5-C_5H_5)Cl(C=C=CPh_2)(P^iPr_3) and the cationic ruthenium derivative [Ru(η^5-C_5Me_5)(C=C=CPh_2)(PEt_3)$_2$]$^+$ but also a chemical behavior intermediate between those previously mentioned for the nucleophilic and γ-electrophilic diarylallenylidene complexes. Thus, the C_3-chain of **8** shows nucleophilic character in the presence of strongly electrophilic reagents and γ-electrophilic character in the presence of strong nucleophiles, while it is inert toward water, alcohols, and amines.

In agreement with the neutral osmium compound Os(η^5-C_5H_5)Cl(C=C=CPh_2)(P^iPr_3), the C_β atom of the C_3-chain of **8** adds the proton of HPF_6. The addition of 1 equiv of this acid to acetone solutions of **8** leads to the dicationic carbyne derivative [Os(η^5-C_5H_5)(CCH=CPh_2)-

(27) Werner, H.; Flügel, R.; Windmüller, B.; Michenfelder, A.; Wolf, J. *Organometallics* **1995**, *14*, 612.

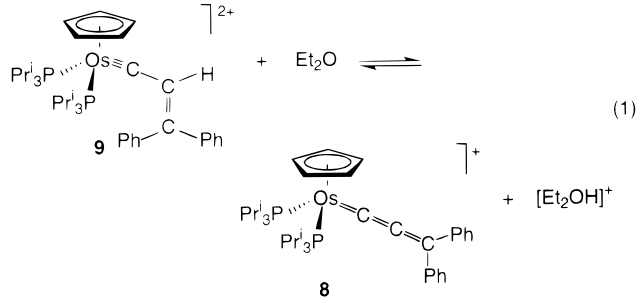
(28) (a) Berke, H.; Huttner, G.; Von Seyerl, J. *Z. Naturforsch.* **1981**, *36B*, 1277. (b) Edwards, A. J.; Esteruelas, M. A.; Lahoz, F. J.; Modrego, J.; Oro, L. A.; Schrickel, J. *Organometallics* **1996**, *15*, 3556.

Scheme 6



$(P^iPr_3)_2](PF_6)_2$ (**9**), which was isolated as a red solid in 86% yield.

The CH= hydrogen atom of the alkenylcarbyne group is relatively acid. When complex **9** is stirred in diethyl ether at room temperature, the C_β atom of the ligand is deprotonated until the equilibrium shown in eq 1 is reached.



(1)

In contrast to $Os(\eta^5\text{-}C_5H_5)Cl(C{=}C{=}CPh_2)(P^iPr_3)$ but in agreement with the γ-electrophilic diarylallenylidene compounds, complex **8** reacts with CH_3Li and acetone and methanol solutions of KOH to give the alkynyl derivatives $Os(\eta^5\text{-}C_5H_5)\{C{\equiv}CC(R)Ph_2\}(P^iPr_3)_2$ (R = CH_3 (**10**), $CH_2C(O)CH_3$ (**11**), OCH_3 (**12**)), as a result of the regioselective addition of the nucleophiles R to the C_γ atom of the allenylidene group. These compounds were isolated as yellow solids in 70−79% yield.

Complex **9** was characterized by MS, elemental analysis, IR and ^1H and $^{31}P\{^1H\}$ NMR spectroscopy, and an X-ray crystallographic study.[29] A view of the molecular geometry of this compound is shown in Figure 2. Selected bond distances and angles are listed in Table 2. The geometry around the osmium center of **9** is close to octahedral, with the cyclopentadienyl ligand occupying three sites of a face. The P−Os−C(carbyne) angles are close to 90°, while the P−Os−P angle (105.12(8)°) strongly deviates from the ideal value of 90°. This is due to the large steric hindrance experienced by the triisopropylphosphine groups, as a consequence of their large cone angle (160°).[30] Transition metal complexes containing bulky phosphine ligands mutually *cis* disposed are rare. P−M−P angles similar to that of **9** have been previously found in the octahedral compounds $[Os(\kappa^2\text{-}O_2CCH_3)\{C(Me)C(OH)Me_2\}(PiPr_3)_2]BF_2$ (103.71(6)°) and $Os\{\eta^2\text{-}CH_2{=}CHC(Ph)_2O\}(k^2\text{-}O_2CCH_3)(PiPr_3)_2$ (106.72(4)°),[31] in the square-planar derivatives $Rh(acac)(PCy_3)_2$ (105.63(4)°),[32] $Rh(\kappa^2\text{-}O_2CCH_3)(P^iPr_3)_2$ (106.00(4)°),[33] and $[Ir(TFB)(P^iPr_3)_2]BF_4$ (TFB = tetrafluorobenzobarrelene; 102.7(1)°),[34] and in the five-coordinate complex $[Rh(acac)\{(E)\text{-}CH{=}CHCy\}(PCy_3)_2]BF_4$ (105.3(1)°).[32]

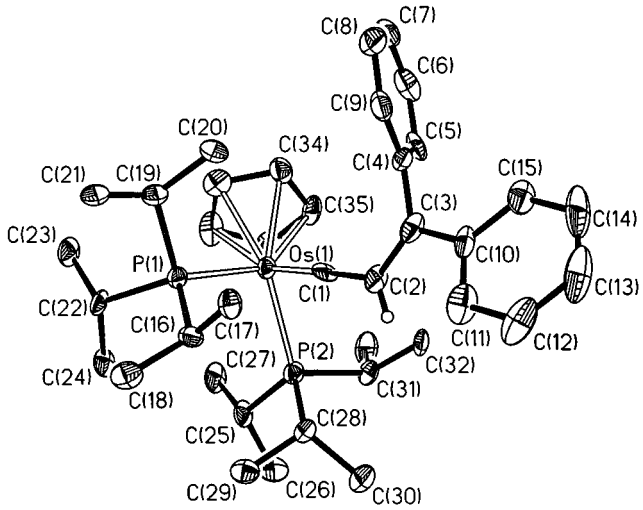


Figure 2. Molecular diagram of the cation of **9**, $[Os(\eta^5\text{-}C_5H_5)(CCH{=}CPh_2)(P^iPr_3)_2]^{2+}$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for the Complex $[Os(\eta^5\text{-}C_5H_5)(CCH{=}Ph_2)(P^iPr_3)_2](PF_6)_2$ (9)

Os(1)−P(1)	2.420(2)	Os(1)−C(1)	1.764(8)
Os(1)−P(2)	2.436(2)	C(1)−C(2)	1.410(12)
Os(1)−C(34)	2.265(9)	C(2)−C(3)	1.366(13)
Os(1)−C(35)	2.283(9)	C(3)−C(4)	1.469(12)
Os(1)−C(36)	2.344(9)	C(3)−C(10)	1.478(12)
Os(1)−C(37)	2.370(9)		
Os(1)−C(38)	2.296(9)		
P(1)−Os(1)−P(2)	105.12(8)	Os(1)−C(1)−C(2)	176.5(7)
P(1)−Os(1)−G(1)[a]	117.2(3)	C(1)−C(2)−C(3)	126.5(9)
P(1)−Os(1)−C(1)	91.9(3)	C(2)−C(3)−C(4)	121.5(9)
P(2)−Os(1)−G(1)[a]	119.2(3)	C(2)−C(3)−C(10)	119.9(8)
P(2)−Os(1)−C(1)	87.8(3)		
G(1)[a]−Os(1)−C(1)	129.3(4)		

[a] G(1) is the midpoint of the C(34)−C(38) Cp ligand.

(29) The low solubility of the complex in acetone-d_6, dichloromethane-d_2, and chloroform-*d* precluded the recording of the $^{13}C\{^1H\}$ NMR spectrum.

(30) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.
(31) Buil, M. L.; Esteruelas, M. A.; García-Yebra, C.; Gutiérrez-Puebla, E.; Oliván, M. *Organometallics*, in press.
(32) Esteruelas M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A.; Rodríguez, L.; Steinert, P.; Werner, H. *Organometallics* **1996**, *15*, 3436.
(33) Werner, H.; Schäfer, M.; Nürnberg, O.; Wolf, J. *J. Chem. Ber.* **1994**, *127*, 27.
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Table 3. Analysis of the Electronic Structures of the Complexes Os(η^5-C_5H_5)Cl(C=C=CH_2)(PH_3) (13), [Os(η^5-C_5H_5)(C=C=CH_2)(PH_3)$_2$]$^+$ (14), and [Os(η^5-C_5H_5)(C=C=CH_2)(CO)(PH_3)]$^+$ (15)'

complex			
	Charge Transfers (e)		
	$[Os]_{HOMO}\rightarrow[C=C=CH_2]_{LUMO}$	$[C=C=CH_2]_{HOMO}\rightarrow[Os]_{LUMO}$	total
13	0.91	0.40	0.44
14	0.87	0.41	0.41
15	0.76	0.41	0.26
	Distribution of the LUMO on the C Atoms of the Allenylidene (%)		
	C_α	C_β	C_γ
13	24	5	30
14	24	5	31
15	28	3	33
	Distribution of the HOMO on the C Atoms of the Allenylidene (%)		
	C_α	C_β	C_γ
13	4	22	0
14	4	25	0
15	5	23	0
	Net Charges on the C Atoms of the Allenylidene (e)		
	C_α	C_β	C_γ
13	−0.46	−0.07	−0.17
14	−0.41	−0.10	−0.15
15	−0.33	−0.08	−0.09

The most conspicuous feature of the structure is the very short Os(1)−C(1) bond length of 1.764(8) Å, which is fully consistent with an Os(1)−C(1) triple bond formulation. Similarly to other carbyne−metal compounds,[35] a slight bending in the Os(1)−C(1)−C(2) moiety is also present (Os(1)−C(1)−C(2) = 176.5(7)°).

The alkenylcarbyne proposal is supported by the bond lengths and angles within the η^1-carbon donor ligand; for example, C(1) and C(2) are separated by 1.410(12) Å and C(2) and C(3) by 1.366(13) Å, and the angles around C(2) and C(3) are in the range 119.9(8)−126.5(9)°.

In agreement with the structure shown in Figure 2, the ^{1}H NMR spectrum of **9** in acetone-d_6 shows a singlet at 6.66 ppm, corresponding to the =CH proton, and the ^{31}P{^{1}H} NMR spectrum contains a singlet at 21.6 ppm.

Complexes **10**−**12** were characterized by MS, elemental analysis, and IR and ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopy. The IR spectrum of **10** in Nujol shows the ν(C≡C) band at 2080 cm^{-1}. In the ^{1}H NMR spectrum in benzene-d_6, the most noticeable resonance is a singlet at 2.06 ppm, corresponding to the methyl group of the alkynyl ligand. The ^{13}C{^{1}H} NMR spectrum shows the resonance corresponding to the OsC_α atom as a triplet, at 75.9 ppm, with a C−P coupling constant of 6.5 Hz, and that due to the C_β atom of the alkynyl group as a singlet at 108.5 ppm. The ^{31}P{^{1}H} NMR spectrum contains a singlet at 4.6 ppm. In agreement with the presence of the functionalized alkynyl ligand of **11**, the IR spectrum of this compound in Nujol shows ν(C≡C) and ν(C=O) bands at 2077 and 1705 cm^{-1}, respectively. In the ^{1}H NMR spectrum, the presence of the ligand in the complex is supported by two singlets at 3.42 and 1.96 ppm, with a 2:3 intensity ratio, which were assigned to the $-CH_2-$ and $-CH_3$ protons. In the ^{13}C{^{1}H} NMR spectrum, the C_α atom of the alkynyl ligand appears as a triplet at 80.1 ppm with a C−P coupling constant of 7.0 Hz, whereas the C_β atom gives rise to a singlet at 106.7 ppm. The ^{31}P{^{1}H} NMR spectrum shows a singlet at 4.6 ppm. In the IR spectrum of **12** in Nujol, the ν(C≡C) band appears at 2071 cm^{-1}. The ^{1}H NMR spectrum in chloroform-*d* shows a singlet at 3.25 ppm, corresponding to the protons of the $-OCH_3$ group. The ^{13}C{^{1}H} NMR spectrum agrees well with those of **10** and **11**, the resonance due to the C_α atom of the alkynyl group is observed as a triplet at 85.9 ppm with a C−P coupling constant of 17.2 Hz, while that corresponding to the C_β atom appears as a singlet at 104.4 ppm. The ^{31}P{^{1}H} NMR spectrum of **12** shows a singlet at 4.9 ppm.

5. Analysis of the Electronic Structures of Os(η^5-C_5H_5)Cl(C=C=CPh_2)(P^iPr_3) and [Os(η^5-C_5H_5)(C=C=CPh_2)L(P^iPr_3)]$^+$ (L = P^iPr_3, CO). To understand the chemical behavior of **8**, we have carried out the analysis of the electronic structures of Os(η^5-C_5H_5)Cl(C=C=CPh_2)(P^iPr_3), **8**, and [Os(η^5-C_5H_5)(C=C=CPh_2)(CO)(P^iPr_3)]$^+$. Although the carbonyl derivative has not been isolated until now, the behavior of the unit [Os(η^5-C_5H_5)(CO)(P^iPr_3)]$^+$, in the presence of terminal alkynes and alkynols,[18a] is similar to the behavior of the metallic fragments which give rise to γ-electrophilic diarylallenylidene compounds. So, we assume that complex Os(η^5-C_5H_5)(C=C=CPh_2)(CO)(P^iPr_3)]$^+$ would be a new example of γ-electrophilic diarylallenylidene derivative. The study has been performed using EHT-MO calculations[36] on the model compounds Os(η^5-C_5H_5)Cl(C=C=CH_2)(PH_3) (**13**), [Os(η^5-C_5H_5)(C=C=CH_2)(PH_3)$_2$]$^+$ (**14**), and [Os(η^5-C_5H_5)(C=C=CH_2)(CO)(PH_3)]$^+$ (**15**), and the results are collected in Table 3.

The orbital scheme of the compounds is related to the interaction of the electronic structures of the corresponding metallic fragments and that of the allenylidene ligand, which are well known.[37] In agreement with previous studies of this type,[10b,13b,28] the allenylidene ligand coordinates to the metal centers as a σ-donor and π-acceptor ligand. The σ-donor component of the bonds, which takes place between the HOMO of the allenylidene and the LUMO orbitals of the metallic fragments, produces charge transfers of about 0.4 e from

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the ligand to the metallic fragments, whereas the interactions between the HOMO orbitals of the metallic fragments and the LUMO of the allenylidene—the π-acceptor component of the metal−allenylidene bonds—lead to charge transfers from the metallic fragments to the organic ligand of 0.91 (**13**), 0.87 (**14**), and 0.76 (**15**) e. So, from the point of view of the charge, the π-acceptor component of the bonds is stronger than the σ-donor one. The resulting bonds, including all contributions, produce total transfers from the metallic fragments to the allenylidene of 0.44 (**13**), 0.41 (**14**), and 0.26 (**15**) e.

The Mulliken population analysis in the three cases indicates that about 60% of the LUMO of the complexes is located on the allenylidene ligand, mainly on the C_α and C_γ atoms, whereas about 25% of the HOMO is located on the C_β atom. Furthermore, the net charge on C_α atoms is significantly higher than those on the C_β and C_γ atoms.

According to the results collected in Table 3, the charge transferred from the metallic fragment $[Os(\eta^5\text{-}C_5H_5)(PH_3)_2]^+$ to the allenylidene ligand is intermediate between those transferred by the metallic fragments of **13** and **15**. This agrees well with the chemical behavior of **8**, which is also intermediate between those of the nucleophilic and γ-electrophilic diarylallenylidene compounds.

In addition, it should be noted that the value of the total charge transfer for **14** is about 7% smaller than that for **13** and about 57% higher than that for **15**. This agrees well with the formation of **9** by protonation of **8** and suggests that the behavior of **8** as γ-electrophile is mainly due to its cationic nature.

The alkenyl group of **9** can be deprotonated by diethyl ether (eq 1). However, under the same conditions, the related compound $[Os(\eta^5\text{-}C_5H_5)Cl(CCH{=}CPh_2)(P^iPr_3)]^+$ is stable. To explain this difference, we have carried out ab initio calculations[38] on the model complexes **13**, **14**, $[Os(\eta^5\text{-}C_5H_5)Cl(CCH{=}CH_2)(PH_3)]^+$ (**16**), and $[Os(\eta^5\text{-}C_5H_5)(CCH{=}CH_2)(PH_3)_2]^{2+}$ (**17**). For comparative purpose, calculations on **15** and $[Os(\eta^5\text{-}C_5H_5)(CCH{=}CH_2)(CO)(PH_3)]^{2+}$ (**18**) were also performed. Figure 3 shows the optimized structures at the MP2 level of the six model species.

The structure of the carbyne compounds **16**−**18** are similar. The structural parameters within the $OsCCH{=}CH_2$ unit of **17** are in excellent agreement with those obtained by X-ray diffraction analysis for the related $OsCCH{=}CPh_2$ unit of **9**. The main difference between the structures of **17** and **9** is the P−Os−P angle. The calculated value (94.9°) is significantly lower than that obtained from the X-ray diffraction analysis (105.12(8)°). This indicates that, in fact, the deviation observed from the ideal value of 90° in **9** is mainly due to the large steric hindrance experienced by the triisopropylphosphine groups.

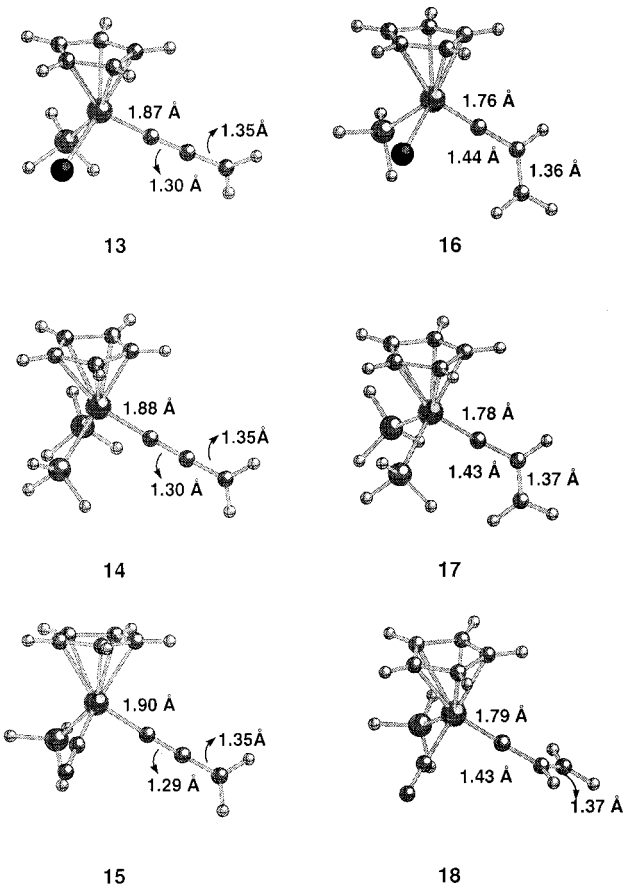

Figure 3. Optimized structures of $Os(\eta^5\text{-}C_5H_5)Cl(C{=}C{=}CH_2)(PH_3)$ (**13**), $[Os(\eta^5\text{-}C_5H_5)(C{=}C{=}CH_2)L(PH_3)]^+$ (L = PH_3 (**14**), CO (**15**)), $[Os(\eta^5\text{-}C_5H_5)Cl(CCH{=}CH_2)(PH_3)]^+$ (**16**), and $[Os(\eta^5\text{-}C_5H_5)(CCH{=}CH_2)L(PH_3)]^{2+}$ (L = PH_3 (**17**), CO (**18**)).

The structures of the allenylidene complexes **13**−**15** are also similar, and the structural parameters of the $OsC{=}C{=}CPh_2$ unit of **13** are in excellent agreement with those obtained by X-ray diffraction analysis for the related $OsC{=}C{=}CPh_2$ unit of $Os(\eta^5\text{-}C_5H_5)Cl(C{=}C{=}CPh_2)(P^iPr_3)$.[7]

For the three metallic fragments, $Os(\eta^5\text{-}C_5H_5)Cl(PH_3)$, $[Os(\eta^5\text{-}C_5H_5)(PH_3)_2]^+$, and $[Os(\eta^5\text{-}C_5H_5)(CO)(PH_3)]^+$, the addition of a naked proton at the allenylidene to give the corresponding carbyne derivatives produces a stabilization of the system. The energy of stabilization by protonation is 267 kcal·mol^{-1} for $Os(\eta^5\text{-}C_5H_5)Cl(PH_3)$, 180 kcal·mol^{-1} for $[Os(\eta^5\text{-}C_5H_5)(PH_3)_2]^+$, and 157 kcal·mol^{-1} for $[Os(\eta^5\text{-}C_5H_5)(CO)(PH_3)]^+$. The difference between the energy of stabilization by protonation obtained for the neutral compound **13** and the cationic complex **14** (87 kcal·mol^{-1}) can explain why complex **9** is deprotonated by diethyl ether, while the carbyne $[Os(\eta^5\text{-}C_5H_5)Cl(CCH{=}CPh_2)(P^iPr_3)]^+$ is inert under the same conditions.

The energy of stabilization by protonation obtained for **15** is 23 kcal·mol^{-1} lower than that for **14**. This, together with the fact that complex **9** is unstable in the presence of very weak bases, can also explain why the γ-electrophilic diarylallenylidene complexes do not react with acids to form carbyne derivatives, under the usual experimental conditions.

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Concluding Remarks

This study has revealed that the combined treatment of the complex $Os(\eta^5\text{-}C_5H_5)Cl(P^iPr_3)_2$ with alkynes, such as phenylacetylene, cyclohexylacetylene, 2-phenyl-3-butyn-2-ol, or 1,1-diphenyl-2-propyn-1-ol and $TlPF_6$ leads to $[OsH(\eta^5\text{-}C_5H_5)(C{\equiv}CR)(P^iPr_3)_2]PF_6$, as a result of the intermolecular H−C(sp) oxidative addition of the alkynes to the metallic fragment $[Os(\eta^5\text{-}C_5H_5)(P^iPr_3)_2]^+$. These complexes are the first examples of hydride−alkynyl−osmium(IV) derivatives and, in contrast to related hydride−alkynyl−ruthenium(IV) compounds, do not rearrange to either vinylidene or π-alkyne isomers in the solid state or in solution.

Complex $[OsH(\eta^5\text{-}C_5H_5)\{C{\equiv}CC(OH)Ph_2\}(P^iPr_3)_2]PF_6$ evolves into the allenylidene derivative $[Os(\eta^5\text{-}C_5H_5)\{C{=}C{=}CPh_2\}(P^iPr_3)_2]PF_6$ in the presence of traces of acid. The reactivity of this allenylidene is a new case in the chemistry of the diarylallenylidene complexes of the iron triad. The behavior of the unsaturated C_3-chain of this ligand is intermediate between those observed for nucleophilic and γ-electrophilic diarylallenylidene derivatives.

In agreement with the nucleophilic diarylallenylidene compounds, complex $[Os(\eta^5\text{-}C_5H_5)(C{=}C{=}CPh_2)(P^iPr_3)_2]PF_6$ reacts with HPF_6 to give $[Os(\eta^5\text{-}C_5H_5)(CCH{=}CPh_2)(P^iPr_3)_2](PF_6)_2$. However, in contrast to nucleophilic diarylallenylidene compounds, but in agreement with the γ-electrophiles, it undergoes the regioselective addition of nucleophilic reagents at the Cγ atom of the allenylidene to give functionalized-alkynyl derivatives.

EHT-MO calculations indicate that the electron density on the C_3-chain of the allenylidene ligand of $[Os(\eta^5\text{-}C_5H_5)(C{=}C{=}CPh_2)(P^iPr_3)_2]^+$ is similar to that on the C_3-chain of the diarylallenylidene ligands of the nucleophilic complexes of this type, while it is significantly higher than that on the allenylidene ligands of the γ-electrophiles. This suggests that the behavior of $[Os(\eta^5\text{-}C_5H_5)(C{=}C{=}CPh_2)(P^iPr_3)_2]^+$ as nucleophile is a consequence of the high electron density of its allenylidene ligand, while the behavior as γ-electrophile is due to the cationic nature of the complex.

Although complex $[Os(\eta^5\text{-}C_5H_5)(C{=}C{=}CPh_2)(P^iPr_3)_2]^+$ is protonated like the nucleophilic diarylallenylidene compounds, ab initio calculations on the model species $Os(\eta^5\text{-}C_5H_5)Cl(C{=}C{=}CH_2)(PH_3)$, $[Os(\eta^5\text{-}C_5H_5)(C{=}C{=}CH_2)(PH_3)_2]^+$, $[Os(\eta^5\text{-}C_5H_5)Cl(CCH{=}CH_2)(PH_3)]^+$, and $[Os(\eta^5\text{-}C_5H_5)(CCH{=}CH_2)(PH_3)_2]^{2+}$ indicate that energy of stabilization by protonation with a naked proton of $Os(\eta^5\text{-}C_5H_5)Cl(C{=}C{=}CH_2)(PH_3)$ is 87 kcal·mol^{-1} higher than that corresponding to the protonation of $[Os(\eta^5\text{-}C_5H_5)(C{=}C{=}CH_2)(PH_3)_2]^+$. This agrees well with experimental observations showing that the =CH hydrogen atom of the carbyne ligand of $[Os(\eta^5\text{-}C_5H_5)(CCH{=}CPh_2)(P^iPr_3)_2]^{2+}$ is fairly acidic and can be deprotonated by weak bases such as diethyl ether, while the complex $[Os(\eta^5\text{-}C_5H_5)Cl(CCH{=}CPh_2)(P^iPr_3)]^+$ is stable under the same conditions.

In conclusion, the unit $[Os(\eta^5\text{-}C_5H_5)(P^iPr_3)_2]^+$ is a useful metallic fragment to stabilize novel hydride−alkynyl, allenylidene, and carbyne compounds, which have a chemical behavior different from those observed for the previously reported compounds of the iron triad containing these functional groups. In particular, the complex $[Os(\eta^5\text{-}C_5H_5)(C{=}C{=}CPh_2)(P^iPr_3)_2]PF_6$ should be mentioned, which shows an amphoteric behavior between nucleophile and γ-electrophile and, from the reactivity point of view, is the first example of a new class of diarylallenylidene derivative within the iron triad.

Experimental Section

All reactions were carried out with exclusion of air using standard Schlenk techniques. Solvents were dried by known procedures and distilled under argon prior to use. The complex $Os(\eta^5\text{-}C_5H_5)Cl(P^iPr_3)_2$ (**1**) was prepared according to the literature method.[16]

In the NMR spectra, chemical shifts are expressed in ppm downfield from Me_4Si (^1H and ^{13}C) and 85% H_3PO_4 (^{31}P).

Preparation of $[OsH(\eta^5\text{-}C_5H_5)(C{\equiv}CPh)(P^iPr_3)_2]PF_6$ (2). A suspension of $TlPF_6$ (79 mg, 0.23 mmol) in 1 mL of acetone was treated with a solution of phenylacetylene (38 μL, 0.35 mmol) in 15 mL of dichloromethane. After the mixture was stirred for 10 min at room temperature, in the absence of light, it was treated with **1** (138 mg, 0.23 mmol). The resulting suspension was stirred for 2 min at room temperature and filtered through Kieselguhr. The solvent was removed in vacuo, and addition of diethyl ether to the residue afforded a white solid, which was washed twice with 5 mL of diethyl ether and twice with 5 mL of a mixture of diethyl ether/methanol (2:1). Yield: 115 mg, 61%. IR (Nujol): ν(C≡C) 2112, $\nu(PF_6)$ 840 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 293 K): δ 7.20−7.03 (m, 5 H, Ph), 5.75 (s, 5 H, Cp), 2.55 (m, 6 H, PCH), 1.38 (dvt, 18 H, J(HH) = 7.1 Hz, N = 14.4 Hz, PCMe), 1.34 (dvt, 18 H, J(HH) = 7.1 Hz, N = 13.8 Hz, PCMe), −13.21 (t, 1 H, J(PH) = 35.7 Hz, OsH). $^{31}P\{^1H\}$ NMR (121.42 MHz, $CDCl_3$, 293 K): δ 6.7 (s, d under off-resonance conditions), −144.8 (sept, J(PF) = 714 Hz, PF_6). $^{13}C\{^1H\}$ NMR (75.42 MHz, $CDCl_3$, 293 K, plus DEPT): δ 130.8 (s, Ph), 128.4 (s, Ph), 126.6 (t, J(PC) = 2.1 Hz, *ipso*-Ph), 126.4 (s, Ph), 118.0 (t, J(PC) = 2.5 Hz, ≡*C*Ph), 85.9 (s, Cp), 57.2 (t, J(PC) = 24.7 Hz, OsC≡), 29.8 (second-order system, PCH), 20.4, 20.3 (both s, PC*Me*). Anal. Calcd for $C_{31}H_{53}F_6OsP_3$ (%): C, 45.25; H, 6.49. Found: C, 44.99; H, 6.13. MS (FAB$^+$): *m/e* 679 (M$^+$).

Preparation of $[OsH(\eta^5\text{-}C_5H_5)(C{\equiv}CCy)(P^iPr_3)_2]PF_6$ (3). A suspension of $TlPF_6$ (141 mg, 0.40 mmol) in 1 mL of acetone was treated with a solution of cyclohexylacetylene (100 μL, 0.76 mmol) in 15 mL of dichloromethane. After the mixture was stirred for 10 min at room temperature, in the absence of light, it was treated with **1** (244 mg, 0.40 mmol). The resulting suspension was stirred for 2 min at room temperature and concentrated to dryness. The residue was extracted with 10 mL of dichloromethane, the suspension was filtered through Kieselguhr, and the solution was concentrated to dryness. The white solid obtained was washed twice with 3 mL of a mixture of diethyl ether/methanol (5:1). Yield: 171.6 mg, 53%. IR (Nujol): ν(C≡C) 2108, $\nu(PF_6)$ 840 cm^{-1}. ^1H NMR (300 MHz, CD_2Cl_2, 293 K): δ 5.63 (s, 5 H, Cp), 2.54 (m, 6 H, PCH), 1.71 (br, 2 H, Cy), 1.64 (br, 2 H, Cy), 1.52 (br, 2 H, Cy), 1.36−1.18 (m, 41 H, PCMe and Cy), −13.50 (t, 1 H, J(PH) = 36.3 Hz, OsH). $^{31}P\{^1H\}$ NMR (121.42 MHz, CD_2Cl_2, 293 K): δ 5.6 (s, d under off-resonance conditions), −144.8 (sept, J(PF) = 714 Hz, PF_6). $^{13}C\{^1H\}$ NMR (75.42 MHz, $CDCl_3$, 293 K): δ 121.4 (t, J(PC) = 2.5 Hz, ≡*C*Cy), 85.5 (s, Cp), 36.4 (t, J(PC) = 24.9 Hz, OsC≡), 33.9, 32.3 (both s, Cy), 29.7 (second-order system, PCH), 25.8, 25.4 (both s, Cy), 20.4, 20.3 (both s, PC*Me*). (Anal. Calcd for $C_{31}H_{59}F_6OsP_3$ (%): C, 44.92; H, 7.17. Found: C, 44.78; H, 7.00. MS (FAB$^+$): *m/e* 685 (M$^+$).

Preparation of $[OsH(\eta^5\text{-}C_5H_5)\{C{\equiv}CC(OH)MePh\}(P^iPr_3)_2]PF_6$ (4). A suspension of $TlPF_6$ (89 mg, 0.25 mmol) in 1 mL of acetone was treated with a solution of 2-phenyl-3-butyn-2-ol (56 mg, 0.38 mmol) in 15 mL of dichloromethane. After the mixture was stirred for 10 min at room temperature, in the absence of light, it was treated with **1** (155 mg, 0.25 mmol).

After the mixture was stirred for 2 min at room temperature, it was filtered through Kieselguhr and concentrated to dryness. The residue was dissolved in 3 mL of methanol, and 15 mL of diethyl ether was added slowly. The mixture was kept for 1 day at −40 °C, and the white crystals obtained were washed with 1 mL of diethyl ether. Yield: 126 mg, 58%. IR (Nujol): ν(OH) 3605, ν(C≡C) 2113, ν(PF_6) 840 cm^{-1}. ^1H NMR (300 MHz, CD_2Cl_2, 293 K): δ 7.52−7.26 (m, 5 H, Ph), 5.68 (s, 5 H, Cp), 2.48 (m, 6 H, PCH), 2.16 (s, 1 H, OH), 1.74 (s, 3 H, Me), 1.28 (dvt, 18 H, J(HH) = 6.9 Hz, N = 13.8 Hz, PCMe), 1.27 (dvt, 18 H, J(HH) = 7.1 Hz, N = 14.0 Hz, PCMe), −13.40 (dd, 1 H, both J(PH) = 35.7 Hz, Os−H). $^{31}P\{^1H\}$ NMR (121.42 MHz, CD_2Cl_2, 293 K): δ 7.0 (part A of AB system, J = 23.5 Hz), 6.6 (part B of AB system, J = 23.5 Hz), d of AB system under off-resonance conditions, −144.8 (sept, J(PF) = 714 Hz, PF_6). $^{13}C\{^1H\}$ NMR (75.42 MHz, CD_2Cl_2, 293 K): δ 147.4 (s, *ipso*-Ph), 128.6, 127.5, 125.1 (all s, Ph), 120.7 (dd, both J(PC) = 2.5 Hz, ≡*C*C), 85.9 (s, Cp), 70.3 (s, COH), 48.1 (dd, both J(PC) = 23.7 Hz, OsC≡), 32.3 (s, Me), 30.2 (d, J(PC) = 28.1 Hz, PCH), 20.6 (s, PC*Me*), 20.5 (d, J(PC) = 2.3 Hz, PCMe). Anal. Calcd for $C_{33}H_{57}F_6OOsP_3$ (%): C, 45.74; H, 6.63. Found: C, 45.82; H, 6.73.

Preparation of [OsH(η5-C5H5){C≡CC(Ph)=CH2}(PiPr3)2]-PF6 (5). A solution of **4** (132 mg, 0.15 mmol) in 15 mL of chloroform was stirred at room temperature for 6 h and then evaporated to dryness. The residue was washed twice with 3 mL of diethyl ether and dried in vacuo to yield a white solid. Yield: 109 mg, 86%. IR (Nujol): ν(C≡C) 2113, ν(Os−H), 2035, ν(PF_6) 840 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 293 K): δ 7.47−7.20 (m, 5 H, Ph), 5.74 (s, 5 H, Cp), 5.38 (s, 1 H, =CH_2), 5.00 (s, 1 H, =CH_2), 2.52 (m, 6 H, PCH), 1.29 (m, PCMe), −13.30 (t, 1 H, J(PH) = 35.6 Hz, OsH). $^{31}P\{^1H\}$ NMR (121.42 MHz, $CDCl_3$, 293 K): δ 6.9 (s, d on off-resonance conditions, −144.8 (sept, J(PF) = 714 Hz, PF_6). $^{13}C\{^1H\}$ NMR (75.42 MHz, $CDCl_3$, 293 K): δ 139.9 (s, *ipso*-Ph), 133.1 (t, J(PC) = 2.0 Hz, =*C*Ph), 128.4, 127.9, 126.1 (all s, Ph), 118.0 (t, J(PC) = 3.1 Hz, ≡*C*C), 117.3 (s, =CH_2), 85.8 (s, Cp), 59.2 (t, J(PC) = 24.3 Hz, OsC≡), 29.7 (second-order system, PCH), 20.4, 20.2 (both s, PC*Me*). Anal. Calcd for $C_{33}H_{55}F_6OsP_3$ (%): C, 46.69; H, 6.53. Found: C, 47.00; H, 6.61.

Preparation of [OsH(η5-C5H5){C≡CC(OH)Ph2}(PiPr3)2]-PF6 (6). A suspension of $TlPF_6$ (88 mg, 0.25 mmol) in 1 mL of acetone was treated with a solution of 1,1-diphenyl-2-propyn-1-ol (79 mg, 0.38 mmol) in 15 mL of dichloromethane. After the mixture was stirred for 10 min at room temperature, in the absence of light, it was treated with **1** (150 mg, 0.25 mmol). The resulting suspension was stirred for 2 min at room temperature and filtered through Kieselguhr. The solvent was removed in vacuo, and addition of diethyl ether to the residue afforded a white solid, which was washed twice with 3 mL of diethyl ether and twice with 3 mL of a mixture of diethyl ether/methanol (4:1) to afford a white solid. Yield: 170 mg, 76%. IR (Nujol): ν(OH) 3543, ν(C≡C) 2116, ν(PF_6) 840 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 293 K): δ 7.39−7.18 (m, 10 H, Ph), 5.73 (s, 5 H, Cp), 2.36 (m, 6 H, PCH), 2.30 (s, 1 H, OH), 1.18 (dvt, 18 H, J(HH) = 6.9 Hz, N = 13.8 Hz, PCMe), 1.13 (dvt, 18 H, J(HH) = 6.9 Hz, N = 14.4 Hz, PCMe), −13.40 (t, 1 H, J(PH) = 35.7 Hz, OsH). $^{31}P\{^1H\}$ NMR (121.42 MHz, $CDCl_3$, 293 K): δ 7.2 (s, d under off-resonance conditions), −144.8 (sept, J(PF) = 714 Hz, PF_6). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K): δ 147.0 (s, *ipso*-Ph), 128.5, 127.9, 126.8 (all s, Ph), 118.4 (s, ≡*C*C), 85.9 (s, Cp), 75.6 (s, COH), 53.3 (t, J(PC) = 23 Hz, OsC≡), 30.2 (second-order system, PCH), 20.6 (s, PC*Me*). Anal. Calcd for $C_{38}H_{59}F_6OOsP_3$ (%): C, 49.15; H, 6.40. Found: C, 48.89; H, 6.15. MS (FAB^+): *m/e* 785 (M^+).

Preparation of Os(η5-C5H5){C≡CC(OH)Ph2}(PiPr3)2 (7). A solution of **6** (115 mg, 0.12 mmol) in 15 mL of methanol was treated with an excess of KOH (18 mg, 0.32 mmol). After the mixture was stirred for 30 min at room temperature, the resultant solution was evaporated to dryness. The residue was extracted with 10 mL of toluene, and the mixture was filtered through Kieselguhr. The solution was concentrated to dryness, and the white solid obtained was washed with 1 mL of pentane and dried in vacuo. Yield: 81 mg, 73%. IR (Nujol): ν(OH) 3532, ν(C≡C) 2115 cm^{-1}. ^1H NMR (300 MHz, C_6D_6, 293 K): δ 8.00 (m, 4 H, *o*-Ph), 7.25−7.10 (m, 6 H, *p*- and *m*-Ph), 4.75 (s, 5 H, Cp), 2.62 (s, 1 H, OH), 2.18 (m, 6 H, PCH), 1.05 (m, 36 H, PCMe). $^{31}P\{^1H\}$ NMR (121.42 MHz, C_6D_6, 293 K): δ 4.7 (s). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K): δ 150.3 (s, *ipso*-Ph), 127.6, 127.5, 126.2 (all s, Ph), 108.7 (s, ≡*C*C), 85.9 (t, J(PC) = 17.5 Hz, OsC≡), 76.0 (s, COH), 74.9 (t, J(PC) = 1.2 Hz, Cp), 30.5 (second-order system, PCH), 21.2, 20.6 (both s, PC*Me*). Anal. Calcd for $C_{38}H_{58}ClOOsP_2$ (%): C, 49.2; H, 6.30. Found: C, 48.96; H, 6.18.

Preparation of [Os(η5-C5H5)(C=C=CPh2)(PiPr3)2]PF6 (8). A solution of **6** (120 mg, 0.13 mmol) in 15 mL of chloroform was heated at reflux temperature for 6 h. The solvent was removed in vacuo, and the residue was washed twice with 3 mL of diethyl ether to afford a green solid. Yield: 105 mg, 89%. IR (Nujol): ν(C=C=C) 1896, ν(PF_6) 840 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 293 K): δ 7.66−7.28 (m, 10 H, Ph), 5.78 (s, 5 H, Cp), 2.31 (m, 6 H, PCH), 1.15 (dd, 18 H, J(HH) = 6.9 Hz, J(PH) = 13.5 Hz, PCMe), 1.04 (dd, 18 H, J(HH) = 7.2 Hz, J(PH) = 13.8 Hz, PCMe). $^{31}P\{^1H\}$ NMR (121.42 MHz, $CDCl_3$, 293 K): δ 7.2 (s), −144.8 (sept, J(PF) = 714 Hz, PF_6). $^{13}C\{^1H\}$ NMR (75.42 MHz, $CDCl_3$, 293 K): δ 255.4 (t, J(PC) = 13.8 Hz, Os=C), 229.8 (s, =C=), 149.7 (s, *ipso*-Ph), 148.4 (s, =CPh_2), 129.9, 139.4, 127.8 (all s, Ph), 86.1 (s, Cp), 31.1 (second-order system, PCH), 20.5, 20.3 (both s, PC*Me*). Anal. Calcd for $C_{38}H_{57}F_6OsP_3$ (%): C, 50.12; H, 6.31. Found: C, 50.24; H, 6.29.

Reaction of Os(η5-C5H5){C≡CC(OH)Ph2}(PiPr3)2 with HPF6. A solution of **7** (8.2 mg, 0.01 mmol) in 0.5 mL of $CDCl_3$ was treated, in a NMR tube at room temperature, with HPF_6 (1.2 μL, 75% in water, 0.01 mmol). The color changed from colorless to green. ^1H and $^{31}P\{^1H\}$ NMR spectra recorded after 10 min showed quantitative formation of **8**.

Reaction of [OsH(η5-C5H5){C≡CC(OH)Ph2}(PiPr3)2]PF6 with HCl. A solution of **6** (12 mg, 0.01 mmol) in 0.5 mL of CD_2Cl_2 was treated, in a NMR tube at room temperature, with HCl (7 μL, 0.14 M in toluene, 0.001 mmol). The color changed from colorless to green. ^1H and $^{31}P\{^1H\}$ NMR spectra recorded after 10 min showed quantitative formation of **8**.

Preparation of [Os(η5-C5H5){CCH=CPh2}(PiPr3)2](PF6)2 (9). A solution of **8** (10 mg, 0.01 mmol) in 0.5 mL of acetone-d_6 in an NMR tube was treated with HPF_6 (1.2 μL, 75% in water, 0.01 mmol), and immediately the color turned from green to red. After 5 min at room temperature, the NMR spectra showed only the presence of the compound [Os(η5-C_5H_5)(CCH=CPh_2)(P^iPr_3)2](PF_6)2. The red solution was then transferred to a Schlenk tube, and the solvent was partially evaporated until a red solid began to precipitate, which was washed twice with 1 mL of cold acetone. Yield: 10 mg (86%). IR (Nujol): ν(PF_6) 840 cm^{-1}. ^1H NMR (300 MHz, $(CD_3)_2CO$, 293 K): 7.85−7.43 (m, 10 H, Ph), 6.66 (s, 1 H, CH), 6.38 (s, 5 H, Cp), 2.94 (m, 6 H, PCH), 1.49 (dd, J(HH) = 7.2 Hz, J(PH) = 15.9 Hz, 18 H, PCMe), 1.41 (dd, J(HH) = 6.9 Hz, J(PH) = 15.3 Hz, PCMe). $^{31}P\{^1H\}$ NMR (121.42 MHz, $(CD_3)_2CO$, 293 K): δ 21.6 (s), −144.8 (sept, J(PF) = 714 Hz, PF_6). Anal. Calcd for $C_{38}H_{58}F_{12}OsP_4$ (%): C, 43.18; H, 5.53. Found: C, 42.82; H, 5.40. MS (FAB^+): *m/e* 767 (M^+ − H).

Preparation of Os(η5-C5H5){C≡CC(CH3)Ph2}(PiPr3)2 (10). A solution of **8** (100 mg, 0.11 mmol) in 7 mL of tetrahydrofuran at −78 °C was treated with methyllithium (69 μL, 1.6 M in diethyl ether, 0.11 mmol). The mixture was stirred for 1 h while the temperature was increased to room temperature. The solvent was removed in vacuo, the residue was extracted with 7 mL of toluene, and the mixture was filtered through Kieselguhr. The solution was concentrated to dryness, and the residue was washed three times with 2 mL of cold methanol to give a yellow solid. Yield: 60 mg (70%). IR (Nujol): ν(C≡C) 2080 cm^{-1}. ^1H NMR (300 MHz, C_6D_6, 293 K): 7.74−7.08 (m, 10 H, Ph), 4.81 (s, 5 H, Cp), 2.24 (m, 6 H,

PCH), 2.06 (s, 3 H, CH_3), 1.09 (dvt, J(HH) = 7.2 Hz, N = 11.1 Hz, 36 H, PCMe). $^{31}P\{^1H\}$ NMR (121.42 MHz, C_6D_6, 293 K): δ 4.6 (s). $^{13}C\{^1H\}$ NMR (75.42 MHz, CD_2Cl_2, 293 K): δ 152.0 (s, *ipso*-Ph), 128.0, 127.6, 125.2 (all s, Ph), 108.5 (s, ≡*C*C), 75.9 (t, J(PC) = 6.5 Hz, OsC≡), 74.7 (s, Cp), 47.2 (s, CPh_2), 31.9 (s, CH_3), 30.9 (second-order system, PCH), 21.6 (s, PC*Me*), 20.9 (s, PC*Me*). Anal. Calcd for $C_{39}H_{60}OsP_2$ (%): C, 59.97; H, 7.74. Found: C, 59.70; H, 7.84. MS (FAB^+): *m/e* 783.5 (M^+ + H).

Preparation of Os(η^5-C_5H_5){C≡CC[$CH_2C(O)CH_3$]Ph_2}-(P^iPr_3)$_2$ (11). A solution of **8** (60 mg, 0.07 mmol) in 8 mL of tetrahydrofuran was treated with a suspension of KOH (50 mg, 85%, 0.76 mmol) in 0.5 mL of acetone, and the mixture was stirred for 1 h at room temperature. The resulting yellow solution was concentrated to dryness, the residue was extracted with 7 mL of toluene, and the mixture was filtered through Kieselguhr. The solvent was removed in vacuo, and the residue was washed three times with 2 mL of methanol to give a yellow solid. Yield: 43 mg (79%). IR (Nujol): ν(C≡C) 2077, ν(C=O) 1705 cm^{-1}. ^1H NMR (300 MHz, C_6D_6, 293 K): 7.40−7.09 (m, 10 H, Ph), 4.82 (s, 5 H, Cp), 3.42 (s, 2 H, CH_2), 2.25 (m, PCH), 1.96 (s, 3 H, CH_3), 1.12 (dvt, 36 H, J(HH) = 10.5 Hz, N = 17.4 Hz, PCMe). $^{31}P\{^1H\}$ NMR (121.42 MHz, C_6D_6, 293 K): δ 4.6 (s). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K): δ 205.6 (s, C=O), 149.7 (s, *ipso*-Ph), 125.5 (s, Ph), 106.7 (s, ≡*C*C), 80.1 (t, J(PC) = 7.0 Hz, OsC≡), 75.0 (s, Cp), 57.8 (s, CH_2), 49.4 (s, CPh_2), 31.1 (s, CH_3), 30.7 (second-order system, PCH), 21.5, 20.7 (both s, PC*Me*). Anal. Calcd for $C_{38}H_{62}OOsP_2$ (%): C, 59.82; H, 7.61. Found: C, 59.50; H, 7.72.

Preparation of Os(η^5-C_5H_5){C≡CC(OCH_3)Ph_2}(P^iPr_3)$_2$ (12). A solution of **8** (65 mg, 0.07 mmol) in 7 mL of tetrahydrofuran was treated with a solution of KOH (50 mg, 85%, 0.76 mmol) in 1 mL of methanol. After the mixture was stirred for 10 min at room temperature, the resulting yellow solution was concentrated to dryness. The residue was extracted with 7 mL of toluene, and the mixture was filtered through Kieselguhr. The solution was concentrated to dryness, and the residue was washed three times with 2 mL of cold pentane to give a yellow solid. Yield: 40 mg (70%). IR (Nujol): ν (C≡C) 2071 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 293 K): 7.51−7.47 (m, 4 H, Ph), 7.23−7.11 (m, 6 H, Ph), 4.84 (s, 5 H, Cp), 3.25 (s, 3 H, OCH_3), 2.27 (m, 6 H, PCH), 1.15 (dvt, J(HH) = 7.0 Hz, N = 11.5 Hz, 18 H, PCMe), 1.12 (dvt, J(HH) = 7.5 Hz, N = 12.3, 18 H, PCMe). $^{31}P\{^1H\}$ NMR (121.42 MHz, C_6D_6, 293 K): δ 4.9 (s). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K): 148.6 (s, *ipso*-Ph), 128.5, 127.5, 126.3 (all s, Ph), 104.4 (s, ≡*C*C), 85.9 (t, J(PC) = 17.2 Hz, OsC≡), 82.4 (s, CPh2), 74.9 (s, Cp), 51.3 (s, OCH_3), 30.6 (second-order system, PCH), 21.4, 20.9 (both s, PC*Me*). Anal. Calcd for $C_{39}H_{60}OOsP_2$ (%): C, 58.76; H, 7.60. Found: C, 58.27; H, 7.62. MS (FAB^+): *m/e* 767 ($M^+ - OCH_3$).

X-ray Structure Determination of [OsH(η^5-C_5H_5)(C≡CPh)(P^iPr_3)$_2$]PF_6 (2) and [Os(η^5-C_5H_5)(CCH=CPh_2)(P^iPr_3)$_2$]-(PF_6)$_2$ (9). A summary of the fundamental crystal and refinement data of the compounds **2** and **9** is given in Table 4. Crystals of **2** and **9** showing well-defined faces were mounted on a Bruker-Siemens Smart CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (Molybdenum radiation, λ = 0.71073 Å) operating at 50 kV and 20 mA. Data were collected over a quadrant of the reciprocal space by a combination of two frame sets for **2** and over a hemisphere by a combination of three sets for **9**. The cell parameters were determinated and refined by least-squares fits of all reflections collected. Each frame exposure time was of 20 s covering 0.3° in ω. Coverage of the unique sets were over 100% complete to at least 27° in θ. The first 50 frames were recollected at the end of the data collection to monitor crystal decay. The absorption correction was made using SADABS.[39] The structure was solved by Multan and Fourier methods using SHELXS.[39] Full-matrix least-squares refinement was carried out using SHELXL97[39] minimizing $w(F_o^2 - F_c^2)^2$. Weighted R factors (R_w) and all goodness of fit S are based on F^2; conventional R factors (R) are based on F.

Table 4. Crystal Data and Data Collection and Refinement for [OsH(η^5-C_5H_5)(C≡CPh)(P^iPr_3)$_2$]PF_6 (2) and [Os(η^5-C_5H_5)(CCH=CPh_2)(P^iPr_3)$_2$](PF_6)$_2$ (9)

	2	9
	Crystal Data	
formula	$C_{31}H_{53}F_6OsP_3$	$C_{38}H_{58}F_{12}OsP_4 \cdot C_3H_6O$
mol wt	822.84	1115.00
color and habit	prismatic, colorless	red, prismatic block
symmetry, space group	monoclinic, $P2_1/c$	triclinic, $P\bar{1}$
a, Å	15.7627(12)	12.2501(9)
b, Å	12.0848(9)	13.3169(10)
c, Å	18.2139(14)	13.9605(10)
α, deg		97.4357(11)
β, deg	99.116(1)	93.0273(11)
γ, deg		91.3774(12)
V, Å^3	3425.7(4)	2254.0(3)
Z	4	2
D_{calc}, g cm^{-3}	1.632	1.643
	Data Collection and Refinement	
diffractometer	Siemens-Bruker CCD	
λ(Mo Kα), Å	0.71073	
monochromator	graphite oriented	
μ, mm^{-1}	3.915	3.052
scan type	ω scans at different φ values	
2θ range, deg	$3° \le 2\theta \le 46.5°$	$3° \le 2\theta \le 52°$
temp, K	294.0(2)	153.0(2)
no. of data collected	7335 (h: −6, 17; k: −7, 12; l: −20, 14)	10 343 (h: −11, 15; k: −16, 13; l: −16, 16)
no. of unique data	4192 (merging R factor 0.0282)	7739 (merging R factor 0.0515)
no. of params refined	335	605
R1[a] [$F^2 > 2\sigma(F^2)$]	0.0527	0.0595
wR2[b] [all data]	0.1430	0.1284
S[c] [all data]	1.071	0.963

[a] $R1(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2(F^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. [c] Goof = $S = \{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$, where n is the number of reflections, and p is the number of refined parameters.

Theoretical Calculations. All the ab initio calculations have been carried out using the Gaussian-98 suite of programs.[38] The calculations have been performed at the MP2 level using the LANL2DZ pseudopotential and basis set for the metal atoms and the 6-31G basis set for the rest of the molecule. The extended Hückel calculations were carried out using the program CACAO and its built-in basis set.[36]

Acknowledgment. We thank the DGES (PROJECT PB-98-1591, Programa de Promoción General del Conocimiento) for financial support. M.B. thanks the DGA (Diputación General de Aragón) for a grant.

Supporting Information Available: Tables of atomic coordinates and equivalent isotropic displacement coefficients, anisotropic thermal parameters, and bond distances and angles for **2** and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM000141+

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