Articles

Ene-Type Reactions between an α-Alkenylphosphine and Terminal Alkynes Promoted by Osmium-Cyclopentadienyl Fragments

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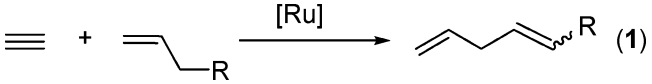
Complex Os(η^5-C_5H_5)Cl{[η^2-CH_2=C(CH_3)]P^{i}Pr$_2$} (**1**) reacts with phenylacetylene to give the dienylphosphine derivative Os(η^5-C_5H_5)Cl{[η^2-(*E*)-PhCH=CHCH$_2$C(=CH$_2$)]P^{i}Pr$_2$} (**2**). The reaction of **1** with PhC≡CD leads to the monodeuterated compound Os(η^5-C_5H_5)Cl{[η^2-(*E*)-PhCH=CDCH$_2$C(=CH$_2$)]P^{i}Pr$_2$} (**2-*d*$_1$**). The position of the deuterium atom in **2-*d*$_1$** is consistent with the participation of π-alkyne intermediates in the formation of **2** and **2-*d*$_1$**. In agreement with this, complex **1** reacts with 1,1-diphenyl-2-propyn-1-ol to give initially Os(η^5-C_5H_5)Cl{η^2-HC≡CC(OH)Ph$_2$}{P^{i}Pr$_2$[C(CH_3)=CH$_2$]} (**3**), which in toluene under reflux evolves into Os(η^5-C_5H_5)Cl{[η^2-(*E*)-{Ph$_2$(OH)C}CH=CHCH$_2$C(=CH$_2$)]P^{i}Pr$_2$} (**4**). Treatment of **1** with lithium phenylacetylide affords the alkynyl derivative Os(η^5-C_5H_5)(C≡CPh){[η^2-CH_2=C(CH_3)]P^{i}Pr$_2$} (**5**). Complex **5** also reacts with 1,1-diphenyl-2-propyn-1-ol. The reaction initially gives Os(η^5-C_5H_5)(C≡CPh){η^2-HC≡CC(OH)Ph$_2$}{P^{i}Pr$_2$[C(CH_3)=CH$_2$]} (**6**), which subsequently affords Os(η^5-C_5H_5)(C≡CPh){[η^2-(*E*)-{Ph$_2$(OH)C}CH=CHCH$_2$C(=CH$_2$)]P^{i}Pr$_2$} (**7**). Triethylamine inhibits the coupling between the isopropenyl group of **1** and phenylacetylene. In the presence of this base, the addition of phenylacetylene to **1** leads to the vinylidene derivative Os(η^5-C_5H_5)Cl(=C=CHPh){P^{i}Pr$_2$[C(CH_3)=CH$_2$]} (**8**). The X-ray structures of **2** and **8** are also reported.

Introduction

The development of efficient and selective methods to form carbon−carbon bonds is a target with high priority.[1] Increasing emphasis is placed upon atom economy in order to utilize raw materials more effectively and to minimize waste production.[2] An example of an atom economical process is the ene-type reaction between an alkene and an alkyne. A variety of transition metal complexes have been reported to catalyze the intramolecular coupling of alkene and alkyne functional groups, to produce cyclic 1,4-dienes.[3] Cationic ruthenium(II) derivatives have been shown to be active catalysts also for the intermolecular version of this reaction (eq 1).[4] Although osmium catalysts for C−C bond formation are known,[5] in the presence of osmium species, neither catalytic nor stoichiometric ene-type reactions between alkene and alkyne groups have been described.



(**1**)

α-Alkenylphosphines are phosphorus-functionalized olefins, which should afford phosphorus-functionalized dienes by means of ene-type reactions with alkynes (eq 2). As ligand, they are attracting increased attention in the chemistry of the metals. α-Alkenylphosphines act as monodentate groups,[6] can bridge to two metal

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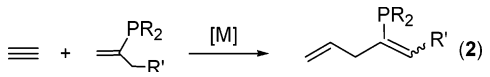
centers,[7] and can act as chelating ligands.[8] Furthermore, the reversible coordination−decoordination of the olefinic moiety gives them hemilabile properties. As a consequence, under appropriate conditions, they can be used to stabilize highly reactive intermediates.[9] Although interest in the preparation of novel functionalized phosphines by their connection with homogeneous catalysis is known,[10] surprisingly, ene-type reactions of the α-alkenylphosphines have not explored.

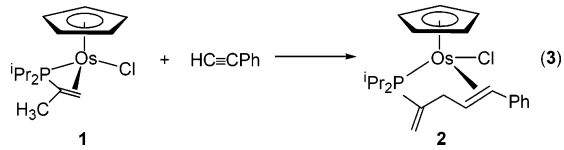


(2)

As part of our work on the chemistry of the Os-cyclopentadienyl unit,[11] we have recently initiated a research program dedicated to the functionalization of trialkylphosphines, in particular triisopropylphosphine. Because, in contrast to alkanes, the reactions involving alkenes are promising processes regarding synthetic applications, the dehydrogenation of an isopropyl group of the phosphine was performed[12] as the first step of the program. In subsequent stages, we have converted the resulting isopropyldi(isopropyl)phosphine into α-allylphosphines by reaction with diazoalkanes via [2+2] cycloaddition reactions[13] and iminophosphines by insertion of the carbon−nitrogen triple bond of benzonitriles into one of the C(sp^2)−H bonds of the isopropenyl group of the isopropenyldi(isopropyl)phosphine.[14] As a continuation of our work in this program, we now report the transformation of the isopropenyl substituent of the phosphine into dienyl groups, by means of ene-type reactions with alkynes.

Results and Discussion

1. Coupling between Isopropenyldi(isopropyl)-phosphine and Phenylacetylene Promoted by the Fragment Os(η^5-C_5H_5)Cl. One of the great utilities of the transition metals is their ability to direct reactivity of organic molecules toward the rarely activated centers. The osmium fragment Os(η^5-C_5H_5)Cl deactivates the phosphorus Lewis base capacity of isopropenyldi(isopropyl)phosphine by coordination, while it activates the isopropenyl carbon−carbon double bond to the coupling with phenylacetylene. Treatment at room temperature of toluene solutions of the complex Os(η^5-C_5H_5)Cl{[η^2-CH_2=C(CH_3)]P^{i}Pr$_2$} (**1**) with 3.6 equiv of the phenylacetylene leads after 7 h to the dienyl phosphine derivative Os(η^5-C_5H_5)Cl{[η^2-(*E*)-PhCH=CHCH_2C(=CH_2)]P^{i}Pr$_2$} (**2**), which was isolated, according to eq 3, as an orange solid in 87% yield.



(3)

Figure 1 shows a view of the structure of this derivative. Selected bond distances and angles are listed in Table 1. The structure proves the formation of the dienyl phosphine, which shows a *gem* disposition for the substituents of the C(1)−C(11) olefinic bond and *E*-stereochemistry at the C(3)−C(4) double bond. The phosphine acts a bidentate ligand through the phosphorus atom and the olefinic C(3)−C(4) bond. Thus, the geometry around the osmium center can be described as a distorted octahedron, with the cyclopentadienyl ligand occupying the three sites of a face, whereas the

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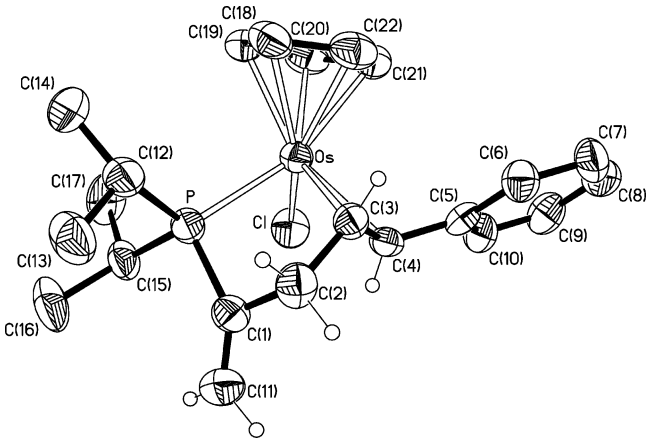


Figure 1. Molecular diagram of complex Os(η^5-C_5H_5)Cl-{[η^2-(*E*)-PhCH=CHCH$_2$C(=CH$_2$)]P^{i}Pr$_2$} (**2**).

Table 1. Selected Bond Distances (Å) and Angles (deg) for the Complex 2[a]

Os−P	2.2990(12)	Os−C(18)	2.171(5)
Os−Cl	2.4268(11)	Os−C(19)	2.236(4)
Os−C(3)	2.203(4)	Os−C(20)	2.274(4)
Os−C(4)	2.184(4)	Os−C(21)	2.256(4)
C(1)−C(11)	1.296(6)	Os−C(22)	2.170(4)
C(1)−C(2)	1.506(6)	C(2)−C(3)	1.529(6)
C(3)−C(4)	1.421(6)	C(4)−C(5)	1.456(6)
P−OsG	129.3	P−C(1)−C(2)	106.9(4)
P−Os−M	89.3	C(11)−C(1)−C(2)	124.5(5)
P−Os−Cl	87.30(4)	C(1)−C(2)−C(3)	111.1(4)
G−Os−M	125.3	C(2)−C(3)−C(4)	119.7(4)
G−Os−Cl	117.6	C(2)−C(3)−H(3)	116(2)
M−Os−Cl	98.4	C(5)−C(4)−H(4)	114(3)
C(3)−Os−C(4)	37.78(15)		

[a] G is the centroid of the C(18)−C(22) Cp ligand. M is the midpoint of the C(3)−C(4) double bond.

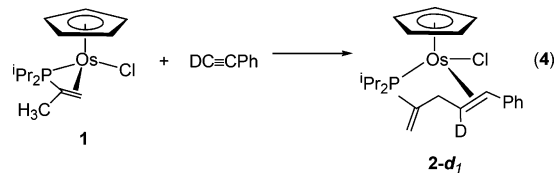
phosphorus atom, the midpoint of the olefinic C(3)−C(4) bond (M), and the chloride ligand are situated on sites of the opposite face. The angles P−Os−Cl, P−Os−M, and M−Os−Cl are 87.30(4)°, 89.3°, and 98.4°, respectively.

The osmium-styryl coordination exhibits Os−C distances of 2.203(4) Å (Os−C(3)) and 2.184(4) Å (Os−C(4)), which agree well with those found in other osmium-olefin complexes (between 2.13 and 2.28 Å).[8d,9b,c,11n,12,15] Similarly, the olefinic bond distance C(3)−C(4) (1.421(6) Å) is within the range reported for transition metal olefin complexes (between 1.340 and 1.455 Å).[16] In agreement with the presence of a C(1)−C(11) double bond, the separation between these atoms is 1.296(6) Å.

The ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra of **2** are consistent with the structure shown in Figure 1. In the ^{1}H NMR the C(sp^2)H$_2$ protons give rise to doublets at 5.28 (*trans* to P) and 4.93 (*cis* to P) ppm, with H−P coupling constants of 27.0 and 11.7 Hz, respectively, while the C(sp^3)H$_2$ protons display multiplets at 2.60 and 2.30 ppm. The olefinic resonances at C(3)H and C(4)H are observed at 4.72 and 4.66 ppm, respectively. The first of them appears as a multiplet, whereas the second one is a doublet with a H−H coupling constant of 9.9 Hz. In the ^{13}C{^{1}H} NMR spectrum, the olefinic carbon atoms C(1) and C(11) display a doublet at 151.9 ppm (C(1)), with a C−P coupling constant of 38.2 Hz, and a singlet at 117.9 ppm (C(11)). The resonance corresponding to the sp^3-C(2) atom is observed at 39.3 ppm, as a doublet with a C−P coupling constant of 25.3 Hz. The resonances due to the coordinated C(3) and C(4) atoms are observed at 39.9 and 53.8 ppm, respectively. The first of them appears as a singlet, while the second one is a doublet with a C−P coupling constant of 2.3 Hz. The ^{31}P{^{1}H} NMR spectrum shows a singlet at 42.5 ppm, shifted 45.4 ppm to lower field in comparison with the resonance of **1**.

The formation of **2** can be certainly rationalized as an ene-type reaction between the isopropenyl substituent of the phosphine of **1** and the alkyne. It is noteworthy the high regioselectivity of the process. Although three stereoisomers are feasible, only that with the smallest steric hindrance between the initial organic moieties is formed.

It is generally believed that this type of reaction proceeds via a metalacyclopentene intermediate,[4h] which is generated by oxidative coupling between the olefin and alkyne substrates. The *E*-configuration at the C(3)−C(4) double bond of **2** and the disposition of the phenyl group, away from the osmium atom, are consistent with this proposal. In favor of the formation of an osmacyclopentene unit, by coupling of coordinated π-olefin and π-alkyne ligands, we have also observed that **1** reacts with PhC≡CD to afford exclusively Os(η^5-C_5H_5)Cl{[η^2-(*E*)-PhCH=CDCH$_2$C(=CH$_2$)]P^{i}Pr$_2$} (**2-*d*$_1$**), containing 1.0 deuterium atom at C(3) (eq 4).



The presence of the deuterium atom at C(3) of **2-*d*$_1$** is demostrated by the ^{1}H and ^{2}H NMR spectra of this compound. The ^{1}H NMR spectrum shows the absence of the resonance at 4.72 ppm, while the ^{2}H NMR spectrum contains a singlet at 4.71 ppm.

Scheme 1 summarizes the elemental steps, which could lead to **2**. The hemilabile properties of the isopropenyldi(isopropyl)phosphine ligand should involve not only the isopropenyl group but also the phosphorus atom. Thus, the decoordination of the latter in **1** should afford an unsaturated intermediate, which by coordination of the alkyne could give the key species, π-olefin-π-alkyne. The oxidative coupling of these unsaturated ligands should afford the osmacyclopentene intermediate, which could evolve by a hydrogen β-elimination reaction on the methyl substituent at the C$_\alpha$(sp^3) atom of the metalacycle. The β-elimination reaction should lead to a hydride-alkenyl intermediate. Thus, the subsequent reductive elimination of olefin followed by the coordination of the phosphorus atom to the metallic center could finally generate **2**.

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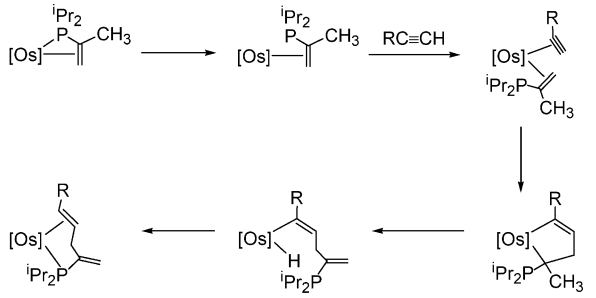
Scheme 1



2. Coupling between Isopropenyldi(isopropyl)phosphine and 1,1-Diphenyl-2-propyn-1-ol Promoted by the Fragment Os(η^5-C_5H_5)Cl. The ene-type reaction shown in eq 3 can be extended to alkynols. In contrast to the formation of **2** the process is a two-step procedure (Scheme 2). The addition at room temperature of 1.5 equiv of 1,1-diphenyl-2-propyn-1-ol to diethyl ether solutions of **1** leads to the π-alkynol derivative Os(η^5-C_5H_5)Cl{η^2-HC≡CC(OH)Ph_2}{P^iPr_2[C(CH_3)=CH_2]} (**3**), which was isolated as a pink solid in 92% yield. The π-coordination of the alkynol is strongly supported by the IR spectrum, in which the C≡C stretching frequency is found at 1808 cm^{-1}, shifted 309 cm^{-1} to lower wavenumbers in comparison with the C≡C stretching frequency in the free alkyne (2117 cm^{-1}).[11d,17] In the ^{1}H NMR spectrum, the most noticeable resonances of the alkynol are a singlet at 6.84 ppm corresponding to the O-H proton and a doublet at 4.40 ppm with a H−P coupling constant of 12.6 Hz due to the C(sp)-H proton. The resonances corresponding to the CH_2 protons of the phosphine isopropenyl group are observed at 5.20 (*trans* to P) and 4.95 (*cis* to P) ppm, as doublets with H−P coupling constants of 30.0 and 12.9 Hz, respectively. These resonances are shifted 1.10 (*trans* to P) and 2.08 (*cis* to P) with regard to those found in the spectrum of **1** (δ, 4.10 and 2.87).[12] In the ^{13}C{^{1}H} NMR spectrum, the resonances due to the propargyl unit of the alkyne appear between 77 and 89 ppm as singlets. The resonances corresponding to the C(sp^2) isopropenyl carbon atoms are observed at 139.6 and 126.2 ppm. The first of them due to the CP atom appears as a doublet with a C−P coupling constant of 35.9 ppm, while the second one is observed as a singlet. The ^{31}P-{^{1}H} NMR spectrum contains a singlet at 15.9 ppm.

In toluene under reflux complex **3** evolves into Os(η^5-C_5H_5)Cl{[η^2-(*E*)-{Ph_2(OH)C}CH=CHCH_2C(=CH_2)]-P^iPr_2} (**4**), which was isolated as a green solid in 74% yield. The formation of **4** indicates that the ene-type reactions between α-alkenylphosphines and alkynols can afford dienylphosphines, which are functionalized with an alcohol group. The process shows the same level of regioselectivity as the formation of **2**. This suggests that the products of these reactions are formed under thermodynamic control.

The presence of an alcohol function in the dienyl substituent of the phosphine of **4** is strongly supported by the IR spectrum of this compound, which shows a ν(O−H) band at 3361 cm^{-1}. In the ^{1}H NMR spectrum the resonance corresponding to the OH proton appears at 6.59 ppm as a singlet. The C(sp^2)H_2 protons of the phosphine display double doublets, at 5.71 (*trans* to P) and 4.89 (*cis* to P) ppm, with a H−H coupling constant of 1.2 Hz and H−P coupling constants of 24.9 and 10.8 Hz, respectively. The C(sp^3)H_2 protons give rise to double doublets at 3.20 and 2.19 ppm, the first of them with a H−H coupling constant of 16.2 Hz and a H−P coupling constant of 31.2 Hz, and the second one with H−H coupling constants of 16.2 and 4.8 Hz. The resonances due to a coordinated olefinic group are observed at 4.80 and 4.04 ppm. The first of them appears as a doublet with a H−H coupling constant of 9.3 Hz, while the second one is a double doublet with H−H coupling constants of 9.3 and 4.8 Hz. In the ^{13}C-{^{1}H} NMR spectrum, the olefinic C=CP carbon atoms display a doublet at 142.5 ppm, with a C−P coupling constant of 33.3 Hz (CP), and a singlet at 122.1 ppm (=CH_2). The resonance corresponding to the C(sp^3)H_2 carbon atom is observed at 43.8 ppm, as a doublet with a C−P coupling constant of 23.4 Hz. The resonances due to the coordinated carbon atoms appear at 57.2 and 44.0 ppm as singlets. The ^{31}P{^{1}H} NMR spectrum shows a singlet at 34.4 ppm.

3. Coupling between Isopropenyldi(isopropyl)phosphine and 1,1-Diphenyl-2-propyn-1-ol Promoted by the Fragment Os(η^5-C_5H_5)(C≡CPh). The replacement of the chloride ligand in the fragment Os-(η^5-C_5H_5)Cl by a phenylacetylide group does not appear to have a significant influence in this type of reaction. Thus, we have observed that the isopropenyldi(isopropyl)phosphine-1,1-diphenyl-2-propyn-1-ol coupling shown in Scheme 2 is also promoted by the fragment Os(η^5-C_5H_5)(C≡CPh) (Scheme 3).

The alkynyl complex Os(η^5-C_5H_5)(C≡CPh){[η^2-CH_2=C(CH_3)]P^iPr_2} (**5**) was prepared by treatment at room temperature of tetrahydrofuran solutions of **1** with 2.0 equiv of lithium phenylacetylide. It was isolated as an orange solid in 65% yield and characterized by MS, elemental analysis, IR, and ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopy. In agreement with the presence of an alkynyl ligand in this compound, its IR spectrum in Nujol shows a band at 2083 cm^{-1} corresponding to the ν(C≡C) vibration. The ^{1}H NMR spectrum is consistent with that of **1**. The olefinic CH_2 protons of the isopropenyl substituent of the phosphine give rise to double doublets at 3.48 (*trans* to P) and 2.41 (*cis* to P) ppm, with a H−H coupling constant of 2.1 Hz and H−P coupling constants of 30.3 and 6.6 Hz, respectively. In the ^{13}C{^{1}H} the C(sp) carbon atoms of the alkynyl ligand display doublets at 111.5 (C_β) and 85.1 (C_α) ppm with C−P coupling constants of 3.8 and 20.3 Hz, respectively, whereas the C(sp^2) carbon atoms of the phosphine give rise to a doublet at 31.2 ppm (CP), with a C−P coupling constant of 18.4 Hz, and a singlet at 24.0 (CH_2) ppm. The ^{31}P{^{1}H} NMR spectrum shows a singlet at −1.85 ppm.

The addition at room temperature of 1.5 equiv of 1,1-diphenyl-2-propyn-1-ol to diethyl ether solutions of **5** leads to the π-alkynol derivative Os(η^5-C_5H_5)(C≡CPh)-{η^2-HC≡CC(OH)Ph_2}{P^iPr_2[C(CH_3)=CH_2]} (**6**), which was isolated as a pale yellow solid in 65% yield. In the

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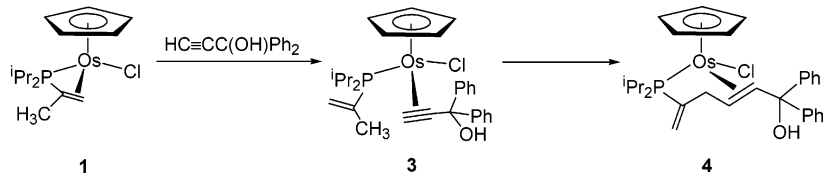
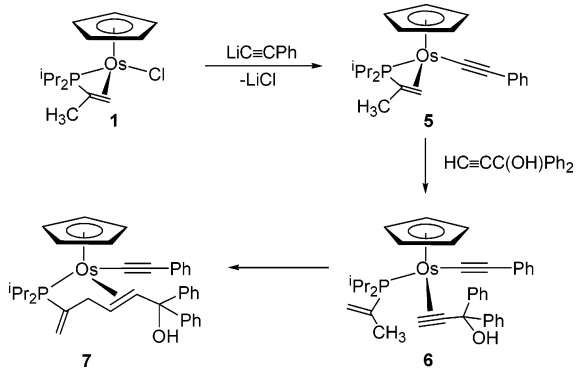
Scheme 2



Scheme 3

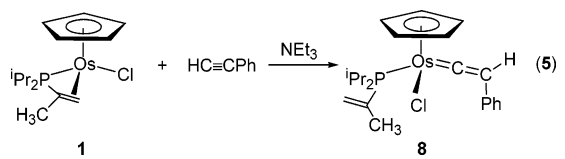


^{1}H NMR spectrum, the most noticeable resonances of the alkynol are a singlet at 4.25 ppm corresponding to the O-H proton and a doublet at 4.04 ppm, with a H−P coupling constant of 9.3 Hz due to the C(sp)-H proton. The resonances corresponding to the CH_2 group of the phosphine are observed at 5.24 (*trans* to P) and 5.03 (*cis* to P), as doublets with H−P coupling constants of 30.3 and 12.6 Hz, respectively. In the $^{13}C\{^1H\}$ NMR spectrum, the resonances due to the C(sp) carbon atoms of the alkynyl ligand appear at 116.5 (C_β) and 78.3 (C_α) ppm, the first of them as a singlet and the second one as a doublet with a C−P coupling constant of 21.6 Hz. The resonances of the C(sp) carbon atoms of the π-alkynol are observed at 125.3 (≡CH) and 75.7 (≡C) ppm, as singlets, whereas the C(sp^2) carbon atoms of the phosphine give rise to a doublet at 143.2 (CP) ppm, with a C−P coupling constant of 36.9 Hz, and a singlet at 124.5 ppm. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 20.3 ppm.

In a manner similar to **3**, in toluene under reflux, complex **6** evolves into the ene-reaction product Os(η^5-C_5H_5)(C≡CPh){[η^2-(*E*)-{Ph_2(OH)C}CH=$CHCH_2C(=CH_2)$]P^iPr_2} (**7**), which was isolated as a white solid in 78% yield. The presence of an OH group in the dienyl substituent of the phosphine is supported by the IR spectrum of the compound, which shows a ν(OH) band at 3368 cm^{-1}. In the ^{1}H NMR spectrum in benzene-d_6, the OH resonance appears masked by the phenyl signals. However in dichlorometane-d_2, it is observed at 6.77 ppm as a singlet. In benzene-d_6, the C(sp^2)H_2 group of the phosphine display two double doublets at 5.53 (*trans* to P) and 4.62 (*cis* to P) ppm with a H−H coupling constant of 2.4 Hz and H−P coupling constants of 24.3 and 10.8 Hz, respectively. The C(sp^3)-H_2 protons give rise to double doublets at 2.94 and 2.11 ppm, the first of them with a H−H coupling constant of 15.6 and a H−P coupling constant of 30.5, and the second one with H−H coupling constants of 15.6 and 4.5 Hz. The resonances due to the coordinated olefinic group are observed at 3.60 and 3.43 ppm. The first of them is a doublet with a H−H coupling constant of 9.9 Hz, while the second one appears as a double doublet with H−H coupling constants of 9.9 and 4.5 Hz. The $^{13}C\{^1H\}$ NMR spectrum of **7** agrees well with that of **4**; the olefinic C=CP group gives rise to a doublet at 144.1 ppm, with a C−P coupling constant of 36.9 Hz, and a singlet at 121.7 ppm. The resonance corresponding to the C(sp^3)H_2 carbon atom of the phosphine appears at 43.6 ppm, as a doublet with a C−P coupling constant of 23.9 Hz, whereas the coordinated C(sp^2) carbon atoms of the chelate ligand display singlets at 51.2 and 37.6 ppm. The resonances due to the C(sp) carbon atoms of the alkynyl ligand are observed at 117.5 (C_β) and 77.1 (C_α) ppm. The first of them appears as a singlet, while the second one is a doublet with a C−P coupling constant of 16.8 Hz. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 38.3 ppm.

4. Triethylamine Inhibits the Coupling. Complex Os(η^5-C_5H_5)Cl(P^iPr_3)$_2$ reacts with terminal alkynes and alkynols to afford π-alkyne and π-alkynol derivatives related to **3** and **6**. In contrast to the isopropenyldi(isopropyl)phosphine complexes, these triisopropylphosphine derivatives evolve into the corresponding vinylidene and hydroxyvinylidene compounds.[11b] From a mechanistic point of view, it has been proposed that the transformation proceeds via 1,2-hydrogen shift on the π-alkyne species or, alternatively, through hydride-alkynyl intermediates.[18] For the latter pathway, Puerta and co-workers have proved that the vinylidene results from the dissociation of the hydride as a proton and the subsequent protonation at the C_β atom of the alkynyl ligand of the metal-alkynyl species.[18f] In agreement with Puerta's results, it has been observed that the presence of bases favors the alkyne-vinylidene isomerization.[11j]

Triethylamine inhibits the ene-type reaction between isopropenyldi(isopropyl)phosphine and alkynes. In contrast to the reaction shown in eq 3, in the presence of 6.0 equiv of triethylamine, the treatment of toluene solutions of **1** with 6.3 equiv of phenylacetylene leads to the vinylidene complex Os(η^5-C_5H_5)Cl(=C=CHPh)-{P^iPr_2[$C(CH_3)$=CH_2]} (**8**), which was isolated as red crystals in 73% yield (eq 5).



Triethylamine accelerates the alkyne-vinylidene transformation. So, the formation of **8** suggests that on Os(η^5-C_5H_5)X fragments the oxidative coupling between the isopropenyl substituent of an isopropenylphosphine and the carbon−carbon triple bond of a terminal alkyne or alkynol (Scheme 1) is faster than the alkyne-vinylidene transformation.

Figure 2 shows a view of the structure of **8**. Selected bond distances and angles are listed in Table 2. The geometry around the osmium center is close to octahe-

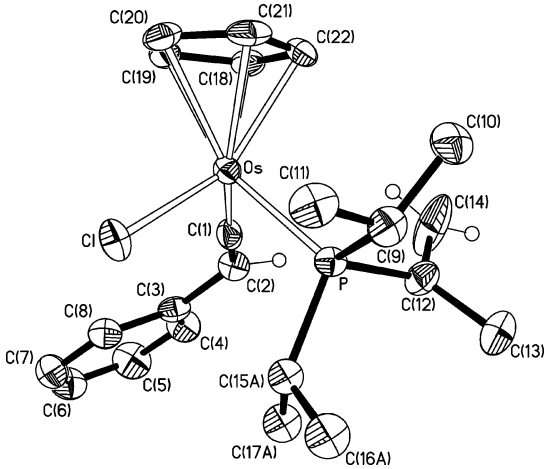


Figure 2. Molecular diagram of complex Os(η^5-C_5H_5)-Cl(=C=CHPh){P^{i}Pr$_2$[C(CH$_3$)=CH$_2$]} (**8**).

Table 2. Selected Bond Distances (Å) and Angles (deg) for the Complex 8[a]

Os−P	2.3028(11)	Os−C(18)	2.195(4)
Os−Cl	2.3906(10)	Os−C(19)	2.289(4)
Os−C(1)	1.817(5)	Os−C(20)	2.322(4)
C(1)−C(2)	1.328(6)	Os−C(21)	2.302(4)
C(2)−C(3)	1.460(6)	Os−C(22)	2.188(4)
C(12)−C(14)	1.334(7)		
P−Os−G	129.9	G−Os−C(1)	120.7
P−Os−Cl	88.51(4)	Cl−Os−C(1)	103.35(13)
P−Os−C(1)	89.05(13)	Os−C(1)−C(2)	170.4(4)
G−Os−Cl	117.8	C(1)−C(2)−C(3)	125.9(4)

[a] G is the centroid of the C(18)−C(22) Cp ligand.

dral, with the cyclopentadienyl ligand occupying a face. The C(1)−Os−P, C(1)−Os−Cl, and P−Os−Cl angles are 89.05(13)°, 103.35(13)°, and 88.51(4)°, respectively.

The vinylidene ligand is bound to the metal in a nearly linear fashion, with an Os−C(1)−C(2) angle of 170.4(4)°. The Os−C(1) (1.817(5) Å) and C(1)−C(2) (1.328(6) Å) bond lengths compare well with those found in other osmium-vinylidene complexes[19] and support the vinylidene formulation.

The presence of a vinylidene ligand in **8** is strongly supported by the ^{1}H and ^{13}C{^{1}H} NMR spectra of this compound. In the ^{1}H NMR spectrum the resonance due to the =CH proton of the vinylidene appears at 2.82 ppm, as a singlet, whereas the CH$_2$ resonances of the isopropenyl substituent of the phosphine are observed at 5.26 (*trans* to P) and 5.06 (*cis* to P) ppm as doublets with H−P coupling constants of 31.5 and 13.5 Hz, respectively. In the ^{13}C{^{1}H} NMR spectrum, the most noticeable resonances of the vinylidene ligand are a doublet at 292.6 ppm, with a C−P coupling constant of 14.3 Hz due to the C$_\alpha$ carbon atom, and a singlet at 117.0 ppm corresponding to the C$_\beta$ carbon atom. The C(sp^2) atoms of the isopropenyl group of the phosphine display doublets at 142.2 (CP) and 125.3 (CH$_2$) ppm, with C−P coupling constants of 39.2 and 4.6 Hz, respectively. The ^{31}P{^{1}H} NMR spectrum shows a singlet at 19.5 ppm.

We note that the indenyl-β-alkenylphosphine-ruthenium(II) cation [Ru(η^5-C_5H_5){[η^2-CH$_2$=CHCH$_2$]PPh$_2$}-(PPh$_3$)]$^+$ reacts with terminal alkynes to afford vinylidene intermediates, which evolve into bicyclic alkylidene compounds by an intramolecular [2+2] cycloaddition process between the olefinic substituent of the phosphine and the C$_\alpha$−C$_\beta$ double bond of the vinylidene ligands.[20] In contrast to this ruthenium system, complex **8** is stable and the coupling between the isopropenyl substituent of the phosphine and the vinylidene is not observed, even in toluene at 80 °C.

Concluding Remarks

This paper reveals that the osmium-cyclopentadienyl Os(η^5-C_5H_5)X fragments (X = Cl, C≡CPh) promote ene-type reactions between the carbon−carbon double bond of an α-alkenylphosphine and the carbon−carbon triple bond of alkyne and alkynol substrates. The carbon−carbon couplings afford dienylphosphine ligands, including those functionalized with an alcohol group. Thus, we show that the reactions of complexes Os(η^5-C_5H_5)X{[η^2-CH$_2$=C(CH$_3$)]P^{i}Pr$_2$} (X = Cl, C≡CPh) with phenylacetylene and 1,1-diphenyl-2-propyn-1-ol lead to the dienylphosphine derivatives Os(η^5-C_5H_5)Cl{[η^2-(*E*)-PhCH=CHCH$_2$C(=CH$_2$)]P^{i}Pr$_2$} and Os(η^5-C_5H_5)X{[η^2-(*E*)-{Ph$_2$(OH)C}CH=CHCH$_2$C(=CH$_2$)]P^{i}Pr$_2$} (X = Cl, C≡CPh).

On the basis of the high regioselectivity of the reactions and the results of an isotope labeling experiment, the formation of the dienylphosphine ligands can be rationalized as olefin-alkyne oxidative couplings on π-alkyne species, which lead to metalacyclopentane intermediates. In agreement with this proposal, the π-alkynol derivatives Os(η^5-C_5H_5)X{η^2-HC≡CC(OH)-Ph$_2$}{P^{i}Pr$_2$[C(CH$_3$)=CH$_2$]} (X = Cl, C≡CPh) have been isolated and characterized.

The oxidative couplings are faster than the isomerization of the alkynes into vinylidenes. Triethylamine accelerates the latter process. As a consequence, in the presence of this amine, the ene-type reactions are inhibited and the formation of vinylidene species takes place.

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(19) See for example: (a) Huang, D. J.; Oliván, M.; Huffman, J. C.; Eisenstein, O.; Caulton, K. G. *Organometallics* **1998**, *17*, 4700. (b) Esteruelas, M. A.; Oliván, M.; Oñate, E.; Ruiz, N.; Tajada, M. A. *Organometallics* **1999**, *18*, 2953. (c) Bohanna, C.; Buil, M. L.; Esteruelas, M. A.; Oñate, E.; Valero, C. *Organometallics* **1999**, *18*, 5176. (d) Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2000**, *19*, 5454. (e) Castarlenas, R.; Esteruelas, M. A.; Gutiérrez-Puebla, E.; Oñate, E. *Organometallics* **2001**, *20*, 1545. (f) Barrio, P.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2002**, *21*, 2491. (g) Barrio, P.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2003**, *22*, 2472.

(20) (a) Alvarez, P.; Lastra, E.; Gimeno, J.; Bassetti, M.; Falvello, L. R. *J. Am. Chem. Soc.* **2003**, *125*, 2386. (b) Braña, P.; Gimeno, J.; Sordo, J. A. *J. Org. Chem.* **2004**, *69*, 2544. (c) Bassetti, M.; Alvarez, P.; Gimeno, J.; Lastra, E. *Organometallics* **2004**, *23*, 5127.

In conclusion, we show a novel method to prepare dienylphosphine derivatives, starting from α-alkenylphosphine complexes and alkynes.

Experimental Section

All reactions were carried out with rigorous exclusion of air using Schlenk-tube techniques. Solvents were dried by the usual procedures and distilled under argon prior to use. The starting material $Os(\eta^5\text{-}C_5H_5)Cl\{[\eta^2\text{-}CH_2{=}C(CH_3)]P^iPr_2\}$ (**1**) was prepared by the published method.[12]

^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra were recorded on either a Varian UNITY 300, a Varian Gemini 2000, a Bruker AXR 300, or a Bruker Avance 300 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. Infrared spectra were run on a Perkin-Elmer 1730 spectrometer (Nujol mulls on polyethylene sheets). C, H, and N analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyzer. Mass spectra analyses were performed with a VG Austospec instrument. In LSIMS$^+$ mode, ions were produced with the standard Cs^+ gun at ca. 30 kV, and 3-nitrobenzyl alcohol (NBA) was used in the matrix.

Preparation of $Os(\eta^5\text{-}C_5H_5)Cl\{[\eta^2\text{-}(E)\text{-}PhCH{=}CHCH_2C(=CH_2)]P^iPr_2\}$ (2). A solution of $Os(\eta^5\text{-}C_5H_5)Cl\{[\eta^2\text{-}CH_2{=}C(CH_3)]P^iPr_2\}$ (**1**) (145 mg, 0.32 mmol) in 9 mL of toluene was treated with PhC≡CH (125 μL, 1.14 mmol) for 7 h. The resulting solution was vacuum-dried, and the residue was washed with pentane (3 × 3 mL). An orange solid was obtained. Yield: 155 mg (87%). Anal. Calcd for $C_{22}H_{30}ClOsP$: C, 47.94; H, 5.49. Found: C, 48.29; H, 5.52. ^1H NMR (300 MHz, C_6D_6, 293 K): δ 7.60−6.90 (5H, Ph); 5.28 (d, 1H, J_{H-P} = 27.0, PC=$CH_{trans\ to\ P}$); 4.93 (d, 1H, J_{H-P} = 11.7, PC=$CH_{cis\ to\ P}$); 4.72 (m, 1H, −C*H*=CHPh); 4.66 (d, 1H, J_{HH} = 9.9, =CHPh); 4.52 (s, 5H, η^5-C_5H_5); 2.71 (m, 1H, one of the PCH); 2.60 (m, 1H, one of the H in $-CH_2-$ group); 2.30 (m, 1H, one of the H in $-CH_2-$ group); 1.87 (m, 1H, one of the PCH); 1.37 (dd, 3H, J_{H-P} = 15.9, J_{H-H} = 7.2, one of the PCHC*H*$_3$); 1.14 (dd, 3H, J_{H-P} = 13.2, J_{H-H} = 7.2, one of the PCHC*H*$_3$); 0.86 (dd, 3H, J_{H-P} = 13.8, J_{H-H} = 7.2, one of the PCHC*H*$_3$); 0.85 (dd, 3H, J_{H-P} = 13.8, J_{H-H} = 7.2, one of the PCHC*H*$_3$). $^{13}C\{^1H\}$ NMR (75.4 MHz, C_6D_6, 293 K, plus APT): δ 151.9 (d, J_{C-P} = 38.2 Hz, P−C=); 150.0 (s, C*ipso* Ph); 128.7, 125.6, and 124.9 (all s, Ph); 117.9 (s, $=CH_2$); 82.1 (s, η^5-C_5H_5); 53.8 (d, J_{C-P} = 2.3, =CHPh); 39.9 (s, −*C*H=CHPh); 39.3 (d, J_{C-P} = 25.3, CH_2); 32.9 (d, J_{C-P} = 31.3, one of the PCH); 23.0 (d, J_{C-P} = 27.7, one of the PCH); 21.1, 20.1, 18.6, and 18.1 (all s CH_3). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6, 293 K): δ 42.5 (s). MS (LSIMS$^+$): *m/z* = 552 (M^+); 515 (M^+ − Cl).

Preparation of $Os(\eta^5\text{-}C_5H_5)Cl\{[\eta^2\text{-}(E)\text{-}PhCH{=}CDCH_2C(=CH_2)]P^iPr_2\}$ (2-d_1). A solution of $Os(\eta^5\text{-}C_5H_5)Cl\{[\eta^2\text{-}CH_2{=}C(CH_3)]P^iPr_2\}$ (**1**) (8 mg, 0.018 mmol) in 0.6 mL of toluene was treated with PhC≡CD (5 μL, 0.045 mmol) for 5 h. The resulting solution was vacuum-dried, and the residue was dissolved in benzene-d_6 (0.5 mL). ^1H NMR (300 MHz, C_6D_6, 293 K): δ 7.60−6.90 (5H, Ph); 5.29 (d, 1H, J_{H-P} = 27.0, PC=$CH_{trans\ to\ P}$); 4.93 (d, 1H, J_{H-P} = 11.4, PC=$CH_{cis\ to\ P}$); 4.67 (s, 1H, =CHPh); 4.52 (s, 5H, η^5-C_5H_5); 2.70 (m, 1H, one of the PCH); 2.60 (dd, 1H, J_{H-P} = 14.7, J_{H-H} = 14.7, one of the H in CH_2); 2.30 (dd, 1H, J_{H-P} = 21.0, J_{H-H} = 14.7, one of the H in CH_2); 1.87 (m, 1H, one of the PCH); 1.37 (dd, 3H, J_{H-P} = 15.9 Hz, J_{H-H} = 7.2 Hz, one of the PCHC*H*$_3$); 1.14 (dd, 3H, J_{H-P} = 13.2, J_{H-H} = 7.2, one of the PCHC*H*$_3$,); 0.86 (dd, 3H, J_{H-P} = 13.8, J_{H-H} = 7.2, one of the PCHC*H*$_3$,); 0.85 (dd, 3H, J_{H-P} = 13.8, J_{H-H} = 7.2, one of the PCHC*H*$_3$). ^2H NMR (46.1 MHz, C_6H_6, 293 K): δ 4.71 (s, CD=CHPh). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6, 293 K): δ 42.5 (s).

Preparation of $Os(\eta^5\text{-}C_5H_5)Cl\{\eta^2\text{-}HC{\equiv}CC(OH)Ph_2\}\{P^iPr_2[C(CH_3){=}CH_2]\}$ (3). A solution of $Os(\eta^5\text{-}C_5H_5)Cl\{[\eta^2\text{-}CH_2{=}C(CH_3)]P^iPr_2\}$ (**1**) (189 mg, 0.42 mmol) in 10 mL of diethyl ether was treated with HC≡C−C(OH)Ph_2 (127 mg, 0.61 mmol) for 30 min. The resulting solution was vacuum-dried, and the residue was washed with pentane (3 × 4 mL). A pink solid was obtained. Yield: 256 mg (92%). Anal. Calcd for $C_{29}H_{36}ClOOsP$: C, 52.99; H, 5.52. Found: C, 53.33; H, 5.63. IR (Nujol, cm^{-1}): ν(O−H) 3331 (f); ν(C≡C) 1808 (s). ^1H NMR (300 MHz, C_6D_6, 293 K): δ 8.10−7.00 (10H, Ph); 6.84 (s, 1H, OH); 5.20 (d, 1H, J_{H-P} = 30.0 Hz, PC=$CH_{trans\ to\ P}$); 4.95 (d, 1H, J_{H-P} = 12.9 Hz, PC=$CH_{cis\ to\ P}$); 4.77 (s, 5H, η^5-C_5H_5); 4.40 (d, 1H, J_{H-P} = 12.6, HC≡); 2.44 (m, 3H, PCH); 1.62 (d, 3H, J_{H-P} = 9.3, P−C(CH_3)=); 0.92 (dd, 6H, J_{H-P} = 14.4, J_{H-H} = 7.2, PCHC*H*$_3$); 0.91 (dd, 6H, J_{H-P} = 14.4, J_{H-H} = 7.2, PCHC*H*$_3$). $^{13}C\{^1H\}$ NMR (75.4 MHz, CD_2Cl_2, 243 K, plus APT): δ 148.2 (s, C*ipso* Ph); 139.6 (d, J_{C-P} = 35.9, PC=); 128.2, 127.3, and 127.0 (all s, Ph); 126.2 (s, $=CH_2$); 88.8, 80.7 and 77.7 (all s, HC≡C−C(OH); 79.3 (s, η^5-C_5H_5); 25.7 (d, J_{C-P} = 30.9, PCH); 23.2 (s, PC(*C*H$_3$)); 19.6 and 19.2 (both s, PCH*C*H$_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6, 293 K): δ 15.9 (s). MS (LSIMS$^+$): *m/z* = 658 (M^+); 639 (M^+ − OH); 623 (M^+ − Cl); 605 (M^+ − OH − Cl).

Preparation of $Os(\eta^5\text{-}C_5H_5)Cl\{[\eta^2\text{-}(E)\text{-}\{Ph_2(OH)C\}CH{=}CHCH_2C(=CH_2)]P^iPr_2\}$ (4). A solution of $Os(\eta^5\text{-}C_5H_5)Cl\{\eta^2\text{-}HC{\equiv}CC(OH)Ph_2\}\{P^iPr_2[C(CH_3){=}CH_2]\}$ (**3**) (91 mg, 0.14 mmol) in 7 mL of toluene was heated to reflux for 6 h. The resulting solution was vacuum-dried, and the residue was washed with pentane (2 × 2 mL). A green solid was obtained. Yield: 67 mg (74%). Anal. Calcd for $C_{29}H_{36}ClOOsP$: C, 52.99; H, 5.52. Found: C, 53.26; H, 5.42. IR (Nujol, cm^{-1}): ν(O−H) 3361 (s). ^1H NMR (300 MHz, C_6D_6, 293 K): δ 8.10−6.90 (10H, Ph); 6.59 (s, 1H, OH); 5.71 (dd, 1H, J_{H-P} = 24.9, J_{H-H} = 1.2, PC=C-$H_{trans\ to\ P}$); 4.89 (dd, 1H, J_{H-P} = 10.8, J_{H-H} = 1.2, PC=$CH_{cis\ to\ P}$); 4.80 (d, 1H, J_{H-H} = 9.3, =C*H*-C(OH),); 4.27 (s, 5H, η^5-C_5H_5); 4.04 (dd, 1H, J_{H-H} = 9.3, J_{H-H} = 4.8, CH_2−C*H*=CH); 3.20 (dd, 1H, J_{H-P} = 31.2, J_{H-H} = 16.2, one of the H in CH_2 group); 2.45 (m, 1H, one of the PCH); 2.19 (dd, 1H, J_{H-H} = 16.2, J_{H-H} = 4.8, one of the H in CH_2 group); 1.64 (m, 1H, one of the PCH); 1.24 (dd, 3H, J_{H-P} = 15.3 Hz, J_{H-H} = 7.2, one of the PCHC*H*$_3$); 1.13 (dd, 3H, J_{H-P} = 15.3 Hz, J_{H-H} = 7.2, one of the PCHC*H*$_3$); 0.69 (dd, 3H, J_{H-P} = 15.3, J_{H-H} = 7.2, one of the PCHC*H*$_3$); 0.45 (dd, 3H, J_{H-P} = 15.3, J_{H-H} = 7.2, one of the PCHC*H*$_3$). $^{13}C\{^1H\}$ NMR (75.4 MHz, CD_2Cl_2, 293 K): δ 152.9, 148.0 (s, C*ipso* Ph); 142.5 (d, J_{C-P} = 33.3, P−C=); 128.5, 128.0, 127.4, 127.1, 126.5, and 126.4 (all s, Ph); 122.1 (s, $=CH_2$); 83.5 (s, η^5-C_5H_5); 61.3 (s, COH); 57.2, and 44.0 (both s, −CH=CH−); 43.8 (d, J_{C-P} = 23.4, CH_2); 32.7 (d, J_{C-P} = 33.3, one of the PCH); 25.5 (d, J_{C-P} = 25.9, one of the PCH); 19.7, 18.2, 17.8, and 16.8 (all s, CH_3). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6, 293 K): δ 34.4 (s). MS (LSIMS$^+$): *m/z* = 658 (M^+); 639 (M^+ − OH); 623 (M^+ − Cl); 605 (M^+ − OH − Cl).

Preparation of $Os(\eta^5\text{-}C_5H_5)(C{\equiv}CPh)\{[\eta^2\text{-}CH_2{=}C(CH_3)]P^iPr_2\}$ (5). A solution of $Os(\eta^5\text{-}C_5H_5)Cl\{[\eta^2\text{-}CH_2{=}C(CH_3)]P^iPr_2\}$ (**1**) (140 mg, 0.31 mmol) in 10 mL of tetrahydrofuran was treated with lithium phenylacetylide (67 mg, 0.62 mmol). The mixture was left to stir for 1 h. The resulting solution was vacuum-dried. The residue was extracted with toluene (15 mL). The resulting solution was vacuum-dried, and the residue was finally washed with methanol (3 × 3 mL). A pale brown solid was obtained. Yield: 107 mg (65%). Anal. Calcd for $C_{22}H_{29}OsP$: C, 51.34; H, 5.68. Found: C, 51.52; H, 5.40. IR (Nujol, cm^{-1}): ν(C≡C) 2083 (s); ν(C=C) 1590 (m). ^1H NMR (300 MHz, C_6D_6, 293 K): δ 7.60−6.90 (5H, Ph); 4.72 (s, 5H, η^5-C_5H_5); 3.48 (dd, 1H, J_{H-P} = 30.3, J_{H-H} = 2.1, PC=$CH_{trans\ to\ P}$); 2.41 (dd, 1H, J_{H-P} = 6.6, J_{H-H} = 2.1, PC=$CH_{cis\ to\ P}$); 2.29 (m, 1H, one of the PCH); 1.62 (m, 1H, one of the PCH); 1.40−1.00 (15H, CH_3). $^{13}C\{^1H\}$ NMR (75.4 MHz, C_6D_6, 293 K, plus APT): δ 132.3, 128.5, 124.2 (all s, Ph); 131.3 (s, C*ipso* Ph); 111.5 (d, J_{C-P} = 3.8, Os−C≡*C*); 85.1 (d, J_{C-P} = 20.3, Os-*C*≡C); 79.4 (s, η^5-C_5H_5); 31.2 (d, J_{C-P} = 18.4, P−C=); 28.7 (d, J_{C-P} = 30.4, one of the PCH); 24.3 (s, one of the CH_3); 24.0 (s, $=CH_2$); 22.7 (d, J_{C-P} = 4.6, one of the CH_3); 22.1 (d, J_{C-P} = 4.6, one of the CH_3); 20.7 (d, J_{C-P} = 2.8, one of the CH_3); 19.1 (d, J_{C-P} = 23.4, one of the

Table 3. Crystal Data and Data Collection and Refinement for 2 and 8

	2	**8**
	Crystal Data	
formula	$C_{22}H_{30}ClOsP$	$C_{22}H_{28}ClOsP\ 0.5(C_5H_{12})$
molecular wt	551.08	585.14
color and habit	orange, irregular block	red, irregular block
symmetry, space group	monoclinic, $P21/n$	triclinic, $P\bar{1}$
a, Å	12.3343(10)	7.6298(5)
b, Å	12.6118(10)	11.3416(7)
c, Å	13.4358(11)	14.0086(8)
α, deg		103.7850(10)
β, deg	95.913(2)	95.9700(10)
γ, deg		91.4870(10)
V, Å^3	2078.9(3)	1169.30(12)
Z	4	2
D_{calc}, g cm^{-3}	1.761	1.662
	Data Collection and Refinement	
diffractometer	Bruker Smart APEX	
λ(Mo Kα), Å	0.71073	
monochromator	graphite oriented	
scan type	ω scans	
μ, mm^{-1}	6.342	5.643
2θ, range, deg	3, 57	3, 57
temp, K	296	100
no. of data collected	24 944	44 897
no. of unique data	4983 (R_{int} = 0.0729)	5449 (R_{int} = 0.0283)
no. of params/ restraints	254/0	257/7
R_1[a][$F^2 > 2\sigma(F^2)$]	0.0297	0.0285
wR_2[b][all data]	0.0402	0.0636
S[c][all data]	0.655	1.009

[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.

PCH); 18.6 (s, one of the CH_3). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6, 293 K): δ −1.85 (s). MS (LSIMS$^+$): *m/z* 515 (M^+).

Preparation of Os(η^5-C_5H_5)(C≡CPh){η^2-HC≡CC(OH)Ph_2}{P^iPr_2[C(CH_3)=CH_2]} (6). A solution of Os(η^5-C_5H_5)(C≡CPh){[η^2-CH_2=C(CH_3)]P^iPr_2} (**5**) (180 mg, 0.35 mmol) in 6 mL of diethyl ether was treated with HC≡C−C(OH)Ph_2 (109 mg, 0.52 mmol) for 30 min. The resulting solution was vacuum-dried, and the residue was washed with pentane (3 × 4 mL). A pale yellow solid was obtained. Yield: 164 mg (65%). Anal. Calcd for $C_{29}H_{36}ClOOsP$: C, 52.99; H, 5.52. Found: C, 53.33; H, 5.63. IR (Nujol, cm^{-1}): ν(O−H) 3310 (s); ν(C≡C) 2075 (s); ν(C=C) 1565 (m). ^1H NMR (300 MHz, C_6D_6, 293 K): δ 8.07−7.05 (m, 15H, Ph); 5.24 (d, 1H, J_{H-P} = 30.3, PC=$CH_{trans\ to\ P}$); 5.03 (d, 1H, J_{H-P} = 12.6, PC=$CH_{cis\ to\ P}$); 4.69 (s, 5H, η^5-C_5H_5); 4.25 (s, 1H, OH); 4.04 (d, 1H, J_{H-P} = 9.3, HC≡); 2.48 (m, 1H, PCH); 2.32 (m, 1H, PCH); 1.63 (d, 3H, J_{H-P} = 8.7, PC(CH_3)=); 1.09 (dd, 3H, J_{H-H} = 7.5, J_{H-P} = 15.0, PCHCH_3); 0.86 (dd, 3H, J_{H-H} = 7.3, J_{H-P} = 12.5, PCHCH_3). $^{13}C\{^1H\}$ NMR (75.4 MHz, C_6D_6, plus APT, plus HSQC): δ 149.6, 148.9 (both s, C*ipso*); 143.2 (d, J_{C-P} = 36.9, PC=); 132.1, 128.4, 128.3, 128.1, 127.2, 127.0, and 126.9 (all s, Ph); 129.6 (s, C*ipso*); 125.3 (s, HC≡); 124.5 (s, =CH_2); 116.5 (s, ≡CPh); 83.0 (s, η^5-C_5H_5); 79.6 (s, CPh_2OH); 78.3 (d, J_{C-P} = 21.6, OsC≡); 75.7 (s, HC≡*C*-C(OH)); 27.2 (d, J_{C-P} = 31.7, PCH); 25.5 (d, J_{C-P} = 33.5, PCH); 20.3 (s, PC(CH_3)); 20.2 and 19.4 (both s, CH_3). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6, 293 K): δ 20.3 (br s). MS (LSIMS$^+$): *m/z* 724 (M^+ + H).

Preparation of Os(η^5-C_5H_5)(C≡CPh){[η^2-(*E*)-{Ph_2(OH)C}-CH=$CHCH_2$C(=CH_2)]P^iPr_2} (7). A solution of Os(η^5-C_5H_5)(C≡CPh){η^2-HC≡CC(OH)Ph_2}{P^iPr_2[C(CH_3)=CH_2]} (**6**) (150 mg, 0.21 mmol) in 7 mL of toluene was heated to reflux for 6 h. The resulting solution was vacuum-dried, and the residue was washed with pentane (2 × 2 mL). A white solid was obtained. Yield: 117 mg (78%). Anal. Calcd for $C_{29}H_{36}ClOOsP$: C, 52.99; H, 5.52. Found: C, 53.26; H, 5.42. IR (Nujol, cm^{-1}): ν(O−H) 3368 (s); ν(C≡C) 2085 (s); ν(C=C) 1594 (m). ^1H NMR (300 MHz, C_6D_6, 293 K): δ 7.83−6.85 (11H, Ph + OH); 5.53 (dd, 1H, J_{H-H} = 2.4, J_{H-P} = 24.3, PC=$CH_{trans\ to\ P}$); 4.62 (dd, 1H, J_{H-H} = 2.4, J_{H-P} = 10.8, PC=$CH_{cis\ to\ P}$); 4.06 (s, 5H, η^5-C_5H_5); 3.60 (d, 1H, J_{H-H} = 9.9, C=CH); 3.43 (dd, 1H, J_{H-H} = 4.5, J_{H-H} = 9.9, HC=C); 2.94 (dd, 1H, J_{H-P} = 30.3, J_{H-H} = 15.6, one of the H in CH_2 group); 2.11 (dd, J_{H-H} = 15.6, J_{H-P} = 4.5, one of the H in CH_2 group); 1.85 (m, 1H, PCH); 1.24 (m, 1H, PCH); 1.09 (dd, 3H, J_{H-P} = 15.6 Hz, J_{H-H} = 6.9, one of the PCHC*H*$_3$); 1.01 (dd, 3H, J_{H-P} = 15.3 Hz, J_{H-H} = 6.9, one of the PCHC*H*$_3$); 0.43 (dd, 3H, J_{H-P} = 12.0, J_{H-H} = 6.6, one of the PCHC*H*$_3$); 0.26 (dd, 3H, J_{H-P} = 14.7, J_{H-H} = 7.2, one of the PCHC*H*$_3$). $^{13}C\{^1H\}$ NMR (75.4 MHz, CD_2Cl_2, plus APT, plus HSQC): δ 152.2, and 148.2 (both s, C*ipso* Ph); 144.1 (d, J_{C-P} = 36.9, PC=); 131.27, 128.7, 128.5, 128.3, 127.9, 127.3, 126.4, 126.3, and 124.8 (all s, Ph); 129.1 (s, C*ipso* Ph); 121.7 (s, =CH_2); 117.5 (s, ≡CPh); 83.3 (s, η^5-C_5H_5); 83.3 (s, COH); 77.1 (d, J_{C-P} = 16.8, OsC≡); 51.2 (s, CH=); 43.6 (d, J_{C-P} = 23.9, CH_2); 37.6 (s, CH=); 32.0 (d, J_{C-P} = 32.7, PCH); 24.2 (d, J_{C-P} = 30.3, PCH); 19.6, 17.6, 17.2, and 16.6 (all s, CH_3). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6, 293 K): δ 38.3 (s). MS (LSIMS$^+$): *m/z* 724 (M^+ + H).

Preparation of Os(η^5-C_5H_5)Cl{=C=CHPh}{P^iPr_2[C(CH_3)=CH_2]} (8). A solution of Os(η^5-C_5H_5)Cl{[η^2-CH_2=C(CH_3)]P^iPr_2} (**1**) (80 mg, 0.18 mmol) in 10 mL of toluene was treated with NEt_3 (0.15 mL, 108 mmol), and after 5 min PhC≡CH was added (125 μL, 1.14 mmol). The mixture was left to stir for 1 h, and the resulting solution was vacuum-dried. The residue was finally washed with pentane (3 × 4 mL), leading to a pale red solid. The compound was purified by crystalization: slow diffusion of pentane over a toluene solution of the isolated solid afforded red crystals. Yield: 72 mg (73%). Anal. Calcd for $C_{22}H_{30}ClOsP$: C, 47.94; H, 5.49. Found: C, 47.91; H, 5.80. IR (Nujol, cm^{-1}): ν(C=C) 1617 (s). ^1H NMR (300 MHz, C_6D_6, 293 K): δ 7.60−6.80 (5H, Ph); 5.26 (d, 1H, J_{H-P} = 31.5, PC=$CH_{trans\ to\ P}$); 5.06 (d, 1H, J_{H-P} = 13.5, PC=$CH_{cis\ to\ P}$); 5.05 (s, 5H, η^5-C_5H_5); 2.82 (s, 1H, Os=C=CH); 2.56 (m, 3H, PCH); 1.83 (d, 3H, J_{H-P} = 9.6, PC(CH_3)=); 1.10−0.90 (12H, PCHC*H*$_3$). $^{13}C\{^1H\}$ NMR (75.4 MHz, C_6D_6, 293 K, plus APT): δ 292.6 (d, J_{C-P} = 14.3, Os=C); 142.2 (d, J_{C-P} = 39.2, P−C=); 131.2 (s, C*ipso* Ph); 128.8, 125.5, and 124.8 (all s, Ph); 125.3 (d, J_{C-P} = 4.6, P−C=*C*H_2); 117.0 (s, =CHPh); 88.7 (s, η^5-C_5H_5); 25.2 (d, J_{C-P} = 11.0, PCH); 20.3 (s, =C*C*H_3); 18.5, 18.3 (both s, CH_3). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6, 293 K): δ 19.5 (s). MS (LSIMS$^+$): *m/z* = 552 (M^+); 515 (M^+ − Cl).

X-ray Analysis of 2 and 8. Two irregular crystals of size 0.12 × 0.12 × 0.10 mm (**2**) and 0.24 × 0.18 × 0.16 mm (**8**) were mounted on a Bruker Smart APEX CCD diffractometer at 296(2) (**2**) and 100.0(2) K (**8**) equipped with a normal focus, 2.4 kW sealed tube source (molybdenum radiation, λ = 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. The cell parameters were determined and refined by least-squares fit of 2872 (**2**) or 6550 (**8**) collected reflections. The first 100 frames were collected at the end of the data collection to monitor crystal decay. Absorption correction was performed with the SADABS program.[21] Lorentz and polarization corrections were also performed. The structures were solved by Patterson and Fourier methods and refined by full matrix least-squares using the Bruker SHELXTL[22] program minimizing $w(F_o^2 - F_c^2)^2$. The hydrogen atoms were observed or calculated and refined riding to bonded carbon atoms. For **8** a molecule of disorder pentane

(21) Blessing, R. H. *Acta Crystallogr., Sect. A* **1995**, *51*, 33. *SADABS*, Area-detector absorption correction; Bruker-AXS: Madison, WI, 1996.

(22) *SHELXTL* Package, v. 6.1; Bruker Analytical, X-ray Systems: Madison, WI, 2000.

was observed in the unit cell. Weighted R factors (R_w) and goodness of fit (S) are based on F^2, and conventional R factors are based on F.

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

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