# Preparation and Characterization of a Monocyclopentadienyl Osmium−Allenylcarbene Complex

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The dihydride−dihydrogen complex $[OsH_2(\eta^5\text{-}C_5H_5)(\eta^2\text{-}H_2)(P^iPr_3)]BF_4$ (**1**) reacts with phenylacetylene to give the allenylcarbene derivative $[Os(\eta^5\text{-}C_5H_5)\{{=}CPh(\eta^2\text{-}CH{=}C{=}CHPh)\}(P^iPr_3)]BF_4$ (**2**) via the $\pi$-phenylacetylene intermediate $[Os(\eta^5\text{-}C_5H_5)(\eta^2\text{-}PhC{\equiv}CH)(P^iPr_3)]BF_4$ (**3**). The reactions of **2** with NaOMe and LiC≡CPh afford 3:1 mixtures of two hydride−osmaindene isomers of formula $OsH(\eta^5\text{-}C_5H_5)\{C(C{\equiv}CPh){=}CHC_6H_4\}(P^iPr_3)$ (**4** and **5**) instead of the expected osmabenzyne complex.

## Introduction

The reactions of osmium hydride complexes with alkynes afford a wide range of organometallic compounds. Their nature depends on both the electronic structure of the starting materials and the electronic character of the substituents of the alkynes.[1]

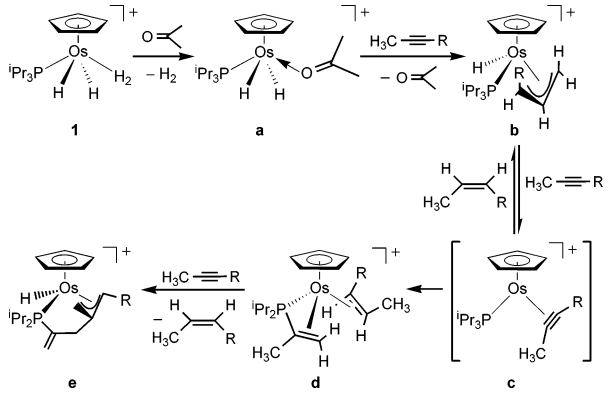
The dihydride−dihydrogen complex $[OsH_2(\eta^5\text{-}C_5H_5)(\eta^2\text{-}H_2)(P^iPr_3)]BF_4$ (**1**) reacts in acetone with 1-phenyl-1-propyne and 2-butyne to give $[OsH(\eta^5\text{-}C_5H_5)\{\kappa^4\text{-}(P,C,C,C)\text{-}CH_2C\text{-}[CH_2C({=}CH_2)P^iPr_2]CHR\}]BF_4$ (R = Ph, $CH_3$) derivatives (**e** in Scheme 1), containing a $\gamma$-($\eta^3$-allyl)-α-alkenylphosphine. These novel ligands are the result of one-pot dehydrogenative additions of an isopropyl group of triisopropylphosphine to the corresponding alkyne.[2]

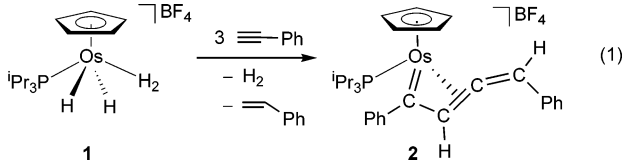
These reactions are tandem processes of four steps (Scheme 1). The first of them involves the dissociation of a dihydrogen ligand from the osmium atom of the starting compound and the stabilization of the resulting unsaturated dihydride with a solvent molecule to form $[OsH_2(\eta^5\text{-}C_5H_5)(\kappa^1\text{-}OCMe_2)(P^iPr_3)]BF_4$ (**a**). During the second one, the displacement of the acetone molecule by an alkyne and the subsequent reduction of the hydrocarbon to give allyl derivatives **b** take place. The third reaction generates isopropenyldi(isopropyl)phosphine species **d** as a consequence of the elimination of *Z*-olefin from the allyl intermediate and a hydrogen transfer from an isopropyl substituent of triisopropylphosphine to a second alkyne molecule of an undetected species **c**.[3] In the fourth step a third alkyne displaces the coordinated olefin from the osmium atom, and it is coupled with the isopropenyl group of the α-alkenylphosphine, to afford the $\gamma$-($\eta^3$-allyl)-α-alkenylphosphine derivatives **e** through ene-type reactions via osmacyclopentene intermediates.[4]

## Results and Discussion

Terminal alkynes, in contrast to 1-phenyl-1-propyne and 2-butyne, have the capacity of forming vinylidene species.[5] As a consequence of this, they quench the third step of the tandem process shown in Scheme 1. Thus, the treatment at 50 °C of acetone solutions of **1** with 3.6 equiv of phenylacetylene for 12 h leads to the allenylcarbene $[Os(\eta^5\text{-}C_5H_5)\{{=}CPh(\eta^2\text{-}CH{=}C{=}CHPh)\}(P^iPr_3)]BF_4$ (**2**) instead of a $\gamma$-($\eta^3$-allyl)-α-alkenylphosphine derivative. This compound is isolated as a brown solid in 56% yield (eq 1).

**Scheme 1**





(1)

The formation of **2** according to eq 1 is notable. Although allenylcarbene complexes have been often proposed as key intermediates for the metal-catalyzed polymerization of terminal alkynes,[6] very few examples of such species have been previously isolated.[7] For osmium, Jia and co-workers[8] have reported

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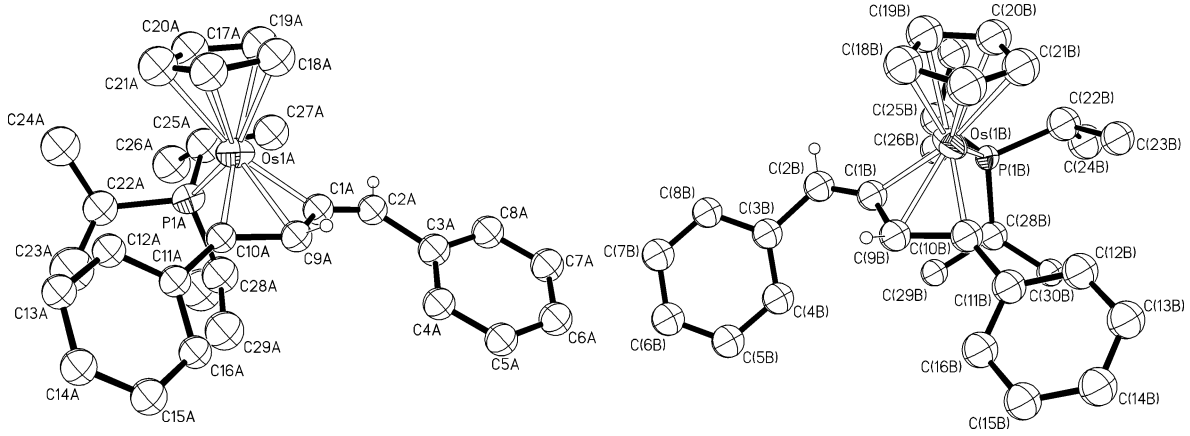


**Figure 1.** Molecular diagram of **2** (cations **A** (left) and **B** (right)), with thermal ellipsoids drawn at the 50% probability level.

**Table 1. Selected Bond Distances (Å) and Angles (deg) for Complex 2 and $OsCl_2\{=CPh(\eta^2\text{-}CH=C=CHPh)\}(PPh_3)_2$ (Jia's Complex)**

| | cation **A** | Jia's complex[a] |
|---|---|---|
| Os−C(1) | 2.015(16) | 2.067(11) |
| Os−C(9) | 2.185(11) | 2.167(11) |
| Os−C(10) | 1.962(15) | 1.894(9) |
| C(1)−C(2) | 1.313(18) | 1.316(16) |
| C(1)−C(9) | 1.420(17) | 1.441(15) |
| C(9)−C(10) | 1.419(17) | 1.437(15) |
| C(1)−C(9)−C(10) | 115.7(10) | 115.9(10) |
| C(1)−Os−C(10) | 74.4(6) | 75.9(4) |
| C(2)−C(1)−C(9) | 134.6(13) | 139.5(11) |

[a] From ref 8b.

that reaction of the vinylidene starting compound $OsCl_2(=C=CHPh)(PPh_3)_2$ with phenylacetylene affords the bisphosphine derivative $OsCl_2\{=CPh(\eta^2\text{-}CH=C=CHPh)\}(PPh_3)_2$. Complex **2** is the first example of a monocyclopentadienyl−osmium compound with an allenylcarbene ligand.

The allenylcarbene derivative **2** was characterized by elemental analysis, MS, IR, and $^1H$, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy. Furthermore, its structure was confirmed by X-ray diffraction analysis. The unit cell contains disordered cations **A** and **B** occupying two alternative orientations in the same region, each showing the stereochemistry illustrated in Figure 1 with approximate occupancy factors of 57% (enantiomer **A**) and 43% (enantiomer **B**) (see Supporting Information). The Os−C and C−C distances within the Os−allenylcarbene unit compare well with those previously reported for Jia's complex $OsCl_2\{=CPh(\eta^2\text{-}CH=C=CHPh)\}(PPh_3)_2$ (Table 1). The Os−C(10) bond length of 1.962(15) Å supports the Os−C double-bond formulation.[9] The Os−C(9) (2.185(11) Å) and Os−C(1) (2.015(16) Å) distances agree with those found in osmium−olefin complexes,[10] whereas the C(9)−C(1) bond length (1.420(17) Å) lies within the range reported for olefin−transition-metal derivatives (1.340−1.455 Å).[11] The C(9)−C(10) distance of 1.419(17) Å is similar to the C(1)−C(9) bond length, indicating the presence of substantial $\pi$-electron delocalization within the Os−C(10)−C(9)−C(1) metallacycle.

The $^1H$ and $^{13}C\{^1H\}$ NMR spectra of **2** are consistent with the structures shown in Figure 1. In the $^1H$ NMR spectrum, the C(9)−H and C(2)−H resonances appear at 3.34 and 6.76 ppm, respectively, whereas in the $^{13}C\{^1H\}$ NMR spectrum the three Os-bound carbon signals are observed at 256.9 (C(10)), 142.2 (C(1)), and 31.1 (C(9)) ppm. A singlet at 22.2 ppm in the $^{31}P\{^1H\}$ NMR spectrum is also characteristic of this compound.

The formation of **2** can be rationalized according to Scheme 2. As in the reactions with 1-phenyl-1-propyne and 2-butyne, the dissociation of a dihydrogen ligand from the starting complex should afford **a**. This dihydride−solvento compound could undergo abstraction of the hydride ligands by action of an alkyne molecule. The reaction should lead to styrene and a highly unsaturated metal fragment, which could coordinate an alkyne molecule to give $[Os(\eta^5\text{-}C_5H_5)(\eta^2\text{-}PhC\equiv CH)(P^iPr_3)]BF_4$ (**3**). This species is the phenylacetylene counterpart to those proposed as intermediates for the formation of complexes **e** by reaction of the allyls **b** with a second molecule of internal alkyne (**c** in Scheme 1). In contrast to 1-phenyl-1-propyne and 2-butyne, where the coordinated alkyne is displaced by *Z*-$CH(CH_3)$=CHR or is reduced by the phosphine, intermediate **3** should coordinate a new phenylacetylene molecule, now as vinylidene, to give **f**. Thus, this vinylidene−$\pi$-alkyne species could generate **2** via a

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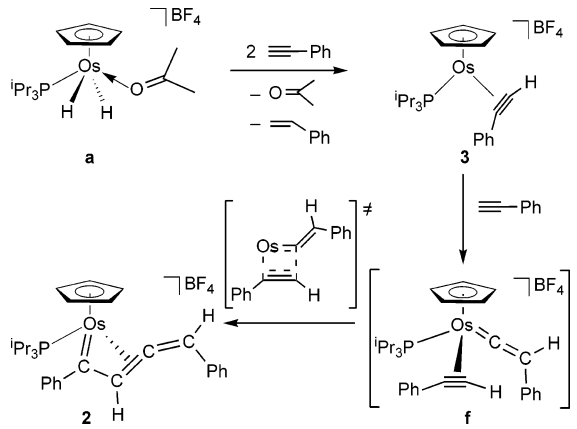
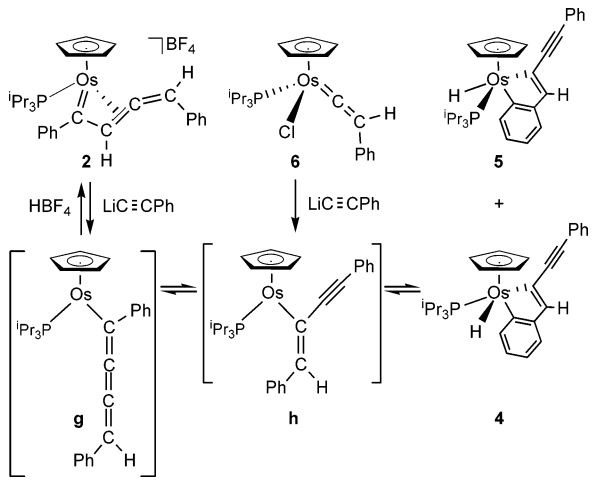
**Scheme 2**



**Scheme 3**



[2+2] cycloaddition reaction between the C−C triple bond of the alkyne and the Os−C vinylidene double bond. We note that Grubbs has previously reported a related process on a ruthenium−carbene complex, which yields a $\eta^3$-vinylcarbene derivative.[12] Tungsten−$\eta^3$-vinylcarbene complexes have also been formed from carbene intermediates upon addition of phenylacetylene.[13] A molybdenum $\eta^3$-iminiumvinylcarbene complex has been obtained via intramolecular reaction of an iminocarbene intermediate with diphenylacetylene.[14] Both the fact that styrene cannot form an allyl ligand related to those of **b** and the trend of phenylacetylene to afford vinylidene complexes can explain the difference in behavior between the internal and terminal alkynes.

The proposal summarized in Scheme 2 is strongly supported by the reaction of **a** with 2.0 equiv of phenylacetylene, in dichloromethane at 0 °C. Under these conditions, in addition to styrene, a mixture of the starting dihydride **a**, **3**, and **2** in a 1:5:1 molar ratio is formed after 30 min. As expected the treatment of the mixture with a third alkyne molecule affords **2**.

Complex **3** is the first member of the novel $[Os(\eta^5\text{-}C_5H_5)(\eta^2\text{-}RC{\equiv}CH)(P^iPr_3)]^+$ series where the $\pi$-alkyne is not an alkynol.[15] The $^1H$ and $^{13}C\{^1H\}$ NMR spectra strongly support the presence of a $\pi$-alkyne group acting as a four-electron donor ligand[16] in the complex. In the $^1H$ NMR spectrum the most noticeable resonance is that corresponding to the C(sp)−H proton, which appears at 10.35 ppm as a doublet with a H−P coupling constant of 27.8 Hz. In accordance with the chemical shifts found for other osmium complexes where the alkyne also acts as a four-electron donor ligand,[10h,15,17] the acetylenic resonances in the $^{13}C\{^1H\}$ NMR spectrum are observed at 167.2 (CPh) and 149.7 (CH) ppm as doublets with C−P coupling constants of 3 and 19 Hz, respectively. A singlet at 19.7 ppm in the $^{31}P\{^1H\}$ NMR spectrum is also characteristic of this compound.

There is a marked difference in behavior between Jia's allenylcarbene and **2**. Complex $OsCl_2\{{=}CPh(\eta^2\text{-}CH{=}C{=}CHPh)\}(PPh_3)_2$ reacts with phenylacetylene in the presence of triethylamine and with $PPh_3AuC{\equiv}CPh$ in the presence of $[HNEt_3]Cl$ to give, in both cases, the osmabenzyne derivative $OsCl_2\{{\equiv}C-C(Ph){=}C(CH_2Ph)-CH{=}C(Ph)\}(PPh_3)_2$.[8b] Under the same conditions, complex **2** affords a 3:1 mixture of two hydride−osmaindene stereoisomers of formula $OsH(\eta^5\text{-}C_5H_5)\{C(C{\equiv}CPh){=}CHC_6H_4\}(P^iPr_3)$ (**4** and **5** in Scheme 3), which are also obtained by treatment of **2** with LiC≡CPh or NaOMe in tetrahydrofuran. The deprotonation is reversible. The addition of 1.0 equiv of $HBF_4{\cdot}Et_2O$ to a dichloromethane solution of **4** and **5** regenerates **2**.

In agreement with the presence of a hydride ligand in **4** and **5**, the $^1H$ NMR spectrum of the isomeric mixture in benzene-$d_6$ at 20 °C shows two doublets at −13.48 (**4**) and −13.55 (**5**) ppm, with H−P coupling constants of 44.9 and 46.7 Hz, respectively, which support the *cisoid* disposition of the hydride and phosphine ligands.[18] In the low-field region of the spectrum, the most noticeable resonances are a doublet at 8.03 ($J_{H-P}$ = 3.4 Hz; **4**) and a singlet at 8.13 (**5**) ppm, corresponding to the $C_\beta$−H hydrogen atoms of the alkenyl units of the metallacycles. In the $^{13}C\{^1H\}$ NMR spectrum, the resonances due to the alkenyl carbon atoms of **4** appear at 157.0 ($C_\beta$) and 119.2 ($C_\alpha$) ppm as doublets with C−P coupling constants of 4 and 16 Hz, respectively, which support the *cisoid* disposition of the phosphine to this alkenyl unit.[19] The metalated carbon atom of the phenyl group gives rise to a doublet at 152.7 ppm with a C−P coupling constant of 4 Hz. The resonances due to the alkenyl carbon atoms of **5** are observed at 151.6 ($C_\beta$) and 127.1 ($C_\alpha$) as doublets. The values of the C−P coupling constants of 2 and 6 Hz, respectively, are consistent with a *transoid* disposition between the phosphine and the alkenyl unit. For this isomer, the resonance corresponding to the metalated carbon atom of the phenyl group appears at 145.3 ppm as a doublet with a C−P coupling constant of 16 Hz. The $^{31}P\{^1H\}$ NMR spectrum shows singlets at 18.3 (**4**) and 18.4 (**5**) ppm. These spectroscopic data

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agree well with those previously reported for the related complex $OsH(\eta^5\text{-}C_5H_4SiPh_3)\{CH{=}C(CH_3)C_6H_4\}(P^iPr_3)$, where the osmaindene nature of the metallabicycle has been stablished by X-ray diffraction analysis.[20]

The formation of **4** and **5** instead of an osmabenzyne derivative appears to be a consequence of the electronic nature of the metal fragment $[Os(\eta^5\text{-}C_5H_5)(P^iPr_3)]^+$, which decreases the p$K_a$ of the allenylcarbene ligand with regard to that coordinated to $OsCl_2(PPh_3)_2$. The deprotonation of the C(9) carbon atom of **2** should generate a buta-1,2,3-trien-4-yl ligand, which could undergo rearrangement into but-1-en-3-yn-2-yl by a 1,3-shift of the metal (Scheme 3). The equilibrium between both types of isomers has been proposed as the key step for the dimerization of terminal alkynes to butatrienes.[21] The subsequent *ortho*-CH bond activation of the phenyl substituent of the alkenyl unit of the resulting intermediate **h** should afford **4** and **5**.

The participation of **h** is strongly supported by the fact that the isomeric mixture is also formed from the treatment of the vinylidene complex $Os(\eta^5\text{-}C_5H_5)Cl(=C{=}CHPh)(P^iPr_3)$ (**6**) with LiC≡CPh in tetrahydrofuran, in agreement with our previous observation that **6** reacts with RMgCl to give the osmaindene derivatives $OsH(\eta^5\text{-}C_5H_5)\{C(R){=}CHC_6H_4\}(P^iPr_3)$ (R = Me, Et, Ph) via $Os(\eta^5\text{-}C_5H_5)\{C(R){=}CHPh\}(P^iPr_3)$ intermediates[22] related to **h** (R = C≡CPh).

In conclusion, in contrast to 1-phenyl-1-propyne and 2-butyne, phenylacetylene reacts with the dihydride−dihydrogen complex $[OsH_2(\eta^5\text{-}C_5H_5)(\eta^2\text{-}H_2)(P^iPr_3)]BF_4$ to afford an allenylcarbene derivative via a $\pi$-phenylacetylene intermediate, where the alkyne acts as a four-electron-donor ligand. This novel compound, which is the first monocyclopentadienyl osmium complex with an allenylcarbene group, undergoes deprotonation in the presence of LiC≡CPh to generate a mixture of hydride−osmaindene isomers instead of giving an osmabenzyne, as is done by Jia's previously reported allenylcarbene complex.

## Experimental Section

**General Procedures.** All reactions were carried out under argon with rigorous exclusion of air using Schlenk-tube or glovebox techniques. Solvents were dried by the usual procedures and distilled under argon prior to use. The starting materials, **1**,[23] **a**,[2] and **6**,[24] were prepared by the published methods. In the NMR spectra chemical shifts (expressed in ppm) are referenced to residual solvent peaks ($^1$H, $^{13}$C) or external $H_3PO_4$ ($^{31}$P). Coupling constants, *J*, are given in hertz.

**Preparation of $[Os(\eta^5\text{-}C_5H_5)\{=CPh(\eta^2\text{-}CH{=}C{=}CHPh)\}(P^iPr_3)]BF_4$ (2). Method a.** A solution of **1** (300 mg, 0.59 mmol) in 4 mL of acetone was treated with phenylacetylene (233 $\mu$L, 2.12 mmol). The solution was allowed to react for 12 h at 50 °C, and then, it was concentrated to ca. 1 mL under reduced pressure. The addition of diethyl ether caused the formation of a brown solid, which was separated by decantation, washed with pentane, and dried in vacuo. The residue was recrystallized from acetone/diethyl ether. Yield: 235 mg (56%).

**Method b.** A solution of **a** (202 mg, 0.36 mmol) in 4 mL of dichloromethane was treated with phenylacetylene (140 $\mu$L, 1.28 mmol). The solution was allowed to react for 30 min at room temperature, and then, it was concentrated to ca. 1 mL under reduced pressure. The addition of diethyl ether caused the formation of a brown solid, which was separated by decantation, washed with pentane, and dried in vacuo. The solid was redissolved in dichloromethane, and the solution was allowed to react for 30 min at 50 °C. Then, it was concentrated to ca. 1 mL under reduced pressure. The addition of diethyl ether caused the formation of a brown solid, which was separated by decantation, washed with pentane, and dried in vacuo. Yield: 208 mg (82%). GC-MS and $^1$H NMR analysis of the mother liquor showed the presence of styrene. Anal. Calcd for $C_{30}H_{38}BF_4OsP$: C, 50.99; H, 5.42. Found: C, 50.53; H, 5.17. IR (ATR, cm$^{-1}$): $\nu$(Ph) 1588 (w). $^1$H NMR (400 MHz, $(CD_3)_2CO$, 298 K): $\delta$ 8.65 (d, $J_{H-H}$ = 7.8, 2H, Ph), 8.11 (t, $J_{H-H}$ = 7.8, 1H, Ph), 7.73 (t, $J_{H-H}$ = 7.8, 2H, Ph), 7.67 (d, $J_{H-H}$ = 7.8, 2H, Ph), 7.47 (t, $J_{H-H}$ = 7.8, 2H, Ph), 7.24 (t, $J_{H-H}$ = 7.8, 1H, Ph), 6.76 (dd, $J_{H-P}$ = 2.5, $J_{H-H}$ = 2.5, 1H, =C*H*Ph), 6.09 (s, 5H, $C_5H_5$), 3.34 (dd, $J_{H-P}$ = 2.5, $J_{H-H}$ = 2.5, 1H, $\eta^2$-C*H*=C), 2.68 (m, 3H, PCH), 1.18 (dd, $J_{H-P}$ = 15.2, $J_{H-H}$ = 7.1, 9H, PCH$CH_3$), 1.07 (dd, $J_{H-P}$ = 14.9, $J_{H-H}$ = 7.1, 9H, PCH$CH_3$). $^{31}$P{$^1$H} NMR (161.99 MHz, $(CD_3)_2CO$, 298 K): $\delta$ 22.2 (s). $^{13}$C{$^1$H} NMR (100.56 MHz, $(CD_3)_2CO$, 298 K): $\delta$ 256.9 (d, $J_{C-P}$ = 7, Os=*C*Ph), 144.5 (s, $C_{ipso}$-Ph), 142.2 (d, $J_{C-P}$ = 13, $\eta^2$-CH=*C*) 137.8 (s, $C_{ipso}$Ph), 137.3, 136.4, 132.9, 130.4, and 129.2 (all s, Ph), 128.9 (d, $J_{C-P}$ = 2, =*C*HPh) 128.5 (s, Ph), 89.0 (s, $C_5H_5$), 31.1 (s, $\eta^2$-*C*H=C), 31.1 (d, $J_{C-P}$ = 30, PCH), 21.1 (s, PCH*C*H$_3$), 20.7 (d, $J_{C-P}$ = 2, PCH*C*H$_3$). MS (MALDI-TOF): *m*/*z* 621.3 ($M^+$).

**Reaction of a with Phenylacetylene: Formation of $[Os(\eta^5\text{-}C_5H_5)(\eta^2\text{-}HC{\equiv}CPh)(P^iPr_3)]BF_4$ (3).** A solution of **a** (152 mg, 0.27 mmol) in 4 mL of dichloromethane was cooled to 0 °C, and then, phenylacetylene (75 $\mu$L, 0.68 mmol) was added. The reaction mixture was stirred for 30 min. After that, the solution was concentrated to ca. 1 mL under reduced pressure. The resultant brown solution was cooled to −70 °C, and diethyl ether was added. Immediately, a brown solid appeared, which was separated by decantation, washed with pentane, and dried in vacuo. The NMR spectra showed the presence of **a**, **3**, and **2** in a 1:5:1 molar ratio. Spectroscopic data for **3**: $^1$H NMR (500 MHz, $CD_2Cl_2$, 293 K): $\delta$ 10.35 (d, $J_{H-P}$ = 27.8, 1H, ≡C−H), 7.75−7.60 (m, 5H, Ph), 5.34 (s, 5H, $C_5H_5$), 2.84 (m, 3H, PCH), 1.14 (dd, $J_{H-P}$ = 14.2, $J_{H-H}$ = 7.1, 18H, PCH$CH_3$). $^{31}$P{$^1$H} NMR (121.49 MHz, $CD_2Cl_2$, 243 K): $\delta$ 38.3 (s). $^{13}$C{$^1$H} NMR (75.47 MHz, $CD_2Cl_2$, 243 K): $\delta$ 167.2 (d, $J_{C-P}$ = 3, ≡*C*Ph), 149.7 (d, $J_{C-P}$ = 19, ≡*C*H) 134.3 (s, $C_{ipso}$Ph), 132.2, 131.5, and 129.6 (all s, Ph), 76.9 (s, $C_5H_5$), 28.1 (d, $J_{C-P}$ = 34, PCH), 19.7 (s, PCH*C*H$_3$). HRMS *m*/*z* 519.182057 ($M^+$), calcd for $[C_{22}H_{32}OsP]^+$: 519.185156.

**Preparation of $OsH(\eta^5\text{-}C_5H_5)\{C(C{\equiv}CPh){=}CHC_6H_4\}(P^iPr_3)$ (4 and 5). Method a.** THF (5 mL) was added to a mixture of 180 mg (0.26 mmol) of **2** and NaOMe (20 mg, 0.37 mmol) or LiC≡CPh (32 mg, 0.30 mmol). The solution was allowed to react for 12 h at room temperature. Then, the solvent was removed, and the crude reaction mixture was extracted with pentane and filtered through Celite. The solution was concentrated to dryness, and a dark brown solid was obtained. The NMR spectra in $C_6D_6$ at room temperature showed the presence of **4** and **5** in a molar ratio of 3:1. Yield of the mixture: 113 mg (72%).

**Method b.** The same procedure described in method a was followed, except that **6** (710 mg, 1.28 mmol) and LiC≡CPh (138 mg, 1.28 mmol) were used. Yield: 505 mg (64%). IR (ATR, cm$^{-1}$): $\nu$(OsH) and $\nu$(C≡C) 2157 (m), 2092 (w), $\nu$(Ph) 1594 (m). Spectroscopic data for **4**: $^1$H NMR (400 MHz, $C_6D_6$, 293 K): $\delta$ 8.07 (d, $J_{H-H}$ = 7.5, 1H, $C_6H_4$), 8.03 (d, $J_{H-P}$ = 3.4, 1H, =C*H*),

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7.65−7.52 (m, 3H, 1H for $C_6H_4$ and 2H for Ph), 7.15−7.00 (m, 4H, 1H for $C_6H_4$ and 3H for Ph), 6.87 (t, $J_{H-H}$ = 7.5, 1H, $C_6H_4$), 4.81 (s, 5H, $C_5H_5$), 2.31 (m, 3H, PCH), 0.90 (dd, $J_{H-P}$ = 14.2, $J_{H-H}$ = 7.0, 9H, PCHC*H*$_3$), 0.77 (dd, $J_{H-P}$ = 12.6, $J_{H-H}$ = 7.1, 9H, PCHC*H*$_3$), −13.48 (d, $J_{H-P}$ = 44.9, 1H, Os−H). $^{31}P\{^1H\}$ NMR (161.99 MHz, $C_6D_6$, 293 K): $\delta$ 18.3 (s). $^{13}C\{^1H\}$ NMR (100.56 MHz, $C_6D_6$, 293 K): $\delta$ 160.8 (d, $J_{C-P}$ = 3, $C_{ipso}C_6H_4$), 157.0 (d, $J_{C-P}$ = 4, =*C*H), 152.7 (d, $J_{C-P}$ = 4, $C_\alpha$ in Os−$C_6H_4$), 146.4 (s, $C_6H_4$), 131.4, 128.6, and 126.7 (all s, Ph), 124.3, 123.1, and 122.4 (all s, $C_6H_4$), 119.2 (d, $J_{C-P}$ = 16, Os−*C*(C≡)), 104.7 (d, $J_{C-P}$ = 3, Os−C(*C*≡)), 92.9 (s, ≡*C*−Ph), 84.1 (d, $J_{C-P}$ = 2, $C_5H_5$), 28.9 (d, $J_{C-P}$ = 30, PCH), 21.1 (s, PCH*C*H$_3$), 19.0 (d, $J_{C-P}$ = 3, PCH*C*H$_3$). $C_{ipso}$Ph could not be assigned. Spectroscopic data for **5**: $^1H$ NMR (400 MHz, $C_6D_6$, 293 K): $\delta$ 8.13 (s, 1H, =C*H*), 7.65−7.52 (m, 4H, 2H for $C_6H_4$ and 2H for Ph), 7.15−7.00 (m, 4H, 1H for $C_6H_4$ and 3H for Ph), 6.84 (t, $J_{H-H}$ = 7.6, 1H, $C_6H_4$), 4.89 (s, 5H, $C_5H_5$), 2.13 (m, 3H, PCH), 0.86 (dd, $J_{H-P}$ = 14.0, $J_{H-H}$ = 7.2, 9H, PCHC*H*$_3$), 0.64 (dd, $J_{H-P}$ = 12.4, $J_{H-H}$ = 7.1, 9H, PCHC*H*$_3$), −13.55 (d, $J_{H-P}$ = 46.7, 1H, Os−H). $^{31}P\{^1H\}$ NMR (161.99 MHz, $C_6D_6$, 293 K): $\delta$ 18.4 (s). $^{13}C\{^1H\}$ NMR (100.56 MHz, $C_6D_6$, 293 K): $\delta$ 163.0 (d, $J_{C-P}$ = 2, $C_{ipso}C_6H_4$), 151.6 (d, $J_{C-P}$ = 2, =*C*H), 145.3 (d, $J_{C-P}$ = 16, $C_\alpha$ in Os−$C_6H_4$), 143.3 (d, $J_{C-P}$ = 3, $C_6H_4$), 131.4 and 128.5 (both s, Ph), 127.1 (d, $J_{C-P}$ = 6, Os−*C*(C≡)), 126.7 (s, Ph), 123.5 and 123.0 (both d, $J_{C-P}$ = 2, $C_6H_4$), 121.3 (s, $C_6H_4$), 107.0 (s, Os−C(*C*≡)), 92.9 (s, ≡*C*−Ph), 83.4 (d, $J_{C-P}$ = 2, $C_5H_5$), 27.5 (d, $J_{C-P}$ = 30, PCH), 20.7 (s, PCH*C*H$_3$), 18.7 (d, $J_{C-P}$ = 3, PCH*C*H$_3$). $C_{ipso}$Ph could not be assigned. HRMS *m*/*z* 621.229558 ($M^+$ + H), calcd for $[C_{30}H_{38}OsP]^+$: 621.232160.

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**Supporting Information Available:** Crystal structure determination and CIF file giving crystal data for compound **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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