# Dehydrogenation of a Coordinated Alkylphosphine as a Method to Prepare Cyclopentadienyl-α-alkenylphosphine-osmium Complexes

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The $\pi$-alkyne complex Os($\eta^5$-$C_5H_5$)Cl($\eta^2$-PhC≡CPh)($P^iPr_3$) (**2**) has been prepared by a two-step procedure involving the oxidative addition of $H_2$ to Os($\eta^5$-$C_5H_5$)Cl($P^iPr_3$)$_2$ (**1**) and the subsequent reaction of the resulting dihydride with diphenylacetylene. In methanol, complex **2** evolves to give the isopropenyldi(isopropyl)phosphine derivative Os($\eta^5$-$C_5H_5$)Cl{[$\eta^2$-$CH_2$=C($CH_3$)]$P^iPr_2$} (**4**) and *Z*-stilbene, by hydrogen transfer from one isopropyl group of the triisopropylphosphine to diphenylacetylene. When the hydrogen transfer reaction is carried out in the presence of $KPF_6$, the cationic *Z*-stilbene compound [Os($\eta^5$-$C_5H_5$){$\eta^2$-(*Z*)-PhCH=CHPh}{[$\eta^2$-$CH_2$=C($CH_3$)]$P^iPr_2$}]$PF_6$ (**5**) is formed. The isopropenyldi(isopropyl)-phosphine ligand of **4** and **5** shows hemilabile properties. The hemilabile character of the isopropenyl substituent of the phosphine of **4** is revealed by the reaction of this complex with $H_2$, which yields an equilibrium mixture of the starting compound and the *transoid*-dihydride $OsH_2$($\eta^5$-$C_5H_5$)Cl{$P^iPr_2$[C($CH_3$)=$CH_2$]} (**6**). The hemilabile character of the phosphine of **5** is shown in the reaction of this compound with MeLi, which affords OsH($\eta^5$-$C_5H_4CH_3$){$\eta^2$-(*Z*)-PhCH=CHPh}{$P^iPr_2$[C($CH_3$)=$CH_2$]} (**7**). In the solid state and in solution the *Z*-stilbene ligand of **7** isomerizes to give OsH($\eta^5$-$C_5H_4CH_3$){$\eta^2$-(*E*)-PhCH=CHPh}{$P^iPr_2$-[C($CH_3$)=$CH_2$]} (**8**). Complexes **5** and **8** have been characterized by X-ray diffraction analysis.



## Introduction

The activation of C−H bonds by transition metal compounds is a type of reaction of general interest due to its connection with the functionalization of nonactivated molecules. An example is the dehydrogenation of alkanes or alkyl groups to produce olefins. The equilibrium is shifted to the right by adding a hydrogen acceptor, such as an olefin or carbonyl compound.[1]

α-Alkenylphosphines are a type of ligand that is attracting increased attention in the chemistry of the metals. They can act as monodentated ligands,[2] can bridge to two metal centers,[3] and can act as chelating ligands.[4]

In addition, the reversible coordination−decoordination of the olefinic group gives them hemilabile properties. As a result, under appropriate conditions, they can stabilize highly reactive intermediates.[5]

The formation of transition metal complexes containing cycloalkenylphosphine ligands by dehydrogenation of coordinated cycloalkylphosphines is a well-known process.[1,6] However, the dehydrogenation of coordinated acyclic alkylphosphines to afford the corresponding transition metal α-alkenylphosphine complexes is scarcely documented. Complex $OsH_2Cl_2(P^iPr_3)_2$ reacts with 2.0 equiv of 1,5-cyclooctadiene or 2,5-norbornadiene to give 1.0 equiv of monoolefin and the isopropenyldi(isopropyl)phosphine derivatives $OsCl_2$($\eta^4$-diolefin){[$\eta^2$-$CH_2$=C($CH_3$)]$P^iPr_2$} (diolefin = COD, NBD).[7] At room temperature, the reactions of the elongated dihydrogen

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complexes $[Os\{C_6X_4C(O)CH_3\}(\eta^2\text{-}H_2)(H_2O)(P^iPr_3)_2]BF_4$ (X = H, F) with phenylacetylene lead to a mixture of compounds containing the 1,4-diphenylbutadiene derivative $[OsH(\eta^4\text{-}C_4H_4Ph_2)\{[\eta^2\text{-}CH_2{=}C(CH_3)]P^iPr_2\}(P^iPr_2{}^nPr)]BF_4$. The diene of this compound is the result of the reductive condensation of two alkyne molecules. The reductor is one of the triisopropylphosphines, which undergoes dehydrogenation of one of the isopropyl groups, to afford the monoisopropenylphosphine.[8] Treatment of the tetrahydride $OsH_4Cl(SnPh_3)(P^iPr_3)_2$ with diphenylacetylene gives rise to the trihydride-isopropenyldi(isopropyl)phosphine derivative $OsH_3(SnClPh_2)\{[\eta^2\text{-}CH_2{=}C(CH_3)]P^iPr_2\}(P^iPr_3)$ in a one-pot synthesis via multiple complex reactions, including the dehydrogenation of one isopropyl group of one phosphine.[9] This trihydride activates an *ortho*-CH bond of aromatic compounds to afford reminiscent species of the intermediates proposed by Murai for the insertion of olefins into aromatic *ortho*-CH bonds of ketones and imines.[10]

The chemistry of the half-sandwich pentamethylcyclopentadienyl-[11] and cyclopentadienylosmium[12] complexes has attracted much less attention than that of the related half-sandwich ruthenium complexes,[13] in particular, the chemistry of the $Os(\eta^5\text{-}C_5H_5)$ unit. Thus, cyclopentadienylosmium complexes containing α-alkenylphosphine ligands are unknown. This is in part due to the lack of convenient $Os(\eta^5\text{-}C_5H_5)$ starting complexes[12a,b,14] and the higher kinetic inertia of the $Os(\eta^5\text{-}C_5H_5)L_3$ species in comparison with the related ruthenium derivatives.[15]

We have previously reported the synthesis of the cyclopentadienyl compound $Os(\eta^5\text{-}C_5H_5)Cl(P^iPr_3)_2$ by reaction of the six-coordinate complex $OsH_2Cl_2(P^iPr_3)_2$ with $Tl(C_5H_5)$.[16] Despite the high kinetic inertia of the $Os(\eta^5\text{-}C_5H_5)L_3$ systems, in solution, this complex dissociates a phosphine to form an unsaturated species that is allowing the development of new cyclopentadienylosmium chemistry.[17] It is now shown that the dehydrogenation of an isopropyl group of one of the phosphines of $Os(\eta^5\text{-}C_5H_5)Cl(P^iPr_3)_2$ is an effective method to prepare cyclopentadienylosmium compounds containing an α-alkenylphosphine ligand.

## Results and Discussion

**1. Preparation of an Os(hydrogen acceptor)-($P^iPr_3$) Precursor.** As it has been previously mentioned, the equilibrium for the dehydrogenation of alkanes and alkyl groups is shifted to the right in the presence of a hydrogen acceptor. Furthermore, diphenylacetylene has shown to be a useful hydrogen acceptor to the dehydrogenation of one of the triisopropylphosphine ligands of the complex $OsH_4Cl(SnPh_3)(P^iPr_3)_2$.[9] So, we decided to prepare a diphenylacetylene derivative as the first step of our strategy to carry out the dehydrogenation of a phosphine of $Os(\eta^5\text{-}C_5H_5)Cl(P^iPr_3)_2$ (**1**).

One of the phosphine ligands of **1** can be easily displaced by methyl vinyl ketone and dimethyl acetylenedicarboxylate. The reactions lead to the derivatives $Os(\eta^5\text{-}C_5H_5)Cl\{\eta^2\text{-}CH_2{=}CHC(O)CH_3\}(P^iPr_3)$ and $Os(\eta^5\text{-}C_5H_5)Cl\{\eta^2\text{-}CH_3CO_2C{\equiv}CCO_2CH_3\}(P^iPr_3)$, respectively, which can be isolated as pure solids.[16] However, the treatment of toluene solutions of **1** with diphenylacetylene gives rise to a equilibrium mixture of **1**, the π-alkyne complex $Os(\eta^5\text{-}C_5H_5)Cl\{\eta^2\text{-}PhC{\equiv}CPh\}(P^iPr_3)$ (**2**), triisopropylphosphine, and diphenylacetylene. Even at 65 °C and in the presence of an excess of alkyne, the quantitative formation of **2** does not take place. This indicates that the direct reaction between **1** and diphenylacetylene is not a useful method to obtain **2**.

In light of this difficulty, we design an alternative pathway (Scheme 1). Bubbling molecular hydrogen through a pentane solution of **1** produces the displacement of a coordinated triisopropylphosphine and the formation of the osmium(IV)-dihydride $OsH_2(\eta^5\text{-}C_5H_5)Cl(P^iPr_3)$ (**3**), which is isolated as a white solid in 67%

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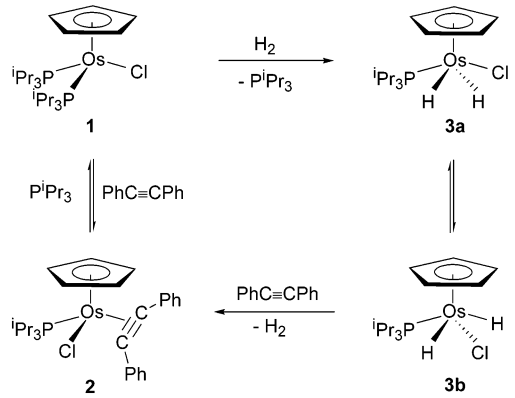
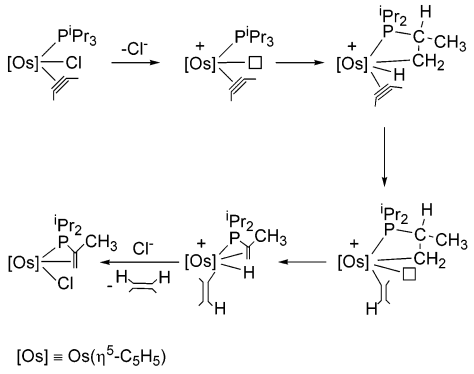
**Scheme 1**



**Scheme 2**

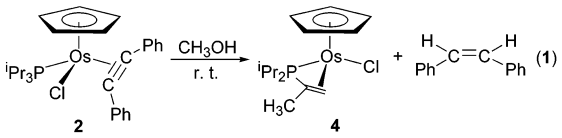


yield. The solid is an equilibrium mixture of the isomers **3a** and **3b**.[17c]

In diethyl ether under reflux and in the presence of 2.7 equiv of diphenylacetylene, the dihydride compounds of the isomeric mixture lose molecular hydrogen and the resulting metallic fragment coordinates an alkyne molecule to afford **2**, which was isolated as a pure dark red solid in 81% yield. The formation of stilbene was not observed during the reaction.

The $\pi$-coordination of the alkyne in **2** is strongly supported by the IR spectrum of the compound, in which the C≡C stretching frequency is found at 1821 $cm^{-1}$, thus shifted 399 $cm^{-1}$ to lower wavenumbers if compared with the free alkyne. In agreement with the chirality of the osmium atom, the $^1H$ NMR spectrum shows two double doublets at 1.04 and 0.83 ppm due to the methyl protons of the phosphine, whereas the $^{13}C\{^1H\}$ NMR spectrum contains two resonances for the C(sp) carbon atoms of the coordinated alkyne: a broad singlet at 92.3 ppm and a doublet with a C−P coupling constant of 3.5 Hz at 71.1 ppm. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 13.2 ppm.

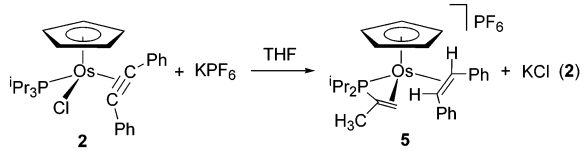
**2. Dehydrogenation of the Phosphine of 2.** At room temperature in toluene or benzene, complex **2** is stable. However in methanol, it evolves into the isopropenyldi(isopropyl)phosphine derivative Os($\eta^5$-$C_5H_5$)Cl{[$\eta^2$-$CH_2$=$C(CH_3)$]$P^iPr_2$} (**4**) and *Z*-stilbene (eq 1). After 24 h the formation of **4** is quantitative, according to the $^1H$ and $^{31}P\{^1H\}$ spectra of the residue obtained from removing the solvent of the reaction under reduced pressure. The extraction of this residue with diethyl ether affords **4** as a pure yellow solid in 70% yield.



The dehydrogenation of an isopropyl group of the phosphine and the formation of the corresponding isopropenyl substituent are strongly supported by the $^1H$ and $^{13}C\{^1H\}$ NMR spectra of **4**. In the $^1H$ NMR spectrum, the olefinic $CH_2$ protons give rise to double doublets at 4.10 (*trans* to P) and 2.87 (*cis* to P) ppm, with a H−H coupling constant of 2.4 Hz and H−P coupling constants of 31.2 and 7.2 Hz, respectively. In the $^{13}C\{^1H\}$ NMR spectrum, the C($sp^2$) carbon atoms of the phosphine display doublets at 36.1 (CP) and 32.6 ($CH_2$) ppm, with C−P coupling constants of 19.7 and 13.8 Hz. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at −2.9 ppm.

The formation of **4** truly involves the hydrogen transfer from an isopropyl group of triisopropylphosphine to the carbon−carbon triple bond of the coordinated alkyne, in **2**. When the reaction is carried out in methanol-$d_4$ as solvent, neither the isopropenyldi(isopropyl)phosphine of **4** nor the obtained stilbene contain any deuterium atom. This clearly indicates that the solvent of the reaction does not play any direct role during the reduction. The role of the methanol is to promote the dissociation of chloride from **2** (Scheme 2). Thus, the C−H activation of a methyl group of an isopropyl substituent of the phosphine, in a cationic unsaturated intermediate, followed by the migratory insertion of the alkyne into the Os−H bond of the resulting hydride affords an unsaturated alkenyl species, containing a metalated phosphine. The $\beta$-hydrogen elimination on the metalated group of the phosphine should give a monoisopropenylphosphine-hydride-alkenyl intermediate, which could evolve into **4** by reductive elimination of *Z*-stilbene, and coordination of the chloride anion dissociated in the first step.

The role of methanol is in fact to promote the dissociation of chloride from **2**. In tetrahydrofuran and in the presence of $KPF_6$, the hydrogen transfer reaction leads to the *Z*-stilbene derivative [Os($\eta^5$-$C_5H_5$){$\eta^2$-(*Z*)-PhCH=CHPh)}{[$\eta^2$-$CH_2$=$C(CH_3)$]$P^iPr_3$}]$PF_6$ (**5**), which was isolated as a white solid in 85% yield (eq 2).



Complex **5** is a rare example of an organometallic compound containing two different Os−olefin bonds. Figure 1 shows a view of the structure of this derivative. Selected bond distances and angles are listed in Table 1. The geometry around the osmium center can be described as a very distorted octahedron, with the cyclopentadienyl ligand occupying the three sites of a face, whereas the phosphorus atom P(1) and the midpoints of the olefinic C(15)−C(17) and C(1)−C(8) bonds (M(1) and M(2), respectively) are situated in the sites of the opposite face. The distortion is mainly due to the ring constraint imposed by the bidentate phosphine, which acts with a bite angle P(1)−Os−M(1) of 57.64(11)°. The P(1)−Os−M(2) angle is 103.64(12)°.

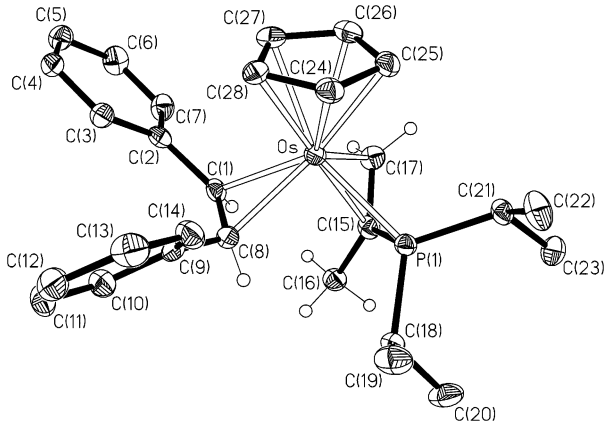



**Figure 1.** Molecular diagram of the cation of complex [Os($\eta^5$-$C_5H_5$)Cl{$\eta^2$-(*Z*)-PhCH=CHPh}{[$\eta^2$-$CH_2$=C($CH_3$)]P$^i$Pr$_2$}]-$PF_6$ (**5**).

**Table 1. Selected Bond Distances (Å) and Angles (deg) for the Complex [Os($\eta^5$-$C_5H_5$){$\eta^2$-(*Z*)-PhCH=CHPh}-{[$\eta^2$-$CH_2$=C($CH_3$)]P$^i$Pr$_3$}]$PF_6$ (5)**

| | | | |
|---|---|---|---|
| Os−P(1) | 2.3093(10) | Os−C(27) | 2.261(4) |
| Os−C(1) | 2.189(4) | Os−C(28) | 2.195(4) |
| Os−C(8) | 2.177(4) | C(1)−C(8) | 1.439(6) |
| Os−C(15) | 2.264(4) | C(15)−C(17) | 1.403(6) |
| Os−C(17) | 2.211(4) | P(1)−C(15) | 1.765(4) |
| Os−C(24) | 2.201(4) | P(1)−C(18) | 1.830(4) |
| Os−C(25) | 2.256(4) | P(1)−C(21) | 1.826(4) |
| Os−C(26) | 2.310(4) | | |

| | | | |
|---|---|---|---|
| P(1)−Os−G[a] | 124.74(13) | Os−C(1)−C(2) | 117.8(3) |
| P(1)−Os−M(1)[b] | 57.64(11) | Os−C(8)−C(9) | 124.4(3) |
| P(1)−Os−M(2)[c] | 103.64(12) | P−C(15)−C(17) | 113.6(3) |
| G[a]−Os−M(1)[b] | 130.37(17) | P(1)−C(15)−C(16) | 124.9(3) |
| G[a]−Os−M(2)[c] | 124.89(17) | C(2)−C(1)−C(8) | 129.3(4) |
| M(1)[b]−Os−M(2)[c] | 95.77(16) | C(1)−C(8)−C(9) | 126.4(4) |
| C(1)−Os−C(8) | 38.48(15) | C(17)−C(15)−C(16) | 121.4(4) |
| Os−C(1)−C(8) | 70.3(2) | | |
| Os−C(8)−C(1) | 71.2(2) | | |

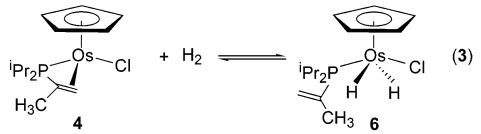
[a] G represents the centroid of the cyclopentadienyl ligand [C(24)−C(28)]. [b] M(1) represents the midpoint of the C(15)−C(17) double bond. [c] M(2) represents the midpoint of the C(1)−C(8) double bond.

The structure proves the *Z*-stereochemistry of the stilbene. The osmium-stilbene coordination exhibits Os−C distances of 2.189(4) (Os−C(1)) and 2.177-(4) (Os−C(8)) Å, which agree well with those found in other osmium-olefin complexes (between 2.13 and 2.28 Å).[7−9,17l,m,18] Similarly, the olefinic bond distance C(1)−C(8) (1.439(6) Å) is within the range reported for transition metal olefin complexes (between 1.340 and 1.445 Å).[19]

The olefinic group of the isopropenyldi(isopropyl)-phosphine ligand coordinates to the osmium atom in an asymmetrical fashion, with Os−C distances of 2.264(1) (Os−C(15)) and 2.211(4) (Os−C(17)) Å. These bond lengths are between 0.03 and 0.09 Å longer than the Os−stilbene distances, which indicates that the Os−isopropenyl interaction is weaker than the Os−stilbene interaction and suggests that the isopropenyl substituent of the phosphine is a more labile group than the *Z*-stilbene ligand. This is also consistent with the C(15)−C(17) bond length (1.403(6) Å), which is about 0.04 Å shorter than the C(1)−C(8) distance. In accordance with the sp$^2$ hybridization for C(15), the angles P(1)−C(15)−C(16) and C(17)−C(15)−C(16) are 124.9(3)° and 121.4-(4)°, respectively. The P(1)−C(15) distance (1.765(4) Å) is about 0.06 Å shorter than the P(1)−C(21) (1.826(4) Å) and P(1)−C(18) (1.830(4) Å) bond lengths.

The $^1$H and $^{13}$C{$^1$H} NMR spectra of **5** are consistent with the asymmetry of the cation. Thus, the $^1$H NMR spectrum contains two resonances for the olefinic protons of the coordinated *Z*-stilbene ligand, at 3.71 and 2.66 ppm. The first of them appears as a double doublet with both H−H and H−P coupling constants of 9.0 Hz, while the second one is observed as a doublet. The olefinic $CH_2$ protons of the isopropenyl group of the phosphine display double doublets at 4.02 (*cis* to P) and 3.63 (*trans* to P) ppm, with a H−H coupling constant of 2.1 Hz and H−P coupling constants of 8.4 and 32.1 Hz, respectively. In the $^{13}$C{$^1$H} NMR spectrum the resonances corresponding to the olefinic carbon atoms of *Z*-stilbene appear at 25.6 and 20.6 ppm, as doublets with the same C−P coupling constant of 7.0 Hz for both, whereas the resonances due to the olefinic carbon atoms of the isopropenyl group of the phosphine are observed at 63.8 (CP) and 31.4 ($CH_2$), also as doublets but with C−P coupling constants of 21.2 and 6.9 Hz, respectively. The $^{31}$P{$^1$H} NMR spectrum shows a singlet at −4.8 ppm.

**3. Hemilabile Character of the Isopropenyl Substituent of the Phosphine of 4.** Despite the kinetic inertia of the saturated Os($\eta^5$-$C_5H_5$)$L_3$ complexes, the isopropenyl substituent of the isopropenyldi(isopropyl)-phosphine of **4** has hemilabile character. This property is revealed in the presence of molecular hydrogen. Under an atmosphere of this gas, complex **4** is in equilibrium with the dihydride derivative $OsH_2$($\eta^5$-$C_5H_5$)Cl{P$^i$Pr$_2$[C($CH_3$)=$CH_2$]} (**6**), which contains a monodentate-phosphorus isopropenyldi(isopropyl)phosphine ligand (eq 3).

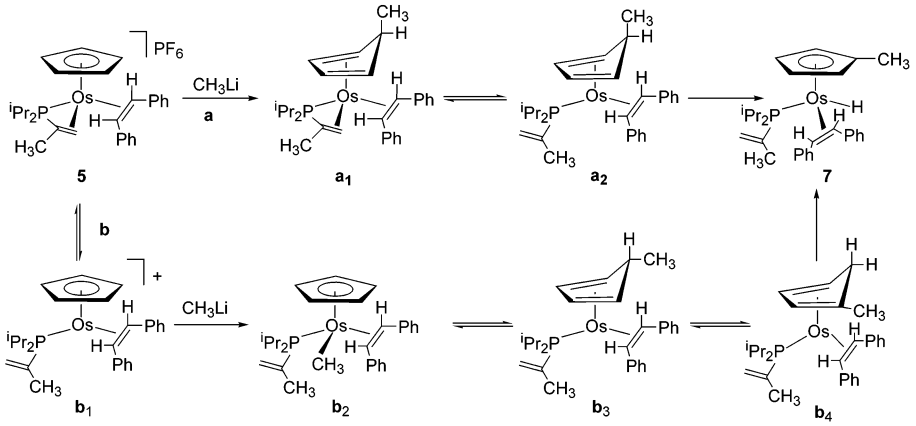



The presence of a free isopropenyl substituent in the phosphine of **6** is strongly supported by the $^{13}$C{$^1$H}, $^1$H, and $^{31}$P{$^1$H} NMR spectra of the complex. In the $^{13}$C-{$^1$H} NMR spectrum, the C(sp$^2$) carbon atoms of the phosphine display doublets at 140.8 (CP) and 130.9 ($CH_2$) ppm with C−P coupling constants of 40.6 and 12.8 Hz, respectively. These resonances appear shifted 104.7 (CP) and 98.3 ($CH_2$) ppm to lower field with regard to those of **4**. In addition, it should be noted that the CP resonance has increased significantly the C−P coupling constant as a consequence of the decoordination (from 19.7 to 40.6 Hz). In the $^1$H NMR spectrum, the resonances corresponding to the $CH_2$ protons of the isopropenyl group are observed at 5.61 (*cis* to P) and 5.44 (*trans* to P) ppm, as doublets with H−P coupling

(18) (a) Johnson, T. J.; Albinati, A.; Koetzle; T. F.; Ricci, J.; Eisenstein, O.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **1994**, *33*, 4966. (b) Edwards, A. J.; Elipe, S.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A.; Valero, C. *Organometallics* **1997**, *16*, 3828. (c) Buil, M. L.; Esteruelas, M. A.; García-Yebra, C.; Gutiérrez-Puebla, E.; Oliván, M. *Organometallics* **2000**, *19*, 2184. (d) Esteruelas, M. A.; García-Yebra, C.; Oliván, M.; Oñate, E. *Organometallics* **2000**, *19*, 3260.

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

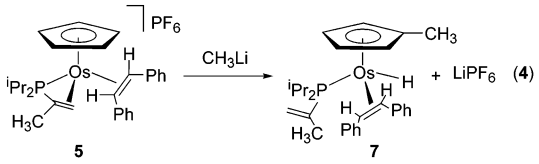
**Scheme 3**



constants of 17.0 and 35.7 Hz, respectively. These resonances are shifted 2.74 (*cis* to P) and 1.34 (*trans* to P) ppm toward lower field with regard to the ones found in the spectrum of **4**. The H−P coupling constants also increase as a consequence of the decoordination, in particular that of the resonance due to the proton disposed *cis* to the phosphorus atom (from 7.2 to 17.0 Hz). The $^1$H NMR spectrum also supports the *transoid* disposition of the hydride ligands, showing at −10.19 ppm only one doublet with a H−P coupling constant of 33.9 Hz for both hydrides. The $^{31}$P{$^1$H} NMR spectrum contains a singlet at 45.2 ppm, shifted 48.2 ppm to lower field if it is compared with the observed one in the spectrum of **4**.

**4. Isomerization of *Z*-Stilbene.** Another illustrative example of the hemilabile properties of the isopropenyldi(isopropyl)phosphine ligand in this type of system is the reaction of **5** with MeLi, which finally produces the isomerization of *Z*-stilbene to *E*-stilbene.

Treatment of tetrahydrofuran solutions of **5** with 1.5 equiv of MeLi leads initially to the hydride-methylcyclopentadienyl derivative OsH($\eta^5$-$C_5H_4CH_3$){$\eta^2$-(*Z*)-PhCH=CHPh)}{P$^i$Pr$_2$[C(CH$_3$)=CH$_2$]} (**7**), which was isolated as a white solid in 55% yield (eq 4).



The presence of a hydride ligand in **7** is strongly supported by the IR and $^1$H NMR spectra of the complex. Thus, the IR spectrum in Nujol shows a $\nu$(Os−H) band at 2083 cm$^{-1}$, whereas the $^1$H NMR spectrum contains at −14.97 ppm a doublet with a H−P coupling constant of 31.5 Hz. The $^1$H NMR spectrum is also consistent with the presence of a methylcyclopentadienyl group and a monodentate-phosphorus isopropenyldi(isopropyl)phosphine ligand. The methylcyclopentadienyl group displays a singlet at 1.96 ppm for the methyl protons, and between 5.10 and 3.70 ppm the expected ABCD spin system for the ring protons. In agreement with the $^1$H NMR spectrum of **6**, the resonances corresponding to the olefinic CH$_2$ protons of the isopropenyl substituent appear at 5.52 (*cis* to P) and 5.46 (*trans* to P) ppm as doublets with H−P coupling constants of 10.5 and 32.2 Hz, respectively. The resonances due to the olefinic protons of the coordinated *Z*-stilbene agree well with those of **5**. These protons display a doublet at 4.25 ppm and a double doublet at 3.32 ppm. Both the H−H and H−P coupling constants are 9.6 Hz. In the $^{13}$C{$^1$H} NMR spectrum the C(sp$^2$)P carbon atom of the phosphine gives rise to a doublet at 139.7 ppm, with a C−P coupling constant of 31.3 Hz, whereas the resonance due to the CH$_2$ carbon atom is observed at 128.6 ppm, partially masked by the solvent ($C_6D_6$) signal. The olefinic carbon atoms of the coordinated *Z*-stilbene display doublets at 33.6 and 26.3 ppm, with C−P coupling constants of 2.7 and 3.2 Hz, respectively. The $^{31}$P{$^1$H} NMR spectrum contains a singlet at 38.5 ppm.

At first glance two reaction pathways are possible for the formation of **7** (Scheme 3): the direct addition of the methyl group to the cyclopentadienyl ligand of **5** (a), or alternatively, the initial attack of the methyl group to the metallic center of **5** and the subsequent Me(Os)/H($C_5H_5$) exchange (b). The formation of substituted cyclopentadienyl derivatives by initial *exo*-addition of nucleophiles to the cyclopentadienyl ring has been proposed for several iron[20] and cobalt[21] systems, while the Nu(Os)/H($C_5H_5$) exchange has been invoked for the formation of functionally substituted cyclopentadienyl osmium(IV) compounds, starting from OsH($\eta^5$-$C_5H_5$)Cl(EPh$_3$)(P$^i$Pr$_3$) (E = Si, Ge) complexes,[17g,i] and recently for the formation of disubstituted cyclopentadienyl cobalt derivatives.[22]

The direct addition of the methyl group to the cyclopentadienyl ligand should give a saturated methylcyclopentadiene-osmium(0) intermediate **a$_1$**, with the hydrogen bonded to the C(sp$^3$) carbon atom of the diene in *endo*-position. Thus, the decoordination of the isopropenyl substituent of the phosphine, followed by the migration of this *endo*-hydrogen atom from the diene to the metallic center of the resulting unsaturated intermediate **a$_2$**, should lead to **7**.

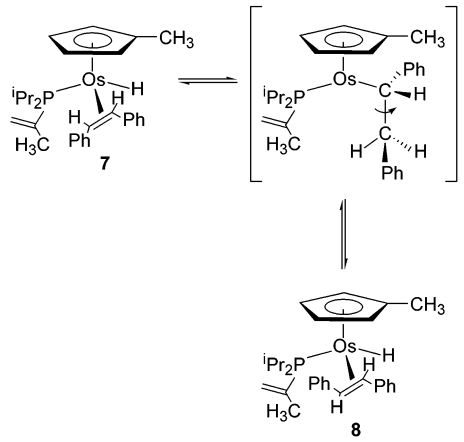
According to the pathway b, the hemilabile character of the isopropenyl substituent of the phosphine of **5**

(20) (a) Reger, D. L.; Belmore, K. A.; Atwood, J. L.; Hunter, W. E. *J. Am. Chem. Soc.* **1983**, *105*, 5701. (b) Reger, D. L.; Belmore, K. A. *Organometallics* **1985**, *4*, 305. (c) Reger, D. L.; Klaeren, S. A.; Lebioda, L. *Organometallics* **1986**, *5*, 1072. (d) Reger, D. L. *Acc. Chem. Res.* **1988**, *21*, 229.

(21) (a) Sternberg, E. D.; Wollhardt, K. P. C. *J. Org. Chem.* **1984**, *49*, 1564. (b) von der Gruen, M.; Schaefer, C.; Gleiter, R. *Organometallics* **2003**, *22*, 2370.

(22) Nomura, M.; Takayama, C.; Janairo, G. C.; Sugiyama, T.; Yokoyama, Y.; Kajitani, M. *Organometallics* **2003**, *22*, 195.

**Scheme 4**




could afford an unsaturated cyclopentadienyl intermediate $\mathbf{b_1}$. Thus, the metallic center of this intermediate could undergo nucleophilic attack of the methyl group, to give a saturated methyl intermediate $\mathbf{b_2}$. The spontaneous migration of the methyl group from the osmium atom to the cyclopentadienyl ligand should lead to a methylcyclopentadiene-osmium(0) intermediate $\mathbf{b_3}$, with the hydrogen bonded to the C($sp^3$) carbon atom of the diene in *exo*-position. Subsequently, this intermediate should evolve by *exo*-1,5-hydride shift within the diene to place the HC($sp^3$) hydrogen atom in *endo*-position, affording $\mathbf{b_4}$. Finally the migration of this *endo*-hydrogen atom from the diene to the osmium atom should give **7**.

In the context of Scheme 3, one should take into account that in accordance with the Davis−Green−Mingos rules[23] the nucleophilic addition to an "*even*" ligand is kinetically favored with regard to the nucleophilic attack to an "*odd*" ligand. Thus, pathway a, involving the methyl attack to an "*odd*" group in the presence of "*even*" ligands, does not appear to be a reasonable proposal, and therefore, we assume that the formation of **7** takes place via the pathway b.

Complex **7** is unstable and evolves into the *E*-stilbene derivative OsH($\eta^5$-$C_5H_4CH_3$){$\eta^2$-(*E*)-PhCH=CHPh}-{$P^iPr_2$[$C(CH_3)$=$CH_2$]} (**8**), even in the solid state at −20 °C under argon atmosphere. In toluene at 80 °C, the isomerization is quantitative after 12 h. The transformation *Z*−*E* is favored by the presence of a hydride ligand in **7**. Thus, the insertion of the *Z*-stilbene ligand into the Os−H bond, followed by the rotation around the C−C single bond of the resulting alkyl group, and the subsequent β-elimination of hydrogen afford **8** (Scheme 4).

Complex **8** was isolated as a white solid in 84% yield. Figure 2 shows a view of the geometry of this compound. Selected bond distances and angles are listed in Table 2.

The geometry around the osmium center is close to octahedral, with the cyclopentadienyl occupying three sites of a face. The angle formed by the isopropenyldi(isoprpyl)phosphine and the midpoint of the olefinic C(1)−C(8) double bond (P−Os−M) is 98.76(13)°.

The structure proves the *E*-stereochemistry of the stilbene ligand, which coordinates to the osmium atom

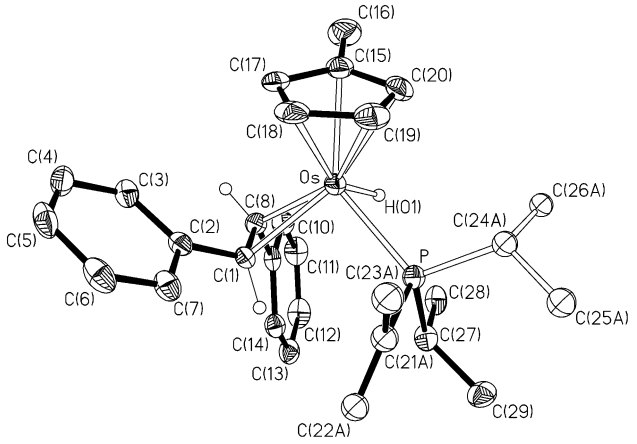



**Figure 2.** Molecular diagram of complex OsH($\eta^5$-$C_5H_4$-$CH_3$){$\eta^2$-(*E*)-PhCH=CHPh}{$P^iPr_2$[$C(CH_3)$=$CH_2$]} (**8**).

**Table 2. Selected Bond Distances (Å) and Angles (deg) for the Complex OsH($\eta^5$-$C_5H_4CH_3$){$\eta^2$-(*E*)-PhHC=CHPh}-[P{$C(CH_3)$=$CH_2$}$^iPr_2$] (8)**

| | | | |
|---|---|---|---|
| Os−P | 2.2886(11) | Os−C(18) | 2.283(5) |
| Os−C(1) | 2.186(4) | Os−C(19) | 2.261(5) |
| Os−C(8) | 2.150(4) | Os−C(20) | 2.201(5) |
| Os−C(15) | 2.220(5) | Os−H(01) | 1.55(6) |
| Os−C(17) | 2.249(4) | C(1)−C(8) | 1.434(6) |
| | | | |
| P−Os−G[a] | 126.32(15) | Os−C(1)−C(8) | 69.4(2) |
| P−Os−M[b] | 98.76(13) | Os−C(1)−C(2) | 117.9(3) |
| P−Os−H(01) | 70(2) | Os−C(8)−C(9) | 123.1(3) |
| G[a]−Os−M[b] | 127.74(19) | C(1)−Os−C(8) | 38.62(15) |
| G[a]−Os−H(01) | 121(2) | C(2)−C(1)−C(8) | 123.5(4) |
| M[b]−Os−H(01) | 97(2) | C(1)−C(8)−C(9) | 124.2(4) |

[a] G represents the centroid of the cyclopentadienyl ligand [C(15)−C(20)]. [b] M represents the midpoint of the C(1)−C(8) double bond.

in an asymmetrical fashion, with Os−C distances of 2.186(4) (Os−C(1)) and 2.150(4) (Os−C(8)) Å and a C(1)−C(8) bond length of 1.434(6) Å. These values agree well with those found for the coordination of the *Z*-stilbene olefin in **5**.

The IR, $^{13}C\{^1H\}$ NMR, and $^{31}P\{^1H\}$ NMR spectra of **8** are consistent with the structure shown in Figure 2. The IR spectrum in Nujol shows a $\nu$(Os−H) band at 2112 $cm^{-1}$. In the $^1H$ NMR spectrum the hydride resonance appears at −15.89 ppm as a doublet with a H−P coupling constant of 35.4 Hz. The methylcyclopentadienyl ligand gives rise to a singlet at 1.95 ppm, due to the methyl protons, and an ABCD spin system corresponding to the ring protons between 4.80 and 4.00 ppm. The coordinated stilbene olefin displays at 5.27 ppm a doublet ($J$(H−H) = 10.2 Hz) and at 3.93 ppm a double doublet ($J$(H−H) = $J$(H−P) = 10.2 Hz). The $CH_2$ resonances of the isopropenyl group of the phosphine are observed at 5.34 (*trans* to P) and 5.23 (*cis* to P) ppm as doublets with H−P coupling constants of 29.1 and 14.1 Hz, respectively. In the $^{13}C\{^1H\}$ NMR spectrum, the olefinic resonances of the coordinated *E*-stilbene appear at 25.2 and 24.6 ppm as doublets with C−P coupling constants of 4.2 and 2.0 Hz, respectively, whereas the olefinic resonances of the isopropenyl group of the phosphine are observed at 142.6 (PC) and 124.8 ($CH_2$) ppm, also as doubletes but with C−P coupling constants of 32.4 and 5.5 Hz, respectively. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 32.8 ppm.

(23) Elschenbroich, Ch.; Salzer, A. *Organometallics: a concise introduction*; VCH Verlagsgesellschaft: Weinheim, 1989; Chapter 15, p 293.

## Concluding Remarks

This paper shows the synthesis and some reactions of cyclopentadienyl-isopropenyldi(isopropyl)phosphine-osmium derivatives. The isopropenyl substituent of the phosphine of these compounds is the result of the dehydrogenation of one of the isopropyl groups of one of the triisopropylphosphines of the complex Os($\eta^5$-$C_5H_5$)Cl($P^iPr_3$)$_2$. The dehydrogenation is promoted by diphenylacetylene, which acts as a hydrogen acceptor.

Although the direct and quantitative formation of a triisopropylphosphine-diphenylacetylene-osmium adduct is not possible, the oxidative addition of molecular hydrogen to Os($\eta^5$-$C_5H_5$)Cl($P^iPr_3$)$_2$ and the subsequent reaction of the resulting dihydride with diphenylacetylene afford Os($\eta^5$-$C_5H_5$)Cl($\eta^2$-PhC≡CPh)($P^iPr_3$). In methanol this compound is unstable and evolves into the isopropenyldi(isopropyl)phosphine derivative Os($\eta^5$-$C_5H_5$)Cl{[$\eta^2$-$CH_2$=C($CH_3$)]$P^iPr_2$} by hydrogen transfer reaction from one isopropyl group of triisopropylphosphine to diphenylacetylene. In tetrahydrofuran and in the presence of $KPF_6$, complex Os($\eta^5$-$C_5H_5$)Cl($\eta^2$-PhC≡CPh)($P^iPr_3$) gives [Os($\eta^5$-$C_5H_5$){[$\eta^2$-(*Z*)-PhCH=CHPh}{[$\eta^2$-$CH_2$=C($CH_3$)]$P^iPr_2$}]$PF_6$.

Despite the high kinetic inertia of the Os($\eta^5$-$C_5H_5$)$L_3$ systems, the isopropenyldi(isopropyl)phosphine displays hemilabile properties. The hemilabile character of the isopropenyl substituent of the phosphine is revealed by the reaction of Os($\eta^5$-$C_5H_5$)Cl{[$\eta^2$-$CH_2$=C($CH_3$)]$P^iPr_2$} with molecular hydrogen, which yields an equilibrium mixture of the starting compound and the dihydride $OsH_2$($\eta^5$-$C_5H_5$)Cl{[$\eta^2$-$CH_2$=C($CH_3$)]$P^iPr_2$}. Another illustrative example of the hemilabile properties of the isopropenyldi(isopropyl)phosphine ligand in cyclopentadienyl-osmium chemistry is the reaction of [Os($\eta^5$-$C_5H_5$)Cl{[$\eta^2$-(*Z*)-PhCH=CHPh}{[$\eta^2$-$CH_2$=C($CH_3$)]$P^iPr_2$}]-$PF_6$ with MeLi, which leads to OsH($\eta^5$-$C_5H_4CH_3$){[$\eta^2$-(*E*)-PhCH=CHPh]{$P^iPr_2$[C($CH_3$)=$CH_2$]} via OsH($\eta^5$-$C_5H_4CH_3$){[$\eta^2$-(*Z*)-PhCH=CHPh]{$P^iPr_2$[C($CH_3$)=$CH_2$]}.

In conclusion, the dehydrogenation of one triisopropylphosphine of the complex Os($\eta^5$-$C_5H_5$)Cl($P^iPr_3$)$_2$ is an easy and effective method to prepare octahedral cyclopentadienyl-isopropenyldi(isopropyl)phosphine-osmium-(II) complexes. These compounds are of interest because due to the hemilabile character of the isopropenyl substituent of the phosphine, they will allow the development of a new chemistry in the field of the cyclopentadienyl-osmium complexes.

## 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 $OsH_2$($\eta^5$-$C_5H_5$)Cl($P^iPr_3$)$_2$ (**1**) was prepared by the published method.[16]

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

**Preparation of Os($\eta^5$-$C_5H_5$)Cl($\eta^2$-PhC≡CPh)($P^iPr_3$) (2).** A solution of $OsH_2$($\eta^5$-$C_5H_5$)Cl($P^iPr_3$) (230 mg, 0.51 mmol) in 50 mL of diethyl ether was treated with diphenylacetylene (245 mg, 1.37 mmol). The mixture was heated under reflux conditions for 6 h, filtered, and then vacuum-dried. The resulting sticky residue was washed with pentane (3 × 4 mL), leading to a red solid. Yield: 260 mg (81%). Anal. Calcd for $C_{28}H_{36}$ClOsP: C, 53.44; H, 5.78. Found: C, 53.90; H, 6.05. IR (Nujol, $cm^{-1}$): $\nu$(C≡C) 1821 (s). $^1$H NMR (300 MHz, $C_6D_6$, 293 K): $\delta$ 8.30−6.90 (10H, Ph); 5.22 (s, 5H, $\eta^5$-$C_5H_5$); 2.47 (m, 3H, PCH); 1.04 (dd, 9H, $J_{H-P}$ = 13.5, $J_{H-H}$ = 7.2, PCHC$H_3$); 0.83 (dd, 9H, $J_{H-P}$ = 13.5, $J_{H-H}$ = 7.2, PCHC$H_3$). $^{13}$C{$^1$H} NMR (75.4 MHz, $CD_3COCD_3$, 293 K): $\delta$ 131.6, 129.0, 127.7, 127.6 (s, C*ortho*, C*meta* Ph); 131.3, 128.5 (both s, C*ipso* Ph); 126.1, 125.7 (s, C*para* Ph); 92.3 (br, ≡C−); 81.1 (s, $\eta^5$-$C_5H_5$); 71.1 (d, $J_{C-P}$ = 3.5, ≡C−,); 24.4 (d, $J_{C-P}$ = 27.7, PCH); 19.8, 18.6 (s, PCH-$CH_3$). $^{31}$P{$^1$H} NMR (121.4 MHz, $C_6D_6$, 293 K): $\delta$ 13.2 (s). MS (FAB$^+$): *m*/*z* 595 ($M^+$ − Cl).

**Preparation of Os($\eta^5$-$C_5H_5$)Cl{[$\eta^2$-$CH_2$=C($CH_3$)]$P^iPr_2$} (4).** A solution of Os($\eta^5$-$C_5H_5$)Cl($\eta^2$-PhC≡CPh)($P^iPr_3$) (299 mg, 0.48 mmol) in 10 mL of methanol was left to stir for 15 h. The resulting solution was vacuum-dried, and the residue was extracted in diethyl ether (50 mL). The filtered solution was again dried in vacuo and finally washed with pentane (3 × 5 mL). A yellow solid was obtained. Yield: 150 mg (70%). Anal. Calcd for $C_{14}H_{24}$ClOsP: C, 37.45; H, 5.39. Found: C, 37.75; H, 5.50. $^1$H NMR (300 MHz, $C_6D_6$, 293 K): $\delta$ 4.62 (s, 5H, $\eta^5$-$C_5H_5$); 4.10 (dd, 1H, $J_{H-P}$ = 31.2, $J_{H-H}$ = 2.4, PC=C$H_{trans\ to\ P}$); 2.87 (dd, 1H, $J_{H-P}$ = 7.2, $J_{H-H}$ = 2.4, =C$H_{cis\ to\ P}$); 2.37 (m, 1H, PCH); 1.56 (m, 1H, PCH); 1.30−1.00 (15H, $CH_3$). $^{13}$C{$^1$H} NMR (75.4 MHz, $C_6D_6$, 293 K, plus APT): $\delta$ 78.0 (+, s, $\eta^5$-$C_5H_5$); 36.1 (−, d, $J_{C-P}$ = 19.7, P−C=); 32.6 (−, d, $J_{C-P}$ = 13.8, = $CH_2$); 27.9 (+, d, $J_{C-P}$ = 30.9, PCH); 23.8 (+, d, $J_{C-P}$ = 2.8, $CH_3$); 23.3 (+, d, $J_{C-P}$ = 6.0, $CH_3$,); 21.8 (+, d, $J_{C-P}$ = 4.6, $CH_3$); 20.7 (+, d, $J_{C-P}$ = 4.6, $CH_3$); 18.8 (+, d, $J_{C-P}$ = 2.3, $CH_3$); 17.0 (+, d, $J_{C-P}$ = 18.0, PCH). $^{31}$P{$^1$H} NMR (121.4 MHz, $C_6D_6$, 293 K): $\delta$ −2.9 (s). MS (FAB$^+$): *m*/*z* 450 ($M^+$); 415 ($M^+$ − Cl).

**Preparation of [Os($\eta^5$-$C_5H_5$)Cl{$\eta^2$-(*Z*)-PhCH=CHPh}-{[$\eta^2$-$CH_2$=C($CH_3$)]$P^iPr_2$}]$PF_6$ (5).** To a solution of Os($\eta^5$-$C_5H_5$)Cl($\eta$-PhC≡CPh)($P^iPr_3$) (422 mg, 0.67 mmol) in 15 mL of THF was added $KPF_6$ (212 mg, 1.15 mmol), and the mixture was left to stir for 3 h. The resulting solution was vacuum-dried, and the residue was extracted in dichloromethane (15 mL). The filtered solution was again dried in vacuo and finally washed with diethyl ether (3 × 6 mL). A white solid was obtained. Yield: 420 mg (85%). Anal. Calcd for $C_{28}H_{36}F_6OsP_2$: C, 45.52; H, 4.92. Found: C, 45.25; H, 5.33. IR (Nujol, $cm^{-1}$): $\nu$($PF_6$) 840 (s). $^1$H NMR (300 MHz, $CDCl_3$, 293 K): $\delta$ 7.40−6.60 (10H, Ph); 5.06 (s, 5H, $\eta^5$-$C_5H_5$); 4.02 (dd, 1H, $J_{H-P}$ = 8.4, $J_{H-H}$ = 2.1, PC=C$H_{cis\ to\ P}$); 3.71 (dd, 1H, $J_{H-P}$ = 9.0, $J_{H-H}$ = 9.0, =CHPh); 3.63 (dd, 1H, $J_{H-P}$ = 32.1, $J_{H-H}$ = 2.1, PC=C$H_{trans\ to\ P}$); 2.72 (m, 1H, PCH); 2.66 (d, 1H, $J_{H-H}$ = 9.0, =CHPh); 2.00−1.40 (16H, PCH and $CH_3$ groups). $^{13}$C{$^1$H} NMR (75.4 MHz, $CDCl_3$, 293 K, plus APT): $\delta$ 145.1; 140.8 (−, s, C*ipso* Ph); 131.6, 128.4, 128.3, 127.6 (+, s, C*ortho*, C*meta* Ph); 126.7, 125.5 (+, s, C*para* Ph); 88.3 (+, s, $\eta^5$-$C_5H_5$); 63.8 (−, d, $J_{C-P}$ = 21.2, P−C=); 41.2 (+, s, $CH_3$); 39.9 (+, d, $J_{C-P}$ = 3.7, $CH_3$); 31.4 (−, d, $J_{C-P}$ = 6.9, =$CH_2$); 30.0 (+, d, $J_{C-P}$ = 29.4, PCH); 25.6 (+, d, $J_{C-P}$ = 7.0, =CHPh); 23.7 (+, d, $J_{C-P}$ = 29.4, PCH); 20.6 (+, d, $J_{C-P}$ = 7.0, =CHPh); 20.1 (+, d, $J_{C-P}$ = 2.7, $CH_3$); 18.5 (+, s, $CH_3$); 9.7 (+, d, $J_{C-P}$ = 3.6, $CH_3$). $^{31}$P{$^1$H} NMR (121.4 MHz, $CDCl_3$, 293 K): $\delta$ −4.8 (s, $P^iPr_2$); −145.1 (sept, $J_{F-P}$ = 717.4, $PF_6$). MS (FAB$^+$): *m*/*z* 595 ($M^+$ − H).

**Reaction of Os($\eta^5$-$C_5H_5$)Cl{[$\eta^2$-$CH_2$=C($CH_3$)]$P^iPr_2$} (4) with $H_2$.** (a) An NMR tube containing a solution of Os($\eta^5$-$C_5H_5$)Cl{[$\eta^2$-$CH_2$=C($CH_3$)]$P^iPr_2$} (**4**) (20 mg, 0.033 mmol) in 0.5 mL of $C_6D_6$ was sealed under hydrogen atmosphere. After 15 min the $^1$H NMR spectrum shows a mixture of Os($\eta^5$-$C_5H_5$)-Cl{[$\eta^2$-$CH_2$=C($CH_3$)]$P^iPr_2$} (**4**) and $OsH_2$($\eta^5$-$C_5H_5$)Cl{$P^iPr_2$-[C($CH_3$)=$CH_2$]} (**6**) in a 3:1 molar ratio.

(b) Molecular hydrogen was bubbled through a stirred solution of Os($\eta^5$-$C_5H_5$)Cl{[$\eta^2$-$CH_2$=C($CH_3$)]$P^iPr_2$} (92 mg, 0.15 mmol) in 8 mL of toluene for 1 h. The solution was concentrated almost to dryness, and the addition of pentane caused the formation of a yellow solid. The solid was washed with pentane and vacuum-dried. The $^1$H NMR spectrum shows a mixture of Os($\eta^5$-$C_5H_5$)Cl{[$\eta^2$-$CH_2$=C($CH_3$)]$P^iPr_2$} (**4**) and $OsH_2$-($\eta^5$-$C_5H_5$)Cl{$P^iPr_2$[C($CH_3$)=$CH_2$]} (**6**) in a 1:2 molar ratio. After

leaving the mixture under vacuo for 2 h, the $^1$H NMR spectrum shows a mixture of Os($\eta^5$-$C_5H_5$)Cl{[$\eta^2$-$CH_2$=C($CH_3$)]P$^i$Pr$_2$} (**4**) and $OsH_2$($\eta^5$-$C_5H_5$)Cl{P$^i$Pr$_2$[C($CH_3$)=$CH_2$]} (**6**) in a 2:1 molar ratio.

**NMR Data for 6.** $^1$H NMR (300 MHz, $C_6D_6$, 293 K): $\delta$ 5.61 (d, 1H, $J_{H-P}$ = 17.0, PC=$CH_{cis\ to\ P}$); 5.44 (d, 1H, $J_{H-P}$ = 35.7, PC=$CH_{trans\ to\ P}$); 4.82 (s, 5H, $\eta^5$-$C_5H_5$); 2.14 (m, 2H, PCH); 1.67 (d, 3H, $J_{H-H}$ = 8.4, PC($CH_3$)); 1.12 (dd, 6H, $J_{H-P}$ = 16.1, $J_{H-H}$ = 6.8, PCHC$H_3$); 0.73 (dd, 6H, $J_{H-P}$ = 15.2, $J_{H-H}$ = 7.0, PCHC$H_3$); −10.19 (d, 2H, $J_{H-P}$ = 33.9, Os−H). $^{13}$C{$^1$H} NMR (75.4 MHz, $C_6DCl_6$, 293 K, plus APT): 140.8 (−, d, $J_{C-P}$ = 40.6, PC=); 130.9 (−, d, $J_{C-P}$ = 12.8, =$CH_2$); 79.7 (−, s, $\eta^5$-$C_5H_5$); 28.4 (+, d, $J_{C-P}$ = 37.4, PCH); 18.8 (+, s, P$CH_3$); 18.6 (+, s, P$CH_3$ plus PC($CH_3$)=). $^{31}$P{$^1$H} NMR (121.4 MHz, $C_6D_6$, 293 K): $\delta$ 45.2 (s).

**Preparation of OsH($\eta^5$-$C_5H_4CH_3$)Cl{$\eta^2$-(*Z*)-PhCH=CHPh}{P$^i$Pr$_2$[C($CH_3$)=$CH_2$]}] (7).** To a solution of [Os($\eta^5$-$C_5H_5$)Cl{$\eta^2$-(*Z*)-PhCH=CHPh}{[$\eta^2$-$CH_2$=C($CH_3$)]PiPr$_2$}]$PF_6$ (120 mg, 0.16 mmol) in 10 mL of THF was added methyllithium (solution in alkanes, 0.15 mL, 1.6 M, 0.24 mmol), and the mixture was left to stir for 1 h. Methanol was added, the resulting solution was vacuum-dried, and the residue was extracted in dichloromethane (15 mL). The filtered solution was again dried in vacuo and finally washed with methanol (2 × 2 mL). A white solid was obtained. Yield: 54 mg (55%). Anal. Calcd for $C_{29}H_{39}OsP_2$: C, 57.21; H, 6.46. Found: C, 57.00; H, 6.38. IR (Nujol, cm$^{-1}$): $\nu$(Os−H) 2083 (m). $^1$H NMR (300 MHz, $C_6D_6$, 293 K): $\delta$ 7.60−6.90 (10 H, Ph); 5.52 (d, 1H, $J_{H-P}$ = 10.5, PC=$CH_{cis\ to\ P}$); 5.46 (d, 1H, $J_{H-P}$ = 32.2, PC=$CH_{trans\ to\ P}$); 5.10−3.70 (ABCD system, 4H, $\eta^5$-$C_5H_4$); 4.25 (d, 1H, $J_{H-P}$ = 9.6, =CHPh); 3.32 (dd, 1H, $J_{H-P}$ = 9.6, $J_{H-H}$ = 9.6, =CHPh); 1.96 (s, $\eta^5$-$C_5H_4CH_3$); 1.81 (m, 2 H, PCH); 1.68 (d, 3H, $J_{H-H}$ = 7.8, PC($CH_3$)); 1.10−0.80 (m, 12H, PCHC$H_3$); −14.97 (d, 1H, $J_{H-P}$ = 31.5, Os−H). $^{13}$C{$^1$H} NMR (75.4 MHz, $C_6DCl_6$, 293 K, plus APT): $\delta$ 151.6, 149.1 (−, s, C*ipso* Ph); 139.7 (−, d, $J_{C-P}$ = 31.3, P−C=); 133.5, 130.4, 127.9, 127.8 (+, s, C*ortho*, C*meta* Ph); 128.6 (−, masked with solvent signals, =$CH_2$); 125.0, 123.4 (+, both s, C*para* Ph); 99.9 (−, s, $\eta^5$-$C_5H_4$); 90.7, 84.6, 78.1, 74.5, (+, all s, $\eta^5$-$C_5H_4$); 33.6 (+, d, $J_{C-P}$ = 2.7, =CHPh); 29.3 (+, d, $J_{C-P}$ = 30.9 Hz, PCH); 27.6 (+, d, $J_{C-P}$ = 30.0 Hz, PCH); 26.3 (+, d, $J_{C-P}$ = 3.2, =CHPh); 23.0−14.0 (+, all s, $CH_3$). $^{31}$P{$^1$H} NMR (121.4 MHz, $CDCl_3$, 293 K): $\delta$ 38.5 (s, d, in *off*-resonance). MS (FAB$^+$): *m*/*z* 610 (M$^+$).

**Preparation of OsH($\eta^5$-$C_5H_4CH_3$){$\eta^2$-(*E*)-PhCH=CHPh}-{P$^i$Pr$_2$[C($CH_3$)=$CH_2$]} (8).** A solution of OsH($\eta^5$-$C_5H_4CH_3$)Cl{$\eta^2$-(*Z*)-PhCH=CHPh}{P$^i$Pr$_2$[C($CH_3$)=$CH_2$]}] (96 mg, 0.16 mmol) in 10 mL of toluene was heated under reflux conditions for 16 h. The mixture was vacuum-dried, and the residue was washed with methanol (2 × 1 mL). A white solid was obtained. Yield: 81 mg (84%). Anal. Calcd for $C_{29}H_{39}OsP$: C, 57.21; H, 6.46. Found: C, 57.30; H, 6.31. IR (Nujol, cm$^{-1}$): $\nu$(Os−H): 2112 (m). $^1$H NMR (300 MHz, $C_6D_6$, 293 K): $\delta$ 7.60−6.90 (10H, Ph); 5.34 (d, 1H, $J_{H-P}$ = 29.1, PC=$CH_{trans\ to\ P}$); 5.27 (d, 1H, $J_{H-P}$ = 10.2, =CHPh); 5.23 (d, 1H, $J_{H-P}$ = 14.1, PC=$CH_{cis\ to\ P}$); 4.80−4.00 (ABCD system, 4H, $\eta^5$-$C_5H_4$); 3.93 (dd, 1H, $J_{H-P}$ = 10.2, $J_{H-H}$ = 10.2, =CHPh); 1.95 (s, 3H, $\eta^5$-$C_5H_4CH_3$); 1.74 (m, 2H, PCH); 1.55 (d, 3H, $J_{H-H}$ = 9.0, PC($CH_3$)=); 1.10−0.60 (m, 12H, PCHC$H_3$); −15.89 (d, 1H, $J_{H-P}$ = 35.4, Os−H). $^{13}$C{$^1$H} NMR (75.4 MHz, $C_6D_6$, 293 K, plus APT): $\delta$ 153.7, 153.6 (−, both s, C*ipso* Ph); 142.6 (−, d, $J_{C-P}$ = 32.4, P−C=); 130.4, 128.6, 128.0, 126.8 (+, s, C*ortho*, C*meta* Ph); 124.8 (−, d, $J_{C-P}$ = 5.5, =$CH_2$); 124.3, 123.7 (+, s, C*para* Ph); 96.7 (−, s, $\eta^5$-$C_5H_4$); 89.9, 84.1, 79.4, 77.3, (+, all s, $\eta^5$-$C_5H_4$); 29.8 (+, d, $J_{C-P}$ = 31.0, PCH); 28.4 (+, d, $J_{C-P}$ = 31.0, PCH); 25.2 (+, d, $J_{C-P}$ = 4.2, =CHPh); 24.6 (+, d, $J_{C-P}$ = 2.0, =CHPh); 23.0−14.0 (+, all s, $CH_3$). $^{31}$P-{$^1$H} NMR (121.4 MHz, $C_6D_6$, 293 K): $\delta$ 32.8 (s, d in *off*-resonance). MS (FAB$^+$): *m*/*z* 610 (M$^+$).

**X-ray Analysis of 5 and 8.** Two irregular crystals of size 0.20 × 0.12 × 0.12 mm (**5**) and 0.16 × 0.12 × 0.08 mm (**8**) were mounted on a Bruker Smart APEX CCD diffractometer at 100.0(2) K equipped with a normal focus, 2.4 kW sealed tube source (molybdenum radiation, $\lambda$ = 0.71073 Å) operating at 50 kV and 35 mA (**5**) or 30 mA (**8**). Data were collected over the complete sphere by a combination of four sets. Each frame exposure time was 10 s covering 0.3° in $\omega$. The cell parameters were determined and refined by least-squares fit of 5034 (**5**) or 7967 (**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 SADABS.[24] 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[25] program package minimizing $w(F_o^2 - F_c^2)^2$. The isopropenyldi(isopropyl)phosphine of complex **8** was observed with the isopropenyl group disordered in two sites and refined with complementary occupancy factors and restrained geometry. The nondisordered non-hydrogen atoms of **5** and **8** were anisotropically refined. The hydrogen atoms were observed or calculated and refined riding on bonded carbon atoms. The hydride ligand of **8** was observed in the difference Fourier maps and refined freely. Weighted *R* factors ($R_w$) and goodness of fit (*S*) are based on $F^2$; conventional *R* factors are based on *F*. Crystal data and details of the data collection and refinement are given in Table 3.

**Table 3. Crystal Data and Data Collection and Refinement for 5 and 8**

| | **5** | **8** |
|---|---|---|
| Crystal Data | | |
| formula | $C_{28}H_{36}F_6OsP_2$ | $C_{29}H_{39}OsP$ |
| molecular wt | 738.71 | 608.77 |
| color and habit | orange, irregular block | yellow, irregular block |
| symmetry, space group | monoclinic, $P2_1/n$ | monoclinic, $P2_1/n$ |
| *a*, Å | 11.2563(9) | 10.0637(5) |
| *b*, Å | 20.2337(16) | 18.3653(9) |
| *c*, Å | 12.3703(10) | 13.7078(7) |
| $\beta$, deg | 92.3440(10) | 90.5290(10) |
| *V*, Å$^3$ | 2815.1(4) | 2533.4(2) |
| *Z* | 4 | 4 |
| $D_{calc}$, g cm$^{-3}$ | 1.743 | 1.596 |
| Data Collection and Refinement | | |
| diffractometer | Bruker Smart APEX | |
| $\lambda$(Mo K$\alpha$), Å | 0.71073 | |
| monochromator | graphite oriented | |
| scan type | $\omega$ scans | |
| $\mu$, mm$^{-1}$ | 4.700 | 5.111 |
| 2$\theta$ range, deg | 3, 56 | 3, 56 |
| temp, K | 100 | 100 |
| no. of data collected | 33 606 | 30 444 |
| no. of unique data | 6741 ($R_{int}$ = 0.0397) | 6065 ($R_{int}$ = 0.0453) |
| no. of params/restraints | 351/0 | 288/14 |
| $R_1$[a] [$F^2 > 2\sigma(F^2)$] | 0.0319 | 0.0326 |
| $wR_2$[b] [all data] | 0.0718 | 0.0723 |
| *S*[c] [all data] | 0.984 | 1.015 |

[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.

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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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