Preparation of Half-Sandwich Osmium-Allyl Complexes by Consecutive C−C Bond Formation and C−H Bond Activation Reactions

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The vinylidene complex Os(η^5-C_5H_5)Cl(=C=CHPh)(P^iPr_3) (**1**) reacts with MeMgCl to give the osmaindene OsH(η^5-C_5H_5){C(CH_3)=CHC_6H_4}(P^iPr_3) (**2**), which isomerizes into the *exo*-allyl compound Os(η^5-C_5H_5)(η^3-*C*H_2*C*H*C*HPh)(P^iPr_3) (**3**) in refluxing toluene. Treatment of **3** with HBF_4·OEt_2 leads to the *endo*-d^4-allyl derivative [OsH(η^5-C_5H_5){η^3-*C*H_2*C*H*C*HPh}(P^iPr_3)]BF_4 (**4**), which can be also obtained by addition of HBF_4·OEt_2 to **2**. Complex **4** contains the terminal CHPh group of the allyl *cisoid* disposed to the phosphine. In dichloromethane at 40 °C, it isomerizes into an *endo*-allyl isomer **5** with the terminal CHPh group *cisoid* disposed to the hydride. Complex **1** also reacts with EtMgCl. The reaction affords OsH(η^5-C_5H_5){C(CH_2CH_3)=CHC_6H_4}(P^iPr_3) (**6**), which in toluene at 70 °C is converted into the *exo*-allyl complex Os(η^5-C_5H_5){η^3-*C*H(CH_3)*C*H*C*HPh}(P^iPr_3) (**7**). Treatment of **7** with HBF_4·OEt_2 leads to an equilibrium mixture of *exo*-d^4-allyl derivatives of formula [OsH(η^5-C_5H_5){η^3-*C*H(CH_3)*C*H*C*HPh}(P^iPr_3)]BF_4 (**8** and **9**). The addition of HBF_4·OEt_2 to **6** gives an *endo*-d^4-allyl isomer, **10**, which is transformed into the equilibrium mixture of **8** and **9** after 7 days in dichloromethane at 40 °C. Treatment of **1** with PhMgCl gives rise to OsH(η^5-C_5H_5){C(Ph)=CHC_6H_4}(P^iPr_3) (**11**), which reacts with HBF_4·OEt_2 in the presence of acetonitrile to afford stilbene and the solvento complex [Os(η^5-C_5H_5)(CH_3CN)$_2$(P^iPr_3)]BF_4 (**12**). The X-ray structures of **3**, **5**, and **8** are also reported.

Introduction

The design of metallic homogeneous systems that are effective in the synthesis of functionalized organic molecules from basic hydrocarbon units is significant and of great interest.[1] In this respect, developing systems that consecutively promote carbon−carbon bond formation and C−H bond activation is an urgent task.[2]

Transition-metal allyl complexes are tools of utmost importance, as they represent real catalysts or reaction intermediates for a number of highly valuable processes including carbon−carbon and carbon−heteroatom coupling reactions.[3] Thus, they have attracted much attention from both experimental[4] and theoretical[5] points of view. Metal−η^3-allyl complexes can exist in different isomers, due to the relative orientations of the allyl ligands. Knowing the factors controlling the relative energy of the isomers should help to understand the regio- and stereochemistry of reactions mediated by π-allyl complexes.[3c,e,5b−d]

In agreement with the tendency shown by Os(η^5-C_5H_5)Cl(P^iPr_3)$_2$ to release a phosphine ligand,[6] and as a part of our work

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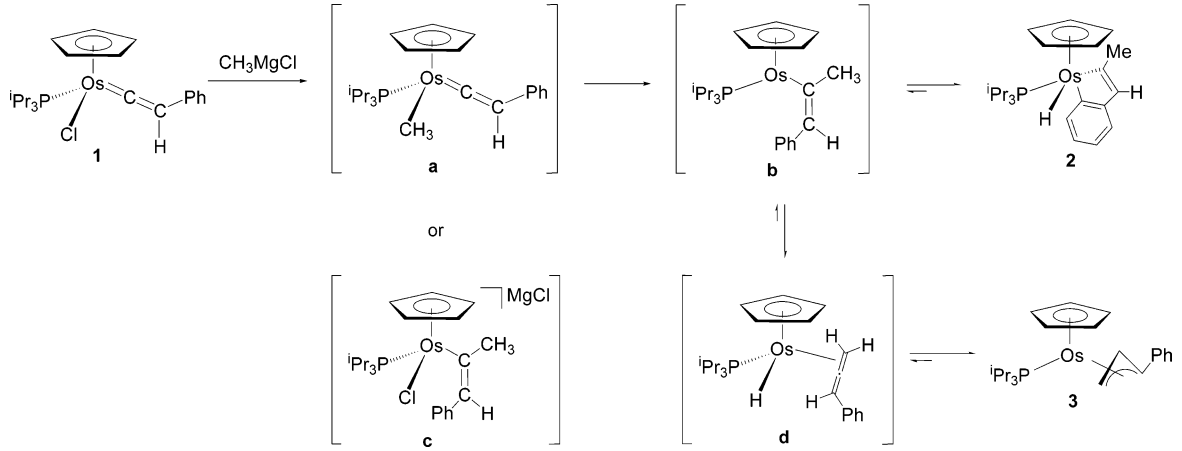
Scheme 1



on the chemistry of the osmium−carbon multiple bonds,[7,8] we have previously proved that the treatment of this cyclopentadienyl derivative with phenylacetylene affords the vinylidene complex Os(η^5-C_5H_5)Cl(=C=CHPh)(P^iPr_3), via the π-alkyne intermediate Os(η^5-C_5H_5)Cl(η^2-HC≡CPh)(P^iPr_3).[9]

The reactivity of the vinylidene−metal moieties is dominated by the electrophilicity and nucleophilicity of the C_α and C_β atoms, respectively. As a result, nucleophiles add to the C_α atom, and the stereoselective coupling of alkyl, aryl, alkenyl, or alkynyl groups with the vinylidene should be expected.[10] The process may be considered as a counterpart to the coupling of a hydrocarbyl unit with a Fischer-type carbene moiety, of which several examples are known.[11] In this paper, we report the coupling between the vinylidene ligand of Os(η^5-C_5H_5)Cl(=C=CHPh)(P^iPr_3) and methyl, ethyl, and phenyl groups, and the transformation of the resulting organic fragments into allyl ligands by means of H−C(sp^3) bond activation reactions.

Results and Discussion

1. Vinylidene−Methyl Coupling. Treatment at 55 °C of a tetrahydrofuran solution of Os(η^5-C_5H_5)Cl(=C=CHPh)(P^iPr_3) (**1**) with 1.2 equiv of MeMgCl leads to the osmaindene derivative OsH(η^5-C_5H_5){$C(CH_3)$=CHC_6H_4}(P^iPr_3) (**2**). Its formation can be rationalized according to Scheme 1. The addition of MeMgCl to **1** could initially produce the nucleophilic substitution of the chloride ligand by a methyl group, to give **a**. The subsequent migratory insertion of the vinylidene into the osmium−methyl bond should afford the unsaturated alkenyl intermediate **b**, which could yield **2** by *ortho*-CH bond activation of the phenyl substituent at the carbon−carbon double bond. The formation of **b** may also occur by direct addition of the C-donor nucleophile to the C_α atom of the vinylidene, followed by the elimination of chloride from the resulting species **c**.

Complex **2** was isolated as a yellow solid in 67% yield. In agreement with the presence of a hydride ligand *cisoid* disposed to the phosphine, at 20 °C, the ^{1}H NMR spectrum in benzene-d_6 of this compound shows at −14.56 ppm a doublet with a H−P coupling constant of 47.2 Hz. In the low-field region of the spectrum the most noticeable resonance is a singlet at 7.44

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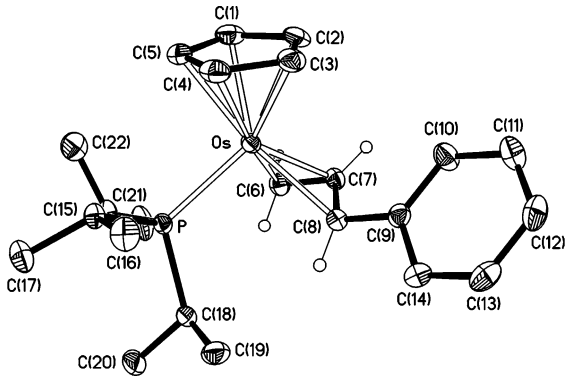

Figure 1. Molecular diagram of complex Os(η^5-C_5H_5)(η^3-$CH_2CHCHPh$)(P^iPr_3) (**3**).

Table 1. Selected Bond Distances (Å) and Angles (deg) for Complex Os(η^5-C_5H_5)(η^3-$CH_2CHCHPh$)(P^iPr_3) (3)

Os−P	2.3170(7)	Os−C(3)	2.213(2)
Os−C(6)	2.197(2)	Os−C(4)	2.218(3)
Os−C(7)	2.115(2)	Os−C(5)	2.216(3)
Os−C(8)	2.229(2)	C(6)−C(7)	1.427(3)
Os−C(1)	2.219(3)	C(7)−C(8)	1.431(3)
Os−C(2)	2.229(2)	C(8)−C(9)	1.485(3)
M[a]−Os−P	124.6	C(6)−Os−C(7)	38.59(9)
M[a]−Os−C(6)	134.2	C(6)−Os−C(8)	66.95(9)
M[a]−Os−C(7)	123.9	C(7)−Os−C(8)	38.35(9)
M[a]−Os−C(8)	130.8	C(6)−C(7)−C(8)	117.4(2)
P−Os−C(6)	86.30(7)	C(7)−C(8)−C(9)	120.1(2)
P−Os−C(7)	111.21(7)		
P−Os−C(8)	95.79(6)		

[a] M is the centroid of the C(1)−C(5) Cp ligand.

ppm, corresponding to the vinylic hydrogen of the alkenyl moiety. In the $^{13}C\{^1H\}$ NMR spectrum, the resonances due to the atoms of the alkenyl carbon−carbon double bond are observed at 142.3 (C_β) and 141.8 (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 Hz. The metalated carbon atom of the phenyl group gives rise to a doublet at 156.4 ppm with a C−P coupling constant of 4 Hz. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 18.5 ppm. These spectroscopic data agree well with those previously reported for the related compound OsH(η^5-$C_5H_4SiPh_3$){CH=C(CH_3)C_6H_4}(P^iPr_3), which has been characterized by X-ray diffraction analysis.[12]

In refluxing toluene, complex **2** isomerizes into the allyl derivative Os(η^5-C_5H_5)(η^3-$CH_2CHCHPh$)(P^iPr_3) (**3**). After 15 h, the rearrangement is quantitative. Complex **3** is the result of a methyl−CH bond activation in the alkenyl ligand of **b** and the subsequent migratory insertion of the resulting allene into the osmium−hydride bond of **d** (Scheme 1).

Since **2** and **3** result from competitive C−H bond activation processes in the undetected alkenyl intermediate **b**, the formation of **2** is in agreement with the kinetic preference of the C−H arene activation over the C−H alkyl, while the formation of **3** agrees well with the higher stability of a M(η^3-allyl) bond with regard to a M−aryl bond.[13]

Complex **3** was isolated as a yellow solid in 83% yield. Figure 1 shows a view of its molecular geometry, whereas selected bond distances and angles are listed in Table 1. The coordination geometry around the osmium atom can be rationalized as being derived from a highly distorted octahedron with the cyclopentadienyl ligand occupying a face. The structure proves the formation of the allyl ligand, which is coordinated by the C(6), C(7), and C(8) carbon atoms, in the *exo* form with the C(7)−H unit pointing to the cyclopentadienyl ring. This agrees well with theoretical results showing that in d^6-(η^5-C_5H_5)ML(η^3-allyl) complexes (L = CO, PR_3, N≡CR, alkyl, H, halides) the *exo* structure form is more stable than the *endo* one. The *exo* structural arrangement of the allyl ligand appears to avoid repulsive interactions between one pair of d electrons and the π_2 electrons of the allyl ligand and to favor the metal(d)-to-η^3-allyl(π^*) back-bonding interactions.[5d] The phenyl substituent is *syn* disposed with regard to C(7)−H, with a C(7)−C(8)−C(9) angle of 120.1(2)°. The allyl moiety coordinates in an asymmetrical fashion, with the separation between the central carbon atom C(7) and the metal (2.115(2) Å) being shorter than the separation between the metal and the terminal carbon atoms C(6) (2.197(2) Å) and C(8) (2.229(2) Å). The angles C(6)−Os−C(8) and C(6)−C(7)−C(8) are 66.95(9)° and 117.4(2)°, respectively. The carbon−carbon distances within the allylic moiety, 1.427(3) Å for C(6)−C(7) and 1.431(3) Å for C(7)−C(8), are in accordance with the values found in Os(η^5-C_5H_5)(η^3-$CH_2CHCHCH_2Ph$)(P^iPr_3)[11b] and [OsH(η^5-$C_5H_4SiPh_3$){η^3-$CH_2C(Ph)CH_2$}(P^iPr_3)]BF_4.[12]

In agreement with the structure shown in Figure 1, the ^1H NMR spectrum in benzene-d_6 at room temperature shows four resonances for the allylic protons at 1.02, 2.58, 2.99, and 4.55 ppm, which were assigned to C(6)H *anti* to C(7)H, C(8)H, C(6)H *syn* to C(7)H, and C(7)H, respectively, on the basis of $^1H-^1H$ COSY, $^1H-^{13}C$ HMQC, and NOE experiments (Table 2). The irradiation of the C(8)HPh resonance increases the Ph

Table 2. NOE Experiments Performed on Complexes 3−5 and 7−10

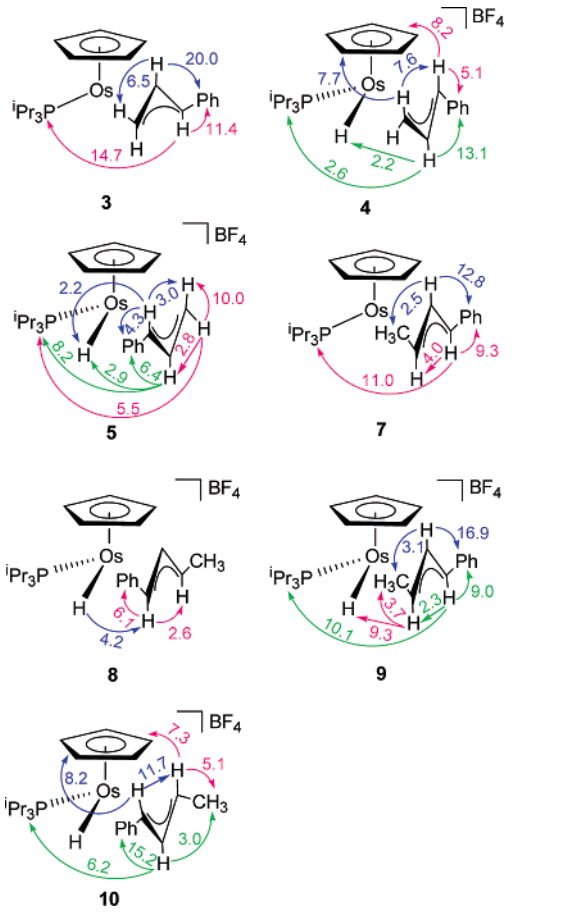

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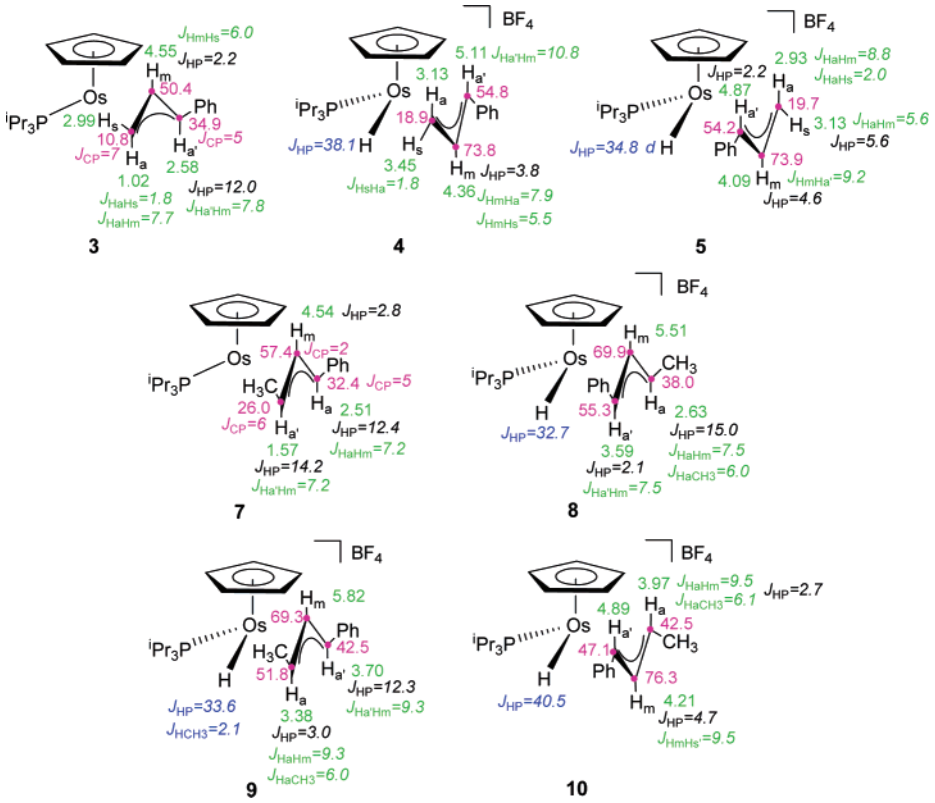
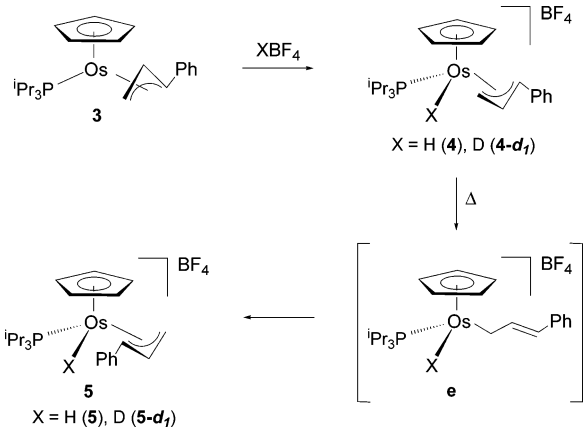
Table 3. Selected ^{1}H (green) and ^{13}C{^{1}H} (purple) NMR Chemical Shifts (δ, ppm) and Coupling Constants (Hz) for Complexes 3−5 and 7−10



(11.4%) and P^{i}Pr$_3$ (14.7%) resonances, while the saturation of the *meso* C(7)H proton enhances the intensity of the C(6)H *syn* (6.5%) and Ph (20%) signals. A NOE effect between C(7)H and the cyclopentadienyl resonance is not observed. In this context, it should be noted that *exo* complexes of this type can be identified by a NOE effect between the *anti* protons and the phosphine, but not by a NOE between the cyclopentadienyl and the *meso* proton. The different coupling constants in these resonances have been deduced by means of the ^{1}H{^{31}P} NMR spectrum and selective homonuclear irradiation in the ^{1}H NMR spectrum and are collected in Table 3. In the ^{13}C{^{1}H} NMR spectrum the most noticeable resonances are a singlet at 50.4 ppm and two doublets at 34.9 and 10.8 ppm with C−P coupling constants of 5 and 7 Hz. On the basis of the ^{1}H−^{13}C HMQC spectrum, these resonances were assigned to the C(7), C(8), and C(6) atoms of the allyl ligand, respectively. The ^{31}P{^{1}H} NMR spectrum shows a singlet at 20.9 ppm.

Treatment of **3** in diethyl ether at 0 °C with 1.0 equiv of HBF$_4$·OEt$_2$ leads to the d^4-allyl derivative [OsH(η^5-C$_5$H$_5$){η^3-*C*H$_2$*C*H*C*HPh}(P^{i}Pr$_3$)]BF$_4$ (**4**) as a result of the protonation of **3**. The addition of the proton of the acid to the metal center is accompanied by a change in the coordination form of the allyl ligand, from *exo* to *endo* (Scheme 2). The latter is the preferred structural form in d^4-M(η^5-C$_5$R$_5$)L$_2$(η^3-allyl) complexes (L ≠ CO),[5d] and it has been found in Os(η^5-C$_5$Me$_5$)X$_2$(η^3-allyl) (X = Br, Me, H),[4d] Ru(η^5-C$_5$H$_5$)X$_2$(η^3-allyl) (X = Cl, Br),[14] Ru(η^5-C$_5$H$_5$)Cl$_2$(η^3-C$_4$H$_4$OMe),[4a] Ru(η^5-C$_5$Me$_5$)(CH$_2$Cl)Cl(η^3-C$_3$H$_5$),[4c] Ru(η^5-C$_5$H$_5$)(R)Br(η^3-C$_3$H$_5$) (R = CH$_3$, CH$_2$SiMe$_3$),[15]

Scheme 2



and [Ru(η^5-C$_5$Me$_5$)(amidinate)(η^3-C$_3$H$_5$)]$^+$.[16] When L = CO, both the *exo* and *endo* structural forms have comparable stability.[4b,17]

The *exo*−*endo* interconversion may proceed by rotation of the planar π-allyl moiety about the osmium−allyl axis or alternatively by an $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ pathway in which an η^1-allyl intermediate is involved. Density functional theory studies on d^4-Mo(η^5-C$_5$H$_5$)(CO)$_2$(η^3-C$_3$H$_5$) and d^6-M(η^5-C$_5$H$_5$)(CO)(η^3-C$_3$H$_5$) (M = Fe, Ru) complexes show that for the d^4-compound

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(15) Itoh, K.; Fukahori, T. *J. Organomet. Chem.* **1988**, *349*, 227.

(16) Kondo, H.; Yamaguchi, Y.; Nagashima, H. *Chem. Commun.* **2000**, 1075.

(17) (a) Faller, J. W.; Incorvia, M. J. *Inorg. Chem.* **1968**, *7*, 840. (b) Faller, J. W.; Chen, C.-C.; Mattina, M. J.; Jakubowski, A. *J. Organomet. Chem.* **1973**, *52*, 361. (c) McCleverty, J. A.; Murray, A. J. *Transition Met. Chem.* **1979**, *4*, 273. (d) Benyunes, S. A.; Binelli, A.; Green, M.; Grimshire, M. J. *J. Chem. Soc.* **1991**, 895. (e) Liao, M.-F.; Lee, G.-H.; Peng, S.-M.; Liu, R.-S. *Organometallics* **1994**, *13*, 4973. (f) van Staveren. D. R.; Weyhermüller, T.; Metzler-Nolte, N. *Organometallics* **2000**, *19*, 3730.

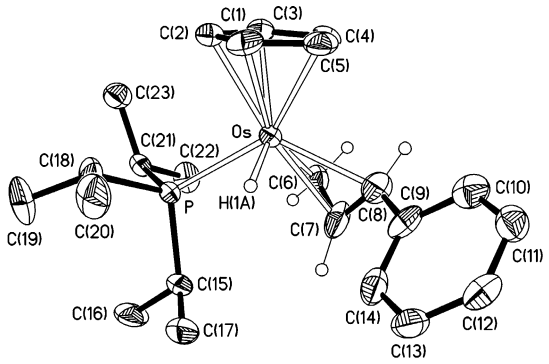


Figure 2. Molecular diagram for the cation of $[OsH(\eta^5\text{-}C_5H_5)\{\eta^3\text{-}CH_2CHCHPh\}(P^iPr_3)]BF_4$ (**5**).

the rotation of the allyl ligand around the metal−allyl axis ($\eta^3 \rightarrow \eta^3 \rightarrow \eta^3$ pathway) is intrinsically more favored than the $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ pathway. However, the η^3-transition states for the Fe and Ru complexes are inaccessible and the $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ pathway is more favorable. The reason for this appears to be that one pair of the six metal d electrons has to occupy a d orbital having significant M−C_5H_5 antibonding character in the transition structure.[5e] According to these results, in our osmium system, the mechanism of the *exo*−*endo* interconversion could depend on when the interconversion process takes place, before the addition of the proton to the metal center or after the protonation. In the first case, which involves the coexistence in equilibrium of **3** with no detectable concentrations of its *endo* isomer, the $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ pathway appears to be a more reasonable proposal than the rotation of the π-allyl around the osmium−allyl axis. However, in the second case an inverse relationship should be expected.

Complex **4** was isolated as a yellow solid in 82% yield. In agreement with the presence of a hydride ligand in the complex, the ^{1}H NMR spectrum in dichloromethane-d_2 at −20 °C shows at −15.12 ppm a doublet with a H−P coupling constant of 38.1 Hz. The resonance due to the CHPh-allyl proton ($H_{a'}$ in Table 3) appears as a doublet at 5.11 ppm. The value of the $H_{a'}$−H_m coupling constant of 10.8 Hz supports the *anti* disposition of this proton with regard to H_m. The resonance corresponding to the latter is observed at 4.36 ppm, whereas those due to the CH_2 protons appear at 3.13 and 3.45 ppm. The *endo* disposition of the allyl with regard to the cyclopentadienyl ligand was inferred on the basis of NOE experiments (Table 2). The saturation of the H_m resonance increases the intensity of the Ph (13.1%), hydride (2.2%), and P^iPr_3 (2.6%) signals, while a NOE effect with the cyclopentadienyl resonance is not observed. However, the saturation of the CHPh-allyl resonance and the CH_2 signal at 3.13 ppm increases the intensity of the Cp resonance (8.2% and 7.7%, respectively). In the $^{13}C\{^1H\}$ NMR spectrum the carbon atoms of the C_3 skeleton of the allyl ligand give rise to singlets at 73.8 (C_{meso}), 54.8 (CHPh), and 18.9 (CH_2) ppm. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 17.7 ppm.

The *cisoid* disposition of the CHPh group of the allyl and the phosphine is unfavorable with regard to that with the CHPh group *cisoid* to the hydride, probably as a consequence of the steric hindrance experienced between the phenyl group and the isopropyl substituents of the phosphine. Thus, complex **4** isomerizes into the *endo*-allyl complex **5** (Scheme 2). In dichloromethane at 40 °C, the transformation is quantitative after 72 h.

Figure 2 shows a view of the molecular geometry of **5**. Selected bond distances and angles are listed in Table 4. The distribution of ligands around the osmium atom can be described as a four-legged piano-stool geometry, where the allyl ligand occupies two *cisoid* positions with a C(6)−Os−C(8) angle of 64.66(17)°. The most noticeable features of the structure are the *cisoid* disposition of the substituted C(8) atom with regard to the hydride ligand, the *endo* coordination of the allyl, and the *syn* disposition of the phenyl group with regard to the *meso* carbon atom (C(7)−C(8)−C(9) = 125.7(5)°). The C_3 skeleton coordinates in an asymmetric fashion. The separation between the central carbon atom, C(7), and the metal (2.180(4) Å) is shorter than the separation between the metal and the terminal carbon atoms C(6) (2.188(4) Å) and C(8) (2.260(5) Å). The carbon−carbon distances within the allylic skeleton are 1.431(7) Å for C(6)−C(7) and 1.365(6) Å for C(7)−C(8). The angle C(6)−C(7)−C(8) is 116.6(5)°.

Table 4. Selected Bond Distances (Å) and Angles (deg) for Complex $[OsH(\eta^5\text{-}C_5H_5)\{\eta^3\text{-}CH_2CHCHPh\}(P^iPr_3)]BF_4$ (5)

Os−P	2.3753(10)	Os−C(3)	2.242(4)
Os−C(6)	2.188(4)	Os−C(4)	2.218(4)
Os−C(7)	2.180(4)	Os−C(5)	2.238(4)
Os−C(8)	2.260(5)	C(6)−C(7)	1.431(7)
Os−C(1)	2.255(4)	C(7)−C(8)	1.365(6)
Os−C(2)	2.254(4)	C(8)−C(9)	1.505(6)
M[a]−Os−H(1A)	116.2	C(6)−Os−C(7)	38.25(18)
M[a]−Os−P	121.8	C(6)−Os−C(8)	64.66(17)
M[a]−Os−C(6)	121.9	C(7)−Os−C(8)	35.75(16)
M[a]−Os−C(7)	140.9	C(6)−C(7)−C(8)	116.6(5)
M[a]−Os−C(8)	112.3	C(7)−C(8)−C(9)	125.7(5)
P−Os−H(1A)	76.5(16)	C(6)−Os−H(1A)	119.7(16)
P−Os−C(6)	86.17(13)	C(7)−Os−H(1A)	85.3(16)
P−Os−C(7)	93.85(14)	C(8)−Os−H(1A)	80.2(16)
P−Os−C(8)	125.89(13)		

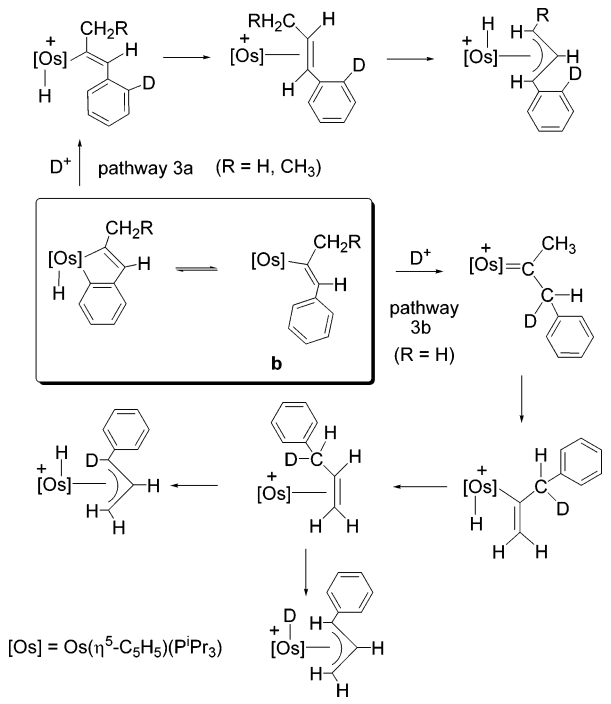
[a] M represents the midpoint of the Cp ring.

In agreement with the structure shown in Figure 2, the ^{1}H NMR spectrum of **5** in dichloromethane-d_2 at 20 °C shows four resonances for the allylic protons at 4.87 (CHPh), 4.09 (H_{meso}), and 3.13 and 2.93 (CH_2) ppm. In the high-field region, the hydride displays a doublet at −15.31 ppm with a H−P coupling constant of 34.8 Hz. In the $^{13}C\{^1H\}$ NMR spectrum, the resonances corresponding to the allyl carbon atoms are observed at 73.9 (C(7)), 54.2 (C(8)), and 19.7 (C(6)) ppm. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 14.0 ppm.

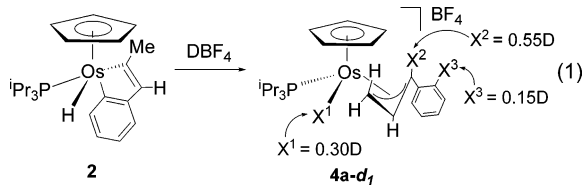
Complexes **4** and **5** are diastereoisomers resulting from the chirality of the osmium atom and the prochirality of the styryl moiety of the allyl. The isomerization process involves the decoordination of the styryl moiety from the metal center of **4**, to afford the η^1-allyl intermediate **e**, and the subsequent coordination of the osmium atom of **e** to the other face of the carbon−carbon double bond. The hydride ligand does not play any role in the transformation. The addition of $DBF_4{\cdot}OD_2$ to a dichloromethane solution of **3** affords $[OsD(\eta^5\text{-}C_5H_5)\{\eta^3\text{-}CH_2CHCHPh\}(P^iPr_3)]BF_4$ (**4-d_1**), which isomerizes into the deuteride derivative **5-d_1**. Deuterium at the allyl positions of **5-d_1** is not observed. The presence of deuterium at the metal center of these compounds is strongly supported by their ^{2}H NMR spectra, which show high-field resonances at −15.1 and −15.3 ppm, respectively.

Complex **4** can be also obtained from **2**. The addition at 0 °C of 1.0 equiv of $HBF_4{\cdot}OEt_2$ to a diethyl ether solution of the latter produces the instantaneous precipitation of **4** in 82% yield. The reaction of **2** with $DBF_4{\cdot}OD_2$ affords **4a-d_1** (eq 1) with the following deuterium distribution: 0.30 deuterium atom at the hydride position, 0.15 deuterium atom at the *ortho* position of the phenyl group, and 0.55 deuterium atom at the terminal allyl CPh carbon atom. In dichloromethane-d_2, complex **4a-d_1** is transformed into **5a-d_1** with the same deuterium distribution as

Scheme 3



4a-*d*$_1$, in agreement with an isomerization process via the η^1-allyl intermediate **e** (Scheme 2) and without the hydride participation. The above-mentioned deuterium distribution is strongly supported by the ^{2}H and ^{1}H NMR spectra of **4a-*d*$_1$** and **5a-*d*$_1$**. The ^{2}H NMR spectra in dichloromethane contain resonances at 7.4, 5.1, and −15.1 (**4a-*d*$_1$**) and 7.4, 4.9, and −15.1 (**5a-*d*$_1$**) ppm in a 0.15:0.55:0.30 intensity ratio, whereas in the ^{1}H NMR spectra in dichloromethane-d_2 the intensity ratio of the resonances at 7.33, 5.11, and −15.12 (**4**) and 7.26, 4.87, and −15.31 (**5**) ppm is 4.85:0.45:0.70.



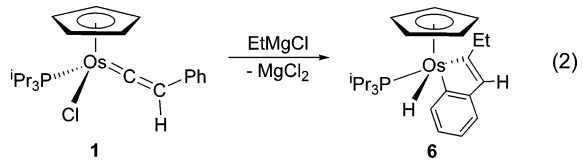
(1)

The results summarized in eq 1 can be rationalized according to Scheme 3. The presence of deuterium at the *ortho* position of the phenyl group appears to be a consequence of the protonation of the orthometalated carbon atom of **2** (pathway 3a), whereas the presence of deuterium at the hydride position and at the terminal-allyl CPh carbon atom appears to be the result of the protonation of the C_β atom of the alkenyl ligand of intermediate **b** (pathway 3b). In this context, it should be noted that alkenyl ligands of electron-rich metals are nucleophilic at the C_β atom and their reactions with electrophiles lead to carbene complexes.[7l,18]

The electrophilic addition of D^+ to the orthometalated carbon atom of **2** should afford a hydride-alkenyl intermediate with a deuterium atom at one of the *ortho* positions of the phenyl substituent of the alkenyl ligand. Its unsaturated character should favor the reductive elimination of the olefin.[12,19] Thus, the C−H bond activation of the methyl substituent of the olefin could finally give **4a-*d*$_1$** containing a deuterium atom at an *ortho* position of the phenyl group.

The electrophilic addition of D^+ to the alkenyl ligand of **b** should yield a benzyl-methyl-carbene intermediate, containing a deuterium atom at the C(sp^3) atom of the benzyl substituent. This species could evolve by a β-hydrogen elimination reaction on the methyl substituent into an unsaturated hydride-alkenyl intermediate. Thus, the reductive elimination of olefin and the subsequent C−H or C−D bond activation of the benzyl substituent of the olefin could give **4a-*d*$_1$** containing a deuterium at the terminal-allyl CPh carbon atom or at the hydride position, respectively.

2. Vinylidene−Ethyl Coupling. Similarly to the reaction of **1** with MeMgCl, the treatment at 55 °C of **1** with EtMgCl in tetrahydrofuran leads to the osmaindene derivative OsH(η^5-C_5H_5){C(CH_2CH_3)=CHC_6H_4}(P^iPr_3) (**6**). In this case, the metallacycle contains an ethyl substituent at the C_α atom of the carbon−carbon double bond (eq 2). Its formation should involve the same sequence of elemental steps as the formation of **2**, with ethyl instead of methyl.



(2)

Complex **6** was isolated as a yellow solid in 74% yield. In agreement with **2**, the hydride resonance in the ^{1}H NMR spectrum of **6** appears at −14.44 ppm as a doublet with a H−P coupling constant of 47.4 Hz. In the low-field region, the vinylic hydrogen of the alkenyl unit of the metallacycle gives rise to a singlet at 7.51 ppm. In the ^{13}C{^{1}H} NMR spectrum, the resonances due to the atoms of the alkenyl carbon−carbon double bond are observed at 141.1 (C_α) and 138.6 (C_β) ppm. The first of them appears as a doublet with a C−P coupling constant of 17 Hz, while the second one is a singlet. The metalated carbon atom of the phenyl group gives rise to a doublet at 162.8 ppm, with a C−P coupling constant of 4 Hz. The ^{31}P{^{1}H} NMR spectrum shows a singlet at 18.6 ppm.

In toluene at 70 °C, complex **6** isomerizes into the allyl derivative Os(η^5-C_5H_5){η^3-*C*H(CH_3)*C*H*C*HPh}(P^iPr_3) (**7**), which was isolated after 72 h as a yellow solid in 82% yield, according to Scheme 4. Its formation can be rationalized as the formation of **3**. A β-hydrogen elimination reaction on the ethyl substituent CH_2 group of the alkenyl ligand of an unsaturated Os(η^5-C_5H_5)-{(E)-C(Et)=CHPh}(P^iPr_3) intermediate should afford a hydride-allene species, which could give **7** by insertion of the allene into the osmium−hydride bond.

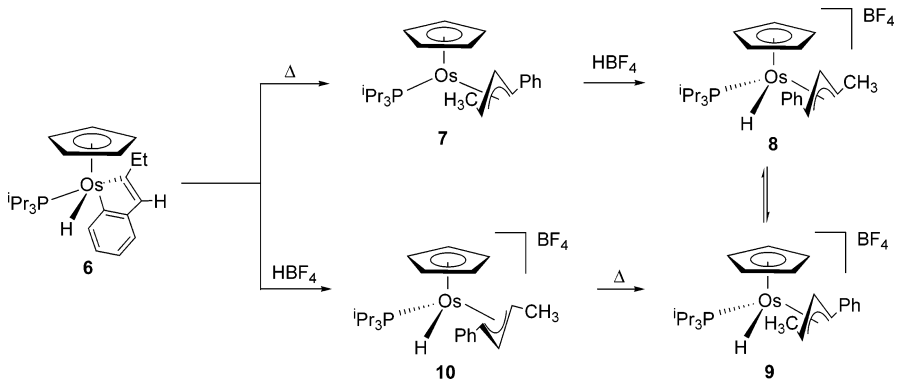
In the ^{1}H NMR spectrum of **7** in benzene-d_6 at 20 °C, the allylic resonances are observed at 4.54 (H_{meso}), 2.51 (CHPh), and 1.57 (CHMe) ppm. The value of the H_{meso}−H coupling constants of 7.2 Hz is in accordance with the *syn* disposition of the phenyl and methyl substituents with regard to H_{meso}.[2a,b,11c,20] This disposition seems to be sterically favored, being that

(18) See for example: Bohanna, C.; Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A. *Organometallics* **1995**, *14*, 4685, and references therein.

(19) (a) Bohanna, C.; Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A.; Sola, E. *Organometallics* **1995**, *14*, 4825. (b) Albéniz, M. J.; Esteruelas, M. A.; Lledós, A.; Maseras, F.; Oñate, E.; Oro, L. A.; Sola, E.; Zeier, B. *J. Chem. Soc., Dalton Trans.* **1997**, 181.

(20) See for example: (a) Clark, H. C.; Hampden-Smith, M. J.; Ruegger, H. *Organometallics* **1988**, *7*, 2085. (b) Krivykh, V. V.; Gusev, O. V.; Petrovskii, P. V.; Rybinskaya, M. I. *J. Organomet. Chem.* **1989**, *366*, 129.

Scheme 4



generally observed in reported complexes structurally characterized by X-ray diffraction.[21] In agreement with the d^6-(η^5-C_5H_5)-ML(η^3-allyl) character of **7**, the allyl ligand is disposed *exo* with regard to the cyclopentadienyl ligand. The orientation was inferred on the basis of a NOE experiment (Table 2). The saturation of the allylic CHPh resonance increases the intensity of the Ph (9.3%), CHMe (4.0%), and P^iPr_3 (11.0%) resonances, while a NOE effect with the cyclopentadienyl signal is not observed. In the $^{13}C\{^1H\}$ NMR spectrum, the most noticeable resonances are three doublets at 57.4, 32.4, and 26.0 ppm with C−P coupling constants of 2, 5, and 6 Hz, which were assigned, on the basis of the $^1H-^{13}C$ HMQC spectrum, to the C_{meso}, CPh, and CMe allylic carbon atoms, respectively. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 19.5 ppm.

In a manner similar to **3**, complex **7** reacts with HBF_4. However, in this case, the oxidation of the metal center does not produce the *exo*−*endo* transformation of the allyl ligand. Treatment at 20 °C of a dichloromethane solution of **7** with 1.0 equiv of HBF_4·OEt_2 leads to a 5:2 equilibrium mixture of the *exo*-d^4-allyl derivatives **8** and **9** ([OsH(η^5-C_5H_5){η^3-*C*H(CH_3)-*C*H*C*HPh}(P^iPr_3)]BF_4), according to Scheme 4.

All attempts to get single crystals of the BF_4^- salt of the thermodynamically favored isomer **8** were unsuccessful. The exchange of BF_4^- by BPh_4^- allowed the crystallization of the salt. Figure 3 shows a view of the molecular geometry of the cation of **8**. Selected bond distances and angles are listed in Table 5.

The distribution of ligands around the osmium atom can be described as a four-legged piano-stool geometry, where the allyl ligand occupies two *cisoid* positions (C(2)−Os−C(4) = 64.5-(4)°), with the terminal CMe carbon atom (C(2)) *cisoid* disposed to the phosphine and the terminal CPh carbon atom (C(4)) *cisoid* disposed to the hydride ligand. The structure proves the *exo* coordination of the allyl ligand and the *syn* disposition of both substituents, the phenyl and methyl groups, with regard to the *meso* carbon atom C(3). The C(1)−C(2)−C(3) and C(3)−C(4)−C(5) angles are 120.5(10)° and 124.0(11)°, respectively. As in **3** and **5**, the C_3 skeleton coordinates in an asymmetrical fashion. The separation between C(3) and the metal (2.079(11) Å) is about 0.2 Å shorter than the separation between the metal and C(4) (2.284(11) Å) and C(2) (2.213(11) Å). The carbon−carbon distances within the C_3 skeleton are 1.394(13) Å for C(2)−C(3) and 1.371(13) Å for C(3)−C(4), whereas the C(2)−C(3)−C(4) angle is 120.3(11)°.

(21) See for example: (a) Tulip, T. H.; Ibers, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 4201. (b) Murrall, N. W.; Welch, A. J. *J. Organomet. Chem.* **1986**, *301*, 109. (c) Henly, T. J.; Wilson, S. R.; Shapley, J. R. *Inorg. Chem.* **1988**, *27*, 2551. (d) Faller, J. W.; Lambert, C.; Mazzieri, M. R. *J. Organomet. Chem.* **1990**, *383*, 161.

Table 5. Selected Bond Distances (Å) and Angles (deg) for Complex [OsH(η^5-C_5H_5){η^3-*C*H(CH_3)*C*H*C*HPh}(P^iPr_3)]BPh_4 (8)

Os−P	2.361(3)	Os−C(14)	2.197(10)
Os−C(2)	2.213(11)	Os−C(15)	2.238(10)
Os−C(3)	2.079(11)	C(1)−C(2)	1.543(13)
Os−C(4)	2.284(11)	C(2)−C(3)	1.394(13)
Os−C(11)	2.279(10)	C(3)−C(4)	1.371(13)
Os−C(12)	2.331(10)	C(4)−C(5)	1.516(13)
Os−C(13)	2.278(11)		
M[a]−Os−H(01)	110.8	C(2)−Os−C(3)	37.8(4)
M[a]−Os−P	124.7	C(2)−Os−C(4)	64.5(4)
M[a]−Os−C(2)	125.4	C(3)−Os−C(4)	36.2(4)
M[a]−Os−C(3)	117.9	C(2)−C(3)−C(4)	120.3(11)
M[a]−Os−C(4)	131.1	C(1)−C(2)−C(3)	120.5(10)
P−Os−H(01)	76.1	C(3)−C(4)−C(5)	124.0(11)
P−Os−C(2)	83.7(3)	C(2)−Os−H(01)	121.6
P−Os−C(3)	112.4(3)	C(3)−Os−H(01)	104.0
P−Os−C(4)	103.0(3)	C(4)−Os−H(01)	67.8

[a] M represents the midpoint of the Cp ring.

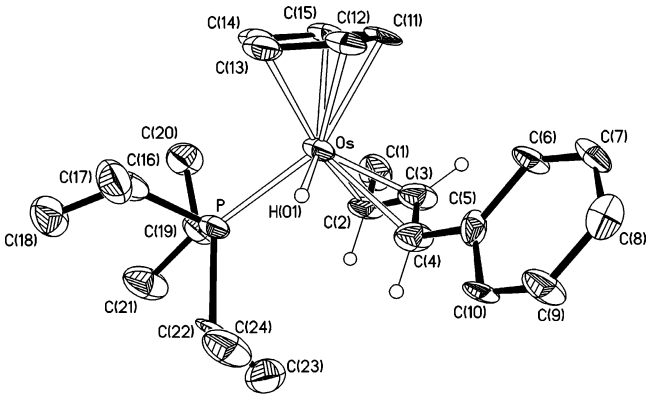


Figure 3. Molecular diagram of the cation [OsH(η^5-C_5H_5){η^3-*C*H(CH_3)*C*H*C*HPh}(P^iPr_3)]$^+$ (**8**).

In the ^1H NMR spectrum of **8** in dichloromethane-d_2 at 20 °C, the hydride resonance appears at −13.30 ppm as a doublet with a H−P coupling constant of 32.7 Hz, in agreement with the *cisoid* disposition of the hydride and phosphine ligands.[22]

(22) See for example: (a) Wilczewski, T. *J. Organomet. Chem.* **1986**, *317*, 307. (b) Rottink, M. K.; Angelici, R. J. *J. Am. Chem. Soc.* **1993**, *115*, 7267. (c) Jia, G.; Ng, W. S.; Yao, J.; Lau, C.-P.; Chen, Y. *Organometallics* **1996**, *15*, 5039. (d) Esteruelas, M. A.; Gómez, A. V.; López, A. M.; Oro, L. A. *Organometallics* **1996**, *15*, 878. (e) Jia, G.; Lau, C.-P. *J. Organomet. Chem.* **1998**, *565*, 37. (f) Baya, M.; Crochet, P.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2001**, *20*, 240. (g) Baya, M.; Buil, M. L.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2004**, *23*, 1416. (h) Esteruelas, M. A.; López, A. M.; Oñate, E.; Royo, E. *Organometallics* **2004**, *23*, 5633. (i) Baya, M.; Esteruelas, M. A.; González, A. I.; López, A. M.; Oñate, E. *Organometallics* **2005**, *24*, 1225. (j) Esteruelas, M. A.; López, A. M.; Oñate, E.; Royo, E. *Inorg. Chem.* **2005**, *44*, 4094.

The allylic resonances are observed at 5.51 (H_{meso}), 3.59 (CHPh), and 2.63 (CHMe) ppm. As for **7**, the value of the $H_{meso}-H$ coupling constants is 7.5 Hz. The *cisoid* disposition of C(4) and the hydride ligand is consistent with the results of the NOE experiments carried out on **8** (Table 2). Thus, the saturation of the hydride resonance produces an enhancement of 4.2% of the intensity of the signal at 3.59 ppm, while a NOE effect with the resonance at 2.63 ppm is not observed. In the $^{13}C\{^1H\}$ NMR spectrum, the most noticeable resonances are three singlets at 69.9, 53.3, and 38.0 ppm, which were assigned to C(3), C(4), and C(2), respectively, on the basis of the $^1H-^{13}C$ HMQC spectrum. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 20.7 ppm.

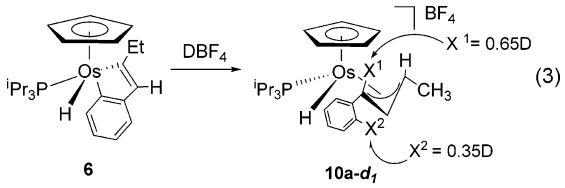
In the ^1H NMR spectrum of **9**, the hydride resonance is observed at −13.76 ppm as a double quartet by spin coupling with the phosphorus atom of the phosphine (33.6 Hz) and the hydrogen atoms of the methyl substituent of the allyl ligand (2.1 Hz). The latter was confirmed by a $^1H-^1H$ COSY NMR spectrum, which shows the cross signals between both resonances. The allylic resonances appear at 5.82 (H_{meso}), 3.70 (CHPh), and 3.38 (CHMe) ppm, with $H_{meso}-H$ coupling constants of 9.3 Hz. In agreement with the *cisoid* disposition of the terminal allylic CHMe group and the hydride ligand, the saturation of the allylic signal at 3.38 ppm produces an enhancement of the hydride resonance of 9.3%. In the $^{13}C\{^1H\}$ NMR spectrum, the allylic carbon atoms give rise to singlets at 69.3 (C_{meso}), 51.8 (CMe), and 42.5 (CPh) ppm. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 20.2 ppm.

In a manner similar to **2**, complex **6** reacts with $HBF_4 \cdot OEt_2$. The addition at 0 °C of 1.0 equiv of the acid to a diethyl ether solution of **6** gives rise to the precipitation of the d^4-allyl derivative **10** (Scheme 4), which is an *endo* isomer of **8** and **9**.

Complex **10** was isolated as a white solid in 91% yield. The ^1H NMR spectrum in dichloromethane-d_2 at −20 °C shows the hydride resonance at −15.10 ppm, as a doublet with a H−P coupling constant of 40.5 Hz. Spin coupling between the hydride and the hydrogen atoms of the methyl substituent of the allyl is not observed, in agreement with the *transoid* disposition of the hydride ligand and the terminal CHMe group. The allylic resonances are observed at 4.89 (CHPh), 4.21 (H_{meso}), and 3.97 (CHMe) ppm, with $H_{meso}-H$ coupling constants of 9.5 Hz. In accordance with the *endo* coordination of the allyl ligand, the saturation of the allyl resonances at 4.89 and 3.97 ppm produces increases of 8.2% and 7.3%, respectively, of the cyclopentadienyl resonance (Table 2). In the $^{13}C\{^1H\}$ NMR spectrum the carbon atoms of the C_3 skeleton of the allyl ligand give rise to singlets at 76.3 (Cmeso), 47.1 (CPh), and 42.5 (CMe) ppm. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 13.4 ppm.

The reaction of **6** with $DBF_4 \cdot OD_2$ affords **10a-*d*$_1$** with 0.35 deuterium atom at the *ortho* position of the phenyl group and 0.65 deuterium atom at the terminal allyl CPh carbon atom (eq 3). Deuterium at the hydride position is not observed. This deuterium distribution is supported by the ^2H and ^1H NMR spectra of **10a-*d*$_1$**. The ^2H NMR spectrum in dichloromethane contains broad singlets at 7.4 and 4.9 ppm in a 0.35:0.65 intensity ratio, whereas in the ^1H NMR spectrum in dichloromethane-d_2 the intensity ratio of the resonances at 7.3 and 4.89 ppm is 4.6:0.3.

The presence of deuterium at the phenyl substituent of the allyl ligand can be rationalized according to pathway 3a of Scheme 3. However, pathway 3b does not justify the presence of the deuterium at the terminal allyl CPh carbon atom and at the same time its absence in the hydride position, since from a statistical point of view, the C−D and C−H bond activations



(3)

in the CHDPh substituent of the olefin should be similarly feasible. The presence of deuterium at CPh and its absence at the hydride position suggests that the C_β atom of the alkenyl unit of the osmaindene of **6** undergoes reversible protonation. Thus, the addition of D^+ and the subsequent dissociation of H^+ should afford **6-*d*$_1$**, containing a deuterium atom at C_β of the alkenyl moiety of the metallacycle (Scheme 5), which could evolve into the allyl derivative via a process similar to that shown in pathway 3a. The presence of deuterium at the CPh carbon atom of **4** is significantly higher than the presence at the hydride position (0.55 versus 0.30). This suggests that, in addition to pathways 3a and 3b of Scheme 3, the C_β atom of the alkenyl unit of **2** also undergoes addition of D^+ and subsequent dissociation of H^+.

Complex **10** is structurally similar to **5**, which is the most stable allyl species resulting from the vinylidene−methyl coupling. However, although the *endo* structural form seems to be preferred in half-sandwich d^4-allyl complexes and the *cisoid* disposition of the hydride ligand and the terminal CHPh group is favored with regard to the *cisoid* disposition of the phosphine and the CHPh group, complex **10** is less stable than **9** despite that the latter contains an *exo*-allyl ligand and a CHPh group *cisoid* disposed to the phosphine. Thus, in dichloromethane at 20 °C, complex **10** isomerizes into **9** in quantitative yield after 24 h. After 7 days in dichloromethane-d_2 at 40 °C, complex **9** reaches equilibrium with **8**.

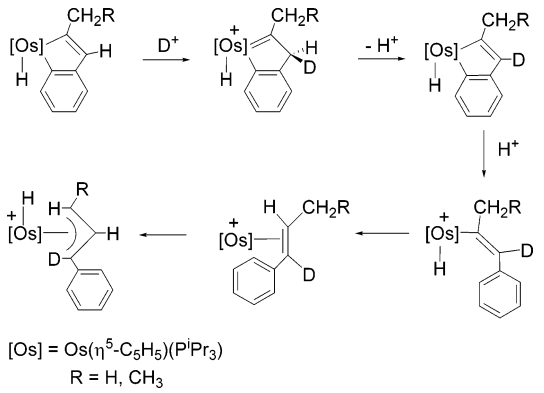
The hydride ligand does not play any role in the isomerization processes from **10** to **9** and from **9** to **8**. In agreement with this, we have observed that the isomerization of **10a-*d*$_1$** into **8a-*d*$_1$** via **9a-*d*$_1$** does not produces any change in the deuterium distribution of the allyl ligand. Like **4** and **5**, complexes **9** and **8** are diastereoisomers resulting from the chirality of the osmium atom and the prochirality of the CH═CHR (R = CH_3, Ph) moieties of the allyl ligand. In a manner similar to the isomerization from **4** to **5**, the transformation of **9** into **8** should occur by decoordination of the styryl moiety from the osmium atom of **9**, to afford the η^1-allyl intermediate $[OsH(\eta^5\text{-}C_5H_5)\{\eta^1\text{-}C(CH_3)HCH{=}CHPh\}(P^iPr_3)]^+$, and the subsequent coordination of the metal center of this species to the other face of the carbon−carbon double bond. This intermediate as well as **e** (Scheme 2) should be favored with regard to those containing an η^1-CH(Ph)CH═CHR (R = H, CH_3) allyl ligand due to the smaller size of H or CH_3 with regard to Ph.

The transformation of **10** into **9** seems to occur via rotation of the allyl ligand around the metal−allyl axis, not only because the $\eta^3 \rightarrow \eta^3 \rightarrow \eta^3$ pathway is intrinsically more favored than the $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ pathway in d^4 compounds of this type, but also because the formation of an η^1-intermediate should give a less stable diastereomer with an *anti* substituent.[23]

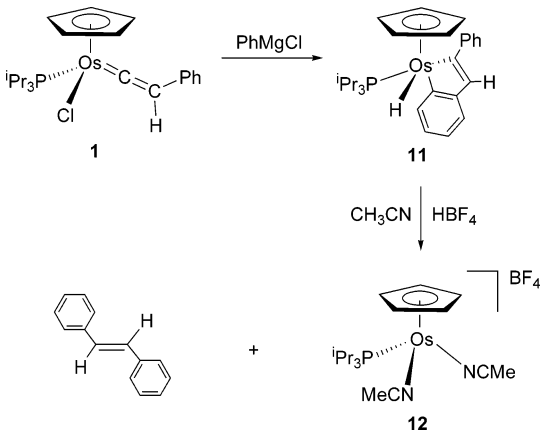
The relative stability of **4** and **5** and **8**−**10** indicates that the *syn* substituents at the η^3-allyl ligand play an important role in determining the relative stability of the *exo* and *endo* coordina-

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

Scheme 5



Scheme 6



tion forms in half-sandwich d^4-η^3-allyl complexes. Faller has observed that the *exo*−*endo* relative stability is also dependent on the *meso*- and *anti*-substitution.[17a,b,24] Jia and co-workers have reported that for Ru(η^3-allyl)Cl(CO)(PR$_3$)$_2$ complexes, an *anti* substituent at one of the terminal carbons destabilizes the *endo* isomer, while a *syn* substituent has a negligible effect.[5b]

3. Vinylidene−**Phenyl Coupling.** Treatment at 55 °C of **1** with 1.2 equiv of PhMgCl in tetrahydrofuran leads to OsH(η^5-C$_5$H$_5$){C(Ph)═CHC$_6$H$_4$}(P^{i}Pr$_3$) (**11**), according to Scheme 6. Its formation should involve the same sequence of elemental steps as the formation of **2** and **6**, with phenyl instead of an alkyl group.

Complex **11** was isolated as a yellow solid in 64% yield. In agreement with the presence of a hydride ligand in the compound, its ^{1}H NMR spectrum in benzene-d_6 at 20 °C contains a doublet at −13.52 ppm with a H−P coupling constant of 48.0 Hz. In the low-field region of the spectrum, the most noticeable resonance is a singlet at 7.88 ppm, corresponding to the C$_\beta$-H hydrogen atom of the alkenyl unit of the metallacycle. In the ^{13}C{^{1}H} NMR spectrum, the resonances due to the alkenyl carbon atoms appear at 144.4 (C$_\beta$) and 142.5 (C$_\alpha$) ppm. The first of them is observed as a singlet, whereas the second one is a doublet with a C−P coupling constant of 17 Hz. The metalated carbon atom of the phenyl group gives rise to a doublet at 156.6 ppm, with a C−P coupling constant of 5 Hz. The ^{31}P{^{1}H} NMR spectrum shows a singlet at 17.7 ppm.

The absence of a hydrogen atom at the phenyl carbon atom bonded to the C$_\alpha$ atom of the alkenyl unit of the metallacycle prevents the transformation of **11** into an allyl derivative. Thus, the addition of HBF$_4$·OEt$_2$ to **11** gives rise to *E*-stilbene and the metallic fragment [Os(η^5-C$_5$H$_5$)(P^{i}Pr$_3$)]$^+$, which is trapped with acetonitrile to afford the solvento complex [Os(η^5-C$_5$H$_5$)(CH$_3$CN)$_2$(P^{i}Pr$_3$)]BF$_4$ (**12**).[25]

Complex **12** is isolated as a yellow solid in 72% yield. In the ^{1}H NMR spectrum, the most noticeable resonance is a doublet at 2.62 ppm, with a H−P coupling constant of 1.2 Hz, corresponding to the methyl groups of the acetonitrile molecules. In the ^{13}C{^{1}H} NMR spectrum, these ligands give rise to singlets at 123.3 (C(sp)) and 4.0 (C(sp^3)) ppm. The ^{31}P{^{1}H} NMR spectrum shows a singlet at 18.3 ppm.

Concluding Remarks

This study reveals that the metal fragment [Os(η^5-C$_5$H$_5$)(P^{i}Pr$_3$)]$^+$ is a useful template to promote the formation of d^6- and d^4-allyl species, by initial carbon−carbon coupling between a vinylidene ligand and carbon nucleophiles, containing hydrogen atoms at the donor atom, and subsequent CH bond activation.

Complex Os(η^5-C$_5$H$_5$)Cl(═C═CHPh)(P^{i}Pr$_3$) reacts with organomagnesium compounds, RMgCl (R = Me, Et, Ph), to give initially hydride−osmaindene derivatives, OsH(η^5-C$_5$H$_5$){C(R)═CHC$_6$H$_4$}(P^{i}Pr$_3$), as a consequence of the addition of the nucleophile to the C$_\alpha$ atom of the vinylidene followed by *ortho*-CH bond activation of the phenyl substituent at the C$_\beta$ atom. When R is Me and Et, the hydride−osmaindene moiety rearranges to afford d^6-*exo*-allyl derivatives, Os(η^5-C$_5$H$_5$){η^3-*C*H(R′)*CHCH*Ph}(P^{i}Pr$_3$) (R′ = H, Me). The transformation involves the reductive elimination of phenyl in the metallacycle and a 1,2-hydrogen shift, through the metal center, from the alkyl substituent to the C$_\alpha$ atom of the resulting unsaturated alkenyl intermediate.

Complexes Os(η^5-C$_5$H$_5$){η^3-*C*H(R′)*CHCH*Ph}(P^{i}Pr$_3$) generate hydride-d^4-allyl derivatives [OsH(η^5-C$_5$H$_5$){η^3-*C*H(R′)*CHCH*Ph}(P^{i}Pr$_3$)]BF$_4$ by protonation with HBF$_4$. The allyl ligands in these compounds coordinate in both *exo* and *endo* forms. The relative stability of the resulting isomers depends on the R′ substituent of the allyl ligand, which is *syn* disposed with regard to H$_{meso}$. When R′ is H, the *endo* coordination is thermodynamically favored. Thus, only *endo* derivatives have been isolated and characterized. However, when R′ is Me the *exo* coordination is the most stable, and although an *endo* isomer has been isolated and characterized, it isomerizes into an equilibrium mixture of *exo* species.

In conclusion, half-sandwich osmium−allyl derivatives can be systematically prepared by reaction of vinylidene complexes with organomagnesium compounds containing hydrogen atoms at the C$_\alpha$ atom of the organic fragment. The coordination form of the allyl ligand depends on both the electronic structure of the metal center and the substituents of the allyl *syn* to H$_{meso}$. While the d^6 ion favors the *exo* coordination, the relative stability of the *exo* and *endo* isomers in d^4-species is governed by the *syn* substituents.

Experimental Section

General Procedures. 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

(24) (a) Faller, J. W.; Rosan, A. M. *J. Am. Chem. Soc*. **1976**, *98*, 3388. (b) Faller, J. W.; Shvo, Y.; Murray, H. H. *J. Organomet. Chem*. **1982**, *226*, 251. (c) Faller, J. W.; Whitmore, B. C. *Organometallics* **1986**, *5*, 752.

(25) A related indenyl derivative has been recently reported; see: Esteruelas, M. A.; López, A. M.; Oñate, E.; Royo, E. *Organometallics* **2005**, *24*, 5780.

starting material Os(η^5-C_5H_5)Cl(=C=CHPh)(P^iPr_3) was prepared by the published method.[9]

NMR spectra were recorded on either a Varian Gemini 2000, a Bruker ARX 300, a Bruker Avance 300 MHz, or a Bruker Avance 400 MHz instrument. Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks (^{1}H, ^{13}C{^{1}H}) or external H_3PO_4 (^{31}P{^{1}H}). 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 analysis 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. For stilbene, GC-MS analysis was run on an Agilent 5973 mass selective detector interfaced to an Agilent 6890 series gas chromatograph system. Sample was injected into a 30 m × 250 μm HP-5MS 5% phenyl methyl siloxane column with a film thickness of 0.25 μm (Agilent). The GC oven temperature was programmed as follows: 35 °C for 6 min, 35 to 280 °C at 25°/min, 280° for 4 min. The carrier gas was helium at a flow rate of 1 mL/min.

Preparation of OsH(η^5-C_5H_5){C(CH_3)=CHC_6H_4}(P^iPr_3) (2). A red solution of **1** (270 mg, 0.49 mmol) in 8 mL of tetrahydrofuran was treated with methylmagnesium chloride (195 μL, 0.58 mmol, 3 M in tetrahydrofuran). The solution was allowed to react for 15 h at 55 °C, and the solvent was removed. The product was extracted from the resultant brown oil with toluene (7 mL), which was filtered through Kieselguhr. The solution was concentrated to dryness, and the addition of 2 mL of methanol caused the precipitation of a yellow solid. The solid was separated by decantation, washed with cold methanol (2 × 1 mL), and dried in vacuo. Yield: 174 mg (67%). Anal. Calcd for $C_{23}H_{35}OsP$: C, 51.85; H, 6.62. Found: C, 51.76; H, 6.82. IR (Nujol, cm^{-1}): ν(OsH) 2133 (w), ν(Ph) 1574 (m). ^{1}H NMR (400 MHz, C_6D_6, 293 K): δ 7.59 and 7.51 (both d, J_{H-H} = 7.6, each 1H, C_6H_4), 7.44 (s, 1H, =C*H*), 7.22 and 6.82 (both t, J_{H-H} = 7.6, each 1H, C_6H_4), 4.67 (s, 5H, C_5H_5), 3.02 (s, 3H, CH_3), 2.14 (m, 3H, PCH), 0.81 (dd, J_{H-P} = 14.6, J_{H-H} = 7.2, 9H, PCHC*H*$_3$), 0.63 (dd, J_{H-P} = 12.0, J_{H-H} = 7.2, 9H, PCHC*H*$_3$), −14.56 (d, J_{H-P} = 47.2, 1H, Os−H). ^{31}P{^{1}H} NMR (161.89 MHz, C_6D_6, 293 K): δ 18.5 (s). ^{13}C{^{1}H} NMR (100.56 MHz, C_6D_6, 293 K, plus APT, plus HSQC, plus HMBC): δ 164.2 (s, $C_{ipso}C_6H_4$), 156.4 (d, J_{C-P} = 4, C_α in Os−C_6H_4), 143.1 (s, C_6H_4), 142.3 (s, =*C*H), 141.8 (d, J_{C-P} = 16, Os−*C*(CH_3)), 123.2, 120.4, and 119.6 (all s, C_6H_4), 82.7 (s, Cp), 42.7 (s, OsC(*C*H$_3$)), 27.5 (d, J_{C-P} = 30, PCH), 20.9 and 18.7 (both s, PCH*C*H$_3$). MS (LSIMS$^+$): *m*/*z* 533 (M$^+$); 489 (M$^+$ − ^{i}Pr).

Preparation of Os(η^5-C_5H_5)(η^3-*C*H_2*C*H*C*HPh)(P^iPr_3) (3). A yellow solution of **2** (150 mg, 0.28 mmol) in 10 mL of toluene was heated under reflux for 15 h. After that period of time, the resultant solution was cooled to room temperature and the solvent was removed. The addition of 2 mL of cold pentane caused the appearance of a yellow solid, which was washed with pentane (2 × 2 mL) and dried in vacuo. Yield: 124 mg (83%). Anal. Calcd for $C_{23}H_{35}OsP$: C, 51.85; H, 6.62. Found: C, 51.54; H, 6.66. IR (Nujol, cm^{-1}): ν(Ph) 1594 (m). ^{1}H NMR (400 MHz, C_6D_6, 293 K, plus COSY): δ 7.35−7.01 (m, 5H, Ph), 4.55 (dddd, J_{H-P} = 2.2, J_{H-Hs} = 6.0, J_{H-Ha} = 7.7, $J_{H-Ha'}$ = 7.8, 1H, H_{meso}), 4.32 (s, 5H, C_5H_5), 2.99 (dd, J_{H-Hm} = 6.0, J_{gem} = 1.8, 1H, H_{syn}), 2.58 (dd, J_{H-P} = 12.0, J_{H-Hm} = 7.8, 1H, C*H*Ph), 1.84 (m, 3H, PCH), 1.02 (dd, J_{H-P} = 12.2, J_{H-H} = 7.4, 10H, PCHC*H*$_3$ + H_a), 1.00 (dd, J_{H-P} = 12.0, J_{H-H} = 7.2, 9H, PCHC*H*$_3$). ^{31}P{^{1}H} NMR (161.89 MHz, C_6D_6, 293 K): δ 20.9 (s). ^{13}C{^{1}H} NMR (100.56 MHz, C_6D_6, 293 K, plus APT, plus HMQC): δ 151.3 (s, C_{ipso}Ph), 128.4, 125.5, and 122.8 (all s, Ph), 73.0 (s, Cp), 50.4 (s, C_{meso}), 34.9 (d, J_{C-P} = 5, *C*HPh), 27.1 (d, J_{C-P} = 25, PCH), 20.8 and 20.1 (both s, PCH*C*H$_3$), 10.8 (d, J_{C-P} = 7, CH_2). MS (LSIMS$^+$): *m*/*z* 533 (M$^+$).

Preparation of [OsH(η^5-C_5H_5){η^3-*C*H_2*C*H*C*HPh}(P^iPr_3)]BF_4 (4). Two different methods were used: (a) A yellow solution of **2** (110 mg, 0.21 mmol) in 7 mL of diethyl ether at 0 °C was treated with HBF_4·Et_2O (28 μL, 0.21 mmol). Immediately, a yellow solid appeared, which was separated by decantation, washed with diethyl ether (2 × 2 mL), and dried in vacuo. Yield: 98 mg (76%). (b) The same procedure was followed starting from **3** (108 mg, 0.21 mmol). Yield: 105 mg (82%). Anal. Calcd for $C_{23}H_{36}BF_4OsP$: C, 44.52; H, 5.85. Found: C, 44.51; H, 5.38. IR (Nujol, cm^{-1}): ν(OsH) 2135 (w), ν(Ph) 1598 (m), ν(BF_4) 1079 (s). ^{1}H NMR (300 MHz, CD_2Cl_2, 253 K, plus COSY): δ 7.40−7.25 (m, 5H, Ph), 5.72 (s, 5H, C_5H_5), 5.11 (d, J_{H-Hm} = 10.8, 1H, C*H*Ph), 4.36 (dddd, J_{H-P} = 3.8, $J_{H-Ha'}$ = 10.8, J_{H-Ha} = 7.9, J_{H-Hs} = 5.5, 1H, H_{meso}), 3.45 (dd, J_{H-Hm} = 5.5, J_{gem} = 1.8, 1H, H_s), 3.13 (dd, J_{H-Hm} = 7.9, J_{gem} = 1.8, 1H, H_{anti}), 1.77 (m, 3H, PCH), 1.02 (dd, J_{H-P} = 13.3, J_{H-H} = 7.1, 9H, PCHC*H*$_3$), 0.83 (dd, J_{H-P} = 15.4, J_{H-H} = 7.1, 9H, PCHC*H*$_3$), −15.12 (d, J_{H-P} = 38.1, 1H, Os−H). ^{31}P{^{1}H} NMR (121.42 MHz, CD_2Cl_2, 253 K): δ 17.7 (s). ^{13}C{^{1}H} NMR (75.42 MHz, CD_2Cl_2, 253 K, plus APT, plus HSQC): δ 137.6 (s, C_{ipso}-Ph), 128.7, 128.7, and 128.6 (all s, Ph), 85.3 (s, Cp), 73.8 (s, C_{meso}), 54.8 (s, *C*HPh), 28.1 (d, J_{C-P} = 29, PCH), 20.5 (s, PCH*C*H$_3$), 19.0 (d, J_{C-P} = 3, PCH*C*H$_3$), 18.9 (s, CH_2).

Preparation of [OsD(η^5-C_5H_5){η^3-*C*H_2*C*H*C*HPh}(P^iPr_3)]BF_4 (4-d_1). An NMR tube containing a yellow solution of **3** (12 mg, 0.02 mmol) in 0.5 mL of dichloromethane-d_2 was treated with DBF_4·OD_2 (6.1 μL, 0.02 mmol) at −20 °C. DBF_4·OD_2 was prepared by adding D_2O (1 mL, 50 mmol) to a commercial solution of HBF_4·OEt_2 (1 mL, 7.35 mmol). The NMR spectra at −20 °C showed the presence of **4**-d_1. ^{1}H NMR (300 MHz, CD_2Cl_2, 253 K) data were identical to those reported for **4** with the exception of the resonance at −15.12, which was missing. ^{2}H NMR (61.5 MHz, CH_2Cl_2, 253 K): δ −5.1 (d, J_{D-P} = 6, OsD).

Preparation of 4a-d_1. An NMR tube was charged with **2** (30 mg, 0.06 mmol) and 0.5 mL of dichloromethane-d_2, the sample was cooled to −20 °C, and DBF_4·OD_2 (15.4 μL, 0.06 mmol) was added. ^{1}H NMR (300 MHz, CD_2Cl_2, 253 K) data were identical to those reported for **4** with the exception of the resonances at 7.33 (m, 4.85H, Ph), 5.11 (d, J_{H-Hm} = 10.8, 0.45H, C*H*Ph), and −15.12 (d, J_{H-P} = 38.1, 0.70H, Os−H). ^{2}H NMR (61.5 MHz, CH_2Cl_2, 253 K): δ 7.4 (br, 0.15D, *o*-Ph), 5.1 (br, 0.55D, CDPh), −15.1 (d, J_{D-P} = 6, 0.30D, OsD).

Isomerization of 4 into 5. A brown solution of **4** (105 mg, 0.17 mmol) in 7 mL of dichloromethane was heated at 40 °C for 72 h. The resultant brown solution was concentrated to ca. 0.5 mL, and diethyl ether (5 mL) was added. A yellow solid precipitated, which was separated by decantation, washed with 2 × 2 mL of diethyl ether, and dried in vacuo. Yield: 94 mg (89%). Anal. Calcd for $C_{23}H_{36}BF_4OsP$: C, 44.52; H, 5.85. Found: C, 44.73; H, 5.90. IR (Nujol, cm^{-1}): ν(OsH) 2109 (w), ν(Ph) 1599 (m), ν(BF_4) 1083 (s). ^{1}H NMR (400 MHz, CD_2Cl_2, 293 K, plus COSY): δ 7.34−7.18 (m, 5H, Ph), 5.67 (s, 5H, C_5H_5), 4.87 (dd, J_{H-P} = 2.2, J_{H-Hm} = 9.2, 1H, C*H*Ph), 4.09 (dddd, J_{H-P} = 4.6, $J_{H-Ha'}$ = 9.2, J_{H-Ha} = 8.8, J_{H-Hs} = 5.6, 1H, H_{meso}), 3.13 (ddd, J_{H-P} = 5.6, J_{H-Hm} = 5.6, J_{gem} = 2.0, 1H, H_{syn}), 2.93 (dd, J_{H-Hm} = 8.8, J_{gem} = 2.0, 1H, H_{anti}), 2.15 (m, 3H, PCH), 1.13 and 1.12 (both dd, J_{H-P} = 14.2, J_{H-H} = 7.0, each 9H, PCHC*H*$_3$), −15.31 (d, J_{H-P} = 34.8, 1H, Os−H). ^{31}P-{^{1}H} NMR (161.89 MHz, CD_2Cl_2, 293 K): δ 14.0 (s). ^{13}C{^{1}H} NMR (100.56 MHz, CD_2Cl_2, 293 K, plus APT, plus HSQC): δ 140.8 (s, C_{ipso}Ph), 129.1, 128.2, and 127.1 (all s, Ph), 86.1 (s, Cp), 73.9 (s, C_{meso}), 54.2 (s, *C*HPh), 28.1 (d, J_{C-P} = 30, PCH), 19.7 (s, CH_2), 19.6 (s, PCH*C*H$_3$), 19.6 (d, J_{C-P} = 4, PCH*C*H$_3$). MS (LSIMS$^+$): *m*/*z* 534 (M$^+$).

Preparation of [OsD(η^5-C_5H_5){η^3-*C*H_2*C*H*C*HPh}(P^iPr_3)]BF_4 (5-d_1). An NMR tube containing a brown solution of **4**-d_1 in dichloromethane-d_2 was heated at 40 °C for 72 h. The NMR spectra at room temperature show the presence of **5**-d_1. ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K) data were identical to those reported for **5** with the exception of the resonance at −15.31, which was missing. ^{2}H NMR (61.5 MHz, CH_2Cl_2, 293 K): δ −15.3 (d, J_{D-P} = 6, OsD).

Preparation of 5a-d_1. An NMR tube containing a brown solution of **4a-d_1** in dichloromethane-d_2 was heated at 40 °C for 72 h. ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K) data were identical to those reported for **5** with the exception of the resonances at 7.26 (m, 4.85H, Ph), 4.87 (d, J_{H-Hm} = 10.8, 0.45H, C*H*Ph), and −15.31 (d, J_{H-P} = 38.1, 0.70H, Os−H). ^{2}H NMR (61.5 MHz, CH_2Cl_2, 293 K): δ 7.4 (br, 0.15D, *o*-Ph), 4.9 (br, 0.55D, CDPh), −15.1 (d, J_{D-P} = 6, 0.30D, OsD).

Preparation of OsH(η^5-C_5H_5){C(CH_2CH_3)=CHC_6H_4}(P^iPr_3) (6). The same procedure described for **2** was followed starting from **1** (200 mg, 0.36 mmol) and ethylmagnesium chloride (217 μL, 0.43 mmol, 2 M in tetrahydrofuran). The product was isolated as a yellow solid. Yield: 196 mg (74%). Anal. Calcd for $C_{24}H_{37}OsP$: C, 52.72; H, 6.82. Found: C, 52.93; H, 7.03. IR (Nujol, cm^{-1}): ν(OsH) 2097 (w), ν(Ph) 1573 (m). ^{1}H NMR (300 MHz, C_6D_6, 293 K): δ 7.61−7.53 (m, 2H, C_6H_4), 7.51 (s, 1H, =C*H*), 7.24−6.84 (m, 2H, C_6H_4), 4.68 (s, 5H, C_5H_5), 3.30−3.17 (m, 1H, CH_2), 3.09−2.95 (m, 1H, CH_2), 2.15 (m, 3H, PCH), 1.48 (dd, J_{H-H} = 7.5, J_{H-H} = 7.5, 3H, $-CH_2CH_3$), 0.80 (dd, J_{H-P} = 14.2, J_{H-H} = 7.0, 9H, PCHCH_3), 0.64 (dd, J_{H-P} = 12.1, J_{H-H} = 7.0, 9H, PCHCH_3), −14.44 (d, J_{H-P} = 47.4, 1H, Os−H). ^{31}P{^{1}H} NMR (121.42 MHz, C_6D_6, 293 K): δ 18.6 (s). ^{13}C{^{1}H} NMR (75.42 MHz, C_6D_6, 293 K, plus APT, plus HSQC): δ 164.6 (s, $C_{ipso}C_6H_4$), 162.8 (d, J_{C-P} = 4, C_α in Os−C_6H_4), 143.1 (s, C_6H_4), 141.1 (d, J_{C-P} = 17, Os−*C*(CH_2CH_3)), 138.6 (s, =CH), 123.1, 120.7, and 119.6 (all s, C_6H_4), 82.5 (s, Cp), 47.9 (s, *C*H_2), 27.2 (d, J_{C-P} = 30, PCH), 20.6 (s, PCH*C*H_3), 18.6 (d, J_{C-P} = 3, PCH*C*H_3), 15.7 (s, CH_2*C*H_3). MS (LSIMS$^+$): *m*/*z* 547 (M^+).

Preparation of Os(η^5-C_5H_5){η^3-*C*H(CH_3)*C*H*C*HPh}(P^iPr_3) (7). A yellow solution of **6** (147 mg, 0.27 mmol) in 10 mL of toluene was stirred at 70 °C for 72 h. The resultant solution was concentrated to dryness, pentane was added (3 mL), and the product appeared as a yellow solid. The solid was washed with pentane (2 × 2 mL) and dried in vacuo. Yield: 120 mg (82%). Anal. Calcd for $C_{24}H_{37}OsP$: C, 52.72; H, 6.82. Found: C, 53.03; H, 6.95. IR (Nujol, cm^{-1}): ν(Ph) 1597 (m). ^{1}H NMR (400 MHz, C_6D_6, 293 K, plus COSY): δ 7.32−7.04 (m, 5H, Ph), 4.54 (ddd, J_{H-P} = 2.8, J_{H-Ha} = $J_{H-Ha'}$ = 7.2, 1H, H_{meso}), 4.32 (s, 5H, C_5H_5), 2.51 (dd, J_{H-P} = 12.4, J_{H-Hm} = 7.2, 1H, C*H*Ph), 1.88 (m, 3H, PCH), 1.79 (d, J_{H-H} = 5.6, 3H, CHCH_3), 1.57 (ddq, J_{H-P} = 14.2, J_{H-Hm} = 7.2, J_{H-HMe} = 5.6, 1H, C*H*CH_3), 1.02 (dd, J_{H-P} = 12.0, J_{H-H} = 7.2, 9H, PCHCH_3), 1.00 (dd, J_{H-P} = 12.0, J_{H-H} = 7.5, 9H, PCHCH_3). ^{31}P{^{1}H} NMR (161.89 MHz, C_6D_6, 293 K): δ 19.5 (s). ^{13}C{^{1}H} NMR (100.56 MHz, C_6D_6, 293 K, plus APT, plus HSQC): δ 151.4 (s, C_{ipso}Ph), 128.3, 125.5, and 122.7 (all s, Ph), 73.6 (s, Cp), 57.4 (d, J_{C-P} = 2, C_{meso}), 32.4 (d, J_{C-P} = 5, *C*HPh), 27.3 (d, J_{C-P} = 25, PCH), 26.0 (d, J_{C-P} = 6, *C*HCH_3), 24.8 (s, CH*C*H_3), 20.6 and 20.3 (both s, PCH*C*H_3). MS (LSIMS$^+$): *m*/*z* 547 (M^+).

Reaction of Os(η^5-C_5H_5){η^3-*C*H(CH_3)*C*H*C*HPh}(P^iPr_3) (7) with HBF_4: Formation of [OsH(η^5-C_5H_5){η^3-*C*H(CH_3)*C*H*C*HPh}(P^iPr_3)]BF_4 (8 and 9). An NMR tube containing an orange solution of **7** (19 mg, 0.03 mmol) in 0.5 mL of dichloromethane-d_2 was treated with HBF_4·Et_2O (5 μL, 0.03 mmol). Immediately, the color of the solution changed from orange to light brown and the NMR spectra, after 7 days, showed the presence of **8** and **9** in a 5:2 molar ratio. Spectroscopic data for **8**: ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K, plus COSY): δ 7.38−7.28 (m, 5H, Ph), 5.51 (s, 6H, C_5H_5 + H_{meso}), 3.59 (dd, J_{H-P} = 2.1, J_{H-Hm} = 7.5, 1H, C*H*Ph), 2.63 (ddq, J_{H-P} = 15.0, J_{H-Hm} = 7.5, J_{H-HMe} = 6.0, 1H, C*H*CH_3), 2.37 (m, 3H, PCH), 1.91 (d, J_{H-H} = 6.0, 3H, CHCH_3), 1.36 (dd, J_{H-P} = 13.8, J_{H-H} = 7.2, 9H, PCHCH_3), 1.32 (dd, J_{H-P} = 15.0, J_{H-H} = 7.0, 9H, PCHCH_3), − 13.30 (d, J_{H-P} = 32.7, 1H, Os−H). ^{31}P{^{1}H} NMR (121.42 MHz, CD_2Cl_2, 293 K): δ 20.7 (s). ^{13}C{^{1}H} NMR (75.42 MHz, CD_2Cl_2, 293 K, plus APT, plus HSQC): δ 139.9 (s, C_{ipso}Ph), 129.2, 127.6, and 126.4 (all s, Ph), 85.8 (s, Cp), 69.9 (s, C_{meso}), 55.3 (s, *C*HPh), 38.0 (s, *C*HCH_3), 28.2 (d, J_{C-P} = 30, PCH), 22.3 (s, CH*C*H_3), 19.7 and 19.7 (both s, PCH*C*H_3). MS (LSIMS$^+$): *m*/*z* 548 (M^+)

Reaction of OsH(η^5-C_5H_5){C(CH_2CH_3)=CHC_6H_4}(P^iPr_3) (6) with HBF_4: Preparation of [OsH(η^5-C_5H_5){η^3-*C*H(CH_3)-*C*H*C*HPh}(P^iPr_3)]BF_4 (10). A yellow solution of **6** (140 mg, 0.26 mmol) in 7 mL of diethyl ether at 0 °C was treated with HBF_4·Et_2O (35 μL, 0.26 mmol). Immediately, a white solid appeared, which was separated by decantation, washed with diethyl ether (2 × 2 mL), and dried in vacuo. Yield: 123 mg (91%). Anal. Calcd for $C_{24}H_{38}BF_4OsP$: C, 45.43; H, 6.04. Found: C, 45.56; H, 6.12. IR (Nujol, cm^{-1}): ν(OsH) 2196 (w), ν(Ph) 1598 (m), ν(BF_4) 1053 (s). ^{1}H NMR (300 MHz, CD_2Cl_2, 253 K, plus COSY): δ 7.35−7.28 (m, 5H, Ph), 5.71 (s, 5H, C_5H_5), 4.89 (d, J_{H-Hm} = 9.5, 1H, C*H*Ph), 4.21 (ddd, J_{H-P} = 4.7, J_{H-Ha} = $J_{H-Ha'}$ = 9.5, 1H, H_{meso}), 3.97 (ddq, J_{H-P} = 2.7, J_{H-Hm} = 9.5, J_{H-HMe} = 6.1, 1H, C*H*CH_3), 2.09 (d, J_{H-H} = 6.1, 3H, CHCH_3), 1.77 (m, 3H, PCH), 1.05 (dd, J_{H-P} = 13.3, J_{H-H} = 7.0, 9H, PCHCH_3), 0.84 (dd, J_{H-P} = 15.0, J_{H-H} = 6.9, 9H, PCHCH_3), −15.10 (d, J_{H-P} = 40.5, 1H, Os−H). ^{31}P{^{1}H} NMR (121.42 MHz, CD_2Cl_2, 253 K): δ 13.4 (s). ^{13}C{^{1}H} NMR (75.42 MHz, CD_2Cl_2, 253 K, plus APT, plus HSQC): δ 137.8 (s, C_{ipso}Ph), 128.5, 128.5, and 128.0 (all s, Ph), 85.4 (s, Cp), 76.3 (s, C_{meso}), 47.1 (s, *C*HPh), 42.5 (s, *C*HCH_3), 27.5 (d, J_{C-P} = 29, PCH), 23.0 (s, CH*C*H_3), 20.1 (s, PCH*C*H_3), 19.0 (d, J_{C-P} = 3, PCH*C*H_3).

Preparation of 10a-d_1. An NMR tube containing a yellow solution of **6** (21 mg, 0.04 mmol) in 0.5 mL of dichloromethane-d_2 was treated with DBF_4·OD_2 (10.3 μL, 0.04 mmol) at −20 °C. The NMR spectra at −20 °C show the presence of **10a-d_1**. ^{1}H NMR (300 MHz, CD_2Cl_2, 253 K) data were identical to those reported for **10** with the exception of the resonances at 7.31 (m, 4.65H, Ph) and 4.89 (d, J_{H-Hm} = 9.5, 0.35H, C*H*Ph). ^{2}H NMR (61.5 MHz, CH_2Cl_2, 253 K): δ 7.4 (br, 0.35D, Ph) and 4.9 (br, 0.65D, CDPh).

Preparation of BPh_4 Salt of 10. A yellow solution of **10** (235 mg, 0.37 mmol) in 8 mL of dichloromethane at −20 °C was treated with $NaBPh_4$ (127 mg, 0.37 mmol). After 2 h, the solution was filtered through Kieselguhr and concentrated to almost dryness. The addition of 4 mL of diethyl ether caused the precipitation of a white solid, which was separated by decantation and dried in vacuo. Yield: 324 mg (89%). The ^{31}P{^{1}H} and ^{1}H NMR (300 MHz, CD_2Cl_2, 253 K) data were identical to those reported for **10** with the exception of the appearance of the resonance at 7.37−6.92 (m, 25H, Ph).

Isomerization of 10 into 9 and 8. A brown solution of **10** (123 mg, 0.19 mmol) in 7 mL of dichloromethane was stirred at room temperature for 24 h. The solution was concentrated to ca. 0.5 mL and cooled to 0 °C. Addition of diethyl ether (5 mL) caused the precipitation of **9** as a white solid. The product was separated by decantation, washed with 2 × 2 mL of diethyl ether, and dried in vacuo. Yield: 112 mg (91%). Anal. Calcd for $C_{24}H_{38}BF_4OsP$: C, 45.43; H, 6.04. Found: C, 45.47; H, 5.94. IR (Nujol, cm^{-1}): ν(OsH) 2197 (w), ν(Ph) 1598 (m), ν(BF_4) 1022 (s). ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K, plus COSY): δ 7.60−7.48 (m, 5H, Ph), 5.82 (dd, J_{H-Ha} = $J_{H-Ha'}$ = 9.3, 1H, H_{meso}), 5.62 (s, 5H, C_5H_5), 3.70 (dd, J_{H-P} = 12.3, J_{H-Hm} = 9.3, 1H, C*H*Ph), 3.38 (ddq, J_{H-P} = 3.0, J_{H-Hm} = 9.3, J_{H-HMe} = 6.0, 1H, C*H*CH_3), 2.74 (m, 3H, PCH), 2.40 (dd, J_{H-H} = 6.0, J_{H-Hhyd} = 2.1, 3H, CHCH_3), 1.49 (dd, J_{H-P} = 13.0, J_{H-H} = 7.0, 9H, PCHCH_3), 1.43 (dd, J_{H-P} = 15.0, J_{H-H} = 7.2, 9H, PCHCH_3), −13.76 (dq, J_{H-P} = 33.6, J_{H-H} = 2.1, 1H, Os−H). ^{31}P{^{1}H} NMR (121.42 MHz, CD_2Cl_2, 293 K): δ 20.2 (s). ^{13}C{^{1}H} NMR (75.42 MHz, CD_2Cl_2, 293 K, plus APT, plus HSQC): δ 140.1 (s, C_{ipso}Ph), 129.4, 127.4, and 126.4 (all s, Ph), 85.8 (s, Cp), 69.3 (s, C_{meso}), 51.8 (s, *C*HCH_3), 42.5 (s, *C*HPh), 28.8 (d, J_{C-P} = 29, PCH), 22.6 (s, CH*C*H_3), 20.7 (s, PCH*C*H_3), 19.7 (d, J_{C-P} = 3, PCH*C*H_3). MS (LSIMS$^+$): *m*/*z* 548 (M^+). A brown solution of **9** (27 mg, 0.04 mmol) in 0.5 mL of dichlo-

Table 6. Crystal Data and Data Collection and Refinement for 3, 5, and 8

	3	5	8
		Crystal Data	
formula	$C_{23}H_{35}OsP$	$C_{23}H_{36}BF_4OsP$	$C_{48}H_{58}BOsP\cdot 1/2CH_2Cl_2$
molecular wt	532.68	620.50	909.39
color and habit	yellow, prism	red, prism	colorless, irregular block
size, mm	0.22,0.20,0.18	0.16,0.10,0.10	0.38,0.02,0.01
symmetry, space group	triclinic, $P\bar{1}$	monoclinic, $P2(1)/n$	triclinic, $P\bar{1}$
a, Å	9.0672(14)	10.2094(13)	9.615(2)
b, Å	10.3723(16)	12.8248(17)	13.811(3)
c, Å	11.6987(18)	17.944(2)	17.423(4)
α, deg	99.221(2)	90.00	85.988(4)
β, deg	95.381(2)	96.363(2)	75.399(5)
γ, deg	105.264(2)	90.00	78.292(5)
V, Å^3	1037.0(3)	2334.9(5)	2191.8(8)
Z	2	4	2
D calc, g cm^{-3}	1.706	1.765	1.378
		Data Collection and Refinement	
diffractometer		Bruker Smart APEX	
λ(Mo Kα), Å		0.71073	
monochromator		graphite oriented	
scan type		ω scans	
μ, mm^{-1}	6.229	5.569	3.038
2θ, range deg	3, 57	4, 57	4, 57
temp, K	100.0(2)	100.0(2)	100.0(2)
no. of data collect	13 064	28 678	25 962
no. of unique data	4967 (R_{int} = 0.0193)	5787 (R_{int} = 0.0325)	10 249 (R_{int} = 0.1627)
no. of params/restraints	248/0	291/18	494/82
R_1[a] [$F^2 > 2\sigma(F^2)$]	0.0174	0.0271	0.0598
wR_2[b] [all data]	0.0421	0.0608	0.1464
S[c] [all data]	1.110	0.974	0.664

[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] Goodness of fit = $S = \{\sum[F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$, where n is the number of reflections and p is the number of refined parameters.

romethane-d_2 was heated at 40 °C. After 7 days, the NMR spectra showed the presence of **8** and **9** in a 5:2 molar ratio.

Preparation of 9a-d_1. An NMR tube containing a brown solution of **10a-d_1** in 0.5 mL of dichloromethane-d_2 was kept at room temperature for 24 h. ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K) data were identical to those reported for **9** with the exception of the resonances at 7.5 (m, 4.65H, Ph) and 3.7 (d, J_{H-Hm} = 10.8, 0.35H, C*H*Ph). ^{2}H NMR (61.5 MHz, CH_2Cl_2, 293 K): δ 7.5 (br, 0.35D, *o*-Ph) and 3.7 (br, 0.65D, CDPh).

Preparation of BPh_4 Salt of 9. A yellow solution of **10-BPh_4** (115 mg, 0.15 mmol) in 7 mL of dichloromethane was stirred at room temperature for 24 h. Then, the solution was concentrated to about dryness and diethyl ether (3 mL) was added. Immediately, a white solid appeared, which was separated by decantation, washed with 2 mL of diethyl ether, and dried in vacuo. Yield: 101 mg (88%). The ^{31}P{^{1}H} and ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K) data were identical to those reported for **9** with the exception of the appearance of the resonance at 7.35−6.98 (m, 25H, Ph).

Formation of 8a-d_1. An NMR tube containing a brown solution of **9a-d_1** in 0.5 mL of dichloromethane-d_2 was heated at 40 °C. After 7 days, the NMR spectra showed the presence of **8a-d_1** and **9a-d_1** in a molar ratio 5:2. ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K) data were identical to those reported for **8** with the exception of the resonances at 7.33 (m, 4.65H, Ph) and 3.59 (d, J_{H-Hm} = 9.5, 0.35H, C*H*Ph). ^{2}H NMR (61.5 MHz, CH_2Cl_2, 293 K): δ 7.3 (br, 0.35D, Ph) and 3.6 (br, 0.65D, CDPh).

Formation of BPh_4 Salt of 8. A yellow solution of **9-BPh_4** (123 mg, 0.16 mmol) in dichloromethane (7 mL) was heated at 40 °C for 7 days. Then, the solution was concentrated to about dryness and diethyl ether (4 mL) was added. Immediately, a white solid appeared, which was separated by decantation, washed with 2 mL of diethyl ether, and dried in vacuo. The NMR spectra showed the presence of **8-BPh_4** and **9-BPh_4** in a molar ratio 5:2. The ^{31}P{^{1}H} and ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K) data were identical to those reported for **8** with the exception of the appearance of the resonance at 7.38−6.92 (m, 25H, Ph).

Preparation of OsH(η^5-C_5H_5){C(Ph)=CHC_6H_4}(P^iPr_3) (11). The same procedure described for **2** was followed starting from **1** (200 mg, 0.36 mmol) and phenylmagnesium chloride (217 μL, 0.43 mmol, 2 M in tetrahydrofuran). The product was isolated as a yellow solid. Yield: 137 mg (64%). Anal. Calcd for $C_{28}H_{37}OsP$: C, 56.54; H, 6.27. Found: C, 56.22; H, 6.43. IR (Nujol, cm^{-1}): ν(OsH) 2189 (w), ν(Ph) 1590 (m). ^{1}H NMR (400 MHz, C_6D_6, 293 K): δ 7.92 (m, 2H, Ph), 7.88 (s, 1H, =C*H*), 7.62−6.86 (m, 7H, Ph), 4.65 (s, 5H, C_5H_5), 2.15 (m, 3H, PCH), 0.79 (dd, J_{H-P} = 14.8, J_{H-H} = 7.0, 9H, PCHCH_3), 0.62 (dd, J_{H-P} = 12.2, J_{H-H} = 7.0, 9H, PCHCH_3), −13.52 (d, J_{H-P} = 48.0, 1H, Os−H). ^{31}P{^{1}H} NMR (161.89 MHz, C_6D_6, 293K): δ 17.7 (s). ^{13}C{^{1}H} NMR (100.56 MHz, C_6D_6, 293K, plus APT, plus HSQC): δ 164.5 and 156.7 (both s, C_{ipso}Ph), 156.6 (d, J_{C-P} = 5, C_α in Os−C_6H_4), 144.4 (s, =*C*H), 143.0 (s, Ph), 142.5 (d, J_{C-P} = 17, Os-*C*(Ph)), 128.4, 127.9, 125.2, 123.2, 122.3, and 120.6 (all s, Ph), 83.3 (s, Cp), 27.5 (d, J_{C-P} = 31, PCH), 21.1 (s, PCH*C*H$_3$), 18.8 (d, J_{C-P} = 3, PCH*C*H$_3$). MS (LSIMS$^+$): *m*/*z* 595 (M$^+$); 435 (M$^+$ − P^iPr_3).

Reaction of OsH(η^5-C_5H_5){C(Ph)=CHC_6H_4}(P^iPr_3) (11) with HBF_4: Preparation of [Os(η^5-C_5H_5)(CH_3CN)$_2$(P^iPr_3)]BF_4 (12). An orange solution of **11** (150 mg, 0.25 mmol) in 7 mL of acetonitrile was treated with $HBF_4\cdot Et_2O$ (45 μL, 0.33 mmol). The color of the solution changed immediately from orange to brown. After 30 min, the solvent was removed and the addition of diethyl ether (2 mL) to the resultant brown oil caused the appearance of a yellow solid. The solid was separated by decantation, washed with diethyl ether (2 × 2 mL), and dried in vacuo. GC-MS analysis of mother liquors showed the presence of stilbene. Yield: 113 mg (77%). Anal. Calcd for $C_{18}H_{32}BF_4N_2OsP$: C, 36.99; H, 5.52; N, 4.79. Found: C, 37.03; H, 5.53; N, 5.09. IR (Nujol, cm^{-1}): ν(CN) 2273 (m), ν(BF_4) 1025 (s). ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ 4.80 (s, 5H, C_5H_5), 2.62 (d, J_{H-P} = 1.2, 6H, CH_3CN), 2.40 (m, 3H, PCH), 1.20 (dd, J_{H-P} = 13.5, J_{H-H} = 7.2, 18H, PCHCH_3). ^{31}P{^{1}H} NMR (121.42 MHz, CD_2Cl_2, 293 K): δ 18.3 (s). ^{13}C-{^{1}H} NMR (75.42 MHz, CD_2Cl_2, 293 K): δ 123.3 (s, CH_3*C*N),

71.4 (s, Cp), 27.0 (d, $J_{C-P} = 26$, PCH), 19.4 (s, PCH*C*H_3), 4.0 (s, *C*H_3CN). MS (LSIMS$^+$): *m*/*z* 457 ($M^+ - CH_3CN$).

Structural Analysis of Complexes 3, 5, and 8. Crystals suitable for the X-ray diffraction were obtained by cooling at 4 °C a solution of **3** in pentane, by slow diffusion of diethyl ether into a concentrated solution of **5** in dichloromethane, and by slow diffusion of diethyl ether into a concentrated solution of a mixture of the BPh_4^- salts of **8** and **9** in dichloromethane. X-ray data were collected for all complexes on a Bruker Smart APEX CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube source (Mo radiation, $\lambda = 0.71073$ Å) operating at 50 kV and 30 mA. Data were collected over the complete sphere by a combination of four sets. Each frame exposure time was 10 s (30 s for **8**) covering 0.3° in ω. Data were corrected for absorption by using a multiscan method applied with the SADABS program.[26] The structures of all compounds were solved by the Patterson method. Refinement, by full-matrix least squares on F^2 with SHELXL97,[27] was similar for all complexes, including isotropic and subsequently anisotropic displacement parameters. The high quality and extended range of diffraction data allowed location of the hydride ligands in **5** and **8** in the difference Fourier maps. However, we observed short Os−H distances due to the well-known behavior of the X-ray experiments that usually show shorter M−H distances than those based on neutron diffraction, a radiation much more appropriate for the precise localization of lighter elements. Unfortunately, none of them supported a free refinement of these atoms and a restrained geometry was used in the last cycles of refinement. Hydrogen atoms (except those corresponding to the allylic carbon atoms, which were observed in the difference Fourier maps and refined as free isotropic atoms) were included in calculated positions and refined riding on their respective carbon atoms with the thermal parameter related to the bonded atoms. For **5**, the BF_4 anion was observed disordered. The anion was defined with four moieties, complementary occupancy factors, isotropic atoms, and restrained geometry. In the last cycles of refinement **8** showed an improper refinement of the thermal parameters of some allyl, Cp, and dichloromethane atoms probably due to the small intensity of the measured reflections (mean $(I/\sigma) = 2.1$). However the poor thermal displacements could be improved by the use of SIMU and DELU restraints (or even ISOR, or combinations thereof). DELU is used to equalize each anisotropic vector parallel to the bond and SIMU was used to atoms that are nonbonded but near in space. All the highest electronic residuals were observed in close proximity of the Os centers and make no chemical sense. A summary of crystal data and data collection and refinement details is reported in Table 6.

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Supporting Information Available: Detailed X-ray crystallographic data (bond distances, bond angles, and anisotropic parameters) for **3**, **5**, and **8** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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