A Four-Electron π-Alkyne Complex as Precursor for Allenylidene Derivatives: Preparation, Structure, and Reactivity of $[Os(\eta^5\text{-}C_5H_5)(C{=}C{=}CPh_2)L(P^iPr_3)]PF_6$ (L = CO, $PHPh_2$)

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The π-alkyne complex $[Os(\eta^5\text{-}C_5H_5)\{\eta^2\text{-}HC{\equiv}CC(OH)Ph_2\}(P^iPr_3)]PF_6$ (**1**), where the alkyne acts as a four-electron donor ligand, reacts with CO to give initially the two-electron π-alkyne derivative $[Os(\eta^5\text{-}C_5H_5)\{\eta^2\text{-}HC{\equiv}CC(OH)Ph_2\}(CO)(P^iPr_3)]PF_6$ (**2**). In dichloromethane, complex **2** isomerizes into the hydroxyvinylidene $[Os(\eta^5\text{-}C_5H_5)\{{=}C{=}CHC(OH)Ph_2\}(CO)(P^iPr_3)]PF_6$ (**3**), which dehydrates to afford the allenylidene $[Os(\eta^5\text{-}C_5H_5)(C{=}C{=}CPh_2)(CO)(P^iPr_3)]PF_6$ (**4**). Complex **1** also reacts with $PHPh_2$. In this case, the reaction initially gives the hydride-hydroxyalkynyl intermediate $[OsH(\eta^5\text{-}C_5H_5)\{C{\equiv}CC(OH)Ph_2\}(PHPh_2)(P^iPr_3)]PF_6$ (**5**). Similar to **2**, in dichloromethane, complex **5** isomerizes into the hydroxyvinylidene $[Os(\eta^5\text{-}C_5H_5)\{{=}C{=}CHC(OH)Ph_2\}(PHPh_2)(P^iPr_3)]PF_6$ (**6**), which dehydrates to afford $[Os(\eta^5\text{-}C_5H_5)(C{=}C{=}CPh_2)(PHPh_2)(P^iPr_3)]PF_6$ (**7**). In the presence of HPF_6, complex **4** isomerizes into $[Os(\eta^5\text{-}C_5H_5)$(3-phenyl-1-indenylidene)$(CO)(P^iPr_3)]PF_6$ (**8**). Under the same conditions, compound **7** affords the dicationic alkenylcarbyne derivative $[Os(\eta^5\text{-}C_5H_5)({\equiv}C{-}CH{=}CPh_2)(PHPh_2)(P^iPr_3)](PF_6)_2$ (**9**). The allenylidene ligand of **4** undergoes the addition of carbodiimides to give iminiumazetidinylidenemethyl derivatives. The reaction with *N*,*N*′-dicyclohexylcarbodiimide affords $[Os(\eta^5\text{-}C_5H_5)\{CH{=}\overline{CC(Ph)_2N(Cy){=}C}{=}N{=}\overline{C(CH_2)_4CH_2}\}(CO)(P^iPr_3)]PF_6$ (**10**), whereas the reaction with *N*,*N*′-diisopropylcarbodiimide leads to $[Os(\eta^5\text{-}C_5H_5)\{CH{=}\overline{CC(Ph)_2N(^iPr){=}C}{=}N{=}C(CH_3)_2\}(CO)(P^iPr_3)]PF_6$ (**11**). Complex **4** also reacts with methanol and aniline. The addition of methanol to the allenylidene **4** gives $[Os(\eta^5\text{-}C_5H_5)\{C(OCH_3)CH{=}CPh_2\}(CO)(P^iPr_3)]PF_6$ (**12**), which undergoes deprotonation at the $CH{=}CPh_2$ group to afford $Os(\eta^5\text{-}C_5H_5)\{C(OCH_3){=}C{=}CPh_2\}(CO)(P^iPr_3)$ (**13**). The addition of aniline leads to $[Os(\eta^5\text{-}C_5H_5)\{C(CH{=}CPh_2){=}NHPh\}(CO)(P^iPr_3)]PF_6$ (**14**). Treatment of **14** with $NaOCH_3$ gives $Os(\eta^5\text{-}C_5H_5)\{C(CH{=}CPh_2){=}NPh\}(CO)(P^iPr_3)$ (**15**). Complexes **4**, **7**, and **8** have been characterized by X-ray diffraction analysis.

Introduction

Allenylidene complexes of the iron triad, in particular cationic half-sandwich ruthenium derivatives, have attracted a great deal of attention in recent years, as a new type of organometallic intermediate that may have unusual reactivity in stoichiometric and catalytic processes.[1]

The reactivity of cationic half-sandwich ruthenium allenylidene compounds is mainly governed by the electron-deficient character of the C_α and C_γ atoms of the cumulene chain. The type of nucleophilic addition and its regioselectivity is controlled by the electronic and steric properties of the auxiliary ligands on the metal.[1b] The coordination of the π-acidic carbonyl group enhances the reactivity associated with the allenylidene spine, favoring the addition of neutral RXH nucleophiles to the $C_\alpha{-}C_\beta$ double bond.[2] However, phosphines inhibit the addition of the latter and direct charged nucleophiles toward the C_γ atom.[3]

The chemistry of the half-sandwich osmium allenylidene complexes is a field much less known than the chemistry of the ruthenium counterparts. Osmium allenylidene complexes are very scarce,[3b,4] and the cationic half-sandwich derivatives are still more rare. Reported compounds of this type include $[Os(\eta^5\text{-}C_9H_7)(C{=}C{=}CR_2)(PPh_3)_2]PF_6$ (R = Ph_2, $C_{12}H_8$),[3b] $[Os(\eta^5\text{-}C_5H_5)(C{=}C{=}CPh_2)(PR_3)_2]PF_6$ (R = ^{i}Pr,[4d] Ph[4g]), $[\overline{Os\{\eta^5\text{-}C_5H_4(CH_2)_2PPh_2\}}(C{=}C{=}CPh_2)(P^iPr_3)]PF_6$,[4h] $[Os(\eta^5\text{-}C_5H_5)\{{=}C{=}C{=}CHC{\equiv}C{-}Os(\eta^5\text{-}C_5H_5)(PPh_3)_2\}(PPh_3)_2]^+$,[4f] and $[Os(\eta^6\text{-arene})(C{=}C{=}CR_2)XL]PF_6$.[4e]

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The limited development of the osmium chemistry in the allenylidenes area is a consequence of the method generally employed to the preparation of cumulene complexes of the iron triad. The procedure widely used in the synthesis of cationic half-sandwich ruthenium- and osmium-allenylidene derivatives involves the treatment of chloro-phosphine or chloro-carbonyl-phosphine starting materials with terminal alkynols in the presence of NH_4PF_6, $NaBPh_4$, or related salts.[3b,4d−h,5] In this context, it should be noted that, in general, the Os(η^5-C_5H_5)L_3 species are more inert than their ruthenium analogues and that the basicity of osmium is higher than the basicity of ruthenium. The great inertness of the Os(η^5-C_5H_5)L_3 complexes hinders the extraction of the chlorine ligand. As a consequence of the high basicity of the metallic center, for the osmium systems, the metalations of the substituents of the phosphines[4h,7] are reactions that can compete with the activation of the alkynol.

Four-electron-alkyne complexes are species where alkyne ⊥ donation supplements classic metal−olefin bonding.[8] Although the chemistry of these compounds has been centered at early transition metals, mainly molybdenum and tungsten,[9] we have recently reported that the π-alkyne complexes Os(η^5-C_5H_5)Cl(η^2-HC≡CR)(P^iPr_3) (R = C(OH)Ph_2, C(OH)Me) can be easily converted into stable [Os(η^5-C_5H_5)(η^2-HC≡CR)(P^iPr_3)]$^+$ derivatives, containing a four-electron-donating alkyne.[10]

We have now observed that the four-electron-alkyne complex [Os(η^5-C_5H_5)(η^2-HC≡CC(OH)Ph_2)(P^iPr_3)]PF_6 is an easy entry to cationic half-sandwich osmium allenylidene compounds. It affords a general method to prepare mixed-ligand derivatives of the type [Os(η^5-C_5H_5)(=C=C=CPh_2)L(P^iPr_3)]$^+$. As a consequence of the latter, this paper reports a comparative study on the formation mechanisms of complexes [Os(η^5-C_5H_5)(=C=C=CPh_2)L(P^iPr_3)]PF_6 (L = CO, $PHPh_2$) and the reactivity of both compounds.

Results and Discussion

1. Preparation and Characterization of [Os(η^5-C_5H_5)(=C=C=CPh_2)(CO)(P^iPr_3)]PF_6. The mixed carbonyl-phosphine complex [Ru(η^5-C_5H_5)(=C=C=CPh_2)-(CO)(P^iPr_3)]BF_4 is the most versatile and one of the best known allenylidenes of ruthenium.[2] It is prepared by a three-step procedure involving the protonation of the monohydride RuH(η^5-C_5H_5)(CO)(P^iPr_3) to give the dihydrogen derivative [Ru(η^5-C_5H_5)(η^2-H_2)(CO)(P^iPr_3)]$^+$, the displacement of the dihydrogen ligand by acetone, and the subsequent reaction of the resulting acetone complex with 1,1-diphenyl-2-propyn-1-ol.[2a] However, attempts to prepare the osmium counterpart by a similar procedure starting from the monohydride OsH-(η^5-C_5H_5)(CO)(P^iPr_3) have been unsuccessful. In contrast to ruthenium, the protonation of the osmium monohydride leads to the osmium(IV) dihydride [OsH_2(η^5-C_5H_5)(CO)(P^iPr_3)]$^+$,[11] which is stable in acetone and quenches the allenylidene preparation. In light of this difficulty, we look for an alternative. An easy and effective method to prepare the allenylidene osmium compound is shown in Scheme 1.

Under 1 atm of carbon monoxide, complex [Os(η^5-C_5H_5){η^2-HC≡CC(OH)Ph_2}(P^iPr_3)]PF_6 (**1**) rapidly coordinates a carbon monoxide molecule, to give the carbonyl intermediate [Os(η^5-C_5H_5){η^2-HC≡CC(OH)Ph_2}-(CO)(P^iPr_3)]PF_6 (**2**). At room temperature in dichloromethane-d_2 as solvent, the transformation from **1** to **2** is quantitative after 1 min, according to the ^1H and $^{13}C\{^1H\}$ NMR spectra of the resulting solution.

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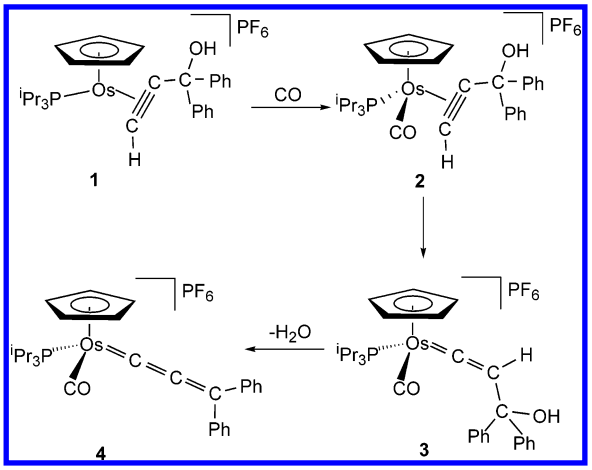
Scheme 1



The ^{1}H and ^{13}C{^{1}H} NMR spectra of **2** reflect the conversion of the π-alkyne ligand, from four-electron donor to two-electron donor, as a consequence of the carbon monoxide coordination. In the ^{1}H NMR spectrum, the C(sp)−H resonance appears at 5.05 ppm as a doublet with a H−P coupling constant of 13.2 Hz. This resonance agrees well with that observed for the complex OsCl(η^5-C_5H_5){η^2-HC≡CC(OH)Ph_2}(P^iPr_3) (d, 4.3, J(HP) = 9.0 Hz),[4a] where the alkyne acts as a two-electron-donor ligand. However, it is shifted 4.4 ppm to higher field with regard to that of **1** (δ, 9.43). The H−P coupling constant is also sensitive to the coordination. Its value is 13.2 Hz smaller in **2** than in **1** (J(PH) = 26.4 Hz). In the ^{13}C{^{1}H} NMR spectrum of **2**, the C(sp) resonances of the alkyne are observed at 79.3 and 51.8 (CH) ppm, as a singlet and as a doublet with a C−P coupling constant of 10 Hz, respectively. The chemical shifts of these resonances also agree well with those of the neutral complex OsCl(η^5-C_5H_5){η^2-HC≡CC(OH)-Ph_2}(P^iPr_3) (δ, 82.2 and 57.2). However, they are shifted about 100 ppm toward higher field with regard to those of **1** (δ, 179 and 146).

The ^{31}P{^{1}H} NMR spectrum of **2** shows a singlet at 18.9 ppm, which is shifted 9.1 ppm toward higher field in comparison with that of **1** (δ, 38.0).

Since complex **1** is a saturated species, at first glance, one could think that the first step for the formation of **2** is the transformation of the π-alkyne ligand from four-electron to two-electron donor. This involves the rupture of the overlap between the $M_\perp$ orbital of the alkyne and the corresponding metal fragment orbital, which is reached when the alkyne rotates 90°. DFT calculations[10] give for the process an energy of 32.7 kcal mol^{-1}, which is too large to be consistent with the observed reaction rate to form the carbonylation product.

Nucleophilic attack at four-electron-donor alkyne ligands is a particular noteworthy class of reaction.[9a,c] In this context it should be mentioned that the $M_\perp$* orbital is of local a_2 symmetry (within the C_{2v} group), which prevents it from significant interaction with the filled d metal orbitals.[10] Because the $M_\perp$* orbital is certainly empty, it seems reasonable to propose that the mechanism of the carbonylation of **1** involves the initial attack of the carbonyl group to the alkyne and its subsequent β-transfer to the metallic center.

In dichloromethane-d_2 at room temperature and under argon atmosphere, complex **2** evolves into the hydroxyvinylidene derivative [Os(η^5-C_5H_5){=C=CHC-(OH)Ph_2}(CO)(P^iPr_3)]PF_6 (**3**), which dehydrates to afford the allenylidene complex [Os(η^5-C_5H_5){=C=C=CPh_2}-(CO)(P^iPr_3)]PF_6 (**4**) before the extinction of **2** is completed.

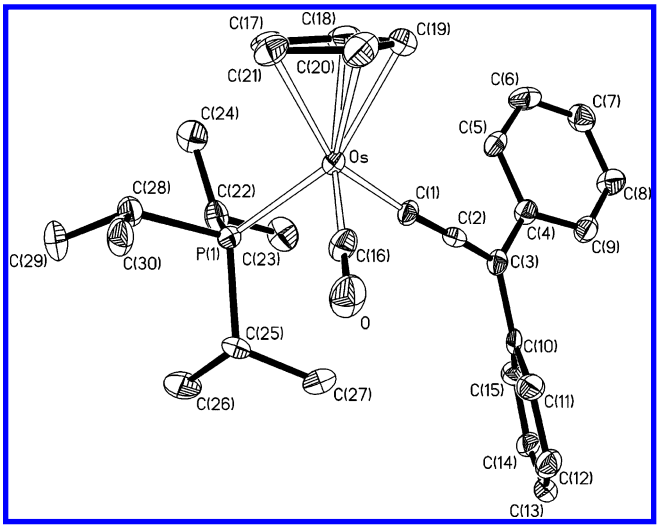


Figure 1. Molecular diagram for the cation of [Os(η^5-C_5H_5){=C=C=CPh_2}(CO)(P^iPr_3)]PF_6 (**4**). Thermal ellipsoids are shown at 50% probability.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complex 4

Os−P(1)	2.3549(14)	Os−C(20)	2.255(6)
Os−C(1)	1.913(5)	Os−C(21)	2.280(5)
Os−C(16)	1.856(6)	C(1)−C(2)	1.246(7)
Os−C(17)	2.298(5)	C(2)−C(3)	1.358(7)
Os−C(18)	2.286(6)	O−C(16)	1.163(6)
Os−C(19)	2.257(6)		
M(1)*[a]−Os−P(1)	123.9	C(1)−Os−C(16)	94.0(2)
M(1)*−Os−C(1)	123.4	Os−C(1)−C(2)	174.4(5)
M(1)*−Os−C(16)	126.0	Os−C(16)−O	175.0(5)
P(1)−Os−C(1)	91.53(15)	C(1)−C(2)−C(3)	175.4(6)
P(1)−Os−C(16)	87.91(18)		

[a] M(1)* is the midpoint of the C(17)−C(21) Cp ligand.

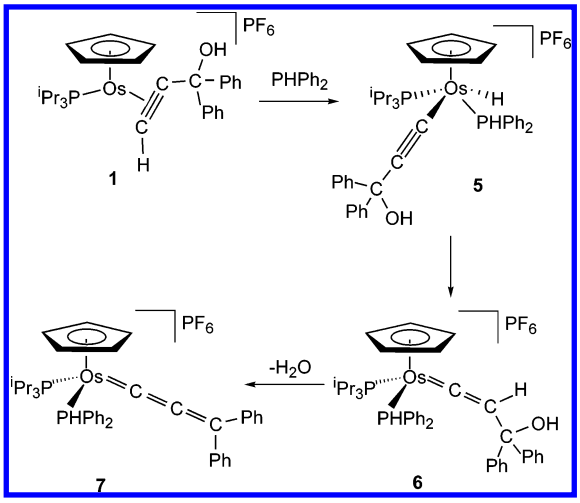
The isomerization of the alkynol to hydroxyvinylidene is strongly supported by the ^{1}H and ^{13}C{^{1}H} NMR spectra of **3**. In the ^{1}H NMR spectrum, the most noticeable resonances are two singlets at 4.00 and 3.23 ppm, corresponding to the =CH and OH protons of the hydroxyvinylidene ligand. In the ^{13}C{^{1}H} NMR spectrum, the OsC_α resonance is observed at 297.0 ppm, as a doublet with a C−P coupling constant of 9 Hz. The ^{31}P{^{1}H} NMR spectrum of **3** shows a singlet at 39.8 ppm.

When the carbonylation of **1** is carried out in a Schlenk tube for 1 min, and the resulting dichloromethane solution is heated at 58 °C under argon atmosphere, the allenylidene complex **4** is directly obtained after 8 h.

This complex was isolated as a brown solid in 86% yield and characterized by elemental analysis, MS, IR, and ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopies, and an X-ray diffraction study. A view of the structure of the cation of **4** is shown in Figure 1. Selected bond distances and angles are listed in Table 1.

The geometry around the osmium center is close to octahedral, with the cyclopentadienyl ligand occupying three sites of a face. The angles C(16)−Os−P(1), C(1)−

Scheme 2



Os−P(1), and C(16)−Os−C(1) are 87.91(18)°, 91.53(15)°, and 94.0(2)°, respectively.

The diphenylallenylidene ligand is bound to the metal in a nearly linear fashion, with Os−C(1)−C(2) and C(1)−C(2)−C(3) angles of 174.4(5)° and 175.4(6)°, respectively. The Os−C(1) and C(1)−C(2) bond lengths of 1.913(5) and 1.246(7) Å, respectively, compare well with those reported for the previous structurally characterized osmium allenylidene complexes. However, the C(1)−C(2) distance is significantly shorter than the bond length expected for a C=C double bond (1.30 Å), indicating a substantial contribution of the canonical form $[M]^-$-C≡C−C^+Ph_2 to the structure of **4**. A similar conclusion has been reached in the structural analysis of other allenylidene complexes.[1b]

In agreement with the presence of an allenylidene ligand in **4**, its IR spectrum in Nujol shows the characteristic ν(C=C=C) band for this type of ligands at 1988 cm^{-1}, and the $^{13}C\{^1H\}$ spectrum contains a doublet at 255.0 ppm with a C−P coupling constant of 10 Hz, which was assigned to the C_α atom, and two singlets at 195.3 and 159.6 ppm, corresponding to the C_β and C_γ atoms, respectively. The $^{31}P\{^1H\}$ NMR spectrum of **4** shows a singlet at 37.2 ppm.

2. Preparation and Characterization of [Os(η^5-C_5H_5)(=C=C=CPh_2)($PHPh_2$)(P^iPr_3)]PF_6. From a mechanistic point of view, it has been proposed that the transformation alkyne−vinylidene proceeds via 1,2-hydrogen migration on a M(η^2-alkyne) intermediate or, alternatively, through hydride-alkynyl species.[3f,5e−h,12] The reactions shown in Scheme 1 are new evidence in favor of the 1,2-hydrogen migration pathway. Scheme 2 shows the formation of an osmium allenylidene compound, starting from the π-alkyne complex **1**, via a hydride-alkynyl intermediate. Treatment at room temperature of dichloromethane solutions of **1** with 1.1 equiv of diphenylphosphine leads after 15 min to the hydride-hydroxyalkynyl-osmium(IV) derivative [OsH(η^5-C_5H_5){C≡CC(OH}Ph_2)($PHPh_2$)(P^iPr_3)]PF_6 (**5**), which was isolated as a white solid in 87% yield.

In a manner similar to **2**, the formation of **5** should involve the initial nucleophilic attack of the phosphine to the coordinated π-alkyne of **1** and its subsequent β-transfer to the metallic center. The resulting diphenylphosphine-triisopropylphosphine intermediate could evolve into **5** by C(sp)−H activation of the alkyne.

In the ^1H NMR spectrum of **5**, in dichloromethane-d_2 at room temperature, the most noticeable resonance of the hydroxyalkynyl ligand is a singlet at 2.71 ppm, which was assigned to the OH proton. In the high-field region of the spectrum, the hydride ligand gives rise to a double doublet at −12.55 ppm. In agreement with the *cisoid* disposition of the hydride to both phosphorus atoms,[4h,7b] the H−P coupling constants are 31.8 and 36.0 Hz. In the $^{13}C\{^1H\}$ NMR spectrum, the resonance due to the C_α atom of the hydroxyalkynyl ligand appears at 59.9 ppm, as a double doublet with C−P coupling constants of 23 and 28 Hz, whereas that corresponding to the C_β atom is observed at 117.7 ppm as a singlet. The $^{31}P\{^1H\}$ NMR spectrum contains two doublets at 22.8 (P^iPr_3) and −11.3 ($PHPh_2$) ppm, with a P−P coupling constant of 17 Hz.

In dichloromethane, complex **5** slowly evolves into its hydroxyvinylidene isomer [Os(η^5-C_5H_5){=C=CHC(OH)-Ph_2}($PHPh_2$)(P^iPr_3)]PF_6 (**6**). At 55 °C, the isomerization is quantitative after 5 h. According to previous studies,[5e] the transformation from **5** to **6** should involve the dissociation of the hydride from **5**, as a proton, and the subsequent protonation at the C_β atom of the hydroxyalkynyl ligand of a neutral metal-hydroxyalkynyl species.

Complex **6** was isolated as an orange solid. In the ^1H NMR spectrum in dichloromethane-d_2 at room temperature, the most noticeable resonances are two singlets at 2.60 and 2.26 ppm, corresponding to the =CH and OH protons of the hydroxyvinylidene ligand, respectively. In the $^{13}C\{^1H\}$ NMR spectrum, the OsC_α resonance is observed at 305.2 ppm, as a double doublet with C−P coupling constants of 9 and 11 Hz, whereas the C_β resonance appears at 123.1 ppm as a singlet. The $^{31}P\{^1H\}$ NMR shows two doublets at 20.8 (P^iPr_3) and −16.6 ($PHPh_2$) ppm, with a P−P coupling constant of 22 Hz.

In dichloromethane at 55 °C, complex **6** dehydrates to afford the allenylidene [Os(η^5-C_5H_5)(=C=C=CPh_2)-($PHPh_2$)(P^iPr_3)]PF_6 (**7**), which is isolated after 24 h as a dark red solid in almost quantitative yield.

Figure 2shows a view of the structure of the cation of **7**. Selected bond distances and angles are listed in Table 2. The geometry around the osmium atom is as that of **4** with C(1)−Os−P(1), C(1)−Os−P(2), and P(1)−Os−P(2) angles of 92.08(8)°, 93.39(8)°, and 88.89(2)°, respectively.

The diphenylallenylidene ligand is bound to the metal in a nearly linear fashion with Os−C(1)−C(2) and C(1)−C(2)−C(3) angles of 169.2(2)° and 175.7(3)°, respectively. The Os−C(1) and C(1)−C(2) bond lengths of 1.890(2) and 1.266(3) Å, respectively, compare well with the related parameters in **4** and in the previous structurally characterized osmium allenylidene complexes.[4] In this

(12) See for example: (a) Silvestre, J.; Hoffmann, R. *Helv. Chem. Acta* **1985**, *6*, 1461. (b) Bruce, M. I. *Organometallics* **1991**, *10*, 197. (c) Wakatsuki, Y.; Koga, N.; Yamazaki, H.; Morokuma, K. *J. Am. Chem. Soc.* **1994**, *116*, 8105. (d) Wakatsuki, Y.; Koga, N.; Werner, H.; Morokuma, K. *J. Am. Chem. Soc.* **1997**, *119*, 360. (e) Stegmann, R.; Frenking, G. *Organometallics* **1998**, *17*, 2089. (f) Baya, M.; Crochet, P.; Esteruelas, M. A.; López, A. M.; Modrego, J.; Oñate, E. *Organometallics* **2001**, *20*, 4291.

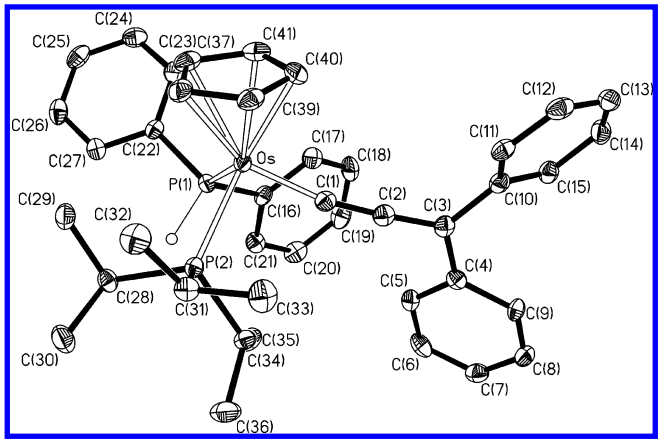


Figure 2. Molecular diagram for the cation of $[Os(\eta^5\text{-}C_5H_5)(=C=C=CPh_2)(PHPh_2)(P^iPr_3)]PF_6$ (**7**). Thermal ellipsoids are shown at 50% probability.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complex 7

Os−P(1)	2.3003(6)	Os−C(41)	2.255(2)
Os−P(2)	2.3736(6)	C(1)−C(2)	1.266(3)
Os−C(1)	1.890(2)	C(2)−C(3)	1.349(4)
Os−C(37)	2.300(2)	P(1)−C(16)	1.816(2)
Os−C(38)	2.303(2)	P(1)−C(22)	1.826(2)
Os−C(39)	2.265(3)	P(1)−H(1)	1.42(3)
Os−C(40)	2.241(3)		
M(1)*[a]−Os−P(1)	123.9	P(1)−Os−C(1)	92.08(8)
M(1)*−Os−P(2)	126.9	P(2)−Os−C(1)	93.39(8)
M(1)*−Os−C(1)	121.9	Os−C(1)−C(2)	169.2(2)
P(1)−Os−P(2)	88.89(2)	C(1)−C(2)−C(3)	175.7(3)

[a] M(1)* is the midpoint of the C(37)−C(41) Cp ligand.

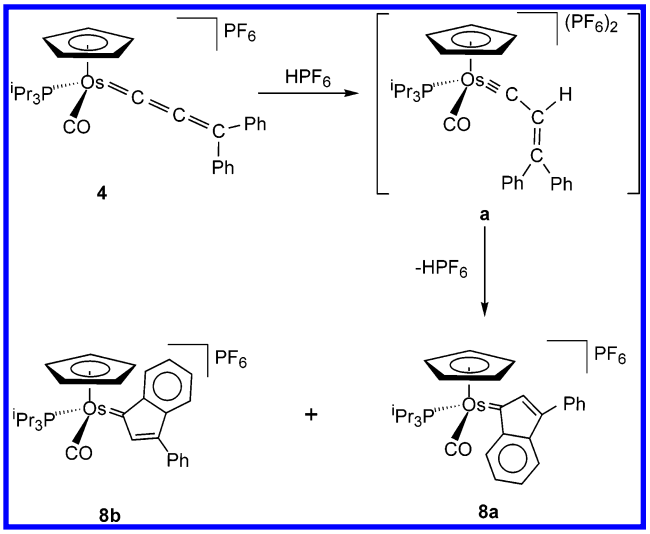
case, a substantial contribution of the canonical form $[M]^-\text{-}C{\equiv}C\text{-}C^+Ph_2$ to the structure of **7** can also to be proposed.

In agreement with the presence of an allenylidene ligand in **7**, its IR spectrum in Nujol shows the characteristic ν(C=C=C) band for this type of ligands at 1926 cm^{-1}, and the $^{13}C\{^1H\}$ NMR spectrum contains a double doublet at 257.0 ppm with C−P coupling constants of 8 and 11 Hz, which was assigned to the C_α atom, and two singlets at 220.6 and 148.2 ppm, corresponding to the C_β and C_γ atoms, respectively. The $^{31}P\{^1H\}$ NMR spectrum contains two doublets at 20.7 (P^iPr_3) and −17.6 ($PHPh_2$) ppm, with a P−P coupling constant of 24 Hz.

3. Reactions of 4 and 7 with H$^+$. EHT-MO calculations on the model complexes $[Os(\eta^5\text{-}C_5H_5)(=C=C=CH_2)(CO)(PH_3)]^+$ and $[Os(\eta^5\text{-}C_5H_5)(=C=C=CH_2)(PH_3)_2]^+$ indicate that the allenylidene coordinates to the metal centers as a σ-donor and π-acceptor ligand.[4d] The latter component of the bond is stronger than the first one. As a result, a net charge is transferred from the metallic fragment to the allenylidene. The value of the total charge on the allenylidene of the bisphosphine complex $[Os(\eta^5\text{-}C_5H_5)(=C=C=CH_2)(PH_3)_2]^+$ is about 57% higher than that on the allenylidene ligand of the carbonylphosphine compound $[Os(\eta^5\text{-}C_5H_5)(=C=C=CH_2)(CO)(PH_3)]^+$. In agreement with this, complexes **4** and **7** show significant differences of behavior in the presence of HPF_6.

Treatment at room temperature of dichloromethane solutions of **4** with 2.3 equiv of $HPF_6{\cdot}H_2O$ gives rise to the indenylidene derivative $[Os(\eta^5\text{-}C_5H_5)$(3-phenyl-1-indenylidene)$(CO)(P^iPr_3)]PF_6$ (**8**), as a result of the isomerization of the allenylidene ligand of **4**.

Scheme 3



The formation of **8** involves the initial attack of the proton of the acid to the C_β atom of the allenylidene of **4**. The addition should afford a dicationic alkenylcarbyne intermediate **a** (Scheme 3), which could evolve into **8** by electrophilic substitution of an *ortho* proton of one of the phenyl groups, by the C_α atom of the alkenylcarbyne unit. In agreement with the participation of the intermediate **a**, we have observed that a monodeuterated 3-phenyl-1-indenylidene cation **8**-d_1, containing a C_β (sp^2)−D bond, is obtained in the presence of CF_3SO_3D.

3-Phenyl-1-indenylidene-ruthenium derivatives, formed by intramolecular rearrangement of a diphenylallenylidene ligand, have been proposed as key intermediates for the olefin metathesis catalyzed by diphenylallenylidene-ruthenium derivatives.[13] As far as we know, related indenylidene-osmium compounds were unknown until now.

The indenylidene complex **8** was isolated as a black solid in 64% yield. The solid is a 1:1 mixture of the two possible rotamers resulting from a high barrier to the rotation of the indenylidene group around the Os−indenylidene bond (**8a** and **8b**). Figure 3 shows a view of the structure of the rotamer containing the C_β (sp^2)−H bond of the indenylidene ligand toward the cyclopentadienyl group (**8a**). Selected bond distances and angles are listed in Table 3.

The geometry around the osmium center is close to octahedral, with the cyclopentadienyl ligand occupying three sites of a face. The angles C(1)−Os−C(16), C(16)−Os−P, and C(1)−Os−P are 95.9(2)°, 88.30(16)°, and 97.15(14)°, respectively.

(13) See for examples: (a) Harlow, K. J.; Hill, A. F.; Wilton-Ely, J. D. E. T. *J Chem. Soc. Dalton Trans.* **1999**, 285. (b) Schanz, H.-J.; Jafarpour, L.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1999**, *18*, 5187. (c) Schanz, H.-J.; Jafarpour, L.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1999**, *18*, 5416. (d) Füstner, A.; Guth, O.; Düffels, A.; Seidel, G.; Liebl, M.; Gabor, B.; Mynott, R. *Chem. Eur. J.* **2001**, *7*, 4811. (e) Fürstner, A.; Jeanjean, F.; Razon, P. *Angew. Chem., Int. Ed.* **2002**, *41*, 2097. (f) Fürstner, A.; Radowski, K.; Wirtz, C.; Goddard, R.; Lehmann, C. W.; Mynott, R. *J. Am. Chem. Soc.* **2002**, *124*, 7061. (g) Opstal, T.; Verpoort, F. *New. J. Chem.* **2003**, *27*, 257. (h) Fürstner, A.; Leitner, A. *Angew. Chem., Int. Ed.* **2003**, *42*, 308. (i) Bassetti, M.; Centola, F.; Sémeril, D.; Bruneau, C.; Dixneuf, P. H. *Organometallics* **2003**, *22*, 4459. (j) Castarlenas, R.; Dixneuf, P. H. *Angew. Chem., Int. Ed.* **2003**, *42*, 4524.

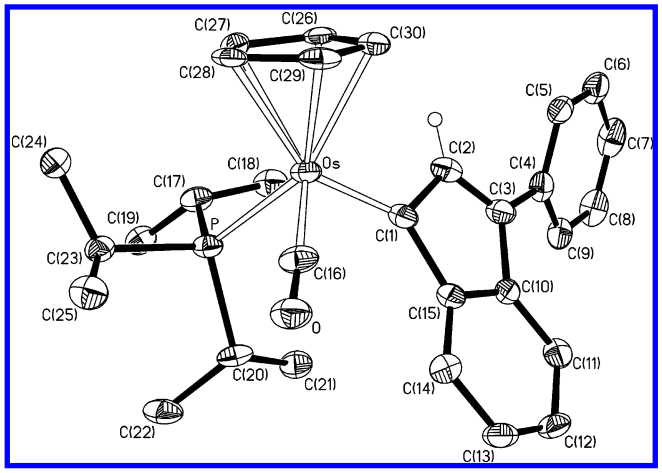


Figure 3. Molecular diagram for the complex $[Os(\eta^5\text{-}C_5H_5)(3\text{-phenyl-1-indenylidene})(CO)(P^iPr_3)]PF_6$ (**8**). Thermal ellipsoids are shown at 50% probability.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for the Complex 8

Os−P	2.3822(13)	Os−C(30)	2.269(4)
Os−C(1)	1.938(5)	C(1)−C(2)	1.483(7)
Os−C(16)	1.847(5)	C(1)−C(15)	1.510(6)
Os−C(26)	2.322(4)	C(2)−C(3)	1.349(7)
Os−C(27)	2.313(4)	C(3)−C(10)	1.492(6)
Os−C(28)	2.308(4)	C(10)−C(15)	1.398(6)
Os−C(29)	2.247(4)		
M(1)*[a]−Os−P	122.9	Os−C(1)−C(2)	123.2(3)
M(1)*−Os−C(1)	120.8	Os−C(1)−C(15)	135.8(4)
M(1)*−Os−C(16)	123.9	C(1)−C(2)−C(3)	113.7(4)
P−Os−C(1)	97.15(14)	C(1)−C(15)−C(10)	110.2(4)
P−Os−C(16)	88.30(16)	C(2)−C(3)−C(10)	107.0(4)
C(1)−Os−C(16)	95.9(2)	C(3)−C(10)−C(15)	107.6(4)
Os−C(16)−O	174.6(4)		

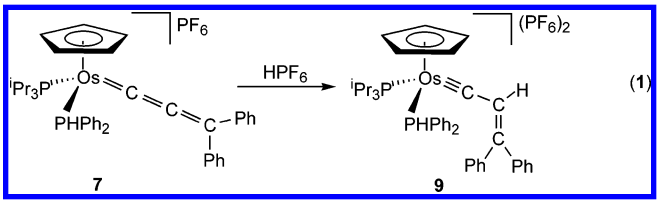
[a] M(1)* is the midpoint of the C(26)−C(30) Cp ligand.

The Os−C(1) bond length of 1.938(5) Å is between 0.04 and 0.05 Å longer than the Os−C distances found in the complexes $OsCl_2(=CHCH_2Ph)(CO)(P^iPR_3)_2$ (1.887(9) Å),[14] $[OsH(\kappa^2\text{-}O_2CCH_3)\{=C(Ph)CH_2\}(P^iPr_3)_2]BF_4$ (1.895(10) and 1.882(11) Å),[15] $[OsH(\kappa^2\text{-}O_2CCH_3)\{=C(Me)C(OH)MePh\}(P^iPr_3)_2]BF_4$ (1.879(6) Å),[16] and $[OsCl\{=CHCH(Ph)N=CMe_2\}(CO)(P^iPr_3)_2][CF_3SO_3]$ (1.890(10) Å),[17] where an Os−C double bond has also been proposed to exist. In agreement with a sp^2 hybridization at C(1), the angles Os−C(1)−C(2) and Os−C(1)−C(15) are 123.2(3)° and 135.8(4)°, respectively. The C(2)−C(3) distance of 1.349(7) Å supports the presence of a double bond between the C(2) and C(3) atoms of the five-membered ring of the indenylidene ligand.

In the ^1H NMR spectrum of **8** in dichloromethane-d_2 at room temperature, the most noticeable resonances are two singlets at 7.08 and 6.72 ppm, corresponding to the $C_\beta(sp^2)$−H protons of the indenylidene ligands of **8a** and **8b**. The $^{13}C\{^1H\}$ NMR spectrum shows the resonances due to the OsC_α carbon atoms at 260.8 and 264.2 ppm. They appear as singlets. In solution, the presence of an indenylidene ligand in **8** is mainly supported by the HMBC spectrum, which shows correlations between the resonances at 7.08 (^1H) and 260.8 ($^{13}C\{^1H\}$) ppm and between the resonances at 6.72 (^1H) and 264.2 ($^{13}C\{^1H\}$) ppm. The $^{31}P\{^1H\}$ NMR spectrum of **8** contains two singlets at 33.6 and 37.0 ppm.

It has been proposed that the intramolecular rearrangement of the diphenylallenylidene ligand into the 3-phenyl-1-indenylidene group is favored on metallic fragments and, therefore, diphenylallenylidene groups, poor in electron density. On the other hand, metallic fragments or allenylidene groups rich in electron density inhibit the isomerization.[13b,i]

In agreement with this proposal, the higher charge on the allenylidene ligand of $[Os(\eta^5\text{-}C_5H_5)(=C=C=CH_2)(PH_3)_2]^+$ with regard to that of $[Os(\eta^5\text{-}C_5H_5)(=C=C=CH_2)(CO)(PH_3)]^+$ and the behavior previously observed for complexes $[Os(\eta^5\text{-}C_5H_5)(=C=C=CPh_2)(P^iPr_3)_2]PF_6$[4d] and $[Os\{\eta^5\text{-}C_5H_4(CH_2)_2PPh_2\}(=C=C=CPh_2)(P^iPr_3)]PF_6$,[4h] the treatment at room temperature of dichloromethane solutions of **7** with 1.2 equiv of $HPF_6{\cdot}H_2O$ leads to the dicationic alkenylcarbyne derivative $[Os(\eta^5\text{-}C_5H_5)(\equiv CCH=CPh_2)(PHPh_2)(P^iPr_3)](PF_6)_2$ (**9**), which does not isomerize into an indenylidene species. The formation of **9** according to eq 1 is additional evidence for the participation of the intermediate **a** in the formation of **8**, according to Scheme 3.



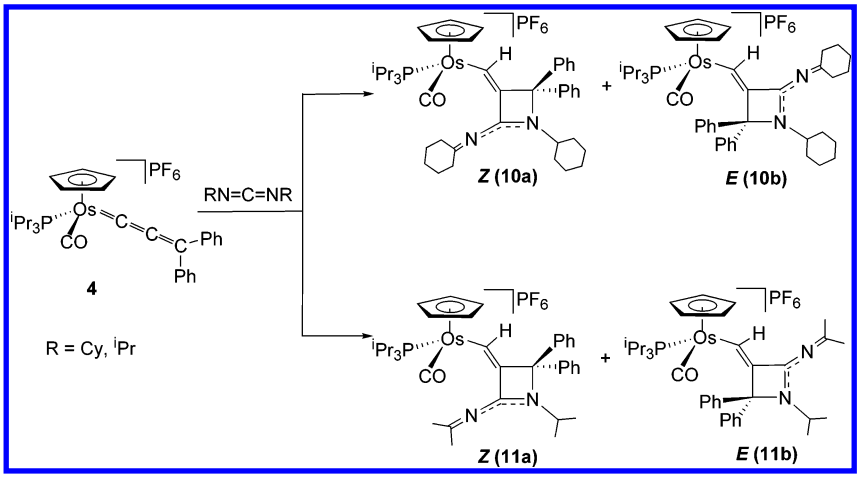
Complex **9** is a result of the acid proton addition to the C_β atom of the allenylidene ligand of **7**. Its formation agrees well with EHT-MO calculations on transition metal allenylidene compounds, which indicate a nucleophilic character of the allenylidene C_β atom.[2b,3b,4d,18]

Complex **9** was isolated as an orange solid in 86% yield. The presence of an alkenylcarbyne ligand in this compound is supported by the ^1H and $^{13}C\{^1H\}$ NMR spectra. The ^1H NMR spectrum in dichloromethane-d_2 at room temperature shows a singlet at 5.10 ppm due to the alkenylcarbyne =CH proton. In the $^{13}C\{^1H\}$ NMR spectrum, the C_α atom of the unsaturated η^1-carbon ligand gives rise to a double doublet at 296.6 ppm, with both C−P coupling constants of 7 Hz. The C_β and C_γ atoms display singlets at 131.2 and 175.7 ppm, respectively. In contrast to **8**, the HMBC spectrum of **9** does not show correlation between the resonances at 5.10 (^1H) and 296.6 ($^{13}C\{^1H\}$) ppm. The $^{31}P\{^1H\}$ NMR spectrum of **9** contains two doublets at 31.0 (P^iPr_3) and −35.2 ($PHPh_2$) ppm, with a P−P coupling constant of 16 Hz.

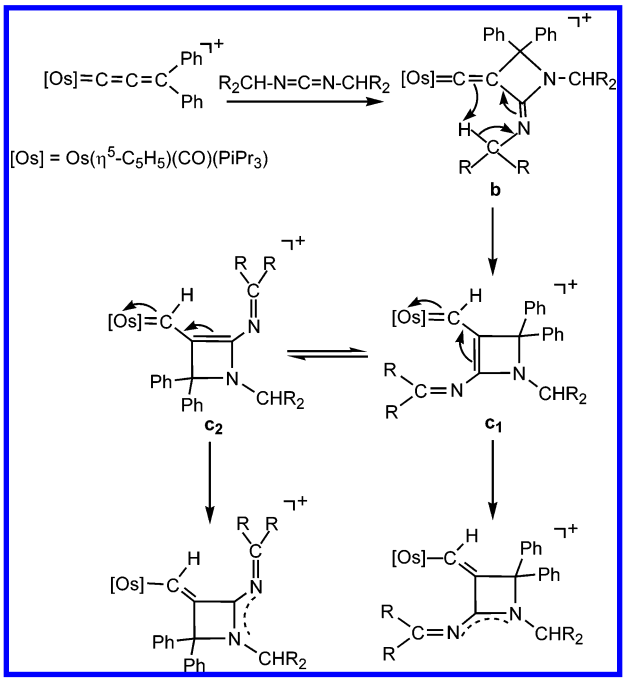
4. Formation of Iminiumazetidinylidenemethylosmium Derivatives. Complexes **4** and **7** show sig-

(14) Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A.; Valero, C.; Zeier, B. *J. Am. Chem. Soc.* **1995**, *117*, 7935.
(15) Buil. M. L.; Eisenstein, O.; Esteruelas, M. A.; García-Yebra, C.; Gutiérrez-Puebla, E.; Oliván, M.; Oñate, E.; Ruiz, N.; Tajada, M. A. *Organometallics* **1999**, *18*, 4949.
(16) Buil, M. L.; Esteruelas, M. A.; García-Yebra, C.; Gutiérrez-Puebla, E.; Oliván, M. *Organometallics* **2000**, *19*, 2184.
(17) Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2001**, *20,* 2294.
(18) (a) Berke, H.; Huttner, G.; Von Seyerl, J. *Z. Naturforsch.* **1981**, *36 B*, 1277. (b) Edwards, A. J.; Esteruelas, M. A.; Lahoz, F. J.; Modrego, J.; Oro, L. A. Schrickel, J. *Organometallics* **1996**, *15*, 3556.

Scheme 4



Scheme 5



nificant differences of behavior not only in the presence of HPF_6 but also in the presence of carbodiimides. Thus, while the addition at room temperature of 2.0 equiv of *N*,*N*′-dicyclohexylcarbodiimide and 1.1 equiv of *N*,*N*′-diisopropylcarbodiimide to dichloromethane solutions of **4** leads to the iminiumazetidinylidenemethyl derivatives $Os(\eta^5\text{-}C_5H_5)\{CH{=}\overline{CC(Ph)_2N(Cy){=}{=}C}{=}{=}N{=}\overline{C(CH_2)_4CH_2}\}(CO)(P^iPr_3)]PF_6$ (**10**) and $[Os(\eta^5\text{-}C_5H_5)\text{-}\{CH{=}\overline{CC(Ph)_2N(^iPr){=}{=}C}{=}{=}N{=}C(CH_3)_2\}(CO)(P^iPr_3)]PF_6$ (**11**), respectively, complex **7** is inert under the same conditions.

Complexes **10** and **11** were isolated as orange solids in 74% (**10**) and 57% (**11**) yield. The solids are 4:1 (**10**) or 1:1 (**11**) mixtures of the isomers *Z* and *E* shown in Scheme 4.

The formation of these compounds (Scheme 5) can be rationalized as [2+2] cycloadditions between one of the carbon−nitrogen double bonds of the carbodiimides and the $C_\beta-C_\gamma$ double bond of the allenylidene of **4**. The cycloadditions give intermediates **b**, which rapidly evolve into **c** by Alder-ene reactions, where the $C_\alpha-C_\beta$ double bond of **b** acts as enophile. The formation of the *Z*−*E* isomeric mixtures suggests that the intermediate **c** exists as mixtures in equilibrium of the isomers $\mathbf{c_1}$ and $\mathbf{c_2}$.

The [2+2] cycloadditions should occur via a polar mechanism, by initial attack of one of the N atoms of the carbodiimides at the C_γ atom of the allenylidene. Thus, the difference in behavior between **4** and **7** could be related to the presence of a carbonyl group in **4**, which enhances the electrophilic character of the C_γ atom of the allenylidene ligand. Similar mechanisms have been proposed for the formation of the ruthenium counterpart $[Ru(\eta^5\text{-}C_5H_5)\{CH{=}\overline{CC(Ph)_2N(Cy){=}{=}C}{=}{=}N{=}\overline{C(CH_2)_4CH_2}\}(CO)(P^iPr_3)]^{+}$[2g] and for the cycloaddition of aromatic imines to the $C_\gamma-C_\delta$ double bond of the butatrienylidene ligand of the cation $[Ru(\eta^5\text{-}C_5H_5)(=C{=}C{=}C{=}CH_2)(PPh_3)_2]^+$.[19]

Transition metal complexes containing unsaturated η^1-carbon ligands with a four-membered heteroring are rare. We note that E. O. Fischer has reported the formation of the iminoazetidinylidene complex $(CO)_5Cr\text{-}\{{=}\overline{CN(Cy)C(=NCy)CH_2}\}$ by reaction of $(OC)_5Cr{=}C(OH)\text{-}Me$ with dicyclohexylcarbodiimide.[20] The alkoxycarbene $(OC)_5W{=}C(OEt)Ph$ reacts with alkenylisocyanides to give 3-aza-1,2,4-pentatriene complexes, which add a second molecule of isocyanide to afford 1-azafulvene and azetidin-2-ylidene derivatives by competitive [4+1] and [3+1] cycloadditions, respectively. Azetidinylidene complexes of tungsten and chromium have also been prepared by addition of imines to carbene or allenylidene compounds.[21] Iron alkoxycarbene complexes undergo formal [1+1+2] cycloadditon reactions with isocyanides to afford iminoazetidinylidene compounds.[22] Similarly, formal [2+2] cycloadditons of iron-,[23] rhe-

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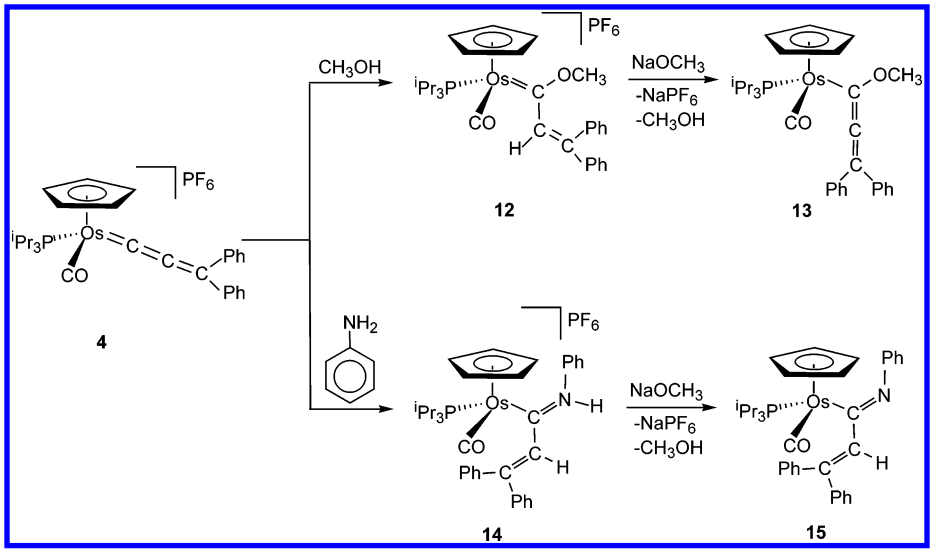
Scheme 6



nium-, and manganese-vinylidene[24] complexes with imines yield azetidinylidene derivatives. Azatitanacyclobutane complexes have been prepared by [2+2] cycloadditons of Ti=C and N=C units.[25]

Complexes **10** and **11** were characterized by elemental analysis and MS, IR, and ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopies.

In the ^{1}H NMR spectrum of **10a**, the most noticeable resonance is a doublet at 10.46 ppm, with a H−P coupling constant of 3.0 Hz, corresponding to the OsCH resonance. In agreement with the *cis* disposition of the proton and CPh_2 group at the OsC=C double bond, the above mentioned resonance shows a NOE effect (18%) with the resonance of the *ortho*-phenyl protons. In the ^{13}C{^{1}H} NMR spectrum, the OsC_α resonance appears at 159.6 ppm, as a doublet with a C−P coupling constant of 10 Hz, whereas the NCN, C_β, and CPh_2 resonances are observed as singlets at 185.4, 143.5, and 61.0 ppm, respectively. The ^{31}P{^{1}H} NMR spectrum shows a singlet at 26.2 ppm.

In the ^{1}H NMR spectrum of **10b**, the OsCH resonance is observed at 10.95 ppm as a doublet with a H−P coupling constant of 3.0 Hz. In agreement with the *E*-stereochemistry around the OsC=C double bond, in this case, a NOE effect between the OsCH resonance and that corresponding to the *ortho*-phenyl protons is not observed. In the ^{13}C{^{1}H} NMR spectrum, the OsC_α resonance appears at 156.3 ppm as a doublet with a C−P coupling constant of 10 Hz, whereas the resonances corresponding to the NCN, C_β, and CPh_2 carbon atoms are observed at 187.5, 143.4, and 61.5 ppm, respectively, as singlets. The ^{31}P{^{1}H} NMR spectrum shows a singlet at 27.6 ppm.

The ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra of **11** agree well with those of **10**. In the ^{1}H NMR spectrum the OsCH resonance of both isomers appears at 10.52 ppm, as a doublet with a H−P coupling constant of 3.7 Hz. In the ^{13}C{^{1}H} NMR spectrum, the OsC_α resonance of both isomers is also observed at the same chemical shift, 160.2 ppm. It appears as a doublet with a C−P coupling constant of 10 Hz. The ^{31}P{^{1}H} NMR spectrum of **11** shows two singlets of the same intensity at 37.2 and 25.3 ppm, one for each isomer.

5. α-Electrophilic Character of the Allenylidene Ligand of 4. The diarylallenylidene complexes with α-electrophilic character are characterized by their strong trend to add RXH molecules at the C_α−C_β double bond, to afford Fischer-type alkenylcarbene derivatives.[2,4d] Complex **4** shows the typical behavior of this type of species (Scheme 6).

In methanol as solvent, the allenylidene complex **4** evolves into the α,β-unsaturated alkoxycarbene derivative [Os(η^5-C_5H_5){=C(OCH$_3$)CH=CPh$_2$}(CO)(P^{i}Pr$_3$)]PF$_6$ (**12**), which was isolated as a yellow solid in 90% yield.

The presence of the α,β-unsaturated alkoxycarbene ligand in **12** is inferred from its ^{1}H and ^{13}C{^{1}H} NMR spectra. In the ^{1}H NMR spectrum, the unsaturated η^1-carbon ligand gives rise to two singlets at 5.86 and 4.25 ppm, which correspond to the CH= and OCH_3 protons, respectively. In the ^{13}C{^{1}H} NMR spectrum, the OsC_α resonance is observed at 268.6 ppm as a singlet, whereas the C_β and C_γ resonances appear at 138.8 and 137.9 ppm, respectively, also as singlets. The OCH_3 group displays a singlet at 65.4 ppm. The ^{31}P{^{1}H} NMR spectrum contains a singlet at 26.4 ppm.

Treatment of **12** with sodium methoxide in tetrahydrofuran produces the deprotonation of the olefinic group of the alkoxycarbene ligand to give the allenyl derivative Os(η^5-C_5H_5){C(OCH$_3$)=C=CPh$_2$}(CO)(P^{i}Pr$_3$) (**13**), which was isolated as a pale yellow solid in 77% yield. Characteristic spectroscopic features of **13** are the C=C=C streching frequency in the IR spectrum at 1855 cm^{-1} and the three resonances in the ^{13}C{^{1}H} NMR spectrum at 197.3 (s), 112.8 (d, J(CP) = 11 Hz), and 103.1 (s) ppm for the C_β, C_α, and C_γ allenyl carbon atoms, respectively. A singlet at 27.5 ppm in the ^{31}P-{^{1}H} NMR spectrum is also characteristic of **13**.

Complex **4** also reacts with aniline. The addition at room temperature of 1.0 equiv of this amine to dichloromethane solutions of **4** affords the azoniabutadienyl derivative [Os(η^5-C_5H_5){C(CH=CPh$_2$)=NHPh}(CO)(P^{i}Pr$_3$)]PF$_6$ (**14**), which was isolated as a yellow solid in 87% yield.

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The spectroscopic data of **14** agree well with those found for related ruthenium compounds.[2h] The IR spectrum in Nujol shows a ν(NH) band at 3347 cm^{-1} and a ν(C=N) band at 1590 cm^{-1}, in agreement with the presence of a C−N double bond in the azoniabutadienyl ligand. In the ^1H NMR spectrum, the most noticeable resonances are those due to the =NH and =CH protons, which are observed as singlets at 10.20 and 6.33 ppm, respectively. In the $^{13}C\{^1H\}$ NMR spectrum, the resonance corresponding to the OsC_α carbon atom appears at 219.4 ppm, as a doublet with a C−P coupling constant of 7 Hz, whereas the resonances due to the =CH and $=CPh_2$ carbon atoms are observed as singlets at 138.1 and 140.8 ppm, respectively. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 21.4 ppm.

The stereochemistry at the C−N double bond of the azoniabutadienyl ligand was inferred on the basis of a NOE experiment. The saturation of the NH resonance increases the intensity of the CH= resonance by about 3%.

Complex **14** also undergoes a deprotonation process in the presence of base. However, the deprotonation does not take place at the $CH{=}CPh_2$ group, as in the case of **12**, but at the nitrogen atom. Thus, the treatment of tetrahydrofuran solutions of **14** with 1.2 equiv of sodium methoxide leads to the azabutadienyl derivative $Os(\eta^5\text{-}C_5H_5)\{C(CH{=}CPh_2){=}NPh\}(CO)(P^iPr_3)$ (**15**), which was isolated as a yellow solid in 65% yield.

Complex **15** was characterized by elemental analysis and MS, IR, and ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopies. In the IR spectrum, the most noticeable absorption is the ν(C=N) band, which appears at 1536 cm^{-1}. In the ^1H NMR spectrum, the CH= resonance is observed at 6.82 ppm, as a singlet. The $^{13}C\{^1H\}$ NMR spectrum shows singlets at 176.6, 144.0, and 141.3 ppm for the C_α, C_β, and C_γ atoms, respectively, of the azabutadienyl ligand. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 22.3 ppm.

In contrast to **4**, complex **7** is stable in methanol, and in dichloromethane in the presence of aniline.

Concluding Remarks

This paper reveals that the π-alkyne complex $[Os(\eta^5\text{-}C_5H_5)\{\eta^2\text{-}HC{\equiv}CC(OH)Ph_2\}(P^iPr_3)]PF_6$, where the alkyne acts as a four-electron donor, is a useful starting material to prepare allenylidene derivatives of formula $[Os(\eta^5\text{-}C_5H_5)(=C=C=CPh_2)L(P^iPr_3)]PF_6$. Thus, we show that the reactions of complex $[Os(\eta^5\text{-}C_5H_5)\{\eta^2\text{-}HC{\equiv}CC(OH)Ph_2\}(P^iPr_3)]PF_6$ with carbon monoxide and diphenylphosphine lead to the mixed-ligand allenylidene compounds $[Os(\eta^5\text{-}C_5H_5)(=C=C=CPh_2)(CO)(P^iPr_3)]PF_6$ and $[Os(\eta^5\text{-}C_5H_5)(=C=C=CPh_2)(PHPh_2)(P^iPr_3)]PF_6$, respectively.

The allenylidene ligand of both complexes is a result of the dehydration of hydroxyvinylidene intermediates. However, the pathway for the formation of the hydroxyvinylidene depends on the ligand L. Carbon monoxide favors the formation of a two-electron π-alkyne intermediate, which evolves via intramolecular 1,2-hydrogen migration. On the other hand, the formation of the diphenylphosphine species takes place via a hydride-hydroxyalkynyl-osmium(IV) intermediate.

The ligand L also determines the electron density on the allenylidene ligand and, therefore, its reactivity. According to a previous theoretical study,[4d] the total charge on the allenylidene ligand of the diphenylphosphine complex is about 57% higher than that on the allenylidene ligand of the carbonyl compound. Thus, the allenylidene of $[Os(\eta^5\text{-}C_5H_5)(=C=C=CPh_2)(CO)(P^iPr_3)]PF_6$ is a weaker nucleophile and a stronger electrophile than the allenylidene of $[Os(\eta^5\text{-}C_5H_5)(=C=C=CPh_2)(PHPh_2)(P^iPr_3)]PF_6$. In agreement with this, the allenylidene ligand of the carbonyl complex isomerizes to 3-phenyl-1-indenylidene in the presence of acid, affords iminiumazetidinylidenemethyl derivatives by reaction with carbodiimides, and adds RXH molecules at the $C_\alpha{=}C_\beta$ double bond to give Fischer-type alkenylcarbene complexes. On the other hand, the diphenylphosphine-allenylidene complex reacts with HPF_6 to give the dicationic carbyne derivative $[Os(\eta^5\text{-}C_5H_5)(\equiv CCH{=}CPh_2)(PHPh_2)(P^iPr_3)](PF_6)_2$, and it is inert toward carbodiimides and RXH molecules, such as alcohols and amines.

In conclusion, the reaction of four-electron π-alkyne complexes with a Lewis base is an easy and useful method to prepare allenylidene-osmium complexes. The formation mechanism of the allenylidene and its reactivity depend on the electronic nature of the Lewis base.

Experimental Section

All manipulations were carried out with rigorous exclusion of air using Schlenk techniques. Solvents were dried by the usual procedures and used freshly distilled. $[Os(\eta^5\text{-}C_5H_5)\{\eta^2\text{-}HC{\equiv}C{-}C(OH)Ph_2\}(P^iPr_3)]PF_6$ (**1**) was prepared by the published method.[10] Infrared spectra were recorded on a Nicolet 550 spectrometer as Nujol mulls on polyethylene sheets. NMR spectra were recorded on a Varian Gemini 2000−300 MHz, Bruker Avance 300, or Bruker Avance 400 spectrometer. ^1H and $^{13}C\{^1H\}$ chemical shifts are reported relative to tetramethylsilane and the $^{31}P\{^1H\}$ ones relative to H_3PO_4 (85%). Coupling constants *J* are given in hertz. C, H, N analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyzer. FAB mass spectra analyses were performed with a VG Auto Spec instrument. The ions were produced with standard Cs^+ gun at 30 kV using 3-nitrobenzyl alcohol (NBA) as matrix.

Reaction of 1 with Carbon Monoxide: Formation of $[Os(\eta^5\text{-}C_5H_5)\{\eta^2\text{-}HC{\equiv}CC(OH)Ph_2\}(CO)(P^iPr_3)]PF_6$ (2) and $[Os(\eta^5\text{-}C_5H_5)\{=C{=}CHC(OH)Ph_2\}(CO)(P^iPr_3)]PF_6$ (3). A brown solution of **1** (25 mg, 0.036 mmol) in 0.5 mL of CD_2Cl_2 was sealed under carbon monoxide atmosphere. Immediately the NMR spectra of the resulting orange solution show the presence of compounds **2**, **3**, and **4** in a 7:3:2 molar ratio.

Spectroscopic data for $[Os(\eta^5\text{-}C_5H_5)\{\eta^2\text{-}HC{\equiv}CC(OH)Ph_2\}(CO)(P^iPr_3)]PF_6$ (2). ^1H NMR (300 MHz, CD_2Cl_2, 293 K): δ 7.50−7.28 (m, 10H, Ph), 5.74 (s, 5H C_5H_5), 5.05 (d, 1H, *J*(HP) = 13.2, ≡CH), 3.18 (s, 1H, COH), 2.55 (m, 3H, PC*H*), 1.20 (dd, 9H, *J*(HH) = 7, *J*(HP) = 14.5, PCHCH_3), 1.06 (dd, 9H, *J*(HH) = 6.7, *J*(HP) = 15.8, PCHCH_3). $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_2Cl_2, 293 K): δ 18.9 (s, P^iPr_3), −144.2 (sept, *J*(PF) = 714, PF_6). $^{13}C\{^1H\}$ NMR (75.4 MHz, CD_2Cl_2, 293 K): δ 179.8 (d, *J*(CP) = 12, CO), 144.2, 143.1 (s, C_{ipso} Ph), 128.7, 128.6, 128.3, 128.2, 126.6, and 126.5 (s, Ph), 88 (s, C_5H_5), 79.3 (s, C_β), 77.7 (s, C_γ), 51.8 (d, *J*(CP) = 10, C_α), 27.8 (d, *J*(CP) = 30, P*C*H), 20.0 and 19.1 (s, PCH*C*H_3). After 2 h, the NMR spectra of the resulting solution show a **2**, **3**, and **4** mixture in a 2:6:3 molar ratio.

Spectroscopic Data for $[Os(\eta^5\text{-}C_5H_5)\{=C{=}CHC(OH)Ph_2\}(CO)(P^iPr_3)]PF_6$ (3). ^1H NMR (300 MHz, CD_2Cl_2, 293 K): δ 7.25−7.47 (m, 10H, Ph), 5.61 (s, 5H, C_5H_5), 4.00 (s, 1H, =CH), 3.23 (s, 1H, OH), 2.38 (m, 9H, PC*H*), 1.30 (dd, 3H, *J*(HH) = 7.1, *J*(HP) = 12.1, PCHCH_3), 1.25 (dd, 9H, *J*(PH) = 7.1, *J*(HP) = 11.5, PCHCH_3). $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_2-

Cl_2, 293 K): δ 39.8 (s, P^iPr_3), −144.3 (sept, J(PF) = 714, PF_6). $^{13}C\{^1H\}$ NMR (75.4 MHz, CD_2Cl_2, 293 K): δ 297 (d, J(CP) = 9, C_α) 177.2 (d, J(CP) = 10, CO), 146.1, 144.9 (s, C_{ipso} Ph), 130.9, 129.5, 128.3, 127.9, 127.5, and 126.2 (s, Ph), 115.2 (s, C_β), 90.0 (s, C_5H_5), 60.0 (s, C_γ), 28.8 (d, J(CP)= 31, P*C*H), 19.5 and 19.3 (s, PCH*C*H_3).

Preparation of [Os(η^5-C_5H_5)(C=C=CPh_2)(CO)(P^iPr_3)$_2$]-PF_6 (4). A brown solution of **1** (500 mg, 0.73 mmol) in 8 mL of dichloromethane was stirred under carbon monoxide atmosphere. After 5 min the carbon monoxide atmosphere was replaced by argon, and the mixture was heated under reflux for 8 h. The solvent was removed under reduced pressure, and the resulting residue was treated with diethyl ether to afford a deep brown solid, which was washed with diethyl ether (3 × 3 mL) and dried in vacuo. Yield: 430 mg (86%). Anal. Calcd for $OsC_{30}H_{36}OP_2F_6$: C, 46.27; H, 4.66. Found: C, 46.10; H, 4.33. IR (Nujol, cm^{-1}): ν(C=C=C) 1988, ν(CO) 1946. MS (FAB$^+$): *m/z* 635 ($M^+ + H^+$). ^1H NMR (300 MHz, CD_2Cl_2, 293 K): δ 7.90−7.48 (m, 10H, Ph), 5.96 (s, 5H, C_5H_5), 2.40 (m, 3H, P*CH*), 1.26 (dd, 9H, J(HH) = 7.1, J(HP) = 12.5, PCHC*H*$_3$), 1.20 (dd, 9H, J(HH) = 7.1, J(HP) = 12.1, PCHC*H*$_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_2Cl_2, 293 K): δ 37.2 (s, P^iPr_3), −144.25 (sept, J(PF) = 709, PF_6). $^{13}C\{^1H\}$ NMR (75.4 MHz, CD_2Cl_2, 293 K): δ 255.0 (d, J(PC) = 10, C_α), 195.3 (s, C_β), 178.9 (d, J(CP) = 11, CO), 159.6 (s, C_γ), 144.9 (s, C_{ipso} Ph), 132.7, 130.9, and 129.7 (s, Ph), 89.5 (s, C_5H_5), 29.6 (d, J(CP) = 31, P*C*H), 19.9 and 19.5 (s, PCH*C*H_3).

Preparation of [OsH(η^5-C_5H_5){C≡C(OH)Ph_2}($PHPh_2$)-(P^iPr_3)]PF_6 (5). A solution of **1** (200 mg, 0.29 mmol) in 6 mL of dichloromethane was treated with diphenylphosphine (55.74 μL, 0.32 mmol), and the mixture was stirred for 15 min. The color turned from brown to yellow, and the solution was filtered through Kieselguhr. The solvent was removed in vacuo. The addition of diethyl ether to the resulting residue led to a white solid, which was washed with diethyl ether (3 × 3 mL) and dried in vacuo. Yield: 243 mg (87%). Anal. Calcd for $OsC_{41}H_{49}OP_3F_6$: C, 51.57; H, 5.17. Found: C, 51.80; H, 4.88. IR (Nujol, cm^{-1}): ν(O−H) 3560, ν(C≡C) + ν(OsH) 2119, ν(PF_6) 838. MS (FAB$^+$): *m/z* 811 ($M^+ + H^+$). ^1H NMR (300 MHz, CD_2Cl_2, 293 K): δ 7.46 (d, 1H, J(PH) = 426.3, $PHPh_2$), 7.39−7.35 (m, 20H, Ph), 5.50 (s, 5H, C_5H_5), 2.71 (s, 1H, OH), 2.31 (m, 3H, P*CH*), 1.04 (dd, 9H, J(HH) =7.1, J(HP) =15.9, PCHC*H*$_3$), 0.97 (dd, 9H, J(HH) = 7.1, J(HP) = 13.9, PCHC*H*$_3$), −12.55 (dd, 1H, J(HP) = 31.8, J(HP′) = 36.0, OsH). $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_2Cl_2, 293 K): δ 22.8 (d, J(PP) = 17, P^iPr_3), −11.3(d, J(PP) = 17, $PHPh_2$), −144.2 (sept, J(PF) =714, PF_6). $^{13}C\{^1H\}$ NMR (75.4 MHz, CD_2Cl_2, 293 K): δ 148.7 (d, J(CP) = 11, C_{ipso} $PHPh_2$), 146.6 (d, J(CP) =13, C_{ipso} $PHPh_2$), 131.7, 130.5 (s, C_{ipso} Ph), 132.5, 132.4, 132.2, 132.1, 129.8, 129.4, 129.3, 127.8, and 127.5 (s, Ph), 117.7 (s, C_β), 87.1(s, C_5H_5), 72.7 (s, C_γ), 59.9 (dd, J(CP) = 23, J(CP′) = 28, C_α), 27.6 (d, J(CP) = 31, P*C*H), 20.1 and 19.6 (s, PCH*C*H_3).

Preparation of [Os(η^5-C_5H_5){=C=CHC(OH)Ph_2}-($PHPh_2$)(P^iPr_3)]PF_6 (6). A solution of **5** (150 mg, 0.16 mmol) in 6 mL of dichloromethane was heated under reflux. After 5 h, the resulting solution was concentrated to ca. 1 mL. The addition of diethyl ether gave rise to the precipitation of an orange solid, which was washed with diethyl ether (3 × 3 mL) and dried in vacuo. Yield: 136 mg (89%). Anal. Calcd for $OsC_{41}H_{49}OP_3F_6$: C, 51.57; H, 5.17. Found: C, 51.80; H, 4.88. MS (FAB$^+$): *m/z* 811 ($M^+ + H^+$). ^1H NMR (300 MHz, CD_2Cl_2, 293 K): δ 7.50 (dd, 1H, J(HP) = 3.9, J(HP′) = 389.1, $PHPh_2$), 7.52−7.24 (m, 20H, Ph), 5.63 (s, 5H, C_5H_5), 2.60 (s, 1H, =CH), 2.26 (s, 1H, OH), 2.42 (m, 3H, P*CH*), 1.16 (dd, 9H, J(HH) = 7.4, J(HP) = 14.9, PCHC*H*$_3$), 1.1 (dd, 9H, J(HH) = 7.2, J(HP) = 14.7, PCHC*H*$_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_2Cl2, 293 K): δ 20.8 (d, J(PP) = 22, P^iPr_3), −16.6 (d, J(PP) = 22, $PHPh_2$), −144.18 (sept, J(PF) = 713, PF_6). $^{13}C\{^1H\}$ NMR (75.4 MHz, CD_2Cl_2, 293 K): δ 305.2 (dd, J(CP) = 9, J(CP′) = 11, C_α), 135.3 (d, J(CP) = 9, C_{ipso} $PHPh_2$), 134.4 (d, J(CP) = 9, C_{ipso} $PHPh_2$), 133.8, 133.5 (s, C_{ipso} Ph), 133.8, 133.6, 130.9, 130.0, 129.2, 129.1, 128.4, 128.2, 127.5, and 126.3 (s, Ph), 123.1 (s, C_β), 88.5 (s, C_5H_5), 66.0 (s, C_γ), 29.7 (d, J(PC) = 30, P*C*H), 19.9 and 19.4 (s, PCH*C*H_3).

Preparation of [Os(η^5-C_5H_5)(=C=C=CPh_2)($PHPh_2$)-(P^iPr_3)]PF_6 (7). A solution of **5** (150 mg, 0.16 mmol) in 6 mL of dichloromethane was heated under reflux during 24 h. Then, the solvent was removed. The treatment of the resulting residue with diethyl ether afforded a dark red solid, which was washed with diethyl ether (3 × 3 mL) and dried in vacuo. Yield: 135 mg (91.7%). Anal. Calcd for $OsC_{41}H_{47}P_3F_6$: C, 52.56; H, 5.06. Found: C, 52.41; H, 5.20. IR (Nujol, cm^{-1}): ν(C=C=C) 1926, ν(PF_6) 840. MS (FAB$^+$): *m/z* 793 ($M^+ + H^+$). ^1H NMR (300 MHz, CD_2Cl_2, 293 K): δ 7.75 (dd, 1H, J(PH) = 6.6, J(P′H) = 382.5), 7.74−7.23 (m, 20H, Ph), 5.60 (s, 5H, C_5H_5), 2.44 (m, 3H, P*CH*), 1.14 (dd, 9H, J(HH) = 7.5, J(HP) = 14.7, PCHC*H*$_3$), 1.88 (dd, 9H, J(HH) = 7.2, J(HP) =15.2, PCHC*H*$_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_2Cl_2, 293 K): δ 20.7 (d, J(PP) = 24, P^iPr_3), −17.6 (d, J(PP) = 24), −144.0 (sept, J(PF) = 716).$^{13}C\{^1H\}$ NMR (75.4 MHz, CD_2Cl_2, 293 K): δ 257.0 (dd, J(CP) = 8, J(CP′) = 11, C_α), 220.6 (s, C_β), 148.2 (s, C_γ), 133.2 (d, J(CP) = 10, C_{ipso} $PHPh_2$), 131.0 (d, J(CP) = 10, C_{ipso} $PhPh_2$), 130.8, 130.2 (s, C_{ipso} Ph), 129.3, 129.1, 128.9, and 128.6 (s,Ph), 88.3 (s, C_5H_5), 28.8 (d, J(CP) = 29, P*C*H), 19.7 (s, PCH*C*H_3).

[Os(η^5-C_5H_5)(3-phenyl-1-indenyl)(CO)(P^iPr_3)]PF_6 (8). A solution of **4** (159 mg, 0.20 mmol) in dichloromethane (6 mL) was treated with HPF_6 (21.2 μL, 60% in water, 0.47 mmol) and stirred at room temperature. After 1 h, NEt_3 (28.5 μL, 0.20 mmol) was added. The mixture was stirred for 30 min and filtered through Kieselguhr. The solvent was removed under reduced pressure. The treatment of the resulting residue with diethyl ether leads to a black solid, which was washed with diethyl ether (3 × 3 mL) and dried in vacuo. Complex **8** was obtained as a 1:1 mixture of the two possible rotamers. Yield: 196 mg (64%). Anal. Calcd for $OsC_{30}F_6H_{36}OP_2$: C, 46.27; H, 4.66. Found: C, 46.67; H, 4.88. IR (Nujol, cm^{-1}): ν (CO) 1940, ν (C=C) 1530, ν(PF_6) 1076. MS (FAB$^+$): *m/z* 635 ($M^+ + H^+$). ^1H NMR (300 MHz, CD_2Cl_2, 293 K): δ 8.30−7.20 (m, 9H, Ph), 7.08 (s, 0.5H, C_β-H), 6.72 (s, 0.5H, C_β-H), 6.10 (s, 5H, C_5H_5), 3.19 (m, 3H, P*CH*), 1.50−0.90 (18H, PCHC*H*$_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_2Cl_2, 293 K): δ 33.6 and 37.0 (s, P^iPr_3). $^{13}C\{^1H\}$ NMR (75.4 MHz, CD_2Cl_2, 293 K): δ 264.2 and 260.8 (s, C_α), 182.3 (d, J(CP) = 9, CO), 181.0 (d, J(CP) = 12, CO), 152.9 (s, =CPh), 152.2 (s, Ph), 150.6 and 150.4 (s, =CH), 149.6 (s, =CPh and Ph), 141.3, 139.9, 133.4, 132.8, 132.5, 132.3, 130.8, 130.7, 130.2, 129.9, 129.5, 129.4, 128.8, 128.7, 127.1, 126.8, 121.2, and 121.0 (s, Ph), 91.6 and 90.1 (s, C_5H_5), 31.4 and 30.7 (d, J(CP) = 30, P*C*H), 19.5, 19.3, 18.9, and 14.9 (s, PCH*C*H_3).

Preparation of [Os(η^5-C_5H_5)(≡C−CH=CPh_2)($PHPh_2$)-(P^iPr_3)]$(PF_6)_2$ (9). A solution of **7** (152 mg, 0.16 mmol) in dichloromethane (6 mL) was treated with HPF_6 (17.2 μL, 60% in water, 0.19 mmol) at room temperature. Immediately the solution changed from dark red to orange. The reaction mixture was stirred for 1 h, and the solution was reduced to ca. 1 mL. Acetone (4 mL) was added to the resulting residue and the mixture was filtered. The solvent was removed under reduced pressure and the solid residue washed with diethyl ether and dried under vacuum to afford an orange solid. Yield: 150 mg (86%). Anal. Calcd for $OsC_{41}F_2H_{48}P_4$: C, 45.47; H, 4.47. Found: C, 45.69; H, 4.54. IR (Nujol, cm^{-1}): ν(C=C) 1592, ν(PF_6) 1058. MS (FAB$^+$): *m/z* 793 (M^+). ^1H NMR (300 MHz, CD_2Cl_2, 293 K): δ 8.6 (dd, J(HP) = 4.8, J(HP′) = 382.5, 1H, $PHPh_2$), 7.71−7.10 (m, 20H, Ph), 5.90 (s, 5H, C_5H_5), 5.10 (s, 1H, =CH), 2.68 (m, 3H, P*CH*), 1.47 (dd, 9H, J(HH) = 7.5, J(HP) = 17.7, PCHC*H*$_3$), 1.22 (dd, 9H, J(HH) = 6.9, J(HP) = 15.9, PCHC*H*$_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_2Cl_2, 293 K): δ 31.0 (d, J(PP) = 16, P^iPr_3), −35.2 (d, J(PP) = 16, $PHPh_2$). $^{13}C\{^1H\}$ NMR (75.4 MHz, CD_2Cl_2, 293 K): δ 296.6 (dd, J(CP) = J(CP′) = 7, C_α), 175.7 (s, C_γ), 137.9, 137.2 (s, C_{ipso} Ph), 135.3, 134.0, 133.9, 133.6, 133.5, 133.3, 132.1, 132.0, 131.4, 130.7,

130.6, 130.5, 130.1, 129.6, and 129.3 (s, Ph), 131.2 (s, C_β), 95.6 (s, C_5H_5), 30.1 (d, J(CP) = 29, PCH), 20.0 and 19.8 (s, PCHCH_3).

Preparation of [Os(η^5-C_5H_5){CH=C$\overline{C(Ph)_2N(Cy)=C=N=C(CH_2)_4CH_2}$}(CO)($P^iPr_3$)]$PF_6$ (10). A solution of **4** (150 mg, 0.19 mmol) in 6 mL of dichloromethane was treated with *N*,*N*′-dicyclohexylcarbodiimide (79 mg, 0.38 mmol). The mixture was stirred at room temperature for 16 h, and a color change from brown to orange was observed. Then, the solvent was removed under reduced pressure. The resulting residue was treated with diethyl ether to afford an orange solid, which was washed with diethyl ether (3 × 3 mL) and dried in vacuo. Complex **10** was obtained as a 4:1 mixture of the *Z* and *E* isomers. Yield: 138 mg (74%). Anal. Calcd for $OsC_{43}H_{58}N_2OP_2F_6$: C, 52.43; H, 5.93; N, 2.84. Found: C, 51.93; H, 5.8; N, 2.64. IR (Nujol, cm^{-1}): ν(CO) 1913, ν(C=N) 1674, ν(C=C) 1575. MS (FAB^+): *m/z* 841 ($M + H^+$).

Spectroscopic Data for *Z* (10a). ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ 10.46 (d, 1H, J(HP) = 3, =CH), 7.47−7.37 (m, 10H, Ph), 5.35 (s, 5H, C_5H_5), 2.65−1.04 (24H, CH_2 + PC*H*), 0.99 (dd, 18H, J(HH) = 5.3, J(HP) = 11, PCHCH_3). $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_2Cl_2): δ 26.2 (s, P^iPr_3), −144.2 (spt, J(PF) = 714, PF_6). $^{13}C\{^1H\}$ NMR (75.4 MHz, CD_2Cl_2, 293 K): δ 186.1 (d, J(PC) = 10, CO), 185.4 (s, N−C−N), 172.3 (s, C=N), 159.6 (d, J(PC) = 10, Os-*C*H=), 143.5 (s, CH=*C*), 138.9 and 137.9 (s, C_{ipso} Ph), 130.3, 129.9, 129.6, 129.5, 129.4, 129.2, 129.1, 129.0, 128.7, and 128.6 (s, Ph), 84.3 (s, C_5H_5), 61.0 (s, CPh_2), 57.2 (s, NCH), 38.9, 38.3, 35.3, 33.0, and 30.2 (s, CH_2), 28.3 (d, J(PC) = 31, P*C*H), 19.7 and 19.3 (s, PCH*C*H_3).

Spectroscopic Data for *E* (10b). ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ 10.95 (d, 1H, J(HP) = 3, =CH), 7.47−7.37 (m, 10H, Ph), 4.99 (s, 5H, C_5H_5), 2.65−1.04 (24H, CH_2 + PC*H*), 0.84 (dd, 18H, J(HH) = 5.3, J(HP) = 10.4, PCHCH_3). $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_2Cl_2, 293 K): δ 27.6 (s, P^iPr_3), −144.2 (spt, J(PF) = 714, PF_6). $^{13}C\{^1H\}$ NMR (75.4 MHz, CD_2Cl_2, 293 K): δ 187.5 (s, N−C−N), 184.9 (d, J(PC) = 12, CO), 172.3 (s, C=N), 156.3 (d, J(PC) = 10, Os−CH=), 143.4 (s, CH=*C*), 138.4 and 136.5 (s, C_{ipso} Ph), 130.6, 130.0, 129.7, 129.5, 129.4, 129.2, 129.1, 129.0, 128.7, and 128.5 (s, Ph), 84.1 (s, C_5H_5), 61.5 (s, CPh_2), 56.3 (s, NCH), 38.4, 37.5, 35.2, 33, 31.3, and 31.2 (s, CH_2), 30.3 (d, J(PC) = 29, P*C*H), 19.6 and 19.5 (s, PCH*C*H_3).

Preparation of [Os(η^5-C_5H_5){CH=C$\overline{C(Ph)_2N(^iPr)=C=N=C(CH_3)_2CH_2}$}(CO)($P^iPr_3$)]$PF_6$ (11). A solution of **4** (150 mg, 0.17 mmol) in 6 mL of dichloromethane was treated with *N*,*N*′-diisopropylcarbodiimide (28.7 μL, 0.18 mmol). The mixture was stirred for 15 h, and a color change from brown to orange was observed. Solvent was evaporated in vacuo, and the residue was treated with diethyl ether to afford a dark orange solid, which was washed with diethyl ether (3 × 3 mL) and dried in vacuo. Complex **11** was obtained as a 1:1 mixture of the *Z* and *E* isomers. Yield: 85 mg (57%). Anal. Calcd for $OsC_{37}H_{50}ON_2P_2F_6$: C, 49.11; H, 5.57; N, 3.10. Found: C, 49.29; H, 5.49; N, 3.10. IR (Nujol, cm^{-1}): ν(CO) 1947, ν(C=N) 1683, ν(C=C) 1589, ν(PF_6) 840. FAB^+: *m/z* 761 ($M^+ + H^+$). ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ 10.52 (d, 1H, J(HP) = 3.7, Os−CH), 7.87−7.38 (m, 10H, Ph), 5.95 (s, 5/2H, C_5H_5), 5.37 (s, 5/2H, C_5H_5), 3.85 (m, 1H, NCH), 2.35 (m, 3/2H, PC*H*), 2.32 (d, 3H, J(HH) = 5.8, NCHCH_3), 1.85 (m, 3/2H, PC*H*), 1.41 (d, 3H, J(HH) = 6.8, NCHCH_3), 1.23 (dd, 9/2H, J(HH) = 7.1, J(HP) = 11.1, PCHCH_3), 1.18 (dd, 9/2H, J(HH) = 7.1, J(HP) = 11.6, PCHCH_3), 1.00 (dd, 9/2H, J(HH) = 7.2, J(HP) = 14.7, PCHCH_3), 0.84 (dd, 9/2H, J(HH) = 7.0, J(HP) = 13.9, PCHCH_3), 0.83 (s, 3H, N=CCH_3), 0.80 (s, 3H, N=CCH_3). $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_2Cl_2, 293 K): δ 37.2 (s, P^iPr_3), 25.3 (s, P^iPr_3), −144.3 (spt, J(PF) = 710, PF_6). $^{13}C\{^1H\}$ NMR (75.4 MHz, CD_2Cl_2, 293 K): δ 186.2 (d, J(CP) = 10, CO), 183.4 and 180.8 (s, NC=N), 179.1 (d, J(CP) = 11, CO), 172.8 (s, N=*C*CH_3), 160.2 (d, J(CP) = 10, OsC_α), 160.1 (s, N=*C*CH_3), 145.1 and 141.5 (s, CH=*C*), 138.8 and 137.6 (s, C_{ipso} Ph), 133.0, 131.2, 130.1, 130, 129.6, 129.5, 129.4, 129.3, 129.1, 129, 128.8, 128.7, and 126.3 (s, Ph), 89.7 and 84.3 (s, C_5H_5), 49.3 (s, N*C*H), 29.8 (d, J(CP) = 31, P*C*H), 28.4 (d, J(CP) = 30, P*C*H), 21.94 (s, NC*C*H_3), 20.1 and 19.7 (s, PCH*C*H_3), 19.3 (s, N=C*C*H_3).

Preparation of [Os(η^5-C_5H_5){=C(OCH$_3$)CH=CPh$_2$}(CO)(P^iPr_3)]PF_6 (12). A solution of **4** (150 mg, 0.19 mmol) in 10 mL of methanol was stirred during 12 h. The color turned from brown to yellow. The solution was concentrated to ca. 1 mL, and diethyl ether was added to afford a light yellow solid. The solid was washed with diethyl ether and dried in vacuo. Yield: 142 mg (90%). Anal. Calcd for $OsC_{31}H_{40}O_2P_2F_6$: C, 45.92; H, 4.97. Found: C, 45.40; H, 4.79. IR (Nujol, cm^{-1}): ν(CO) 1593, ν(C=C) 1597. MS (FAB^+): *m/z* 667 ($M^+ + H^+$). ^{1}H NMR (300 MHz, $CDCl_3$, 293 K): δ 7.50−7.16 (m, 10H, Ph), 5.86 (s, 1H, =CH), 5.18 (s, 5H, C_5H_5), 4.25 (s, 3H, OCH_3), 2.36 (m, 3H, PC*H*), 1.29 (dd, 9H, J(HH) = 7.2, J(HP) = 15.0, PCHCH_3), 1.20 (dd, 9H, J(HH) = 7.2, J(HP) = 14.7, PCHCH_3). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$, 293 K): δ 26.4 (s, P^iPr_3), −145.1 (spt, J(PF) = 717, PF_6). $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$, 293 K): δ 268.6 (s, C_α), 181.7 (d, J(CP) = 8, CO), 139.9 (s, C_{ipso}), 138.8 (s, C_β), 137.9 (s, C_γ), 131.1, 129.5, 129.4, 128.7, 128.6, and 128.4 (s, Ph), 87.4 (s, C_5H_5), 65.4 (s, OCH_3), 30.2 (d, J(PC) = 23, P*C*H), 19.8 and 19.4 (s, PCH*C*H_3).

Preparation of Os(η^5-C_5H_5){C(OCH$_3$)=C=CPh$_2$}(CO)(P^iPr_3) (13). A solution of **12** (142 mg, 0.21 mmol) in 5 mL of tetrahydrofuran was treated with sodium methoxide (15 mg, 0.25 mmol) at room temperature. The reaction mixture was stirred for 24 h, and the solvent was removed in vacuo. The residue was treated with 8 mL of toluene and the resulting suspension filtered through Kieselguhr to eliminate $NaPF_6$. The solvent was removed under reduced pressure and the residue washed with pentane to give a pale yellow solid, which was dried in vacuo. Yield: 110 mg (77%). Anal. Calcd for $OsC_{31}H_{39}O_2P$: C, 56.00; H, 5.91. Found: C, 55.88; H, 5.83. IR (Nujol, cm^{-1}): ν(CO) 1855, ν(=C=C=C) 1855. MS (FAB^+): *m/z* 667 ($M^+ + 2H^+$). ^{1}H NMR (300 MHz, C_6D_6, 293 K): δ 7.75−7.24 (m, 10H, Ph), 4.9 (s, 5H, C_5H_5), 3.51 (s, 3H, OCH_3), 2.06 (m, 3H, PC*H*), 0.98 (dd, 9H, J(HH) = 7.2, J(HP) = 13.8, PCHCH_3), 0.83 (dd, 9H, J(HH) = 7.2, J(HP) = 13.2, PCHCH_3). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6, 293 K): δ 27.5 (s, P^iPr_3). $^{13}C\{^1H\}$ NMR (75.4 MHz, C_6D_6, 293 K): δ 197.3 (s, C_β), 181.3 (d, J(CP) = 11, CO), 137.4 and 137.2 (s, C_{ipso} Ph), 124.5, 124.0, 123.6, 123.5, 121.2, and 121.1 (s, Ph), 112.8 (d, J(CP) = 11, *C*(OCH_3)), 103.1 (s,C_γ), 77.5 (s, C_5H_5), 53.0 (s, O*C*H_3), 23.3 (d, J(PC) = 29, P*C*H), 15.1 and 14.7 (s, PCH*C*H_3).

[Os(η^5-C_5H_5){C(CH=CPh$_2$)=NHPh}(CO)(P^iPr_3)]PF_6 (14). A solution of **4** (150 mg, 0.19 mmol) in dichloromethane (6 mL) was treated with aniline (19 μL, 0.20 mmol) and the mixture stirred for 8 h at room temperature. The solvent was concentrated to dryness, and the residue treated with diethyl ether to afford a yellow solid, which was washed with diethyl ether (3 × 3 mL) and dried in vacuo. Yield: 147 mg (87%). Anal. Calcd for $OsC_{36}H_{43}ONP_2F_6$: C, 49.59; H, 4.97; N, 1.61. Found: C, 49.37; H, 4.83; N, 1.72. IR (Nujol, cm^{-1}): ν(NH) 3347, ν(CO) 1942, ν(C=N) 1590, ν(PF_6) 852. MS (FAB^+): *m/z* 728 ($M^+ + H^+$). ^{1}H NMR (300 MHz, $CDCl_3$, 293 K): δ 10.20 (br s, 1H, NH), 7.40−7.02 (m, 15H, Ph), 6.33 (s, 1H, =CH), 5.18 (s, 5H, C_5H_5), 2.42 (m, 3H, PC*H*), 1.31 (dd, 9H, J(HH) = 7.2, J(HP) = 14.7, PCHCH_3), 1.29 (dd, 9H, J(HH) = 7.1, J(HP) = 14.4, PCHCH_3). $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_3Cl_3, 293 K): δ 21.4 (s, P^iPr_3), −143.8 (spt, J(PF) = 704, PF_6). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3Cl_3, 293 K): δ 219.4 (d, J(CP) = 7, C_α), 182.9 (d, J(CP) = 10, CO), 141.1 and 140.9 (s, C_{ipso} CPh_2), 140.8 (s, C_γ), 138.6 (s, C_{ipso} =NPh), 138.1 (s, C_β), 130.4, 129.4, 129.2, 128.8, 128.5, 128.3, 128.2, 127.9, and 122.9 (s, Ph), 84.9 (s, C_5H_5), 30.1 (d, J(PC) = 30, P*C*H), 20.0 and 19.7 (s, PCH*C*H_3).

Preparation of Os(η^5-C_5H_5){C(CH=CPh$_2$)=NPh}(CO)(P^iPr_3) (15). A solution of **14** (150 mg, 0.17 mmol) in 6 mL of tetrahydrofuran was treated with sodium methoxide (11 mg, 0.20 mmol), and the mixture was stirred for 1 h. The color turned from orange to yellow, and the solvent was evaporated.

Table 4. Crystal Data and Data Collection and Refinement for 4, 7, and 8

	4	7	8
		Crystal Data	
formula	$C_{30}H_{36}F_6OOsP_2$	$C_{41}H_{47}F_6OsP_3$	$C_{30}H_{36}BF_4OOsP$
molecular wt	778.73	936.90	720.57
color and habit	brown plate	black irregular prism	black plate
symmetry, space group	monoclinic, *Cc*	orthorhombic, $Pna2_1$	monoclinic, $P2_1/c$
a, Å	8.2926(4)	19.0275(9)	14.1963(11)
b, Å	32.7606(17)	15.9489(7)	8.1286(7)
c, Å	11.0558(6)	12.4803(6)	24.719(2)
β, deg	94.9650(10)		105.8000(10)
V, Å^3	2992.3(3)	3787.4(3)	2744.7(4)
Z	4	4	4
diffractometer		Bruker Smart APEX	
λ(Mo Kα), Å		0.71073	
monochromator		graphite oriented	
scan type		ω scans	
μ, mm^{-1}	4.429	3.553	4.754
2θ, range deg	3, 57	3, 57	3, 57
temp, K	100	100	100
no. of data collect	18 658	45 945	26 767
no. of unique data	7159 (R_{int} = 0.0398)	9338 (R_{int} = 0.0264)	6690 (R_{int} = 0.0586)
no. of params/restraints	355/20	471/1	353/0
$R_1{}^a[F^2 > 2\sigma(F^2)]$	0.0305	0.0180	0.0357
$wR_2{}^b$[all data]	0.0644	0.0410	0.0626
S^c[all data]	0.837	0.783	0.845

[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.

The residue was treated with toluene (9 mL), and the resulting suspension was filtered through Kieselguhr to eliminate $NaPF_6$. The solvent was removed in vacuo and the residue treated with pentane to afford a yellow solid, which was washed with pentane (3 × 3 mL). Yield: 0.16 g (65%). Anal. Calcd for $OsC_{36}H_{42}ONP$: C, 59.09; H, 5.83. Found: C, 59.09, H, 5.55. IR (Nujol, cm^{-1}): ν(C═N) 1535, ν(CO) 1895. MS (FAB$^+$): *m/z* 727 ($M^+ + H^+$). ^{1}H NMR (300 MHz, C_6D_6, 293 K): δ 7.45−6.80 (m, Ph, 15H), 6.82 (s, ═CH), 4.66 (s, 5H, C_5H_5), 2.19 (m, 3H, PC*H*), 1.10 (dd, 9H, *J*(HH) = 7.1, *J*(HP) = 13.4, PCC*H*$_3$), 0.92 (dd, 9H, *J*(HH) = 7.1, *J*(HP) = 13.4, PCC*H*$_3$). ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6, 293 K): δ 22.3 (s, P^{i}Pr$_3$). ^{13}C{^{1}H} NMR (75.4 MHz, C_6D_6, 293 K): δ 176.6 (s, C$_\alpha$), 144.0 (s, C$_\beta$), 141.3 (s, C$_\gamma$), 141.3 and 140.2 (s, C$_{ipso}$ Ph), 130.9, 128.7, 128.6, 128.4, 128.3, 128, 127.8, 127.7, 127.3, 125.9, and 121.3 (s, Ph), 84.5 (s, C_5H_5), 28.7 (d, *J*(CP) = 29, P*C*H), 20.2 and 19.6 (s, PCH*C*H$_3$).

Structural Analysis of Complexes 4, 7, and 8. 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 (molybdenum radiation, λ = 0.71073 Å) operating at 50 kV and 40 mA (**4**) or 30 mA (**7**, **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 ω. Data were corrected for absorption by using a multiscan method applied with the SADABS[26] program. The structures for 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 hydrogen atoms were observed or calculated and refined using a restricted riding model or freely. All the highest electronic residuals were observed in close proximity of the Os centers and make no chemical sense. Crystal data and details of the data collection and refinement are given in Table 4.

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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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