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# Assembly of an Allenylidene Ligand, a Terminal Alkyne, and an Acetonitrile Molecule: Formation of Osmacyclopentapyrrole Derivatives

Tamara Bolaño, Ricardo Castarlenas, Miguel A. Esteruelas,* and Enrique Oñate

*Contribution from the Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC, 50009 Zaragoza, Spain*

Received December 9, 2005; E-mail: maester@posta.unizar.es

***Abstract:*** Treatment in acetonitrile at −30 °C of the hydride−alkenylcarbyne complex [OsH(≡CCH=$CPh_2$)$(CH_3CN)_2(P^iPr_3)_2$][$BF_4$]$_2$ (**1**) with $^t$BuOK produces the selective deprotonation of the alkenyl substituent of the carbyne and the formation of the bis-solvento hydride−allenylidene derivative [OsH(=C=C=$CPh_2$)$(CH_3CN)_2(P^iPr_3)_2$]$BF_4$ (**2**), which under carbon monoxide atmosphere is converted into [Os(CH=C=$CPh_2$)(CO)$(CH_3CN)_2(P^iPr_3)_2$]$BF_4$ (**3**). When the treatment of **1** with $^t$BuOK is carried out in dichloromethane at room temperature, the fluoro−alkenylcarbyne [OsHF(≡CCH=$CPh_2$)$(CH_3CN)(P^iPr_3)_2$]$BF_4$ (**4**) is isolated. Complex **2** reacts with terminal alkynes. The reactions with phenylacetylene and cyclohexylacetylene afford [Os{(*E*)-CH=CHR}(=C=C=$CPh_2$)$(CH_3CN)_2(P^iPr_3)_2$]$BF_4$ (R = Ph (**5**), Cy (**6**)), containing an alkenyl ligand beside the allenylidene, while the reaction with acetylene in dichloromethane at −20 °C gives the hydride−allenylidene−$\pi$-alkyne [OsH(=C=C=$CPh_2$)($\eta^2$-HC≡CH)$(P^iPr_3)_2$]$BF_4$ (**7**), with the alkyne acting as a four-electron donor ligand. In acetonitrile under reflux, complexes **5** and **6** are transformed into the osmacyclopentapyrrole compounds [Os{C=C($CPh_2$CR=CH)CMe=NH}$(CH_3CN)_2$]$BF_4$ (R = Ph (**8**), Cy (**9**)), as a result of the assembly of the allenylidene ligand, the alkenyl group, and an acetonitrile molecule. The X-ray structures of **2**, **5**, and **8** are also reported.

## Introduction

The development of highly efficient and selective synthetic methods is one of the tasks for chemical science. In this context, to assemble organic fragments, in the manner like a child plays with a LEGO, is a fascinating challenge.

Allenylidene complexes belong to the series of unsaturated derivatives $L_mM{=}C(=C)_n{=}CRR'$ with $n > 0$.[1] They are generally prepared by following Selegue's protocol involving propargyl alcohols, which are converted into C=C=CRR′ units in the coordination sphere of a transition metal center by elimination of water.[2] Recent studies indicate that these $C_3$-unsaturated species are an option with a promising future, in both stoichiometric[3] and catalytic[4] processes. Their potentiality can become greater than that of the classical carbene derivatives. It stems from the presence in the carbon chain of both electrophilic ($C_\alpha$ and $C_\gamma$) and nucleophilic ($C_\beta$) sites, which provide unusually versatile reactivities.[5]

The allenylidene ligands coordinate to the metal center as $\sigma$-donor and $\pi$-acceptor groups. The resulting bond produces a charge transfer from the metal center to the allenylidene, which mainly depends on the co-ligands. As a result, the reactivity of the $C_3$-organic unit is a function of the particular metallic fragment stabilizing the unsaturated ligand. According to the behavior reported until now and in agreement with the presence of electrophilic and nucleophilic sites in the $C_3$ chain, the allenylidene complexes have been classified in three groups:[5e] α-electrophiles, γ-electrophiles, and nucleophiles. While α- and

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$\gamma$-electrophiles have attracted great attention,[6] nucleophiles have been very little studied. The most noticeable feature of the latter is their tendency to add a proton at the $C_\beta$ atom, to afford $\alpha,\beta$-unsaturated alkenylcarbyne derivatives.[5e,6n,7]

Hydrides are one of the best anchors to nail unsaturated organic molecules in transition metal compounds. As a consequence, transition metal hydride complexes are involved in many stoichiometric and catalytic reactions, including carbon−carbon and carbon−heteroatom coupling processes.[8] Hydride−allenylidene compounds are very rare. As far as we know, reported derivatives of this type only include $IrHCl_2(=C=C=CPhR)(P^iPr_3)_2$ (R = Ph, $^t$Bu), which have been obtained by oxidative addition of HCl to the corresponding iridium (I) starting complexes $IrCl(=C=C=CPhR)(P^iPr_3)_2$.[9] Hydride−allenylidene species have been also proposed as intermediates for the formation of $Os(CH=C=CPh_2)Cl_2(NO)(P^iPr_2R)_2$ (R = $^i$Pr, Ph), by treatment of $OsHCl\{C\equiv CC(OH)Ph_2\}(NO)(P^iPr_2R)_2$ with acidic alumina.[10]

The acid−base properties are among the most important and fundamental characteristics of the metal−hydride bond. They depend on the electron density of the metal fragment. The p$K_a$ values increase as the electron richness of the metal center also increases.[11] In some cases, the hydride complexes of electron-rich metals also bear a carbyne ligand.[12] Those with a $CH_2R$ group are known to have rather acidic properties.[13] In agreement with the acidity of the $C_\beta$−H bond, a few hydride−vinylidene complexes have been prepared by selective deprotonation of a carbyne group in the presence of a hydride ligand.[14]

Hydride−carbyne complexes of electron-rich metal centers are inert toward the 1,2-hydrogen shift from the metal to the carbyne carbon atom.[15] Recently, we have reported evidences proving that the activation energy for the hydride migration increases as the electron richness of the metal center augments, that is, as the acidity of the hydride ligand decreases. Thus, in contrast to $OsHCl_2(\equiv CCH=CR_2)(P^iPr_3)_2$, in acetonitrile, the dicationic hydride−alkenylcarbyne complexes $[OsH(\equiv CCH=CR_2)S_2(P^iPr_3)_2][BF_4]_2$ (R = Ph, Me; S = $H_2O$, $CH_3CN$) are converted into dicationic alkenylcarbene derivatives as expected for an electron-poor metal center.[16]

In this paper we show (i) the selective deprotonation of the alkenyl substituent of the carbyne group of complex $[OsH(\equiv CCH=CPh_2)(CH_3CN)_2(P^iPr_3)_2][BF_4]_2$ in the presence of the hydride ligand, despite the electron-poor character of the metal center, and the corresponding formation of a novel hydride−allenylidene compound; (ii) the use of the hydride ligand as a useful anchor to nail alkynes beside an allenylidene; and (iii) the assembly of the alkynes, the allenylidene, and acetonitrile to form osmacyclopentapyrrole derivatives.

## Results and Discussion

**1. Selective Deprotonation of the Alkenyl Substituent of an Alkenylcarbyne Ligand: Formation and Characterization of a Novel Hydride−Allenylidene Derivative.** Despite the expected acidity of the hydride ligand of $[OsH(\equiv CCH=$

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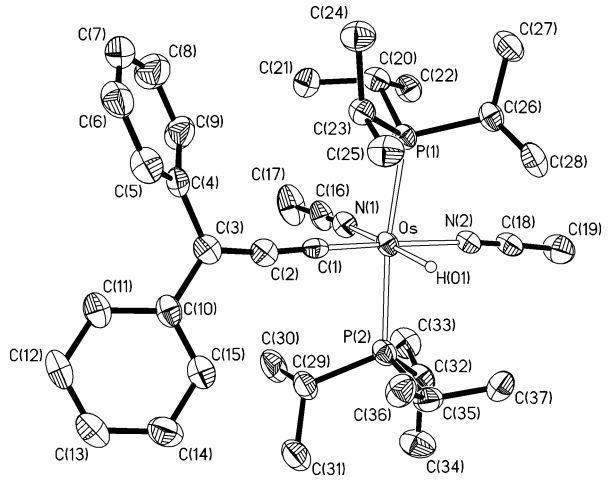
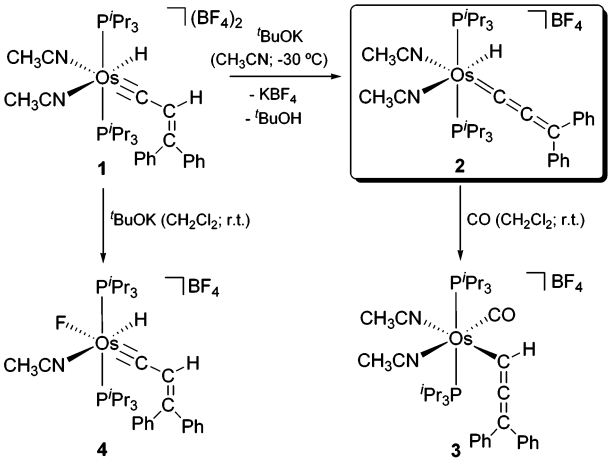



***Figure 1.*** Molecular diagram of the cation of complex $[OsH(=C=C=CPh_2)(CH_3CN)_2(P^iPr_3)_2]BF_4$ (**2**). Selected bond distances (Å) and angles (deg): Os−P(1) 2.3997(17), Os−P(2) 2.3797(17), Os−N(1) 2.218(5), Os−N(1) 2.218(5), Os−N(2) 2.116(5), Os−C(1) 1.854(6), Os−H(01) 1.57(1), C(1)−C(2) 1.275(8), C(2)−C(3) 1.347(8), P(1)−Os−P(2) 167.89(5), N(1)−Os−N(2) 85.93(18), N(1)−Os−H(01) 169.6(19), N(2)−Os−C(1) 176.2(2), Os−C(1)−C(2) 177.5(5), C(1)−C(2)−C(3) 173.2(7).

***Scheme 1***




$CPh_2)(CH_3CN)_2(P^iPr_3)_2][BF_4]_2$ (**1**), the treatment at −30 °C of acetonitrile solutions of this dicationic hydride−alkenylcarbyne complex with 1.5 equiv of $^t$BuOK produces the selective abstraction of the $C_\beta$−H hydrogen atom of the alkenylcarbyne group. The abstraction of the latter instead of the hydride ligand could be a consequence of the steric requirement of the base and/or of the fact of that the abstraction of the hydride involves the reduction of the metal center from +2 to 0. The deprotonation gives rise to the formation of the monocationic hydride−allenylidene derivative $[OsH(=C=C=CPh_2)(CH_3CN)_2(P^iPr_3)_2]$-$BF_4$ (**2**), which is isolated as a green solid in 77% yield, according to Scheme 1. The bis-solvento complex **2** is notable not only because it is a rare example of a hydride−allenylidene compound but also due to its cationic nature.

Figure 1 shows a view of the geometry of the cation of **2**. The coordination around the osmium atom can be rationalized as a distorted octahedron with the phosphorus atoms of the phosphine ligands occupying trans positions (P(1)−Os−P(2) = 167.89(5)°). The perpendicular plane is formed by the acetonitrile molecules cis disposed (N(1)−Os−N(2) = 85.93(18)°), the hydride ligand trans disposed to N(1), and the allenylidene group trans disposed to N(2) (N(2)−Os−C(1) = 176.2(2)°).

The diphenylallenylidene ligand is bonded to the metal in a nearly linear fashion with Os−C(1)−C(2) and C(1)−C(2)−C(3) angles of 177.5(5) and 173.2(7)°, respectively. The Os−C(1), C(1)−C(2), and C(2)−C(3) bond lengths of 1.854(6), 1.275(8), and 1.347(8) Å, respectively, compare well with those reported for the previously structurally characterized osmium−allenylidene complexes.[5b,6a,7a,17] In this context, it should be noted that C(1)−C(2) and C(2)−C(3) are shorter and longer, respectively, than the bond length expected for a carbon−carbon double bond (about 1.30 Å), indicating a substantial contribution of the canonical form $[M]^--C\equiv C-C^+Ph_2$ to the structure of **2**. A similar conclusion has been reached in structural analysis of other allenylidene complexes.[1b,c]

In agreement with the presence of the hydride and the allenylidene ligands in **2**, its IR spectrum in Nujol shows the characteristic $\nu$(Os−H) and $\nu$(C=C=C) bands for these ligands at 2129 and 1886 $cm^{-1}$, respectively. In the $^1H$ NMR spectrum in dichloromethane-$d_2$, the hydride resonance appears at −10.66 ppm, as a triplet ($J_{H-P}$ = 17.5 Hz). In the $^{13}C\{^1H\}$ NMR spectrum, the allenylidene ligand gives rise to a singlet at 137.5 ppm, corresponding to the $C_\gamma$ atom, and two triplets at 267.8 ($J_{C-P}$ = 13.4 Hz) and 252.2 ppm ($J_{C-P}$ = 8.1 Hz), which are assigned to the $C_\alpha$ and $C_\beta$ atoms, respectively, on the basis of the HMBC spectrum. The $^{31}P\{^1H\}$ spectrum contains a singlet at 11.8 ppm.

Complex **2** is immediately converted into the allenyl derivative $[Os(CH=C=CPh_2)(CO)(CH_3CN)_2(P^iPr_3)_2]BF_4$ (**3**) in dichloromethane under 1 atm of carbon monoxide. The transformation of **2** into **3** involves the migratory insertion of the allenylidene ligand into the metal−hydride bond and the coordination of carbon monoxide to the osmium atom.

Complex **3** is isolated as a red solid in 86% yield. In the IR spectrum of this compound in Nujol, the most noticeable feature is the presence of a $\nu$(CO) band at 1927 $cm^{-1}$. In the $^1H$ NMR spectrum in dichloromethane-$d_2$ at room temperature, the $C_\alpha$−H resonance of the allenyl ligand appears at 7.06 ppm, as a triplet ($J_{H-P}$ = 2.4 Hz). The mutually cis disposition of the acetonitrile molecules is strongly supported by the $^{13}C\{^1H\}$ NMR spectrum, which shows four singlets for these ligands at 125.6 and 125.4 (CN), and 4.1 and 3.4 ($CH_3$) ppm. The CO resonance is observed at 183.5 ppm. The allenyl ligand displays a singlet at 101.0 ppm, corresponding to the $C_\gamma$ atom, and two triplets at 206.1 ($J_{C-P}$ = 2.6 Hz) and 69.1 ppm ($J_{C-P}$ = 7.7 Hz), due to the $C_\beta$ and $C_\alpha$ atoms, respectively. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 3.7 ppm.

Because in the presence of strong bases the $BF_4^-$ anion shows a high trend to decompose releasing fluoride, the preparation of **2** requires the previously mentioned specific reaction conditions. When the treatment of **1** with $^t$BuOK is carried out in dichloromethane at room temperature, instead of acetonitrile at −30 °C, the hydride−fluoro−alkenylcarbyne derivative $[OsHF(\equiv CCH=CPh_2)(CH_3CN)(P^iPr_3)_2]BF_4$ (**4**) is obtained as a brown

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solid in 75% yield (Scheme 1). The formation of **4** seems to be a result of the replacement of one of the acetonitrile molecules of the cation of **2** by the fluoride resulting from the partial decomposition of the $BF_4^-$ anion. In agreement with this, the addition of 1 equiv of CsF to **1** gives **4**.

Complex **4** is also notable. Although there are experimental evidences suggesting that the fluoro complexes are stable when $\pi$-back-bonding ligands are also present in the coordination sphere of the metal, the chemistry of these compounds is relatively unexplored.[18] To date, only a few osmium−fluoride organometallic compounds have been reported, among them the derivatives $OsF(CO)_2(N{=}NPh)(PPh_3)_2$,[19] $[OsF_2(CO)_3]_4$,[20] $OsF(COF)(CO)_2(PPh_3)_2$,[21] and $OsF_2(CO)_2(PR_3)_2$ (R = Ph, Cy).[22] In general, fluoro−carbyne complexes are very rare,[23] as far as we know, the fluoro−osmium−carbyne compounds previously described only include $[OsHF(\equiv CCH_2Ph)(Hpz)(P^iPr_3)_2]BF_4$[13b] and $[OsH\{F\cdots HON{=}C(CH_3)_2\}(\equiv CCH_2R)(P^iPr_3)_2]BF_4$ (R = Ph, Cy, $^t$Bu).[14c] Alkenylcarbyne derivatives were unknown.

The $^1$H NMR spectrum of **4** in dichloromethane-$d_2$ at room temperature supports the presence of the alkenylcarbyne and hydride ligands. The most noticeable resonance of the alkenylcarbyne group is a singlet at 5.26 ppm, corresponding to the $C_\beta$−H hydrogen atom. The hydride ligand gives rise to a triplet ($J_{H-P}$ = 17.4 Hz) of doublets ($J_{H-F}$ = 10.3 Hz) at −5.65 ppm. In the $^{13}C\{^1H\}$ NMR spectrum, the $C_\alpha$ resonance of the alkenylcarbyne group appears 263.3 ppm, as a doublet of triplets with a C−P coupling constant of 9.9 Hz. The value of the C−F coupling constant of 129.7 Hz is consistent with the trans disposition of the alkenylcarbyne and fluoride ligands. The $C_\beta$ resonance is observed at 133.8 ppm as a doublet ($J_{C-F}$ = 9.0 Hz), while the $C_\gamma$ resonance appears at 161.1 ppm as a singlet. In the $^{19}$F NMR spectrum, the fluoride ligand displays a multiplet at −298.0 ppm. The $^{31}P\{^1H\}$NMR spectrum contains a doublet at 37.4 ppm with a P−F coupling constant of 44.3 Hz.

**2. Reactions of $[OsH(=C=C=CPh_2)(CH_3CN)_2(P^iPr_3)_2]BF_4$ with Alkynes: Formation and Characterization of Alkenyl−Allenylidene Derivatives.** The bis-solvento complex **2** reacts in dichloromethane at room temperature with terminal alkynes, such as phenylacetylene and cyclohexylacetylene, to afford the alkenyl−allenylidene derivatives $[Os\{(E)\text{-}CH{=}CHR\}(=C=C=CPh_2)(CH_3CN)_2(P^iPr_3)_2]BF_4$ (R = Ph (**5**), Cy (**6**)), as a result of the insertion of the carbon−carbon triple bond of the alkynes into the Os−H bond of **2**. Complexes **5** and **6** are isolated as orange solids in high yield, 93% (**5**) and 89% (**6**), according to Scheme 2.

Figure 2 shows a view of the geometry of the cation of **5**. The coordination around the osmium atom can be rationalized as a distorted octahedron with the phosphorus atoms of the phosphine ligands occupying trans positions (P(1)−Os−P(2) = 178.74(3)°). The perpendicular plane is formed by the alkenyl and the allenylidene ligands cis disposed (C(1)−Os−C(16) = 90.84(12)°) and the two acetonitrile molecules. The alkenyl ligand is trans disposed to N(1) (N(1)−Os−C(16) = 169.33(10)°), while the allenylidene group is trans disposed to N(2) (N(2)−Os−C(1) = 174.49(10)°).

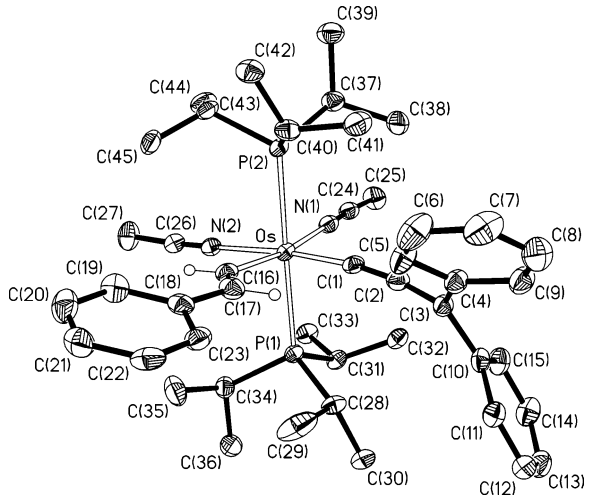
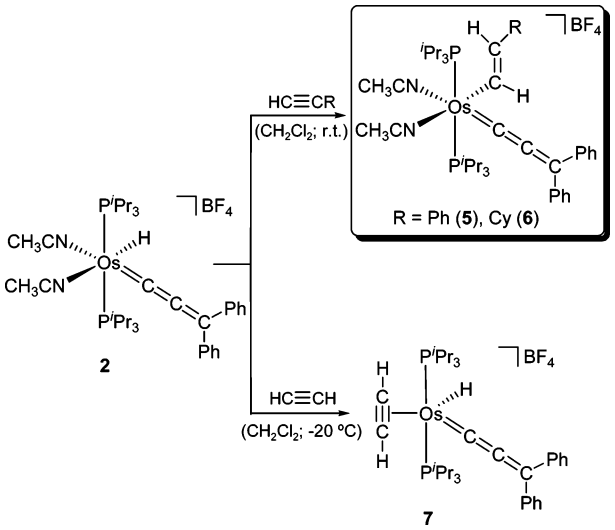



***Figure 2.*** Molecular diagram of the cation of complex $[Os\{(E)\text{-}CH{=}CHPh\}(=C=C=CPh_2)(CH_3CN)_2(P^iPr_3)_2]BF_4$ (**5**). Selected bond distances (Å) and angles (deg): Os−P(1) 2.4426(7), Os−P(2) 2.4255(7), Os−N(1) 2.122(2), Os−N(2) 2.134(2), Os−C(1) 1.866(3), Os−C(16) 2.053(3), C(1)−C(2) 1.274(4), C(2)−C(3) 1.351(4), C(16)−C(17) 1.307(4), P(1)−Os−P(2) 178.74(3), N(1)−Os−C(16) 169.33(10), N(2)−Os−C(1) 174.49(10), C(1)−Os−C(16) 90.84(12), Os−C(1)−C(2) 171.9(2), C(1)−C(2)−C(3) 172.3(3), Os−C(16)−C(17) 135.1(3), C(16)−C(17)−C(18) 130.6(3).

***Scheme 2***




The alkenyl ligand shows an *E* stereochemistry at the C(16)−C(17) double bond. The Os−C(16) bond length of 2.053(3) Å compares well with the Os−C($sp^2$) single bond distances found in other osmium−alkenyl complexes,[8b,e,24] whereas the C(16)−C(17) distance of 1.307(4) Å agrees well with the average

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carbon−carbon double bond distance (1.32(1) Å).[25] In accordance with the $sp^2$ hybridization at C(16) and C(17), the Os−C(16)−C(17) and C(16)−C(17)−C(18) angles are 135.1(3) and 130.6(3)°, respectively.

Like in **2**, the allenylidene ligand is bonded to the metal in a nearly linear fashion. In this case, the Os−C(1)−C(2) and C(1)−C(2)−C(3) angles are 171.9(2) and 172.3(3)°, respectively. The Os−C(1), C(1)−C(2), and C(2)−C(3) distances of 1.866(3), 1.274(4), and 1.351(4) Å, respectively, are statistically identical with the related bond lengths in **2**.

In agreement with the presence of the allenylidene ligands, the IR spectra of **5** and **6** in Nujol show the characteristic $\nu$(C=C=C) bands for this type of ligands at 1899 (**5**) and 1885 (**6**) $cm^{-1}$. In the $^1H$ NMR spectra in dichloromethane-$d_2$ at room temperature, the vinylic $C_\alpha$−H resonances of the alkenyl ligands are observed at 10.33 (**5**) and 8.84 (**6**) ppm, while the vinylic $C_\beta$−H resonances appear at 6.08 (**5**) and 4.81 (**6**) ppm. In accordance with the *E* stereochemistry at the carbon−carbon double bonds, the values of the H−H coupling constants between the vinylic protons are 16.8 (**5**) and 16.5 (**6**) Hz. Characteristic resonances of the allenylidene ligands in the $^{13}C\{^1H\}$ NMR spectra are triplets at 272.4 (**5**) and 268.4(**6**), and 250.8 (**5**) and 252.9 (**6**) ppm, with C−P coupling constants of 13.3 (**5**) and 13.1 (**6**), and 3.0 (**5**) and 6.2 (**6**) Hz, corresponding to the $C_\alpha$ and $C_\beta$ atoms, respectively, and singlets at 145.2 (**5**) and 142.2 (**6**) ppm due to the $C_\gamma$ atoms. The alkenyl ligands display triplets at 132.4 (**5**) and 121.0 (**6**) ppm, with C−P coupling constants of 10.0 (**5**) and 9.5 (**6**) Hz, assigned to the $C_\alpha$ atoms, and singlets at 137.4 (**5**) and 142.5 (**6**) ppm for the $C_\beta$ atoms. The $^{31}P\{^1H\}$ NMR spectra contain singlets at −9.4 (**5**) and −12.0 (**6**) ppm.

Complex **2** also reacts with acetylene. However, there are marked differences in behavior between the latter and the monosubstituted alkynes. In contrast to phenylacetylene and cyclohexylacetylene, the reaction of **2** with acetylene in dichloromethane at room temperature leads to an *ill-defined* straw-colored solid. In acetonitrile, the decomposition does not take place, but **2** is recovered unaltered. Under acetylene at −20 °C, the dichloromethane solutions of **2** afford the hydride−$\pi$-alkyne−allenylidene derivative $[OsH(=C=C=CPh_2)(\eta^2\text{-}HC\equiv CH)(P^iPr_3)_2]BF_4$ (**7**), which is isolated at −20 °C as a brown solid in 94% yield.

Complex **7** is the first member of the novel $[OsH\{=C(=C)_n=CRR'\}(\eta^2\text{-}HC\equiv CR'')(P^iPr_3)]^+$ series with $n > 0$.[26] The NMR spectra of **7** strongly support the presence in the compound of a $\pi$-acetylene group acting as a four-electron donor ligand.[27] Furthermore, they indicate that its structure is like that of $[OsH(=C=CHR)(\eta^2\text{-}HC\equiv CH)(P^iPr_3)_2]^+$, which, on the basis of an X-ray diffraction study on $[OsH(=C=CH_2)(\eta^2\text{-}HC\equiv CH)(P^iPr_3)_2]BF_4$, has been described as a trigonal bipyramid with apical phosphines and inequivalent angles within the equatorial plane.[26] In this context, it should be noted that for five-coordinate complexes an L ligand with $\sigma$- and $\pi$-donating capabilities stabilizes the trigonal bipyramid, with the L ligand in the foot of the Y.[28]

In agreement with the structure proposed in Scheme 2, in the $^1H$ NMR spectrum of **7** in dichloromethane at −20 °C, the resonance corresponding to the protons of the alkyne appears at 10.51 ppm as the AA′ part of an AA′XX′ spin system. The hydride ligand gives rise to a triplet ($J_{H-P} = 22.8$ Hz) at −5.05 ppm. In accordance with the chemical shifts found for other complexes where the alkynes also act as four-electron donor ligands,[26,27,29] the acetylenic resonance in the $^{13}C\{^1H\}$ NMR spectrum is observed at 146.6 ppm as a triplet ($J_{C-P} = 3.1$ Hz). Characteristic resonances of the allenylidene ligand are two triplets at 236.7 ($J_{C-P} = 16.2$ Hz) and 208.8 ppm ($J_{C-P} = 6.0$ Hz) corresponding to the $C_\alpha$ and $C_\beta$ atoms, respectively, and a singlet at 137.0 ppm due to the $C_\gamma$ atom. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 37.6 ppm.

The difference in behavior between the substituted alkynes and acetylene merits further comment. The insertion of the C−C triple bond of an alkyne into the Os−H bond of **2** requires that the C−C triple bond, the metal center, and the hydride ligand lie in the same plane. This occurs when the four-electron donor $\pi$-alkyne ligand, with the C−C triple bond parallel disposed to the P−Os−P direction, rotates 90° and it is converted into a two-electron donor ligand.[27] The steric hindrance experienced between the substituent of phenylacetylene or cyclohexylacetylene and the phosphines in the four-electron donor disposition (triple bond parallel to the P−Os−P direction) favors the rotation of these alkynes and, therefore, the insertion of the C−C triple bond into the Os−H bond. In this context, it should be noted that, in contrast to the related phenylacetylene and cyclohexylacetylene derivatives, complex $[OsH(=C=CH_2)(\eta^2\text{-}HC\equiv CH)(P^iPr_3)_2]BF_4$ has been isolated at room temperature and characterized by X-ray diffraction analysis.[26]

**3. Alkenyl−Allenylidene−Acetonitrile Coupling: Formation and Characterization of Osmacyclopentapyrrole Derivatives.** In acetonitrile under reflux, the alkenyl−allenylidene complexes **5** and **6** are converted into the osmacyclopentapyrrole derivatives $[Os\{C=C(CPh_2CR=CH)CMe=NH\}(CH_3CN)_2(P^iPr_3)_2]BF_4$ (R = Ph (**8**), Cy (**9**)) as a result of a triple carbon−carbon coupling involving the alkenyl and allenylidene ligands and an acetonitrile molecule. Complexes **8** and **9** are isolated as dark red (**8**) or brown (**9**) solids in high yield, 83 (**8**) and 79% (**9**), according to eq 1.

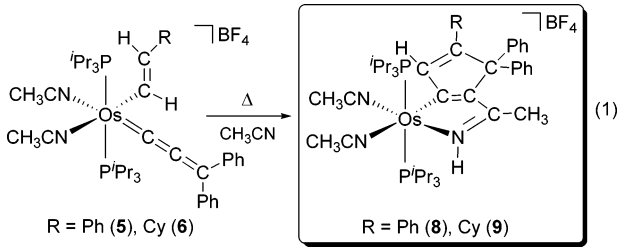


Figure 3 shows a view of the geometry of the cation of **8**. The structure proves the assembly of the three organic fragments to form a 1-osma-4-hydrocyclopenta[*c*]pyrrole skeleton, where the coordination around the metal center can be described as a distorted octahedron with the phosphorus atoms of the phosphine

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(29) See for example: (a) Templeton, J. L. *Adv. Organomet. Chem.* **1989**, *19*, 1 and references therein. (b) Baker, P. K. *Adv. Organomet. Chem.* **1996**, *40*, 45 and references therein. (c) Frohnapfel, D. S.; Reinartz, S.; White, P. S.; Templeton, J. L. *Organometallics* **1998**, *17*, 3759. (d) Frohnapfel, D. S.; Enriquez, A. E.; Templeton, J. L. *Organometallics* **2000**, *19*, 221.

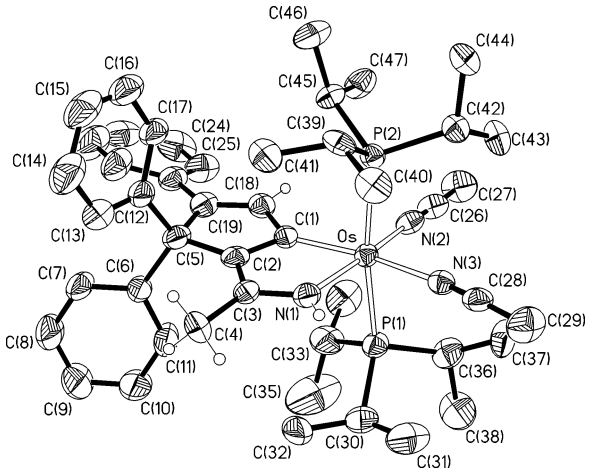


***Figure 3.*** Molecular diagram of the cation of complex [Os{C═C(CPh$_2$-CPh═CH)CMe═NH}(CH$_3$CN)$_2$(P$^i$Pr$_3$)$_2$]BF$_4$ (**8**). Selected bond distances (Å) and angles (deg): Os−P(1) 2.4149(16), Os−P(2) 2.3921(16), Os−N(1) 2.044(5), Os−N(2) 1.974(5), Os−C(1) 1.996(6), Os−N(3) 2.084(5), C(1)−C(2) 1.386(8), C(2)−C(3) 1.422(8), C(3)−N(1) 1.316(7), C(18)−C(19) 1.344(8), C(1)−C(18) 1.473(8), C(5)−C(19) 1.560(8), C(2)−C(5) 1.545(7), P(1)−Os−P(2) 170.76(6), N(1)−Os−N(2) 171.1(2), N(1)−Os−C(1) 76.4(2), N(3)−Os−C(1) 164.3(2), Os−N(1)−C(3) 119.5(4), Os−C(1)−C(2) 117.0(4), C(1)−C(2)−C(3) 114.6(5), C(2)−C(3)−N(1) 112.4(6).

ligands occupying trans positions (P(1)−Os−P(2) = 170.76(6)°). The perpendicular plane is formed by the chelate group, which acts with a bite angle N(1)−Os−C(1) of 76.4(2)°, and the acetonitrile molecules with N(2) disposed trans to N(1) (N(1)−Os−N(2) = 171.1(2)°) and N(3) disposed trans to C(1) (N(3)−Os−C(1) = 164.3(2)°).

The osmahydrocyclopentapyrrole skeleton is almost planar. The deviations (in Å) from the best plane are 0.022(3) (Os), −0.033(5) (C(1)), −0.010(5) (C(18)), 0.013(5) (C(19)), 0.037(4) (C(5)), −0.028(5) (C(2)), −0.030(4) (C(3)), and 0.030(4) (N(1)). The imine group is bonded to the osmium atom with an Os−N(1)−C(3) angle of 119.5(4)°. The Os−N(1) (2.044(5) Å), C(3)−N(1) (1.316(7) Å), C(2)−C(3) (1.422(8) Å), and C(1)−C(2) (1.386(8) Å) bond lengths are statistically identical with the related distances in the complex [OsH($\eta^5$-C$_5$H$_5$){NH═C(*p*-C$_6$H$_4$Cl)CH═C(CH$_3$)}(PH$^i$Pr$_2$)]BF$_4$[30] and indicate a low degree of electronic delocalization in the azametallacyclopentadienyl ring. This agrees well with that observed for tungstenapyrrole compounds by Legzdins and co-workers.[31] However, it is in contrast with the aromaticity invoked by Carmona's group for iridapyrrole derivatives.[32] In accordance with a low contribution of the carbene resonance form to the osmium−carbon bond, the Os−C(1) distance of 1.996(6) Å is only about 0.03 Å shorter than the Os−C(16) bond length in **5**. The C(18)−C(19) distance of 1.344(8) Å strongly supports the presence of a double bond between these atoms of the fused C$_5$-ring.

The IR spectra of **8** and **9** in Nujol are consistent with the presence of an osmahydrocyclopentapyrrole skeleton in these compounds. Thus, they show $\nu$(N−H) bands at 3318 (**8**) and 3322 (**9**) cm$^{-1}$. In the $^1$H NMR spectra in dichloromethane-$d_2$ at room temperature, the NH resonances are observed at 7.97 (**8**) and 7.60 (**9**) ppm, as broad signals, whereas the C(18)−H resonances of the fused C$_5$-ring appear at 7.60 (**8**) and 6.95 (**9**) ppm as singlets. The $^{13}$C{$^1$H} NMR spectra also support a low degree of electronic delocalization in the OsNC$_3$-ring. Thus, the OsC(1) resonances appear at 204.2 (**8**) and 209.7 (**9**) ppm, as triplets with C−P coupling constants of 7.0 (**8**) and 5.3 (**9**) Hz. These resonances are shifted about 10 ppm toward lower field with regard to the chemical shifts observed for the hydride−osmium(IV) complexes [OsH($\eta^5$-C$_5$H$_5$){NH═C(*p*-C$_6$H$_4$R)CH═C(CH$_3$)](PH$^i$Pr$_2$)]BF$_4$ (R = CH$_3$, H, Cl), and about 20 ppm toward higher field with regard to the chemical shifts observed for the corresponding deprotonated osmium(II) derivatives, where, in contrast to the hydride−osmium(IV) precursors, aromaticity has been invoked in order to describe the bonding situation in the five-membered heterometallaring.[30] On the basis of the APT, HMBC, and the HSQC spectra, singlets at 176.3 (**8**) and 175.9 (**9**), 159.6 (**8**) and 168.6 (**9**), 156.7 (**8**) and 149.7 (**9**), 140.0 (**8**) and 135.9 (**9**), and 69.5 (**8**) and 70.6 (**9**) ppm are assigned to the C(3), C(19), C(2), C(18), and C(5) atoms, respectively. The $^{31}$P{$^1$H} NMR spectra contains singlets at −6.1 (**8**) and −5.0 (**9**) ppm.

Reactions involving one nitrile and unsaturated organic fragments have provided convenient routes to interesting metallacyclic imines.[33] In this context, we note that Buchwald and co-workers have reported a wide series of nitrile coupling reactions with zirconocene precursors to form azametallacycles with extremely good regiochemical control.[34] However, as far as we know, couplings involving one nitrile and two different organic fragments, like that shown in eq 1, have not been previously reported.

The formation of the osmabicycles of **8** and **9** can be rationalized according to Scheme 3. The migratory insertion of the allenylidene ligands of **5** and **6** into the Os−alkenyl bonds should give allenyl species **a**, which by coordination of an acetonitrile molecule could afford the intermediates **b** related to complex **3**. Nitriles exhibit electrophilic reactivity at the C(sp) atom,[35] by virtue of the contribution of a dipolar resonance form

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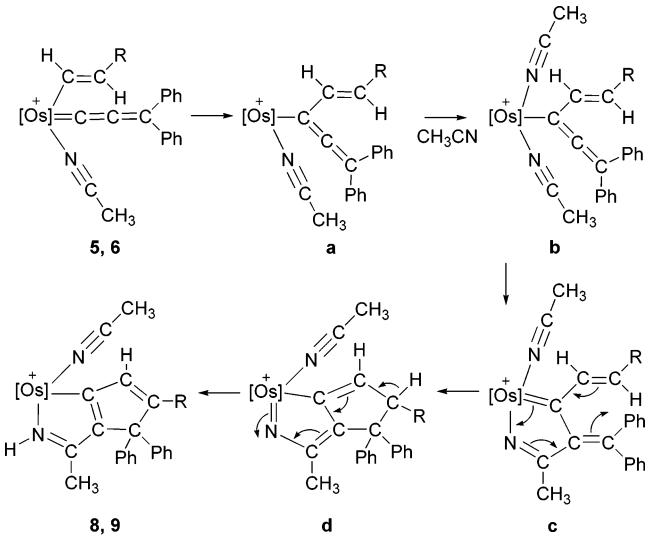
***Scheme 3***




to the carbon−nitrogen triple bond. Thus, the electrophilic attack of the C(sp) atom of acetonitrile to the $C_\beta$ atom of the cumulene should lead to **c**. This attack is consistent with EHT-MO calculations showing the nucleophilic character of the $C_\beta$ atom in these types of cumulenes.[5] The ring-closure of **c** should give **d**, which could generate **8** and **9** by dissociation of the RCH− hydrogen atom as $H^+$ and subsequent protonation of the nitrogen atom. In agreement with this, we have observed that, in the presence of $D_2O$, the formation of **8** takes place with the deuteration of the nitrogen atom, while the addition of $D_2O$ to an acetonitrile solution of **8** does not give to the deuteration of the heteroatom.

## Concluding Remarks

This study shows, step by step, the formation of osmacyclopentapyrrole derivatives, starting from a dicationic bis-solvento hydride−alkenylcarbyne compound, terminal alkynes, and acetonitrile.

The selective deprotonation of the alkenyl substituent of the alkenylcarbyne group of the hydride complex $[OsH(\equiv CCH{=}CPh_2)(CH_3CN)_2(P^iPr_3)_2][BF_4]_2$ affords the novel hydride−allenylidene derivative $[OsH(=C{=}C{=}CPh_2)(CH_3CN)_2(P^iPr_3)_2]BF_4$, which is the key species to assemble the organic fragments, in a LEGO manner, until the osmabicycles are obtained.

The hydride ligand of this cumulene compound is an efficient anchor to nail terminal alkynes beside the allenylidene ligand. Thus, it reacts with phenylacetylene and cyclohexylacetylene to give the alkenyl−allenylidene derivatives $[Os\{(E)\text{-}CH{=}CHR\}(=C{=}C{=}CPh_2)(CH_3CN)_2(P^iPr_3)_2]BF_4$ (R = Ph, Cy), which in acetonitrile are converted into $[Os\{C{=}C(CPh_2\text{-}CR{=}CH)CMe{=}NH\}(CH_3CN)_2(P^iPr_3)_2]BF_4$ by means of the formation of three carbon−carbon bonds involving the three carbon atoms of the cumulene. The $C_\alpha$ and $C_\gamma$ atoms of the allenylidene ligand are coupled with the $C_\alpha$ and $C_\beta$ atoms, respectively, of the alkenyl group, while the $C_\beta$ atom of the allenylidene is added to the C(sp) atom of an acetonitrile molecule.

In conclusion, metallacyclopentapyrrole derivatives can be formed by assembling an allenylidene ligand with an alkyne and a nitrile, via hydride−allenylidene and alkenyl−allenylidene intermediates.

## Experimental Section

All reactions were carried out with rigorous exclusion of air using Schlenk-tube techniques. Solvents were dried by the usual procedures and distilled under argon prior to use. The starting material $[OsH(\equiv CCH{=}CPh_2)(CH_3CN)_2(P^iPr_3)_2][BF_4]_2$ (**1**) was prepared by the published method.[16] $^1H$, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra were recorded on either a Varian Gemini 2000, a Bruker AXR 300, or a Bruker Avance 400 MHz instrument. Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks ($^1H$, $^{13}C\{^1H\}$) or external $H_3PO_4$ ($^{31}P\{^1H\}$). Coupling constants, *J* and *N*, are given in hertz. Infrared spectra were run on a Perkin-Elmer 1730 spectrometer (Nujol mulls on polyethylene sheets). C, H, and N analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyzer. Mass spectra analyses were performed with a VG Austospec instrument in $LSIMS^+$ mode, ions were produced with the standard $Cs^+$ gun at ca. 30 kV, and 3-nitrobenzyl alcohol (NBA) was used in the matrix.

**Preparation of $[OsH(=C{=}C{=}CPh_2)(CH_3CN)_2(P^iPr_3)_2]BF_4$ (2).** A red solution of **1** (500 mg, 0.522 mmol) in 12 mL of acetonitrile at −30 °C was treated with $^t$BuOK (88 mg, 0.782 mmol), and the mixture was stirred for 4 h until reaching room temperature. Then, the suspension was filtered through Celite, and the filtrate was evaporated. The addition of diethyl ether afforded a green solid, which was washed with a mixture of diethyl ether/pentane (1:3) and dried in vacuo. Yield: 350 mg (77%). Anal. Calcd for $C_{37}H_{59}BF_4N_2OsP_2$: C 51.03; H 6.83; N 3.21. Found: C 50.53; H 6.50; N 2.99. IR (Nujol, $cm^{-1}$): $\nu$(C≡N) 2325 (w); $\nu$(OsH) 2129 (m); $\nu$(C=C=C) 1886 (s); $\nu$(BF) 1058 (vs). MS: *m*/*z* 723 $[M + HF]^+$. $^1H$ NMR (300 MHz, $CD_2Cl_2$, 293 K): $\delta$ 7.73 (tt, $J_{H-H}$ = 7.5 and 1.2, 2H, *p*-Ph), 7.64 (d, $J_{H-H}$ = 7.2, 4H, *o*-Ph), 7.31 (dd, $J_{H-H}$ = 7.5 and 7.2, 4H, *m*-Ph), 3.01 and 2.77 (both s, 6H, $CH_3CN$), 2.40 (m, 6H, PCH), 1.19 (dvt, *N* = 13.2, $J_{H-H}$ = 7.2, 18H, PCHC$H_3$), 1.15 (dvt, *N* = 14.5, $J_{H-H}$ = 7.3, 18H, PCHC$H_3$), −10.66 (t, $J_{P-H}$ = 17.5, 1H, OsH). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CD_2Cl_2$, 293 K): $\delta$ 11.8 (s). $^{19}F$ NMR (282.3 MHz, $CD_2Cl_2$, 293 K): $\delta$ −152.7 (br). $^{13}C\{^1H\}$-APT NMR plus HMBC and HSQC (75.4 MHz, $CD_2Cl_2$, 293 K): $\delta$ 267.8 (t, $J_{C-P}$ = 13.4, Os=C), 252.2 (t, $J_{C-P}$ = 8.1, =C=), 154.2 (s, $C_{ipso}$−Ph), 142.3 and 131.9 (both s, CN), 137.5 (s, =$CPh_2$), 129.2 (s, *m*-Ph), 128.0 (s, *p*-Ph) and 126.2 (s, *o*-Ph), 25.5 (vt, *N* = 12.3, PCH), 19.0 and 18.7 (both s, PCH$CH_3$), 3.8 (s, $CH_3$-CN).

**Preparation of $[Os(CH{=}C{=}CPh_2)(CH_3CN)_2(CO)(P^iPr_3)_2]BF_4$ (3).** A green solution of **2** (220 mg, 0.253 mmol) in 8 mL of dichloromethane was stirred under carbon monoxide atmosphere. Immediately, the reaction mixture became red. After 15 min, the solution was filtered through Celite, and the solvent was removed in vacuo. The residue was washed with diethyl ether to afford a red solid. Yield: 195 mg (86%). Anal. Calcd for $C_{38}H_{59}BF_4N_2OOsP_2$: C 50.77; H 6.61; N 3.11. Found: C 50.53; H 6.28; N 2.98. IR (Nujol, $cm^{-1}$): $\nu$(C≡N) 2328 (w); $\nu$(C≡O) 1927 (s); $\nu$(BF) 1058 (vs). MS: *m*/*z* 731 $[M - 2CH_3CN]^+$. $^1H$ NMR (300 MHz, $CD_2Cl_2$, 293 K): $\delta$ 7.30−7.14 (m, 10H, Ph), 7.06 (t, $J_{H-P}$ = 2.4, OsCH), 2.56 and 2.51 (both s, 6H, $CH_3$-CN), 2.56 (m, 6H, PCH), 1.26 (dvt, *N* = 22.3, $J_{H-H}$ = 6.7, 18H, PCHC$H_3$), 1.23 (dvt, *N* = 22.5, $J_{H-H}$ = 6.9, 18H, PCHC$H_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CD_2Cl_2$, 293 K): $\delta$ 3.7 (s). $^{19}F$ NMR (282.3 MHz, $CD_2Cl_2$, 293 K): $\delta$ −152.1 (br). $^{13}C\{^1H\}$-APT NMR plus HMBC and HSQC (75.4 MHz, $CD_2Cl_2$, 293 K): $\delta$ 206.1 (t, $J_{C-P}$ = 2.6, =C=),

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183.5 (t, $J_{C-P}$ = 9.8, C≡O), 139.8 (s, $C_{ipso}$−Ph), 101.0 (s, =$CPh_2$), 125.6 and 125.4 (both s, CN), 128.4, 128.0 and 125.6 (all s, $CH_{Ph}$), 69.1 (t, $J_{C-P}$ = 7.7, OsCH), 25.3 (vt, $N$ = 12.2, PCH), 19.0 and 18.8 (both s, PCH$CH_3$), 4.1 and 3.4 (s, $CH_3$CN).

**Preparation of [OsHF(≡CCH=$CPh_2$)($CH_3CN$)($P^iPr_3$)$_2$]$BF_4$ (4). Method a:** A red solution of **1** (150 mg, 0.156 mmol) in 7 mL of dichloromethane was treated with $^t$BuOK (26 mg, 0.235 mmol). After stirring the mixture for 5 h at room temperature, the suspension was filtered through Celite, and the filtrate was evaporated. The addition of diethyl ether gave rise to the formation of a brown solid, which was washed with diethyl ether and dried in vacuo. Yield: 100 mg (75%). **Method b:** A red solution of **1** (120 mg, 0.125 mmol) in 7 mL of dichloromethane was treated with CsF (19 mg, 0.125 mmol). After stirring the mixture for 2 h at room temperature, the suspension was filtered through Celite, and the filtrate was evaporated. The addition of diethyl ether gave rise to the formation of a brown solid, which was washed with diethyl ether and dried in vacuo. Yield: 95 mg (79%). Anal. Calcd for $C_{35}H_{57}BF_5NOsP_2$: C 49.47; H 6.76; N 1.65. Found: C 48.99; H 6.51; N 1.50. IR (Nujol, cm$^{-1}$): $\nu$(C≡N) 2330 (w); $\nu$(OsH) 2168 (m); $\nu$(C=C) 1535 (m); $\nu$(BF) 1061 (vs). MS: $m/z$ 723 [M − $CH_3CN$]$^+$. $^1$H NMR (300 MHz, $CD_2Cl_2$, 293 K): $\delta$ 7.78−7.21 (m, 10H, Ph), 5.26 (s, 1H, =CH−), 2.68 (s, 3H, $CH_3CN$), 2.48 (m, 6H, PCH), 1.31 (dvt, $N$ = 13.8, $J_{H-H}$ = 7.0, 36H, PCHC$H_3$), −5.65 (td, $J_{H-P}$ = 17.4, $J_{H-F}$ = 10.3, 1H, OsH). $^{31}$P{$^1$H} NMR (121.4 MHz, $CD_2Cl_2$, 293 K): $\delta$ 37.4 (d, $J_{P-F}$ = 44.3). $^{19}$F NMR (282.3 MHz, $CD_2Cl_2$, 293 K): $\delta$ −151.6 (br, $BF_4$), −298.0 (m, Os−F). $^{13}$C{$^1$H}-APT NMR plus HMBC and HSQC (75.4 MHz, $CD_2Cl_2$, 293 K): $\delta$ 263.3 (dt, $J_{C-F}$ = 129.7, $J_{C-P}$ = 9.9, Os≡C), 161.1 (s, =$CPh_2$), 139.1 and 139.0 (both s, $C_{ipso}$−Ph), 133.8 (d, $J_{C-F}$ = 9.0, −CH=), 131.5, 131.4, 130.5, 129.3, 129.1 and 128.5 (all s, $CH_{Ph}$), 129.0 (s, CN), 25.5 (vt, $N$ = 13.0, PCH), 19.2 and 18.9 (both s, PCH$CH_3$), 3.7 (s, $CH_3$CN).

**Preparation of [Os{(*E*)-CH=CHPh}(=C=C=$CPh_2$)($CH_3CN$)$_2$($P^iPr_3$)$_2$]$BF_4$ (5).** A green solution of **2** (288 mg, 0.331 mmol) in 10 mL of dichloromethane was treated with phenylacetylene (37 $\mu$L, 0.331 mmol). After the mixture was stirred for 30 min at room temperature, it was filtered through Celite, and the filtrate was evaporated. The addition of diethyl ether afforded an orange solid, which was washed with a mixture of diethyl ether/pentane (1:3) and dried in vacuo. Yield: 300 mg (93%). Anal. Calcd for $C_{45}H_{65}BF_4N_2OsP_2$: C 55.55; H 6.73; N 2.88. Found: C 55.46; H 6.28; N 2.81. IR (Nujol, cm$^{-1}$): $\nu$(C≡N) 2317 (w); $\nu$(C=C=C) 1899 (s); $\nu$(C=C) 1550 (m); $\nu$(BF) 1059 (vs). MS: $m/z$ 804 [M − 2$CH_3CN$]$^+$; 643 [M − 2$CH_3CN$ − $P^iPr_3$]$^+$. $^1$H NMR (400 MHz, $CD_2Cl_2$, 293 K): $\delta$ 10.33 (dt, $J_{H-H}$ = 16.8, $J_{H-P}$ = 2.0, 1H, OsCH=), 7.82 (d, $J_{H-H}$ = 7.2, 4H, *o*-$Ph_{allen}$), 7.76 (t, $J_{H-H}$ = 7.6, 2H, *p*-$Ph_{allen}$), 7.31 (dd, $J_{H-H}$ = 7.6 and 7.2, 4H, *m*-$Ph_{allen}$), 7.26 (dd, $J_{H-H}$ = 7.6 and 7.2, 2H, *m*-$Ph_{vinyl}$), 7.06 (d $J_{H-H}$ = 7.2, 1H, *o*-$Ph_{vinyl}$), 6.92 (t, $J_{H-H}$ = 7.6, 2H, *p*-$Ph_{vinyl}$), 6.08 (d, $J_{H-H}$ = 16.8, 1H, =C*H*Ph), 3.23 and 2.90 (both s, 6H, $CH_3CN$), 2.51 (m, 6H, PCH), 1.20 (dvt, $N$ = 12.6, $J_{H-H}$ = 6.6, 18H, PCHC$H_3$), 1.16 (dvt, $N$ = 13.0, $J_{H-H}$ = 6.6, 18H, PCHC$H_3$). $^{31}$P{$^1$H} NMR (121.4 MHz, $CD_2Cl_2$, 293 K): $\delta$ −9.4 (s). $^{19}$F NMR (282.3 MHz, $CD_2Cl_2$, 293 K): $\delta$ −152.2 (br). $^{13}$C{$^1$H}-APT NMR plus HMBC and HSQC (100.5 MHz, $CD_2Cl_2$, 293 K): $\delta$ 272.4 (t, $J_{C-P}$ = 13.3, Os=C), 250.8 (t, $J_{C-P}$ = 3.0, =C=), 154.3 (s, $C_{ipso}$−$Ph_{allen}$), 145.2 (s, =$CPh_2$), 143.1 and 131.8 (both s, CN), 141.8 (s, $C_{ipso}$−$Ph_{vinyl}$), 137.4 (s, =*C*HPh), 132.4 (t, $J_{C-P}$ = 10.0, OsCH), 129.4 (s, *m*-$Ph_{allen}$), 129.1 (s, *p*-$Ph_{allen}$), 128.3 (s, *m*-$Ph_{vinyl}$), 127.4 (s, *o*-$Ph_{allen}$), 124.9 (s, *o*-$Ph_{vinyl}$), 124.3 (s, *p*-$Ph_{vinyl}$), 24.5 (vt, $N$ = 11.6, PCH), 19.4 and 19.3 (both s, PCH$CH_3$), 4.8 and 4.0 (s, $CH_3$CN).

**Preparation of [Os{(*E*)-CH=CHCy}(=C=C=$CPh_2$)($CH_3CN$)$_2$($P^iPr_3$)$_2$]$BF_4$ (6).** This complex was prepared as described for **5**, starting from **2** (200 mg, 0.230 mmol) and cyclohexylacetylene (30 $\mu$L, 0.23 mmol). An orange solid was obtained. Yield: 200 mg (89%). Anal. Calcd for $C_{45}H_{71}BF_4N_2OsP_2$: C 55.2; H 7.31; N 2.86. Found: C 54.80; H 7.25; N 2.96. IR (Nujol, cm$^{-1}$): $\nu$(C≡N) 2349 (w); $\nu$(C=C=C) 1885 (s); $\nu$(BF) 1060 (vs). MS: $m/z$ 811 [M − 2$CH_3CN$]$^+$; 651 [M − 2$CH_3$-CN − $P^iPr_3$]$^+$. $^1$H NMR (300 MHz, $CD_2Cl_2$, 293 K): $\delta$ 8.84 (d, $J_{H-H}$ = 16.5, 1H, OsCH), 7.75−7.73 (m, 6H, *o*-Ph and *p*-Ph), 7.24 (dd, $J_{H-H}$ = 7.5 and 7.2, 4H, *m*-Ph), 4.81 (dd, $J_{H-H}$ = 16.5 and 6.7, 1H, =C*H*Cy), 3.15 and 2.85 (both s, 6H, $CH_3CN$), 2.55 (m, 6H, PCH), 1.8−0.8 (m, 11H, Cy), 1.18 (dvt, $N$ = 12.9, $J_{H-H}$ = 7.2, 18H, PCHC$H_3$), 1.16 (dvt, $N$ = 14.2, $J_{H-H}$ = 7.3, 18H, PCHC$H_3$). $^{31}$P{$^1$H} NMR (121.4 MHz, $CD_2Cl_2$, 293 K): $\delta$ −12.0 (s). $^{19}$F NMR (282.3 MHz, $CD_2Cl_2$, 293 K): $\delta$ −152.4 (br). $^{13}$C{$^1$H}-APT NMR plus HMBC and HSQC (100.5 MHz, $CD_2Cl_2$, 293 K): $\delta$ 268.4 (t, $J_{C-P}$ = 13.1, Os=C), 252.9 (t, $J_{C-P}$ = 6.2, =C=), 154.1 (s, $C_{ipso}$−Ph), 142.6 and 132.3 (both s, CN), 142.5 (s, =*C*HCy), 142.2 (s, =$CPh_2$), 129.0 (s, *m*-Ph), 128.5 (s, *p*-Ph) and 127.0 (s, *o*-Ph), 121.0 (t, $J_{C-P}$ = 9.5, OsCH), 46.7 (s, $CH_{Cy}$), 34.4, 26.7, and 26.6 (all s, $CH_2$), 23.6 (vt, $N$ = 11.7, PCH), 18.9 and 18.7 (both s, PCH$CH_3$), 4.6 and 3.8 (both s, $CH_3$CN).

**Preparation of [OsH(=C=C=$CPh_2$)($\eta^2$-HC≡CH)($P^iPr_3$)$_2$]$BF_4$ (7).** A green solution of **2** (250 mg, 0.287 mmol) in 7 mL of dichloromethane at 253 K was stirred under acetylene atmosphere. After 3 h at 253 K, the resulting mixture was concentrated. The addition of diethyl ether at 253 K gave rise to the formation of a brown solid, which was washed with diethyl ether and dried in vacuo. Yield: 219 mg (94%). Anal. Calcd for $C_{35}H_{53}BF_4OsP_2$: C 51.72; H 6.57. Found: C 51.35; H 6.75. IR (Nujol, cm$^{-1}$): $\nu$(OsH) 2115 (w); $\nu$(C=C=C) 1919 (s); $\nu$(BF) 1061 (vs). MS: $m/z$ 701 [M − $C_2H_2$]$^+$. $^1$H NMR (300 MHz, $CD_2Cl_2$, 253 K): $\delta$ 10.51 (part AA′ of an AA′XX′ spin system, AA′ = $H_2C_2$ and XX′ = ($P^iPr_3$)$_2$), 7.61 (t, $J_{H-H}$ = 7.0, 2H, *p*-Ph), 7.38 (d, $J_{H-H}$ = 7.3, 4H, *o*-Ph), 7.30 (dd, $J_{H-H}$ = 7.3 and 7.0, 4H, *m*-Ph), 2.88 (m, 6H, PCH), 1.19 (dvt, $N$ = 13.5, $J_{H-H}$ = 6.9, 18H, PCHC$H_3$), 1.10 (dvt, $N$ = 14.2, $J_{H-H}$ = 6.8, 18H, PCHC$H_3$), −5.05 (t, $J_{H-P}$ = 22.8, 1H, OsH). $^{31}$P{$^1$H} NMR (121.4 MHz, $CD_2Cl_2$, 253 K): $\delta$ 37.6 (s). $^{19}$F NMR (282.3 MHz, $CD_2Cl_2$, 253 K): $\delta$ −152.8 (br). $^{13}$C{$^1$H}-APT NMR plus HMBC and HSQC (75.4 MHz, $CD_2Cl_2$, 253 K): $\delta$ 236.7 (t, $J_{C-P}$ = 16.2, Os=C), 208.8 (t, $J_{C-P}$ = 6.0, =C=), 146.6 (t, $J_{C-P}$ = 3.1, $H_2C_2$), 143.4 (s, $C_{ipso}$−Ph), 137.0, (s, =$CPh_2$), 129.4 (s, *p*-Ph), 129.0 (s, *m*-Ph) and 127.3 (s, *o*-Ph), 24.6 (vt, $N$ = 14.6, PCH), 20.4 and 19.1 (both s, PCH$CH_3$).

**Preparation of [Os{C=C(CPh$_2$CPh=CH)CMe=NH}($CH_3CN$)$_2$($P^iPr_3$)$_2$]$BF_4$ (8).** An orange solution of **5** (150 mg, 0.154 mmol) in 12 mL of acetonitrile was heated under reflux for 8 h. The solution was filtered through Celite, and the solvent was removed in vacuo. The addition of diethyl ether to the resulting residue led to a dark red solid, which was washed with diethyl ether and dried in vacuo. Yield: 130 mg (83%). Anal. Calcd for $C_{47}H_{68}BF_4N_3OsP_2$: C 55.67; H 6.76; N 4.14. Found: C 55.54; H 6.24; N 4.32. IR (Nujol, cm$^{-1}$): $\nu$(NH) 3318 (w); $\nu$(C≡N) 2327 (w), 2230 (w); $\nu$(BF) 1059 (vs). MS: $m/z$ 887 [M − $CH_3CN$]$^+$; 842 [M − 2$CH_3CN$]$^+$. $^1$H NMR (300 MHz, $CD_2Cl_2$, 293 K): $\delta$ 7.97 (br, 1H, NH), 7.60 (s, 1H, =CH), 7.33−7.16 (m, 15H, Ph), 2.77 and 2.64 (both s, 6H, $CH_3CN$), 2.28 (m, 6H, PCH), 2.14 (s, 3H, $CH_3$), 1.30 (dvt, $N$ = 13.5, $J_{H-H}$ = 6.9, 18H, PCHC$H_3$), 0.99 (dvt, $N$ = 12.4, $J_{H-H}$ = 6.4, 18H, PCHC$H_3$). $^{31}$P{$^1$H} NMR (121.4 MHz, $CD_2Cl_2$, 293 K): $\delta$ −6.1 (s). $^{19}$F NMR (282.3 MHz, $CD_2Cl_2$, 293 K): $\delta$ −152.4 (br). $^{13}$C{$^1$H}-APT NMR plus HMBC and HSQC (75.4 MHz, $CD_2Cl_2$, 293 K): $\delta$ 204.2 (t, $J_{C-P}$ = 7.0, C(1)), 176.3 (s, C(3)), 159.6 (s, C(19)), 156.7 (s, C(2)), 140.5 and 136.0 (both s, $C_{ipso}$−Ph), 140.0 (s, C(18)), 127.5 and 120.8 (both s, CN), 129.3, 128.8, 128.2, 128.1, 127.8, and 126.8 (all s, $CH_{Ph}$), 69.5 (s, C(5)), 24.7 (vt, $N$ = 11.3, PCH), 22.4 (s, C(4)), 19.6 and 18.7 (both s, PCH$CH_3$), 4.7 and 4.0 (both s, $CH_3$CN).

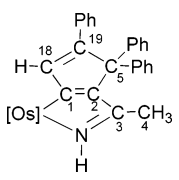
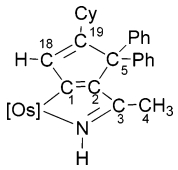


***Table 1.*** Crystal Data and Data Collection and Refinement for **2**, **5**, and **8**

| | **2** | **5** | **8** |
|---|---|---|---|
| | | Crystal Data | |
| formula | $C_{37}H_{58}BF_4N_2OsP_2 \cdot CH_2Cl_2$ | $C_{45}H_{65}BF_4N_2OsP_2$ | $C_{47}H_{68}BF_4N_3OsP_2$ |
| molecular wt | 955.74 | 972.94 | 1013.99 |
| color and habit | orange, irregular block | red, irregular block | orange, irregular block |
| size, mm | 0.80, 0.08, 0.06 | 0.20, 0.016, 0.16 | 0.10, 0.06, 0.06 |
| symmetry, space group | monoclinic, $P2_1/n$ | triclinic, $P\bar{1}$ | monoclinic, $P2_1/c$ |
| *a*, Å | 11.5033(12) | 7.4633(6) | 11.3003(14) |
| *b*, Å | 33.861(4) | 11.2428(9) | 10.9934(13) |
| *c*, Å | 11.8212(13) | 13.7705(11) | 38.071(5) |
| α, deg | | 84.140(2) | |
| *β*, deg | 111.056(2) | 83.248(3) | 94.455(2) |
| *γ*, deg | | 81.579(2) | |
| *V*, Å$^3$ | 4297.1(8) | 2205.4(6) | 4715.3(10) |
| *Z* | 4 | 2 | 4 |
| $D_{calc}$, g cm$^{-3}$ | 1.477 | 1.465 | 1.428 |
| | | Data Collection and Refinement | |
| diffractometer | | Bruker Smart APEX | |
| *λ*(Mo Kα), Å | | 0.71073 | |
| monochromator | | graphite oriented | |
| scan type | | *ω* scans | |
| *μ*, mm$^{-1}$ | 3.212 | 3.013 | 2.823 |
| 2*θ*, range deg | 3, 57 | 3, 57 | 3, 57 |
| temp, K | 173.0(2) | 100.0(2) | 100.0(2) |
| no. of data collect | 53716 | 26188 | 41140 |
| no. of unique data | 10629 ($R_{int}$ = 0.0870) | 10513 ($R_{int}$ = 0.0284) | 11465 ($R_{int}$ = 0.0971) |
| no. of params/restrains | 458/20 | 518/0 | 540/39 |
| $R_1$[a] [$F^2 > 2\sigma(F^2)$] | 0.0499 | 0.0258 | 0.0503 |
| $wR_2$[b] [all data] | 0.0892 | 0.0508 | 0.0803 |
| $S$[c] [all data] | 0.880 | 0.876 | 0.784 |

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

**Preparation of [Os{C=C(CPh$_2$CCy=CH)CMe=NH}(CH$_3$CN)$_2$(P$^i$Pr$_3$)$_2$]BF$_4$ (9).** This complex was prepared as described for **8**, starting from 120 mg (0.123 mmol) of **6**. A brown solid was obtained. Yield: 99 mg (79%). Anal. Calcd for $C_{47}H_{68}BF_4N_3OsP_2$: C 55.34; H 7.31; N 4.12. Found: C 55.37; H 6.88; N 4.64. IR (Nujol, cm$^{-1}$): *ν*(NH) 3322 (w); *ν*(C≡N) 2326 (w), 2239 (w); *ν*(BF) 1061 (vs). MS: *m*/*z* 893 [M − CH$_3$CN]$^+$. $^1$H NMR (300 MHz, $CD_2Cl_2$, 293 K): *δ* 7.60 (s, 1H, NH), 6.95 (s, 1H, =CH), 7.52−7.18 (m, 10H, Ph), 2.73 and 2.60 (both s, 6H, $CH_3CN$), 2.24 (m, 6H, PCH), 2.14 (s, 3H, $CH_3$), 1.72−1.60 (m, 11H, Cy), 1.24 (dvt, $N$ = 13.2, $J_{H-H}$ = 6.6, 18H, PCHC*H*$_3$), 0.97 (dvt, $N$ = 12.4, $J_{H-H}$ = 6.7, 18H, PCHC*H*$_3$). $^{31}$P{$^1$H} NMR (121.4 MHz, $CD_2Cl_2$, 293 K): *δ* −5.0 (s). $^{19}$F NMR (282.3 MHz, $CD_2Cl_2$, 293 K): *δ* −152.4 (br). $^{13}$C{$^1$H}-APT NMR plus HMBC and HSQC (100.5 MHz, $CD_2Cl_2$, 293 K): *δ* 209.7 (t, $J_{C-P}$ = 5.3, C(1)), 175.9 (s, C(3)), 168.6 (s, C(19)), 149.7 (s, C(2)), 142.0 (s, $C_{ipso}$−Ph), 135.9 (s, C(18)), 128.6, 128.0, and 126.4 (all s, $CH_{Ph}$), 127.4 and 120.5 (both s, CN), 70.6 (s, C(5)), 38.2 (s, $CH_{Cy}$), 35.2, 27.2, and 26.6 (all s, $CH_2$), 25.0 (vt, N = 11.2, PCH), 23.1 (s, C(4)), 20.2 and 19.2 (both s, PCH*C*H$_3$), 5.2 and 4.5 (both s, *C*H$_3$CN).




**Structural Analysis of Complexes 2, 5, and 8.** X-ray data were collected for all complexes at low temperature on a Bruker Smart APEX CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube source (molybdenum radiation, $\lambda$ = 0.71073 Å) operating at 50 kV and 40 mA. Data were collected over the complete sphere by a combination of four sets. Each frame exposure time was 10 or 30 s covering 0.3° in *ω*. Data were corrected for absorption by using a multiscan method applied with the Sadabs[36] program. The structures for all compounds were solved by the Patterson method. Refinement, by full-matrix least squares on $F^2$ with SHELXL97,[37] was similar for all complexes, including isotropic and subsequently anisotropic displacement parameters for all non-hydrogen atoms. The hydrogen atoms were observed or calculated and refined freely or using a restricted riding model, respectively.

For **2**, a molecule of dichloromethane was observed in the least cycles of refinement in the asymmetric cell. This molecule was refined with restrains in the geometry and thermal parameters. For **8**, the $BF_4^-$ anion was observed disordered over two sites. These molecules were also refined with restrains in the their geometry and thermal parameters.

A summary of crystal data and data collection and refinement details is reported in Table 1.

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**Supporting Information Available:** Crystal structure determinations, including bond lengths and angles of compounds **2**, **5**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

JA058355B

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