Synthesis and Reactivity of Osmium Complexes Containing a Cyclopentadienyl Ligand with a Pendant Phosphine Donor Group

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The unsaturated six-coordinate complex $OsH_2Cl_2(P^iPr_3)_2$ (**1**) reacts with $Li[C_5H_4(CH_2)_2PPh_2]$ to give $[OsH_2\{\eta^5\text{-}C_5H_4(CH_2)_2PPh_2\}(P^iPr_3)]Cl$ (**2**). This dihydride is fairly acidic and can be deprotonated with KOH in methanol. The reaction of the resulting monohydride $OsH\{\eta^5\text{-}C_5H_4(CH_2)_2PPh_2\}(P^iPr_3)$ (**3**) with chloroform affords $Os\{\eta^5\text{-}C_5H_4(CH_2)_2PPh_2\}Cl(P^iPr_3)$ (**4**). The extraction of the chloride ligand with $TlPF_6$ causes the selective C−H activation of one of the methyl groups of the triisopropylphosphine ligands to give $[\{CH_2CH(CH_3)P^iPr_2\}OsH\{\eta^5\text{-}C_5H_4(CH_2)_2PPh_2\}]PF_6$ (**5**), which is isolated as a mixture of stereoisomers. Complex **4** also reacts with phenylacetylene in the presence of $TlPF_6$. The reaction leads to the hydride-alkynyl-osmium(IV) derivative $[OsH\{\eta^5\text{-}C_5H_4(CH_2)_2PPh_2\}(C{\equiv}CPh)(P^iPr_3)]PF_6$ (**6**), which is not stable and evolves into the vinylidene $[Os\{\eta^5\text{-}C_5H_4(CH_2)_2PPh_2\}(=C=CHPh)(P^iPr_3)]PF_6$ (**7**). Deprotonation of **7** with methanol solutions of KOH yields the neutral alkynyl compound $[Os\{\eta^5\text{-}C_5H_4(CH_2)_2PPh_2\}(C{\equiv}CPh)(P^iPr_3)]$ (**8**). The addition of $HPF_6{\cdot}H_2O$ to **8** regenerates **7**. Similarly to phenylacetylene, 1,1-diphenyl-2-propyn-1-ol reacts with **4** and $TlPF_6$ to give the hydride-hydroxyalkynyl derivative $[OsH\{\eta^5\text{-}C_5H_4(CH_2)_2PPh_2\}\{C{\equiv}CC(OH)Ph_2\}(P^iPr_3)]PF_6$ (**9**), which dehydrates to produce the allenylidene $[Os\{\eta^5\text{-}C_5H_4(CH_2)_2PPh_2\}(=C=C=CPh_2)(P^iPr_3)]PF_6$ (**10**). Addition of $HPF_6{\cdot}H_2O$ to **10** affords the dicationic alkenyl carbyne $[Os\{\eta^5\text{-}C_5H_4(CH_2)_2PPh_2\}(\equiv CCH=CPh_2)(P^iPr_3)](PF_6)_2$ (**11**). Complexes **2** and **4** have been characterized by X-ray diffraction analysis.

Introduction

Cyclopentadienyl ligands bearing pendant donor groups are attracting increased interest in the chemistry of the metals.[1] The complexes containing this type of ligands are expected to perform chemistry different from that of usual cyclopentadienyl complexes. Indeed, the reversible coordination−decoordination of the pendant donor group facilitates the stabilization of highly reactive centers.[2] This has a strong influence on the catalytic properties of the active systems and facilitates the study of the catalytic mechanisms.[3]

For the iron triad, the chemistry of the half-sandwich osmium complexes with the pentamethylcyclopentadienyl[4] and particularly cyclopentadienyl[5] ligands is a field much less known than the chemistry of related half-sandwich iron and ruthenium compounds.[6] In accordance with this, a significant number of phosphinoalkylcyclopentadienyl complexes of iron and ruthenium have been prepared by a variety of methods,[1c] while the osmium counterparts are unknown.

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The limited development of the chemistry of the Os(η^5-C_5H_5) unit is in part due to the lack of convenient Os(η^5-C_5H_5) starting complexes[5a,b,7] and the greater inertness of the Os(η^5-C_5H_5)L_3 species in comparison with the related ruthenium derivatives.[8] Seven years ago, we reported that the six-coordinate complex $OsH_2Cl_2(P^iPr_3)_2$ reacts with Tl(C_5H_5) to afford the cyclopentadienyl compound Os(η^5-C_5H_5)Cl(P^iPr_3)$_2$,[9] which allows the development of new cyclopentadienyl osmium chemistry.[10] Despite the high kinetic inertness of the Os(η^5-C_5H_5)L_3 systems, the complex Os(η^5-C_5H_5)Cl(P^iPr_3)$_2$ dissociates the chloride ligand in methanol, and the resulting fragment is capable of activating a methyl C−H bond of one of the triisopropylphosphine ligands to give $[OsH\{\eta^5\text{-}C_5H_4\{CH_2CH(CH_3)P^iPr_2\}(P^iPr_3)]^+$, as a mixture of two pairs of diastereoisomers.[9] Previously, Tilley and co-workers had observed that in dichloromethane the bis(triphenylphosphine) derivative Os(η^5-C_5H_5)(OTf)(PPh_3)$_2$ evolves in a similar way into the orthometalated species $[OsH\{\eta^5\text{-}C_5H_5\}(PPh_2C_6H_4)(PPh_3)]$-OTf.[11]

Although the arene C−H bond is between 14 and 8 kcal·mol^{-1} stronger than the alkane C−H bond, in general, the activation of the first one is kinetically and thermodynamically favored. The kinetic advantage of the arene activation appears to be due to its prior π-coordination, while the thermodynamic preference has been largely attributed to a metal−carbon bond much stronger for aryl than for alkyl.[12] In agreement with the preferred arene C−H activation, the mixed-phosphine ligand complex Os(η^5-C_5H_5)Cl(PPh_3)(P^iPr_3) reacts with thallium hexafluorophosphate to give $[OsH\{\eta^5\text{-}C_5H_5\}(PPh_2C_6H_4)(P^iPr_3)]PF_6$ as a result of the selective activation of a phenyl ring in the presence of the alkyl groups of the triisopropylphosphine.[10d]

When terminal alkynes and alkynols are present, the H−C(sp) activation of the organic substrate is favored with regard to the intramolecular activation of the phosphine ligands. According to this, treatment of Os(η^5-C_5H_5)Cl(P^iPr_3)$_2$ with thallium hexafluorophosphate and terminal alkynes or alkynols leads to hydride-alkynyl-osmium(IV) complexes, $[OsH(\eta^5\text{-}C_5H_5)(C{\equiv}CR)(P^iPr_3)_2]PF_6$, as a result of the H−C(sp) oxidative addition of the alkyne or alkynol to the $[Os(\eta^5\text{-}C_5H_5)(P^iPr_3)_2]^+$ metallic fragment.[10e] In contrast to the ruthenium analogues,[13] these compounds are stable under the reaction conditions and do not evolve spontaneously into the corresponding cumulenes. The formation of vinylidene or allenylidene derivatives requires the deprotonation of the hydride-alkynyl-osmium(IV) compounds with strong bases and the subsequent protonation of the resulting alkynyl-osmium(II) complexes.[10e,h]

We are interested in getting information about how the presence of a donor group tied to the cyclopentadienyl ring influences the chemistry of half-sandwich cyclopentadienyl osmium complexes. This led us to wonder whether the six-coordinate compound $OsH_2Cl_2(P^iPr_3)_2$ could be also useful to prepare osmium derivatives containing a cyclopentadienyl ligand bearing a pendant phosphino group. In this paper, we report the first osmium complexes with a ligand of this type, 2-diphenylphosphinoethylcyclopentadienyl. Furthermore, we show the influence of the CH_2CH_2 chain on the competitive alkane-arene intramolecular C−H activation and the influence of the diphenylphosphino group on the stability of hydride-alkynyl-osmium(IV) species.

Results and Discussion

1. Reaction of $OsH_2Cl_2(P^iPr_3)_2$ with Li[$C_5H_4(CH_2)_2PPh_2$]. The dihydride-dichloro complex OsH_2-

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Table 1. Selected Bond Distances (Å) and Angles (deg) for [$OsH_2\{\eta^5\text{-}C_5H_4(CH_2)_2PPh_2\}(P^iPr_3)$]Cl (2)

	molecule **a**	molecule **b**		molecule **a**	molecule **b**
Os(1)−P(1)	2.2746(19)	2.2664(19)	Os(1)−C(3)	2.241(7)	2.251(7)
Os(1)−P(2)	2.3157(18)	2.3191(19)	Os(1)−C(4)	2.258(7)	2.283(7)
Os(1)−H(1)	1.37(6)	1.33(6)	Os(1)−C(5)	2.249(7)	2.255(7)
Os(1)−H(2)	1.46(6)	1.46(6)	C(1)−C(6)	1.494(10)	1.509(10)
Os(1)−C(1)	2.233(7)	2.204(7)	C(6)−C(7)	1.521(9)	1.529(9)
Os(1)−C(2)	2.176(7)	2.177(6)	C(7)−P(1)	1.840(7)	1.844(7)
P(1)−Os(1)−P(2)	111.98(7)	111.82(7)	H(2)−Os(1)−P(2)	65(2)	77(2)
H(1)−Os(1)−H(2)	115(3)	133(3)	C(6)−C(7)−P(1)	109.0(5)	107.9(5)
H(1)−Os(1)−P(1)	90(3)	65(3)	C(7)−P(1)−Os(1)	100.8(2)	101.5(2)
H(1)−Os(1)−P(2)	63(2)	79(3)	C(1)−C(6)−C(7)	112.6(6)	113.8(6)
H(2)−Os(1)−P(1)	75(2)	87(2)			

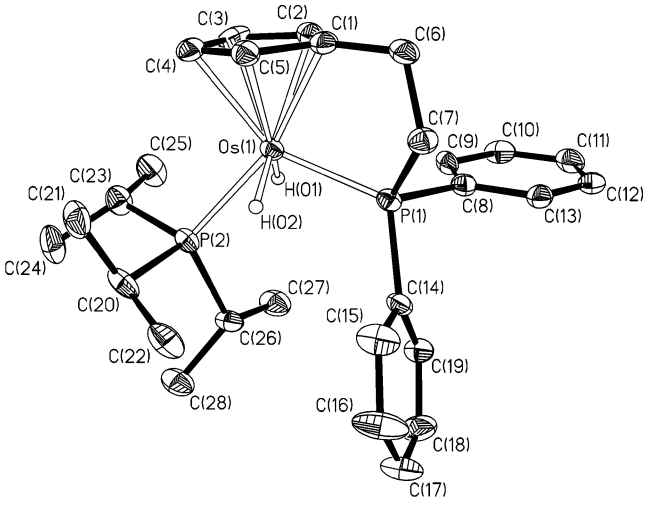
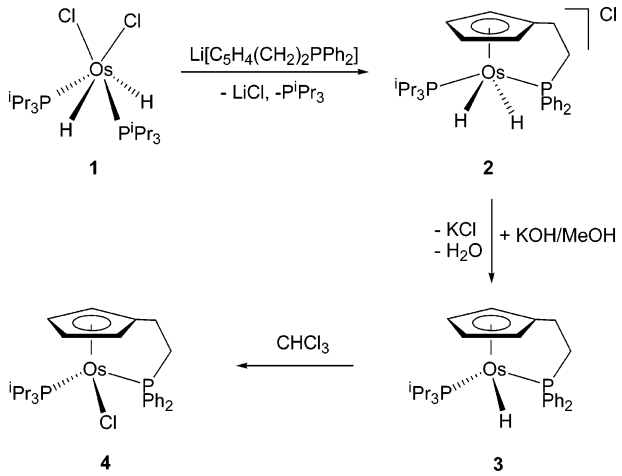


Figure 1. Molecular diagram of [$OsH_2\{\eta^5\text{-}C_5H_4(CH_2)_2PPh_2\}(P^iPr_3)$]Cl (**2**). Thermal ellipsoids are shown at 50% probability.

Scheme 1



$Cl_2(P^iPr_3)_2$ (**1**) is certainly useful to prepare compounds containing a 2-diphenylphosphinoethylcyclopentadienyl ligand. At room temperature, the reaction of **1** with $Li[C_5H_4(CH_2)_2PPh_2]$ in toluene leads, after 12 h, to the dihydride-osmium(IV) derivative [$OsH_2\{\eta^5\text{-}C_5H_4(CH_2)_2PPh_2\}(P^iPr_3)$]Cl (**2**), in 64% yield (Scheme 1).

The coordination of the diphenylphosphino group to the metallic center of **2** was confirmed by an X-ray diffraction study. The structure has two chemically equivalent but crystallographically independent molecules in the asymmetric unit. A drawing of one of them is shown in Figure 1. Selected bond distances and angles for both molecules are listed in Table 1.

The distribution of ligands around the osmium atom can be described as a four-legged piano stool geometry, with the cyclopentadienyl ring occupying the three-membered face while the phosphorus donor atoms lie in the four-membered face mutually *transoid* disposed. The P(1)−Os−P(2) bond angle is 111.98(7)° for molecule **a** and 111.82(7)° for molecule **b**. Interestingly, the Os−PPh_2 bond appears to be stronger than the Os−P^iPr_3 bond. Thus, the Os(1)−P(1) bond length (2.2746(19) Å in molecule **a** and 2.2664(19) Å in molecule **b**) is about 0.04 Å shorter than the Os(1)−P(2) distance (2.3157(18) Å in molecule **a** and 2.3191(19) Å in molecule **b**).

The IR and the ^1H and $^{31}P\{^1H\}$ NMR spectra of **2** are consistent with the structure shown in Figure 1. In the IR spectrum in Nujol, the most noticeable feature is the presence of a ν(Os−H) band at 2133 cm^{-1}. In agreement with the *transoid* disposition of the hydride ligands, the ^1H NMR spectrum in dichloromethane-d_2 contains only one hydride resonance at −13.10 ppm, which is observed as a double doublet with P−H coupling constants of 25.5 and 30.9 Hz. In addition, the spectrum reflects the rigidity of the CH_2−CH_2 chain, which is a consequence of the coordination of the phosphorus atom of the pendant group to the metallic center. Thus, it shows an AA′BB′X spin system between 3.85 and 2.09 ppm for the methylene protons. The $^{31}P\{^1H\}$NMR spectrum displays two doublets at 44.7 and 30.1 ppm, with a P−P coupling constant of 30 Hz.

Complex **2** can be deprotonated by reaction with a methanol solution of potassium hydroxide. The addition of this base to tetrahydrofuran solutions of **2** gives rise to the formation of the neutral compound [$OsH\{\eta^5\text{-}C_5H_4(CH_2)_2PPh_2\}(P^iPr_3)$] (**3**), as a result of the extraction of one of the hydride ligands. Complex **3** was isolated as a yellow oil in a 98% yield. Due to the chirality of the osmium atom, the ^1H NMR spectrum of **3** in benzene-d_6 shows an ABCDX spin system for the methylene resonances, which appear between 3.08 and 1.69 ppm, whereas the hydride signal is observed at −14.40 ppm as a double doublet with P−H coupling constants of 21.6 and 32.7 Hz. The $^{31}P\{^1H\}$ NMR spectrum shows two doublets at 41.7 and 27.9 ppm, with a P−P coupling constant of 5 Hz.

In chloroform, complex **3** is unstable and evolves into the chloro derivative [$Os\{\eta^5\text{-}C_5H_4(CH_2)_2PPh_2\}Cl(P^iPr_3)$] (**4**), which is analogous to the mixed-ligand complex Os(η^5-C_5H_5)Cl(PPh_3)(P^iPr_3) but with the PPh_2-phosphorus atom connected to the cyclopentadienyl ring.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Os{η^5-$C_5H_4(CH_2)_2PPh_2$}Cl(P^iPr_3) (4)

	molecule **a**	molecule **b**		molecule **a**	molecule **b**
Os(1)−P(1)	2.2816(12)	2.2792(12)	Os(1)−C(4)	2.239(4)	2.235(4)
Os(1)−P(2)	2.3443(12)	2.3552(12)	Os(1)−C(5)	2.199(4)	2.194(4)
Os(1)−Cl	2.4489(11)	2.4555(11)	C(1)−C(6)	1.501(6)	1.495(5)
Os(1)−C(1)	2.178(4)	2.181(4)	C(6)−C(7)	1.524(5)	1.532(5)
Os(1)−C(2)	2.193(4)	2.197(4)	C(7)−P(1)	1.847(4)	1.846(4)
Os(1)−C(3)	2.215(4)	2.217(4)			
P(1)−Os(1)−P(2)	101.04(4)	100.52(4)	C(7)−P(1)−Os(1)	102.10(15)	102.59(14)
P(1)−Os(1)−Cl	99.06(4)	99.75(4)	C(6)−C(7)−P(1)	106.2(3)	106.1(3)
P(2)−Os(1)−Cl	87.43(4)	88.09(4)	C(1)−C(6)−C(7)	111.6(3)	110.4(3)

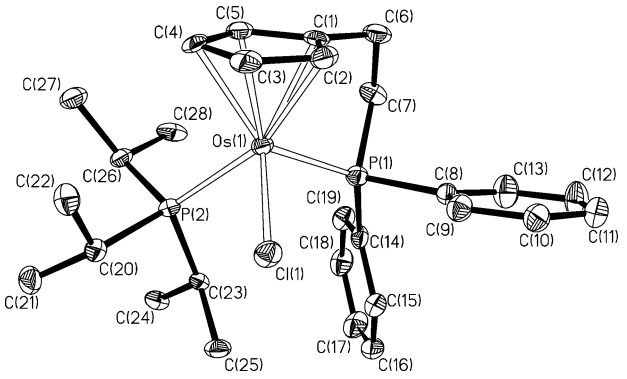


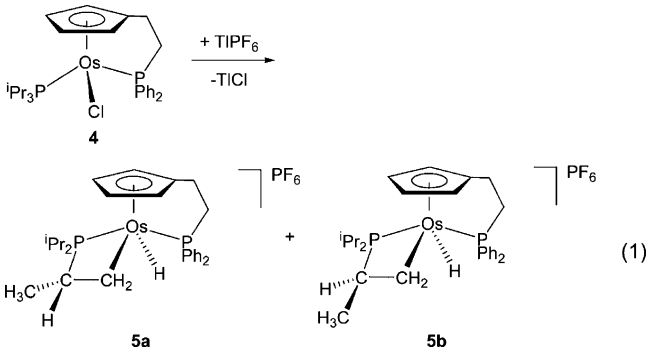
Figure 2. Molecular diagram of [Os{η^5-$C_5H_4(CH_2)_2PPh_2$}Cl(P^iPr_3) (**4**). Thermal ellipsoids are shown at 50% probability.

Complex **4** was isolated as a yellow solid in 79% yield and characterized by MS, elemental analysis, IR, and ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopy as well as by an X-ray crystallographic study. Analogously to compound **2**, the structure of **4** has two chemically equivalent but crystallographically independent molecules in the asymmetric unit. A drawing of one of them is shown in Figure 2. Selected bond distances and angles for both molecules are listed in Table 2.

The geometry around the osmium center can be described as a very distorted octahedron, with the cyclopentadienyl ring occupying the three sites of a face. The $^iPr_3P$−Os−Cl angle (87.43(4)° for molecule **a** and 88.09(4)° for molecule **b**) is close to 90°. However, the P−Os−P (101.04(4)° for molecule **a** and 100.52(4)° for molecule **b**) and Ph_2P−Os−Cl (99.06(4)° for molecule **a** and 99.75(4)° for molecule **b**) angles strongly deviate from the ideal value of 90°. This suggests that the distortion of the octahedron is in part due to the constriction imposed by the CH_2−CH_2 string in the 2-diphenylphosphinoethylcyclopentadienyl ligand. However, this constriction does not appear to give rise to an Os−PPh_2 bond less stable than the Os−P^iPr_3 bond. In fact, in a manner similar to **2**, the Os−PPh_2 bond seems to be even stronger than the Os−P^iPr_3 one. Thus, the distance between the metal center and the phosphorus atom of the diphenylphosphinoethyl group of **4** (Os(1)−P(1) = 2.2816(12) (**a**), 2.2792(12) (**b**) Å) is about 0.06 Å shorter than the Os−P^iPr_3 bond length (Os(1)−P(2) = 2.3443(12) (**a**), 2.3552(12) (**b**) Å).

The ^1H and $^{31}P\{^1H\}$ NMR spectra of **4** are consistent with the structure shown in Figure 2 and with the high stability of the [Os{η^5-$C_5H_4(CH_2)_2PPh_2$} unit. In the ^1H NMR spectrum, which is temperature invariant between −80 and 80 °C, the most noticeable feature is the presence between 3.18 and 1.37 ppm of an ABCDX spin system corresponding to the methylene protons of the CH_2−CH_2 chain. This strongly supports the coordination of the phosphorus atom to the metallic center in solution, even at high temperature. In accordance with it, the $^{31}P\{^1H\}$ NMR spectrum exhibits two doublets at 11.4 and 7.4 ppm with a P−P coupling constant of 13 Hz.

2. Competitive Alkane−Arene Intramolecular C−H Activation in 4. Similarly to the mixed-phosphine ligand complex Os(η^5-C_5H_5)Cl(PPh_3)(P^iPr_3), the chloride ligand of **4** can be extracted from the osmium atom with thallium hexafluorophosphate. The resulting metallic center is capable of activating a C−H bond of one of the substituents of the phosphine ligands. However, in this case, the C−H activation does not take place on a phenyl group, as it is observed for Os(η^5-C_5H_5)Cl(PPh_3)(P^iPr_3), but on an isopropyl group. Thus, at room temperature, the treatment of **4** with 1.0 equiv of thallium hexafluorophosphate in acetone affords the yellow metalated derivative [{$CH_2CH(CH_3)^iPr_2P$}OsH{η^5-$C_5H_4(CH_2)_2PPh_2$}]PF_6 (**5**). Complex **5** was isolated as a 1:1 mixture of the stereoisomers **5a** and **5b** shown in eq 1, in 94% yield.



(1)

The formation of **5** is a rare case of selective alkyl C−H activation in the presence of phenyl groups, which is in contrast with the kinetic and thermodynamic preference of the C−H arene activation over the C−H alkyl one. It is easily seen by using a molecular model that the constriction imposed by the CH_2−CH_2 chain in the functionalized cyclopentadienyl ligand should not influence significantly the stability of the orthometalated ring, resulting from the aryl C−H activation. So, we assume that the isopropyl C−H activation in **4** is kinetic in origin. In agreement with this, it has been previously observed that the short-lived ruthenium(0) species Ru(η^6-C_6Me_6)(PPh_2R) (R = ^{i}Pr, ^{t}Bu), containing an alkyldiphenylphosphine ligand, evolve initially into cyclometalated complexes, as a result of the C−H activation of the alkyl substituent. In solution, these

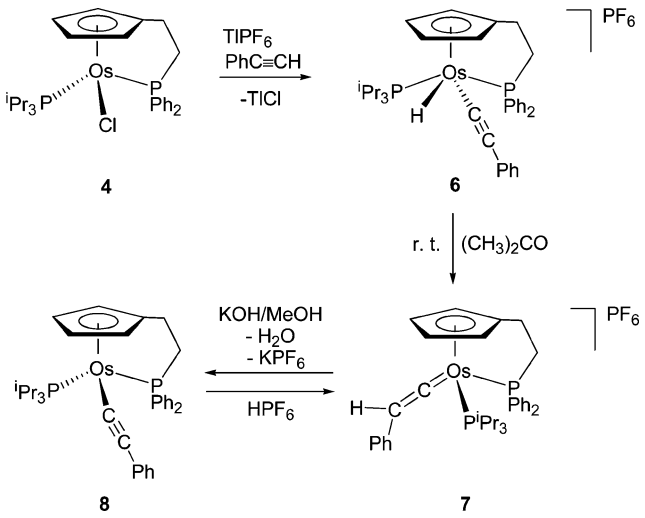
cyclometalated species rapidly isomerize into the thermodynamically favored aryl orthometalated derivatives.[14]

As it has been previously mentioned, the kinetic advantage of the arene activation is related to its prior π-coordination. For arylphosphine ligands, the coordination of the phosphorus atom to the metal makes the π-coordination of the aryl group unfavorable. As a result, the barrier for the aryl activation increases with regard to the barrier of the simple arene activation. The rise can locate the aryl activation barrier over the alkyl activation one. In this case, the kinetic advantage for the arene activation disappears and the weaker alkyl C−H bond is initially activated. In contrast to the previously mentioned metalated ruthenium derivatives, complex **5** does not evolve into an orthometalated isomer. This suggests that the increase of the activation barrier for the arene activation in the case of arylphosphines is associated with the prior dissociation of the M−P bond. Thus the strength of the Os−PPh_2 bond in the [Os{η^5-$C_5H_4(CH_2)_2PPh_2$} moiety could explain why **5** does not evolve into an orthometalated isomer.

In solution, the presence of isomers **5a** and **5b** is strongly supported by the ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra of **5**. In the ^{1}H NMR spectrum in acetone-d_6, the hydride resonances appear at −12.38 and −12.84 ppm as double doublets with H−P coupling constants of 31.2 and 25.8 Hz and 29.7 and 25.2 Hz, respectively. Similar P−H coupling constants have been observed for the monohydride derivatives RuH(η^5-C_5Me_5){$CH_2CH(CH_3)P^iPr_2$}{$Si(CH_3)Ph_2$} (22.5 Hz)[15] and [OsH{η^5-C_5H_5-$(PPh_2C_6H_4)$}(P^iPr_3)]PF_6 (35.7 and 26.4 Hz),[10d] whose *cisoid*-(P,H) four-legged piano-stool geometries have been determined by X-ray diffraction studies. In the ^{13}C{^{1}H} NMR spectrum, the Os−CH_2 and PCH signals of the metalated isopropyl group are observed at −22.5 and −24.3 ppm and 46.6 and 43.4 ppm, respectively. These chemical shifts agree well with those previously reported for the complexes [OsH(η^5-C_5H_5){$CH_2CH(CH_3)P^iPr_2$}($PiPr_3$)]PF_6 (−36.9 and −37.4 ppm and 49.9 and 46.9 ppm),[9] RuH(η^5-C_5Me_5){$CH_2CH(CH_3)P^iPr_2$}{$Si(CH_3)Ph_2$} (−31.5 and 42.8 ppm),[15] and RuH(η^6-C_6H_6){$CH_2CH(CH_3)P^iPr_2$} (−10.74 and 42.80 ppm).[16] The ^{31}P{^{1}H} NMR spectrum shows four doublets at 33.0 and −17.3 and 31.3 and −11.1 ppm, with P−P coupling constants of 31 and 25 Hz, respectively.

3. Reaction of 4 with $TlPF_6$ and HC≡CPh. Cationic half-sandwich osmium vinylidene complexes are very scarce. The compounds of this type previously reported include [Os{η^5-C_5Me_5}(=C=CHR)(CO)(PPh_3)]PF_6 (R = ^{t}Bu, Ph),[4b] [Os(η^5-C_5H_5)(=C=CHR)(CO)(P^iPr_3)]BF_4 (R = Ph, C=C$(CH_2)_3CH_2$),[7c] [Os(η^5-C_9H_7)(=C=CHR)(PPh_3)$_2$]PF_6 (R = H, $CH_2(CH_2)_2CH_2OH$, ^{t}Bu, C=C$(CH_2)_nCH_2$),[17] and [Os{η^5-C_5H_5)(=C=CHR)(P^iPr_3)$_2$]-PF_6 (R = Ph, Cy).[10h] The procedure used for the preparation of these complexes and related ruthenium derivatives involves the treatment of the corresponding chloro starting materials with terminal alkynes in the presence of NH_4PF_6, $NaBPh_4$, or analogous salts.[13,18] From a mechanistic point of view, it has been proposed that the reactions proceed via 1,2-hydrogen migration on a M(η^2-alkyne) intermediate or, alternatively, through hydride-alkynyl species.[13,18,19] For the latter pathway, Puerta and co-workers have proved that the vinylidene results from the dissociation of the hydride as a proton and the subsequent protonation at the C_β atom of the alkynyl ligand of a metal-alkynyl species.[13b] For the osmium-bis(triisopropylphosphine) system, the high basicity of the alkynyl complexes of general formula Os(η^5-C_5H_5)(C≡CR)(P^iPr_3)$_2$ imposes a high energy for the dissociation of H^+ from [OsH(η^5-C_5H_5)(C≡CR)(P^iPr_3)$_2$]$^+$, which makes nonviable the hydride-alkynyl isomerization into the vinylidene derivative.[10h]

Scheme 2



The replacement of a triisopropylphosphine ligand and the cyclopentadienyl group by the 2-diphenylphosphinoethylcyclopentadienyl ligand increases the acidity of the hydride-alkynyl intermediate. At −20 °C, the treatment of **4** with phenylacetylene in the presence of thallium hexafluorophosphate initially leads to [OsH{η^5-$C_5H_4(CH_2)_2PPh_2$}(C≡CPh)(P^iPr_3)]PF_6 (**6**). However, in contrast to that observed for [OsH(η^5-C_5H_5)(C≡CPh)(P^iPr_3)$_2$]PF_6, compound **6** isomerizes into the vinylidene [Os{η^5-$C_5H_4(CH_2)_2PPh_2$}(=C=CHPh)(P^iPr_3)]PF_6 (**7**) (Scheme 2). In acetone at room temperature, the transformation is quantitative after 12 h.

(14) Bennett, M. A.; Huang, T.-N.; Latten, J. L. *J. Organomet. Chem.* **1984**, *272*, 189.
(15) Campion, B. K.; Heyn, R. H.; Tilley, T. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **1993**, *115*, 5527.
(16) Kletzin, H.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 873.
(17) Gamasa, M. P.; Gimeno, J.; González-Cueva, M.; Lastra, E. *J. Chem. Soc., Dalton Trans.* **1996**, *12*, 2547.
(18) See for example: (a) Lagadec, R. L.; Roman, E.; Toupet, L.; Müller, U.; Dixneuf, P. H. *Organometallics* **1994**, *13*, 5030. (b) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; Pérez-Carreño, E.; García-Granda, S. *Organometallics* **1999**, *18*, 2821.
(19) See for example: (a) Silvestre, J.; Hoffmann, R. *Helv. Chim. 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.

The presence of a hydride ligand in **6** is supported by the ^{1}H NMR spectrum in acetone-d_6, which contains a double doublet at −12.35 ppm, with H−P coupling constants of 36.9 and 26.4 Hz. In the low-field region of the spectrum, the most noticeable feature is the presence, between 4.26 and 2.10 ppm, of the ABCDX spin system due to the methylene protons of the 2-diphenylphosphinoethylcyclopentadienyl ligand. In the ^{13}C{^{1}H} NMR spectrum, the resonances corresponding to the C(sp) carbon atoms of the alkynyl group are observed at 115.4 and 65.6 ppm. The first of them, due to the C_β carbon atom, appears as a broad signal, while the second one assigned to the C_α carbon atom is observed as a double doublet with both C−P coupling constants of 25 Hz.

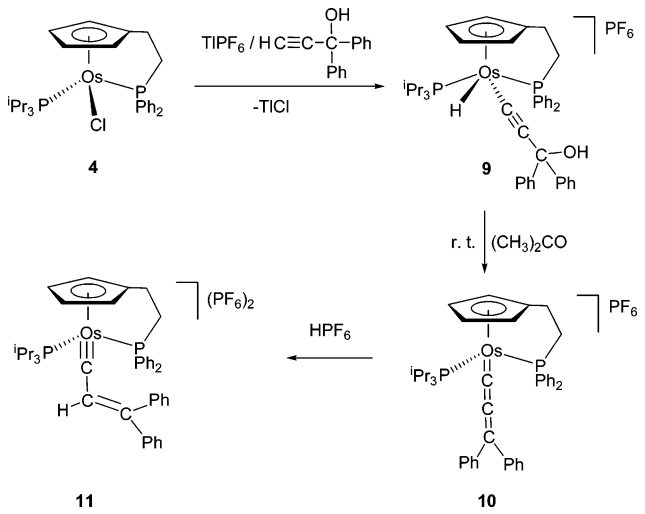
The vinylidene complex **7** was isolated as a red solid in 82% yield. The ^{1}H NMR spectrum shows the resonance due to the =CH proton of the vinylidene ligand at 3.43 ppm as a doublet with a P−H coupling constant of 3 Hz. The ABCDX spin system due to the CH_2−CH_2 chain is observed between 3.98 and 1.94 ppm. In the ^{13}C{^{1}H} NMR spectrum, the C_α carbon atom of the vinylidene unit displays a double doublet at 309.5 ppm, with C−P coupling constants of 6 and 13 Hz, whereas the resonance corresponding to the C_β atom appears as a singlet at 115.2 ppm. The ^{31}P{^{1}H} NMR spectrum shows two doublets at 20.7 and 15.9 ppm, with a P−P coupling constant of 12 Hz.

Because the rate-determining step for the isomerization of the hydride-alkynyl to the vinylidene is the H^+ dissociation from the hydride-alkynyl and, therefore, the protonation of the neutral alkynyl intermediate is very fast,[10h] the Os{η^5-$C_5H_4(CH_2)_2PPh_2$}(C≡CPh)(P^iPr_3) (**8**) species was not detected during the isomerization of **6** into **7**. However, compound **8** can be prepared by deprotonation of the vinylidene ligand of **7** with potassium hydroxide in methanol (Scheme 2). In agreement with the higher stability of **7** with regard to **6**, the addition of 1.2 equiv of HPF_6·H_2O to diethyl ether solutions of **8** produces the instantaneous precipitation of **7** in almost quantitative yield.

Intermediate **8** was obtained as a pale yellow solid in 88% yield. In the IR spectrum in Nujol of this complex, the most noticeable feature is the ν(C≡C) vibration, which is observed at 2059 cm^{-1}. The ^{1}H NMR spectrum shows the ABCDX spin system due to the CH_2CH_2 fragment of the 2-diphenylphosphinoethylcyclopentadienyl ligand between 3.09 and 1.43 ppm. In the ^{13}C{^{1}H} NMR spectrum, the C(sp) resonances of the alkynyl ligand are observed as broad signals at 110.7(C_β) and 94.5(C_α) ppm. The ^{31}P{^{1}H} NMR spectrum exhibits two doublets at 17.2 and 9.3 ppm, with a P−P coupling constant of 11 Hz.

4. Reaction of 4 with 1,1-Diphenyl-2-propyn-1-ol and $TlPF_6$. Treatment of acetone solutions of **4** with 1.1 equiv of 1,1-diphenyl-2-propyn-1-ol and 1.0 equiv of thallium hexafluorophosphate at 10 °C leads, after 45 min, to the hydride-hydroxyalkynyl-osmium(IV) complex [OsH{η^5-$C_5H_4(CH_2)_2PPh_2$}{C≡CC(OH)Ph_2}(P^iPr_3)]PF_6 (**9**), as a result of the extraction of the chloride ligand from compound **4** and the oxidative addition of the alkynol H−C(sp) bond to the unsaturated [Os{η^5-$C_5H_4(CH_2)_2PPh_2$}(P^iPr_3)]$^+$ metallic fragment (Scheme 3).

Scheme 3



In the ^{1}H NMR spectrum, the most noticeable resonance of the hydroxyalkynyl ligand is a broad signal centered at 2.96 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 −12.54 ppm. In agreement with the *cisoid* disposition of the hydride to both phosphorus atoms[10d,e] the H−P coupling constants are 37.2 and 26.7 Hz. In the ^{13}C{^{1}H} NMR spectrum, the resonance due to the C_α carbon atom of the hydroxyalkynyl ligand appears at 60.3 ppm as a double doublet with both C−P coupling constants of 24 Hz, whereas that corresponding to the C_β carbon atom is observed at 116.0 ppm also as a double doublet but with both C−P coupling constants of 3 Hz. The ^{31}P{^{1}H} NMR spectrum contains two doublets at 25.6 and 13.9 ppm, with a P−P coupling constant of 34 Hz.

The replacement of a triisopropylphosphine ligand and the cyclopentadienyl ring by the 2-diphenylphosphinoethylcyclopentadienyl group also produces an increase of the acidity of the hydride-hydroxyalkynyl-osmium(IV) complexes. The fact becomes apparent when compound **9** is compared with the related bis(triisopropylphosphine) derivative [OsH(η^5-C_5H_5){C≡CC(OH)Ph_2}(P^iPr_3)$_2$]PF_6. In contrast to the latter but in agreement with **6**, complex **9** is unstable and evolves into the allenylidene derivative [Os{η^5-$C_5H_4(CH_2)_2PPh_2$}(=C=C=CPh_2)(P^iPr_3)]PF_6 (**10**). In acetone solution at room temperature, the transformation is quantitative after 12 h. According to that observed for half-sandwich ruthenium systems,[13] the dehydration of **9** to give **10** should involve the formation of a hydroxyvinylidene intermediate.

Complex **10** was isolated as a very dark yellow solid in 88% yield. The presence of the allenylidene ligand in this derivative is strongly supported by the IR and ^{13}C{^{1}H} NMR spectra. The IR spectrum in Nujol shows the characteristic ν(C=C=C) vibration band for this type of ligands[20] at 1909 cm^{-1}, and the ^{13}C{^{1}H} NMR spectrum exhibits resonances at 260.5, 227.2, and 150.7

(20) (a) Bruce, M. I. *Chem. Rev.* **1998**, *98*, 2797. (b) Cadierno, V.; Gamasa, M. P.; Gimeno, J. *Eur. J. Inorg. Chem.* **2001**, 571.

ppm, corresponding to the C_α, C_β, and C_γ carbon atoms of the allenylidene group, respectively. The $^{31}P\{^1H\}$ NMR spectrum shows two doublets at 19.1 and 16.9 ppm, with a P−P coupling constant of 14 Hz.

Exploratory studies show that the reactivity of **10** is similar to that of the related bis(triisopropylphosphine) derivative $[Os(\eta^5\text{-}C_5H_5)(=C=C=CPh_2)(P^iPr_3)_2]PF_6$. Thus, complex **10** is stable in the presence of alcohols and amines. However it reacts with strong acids. The addition of 1.0 equiv of $HPF_6{\cdot}H_2O$ to diethyl ether solutions of **10** affords the dicationic carbyne derivative $[Os\{\eta^5\text{-}C_5H_4(CH_2)_2PPh_2\}(\equiv CCH=CPh_2)(P^iPr_3)](PF_6)_2$ (**11**), as result of the acid proton addition to the C_β carbon atom of the allenylidene ligand in **10**. The formation of **11** agrees well with EHT-MO calculations on transition metal allenylidene compounds, which indicate a nucleophilic character of the allenylidene C_β carbon atom.[10e,21] In addition, it should be mentioned that in contrast to $[Os(\eta^5\text{-}C_5H_5)\equiv CCH=CPh_2)(P^iPr_3)_2](PF_6)_2$, complex **11** does not undergo the deprotonation of the alkenylcarbene ligand in diethyl ether. This indicates that the alkenylcarbyne ligand at **11** is a weaker Brönsted acid than that of the cyclopentadienyl-bis(triisopropylphosphine) compound.[10e]

Complex **11** was isolated as an orange solid in 94% yield. The presence of an alkenylcarbyne ligand in this complex is supported by the ^1H and $^{13}C\{^1H\}$ NMR spectra. The ^1H NMR spectrum shows a singlet at 6.01 ppm due to the alkenylcarbyne =CH proton. In the $^{13}C\{^1H\}$ NMR spectrum, the C_α carbon atom of the unsaturated η^1-carbon ligand gives rise to a double doublet at 297.0 ppm, with C−P coupling constants of 6 and 11 Hz. The C_β and C_γ carbon atoms display singlets at 132.5 and 174.8 ppm, respectively. The $^{31}P\{^1H\}$ NMR spectrum shows two doublets at 25.7 and 22.3 ppm, with a P−P coupling constant of 7 Hz.

Concluding Remarks

This paper reveals that the unsaturated six-coordinate complex $OsH_2Cl_2(P^iPr_3)_2$ is a useful starting material to obtain osmium compounds with a cyclopentadienyl ligand bearing a pendant donor group. Thus, the preparation and full characterization of the first osmium(IV) and osmium(II) derivatives with the 2-diphenylphosphinoethylcyclopentadienyl ligand are reported.

Complex $OsH_2Cl_2(P^iPr_3)_2$ reacts with $Li[C_5H_4(CH_2)_2PPh_2]$ to give the dihydride-osmium(IV) compound $[OsH_2\{\eta^5\text{-}C_5H_4(CH_2)_2PPh_2\}(P^iPr_3)]Cl$, which can be transformed into the chloro-osmium(II) derivative $[Os\{\eta^5\text{-}C_5H_4(CH_2)_2PPh_2\}Cl(P^iPr_3)$, by a two-step procedure involving the deprotonation of the dihydride and the subsequent chlorination of the resulting monohydride complex. This chloro-osmium(II) species is a useful compound to study the chemistry of the 2-diphenylphosphinoethylcyclopentadienyl-osmium complexes and to gain information about how the fact of tethering a phosphorus group to a cyclopentadienyl ring influences the chemistry of half-sandwich cyclopentadienyl-osmium compounds. We have proved that the CH_2CH_2 chain has a strong influence on the competitive alkane-arene intramolecular C−H activation in mixed-ligand alkylphosphine-arylphosphine compounds. Thus, while the extraction of the chloride ligand from $Os(\eta^5\text{-}C_5H_5)Cl(P^iPr_3)(PPh_3)$ gives rise to the selective ortho-C−H activation of one of the triphenylphosphine aryl groups, the extraction of the chloride ligand from $[Os\{\eta^5\text{-}C_5H_4(CH_2)_2PPh_2\}Cl(P^iPr_3)$ causes the selective C−H activation of one of the methyl groups of the triisopropylphosphine ligand. The reason for this difference in reactivity seems to be the greater strength of the Os−PPh_2 bond in the 2-diphenylphosphinoethylcyclopentadienyl osmium complex with regard to that of the triphenylphosphine derivative. The CH_2CH_2 chain prevents the Os−PPh_2 dissociation, which is crucial for the activation of an aryl substituent.

Substitution of a triisopropylphosphine ligand and the cyclopentadienyl ring by the 2-diphenylphosphinoethylcyclopentadienyl ligand also affects the stability of the half-sandwich cyclopentadienyl-hydride-alkynyl-osmium(IV) compounds. In contrast to the bis(triisopropylphosphine) derivatives of the type $[OsH(\eta^5\text{-}C_5H_5)(C\equiv CR)(P^iPr_3)_2]PF_6$, complexes of formula $[OsH\{\eta^5\text{-}C_5H_4(CH_2)_2PPh_2\}(C\equiv CR)(P^iPr_3)][PF_6]$ (R = Ph, $C(OH)Ph_2$) are not stable and evolve into the corresponding metal-cumulene compounds. The lower stability of the corresponding substituted cyclopentadienyl complexes seems to be a consequence of the lower basicity of the intermediate species $[Os\{\eta^5\text{-}C_5H_4(CH_2)_2PPh_2\}(C\equiv CR)(P^iPr_3)$, isolated for R = Ph, with regard to that of $Os(\eta^5\text{-}C_5H_5)(C\equiv CR)(P^iPr_3)_2$.

In comparison with the corresponding bis(triisopropylphosphine)cyclopentadienyl derivative, the presence of the 2-diphenylphosphinoethylcyclopentadienyl system also causes a decrease of the Brönsted acid character of the $[\equiv CCH=CPh_2]^+$ carbyne ligand. Thus, while $[Os\{\eta^5\text{-}C_5H_4(CH_2)_2PPh_2\}(\equiv CCH=CPh_2)(P^iPr_3)](PF_6)_2$ is stable in diethyl ether, the analogous bis(triisopropylphosphine) derivative undergoes a deprotonation reaction in that solvent.

In conclusion, we have shown an entry into the chemistry of osmium derivatives containing a cyclopentadienyl ligand bearing a pendant donor function, as well as some of the differences in reactivity between 2-diphenylphosphinoethylcyclopentadienyl complexes and related cyclopentadienyl-phosphine-osmium derivatives.

Experimental Section

General Information. All manipulations were performed at an argon/vacuum manifold using standard Schlenk techniques. Solvents were dried by known procedures and used freshly distilled. $OsH_2Cl_2(P^iPr_3)_2$[22] (**1**) and $Li[C_5H_4(CH_2)_2PPh_2]$[23] were prepared according to previous reports. Infrared

(21) (a) Berke, H.; Huttner, G.; Von Seyerl, J. N. *Naturforsch.* **1981**, *36B*, 1277. (b) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; González-Cueva, M.; Lastra, E.; Borge, J.; García-Granda, S.; Pérez-Carreño, E. *Organometallics*, **1996**, *15*, 2137. (c) Edwards, A. J.; Esteruelas, M. A.; Lahoz, F. J.; Modrego, J.; Oro, L. A.; Schrickel, J. *Organometallics* **1996**, *15*, 3556. (d) Esteruelas, M. A.; Gómez, A. V.; López, A. M.; Modrego, J.; Oñate, E. *Organometallics* **1997**, *16*, 5826.

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spectra were recorded on a Nicolet 550 spectrometer as Nujol mulls on polyethylene sheets. NMR spectra were recorded on a Varian UNITY 300, Varian GEMINI 2000−300 MHz, or Bruker ARX 300 spectrometer. ^{1}H and ^{13}C{^{1}H} chemical shifts are reported relative to tetramethylsilane, and those of ^{31}P{^{1}H} relative to H_3PO_4 (85%). Coupling constants J are given in hertz. C, H 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 a standard Cs^- gun at 30 kV using 3-nitrobenzyl alcohol (NBA) as matrix.

Preparation of [OsH$_2${η^5-C$_5$H$_4$(CH$_2$)$_2$PPh$_2$}(P^{i}Pr$_3$)]Cl (2). To a suspension of Li[$C_5H_4(CH_2)_2PPh_2$] (0.54 g, 1.90 mmol) and **1** (1.0 g, 1.71 mmol) in 20 mL of toluene was added P^iPr_3 (0.10 mL, 0.52 mmol). Stirring of the reaction mixture for 12 h at room temperature gave a yellow solution and a white precipitate. The solvent was removed under vacuum, and dichloromethane (3 × 5 mL) was then added to the solid residue. The resulting suspension was filtered to separate the LiCl precipitate and the combined filtrate concentrated under reduced pressure. The solid residue was washed with toluene (1 × 5 mL) and pentane (1 × 5 mL) and dried under vacuum to give a white powder. Yield: 64% (0.73 g, 1.10 mmol). Anal. Calcd for $C_{28}ClH_{41}OsP_2$: C, 50.55; H, 6.41. Found: C, 50.39; H, 6.44. IR (Nujol): ν(Os−H) 2133 cm^{-1}. MS (FAB$^+$): *m/e* 630 (M$^+$). ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ 7.72−7.65 (m, 4H, PPh_2), 7.50−7.47 (m, 6H, PPh_2), 6.06, 5.45 (both m, each 2H, C_5H_4), 3.85 (m, 2H, CH_2CH_2P), 2.19, 2.09 (both m, each 1H, CH_2CH_2P), 1.67 (m, 3H, PCH), 0.95 (dd, 9H, J(HH) = 7.2, J(PH) = 15.0, $PCCH_3$), −13.10 (dd, 2H, J(P′H) = 25.5, J(PH) = 30.9, Os−H). ^{31}P{^{1}H} NMR (121.4 MHz, CD_2Cl_2, 293 K): δ 44.7, 30.1 (both d, J(PP′) = 30). ^{13}C{^{1}H} NMR (75.4 MHz, CD_2Cl_2, 293 K, plus APT): δ 133.3 (−, d, J(PC) = 46, ipso-C_6H_5), 132.9 (+, d, J(PC) = 11, C_6H_5), 131.7 (+, d, J(PC) = 2, C_6H_5), 129.0 (+, d, J(PC) = 11, C_6H_5), 119.9 (−, dd, J(PC) = 4, J(P′C) = 9, ipso-C_5H_4), 85.3 (+, s, C_5H_4), 78.9 (+, d, J(PC) = 4, C_5H_4), 59.3 (−, d, J(PC) = 38, $-CH_2CH_2P$), 29.7 (+, d, J(PC) = 33, PCH), 20.6 (−, s, $-CH_2CH_2P$), 19.6 (+, s, $PCCH_3$).

Preparation of [OsH{η^5-C$_5$H$_4$(CH$_2$)$_2$PPh$_2$}(P^{i}Pr$_3$) (3). To a solution of **2** (1.40 g, 2.10 mmol) in 20 mL of tetrahydrofuran was added a 0.19 M solution of KOH in methanol (13.3 mL, 2.52 mmol). The reaction mixture was stirred for 12 h at room temperature. The solvent was removed under reduced pressure and the residue extracted with pentane (3 × 10 mL). The combined filtrate was concentrated to dryness and the resulting yellow oil washed with cold propan-2-ol and dried under vacuum. Yield: 98% (1.30 g, 2.06 mmol). MS (FAB$^+$): *m/e* 629 (M$^+$). ^{1}H NMR (300 MHz, C_6D_6, 293 K): δ 8.30 (m, 2H, p-C_6H_5), 7.33−6.97 (m, 8H, o-, m-C_6H_5), 4.93, 4.82, 4.79, 4.61 (all m, each 1H, C_5H_4), 3.08 (m, 2H, CH_2CH_2P), 1.84, 1.69 (both m, each 1H, CH_2CH_2P), 1.51 (m, 3H, PCH), 1.01 (dd, 9H, J(HH) = 7.2, J(PH) = 13.2, $PCCH_3$), 0.88 (dd, 9H, J(HH) = 7.2, J(PH) = 15.9, $PCCH_3$), −14.40 (dd, 1H, J(PH) = 21.6, J(P′H) = 32.7, Os−H). ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6, 293 K): δ 41.7, 27.9 (both d, J(PP′) = 5). ^{13}C{^{1}H} NMR (75.4 MHz, C_6D_6, 293 K, plus APT): δ 143.2 (−, d, J(PC) = 32, ipso-C_6H_5), 140.5 (−, d, J(PC) = 38, ipso-C_6H_5), 136.0 (+, m, C_6H_5), 132.1 (+, d, J(PC) = 9, C_6H_5), 129.5, 128.2 (+, both s, C_6H_5), 127.7 (+, d, J(PC) = 9, C_6H_5), 127.5 (+, d, J(PC) = 8, C_6H_5), 108.0 (−, dd, J(PC) = J(P′C) = 5, ipso-C_5H_4), 78.1 (+, d, J(PC) = 6, C_5H_4), 67.8 (+, s, C_5H_4), 67.7 (+, s, C_5H_4), 65.4 (+, d, J(PC) = 8, C_5H_4), 58.0 (−, d, J(PC) = 35, $-CH_2CH_2P$), 29.3 (+, d, J(PC) = 25, PCH), 22.4 (−, d, J(PC) = 4, $-CH_2CH_2P$), 21.4, 20.2 (+, both s, $PCCH_3$).

Preparation of [Os{η^5-C$_5$H$_4$(CH$_2$)$_2$PPh$_2$}Cl(P^{i}Pr$_3$) (4). A solution of **3** (1.20 g, 1.91 mmol) in 20 mL of chloroform was stirred at room temperature for 12 h. The resulting orange solution was concentrated to dryness. Addition of ca. 20 mL of toluene and filtration resulted in a clear solution, from which traces of derivative **2** formed during the process were removed by precipitation with ca. 5 mL of pentane. The suspension was filtered, the combined filtrate concentrated under reduced pressure, and the resulting yellow solid washed with cold pentane and dried under vacuum. Yield: 79% (1.0 g, 1.51 mmol). Anal. Calcd for $C_{28}ClH_{39}OsP_2$: C, 50.70; H, 5.93. Found: C, 50.68; H, 6.20. MS (FAB$^+$): *m/e* 664 (M$^+$), 627 (M$^+$ − Cl). ^{1}H NMR (300 MHz, C_6D_6 293 K): δ 8.46 (m, 2H, C_6H_5), 7.21 (m, 4H, C_6H_5), 6.92 (m, 4H, C_6H_5), 5.39, 4.91, 4.71, 4.08 (all m, each 1H, C_5H_4), 3.18, 2.59 (both m, each 1H, CH_2CH_2P), 2.05 (m, 3H, PCH), 1.37 (m, 2H, CH_2CH_2P), 1.15 (dd, 9H, J(HH) = 7.2, J(PH) = 13.8, $PCCH_3$), 0.79 (dd, 9H, J(HH) = 7.2, J(PH) = 11.4, $PCCH_3$). ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6, 293 K): δ 11.4, 7.4 (both d, J(PP′) = 13). ^{13}C{^{1}H} NMR (75.4 MHz, C_6D_6, 293 K, plus APT, plus HMQC): δ 141.9 (−, d, J(PC) = 32, ipso-C_6H_5), 141.8 (−, d, J(PC) = 32, ipso-C_6H_5), 136.3, 132.6 (+, both d, J(PC) = 10, C_6H_5), 129.9, 129.0, 127.8 (+, all m, C_6H_5), 105.2 (−, d, J(PC) = 6, ipso-C_5H_4), 86.3 (+, d, J(PC) = 7, C_5H_4), 75.3 (+, d, J(PC) = 8, C_5H_4), 70.2 (+, d, J(PC) = 11, C_5H_4), 57.6 (−, d, J(PC) = 40, $-CH_2CH_2P$), 26.1 (+, d, J(PC) = 24, PCH), 21.6 (+, s, $PCCH_3$), 20.8 (−, s, $-CH_2CH_2P$), 19.7 (+, s, $PCCH_3$).

Preparation of [{CH$_2$CH(CH$_3$)P^{i}Pr$_2$}OsH{η^5-C$_5$H$_4$(CH$_2$)$_2$PPh$_2$}]PF$_6$ (5). Acetone (10 mL) was added to a dry mixture of **4** (0.25 g, 0.37 mmol) and $TlPF_6$ (0.13 g, 0.38 mmol). Stirring of the reaction mixture at room temperature for 3 h afforded an orange solution and a white precipitate. The suspension was filtered, the filtrate concentrated under reduced pressure, and the resulting yellow solid washed with cold pentane and dried under vacuum. Complex **5** was obtained as a 1:1 mixture of stereoisomers. Yield: 94% (0.27 g, 0.35 mmol). Anal. Calcd for $C_{28}F_6H_{39}OsP_3$: C, 43.52; H, 5.09. Found: C, 43.32; H, 5.00. IR (Nujol): ν(Os−H) 2120 cm^{-1}, $\nu(PF_6)$ 839 cm^{-1}. ^{1}H NMR (300 MHz, $(CD_3)_2CO$, 293 K, plus ^{1}H{^{31}P}): δ 8.21−8.14 (m, 4H, C_6H_5), 7.73−7.50 (m, 16H, C_6H_5), 6.18, 6.13, 6.03, 6.02, 6.00, 5.97, 5.88, 5.83 (all m, each 1H, C_5H_4), 4.10−3.70 (m, 4H), 3.45 (m, 1H), 3.11 (ddd, 1H, J^2(HH) = J^3(HH) = 9.3, J(PH) = 29.7, Os−CH_2), 2.69−2.36 (m, 7H), 2.05−1.94 (m, 6H), 1.40−1.16 (m, 25H, $PCCH_3$ + Os−CH_2), 0.89 (ddd, 3H, J^3(HH) = 15.4, J^4(HH) = 7.0, J(PH) = 15.9, PCH(CH_3)-CH_2), 0.44 (ddd, 1H, J^2(HH) = 9.3, J^3(HH) = 6.8, J(PH) = 15.8, Os−CH_2), −12.38 (dd, 1H, J(PH) = 31.2, J(P′H) = 25.8, Os−H), −12.84 (dd, 1H, J(PH) = 29.7, J(P′H) = 25.2, Os−H). ^{31}P{^{1}H} NMR (121.4 MHz, $(CD_3)_2CO$, 293 K): δ 33.0, −17.3 (both d, J(PP′) = 31), δ 31.3, −11.1 (both d, J(PP′) = 25), −139.8 (sept, J(PF) = 712). ^{19}F{^{1}H} NMR (282.3 MHz, $(CD_3)_2CO$, 293 K): δ −73.0 (d, J(PF) = 712). ^{13}C{^{1}H} NMR (75.4 MHz, $(CD_3)_2CO$, 293 K, plus APT plus HETCOR): δ 134.4 (+, d, J(PC) = 11, C_6H_5), 132.4, 132.3 (+, both d, J(PC) = 8, C_6H_5), 132. 3, 131.8 (−, both d, J(PC) = 38, ipso-C_6H_5), 131.9 (+, m, C_6H_5), 131.3, 131.2 (+, both d, J(PC) = 3, C_6H_5), 129.4 (−, d, J(PC) = 52, ipso-C_6H_5), 129.1 (+, d, J(PC) = 10, C_6H_5), 129.0 (+, d, J(PC) = 10, C_6H_5), 128.8 (+, d, J(PC) = 10, C_6H_5), 128.7 (+, d, J(PC) = 10, C_6H_5), 128.6 (−, d, J(PC) = 68, ipso-C_6H_5), 128.6 (+, d, J(PC) = 10, C_6H_5), 122.8 (−, dd, J(PC) = 9, J(P′C) = 4, ipso-C_5H_4), 122.6 (−, dd, J(PC) = 9, J(P′C) = 4, ipso-C_5H_4), 90.6 (+, d, J(PC) = 4, C_5H_4), 89.9 (+, d, J(PC) = 2, C_5H_4), 83.4, 83.2 (+, both s, C_5H_4), 81.5 (+, d, J(PC) = 7, C_5H_4), 78.5 (+, d, J(PC) = 7, C_5H_4), 75.7, 75.5 (+, both d, J(PC) = 5, C_5H_4), 56.2, (−, d, J(PC) = 37, $-CH_2CH_2P$), 55.2 (−, d, J(PC) = 37, $-CH_2CH_2P$), 46.6 (+, dd, J(PC) = 34, J(P′C) = 3, $^iPr_2PCH$), 43.4 (+, d, J(PC) = 36, $^iPr_2PCH$), 29.4 (+, d, J(PC) = 26, $PCH(CH_3)_2$), 26.5 (+, d, J(PC) = 19, $PCH(CH_3)_2$), 25.6 (+, d, J(PC) = 22, $PCH(CH_3)_2$), 23.9 (+, s, $^iPr_2PCHCH_3$), 23.8 (+, s, $^iPr_2PCHCH_3$), 23.6 (+, d, J(PC) = 17, $PCH(CH_3)_2$), 21.1, 20.5 (+, both s, $PCHCH_3$), 20.1 (−, s, $-CH_2CH_2P$), 20.0 (+, s, $PCHCH_3$), 19.9 (−, s, $-CH_2CH_2P$), 19.8 (+, s, $PCHCH_3$), 19.3 (+, d, J(PC) = 2, $PCHCH_3$), 19.1 (+, d,

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J(PC) = 5, PCHCH$_3$), −22.5 (−, dd, J(PC) = 39, J(P′C) = 7, Os−CH$_2$−), −24.3 (−, dd, J(PC) = 37, J(P′C) = 8, Os−CH$_2$).

Reaction of 4 with Phenylacetylene and TlPF$_6$: Preparation of [Os{η^5-C$_5$H$_4$(CH$_2$)$_2$PPh$_2$}(=C=CHPh)(P^{i}Pr$_3$)]PF$_6$ (7). A solution of **4** (0.80 g, 1.2 mmol) and phenylacetylene (0.14 mL, 1.3 mmol) in 10 mL of acetone was treated with TlPF$_6$ (0.42 g, 1.2 mmol) at −20 °C. After stirring of the mixture for 1 h at the same temperature, the suspension was filtered. NMR spectra of an aliquot of the pale yellow solution showed the presence of compounds **6** and **7** in ca. 8:2 molar ratio. Spectroscopic data for [OsH{η^5-C$_5$H$_4$(CH$_2$)$_2$PPh$_2$}(C≡CPh)(P^{i}Pr$_3$)]PF$_6$, **6**: ^{1}H NMR (300 MHz, (CD$_3$)$_2$CO, 273 K): δ 8.05 (m, 2H, C$_6$H$_5$), 7.74−7.08 (m, 13H, C$_6$H$_5$), 6.35, 6.24, 6.14, 5.83 (all m, each 1H, C$_5$H$_4$), 4.26, 4.07 (both m, each 1H, −CH$_2$C*H$_2$*P), 2.60 (m, 3H, PCH), 2.45, 2.10 (both m, each 1H, −C*H$_2$*CH$_2$P), 1.14 (dd, 9H, J(HH) = 6.9, J(PH) = 15, PCCH$_3$), 1.03 (dd, 9H, J(HH) = 8.7, J(PH) = 15, PCCH$_3$), −12.35 (dd, 1H, J(PH) = 36.9, J(P′H) = 26.4, Os−H). ^{31}P{^{1}H} NMR (121.4 MHz, (CD$_3$)$_2$CO, 273 K): δ 23.2, 13.5 (d, J(PP′) = 35), −144.3 (sept, J(PF) = 708). ^{13}C{^{1}H} NMR (75.4 MHz, (CD$_3$)$_2$CO, 253 K, plus APT): δ 134.3 (+, d, J(PC) = 10, PC$_6$H$_5$), 134.0 (+, d, J(PC) = 8, PC$_6$H$_5$), 132.1 (+, d, J(PC) = 3, PC$_6$H$_5$), 131.2 (+, s, C$_6$H$_5$), 131.1 (−, d, J(PC) = 67, ipso-PC$_6$H$_5$), 130.3 (−, d, J(PC) = 55, ipso-PC$_6$H$_5$), 129.3 (+, d, J(PC) = 10, PC$_6$H$_5$), 128.2 (+, s, C$_6$H$_5$), 127.9 (+, d, J(PC) = 11, PC$_6$H$_5$), 127.7 (−, s, ipso-C$_6$H$_5$), 126.1 (+, s, C$_6$H$_5$), 123.4 (−, dd, J(PC) = 4, J(P′C) = 9, ipso-C$_5$H$_4$), 115.4 (−, br, ≡*C*C$_6$H$_5$), 97.9, 84.3 (+, s, C$_5$H$_4$), 83.8 (+, d, J(PC) = 6, C$_5$H$_4$), 79.4 (+, s, C$_5$H$_4$), 65.6 (−, dd, J(PC) = J(P′C) = 25, Os−C≡), 57.7 (−, d, J(PC) = 40, −CH$_2$*C*H$_2$P), 28.0 (+, d, J(PC) = 32, PCH), 19.7 (+, s, PC*C*H$_3$), 18.9 (−, s, *C*H$_2$CH$_2$P), 18.8 (+, s, PC*C*H$_3$).

The solution was warmed to room temperature and periodically monitored by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. After 12 h at room temperature, only complex **7** was observed. The light red solution was concentrated under reduced pressure and the resulting red solid washed with cold pentane (3 × 5 mL) and dried under vacuum. Yield: 82% (0.86 g, 0.98 mmol). Anal. Calcd for C$_{36}$H$_{45}$OsP$_3$F$_6$: C, 49.42; H, 5.18. Found: C, 49.60; H, 4.99. IR (Nujol): ν(C=C) 1623, 1592 cm^{-1}, ν(PF$_6$) 838 cm^{-1}. MS (FAB$^+$): *m/e* 729 (M$^+$). ^{1}H NMR (300 MHz, (CD$_3$)$_2$CO, 293 K, plus ^{1}H{^{31}P} plus COSY): δ 8.01−7.94 (m, 2H, C$_6$H$_5$), 7.70−7.38 (m, 8H, C$_6$H$_5$), 7.30−7.25 (m, 2H, C$_6$H$_5$), 7.08−7.02 (m, 3H, C$_6$H$_5$), 6.49 (m, 1H, C$_5$H$_4$), 6.14, (m, 2H, C$_5$H$_4$), 6.08 (m, 1H, C$_5$H$_4$), 3.98, 3.87 (both m, each 1H, PC*H$_2$*CH$_2$), 3.43 (d, 1H, J(PH) = 3.0, Os=C=CH), 2.70 (m, 1H, PCH$_2$C*H$_2$*), 2.13 (m, 3H, PCH), 1.94 (m, 1H, PCH$_2$C*H$_2$*), 1.22 (dd, 9H, J(HH) = 7.2, J(PH) = 14.8, PCCH$_3$), 1.11 (dd, 9H, J(HH) = 7.2, J(PH) = 13.4, PCCH$_3$). ^{31}P{^{1}H} NMR (121.4 MHz, CD$_2$Cl$_2$, 293 K): δ 20.7, 15.9 (both d, J(PP′) = 12), −144.2 (sept, J(PF) = 714). ^{19}F{^{1}H} NMR (282.3 MHz, CD$_2$Cl$_2$, 293 K): δ −73.0 (d, J(PF) = 714). ^{13}C{^{1}H} NMR (75.4 MHz, (CD$_3$)$_2$CO, 293 K, plus APT): δ 309.5 (−, dd, J(PC) = 6, J(P′C) = 13, Os=C), 132.9 (−, d, J(PC) = 49, ipso-PC$_6$H$_5$), 132.3 (−, d, J(PC) = 59, ipso-PC$_6$H$_5$), 131.1 (+, d, J(PC) = 9, PC$_6$H$_5$), 130.6 (+, d, J(PC) = 2.8, PC$_6$H$_5$), 130.4 (+, d, J(PC) = 2.4, PC$_6$H$_5$), 128.5 (−, d, J(PC) = 10, ipso-C$_5$H$_4$), 127.7 (+, d, J(PC) = 13, PC$_6$H$_5$), 127.5 (+, d, J(PC) = 14, PC$_6$H$_5$), 127.0, 125.4 (+, both s, =C*C$_6$H$_5$), 125.3 (−, s, ipso-C$_6$H$_5$), 124.4 (+, s, =C*C$_6$H$_5$), 115.2 (+, s, =CH), 86.0 (+, d, J(PC) = 7, C$_5$H$_4$), 85.2 (+, d, J(PC) = 5, C$_5$H$_4$), 83.1 (+, d, J(PC) = 3, C$_5$H$_4$), 76.9 (+, s, C$_5$H$_4$), 52.5 (−, d, J(PC) = 37, PC*H$_2$*CH$_2$), 27.1 (+, d, J(PC) = 29, PCH), 18.7 (+, s, PC*C*H$_3$), 18.0 (−, s, PCH$_2$C*H$_2$*), 17.8(+, s, PC*C*H$_3$).

Preparation of [Os{η^5-C$_5$H$_4$(CH$_2$)$_2$PPh$_2$}(C≡CPh)(P^{i}Pr$_3$) (8). To a solution of **7** (0.15 g, 0.17 mmol) in 5 mL of tetrahydrofuran was added a 0.19 M solution of KOH in MeOH (1.0 mL, 0.19 mmol). Stirring of the mixture for 6 h at room temperature afforded a pale yellow suspension. Solvents were evaporated to dryness, and the resulting solid residue was extracted with toluene (2 × 5 mL). The combined filtrate was concentrated under reduced pressure and the pale yellow solid washed with cold pentane (2 × 5 mL) and dried under vacuum. Yield: 88% (0.11 g, 0.15 mmol). Anal. Calcd for C$_{36}$H$_{44}$OsP$_2$: C, 59.35; H, 6.04. Found: C, 59.14; H, 5.99. MS (FAB$^+$): *m/e* 731 (M$^+$), *m/e* 569 (M$^+$ − P^{i}Pr$_3$). IR (Nujol): ν(C≡C) 2059 cm^{-1}. ^{1}H NMR (300 MHz, C$_6$D$_6$, 273 K): δ 8.60 (dd, 2H, J(HH) = 8.1, J(HH) = 9.6, C$_6$H$_5$), 7.63 (d, 2H, J(HH) = 8.1, C$_6$H$_5$), 7.25 (m, 5H, C$_6$H$_5$), 7.16 (m, 2H, C$_6$H$_5$), 6.92 (m, 4H, C$_6$H$_5$), 5.27, 4.83, 4.66, 4.43 (all m, each 1H, C$_5$H$_4$), 3.09, 2.76 (both m, each 1H, PC*H$_2$*CH$_2$), 2.00 (m, 3H, PCH), 1.55, 1.43 (both m, each 1H, PCH$_2$C*H$_2$*), 1.15 (dd, 9H, J(HH) = 6.9, J(PH) = 13.5, PCCH$_3$), 0.80 (dd, 9H, J(HH) = 7.2, J(PH) = 11.7, PCCH$_3$). ^{31}P{^{1}H} NMR (121.4 MHz, C$_6$D$_6$, 273 K): δ 17.2, 9.3 (both d, J(PP′) = 11). ^{13}C{^{1}H} NMR (100 MHz, (C$_6$D$_6$, 273 K, plus APT): δ 141.1 (−, d, J(PC) = 34, ipso-PC$_6$H$_5$), 139.9 (−, d, J(PC) = 37, ipso-PC$_6$H$_5$), 135.8 (+, d, J(PC) = 10, PC$_6$H$_5$), 132.2 (+, d, J(PC) = 9, PC$_6$H$_5$), 131.4 (+, s, C$_6$H$_5$), 129.6 (+, d, J(PC) = 2, PC$_6$H$_5$), 128.6 (+, d, J(PC) = 2, PC$_6$H$_5$), 128.2 (+, s, C$_6$H$_5$), 127.7 (+, d, J(PC) = 9, PC$_6$H$_5$), 127.3 (+, d, J(PC) = 8, PC$_6$H$_5$), 123.0 (+, s, C$_6$H$_5$), 113.1 (−, dd, J(PC) = 2, J(P′C) = 6, ipso-C$_5$H$_4$), 110.7 (−, br, ≡*C*C$_6$H$_5$), 94.5 (−, br, Os−C≡), 78.5, 78.1 (+, both d, both J(PC) = 7, C$_5$H$_4$), 72.1 (+, d, J(PC) = 10, C$_5$H$_4$), 65.9 (+, s, C$_5$H$_4$), 57.5 (−, d, J(PC) = 48, P*C*H$_2$CH$_2$), 26.8 (+, d, J(PC) = 26, PCH), 21.6 (+, s, PC*C*H$_3$), 20.4 (−, d, J(PC) = 3, PCH$_2$*C*H$_2$), 19.5 (+, d, J(PC) = 2, PC*C*H$_3$).

Reaction of 4 with 1,1-Diphenyl-2-propyn-1-ol and TlPF$_6$: Preparation of [Os{η^5-C$_5$H$_4$(CH$_2$)$_2$PPh$_2$}(=C=C=CPh$_2$)(P^{i}Pr$_3$)]PF$_6$ (10). A solution of **4** (0.60 g, 0.90 mmol) and 1,1-diphenyl-2-propyn-1-ol (0.23 g, 1.1 mmol) in 10 mL of acetone was reacted with TlPF$_6$ (0.31 g, 0.90 mmol) at 10 °C. After stirring of the mixture for 45 min at that temperature, the suspension was filtered. NMR spectra of an aliquot of the resulting orange solution showed the presence of compounds **9** and **10** in ca. 9:1 molar ratio. Spectroscopic data for [OsH{η^5-C$_5$H$_4$(CH$_2$)$_2$PPh$_2$}{C≡CC(OH)Ph$_2$}(P^{i}Pr$_3$)]PF$_6$, **9**: ^{1}H NMR (300 MHz, CD$_2$Cl$_2$, 283 K): δ 7.79 (m, 2H, C$_6$H$_5$), 7.60 (m, 7H, C$_6$H$_5$), 7.56−7.18 (m, 11H, C$_6$H$_5$), 6.03, 6.02, 5.79, 5.43 (all m, each 1H, C$_5$H$_4$), 3.96, 3.81 (both m, each 1H, PC*H$_2$*CH$_2$), 2.96 (br, 1H, OH), 2.49 (m, 1H, PCH$_2$C*H$_2$*), 2.31 (m, 3H, PCH), 2.03 (m, 1H, PCH$_2$C*H$_2$*), 0.95 (dd, 9H, J(HH) = 7.1, J(PH) = 15.3, PCCH$_3$), 0.85 (dd, 9H, J(HH) = 7.0, J(PH) = 14.2, PCCH$_3$), −12.54 (dd, 1H, J(PH) = 37.2, J(P′H) = 26.7, Os−H). ^{31}P{^{1}H} NMR (121.4 MHz, CD$_2$Cl$_2$, 283 K): δ 25.6, 13.9 (d, J(PP′) = 34), −144.2 (sept, J(PF) = 708). ^{13}C{^{1}H} NMR (75.4 MHz, CD$_2$Cl$_2$, 253 K, plus APT): δ 146.6 (−, d, J(PC) = 61, ipso-PC$_6$H$_5$), 133.9 (+, d, J(PC) = 8, PC$_6$H$_5$), 133.7 (+, d, J(PC) = 10, PC$_6$H$_5$), 132.2, 131.5 (+, both d, J(PC) = 2, PC$_6$H$_5$), 130.6 (−, d, J(PC) = 58, ipso-PC$_6$H$_5$), 130.1 (−, s, ipso-C$_6$H$_5$), 129.4 (+, d, J(PC) = 10, PC$_6$H$_5$), 128.3, 127.9 (+, s, C*C$_6$H$_5$), 127.8 (+, d, J(PC) = 11, PC$_6$H$_5$), 126.9, 126.4, 125.7 (+, all s, C*C$_6$H$_5$), 122.6 (−, dd, J(PC) = 4, J(PC) = 9, ipso-*C$_5$*H$_4$), 116.0 (−, dd, J(PC) = 3 = J(P′C), Os−C≡*C*), 97.8, 83.6 (+, both s, C$_5$H$_4$), 82.7 (+, d, J(PC) = 6, *C$_5$*H$_4$), 78.7 (+, s, *C$_5$*H$_4$), 75.1 (−, s, CPh$_2$), 60.3 (−, dd, J(PC) = J(P′C) = 24, Os−C≡), 56.2 (−, d, J(PC) = 39, P*C*H$_2$CH$_2$), 27.9 (+, d, J(PC) = 32, PCH), 19.8 (+, s, PC*C*H$_3$), 18.8 (−, s, PCH$_2$C*H$_2$*), 18.7 (+, s, PC*C*H$_3$).

The solution was warmed to room temperature, and the reaction was periodically monitored by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. After 12 h at room temperature, only complex **10** was observed. The dark yellow solution was concentrated under reduced pressure and the resulting very dark yellow solid washed with cold diethyl ether and pentane (3 × 5 mL) and dried under vacuum. Yield: 88% (0.76 g, 0.79 mmol). Anal. Calcd for C$_{43}$H$_{49}$OsP$_3$F$_6$: C, 53.65; H, 5.09. Found: C, 53.40; H, 4.98. IR (Nujol): ν (C=C=C) 1909 cm^{-1}, ν (PF$_6$) 838 cm^{-1}. MS (FAB$^+$): *m/e* 819 (M$^+$), 659 (M$^+$ − P^{i}Pr$_3$). ^{1}H NMR (300 MHz (CD$_3$)$_2$CO, 293 K): δ 7.95 (m, 4H, C$_6$H$_5$), 7.89−7.74 (m, 4H, C$_6$H$_5$), 7.65 (m, 4H, C$_6$H$_5$), 7.52 (m, 4H, C$_6$H$_5$), 7.46−7.35 (m, 4H, C$_6$H$_5$), 6.60, 6.51, 6.07, 5.97 (all m, each 1H, C$_5$H$_4$),

3.98, 3.78 (both m, each 1H, PCH_2CH_2), 2.69−2.43 (m, 1H, PCH_2CH_2), 2.14 (m, 3H, PCH), 1.84 (m, 1H, PCH_2CH_2), 1.16 (dd, 9H, J(HH) = 7.2, J(PH) = 14.7, $PCCH_3$), 1.11 (dd, 9H, J(HH) = 6.9, J(PH) = 13.5, $PCCH_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_2Cl_2, 293 K): δ 19.1, 16.9 (both d, $J(PP') = 14$), −144.9 (sept, J(PF) = 734). $^{19}F\{^1H\}$ NMR (282.3 MHz, CD_2Cl_2, 293 K): δ −69.3 (d, J(PF) = 734). $^{13}C\{^1H\}$ NMR (75.4 MHz, CD_2Cl_2, 293 K, plus APT): δ 260.5 (−, br, Os=C), 227.2 (−, br, =C=) 150.7 (−, d, J(PC) = 1, $=CPh_2$), 149.4 (−, s, ipso-C_6H_5), 134.6 (−, d, J(PC) = 45, ipso-PC_6H_5), 134.1 (−, d, J(PC) = 31, ipso-PC_6H_5), 134.5 (+, d, J(PC) = 11, PC_6H_5), 132.4 (+, d, J(PC) = 9, PC_6H_5), 131.7 (+, d, J(PC) = 3, PC_6H_5), 131.5 (+, d, J(PC) = 2, PC_6H_5), 130.4, 129.6, 128.9 (+, s, C_6H_5), 128.8 (+, d, J(PC) = 8, PC_6H_5), 128.7 (+, d, J(PC) = 11, PC_6H_5), 125.4 (−, dd, J(PC) = 3, $J(P'C)$ = 8, ipso-C_5H_4), 87.5 (+, d, J(PC) = 6, C_5H_4), 86.5 (+, d, J(PC) = 5, C_5H_4), 85.4 (+, d, J(PC) = 5, C_5H_4), 77.6 (+, s, C_5H_4), 55.0 (−, d, J(PC) = 23, PCH_2CH_2), 29.5 (+, d, J(PC) = 29, PCH), 20.5 (+, s, $PCCH_3$), 19.8 (−, s, PCH_2CH_2), 19.5 (+, d, J(PC) = 2, $PCCH_3$).

Preparation of [Os{η^5-$C_5H_4(CH_2)_2PPh_2$}(≡CCH=CPh_2)-(P^iPr_3)](PF_6)$_2$ (11). A suspension of **10** (0.30 g, 0.31 mmol) in 5 mL of diethyl ether was treated with $HPF_6 \cdot H_2O$ (27.5 μL, 0.31 mmol) at room temperature. Stirring of the mixture for 1 h afforded an orange solid, which was isolated by filtration, washed with diethyl ether and pentane (3 × 5 mL), and dried under vacuum. Yield: 94% (0.32 g, 0.29 mmol). Anal. Calcd for $C_{43}H_{50}OsP_4F_{12}$: C, 46.59; H, 4.51. Found: C, 46.34; H, 4.35. MS (FAB$^+$): *m/e* 820 (M^+). IR (Nujol): ν(C=C) 1511 cm^{-1}, $\nu(PF_6)$ 838 cm^{-1}. ^1H NMR (300 MHz, CD_2Cl_2, 293 K): δ 7.79−7.62 (m, 15H, C_6H_5), 7.45 (m, 3H, C_6H_5), 7.33 (m, 2H, C_6H_5), 6.52, 6.40 (both m, each 1H, C_5H_4), 6.01 (s, 1H, =CH), 5.89, 5.36 (both m, each 1H, C_5H_4), 4.13, 3.63 (both m, each 1H, PCH_2CH_2) 2.95, 2.16 (both m, each 1H, PCH_2CH_2), 1.93 (m, 3H, PCH), 1.05 (dd, 9H, J(HH) = 7.2, J(PH) = 14.7, $PCCH_3$), 1.03 (dd, 9H, J(HH) = 9.0, J(PH) = 16.5, $PCCH_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_2Cl_2, 293 K): δ 25.7, 22.3 (both d, $J(PP') = 7$), −144.9 (sept, J(PF) = 716). $^{19}F\{^1H\}$ NMR (282.3 MHz, CD_2Cl_2, 293 K): δ −72.1 (d, J(PF) = 716). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2, 293 K, plus APT plus HMQC): δ 297.0 (−, dd, J(PC) = 6, $J(P'C)$ = 11, Os≡C), 174.8 (−, s, $=CPh_2$), 135.3 (+, s, C_6H_5), 134.8 (+, d, J(PC) = 14, PC_6H_5), 134.5 (+, d, J(PC) = 4, PC_6H_5), 134.0 (+, d, J(PC) = 4, PC_6H_5), 133.7 (+, s, C_6H_5), 133.1 (+, d, J(PC) = 12, PC_6H_5), 132.5 (+, s, =CH), 131.2, 130.6, 130.4, 130.3, 130.2 (+, all s, C_6H_5), 97.1, 91.1 (+, br, C_5H_4), 88.9 (+, d, J(PC) = 2, C_5H_4), 83.7 (+, d, J(PC) = 1, C_5H_4), 53.6 (−, obscured by CD_2Cl_2, PCH_2CH_2), 30.6 (+, d, J(PC) = 37, PCH), 20.4 (+, s, $PCCH_3$), 19.4 (−, s, PCH_2CH_2), 19.5 (+, d, J(PC) = 4, $PCCH_3$).

X-ray Analysis of 2 and 4. Crystals suitable for X-ray diffraction were grown from toluene (**2**) and pentane (**4**) solutions cooled at −30 °C. Two irregular crystals of size 0.16 × 0.12 × 0.06 mm (**2**) and 0.28 × 0.06 × 0.04 mm (**4**) were mounted on a Bruker Smart APEX CCD diffractometer at 100.0(2) K equipped with a normal focus, 2.4 kW sealed tube source (molybdenum radiation, λ = 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 s covering 0.3° in ω. The cell parameters were determined and refined by least-squares fit of 7013 (**2**) or 959 (**4**) collected reflections. The first 100 frames were collected at the end of the data collection to monitor crystal decay. Absorption correction was performed with the SADABS program.[24] Lorentz and polarization corrections were also performed. The structures were solved by Patterson and Fourier methods and refined by full matrix least-squares using the Bruker SHELXTL program package[25] minimizing $w(F_o^2 - F_c^2)^2$. A molecule of water (**2**) and toluene (**4**) were observed in the refinement. The hydride ligands of **2** were observed and refined as free isotropic atoms with the same thermal parameter. Weighted R factors (R_w) and goodness of fit (S) are based on F^2; conventional R factors are based on F. Crystal data and details of the data collection and refinement are given in Table 3.

Table 3. Crystal Data and Data Collection and Refinement for 2 and 4

	2	**4**
	Crystal Data	
formula	$C_{28}H_{41}ClOsP_2O_{0.50}H$	$C_{28}H_{39}ClOsP_2C_{3.5}H_4$
molecular wt	674.21	709.25
color and habit	light yellow, block	light yellow, block
symmetry, space group	triclinic, $P\bar{1}$	triclinic, $P\bar{1}$
a, Å	12.3939(11)	10.987(2)
b, Å	13.5863(13)	15.170(3)
c, Å	17.2113(16)	18.254(4)
α, deg	98.701(2)	88.250(3)
β, deg	104.801(2)	76.352(3)
γ, deg	91.190(2)	80.402(3)
V, Å^3	2764.4(4)	2915.1(10)
Z	4	4
D_{calc}, g cm^{-3}	1.620	1.616
	Data Collection and Refinement	
diffractometer	Bruker Smart APEX	
λ(Mo Kα)	0.71073	
monochromator	graphite oriented	
scan type	ω scans	
μ, mm^{-1}	4.842	4.595
2θ, range deg	3, 56	3, 56
temp, K	100	100
no. of data collected	33 425	34 982
no. of unique data	12 776 (R_{int} = 0.0610)	13 397 (R_{int} = 0.0366)
no. of params/restraints	619/3	653/0
R_1[a] [$F^2 > 2\sigma(F^2)$]	0.0391	0.0303
wR_2[b] [all data]	0.0761	0.0566
S[c] [all data]	0.860	0.861

[a] $R_1(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2(F^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. [c] Goof = $S = \{\sum[F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$, where n is the number of reflections and p is the number of refined parameters.

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Supporting Information Available: Tables of crystallographic data and bond lengths and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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