New Cyclopentadienylosmium Compounds Containing Unsaturated Carbon Donor Coligands: Synthesis, Structure, and Reactivity of $Os(\eta^5\text{-}C_5H_5)Cl({=}C{=}C{=}CPh_2)(P^iPr_3)$

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The addition of 1,1-diphenyl-2-propyn-1-ol to pentane solutions of the cyclopentadienyl compound $Os(\eta^5\text{-}C_5H_5)Cl(P^iPr_3)_2$ (**1**) produces the displacement of a phosphine ligand from **1** and the formation of the π-alkyne complex $Os(\eta^5\text{-}C_5H_5)Cl\{\eta^2\text{-}HC{\equiv}C{-}C(OH)Ph_2\}(P^iPr_3)$ (**2**), which affords the allenylidene derivative $Os(\eta^5\text{-}C_5H_5)Cl({=}C{=}C{=}CPh_2)(P^iPr_3)$ (**3**) in toluene at 85 °C. The structure of **3** has been determined by X-ray diffraction. The $Os{-}C_\alpha$, $C_\alpha{-}C_\beta$, and $C_\beta{-}C_\gamma$ bond lengths are 1.875(6), 1.222(9), and 1.344(9) Å, respectively, while the $Os{-}C_\alpha{-}C_\beta$ and $C_\alpha{-}C_\beta{-}C_\gamma$ angles are 171.6(6)° and 172.0(7)°, respectively. Protonation of **3** with $HBF_4{\cdot}OEt_2$ leads to the α,β-unsaturated carbyne $[Os(\eta^5\text{-}C_5H_5)Cl({\equiv}C{-}CH{=}CPh_2)(P^iPr_3)]BF_4$ (**4**), as a result of the attack of the proton from the acid at the C_β carbon atom of the allenylidene. The nucleophilicity of this atom is also revealed by the reaction of **3** with dimethyl acetylenedicarboxylate, which leads to the allenylvinylidene $Os(\eta^5\text{-}C_5H_5)Cl\{{=}C{=}C(CO_2Me)C(CO_2Me){=}C{=}CPh_2\}(P^iPr_3)$ (**5**). A second $C_3 + C_2$ coupling process is the formation of the pentatrienyl complex $Os(\eta^5\text{-}C_5H_5)\{(3{-}5\text{-}\eta)CH_2CHC{=}C{=}CPh_2\}(P^iPr_3)$ (**6**) by reaction of **3** with $CH_2{=}CHMgBr$. Complex **3** also reacts with KI to give $Os(\eta^5\text{-}C_5H_5)I({=}C{=}C{=}CPh_2)(P^iPr_3)$ (**7**). The reduction of the $C_\beta{-}C_\gamma$ double bond of the allenylidene ligand of **3**, to form the vinylidene complex $Os(\eta^5\text{-}C_5H_5)Cl({=}C{=}CH{-}CHPh_2)(P^iPr_3)$ (**8**), has been carried out in the presence of $NaBH_4$ and methanol.

Introduction

The chemistry of the $Os(\eta^5\text{-}C_5H_5)$ unit is a little-known field[1] due to the lack of convenient osmium synthetic precursors[2] and the higher kinetic stability of the $CpOsL_3$ compounds in comparison with the related iron and ruthenium species.[3]

We have recently reported that the five-coordinate complex $OsHCl(CO)(P^iPr_3)_2$ reacts with cyclopentadiene to afford $OsH(\eta^5\text{-}C_5H_5)(CO)(P^iPr_3)$, which has been the starting point for new half-sandwich osmium complexes including hydrido, halide, vinylidene, and alkenylvinylidene derivatives.[4] Subsequently, as a part of our study on the chemical properties of the six-coordinate osmium (IV) complex $OsH_2Cl_2(P^iPr_3)_2$,[5] we have observed that its reaction with cyclopentadienylthallium leads to $Os(\eta^5\text{-}C_5H_5)Cl(P^iPr_3)_2$, which is also a useful starting material for the preparation of new cyclopentadienylosmium compounds.[6]

The chemical behavior of $Os(\eta^5\text{-}C_5H_5)Cl(P^iPr_3)_2$ is a result of two factors: the high basicity of the metallic center, as a consequence of the presence of the strong donor phosphine and the chlorine ligands in the complex, and the large steric hindrance experienced by the triisopropylphosphine groups, which are mutually cis disposed. This mixture allows access to reactive points on the osmium center by activation of Os−P and Os−Cl bonds. In polar solvents such as methanol and

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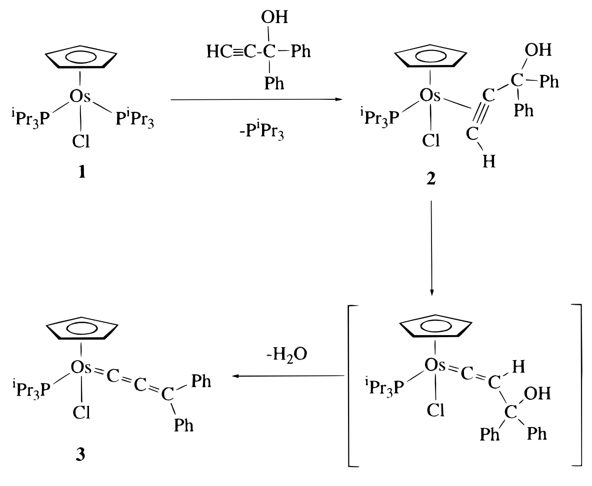
acetone, the dissociation of the chlorine ligand occurs, and the resulting metallic fragment is capable of activating a methyl C−H bond of a triisopropylphosphine to give $[OsH(\eta^5\text{-}C_5H_5)\{CH_2CH(CH_3)P^iPr_2\}(P^iPr_3)]^+$. On the other hand, in pentane and toluene, the splitting of an Os−P bond is favored, and the reactions of $Os(\eta^5\text{-}C_5H_5)Cl(P^iPr_3)_2$ with olefins and alkynes lead to π-olefin and π-alkyne complexes.[6]

In 1982, Selegue illustrated that propargylic alcohols HC≡C−CRR′OH can be converted quite smoothly into a C=C=CRR′ unit in the coordination sphere of an electron-rich transition-metal center by elimination of water.[7] Since then, a variety of allenylidene−metal complexes has been prepared, the elements of chromium and manganese triads, as well as rhodium and ruthenium, thereby playing a dominant role.[8,9]

Allenylidene complexes of the third-row platinum group metals are rare. For osmium, Gimeno and co-workers have reported that the reactions of $Os(\eta^5\text{-}C_9H_7)Cl(PPh_3)_2$ with propargylic alcohols in the presence of $NaPF_6$ lead to $[Os(\eta^5\text{-}C_9H_7)(=C=C=CR_2)(PPh_3)_2]PF_6$ (R_2 = Ph_2, $C_{12}H_8$),[10] and we have described the formation of the complex $[Os\{C[C(O)OCH_3]=CH_2\}(=C=C=CPh_2)(CO)(P^iPr_3)_2]BF_4$, which in the presence of NaCl and in toluene at 60 °C evolves to the allenyl derivative $Os\{C[C(=CH_2)C(O)OCH_3]=C=CPh_2\}Cl(CO)(P^iPr_3)_2$ via the intermediate $Os\{C(CO_2CH_3)=CH_2\}Cl(=C=C=CPh_2)(CO)(P^iPr_3)_2$, which is isolated as a mixture of two different isomers.[11] Other neutral osmium−allenylidene compounds are not known. For iridium, the neutral allenylidene complex $IrCl(=C=C=CPh_2)(P^iPr_3)_2$ has been reported by Werner and co-workers. Its formation involves alkynylhydridoiridium (III) or alternatively square-planar hydroxyvinylidene intermediates, which are catalytically converted into the allenylidene in the presence of trifluoroacetic acid.[12] We had previously observed the formation of square-planar cationic species containing an $Ir=C=C=CPh_2$ unit as a result of the protonation of $Ir\{C\equiv C-C(OH)Ph_2\}(diene)(PR_3)$ complexes.[13] To the best of our knowledge, platinum−allenylidene compounds have not been reported.

Scheme 1



The lability of one of the two Os−P bonds in $Os(\eta^5\text{-}C_5H_5)Cl(P^iPr_3)_2$ prompted us to carry out the reaction of this complex with 1,1-diphenyl-2-propyn-1-ol, to prepare $Os(\eta^5\text{-}C_5H_5)Cl(=C=C=CPh_2)(P^iPr_3)$, and to study the influence of the $Os(\eta^5\text{-}C_5H_5)$ unit on the chemical properties of the allenylidene ligand. In this paper, we report the synthesis, the structure, and some reactivity of this complex.

Results and Discussion

1. Synthesis and X-ray Structure of $Os(\eta^5\text{-}C_5H_5)Cl(=C=C=CPh_2)(P^iPr_3)$. In agreement with the tendency shown by the complex $Os(\eta^5\text{-}C_5H_5)Cl(P^iPr_3)_2$ (**1**) to release a phosphine ligand, the treatment of this compound with 1 equiv of 1,1-diphenyl-2-propyn-1-ol in pentane at room temperature led to the π-alkynol complex $Os(\eta^5\text{-}C_5H_5)Cl\{\eta^2\text{-}HC\equiv C-C(OH)Ph_2\}(P^iPr_3)$ (**2**, Scheme 1), which was isolated as a violet solid in 80% yield.

The π-coordination of the alkynol in **2** is strongly supported by the IR spectrum, in which the C≡C stretching frequency is found at 1801 cm^{-1}, shifted 316 cm^{-1} to lower wavenumbers in comparison with the C≡

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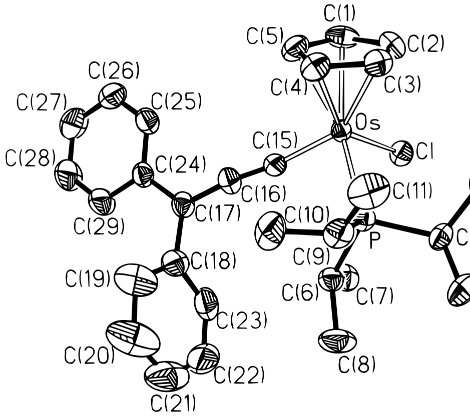

Figure 1. Molecular diagram of the complex $Os(\eta^5\text{-}C_5H_5)Cl({=}C{=}C{=}CPh_2)(P^iPr_3)$ (**3**). Thermal ellipsoids are shown at 50% probability.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for the Complex $Os(\eta^5\text{-}C_5H_5)Cl({=}C{=}C{=}CPh_2)(P^iPr_3)$ (3)

Os−C(1)	2.278(6)	Os−P	2.311(2)
Os−C(2)	2.344(7)	Os−Cl	2.457(2)
Os−C(3)	2.330(6)	Os−C(15)	1.875(6)
Os−C(4)	2.273(7)	C(15)−C(16)	1.222(9)
Os−C(5)	2.262(7)	C(16)−C(17)	1.344(9)
P−Os−Cl	86.42(5)	Os−C(15)−C(16)	171.6(6)
P−Os−C(15)	84.5(2)	C(15)−C(16)−C(17)	172.0(7)
P−Os−G(1)[a]	132.8(2)	C(16)−C(17)−C(18)	118.6(6)
Cl−Os−C(15)	104.1(2)	C(16)−C(17)−C(24)	120.7(6)
Cl−Os−G(1)[a]	118.0(2)	C(18)−C(17)−C(24)	120.6(6)
C(15)−Os−G(1)[a]	122.2(3)		

[a] G(1) is the midpoint of the C(1)−C(5) Cp ligand.

C stretching frequency in the free alkyne (2117 cm^{-1}).[14] In the $^{13}C\{^1H\}$ NMR spectrum, the resonance of the HC≡ carbon atom appears at 122.9 ppm as a singlet, whereas the other acetylenic carbon atom gives rise at 82.2 ppm to a doublet with a P−C coupling constant of 6.5 Hz. In the ^1H NMR spectrum, the most noticeable resonances are a singlet at 6.93 ppm corresponding to the O−H proton and a doublet at 4.32 ppm with a P−H coupling constant of 9.0 Hz due to the HC≡ proton.

In toluene at room temperature, complex **2** is stable. However, at 85 °C, it evolves into the allenylidene derivative $Os(\eta^5\text{-}C_5H_5)Cl({=}C{=}C{=}CPh_2)(P^iPr_3)$ (**3**) in quantitative yield after 15 h. The reaction most probably involves the formation of a hydroxyvinylidene intermediate, which dehydrates spontaneously[7] (Scheme 1).

Complex **3** was isolated as a green solid and characterized by elemental analysis, IR, ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ spectroscopies, and an X-ray diffraction study. A view of the molecular geometry is shown in Figure 1. Selected bond distances and angles are listed in Table 1. The geometry around the osmium center is close to octahedral, with the cyclopentadienyl ligand occupying three sites of a face. The angles P−Os−Cl, P−Os−C(15), and Cl−Os−C(15) are 86.42(5)°, 84.5(2)°, and 104.1(2)°, respectively.

The diphenylallenylidene ligand is bound to the metal in a nearly linear fashion, with Os−C(15)−C(16) and C(15)−C(16)−C(17) angles of 171.6(6)° and 172.0(7)°, respectively. The Os−C(15) bond length of 1.875(6) Å is statistically identical with that found in the cationic indenyl complex $[Os(\eta^5\text{-}C_9H_7)({=}C{=}C{=}CPh_2)(PPh_3)_2]PF_6$ [1.895(4) Å][10] and about 0.05 Å shorter than the related bond length in $[\overline{\mathrm{Os\{C[C(O}})\mathrm{OCH_3]{=}CH_2\}({=}C{=}C{=}CPh_2)(CO)(P^iPr_3)_2]BF_4}$ [1.947(6) Å].[11] The C(15)−C(16) distance [1.222(9) Å] compares well with those found in the previously reported two osmium−allenylidene compounds [1.265(6) and 1.250(8) Å, respectively]. However, it is significantly shorter than the bond length expected for a carbon−carbon double bond (1.30 Å),[15] indicating a substantial contribution of the canonical form $[Os]^-\text{-}C{\equiv}C{-}C^+Ph_2$ to the structure of **3**. A similar conclusion has been reached in the structural analysis of the other allenylidene complexes.[10,11]

In agreement with the presence of the allenylidene ligand in **3**, the IR spectrum shows the characteristic $\nu(C{=}C{=}C)$ band for this type of ligands at 1874 cm^{-1}, and the $^{13}C\{^1H\}$ NMR spectrum contains a doublet at 225.1 ppm with a P−C coupling constant of 15.2 Hz, which was assigned to the α-carbon atom, and two singlets at 238.5 and 129.1 ppm, corresponding to β- and γ-carbon atoms, respectively.

In addition, the atypical chemical shift for the β-carbon atom, which appears at lower field than even that for the α-carbon atom, should be noted. This unexpected finding has been previously observed in the μ-dicyanoallenylidene complex $(\eta^5\text{-}C_5H_5)_2Fe_2(\mu\text{-}CO)(\mu\text{-}dppe)\{\mu\text{-}C{=}C{=}C(CN)_2\}$ and in the complexes $Cp^*{}_2Fe_2(\mu\text{-}C{=}C{=}CR'R'')(\mu\text{-}CO)(CO)_2$.[16]

2. Reactivity of 3. EHT-MO calculations on the allenylidene complexes $Mn(\eta^5\text{-}C_5H_5)(CO)_2({=}C{=}C{=}CH_2)$,[17] $[Rh_2(\mu\text{-}OOCH)(\mu\text{-}\sigma,\sigma\text{-}C{=}C{=}CH_2)(CO)_2(PH_3)_2]^+$,[8v] $[Ru(\eta^5\text{-}C_5H_5)({=}C{=}C{=}CH_2)(CO)(PH_3)]^+$,[18] and $[Ru(\eta^5\text{-}C_9H_7)({=}C{=}C{=}CH_2)(PH_3)_2]^+$ [10] suggest, in all the cases, that the C_α and C_γ carbon atoms of the allenylidene unit are electrophilic centers, while the C_β carbon atom is nucleophilic. In agreement with the electrophilic character of the C_α and C_γ carbon atoms, cationic allenylidene−ruthenium(II) complexes and the cationic allenylidene−osmium(II) compound $[\overline{\mathrm{Os\{C[C(O}})\mathrm{OCH_3]{=}CH_2\}({=}C{=}C{=}CPh_2)(CO)(P^iPr_3)_2]BF_4}$ are quite reactive toward nucleophiles. Work by Dixneuf and co-workers,[8a,e,f,n,p,s] Gimeno and co-workers,[8j,k,m,9e−h,10] and our group[8w,11,18] has shown that such compounds are easily attacked by alcohols, thiols, alcoholates, acetylides, phosphines, and amines. In addition, Werner and co-workers have reported the formation of γ-functionalized alkynyl groups by migratory insertion of an allenylidene unit into Rh−OR (R = Ph, CH_3CO) bonds of neutral rhodium species.[9i,19]

The behavior of **3** toward nucleophilic reagents markedly differs from that previously mentioned. The allenylidene ligand is inert in the presence of alcohols, diphenylphosphine, benzophenone imine, pyrazole, and

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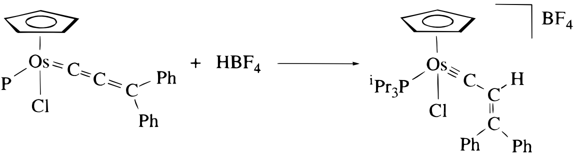
acetate. In methanol, the dissociation of the chlorine and the subsequent activation of a methyl C−H bond of the phosphine are also not observed. However, in agreement with the expected nucleophilic character of the C_β carbon atom, complex **3** reacts with 1 equiv of $HBF_4{\cdot}OEt_2$ to afford the α,β-unsaturated carbyne derivative $[Os(\eta^5\text{-}C_5H_5)Cl\{{\equiv}C{-}CH{=}CPh_2\}(P^iPr_3)]BF_4$ (**4**), which is a result of the attack of the proton from the acid to the C_β carbon atom of the allenylidene ligand (eq 1). We note that Kolobova and co-workers have previously reported the synthesis of related manganese complexes by protonation of the corresponding allenylidene starting materials.[20]

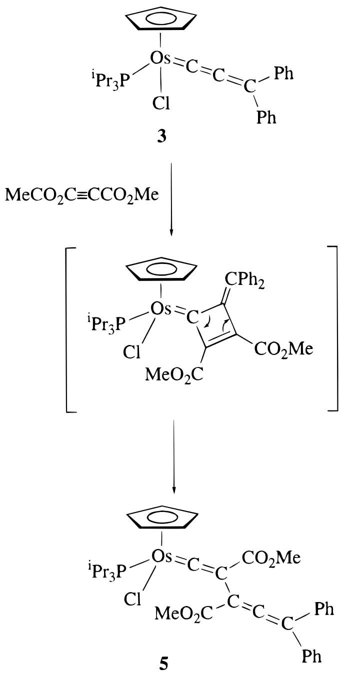


3 **4** (1)

Although binuclear μ-alkenylcarbyne complexes are well known,[21] the mononuclear alkenylcarbyne compounds are rare, in particular those containing osmium. The latter have been prepared using dihydridoosmium(IV) complexes and alkynols as precursors.[5b,22] Recently, we have also observed that the protonation of α,β-unsaturated vinylidene−osmium(II) compounds affords α,β-unsaturated carbyne derivatives.[6] Previously, the same method of synthesis has been used to prepare related compounds of manganese,[23] tungsten,[24] and rhodium.[25]

The protonation of **3** to give **4** was carried out in dichloromethane-d_2 as solvent, and complex **4** was isolated as a green solid in 93% yield. The IR spectrum in Nujol shows the absorption due to the $[BF_4]^-$ anion with T_d symmetry centered at 1065 cm^{-1}, which indicates that this anion is not coordinated to the metallic center. In the ^{1}H NMR spectrum in dichloromethane-d_2, the most noticeable resonance is a singlet at 6.01 ppm, assigned to the =CH proton. In the $^{13}C\{^1H\}$ NMR spectrum, the resonance due to the sp carbon atom of the η^1-unsaturated ligand appears at 289.1 ppm as a doublet, with a P−C coupling constant of 10.1 Hz, whereas the resonances of the sp^2 carbon atoms are observed at 169.1 (=CPh$_2$) and 135.6 (CH=) ppm as singlets. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 37.7 ppm.

Scheme 2



The nucleophilicity of the C_β carbon atom of the allenylidene of **3** is also revealed by its reaction with the electron-withdrawing alkyne dimethyl acetylenedicarboxylate. This alkyne contains two ester functionalities that draw electron density from the carbon−carbon triple bond, activating it toward nucleophilic attack by the electron-rich allenylidene C_β atom. Thus, the treatment of **3** with dimethyl acetylenedicarboxylate in toluene under reflux leads, after 20 h, to the allenylvinylidene $Os(\eta^5\text{-}C_5H_5)Cl\{{=}C{=}C(CO_2CH_3)C(CO_2CH_3){=}C{=}CPh_2\}(P^iPr_3)$ (**5**). The insertion of the alkyne into the $C_\alpha{-}C_\beta$ double bond of the allenylidene can be rationalized as a stepwise cycloaddition to form an η^1-cyclobutenyl intermediate, which rapidly ring-opens to form the allenylvinylidene product (Scheme 2). A similar reaction pathway has been previously proposed for the addition of dimethyl acetylenedicarboxylate to the vinylidene ligand of *mer*-(dppe)(OC)$_3$W=C=CHPh, which yields an alkenylvinylidene derivative.[26]

Complex **5** was isolated as an orange solid in 72% yield. The IR spectrum in Nujol shows the C=C=C stretching frequency at 1719 cm^{-1}, along with two ν(CO) bands at 1678 and 1576 cm^{-1} corresponding to the carboxylato groups. In the ^{1}H NMR spectrum, the most noticeable resonances are two singlets at 3.52 and 3.37 ppm due to the methyl protons of the η^1-unsaturated carbon ligand. The presence of an allenylvinylidene ligand in **5** is also supported by the $^{13}C\{^1H\}$ NMR spectrum, which contains at 286.6 ppm a doublet with a P−C coupling constant of 12.5 Hz, due to the C_α carbon atom, and at 215.5 ppm a singlet corresponding to the central carbon atom of the allenyl unit. The C_β carbon atom of the vinylidene and the C_α and C_γ carbon atoms of allenyl unit are observed as singlets at 114.3,

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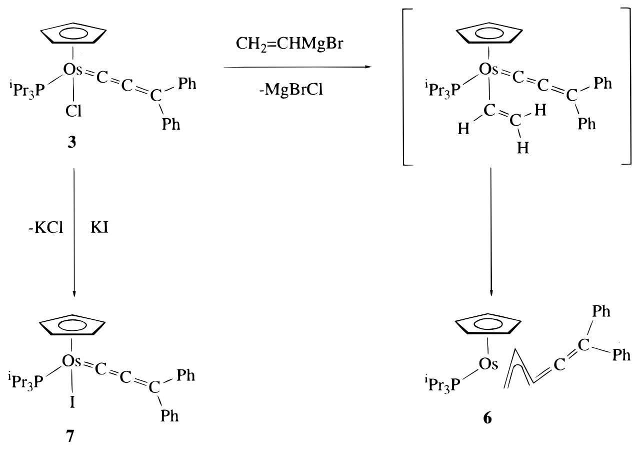
Scheme 3



112.5, and 92.7 ppm. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 21.9 ppm.

The formation of **5** according to Scheme 2 is a novel $C_3 + C_2$ coupling reaction. A second $C_3 + C_2$ coupling process is shown in Scheme 3. Treatment of a solution of **3** in toluene with 1 equiv of CH_2=CHMgBr in tetrahydrofuran leads to a rapid change of color from green to yellow and finally to the isolation of yellow microcrystals of the pentatrienyl complex Os(η^5-C_5H_5)-{(3−5-η)CH_2CHC=C=CPh$_2$}(P^{i}Pr$_3$) (**6**) in 73% yield.

The IR spectrum of **6** shows the characteristic C=C=C stretching frequency at 1939 cm^{-1}. The resonances corresponding to the allyl protons are observed, in the ^{1}H NMR spectrum, as three multiplets at 3.98 (H_{meso}), 2.92 (H_{syn}), and 2.01 (H_{anti}) ppm. The $^{13}C\{^1H\}$ NMR spectrum displays two low-field signals for the allene-like carbon atoms =C= and =CPh$_2$ at 192.4 and 103.2 ppm, which appear as doublets with P−C coupling constants of 3.8 and 1.8 Hz, respectively, and three resonances due to the allyl carbons at 91.4 (C=), 33.1 (CH), and 11.8 (CH$_2$) ppm, which are also observed as doublets but with P−C coupling constants of 11.5, 2.8, and 6.0 Hz, respectively.

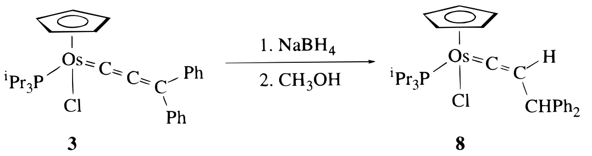
Complex **6** is a rare case of a transition-metal pentatrienyl complex. We note that related ruthenium[27] and rhodium[28] compounds have been previously prepared by a similar procedure. With regard to the mechanism of formation of the pentatrienyl ligand, we assume that initially a nucleophilic substitution of the chloro ligand takes place and a vinylmetal intermediate is generated. This could rearrange by migratory insertion of the allenylidene ligand into the Os−CH=CH$_2$ bond to give the final product. In this context, it should be noted that the rhodium complexes *trans*-RhCl(=C=CHR)(P^{i}Pr$_3$)$_2$ (R = ^{t}Bu, Ph) react with CH_2=CHMgBr to afford *trans*-Rh(CH=CH$_2$)(=C=CHR)(P^{i}Pr$_3$)$_2$, which upon heating to 50 °C in benzene isomerize to give the butadienyl derivatives Rh{(2−4-η)-CH_2CHC=CHR}-(P^{i}Pr$_3$)$_2$.[29]

Taking into account the kinetic inertia of the CpOsL$_3$ complexes toward substitution reactions, an alternative pathway leading to **6**, namely the direct attack of the vinyl nucleophile to the C_α carbon atom of the allenylidene ligand followed by elimination of chloride with concomitant η^1 to η^3 rearrangement, could be also considered but seems less likely, since the allenylidene ligand is inert in the presence of nucleophiles, as has been previously mentioned.

To confirm the lability of the chloro ligand in **3**, we have also carried out the reaction of this complex with potassium iodide. As expected, the addition of this salt to **3** in methanol affords the iodo complex Os(η^5-C_5H_5)I(=C=C=CPh$_2$)(P^{i}Pr$_3$) (**7**, in Scheme 3), which was isolated as a brown solid in 64% yield.

The most characteristic spectroscopic features of **7** are, in the IR spectrum, the ν(C=C=C) band at 1872 cm^{-1} and, in the $^{13}C\{^1H\}$ NMR spectrum, a doublet at 234.1 ppm with a P−C coupling constant of 14.3 Hz, which was assigned to the C_α carbon atom, and two singlets at 243.3 and 132.0 ppm, corresponding to the C_β and C_γ carbon atoms, respectively. As for **3**, the resonance due to the C_β atoms appears at lower field than that due to the C_α carbon atom.

A general procedure to generate ruthenium and osmium hydrido compounds is the treatment of chloro precursors with NaBH$_4$ in the presence of methanol.[5a,30] However, an unexpected reaction occurs if a toluene solution of **3** is treated with NaBH$_4$ and subsequently with some drops of methanol. Under these conditions, the substitution of the chloro ligand by hydride does not take place, but the formation of the vinylidene derivative Os(η^5-C_5H_5)Cl(=C=CH−CHPh$_2$)(P^{i}Pr$_3$) (**8**), as a result of the reduction of the C_β−C_γ double bond of the allenylidene ligand of **3**, is observed (eq 2). We note that, in contrast to the reaction shown in eq 2, the reduction of the neutral allenylidene complexes MCl(=C=C=CPh$_2$)(P^{i}Pr$_3$)$_2$ (M = Rh, Ir) with molecular hydrogen leads to allene compounds.[12,31]



(**2**)

Complex **8** was isolated as an orange solid in 65% yield. The IR spectrum in Nujol shows the ν(C=C) band due to the vinylidene ligand at 1656 cm^{-1}. In the ^{1}H NMR spectrum, the most noticeable resonances are two doublets at 5.24 and 2.38 ppm with a H−H coupling constant of 10.3 Hz, corresponding to the =CH and −CH− protons, respectively. In the $^{13}C\{^1H\}$ NMR spectrum, the resonance due to the C_α carbon atom of the vinylidene appears at 283.7 ppm as a doublet with a P−C coupling constant of 13.4 Hz, whereas the signal corresponding to the C_β carbon atom is observed at 126.1 ppm as a singlet, and the resonance due to the *C*HPh$_2$ carbon atom appears at 40.2 ppm, also as a singlet. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 20.4 ppm.

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Concluding Remarks

This study has revealed that the lability of an Os−P bond of $Os(\eta^5\text{-}C_5H_5)Cl(P^iPr_3)_2$ also allows the preparation of the allenylidene compound $Os(\eta^5\text{-}C_5H_5)Cl(=C=C=CPh_2)(P^iPr_3)$ containing the unusual $Os(\eta^5\text{-}C_5H_5)$ unit. This complex is obtained via the *isolable* intermediate $Os(\eta^5\text{-}C_5H_5)Cl\{\eta^2\text{-}HC\equiv C-C(OH)Ph_2\}(P^iPr_3)$ and has a very remarkable nucleophlic character.

As a result of its high nucleophilicity, which is mainly concentrated on the C_β carbon atom of the diphenylallenylidene ligand, marked differences in reactivity are observed between this allenylidene complex and those stabilized by cationic ruthenium and osmium fragments. Previous EHT-MO calculations[8v,10,17,18] indicate that the allenylidenes are π-acceptor groups and that the HOMO of this type of complexes is mainly located on the C_β carbon atom of the allenylidene. Thus, the differences in reactivity seem to be not only a consequence of the neutral charge of the $Os(\eta^5\text{-}C_5H_5)Cl(P^iPr_3)$ fragment but also a result of the high basicity of the phosphine, the large π-donor power of the chlorine, and the intrinsically higher basicity of the osmium atom in comparison with ruthenium.[32]

The marked nucleophilic character of the allenylidene ligand of $Os(\eta^5\text{-}C_5H_5)Cl(=C=C=CPh_2)(P^iPr_3)$ is revealed by the inert behavior toward alcohols, diphenylphosphine, benzophenone imine, pyrazole, and acetate and in its reactions with HBF_4 and dimethyl acetylenedicarboxylate, which afford $[Os(\eta^5\text{-}C_5H_5)Cl(\equiv C-CH=CPh_2)(P^iPr_3)]BF_4$ and $Os(\eta^5\text{-}C_5H_5)Cl\{=C=C(CO_2Me)C(CO_2Me)=C=CPh_2\}(P^iPr_3)$. The latter complex, which is a result of a novel $C_3 + C_2$ coupling reaction, involves the insertion of the electron-withdrawing alkyne into the $C_\alpha-C_\beta$ double bond of the allenylidene ligand.

Not only is the reactivity of the complex $Os(\eta^5\text{-}C_5H_5)Cl(=C=C=CPh_2)(P^iPr_3)$ limited to the nucleophilic power of the C_β carbon atom of the allenylidene, but the chloro ligand is also activated toward the nucleophilic substitution, as is revealed by its reaction with KI to give $Os(\eta^5\text{-}C_5H_5)I(=C=C=CPh_2)(P^iPr_3)$. This property is most probably responsible for the formation of the pentatrienyl complex $Os(\eta^5\text{-}C_5H_5)\{(3-5\text{-}\eta)CH_2CHC=C=CPh_2\}(P^iPr_3)$, as a result of the reaction of $Os(\eta^5\text{-}C_5H_5)Cl(=C=C=CPh_2)(P^iPr_3)$ with $CH_2=CHMgBr$, which is another $C_3 + C_2$ coupling reaction. In this respect, the complex $Os(\eta^5\text{-}C_5H_5)Cl(=C=C=CPh_2)(P^iPr_3)$ shows a behavior similar to that previously reported for the complexes $MCl(=C=C=CPh_2)(P^iPr_3)_2$ (M = Rh, Ir),[9i] which are related to the Vaska compound and, therefore, are also strong Lewis bases.

Finally, the synthesis of the vinylidene complex $Os(\eta^5\text{-}C_5H_5)Cl(=C=CH-CHPh_2)(P^iPr_3)$ by reduction of the $C_\beta-C_\gamma$ double bond of the allenylidene ligand of $Os(\eta^5\text{-}C_5H_5)Cl(=C=C=CPh_2)(P^iPr_3)$ in the presence of $NaBH_4$ and methanol should be pointed out. This reaction is a new entry into the preparation of vinylidene derivatives starting from allenylidene precursors.

Experimental Section

Physical Measurements. Infrared spectra were recorded as Nujol mulls on polyethylene sheets using a Nicolet 550 spectrometer. NMR spectra were recorded on a Varian Unity 300, Varian Gemini 2000 (300 MHz), or a Bruker ARX 300. ^1H and $^{13}C\{^1H\}$ chemical shifts were measured relative to partially deuterated solvent peaks but are reported relative to tetramethylsilane. $^{31}P\{^1H\}$ chemical shifts are reported relative to H_3PO_4 (85%). Coupling constants J are given in hertz. C, H, and N analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyzer. Mass spectra analyses were performed with a VG Auto Spec instrument. The ions were produced, FAB^+ mode, with the standard Cs^+ gun at ca. 30 kV, and 3-nitrobenzyl alcohol (NBA) was used as the matrix.

Synthesis. All reactions were carried out with exclusion of air using standard Schlenk techniques. Solvents were dried by known procedures and distilled under argon prior to use. The complex $Os(\eta^5\text{-}C_5H_5)Cl(P^iPr_3)_2$ (**1**) was prepared according to the literature method.[6]

Preparation of $Os(\eta^5\text{-}C_5H_5)Cl\{\eta^2\text{-}HC\equiv C-C(OH)Ph_2\}(P^iPr_3)$ (2). A suspension of $Os(\eta^5\text{-}C_5H_5)Cl(P^iPr_3)_2$ (**1**) (200 mg, 0.33 mmol) in 10 mL of pentane was treated with 81.8 mg (0.39 mmol) of 1,1-diphenyl-2-propyn-1-ol. After the mixture was stirred for 30 min at room temperature, a violet solid was formed, which was separated by decantation, washed with pentane, and dried in vacuo. Yield: 170 mg (80%). IR (Nujol): ν(OH) 3353−3337 cm^{-1}, ν(C≡C) 1801 cm^{-1}. ^1H NMR (300 MHz, C_6D_6, 293 K): δ 7.98 (d, $^3J(HH) = 7.5$ Hz, 4 H, *o*-Ph), 7.23 (dd, $^3J(HH) = 7.5$ Hz, $^3J(HH) = 6.9$ Hz, 4 H, *m*-Ph), 7.07 (t, $^3J(HH) = 6.9$ Hz, 2 H, *p*-Ph), 6.93 (s, 1 H, OH), 4.83 (s, 5 H, Cp), 4.32 (d, $^3J(PH) = 9.0$ Hz, 1 H, ≡CH), 2.33 (m, 3 H, PCH), 0.85 (dd, $^3J(HH) = 7.2$ Hz, $^3J(PH) = 12.9$ Hz, 18 H, $PCCH_3$). $^{31}P\{^1H\}$ NMR (121.42 MHz, C_6D_6, 293 K): δ 10.0 (s). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K, plus APT): δ 152.2, 151.7 (−, both s, *ipso*-Ph), 127.9, 127.1, 126.6 (+, all s, Ph), 122.9 (+, s, ≡CH), 82.2 (−, d, $^2J(PC) = 6.5$ Hz, ≡C−), 79.9 (+, d, $^2J(PC) = 1.9$ Hz, Cp), 71.1 (−, s, −C(OH)), 24.1 (+, d, $^1J(PC) = 20.1$ Hz, PCH), 19.4 (+, s, $PC\mathit{C}H_3$). Anal. Calcd for $C_{29}H_{38}ClOOsP$: C, 52.83; H, 5.81. Found: C, 52.61; H, 5.92. MS (FAB^+): *m/e* 625 ($M^+ - Cl$).

Preparation of $Os(\eta^5\text{-}C_5H_5)Cl(=C=C=CPh_2)(P^iPr_3)$ (3). A solution of $Os(\eta^5\text{-}C_5H_5)Cl(P^iPr_3)_2$ (**1**) (200 mg, 0.33 mmol) in 10 mL of toluene was treated with 81.8 mg (0.39 mmol) of 1,1-diphenyl-2-propyn-1-ol. The mixture was heated at 85 °C for 15 h, and a green solution was obtained. The resulting green solution was cooled to room temperature and filtered through Kieselguhr. The solution was concentrated to dryness, and the addition of pentane caused the precipitation of a green solid, which was separated by decantation, washed with pentane, and dried in vacuo. Yield: 179 mg (85%). IR (Nujol): ν(C=C=C) 1874 cm^{-1}. ^1H NMR (300 MHz, CD_2Cl_2, 293 K): δ 7.80 (d, $^3J(HH) = 7.2$ Hz, 4 H, *o*-Ph), 7.66 (t, $^3J(HH) = 7.5$ Hz, 2 H, *p*-Ph), 7.02 (t, $^3J(HH) = 7.5$ Hz, 4 H, *m*-Ph), 5.67 (s, 5 H, Cp), 2.72 (m, 3 H, PCH), 1.17 (dd, $^3J(HH) = 7.2$ Hz, $^3J(PH) = 13.5$ Hz, 9 H, $PCCH_3$), 1.08 (dd, $^3J(HH) = 6.9$ Hz, $^3J(PH) = 13.2$ Hz, 9 H, $PCCH_3$). $^{31}P\{^1H\}$ NMR (121.42 MHz, CD_2Cl_2, 293 K): δ 18.6 (s). $^{13}C\{^1H\}$ NMR (75.42 MHz, CD_2Cl_2, 293 K): δ 238.5 (s, $Os=C=\mathit{C}=C$), 225.1 (d, $^2J(PC) = 15.2$ Hz, $Os=\mathit{C}=C=C$), 152.5 (s, *ipso*-Ph), 129.6, 127.5, 127.0 (all s, Ph), 129.1 (s, $Os=C=C=\mathit{C}$), 88.1 (s, Cp), 25.6 (d, $^1J(PC) = 29.0$ Hz, PCH), 19.7, 19.5 (both s, $PC\mathit{C}H_3$). Anal. Calcd for $C_{29}H_{36}ClOsP$: C, 54.32; H, 5.65. Found: C, 54.11; H, 5.52. MS (FAB^+): *m/e* 643 ($M^+ + H$).

Preparation of $[Os(\eta^5\text{-}C_5H_5)Cl(\equiv C-CH=CPh_2)(P^iPr_3)]BF_4$ (4). A solution of $Os(\eta^5\text{-}C_5H_5)Cl(=C=C=CPh_2)(P^iPr_3)$ (**3**) (52.0 mg, 0.08 mmol) in 0.5 mL of CD_2Cl_2 was treated with 11.0 μL (0.08 mmol) of $HBF_4\cdot OEt_2$. After 2 min at room temperature, the NMR spectra showed only the presence of the compound $[Os(\eta^5\text{-}C_5H_5)Cl(\equiv C-CH=CPh_2)(P^iPr_3)]BF_4$. The green solution was then transferred to a Schlenk tube and concentrated to dryness. The addition of diethyl ether caused the precipitation of a green solid, which was separated by decantation, washed with diethyl ether, and dried in vacuo. Yield: 54.2 mg (93%). IR (Nujol): $\nu(BF_4)$ 1065 cm^{-1}. ^1H NMR (300 MHz, CD_2Cl_2, 293 K): δ 7.66−7.42 (m, 10 H, Ph), 6.01

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(s, 1 H, =CH), 5.94 (s, 5 H, Cp), 2.61 (m, 3 H, PCH), 1.26 (dd, ^3J(HH) = 7.2 Hz, ^3J(PH) = 15.0 Hz, 9 H, PCCH$_3$), 1.21 (dd, ^3J(HH) = 6.9 Hz, ^3J(PH) = 15.9 Hz, 9 H, PCCH$_3$). ^{31}P{^{1}H} NMR (121.42 MHz, CD_2Cl_2, 293 K): δ 37.7 (s). ^{13}C{^{1}H} NMR (75.42 MHz, CD_2Cl_2, 293 K, plus APT): δ 289.1 (−, d, ^2J(PC) = 10.1 Hz, Os≡C), 169.1 (−, s, −CH=*C*), 138.2, 137.5 (−, both s, *ipso*-Ph), 135.6 (+, s, −*C*H=C), 133.3, 131.8, 131.6, 129.9, 129.7, 129.4 (+, all s, Ph), 94.3 (+, s, Cp), 27.8 (+, d, ^1J(PC) = 29.5 Hz, PCH), 19.9 (+, s, PC*C*H$_3$), 19.4 (+, d, ^2J(PC) = 2.7 Hz, PC*C*H$_3$). Anal. Calcd for $C_{29}H_{37}BF_4ClOsP$: C, 47.77; H, 5.11. Found: C, 47.54; H, 5.13. MS (FAB$^+$): *m/e* 643 (M$^+$).

Preparation of Os(η^5-C_5H_5)Cl{=C^1=C^2(CO$_2$Me)C^3(CO$_2$Me)=C^4=C^{5}Ph$_2$}(P^{i}Pr$_3$) (5). A solution of Os(η^5-C_5H_5)Cl(=C=C=CPh$_2$) (**3**) (313 mg, 0.49 mmol) in 15 mL of toluene was treated with dimethyl acetylenedicarboxylate (55 μL, 0.61 mmol). The mixture was heated 20 h at reflux temperature. The brown resulting solution was evaporated to dryness, and the residue was washed twice with 5 mL of pentane. Elution with a mixture of ether and THF (1/1) on aluminum oxide and further evaporation affords an orange solid. Yield: 276 mg (72%). IR (Nujol): ν(C=C=C) 1719 cm^{-1}, ν(C=O) 1678 cm^{-1}, ν(C=O) 1576 cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6, 293 K): δ 7.81 (d, ^3J(HH) = 7.7 Hz, 2 H, *o*-Ph), 7.72 (d, ^3J(HH) = 7.7 Hz, 2 H, *o*-Ph), 7.28 (t, ^3J(HH) = 7.7 Hz, 2 H, *m*-Ph), 7.16 (t, ^3J(HH) = 7.2 Hz, 2 H, *m*-Ph), 7.07 (t, ^3J(HH) = 7.7 Hz, 1 H, *p*-Ph), 7.03 (t, ^3J(HH) = 7.2 Hz, 1 H, *p*-Ph), 5.16 (s, 5 H, Cp), 3.52 (s, 3 H, CO$_2$Me), 3.37 (s, 3 H, CO$_2$Me), 2.65 (m, 3 H, PCH), 1.02 (dd, ^3J(HH) = 7.2 Hz, ^3J(PH) = 14.1 Hz, 9 H, PCCH$_3$), 1.00 (dd, ^3J(HH) = 7.1 Hz, ^3J(PH) = 13.1 Hz, 9 H, PCCH$_3$). ^{31}P{^{1}H} NMR (121.42 MHz, C_6D_6, 293 K): δ 21.9 (s). ^{13}C{^{1}H} NMR (75.42 MHz, C_6D_6, 293 K, plus APT): δ 286.6 (−, d, ^2J(PC) = 12.5 Hz, C^1), 215.5 (−, s, C^4), 167.6 (−, s, *C*O$_2$Me), 163.3 (−, s, *C*O$_2$Me), 136.2 (−, s, *ipso*-Ph), 135.6 (−, s, *ipso*-Ph), 129.8, 129.7, 129.3, 128.9, 128.2 (+, all s, Ph, 1 signal masked), 114.3, 112.5, 92.7 (−, all s, C^2, C^3, C^5), 88.9 (+, s, Cp), 52.0 (+, s, CO$_2$*Me*), 50.6 (+, s, CO$_2$*Me*), 24.9 (+, d, ^1J(PC) = 29.5 Hz, PCH), 19.8 (+, s, PC*C*H$_3$), 19.0 (+, d, ^2J(PC) = 1.8 Hz, PC*C*H$_3$). Anal. Calcd for $C_{35}H_{42}ClO_4OsP$: C, 53.67; H, 5.40. Found: C, 53.58; H, 5.43. MS (FAB$^+$): *m/e* 784 (M$^+$).

Preparation of Os(η^5-C_5H_5){(3−5-η)C^{5}H$_2$C^{4}HC^3=C^2=C^{1}Ph$_2$}(P^{i}Pr$_3$) (6). A solution of Os(η^5-C_5H_5)Cl(=C=C=CPh$_2$)(P^{i}Pr$_3$) (**3**) (107 mg, 0.17 mmol) in 10 mL of toluene was treated with vinylmagnesium bromide (0.17 mL, 0.17 mmol). The mixture was stirred at room temperature for 10 min, filtered through Kieselguhr, and concentrated to dryness. Ten milliliters of pentane was added, and the solution was again filtered through Kieselguhr and concentrated to dryness. The addition of 5 mL of methanol caused the precipitation of a yellow solid, which was separated by decantation, washed with methanol, and dried in vacuo. Yield: 76.7 mg (73%). IR (Nujol): ν(C=C=C) 1939 cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6, 293 K): δ 7.76 (d, ^3J(HH) = 8.4 Hz, 1 H, *o*-Ph), 7.75 (d, ^3J(HH) = 7.8 Hz, 1 H, *o*-Ph), 7.53 (d, ^3J(HH) = 7.8 Hz, 1 H, *o*-Ph), 7.52 (d, ^3J(HH) = 8.1 Hz, 1 H, *o*-Ph), 7.25 (t, ^3J(HH) = 7.5 Hz, 2 H, Ph), 7.13 (t, ^3J(HH) = 8.4 Hz, 2 H, Ph), 7.10 (t, ^3J(HH) = 8.2 Hz, 2 H, Ph), 4.61 (s, 5 H, Cp), 3.98 (ddd, ^3J(H$_{syn}$H$_{meso}$) = 6.4 Hz, ^3J(H$_{anti}$H$_{meso}$) = 7.5 Hz, ^3J(PH$_{meso}$) = 3.3 Hz, 1 H, H$_{meso}$), 2.92 (ddd, ^3J(H$_{syn}$H$_{meso}$) = 6.4 Hz, ^2J(H$_{anti}$H$_{syn}$) = 2.1 Hz, ^3J(PH$_{syn}$) = 1.5 Hz, 1 H, H$_{syn}$), 2.01 (ddd, ^3J(H$_{anti}$H$_{meso}$) = 7.5 Hz, ^2J(H$_{anti}$H$_{syn}$) = 2.1 Hz, ^3J(PH$_{anti}$)= 13.5 Hz, 1 H, H$_{anti}$), 1.83 (m, 3 H, PCH), 0.85 (dd, ^3J(HH) = 7.2 Hz, ^3J(PH) = 12.5 Hz, 9 H, PCCH$_3$), 0.84 (dd, ^3J(HH) = 7.2 Hz, ^3J(PH) = 12.9 Hz, 9 H, PCCH$_3$). ^{31}P{^{1}H} NMR (121.42 MHz, C_6D_6, 293 K): δ 18.5 (s). ^{13}C{^{1}H} NMR (75.42 MHz, C_6D_6, 293 K, plus APT): δ 192.4 (−, d, ^3J(PC) = 3.8 Hz, C^2), 142.2 (−, d, ^5J(PC) = 1.9 Hz, *ipso*-Ph), 142.1 (−, d, ^5J(PC) = 1.8 Hz, *ipso*-Ph), 129.2, 128.7, 128.3, 127.7, 125.6, 124.9 (+, all s, Ph), 103.2 (−, d, ^4J(PC) = 1.8 Hz, C^1), 91.4 (−, d, ^2J(PC) = 11.5 Hz, C^3), 74.1 (+, d, ^2J(PC) = 2.0 Hz, Cp), 33.1 (+, d, ^2J(PC) = 2.8 Hz, C^4), 27.6 (+, d, ^1J(PC) = 26.7 Hz, PCH), 20.4, 19.9 (+, both s, PC*C*H$_3$), 11.8 (−, d, ^2J(PC) = 6.0 Hz, C^5). Anal. Calcd for $C_{31}H_{39}OsP$: C, 58.83; H, 6.21. Found: C, 58.35; H, 5.84.

Table 2. Crystal Data and Data Collection and Refinement for Os(η^5-C_5H_5)Cl(=C=C=CPh$_2$)(P^{i}Pr$_3$) (3)

Crystal Data	
formula	$C_{29}H_{36}ClOsP$
molecular wt	641.20
color and habit	black, prismatic block
symmetry	triclinic
space group	$P\bar{1}$
a, Å	10.770(1)
b, Å	11.323(1)
c, Å	11.319(1)
α, deg	77.58(1)
β, deg	84.28(1)
γ, deg	86.78(1)
V, Å^3	1340.5(2)
Z	2
D_{calc}, g cm^{-3}	1.589
Data Collection and Refinement	
diffractometer	four-circle Siemens-STOE AED
λ(MoKα), Å; technique	0.710 73; bisecting geometry
monochromator	graphite oriented
μ, mm^{-1}	4.93
scan type	$\omega/2\theta$
2θ range, deg	$3 \le 2\theta \le 50°$
temp, K	253.0(2)
no. of data collect	5505
no. of unique data	4721 (R_{int} = 0.0198)
no. of params refined	296
R_1^{a} [$F^2 > 2\sigma(F^2)$]	0.0277
wR_2^{b} (all data)	0.0951
S^c (all data)	1.289

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

Preparation of Os(η^5-C_5H_5)I(=C=C=CPh$_2$)(P^{i}Pr$_3$) (7). A solution of Os(η^5-C_5H_5)Cl(=C=C=CPh$_2$) (**3**) (250 mg, 0.39 mmol) in 15 mL of methanol was treated with potassium iodide (70 mg, 0.42 mmol). After stirring 4 h at room temperature, the resulting solution was evaporated to dryness. The residue was extracted with 15 mL of dichloromethane and filtered through Kieselguhr. The filtrate was evaporated to dryness. The brown-orange solid was washed twice with 3 mL of pentane and dried in vacuo. Yield: 183 mg (64%). IR (Nujol): ν(C=C=C) 1872 cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6, 293 K): δ 7.94 (d, ^3J(HH) = 7.5 Hz, 4 H, *o*-Ph), 7.42 (t, ^3J(HH) = 7.5 Hz, 2 H, *p*-Ph), 6.96 (t, ^3J(HH) = 7.5 Hz, 4 H, *m*-Ph), 5.31 (s, 5 H, Cp), 2.64 (m, 3 H, PCH), 1.00 (dd, ^3J(HH) = 7.2 Hz,^3J(PH) = 13.8 Hz, 9 H, PCCH$_3$), 0.96 (dd, ^3J(HH) = 7.2 Hz, ^3J(PH) = 13.8 Hz, 9 H, PCCH$_3$). ^{31}P{^{1}H} NMR (121.42 MHz, C_6D_6, 293 K): δ 14.27 (s). ^{13}C{^{1}H} NMR (75.42 MHz, C_6D_6, 293 K): δ 243.3 (s, Os=C=*C*=C), 234.1 (d, ^2J(PC) = 14.3 Hz, Os=*C*=C=C), 132.0 (s, Os=C=C=*C*), 129.5, 127.3, 127.0, 126.9 (all s, Ph), 86.76 (s, Cp), 27.78 (d, ^1J(PC) = 29.5 Hz, PCH), 20.48 (s, PC*C*H$_3$), 19.79 (s, PC*C*H$_3$). Anal. Calcd for $C_{29}H_{36}IOsP$: C, 47.54; H, 4.95. Found: C, 47.94; H, 4.99. MS (FAB$^+$): *m/e* 734 (M$^+$).

Preparation of Os(η^5-C_5H_5)Cl(=C=CH−CHPh$_2$)(P^{i}Pr$_3$) (8). A solution of Os(η^5-C_5H_5)Cl(=C=C=CPh$_2$)(P^{i}Pr$_3$) (**3**) (135 mg, 0.210 mmol) in 10 mL of toluene was treated with 82 mg (2.10 mmol) of NaBH$_4$ and, after 2 min, dropwise with 1.5 mL of methanol. After the mixture was stirred for 15 min at room temperature, the solution was filtered through Kieselguhr. The solvent was removed to dryness, and 16 mL of pentane was added. The orange solution was filtered through Kieselguhr and concentrated until a orange solid began to precipitate. After the suspension was kept at −78 °C for 45 min, the orange solid was separated by decantation and dried in vacuo. Yield: 87.8 mg (65%). IR (Nujol): ν(=C=C) 1656 cm^{-1}. ^{1}H

NMR (300 MHz, C_6D_6, 293 K): δ 7.34 (d, ^3J(HH) = 7.2 Hz, 1 H, *o*-Ph), 7.27 (d, ^3J(HH) = 7.5 Hz, 1 H, *o*-Ph), 7.01 (m, 8 H, Ph), 5.24 (d, ^3J(HH) = 10.3 Hz, 1 H, =C=C*H*), 5.11 (s, 5 H, Cp), 2.55 (m, 3 H, PCH), 2.38 (d, ^3J(HH) = 10.3 Hz, 1 H, C*H*Ph$_2$), 0.99 (dd, ^3J(HH) = 7.2 Hz, ^3J(PH) = 13.8 Hz, 9 H, PCCH$_3$), 0.87 (dd, ^3J(HH) = 7.2 Hz, ^3J(PH) = 12.9 Hz, 9 H, PCCH$_3$). ^{31}P{^{1}H} NMR (121.42 MHz, C_6D_6, 293 K): δ 20.4 (s). ^{13}C{^{1}H} NMR (75.42 MHz, C_6D_6, 293 K, plus APT): δ 283.7 (−, d, ^2J(PC) = 13.4 Hz, Os=C), 148.6, 147.9 (−, both s, *ipso*-Ph), 128.6, 128.5, 128.4 128.3 128.1 (+, all s, Ph) 126.1 (+, s, C=*C*H), 86.8 (+, s, Cp), 40.2 (+, s, *C*HPh$_2$), 24.3 (+, d, ^1J(PC) = 29.5 Hz, PCH), 19.6, 19.3 (+, both s, PC*C*H$_3$). Anal. Calcd for $C_{29}H_{38}ClOsP$: C, 54.14; H, 5.94. Found: C, 54.59; H, 5.85. MS (FAB$^+$): *m*/*e* 645 (M$^+$ + H).

X-ray Structure Analysis of Os(η^5-C_5H_5)Cl(=C=C=CPh$_2$)(P^{i}Pr$_3$) (3). Crystals suitable for the X-ray diffraction study were obtained by slow diffusion of pentane into a concentrated solution of **3** in toluene. A summary of crystal data and refinement parameters is reported in Table 2. The black, prismatic crystal, of approximate dimensions 0.3 × 0.2 × 0.2 mm, was glued on a glass fiber and mounted on a Siemens-STOE AED-2 diffractometer. A group of 48 reflections in the range $23 \leq 2\theta \leq 37°$ were carefully centered at 253 K and used to obtain by least-squares methods the unit cell dimensions. Three standard reflections were monitored at periodic intervals throughout data collection: no significant variations were observed. All data were corrected for absorption using a semiempirical method.[33] The structure was solved by Patterson (Os atom, SHELXTL-PLUS[34]) and conventional Fourier techniques and refined by full-matrix least-squares on F^2 (SHELXL93[35]). Anisotropic parameters were used in the last cycles of refinement for all non-hydrogen atoms. The hydrogen atoms were fixed in idealized positions and refined riding on carbon atoms with a common isotropic thermal parameter. Atomic scattering factors, corrected for anomalous dispersion for Os and P, were implemented by the program. The refinement converge to $R_1 = 0.0277$ [$F^2 > 2\sigma(F^2)$] and $wR_2 = 0.0951$ (all data), with weighting parameters $x = 0.0542$ and $y = 0$.

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Supporting Information Available: Tables of atomic coordinates and equivalent isotropic displacement coefficients, anisotropic thermal parameters, experimental details of the X-ray study, and bond distances and angles for **3** (11 pages). Ordering information is given on any current masthead page.

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