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The Five-Coordinate Hydrido−Dihydrogen Complex $[OsH(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2]BF_4$ Acting as a Template for the Carbon−Carbon Coupling between Methyl Propiolate and 1,1-Diphenyl-2-propyn-1-ol

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The five-coordinate hydrido−dihydrogen complex $[OsH(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2]BF_4$ (**1**) reacts with methyl propiolate in acetone to give $[\overline{Os\{C[C(O})OCH_3]{=}CH_2\}\{\eta^1\text{-}OC(CH_3)_2\}(CO)(P^iPr_3)_2]BF_4$ (**2**). The acetone ligand of **2** can be easily displaced by methyl propiolate and 1,1-diphenyl-2-propyn-1-ol to afford $[\overline{Os\{C[C(O})OCH_3]{=}CH_2\}(C{=}CHCO_2CH_3)(CO)(P^iPr_3)_2]BF_4$ (**3**) and $[\overline{Os\{C[C(O})OCH_3]{=}CH_2\}(C{=}C{=}CPh_2)(CO)(P^iPr_3)_2]BF_4$ (**4**), respectively. The structure of **4** has been determined by X-ray diffraction. The geometry around the osmium atom can be rationalized as a distorted octahedron with the phosphine ligands occupying opposite positions. The remaining perpendicular plane is formed by the chelating alkenyl ligand, which acts with a bite angle of 62.8(2)°, the carbonyl group disposed trans to the oxygen atom. Complex **4** reacts with methyllithium to give the alkynyl derivative $[\overline{Os\{C[C(O}){\text{-}}OCH_3]{=}CH_2\}(C{\equiv}CCPh_2CH_3)(CO)(P^iPr_3)_2$ (**5**), which is unstable in methanol and quantitatively evolves into $[\overline{Os\{C[C(O}})OCH_3]{=}CH_2\}(C{\equiv}CCPh_2OCH_3)(CO)(P^iPr_3)_2$ (**6**). Complex **6** can be alternatively obtained from the reaction of **4** with $NaOCH_3$. Complex **4** also reacts with NaCl to afford *trans*-chlorocarbonyl $Os\{C[C(O)OCH_3]{=}CH_2\}Cl(C{=}C{=}CPh_2)(CO)(P^iPr_3)_2$ (**7**) and *cis*-chlorocarbonyl $Os\{C[C(O)OCH_3]{=}CH_2\}Cl(C{=}C{=}CPh_2)(CO)(P^iPr_3)_2$ (**8**). At 60 °C, toluene solutions of **7** and **8** yield the allenyl derivative $\overline{Os\{C[C({=}CH_2)C(O}){\text{-}}OCH_3]{=}C{=}CPh_2]Cl(CO)(P^iPr_3)_2$ (**9**) as a result from the migratory insertion of the allenylidene ligand into the Os−C(alkenyl) bond of **7** and **8**. The structure of **9** has been also determined by X-ray diffraction. The geometry around the osmium atom can be described as a distorted octahedron with the phosphine ligands occupying two relative trans positions. The ideal equatorial plane is formed by the chelate allenyl ligand which acts with a bite angle of 78.66(12)°, the carbonyl group disposed trans to the oxygen atom.

Introduction

The formation of carbon−carbon bonds mediated by transition metal complexes has emerged in its own right over the last few years as an important step in organic synthesis.[1] In an effort to develop new models for homogeneous systems effective in the synthesis of functionalized organic molecules from basic hydrocarbon units, we are carrying out a research program centered in the use of osmium and ruthenium hydrido complexes as precursors for C−C bonds.

In 1986 we observed that the reactions of the five-coordinate hydrido complexes $MHCl(CO)(P^iPr_3)_2$ with terminal alkynes led to the alkenyl derivatives $M\{(E)\text{-}CH{=}CHR\}Cl(CO)(P^iPr_3)_2$ (M = Os, Ru; R = Ph, H).[2] Recently, we have observed that treatment of these alkenyl complexes with main group organometallic compounds (R'Li, R'MgBr) produces olefin species of type $M(R'CH{=}CHR)(CO)(P^iPr_3)_2$.[3] These transformations most probably involve the replacement of the Cl^- anion by the organic fragment R′ and the subsequent reductive carbon−carbon coupling of the η^1-carbon

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ligand.[3,4] In agreement with this, it has also been observed that the chloro-styryl ruthenium(II) complex $\mathrm{Ru\{(\mathit{E})\text{-}CH{=}CHPh\}Cl(CO)(P^iPr_3)_2}$ reacts with $\mathrm{CH_2{=}CHMgBr}$ to give the styryl-vinyl derivative $\mathrm{Ru(CH{=}CH_2)\{\text{-}(\mathit{E})\text{-}CH{=}CHPh\}(CO)(P^iPr_3)_2}$ which affords the π-(phenyl)butadiene complex $\mathrm{Ru(\eta^4\text{-}C_4H_5Ph)(CO)(P^iPr_3)_2}$.[3a] In contrast to the five-coordinate derivative $\mathrm{Ru(CH{=}CH_2)\{(\mathit{E})\text{-}CH{=}CHPh\}(CO)(P^iPr_3)_2}$, the reductive elimination of 2-methylhexatriene from the six-coordinate complex $\mathrm{Ru(CH{=}CH_2)\{(\mathit{E})\text{-}CH{=}CHC(CH_3){=}CH_2\}(CO)_2(P^iPr_3)_2}$ is not thermally activated. However, the carbon−carbon coupling of the alkenyl ligands to give $\mathrm{[Ru\{\eta^3\text{-}CH_2CHCHCH{=}C(CH_3)_2\}(CO)_2(P^iPr_3)_2]BF_4}$ can be carried out by protonation with $\mathrm{HBF_4}$.[5]

Most recently, we have reported that the dihydrogen complex $\mathrm{OsH_2(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2}$ reacts with phenylacetylene to give the bis-alkynyl compound $\mathrm{Os(C_2Ph)_2(CO)(P^iPr_3)_2}$.[6] In 2-propanol, the C≡C triple bond of one of the two alkynyl ligands of this complex can be selectively broken by reaction with water to give $\mathrm{Os(CH_2Ph)(C_2Ph)(CO)_2(P^iPr_3)_2}$. In methanol and in the presence of trifluoroacetic acid, the alkynyl-benzyl compound isomerizes into the osmaindene derivative $\mathrm{Os\{C(CH_2Ph){=}CHC_6H_4\}(CO)_2(P^iPr_3)_2}$. In the presence of tetrafluoroboric acid, in addition to the isomerization, the π-allyl derivative $\mathrm{[Os\{\eta^3\text{-}CH(Ph)CHCH(Ph)\}(CO)_2(P^iPr_3)_2]BF_4}$ is produced as a result of the addition of the proton from the acid and the carbon−carbon coupling of the benzyl and alkynyl fragments of $\mathrm{Os(CH_2Ph)(C_2Ph)(CO)_2(P^iPr_3)_2}$.[7]

Several hundred stable dihydrogen compounds have been prepared since the discovery of complex $\mathrm{W(\eta^2\text{-}H_2)(CO)_3(P^iPr_3)_2}$ by Kubas *et al.* in 1984.[8] The spectroscopic characterization, some theoretical aspects on the nature and stabilization on the $\mathrm{M(\eta^2\text{-}H_2)}$ bond and the roles they can play during some homogeneous catalytic processes have been also the subject of intensive studies in recent years.[9] Initially, they were viewed as reaction intermediates stabilized by sterically demanding phosphines. However, the known dihydrogen chemistry now indicates that dihydrogen complexes are more than reactive intermediates and, therefore, must be considered to have an identity and chemistry of their own.

In this context and as a continuation of our research program, we prove that dihydrogen complexes are also useful starting materials to carry out carbon−carbon coupling reactions. In this paper we report the introduction in a sequential manner of methyl propiolate and 1,1-diphenyl-2-propyn-1-ol to the osmium atom of the unsaturated dihydrogen complex $\mathrm{[OsH(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2]BF_4}$ and the carbon−carbon coupling between the resulting organic ligands.

Results and Discussion

1. Sequential Introduction of Methyl Propiolate and 1,1-Diphenyl-2-propyn-1-ol. The addition of 1 equiv of methyl propiolate to an acetone solution of $\mathrm{[OsH(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2]BF_4}$ (**1**) affords a yellow solution from which a crystalline solid analyzing for $\mathrm{[Os\{C[C(O)OCH_3]{=}CH_2\}\{\eta^1\text{-}OC(CH_3)_2\}(CO)(P^iPr_3)_2]BF_4{\cdot}(CH_3)_2CO}$ (**2**) was isolated in 67% yield, by addition of diethyl ether (Scheme 1).

In the IR spectrum of **2**, the most noticeable features are the absorptions due to the $[\mathrm{BF_4}]^-$ anion with T_d symmetry centered at 1060 $\mathrm{cm^{-1}}$ indicating that the anion is not coordinated to the metallic center, and the ν(C=O) band of the carbonyl group of the coordinated acetone molecule at 1635 $\mathrm{cm^{-1}}$, suggesting that the acetone ligand coordinates to the metal atom by the oxygen atom.[10] In addition, a C=O stretching frequency at 1564 $\mathrm{cm^{-1}}$ corresponding to the coordinated ester group of the alkenyl ligand should be mentioned.[11] In agreement with η^1-oxygen coordination bonding mode of the acetone ligand, the $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR spectrum of **2** shows a singlet at 222.8 ppm for the carbon atom of the acetone carbonyl group. The resonance of the α-carbon atom of the alkenyl ligand appears at 121.7 ppm as a triplet with a C−P coupling constant of 6.8 Hz, while that corresponding to the β-carbon atom is observed at 127.5 ppm as a singlet. In the ^{1}H NMR spectrum, the $=\mathrm{CH_2}$ protons give rise to two broad singlets at 6.74 and 5.44 ppm. The $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum contains a singlet at 13.1 ppm.

The acetone ligand of **2** can be easily displaced by a second molecule of methyl propiolate. Thus, treatment of **2** in acetone with 1.3 equiv of methyl propiolate affords the vinylidene derivative $\mathrm{[Os\{C[C(O)OCH_3]{=}CH_2\}\{C{=}CHCO_2CH_3\}(CO)(P^iPr_3)_2]BF_4}$ (**3**) which was isolated as an ocher solid in 60% yield (Scheme 1).

The presence of a vinylidene ligand in **3** is strongly supported by the $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR spectrum, which shows a triplet at 311.7 ppm with a C−P coupling constant of 7.2 Hz corresponding to the $\mathrm{Os{=}\mathit{C}{=}}$ carbon atom. The resonance of the β-carbon atom of the vinylidene ligand appears at 105.2 ppm as a singlet, while the resonances of the alkenyl group are observed at 137.2 (t, $J_{\mathrm{C-P}}$ = 8.9 Hz, Os−C) and 136.8 (s, $=\mathrm{CH_2}$) ppm. In the ^{1}H NMR spectrum the $=\mathrm{CH_2}$ protons give rise to two broad singlets at 7.58 and 6.51 ppm. The resonance of the $=$CH− proton of the vinylidene ligand is also observed as a broad singlet at 2.94 ppm. The $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum contains a singlet at 25.1 ppm.

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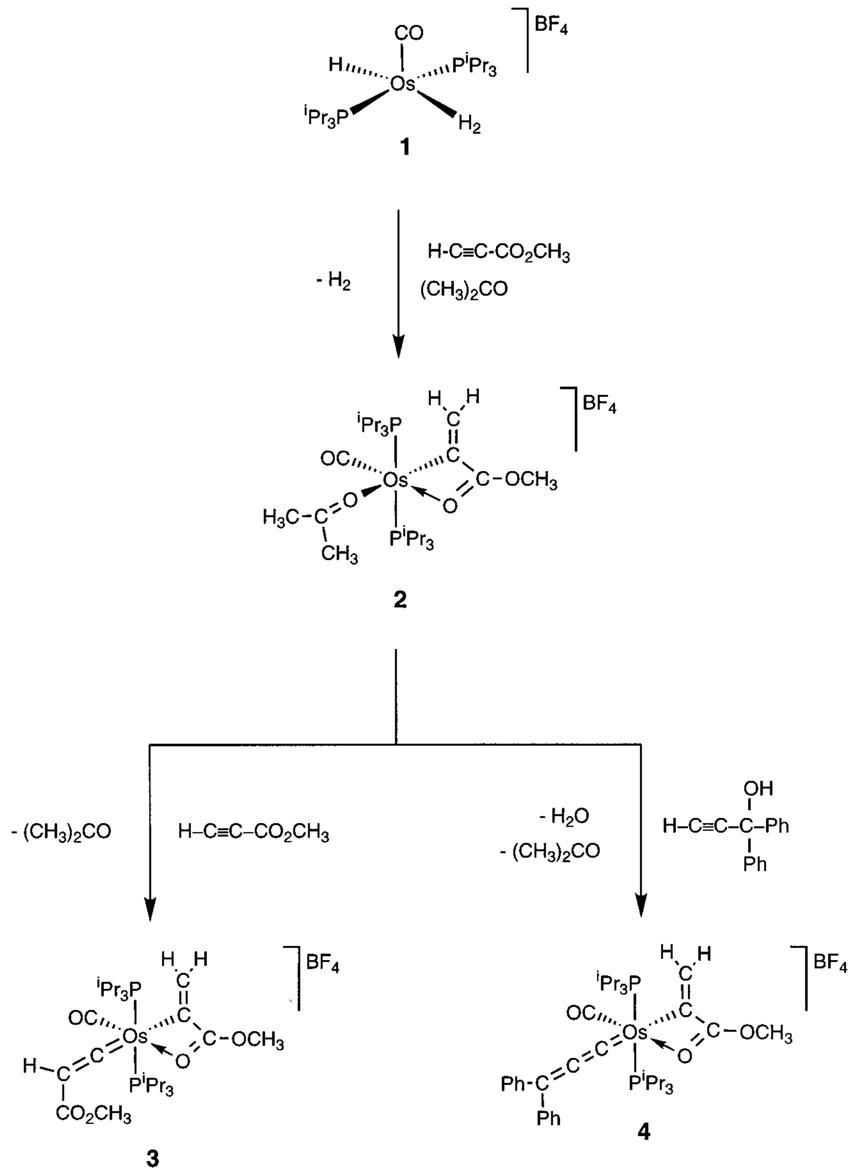
Scheme 1



The acetone molecule of **2** can be also displaced by 1,1-diphenyl-2-propyn-1-ol. In this case the reaction product is the allenylidene derivative $[Os\{C[C(O)\text{-}OCH_3]{=}CH_2\}\{C{=}C{=}CPh_2\}(CO)(P^iPr_3)_2]BF_4$ (**4**, in Scheme 1). The reaction most probably involves the formation of a hydroxyvinylidene intermediate, which dehydrates spontaneously.[12]

Complex **4** was isolated as a dark red solid in 94% yield and characterized by elemental analysis, IR, ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopy, and X-ray diffraction. A view of the molecular geometry is shown in Figure 1. Selected bond distances and angles are listed in Table 1.

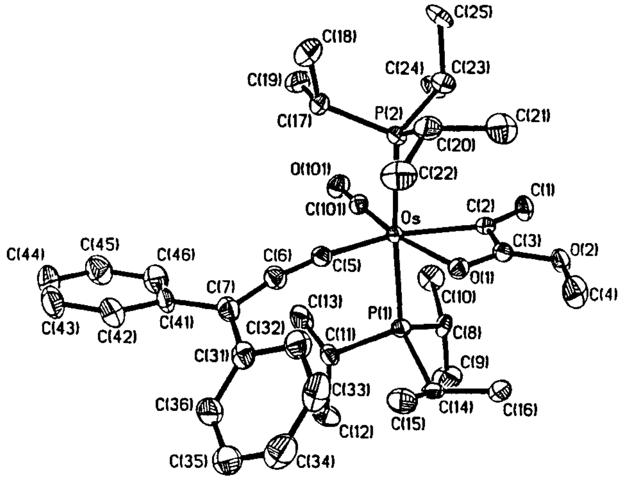


Figure 1. Molecular diagram of complex $[Os\{C[C(O)\text{-}OCH_3]{=}CH_2\}(C{=}C{=}CPh_2)(CO)(P^iPr_3)_2]BF_4$ (**4**).

The geometry of the complex can be rationalized as a distorted octahedron with the two phosphorus atoms of the triisopropylphosphine ligands occupying opposite positions (P(1)−Os−P(2) = 175.67(5)°). The ideal equatorial plane is formed by the atoms C(2) and O(1) of the chelating alkenyl ligand, defining a four-membered ring with the osmium atom (C(2)−Os−O(1) = 62.8(2)°—the atom C(5) of the allenylidene group disposed *trans* to

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Table 1. Selected Bond Lengths (Å) and Angles (deg) for the Complex $[Os\{C[C(O)OCH_3]{=}CH_2\}(C{=}C{=}CPh_2)(CO)(P^iPr_3)_2]BF_4$ (4)

Os−P(1)	2.457(2)	C(3)−O(1)	1.259(7)
Os−P(2)	2.446(2)	C(3)−O(2)	1.317(6)
Os−O(1)	2.242(4)	O(2)−C(4)	1.456(7)
Os−C(2)	2.146(6)	C(101)−O(101)	1.158(6)
Os−C(101)	1.826(5)	C(5)−C(6)	1.250(8)
Os−C(5)	1.947(6)	C(6)−C(7)	1.376(9)
C(1)−C(2)	1.325(8)	C(7)−C(31)	1.472(10)
C(2)−C(3)	1.464(7)	C(7)−C(41)	1.462(9)

P(1)−Os−P(2)	175.67(5)	Os−C(2)−C(1)	147.6(4)
P(1)−Os−O(1)	88.4(2)	Os−C(2)−C(3)	90.8(3)
P(1)−Os−C(2)	87.6(2)	Os−O(1)−C(3)	92.3(3)
P(1)−Os−C(101)	91.5(3)	Os−C(101)−O(101)	178.9(6)
P(1)−Os−C(5)	90.7(2)	Os−C(5)−C(6)	173.5(6)
P(2)−Os−O(1)	88.9(2)	C(1)−C(2)−C(3)	121.5(5)
P(2)−Os−C(2)	88.1(2)	C(2)−C(3)−O(1)	114.1(5)
P(2)−Os−C(101)	90.4(3)	C(2)−C(3)−O(2)	123.0(5)
P(2)−Os−C(5)	93.0(2)	C(3)−O(2)−C(4)	117.3(5)
O(1)−Os−C(2)	62.8(2)	O(1)−C(3)−O(2)	122.9(5)
O(1)−Os−C(101)	169.2(2)	C(5)−C(6)−C(7)	171.2(7)
O(1)−Os−C(5)	96.3(2)	C(6)−C(7)−C(31)	118.2(6)
C(2)−Os−C(101)	106.5(2)	C(6)−C(7)−C(41)	120.2(6)
C(2)−Os−C(5)	159.0(2)	C(31)−C(7)−C(41)	121.6(6)
C(101)−Os−C(5)	94.5(2)		

C(2) (C(5)−Os−C(2) = 159.0(2)°) and the carbonyl ligand located *trans* to O(1) (C(101)−Os−O(1) = 169.2(2)°).

The four-membered metallacycle is almost planar (maximum deviation 0.014 Å). The Os−C(2) distance is 2.146(6) Å, longer than the Os−C distances found in the alkenylosmium(II) complexes $Os\{(E)\text{-}CH{=}CHPh\}Cl(CO)(P^iPr_3)_2$ (1.99(1) Å),[2] $[Os\{CH{=}C(I)C(OCH_3){=}O\}(\eta^6\text{-}C_6H_6)(P^iPr_3)]^+$ (2.02(1) Å),[11a] and $Os\{CH{=}CHC(OCH_3){=}O\}(C_2CO_2CH_3)(CO)(P^iPr_3)_2$ (2.103(4) Å).[6a] The Os−O(1) distance of 1.242(4) Å is about 0.05 Å longer than the related bond length in the complex $Os\{CH{=}CHC(OCH_3){=}O\}(C_2CO_2CH_3)(CO)(P^iPr_3)_2$ (2.188(2) Å), where the metallacycle is a five-membered ring. The C=O bond in the four-membered ring of **4** is also longer than that found in the five-membered ring of the above mentioned complex (1.259 (7) *versus* 1.244(5) Å). However, the exocyclic C(1)−C(2) double bond (1.325(8) Å) is shorter than the endocyclic carbon−carbon double bond contained inside the five-membered ring of $Os\{CH{=}CHC(OCH_3){=}O\}(C_2CO_2CH_3)(CO)(P^iPr_3)_2$ (1.351(6) Å).

The diphenylallenylidene ligand is bound to the metal in a nearly linear fashion with Os−C(5)−C(6) and C(5)−C(6)−C(7) angles of 173.5(6) and 171.2(7)°, respectively. The Os−C(5) bond length of 1.947(6) Å is about 0.5 Å longer than the osmium−diphenylallenylidene separation found in the complex $[Os(\eta^5\text{-}C_9H_7)(C{=}C{=}CPh_2)(PPh_3)_2]^+$ (1.895(4) Å).[13] The value of the osmium−diphenylallenylidene separation in **4** lies between the values found for the osmium−alkynyl separation in $Os\{CH{=}CHC(OCH_3){=}O\}(C_2CO_2CH_3)(CO)(P^iPr_3)_2$ (1.977(4) Å)[6a] and the osmium−carbene separation in $OsCl_2(CHCH_2Ph)(CO)(P^iPr_3)_2$ (1.887(9) Å).[14] The C(5)−C(6) distance (1.250(8) Å) compares well with the related bond length found in the complex $[Os(\eta^5\text{-}C_9H_7)(C{=}C{=}CPh_2)(PPh_3)_2]^+$ (1.265(6) Å).[13] However, it is significantly shorter than the bond length of the exocyclic carbon−carbon double bond C(1)−C(2) and longer than the bond length of the carbon−carbon triple bond in the alkynyl ligand of the complex $Os\{CH{=}CHC(OCH_3){=}O\}(C_2CO_2CH_3)(CO)(P^iPr_3)_2$ (1.212(6) Å).[6a] These structural parameters indicate a substantial contribution of the canonical form $[M]{-}C{\equiv}C{-}C^+Ph_2$ to the structure of **4**. A similar conclusion has been reached in the structural analysis of other allenylidene complexes.[12,13,15]

In agreement with the presence of the allenylidene ligand in **4**, the IR spectrum shows the characteristic ν(C=C=C) band for this type of ligands[16] at 1954 cm^{-1} and the $^{13}C\{^1H\}$ NMR spectrum contains a triplet at 279.3 ppm with a C−P coupling constant of 9.1 Hz, which was assigned to the α-carbon atom, and two singlets at 197.9 and 156.0 ppm corresponding to β- and γ-carbon atoms, respectively. Furthermore, the spectrum contains a triplet at 139.7 ppm with a C−P coupling constant of 11.2 Hz and a singlet at 139.6 ppm, due to the C(2) and C(1) atoms of the alkenyl ligand. In the ^1H NMR spectrum, the most noticeable resonances of this ligand are two double triplets at 7.20 and 6.48 ppm with H−H and H−P coupling constants of 2.1 and 2.4 Hz, respectively, corresponding to the $=CH_2$ protons. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 19.7 ppm.

Complex **4** reacts with methyllithium to give the alkynyl derivative $Os\{C[C(O)OCH_3]{=}CH_2\}(C{\equiv}CCPh_2CH_3)(CO)(P^iPr_3)_2$ (**5**) in 82% yield. This complex, which is a result of the addition of the methyl group at the γ-carbon atom of the allenylidene of **4**, is unstable in methanol and quantitatively evolves into $Os\{C[C(O)OCH_3]{=}CH_2\}(C{\equiv}CCPh_2OCH_3)(CO)(P^iPr_3)_2$ (**6**) and methane. Alternatively, complex **6** can be obtained in 69% yield by reaction of **4** with sodium methoxide in dichloromethane. Complex **5** regenerates **4** in the presence of HBF_4 (Scheme 2).

We note that the ruthenium−allenylidene complexes $[Ru(\eta^5\text{-}C_9H_7)(C{=}C{=}CPh_2)L(PPh_3)]PF_6$ (L = CO, PPh_3) also undergo regioselective nucleophilic attacks at C_γ to yield alkynyl derivatives of the type $Ru(\eta^5\text{-}C_9H_7)\{C{\equiv}C{-}C(Nu)Ph_2\}L(PPh_3)$.[15f,17] In addition, it should be mentioned that rhodium compounds containing γ-functionalized alkynyl groups have been recently prepared

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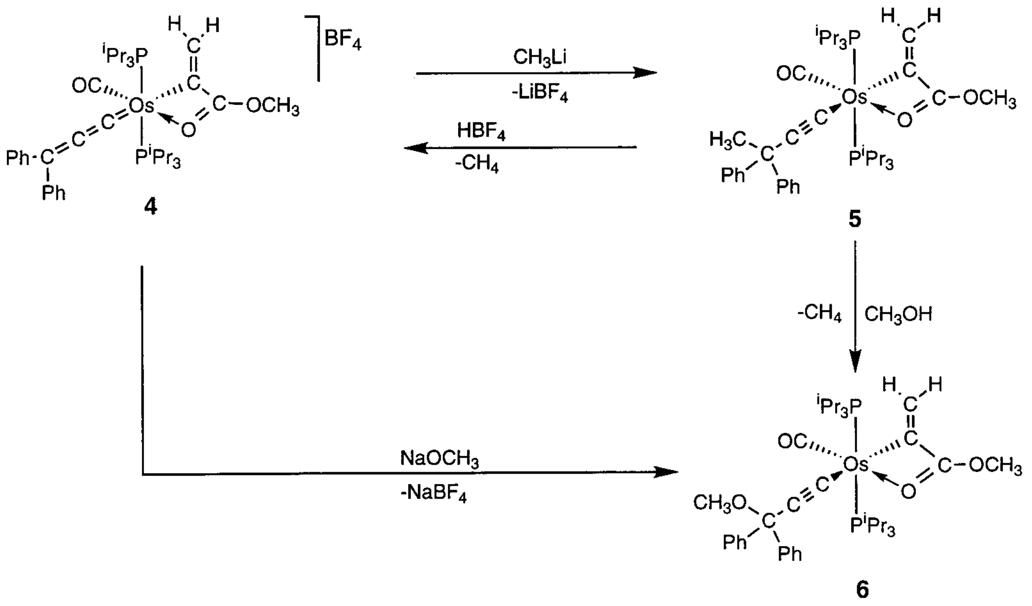
Scheme 2



by migratory insertion of an allenylidene unit into Rh−OR (R = Ph, CH_3CO) bonds.[18]

Complexes **5** and **6** were isolated as red (**5**) or yellow (**6**) solids and characterized by elemental analysis, IR, ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopy. The most noticeable absorptions in the IR spectra are the $\nu(C{\equiv}C)$ bands corresponding to the alkynyl ligands which appear at 2088 (**5**) and 2061 (**6**) cm^{-1}. In the $^{13}C\{^1H\}$ NMR spectra, these ligands displayed triplets at 103.3 (**5**) and 110.9 (**6**) ppm with C−P coupling constants of 12.4 and 11.9 Hz, respectively, which were assigned to the Os−C≡ carbon atoms and two singlets at 119.8 (**5**) and 114.4 (**6**) ppm corresponding to the β-carbon atoms. The resonances due to the α- and β-carbon atoms of the alkenyl group appeared at about 145 and 127 ppm, respectively, the first ones as triplets with C−P coupling constants of 7.4 (**5**) and 7.5 Hz (**6**) and the second ones as singlets. The $^{31}P\{^1H\}$ NMR spectra show singlets at 14.0 (**5**) and 13.8 (**6**) ppm.

2. Carbon−Carbon Coupling between the Allenylidene and Alkenyl Ligands of 4. The carbonyl group of the ester coordinated to the osmium atom in **4** can be easily displaced from the metal by reaction with NaCl. Treatment of a methanol solution of **4** with sodium chloride at room temperature gives after 1 h a purple solid (40% yield) and a purple solution. From the solution, other purple solid was obtained in 16% yield.

According to the elemental analysis, the composition of both solids corresponds to a 1:1 adduct of the fragments $Os\{C[C(O)OCH_3]{=}CH_2\}(C{=}C{=}CPh_2)(CO)(P^iPr_3)_2$ and Cl. However, there are significant differences between them as far as their spectroscopic data are concerned, mainly between the values of the stretching frequency of the carbonyl ligands and the chemical shifts of the Os=C= resonances in the $^{13}C\{^1H\}$ NMR spectra. The $\nu(C{\equiv}O)$ band of the first solid appears at 1901 cm^{-1}, while that of the second solid is shifted by 13 cm^{-1} to higher wavenumbers (1914 cm^{-1}). The resonance of the α-carbon atom of the allenylidene ligand of the first solid is observed at 268.0 (t, J_{C-P} = 10.1 Hz) ppm, while the resonance of the α-carbon atom of the allenylidene ligand of the second solid appears at 284.1 (t, J_{C-P} = 11.0 Hz) ppm, thus shifted by 16.1 ppm to lower field. Because the chloride ligand has a higher π-donor power than the α-carbon atom of the alkenyl ligand and the carbonyl and allenylidene ligands are π-acceptor groups,[19] we assume that the first solid corresponds to *trans*-chlorocarbonyl-$Os\{C[C(O)OCH_3]{=}CH_2\}Cl(C{=}C{=}CPh_2)(CO)(P^iPr_3)_2$ (**7**) and the second solid to *cis*-chlorocarbonyl-$Os\{C[C(O)OCH_3]{=}CH_2\}Cl(C{=}C{=}CPh_2)(CO)(P^iPr_3)_2$ (**8**).

At 60 °C, toluene solutions of **7** and **8** yield $Os\{C[C({=}CH_2)C(O)OCH_3]{=}C{=}CPh_2\}Cl(CO)(P^iPr_3)_2$ (**9**) after 23 h. This allenyl complex, which is the result of the coupling between the allenylidene and alkenyl ligands, was obtained as an orange solid in 82% yield (Scheme 3).

A view of the molecular geometry of **9** is shown in Figure 2. Selected bond distances and angles are listed in Table 2. The geometry of the complex can be rationalized as a distorted octahedron with the two phosphorus atoms of the triisopropylphosphine ligands occupying opposite positions (P(1)−Os−P(2) = 172.85(4)°). The ideal equatorial plane is formed by atoms C(24) and O(2) of the chelating allenyl ligand —defining with the osmium atom a five-membered ring (C(24)−Os−O(2) = 78.66(12)°)—the carbonyl group disposed trans to O(2) (C(19)−Os−O(2) = 173.45(14)°) and the chlorine atom located trans to C(24) (Cl−Os−C(24) = 161.02(10)°).

The five-membered metallacycle is not strictly planar; the atoms C(24) and C(22) deviate from the best plane through the five atoms by 0.159(4) and −0.147(4) Å, respectively. The bond length Os−C(24) (2.091(4) Å) is that expected for an $Os{-}C_{sp^2}$ single bond and comparable to the related distance in $Os(CH{=}C{=}CPh_2)Cl_2$-

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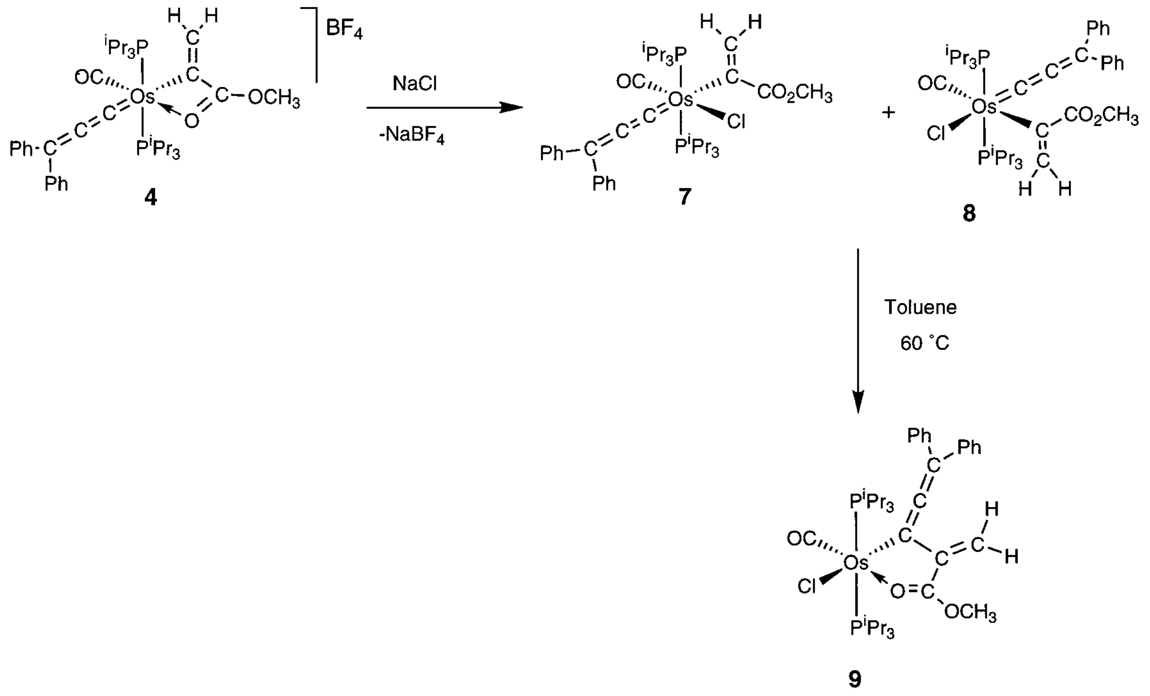
Scheme 3



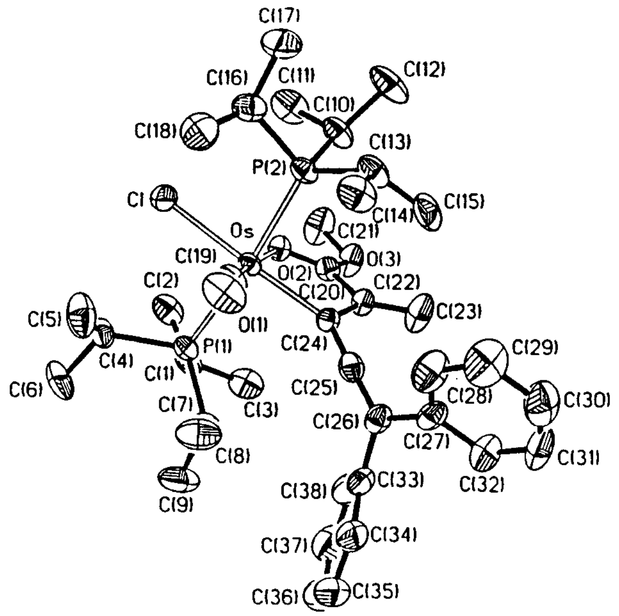


Figure 2. Molecular diagram of complex $[Os\{C[C(=CH_2)C(O)OCH_3]=C=CH_2\}Cl(CO)(P^iPr_3)_2$ (**9**).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for the Complex $Os\{C[C=CH_2)C(O)$-$OCH_3]=C=CPh_2\}Cl(CO)(P^iPr_3)_2$ (9)

Os–P(1)	2.4257(10)	O(3)–C(21)	1.457(5)
Os–P(2)	2.4375(10)	C(20)–C(22)	1.457(5)
Os–Cl	2.4875(10)	C(22)–C(23)	1.327(6)
Os–C(19)	1.818(4)	C(22)–C(24)	1.510(5)
Os–C(24)	2.091(4)	C(24)–C(25)	1.304(5)
Os–O(2)	2.214(2)	C(25)–C(26)	1.322(6)
C(19)–O(1)	1.166(4)	C(26)–C(27)	1.505(5)
O(2)–C(20)	1.241(4)	C(26)–C(33)	1.485(6)
C(20)–O(3)	1.326(5)		

P(1)–Os–P(2)	172.85(4)	Os–C(24)–C(25)	135.8(3)
P(1)–Os–Cl	86.55(4)	Os–C(24)–C(22)	110.7(3)
P(1)–Os–C(19)	90.32(12)	Os–O(2)–C(20)	112.7(2)
P(1)–Os–C(24)	91.19(10)	C(25)–C(24)–C(22)	113.5(4)
P(1)–Os–O(2)	92.77(7)	C(24)–C(25)–C(26)	173.7(4)
P(2)–Os–Cl	86.74(4)	C(25)–C(26)–C(27)	120.6(4)
P(2)–Os–C(19)	88.83(12)	C(25)–C(26)–C(33)	121.1(4)
P(2)–Os–C(24)	95.96(10)	C(27)–C(26)–C(33)	118.3(4)
P(2)–Os–O(2)	88.81(7)	C(24)–C(22)–C(23)	127.1(4)
Cl–Os–C(19)	103.33(14)	C(24)–C(22)–C(20)	112.8(3)
Cl–Os–C(24)	161.02(10)	C(23)–C(22)–C(20)	120.1(4)
Cl–Os–O(2)	82.63(7)	C(22)–C(20)–O(3)	117.2(4)
C(19)–Os–C(24)	95.5(2)	C(22)–C(20)–O(2)	122.0(4)
C(19)–Os–O(2)	173.45(14)	O(3)–C(20)–O(2)	120.7(4)
C(24)–Os–O(2)	78.66(12)	C(20)–O(3)–C(21)	117.1(3)
Os–C(19)–O(1)	176.3(4)		

$(NO)(P^iPr_3)_2$ (2.110(5) Å),[20] **4** (2.146(6) Å), and the previously mentioned alkenyl complexes. The C(24)–C(25) (1.304(5) Å) and C(25)–C(26) (1.322(6) Å) distances, as well as the C(24)–C(25)–C(26) angle (173.7(4)°), which are in agreement with those reported for other transition metal compounds of this type,[21] strongly support the allenyl formulation.[22]

Characteristic spectroscopic features of **9** are the C=C=C stretching frequency in the IR spectrum at 1919 cm^{-1} and the three resonances in the $^{13}C\{^1H\}$ NMR spectrum at 210.4, 140.6, and 88.3 ppm attributable to the C(25), C(26), and C(24) allenyl carbon atoms. The first and third resonances appear as triplets with C–P coupling constants of 2.3 and 6.4 Hz, respectively,

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while the second one is observed as a singlet. The resonances of the C(22) and C(23) olefinic carbon atoms are observed at 122.6 and 105.3 ppm as singlets. In the ^1H NMR spectrum, the vinylic $CH_2{=}$ resonances appear at 5.95 and 5.74 ppm as singlets. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 7.5 ppm.

Concluding Remarks

This study has revealed that the five-coordinate hydrido−dihydrogen complex $[OsH(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2]BF_4$ allows the access of methyl propiolate and 1,1-diphenyl-2-propyn-1-ol into the osmium atom and the C−C coupling between the resulting carbon-donor ligands.

In an initial stage the alkyne molecules are introduced in a sequential manner. Thus, the complex $[OsH(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2]BF_4$ reacts with methyl propiolate in acetone to give the alkenyl derivative $[\overline{Os\{C[C(O}})OCH_3]{=}CH_2\}\{\eta^1\text{-}OC(CH_3)_2\}(CO)(P^iPr_3)_2]BF_4$, which by addition of 1,1-diphenyl-2-propyn-1-ol affords the alkenyl-allenylidene compound $[\overline{Os\{C[C(O}})OCH_3]{=}CH_2\}(C{=}C{=}CPh_2)(CO)(P^iPr_3)_2]BF_4$.

Despite the fact that the above mentioned alkenyl−allenylidene complex is stable in solution and does not evolve by migratory insertion of the allenylidene ligand into the Os−C(alkenyl) bond, in the subsequent stage of the process, we prove that the addition of NaCl leads to the C−C coupling to give the allenyl derivative $\overline{Os\{C[C({=}CH_2)C(O}})OCH_3]{=}C{=}CPh_2\}Cl(CO)(P^iPr_3)_2]BF_4$ *via* the intermediate $Os\{C[C(O)OCH_3]{=}CH_2\}Cl(C{=}C{=}CPh_2)(CO)(P^iPr_3)_2$, which is isolated as two different isomers.

In conclusion, dihydrogen complexes are useful starting materials to carry out C−C coupling reactions, thus confirming that they have an identity and chemistry of their own.

Experimental Section

General Considerations. All reactions were carried out with rigorous exclusion of air using Schlenk-tube techniques. Solvents were dried by known procedures and distilled prior to use. $[OsH(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2]BF_4$ (**1**) was prepared by a published method.[23] 1,1-Diphenyl-2-propyn-1-ol (ABCR) was purified by column chromatography (Silica-gel) prior to use. Methyl propiolate was used as purchased.

Physical Measurements. Infrared spectra were run on either a Perkin-Elmer 883 or a Nicolet 550 spectrometer as either solids (Nujol mulls or polyethylene sheets) or solutions (NaCl cell windows). Elemental analyses were performed with a Perkin-Elmer 2400 CHNS/O analyzer. NMR spectra were recorded on a Varian UNITY 300, a GEMINI 300, or a Bruker 300 AXR spectrometer. Chemical shifts are expressed in ppm upfield from Me_4Si (^1H and ^{13}C) and (85%) H_3PO_4 (^{31}P). Coupling constants J and N ($N = J(HP) + J(HP')$ for ^1H and $N = J(CP) + J(CP')$ for ^{13}C) are given in hertz.

Preparation of $[\overline{Os\{C[C(O}})OCH_3]{=}CH_2\}\{\eta^1\text{-}OC(CH_3)_2\}(CO)(P^iPr_3)_2]BF_4\cdot(CH_3)_2CO$ (2). A solution of $OsH(CO)(\eta^2\text{-}H_2)(P^iPr_3)_2BF_4$ (**1**) (500 mg, 0.79 mmol) in acetone (10 mL) was treated with methyl propiolate (66.6 μL, 0.80 mmol). After the mixture was stirred for 1 h at room temperature, a beige solid was obtained. It was separated by decantation, washed with ether, and dried *in vacuo*. Yield: 434 mg (67%). IR (Nujol, cm^{-1}): $\nu(C{\equiv}O)$ 1894 vs; $\nu(C{=}O)_{free}$ 1703 s; $\nu(C{=}O)_{coord}$ 1635 vs; $\nu(C{=}O)$ 1564 s; $\nu(BF_4)$ 1060 br. ^1H NMR (300 MHz, 233 K, CD_2Cl_2) δ: 6.74, 5.44 (both s, 1H each, $=CH_2$), 3.95 (s, 3H, OCH_3), 2.49 (s, 6H, $OC(CH_3)_{2\,coord}$), 2.22 (m, 6H, PCH), 2.11 (s, 6H, $OC(CH_3)_{2\,free}$), 1.25 (dvt, 36H, $J(HH) = 7.1$ Hz, $N = 14.2$ Hz, $PCCH_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, 233 K, CD_2Cl_2) δ 13.1 (s). $^{13}C\{^1H\}$ NMR (75.4 MHz, 233 K, CD_2Cl_2) δ: 222.8 (s, $OC(CH_3)_{2\,coord}$), 207.8 (s, $OC(CH_3)_{2\,free}$), 183.0 (s, $C(O)OCH_3$), 181.3 (t, $J(PC) = 8.3$ Hz, $C{\equiv}O$), 127.5 (s, $Os{-}C{=}CH_2$), 121.7 (t, $J(PC) = 6.8$ Hz, $Os{-}C{=}CH_2$), 53.4 (s, OCH_3), 32.2 (s, $OC(CH_3)_{2\,coord}$), 30.9 (s, $OC(CH_3)_{2\,free}$), 24.2 (vt, $N = 24.7$ Hz, PCH), 18.7, 18.4 (both s, $PCHCH_3$). Anal. Calcd for $C_{29}H_{59}BF_4O_5OsP_2$: C, 42.12; H, 7.20. Found: C, 41.98; H, 6.65.

Preparation of $[\overline{Os\{C[C(O}})OCH_3]{=}CH_2\}(C{=}CHCO_2CH_3)(CO)(P^iPr_3)_2]BF_4$ (3). A yellow solution of **2** (134 mg, 0.19 mmol) in acetone (8 mL) was treated with methyl propiolate (20 μL, 0.24 mmol). After it was stirred for 2 h at room temperature, the solution was concentrated to 1 mL and 6 mL of diethyl ether was added. An ocher precipitate was formed. The solid was decanted, washed with 1 mL of diethyl ether, and dried *in vacuo*. The product is an ocher solid. Yield 90 mg (60%). IR (Nujol, cm^{-1}): $\nu(C{\equiv}O)$ 2060 s, $\nu(C{=}C{=}Os)$ 1710 m, $\nu(C{=}C)$ 1610 m, $\nu(C{=}O)$ 1570 s, $\nu(BF_4)$ 1060 br. ^1H NMR (300 MHz, 293 K, $CDCl_3$) δ: 7.58 and 6.51 (both br, 1H each, $=CH_2$), 4.04 and 3.60 (both s, 3H each, $-OCH_3$), 2.94 (s, 1H, $=CHCO_2CH_3$), 2.70 (m, 6H, $PCHCH_3$), 1.30 (dvt, 36H, $J(HH) = 7.2$ Hz, $N = 14.7$ Hz, $PCHCH_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, 293 K, $CDCl_3$) δ: 25.1 (s). $^{13}C\{^1H\}$ NMR (75.4 MHz, 293 K, $CDCl_3$) δ 311.7 (t, $J(PC) = 7.2$, $Os{=}C$), 186.3 (s, $OsOCOCH_3$), 185.0 (t, $J(PC) = 8.1$ Hz, $Os{-}CO$), 160.0 (s, CO_2CH_3), 137.2 (t, $J(PC) = 8.9$ Hz, $Os{-}C(CO_2CH_3){=}CH_2$), 136.8 (s, $Os{-}C(CO_2CH_3){=}CH_2$), 105.2 (s, $Os{=}C{=}C$), 54.3 and 51.5 (s, both OCH_3), 25.3 (vt, $N = 25.8$ Hz, PCH), 20.6 and 19.1 (both s, $PCHCH_3$). Anal. Calcd for $C_{27}H_{51}BF_4O_5OsP_2$: C, 40.80; H, 6.47. Found: C, 40.43; H, 6.38.

Preparation of $[\overline{Os\{C[C(O}})OCH_3]{=}CH_2\}(C{=}C{=}CPh_2)(CO)(P^iPr_3)_2]BF_4$ (4). A solution of **2** (450 mg, 0.54 mmol) in dichloromethane (10 mL) was treated with 1,1-diphenyl-2-propyn-1-ol (128.2 mg, 0.61 mmol). The solution became purple instantaneously. After the mixture was stirred for 6 h at room temperature, the solution was concentrated to 1 mL. Addition of ether caused the precipitation of a purple solid, which was decanted, washed with ether, and dried *in vacuo*. Yield: 481 mg (94%). IR (Nujol, cm^{-1}): $\nu(C{=}C{=}C)$ 1954 s, $\nu(C{\equiv}O)$ 1915 vs, $\nu(C{=}C)$ 1600 w, $\nu(C{=}O)$ 1552 s, $\nu(BF_4)$ 1050 br. ^1H NMR (300 MHz, 293 K, $CDCl_3$) δ: 7.88 (m, 4H, C_6H_5), 7.81 (m, 4H, C_6H_5), 7.46 (m, 2H, C_6H_5), 7.20 and 6.48 (both dt, 1H each, $J(HH) = 2.1$ Hz, $J(PH) = 2.4$ Hz, $=CH_2$), 4.01 (s, 3H, OCH_3), 2.45 (m, 6H, PCH), 1.22 (dvt, 36H, $J(HH) = 6.9$ Hz, $N = 13.5$ Hz, $PCHCH_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, 293 K, $CDCl_3$) δ: 19.7 (s). $^{13}C\{^1H\}$ NMR (75.4 MHz, 293 K, $CDCl_3$) δ 279.3 (t, $J(PC) = 9.1$ Hz, $Os{=}C$), 197.9 (s, $Os{=}C{=}C$), 187.7 (s, $C(O)OCH_3$), 178.9 (t, $J(PC) = 9.3$ Hz, $C{\equiv}O$), 156.0 (s, $Os{=}C{=}C{=}C$), 143.4 (s, C_{ipso}), 139.7 (t, $J(PC) = 11.2$ Hz, $Os{-}C{=}CH_2$), 139.6 (s, $Os{-}C{=}CH_2$), 132.7, 131.4, 129.8 (all s, C_6H_5), 53.9 (s, OCH_3), 26.0 (vt, $N = 26.1$ Hz, $PCHCH_3$), 19.8, 19.2 (both s, $PCHCH_3$). Anal. Calcd for $C_{38}H_{57}BF_4O_3OsP_2$: C, 50.67; H, 6.38. Found: C, 50.60; H, 6.87.

Preparation of $[\overline{Os\{C[C(O}})OCH_3]{=}CH_2\}(C{\equiv}CCPh_2CH_3)(CO)(P^iPr_3)_2$ (5). A solution of **4** (100 mg, 0.11 mmol) in tetrahydrofuran (10 mL) was treated with methyllithium (133 μL, 0.21 mmol). After the mixture was stirred for 1 h at room temperature, 2 mL of acetone was added to destroy the excess of methyllithium. The solution was evaporated to dryness. After the residual solid was treated with 20 mL of pentane, the solution was filtered through Kieselguhr and concentrated to 2 mL. The resulting red solid was separated by decantation,

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Table 3. Crystal Data and Data Collection and Refinement for $[\mathrm{Os\{C[C(O)OCH_3]{=}CH_2\}(C{=}C{=}CPh_2)(CO)(P^iPr_3)_2]BF_4\cdot 1/4(CH_2CH_3)_2O}$ (4) and $\mathrm{Os\{C[C({=}CH_2)C(O)OCH_3]{=}C{=}CPh_2\}Cl(CO)(P^iPr_3)_2}$ (9)

	4	**9**
formula	$C_{37}H_{57}BF_4O_3OsP_2\cdot 1/4C_4H_{10}O$	$C_{38}H_{57}ClO_3OsP_2$
mol wt	919.32	849.43
color, habit	violet, irregular prism	orange, irregular prism
crystal size, mm	0.34 × 0.30 × 0.30	0.34 × 0.44 × 0.20
space group	monoclinic, $P2_1/c$	monoclinic, $P2_1/n$
a, Å	19.385(2)	12.968(1)
b, Å	12.931(2)	14.058(1)
c, Å	17.677(2)	21.703(2)
β, deg	110.48(1)	100.188(7)
V, Å^3	4151.0(9)	3894.2(5)
Z	4	4
D (calcd), g cm^{-3}	1.471	1.449
μ, mm^{-1}	3.20	3.46
scan type	$\omega/2\theta$	$\omega/2\theta$
2θ range, deg	$5 \le 2\theta \le 50$	$2 \le 2\theta \le 51$
temp, K	173.0(2)	193.0(2)
no. of data collctd	7908	9253
no. of unique data	7291 ($R_{int} = 0.0150$)	7179 ($R_{int} = 0.0242$)
no. of params refined	474	420
$R_1{}^a$ ($F_o \ge 4.0\sigma(F_o)$)	0.0350	0.0262
w$R_2{}^b$ (all data)	0.0935	0.0522
S^c (all data)	1.132	0.856

[a] $R_1(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2(F^2) = [\Sigma[w(F_o{}^2 - F_c{}^2)^2]/\Sigma[w(F_o{}^2)^2]]^{1/2}$; $w^{-1} = [\sigma^2(F_o{}^2) + (aP)^2 + bP]$, where $P = [\max(F_o{}^2, 0) + 2F_c{}^2)]/3$ (for **4**, $a = 0.0372$ and $b = 3.37$; for **9**, $a = 0.0242$ and $b = 0$). [c] $S = [\Sigma[w(F_o{}^2 - F_c{}^2)^2]/(n - p)]^{1/2}$, where n is the number of reflections and p the number of parameters.

washed twice with 2 mL pentane, and dried *in vacuo*. Yield: 75 mg (82%). IR (Nujol, cm^{-1}): ν(C≡C) 2088 w, ν(C≡O) 1882 s, ν(C═O) 1560 s. ^{1}H NMR (300 MHz, 293 K, C_6D_6) δ: 7.68 (m, 4H, C_6H_5), 7.27 (m, 4H, C_6H_5), 7.09 (m, 2H, C_6H_5), 7.44, 6.23 (both br, 1H each, ═CH_2), 3.16 (s, 3H, OCH_3), 2.71 (m, 6H, PCH), 2.12 (s, 3H, CH_3), 1.25 (dvt, 36H, J(PH) = 6.9 Hz, N = 11.1 Hz, PCHC*H*$_3$). ^{31}P{^{1}H} NMR (121.4 MHz, 293 K, C_6D_6) δSPCLN 14.0 (s). ^{13}C{^{1}H} NMR (75.4 MHz, 293 K, C_6D_6) δ: 186.4 (t, J(PC) = 9.6 Hz, C≡O), 186.0 (s, *C*(O)CH$_3$), 150.4 (s, C$_{ipso}$), 145.6 (t, J(PC) = 7.4 Hz, −*C*═CH$_2$), 128.3, 127.9, 125.6 (all s, C_6H_5), 127.0 (s, −C═CH$_2$), 119.8 (s, Os−C≡*C*−), 103.2 (t, J(PC) = 12.4 Hz, Os−*C*≡C), 50.5 (s, OCH_3), 47.1 (s, Os−C≡C−*C*), 31.5 (s, CH_3), 24.9 (vt, N = 24.8 Hz, P*C*HCH$_3$), 19.9, 19.6 (both s, PCH*C*H$_3$). Anal. Calcd for $C_{39}H_{60}O_3OsP_2$: C, 55.04; H, 7.30. Found: C, 55.18; H, 7.29.

Preparation of $\mathrm{Os\{C[C(O)OCH_3]{=}CH_2\}(C{\equiv}CCPh_2OCH_3)(CO)(P^iPr_3)_2}$ (6). A solution of **4** (111 mg, 0.12 mmol) in dichloromethane (10 mL) was treated with sodium methoxide (13.30 mg, 0.25 mmol). The mixture was stirred for 1 h at room temperature and filtered through Kieselguhr. The filtrate was dried *in vacuo*. The residual solid was treated with 2 mL of methanol, and a yellow solid was obtained. It was separated by decantation, washed twice with 2 mL of methanol, and dried *in vacuo*. Yield: 70 mg (69%). IR (Nujol, cm^{-1}): ν(C≡C) 2061 w, ν(C≡O) 1886 s, ν(C═O) 1562 s. ^{1}H NMR (300 MHz, 293 K, C_6D_6) δ: 7.97 (m, 4H, C_6H_5), 7.26 (m, 4H, C_6H_5), 7.15 (m, 2H, C_6H_5), 7.48, 6.27 (both dt, 1 H each, J(HH) = 3.0 Hz, J(PH) = 2.1 Hz, ═CH_2), 3.61 and 3.19 (both s, 3H each, OCH_3), 2.77 (m, 6H, PCH), 1.30 (dvt, 36H, J(HH) = 7.2 Hz, N = 12.6 Hz, PCHC*H*$_3$). ^{31}P{^{1}H} NMR (121.4 MHz, 293 K, C_6D_6) δ: 13.8 (s). ^{13}C{^{1}H} NMR (75.4 MHz, 293 K, C_6D_6) δ: 186.1 (s, *C*(O)OCH$_3$), 185.9 (t, J(PC) = 9.8 Hz, C≡O), 147.5 (s, C$_{ipso}$), 144.8 (t, J(PC) = 7.5 Hz, −*C*═CH$_2$), 127.9, 127.4, 126.3 (all s, C_6H_5), 127.1 (s, −C═CH$_2$), 114.4 (s, Os−C≡*C*−), 110.9 (t, J(PC) = 11.9 Hz, Os−*C*≡C−), 82.7 (s, Os−C≡C−*C*), 51.8 (s, OCH_3), 50.7 (s, OCH_3), 25.2 (vt, N = 24.7 Hz, P*C*HCH$_3$), 19.9, 19.7 (both s, PCH*C*H$_3$). Anal. Calcd for $C_{39}H_{60}O_4OsP_2$: C, 55.42; H, 7.17. Found: C, 55.14; H, 7.06.

Reaction of $\mathrm{Os\{C[C(O)OCH_3]{=}CH_2\}(C{\equiv}CCPh_2CH_3)(CO)(P^iPr_3)_2}$ (5) with HBF_4. A solution of **5** (75 mg, 0.09 mmol) was treated with $HBF_4\cdot OEt_2$ (12.3 μL, 0.09 mmol). The mixture was stirred for 2 h at room temperature, and a purple solid was obtained. It was separated by decantation, washed with diethyl ether, and dried *in vacuo*. Yield: 55 mg (65%). This solid was characterized by ^{1}H and ^{31}P{^{1}H} NMR as $\mathrm{Os\{C[C(O)OCH_3]{=}CH_2\}(C{=}C{=}CPh_2)(CO)(P^iPr_3)_2]BF_4}$ (**4**).

Reaction of $\mathrm{Os\{C[C(O)OCH_3]{=}CH_2\}(C{\equiv}CCPh_2CH_3)(CO)(P^iPr_3)_2}$ (5) with CH_3OH. A solution of **5** (100 mg, 0.12 mmol) in methanol (10 mL) was stirred for 1 h at room temperature, and a yellow solid was obtained. It was separated by decantation, washed with methanol and dried *in vacuo*. Yield: 90 mg (88%). This solid was characterized by ^{1}H and ^{31}P{^{1}H} NMR as $\mathrm{Os\{C[C(O)OCH_3]{=}CH_2\}[C{\equiv}CCPh_2OCH_3)(CO)(P^iPr_3)_2]}$ (**6**).

Preparation of the mixture of isomers *trans*- and *cis*-$\mathrm{Os\{C[C(O)OCH_3]{=}CH_2\}Cl(C{=}C{=}CPh_2)(CO)(P^iPr_3)_2}$ (7 and 8). A solution of **4** (400 mg, 0.43 mmol) in methanol (10 mL) was treated with sodium chloride (49.86 mg, 0.85 mmol). The mixture was stirred for 1 h at room temperature, giving a purple solid and a purple methanol solution. This purple solid was separated by decantation, washed twice with methanol, and dried *in vacuo*. The purple solid obtained was characterized as $\mathrm{Os\{C[C(O)OCH_3]{=}CH_2\}Cl(C{=}C{=}CPh_2)(CO)(P^iPr_3)_2}$ (**7**). Yield: 145 mg (40%). IR (Nujol, cm^{-1}): ν(C═C═C) 1961 m, ν(C≡O) 1901 s, ν(C═O) 1695 s. ^{1}H NMR (300 MHz, 293 K, C_6D_6) δSPCLN 8.13 (m, 4H, C_6H_5), 7.33 (m, 4H, C_6H_5), 7.10 (m, 2H, C_6H_5), 6.67, 6.52 (both m, 1H each, ═CH_2), 3.36 (s, 3H, OCH_3), 2.91 (m, 6H, PCH), 1.36 (dvt, 18H, J(HH)= 7.1 Hz, N = 14.2 Hz, PCHC*H*$_3$), 1.04 (dvt, 18H, J(HH) = 6.9 Hz, N = 13.2 Hz, PCHC*H*$_3$). ^{31}P{^{1}H} NMR (121.4 MHz, 293 K, C_6D_6) δ 6.8 (s). ^{13}C{^{1}H} NMR (75.4 MHz, 293 K, C_6D_6) δ 268.0 (t, J(PC) = 10.1 Hz, Os═C), 232.5 (s, Os═C═*C*), 181.6 (t, J(PC) = 8.7 Hz, C≡O), 180.9 (s, *C*(O)OCH$_3$), 151.2 (t, J(PC) = 11.1 Hz, −*C*═CH$_2$), 150.0 (s, C$_{ipso}$), 139.3 (s, Os═C═C═*C*), 129.3, 129.2, 128.7 (all s, C_6H_5), 125.5 (br, −C═CH$_2$), 49.6 (s, OCH_3), 24.5 (vt, N = 24.4 Hz, PCH), 20.9, 19.4 (both s, PC*C*H$_3$).

The purple methanol solution was concentrated to dryness. After the residual solid was treated with 20 mL of pentane, the solution was filtered through Kieselguhr and concentrated to 2 mL. The resulting purple solid was separated by decantation, washed twice with 2 mL of pentane, and dried *in vacuo*. The purple solid obtained was characterized as $Os\{C[C(O)OCH_3]{=}CH_2\}Cl(C{=}C{=}CPh_2)(CO)(P^iPr_3)_2$ (**8**). Yield: 55 mg (16%). IR (Nujol, cm^{-1}): ν(C=C=C) 1954 m, ν(C≡O) 1914 s, ν(C=O) 1691 s. ^1H NMR (300 MHz, 293 K, C_6D_6) δ: 8.13 (m, 4H, C_6H_5), 7.32 (m, 3H, C_6H_5 and 1H from $=CH_2$), 7.02 (t, 4H, J(HH) = 8.0 Hz, m-C_6H_5), 7.23 (dt, 1H, J(HH) = 4.5 Hz, J(PH) = 3.6 Hz, $=CH_2$) (the signal due to the other vinyl proton is masked by the phenyl resonances), 3.65 (s, OCH_3), 2.70 (m, 6H, PCH), 1.23 (dvt, 36H, J(HH) = 7.2 Hz, N = 15.0 Hz, PCHCH_3). $^{31}P\{^1H\}$ NMR (121.4 MHz, 293 K, C_6D_6) δSPCLN 1.7 (s). $^{13}C\{^1H\}$ NMR (75.4 MHz, 293 K, C_6D_6) δ: 284.1 (t, J(PC) = 11.0 Hz, Os=C), 221.6 (s, Os=C=*C*), 180.4 (s, *C*(O)-OCH_3), 178.0 (t, J(PC) = 8.7 Hz, C≡O), 152.7 (t, J(PC) = 12.4 Hz, $-C{=}CH_2$), 147.6 (s, C_{ipso}), 142.3 (br, $-C{=}CH_2$), 135.4 (s, Os=C=C=*C*), 129.7, 129.4, 129.3 (all s, C_6H_5), 50.5 (s, OCH_3), 24.5 (vt, N = 24.4 Hz, PCH), 20.9, 19.4 (both, PC*C*H_3). Anal. Calcd for $C_{38}ClH_{57}O_3OsP_2$: C, 53.72; H, 6.78. Found: C, 53.17; H, 6.70.

Preparation of $\overline{Os[\{C[C(=CH_2)C(O}){OCH_3}]{=}C{=}CPh_2\}Cl(CO)(P^iPr_3)_2$ (9). A solution of a mixture of 7 and 8 (150 mg, 0.18 mmol) in toluene (10 mL) was stirred and heated at 60 °C for 23 h. The solution was filtered through Kieselguhr and evaporated to dryness. The residual solid was treated with 3 mL of pentane, and an orange solid was obtained. It was separated by decantation, washed twice with pentane, and dried *in vacuo*. Yield: 125 mg (82%). IR (Nujol, cm^{-1}): ν(C=C=C) 1919 m, ν(C≡O) 1914 s, ν(C=O) 1630 s, ν(C=C) 1582 m. ^1H NMR (300 MHz, 293 K, C_6D_6) δ: 7.52 (m, 4H, C_6H_5), 7.17 (m, 4H, C_6H_5), 7.11 (m, 2H, C_6H_5), 5.95, 5.74 (both s, 1H each, $=CH_2$), 3.39 (s, 3H, OCH_3), 2.70 (m, 6H, PCH), 1.33 (dvt, 18H, J(HH) = 7.6 Hz, N = 13.5 Hz, PCHCH_3), 1.13 (dvt, 18H, J(HH) = 6.9 Hz, N = 13.5 Hz, PCHCH_3). $^{31}P\{^1H\}$ NMR (121.4 MHz, 293 K, C_6D_6) δSPCLN 7.5 (s). $^{13}C\{^1H\}$ NMR (75.4 MHz, 293 K, C_6D_6) δ 210.4 (t, J(PC) = 2.3 Hz, Os−C=*C*), 186.2 (t, J(PC) = 10.1 Hz, C≡O), 179.9 (s, *C*(O)OCH_3), 145.3 (s, C_{ipso}), 140.6 (s, Os−C=C=*C*), 129.8, 128.4, 126.5 (all s, C_6H_5), 122.6 (s, $-C{=}CH_2$), 105.3 (s, $-C{=}CH_2$), 88.3 (t, J(PC) = 6.4 Hz, Os−C=C=C), 54.3 (s, OCH_3), 23.8 (vt, N = 28.8 Hz, PCH), 19.9, 18.6 (both s, PCHCH_3). Anal. Calcd for $C_{38}ClH_{57}O_3OsP_2$: C, 53.72; H, 6.78. Found: C, 53.88; H, 7.08.

Crystal Data for 4 and 9. Crystals suitable for the X-ray diffraction study were obtained by slow diffusion of diethyl ether into a concentrated solution of **4** in dichloromethane or from a toluene/pentane solution (**9**). A summary of crystal data and refinement parameters is reported in Table 3. A violet (**4**) and an orange prismatic crystal (**9**) were glued on glass fibers and mounted on a Siemens-STOE AED (**4**) or Siemens P4 (**9**) four-circle diffractometer, with graphite-monochromated Mo Kα radiation. A group of 24 reflections in the range $18 \le 2\theta \le 25°$ (for **4**) or 49 reflections in the range $29 \le 2\theta \le 39°$ (for **9**) were carefully centered at 173 (**4**) or 193 K (**9**) 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.[24] The structures were solved by Patterson (Os atom, SHELXTL-PLUS[25]) and conventional Fourier techniques. Refinement was carried out by full-matrix least-squares on F^2 (SHELXL-93[26]) with initial isotropic thermal parameters. Anisotropic thermal parameters were used in the last cycles of refinement for all non-hydrogen atoms. In **4** some residual peaks evidenced the presence of a crystallization solvent molecule (most probably diethyl ether), highly disordered around a center of symmetry. Several attempts carried out to build-up a geometrically reasonable model to interpret these residuals were unfortunately unsuccessful. Eventually, the three more intense peaks were included in the final refinement with partial occupancy factors ($^1/_4$ diethyl ether molecule) to take account of this residual electron density. All hydrogens for both structures (except H(1) and H (29 in **4**, refined as isotropic atoms) were included in calculated positions and refined riding on their carbon atoms; isotropic displacement parameters proportional to those of the carbon atoms (1.2 times) in **4**, or a common value for all hydrogens in **9**, were also included in the refinement. Atomic scattering factors, corrected for anomalous dispersion for Os and P were implemented by the program. The refinements converge to R_1 ($F^2 > 2\sigma(F^2)$) = 0.0350 (**4**) or 0.0262 (**9**) and wR_2 (all data) = 0.0935 (**4**) or 0.0522 (**9**), with weighting parameters $x = 0.0372$, $y = 3.37$ (**4**) and $x = 0.0242$, $y = 0$ (**9**).

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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 **4** and **9** (23 pages). Ordering information is given on any current masthead page.

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