Hydride−Hydroxyosmacyclopropene versus Hydride−Hydroxycarbyne and Cyclic Hydroxycarbene: Influence of the Substituents at the C(OH) Carbon Atom of the Carbon Donor Ligand

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Received December 3, 1999

The dihydride $[OsH_2(\kappa^2\text{-}O_2CCH_3)(H_2O)(P^iPr_3)_2]BF_4$ (**1**) reacts with 2-phenyl-3-butyn-2-ol and 2-methyl-3-butyn-2-ol to give isomeric mixtures of the corresponding hydride−hydroxyosmacyclopropene, $[OsH(\kappa^2\text{-}O_2CCH_3)\{C[C(OH)MeR]CH_2\}(P^iPr_3)_2]BF_4$ (R = Ph (**3**), Me (**5**)), and hydride−hydroxycarbyne, $[OsH(\kappa^2\text{-}O_2CCH_3)\{\equiv CCH_2C(OH)MeR\}(P^iPr_3)_2]BF_4$ (R = Ph (**4**), Me (**6**)), derivatives. In solution, complexes **3** and **5** and the related compound $[OsH(\kappa^2\text{-}O_2CCH_3)\{C[C(OH)Ph_2]CH_2\}(P^iPr_3)_2]BF_4$ (**2**) isomerize into the cyclic hydroxycarbenes $[Os(\kappa^2\text{-}O_2CCH_3)\{C(Me)C(OH)RR'\}(P^iPr_3)_2]BF_4$ (R = R′ = Ph (**7**); R = Ph, R′ = Me (**8**); R = R′ = Me (**9**)). The structure of **8** in the solid state has been determined by X-ray diffraction analysis. The geometry around the osmium center can be rationalized as a very distorted octahedron, with the phosphine ligands occupying *cis* positions (P−Os−P = 103.71(6)°). Reaction of **2** with sodium methoxide leads to the η^2-vinyl alkoxide derivative $Os\{\eta^2\text{-}CH_2{=}CHC(Ph)_2O\}(\kappa^2\text{-}O_2CCH_3)(P^iPr_3)_2$ (**10**), which by protonation with HBF_4 affords the η^2-1,1-diphenyl-2-propenol complex $[Os(\kappa^2\text{-}O_2CCH_3)\{\eta^2\text{-}CH_2{=}CHC(OH)Ph_2\}(P^iPr_3)_2]BF_4$ (**11**). The structure of **10** has also been determined by X-ray diffraction analysis. As for **8**, the geometry around the osmium atom can be rationalized as a very distorted octahedron with the phosphine ligands occupying *cis* positions (P−Os−P = 106.72(4)°). The reaction of **8** with sodium methoxide leads to the osmaoxacyclobutene derivative $Os\{C(Me)C(O)MePh\}(\kappa^2\text{-}O_2CCH_3)(P^iPr_3)_2$ (**12**), which on protonation with $HBF_4{\cdot}OEt_2$ regenerates **8**. Treatment of **4** with sodium methoxide gives the hydride−vinylidene $OsH(\kappa^2\text{-}O_2CCH_3)\{{=}C{=}CHC(Ph){=}CH_2\}(P^iPr_3)_2$ (**13**). The formation of the hydride−alkenylcarbynes $[OsH(\kappa^2\text{-}O_2CCH_3)(\equiv CCH{=}CRMe)(P^iPr_3)_2]BF_4$ (R = Ph (**14**), Me (**15**)) by dehydration of **4** and **6** is also reported.

Introduction

Harman[1] has recently reported that the pentaammineosmium(II) unit, $[Os(NH_3)_5]^{2+}$, despite its divalent character, acts as an electron donor through a substantial interaction with the olefin π^* orbital. Thus, in the case of a vinyl ether or vinyl ester complex, coordination by osmium(II) facilitates the loss of the oxygen substituent through the stabilization of the resulting osmacyclopropene. When the Os=C carbon atom carries an alkyl substituent, the complex can be isolated. In contrast, when the Os=C carbon atom bears a hydrogen atom, the metallacyclopropene evolves into the carbyne isomer by an intramolecular 1,2-hydrogen shift.

Metallacyclopropene complexes are considered important intermediates in several catalytic reactions, including alkyne oligomerization,[2] alkyne cyclization,[3] and hydrodesulfurization.[4] However, few compounds of this type are known. They are limited to early transition metals, mainly Mo,[5] W,[6] and Re,[7] and, in general, have been prepared by external nucleophilic attack on coordinated alkyne ligands.[8]

For osmium, in addition to Harman's work, we have recently reported that the dihydride compound $[OsH_2(\kappa^2\text{-}O_2CCH_3)(H_2O)(P^iPr_3)_2]BF_4$ (**1**) reacts with phenylacetylene to give the hydride−osmacyclopropene derivative $[Os(\kappa^2\text{-}O_2CCH_3)\{C(Ph)CH_2\}(P^iPr_3)_2]BF_4$ and with *tert*-butylacetylene and (trimethylsilyl)acetylene to afford the hydride−carbyne complexes $[OsH(\kappa^2\text{-}O_2C$-

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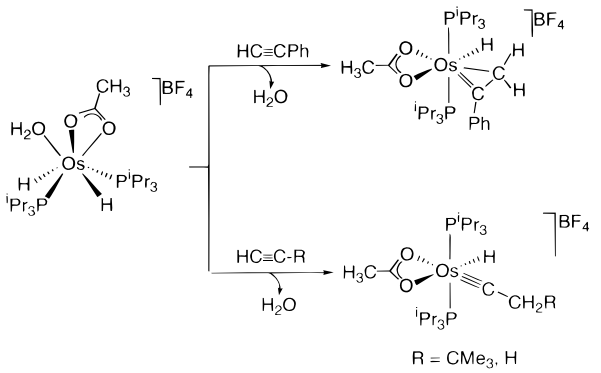
10.1021/om9909542 CCC: $19.00
Publication on Web 05/05/2000

Scheme 1



CH_3)(≡CCH_2CMe_3)(P^iPr_3)$_2$]BF_4 and [OsH(κ^2-O_2CCH_3)-(≡CCH_3)(P^iPr_3)$_2$]BF_4, respectively (Scheme 1). In agreement with these observations, theoretical calculations indicate that the relative stabilities of the metallacyclopropene and carbyne structures depend on the substituent on the alkyne precursor. There is a strong energy preference for the carbyne for R = H, and any substitution stabilizes the metallacyclopropene form more than the carbyne. The stabilization already operative for alkyl substitution through hyperconjugation of the alkyl group is magnified for a phenyl group, where conjugation with a true π system is possible. This means that the metallacyclopropene isomer is thermodynamically more stable than the carbyne isomer when the substituent is a phenyl group, while the opposite is observed for alkyl substituents.[9]

As part of our work on the reactivity of transition-metal complexes toward alkynols,[10] we have also reported that the treatment of dichloromethane solutions of **1** with 1.2 equiv of 1,1-diphenyl-2-propyn-1-ol, at −65 °C, leads to the hydride−hydroxyosmacyclopropene complex [OsH(κ^2-O_2CCH_3){C[C(OH)Ph_2]CH_2}(P^iPr_3)$_2$]-BF_4 (**2**) in 87% yield (Scheme 2).[9] Our interest in determining the influence of the substituents at the C−OH carbon atom of the alkynol on the hydroxymetallacyclopropene−hydroxycarbyne molar ratio, resulting from the reactions of **1** with alkynols, led us to study the reaction of **1** with 2-phenyl-3-butyn-2-ol or 2-methyl-3-butyn-2-ol. In this paper we report: (i) the results of this study, (ii) the isomerization of the hydride−hydroxyosmacyclopropenes into cyclic hydroxycarbenes, and (iii) the behavior of the above-mentioned types of compounds in the presence of sodium methoxide.

Results and Discussion

1. Reactions of [OsH_2(κ^2-O_2CCH_3)(H_2O)(P^iPr_3)$_2$]-BF_4 with 2-Phenyl-3-butyn-2-ol and 2-Methyl-3-butyn-2-ol. The reaction of **1** with 2-phenyl-3-butyn-2-ol under the conditions previously mentioned for 1,1-diphenyl-2-propyn-1-ol affords a yellow solid, which is a 2:3 mixture of the isomeric hydroxyosmacyclopropene [OsH(κ^2-O_2CCH_3){C[C(OH)MePh]CH_2}(P^iPr_3)$_2$]BF_4 (**3**) and the hydroxycarbyne [OsH(κ^2-O_2CCH_3){≡C-CH_2C(OH)MePh}(P^iPr_3)$_2$]BF_4 (**4**), according to the IR and ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectra of the mixture (Scheme 2). The most noticeable spectroscopic features of **3** are a broad signal at 1.89 ppm in the ^{1}H NMR spectrum, corresponding to the OsCH_2 protons of the metallacyclopropene group, and a broad resonance at 280.6 ppm and a singlet at 5.8 ppm in the ^{13}C{^{1}H} NMR spectrum, due to the Os=C and OsCH_2 carbon atoms, respectively. The ^{13}C{^{1}H} NMR spectrum of **4** shows the resonance due to the sp carbon atom as a broad singlet at 288.8 ppm and the CH_2 resonance of the η^1-carbon donor ligand as a singlet at 65.4 ppm.

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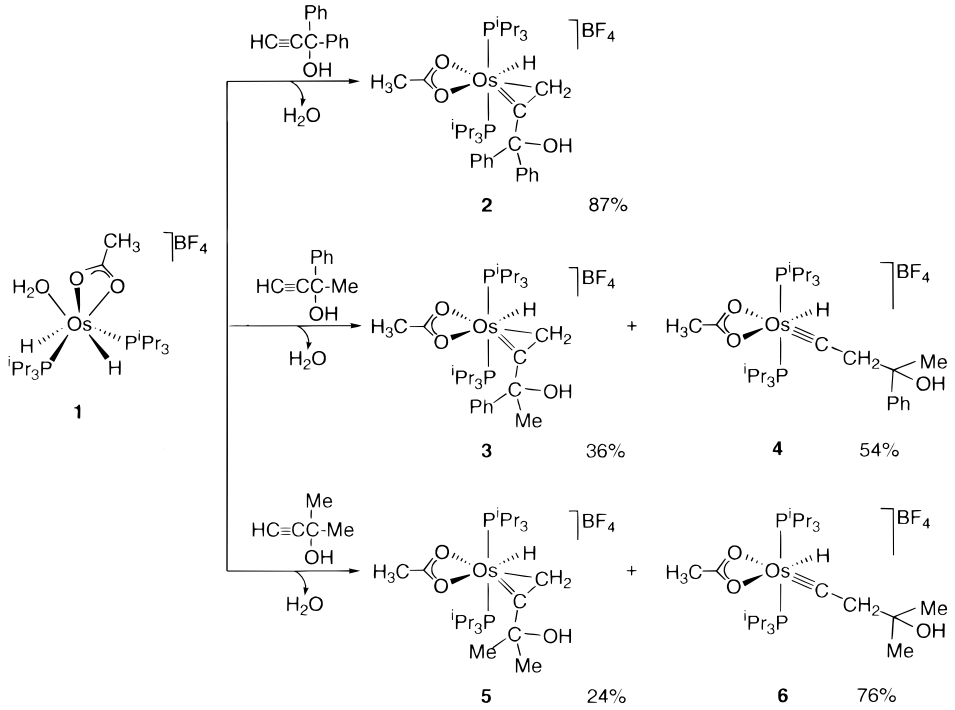
Scheme 2

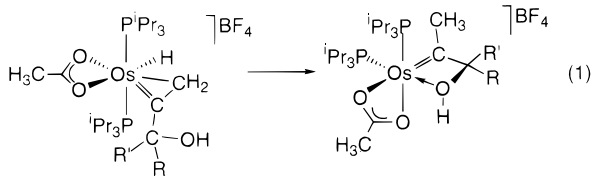


The reaction of **1** with 2-methyl-3-butyn-2-ol under the same conditions as those for 2-phenyl-3-butyn-2-ol affords a yellow solid, which in this case is a 1:3 isomeric mixture of the hydroxyosmacyclopropene [OsH(κ^2-O_2-CCH_3){C[C(OH)Me_2]CH_2}(P^iPr_3)$_2$]BF_4 (**5**) and the hydroxycarbyne [OsH(κ^2-O_2CCH_3){≡$CCH_2C(OH)Me_2$}-(P^iPr_3)$_2$]BF_4 (**6**) (Scheme 2).

The $^{13}C\{^1H\}$ NMR spectrum of **5** agrees well with that of **3**. The resonance due to the Os=C carbon atoms appears as a triplet at 268.5 ppm with a C−P coupling constant of 7.5 Hz. In the $^{13}C\{^1H\}$ NMR spectrum of **6** the resonance due to the sp carbon atom of the η^1-carbon ligand is observed as a triplet at 290.9 ppm with a C−P coupling constant of 7.5 Hz, and the $-CH_2-$ resonance appears as a singlet at 65.8 ppm.

The above data indicate that the reaction of **1** with alkynols (Scheme 2) leads to isomeric mixtures of hydride−hydroxyosmacyclopropenes and hydride−hydroxycarbynes. The molar ratio of the isomers in the mixture depends on the nature of the substituents at the C−OH carbon atom of the alkynol. With two phenyl substituents the hydroxyosmacyclopropene isomer is the only reaction product. The consecutive substitution of phenyl by methyl groups produces an increase in the amount of the hydroxycarbyne isomer and a decrease in the amount of the hydroxyosmacyclopropene isomer. Therefore, the presence of phenyl substituents in the alkyne precursor favors not only the formation of osmacyclopropene derivatives[9] but also the formation of hydroxyosmacyclopropene compounds.

2. Isomerization of Hydride−Hydroxyosmacyclopropenes into Cyclic Hydroxycarbenes. At room temperature, in dichloromethane solution, the hydride−hydroxyosmacyclopropene complexes **2**, **3**, and **5** are unstable and evolve into the corresponding cyclic hydroxycarbene complexes [Os(κ^2-O_2CCH_3){C(Me)C(OH)-RR′}(P^iPr_3)$_2$]BF_4 (R = R′ = Ph (**7**); R = Ph, R′ = Me (**8**); R = R′ = Me (**9**)), according to eq 1. This transformation



R = R' = Ph (**2**)
R = Ph, R' = Me (**3**)
R = R' = Me (**5**)

R = R' = Ph (**7**)
R = Ph, R' = Me (**8**)
R = R' = Me (**9**)

(1)

involves a 1,2-migration of the hydride ligand from the osmium atom to the CH_2 group of the osmacyclopropene and subsequent coordination of the hydroxy group of the resulting carbene ligand. During this process a significant rearrangement of the coordination environment at the osmium atom also takes place. The phosphine ligands, mutually *trans*-disposed in the starting material, lie mutually *cis* in the isomerization products.

The rate of the isomerization shown in eq 1 depends on the nature of the substituents at the C−OH carbon atom. Thus, while complex **2** quantitatively disappears after 24 h, the quantitative formation of **8** and **9** occurs after only 3 h. The stability of the products resulting from the isomerization also depends on these substituents. In solution, complexes **8** and **9** are stable for long periods of time; compound **7**, however, decomposes into unidentified species before the transformation of **2** into **7** is complete.

Complex **7** was characterized in solution by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy, while complexes **8** and **9** were characterized by MS, elemental analysis, and IR and ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy. Complex **8** was further characterized by an X-ray crystallographic study. A view of the molecular geometry of

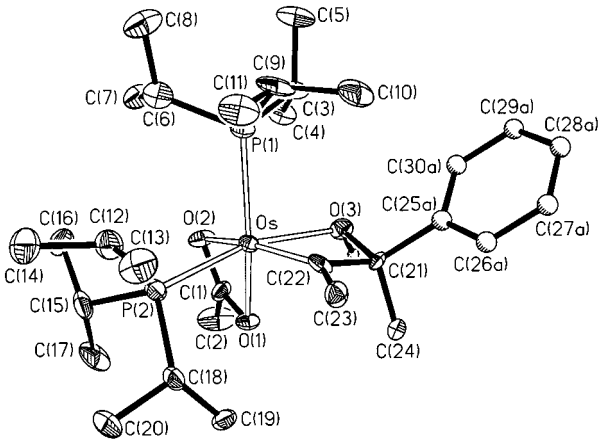


Figure 1. Molecular diagram of the cation of the complex $[Os(\kappa^2\text{-}O_2CCH_3)\{C(Me)C(OH)MePh\}(P^iPr_3)_2]BF_4$ (**8**).

Table 1. Selected Bond Lengths (Å) and Angles (deg) for the Complex $[Os(\kappa^2\text{-}O_2CCH_3)\{C(Me)C(OH)MePh\}(P^iPr_3)_2]BF_4$ (8)

Os−C(22)	1.879(6)	C(21)−O(3)	1.465(7)
Os−O(1)	2.117(4)	C(21)−C(22)	1.558(9)
Os−O(2)	2.304(4)	C(21)−C(24)	1.538(9)
Os−O(3)	2.188(5)	C(22)−C(23)	1.484(8)
Os−P(1)	2.384(2)	Os−P(2)	2.322(2)
C(22)−Os−O(1)	102.8(2)	O(2)−Os−P(2)	95.47(13)
C(22)−Os−O(2)	154.4(3)	O(3)−Os−P(1)	90.33(13)
C(22)−Os−O(3)	67.7(2)	O(3)−Os−P(2)	163.67(13)
C(22)−Os−P(1)	96.6(2)	P(1)−Os−P(2)	103.71(6)
C(22)−Os−P(2)	101.9(2)	O(3)−C(21)−C(22)	97.8(5)
O(1)−Os−O(2)	58.5(2)	O(3)−C(21)−C(24)	110.0(5)
O(1)−Os−O(3)	81.7(2)	C(22)−C(21)−C(24)	110.9(5)
O(1)−Os−P(1)	154.22(12)	C(21)−C(22)−C(23)	117.0(6)
O(1)−Os−P(2)	88.78(13)	Os−C(22)−C(21)	101.0(4)
O(2)−Os−O(3)	90.8(2)	Os−C(22)−C(23)	140.7(5)
O(2)−Os−P(1)	97.40(11)		

the cation of this compound is shown in Figure 1. Selected bond distances and angles are listed in Table 1.

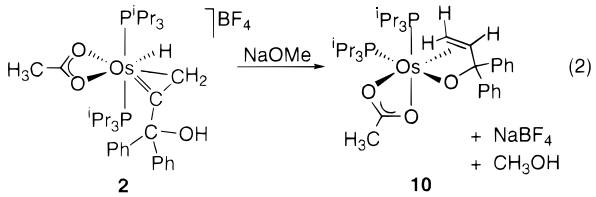
The geometry around the osmium center can be rationalized as a very distorted octahedron with the O(1) oxygen atom of the acetate group and a phosphine ligand occupying pseudo-*trans* positions (O(1)−Os−P(1) = 154.22(12)°). The perpendicular plane is formed by the other phosphine ligand, which is pseudo-*trans* to the O(3) oxygen atom of the hydroxycarbene group (O(3)−Os−P(2) = 163.67(13)°), and the C_α atom of the carbene (C(22)), which is pseudo-*trans* to the O(2) oxygen atom of the carboxylate ligand (C(22)−Os−O(2) = 154.4(3)°).

The observed distortion is due to two factors: (i) the bite angle of the chelating ligands, 58.5(2)° for the acetate and 67.7(2)° for the hydroxycarbene, and (ii) the mutual *cis* arrangement of the phosphine ligands, which experience a large steric hindrance due to their large cone angle (160°).[11] As a result, the P−Os−P angle (103.71(6)°) strongly deviates from the ideal value of 90°. P−M−P angles similar to that of **8** have previously been found in the square-planar complexes Rh(acac)$(PCy_3)_2$ (105.63(4)°),[12] Rh$(\kappa^2\text{-}O_2CCH_3)(P^iPr_3)_2$ (106.00(4)°),[13] and $[Ir(TFB)(P^iPr_3)_2]BF_4$ (TFB = tetrafluorobenzobarrelene; 102.7(1)°)[14] and in the five-coordinate derivative [Rh(acac){(*E*)-CH=CHCy}$(PCy_3)_2]BF_4$ (105.3(1)°).[12]

The most important features of the structure are the Os−C(22) bond length (1.879(6) Å), which is consistent with an Os−C(22) double-bond formulation, and the angles around C(22), between 101.0(4) and 140.7(5)°, which indicates an sp^2 hybridization for this carbon atom. Similar values have been reported for other osmium−carbene complexes.[15]

The presence of a hydroxy group in the carbene ligand of these compounds is also supported by the IR spectra (KBr) of **8** and **9**, which contain a ν(O−H) band at 3217 cm^{-1} (**8**) and 3280 cm^{-1} (**9**). In agreement with the structure shown in Figure 1, the $^{31}P\{^1H\}$ NMR spectra of **7**−**9** show two doublets at 15.2 and −22.3 ppm (**7**), 13.0 and −22.7 ppm (**8**), and 13.9 and −18.6 ppm (**9**), with a P−P coupling constant of about 6.5 Hz. In the ^1H NMR spectra of all three compounds, the most noticeable resonances are those corresponding to the O−H and =CCH_3 protons, which appear as singlets at 7.68 and 1.77 ppm (**7**), 7.39 and 1.90 ppm (**8**), and 6.41 and 1.44 ppm (**9**), respectively. The $^{13}C\{^1H\}$ NMR spectra of **8** and **9** also support the carbene formulation. Thus, they show doublets of doublets at 266.1 (**8**) and 268.7 ppm (**9**), with C−P coupling constants of about 7.5 Hz for the Os=C carbon atoms.

3. Reaction of $[OsH(\kappa^2\text{-}O_2CCH_3)\{C[C(OH)Ph_2]CH_2\}(P^iPr_3)_2]BF_4$ with Sodium Methoxide. Harman has previously reported that his osmacyclopropene complexes undergo nucleophilic addition of alkoxides at the Os=C carbon atom to give η^2-vinyl ether derivatives.[1] However, our system shows a significantly different behavior. Treatment of **2** with 1.4 equiv of sodium methoxide in tetrahydrofuran at room temperature does not give rise to the corresponding hydride−η^2-vinyl ether complex but to the η^2-vinyl alkoxide compound $Os\{\eta^2\text{-}CH_2{=}CHC(Ph)_2O\}(\kappa^2\text{-}O_2CCH_3)(P^iPr_3)_2$ (**10**), which was isolated as an orange solid in 65% yield, according to eq 2.



2 **10** (2)

The formation of **10** can be rationalized as the deprotonation of the OH group of the hydroxyosmacyclopropene ligand of **2**, together with a 1,2-hydride shift from the metal to the Os=C carbon atom. Similarly to the isomerization of **2**, **3**, and **5** to **7**−**9**, the transforma-

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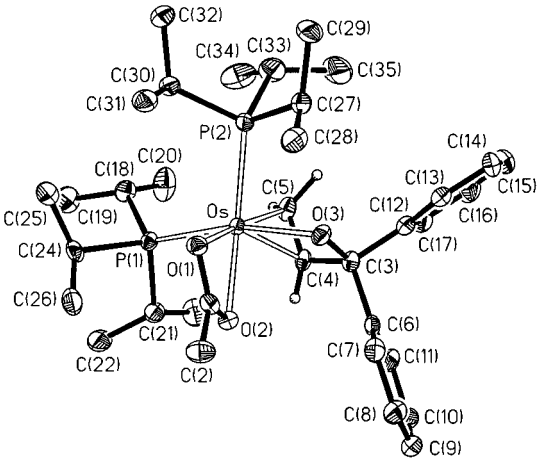
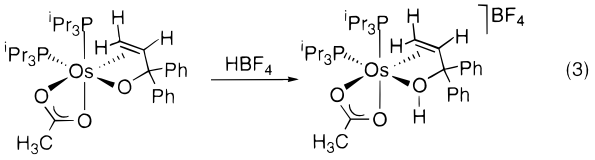


Figure 2. Molecular diagram of the complex $Os\{\eta^2\text{-}CH_2{=}CHC(Ph)_2O\}(\kappa^2\text{-}O_2CCH_3)(P^iPr_3)_2$ (**10**).

tion of **2** into **10** involves a significant rearrangement of the coordination environment at the osmium atom. The phosphine ligands which were mutually *trans* in **2** are now mutually *cis*.

The reaction is not reversible. Addition of 1 equiv of $HBF_4{\cdot}OEt_2$ to dichloromethane solutions of **10** affords the η^2-1,1-diphenyl-2-propenol complex $[Os(\kappa^2\text{-}O_2CCH_3)\{\eta^2\text{-}CH_2{=}CHC(OH)Ph_2\}(P^iPr_3)_2]BF_4$ (**11**), as a result of the protonation of the oxygen atom of the η^2-vinyl alkoxide ligand of **10** (eq 3). Complex **11**, which is a stable isomer of **2** and **7**, was isolated as a white solid in 65% yield.



10 **11** (3)

A view of the molecular geometry of **10** is shown in Figure 2. Selected bond distances and angles are listed in Table 2. The coordination geometry around the osmium atom can be rationalized as being derived from a highly distorted octahedron with the O(2) oxygen atom of the acetate group and a phosphine ligand occupying pseudo-*trans* positions (O(2)−Os−P(2) = 151.99(7)°), at opposite sides of an ideal coordination plane defined by the other phosphine ligand, which is *trans* to the O(3) oxygen atom of the coordinated vinyl alkoxide ligand (O(3)−Os−P(1) = 166.16(8)°), and the O(1) oxygen atom of the acetate group, which is *trans* to the midpoint (M) of the carbon−carbon double bond of the olefin (M−Os−O(1) = 155.30(11)°). In this case, the distortion of the ideal octahedron appears to be a consequence of the bite angles of the acetate group (O(1)−Os−O(2) = 60.25(10)°) and of the vinyl alkoxide ligand (O(3)−Os−M = 75.58(13)°), and the steric hindrance experienced by the phosphine ligands, which are mutually *cis* (P(2)−Os-P(1) = 106.72(4)°).

The osmium−olefin bond lengths, 2.120(4) Å (Os−C(4)) and 2.214(4) Å (Os−C(5)), agree well with those found in other osmium−olefin complexes (between 2.10 and 2.30 Å).[16] Similarly, the olefinic bond distance C(4)−C(5) (1.407(6) Å) is within the range reported for transition-metal olefin complexes (between 1.340 and 1.445 Å).[17] The dihedral angle between the O(2)−Os−P(2) and Os−C(4)−C(5) planes is 48.7(2)°.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for the Complex $Os\{\eta^2\text{-}CH_2{=}CHC(Ph)_2O\}(\kappa^2\text{-}O_2CCH_3)(P^iPr_3)_2$ (10)

Os−O(1)	2.142(3)	Os−C(4)	2.120(4)
Os−O(2)	2.195(3)	Os−C(5)	2.214(4)
Os−O(3)	2.097(3)	C(4)−C(5)	1.407(6)
Os−P(1)	2.3671(10)	C(3)−C(4)	1.540(5)
Os−P(2)	2.3660(10)	C(3)−O(3)	1.406(5)
O(1)−Os−O(2)	60.25(10)	O(3)−Os−P(1)	166.16(8)
O(1)−Os−O(3)	84.49(11)	O(3)−Os−P(2)	87.12(8)
O(1)−Os−C(4)	136.63(13)	O(3)−Os−MP[a]	75.58(13)
O(1)−Os−C(5)	170.55(13)	C(4)−Os−C(5)	37.8(2)
O(1)−Os−P(1)	94.69(8)	C(4)−Os−P(1)	106.91(11)
O(1)−Os−P(2)	93.60(8)	C(4)−Os−P(2)	114.45(12)
O(1)−Os−MP	155.30(11)	C(5)−Os−P(1)	94.63(11)
O(2)−Os−O(3)	80.92(10)	C(5)−Os−P(2)	85.22(12)
O(2)−Os−C(4)	83.49(13)	P(1)−Os−P(2)	106.72(4)
O(2)−Os−C(5)	118.81(13)	C(3)−C(4)−C(5)	120.0(4)
O(2)−Os−P(1)	86.67(7)	C(3)−O(3)−Os	98.6(2)
O(2)−Os−P(2)	151.99(7)	C(3)−C(4)−Os	93.5(2)
O(3)−Os−C(4)	65.76(13)	C(5)−C(4)−Os	74.7(2)
O(3)−Os−C(5)	86.09(13)	C(4)−C(5)−Os	67.5(2)

[a] MP is the midle point between C(4) and C(5).

In agreement with the structure shown in Figure 2, the $^{31}P\{^1H\}$ NMR spectrum of **10** contains two singlets at −11.2 and −17.4 ppm. In the ^1H NMR spectrum, the most noticeable resonances are a doublet of doublets of doublets at 5.33 ppm and two doublets of doublets at 3.79 and 3.76 ppm, respectively, which were assigned to the olefinic protons. In the $^{13}C\{^1H\}$ NMR spectrum, the olefinic carbon atoms give rise to a singlet at 50.9 ppm and a doublet at 23.1 ppm with a C−P coupling constant of 7.7 Hz.

In agreement with the presence of a coordinated 1,1-diphenyl-2-propenol ligand in **11**, its IR spectrum in KBr contains a ν(O−H) band at 3335 cm^{-1}. In the ^1H NMR spectrum, the resonance corresponding to the OH proton appears as a singlet at 5.96 ppm, whereas the resonances due to the olefinic protons are observed as doublets of doublets of doublets at 5.68, 4.32, and 3.89 ppm. In the $^{13}C\{^1H\}$ NMR spectrum, the olefinic carbon atoms give rise to a singlet at 48.3 ppm and a broad resonance at 24.0 ppm. The $^{31}P\{^1H\}$ NMR spectrum shows two doublets at −14.8 and −24.3 ppm, with a P−P coupling constant of 2.2 Hz, in accordance with the mutually *cis* arrangement of the phosphine ligands.

4. Reaction of $[Os(\kappa^2\text{-}O_2CCH_3)\{C(Me)C(OH)MePh\}(P^iPr_3)_2]BF_4$ with Sodium Methoxide. It has previously been mentioned that, in solution, the hydride−hydroxyosmacyclopropene complex **2** slowly evolves into the cyclic hydroxycarbene compound **7**. After taking this into account, we asked ourselves whether complex **7** could participate in the formation of **10**. Unfortunately, complex **7** cannot be isolated as a

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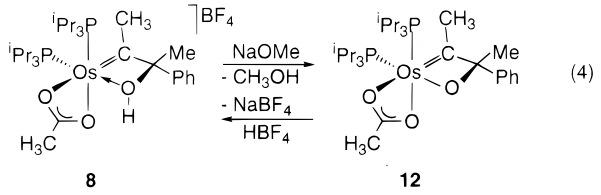
pure solid due to its high instability. However, the related cyclic hydroxycarbene complex **8**, which contains a phenyl and a methyl at the COH carbon atom instead of two phenyl groups, is stable and can be obtained as a pure solid in moderate yield (about 40%). This prompted us to carry out the reaction of **8** with sodium methoxide in order to get information about the participation of the cyclic hydroxycarbene in the formation of **10**. Treatment of **8** with 1 equiv of sodium methoxide in tetrahydrofuran at 0 °C rapidly affords the osmaoxacyclobutene derivative $\overline{Os\{C(Me)C(O)MePh\}}(\kappa^2\text{-}O_2CCH_3)(P^iPr_3)_2$ (**12**) as a result of the deprotonation of the OH group of the cyclic hydroxycarbene ligand of **8** (eq 4). Evidence for the formation of a species related



(4)

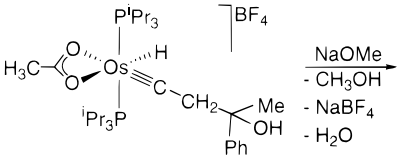
to **10** was not found. This seems to suggest that the isomerization of the hydride−hydroxyosmacyclopropene into the cyclic hydroxycarbene has no influence on the deprotonation of **2** to give **7**. In contrast with the reaction shown in eq 3, the deprotonation of **8** is reversible. Addition of 1 equiv of $HBF_4{\cdot}OEt_2$ to a dichloromethane solution of **12** regenerates **8**.

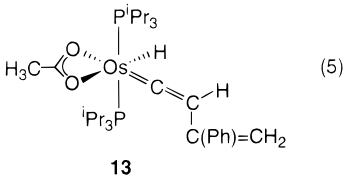
Complex **12** was isolated as a blue crystalline solid in 50% yield. In the IR spectrum (KBr), the most noticeable feature is the absence of any ν(OH) band. The ^{1}H NMR spectrum shows two singlets at 1.81 and 1.80 ppm, respectively, corresponding to the methyl substitutents of the carbocyclic ligand. In the $^{13}C\{^1H\}$ NMR spectrum, the resonance corresponding to the Os=C carbon atom appears as a broad signal at 274.7 ppm. The $^{31}P\{^1H\}$ NMR spectrum contains two singlets at 16.1 and −17.8 ppm, respectively, in agreement with the presence in the complex of two mutually *cis* phosphine ligands.

5. Reaction of $[OsH(\kappa^2\text{-}O_2CCH_3)\{\equiv CCH_2C(OH)MePh\}(P^iPr_3)_2]BF_4$ with Sodium Methoxide. The hydride−hydroxyosmacyclopropene and cyclic hydroxycarbene are isomeric forms which show different behaviors in the presence of sodium methoxide. The first of them affords η^2-vinyl alkoxide species, while the second one gives osmaoxacyclobutene derivatives. Both starting forms are also isomers of the corresponding hydride−hydroxycarbyne compounds.

To determine the behavior of the hydride−hydroxycarbyne form in the presence of sodium methoxide, we treated a 1:1.5 isomeric mixture of **3** and **4**[18] with sodium methoxide in tetrahydrofuran at −20 °C. Under these conditions, after removal of the solvent, a green residue was obtained. According to its $^{31}P\{^1H\}$ NMR spectrum, this mixture contains **12** and a complex displaying a singlet at 27.7 ppm. The latter complex was isolated as an orange solid by treatment of the residue with a 3:1 pentane−toluene mixture and subsequently with diethyl ether at −75 °C. The solid was characterized as the hydride−alkenylvinylidene derivative $OsH(\kappa^2\text{-}O_2CCH_3)\{=C=CHC(Ph)=CH_2\}(P^iPr_3)_2$ (**13**) by MS, elemental analysis, and IR and ^{1}H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy.

The formation of compounds **12** and **13** can be rationalized as follows: compound **12** is the result of the isomerization of **3** into **8** and subsequent deprotonation of **8**, while complex **13** is the result of the deprotonation and dehydration of **4** (eq 5).

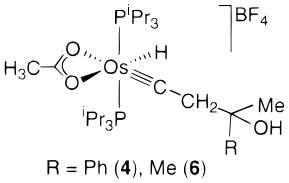


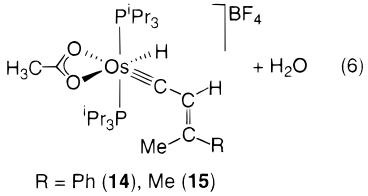


(5)

The presence of a hydride ligand in **13** was inferred from its ^{1}H NMR spectrum, which contains a triplet at −11.86 ppm with an H−P coupling constant of 15.9 Hz. In the $^{13}C\{^1H\}$ NMR spectrum, the resonances due to the C_α and C_β atoms of the vinylidene group appear at 292.7 and 105.7 ppm, respectively, the first of them as a broad signal and the second as a triplet with a C−P coupling constant of 3.1 Hz, while the vinyl carbon atoms give rise to singlets at 144.9 and 103.4 ppm. As has previously been mentioned, the $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 27.7 ppm. Under off-resonance conditions, this singlet is split into a doublet by spin coupling with the hydride.

The dehydration process in **4** probably occurs before the deprotonation. Thus, we have observed that in chloroform-*d* and in the absence of sodium methoxide complexes **4** and **6** slowly lose a water molecule to give the hydride−alkenylcarbyne complexes $[OsH(\kappa^2\text{-}O_2CCH_3)(\equiv CCH=CRMe)(P^iPr_3)_2]BF_4$ (R = Ph (**14**), Me (**15**)). This dehydration is accelerated by the presence of Al_2O_3 in the reaction medium (eq 6). As expected, treatment of **14** with sodium methoxide affords **13**.





(6)

Complex **14** was isolated as red crystals. In agreement with the presence of a hydride ligand in this complex, its IR spectrum (KBr) contains a ν(Os−H) band at 2195 cm^{-1}, and the ^{1}H NMR spectrum shows a triplet at

(18) Attempts to separate the two isomers by fractional crystallization or column chromatography were unsuccessful.

−8.12 ppm with an H−P coupling constant of 15.6 Hz. In addition, the spectrum contains two singlets at 5.34 and 1.80 ppm, which were assigned to the =CH and $=CCH_3$ protons of the alkenyl unit of the unsaturated η^1-carbon ligand, along with the resonances corresponding to the phenyl group, and acetate and the phosphine ligands. The mutually *cis* arrangement of the hydrogen atom and the phenyl group at the carbon−carbon double bond of the alkenylcarbyne ligand was inferred by means of an NOE experiment. Irradiation of the resonance at 5.34 ppm gave an increase in the phenyl resonances (9.5%), whereas the resonance at 1.80 ppm was unaffected. The $^{13}C\{^1H\}$ NMR spectrum shows a broad resonance at 273.6 ppm corresponding to the sp carbon atom of the alkenylcarbyne ligand. The resonances due to the sp^2 carbon atoms appear as singlets at 161.6 and 132.3 ppm. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 41.3 ppm, in accordance with the mutually *trans* arrangement of the phosphine ligands. Under off-resonance conditions this singlet is split into a doublet by spin coupling with the hydride ligand. The aforementioned spectroscopic data agree well with those previously reported for the compound $[OsH(\kappa^2\text{-}O_2CCH_3)\{\equiv CCH{=}C(CH_3)_2\}(P^iPr_3)_2]BF_4$ (**15**).[19]

Concluding Remarks

This study has revealed that at least three types of isomeric compounds can be obtained by reaction of dihydride−osmium compounds with alkynols: hydride−hydroxyosmacyclopropenes, cyclic hydroxycarbenes, and hydride−hydroxycarbynes. In the presence of sodium methoxide, the behaviors of the three isomeric forms are significantly different and afford η^2-vinyl alkoxide, osmaoxacyclobutene, and hydride−alkenylvinylidene complexes, respectively.

Experimental Section

All reactions were carried out with rigorous exclusion of air using standard Schlenk techniques. Solvents were dried by known procedures and distilled under argon prior to use. $[OsH_2(\kappa^2\text{-}O_2CCH_3)(H_2O)(P^iPr_3)_2]BF_4$ (**1**) and $[OsH(\kappa^2\text{-}O_2CCH_3)\{C[C(OH)Ph_2]CH_2\}(P^iPr_3)_2]BF_4$ (**2**) were prepared as previously reported.[9] Infrared spectra were recorded on a Nicolet 550 spectrometer as solids (KBr pellet or Nujol mull). ^1H, $^{13}C\{^1H\}$, ^{19}F, and ^{31}P NMR spectra were recorded on either a Varian Gemini 2000 or a Bruker AXR 300 instrument. Chemical shifts are referenced to residual solvent peaks (^1H, $^{13}C\{^1H\}$) or external H_3PO_4 (^{31}P). Coupling constants, J and N ($N = J_{P-H} + J_{P'-H}$ for ^1H; $N = J_{P-C} + J_{P'-C}$ for $^{13}C\{^1H\}$), are given in hertz. C, H, and N analyses were measured on a Perkin-Elmer 2400 CHNS/O analyzer. Mass spectral 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 with 3-nitrobenzyl alcohol (NBA) as the matrix.

Reaction of $[OsH_2(\kappa^2\text{-}O_2CCH_3)(H_2O)(P^iPr_3)_2]BF_4$ with 2-Phenyl-3-butyn-2-ol. A solution of 2-phenyl-3-butyn-2-ol (133 mg, 0.91 mmol) in 3.5 mL of CH_2Cl_2 was cooled to −65 °C and then added to a Schlenk apparatus containing complex **1** (515 mg, 0.76 mmol). The reaction mixture was stirred for 30 min at −65 °C, and then diethyl ether (30 mL) was added to precipitate a yellow solid, which was subsequently washed three times with diethyl ether and dried in vacuo. Yield: 549 mg (90%). Anal. Calcd for $C_{30}H_{57}BF_4O_3OsP_2$: C, 44.70; H, 7.13. Found: C, 45.01; H, 6.67. MS (FAB^+): *m/z* (relative intensity) 719 (100) (M^+), 701 (88) ($M^+ - H - OH$), 559 (25) ($M^+ - P^iPr_3$). ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra of this yellow solid, recorded at −65 °C in CD_2Cl_2, showed a 2:3 mixture of the isomers $[OsH(\kappa^2\text{-}O_2CCH_3)\{C[C(OH)MePh]CH_2\}(P^iPr_3)_2]BF_4$ (**3**) and $[OsH(\kappa^2\text{-}O_2CCH_3)\{\equiv CCH_2C(OH)MePh\}(P^iPr_3)_2]BF_4$ (**4**).

3: IR (KBr, cm^{-1}) ν(O−H) 3515, ν(Os−H) 2186, ν_{asym}(OCO) 1529, ν_{sym}(OCO) 1469, ν(B−F) 1064; ^1H NMR (300 MHz, CD_2Cl_2, −65 °C) δ 7.70−7.60 (d, $^3J_{H-H} = 6.9$, 2 H, *o*-C_6H_5), 7.40−7.20 (m, 3 H, *m*- and *p*-C_6H_5), 5.68 (s, 1 H, OH), 2.45−2.20 (m, 6 H, PC*H*$(CH_3)_2$), 2.00 (s, 3 H, O_2CCH_3), 1.89 (br s, 2 H, OsCH_2), 1.78 (s, 3 H, C(OH)PhCH_3), 1.50−1.20 (m, 18 H, PCH(CH_3)$_2$), 1.15−1.04 (m, 9 H, PCH(CH_3)$_2$), 0.79 (dvt, $N = 14.6$, $^3J_{H-H} = 7.2$, 9 H, PCH(CH_3)$_2$), −7.83 (t, $^2J_{P-H} = 15.8$, 1 H, Os−H); $^{31}P\{^1H\}$ NMR (121.42 MHz, CD_2Cl_2, −65 °C) δ 27.2 (s); $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2, −65 °C, plus APT) δ 280.6 (br s, Os=*C*), 189.1 (s, O_2CCH_3), 139.2 (s, C-*ipso* C_6H_5), 128.9, 127.8, 124.7 (s, *o*-, *m*-, and *p*-C_6H_5), 91.8 (s, *C*(OH)MePh), 28.9 (s, O_2CCH_3), 22.5 (m, P*C*H$(CH_3)_2$), 22.0 (s, C(OH)*Me*Ph), 18.3 (s, PCH(*C*H_3)$_2$), 18.1 (s, PCH(*C*H_3)$_2$), 5.8 (s, Os*C*H_2).

4: IR (KBr, cm^{-1}) ν(O−H) 3485, ν(Os−H) 2205, ν_{asym}(OCO) 1529, ν_{sym}(OCO) 1469, ν(B−F) 1064; ^1H NMR (300 MHz, CD_2Cl_2, −65 °C) δ 7.40−7.20 (m, 5 H, *o*-, *m*-, and *p*-C_6H_5), 7.35 (s, 1 H, OH), 2.70−2.50 (m, 6 H, PC*H*$(CH_3)_2$), 2.09 (br s, 2 H, CH_2), 1.73 (s, 3 H, O_2CCH_3), 1.56 (s, 3 H, C(OH)PhCH_3), 1.50−1.10 (m, 36 H, PCH(CH_3)$_2$), −7.63 (t, $^2J_{P-H} = 15.8$, 1 H, Os−H); $^{31}P\{^1H\}$ NMR (121.42 MHz, CD_2Cl_2, −65 °C) δ 40.2 (s); $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2, −65 °C, plus APT) δ 288.8 (br s, Os≡*C*), 186.6 (s, O_2CCH_3), 144.9 (s, C-*ipso* C_6H_5), 128.1, 127.3, 123.9 (all s, *o*-, *p*-, and *m*-C_6H_5), 71.6 (s, *C*(OH)MePh), 65.4 (s, ≡CCH_2), 30.2 (s, O_2CCH_3), 26.1 (m, P*C*H$(CH_3)_2$), 25.3 (s, C(OH)*Me*Ph), 18.7 (s, PCH(*C*H_3)$_2$), 18.7 (s, PCH(*C*H_3)$_2$).

Reaction of $[OsH_2(\kappa^2\text{-}O_2CCH_3)(H_2O)(P^iPr_3)_2]BF_4$ with 2-Methyl-3-butyn-2-ol. To a solution of complex **1** (256 mg, 0.38 mmol) in 1.5 mL of dichloromethane at −65 °C was added 2-methyl-3-butyn-2-ol (55.4 μL, 0.57 mmol). The reaction mixture was stirred for 20 min, and then diethyl ether was added at −65 °C to precipitate a yellow solid, which was subsequently washed twice with diethyl ether and dried under vacuum. Yield: 283 mg (99%). Anal. Calcd for $C_{25}H_{55}BF_4O_3OsP_2$: C, 40.42; H, 7.46. Found: C, 40.37; H, 8.04. MS (FAB^+): *m/z* (relative intensity) 657 (18) (M^+), 639 (35) ($M^+ - OH - H$), 479 (12) ($M^+ - P^iPr_3$). ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra of this yellow solid, recorded at −65 °C in CD_2Cl_2, showed a 1:3 mixture of the isomers $[OsH(\kappa^2\text{-}O_2CCH_3)\{C[C(OH)Me_2]CH_2\}(P^iPr_3)_2]BF_4$ (**5**) and $[OsH(\kappa^2\text{-}O_2CCH_3)\{\equiv CCH_2C(OH)Me_2\}(P^iPr_3)_2]BF_4$ (**6**).

5: IR (Nujol, cm^{-1}) ν(O−H) 3510, ν(Os−H) 2171; ^1H NMR (300 MHz, CD_2Cl_2, −65 °C) δ 4.93 (s, 1 H, OH), 2.30−2.10 (m, 6 H, PC*H*$(CH_3)_2$), 1.96 (s, 3 H, O_2CCH_3), 1.53 (t, $^3J_{P-H} = 6.0$, 2 H, Os−CH_2), 1.41 (s, 6 H, −C(OH)Me_2), 1.47−1.15 (m, 36 H, PCH(CH_3)$_2$), −7.99 (t, $^2J_{P-H} = 15.0$, 1 H, Os−H); $^{31}P\{^1H\}$ NMR (121.42 MHz, CD_2Cl_2, −65 °C) δ 27.6 (s); $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2, −65 °C, plus DEPT) δ 268.5 (t, $^2J_{P-C} = 7.5$, Os=*C*), 190.4 (s, O_2CCH_3), 92.9 (s, *C*(OH)Me_2), 27.1 (s, O_2CCH_3), 26.2 (m, P*C*H$(CH_3)_2$), 25.0 (s, C(OH)*Me*$_2$), 19.1 (s, PCH(*C*H_3)$_2$), 18.7 (s, PCH(*C*H_3)$_2$) (the peak corresponding to Os−CH_2 was not observed, even at long acquisition times, due to the low proportion of compound **5** in the mixture).

6: IR (Nujol, cm^{-1}) ν(O−H) 3490, ν(Os−H) 2181, ν_{asym}(OCO) 1524, ν_{sym}(OCO) 1472, ν(B−F) 1062; ^1H NMR (300 MHz, CD_2Cl_2, −65 °C) δ 3.02 (s, 1 H, OH), 2.80−2.60 (m, 6 H, PC*H*$(CH_3)_2$), 1.77 (s, 3 H, O_2CCH_3), 1.76 (t, $^4J_{P-H} = 1.0$, 6 H, −C(OH)Me_2), 1.58 (br s, 2 H, CH_2), 1.47−1.15 (m, 36 H, PCH(CH_3)$_2$), −7.98 (t, $^2J_{P-H} = 15.6$, 1 H, Os−H); $^{31}P\{^1H\}$ NMR (121.42 MHz, CD_2Cl_2, −65 °C) δ 40.5 (s); $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2, −65 °C, plus DEPT) δ 290.9 (t, $^2J_{P-C} = 7.5$, Os≡*C*), 187.6 (s, O_2CCH_3), 69.8 (s, *C*(OH)Me_2), 65.8 (s, ≡CCH_2),

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30.4 (s, O_2CCH_3), 26.7 (vt, N = 26.9 Hz, $PCH(CH_3)_2$), 25.7 (s, $C(OH)Me_2$), 19.1 (s, $PCH(CH_3)_2$), 18.7 (s, $PCH(CH_3)_2$).

Preparation of [Os(κ²-O₂CCH₃){C(Me)C(OH)Ph₂}(P^{i}Pr₃)₂]BF₄ (7). Complex **2** (40 mg, 0.05 mmol) was placed in an NMR tube and 0.5 mL of CD_2Cl_2 added. The solution was left to stand for 24 h at room temperature, during which time the color changed from light orange to purple. The sample was then checked by NMR and, among other decomposition products, complex **7** could be detected by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. Isolation of this compound as a pure solid was not possible, as total decomposition of the mixture occurs. ^1H NMR (300 MHz, CD_2Cl_2, 25 °C): δ 7.70−7.57 (m, 4 H, *o*-C_6H_5), 7.68 (s, 1 H, OH), 7.48−7.22 (m, 6 H, *m*- and *p*-C_6H_5), 2.70−2.50 (m, 3 H, $PCH(CH_3)_2$), 2.50−2.32 (m, 3 H, $PCH(CH_3)_2$), 2.04 (s, 3 H, O_2CCH_3), 1.77 (s, 3 H, =C*Me*), 1.50−1.06 (m, 36 H, $PCH(CH_3)_2$). $^{31}P\{^1H\}$ NMR (121.42 MHz, CD_2Cl_2, 25 °C): δ 15.2 (d, $^2J_{P-P}$ = 6.2), −22.3 (d, $^2J_{P-P}$ = 6.2).

Preparation of [Os(κ²-O₂CCH₃){C(Me)C(OH)MePh}(P^{i}Pr₃)₂]BF₄ (8). A solution of **1** (154 mg, 0.23 mmol) in 4 mL of CH_2Cl_2 was treated with 2-phenyl-3-butyn-2-ol (40 mg, 0.27 mmol), and the resulting mixture was stirred for 3 h at room temperature. The purple solution obtained was concentrated to ca. 2 mL and diethyl ether added to precipitate a purple solid, which was washed three times with diethyl ether and dried under vacuum. Yield: 64 mg (35%). Anal. Calcd for $C_{30}H_{57}BF_4O_3OsP_2$: C, 44.70; H, 7.13. Found: C, 45.00; H, 6.80. MS (FAB$^+$): *m*/*z* 719 (66) (M^+), 659 (48) ($M^+ - H - O_2CCH_3$), 598 (60) (M^+ − C(OH)MePh). IR (KBr, cm^{-1}): ν(O−H) 3217, ν_{asym}(OCO) 1545, ν_{sym}(OCO) 1464, ν(B−F) 1100. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.57 (br d, $^3J_{H-H}$ = 7.5, 2 H, *o*-C_6H_5), 7.39 (s, 1 H, OH), 7.33 (dd, $^3J_{H-H}$ = 7.5, $^3J_{H-H}$ = 7.2, 2 H, *m*-C_6H_5), 7.20 (t, $^3J_{H-H}$ = 7.2, 1 H, *p*-C_6H_5), 2.60−2.40 (m, 6 H, $PCH(CH_3)_2$), 2.11 (s, 3 H, O_2CCH_3), 1.90 (s, 3 H, =C*Me*), 1.75 (s, 3 H, −C(OH)*Me*Ph), 1.28 (dd, $^4J_{P-H}$ = 12.5, $^3J_{H-H}$ = 7.2, 9 H, $PCH(CH_3)_2$), 1.26 (dd, $^4J_{P-H}$ = 13.1, $^3J_{H-H}$ = 7.2, 9 H, $PCH(CH_3)_2$), 1.16 (dd, $^4J_{P-H}$ = 14.0, $^3J_{H-H}$ = 7.1, 9 H, $PCH(CH_3)_2$), 0.93 (dd, $^4J_{P-H}$ = 13.0, $^3J_{H-H}$ = 6.6, 9 H, $PCH(CH_3)_2$). $^{31}P\{^1H\}$ NMR (121.42 MHz, $CDCl_3$, 25 °C): δ 13.0 (d, $^2J_{P-P}$ = 6.2), −22.7 (d, $^2J_{P-P}$ = 6.2). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2, 25 °C): δ 266.1 (dd, $^2J_{P-C}$ = 8.2, $^2J_{P-C}$ = 7.3, Os=*C*), 190.8 (s, O_2CCH_3), 142.9 (s, C-*ipso* C_6H_5), 128.8, 128.0, 123.9 (s, *o*-, *p*-, and *m*-C_6H_5), 124.1 (s, *C*(OH)MePh), 48.9 (s, =C*Me*), 25.4 (d, $^4J_{P-C}$ = 1.8, O_2CCH_3), 29.5 (d, $^1J_{P-C}$ = 27.5, $PCH(CH_3)_2$), 23.1 (s, C(OH)*Me*Ph), 20.5, 20.0, 20.0, 19.6 (all s, $PCH(CH_3)_2$).

Preparation of [Os(κ²-O₂CCH₃){C(Me)C(OH)Me₂}(P^{i}Pr₃)₂]BF₄ (9). A 1:3 mixture of complexes **5** and **6** (30 mg, 0.04 mmol) was placed in an NMR tube and 0.5 mL of CD_2Cl_2 added. The solution was left to stand for 3 h at room temperature, and during this time the color of the solution changed from yellow to purple. The ^1H and $^{31}P\{^1H\}$ NMR spectra recorded after this time showed a 1:3 mixture of complexes **9** and **6** as a result of the evolution of complex **5** into **9**. Crystallization of the mixture from CH_2Cl_2/diethyl ether gave rise to some deep purple crystals of **9** and yellow crystals of complex **6**, which could be separated by hand. Anal. Calcd for $C_{25}H_{55}BF_4O_3OsP_2$: C, 40.42; H, 7.46. Found: C, 40.37; H, 7.60. MS (FAB$^+$): *m*/*z* 657 (100) (M^+), 597 (96) (M^+ -H − O_2CCH_3). IR (KBr, cm^{-1}): ν(O−H) 3280, ν_{asym}(OCO) 1542, ν_{sym}(OCO) 1466, ν(B−F) 1097. ^1H NMR (300 MHz, CD_2Cl_2, 25 °C): δ 6.41 (s, 1 H, OH), 2.62−2.42 (m, 6 H, $PCH(CH_3)_2$), 2.0 (s, 3 H, O_2CCH_3), 1.59, 1.58 (both s, 3 H, −C(OH)*Me*$_2$), 1.44 (s, 3 H, =C*Me*), 1.38−1.18 (m, 36 H, $PCH(CH_3)_2$). $^{31}P\{^1H\}$ NMR (121.42 MHz, CD_2Cl_2, 25 °C): δ 13.9 (d, $^2J_{P-P}$ = 7.0), −18.6 (d, $^2J_{P-P}$ = 7.0). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2, 25 °C): δ 268.7 (dd, $^2J_{P-C}$ = $^2J_{P-C}$ = 7.4, Os=*C*), 190.5 (s, O_2CCH_3), 121.5 (s, *C*(OH)Me$_2$), 46.3 (s, =C*Me*), 28.6 (d, $^1J_{P-C}$ = 26.2, $PCH(CH_3)_2$), 25.8 (s, O_2CCH_3), 25.1, 25.0 (both s, C(OH)*Me*$_2$), 20.10, 20.0, 19.6, 19.6 (all s, $PCH(CH_3)_2$).

Preparation of Os{η²-CH₂=CHC(Ph)₂O}(κ²-O₂CCH₃)(P^{i}Pr₃)₂ (10). An excess of NaOMe (15 mg, 0.28 mmol) was added to a solution of **2** (177 mg, 0.20 mmol) in 8 mL of THF. The reaction mixture was stirred for 1 h and then evaporated to dryness to give an oily orange solid, which was subsequently extracted with 2 mL of toluene. The solvent was removed under vacuum, and then cold pentane (−30 °C) was added to precipitate an orange solid, which was washed three times with pentane at −30 °C and then dried under vacuum. Yield: 101 mg (65%). Anal. Calcd for $C_{35}H_{58}O_3OsP_2$: C, 53.96; H, 7.50. Found: C, 53.68; H, 7.72. MS (FAB$^+$): *m*/*z* (relative intensity) 781 (20) (M^+ + 1), 721 (22) ($M^+ - O_2CCH_3$), 620 (100) (M^+ − P^{i}Pr$_3$), 560 (73) ($M^+ - O_2CCH_3$ − P^{i}Pr$_3$). IR (Nujol, cm^{-1}): ν_{asym}(OCO) 1531, ν_{sym}(OCO) 1485. ^1H NMR (300 MHz, C_6D_6, 25 °C): δ 8.10 (dd, $^3J_{H-H}$ = 8.2, $^4J_{H-H}$ = 1.2, 2 H, *o*-C_6H_5), 7.88 (dd, $^3J_{H-H}$ = 8.1, $^4J_{H-H}$ = 1.2, 2 H, *o*-C_6H_5), 7.36−7.08 (m, 4 H, *m*-C_6H_5, both phenyl groups), 7.03 (tt, $^3J_{H-H}$ = 7.2, $^4J_{H-H}$ = 1.2, 1 H, *p*-C_6H_5), 6.94 (tt, $^3J_{H-H}$ = 7.5, $^4J_{H-H}$ = 1.2, 1 H, *p*-C_6H_5), 5.33 (ddd, $^3J_{H-H}$ = 8.2, $^3J_{P-H}$ = $^3J_{P-H}$ = 0.99, 1 H, −C*H*=CH_2), 3.79 (dd, $^3J_{H-H}$ = 8.2, $^3J_{P-H}$ = 1.2, 1 H, =CH_2), 3.76 (dd, $^3J_{H-H}$ = 8.2, $^3J_{P-H}$ = 14.4, 1 H, =CH_2), 2.65−2.45 (m, 3 H, $PCH(CH_3)_2$), 2.20−2.00 (m, 3 H, $PCH(CH_3)_2$), 1.76 (s, 3 H, O_2CCH_3), 1.3 (dd, $^4J_{P-H}$ = 12.3, $^3J_{H-H}$ = 6.9, 9 H, $PCH(CH_3)_2$), 1.12 (dd, $^4J_{P-H}$ = 11.5, $^3J_{H-H}$ = 7.2, 9 H, $PCH(CH_3)_2$), 1.06 (dd, $^4J_{P-H}$ = 11.8, $^3J_{H-H}$ = 6.9, 9 H, $PCH(CH_3)_2$), 0.99 (dd, $^4J_{P-H}$ = 11.4, $^3J_{H-H}$ = 7.2, 9 H, $PCH(CH_3)_2$). $^{31}P\{^1H\}$ NMR (121.42 MHz, C_6D_6, 25 °C): δ −11.2 (s), −17.4 (s). $^{13}C\{^1H\}$ NMR (75.47 MHz, C_6D_6, 25 °C, plus APT): δ 188.1 (s, O_2CCH_3), 159.1 (d, $^4J_{P-C}$ = 2.1, C-*ipso* C_6H_5), 156.2 (s, C-*ipso* C_6H_5), 127.2 and 127.1 (both s, *o*-C_6H_5), 126.0 and 125.5 (both s, *m*-C_6H_5), 125.0 and 124.8 (both s, *p*-C_6H_5), 94.7 (d, $^3J_{P-C}$ = 3.5, −O*C*Ph$_2$-), 50.9 (s, *C*H=), 28.6 (d, $^1J_{P-C}$ = 21.0, $PCH(CH_3)_2$), 27.1 (d, $^1J_{P-C}$ = 24.6, $PCH(CH_3)_2$), 25.6 (s, O_2CCH_3), 23.1 (d, $^2J_{P-C}$ = 7.7, =*C*H_2), 20.5 (d, $^2J_{P-C}$ = 1.4, $PCH(CH_3)_2$), 20.2 (s, $PCH(CH_3)_2$), 20.1 (d, $^2J_{P-C}$ = 2.8, $PCH(CH_3)_2$), 20.0 (d, $^2J_{P-C}$ = 1.43, $PCH(CH_3)_2$).

Preparation of [Os{η²-CH₂=CHC(Ph)₂OH}(κ²-O₂CCH₃)(P^{i}Pr₃)₂]BF₄ (11). HBF_4·OEt_2 (4 μL, 0.029 mmol) was added to a solution of **10** (22.3 mg, 0.029 mmol) in 2 mL of CH_2Cl_2 at 0 °C. The reaction mixture was stirred for 10 min, and then the solvent was removed under vacuum. Diethyl ether was added to precipitate an off-white solid, which was washed with diethyl ether and dried under vacuum. Yield: 16.1 mg (65%). Anal. Calcd for $C_{35}H_{59}BF_4O_3OsP_2$: C, 48.50; H, 6.86. Found: C, 48.23; H, 7.07. MS (FAB$^+$): *m*/*z* (relative intensity) 781 (43) (M^+), 721 (53) ($M^+ - H - O_2CCH_3$), 620 (64) (M^+ − H − P^{i}Pr$_3$). IR (Nujol, cm^{-1}): ν(OH) 3335, ν_{asym}(OCO) 1521, ν_{sym}(OCO) 1486. ^1H NMR (300 MHz, CD_2Cl_2, 25 °C): δ 7.64 (d, $^3J_{H-H}$ = 7.2, 4 H, *o*-C_6H_5), 7.50−7.30 (m, 6 H, *m*- and *p*-C_6H_5), 5.96 (s, 1 H, OH), 5.68 (ddd, $^3J_{H-H}$ = 8.2, $^3J_{H-H}$ = 7.2, $^3J_{P-H}$ = 1.2, 1 H, −C*H*=), 4.32 (ddd, $^3J_{H-H}$ = 7.2, $^2J_{H-H}$ = 3.0, $^3J_{P-H}$ = 2.0, 1 H, =CH_2), 3.89 (ddd, $^3J_{P-H}$ = 15.4, $^3J_{H-H}$ = 8.2, $^2J_{H-H}$ = 3.0, 1 H, =CH_2), 2.72−2.50 (m, 3 H, $PCH(CH_3)_2$), 2.30−2.12 (m, 3 H, $PCH(CH_3)_2$), 1.98 (s, 3 H, O_2CCH_3), 1.37−1.20 (m, 36 H, $PCH(CH_3)_2$). $^{31}P\{^1H\}$ NMR (121.42 MHz, CD_2Cl_2, 25 °C): δ −14.8 (d, $^2J_{P-P}$ = 2.2), −24.3 (d, $^2J_{P-P}$ = 2.2). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2, −30 °C, plus DEPT): δ 193.3 (s, O_2CCH_3), 149.3, 143.4 (both s, C-*ipso* C_6H_5), 128.4 and 128.2 (both s, *o*-C_6H_5), 127.6 and 127.1 (both s, *p*-C_6H_5), 125.0 and 124.3 (both s, *m*-C_6H_5), 100.2 (s, *C*(OH)Ph$_2$), 48.3 (s, *C*H=), 28.2 (d, $^1J_{P-C}$ = 28.1, $PCH(CH_3)_2$), 27.0 (d, $^1J_{P-C}$ = 25.8, $PCH(CH_3)_2$), 25.9 (s, $OCOCH_3$), 24.0 (br s, =*C*H_2), 20.1 (s, $PCH(CH_3)_2$).

Preparation of Os{C(Me)C(O)MePh}(κ²-O₂CCH₃)(P^{i}Pr₃)₂]BF₄ (12). To a cold (0 °C) solution of **8** (83 mg, 0.10 mmol) in 4 mL of THF was added NaOMe (5.60 mg, 0.10 mmol). A rapid color change from purple to blue was observed, indicating the end of the reaction. The blue solution was evaporated to dryness and extracted at 0 °C with a 2:1 pentane/toluene mixture. The solvents were removed under

vacuum, and pentane was added at −65 °C to precipitate a blue crystalline solid, which was washed twice with the same solvent, at the same temperature, and dried in vacuo. Yield: 36 mg (50%). Anal. Calcd for $C_{30}H_{56}O_3OsP_2$: C, 50.26; H, 7.87. Found: C, 49.90; H, 8.09. MS (FAB$^+$): *m*/*z* (relative intensity) 719 (29) ($M^+ + 1$), 659 (30) ($M^+ - O_2CCH_3$), 438 (100) ($M^+ - P^iPr_3 - C(O)MePh$). IR (KBr, cm^{-1}): ν_{asym}(OCO) 1546, ν_{sym}(OCO) 1472. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 8.01 (d, $^3J_{H-H} = 7.5$, 2 H, *o*-C_6H_5), 7.27 (dd, $^3J_{H-H} = 7.5$, $^3J_{H-H} = 8.1$, 2 H, *m*-C_6H_5), 7.08 (t, $^3J_{H-H} = 8.1$, 1 H, *p*-C_6H_5), 2.26−2.25 (m, 6 H, PC*H*$(CH_3)_2$), 1.94 (s, 3 H, O_2CCH_3), 1.81 (s, 3 H, =C*Me*), 1.80 (s, 3 H, −C(O)*Me*Ph), 1.28 (dd, $^4J_{P-H} = 12.1$, $^3J_{H-H} = 7.2$, 9 H, PCH(CH_3)$_2$), 1.20 (dd, $^4J_{P-H} = 11.5$, $^3J_{H-H} = 7.2$, 9 H, PCH(CH_3)$_2$), 1.13 (dd, $^4J_{P-H} = 13.3$, $^3J_{H-H} = 6.9$, 9 H, PCH-(CH_3)$_2$), 0.86 (dd, $^4J_{P-H} = 11.4$, $^3J_{H-H} = 6.9$, 9 H, PCH(CH_3)$_2$). ^{31}P{^{1}H} NMR (121.42 MHz, C_6D_6, 25 °C): δ 16.1 (s), −17.8 (s). ^{13}C{^{1}H} NMR (75.47 MHz, C_7D_8, −20 °C): δ 274.7 (br, Os=*C*), 186.1 (s, O_2CCH_3), 150.0 (s, C-*ipso* C_6H_5), 127.1 and signals overlapping with the solvent peak (s, *o*-, *m*-, and *p*-C_6H_5), 117.3 (s, *C*(O)MePh), 48.5 (s, =C*Me*), 29.4 (m, P*C*H-$(CH_3)_2$), 25.9 (s, O_2CCH_3), 25.5 (s, C(O)*Me*Ph), 20.8, 20.4, 19.9, 19.7 (all s, PCH(*C*H_3)$_2$).

Preparation of OsH(κ^2-O_2CCH_3)(=C=CHC(Ph)=CH_2)(P^iPr_3)$_2$ (13). A 1:1.5 mixture of complexes **3** and **4** (89 mg, 0.01 mmol) in 2 mL of THF at −20 °C was treated with NaOMe (6 mg, 0.01 mmol). The mixture was stirred for 30 min at −20 °C, and then the solvent was removed under vacuum. The oily green solid obtained was extracted with 2 mL of a 3:1 mixture of pentane/toluene to give a green solution, which was evaporated to dryness. Diethyl ether at −75 °C was then added to precipitate an orange solid, which was dried under vacuum. Yield: 11 mg (15%). Anal. Calcd for $C_{30}H_{54}O_2OsP_2$: C, 51.56; H, 7.79. Found: C, 51.95; H, 7.43. MS (FAB$^+$): *m*/*z* (relative intensity) 701 (100) ($M^+ + 1$), 541 (70) ($M^+ - H - P^iPr_3$). IR (KBr, cm^{-1}): ν(Os−H) 2154. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 7.70−7.50 (d, $^3J_{H-H} = 8.1$, 2 H, *o*-C_6H_5), 7.30−7.00 (m, 3 H, *m*- and *p*-C_6H_5), 5.37 and 5.05 (both br s, 1 H each, =CH_2), 2.70−2.40 (m, 6 H, PC*H*$(CH_3)_2$), 2.03 (br s, 1 H, =C=C*H*), 1.61 (s, 3 H, O_2CCH_3), 1.35 (dvt, $N = 13.2$, $^3J_{H-H} = 6.9$, 18 H, PCH-(CH_3)$_2$), 1.28 (dvt, $N = 13.2$, $^3J_{H-H} = 6.9$, 18 H, PCH(CH_3)$_2$), −11.86 (t, $^3J_{P-H} = 15.9$, 1 H, Os−H). ^{31}P{^{1}H} NMR (121.42 MHz, C_6D_6, 25 °C): δ 27.7 (s). ^{13}C{^{1}H} NMR (75.47 MHz, C_6D_6, 25 °C): δ 292.7 (br s, Os=*C*), 182.7 (s, O_2CCH_3), 144.9 (s, −*C*(Ph)=CH_2), 136.3 (s, C-*ipso* C_6H_5), 127.0 (s, *p*-C_6H_5), 126.4 (s, *o*- and *m*-C_6H_5), 105.7 (t, $^3J_{P-C} = 3.1$, =C=C*H*), 103.4 (s, =*C*H_2), 24.9 (s, O_2CCH_3), 24.7 (vt, $N = 24.3$, P*C*H$(CH_3)_2$), 19.6, 19.1 (both s, PCH(*C*H_3)$_2$).

Preparation of [OsH(κ^2-O_2CCH_3){≡CCH=CMePh}-(P^iPr_3)$_2$]BF_4 (14). Method A. A 1:1 mixture of compounds **4** and **8** (60 mg, 0.07 mmol) was placed in an NMR tube, and 0.5 mL of $CDCl_3$ was added. After 1 month at room temperature, a 1:0.5:0.5 mixture of compounds **4**, **8**, and **14** was observed by NMR spectroscopy. An equilibrium was established, and a greater conversion of compound **4** to **14** was not observed at longer reaction times. Crystallization of the mixture from CH_2Cl_2/diethyl ether allowed the separation (by hand) of red crystals of **14**.

Method B. A 1:1 mixture of complexes **4** and **8** (93 mg, 0.11 mmol) was dissolved in 4 mL of CH_2Cl_2, and the acid Al_2O_3 (300 mg) was added. The reaction mixture was stirred for 1 h and then filtered through Celite and the filtrate evaporated to dryness. The red solid which precipitated was washed twice with diethyl ether and subsequently identified as a 1:1 mixture of compounds **8** and **14**. Yield: 61.2 mg (67%). The red solid was crystallized from CH_2Cl_2/diethyl ether to give red and purple crystals of complexes **14** (separated by hand) and **8**, respectively. Anal. Calcd for $C_{30}H_{55}BF_4O_2OsP_2$: C, 45.80; H, 7.05. Found: C, 45.86; H, 7.10. MS (FAB$^+$): *m*/*z* (relative intensity) 701 (58) (M^+), 541 (27) ($M^+ - P^iPr_3$). IR (KBr, cm^{-1}): ν(Os−H) 2195, ν(C=C) 1583, ν_{asym}(OCO) 1548, ν_{sym}(OCO) 1470, ν(B−F) 1064. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.70−7.52 (m, 3 H, *o*- and *p*-C_6H_5), 7.50−7.38 (m, 2 H, *m*-C_6H_5), 5.34 (s, 1 H, C*H*=C), 2.64−2.46 (m, 6 H, PC*H*$(CH_3)_2$), 2.33 (s, 3 H, O_2CCH_3), 1.80 (s, 3 H, =C*Me*Ph), 1.41 (dvt, $N = 14.4$, $^3J_{H-H} = 7.2$, 18 H, PCH(CH_3)$_2$), 1.36 (dvt, $N = 15.0$, $^3J_{H-H} = 7.2$, 18 H, PCH(CH_3)$_2$), −8.12 (t, $^3J_{P-H} = 15.6$, 1 H, Os−H). Irradiation of the signal at 5.34 ppm produces an NOE of 9.5% in the multiplet at 7.50−7.38 ppm. ^{31}P{^{1}H} NMR (121.42 MHz, $CDCl_3$, 25 °C): δ 41.3 (s). ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$, 25 °C): δ 273.6 (br, Os≡*C*), 186.5 (s, O_2CCH_3), 161.6 (s, =*C*MePh), 136.8 (s, C-*ipso* C_6H_5), 132.3 (s, *C*H=), 131.9 (s, *p*-C_6H_5), 129.6 (s, *m*-C_6H_5), 125.7 (s, *o*-C_6H_5), 26.2 (t, $^1J_{P-C} = 13.3$, P*C*H$(CH_3)_2$), 25.5 (s, O_2CCH_3), 21.0 (s, =C*Me*Ph), 19.6, 19.0 (both s, PCH(*C*H_3)$_2$).

Preparation of [OsH(κ^2-O_2CCH_3){≡CCH=CMe_2}(P^iPr_3)$_2$]-BF_4 (15). Method A. A 3:1 mixture of compounds **6** and **9** (70 mg, 0.09 mmol) was placed in an NMR tube, and 0.5 mL of $CDCl_3$ was added. The reaction was complete within 5 days at room temperature, and a 1:3 mixture of complexes **9** and **15** was obtained. Crystallization of the mixture from CH_2Cl_2/diethyl ether gave rise to orange and purple crystals, corresponding to compounds **15** and **9**, respectively.

Method B. A 3:1 mixture of complexes **6** and **9** (280 mg, 0.38 mmol) in 6 mL of dichloromethane was treated with 500 mg of the acid Al_2O_3. The obtained suspension was stirred for 1 h and then filtered. The filtrate was evaporated to dryness and diethyl ether added to precipitate a brown solid (1:3 mixture of complexes **9** and **15**), which was washed twice with diethyl ether and dried under vacuum. Yield: 200 mg (73%). Crystallization of this solid from CH_2Cl_2/diethyl ether gave rise to orange and purple crystals corresponding to compounds **15** and **9**, respectively, which could be separated by hand. Anal. Calcd for $C_{25}H_{53}BF_4O_2OsP_2$: C, 41.44; H, 7.37. Found: C, 40.82; H, 7.10. MS (FAB$^+$): *m*/*z* (relative intesity) 639 (100) (M^+), 638 (24) ($M^+ - H$), 479 (37) ($M^+ - P^iPr_3$). IR (KBr, cm^{-1}): ν(Os−H) 2175, ν(C=C) 1588, ν_{asym}(OCO) 1521, ν_{sym}(OCO) 1471, ν(B−F) 1060. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 4.78 (s, 1 H, C*H*=C), 2.60−2.40 (m, 6 H, PC*H*$(CH_3)_2$), 2.02 (s, 3 H,

Table 3. Crystal Data and Data Collection and Refinement Parameters for [Os(κ^2-O_2CCH_3){C(Me)C(OH)MePh}(P^iPr_3)$_2$]BF_4 (8) and Os{η^2-CH_2=CHC(Ph)$_2$O}(κ^2-O_2CCH_3)(P^iPr_3)$_2$ (10)

	8	**10**
formula	$C_{30}H_{57}BF_4O_3OsP_2 \cdot {}^1/_2OEt_2$	$C_{28}H_{53}BF_4O_2OsP_2$
mol wt	841.77	778.95
color, habit	dark purple, prismatic block	dark orange, prismatic block
cryst size, mm	0.36 × 0.2 × 0.1	0.6 × 0.24 × 0.12
space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
a, Å	8.6254(5)	10.1295(6)
b, Å	20.6339(12)	11.5310(9)
c, Å	21.3312(13)	15.5410(9)
α, deg	90	106.3196(9)
β, deg	99.9860(10)	92.0251(10)
γ, deg	90	97.5770(10)
V, Å^3	3738.9(4)	1721.9(2)
Z	4	2
D(calcd), g cm^{-3}	1.495	1.502
μ, mm^{-1}	3.547	3.828
scan type	ω scans at diff φ values	ω scans at diff φ values
2θ range, deg	$5 \le 2\theta \le 53$	$5 \le 2\theta \le 53$
temp, K	143(2)	143(2)
no. of data collcd	10852	8163
no. of unique data	5533	5983
no. of params refined	373	383
R1[a] ($F_o \ge 4.0\sigma(F_o)$)	0.0379	0.0256
wR2[b] (all data)	0.0991	0.0599
S[c] (all data)	1.054	1.134

O_2CCH_3), 1.61, 1.56 (both s, each 3 H, =C*Me*$_2$), 1.45−1.15 (m, 36 H, PCH(C*H*$_3$)$_2$), −8.31 (t, $^2J_{P-H}$ = 15.6, 1 H, Os−H). ^{31}P-{^{1}H} NMR (121.42 MHz, $CDCl_3$, 25 °C): δ 40.8 (s). ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$, 25 °C): δ 274.4 (t, $^2J_{P-C}$ = 8.3, Os≡*C*), 187.6 (s, O_2CCH_3), 169.0 (s, = *C*Me$_2$), 134.4 (s, *C*H=), 35.5 (s, O_2CCH_3), 26.4 (vt, *N* = 26.7, P*C*H(CH$_3$)$_2$), 25.6, 24.3 (both s, =C*Me*$_2$), 19.5, 19.0 (both s, PCH(*C*H$_3$)$_2$).

Crystal Data for 8 and 10. Crystals suitable for the X-ray diffraction study were obtained by slow diffusion of diethyl ether into a concentrated solution of **8** in dichloromethane and by slow diffusion of pentane into a concentrated solution of **10** in toluene. A summary of crystal data and refinement parameters is reported in Table 3. The dark purple (**8**) and dark orange (**10**) crystals were glued on a glass fiber and mounted on a Siemens CCD diffractometer with graphite-monochromated Mo Kα radiation. All data were corrected for absorption using a semiempirical method.[20] The structures were solved by Patterson (Os atom, SHELX97)[ref] and conventional Fourier techniques and refined by full-matrix least squares on F^2 (SHELX97).[21] Anisotropic parameters were used in the last cycles of refinement for all nondisordered atoms (excluding the hydrogen atoms). The hydrogen atoms (included in nondisordered groups) were observed or calculated in idealized positions and, most of them, refined riding on carbon atoms using a common isotropic thermal parameter (**8**) or using thermal parameters related to bonded atoms (**10**). The hydrogen atom H(1) (**8**) was refined as a free isotropic atom from an observed position. The phenyl group of **8** and a diethyl ether molecule in **10** were found to be disordered and were refined using geometry restraints and complementary occupancy factors.[21] Atomic scattering factors, corrected for anomalous dispersion of Os and P, were implemented by the program. The refinements converged to R1 = 0.0379 (**8**), 0.0256 (**10**) ($F^2 > 2\sigma(F^2)$) and wR2 = 0.0991 (**8**), 0.0599 (**10**) (all data).

Acknowledgment. We acknowledge financial support from the DGES of Spain (Project PB98-1591). C.G.-Y. thanks the CSIC-Repsol YPF for a postdoctoral grant.

Supporting Information Available: Tables of atomic coordinates and equivalent isotropic displacement coefficients, anisotropic thermal parameters, experimental details of the X-ray studies, and bond distances and angles for **8** and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM9909542

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