Reactions of New Osmium−Dihydride Complexes with Terminal Alkynes: Metallacyclopropene versus Metal−Carbyne. Influence of the Alkyne Substituent

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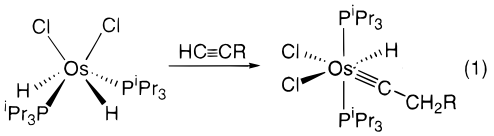
Reaction of $OsH_2(\kappa^2\text{-}OCOCH_3)\{\kappa^1\text{-}OC(O)CH_3\}(P^iPr_3)_2$ (**1**) with $1/2HBF_4{\cdot}OEt_2$ leads to the dimer $[\{OsH_2(\kappa^2\text{-}OCOCH_3)(P^iPr_3)_2\}_2(\mu\text{-}OCOCH_3)]BF_4$ (**2**), while the reaction with $HBF_4{\cdot}OH_2$ gives the aquo-derivative $[OsH_2(\kappa^2\text{-}OCOCH_3)(H_2O)(P^iPr_3)_2]BF_4$ (**3**). The structure of **2** in the solid state has been determined by an X-ray diffraction study. The structure consists of two $OsH_2(\kappa^2\text{-}OCOCH_3)(P^iPr_3)_2$ units connected through an acetate bridge. Complex **3** reacts with phenylacetylene and 1,1-diphenyl-2-propyn-1-ol to give the metallacyclopropene complexes $[OsH(\kappa^2\text{-}OCOCH_3)\{C(Ph)CH_2\}(P^iPr_3)_2]BF_4$ (**4**) and $OsH(\kappa^2\text{-}OCOCH_3)\{C[C(OH)Ph_2]CH_2\}(P^iPr_3)_2]BF_4$ (**7**), respectively. The structure of **4** in the solid state has been determined by an X-ray diffraction study. The geometry around the metal center can best be described as a pentagonal bipyramid with the two phosphorus atoms of the phosphines occupying apical positions. The equatorial plane is defined by the hydride, the acetate ligand, and the two carbon atoms of the metallacyclopropene. Reaction of **3** with *tert*-butylacetylene or trimethylsilylacetylene affords the carbyne complexes $[OsH(\kappa^2\text{-}OCOCH_3)(\equiv CCH_2R)(P^iPr_3)_2]BF_4$ [R = CMe_3 (**8**), H (**9**)], respectively. Deprotonation of **8** and **9** with KOH gives the vinylidene derivatives $OsH(\kappa^2\text{-}OCOCH_3)(=C=CHR)(P^iPr_3)_2$ [R = CMe_3 (**10**), H (**11**)]. The carbyne analogue of **8** and **9** bearing a phenyl group, $[OsH(\kappa^2\text{-}OCOCH_3)(\equiv CCH_2Ph)(P^iPr_3)_2]BF_4$ (**5**), can be obtained upon protonation of $OsH(\kappa^2\text{-}OCOCH_3)(=C=CHPh)(P^iPr_3)_2$ (**6**) with $HBF_4{\cdot}OEt_2$. In agreement with the experimental results, DFT (B3PW91) calculations show that the cyclopropene product is thermodynamically preferred for phenylacetylene, while the carbyne isomer is preferred for *tert*-butylacetylene.

Introduction

Reactions between transition metal hydride complexes and alkynes are fundamental steps in many catalytic cycles.[1] These reactions generally result in the formation of alkenyl derivatives as a result of the insertion of the alkyne into the M−H bond.[2]

In contrast to the general trend, the six-coordinate osmium(IV)−dihydride $OsH_2Cl_2(P^iPr_3)_2$ reacts with phenylacetylene, cyclohexylacetylene, 1-(trimethylsilyl)-1,4-pentadiyne, or trimethylsilylacetylene to give the hydrido−carbyne derivatives $OsHCl_2(\equiv CCH_2R)(P^iPr_3)_2$ (R = Ph, Cy, $CH_2C{\equiv}CSiMe_3$, H), according to eq 1.[3]



(1)

R = Ph, Cy, $CH_2C{\equiv}C(SiMe_3)$, H

Osmium(II) dihydrogen−vinylidene species have been proposed as the key intermediates in this process. Thus, the reactions were rationalized as the electrophilic attack of the acidic hydrogen atom of the dihydrogen ligand at the C_β atom of the vinylidene group. In agreement with this, the five-coordinate hydrido−vinylidene complex $OsHCl(=C=CHPh)(P^iPr_3)_2$ reacts with HCl to give $OsHCl_2(\equiv CCH_2Ph)(P^iPr_3)_2$.[4] Related five-

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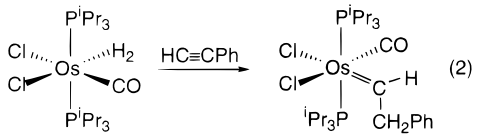
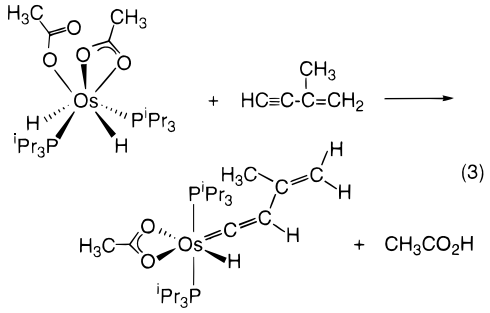
coordinate hydrido−vinylidene derivatives of osmium and ruthenium have recently been prepared by reaction of the trihydride compounds $MH_3Cl(PR_3)_2$ (M = Ru, Os; PR_3 = P^tBu_2Me, P^iPr_3) with terminal alkynes.[5]

In contrast to $OsH_2Cl_2(P^iPr_3)_2$, the dichloro−dihydrogen complex $OsCl_2(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2$ reacts with phenylacetylene to give the carbene complex $OsCl_2(=CHCH_2Ph)(CO)(P^iPr_3)_2$ (eq 2).



The formation of this carbene derivative proceeds by elimination of HCl to afford, initially, a six-coordinate hydride−π-alkyne intermediate, which evolves to the insertion product. Subsequently, the alkenyl complex undergoes an electrophilic attack by the HCl proton at the C_β carbon atom.[6]

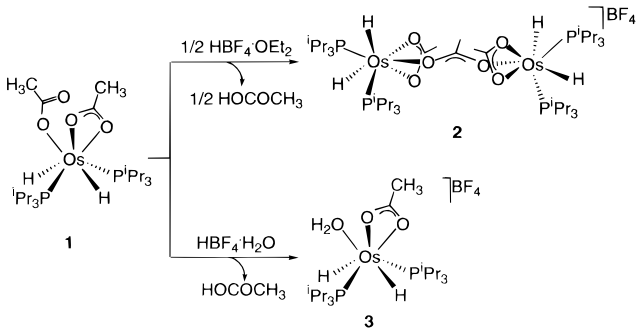
The seven-coordinate dihydride $OsH_2(\kappa^2\text{-}OCOCH_3)\{\kappa^1\text{-}OC(O)CH_3\}(P^iPr_3)_2$ neither follows the general trend nor shows a behavior similar to $OsH_2Cl_2(P^iPr_3)_2$ and $OsCl_2(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2$. Thus, reaction of $OsH_2(\kappa^2\text{-}OCOCH_3)\{\kappa^1\text{-}OC(O)CH_3\}(P^iPr_3)_2$ with 2-methyl-1-buten-3-yne affords the alkenylvinylidene complex $OsH(\kappa^2\text{-}OCOCH_3)\{=C=CHC(CH_3)=CH_2\}(P^iPr_3)_2$ (eq 3).[7]



The formation of this hydrido−alkenylvinylidene complex involves, as in the other two cases, the initial formation of an acid (acetic acid). However, in this case, the proton of the acid is not capable of attacking the vinylidene ligand.

The reactions shown in eqs 1−3, along with those reported for the complexes $OsHCl(CO)(P^iPr_3)_2$,[8] $[OsH(CO)_2\{\eta^1\text{-}OC(CH_3)_2\}(P^iPr_3)_2]^+$,[9] $OsH_3(\kappa^2\text{-}OCOCH_3)(P^iPr_3)_2$,[10] and $OsH_2(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2$,[11] indicate that the addition of terminal alkynes to osmium hydride complexes can afford not only alkenyl, but also carbyne, carbene, vinylidene, and alkynyl derivatives, and that new reaction patterns should be found during the study of the reactivity of this type of compounds, if the electronic properties of the metallic center are significantly changed.

Scheme 1



In the search for new reactions between transition metal complexes and alkynes, we have prepared novel seven-coordinate cationic dihydride compounds of osmium(IV) and have studied their reactivity toward phenylacetylene, *tert*-butylacetylene, trimethylsilylacetylene, or 1,1-diphenyl-2-propyn-1-ol. In this paper, we show that the preparation of osmacyclopropene derivatives, by reaction of osmium dihydride complexes with terminal alkynes, is also possible if the substituent of the alkyne is appropriately selected.

Results and Discussion

1. Synthesis and Characterization of $[\{OsH_2(\kappa^2\text{-}OCOCH_3)(P^iPr_3)_2\}_2(\mu\text{-}OCOCH_3)]BF_4$ and $[OsH_2(\kappa^2\text{-}OCOCH_3)(H_2O)(P^iPr_3)_2]BF_4$. Treatment of 7:1 diethyl ether/dichloromethane solutions of $OsH_2(\kappa^2\text{-}OCOCH_3)\{\kappa^1\text{-}OC(O)CH_3\}(P^iPr_3)_2$ (**1**) with 0.5 equiv of $HBF_4{\cdot}OEt_2$ leads to the cationic tetrahydride compound $[\{OsH_2(\kappa^2\text{-}OCOCH_3)(P^iPr_3)_2\}_2(\mu\text{-}OCOCH_3)]BF_4$ (**2**), which was isolated as a pale yellow solid in 82% yield (Scheme 1). The formation of this complex can be rationalized as a result of the protonation of an acetate ligand of 0.5 equiv of the starting material and the subsequent coordination of the monodentate acetate ligand of the other 0.5 equiv of **1** to the resulting fragment $[OsH_2(\kappa^2\text{-}OCOCH_3)(P^iPr_3)_2]^+$. In agreement with this, we have observed that the addition of 5 equiv of water to a chloroform-*d* solution of **2** regenerates 0.5 equiv of **1** and gives 0.5 equiv of the mononuclear complex $[OsH_2(\kappa^2\text{-}OCOCH_3)(H_2O)(P^iPr_3)_2]BF_4$ (**3**), which can also be obtained, in 97% yield, by treatment of 7:1 diethyl ether/acetone solutions of **1** with 1.5 equiv of $HBF_4{\cdot}H_2O$ (Scheme 1).

Complexes **2** and **3** were characterized by elemental analysis, IR, and ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopies. Complex **2** was further characterized by an X-ray crystallographic study. A view of the cation of **2** is presented in Figure 1. Selected bond distances and angles are listed in Table 1.

The cation is dinuclear and consists of two $OsH_2(\kappa^2\text{-}OCOCH_3)(P^iPr_3)_2$ fragments connected through an acetate bridge. Although the related structural parameters of the two fragments are not strictly equal, they can be considered equivalent due to the presence of a pseudo-C_2 axis, which contains the C(40)−C(39) bond of the acetate bridge.

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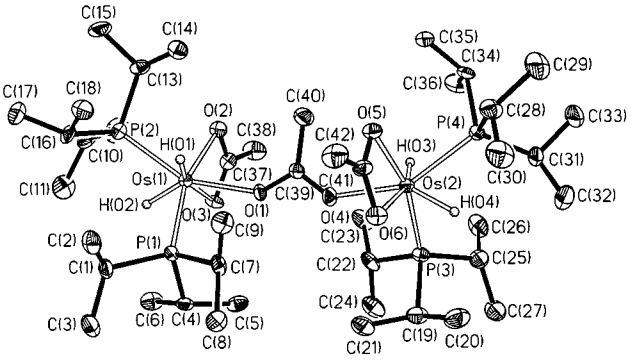


Figure 1. Molecular diagram of the cation of **2**, $[\{OsH_2(\kappa^2\text{-}OCOCH_3)(P^iPr_3)_2\}_2(\mu\text{-}OCOCH_3)]^+$.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for the Complex $[\{OsH_2(\kappa^2\text{-}OCOCH_3)(P^iPr_3)_2\}_2(\mu\text{-}OCOCH_3)]BF_4$ (2)

Os(1)−O(1)	2.122(4)	Os(2)−O(4)	2.113(4)
Os(1)−O(2)	2.197(4)	Os(2)−O(5)	2.207(4)
Os(1)−O(3)	2.251(4)	Os(2)−O(6)	2.232(4)
Os(1)−P(1)	2.3243(15)	Os(2)−P(3)	2.3142(16)
Os(1)−P(2)	2.2908(16)	Os(2)−P(4)	2.3006(16)
Os(1)−H(01)	1.50(3)	Os(2)−H(03)	1.51(3)
Os(1)−H(02)	1.51(3)	Os(2)−H(04)	1.51(3)
O(1)−Os(1)−O(2)	81.04(15)	O(4)−Os(2)−O(5)	80.83(16)
O(1)−Os(1)−O(3)	79.10(15)	O(4)−Os(2)−O(6)	78.99(15)
O(2)−Os(1)−O(3)	58.80(15)	O(5)−Os(2)−O(6)	59.08(15)
P(1)−Os(1)−P(2)	114.04(5)	P(3)−Os(2)−P(4)	112.84(6)
P(1)−Os(1)−O(1)	84.33(11)	P(3)−Os(2)−O(4)	86.17(12)
P(1)−Os(1)−O(2)	161.08(11)	P(3)−Os(2)−O(5)	162.42(11)
P(1)−Os(1)−O(3)	106.66(11)	P(3)−Os(2)−O(6)	106.90(12)
P(2)−Os(1)−O(1)	151.30(12)	P(4)−Os(2)−O(4)	149.94(12)
P(2)−Os(1)−O(2)	84.18(11)	P(4)−Os(2)−O(5)	83.94(11)
P(2)−Os(1)−O(3)	113.52(11)	P(4)−Os(2)−O(6)	114.55(12)
O(1)−Os(1)−H(01)	86(2)	O(4)−Os(2)−H(03)	86(2)
O(2)−Os(1)−H(01)	111(2)	O(5)−Os(2)−H(03)	111(2)
O(3)−Os(1)−H(01)	163(2)	O(6)−Os(2)−H(03)	163(2)
P(1)−Os(1)− H(01)	80(2)	P(3)−Os(2)−H(03)	79(2)
P(2)−Os(1)− H(01)	76(2)	P(4)−Os(2)−H(03)	76(2)
O(1)−Os(1)−H(02)	138(2)	O(4)−Os(2)−H(04)	143(2)
O(2)−Os(1)−H(02)	106(2)	O(5)−Os(2)−H(04)	110(2)
O(3)−Os(1)−H(02)	71(2)	O(6)−Os(2)−H(04)	78(2)
P(1)−Os(1)−H(02)	78(2)	P(3)−Os(2)−H(04)	74(2)
P(2)−Os(1)−H(02)	70(2)	P(4)−Os(2)−H(04)	66(2)
H(01)−Os(1)−H(02)	126(3)	H(03)−Os(2)−H(04)	119(3)

The two fragments have no symmetry elements other than a C_1 axis. At first glance, the coordination polyhedron around each osmium atom could be described as a capped trigonal prism. The two trigonal faces are made up by an oxygen atom of the bidentate acetate ligand, a hydride ligand, and a phosphorus atom of the triisopropylphosphine. The remaining vertex is occupied by the oxygen atom of the bridging acetate.

At room temperature complex **2** is fluxional in solution, as can be seen from the ^1H and $^{31}P\{^1H\}$ NMR spectra. Although inspection of the structure shown in Figure 1 predicts two different chemical shifts for the hydride ligands and two different chemical shifts for the phosphine ligands,[13] both the ^1H and the $^{31}P\{^1H\}$ NMR spectra show only one resonance for the corresponding nucleus. In the ^1H NMR spectrum the hydride resonance appears at −16.92 ppm as a triplet with a H−P coupling constant of 37.2 Hz. Lowering the sample temperature leads to broadening of this resonance. Between 233 and 223 K decoalescence occurs, and at 173 K four triplets and a broad signal are observed. The $^{31}P\{^1H\}$ NMR spectrum shows a behavior similar to that of the ^1H NMR spectrum. At room temperature, the spectrum contains a singlet at 31.7 ppm, while lowering the sample temperature leads to a broadening of the resonance. Between 223 and 213 K decoalescence occurs, and at 173 K, in addition to a broad resonance, five signals (two of them overlapping) are observed.

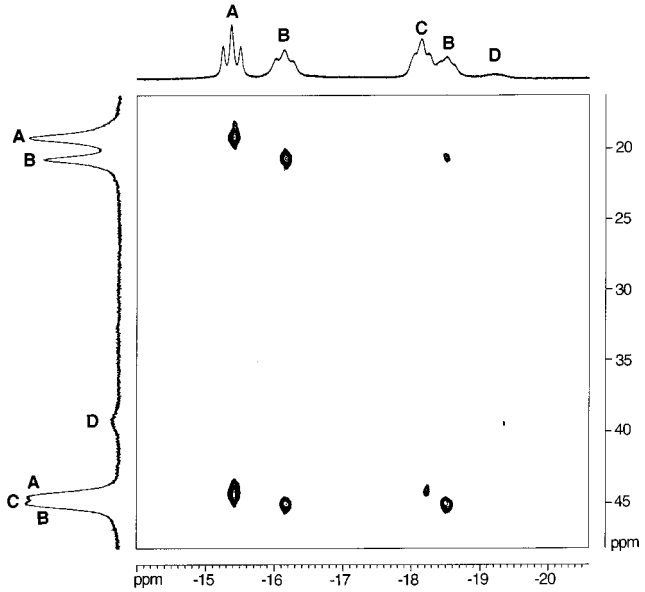


Figure 2. HMQC (^1H, ^{31}P) NMR spectrum of **2** at 173 K. Only the high-field region of the ^1H NMR spectrum is shown.

Figure 2 shows the HMQC (^1H, ^{31}P) NMR spectrum at 173 K. According to this spectrum, at 173 K, four environments around the osmium atoms, **A**, **B**, **C**, and **D**, coexist in solution. Environment **B** involves chemically inequivalent hydrides and chemically inequivalent phosphines and is the only distribution of ligands around the osmium atoms that is consistent with the one found in Figure 1. Environment **A** involves chemically equivalent hydrides and chemically inequivalent phosphines, while environment **C** contains chemically equivalent hydrides and phosphines. Environment **D** is fluxional even at 173 K.

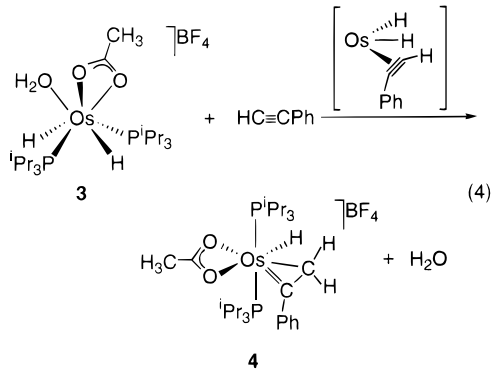
Complex **3** is also fluxional in solution, and the changes in the coordination polyhedron around the osmium atom occur with lower energy barriers than in the case of **2**. At room temperature, the ^1H NMR spectrum of **3** shows a triplet, at −16.90 ppm, with a H−P coupling constant of 35.5 Hz. Although decoalescence is not observed even at 173 K, lowering the sample temperature leads to a broadening of the abovementioned triplet. The presence of a water ligand in this complex is strongly supported by the ^1H NMR spectrum at 193 K, which contains a broad resonance, centered at 6.33 ppm, corresponding to the water hydrogen atoms. The $^{31}P\{^1H\}$ NMR spectrum shows a behavior similar to that of the ^1H NMR spectrum. At room temperature, the spectrum shows a singlet at 35.2 ppm. Again, although decoalescence is not observed at 173 K, lowering the sample temperature leads to a broadening of the signal.

(12) The hydride ligands were located in the different Fourier maps and refined as isotropic atoms along with the rest of the non-hydrogen atoms of the structure.

(13) From a spectroscopic point of view, the fragments are chemically equivalent. However, both hydrides and phosphines occupy chemically inequivalent positions within each fragment.

The IR spectrum of **2** in Nujol shows the inequivalence of the four hydrides in the solid state, displaying four ν(Os−H) bands at 2233, 2207, 2181, and 2154 cm^{-1}, while the IR spectrum in Nujol of complex **3** shows two ν(Os−H) bands at 2225 and 2192 cm^{-1}, characteristic for this type of arrangement.[7,14]

2. Reactions of [OsH$_2$(κ^2-OCOCH$_3$)(H$_2$O)(P^{i}Pr$_3$)$_2$]-BF$_4$ with Phenylacetylene and 1,1-Diphenyl-2-propyn-1-ol. Treatment of dichloromethane solutions of **3** with 1 equiv of phenylacetylene leads to the osmacyclopropene complex [OsH(κ^2-OCOCH$_3$){C(Ph)CH$_2$}(P^{i}Pr$_3$)$_2$]BF$_4$ (**4**), as a result of the displacement of the water molecule of **3** by the alkyne, and the subsequent Markovnikov insertion of the C−C triple bond of the alkyne into one of the two Os−H bonds of a π-alkyne intermediate (eq 4).



Few metallacyclopropene complexes are known to date. In general, they have been prepared by external nucleophilic attack on coordinated alkyne ligands[15] and have been limited to early transition metals, mainly Mo,[16] W,[17] and Re.[18] As far as we know, the only example of an osmacyclopropene is the complex [Os{C(CH$_3$)CH$_2$}(NH$_3$)$_5$](OTf)$_3$, reported by Harman and coworkers.[19] In contrast to **4**, this compound is obtained by electrophilic extraction of the methoxy group of the coordinated olefin in the complex [Os(η^2-CH$_2$=C(OMe)-CH$_3$}(NH$_3$)$_5$](OTf)$_2$.

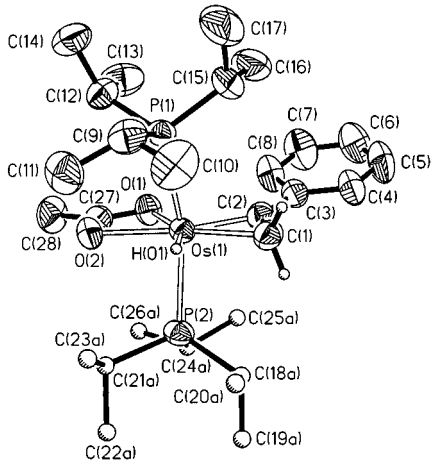


Figure 3. Molecular diagram of one of the two independent cations of **4**, [OsH(κ^2-OCOCH$_3$){C(Ph)CH$_2$}(P^{i}Pr$_3$)$_2$]$^+$.

The osmacyclopropene complex **4** was isolated as a purple solid in 55% yield and characterized by elemental analysis, IR, and ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopies, and by an X-ray crystallographic study. The structure has two chemically equivalent, but crystallographically independent, molecules of complex **4** in the asymmetric unit. A drawing of one of them is shown in Figure 3. Selected bond distances and angles for both molecules are listed in Table 2.

The coordination geometry around the osmium atom can be rationalized as a distorted pentagonal bipyramid with the two phosphorus atoms of the triisopropylphosphine ligands occupying trans positions [P(1)−Os(1)−P(2) = 161.37(9)° (molecule *a*) and 160.7(1)° (molecule *b*)]. The osmium coordination sphere is completed by the acetate ligand, which acts with a bite angle O(1)−Os(1)−O(2) of 59.3(3)° in molecule *a* and 59.6(3)° in molecule *b*, the hydride ligand, and the atoms C(1) and C(2) of the carbon donor ligand, which are coordined to the osmium atom to form a three-membered ring [C(1)−Os(1)−C(2) = 40.2(4)° in both molecules].

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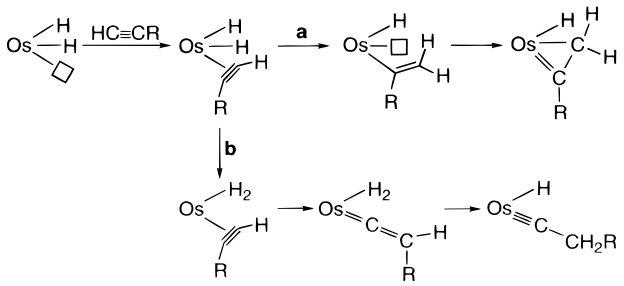
Table 2. Selected Bond Lengths (Å) and Angles (deg) for the Complex $[OsH(\kappa^2\text{-}OCOCH_3)\{C(Ph)CH_2\}(P^iPr_3)_2]BF_4$

molecule *a*		molecule *b*	
Os(1)−C(1)	2.141(11)	Os(2)−C(51)	2.146(12)
Os(1)−C(2)	1.895(10)	Os(2)−C(52)	1.882(11)
Os(1)−O(1)	2.211(7)	Os(2)−O(51)	2.219(7)
Os(1)−O(2)	2.162(7)	Os(2)−O(52)	2.158(7)
Os(1)−P(1)	2.433(2)	Os(2)−P(51)	2.433(3)
Os(1)−P(2)	2.434(3)	Os(2)−P(52)	2.435(3)
Os(1)−H(01)	1.43(9)	Os(2)−H(02)	1.56(9)
C(1)−C(2)	1.40(2)	C(51)−C(52)	1.41(2)
P(1)−Os(1)−P(2)	161.37(9)	P(51)−Os(2)−P(52)	160.74(10)
O(1)−Os(1)−O(2)	59.3(3)	O(51)−Os(2)−O(52)	59.6(3)
O(1)−Os(1)−C(1)	137.3(4)	O(51)−Os(2)−C(51)	137.0(4)
O(1)−Os(1)−C(2)	97.2(4)	O(51)−Os(2)−C(52)	96.8(4)
O(2)−Os(1)−C(1)	163.3(4)	O(52)−Os(2)−C(51)	163.5(4)
O(2)−Os(1)−C(2)	156.4(4)	O(52)−Os(2)−C(52)	156.3(4)
C(1)−Os(1)−C(2)	40.2(4)	C(51)−Os(2)−C(52)	40.2(4)
P(1)−Os(1)−O(1)	95.1(2)	P(51)−Os(2)−O(51)	96.0(2)
P(1)−Os(1)−O(2)	84.5(2)	P(51)−Os(2)−O(52)	85.2(2)
P(1)−Os(1)−C(1)	92.6(3)	P(51)−Os(2)−C(51)	92.2(4)
P(1)−Os(1)−C(2)	96.5(3)	P(51)−Os(2)−C(52)	99.5(3)
P(2)−Os(1)−O(1)	92.4(2)	P(52)−Os(2)−O(51)	91.9(2)
P(2)−Os(1)−O(2)	84.7(2)	P(52)−Os(2)−O(52)	83.6(2)
P(2)−Os(1)−C(1)	93.5(3)	P(52)−Os(2)−C(51)	94.0(4)
P(2)−Os(1)−C(2)	99.5(3)	P(52)−Os(2)−C(52)	97.1(3)
P(1)−Os(1)−H(01)	81(3)	P(51)−Os(2)−H(02)	78(4)
P(2)−Os(1)−H(01)	84(3)	P(52)−Os(2)−H(02)	88(3)
O(1)−Os(1)−H(01)	153(3)	O(51)−Os(2)−H(02)	153(4)
O(2)−Os(1)−H(01)	93(3)	O(52)−Os(2)−H(02)	93(4)
C(1)−Os(1)−H(01)	70(3)	C(51)−Os(2)−H(02)	70(4)
C(2)−Os(1)−H(01)	110(3)	C(52)−Os(2)−H(02)	110(4)

The M−C bond to the monosubtituted carbon [C(2)] is substantially shorter than the M−C bond to the disubstituted carbon [C(1)]. Thus, the Os−C(2) bond length [1.895(10) Å in molecule *a* and 1.882(11) Å in molecule *b*] is statistically identical with the Os−C double bond distance found in the carbene complex $OsCl_2(CHCH_2Ph)(CO)(P^iPr_3)_2$ [1.887(9) Å],[6] while the Os−C(1) bond length [2.141(1) Å in molecule *a* and 2.146(12) Å in molecule *b*] agrees well with the values previously reported for Os−C(alkyl) distances [mean value 2.16(5) Å].[20] The C(1)−C(2) distance [1.405(15) Å in molecule *a* and 1.407(16) Å in molecule *b*] is consistent with a metallacyclopropene formulation. Similar values have been reported for the related compounds of Mo,[16] W,[17] and Re.[18]

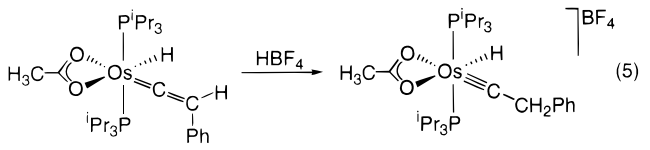
In agreement with the M−C(2)−carbene and M−C(1)−alkyl formulation the resonances of the C(2) and C(1) carbon atoms appear in the $^{13}C\{^1H\}$ NMR spectrum at 263.2 and −0.7 ppm, respectively. In the ^1H NMR spectrum the most notable resonances are those corresponding to the Os−CH_2− and Os−H hydrogen atoms, which are observed at 1.47 and −8.62 ppm, as triplets with H−P coupling constants of 6.9 and 15.3 Hz, respectively. The presence of a hydride ligand in **4** is also supported by the IR spectrum in Nujol and the ^{31}P NMR spectrum. The IR spectrum shows a ν(Os−H) band at 2236 cm^{-1}, whereas the $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 25.5 ppm which, under *off-resonance* conditions, is split into a doublet as a result of coupling to the hydride ligand.

Scheme 2



The different behavior of the complex $OsH_2Cl_2(P^iPr_3)_2$ and that of the fragment $[OsH_2(\kappa^2\text{-}OCOCH_3)(P^iPr_3)_2]^+$ should be noted (eqs 1 and 4). The reaction of the complex $OsH_2Cl_2(P^iPr_3)_2$ with phenylacetylene to afford the hydrido−carbyne derivative $OsHCl_2(\equiv CCH_2Ph)(P^iPr_3)_2$ involves initial coordination of the alkyne to give a dihydride−π-alkyne osmium(IV) intermediate, in equilibrium with a dihydrogen−π-alkyne osmium(II) species. Subsequently, a π-alkyne−vinylidene isomerization occurs. Thus, the electrophilic attack of the acidic hydrogen proton of the dihydrogen at the C_β atom of the vinylidene leads to the carbyne[3] (route b in Scheme 2). The formation of the osmacyclopropene complex **4** also involves initial coordination of the alkyne to give a dihydride−π-alkyne osmium(IV) intermediate. However, this intermediate evolves by insertion of the C−C triple bond into one of the two Os−H bonds to give an alkenyl intermediate, which subsequently should afford **4** (route a in Scheme 2). So, the formation of a hydrido−carbyne derivative or a hydride−osmacyclopropene complex appears to depend on two factors: (i) the tendency of the starting metallic fragment to promote a dihydride−dihydrogen transformation and (ii) the tendency of the coordinated alkyne to undergo isomerization into vinylidene.

The complex $OsH_2Cl_2(P^iPr_3)_2$ shows a high tendency to form elongated-dihydrogen compounds, as is revealed by its chemistry in the presence of nucleophilic reagents.[21] For example, simple addition of monodentate ligands to $OsH_2Cl_2(P^iPr_3)_2$ produces a dihydride-elongated dihydrogen transformation.[21] The fragment $[OsH_2(\kappa^2\text{-}OCOCH_3)(P^iPr_3)_2]^+$ has a lower tendency to form dihydrogen derivatives,[7] and according with this, complex **3** is a dihydride derivative. This behavior could explain why this fragment reacts with phenylacetylene to give the osmacyclopropene **4** instead of the hydrido−carbyne $[OsH(\kappa^2\text{-}OCOCH_3)(\equiv CCH_2Ph)(P^iPr_3)_2]BF_4$ (**5**), which can be obtained in 65% yield, by reaction of the hydrido−vinylidene $OsH(\kappa^2\text{-}OCOCH_3)(=C=CHPh)(P^iPr_3)_2$ (**6**) with $HBF_4\cdot Et_2O$ in diethyl ether as solvent (eq 5).



(5)

6 **5**

The presence of a hydride ligand in **5** is supported by the IR, ^1H, and ^{31}P NMR spectra. The IR spectrum in

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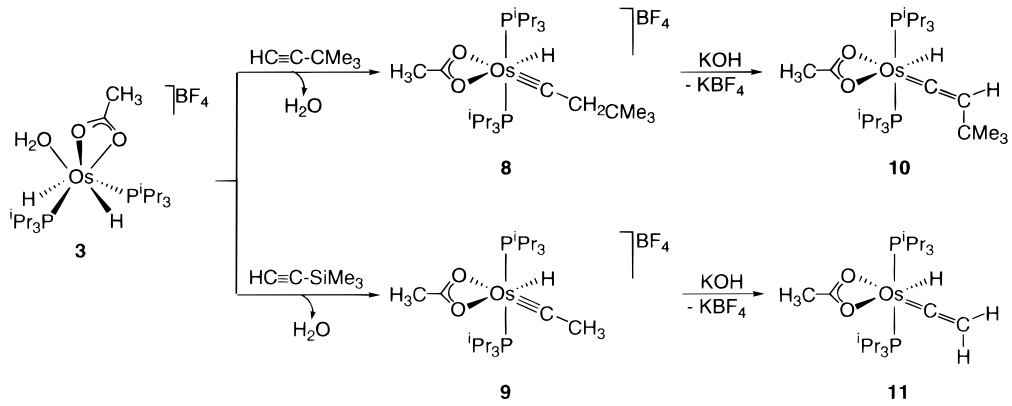
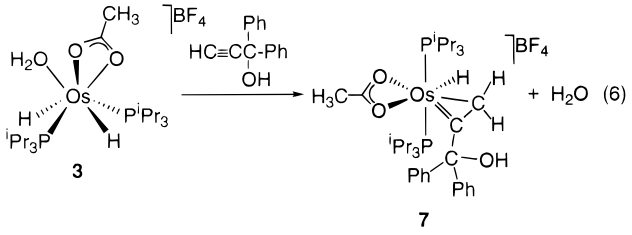
Scheme 3



Nujol shows a ν(Os−H) absorption at 2180 cm^{-1}, while the ^{1}H NMR spectrum in dichloromethane-d_2 contains a triplet, with a H−P coupling constant of 15.6 Hz, at −7.69 ppm. The ^{31}P{^{1}H} NMR spectrum shows a singlet at 43.7 ppm, which is split into a doublet under *off-resonance* conditions, as a result of the coupling with the hydride ligand. In the ^{13}C{^{1}H} NMR spectrum the most noticeable resonances are a triplet at 287.1 with a C−P coupling constant of 8.3 Hz and a singlet at 60.3 ppm, which were assigned to the C_α and C_β carbon atoms of the carbyne ligand, respectively.

Similarly to the reaction of **3** with phenylacetylene, treatment of dichloromethane solutions of **3** with 1.2 equiv of 1,1-diphenyl-2-propyn-1-ol, at 208 K, leads to the hydrido−hydroxy−osmacyclopropene complex [OsH(κ^2-OCOCH$_3$){C[C(OH)Ph$_2$]H$_2$}(P^{i}Pr$_3$)$_2$]BF$_4$ (**7**), which was isolated as yellow solid in 87% yield, according to eq 6.



In the IR spectrum of **7**, the most noticeable absorptions are those corresponding to the O−H and Os−H bonds, which appear at 3540 and 2203 cm^{-1}, respectively. In the ^{1}H NMR spectrum in chloroform-*d*, the OH resonance is observed as a singlet at 6.13 ppm, while the resonance corresponding to the −CH$_2$− hydrogen atoms of the carbon donor ligand appears as a triplet at 2.17 with a H−P coupling constant of 8.1 Hz. Furthermore, in the high-field region, the spectrum contains a triplet at −8.14 ppm with a H−P coupling constant of 16.2 Hz. The mutually cisoid disposition of the hydride ligand and the −CH$_2$− group of the three-membered ring was confirmed by a NOE experiment. Irradiation of the hydride resonance gave an increase of 4.6% in the triplet at 2.17 ppm, whereas the resonances of the phenyl groups were not affected.

The ^{13}C{^{1}H} NMR spectrum of **7** agrees well with that of **4**. The resonance corresponding to the monosubstituted carbon atom appears at 279.8 ppm, while the resonance due to the disubstituted carbon atom is observed at 9.6 ppm. The C(OH)Ph$_2$ carbon atom gives rise to a singlet at 95.0 ppm. The ^{31}P{^{1}H} NMR spectrum contains a singlet at 28.2 ppm, which splits into a doublet under *off-resonance* conditions, as a result of the coupling with the hydride ligand.

Complexes **4** and **7** can also be obtained, in about 50% yield, by reaction of the dinuclear complex **2** with 1 equiv of the corresponding alkyne. In addition to the cyclopropene derivatives, these reactions also give compound **1**. This indicates that the dinuclear complex **2** is a result of the stabilization of the unsaturated fragment [OsH$_2$(κ^2-OCOCH$_3$)(P^{i}Pr$_3$)$_2$]$^+$ by **1**.

3. Reaction of [OsH$_2$(κ^2-OCOCH$_3$)(H$_2$O)(P^{i}Pr$_3$)$_2$]BF$_4$ with *tert*-Butylacetylene or Trimethylsilylacetylene. It has previously been mentioned that the formation of a hydrido−osmacyclopropene derivative or a hydrido−carbyne complex, by reaction of an unsaturated osmium(IV) dihydride compound with a terminal alkyne, appears to depend on two factors, one of them characteristic of the starting metallic fragment and the other one characteristic of the alkyne. In agreement with the second factor, we have observed that the reaction of **3** with *tert*-butylacetylene or trimethylsilylacetylene does not lead to the corresponding osmacyclopropene compounds, related to **4** and **7**, but instead affords hydrido−carbyne complexes (Scheme 3). Treatment of dichloromethane solutions of **3** with 1 equiv of *tert*-butylacetylene leads to [OsH(κ^2-OCOCH$_3$)(≡CCH$_2$CMe$_3$)(P^{i}Pr$_3$)$_2$]BF$_4$ (**8**), which was isolated as a yellow solid in 68% yield. Similarly, the addition of 2 equiv of trimethylsilylacetylene to dichloromethane solutions of **3** affords [OsH(κ^2-OCOCH$_3$)(≡CCH$_3$)(P^{i}Pr$_3$)$_2$]BF$_4$ (**9**), as a yellowish solid in 60% yield. Alternatively, **9** can be prepared in 97% yield starting from **2**.

The formation of **8** and **9**, as shown in Scheme 3, suggests that the π-alkyne−vinylidene isomerization shown in Scheme 2 is more favored for *tert*-butylacetylene or trimethylsilylacetylene than for phenylacetylene or 1,1-diphenyl-2-propyn-1-ol. Furthermore, the cleavage of the Si−C bond in the formation of **9** agrees well with the participation of a vinylidene species as the key intermediate. A similar desilylation has previously been observed in the reaction of the dihydrido−dichloro OsH$_2$Cl$_2$(P^{i}Pr$_3$)$_2$ with trimethylsilylacetylene to give OsHCl$_2$(≡CCH$_3$)(P^{i}Pr$_3$)$_2$. This desilylation has been attributed to the presence in the reaction medium of slight traces of water, which acts as an electrophilic reagent.[3]

The IR spectra of **8** and **9** in Nujol show the characteristic ν(Os−H) band at 2178 (**8**) or 2170 cm^{-1} (**9**). In the ^{1}H NMR spectra the resonance corresponding to the hydride ligand appears at −8.04 (**8**) or −8.36 ppm (**9**), as triplets with H−P coupling constants of 16.2 (**8**) or 15.6 Hz (**9**). The presence of a carbyne ligand in these compounds is mainly supported by the ^{13}C{^{1}H} NMR spectra. In the ^{13}C{^{1}H} NMR spectrum of **8**, the resonance due to the C_α atom of the carbyne appears as a triplet at 292.5 ppm, with a C−P coupling constant of 6.9 Hz, while the resonance corresponding to the C_β atom is observed as a singlet at 65.9 ppm. In the ^{13}C{^{1}H} NMR spectrum of **9**, the C_α atom of the carbyne gives rise to a triplet at 286.3 ppm with a C−P coupling constant of 8.4 Hz, whereas the $-CH_3$ carbon atom appears as a singlet at 40.1 ppm. The ^{31}P{^{1}H} NMR spectra of both compounds contain singlets at 41.8 (**8**) and 42.3 ppm (**9**). Under *off-resonance* conditions, these singlets are split into doublets, as a result of coupling to the hydride ligands.

The hydrido−carbyne complexes **8** and **9** show a behavior similar to the chloro derivatives $OsHCl_2(\equiv CCH_2R)(P^iPr_3)_2$.[4] Thus, treatment of methanol solutions of **8** or **9** with KOH leads to the corresponding hydrido−vinylidene compounds $OsH(\kappa^2\text{-}OCOCH_3)(=C=CHCMe_3)(P^iPr_3)_2$ (**10**) and $OsH(\kappa^2\text{-}OCOCH_3)(=C=CH_2)(P^iPr_3)_2$ (**11**), respectively, as a result of the deprotonation of the C_β atom of the carbyne ligand of the starting materials (Scheme 3). Complex **10** was isolated as an orange-yellow solid in 40% yield and characterized by IR, ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectroscopies. In the ^{1}H NMR spectrum in benzene-d_6, the most notable resonances are a triplet at 0.23 ppm with a H−P coupling constant of 3.0 Hz, corresponding to the =CH hydrogen atom of the vinylidene, and another triplet at −12.82 ppm with a H−P coupling constant of 15.9 Hz, due to the hydride ligand. In the ^{13}C{^{1}H} NMR spectrum, the resonance corresponding to the C_α of the vinylidene appears as a triplet at 288.8 ppm, with a C−P coupling constant of 10.1 Hz, while the resonance due to the C_β atom is observed as a singlet at 114.3 ppm. The ^{31}P{^{1}H} NMR spectrum shows a singlet at 24.0 which, under *off-resonance* conditions, is split into a doublet as a result of coupling to the hydride ligand.

Although the reaction is quantitative (by NMR spectroscopies), the isolated yield (23%) of complex **11** is quite low, as its high solubility does not easily permit us to precipitate it from solution. In the IR spectrum in Nujol, the most noticeable feature is the presence of a ν(Os−H) band at 2140 cm^{-1}. The ^{1}H NMR spectrum shows the $=CH_2$ resonance of the vinylidene as a triplet at 0.45 ppm, with a H−P coupling constant of 2.7 Hz. The hydride ligand gives rise to another triplet at −12.87 ppm with a H−P coupling constant of 15.6 Hz. In the ^{13}C{^{1}H} NMR spectrum the resonance due to the C_α atom of the vinylidene appears at 289.8 ppm as a triplet with a C−P coupling constant of 10.7 Hz, and the C_β atom also appears as a triplet at 84.1 ppm with a C−P coupling constant of 1.8 Hz. As is seen in the ^{31}P{^{1}H} NMR spectrum of **10**, the ^{31}P{^{1}H} NMR spectrum of **11** contains a singlet at 25.3 ppm which, under *off-resonance* conditions, is split into a doublet as a result of coupling to the hydride ligand.

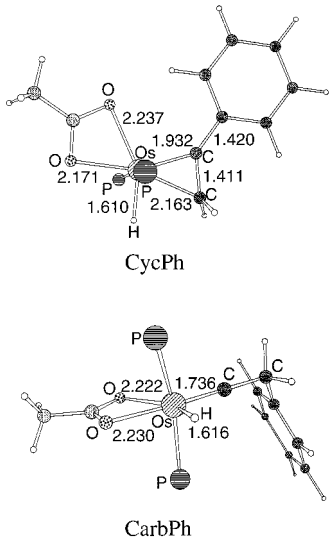


Figure 4. Optimized (B3PW91) geometries of the metallacyclopropene (**CycR**) and the carbyne (**CarbR**) for R = Ph.

We note that Allen et al.[16i] have previously observed the rearrangement of the trimethylsilyl−metallacyclopropene complexes $Mo(\eta^5\text{-}C_9H_7)\{C(SiMe_3)CHR\}\{P(OMe)_3\}_2$ (R = H, Ph) to the corresponding carbyne isomers, by an 1,2-shift of the silyl group from the monosubstituted carbon atom into the disubstituted carbon atom of the metallacyclopropene. The formation of **8** and **9** by a similar procedure, involving metallacyclopropene intermediates related to **4** and **7**, does not seem to be a reasonable proposal since the formation of **8** should require the 1,2-shift of the *tert*-butyl group, and the activation barrier for this migration should be very high. Furthermore, in agreement with the participation of vinylidene intermediates during the formation of **8** and **9**, we have observed that addition of 1 equiv of $HBF_4{\cdot}OEt_2$ to diethyl ether solutions of **10** and **11** rapidly regenerates **8** and **9**, respectively.

4. Theoretical Analysis. The two isomeric forms, metallacyclopropene (**CycR**) and carbyne (**CarbR**), were optimized with DFT(B3PW91)[22] for R = H, Me, and Ph. The structures of **CycR** and **CarbR** (Figure 4) show no remarkable features. The three ligands, acetate, hydride, and metallacyclopropene or carbyne, are situated in a plane that is perpendicular to the Os−P direction. To compare the structure of **CycPh** with the experimental structure of **4**, we present only the geometrical calculated parameters for R = Ph. In **CycPh**, the Os−C(2) is shorter (1.932 Å) than Os−C(1) (2.163 Å), as expected from the partial Os−C(2) double bond. The Os−C bond (1.736 Å) in **CarbPh** is the shortest.

(22) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Revision A.6; Gaussian, Inc.: Pittsburgh, PA, 1998.

In **CycPh** the Os−O bond pseudo-trans to H is slightly longer (2.237 Å) than the Os−O bond (2.171 Å) trans to C(1). In **CarbPh** the two Os−O bond lengths are more equal (2.222 and 2.230 Å, respectively). As the rotation of the C−C bond is essentially free, the conformation of the phenyl group in **CarbPh** has no real significance. The calculated structure of **CycPh** is close to the X-ray structure of **4** (Figure 3)

The dependence on R of the relative energies of **CycR** and **CarbR** is remarkable. While for R = H, **CycH** is calculated to be 18 kcal·mol^{-1} *above* **CarbH**. **CycMe** is calculated to be only 8.7 kcal·mol^{-1} above **CarbMe**. There is a reversal in the relative energy of the isomers for R = Ph since **CycPh** is calculated to be 3.2 kcal·mol^{-1} *below* **CarbPh**. Steric factors should not modify the relative energies calculated for a model deprived of steric effects (PH_3 as model phosphine, Me as a model for ^{t}Bu). The Ph group has no large steric effect. In addition, the phenyl group is calculated to be lying on the Os−C(1)−C(2) in the metallacyclopropene isomer, which minimizes the steric effects with the phosphine ligands. **CycPh** should thus remain the preferred isomer. In the case of R = ^{t}Bu, the carbyne isomer is the least sterically hindered, and the electronic preference for **CarbMe** should also be found for R = ^{t}Bu.

While there is a strong energy preference for the carbyne form for R = H, any substitution stabilizes more the metallacyclopropene form than the carbyne (9.3 kcal·mol^{-1} for Me and 21.2 kcal·mol^{-1} for Ph). 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. The conjugating effect of the phenyl group has several structural consequences. The phenyl ring lies on the Os−C(1)−C(2) plane. The Os−C(2) bond is longer for R = Ph (1.932 Å) than for R = H (1.875 Å), which indicates that the phenyl π-orbitals and one occupied osmium d-orbital compete to conjugate with the π-orbital of C(2). Finally, the conjugation of Ph with C(2) is shown through the bond alternation, which is more accentuated in **CycPh**—a difference of 0.03 Å between short and long bonds—than in **CarbPh** (where the difference is only 0.006 Å). As should be expected, the geometries calculated for R = H and Me are very similar, which shows that there is little effect caused by hyperconjugation of Me with C(2) in the metallacyclopropene isomer.

Concluding Remarks

We have previously reported the synthesis of the complexes $OsH_2Cl_2(P^iPr_3)_2$,[14a] $OsCl_2(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2$,[6] and $OsH_2(\kappa^2\text{-}OCOCH_3)\{\kappa^1\text{-}OC(O)CH_3\}(P^iPr_3)_2$,[7] which contain two hydrogen atoms bonded to the metallic center. A study of their reactivities toward terminal alkynes revealed new reaction patterns between transition metal hydride compounds and alkynes, giving carbyne,[3] carbene,[6] and vinylidene[7] derivatives. In this paper we have described the synthesis of two new compounds containing two hydrogen atoms bonded to osmium, the tetrahydride $[\{OsH_2(\kappa^2\text{-}OCOCH_3)(P^iPr_3)_2\}_2(\mu\text{-}OCOCH_3)]BF_4$ and the dihydride $[OsH_2(\kappa^2\text{-}OCOCH_3)(H_2O)(P^iPr_3)_2]BF_4$, which are of interest not only because they have no precendent in transition metal hydride chemistry but also because they have allowed us to find a new reaction pattern between a transition metal hydride complex and a terminal alkyne. Thus, the reactions of these novel compounds with phenylacetylene or 1,1-diphenyl-2-propyn-1-ol afford the hydride osmacyclopropene derivatives $[OsH(\kappa^2\text{-}OCOCH_3)\{C(Ph)CH_2\}(P^iPr_3)_2]BF_4$ and $[OsH(\kappa^2\text{-}OCOCH_3)\{C[C(OH)Ph_2]CH_2\}(P^iPr_3)_2]BF_4$, respectively.

Although there is a marked difference in reactivity toward phenylacetylene and 1,1-diphenyl-2-propyn-1-ol between the metallic fragment $[OsH(\kappa^2\text{-}OCOCH_3)(P^iPr_3)_2]^+$ and the complex $OsH_2Cl_2(P^iPr_3)_2$, in the presence of *tert*-butylacetylene or trimethylsilylacetylene the behavior of both species is the same. Thus it is also observed that the reactions of $[OsH_2(\kappa^2\text{-}OCOCH_3)(H_2O)(P^iPr_3)_2]BF_4$ with the above-mentioned alkynes lead to the hydride−carbyne derivatives $[OsH(\kappa^2\text{-}OCOCH_3)(\equiv CCH_2CMe_3)(P^iPr_3)_2]BF_4$ and $[OsH(\kappa^2\text{-}OCOCH_3)(\equiv CCH_3)(P^iPr_3)_2]BF_4$, respectively. The related compound $[OsH(\kappa^2\text{-}OCOCH_3)(\equiv CCH_2Ph)(P^iPr_3)_2]BF_4$, an isomer of $[OsH(\kappa^2\text{-}OCOCH_3)\{C(Ph)CH_2\}(P^iPr_3)_2]BF_4$, is also accessible, and its preparation involves the protonation of the hydride−vinylidene $OsH(\kappa^2\text{-}OCOCH_3)(=C=CHPh)(P^iPr_3)_2$.

Theoretical calculations indicate that the relative stability of the metallacyclopropene and carbyne structures depends on the substituent of the alkyne precursors. The metallacyclopropene isomer is thermodynamically more stable than the carbyne isomer when the substituent is a phenyl group, while an inverse relationship is observed for alkyl substituents.

In conclusion, the reactions of osmium compounds containing two hydrogen atoms bonded to the metallic center with terminal alkynes give not only carbyne, carbene, and vinylidene but also osmacyclopropene derivatives. The nature of the obtained products depends on all the factors related to the electronic nature of the starting material and also on the nature of the substituent, R, of the alkyne.

In light of these results, it is clear that further work needs to be done in order to be able to predict the result of the addition of terminal alkynes to this type of system, since the four dihydride compounds studied so far lead to four different types of organometallic compounds, all of them different from the usual alkenyl derivatives.

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. $OsH_2(\kappa^2\text{-}OCOCH_3)(\kappa^1\text{-}OCOCH_3)(P^iPr_3)_2$ (**1**)[7] and $OsH(\kappa^2\text{-}OCOCH_3)(=C=CHPh)(P^iPr_3)_2$ (**6**)[10] were prepared as previously reported. Infrared spectra were run on a Nicolet 550 spectrometer as solids (KBr pellet or Nujol mull). ^{1}H, ^{31}P, and ^{13}C{^{1}H} NMR spectra were recorded either on a Varian Gemini 2000 or on a Bruker AXR 300 instrument. Chemical shifts are referenced to residual solvent peaks (^{1}H, ^{13}C{^{1}H}) or external H_3PO_4 (^{31}P). Coupling constants, J and N ($N = J_{P-H} + J_{P'-H}$ for ^{1}H and $N = J_{P-C} + J_{P'-C}$ for ^{13}C{^{1}H}), are given in hertz. C, H, and N analyses were carried out either on a Perkin-Elmer 2400 CHNS/O or on a C.E. Instruments EA1108 analyzer. Mass spectrum analysis was performed with a VG Auto Spec

instrument. The ions were produced, FAB$^+$ mode, with the stardard Cs^+ gun at ca. 30 kV, and 3-nitrobenzyl alcohol (NBA) was used as the matrix.

Preparation of [{OsH$_2$(κ^2-OCOCH$_3$)(P^{i}Pr$_3$)$_2$}$_2$(μ-OCOCH$_3$)]BF$_4$ (2). To a solution of **1** (100 mg, 0.16 mmol) in diethyl ether/dichloromethane (7:1, 16 mL) was added HBF_4·Et_2O (11 μL, 0.08 mmol). The resulting mixture was stirred for 45 min at room temperature and then was evaporated to dryness. Subsequent addition of diethyl ether (20 mL) caused the precipitation of a pale yellow solid, which was washed with further portions of diethyl ether and dried in vacuo. Yield: 84 mg (82%). Anal. Calcd for $C_{42}H_{97}BF_4O_6Os_2P_4$: C, 39.20; H, 7.50. Found: C, 39.01; H, 7.51. IR (Nujol, cm^{-1}): ν(Os−H) 2233 (m), 2207 (m), 2181 (s), 2154 (s), ν_{asym}(OCO) 1550 (s), ν(B−F) 1150−1000 (s). ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ 2.24 (s, 3H, OCOC*H*$_3$), 2.24 (m, 12H, PC*H*(CH$_3$)$_2$), 1.72 (s, 6H, OCOCH$_3$), 1.25 (dd, J_{H-H} = 7.2 Hz, J_{P-H} = 13.8 Hz, 72H, PCH(C*H*$_3$)$_2$), −16.92 (t, J_{P-H} = 37.2 Hz, 4H, Os−H). ^{31}P{^{1}H} NMR (121.42 MHz, CD_2Cl_2, 293 K): δ 30.5 (s). ^{13}C{^{1}H} NMR (75.47 MHz, CD_2Cl_2, 293 K): δ 191.7 (s, O*C*OCH$_3$), 181.2 (s, O*C*OCH$_3$), 28.4 (s, OCO*C*H$_3$), 28.0 (d, J_{P-C} = 32.8 Hz, P*C*H(CH$_3$)$_2$), 26.7 (s, OCO*C*H$_3$), 18.92 (s, PCH(*C*H$_3$)$_2$), 18.89 (s, PCH(*C*H$_3$)$_2$).

Preparation of [OsH$_2$(κ^2-OCOCH$_3$)(H$_2$O)(P^{i}Pr$_3$)$_2$]BF$_4$ (3). To a solution of **1** (222 mg, 0.35 mmol) in diethyl ether/acetone (7:1, 16 mL) was added HBF_4·H_2O (63 μL, 0.53 mmol). The resulting mixture was stirred for 15 min at room temperature and then was evaporated to dryness. Subsequent addition of diethyl ether (20 mL) caused the precipitation of a pale yellow solid, which was washed with diethyl ether and dried in vacuo. Yield: 231 mg (97%). Anal. Calcd for $C_{20}H_{49}BF_4O_3OsP_2$: C, 35.50; H, 7.20. Found: C, 35.25; H, 7.46. IR (Nujol, cm^{-1}): ν(H$_2$O) 3350 (vs, br), ν(Os−H) 2225 (s), 2192 (s), ν(H$_2$O) 1685 (s), ν_{asym}(OCO) 1555 (s), ν_{sym}(OCO) 1390, ν(B−F) 1150−1000 (s). ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ 3.75 (br, 2H, H$_2$O), 2.24 (m, 6H, PC*H*(CH$_3$)$_2$), 1.85 (s, 3H, OCOCH$_3$), 1.28 (dd, J_{H-H} = 7.5 Hz, J_{P-H} = 14.4 Hz, 36H, PCH(C*H*$_3$)$_2$), −16.90 (t, J_{P-H} = 35.5 Hz, 2H, Os−H). ^{31}P{^{1}H} NMR (121.42 MHz, CD_2Cl_2, 293 K): δ 35.2 (s). ^{13}C{^{1}H} NMR (75.47 MHz, CD_2Cl_2, 293 K): δ 193.8 (s, O*C*OCH$_3$), 28.2 (d, J_{P-C} = 33.2 Hz, P*C*H(CH$_3$)$_2$), 26.0 (s, OCO*C*H$_3$), 18.9 (s, PCH(*C*H$_3$)$_2$).

Preparation of [OsH(κ^2-OCOCH$_3$){C(Ph)CH$_2$}(P^{i}Pr$_3$)$_2$]BF$_4$ (4). A stoichiometric amount of phenylacetylene (16.2 μL, 0.15 mmol) was added, via syringe, to a solution of **3** (100 mg, 0.15 mmol) in dichloromethane (10 mL). An immediate color change from pale yellow to purple was observed. The resulting mixture was stirred for 15 min at room temperature and then was evaporated to dryness. Subsequent addition of diethyl ether caused the precipitation of a purple solid, which was washed with diethyl ether and dried in vacuo. Yield: 62 mg (55%). Anal. Calcd for $C_{28}H_{53}BF_4O_2OsP_2$: C, 44.21; H, 7.02. Found: C, 44.46; H, 6.36. IR (Nujol, cm^{-1}): ν(Os−H) 2236 (w), ν(C=C) 1590 (s), ν_{asym}(OCO) 1511 (m), ν(B−F) 1150−1000 (s). ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ 9.40 (br, 1H, Ph), 8.06 (t, J_{H-H} = 7.5 Hz, 1H, Ph), 7.90 (br, 1H, Ph), 7.59 (br, 2H, Ph), 2.25 (m, 6H, PC*H*(CH$_3$)$_2$), 2.09 (s, 3H, OCOCH$_3$), 1.47 (t, 2H, J_{P-H} = 6.9 Hz, Os−CH$_2$-), 1.37 (dvt, J_{H-H} = 7.2 Hz, N = 14.1 Hz, 18H, PCH(C*H*$_3$)$_2$), 0.99 (dvt, J_{H-H} = 7.2 Hz, N = 14.1 Hz, 18H, PCH(C*H*$_3$)$_2$), −8.62 (t, J_{P-H} = 15.3 Hz, 1H, Os−H). ^{1}H NMR (300 MHz, CD_2Cl_2, 213 K, aromatic region): δ 9.43 (d, J_{H-H} = 7.5 Hz, 1H), 8.05 (t, J_{H-H} = 7.5 Hz, 1H), 7.90 (d, J_{H-H} = 7.2 Hz, 1H), 7.65 (t, J_{H-H} = 7.5 Hz, 1H), 7.53 (t, J_{H-H} = 7.5 Hz, 1H); there are no significant changes in the other signals. ^{31}P{^{1}H} NMR (121.42 MHz, CD_2Cl_2, 293 K): δ 25.5 (s, doublet under *off-resonance* conditions). ^{13}C{^{1}H} NMR (75.47 MHz, CD_2Cl_2, 213 K plus apt): δ 263.2 (s, Os=C), 188.5 (s, O*C*OCH$_3$), 142.9 (s, C$_{ipso}$ Ph), 133.5, 132.2, 131.9, 131.3, 130.9 (each one s, Ph), 26.8 (s, OCO*C*H$_3$), 23.0 (br, P*C*H(CH$_3$)$_2$), 19.1 (s, PCH(*C*H$_3$)$_2$), 18.0 (s, PCH(*C*H$_3$)$_2$), −0.7 (s, Os-*C*H$_2$).

Preparation of [OsH(κ^2-OCOCH$_3$)(≡CCH$_2$Ph)(P^{i}Pr$_3$)$_2$]BF$_4$ (5). A solution of **6** (312.4 mg, 0.46 mmol) in 10 mL of diethyl ether was treated with HBF_4·H_2O (106 μL, 0.78 mmol). A brown precipitate was immediately formed. After stirring for 5 min at room temperature, the brown solid was separated by filtration, washed with diethyl ether, and dried in vacuo. Yield: 229.6 mg (65%). Anal. Calcd for $C_{28}H_{53}BF_4O_2OsP_2$: C, 44.21; H, 7.02. Found: C, 43.90; H, 7.45. IR (Nujol, cm^{-1}): ν(Os−H) 2180 (m), ν_{asym}(OCO) 1520 (m), ν_{sym}(OCO) 1395 (m), ν(B−F) 1150−1000 (s). ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ 7.40−7.20 (m, 5H, Ph), 2.79 (s, 2H, Os≡CC*H*$_2$Ph), 2.41 (m, 6H, PC*H*(CH$_3$)$_2$), 1.76 (s, 3H, OCOCH$_3$), 1.36 (dvt, J_{H-H} = 7.5 Hz, N = 14.4 Hz, 18H, PCH(C*H*$_3$)$_2$), 1.30 (dvt, J_{H-H} = 7.2 Hz, N = 14.1 Hz, 18H, PCH(C*H*$_3$)$_2$), −7.69 (t, J_{P-H} = 15.6 Hz, 1H, Os−H). ^{31}P{^{1}H} NMR (121.42 MHz, CD_2Cl_2, 293 K): δ 43.7 (s). ^{13}C{^{1}H} NMR (75.47 MHz, CD_2Cl_2, 293 K): δ 287.1 (t, J_{P-C} = 8.3 Hz, Os≡C), 189.9 (t, J_{P-C} = 1.9 Hz, O*C*OCH$_3$), 131.7, 131.3, 131.0, 128.8 (each one s, Ph), 60.3 (s, Os≡C*C*H$_2$Ph), 28.4 (vt, N = 27 Hz, P*C*H(CH$_3$)$_2$) 27.6 (s, OCO*C*H$_3$), 21.2 (s, PCH(*C*H$_3$)$_2$), 20.9 (s, PCH(*C*H$_3$)$_2$).

Preparation of [OsH(κ^2-OCOCH$_3$){C[C(OH)Ph$_2$]CH$_2$}(P^{i}Pr$_3$)$_2$]BF$_4$ (7). To a solution of **3** (258 mg, 0.38 mmol) in dichloromethane (2 mL) at −65 °C was added 1,1-diphenyl-2-propyn-1-ol (95.5 mg, 0.46 mmol). The resulting mixture was stirred for 15 min at −65 °C, and then diethyl ether was added to precipitate a yellow solid, which was washed three times with diethyl ether at −65 °C and dried in vacuo. Yield: 288 mg (87%). Anal. Calcd for $C_{35}H_{59}BF_4O_3OsP_2$: C, 48.49; H, 6.86. Found: C, 48.23; H, 7.06. IR (KBr, cm^{-1}): ν(OH) 3540, ν(Os−H) 2203, ν(B−F) 1000−1100 (vs). ^{1}H NMR (300 MHz, $CDCl_3$, 253 K): δ 7.86 (d, J_{H-H} = 7.8 Hz, 4H, *o*-C$_6$H$_5$), 7.24 (t, J_{H-H} = 7.8 Hz, 4H, *m*-C$_6$H$_5$), 7.11 (t, J_{H-H} = 7.8 Hz, 2H, *p*-C$_6$H$_5$), 6.13 (s, 1H, OH), 2.17 (t, 2H, J_{P-H} = 8.1 Hz, CH$_2$, s in ^{1}H{^{31}P} NMR), 2.10−1.92 (m, 6H, PC*H*(CH$_3$)$_2$), 2.00 (s, 3H, OCOCH$_3$), 1.20 (dvt, J_{H-H} = 6.9 Hz, N = 13.8 Hz, 18H, PCH(C*H*$_3$)$_2$), 0.84 (dvt, J_{H-H} = 7.05 Hz, N = 14.5 Hz, 18H, PCH(C*H*$_3$)$_2$), −8.14 (t, J_{P-H} = 16.2 Hz, 1H, OsH). Irradiation of the signal at −8.14 ppm produces a NOE of 4.6% in the triplet at 2.17 ppm. ^{31}P{^{1}H} NMR (121.42 MHz, $CDCl_3$, 253 K): δ 28.2 (s). ^{13}C{^{1}H} NMR (75.47 MHz, CD_2Cl_2, 233K): δ 279.8 (s br, Os=C), 188.9 (s, O*C*OCH$_3$), 140.6 (s, C$_{ipso}$ Ph), 128.7, 128.3 (both s, *o*-C$_6$H$_5$), 128.0, 127.6 (both s, *p*-C$_6$H$_5$), 124.6 (s, *m*-C$_6$H$_5$), 95.0 (s, *C*(OH)Ph$_2$), 26.3 (s, OCO*C*H$_3$), 23.0 (vt, N = 25.6 Hz, P*C*H(CH$_3$)$_2$), 18.7 (s, PCH(*C*H$_3$)$_2$), 18.2 (s, PCH(*C*H$_3$)$_2$), 9.6 (s, Os−*C*H$_2$−). MS (FAB+): *m/e* (relative intesity) 781 (88) ([M]$^+$), 780 (41) ([M]$^+$ − H), 763 (23) ([M]$^+$ − H − OH), 721 (66) ([M]$^+$ − H − OCOCH$_3$).

Reaction of [{OsH$_2$(κ^2-OCOCH$_3$)(P^{i}Pr$_3$)$_2$}$_2$(μ-OCOCH$_3$)]BF$_4$ with PhC≡CH. In a 5 mm NMR tube, **2** (11.6 mg, 9 × 10^{-3} mmol) was disolved in CD_2Cl_2 (0.5 mL). To this solution was added PhC≡CH (1 μL, 9 × 10^{-3} mmol) via syringe. The color of the resulting solution changed within time of mixing from yellow to purple. ^{1}H and ^{31}P NMR spectra were immediately recorded. Both ^{1}H and ^{31}P{^{1}H} NMR spectra showed peaks corresponding to OsH$_2$(κ^2-OCOCH$_3$)(κ^1-OCOCH$_3$)(P^{i}Pr$_3$)$_2$ (50%)[7] and [OsH(κ^2-OCOCH$_3$){C(Ph)CH$_2$}(P^{i}Pr$_3$)$_2$]BF$_4$ (50%), by comparison with pure samples.

Reaction of [{OsH$_2$(κ^2-OCOCH$_3$)(P^{i}Pr$_3$)$_2$}$_2$(μ-OCOCH$_3$)]BF$_4$ with HC≡CC(OH)Ph$_2$. A 37 mg (2.9 × 10^{-2} mmol) sample of **2** was reacted with 6 mg (2.9 × 10^{-2} mmol) of 1,1-diphenyl-2-propyn-1-ol in 2 mL of dichloromethane at −40 °C. The reaction mixture was stirred for 1 h and 30 min, while warming to −10 °C. After this time, the solvent was evaporated to dryness and diethyl ether added to precipitate a yellow solid, which was extracted three times with the same solvent. The diethyl ether solution was then evaporated to dryness and cold pentane added to precipitate a yellow solid, which was dried under vacuo and subsequently identified as OsH$_2$(κ^2-OCOCH$_3$)(κ^1-OCOCH$_3$)(P^{i}Pr$_3$)$_2$ (10 mg, 1.58 × 10^{-2} mmol). The yellow solid, originally precipitated from diethyl ether, was identified as a mixture of compounds [{OsH$_2$(k^2-OCOCH$_3$)(P^{i}Pr$_3$)$_2$}$_2$(μ-

$OCOCH_3$)]BF_4 (14%) and [OsH(κ^2-$OCOCH_3$){C[C(OH)Ph_2]-CH_2}(P^iPr_3)$_2$]BF_4 (86%).

Preparation of [OsH(κ^2-$OCOCH_3$)(≡CCH_2CMe_3)(P^iPr_3)$_2$]BF_4 (8). To a solution of **3** (100 mg, 0.15 mmol) in 10 mL of dichloromethane was added HC≡C^{t}Bu (18 μL, 0.15 mmol). The resulting solution was stirred for 20 min at room temperature and then evaporated to ca. 0.5 mL. Addition of diethyl ether caused the precipitation of a pale yellow solid, which was washed with diethyl ether and dried in vacuo. Yield: 75 mg (68%). Anal. Calcd for $C_{26}H_{57}BF_4O_2OsP_2$·CH_2Cl_2: C, 39.28; H, 7.20. Found: C, 39.17; H, 7.19. IR (Nujol, cm^{-1}): ν(Os−H) 2178, ν_{asym}(OCO) 1514, ν_{sym}(OCO) 1406, ν(BF_4) 1100−1000. ^{1}H NMR (300 MHz, $CDCl_3$, 293 K): δ 2.55 (m, 6H, PC*H*(CH_3)$_2$), 1.73 (s, 3H, $OCOCH_3$), 1.56 (s, 2H, Os≡CCH_2−), 1.38 (dvt, J_{H-H} = 6.6 Hz, N = 13.5 Hz, 18H, PCH(C*H*$_3$)$_2$), 1.35 (dvt, J_{H-H} = 7.2 Hz, N = 14.7 Hz, 18H, PCH(C*H*$_3$)$_2$), 1.08 (s, 9H, C*Me*$_3$), −8.04 (t, J_{P-H} = 16.2 Hz, 1H, Os−H). ^{31}P{^{1}H} NMR (121.42 MHz, CD_2Cl_2, 293 K): δ 41.8 (s, doublet under off-resonance conditions). ^{13}C{^{1}H} NMR (75.47 MHz, CD_2Cl_2, 293 K): δ 292.5 (t, J_{P-C} = 6.9 Hz, Os≡*C*), 187.2 (s, O*C*OCH_3), 65.9 (s, −CH_2−), 32.3 (s, C(*C*H$_3$)$_3$), 30.6 (s, *C*(CH_3)$_3$), 27.0 (s, OOC*C*H_3), 26.1 (vt, N = 26.5 Hz, P*C*H(CH_3)$_2$), 19.5, 19.4 (both s, PCH(*C*H$_3$)$_2$).

Preparation of [OsH(κ^2-$OCOCH_3$)(≡CCH_3)(P^iPr_3)$_2$]BF_4 (9). This compound was prepared using two different procedures. Method a: To a solution of **3** (100 mg, 0.15 mmol) in 10 mL of dichloromethane was added HC≡$CSiMe_3$ (21 μL, 0.15 mmol). The resulting solution was stirred for 10 min at room temperature and then evaporated to ca. 0.5 mL. Addition of diethyl ether caused the precipitation of a yellowish solid, which was washed with diethyl ether and dried in vacuo. Yield: 63 mg (60%). Method b: HC≡$CSiMe_3$ (76 μL, 0.53 mmol) was added to a solution of **2** (400 mg, 0.36 mmol) in 10 mL of dichloromethane. The resulting solution was stirred for 45 min at room temperature and then evaporated to ca. 0.5 mL. Addition of diethyl ether caused the precipitation of a light yellow solid, which was washed with diethyl ether and dried in vacuo. Yield: 242 mg (97%). Anal. Calcd for $C_{22}H_{49}BF_4O_2OsP_2$: C, 38.60; H, 7.21. Found: C, 38.69; H, 6.73. IR (Nujol, cm^{-1}): ν(Os−H) 2170 (m), ν_{asym}(OCO) 1525 (m), ν_{sym}(OCO) 1396 (m), ν(B−F) 1150−1000 (s). ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ 2.54 (m, 6H, PC*H*(CH_3)$_2$), 1.75 (s, 3H, $OCOCH_3$) 1.39 (dvt, 36H, J_{H-H} = 7.5 Hz, N = 14.7 Hz, PCH(C*H*$_3$)$_2$), 1.30 (s, 3H, Os≡CC*H*$_3$), −8.36 (t, 1H, J_{P-H} = 15.6 Hz). ^{31}P{^{1}H} NMR (121.42 MHz, CD_2Cl_2, 293 K): δ 42.3 (s, doublet under off-resonance conditions). ^{13}C{^{1}H} NMR (75.47 MHz, CD_2Cl_2, 293 K): δ 286.3 (t, J_{P-C} = 8.4 Hz, Os≡*C* CH_3), 187.8 (br s, O*C*OCH_3), 40.1 (s, Os≡C*C*H_3), 26.5 (vt, N = 27.5 Hz, P*C*H-(CH_3)$_2$), 25.9 (s, OOC*C*H_3), 19.9 (s, PCH(*C*H$_3$)$_2$), 19.4 (s, PCH-(*C*H$_3$)$_2$).

Preparation of OsH(κ^2-$OCOCH_3$)(=C=$CHCMe_3$)(P^iPr_3)$_2$ (10). A solution of **8** (100 mg, 0.13 mmol) in methanol (10 mL) was treated with a solution (0.189 N) of KOH in methanol (0.7 mL, 0.13 mmol). The resulting mixture was stirred for 5 min at room temperature and then evaporated to dryness. KBF_4 was filtered away by adding toluene and filtering the resulting suspension through Celite. The resulting toluene solution was evaporated to dryness, and further addition of methanol caused the precipitation of an orange-yellow solid, which was washed with methanol and dried in vacuo. Yield: 35 mg (40%). Anal. Calcd for $C_{26}H_{56}O_2OsP_2$: C, 47.83; H, 8.64. Found: C, 47.84; H, 8.60. IR (Nujol, cm^{-1}): ν(Os−H) 2125 (m), ν(C=C) 1640 (m), ν_{asym}(OCO) 1544 (s), ν_{sym}(OCO) 1383 (s). ^{1}H NMR (300 MHz, C_6D_6, 293 K): δ 2.72 (m, 6H, PC*H*(CH_3)$_2$), 1.64 (s, 3H, OOCC*H*$_3$), 1.37 (dvt, J_{H-H} = 6.9 Hz, N = 13.5 Hz, 18H, PCH(C*H*$_3$)$_2$), 1.28 (dvt, J_{H-H} = 6.6 Hz, N = 12.6 Hz, 18H, PCH-(C*H*$_3$)$_2$), 1.19 (s, 9H, ^{t}Bu), 0.23 (t, J_{P-H} = 3.0 Hz, 1H, Os=C=C*H*^{t}Bu), −12.81 (t, J_{P-H} = 15.9 Hz, 1H, Os−H). ^{31}P{^{1}H} NMR (121.42 MHz, C_6D_6, 293 K): δ 24.0 (s, doublet under off-resonance conditions). ^{13}C{^{1}H} NMR (75.47 MHz, C_6D_6, 293 K): δ 288.8 (t, J_{P-C} = 10.1 Hz, Os=*C*=CH^{t}Bu), 181.9 (s, O*C*OCH_3), 114.3 (t, J_{P-C} = 3.2 Hz, Os=C=*C*HCMe$_3$), 33.5 (s, C(*C*H$_3$)$_3$), 25.4 (s, OOC*C*H_3), 24.8 (vt, N = 23.4 Hz, P*C*H(CH_3)$_2$), 24.5 (s, *C*(CH_3)$_3$), 19.9, 19.5 (both s, PCH(*C*H$_3$)$_2$).

Table 3. Crystal Data and Data Collection and Refinement Parameters for [{OsH_2(κ^2-$OCOCH_3$)(P^iPr_3)$_2$}$_2$(μ-$OCOCH_3$)]BF_4 (2) and [OsH(κ^2-$OCOCH_3$){C(Ph)CH_2}(P^iPr_3)$_2$]BF_4 (4)

	2	**4**
formula	$C_{42}H_{97}BF_4O_6Os_2P_4$	$C_{28}H_{53}BF_4O_2OsP_2$
mol wt	1289.29	760.65
color, habit	pale yellow, prismatic block	dark purple, prismatic block
cryst size, mm	0.4 × 0.3 × 0.2	0.49 × 0.31 × 0.31
space group	$P2_1/c$ (14)	$P2_1/n$ (14)
a, Å	18.693(1)	17.770(2)
b, Å	18.190(1)	12.928(2)
c, Å	17.778(1)	29.723(5)
α, deg	90	90
β, deg	114.737(10)	102.22(3)
γ, deg	90	90
V, Å^3	5490.3(5)	6673.6(17)
Z	4	8
D(calcd), g cm^{-3}	1.560	1.514
μ, mm^{-1}	4.793	3.97
scan type	ω scans at different φ values	$\omega/2\theta$
2θ range, deg	$5 \le 2\theta \le 46$	$3 \le 2\theta \le 50$
temp, K	153.0(2)	293.0(2)
no. of data collcd	12757	13437
no. of unique data	7588	11729
no. of params refined	574	706
R_1[a] ($F_o \ge 4.0\sigma(F_o)$)	0.0313	0.0443
wR_2[b] (all data)	0.0724	0.1226
S[c] (all data)	1.059	0.909

[a] $R_1(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2(F^2) = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$; $w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [\max(F_o^2, 0) + 2F_c^2]/3$ (**2**, a = 0.0346, b = 1.7805; **3**, a =0.0326, b = 1.4359). [c] $S = [\sum[w(F_o^2 - F_c^2)2]/(n - p)]^{1/2}$, where n is the number of reflections and p the number of parameters.

Preparation of OsH(κ^2-$OCOCH_3$)(=C=CH_2)(P^iPr_3)$_2$ (11). Compound **11** was prepared analogously as described for **10**, starting from **9** (100 mg, 0.146 mmol) and a solution (0.195 N) of KOH in methanol (766 μL, 0.146 mmol). Compound **11** was isolated as a yellow-greenish solid. Yield: 20 mg (23%). Anal. Calcd for $C_{22}H_{48}O_2OsP_2$: C, 44.28; H, 8.11. Found: C, 43.96; H, 8.10. IR (Nujol, cm^{-1}): ν(Os−H) 2140 (s), ν(C=C) 1613 (s), ν_{asym}(OCO) 1541(s), ν_{sym}(OCO) 1430 (s). ^{1}H NMR (300 MHz, C_6D_6, 293 K): δ 2.72 (m, 6H, PC*H*(CH_3)$_2$), 1.62 (s, 3H, OOCC*H*$_3$), 1.35 (dvt, J_{H-H} = 6.9 Hz, N = 13.2 Hz, 36H, PCH-(C*H*$_3$)$_2$), 0.45 (t, 2H, J_{P-H} = 2.7 Hz Os=C=C*H*$_2$), −12.87 (t, 1H, J_{P-H} = 15.6 Hz, Os−H). ^{31}P{^{1}H} NMR (121.42 MHz, C_6D_6, 293 K): δ 25.3 (s, doublet under off-resonance conditions). ^{13}C-{^{1}H} NMR (75.47 MHz, C_6D_6, 293 K): δ 289.8 (t, J_{P-C} = 10.7 Hz, Os=*C*=CH_2), 182.5 (br s, O*C*OCH_3), 84.1 (br t, J_{P-C} = 1.8 Hz, Os=C=*C*H$_2$), 24.9 (s, OCO*C*H_3), 23.9 (vt, N = 24.4 Hz, P*C*H(CH_3)$_2$), 19.4 (s, PCH(*C*H$_3$)$_2$), 19.1 (s, PCH(*C*H$_3$)$_2$).

Reaction of [{OsH_2(κ^2-$OCOCH_3$)(P^iPr_3)$_2$}$_2$(μ-$OCOCH_3$)]BF_4 with Me_3SiC≡CH. In a 5 mm NMR tube, **2** (9.25 mg, 7 × 10^{-3} mmol) was dissolved in CD_2Cl_2 (0.5 mL). To this solution was added HC≡$CSiMe_3$ (1 μL, 7 × 10^{-3} mmol) via syringe. After 15 min, the ^{1}H and ^{31}P{^{1}H} NMR spectra showed peaks corresponding to [OsH(κ^2-$OCOCH_3$)(≡CCH_3)(P^iPr_3)$_2$]BF_4 (45%), OsH_2(κ^2-$OCOCH_3$)(κ^1-$OCOCH_3$)(P^iPr_3)$_2$ (45%), and [{OsH_2-(κ^2-$OCOCH_3$)(P^iPr_3)$_2$}$_2$(μ-$OCOCH_3$)]BF_4 (10%).

Reaction of OsH(κ^2-$OCOCH_3$)(=C=$CHCMe_3$)(P^iPr_3)$_2$ with HBF_4·OEt_2. In a 5 mm NMR tube, complex **10** (16.5 mg, 2.5 × 10^{-2} mmol) was dissolved in $CDCl_3$ (0.5 mL). To this solution was added HBF_4·OEt_2 (3 μL, 2.5 × 10^{-2} mmol) via syringe. ^{1}H and ^{31}P NMR spectra recorded immediately showed quantitative formation of **8**.

Reaction of OsH(κ^2-$OCOCH_3$)(=C=CH_2)(P^iPr_3)$_2$ with HBF_4·OEt_2. In a 5 mm NMR tube, complex **11** (5.4 mg, 9 ×

10^{-3} mmol) was disolved in CD_2Cl_2 (0.5 mL). To this solution was added $HBF_4 \cdot OEt_2$ (1 μL, 9×10^{-3} mmol) via syringe. ^1H and ^{31}P NMR spectra recorded after 5 min showed quantitative formation of **9**.

Computational Details. The calculations were carried out with the Gaussian 98 suite of programs.[22] Os was represented with the Hay−Wadt relativistic core potential (ECP) for the 46 innermost electrons and its associated double-ζ basis set.[23] P is also described with the Los Alamos ECPs and its associated double-ζ basis set augmented by a d polarization function.[24,25] A 6-31G(d,p) basis set[26] was used for all other atoms. The phenyl group was represented with a 6-31G for the geometry optimization process, and the energies of the resulting geometries were recalculated with a 6-31G(d,p) on the phenyl group. Full optimizations without symmetry constraint have been carried out at the B3PW91 level.[27,28]

Crystal Data for 2 and 4. Crystals suitable for the X-ray diffraction study were obtained by slow diffusion of diethyl ether into concentrated solutions of **2** and **4** in acetone at room temperature. A summary of crystal data and refinement parameters is reported in Table 3. The yellow (**2**) and deep purple (**4**) crystals were glued on a glass fiber and mounted on Siemens CCD (**2**) and Siemens-STOE (**4**) diffractometers with graphite-monochromated Mo Kα radiation. All data were corrected for absorption using the SADABS program (**2**)[29] or a semiempirical method (**4**).[30] The structures were solved by Patterson (Os atoms, SHELX97)[31] and conventional Fourier techniques and refined by full-matrix least-squares on F^2 (SHELX97). Anisotropic parameters were used in the last cycles of refinement for all nondisordered atoms (excluding the hydrogen atoms). This 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. The hydrogen atoms H(01), H(02), H(03), and H(04) of **2** were refined as isotropic atoms with the same Os−H distance and thermal parameter, while the H(01), H(1A), H(1B), H(02), H(51A), and H(51B) atoms of **4** were refined with all free variables. One of the four phosphine ligands of the cation of **4** and both BF_4 anions of the same molecule were found to be disordered and were refined using geometry restraints and complementary occupancy factors. Atomic scattering factors were implemented by the program. The refinement converged to $R_1[F, F^2 > 2\sigma(F^2)]$ 0.0313 (**2**) or 0.0443 (**4**) and ωR^2 (F^2, all data) 0.0724 (**2**) or 0.1293 (**4**).

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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 studies, and bond distances and angles for **2** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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