Seven-Coordinate Dihydrido Complex $OsH_2(\kappa^2\text{-}O_2CCH_3)\{\kappa^1\text{-}OC(O)CH_3\}(P^iPr_3)_2$ as Precursor of New Organometallic Compounds Containing Unsaturated η^1-Carbon Ligands

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The dichloro−dihydrido complex $OsH_2Cl_2(P^iPr_3)_2$ (**1**) reacts with $K[CH_3CO_2]$ to give the seven-coordinate dihydrido $OsH_2Cl(\kappa^2\text{-}O_2CCH_3)(P^iPr_3)_2$ (**2**), while the reaction of **1** with $Ag[CH_3CO_2]$ affords $OsH_2(\kappa^2\text{-}O_2CCH_3)\{\kappa^1\text{-}OC(O)CH_3\}(P^iPr_3)_2$ (**3**). The structure of **3** in the solid state has been determined by X-ray diffraction analysis. The geometry around the metal center could ideally be described as derived from a distorted square antiprism with a missing vertice. One of the two square planes is made up by the two phosphorus atoms and the hydrido ligands. The oxygen atoms of the acetato ligands are located in the second plane, which is rotated by 24.7° from the first one. Complex **3** reacts with 2-methyl-1-buten-3-yne to give the α,β-unsaturated vinylidene derivative $OsH\{{=}C{=}CHC(CH_3){=}CH_2\}(\kappa^2\text{-}O_2CCH_3)(P^iPr_3)_2$ (**4**), which by reaction with $HBF_4{\cdot}OEt_2$ affords the cationic carbyne complex $[OsH\{{\equiv}CCH{=}C(CH_3){=}CH_2\}(\kappa^2\text{-}O_2CCH_3)(P^iPr_3)_2]BF_4$ (**5**). The structure of **5** has been also determined by X-ray diffraction analysis. The coordination geometry around the osmium atom could be rationalized as a distorted octahedron with the two phosphorus atoms of the phosphine ligands occupying apical positions. The equatorial plane is formed by the bidentate ligand, the hydrido, and the carbyne group. Under carbon monoxide atmosphere, complex **5** evolves into the (*Z*)-dienyl complex $Os\{(Z)\text{-}CH{=}CHC(CH_3){=}CH_2\}\{\kappa^1\text{-}OC(O)CH_3\}(CO)_2(P^iPr_3)_2$ (**6**), which does not isomerize into the (*E*)-dienyl isomer $Os\{(E)\text{-}CH{=}CHC(CH_3){=}CH_2\}\{\kappa^1\text{-}OC(O)CH_3\}(CO)_2(P^iPr_3)_2$ (**7**). Treatment of **6** with $HBF_4{\cdot}OEt_2$ produces isoprene and the *cis*-dicarbonyl $[Os(\kappa^2\text{-}O_2CCH_3)(CO)_2(P^iPr_3)_2]BF_4$ (**8**). The (*E*)-dienyl complex **7** has been prepared according to the following reaction sequence: the reaction of $Os\{(E)\text{-}CH{=}CHC(CH_3){=}CH_2\}Cl(CO)(P^iPr_3)_2$ (**9**) with $Ag[CH_3CO_2]$ leads to $Os\{(E)\text{-}CH{=}CHC(CH_3){=}CH_2\}(\kappa^2\text{-}O_2CCH_3)(CO)(P^iPr_3)_2$ (**10**), which under carbon monoxide atmosphere gives **7**. The related chloro complex $Os\{(E)\text{-}CH{=}CHC(CH_3){=}CH_2\}Cl(CO)_2(P^iPr_3)_2$ (**11**) is similarly prepared by starting from **9**. The protonation of **10** with $HBF_4{\cdot}OEt_2$ leads to the α,β-unsaturated carbene $[Os\{{=}CHCH{=}C(CH_3)_2\}(\kappa^2\text{-}O_2CCH_3)(CO)(P^iPr_3)_2]BF_4$ (**12**).

Introduction

The complex $OsH_2Cl_2(P^iPr_3)_2$ is an unusual example of a six-coordinate osmium(IV) molecule. Its solid-state structure, significantly distorted from octahedral, has only C_2 symmetry and can be described as a square antiprism with two missing vertexes.[1] In solution, it exists as two rapidly interconverting isomers, one having C_2 symmetry and the other with no symmetry.[2]

The chemical behavior of this complex is unique. It catalyzes the reduction of ketones, olefins, and diolefins[1,3] and is a useful starting material to prepare polyhydrido,[4] diolefin,[5] and cyclopentadienyl[6] derivatives of osmium(II) and -(IV). The reactions with $K[EtOCS_2]$, $K[CH_3COS]$, 2,2′-biimidazole (H_2bim), and pyrazole (Hpz) are of particular interest (Scheme 1). Substitution of the chloride anions in $OsH_2Cl_2(P^iPr_3)_2$

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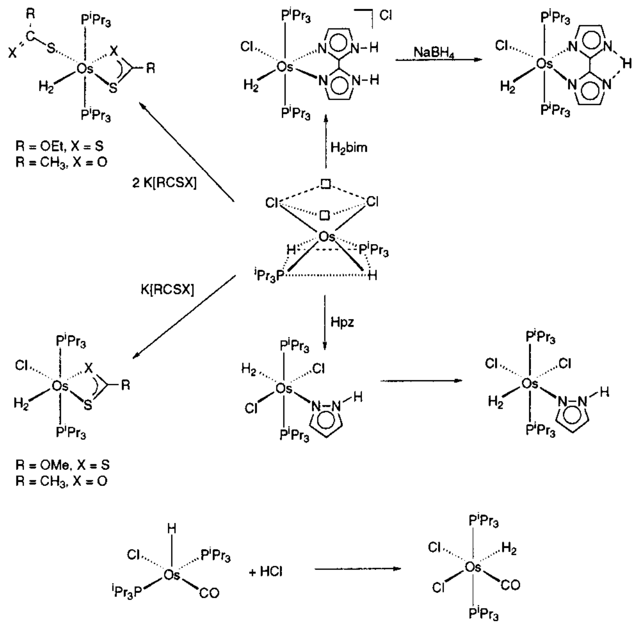
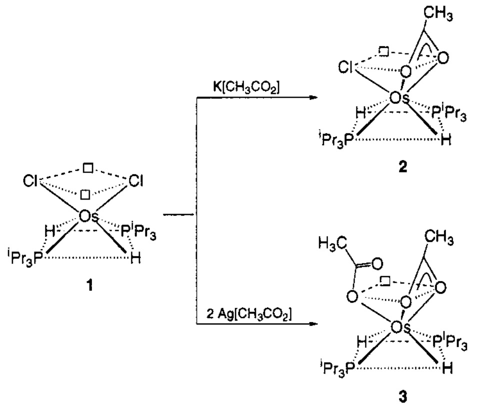
Scheme 1



Scheme 2



by $[EtOCS_2]^-$ and $[CH_3COS]^-$ produces dihydrido-elongated dihydrogen transformations.[7] Similarly, the addition of 2,2′-biimidazole leads to the cationic elongated dihydrogen $[OsCl(\eta^2\text{-}H_2)(H_2bim)(P^iPr_3)_2]Cl$, which by deprotonation with $NaBH_4$ yields $Os(Hbim)Cl(\eta^2\text{-}H_2)(P^iPr_3)_2$. Addition of pyrazole to $OsH_2Cl_2(P^iPr_3)_2$ affords the *trans-dichloro*-$OsCl_2(\eta^2\text{-}H_2)(Hpz)(P^iPr_3)_2$, which is transformed into its *cis-dichloro* isomer by stirring in hexane at 60 °C.[8] The related carbonyl derivative *cis-dichloro*-$OsCl_2(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2$ has been prepared by reaction of the five-coordinate complex $OsHCl(CO)(P^iPr_3)_2$ with HCl.[9]

The tendency of $OsH_2Cl_2(P^iPr_3)_2$ to form elongated dihydrogen complexes appears to determine its reactivity toward terminal alkynes, 1-alkyn-3-ols, and unsaturated alkynes. The reactions with terminal alkynes lead to hydrido−carbyne compounds, while hydrido−alkenylcarbyne derivatives are formed from 1-alkyn-3-ols and unsaturated alkynes.[10] Osmium(II) dihydrogen−vinylidene species have been proposed as the key intermediates of these processes; thus, the reactions are rationalized as the electrophilic attack of the acidic hydrogen proton of the dihydrogen ligand on 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 $OsHCl_2({\equiv}CCH_2Ph)(P^iPr_3)_2$.[11] Related five-coordinate hydrido−vinylidene derivatives of osmium and ruthenium have been recently prepared by reaction of the trihydrido compounds $MH_3Cl(PR_3)_2$ (M = Ru, Os; $PR_3 = P^tBu_2Me$, P^iPr_3) with terminal alkynes.[12]

The dichloro−dihydrogen compound $OsCl_2(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2$ reacts with terminal alkynes, 1-alkyn-3-ols, and unsaturated alkynes to give carbene and alkenylcarbene derivatives. The formation of these derivatives goes by elimination of HCl to afford initially a six-coordinate hydrido−π-alkyne intermediate, which evolves to the insertion product. Subsequently, the alkenyl complex undergoes the electrophilic attack of the HCl proton at the nucleophilic center of the unsaturated organic ligand (β or δ carbon atom) to give the carbene species.[9]

For the reaction types mentioned above for complexes containing two hydrogen atoms in the coordination sphere of the metal, two types of organometallic compounds have been previously obtained: carbynes, when the hydrogen atoms form a dihydrido, and carbenes, when the hydrogen atoms form a dihydrogen. In this context, it should be mentioned that the organometallic products obtained from the reactions of osmium hydrido compounds with terminal alkynes depend on the number of hydrogen atoms bonded to the metallic center and the nature of these hydrogens.[9,10,12,13]

In this paper, we show that the behavior of the dichloro−dihydrido complex $OsCl_2H_2(P^iPr_3)_2$ toward $[CH_3CO_2]^-$ is different from that previously observed in the presence of $[EtOCS_2]^-$ and $[CH_3COS]^-$ and that the reactivity of the resulting compound toward 2-methyl-1-buten-3-yne is also different from the reactivity of the compounds $OsCl_2H_2(P^iPr_3)_2$ and $OsCl_2(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2$. In addition, we report the synthesis and characterization of new carbyne, carbene, and alkenyl derivatives of osmium(II).

Results and Discussion

1. Reactions of $OsCl_2H_2(P^iPr_3)_2$ with $M[CH_3CO_2]$ (M = K, Ag). Treatment of tetrahydrofuran solutions of $OsCl_2H_2(P^iPr_3)_2$ (**1**) with 1 or 2 equiv of $K[CH_3CO_2]$ produces the substitution of a chloride anion of **1** by $[CH_3CO_2]^-$, to afford the dihydrido $OsH_2Cl(\kappa^2\text{-}O_2CCH_3)(P^iPr_3)_2$ (**2**, Scheme 2), which was isolated as a yellow solid

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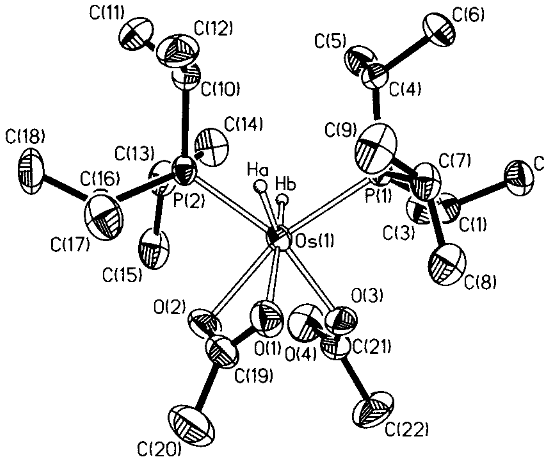

Figure 1. Molecular diagram of the complex $OsH_2(\kappa^2\text{-}O_2CCH_3)\{\kappa^1\text{-}OC(O)CH_3\}(P^iPr_3)_2$ (**3**). Thermal ellipsoids are shown at 50% probability.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for the Complex $OsH_2(\kappa^2\text{-}O_2CCH_3)\{\kappa^1\text{-}OC(O)CH_3\}(P^iPr_3)_2$ (3)

Os(1)−P(1)	2.310(2)	Os(1)−Hb	1.51(6)
Os(1)−P(2)	2.292(2)	O(1)−C(19)	1.255(8)
Os(1)−O(1)	2.273(4)	O(2)−C(19)	1.261(8)
Os(1)−O(2)	2.194(4)	O(3)−C(21)	1.279(7)
Os(1)−O(3)	2.100(4)	O(4)−C(21)	1.223(8)
Os(1)−Ha	1.54(6)		
P(1)−Os(1)-P(2)	112.62(5)	O(1)−Os(1)-Ha	78(2)
P(1)−Os(1)-O(1)	109.74(11)	O(1)−Os(1)-Hb	170(2)
P(1)−Os(1)-O(2)	162.94(12)	O(2)−Os(1)-O(3)	77.7(2)
P(1)−Os(1)-O(3)	87.82(11)	O(2)−Os(1)-Ha	110(2)
P(1)−Os(1)-Ha	77(2)	O(2)−Os(1)-Hb	112(2)
P(1)−Os(1)-Hb	78(2)	O(3)−Os(1)-Ha	144(2)
P(2)−Os(1)-O(1)	114.42(12)	O(3)−Os(1)-Hb	98(2)
P(2)−Os(1)-O(2)	84.27(13)	Ha-Os(1)−Hb	110(3)
P(2)−Os(1)-O(3)	149.42(11)	Os(1)−O(1)-C(19)	89.1(4)
P(2)−Os(1)-Ha	66(2)	Os(1)−O(2)-C(19)	92.6(4)
P(2)−Os(1)-Hb	67(2)	Os(1)−O(3)-C(21)	123.5(4)
O(1)−Os(1)-O(2)	58.3(2)	O(1)−C(19)-O(2)	119.7(6)
O(1)−Os(1)-O(3)	76.4(2)	O(3)−C(21)-O(4)	127.2(6)

in 76% yield. In contrast to the reactions of **1** with K[EtOCS$_2$] and K[CH$_3$COS], the substitution of the second chloride ligand of **1** does not occur, even, by treatment of **2** with 3 equiv of K[CH$_3$CO$_2$]. The formation of the bis(acetato) complex $OsH_2(\kappa^2\text{-}O_2CCH_3)\{\kappa^1\text{-}OC(O)CH_3\}(P^iPr_3)_2$ (**3**) needs the addition of 2 equiv of Ag[CH$_3$CO$_2$] to dichloromethane solutions of **1**. Complex **3** was isolated as a yellow solid in 50% yield.

In contrast to the reactions collected in Scheme 1, a dihydrido-elongated dihydrogen transformation does not take place in the reactions shown in Scheme 2. This indicates that for these systems the change six-coordinate/seven-coordinate is not a sufficient condition to produce the dihydrido-elongated dihydrogen transformation, but the nature of the donor atoms of the coligands also plays a main role. According to the reactions shown in Schemes 1 and 2, the S- and N-donor ligands appear to have more tendency to afford elongated dihydrogen ligands than the O-donor ligands. In this context, it should be mentioned that we have previously observed[14] that the protonation in dichloromethane of the dithioformato complex $OsH(\kappa^2\text{-}S_2CH)(CO)(P^iPr_3)_2$ gives the elongated dihydrogen compound $[Os(\kappa^2\text{-}S_2CH)(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2]^+$ while, under the same conditions, the protonation of the formato complex $OsH(\kappa^2\text{-}O_2CH)(CO)(P^iPr_3)_2$ affords a mixture of elongated dihydrogen and dihydrido derivatives.[15]

Complexes **2** and **3** were characterized by elemental analysis and IR and ^{1}H and ^{31}P{^{1}H} NMR spectroscopies. Complex **3** was further characterized by an X-ray crystallographic study. The molecular structure of **3** is presented in Figure 1. Selected bond distances and angles are listed in Table 1.

The molecule has no symmetry elements other than a C_1 axis, and the bond angles can be hardly fitted to a typical geometry of a seven-coordinate compound. At first glance, the structure of **3** could be described as a halfway situation between a capped trigonal prism and a piano stool geometry. If one takes as a base the structure of **1** and the related dihydrido $OsH_2\{\kappa^2\text{-}OC({=}O)CH[NHC({=}O)CH_3]CH_2S\}(P^iPr_3)_2$,[16] the geometry around the metal center of **3** could be described as derived from a distorted square antiprism with a missing vertice (Scheme 2). One of the two square planes is made up by the two phosphorus atoms and the two hydrido ligands,[17] which occupy alternate positions. The oxygen atoms of the bidentate [O(1) and O(2)] and the monodentate [O(3)] acetato ligands are located in the second plane, which is rotated by 24.7° from the first one.

Although **1** is six-coordinate and **3** is seven-coordinate, the P(1)−Os−P(2) angle and the Os−P distances of both compounds are similar [P(1)−Os−P(2), 112.62(5)° in **3** vs 112.15(5)° in **1**, and Os−P, 2.310(2) and 2.292(2) Å in **3** vs 2.304(2) and 2.289(3) Å in **1**]. The bidentate acetato ligand, which acts with a bite angle O(1)−Os−O(2) of 58.3(2)°, coordinates to the osmium atom in an asymmetric manner. The Os−O(1) [2.273(4) Å] is about 0.08 Å longer than the Os−O(2) [2.194(4) Å] bond length, and both distances are longer than the osmium−monodentate acetato separation [Os−O(3) = 2.100(4) Å]. The Os−O(4) distance (3.28 Å) is long enough to exclude any interaction between the osmium and O(4)

The IR spectrum of **2** in Nujol shows the ν_{asym}(OCO) band at 1537 cm^{-1} and the ν_{sym}(OCO) band at 1420 cm^{-1}. The value of $\Delta\nu$ [$\Delta\nu = \nu_{asym}(OCO) - \nu_{sym}(OCO)$], 117 cm^{-1}, agrees well with a bidentate coordination mode for the acetato group.[18] In the IR spectrum of **3** in Nujol the ν(OCO) bands of the bidentate acetato ligand appear at 1543 and 1440 cm^{-1} ($\Delta\nu = 103$ cm^{-1}), while those corresponding to the monodentate acetato group are observed at 1636 and 1370 cm^{-1} ($\Delta\nu = 266$ cm^{-1}).

In solution the coordination modes for the acetato ligands of **2** and **3** do not undergo any changes. Thus, the IR spectra in dichloromethane show the ν(OCO) bands at the same wavenumbers as in Nujol. On the other hand, complexes **2** and **3** have not a rigid structure in solution at room temperature, as is inferred from the ^{1}H and ^{31}P{^{1}H} NMR spectra.

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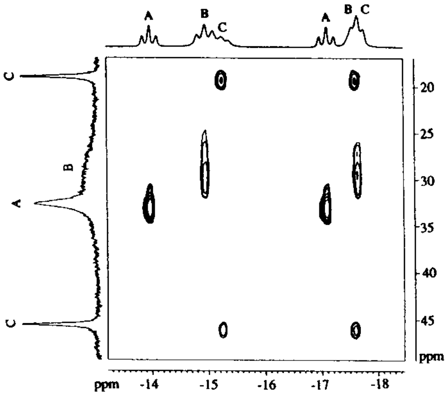


Figure 2. HMQC(^{1}H, ^{31}P) spectrum of **2** at 173 K. Only the high-field region of the ^{1}H spectrum is shown.

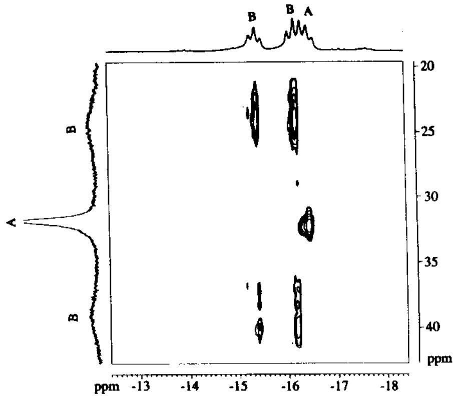


Figure 3. HMQC(^{1}H, ^{31}P) spectrum of **3** at 173 K. Only the high-field region of the ^{1}H spectrum is shown.

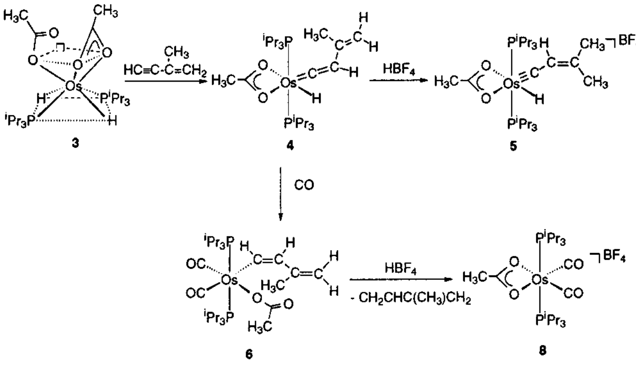
Inspection of the structures shown in Scheme 2 predicts two different chemical shifts for the hydrido ligands and two different chemical shifts for the phosphine ligands. Both, hydridos and phosphines, occupy chemically inequivalent positions. However, at room temperature, the ^{1}H NMR spectrum of **2** in dichloromethane-d_2 shows only one triplet at -15.76 ppm, with a P$-$H coupling constant of 38.1 Hz. Lowering the sample temperature leads to broadening of the resonance. At very low temperature (183 K) decoalescence occurs, and at 173 K six triplets (two of them overlapping) are observed. The ^{31}P{^{1}H} NMR spectrum of **2** shows a coherent behavior with that of the ^{1}H NMR spectrum. At room temperature, the spectrum contains only one singlet at 31.5 ppm, while lowering the sample temperature leads to a broadening of the resonance. Between 193 and 183 K decoalescence occurs, and at 173 K, in addition to a very broad resonance, three signals are observed.

Figure 2 shows the HMQC(^{1}H, ^{31}P) spectrum at 173 K. According to this spectrum, at 173 K, three isomers, A, B, and C, coexist. Isomers B and C contain hydridos and phosphines chemically inequivalent, indicating that these molecules have no symmetry elements other than a C_1 axis, while isomer A contains chemically inequivalent hydridos and chemically equivalent phosphines, which is consistent with a pentagonal bipyramid arrangement of ligands around the osmium atom, with the phosphine ligands in the axial positions and the chloro ligand located in the equatorial plane between a hydrido and the acetato group.

At room temperature, the ^{1}H NMR spectrum of **3** also contains only one triplet at -15.75 ppm with a P$-$H coupling constant of 37.9 Hz, and the ^{31}P{^{1}H} NMR spectrum shows only one singlet at 33.4 ppm.

The variations of the ^{1}H and ^{31}P{^{1}H} NMR spectra of **3** with the temperature are similar to the case for **2**, with the notable exception of the HMQC(^{1}H, ^{31}P) spectrum at 173 K (Figure 3), which shows the coexistence in equilibrium of only two isomers, A and B. Isomer A contains chemically equivalent hydridos and chemically equivalent phosphine ligands, while isomer B contains chemically inequivalent hydridos and chemically inequivalent phosphine ligands.

Scheme 3



The equivalence of both, hydridos and phosphines, indicates that the isomer A is a molecule with high symmetry, which is consistent with a pentagonal bipyramid arrangement of ligands around the metallic center, where the phosphine ligands are situated in the axial positions and the monodentated acetato group lies in the equatorial plane between the hydrido ligands. ^{1}H and ^{31}P{^{1}H} NMR spectra of isomer B are consistent with the structure shown in Figure 1.

2. Reaction of OsH$_2$(κ^2-O$_2$CCH$_3$){κ^1-OC(O)CH$_3$}(P^{i}Pr$_3$)$_2$ with 2-Methyl-1-buten-3-yne. Treatment of **3** with 1.5 equiv of 2-methyl-1-buten-3-yne in toluene under reflux gives, after 2 h, a brown solution from which the hydrido$-$vinylidene complex OsH{κ^2-O$_2$CCH$_3$}{$=$C$=$CHC(CH$_3$)$=$CH$_2$}(P^{i}Pr$_3$)$_2$ (**4**, in Scheme 3) is separated at -78 °C by addition of pentane in 38% yield, as a result of its high solubility in the alkane.

The presence of a hydrido ligand in **4** was inferred from its ^{1}H NMR spectrum, which contains a triplet at -11.96 ppm, with a P$-$H coupling constant of 15.7 Hz. In the ^{13}C{^{1}H} NMR spectrum, the resonances due to the C$_\alpha$ and C$_\beta$ atoms of the vinylidene group appear at 292.4 and 110.5 ppm as triplets with P$-$C coupling constants of 10.6 and 4.1 Hz, respectively, while the vinyl carbon atoms give rise to a triplet at 133.3 (J(PC) $=$ 2.3 Hz) and a singlet at 99.6 ppm. The ^{31}P{^{1}H} NMR spectrum shows a singlet at 25.6 ppm, which under off-resonance condition splits into a doublet due to the coupling with the hydrido ligand.

Although hydrido$-$vinylidene complexes are considered important intermediates in several homogeneous and heterogeneous catalytic reactions, including alkene oligomerization, polymerization, metathesis of olefins,[19]

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(19) (a) Turner, H. W.; Schrock, R. R.; Fellman, J. D.; Holmes, S. J. *J. Am. Chem. Soc.* **1983**, *105*, 4942. (b) Green, J. C.; Green, M. L. H.; Morley, C. P. *Organometallics* **1985**, *4*, 1302. (c) Beckhaus, R. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 686.

and Fischer−Tropsch synthesis,[20] the isolated compounds of this type are very rare. In addition to the five-coordinated hydrido−vinylidene complexes reported by Caulton[12] and our group,[11] Werner has observed that the treatment of $IrCl(=C=CHR)(P^iPr_3)_2$ with HBF_4 in ether results in the formation of $[IrHCl(=C=CHR)(P^iPr_3)_2]BF_4$ (R = H, Me, Ph), which in solution smoothly rearrange by a 1,3-hydrido shift to afford the isomers $[IrCl(\equiv CCH_2R)(P^iPr_3)_2]BF_4$ (R = H, Me).[21] Bercaw has described that the reaction of $Cp^*{}_2TaCl_2$ with vinylmagnesium bromide gives the neutral hydrido−vinylidene $Cp^*{}_2TaH(=C=CH_2)$, which leads to $Cp^*{}_2Ta(CH=CH_2)(CO)$ by reaction with carbon monoxide.[22] Bianchini has observed that the 16-electron fragment $[(PP_3)OsH]^+$ ($PP_3 = P(CH_2CH_2PPh_2)_3]$ is capable of promoting the terminal alkyne to vinylidene tautomerism.[23] We have shown that the reaction of $OsHCl(CO)(P^iPr_3)_2$ with cyclohexylacetylene leads to $OsHCl(=C=CHCy)(CO)(P^iPr_3)_2$, which in solution evolves to $Os\{(E)\text{-}CH=CHCy\}Cl(CO)(P^iPr_3)_2$.[13g]

Hydrido−alkenylvinylidene complexes are even more rare. To the best of our knowledge, the only one derivative of this type previously reported is the compound $OsH(\kappa^2\text{-}O_2CCH_3)\{=C=CHC=CH(CH_2)_3CH_2\}(P^iPr_3)_2$.[11]

The reactions of $OsH_2Cl_2(P^iPr_3)_2$ and $OsCl_2(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2$ with 2-methyl-1-buten-3-yne to afford the derivatives $OsHCl_2\{\equiv CCH=C(CH_3)_2\}(P^iPr_3)_2$ and $OsCl_2\{=CHCH=C(CH_3)_2\}(CO)(P^iPr_3)_2$, respectively, involve the electrophilic attack of a proton to the nucleophilic center (C_β or C_δ) of vinylidene or alkenyl intermediates. The formation of **4** involves the elimination of acetic acid. However, in this case, the proton of the acid is not capable of attacking the vinylidene ligand, suggesting that the pK_a of the formed acid in these reactions plays a main role in the obtained product. So, the reactivity of the OsH_2 complexes toward terminal alkynes depends not only on the nature of the hydrogen atoms bonded to the metallic center (as it has been previously mentioned) but also on the nature of the one-electron coligands contained in the complexes.

In the presence of a stronger acid than acetic acid, complex **4** affords a carbyne derivative. Thus, the addition of 1 equiv of $HBF_4{\cdot}OEt_2$ to diethyl ether solutions of **4** produces the precipitation of the hydrido−carbyne compound $[OsH\{\equiv CCH=C(CH_3)_2\}(\kappa^2\text{-}O_2CCH_3)(P^iPr_3)_2]BF_4$ (**5**), which was isolated as a yellow solid in 86% yield (Scheme 3).

A view of the molecular geometry of **5** is shown in Figure 4. Selected bond distances and angles are listed in Table 2. Although the hydrido ligand could not be located, the presence of this ligand in the complex is supported by the IR and ^1H and $^{31}P\{^1H\}$ NMR spectra. The IR spectrum in Nujol shows a ν(Os−H) absorption at 2176 cm^{-1}, while the ^1H NMR spectrum in $CDCl_3$ contains a triplet with a P−H coupling constant of 15.4 Hz, at −8.34 ppm. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 40.7 ppm, which is split into a doublet under off-resonance conditions, as a result of the coupling with the hydrido ligand.

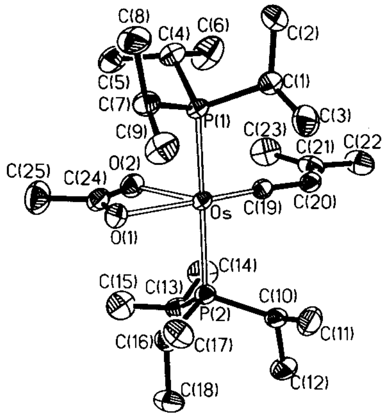

Figure 4. Molecular diagram of the cation of **5**, $[OsH\{\equiv CCH=C(CH_3)_2\}(\kappa^2\text{-}O_2CCH_3)(P^iPr_3)_2]^+$. Thermal ellipsoids are shown at 50% probability.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for the Complex $[OsH(\kappa^2\text{-}O_2CCH_3)\{\equiv CCH=C(CH_3)_2\}(P^iPr_3)_2]BF_4$ (5)

Os−P(1)	2.416(2)	C(20)−C(21)	1.338(9)
Os−P(2)	2.412(2)	C(21)−C(22)	1.499(10)
Os−O(1)	2.236(5)	C(21)−C(23)	1.484(11)
Os−O(2)	2.204(5)	C(24)−C(25)	1.511(10)
Os−C(19)	1.734(6)	C(24)−O(1)	1.264(9)
C(19)−C(20)	1.418(9)	C(24)−O(2)	1.261(9)
P(1)−Os-C(19)	94.3(2)	O(1)−Os-O(2)	58.4(2)
P(1)−Os-P(2)	168.27(5)	Os−C(19)−C(20)	177.4(5)
P(1)−Os-O(1)	88.12(13)	C(19)−C(20)-C(21)	123.6(7)
P(1)−Os-O(2)	93.40(13)	C(20)−C(21)-C(22)	120.8(7)
C(19)−Os-P(2)	91.7(2)	C(20)−C(21)-C(23)	123.0(7)
C(19)−Os-O(1)	173.0(2)	C(23)−C(21)-C(22)	116.2(6)
C(19)−Os-O(2)	114.9(2)	O(1)−C(24)-O(2)	118.1(6)
P(2)−Os-O(1)	87.10(13)	O(1)−C(24)-C(25)	120.4(7)
P(2)−Os-O(2)	93.20(13)	O(2)−C(24)-C(25)	121.5(7)

The coordination geometry around the osmium atom could be rationalized as a distorted octahedron with the two phosphorus atoms of the phosphine ligands occupying the apical positions [P(1)−Os−P(2) = 168.27(5)°]. The equatorial plane is formed by the bidentate ligand, which acts with a bite angle O(1)−Os−O(2) of 58.4(2)°, the hydrido ligand *trans*-disposed to O(2), and the carbyne group *trans*-disposed to O(1) [C(19)−Os−O(1) = 173.0(2)°].

The most conspicuous feature of the structure is the very short Os−C(19) bond length of 1.734(6) Å, which is fully consistent with a Os−C(19) triple bond formulation. Similarly to other (carbyne)metal compounds,[24] a slight bending in the Os−C(19)−C(20) moiety is also present [Os−C(19)−C(20) = 177.4(5)°].

The alkenylcarbyne proposal is supported by the bond lengths and angles within the η^1-carbon donor ligand; e.g., C(19) and C(20) are separated by 1.418(9) Å and C(20) and C(21) by 1.338(9) Å, and the angles around C(20) and C(21) are in the range 116.2−123.6°.

In agreement with the X-ray diffraction study, the $^{13}C\{^1H\}$ NMR spectrum of **5** shows a triplet at 274.6

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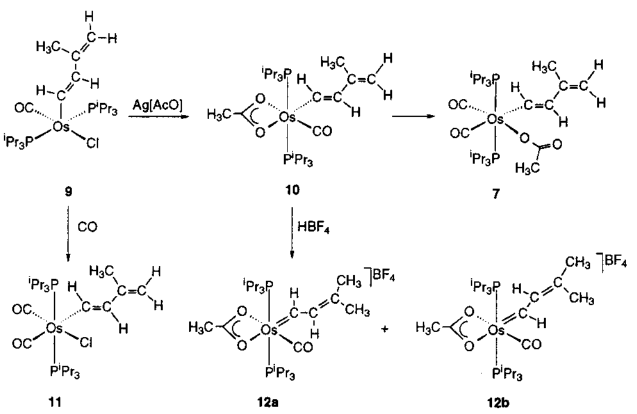
ppm with a P−C coupling constant of 8.5 Hz, corresponding to the sp-carbon atom of the alkenylcarbyne ligand. The resonances due to the sp^2-carbon atoms appear at 169.1 [=*C*(CH$_3$)$_2$] and 134.7 (=*C*H), the first resonance as a singlet and the second one as a triplet with a P−C coupling constant of 4.5 Hz.

The ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectra of **4** are temperature invariant between 60 and −80 °C. This suggest that the exchange of the relative positions of the H and C(CH$_3$)=CH$_2$ groups in the vinylidene ligand are blocked or, alternatively, that the exchange has a very low activation barrier. The exchange barriers of vinylidene ligands have been found experimentally to be in the range from 7 to 20 kcal mol^{-1}.[25] Interestingly, complex **4** reacts with carbon monoxide to give selectively the (*Z*)-dienyl derivative Os{(*Z*)-CH=CHC(CH$_3$)=CH$_2$}{κ^1-OC(O)CH$_3$}(CO)$_2$(P^{i}Pr$_3$)$_2$ (**6**), as a result of the migratory insertion of the vinylidene ligand into the Os−H bond (Scheme 3). The selective formation of the dienyl ligand with a *Z*-stereochemistry suggests that of the two possible isomers of **4** only one is present in solution, that shown in Scheme 3.

The reaction of **4** with carbon monoxide was carried out in toluene and benzene-*d*$_6$ as solvents, under atmospheric pressure. Although the reaction spectroscopically proceeds nearly quantitatively, complex **6** was obtained in 50% yield as a result of its high solubility in pentane, which was used to precipitate it as a pink solid.

In accordance with the mutually cis disposition of the carbonyl ligands, the IR spectrum of **6** in Nujol shows two ν(CO) absorptions at 2012 and 1926 cm^{-1}. Furthermore, the spectrum reflects the conversion of the acetato group from bidentate in **4** to monodentate in **6**. Thus, the asymmetric ν(OCO) stretching, which appears in **4** at 1598 cm^{-1}, is now observed at 1630 cm^{-1}, in line with those of monodentate acetato species.[18] In the ^{1}H NMR spectrum, the most noticeable signals are two double triplets at 8.16 and 7.40 ppm, with a H−H coupling constant of 14.7 Hz and P−H coupling constants of 2.2 and 2.9 Hz, corresponding to the H$_\alpha$ and H$_\beta$ atoms, respectively. The *Z*-stereochemistry of the OsCH=CHR unit was supported by means of a NOE experiment. The irradiation of the H$_\alpha$ resonance (δ = 8.16 ppm) gave an increase in the H$_\beta$ resonance (19%), whereas the −CH$_3$ resonance of the −C(CH$_3$)=CH$_2$ group was not affected. Although the value of ^3J(HH) coupling constant is slightly bigger than that expected for a (*Z*)-dienyl ligand, it is smaller than the ^3J(HH) coupling constant (18.5 Hz) in the (*E*)-dienyl isomer Os{(*E*)-CH=CHC(CH$_3$)=CH$_2$}{κ^1-OC(O)CH$_3$}(CO)$_2$(P^{i}Pr$_3$)$_2$ (**7**; vide infra). The ^{13}C{^{1}H} NMR spectrum confirms the presence of two carbonyl ligands in the complex, showing two triplets at 186.3 and 184.5 ppm, with P−C coupling constants of 7.4 and 7.8 Hz, respectively. The dienyl ligand gives rise to a triplet at 154.0 ppm with a P−C coupling constant of 12.9 Hz, corresponding to the Os*C*H atom, and three singlets at 146.4, 141.4 and 109.6 ppm, due to the sp^2-carbon atoms *C*(CH$_3$)$_2$, =*C*H, and =*C*H$_2$, respectively. The ^{31}P{^{1}H} NMR spectrum contains a singlet at 8.1 ppm.

Scheme 4



The five-coordinate dienyl complexes M{(*E*)-CH=CH−CR=CR′$_2$}Cl(CO)(P^{i}Pr$_3$)$_2$ (M = Ru, Os)[9,26] and the indenyl−dienyl complexes Ru(η^5-C$_7$H$_9$){(*E*)-CH=CH−CR=CR′$_2$}(dppe)[27] react with acids to afford the corresponding α,β-unsaturated carbene derivatives. In this respect, complex **6** shows a different behavior. The protonation of **6** with HBF$_4$ in diethyl ether produces isoprene and the *cis*-dicarbonyl compound [Os(κ^2-O$_2$CCH$_3$)(CO)$_2$(P^{i}Pr$_3$)$_2$]BF$_4$ (**8**), isolated as a pink solid in 83% yield.

The IR spectrum of **8** in Nujol shows the absorption due to the [BF$_4$]$^-$ anion with T_d symmetry centered at 1064 cm^{-1}, indicating that the anion is not coordinated to the metallic center. In agreement with the mutually cis-disposition of the carbonyl ligands two ν(CO) bands at 2039 and 1969 cm^{-1} are also observed. In addition, the spectrum reflects the conversion of the acetato form monodentate to bidentate. Thus, the symmetric and asymmetric ν(OCO) stretchings appear at 1404 and 1593 cm^{-1}. The ^{31}P{^{1}H} NMR spectrum contains a singlet at 30.4 ppm.

3. Synthesis and Characterization of Os{(*E*)-CH=CHC(CH$_3$)=CH$_2$}{κ^1-OC(O)CH$_3$}(CO)$_2$(P^{i}Pr$_3$)$_2$ (7). Although, in general, the (*Z*)-dienyl complexes are less stable than the corresponding (*E*)-dienyl isomers, in solution, complex **6** does not isomerizes into **7** even after 1 week at room temperature. However, the (*E*)-dienyl complex **7** can be prepared by the synthetic strategy shown in Scheme 4.

The five-coordinate (*E*)-dienyl compound Os{(*E*)-CH=CHC(CH$_3$)=CH$_2$}Cl(CO)(P^{i}Pr$_3$)$_2$ (**9**), which is prepared in high yield by reaction of OsHCl(CO)(P^{i}Pr$_3$)$_2$ with 2-methyl-1-buten-3-yne,[9] reacts with Ag[CH$_3$CO$_2$] in toluene to give Os{(*E*)-CH=CHC(CH$_3$)=CH$_2$}(κ^2-O$_2$CCH$_3$)(CO)(P^{i}Pr$_3$)$_2$ (**10**) as a pale yellow solid in 83% yield. Under carbon monoxide atmosphere this complex affords **7** in 86% yield. The related chloro complex Os{(*E*)-CH=CHC(CH$_3$)=CH$_2$}Cl(CO)$_2$(P^{i}Pr$_3$)$_2$ (**11**) is similarly prepared starting from **9**.

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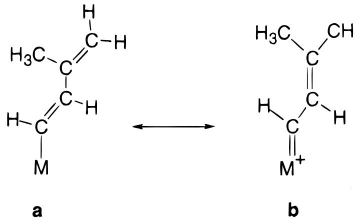
The most noticeable spectroscopic feature of compounds **7**, **10**, and **11** is the presence of two double triplets in the ^{1}H NMR spectrum, at about 8 and 7 ppm, which correspond to the H_α and H_β protons of the dienyl ligand and show ^3J(HH) coupling constants of about 18.5 Hz. This value, which is typical for a mutually trans-disposition of two vinylic hydrogen atoms, is similar to that found recently by Ozawa and co-workers in ruthenium complexes having *trans*-dienyl ligands.[28] The *E* stereochemistry at the Os−CH=CH carbon−carbon double bond of **10** was further confirmed by means of a NOE experiment. The irradiation of the H_α resonance ($\delta = 8.07$ ppm) gave an increase in the $-CH_3$ resonance of the $-C(CH_3)=CH_2$ group (10%), whereas the H_β resonance was not affected.

In addition, it should be mentioned the different behavior of the monocarbonyl complex **10** and the dicarbonyl compound **6** in the presence of HBF_4. The protonation of **10** in diethyl ether as solvent, in contrast to the protonation of **6**, leads to the α,β-unsaturated carbene derivative $[Os\{=CHCH=C(CH_3)_2\}(\kappa^2\text{-}O_2CCH_3)(CO)(P^iPr_3)_2]BF_4$ (**12**), which is isolated as a yellow solid in 86% yield.

In solution, complex **12** exists as a mixture of the isomers **12a** (87%) and **12b** (13%). In the ^{1}H NMR spectrum of the mixture the most noticeable resonances are those corresponding to the H_α and H_β hydrogen atoms of the alkylidene ligand. The resonances of both protons appear as doublets with H−H coupling constants of 12.2 (**12a**) and 13.4 (**12b**) Hz. In the isomer **12a** the chemical shifts are 16.74 (H_α) and 7.30 ppm (H_β), and in the isomer **12b** the chemical shifts are 16.51 (H_α) and 7.98 ppm (H_β). In the $^{13}C\{^1H\}$ NMR spectrum the resonances corresponding to the C_α atom of the unsaturated η^1-carbon ligands are observed at 258.8 (**12a**) and 261.6 ppm (**12b**), and the resonances due to the carbonyl groups appear at 181.1 (**12a**) and 180.0 ppm (**12b**). The $^{31}P\{^1H\}$ NMR spectrum of the mixture contains two singlets at 37.2 (**12a**) and 34.4 ppm (**12b**). We have assigned the major isomer to **12a** and the minor isomer to **12b** (Scheme 4), on the basis of the chemical shifts of the resonances of the carbonyl ligand of both isomers, assuming that the carbonyl ligand of isomer **12a** lies in the region of a negative shielding contribution due to the magnetic anisotropy of the carbon−carbon double bond of the alkylidene,[29] and therefore, its chemical shift is found to lower field than that of the carbon atom of the carbonyl group of **12b**.

The different behaviors of **6** and **10**, in the presence of HBF_4, merits some additional comments. X-ray diffraction and reactivity studies on dienyl complexes indicate that for an adequate description of the bonding situation in this type of compounds a second zwitterionic resonance form (**b**, Scheme 5) must be considered. As a result of the significant contribution of the zwitterionic resonance form, the C_γ atoms of the dienyl ligands have a marked nucleophilic character, and their reactions with electrophilic reagents afford α,β-unsaturated carbene derivatives.[9,26] The behavior of **10** is in agreement with this. However, the behavior of **6** markedly differs. The main difference between **10** and **6** is the presence of a carbonyl group, *trans*-disposed to the dienyl ligand, in the last compound.

Scheme 5



An important contribution of the resonance form **b** requires the donation of electron density from the metal to the dienyl ligand [M(dπ) → C(pπ) contribution]. The presence of a carbonyl group (a strong π-acceptor ligand) trans to the dienyl reduces the M(dπ) → C(pπ) contribution and, therefore, the nucleophilicity of the unsaturated η^1-carbon ligand. Then the nucleophilic center of the molecule is not the alkenyl ligand but the metallic center, and the protonation at the metal leads to the olefin via a reductive elimination in a hydrido−dienyl intermediate.[30]

The *cis*−*trans* isomerization of alkenyl ligands in transition-metal alkenyl compounds is proposed to occur via zwitterionic carbene intermediates.[31] According with this, the low contribution of the form **b** to the metal−dienyl bond in **6** could explain why **6** does not isomerize into **7**.

In other words, the nonisomerization of **6** into **7** and the behavior of **6** in the presence of HBF_4 could have the same origin: the presence of a carbonyl group *trans*-disposed to the dienyl ligand.

Concluding Remarks

We have previously reported that the reactions of $OsH_2Cl_2(P^iPr_3)_2$ with anionic and neutral bidentate and neutral monodentate nucleophilic ligands lead to Os-(η^2-H_2) derivatives. Although this is true for Lewis bases such as $[RCOS]^-$, $[RCS_2]^-$, H_2bim, $[Hbim]^-$, and Hpz (Scheme 1),[7,8] this study has revealed that the nature of the donor atoms of the nucleophilic reagents must be also taken into account. Thus, the reactions of $OsH_2Cl_2(P^iPr_3)_2$ with $[CH_3CO_2]^-$ do not lead to Os-(η^2-H_2) derivatives, but the seven-coordinate dihydrido complexes $OsH_2Cl(\kappa^2\text{-}O_2CCH_3)(P^iPr_3)_2$ and $OsH_2(\kappa^2\text{-}O_2CCH_3)\{\kappa^1\text{-}OC(O)CH_3\}(P^iPr_3)_2$ are obtained. In the solid state the structures of these compounds are so fascinating as that of their precursor and can also be described as square antiprisms but with only one missing vertice. In solution, complex $OsH_2Cl(\kappa^2\text{-}O_2CCH_3)(P^iPr_3)_2$ exists as three rapidly interconverting isomers. Two of them have no symmetry elements other than the C_1 axis, while the third one could have a pentagonal bipyramid arrangement of ligands around the osmium atom, with the phosphine ligands in the axial positions and the chloro ligand located in the equatorial plane between a hydrido and the bidentate acetato group. In solution, complex $OsH_2(\kappa^2\text{-}O_2CCH_3)\{\kappa^1\text{-}OC(O)CH_3\}(P^iPr_3)_2$ exists as two rapidly interconverting isomers. One of them

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has no symmetry elements other than a C_1 axis, while the other one has a high symmetry, consistent with a pentagonal bipyramid arrangement of ligands around the metallic center. However, in this case, the monodentate anionic ligand appears to be located in the equatorial plane between the hydrido ligands.

In the presence of 2-methyl-1-buten-3-yne, the complex $OsH_2(\kappa^2\text{-}O_2CCH_3)\{\kappa^1\text{-}OC(O)CH_3\}(P^iPr_3)_2$ and its precursor $OsH_2Cl_2(P^iPr_3)_2$ show a different behavior. The reaction of the diacetato compound leads to the vinylidene derivative $OsH\{{=}C{=}CHC(CH_3){=}CH_2\}(\kappa^2\text{-}O_2CCH_3)(P^iPr_3)_2$ and acetic acid, while the reaction of the dichloro complex affords the carbyne compound $OsHCl_2\{{\equiv}CCH{=}C(CH_3)_2\}(P^iPr_3)_2$ via a $Os\{{=}C{=}CHC(CH_3){=}CH_2\}$ intermediate, which undergoes the electrophilic attack of H^+.[10,11] The reason for the nonformation of a bis(acetato)−carbyne derivative appears to be the low pK_a of the acetic acid. Thus, the reaction of $OsH\{{=}C{=}CHC(CH_3){=}CH_2\}(\kappa^2\text{-}O_2CCH_3)(P^iPr_3)_2$ with HBF_4, stronger than acetic acid, leads to the cationic carbyne $[OsH\{{\equiv}CCH{=}C(CH_3){=}CH_2\}(\kappa^2\text{-}O_2CCH_3)(P^iPr_3)_2]BF_4$.

In solution under atmospheric pressure of carbon monoxide the vinylidene $OsH\{{=}C{=}CHC(CH_3){=}CH_2\}(\kappa^2\text{-}O_2CCH_3)(P^iPr_3)_2$ selectively evolves to the (*Z*)-dienyl derivative $Os\{(Z)\text{-}CH{=}CHC(CH_3){=}CH_2\}\{\kappa^1\text{-}OC(O)CH_3\}(CO)_2(P^iPr_3)_2$, as a result of the migratory insertion of the vinylidene into the Os−H bond. The selective formation of the (*Z*)-dienyl ligand suggests that, of two possible orientations of the vinylidene in the coordination sphere of the metal, only one is present in solution, that shown in Scheme 3.

In conclusion, we report the synthesis and the characterization of a new seven-coordinate osmium(IV) dihydrido compound, which has an unusual structure and is a useful starting material to prepare new organometallic complexes containing an unsaturated η^1-carbon ligand, including α,β-unsaturated vinylidene, -carbyne, and -alkenyl.

Experimental Section

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

Synthesis. All reactions were carried out with exclusion of air using standard Schlenk techniques. Solvents were dried by known procedures and distilled under argon prior to use. The complexes $OsH_2Cl_2(P^iPr_3)_2$[1] (**1**) and $Os\{(E)\text{-}CH{=}CHC(CH_3){=}CH_2\}Cl(CO)(P^iPr_3)_2$[9] (**9**) were prepared according to the literature method.

Preparation of $OsH_2Cl(\kappa^2\text{-}O_2CCH_3)(P^iPr_3)_2$ (2). A solution of $OsH_2Cl_2(P^iPr_3)_2$ (**1**) (617 mg, 1.06 mmol) in 20 mL of THF was treated with 2 equiv of potassium acetate (206 mg, 2.12 mmol). After being stirred for 45 min at room temperature, the mixture was evaporated to dryness and extracted with 10 mL of toluene. The resulting solution was concentrated to ca. 1 mL. Addition of pentane caused the precipitation of a yellow solid, which was separated by decantation, washed twice with pentane, and dried in vacuo: yield 491 mg (76%). IR (Nujol, cm^{-1}): ν(OsH) 2207, 2185, 2166, 2155; ν_{asym}(OCO) 1537, ν_{sym}(OCO) 1420. ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ 2.29 (m, 6 H, PCH), 1.74 (s, 3 H, O_2CMe), 1.26 (dd, 36 H, $^3J(HH) = 6.3$ Hz, $^3J(PH) = 13.5$ Hz, PCMe), −15.76 (t, 2 H, $^2J(PH) = 38.1$ Hz, OsH_2). ^{31}P{^{1}H} NMR (121.42 MHz, CD_2Cl_2, 293 K): δ 31.5 (s, t under off resonance condition). Anal. Calcd for $C_{20}H_{47}ClO_2OsP_2$: C, 39.56; H, 7.80. Found: C, 39.72; H, 7.06.

Preparation of $OsH_2(\kappa^2\text{-}O_2CCH_3)\{\kappa^1\text{-}OC(O)CH_3\}(P^iPr_3)_2$ (3). A solution of $OsH_2Cl_2(P^iPr_3)_2$ (**1**) (958 mg, 1.64 mmol) in 20 mL of dichloromethane was treated with silver acetate (604 mg, 3.62 mmol). After the mixture was stirred for 2 h at room temperature, the suspension was filtered through Kieselguhr and the filtrate was evaporated to dryness. The residue was washed twice with pentane to afford a yellow solid: yield 513 mg (50%). IR (Nujol, cm^{-1}): ν(OsH) 2203, 2177; ν_{asym}(OCO) 1636, 1543; ν_{sym}(OCO) 1440, 1370. ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ 2.27 (m, 6 H, PCH), 1.87 (s, 6 H, O_2CMe), 1.33 (dd, 36 H, $^3J(HH) = 7.1$ Hz, $^3J(PH) = 13.6$ Hz, PCMe), −15.75 (t, 2 H, $^2J(PH) = 37.9$ Hz, OsH_2). ^{31}P{^{1}H} NMR (121.42 MHz, CD_2Cl_2, 293 K): δ 33.4 (s, t under off resonance condition). Anal. Calcd for $C_{22}H_{50}O_4OsP_2$: C, 41.89; H, 7.99. Found: C, 41.67; H, 7.99.

Preparation of $OsH\{{=}C{=}CHC(CH_3){=}CH_2\}(\kappa^2\text{-}O_2CCH_3)(P^iPr_3)_2$ (4). A solution of **3** (284 mg, 0.45 mmol) in 10 mL of toluene was treated with 2-methyl-1-buten-3-yne (57 μL, 0.68 mmol), and the mixture was heated for 2 h at reflux temperature. The solution was filtered through Kieselguhr, and the filtrate was evaporated to dryness. A total of 4 mL of pentane was added, and the solution was kept at −78 °C for 48 h. The resulting brown solid was separated by decantation and dried in vacuo: yield 110 mg (38%). IR (Nujol, cm^{-1}): ν(OsH) 2158, ν(Os=C=C) 1598; ν_{asym}(OCO) 1541; ν_{sym}(OCO) 1440. ^{1}H NMR (300 MHz, C_6D_6, 293 K): δ 4.55 (s broad, 1 H, $=CH_2$), 4.01 (s broad, 1 H, $=CH_2$), 2.58 (m, 6 H, PCH), 1.97 (s, 3 H, O_2CMe), 1.95 (t, 1 H, $^4J(PH) = 2.7$ Hz, =CH−), 1.60 (s, 3 H, =CMe), 1.31 (dvt, 18 H, $^3J(HH) = 6.9$ Hz, $N = 13.2$ Hz, PCMe), 1.25 (dvt, 18 H, $^3J(HH) = 7.2$ Hz, $N = 12.9$ Hz, PCMe), −11.96 (t, 1 H, $^2J(PH) = 15.7$ Hz, OsH). ^{31}P{^{1}H} NMR (121.42 MHz, C_6D_6, 293 K): δ 25.6 (s, d under off resonance condition). ^{13}C{^{1}H} NMR (75.47 MHz, C_6D_6, 293 K): δ 292.4 (t, $^2J(PC) = 10.6$ Hz, Os=C), 182.5 (s, O_2CMe), 133.3 (t, $^4J(PC) = 2.3$ Hz, =*C*Me), 110.5 (t, $^3J(PC) = 4.1$ Hz, =CH−), 99.6 (s, $=CH_2$), 25.1 (s, O_2C*Me*), 24.9 (vt, $N = 24.4$ Hz, PCH), 22.5 (s, =C*Me*), 19.7 (s, PC*Me*), 19.3 (s, PC*Me*). Anal. Calcd for $C_{25}H_{52}O_2OsP_2$: C, 47.15; H, 8.23. Found: C, 47.60; H, 7.91.

Preparation of $[OsH\{{\equiv}CCH{=}C(CH_3)_2\}(\kappa^2\text{-}O_2CCH_3)(P^iPr_3)_2]BF_4$ (5). A solution of **4** (82 mg, 0.13 mmol) in 10 mL of ether was treated with $HBF_4{\cdot}OEt_2$ (18 μL, 0.13 mmol). The mixture was stirred for 30 min at room temperature, and then the yellow solid obtained was separated by decantation, washed twice with ether, and dried in vacuo: yield 80 mg (86%). IR (Nujol, cm^{-1}): ν(OsH) 2176, ν_{asym}(OCO) 1587; ν_{sym}(OCO) 1445; ν(BF_4) 1057. ^{1}H NMR (300 MHz, $CDCl_3$, 293 K): δ 4.78 (s, 1 H, =CH−), 2.51 (m, 6 H, PCH), 1.96 (s, 3 H, O_2CMe), 1.75 (s, 3 H, =CMe), 1.71 (s, 3 H, =CMe), 1.37 (dvt, 18 H, $^3J(HH) = 7.2$ Hz, $N = 11.7$ Hz, PCMe), 1.32 (dvt, 18 H, $^3J(HH) = 7.2$ Hz, $N = 12.6$ Hz, PCMe), −8.34 (t, 1 H, $^2J(PH) = 15.4$ Hz, OsH). ^{31}P{^{1}H} NMR (121.42 MHz, $CDCl_3$, 293 K): δ 40.7 (s, d under off resonance condition). ^{13}C{^{1}H} NMR (75.47 MHz, CD_2Cl_2, 293 K): δ 274.6 (t, $^2J(PC) = 8.5$ Hz, Os≡C), 187.8 (t, $^3J(PC) = 2.0$ Hz, O_2CMe), 169.1 (s, $=CMe_2$), 134.7 (t, $^3J(PC) = 4.5$ Hz, =CH−), 26.9 (s, O_2C*Me*), 26.6 (vt, $N = 27.1$ Hz, PCH), 25.8 (s, =C*Me*), 24.5 (s, =C*Me*), 19.8 (s, PC*Me*), 19.3 (s, PC*Me*). Anal. Calcd for $C_{25}H_{53}BF_4O_2OsP_2$: C, 41.44; H, 7.37. Found: C, 41.70; H, 6.69.

Preparation of $Os\{(Z)\text{-}CH{=}CHC(CH_3){=}CH_2\}\{\kappa^1\text{-}OC(O)$-

CH$_3$}(CO)$_2$(P^{i}Pr$_3$)$_2$ (6). A solution of **4** (110 mg, 0.17 mmol) in 10 mL of toluene was stirred for 5 h under carbon monoxide atmosphere. The resulting solution was filtered through Kieselguhr, and the filtrate was evaporated to dryness. Addition of cold pentane afforded a pink solid, which was separated by decantation, washed twice with pentane, and dried in vacuo: yield 58.1 mg (50%). IR (Nujol, cm^{-1}): ν(C≡O) 2012, 1926; ν_{asym}(OCO) 1630; ν_{sym}(OCO) 1376. ^{1}H NMR (300 MHz, C$_6$D$_6$, 293 K): δ 8.16 (dt, 1 H, ^3J(HH) = 14.7 Hz, ^3J(PH) = 2.2 Hz, OsCH), 7.40 (dt, 1 H, ^3J(HH) = 14.7 Hz, ^4J(PH) = 2.9 Hz, ═CH−), 5.57 (s broad, 1 H, ═CH$_2$), 4.99 (s broad, 1 H, ═CH$_2$), 2.52 (m, 6 H, PCH), 2.19 (s, 3 H, O$_2$CMe), 1.96 (s, 3 H, ═CMe), 1.23 (dvt, 18 H, ^3J(HH) = 7.2 Hz, *N* = 13.5 Hz, PCMe), 1.14 (dvt, 18 H, ^3J(HH) = 6.9 Hz, *N* = 13.5 Hz, PCMe). ^{31}P{^{1}H} NMR (121.42 MHz, C$_6$D$_6$, 293 K): δ 8.1 (s). ^{13}C{^{1}H} NMR (75.47 MHz, C$_6$D$_6$, 293 K): δ 186.3 (t, ^2J(PC) = 7.4 Hz, C≡O), 184.5 (t, ^2J(PC) = 7.8 Hz, C≡O), 176.1 (s, O$_2$*C*Me), 154.0 (t, ^2J(PC) = 12.9 Hz, OsCH), 146.4 (s broad, ═*C*Me), 141.4 (s, ═CH−), 109.6 (s, ═CH$_2$), 25.8 (vt, *N* = 25.3 Hz, PCH), 24.4 (s, O$_2$C*Me*), 24.0 (s, ═C*Me*), 19.3 (s, PC*Me*), 19.1 (s, PC*Me*). Anal. Calcd for C$_{27}$H$_{52}$O$_4$OsP$_2$: C, 46.81; H, 7.56. Found: C, 47.17; H, 7.74.

Preparation of Os{(*E*)-CH═CHC(CH$_3$)═CH$_2$}{κ^1-OC(O)-CH$_3$}(CO)$_2$(P^{i}Pr$_3$)$_2$ (7). A solution of **10** (120 mg, 0.18 mmol) in 10 mL of dichloromethane was stirred for 3 h under carbon monoxide atmosphere. The solution was filtered through Kieselguhr, and the filtrate was evaporated to dryness. The resulting residue was washed with 2 mL of cold methanol to afford a beige solid: yield 108 mg (86%). IR (Nujol, cm^{-1}): ν(C≡O) 2000, 1922; ν_{asym}(OCO) 1629, 1604. ^{1}H NMR (300 MHz, C$_6$D$_6$, 293 K): δ 8.07 (dt, 1 H, ^3J(HH) = 18.5 Hz, ^3J(PH) = 1.8 Hz, OsCH═), 7.10 (dt, 1 H, ^3J(HH) = 18.5 Hz, ^4J(PH) = 2.5 Hz, ═CH−), 4.93 (s broad, 1 H, ═CH$_2$), 4.84 (s broad, 1 H, ═CH$_2$), 2.43 (m, 6 H, PCH), 2.19 (s, 3 H, O$_2$CMe), 2.06 (s, 3 H, ═CMe), 1.16 (dvt, 18 H, ^3J(HH) = 6.9 Hz, *N* = 13.5 Hz, PCMe), 1.15 (dvt, 18 H, ^3J(HH) = 6.9 Hz, *N* = 14.7 Hz, PCMe). ^{31}P{^{1}H} NMR (121.42 MHz, C$_6$D$_6$, 293 K): δ 8.2 (s).^{13}C{^{1}H} NMR (75.47 MHz, C$_6$D$_6$, 293 K, plus DEPT): δ 187.1 (t, ^2J(PC) = 6.9 Hz, C≡O), 184.7 (t, ^2J(PC) = 8.0 Hz, C≡O), 176.1 (s, O$_2$*C*Me), 149.2 (+, t, ^2J(PC) = 13.2 Hz, OsCH═), 146.4 (t, ^4J(PC) = 2.5 Hz, ═*C*Me), 143.6 (+, t, ^3J(PC) = 3.7 Hz, ═CH−), 108.1 (−, s, ═CH$_2$), 25.1 (+, vt, *N* = 25.4 Hz, PCH), 23.8 (+, s, O$_2$C*Me*), 19.3 (+, s broad, PC*Me* and ═C*Me* overlapped), 19.1 (+, s, PC*Me*). Anal. Calcd for C$_{27}$H$_{52}$O$_4$OsP$_2$: C, 46.81; H, 7.56. Found: C, 46.53; H, 7.49. MS (FAB$^+$): *m*/*e* 693 (M$^+$ − H), 666 (M$^+$ − CO), 633 (M$^+$ − O$_2$CMe).

Preparation of [Os(κ^2-O$_2$CCH$_3$)(CO)$_2$(P^{i}Pr$_3$)$_2$]BF$_4$ (8). A solution of **6** (23 mg, 0.034 mmol) in 5 mL of diethyl ether was treated with 1 equiv of HBF$_4$·OEt$_2$ (5 μL, 0.034 mmol). After being stirred for 45 min at room temperature, the mixture was concentrated to ca. 1 mL. The pink solid obtained was washed twice with diethyl ether and dried in vacuo: yield 20 mg (83%). IR (Nujol, cm^{-1}): ν(C≡O) 2039, 1969; ν_{asym}(OCO) 1593; ν_{sym}(OCO) 1404; ν(BF$_4$) 1064. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$, 293 K): δ 2.65 (m, 6 H, PCH), 1.97 (s, 3 H, O$_2$CMe), 1.40 (dvt, 36 H, ^3J(HH) = 7.2 Hz, *N* = 15.0 Hz, PCMe). ^{31}P{^{1}H} NMR (121.42 MHz, CD$_2$Cl$_2$, 293 K): δ 30.4 (s). Anal. Calcd for C$_{22}$H$_{45}$BF$_4$O$_4$OsP$_2$ + $^1/_2$ Et$_2$O: C, 38.46; H, 6.72. Found: C, 38.80; H, 6.40. MS (FAB$^+$): *m*/*e* 627 (M$^+$). Concomitant formation of isoprene was proved by ^{1}H NMR spectroscopy: in an NMR tube, a solution of **6** (9 mg, 0.014 mmol) in 0.5 mL of CDCl$_3$ was treated with HBF$_4$·OEt$_2$ (2 μL, 0.014 mmol). After 2 min at room temperature, the NMR spectra of the mixture showed only the signals of **8** and isoprene. ^{1}H NMR (300 MHz, CDCl$_3$, 293 K) spectroscopic data for H^{1}H^{2}C═CH^{3}C-(Me)═CH^{4}H:^{5} δ 6.42 (dd, 1 H, ^3J(HH) = 10.5 Hz, ^3J(HH) = 17.5 Hz, H^3), 5.16 (d, 1 H, ^3J(HH) = 17.5 Hz, H^2), 5.05 (d, 1 H, ^3J(HH) = 10.5 Hz, H^1), 4.98 (m, 2 H, H^{4}H^5), 1.82 (s broad, 3 H, Me).

Preparation of Os{(*E*)-CH═CHC(CH$_3$)═CH$_2$}(κ^2-O$_2$CCH$_3$)-(CO)(P^{i}Pr$_3$)$_2$ (10). A solution of **9** (125 mg, 0.19 mmol) in 15 mL of toluene was treated with silver acetate (32 mg, 0.19 mmol). After the mixture was stirred for 30 min at room temperature, the suspension was filtered through Kieselguhr and the filtrate was evaporated to dryness. The resulting residue was washed twice with 2 mL of cold methanol to afford pale yellow solid: yield 105 mg (83%). IR (Nujol, cm^{-1}): ν(C≡O) 1877, ν_{asym}(OCO) 1596; 1547; ν(C═C) 1528. ^{1}H NMR (300 MHz, C$_6$D$_6$, 293 K): δ 8.51 (d, 1 H, ^3J(HH) = 15.6 Hz, OsCH), 6.44 (dt, 1 H, ^3J(HH) = 15.6 Hz, ^4J(PH) = 0.2 Hz, ═CH−), 4.81 (d broad, 1 H, *J* = 2.4 Hz, ═CH$_2$), 4.57 (s broad, 1 H, ═CH$_2$), 2.45 (m, 6 H, PCH), 2.08 (s, 3 H, O$_2$CMe), 1.58 (t, 3 H, ^4J(HH) = 0.8 Hz, MeC═), 1.27 (dvt, 18 H, ^3J(HH) = 7.2 Hz, *N* = 13.2 Hz, PCMe), 1.21 (dvt, 18 H, ^3J(HH) = 7.2 Hz, *N* = 13.2 Hz, PCMe). ^{31}P{^{1}H} NMR (121.42 MHz, C$_6$D$_6$, 293 K): δ 15.6 (s). ^{13}C{^{1}H} NMR (75.47 MHz, C$_6$D$_6$, 293 K, plus DEPT): δ 186.6 (t, ^2J(PC) = 9.5 Hz, C≡O), 183.7 (s, O$_2$*C*Me), 145.0 (t, ^4J(PC) = 2.1 Hz, ═*C*Me), 136.7 (+, t, ^2J(PC) = 8.3 Hz, OsCH═), 136.6 (+, s, ═CH−), 104.1 (−, s, ═CH$_2$), 25.01 (+, s, O$_2$C*Me*), 24.62 (+, vt, *N* = 24.0 Hz, PCH), 19.7 (+, s, ═C*Me*), 19.5 (+, s, PC*Me*), 19.4 (+, s, PC*Me*). Anal. Calcd for C$_{26}$H$_{52}$O$_3$OsP$_2$: C, 46.97; H, 7.88. Found: C, 47.22; H, 7.56. MS (FAB$^+$): *m*/*e* 667 (M$^+$ + H), 479 (M$^+$ − CO − P^{i}Pr$_3$).

Preparation of Os{(*E*)-CH═CHC(CH$_3$)═CH$_2$}Cl(CO)$_2$-(P^{i}Pr$_3$)$_2$ (11). A solution of **9** (237 mg, 0.37 mmol) in 10 mL of dichloromethane was stirred for 1 h under carbon monoxide atmosphere. The resulting orange solution was filtered through Kieselguhr, and the filtrate was evaporated to dryness. The residue was washed twice with 2 mL of cold methanol to afford beige solid: yield 126 mg (51%). IR (Nujol, cm^{-1}): ν(C≡O) 1998, 1925; ν(C═C) 1605. ^{1}H NMR (300 MHz, C$_6$D$_6$, 293 K): δ 8.13 (dt, 1 H, ^3J(HH) = 18.4 Hz, ^3J(PH) = 2.0 Hz, OsCH═), 7.08 (dt, 1 H, ^3J(HH) = 18.4 Hz, ^4J(PH) = 2.2 Hz, ═CH−), 4.92 (s broad, 1 H, ═CH$_2$), 4.84 (s broad, 1 H, ═CH$_2$), 2.63 (m, 6 H, PCH), 2.10 (s, 3 H, ═CMe), 1.30 (dvt, 18 H, ^3J(HH) = 7.2 Hz, *N* = 14.4 Hz, PCMe), 1.07 (dvt, 18 H, ^3J(HH) = 6.9 Hz, *N* = 12.9 Hz, PCMe). ^{31}P{^{1}H} NMR (121.42 MHz, C$_6$D$_6$, 293 K): δ 3.53 (s). ^{13}C{^{1}H} NMR (75.47 MHz, C$_6$D$_6$, 293 K, plus DEPT): δ 185.8 (t, ^2J(PC) = 7.4 Hz, C≡O), 181.2 (t, ^2J(PC) = 7.4 Hz, C≡O), 150.3 (+, t, ^2J(PC) = 12.0 Hz, OsCH), 146.5 (t, ^4J(PC) = 2.5 Hz, ═*C*Me), 144.0 (+, t, ^3J(PC) = 3.7 Hz, ═CH−), 108.4 (−, s broad, ═CH$_2$), 24.3 (vt, *N* = 25.8 Hz, PCH), 20.1 (s, PC*Me*), 19.1 (s, ═C*Me*), 18.9 (s, PC*Me*). Anal. Calcd for C$_{25}$H$_{49}$ClO$_2$OsP$_2$: C, 44.87; H, 7.38. Found: C, 44.69; H, 7.16. MS (FAB$^+$): *m*/*e* 669 (M$^+$ − H), 642 (M$^+$ − CO).

Preparation of [Os{═CHCH═C(CH$_3$)$_2$}(κ^2-O$_2$CCH$_3$)-(CO)(P^{i}Pr$_3$)$_2$]BF$_4$ (12). A solution of **10** (135 mg, 0.20 mmol) in 10 mL of diethyl ether was treated with HBF$_4$·OEt$_2$ (28 μL, 0.20 mmol). After the mixture was stirred for 5 min at room temperature, the suspension was concentrated to ca. 4 mL. The yellow solid obtained was separated by decantation, washed twice with 2 mL of diethyl ether, and dried in vacuo: yield 129 mg (86%). IR (Nujol, cm^{-1}): ν(C≡O) 1929; ν_{asym}(OCO) 1579; ν(BF$_4$) 1058. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$, 293 K): δ(**12a**) (87%) 16.74 (d, 1 H, ^3J(HH) = 12.2 Hz, Os═CH−), 7.30 (d, 1 H, ^3J(HH) = 12.2 Hz, ═CH−), 2.44 (m, 6 H, PCH), 1.97 (s, 3 H, Me), 1.65 (s, 3 H, Me), 1.51 (s, 3 H, Me), 1.30 (dvt, 18 H, ^3J(HH) = 6.9 Hz, *N* = 14.4 Hz, PCMe), 1.23 (dvt, ^3J(HH) = 7.1 Hz, *N* = 14.6 Hz, PCMe); δ(**12b**) (13%) 16.51 (d, 1 H, ^3J(HH) = 13.4 Hz, Os═CH), 7.98 (d, 1 H, ^3J(HH) = 13.4 Hz, ═CH−), 2.01 (s, 3 H, Me), 1.61 (s, 3 H, Me), 1.54 (s, 3 H, Me), PCH and PCMe signals are overlapped by the PCH and PCMe signals of the **12a**. ^{31}P{^{1}H} NMR (121.42 MHz, CD$_2$Cl$_2$, 293 K): δ 37.2 (s, **12a**), 34.4 (s, **12b**). ^{13}C{^{1}H} NMR (75.47 MHz, CD$_2$Cl$_2$, 293 K, plus DEPT): δ(**12a**) 258.8 (t, ^2J(PC) = 4.6 Hz, Os═CH), 188.3 (t, ^3J(PC) = 1.8 Hz, Me*C*O$_2$), 181.1 (t, ^2J(PC) = 8.3 Hz, C≡O), 160.8 (s, ═*C*Me$_2$), 150.1 (s, ═CH−), 28.4 (s, Me), 26.1 (vt, *N* = 25.8 Hz, PCH), 25.3 (s, Me), 22.3 (s, Me), 19.4 (s, PC*Me*), 19.3 (s, PC*Me*); δ(**12b**) 261.6 (br, Os═CH), 180.0 (t, ^2J(PC) = 8.5 Hz, CO), 155.2 (s, ═*C*Me$_2$), 144.4 (s, ═CH−), 28.9 (s, Me), 26.2 (vt, *N* = 24.2 Hz, PCH), 22.1 (s, Me), one Me, two PC*Me*, and the Me*C*O$_2$ signals are

Table 3. Crystal Data and Data Collection and Refinement for $OsH_2(\kappa^2\text{-}O_2CCH_3)\{\kappa^1\text{-}OC(O)CH_3\}(P^iPr_3)_2$ (3) and $[OsH(\kappa^2\text{-}O_2CCH_3)\{\equiv CCH{=}C(CH_3)_2\}(P^iPr_3)_2]BF_4$ (5)

	3	5
formula	$C_{22}H_{50}O_4OsP_2$	$C_{25}H_{53}BF_4O_2OsP_2$
mol wt	630.76	724.62
color, habit	pale yellow, prismatic block	pale brown, irregular block
cryst size, mm	0.49 × 0.46 × 0.30	0.53 × 0.30 × 0.13
space group	monoclinic, $P2_1/c$	triclinic, $P\bar{1}$
a, Å	18.156(5)	9.858(2)
b, Å	9.549(3)	11.793(2)
c, Å	17.056(4)	14.260(2)
α, deg	90	76.808(10)
β, deg	111.21(2)	79.217(9)
γ, deg	90	82.042(6)
V, Å^3	2757(1)	1577.6(5)
Z	4	2
D(calcd), g cm^{-3}	1.520	1.525
μ, mm^{-1}	4.76	4.19
scan type	$\omega/2\theta$	$\theta/2\theta$
2θ range, deg	$3 \le 2\theta \le 50$	$3 \le 2\theta \le 50$
temp, K	223.0(2)	193.0(2)
no. of data collcd	5025	6564
no. of unique data	4863 ($R_{int} = 0.0154$)	5511 ($R_{int} = 0.0369$)
no. of params refined	284	332
$R_1{}^a$ ($F_o \ge 4.0\sigma(F_o)$)	0.0352	0.0394
$wR_2{}^b$ (all data)	0.0950	0.1031
S^c (all data)	1.033	1.032

[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 $P = [\max(F_o{}^2, 0) + 2F_c{}^2)]/3$ (**3**, $a = 0.066$, $b = 2.40$; **5**, $a = 0.0756$, $b = 1.29$). [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.

masked by the signals of **12a**. Anal. Calcd for $C_{26}H_{53}BF_4O_3OsP_2$: C, 41.49; H, 7.10. Found: C, 41.15; H, 6.83. MS (FAB$^+$): *m*/*e* 667 (M$^+$), 507 (M$^+$ − P^{i}Pr$_3$), 479 (M$^+$ − CO − P^{i}Pr$_3$).

Crystal Data for 3 and 5. Crystals suitable for the X-ray diffraction study were obtained by slow diffusion of pentane into a concentrated solution of **3** in toluene or from ether/tetrahydrofuran (**5**). A summary of crystals data and refinement parameters is reported in Table 3. The yellow (**3**) and pale brown (**5**) crystals (0.49 × 0.46 × 0.30 (**3**) and 0.53 × 0.30 × 0.13 (**5**)) were glued on a glass fiber and mounted on a Siemens STOE AED-2 (**3**) or Siemens P4 four-circle (**5**) diffractometer, with graphite-monochromated Mo Kα radiation. A group of 60 reflections in the range $20 \le 2\theta \le 38°$ (**3**) or 44 reflections in the range $29 \le 2\theta \le 48°$ (**5**) were carefully centered at 223 K (**3**) or 193 K (**5**) and used to obtain by least-squares methods the unit cell dimensions. Three standard reflections were monitored at periodic intervals throughout data collection: a significant decay (38%) was observed for **3**. All data were corrected for absorption using a numerical (**3**)[32] or a semiempirical method (**5**).[33] The structures were solved by Patterson (Os atom, SHELXTL v. 5.0)[32] and conventional Fourier techniques and refined by full-matrix least-squares on F^2 (SHELXTL v. 5.0).[32] Anisotropic parameters were used in the last cycles of refinement for all non-hydrogen atoms. The hydrogen atoms were fixed in idealized positions and refined riding on carbon atoms using thermal parameters related to bonded atoms (**3**) or a common isotropic thermal parameter (**5**). The two hydrido ligands of **3** were refined as free isotropic atoms from observed positions with a common isotropic thermal parameter. The hydrido ligand of **5** was not located. Atomic scattering factors, corrected for anomalous dispersion for Os and P, were implemented by the program. The refinement converge to $R_1 = 0.0352$ (**3**) or 0.0394 (**5**) [$F^2 > 2\sigma(F^2)$] and wR_2 (all data) = 0.0950 (**3**) or 0.1031 (**5**), with weighting parameters $x = 0.0662$, $y = 2.40$ (**3**) and $x = 0.0756$, $y = 1.2858$ (**5**).

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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 **3** and **5** (24 pages). Ordering information is given on any current masthead page.

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