

Synthesis, Spectroscopic Characterization, and Reactivity of the Unusual Five-Coordinate Hydrido–Vinylidene Complex $\text{OsHCl}(\text{C}=\text{CHPh})(\text{P}i\text{Pr}_3)_2$: Precursor for Dioxygen Activation

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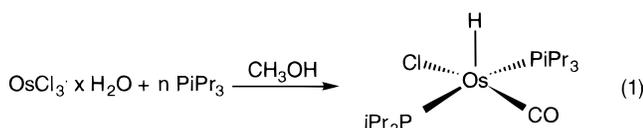
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The hydrido–carbyne complex $\text{OsHCl}_2(\text{CCH}_2\text{Ph})(\text{P}i\text{Pr}_3)_2$ (**1**) reacts with sodium methoxide in 1:1 molar ratio to give the five-coordinate hydrido–vinylidene $\text{OsHCl}(\text{C}=\text{CHPh})(\text{P}i\text{Pr}_3)_2$ (**2**), which affords $[\text{OsHCl}(\text{CCH}_2\text{Ph})(\text{H}_2\text{O})(\text{P}i\text{Pr}_3)_2]\text{BF}_4$ (**3**) by reaction with $\text{HBF}_4 \cdot \text{H}_2\text{O}$. The spectroscopic data obtained for **2** indicate that in solution, it is a mixture of two conformers in equilibrium. The thermodynamic magnitudes involved in the equilibrium as well as the activation parameters for the conversion between them were determined by ^1H NMR spectroscopy in toluene- d_8 . The values obtained were $\Delta H^\ddagger = -0.7 (\pm 0.1) \text{ kcal mol}^{-1}$, $\Delta S^\ddagger = -2.3 (\pm 0.6) \text{ cal K}^{-1} \text{ mol}^{-1}$, $\Delta H^\ddagger = 11.0 (\pm 0.2) \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = 3.2 (\pm 0.6) \text{ cal K}^{-1} \text{ mol}^{-1}$. At room temperature under argon, complex **2** is stable in the solid state and in solution. However in the presence of air, it activates molecular oxygen to give the dioxo–styryl compound $\text{OsCl}\{(\text{E})\text{-CH}=\text{CHPh}\}(\text{O})_2(\text{P}i\text{Pr}_3)_2$ (**4**), which has been characterized by X-ray diffraction analysis. The geometry around of the osmium atom can be described as a distorted octahedron with the two oxygen atoms occupying two relative *trans* positions ($\text{O}(1)\text{-Os-O}(2) = 179.5(5)^\circ$). Complex **2** also reacts with trimethylphosphite, sodium acetylacetonato (acetylacetonato = acac), and sodium acetato to give the six-coordinate hydrido–vinylidene derivatives $\text{OsHCl}(\text{C}=\text{CHPh})\{(\text{P}(\text{OMe})_3\})(\text{P}i\text{Pr}_3)_2$ (**8**), $\text{OsH}(\text{acac})(\text{C}=\text{CHPh})(\text{P}i\text{Pr}_3)_2$ (**9**), and $\text{OsH}(\eta^2\text{-O}_2\text{CCH}_3)(\text{C}=\text{CHPh})(\text{P}i\text{Pr}_3)_2$ (**10**), respectively. Complex **10** can also be prepared by treatment of $\text{OsH}_3(\eta^2\text{-O}_2\text{CCH}_3)(\text{P}i\text{Pr}_3)_2$ (**11**) with phenylacetylene. Similarly, the reactions of **11** with 1,1-diphenyl-2-propyn-1-ol and 1-ethynyl-1-cyclohexanol lead to $\text{OsH}(\eta^2\text{-O}_2\text{CCH}_3)\{\text{C}=\text{CHC}(\text{OH})\text{Ph}_2\}(\text{P}i\text{Pr}_3)_2$ (**12**) and $\text{OsH}(\eta^2\text{-O}_2\text{CCH}_3)\{\text{C}=\text{CHC}=\text{CH}(\text{CH}_2)_3\text{CH}_2\}(\text{P}i\text{Pr}_3)_2$ (**13**), respectively.

Introduction

Our previous osmium chemistry has its starting point in the five-coordinate complex $\text{OsHCl}(\text{CO})(\text{P}i\text{Pr}_3)_2$, which is prepared in nearly quantitative yield by treatment of $\text{OsCl}_3 \cdot x\text{H}_2\text{O}$ with triisopropylphosphine in refluxing methanol (eq 1). During the reaction, the alcohol is de-



hydrogenated by the metal trichloride to give methanal, which is probably the source of the carbonyl ligand.¹ The complex $\text{OsHCl}(\text{CO})(\text{P}i\text{Pr}_3)_2$ is an active and highly selective catalyst for the reduction of unsaturated organic substrates² and for the addition of HSiEt_3 to phenylacetylene.³ In addition, it has been found to be the master key for the development of extensive orga-

nometallic chemistry, including dihydrogen,^{3,4} mono and binuclear tetrahydridoborato,^{4b,5} alkenyl,⁶ alkynyl,^{4c,7} vinylacetato,⁸ carbene,^{4e,9} aryl,¹⁰ π -butadiene,¹¹ π -alkyne,¹² and cyclopentadienyl¹³ compounds.

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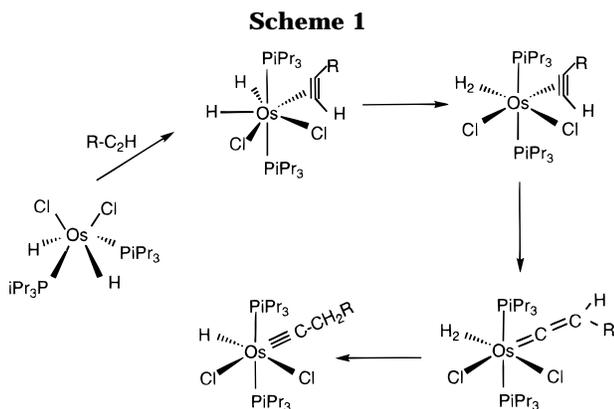
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In agreement with the proposal that the carbonyl ligand of $\text{OsHCl}(\text{CO})(\text{P}i\text{Pr}_3)_2$ is generated from methanol through methanal, Meyer has found that the treatment of $\text{OsCl}_2 \cdot x\text{H}_2\text{O}$ with triisopropylphosphine in refluxing 2-propanol leads to $\text{OsH}_2\text{Cl}_2(\text{P}i\text{Pr}_3)_2$ in ca. 80% yield.¹⁴ This complex reacts with terminal alkynes $\text{H}-\text{C}\equiv\text{C}-\text{R}$ to give the hydrido-carbyne compounds $\text{OsHCl}_2(\text{C}\equiv\text{C}-\text{R})(\text{P}i\text{Pr}_3)_2$. The mechanistic proposal for this transformation (Scheme 1) involves the initial coordination of the alkyne to the osmium atom of $\text{OsH}_2\text{Cl}_2(\text{P}i\text{Pr}_3)_2$ to give dihydrido- π -alkyne-osmium(IV) intermediates, in equilibrium with dihydrogen- π -alkyne-osmium(II) species. The formal $d^4 \rightarrow d^6$ reduction should favor the isomerization of the π -alkyne complexes into vinylidene intermediates. In this way, the subsequent electrophilic attack of the acidic hydrogen of the dihydrogen ligand to the C_β carbon atom of the vinylidene groups could give the hydrido-carbyne complexes.¹⁵

According to Scheme 1, the key intermediates in the formation of the hydrido-carbyne complexes are the species $\text{OsCl}_2(\eta^2-\text{H}_2)(\text{C}=\text{CHR})(\text{P}i\text{Pr}_3)_2$. Complexes of this type have not been previously isolated. However, the related carbonyl compound $\text{OsCl}_2(\eta^2-\text{H}_2)(\text{CO})(\text{P}i\text{Pr}_3)_2$ has been recently reported. In solution, this complex is highly activated toward HCl elimination, as a result of the heterolytic cleavage of the dihydrogen ligand.^{4e}

If the mechanistic proposal shown in Scheme 1 is correct, in solution, one should expect an equilibrium between the hydrido-carbyne complexes and no detectable concentrations of $\text{OsCl}_2(\eta^2-\text{H}_2)(\text{C}=\text{CHR})(\text{P}i\text{Pr}_3)_2$. As the related carbonyl complex, the dihydrogen-vinylidene species should be activated toward HCl elimination. So, the treatment of the hydrido-carbyne complexes with stronger bases than the C_β carbon atom of a vinylidene group may afford five-coordinate hydrido-vinylidene complexes $\text{OsHCl}(\text{C}=\text{CHR})(\text{P}i\text{Pr}_3)_2$, related to $\text{OsHCl}(\text{CO})(\text{P}i\text{Pr}_3)_2$.

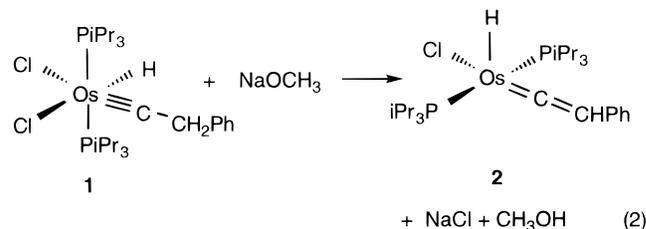
Although hydrido-vinylidene complexes are considered important intermediates in several homogeneous

and heterogeneous catalytic reactions, including alkene oligomerization, polymerization, metathesis of olefins,¹⁶ and Fischer-Tropsch synthesis,¹⁷ the isolated compounds of this type are very rare. Werner has reported that the treatment of $\text{IrCl}(\text{C}=\text{CHR})(\text{P}i\text{Pr}_3)_2$ with HBF_4 in ether results in the formation of $[\text{IrHCl}(\text{C}=\text{CHR})(\text{P}i\text{Pr}_3)_2]^+$ ($\text{R} = \text{H}, \text{Me}, \text{Ph}$), which, in solution, smoothly rearranges by a 1,3-hydrido shift to afford the isomers $[\text{IrCl}(\text{C}\equiv\text{C}\text{H}_2\text{R})(\text{P}i\text{Pr}_3)_2]^+$ ($\text{R} = \text{H}, \text{Me}$).¹⁸ Bercaw has described that the reaction of $\text{Cp}_2^*\text{TaCl}_2$ with vinylmagnesium bromide gives the neutral hydrido-vinylidene $\text{Cp}_2^*\text{TaH}(\text{C}=\text{CH}_2)$, which leads to $\text{Cp}_2^*\text{Ta}(\text{CH}=\text{CH}_2)(\text{CO})$ by reaction with carbon monoxide.¹⁹ Bianchini has observed that the 16-electron fragment $[(\text{PP}_3)\text{OsH}]^+$ ($\text{PP}_3 = \text{P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3$) is capable of promoting the terminal alkyne to vinylidene tautomerism.²⁰ We have shown that the reaction of $\text{OsHCl}(\text{CO})(\text{P}i\text{Pr}_3)_2$ with cyclohexylacetylene leads to $\text{OsHCl}(\text{C}=\text{CHC}_6\text{H}_{11})(\text{CO})(\text{P}i\text{Pr}_3)_2$, which evolves to $\text{Os}\{\text{E}-\text{CH}=\text{CHC}_6\text{H}_{11}\}\text{Cl}(\text{CO})(\text{P}i\text{Pr}_3)_2$ in solution.²¹

With the notable exception of Werner's complexes, the above mentioned hydrido-vinylidene derivatives are species of 18 valence electrons. The interest and the novelty of the unsaturated hydrido-vinylidene compounds prompted us to carry out the reaction of $\text{OsHCl}_2(\text{C}\equiv\text{C}\text{HPh})(\text{P}i\text{Pr}_3)_2$ with sodium methoxide in order to prepare $\text{OsHCl}(\text{C}=\text{CHPh})(\text{P}i\text{Pr}_3)_2$. In this paper, we report the synthesis and spectroscopic characterization of this unusual complex, which is capable of activating molecular oxygen, and the synthesis and characterization of new six-coordinate hydrido-vinylidene derivatives.

Results and Discussion

1. Synthesis and Characterization of $\text{OsHCl}(\text{C}=\text{CHPh})(\text{P}i\text{Pr}_3)_2$. Treatment at room temperature of a tetrahydrofuran solution of the hydrido-carbyne complex $\text{OsHCl}_2(\text{C}\equiv\text{C}\text{HPh})(\text{P}i\text{Pr}_3)_2$ (**1**) with sodium methoxide in a 1:1 molar ratio for 15 min gives, after solvent removal, a sticky residue. Pentane extraction of the residue and filtration to remove NaCl affords a green solution, from which the five-coordinate hydrido-vinylidene complex $\text{OsHCl}(\text{C}=\text{CHPh})(\text{P}i\text{Pr}_3)_2$ (**2**) was isolated as a green solid in 82% yield (eq 2).



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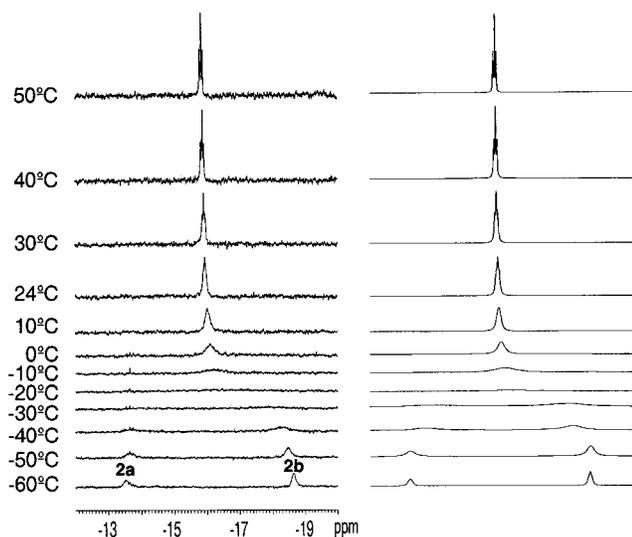
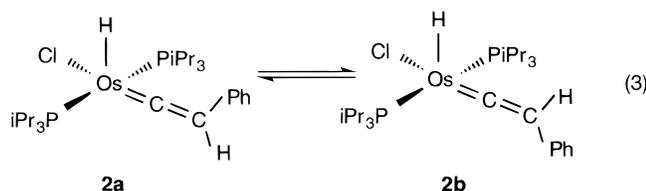


Figure 1. Hydrido region of the ^1H NMR spectrum of **2** at different temperatures: experimental in toluene- d_8 (left) and calculated (right).

In the IR spectrum of **2** in Nujol, the most noticeable absorption is that corresponding to the vibration $\nu(\text{Os}-\text{H})$, which appears at 2019 cm^{-1} . At room temperature, the ^1H NMR spectrum shows the expected resonances for the triisopropylphosphine ligands and the phenyl group of the vinylidene, along with a triplet at 2.03 ppm ($J_{\text{P}-\text{H}} = 2.6\text{ Hz}$) assigned to the $=\text{CHPh}$ proton, and a broad triplet at -15.82 ppm ($J_{\text{P}-\text{H}} = 19\text{ Hz}$) corresponding to the hydrido ligand. At the same temperature, the C_α and C_β carbon atoms of the vinylidene group appear in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum as triplets at 283.9 and 109.0 ppm with P-C coupling constants of 10.2 and 3.3 Hz, respectively. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows a singlet a 37.0 ppm.

The ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **2** are temperature-dependent. Figure 1 shows the hydrido region of the ^1H NMR spectra in toluene- d_8 between -60 and $50\text{ }^\circ\text{C}$. At $-60\text{ }^\circ\text{C}$, the spectrum contains two broad hydrido resonances at -13.5 and -18.7 ppm . On raising the temperature, they coalesce, and the resulting averaged signal finally sharpens to give a triplet, the chemical shift of this triplet being temperature-dependent. This behavior can be understood as the result of the equilibrium between the two possible conformers of **2** (eq 3). The lower field hydrido resonance at -13.5



ppm is assignable to the conformer **2a**, because we assume that the ring current effects of the aromatic ring of the vinylidene group on the hydrido ligand should be greater in **2a** than that in **2b**. At $-60\text{ }^\circ\text{C}$, the $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra also support the presence of **2a** and **2b** in solution. Thus, the $^{13}\text{C}\{^1\text{H}\}$ NMR shows four broad resonances for the C_α and C_β carbon atoms of the vinylidene ligand at 283.5 and 282.7 (C_α) and 104.1 and 103.2 (C_β) ppm, and the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum contains two singlets at 38.6 and 36.9 ppm.

The presence of two singlets in this spectrum suggests that for both **2a** and **2b**, the mutually *trans* disposed

Table 1. Equilibrium Constants and Rates for Conversion of **2a** into **2b** in Toluene- d_8

temp ($^\circ\text{C}$)	K	k_1 (s^{-1})
-70	1.653	7×10^1
-60	1.538	1×10^2
-50	1.439	3×10^2
-40		8×10^2
-30		25×10^2
-20		80×10^2
-10	1.146	18×10^3
0	1.088	55×10^3
10	1.030	10×10^4
24	0.976	30×10^4
30	0.953	50×10^4
40	0.934	70×10^4
50	0.912	12×10^5
60	0.885	

phosphine ligands are equivalent. This indicates that C_α , C_β , and the substituents of the vinylidene group lie in a plane, which is perpendicular to the P-Os-P plane, in agreement with that observed by X-ray diffraction analysis in substituted vinylidene compounds containing two bulky phosphine ligands.²² The structure of **2**, therefore, is as that of the five-coordinate carbonyl complex $\text{OsHCl}(\text{CO})(\text{P}^i\text{Pr}_3)_2$,¹ with the vinylidene ligand in the position of the carbonyl group. Previous results obtained by Caulton and co-workers on the related system $\text{RuHX}(\text{CO})(\text{P}^i\text{Bu}_2\text{Me})_2$ suggest that the high stability of the T shape with X disposed *trans* to the π -acceptor ligand is a result of a push-pull mechanism between the π -donor and the π -acceptor groups.²³ Although the vinylidene is a less efficient π -acceptor ligand than the carbonyl group, complex **2** also shows a disposition of this type, most probably because the methyl groups of the phosphine ligands have an important contribution to the stabilization of the T shape. In this context, it should be noted that all five-coordinate ruthenium(II) and osmium(II) complexes, containing two triisopropylphosphine ligands and characterized by X-ray diffraction analysis, show a square-pyramidal arrangement of ligands around of the metallic center, with the phosphine ligands mutually *trans* disposed. The sixth (formally unoccupied) position of the octahedron is well-shielded by 4 of the 12 methyl groups of the phosphines, which surround the metal like an umbrella.^{6a,24ab}

The constants for the equilibrium between **2a** and **2b** were measured in the range from -70 to $50\text{ }^\circ\text{C}$ (Table 1). The temperature dependence of the equilibrium (Figure 2) provides values for ΔH° and ΔS° of -0.7 (± 0.1) kcal mol $^{-1}$ and -2.3 (± 0.6) cal K $^{-1}$ mol $^{-1}$, respectively. The obtained values for ΔH° and ΔS° suggest that both conformers have a similar thermody-

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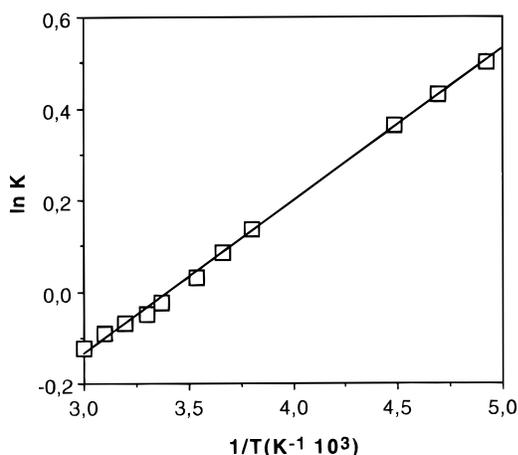


Figure 2. Arrhenius plot of the equilibrium constants for conversion of conformer **2a** into conformer **2b**.

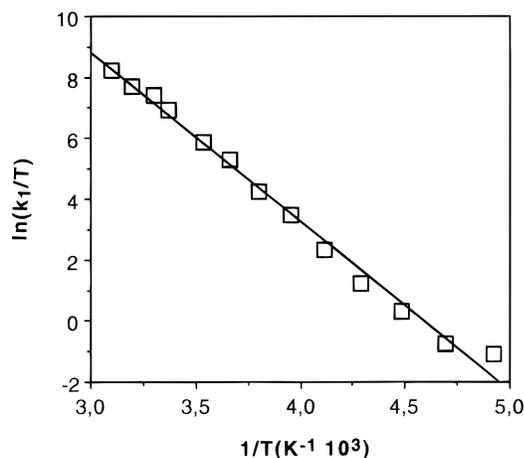


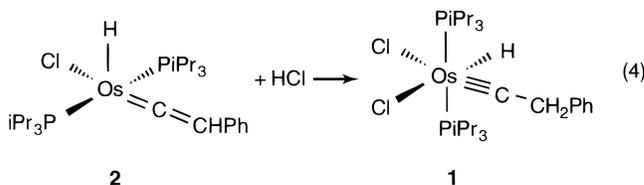
Figure 3. Eyring plot of the rate constants for conversion of conformer **2a** into conformer **2b**.

namic stability, as, at first glance, could be expected from the proposed structures. At low temperatures, the concentration of **2b** is slightly higher than the concentration of **2a**. However at high temperatures, the latter conformer is slightly more stable than the first one.

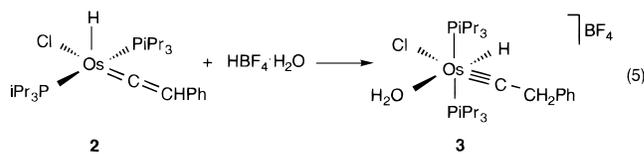
Line shape analysis of the spectra of Figure 1 allows the calculation of the rate constants for the exchange process between the relative positions of the vinylidene substituents (Table 1). The activation parameters obtained from the Eyring analysis (Figure 3) are $\Delta H^\ddagger = 11.0 (\pm 0.2) \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = 3.2 (\pm 0.6) \text{ cal K}^{-1} \text{ mol}^{-1}$. The activation entropy is nearly zero, suggesting that the exchange process is intramolecular. The value of the activation enthalpy is significantly lower than those found for the related process in the vinylidene complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(=\text{C}=\text{CHR})]^+$ (about 20 kcal mol^{-1}), where it has been proposed that the $\text{Re}=\text{C}=\text{C}$ isomerization occurs predominantly by simple rotation around the $\text{Re}-\text{C}_\alpha$ bond.²⁵ In addition, it should be noted that complex **2** is isoelectronic and contains the same ligands as the $[\text{IrHCl}(\text{C}=\text{CHR})(\text{P}i\text{Pr}_3)_2]^+$ complexes, which in solution are in equilibrium with the carbyne isomers $[\text{IrCl}(\text{CCH}_2\text{R})(\text{P}i\text{Pr}_3)_2]^+$.¹⁸ So, it appears reasonable to think that in solution, complex **2** affords the short-lived species $\text{OsCl}(\text{CCH}_2\text{Ph})(\text{P}i\text{Pr}_3)_2$ by a 1,3-hydrido shift. Thus, the rotation of the $-\text{CH}_2\text{Ph}$ group around the single $\text{C}-\text{C}$ bond of

the carbyne ligand could explain the low value of the activation enthalpy.

The five-coordinate carbonyl complex $\text{OsHCl}(\text{CO})(\text{P}i\text{Pr}_3)_2$ reacts with HCl to give the dihydrogen derivative $\text{OsCl}_2(\eta^2\text{-H}_2)(\text{CO})(\text{P}i\text{Pr}_3)_2$.^{4e} The related five-coordinate vinylidene complex **2** also reacts with HCl . However, the isolated product from the reaction is not $\text{OsCl}_2(\eta^2\text{-H}_2)(\text{C}=\text{CHPh})(\text{P}i\text{Pr}_3)_2$ but the hydrido-carbyne **1** (eq 4).



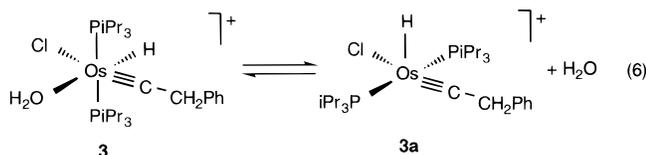
The formation of **1**, according to eq 4, is in agreement with the participation of the vinylidene intermediates during the last step of the reaction of the dihydrodichloro $\text{OsH}_2\text{Cl}_2(\text{P}i\text{Pr}_3)_2$ with terminal alkynes (Scheme 1) and suggests that the most basic center of **2** is the C_β carbon atom of the vinylidene ligand. In agreement with this, we have also observed that the addition of the stoichiometric amount of a water solution of HBF_4 to a toluene solution of **2** produces a beige solid in 65% yield, which was characterized as the cationic hydrido-carbyne complex $[\text{OsHCl}(\text{CCH}_2\text{Ph})(\text{H}_2\text{O})(\text{P}i\text{Pr}_3)_2]\text{BF}_4$ (**3**, eq 5).



The IR spectrum of **3** in Nujol shows the characteristic $\nu(\text{Os}-\text{H})$ band at 2156 cm^{-1} , along with absorptions due to $[\text{BF}_4]^-$ at 1071 , 1061 , and 1036 cm^{-1} . The splitting of the T_d symmetry of the anion suggests that in the solid state, it interacts with the water molecule.^{24c} At room temperature, the ^1H NMR spectrum in dichloromethane- d_2 contains the expected resonances for the phosphine ligands and the phenyl group of the carbyne ligand, a singlet at 2.86 ppm , corresponding to the $-\text{CH}_2\text{Ph}$ protons, and two broad resonances, one of them due to the water molecule at about 3.0 ppm and the other corresponding to the hydrido ligand between -7 and -8 ppm . At -60°C , the resonance of the water molecule appears as a broad singlet located at 4.39 ppm , while the hydrido resonance is observed at -6.36 ppm as a triplet with a $\text{P}-\text{H}$ coupling constant of 15.8 Hz . At room temperature, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows a broad signal centered at 37.5 ppm . At -60°C , this signal is converted into a singlet at 30.1 ppm . At -60°C , the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum contains a triplet at 278.9 ppm with a $\text{P}-\text{C}$ coupling constant of 9 Hz and a singlet at 57.3 ppm , which were assigned to the C_α and C_β carbon atoms of the carbyne ligand, respectively. The above mentioned spectroscopic data suggest that in solution, the cation of **3** is in equilibrium with a five-coordinate hydrido-carbyne cation **3a**, which is formed as a result of the dissociation of the water molecule from **3** (eq 6).

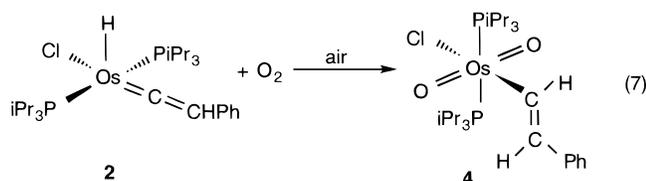
Activation of Molecular Oxygen by 2. Transition metal oxo complexes offer application in homogeneous catalysis, including the oxidation of organic substrates

(25) Senn, D. R.; Wong, A.; Patton, A. T.; Marsi, M.; Strouse, C. E.; Gladysz, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 6096.



with molecular oxygen. From a mechanistic point of view, the reduction of the oxo complexes by the organic substrates could directly occur. However, in general, the reduced species of the oxo complex reagents cannot be reoxidized by air but require stronger oxidants.²⁶ In this context, the formation of dioxo complexes by dioxygen activation is a reaction of general interest.

In the solid state and in solution, complex **2** is stable if kept under argon. However, at room temperature under air, it is capable of activating the oxygen–oxygen double bond of the molecular oxygen from the air to give the dioxo compound $\text{OsCl}\{(\text{E})\text{-CH=CHPh}\}(\text{O})_2(\text{P}i\text{Pr}_3)_2$ (**4**)²⁷ as an air-stable dark brown solid. The formation of **4** further involves the migration of the hydrido ligand at the C_α carbon atom of the vinylidene group (eq 7).



Complex **4** was characterized by elemental analysis, IR and ^1H , $^{31}\text{P}\{^1\text{H}\}$, and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopies, and X-ray diffraction. Figure 4 shows the molecular diagram of the structure of **4**. Selected bond distances and angles are listed in Table 2.

The geometry of the complex can be rationalized as a distorted octahedron with the two phosphorus atoms of the triisopropylphosphine ligands occupying the apical positions ($\text{P}(1)\text{-Os-P}(2) = 178.2(2)^\circ$). The equatorial plane is formed by the two oxygen atoms mutually *trans* disposed ($\text{O}(1)\text{-Os-O}(2) = 179.5(5)^\circ$) and the chlorine atom and the styryl ligand also in relative *trans* positions ($\text{Cl-Os-C}(1a) = 172.2(5)^\circ$, $\text{Cl-Os-C}(1b) = 170(1)^\circ$).

The osmium oxygen distances ($\text{Os-O}(1) = 1.701(11)$ Å and $\text{Os-O}(2) = 1.718(12)$ Å) are statistically identical and very similar to the ones previously reported for the complexes $\text{Os}(\text{mes})_2(\text{O})_2$ (1.700(7) and 1.690(7) Å),²⁸ $[\text{Me}_4\text{N}]_2[\text{Os}(\text{O})_2(\text{COOMe})_2(\mu\text{-OMe})_2]$ (1.728(5) and 1.722(5) Å),²⁹ $\text{Os}(\text{CH}_3)_2(\text{O})_2(\text{py})_2$ (1.723(3) and 1.648(2) Å), $\text{Os}\{\text{CH}_2\text{Si}(\text{CH}_3)_3\}_2(\text{O})_2(\text{py})_2$ (1.716(4) and 1.724(3) Å),³⁰ $\text{Os}(\text{C}_6\text{F}_5)_2(\text{O})_2(\text{py})_2$ (1.706(5) and 1.737(5) Å),³¹ and $[(\text{mes})\text{-}$

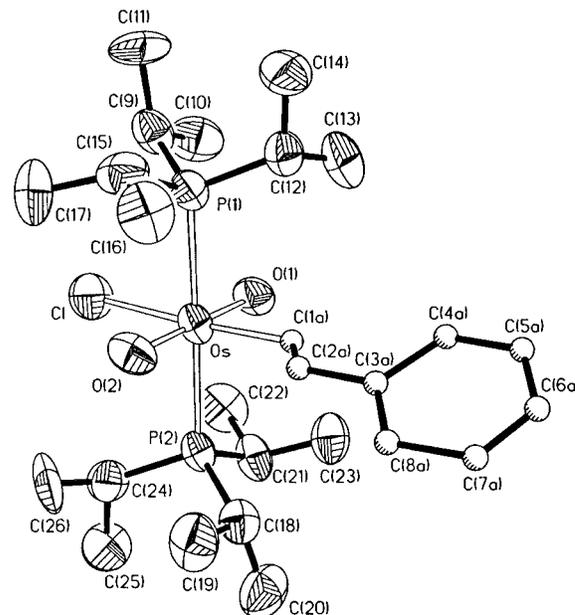


Figure 4. Molecular diagram of the complex $\text{OsCl}\{(\text{E})\text{-CH=CHPh}\}(\text{O})_2(\text{P}i\text{Pr}_3)_2$ (**4**).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for the Complex $\text{OsCl}\{(\text{E})\text{-CH=CHPh}\}(\text{O})_2(\text{P}i\text{Pr}_3)_2$ (**4**)

Bond Lengths			
Os–P(1)	2.476(6)	Os–C(1b)	1.979(30)
Os–P(2)	2.496(6)	C(1a)–C(2a)	1.297(28)
Os–Cl	2.519(5)	C(2a)–C(3a)	1.502(31)
Os–O(1)	1.701(11)	C(1b)–C(2b)	1.292(45)
Os–O(2)	1.718(12)	C(2b)–C(3b)	1.500(82)
Os–C(1a)	1.985(14)		
Bond Angles			
P(1)–Os–P(2)	178.2(2)	Cl–Os–C(1b)	170(1)
P(1)–Os–Cl	88.7(2)	O(1)–Os–O(2)	179.5(5)
P(1)–Os–O(1)	88.9(4)	O(1)–Os–C(1a)	82.4(6)
P(1)–Os–O(2)	91.5(5)	O(1)–Os–C(1b)	100(1)
P(1)–Os–C(1a)	91.2(5)	O(2)–Os–C(1a)	97.2(7)
P(1)–Os–C(1b)	93(1)	O(2)–Os–C(1b)	80(1)
P(2)–Os–Cl	89.5(2)	Os–C(1a)–C(2a)	124(2)
P(2)–Os–O(1)	90.9(4)	C(1a)–C(2a)–C(3a)	127(2)
P(2)–Os–O(2)	88.8(5)	C(2a)–C(3a)–C(4a)	121(3)
P(2)–Os–C(1a)	90.7(5)	C(2a)–C(3a)–C(8a)	125(3)
P(2)–Os–C(1b)	89(1)	Os–C(1b)–C(2b)	131(3)
Cl–Os–O(1)	89.8(4)	C(1b)–C(2b)–C(3b)	125(4)
Cl–Os–O(2)	90.6(5)	C(2b)–C(3b)–C(4b)	122(6)
Cl–Os–C(1a)	172.2(5)	C(2b)–C(3b)–C(8b)	124(6)

$\text{N}_2][\text{Os}(\text{mes})(\text{O})_2(\text{ONO})_2]$ (1.718(10) and 1.710(9) Å).³² In agreement with the relative *trans* position of the oxygen atoms, the IR spectrum of **4** in Nujol contains a single Os–O stretch at 841 cm^{-1} .

It has been previously proposed that the formation of oxo compounds involves the participation of μ -peroxo intermediates.^{26a} The relative *trans* position of the oxo ligands in **4** is in agreement with this proposal. In this case, the μ -peroxo intermediates could be formed according to Scheme 2. The five-coordinate carbonyl complex $\text{OsHCl}(\text{CO})(\text{P}i\text{Pr}_3)_2$ reacts with molecular oxygen to give the peroxo compound $\text{OsHCl}(\eta^2\text{-O}_2)(\text{CO})(\text{P}i\text{Pr}_3)_2$, which is stable.^{4a} Similarly, the hydrido-vinylidene complex **2** could coordinate dioxygen to afford the peroxo–vinylidene complex **5**. The six-coordinate hydrido-carbonyl compounds show a low tendency to give formyl derivatives by migratory CO insertion in the hydrido ligand. In contrast, the six-coordinate hydrido–

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(27) This complex can also be prepared with pure dioxygen with pentane as the solvent.

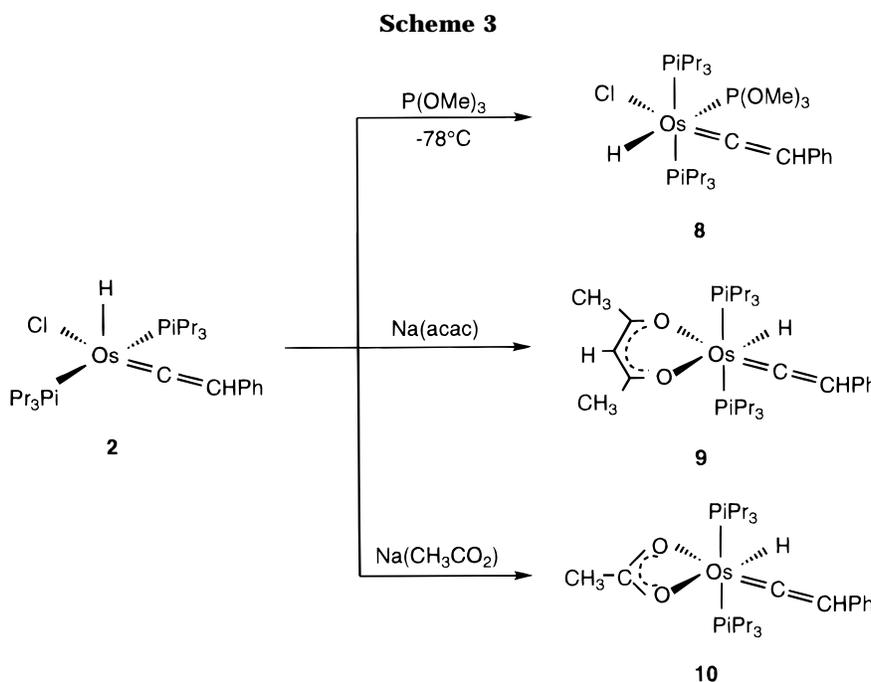
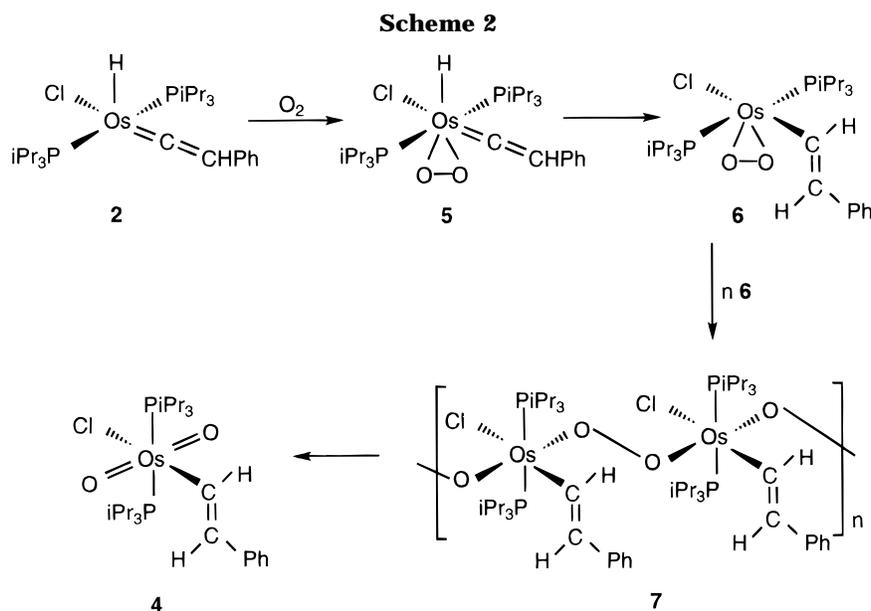
(28) Stravropoulos, P.; Edwards, P. G.; Behling, T.; Wilkinson, G.; Motevalli, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1987**, 169.

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(31) Herrmann, W. A.; Eder, S. J.; Kiprof, P. *J. Organomet. Chem.* **1991**, *412*, 407.

(32) McGilligan, B. S.; Arnold, J.; Wilkinson, G.; Hussain-Bates, B.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1990**, 2465.



vinylidene complexes generally evolve to alkenyl derivatives by migratory insertion of the C_α carbon atom of the vinylidene ligand into the metal–hydrido bond.^{21,33} So, the insertion of the C_α carbon atom of the vinylidene ligand of **5** into the osmium–hydrido bond could afford unsaturated peroxy-styryl species (**6**). The coupling of several units of **6** by one oxygen atom of the peroxy ligand could give **7**, which finally should lead to **4**.

In the X-ray experiment, the styryl group of **4** was found to be disordered. So, it was modeled using two different moieties and refined with a complementary occupancy factor (see Experimental Section). Despite this, we can without a doubt say that the styryl group has an *E*-stereochemistry. Thus, the ^1H NMR spectrum of **4** shows, for the H_α and H_β protons of the styryl ligand, two doublets at 9.69 and 7.03 ppm, with a H–H coupling constant of 16 Hz, a value which is characteristic for this arrangement.^{6a} In the $^{13}\text{C}\{^1\text{H}\}$ NMR

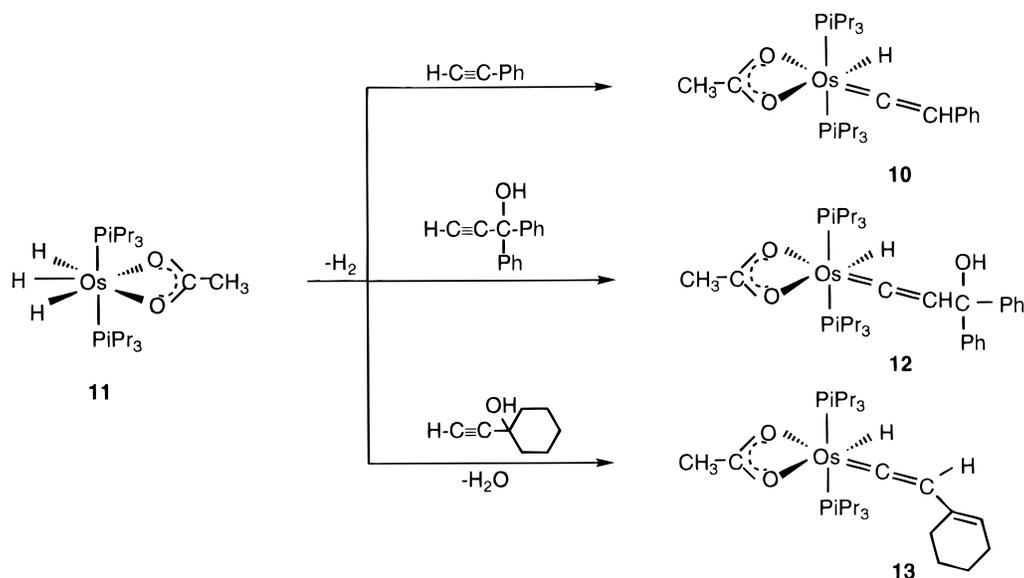
spectrum, the olefinic carbon atoms of the alkenyl group display two triplets at 135.6 and 77.6 ppm with P–C coupling constants of 6.2 and 16.2 Hz, respectively. The –CH groups of the phosphines give a virtual triplet at 23.8 ppm ($N = 22.1$ Hz), which is characteristic of two equivalent triisopropylphosphine ligands in a relative *trans* position. This is in agreement with the singlet at 2.1 ppm found in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum.

Synthesis of Six-Coordinate Hydrido–Vinylidene Complexes. In pentane at -78°C , the five-coordinate hydrido–vinylidene complex **2** adds trimethylphosphite to form the six-coordinate hydrido–vinylidene compound $\text{OsHCl}(\text{C}=\text{CHPh})\{\text{P}(\text{OMe})_3\}(\text{PiPr}_3)_2$ (**8**), which was isolated at -78°C as a pink solid in 74% yield (Scheme 3). Under argon in the solid state, the complex is stable at 0°C . However, in solution, it decomposes to a mixture from which was isolated an ill-defined straw-colored solid.

The spectroscopic data obtained for **8** at -30°C support the structure proposed in Scheme 3. The ^{31}P -

(33) Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A.; Rodriguez, L.; Steinert, P.; Werner, H. *Organometallics*, in press.

Scheme 4



$\{^1\text{H}\}$ NMR spectrum consists of a triplet at 98.0 ppm and a doublet at 9.8 ppm ($J_{\text{P-H}} = 18.6$ Hz), in agreement with a phosphite ligand *cis* to two equivalent triisopropylphosphine ligands. The proposed *trans* disposition of the hydrido and phosphite ligands is supported by the ^1H NMR spectrum, which contains, at -4.5 ppm, a doublet ($J_{\text{P-H}} = 139.5$ Hz) of triplets ($J_{\text{P-H}} = 22.8$ Hz). In the low-field region, the spectrum exhibits the expected resonances for the phosphorus donor ligands and the aromatic protons of the phenyl ring of the vinylidene ligand, along with a broad signal at 1.58 ppm corresponding to the $=\text{CHPh}$ proton. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, the C_α and C_β carbon atoms appear at 296.4 and 106.8 ppm as two broad signals.

Using complex **2** as the starting material, octahedral six-coordinate hydrido–vinylidene complexes cannot only be obtained by addition of ligands L, such as trimethylphosphite, but also by displacement of the chloride by acetylacetonato (acac) and acetato anions (Scheme 3). The acetylacetonato complex $\text{OsH}(\text{acac})(\text{C}=\text{CHPh})(\text{P}i\text{Pr}_3)_2$ (**9**), was isolated as a brown solid in 42% yield. The IR spectrum of **9** in Nujol shows a $\nu(\text{Os-H})$ band at 2093 cm^{-1} . In the ^1H NMR spectrum, the hydrido signal appears as a triplet at -10.36 ppm, with a P–H coupling constant of 16.5 Hz, and the $=\text{CHPh}$ proton gives a triplet at 2.32 ppm with a P–H coupling constant of 2.5 Hz. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, the C_α carbon atom of the vinylidene ligand gives rise to a triplet at 289.7 ppm with a P–C coupling constant of 10.2 Hz. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows a singlet at 24.9 ppm.

The acetato complex $\text{OsH}(\eta^2\text{-O}_2\text{CCH}_3)(\text{C}=\text{CHPh})(\text{P}i\text{Pr}_3)_2$ (**10**) can also be obtained from the reaction of the trihydrido–acetato compound $\text{OsH}_3(\eta^2\text{-O}_2\text{CCH}_3)(\text{P}i\text{Pr}_3)_2$ (**11**) with the stoichiometric amount of phenylacetylene.³⁴ Hydroxyvinylidene and vinylvinylidene complexes can be similarly prepared by reaction of **11** with alkynols. Thus, the complexes $\text{OsH}(\eta^2\text{-O}_2\text{CCH}_3)\{\text{C}=\text{CHC}(\text{OH})\text{Ph}_2\}(\text{P}i\text{Pr}_3)_2$ (**12**) and $\text{OsH}(\eta^2\text{-O}_2\text{CCH}_3)\{\text{C}=\text{CHC}=\text{CH}(\text{CH}_2)_3\text{CH}_2\}(\text{P}i\text{Pr}_3)_2$ (**13**) were synthesized starting from 1,1-diphenyl-2-propyn-1-ol and 1-ethynyl-1-cyclohexanol, respectively (Scheme 4).

Complex **12**, which is the first known hydrido–hydroxyvinylidene compound, was isolated as an orange solid in 60% yield. In the IR spectrum of **12** in Nujol, the most noticeable absorptions are those corresponding to the $\nu(\text{O-H})$ and $\nu(\text{Os-H})$ vibrations, which appear at 3500 and 2104 cm^{-1} . In the ^1H NMR spectrum, the hydrido ligand gives a triplet at -11.51 ppm with a P–H coupling constant of 14.7 Hz. The low-field region contains the expected resonances for the triisopropylphosphine ligands and the phenyl protons of the hydroxyvinylidene group, along with a singlet at 3.01 ppm corresponding to the $-\text{OH}$ proton, and a triplet ($J_{\text{P-H}} = 3.0$ Hz) at 1.74 ppm due to the $=\text{CH}$ proton. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, the C_α and C_β carbon atoms of the hydroxyvinylidene ligand appear at 282.9 and 113.3 ppm as triplets, with P–C coupling constants of 10.5 and 3.1 Hz, respectively, while the COH carbon atom is observed at 66.0 ppm as a singlet. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows a singlet at 24.1 ppm.

Complex **13**, which is also the first known hydrido–vinylvinylidene compound, was isolated as an orange solid in 45% yield. The presence of a hydrido ligand in **13** was inferred from its ^1H NMR spectrum, which contains a triplet at -12.22 ppm with a P–H coupling constant of 15.7 Hz. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, the C_α and C_β carbon atoms of the vinylidene group appear at 292.7 and 110.5 ppm as triplets with P–C coupling constants of 10.5 and 3.2 Hz, respectively, while the vinylic carbon atoms give rise to a triplet at 126.0 ppm ($J_{\text{P-C}} = 2.3$ Hz) and a singlet at 110.7 ppm. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows a singlet at 25.2 ppm.

The formation of **13** most probably involves the participation of an hydroxyvinylidene intermediate, which dehydrates under the reaction conditions. The dehydration of hydroxyvinylidenes containing hydrogen atoms adjacent to the hydroxy group can occur in two different directions to give either vinylvinylidene or allenylidene derivatives, depending on the electronic and steric properties of the metal.³⁵ Vinylvinylidene products are obtained exclusively from reactions of the rich electron fragment $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PMe}_3)_2]^+$ with alkyn-1-ols containing hydrogen atoms adjacent to the hydroxy

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(35) (a) Selegue, J. P. *Organometallics* **1982**, *1*, 217. (b) Selegue, J. P. *J. Am. Chem. Soc.* **1983**, *105*, 5921.

group.³⁶ A similar behavior has been observed for the fragment [Os(η^5 -C₅H₅)(CO)(P*i*Pr₃)⁺], which reacts with 1-ethynyl-1-cyclohexanol to afford the vinylvinylidene [Os(η^5 -C₅H₅){C=CHC=CH(CH₂)₃CH₂}(CO)(P*i*Pr₃)⁺ in 78% yield.¹³ The behavior of this electron rich fragment is in contrast with that observed for [Ru(η^5 -C₅H₅)(CO)(P*i*Pr₃)⁺]³⁷ and the arene system [RuCl₂(η^6 -C₆H₆)(PMe₃)] studied by Dixneuf,³⁸ which give hydroxycarbene and alkoxy carbene derivatives via allenylidene intermediates.

Concluding Remarks

This study has revealed that the hydrido-carbyne complex OsHCl₂(CCH₂Ph)(P*i*Pr₃)₂ reacts with sodium methoxide to give the five-coordinate hydrido-vinylidene derivative OsHCl(C=CHPh)(P*i*Pr₃)₂, which has a square-pyramidal structure like that of the well-known carbonyl complex OsHCl(CO)(P*i*Pr₃)₂,¹ with the vinylidene ligand in the position of the carbonyl group. However, there is a marked difference in the behavior of these complexes toward HCl. Whereas the dihydrogen compound OsCl₂(η^2 -H₂)(CO)(P*i*Pr₃)₂ is obtained from OsHCl(CO)(P*i*Pr₃)₂ and HCl,^{4e} the reaction of OsHCl(C=CHPh)(P*i*Pr₃)₂ with HCl regenerates OsHCl₂(CCH₂Ph)(P*i*Pr₃)₂. The formation of this complex is in agreement with the participation of vinylidene intermediates during the last step of the reaction of OsH₂Cl₂(P*i*Pr₃)₂ with terminal alkynes to afford hydrido-carbyne derivatives¹⁵ and suggests that the most basic center of OsHCl(C=CHPh)(P*i*Pr₃)₂ is the C _{β} carbon atom of the vinylidene ligand. In agreement with this, we also report that the reaction of the vinylidene complex with a water solution of HBF₄ leads to [OsHCl(CCH₂Ph)(H₂O)(P*i*Pr₃)₂] BF₄.

In solution, the compound OsHCl(C=CHPh)(P*i*Pr₃)₂ has been characterized as a mixture of two conformers of similar thermodynamic stability ($\Delta H^\ddagger = -0.7 (\pm 0.1)$ kcal mol⁻¹ and $\Delta S^\ddagger = -2.3 (\pm 0.6)$ cal K⁻¹ mol⁻¹), which is a result of the intramolecular exchange between the relative positions of the vinylidene substituents. The activation parameters for the exchange process ($\Delta H^\ddagger = 11.0 (\pm 0.2)$ kcal mol⁻¹ and $\Delta S^\ddagger = 3.2 (\pm 0.6)$ cal K⁻¹ mol⁻¹) are in agreement with the participation of a OsCl(CCH₂Ph)(P*i*Pr₃)₂ intermediate, which is formed by a 1,3-hydrido shift.

Complex OsHCl(C=CHPh)(P*i*Pr₃)₂ is capable of activating the oxygen-oxygen double bond of the molecular oxygen contained in the air, to give the dioxo compound OsCl{(E)-CH=CHPh}(O)₂(P*i*Pr₃)₂, which has been characterized by X-ray diffraction analysis. From a structural point of view, it should be mentioned that the oxygen atoms occupy relative *trans* positions in an octahedral environment.

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The five-coordinate complex OsHCl(C=CHPh)(P*i*Pr₃)₂ is also a useful starting material for the preparation of new six-coordinate hydrido-vinylidene-osmium(II) derivatives by addition of ligands, such as trimethylphosphite, and by replacement of the chloride by the acetato and acetylacetonato anions.

In conclusion, we report the synthesis and spectroscopic characterization of the unusual hydrido-vinylidene complex OsHCl(C=CHPh)(P*i*Pr₃)₂, which activates the oxygen-oxygen double bond of the molecular oxygen from the air and is a useful starting material to prepare new and unusual vinylidene complexes.

Experimental Section

All reactions were carried out under an argon atmosphere using standard Schlenk techniques. Solvents were dried using the appropriate drying agents and were freshly distilled under argon before use. ¹H, ³¹P{¹H}, and ¹³C{¹H} NMR spectra were recorded on either a Varian UNITY 300 or on a Bruker 300 AXR spectrometer. Chemical shifts are expressed in ppm upfield from Me₄Si (¹H and ¹³C) and 85% H₃PO₄ (³¹P). Coupling constants (*J* and *N* [*N* = *J*_{P-H} + *J*_{P-H} or *J*_{P-C} + *J*_{P-C}]) are given in hertz. IR data were recorded on a Perkin-Elmer 783 or on a Nicolet 550 spectrophotometer. Elemental analyses were carried out with a Perkin-Elmer 240C microanalyser. Mass spectra analyses were performed with a VG Autospec instrument. In FAB⁺ mode (used for complexes **2** and **4**), ions were produced with the standard Cs⁺ gun at ca. 30 kV, and 2-nitrophenyl octyl ether (N-POE) for **2** and 3-nitrobenzyl alcohol (NBA) for **4** were used as the matrix. The reagents 1,1-diphenyl-2-propyn-1-ol (ABCR) and 1-ethynyl-1-cyclohexanol (Fluka) were obtained from commercial sources as indicated and used without further purification. The starting complexes OsH₂Cl₂(P*i*Pr₃)₂, OsH₆(P*i*Pr₃)₂, and OsHCl₂(CCH₂Ph)(P*i*Pr₃)₂ (**1**) were prepared by published methods.^{14b,15}

Kinetic Analysis. The equilibrium constants $K = k_1/k_{-1} = [2b]/[2a]$ were calculated by ¹H NMR spectroscopy in toluene-*d*₆. At temperatures below the coalescence point, the ratio was calculated by integration of the hydrido signals corresponding to **2a** and **2b** and above the coalescence temperature by measuring the chemical shift of the exchange-averaged hydrido resonance. A least-squares fit of the values of ln *K* vs 1/*T* gave the thermodynamic magnitudes ΔH^\ddagger and ΔS^\ddagger involved in this equilibrium. Error analysis assumed a 10% error in the value of the equilibrium constant, whereas the error in temperature was estimated at 1 K. Errors were computed by standard error propagation formulas for least-squares fitting.³⁹

The two parameters *K* and *k*₁ are sufficient to characterize and simulate the hydrido regions of the variable-temperature ¹H NMR spectra. Complete line shape analysis of the ¹H NMR spectra was achieved using the program DNMR6 (QCPE, Indiana University). The rate constants (*k*₁) for various temperatures were obtained by visually matching observed and calculated spectra. Due to the broadness of the signals obtained at the lowest temperature reached, the individual coupling constants *J*_{P-H} for the two hydrides could not be evaluated; thus, the averaged value of *J*_{P-H} was used for both hydrides. The transverse relaxation time *T*₂ used was common for the two signals for all temperatures recorded and was obtained from the line width of the exchange-averaged resonance above the fast-exchange limit. To avoid the influence of these mentioned simplifications in the calculation of the activation parameters, only data for the spectra that exhibited significant line broadening were included. The activation parameters ΔH^\ddagger and ΔS^\ddagger were calculated by least-squares fit of ln(*k*₁/*T*) vs 1/*T* (Eyring equation). Error analysis assumed

(39) Bevington, P. R. *Data Reduction and Error Analysis for the Physical Sciences*; McGraw-Hill, New York, 1969; Chapter 4.

a 10% error in the rate constant and 1 K in the temperature. Errors were computed by published methods.⁴⁰

Preparation of OsHCl(C=CPh)(P*i*Pr₃)₂ (2). A solution of OsHCl₂(CCH₂Ph)(P*i*Pr₃)₂ (1) (110 mg, 0.16 mmol) in 20 mL of THF was treated with sodium methoxide (9 mg, 0.16 mmol). After 15 min of stirring, the solution became green. The solvent was evaporated to dryness, and the residue was dissolved in 20 mL of pentane. After filtration and concentration to 1 mL, the solution was left 15 h at -20 °C. The resulting green solid was decanted, washed with 1 mL of cold pentane, and dried in vacuo. Yield: 86 mg (82%). Anal. Calcd for C₂₆H₄₉ClOsP₂: C, 48.10; H, 7.61. Found: C, 47.94; H, 8.07. IR (Nujol, cm⁻¹): ν(Os-H) 2019. ¹H NMR (300 MHz, C₆D₆, 20 °C): δ 7.19 (m, 2 H, *m*-C₆H₅), 7.07 (d, *J*_{H-H} = 7.0 Hz, 2 H, *o*-C₆H₅), 6.76 (m, 1H, *p*-C₆H₅), 2.63 (m, 6 H, PCHCH₃), 2.03 (t, *J*_{P-H} = 2.6 Hz, 1 H, =CH), 1.22 (dvt, *N* = 13.2 Hz, *J*_{H-H} = 7.1 Hz, 18 H, PCHCH₃), 1.19 (dvt, *N* = 13.7 Hz, *J*_{H-H} = 7.1 Hz, 18 H, PCHCH₃), -15.82 (t, *J*_{P-H} = 19 Hz, 1 H, OsH). ³¹P{¹H} NMR (121.42 MHz, C₆D₆, 20 °C): δ 37.0 (s, PiPr₃). ¹³C{¹H} NMR (75.43 MHz, C₆D₆, 20 °C): δ 283.9 (t, *J*_{P-C} = 10.2 Hz, Os=C=C), 130.4, 123.3, 122.9 (3 s, C₆H₅), 109.0 (t, *J*_{P-C} = 3.3 Hz, Os=C=C), 25.5 (vt, *N* = 24.5 Hz, PCHCH₃), 20.3, 20.2 (2 s, PCHCH₃). ³¹P{¹H} NMR (121.42 MHz, C₇D₈, -80 °C): δ 38.6, 36.9 (2 s, PiPr₃). ¹³C{¹H} NMR (75.43 MHz, C₇D₈, -60 °C): δ 283.5, 282.7 (2 br, Os=C=C), 124.6-118.0 (C₆H₅), 104.1, 103.2 (2 br, Os=C=C), 21.3, 19.6 (2 br, PCHCH₃), 16.7-15.4 (m, PCHCH₃). MS (FAB): *m/e* 650 (M⁺).

Preparation of [OsHCl(CCH₂Ph)(H₂O)(P*i*Pr₃)₂] BF₄ (3). HBF₄ in water (21 μL, 0.154 mmol) was added to a solution of OsHCl(C=CPh)(P*i*Pr₃)₂ (2) (100 mg, 0.154 mmol) in 20 mL of toluene. The solution changed from green to yellow, and a white precipitate was formed. After 1 h, the solvent was removed and the residual solid was washed with 3 mL of toluene and subsequently dried in vacuo, giving a beige powder. Yield: 76 mg (65%). Anal. Calcd for C₂₆H₅₂BClF₄O₂OsP₂: C, 41.34; H, 6.89. Found: C, 40.77; H, 6.92. IR (Nujol, cm⁻¹): ν(Os-H) 2156, ν(BF₄) 1071, 1061, 1036. ¹H NMR (300 MHz, CD₂Cl₂, 20 °C): δ 7.43-7.15 (m, 5 H, C₆H₅), 2.95 (br, 2 H, H₂O), 2.86 (s, 2 H, CH₂), 2.47 (m, 6 H, PCHCH₃), 1.38 (dvt, *N* = 14.3 Hz, *J*_{H-H} = 7.1 Hz, 18 H, PCHCH₃), 1.34 (dvt, *N* = 14.4 Hz, *J*_{H-H} = 7.2 Hz, 18 H, PCHCH₃), -7.5 (br, 1 H, OsH). ³¹P{¹H} NMR (121.42 MHz, CD₂Cl₂, 20 °C): δ 37.5 (br, PiPr₃). ¹H NMR (300 MHz, CD₂Cl₂, -60 °C): δ 7.39-7.19 (m, 5 H, C₆H₅), 4.39 (s, 2 H, H₂O), 2.71 (s, 2 H, CH₂), 2.26 (br, 6 H, PCHCH₃), 1.29 (br, 36 H, PCHCH₃), -6.36 (t, *J*_{P-H} = 15.8 Hz, 1 H, OsH). ³¹P{¹H} NMR (121.42 MHz, CD₂Cl₂, 20 °C): δ 30.1 (s, PiPr₃). ¹³C{¹H} NMR (75.43 MHz, CD₂Cl₂, -60 °C): δ 278.9 (t, *J*_{P-C} = 9 Hz, OsC), 129.1, 128.8, 128.2, 126.9 (4 s, C₆H₅), 57.3 (s, CH₂), 26.0 (br, PCHCH₃), 18.8 (s, PCHCH₃).

Preparation of OsCl{(E)-CH=CPh}(O)₂(P*i*Pr₃)₂ (4). A solution of OsHCl(C=CPh)(P*i*Pr₃)₂ (2) (142 mg, 0.22 mmol) in 20 mL of pentane was left 1 h in air atm, causing the precipitation of a dark brown solid. After decantation, the precipitate was washed twice with 2 mL of pentane and then dried in vacuo. Yield: 120 mg (80%). Anal. Calcd for C₂₆H₄₉ClO₂OsP₂: C, 45.79; H, 7.19. Found: C, 45.68; H, 7.04. IR (Nujol, cm⁻¹): ν(Os-O) 841. ¹H NMR (300 MHz, CD₂Cl₂, 20 °C): δ 9.69 (d, *J*_{H-H} = 16.0 Hz, 1 H, HC=CH(C₆H₅)), 7.26-6.84 (m, 5 H, C₆H₅), 7.03 (d, *J*_{H-H} = 16.0 Hz, 1 H, HC=CH(C₆H₅)), 2.99 (m, 6 H, PCHCH₃), 1.17 (dvt, *N* = 13.8 Hz, *J*_{H-H} = 6.9 Hz, 36 H, PCHCH₃). ³¹P{¹H} NMR (121.42 MHz, CD₂Cl₂, 20 °C): δ 2.1 (s, PiPr₃). ¹³C{¹H} NMR (75.43 MHz, CD₂Cl₂, 20 °C): δ 135.6 (t, *J*_{P-C} = 6.2 Hz, Os=C=C), 141.7, 134.7, 126.5, 126.1 (4 s, C₆H₅), 77.6 (t, *J*_{P-C} = 16.2 Hz, Os=C=C), 23.8 (vt, *N* = 22.1 Hz, PCHCH₃), 18.3 (s, PCHCH₃). MS (FAB): *m/e* 647 (M⁺ - Cl).

Preparation of OsHCl(C=CPh)(P(OMe)₃)(P*i*Pr₃)₂ (8). P(OMe)₃ (26 μL, 0.175 mmol) was added to a solution of OsHCl(C=CPh)(P*i*Pr₃)₂ (2) (114 mg, 0.175 mmol) in 10 mL of pentane at -78 °C. The solution changed immediately from

green to pink. After 5 min of stirring at -78 °C, the pink solid formed was decanted, washed twice with 2 mL of pentane at -78 °C, and dried in vacuo. Yield: 101 mg (74%). Anal. Calcd for C₂₉H₅₈ClO₃OsP₃: C, 45.05; H, 8.27. Found: C, 45.64; H, 8.27. ¹H NMR (300 MHz, CD₂Cl₂, -30 °C): δ 7.05 (m, 2 H, *m*-C₆H₅), 6.84 (d, *J*_{H-H} = 7.0 Hz, 2 H, *o*-C₆H₅), 6.66 (m, 1H, *p*-C₆H₅), 3.81 (d, *J*_{P-H} = 10.0 Hz, 9 H, P(OMe)₃), 2.71 (m, 6 H, PCHCH₃), 1.58 (br, 1 H, =CH), 1.29 (dvt, *N* = 12.9 Hz, *J*_{H-H} = 6.6 Hz, 18 H, PCHCH₃), 1.24 (dvt, *N* = 13.5 Hz, *J*_{H-H} = 6.9 Hz, 18 H, PCHCH₃), -4.5 (dt, *J*_{P-H} = 139.5 Hz, *J*_{P-H} = 22.8 Hz, 1 H, OsH). ³¹P{¹H} NMR (121.42 MHz, CD₂Cl₂, -30 °C): δ 98.0 (t, *J*_{P-P} = 18.6 Hz, P(OMe)₃), 9.8 (d, *J*_{P-P} = 18.6 Hz, PiPr₃). ¹³C{¹H} NMR (75.43 MHz, C₇D₈, -30 °C): δ 296.4 (br, Os=C=C), 131.4, 127.4, 123.3, 121.5 (4 s, C₆H₅), 106.8 (br, Os=C=C), 53.8 (dt, *J*_{P-C} = 54.5 Hz, *J*_{P-C} = 27.2 Hz, P(OMe)₃), 24.5 (vt, *N* = 24.9 Hz, PCHCH₃), 19.8, 19.4 (2 s, PCHCH₃).

Preparation of OsH(acac)(C=CPh)(P*i*Pr₃)₂ (9). Sodium acetylacetonato (29 mg, 0.23 mmol) was added to a solution of OsHCl(C=CPh)(P*i*Pr₃)₂ (2) (151 mg, 0.23 mmol) in 20 mL of dichloromethane. After the mixture was stirred for 30 min at room temperature, the mixture was filtered through kieselguhr and the solvent was evaporated in vacuo. The residual brown oil was dissolved in 2 mL of ether, and after 14 h at -20 °C, a pale brown solid precipitated. After decantation, the solid was washed twice with 2 mL of pentane and dried in vacuo. Yield: 75 mg (42%). Anal. Calcd for C₃₁H₅₆O₂OsP₂: C, 52.22; H, 7.92. Found: C, 51.78; H, 7.47. IR (Nujol, cm⁻¹): ν(Os-H) 2093. ¹H NMR (300 MHz, C₆D₆, 20 °C): δ 7.3-6.8 (m, 5 H, C₆H₅), 5.06 (t, *J*_{P-H} = 2.4 Hz, 1 H, CH of acac), 2.48 (m, 6 H, PCHCH₃), 2.32 (t, *J*_{P-H} = 2.5 Hz, 1 H, =CH), 1.75, 1.58 (2 s, 6 H, O-C-CH₃), 1.34 (dvt, *N* = 13.0 Hz, *J*_{H-H} = 6.9 Hz, 18 H, PCHCH₃), 1.19 (dvt, *N* = 12.6 Hz, *J*_{H-H} = 7.0 Hz, 18 H, PCHCH₃), -10.36 (t, *J*_{P-H} = 16.5 Hz, 1 H, OsH). ³¹P{¹H} NMR (121.42 MHz, C₆D₆, 20 °C): δ 24.9 (s, PiPr₃). ¹³C{¹H} NMR (75.43 MHz, C₆D₆, 20 °C): δ 289.7 (t, *J*_{P-C} = 10.2 Hz, Os=C=C), 185.0, 182.8 (2 s, O-C-CH₃), 133.7, 128.9, 123.6, 121.7, 109.6, 101.2 (6 s, C₆H₅, CH of acac and Os=C=C), 28.2, 27.3 (2 s, O-C-CH₃), 24.4 (vt, *N* = 23.0 Hz, PCHCH₃), 19.8, 19.5 (2 s, PCHCH₃).

Preparation of OsH(η²-O₂CCH₃)(C=CPh)(P*i*Pr₃)₂ (10). This complex was prepared analogously to 9, starting from 2 (151 mg, 0.23 mmol) and sodium acetato (20 mg, 0.24 mmol). After the mixture was stirred for 40 min, the mixture was filtered through kieselguhr. The filtrate was evaporated in vacuo, and the residual oil was dissolved in 2 mL of pentane. After 15 h at -20 °C, a brown solid precipitated. The resulting brown solid was decanted, washed with cold pentane, and dried in vacuo. Yield: 52 mg (33%). Anal. Calcd for C₂₈H₅₂O₂OsP₂: C, 49.97; H, 7.80. Found: C, 49.62; H, 8.30. IR (Nujol, cm⁻¹): ν(Os-H) 2130, ν(OCO) 1555, 1460. ¹H NMR (300 MHz, C₆D₆, 20 °C): δ 7.25-6.83 (m, 5H, C₆H₅), 2.59 (m, 6H, PCHCH₃), 2.25 (t, 2 H, *J*_{P-H} = 2.5 Hz, 1 H, =CH), 1.67 (s, 3 H, CH₃), 1.33 (dvt, *N* = 13.3 Hz, *J*_{H-H} = 7.1 Hz, 18 H, PCHCH₃), 1.30 (dvt, *N* = 12.8 Hz, *J*_{H-H} = 6.9 Hz, 18 H, PCHCH₃), -11.51 (t, *J*_{P-H} = 15.6 Hz, 1 H, OsH). ³¹P{¹H} NMR (121.42 MHz, C₆D₆, 20 °C): δ 26.8 (s, PiPr₃). ¹³C{¹H} NMR (75.43 MHz, C₆D₆, 20 °C): δ 291.5 (t, *J*_{P-C} = 10.5 Hz, Os=C), 182.6 (s, OCO), 132.1, 123.3, 122.0 (3 s, C₆H₅), 107.5 (t, *J*_{P-C} = 2.8 Hz, =CH), 25.3 (s, CH₃), 25.0 (vt, *N* = 23.9 Hz, PCHCH₃), 19.9, 19.5 (2 s, PCHCH₃).

Preparation of OsH(η²-O₂CCH₃)(C=CCH(OH)Ph)₂(P*i*Pr₃)₂ (12). A solution of OsH₆(P*i*Pr₃)₂ (187 mg, 0.36 mmol) in 12 mL of toluene was treated with acetic acid (22.5 μL, 0.36 mmol) and heated under reflux for 30 min. After the mixture was cooled at room temperature, the solution was filtered through kieselguhr and the filtrate (OsH₃(η²-O₂CCH₃)(P*i*Pr₃)₂) treated with 1,1-diphenyl-2-propyn-1-ol (97.56 mg, 0.47 mmol). After it was stirred for 17 h at room temperature, the solution was filtered through kieselguhr and concentrated until an orange-colored solid precipitated. This solid was stored at -78 °C, decanted, washed with acetone, and dried in vacuo. Yield: 160 mg (60%). Anal. Calcd. for C₃₅H₅₂O₃OsP₂: C, 53.84; H, 6.66. Found: C, 53.57; H, 6.97. IR (Nujol, cm⁻¹): ν

(40) Morse, P. M.; Spencer, M. O.; Wilson, S. R.; Girolami, G. S. *Organometallics* 1994, 13, 1646 and references therein.

(OH) 3500, ν (Os–H) 2104. ¹H NMR (300 MHz, C₆D₆, 20 °C): δ 7.7 (d, $J_{\text{H-H}} = 7.5$ Hz, 4 H, o-C₆H₅), 7.20 (m, 4 H, m-C₆H₅), 7.00 (m, 2 H, p-C₆H₅), 3.01 (s, 1 H, OH), 2.58 (m, 6 H, PCHCH₃), 1.74 (t, $J_{\text{P-H}} = 3.0$ Hz, =CH), 1.63 (s, 3 H, CH₃), 1.31 (dvt, $N = 13.8$ Hz, $J_{\text{H-H}} = 7.2$ Hz, 18 H, PCHCH₃), 1.26 (dvt, $N = 13.5$ Hz, $J_{\text{H-H}} = 6.9$ Hz, 18 H, PCHCH₃), –11.51 (t, $J_{\text{P-H}} = 14.7$ Hz, 1 H, OsH). ³¹P{¹H} NMR (121.42 MHz, C₆D₆, 20 °C): δ 24.1 (s, PiPr₃). ¹³C{¹H} NMR (75.43 MHz, C₆D₆, 20 °C): δ 282.9 (t, $J_{\text{P-C}} = 10.5$ Hz, Os=C), 182.3 (s, OCO), 152.3 (s, C_{ipso}), 127.9, 126.1, 126.0 (3 s, C₆H₅), 113.3 (t, $J_{\text{P-C}} = 3.1$ Hz, =CH), 66.0 (s, COH), 25.1 (s, CH₃), 25.0 (vt, $N = 23.8$ Hz, PCHCH₃), 19.6, 19.2 (2 s, PCHCH₃).

Preparation of OsH(η^2 -O₂CCH₃){C=CHC=CH-(CH₂)₃CH₂}(PiPr₃)₂ (13). This complex was prepared analogously to **12**, starting from OsH₆(PiPr₃)₂ (295 mg, 0.57 mmol), acetic acid (33.53 μ L, 0.57 mmol), and 1-ethynyl-1-cyclohexanol (92 mg, 0.74 mmol). After the mixture was stirred for 30 min at room temperature, the solution was concentrated to dryness. Addition of acetone caused the precipitation of an orange solid after storing at –78 °C for 2 days. The resulting orange solid was decanted, washed with acetone, stored at –70 °C, and dried in vacuo. Yield 202 mg (45%). Anal. Calcd. for C₂₃H₅₆O₂OsP₂: C, 49.73; H, 8.28. Found: C, 49.70; H, 8.18. IR (Nujol, cm⁻¹): ν (Os–H) 2160, 2138. ¹H NMR (300 MHz, C₆D₆, 20 °C): δ 5.07 (unresolved t, 1 H, –C=CH(CH₂)₃CH₂), 2.61 (m, 6 H, PCHCH₃), 2.53 (br m, 2 H, allylic CH₂), 2.24 (br, 3 H, OsC=CH and allylic CH₂), 1.72 (br m, 4 H, alkyl CH₂), 1.62 (s, 3 H, CH₃), 1.33 (dvt, $N = 13.2$ Hz, $J_{\text{H-H}} = 7.0$ Hz, 18 H, PCHCH₃), 1.27 (dvt, $N = 12.6$ Hz, $J_{\text{H-H}} = 7.0$ Hz, 18 H, PCHCH₃), –12.22 (t, $J_{\text{P-H}} = 15.7$ Hz, 1 H, OsH). ³¹P{¹H} NMR (121.42 MHz, C₆D₆, 20 °C): δ 25.2 (s, PiPr₃). ¹³C{¹H} NMR (75.43 MHz, C₆D₆, 20 °C): δ 292.7 (t, $J_{\text{P-C}} = 10.5$ Hz, Os=C), 182.2 (t, $J_{\text{P-C}} = 1.5$ Hz, OCO), 126.0 (t, $J_{\text{P-C}} = 2.3$ Hz, =CH–C=CH), 110.7 (s, =CH–C=CH), 110.5 (t, $J_{\text{P-C}} = 3.2$ Hz, =CH–C=CH), 29.4, 25.5 (2 s, allylic CH₂), 25.3 (s, CH₃), 24.9 (vt, $N = 23.9$ Hz, PCHCH₃), 23.9, 23.7 (2 s, alkyl CH₂), 19.9, 19.5 (2 s, PCHCH₃).

X-ray Structure Analysis of Complex OsCl{(E)-CH=CHPh}(O₂)(PiPr₃)₂ (4). All attempts at preparing crystals of **4** from solutions of **4** in toluene or pentane were unsuccessful. The only suitable crystal was grown in a solution of complex **2** in toluene left under an air atmosphere for 3 weeks. A summary of the crystal data and refinement parameters is reported in Table 3. The dark brown irregular crystal, of approximate dimensions 0.21 \times 0.14 \times 0.24 mm, was glued on a glass fiber and mounted on a Siemens P4 diffractometer. A group of 50 reflections in the range 20° \leq 2θ \leq 25° were carefully centered and used to obtain, by least-squares methods, the unit cell dimensions. Three standard reflections were monitored at periodic intervals throughout data collection: no significant variations were observed. All data were corrected for absorption using a semiempirical method.⁴¹ The structure was solved by Patterson (Os atom, SHELXTL-PLUS⁴²) and conventional Fourier techniques and was refined by full-matrix least-squares on F^2 (SHELXL93).⁴³ The styryl group of **4** was found to be disordered. This disorder could result from a rotation of approximately 180° around the Os–C(1) bond and was modeled by including two different moieties (C(1a) to C(8a) and C(1b) to C(8b)) with complementary occupancy factors, initially assigned on the basis of thermal parameters and refined to a final value of 0.71(2) for the

Table 3. Crystal Data and Data Collection and Refinement for OsCl{(E)-CH=CHPh}(O₂)(PiPr₃)₂ (4)

Crystal Data	
formula	C ₂₆ H ₄₀ ClO ₂ OsP ₂
mw	681.27
color and habit	dark brown, irregular prism
cryst size, mm	0.21 \times 0.14 \times 0.24
symmetry	triclinic
space group	$P\bar{1}$ (No. 2)
<i>a</i> , Å	9.759(3)
<i>b</i> , Å	10.419(3)
<i>c</i> , Å	15.363(5)
α , deg	70.81(2)
β , deg	89.24(2)
γ , deg	83.26(2)
<i>V</i> , Å ³	1464.6(8)
<i>Z</i>	2
<i>D</i> _{calcd} , g cm ⁻³	1.545
Data Collection and Refinement	
diffractometer	four-circle Siemens-P4
λ (Mo K α), Å; technique	0.710 73; bisecting goniometer
monochromator	graphite oriented
μ , mm ⁻¹	4.57
scan type	$\theta/2\theta$
2θ range, deg	2 \leq 2θ \leq 50
temp, K	293
no. of data colld	5690
no. of unique data	4845 ($R_{\text{int}} = 0.0503$)
no. of params refined	286
$R1^a$ [$F^2 > 2\sigma(F^2)$]	0.0731
$wR2^b$ [all data ($F_o \geq 0$)]	0.1840
S^c	0.983

^a $R1(F) = \sum |F_o| - |F_c| / \sum |F_o|$. ^b $wR2(F^2) = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$. ^c Goodness of fit = $S = \{ \sum [w(F_o^2 - F_c^2)^2] / (n - p) \}^{1/2}$, where n is the number of observed reflections and p is the number of refined parameters.

a-labeled atoms and 0.29(2) for the *b* ones. The styryl groups were refined including geometrical restrictions, the distances C(1)–C(2) and C(2)–C(3) were fixed to 1.29(1) and 1.49(1) Å (medium values observed in the CSD⁴⁴ for related styryl complexes of osmium: DFIX⁴³ facility), and both groups were refined with the identical geometry (SAME⁴³ facility). Anisotropic parameters were used in the last cycles of refinement for all non-hydrogen atoms, except those involved in disorder. The hydrogen atoms for the nondisordered carbon atoms were calculated (C–H = 0.96 Å) and refined riding on carbon atoms with a common isotropic thermal parameter. Atomic scattering factors, corrected for anomalous dispersion for Os and P were implemented by the program.⁴³ The refinement converge to $R_1 = 0.073$ [$F^2 > 2\sigma(F^2)$] and $wR_2 = 0.184$ (all data, $F^2 > 0$), with weighting parameters $x = 0.1004$ and $y = 0$.

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Supporting Information Available: Tables of anisotropic thermal parameters, atomic coordinates and thermal parameters for hydrogen atoms, experimental details of the X-ray study, bond distances and angles, and selected least-squares planes and interatomic distances (15 pages). Ordering information is given on any current masthead page.

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