Reaction of $OsHCl(CO)(PiPr_3)_2$ with Cyclohexylacetylene: Formation of a Hydrido–Vinylidene Complex via a 1,3-Hydrogen Shift

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*Summary: The complex $OsHCl(CO)(PiPr_3)_2$ (**1**) reacts with cyclohexylacetylene to give $OsHCl(=C=CHCy)(CO)(PiPr_3)_2$ (**2**), which evolves in solution to $OsCl\{(E)\text{-}CH=CHCy\}(CO)(PiPr_3)_2$ (**3**). Complex **3** reacts with HCl to afford $OsCl_2(=CHCH_2Cy)(CO)(PiPr_3)_2$ (**4**). The reaction of $OsDCl(CO)(PiPr_3)_2$ (**1-d**) with cyclohexylacetylene leads to a mixture of $OsDCl(=C=CHCy)(CO)(PiPr_3)_2$ (**2-d_a**) and $OsHCl(=C=CDCy)(CO)(PiPr_3)_2$ (**2-d_b**) in a ca. 1:1 molar ratio, indicating that the formation of **2** involves a 1,3-hydrogen shift via an alkynyl intermediate. The dihydrogen or dihydride nature of this alkynyl intermediate is discussed.*

Introduction

During studies designed to determine the mechanism of the reduction[1] and hydrosilylation[2] of terminal alkynes catalyzed by $OsHCl(CO)(PiPr_3)_2$, we have observed that the nature of the alkyne R group determines the type of the organometallic complexes obtained by reaction of the hydrido-osmium complex $OsHCl(CO)(PiPr_3)_2$ with terminal alkynes. Thus, it has been reported that this monohydrido compound reacts with acetylene, propyne, and phenylacetylene by insertion to give the five-coordinate vinyl–osmium compounds $OsCl\{(E)\text{-}CH=CHR\}(CO)(PiPr_3)_2$ (R = H, Me, Ph),[3] while the reactions of the monohydride with $HC{\equiv}CC(OH)R^1R^2$ afford, in one step, vinylcarbene compounds of the type $OsCl_2(=CHCH=CR^1R^2)(CO)(PiPr_3)_2$ in about 40% yield. When R^1 is hydrogen, small amounts of the complexes $OsCl\{CHCHC(O)R^2\}(CO)(PiPr_3)_2$ can also be obtained.[4] We have now observed that the reaction of $OsHCl(CO)(PiPr_3)_2$ with cyclohexylacetylene leads to the hydrido–vinylidene species $OsHCl(=C=CHCy)(CO)(PiPr_3)_2$.

Hydrido–vinylidene complexes are considered important intermediates in several homogeneous and heterogeneous catalytic reactions, including alkene oligomerization, polymerization, metathesis of olefins,[5] and Fischer–Tropsch synthesis.[6] To the best of our knowledge, only three hydrido–vinylidene complexes have been previously isolated. Bercaw *et al.* have reported that the reaction of $Cp^*_2TaCl_2$ and vinylmagnesium bromide gives the neutral hydrido–vinylidene species $Cp^*_2Ta(H)(=C=CH_2)$, which affords $Cp^*_2Ta(CH=CH_2)(CO)$ by reaction with CO.[7] Bianchini *et al.* have observed that the 16-electron fragment $[(PP_3)OsH]^+$ (PP_3 = $P(CH_2CH_2P)_3$) is capable of promoting the terminal alkyne to vinylidene tautomerism.[8] We have shown that the $OsH_3(\eta^2\text{-}O_2CCH_3)(PiPr_3)_2$ complex reacts with phenylacetylene to give $OsH(\eta^2\text{-}O_2CCH_3)(=C=CHPh)(PiPr_3)_2$ and molecular hydrogen.[9]

In this note, we report on the reaction of $OsHCl(CO)(PiPr_3)_2$ (**1**) with cyclohexylacetylene to give $OsHCl(=C=CHCy)(PiPr_3)_2$ (**2**), its transformation into $OsCl\{(E)\text{-}CH=CHCy\}(CO)(PiPr_3)_2$ (**3**), and the reaction of **3** with HCl to afford $OsCl_2(=CHCH_2Cy)(CO)(PiPr_3)_2$ (**4**) (Scheme 1).

Results and Discussion

The reaction of the hydrido–osmium complex **1** with cyclohexylacetylene to give **2** was carried out in toluene at room temperature. Complex **2** was isolated after 30 min as a pale green solid in 70% yield by addition of pentane and was characterized by elemental analysis, IR, and ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopy.

The most noticeable absorptions of the IR spectrum in Nujol are three bands at 2030, 1935, and 1670 cm^{-1}, assigned to the ν(OsH), ν(CO), and ν(C=C) vibrations, respectively. The presence of a hydrido ligand in **2** was mainly inferred from ^1H and $^{31}P\{^1H\}$ NMR spectra. In agreement with the mutually *trans* disposition of the hydrido and carbonyl ligands, the ^1H NMR spectrum in benzene-d_6 contains a triplet at −4.62 ppm[10] with a P–H coupling constant of 28.8 Hz. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 44.8 ppm, which under off-resonance conditions splits into a doublet. The vinylidene group was characterized by a doublet of triplets at 3.19 ppm with P–H and H–H coupling constants of 4.1 and 10.6 Hz, respectively, and, in the $^{13}C\{^1H\}$ NMR spectrum, by a triplet at 326.9 ppm due to the α-carbon atom with a P–C coupling constant of 2.0 Hz and a singlet at 121.9 ppm due to the β-carbon atom. Similar

⊗ Abstract published in *Advance ACS Abstracts*, June 1, 1995.

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(10) A similar δ value for Os–H has been found for related compounds containing a carbonyl ligand *trans* to a hydrido ligand. See: (a) Esteruelas, M. A.; Werner, H. *J. Organomet. Chem.* **1986**, *303*, 221. (b) Werner, H.; Esteruelas, M. A.; Meyer, U.; Wrackmeyer, B. *Chem. Ber.* **1987**, *120*, 11.

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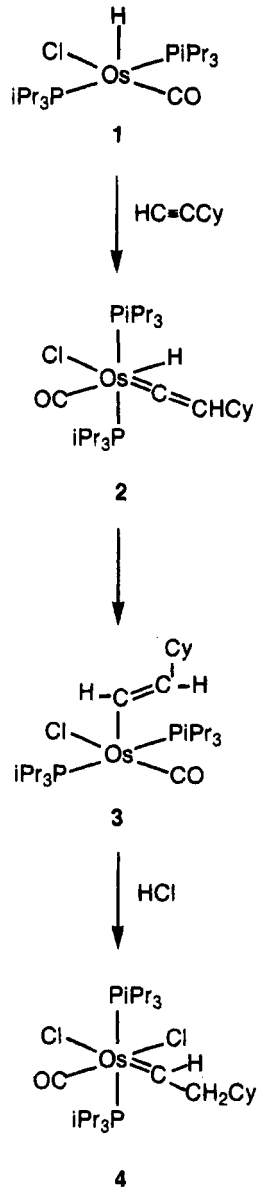
Scheme 1



chemical shifts have been observed for related vinylidene compounds.[11]

The reaction of **1** with cyclohexylacetylene to form **2** can be easily monitored by $^{31}P\{^1H\}$ NMR spectroscopy. Kinetic measurements for two different concentrations of **1** yield a second-order rate constant of $(6.0 \pm 0.2) \times 10^{-3}$ M^{-1} s^{-1} at −29 °C.

The addition of terminal alkynes to coordinatively unsaturated metal-complex fragments is a general method of preparing vinylidene compounds.[12] It is generally agreed that, in the initial step, the alkyne molecule coordinates in a η^2-fashion to the metallic center, undergoing transformation in the coordination sphere of the metal to give the corresponding vinylidene species. This transformation is generally viewed either as a 1,2-hydrogen shift or as a 1,3-hydrogen shift via hydrido−alkynyl intermediates.[13] Theoretical studies suggest that the expenditure of energy to promote the concerted migration of the hydrido ligand from the metal to the β-carbon atom of the alkyne group in the 1,3-hydrogen shift is prohibitive.[14] In agreement with this, Werner *et al.* have proved that the mechanism for the formation of the complex $Rh(\eta^5\text{-}C_5H_5)(C{=}CHPh)(P\textit{i}Pr_3)_2$ via a hydrido−alkynyl intermediate does not involve an intramolecular 1,3-hydrogen shift but a two-step elimination−addition reaction, in which the last step involves the protonation of the alkynyl ligand.[15]

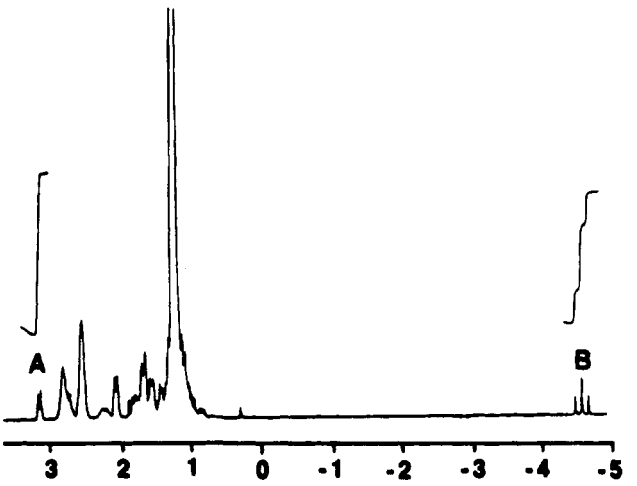


Figure 1. ^1H NMR spectrum of the reaction of $OsDCl(CO)(P\textit{i}Pr_3)_2$ (**1-*d***) with cyclohexylacetylene after 20 min in benzene-d_6.

In order to obtain information about the mechanism of formation of **2**, the reaction of $OsDCl(CO)(P\textit{i}Pr_3)_2$ (**1-*d***) with cyclohexylacetylene was studied by ^1H and ^2H NMR spectroscopy. Figure 1 shows the ^1H NMR spectrum of the solution formed by addition of the stoichiometric amount of cyclohexylacetylene to a benzene-d_6 solution of **1-*d***, after 20 min. The most noticeable signals of this spectrum are the two resonances A (δ 3.19, dt, J(HH) = 10.6, J(HP) = 4.1 Hz) and B (δ −4.62, t, J(HP) = 28.8 Hz). Resonance A can be assigned to $OsDCl(=C{=}CH\textit{C}Cy)(P\textit{i}Pr_3)_2$ (**2-*d*$_a$**), while resonance B can be assigned to $Os\textit{H}Cl(=C{=}CDCy)(P\textit{i}Pr_3)_2$ (**2-*d*$_b$**). The presence of the OsD and =C=CDCy fragments in complexes **2-*d*$_a$** and **2-*d*$_b$**, respectively, is strongly supported by the ^2H NMR spectrum, which contains two resonances, a broad singlet at 3.0 ppm for the =C=C*D*Cy group of **2-*d*$_b$** and a triplet at −4.6 ppm with a P−D coupling constant of 4.0 Hz, assigned to Os−*D* of **2-*d*$_a$**. H,D-exchange between **1-*d*** and **2** was not observed in an additional experiment. This observation together with the formation of **2-*d*$_a$** and **2-*d*$_b$** in a ca. 1:1 molar ratio no doubt indicates that the alkyne → vinylidene transformation involves a 1,3-hydrogen shift via an alkynyl intermediate. Furthermore, the second-order rate law for the reaction of **1** with cyclohexylacetylene suggests an intramolecular 1,3-hydrogen shift.

(11) See, for example: (a) Werner, H.; Rappert, T.; Wiedemann, R.; Wolf, J.; Mahr, N. *Organometallics* **1994**, *13*, 2721. (b) Ting, P. C.; Lin, Y. C.; Cheng, M. C.; Wang, Y. *Organometallics* **1994**, *13*, 2150.

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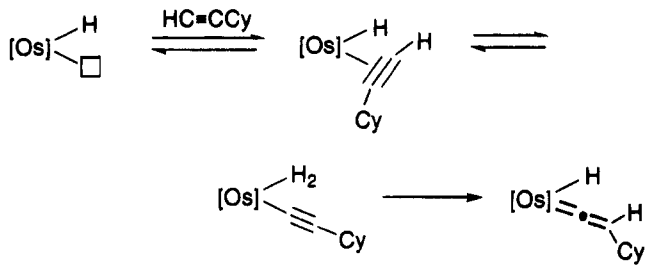
(14) Silvestre, J.; Hoffmann, R. *Helv. Chim. Acta* **1985**, *68*, 1461.

(15) Wolf, J.; Werner, H.; Serhadli, O.; Ziegler, M. L. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 414.

Scheme 2



[Os] = OsCl(CO)($PiPr_3$)$_2$

The nature of this alkynyl intermediate merits further consideration. Its formation should occur by oxidative addition of the H−C_{sp} alkyne bond to give, at first glance, a dihydrido−osmium(IV) species, where both hydrido ligands should be nucleophilic centers. In addition, it should be noted that coordination of an acetylide, $[RC{\equiv}C]^-$, to a metal center transfers the nucleophilicity from the α- to the β-carbon atom, and it has been proved that for these types of osmium systems the transfer is efficient.[16] Thus, the direct attack of one of the two hydrido ligands at the β-carbon atom of the alkynyl group does not seem likely, given the nucleophilicity of these centers. Hence, it can be proposed that the H−C_{sp} activation leads to dihydrogen species. In this way, the formation of **2** could be rationalized as the electrophilic attack of an acidic proton of the dihydrogen ligand at the β-carbon atom of the alkynyl group (Scheme 2).

In favor of a dihydrogen intermediate, the following should be noted. (i) The addition of HX molecules to hydrido−osmium(II) complexes has been found to be an useful synthetic route for dihydrogen compounds. Thus, the alkynyl−hydrido−dihydrogen derivative OsH(C_2R)(η^2-H_2)(CO)($PiPr_3$)$_2$ (R = Ph, $SiMe_3$),[17] the silyl−dihydrogen derivative Os($SiEt_3$)Cl(η^2-H_2)(CO)($PiPr_3$)$_2$,[2] and the dichloro−dihydrogen complex $OsCl_2$(η^2-H_2)(CO)($PiPr_3$)$_2$[18] have been prepared by reaction of OsH_2(CO)($PiPr_3$)$_2$ with HC≡CR (R = Ph, $SiMe_3$) or OsHCl(CO)($PiPr_3$)$_2$ with $HSiEt_3$ or HCl, respectively. (ii) The electrophilic character of the dihydrogen complexes has been previously demonstrated. A common feature of the dihydrogen complexes is that the coordinated dihydrogen ligand is readily deprotonated.[19] (iii) The addition of electrophiles to metal alkynyl complexes is a general method of preparing vinylidene compounds.[12]

In benzene-d_6 or toluene as solvent, **2** evolves after 3 days into the vinyl derivative **3**. Complex **3** was isolated as a dark blue solid in 88% yield by addition of pentane. The IR spectrum of this solid in Nujol shows the ν(CO) and ν(C=C) absorptions at 1895 and 1590 cm^{-1}, respectively. The most noticeable resonances in the ^1H NMR spectrum are a doublet at 6.80 ppm with an H−H coupling constant of 12.6 Hz and a doublet of doublets of triplets at 4.60 ppm with H−H coupling constants of 12.6 and 7.2 Hz and a P−H coupling constant of 2.1 Hz. These resonances are assigned to the protons attached to the α- and β-carbon atoms of the vinyl ligand, respectively. The α-carbon atom of the vinyl group appears in the $^{13}C\{^1H\}$ NMR spectrum at 105.9 ppm with a P−C coupling constant of 7.0 Hz, while the β-carbon atom appears at 139.6 ppm as a triplet with a P−C coupling constant of 3.0 Hz. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 22.3 ppm.

These spectroscopic data agree well with those previously reported for the related compounds OsCl{(*E*)-CH=CHR}(CO)($PiPr_3$)$_2$ (R = H, Me, Ph), where the square-pyramidal coordination of the osmium atom, and the *trans* position of the two substituents at the carbon−carbon double bond, have been determined by a single-crystal X-ray diffraction study on OsCl{(*E*)-CH=CHPh}-(CO)($PiPr_3$)$_2$.[3]

Previous studies of vinyl compounds have identified the localization of electron density at the β-carbon atom of the vinyl ligand. The chemical reactivity at this atom is thus oriented toward electrophiles.[20] In agreement with this, **3** reacts with a stoichiometric amount of a toluene−HCl solution to afford the dichloro−carbene compound **4**.

Complex **4** was isolated as a yellow solid in 70% yield. The presence of the carbene ligand in this complex can be inferred from the ^1H and the $^{13}C\{^1H\}$ spectra. The ^1H NMR spectrum exhibits the Os=CH resonance at 19.20 ppm as a triplet with a H−H coupling constant of 5.7 Hz. In the $^{13}C\{^1H\}$ NMR spectrum, the Os=C signal appears as a triplet at 273.05 ppm with a P−C coupling constant of 7.6 Hz. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 11.10 ppm, indicating that both triisopropylphosphine ligands are equivalent.

In conclusion, the reaction of the monohydrido−osmium(II) compound OsHCl(CO)($PiPr_3$)$_2$ (**1**) with cyclohexylacetylene initially leads to the hydrido−vinylidene species OsHCl(=C=CHCy)(CO)($PiPr_3$)$_2$ (**2**), which evolves in solution into OsCl{(*E*)-CH=CHCy}-(CO)($PiPr_3$)$_2$ (**3**). The reaction of this vinyl compound with HCl affords $OsCl_2$(=CHCH_2Cy)(CO)($PiPr_3$)$_2$ (**4**). The process of formation of the vinylidene complex **2** is a real 1,3-hydrogen shift, which takes place via an alkynyl intermediate. The 1,3-hydrogen shift, most probably implies the presence of a dihydrogen molecule instead of two hydrido ligands in the alkynyl intermediate.

Experimental Section

General Considerations. All reactions were carried out with rigorous exclusion of air by using Schlenk-tube techniques. Solvents were dried by known procedures and distilled under argon prior to use. OsHCl(CO)($PiPr_3$)$_2$[10a] and OsDCl-(CO)($PiPr_3$)$_2$[1] were prepared by a published method.

Physical Measurements. Infrared spectra were recorded as Nujol mulls on polyethylene sheets using a Perkin-Elmer 883 or a Nicolet 550 spectrometer. NMR spectra were recorded on a Varian UNITY 300 or on a Bruker 300 AXR. Chemical shifts are expressed in ppm using C_6D_6 (7.15 ppm) as internal

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standard (^{2}H) or upfield from Me_4Si (^{13}C, ^{1}H) or 85% H_3PO_4 (^{31}P). Coupling constants J and N ($N = J(HP) + J(HP')$ for ^{1}H, and $N = J(CP) + J(CP')$ for ^{13}C) are given in hertz. C and H analyses were carried out with a Perkin-Elmer 2400 CHNS/O analyzer.

Reaction of OsHCl(CO)(P*i*Pr$_3$)$_2$ (1) with Cyclohexylacetylene: Preparation of OsHCl(=C=CHCy)(CO)(P*i*Pr$_3$)$_2$ (2). A solution of **1** (217 mg, 0.38 mmol) in 8 mL of toluene was treated with cyclohexylacetylene (63 μL, 0.49 mmol). After the mixture was stirred for 30 min at room temperature, it was evaporated to dryness. The green-violet residue was washed three times (3 mL) with cold pentane and dried in vacuo. The product is a pale green solid. Yield 181 mg (70%). Anal. Calcd for $C_{27}H_{55}ClOP_2Os$: C, 47.43; H, 8.11. Found: C, 47.41; H, 7.85. IR (Nujol): ν(OsH) 2030 (w), ν(C≡O) 1935 (s), ν(Os=C=C) 1670 (m) cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6): δ 3.19 (dt, J(HH) = 10.6, J(HP) = 4.1; =C=C*H*Cy), 2.76 (m; PCH), 2.1−1.4 (H of Cy), 1.24 and 1.23 (both dvt, N = 14.1, J(HH) = 6.9; PCCH_3), −4.62 (t, J(HP) = 28.8; OsH). ^{13}C{^{1}H} NMR (75.43 MHz, C_6D_6): δ 326.9 (t, J(CP) = 2.0; OsC_α), 179.3 (t, J(CP) = 8.6; OsCO), 121.9 (br; =CC_β), 36.4, 32.4, 26.6, and 25.9 (each s; C of Cy), 24.9 (vt, N = 28.0; PCH), 19.1, 18.9 (both s; PC*C*H$_3$). ^{31}P{^{1}H} NMR (121.42 MHz, C_6D_6): δ 44.8 (s, d in off-resonance).

Reaction of OsDCl(CO)(P*i*Pr$_3$)$_2$ (1-*d*) with Cyclohexylacetylene: Formation of OsDCl(=C=CHCy)(CO)(P*i*Pr$_3$)$_2$ (2-*d*$_a$) and OsHCl(=C=CDCy)(CO)(P*i*Pr$_3$)$_2$ (2-*d*$_b$). To an NMR tube containing a benzene-d_6 solution of **1-*d*** (0.035 mmol in 0.5 mL) was added cyclohexylacetylene (5 μL, 0.037 mmol). The reaction was followed by ^{1}H and ^{2}H NMR analysis. After 20 min, the two isotopomers were formed in the ratio **2-*d*$_a$**:**2-*d*$_b$** = 1:0.84. Data for **2-*d*$_a$** are as follows. ^{1}H NMR (300 MHz, C_6D_6): δ 3.19 (dt, J(HH) = 10.6, J(HP) = 4.1; =C=C*H*Cy), 2.76 (m; PCH), 2.1−1.4 (H of Cy), 1.24 and 1.23 (both dvt, N = 14.1, J(HH) = 6.9; PCCH_3). ^{2}H NMR (46.07 MHz, C_6H_6): δ −4.6 (t, J(DP) = 4.0; OsD). Data for **2-*d*$_b$** are as follows. ^{1}H NMR (300 MHz, C_6D_6): δ 2.76 (m; PCH), 2.1−1.4 (H of Cy), 1.24 and 1.23 (both dvt, N = 14.1, J(HH) = 6.9; PCCH_3), −4.62 (t, J(HP) = 28.8; OsH). ^{2}H NMR (46.07 MHz, C_6H_6): δ 3.0 (br; =C=CDCy). ^{31}P{^{1}H} NMR (121.42 MHz, C_6D_6) for **2-*d*$_a$** and **2-*d*$_b$**: δ 44.8 (br s).

Reaction of OsDCl(CO)(P*i*Pr$_3$)$_2$ (1-*d*) with OsHCl(=C=CHCy)(CO)(P*i*Pr$_3$)$_2$ (2). Complexes **1-*d*** (15 mg, 0.026 mmol) and **2** (18 mg, 0.026 mmol) were dissolved in 0.5 mL of benzene-d_6, and the resulting solution was transferred to an NMR tube. The ^{1}H NMR spectrum was recorded over the time. No reaction was observed after 1 h.

Preparation of OsCl{(*E*)-CH=CHCy}(CO)(P*i*Pr$_3$)$_2$ (3). A solution of **2** (125 mg, 0.22 mmol) in 5 mL of toluene was stirred at room temperature under an argon atmosphere. After 3 days, the purification procedure was analogous to that described for **2**. The product is a dark blue solid. Yield: 132 mg (88%). Anal. Calcd for $C_{27}H_{55}ClOP_2Os$: C, 47.43; H, 8.11. Found: C, 47.38; H, 7.80. IR (Nujol): ν(C≡O) 1895 (vs), ν(C=C) 1590 (s) cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6): δ 6.8 (d, J(HH) = 12.6; OsCH=), 4.6 (ddt, J(HH) = 12.6 and 7.2, J(HP) = 2.1; =C*H*Cy), 2.90 (m; PCH), 2.4−1.4 (H of Cy), 1.22 (dvt, N = 12.6, J(HH) = 6.0; PCCH_3). ^{13}C NMR (75.43 MHz, C_6D_6): δ 182.9 (t, J(CP) = 9.2; OsCO), 139.6 (t, J(CP) = 3.0; CC_β), 105.9 (t, J(CP) = 7.0; OsC_α), 45.0, 34.8 and 26.8 (each s; C of Cy), 24.9 (vt, N = 23.8; PCH), 20.0 and 19.78 (both s; PC*C*H$_3$). ^{31}P{^{1}H} NMR (121.42 MHz,C_6D_6): δ 22.3 (s).

Reaction of 3 with HCl: Preparation of OsCl$_2$(=CHCH$_2$Cy)(CO)(P*i*Pr$_3$)$_2$ (4). A solution of **3** (70 mg, 0.10 mmol) in 4 mL of toluene was treated dropwise with toluene−HCl (0.123N; 0.8 mL, 0.31 mmol). After the mixture was stirred for 20 min at room temperature, the yellow-green solution was evaporated to dryness. The residue was washed twice for 10 min with 2 mL of pentane and dried in vacuo. The product is a yellow solid. Yield: 50 mg (70%). Anal. Calcd for $C_{27}H_{56}Cl_2OP_2Os$: C, 44.96; H, 7.82. Found: C, 45.38; H, 7.83. IR (Nujol): ν(C≡O) 1930 (s) cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6): δ 19.20 (t, J(HH) = 5.7; Os=CH), 2.75 (m; PCH), 2.15 (pseudo t, J(HH) = 6.05; =CCH_2), 2.0−1.1 (H of Cy), 1.35 (dvt, N = 14.0, J(HH) = 7.1; PCCH_3), 1.15 (dvt, N = 13.7, J(HH) = 6.8; PCCH_3). ^{13}C{^{1}H} NMR (75.43 MHz, C_6D_6): δ 273.05 (t, J(CP) = 7.6; OsC_α), 176 (t, J(CP) = 8.5; OsCO), 68.9 (s, =CC_β), 38.60, 33.50, 26.54, and 26.47 (each s; C of Cy), 25.3 (vt, N = 25.1; PCH), 20.1 and 19.4 (both s; PC*C*H$_3$). ^{31}P{^{1}H} NMR (121.42 MHz, $CDCl_3$): δ 11.1 (s).

Kinetics of formation of 2. The reaction of **1** with cyclohexylacetylene was monitored by ^{31}P{^{1}H} NMR at −29 °C, assuming that the reaction occurs in a 1:1 molar ratio. Samples of **1** and cyclohexylacetylene in 0.5 mL of toluene-d_8 were stored under argon in NMR tubes at −120 °C prior to measurements. Second-order rate constants were calculated by linear least-squares fitting of the kinetic data to the integrated second-order rate law

$$\ln(C_a/C_b) = (C^\circ_a - C^\circ_b)kt + \ln(C^\circ_a/C^\circ_b)$$

For two different samples of reactant **1** (0.052 M and 0.07 M) and cyclohexylacetylene (0.233 M), the calculated rate constants were (6.1 ± 0.3) × 10^{-3} and of (5.9 ± 0.1) × 10^{-3} M^{-1} s^{-1}, respectively.

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