

Synthesis and Characterization of Dihydrogen(olefin)osmium Complexes with (E)-Ph₂P(CH₂)₂CH=CH(CH₂)₂PPh₂

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Treatment of [OsClH₃(PPh₃)₃] with (E)-Ph₂P(CH₂)₂CH=CH(CH₂)₂PPh₂ produced [OsClH(PPh₃){Ph₂P(CH₂)₂CH=CH(CH₂)₂PPh₂}], which reacted with HOTf to give the dihydrogen(olefin) complex [OsCl(H₂)(PPh₃){Ph₂P(CH₂)₂CH=CH(CH₂)₂PPh₂}]OTf. Treatment of the latter complex with H₂ did not result in hydrogenation of the olefin double bond, but gave the (hydrido)dihydrogen complex [OsH(H₂)-

(PPh₃){Ph₂P(CH₂)₂CH=CH(CH₂)₂PPh₂}]OTf. A density functional theory study suggested that hydrogenation of the double bond in [OsCl(H₂)(PPh₃){Ph₂P(CH₂)₂CH=CH(CH₂)₂PPh₂}]OTf was thermodynamically feasible but kinetically unfavorable.

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Introduction

Since the first report of dihydrogen complexes by Kubas and his co-workers in 1984,^[1] this unique class of complexes has been intensively investigated, especially with regard to their preparation, characterization, and structural and catalytic properties.^[2–4] Previous studies have established that dihydrogen complexes may have their own individual reactivity and play active roles in catalytic reactions. In catalytic hydrogenation reactions, there are several possible ways in which dihydrogen complexes may play active roles. Among them, intramolecular hydrogen transfer from a coordinated dihydrogen ligand to the α -carbon atom of a σ -bonded carbon ligand has been recognized as one of the key steps in the catalytic cycles. In particular, (alkyl)dihydrogen and (alkenyl)dihydrogen complexes have been proposed or inferred as the key intermediates in the hydrogenation of olefins and acetylenes under catalysis by group-8 metal complexes such as [MH(H₂)(PP₃)]⁺ [M = Fe, Ru; PP₃ = P(CH₂-CH₂PPh₂)₃],^[5] [OsClH(CO){P(*i*Pr)₃}₂],^[6] [RuClH-(PPh₃)₃],^[7] and [RuH(Tp)(L)(PPh₃)] [Tp = hydrotris(1-pyrazolyl)borate; L = PPh₃, CH₃CN].^[8] As model complexes for reactions involving intramolecular hydrogen transfer from a coordinated dihydrogen ligand to the α -carbon atom of a σ -bonded carbon ligand, several well-characterized dihydrogen complexes containing σ -bonded carbon ligands (such as alkynyl,^[9] alkenyl,^[10] and aryl^[11]) have been synthesized in recent years.

In addition, there are reports that hydrogenation may also proceed through hydrogen transfer from a coordinated dihydrogen ligand to an olefin ligand. The complexes [M(H₂)(η^4 -NBD)(CO)₃] and [M(H₂)(η^2 -NBD)(CO)₄] (M = Cr, Mo, and W) have been proposed as the intermediates in the photocatalytic hydrogenation of norbornadiene with [M(CO)₆].^[12,13] Dihydrogen(olefin) complexes have also been proposed (but not detected) as the intermediates in catalytic hydrogenation of olefins with [Ru(Tp)(PPh₃)_x(CH₃CN)_{3-x}]⁺ ($x = 1, 2$),^[8] and in the protonation reaction of [Ru(Cp*)H(NBD)].^[14a] However, well-characterized dihydrogen(olefin) complexes are rare.^[12–14] Reported dihydrogen(olefin) complexes include [M(H₂)(η^2 -NBD)(CO)₄] (M = Mo and W),^[12] [M(H₂)(η^4 -NBD)(CO)₄] (M = Cr, Mo, and W),^[12] and [Fe(H₂)(CO)₃(MeO₂CCH=CHCO₂Me)],^[13] which have been detected by IR spectroscopy, and [Ru(Cp*)(H₂)(COD)]⁺, which has been detected by NMR spectroscopy.^[14a] In this paper we wish to report the synthesis and characterization of new dihydrogen(olefin) complexes.

Results and Discussion

Synthesis and Characterization of

[OsClH(PPh₃){Ph₂P(CH₂)₂CH=CH(CH₂)₂PPh₂}]

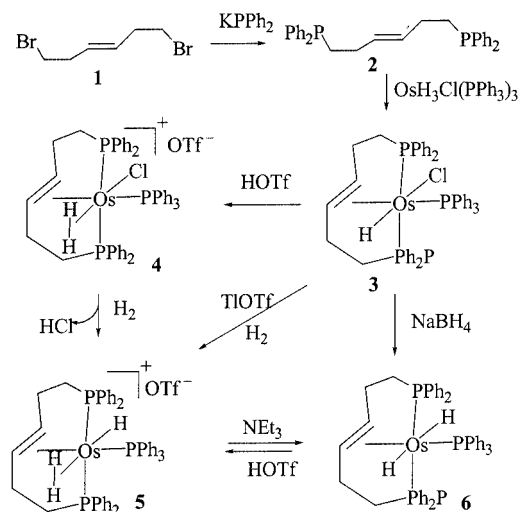
Complexes of the type [MCl(H₂)L₄]⁺ (M = Ru, Os; L = phosphane, CO, pyridine) are known to contain a dihydrogen ligand.^[15,16] One might therefore expect that protonation of [MClH(olefin)(PR₃)₃] might produce dihydrogen complexes [MCl(H₂)(olefin)(PR₃)₃]⁺. To test this possibility, we prepared the hydrido(olefin) complex [OsClH(PPh₃)(Ph₂P(CH₂)₂CH=CH(CH₂)₂PPh₂)], hoping that subsequent protonation would produce the corres-

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ponding dihydrogen(olefin) complex. Osmium metal and the bidentate phosphane ligand with an olefinic functionality in the backbone were used in the project because of the expectation that such systems may give thermally stable dihydrogen(olefin) complexes.

The ligand (*E*)-Ph₂P(CH₂)₂CH=CH(CH₂)₂PPh₂ (**2**)^[17] was prepared by treatment of (*E*)-Br(CH₂)₂CH=CH(CH₂)₂Br (**1**) with excess KPPH₂ in THF (Scheme 1). Ligand **2** was characterized by ¹H, ¹³C{¹H}, and ³¹P{¹H} NMR spectroscopy and by elemental analysis. In particular, the ¹H NMR spectrum (in C₆D₆) showed the olefinic proton signal at δ = 5.4 ppm, while the ³¹P{¹H} NMR spectrum (in C₆D₆) showed a singlet at δ = -17.0 ppm. The closely related ligand (*E*)-(tBu)₂P(CH₂)₂CH=CH(CH₂)₂-P(tBu)₂ has also been reported previously.^[18]



Scheme 1

Treatment of a benzene solution of [OsClH₃(PPh₃)₃] with ligand **2** for 5 h produced [OsClH(PPh₃){Ph₂P(CH₂)₂CH=CH(CH₂)₂PPh₂}] (**3**), which was isolated as a gray solid in ca. 79% yield. The structure of complex **3** could readily be assigned by its ¹H, ¹³C{¹H}, ³¹P{¹H}, and ¹H-³¹P-COSY NMR spectra and by elemental analysis. The ³¹P{¹H} NMR spectrum (in C₆D₆) showed three doublets of doublets at δ = -7.7, 7.3, and 23.8 ppm. A large ²J_{P,P} coupling (290.6 Hz) for the ³¹P signals at δ = 7.3 and 23.8 ppm was observed, indicating that two of the phosphorus atoms in **3** were *trans* to each other. A ¹H-³¹P-COSY NMR experiment suggested that the two *trans*-disposed phosphorus atoms were associated with the two PPh₂ groups of ligand **2**. In the ¹H NMR spectrum (in C₆D₆), the olefinic proton signals appeared at δ = 3.88 ppm, significantly upfield from their counterparts in free ligand **2**, confirming that the olefin double bond was coordinated to the osmium center. Complex **3** exhibited a hydride signal at δ = -16.40 ppm (dt, ²J_{P,H} = 27.0, 15.0 Hz). The magnitude of the coupling constants indicated that the hydride ligand was *cis* to the three phosphorus atoms. The chemical shift of the hydride signal was quite strongly upfield, consistently with a struc-

ture in which the hydride ligand is *trans* to a chloride ligand. During the course of this work, the closely related complex [OsClH(PPh₃)(Ph₂P-C₆H₃Me-CH=CH-C₆H₃Me-PPh₂)] was reported.^[19]

Synthesis and Characterization of [OsCl(H₂)(PPh₃){Ph₂P(CH₂)₂CH=CH(CH₂)₂PPh₂}]OTf

Protonation of complex **3** with HOTf produced the dihydrogen(olefin) complex [OsCl(H₂)(PPh₃)(Ph₂P(CH₂)₂CH=CH(CH₂)₂PPh₂)]OTf (**4**). Complex **4** was unstable and decomposed under vacuum. The compound could therefore not be isolated as a pure solid, so it was characterized in situ. The ³¹P{¹H} NMR spectrum of complex **4** (in CD₂Cl₂) exhibited the PPh₃ signal at δ = -8.9 ppm and the PPh₂ signals at δ = 14.2 and 16.8 ppm. The ³¹P signals of the PPh₂ groups at δ = 14.2 and 16.8 ppm had a large ²J_{P,P} coupling constant (243.6 Hz), indicating that the PPh₂ groups were *trans* to each other in **4**. The ¹H NMR spectrum (in CD₂Cl₂) exhibited a broad signal attributable to a dihydrogen ligand at δ = -9.57 ppm. The broad hydride signal had a T₁ (min) of 27.0 ms (at 300 MHz) at 258 K. The short T₁ (min) value strongly suggested that complex **4** contained a dihydrogen ligand. Further support for the existence of the dihydrogen ligand in **4** was provided by the ¹H NMR spectrum of the HD isotopomer [OsCl(HD)(PPh₃){Ph₂P(CH₂)₂CH=CH(CH₂)₂PPh₂}]⁺, which was generated in situ by protonation of complex **3** with DOTf. The ¹H NMR spectrum of the HD isotopomer (in CD₂Cl₂) displayed the HD signal as a 1:1:1 triplet at δ = -9.58 ppm, with a ¹J(HD) coupling constant of 14.1 Hz. A d(HH) of 1.18 Å was obtained by application of the relationship d(HH) = -0.0167J(HD) + 1.42 and ¹J(HD) = 14.1 Hz.^[15a] On the basis of the T₁ (min) of 27 ms, the H-H bond length was calculated to be 1.13 Å for a non-spinning H₂ or 0.98 Å for a spinning dihydrogen ligand.^[20]

Treatment of [OsCl(H₂)(PPh₃){Ph₂P(CH₂)₂CH=CH(CH₂)₂PPh₂}]OTf with H₂

We tried to hydrogenate the coordinated olefin double bond in **4** by storing a solution of **4** in CD₂Cl₂ under H₂. However, the expected hydrogenated product [OsClH_x(PPh₃){Ph₂P(CH₂)₂PPh₂}]⁺ was apparently not produced from the reaction, as indicated by in situ NMR studies. Instead, the fluxional (hydrido)dihydrogen complex [OsH(H₂)(PPh₃){Ph₂P(CH₂)₂CH=CH(CH₂)₂PPh₂}]OTf (**5**) was slowly produced under these reaction conditions. A molecule of HCl in **4** was thus apparently replaced by a H₂ molecule in the reaction. Mechanistically, complex **5** could be formed by initial displacement of Cl⁻ in **4** with an H₂ molecule to give the dicationic dihydrogen complex [Os(H₂)₂(PPh₃){Ph₂P(CH₂)₂CH=CH(CH₂)₂PPh₂}]²⁺, followed by deprotonation.

The presence of a coordinated CH=CH moiety in **5** was supported by the ¹³C NMR spectrum (in CD₂Cl₂), which displayed the coordinated olefinic CH carbon signals at δ = 56.9 and 65.7 ppm. The ³¹P{¹H} NMR spectrum (in CD₂Cl₂) at 230 K showed the PPh₃ signal at δ = 4.0 ppm

and the PPh₂ signals at $\delta = 29.1$ and 36.5 ppm. The two PPh₂ groups in **5** had to be *trans* to each other for the large $^2J_{\text{P,P}}$ coupling constant (201.7 Hz) observed for the PPh₂ signals at $\delta = 29.1$ and 36.5 ppm. In the room-temperature ^1H NMR spectrum (in CD₂Cl₂), a broad hydride signal was observed at $\delta = -5.30$ ppm. When the temperature was below 275 K, the hydride signal was split into two with a relative intensity ratio of 1:2. For example, the ^1H NMR spectrum at 230 K showed a doublet of triplets at $\delta = -6.70$ ppm ($^2J_{\text{P,H}} = 33.0, 19.5$ Hz) and a broad singlet at $\delta = -4.74$ ppm, corresponding to one and two hydrogen atoms, respectively. T_1 measurements showed that the broad hydride signal at $\delta = -4.74$ ppm had a T_1 (min) of 10.1 ms (on 300 MHz) at 232 K. The short T_1 (min) value strongly suggested that complex **5** contained a dihydrogen ligand. Furthermore, a partially deuterated sample of [OsD_{3-x}H_x(PPh₃)₂{Ph₂P(CH₂)₂CH=CH(CH₂)₂PPh₂}]⁺ (in CD₂Cl₂ at 235 K) showed a 1:1:1 triplet at $\delta = -4.69$ ppm with a $^1J(\text{HD})$ coupling constant of 26.7 Hz. The $d(\text{HH})$ value in **5** was estimated to be 0.97 Å by application of the relationship $d(\text{HH}) = -0.0167 J(\text{HD}) + 1.42$ and $^1J(\text{HD}) = 26.7$ Hz.^[15a] On the basis of the T_1 (min) of 10.1 ms, the H–H bond length was calculated to be 1.04 Å for a nonspinning H₂ or 0.83 Å for a spinning H₂ ligand.^[20] The H–H distance in the (hydrido)dihydrogen complex **5** was shorter than that in the (chloro)dihydrogen complex **4**; a similar trend has been observed for [MX(H₂)(dppe)₂]⁺ (M = Ru, Os; X = H, Cl).^[15a]

Deprotonation of complex **5** with NEt₃ produced the neutral dihydride complex *trans*-[OsH₂(PPh₃)₂{Ph₂P(CH₂)₂CH=CH(CH₂)₂PPh₂}] (**6**), which could also be obtained by treatment of complex **3** with NaBH₄. Complex **5** was regenerated when **6** was treated with HOTf. The geometry of complex **6** could readily be assigned from its NMR spectroscopic data. In particular, the ^1H NMR spectrum (in CD₂Cl₂) displayed only one hydride signal at $\delta = -9.13$ ppm, indicating that the molecule had high symmetry. Consistently with the structure, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (in CD₂Cl₂) showed a doublet at $\delta = 41.2$ ppm for the PPh₂ groups and a triplet at $\delta = 17.6$ ppm for the PPh₃ ligand; the $^{13}\text{C}\{^1\text{H}\}$ NMR showed the coordinated olefinic CH carbon signal at $\delta = 37.6$ ppm.

Structural Study Using Quantum Chemical Calculations

To obtain a better understanding of the interesting chemistry described above, we calculated the structures of complexes [OsClH(PH₃)₂{H₂P(CH₂)₂CH=CH(CH₂)₂PH₂}] (**3'**), [OsCl(H₂)(PH₃)₂{H₂P(CH₂)₂CH=CH(CH₂)₂PH₂}]⁺ (**4'**), and [OsH(H₂)(PH₃)₂{H₂P(CH₂)₂CH=CH(CH₂)₂PH₂}]⁺ (**5'**), by the density functional theory B3LYP technique. The calculated structures of complexes **3'**, **4'**, and **5'** should provide enlightening geometric information regarding complexes **3**, **4**, and **5**. We also calculated the structure of [OsCl(H₂)(PH₃)₂{H₂P(CH₂)₂PH₂}]⁺ (**7'**), a model complex for a hydrogenated product of complex **4**. The optimized structures are shown in Figure 1. Complex **3'** is a typical hydrido(olefin) complex with strong Os–olefin interaction. The protonated species **4'** is confirmed to be a dihydrogen

complex. The H–H distance in the dihydrogen complex is calculated to be 1.011 Å, which is close to the experimentally predicted value in **4** based on the $^1J(\text{HD})$ coupling constant and T_1 (min) value. In a similar manner to complex **4'**, complex **5'** is another dihydrogen(olefin) species. In **5'**, the H–H distance is significantly shorter (0.853 Å), due to the presence of the strongly *trans*-influencing hydride ligand, which gives weaker Os–H₂ interaction.

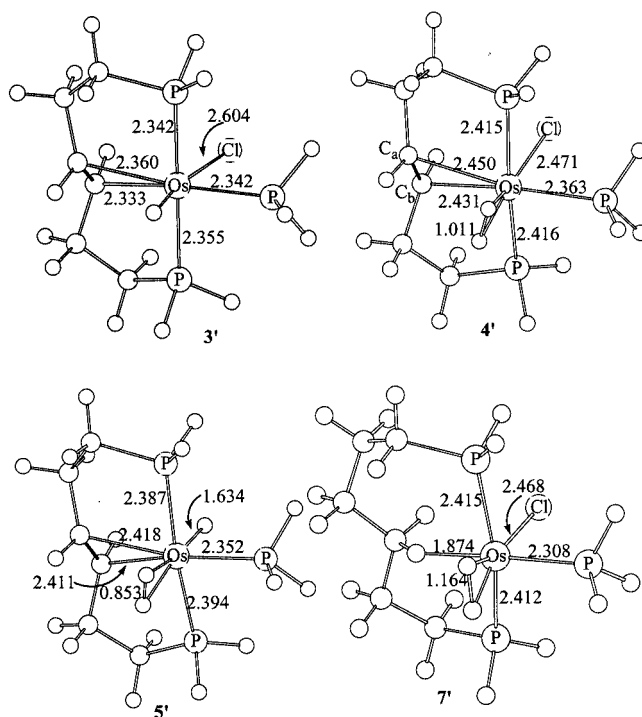


Figure 1. Optimized structures together with selected bond lengths [Å]

Experimentally, it is interesting that under H₂ the coordinated $\eta^2\text{-H}_2$ did not hydrogenate the olefin unit. The calculated free energy change (ΔG^0) for the process of **4'** + H₂ → **7'** (see Figure 1 for **7'**, the hydrogenated product featuring an agostic interaction) is ca. –1.0 kcal/mol. This result suggests that the hydrogenation is thermodynamically feasible, and we therefore feel that kinetic factors are probably responsible for the hydrogenation not occurring. Careful examination of the structure of complex **4'** (Figure 1) allows one to see that the orientation of the coordinated –HC=CH– unit is in such a manner that one olefinic carbon atom (C_a) is closer to the $\eta^2\text{-H}_2$ ligand while the other is further away. The hydrogenation of a coordinated olefin by an $\eta^2\text{-H}_2$ unit can occur through the formation of an agostic intermediate by transfer of one hydrogen atom of the H₂ ligand to one of the two olefinic carbon atoms. A reductive elimination then follows, to complete the hydrogenation process. If the transfer of one H atom from the $\eta^2\text{-H}_2$ ligand to the closer olefinic carbon atom (C_a) in **4'** is regarded as the first step, it is found that the assumed agostic species does not correspond to a stationary point in the potential energy surface. An agostic structure can be calculated (optimized) by fixing the C_a–H bond length at 1.20 Å.

However, the partially optimized structure is 20 kcal/mol higher in energy than complex **4'** and adopts a pseudopentagonal-bipyramidal (PB) structure in which the equatorial plane is formed by one hydride ligand, the chloride ion, the PH_3 molecule, the $\text{C}_a\text{--H}$ agostic ligand, and the bonded C_b alkyl moiety. In the PB structure, the hydride ligand and the bonded C_b alkyl moiety are separated by the $\text{C}_a\text{--H}$ agostic ligand. In such a ligand arrangement, reductive elimination starting from the high-energy partially optimized structure is difficult. Considering the PB structure, one might also take account of the possibility of pushing the $\text{C}_a\text{--H}$ agostic ligand away and then binding an additional H_2 molecule so that reductive elimination becomes possible. Calculations showed that such a structure was again not a stationary point and had an even higher energy, due to the crowded ligand environment. When the transfer of one H atom from the $\eta^2\text{-H}_2$ ligand to the further olefinic carbon atom (C_b) was considered as the first step, we found that the activation energy (50 kcal/mol) was too high for such a transfer under the given reaction conditions. The high activation energy for such a process was not surprising, because of the geometric separation of the H and the C_b atoms. A concerted process in which both hydrogen atoms in the $\eta^2\text{-H}_2$ ligand would transfer simultaneously to the two olefinic carbon atoms seemed unlikely on the basis of our previous calculations on related systems.^[21]

Conclusion

The dihydrogen(olefin) complex $[\text{OsCl}(\text{H}_2)(\text{PPh}_3)\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{CH}=\text{CH}(\text{CH}_2)_2\text{PPh}_2\}]\text{OTf}$ has been prepared and characterized by NMR spectroscopy. Treatment of $[\text{OsCl}(\text{H}_2)(\text{PPh}_3)\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{CH}=\text{CH}(\text{CH}_2)_2\text{PPh}_2\}]\text{OTf}$ with H_2 produced the (hydrido)dihydrogen complex $[\text{OsH}(\text{H}_2)\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{CH}=\text{CH}(\text{CH}_2)_2\text{PPh}_2\}]\text{OTf}$ rather than the hydrogenated products. A computational study suggested that the hydrogenation was thermodynamically feasible but kinetically unfavorable. This work provides rare examples of dihydrogen(olefin) complexes that are characterizable by NMR spectroscopy.

Experimental Section

General: All manipulations were carried out at room temperature under nitrogen by standard Schlenk techniques unless otherwise stated. Solvents were distilled under nitrogen from sodium/benzophenone (hexane, diethyl ether, THF, benzene) or calcium hydride (dichloromethane, CHCl_3). The starting materials $\text{Br}(\text{CH}_2)_2\text{CH}=\text{CH}(\text{CH}_2)_2\text{Br}$ ^[22] and $[\text{OsClH}_3(\text{PPh}_3)_3]$ ^[23] were prepared by literature methods. Microanalyses were performed by M-H-W Laboratories (Phoenix, AZ). ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were measured with a Bruker ARX 300 spectrometer (300 MHz). ^1H and ^{13}C NMR chemical shifts are relative to TMS, and ^{31}P NMR chemical shifts are relative to 85% H_3PO_4 .

(*E*)- $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{CH}=\text{CH}(\text{CH}_2)_2\text{PPh}_2$ (2**):** A THF solution of KPPH_2 (50 mL, 0.50 M, 25 mmol) was added slowly to a solution of (*E*)- $\text{Br}(\text{CH}_2)_2\text{CH}=\text{CH}(\text{CH}_2)_2\text{Br}$ (3.00 g, 12.4 mmol) in 30 mL of

THF. The reaction mixture was stirred at room temperature for 3 h. A deep red solid was obtained after the solvent had been removed. Addition of water (10 mL) and methanol (40 mL) to the reaction mixture gave a pale yellow solid. The solid was collected on a filter frit, washed with $\text{MeOH}/\text{H}_2\text{O}$ (4:1, 6×50 mL) and MeOH (4×40 mL), and dried under vacuum. Yield, 4.2 g, 76%. ^1H NMR (300.13 MHz, C_6D_6): δ = 2.03–2.08 (m, 4 H, $\text{CH}_2\text{CH}_2\text{PPh}_2$), 2.14–2.24 (m, 4 H, CH_2PPh_2), 5.38–5.41 (m, 2 H, $\text{HC}=\text{CH}$), 7.12–7.52 ppm (m, 20 H, Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, C_6D_6): δ = –17.0 ppm (s, PPh_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.48 MHz, C_6D_6): δ = 28.0 (d, $J_{\text{P,C}}$ = 12.8 Hz, $\text{CH}_2\text{CH}_2\text{PPh}_2$), 28.9 (d, $J_{\text{P,C}}$ = 17.7 Hz, $\text{CH}_2\text{CH}_2\text{PPh}_2$), 128.1 (s, *p*-Ph), 128.2 (d, $J_{\text{P,C}}$ = 6.2 Hz, *m*-Ph), 130.2 (d, $J_{\text{P,C}}$ = 13.3 Hz, =CH), 132.6 (d, $J_{\text{P,C}}$ = 18.6 Hz, *o*-Ph), 139.2 ppm (d, $J_{\text{P,C}}$ = 14.6 Hz, *ipso*-Ph). $\text{C}_{30}\text{H}_{30}\text{P}_2$ (452.52): calcd. C 79.63, H 6.68; found C 79.72, H 6.56.

$[\text{OsClH}(\text{PPh}_3)\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{CH}=\text{CH}(\text{CH}_2)_2\text{PPh}_2\}]\text{OTf}$ (3**):** A mixture of $[\text{OsClH}_3(\text{PPh}_3)_3]$ (1.37 g, 1.35 mmol) and (*E*)- $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{CH}=\text{CH}(\text{CH}_2)_2\text{PPh}_2$ (0.71 g, 1.6 mmol) in benzene (110 mL) was stirred for 5 h. The volume of the reaction mixture was reduced to ca. 7 mL under vacuum. A gray solid was formed when hexane (60 mL) was added. The solid was collected by filtration, washed with hexane (3×15 mL), and dried under vacuum. Yield: 1.0 g, 79%. ^1H NMR (300.13 MHz, C_6D_6): δ = –16.40 (dt, $J_{\text{P,H}}$ = 27.0, 15.0 Hz, 1 H, Os–H), 1.96–3.88 [m, 10 H, $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{CH}=\text{CH}(\text{CH}_2)_2\text{PPh}_2$], 6.87–8.55 ppm (m, 35 H, Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.50 MHz, C_6D_6): δ = –7.7 (dd, $J_{\text{P,P}}$ = 15.0, 14.2 Hz PPh_3), 7.3 (dd, $J_{\text{P,P}}$ = 290.6, 15.0 Hz, PPh_2), 23.8 ppm (dd, $J_{\text{P,P}}$ = 290.6, 14.2 Hz, PPh_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.48 MHz, C_6D_6): δ = 28.1–33.5 (m, $\text{CH}_2\text{CH}_2\text{PPh}_2$), 56.4 (m, HC=), 56.7 (d, $J_{\text{P,C}}$ = 21.9 Hz, =CH), 126.8–143.0 ppm (m, Ph). $\text{C}_{48}\text{H}_{46}\text{ClP}_3\text{Os}$ (941.47): calcd. C 61.24, H 4.93; found C 61.06, H 5.13.

$[\text{OsCl}(\text{H}_2)(\text{PPh}_3)\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{CH}=\text{CH}(\text{CH}_2)_2\text{PPh}_2\}]\text{OTf}$ (4**):** Because of its low stability, the compound was not isolated but was characterized in situ. HOTf (5 μL , 0.06 mmol) was added to a CD_2Cl_2 solution (0.5 mL) containing $[\text{OsClH}(\text{PPh}_3)\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{CH}=\text{CH}(\text{CH}_2)_2\text{PPh}_2\}]$ (20 mg, 0.021 mmol) in an NMR tube. ^1H , ^{13}C , and ^{31}P NMR spectra were measured immediately. ^1H NMR (300.13 MHz, CD_2Cl_2): δ = –9.57 (br, Os– H_2), 2.15–3.10 (m, 8 H, $\text{CH}_2\text{CH}_2\text{PPh}_2$), 4.77 (br, 1 H, HC=), 5.58 (br, 1 H, =CH), 6.86–7.82 ppm (m, 35 H, Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.50 MHz, CD_2Cl_2): δ = –8.9 (dd, $J_{\text{P,P}}$ = 14.1, 15.5 Hz, PPh_3), 14.2 (dd, $J_{\text{P,P}}$ = 243.6, 15.5 Hz, PPh_2), 16.8 ppm (dd, $J_{\text{P,P}}$ = 243.6, 14.1 Hz, PPh_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.48 MHz, CD_2Cl_2): δ = 28.6–37.4 (m, $\text{CH}_2\text{CH}_2\text{PPh}_2$), 89.0 (br, HC=), 96.0 (br, =CH), 118.8–137.2 ppm (m, Ph). T_1 [ms] of $\text{Os}(\text{H}_2)$ (300 MHz, CD_2Cl_2) (temperature) = 35.2 (298 K), 31.3 (273 K), 29.1 (263 K), 27.0 (258 K), 27.5 (253 K), 29.5 (243 K), 32.5 (233 K).

$[\text{OsCl}(\text{HD})(\text{PPh}_3)\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{CH}=\text{CH}(\text{CH}_2)_2\text{PPh}_2\}]\text{OTf}$ ([D₁]-4**):** The compound was prepared similarly, except that DOTf was used instead of HOTf . The $\eta^2\text{-HD}$ signal was observed after cancellation of the $\eta^2\text{-H}_2$ peak at δ = –9.57 ppm by the inversion-recovery method. ^1H NMR (300.13 MHz, CD_2Cl_2): δ = –9.58 ppm [1:1:1 triplet, $J(\text{HD})$ = 14.1 Hz, $\text{Os}(\text{HD})$].

Characterization of $[\text{OsH}(\text{H}_2)(\text{PPh}_3)\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{CH}=\text{CH}(\text{CH}_2)_2\text{PPh}_2\}]\text{OTf}$ (5**):** Because of its low stability, this compound was not isolated but was characterized in situ. **Method A:** HOTf (5 μL , 0.06 mmol) was added to a CD_2Cl_2 solution (0.5 mL) containing $[\text{OsH}_2(\text{PPh}_3)\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{CH}=\text{CH}(\text{CH}_2)_2\text{PPh}_2\}]$ (20 mg, 0.020 mmol) in an NMR tube. NMR spectra were then measured immediately. **Method B:** A CD_2Cl_2 solution (0.5 mL) containing $[\text{OsClH}(\text{PPh}_3)\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{CH}=\text{CH}(\text{CH}_2)_2\text{PPh}_2\}]$ (20 mg,

0.021 mmol) and TlOTf (20 mg, 0.057 mmol) in an NMR tube was stored under H₂ for 5 h. ¹H, ¹³C, and ³¹P NMR spectra were then measured. **Method C:** A CD₂Cl₂ solution of **4** was stored under H₂ for 18 h, and ¹H and ³¹P{¹H} NMR spectra were then measured. ¹H NMR (300.13 MHz, CD₂Cl₂, 230 K): δ = -6.70 (dt, J_{P,H} = 33.0, 19.5 Hz, 1 H, Os-H), -4.74 (br, 2 H, OsH₂), 1.60–3.80 [m, 10 H, Ph₂P(CH₂)₂CH=CH(CH₂)₂PPh₂], 6.86–7.70 ppm (m, 35 H, Ph). ¹H NMR (300.13 MHz, CD₂Cl₂, 298 K): δ = -5.30 (br, 3 H, Os-H, Os-H₂), 1.60–3.80 [m, 12 H, Ph₂P(CH₂)₂CH=CH(CH₂)₂PPh₂], 6.86–7.64 ppm (m, 35 H, Ph). ³¹P{¹H} NMR (121.50 MHz, CD₂Cl₂, 230 K): δ = 4.0 (dd, J_{P,P} = 11.0, 12.8 Hz, PPh₃), 29.1 (dd, J_{P,P} = 201.7, 12.8 Hz, PPh₂), 36.5 ppm (dd, J_{P,P} = 201.7, 11.0 Hz, PPh₂). ³¹P{¹H} NMR (121.50 MHz, CD₂Cl₂, 298 K): δ = 4.4 (dd, J_{P,P} = 12.4, 12.5 Hz, PPh₃), 29.8 (br. d, J_{P,P} = 181.5 Hz, PPh₂), 36.2 ppm (br. d, J_{P,P} = 181.5 Hz, PPh₂). ¹³C{¹H} NMR (75.48 MHz, CD₂Cl₂, 233 K): δ = 28.6–35.1 (m, CH₂CH₂P), 56.9 (br, HC=), 65.7 (br, =CH), 128.2–138.8 ppm (m, Ph). T₁ [ms] (300 MHz, CD₂Cl₂) (temperature): δ = -4.80: 13.8 (272 K), 12.2 (252 K), 10.1 (232 K), 14.2 (213 K); δ = -6.58: 14.9 (272 K), 65.16 (252 K), 204.9 (232 K), 301.5 (213 K).

[OsD_{3-x}H_x(PPh₃)₃][Ph₂P(CH₂)₂CH=CH(CH₂)₂PPh₂][BF₄]: CD₃OD (0.05 mL) was added to a solution of [OsH(H₂)-(PPh₃)₃][Ph₂P(CH₂)₂CH=CH(CH₂)₂PPh₂][BF₄] in CD₂Cl₂, prepared by protonation of **6** (20 mg, 0.020 mmol) with HBF₄·Et₂O (5 μL, 0.04 mmol). The mixture was stored at room temperature for 2 h, and ¹H NMR spectrum was measured at 235 K. The η²-HD signal was observed after cancellation of the η²-H₂ peak at δ = -4.74 ppm by the inversion-recovery method. ¹H NMR (300.13 MHz, CD₂Cl₂, 235 K): δ = -4.69 ppm [1:1:1 triplet, J(HD) = 26.7 Hz, Os(HD)].

trans-[OsH₂(PPh₃)₃][Ph₂P(CH₂)₂CH=CH(CH₂)₂PPh₂] (**6**): A mixture of NaBH₄ (0.20 g, 5.3 mmol) and [OsClH(PPh₃)₃][Ph₂P(CH₂)₂CH=CH(CH₂)₂PPh₂] (0.50 g, 0.53 mmol) in 20 mL of ethanol was stirred at room temperature for 30 min. The solvent was removed under vacuum and the residue was extracted with benzene (20 mL). The volume of the extracted solution was reduced to ca 3 mL. A yellow solid was formed when hexane (40 mL) was added. The solid was collected by filtration, washed with hexane (3 × 15 mL), and dried under vacuum. Yield: 0.25 g, 52%. The complex was also produced when complex **5** was treated with NEt₃. ¹H NMR (300.13 MHz, CD₂Cl₂): δ = -9.13 (dt, J_{P,H} = 29.7, 12.6 Hz, 2 H, Os-H), 1.80–2.74 [m, 10 H, Ph₂P(CH₂)₂CH=CH(CH₂)₂PPh₂], 6.74–7.80 ppm (m, 35 H, Ph). ³¹P{¹H} NMR (121.50 MHz, CD₂Cl₂): δ = 17.6 (t, J_{P,P} = 15.1 Hz, PPh₃), 41.2 ppm (d, J_{P,P} = 15.0 Hz, PPh₂). ¹³C NMR (75.48 MHz, CD₂Cl₂): δ = 30.4 (t, J_{P,C} = 13.5 MHz, CH₂P), 34.2 (t, J_{P,C} = 7.3 MHz, CH₂CH₂P), 37.6 (d, J_{P,C} = 12.1 MHz, HC=), 126.8–143.1 ppm (m, Ph). C₄₈H₄₇P₃Os·3H₂O (961.06): calcd. C 59.99, H 5.56 (the water was probably from the solvents); found C 59.98, H 6.00.

Computational Details: In our calculations, the Ph group on the phosphorus atom was modeled by an H atom. Geometry optimizations and frequency calculations were carried out for all species involved in the reactions with the Gaussian 98 program^[24] installed on Pentium III personal computers with Linux (Red Hat) operating systems. Molecular geometries of the model complexes were optimized at the Becke3LYP (B3LYP) level of density functional theory.^[25] The LANL2DZ effective core potentials and basis sets^[26] were used to describe Os, P, and Cl. Polarization functions [ξ(d) = 0.340]^[27] were added for P and [ξ(d) = 0.514]^[27] for Cl. Additionally, better to describe the electronic properties of both hydride and dihydrogen ligands, polarization functions with ξ(p) = 0.11^[27] were

also added to the standard basis set for H atoms of these two ligands. The standard 6–31G basis set was used for all other atoms.

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