Synthesis and Characterization of Dihydrogen(olefin)osmium Complexes with (E)-$Ph_2P(CH_2)_2CH{=}CH(CH_2)_2PPh_2$

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Treatment of $[OsClH_3(PPh_3)_3]$ with (*E*)-$Ph_2P(CH_2)_2CH{=}CH(CH_2)_2PPh_2$ produced $[OsClH(PPh_3)\{Ph_2P(CH_2)_2CH{=}CH(CH_2)_2PPh_2\}]$, which reacted with HOTf to give the dihydrogen(olefin) complex $[OsCl(H_2)(PPh_3)\{Ph_2P(CH_2)_2CH{=}CH(CH_2)_2PPh_2\}]OTf$. Treatment of the latter complex with H_2 did not result in hydrogenation of the olefin double bond, but gave the (hydrido)dihydrogen complex $[OsH(H_2)(PPh_3)\{Ph_2P(CH_2)_2CH{=}CH(CH_2)_2PPh_2\}]OTf$. A density functional theory study suggested that hydrogenation of the double bond in $[OsCl(H_2)(PPh_3)\{Ph_2P(CH_2)_2CH{=}CH(CH_2)_2PPh_2\}]OTf$ was thermodynamically feasible but kinetically unfavorable.

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 $[MH(H_2)(PP_3)]^+$ [M = Fe, Ru; PP_3 = $P(CH_2CH_2PPh_2)_3$],[5] $[OsClH(CO)\{P(iPr)_3\}_2]$,[6] $[RuClH(PPh_3)_3]$,[7] and $[RuH(Tp)(L)(PPh_3)]$ [Tp = hydrotris(1-pyrazolyl)borate; L = PPh_3, CH_3CN].[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 $[M(H_2)(\eta^4\text{-NBD})(CO)_3]$ and $[M(H_2)(\eta^2\text{-NBD})(CO)_4]$ (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 $[Ru(Tp)(PPh_3)_x(CH_3CN)_{3-x}]^+$ (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 $[M(H_2)(\eta^2\text{-NBD})(CO)_4]$ (M = Mo and W),[12] $[M(H_2)(\eta^4\text{-NBD})(CO)_4]$ (M = Cr, Mo, and W),[12] and $[Fe(H_2)(CO)_3(MeO_2CCH{=}CHCO_2Me)]$,[13] which have been detected by IR spectroscopy, and $[Ru(Cp^*)(H_2)(COD)]^+$, 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 $[OsClH(PPh_3)\{Ph_2P(CH_2)_2CH{=}CH(CH_2)_2PPh_2\}]$

Complexes of the type $[MCl(H_2)L_4]^+$ (M = Ru, Os; L = phosphane, CO, pyridine) are known to contain a dihydrogen ligand.[15,16] One might therefore expect that protonation of $[MClH(olefin)(PR_3)_3]$ might produce dihydrogen complexes $[MCl(H_2)(olefin)(PR_3)_3]^+$. To test this possibility, we prepared the hydrido(olefin) complex $[OsClH(PPh_3)(Ph_2P(CH_2)_2CH{=}CH(CH_2)_2PPh_2]$, hoping that subsequent protonation would produce the corres-

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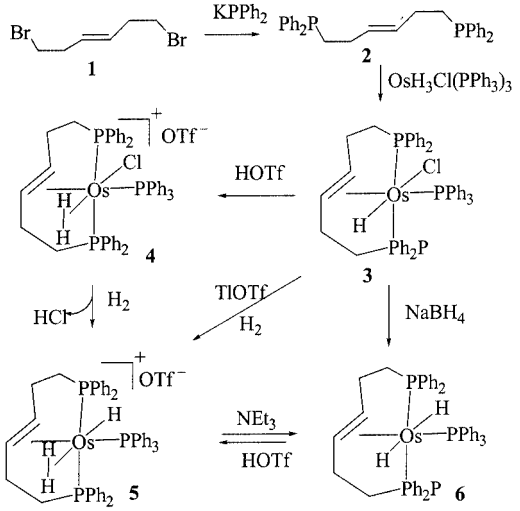
ponding dihydrogen(olefin) complex. Osmium metal and the bidentate phosphane ligand with an olefinic functionality in the backbone were used in the project because of the expectation that such systems may give thermally stable dihydrogen(olefin) complexes.

The ligand (*E*)-$Ph_2P(CH_2)_2CH{=}CH(CH_2)_2PPh_2$ (**2**)[17] was prepared by treatment of (*E*)-$Br(CH_2)_2CH{=}CH(CH_2)_2Br$ (**1**) with excess $KPPh_2$ in THF (Scheme 1). Ligand **2** was characterized by ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy and by elemental analysis. In particular, the ^1H NMR spectrum (in C_6D_6) showed the olefinic proton signal at $\delta = 5.4$ ppm, while the $^{31}P\{^1H\}$ NMR spectrum (in C_6D_6) showed a singlet at $\delta = -17.0$ ppm. The closely related ligand (*E*)-$(t\mathrm{Bu})_2P(CH_2)_2CH{=}CH(CH_2)_2P(t\mathrm{Bu})_2$ has also been reported previously.[18]



Scheme 1

Treatment of a benzene solution of $[OsClH_3(PPh_3)_3]$ with ligand **2** for 5 h produced $[OsClH(PPh_3)\{Ph_2P(CH_2)_2CH{=}CH(CH_2)_2PPh_2\}]$ (**3**), which was isolated as a gray solid in ca. 79% yield. The structure of complex **3** could readily be assigned by its ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, and ^1H-^{31}P-COSY NMR spectra and by elemental analysis. The $^{31}P\{^1H\}$ NMR spectrum (in C_6D_6) showed three doublets of doublets at $\delta = -7.7$, 7.3, and 23.8 ppm. A large $^2J_{P,P}$ coupling (290.6 Hz) for the ^{31}P signals at $\delta = 7.3$ and 23.8 ppm was observed, indicating that two of the phosphorus atoms in **3** were *trans* to each other. A ^1H-^{31}P-COSY NMR experiment suggested that the two *trans*-disposed phosphorus atoms were associated with the two PPh_2 groups of ligand **2**. In the ^1H NMR spectrum (in C_6D_6), the olefinic proton signals appeared at $\delta = 3.88$ 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 $\delta = -16.40$ 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 structure in which the hydride ligand is *trans* to a chloride ligand. During the course of this work, the closely related complex $[OsClH(PPh_3)(Ph_2P{-}C_6H_3Me{-}CH{=}CH{-}C_6H_3Me{-}PPh_2)]$ was reported.[19]

Synthesis and Characterization of $[OsCl(H_2)(PPh_3)\{Ph_2P(CH_2)_2CH{=}CH(CH_2)_2PPh_2\}]OTf$

Protonation of complex **3** with HOTf produced the dihydrogen(olefin) complex $[OsCl(H_2)(PPh_3)(Ph_2P(CH_2)_2CH{=}CH(CH_2)_2PPh_2)]OTf$ (**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 $^{31}P\{^1H\}$ NMR spectrum of complex **4** (in CD_2Cl_2) exhibited the PPh_3 signal at $\delta = -8.9$ ppm and the PPh_2 signals at $\delta = 14.2$ and 16.8 ppm. The ^{31}P signals of the PPh_2 groups at $\delta = 14.2$ and 16.8 ppm had a large $^2J_{P,P}$ coupling constant (243.6 Hz), indicating that the PPh_2 groups were *trans* to each other in **4**. The ^1H NMR spectrum (in CD_2Cl_2) exhibited a broad signal attributable to a dihydrogen ligand at $\delta = -9.57$ ppm. The broad hydride signal had a T_1 (min) of 27.0 ms (at 300 MHz) at 258 K. The short T_1 (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 $[OsCl(HD)(PPh_3)\{Ph_2P(CH_2)_2CH{=}CH(CH_2)_2PPh_2\}]^+$, which was generated in situ by protonation of complex **3** with DOTf. The ^1H NMR spectrum of the HD isotopomer (in CD_2Cl_2) displayed the HD signal as a 1:1:1 triplet at $\delta = -9.58$ 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 T_1 (min) of 27 ms, the H−H bond length was calculated to be 1.13 Å for a nonspinning H_2 or 0.98 Å for a spinning dihydrogen ligand.[20]

Treatment of $[OsCl(H_2)(PPh_3)\{Ph_2P(CH_2)_2CH{=}CH(CH_2)_2PPh_2\}]OTf$ with H_2

We tried to hydrogenate the coordinated olefin double bond in **4** by storing a solution of **4** in CD_2Cl_2 under H_2. However, the expected hydrogenated product $[OsClH_x(PPh_3)\{Ph_2P(CH_2)_6PPh_2\}]^+$ was apparently not produced from the reaction, as indicated by in situ NMR studies. Instead, the fluxional (hydrido)dihydrogen complex $[OsH(H_2)(PPh_3)\{Ph_2P(CH_2)_2CH{=}CH(CH_2)_2PPh_2\}]OTf$ (**5**) was slowly produced under these reaction conditions. A molecule of HCl in **4** was thus apparently replaced by a H_2 molecule in the reaction. Mechanistically, complex **5** could be formed by initial displacement of Cl^- in **4** with an H_2 molecule to give the dicationic dihydrogen complex $[Os(H_2)_2(PPh_3)\{Ph_2P(CH_2)_2CH{=}CH(CH_2)_2PPh_2\}]^{2+}$, followed by deprotonation.

The presence of a coordinated CH=CH moiety in **5** was supported by the ^{13}C NMR spectrum (in CD_2Cl_2), which displayed the coordinated olefinic CH carbon signals at $\delta = 56.9$ and 65.7 ppm. The $^{31}P\{^1H\}$ NMR spectrum (in CD_2Cl_2) at 230 K showed the PPh_3 signal at $\delta = 4.0$ ppm

and the PPh_2 signals at δ = 29.1 and 36.5 ppm. The two PPh_2 groups in **5** had to be *trans* to each other for the large $^2J_{P,P}$ coupling constant (201.7 Hz) observed for the PPh_2 signals at δ = 29.1 and 36.5 ppm. In the room-temperature ^1H NMR spectrum (in CD_2Cl_2), a broad hydride signal was observed at δ = −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 δ = −6.70 ppm ($^2J_{P,H}$ = 33.0, 19.5 Hz) and a broad singlet at δ = −4.74 ppm, corresponding to one and two hydrogen atoms, respectively. T_1 measurements showed that the broad hydride signal at δ = −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 $[OsD_{3-x}H_x(PPh_3)\{Ph_2P(CH_2)_2CH{=}CH(CH_2)_2PPh_2\}]^+$ (in CD_2Cl_2 at 235 K) showed a 1:1:1 triplet at δ = −4.69 ppm with a ^1J(HD) coupling constant of 26.7 Hz. The *d*(HH) value in **5** was estimated to be 0.97 Å by application of the relationship *d*(HH) = −0.0167 *J*(HD) + 1.42 and ^1J(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 H_2 or 0.83 Å for a spinning H_2 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 $[MX(H_2)(dppe)_2]^+$ (M = Ru, Os; X = H, Cl).[15a]

Deprotonation of complex **5** with NEt_3 produced the neutral dihydride complex *trans*-$[OsH_2(PPh_3)\{Ph_2P(CH_2)_2CH{=}CH(CH_2)_2PPh_2\}]$ (**6**), which could also be obtained by treatment of complex **3** with $NaBH_4$. 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 CD_2Cl_2) displayed only one hydride signal at δ = −9.13 ppm, indicating that the molecule had high symmetry. Consistently with the structure, the $^{31}P\{^1H\}$ NMR spectrum (in CD_2Cl_2) showed a doublet at δ = 41.2 ppm for the PPh_2 groups and a triplet at δ = 17.6 ppm for the PPh_3 ligand; the $^{13}C\{^1H\}$ NMR showed the coordinated olefinic CH carbon signal at δ = 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 $[OsClH(PH_3)\{H_2P(CH_2)_2CH{=}CH(CH_2)_2PH_2\}]$ (**3′**), $[OsCl(H_2)(PH_3)\{H_2P(CH_2)_2CH{=}CH(CH_2)_2PH_2\}]^+$ (**4′**), and $[OsH(H_2)(PH_3)\{H_2P(CH_2)_2CH{=}CH(CH_2)_2PH_2\}]^+$ (**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 $[OsCl(H_2)(PH_3)\{H_2P(CH_2)_6PH_2\}]^+$ (**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(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−H_2 interaction.

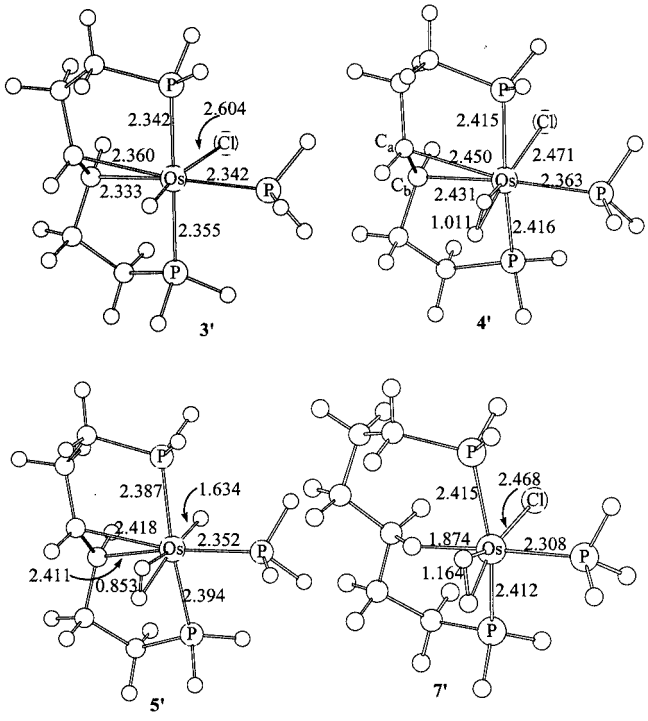


Figure 1. Optimized structures together with selected bond lengths [Å]

Experimentally, it is interesting that under H_2 the coordinated η^2-H_2 did not hydrogenate the olefin unit. The calculated free energy change (ΔG^0) for the process of **4′** + H_2 → **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 η^2-H_2 ligand while the other is further away. The hydrogenation of a coordinated olefin by an η^2-H_2 unit can occur through the formation of an agostic intermediate by transfer of one hydrogen atom of the H_2 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 η^2-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 C_a-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 C_a-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 C_a-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 η^2-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 η^2-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 $[OsCl(H_2)(PPh_3)\{Ph_2P(CH_2)_2CH=CH(CH_2)_2PPh_2\}]OTf$ has been prepared and characterized by NMR spectroscopy. Treatment of $[OsCl(H_2)(PPh_3)\{Ph_2P(CH_2)_2CH=CH(CH_2)_2PPh_2\}]OTf$ with H_2 produced the (hydrido)dihydrogen complex $[OsH(H_2)\{Ph_2P(CH_2)_2CH=CH(CH_2)_2PPh_2\}]OTf$ 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 $Br(CH_2)_2CH=CH(CH_2)_2Br$[22] and $[OsClH_3(PPh_3)_3]$[23] were prepared by literature methods. Microanalyses were performed by M-H-W Laboratories (Phoenix, AZ). ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ 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*)-$Ph_2P(CH_2)_2CH=CH(CH_2)_2PPh_2$ (2): A THF solution of $KPPh_2$ (50 mL, 0.50 M, 25 mmol) was added slowly to a solution of (*E*)-$Br(CH_2)_2CH=CH(CH_2)_2Br$ (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 MeOH/H_2O (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, $CH_2CH_2PPh_2$), 2.14−2.24 (m, 4 H, CH_2PPh_2), 5.38−5.41 (m, 2 H, *H*C=C*H*), 7.12−7.52 ppm (m, 20 H, Ph). $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6): δ = −17.0 ppm (s, PPh_2). $^{13}C\{^1H\}$ NMR (75.48 MHz, C_6D_6): δ = 28.0 (d, $J_{P,C}$ = 12.8 Hz, $CH_2CH_2PPh_2$), 28.9 (d, $J_{P,C}$ = 17.7 Hz, $CH_2CH_2PPh_2$), 128.1 (s, *p*-Ph), 128.2 (d, $J_{P,C}$ = 6.2 Hz, *m*-Ph), 130.2 (d, $J_{P,C}$ = 13.3 Hz, =CH), 132.6 (d, $J_{P,C}$ = 18.6 Hz, *o*-Ph), 139.2 ppm (d, $J_{P,C}$ = 14.6 Hz, *ipso*-Ph). $C_{30}H_{30}P_2$ (452.52): calcd. C 79.63, H 6.68; found C 79.72, H 6.56.

$[OsClH(PPh_3)\{Ph_2P(CH_2)_2CH=CH(CH_2)_2PPh_2\}]$ (3): A mixture of $[OsClH_3(PPh_3)_3]$ (1.37 g, 1.35 mmol) and (*E*)-$Ph_2P(CH_2)_2CH=CH(CH_2)_2PPh_2$ (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, $J_{P,H}$ = 27.0, 15.0 Hz 1 H, Os−*H*), 1.96−3.88 [m, 10 H, $Ph_2PCH_2)_2CH=CH(CH_2)_2PPh_2$], 6.87−8.55 ppm (m, 35 H, Ph). $^{31}P\{^1H\}$ NMR (121.50 MHz, C_6D_6): δ = −7.7 (dd, $J_{P,P}$ = 15.0, 14.2 Hz PPh_3), 7.3 (dd, $J_{P,P}$ = 290.6, 15.0 Hz, PPh_2), 23.8 ppm (dd, $J_{P,P}$ = 290.6, 14.2 Hz, PPh_2). $^{13}C\{^1H\}$ NMR (75.48 MHz, C_6D_6): δ = 28.1−33.5 (m, $CH_2CH_2PPh_2$), 56.4 (m, H*C*=), 56.7 (d, $J_{P,C}$ = 21.9 Hz, =*C*H), 126.8−143.0 ppm (m, Ph). $C_{48}H_{46}ClP_3Os$ (941.47): calcd. C 61.24, H 4.93; found C 61.06, H 5.13.

$[OsCl(H_2)(PPh_3)\{Ph_2P(CH_2)_2CH=CH(CH_2)_2PPh_2\}]OTf$ (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 $[OsClH(PPh_3)\{Ph_2P(CH_2)_2CH=CH(CH_2)_2PPh_2\}]$ (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, $CH_2CH_2PPh_2$), 4.77 (br, 1 H, *H*C=), 5.58 (br, 1 H, =C*H*), 6.86−7.82 ppm (m, 35 H, Ph). $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2): δ = −8.9 (dd, $J_{P,P}$ = 14.1, 15.5 Hz, PPh_3), 14.2 (dd, $J_{P,P}$ = 243.6, 15.5 Hz, PPh_2), 16.8 ppm (dd, $J_{P,P}$ = 243.6, 14.1 Hz, PPh_2). $^{13}C\{^1H\}$ NMR (75.48 MHz, CD_2Cl_2): δ = 28.6−37.4 (m, $CH_2CH_2PPh_2$), 89.0 (br, H*C*=), 96.0 (br, =*C*H), 118.8−137.2 ppm (m, Ph). T_1 [ms] of Os(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).

$[OsCl(HD)(PPh_3)\{Ph_2P(CH_2)_2CH=CH(CH_2)_2PPh_2\}]OTf$ ($[D_1]$-4): The compound was prepared similarly, except that DOTf was used instead of HOTf. The η^2-HD signal was observed after cancellation of the η^2-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(HD) = 14.1 Hz, Os(HD)].

Characterization of $[OsH(H_2)(PPh_3)\{Ph_2P(CH_2)_2CH=CH(CH_2)_2PPh_2\}]OTf$ (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 $[OsH_2(PPh_3)\{Ph_2P(CH_2)_2CH=CH(CH_2)_2PPh_2\}]$ (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 $[OsClH(PPh_3)\{Ph_2P(CH_2)_2CH=CH(CH_2)_2PPh_2\}]$ (20 mg,

0.021 mmol) and TlOTf (20 mg, 0.057 mmol) in an NMR tube was stored under H_2 for 5 h. ^1H, ^{13}C, and ^{31}P NMR spectra were then measured. **Method C:** A CD_2Cl_2 solution of **4** was stored under H_2 for 18 h, and ^1H and $^{31}P\{^1H\}$ NMR spectra were then measured. ^1H NMR (300.13 MHz, CD_2Cl_2, 230 K): δ = −6.70 (dt, $J_{P,H}$ = 33.0, 19.5 Hz, 1 H, Os−*H*), −4.74 (br, 2 H, OsH_2), 1.60−3.80 [m, 10 H, $Ph_2P(CH_2)_2CH=CH(CH_2)_2PPh_2$], 6.86−7.70 ppm (m, 35 H, Ph). ^1H NMR (300.13 MHz, CD_2Cl_2, 298 K): δ = −5.30 (br, 3 H, Os−*H*, Os−H_2), 1.60−3.80 [m, 12 H, $Ph_2P(CH_2)_2CH=CH(CH_2)_2PPh_2$], 6.86−7.64 ppm (m, 35 H, Ph). $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2, 230 K): δ = 4.0 (dd, $J_{P,P}$ = 11.0, 12.8 Hz, PPh_3), 29.1 (dd, $J_{P,P}$ = 201.7, 12.8 Hz, PPh_2), 36.5 ppm (dd, $J_{P,P}$ = 201.7, 11.0 Hz, PPh_2). $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2, 298 K): δ = 4.4 (dd, $J_{P,P}$ = 12.4, 12.5 Hz, PPh_3), 29.8 (br. d $J_{P,P}$ = 181.5 Hz, PPh_2), 36.2 ppm (br. d, $J_{P,P}$ = 181.5 Hz, PPh_2). $^{13}C\{^1H\}$ NMR (75.48 MHz, CD_2Cl_2, 233 K): δ = 28.6−35.1 (m, CH_2CH_2P), 56.9 (br, H*C*=), 65.7 (br, =*C*H), 128.2−138.8 ppm (m, Ph). T_1 [ms] (300 MHz, CD_2Cl_2) (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).

$[OsD_{3-x}H_x(PPh_3)\{Ph_2P(CH_2)_2CH=CH(CH_2)_2PPh_2\}]BF_4$: CD_3OD (0.05 mL) was added to a solution of $[OsH(H_2)(PPh_3)\{Ph_2P(CH_2)_2CH=CH(CH_2)_2PPh_2\}]BF_4$ in CD_2Cl_2, prepared by protonation of **6** (20 mg, 0.020 mmol) with $HBF_4{\cdot}Et_2O$ (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 η^2-HD signal was observed after cancellation of the η^2-H_2 peak at δ = −4.74 ppm by the inversion-recovery method. ^1H NMR (300.13 MHz, CD_2Cl_2, 235 K): δ = −4.69 ppm [1:1:1 triplet, J(HD) = 26.7 Hz, Os(HD)].

***trans*-$[OsH_2(PPh_3)\{Ph_2P(CH_2)_2CH=CH(CH_2)_2PPh_2\}]$ (6):** A mixture of $NaBH_4$ (0.20 g, 5.3 mmol) and $[OsClH(PPh_3)\{Ph_2P(CH_2)_2CH=CH(CH_2)_2PPh_2\}]$ (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 NEt_3. ^1H NMR (300.13 MHz, CD_2Cl_2): δ = −9.13 (dt, $J_{P,H}$ = 29.7, 12.6 Hz, 2 H, Os−*H*), 1.80−2.74 [m, 10 H, $Ph_2P(CH_2)_2CH=CH(CH_2)_2PPh_2$], 6.74−7.80 ppm (m, 35 H, Ph). $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2): δ = 17.6 (t, $J_{P,P}$ = 15.1 Hz, PPh_3), 41.2 ppm (d, $J_{P,P}$ = 15.0 Hz, PPh_2). ^{13}C NMR (75.48 MHz, CD_2Cl_2): δ = 30.4 (t, $J_{P,C}$ = 13.5 MHz, CH_2P), 34.2 (t, $J_{P,C}$ = 7.3 MHz, CH_2CH_2P), 37.6 (d, $J_{P,C}$ = 12.1 MHz, H*C*=), 126.8−143.1 ppm (m, Ph). $C_{48}H_{47}P_3Os{\cdot}3H_2O$ (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 ato 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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