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Preparation, Characterization, and Reactivity of an Osmium Alkenyl Dihydrogen Complex

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Treatment of $OsCl_2(PPh_3)(PNP)$ (PNP = 2,6-$(Ph_2PCH_2)_2C_5H_3N$) with $LiC{\equiv}CPh$ produced $OsCl(PPh_3)$(2-$Ph_2PCH(CPh{=}CH)$-6-$Ph_2PCH_2C_5H_3N$). The structure of the latter, unusual complex has been confirmed by an X-ray diffraction study. Reaction of $OsCl(PPh_3)$(2-$Ph_2PCH(CPh{=}CH)$-6-$Ph_2PCH_2C_5H_3N$) with H_2 and K_2CO_3 in the presence of $NaBF_4$ in methanol produced $OsH(PPh_3)$(2-$Ph_2PCH(CPh{=}CH)$-6-$Ph_2PCH_2C_5H_3N$). Protonation of $OsH(PPh_3)$(2-$Ph_2PCH(CPh{=}CH)$-6-$Ph_2PCH_2C_5H_3N$) with HBF_4 gave $[Os(H_2)(PPh_3)$(2-$Ph_2PCH(CPh{=}CH)$-6-$Ph_2PCH_2C_5H_3N)]BF_4$, which reacted with H_2 to give $[OsH(H_2)(PPh_3)$(2-$Ph_2PCH(CPh{=}CH_2)$-6-$Ph_2PCH_2C_5H_3N)]BF_4$.

Introduction

Dihydrogen complexes have been intensively investigated, especially their preparation, characterization, structural, and catalytic properties.[1−3] These studies have established that dihydrogen complexes are more than arrested intermediates in the oxidative addition of the H_2 molecule; they can have their own reactivity and play active roles in catalytic reactions. In catalytic hydrogenation reactions, there are several possible ways in which dihydrogen complexes can play active roles.[2] Among them, intramolecular hydrogen transfer from a coordinated dihydrogen ligand to the α-carbon of a σ-bonded carbon ligand has been recognized as one of the key steps in the catalytic cycles. For example, alkyl−dihydrogen and alkenyl−dihydrogen complexes have been proposed or implied as the key intermediates in the hydrogenation of acetylenes and olefins catalyzed by group 8 metal complexes such as $[MH(H_2)(PP_3)]^+$ (M = Fe, Ru; PP_3 = $P(CH_2CH_2PPh_2)_3$),[4] $OsHCl(CO)(P(i\text{-}Pr)_3)_2$,[5] $RuHCl(PPh_3)_3$, [6] and $TpRuH(L)(PPh_3)$ (L = PPh_3, CH_3CN).[7] The mechanism is interesting, as hydrogenation could proceed without going through oxidative addition of the H_2 molecule. However, the proposed dihydrogen intermediates are usually too reactive to be observed. In fact, well-characterized dihydrogen complexes containing σ-bonded carbon ligands are still rare, despite the fact that a large number of dihydrogen complexes have been reported.[1] Previously reported complexes containing both a dihydrogen and a σ-bonded carbon ligand are limited to a few of those with alkynyl ligands (for example, $[Ru(H_2)(C{\equiv}CPh)(dippe)_2]BPh_4$,[8] $OsH(H_2)(C{\equiv}CPh)(CO)(P(i\text{-}Pr)_3)_2$ [9]) and aryl ligands (for example, $OsCl(H_2)(NH{=}CPhC_6H_4)(P(i\text{-}Pr)_3)_2$,[10] $[IrH(H_2)(bq)(PPh_3)_2]^+$ (bq = 7,8-benzoquinolinate)[11]).

To model intramolecular hydrogen transfer from a dihydrogen ligand to the α-carbon of a σ-bonded carbon ligand, we have attempted to prepare and characterize dihydrogen complexes $[L_nM(H_2)(R)]^+$ (R = σ-bonded carbon ligands) by protonation of $L_nMH(R)$. In this report, we wish to describe the synthesis of an alkenyl−dihydrogen complex and its reaction with hydrogen.

Results and Discussion

Preparation and Characterization of $OsH(PPh_3)$(2-$Ph_2PCH(CPh{=}CH)$-6-$Ph_2PCH_2C_5H_3N$). Protonation of hydride complexes is one of the most common methods to prepare dihydrogen complexes.[1] As stable dihydrogen complexes have been reported for $[Os(H_2)Cl(PPh_3)(PNP)]^+$ [12] and $[OsH(H_2)(P_4)]^+$ (P = phosphorus donor ligands),[13] one might expect that dihydrogen complexes $[Os(H_2)(R)(PPh_3)(PNP)]^+$ (R = σ-bonded car-

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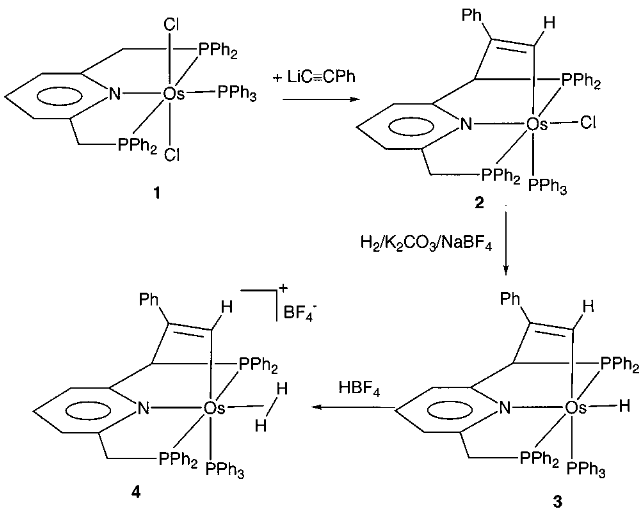
Scheme 1



bon ligands) may be obtained by protonation of OsH(R)(PPh_3)(PNP). With the hope to obtain OsH(R)(PPh_3)(PNP), we have treated $OsCl_2(PPh_3)(PNP)$ (**1**) with various alkylating agents. Treatment of **1** with excess PhC≡CLi in THF or toluene produced the alkenyl complex $OsCl(PPh_3)(2\text{-}Ph_2PCH(CPh{=}CH)\text{-}6\text{-}Ph_2PCH_2C_5H_3N)$ (**2**), which can be isolated in 80% yield (Scheme 1). Attempts to obtain pure compounds from the reactions of **1** with other reagents such as MeLi, PhLi, PhMgBr, and $CH_2{=}CHMgBr$ failed.

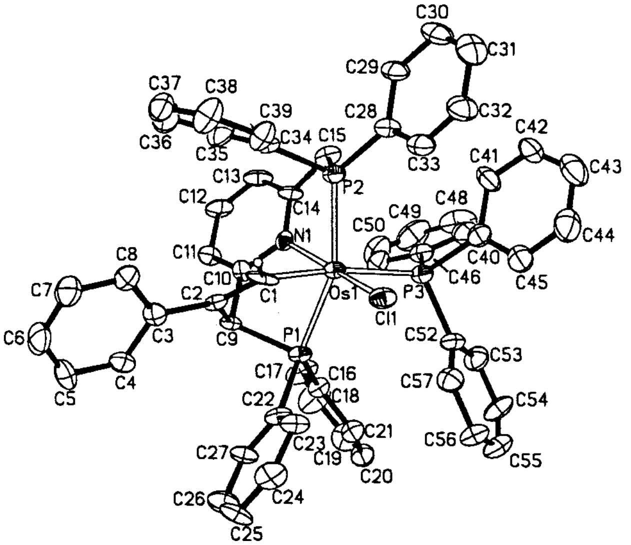


Figure 1. Molecular structure for $OsCl(PPh_3)(2\text{-}Ph_2PCH(CPh{=}CH)\text{-}6\text{-}Ph_2PCH_2C_5H_3N)$.

Table 1. Crystal Data and Refinement Details for $OsCl(PPh_3)(2\text{-}Ph_2PCH(CPh{=}CH)\text{-}6\text{-}Ph_2PCH_2C_5H_3N)\cdot 3.5C_6H_6$

formula	$C_{78}H_{68}ClNP_3Os$
fw	1337.89
cryst sys	monoclinic
space group	*C*2/*c*
a, Å	39.570(8)
b, Å	15.429(3)
c, Å	28.322(6)
β, deg	126.06(3)
V, Å^3	13978(5)
Z	8
d_{calc}, g cm^{-3}	1.272
radiation, Mo Kα, Å	0.071073
θ range, deg	1.99–27.58
no. of reflns collected	45 699
no. of ind reflns	15 984 (R_{int} = 16.93%)
no. of obsd reflns	5086 ($I > 2\sigma(I)$)
no. of params refined	676
final *R* indices (obsd data)	R = 7.21%, R_w = 14.60%
goodness of fit	0.853
largest diff peak, e Å^{-3}	1.699
largest diff hole, e Å^{-3}	−1.411

Table 2. Selected Bond Distances and Angles for $OsCl(PPh_3)(2\text{-}Ph_2PCH(CPh{=}CH)\text{-}6\text{-}Ph_2PCH_2C_5H_3N)\cdot 3.5C_6H_6$

Bond Distances (Å)			
Os(1)–C(1)	1.897(4)	Os(1)–P(1)	2.3275(13)
Os(1)–P(2)	2.3028(14)	Os(1)–P(3)	2.385(14)
Os(1)–Cl(1)	2.4670(5)	Os(1)–N(1)	2.103(3)
C(1)–C(2)	1.338(5)	C(2)–C(9)	1.560(6)
Bond Angles (deg)			
C(1)–Os(1)–P(1)	74.86(16)	C(1)–Os(1)–P(2)	91.45(16)
C(1)–Os(1)–P(3)	171.93(15)	C(1)–Os(1)–Cl(1)	87.94(13)
C(1)–Os(1)–N(1)	81.54(15)	P(1)–Os(1)–P(2)	56.37(3)
P(1)–Os(1)–P(3)	98.43(5)	P(1)–Os(1)–Cl(1)	102.00(4)
P(1)–Os(1)–N(1)	81.71(10)	P(2)–Os(1)–P(3)	96.36(5)
P(2)–Os(1)–Cl(1)	96.53(5)	P(2)–Os(1)–N(1)	77.21(10)
P(3)–Os(1)–Cl(1)	89.13(4)	P(3)–Os(1)–N(1)	102.15(8)
Cl(1)–Os(1)–N(1)	81.54(15)	Os(1)–C(1)–C(2)	128.5(4)

The structure of **2** could not be assigned confidently on the basis of the spectroscopic data. Thus a single-crystal X-ray diffraction study on **2** was carried out. The molecular geometry of **2** is depicted in Figure 1. The crystallographic details and selected bond distances and angles are given in Tables 1 and 2, respectively. The X-ray diffraction study reveals that one phenylacetylene has incorporated into the PNP ligand in the form of an alkenyl group. The geometry around osmium can be viewed as a distorted octahedron with two trans PPh_2 groups and an alkenyl ligand trans to the PPh_3 ligand. The distortion could be mainly attributed to the small bite angle of the chelating ligand, as reflected by the P(1)–Os(1)–P(2) angle (156.37(3)°). The angle is similar to those observed for other PNP complexes, for example, $RuCl_2(PPh_3)(PNP)$ (158.1(1)°),[12] RuHCl(PPh_3)(PNP) (155.97(3)°),[14] [Rh($CH_2{=}CH_2$)(PNP)]BF_4 (161.39(1)°),[15] and [Pd($CH_2{=}CHPh$)(PNP)]$(BF_4)_2$ (162.4(1)°).[16] The Os–C(alkenyl) bond distance (1.897(4) Å) is near the lower end of those observed for osmium alkenyl complexes,[17] for example, $OsCl(CH{=}CHSiMe_3)({=}C{=}CHSiMe_3)(P(i\text{-}Pr)_3)_2$ (1.92(3) Å),[17a] $OsCl(CH{=}CHPh)(O)_2(P(i\text{-}Pr)_3)_2$ (1.985(4) Å),[17b] and $OsCl(CH{=}CHPh)(CO)(P(i\text{-}Pr)_3)_2$ (1.99(1) Å).[17c] Consistent with the solid-state structure, the $^{31}P\{^1H\}$ NMR spectrum in C_6D_6 displayed a PPh_3 signal at −6.2 ppm as a doublet of doublets and PPh_2 signals at −2.4 and 30.6 ppm with a large $^2J(PP)$ coupling constant (336.7 Hz). The ^1H NMR spectrum in C_6D_6 showed the Os–C*H*= signal at 9.99 ppm.

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It has been shown that methylene protons of complexed PNP ligand are acidic. For example, the methylene protons of PNP in $RuH(OAc)(PPh_3)(PNP)$ can undergo H/D exchange reactions with CD_3OD; the methylene protons of PNP in $Rh(CH_3)(PNP)$ can be deprotonated by $LiCH_3$ to give $[Rh(CH_3)(2,6\text{-}(Ph_2PCH)_2C_5H_3N)]Li_2$.[18] Formation of complex **2** from the reaction of **1** with $PhC{\equiv}CLi$ is likely related to this property. It is speculated that reaction of $OsCl_2(PPh_3)(PNP)$ with the first equivalent of $PhC{\equiv}CLi$ might lead to the deprotonation of a benzyl CH to give $OsCl(PPh_3)(2\text{-}Ph_2PCH\text{-}6\text{-}Ph_2PCH_2C_5H_3N)$, $PhC{\equiv}CH$, and LiCl. The 16-electron complex $OsCl(PPh_3)(2\text{-}Ph_2PCH\text{-}6\text{-}Ph_2PCH_2C_5H_3N)$ can coordinate a molecule of $PhC{\equiv}CH$ to give $OsCl(\eta^2\text{-}PhC{\equiv}CH)(PPh_3)(2\text{-}Ph_2PCH\text{-}6\text{-}Ph_2PCH_2C_5H_3N)$. The nucleophilic carbon center ($Ph_2P\mathit{C}H$) could then attack the coordinated $PhC{\equiv}CH$ to give **2**. Unfortunately, we have not been able to detect any of the intermediates. When $OsCl_2(PPh_3)(PNP)$ was treated with 1 equiv of $HC{\equiv}CPh$, only the C−C bond formation product **2** and the starting material **1** were obtained, and no other products could be detected.

Complex **2** can be easily converted to the alkenyl−hydride complex $OsH(PPh_3)(2\text{-}Ph_2PCH(CPh{=}CH)\text{-}6\text{-}Ph_2PCH_2C_5H_3N)$ (**3**) by treating **2** with H_2 in the presence of K_2CO_3 and $NaBF_4$ in methanol (Scheme 1). In this reaction, the hydride complex **3** is presumably formed by deprotonation of the dihydrogen intermediate $[Os(H_2)(PPh_3)(2\text{-}Ph_2PCH(CPh{=}CH)\text{-}6\text{-}Ph_2PCH_2C_5H_3N)]BF_4$. A similar strategy has been previously used to prepare $RuH_2(dppe)_2$ from $RuCl_2(dppe)_2$ [19] and $OsH_2(dppp)_2$ from $OsCl_2(dppp)_2$.[13a] In principle, complex **3** could undergo reductively elimination of the alkenyl and the hydride ligands under a H_2 atmosphere to form a dihydride complex. However such reaction was not observed.

Complex **3** can be readily characterized by ^1H and ^{31}P NMR spectroscopy. In particular, the $^{31}P\{^1H\}$ NMR spectrum (in C_6D_6) displayed a PPh_3 signal at 22.7 ppm and PPh_2 signals at 38.0 and 68.6 ppm. The two PPh_2 groups are trans to each other, as they have large $^2J(PP)$ coupling (298.8 Hz). The ^1H NMR spectrum (in C_6D_6) showed the alkenyl proton signal at 11.21 ppm and the hydride signal at −6.81 ppm (ddd, $J(PH) = 25.8$, 13.4, 12.5 Hz). The hydride must be cis to the three phosphorus atoms, as judged from the magnitude of the $^2J(PH)$ coupling constants. The hydride is also cis to the alkenyl group, as the alkenyl proton signal at 11.21 ppm was enhanced when the hydride signal at −6.81 ppm was irradiated.

Preparation and Characterization of the Dihydrogen Complex $[Os(H_2)(PPh_3)(2\text{-}Ph_2PCH(CPh{=}CH)\text{-}6\text{-}Ph_2PCH_2C_5H_3N)]BF_4$. Protonation of **3** with $HBF_4{\cdot}Et_2O$ in dichloromethane gave the molecular dihydrogen complex $[Os(H_2)(PPh_3)(2\text{-}Ph_2PCH(CPh{=}CH)\text{-}6\text{-}Ph_2PCH_2C_5H_3N)]BF_4$ (**4**). The existence of the η^2-H_2 moiety in **4** was confirmed by the variable-temperature T_1 measurements and the observation of a large $^1J(HD)$ for the corresponding isotopomer $[Os(HD)(PPh_3)(2\text{-}Ph_2PCH(CPh{=}CH)\text{-}6\text{-}Ph_2PCH_2C_5H_3N)]^+$. The ^1H NMR spectrum of **4** in CD_2Cl_2 showed a broad hydride signal at δ −3.14 ppm. A minimum T_1 value of 16.2 ms (300 MHz) was obtained for the broad hydride signal at −3.14 ppm, assignable to the $Os(H_2)$, at 273 K. Acidification of **3** in CD_2Cl_2 with CF_3CO_2D gave the η^2-HD isotopomer, $[Os(HD)(PPh_3)(2\text{-}Ph_2PCH(CPh{=}CH)\text{-}6\text{-}Ph_2PCH_2C_5H_3N)]O_2CCF_3$, which showed a 1:1:1 triplet centered at δ −3.15 ppm with $^1J(HD) = 29.7$ Hz in the ^1H NMR spectrum. The pattern of the ^{31}P NMR spectrum is similar to those of **2** and **3**, indicating that they have similar coordination spheres. The dihydrogen ligand is cis to the alkenyl group, as a positive NOE effect was observed for the alkenyl proton signal at 8.68 ppm when the dihydrogen signal at −3.14 ppm was irradiated.

The H−H distance in complex **4** can be estimated from the T_1(min) value[20] and J(HD) data.[21] Based on the T_1(min) value of 16.2 ms (at 300 MHz), the d(HH) was estimated to be 1.13 Å for a slowly spinning dihydrogen ligand, or 0.90 Å for a fast spinning dihydrogen ligand. It should be mentioned that the calculated d(HH) values are the minimum H−H distances, as contributions to the T_1(min) from other groups are not corrected for here. A d(HH) of 0.92 Å can be obtained by use of the relationship $d(HH) = -0.0167J(HD) + 1.42$ and $J(HD) = 29.7$ Hz.[21] The H−H bond distance in **4** is significantly shorter than that in the related dihydrogen complex $[OsCl(H_2)(PPh_3)(PNP)]^+$ (1.12 Å based on $J(HD) = 17.7$ Hz).[12]

As mentioned previously, reported complexes containing both a dihydrogen and a σ-bonded carbon ligand are limited to a few of those with alkynyl[8,9] and aryl ligands.[9,10] Complex **4** appears to be the first spectroscopically characterized alkenyl−dihydrogen complex.

Reactions of Dihydrogen Complex 4. The dihydrogen ligand in **4** is weakly coordinated to osmium and can be removed by evacuation to give the unsaturated complex $[Os(PPh_3)(2\text{-}Ph_2PCH(CPh{=}CH)\text{-}6\text{-}Ph_2PCH_2C_5H_3N)]BF_4$ (**5**) (see Scheme 2). The process is reversible, and the dihydrogen complex **4** was rapidly regenerated upon exposure of **5** to H_2. The Os−alkenyl bond in the dihydrogen complex **4** was slowly cleaved if solutions of **4** were stored under a H_2 atmosphere. For example, **4** was completely converted to $[OsH(H_2)(PPh_3)(2\text{-}Ph_2PCH(CPh{=}CH_2)\text{-}6\text{-}Ph_2PCH_2C_5H_3N)]BF_4$ (**6**) after a solution of **4** in dichloromethane was stored under a dihydrogen atmosphere for 22 h.

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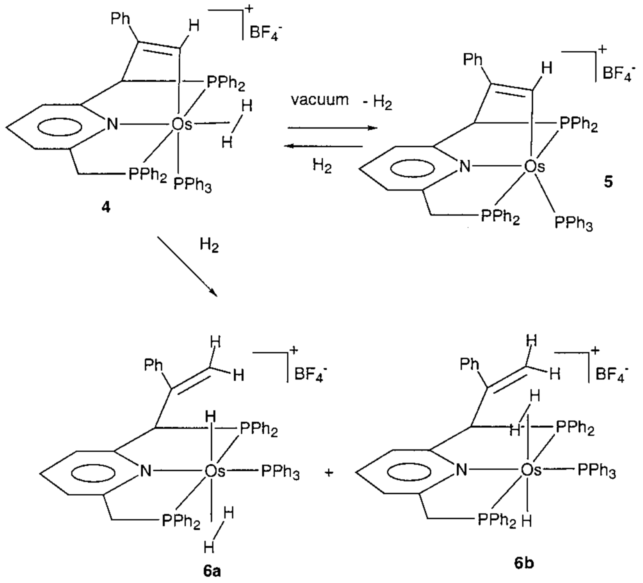
Scheme 2



Complex **6** is air-sensitive, and thus it was characterized in situ. As indicated by NMR, complex **6** in solution exists as two isomers in a ratio of ca. 2:1. In the ^{1}H NMR spectrum in CD_2Cl_2, the major isomer **6a** displayed alkenyl $=CH_2$ signals at 5.33 and 3.77 ppm, a terminal Os-H signal at −6.65 ppm, and an Os(H_2) signal at −3.48 ppm; the minor isomer **6b** displayed alkenyl $=CH_2$ signals at 4.27 and 5.37 ppm, a terminal Os-H signal at −6.42 ppm, and an Os(H_2) signal at −3.20 ppm. The existence of the η^2-H_2 moieties in **6** was confirmed by the variable-temperature T_1 measurements and the observation of a large ^1J(HD) for the corresponding isotopomers of **6**. A minimum T_1 value of 14.5 ms (300 MHz) was obtained for the broad Os(H_2) signal of **6a** at −3.48 ppm, and 15.2 ms (300 MHz) was obtained for the broad Os(H_2) signal of **6b** at −3.20 ppm at 243 K. The ^1J(HD) coupling constants were determined to be 30.0 Hz for the η^2-HD isotopomer of **6a** and 29.7 Hz for that of **6b**.

In both isomers of **6**, the two PPh_2 groups must be trans to each other, as they have large ^2J(PP) coupling (ca. 220 Hz); the terminal hydride must be cis to the three phosphorus atoms, as judged from the magnitude of the ^2J(PH) constants. ^{1}H NOE experiments confirmed that the dihydrogen ligand is trans to the terminal hydride and cis to the three phosphorus atoms. In isomer **6b**, the dihydrogen ligand is on the same side of the alkenyl group, as a positive NOE effect was observed for one of the $=CH_2$ signals at 5.36 ppm when the dihydrogen signal at −3.20 ppm was irradiated. In isomer **6a**, the dihydrogen ligand is on the opposite side of the alkenyl group, as a positive NOE effect was observed for the CH-PPh_2 signal at 5.51 ppm when the dihydrogen signal at −3.48 ppm was irradiated.

Intramolecular hydrogen transfer from a dihydrogen ligand to the α-carbon of alkyl or alkenyl ligands has been invoked to explain the catalytic activity of $RuHCl(PPh_3)_3$,[6] $[MH(H_2)(PP_3)]^+$ (M = Fe, Ru; $PP_3 = P(CH_2CH_2PPh_2)_3$),[4] and $TpRuH(PPh_3)_2$ [7] for hydrogenation of acetylenes and olefins. The reactions are also thought to be involved in the reactions of some d^0 alkyl complexes with H_2 to give hydride complexes and alkanes.[22] However, such reactions have rarely been demonstrated with well-defined alkyl− or alkenyl−dihydrogen complexes. Previously reported intramolecular hydrogen transfer from a dihydrogen ligand to the α-carbon of a σ-bonded carbon ligand are limited to a few of those with alkynyl ligands and aryl ligands. For example, Crabtree et al. have shown that reaction of $[Ir(diphpyH)H(H_2)(PR_3)_2]SbF_6$ with H_2 gives $[Ir(diphpyH_2)H(H_2)(PR_3)_2]SbF_6$ ($diphpyH_2 = 2,6\text{-}(C_6H_5)_2C_5H_3N$);[11c] Puerta et al. have shown that $[RuH(dippe)_2]^+$ reacts reversibly with $HC\equiv CPh$ to give $[Ru(H_2)(C\equiv CPh)(dippe)_2]^+$;[8] Oro et al. have shown that $OsH(H_2)(C\equiv CPh)(CO)(P(i\text{-}Pr)_3)_2$ reacts with H_2 to give $OsH_2(CH_2{=}CHPh)(CO)(P(i\text{-}Pr)_3)_2$.[9] Reaction of H_2 with **4** to give **6** provides a rare example of intramolecular hydrogen transfer from a dihydrogen ligand to the α-carbon of an alkenyl ligand.

It is noted that the alkenyl−osmium bond in the hydride complex **3** could not be cleaved when **3** is allowed to react with H_2 under similar condition. Thus reaction of **4** with H_2 gas to give **6** is significant. It implies that intramolecular hydrogen transfer from H_2 to the α-carbon of alkyl or alkenyl ligands could be more facile than reductive elimination of alkyl and hydride ligands for certain systems. Thus our results support the idea that intramolecular hydrogen transfer from a dihydrogen ligand to the α-carbon of an alkyl or alkenyl ligand can be operative in catalytic hydrogenation of unsaturated substrates in certain systems.

Conclusion. We have prepared and characterized $[Os(H_2)(PPh_3)(2\text{-}Ph_2PCH(CPh{=}CH)\text{-}6\text{-}Ph_2PCH_2C_5H_3N)]BF_4$, the first example of alkenyl−dihydrogen complexes characterized by NMR spectroscopy. The dihydrogen complex reacted with H_2 to give $[OsH(H_2)(PPh_3)(2\text{-}Ph_2PCH(CPh{=}CH_2)\text{-}6\text{-}Ph_2PCH_2C_5H_3N)]BF_4$. In contrast, the alkenyl−osmium bond in $OsH(PPh_3)(2\text{-}Ph_2PCH(CPh{=}CH)\text{-}6\text{-}Ph_2PCH_2C_5H_3N)$ could not be cleaved upon treatment with H_2 under similar condition. The results suggest that intramolecular hydrogen transfer from H_2 to the α-carbon of alkyl or alkenyl could be more facile than reductive elimination of alkyl and hydride ligands for certain systems.

Experimental Section

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques. Solvents were distilled under dinitrogen from sodium benzophenone (hexane, diethyl ether, THF, benzene) and calcium hydride (CH_2Cl_2). The starting materials PNP,[23] $OsCl_2(PPh_3)_3$,[24] and $OsCl_2(PPh_3)(PNP)$[12] were prepared according to literature methods. All other reagents were used as purchased from Aldrich. Microanalysis were performed by M-H-W Laboratories (Phoenix, AZ). ^{1}H and $^{31}P\{^1H\}$ NMR spectra were collected on a Bruker ARX-300 spectrometer. ^{1}H chemical shifts are relative to TMS, and ^{31}P NMR chemical shifts are relative to 85% H_3PO_4.

$OsCl(PPh_3)(2\text{-}Ph_2PCH(CPh{=}CH)\text{-}6\text{-}Ph_2PCH_2C_5H_3N)$ (2). A solution of $PhC\equiv CLi$ (4 mL of 1 M in THF, 4 mmol) was added to a solution of $OsCl_2(PPh_3)(PNP)$ (1.3 g, 1.3 mmol) in toluene (40 mL). The mixture was stirred at room temperature for 5 h. The reaction was then quenched by addition of 0.5 mL of water, and the resulting mixture was stirred for another 5 min. After filtration, the filtrate was concentrated to ca. 5

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mL. An orange-red 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: 1.1 g, 80%. Anal. Calcd for $C_{57}H_{47}ClNP_3Os$: C, 64.31; H, 4.45; N, 1.32. Found: C, 64.61; H, 4.80; N, 1.34. ^1H NMR (300.13 MHz, C_6D_6): δ 3.45 (dd, J(HH) = 15.0 Hz, J(PH) = 6.1 Hz, 1 H, CH_2PPh_2), 4.18 (dd, J(HH) = 15.0 Hz, J(PH) = 11.2 Hz, 1 H, CH_2PPh_2), 5.74 (d, J(PH) = 8.8 Hz, 1 H, $CHPPh_2$), 6.79−8.78 (m, 43 H, PPh_3, 2 PPh_2, Ph, Py-3,4,5-H), 9.99 (d, J(PH) = 5.8 Hz, Os−C*H*═). $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6): δ −6.2 (dd J(PP) = 16.7, 9.3 Hz, PPh_3), −2.4 (dd, J(PP) = 336.7, 9.3 Hz, PPh_2), 30.6 (dd, J(PP) = 336.7, 16.7 Hz, PPh_2).

OsH(PPh$_3$)(2-Ph$_2$PCH(CPh═CH)-6-Ph$_2$PCH$_2$C$_5$H$_3$N) (3). A mixture of **2** (0.50 g, 0.47 mmol), $NaBF_4$ (2.00 g, 18.2 mmol), and K_2CO_3 (2.00 g, 14.5 mmol) in 60 mL of methanol was refluxed under a hydrogen atmosphere for 2 days. The color of the reaction mixture changed from red to yellow. The solvent was then removed under vacuum, and the yellow residue was extracted with 60 mL of benzene. The extraction was filtered using a filter frit containing Celite. The yellow filtrate was concentrated to dryness to give a yellow solid (0.36 g, 74%). Anal. Calcd for $C_{57}H_{48}NP_3Os$: C, 66.46; H, 4.70; N, 1.36. Found: C, 66.20; H, 4.66; N, 1.31. ^1H NMR (300.13 MHz, C_6D_6): δ −6.81 (ddd, J(PH) = 25.8, 13.4, 12.5 Hz, 1 H, Os-*H*), 4.02 (m, 2 H, CH_2PPh_2), 6.14 (d, 1 H, J(PH) = 9.0, $CHPPh_2$), 6.39−8.40 (m, 43 H, PPh_3, 2 PPh_2, Ph, Py-3,4,5-H), 11.21 (s, Os−CH═). $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6): δ 22.7 (t, J(PP) = 16.5 Hz, PPh_3), 38.0 (dd, J(PP) = 298.8, 16.2 Hz, PPh_2), 68.6 (dd, J(PP) = 298.8, 16.8 Hz, PPh_2).

[Os(H$_2$)(PPh$_3$)(2-Ph$_2$PCH(CPh═CH)-6-Ph$_2$PCH$_2$C$_5$H$_3$N)]-BF$_4$ (4). Due to its low stability, this compound was not isolated but was characterized in situ. To a dichloromethane-*d*$_2$ solution (0.7 mL) containing **3** (20 mg, 0.019 mmol) in an NMR tube was added $HBF_4{\cdot}Et_2O$ (5 μL). ^1H and ^{31}P NMR spectra were then collected immediately. ^1H NMR (300.13 MHz, CD_2Cl_2): δ −3.14 (br, Os(*H*$_2$)), 3.90 (dd, J(HH) = 16.5 Hz, J(PH) = 6.3 Hz, 1 H, CH_2PPh_2), 4.62 (dd, J(HH) = 16.5 Hz, J(PH) = 11.9 Hz, 1 H, CH_2PPh_2), 5.93 (d, J(PH) = 10.2 Hz, 1 H, $CHPPh_2$), 6.9−8.0 (m, PPh_3, 2 PPh_2, Ph, Py-3,4,5-H), 8.68 (s, Os−C*H*═). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): δ 5.9 (dd, J(PP) = 15.7, 13.8 Hz, PPh_3), 24.2 (dd, J(PP) = 265.6, 13.8 Hz, PPh_2), 55.0 (dd, J(PP) = 265.6, 15.7 Hz, PPh_2). T_1(300 MHz, CD_2Cl_2): ms (temperature) 21.2 (298 K), 18.4 (283 K), 16.2 (273 K), 16.7 (253 K), 16.6 (243 K).

[Os(HD)(PPh$_3$)(2-Ph$_2$PCH(CPh═CH)-6-Ph$_2$PCH$_2$C$_5$H$_3$N)]-O$_2$CCF$_3$ (4d$_1$). The compound was prepared similarly except that DO_2CCF_3 was used instead of $HBF_4{\cdot}Et_2O$. The η^2-HD signal was observed after nulling the η^2-H_2 peak at δ −3.14 ppm by the inversion−recovery method. ^1H NMR (300.13 MHz, CD_2Cl_2): δ −3.15 (br 1:1:1 triplet, J(HD) = 29.7 Hz, Os(HD)).

[Os(PPh$_3$)(2-Ph$_2$PCH(CPh═CH)-6-Ph$_2$PCH$_2$C$_5$H$_3$N)]-BF$_4$ (5). A 0.20 mL sample of $HBF_4{\cdot}Et_2O$ was added to 20 mL of Et_2O. The clear ether solution of HBF_4 was then added to a solution of **3** (0.20 g, 0.19 mmol) in 20 mL of ether. The mixture was stirred at room temperature for 15 min to give a pale green solid. The solid was collected on a filter frit, washed with 2 × 10 mL of ether, and dried under vacuum for 1 h to give 0.17 g of product. $^{31}P\{^1H\}$ and ^1H NMR spectra of the solid indicated that the solid is a mixture of **4** and **5**. The mixture was then redissolved in 10 mL of CH_2Cl_2, and the solvent was removed. The procedure was repeated three times to give a dark blue solid of **5**. Yield: 0.15 g, 69%. Anal. Calcd for $C_{57}H_{47}BF_4NP_3$-$Os{\cdot}1.5CH_2Cl_2$: C, 56.51; H, 4.65; N, 1.13. Found: C, 56.10; H, 4.38; N, 1.29. ^1H NMR (300.13 MHz, CD_2Cl_2): δ 4.40 (dd, J(HH) = 16.9 Hz, J(PH) = 13.4 Hz, 1 H, CH_2PPh_2), 4.82 (dd, J(HH) = 16.9 Hz, J(PH) = 9.0 Hz, 1 H, CH_2PPh_2), 6.25 (d, 1 H, J(PH) = 9.8 Hz, $CHPPh_2$), 7.10−7.84 (m, 43 H, PPh_3, 2 PPh_2, Ph, Py-3,4,5-H), 9.70 (dd, J(PH) = 13.4, 2.9 Hz, Os−C*H*═). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): δ −13.5 (dd, J(PP) = 16.7, 14.1 Hz, PPh_3), −1.4 (dd, J(PP) = 333.6, 14.1 Hz, PPh_2), 18.1 (dd, J(PP) = 333.6, 16.7 Hz, PPh_2).

[OsH(H$_2$)(PPh$_3$)(2-Ph$_2$PCH(CPh═CH$_2$)-6-Ph$_2$PCH$_2$C$_5$-H$_3$N)]BF$_4$ (6). Due to its low stability, this compound was not isolated but was characterized in situ. To an NMR tube was added a mixture of **4** and **5** (20 mg) and CD_2Cl_2 (0.7 mL). The NMR tube was then attached to a hydrogen balloon, and the mixture was then allowed to stand at room temperature for 22 h. NMR spectra showed that all **4** and **5** had been converted to **6**, which exists in two isomers in a ratio of ca. 2:1. Selected characterization data for **6a**, the major isomer: $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): δ 13.4 (dd, J(PP) = 14.0, 12.4 Hz, PPh_3), 28.7 (dd, J(PP) = 217.6, 12.4 Hz, PPh_2), 48.2 (dd, J(PP) = 217.6, 14.0 Hz, PPh_2). ^1H NMR (300.13 MHz, CD_2Cl_2): δ −6.65 (dt, J(PH) = 20.7, 15.6 Hz, 1 H, Os-*H*), −3.48 (br s, 2H, Os-(*H*$_2$)), 3.77 (d, J(HH) = 2.3 Hz, PhC═C*H*H), 4.22 (dd, J(HH) = 16.6 Hz, J(PH) = 10.2 Hz, 1 H, CH_2PPh_2), 4.65 (dd, J(HH) = 16.6 Hz, J(PH) = 10.4 Hz, 1 H, CH_2PPh_2), 5.33 (d, 1 H, J(HH) = 2.3 Hz, PhC═CH*H*), 5.58 (d, J(PH) = 13.8 Hz, $CHPPh_2$), 6.89−7.42 (m, other proton signals mixed with those of **6b**). T_1(300.13 MHz, CD_2Cl_2): ms (temperature) 23.7 (298 K), 17.4 (273 K), 15.3 (253 K), 14.5 (243 K), 15.8 (233 K), 15.9 (220 K). Selected characterization data for **6b**, the minor isomer: $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): δ 13.8 (dd, J(PP) = 14.8, 12.2 Hz, PPh_3), 24.9 (dd, J(PP) = 220.7, 14.8 Hz, PPh_2), 46.1 (dd, J(PP) = 220.7, 12.2 Hz, PPh_2). ^1H NMR (300.13 MHz, CD_2Cl_2): δ -6.42 (dt, J(PH) = 21.9, 16.2 Hz, 1 H, Os-*H*), −3.20 (br s, 2 H, Os(*H*$_2$)), 4.28(d, J(HH) = 2.8 Hz, PhC═CH*H*), 4.40 (dd, J(HH) = 16.0 Hz, J(PH) = 10.4 Hz, 1 H, CH_2PPh_2), 4.73 (dd, J(HH) = 16.0 Hz, J(PH) = 11.2 Hz, 1 H, CH_2PPh_2), 5.36 (d, 1 H, J(HH) = 2.8 Hz PhC═C*H*H), 5.51 (d, J(PH) = 13.8 Hz, $CHPPh_2$), 6.89−7.42 (m, other proton signals mixed with those of **6a**). T_1(300.13 MHz, CD_2Cl_2): ms (temperature) 25.8 (298 K), 17.9 (273 K), 15.2 (253 K), 18.5 (243 K), 18.8 (233 K).

[OsH(HD)(PPh$_3$)(2-Ph$_2$PCH(CPh═CH$_2$)-6-Ph$_2$PCH$_2$C$_5$-H$_3$N)]BF$_4$. To a solution of **6** in CD_2Cl_2 prepared as above was added 0.05 mL of CD_3OD. The mixture was then store at room temperature for 30 min, and then the ^1H NMR spectrum was collected. The η^2-HD signals were observed after nulling the η^2-H_2 peaks by the inversion−recovery method. ^1H NMR (300 MHz, CD_2Cl_2): δ −3.41 (t, J(HD) = 30.0 Hz, Os(HD), isomer **6a-d$_1$**), −3.13 (br t, J(HD) = 29.7 Hz, Os(HD), isomer **6b-d$_1$**).

Crystallographic Analysis for OsCl(PPh$_3$)(2-Ph$_2$PCH-(CPh═CH)-6-Ph$_2$PCH$_2$C$_5$H$_3$N)·3.5C$_6$H$_6$. Suitable crystals for X-ray diffraction study were obtained by standing a saturated solution of **2** in benzene. An orange prismatic single crystal with dimensions of 0.24 × 0.16 × 0.14 mm was mounted on a glass fiber for the diffraction experiment. Intensity data were collected on a Bruker SMART CCD area detector and corrected for SADABS (Siemens area detector absorption)[25] (from 0.512 to 0.967 on *I*). The structure was solved by direct methods, expanded by difference Fourier syntheses, and refined by full-matrix least-squares on F^2 using the Bruker SHELXTL (Version 5.10)[26] program package. All non-hydrogen atoms were refined anisotropically except the carbons of the benzene solvent molecules, which were refined isotropically with similar C−C bond distances and planarity restraints. Hydrogen atoms were placed in the ideal positions and refined as riding atoms. Further details of the data collection are summarized in Table 1, and selected bond distances and angles are listed in Table 2.

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(26) Bruker. *SHELXTL Reference Manual* (Version 5.1); Bruker Analytical X-Ray Systems Inc.: Madison, WI, 1997.

Supporting Information Available: Tables of crystallographic details, bond distances and angles, atomic coordinates and equivalent isotropic displacement coefficients, and anisotropic displacement coefficients for $OsCl(PPh_3)(2\text{-}Ph_2PCH(CPh{=}CH)\text{-}6\text{-}Ph_2PCH_2C_5H_3N)\cdot 3.5C_6H_6$. The material is available free of charge via the Internet at http://pubs.acs.org.

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