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Sequential and Selective Hydrogenation of the $C_\alpha-C_\beta$ and $M-C_\alpha$ Double Bonds of an Allenylidene Ligand Coordinated to Osmium: New Reaction Patterns between an Allenylidene Complex and Alcohols

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Abstract: Complex $[OsH(=C=C=CPh_2)(CH_3CN)_2(P^iPr_3)_2]BF_4$ (**1**) reacts with primary and secondary alcohols to give the corresponding dehydrogenated alcohols and the hydride-carbene derivative $[OsH(=CHCH=CPh_2)(CH_3CN)_2(P^iPr_3)_2]BF_4$ (**2**), as a result of hydrogen transfer reactions from the alcohols to the $C_\alpha-C_\beta$ double bond of the allenylidene ligand of **1**. The reactions with phenol and *t*-butanol, which do not contain any β-hydrogen, afford the alkoxy-hydride-carbyne complexes $[OsH(OR)(\equiv CCH=CPh_2)(CH_3CN)(P^iPr_3)_2]BF_4$ (R = Ph (**3**), ^{t}Bu (**4**)), as a consequence of the 1,3-addition of the O−H bond of the alcohols to the metallic center and the C_β atom of the allenylidene of **1**. On the basis of the reactions of **1** with these tertiary alcohols, deuterium labeling experiments, and DFT calculations, the mechanism of the hydrogenation is proposed. In acetonitrile under reflux, the Os−C double bond of **2** undergoes hydrogenation to give 1,1-diphenylpropene and $[Os\{CH_2CH(CH_3)\}P^iPr_2(CH_3CN)_3(P^iPr_3)]BF_4$ (**11**), containing a metalated phosphine ligand. This reaction is a first-order process with activation parameters of $\Delta H^\ddagger = 89.0 \pm 6.3$ kJ mol^{-1} and $\Delta S^\ddagger = -43.5 \pm 9.6$ J mol^{-1} K^{-1}. The X-ray structures of **2** and **3** are also reported.

Introduction

The term "hydrogenation" refers to a chemical reaction in which one or more hydrogen atoms (and only those) are incorporated in the product(s) of the reaction. The chemoselective hydrogenation of a specific carbon−carbon double bond in compounds containing several of them is a challenging problem in synthetic organic and organometallic chemistry.[1]

Transition metal allenylidene complexes are a class of compounds with three consecutive double bonds: one metal−carbon and two carbon−carbon. Their chemistry has been subject of special attention in recent years due to their potential as organometallic intermediates that may have unusual reactivity in stoichiometric[2] and catalytic reactions.[3] The presence of three reactive centers (unsaturated C_3 chain) or more (unsaturated chain plus substituents) in the η^1-carbon ligand allows one to build, in one or two steps, organic skeletons (naphthofuranyl,[4] pyrazolopyrazolyl,[5] azetidine, hexahydroquinoline,[6] pyridopyridinyl, thiazinyl,[7] dihydronapthopyrrolyl,[8] etc.[9]), which require multistep procedures in conventional organic synthesis.

The reactivity of the C_3-organic unit is a function of the particular metallic fragment stabilizing the allenylidene ligand. In agreement with the presence of electrophilic (C_α and C_γ) and nucleophilic (C_β) sites in the C_3-chain,[10] three types of behaviors have been observed for the allenylidene complexes:[11] α-electrophilic, γ-electrophilic, and nucleophilic. The most noticeable feature of the first of them is the formation of Fischer type alkenylcarbene derivates by addition of RXH molecules (alcohols, amines, etc.) to the $C_\alpha-C_\beta$ double bond.[12] In contrast to the α-electrophilic compounds, the γ-electrophilic ones do not undergo intermolecular addition of weak nucleophilic reagents and the reactions with strong nucleophiles lead to alkynyl complexes.[13] The nucleophilic behavior involves addition of electrophiles at C_β.[12j,14]

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The hydrogenation of allenylidene compounds has received scarce attention and has been centered on the $M-C_\alpha$ and $C_\beta-C_\gamma$ double bonds. As far as we know, the addition of two hydrogen atoms to the $C_\alpha-C_\beta$ bond has not been achieved. Werner and co-workers have reported the hydrogenation with molecular hydrogen of the M−C double bonds of $MCl\{=C=C=C(R)Ph\}(P^iPr_3)_2$ to afford the allene derivatives $MCl\{\eta^2\text{-}CH_2=C=C(R)Ph\}(P^iPr_3)_2$ (M = Rh,[15] Ir[16]). We have described the formation of the vinylidene $Os(\eta^5\text{-}C_5H_5)Cl(=C=CHCHPh_2)(P^iPr_3)_2$ by reduction of the $C_\beta-C_\gamma$ bond of the allenylidene ligand of $Os(\eta^5\text{-}C_5H_5)Cl(=C=C=CPh_2)(P^iPr_3)_2$ with $NaBH_4$ and some drops of methanol.[17] In the same line, Che, Phillips, and co-workers have observed that complex *trans*-[Cl(16-TMC)Ru(=C=C=CPh$_2$)]PF_6 (16-TMC = 1,5,9,13-tetramethyl-1,5,9,13-tetraazacyclohexadecane) can be converted to *trans*-[Cl(16-TMC)Ru(=C=CHCHPh$_2$)]PF_6 by treatment with Zn/Hg in methanol under reflux.[18] These $C_\beta-C_\gamma$ reductions appear to be two-step processes: addition of H^- to C_γ and H^+ to C_β, in agreement with the respective electrophilic and nucleophilic character of the carbon atoms. Thus, Dixneuf and co-workers have shown that complexes $[RuCl(=C=C=CR_2)(dppm)_2]PF_6$ (dppm = $Ph_2PCH_2PPh_2$) react with $NaBH_4$ to give the corresponding alkynyl derivatives $RuCl(C\equiv CCHR_2)(dppm)_2$.[19] The addition of H^+ to the C_β atom of alkynyl compounds to form vinylidenes is a well-known process.[20]

Alcohols have proven to be useful hydrogen donors and an important alternative to molecular hydrogen for the hydrogenation of unsaturated molecules.[21] We have recently reported the preparation of the bis-solvento hydride-allenylidene complex $[OsH(=C=C=CPh_2)(CH_3CN)_2(P^iPr_3)_2]BF_4$, which allows us to assemble the allenylidene ligand with a terminal alkyne and an acetonitrile molecule to afford osmacyclopentapyrrole derivatives.[22] Now, we show that alcohols hydrogenate the $C_\alpha-C_\beta$ double bond of the allenylidene ligand of this compound to give a bis-solvento hydride-alkenylcarbene derivative.

In this Article, we report the following: (i) the hydrogenation of the $C_\alpha-C_\beta$ bond of $[OsH(=C=C=CPh_2)(CH_3CN)_2(P^iPr_3)_2]BF_4$, (ii) the mechanism of the hydrogenation, (iii) a theoretical study on the mechanism, and (iv) the subsequent hydrogenation of the Os−C double bond to give 1,1-diphenylpropene.

Results and Discussion

1. Hydrogenation of the $C_\alpha-C_\beta$ Double Bond of the Allenylidene Ligand of $[OsH(=C=C=CPh_2)(CH_3CN)_2(P^iPr_3)_2]BF_4$. In contrast to the diphenylallenylidene complexes of the iron triad with α-electrophilic character, which, in alcohols, afford α,β-unsaturated alkoxycarbene derivatives, as a result of the addition of the O−H bond of the alcohols to the $C_\alpha-C_\beta$ double bond of the C_3-chain of the η^1-carbon donor ligand, the hydride-allenylidene complex $[OsH(=C=C=CPh_2)(CH_3CN)_2(P^iPr_3)_2]BF_4$ (**1**) in methanol, ethanol, *n*-propanol, or 2-propanol evolves to the hydride-alkenylcarbene derivative $[OsH(=CHCH=CPh_2)(CH_3CN)_2(P^iPr_3)_2]BF_4$ (**2**). The hydrogenation of the $C_\alpha-C_\beta$ double bond of the allenylidene ligand of **1** takes place by means of hydrogen transfer from the alcohols, which undergo dehydrogenation to give the carbonyl compounds (eq 1). The rates of the hydrogenation depend upon the nature of the alcohols. While the quantitative reduction with

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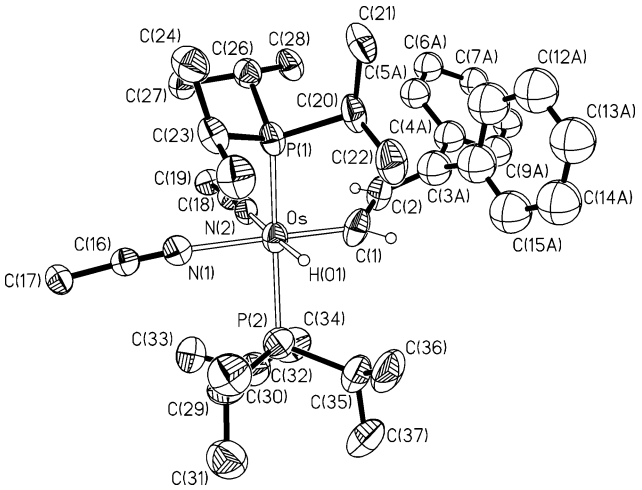
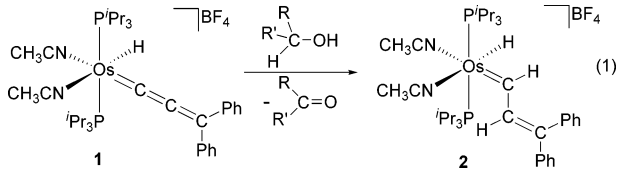


Figure 1. Molecular diagram of the cation of **2**. Selected bond lengths (Å) and angles (deg): Os−N(1) 2.165(6), Os−N(2) 2.132(6), Os−C(1) 1.892(8), C(1)−C(2) 1.472(11); P(1)−Os−P(2) 158.64(7), Os−C(1)−C(2) 129.3(6), N(1)−Os−N(2) 85.5(2), H(01)−Os−N(2) 175(3), C(1)−Os−N(1) 176.5(3).

primary alcohols occurs after 1 h, with 2-propanol 5 h is necessary to obtain **2** in high yield.

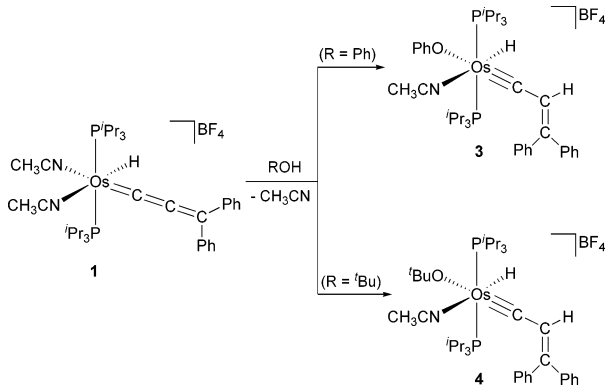


The carbonyl compounds, RR′CO, were characterized by GC−MS, whereas complex **2**, which is isolated as a green solid, was characterized by elemental analysis, IR, ^{1}H, ^{31}P{^{1}H}, ^{13}C{^{1}H} NMR spectroscopy, and by an X-ray crystallographic study. Figure 1 shows an ORTEP drawing of the cation.

The geometry around the osmium atom can be described as a distorted octahedron with the phosphorus atoms of the phosphine ligands occupying trans positions (P(1)−Os−P(2) = 158.64(7)°). The perpendicular plane is formed by the acetonitrile molecules cis disposed (N(1)−Os−N(2) = 85.5(2)°), the hydride ligand trans disposed to N(2) (H(01)−Os−N(2) = 175(3)°), and the carbene group trans disposed to N(1) (C(1)−Os−N(1) = 176.5(3)°). The Os−C(1) bond length of 1.892(8) Å supports the Os−C double bond formulation.[23] In agreement with the sp^2 hybridization at C(1), the angles around this atom are between 108(5)° and 129.3(6)°.

The IR spectrum of **2** in Nujol shows two ν(C≡N) absorptions at 2331 and 2265 cm^{-1} along with a band at 2172 cm^{-1}, corresponding to the Os−H vibration, and the absorption due to the [BF$_4$]$^-$ anion with T_d symmetry centered at 1061 cm^{-1}. In the ^{1}H NMR spectrum in dichloromethane-d_2, the most noticeable resonance is that due to the Os=CH proton, which appears at 21.35 ppm, as a doublet with an H−H coupling constant of 13.2 Hz. The acetonitrile resonances are observed at 2.90 and 2.80 ppm as singlets. In the high field region of the spectrum, the hydride ligand gives rise to a triplet at −16.27 ppm, with an H−P coupling constant of 21.4 Hz. In the ^{13}C{^{1}H} NMR spectrum, the Os=C resonance is observed at 265.1 ppm, as a triplet with a C−P coupling constant of 8.1 Hz. In accordance with the mutually cis disposition of the acetonitrile molecules, these ligands display two CN resonances at 141.5 and 125.3 ppm. The ^{31}P{^{1}H} NMR spectrum contains a singlet at 22.4 ppm, which is consistent with the mutually trans disposition of the phosphine ligands, and with the fact that the hydrogen and alkenyl substituents of the alkylidene carbon atom lie in the plane containing the nitrogen atoms.

Scheme 1



2. Mechanism of the Hydrogenation: Reactions with Phenol and *t*-Butanol. Although tertiary alcohols can undergo heterolytic activation of the O−H bond, they are not a suitable source of hydrogen for the hydrogenation of a C−C double bond, because they do not contain a geminal hydrogen. Thus, to obtain information about the first step of the reaction shown in eq 1, we have also investigated the behavior of **1** in the presence of phenol and *t*-butanol (Scheme 1).

Treatment at room temperature of dichloromethane solutions of **1** with 1.1 equiv of phenol leads to the phenoxy-carbyne derivative [OsH(OPh)(≡CCH=CPh$_2$)(CH$_3$CN)(P^{i}Pr$_3$)$_2$]BF$_4$ (**3**), as a result of a 1,3-addition of the O−H bond of the alcohol to the Os-allenylidene unit of **1**. Similarly, the stirring of **1** in *t*-butanol as solvent affords [OsH(O^{t}Bu)(≡CCH=CPh$_2$)(CH$_3$CN)(P^{i}Pr$_3$)$_2$]BF$_4$ (**4**). The formation of **3** and **4** is in agreement with the nucleophilic character of the C_β atom of the C_3-chain of the allenylidene and reveals the Lewis base nature of **1**, which is able to undergo the oxidative addition of alcohols.

Complexes **3** and **4** are isolated as red and brown solids in 90% and 72% yield, respectively, and were characterized by elemental analysis, IR, and ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopy. Complex **3** was further characterized by an X-ray crystallographic study. An ORTEP drawing of the cation of this compound is shown in Figure 2.

The coordination around the osmium atom can be rationalized as a distorted octahedron with the phosphine ligands occupying trans positions (P(1)−Os−P(2) = 166.18(5)°). The perpendicular plane is formed by the phenoxide, acetonitrile, hydride, and

(23) (a) Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A.; Zeier, B. *Organometallics* **1994**, *13*, 1662. (b) Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A.; Valero, C.; Zeier, B. *J. Am. Chem. Soc.* **1995**, *117*, 7935. (c) Brumaghim, J. L.; Girolami, G. S. *Chem. Commun.* **1999**, 953. (d) Werner, H.; Stüer, W.; Wolf, J.; Laubender, M.; Weberndörfer, B.; Herbst-Irmer, R.; Lehmann, C. *Eur. J. Inorg. Chem.* **1999**, 1889. (e) Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2001**, *20*, 2294. (f) Gusev, D. G.; Lough, A. J. *Organometallics* **2002**, *21*, 2601. (g) Weberndörfer, B.; Henig, G.; Hockless, D. C. R.; Bennett, M. A.; Werner, H. *Organometallics* **2003**, *22*, 744. (h) Esteruelas, M. A.; González, A. I.; López, A. M.; Oñate, E. *Organometallics* **2004**, *23*, 4858. (i) Bolaño, T.; Castarlenas, R.; Esteruelas, M. A.; Modrego, F. J.; Oñate, E. *J. Am. Chem. Soc.* **2005**, *127*, 11184. (j) Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2005**, *24*, 4343. (k) Esteruelas, M. A.; Fernández-Alvarez, F. J.; Oliván, M.; Oñate, E. *J. Am. Chem. Soc.* **2006**, *128*, 4596. (l) Esteruelas, M. A.; Fernández-Alvarez, F.; Oñate, E. *J. Am. Chem. Soc.* **2006**, *128*, 13044.

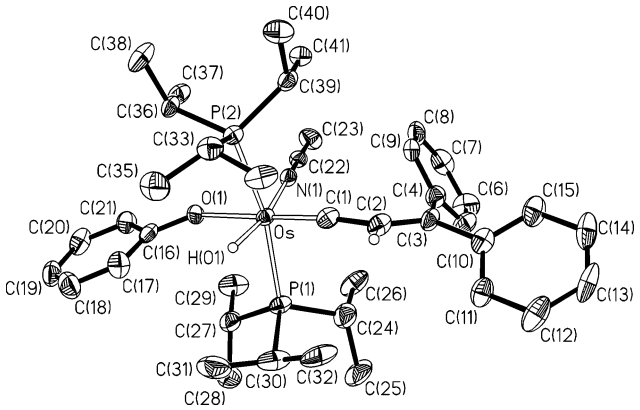
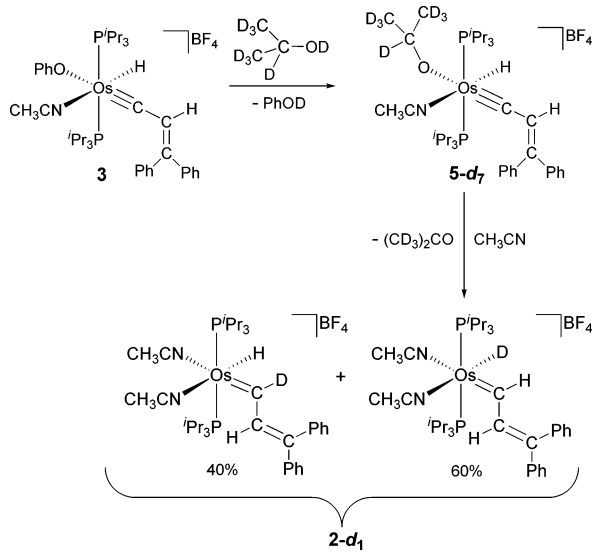


Figure 2. Molecular diagram of the cation of **3**. Selected bond lengths (Å) and angles (deg): Os−N(1) 2.154(4), Os−O(1) 2.061(3), Os−C(1) 1.740(5), C(1)−C(2) 1.432(6), C(2)−C(3) 1.343(7); P(1)−Os−P(2) 166.18-(5), Os−C(1)−C(2) 172.9(4), O(1)−Os−C(1) 178.91(19), N(1)−Os−O(1) 79.07(13), N(1)−Os−H(01) 165.7(14), O(1)−Os−H(01) 86.6(14).

carbyne ligands. The phenoxide group lies trans to the carbyne ligand (O(1)−Os−C(1) = 178.91(19)°), whereas the hydride and acetonitrile ligands are also mutually trans disposed (H(01)−Os−N(1) = 165.7(14)°). The Os−C(1) bond length of 1.740-(5) Å is fully consistent with an Os−C triple bond formulation.[23i,24] Similarly to other carbyne−metal compounds,[13d,e,25] a slight bending in the Os−C(1)−C(2) moiety is also present (Os−C(1)−C(2) = 172.9(4)°). The alkenyl carbyne proposal is supported by the bond lengths and angles within the η^1-carbon donor ligand; for example, C(1) and C(2) are separated by 1.432-(6) Å and C(2) and C(3) by 1.343(7) Å, and the angles around C(2) and C(3) are in the range 111−125°. The Os−O(1) distance of 2.061(3) Å compares well with those found in other alkoxy− and hydroxy−osmium complexes.[26]

In agreement with the presence of a hydride ligand in **3** and **4**, their ^{1}H NMR spectra in the high field region show triplets at −6.72(**3**) and −3.90(**4**) ppm, with H−P coupling constants of 16.8 and 17.4 Hz, respectively. In the low field region, the C_β−H proton of the alkenyl substituent of the carbyne ligands gives rise to singlets at 5.40 (**3**) and 5.22 (**4**) ppm. In the ^{13}C-{^{1}H} NMR spectra, the Os−C_α resonances are observed at 261.0 (**3**) and 270.7 (**4**) ppm, as triplets with C−P coupling constants of 12.3 and 9.0 Hz, respectively. The ^{31}P{^{1}H} NMR spectra contain singlets at 27.4 (**3**) and 26.1 (**4**) ppm.

Scheme 2



In the presence of acetonitrile, the *n*-propanol solutions of **3** and **4** evolve to afford the hydride−carbene complex **2**. The first step of these transformations is the exchange of the coordinated alkoxy group by reaction with *n*-propanol, which acts as solvent. The exchange between the hydrogen-bonded alcohol and a coordinated alkoxide is a well-known process.[27] In agreement with this, we have observed that at −30 °C, the ^{1}H NMR spectra of the freshly prepared solutions of **3** in 2-propanol-d_8 contain, in addition to the resonances of **3**, a triplet (J_{H-P} = 17.7 Hz) at −6.28 ppm and a singlet at 5.38 ppm, which can be assigned to the hydride ligand and to the C_β−H hydrogen atom of the alkenyl substituent of the carbyne group of [OsH{OCD(CD$_3$)$_2$}(≡CCH═CPh$_2$)(CH$_3$CN)(P^{i}Pr$_3$)$_2$]$^+$ (**5-*d*$_7$**). At temperatures higher than −30 °C, the latter is unstable and decomposes into a complex mixture of unidentified products. However, in the presence of acetonitrile the evolution takes place in a controlled way, and the hydride-carbene **2-*d*$_1$** is formed. Interestingly, the ^{1}H and ^{2}H NMR spectra of **2-*d*$_1$** indicate the presence of 0.4 deuterium atoms at the C_α position and 0.6 deuterium atoms at the hydride position. This deuterium distribution suggests that **2-*d*$_1$** is a 4:6 mixture of the isomers shown in Scheme 2.

Scheme 3 shows a mechanism for the hydrogenation of the $C_\alpha-C_\beta$ double bond of the allenylidene of **1**, which is consistent with the experimental observations summarized in Schemes 1 and 2. The reactions involve the ruptures of the O−H and OC−H bonds of the alcohols, and the additions of the hydrogen atoms to the $C_\alpha-C_\beta$ double bond of the allenylidene. In accordance with Scheme 1, the 1,3-addition of the O−H bond of the alcohols to the Os-allenylidene unit should afford alkoxy-hydride-carbyne intermediates related to **3**, **4**, and **5-*d*$_7$**. The composition of **2-*d*$_1$** indicates that the rupture of the OC−H bond takes place before the formation of the C_α−H one. The β-hydrogen elimination from the alcoholates should give dihydride-carbyne intermediates, which could form **2** by migratory insertion of the carbyne ligand into one of the Os−H bonds.

3. Theoretical Calculations on the Mechanism. The mechanism for the hydrogenation of the $C_\alpha-C_\beta$ double bond of the

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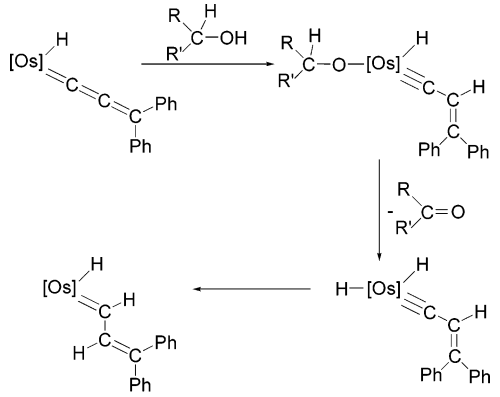
(25) (a) Esteruelas, M. A.; López, A. M.; Ruiz, N.; Tolosa, J. I. *Organometallics* **1997**, *16*, 4657. (b) Crochet, P.; Esteruelas, M. A.; López, A. M.; Martínez, M.-P.; Oliván, M.; Oñate, E.; Ruiz, N. *Organometallics* **1998**, *17*, 4500.

(26) See, for example: (a) Che, C.-M.; Huang, J.-S.; Li, Z.-Y.; Poon, C.-K.; Tong, W.-F.; Lai, T.-F.; Cheng, M.-C.; Wang, C.-C.; Wang, Y. *Inorg. Chem.* **1992**, *31*, 5220. (b) Edwards, A. J.; Elipe, S.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A.; Valero, C. *Organometallics* **1997**, *16*, 3828. (c) Renkema, K. B.; Huffman, J. C.; Caulton, K. G. *Polyhedron* **1999**, *18*, 2575. (d) Bhattacharya, S.; Gupta, P.; Basuli, F.; Pierpont, C. G. *Inorg. Chem.* **2002**, *41*, 5810. (e) Dickinson, P. W.; Girolami, G. S. *Inorg. Chem.* **2006**, *45*, 5215. (f) Wu, A.; Dehestani, A.; Saganic, E.; Crevier, T. J.; Kaminsky, W.; Cohen, D. E.; Mayer, J. M. *Inorg. Chim. Acta* **2006**, *359*, 2842.

(27) Esteruelas, M. A.; Oro, L. A. *Coord. Chem. Rev.* **1999**, *193*−*195*, 557 and references therein.

Scheme 3



allenylidene of **1**, by hydrogen transfer from alcohols, has been analyzed by DFT calculations (B3PW91) using PH_3, CCH═CH_2, and $(CH_3)_2CO$ as models of triisopropylphosphine, alkenylcarbyne, and dehydrogenated alcohol, respectively. Because the alkoxy-hydride-carbyne complexes **3** and **4** have been isolated and characterized, including the X-ray structure of **3**, the theoretical study is centered on the rupture of the OC−H bond of the alkoxide ligand and the formation of the C_α−H bond. So, the analysis starts from the model alkoxy-hydride-carbyne intermediate $[OsH\{OCH(CH_3)_2\}(\equiv CCHCH_2)(CH_3CN)(PH_3)_2]^+$ (**5t**). The changes in free energy (ΔG) have been computed at 298.15 K and $P = 1$ atm. Figure 3 shows the energy profile, whereas Figure 4 collects the optimized structures and selected structural parameters.

The β-hydrogen elimination reaction on the alkoxide ligand of **5t** needs a coordination vacancy at the metal center. So, because **5t** is a saturated species, the dissociation of the acetonitrile molecule should be the first step of the transformation from **5t** into $[OsH(=CHCH=CH_2)(CH_3CN)_2(PH_3)_2]^+$ (**2t**). This release leads to $[OsH\{OCH(CH_3)_2\}(\equiv CCH=CH_2)(PH_3)_2]^+$ (**6t**), which has two minima, **a** and **b**. The first of them, **6t-a**, lies 90.7 kJ mol^{-1} above **5t**. The second one, **6t-b**, is 13.0 kJ mol^{-1} more stable than **6t-a**. From a structural point of view, they show significant differences. The geometry around the osmium atom of **6t-a** can be described as a distorted trigonal bipyramid with apical phosphines (P−Os−P = 176.5°) and inequivalent angles within the Y-shaped equatorial plane (O−Os−H(1) = 137.7°, O−Os−C(1) = 133.2°, and H(1)−Os−C(1) = 89.1°), whereas the structure of **6t-b** can be rationalized as a square-pyramidal with the phosphines, mutually trans disposed (P−Os−P = 164.5°), the alkoxide and alkenylcarbyne group (O−Os−C(1) = 174.7°) occupying the basal sites, and the hydride ligand located at the apex. The separation between the β-hydrogen atom H(2) of the alkoxide ligand and the metal center in **6t-b** (1.945 Å) is about 0.16 Å shorter than in **6t-a** (2.111 Å).

The proximity of H(2) and the osmium atom in **6t-b** favors the β-hydrogen elimination reaction. Thus, the activation barrier for the process in **6t-b** (**TS1-b**) is 81.1 kJ mol^{-1} above **5t** and 26.7 kJ mol^{-1} lower than in **6t-a** (**TS1-a**; 107.8 kJ mol^{-1}). The transition states **TS1-a** and **TS1-b** are also structurally different. In **TS1-a**, the β-hydrogen atom H(2) of the alkoxide group lies cisoid disposed to the hydride H(1) (H(2)−Os−H(1) = 73.4°) and 1.795 Å from the metal center. However, in **TS1-b**, the H(2) atom is transoid with regard to H(1) (H(2)−Os−H(1) = 155.4°) and is separated by 1.754 Å from the osmium atom. The disposition of H(2) in the transition state determines the stereochemistry of the resulting dihydride intermediates $[OsH_2(\equiv CCH=CH_2)\{\kappa^1\text{-}OC(CH_3)_2\}(PH_3)_2]^+$ (**7t**). The β-elimination through **TS1-a** gives the *cis*-dihydride **7t-a** (H(1)−Os−H(2) = 73.2°), while the β-elimination via **TS1-b** affords the *trans*-dihydride **7t-b** (H(1)−Os−H(2) = 157.9°).

There is a noticeable difference in the Os−H bond lengths of **7t-a**, which is consistent with the marked difference in trans influence between the carbyne and acetone ligands. The distance between the osmium atom and the hydride ligand trans disposed to the carbyne group (H(2)) is 0.118 Å longer than the distance between the metal center and the hydride ligand, H(1), trans disposed to the acetone molecule (1.724 Å versus 1.606 Å). The trans influence of a hydride ligand is intermediate between those of the carbyne and acetone groups. In accordance with this, the Os−H bond lengths in **7t-b** of 1.685 Å (Os−H(1)) and 1.674 Å (Os−H(2)) are intermediate between those of **7t-a**. Both dihydride intermediates are less stable than **5t**, the first of them by 24.2 kJ mol^{-1} and the second one by 7.1 kJ mol^{-1}. The lower stability of **7t-a** with regard to **7t-b** appears to be a consequence of the trans disposition of the two ligands with the highest trans influences of the complex, carbyne and hydride.

The migration of the hydride ligand H(1) to the carbyne group in **7t-a** gives the five-coordinate alkenylcarbene intermediate $[OsH(=CHCH=CH_2)\{\kappa^1\text{-}OC(CH_3)_2\}(PH_3)_2]^+$ (**8t**). Similarly, the migration of H(1) to the carbyne ligand in **7t-b** leads to **8t**. The latter, which is 3.3 kJ mol^{-1} more stable than **7t-a** and 13.8 kJ mol^{-1} less stable than **7t-b**, lies 20.9 kJ mol^{-1} above **5t**. Intermediate **8t** can be described as a five-coordinate species with trans phosphines (P−Os−P = 168.6°) and O−Os−H(1), O−Os−C(1), and H(1)−Os−C(1) angles of 144.4°, 129.6°, and 85.9°, respectively, within the Y-shaped perpendicular plane.

The activation energy for the insertion has a marked dependence upon the strength of the bond between the metal center and the emigrant hydride, which is determined by the group disposed trans to this hydride, and therefore depends upon the stereochemistry cis or trans of the dihydrides **7t**. The Os−H(1) distance in the *cis*-dihydride **7t-a** is 0.079 Å shorter than the Os−H(1) bond length in its *trans*-dihydride isomer **7t-b**. In agreement with an Os−H(1) bond stronger in **7t-a** than in **7t-b**, the activation barrier for the migration of the H(1) hydride ligand of **7t-a** from the metal center to the carbyne carbon atom (**TS2-a**) is higher than that (**TS2-b**) for the migration of the hydride ligand H(1) of **7t-b** (160.1 versus 62.3 kJ mol^{-1}). The value calculated for the migration of H(1) of **7t-a** is also higher than those previously reported for related processes.[23i,28] According to the obtained value, the acetone dissociation should occur before the migration takes place. The release of acetone should afford $[OsH_2(\equiv CCHCH_2)(PH_3)_2]^+$ species, which lie between 67 and 100 kJ mol^{-1} above **5t**. Although both **TS2-a** and **TS2-b** can be described as η^2-carbene species,[29] as expected from the energy difference between them, the three-membered Os−C−H rings are very different. That of **TS2-a** has Os−H, Os−C, and C−H distances of 2.089, 1.866, and 1.164 Å,

(28) Bolaño, T.; Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2007**, *26*, 2037.
(29) (a) Schultz, A. J.; Williams, J. M.; Schrock, R. R.; Rupprecht, G. A.; Fellmann, J. D. *J. Am. Chem. Soc.* **1979**, *101*, 1593. (b) Goddard, R. J.; Hoffman, R.; Jemmis, E. D. *J. Am. Chem. Soc.* **1980**, *102*, 7667.

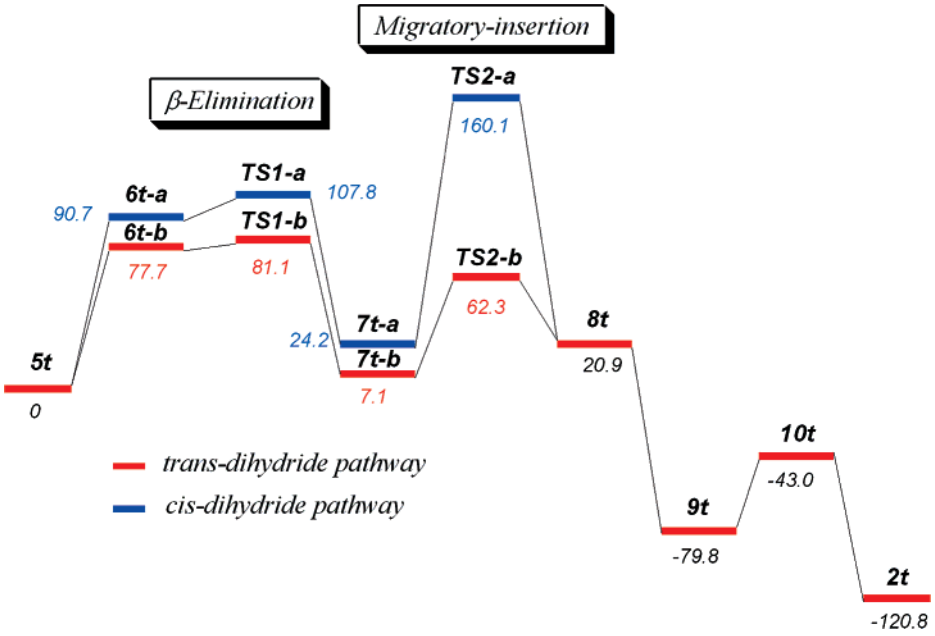


Figure 3. Relative energies (ΔG, 298 K, 1 atm; kJ mol^{-1}) for the transformation of **5t** to **2t**.

respectively, and the triangle angles are between 33.6° and 83.7°. In **TS2-b**, not only the three sides of the triangle are similar (1.774 (Os−H), 1.758 (Os−C), and 1.526 (C−H)) but also the angles (between 52.5° and 63.2°).

The coordination of acetonitrile to **8t** gives [OsH(=CHCH=CH_2){κ^1-OC(CH_3)$_2$}(CH_3CN)(PH_3)$_2$]$^+$ (**9t**). The saturation of the metal center produces a strong stabilization. Intermediate **9t** is 79.8 kJ mol^{-1} more stable than **5t**. It can be described as an octahedral *cis*-hydride-carbene intermediate (H(2)−Os−C(1) = 87.6°) with trans phosphines (P−Os−P = 171.4°). The remaining coordination sites involve the acetonitrile molecule and the carbene group trans disposed (N−Os−C(1) = 171.1°), and the acetone molecule and the hydride ligand also trans disposed (O−Os−H(2) = 163.9°).

The substitution of the acetone ligand of **9t** by a second acetonitrile molecule gives rise to an additional stabilization of the system. The formation of **2t**, which is 120.8 kJ mol^{-1} more stable than **5t**, from **9t** implies the dissociation of acetone to afford [OsH(=CHCH=CH_2)(CH_3CN)(PH_3)$_2$]$^+$ (**10t**) and the subsequent coordination of acetonitrile to the metal center of the latter. The acetone dissociation produces a light destabilization with regard to **9t**. The five-coordinate intermediate **10t** is only 43.0 kJ mol^{-1} more stable than **5t**. In contrast to the acetone derivative **8t**, the structure of **10t** can be rationalized as square-pyramidal with the phosphines mutually trans disposed (P−Os−P = 169.0°), the acetonitrile and alkenylcarbene (also trans disposed; N−Os−C(1) = 175.5°) occupying the basal sites, and the hydride ligand located at the apex.

The visual examination of the energy profile depicted in Figure 3 shows that the transformation from **5t** to **2t** through the pathway **b** (red) via the *trans*-dihydride intermediate **7t-b** is strongly favored over the pathway **a** (blue) via the *cis*-dihydride **7t-a**. The highest barrier of pathway **b** is the β-hydrogen elimination on the alkoxide ligand of **5t** and appears to be the rate-determining step for the reduction. This is consistent with the previously mentioned dependence of the rate of the hydrogenation on the nature of the alcohol and with the moderated stability of the intermediate **5-*d*$_7$**, which can be spectroscopically detected. The conversion of **5t** into **7t-b** is a combined step, which implies the initial dissociation of acetonitrile to give **6t-b**, and the subsequent β-elimination on the alkoxide ligand. In agreement with the initial dissociation of acetonitrile, we have also observed that the reaction of **3** with *n*-propanol is inhibited in acetonitrile as solvent.

The β-hydrogen elimination in **5t** is certainly favored with regard to the migratory insertion of the carbyne ligand into the Os−H bond. The energy barrier calculated for the latter of 114.1 kJ mol^{-1} is higher than that for the β-hydrogen elimination. Although the resulting alkoxide-carbene is unsaturated, the β-elimination reaction in this species has also an energy barrier higher than in **5t**. Thus, the transition state for the process lies 94.9 kJ mol^{-1} above **5t**, that is, 13.8 kJ mol^{-1} above **TS1-b**.

4. Hydrogenation of the Os−C Double Bond of [OsH(=CHCH=CPh$_2$)(CH_3CN)$_2$(P^iPr_3)$_2$]BF_4. Complex **2** is notable because it is a rare example of hydride-alkenylcarbene derivative and by the mutually cis disposition of the hydride and Os−C double bond. As far as we know, the only hydride−carbene complexes previously reported in the osmium-chemistry are the carbonyl derivatives OsHX(CO)(=CHR)(PR′$_3$)$_2$ (X = Cl, O_2CCF_3; R = H, Ph, CO_2Et, $SiMe_3$; PR′$_3$ = P^iPr_3, PMe^tBu_2), with the hydride and carbene ligands mutually trans disposed.[30] In benzene at 25 °C, complex OsHCl(CO)(=CH_2)(P^iPr_3)$_2$ decomposes unselectively to give a mixture of several products.[30a] On the other hand, the related ^{t}Bu$_2$MeP derivative OsHCl(CO)(=CH_2)(PMe^tBu_2)$_2$ isomerizes into the five-coordinate methyl compound Os(CH_3)Cl(CO)(PMe^tBu_2)$_2$.[30b,d]

The behavior of **2** differs from those previously mentioned. In acetonitrile under reflux, complex **2** releases 1,1-diphenyl-

(30) (a) Werner, H.; Stüer, W.; Laubender, M.; Lehmann, C.; Herbst-Irmer, R. *Organometallics* **1997**, *16*, 2236. (b) Huang, D.; Spivak, G. J.; Caulton, *New J. Chem.* **1998**, *22*, 1023. (c) Werner, H.; Stüer, W.; Wolf, J.; Laubender, M.; Weberndörfer, B.; Herbst-Irmer, R.; Lehmann, C. *Eur. J. Inorg. Chem.* **1999**, 1889. (d) Gérard, H.; Clot, E.; Eisenstein, O. *New J. Chem.* **1999**, *23*, 495. (e) Gandelman, M.; Rybtchinski, B.; Ashkenazi, N.; Gauvin, R. M.; Milstein, D. *J. Am. Chem. Soc.* **2001**, *123*, 5372. (f) Gondelman, M.; Naing, K. M.; Rybtchinski, B.; Poverenov, E.; Ben-David, Y.; Ashkenazi, N.; Gauvin, R. M.; Milstein, D. *J. Am. Chem. Soc.* **2005**, *127*, 15265.

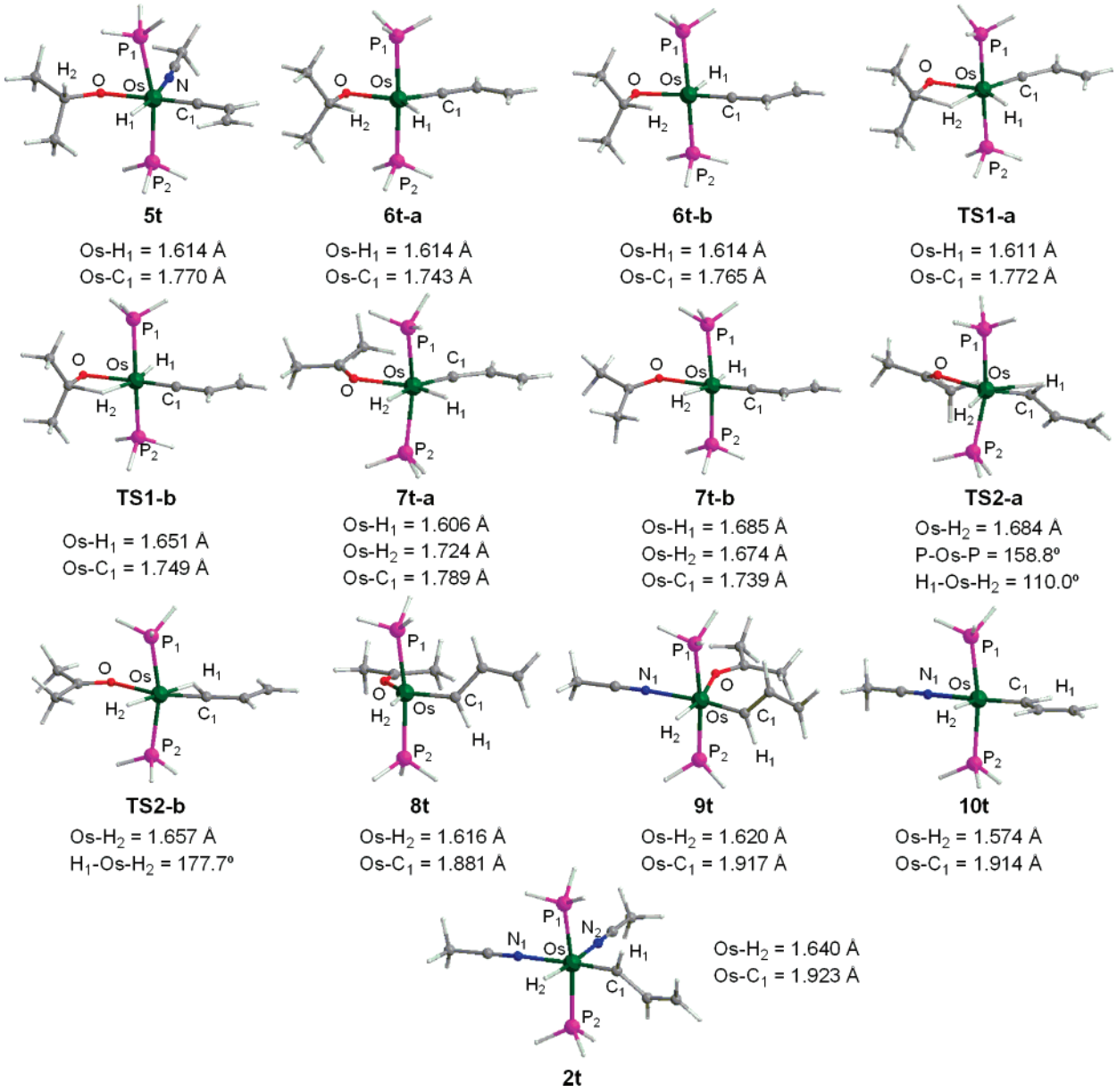
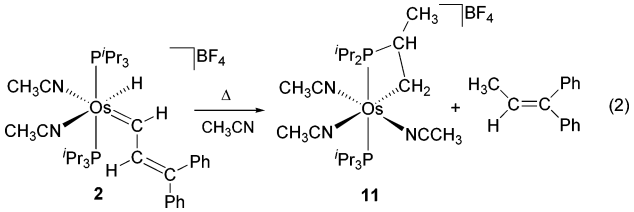


Figure 4. B3PW91 optimized geometries of the intermediates and the transition states for the transformation of **5t** to **2t**.

propene (eq 2) as a result of the hydrogenation of its Os−C double bond. The new hydrogen atoms of the olefin come from the metal center, and from a methyl group of one of the phosphine ligands, which undergoes metalation with the osmium atom. The reaction affords [Os{$CH_2CH(CH_3)$P^{i}Pr$_2$}$(CH_3CN)_3$-(P^{i}Pr$_3$)]BF_4 (**11**) as a brown solid in 83% yield.



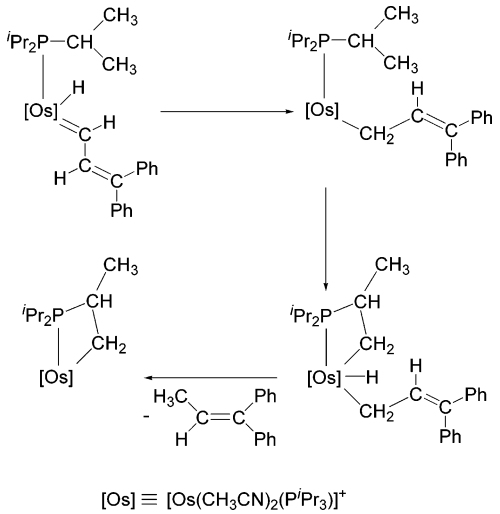
(2)

The presence of a metalated triisopropylphosphine ligand in **11** is strongly supported by its ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra in acetonitrile-d_3. In the ^{1}H NMR spectrum, the most noticeable resonances are those due to the CH_2-protons of the metalated carbon atom, which appear at 1.69 and 0.60 ppm. In the ^{13}C{^{1}H} NMR spectrum, the Os−CH_2 and CH signals of the metalated isopropyl group are observed at −15.6 and 48.4 ppm, respectively. These chemical shifts are similar to those previously reported for related cyclopentadienyl-[14d,25a] and indenyl-osmium compounds.[31] The ^{31}P{^{1}H} NMR spectrum shows two doublets. That corresponding to the metalated phosphine appears at −27.7 ppm, while the other one is observed at 3.0 ppm. In agreement with the mutually trans disposition of these ligands, the P−P coupling constant is 266 Hz.

The formation of the olefin can be rationalized according to Scheme 4. The migration of the hydride ligand to the carbene carbon atom in **2** should lead to an unsaturated σ-allyl intermediate. Thus, the metal center could promote the C(sp^3)−H bond activation of a methyl group of an isopropyl substituent of one of the phosphine ligands, to give a hydride-σ-allyl

(31) Esteruelas, M. A.; López, A. M.; Oñate, E.; Royo, E. *Organometallics* **2005**, *24*, 5780.

Scheme 4



intermediate containing a metalated phosphine. The carbon–hydrogen coupling on the osmium atom should finally afford the olefin, reducing the metal center.

The reaction shown in eq 2 was followed by ^{1}H NMR spectroscopy by measuring the disappearance of the C_α–H resonance of the carbene ligand of **2**, and the appearance of both the CH= resonance of the olefin and one of the Os–CH_2 resonances of **11**. As shown in Figure 5, in acetonitrile-d_3, the decrease of **2** and the increases of the olefin and **11** are exponential functions of the time, in agreement with first-order processes. The three first-order rate constants, collected between 40 and 80 °C, have the same value. The activation parameters obtained from the Eyring analysis are $\Delta H^{\ddagger} = 89.0 \pm 6.3$ kJ mol^{-1} and $\Delta S^{\ddagger} = -43.5 \pm 9.6$ J mol^{-1} K^{-1}. These observations are consistent with the proposal depicted in Scheme 4 and suggest that the rate-determining step for the formation of the olefin is the migratory insertion of the carbene ligand into the Os–H bond of **2**. The negative value of the activation entropy is similar to that reported for the migration of the hydride ligand of $(P^iPr_3)_2(CO)ClRu\{(E)$-CH=CH–$C(CH_2)_4$–CH=C=$\}OsHCl(CO)(P^iPr_3)_2$ from the osmium atom to the C_α atom of the vinylidene group[32] and indicates that the insertion occurs by a concerted mechanism with a geometrically highly oriented transition state.

Concluding Remarks

Until now, the transition metal allenylidenes complexes had shown two different behaviors with alcohols. Those with α-electrophilic nature form α,β-unsaturated alkoxycarbene derivatives, as a result of the 1,2-addition of the O–H bond of the alcohols to the C_α–C_β double bond of the allenylidenes, while those with γ-electrophilic or nucleophilic nature are inert. This Article illustrates new reaction patterns. They appear to be characteristic of very strong nucleophilic species with weak coordinating co-ligands in the sphere of the metal. One of them, general for all alcohols, implies the 1,3-addition of the O–H bond of the alcohols to the metallic center and the C_β atom of the allenylidene and affords novel alkoxy-carbyne derivatives. The other one is particular for primary and secondary alcohols, which can transfer a β-hydrogen to the C_α atom of the carbyne ligand of an alkoxy-carbyne intermediate. The last pattern has afforded the preparation of the novel hydride-alkenylcarbene derivative $[OsH(=CHCH=CPh_2)(CH_3CN)_2(P^iPr_3)_2]BF_4$, as a consequence of the unprecedented hydrogenation of the C_α–C_β double bond of an allenylidene ligand, that of complex $[OsH(=C=C=CPh_2)(CH_3CN)_2(P^iPr_3)_2]BF_4$.

Deuterium labeling experiments and theoretical calculations on this hydrogenation indicate that the β-hydrogen elimination in the alkoxide ligand of the key intermediates $[OsH(OCHR_2)(\equiv CCH=CPh_2)(CH_3CN)(P^iPr_3)_2]^+$ is favored with regard to the migratory insertion of the carbyne into the Os–H bond. However, the presence of a hydride co-ligand in the starting allenylidene complex seems to be determinant for the viability of the reduction. Because the β-hydrogen elimination is the favored reaction in the alkoxide-hydride-carbyne intermediate, the hydrogenation proceeds via a dihydride carbyne species, and the cis disposition of the carbyne group to both hydride ligands (trans between them) is essential to the insertion. While the activation energy for the migratory insertion of the carbyne into an Os–H bond of the *trans*-dihydride is only 62.3 kJ mol^{-1}, it is increased until 160.1 kJ mol^{-1} in the *cis*-dihydride isomer.

Complex $[OsH(=CHCH=CPh_2)(CH_3CN)_2(P^iPr_3)_2]BF_4$ is the unique hydride-carbene known in the osmium-chemistry with the hydride and carbene ligand mutually cis disposed. Its behavior also differs from the behavior observed for the scarce *trans*-hydride-carbene-osmium complexes reported until now. In contrast to the latter, it undergoes hydrogenation of the Os–C double bond. Thus, 1,1-diphenylpropene and the complex $[Os\{CH_2CH(CH_3)P^iPr_2\}(CH_3CN)_3(P^iPr_3)]BF_4$, containing a metalated phosphine, are formed in acetonitrile.

In conclusion, we report an unprecedented sequential and selective hydrogenation of a diphenylallenylidene ligand coordinated to osmium and the mechanism of the formation of the reduced products.

Experimental Section

All reactions were carried out with rigorous exclusion of air using Schlenk-tube techniques. Solvents were dried by the usual procedures and distilled under argon prior to use. The starting material $[OsH(=C=C=CPh_2)(CH_3CN)_2(P^iPr_3)_2]BF_4$ (**1**) was prepared by the published method.[22] ^{1}H, ^{31}P{^{1}H}, ^{19}F, and ^{13}C{^{1}H} NMR spectra were recorded on either a Varian Gemini 2000, a Bruker AXR 300, a Bruker Avance 400 MHz, or a Bruker Avance 500 MHz instrument. Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks (^{1}H, ^{13}C{^{1}H}) or external H_3PO_4 (^{31}P{^{1}H}). Coupling constants, *J* and *N*, are given in hertz. Infrared spectra were run on a Perkin-Elmer 1730 spectrometer (Nujol mulls on polyethylene sheets). C, H, and N analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyzer. GC–MS experiments were run on an Agilent 5973 mass selective detector interfaced to an Agilent 6890 series gas chromatograph system. Samples were injected into a 30 m × 250 μm HP-5MS 5% phenyl methyl siloxane column with a film thickness of 0.25 μm.

Hydrogenation of $[OsH(=C=C=CPh_2)(CH_3CN)_2(P^iPr_3)_2]BF_4$: Formation of $[OsH(=CHCH=CPh_2)(CH_3CN)_2(P^iPr_3)_2]BF_4$ (2). A green solution of **1** (569 mg, 0.653 mmol) in 12 mL of *n*-propanol was stirred for 1 h. The solvent was removed in vacuo. The addition of diethyl ether to the resulting residue led to a green solid, which was washed with diethyl ether and dried in vacuo. Yield: 486 mg (85%). GC–MS analysis of the mother liquor showed the presence of propanal. Anal. Calcd for $C_{37}H_{61}BF_4N_2OsP_2$: C, 50.91; H, 7.04; N, 3.21. Found: C, 50.66; H, 6.96; N, 3.07. IR (Nujol, cm^{-1}): ν(C≡N) 2331 (w), 2265

(32) Buil, M. L.; Esteruelas, M. A. *Organometallics* **1999**, *18*, 1798.

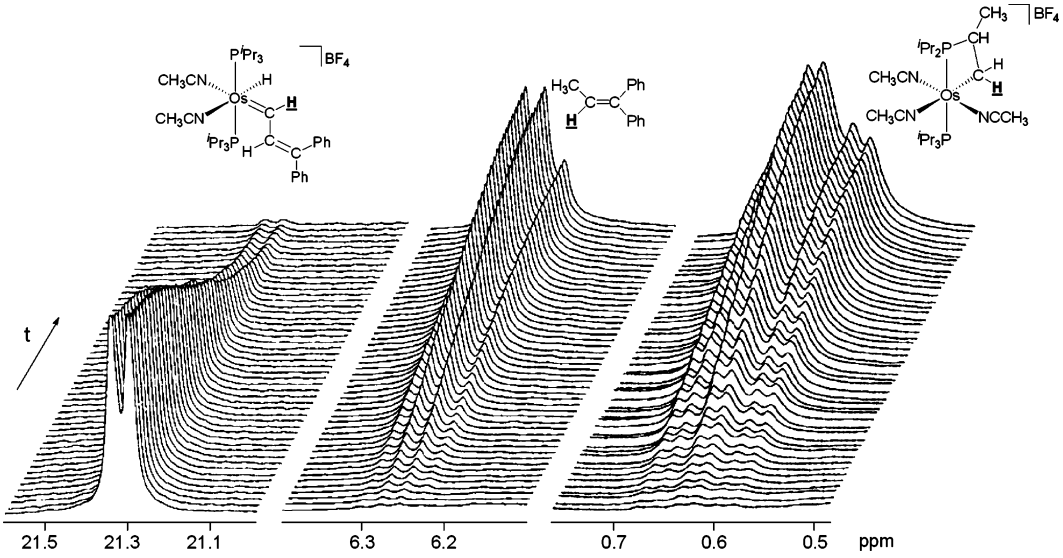


Figure 5. Stacked ^{1}H NMR spectra illustrating the transformation of **2** into **11** and 1,1-diphenylpropene in CD_3CN at 313 K.

(w); ν(OsH) 2172 (m); ν(C═C) 1538 (m); ν(BF) 1061 (vs). ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ 21.35 (d, J_{H-H} = 13.2, 1H, Os═CH), 7.6−7.1 (m, 11H, Ph, −CH═), 2.90 and 2.80 (both s, 6H, CH_3CN), 2.03 (m, 6H, PCH), 1.26 (dvt, N = 13.3 Hz, J_{H-H} = 6.7, 18H, PCHCH_3), 1.15 (dvt, N = 13.5, J_{H-H} = 6.9, 18H, PCHCH_3), −16.27 (t, J_{H-P} = 21.4, 1H, OsH). ^{31}P{^{1}H} NMR (121.4 MHz, CD_2Cl_2, 293 K): δ 22.4 (s). ^{19}F NMR (282.3 MHz, CD_2Cl_2, 293 K): δ −151.8 (br). ^{13}C{^{1}H}-APT NMR plus HMBC and HSQC (75.4 MHz, CD_2Cl_2, 293 K): δ 265.1 (t, J_{C-P} = 8.1, Os═CH), 156.4 (s, −CH═), 143.6 and 142.2 (both s, C_{ipso}−Ph), 141.5 and 125.3 (s, CN), 140.5 (s, ═CPh_2), 129.6, 128.5, 128.0, 127.7, 127.5 and 126.9 (all s, CH_{Ph}), 27.6 (vt, N = 12.7, PCH), 18.7 and 18.6 (both s, PCHCH_3), 3.6 (s, CH_3-CN).

Reaction of [OsH(═C═C═CPh$_2$)(CH$_3$CN)$_2$(P^{i}Pr$_3$)$_2$]BF$_4$ with Phenol: Formation of [OsH(OPh)(≡CCH═CPh$_2$)(CH$_3$CN)(P^{i}Pr$_3$)$_2$]BF$_4$ (3). A green solution of **1** (260 mg, 0.298 mmol) in 10 mL of dichloromethane was treated with phenol (31 mg, 0.328 mmol). After the mixture was stirred for 30 min at room temperature, it was filtered through Celite and the filtrate was evaporated. The addition of diethyl ether afforded a red solid, which was washed with a mixture of diethyl ether/pentane (1:3) and dried in vacuo. Yield: 250 mg (90%). Anal. Calcd for $C_{41}H_{62}BF_4NOOsP_2$: C, 53.30; H, 6.76; N, 1.52. Found: C, 53.53; H, 6.59; N, 1.52. IR (Nujol, cm^{-1}): ν(C≡N) 2319 (w); ν(OsH) 2156 (m); ν(C═C) 1537 (m); ν(BF) 1058 (vs). ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ 7.8−7.2 (m, 10H, Ph), 7.0−6.4 (m, 5H, OPh), 5.40 (s, 1H, ═CH−), 2.74 (s, 3H, CH_3CN), 2.28 (m, 6H, PCH), 1.28 (dvt, N = 13.9 Hz, J_{H-H} = 7.0, 18H, PCHCH_3), 1.27 (dvt, N = 13.9, J_{H-H} = 7.0, 18H, PCHCH_3), −6.72 (t, J_{H-P} = 16.8, 1H, OsH). ^{31}P{^{1}H} NMR (121.4 MHz, CD_2Cl_2, 293 K): δ 27.4 (s). ^{19}F NMR (282.3 MHz, CD_2Cl_2, 293 K): δ −153.0 (br). ^{13}C{^{1}H}-APT NMR plus HMBC and HSQC (75.4 MHz, CD_2Cl_2, 293 K): δ 261.0 (t, J_{C-P} = 12.3, Os≡C), 163.1 (t, J_{C-P} = 8.4, C_{ipso}−OPh), 160.0 (s, ═CPh_2), 139.5 and 138.6 (s, C_{ipso}−Ph), 135.4 (s, −CH═), 131.8, 131.5, 130.7, 129.5, 129.4 and 128.8 (all s, CH_{Ph}), 127.7 (s, CN), 26.9 (vt, N = 12.5, PCH), 19.9 and 19.3 (both s, PCHCH_3), 3.7 (s, CH_3CN).

Reaction of [OsH(═C═C═CPh$_2$)(CH$_3$CN)$_2$(P^{i}Pr$_3$)$_2$]BF$_4$ with *t*-Butanol: Formation of [OsH(O^{t}Bu)(≡CCH═CPh$_2$)(CH$_3$CN)(P^{i}Pr$_3$)$_2$]BF$_4$ (4). A green solution of **1** (150 mg, 0.172 mmol) in 12 mL of *t*-butanol was stirred for 12 h. The solvent was removed in vacuo. The addition of diethyl ether to the resulting residue led to a brown solid, which was washed with diethyl ether and dried in vacuo. Yield: 113 mg (72%). Anal. Calcd for $C_{39}H_{66}BF_4NOOsP_2$: C, 51.82; H, 7.35; N, 1.55. Found: C, 51.53; H, 7.27; N, 1.52. IR (Nujol, cm^{-1}): ν(C≡N) 2313 (w); ν(OsH) 2178 (m); ν(C═C) 1532 (m); ν(BF) 1055 (vs). ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ 7.7−6.6 (m, 10H, Ph), 5.22 (s, 1H, ═CH−), 2.60 (s, 3H, CH_3CN), 2.42 (m, 6H, PCH), 1.32 (dvt, N = 13.6 Hz, J_{H-H} = 7.0, 18H, PCHCH_3), 1.27 (dvt, N = 14.5, J_{H-H} = 7.0, 18H, PCHCH_3), 1.21 (s, −OC(CH_3)$_3$), −3.90 (t, J_{H-P} = 17.4, 1H, OsH). ^{31}P{^{1}H} NMR (121.4 MHz, CD_2Cl_2, 293 K): δ 26.1 (s). ^{19}F NMR (282.3 MHz, CD_2Cl_2, 293 K): δ −153.0 (br). ^{13}C{^{1}H}-APT NMR plus HMBC and HSQC (75.4 MHz, CD_2Cl_2, 293 K): δ 270.7 (t, J_{C-P} = 9.0, Os≡C), 159.1 (s, ═CPh_2), 139.9 and 138.4 (s, C_{ipso}−Ph), 134.1 (s, −CH═), 131.6, 131.3, 130.4, 129.5, 129.4 and 128.7 (all s, CH_{Ph}), 127.0 (s, CN), 68.5 (s, −OC(CH_3)$_3$), 31.0 (s, −OC(CH_3)$_3$), 27.0 (vt, N = 12.4, PCH), 19.8 and 19.2 (both s, PCHCH_3), 3.7 (s, CH_3CN).

Formation of [Os{CH$_2$CH(CH$_3$)}P^{i}Pr$_2$(CH$_3$CN)$_3$(P^{i}Pr$_3$)]BF$_4$ (11). A green solution of **2** (300 mg, 0.344 mmol) in 12 mL of acetonitrile was heated under reflux for 3 h. The solution was filtered through Celite, and the solvent was removed in vacuo. The olefin 1,1-diphenylpropene was extracted from the resultant brown oil with diethyl ether. The subsequent addition of *n*-pentane to the residue led to a brown solid, which was washed with *n*-pentane and dried in vacuo. Yield: 225 mg (83%). Anal. Calcd for $C_{24}H_{47}BF_4N_3OsP_2$: C, 40.22; H, 6.61; N, 5.86. Found: C, 40.64; H, 6.83; N, 5.65. IR (Nujol, cm^{-1}): ν(C≡N) 2238 (w); ν(BF) 1056 (vs). ^{1}H NMR plus ^{1}H{^{31}P} (500 MHz, CD_3CN, 293 K): δ 3.07 (m, 1H, OsCH$_2$CH), 2.59 (s, 6H, CH_3CN), 2.47 (s, 3H, CH_3CN), 2.45 (m, 5H, PCH), 1.69 (dddd, J_{H-P} = 36.5, J_{H-P} = 4.0, J_{H-H} = 9.5, J_{H-H} = 9.5, 1H, OsCH$_2$), 1.4−1.2 (m, 30H, PCHCH_3), 1.45 (dd, J_{H-P} = 12, J_{H-H} = 7, 3H, OsCH$_2$CH(CH_3)), 0.60 (ddd, J_{H-H} = 9.5, J_{H-H} = 9.5, J_{H-P} = 4.5, 1H, OsCH$_2$). ^{31}P{^{1}H} NMR (202.3 MHz, CD_3CN, 293 K): δ 3.0 (d, J_{P-P} = 266, P^{i}Pr$_3$), −27.7 (d, J_{P-P} = 266, P^{i}Pr$_2$CH(CH$_3$)CH$_2$). ^{19}F NMR (282.3 MHz, CD_3CN, 293 K): δ −152.5 (br). ^{13}C{^{1}H}-APT NMR plus HMBC and HSQC (125.6 MHz, CD_3CN, 293 K): δ 121.4, 117.5, and 115.6 (all s, CN), 48.4 (d, J_{C-P} = 27.0, OsCH$_2$CH(CH$_3$)P), 25.7 (d, J_{C-P} = 5.3, OsCH$_2$CH(CH_3)P), 25.4 (d, J_{C-P} = 13.2, PCH), 23.2 (dd, J_{C-P} = 9.9, J_{C-P} = 3.9, PCH), 20.7 (d, J_{C-P} = 15.3, PCH), 21.4, 21.1, 20.1, 20.0, 19.6, and 19.3 (all s, PCHCH_3), 4.6, 4.5, and 3.7 (all s, CH_3CN), −15.6 (dd, J_{C-P} = 18.2, J_{C-P} = 5.3, OsCH$_2$).

1,1-Diphenylpropene. The product was extracted from the residue obtained during the preparation of **11** with diethyl ether. The solution was filtered through Celite and concentrated to dryness. An uncolored oil was obtained. This compound was identified by GC−MS and ^{1}H and ^{13}C{^{1}H} NMR. ^{1}H NMR (500 MHz, CD_3CN, 293 K): δ 7.4−7.1 (m, 10H, Ph), 6.22 (q, J_{H-H} = 7.0, 1H, ═CHCH$_3$), 1.73 (d, J_{H-H} = 7.0, 3H, CH_3). ^{13}C{^{1}H}-APT NMR plus HMBC and HSQC (125.6

MHz, CD_3CN, 293 K): δ 143.9 and 140.9 (s, C_{ipso}–Ph), 143.3 (s, CPh_2), 130.7, 129.2, 129.1, 127.9 and 127.7 (all s, Ph), 125.0 (s, $=CHCH_3$), 15.8 (CH_3).

Preparation of BPh_4 Salt of 2. A green solution of **2** (200 mg, 0.229 mmol) in 10 mL of dichloromethane was treated with $NaBPh_4$ (157 mg, 0.458 mmol). After the mixture was stirred for 1 h at room temperature, the suspension was filtered through Celite and the filtrate was evaporated to dryness. The addition of diethyl ether afforded a green solid, which was washed with diethyl ether and dried in vacuo. Yield: 225 mg (89%). The $^{31}P\{^1H\}$ and ^1H NMR (300 MHz, CD_2Cl_2, 293 K) data are identical to those reported for **2** with the exception of the appearance of the resonance at 7.6−6.9 (m, 30 H, Ph).

Reaction of [OsH(OPh)(=CCH=CPh$_2$)(CH$_3$CN)(P^{i}Pr$_3$)$_2$][BF$_4$] with 2-Propanol-d_8. An NMR tube charged with **3** (20 mg, 0.022 mmol) was cooled to −30 °C, and then 0.5 mL of 2-propanol-d_8 was added. At this temperature, the ^1H and ^{31}P NMR spectra of the resulting brown solution showed, in addition to the resonances of **3**, the following representative signals: ^1H NMR (400 MHz, ^{i}PrOD, 243 K): δ 5.38 (s, 1H, =CH−), −6.28 (t, J_{H-P} = 17.7, 1H, OsH). $^{31}P\{^1H\}$ NMR (161.9 MHz, ^{i}PrOD, 243 K): δ 28.7 (s). The solution was led to reach room temperature, and, after addition of 20 μL of CH_3CN, the ^1H and ^{31}P NMR spectra showed the appearance of **2-d_1**. Next, the solution was concentrated to dryness, and 0.5 mL of 2-propanol was added. ^2H NMR (61.5 MHz, ^{i}PrOH, 293 K): δ 21.35 (br, 0.4D, Os=CD), −16.27 (br, 0.6D, OsD).

Kinetic Analysis for Hydrogenation of the Os−C Double Bond. The formation of 1,1-diphenylpropene and **11** was followed quantitatively by ^1H NMR spectroscopy in CD_3CN. The decrease of the intensity of low field carbene-proton was measured automatically at intervals in a Varian Gemini 2000 spectrometer. Rate constants and errors were obtained fitting the data to an exponential decay function using the routine programs of the spectrometer. Activation parameters $\Delta H^\ddagger$ and $\Delta S^\ddagger$ were obtained by least-squares fit of the Eyring plot. Errors were computed by published methods.[33]

Computational Details. The calculations have been carried out using the Gaussian 03 computational package.[34] All the structures have been optimized using DFT and the B3PW91 functional. The 6-31g** basis set has been used for all the non-hydrogen atoms and hydride ligands (6-31g for the rest of hydrogens) but the Os, where the LANL2DZ basis and pseudopotential has been used instead. The transition states found have been confirmed by frequency calculations, and the connection between the starting and final reactants has been checked by slightly perturbing the TS geometry toward the minima geometries and reoptimizing.

Crystal Data for 2 and 3. Complex **2**: $C_{37}H_{61}N_2OsP_2$,$C_{24}H_{20}B\cdot0.25CH_2Cl_2$, M_w 1126.46, green, irregular block (0.10 × 0.8 × 0.02 mm), monoclinic, space group *P*2/*c*, *a* 18.323(2) Å, *b* 18.073(2) Å, *c* 17.688(2) Å, β 93.657(2)°, V = 5845.5(12) Å^3, Z = 4, D_{calc} 1.280 g cm^{-3}, F (000) 2330, T = 100.0(2) K. Bruker SMART APEX CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube source (Molybdenum radiation, λ = 0.71073 Å, μ 2.296 mm^{-1}) operating at 50 kV and 40 mA. 50 743 measured reflections (2θ: 3−55°, ω scans 0.3°), 13 312 unique (R_{int} = 0.0732); multiscan absorption correction applied (SADABS program),[35] with min./max.transm.factors 0.750/0.955. Structure solved by Patterson and difference Fourier maps; refined using SHELXTL.[36] Final agreement factors were R1 = 0.0668 (8562 observed reflections, $I > 2\sigma(I)$) and wR^2 = 0.1735; data/restrains/parameters 13 312/106/583; GoF = 1043. Largest peak and hole 2.742 and −0.960 e/Å^3. Complex **3**: $C_{41}H_{62}NP_2OOs$, $BF_4\cdot0.5OC_4H_{10}$, M_w 960.93, orange, irregular block (0.18 × 0.12 × 0.09 mm), monoclinic, space group $P2_1/c$, *a* 14.6813(19) Å, *b* 13.9813(17) Å, *c* 21.656(3) Å, β 90.816(2)°, V = 4444.8(10) Å^3, Z = 4, D_{calc} 1.436 g cm^{-3}, F (000) 1964, T = 100.0(2) K. Bruker SMART APEX CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube source (Molybdenum radiation, λ = 0.71073 Å, μ 2.991 mm^{-1}) operating at 50 kV and 40 mA. 28 234 measured reflections (2θ: 3−56°, ω scans 0.3°), 10 722 unique (R_{int} = 0.0544); multiscan absorption correction applied (SADABS program),[35] with min./max.transm.factors 0.621/0.745. Structure solved by Patterson and difference Fourier maps; refined using SHELXTL.[36] Final agreement factors were R1 = 0.0453 (7467 observed reflections, $I > 2\sigma(I)$) and wR^2 = 0.0753; data/restrains/parameters 10 722/1/513; GoF = 0.886. Largest peak and hole 1.847 and −1.421 e/Å^3.

The carbene ligand of complex **2** shows static disorder over the carbene ligand due to a small rotation of about 10° around the C(2)−C(3) single bond. This disorder is modeled with two moieties with complementary occupancy factors (0.23/0.77) and isotropic thermal parameters due to the proximity of the atoms. The solvent CH_2Cl_2 and $CH_3CH_2OCH_2CH_3$ molecules of **2** and **3** were also observed disordered. Furthermore, the hydride ligands did not refine properly neither for **2** nor for **3**. Because of that, the Os−H distances were fixed to 1.59(1) (average value found in The Cambridge Structural Database).

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Supporting Information Available: Complete ref 34, orthogonal coordinates of theoretical structures, and crystal structure determinations, including bond lengths and angles of compounds **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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