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Hydride-Carbyne to Carbene Transformation in an Osmium-Acetate-Bis(triisopropylphosphine) System: Influence of the Coordination Mode of the Carboxylate and the Reaction Solvent

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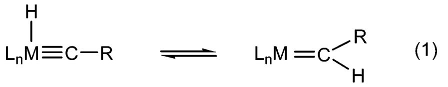
The bis-solvato hydride-allenylidene complex $[OsH({=}C{=}C{=}CPh_2)(CH_3CN)_2(P^iPr_3)_2]BF_4$ (**1**) reacts with acetic acid to give the hydride-carbyne $[OsH(\kappa^2\text{-}O_2CCH_3)({\equiv}CCH{=}CPh_2)(P^iPr_3)_2]BF_4$ (**2**), which in 1,2-dichloroethane under reflux is stable and does not evolve into its five-coordinate carbene isomer. In acetonitrile at room temperature, complex **2** is in equilibrium with $[OsH\{\kappa^1\text{-}OC(O)CH_3\}({\equiv}CCH{=}CPh_2)(CH_3CN)(P^iPr_3)_2]BF_4$ (**4**; $\Delta H° = -6.4 \pm 0.3$ kcal·mol^{-1}, $\Delta S° = -22.9 \pm 1.1$ eu). At 353 K, complex **4** is transformed into the carbene $[Os\{\kappa^1\text{-}OC(O)CH_3\}({=}CHCH{=}CPh_2)(CH_3CN)_2(P^iPr_3)_2]BF_4$ (**5**; 40%), which is obtained in high yield (88%) by reaction of $[Os({=}CHCH{=}CPh_2)(CH_3CN)_3(P^iPr_3)_2][BF_4]_2$ with sodium acetate in 2-propanol. The hydride-carbyne to carbene transformation is analyzed by DFT calculations.

Introduction

Rates and equilibrium positions of chemical reactions, including intramolecular redox processes, are solvent-dependent. Responsible for this medium effect is the different solvation of reactants and products (position of the equilibria) or reactants and activated species (rates of chemical reactions).[1]

One of the most relevant redox processes in the organometallic field is the C−H reductive elimination.[2] For alkyl and hydrocarbyl hydride complexes of late transition metals Pt, Ir, Rh, Os, and Ru, some reactions are proposed to go by direct elimination, while others require ligand dissociation prior to the C−H coupling.[3] For both cases, the presence of a chelate ligand *trans* disposed to the coupled fragments prevents the C−H bond formation.[4]

Complexes $OsHCl_2({\equiv}CR)(PR'_3)_2$[5] are stable isomers of the unknown compounds $OsCl_2({=}CHR)(PR'_3)_2$, which should be the osmium counterparts to the Grubbs-type carbene-ruthenium derivatives, $RuCl_2({=}CHR)(PR'_3)_2$.[6] In order to rationalize these findings, one can argue that the migration of the hydride from the metal center to the carbyne carbon atom (eq 1) involves a simple intramolecular reductive elimination.[7] It is well-known that 5d metals favor the oxidized species, while the 4d counterparts protect the reduced ones. In agreement with the redox character of eq 1, we have recently shown that the position of the equilibrium and the activation energy from the hydride migration are governed by the co-ligands, which determine the electron richness of the metal center.[8]



(1)

Electron-rich compounds are susceptible to oxidation. In this context it should be mentioned that there is a class of allenylidene derivatives, $L_nM{=}C{=}C{=}CR_2$, that show the typical behavior of Lewis base transition metal complexes.[9] EHT-MO

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[1] See for example: (a) Weaver, M. J. *Chem. Rev.* **1992**, *92*, 463. (b) Reichardt, C. *Chem. Rev.* **1994**, *94*, 2319.

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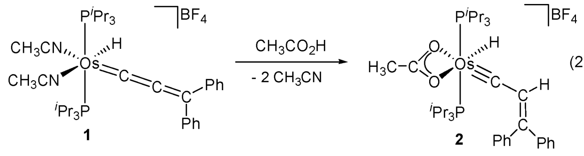
calculations indicate that the HOMO orbital of these species is mainly located at the C_β atom of the unsaturated chain.[10] In accordance with this, the reactions of these compounds with electrophiles lead to alkenylcarbyne derivatives, which are stable with electron-rich coligands.[11] When some of the R substituents of the unsaturated chain are phenyl groups and the complex contains π-acidic ligands, the reduction into the corresponding metal-indenylidene compound, an isomer of the starting allenylidene, is observed.[12]

Results and Discussion

The recently reported[13] bis-solvento hydride-allenylidene complex $[OsH(=C=C=CPh_2)(CH_3CN)_2(P^iPr_3)_2]BF_4$ (**1**) appears to be a member of the family of electron-rich species, despite that one should expect an electron-poor character for the metal center. Thus, in dichloromethane at room temperature, it reacts with a stoichiometric amount of acetic acid to afford the hydride-alkenylcarbyne derivative $[OsH(\kappa^2\text{-}O_2CCH_3)(\equiv CCH=CPh_2)(P^iPr_3)_2]BF_4$ (**2**), containing a chelate acetate ligand (eq 2). This complex, which is isolated as a pink solid in 93% yield, is the result of the addition of the proton of the weak acid to the C_β atom of the allenylidene ligand and the carboxylate group to the metal center.



(2)

Figure 1 shows a view of the geometry of the cation of **2**. The coordination around the osmium atom can be rationalized as a distorted octahedron with the phosphorus atoms of the phosphine ligands occupying *trans* positions (P(1)−Os−P(2) = 166.47(4)°). The perpendicular plane is formed by the bidentate ligand, which acts with a bite angle O(1)−Os−O(2) of 58.66(10)°, the hydride *trans* disposed to O(2) (O(2)−Os−H(O1) = 153.5(15)°) and the carbyne group *trans* disposed to O(1) (C(1)−Os−O(1) = 177.62(15)°). The acetate group coordinates in an asymmetrical fashion, with the separation between the metal center and O(2) (2.203(3) Å) being about 0.02 Å shorter than the Os−O(1) distance (2.228(3) Å). The Os−C(1) bond length of 1.740(4) Å is fully consistent with an Os−C triple bond formulation.[5a,8,14] Similarly to other carbyne-metal compounds[15] a slight bending in the Os−C(1)−C(2) moiety is also present (Os−C(1)−C(2) = 171.2(3)°). 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 1.415(5) Å, and C(2) and C(3) by 1.358(6) Å, and the angles around C(2) and C(3) are in the range 111−125°.

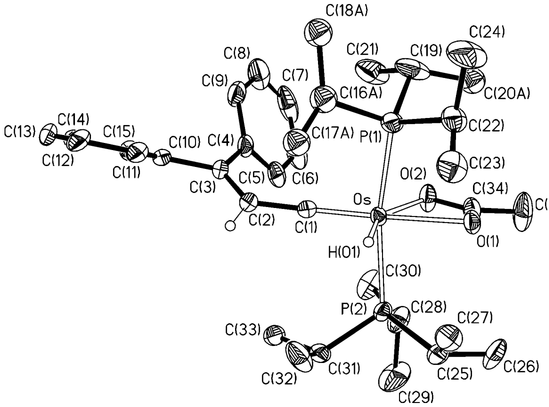


Figure 1. Molecular diagram of the cation of **2**. Selected bond lengths (Å) and angles (deg): Os−O(1) 2.228(3), Os−O(2) 2.203(3), Os−C(1) 1.740(4), C(1)−C(2) 1.415(5), C(2)−C(3) 1.358(6); P(1)−Os−P(2) 166.47(4), O(1)−Os−O(2) 58.66(10), O(1)−Os−C(1) 177.62(15), O(2)−Os−H(01) 153.5(15).

The IR spectrum of **2** in dichloromethane shows the ν_{asym}(OCO) band at 1535 cm^{-1} and the ν_{sym}(OCO) band at 1471 cm^{-1}. The value of $\Delta\nu$ ($\Delta\nu = \nu_{\text{asym}}(\text{OCO}) - \nu_{\text{sym}}(\text{OCO})$) of 64 cm^{-1} is consistent with the bidentate coordination mode of the acetate group.[16] In agreement with the presence of a hydride ligand in the complex, its ^{1}H NMR spectrum shows a triplet at −7.80 ppm with a H−P coupling constant of 15.7 Hz. In the low-field region of the spectrum, the most noticeable signal is a singlet at 5.14 ppm corresponding to the C(sp^2)−H proton of the alkenyl substituent of the carbyne ligand. In the $^{13}C\{^1H\}$ NMR spectrum the Os−C_α resonance appears at 272.7 ppm, as a triplet with a C−P coupling constant of 8.0 Hz. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 42.6 ppm.

Complex **2** is stable in 1,2-dichloroethane, even under reflux for 24 h. It does not undergo reduction into an indenylidene species by loss of molecular hydrogen, acetic acid, or tetrafluoroboric acid, nor is its transformation into a five-coordinate carbene isomer observed. In agreement with this, DFT calculations on the model system $[Os(HCO_2)H(\equiv CCH=CH_2)(PMe_3)_2]^+$ indicate that the five-coordinate carbene cation $[Os(\kappa^2\text{-}O_2CH)$-

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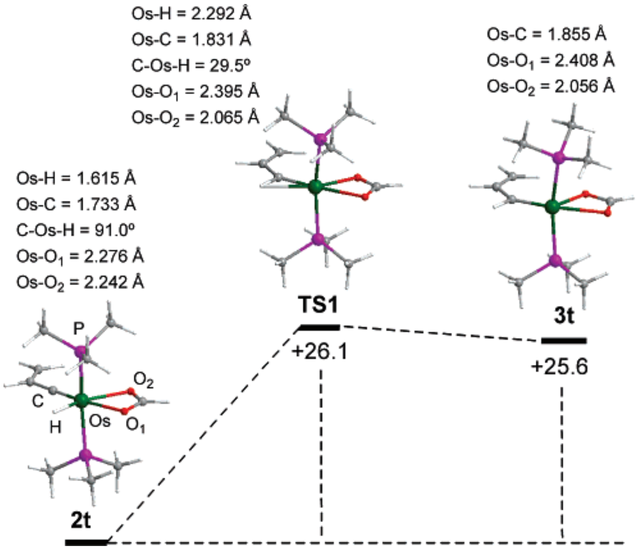
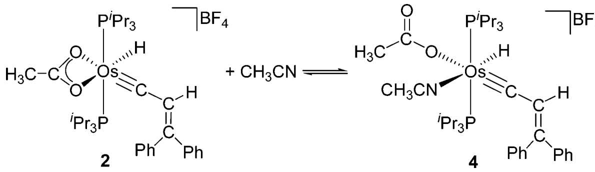


Figure 2. Optimized structures and relative energies (kcal·mol^{-1}) of **2t**, **TS1**, and **3t**.

(=CHCH=CH$_2$)(PMe$_3$)$_2$]$^+$ (**3t**) lies 25.6 kcal·mol^{-1} above the hydride-carbyne [OsH(κ^2-O$_2$CH)(≡CCH=CH$_2$)(PMe$_3$)$_2$]$^+$ (**2t**). Furthermore the activation barrier for the transformation from **3t** into **2t** via an η^2-carbene transition state [Os(κ^2-O$_2$CH){=C(CH=CH$_2$)H}(PMe$_3$)$_2$]$^+$ (**TS1**), similar to those proposed for related systems containing only monodentate ligands,[8] is very low (0.5 kcal·mol^{-1}). The η^2-coordination mode shown in Figure 2 for the carbene ligand of **TS1** has been observed in alkylidene complexes of electron-deficient transition metals.[17]

In acetonitrile, complex **2** is in equilibrium with the solvento species [OsH{κ^1-OC(O)CH$_3$}(≡CCH=CPh$_2$)(CH$_3$CN)(P^{i}Pr$_3$)$_2$]BF$_4$ (**4**), resulting from the displacement of the oxygen atom of the carboxylate, *trans* disposed to the hydride ligand, by a solvent molecule (eq 3).



(3)

The monodentate coordination mode of the carboxylate in **4** is strongly supported by the IR spectrum of this compound in acetonitrile, which shows the ν(OCO) bands at 1639 and 1310 cm^{-1} ($\Delta\nu$ = 329 cm^{-1}). The replacement of the oxygen atom by the acetonitrile molecule produces slight changes on the electron density at the metal center, which are evident in the chemical shifts of the hydride, carbyne carbon atom, and phosphine resonances in the ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra. These resonances appear at −5.7 (J_{H-P} = 17.1 Hz), 268.5 (J_{C-P} = 10.6 Hz), and 28.5 ppm. In comparison with **2**, they are shifted 2.1 ppm toward lower field, 4.2 ppm toward higher field, and 14.1 ppm toward higher field, respectively.

The constants for the equilibrium shown in eq 3 were determined, between 233 and 303 K, by integration of the hydride resonances. A linear-square analysis of ln K versus 1/T provides values of $\Delta H° = -6.4 \pm 0.3$ kcal·mol^{-1} and $\Delta S° = -22.9 \pm 1.1$ eu. The value of $\Delta H°$ agrees with DFT calculations, indicating that the formation of the model cation [OsH{κ^1-OC(O)H}(≡CCH=CH$_2$)(CH$_3$CN)(PMe$_3$)$_2$]$^+$ (**4t**), from **2t** and acetonitrile, is exothermic by 11.1 kcal·mol^{-1}.

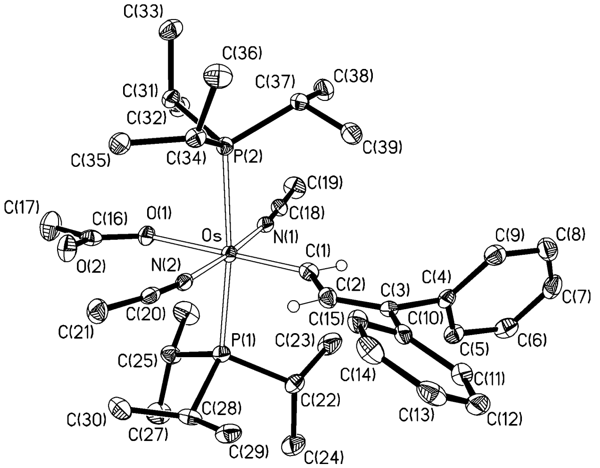
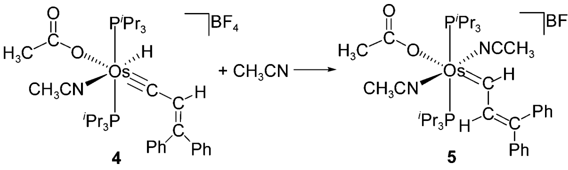


Figure 3. Molecular diagram of the cation of **5**. Selected bond lengths (Å) and angles (deg): Os−O(1) 2.1750(18), Os−C(1) 1.909(3), O(1)−C(16) 1.275(3), O(2)−C(16) 1.229(3), C(1)−C(2) 1.439(4), C(2)−C(3) 1.355(4); P(1)−Os−P(2) 172.93(2), O(1)−Os−C(1) 174.21(10), N(1)−Os−N(2) 175.79(9).

Complex **4** has a higher tendency than **2** to undergo reduction into the carbene form. Thus, the acetonitrile solution of **4** affords the carbene derivative [Os{κ^1-OC(O)CH$_3$}(=CHCH=CPh$_2$)(CH$_3$CN)$_2$(P^{i}Pr$_3$)$_2$]BF$_4$ (**5**) in 40% yield, after 12 h at 353 K (eq 4). In addition to **5**, a complex mixture of other unidentified products without any acetate ligand is also formed. Complex **5** is obtained as a pure yellow solid in 88% yield, by treatment at room temperature of 2-propanol solutions of the previously reported carbene compound [Os(=CHCH=CPh$_2$)(CH$_3$CN)$_3$(P^{i}Pr$_3$)$_2$][BF$_4$]$_2$[8] with 5.0 equiv of sodium acetate.



(4)

Figure 3 shows a view of the geometry of the cation of **5**. The coordination 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) = 172.93(2)°). The perpendicular plane is formed by the acetonitrile molecules *trans* disposed (N(1)−Os−N(2) = 175.79(9)°) and the carbene ligand *trans* disposed to the monodentate acetate group (C(1)−Os−O(1)) = 174.21(10)°). The Os−C(1) bond length of 1.909(3) Å supports the Os−C double bond formulation.[8,18] In agreement with the sp^2 hybridization at C(1), the angles around this atom are between 110.9(17)° and 129.5(2)°. The parameters of the alkenyl moiety agree well with those of **2**. The C(1)−C(2) distance is 1.439(4) Å, whereas the C(2)−C(3) bond length is 1.355(4) Å, and the angles around C(2) and C(3) are in the range 112−128°.

In the IR spectrum of **5** in Nujol the ν(OCO) bands of the monodentate acetate ligand appear at 1611 and 1324 cm^{-1} ($\Delta\nu$ = 287 cm^{-1}). In dichloromethane at room temperature, the coordination mode of the acetate does not undergo any changes. Thus, the IR spectrum in this solvent shows the ν(OCO) bands

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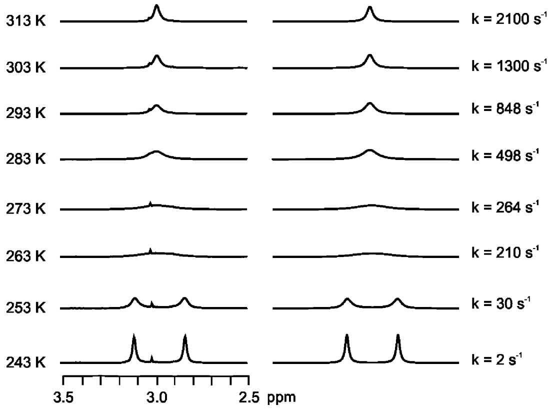

Figure 4. Variable-temperature $^1H\{^{31}P\}$ NMR spectra in the acetonitrile region of $[Os\{\kappa^1\text{-}OC(O)CH_3\}(=CHCH=CPh_2)(CH_3CN)_2(P^iPr_3)_2]BF_4$ (**5**): experimental (left) and calculated (right).

at the same wavenumbers as in Nujol. In dichloromethane-d_2, the ^1H and $^{13}C\{^1H\}$ NMR spectra are temperature-dependent. Figure 4 shows the variable-temperature $^1H\{^{31}P\}$ NMR spectra in the acetonitrile region. According to Figure 3, the hydrogen and alkenyl substituents of the carbene carbon atom lie in the plane containing the nitrogen atoms. As a result, the acetonitrile molecules are chemically inequivalent. In agreement with this, the spectrum at 233 K contains two resonances for the acetonitrile methyl groups at 3.14 and 2.93 ppm. On raising the temperature, they coalesce to give only one resonance. This behavior can be understood as the result of the rotation of the alkenylcarbene ligand around the Os−C double bond. Line shape analysis of the acetonitrile methyl resonances allows the calculation of the rate constants for the rotation process. The activation parameters obtained from the corresponding Eyring analysis are $\Delta H^‡ = 12.8 \pm 0.5$ kcal·mol^{-1} and $\Delta S^‡ = -1.0 \pm 1.1$ eu. The value of the activation entropy, near zero, is consistent with a rotational process, whereas the value of the activation enthalpy lies within the range reported for other transition metal complexes.[8,19] In addition to the acetonitrile methyl resonances, those corresponding to the C_α-H and C_β−H protons of the carbene ligand should be mentioned, which appear at 20.70 and 7.99 ppm as doublets with a H−H coupling constant of 13.5 Hz. In the $^{13}C\{^1H\}$ NMR spectrum the Os−C_α resonance is observed at 259.5 ppm, as a triplet with a C−P coupling constant of 8.7 Hz. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 0.9 ppm.

The formation of **5** according to eq 4 indicates that, in contrast to 1,2-dichloroethane, acetonitrile favors the hydride-carbyne to carbene transformation. DFT calculations shows that the formation of the six-coordinate carbene cation $[Os\{\kappa^1\text{-}OC(O)H\}(=CHCH=CH_2)(CH_3CN)_2(PMe_3)_2]^+$ (**5t**) from the hydride-carbyne **4t** takes place via the five-coordinate intermediate $[Os\{\kappa^1\text{-}OC(O)H\}(=CHCH=CH_2)(CH_3CN)(PMe_3)_2]^+$ (**6t**), which lies 21.9 kcal·mol^{-1} above **4t**. The coordination of an acetonitrile molecule to **6t** is exothermic by 44.9 kcal·mol^{-1}.

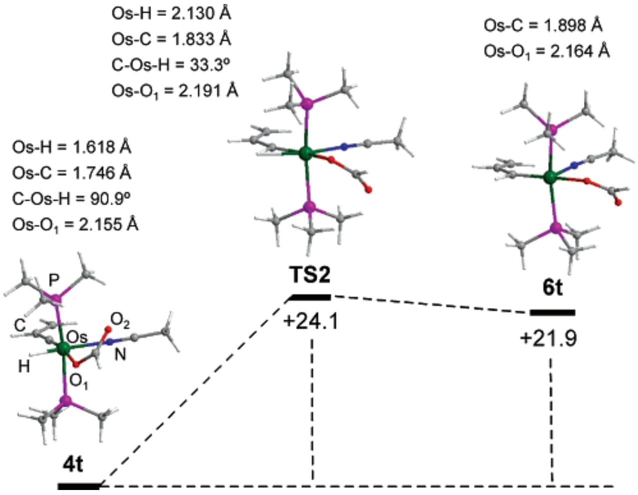

Figure 5. Optimized structures and relative energies (kcal·mol^{-1}) of **4t**, **TS2**, and **6t**.

The η^2-carbene transition state $[Os\{\kappa^2\text{-}OC(O)H\}\{=C(CH=CH_2)H\}(CH_3CN)(PMe_3)_2]^+$ (**TS2**) connecting **4t** and **6t** (Figure 5) is 24.1 kcal above **4t**. Since the $\kappa^2-\kappa^1$ transformation of the acetate group by addition of acetonitrile to **2t**, to form **4t**, is exothermic by 11.1 kcal·mol^{-1}, and the difference in energy between **TS1** and **2t** of 26.1 kcal·mol^{-1} is higher than that between **TS2** and **4t**, one can assert that the $\kappa^2-\kappa^1$ transformation of the acetate group facilitates the hydride-carbyne to carbene transformation.

In conclusion, for this osmium-acetate-bis(phosphine) system, the κ^2-coordination of the acetate increases the difference in stability between the stable hydride-carbyne form and the carbene, while the κ^1-coordination facilitates the hydride-carbyne to carbene transformation, lowering its activation energy. A coordinating solvent such as acetonitrile stabilizes the carbene form, by coordination to the five-coordinate intermediate resulting from the migratory insertion of the carbyne into the metal−hydride bond.

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 materials **1** and $[Os(=CHCH=CPh_2)(CH_3CN)_3(P^iPr_3)_2][BF_4]_2$ were prepared by published methods.[8,13] Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks (^1H, $^{13}C\{^1H\}$) or external H_3PO_4 ($^{31}P\{^1H\}$). Coupling constants, *J* and *N*, are given in hertz.

Preparation of $[OsH(\kappa^2\text{-}O_2CCH_3)(\equiv CCH=CPh_2)(P^iPr_3)_2]BF_4$ (2). A solution of **1** (100 mg, 0.114 mmol) in 5 mL of dichloromethane was treated with acetic acid (7 μL, 0.114 mmol). After stirring the mixture for 30 min at room temperature, it was filtered through Celite, and the filtrate was evaporated. The addition of diethyl ether to the resulting residue led to a pink solid, which was washed with diethyl ether and dried in vacuo. Yield: 89 mg (93%). Anal. Calcd for $C_{35}H_{57}BF_4O_2OsP_2$: C 49.53; H 6.77. Found: C 49.36; H 6.33. IR (Nujol, cm^{-1}): ν(OsH) 2179 (m); ν_{asym}(OCO) 1530 (s); ν_{sym}(OCO) 1465 (s); ν(BF) 1051 (vs). MS: *m/z* 762 (M)$^+$. ^1H NMR (300 MHz, CD_2Cl_2, 293 K): δ 7.6−7.2 (m, 10H, Ph),

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(18) See for example: (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) Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2005**, *24*, 4343. (j) Esteruelas, M. A.; Fernández-Álvarez, F. J.; Oliván, M.; Oñate, E. *J. Am. Chem. Soc.* **2006**, *128*, 4596. (k) Esteruelas, M. A.; Fernández-Álvarez, F. J.; Oñate, E. *J. Am. Chem. Soc.* **2006**, *128*, 13044.

(19) See for example: (a) Kegley, S. E.; Brookhart, M.; Husk, G. R. *Organometallics* **1982**, *1*, 760. (b) Gunnoe, T. B.; White, P. S.; Templeton, J. L. *Organometallics* **1997**, *16*, 370.

5.14 (s, 1H, $=$CH$-$), 2.43 (m, 6H, PCH), 1.79 (s, 3H, O$_2$CCH$_3$), 1.33 (dvt, $N = 14.1$, $J_{\mathrm{H-H}} = 7.2$, 18H, PCHCH_3), 1.28 (dvt, $N = 15.0$, $J_{\mathrm{H-H}} = 7.2$, 18H, PCHCH_3), -7.80 (t, $J_{\mathrm{H-P}} = 15.7$, 1H, OsH). ^{31}P{^{1}H} NMR (121.4 MHz, CD$_2$Cl$_2$, 293 K): δ 42.6 (s). ^{19}F NMR (282.3 MHz, CD$_2$Cl$_2$, 293 K): δ -153.6 (br). ^{13}C{^{1}H}-APT NMR plus HMBC and HSQC (100.5 MHz, CD$_2$Cl$_2$, 293 K): δ 272.7 (t, $J_{\mathrm{C-P}} = 8.0$, Os$\equiv$C), 187.2 (t, $J_{\mathrm{C-P}} = 2.3$, C$=$O), 162.6 (s, $=$$CPh_2$), 139.2 and 137.9 (both s, C$_{\mathrm{ipso}}$$-$Ph), 132.5 (s, $-$CH$=$), 132.0, 130.3, 129.5, 129.4, 129.5, and 128.8 (all s, CH$_{\mathrm{Ph}}$), 27.1 (vt, $N = 13.5$, PCH), 25.8 (s, O$_2$CCH$_3$), 19.5 and 19.2 (both s, PCHCH$_3$).

Formation and Characterization of [OsH(κ^1-O$_2$CCH$_3$)(CD$_3$CN)($\equiv$CCH$=$CPh$_2$)(P^{i}Pr$_3$)$_2$]BF$_4$ (4). Complex **2** in acetonitrile-d_3 gave an equilibrium mixture with **4**. IR (CH$_3$CN, cm^{-1}): ν(OsH) 2191 (m); ν_{asym}(OCO) 1639 (s); ν_{sym}(OCO) 1310 (s); ν(BF) 1105 (vs). Spectroscopy data for **4**: ^{1}H NMR (300 MHz, CD$_3$CN, 233 K): δ 7.8$-$7.3 (m, 10H, Ph), 5.38 (s, 1H, $=$CH$-$), 2.33 (m, 6H, PCH), 1.70 (s, 3H, O$_2$CCH$_3$), 1.31 (dvt, $N = 13.9$, $J_{\mathrm{H-H}} = 7.0$, 18H, PCHCH_3), 1.28 (dvt, $N = 13.9$, $J_{\mathrm{H-H}} = 6.7$, 18H, PCHCH_3), -5.7 (t, $J_{\mathrm{H-P}} = 17.1$, 1H, OsH). ^{31}P{^{1}H} NMR (121.4 MHz, CD$_2$Cl$_2$, 293 K): δ 28.5 (s). ^{13}C{^{1}H}-APT NMR plus HMBC and HSQC (75.4 MHz, CD$_3$CN, 233 K): δ 268.5 (t, $J_{\mathrm{C-P}} = 10.6$, Os$\equiv$C), 173.9 (s, C$=$O), 162.8 (s, $=$$CPh_2$), 139.7 and 138.9 (both s, C$_{\mathrm{ipso}}$$-$Ph), 135.4 (s, $-$CH$=$), 132.2, 132.1, 131.4, 129.9, 129.8, and 129.7 (all s, CH$_{\mathrm{Ph}}$), 118.7 (s, CN), 27.7 (br, PCH), 24.3 (s, O$_2$CCH$_3$), 20.1 and 18.9 (both s, PCHCH$_3$), 1.24 (CH$_3$CN).

Preparation of [Os(κ^1-O$_2$CCH$_3$)($=$CHCH$=$CPh$_2$)(CH$_3$CN)$_2$(P^{i}Pr$_3$)$_2$]BF$_4$ (5). A solution of [Os($=$CHCH$=$CPh$_2$)(CH$_3$CN)$_3$(P^{i}Pr$_3$)$_2$][BF$_4$]$_2$ (155 mg, 0.155 mmol) in 10 mL of 2-propanol was treated with sodium acetate (107 mg, 0.775 mmol). After stirring the mixture for 12 h at room temperature, the solvent was removed in vacuo. Then, 10 mL of dichloromethane was added, the suspension was filtered through Celite, and the filtrate was evaporated to dryness. The residue was washed with diethyl ether to afford a yellow solid. Yield: 127 mg (88%). Anal. Calcd for C$_{39}$H$_{63}$BF$_4$N$_2$O$_2$OsP$_2$: C 47.29; H 6.45; N 2.76. Found: C 47.56; H 6.13; N 2.77. IR (Nujol, cm^{-1}): ν(C$\equiv$N) 2327 (w), 2273 (w); ν_{asym}(OCO) 1611 (s); ν_{sym}(OCO) 1324 (s); ν(BF) 1056 (vs). MS: m/z 846 [M + H]$^+$, 685 [M $-$ P^{i}Pr$_3$]$^+$, 603 [M $-$ P^{i}Pr$_3$ $-$ 2CH$_3$CN]$^+$. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$, 233 K): δ 20.70 (d, $J_{\mathrm{H-H}} = 13.5$, 1H, Os$=$CH), 7.99 (d, $J_{\mathrm{H-H}} = 13.5$, 1H, $-$CH$=$), 7.9$-$7.1 (m, 10H, Ph), 3.14 and 2.93 (both s, 6H, CH$_3$CN), 2.29 (m, 6H, PCH), 2.03 (s, 3H, O$_2$CCH$_3$), 1.20 (m, 36H, PCHCH_3). ^{31}P{^{1}H} NMR (121.4 MHz, CD$_2$Cl$_2$, 233 K): δ 0.9 (s). ^{19}F NMR (282.3 MHz, CD$_2$Cl$_2$, 293 K): δ -152.9 (br). ^{13}C{^{1}H}-APT NMR plus HMBC and HSQC (75.4 MHz, CD$_2$Cl$_2$, 233 K): δ 259.5 (t, $J_{\mathrm{C-P}} = 8.7$, Os$=$CH), 179.7 (s, C$=$O), 149.0 (s, $-$CH$=$), 142.3 and 142.1 (both s, C$_{\mathrm{ipso}}$$-$Ph), 140.6 (s, $=$$CPh_2$), 129.7, 129.5, 128.5, 128.4, 127.7, and 127.6 (all s, CH$_{\mathrm{Ph}}$), 123.7 and 123.2 (both s, CN), 25.3 (s, O$_2$CCH$_3$), 25.2 (vt, $N = 11.8$, PCH), 19.1 and 18.8 (both s, PCHCH$_3$), 5.0 and 4.5 (both s, CH$_3$CN).

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Supporting Information Available: X-ray analysis, computational details, determination of the rotational barrier of the carbene ligand on complex **5**, determination of thermodynamic parameters for the equilibrium **2** to **4**, orthogonal coordinates of theoretical structures, and crystal structure determinations, including bond lengths and angles of compounds **2** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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