$C_\beta(sp^2)-H$ Bond Activation of α,β-Unsaturated Ketones Promoted by a Hydride-Elongated Dihydrogen Complex: Formation of Osmafuran Derivatives with Carbene, Carbyne, and NH-Tautomerized α-Substituted Pyridine Ligands

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Complex $[OsH(\eta^2\text{-}H_2)(\eta^2\text{-}CH_2{=}CH\text{-}o\text{-}C_5H_4N)(P^iPr_3)_2]BF_4$ (**1**) reacts with methyl vinyl ketone in the absence of solvent to give $[Os\{CHCHC(O)CH_3\}_2(P^iPr_3)_2]BF_4$ (**2**), which can be described as two osmafurans joined by a common $[OsH(P^iPr_3)_2]^+$ fragment. The hydride ligand of **2** is fairly acidic. Thus, its treatment with sodium methoxide produces the deprotonation of the metal center to give $Os\{CHCHC(O)CH_3\}_2(P^iPr_3)_2$ (**3**). The reaction is not reversible; the protonation of **3** with $HBF_4\cdot OEt_2$ leads to $[Os\{CHCHC(O)CH_3\}\{{=}CHCH_2C(=O)CH_3\}(P^iPr_3)_2]BF_4$ (**4**), which in dichloromethane is unstable and evolves into $[Os\{CHCHC(O)CH_3\}Cl\{{\equiv}CCH{=}C(CH_3)OH\}(P^iPr_3)_2]BF_4$ (**5**), containing an enolcarbyne ligand. In the solid state the anion of **5** is associated with the OH-hydrogen of the enol, by means of an H···F hydrogen bond. In dichloromethane the H···F hydrogen bond is broken and DFT calculations suggest that the OH-hydrogen atom forms an H···Cl hydrogen bond with the chlorine ligand. In the absence of solvent, complex **1** reacts with benzylideneacetophenone and benzylideneacetone to give $[Os\{C(Ph)CHC(O)R\}(\eta^2\text{-}H_2)\{\kappa\text{-}C\text{-}[HNC_5H_3Et]\}(P^iPr_3)_2]BF_4$ (R = Ph (**6**), CH_3 (**10**)), containing a NH-tautomerized 2-ethylpyridine ligand. Complexes $[Os\{C(Ph)CHC(O)R\}(\eta^2\text{-}H_2)\{(CH_3CN)\}(P^iPr_3)_2]BF_4$ (R = Ph (**8**), CH_3 (**11**)) and $[Os\{C_6H_4C(O)CH{=}CHPh\}(\eta^2\text{-}H_2)\{(CH_3CN)\}(P^iPr_3)_2]BF_4$ (**9**) have been also isolated and characterized. The X-ray structures of **2**, **5**, and **6** are reported.

Introduction

One of the most typical reactions of transition-metal hydride complexes is the insertion of alkenes into the metal−hydride bond, which leads to alkyl derivatives and constitutes a key step in a variety of catalytic reactions.[1] The insertion is particularly favored for metal centers in high oxidation states. The thermodynamic stability of the resulting alkyl derivatives also depends on the particular alkyl group. The presence of a donor heteroatom at the γ-position increases the stability of the system, as a consequence of its coordination to the metal center and the formation of five-membered heterometallarings.[2]

The activation of C−H bonds by transition-metal compounds is another reaction of great interest[3] due to its importance in organometallic synthesis[4] and by its connection with the functionalization of organic molecules.[5] An example is the addition of $C(sp^2)-H$ bonds to unsaturated hydrocarbons. The formation of the new carbon−carbon bond requires, as a

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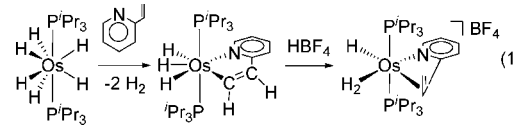
previous step, the C−H activation of the added bond. The C−H bond activation is promoted by low-valent metal complexes. Among the various strategies used, chelation assistance utilizing cyclometallation is considered to be one of the most promising ways.[6]

Complex $[OsH_2(\eta^5\text{-}C_5H_5)(\eta^2\text{-}H_2)(P^iPr_3)]BF_4$ reacts with α,β-unsaturated ketones,[7] aldehydes,[8] and alkynes[9] to give the corresponding reduced organic substrates and the 14-valence-electron fragment $[Os(\eta^5\text{-}C_5H_5)(P^iPr_3)]^+$, which activates C(sp^3)−H and C(sp^2)−H bonds. The reactions with α,β-unsaturated ketones afford hydride−osmafuran derivatives.[7,10] In contrast to this hydride-elongated dihydrogen complex, the 14-valence-electron monohydride $OsH(SnPh_2Cl)(P^iPr_3)_2$, which is generated *in situ* from the trihydride $OsH_3(SnPh_2Cl)\{[\eta^2\text{-}CH_2{=}C(CH_3)]P^iPr_2\}(P^iPr_3)$ by hydrogen transfer from the metal center to the carbon−carbon double bond of the unsaturated phosphine,[11] is inactive toward the insertion of unsaturated organic molecules into the osmium−hydride bond. However, in agreement with a strong base character of the metal center,[12] it activates C(sp^2)−H bonds of aromatic ketones and aldehydes, α,β-unsaturated ketones and aldehydes, aromatic imines, 2-vinylpyridine, and (*E*)-*N*-(phenylmethylene)-2-pyridinamine.[13]

C−H bond activation with high-valent metal complexes is difficult, and it has been rarely observed. The saturated d^2 hexahydride $OsH_6(P^iPr_3)_2$ is thermally activated to afford a 16-valence-electron fragment, $OsH_4(P^iPr_3)_2$. This species is capable of producing a triple C(sp^3)−H bond activation of cyclohexyl methyl ketone to give a trihydride−osmafuran derivative.[14] It also activates a C(sp^3)−H bond of the methyl groups of 8-methylquinoline and 2-dimethylaminopyridine,[15] a C(sp^2)−H bond of aromatic ketones[16] and imines,[17] and the OC−H bond of aldehydes.[18] The reactions with RCH═E-py substrates (E = CH, N) lead to products resulting from C(sp^2)−H bond activation or insertion reactions. They are competitive and depend on the nature of both E and R, which determine the polarity of the C═E double bond and the steric hindrance of the RCH group. For E = CH the C(sp^2)−H bond activation of the RCH group is preferred over the hydride migration. Thus, the reaction of $OsH_6(P^iPr_3)_2$ with 2-vinylpyridine gives the metalated compound $OsH_3(NC_5H_4\text{-}o\text{-}CH{=}CH)(P^iPr_3)_2$, which affords the hydride-elongated dihydrogen complex $[OsH(\eta^2\text{-}H_2)(\eta^2\text{-}CH_2{=}CH\text{-}o\text{-}C_5H_4N)(P^iPr_3)_2]BF_4$ in the presence of HBF_4. The formation of this compound is a consequence of the protonation of the OsCH-carbon atom with concomitant transformation of a pair of hydride ligands into a dihydrogen ligand (eq 1).[19]



(1)

We have recently reported that complex $[OsH(\eta^2\text{-}H_2)(\eta^2\text{-}CH_2{=}CH\text{-}o\text{-}C_5H_4N)(P^iPr_3)_2]BF_4$ reacts with benzophenone to give $[Os\{C_6H_4C(O)Ph\}(\eta^2\text{-}H_2)\{\kappa\text{-}C\text{-}[HNC_5H_3Et]\}(P^iPr_3)_2]BF_4$.[20] The formation of this compound is a one-pot tandem process of three reactions: (i) hydrogenation of the vinyl substituent of the pyridine as a result of the transfer of the coordinated hydrogen molecule from the metal center to the carbon−carbon double bond, in agreement with the behavior of the trihydride $OsH_3(SnPh_2Cl)\{[\eta^2\text{-}CH_2{=}C(CH_3)]P^iPr_2\}(P^iPr_3)$; (ii) *ortho*-CH bond activation of the ketone by the resulting monohydride, in accordance with the trend shown by the 14-valence-electron monohydride $OsH(SnPh_2Cl)(P^iPr_3)_2$ to add aromatic ketones; and (iii) a C,N-1,2-H rearrangement of 2-ethylpyridine.

Now, we have studied the reactions of the complex $[OsH(\eta^2\text{-}H_2)(\eta^2\text{-}CH_2{=}CH\text{-}o\text{-}C_5H_4N)(P^iPr_3)_2]BF_4$ with methyl vinyl ketone, benzylideneacetophenone, and benzylideneacetone. This paper reports the formation of novel osmafuran complexes, including derivatives with double and triple Os−C bonds, and shows the selectivity of the olefinic versus aromatic C−H bond activation and the influence of the substituent at the β-carbon atom of the α,β-unsaturated ketone on the reaction products.

Results and Discussion

1. Reaction with Methyl Vinyl Ketone: Formation of Osmafuran Derivatives Containing Double and Triple Os−C Bonds. Treatment at room temperature of the hydride−dihydrogen complex $[OsH(\eta^2\text{-}H_2)(\eta^2\text{-}CH_2{=}CH\text{-}o\text{-}C_5H_4N)(P^iPr_3)_2]BF_4$ (**1**) with 5.0 equiv of methyl vinyl ketone in the absence of solvent gives rise after 24 h to a red melt, which, by stirring in a 5:3 diethyl ether/toluene mixture, affords $[OsH\{CHCHC(O)CH_3\}_2(P^iPr_3)_2]BF_4$ (**2**) as an orange solid in 80% yield. Complex **2** is the result of the hydrogenation of the vinyl substituent of the pyridine ligand of **1** to yield 2-ethylpyridine, which was detected by GC-MS in the discarded diethyl ether/toluene solution, and of the C_β(sp^2)−H bond activation of 2 equiv of the α,β-unsaturated ketone with the release of a hydrogen molecule (Scheme 1).

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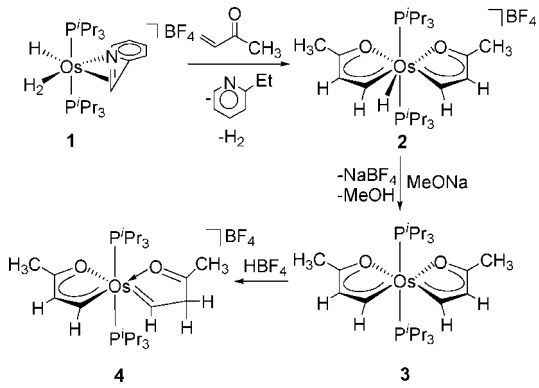
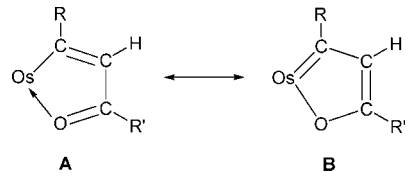
Scheme 1



Scheme 2



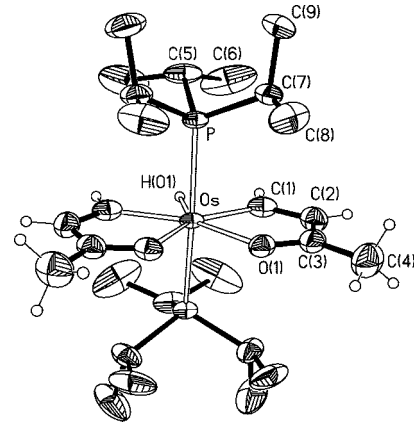


Figure 1. Molecular diagram of **2**. Selected bond lengths (Å) and angles (deg): Os−C(1) 2.046(13), C(1)−C(2) 1.374(18), C(2)−C(3) 1.395(18), Os−O(1) 2.106(8), C(3)−O(1) 1.264(16); P(1)−Os−P(2) 170.58(11), C(1)−Os−O(1) 74.2(4).

Figure 1 shows a view of the geometry of **2**. The complex can be described as two osmafurans joined by a common osmium atom. Thus, the coordination around the metal center can be rationalized as a pentagonal bipyramid of C_{2v} symmetry with the phosphine ligands in apical positions (P−Os−P = 170.58(11)°) and the C_2 axis on the Os−H bond.

The Os−C(1) bond lengths of 2.046(13) Å agree well with that expected for an osmafurane derivative where the resonance forms shown in Scheme 2 should be taken into account to describe the bonding situation in the heterometallacycles.[7,13b,c,21] In agreement with this, the C(1)−C(2) and C(2)−C(3) distances of 1.374(18) and 1.395(18) Å, respectively, are between those expected for single and double carbon−carbon bonds. The Os−O(1) and C(3)−O(1) bond lengths of 2.106(8) and 1.264(16) Å also support the metallafuran resonance forms.[22]

A main contribution of the resonance form **B** to the structure **2** is also supported by the $^{13}C\{^1H\}$ NMR spectrum, which shows the resonance due to the metalated carbon atoms C(1) at 207.8 ppm, shifted more than 50 ppm to lower field with regard to the chemical shifts found for the OsC_α resonances of the alkenyl complexes $Os(C_2Ph)\{(E)\text{-}CH{=}CHPh\}(\equiv CCH_2Ph)(P^iPr_3)_2$ (δ, 155.7),[23] $OsH(\eta^5\text{-}C_5H_5)\{(E)\text{-}CH{=}CHPh\}\{P(OMe)_3\}(P^iPr_3)$ (δ, 136.9),[24] $[Os\{(E)\text{-}CH{=}CHCy\}Cl(=N{=}CMe_2)(P^iPr_3)_2][CF_3SO_3]$ (δ, 143.1),[25] $Os\{(Z)\text{-}CH{=}C(Ph)N{=}CR_2\}Cl(CO)_2(P^iPr_3)_2$ (δ between 158 and 145),[26] and $[Os\{(E)\text{-}CH{=}CHR\}(=C{=}C{=}CPh_2)(CH_3CN)_2(P^iPr_3)_2]BF_4$ (δ between 153 and 150).[27] This resonance is however shifted between 20 and 40 ppm to higher field with regard to the chemical shift corresponding to the metalated carbon atoms of the complexes $Os\{CHCHC(O)Ph\}Cl(CO)(P^iPr_3)_2$ (δ, 230.13),[21] $Os(SnPh_2Cl)\{C_4(O)H_2C(O)H\}(\eta^2\text{-}H_2)(P^iPr_3)_2$ (δ, 230.6),[13b] $OsH\{CHCHC(O)CH_3\}(P^iPr_3)_2$ (δ, 250.8),[28] and $OsH_3\{C_6H_8C(O)CH_3\}(P^iPr_3)_2$ (255.7),[14] suggesting that, although the contribution of the resonance form **B** to the bonding situation in **2** is important, it is significantly lower than those to these derivatives.

The ^1H and $^{31}P\{^1H\}$ NMR spectra of **2** are also consistent with the structure shown in Figure 1. In agreement with its position between the metalated carbon atoms C(1), the hydride ligand undergoes spin coupling with the C(1)−H-protons. Thus, the hydride resonance appears at −6.13 ppm as a triple triplet with H−H and H−P coupling constants of 8.5 and 10.6 Hz, respectively. In the low-field region of the spectrum the resonance corresponding to the C(1)−H-protons (H_α) appears at 11.43 ppm, as a double doublet with a $H_\alpha-H_\beta$ coupling constant of 8.5 Hz, whereas the resonance due to the C(2)−H-protons (H_β) is observed at 7.48 ppm. In accordance with the equivalence of the phosphine ligands, the $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 8.4 ppm.

Complex **2** can be deprotonated by reaction with sodium methoxide. The addition of 1.3 equiv of this base to a tetrahydrofuran solution of **2** gives rise to the neutral compound $Os\{CHCHC(O)CH_3\}_2(P^iPr_3)_2$ (**3**), as a result of the extraction of the hydride ligand. Complex **3** is isolated as a dark brown oil in 86% yield, according to Scheme 1.

The deprotonation of the metal center produces an increase of the contribution of the resonance form **B** to the bonding in the five-membered heterometallaring, in agreement with the formal reduction of the metal center, which increases the back-bonding $Os(d\pi)\rightarrow C(p\pi)$ interaction. This is revealed by the ^1H and $^{13}C\{^1H\}$ NMR spectra of **3**. The ^1H NMR spectrum, in addition to the absence of any hydride resonance, shows the H_α resonance of the osmafuran rings at 16.78 ppm, shifted about 5 ppm to lower field with regard to the chemical shift of **2**, whereas in the $^{13}C\{^1H\}$ NMR spectrum the OsC_α resonance is observed at 237.2 ppm, shifted about 27 ppm to lower field with regard to that of **1**. These chemical shifts are similar to those observed for the related resonances of the phenylmethylene ligand in the half-sandwich complexes $Os(\eta^5\text{-}C_5H_5)Cl(=CHPh)\text{-}$

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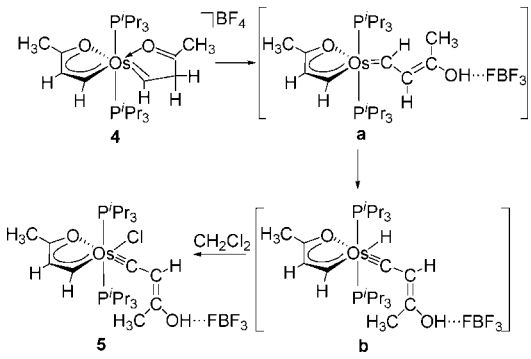
Scheme 3



{[η^2-CH$_2$=C(CH$_3$)]P^{i}Pr$_2$} (δ_H, 18.50; δ_C, 234.2)[29] and Os(η^5-C$_5$H$_5$)Cl(=CHPh)(P^{i}Pr$_3$) (δ_H, 19.17; δ_C, 235.0).[30] The ^{31}P{^{1}H} NMR spectrum contains a singlet at 17.7 ppm.

The increase of the back-bonding Os(dπ)→C(pπ) interaction produces the nuclephilicity transfer from the metal center to the C$_\beta$ atoms of the five-membered rings. As a consequence of this, the deprotonation of **2** is not reversible. The addition at −40 °C of 1.2 equiv of HBF$_4$·OEt$_2$ to a diethyl ether solution of **3** affords [Os{CHCHC(O)CH$_3$}{=CHCH$_2$C(=O)CH$_3$}(P^{i}Pr$_3$)$_2$]BF$_4$ (**4**), which is isolated as a green solid in 67% yield (Scheme 1). Complex **4**, containing two different heterometallacycles joined by a common osmium atom, is the result of the addition of the proton of the acid to the C$_\beta$ atom of one of the osmafurans of **3**.

The protonation produces an increase in the double-bond character of the Os−C bond of the protonated heterometallacycle and a slight decrease in the contribution of the resonance form **B** to the osmafuran structure of the nonprotonated heterometallacycle. Thus, in the ^{13}C{^{1}H} NMR spectrum of **4** the OsC$_\alpha$ resonance of the protonated ring appears at 263.7 ppm, shifted about 27 ppm to lower field with regard to the related resonance of **3**, while the OsC$_\alpha$ resonance of the osmafuran is observed at 223.0 ppm, shifted about 14 ppm to higher field with regard to that of **3**. The ^{1}H NMR spectrum is consistent with the ^{13}C{^{1}H} NMR spectrum: the H$_\alpha$ resonance of the protonated ring appears at 22.28 ppm, shifted about 5 ppm to lower field with regard to the related resonance of **3**, while the H$_\alpha$ resonance of the osmafuran is observed at 14.90 ppm, shifted about 2 ppm to higher field with regard to that of **3**. The ^{31}P{^{1}H} NMR spectrum is in accordance with the structure proposed for **4** in Scheme 1. Thus, it contains a singlet at 21.0 ppm.

Complex **4** is unstable in dichloromethane. Under reflux, it evolves into the osmafuran−carbyne derivative [Os{CHCHC(O)CH$_3$}Cl{≡CCH=C(CH$_3$)OH}(P^{i}Pr$_3$)$_2$]BF$_4$ (**5**), which is isolated as a yellow solid in 34% yield after 6 days. Its formation can be rationalized according to Scheme 3. The dissociation followed by keto−enol tautomerization of the keto moiety of the protonated ring of **4** should afford a five-coordinate carbene intermediate **a**. In agreement with the osmium preference for the coordination saturation and redox isomers with a higher multiplicity of the metal−carbon bond,[10,31] intermediate **a** could evolve into the hydride−carbyne **b** as a result of a 1,2-hydrogen shift from the carbene carbon atom to the metal center. Thus, the hydride chlorination[32] should lead to **5**.

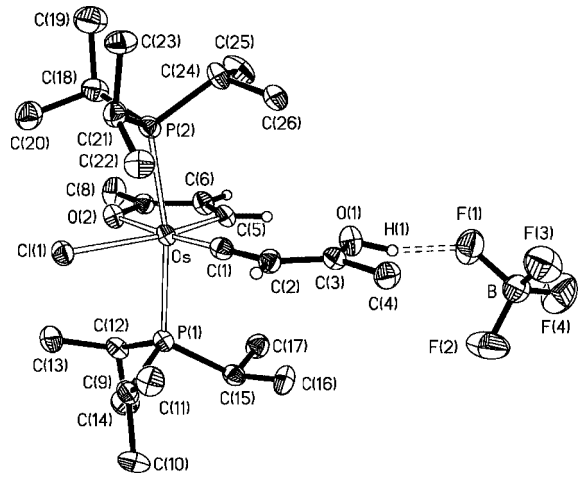


Figure 2. Molecular diagram of **5**. Selected bond lengths (Å) and angles (deg): Os−C(1) 1.746(7), C(1)−C(2) 1.408(9), C(2)−C(3) 1.362(9), C(3)−O(1) 1.330(8), Os−C(5) 1.993(6), C(5)−C(6) 1.374(9), C(6)−C(7) 1.387(8), C(7)−O(2) 1.271(7), O(2)−Os 2.171(4), H(1)···F(1) 1.68(7); P(1)−Os−P(2) 170.21(15), C(5)−Os−O(2) 75.4, C(2)−C(1)−Os 179.4(5), C(1)−Os−O(2) 171.2(2), Cl(1)−Os−C(5) 158.73(19).

Complex **5** has been characterized by an X-ray crystallographic study. A view of the molecular geometry is shown in Figure 2. The structure proves the formation of the novel enol−carbyne ligand, which in the solid state is associated with the BF$_4$ anion by means of a H···F hydrogen bond between the OH-proton of the enol and one of the fluorine atoms of the anion. The hydrogen bond is supported by the H(1)···F(1) separation of 1.68(7) Å, which is shorter than the sum of the van der Waals radii of hydrogen and fluorine (r_{vdw}(H) = 1.20 Å, r_{vdw}(F) = 1.47 Å).[33] The association is consistent with the IR in Nujol, which shows the characteristic absorptions of a [BF$_4$]$^-$ anion with C_{2v} symmetry at 1091 and 984 cm^{-1}.

The coordination geometry around the osmium atom can be rationalized as a distorted octahedron with the two phosphorus atoms occupying relative *trans* positions (P(1)−Os−P(2) = 170.21(15)°). The remaining coordination sites involve the C(5) and O(2) atoms of the osmafuran, the carbyne ligand *trans* disposed to O(2) (C(1)−Os−O(2) = 171.2(2)°), and the chlorine *trans* disposed to C(5) (Cl(1)−Os−C(5) = 158.73(19)°). The Os−C(5), C(5)−C(6), C(6)−C(7), C(7)−O(2), and O(2)−Os bond lengths of 1.993(6), 1.374(9), 1.387(8), 1.271(7), and 2.171(4) Å, respectively, agree well with those of **2** and support the osmafuran formulation. The Os−C(1) distance of 1.746(7) Å is fully consistent with an Os−C triple-bond formulation.[34] The enol 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 1.408(9) Å, C(2) and C(3) by 1.362(9) Å, and C(3) and O(1) by 1.330(8) Å, and the angles around C(2) and C(3) are in the range 119−124°.

In solution the H(1)···F(1) hydrogen bond should be evident from the OH-resonance in the ^{1}H NMR spectrum, which should

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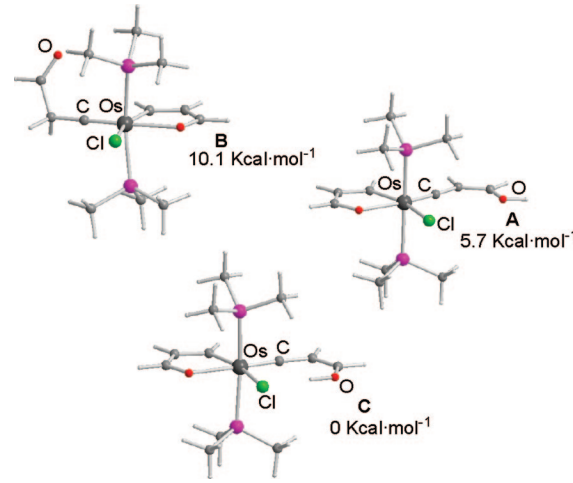
show spin coupling with the ^{19}F nuclei of the $[BF_4]^-$ anion. Unfortunately, this resonance was not found in the ^1H NMR spectra between 293 and 203 K. The ^{19}F NMR spectrum is not very informative. In order to investigate the presence or absence of the H(1)···F(1) hydrogen bond, we carried out a ^1H NMR diffusion-ordered spectroscopy (^1H-DOSY) experiment in dichloromethane-d_2. Pulsed field gradient (PFG) NMR is a method for measuring diffusion rates, which provides information about the size of molecules in solution.[35] Self-diffusion of a chemical species in a solvent depends on its molecular size and its hydrodynamic volume. According to this principle, molecular association can promote changes in self-diffusion coefficients, which can allow detecting the presence of a hydrogen-bonded species in solution,[36] including ion pairs and other organometallic assemblies.[37] At 303 K, the obtained diffusion coefficient for **5** is 1.05×10^{-9} $m^2 \cdot s^{-1}$, which corresponds to a hydrodynamic radius of 5.0 Å. By means of the X-ray experiment, we have calculated a hydrodynamic radius for the free cation of **5** of 5.6 Å, which increases to 6.3 Å when the cation−anion entity is taken into account. The comparison of these values suggests that in dichloromethane solution the H(1)···F(1) hydrogen bond is broken.

In spite of the absence of the H(1)···F(1) hydrogen bond, the enol form of the substituent of the carbyne ligand is retained in solution. In accordance with this, the ^1H NMR spectrum shows a poorly resolved signal at 4.18 ppm corresponding to the C(2)−H hydrogen atom of the enolcarbyne ligand. The C(5)−H resonance of the osmafuran is observed at 13.29 ppm. The $^{13}C\{^1H\}$ NMR spectrum is also consistent with the presence of the enolcarbyne ligand in solution. The resonance due to C(1) appears at 284.4 ppm, whereas those corresponding to C(2) and C(3) are observed at 118.0 and 191.1 ppm, respectively. The osmafuran C(5) resonance appears at 222.3 ppm. The $^{31}P\{^1H\}$NMR spectrum contains a singlet at 13.3 ppm, in agreement with the equivalence of the phosphine ligands.

In order to understand the higher stability of the enolcarbyne with regard to the keto carbyne, we have also carried out DFT calculations on the model system $[Os\{CHCHC(O)H\}Cl\{\equiv CC_2H_3O\}(PMe_3)_2]^+$ (Chart 1). The results indicate that the enol is more stable than the keto carbyne in the absence of any hydrogen bond, probably as a consequence of the conjugation between the triple Os−C and the double C−C bonds. Thus, the enolcarbyne structure **A** is 4.4 kcal·mol^{-1} more stable than the keto carbyne structure **B**. The *cis* disposition of the chlorine ligand and the carbyne group allows a Cl···H hydrogen bond between the chlorine and the OH hydrogen bond of the enol. This hydrogen bond produces an additional stabilization in the enol carbyne form. The structure **C**, in which the OH-hydrogen atom of the enolcarbyne group and the chlorine ligand are involved in a H···Cl hydrogen bond, is 5.7 kcal·mol^{-1} more stable than the enolcarbyne structure **A**. The H···Cl hydrogen bond is supported by the separation between the involved atoms

Chart 1



(2.58 Å), which is shorter than the sum of the van der Waals radii of hydrogen and chlorine.[38]

2. Reaction with Benzylideneacetophenone: Selectivity of the Olefinic versus Aromatic C−H Bond Activation. As noted in the Introduction, we have shown in a recent communication that complex **1** activates an *ortho*-CH bond of benzophenone to give $[Os\{C_6H_4C(O)Ph\}(\eta^2\text{-}H_2)\{\kappa\text{-}C\text{-}[HNC_5H_3Et]\}(P^iPr_3)_2]BF_4$, containing, in addition to an *ortho*-metalated ketone, a tautomerized 2-ethylpyridine ligand.[20] The previous section describes the $C_\beta(sp^2)$−H bond activation of 2 equiv of methyl vinyl ketone to afford **2** and free 2-ethylpyridine. Benzylideneacetophenone contains both functionalities bonded to the carbonyl unit, a phenyl group, and olefinic moiety with a $C(sp^2)$−H bond, which could be activated in a competitive manner. In order to study the preference for one of both C−H bond activations and the influence of the ketone type on the behavior of the pyridine ligand, we have studied the reaction of **1** with benzylideneacetophenone under the same conditions as those used for the reaction with benzophenone.

Treatment at 60 °C of **1** with 5.0 equiv of benzylideneacetophenone in the absence of solvent leads after 24 h to a red melt, which, by stirring at room temperature in a 6:5 diethyl ether/toluene mixture, gives $[Os\{C(Ph)CHC(O)Ph\}(\eta^2\text{-}H_2)\{\kappa\text{-}C\text{-}[HNC_5H_3Et]\}(P^iPr_3)_2]BF_4$ (**6**) as a brown solid in 52% yield, according to Scheme 4. Complex **6** is the result of a process similar to the formation of the previously mentioned *ortho*-metalated benzophenone derivative, involving the olefinic $C_\beta(sp^2)$−H bond activation of the α,β-unsaturated ketone instead of the *ortho*-CH bond of one of the phenyl groups of the aromatic ketone. It should be noted that the greater steric demand of benzylideneacetophenone, with phenyl substituents at the C_β atom of the olefinic moiety and the carbonyl group, with regard to methyl vinyl ketone prevents the $C_\beta(sp^2)$−H bond activation of a second equivalent of substrate and favors the tautomerization of the 2-ethylpyridine ligand.

N−H tautomers of α-substituted pyridines were postulated 70 years ago.[39] However, the first tautomerizations of these six-membered heterorings were reported in 2006 by Carmona's

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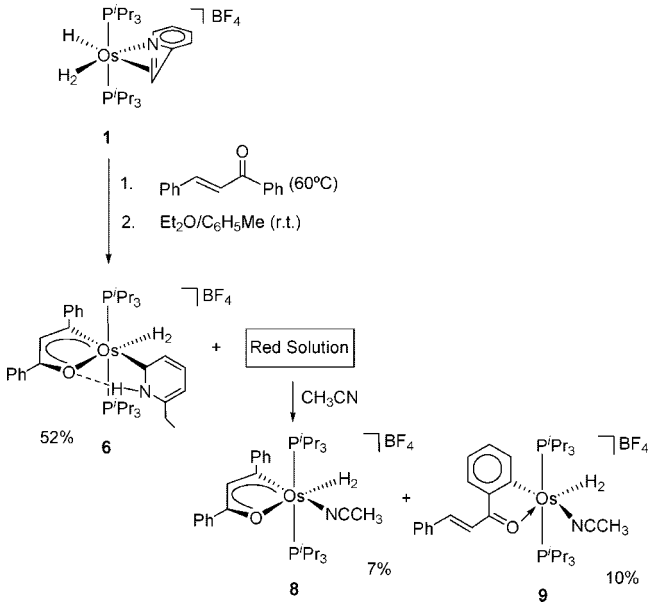
Scheme 4



group.[40] At the same time, we showed the stabilization of N−H tautomers of quinolines.[41] Subsequently Ruiz et al. described the base-promoted tautomerization of imidazole ligands to N-heterocyclic carbenes[42] and Whittlesey et al. reported ruthenium isomers resulting from the N- or C-bond tautomers of isopropyl-4,5-dimethylimidazole,[43] in agreement with the paper of Sini, Eisenstein, and Crabtree about the possibility that C-bound imidazoles could exist in metalloprotein chemistry.[44] This type of tautomerization has been also proposed as a key step in some relevant catalytic reactions,[45] including the Rh(I)-catalyzed *ortho* alkylation of pyridines and quinolines recently reported by Bergman and Ellman.[5f,h,i]

We note that a 2,6-lutidium ylide bound to osmium through the carbon atom at the 4-position has been produced by isomerization of an η^2-C,C,-2,6-lutidine species.[46] A few pyridine or *N*-alkylpyridine-2-ylidene and -4-ylidine complexes of metals other than osmium have also been prepared by indirect methods from suitable precursors.[47]

Complex **6** has been characterized by an X-ray crystallographic study. A view of the cation is shown in Figure 3. As observed for **5**, the coordination geometry around the osmium atom can be rationalized as a distorted octahedron with the phosphine ligands occupying mutually *trans* positions (P(1)−Os−P(2) = 162.68(5)°). The remaining coordination sites involve the C(8) and O(1) atoms of the activated ketone, the tautomerized pyridine *trans* disposed to C(8) (C(1)−Os−C(8) = 156.7(2)°), and the hydrogen atoms H(01) and H(02) *trans* disposed to O(1). The C(8) and O(1) atoms form with the metal center an osmafuran ring. The Os−C(8), C(8)−C(15), C(15)−C(16), C(16)−O(1), and O(1)−Os bond lengths of 2.086(5), 1.393(7), 1.385(7), 1.296(6), and 2.148(3) Å, respectively, agree well with those of **2** and **5** and support this formulation. The Os−C(1) distance of 2.137(5) Å, which is about 0.05 Å longer than Os−C(8), compares well with Os−C bond lengths in [Os{$C_6H_4C(O)$-Ph}(η^2-H_2){κ-C-[HNC_5H_3Et]}(P^iPr_3)$_2$]BF_4 (2.110(5) Å),[20] the tautomerized quinoline derivatives $OsCl_2${κ-*C*-[$HNC_{10}H_8$]}(η^2-H_2)(P^iPr_3)$_2$ (2.005(6) Å)[41a] and $OsCl_2${κ-*C*-[HNbq]}(η^2-H_2)-(P^iPr_3)$_2$ (bq = benzo[*h*]quinoline; 2.055(11) and 2.030(10) Å),[41b] and the scarce Os−imidazolydene complexes characterized by X-ray diffraction analysis (1.993(9)−2.123(6) Å).[48] As in the above-mentioned pyridine and quinoline complexes, a hydrogen bond involving the NH group plays an important role in the stabilization of the tautomeric form. In accordance with the hydrogen bond, the NH-hydrogen points out the oxygen atom of the ketone O(1). The separation between them of 1.99(4) is shorter than the sum of the van der Waals radii of hydrogen and oxygen.[13a] The OsH_2 unit forms an osmium-elongated dihydrogen,[49] with a H−H separation of 1.47(6) Å.

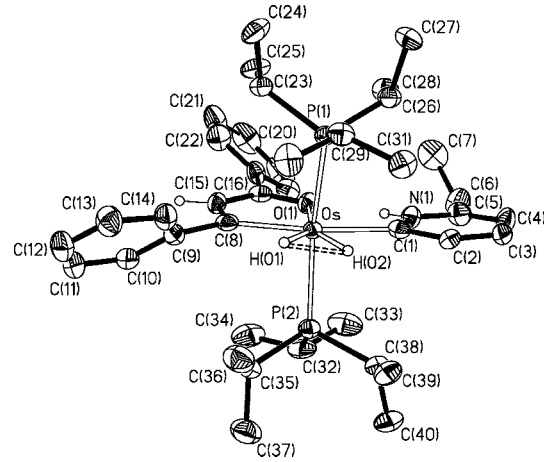


Figure 3. Molecular diagram of **6**. Selected bond lengths (Å) and angles (deg): Os−C(1) 2.137(5) Å, Os−C(8) 2.086(5), C(8)−C(15) 1.393(7), C(15)−C(16) 1.385(7), C(16)−O(1) 1.296(6), O(1)−Os 2.148(3), H(01)···H(02) 1.47(6), NH···O(1) 1.99(4); P(1)−Os−P(2) 162.68(5), C(1)−Os−C(8) 156.7(2).

The $^{13}C\{^1H\}$ NMR spectrum is consistent with the osmafuran formulation and with the presence of a tautomerized 2-ethylpyridine ligand in the complex. Thus, the resonance due to C(8) appears at 250.2 ppm, whereas, in agreement with the previously reported osmium compounds containing tautomerized quinoline and pyridine ligands, [20,41] the C(1) resonance is observed at 189.5 ppm.

The ^1H NMR spectrum in dichloromethane-d_2 supports the NH···O(1) hydrogen bond, the osmafuran formulation, and the presence of an elongated dihydrogen in the complex. As expected for the hydrogen bond, the NH resonance is observed

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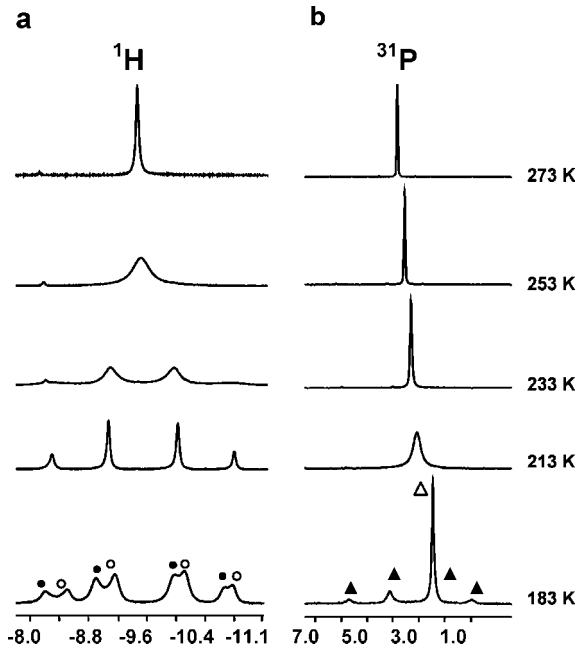
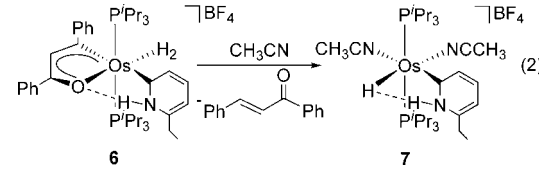


Figure 4. Variable-temperature NMR spectra (300 MHz, CD_2Cl_2) of **6**: (a) $^1H\{^{31}P\}$ in the high-field region and (b) $^{31}P\{^1H\}$.

at unusually low field,[50] 14.19 ppm. The most noticeable resonance of the osmafuran ring is a singlet at 8.50 ppm corresponding to the C(15)H-hydrogen atom. In the high-field region of the spectrum, the elongated dihydrogen ligand gives rise to a triplet at −9.43 ppm with an H−P coupling constant of 12.2 Hz. This resonance is temperature dependent. At about 243 K decoalescence occurs, and between 233 and 203 K an ABX_2 (X = ^{31}P) spin system centered at −9.51 ppm with $\Delta\nu$ = 461 Hz and J_{A-B} = 211 Hz is observed. The value of the H−H coupling constant suggests the operation of a quantum exchange coupling[51] between the hydrogen atoms, in addition to the thermally activated site exchange process. For this resonance, at 300 MHz, a $T_{1(min)}$ value of 50 ± 1 ms was obtained at 228 K, which corresponds to a H−H separation of 1.36 Å, in agreement with the elongated dihydrogen character of the compound. Complex **6** is a new example of blocked rotation of the dihydrogen ligand on the NMR time scale.[12,13,17,49,52] Assuming an entropy of activation close to 0, a $\Delta H^{\ddagger}$ value of 11 kcal·mol^{-1} can be estimated as the rotation barrier, on the basis of the spectra shown in Figure 4a, which is similar to those found for blocked rotation processes in other elongated dihydrogen complexes.

Figure 4a also shows that at 183 K the AB spin system splits into two. This is consistent with the presence of two elongated dihydrogen species in solution at this temperature. At room temperature the $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 4.7 ppm. This resonance is also temperature dependent. Its behavior with the temperature is consistent with that of the elongated dihydrogen resonance (Figure 4b). Thus, at 183 K, the $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 2.4 ppm and an AB spin system centered at 3.9 ppm and defined by $\Delta\nu$ = 340 Hz and J_{A-B} = 189 Hz. These observations can be rationalized in terms of the existence of an equilibrium between two rotamer structures. One of them contains equivalent phosphines, while the other one has lower symmetry by virtue of the alternate disposition of the isopropyl groups. The rotamers are the result of the hindered rotation around the Os−P bond. The phenomenon is common for bis-phosphine complexes, and it has been observed for five- and six-coordinate ruthenium and osmium compounds containing bulky phosphine ligands.[13,53]

Although the Os−C(8) distance is slightly shorter than the Os−C(1) bond length, and despite the chelate nature of the activated ketone, the elimination of the latter from **6** is favored with regard to the retrotautomerization of the heterocycle or the elimination of the 2-ethylpyridinium. Thus, at room temperature in acetonitrile, complex **6** evolves to the previously reported compound $[OsH(CH_3CN)_2\{\kappa\text{-C-}[HNC_5H_3Et]\}(P^iPr_3)_2]BF_4$[20] (**7**) in almost quantitative yield (eq 2).



In contrast to **6**, the addition of acetonitrile to the diethyl ether/toluene solution obtained from the workup of the reaction depicted in Scheme 4 produces the precipitation of a 5:7 mixture of the side compounds $[Os\{C(Ph)CHC(O)Ph\}(\eta^2\text{-}H_2)(CH_3CN)(P^iPr_3)_2]BF_4$ (**8**) and $[Os\{C_6H_4C(O)CH{=}CHPh\}(\eta^2\text{-}H_2)(CH_3CN)(P^iPr_3)_2]BF_4$ (**9**). These complexes are obtained in 7% and 10% yield, respectively. They result from the release of the 2-ethylpyridine ligand from the metal center before the tautomerization process.

The osmafuran character of **8** is supported by its $^{13}C\{^1H\}$ NMR spectrum, which shows at 232.2 ppm a triplet with a C−P coupling constant of 3.8 Hz, corresponding to the OsC-carbon atom. In the ^{1}H NMR spectrum, the elongated dihydrogen ligand displays at −8.15 ppm a triplet with a H−P coupling constant of 9.0 Hz. At 300 MHz, a $T_{1(min)}$ value of 32 ± 1 ms at 228 K was obtained for this resonance, which corresponds to a H−H separation of 1.27 Å, in agreement with the elongated dihydrogen character of the compound. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 9.5 ppm.

The presence of an intact CH=CHPh moiety in the ketone ligand of **9** is strongly supported by the ^{1}H NMR spectrum of this compound, which shows two doublets at 8.03 and 7.71 ppm with a coupling constant of 15.5 Hz. In the high-field region of the spectrum, the elongated dihydrogen ligand gives rise to a triplet at −8.86 ppm with a H−P coupling constant of 9.8 Hz. In this case, at 300 MHz, a $T_{1(min)}$ value of 39 ± 1 ms was found for this resonance, which corresponds to a H−H separation of 1.31 Å. In the $^{13}C\{^1H\}$ NMR spectrum, the most noticeable resonance is that due to the *ortho*-metalated carbon atom, which appears at 183.1 ppm as a triplet with a C−P

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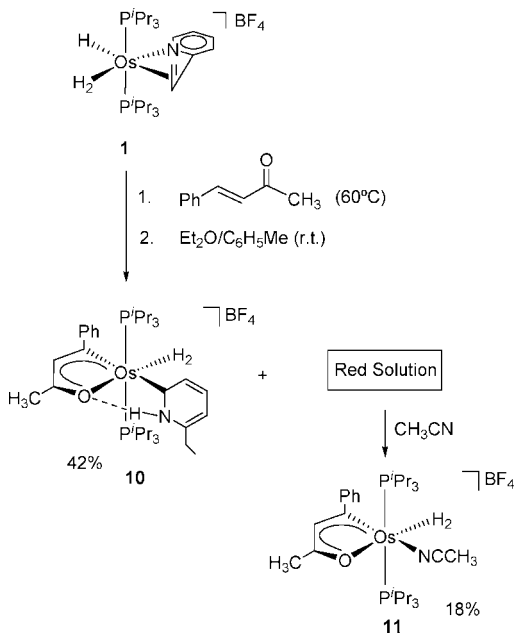
Scheme 5



coupling constant of 5.8 Hz. A singlet at 11.1 ppm in the $^{31}P\{^1H\}$ NMR spectrum is also characteristic of this complex.

Complex **8** is the result of the olefinic $C_\beta(sp^2)-H$ bond activation of the α,β-unsaturated ketone, while complex **9** is a consequence of the *ortho*-CH bond activation of the phenyl substituent of the carbonyl group of the substrate. According to the yields obtained for the formation of **6**, **8**, and **9**, it is clear that the olefinic $C_\beta(sp^2)-H$ bond activation is favored with regard to the *ortho*-CH bond activation of the phenyl group.

The trihydride $OsH_3(SnPh_2Cl)\{[\eta^2\text{-}CH_2{=}C(CH_3)]P^iPr_2\}(P^iPr_3)$, through the 14-valence electron monohydride $OsH(SnPh_2Cl)(P^iPr_3)_2$, also activates both the $C_\beta(sp^2)-H$ bond of the olefinic moiety and an *ortho*-CH bond of the phenyl substituted at the carbonyl group of benzylideneacetophenone. In this case, the olefinic $C_\beta(sp^2)-H$ bond activation is kinetically favored with regard to the *ortho*-CH bond activation. However, the *ortho*-metalated product is thermodynamically more stable than the osmafuran derivative.[13c] In contrast to the trihydride, the half-sandwhich complex $[OsH_2(\eta^5\text{-}C_5H_5)(\eta^2\text{-}H_2)(P^iPr_3)]BF_4$ exclusively activates the olefinic $C_\beta(sp^2)-H$ bond of benzylideneacetophenone.[7]

3. Reaction with Benzylideneacetone: Influence of the Substituent at the β-Carbon Atom of the α,β-Unsaturated Ketone. The different behavior of benzylideneacetophenone with regard to methyl vinyl ketone could be a consequence of the presence of a phenyl group, instead of a hydrogen atom, at the C_β atom of the olefinic moiety or alternatively of the presence of a phenyl group, instead of a methyl substituent, at the carbonyl. In order to know which phenyl determines the behavior of the ketone, we have carried out the reaction of **1** with benzylideneacetone. The latter substrate contains a phenyl substituent at the C_β atom, as benzylideneacetophenone, and a methyl substituent at the carbonyl, as methyl vinyl ketone.

Treatment at 60 °C of **1** with 2.0 equiv of benzylideneacetone in the absence of solvent for 24 h gives a red melt, which, by stirring at room temperature in a 5:3 diethyl ether/toluene mixture, affords $[Os\{C(Ph)CHC(O)CH_3\}(\eta^2\text{-}H_2)\{\kappa\text{-}C\text{-}[HNC_5H_3Et]\}(P^iPr_3)_2]BF_4$ (**10**) as an orange solid in 42% yield, according to Scheme 5.

Complex **10** is an osmafuran species containing a tautomerized 2-ethylpyridine ligand as **6**. So, the $^{13}C\{^1H\}$, ^1H, and $^{31}P\{^1H\}$ NMR spectra of **10** are fully consistent with those of the latter. In the $^{13}C\{^1H\}$ NMR spectrum, the osmafuran OsC resonance appears at 250.1 ppm, whereas that corresponding to the metalated carbon atom of the tautomerized pyridine is observed at 189.0 ppm. At room temperature, the ^1H NMR spectrum shows the NH resonance at 14.0 ppm, as a singlet, while the elongated dihydrogen ligand gives rise to a triplet at −9.83 ppm with an H−P coupling constant of 12.0 Hz. The latter resonance is temperature dependent; thus at 213K, it appears as an ABX_2 spin system centered at −9.93 ppm and defined by $\Delta\nu = 657$ Hz and $J_{A-B} = 211$ Hz. At 183 K, the second-order spin system splits into two. At 400 MHz, a $T_{1(min)}$ value of 73 ± 1 ms at 253 K was found for the resonance, which corresponds to a H−H separation of 1.38 Å. At room temperature the $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 3.7 ppm, while at 183 K a singlet at 2.1 ppm and an AB spin system centered at 2.7 ppm and defined by $\Delta\nu = 470$ Hz and $J_{A-B} = 189$ Hz are observed.

Complex **10** also reacts with acetonitrile to give **7**. Similarly to the diethyl ether/toluene solution obtained from the workup of the reaction depicted in Scheme 4, the addition of acetonitrile to that resulting from the reaction depicted in Scheme 5 produces the precipitation of $[Os\{C(Ph)CHC(O)CH_3\}(\eta^2\text{-}H_2)(CH_3CN)(P^iPr_3)_2]BF_4$ (**11**) as an orange solid in 18% yield.

The $^{13}C\{^1H\}$, ^1H, and $^{31}P\{^1H\}$ NMR spectra of **11** are consistent with those of **8**. The $^{13}C\{^1H\}$ NMR spectrum shows the osmafuran OsC resonance at 231.9 ppm. In the ^1H NMR spectrum, the elongated dihydrogen ligand displays at −8.58 ppm a triplet with an H−P coupling constant of 10.0 Hz. In this case, at 300 MHz, a $T_{1(min)}$ value of 44 ± 1 ms was obtained at 238 K, which corresponds to a H−H separation of 1.33 Å. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 8.9 Hz.

The formation of **10** and **11**, which are the analogues to **6** and **8** containing an activated benzylideneacetone instead of benzylideneacetophenone, prove that the presence of a phenyl substituent at the C_β atom of the olefinic moiety is the factor determining the different behavior of benzylideneacetophenone with regard to methyl vinyl ketone.

Concluding Remarks

This study has revealed that the hydride-elongated dihydrogen complex $[OsH(\eta^2\text{-}H_2)(\eta^2\text{-}CH_2{=}CH\text{-}o\text{-}C_5H_4N)(P^iPr_3)_2]BF_4$ activates not only an *ortho*-CH bond of aromatic ketones but also an olefinic $C_\beta(sp^2)-H$ bond of α,β-unsaturated ketones. The latter activation is preferred over the first one in substrates with both phenyl and olefinic substituents.

The olefinic $C_\beta(sp^2)-H$ activations have given rise to two types of products: complex $[OsH\{CHCHC(O)CH_3\}_2(P^iPr_3)_2]BF_4$, formed by two osmafurans joined by a common $[OsH(P^iPr_3)_2]^+$ fragment, and the dihydrogen elongated-osmafuran derivatives $[Os\{C(Ph)CHC(O)R\}(\eta^2\text{-}H_2)\{\kappa\text{-}C\text{-}[HNC_5H_3Et]\}(P^iPr_3)_2]BF_4$, containing a NH-tautomerized 2-ethylpyridine ligand. The first of them is the product from the reaction with methyl vinyl ketone, while the second ones are obtained when one of the $C_\beta-H$ hydrogen atoms of the vinylic group is replaced by a phenyl substituent. The deprotonation of $[OsH\{CHCHC(O)CH_3\}_2(P^iPr_3)_2]BF_4$ and the subsequent protonation of the resulting neutral species affords an osmafuran ring with a cyclic carbene bonded at the osmium atom, which

is unstable in dichloromethane and evolves into [Os{CH-CHC(O)CH_3}Cl{≡CCH=C(CH_3)OH}(P^iPr_3)$_2$]BF_4, containing a novel enolcarbyne ligand.

In conclusion, we report new $C_\beta(sp^2)$−H bond activation processes promoted by a hydrido-elongated dihydrogen complex that are the entry to novel osmafuran compounds with double and triple Os−C bonds, even some of them with a NH-tautomerized 2-ethylpyridine ligand.

Experimental Section

All reactions were carried out with rigorous exclusion of air using Schlenk-tube techniques. Organic solvents were dried by standard procedures and distilled under argon prior to use. The starting material **1** was prepared as previously described in the literature.[19] ^1H, ^{19}F, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra were recorded on either a Bruker ARX 300, a Bruker Avance 300, a Bruker Avance 400, or a Bruker Avance 500 MHz instrument. 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. 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.

Preparation of [OsH{CHCHC(O)CH_3}$_2$(P^iPr_3)$_2$]BF_4 (2). In a Schlenk tube were added [OsH(η^2-H_2)(η^2-CH_2=CH-*o*-C_5H_4N)(P^iPr_3)$_2$]BF_4 (**1**) (194 mg, 0.28 mmol) and 5.0 equiv of methyl vinyl ketone (116 μL, 1.37 mmol), and the mixture was stirred for 24 h at room temperature. The addition of a mixture of diethyl ether/toluene (5:3) in a cold bath caused the precipitation of an orange solid, which was decanted, washed with further portions of cold diethyl ether, and dried *in vacuo*. Yield: 162 mg (80%). Anal. Calcd for $C_{26}H_{53}BF_4O_2OsP_2$: C, 42.39; H, 7.25. Found: C, 42.23; H, 7.18. IR (Nujol, cm^{-1}): ν(C=O) 1720 (m); ν(C=C) 1539 (s); ν(BF_4) 1060 (vs). ^1H NMR and COSY (500 MHz, CD_2Cl_2, 293 K): δ 11.43 (dd, $J_{H-H\alpha}$ = 8.5, $J_{H\alpha-H\beta}$ = 8.5, 2H, $OsCH_\alpha$), 7.48 (d, $J_{H\alpha-H\beta}$ = 8.5, 2H, $OsCHCH_\beta$), 2.78 (t, J_{H-P} = 2.0, 6H, CH_3), 1.82 (m, 6H, $PCHCH_3$), 1.09 (dvt, *N* = 13.8, J_{H-H} = 7.3, 36H, $PCHCH_3$), −6.13 (tt, $J_{H-H\alpha}$ = 8.5, J_{H-P} = 10.6, 1H, OsH). $^{31}P\{^1H\}$ NMR (202.46 MHz, CD_2Cl_2, 293 K): δ 8.4 (s). $^{13}C\{^1H\}$-APT NMR plus HMBC and HSQC (75.43 MHz, CD_2Cl_2, 293 K): δ 209.8 (t, J_{C-P} = 2.1, CO), 207.8 (t, J_{C-P} = 5.9, OsCH), 135.1 (s, OsCHCH), 26.4 (s, CH_3), 22.6 (vt, *N* = 25.2, $PCHCH_3$), 19.7 (s, $PCHCH_3$).

Preparation of Os{CHCHC(O)CH_3}$_2$(P^iPr_3)$_2$ (3). To a solution of [OsH{CHCHC(O)CH_3}$_2$(P^iPr_3)$_2$]BF_4 (**2**) (413 mg, 0.56 mmol) in 8 mL of THF was added sodium methoxide (40 mg, 0.73 mmol). The solution was stirred for 1 h at room temperature, and the solvent was removed *in vacuo*. The residue was extracted with toluene (12 mL) and filtered through Celite. Then, the solvent was removed, and the resultant oil was washed with pentane (2 mL) in a 2-propanol/dry ice bath. Finally, the solution was concentrated to dryness and a dark brown oil was obtained. Yield: 313 mg (86%). Anal. Calcd for $C_{26}H_{52}O_2OsP_2$: C, 48.13; H, 8.08. Found: C, 48.06; H, 7.99. IR (Nujol, cm^{-1}): ν(C=O) 1464 (s). ^1H NMR (300 MHz, C_6D_6, 293 K): δ 16.78 (d, J_{H-H} = 6.0, 2H, OsCH), 7.27 (d, J_{H-H} = 6.0, 2H, OsCHCH), 2.17 (s, 6H, CH_3), 1.85 (m, 6H, $PCHCH_3$), 1.08 (dvt, *N* = 12.5, J_{H-H} = 6.5, 36H, $PCHCH_3$). $^{31}P\{^1H\}$ NMR (121.42 MHz, C_6D_6, 293 K): δ 17.7 (s). $^{13}C\{^1H\}$-APT NMR plus HMBC and HSQC (75.43 MHz, C_6D_6, 293 K): δ 237.2 (t, J_{C-P} = 5.8, OsCH), 196.4 (s, CO), 132.7 (s, OsCHCH), 24.0 (s, CH_3), 21.2 (vt, *N* = 22.8, $PCHCH_3$), 19.8 (s, $PCHCH_3$).

Preparation of [Os{CHCHC(O)CH_3}{=CHCH$_2$C(O)CH_3}(P^iPr_3)$_2$]BF_4 (4). A dark brown solution of [Os{CHCHC(O)CH_3}$_2$(P^iPr_3)$_2$] (**3**) (313 mg, 0.48 mmol) in 10 mL of diethyl ether at −40 °C was treated with 1.2 equiv of $HBF_4 \cdot Et_2O$ (79 μL, 0.58 mmol) and stirred for 30 min at this temperature. During the course of the reaction a green solid was formed. The solvent was removed, and the solid was washed with further portions of diethyl ether in a cold bath and dried *in vacuo*. Yield: 238 mg (67%). Anal. Calcd for $C_{26}H_{53}BF_4O_2OsP_2$: C, 42.39; H, 7.25. Found: C, 42.45; H, 7.13. IR (Nujol, cm^{-1}): ν(C=C) 1627 (w); ν(C=O) 1452 (m). ^1H NMR (300 MHz, CD_2Cl_2, 263 K): δ 22.28 (br, 1H, Os=CH), 14.90 (d, J_{H-H} = 6.6, 1H, OsCH), 6.86 (d, J_{H-H} = 6.6, 1H, OsCHCH), 2.88 (s, 3H, Os=$CHCH_2COCH_3$), 2.29 (s, 3H, $OsC_2H_4COCH_3$), 1.58 (m, 6H, $PCHCH_3$), 1.04 (m, 2H, CH_2,), 0.96 (dvt, *N* = 13.2, J_{H-H} = 6.9, 36H, $PCHCH_3$). $^{31}P\{^1H\}$ NMR (121.42 MHz, CD_2Cl_2, 263 K): δ 21.0 (s). $^{13}C\{^1H\}$-APT NMR plus HMBC and HSQC (75.43 MHz, CD_2Cl_2, 263 K): δ 263.7 (t, J_{C-P} = 7.5, Os=CH), 226.6 (s, Os=$CHCH_2CO$), 223.0 (t, J_{C-P} = 4.4, OsCH), 203.0 (t, J_{C-P} = 1.9, OsC_2H_4CO), 136.2 (s, OsCHCH), 79.23 (s, Os=$CHCH_2$), 27.7 (s, Os=$CHCH_2COCH_3$), 25.2 (s, $OsC_2H_4COCH_3$), 21.4 (vt, *N* = 23.9, $PCHCH_3$), 19.0 (s, $PCHCH_3$).

Preparation of [Os{CHCHC(O)CH_3}Cl{≡CCH=C(CH_3)OH}(P^iPr_3)$_2$]BF_4(5). A green solution of [Os{CHCHC(O)CH_3}{=$CHCH_2C$(=O)CH_3}(P^iPr_3)$_2$]BF_4 (**4**) (197 mg, 0.27 mmol) in 15 mL of dichloromethane was heated under reflux for 6 days. The solution was filtered through Celite, and the solvent was removed *in vacuo*. The crude of the reaction was extracted with cold diethyl ether (20 mL), and the solvent was removed *in vacuo*. The addition of pentane in a 2-propanol/dry ice bath caused the precipitation of a yellow solid, which was washed with further portions of cold pentane and dried *in vacuo*. Yield: 70 mg (34%). Anal. Calcd for $C_{26}H_{52}BClF_4O_2OsP_2$: C, 40.50; H, 6.77. Found: C, 40.45; H, 7.25. IR (Nujol, cm^{-1}): ν(C=C) 1606 (m); ν(C=O) 1507 (s); ν(BF_4) 1091, 984. ^1H NMR (400 MHz, CD_2Cl_2, 293 K): δ 13.29 (dd, J_{H-H} = 7.6, $J_{H-H'}$ = 2, 1H, OsCH), 7.17 (d, J_{H-H} = 7.6, 1H, OsCHCH), 4.18 (br, 1H, Os≡C−CH), 2.54 (m, 6H, $PCHCH_3$), 2.31 (t, J_{H-P} = 1.4, 3H, $OsC_2H_4COCH_3$), 2.04 (s, 3H, CH=C(CH_3)OH), 1.33 (dvt, *N* = 14.8, J_{H-H} = 7.2, 18H, $PCHCH_3$), 1.21 (dvt, *N* = 13.2, J_{H-H} = 7.2, 18H, $PCHCH_3$). $^{31}P\{^1H\}$ NMR (161.99 MHz, CD_2Cl_2, 293 K): δ 13.3 (s). ^{19}F NMR (376.49 MHz, CD_2Cl_2, 293 K): −148.1 (br), −151.6 (br). $^{13}C\{^1H\}$-APT NMR plus HMBC and HSQC (100 MHz, CD_2Cl_2, 293 K): δ 284.4 (t, J_{C-P} = 10.0, Os≡C), 222.3 (t, J_{C-P} = 4.8, OsCH), 205.0 (s, OsC_2H_4CO), 191.1 (s, Os≡C−CH=C), 130.4 (s, OsCHCH), 118.0 (s, Os≡C−CH), 25.5 (s, $OsC_2H_4COCH_3$), 23.3 (vt, *N* = 25.3, $PCHCH_3$), 22.9 (s, CH=C(CH_3)OH), 19.8 and 19.4 (both s, $PCHCH_3$).

Preparation of [Os{C(Ph)CHC(O)Ph}(η^2-H_2){κ-C-[HNC_5H_3-Et]}(P^iPr_3)$_2$]BF_4 (6). In a Schlenk tube were added [OsH(η^2-H_2)(η^2-CH_2=CH-*o*-C_5H_4N)(P^iPr_3)$_2$]BF_4 (**1**) (193 mg, 0.273 mmol) and 5.0 equiv of benzylideneacetophenone (285 mg, 1.37 mmol), and the mixture was heated to 60 °C for 24 h. The addition of cold diethyl ether (6 mL) with toluene (5 mL) to the crude reaction caused the formation of a brown solid, which was washed with further portions of a mixture of cold diethyl ether/toluene (4:1) and dried *in vacuo*. Yield: 130 mg (52%). Anal. Calcd for $C_{40}H_{64}BF_4NOOsP_2$: C, 52.57; H, 7.06; N, 1.53. Found: C, 52.80; H, 7.21; N, 1.53. IR (KBr, cm^{-1}): ν(N−H) 3236 (m); ν(OsH) 2180 (w); ν(CO) 1606 (s); ν(C=C) 1581 (s); ν(BF_4) 1053 (vs). ^1H NMR (500 MHz, CD_2Cl_2, 293 K): δ 14.19 (br, 1H, N−H), 8.50 (s, 1H, CH), 8.21−8.16 (m, 2H, Ph), 8.11 (d, J_{H-H} = 7.8, 1H, H_{py}), 8.08−8.03 (m, 3H, Ph), 7.77−7.36 (m, 6H, Ph + H_{py}), 7.23 (d, J_{H-H} = 7.8, 1H, H_{py}), 3.13 (q, J_{H-H} = 7.5, 2H, CH_2CH_3), 1.88 (m, 6H, $PCHCH_3$), 1.59 (t, J_{H-H} = 7.5, 3H, CH_2CH_3), 1.02 (dvt, *N* = 13.5, J_{H-H} = 7.0, 18H, $PCHCH_3$), 0.99 (dvt, *N* = 13.5, J_{H-H} = 7.0, 18H, $PCHCH_3$), −9.43 (t, J_{H-P} = 12.2, 2H, OsH_2). ^1H NMR (300 MHz, CD_2Cl_2, 213 K, hydride region): δ −9.51 (ABX_2 spin system, Δν = 461 Hz, J_{A-B} = 211 Hz). ^1H NMR (300 MHz, CD_2Cl_2, 183 K, high-field region): δ −9.41 (ABX_2 spin system, Δν = 487 Hz, J_{A-B} = 204), −9.62

Table 1. Crystal Data and Data Collection and Refinement for 2, 5, and 6

	2	5	6
		Crystal Data	
formula	$C_{26}H_{53}BF_4O_2OsP_2$	$C_{26}H_{52}BCl_1F_4O_2OsP_2 \times 0.5CH_2Cl_2 \times 0.4C_5H_{12}$	$C_{40}H_{64}BF_4NOOsP_2$
molecular wt	736.63	842.40	913.87
color and habit	red, needle	yellow, irregular block	colorless, irregular block
symmetry, space group	orthorhombic, *Pmmn*	triclinic, $P\bar{1}$	triclinic, $P\bar{1}$
a, Å	13.041(4)	7.890(3)	10.258(2)
b, Å	14.089(4)	15.363(6)	14.422(3)
c, Å	8.462(2)	16.115(6)	14.825(3)
α, deg		71.071(6)	92.738(4)
β, deg		82.244(6)	92.738(4)
γ, deg		82.111(6)	107.905(4)
V, Å^3	1554.9(7)	1821.7(12)	2075.1(8)
Z	2	2	2
D_{calc}, g cm^{-3}	1.573	1.536	1.463
		Data Collection and Refinement	
diffractometer		Bruker Smart APEX	
λ(Mo Kα), Å		0.71073	
monochromator		graphite oriented	
scan type		*ω* scans	
μ, mm^{-1}	4.249	3.779	3.198
2*θ*, range, deg	3, 57	3, 57	3, 57
temp, K	100	100	173
no. of data collected	18 234	22 774	25 911
no. of unique data	2106 (R_{int} = 0.0419)	8707 (R_{int} = 0.1102)	9835 (R_{int} = 0.0614)
no. of params/restraints	109/22	398/21	476/3
R_1[a] [$F^2 > 2\sigma(F^2)$]	0.0588	0.0565	0.0480
wR_2[b] [all data]	0.1361	0.1069	0.1012
S[c] [all data]	1.094	0.933	1.040

[a] $R_1(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2(F^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)\}^{1/2}$. [c] Goof = $S = \{\sum[F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$, where n is the number of reflections and p is the number of refined parameters.

(ABX_2 spin system, $\Delta\nu$ = 443 Hz, J_{A-B} = 198). $^{31}P\{^1H\}$ NMR (121.42 MHz, CD_2Cl_2, 293 K): δ 4.7 (s). $^{31}P\{^1H\}$ NMR (121.42 MHz, CD_2Cl_2, 183 K): δ 3.9 (AB spin system, $\Delta\nu$ = 340 Hz, J_{A-B} = 189), 3.0 (s). $^{13}C\{^1H\}$-APT NMR plus HMBC and HSQC (75.43 MHz, CD_2Cl_2, 293 K): δ 250.2 (t, J_{C-P} = 4.8, OsC), 193.6 (t, J_{C-P} = 2.2, CO), 189.5 (t, J_{C-P} = 9.1, OsCNH), 154.9 (s, CCH_2CH_3), 153.2 (s, C_{ipso}Ph), 145.7 and 138.8 (both s, C_{py}), 136.5 (s, C_{ipso}Ph), 134.6 (s, Ph), 132.8 (s, CH), 132.3, 130.9, 130.4, 130.3, 130.1, 130.0, 129.4, 129.0, 128.6 (all s, Ph), 118.8 (s, C_{py}), 28.7 (vt, N = 25.8, $PCHCH_3$), 28.3 (s, CH_2CH_3), 20.2 and 19.7 (both s, $PCHCH_3$), 13.2 (s, CH_2CH_3). $T_{1(min)}$ (ms, OsH_2, 300 MHz, CD_2Cl_2, 228 K): 50 ± 1.

Preparation of a Mixture of [Os{C(Ph)CHC(O)Ph}(η^2-H$_2$)(CH$_3$CN)(P^{i}Pr$_3$)$_2$]BF$_4$ (8) and [Os{C$_6$H$_4$C(O)CH=CHPh}(η^2-H$_2$)(CH$_3$CN)(P^{i}Pr$_3$)$_2$]BF$_4$(9). The diethyl ether/toluene solution recovered from the workup of complex [Os{C(Ph)CHC(O)Ph}(η^2-H_2){κ-C-[HNC_5H_3Et]}(P^iPr_3)$_2$]BF_4 (**6**) was concentrated under reduced pressure to ca. 2 mL, and acetonitrile (1 mL) was added, getting a brown solid, which was washed with a cold mixture of diethyl ether/toluene/pentane (3:1:1) and dried *in vacuo*. A 5:7 mixture of complexes **8** and **9** was obtained. Yield: 42 mg (17%). Anal. Calcd for $C_{35}H_{58}BF_4NOOsP_2$: C, 45.86; H, 7.18; N, 1.78. Found: C, 46.13; H, 7.03; N, 1.68.

Spectroscopic data of **8**: ^1H NMR (500 MHz, CD_2Cl_2, 293 K): δ 8.16−7.42 (m, 10H, Ph), 8.08 (s, 1H, CH), 2.78 (s, 3H, C*H*$_3$CN), 2.12 (m, 6H, PC*H*CH_3), 1.15 (dvt, N = 13.5, J_{H-H} = 7.0, 18H, PCHC*H*$_3$), 1.05 (dvt, N = 13.5, J_{H-H} = 7.0, 18H, PCHC*H*$_3$), −8.15 (t, J_{H-P} = 9.0, 2H, OsH_2). $^{31}P\{^1H\}$ NMR (202.46 MHz, CD_2Cl_2, 293 K): δ 9.5 (s). $^{13}C\{^1H\}$-APT NMR plus HMBC and HSQC (125.78 MHz, CD_2Cl_2, 293 K): δ 232.2 (t, J_{C-P} = 3.8, OsC), 194.3 (t, J_{C-P} = 2.1, CO), 152.0 (s, C_{ipso}Ph), 145.5 and 135.4 (both s, OsC_6H_4), 135.2 (s, C_{ipso}Ph), 131.9 (s, OsC_6H_4), 129.8 (s, CH_3CN), 126.4 (s, CH), 26.5 (vt, N = 25.5, P*C*HCH_3), 19.7 and 19.4 (both s, PCH*C*H_3), 4.4 (s, *C*H_3CN). $T_{1(min)}$ (ms, OsH_2, 300 MHz, CD_2Cl_2, 228 K): 32 ± 1.

Spectroscopic data of **9**: ^1H NMR (500 MHz, CD_2Cl_2, 293 K): 8.16−7.42 (m, 5H, Ph), 8.03 (d, J_{H-H} = 15.5, 1H, C*H*=CHPh), 7.98 (d, J_{H-H} = 7.5, OsC_6H_4), 7.92 (d, J_{H-H} = 7.5, OsC_6H_4), 7.71 (d, J_{H-H} = 15.5, 1H, CH=C*H*Ph), 7.07 (t, J_{H-H} = 7.5, 1H, OsC_6H_4), 7.03 (t, J_{H-H} = 7.5, 1H, OsC_6H_4), 2.75 (s, 3H, C*H*$_3$CN), 2.01 (m, 6H, PC*H*CH_3), 1.14 (dvt, N = 13.5, J_{H-H} = 7.0, 18H, PCHC*H*$_3$), 0.97 (dvt, N = 13.5, J_{H-H} = 7.0, 18H, PCHC*H*$_3$), −8.86 (t, J_{H-P} = 9.8, 2H, OsH_2). $^{31}P\{^1H\}$ NMR (202.46 MHz, CD_2Cl_2, 293 K): δ 11.1 (s). $^{13}C\{^1H\}$-APT NMR plus HMBC and HSQC (125.78 MHz, CD_2Cl_2, 293 K): δ 198.0 (t, J_{C-P} = 2.4, CO), 183.1 (t, J_{C-P} = 5.8, OsC), 147.1 (s, *C*H=CHPh), 145.5 (s, OsC_6H_4), 142.6 (s, *C*CO), 135.4 (s, OsC_6H_4), 132.0 (s, OsC_6H_4), 121.3 (s, OsC_6H_4), 129.2 (s, CH_3CN), 118.5 (s, CH=*C*HPh), 25.0 (vt, N = 25.3, P*C*HCH_3), 19.5 and 19.3 (both s, PCH*C*H_3), 4.5 (s, *C*H_3CN). $T_{1(min)}$ (ms, OsH_2, 300 MHz, CD_2Cl_2, 228 K): 39 ± 1.

Preparation of [Os{C(Ph)CHC(O)CH$_3$}(η^2-H$_2$){κ-C-[HNC$_5$H$_3$Et]}(P^{i}Pr$_3$)$_2$]BF$_4$(10). In a Schlenk flask were added [OsH(η^2-H_2)(η^2-CH_2=CH-*o*-C_5H_4N)(P^iPr_3)$_2$]BF_4 (**1**) (209 mg, 0.30 mmol) and 2 equiv of benzylideneacetone (87 mg, 0.60 mmol), and the mixture was heated at 60 °C for 24 h. The addition of a mixture of diethyl ether/toluene (5:3, 8 mL) in a cold bath to the resulting residue led to an orange solid, which was washed with further portions of cold diethyl ether and dried *in vacuo*. Yield: 106 mg (42%). Anal. Calcd for $C_{35}H_{62}BF_4NOOsP_2$: C, 49.35; H, 7.34; N, 1.64. Found: C 49.83; H, 6.77; N, 1.60. IR (KBr, cm^{-1}): ν(N−H) 3239 (s); ν(Os−H) 2184 (m); ν(C=O) 1718 (s); ν(C=C) 1583 (s); $\nu(BF_4)$ 1079 (vs). ^1H NMR (400 MHz, CD_2Cl_2, 293 K): δ 14.00 (br, 1H, N−H), 8.00 (d, J_{H-H} = 8.0, 1H, H_{py}), 7.93−7.90 (m, 2H, Ph), 7.79 (s, 1H, OsCCH), 7.55 (t, J_{H-H} = 8.0, 1H, H_{py}), 7.47−7.36 (m, 3H, Ph), 7.09 (d, J_{H-H} = 8.0, 1H, H_{py}), 3.03 (q, J_{H-H} = 7.6, 2H, CH_2CH_3), 2.73 (t, J_{H-P} = 1.8, 3H, CH_3), 1.80 (m, 6H, $PCHCH_3$), 1.55 (t, J_{H-H} = 7.6, 3H, CH_2CH_3), 0.96 (dvt, N = 13.2, J_{H-H} = 6.8, 18H, $PCHCH_3$), 0.95 (dvt, N = 13.0, J_{H-H} = 7.0, 18H, $PCHCH_3$), −9.83 (t, J_{H-P} = 12.0, 2H, OsH_2). ^1H NMR (400 MHz, CD_2Cl_2, 213 K, high-field region): δ −9.93 (ABX_2 spin

system, $\Delta\nu = 657$ Hz, $J_{A-B} = 211$). ^{1}H NMR (400 MHz, CD_2Cl_2, 183 K, high-field region): δ −9.79 (ABX_2 spin system, $\Delta\nu = 695$ Hz, $J_{A-B} = 209$), −10.0 (ABX_2 spin system, $\Delta\nu = 634$ Hz, $J_{A-B} = 181$). ^{31}P{^{1}H} NMR (161.89 MHz, CD_2Cl_2, 293 K): δ 3.7 (s). ^{31}P{^{1}H} NMR (161.89 MHz, CD_2Cl_2, 183 K): δ 2.7 (AB spin system, $\Delta\nu = 470$ Hz, $J_{A-B} = 189$), 2.1 (s). ^{13}C{^{1}H}-APT NMR plus HMBC and HSQC (75.43 MHz, CD_2Cl_2, 293 K): δ 250.1 (t, $J_{C-P} = 5.0$, OsC), 201.2 (t, $J_{C-P} = 1.7$, CO), 189.0 (t, $J_{C-P} = 9.1$, OsCNH), 154.4 (s, CCH_2CH_3), 152.4 (s, C_{ipso}Ph), 145.5 (s, C_{py}), 138.5 (s, C_{py}), 135.1 (s, CH), 130.8, 130.2, 128.8 (all s, Ph), 118.7 (s, C_{py}), 28.5 (vt, $N = 25.6$, $PCHCH_3$), 27.8 (s, CH_2CH_3), 25.0 (s, CH_3), 20.1 and 19.6 (both s, $PCHCH_3$), 12.2 (s, CH_2CH_3). $T_{1(min)}$ (ms, OsH_2, 400 MHz, CD_2Cl_2, 253 K): 73 ± 1.

Preparation of [Os{C(Ph)CHC(O)CH$_3$}(η^2-H$_2$)(CH$_3$CN)(P^{i}Pr$_3$)$_2$]BF$_4$(11). The diethyl ether/toluene solution recovered from the workup of complex [Os{C(Ph)CHC(O)CH$_3$}(η^2-H$_2$){κ-C-[HNC$_5$H$_3$Et]}(P^{i}Pr$_3$)$_2$]BF_4 (**10**) was concentrated under reduced pressure to ca. 5 mL, and acetonitrile (1 mL) was added, getting an orange solid, which was washed with cold mixture of diethyl ether/pentane (4:1) and dried *in vacuo*. Yield: 42 mg (18%). Anal. Calcd for $C_{30}H_{56}BF_4NOOsP_2$: C, 45.86; H, 7.18; N, 1.78. Found: C, 45.97; H, 7.07; N, 1.61. IR (Nujol, cm^{-1}): ν(C≡N) 2319 (w); ν(OsH) 2286 (w), 2155 (w); ν(C═O) 1514 (m); $\nu(BF_4)$ 1049 (vs). ^{1}H NMR (400 MHz, CD_2Cl_2, 293 K): δ 7.81−7.77 (m, 2H, Ph), 7.39−7.36 (m, 4H, Ph + CH), 2.70 (t, $J_{H-P} = 1.2$, 3H, CH_3CN), 2.55 (t, $J_{H-P} = 2.0$, 3H, CH_3), 2.09 (m, 6H, $PCHCH_3$), 1.14 (dvt, $N = 13.6$, $J_{H-H} = 7.2$, 18H, $PCHCH_3$), 1.07 (dvt, $N = 13.2$, $J_{H-H} = 7.2$, 18H, $PCHCH_3$), −8.58 (t, $J_{H-P} = 10.0$, 2H, OsH_2). ^{31}P{^{1}H} NMR (161.99 MHz, CD_2Cl_2, 293 K): δ 8.9 (s). ^{13}C{^{1}H}-APT NMR plus HMBC and HSQC (100 MHz, CD_2Cl_2, 293 K): δ 231.9 (t, $J_{C-P} = 3.7$, OsC), 202.7 (t, $J_{C-P} = 2.0$, CO), 151.3 (s, C_{ipso}Ph), 131.0 (s, Ph), 132.1 (s, CH), 130.0 (s, Ph), 129.5 (s, CH_3CN), 129.0 (s, Ph), 26.5 (vt, $N = 25.5$, $PCHCH_3$), 24.7 (s, CH_3), 19.7 and 19.4 (both s, $PCHCH_3$), 4.3 (s, CH_3CN). $T_{1(min)}$ (ms, OsH_2, 300 MHz, CD_2Cl_2, 238 K): 44 ± 1.

Reaction of 6 and 10 with CH$_3$CN. Formation of [OsH(CH$_3$CN)$_2${κ-C-[HNC$_5$H$_3$Et]}(P^{i}Pr$_3$)$_2$]BF$_4$(7). Solutions of **6** and **10** (130 mg) in 10 mL of acetonitrile were stirred for 4 days at room temperature. After this time the solvent was removed *in vacuo*, and the resulting residues were dissolved in 0.5 mL of CD_2Cl_2. ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ 10.17 (br, 1H, N−H), 7.65 (d, $J_{H-H} = 7.8$, 1H, H_{py}), 6.94 (t, $J_{H-H} = 7.8$, 1H, H_{py}), 6.28 (d, $J_{H-H} = 7.8$, 1H, H_{py}), 2.59 (s, 3H, CH_3CN), 2.44 (q, $J_{H-H} = 8.0$, 2H, CH_2CH_3), 2.43 (s, 3H, CH_3CN), 2.01 (m, 6H, $PCHCH_3$), 1.15 (dvt, $N = 13.1$, $J_{H-H} = 7.1$, 18H, $PCHCH_3$), 1.23 (dvt, $N = 12.9$, $J_{H-H} = 6.6$, 18H, $PCHCH_3$), the triplet corresponding to the methyl of the CH_2CH_3 group is under the peaks of the P^{i}Pr$_3$ ligand, −16.22 (t, $J_{H-P} = 19.5$, 1H, OsH). ^{31}P{^{1}H} NMR (121.42 MHz, CD_2Cl_2, 293 K): δ 17.0 (s). ^{13}C{^{1}H}-APT NMR plus HMBC and HSQC (75.43 MHz, CD_2Cl_2, 293 K): δ 196.7 (t, $J_{C-P} = 8.0$, OsCNH), 152.4 (s, CCH_2CH_3), 139.1 (s, C_{py}), 130.9 (s, C_{py}), 123.9 and 121.3 (both s, CH_3CN), 111.2 (s, C_{py}), 27.4 (s, CH_2CH_3), 26.5 (vt, $N = 23.0$, $PCHCH_3$), 19.4 and 19.3 (both s, $PCHCH_3$), 12.5 (s, CH_2CH_3), 5.0 and 4.2 (both s, CH_3CN).

Computational Details. The theoretical calculations were carried out on the model complexes **A**, **B**, and **C** by optimizing the structure at the b3pw91-DFT level with the Gaussian 03 program.[54] The basis sets used were LANL2DZ basis and pseudopotentials for Os, and 6-31G(d,p) for the rest of the atoms.

Structural Analysis of Complexes 2, 5, and 6. X-ray data were collected for all complexes on a Bruker Smart APEX CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube source (Mo radiation, $\lambda = 0.71073$ Å) operating at 50 kV and 30 mA (**2**) or 40 mA (**5**, **6**). Data were collected over the complete sphere by a combination of four sets. Each frame exposure time was 10 s (**6**) or 20 s (**2**, **5**) covering 0.3° in ω. Data were corrected for absorption by using a multiscan method applied with the SADABS program.[55] The structures of all compounds were solved by the Patterson method. Refinement, by full-matrix least-squares on F^2 with SHELXL97,[56] was similar for all complexes, including isotropic and subsequently anisotropic displacement parameters. The hydrogen atoms were observed or calculated and refined freely or using a restricted riding model. Hydride ligands were observed in the difference Fourier maps but refined with restrained Os−H bond lengths (1.59(1) Å, CSD, **2** and **6**). All the highest electronic residuals were observed in close proximity of the Os centers and make no chemical sense. For **5**, 0.4 (pentane) and 0.5 (dichloromethane) molecules were observed in the asymmetric unit as crystallization solvents. Selected crystal data and data collection and refinement parameters for **2**, **5**. and **6** are shown in Table 1.

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Supporting Information Available: Optimized coordinates for complexes **A**, **B**, and **C**, and a CIF file giving crystal data for compounds **2**, **5**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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