Reduction and C(sp²)−H Bond Activation of Ketones Promoted by a Cyclopentadienyl-Osmium-Dihydride-Dihydrogen Complex

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The dihydride-dihydrogen complex $[OsH_2(\eta^5\text{-}C_5H_5)(\eta^2\text{-}H_2)(P^iPr_3)]BF_4$ (**2**) has been prepared by addition of $HBF_4{\cdot}OEt_2$ to $OsH_3(\eta^5\text{-}C_5H_5)(P^iPr_3)$ (**1**), and its reactions with benzylideneacetone, methyl vinyl ketone, acetophenone, and benzylideneacetophenone have been studied. The reaction with benzylideneacetone leads initially to $[OsH_2(\eta^5\text{-}C_5H_5)\{\kappa^1\text{-}OC(CH_3)CH{=}CHPh\}(P^iPr_3)]BF_4$ (**3**), which in dichloromethane is converted to the hydroxyallyl derivative $[OsH(\eta^5\text{-}C_5H_5)\{\eta^3\text{-}CH_2C(OH)CHCH_2Ph\}(P^iPr_3)]BF_4$ (**4**). Complex **4** releases 4-phenylbutan-2-one, and the resulting metallic fragment activates a $C_\beta(sp^2)$−H bond of a new molecule of benzylideneacetone to give $[OsH(\eta^5\text{-}C_5H_5)\{C(Ph)CHC(O)CH_3\}(P^iPr_3)]BF_4$ (**5**), which affords $Os(\eta^5\text{-}C_5H_5)\{C(Ph)CHC(O)CH_3\}(P^iPr_3)$ (**6**) by deprotonation with $NaOCH_3$. The reaction of **2** with methyl vinyl ketone gives ethyl methyl ketone and $[OsH(\eta^5\text{-}C_5H_5)\{CHCHC(O)CH_3\}(P^iPr_3)]BF_4$ (**9**). The latter can also be obtained from $Os(\eta^5\text{-}C_5H_5)Cl\{\eta^2\text{-}CH_2{=}CHC(O)CH_3\}(P^iPr_3)$ (**7**) via the intermediate $[Os(\eta^5\text{-}C_5H_5)\{CH_2CHC(O)CH_3\}(P^iPr_3)]BF_4$ (**8**). Treatment of **9** with $NaOCH_3$ leads to an equilibrium mixture of $Os(\eta^5\text{-}C_5H_5)\{CHCHC(O)CH_3\}(P^iPr_3)$ (**10**) and the hydride-vinylidene $OsH(\eta^5\text{-}C_5H_5)\{{=}C{=}CHC(O)CH_3\}(P^iPr_3)$ (**11**). The reaction of **2** with acetophenone gives 1-phenylethanol and the orthometalated derivative $[OsH(\eta^5\text{-}C_5H_5)\{C_6H_4C(O)CH_3\}(P^iPr_3)]BF_4$ (**13**), which is deprotonated with $NaOCH_3$ to give $Os(\eta^5\text{-}C_5H_5)\{C_6H_4C(O)CH_3\}(P^iPr_3)$ (**14**), while the reaction of **2** with benzylideneacetophenone leads to $[OsH(\eta^5\text{-}C_5H_5)\{C(Ph)CHC(O)Ph\}(P^iPr_3)]BF_4$ (**15**), which yields $Os(\eta^5\text{-}C_5H_5)\{C(Ph)CHC(O)Ph\}(P^iPr_3)$ (**16**) by deprotonation. Complexes **3**, **10**, and **13** have been characterized by X-ray diffraction analysis.

Introduction

A large part of the reactions involving dihydrogen compounds proceed by loss of molecular hydrogen.[1] The weak binding of the H_2 molecule to transition metals makes this ligand a good leaving group, which stabilizes unsaturated species without hindering the coordination of substrates to the metal centers. Several catalytic systems for the reduction of ketones and α,β-unsaturated ketones, by both hydrogenation and hydrogen transfer, are based upon this strategy.[2]

The coordination of the C−C double bond of α,β-unsaturated ketones to the catalyst has been proposed as the key step to the selective formation of the saturated ketone, while the coordination of the oxygen atom is thought to be determinant to the hydrogenation of the carbonyl group (Scheme 1).[3] Thus, the selectivity in the reduction of this type of compounds has been mainly associated with the steric crowding around the metal center of the catalyst. In both cases the direct addition of two hydrogen atoms to the double bond is proposed to occur.[4]

The activation of C(sp²)−H bonds by transition-metal compounds is another reaction of great importance,[5] due

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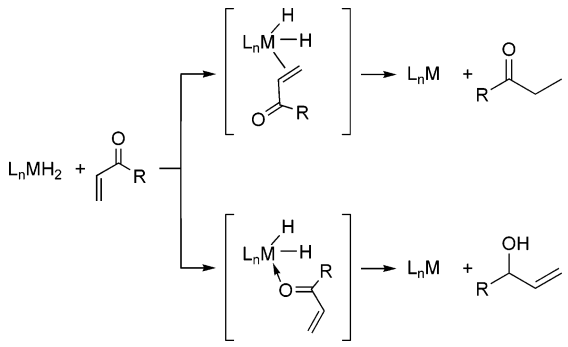
Scheme 1



to its connection with the addition of vinylic and aromatic C(sp^2)−H bonds to unsaturated hydrocarbons.[6] Among the various strategies used, chelate assistance to promote cyclometalation is considered to be a promising way. In this context, the study of the behavior of α,β-unsaturated[7] and aromatic ketones[8] is of particular interest.

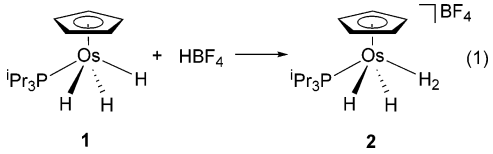
The C−H bond activation reactions with hydride-dihydrogen or polyhydride precursors are little studied.[9] They compete with the reduction of the substrate, and the selectivity toward one of the processes is not always high.[10]

As a part of our work on the chemistry of the cyclopentadienyl-osmium moiety,[11] we have previously reported the preparation of the trihydride-osmium(IV) derivative $OsH_3(\eta^5\text{-}C_5H_5)(P^iPr_3)$.[12] Now, we have observed that the latter affords the dihydride-dihydrogen derivative $[OsH_2(\eta^5\text{-}C_5H_5)(\eta^2\text{-}H_2)(P^iPr_3)]BF_4$ by protonation with $HBF_4{\cdot}OEt_2$. Our interest in learning to rationalize the reactivity of this type of species toward unsaturated organic molecules[13] prompted us to investigate its reactions with α,β-unsaturated and aromatic ketones.

This paper reports the preparation of $[OsH_2(\eta^5\text{-}C_5H_5)(\eta^2\text{-}H_2)(P^iPr_3)]BF_4$ and shows the sequence of steps that leads to the reduction and subsequent C(sp^2)−H bond activation of these substrates, by means of the characterization of intermediates.

Results and Discussion

1. Preparation of $[OsH_2(\eta^5\text{-}C_5H_5)(\eta^2\text{-}H_2)(P^iPr_3)]BF_4$. The addition of 1.2 equiv of $HBF_4{\cdot}OEt_2$ to a diethyl ether solution of the trihydride-osmium(IV) complex $OsH_3(\eta^5\text{-}C_5H_5)(P^iPr_3)$ (**1**) leads to the dihydride-elongated dihydrogen derivative $[OsH_2(\eta^5\text{-}C_5H_5)(\eta^2\text{-}H_2)(P^iPr_3)]BF_4$ (**2**), which is isolated as a white solid in 93% yield, according to eq 1.



The most noticeable signal in the ^{1}H NMR spectrum of **2** in dichloromethane-d_2 at room temperature is a doublet at −10.70 ppm, with a H−P coupling constant of 14.1 Hz, corresponding to the dihydride-elongated dihydrogen unit. A variable-temperature 300 MHz study of this resonance gives a T_1 value of 950 ± 20 ms at 273 K, which decreases to 106 ± 1 ms at 180 K. In this temperature range, the T_1(min) value was not found. The reaction of **1** with trifluoromethanesulfonic acid-d_1 (DOTf) in dichloromethane-d_2 gives the [**2**-d_1]OTf salt, which shows a H−D coupling constant of 3.6 Hz. This value is average owing to the exchange process in the dihydride-elongated dihydrogen unit. Assuming that the hydride-dihydrogen H−D coupling constants are all between 0 and 1 Hz,[14] then the H−D coupling constant in the dihydrogen ligand is between 20.6 and 21.6 Hz. According to the standard Morris' empirical equation,[1a] the calculated H−D coupling constant yields a H−H separation of about 1.1 Å, which agrees well with that found in the related pentamethylcyclopentadienyl complex $[OsH_2(\eta^5\text{-}C_5Me_5)(\eta^2\text{-}H_2)(PPh_3)]BF_4$ by spectroscopic methods (1.06−1.08 Å) and a single-crystal neutron diffraction study (1.014(11) Å).[15] A singlet at 43.3 ppm in the $^{31}P\{^1H\}$ NMR spectrum is also characteristic of **2**.

2. Elementary Steps for the C−C Double Bond Reduction. In the presence of benzylideneacetone, complex **2** loses a hydrogen molecule and the resulting unsaturated dihydride coordinates the ketone to afford $[OsH_2(\eta^5\text{-}C_5H_5)\{\kappa^1\text{-}OC(CH_3)CH{=}CHPh\}(P^iPr_3)]BF_4$ (**3**), which is isolated as a yellow solid in 79% yield, according to Scheme 2.

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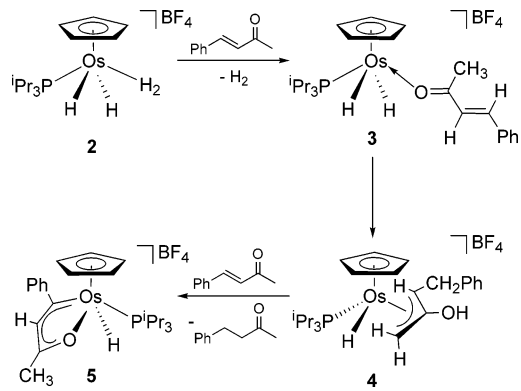
Scheme 2



The coordination of benzylideneacetone to the osmium atom, by the carbonyl group, was proved by an X-ray diffraction analysis experiment on a single crystal of the BAr^F_4 salt of **3** (BAr^F_4 = tetrakis(3,5-bis(trifluoromethyl)phenyl)borate). This salt was prepared by reaction of benzylideneacetone with the BAr^F_4 salt of **2**. Figure 1 shows a view of the structure of the cation, whereas Table 1 collects selected bond distances and angles.

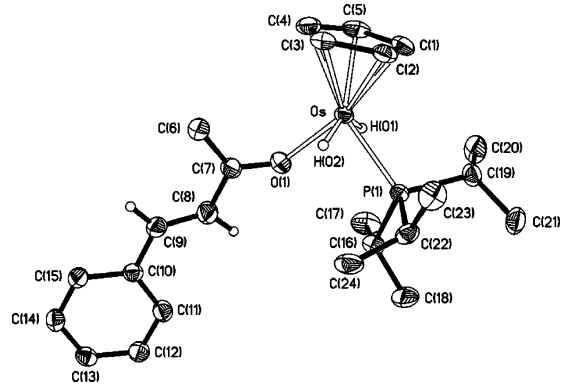


Figure 1. Molecular diagram of the cation of $[OsH_2(\eta^5\text{-}C_5H_5)\{\kappa^1\text{-}OC(CH_3)CH{=}CHPh\}(P^iPr_3)]BAr^F_4$ (**3**).

The distribution of ligands around the osmium atom can be described as a four-legged piano stool geometry, with the cyclopentadienyl ring occupying the three-membered face, while the monodentate ligands lie in the four-membered face. Although the O(1)−Os−P(1) angle of 88.77(7)° is noticeably small, like in other cyclopentadienyl-osmium(IV)-dihydride complexes,[12,16] the bulky ligands are mutually *transoid* disposed. The Os−O(1) bond length of 2.128(2) Å agrees well with the osmium−oxygen distances found in osmium-ketone compounds,[7i,8b,d,9e,17] whereas the O(1)−C(7) bond length of 1.247(4) Å is slightly longer than that observed in free benzylideneacetone (1.2242(13) Å).[18] This suggests a weakening of the C−O double bond of the ketone as a consequence of the coordination of the oxygen atom to the metal center. The effect of the coordination is also evident in the IR spectrum of **3**, which shows the ν(CO) band at 1616 cm^{-1}, shifted 64 cm^{-1} to lower wavenumbers if compared with the free molecule. In agreement with the coordination of the oxygen atom,[19] the carbonyl resonance in the $^{13}C\{^1H\}$ NMR spectrum is observed at 213.6 ppm, shifted 15.5 ppm to lower field with regard to the resonance of the free benzylideneacetone. As expected for the *transoid* disposition of the hydride ligands, the ^1H NMR spectrum contains only one high-field resonance. It appears as a doublet at −7.6 ppm with a H−P coupling constant of 32.0 Hz. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 42.1 ppm, which under off-resonance conditions is split into a triplet, as a result of the P−H coupling with two hydride ligands.

Table 1. Selected Bond Distances (Å) and Angles (deg) for the Complex $[OsH_2(\eta^5\text{-}C_5H_5)\{\kappa^1\text{-}OC(CH_3)\text{-}CH{=}CHPh\}(P^iPr_3)]BAr^F_4$ (3)

Os−O(1)	2.128(2)	Os−C(3)	2.232(3)
Os−P(1)	2.3136(9)	Os−C(4)	2.295(3)
Os−H(01)	1.37(4)	Os−C(5)	2.241(3)
Os−H(02)	1.52(4)	O(1)−C(7)	1.247(4)
Os−C(1)	2.163(3)	C(7)−C(8)	1.455(5)
Os−C(2)	2.158(3)	C(8)−C(9)	1.334(5)
M[a]−Os−O(1)	136.6	P(1)−Os−H(02)	77.8(15)
M[a]−Os−P(1)	134.6	H(01)−Os−H(02)	138(2)
M[a]−Os−H(01)	113.7	Os−O(1)−C7)	133.6(2)
M[a]−Os−H(02)	107.1	O(1)−C(7)−C(8)	115.6(3)
O(1)−Os−P(1)	88.77(7)	O(1)−C(7)−C(6)	121.1(3)
O(1)−Os−H(01)	76.0(17)	C(6)−C(7)−C(8)	123.3(3)
O(1)−Os−H(02)	80.1(15)	C(7)−C(8)−C(9)	123.7(4)
P(1)−Os−H(01)	68.3(17)	C(8)−C(9)−C(10)	126.8(4)

[a] M represents the midpoint of the Cp ring.

In dichloromethane at room temperature, complex **3** is converted to the hydroxyallyl derivative $[OsH(\eta^5\text{-}C_5H_5)\{\eta^3\text{-}CH_2C(OH)CHCH_2Ph\}(P^iPr_3)]BF_4$ (**4**). After 12 h, this monohydride is isolated as a green solid in 82% yield.

In the ^1H NMR spectrum, the resonance corresponding to the OH group appears at 7.56 ppm, as a broad signal. The $H_2C(sp^2)$ hydrogen atoms of the hydroxyallyl ligand display a doublet at 4.40 ppm, with a H−H coupling constant of 5.2 Hz, and a multiplet at 2.27 ppm, whereas the $HC(sp^2)$ hydrogen atom gives rise to a double doublet of doublets at 2.99 ppm, with H−H coupling constants of 11.2 and 2.2 Hz and a H−P coupling constant of 11.0 Hz. The resonances due to CH_2 protons of the benzyl substituent of the allyl group appear as the AB part of an ABC spin system with δ_A = 3.65, δ_B = 3.17, and J_{AB} = 14.2 Hz. The hydride resonance appears at −13.63 ppm as a doublet with a H−P coupling constant of 31.1 Hz. In the $^{13}C\{^1H\}$ NMR spectrum, the resonances corresponding to the allyl carbon atoms are observed at 130.7 (COH), 37.1 (CH), and 19.5 (CH_2) ppm. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 18.0 ppm, which under off-resonance conditions is split into a doublet. With the exception of the chemical shifts of the ^1H and ^{13}C COH resonances, which agree well with those reported for

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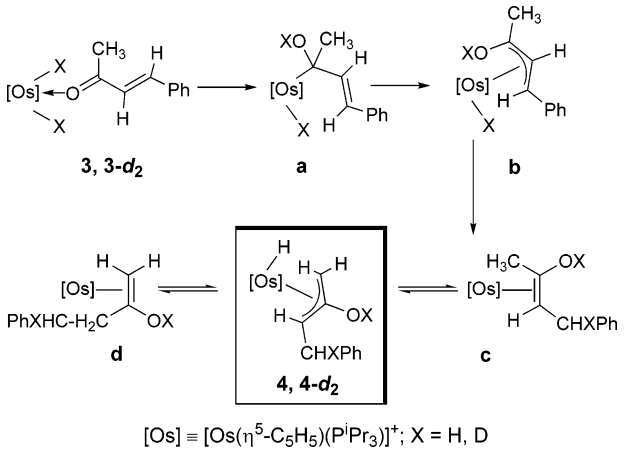
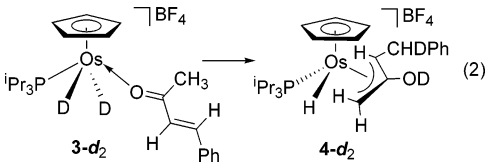
Scheme 3



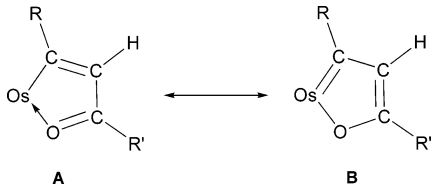
other hydroxyallyl complexes of late transition metals,[20] these spectroscopic data are very similar to those found for the silylcyclopentadienyl compound $[OsH(\eta^5\text{-}C_5H_4SiPh_3)\{\eta^3\text{-}CH_2C(Ph)CH_2\}(P^iPr_3)]BF_4$, where the disposition of the allyl ligand with regard to the $[OsH(\eta^5\text{-}C_5H_4SiPh_3)(P^iPr_3)]^{2+}$ skeleton has been confirmed by X-ray diffraction analysis.[21] In addition, the *cisoid* disposition of the hydride and the $H_2C(sp^2)$ group of the hydroxyallyl ligand in **4** is proved by the $^1H-^1H$ NOESY NMR spectrum, which shows the cross-peaks between the hydride resonance and those due to the $H_2C(sp^2)$ protons.

To obtain information about the formation of **4**, we prepared $[OsD_2(\eta^5\text{-}C_5H_5)\{\kappa^1\text{-}OC(CH_3)CH{=}CHPh\}(P^iPr_3)]BF_4$ (**3-*d*$_2$**), in situ, by reaction of $[OsD_2(\eta^5\text{-}C_5H_5)(\eta^2\text{-}D_2)(P^iPr_3)]BF_4$ (**2-*d*$_4$**) with benzylideneacetone. Under the same conditions as **3**, complex **3-*d*$_2$** is selectively transformed into $[OsH(\eta^5\text{-}C_5H_5)\{\eta^3\text{-}CH_2C(OD)CHCHDPh\}(P^iPr_3)]BF_4$ (**4-*d*$_2$**), containing a deuterium atom at the oxygen atom and the other one at the benzyl substituent of the allyl ligand (eq 2). The positions of these atoms are supported by the ^2H NMR spectrum of **4-*d*$_2$**, which shows three broad singlets at 7.6, 3.5, and 3.0 ppm with a 1:0.5:0.5 intensity ratio.

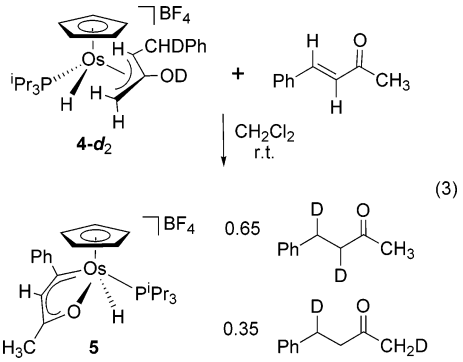


Scheme 3 shows a sequence of reactions that allows to rationalize the formation of **4** (X = H) and **4-*d*$_2$** (X = D). The 1,2-hydrogen or 1,2-deuterium shift from the metal to the oxygen atom of the ketone in **3** or **3-*d*$_2$** could afford the η^1-hydroxyallyl intermediate **a**, which should give **b** by $\eta^1-\eta^3$ rearrangement. A second hydrogen or deuterium migration from the metal, now, to the terminal CHPh carbon atom of the η^3-hydroxyallyl ligand of **b** could lead to the enol species **c**, which by $C(sp^3)-H$ bond activation of the methyl group should yield **4** or **4-*d*$_2$**.

Scheme 4



In the presence of benzylideneacetone, complex **4** releases 4-phenylbutan-2-one, and the resulting metallic fragment activates a $C(sp^2)-H$ bond of the α,β-unsaturated substrate to give $[OsH(\eta^5\text{-}C_5H_5)\{C(Ph)CHC(O)CH_3\}(P^iPr_3)]BF_4$ (**5**), which is isolated as a yellow solid in 79% yield, according to Scheme 2. Under the same conditions, **4-*d*$_2$** affords **5** and dideuterated saturated ketone containing one deuterium at position 4, 0.65 at position 3, and 0.35 at position 1. This deuterium distribution is consistent with a 1.8:1 mixture of the ketones shown in eq 3. The formation of both ketones indicates that **4** and **4-*d*$_2$** undergo the reversible migration of the hydride ligand from the metal center to both terminal carbon atoms of the hydroxyallyl group, to form the enol species **c** and **d** shown in Scheme 3. These intermediates release the saturated ketone in an irreversible manner. In agreement with this, reaction between **4-*d*$_2$** and 4-phenylbutan-2-one is not observed. According to the deuterium ratio between the positions 3 and 1 of the ketone, the migration to the CH_2-terminal group appears to be favored with regard to the migration to the terminal CH carbon atom.



In the ^1H NMR spectrum of **5** the most noticeable features are the presence of a singlet at 7.33 ppm, corresponding to the CH hydrogen atom of the five-membered heterometallacycle, and a doublet at −12.84 ppm with a H−P coupling constant of 34.4 Hz due to the hydride ligand. The $^{13}C\{^1H\}$ NMR spectrum suggests that for an adequate description of the bonding situation in **5** the resonance forms shown in Scheme 4 should be taken into account. Thus, it shows the resonance due to the metalated carbon

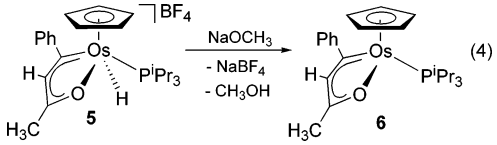
(20) See for example: (a) Huang, T.-M.; Hsu, R.-H.; Yang, C.-S.; Chen, J.-T.; Lee, G.-H.; Wang, Y. *Organometallics* **1994**, *13*, 3657. (b) Arndtsen, B. A.; Bergman, R. G. *J. Organomet. Chem.* **1995**, *504*, 143. (c) Casey, C. P.; Nash, J. R.; Yi, C. S.; Selmeczy, A. D.; Chung, S.; Powell, D. R.; Hayashi, R. K. *J. Am. Chem. Soc.* **1998**, *120*, 722.

(21) Baya, M.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2001**, *20*, 4875.

(22) This resonance appears shifted 5.7 and 7.7 ppm, respectively, to higher field with regard to the chemical shifts observed for the carbene atoms of the Fischer carbene derivatives $OsH(\eta^5\text{-}C_5H_5)\{{=}C(OMe)Ph\}(P^iPr_3)$ (δ 242.6)[23] and $OsH(\eta^5\text{-}C_5H_5)\{{=}C(OMe)Ph\}\{P^iPr_2[C(CH_3){=}CH_2]\}$ (δ 244.6).[24] However, it appears shifted more than 77 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),[25] $OsH(\eta^5\text{-}C_5H_5)\{(E)\text{-}CH{=}CHPh\}\{P(OMe)_3\}(P^iPr_3)$ (δ 136.9),[26] $[Os\{(E)\text{-}CH{=}CHCy\}Cl(=N{=}CMe_2)(P^iPr_3)_2][CF_3SO_3]$ (δ 143.1),[27] and $[Os\{(Z)\text{-}CH{=}C(Ph)NH{=}CR_2\}Cl(CO)_2(P^iPr_3)_2]^+$ (δ 158−145).[28]

atom at 236.9 ppm.[22] This chemical shift agrees with those corresponding to the related resonances of the complexes $OsCl\{CHCHC(O)Ph\}(CO)(P^iPr_3)_2$ (δ 230.13),[29] $Os(SnPh_2Cl)\{C_4(O)H_2C(O)H\}(\eta^2\text{-}H_2)(P^iPr_3)_2$ (δ 230.6), $Os(SnPh_2Cl)\{C_6H_8C(O)H\}(\eta^2\text{-}H_2)(P^iPr_3)_2$ (δ 242.9),[9e] $Os(SnPh_2Cl)\{CRCHC(O)R'\}(\eta^2\text{-}H_2)(P^iPr_3)_2$ (δ between 233 and 242),[7i] $OsH\{CHCHC(O)CH_3\}(CO)(P^iPr_3)_2$ (δ 250.8),[30] and $OsH_3\{C_6H_8C(O)CH_3\}(P^iPr_3)_2$ (δ 255.7),[9b] where bonding situations intermediate between resonance forms analogous to **A** and **B** have been proposed to exist. The OsC_α resonance of **5** is observed as a doublet with a C−P coupling constant of 4 Hz. This value strongly supports the *transoid* disposition of the metalated carbon atom of the ketone with regard to the phosphine ligand.[16e,21] The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 24.6 ppm, which under off-resonance conditions is split into a doublet.

Complex **5** can be deprotonated by reaction with sodium methoxide. The addition of this base to a tetrahydrofuran solution of **5** gives rise to the formation of the neutral compound $Os(\eta^5\text{-}C_5H_5)\{C(Ph)CHC(O)CH_3\}(P^iPr_3)$ (**6**), as a result of the extraction of the hydride ligand (eq 4). The reaction is reversible: the addition of 1.0 equiv of $HBF_4{\cdot}OEt_2$ to a dichloromethane-d_2 solution of **6** regenerates **5**. Complex **6**, which is a brown oil, is isolated in 88% yield.

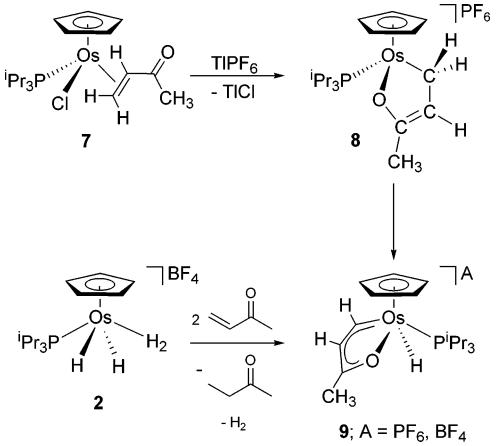


(4)

In the ^1H NMR spectrum of **6**, the most noticeable feature is the absence of any hydride resonance. The CH hydrogen of the heterometallacycle gives rise to a singlet at 7.51 ppm. The $^{13}C\{^1H\}$ NMR spectrum reveals an increase of the contribution of the resonance form **B** to the bonding in the five-membered ring, as a consequence of the deprotonation of the metal center. Thus, the OsC_α resonance is observed at 249.0 ppm, shifted about 12 ppm to lower field with regard to the chemical shift of **5**. This increase of the carbene resonance form is in agreement with the formal reduction of the metal center, which increases the back-bonding $Os(d\pi)\rightarrow C(p\pi)$ interaction. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 22.8 ppm.

3. Elementary Steps for the C(sp²)−H Bond Activation. The formation of **5** involves the coordination of benzylideneacetone to the osmium atom, after the release of the saturated ketone from **4**, as a previous step to the C(sp²)−H bond activation. All attempts to isolate this intermediate were unsuccessful. To obtain information about its nature, we note, however, that one of the phosphine ligands of $Os(\eta^5\text{-}C_5H_5)Cl(P^iPr_3)_2$ can be easily displaced by methyl vinyl ketone to afford $Os(\eta^5\text{-}C_5H_5)Cl\{\eta^2\text{-}CH_2{=}CHC(O)CH_3\}(P^iPr_3)$ (**7**) in high yield.[31] Treatment at −70 °C of an acetone solution of **7** with 1.3 equiv of $TlPF_6$ produces the abstraction of the chloride ligand and the intramolecular coordination of the carbonyl group of the ketone to give the intermediate $[Os(\eta^5\text{-}C_5H_5)\{CH_2CHC(O)CH_3\}(P^iPr_3)]PF_6$ (**8**), which is isolated as a green solid in 83% yield, according to Scheme 5.

Scheme 5

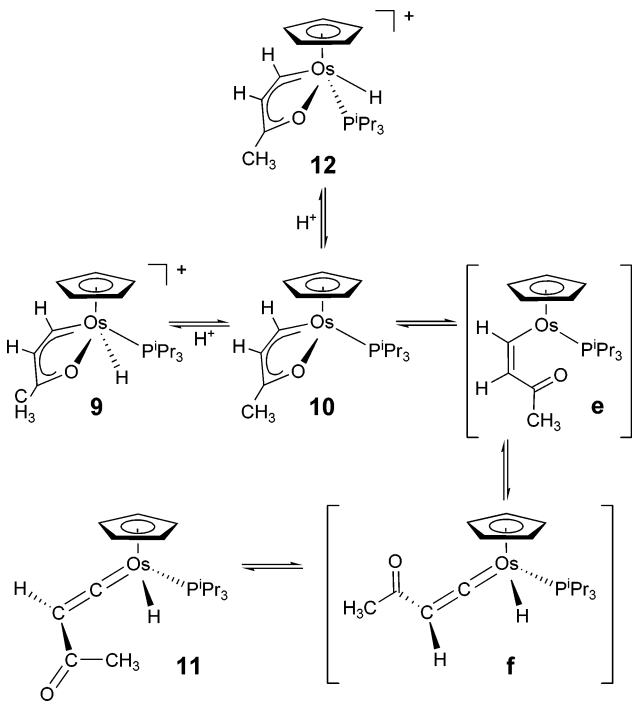


In the ^1H NMR spectrum, the resonances of the coordinated ketone appear at 5.78 (CH), 3.51 and 1.70 (CH_2), and 2.70 (CH_3) ppm, whereas in the $^{13}C\{^1H\}$ NMR spectrum they are observed at 141.3 (CO), 67.2 (CH), 31.4 (CH_2), and 20.4 (CH_3). These chemical shifts are similar to those corresponding to the related atoms of complexes $[OsH\{CH_2CHC(O)CH_3\}(CO)(P^iPr_3)_2]BF_4$,[32] $Ru\{CH_2CHC(O)CH_3\}$(triphos) (triphos = ttp, Cyttp),[33] $Ru\{CH_2C(CH_3)C(O)H\}(CO)(PPh_3)_2$,[34] and $Ru\{CH_2CHC(O)R\}(PEt_3)_3$ (R = H, CH_3).[35] It must be pointed out that the CH hydrogen atom has the same spin coupling with both hydrogen atoms of the CH_2 group. This indicates that the Karplus angle in both cases is the same, which suggests a significant contribution of the $\sigma^2-\pi$ resonance form to the Os−ketone bonding. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 9.6 ppm.

In dichloromethane at room temperature, complex **8** is rapidly converted into $[OsH(\eta^5\text{-}C_5H_5)\{CHCHC(O)CH_3\}(P^iPr_3)]PF_6$ (**9**). After 15 min the transformation is quantitative. If complex **8** is considered a 16-valence-electron osmium(IV) species, the formation of **9** can be rationalized as a 1,2-hydrogen shift from the CH_2 carbon atom of the ketone to the unsaturated metal center of

(23) Esteruelas, M. A.; González, A. I.; López, A. M.; Oñate, E. *Organometallics* **2003**, *22*, 414.
(24) Esteruelas, M. A.; González, A. I.; López, A. M.; Oñate, E. *Organometallics* **2004**, *23*, 4858.
(25) Barrio, P.; Esteruelas, M. A.; Oñate, E. *J. Am. Chem. Soc.* **2004**, *126*, 1946.
(26) Baya, M.; Esteruelas, M. A. *Organometallics* **2002**, *21*, 2332.
(27) Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2001**, *20*, 3283.
(28) Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2001**, *20*, 2294.
(29) Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A.; Zeier, B. *Organometallics* **1994**, *13*, 1662.
(30) Edwards, A. J.; Elipe, S.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A.; Valero, C. *Organometallics* **1997**, *16*, 3828.
(31) Esteruelas, M. A.; López, A. M.; Ruiz, N.; Tolosa, J. I. *Organometallics* **1997**, *16*, 4657.
(32) Esteruelas, M. A.; García, M. P.; López, A. M.; Oro, L. A.; Ruiz, N.; Schlünken, C.; Valero, C.; Werner, H. *Inorg. Chem.* **1992**, *31*, 5580.
(33) Jia, G.; Meek, D. W.; Gallucci, J. C. *Organometallics* **1990**, *9*, 2549.
(34) Hiraki, K.; Nonaka, A.; Matsunaga, T.; Kawano, H. *J. Organomet. Chem.* **1999**, *574*, 121.
(35) Kanaya, S.; Imai, Y.; Komine, N.; Hirano, M.; Komiya, S. *Organometallics* **2005**, *24*, 1059.

Scheme 6



8. In this context, it should be mentioned that in acetone the isomerization is significantly slower than in dichloromethane. As expected, the BF_4 salt of **9** and ethyl methyl ketone are obtained from the reaction of **2** with vinyl methyl ketone (Scheme 5). By this procedure, complex **9** is isolated as a yellow solid in 73% yield.

The ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra of **9** are consistent with those of **5** and with a notable contribution of the resonance form **B** (Scheme 4) to its structure. The OsCH resonance is observed at 12.70 ppm, as a double doublet of doublets by spin coupling with the phosphine (1.4 Hz), the hydride ligand (5.1 Hz), and the $C_\beta H$-hydrogen atom (7.3 Hz), which gives rise to a doublet at 7.29 ppm. The hydride resonance appears as a double doublet at −13.41 ppm, with a H−P coupling constant of 31.5 Hz. In the $^{13}C\{^1H\}$ NMR spectrum, the resonances corresponding to the carbon atoms of the heterometallacycle are observed at 222.8 (OsC), 214.5 (CO), and 137.2 (*C*CO) ppm. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 30.2 ppm, which under off-resonance conditions is split into a doublet.

Like **5**, complex **9** can be deprotonated with sodium methoxide. The addition of the base to a tetrahydrofuran solution of this compound leads to an equilibrium mixture of $Os(\eta^5\text{-}C_5H_5)\{CHCHC(O)CH_3\}(P^iPr_3)$ (**10**) and its hydride-vinylidene isomer $OsH(\eta^5\text{-}C_5H_5)\{{=}C{=}CHC(O)CH_3\}(P^iPr_3)$ (**11**), according to Scheme 6. In benzene-d_6 at room temperature the **10**:**11** molar ratio is 5:1.

The crystallization of the mixture in pentane at −78 °C affords crystals of **10** suitable for an X-ray diffraction analysis. Figure 2 shows a view of the structure of the molecule. Selected bond distances and angles are collected in Table 2. The geometry around the osmium center is close to octahedral, with the cyclopentadienyl ligand occupying three sites of a face. The angles formed by the triisopropylphosphine and the C(1) and O atoms of the metalated ketone are 93.16(10)° and 90.75(7)°,

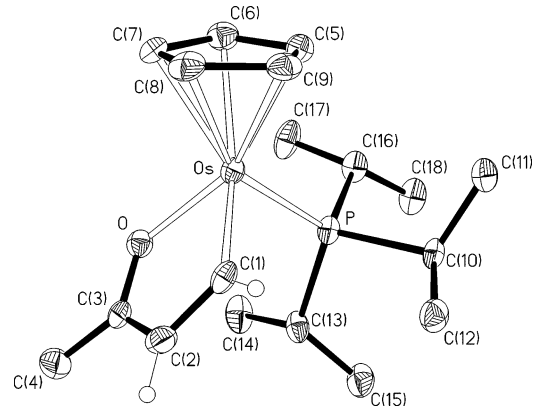


Figure 2. Molecular diagram of $Os(\eta^5\text{-}C_5H_5)\{CHCHC(O)CH_3\}(P^iPr_3)$ (**10**).

Table 2. Selected Bond Distances (Å) and Angles (deg) for the Complex $Os(\eta^5\text{-}C_5H_5)\{CHCHC(O)CH_3\}(P^iPr_3)$ (10)

Os−C(1)	1.989(4)	Os−C(8)	2.229(3)
Os−O	2.121(2)	Os−C(9)	2.187(3)
Os−P	2.3191(9)	C(1)−C(2)	1.384(5)
Os−C(5)	2.187(3)	C(2)−C(3)	1.396(5)
Os−C(6)	2.285(3)	C(3)−O	1.288(4)
Os−C(7)	2.246(3)		
M[a]−Os−C(1)	128.0	Os−C(1)−C(2)	118.7(3)
M[a]−Os−O	129.0	C(1)−C(2)−C(3)	113.0(3)
M[a]−Os−P	125.5	C(2)−C(3)−C(4)	125.6(3)
C(1)−Os−O	75.60(12)	O−C(3)−C(4)	117.6(3)
C(1)−Os−P	93.16(10)	C(2)−C(3)−O	116.8(3)
O−Os−P	90.75(7)	C(3)−O−Os	115.8(2)

[a] M represents the midpoint of the Cp ring.

respectively, whereas the C(1)−Os−O bite angle (75.60(12)°) of this group strongly deviates from 90°.

The five-membered heterometallacycle is almost planar (maximum deviation 0.0198(54) Å, C(4)). The Os−C(1) bond length of 1.989(4) Å agrees well with the osmium−carbon distances found in the complexes $Os(SnPh_2Cl)\{CHCHC(O)CH_3\}(\eta^2\text{-}H_2)(P^iPr_3)_2$ (2.035(2) Å),[7i] $Os\{CHCHC(O)Ph\}Cl(CO)(P^iPr_3)_2$ (1.921(3) Å),[29] and $Os(SnPh_2Cl)\{C_4(O)H_2C(O)H\}(\eta^2\text{-}H_2)(P^iPr_3)_2$ (2.021(4) Å),[9c] where the resonance forms shown in Scheme 4 have been taken into account to describe the bonding situation in the metallacycles. In agreement with this, the C(1)−C(2) and C(2)−C(3) distances of 1.384(5) and 1.396(5) Å, respectively, are between those expected for single and double carbon−carbon bonds. The Os−O and C(3)−O bond lengths of 2.121(2) and 1.288(4) Å also support the metallafuran resonance forms.[36]

In the ^1H NMR spectrum, the C(1)−H and C(2)−H resonances appear as doublets at 13.39 and 7.42 ppm, respectively, with a H−H coupling of 7.3 Hz. The $^{13}C\{^1H\}$ NMR spectrum, in a manner similar to that of **6**, makes clear the increase of the contribution of the resonance form **B** to the structure of the metallacycle as a result of the deprotonation of the metal center of **9**. Thus, the C(1) resonance is observed at 237.8 ppm, shifted 15 ppm to lower field with regard to that of **9**. This resonance appears as a doublet with a C−P

(36) Stone, K. C.; Jamison, G. M.; White, P. S.; Templeton, J. L. *Organometallics* **2003**, *22*, 3083, and references therein.

coupling constant of 6 Hz, while the C(2) resonance (δ 131.0) is a singlet. The C(3) atom displays a doublet at 203.8 ppm, with a C−P coupling constant of 2 Hz. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 30.4 ppm.

In the ^1H NMR spectrum of the hydride-vinylidene isomer **11**, the most noticeable features are a broad double doublet at 3.00 ppm, corresponding to the C_β−H of the vinylidene, and the hydride resonance. The latter is observed at −14.12 ppm as a double doublet by spin coupling with the C_β−H proton of the vinylidene (2.0 Hz) and the phosphorus of the phosphine (29.2 Hz). In dichloromethane-d_2, these resonances are temperature invariant between 183 and 298 K, suggesting that the vinylidene group does not rotate around the double bonds. The *cisoid* disposition of the hydride ligand and the acyl substituent is supported by the $^1H-^1H$ NOESY NMR spectrum, which shows the cross-peaks between the hydride and CH_3CO (δ 2.51) resonances. In the $^{13}C\{^1H\}$ NMR spectrum, the C_α resonance of the vinylidene appears at 289.7 ppm, as a doublet with a C−P coupling constant of 11 Hz, while the resonance due to the C_β atom is observed at 118.1 ppm, as a singlet. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 42.9 ppm, which under off-resonance conditions is split into a doublet.

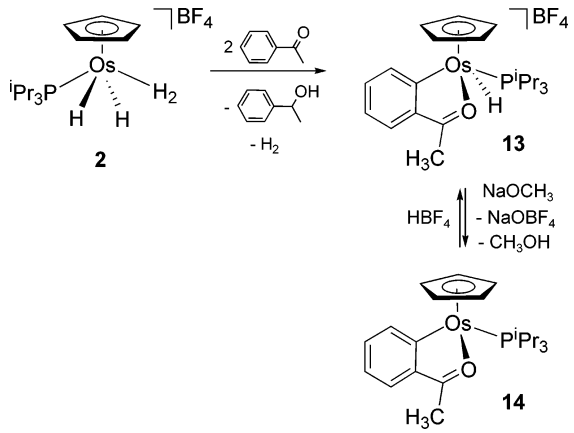
The formation of **11** can be rationalized according to Scheme 6. The decoordination of the oxygen atom in **10** should give an unsaturated alkenyl intermediate **e**, which could evolve into the hydride-vinylidene **f** by 1,2-hydrogen shift from the η^1-carbon donor ligand to the metal center. The formation of hydride-vinylidene complexes by an α-elimination reaction in alkenyl compounds is a well-known process.[37] Finally the rotation of the vinylidene of **f** around the Os−vinylidene bond should afford **11**. The driving force for this process must be the steric hindrance experienced by the acyl substituent and the isopropyl groups of the phosphine.

The deprotonation of **9** is reversible. Thus, the addition of 1.0 equiv of $HBF_4{\cdot}OEt_2$ to a dichloromethane solution of the equilibrium mixture of **10** and **11** initially leads to a mixture of **9** and its isomer **12** (Scheme 6). After 30 min, the **9**:**12** molar ratio is 1:2. After 12 h at room temperature the quantitative isomerization of **12** into **9** occurs.

The addition of the proton of the acid to **10** can take place between the phosphine and the oxygen atom or alternatively between the phosphine and the metalated carbon atom. The first addition leads to **12**, containing the metalated carbon atom *cisoid* disposed to the phosphine, while the second one directly gives **9**. Since complex **12** is the product of kinetic control and **9** is the product of thermodynamic control, the previously mentioned observations indicate that the addition between the phosphine and the oxygen is kinetically favored, whereas the *transoid* disposition of the metalated carbon atom and the phosphine is thermodynamically favored.

In contrast to **9**, in the ^1H NMR spectrum of **12**, the OsCH (δ 11.71) and CHCO (δ 7.22) resonances appear as double doublets with a H−H coupling constant of 7.7 Hz and H−P coupling constants of 1.6 and 2.6 Hz, respectively. The hydride ligand displays a doublet at −9.40 ppm, with a H−P coupling constant of 37.4 Hz. In the $^{13}C\{^1H\}$ NMR spectrum the OsC resonance is observed at 210.0 ppm as a doublet. The value of 14 Hz for the C−P coupling constant strongly supports the *cisoid* disposition of the metalated carbon atom and the phosphine. In addition, it should be noted that this resonance is shifted 12.8 ppm toward higher field with regard to that of **9**, suggesting a lower contribution of the resonance form **B** to the structure of **12** than to the structure of **9**. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 21.7 ppm, which under off-resonance conditions is split into a doublet.

Scheme 7



4. Olefinic C(sp²)−H versus Aromatic C(sp²)−H Activation. Treatment of **2** with 3.0 equiv of acetophenone produces the loss of a hydrogen molecule from the starting compound and the formation of 1.0 equiv of 1-phenylethanol and the orthometalated compound $[OsH(\eta^5\text{-}C_5H_5)\{C_6H_4C(O)CH_3\}(P^iPr_3)]BF_4$ (**13**), which is isolated as a yellow solid in 87% yield, according to Scheme 7. The reaction of **2-*d*₄** with 3.0 equiv of acetophenone also affords **13**. This indicates that **13** is a result of *ortho*-CH bond activation of the ketone by the $[Os(\eta^5\text{-}C_5H_5)(P^iPr_3)]^+$ metal fragment.

A view of the structure of the cation of **13** is shown in Figure 3. Selected bond distances and angles are listed in Table 3. The distribution of ligands around the osmium atom can be described as a four-legged piano stool geometry with the orthometalated carbon atom C(1) *transoid* to the phosphine ligand. The C(1) −Os−P and O−Os−H(01) angles are 106.24(12)° and 128.2(18)°, respectively.

The orthometalated ketone acts with a bite angle of 76.08(15)°. The Os−C(1) bond length of 2.016(5) Å is typical for an Os−C(aryl) single bond and agrees well with the values previously found in other orthometa-

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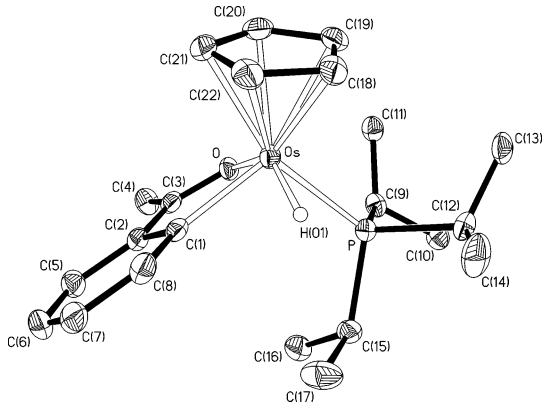


Figure 3. Molecular diagram of the cation of [OsH(η^5-C_5H_5){$C_6H_4C(O)CH_3$}(P^iPr_3)]BF_4 (**13**).

Table 3. Selected Bond Distances (Å) and Angles (deg) for the Complex [OsH(η^5-C_5H_5){$C_6H_4C(O)CH_3$}(P^iPr_3)]BF_4 (13)

Os−O	2.082(3)	Os−C(20)	2.294(5)
Os−P	2.3470(11)	Os−C(21)	2.229(4)
Os−H(01)	1.585(10)	Os−C(22)	2.156(4)
Os−C(1)	2.016(5)	O−C(3)	1.261(5)
Os−C(18)	2.168(5)	C(1)−C(2)	1.432(6)
Os−C(19)	2.297(5)	C(2)−C(3)	1.416(6)
M[a]−Os−C(1)	124.4	O−Os−P	82.09(8)
M[a]−Os−O	115.9	O−Os−H(01)	128.2(18)
M[a]−Os−P	128.6	P−Os−H(01)	76.0(18)
M[a]−Os−H	114.4	O−C(3)−C(2)	117.2(4)
C(1)−Os−O	76.08(15)	C(3)−O−Os	118.1(3)
C(1)−Os−P	106.24(12)	C(1)−C(2)−C(3)	111.5(4)
C(1)−Os−H(01)	66.4(18)		

[a] M represents the midpoint of the Cp ring.

lated osmium compounds.[8b,d,9a,e,16a,c,17,21,38] The Os−O bond length of 2.082(3) Å is about 0.04 Å shorter than those in **3** and **10**, while the O−C(3) distance of 1.261(5) Å is about 0.04 Å longer than that found in the free acetophenone.[39]

In agreement with the presence of a hydride ligand in **13**, its ^1H NMR spectrum contains a doublet at −13.80 ppm, with a H−P coupling constant of 32.9 ppm. In the $^{13}C\{^1H\}$ NMR spectrum the resonance corresponding to the metalated carbon atom of the ketone appears as a doublet at 179.3 ppm, with a C−P coupling constant of 3 Hz. The $^{31}P\{^1H\}$ NMR spectum shows a singlet at 28.0 ppm, which under off-resonance conditions is split into a doublet.

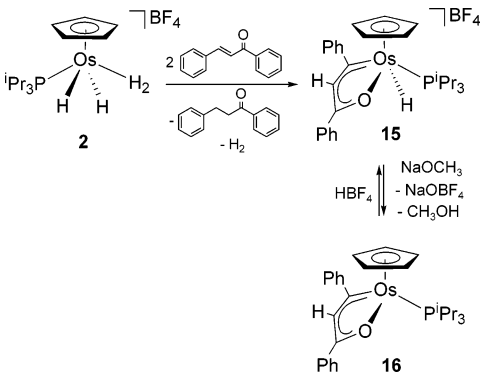
Like **5** and **9**, complex **13** can be deprotonated with sodium methoxide. The addition of 1.6 equiv of the base to a tetrahydrofuran solution of **13** leads to the neutral derivative Os(η^5-C_5H_5){$C_6H_4C(O)CH_3$}(P^iPr_3) (**14**), as a result of the abstraction of the hydride ligand of **13**. The reaction is reversible. The addition of 1.0 equiv of HBF_4·OEt_2 to a dichloromethane-d_2 solution of **14** regenerates **13**.

In the ^1H NMR spectrum of **14**, which is isolated as a brown oil in 74% yield, the most noticeable feature is the absence of any hydride resonance. In the $^{13}C\{^1H\}$ NMR spectrum the resonance of the metalated carbon atom of the ketone is observed as a doublet at 202.7 ppm, with a C−P coupling constant of 7 Hz. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 23.5 ppm.

We have shown that the metal fragment [Os(η^5-C_5H_5)(P^iPr_3)]$^+$ activates a $C_\beta(sp^2)$−H bond of α,β-unsaturated ketones and an *ortho*-CH bond of an aromatic ketone such as acetophenone. To study the preference for the olefinic $C_\beta(sp^2)$−H activation or aromatic *ortho*-CH activation, we have also investigated the reaction of **2** with benzylideneacetophenone. This substrate contains both functionalities bonded to the carbonyl unit, a phenyl group and a carbon−carbon double bond, which could be activated in a competitive manner. Thus, we have previously observed that the 14-valence-electron monohydride OsH($SnPh_2Cl$)(P^iPr_3)$_2$, generated from $OsH_3(SnPh_2Cl)$\{[η^2-CH_2=$C(CH_3)$]-P^iPr_2\}(P^iPr_3), activates both the $C_\beta(sp^2)$−H of the olefinic moiety and an *ortho*-CH bond of the phenyl group. The activation of the $C_\beta(sp^2)$−H bond of the olefin is kinetically favored with regard to the *ortho*-CH bond activation of the phenyl group. However, the orthometalated product is thermodynamically more stable than that resulting from the $C_\beta(sp^2)$−H bond activation.[7i]

In contrast to the monohydride OsH($SnPh_2Cl$)-(P^iPr_3)$_2$, complex **2** exclusively activates the $C_\beta(sp^2)$−H bond of benzylideneacetophenone. Treatment of this compound with 3.0 equiv of the α,β-unsaturated ketone leads to 1.0 equiv of saturated ketone and the complex [OsH(η^5-C_5H_5){C(Ph)CHC(O)Ph}(P^iPr_3)]BF_4 (**15**), which is isolated according to Scheme 8 as a green solid in 88% yield.

Scheme 8



The ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra of **15** agree well with those of **5** and **9**. In the ^1H NMR spectrum, the hydride resonance appears at −12.50 ppm as a doublet with a H−P coupling constant of 34.4 Hz. In the $^{13}C\{^1H\}$ NMR spectrum, the OsC resonance is observed as a doublet at 237.4 ppm, with a C−P coupling constant of 3 Hz. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 28.5 ppm, which under off-resonance conditions is split into a doublet.

The hydride ligand of **15** is also fairly acidic. Thus, the treatment of **15** with 1.3 equiv of sodium methoxide in tetrahydrofuran produces its deprotonation and the formation of the neutral derivative Os(η^5-C_5H_5){C(Ph)-CHC(O)Ph}(P^iPr_3) (**16**), which is isolated as a brown oil in 82% yield. The reaction is reversible. The addition of

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1.0 equiv of $HBF_4 \cdot OEt_2$ to a dichloromethane-d_2 solution of **16** regenerates **15**. The formation of an isomer of **15** with a stereochemistry as that of **12** is not observed.

In the $^{13}C\{^1H\}$ NMR spectrum, the metalated carbon atom of the ketone of **16** gives rise to a doublet at 249.8 ppm with a C−P coupling constant of 4 Hz. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 23.7 ppm.

Concluding Remarks

This study reveals that, in the presence of α,β-unsaturated and aromatic ketones, the dihydride-dihydrogen complex $[OsH_2(\eta^5\text{-}C_5H_5)(\eta^2\text{-}H_2)(P^iPr_3)]BF_4$ loses a hydrogen molecule, subsequently it reduces 1.0 equiv of substrate, and finally the resulting $[Os(\eta^5\text{-}C_5H_5)(P^iPr_3)]^+$ metal fragment activates a C(sp²)−H bond to give $[OsH(\eta^5\text{-}C_5H_5)\{C(R)CHC(O)R'\}(P^iPr_3)]BF_4$ or $[OsH(\eta^5\text{-}C_5H_5)\{C_6H_4C(O)R\}(P^iPr_3)]BF_4$, depending on the nature of the ketone.

The reduction of α,β-unsaturated ketones affords saturated ketones. The reactions are initiated with the coordination of the oxygen atom of the carbonyl group and involve the transfer of two hydrogen atoms from the metal center to the oxygen and C_β atoms of the substrates.

The $C_\beta(sp^2)$−H bond activation probably takes place by means of the initial $\sigma^2-\pi$ coordination of the α,β-unsaturated ketone to the metal fragment $[Os(\eta^5\text{-}C_5H_5)(P^iPr_3)]^+$ and most likely involves the 1,2-hydrogen shift from the CHR carbon atom to the metal center of the intermediates $[Os(\eta^5\text{-}C_5H_5)\{CH(R)CHC(O)R'\}(P^iPr_3)]^+$.

Although the metal fragment $[Os(\eta^5\text{-}C_5H_5)(P^iPr_3)]^+$ activates a $C_\beta(sp^2)$−H olefinic bond of α,β-unsaturated ketones and an *ortho*-CH bond of aromatic ketones, the exclusive activation of the olefinic $C_\beta(sp^2)$−H bond is observed in substrates such as benzylideneacetophenone, which contains both types of organic moieties bonded to the carbonyl group.

In conclusion, we show the sequence of steps for the selective carbon−carbon reduction and selective $C_\beta(sp^2)$−H bond activation of α,β-unsaturated ketones promoted by a new dihydride-dihydrogen complex.

Experimental Section

General Methods and Instrumentation. All reactions were carried out under argon with rigorous exclusion of air using Schlenk-tube or glovebox techniques. Solvents were dried by the usual procedures and distilled under argon prior to use. ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra were recorded on either a Varian UNITY 300, a Varian Gemini 2000, a Bruker ARX 300, a Bruker Avance 300 MHz, or a Bruker Avance 400 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*, are given in hertz. Spectral assignments were achieved by $^1H-^1H$ COSY and NOESY, $^1H\{^{31}P\}$, ^{13}C APT, $^1H-^{13}C$ HMQC, and $^1H-^{13}C$ HMBC experiments. Infrared spectra were run on a Perkin-Elmer 1730 spectrometer (Nujol mulls on polyethylene sheets). C and H analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyzer. Mass spectra analyses were performed with a VG Austospec instrument. In $LSIMS^+$ mode, ions were produced with the standard Cs^+ gun at ca. 30 kV, and 3-nitrobenzyl alcohol (NBA) was used in the matrix. 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.

Preparation of $[OsH_2(\eta^5\text{-}C_5H_5)(\eta^2\text{-}H_2)(P^iPr_3)]BF_4$ (2). A brown solution of **1** (290 mg, 0.69 mmol) in 5 mL of diethyl ether was treated with $HBF_4 \cdot Et_2O$ (113 μL, 0.83 mmol). Immediately a grayish white solid appeared. The solid was separated by decantation, washed with diethyl ether, and dried in vacuo. Yield: 325 mg (93%). Anal. Calcd for $C_{14}H_{30}BF_4OsP$: C, 33.21; H, 5.97. Found: C, 33.35; H, 5.59. IR (Nujol, cm^{-1}): ν(OsH) 2142 (m), 2108 (m). ^1H NMR (300 MHz, CD_2Cl_2, 293 K): δ 5.78 (s, 5H, C_5H_5), 2.19 (m, 3H, PCH), 1.18 (dd, $^3J_{HP}$ = 15.9, $^3J_{HH}$ = 7.2, 18H, PCHC*H*$_3$), −10.70 (d, $^2J_{HP}$ = 14.1, 4H, OsH). $^{31}P\{^1H\}$ NMR (121.42 MHz, CD_2Cl_2, 293 K): δ 43.3 (s). MS ($LSIMS^+$): *m/z* 421 (M^+). T_1 (ms, 300 MHz, CD_2Cl_2): 950 ± 20 (273 K), 940 ± 20 (263 K), 690 ± 10 (243 K), 420 ± 10 (223 K), 224 ± 2 (203 K), 168 ± 2 (193 K), 106 ± 1 (180 K).

Preparation of 2-d_1. An NMR tube containing a brown solution of **1** (24 mg, 0.06 mmol) in 0.5 mL of dichloromethane-d_2 was treated with trifluoromethanesulfonic acid-d_1 (7 μL, 0.08 mmol). The solution color changed from brown to light orange. ^1H NMR data were identical to those reported for **2** with the exception of the resonance at −10.69 (dt (1:1:1), $^2J_{HP}$ = 13.8, $J_{HD\ (average)}$ = 3.6, 3H, OsH). $^{31}P\{^1H\}$ NMR (121.42 MHz, CD_2Cl_2, 293 K): δ 43.3 (br).

Preparation of $[OsD_2(\eta^5\text{-}C_5H_5)(\eta^2\text{-}D_2)(P^iPr_3)]BF_4$ (2-d_4). An NMR tube was charged with **2** (20 mg, 0.04 mmol), and 0.2 mL of methanol-d_4 was added. After 5 min, the solvent was removed in vacuo, and the grayish solid was dissolved in dichloromethane-d_2. ^1H NMR data were identical to those reported for **2** with the exception of the absence of the resonance at −10.70 ppm. ^2H NMR (61.42 MHz, CH_2Cl_2, 293 K): δ −10.0 (br). $^{31}P\{^1H\}$ NMR (121.42 MHz, CD_2Cl_2, 293 K): δ 43.3 (br).

Preparation of BAr^F_4 Salt of 2. A Schlenk flask was charged with **2** (200 mg, 0.40 mmol) and $NaBAr^F_4$ (318 mg, 0.36 mmol). Diethyl ether (5 mL) was added, and the mixture was stirred for 1 h at room temperature. The resultant light orange solution was filtered through Celite and concentrated to ca. 1 mL under reduced pressure. The addition of pentane (10 mL) caused the formation of a white solid, which was separated by decantation and dried in vacuo. Yield: 418 mg (91%). The $^{31}P\{^1H\}$ and ^1H NMR (300 MHz, CD_2Cl_2, 293 K) data were identical to those reported for **2** with the exception of the appearance of the resonances at 7.74 (br s, 8H, *o*-BAr^F_4) and 7.58 (s, 4H, *p*-BAr^F_4) ppm.

Preparation of $[OsH_2(\eta^5\text{-}C_5H_5)\{\kappa^1\text{-}OC(CH_3)CH{=}CHPh\}(P^iPr_3)]BF_4$ (3). In a Schlenk flask in a glovebox were added **2** (50 mg, 0.10 mmol) and benzylideneacetone (150 mg, 1.03 mmol). The flask was removed from the glovebox and placed on a vacuum line under argon. The reaction mixture was stirred for 5 min under reduced pressure. The resultant orange slurry was cooled to −70 °C, and cold diethyl ether (20 mL) was added. Immediately, a light yellow solid appeared, which was washed with cold diethyl ether (3 × 5 mL), cold toluene (3 × 5 mL), and then with pentane (3 × 5 mL). The product was recrystallized from cold dichloromethane (2 mL) and diethyl ether (20 mL). The light yellow solid was separated by decantation and dried in vacuo. Yield: 51 mg (79%). Anal. Calcd for $C_{24}H_{38}BF_4OOsP$: C, 44.31; H, 5.89. Found: C, 44.63; H, 6.07. IR (Nujol, cm^{-1}): ν(OsH) 2116 (w), ν(CO) 1616 (m). ^1H NMR (400 MHz, CD_2Cl_2, 223 K): δ 7.71 (d, $^3J_{HH}$ = 16.9, 1H, PhC*H*), 7.68 (m, 2H, Ph), 7.54 (m, 3H, Ph), 6.81 (d, $^3J_{HH}$ = 16.9, 1H, CHCO), 5.47 (s, 5H, C_5H_5), 2.43 (s, 3H, CH_3), 2.10 (br, 3H, PC*H*CH_3), 1.24 (dd, $^3J_{HP}$ = 14.5, $^3J_{HH}$ = 6.6, 18H, PHC*H*$_3$), −7.61 (d, $^2J_{HP}$ = 32.0, 2H, OsH). $^{31}P\{^1H\}$ NMR (161.99 MHz, CD_2Cl_2, 223 K): δ 42.1 (s, t in off-resonance). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2, 223 K): δ 213.6 (s, CO), 150.0 (s, Ph*C*H), 132.6 (s, C_{ipso}Ph), 132.4, 129.1, 129.0 (all s, Ph),

124.7 (s, *C*HCO), 77.9 (d, J_{CP} = 2, C_5H_5), 27.5 (br d, J_{CP} = 32, P*C*HCH$_3$), 27.2 (br, CH_3), 18.6 (s, PCH*C*H$_3$).

Preparation of BAr$^F_4$ Salt of 3. This complex was prepared as described for **3** starting from 125 mg (0.10 mmol) of the BAr$^F_4$ salt of **2** and benzylideneacetone (150 mg, 1.03 mmol), but it was precipitated by addition of pentane. A light yellow solid was obtained. Yield: 107 mg (75%). Crystals suitable for the X-ray diffraction were obtained at 233 K by slow diffusion of pentane into a concentrated solution of the BAr$^F_4$ salt of **3** in toluene. The $^{31}P\{^1H\}$ and ^1H NMR (400 MHz, CD_2Cl_2, 233 K) data were identical to those reported for **3** with the exception of the appearance of the resonances at 7.70 (br s, 8H, *o*-BAr$^F_4$) and 7.52 (s, 4H, *p*-BAr$^F_4$) ppm.

Preparation of [OsH(η^5-C_5H_5){η^3-$CH_2C(OH)CHCH_2Ph$}-(P^{i}Pr$_3$)]BF$_4$ (4). An orange solution of **3** (51 mg, 0.08 mmol) in 4 mL of dichloromethane was stirred at room temperature for 12 h. The solution was concentrated to ca. 1 mL under reduced pressure. The addition of diethyl ether (10 mL) caused the formation of a light green solid, which was separated by decantation, washed with diethyl ether (3 × 5 mL), and dried in vacuo. Yield: 42 mg (82%). Anal. Calcd for $C_{24}H_{38}BF_4OOsP$: C, 44.31; H, 5.89. Found: C, 43.97; H, 5.69. ^1H NMR (400 MHz, CD_2Cl_2, 293 K): δ 7.56 (br, 1H, OH), 7.50 (m, 2H, Ph), 7.36 (m, 2H, Ph), 7.32 (m, 1H, Ph), 5.48 (s, 5H, C_5H_5), 4.40 (d, $^2J_{HH}$ = 5.2, 1H, OsCH$_2$), 3.65 (dd, $^2J_{HH}$ = 14.2, $^3J_{HH}$ = 11.2, 1H, CH$_2$Ph), 3.17 (dd, $^2J_{HH}$ = 14.2, $^3J_{HH}$ = 2.2, 1H, CH$_2$Ph), 2.99 (ddd, $^3J_{HH}$ =11.2, $^3J_{HP}$ =11.0, $^3J_{HH}$ = 2.2, 1H, CH), 2.27 (br, 1H, OsCH$_2$), 2.16 (m, 3H, PC*H*CH$_3$), 1.27 (dd, $^3J_{HP}$ = 14.6, $^3J_{HH}$ = 7.3, 9H, PCHC*H*$_3$), 1.16 (dd, $^3J_{HP}$ = 14.6, $^3J_{HH}$ = 7.3, 9H, PCHC*H*$_3$), −13.63 (d, $^2J_{HP}$ = 31.1, 1H, OsH). $^{31}P\{^1H\}$ NMR (161.99 MHz, CD_2Cl_2, 293 K): δ 18.0 (s, d in off-resonance). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2, 293 K): δ 141.6 (s, C_{ipso}Ph), 130.7 (s, CO), 129.3, 129.0, 128.6 (all s, Ph), 85.9 (d, J_{CP} = 2, C_5H_5), 37.9 (s, *C*H$_2$Ph), 37.1 (d, J_{CP} = 5, CH), 27.5 (d, J_{CP} = 29, P*C*HCH$_3$), 20.0 (s, PCH*C*H$_3$), 19.6 (d, J_{CP} = 2, PCH*C*H$_3$), 19.5 (s, OsCH$_2$).

Preparation of [OsH(η^5-C_5H_5){C(Ph)CHC(O)CH$_3$}(P^{i}Pr$_3$)]BF$_4$ (5). In a Schlenk flask in a glovebox were added **2** (102 mg, 0.20 mmol) and benzylideneacetone (125 mg, 0.86 mmol). The flask was removed from the glovebox and placed on a vacuum line under argon. The argon pressure inside the flask was slightly reduced, and then it was heated to 50 °C. After 2 h, the resulting orange solution was cooled to −78 °C. The addition of diethyl ether (15 mL) caused the formation of a light yellow solid, which was washed with cold diethyl ether and dried in vacuo. Yield: 103 mg (79%). GC-MS analysis of the mother liquor showed the presence of benzylideneacetone and 4-phenylbutan-2-one. Anal. Calcd for $C_{24}H_{36}BF_4OOsP$: C, 44.45; H, 5.60. Found: C, 44.36; H, 5.66. ^1H NMR (400 MHz, CD_2Cl_2, 293 K): δ 7.83 (m, 2H, Ph), 7.49 (m, 3H, Ph), 7.33 (s, 1H, CH), 5.57 (s, 5H, C_5H_5), 2.65 (s, 3H, CH$_3$), 2.42 (m, 3H, PC*H*CH$_3$), 1.25 (dd, $^3J_{HP}$ = 14.6, $^3J_{HH}$ = 7.3, 9H, PCHC*H*$_3$), 1.14 (dd, $^3J_{HP}$ = 14.6, $^3J_{HH}$ = 7.3, 9H, PCHC*H*$_3$), −12.84 (d, $^2J_{HP}$ = 34.4, 1H, OsH). $^{31}P\{^1H\}$ NMR (161.99 MHz, CD_2Cl_2, 293 K): δ 24.6 (s, d in off-resonance). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2, 293 K): δ 236.9 (d, J_{CP} = 4, OsC), 214.6 (d, J_{CP} = 2, CO), 149.7 (s, C_{ipso}Ph), 134.6 (s, CH), 131.7 (s, *p*-Ph), 129.3 (s, *o*- and *m*-Ph), 87.3 (d, J_{CP} = 2, C_5H_5), 27.7 (d, J_{CP} = 30, P*C*HCH$_3$), 23.4, (s, CH$_3$), 20.2 (d, J_{CP} = 2, PCH*C*H$_3$), 19.3 (d, J_{CP} = 2, PCH*C*H$_3$). MS (LSIMS$^+$): *m/z* 563 (M$^+$).

Reaction of [OsD$_2$(η^5-C_5H_5)(η^2-D$_2$)(P^{i}Pr$_3$)]BF$_4$ (2-*d*$_4$) with Benzylideneacetone: Formation of [OsD$_2$(η^5-C_5H_5){κ^1-OC(CH$_3$)CH=CHPh}(P^{i}Pr$_3$)]BF$_4$ (3-*d*$_2$), [OsH(η^5-C_5H_5)-{η^3-$CH_2C(OD)CHCHDPh$}(P^{i}Pr$_3$)]BF$_4$ (4-*d*$_2$), 5, and 4-Phenylbutan-2-one-*d*$_2$. Two NMR tubes were charged with **2**-*d*$_4$ (20 mg, 0.04 mmol) and benzylideneacetone (18 mg, 0.12 mmol). To the first NMR tube, 0.5 mL of dichloromethane was added, and to the second 0.5 mL of dichloromethane-d_2 was added. After that, ^1H and ^2H NMR were recorded. The ^1H NMR (400 MHz, CD_2Cl_2, 293 K) data were identical to those reported for **3** with the exception of the absence of the resonance at −7.61 ppm. ^2H NMR (61.42 MHz, CH_2Cl_2, 293 K): δ −7.3 (br d, $^2J_{DP}$ = 4.2, OsD).

Both samples were stored at room temperature for 2 h. Then, ^1H and ^2H NMR were recorded. The ^1H NMR (400 MHz, CD_2Cl_2, 293 K) data were identical to those reported for **4** with the exception of the absence of the resonance at 7.56 ppm and the intensity of the signals at 3.65 (0.5H, CH$_2$Ph) and 3.17 (0.5H, CH$_2$Ph). ^2H NMR (61.42 MHz, CH_2Cl_2, 293 K): δ 7.6 (br, OD), 3.5 (br, CHDPh), and 3.0 (br, CHDPh).

After 12 h at room temperature, ^1H NMR showed the presence of **5** and 4-phenylbutan-2-one-d_2. The ^1H NMR (400 MHz, CD_2Cl_2, 293 K) data were identical to those reported for **5** and 4-phenylbutan-2-one with the exception of the integral ratio between the resonances at 2.85 (br t, 1H, CHDPh), 2.74 (br t, 1.35H, CHDCO), and 2.10 (br s, 2.65H, CH$_2$D) corresponding to that of 4-phenylbutan-2-one-d_2.

Preparation of Os(η^5-C_5H_5){C(Ph)CHC(O)CH$_3$}(P^{i}Pr$_3$) (6). In a flame-dried Schlenk flask in a glovebox were added 113 mg (0.17 mmol) of **5** and sodium methoxide (12 mg, 0.22 mmol). The flask was removed from the glovebox and placed on a vacuum line under argon. THF (5 mL) was added, and after 15 min the solvent was removed in vacuo. The product was extracted in toluene (10 mL) and filtered through Celite. Then, the solvent was removed, and the resultant oil was extracted with pentane (10 mL). The solution was concentrated to dryness, and a dark brown oil was obtained.[40] Yield: 86 mg (88%). ^1H NMR (400 MHz, C_6D_6, 293 K): δ 8.02 (d, J_{HH} = 8.0, 2H, *o*-Ph), 7.51 (s, 1H, CH), 7.33 (dd, $^3J_{HH}$ = 8.0, $^3J_{HH}$ = 7.3, 2H, *m*-Ph), 7.17 (t, $^3J_{HH}$ = 7.3, 1H, *p*-Ph), 4.54 (s, 5H, C_5H_5), 2.44 (s, 3H, CH$_3$), 1.88 (m, 3H, PC*H*CH$_3$), 1.11 (dd, $^3J_{HP}$ = 13.2, $^3J_{HH}$ = 7.3, 9H, PCHC*H*$_3$), 0.92 (dd, $^3J_{HP}$ = 13.2, $^3J_{HH}$ = 7.3, 9H, PCHC*H*$_3$). $^{31}P\{^1H\}$ NMR (161.99 MHz, C_6D_6, 293 K): δ 22.8 (s). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6, 293 K): δ 249.0 (d, J_{CP} = 4, OsC), 203.8 (d, J_{CP} = 4, CO), 155.5 (s, C_{ipso}Ph), 130.0 (d, J_{CP} = 2, CH), 129.9 (s, *o*-Ph), 128.9 (s, *p*-Ph), 128.3 (s, *m*-Ph), 72.6 (d, J_{CP} = 2, C_5H_5), 26.7 (d, J_{CP} = 25, P*C*HCH$_3$), 22.3, (d, J_{CP} = 2, CH$_3$), 20.8 (s, PCH*C*H$_3$), 20.6 (s, PCH*C*H$_3$). MS (LSIMS$^+$): *m/z* 562 (M$^+$).

Preparation of [Os(η^5-C_5H_5){CH$_2$CHC(O)CH$_3$}(P^{i}Pr$_3$)]-PF$_6$ (8). A flame-dried Schlenk flask was charged with **7** (148 mg, 0.28 mmol). Acetone (18 mL) was added to the flask, and it was cooled to −70 °C in a dry ice/2-propanol bath. Then, thallium(I) hexafluorophosphate (126 mg, 0.36 mmol) was added, the reaction mixture was stirred for 20 min, and the solvent was removed in vacuo. The crude reaction mixture was cooled to −70 °C and extracted with cold dichloromethane (30 mL). The orange slurry was filtered through Celite and concentrated to ca. 1 mL under reduced pressure. The addition of cold diethyl ether (15 mL) caused the formation of a light green solid, which was separated by decantation, washed with cold diethyl ether (3 × 5 mL), and dried in vacuo. Yield: 149 mg (83%). Anal. Calcd for $C_{18}H_{32}F_6OOsP_2$: C, 34.28; H, 5.12. Found: C, 34.12; H, 4.98. ^1H NMR (300 MHz, CD_2Cl_2, 233 K): δ 5.78 (ddd, $^3J_{HH}$ = 7.5, $^3J_{HH}$ = 7.5, $^3J_{HP}$ = 2.4, 1H, CH), 5.60 (s, 5H, C_5H_5), 3.51 (dd, $^3J_{HH}$ = 7.5, $^2J_{HH}$ = 1.5, 1H, CH$_2$), 2.70 (s, 3H, CH$_3$), 2.62 (m, 3H, PC*H*CH$_3$), 1.70 (ddd, $^3J_{HP}$ = 14.1, $^3J_{HH}$ = 7.5, $^2J_{HH}$ = 1.5, 1H, CH$_2$), 1.38 (dd, $^3J_{HP}$ = 14.1, $^3J_{HH}$ = 6.9, 9H, PCHC*H*$_3$), 1.35 (dd, $^3J_{HP}$ = 14.1, $^3J_{HH}$ = 6.9, 9H, PCHC*H*$_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_2Cl_2, 233 K): δ 9.6 (s, PCHCH$_3$), −144.2 (sept, J_{FP} = 714, PF$_6$). $^{13}C\{^1H\}$ NMR (75.4 MHz, CD_2Cl_2, 233 K): δ 141.3 (s, CO), 79.4 (s, C_5H_5), 67.2 (s, CH) 31.4 (d, J_{CP} = 6, CH$_2$), 26.2 (d, J_{CP} = 28, P*C*HCH$_3$), 20.4, (s, CH$_3$), 19.5 (s, PCH*C*H$_3$), 19.1 (s, PCH*C*H$_3$).

Preparation of [OsH(η^5-C_5H_5){CHCHC(O)CH$_3$}(P^{i}Pr$_3$)]A (9) (A = PF$_6$, BF$_4$). 9-PF$_6$ Salt. An orange solution of **7** (668

(40) All our attempts to achieve a valid elemental analysis determination for this complex were unsuccessful due to the presence of impurity traces (including solvents) in the sample.

mg, 1.28 mmol) in 10 mL of acetone was treated with thallium(I) hexafluorophosphate (493 mg, 1.41 mmol). The solution was allowed to react for 15 min at room temperature, the solvent was removed in vacuo, and the crude reaction mixture was dissolved in dichloromethane (10 mL). The orange solution was filtered through Celite and concentrated to ca. 1 mL under reduced pressure. The addition of diethyl ether (15 mL) caused the formation of a yellow solid, which was separated by decantation and dried in vacuo. Yield: 660 mg (82%). Anal. Calcd for $C_{18}H_{32}F_6OOsP_2$: C, 34.28; H, 5.12. Found: C, 34.19; H, 5.04. ^{1}H NMR (400 MHz, CD_2Cl_2, 293 K): δ 12.70 (ddd, $^3J_{HH}$ = 7.3, $^3J_{HH}$ = 5.1, $^3J_{HP}$ = 1.4, 1H, OsCH), 7.29 (d, $^3J_{HH}$ = 7.3, 1H, OsCHC*H*), 5.63 (s, 5H, C_5H_5), 2.62 (s, 3H, CH_3), 2.24 (m, 3H, PC*H*CH_3), 1.23 (dd, $^3J_{HP}$ = 14.6, $^3J_{HH}$ = 6.6, 9H, PCHC*H*$_3$), 1.10 (dd, $^3J_{HP}$ = 14.6, $^3J_{HH}$ = 6.6, 9H, PCHC*H*$_3$), −13.41 (dd, $^2J_{HP}$ = 31.5, $^3J_{HH}$ = 5.1, 1H, OsH). ^{31}P{^{1}H} NMR (161.99 MHz, CD_2Cl_2, 293 K): δ 30.2 (s, d in off-resonance, ^{i}Pr$_3$), −144.4 (sept, PF_6). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2, 293 K): δ 222.8 (br, OsCH), 214.5 (d, J_{CP} = 2, CO), 137.2 (s, OsCHC*H*), 86.7 (s, C_5H_5), 27.0 (d, J_{CP} = 29, P*C*HCH$_3$), 23.4, (s, CH_3), 20.0 (d, J_{CP} = 2, PCH*C*H$_3$), 19.2 (d, J_{CP} = 2, PCH*C*H$_3$). MS (LSIMS$^+$): *m/z* 487 (M^+).

9-BF$_4$ Salt. This complex was prepared as described for **5** starting from 100 mg (0.20 mmol) of **2** and methyl vinyl ketone (49 μL, 0.59 mmol). A yellow solid was obtained. Yield: 83 mg (73%). Anal. Calcd for $C_{18}H_{32}BF_4OOsP$: C, 37.77; H, 5.63. Found: C, 37.42; H, 5.36. GC-MS analysis of the mother liquor showed the presence of methyl vinyl ketone and ethyl methyl ketone.

Reaction of [OsH(η^5-C_5H_5){CHCHC(O)CH_3}(P^iPr_3)]PF_6 (9) with Sodium Methoxide: Formation of Os(η^5-C_5H_5)-{CHCHC(O)CH_3}(P^iPr_3) (10) and OsH(η^5-C_5H_5)(=C=CHC(O)CH_3)(P^iPr_3) (11). A procedure analogous to that described for **6** was followed starting from **9-PF$_6$** (250 mg, 0.40 mmol) and sodium methoxide (25 mg, 0.46 mmol). A dark brown thick oil was obtained. The NMR spectra in C_6D_6 at room temperature showed the presence of **10** and **11** in a molar ratio 5:1. Yield of the mixture: 153 mg (80%). Complex **10** could be isolated pure by crystallization of the mixture from pentane at −78 °C. Spectroscopic data for **10**: ^{1}H NMR (400 MHz, C_6D_6, 293 K): δ 13.39 (d, $^3J_{HH}$ = 7.3, 1H, OsCH), 7.42 (d, $^3J_{HH}$ = 7.3, 1H, OsCHC*H*), 4.60 (s, 5H, C_5H_5), 2.46 (d, J_{HP} = 2.2, 3H, CH_3), 1.70 (m, 3H, PC*H*CH_3), 1.02 (dd, $^3J_{HP}$ = 13.2, $^3J_{HH}$ = 7.3, 9H, PCHC*H*$_3$), 0.98 (dd, $^3J_{HP}$ = 13.2, $^3J_{HH}$ = 7.3, 9H, PCHC*H*$_3$). ^{31}P{^{1}H} NMR (161.99 MHz, C_6D_6, 293 K): δ 30.4 (s). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 293 K): δ 237.8 (d, J_{CP} = 6, OsCH), 203.8 (d, J_{CP} = 2, CO), 131.0 (s, OsCHC*H*), 71.9 (d, J_{CP} = 2, C_5H_5), 25.8 (d, J_{CP} = 26, P*C*HCH$_3$), 22.3 (s, CH_3), 20.6 (s, PCH*C*H$_3$), 20.5 (s, PCH*C*H$_3$). Spectroscopic data for **11**: ^{1}H NMR (400 MHz, C_6D_6, 293 K): δ 4.89 (s, 5H, C_5H_5), 3.00 (br, 1H, CH), 2.51 (s, 3H, CH_3), 1.83 (m, 3H, PC*H*CH_3), 0.85 (dd, $^3J_{HP}$ = 14.0, $^3J_{HH}$ = 7.2, 9H, PCHC*H*$_3$), 0.83 (dd, $^3J_{HP}$ = 14.0, $^3J_{HH}$ = 7.2, 9H, PCHC*H*$_3$), −14.12 (dd, $^2J_{HP}$ = 29.2, $^4J_{HH}$ = 2.0, 1H, OsH). ^{31}P{^{1}H} NMR (161.99 MHz, C_6D_6, 293 K): δ 42.9 (s, d in off-resonance). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 293 K): δ 289.7 (d, J_{CP} = 11, OsC), 191.8 (s, CO), 118.1 (s, CH), 84.5 (d, J_{CP} = 2, C_5H_5), 28.5 (d, J_{CP} = 31, P*C*HCH$_3$), 28.5, (s, CH_3), 20.5 (s, PCH*C*H$_3$), 20.2 (s, PCH*C*H$_3$). MS (LSIMS$^+$): *m/z* 486 (M^+).

Reaction of 10 and 11 with HBF$_4$. An NMR tube containing a dark brown solution of **10** and **11** (24 mg, 0.05 mmol) in 0.5 mL of dichloromethane-d_2 was treated with HBF_4·Et_2O (6.6 μL, 0.05 mmol). The solution color changed immediately from dark brown to light yellow. After 30 min at room temperature, the NMR spectra at −40 °C showed the presence of **9** and **12** in a molar ratio of 1:2. After 12 h at room temperature, **9** was the only isomer observed. Spectroscopic data for **12**: ^{1}H NMR (300 MHz, CD_2Cl_2, 233 K): δ 11.71 (dd, $^3J_{HH}$ = 7.7, $^3J_{HP}$ = 1.6, 1H, OsCH), 7.22 (dd, $^3J_{HH}$ = 7.7, $^4J_{HP}$ = 2.6 1H, OsCHC*H*), 5.71 (s, 5H, C_5H_5), 2.68 (s, 3H, CH_3), 2.26 (m, 3H, PC*H*CH_3), 1.22 (dd, $^3J_{HP}$ = 14.8, $^3J_{HH}$ = 6.6, 9H, PCHC*H*$_3$), 1.20 (dd, $^3J_{HP}$ = 14.3, $^3J_{HH}$ = 7.2, 9H, PCHC*H*$_3$), −9.40 (d, $^2J_{HP}$ = 37.4, 1H, OsH). ^{31}P{^{1}H} NMR (121.4 MHz, CD_2Cl_2, 293 K): δ 21.7 (s, d in off-resonance). ^{13}C{^{1}H} NMR (75.4 MHz, CD_2Cl_2, 233 K): δ 217.4 (s, CO), 210.0 (d, J_{CP} = 14, OsCH), 138.1 (d, J_{CP} = 3, OsCHC*H*), 84.4 (s, C_5H_5), 28.4 (d, J_{CP} = 33, P*C*HCH$_3$), 24.5 (s, CH_3), 19.7 (s, PCHC*H*$_3$), 18.9 (d, J_{CP} = 2, PCHC*H*$_3$).

The same procedure was followed in all of the reported protonation reactions starting from the corresponding osmium derivatives, **6** (24 mg, 0.04 mmol), **14** (30 mg, 0.06 mmol), or **16** (33 mg, 0.05 mmol) and HBF_4·Et_2O (5.5 μL, 0.04 mmol; 8.2 μL, 0.06 mmol; and 7.3 μL, 0.05 mmol, respectively). ^{1}H and ^{31}P{^{1}H} NMR spectra recorded after 20 min were identical to those reported for **5**, **13**, and **15**, respectively.

Preparation of [OsH(η^5-C_5H_5){$C_6H_4C(O)CH_3$}(P^iPr_3)]-BF_4 (13). This complex was prepared as described for **5** starting from 200 mg (0.40 mmol) of **2** and acetophenone (150 μL, 1.29 mmol). A light yellow solid was obtained. Yield: 213 mg (87%). GC-MS analysis of the mother liquor showed the presence of acetophenone and 1-phenylethanol. Anal. Calcd for $C_{22}H_{34}BF_4OOsP$: C, 42.45; H, 5.51. Found: C, 42.30; H, 5.24. IR (Nujol, cm^{-1}): ν(OsH) 2171 (m), ν(CO) 1588 (s). ^{1}H NMR (400 MHz, CD_2Cl_2, 293 K): δ 8.19 (d, $^3J_{HH}$ = 8.0, 1H, Ph), 8.00 (d, $^3J_{HH}$ = 8.0, 1H, Ph), 7.30 (vt, $^3J_{HH}$ = 8.0, 1H, Ph), 7.14 (vt, $^3J_{HH}$ = 8.0, 1H, Ph), 5.66 (s, 5H, C_5H_5), 2.91 (s, 3H, CH_3), 2.33 (m, 3H, PC*H*CH_3), 1.21 (dd, $^3J_{HP}$ = 14.6, $^3J_{HH}$ = 7.3, 9H, PCHC*H*$_3$), 0.98 (dd, $^3J_{HP}$ = 13.9, $^3J_{HH}$ = 7.3, 9H, PCHC*H*$_3$), −13.80 (d, $^2J_{HP}$ = 32.9, 1H, OsH). ^{31}P{^{1}H} NMR (161.99 MHz, CD_2Cl_2, 293 K): δ 28.0 (s, d in off-resonance). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2, 293 K): δ 220.9 (d, J_{CP} = 3, CO), 179.3 (d, J_{CP} = 3, OsC), 145.1 (s, Ph), 145.0 (s, C_{ipso}Ph), 134.7 (s, Ph), 133.4 (s, Ph), 124.2 (s, Ph), 86.5 (d, J_{CP} = 2, C_5H_5), 27.6 (d, J_{CP} = 29, P*C*HCH$_3$), 23.5 (s, CH_3), 20.0 (s, PCH*C*H$_3$), 18.8 (d, J_{CP} = 3, PCH*C*H$_3$). MS (LSIMS$^+$): *m/z* 537 (M^+).

Preparation of Os(η^5-C_5H_5){$C_6H_4C(O)CH_3$}(P^iPr_3) (14). This complex was prepared as described for **6** starting from 113 mg (0.18 mmol) of **13** and sodium methoxide (15 mg, 0.28 mmol). A dark brown oil was obtained.[40] Yield: 72 mg (74%). ^{1}H NMR (400 MHz, C_6D_6, 293 K): δ 8.49 (m, 1H, Ph), 7.55 (m, 1H, Ph), 6.82 (m, 2H, Ph), 4.60 (s, 5H, C_5H_5), 2.56 (s, 3H, CH_3), 1.70 (m, 3H, PC*H*CH_3), 1.02 (dd, $^3J_{HP}$ = 13.0, $^3J_{HH}$ = 7.2, 9H, PCHC*H*$_3$), 0.82 (dd, $^3J_{HP}$ = 12.4, $^3J_{HH}$ = 7.2, 9H, PCHC*H*$_3$). ^{31}P{^{1}H} NMR (161.99 MHz, C_6D_6, 293 K): δ 23.5 (s). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 293 K): δ 214.9 (d, J_{CP} = 3, CO), 202.7 (d, J_{CP} = 7, OsC), 145.3 (s, C_{ipso}Ph), 143.9, 133.3, 131.1, 117.7 (all s, Ph), 70.7 (d, J_{CP} = 2, C_5H_5), 27.0 (d, J_{CP} = 25, P*C*HCH$_3$), 22.2 (s, CH_3), 20.8 (s, PCH*C*H$_3$), 19.9 (s, PCH*C*H$_3$). MS (LSIMS$^+$): *m/z* 536 (M^+).

Preparation of [OsH(η^5-C_5H_5){C(Ph)CHC(O)Ph}(P^iPr_3)]-BF_4 (15). This complex was prepared as described for **5** starting from 160 mg (0.32 mmol) of **2** and benzylideneacetophenone (284 mg, 1.37 mmol), but heating the reaction mixture for 8 h. A green solid was obtained. Yield: 198 mg (88%). GC-MS analysis of the mother liquor showed the presence of benzylideneacetonephenone and benzylacetophenone. Anal. Calcd for $C_{29}H_{38}BF_4OOsP$: C, 49.02; H, 5.39. Found: C, 48.98; H, 5.19. ^{1}H NMR (400 MHz, CD_2Cl_2, 293 K): δ 8.02 (m, 3H, Ph), 7.91 (m, 2H, Ph), 7.59−7.52 (m, 6H, Ph plus CH), 5.65 (s, 5H, C_5H_5), 2.48 (m, 3H, PC*H*CH_3), 1.28 (dd, $^3J_{HP}$ = 15.4, $^3J_{HH}$ = 6.6, 9H, PCHC*H*$_3$), 1.14 (dd, $^3J_{HP}$ = 14.6, $^3J_{HH}$ = 7.0, 9H, PCHC*H*$_3$), −12.50 (d, $^2J_{HP}$ = 34.4, 1H, OsH). ^{31}P{^{1}H} NMR (161.99 MHz, CD_2Cl_2, 293 K): δ 28.5 (s, d in off-resonance). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2, 293 K): δ 237.4 (d, J_{CP} = 3, OsC), 205.7 (d, J_{CP} = 2, CO), 150.5 (s, C_{ipso}Ph), 133.9 (s, C_{ipso}Ph), 133.8 (s, CH), 131.9 (s, *p*-Ph), 131.2 (s, *p*-Ph), 129.6, 129.5, 129.4, 129.3 (all s, *o*- and *m*-Ph), 87.6

Table 4. Crystal Data and Data Collection and Refinement for 3, 10, and 13

	3	10	13
Crystal Data			
formula	$C_{56}H_{50}BF_{24}OOsP$	$C_{18}H_{31}OOsP$	$C_{22}H_{34}BF_4OOsP$
molecular wt	1426.94	484.60	622.47
color and habit	yellow, irregular prism	brown, irregular block	colorless, irregular block
size, mm	0.30, 0.20, 0.22	0.18, 0.16, 0.12	0.12, 0.08, 0.02
symmetry, space group	triclinic, $P\bar{1}$	triclinic, $P\bar{1}$	triclinic, $P\bar{1}$
a, Å	12.1960(16)	9.2950(6)	8.9899(8)
b, Å	12.8102(17)	9.3678(6)	11.2125(10)
c, Å	18.322(2)	11.0350(8)	11.9126(11)
α, deg	87.708(2)	81.6970(10)	78.686(2)
β, deg	82.980(2)	77.1260(10)	82.2820(10)
γ, deg	88.746(2)	81.0550(10)	78.1240(10)
V, Å^3	2838.3(6)	919.28(11)	1146.71(18)
Z	2	2	2
D_{calc}, g cm^{-3}	1.670	1.751	1.803
Data Collection and Refinement			
diffractometer		Bruker Smart APEX	
λ(Mo Kα), Å		0.71073	
monochromator		graphite oriented	
scan type		ω scans	
μ, mm^{-1}	2.393	7.020	5.674
2θ, range deg	3, 57	3, 57	3, 57
temp, K	100.0(2)	100.0(2)	100.0(2)
no. of data collected	37 705	8579	12 019
no. of unique data	13 611 (R_{int} = 0.0293)	4192 (R_{int} = 0.0204)	5414 (R_{int} = 0.0348)
no. of params/restraints	790/24	205/0	282/1
R_1[a] [$F^2 > 2\sigma(F^2)$]	0.0347	0.0222	0.0333
wR_2[b] [all data]	0.0832	0.0445	0.0552
S[c] [all data]	1.144	0.990	0.893

[a] $R_1(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2(F^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. [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.

(d, J_{CP} = 2, C_5H_5), 27.9 (d, J_{CP} = 29, P*C*HCH$_3$), 20.4 (s, PCH*C*H$_3$), 19.3 (d, J_{CP} = 2, PCH*C*H$_3$). MS (LSIMS$^+$): *m/z* 625 (M$^+$).

Preparation of [Os(η^5-C_5H_5){C(Ph)CHC(O)Ph}(P^iPr_3) (16). This complex was prepared as described for **6** starting from 148 mg (0.21 mmol) of **15** and sodium methoxide (19 mg, 0.35 mmol). A dark brown oil was obtained.[40] Yield: 106 mg (82%). ^{1}H NMR (400 MHz, C_6D_6, 293 K): δ 8.23 (s, 1H, CH), 8.18 (m, 2H, Ph), 8.06 (m, 2H, Ph), 7.36 (m, 2H, Ph), 7.22−7.14 (m, 2H, Ph), 7.03 (m, 2H, Ph), 4.58 (s, 5H, C_5H_5), 1.83 (m, 3H, PC*H*CH$_3$), 1.06 (dd, $^3J_{HP}$ = 12.9, $^3J_{HH}$ = 7.1, 9H, PCHC*H*$_3$), 0.89 (dd, $^3J_{HP}$ = 13.1, $^3J_{HH}$ = 7.2, 9H, PCHC*H*$_3$). ^{31}P{^{1}H} NMR (161.99 MHz, C_6D_6, 293 K): δ 23.7 (s). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 293 K): δ 249.8 (d, J_{CP} = 4, OsC), 198.2 (d, J_{CP} = 3, CO), 156.3 (s, C_{ipso}Ph), 137.3 (s, C_{ipso}Ph), 130.0, 129.7, 129.1, 128.9, 128.8, 128.5 (all s, Ph), 127.7 (s, CH), 73.3 (d, J_{CP} = 2, C_5H_5), 26.6 (d, J_{CP} = 26, P*C*HCH$_3$), 20.7 (s, PCH*C*H$_3$), 20.5 (s, PCH*C*H$_3$). MS (LSIMS$^+$): *m/z* 624 (M$^+$).

Structural Analysis of Complexes 3, 10, and 13. 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, λ = 0.71073 Å) operating at 50 kV and 30 mA. Data were collected over the complete sphere by a combination of four sets. Each frame exposure time was 10 s covering 0.3° in ω. Data were corrected for absorption by using a multiscan method applied with the SADABS program.[41] The structures of all compounds were solved by the Patterson method. Refinement, by full-matrix least squares on F^2 with SHELXL97,[42] 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 and refined as free isotropic atoms (**3**) or with restrained Os−H bond length (**13**, 1.59 Å, CSD). For **3**, one of the CF_3 groups of the BAr^F_4 anion was observed disordered. This group was defined with four moieties, complementary occupancy factors, isotropic atoms, and restrained geometry. All the highest electronic residuals were observed in close proximity of the Os centers and make no chemical sense. Crystal data and details of the data collection and refinement are given in Table 4.

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Supporting Information Available: CIF files giving positional and displacement parameters, crystallographic data, and bond lengths and angles of compounds **3**, **10**, and **13**. This material is available free of charge via the Internet at http://pubs.acs.org.

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