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Sequential Protonation and Methylation of a Hydride–Osmium Complex Containing a Cyclopentadienyl Ligand with a Pendant Amine Group

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Complex OsH{η^5-$C_5H_4(CH_2)_2NMe_2$}(P^iPr_3)$_2$ (**1**) reacts with 1 equiv of trifluoromethanesulfonic acid (HOTf) and trifluoromethanesulfonic acid-d_1 (DOTf) to produce the dihydride and hydride–deuteride complexes, [OsHE{η^5-$C_5H_4(CH_2)_2NMe_2$}(P^iPr_3)$_2$]OTf (E = H (**2**), D (**2-*d*$_1$**)), respectively. Treatment of **2** and **2-*d*$_1$** with a second equivalent of HOTf gives [OsHE{η^5-$C_5H_4(CH_2)_2NHMe_2$}(P^iPr_3)$_2$][OTf]$_2$ (E = H (**3**), D (**3-*d*$_1$**)) as a result of the protonation of the nitrogen atom. While the hydride and deuteride ligands of **2**, **2-*d*$_1$**, **3**, and **3-*d*$_1$** do not undergo any H/D exchange process with the solvent, in acetone-d_6, the NH proton of **3** and **3-*d*$_1$** changes places with a deuterium atom of the solvent to yield [OsHE{η^5-$C_5H_4(CH_2)_2NDMe_2$}(P^iPr_3)$_2$][OTf]$_2$ (E = H (**3-*Nd*$_1$**), D (**3-*d*$_2$**)). Complex **3-*Nd*$_1$** can also be obtained from the treatment of complex **2** with DOTf in dichloromethane. No exchange process between the hydride and the ND positions in **3-*Nd*$_1$** or between the deuteride and NH positions in **3-*d*$_1$** has been observed. Treatment of **3-*Nd*$_1$** and **3-*d*$_1$** with sodium methoxide results in a selective reaction of the base with the ammonium group to regenerate **2** and **2-*d*$_1$**, respectively. Complex **1** also reacts with methyl and methyl-d_3 trifluoromethanesulfonate (CH_3OTf and CD_3OTf, respectively) to give [OsH{η^5-$C_5H_4(CH_2)_2NMe_2CE_3$}(P^iPr_3)$_2$]OTf (E = H (**4**), D (**4-*d*$_3$**)) as a result of the addition of the CE_3 (E = H, D) group to the nitrogen atom. Complex **4** has been characterized by an X-ray diffraction analysis. It reacts with a second molecule of CH_3OTf or CD_3OTf to produce [OsH{η^5-$C_5H_4(CH_2)_2NMe_3$}{$CH_2CH(CH_3)P^iPr_2$}(P^iPr_3)][OTf]$_2$ (**5**). Similarly, complex **4-*d*$_3$** reacts with a second molecule of CH_3OTf or CD_3OTf to yield [OsH{η^5-$C_5H_4(CH_2)_2NMe_2CD_3$}{$CH_2CH(CH_3)P^iPr_2$}(P^iPr_3)][OTf]$_2$ (**5-*d*$_3$**). In acetonitrile, complex **5** evolves to an equilibrium mixture of the acetonitrile adducts [Os{η^5-$C_5H_4(CH_2)_2NMe_3$}($NCCH_3$)(P^iPr_3)$_2$][OTf]$_2$ (**7**) and [Os{η^5-$C_5H_4(CH_2)_2NMe_3$}($NCCH_3$)$_2$(P^iPr_3)][OTf]$_2$ (**8**). In methanol or methanol-d_4, complex **4** is not stable and loses trimethylamine to give the vinylcyclopentadienyl derivatives [OsHE(η^5-$C_5H_4CH{=}CH_2$)(P^iPr_3)$_2$]OTf (E = H (**9**), D (**9-*d*$_1$**)) as a result of the protonation or deuteration of the metallic center and a subsequent Hofmann elimination. Protonation of **4** with HOTf gives the dihydride–trimethylammonium derivative [OsH_2\{η^5-$C_5H_4(CH_2)_2NMe_3$\}(P^iPr_3)$_2$]-[OTf]$_2$ (**10**). Treatment of **9** with sodium methoxide produces OsH(η^5-$C_5H_4CH{=}CH_2$)(P^iPr_3)$_2$ (**11**).

Introduction

Cyclopentadienyl ligands bearing pendant donor groups are attracting increased interest from those who study the chemistry of metals.[1] Complexes with this type of ligand are expected to perform chemistry in a manner different from that of usual cyclopentadienyl complexes.[2] Indeed, the presence of the pendant donor group facilitates the study of some reaction mechanisms.[3]

There is increasing evidence showing that polar C=X bonds (X = N, O) can be reduced by an ionic mechanism.[4] The intramolecular cleavage of η^2-H_2 is a result of its deprotonation by the basic site of a coligand.[5] Then, H^+ and H^- are transferred to the substrate.[6] The catalyst is regenerated by coordination of molecular hydrogen to the metal[4,5] (Scheme 1).

Formic acid has been obtained by reduction of carbon dioxide with molecular hydrogen in the presence of [Ru{η^5-$C_5H_4(CH_2)_nNMe_2$}(dppm)]BF_4 (n = 2 or 3, dppm

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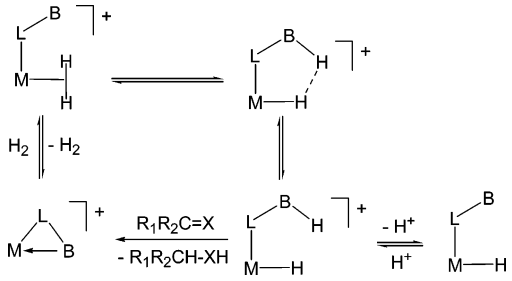
Scheme 1



$= Ph_2PCH_2PPh_2$) complexes.[7] The proposed catalytic cycle[8] is similar to that shown in Scheme 1. The proposal is supported by the observation that the addition of HBF_4 to the $RuH\{\eta^5\text{-}C_5H_4(CH_2)_nNMe_2\}$(dppm) monohydrides leads to the intramolecular dihydrogen-bonded Ru−H···H−N $[RuH\{\eta^5\text{-}C_5H_4(CH_2)_nNHMe_2\}(dppm)]BF_4$ complexes, which show rapid and reversible hydride−proton exchange via the intermediacy of the η^2-dihydrogen $[Ru\{\eta^5\text{-}C_5H_4(CH_2)_n\text{-}NMe_2\}(\eta^2\text{-}H_2)(dppm)]BF_4$ tautomers.[7] The strength of the Ru−H···H−N interaction is very sensitive to the basicity of the metal center. The replacement of the dppm ligand by the more weakly donating triphenyl phosphite ligands results in the $RuH\{\eta^5\text{-}C_5H_4(CH_2)_nNHMe_2\}\{P(OPh)_3\}_2$ species ($n = 2$) in which no Ru−H···H−N dihydrogen-bonding interaction is present between the hydride and the ammonium proton.[9] Sabo-Etienne, Chaudret, and co-workers have reported that the related triphenylphosphine derivative $RuH\{\eta^5\text{-}C_5H_4(CH_2)_2NMe_2\}(PPh_3)_2$ reacts with $[HNEt_3][BPh_4]$ or $[HPBu_3][BPh_4]$ to produce $[RuH\{\eta^5\text{-}C_5H_4(CH_2)_2NHMe_2\}\text{-}(PPh_3)_2]^+$, which also undergoes a proton−hydride intramolecular exchange process. However, in this case, the intermediacy of a η^2-dihydrogen tautomer does not seem to be necessary. In agreement with this, the addition of HBF_4 to $RuH\{\eta^5\text{-}C_5H_4(CH_2)_2NMe_2\}(PPh_3)_2$ promotes the loss of molecular hydrogen and the formation of $[Ru\{\eta^5\text{-}C_5H_4\text{-}(CH_2)_2NMe_2\}(PPh_3)_2]BF_4$.[10]

For the iron triad, numerous iron and ruthenium complexes containing a cyclopentadienyl ligand with a pendant donor group have been reported.[1c] However, the osmium counterparts are very scarce, and they were unknown until very recently.[2j] As a part of our work on the osmium cyclopentadienyl unit,[11] we have recently described the preparation of the first osmium compounds containing a cyclopentadienyl ligand with a pendant donor group,[2j,12] including the synthesis of the monohydride $OsH\{\eta^5\text{-}C_5H_4(CH_2)_2NMe_2\}(P^iPr_3)_2$.[12] We are now interested in determining how the change from ruthenium to osmium influences the chemistry of the half-sandwich cyclopentadienyl complexes. Thus, we have studied the behavior of the latter monohydride toward electrophiles. In this paper, we report the reactions of $OsH\{\eta^5\text{-}C_5H_4(CH_2)_2NMe_2\}(P^iPr_3)_2$ with HOTf, DOTf, CH_3OTf, and CD_3OTf as well as the

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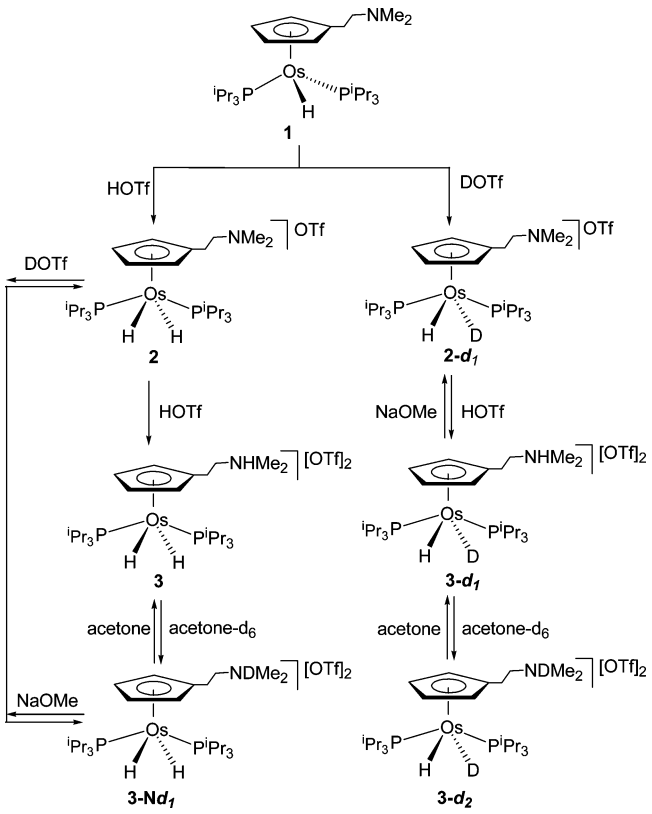
Scheme 2



dehydroamination reaction on the pendant substituent of the cyclopentadienyl ligand.

Results and Discussion

1. Reactions of OsH{η^5-$C_5H_4(CH_2)_2NMe_2$}(P^iPr_3)$_2$ (1) with HOTf and DOTf. The investigations that aimed to elucidate the behavior of **1** in the presence of HOTf and DOTf are summarized in Scheme 2.

Between −80 °C and room temperature, the addition of 1.0 equiv of HOTf to dichloromethane solutions of **1** results in the instantaneous and quantitative formation of dihydride $[OsH_2\{\eta^5\text{-}C_5H_4(CH_2)_2NMe_2\}(P^iPr_3)_2][OTf]_2$ (**2**), which is represented by a triplet at −14.19 ppm with a ^2J(HP) coupling constant of 29.1 Hz in the ^{1}H NMR spectrum. In dichloromethane-d_2 and in acetone-d_6, exchange between the hydride positions and the solvent is not observed.

The addition of 1.0 equiv of HOTf to dichloromethane solutions of **2** leads to the formation of $[OsH_2\{\eta^5\text{-}C_5H_4(CH_2)_2NHMe_2\}(P^iPr_3)_2][OTf]_2$ (**3**) as result of the protonation of the nitrogen atom of the pendant group. The most noticeable resonances of this compound in the ^{1}H NMR spectrum in dichloromethane-d_2 are a broad singlet at 8.94 ppm, corresponding to the NH proton, and a triplet, assigned to the hydride ligands, at −14.19 ppm with a ^2J(HP) coupling constant of 28.8 Hz. These signals are temperature invariant between −80 °C and room temperature.

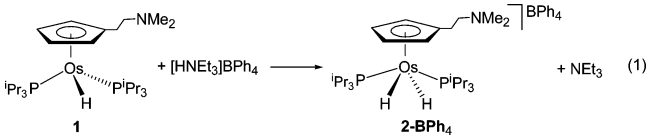
In contrast to the hydride ligands, in acetone-d_6 at room temperature, the NH proton of complex **3** undergoes an H−D exchange process with the solvent to produce the monodeuterated derivative $[OsH_2\{\eta^5\text{-}C_5H_4(CH_2)_2NDMe_2\}(P^iPr_3)_2][OTf]_2$ (**3-*Nd*$_1$**), which can also be obtained by treatment of **2** with DOTf in dichloromethane. In acetone, complex **3-*Nd*$_1$** regenerates **3**. The presence of a deuterium at the nitrogen atom of **3-*Nd*$_1$** is strongly supported not only by the absence of any NH resonance in the ^{1}H NMR spectrum of this compound but also by the presence of a broad singlet at 8.90 ppm in the ^{2}H NMR spectrum in dichloromethane. The chemical shifts of the resonance of the NH proton in acetone-d_6 (**3**) or the ND deuterium atom in acetone (**3-*Nd*$_1$**) are dependent on the sample concentration because of the NH···O=$C(CD_3)_2$ and ND···O=$C(CH_3)_2$ interactions, respectively. The influence of sample concentration on these chemical shifts is not observed in dichloromethane, in which no H−D exchange is observed. This suggests that NH···O=$C(CD_3)_2$ and ND···O=$C(CH_3)_2$ interactions are the first step in the H−D exchanges between the ammonium group and the oxygenated solvent, which could occur according to the mechanism previously proposed by Bianchini.[13]

In dichloromethane-d_2 and acetone-d_6, exchange between the hydride positions of **3-*Nd*$_1$** and the deuterium at the nitrogen atom is not observed. Any preference of the metallic center for the hydrogen atom must be excluded. Indeed, the addition of 1.0 equiv of DOTf to dichloromethane solutions of **1** leads to the hydride-deuteride $[OsHD\{\eta^5\text{-}C_5H_4(CH_2)_2NMe_2\}(P^iPr_3)_2]OTf$ (**2-*d*$_1$**), which is seen in the ^{2}H NMR spectrum as a triplet at −13.80 ppm with a ^2J(DP) coupling constant of 4.1 Hz. Exchange between the deuteride position and the solvent is not observed either in dichloromethane or in acetone.

Complex **2-*d*$_1$** in dichloromethane reacts with 1.0 equiv of HOTf to produce $[OsHD\{\eta^5\text{-}C_5H_4(CH_2)_2NHMe_2\}(P^iPr_3)_2][OTf]_2$ (**3-*d*$_1$**) as a result of the protonation of the nitrogen atom of **2-*d*$_1$**. Exchange between the deuteride and NH positions, in dichloromethane-d_2 or acetone-d_6, is not observed. In acetone-d_6, the NH proton exchanges with a deuterium atom of the solvent to give $[OsHD\{\eta^5\text{-}C_5H_4(CH_2)_2NDMe_2\}(P^iPr_3)_2][OTf]_2$ (**3-*d*$_2$**), which contains deuterium at both the metallic center and the nitrogen atom of the pendant group.

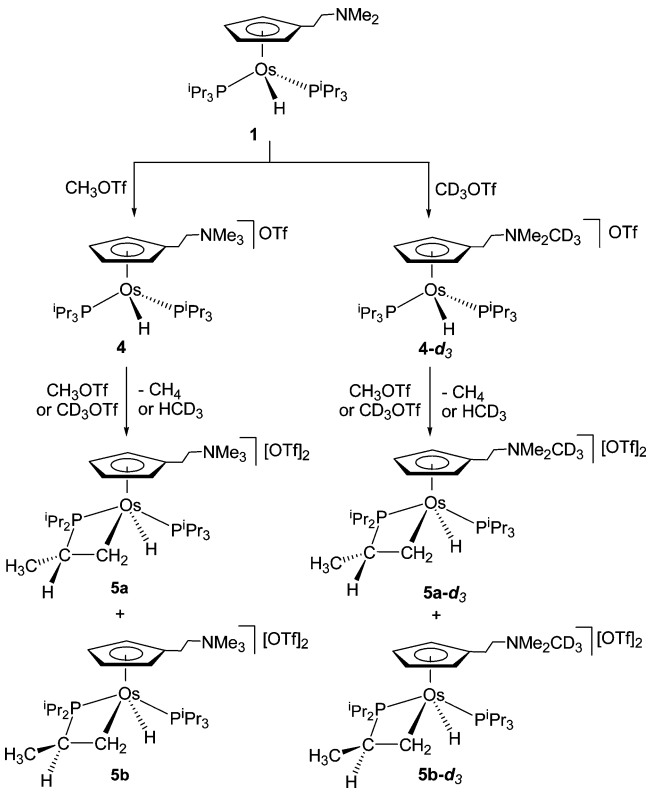
The reactions shown in Scheme 2 merit further comment. Complex **1** contains three basic sites, namely, the metal, the hydride, and the amino group, each one able to react with an electrophile, in this case the proton. The results collected in Scheme 2 clearly indicate that, from a thermodynamic point of view, the preference of each site for the proton decreases in the following sequence: metal > amino group > hydride. This is in contrast with the results obtained from the theoretical calculations on the ruthenium-monohydride $RuH\{\eta^5\text{-}C_5H_4(CH_2)_2NMe_2\}(PH_3)_2$, which do not show any strong thermodynamic preference for one site.[10]

We have also observed that complex **1** reacts with triethylammonium tetraphenylborate in dichloromethane to give $[OsH_2\{\eta^5\text{-}C_5H_4(CH_2)_2NMe_2\}(P^iPr_3)_2]BPh_4$ (**2-BPh$_4$**), and triethylamine (eq 1), which is in agreement with the thermodynamic preference of the metallic center over the amino group.



(1)

Scheme 3



In addition, the deprotonation of the ammonium group is not only thermodynamically but also kinetically favored in comparison with the deprotonation of the osmium atom. Thus, treatment at room temperature of the tetrahydrofuran solutions of **3-*Nd*$_1$** with 1.0 equiv of sodium methoxide regenerates **2**. Deuterium is not observed at the hydride positions. In agreement with this, the addition of sodium methoxide to **3-*d*$_1$** in THF selectively yields **2-*d*$_1$**.

2. Reactions of 1 with CH_3OTf and CD_3OTf. In contrast to the reaction with 1.0 equiv of HOTf, the treatment at room temperature of dichloromethane solutions of **1** with 1.0 equiv of CH_3OTf promotes the quaternization of the amino group of the pendant substituent as a consequence of the addition of the methyl group to the nitrogen atom (Scheme 3).

The formation of $[OsH\{\eta^5\text{-}C_5H_4(CH_2)_2NMe_3\}(P^iPr_3)_2]OTf$ (**4**) suggests that, in complex **1**, the nitrogen atom is the kinetically favored site for the electrophilic addition. Complex **4** was isolated as a white solid in almost quantitative yield and characterized by elemental analysis, IR, ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy, and X-ray diffraction analysis. A drawing of the cation of **4** is shown in Figure 1. Selected bond distances and angles are listed in Table 1.

The structure shows that there is a quaternary ammonium group in the complex; it has a tetrahedral arrangement around the nitrogen atom with C−N−C angles between 107.3(2)° and 111.5(2)°. The geometry around the osmium center can be described as a very distorted octahedron with the cyclopentadienyl ring occupying the three sites of a face. The distortion is mainly caused by the mutual cis disposition

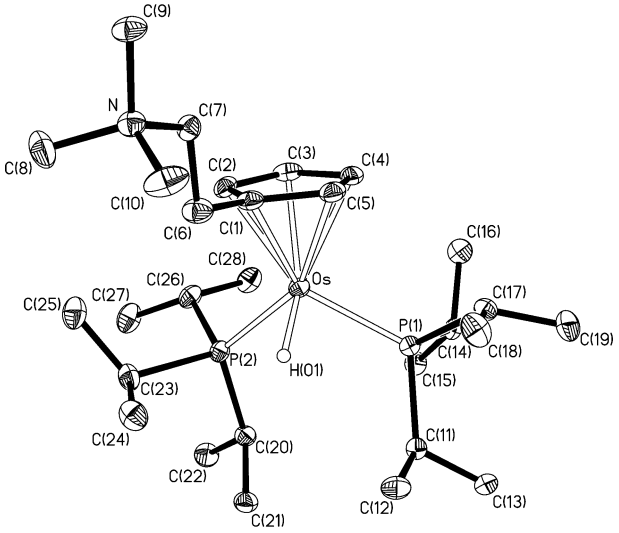


Figure 1. Molecular diagram of the cation of $[OsH\{\eta^5\text{-}C_5H_4(CH_2)_2\text{-}NMe_3\}(P^iPr_3)]_2OTf$ (**4**). Thermal ellipsoids are shown at 50% probability.

Table 1. Selected Bond Distances (Å) and Angles (deg) for Complex $[OsH\{\eta^5\text{-}C_5H_4(CH_2)_2NMe_3\}(P^iPr_3)_2]OTf$ (**4**)

Os−P(1)	2.3002(8)	Os−H(01)	1.45(3)
Os−P(2)	2.2928(8)	N−C(7)	1.508(3)
Os−C(1)	2.222(3)	N−C(8)	1.489(4)
Os−C(2)	2.246(3)	N−C(9)	1.500(3)
Os−C(3)	2.271(3)	N−C(10)	1.489(4)
Os−C(4)	2.231(3)	C(1)−C(6)	1.510(4)
Os−C(5)	2.225(3)	C(6)−C(7)	1.515(4)

P(1)−Os−P(2)	104.14(3)	N−C(7)−C(6)	115.8(2)
P(1)−Os−M[a]	124.2	C(7)−N−C(8)	111.5(2)
P(1)−Os−H(01)	85.1(10)	C(7)−N−C(9)	107.3(2)
P(2)−Os−M[a]	124.8	C(7)−N−C(10)	111.1(2)
P(2)−Os−H(01)	77.4(11)	C(8)−N−C(9)	108.5(2)
M[a]−Os−H(01)	127.0	C(8)−N−C(10)	109.9(2)
C(9)−N−C(10)	108.4(2)		

[a] M represents the midpoint of the C(1)−C(5) Cp ligand.

of the phosphine ligands, which experience a large steric hindrance as a consequence of their large cone angle (160°).[14] Thus, the P−Os−P angle (104.14(3)°) strongly deviates from the ideal value of 90°. P−M−P angles similar to those of **4** have previously been found in the square-planar complexes $Rh(acac)(PCy_3)_2$ (105.63(4)°),[15] $Rh(\kappa^2\text{-}O_2CCH_3)(P^iPr_3)_2$ (106.00(4)°),[16] and $[Ir(TFB)(P^iPr_3)_2]BF_4$ (TFB = tetrafluorobarralene, 102.7(1)°),[17] the five-coordinate derivative $[Rh(acac)\{(E)\text{-}CH{=}CHCy\}(PCy_3)_2]BF_4$ (105.3(1)°),[15] and the octahedral compounds $[Os(\kappa^2\text{-}O_2CCH_3)\{C(Me)C(OH)\text{-}MePh\}(P^iPr_3)_2]BF_4$ (103.71(6)°)[18] and $Os\{\eta^2\text{-}CH_2{=}CHC(OH)Ph_2\}(\kappa^2\text{-}O_2CCH_3)(P^iPr_3)_2$ (106.72(4)°).[18]

In agreement with the presence of a hydride ligand in **4**, its IR spectrum in Nujol shows a ν(Os−H) band at 2052

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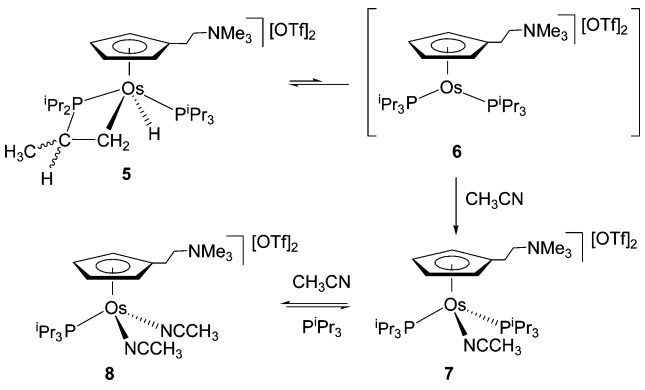
cm^{-1}. In the ^{1}H NMR spectrum in acetone-d_6 at room temperature, the hydride ligand results in a triplet at −15.68 ppm with a ^2J(HP) coupling constant of 30.6 Hz. The ^{31}P{^{1}H} NMR spectrum shows a singlet at 32.9 ppm.

Complex **4** reacts with a second molecule of CH_3OTf. The treatment at room temperature of dichloromethane solutions of the monohydride with 1.0 equiv of the electrophile produces, in an 83% yield, the white metalated derivative [Os{η^5-$C_5H_4(CH_2)_2NMe_3$}{$CH_2CH(CH_3)P^iPr_2$}(P^iPr_3)][OTf]$_2$ (**5**). This compound was isolated as a 1:1 equilibrium mixture[19] of stereoisomers **5a** and **5b** shown in Scheme 3.

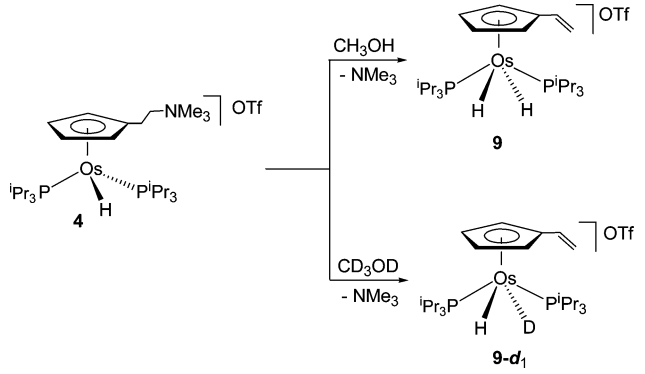
In solution, the presence of isomers **5a** and **5b** is strongly supported by the ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} spectra of **5**. In the ^{1}H NMR spectrum in acetone-d_6, the hydride resonances appear at −13.96 and −13.70 ppm as a doublet of doublets with ^2J(HP) coupling constants of 34.8 and 26.0 Hz, and 36.8 and 28.8 Hz, respectively. In the ^{13}C{^{1}H} NMR spectrum, the Os−CH_2 and PCH signals of the metalated isopropyl group are observed at −27.1 and 49.9 ppm, and −27.0 and 47.6 ppm, respectively. These chemical shifts agree well with those previously reported for the complexes [OsH(η^5-C_5H_5){$CH_2CH(CH_3)P^iPr_2$}(P^iPr_3)]PF_6 (−36.9 and 49.9 ppm and −37.4 and 46.9 ppm),[11b] [{$CH_2CH(CH_3)^iPr_2P$}OsH{η^5-$C_5H_4(CH_2)_2PPh_2$}]PF_6 (−22.5 and 46.6 ppm and −24.3 and 43.4 ppm),[2j] RuH(η^5-C_5H_5){$CH_2CH(CH_3)P^iPr_2$}($SiMePh_2$) (−31.5 and 42.8 ppm),[20] and RuH(η^6-C_6H_6){$CH_2CH(CH_3)P^iPr_2$} (−10.7 and 42.8 ppm).[21] The ^{31}P{^{1}H} NMR spectrum shows four doublets for isomers **5a** and **5b** at 11.4 and −29.5 ppm, and 10.1 and −31.3 ppm, with ^2J(PP) coupling constants of 26 and 21 Hz, respectively.

Complex **5** is certainly the result of the reaction of an external methyl group with the hydride ligand of **4** and the subsequent C−H activation of an isopropyl group of one of the phosphine ligands. Thus, we have observed that **5** can be also obtained by addition of 1.0 equiv of CD_3OTf to dichloromethane solutions of **4**. The formation of a metalated species containing a CD_3 group at the ammonium fragment, [OsH{η^5-$C_5H_4(CH_2)_2NMe_2CD_3$}{$CH_2CH(CH_3)P^iPr_2$}(P^iPr_3)][OTf]$_2$, in spectroscopically detectable concentrations, does not take place. This complex, **5-*d*$_3$** in Scheme 3, was obtained in a two-step procedure via the monohydride intermediate [OsH{η^5-$C_5H_4(CH_2)_2NMe_2CD_3$}(P^iPr_3)$_2$]OTf (**4-*d*$_3$**), which is a result of the addition of 1.0 equiv of CD_3OTf to a dichloromethane solution of **1**. The presence of a CD_3 group at the ammonium fragments of **4-*d*$_3$** and **5-*d*$_3$** is strongly supported by the ^{2}H NMR spectra of these compounds, which show singlets at 3.49 and 3.22 ppm, respectively.

Scheme 4



Scheme 5



The formation of **5** takes place via the unsaturated intermediate **6** (Scheme 4), which can be trapped as a 2:1 equilibrium mixture of adducts [Os{η^5-$C_5H_4(CH_2)_2NMe_3$}($NCCH_3$)(P^iPr_3)$_2$][OTf]$_2$ (**7**) and [Os{η^5-$C_5H_4(CH_2)_2NMe_3$}($NCCH_3$)$_2$(P^iPr_3)][OTf]$_2$ (**8**). Adducts **7** and **8** were fully characterized by ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopy.

In the ^{1}H NMR spectrum of the mixture, the most noticeable feature is the absence of any hydride resonance and the presence of a triplet at 2.82 ppm and a doublet at 2.66 ppm both with ^5J(HP) coupling constants of 1.2 Hz, corresponding to the acetonitrile ligands of **7** and **8**, respectively. The ^{13}C{^{1}H} NMR spectrum for the acetonitrile ligand of **7** shows a broad triplet at 96.0 ppm and a singlet at 5.2 ppm; they were assigned to the C(sp) atom and the CH_3 group, respectively. The resonances of the acetonitrile ligands present in **8** appear as a doublet at 88.7 ppm, with a ^3J(CP) coupling constant of 7.0 Hz, and a singlet at 4.5 ppm. The ^{31}P{^{1}H} NMR spectrum contains singlets at 0.0 and 17.5 ppm corresponding to **7** and **8**, respectively.

3. Reactions of 4 with CH_3OH and CD_3OD: Dehydroamination of the Pendant Substituent. In methanol, the monohydride−osmium(II) complex, **4**, is unstable and evolves into trimethylamine and the dihydride−osmium(IV) vinylcyclopentadienyl derivative [OsH_2(η^5-$C_5H_4CH{=}CH_2$)(P^iPr_3)$_2$]OTf (**9**), which was isolated as a white solid in a 68% yield (Scheme 5). The presence of a vinyl substituent at the cyclopentadienyl ligand of **9** is strongly supported by the ^{1}H and ^{13}C{^{1}H} NMR spectra of this compound. In the ^{1}H NMR spectrum in dichloromethane-d_2 at room temperature, the −CH= resonance of the vinyl group appears at 6.40 ppm as a doublet of doublets with ^3J(HH) coupling

(19) When the reaction was carried out in toluene, a white solid was formed. Its NMR spectra in CD_2Cl_2 revealed the presence of **5a** and **5b** in a 9:1 molar ratio. After 5 h at room temperature, the 1:1 equilibrium mixture is reached.

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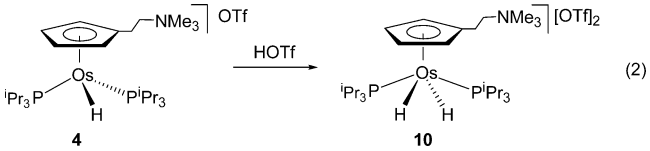
constants of 17.6 and 10.8 Hz, whereas the $=CH_2$ resonances are observed as doublets at 5.64 (trans to H) and 5.43 (cis to H) ppm. In the high field region, the spectrum shows a triplet at −14.22 ppm, corresponding to the hydride ligands, with a ^2J(HP) coupling constant of 29.2 Hz. In the $^{13}C\{^1H\}$ NMR spectrum, the vinyl resonances are observed as singlets at 127.3 (CH) and 120.5 (CH_2) ppm. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 32.2 ppm.

In methanol-d_4, complex **4** produces [OsHD(η^5-C_5H_4CH=CH_2)(P^iPr_3)$_2$]OTf (**9-*d*$_1$**) which contains a deuterium atom at the position of one of the hydride ligands of **9**. Its presence is supported by the ^{2}H NMR spectrum in dichloromethane which contains a triplet at −14.13 ppm with a ^2J(DP) coupling constant of 4 Hz.

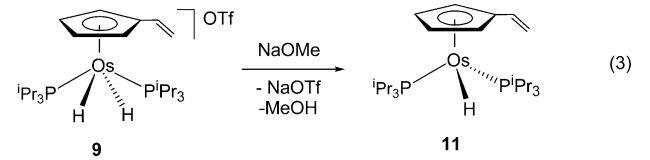
The position of the deuterium atom in **9-*d*$_1$** suggests that the transformation from **4** to **9** is a one-pot synthesis of two reactions. They are the protonation of the metallic center by action of methanol and a Hofmann elimination[22] on the ammonium group, promoted by the methoxide anion which was generated from the metal protonation. We have also observed that the addition of 1.0 equiv of HOTf to dichloromethane solutions of **4** yields dihydride [$OsH_2\{\eta^5$-$C_5H_4(CH_2)_2NMe_3\}(P^iPr_3)_2$][OTf]$_2$ (**10** in eq 2) and treatment of **10** with 1.0 equiv of sodium methoxide in tetrahydrofuran produces **9**, which supports the proposed mechanism.



(2)

Complex **10** was isolated as a white solid in a 90% yield and characterized by MS, elemental analysis, IR, and ^{1}H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy. The most noticeable feature of this compound, in the ^{1}H NMR spectrum in acetone-d_6 at room temperature, is a triplet at −14.09 ppm with a ^2J(HP) coupling constant of 29.2 Hz. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 32.8 ppm.

Unlike the OsH_2 unit of **10**, the OsH_2 unit of **9** can be deprotonated. Treatment of **9** with 1.1 equiv of sodium methoxide in tetrahydrofuran produces monohydride OsH(η^5-C_5H_4CH=CH_2)(P^iPr_3)$_2$ (**11**), which was isolated as a yellow solid in a 64% yield (eq 3).



(3)

In the ^{1}H NMR spectrum of **11** in benzene-d_6 at room temperature, the −CH= resonance of the vinyl substituent of the cyclopentadienyl ligand appears at 6.55 ppm as a doublet of doublets with ^3J(HH) coupling constants of 17.2 and 10.8 Hz, whereas the $=CH_2$ resonances are observed at 5.22 (trans to H) and 5.0 (cis to H) ppm as doublets. The hydride ligand appears as a triplet at −16.67 ppm with a ^2J(HP) coupling constant of 31.6 Hz. In the $^{13}C\{^1H\}$ NMR spectrum, the vinyl group is represented by singlets at 134.5 (CH) and 107.9 (CH_2) ppm. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 27.7 ppm. The reaction shown in eq 3 is reversible. Thus, the addition of 1.0 equiv of NaOTf to a methanol solution of **11** produces **9**.

Concluding remarks

This study revealed that complex OsH{η^5-$C_5H_4(CH_2)_2$-NMe_2}(P^iPr_3)$_2$ has two nucleophilic centers, which undergo attack by electrophiles, such as proton and methyl groups. From a thermodynamic point of view, the protonation of the metallic center is preferred over that of the nitrogen atom. Thus, complex OsH{η^5-$C_5H_4(CH_2)_2NMe_2$}(P^iPr_3)$_2$ reacts with HOTf to give [$OsH_2\{\eta^5$-$C_5H_4(CH_2)_2NMe_2\}(P^iPr_3)_2$]OTf and [$OsH_2\{\eta^5$-$C_5H_4(CH_2)_2NHMe_2\}(P^iPr_3)_2$][OTf]$_2$ in a sequential manner. However, from a kinetic point of view, the addition of electrophiles to the nitrogen atom appears to be favored with regard to the osmium atom. In agreement with this, complex OsH{η^5-$C_5H_4(CH_2)_2NMe_2$}(P^iPr_3)$_2$ reacts with CH_3OTf to produce [OsH{η^5-$C_5H_4(CH_2)_2NMe_3$}(P^iPr_3)$_2$]OTf as result of the addition of the methyl group to the nitrogen atom. Treatment of the latter complex with a second molecule of CH_3OTf promotes the attack of a new methyl group, now to the osmium atom. As a result of this addition and the subsequent elimination of methane, the unsaturated intermediate [$Os\{\eta^5$-$C_5H_4(CH_2)_2NMe_3\}(P^iPr_3)_2]^{2+}$ is formed. This short-lived species evolves into [$Os\{\eta^5$-$C_5H_4(CH_2)_2NMe_3\}$-{$CH_2CH(CH_3)P^iPr_2$}(P^iPr_3) by methyl C−H activation of an isopropyl group of one of the phosphine ligands.

In methanol, the metallic center of [OsH{η^5-$C_5H_4(CH_2)_2$-NMe_3}(P^iPr_3)$_2$]OTf undergoes the attack of a proton from the solvent to yield the dicationic dihydride complex [OsH_2-$\{\eta^5$-$C_5H_4(CH_2)_2NMe_3\}(P^iPr_3)_2]^{2+}$. The oxidation of the osmium atom results in an acidity increase of the Cp-CH_2 group of the cyclopentadienyl chain, which becomes higher than that of the OsH_2 unit. Thus, the first deprotonation of dihydride [$OsH_2\{\eta^5$-$C_5H_4(CH_2)_2NMe_3\}(P^iPr_3)_2]^{2+}$ occurs at the Cp-CH_2 group. As a consequence of this extraction, trimethylamine is eliminated from the pendant substituent, and the dihydride vinylcyclopentadienyl derivative [OsH_2-(η^5-C_5H_4CH=CH_2)(P^iPr_3)$_2]^+$ is formed. The deprotonation of the latter (second deprotonation) gives the monohydride OsH(η^5-C_5H_4CH=CH_2)(P^iPr_3)$_2$.

In conclusion, we showed that in an osmium hydride complex containing a cyclopentadienyl ligand with an amino pendant substituent, both the amino group and the metallic center undergo sequential protonation and methylation. Furthermore, the pendant group is transformed into a vinyl substituent by a Hofmann elimination of amine, which is promoted by the oxidation of the metallic center.

Experimental Section

General Information. All manipulations were performed using an argon vacuum manifold and standard Schlenk techniques. Solvents were dried by known procedures and were used freshly

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distilled. OsH{η^5-$C_5H_4(CH_2)_2NMe_2$}(P^iPr_3)$_2$ (**1**) was prepared according to previous report.[12] IR spectra were recorded on a Nicolet 550 spectrometer as Nujol mulls on polyethylene sheets. NMR spectra were recorded on a Varian UNITY 300, a Varian GEMINI 2000−300 MHz, or a Bruker ARX 400 spectrometer. ^{1}H and ^{13}C{^{1}H}, ^{31}P{^{1}H}, and ^{19}F chemical shifts are reported relative to external tetramethylsilane, H_3PO_4 (85%), and $CFCl_3$, respectively. Coupling constants, *J*, are given in hertz. C, H analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyzer. FAB mass spectra analyses were performed with a VG Auto Spec instrument. The ions were produced with a standard Cs^+ gun at 30 kV using 3-nitrobenzyl alcohol (NBA) as the matrix.

Reaction of 1 with HOTf: Formation of [OsH_2\{η^5-$C_5H_4(CH_2)_2NMe_2$\}(P^iPr_3)$_2$]OTf (2). A solution of **1** (0.20 g, 031 mmol) in dichloromethane (0.5 mL) was treated with HOTf (27 μL, 0.31 mmol), and the mixture was stirred for 4 h at room temperature. The solvent was removed, and the solid residue was washed with pentane (2 × 3 mL) and dried under vacuum to give a white powder. Yield: 0.18 g (73%). Anal. Calcd for $C_{28}H_{58}F_3NO_3OsP_2S$: C, 42.17; H, 7.27; N, 1.75; S, 4.02. Found: C, 42.32; H, 7.10; N, 1.78; S, 4.37. IR (Nujol, cm^{-1}): ν (Os−H) 2136, 2105 (w), ν (SO_3) and ν (CF_3) 1270 (br, s), 1148 (s), 1030 (s). MS (FAB$^+$, *m*/*e*): 650 (M^+). ^{1}H NMR (400 MHz, CD_2Cl_2, 293 K): δ 5.37, 5.18 (both m, each 2H, C_5H_4), 2.58, 2.56 (both m, each 2H, CH_2CH_2N), 2.18 (s, 6H, $N(CH_3)_2$), 2.05 (m, 6H, PCH), 1.22 (dd, 36H, ^3J(HH) = 6.9, ^3J(PH) = 13.8, $PCCH_3$), −14.19 (t, 2H, ^2J(PH) = 29.1, Os−H). ^{1}H NMR (400 MHz, $(CD_3)_2CO$, 293 K): δ 5.77, 5.46 (both m, each 2H, C_5H_4), 2.73, 2.48 (both m, each 2H, CH_2CH_2N), 2.29 (m, 6H, PCH), 2.19 (s, 6H, $N(CH_3)_2$), 1.31 (dd, 36H, ^3J(HH) = 7.2, ^3J(PH) = 13.6, $PCCH_3$), −14.09 (t, 2H, ^2J(PH) = 29.2, Os−H). ^{31}P{^{1}H} NMR (161.9 MHz, $(CD_3)_2CO$, 293 K): δ 32.6 (s). ^{19}F NMR (376.3 MHz, $(CD_3)_2CO$, 293 K): δ −80 (s). ^{13}C{^{1}H} NMR (100 MHz, $(CD_3)_2CO$, 293 K, plus APT): δ 112.2 (−, s, ipso-C_5H_4), 87.0, 79.2 (+, s, C_5H_4), 62.9 (−, s, CH_2CH_2N), 46.5 (+, s, $N(CH_3)_2$), 31.9 (+, second-order system, PCH), 28.8 (−, s, CH_2CH_2N), 20.9 (+, s, $PCCH_3$).

Reaction of 1 with Triethylammonium Tetraphenylborate: Formation of [OsH_2\{η^5-$C_5H_4(CH_2)_2NMe_2$\}(P^iPr_3)$_2$]BPh_4 (2-BPh_4). Dichloromethane (2 mL) was added to a mixture of **1** (0.12 g, 0.18 mmol) and triethylammonium tetraphenylborate (0.08 g, 0.18 mmol) at room temperature. The mixture was stirred for 4 h; the suspension formed was filtered through Celite, and the product was isolated by precipitation with pentane (1−2 mL) and dried under vacuum to give a white solid. Yield: 0.13 g (76%). Anal. Calcd for $C_{51}H_{78}BNOsP_2$: C, 63.27; H, 8.12; N, 1.45. Found: C, 63.15; H, 7.99; N, 1.52. IR (Nujol, cm^{-1}): ν (Os−H) 2139, 2108 (w), ν (arC−C) 1580 (m). ^{1}H NMR (400 MHz, CD_2Cl_2, 293 K): δ 7.32, 7.04 (both m, each 8H, BPh_4), 6.89 (m, 4H, BPh_4), 5.31, 5.11 (both m, each 2H, C_5H_4), 2.60, 2.42 (both m, each 2H, CH_2CH_2N), 2.21 (s, 6H, $N(CH_3)_2$), 2.04 (m, 6H, PCH), 1.23 (dd, 36H, ^3J(HH) = 7.2, ^3J(PH) = 13.8, $PCCH_3$), −14.19 (t, 2H, ^2J(PH) = 28.8, Os−H). ^{31}P{^{1}H} NMR (161.9 MHz, $(CD_3)_2CO$, 293 K): δ 32.9 (s). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2, 293 K + APT): δ 165.4, 164.8, 164.1, 163.5 (−, all s, ipso-C_6H_5), 136.3, 126.0, 125.9, 125.8, 125.7, 122.0 (+, all s, C_6H_5), 110.92 (−, s, ipso-C_5H_4), 84.9, 77.2 (+, both s, C_5H_4), 61.5 (−, s, CH_2CH_2N), 45.5 (+, s, $N(CH_3)_2$), 30.6 (+, second-order system, PCH), 27.7 (−, s, CH_2CH_2N), 19.8 (+, s, $PCCH_3$).

Reaction of 1 with DOTf: Formation of [OsHD\{η^5-$C_5H_4(CH_2)_2NMe_2$\}(P^iPr_3)$_2$]OTf (2-d_1). A procedure analogous to that described for **2** was followed starting from a solution of **1** (0.20 g, 0.31 mmol) in dichloromethane (0.5 mL) and DOTf (27 μL, 0.31 mmol). Complex **2-d_1** was obtained as a white powder solid. Yield: 0.16 g (65%). The ^{19}F and ^{1}H NMR data were identical to those reported for **2** with exception of the resonance at −14.09 (t, 1H, ^2J(PH) = 29.2, Os−H). ^{31}P{^{1}H} NMR (161.9 MHz, $(CD_3)_2CO$, 293 K): δ 32.6 (t, 1:1:1, ^2J(PD) = 4.1). ^{2}H NMR (46.05 MHz, $(CH_3)_2CO$, 293 K): δ −13.8 (t, ^2J(PD) = 4.1, Os−D).

Reaction of 2 with HOTf: Formation of [OsH_2\{η^5-$C_5H_4(CH_2)_2NHMe_2$\}(P^iPr_3)$_2$][OTf]$_2$ (3). A suspension of **2** (0.10 g, 0.12 mmol) in dichloromethane (0.5 mL) was treated with HOTf (10 μL, 0.12 mmol), and the resulting colorless mixture was stirred for 3 h at room temperature. The solvent was removed, and the solid residue was washed with pentane (2 × 3 mL) and dried under vacuum to give a white solid. Yield: 0.08 g (70%). Anal. Calcd for $C_{29}H_{59}F_6NO_6OsP_2S_2$: C, 36.80; H, 6.23; N, 1.48; S, 6.77. Found: C, 36.81; H, 6.31; N, 1.45; S, 7.00. IR (Nujol, cm^{-1}): ν (N−H) 3100 (m), ν (Os−H) 2141, 2117 (w), ν (SO_3) and ν (CF_3) 1270 (br s), 1156 (s), 1031 (s). MS (FAB$^+$, *m*/*e*): 800 ([M − OTf]$^+$), 650 ([M − H]$^+$). ^{1}H NMR (400 MHz, $(CD_3)_2CO$, 293 K): δ 8.77 (br, 1H, NH), 6.07, 5.67 (both m, each 2H, C_5H_4), 3.68, 3.29 (both m, each 2H, CH_2CH_2N), 3.21 (s, 6H, $N(CH_3)_2$), 2.39 (m, 6H, PCH), 1.42 (dd, 36H, ^3J(HH) = 7.5, ^3J(PH) = 14.4, $PCCH_3$), −14.19 (t, 2H, ^2J(PH) = 28.8, Os−H). ^{1}H NMR (400 MHz, CD_2Cl_2, 293 K): δ 8.94 (br, 1H, NH), 5.82, 5.20 (both m, each 2H, C_5H_4), 3.44, 2.97 (both m, each 2H, CH_2CH_2N), 2.95, 2.93 (both s, each 3H, $N(CH_3)_2$), 2.12 (m, 6H, PCH), 1.24 (dd, 36H, ^3J(HH) = 7.2, ^3J(PH) = 14.1, $PCCH_3$), −14.19 (t, 2H, ^2J(PH) = 28.8, Os−H). ^{31}P{^{1}H} NMR (161.9 MHz, CD_2Cl_2, 293 K): δ 31.3 (s). ^{19}F NMR (376.3 MHz, CD_2Cl_2, 293 K): δ −78.6 (s). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2, 293 K): δ 122.9 (−, q, ^1J(CF) = 320, CF_3), 104.3 (−, s, ipso-C_5H_4), 85.8, 78.6 (+, s, C_5H_4), 58.9 (−, s, CH_2CH_2N), 43.3 (+, s, $N(CH_3)_2$), 30.4 (+, second-order system, PCH), 24.4 (−, s, CH_2CH_2N), 19.6 (+, s, $PCCH_3$).

Reaction of 2 with DOTf: Formation of [OsH_2\{η^5-$C_5H_4(CH_2)_2NDMe_2$\}(P^iPr_3)$_2$][OTf]$_2$ (3-Nd_1). A procedure analogous to that described for **3** was followed starting from a solution of **2** (0.10 g, 0.12 mmol) in dichloromethane (0.5 mL) and DOTf (10 μL, 0.12 mmol). Complex **3-Nd_1** was obtained as a white powder solid. Yield: 0.08 g (70%). The ^{1}H, ^{31}P{^{1}H}, and ^{19}F NMR data were identical to those reported for **3** with exception of the absence of the resonance at 8.94 ppm in the ^{1}H NMR spectrum. ^{2}H NMR (46.05 MHz, 293 K): $(CH_3)_2CO$ δ 8.62 (br); CH_2Cl_2 δ 8.90 (br).

Reaction of 2-d_1 with HOTf: Formation of [OsHD\{η^5-$C_5H_4(CH_2)_2NHMe_2$\}(P^iPr_3)$_2$][OTf]$_2$ (3-d_1). A procedure analogous to that described for **3** was followed starting from a solution of **2-d_1** (0.10 g, 0.12 mmol) in dichloromethane (0.5 mL) and HOTf (10 μL, 0.12 mmol). Yield: 0.08 g (70%). The ^{19}F and ^{1}H NMR data were identical to those reported for **3** with exception of the resonance at −14.19 (t, 1H, ^2J(PH) = 28.8, Os−H). ^{31}P{^{1}H} NMR (161.9 MHz, CD_2Cl_2, 293 K): δ 31.3 (t (1:1:1), ^2J(PD) = 3.9). ^{2}D NMR (46.05 MHz, 293 K): $(CH_3)_2CO$ δ −13.79 (t, ^2J(PD) = 3.9); CH_2Cl_2 δ −13.99 (t, ^2J(PD) = 3.9).

Reaction of 3-d_1 with Acetone-d_6: Formation of [OsHD\{η^5-$C_5H_4(CH_2)_2NDMe_2$\}(P^iPr_3)$_2$][OTf]$_2$ (3-d_2). A solution of **3-d_1** (0.10 g, 0.12 mmol) in acetone-d_6 (0.5 mL) was stirred for 6 h at room temperature. The mixture was evaporated to dryness, and the resulting white solid was washed twice with pentane (2 × 1 mL). The ^{19}F and ^{1}H NMR data were identical to those reported for **3** with exception of the resonance at −14.19 (t, 1H, ^2J(PH) = 28.8, Os−H) and the absence of the one assigned to the NH proton. ^{31}P-{^{1}H} NMR (161.9 MHz, CD_2Cl_2, 293 K): δ 31.3 (t (1:1:1), ^2J(PD) = 3.9). ^{2}H NMR (46.05 MHz, CH_2Cl_2, 293 K): δ 8.90 (br, ND), −13.99 (t, ^2J(PD) = 3.9).

Reaction of 1 with CH_3OTf: Formation of [OsH\{η^5-$C_5H_4(CH_2)_2NMe_3$\}(P^iPr_3)$_2$]OTf (4). A solution of **1** (0.25 g, 0.38 mmol)

in toluene (0.5 mL) was treated with CH_3OTf (39 μL, 0.34 mmol) at room temperature, and the reaction mixture was stirred for 12 h. The solvent was removed under reduced pressure, and the solid residue was washed with pentane (2 × 3 mL) and dried under vacuum to give a white solid. Yield: 0.29 g (93%). Anal. Calcd for $C_{29}H_{60}F_3NO_3OsP_2S$: C, 42.89; H, 7.45; N, 1.72; S, 3.95. Found: C, 43.09; H, 7.51; N, 1.89; S, 4.05. IR (Nujol, cm^{-1}): ν (Os−H) 2052 (m), ν (SO_3) and ν (CF_3) 1259 (br, s), 1154 (s) and 1031 (s). MS (FAB^+, *m*/*e*): 813 ($[M + H]^+$). ^1H NMR (400 MHz, CD_2Cl_2, 293 K): δ 4.80, 4.00 (both m, each 2H, C_5H_4), 3.73 (m, 2H, CH_2CH_2N), 3.21 (s, 9H, NCH_3), 2.70 (m, 2H, CH_2CH_2N), 2.01 (m, 6H, PCH), 1.09 (dd, 18H, ^3J(HH) = 7.2, ^3J(PH) = 12.0, $PCCH_3$), 1.07 (dd, 18H, ^3J(HH) = 7.2, ^3J(PH) = 11.6, $PCCH_3$), −15.67 (t, 1H, ^2J(PH) = 30.4, Os−H). ^1H NMR (400 MHz, $(CD_3)_2CO$, 293 K): δ 4.75, 4.13 (both m, each 2H, C_5H_4), 3.82 (m, 2H, CH_2CH_2N), 3.34 (s, 9H, NCH_3), 2.89 (m, 2H, CH_2CH_2N), 2.01 (m, 6H, PCH), 1.13 (dd, 18H, ^3J(HH) = 7.2, ^3J(PH) = 11.6, $PCCH_3$), 1.17 (dd, 18H, ^3J(HH) = 7.2, ^3J(PH) = 12.0, $PCCH_3$), −15.68 (t, 1H, ^2J(PH) = 30.6, Os−H). $^{31}P\{^1H\}$ NMR (161.9 MHz, $(CD_3)_2CO$, 293 K): δ 32.9 (s). ^{19}F NMR (376.3 MHz, $(CD_3)_2CO$, 293 K): δ −75.5 (s). $^{13}C\{^1H\}$ NMR (100 MHz, $(CD_3)_2CO$, 293 K, plus HMQC plus APT): δ 88.4 (−, s, ipso-C_5H_4), 73.3 (+, s, C_5H_4), 69.9 (−, s, CH_2CH_2N), 68.5 (+, second-order system, C_5H_4), 53.6 (+, t (1:1:1), ^1J(NC) = 4, NMe_3), 31.7 (+, second-order system, PCH), 23.6 (−, s, CH_2CH_2N), 20.9, 20.8 (+, s, $PCCH_3$).

Reaction of 4 with CH_3OTf: Formation of [OsH{η^5-C_5H_4}-(CH_2)$_2$$NMe_3$}{$CH_2CH(CH_3)P^iPr_2$}($P^iPr_3$)][OTf] (5). A solution of **4** (0.25 g, 0.31 mmol) in dichloromethane (1 mL) was treated with CH_3OTf (35 μL, 0.31 mmol) at room temperature. The reaction mixture was stirred for 1 h; the solvent was removed under reduced pressure, and the solid residue was washed with pentane and dried under vacuum to produce a white solid. Complex **5** was obtained as a 1:1 mixture of isomers. Yield: 0.30 g (83%). Anal. Calcd for $C_{29}H_{59}F_6NOsO_6P_2S_2$: C, 37.45; H, 6.39; N, 1.46; S, 6.67. Found: C, 37.75; H, 6.22; N, 1.59; S, 6.45. IR (Nujol, cm^{-1}): ν (Os−H) 2053 (w), ν (SO_3) and ν (CF_3) 1259 (br, s), 1153 (s), 1030 (s). MS (FAB^+, *m*/*e*): 330 ($[M/2]^+$), 812 ($[M + OTf]^+$). **5a** or **5b** isomer. ^1H NMR (400 MHz, $(CD_3)_2CO$, 293 K, plus $^1H\{^{31}P\}$): δ 6.21, 5.90, 5.44, 5.38 (all m, each 1H, C_5H_4), 3.91 (m, 2H, NCH_2CH_2), 3.50 (m, 1H, CH_2CHCH_3), 3.40 (s, 9H, NMe_3), 2.90 (m, 2H, NCH_2CH_2), 2.56 (m, 3H, PCH), 2.40−2.10 (m, 4H, 2 PCH + Os−CH_2), 1.54−1.17 (m, 33H, $PCCH_3$), − 13.96 (dd, 1H, ^2J(P′H) = 26.0, ^2J(PH) = 34.8, Os−H). $^{31}P\{^1H\}$ NMR (161.9 MHz, $(CD_3)_2CO$, 293 K): δ 11.4, −29.5 (both d, ^2J(PP′) = 26). $^{19}F\{^1H\}$ NMR (376.3 MHz, $(CD_3)_2CO$, 293 K): δ −75.5 (s, CF_3).$^{13}C\{^1H\}$ NMR (100 MHz, $(CD_3)_2CO$, 283 K, plus APT plus HETCOR): δ 123.1 (−, q, ^1J(CF) = 331, CF_3), 108.7 (−, s, ipso-C_5H_4), 90.7 (+, d, ^2J(PC) = 4, C_5H_4), 85.0 (+, d, ^2J(PC) = 6, C_5H_4), 81.2, 77.2 (+, both s, C_5H_4), 67.8 (−, s, CH_2CH_2N), 54.7 (+, t(1:1:1), ^1J(NC) = 4, $N(CH_3)_3$), 49.9 (+, d, ^1J(PC) = 35, CH_2CHCH_3), 36.2 (+, d, ^1J(PC) = 22, PCH), 31.5 (+, d, ^1J(PC) = 28, PCH), 28.1 (+, d, ^1J(PC) = 20, PCH), 26.1 (+, d, ^2J(PC) = 6, CH_2CHCH_3), 23.5 (+, s, CH_2CH_2N), 22.2, 22.1, 22.0, 21.8 (+, all s, $PCHCH_3$), 21.7 (+, d, ^2J(CP) = 3, $PCHCH_3$), 21.4 (+, d, ^2J(PC) = 5, $PCHCH_3$), 19.9 (+, s, $PCHCH_3$), −27.1 (-, dd, ^2J(PC) = 9, ^2J(P′C) = 36, Os−CH_2). **5a** or **5b** isomer. ^1H NMR (400 MHz, $(CD_3)_2CO$, 293 K, plus $^1H\{^{31}P\}$): δ 5.95, 5.74, 5.73, 5.26 (all m, each 1H, C_5H_4), 3.91 (m, 2H, NCH_2CH_2), 3.40 (s, 9H, NMe_3), 3.19 (m, 1H, CH_2CHMe), 2.97 (m, 2H, NCH_2CH_2), 2.90−2.70 (m, 2H, Os−CH_2), 2.56 (m, 3H, PCH), 2.40−2.10 (m, 2H, PCH), 1.54−1.17 (m, 33H, $PCCH_3$), − 13.70 (dd, 1H, ^2J(P′H) = 28.8, ^2J(PH) = 36.8, Os−H). $^{31}P\{^1H\}$ NMR (161.9 MHz, $(CD_3)_2CO$, 293 K): δ 10.1, −31.3 (both d, ^2J(PP′) = 21). $^{19}F\{^1H\}$ NMR (376.3 MHz, $(CD_3)_2CO$, 293 K): δ −75.5 (s, CF_3).$^{13}C\{^1H\}$ NMR (100 MHz, $(CD_3)_2CO$, 283 K, plus APT plus HETCOR): δ 123.1 (−, q, ^1J(CF) = 331, CF_3), 111.4 (−, s, ipso-C_5H_4), 92.3 (+, d, ^2J(PC) = 5, C_5H_4), 84.3 (+, d, ^2J(PC) = 6, C_5H_4), 79.9, 75.8 (+, both s, C_5H_4), 67.6 (−, s, CH_2CH_2N), 54.7 (+, t(1:1:1), ^1J(NC) = 4, $N(CH_3)_3$), 47.6 (+, d, ^1J(PC) = 36, CH_2CHCH_3), 36.0 (+, d, ^1J(PC) = 22, PCH), 32.4 (+, d, ^2J(PC) = 27, PCH), 23.8, (−, s, NCH_2CH_2), 23.4 (+, d, ^2J(PC) = 6, CH_2CHCH_3), 22.1, 21.9, (+, both s, $PCHCH_3$), 21.7 (+, d, ^2J(CP) = 3, $PCHCH_3$), 21.2 (+, d, ^2J(PC) = 6, $PCHCH_3$), 20.9 (+, s, $PCHCH_3$), 20.8 (+, d, ^2J(PC) = 5, $PCHCH_3$), 19.0 (+, s, $PCHCH_3$), −27.0 (−, dd, ^2J(PC) = 9, ^2J(P′C) = 37, Os−CH_2).

Reaction of 1 with CD_3OTf: Formation of [OsH{η^5-C_5H_4-(CH_2)$_2$$NMe_2CD_3$}($P^iPr_3$)$_2$]OTf (4-*d*$_3$). A procedure analogous to that described for **4** was followed starting from a solution of **1** (0.15 g, 0.23 mmol) in toluene (0.5 mL) and CD_3OTf (24 μL, 0.22 mmol). Complex **4-*d*$_3$** was obtained as a white powder. Yield: 0.16 g (89%). $^{31}P\{^1H\}$, ^{19}F, and ^1H NMR data were identical to those reported for **4** with exception of the resonance at 3.34 (s, 6H, $N(CH_3)_2$). ^2H NMR (46.05 MHz, $(CH_3)_2CO$, 293 K): δ 3.49 (s, CD_3).

Reaction of 4-*d*$_3$ with CH_3OTf or CD_3OTf: Formation of [OsH{η^5-C_5H_4(CH_2)$_2$$NMe_2CD_3$}{$CH_2CH(CH_3)P^iPr_2$}($P^iPr_3$)][OTf]$_2$ (5-*d*$_3$). A procedure analogous to that described for **5** was followed starting from a solution of **4-*d*$_3$** (0.15 g, 0.18 mmol) in toluene (0.5 mL) and CH_3OTf or CD_3OTf (20 or 20 μL, respectively, 0.18 mmol). $^{31}P\{^1H\}$, ^{19}F, and ^1H NMR data were identical to those reported for **5** with exception of the resonance at 3.40 (s, 12H, NMe_2 of isomer **5a-*d*$_3$** and **5b-*d*$_3$**). ^2H NMR (46.05 MHz, $(CH_3)_2CO$, 293 K): δ 3.22 (s, NCD_3 of isomers **5a-*d*$_3$** and **5b-*d*$_3$**).

Reaction of 5 with Acetonitrile: Formation of [Os{η^5-C_5H_4-(CH_2)$_2$$NMe_3$}(NCMe)($P^iPr_3$)$_2$][OTf]$_2$(7) and [Os{$\eta^5$-$C_5H_4$-($CH_2$)$_2$$NMe_3$}(NCMe)$_2$($P^iPr_3$)][OTf]$_2$(8). A solution of **5** (0.30 g, 0.31 mmol) in acetonitrile (0.5 mL) was stirred at room temperature for 12 h. The solvent was removed under reduced pressure, and the solid residue was washed with pentane (2 × 3 mL) and dried under vacuum to give a light red solid. NMR spectra of this solid showed the presence of **7** and **8** in a 2:1 molar ratio. IR (Nujol, cm^{-1}): ν (C≡N) 2250 (br), ν (SO_3) and ν (CF_3) 1270 (br, s), 1148 (s), 1030 (s). MS (FAB^+, *m*/*e*): 652 ([Os{η^5-C_5H_4(CH_2)$_2$$NMe_3$}($P^iPr_3$)][OTf]). Complex **7**. ^1H NMR (400 MHz, CD_2Cl_2, 293 K, plus COSY plus HMQC): δ 5.13, 4.94 (both m, each 2H, C_5H_4), 3.75 (m, 2H, CH_2CH_2N), 3.25 (s, 9H, NCH_3), 2.82 (t, 3H, ^5J(PH) = 1.2, $NCCH_3$), 2.56 (m, 2H, CH_2CH_2N), 2.48 (m, 6H, PCH), 1.23 (dd, 18H, ^3J(HH) = 6.8, ^3J(PH) = 13.2, $PCCH_3$), 1.18 (dd, 18H, ^3J(HH) = 7.2, ^3J(PH) = 13.6, $PCCH_3$). $^{31}P\{^1H\}$ NMR (161.9 MHz, CD_2Cl_2, 293 K): δ 0.0 (s). ^{19}F NMR (376.3 MHz, CD_2Cl_2, 293 K): δ −74.3 (s). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2, 293 K, plus HMQC plus APT): δ 123.5 (−, s, ipso-C_5H_4), 121.0 (−, q, ^1J(FC) = 321, CF_3SO_3), 96.0 (−, br, N≡C), 73.1, 69.0 (+, s, C_5H_4), 66.3 (−, s, CH_2CH_2N), 53.8 (+, t(1:1:1), ^1J(NC) = 4, NMe_3), 30.0 (+, second-order system, PCH), 21.0 (−, s, CH_2CH_2N), 20.7, 20.6 (+, both s, $PCCH_3$), 5.2 (+, s, N≡CCH_3). Complex **8**. ^1H NMR (400 MHz, CD_2Cl_2, 293 K, plus COSY plus HMQC): δ 4.94, 4.57 (both m, each 2H, C_5H_4), 3.66 (m, 2H, CH_2CH_2N), 3.26 (s, 9H, NCH_3), 2.81 (m, 2H, CH_2CH_2N), 2.66 (d, 6H, ^5J(PH) = 1.2, $NCCH_3$), 2.37 (m, 3H, PCH), 1.23 (dd, 9H, ^3J(HH) = 6, ^3J(PH) = 12.4, $PCCH_3$). $^{31}P\{^1H\}$ NMR (161.9 MHz, CD_2Cl_2, 293 K): δ 17.5 (s). ^{19}F NMR (376.3 MHz, CD_2Cl_2, 293 K): δ −74.3 (s). $^{13}C\{^1H\}$ NMR (100.57 MHz, CD_2Cl_2, 293 K, plus HMQC plus APT): δ 124.6 (−, s, ipso-C_5H_4), 121.0 (−, q, ^1J(FC) = 321, CF_3SO_3), 88.7 (−, d, ^3J(PC) = 7.0, N≡C), 72.5, 67.5 (+, s, C_5H_4), 66.3 (−, s, CH_2CH_2N), 53.6 (+, t(1:1:1), ^1J(NC)

= 3, NMe_3), 27.1 (+, d, ^1J(PC) = 26, PCH), 21.0 (−, s, *C*H_2-CH_2N), 19.6 (+, s, PC*C*H_3), 4.5 (+, s, N≡C*C*H_3).

Reaction of 4 with Methanol: Formation of [OsH$_2$(η^5-C$_5$H$_4$CH=CH$_2$)(P^{i}Pr$_3$)$_2$]OTf (9). A solution of **4** (0.15 g, 0.15 mmol) in methanol was stirred at room temperature for 24 h. The resulting colorless solution was evaporated to dryness, and the product was extracted with dichloromethane, filtered through Celite/alumina (9:1), and washed twice with pentane to yield a white solid. Yield: 9.6 × 10^{-2} g (63%). Anal. Calcd for $C_{26}H_{51}F_3OsO_3P_2S$: C, 41.47; H, 6.83; S, 4.26. Found C, 41.56; H, 6.82; S, 4.12. IR (Nujol, cm^{-1}): ν (Os−H) 2145, 2111, ν (C=C) 1633, ν (SO_3) and ν (CF_3) 1270 (br, s), 1148 (s), 1030 (s). MS (FAB$^+$, *m*/*e*): 605 (M^+). ^{1}H NMR (400 MHz, CD_2Cl_2, 293 K, plus ^{1}H{^{31}P} plus COSY): δ 6.40 (dd, 1H, ^3J(HH_{cis}) = 10.8, ^3J(HH_{trans}) = 17.6, −CH=), 5.64 (d, 1H, ^3J(HH_{trans}) = 17.6, C=CH_{trans}), 5.55 (m, 2H, C_5H_4), 5.43 (d, 1H, ^3J(HH_{cis}) = 10.8, C=CH_{cis}), 5.30 (m, 2H, C_5H_4), 2.10 (m, 6H, PCH), 1.23 (dd, 36H, ^3J(HH) = 6.8, ^3J(PH) = 14.0, $PCCH_3$), −14.22 (t, 2H, ^2J(PH) = 29.2, Os−H). ^{31}P{^{1}H} NMR (161.9 MHz, CD_2Cl_2, 293 K): δ 32.2 (s). ^{19}F NMR (376.3 MHz, CD_2Cl_2, 293 K): δ −78.8 (s) ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2, 293 K, plus HMQC plus APT): δ 127.3 (+, s, −CH=), 120.5 (−, s, $=CH_2$), 107.6 (−, s, ipso-C_5H_4), 82.3, 78.4 (+, both s, C_5H_4), 30.6 (+, second-order system, PCH), 19.7 (+, s, PC*C*H_3).

Reaction of 4 with Methanol-*d*$_4$: Formation of [OsHD(η^5-C$_5$H$_4$CH=CH$_2$)(P^{i}Pr$_3$)$_2$]OTf (9-*d*$_1$). A procedure analogous to that described for **9** was followed starting from a solution of **4** in methanol-d_4. Complex **9-*d*$_1$** was obtained as a white solid. ^{1}H NMR data were identical to those reported for **9** with exception of the resonance at −14.22 (t, 1H, ^2J(PH) = 29.2, Os−H). ^{31}P{^{1}H} NMR (161.9 MHz, CD_2Cl_2, 293 K): δ 32.2 (t, ^2J(PD) = 4). ^{2}H NMR (46.05 MHz, CH_2Cl_2, 293 K): δ −14.13 (t, ^2J(PD) = 4, Os-D).

Reaction of 4 with HOTf: Formation of [OsH$_2${η^5-C$_5$H$_4$(CH$_2$)$_2$NMe$_3$}(P^{i}Pr$_3$)$_2$][OTf]$_2$(10). A solution of **4** (0.25 g, 0.31 mmol) in dichloromethane (0.5 mL) was treated with HOTf (27 μL, 0.31 mmol) at room temperature, and the reaction mixture was stirred for 1 h. The solvent was removed under reduced pressure, and the solid residue was washed with pentane (2 × 3 mL) and dried under vacuum to give a white solid. Yield: 0.27 g (90%). Anal. Calcd for $C_{30}H_{61}F_6NOsO_6P_2S_2$: C, 37.45; H, 6.39; N, 1.46; S, 6.67. Found C, 37.31; H, 5.98; N, 1.40; S, 6.98. IR (Nujol, cm^{-1}): ν (Os−H) 2044, 2020 (w), ν (SO_3) and ν (CF_3) 1270 (br, s), 1148 (s), 1030 (s). MS (FAB$^+$, *m*/*e*): 814 ([M − OTf]$^+$). ^{1}H NMR (400 MHz, CD_2Cl_2, 293 K): δ 5.99, 5.22 (both m, each 2H, C_5H_4), 3.73 (m, 2H, CH_2CH_2N), 3.23 (s, 9H, NCH_3), 2.97 (m, 2H, CH_2CH_2N), 2.15 (m, 6H, PCH), 1.24 (dd, 36H, ^3J(HH) = 7.2, ^3J(PH) = 14.1, $PCCH_3$), −14.22 (t, 2H, ^2J(PH) = 29.1, Os−H). ^{1}H NMR (400 MHz, $(CD_3)_2CO$, 293 K): δ 6.02, 5.54 (both m, each 2H, C_5H_4), 3.84 (m, 2H, CH_2CH_2N), 3.38 (s, 9H, NCH_3), 3.30 (m, 2H, CH_2CH_2N), 2.30 (m, 6H, PCH), 1.31 (dd, 36H, ^3J(HH) = 7.2, ^3J(PH) = 14.0, $PCCH_3$), −14.09 (t, 2H, ^2J(PH) = 29.2, Os−H). ^{31}P{^{1}H} NMR (161.9 MHz, $(CD_3)_2CO$, 293 K): δ 32.8 (s). ^{19}F NMR (376.3 MHz, $(CD_3)_2CO$, 293 K): δ −74.3 (s). ^{13}C{^{1}H} NMR (100 MHz, $(CD_3)_2CO$, 293 K, plus HMQC plus APT): δ 106.0 (−, s, ipso-C_5H_4), 87.9, 80.7 (+, s, C_5H_4), 68.7 (−, s, CH_2CH_2N), 54.8 (+, t(1:1:1), ^1J(NC) = 4, NMe_3), 32.0 (+, second-order system, PCH), 24.8 (−, s, CH_2CH_2N), 20.9 (+, s, PC*C*H_3).

Reaction of 9 with Sodium Methoxide: Formation of OsH(η^5-C$_5$H$_4$CH=CH$_2$)(P^{i}Pr$_3$)$_2$ (11). Tetrahydrofurane (2 mL) was added to a mixture of complex **9** (0.25 g, 0.33 mmol) and sodium methoxide (19 × 10^{-3} g, 0.36 mmol) at room temperature, and the reaction mixture was stirred for 24 h. The solvent was removed under reduced pressure, and the solid residue was extracted with pentane (2 × 2 mL). The pale yellow solution was separated from the white precipitate by filtration through Celite, evaporated to dryness, and dried under vacuum to yield a yellow powder. Yield: 0.10 g (64%). Anal. Calcd for $C_{25}H_{50}OsP_2$: C, 49.81; H, 8.36. Found: C, 50.04; H, 8.43. IR (Nujol, cm^{-1}): ν (Os−H) 2083, ν (C=C) 1615. MS (FAB$^+$, *m*/*e*): 605 ([M + H]$^+$). ^{1}H NMR (400 MHz, C_6D_6, 293 K, plus ^{1}H{^{31}P} plus COSY): δ 6.55 (dd, 1H, ^3J(HH_{cis}) = 10.8, ^3J(HH_{trans}) = 17.2, =CH), 5.22 (d, 1H, ^3J(HH_{trans}) = 17.2, =C*H*$_{trans}$), 5.00 (d, 1H, ^3J(HH_{cis}) = 10.8, =C*H*$_{cis}$), 4.64, 4.52 (both m, each 2H, C_5H_4), 1.94 (m, 6H, PCH), 1.12 (dd, 18H, ^3J(HH) = 7.2, ^3J(PH) = 12.4, $PCCH_3$), 1.15 (dd, 18H, ^3J(HH) = 7.2, ^3J(PH) = 12.4, $PCCH_3$), −16.67 (t, 2H, ^2J(PH) = 31.6, Os−H). ^{31}P{^{1}H} NMR (161.9 MHz, C_6D_6, 293 K): δ 27.7 (s). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 293 K, plus HMQC plus APT): δ 134.5 (+, s, =CH), 107.9 (−, s, $=CH_2$), 87.9 (−, s, ipso-C_5H_4), 72.8, 69.3 (+, both s, C_5H_4), 31.1 (+, d, ^1J(PC) = 24, PCH), 21.1, 20.6 (+, both s, PC*C*H_3). The same procedure was followed in all of the reported deprotonation reactions starting from the corresponding osmium derivatives, **3-*Nd*$_1$** (0.15 g, 0.16 mmol), **3-*d*$_1$** (0.15 g, 0.16 mmol), or **10** (0.30 g, 0.31 mmol) and sodium methoxide (8.6 × 10^{-3} g, 0.16 mmol (**3-*Nd*$_1$**), 8.6 × 10^{-3} g, 0.16 mmol (**3-*d*$_1$**), or 18 × 10^{-3} g, 0.34 mmol (**10**), respectively. ^{1}H, ^{31}P{^{1}H}, and ^{19}F NMR spectra of the corresponding solids were identical to those reported for **2**, **2-*d*$_1$**, and **9**, respectively.

Table 2. Crystal Data and Data Collection and Refinement for **4**

Crystal Data	
formula	$C_{29}H_{60}F_3NO_3OsP_2S$
mol wt	811.98
color and habit	colorless, irregular block
symmetry, space group	triclinic, $P\bar{1}$
a, Å	8.5873(4)
b, Å	10.3482(5)
c, Å	20.1959(10)
α, deg	77.9920(10)
β, deg	83.5540(10)
γ, deg	83.3500(10)
V, Å^3	1736.39(14)
Z	2
D_{calc}, g cm^{-3}	1.553
Data Collection and Refinement	
diffractometer	Bruker Smart APEX
λ(Mo Kα), Å	0.71073
monochromator	graphite oriented
scan type	*ω* scans
μ, mm^{-1}	3.869
2*θ*, range deg	3, 57
temp, K	100
no. of data collected	21900
no. of unique data	8307 (R_{int} = 0.0323)
no. of params/restraints	380/0
R_1[a] [$F^2 > 2\sigma(F^2)$]	0.0261
R_2[b] (all data)	0.0451
S[c] (all data)	0.842

[a] $R_1(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_2(F^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. [c] GOF = $S = \{\sum[F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$ where *n* is the number of reflections and *p* is the number of refined parameters.

X-ray Analysis of 4. An irregular crystal of 0.20 × 0.12 × 0.08 mm was mounted on a Bruker Smart APEX CCD diffractometer, equipped with a normal focus and a 2.4 kW sealed tube source (molybdenum radiation, λ = 0.71073 Å) operating at 50 kV and 40 mA, at 100.0(2) K. 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. The cell parameters were determined and refined by the least-squares fit of 7645 collected reflections. The first 100 frames were collected at the end of the data collection to monitor crystal decay. The absorption correction was performed with the SADABS program which is based on the Blessing method.[23] Lorentz and polarization corrections were also performed. The structure was solved by Patterson and Fourier methods and refined

by full matrix least-squares using the Bruker SHELXTL program package[24] minimizing $w(F_o^2 - F_c^2)^2$. The hydride was refined as a free isotropic atom. The weighted R factors (R_2) and goodness of fit (S) are based on F^2, and the conventional R factors are based on F. Crystal data and details of the data collection and refinement are given in Table 2.

(23) Blessing, R. H. *Acta Crystallogr., Sect. A.* **1995**, *51*, 33.
(24) *SHELXTL Package*, version 6.1; Bruker-AXS: Madison, WI, 2000.

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Supporting Information Available: Tables of crystallographic data and bond lengths and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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