Activation of C(sp²)−H and Reduction of C=E (E = CH, N) Bonds with an Osmium-Hexahydride Complex: Influence of E on the Behavior of RCH=E-py Substrates

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The hexahydride complex $OsH_6(P^iPr_3)_2$ (**1**) reacts with 2-vinylpyridine to give the trihydride derivative $OsH_3(NC_5H_4\text{-}o\text{-}CH{=}CH)(P^iPr_3)_2$ (**2**). The β- and γ-positions of the pyridine ring are quantitatively and selectively deuterated by addition of **1** (5%) to toluene-d_8 and benzene-d_6 solutions of **2**. Under hydrogen atmosphere, **2** reacts with $HBF_4{\cdot}OEt_2$ to afford $[HNC_5H_4\text{-}o\text{-}Et]BF_4$ and regenerate **1**. Under argon atmosphere, the addition of $HBF_4{\cdot}OEt_2$ to dichloromethane solutions of **2** leads to the hydride-dihydrogen $[OsH(\eta^2\text{-}H_2)(\eta^2\text{-}CH_2{=}CH\text{-}o\text{-}C_5H_4N)(P^iPr_3)_2]BF_4$ (**3**), which catalyzes the hydrogenation of 2-vinylpyridine to 2-ethylpyridine. In dichloromethane **3** evolves into the neutral chloro-dihydrogen compound $Os(NC_5H_4\text{-}o\text{-}CH{=}CH)Cl(\eta^2\text{-}H_2)(P^iPr_3)_2$ (**4**). Complex **1** also reacts with *N*-methylene-2-pyridinamine and (*E*)-*N*-(phenylmethylene)-2-pyridinamine. The reaction with the first pyridinamine leads to a 3:1 mixture of the trihydride complexes $OsH_3(NC_5H_4\text{-}o\text{-}NCH_3)(P^iPr_3)_2$ (**5**) and $OsH_3(NC_5H_4\text{-}o\text{-}N{=}CH)(P^iPr_3)_2$ (**6**), while the reaction with the second one selectively affords $OsH_3(NC_5H_4\text{-}o\text{-}NCH_2Ph)(P^iPr_3)_2$ (**7**). Similarly to **2**, the addition of **1** (5%) to toluene-d_8 and benzene-d_6 solutions of **6** produces the quantitative and selective deuteration of the β- and γ-positions of the pyridine ring. The addition of $HBF_4{\cdot}OEt_2$ to diethyl ether solutions of **5** leads to $[OsH_3(NC_5H_4\text{-}o\text{-}NHCH_3)(P^iPr_3)_2]BF_4$ (**8**). Isotope labeling experiments suggest that the reduction of the C=C double bond of 2-vinylpyridine takes place by concerted addition of a dihydrogen ligand, while the reduction of the C=N double bond of *N*-methylene-2-pyridinamine occurs by sequential addition of H^- and H^+. In solution the hydride ligands of these compounds undergo two different site exchange processes. Their activation parameters have been calculated by ^1H NMR spectroscopy. Complexes **2**, **3**, and **5** have been characterized by X-ray diffraction analyses.

Introduction

The activation of C−H bonds by transition metal compounds is a type of reaction of general interest due to its connection with the functionalization of nonactivated organic molecules.[1] Although it is rare with high-valent metal complexes, we have recently shown that the saturated d² hexahydride $OsH_6(P^iPr_3)_2$ can be thermally activated to generate the unsaturated short-lived dihydride-dihydrogen $OsH_2(\eta^2\text{-}H_2)(P^iPr_3)_2$, which activates *ortho*-CH bonds of aromatic ketones and imines[3] and *ortho*-CF bonds of partially fluorinated ketones.[2] The reactions give complexes that are reminiscent species of the intermediates proposed by Murai for the insertion of olefins into *ortho*-CH bonds of ketones and imines[4] and for the arylation of aromatic ketones with arylboronates.[5]

In addition to aromatic ketones and imines, intermediate $OsH_2(\eta^2\text{-}H_2)(P^iPr_3)_2$ activates cyclohexylmethyl ketone and aromatic and alkyl aldehydes. The reaction with cyclohexylmethyl ketone affords the cyclohexenyl-keto complex $OsH_3\{C_6H_8C(O)CH_3\}(P^iPr_3)_2$, as a result of a triple $C(sp^3)$−H activation of the cyclohexyl substituent.[6] The reactions with aldehydes lead to acyl species, as a consequence of $C(sp^2)$−H_α activation processes. These acyl derivatives are highly unstable and rapidly evolve to different types of isolated com-

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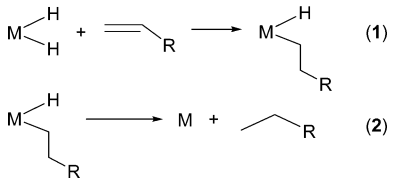
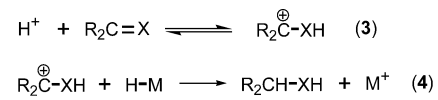
pounds, including $OsH_2(CO)_2(P^iPr_3)_2$, $OsHPh(CO)_2(P^iPr_3)_2$, and $OsH_3(\kappa^2\text{-}O_2CR)(P^iPr_3)_2$.[7]

Hydride complexes of platinum group metals have shown to be effective reducing agents for the transformation of olefins to alkanes. It is assumed that two hydrides are transferred sequentially to the olefin. The transfer of the first of them yields hydride-alkyl species, which evolve into the alkane by intramolecular reductive elimination (eqs 1 and 2).[8]



The mechanism of the addition of molecular hydrogen to transition metal complexes goes through a dihydrogen intermediate. The kinetic acidity of dihydrogen complexes is much greater than their corresponding dihydrides.[9] In agreement with this, there is increasing evidence showing that polar C═X bonds (X = N, O) can be also reduced by an ionic mechanism involving the rapid and reversible protonation of the substrate, followed by the hydride transfer from the metal (eqs 3 and 4).[10]



At first glance, the short-lived dihydride-dihydrogen $OsH_2(\eta^2\text{-}H_2)(P^iPr_3)_2$ has all the qualities to be an active species for the following reactions: (i) the activation of $C(sp^2)-H$ bonds of olefins and aldimines, in a manner similar to the previously mentioned activations; (ii) the reduction of olefins according to eqs 1 and 2, due to its hydride character; and (iii) the reduction of aldimines according to eqs 3 and 4, or by a similar pathway, because its dihydrogen ligand is expected to be fairly acidic.

Ruthenium- and osmium-polyhydride complexes have shown to be useful templates to carbon−carbon and carbon−heteroatom coupling reactions. The processes involve the entry, in a consecutive and controlled way, of organic molecules into the metallic center of the polyhydride. The field needs much more research effort, mainly on the control of the products from the first step of the global process.[11] Our interest in learning to control the products of these reactions prompted us to study the reactivity of the hexahydride $OsH_6(P^iPr_3)_2$ toward olefin and aldimine substrates containing a pyridyl group. This substituent was used in order to facilitate stable metallacycles, resulting from $C(sp^2)-H$ activation reactions.[12]

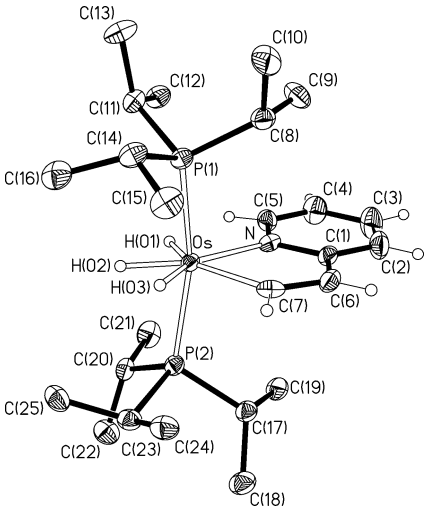


Figure 1. Molecular diagram of complex $OsH_3(NC_5H_4\text{-}o\text{-}CH{=}CH)(P^iPr_3)_2$ (**2**).

In this paper, we report the results of this study.

Results and Discussion

1. Reactions of $OsH_6(P^iPr_3)_2$ with 2-Vinylpyridine. Treatment under reflux of toluene solutions of the hexahydride $OsH_6(P^iPr_3)_2$ (**1**) with 1.6 equiv of 2-vinylpyridine affords after 5 h orange solutions, from which the trihydride $OsH_3(NC_5H_4\text{-}o\text{-}CH{=}CH)(P^iPr_3)_2$ (**2**) was isolated as a yellow solid in 83% yield (eq 5). Complex **2** is the result of the $C(sp^2)-H$ bond activation of the CH_2 olefinic group of the substituent of the pyridine, by the short-lived intermediate $OsH_2(\eta^2\text{-}H_2)(P^iPr_3)_2$. The formation of ethylpyridine or organometallic products resulting from the insertion of the vinyl substituent of the substrate into any of the Os−H bonds of the starting complex was not observed during the reaction.

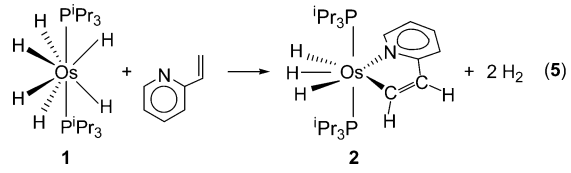


Figure 1 shows a view of the molecular geometry of **2**. Selected bond distances and angles are listed in Table 1. The coordination geometry around the osmium atom can be rationalized as a distorted pentagonal bipyramid with the two phosphorus atoms of the triisopropylphosphine ligands occupying axial positions (P(1)−Os−P(2) = 165.12(4)°). The osmium sphere is completed by the hydride ligands and the metalated group, which acts with a bite angle of 75.40(18)°.

The bond length Os−C(7) (2.073(5) Å) is as expected for an $Os-C(sp^2)$ single bond and similar to those found in other alkenyl-osmium complexes (between 1.99(1) and 2.195(5) Å).[13] The C(6)−C(7) bond length of 1.347(7)

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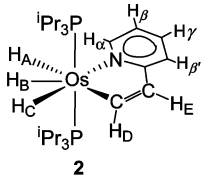
Table 1. Selected Bond Lengths (Å) and Angles (deg) for the Complex $OsH_3(NC_5H_4$-*o*-$CH{=}CH)(P^iPr_3)_2$ (2)

Os−P(1)	2.3380(13)	Os−H(02)	1.45(4)
Os−P(2)	2.3253(13)	Os−H(03)	1.43(4)
Os−N	2.148(4)	N−C(1)	1.371(5)
Os−C(7)	2.073(5)	C(1)−C(6)	1.422(7)
Os−H(01)	1.43(4)	C(6)−C(7)	1.347(7)
P(1)−Os−P(2)	165.12(4)	N−Os−H(02)	145.1(16)
P(1)−Os−N	97.36(10)	N−Os−H(03)	152.0(16)
P(1)−Os−C(7)	92.53(13)	C(7)−Os−H(01)	146.8(16)
P(1)−Os−H(01)	94.6(16)	C(7)−Os−H(02)	139.0(16)
P(1)−Os−H(02)	88.0(16)	C(7)−Os−H(03)	76.6(16)
P(1)−Os−H(03)	83.5(16)	H(01)−Os−H(02)	74(2)
P(2)−Os−N	97.46(10)	H(01)−Os−H(03)	136(2)
P(2)−Os−C(7)	92.39(13)	H(02)−Os−H(03)	63(2)
P(2)−Os−H(01)	88.9(16)	Os−N−C(1)	115.7(3)
P(2)−Os−H(02)	79.1(16)	Os−C(7)−C(6)	118.4(4)
P(2)−Os−H(03)	84.0(16)	N−C(1)−C(6)	114.5(4)
N−Os−C(7)	75.40(18)	C(1)−C(6)−C(7)	116.0(4)
N−Os−H(01)	71.5(16)		

Å agrees well with the average carbon−carbon double bond distances in vinyl groups (1.35(2) Å).[14] In accordance with the sp^2 hybridization at C(6) and C(7), the angles C(7)−C(6)−C(1) and C(6)−C(7)−Os are 116.0(4)° and 118.4(4)°, respectively.

The spectroscopic data of **2** are consistent with the structure shown in Figure 1. The IR spectrum in KBr contains two bands at 2173 and 2118 cm^{-1}, corresponding to the hydride ligands. In the $^{13}C\{^1H\}$ NMR spectrum in toluene-d_8 at room temperature, the resonances due to the CH═CH substituent of the pyridine are observed at 203.9 and 158.6 ppm. The first of them, assigned to the OsCH-carbon atom, appears as a triplet with a C−P coupling constant of 6.4 Hz. The second one, corresponding to the HCpy-carbon atom, is observed as a singlet. In agreement with the mutually *trans* disposition of the phosphine ligands, the $^{31}P\{^1H\}$ NMR spectrum in toluene-d_8 contains a singlet at 26.8 ppm, which is temperature invariant between 363 and 193 K.

In contrast to the $^{31}P\{^1H\}$ NMR spectrum, the ^1H NMR spectrum is temperature-dependent. In toluene-d_8 at 363 K, it shows in the hydride region a single broad resonance centered at −9.4 ppm. This observation is consistent with the operation of two thermally activated site exchange processes, which proceed at rates sufficient to lead to the single resonance. Consistent with this, lowering the sample temperature produces broadening of the resonance. Between 343 and 333 K, the first decoalescence occurs, and at about 223 K, the second one takes place. At 193 K, three broad resonances at −5.05 (H_A), −11.33 (H_B), and −12.20 (H_C) are observed. In the low-field region of the spectrum, the resonance corresponding to the OsCH-proton of the substituent of the pyridine appears at 11.47 ppm (H_D), while the HCpy-proton displays a doublet at 7.91 ppm (H_E). The resonance H_D is observed as a double doublet by spin coupling with H_E ($J_{H_D-H_E}$ = 10 Hz) and H_C ($J_{H_C-H_D}$ = 8 Hz). The spin coupling between the hydride H_C and the vinylic proton H_D was confirmed by a $^1H-^1H$ COSY



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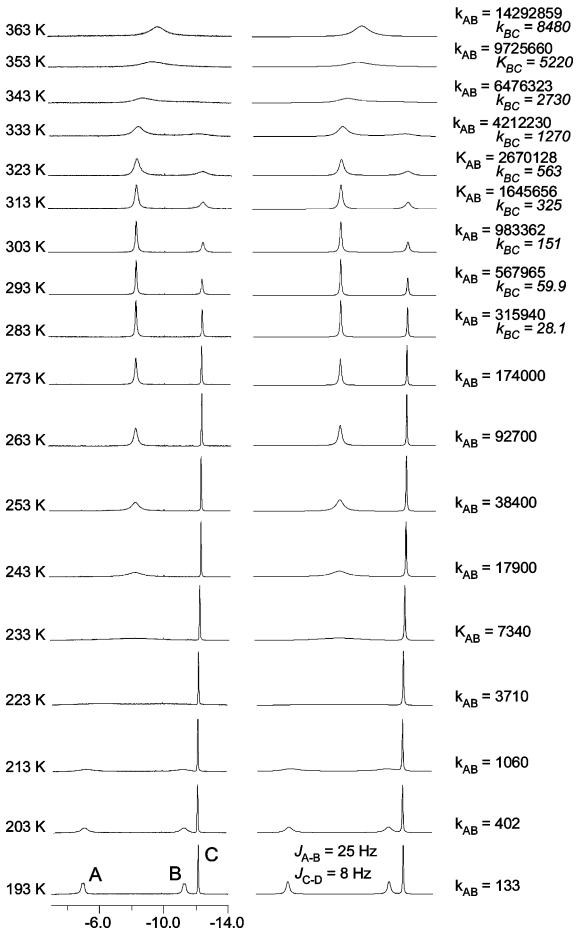

Figure 2. Left: Variable-temperature $^1H\{^{31}P\}$ NMR spectra (300 MHz) in the high-field region of $OsH_3(NC_5H_4$-*o*-$CH{=}CH)(P^iPr_3)_2$ (**2**). Right: Simulated spectra and rate constants (s^{-1}) for the intramolecular hydrogen site-exchange processes.

NMR spectrum at 193 K, which shows the cross signals between both resonances. On the basis of this spectrum, the resonance H_C was assigned to the hydride ligand disposed *cisoid* to the OsCH-carbon atom of the substituent of the pyridine. In agreement with this, the saturation of H_D increases the intensities of H_C (2%) and H_E (12%), while H_A and H_B do not show any NOE effect. In the $^1H\{^{31}P\}$ NMR spectrum, the resonances H_A, H_B, and H_C are simplified to doublets. The resonances H_A and H_B show a H_A-H_B coupling constant of 25 Hz.

The T_1 values of the hydrogen nuclei of the OsH_3 unit of **2** were determined over the temperature range 253−183 K. $T_{1(min)}$ values of 108 ± 3 ms for H_A, 102 ± 2 ms for H_B, and 114 ± 1 ms for H_C were obtained at 203 K. They support the trihydride character of the complex and suggest that the central atom of the OsH_3 unit is H_B. So, H_A is the hydride situated *cisoid* to the nitrogen atom of the pyridine.

Figure 2 shows the $^1H\{^{31}P\}$ NMR spectra of **2** in the hydride region, as a function of the temperature. Line-

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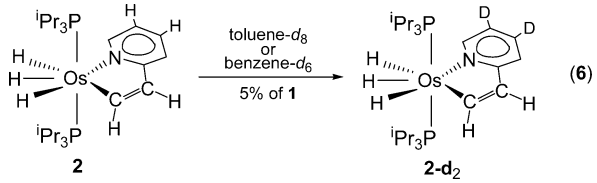
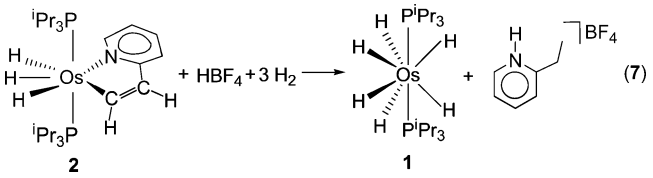
shape analyses of these spectra allow the calculation of the rate constants for the thermal exchange processes at different temperatures. The activation parameters obtained from the corresponding Eyring analysis are $\Delta H^{\ddagger} = 9.1 \pm 0.2$ kcal·mol^{-1} and $\Delta S^{\ddagger} = 1.1 \pm 0.7$ cal·mol^{-1}·K^{-1} for the H_A/H_B exchange and $\Delta H^{\ddagger} = 14.1 \pm 0.6$ kcal·mol^{-1} and $\Delta S^{\ddagger} = -1.9 \pm 1.2$ cal·mol^{-1}·K^{-1} for the H_B/H_C exchange. The values for the entropy of activation, close to zero, are in agreement with an intramolecular process, whereas the values for the enthalpy of activation lie in the range reported for thermal exchange processes in related osmium-trihydride complexes.[2,3,15]

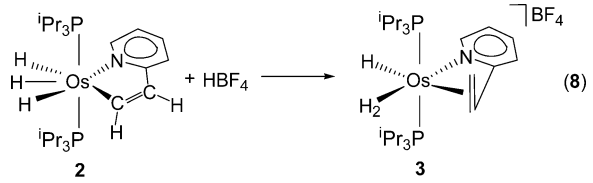
In addition to the vinylic resonances, four signals at 9.57 (d), 7.06 (d), 6.85 (dd), and 6.09 (dd) ppm are observed in the low-field region of the ^{1}H NMR spectrum. They were assigned to the pyridinic protons H_α, $H_{\beta'}$, H_γ, and H_β (see Figure 2), respectively, on the basis of their multiplicities and the ^{1}H−^{1}H COSY NMR spectrum at 193 K. The addition of 0.05 equiv of **1** to an NMR tube containing toluene-d_8 or benzene-d_6 solutions of **2** produces after 10 h the extinction of the resonances at 6.85 (H_γ) and 6.09 (H_β) ppm, whereas the resonances at 9.57 (H_α) and 7.06 ($H_{\beta'}$) are converted into singlets. Changes in the vinylic, phosphine, and hydride resonances are not observed. In the ^{13}C{^{1}H} NMR spectrum of these solutions, the resonances corresponding to the CH_β- and CH_γ-carbon atoms of the pyridine (132.4 and 115.5 ppm) appear as 1:1:1 triplets with C−D coupling constants of 24.3 and 24.6 Hz, respectively. The ^{2}H NMR spectrum in benzene of the residue resulting from removing the deuterated solvent under reduced pressure shows two singlets at 6.98 and 6.20 ppm. Resonances in the high-field region are not observed. The above-mentioned facts indicate that the hexahydride **1** selectively catalyzes the H/D exchange between the less handicapped β- and γ-positions of the pyridine of **2** and the deuterated solvent, in the presence of the hydride ligands of the OsH_3 unit (eq 6). The process should involve C−H_β and C−H_γ activations of the pyridine and C−D activations of the deuterated solvent on the short-lived intermediate $OsH_2(\eta^2\text{-}H_2)(P^iPr_3)_2$.



Under hydrogen atmosphere, complex **2** is stable and does not evolve into **1** and 2-vinylpyridine, or 2-ethylpyridine, even at 80 °C. However, at room temperature in dichloromethane and in the presence of 1.0 equiv of HBF_4·OEt_2, the formation of **1** and the tetrafluoroborate salt of 2-ethylpyridinium takes place after 4 h, according to eq 7.



Under argon atmosphere the addition of 1.0 equiv of HBF_4·OEt_2 to a diethyl ether solution of **2** produces the precipitation of the cationic hydride-dihydrogen complex $[OsH(\eta^2\text{-}H_2)(\eta^2\text{-}CH_2{=}CH\text{-}o\text{-}C_5H_4N)(P^iPr_3)_2]BF_4$ (**3**), as a result of the formal protonation of the OsCH-carbon atom of the substituent of the pyridine of **2**, and the conversion of the H_B and H_C hydrides into an elongated dihydrogen ligand (eq 8).



Complex **3** was isolated as a white solid in 92% yield and characterized by elemental analyses, MS, IR, and ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} spectroscopy, and by an X-ray crystallographic study. The structure has two chemically equivalent but crystallographically independent molecules in the asymmetric unit. A drawing of the cation of one of them is shown in Figure 3. Selected bond distances and angles for both molecules are listed in Table 2.

The coordination geometry around the osmium atom could be rationalized as being derived from a highly distorted octahedron with the two phosphorus atoms of the triisopropylphosphine ligands occupying *pseudo-trans* positions (P(1)−Os(1)−P(2) = 152.45(4)° in molecule **a** and 149.88(4)° in molecule **b**) at opposite sides of an ideal coordination plane defined by the nitrogen atom, the midpoint (M) of the carbon−carbon double bond of the substituent of the pyridine (N(1)−Os(1)−M = 68.8° in molecule **a** and 69.0° in molecule **b**), the hydride, and the dihydrogen ligand. The strong deviation of the P(1)−Os(1)−P(2) angle from the ideal value of 180° is most probably a result of a large steric hindrance between the phosphines and the substituent of the pyridine. The vinyl group lies almost parallel to the phosphorus−phosphorus vector, the dihedral angle between the P(1)−Os(1)−P(2) and C(2)−Os(1)−C(3) planes being 22.85° in molecule **a** and 19.86° in molecule **b**.

The intrinsic asymmetry of the olefin produces a loss of symmetry in the cation, which is seen in the structural parameters by the two different Os−P distances. The Os(1)−P(1) bond length (2.3857(12) Å in molecule **a** and 2.3827(11) Å in molecule **b**) is approximately 0.01 Å longer than the Os(1)−P(2) bond length (2.3740(11) Å in molecule **a** and 2.3724(11) Å in molecule **b**). This fact can also be observed in the ^{31}P{^{1}H} NMR spectrum, which shows an AB spin system centered at 20.1 ppm, and defined by $\Delta\nu = 189$ Hz and $J_{AB} = 157$ Hz.

The osmium-vinyl coordination exhibits Os−C distances of 2.222(4) (molecule **a**) and 2.220(4) (molecule **b**) Å (Os(1)−C(2)) and 2.225(4) (molecule **a**) and 2.220(4)

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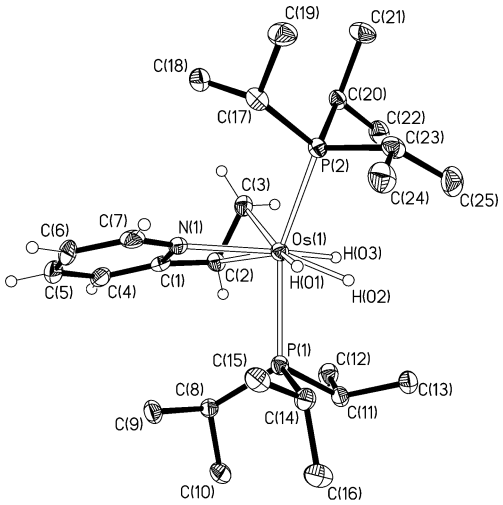

Figure 3. Molecular diagram of the cation of complex $[OsH(\eta^2\text{-}H_2)(\eta^2\text{-}CH_2{=}CH\text{-}o\text{-}C_5H_4N)(P^iPr_3)_2]BF_4$ (**3**).

(molecule **b**) Å (Os(1)−C(3)), which agree well with those found in other osmium-olefin complexes (between 2.13 and 2.28 Å).[16] Similarly, the olefinic bond distance C(2)−C(3) (1.395(5) Å in molecule **a** and 1.415(5) Å in molecule **b**) is within the range reported for transition metal olefin complexes (between 1.340 and 1.445 Å).[17] In accordance with the coordination of the C(2)−C(3) double bond to the osmium atom, in the $^{13}C\{^1H\}$ NMR spectrum, the resonances due to C(2) and C(3) are observed at 42.8 and 46.7 ppm, respectively.

In the high-field region of the ^1H NMR spectrum, in dichloromethane-d_2 at 253 K, the hydride ligand gives rise to a double doublet at −4.55 ppm, with H−P coupling constants of 23.7 and 16.8, whereas the elongated dihydrogen displays an apparent triplet at −13.30 ppm with a H−P coupling constant of 11.4 Hz. The *cis* disposition of the latter with regard to the coordinated olefin group was inferred from a NOESY ^1H NMR experiment at 253 K. The spectrum shows cross-peaks between the hydride resonance and the H_α signal of the pyridine ring (δ 8.16) and between the dihydrogen resonance and two of those corresponding to the olefinic protons (δ 4.16 and 3.13).

A variable-temperature 300 MHz T_1 study between 253 and 173 K of these resonances gives $T_{1(min)}$ values of 129 ± 6 ms for the hydride resonance and 48 ± 2 ms for the dihydrogen resonance, at 193 K. These values support the hydride-elongated dihydrogen character of the complex. In particular, the $T_{1(min)}$ value of the dihydrogen resonance corresponds to a hydrogen−hydrogen distance of 1.35 Å (slow spinning).[9,18]

Treatment of **2** with DBF_4 yields **3** partially deuterated, including the dihydrogen position. The H−D coupling constant for the η^2-HD resonance, obtained from the ^2H NMR spectrum at 253 K, is 4.7 Hz. According to the standard equation,[19] this value allows the calculation of a separation between the hydrogen atoms of the dihydrogen ligand of 1.34 Å, which agrees well with that obtained from the T_1 study.

The deuterium distribution in the partially deuterated complex **3** is 0.17 at the dihydrogen, 0.09 at the hydride, 0.50 at C(3) (0.25 at each position), and 0.24 at C(2). The presence of deuterium at the osmium atom and at all positions of the olefinic group, equally distributed, suggests that the protonation of **2** initially occurs on one of its hydride ligands. From a classical point of view, one could argue that the amounts of deuterium at C(2) and C(3) are the result of Markovnikov and anti-Markovnikov insertion equilibria equally favored. However, it should be noted that the stability of the resulting metallacycles should be very different. So, classical consecutive insertion equilibria cannot explain the observed deuterium distribution.

Jia and co-workers have recently shown that the dihydrogen ligand can be transferred to an olefin by a process similar to the [2 + 2] cycloaddition between olefins.[20] In this context, it should be noted that dihydrogen and olefins are similar in terms of their bonding interaction with transition metal centers.[21] Dihydrogen forms metal−ligand σ bonds by donating its σ-bonding electron pair to an empty orbital of the metal and metal−ligand π bonds by back-donation of metal d_π electrons to the σ^* orbital.[22] Olefins form metal−ligand σ bonds by donating their π-bonding electron pairs to empty orbitals of the metal and metal−ligand π bonds by back-donation of metal d_π electrons to the π^* orbitals.[23]

A transfer of this type allows us to rationalize our observations. Scheme 1 shows the elemental steps for the protonation of **2**, which could lead to the obtained deuterium distribution in **3**.

The addition of D^+ to one of the hydride ligands of **2** should afford a deuterated **a** intermediate with 0.25 deuterium atom in each position of the OsH_4 unit, as a consequence of exchange processes between the hydrides and between the hydrides and the dihydrogen. Thus, the migration of one of the hydrides from the metallic center to the metalated carbon atom of the substituent of the pyridine in **2** should initially move 0.25 deuterium atom to C(3). Then, the subsequent concerted addition of the dihydrogen ligand to the

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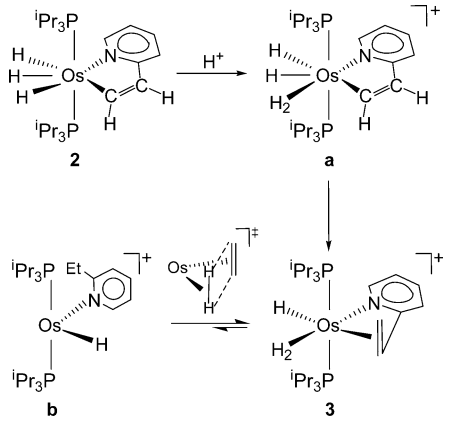
(23) Crabtree, R. H. *The Organometallics Chemistry of The Transition Metals*, 3rd ed.; Wiley: New York, 2001.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for the Complex $[OsH(\eta^2\text{-}H_2)(\eta^2\text{-}CH_2{=}CH\text{-}o\text{-}C_5H_4N)(P^iPr_3)_2]BF_4$ (3)

	molecule **a**	molecule **b**		molecule **a**	molecule **b**
Os(1)−P(1)	2.3857(12)	2.3827(11)	Os(1)−C(3)	2.225(4)	2.220(4)
Os(1)−P(2)	2.3740(11)	2.3724(11)	N(1)−C(1)	1.358(4)	1.360(4)
Os(1)−N(1)	2.168(3)	2.161(3)	C(1)−C(2)	1.478(5)	1.466(5)
Os(1)−C(2)	2.222(4)	2.220(4)	C(2)−C(3)	1.395(5)	1.415(5)
P(1)−Os(1)−P(2)	152.45(4)	149.88(4)	N(1)−Os(1)−H(03)	152.4(12)	150.5(12)
P(1)−Os(1)−N(1)	92.73(8)	92.53(9)			
P(1)−Os(1)−M[a]	103.7	108.2	M[a]−Os(1)−H(01)	161.3	159.3
P(1)−Os(1)−H(01)	76.0(13)	81.0(13)	M[a]−Os(1)−H(02)	130.8	132.2
P(1)−Os(1)−H(02)	68(2)	77.4(17)	M[a]−Os(1)−H(03)	84.7	85.1
P(1)−Os(1)−H(03)	87.5(13)	82.0(12)	H(01)−Os(1)−H(02)	67.0(15)	67.3(15)
P(2)−Os(1)−N(1)	102.42(9)	100.92(9)	H(01)−Os(1)−H(03)	114.3(14)	115.0(14)
P(2)−Os(1)−M[a]	103.7	101.8	H(02)−Os(1)−H(03)	48.2(14)	47.8(14)
P(2)−Os(1)−H(01)	80.4(13)	71.7(12)	Os(1)−N(1)−C(1)	97.8(2)	97.9(2)
P(2)−Os(1)−H(02)	90(2)	80.5(17)	Os(1)−C(2)−C(3)	71.9(2)	71.4(2)
P(2)−Os(1)−H(03)	89.4(13)	97.9(12)	Os(1)−C(2)−C(1)	91.9(2)	92.2(2)
N(1)−Os(1)−M[a]	68.8	69.0	Os(1)−C(3)−C(2)	71.6(2)	71.4(2)
N(1)−Os(1)−H(01)	92.4(12)	92.5 (11)	N(1)−C(1)−C(2)	106.3(3)	106.4(3)
N(1)−Os(1)−H(02)	154.0(18)	158.4(15)	C(1)−C(2)−C(3)	114.1(4)	113.6(4)

[a] M represents the midpoint of the C(2)−C(3) double bond.

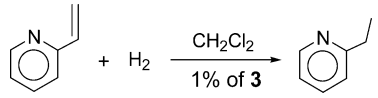
Scheme 1



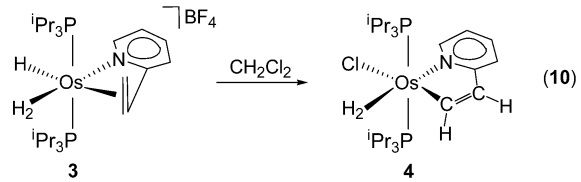
coordinated olefin group in **3** could give a 14-e$^-$ unsaturated species **b**, containing in the resulting ethyl substituent of the pyridine 0.50 deuterium atom at the methyl group and 0.25 deuterium atom at the CH_2 group. The remaining 0.25 deuterium atom should lie at the hydride position. Finally, the concerted extraction of H_2 from the ethyl substituent of the pyridine in **b** should afford **3**, which could distribute 0.25 deuterium atom between the positions of the OsH_3 unit by means of a hydride−dihydrogen exchange process, to show the observed deuterium distribution. The extraction of H_2 instead D_2 or HD is in agreement with the higher strength of the alkyl−D bond in comparison with the alkyl−H bond.[24]

We have recently reported that the trihydride-isopropenyl complex $OsH_3(SnPh_2Cl)\{\eta^2\text{-}CH_2{=}C(CH_3)P^iPr_2\}(P^iPr_3)$ activates *ortho*-CH bonds of aromatic ketones and imines via the 14-electron monohydride intermediate $OsH(SnPh_2Cl)(P^iPr_3)_2$, which is formed by reversible transfer of two hydrides from the metallic center to the olefin group of the isopropenylphosphine.[16i] Although from an intimate point of view, the transformation from **3** to **b** appears to be significantly different from the conversion of the trihydride-isopropenylphosphine complex into the 14-electron monohydride, it should be noted the similarity between both equilibria. Direct experimental evidence for the existence of related 14-electron transition metal complexes has been reported by Caulton and co-workers.[25] They prove that agostic interactions are not inevitable in this type of unsaturated species, but that a triplet state with half-filling of two orbitals is another way to make the best outcome of an otherwise electron-deficient situation.[26]

In agreement with an accessible species **b**, complex **3** is an active catalyst for the hydrogenation of 2-vinylpyridine to 2-ethylpyridine, in dichloromethane, at room temperature and under hydrogen atmospheric pressure (eq 9). However its stability under the reaction



conditions is very low, and it rapidly undergoes deactivation. Using a 1:100 catalyst:substrate molar ratio, after 1, 4, and 50 h, the yields of the reaction are 10%, 20%, and 39%, respectively. The resulting species from the deactivation process is the elongated dihydrogen complex $Os(NC_5H_5\text{-}o\text{-}CH{=}CH)Cl(\eta^2\text{-}H_2)(P^iPr_3)_2$ (**4**). This is supported by the ^1H and $^{31}P\{^1H\}$ NMR spectra of the residue obtained from removing the volatiles of the catalytic mixture, after 50 h of reaction, which show the characteristic resonances of **4**. This complex is formed by reaction of the catalyst with the solvent. Thus, we have observed that in the absence of 2-vinylpyridine, under argon, the dichloromethane solutions of **3** evolve into **4** (eq 10).



Complex **4** was isolated as a yellow oil and characterized by MS, IR, and $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, and ^1H NMR

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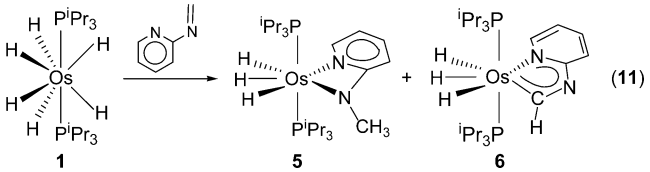
spectroscopy. In agreement with the mutually *trans* disposition of the phosphine ligands, the $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 9.02 ppm. In the $^{13}C\{^1H\}$ NMR spectrum, the resonances due to the CH=CH substituent of the pyridine are observed at 180.6 and 151.1 ppm. The first of them, assigned to the OsCH-carbon atom, appears as a triplet with a C−P coupling constant of 6.1 Hz. The second one, corresponding to the pyCH-carbon atom, is observed as a singlet. In the ^1H NMR spectrum the vinylic resonances are observed at 7.32 (CH) and 10.06 (OsCH) ppm. The CH-proton displays a doublet, while the OsCH resonance is observed as a double (J_{H-H} = 7.3 Hz) triplet (J_{H-H} = 4.6 Hz) by spin coupling with the CH-proton and the dihydrogen ligand. The latter was confirmed by a $^1H-^1H$ COSY NMR spectrum, which shows the cross-peaks between the OsCH signal and the dihydrogen resonance (δ −7.71; J_{H-P} = 12.5 Hz).

A variable-temperature 300 MHz T_1 study of the dihydrogen resonance gives a $T_{1(min)}$ value of 39 ± 1 ms at 193 K. The treatment of **4** with methanol-d_4 yields the partially deuterated derivative $Os(NC_5H_5\text{-}o\text{-}CH{=}CH)Cl(\eta^2\text{-}HD)(P^iPr_3)_2$ (**4-*d*$_1$**), which has a H−D coupling constant of 6.3 Hz. $T_{1(min)}$ and J(H−D) values suggest that the separation between the hydrogen atoms of the dihydrogen ligand is about 1.32 Å.[9,18,19]

2. Reactions of $OsH_6(P^iPr_3)_2$ with *N*-Methylene-2-pyridinamines. The replacement of the CH group of the substituent of the pyridine by a nitrogen atom has a marked influence on the reactions of this type of organic substrates with the short-lived intermediate $OsH_2(\eta^2\text{-}H_2)(P^iPr_3)_2$. The substitution produces an increase of the electrophilic character of the terminal group of the double bond, which favors the migration of a hydride ligand to the carbon atom. Thus, in contrast to 2-vinylpyridine, the treatment under reflux of toluene solutions of **1** with 1.4 equiv of *N*-methylene-2-pyridinamine leads after 5 h to a mixture of the trihydride derivatives $OsH_3(NC_5H_4\text{-}o\text{-}NCH_3)(P^iPr_3)_2$ (**5**) and $OsH_3(NC_5H_4\text{-}o\text{-}N{=}CH)(P^iPr_3)_2$ (**6**) in a 3:1 molar ratio, according to the ^1H and $^{31}P\{^1H\}$ NMR spectra of the residue obtained from removing the reaction solvent under reduced pressure (eq 11).



Complex **5** was obtained as a pure yellow solid in 52% yield by crystallization of the above-mentioned residue in toluene−methanol and characterized by elemental analysis, MS, IR, and ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopy, and by an X-ray crystallographic study. The structure has two chemically equivalent but crystallographically independent molecules in the asymmetric unit. A drawing of one of them is shown in Figure 4. Selected bond distances and angles for both molecules are listed in Table 3.

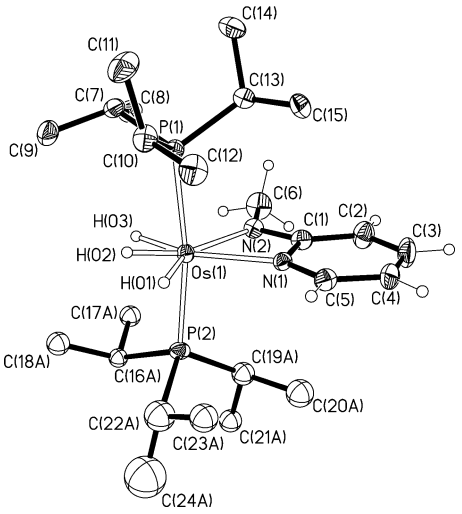


Figure 4. Molecular diagram of complex $OsH_3(NC_5H_4\text{-}o\text{-}NCH_3)(P^iPr_3)_2$ (**5**).

The coordination geometry around the osmium atom can be rationalized as a distorted pentagonal bipyramid with the two phosphorus atoms of the triisopropylphosphine ligands occupying axial positions (P(1)−Os−P(2) = 170.67(3)° (molecule **a**) and 171.50(3)° (molecule **b**)). The osmium sphere is completed by the hydride ligands and the chelate nitrogen donor group, which acts with a bite angle of 60.85(11)° in molecule **a** and 60.60(11)° in molecule **b**.

The spectroscopic data of **5** are consistent with the structure shown in Figure 4. The IR spectrum in KBr contains two bands at 2134 and 2116 cm^{-1}, corresponding to the hydride ligands. In the $^{13}C\{^1H\}$ NMR spectrum, the most noticeable feature is the presence of a singlet at 36.0 ppm, due to the methyl group of the chelate ligand. In agreement with the mutually *trans* disposition of the phosphine ligands, the $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 26.4 ppm, which is temperature invariant between 353 and 193 K.

In contrast to the $^{31}P\{^1H\}$ NMR spectrum, the ^1H NMR spectrum is temperature-dependent. The behavior of the hydride ligands of **5** with the temperature is similar to that found for **2**. In toluene-d_8, at 353 K, the spectrum contains a triplet at −11.88 ppm with a H−P coupling constant of 13.5 Hz. Lowering the sample temperature leads to broadening of the resonance. Between 273 and 263 K, the first decoalescence occurs, and between 223 and 213, the second one. At 183 K, an $ABCX_2$ (X = ^{31}P) spin system is observed. The $^1H\{^{31}P\}$ spectrum is simplified to the expected ABC spin system, which is defined by δ_A = −10.97, δ_B = −11.65, δ_C = −12.24, J_{AC} = 11.6 Hz, J_{BC} = 24.7 Hz, and J_{AB} = 0. The activation parameters obtained from the corresponding Eyring analysis are $\Delta H^{\ddagger}$ = 9.9 ± 0.5 kcal·mol^{-1} and $\Delta S^{\ddagger}$ = −0.3 ± 1.5 cal·mol^{-1}·K^{-1} for the H_B-H_C exchange and $\Delta H^{\ddagger}$ = 12.6 ± 0.3 kcal·mol^{-1} and $\Delta S^{\ddagger}$ = 2.4 ± 0.8 cal·mol^{-1}·K^{-1} for the H_A-H_C exchange. In

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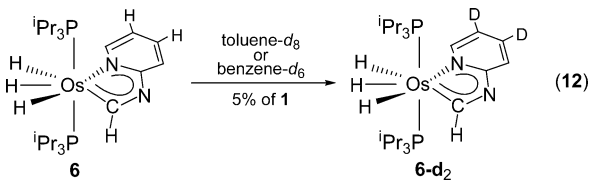
Table 3. Selected Bond Lengths (Å) and Angles (deg) for the Complex $OsH_3(NC_5H_4$-*o*-$NCH_3)(P^iPr_3)_2$ (5)

	molecule **a**	molecule **b**		molecule **a**	molecule **b**
Os(1)−P(1)	2.3377(9)	2.3390(9)	Os(1)−H(02)	1.34(5)	1.29(5)
Os(1)−P(2)	2.3228(10)	2.3335(9)	Os(1)−H(03)	1.53(4)	1.56(4)
Os(1)−N(1)	2.152(3)	2.158(3)	N(1)−C(1)	1.376(4)	1.375(4)
Os(1)−N(2)	2.151(3)	2.140(3)	N(2)−C(1)	1.324(5)	1.322(4)
Os(1)−H(01)	1.50(4)	1.49(5)	N(2)−C(6)	1.432(4)	1.449(4)
P(1)−Os(1)−P(2)	170.67(3)	171.50(3)	N(1)−Os(1)−H(02)	148(2)	152(2)
P(1)−Os(1)−N(1)	94.76(8)	93.54(8)	N(1)−Os(1)−H(03)	152.7(16)	151.8(16)
P(1)−Os(1)−N(2)	92.30(8)	92.42(8)	N(2)−Os(1)−H(01)	152.7(15)	150.0(16)
P(1)−Os(1)−H(01)	94.3(14)	88.9(16)	N(2)−Os(1)−H(02)	150(2)	148(2)
P(1)−Os(1)−H(02)	78.2(18)	87(2)	N(2)−Os(1)−H(03)	91.9(16)	91.3(16)
P(1)−Os(1)−H(03)	84.4(15)	90.0(15)	H(01)−Os(1)−H(02)	57(2)	62(3)
P(2)−Os(1)−N(1)	94.54(8)	94.89(8)	H(01)−Os(1)−H(03)	115(2)	119(2)
P(2)−Os(1)−N(2)	92.90(8)	92.72(8)	H(02)−Os(1)−H(03)	59(2)	56(2)
P(2)−Os(1)−H(01)	84.5(14)	90.0(16)	Os(1)−N(1)−C(1)	95.0(2)	94.9(2)
P(2)−Os(1)−H(02)	93.5(18)	85(2)	Os(1)−N(2)−C(1)	96.5(2)	97.4(2)
P(2)−Os(1)−H(03)	87.7(15)	83.1(15)	Os(1)−N(2)−C(6)	141.6(3)	139.7(3)
N(1)−Os(1)−N(2)	60.85(11)	60.60(11)	N(1)−C(1)−N(2)	107.7(3)	107.0(3)
N(1)−Os(1)−H(01)	92.2(15)	89.4(16)	C(1)−N(2)−C(6)	121.8(3)	122.9(3)

agreement with the trihydride character of the complex, $T_{1(min)}$ values of 109 ± 2 (δ_A), 94 ± 1 (δ_B), and 87 ± 1 (δ_C) ms were found at 208 K.

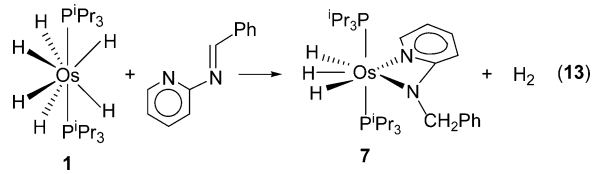
Complex **6** was characterized by $^{13}C\{^1H\}$, ^1H, and $^{31}P\{^1H\}$ NMR spectroscopy. The $^{13}C\{^1H\}$ NMR spectrum reveals a significant contribution of the aminocarbene resonance form to the structure of the complex. Thus, the OsCN resonance appears at 251.7 ppm as a triplet with a C−P coupling constant of 4.6 Hz. The behavior of the hydride ligands with the temperature is similar to those found for **2** and **5**. In toluene-d_8 at 343 K, the ^1H NMR spectrum shows a broad resonance centered at −9.1 ppm for the three hydride ligands. Between 323 and 313 K, the first decoalescence takes place, and between 223 and 218, the second one. At 193 K, an $ABCX_2$ (X = ^{31}P) spin system with $\delta_A = -5.77$, $\delta_B = -10.53$, and $\delta_C = -11.33$ is observed. In the low-field region of the spectrum the OsCH-proton displays at 14.30 ppm a doublet (J_{H-H} = 9 Hz), by spin coupling with the H_C hydride ligand. The estimated activation enthalpies for the site exchange processes of the hydride ligands are 9 kcal·mol^{-1} for the H_A-H_B exchange and 15 kcal·mol^{-1} for the H_B-H_C exchange. The trihydride character of **6** is supported by $T_{1(min)}$ values of 94 ± 5 (δ_A), 85 ± 4 (δ_B), and 126 ± 2 (δ_C) ms. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 30.8 ppm.

Complex **6** can also be selectively deuterated at the β- and γ-positions of the pyridine ring (eq 12). Thus, the addition of 0.05 equiv of **1** to toluene-d_8 or benzene-d_6 solutions of **6** produces the extinction of the H_γ and H_β resonances (7.01 and 6.16 ppm), in the ^1H NMR spectrum, while the H_α and $H_{\beta'}$ resonances are converted into singlets.



6 **6-d$_2$** (12)

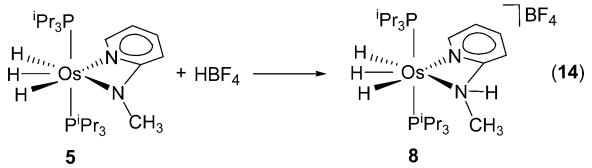
Complex **5** is the result of the insertion of the C═N double bond of *N*-methylene-2-pyridinamine into one of the Os−H bonds of the short-lived intermediate $OsH_2(\eta^2\text{-}H_2)(P^iPr_3)_2$, while complex **6** is a consequence of the C−H activation of the terminal CH_2 group. The replacement of a hydrogen atom in the latter by a phenyl group favors the insertion with regard to the C−H activation. Thus, the treatment under reflux of toluene solutions of **1** with 1.3 equiv of (*E*)-*N*-(phenylmethylene)-2-pyridinamine selectively affords after 5 h the trihydride $OsH_3(NC_5H_4$-*o*-$NCH_2Ph)(P^iPr_3)_2$ (**7**), as result of the insertion of the C═N double bond of the organic substrate into one of the Os−H bonds of the starting complex (eq 13). The role of the phenyl group is double. On one hand it increases the electrophilic character of the carbon atom of the C═N double bond, favoring the migration of the hydride ligand; on the other its steric hindrance prevents the coordination of the activated CPh group to the osmium atom.



1 **7** + H_2 (13)

Complex **7** was isolated as a yellow solid in 75% yield. Its spectroscopic data agree well with those of **5**. The IR spectrum in KBr shows the ν(Os−H) vibrations at 2117 and 2102 cm^{-1}. In the $^{13}C\{^1H\}$ NMR spectrum the C(sp^3) carbon atom of the benzyl group displays a singlet at 54.6 ppm. At 343 K, the ^1H NMR spectrum in toluene-d_8 shows a triplet at −12.04 ppm, with a H−P coupling constant of 13.5 Hz, for the three hydride ligands. The first decoalescence of this resonance occurs between 273 and 263 K, whereas the second one is observed at 213 K. At 193 K, the spectrum shows an $ABCX_2$ (X = ^{31}P) spin system. The $^1H\{^{31}P\}$ NMR spectrum is simplified to the expected ABC spin system with $\delta_A = -10.89$, $\delta_B = -12.11$, $\delta_C = -12.32$, $J_{AC} = 11.8$ Hz, J_{BC} = 22.3 Hz, and J_{AB} = 0. The activation parameters for the site exchange processes between the hydride ligands are $\Delta H^\ddagger = 10.8 \pm 1.1$ kcal·mol^{-1} and $\Delta S^\ddagger = 0.3 \pm 3.2$ cal·mol^{-1}·K^{-1} for the H_B-H_C exchange and $\Delta H^\ddagger = 12.7 \pm 0.3$ kcal·mol^{-1} and $\Delta S^\ddagger = 3.4 \pm 0.8$ cal·mol^{-1}·K^{-1} for the H_A-H_C exchange. In agreement with the trihydride character of the complex, $T_{1(min)}$ values of 96 ± 2 (δ_A) and 80 ± 2 (δ_B and δ_C) were found at 223 K, before the second decoalescence. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 25.0 ppm.

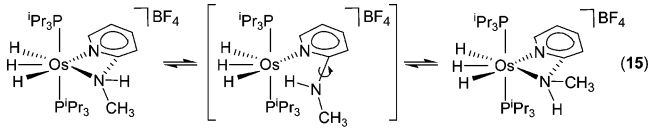
Under atmospheric hydrogen pressure, 2-vinylpyridine and the studied pyridinamines show significant differences in reactivity. The toluene solutions of **5** and **7** are stable under hydrogen atmosphere. The addition of 1.0 equiv of $HBF_4{\cdot}OEt_2$ to the diethyl ether solutions of **5** affords the cationic trihydride derivative $[OsH_3(NC_5H_4\text{-}o\text{-}NHCH_3)(P^iPr_3)_2]BF_4$ (**8**) as a result of the formal addition of the proton of the acid to the CH_3N-nitrogen atom of **5** (eq 14). In contrast to **3**, the dichloromethane solutions of **8** are also stable under hydrogen atmosphere, even in the presence of *N*-methylene-2-pyridinamine. So, the catalytic reduction of the C=N double bond of this organic substrate is not achieved.



(14)

5 **8**

Complex **8** was isolated as a white solid in 82% yield. In agreement with the presence of a NH group in the complex, its IR spectrum in KBr shows a ν(N−H) band at 3264 cm^{-1}, along with the ν(Os−H) vibrations at 2157 and 2122 cm^{-1}. In the $^{13}C\{^1H\}$ NMR spectrum, the methyl group of the amino substituent of the pyridine gives rise to a singlet at 42.1 ppm. The $^{31}P\{^1H\}$ NMR spectrum is temperature dependent. In dichloromethane-d_2 at 303 K, the spectrum shows a singlet at 27.4 ppm. Lowering the sample temperature produces broadening of the resonance. At 198 K, an AB spin system centered at 25.2 ppm and defined by $\Delta\nu = 429$ Hz and $J_{AB} = 245$ Hz is observed. This behavior suggests that in solution the nitrogen atom of the methylamino substituent is involved in a dynamic process of inversion of its configuration. Line-shape analyses of the $^{31}P\{^1H\}$ NMR spectra allows the calculation of the rate constants of the process at different temperatures. The activation parameters obtained from the corresponding Eyring analysis are $\Delta H^{\ddagger} = 18.9 \pm 0.3$ kcal·mol^{-1} and $\Delta S^{\ddagger} = 23.2 \pm 0.7$ cal·mol^{-1}·K^{-1}. The value of the activation entropy is consistent with an unsaturated intermediate containing the nitrogen donor ligand coordinated as monodentated (eq 15).

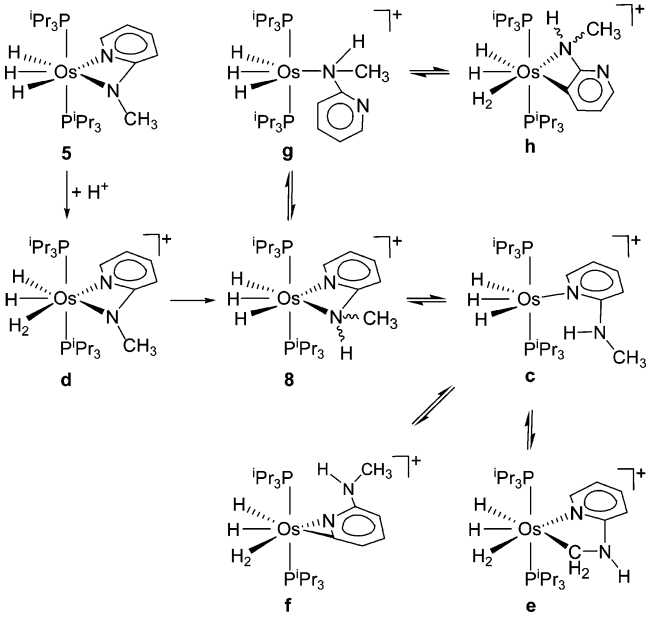


(15)

c

The dynamic equilibrium shown in eq 15 is also supported by the ^1H NMR spectrum. In dichloromethane-d_2 at 303 K, the spectrum shows two broad resonances at 5.27 and 3.19 ppm for the NH and methyl protons of the methylamino substituent, respectively. At temperatures lower than 293 K, these resonances are split into a quartet and a doublet, respectively, with a H−H coupling constant of 5.9 Hz. Like in the trihydride compounds previously mentioned, the hydrides of **8** are involved in two different site exchange processes. At 303 K, the spectrum in the high-field region contains a broad resonance at −12.81 ppm for the three hydride ligands. Between 283 and 273 K, the first decoalescence occurs, and between 243 and 233 K the second one. At 193 K, the characteristic $ABCX_2$ ($X = {}^{31}P$) spin system for this type of derivatives is observed. The ABC spin system in the $^1H\{^{31}P\}$ NMR spectrum is defined by $\delta_A = -10.59$, $\delta_B = -12.65$, $\delta_C = -15.19$, $J_{AB} = 63.7$ Hz, $J_{BC} = 15.9$ Hz, and $J_{AC} = 0$ Hz. The activation parameters for the exchanges are $\Delta H^{\ddagger} = 10.4 \pm 0.5$ kcal·mol^{-1} and $\Delta S^{\ddagger} = 0.9 \pm 1.5$ cal·mol^{-1}·K^{-1} for the H_A-H_B exchange and $\Delta H^{\ddagger} = 14.1 \pm 0.6$ kcal·mol^{-1} and $\Delta S^{\ddagger} = 8.5 \pm 1.3$ cal·mol^{-1}·K^{-1} for the H_B-H_C exchange. In accordance with the trihydride character of **8**, $T_{1(min)}$ values of 71 ± 3 (δ_A), 69 ± 3 (δ_B), and 101 ± 1 (δ_C) ms were obtained at 203 K.

Scheme 2



Treatment of **5** with DBF_4 yields **8** partially deuterated. According to the ^2H NMR spectrum of this species, the deuterium atom is distributed as follows: 0.07 and 0.14 at the α- and β′-position respectively, of the pyridine ring, 0.47 at the nitrogen atom of the methylamino substituent, 0.27 at the methyl group, and 0.05 at the hydride positions.

The observed deuterium distribution can be rationalized according to Scheme 2. The initial addition of the acid to one of the hydride ligands of **5** should afford a dihydride-dihydrogen intermediate **d**, with half of the atoms of the dihydrogen being deuterium. The transfer of one of these atoms to the CH_3-N nitrogen atom should give **8** with 0.5 deuterium at the methylamino nitrogen atom. Since this is the amount found at this atom, the migration from the dihydrogen appears to be faster than the site exchange processes between the dihydrogen and the hydrides. The remaining 0.50 deuterium should initially lie in the hydride positions. It could be distributed between the α, β′, and methyl positions of the pyridine via the unsaturated intermediates **c** and **g** through reversible C−H activation processes (intermediates **e**, **f**, and **h**). The formation of η^2-C, N-pyridyl complexes, related to intermediate **f**, by reaction of a polyhydride compound with pyridines has been recently

shown.[27] In addition, it should be noted that the amount of deuterium at the carbon atoms of the pyridine increases (C_α < $C_{\beta'}$ < C-methyl) as the number of members, and therefore the stability, of the heterometallacycles of **f**, **h**, and **e** increases.

Equations 11 and 14 represent the ionic stoichiometric reduction of the C=N double bond of *N*-methylene-2-pyridinamine. The hydride transfer together with the addtion of H^+, in a subsequent reaction, have been proposed by Bäckvall and co-workers as the key elemental steps for the $[Ru_2(CO)_4(\mu\text{-}H)(C_4Ph_4COHOCC_4Ph_4)]$-catalyzed transfer hydrogenation of imines by 2-propanol in benzene.[28] Stoichiometric ionic reductions of carbonyl groups,[29] olefins,[30] and imines[31] have also been reported.

Concluding Remarks

This study reveals that the short-lived intermediate species $OsH_2(\eta^2\text{-}H_2)(P^iPr_3)_2$, generated by thermal activation of the hexahydride $OsH_6(P^iPr_3)_2$, reacts with RCH=E-py organic substrates (E = CH, N) to give derivatives resulting from C(sp^2)−H activation or insertion reactions. They are competitive and depend on the nature of both E and R, which determine the polarity of the C=E double bond and the steric hindrance of the RCH group.

For E = N the migration of a hydride ligand from the metal to the RCH-carbon atom is favored with regard to the C−H activation. On the other hand, for E = CH the C(sp^2)−H activation of the RCH group is preferred over the hydride migration. Bulky substituents at the RCH group prevent the coordination of the RC-carbon atom to the metal, favoring the insertion of the double bond.

In the presence of HBF_4 both C=C and C=N double bonds are reduced. However, isotope labeling experiments suggest that there are strong differences between the intimate details of each process. The C=C double bond, less polar than C=N, appears to undergo the concerted addition of a dihydrogen ligand, while the C=N double bond adds H^- and H^+ in a sequential manner.

Experimental Section

All reactions were carried out with rigorous exclusion of air using Schlenk-tube techniques. Solvents were dried by the usual procedures and distilled under argon prior to use. The starting materials $OsH_6(P^iPr_3)_2$ and $DBF_4{\cdot}D_2O$ were prepared by the published methods.[32] The aldimines were synthesized as follows: 1 equiv of 2-aminopyridine (1.5 g, 0.016 mol) and 1 equiv of the corresponding aldehyde, benzaldehyde (1.6 mL, 0.016 mol) or paraformaldehyde (0.5 g, 0.016 mol), were solved in 8 mL of toluene. A catalytic quantity of *p*-toluenesulfonic acid was added. In both cases, the resulting solution was heated under reflux overnight with a Dean−Stark apparatus as water collector. Then the solvent was removed in vacuo, and pentane was added to afford a white solid, which was washed with further portions of pentane and dried in vacuo. Yield: 1.89 g (65%) for (*E*)-*N*-(phehylmethylene)-2-pyridinamine and 0.92 g (54%) for *N*-methylene-2-pyridinamine. Data for *N*-methylene-2-pyridinamine (py-N=CH_2): Anal. Calcd for $C_6H_6N_2$: C 67.90, H 5.70, N 26.40. Found: C 67.90, H 5.67, N 26.50. IR (KBr, cm^{-1}): ν(C=N) 1591 (s). ^{1}H NMR (300 MHz, C_6D_6, 293 K): δ 8.16, 6.98, 6.88, and 6.25 (all m, 1H, py), 5.45 (s, 2H, CH_2). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K): δ 158.0 (s, $C_{ipso(py)}$), 148.1, 137.5, 114.2, and 108.4 (all s, py), 60.0 (s, CH_2). MS (EI): *m*/*z* 106 ($M^+ - H$).

^{1}H, ^{2}H, ^{19}F, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra were recorded on either a Varian UNITY 300, Varian Gemini 2000, Bruker AXR, or Bruker Avance 300 MHz instrument. Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks (^{1}H, $^{13}C\{^1H\}$), external 85% H_3PO_4 ($^{31}P\{^1H\}$), or external $CFCl_3$ (^{19}F). Coupling constants, *J* and *N* ($N = J_{P-H} + J_{P'-H}$ for ^{1}H and $N = J_{P-C} + J_{P'-C}$ for $^{13}C\{^1H\}$) are given in hertz. Infrared spectra were run on a Perkin-Elmer 1730 spectrometer as solids (KBr pellet). C, H, and N analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyzer. For organometallic compounds, mass spectra analyses were performed with a VG Austospec instrument. In FAB^+ mode, ions were produced with the standard Cs^+ gun at ca. 30 kV, and 3-nitrobenzyl alcohol (NBA) was used in the matrix. For the organic products, GC−MS analyses 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 (Agilent).

Kinetic Analysis. Complete line-shape analyses of the $^1H\{^{31}P\}$ NMR spectra of the complexes **2**, **5**, **7**, and **8** were achieved using the program gNMR (Cherwell Scientific Publishing Limited). The rate constants for various temperatures were obtained by fitting calculated to experimental spectra by full line-shape iterations. The transverse relaxation time, T_2, was estimated at the lowest interval of temperatures using the resonances corresponding to the hydride ligands. The activation parameters $\Delta H^\ddagger$ and $\Delta S^\ddagger$ were calculated by least-squares fit of $\ln(k_1/T)$ versus $1/T$ (Eyring equation). Error analysis assumed a 10% error in the rate constant and 1 K in the temperature. Errors were computed by published methods.[33]

Preparation of $OsH_3(NC_5H_4\text{-}o\text{-}CH{=}CH)(P^iPr_3)_2$ (2). A colorless solution of $OsH_6(P^iPr_3)_2$ (212.6 mg, 0.412 mmol) in 15 mL of toluene was treated with 1.6 equiv of 2-vinylpyridine (71 μL, 0.659 mmol) and heated under reflux for 5 h. The resulting orange solution was filtered through Celite and dried in vacuo. Pentane was added to afford a yellow solid, which was washed with further portions of pentane at 223 K and dried in vacuo. Yield: 211.0 mg (83%). Anal. Calcd for $C_{25}H_{51}NOsP_2$: C 48.60, H 8.32, N 2.27. Found: C 48.40, H 8.02, N 2.01. IR (KBr, cm^{-1}): ν(OsH) 2173 (m), 2118 (m); ν(C=C) 1599 (s). ^{1}H NMR (300 MHz, C_7D_8, 293 K, plus COSY): δ 11.51 (double virtual quartet, J_{H-H} = 10 Hz, $J_{H-H(OsH_3)}$ = 3 Hz, 1H, $OsCH_D$), 9.57 (d, J_{H-H} = 7.1 Hz, 1H, H_α py), 7.91 (d, J_{H-H} = 10 Hz, 1H, $=CH_E$), 7.06 (d, J_{H-H} = 7.1 Hz, 1H, $H_{\beta'}$ py), 6.85 and 6.09 (both dd, $J_{H-H} = J_{H-H}$ = 7.1 Hz, 1H, H_γ and H_β py), 1.87 (m, 6H, PC*H*), 1.24 and 0.99 (both dvt, *N* = 12.9 Hz, J_{H-H} = 6.6 Hz, 18H, PCHCH_3), −8.22 (br, 2H, OsH), −12.22 (br, 1H, OsH). $^1H\{^{31}P\}$ NMR (300 MHz, C_7D_8, 193 K (plus ^{1}H COSY), only variable-temperature signals): low-field ($OsCH_D$),

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δ 11.47 (dd, $J_{H_D-H_E}$ = 10 Hz, $J_{H_D-H_C}$ = 8 Hz, 1H, $OsCH_D$); high-field region (OsH_3 unit), δ −5.05 and −11.33 (both d, $J_{H_A-H_B}$ = 25 Hz, 1H, H_A and H_B), −12.20 (d, $J_{H_C-H_D}$ = 8 Hz, 1H, H_C). $^{31}P\{^1H\}$ NMR (121.42 MHz, C_7D_8, 293 K): δ 26.8 (s). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_7D_8, 293 K): δ 203.9 (t, J_{P-C} = 6.4 Hz, OsCH), 169.6 (s, C_{ipso}), 158.6 (s, CH), 132.4, 127.2, 119.3, and 115.5 (all s, py), 27.7 (vt, N = 24.4 Hz, P*C*H), 20.1 and 19.8 (both s, PCH*C*H_3). MS (FAB^+): m/z 613 (M^+ − 2H). $T_{1(min)}$ (ms, OsH_3, 300 MHz, C_7D_8, 203 K): 108 ± 3 (−5.05 ppm, 1H), 102 ± 2 (−11.33 ppm, 1H), 114 ± 1 (−12.20 ppm, 1H).

The addition of 0.05 equiv of $OsH_6(P^iPr_3)_2$ to an NMR tube containing **2** in toluene-d_8 or benzene-d_6 gives, after 10 h, the complex **2** partially deuterated in the pyridine ring. ^1H NMR (300 MHz, C_6D_6 or C_7D_8, 293 K, pyridine ring): δ 9.57 (s, 1H, H_α py), 7.06 (s, 1H, $H_{\beta'}$ py). ^2H NMR (300 MHz, C_6H_6, 293 K): δ 6.98 and 6.20 (both s, 1D, D_γ and D_β py). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_7D_8, 293 K, C_γ and C_β of the pyridine ring, no changes in the other signals): δ 115.5 (t(1:1:1), J_{C-D} = 24.6 Hz), 132.4 (t(1:1:1), J_{C-D} = 24.3 Hz).

Reaction of 2 with $HBF_4{\cdot}OEt_2$ and H_2. A yellow solution of **2** (20.0 mg, 0. 032 mmol) in CD_2Cl_2 in an NMR tube was treated with 1.0 equiv of $HBF_4{\cdot}OEt_2$ (4 μL, 0.032 mmol), and the tube was sealed under hydrogen atmosphere. After 4 h, the ^1H and $^{31}P\{^1H\}$ NMR spectra of the resulting solution revealed the formation of complex **1** and $[HNC_5H_5\text{-}o\text{-}CH_2CH_3]BF_4$. Data for $[HNC_5H_5\text{-}o\text{-}CH_2CH_3]BF_4$: ^1H NMR (300 MHz, CD_2Cl_2, 293 K): δ 12.99 (br, 1H, NH), 8.66 (d, J_{H-H} = 7.7 Hz, 1H, py), 8.51 (vt, J_{H-H} = 7.7 Hz, 1H, py), 7.89 (d, J_{H-H} = 7.7 Hz, 1H, py), 7.87 (vt, J_{H-H} = 7.7 Hz, 1H, py), 3.14 (quartet, J_{H-H} = 7.5 Hz, 2H, CH_2), 1.43 (t, J_{H-H} = 7.5 Hz, 3H, CH_3). ^{19}F NMR (282.33 MHz, CD_2Cl_2, 293 K): δ −151.0 (br).

Preparation of $[\overline{OsH(\eta^2\text{-}H_2)(\eta^2\text{-}CH_2{=}CH\text{-}o\text{-}C_5H_4N)}(P^iPr_3)_2]BF_4$ (3). A yellow solution of **2** (131.4 mg, 0.213 mmol) in 30 mL of diethyl ether was treated with 1 equiv of $HBF_4{\cdot}OEt_2$ (29 μL, 0.213 mmol) and stirred for 40 min at room temperature. During the course of the reaction a white solid formed. The solvent was removed, and the solid was washed with further portions of diethyl ether and dried in vacuo. Yield: 137.6 mg (92%). Anal. Calcd for $C_{25}H_{52}BF_4NOsP_2$: C 42.55, H 7.43, N 1.98. Found: C 42.37, H 7.85, N 1.97. IR (KBr, cm^{-1}): ν(OsH) 2152 (s), 2098 (m); ν(C=C) 1603 (s); $\nu(BF_4)$ 1050 (br). ^1H NMR (300 MHz, CD_2Cl_2, 293 K): δ 8.18 (d, J_{H-H} = 7.0 Hz, 1H, H_α py), 7.74 and 7.22 (both vt, J_{H-H} = 7.0 Hz, 1H, H_β and H_γ py), 7.04 (d, J_{H-H} = 7.0 Hz, 1H, $H_{\beta'}$ py), 4.23 (br, 1H, CH_2), 3.40 (br, 1H, CH_2), 3.16 (d, J_{H-H} = 7.8 Hz, 1H, CH), 2.42 and 2.21 (both m, 3H, P*C*H), 1.16 (dvt, N = 12.6 Hz, J_{H-H} = 6.9 Hz, 27H, PCHCH_3), 0.92 (br, 9H, PCCH_3), −4.53 (br, 1H, OsH), −13.29 (br, 2H, OsH). ^1H NMR (300 MHz, CD_2Cl_2, 253 K): δ 8.16 (d, J_{H-H} = 7.0 Hz, 1H, H_α py), 7.72 and 7.21 (both vt, J_{H-H} = 7.0 Hz, 1H, H_β and H_γ py), 7.03 (d, J_{H-H} = 7.0 Hz, 1H, $H_{\beta'}$ py), 4.16 (ddd, J_{H-P} = 8.1 Hz, J_{H-H} = 8.1 Hz, J_{H-H} = 7.6 Hz, 1H, CHpy), 3.36 (dd, J_{H-P} = 13.2 Hz, J_{H-H} = 8.1 Hz, 1H, CH *cis* to py), 3.13 (d, J_{H-H} = 7.6 Hz, 1H, CH *trans* to py), 2.40 and 2.18 (both m, 3H, PCH), 1.13 (dvt, N = 12.6 Hz, J_{H-H} = 6.9 Hz, 27H, PCCH_3), 1.13 (dvt, N = 12.6 Hz, J_{H-H} = 6.9 Hz, 9H, PCCH_3), −4.55 (dd, J_{H-P} = 23.7 Hz, $J_{H-P'}$ = 16.8 Hz, 1H, OsH), −13.30 (dd, J_{H-P} = $J_{H-P'}$ = 11.4 Hz, 2H, OsH_2). $^{31}P\{^1H\}$ NMR (121.42 MHz, CD_2Cl_2, 293 K): AB spin system, δ 20.1, $\Delta\nu$ = 189 Hz, J_{AB} = 157 Hz. ^{19}F NMR (282.33 MHz, CD_2Cl_2, 293 K): δ −155.4 (br). $^{13}C\{^1H\}$ NMR (75.42 MHz, CD_2Cl_2, 233 K, plus APT): δ 165.6 (s, C_{ipso}), 149.1, 136.7, 124.5, and 122.9 (all s, py), 46.7 (s, CH_2), 42.8 (s, CH), 27.9 (d, J_{C-P} = 25.5 Hz, P*C*H), 27.0 (d, J_{C-P} = 26.3 Hz, P*C*H), 19.7, 19.6, 19.3, and 18.5 (all s, PCH*C*H_3). MS (FAB^+): m/z 610 (M^+ − 10H). $T_{1(min)}$ (ms, OsH_3, 300 MHz, CD_2Cl_2, 193 K): 129 ± 6 (−4.58 ppm, 1H), 48 ± 2 (−13.35 ppm, 2H).

Preparation of $[\overline{OsH(\eta^2\text{-}H_2)(\eta^2\text{-}CH_2{=}CH\text{-}o\text{-}C_5H_4N)}\text{-}(P^iPr_3)_2]BF_4$ Partially Deuterated. This complex was prepared as described for **3** starting from **2** (106.1 mg, 0.172 mmol) and $DBF_4{\cdot}D_2O$ (33 μL, 0.173 mmol). A white solid was obtained. Yield: 81.6 mg (67%). ^2H NMR (46.03 MHz, CH_2Cl_2, 253 K): δ 4.2 (s, 0.24D, CDpy), 3.4 and 3.1 (both s, 0.25D, CDH), −4.5 (br, 0.09D, OsD), −13.3 (t(1:1:1)dd, J_{H-D} = 4.7 Hz, J_{P-D} = $J_{P'-D}$ ≈ 2 Hz, 0.17D, Os(η^2-HD)).

Catalytic Hydrogenation of 2-Vinylpyridine. A solution of **3** (114.0 mg, 0.162 mmol) and 2-vinylpyridine (1.75 mL, 16.2 mmol) in 15 mL of dichloromethane was stirred under a hydrogen atmosphere. The reaction was monitored by GC−MS. The products were identified by comparison of their mass spectra with those of the G1045B Spectral Library (Willey 7N, Agilent Technologies, 2000). The yields of formation of 2-ethylpyridine after 1, 4, and 50 h were 10%, 20%, and 39%, respectively. After 50 h, the reaction was stopped and the resulting solution was concentrated in vacuo. The ^1H and $^{31}P\{^1H\}$ NMR spectra of the residue obtained, in CD_2Cl_2, revealed the formation of **4**.

Preparation of $\overline{Os(NC_5H_4\text{-}o\text{-}CH{=}CH)}Cl(\eta^2\text{-}H_2)(P^iPr_3)_2$ (4). A yellow solution of **3** (203.1 mg, 0.288 mmol) in 15 mL of dichloromethane was heated under reflux for 16 h. The yellow solution was filtered through Celite and dried in vacuo. Pentane was added to afford a yellow oil, which was washed with further portions of pentane at 223 K and dried in vacuo. Yield: 63.2 mg (34%). IR (KBr, cm^{-1}): ν(OsH) 2174 (m); ν(C=C) 1602 (s). ^1H NMR (300 MHz, C_6D_6, 293 K, plus COSY): δ 10.57 (d, J_{H-H} = 6.7 Hz, 1H, H_α py), 10.06 (dt, J_{H-H} = 7.3 Hz, J_{H-H} = 4.6 Hz, 1H, OsCH), 7.32 (d, J_{H-H} = 7.3 Hz, 1H, CH), 6.98 (d, J_{H-H} = 6.7 Hz, 1H, $H_{\beta'}$ py), 6.92 and 6.48 (both vt, J_{H-H} = 6.7 Hz, 1H, H_β and H_γ py), 2.30 (m, 6H, P*C*H), 1.08 and 0.96 (both dvt, N = 12.6 Hz, J_{H-H} = 6.9 Hz, 18H, PCCH_3), −7.71 (td, J_{H-P} = 12.5 Hz, J_{H-H} = 4.6 Hz, 2H, OsH). $^{31}P\{^1H\}$ NMR (121.42 MHz, C_6D_6, 293 K): δ 9.02 (s). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K, plus APT): δ 180.6 (t, J_{P-C} = 6.1 Hz, OsCH), 167.8 (s, C_{ipso}), 151.1 (s, =CH), 134.6, 125.1, 118.5 and 114.3 (all s, py), 25.6 (vt, N = 23.7 Hz, P*C*H), 19.5 and 19.4 (both s, PC*C*H_3). MS (FAB^+): m/z 651 (M^+ − 2H). $T_{1(min)}$ (ms, OsH_2, 300 MHz, CD_2Cl_2, 193 K): 39 ± 1 (−7.75 ppm, 2H).

$\overline{Os(NC_5H_4\text{-}o\text{-}CH{=}CH)}Cl(\eta^2\text{-}HD)(P^iPr_3)_2$ was obtained from **4** stirred in CD_3OD for 1 day. ^1H NMR (300 MHz, CD_3OD, 293 K, high-field region): δ −7.71 (tt(1:1:1) d, J_{H-P} = 12.5 Hz, J_{H-D} = 6.3 Hz, J_{H-H} = 4.6 Hz).

Reaction of $OsH_6(P^iPr_3)_2$ with *N*-Methylene-2-pyridinamine. A colorless solution of $OsH_6(P^iPr_3)_2$ (207.0 mg, 0.401 mmol) in 15 mL of toluene was treated with 1.4 equiv of *N*-methylene-2-pyridinamine (59.4 mg, 0.560 mmol) and heated under reflux for 5 h. The resulting orange solution was filtered through Celite and dried in vacuo. The ^1H and $^{31}P\{^1H\}$ NMR spectra of the residue, in benzene-d_6, indicated the formation of two products: **5** and **6** in a 3:1 ratio. Methanol was added to afford complex **5** as a yellow solid, which was washed with further portions of methanol at 223 K and dried in vacuo. Complex **6** was the major component in the supernatant solution, but it could not be isolated purely.

Data for $\overline{OsH_3(NC_5H_4\text{-}o\text{-}NCH_3)}(P^iPr_3)_2$ (5). Yield: 129.3 mg (52%). Anal. Calcd for $C_{24}H_{52}N_2OsP_2$: C 46.43, H 8.44, N 4.51. Found: C 46.56, H 8.24, N 4.92. IR (KBr, cm^{-1}): ν(OsH) 2134 (s), 2116 (s). ^1H NMR (300 MHz, C_7D_8, 293 K): δ 7.88 (d, J_{H-H} = 7.0 Hz, 1H, H_α py), 6.88 and 5.87 (both vt, J_{H-H} = 7.0 Hz, 1H, H_β and H_γ py), 5.55 (d, J_{H-H} = 7.0 Hz, 1H, $H_{\beta'}$ py), 3.05 (s, 3H, CH_3), 1.93 (m, 6H, P*C*H), 1.14 and 1.08 (both dvt, N = 12.5 Hz, J_{H-H} = 6.3 Hz, 18H, PCHCH_3), −11.88 (br, 3H, OsH). $^1H\{^{31}P\}$ NMR (300 MHz, C_7D_8, 183 K, in the high-field region): δ −10.97 (d, J_{H-H} = 11.6, 1H), −11.65 (d, J_{H-H} = 24.7, 1H), −12.24 (dd, J_{H-H} = 24.7, J_{H-H} = 11.6, 1H). $^{31}P\{^1H\}$ NMR (121.42 MHz, C_7D_8, 293 K): δ 26.4 (s). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_7D_8, 293 K): δ 167.5 (s, C_{ipso}), 149.2, 133.1, 102.9, and 102.1 (all s, py), 36.0 (s, CH_3), 27.3 (vt, N = 23.0 Hz, P*C*H), 20.3 and 20.1 (both s, PCH*C*H_3). MS (FAB^+): m/z 619 (M^+ − 3H). $T_{1(min)}$ (ms, OsH_3, 300 MHz, C_7D_8, 208 K): 109 ± 2 (−10.97 ppm, 1H), 94 ± 1 (−11.65 ppm, 1H), 87 ± 1 (−12.24 ppm, 1H).

Table 4. Crystal Data and Data Collection and Refinement for 2, 3, and 5

	2	3	5
Crystal Data			
formula	$C_{25}H_{51}NOsP_2$	$C_{25}H_{52}BF_4NOsP_2 \cdot 0.5(C_4H_{10}O)$	$C_{24}H_{52}N_2OsP_2$
molecular wt	617.81	742.69	620.82
color and habit	orange, irregular block	dark red, irregular block	orange, irregular block
symmetry, space group	triclinic, $P\bar{1}$	triclinic, $P\bar{1}$	monoclinic, $P2_1/c$
a, Å	7.5678(6)	8.947(2)	7.7832(7)
b, Å	12.1370(10)	11.992(3)	38.317(3)
c, Å	15.4192(13)	32.215(8)	18.7027(17)
α, deg	79.5480(10)	84.276(4)	
β, deg	89.0740(10)	83.400(4)	96.8040(10)
γ, deg	82.6080(10)	69.593(4)	
V, Å^3	1381.1(2)	3211.2(13)	5538.4(9)
Z	2	4	8
D_{calc}, g cm^{-3}	1.486	1.536	1.489
Data Collection and Refinement			
diffractometer		Bruker Smart APEX	
λ(Mo Kα), Å		0.71073	
monochromator		graphite oriented	
scan type		ω scans	
μ, mm^{-1}	4.744	4.112	4.733
2θ, range, deg	3, 57	3, 57	3, 57
temp, K	100	100	100
no. of data collected	16 410	39 261	67 277
no. of unique data	6356 (R_{int} = 0.0442)	14 903 (R_{int} = 0.0410)	13 337 (R_{int} = 0.0372)
no. of params/restraints	307/0	734/10	563/54
R_1[a] [$F^2 > 2\sigma(F^2)$]	0.0351	0.0307	0.0269
wR_2[b] [all data]	0.0603	0.0516	0.0599
S[c] [all data]	0.848	0.777	0.946

[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.

Data for $OsH_3(NC_5H_4$-*o*-N=CH)$(P^iPr_3)_2$ (6). ^{1}H NMR (300 MHz, C_7D_8, 293 K): δ 14.26 (virtual quartet, $J_{H-H(OsH_3)}$ = 3 Hz, 1H, OsCH), 9.40 and 7.85 (d, J_{H-H} = 6.8 Hz, 1H, H_α and $H_{\beta'}$ py), 7.01 and 6.16 (both dd, $J_{H-H} = J_{H-H}$ = 6.8 Hz, 1H, H_γ and H_β py), 1.70 (m, 6H, PC*H*), 0.93 and 0.92 (both dvt, N = 12.7 Hz, J_{H-H} = 7.0 Hz, 18H, PCHCH_3), −8.19 (br, 2H, OsH), −11.42 (br, 1H, OsH). ^{1}H{^{31}P} NMR (300 MHz, C_7D_8, 193 K, only variable-temperature signals): low-field (OsCH), δ 14.30 (d, J_{H-H} = 9 Hz, 1H, OsCH); high-field region, δ −5.77 and −10.53 (both d, $J_{H_A-H_B}$ = 22 Hz, 1H, H_A and H_B), −11.33 (d, J_{H-H} = 9 Hz, 1H, OsH_3). ^{31}P{^{1}H} NMR (121.42 MHz, C_7D_8, 293 K): δ 30.8 (s). ^{13}C{^{1}H} NMR (75.42 MHz, C_7D_8, 293 K): δ 251.7 (t, J_{C-P} = 4.6 Hz, OsC), 172.5 (s, C_{ipso}), 155.6, 134.7, 119.3, and 116.3 (all s, py), 27.9 (vt, N = 25.7 Hz, P*C*H), 19.8 and 19.7 (both s, PCH*C*H$_3$). $T_{1(min)}$ (ms, OsH_3, 300 MHz, C_7D_8, 213 K): 94 ± 5 (−5.77 ppm, 1H), 85 ± 4 (−10.53 ppm, 1H), 126 ± 2 (−11.33 ppm, 1H).

The addition of 0.05 equiv of $OsH_6(P^iPr_3)_2$ to an NMR tube containing **6** in toluene-d_8 or benzene-d_6 gives, after 10 h, complex **6** partially deuterated in the pyridine ring. ^{1}H NMR (300 MHz, C_6D_6 or C_7D_8, 293 K, pyridine ring): δ 9.40 (s, 1H, H_α py), 7.85 (s, 1H, $H_{\beta'}$ py). ^{2}H NMR (300 MHz, C_6H_6, 293 K): δ 7.12 and 6.27 (both s, 1D, D_γ and D_β py). ^{13}C{^{1}H} NMR (75.42 MHz, C_7D_8, 293 K, C_γ and C_β of the pyridine ring, no changes in the other signals): δ 116.3 (t(1:1:1), J_{C-D} = 24.4 Hz), 134.7 (t(1:1:1), J_{C-D} = 23.9 Hz).

Preparation of $OsH_3(NC_5H_4$-*o*-NCH_2Ph)$(P^iPr_3)_2$ (7). A colorless solution of $OsH_6(P^iPr_3)_2$ (173.1 mg, 0.335 mmol) in 15 mL of toluene was treated with 1.3 equiv of (*E*)-*N*-(phenylmethylene)-2-pyridinamine (79.2 mg, 0.435 mmol) and heated under reflux for 5 h. The resulting yellow solution was filtered through Celite and dried in vacuo. Pentane was added to afford a yellow solid, which was washed with further portions of pentane at 223 K and dried in vacuo. Yield: 175.1 mg (75%). Anal. Calcd for $C_{30}H_{56}N_2OsP_2$: C 51.70, H 8.10, N 4.02. Found: C 51.63, H 8.05, N 4.17. IR (KBr, cm^{-1}): ν(OsH) 2117 (s), 2102 (s). ^{1}H NMR (300 MHz, C_7D_8, 293 K): δ 7.96 (d, J_{H-H} = 6.7 Hz, 1H, H_α py), 7.40 (d, J_{H-H} = 7.5 Hz, 2H, *o*-Ph), 7.18 (vt, J_{H-H} = 7.5 Hz, 2H, *m*-Ph), 7.09 (vt, J_{H-H} = 6.7 Hz, 1H, H_γ py), 6.84 (vt, J_{H-H} = 7.5 Hz, 1H, *p*-Ph), 5.93 (vt, J_{H-H} = 6.7 Hz, 1H, H_β py), 5.82 (d, J_{H-H} = 6.7 Hz, 1H, $H_{\beta'}$ py), 4.58 (s, 2H, CH_2), 1.91 (m, 6H, PC*H*), 1.11 and 1.01 (both dvt, N = 12.7 Hz, J_{H-H} = 6.5 Hz, 18H, PCHCH_3), −11.92 (br, 3H, OsH). ^{1}H{^{31}P} NMR (300 MHz, C_7D_8, 193 K, in the high-field region): δ −10.89 (d, J_{H-H} = 11.8, 1H), −12.11 (d, J_{H-H} = 22.3, 1H), −12.32 (dd, J_{H-H} = 22.3, J_{H-H} = 11.8, 1H). ^{31}P{^{1}H} NMR (121.42 MHz, C_7D_8, 293 K): δ 25.0 (s). ^{13}C{^{1}H} NMR (75.42 MHz, C_7D_8, 293 K, plus HETCOR): δ 168.4 (s, $C_{ipso(py)}$), 149.4 (s, py), 142.9 (s, $C_{ipso(Ph)}$), 133.1 (s, *p*-Ph), 128.5 (s, *o*-Ph), 128.1 (s, *m*-Ph), 126.5, 103.9, and 103.7 (all s, py), 54.6 (s, CH_2), 27.5 (vt, N = 23.0 Hz, P*C*H), 20.5 and 19.8 (both s, PCH*C*H$_3$). MS (FAB$^+$): m/z 698 (M^+). $T_{1(min)}$ (ms, OsH_3, 300 MHz, C_7D_8, 223 K): 96 ± 2 (−10.90 ppm, 1H), 80 ± 2 (−12.22 ppm, 2H).

Preparation of $[OsH_3(NC_5H_4$-*o*-NH$CH_3)(P^iPr_3)_2]BF_4$ (8). A yellow solution of **5** (129.0 mg, 0.208 mmol) in 30 mL of diethyl ether was treated with 1 equiv of $HBF_4 \cdot OEt_2$ (29 μL, 0.213 mmol) and stirred for 40 min at room temperature. During the course of the reaction a white solid formed. The solvent was removed, and the solid was washed with further portions of diethyl ether and dried in vacuo. Yield: 121.5 mg (82%). Anal. Calcd for $C_{24}H_{53}BF_4N_2OsP_2$: C 40.68, H 7.54, N 3.95. Found: C 40.54, H 7.73, N 4.01. IR (KBr, cm^{-1}): ν(NH) 3264 (m); ν(OsH) 2157 (s), 2122 (m); $\nu(BF_4)$ 1050 (br). ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ 8.47 (d, J_{H-H} = 7.1 Hz, 1H, H_α py), 7.86 and 7.45 (both vt, J_{H-H} = 7.1 Hz, 1H, H_γ and H_β py), 7.42 (d, J_{H-H} = 7.1 Hz, 1H, $H_{\beta'}$ py), 5.42 (br quartet, J_{H-H} = 5.9 Hz, 1H, NH), 3.28 (d, J_{H-H} = 5.9 Hz, 3H, CH_3), 2.10 (m, 6H, PC*H*), 1.19 and 0.96 (both dvt, N = 13.4 Hz, J_{H-H} = 6.7 Hz, 18H, PCHCH_3), −12.80 (br, 3H, OsH). ^{1}H{^{31}P} NMR (300 MHz, CD_2Cl_2, 193 K, in the high-field region): δ −10.59 (d, $J_{H_A-H_B}$ = 63.7 Hz, 1H), −12.65 (dd, $J_{H_A-H_B}$ = 63.7 Hz, $J_{H_B-H_C}$ = 15.9 Hz, 1H), −15.19 (d, $J_{H_B-H_C}$ = 15.9 Hz, 1H). ^{31}P{^{1}H} NMR (121.42 MHz, CD_2Cl_2, 303 K): δ 27.4 (s). ^{31}P{^{1}H} NMR (121.42 MHz, CD_2Cl_2, 198 K): AB spin system, δ 25.2, $\Delta\nu$ = 429 Hz, J_{AB} = 245 Hz. ^{19}F NMR (282.33 MHz, CD_2Cl_2, 293 K): δ −154.9 (br). ^{13}C{^{1}H} NMR (75.42 MHz, CD_2Cl_2, 293 K, plus APT): δ 161.5 (s, C_{ipso}), 150.1, 137.6, 127.1, and 120.3 (all s, py), 42.1 (s, CH_3), 27.6 (vt, N = 25.5 Hz, P*C*H), 20.3 and 19.4

(both s, $PCHCH_3$). MS (FAB^+): *m*/*z* 621 ($M^+ - 2H$). $T_{1(min)}$ (ms, OsH_3, 300 MHz, CD_2Cl_2, 203 K): 71 ± 3 (−10.59 ppm, 1H), 69 ± 3 (−12.65 ppm, 1H), 101 ± 1 (−15.19 ppm, 1H).

Preparation of $[OsH_3(NC_5H_4$-*o*-$NHCH_3)(P^iPr_3)_2]BF_4$ Partially Deuterated. This complex was prepared as described for **8** starting from **5** (78.6 mg, 0.127 mmol) and $DBF_4 \cdot D_2O$ (24 μL, 0.127 mmol). A white solid was obtained. Yield: 32.8 mg (36%). ^2H NMR (46.03 MHz, CH_2Cl_2, 293 K): δ 8.5 (s, 0.07D, D_α py), 7.4 (s, 0.14D, $D_{\beta'}$ py), 5.4 (s, 0.47D, ND), 3.3 (s, 0.27D, CDH_2), −12.4 (br, 0.05D, OsD).

Structural Analysis of Complexes 2, 3, and 5. Suitable crystals for X-ray diffraction were obtained by slow diffusion of pentane into a saturated solution of **2** in toluene, diethyl ether into a saturated solution of **3** in dichloromethane, or methanol into a saturated solution of **5** in toluene. 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 (molybdenum radiation, $\lambda = 0.71073$ Å) operating at 50 kV and 40 (**2**) or 30 (**3** and **5**) mA. Data were collected over the complete sphere by a combination of four sets. Each frame exposure time was 10 (**3**) or 20 (**2** and **5**) s covering 0.3° in ω. Data were corrected for absorption by using a multiscan method applied with the SADABS[34] program. The structures for all compounds were solved by the Patterson method. Refinement, by full-matrix least squares on F^2 with SHELXL97,[35] was similar for all complexes, including isotropic and subsequently anisotropic displacement parameters. For **3** and **5** the asymmetric unit shows two independent, but chemically equivalent molecules, and a solvent molecule of diethyl ether was observed in **3**. In the last cycles of anisotropic refinement, the shape and size of some thermal ellipsoids suggest the presence of disorder in a phosphine ligand of molecule **a** in **5** due to a rotation about the P−Os bond. This ligand was refined with two moieties with isotropic thermal parameters and complementary occupancy factors. The hydrogen atoms for nondisordered groups were observed or calculated and refined using a restricted riding model or freely. Hydride ligands were located, but not all of them refined appropriately, and some restraints were used in **2** (thermal parameters) and **3** (Os−H bonds). All the highest electronic residuals were observed in the 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: Tables of positional and displacement parameters, 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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