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C(sp^2)−H Activation of RCH=E−py (E = CH, N) and RCH=CHC(O)R′ Substrates Promoted by a Highly Unsaturated Osmium−Monohydride Complex

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The 14-valence-electron monohydride $OsH(SnPh_2Cl)(P^iPr_3)_2$ (**a**), generated from $OsH_3(SnPh_2Cl)\{\eta^2\text{-}CH_2{=}C(CH_3)P^iPr_2\}(P^iPr_3)$ (**1**), activates a C(sp^2)−H bond of 2-vinylpyridine, (*E*)-*N*-(phenylmethylene)-2-pyridinamine, and α,*β*-unsaturated ketones. The activation of 2-vinylpyridine affords the elongated dihydrogen ($d_{H-H} = 1.41$ Å) derivative $Os(SnPh_2Cl)(NC_5H_4\text{-}o\text{-}CH{=}CH)(\eta^2\text{-}H_2)(P^iPr_3)_2$ (**2**) in equilibrium ($\Delta H° = -2.5 \pm 0.2$ kcal mol^{-1} and $\Delta S° = -14.8 \pm 1.0$ cal mol^{-1} K^{-1}) with the tautomer $OsH(NC_5H_4\text{-}o\text{-}CH{=}CH)(HSnPh_2Cl)(P^iPr_3)_2$ (**3**), where the stannane is bonded to the transition metal by an Os−H−Sn three-center bond (J_{H-Sn} = 183 Hz). The activation of (*E*)-*N*-(phenylmethylene)-2-pyridinamine gives rise to $Os(SnPh_2Cl)(NC_5H_4\text{-}o\text{-}NCPh)(\eta^2\text{-}H_2)(P^iPr_3)_2$ (**4**; $d_{H-H} = 1.32$ Å), whereas the treatment of **1** with methyl vinyl ketone and benzylidenacetone leads to $Os(SnPh_2Cl)\{C(R)CHC(O)CH_3\}(\eta^2\text{-}H_2)(P^iPr_3)_2$ (R = H (**5**), Ph (**6**)), which show blocked rotation of the dihydrogen ligand ($d_{H-H} = 1.45$ (**5**), $d_{H-H} = 1.42$ (**6**) Å) on the NMR time scale ($\Delta H^‡ = 11.7 \pm 0.4$ kcal mol^{-1} and $\Delta S^‡ = -1 \pm 1$ cal mol^{-1} K^{-1} (**5**), $\Delta H^‡ = 10.8 \pm 0.5$ kcal mol^{-1} and $\Delta S^‡ = 0.4 \pm 1$ cal mol^{-1} K^{-1} (**6**)). Complex **1** also reacts with benzylidenacetophenone. The reaction initially gives $Os(SnPh_2Cl)\{C(Ph)CHC(O)Ph\}(\eta^2\text{-}H_2)(P^iPr_3)_2$ (**7**), which isomerizes into $Os(SnPh_2Cl)\{C_6H_4C(O)CH{=}CHPh\}(\eta^2\text{-}H_2)(P^iPr_3)_2$ (**8**), resulting from the *o*-CH activation of the PhCO aryl group. Complex **8** is other example of blocked rotation of the dihydrogen ligand ($d_{H-H} = 1.45$ Å) on the NMR time scale ($\Delta H^‡ = 10.6 \pm 0.6$ kcal mol^{-1} and $\Delta S^‡ = -6.3 \pm 1.5$ cal mol^{-1} K^{-1}). The structures of **2** and **5** have been determined by X-ray diffraction analysis.

Introduction

The activation of C−H bonds by transition-metal compounds[1] is a type of reaction of great importance, due to its connection with the functionalization of organic molecules.[2] An example is the addition of vinylic C(sp^2)−H bonds to unsaturated hydrocarbons.[3] The formation of the new carbon−carbon bond requires, as a previous step, the C−H activation of the added bond, which is promoted by a low-valent metal complex.[4]

Among the various strategies to activate C−H bonds, chelation assistance utilizing cyclometalation is considered to be one of the most promising ways.[5] In this context, the C(sp^2)−H activation in C=E groups (E = C, N) contained in substrates such as 2-vinylpyridine,[6] aldimines,[7] and α,*β*-unsaturated ketones[8] is of particular interest.

The C−H activation reactions with high-valent metal complexes are rare, in particular those using hydride compounds.[6f,l,9] Despite this, it has been shown that the

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thermal activation of the hexahydride $OsH_6(P^iPr_3)_2$ affords a short-lived species, $OsH_2(\eta^2\text{-}H_2)(P^iPr_3)_2$, which activates cyclohexyl methyl ketone,[10] an *o*-CH bond of aromatic ketones[11] and imines,[12] and the $C(sp^2)-H_\alpha$ bond of aldehydes.[13]

One of the most typical reactions of transition-metal hydride complexes is the insertion of alkenes into the metal−hydride bond, which leads to alkyl derivatives and constitutes a key step in a variety of catalytic reactions.[14] The thermodynamic stability of the resulting alkyl compounds depends on the particular alkyl group. The presence of a donor heteroatom at the C_γ carbon atom increases the stability of the system, as a result of its coordination to the metallic center.[15]

The reactions of the 16-valence-electron dihydride−dihydrogen derivative $OsH_2(\eta^2\text{-}H_2)(P^iPr_3)_2$ with $RCH{=}E\text{-}py$ substrates (E = CH, N) lead to products resulting from both insertion and C(sp^2)−H activation reactions. They are competitive and depend on the nature of E and R, which determine the polarity of the C=E double bond and the steric hindrance of the RCH group.[16]

Complexes with formally 14 valence electrons are recognized as the active catalytic component of olefin polymerization, with both early and late transition metals.[17] For the iron triad, direct experimental evidence for the existence of this type of compound has been reported by the groups of Caulton,[18] Grubbs,[19] and Baratta.[20] The accessible systems are very scarce, and as a consequence, their chemistry is much less known than that of the also unsaturated 16-valence-electron compounds.

In an effort to introduce the advantages of the tin ligands[21] into osmium−polyhydride chemistry, we have recently prepared a family of polyhydride−tin−osmium complexes,[22] including the trihydride−isopropenyldiisopropylphosphine derivative $OsH_3(SnPh_2Cl)\{\eta^2\text{-}CH_2{=}C(CH_3)P^iPr_2\}(P^iPr_3)$,[23] which is a synthon for the 14-valence-electron monohydride $OsH(SnPh_2Cl)(P^iPr_3)_2$. Like the 16-valence-electron derivative $OsH_2(\eta^2\text{-}H_2)(P^iPr_3)_2$, this monohydride activates an *o*-CH bond of aromatic ketones and an *o*-CH bond of aromatic imines.[24] However, in contrast to $OsH_2(\eta^2\text{-}H_2)(P^iPr_3)_2$, it also activates an *o*-CH bond of benzaldehyde and para- and meta-substituted benzaldehydes.[25] As a continuation of our work on the chemistry of the 14-valence-electron monohydride $OsH(SnPh_2Cl)(P^iPr_3)_2$, we now report the reactions of this species with 2-vinylpyridine, (*E*)-*N*-(phenylmethylene)-2-pyridinamine, and α,*β*-unsaturated ketones, including benzylidenacetophenone.

Results and Discussion

1. Reaction with 2-Vinylpyridine. Treatment at room temperature of toluene solutions of $OsH_3(SnPh_2Cl)\{\eta^2\text{-}CH_2{=}C(CH_3)P^iPr_2\}(P^iPr_3)$ (**1**) with 1.4 equiv of 2-vinylpyridine affords brown solutions after 24 h, from which the elongated dihydrogen derivative $Os(SnPh_2Cl)(NC_5H_4\text{-}o\text{-}CH{=}CH)(\eta^2\text{-}H_2)(P^iPr_3)_2$ (**2**) was isolated as a dark beige solid in 53% yield. The formation of **2** involves the reduction of the isopropenyl group of the isopropenyldiisopropylphosphine of **1** and subsequent C(sp^2)−H bond activation of the olefinic CH_2 group of

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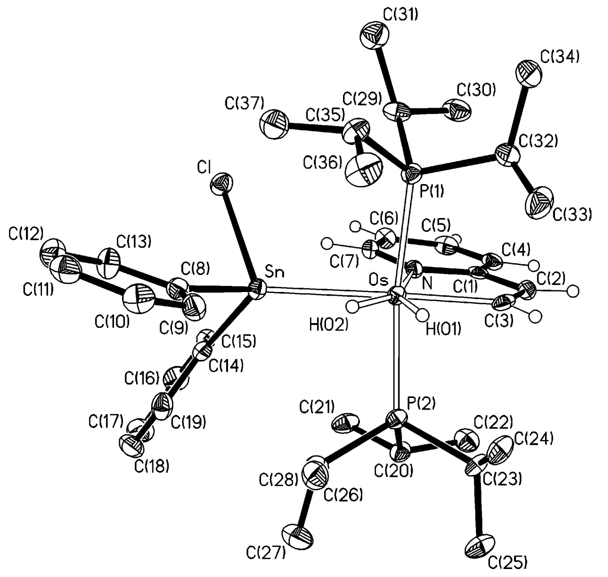
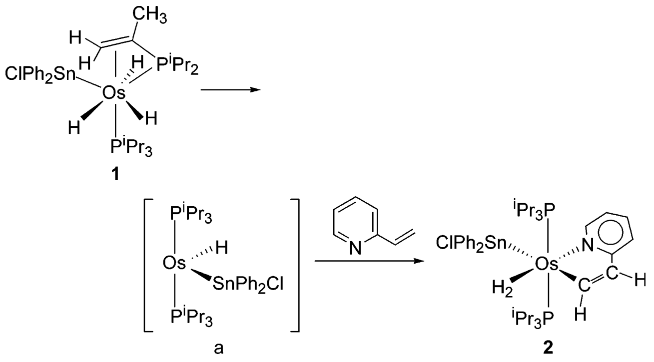


Figure 1. Molecular diagram of the complex $Os(SnPh_2Cl)(NC_5H_4\text{-}o\text{-}CH{=}CH)(\eta^2\text{-}H_2)(P^iPr_3)_2$ (**2**).

Scheme 1



the substituent of the pyridine, by the 14-valence-electron monohydride $OsH(SnPh_2Cl)(P^iPr_3)_2$ (**a** in Scheme 1). 2-Ethylpyridine or organometallic products resulting from the insertion of the vinyl substituent of the substrate into any of the Os−H bonds of **1** or **a** were not observed during the reaction.

The behavior of **a** is similar to that previously observed for the 14-valence-electron ruthenium monohydride $RuHCl(P^iPr_3)_2$, which reacts with 2-vinylpyridine to give $Ru(NC_5H_4\text{-}o\text{-}CH{=}CH)Cl(P^iPr_3)_2$ and molecular hydrogen.[26] However, it should be noted that, in contrast to the ruthenium system, the bonding in the OsH_2 unit of **2** is stable. Since 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,[27] the stability of the OsH_2 unit of **2** appears to be a consequence of the intrinsically higher basicity of the osmium atom in comparison with ruthenium.[28]

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 octahedron, with the two phosphorus atoms of the triisopropylphosphine ligands occupying apical positions (P−Os−P = 167.07(3)°). The osmium sphere is completed by the metalated group, which acts with a bite angle of 74.68(12)°, the stannyl ligand disposed cis to the nitrogen atom of the pyridine (Sn−Os−N = 91.89(7)°), and the hydrogen atoms H(01) and H(02).

Table 1. Selected Bond Lengths (Å) and Angles (deg) for the Complex $Os(SnPh_2Cl)(NC_5H_4\text{-}o\text{-}CH{=}CH)(\eta^2\text{-}H_2)(P^iPr_3)_2$ (2)

Os−Sn	2.6987(4)	Sn−Cl	2.4542(9)
Os−P(1)	2.3942(9)	N−C(7)	1.348(4)
Os−P(2)	2.3822(9)	C(1)−C(2)	1.431(5)
Os−N	2.195(3)	C(2)−C(3)	1.336(5)
Os−C(3)	2.068(4)	C(7)−C(6)	1.374(4)
Os−H(01)	1.40(3)	C(6)−C(5)	1.379(4)
Os−H(02)	1.35(4)	C(5)−C(4)	1.365(4)
H(01)···H(02)	1.31(4)	N−C(1)	1.365(4)
Sn−Os−P(1)	96.43(2)	N−Os−C(3)	74.68(12)
Sn−Os−P(2)	91.70(2)	N−Os−H(01)	151.0(13)
Sn−Os−N	91.89(7)	N−Os−H(02)	152.2(16)
Sn−Os−C(3)	165.74(9)	C(8)−Sn−C(14)	98.13(13)
Sn−Os−H(01)	117.1(13)	C(8)−Sn−Cl	97.77(9)
Sn−Os−H(02)	60.4(16)	C(14)−Sn−Cl	92.71(9)
P(1)−Os−P(2)	167.07(3)	C(8)−Sn−Os	120.80(9)
P(1)−Os−N	92.50(7)	C(14)−Sn−Os	126.71(9)
P(2)−Os−N	97.28(7)	C(3)−Os−H(01)	76.3(13)
P(1)−Os−C(3)	89.07(9)	C(3)−Os−H(02)	133.1(16)
P(2)−Os−C(3)	85.39(9)	H(01)−Os−H(02)	56.8(17)
P(1)−Os−H(01)	86.1(12)	Os−N−C(1)	115.2(2)
P(2)−Os−H(01)	81.3(12)	Os−C(3)−C(2)	119.4(3)
P(1)−Os−H(02)	88.8(15)	C(1)−C(2)-C(3)	116.7(3)
P(2)−Os−H(02)	86.5(15)		

The bond length Os−C(3) (2.068(4) Å) is as expected for an Os−C(sp^2) single bond and is similar to those found in $OsH_3(NC_5H_4\text{-}o\text{-}CH{=}CH)(P^iPr_3)_2$ (2.073(5) Å)[16] and in other alkenyl−osmium complexes (between 1.99(1) and 2.195(5) Å).[29] The C(2)−C(3) bond length (1.336(5) Å) agrees well with the average carbon−carbon double-bond distances in vinyl groups (1.35(2) Å).[30] In accordance with the sp^2 hybridization at C(2) and C(3) the angles C(1)−C(2)−C(3) and Os−C(3)−C(2) are 116.7(3) and 119.4(3)°, respectively.

The Os−Sn distance (2.6987(4) Å) agrees well with those reported for other mononuclear osmium−stannyl derivatives (2.6−2.7 Å),[22−25,31] while it is about 0.1 Å shorter than the Os(μ−H) Sn−osmium−tin bond length in the cluster $Os_3SnH_2(CO)_{10}\{CH(SiMe_3)_2\}_2$ (2.855(3) Å).[32] The environment of the tin atom is tetrahedral, with the chlorine atom lying in the equatorial plane of

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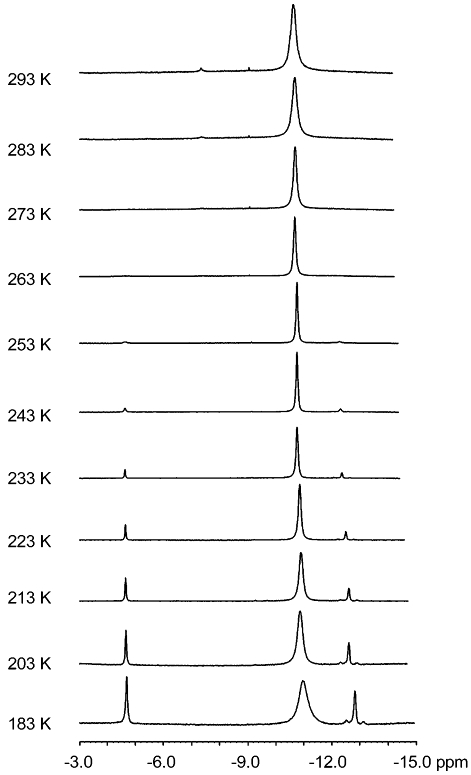
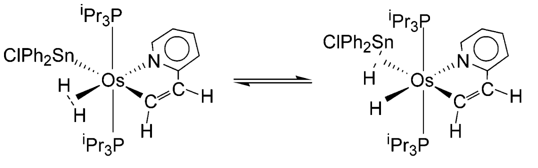


Figure 2. Variable-temperature $^1H\{^{31}P\}$ NMR spectra (300 MHz) in toluene-d_8 in the high-field region of $Os(SnPh_2Cl)(NC_5H_4\text{-}o\text{-}CH{=}CH)(\eta^2\text{-}H_2)(P^iPr_3)_2$ (**2**) and $OsH(NC_5H_4\text{-}o\text{-}CH{=}CH)(HSnPh_2Cl)(P^iPr_3)_2$ (**3**).

the bipyramid. The angles around the tin atom are between 92.71(9)° (C(14)−Sn−Cl) and 126.71(9)° (C(14)−Sn−Os).

The C−H activation of the vinyl substituent of the pyridine is also supported by the $^{13}C\{^1H\}$ NMR spectrum of **2** in benzene-d_6 at room temperature. In agreement with the presence of an alkenyl ligand in the complex, the spectrum shows two singlets at 161.2 and 130.5 ppm corresponding to C(3) and C(2), respectively.

The ^1H NMR spectra in toluene-d_8 indicate that in solution complex **2** is in equilibrium with the tautomer $OsH(NC_5H_4\text{-}o\text{-}CH{=}CH)(HSnPH_2Cl)(P^iPr_3)_2$ (**3**), where the stannane is bonded to the transition metal by an Os−H−Sn three-center bond (eq 1). Figure 2 shows the $^1H\{^{31}P\}$ NMR spectra of the equilibrium mixture, in the hydride region, as a function of the temperature. At temperatures higher than 273 K the only spectroscopically detected species is the elongated dihydrogen **2**, while at temperatures lower than 263 K the presence of **3** is evident in the spectra.



(1)

2 **3**

In the ^1H NMR spectrum at 348 K, the resonance due to the elongated dihydrogen ligand of **2** appears at −11.11 ppm, as a double triplet by spin coupling with the OsCH hydrogen (δ, 9.99) of the substituent of the pyridine (J_{H-H} = 5.1) and the phosphorus of the phosphine ligands (J_{H-P} = 11.6 Hz). The spin coupling between the dihydrogen and the vinyl OsCH proton was confirmed by a $^1H-^1H$ COSY NMR spectrum, which shows the cross signals between both resonances. Lowering the sample temperature produces a broadening of the dihydrogen resonance. However, decoalescence is not observed at 183 K. A variable-temperature 300 MHz T_1 study between 273 and 203 K of this resonance gives a T_1(min) value of 61 ± 1 ms at 228 K. Assuming slow spinning, this value corresponds to a hydrogen−hydrogen distance of 1.41 Å,[33] which lies within the range of distances found in the so-called elongated dihydrogen complexes.[34]

Table 2. Calculated Values for K (K = [3]/[2])

temp (K)	K	temp (K)	K
193	0.4427	233	0.1706
203	0.2842	243	0.1154
213	0.2630	253	0.0783
223	0.1998		

The most noticeable spectroscopic data of **3** are two resonances with a 1:1 intensity ratio, in the high-field region of the ^1H NMR spectrum. These resonances are observed at −4.70 and −12.87 ppm and were assigned to the hydride ligand atom and the Sn−H hydrogen, respectively. In agreement with a three-center Sn−H−Os interaction, the resonance at −12.87 ppm shows tin satellites with H−^{119}Sn and H−^{117}Sn coupling constants of 183 Hz. This value is situated within the range distinctive of compounds exhibiting three-center Sn−H−M interactions (150−300 Hz).[32,35] The stereochemistry of **3**, with the hydride ligand disposed cis to the metalated carbon atom of the substituent of the pyridine, was inferred from a NOESY ^1H NMR spectrum at 203 K. The spectrum shows cross-peaks between the hydride resonance (δ −4.70) and the OsCH signal (δ 9.70).

The $^{31}P\{^1H\}$ NMR spectra also support the existence of an equilibrium mixture between **2** and **3**. At 353 K in toluene-d_8, the spectrum shows a singlet at 6.2 ppm, along with the tin satellites ($J_{P-^{117}Sn} = J_{P-^{119}Sn}$ = 111 Hz). At 183 K, in addition to the resonance of **2** a singlet at −3.3 ppm for **3** is observed. In this case, the tin satellites indicate P−^{117}Sn and P−^{119}Sn coupling constants of 87 Hz.

The equilibrium constant between **2** and **3** was calculated for each temperature (Table 2) by integration

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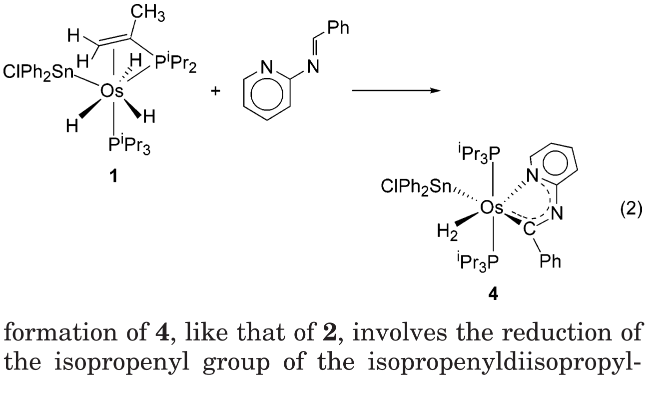
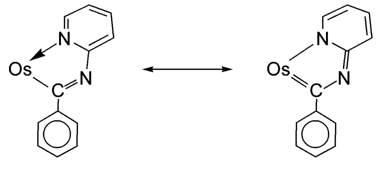
of the resonances shown in Figure 2. Linear least-squares analysis of ln K versus $1/T$ provides values for $\Delta H°$ and $\Delta S°$ of -2.5 ± 0.2 kcal mol^{-1} and -14.8 ± 1.0 cal mol^{-1} K^{-1}, respectively.

The equilibrium shown in eq 1 is a rare case of coexistence of the two possible coordination modes of a "H_2MR_3" moiety (M = group 14 element) to a transition metal. A theoretical study on the model $OsCl(H_2SiH_3)(CO)(PH_3)_2$ system has predicted the existence of two stable octahedral six-coordinate species of very close energy: the dihydrogen complex $OsCl(SiH_3)(CO)(\eta^2\text{-}H_2)(PH_3)_2$ and the η^2-H$-$SiH$_3$ compound $OsHCl(CO)(\eta^2\text{-}HSiH_3)(PH_3)_2$.[36] However, only the dihydrogen derivative $OsCl(SiEt_3)(CO)(\eta^2\text{-}H_2)(P^iPr_3)_2$ has been experimentally found.[37] In contrast to the latter, the η^2-HMR$_3$ complexes $[IrH_2(\eta^2\text{-}HSiEt_3)_2(PPh_3)_2]^+$,[38] $RuH_2(\eta^2\text{-}H_2)(\eta^2\text{-}HMPh_3)(PCy_3)_2$ (M = Si, Ge),[39] $RuH_2\{\eta^2\text{-}HSi(OEt)_3\}_2(PCy_3)_2$,[40] and $RuH_2\{(\eta^2\text{-}HSiMe_2)_2X\}(PCy_3)_2$[41] have been reported.

2. Reaction with (*E*)-*N*-(Phenylmethylene)-2-pyridinamine. The presence of a bulky phenyl group at the metalated carbon atom of **2** or **3** should increase the steric hindrance between the chelating ligand and the phosphines, decreasing the stability of the five-membered ring. In addition, it should be noted that, in 2-vinylpyridine, the replacement of the olefinic CH group by a nitrogen atom increases the electrophilicity of the terminal group of the double bond, which should favor the insertion of the substrate into the Os$-$H bond of **a**. (*E*)-*N*-(phenylmethylene)-2-pyridinamine is a substrate that, in contrast to 2-vinylpyridine, contains a phenyl group at the terminal carbon atom of the substituent of the pyridine, and where the olefinic CH unit has been replaced by a nitrogen atom. Despite these differences between (*E*)-*N*-(phenylmethylene)-2-pyridinamine and 2-vinylpyridine, the behaviors of both substrates are similar. Treatment at room temperature of toluene solutions of **1** with 1.4 equiv of (*E*)-*N*-(phenylmethylene)-2-pyridinamine leads after 5 days to orange solutions, from which the elongated dihydrogen complex $\overline{Os(SnPh_2Cl)(NC_5H_4\text{-}o\text{-}NC}Ph)(\eta^2\text{-}H_2)(P^iPr_3)_2$ (**4**) was isolated as a beige solid in 60% yield (eq 2). The formation of **4**, like that of **2**, involves the reduction of the isopropenyl group of the isopropenyldiisopropylphosphine of **1** to afford **a** and the subsequent C(sp^2)$-$H bond activation of the vinylic CHPh group of the substituent of the pyridine by the monohydride $OsH(SnPh_2Cl)(P^iPr_3)_2$.



Scheme 2



4A **4B**

The $^{13}C\{^1H\}$ NMR spectrum of **4** in benzene-d_6 at room temperature reveals that for an adequate description of the bonding situation in this compound the resonance forms shown in Scheme 2 should be taken into account. In agreement with a significant contribution of the amino$-$carbene resonance form **4B** to the structure of this compound, the OsC resonance appears as a triplet at 237.1 ppm with a C$-$P coupling constant of 7.2 Hz.

The ^1H NMR spectra of **4** in toluene-d_8, in contrast to those of **2**, does not show any evidence for the formation of an η^2-H$-$SnPh$_2$Cl tautomer. In these spectra the most noticeable resonance is that due to the elongated dihydrogen ligand. At room temperature, it appears as a triplet at -10.09 ppm with an H$-$P coupling constant of 10.5 Hz. Lowering the sample temperature produces a broadening of the resonance. However, decoalescence is not observed upon 183 K. A variable-temperature 300 MHz T_1 study between 273 and 203 K of the elongated dihydrogen resonance gives a T_1(min) value of 42 ± 4 ms at 248 K. Assuming slow spinning, this value corresponds to a hydrogen$-$hydrogen separation of 1.32 Å, which is about 0.1 Å shorter than that in **2**. This difference agrees well with the lower nucleophilic power of the metalated carbon atom of **4** in comparison with that of **2**.[34,42]

The $^{31}P\{^1H\}$ NMR spectrum at room temperature contains a singlet at -2.6 ppm along with tin satellites ($J_{P-^{117}Sn} = J_{P-^{119}Sn} = 122$ Hz). At 193 K, the singlet is converted into an AB spin system centered at -3.3 ppm and defined by $\Delta\nu = 492$ Hz and $J_{A-B} = 186$ Hz. The presence of an AB spin system at 193 K is consistent with the existence at this temperature of a single conformer, in which the trans phosphines are inequivalent due to hindered rotation about the Os$-$P or/and Os$-$Sn bonds. Resistance to rotation about these single bonds could be a consequence of the steric hindrance experienced by the isopropyl groups of the phosphines and the phenyl groups of the stannyl ligand. A similar behavior has been previously observed for some five-, six-, and seven-coordinate ruthenium and osmium complexes containing bulky phosphine ligands.[24,25,43]

3. Reactions with Methyl Vinyl Ketone and Benzylideneacetone. The 14-valence-electron monohydride **a** also activates a C$_\beta$(sp^2)$-$H bond of α,β-unsaturated ketones. Treatment at room temperature

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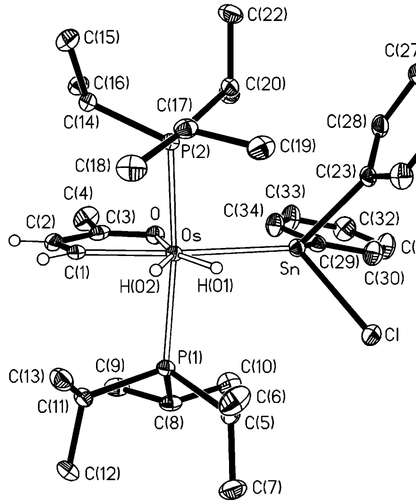
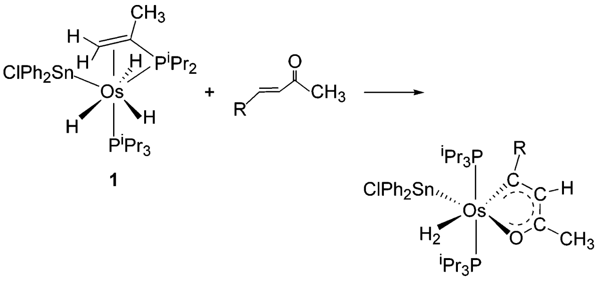


Figure 3. Molecular diagram of the complex Os(SnPh$_2$Cl){CHCHC(O)CH$_3$}(η^2-H$_2$)(P^{i}Pr$_3$)$_2$ (**5**).

of toluene solutions of **1** with 1.4 equiv of methyl vinyl ketone and benzylideneacetone affords after 24 h the corresponding elongated dihydrogen derivatives Os(SnPh$_2$Cl){C(R)CHC(O)CH$_3$)(η^2-H$_2$)(P^{i}Pr$_3$)$_2$ (R = H (**5**), Ph (**6**)), as a consequence of the reduction of the carbon−carbon double bond of the isopropenyldiisopropylphosphine of **1** and the C$_\beta$(sp^2)−H bond activation of the ketones (eq 3).



(3)

R = H (**5**), Ph (**6**)

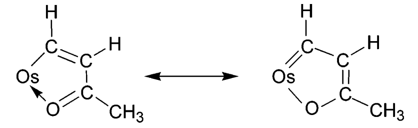
Complexes **5** and **6** were isolated as orange solids in high yield (60−70%) and characterized by elemental analysis, IR, and ^{1}H, ^{31}P{^{1}H}, ^{13}C{^{1}H}, and ^{119}Sn{^{1}H} NMR spectroscopy. Complex **5** was further characterized by an X-ray crystallographic study. A view of the molecular geometry of this complex is shown in Figure 3. Selected bond distances and angles are listed in Table 3.

In a manner similar to that for **2**, the coordination geometry around the osmium atom of **5** can be rationalized as a distorted octahedron with the two phosphorus atoms occupying relative trans positions (P(1)−Os−P(2) = 161.16(2)°). The remaining coordination sites involve the C(1) and O atoms of the chelating CHCHC(CH$_3$)O ligand, which form with the osmium atom a five-membered ring (C(1)−Os−O = 74.83(8)°), the stannyl ligand disposed cis to the oxygen atom of the activated ketone (Sn−Os−O = 84.10(4)°), and the hydrogen atoms H(01) and H(02) of the elongated dihydrogen ligand.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for the Complex Os(SnPh$_2$Cl){CHCHC(O)CH$_3$}(η^2-H$_2$)(P^{i}Pr$_3$)$_2$ (5)

Os−Sn	2.7219(3)	Sn−Cl	2.4549(6)
Os−P(1)	2.3809(6)	O−C(3)	1.273(3)
Os−P(2)	2.3799(6)	C(1)−C(2)	1.362(3)
Os−O	2.1657(15)	C(2)−C(3)	1.401(3)
Os−C(1)	2.035(2)	Os−H(01)	1.41(2)
Os−H(02)	1.48(2)	H(01)···H(02)	1.29(3)
Sn−Os−P(1)	96.442(14)	P(2)−Os−H(02)	84.6(9)
Sn−Os−P(2)	94.490(14)	O−Os−C(1)	74.83(8)
Sn−Os−O	84.10(4)	O−Os−H(01)	152.7(10)
Sn−Os−C(1)	158.92(7)	O−Os−H(02)	154.2(9)
Sn−Os−H(01)	68.8(10)	C(1)−Os-H(01)	132.2(10)
Sn−Os−H(02)	121.6(9)	C(1)−Os−H(02)	79.4(9)
P(1)−Os-P(2)	161.16(2)	H(01)−Os−H(02)	52.8(11)
P(1)−Os-O	99.52(4)	Os−O(1)−C(3)	114.93(14)
P(2)−Os-O	96.83(4)	Os−Sn−Cl	118.553(15)
P(1)−Os-C(1)	86.50(6)	Os−Sn−C(23)	124.02(6)
P(2)−Os-C(1)	88.80(6)	Os−Sn−C(29)	122.47(6)
P(1)−Os-H(01)	81.0(9)	C(23)−Sn-Cl	90.69(6)
P(2)−Os-H(01)	88.7(9)	C(29)−Sn-Cl	97.44(6)
P(1)−Os-H(02)	76.6(9)	C(23)−Sn-C(29)	96.36(8)

Scheme 3



5A **5B**

The five-membered heterometallacycle is almost planar (maximum deviation −0.009(1) Å, C(2)). The Os−C(1) bond length (2.035(2) Å) is slightly longer than the osmium−carbon distances found in the complexes OsCl{CHCHC(O)Ph}(CO)(P^{i}Pr$_3$)$_2$ (1.921(3) Å)[44] and Os(SnPh$_2$Cl){C$_4$(O)H$_2$C(O)H}(η^2-H$_2$)(P^{i}Pr$_3$)$_2$ (2.021(4) Å).[25] The C(1)−C(2) and C(2)−C(3) distances are 1.362(3) and 1.401(3) Å, respectively. These values are between those expected for single and double carbon−carbon bonds and suggest that for an adequate description of the bonding situation in this compound the resonance forms shown in Scheme 3 should be taken into account.

A significant contribution of the osmafuran resonance form **5B** to the structure of **5** is also supported by the ^{13}C{^{1}H} NMR spectrum, which shows the resonance due to the metalated carbon atom at 233.1 ppm. This resonance appears shifted 9.5 and 11.5 ppm, respectively, to higher field with regard to the chemical shifts observed for the carbon atoms of the Fischer carbene derivatives OsH(η^5-C$_5$H$_5$){=C(OMe)Ph}(P^{i}Pr$_3$) (δ 242.6)[45] and OsH(η^5-C$_5$H$_5$){=C(OMe)Ph}{P^{i}Pr$_2$[C(CH$_3$)=CH$_2$]} (δ 244.6).[46] However, it appears shifted more than 75 ppm to lower field with regard to the chemical shifts found for the OsC$_\alpha$ resonance of the alkenyl complexes Os(C$_2$Ph){(*E*)-CH=CHPh}(≡CCH$_2$Ph)(P^{i}Pr$_3$)$_2$ (δ 155.7),[47] OsH(η^5-C$_5$H$_5$){(*E*)-CH=CHPh}{P(OMe)$_3$}(P^{i}Pr$_3$) (δ 136.9),[48] [Os{(*E*)-CH=CHCy}Cl(=N=CMe$_2$)(P^{i}Pr$_3$)$_2$][CF$_3$SO$_3$] (δ 143.1),[49] and [Os{(*Z*)-CH=C(Ph)NH=CR$_2$}Cl(CO)$_2$(P^i-

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$Pr_3)_2]^+$ (δ between 158 and 145).[50] The chemical shift of the resonance due to C(1) agrees well with those corresponding to the related resonances of the complexes $OsCl\{CHCHC(O)Ph\}(CO)(P^iPr_3)_2$ (δ 230.13),[44] $Os(SnPh_2Cl)\{C_4(O)H_2C(O)H\}(\eta^2\text{-}H_2)(P^iPr_3)_2$ (δ 230.6), $Os(SnPh_2Cl)\{C_6H_8C(O)H\}(\eta^2\text{-}H_2)(P^iPr_3)_2$ (δ 242.9),[25] $OsH\{CHCHC(O)CH_3\}(P^iPr_3)_2$ (δ 250.8),[51] and $OsH_3\{C_6H_8C(O)CH_3\}(P^iPr_3)_2$ (δ 255.7),[10] where bonding situations intermediate between resonance forms analogous to **5A** and **5B** have been proposed to exist. In agreement with the $^{13}C\{^1H\}$ NMR spectrum of **5**, the $^{13}C\{^1H\}$ NMR spectrum of **6** shows a triplet at 241.4 ppm with a C−P coupling constant of 5.5 Hz, due to the OsC carbon atom of the activated benzylideneacetone.

The Os−Sn distance (2.7219(3) Å) is about 0.02 Å longer than that found in **2**. As in the latter, the environment of the tin atom is tetrahedral, with angles around the tin atom between 90.69(6)° (C(23)−Sn−Cl) and 124.02(6)° (Os−Sn−C(23)). In accordance with the presence of the stannyl ligand in these compounds, the $^{119}Sn\{^1H\}$ NMR spectra of **5** and **6** show triplets at 43.7 (**5**) and −47.5 (**6**) ppm, with Sn−P coupling constants of 119 and 136 Hz, respectively.

The ^1H NMR spectra of **5** are temperature-dependent. At 293 K in toluene-d_8 as solvent, the spectrum shows in the hydride region a broad resonance centered at −11.76 ppm. At about 273 K decoalescence occurs, and at 213 K an ABX_2 spin system defined by δ_A −10.79, δ_B −12.69, $J_{A-X} = 9$ Hz, $J_{B-X} = 13$ Hz, and $J_{A-B} = 27$ Hz is observed.

The variation of the OsH_2 resonance of **6** with the temperature is similar to that of **5**. At 293 K, the spectrum contains a triplet at −11.29 ppm, with a H−P coupling constant of 13.2 Hz. At about 223 K decoalescence occurs, and at 213 K a nonresolved ABX_2 spin system centered at −11.36 ppm with $\Delta\nu = 100$ Hz and $J_{A-B} = 84$ Hz is observed.

To estimate the separation between the hydrogen atoms of the OsH_2 units of **5** and **6**, T_1 values of the aforementioned resonances were determined over the temperature range 273-213 K. For **5** a T_1(min) value of 71 ± 1 ms was obtained for both resonances, after decoalescence, at 233 K. For **6**, the T_1(min) value (63 ± 3 ms) was obtained before decoalescence, at 243 K. The obtained T_1(min) values correspond to hydrogen−hydrogen distances of 1.45 Å (**5**) and 1.42 Å (**6**), which lie within the range of distances reported in the so-called elongated dihydrogen complexes,[34] as do those of **2** and **4**.

Complexes **5** and **6** are new examples of blocked rotation of the dihydrogen ligand on the NMR time scale.[12,25,34,52] Line shape analysis of the $^1H\{^{31}P\}$ NMR spectra (Figure 4 shows those of **5**) allows the calculation of the rate constants for the rotation at each temperature (Table 4). The activation parameters obtained from the corresponding Eyring analysis are $\Delta H^{\ddagger} = 11.7 \pm 0.4$ kcal mol^{-1} and $\Delta S^{\ddagger} = -1.0 \pm 1$ cal mol^{-1} K^{-1} for **5** and $\Delta H^{\ddagger} = 10.8 \pm 0.5$ kcal mol^{-1} and $\Delta S^{\ddagger} = -0.4 \pm 1$ cal mol^{-1} K^{-1} for **6**. The values for the entropy of activation, close to zero, are in agreement with an intramolecular process, while the values for the enthalpy of activation are similar to those found for blocked rotation processed in other elongated dihydrogen complexes.

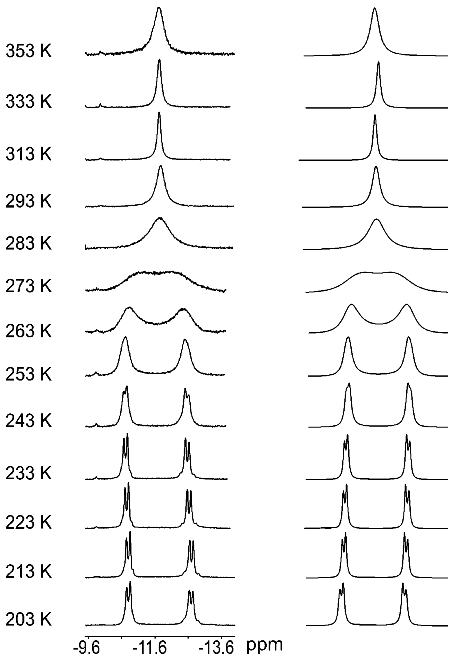

Figure 4. (left) Variable-temperature $^1H\{^{31}P\}$ NMR spectra (300 MHz) in toluene-d_8 in the high-field region of $Os(SnPh_2Cl)\{CHCHC(O)CH_3\}(\eta^2\text{-}H_2)(P^iPr_3)_2$ (**5**). (right) Simulated spectra.

Table 4. Rate Constants for the Hydride Exchange of Complexes 5, 6, and 8

	rate (s^{-1})		
temp (K)	**5**	**6**	**8**
213		2.03 × 10^2	
223		3.26 × 10^2	
233		6.23 × 10^2	
243		2.10 × 10^3	56
253	1.99 × 10^2	7.33 × 10^3	1.35 × 10^2
263	5.41 × 10^2	1.46 × 10^4	3.18 × 10^2
273	1.20 × 10^3	2.98 × 10^4	6.30 × 10^2
283	3.31 × 10^3	6.86 × 10^4	13.9 × 10^3
293	7.76 × 10^3	14.6 × 10^5	30.5 × 10^3
313	1.89 × 10^4	30.6 × 10^5	

The $^{31}P\{^1H\}$ NMR spectrum of **5** at room temperature shows a singlet at 17.4 ppm along with tin satellites ($J_{P-^{117}Sn} = J_{P-^{119}Sn} = 119$ Hz). Lowering the sample temperature produces a broadening of the resonance. However, decoalescence is not observed at 183 K. The $^{31}P\{^1H\}$ NMR spectrum of **6** at room temperature also contains a singlet, in this case at 4.6 ppm, along with tin satellites ($J_{P-^{117}Sn} = J_{P-^{119}Sn} = 136$ Hz). At 183 K, the spectrum of **6** shows an AB spin system centered at

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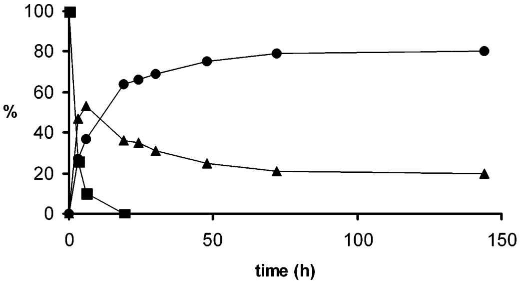


Figure 5. Time vs composition of the reaction mixture of **1** with benzylidenacetophenone: (■) percent of remaining **1**; (▲) percent of $\overline{\text{Os}(\text{SnPh}_2\text{Cl})\{\text{C(Ph)CHC(O}}\text{)Ph}\}(\eta^2\text{-H}_2)(\text{P}^i\text{Pr}_3)_2$ (**7**); (●) percent of $\overline{\text{Os}(\text{SnPh}_2\text{Cl})\{\text{C}_6\text{H}_4\text{C(O}}\text{)CH=CHPh}\}(\eta^2\text{-H}_2)(\text{P}^i\text{Pr}_3)_2$ (**8**).

3.1 ppm and defined by $\Delta\nu = 655$ Hz and $J_{A-B} = 188$ Hz. The behavior of the ^{31}P{^{1}H} NMR spectrum of **6** is consistent with that of the spectra of **5**. Their dependence on the temperature agrees well with the dependence of the spectra of **4**, and it indicates that in this type of compounds the rotation of the phosphine ligands around the Os−P bond can be also blocked on the NMR time scale. The blockage affords a single conformer with inequivalent phosphines.

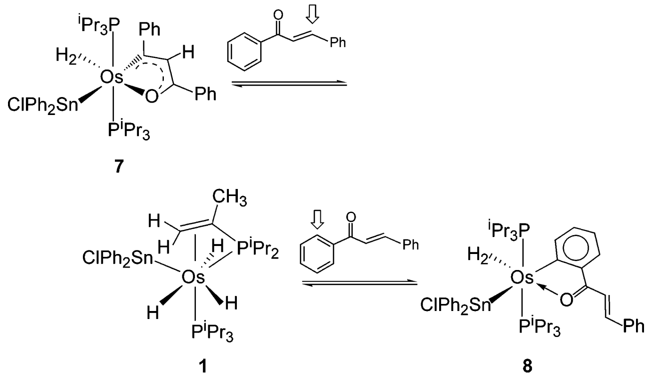
4. Reaction with Benzylideneacetophenone. In a previous work, we have shown that the 14-valence-electron monohydride **a** activates an *o*-CH bond of aromatic ketones.[24] The previous section describes the C$_\beta$(sp^2)−H bond activation of α,β-unsaturated ketones promoted by the monohydride **a**. To study the preference for *o*-CH activation or C$_\beta$(sp^2)−H activation, we have investigated the reaction of **1** with benzylideneacetophenone. This substrate contains both functions bonded to the carbonyl unit, a phenyl group and a carbon−carbon double bond, which could be activated in a competitive manner.

The reaction was carried out at room temperature in a NMR tube using benzene-d_6 or toluene-d_8 as solvent and a **1** to ketone molar ratio of 1:1.52. This was followed by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. Figure 5 summarizes the composition of the reaction mixture as a function of time.

Monohydride **a** activates both the C$_\beta$(sp^2)−H of the olefinic moiety and an *o*-CH bond of the phenyl group, to give $\overline{\text{Os}(\text{SnPh}_2\text{Cl})\{\text{C(Ph)CHC(O}}\text{)Ph}\}(\eta^2\text{-H}_2)(\text{P}^i\text{Pr}_3)_2$ (**7**) and $\overline{\text{Os}(\text{SnPh}_2\text{Cl})\{\text{C}_6\text{H}_4\text{C(O}}\text{)CH=CHPh}\}(\eta^2\text{-H}_2)(\text{P}^i\text{Pr}_3)_2$ (**8**), respectively (Scheme 4). The activation of the C$_\beta$(sp^2)−H bond of the olefin is kinetically favored with regard to the *o*-CH bond activation of the phenyl group. However, complex **8** resulting from the *o*-CH bond activation of the phenyl group is thermodynamically more stable than **7**. Thus, after 6 h, the ^{1}H and ^{31}P{^{1}H} NMR spectra of the solutions resulting from the addition of 1.52 equiv of benzylidenacetophenone to **1** show a 1:5.3:3.7 mixture of **1**, **7**, and **8** while, after 144 h, the starting complex has disappeared and the **7** to **8** molar ratio is 1:4.

The lower strength of a H−vinyl bond with regard to a H−Ph bond could be the reason for the kinetic preference for the C$_\beta$(sp^2)−H bond activation over the *o*-CH bond activation, whereas the Os−Ph bond being stronger than the Os−vinyl bond appears to be the driving force for the thermodynamic preference for the formation of **8** over the formation of **7**.[1a,53]

Scheme 4



In the ^{1}H NMR spectrum of **7** at room temperature the most noticeable features are the presence of a singlet at 6.46 ppm, corresponding to the CH proton of the five-membered heterometalla ring, and a triplet at −10.97 ppm with a H−P coupling constant of 12.8 Hz due to the elongated dihydrogen ligand. At about 223 K the decoalescence of the latter resonance takes place, and at 213 K two broad signals at −10.9 and −11.2 ppm are observed. In agreement with a significant contribution of the osmafuran resonance form to the structure of **7**, in the ^{13}C{^{1}H} NMR spectrum, the OsC resonance appears as a triplet at 240.4 ppm with a C−P coupling constant of 6 Hz. At room temperature, the ^{31}P{^{1}H} NMR spectrum shows a singlet at 4.3 ppm, along with the tin satellites ($J_{P-^{117}Sn} = J_{P-^{119}Sn} = 134$ Hz). At 193 K, the singlet is converted into an AB spin system centered at 3.2 ppm and defined by $\Delta\nu = 616$ Hz and $J_{A-B} = 181$ Hz. The ^{119}Sn{^{1}H} NMR spectrum at room temperature contains a triplet at −36.5 ppm.

When the reaction of **1** with benzylideneacetophenone is carried out in a Schlenk tube for 9 days at room temperature, complex **8** can be isolated as a violet solid in 52% yield.

The presence of an intact CH=CHPh moiety in the ketone ligand of **8** is strongly supported by the ^{1}H NMR spectrum of this compound at room temperature, which shows two doublets at 8.72 and 7.50 ppm with a H−H coupling constant of 15.6 Hz, due to the olefinic protons of the ortho-metalated ketone. At this temperature, the elongated dihydrogen ligand gives rise to a broad signal centered at −11.22 ppm. In agreement with the behavior of **5** and **6**, this resonance is temperature dependent. At 353 K, it appears as a triplet with a H−P coupling constant of 12.5 Hz. At about 283 K decoalescence occurs, and at 233 K an ABX$_2$ spin system defined by δ_A −10.49, δ_B −12.12, $J_{A-X} = 9.5$ Hz, $J_{B-X} = 13.8$ Hz, and $J_{A-B} = 37$ Hz is observed.

The T_1 values of the OsH$_2$ resonance of **8** were determined over the temperature range 273−223 K. In agreement with the elongated dihydrogen character of the compound, a T_1(min) value of 68 ± 1 ms was found for both resonances at 243 K, after the decoalescence. It leads to a separation between the hydrogens atom of the dihydrogen of 1.45 Å.

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Complex **8** is other example of blocked rotation of the dihydrogen ligand on the NMR time scale. In this case, the activation parameters for the rotation process are $\Delta H^{\ddagger} = 10.6 \pm 0.6$ kcal mol^{-1} and $\Delta S^{\ddagger} = -6.3 \pm 1.5$ cal mol^{-1} K^{-1}.

In the ^{13}C{^{1}H} NMR spectrum, the most noticeable resonance is that due to the metalated carbon atom of the ketone, which appears as a triplet at 195.4 ppm with a C−P coupling constant of 8.3 Hz. The ^{31}P{^{1}H} NMR spectrum at room temperature shows a singlet at 8.0 ppm, along with the tin satellites. At 183 K, the singlet is converted into an AB spin system centered at 6.1 ppm and defined by $\Delta\nu = 739$ Hz and $J_{A-B} = 204$ Hz. The ^{119}Sn{^{1}H} NMR spectrum at room temperature contains a triplet at 10.1 ppm, with a ^{119}Sn−P coupling constant of 113 Hz.

Concluding Remarks

The 14-valence-electron monohydride OsH($SnPh_2Cl$)(P^iPr_3)$_2$, in contrast to the 16-valence-electron species $OsH_2(\eta^2\text{-}H_2)(P^iPr_3)_2$, activates a terminal C(sp^2)−H bond of both types of pyridinic substrates, RCH=CH−py and RCH=N−py. The activation of 2-vinylpyridine (R = H) leads to the elongated dihydrogen derivative Os($SnPh_2Cl$)(NC_5H_4-*o*-CH=CH)(η^2-H_2)(P^iPr_3)$_2$, which in solution is in equilibrium with its tautomer OsH(NC_5H_4-*o*-CH=CH)($HSnPh_2Cl$)(P^iPr_3)$_2$. In the latter, the stannane is bonded to the transition metal by an Os−H−Sn three-center bond. The activation of (*E*)-*N*-(phenylmethylene)-2-pyridinamine (R = Ph) affords Os($SnPh_2Cl$)(NC_5H_4-*o*-NCPh)(η^2-H_2)(P^iPr_3)$_2$. According to the ^{13}C{^{1}H} NMR spectrum of this compound, the Os−C bond in the heterometallacycle is intermediate between single and double.

The monohydride OsH($SnPh_2Cl$)(P^iPr_3)$_2$ also activates a C$_\beta$(sp^2)−H bond of α,β-unsaturated ketones to give elongated dihydrogen derivatives, Os($SnPh_2Cl$){C(R)-CHC(O)R′}(η^2-H_2)(P^iPr_3)$_2$, which show blocked rotation of the dihydrogen ligand on the NMR time scale. The ^{13}C{^{1}H} NMR spectra of those compounds and the X-ray diffraction structure of Os($SnPh_2Cl$){CHCHC(O)CH_3}(η^2-H_2)(P^iPr_3)$_2$ indicate that the osmafuran resonance form **5B** (Scheme 3) makes a very important contribution to the bonding in the heterometallacycle.

These five-membered rings are less stable than that formed by the osmium atom and an ortho-metalated ketone. However, the activation of a C$_\beta$(sp^2)−H bond of an α,β-unsaturated ketone is kinetically favored with regard to the *o*-CH bond activation of the aryl group of an aromatic ketone. In agreement with this, the complex OsH_3($SnPh_2Cl$){η^2-CH_2=C(CH_3)P^iPr_2}(P^iPr_3) reacts with benzylideneacetophenone to afford initially Os($SnPh_2Cl$){C(Ph)CHC(O)Ph}(η^2-H_2)(P^iPr_3)$_2$, as a consequence of the C$_\beta$(sp^2)−H bond activation of the olefin moiety. In toluene or benzene, the latter isomerizes into Os($SnPh_2Cl$){C_6H_4C(O)CH=CHPh}(η^2-H_2)(P^iPr_3)$_2$, resulting from the *o*-CH activation of the PhCO aryl group.

In conclusion, the 14-valence-electron monohydride OsH($SnPh_2Cl$)(P^iPr_3)$_2$ activates vinylic C−H bonds disposed in a γ-position with regard to a donor heteroatom, which acts as a leading group. The resulting products are elongated dihydrogen derivatives, which show blocked rotation of the dihydrogen on the NMR time scale and where the formed Os−C bonds are intermediate between single and double.

Experimental Section

All reactions were carried out under an argon atmosphere using Schlenk tube techniques. Solvents were dried and purified by known procedures and distilled under argon prior to use. The complex OsH_3($SnPh_2Cl$){η^2-CH_2=C(CH_3)P^iPr_2}(P^iPr_3) (**1**)[23] and (*E*)-*N*-(phenylmethylene)-2-pyridinamine[16] were prepared as previously described. Infrared spectra were recorded on a Perkin-Elmer Spectrum One spectrometer as solids (Nujol mull). ^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H}, and ^{119}Sn{^{1}H} NMR spectra were recorded on Varian Gemini 2000, Varian UNITY 300, Bruker AXR 300, and Bruker Avance 400 instruments. Chemical shifts are referenced to residual solvent peaks (^{1}H and ^{13}C{^{1}H}), external H_3PO_4 (^{31}P{^{1}H}), or Me_4Sn (^{119}Sn{^{1}H}). The coupling constants *J* and *N* ($N = J_{P-H} + J_{P'-H}$ for ^{1}H; $N = J_{P-C} + J_{P'-C}$ for ^{13}C{^{1}H}) are given in hertz. C, H, and N analyses were measured on a Perkin-Elmer 2400 CHNS/O analyzer.

Preparation of Os($SnPh_2Cl$)(NC_5H_4-*o*-CH=CH)(η^2-H_2)(P^iPr_3)$_2$ (2). 2-Vinylpyridine (29.1 μL, 0.27 mmol) was added to a solution of **1** (150 mg, 0.19 mmol) in toluene (10 mL). After the solution was stirred for 24 h at room temperature, the color changed from yellow to brown. The resulting solution was filtered through Celite and was taken to dryness. Subsequent addition of pentane caused the precipitation of a dark beige solid, which was washed with pentane and dried in vacuo. Yield: 87 mg (53%). Anal. Calcd for $C_{37}H_{60}ClNOsP_2Sn$: C, 48.03; H, 6.53. Found: C, 48.01; H, 6.70. IR (Nujol, cm^{-1}): ν(OsH) 2018 (w). ^{1}H NMR (300 MHz, C_7D_8, 348 K): δ 10.88 (d, $J_{H-H} = 9.6$, 1H, −NC_5H_4), 9.99 (dt, $J_{H-H} = 9.6$, $J_{H-H} = 5.1$, 1H, Os−C*H*=CH), 8.17 (d, $J_{H-H} = 7.1$, 4H, SnPh H_{ortho}), 7.34 (d, $J_{H-H} = 9.6$, 1H, −CH=C*H*), 7.28 (t, $J_{H-H} = 7.1$, 4H, SnPh H_{meta}), 7.13 (t, $J_{H-H} = 7.1$, 2H, SnPh H_{para}), 6.97−6.88 (m, $J_{H-H} = 7.2$, $J_{H-H} = 6.6$, 2H, −NC_5H_4), 6.54 (dt, $J_{H-H} = 7.1$, $J_{H-H} = 1.8$, 1H, −NC_5H_4), 2.24 (m, 6H, PC*H*(CH_3)$_2$), 1.01 (dvt, *N* = 20.0, $J_{H-H} = 7.1$, 18H, PCH(CH_3)$_2$), 0.83 (dvt, *N* = 19.5, $J_{H-H} = 6.9$, 18H, PCH(CH_3)$_2$), −11.11 (td, $J_{H-P} = 11.6$, $J_{H-H} = 5.1$, 2H, OsH). ^{31}P{^{1}H} NMR (121.42 MHz, C_7D_8, 353 K): δ 6.2 (s with tin satellites $J_{P-^{119}Sn} = J_{P-^{117}Sn} = 111$). ^{13}C{^{1}H} NMR (100.56 MHz, C_6D_6, 293 K, plus apt): δ 170.0 (s, −NC_5H$_4$), 161.2 (s, Os*C*), 156.4 (s, C$_{ipso}$, $SnPh_2Cl$), 137.8 (s, −NC_5H$_4$), 136.8 (s, $SnPh_2Cl$), 136.0 (s, −NC_5H$_4$), 130.5 (br, −*C*H=), 127.6 (s, $SnPh_2Cl$), 127.3 (s, $SnPh_2Cl$), 120.0 (s, −NC_5H$_4$), 118.4 (s, −NC_5H$_4$), 29.0 (vt, *N* = 20.9, P*C*H(CH_3)$_2$), 20.3, 19.6 (both s, PCH(*C*H$_3$)$_2$). ^{119}Sn{^{1}H} NMR (111.83 MHz, C_6D_6, 293 K): δ −3.1 (t, $J_{P-^{119}Sn} = 111$). T_1(min) (ms, OsH_2, 300 MHz, C_7D_8, 228 K): 61 ± 1 (−11.19 ppm).

Preparation of Os($SnPh_2Cl$)(NC_5H_4-*o*-NCPh)(η^2-H_2)(P^iPr_3)$_2$ (4). (*E*)-*N*-(Phenylmethylene)-2-pyridinamine (49.8 mg, 0.27 mmol) was added to a solution of **1** (150 mg, 0.19 mmol) in toluene (10 mL). After the solution was stirred for 5 days at room temperature, the color changed from yellow to orange. The resulting solution was filtered through Celite and was taken to dryness. Subsequent addition of pentane caused the precipitation of a beige solid, which was washed with pentane and dried in vacuo. Yield: 162 mg (60%). Anal. Calcd for $C_{42}H_{63}ClN_2OsP_2Sn$: C, 50.33; H, 6.33. Found: C, 50.15; H, 6.42. IR (Nujol, cm^{-1}): ν(OsH) 2019 (w), ν(CN) 1604 (w). ^{1}H NMR (300 MHz, C_6D_6, 293 K): δ 11.19 (d, $J_{H-H} = 6.5$, 1H,

$-\mathrm{NC_5}H_4$), 8.96 (d, $J_{\mathrm{H-H}} = 7.5$, 2H, Ph), 8.26 (d, $J_{\mathrm{H-H}} = 8.1$, 4H, SnPh H_{ortho}), 7.86, (d, $J_{\mathrm{H-H}} = 6.5$, 1H, $-\mathrm{NC_5}H_4$), 7.30 (t, $J_{\mathrm{H-H}} = 8.1$, 4H, SnPh H_{meta}), 7.18 (t, $J_{\mathrm{H-H}} = 8.1$, 2H, SnPh H_{para}), 7.33−7.15 (m, 3H, Ph), 7.08 (t, $J_{\mathrm{H-H}} = 6.5$, 1H, $-\mathrm{NC_5}H_4$), 6.62 (t, $J_{\mathrm{H-H}} = 6.5$, 1H, $-\mathrm{NC_5}H_4$), 2.15 (m, 6H, $\mathrm{PC}H\mathrm{(CH_3)_2}$), 0.79 (dvt, $N = 13.2$, $J_{\mathrm{H-H}} = 6.6$, 18H, $\mathrm{PCH(C}H_3)_2$), 0.70 (dvt, $N = 12.9$, $J_{\mathrm{H-H}} = 6.9$, 18H, $\mathrm{PCH(C}H_3)_2$), −10.09 (t, $J_{\mathrm{H-P}} = 10.5$, 2H, OsH). ^{1}H NMR (300 MHz, $\mathrm{C_7D_8}$, 183 K, hydride region): δ −10.10 (br, 2H, OsH). ^{31}P{^{1}H} NMR (121.42 MHz, $\mathrm{C_6D_6}$, 293 K): δ −2.6 (s, with tin satellites $J_{\mathrm{P-^{119}Sn}} = J_{\mathrm{P-^{117}Sn}} = 122$). ^{31}P{^{1}H} NMR (121.42 MHz, $\mathrm{C_7D_8}$, 193 K): δ −3.3 (AB spin system, $\Delta\nu = 492$ Hz, $J_{\mathrm{A-B}} = 186$). ^{13}C{^{1}H} NMR (100.56 MHz, $\mathrm{C_6D_6}$, 293 K, plus apt): δ 237.1 (t, $J_{\mathrm{C-P}} = 7.2$, Os*C*), 173.2 (s, $\mathrm{N}C_5\mathrm{H_4}$), 158.7 (s, $\mathrm{N}C_5\mathrm{H_4}$), 154.9 (s, $\mathrm{C_{ipso}}$, $\mathrm{SnPh_2Cl}$), 150.1 (s, Ph), 138.1 (s, Ph), 137.9 (s, $\mathrm{SnPh_2Cl}$), 134.9 (s, Ph), 130.8 (s, $\mathrm{SnPh_2Cl}$), 128.5 (s, Ph), 120.8 (s, Ph), 118.4 (s, Ph), 30.4 (vt, $N = 24.8$, $\mathrm{P}C\mathrm{H(CH_3)_2}$), 20.6, 20.2,(both s, $\mathrm{PCH(}C\mathrm{H_3)_2}$). ^{119}Sn{^{1}H} NMR (111.83 MHz, $\mathrm{C_6D_6}$, 293 K): δ −0.33 (t, $J_{\mathrm{P-^{119}Sn}} = 122$). T_1(min) (ms, $\mathrm{OsH_2}$, 300 MHz, $\mathrm{C_7D_8}$, 248 K): 42 ± 4 (−10.13 ppm).

Preparation of $\mathbf{Os(SnPh_2Cl)\{CHCHC(O)CH_3\}(\eta^2\text{-}H_2)(P^iPr_3)_2}$ (5). Methyl vinyl ketone (22.4 μL, 0.27 mmol) was added to a solution of **1** (150 mg, 0.19 mmol) in toluene (10 mL). After the solution was stirred for 24 h at room temperature, the color had changed from yellow to orange. The resulting solution was filtered through Celite and was taken to dryness. Subsequent addition of pentane caused the precipitation of an orange solid, which was washed with pentane and dried in vacuo. Yield: 120 mg (70%). Anal. Calcd for $\mathrm{C_{34}H_{59}ClOOsP_2Sn}$: C, 45.87; H, 6.68. Found: C, 45.56; H, 6.72. IR (Nujol, cm^{-1}): ν(OsH) 2021 (w), ν(CO) 1575 (m). ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$, 293 K): δ 11.77 (q, $J_{\mathrm{H-H}} = 6.3$, $J_{\mathrm{H-H}} = 8.4$, 1H, $=\mathrm{C}H$), 8.39 (d, $J_{\mathrm{H-H}} = 7.2$, 4H, SnPh H_{ortho}), 7.32 (t, $J_{\mathrm{H-H}} = 7.2$, 4H, SnPh H_{meta}), 7.18 (t, $J_{\mathrm{H-H}} = 7.2$, 2H, SnPh H_{para}), 6.87 (d, $J_{\mathrm{H-H}} = 8.4$, 1H, $\mathrm{Os-C}H=$), 2.27 (s, 3H, $\mathrm{C}H_3$), 2.16 (m, 6H, $\mathrm{PC}H\mathrm{(CH_3)_2}$), 1.03 (dvt, $N = 13.4$, $J_{\mathrm{H-H}} = 6.9$, 18H, $\mathrm{PCH(C}H_3)_2$), 0.91 (dvt, $N = 13.1$, $J_{\mathrm{H-H}} = 6.9$, 18H, $\mathrm{PCH(C}H_3)_2$), −11.76 (br, 2H, OsH). ^{1}H NMR (300 MHz, $\mathrm{C_7D_8}$, 213 K, hydride region): δ −10.79 (part A of an $\mathrm{ABX_2}$ spin system, 1H, $J_{\mathrm{A-X}} = 9$, $J_{\mathrm{A-B}} = 27$), −12.69 (part B of an $\mathrm{ABX_2}$ spin system, 1H, $J_{\mathrm{B-X}} = 13$, $J_{\mathrm{A-B}} = 27$). ^{31}P{^{1}H} NMR (121.42 MHz, $\mathrm{C_6D_6}$, 293 K): δ 17.4 (s with tin satellites $J_{\mathrm{P-^{117}Sn}} = J_{\mathrm{P-^{119}Sn}} = 119$). ^{13}C{^{1}H} NMR (100.56 MHz, $\mathrm{C_6D_6}$, 293 K, plus apt): δ 233.1 (s, Os*C*), 207.1 (s, *C*O), 156.2 (s, $\mathrm{C_{ipso}}$, $\mathrm{SnPh_2Cl}$), 137.8 (s, $\mathrm{SnPh_2Cl}$), 129.1 (s, $\mathrm{SnPh_2Cl}$), 128.8 (s, $-C\mathrm{H}=$), 127.5 (s, $\mathrm{SnPh_2Cl}$), 28.4 (vt, $N = 26.6$, $\mathrm{P}C\mathrm{H(CH_3)_2}$), 19.9 (s, $\mathrm{PCH(}C\mathrm{H_3)_2}$). ^{119}Sn{^{1}H} NMR (111.83 MHz, $\mathrm{C_6D_6}$, 293 K): δ 43.7 (t, $J_{\mathrm{P-^{119}Sn}} = 119$). T_1(min) (ms, $\mathrm{OsH_2}$, 300 MHz, $\mathrm{C_7D_8}$, 233 K): 71 ± 1 (−10.87 ppm, −12.84 ppm).

Preparation of $\mathbf{Os(SnPh_2Cl)\{C(Ph)CHC(O)CH_3\}(\eta^2\text{-}H_2)(P^iPr_3)_2}$ (6). Benzylideneacetone (39.9 μL, 0.27 mmol) was added to a solution of **1** (150 mg, 0.19 mmol) in toluene (10 mL). After the solution was stirred for 24 h at room temperature, the color had changed from yellow to orange. The resulting solution was filtered through Celite and was taken to dryness. Subsequent addition of pentane caused the precipitation of a red solid, which was washed with pentane and dried in vacuo. Yield: 147.6 mg (60%). Anal. Calcd for $\mathrm{C_{61}H_{40}ClOOsP_2Sn}$: C, 49.82; H, 6.38. Found: C, 49.99; H, 6.21. IR (Nujol, cm^{-1}): ν(OsH) 2021 (w), ν(CO) 1575 (m). ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$, 293 K): δ 8.42 (d, $J_{\mathrm{H-H}} = 7.5$, 4H, SnPh H_{ortho}), 8.13 (d, $J_{\mathrm{H-H}} = 7.5$, 2H, Ph), 7.34 (s, 1H, $-\mathrm{C}H=$), 7.30 (t, $J_{\mathrm{H-H}} = 7.5$, 4H, SnPh H_{meta}), 7.19−7.12 (m, 2H, Ph), 7.16 (t, $J_{\mathrm{H-H}} = 7.5$, 2H, SnPh H_{para}), 7.07 (d, $J_{\mathrm{H-H}} = 6.9$, 1H, Ph), 2.42 (t, $J_{\mathrm{H-P}} = 1.8$, 3H, $\mathrm{C}H_3$), 2.23 (m, 6H, $\mathrm{PC}H\mathrm{(CH_3)_2}$), 0.93 (dvt, $N = 13.5$, $J_{\mathrm{H-H}} = 6.9$, 18H, $\mathrm{PCH(C}H_3)_2$), 0.86 (dvt, $N = 13.2$, $J_{\mathrm{H-H}} = 6.6$, 18H, $\mathrm{PCH(C}H_3)_2$), −11.29 (t, $J_{\mathrm{H-P}} = 13.2$, 2H, OsH). ^{1}H NMR (300 MHz, $\mathrm{C_7D_8}$, 213 K, hydride region): δ −11.36 (nonresolved $\mathrm{ABX_2}$ spin system, $\Delta\nu = 100$ Hz, $J_{\mathrm{A-B}} = 84$). ^{31}P{^{1}H} NMR (121.42 MHz, $\mathrm{C_6D_6}$, 293 K): δ 4.6 (s with tin satellites $J_{\mathrm{P-^{119}Sn}} = J_{\mathrm{P-^{117}Sn}} = 136$). ^{31}P{^{1}H} NMR (121.42 MHz, $\mathrm{C_7D_8}$, 183 K): δ 3.1 (AB spin system $\Delta\nu = 655$ Hz, $J_{\mathrm{A-B}} = 188$). ^{13}C{^{1}H} NMR (100.56 MHz, $\mathrm{C_6D_6}$, 293 K plus apt): δ 241.4 (t, $J_{\mathrm{C-P}} = 5.5$, Os*C*), 204.6 (t, $J_{\mathrm{C-P}} = 1.8$, *C*O), 156.2 (s, $C_{\mathrm{ipso,}}$ $\mathrm{SnPh_2Cl}$), 149.2 (s, $C_{\mathrm{ipso,}}$ Ph), 137.6 (s, $\mathrm{SnPh_2Cl}$), 131.1 (br, Ph), 130.3 (s, Ph), 128.6 (s, Ph), 128.3 (s, $=C\mathrm{H}-$), 127.5 (s, $\mathrm{SnPh_2Cl}$), 127.2 (s, $\mathrm{SnPh_2Cl}$), 30.4 (vt, $N = 25.3$, $\mathrm{P}C\mathrm{H(CH_3)_2}$), 23.9 (s, $C\mathrm{H_3}$), 20.8, 20.3 (both s, $\mathrm{PCH(}C\mathrm{H_3)_2}$). ^{119}Sn{^{1}H} NMR (111.83 MHz, $\mathrm{C_6D_6}$, 293K): δ −47.5 (t, $J_{\mathrm{P-^{119}Sn}} = 136$). T_1(min) (ms, $\mathrm{OsH_2}$, 300 MHz, $\mathrm{C_7D_8}$, 243 K): 63 ± 3 (−11.33 ppm).

Reaction of 1 with Benzylideneacetophenone. In a 5 mm NMR tube **1** (20 mg, 0.025 mmol) and benzylideneacetophenone (8.0 mg, 0.038 mmol) were dissolved in 0.4 mL of benzene-d_6, and the reaction was followed by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. After 6 h, the ^{1}H and ^{31}P{^{1}H} NMR spectra showed a 10:53:37 mixture of **1**, $\mathrm{Os(SnPh_2Cl)\{C(Ph)CHC(O)Ph\}(\eta^2\text{-}H_2)(P^iPr_3)_2}$ (**7**), and $\mathrm{Os(SnPh_2Cl)\{C_6H_4C(O)CH{=}CHPh\}(\eta^2\text{-}H_2)(P^iPr_3)_2}$ (**8**). After 144 h, the ^{1}H and ^{31}P{^{1}H} NMR spectra showed a 20:80 mixture of complexes **7** and **8**. Complex **8** could be isolated in pure form as follows: benzylideneacetophenone (56.5 mg, 0.27 mmol) was added to a solution of **1** (150 mg, 0.19 mmol) in toluene (10 mL). After the solution was stirred for 9 days at room temperature, the color had changed from yellow to deep violet. The resulting solution was filtered through Celite and was taken to dryness. Subsequent addition of pentane caused the precipitation of a violet solid, which was washed with pentane and dried in vacuo. Yield: 92 mg (52%). Anal. Calcd for $\mathrm{C_{45}H_{63}ClOOsP_2Sn}$: C, 52.66; H, 6.19. Found: C, 52.60; H, 6.79. IR (Nujol, cm^{-1}): ν(OsH) 2023 (w), ν(CO) 1586 (m).

Spectroscopic data of **7** are as follows. ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$, 293 K): δ 8.40 (d, $J_{\mathrm{H-H}} = 6.8$, 4H, SnPh H_{ortho}), 7.33−7.25 (m, overlapped signals 4H, SnPh H_{meta}), 7.17−7.09 (m, overlapped signals 2H, SnPh H_{para}), 7.33−6.98 (m, overlapped signals, 10H, Ph), 6.46 (s, 1H, $-\mathrm{C{=}C}H$), 2.21 (m, 6H, $\mathrm{PC}H\mathrm{(CH_3)_2}$), 0.96 (dvt, $N = 10.2$, $J_{\mathrm{H-H}} = 5.1$, 18H, $\mathrm{PCH(C}H_3)_2$), 0.83 (dvt, $N = 9.9$, $J_{\mathrm{H-H}} = 5.1$, 18H, $\mathrm{PCH(C}H_3)_2$), −10.97 (t, $J_{\mathrm{H-H}} = 12.8$, 2H, OsH). ^{1}H NMR (300 MHz, $\mathrm{C_7D_8}$, 213 K, hydride region): nonresolved $\mathrm{ABX_2}$ spin system, −10.90 (part A), −11.20 (part B). ^{31}P{^{1}H} NMR (161.9 MHz, $\mathrm{C_6D_6}$, 293 K): δ 4.3 (s with tin satellites $J_{\mathrm{P-^{119}Sn}} = J_{\mathrm{P-^{117}Sn}} = 134$). ^{31}P{^{1}H} NMR (121.42 MHz, $\mathrm{C_7D_8}$, 193 K): δ 3.2 (AB spin system $\Delta\nu = 616$ Hz, $J_{\mathrm{A-B}} = 181$). ^{13}C{^{1}H} NMR (100.56 MHz, $\mathrm{C_6D_6}$, 293 K, plus apt): δ 240.4 (t, $J_{\mathrm{C-P}} = 6.0$, Os*C*), 198.2 (t, $J_{\mathrm{C-P}} = 2.1$, *C*O), 156.0 (s, $\mathrm{C_{ipso}}$, $\mathrm{SnPh_2Cl}$), 150.0 (s, $\mathrm{C_{ipso}}$, Ph), 138.9 (s, $\mathrm{C_{ipso}}$, Ph), 137.3 (s, $\mathrm{SnPh_2Cl}$), 131.9 (s, Ph), 130.3 (s, Ph), 129.2 (s, Ph), 128.8 (s, Ph), 128.7 (s, Ph), 128.6 (s, Ph), 127.5 (s, $\mathrm{SnPh_2Cl}$), 127.3 (s, $\mathrm{SnPh_2Cl}$), 126.5 (s, $-C\mathrm{H{=}C}$), 30.4 (vt, $N = 25.1$, $\mathrm{P}C\mathrm{H(CH_3)_2}$), 20.9, 20.3 (both s, $\mathrm{PCH(}C\mathrm{H_3)_2}$). ^{119}Sn{^{1}H} NMR (111.83 MHz, $\mathrm{C_6D_6}$, 293 K): δ −36.5 (t, $J_{\mathrm{P-^{119}Sn}} = 134$).

Spectroscopic data of **8** are as follows. ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$, 293 K): δ 8.72 (d, $J_{\mathrm{H-H}} = 15.6$, 1H, $-\mathrm{C}H\mathrm{{=}CH}$-), 8.39 (d, $J_{\mathrm{H-H}} = 7.5$, 4H, SnPh H_{ortho}), 8.33 (d, $J_{\mathrm{H-H}} = 7.5$, 1H, Ph), 7.69 (d, $J_{\mathrm{H-H}} = 6.6$, $\mathrm{C_6}H_4$), 7.55 (d, $J_{\mathrm{H-H}} = 6.6$, 2H, $\mathrm{C_6}H_4$), 7.50 (d, $J_{\mathrm{H-H}} = 15.6$, 1H, $-\mathrm{CH{=}C}H-$), *7.32 (t,* $J_{\mathrm{H-H}} = 7.5$, 4H, SnPh H_{meta}), 7.10 (t, $J_{\mathrm{H-H}} = 7.5$, 2H, SnPh H_{para}), 7.06 (m, 2H, Ph), 6.94 (t, $J_{\mathrm{H-H}} = 6.9$, 1H, Ph), 6.85 (t, $J_{\mathrm{H-H}} = 6.9$, 1H, Ph), 2.20 (m, 6H, $\mathrm{PC}H\mathrm{(CH_3)_2}$), 1.04 (dvt, $N = 13.5$, $J_{\mathrm{H-H}} = 6.9$, 18H, $\mathrm{PCH(C}H_3)_2$), 0.71 (dvt, $N = 12.9$, $J_{\mathrm{H-H}} = 6.6$, 18H, $\mathrm{PCH(C}H_3)_2$), −11.22 (br, 2H, OsH). ^{1}H NMR (300 MHz, $\mathrm{C_7D_8}$, 233 K, hydride region): δ −10.49 (part A of an $\mathrm{ABX_2}$ spin system, $J_{\mathrm{A-X}} = 9.5$, $J_{\mathrm{A-B}} = 37$) −12.12 (part B of an $\mathrm{ABX_2}$ spin system, $J_{\mathrm{B-X}} = 13.8$, $J_{\mathrm{A-B}} = 37$). ^{31}P{^{1}H} NMR (121.42 MHz, $\mathrm{C_6D_6}$, 293 K): δ 8.0 (s with tin satellites $J_{\mathrm{P-^{119}Sn}} = J_{\mathrm{P-^{117}Sn}} = 113$). ^{31}P{^{1}H} NMR (121.42 MHz, $\mathrm{C_7D_8}$, 183 K): δ 6.1 (AB spin system $\Delta\nu = 739$ Hz, $J_{\mathrm{A-B}} = 204$). ^{13}C{^{1}H} NMR (100.56 MHz, $\mathrm{C_6D_6}$, 293 K, plus apt): δ 201.6 (s, *C*O), 195.4, (t, $J_{\mathrm{C-P}} = 8.3$, Os*C*), 156.2 (s, $\mathrm{C_{ipso}}$, $\mathrm{SnPh_2Cl}$), 147.5 (s, $-C\mathrm{H{=}CH}-$), 144.0 (s, $C_6\mathrm{H_4}$), 142.5 (s, $C_6\mathrm{H_4}$), 137.1 (s, $\mathrm{SnPh_2Cl}$), 135.5 (s, $\mathrm{C_{ipso}}$, Ph), 132.6 (s, $C_6\mathrm{H_4}$), 130.9 (s, $C_6\mathrm{H_4}$), 130.6 (s, $C_6\mathrm{H_4}$), 129.2 (s, Ph), 129.1 (s, Ph), 127.6 (s, $\mathrm{SnPh_2Cl}$), 127.3 (s, $\mathrm{SnPh_2Cl}$), 120.4 (s, Ph), 118.2 (s,

Table 5. Crystal Data and Data Collection and Refinement Details for 2 and 5

	2	**5**
	Crystal Data	
formula	$C_{37}H_{60}ClNOsP_2Sn$	$C_{34}H_{59}ClOOsP_2Sn$
mol wt	925.14	890.09
color, habit	yellow, prism	orange, irregular block
symmetry, space group	triclinic, $P\bar{1}$	monoclinic, $P2_1/n$
a, Å	11.0322(12)	10.5516(8)
b, Å	11.7494(13)	19.3519(14)
c, Å	16.8982(18)	17.6856(13)
α, deg	102.092(2)	
β, deg	91.235(2)	94.7080(10)
γ, deg	117.825(2)	
V, Å^3	1876.0(4)	3599.1(5)
Z	2	4
D_{calcd}, g cm^{-3}	1.638	1.643
	Data Collection and Refinement	
diffractometer	Bruker Smart APEX	
λ(Mo Kα), Å	0.710 73	
monochromator	graphite oriented	
scan type	ω scans	
μ, mm^{-1}	4.231	4.409
2θ range, deg	3−57	3−57
temp, K	100	100
no. of data collected	18 845	44 897
no. of unique data	8787 (R_{int} = 0.030)	8779 (R_{int} = 0.0308)
no. of params/restraints	414/0	388/0
R1^a ($F^2 > 2\sigma(F^2)$)	0.0278	0.0185
wR2^b (all data)	0.0417	0.0380
S^c (all data)	0.782	0.944

^{a} $R1(F) = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $wR2(F^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. ^{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.

CH=*C*H), 28.3 (vt, N = 25.7, P*C*H$(CH_3)_2$), 20.4, 19.5 (both s, PCH$(\mathit{C}H_3)_2$). $^{119}Sn\{^1H\}$ NMR (111.83 MHz, C_6D_6, 293 K): δ 10.1 (t, $J_{P-^{119}Sn}$ = 113). T_1(min) (ms, OsH_2, 300 MHz, C_7D_8, 248 K): 68 ± 1 (−10.54, −12.08 ppm).

Structural Analysis of Complexes 2 and 5. X-ray data were collected on a Bruker Smart APEX CCD diffractometer equipped with a normal-focus, 2.4 kW sealed-tube source (molybdenum radiation, λ = 0.710 73 Å) operating at 50 kV and 30 mA. Data were collected over the complete sphere by a combination of four sets. Each frame exposure time was 10 s (**2**) or 20 s (**5**), covering 0.3° in ω. Data were corrected for absorption by using a multiscan method applied with the SADABS[54] programs. The structures were solved by direct methods. Refinement, by full-matrix least squares on F^2 with SHELXS-97,[55] was similar for both complexes, including isotropic and subsequently anisotropic displacement parameters. The hydrogen atoms were observed or calculated and refined using a restricted riding model or refined freely. Hydride ligands were observed in the difference Fourier maps and refined as free isotropic atoms. All the highest electronic residuals were observed in close proximity to the Os centers and make no chemical sense. Crystal data and details of the data collection and refinement are given in Table 5.

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Supporting Information Available: CIF files giving positional and displacement parameters, crystallographic data, and bond lengths and angles of complexes **2** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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