Notes

Preparation, X-ray Structures, and NMR Spectra of Elongated Dihydrogen Complexes with Four- and Five-Coordinate Tin Centers

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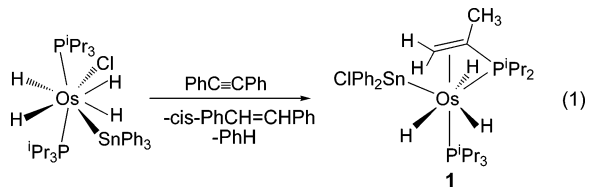
*Summary: Complex $OsH_3(SnPh_2Cl)\{[\eta^2\text{-}CH_2{=}C(CH_3)]P^iPr_2\}(P^iPr_3)$ (**1**) undergoes protonation−addition of benzoic acid to give the elongated dihydrogen derivative $Os(SnPh_2Cl)(\kappa^2\text{-}O_2CPh)(\eta^2\text{-}H_2)(P^iPr_3)_2$ (**2**). In solution the tin atom exchanges with the osmium on the chloride ligand by one of the oxygen atoms of the carboxylate group to afford $OsCl\{OC(Ph)OSnPh_2\}(\eta^2\text{-}H_2)(P^iPr_3)_2$ (**3**). Treatment of the latter with 1.0 equiv of benzoic acid leads to $OsCl\{OC(Ph)OSn(\kappa^2\text{-}O_2CPh)Ph\}(\eta^2\text{-}H_2)(P^iPr_3)_2$ (**4**). The elongated dihydrogen ligands of **2** and **3** show blocked rotation on the NMR time scale, whereas the hydrogen atoms undergo quantum exchange coupling. The X-ray structures of **3** and **4** are also reported.*

Transition-metal hydride compounds play a central role in modern chemistry, including homogeneous catalysis.[1] Some of them, with two hydrogen atoms bonded to the metal, have H−H separations between the dihydrogen (0.8−1.0 Å) and dihydride (>1.6 Å) limits.[2] The intermediate or stretched dihydrogen (so-called elongated dihydrogen or compressed dihydride) complexes of osmium have shown to be useful templates for carbon−carbon and carbon−heteroatom coupling reactions.[3] The study of the parameters depending on the OsH_2 interactions is essential to determine the nature of the bonding and rationalize the chemistry of this type of species.[4]

We have recently reported that the tetrahydride−stannyl−osmium(VI) complex $OsH_4Cl(SnPh_3)(P^iPr_3)_2$ reacts with diphenylacetylene to give $OsH_3(SnPh_2Cl)\{[\eta^2\text{-}CH_2{=}C(CH_3)]P^iPr_2\}(P^iPr_3)$ (**1**) in a one-pot synthesis of multiple complex reactions, among them, the migration of the chloride ligand from the osmium to the tin atom (eq 1).[5]



(1)

Complex **1** is a synthon for the 14-valence electron monohydride $OsH(SnPh_2Cl)(P^iPr_3)_2$, which is formed by transfer of two hydrogen atoms from the metal center to the C−C double bond of the isopropenyl substituent of the unsaturated phosphine. This species reveals its nucleophilic nature in the $C(sp^2)$−H bond activation of aldehyde, ketone, and RCH═E-py (E = CH, N) substrates.[6] In agreement with the base character of the metal center, complex **1** undergoes protonation−addition of benzoic acid to give the elongated dihydrogen derivative $Os(SnPh_2Cl)(\kappa^2\text{-}O_2CPh)(\eta^2\text{-}H_2)(P^iPr_3)_2$ (**2**), which is isolated as a yellow solid in 73% yield, according to Scheme 1.

In the $^1H\{^{31}P\}$ NMR spectrum of **2** in toluene-d_8, the most noticeable signal is that due to the elongated dihydrogen ligand. At room temperature, it appears at −13.02 ppm. Lowering the sample temperature produces a broadening of the resonance. Between 223 and 213 K decoalescence occurs, and at 203 K an AB spin system centered at −12.93 ppm and defined by $\Delta\nu$ = 182.8 Hz and J_{A-B} = 242.6 Hz is observed. A $T_{1(min)}$ value of 74 ± 1 ms was obtained at 243 K for this signal. Assuming slow spinning, it corresponds to a H−H distance of 1.50 Å,[7] which is consistent with the elongated dihydrogen character.

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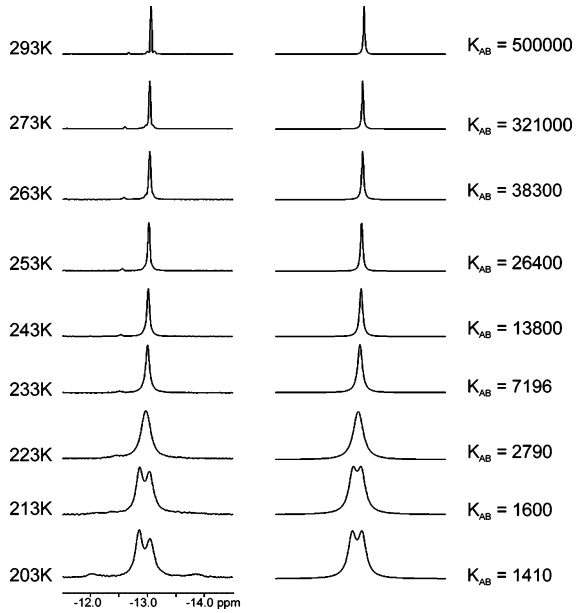
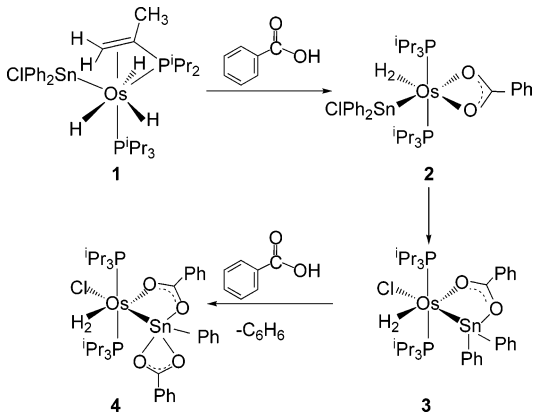


Figure 1. Left: Variable-temperature $^1H\{^{31}P\}$ NMR spectra (300 MHz) in the high-field region of **2**. Right: Simulated spectra and rate constant (s^{-1}) for the intramolecular hydrogen site-exchange processes.

Scheme 1



The J_{A-B} value supports the operation of quantum exchange coupling between the hydrogen atoms.[8]

Complex **2** is a rare example of blocked rotation of the H_2 ligand on the NMR time scale. Line-shape analysis of the $^1H\{^{31}P\}$ NMR spectra (Figure 1) allows the calculation of the rate constants for the process at each temperature. The activation parameters obtained from the Eyring analysis are $\Delta H^{\ddagger} = 9.7 \pm 0.2$ kcal·mol^{-1} and $\Delta S^{\ddagger} = 0.4 \pm 0.8$ cal·mol^{-1}·K^{-1}. The value for the entropy of activation, close to 0, is in agreement with an intramolecular process, while the value for the enthalpy of activation lies in the range previously reported for other blocked rotation processes.[4,6b,c,9]

In solution the tin atom exchanges with the osmium on the chloride ligand by one of the oxygen atoms of the carboxylate group. Thus, complex **2** is slowly converted into the chloro-elongated dihydrogen derivative $\overline{OsCl\{OC(Ph)OSnPh_2\}}(\eta^2\text{-}H_2)(P^iPr_3)_2$ (**3**), containing a chelate O,Sn donor ligand. After 12 h at room temperature in toluene, the **2**:**3** molar ratio is 6:4. At 243 K, crystallization of the mixture from toluene/methanol yields **3** as pure yellow crystals suitable for an X-ray diffraction study. The structure (Figure 2) proves the exchange process. The coordination around the osmium can be rationalized as a distorted octahedron with the phosphorus atoms occupying apical positions (P(1)−Os−P(2) = 164.62(5)°). The osmium sphere is completed by the chelate oxygen−tin ligand, which acts with a bite angle O(1)−Os−Sn of 76.45(11)°, the chloride *trans* disposed to the tin atom (Cl−Os−Sn = 154.91(4)°), and the hydrogen atoms H(01) and H(02) separated by 1.39(9) Å. The Os−Sn distance of 2.5996(6) Å is slightly shorter than the Os−Sn bond length found in complexes containing monodentate stannyl groups (about 2.65 Å).[5,6,10] The environment of the tin is tetrahedral, with angles between 95.7(2)° (C(8)−Sn−C(14)) and 131.29(19)° (C(8)−Sn−Os).

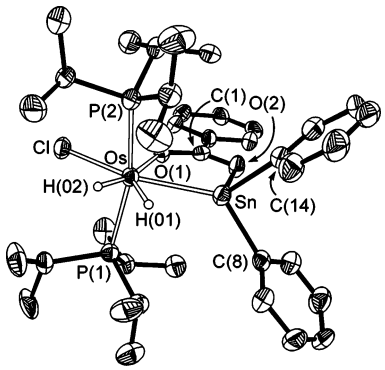


Figure 2. Molecular diagram of **3**. Selected bond lengths (Å) and angles (deg): Os−Sn 2.5996(6), H(01)−H(02) 1.39(9); P(1)−Os−P(2) 164.62(5), Sn−Os−Cl 154.91(4), Sn−Os−O(1) 76.45(11), C(8)−Sn−Os 131.29(19), C(8)−Sn−C(14) 95.7(2).

In the $^1H\{^{31}P\}$ NMR spectrum in toluene-d_8 at room temperature, the signal corresponding to the elongated dihydrogen ligand appears at −12.60 ppm. The behavior of this resonance with the temperature is similar to that of **2**. Thus, at 193 K, an AB spin system centered at −12.60 ppm and defined by $\Delta\nu = 476$ Hz and, in agreement with a quantum exchange process between the hydrogen atoms, by $J_{A-B} = 303$ Hz is observed. In this case, a $T_{1(min)}$ value of 80 ± 1 ms was found at 243 K. It leads to a H−H separation of 1.5 Å, which agrees well with that of **2** and that found by X-ray diffraction analysis.

Complex **3** is another example of blocked rotation of the dihydrogen ligand on the NMR time scale. The activation

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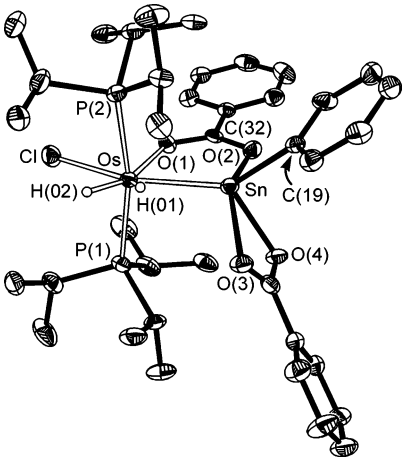

Figure 3. Molecular diagram of **4**. Selected bond lengths (Å) and angles (deg): Os−Sn 2.5974(4), H(01)−H(02) 1.52(4), Sn−O(2) 2.159(3), Sn−O(3) 2.380(3), Sn−O(4) 2.148(3); P(1)−Os−P(2) 168.14(5), Sn−Os−Cl 160.76(3), Sn−Os−O(1) 74.42(8), O(3)−Sn−O(4) 57.66(12), O(2)−Sn−O(3) 147.61(12).

parameters obtained for the rotation are similar to those of **2**, $\Delta H^{\ddagger} = 8.3 \pm 0.2$ kcal·mol^{-1} and $\Delta S^{\ddagger} = -3 \pm 1$ cal·mol^{-1}·K^{-1}.

In the presence of benzoic acid, one of the phenyl groups of **3** undergoes hydrogenolysis. The resulting tin is sufficiently electrophilic to increase its coordination to five by addition of the carboxylate group.[11] Thus, the treatment of a toluene solution of **3** with 1.0 equiv of benzoic acid leads to $\overline{\text{OsCl}\{\text{OC(Ph)OSn-}(\kappa^2\text{-O}_2\text{CPh})\text{Ph}\}(\eta^2\text{-H}_2)(\text{P}^i\text{Pr}_3)_2}$ (**4**), which is obtained in a one-pot synthesis by reaction of **1** with 2.0 equiv of benzoic acid, in toluene at room temperature. By the latter procedure, complex **4** is isolated as yellow crystals in 73% yield. It has been also characterized by X-ray diffraction analysis. The structure (Figure 3) proves the presence of a five-coordinate tin center in the complex. The change in the coordination number of the tin atom is also revealed by the ^{119}Sn{^{1}H} NMR spectrum of **4**, which shows a triplet ($J_{\text{P}-^{119}\text{Sn}} = 120$ Hz) at −178.2 ppm, shifted more than 200 ppm toward higher field with regard to **3** (δ, 53.3) and **2** (δ, 66.4).

All angles around the tin atom are different. They are between 57.66(12)° (O(3)−Sn−O(4)) and 147.61(12)° (O(2)−Sn−O(3)). The chelate carboxylate group coordinates in an asymmetrical fashion with Sn−O(4) and Sn−O(3) distances of 2.148(3) and 2.380(3) Å, respectively. The first of them is statistically identical with the Sn−O(2) bond length (2.159(3) Å), while the second one is about 0.2 Å longer. The separation between the tin and osmium atoms (2.5575(4) Å) is slightly shorter than in **3**. The coordination geometry around the osmium atom can be described as a distorted octahedron with P(1)−Os−P(2), Cl−Os−Sn, and O(1)−Os−Sn angles of 168.14(5)°, 160.76(3)°, and 79.42(8)°, respectively. In agreement with the elongated dihydrogen character of the complex, the separation between H(01) and H(02) is 1.52(5) Å.

(11) In the presence of suitable ligands, tin can increases its coordination from four to five or even six. See for example: (a) Buil, M. L.; Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A. *J. Am. Chem. Soc.* **1995**, *117*, 3619. (b) Biesemans, M.; Willem, R.; Damoun, S.; Geerlings, P.; Lahcini, M.; Jaumier, P.; Jousseaume, B. *Organometallics* **1996**, *15*, 2237. (c) Jaumier, P.; Jousseame, B.; Tiekink, E. R. T.; Biesemans, M.; Willem, R. *Organometallics* **1997**, *16*, 5124. (d) Dakternieks, D.; Duthie, A.; Smyth, D. R.; Stapleton, C. P. D.; Tiekink, E. R. T. *Organometallics* **2003**, *22*, 4599.

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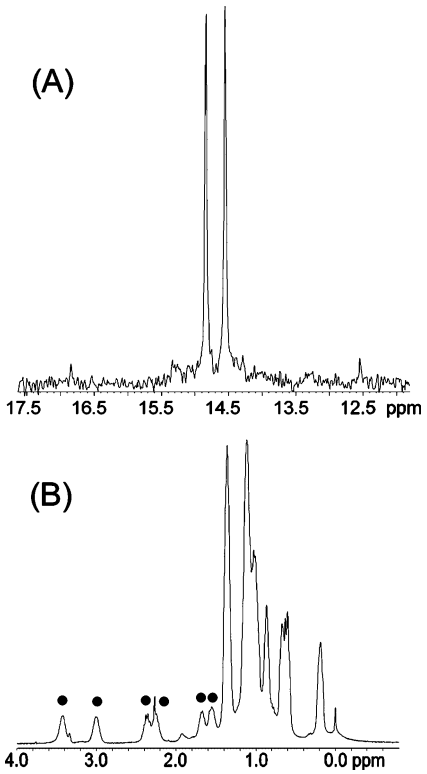

Figure 4. (A) ^{31}P{^{1}H} NMR spectrum of complex **4** at 193 K and (B) ^{1}H NMR spectrum of complex **4** at 193 K in the P^{i}Pr$_3$ region (● denotes each of the CH protons of the phosphines).

In the ^{1}H NMR spectrum at room temperature, the elongated dihydrogen ligand of **4** gives rise to a triplet ($J_{\text{H}-\text{P}} = 11.4$ Hz) at −11.86 ppm. Lowering the sample temperature produces a broadening of the signal. However, in this case, decoalescence is not observed at 183 K. A $T_{1(\text{min})}$ value of 64 ± 1 ms was obtained at 223 K for this resonance. It corresponds to a H−H distance of 1.46 Å, which agrees well with that obtained by X-ray diffraction analysis.

Gusev, Heinekey, and co-workers have recently studied by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy the behavior of our complex $\overline{\text{OsCl}\{\text{NH=C(Ph)C}_6\text{H}_4\}(\eta^2\text{-H}_2)\text{P}^i\text{Pr}_3)_2}$[9d] in $CDFCl_2$−CDF_2Cl. They have observed complex ^{1}H NMR spectra between 156 and 135 K and a ^{31}P{^{1}H} NMR spectrum at 150 K that is consistent with an equilibrium mixture of two rotamer structures. One of them contains equivalent phosphines, while the other one has lower symmetry by virtue of the alternate disposition of the isopropyl groups. The rotamers are the result of the hindered rotation around the Os−P bonds. This phenomenon is common for bis-phosphine complexes. The temperature at which this is observed depends on the steric hindrance experienced by the ligands of the particular species.[6] The tin ligands of **2**−**4** have a steric requirement higher than an orthometalated benzophenone imine ligand. As a consequence, the rotation of the phosphine ligands around the Os−P bonds in **2**−**4** is stopped at temperatures higher than for the previously reported benzophenone imine derivative. In contrast to $\overline{\text{OsCl}\{\text{NH=C(Ph)C}_6\text{H}_4\}(\eta^2\text{-H}_2)\text{P}^i\text{Pr}_3)_2}$, only one rotamer is observed for **2**−**4**. In agreement with this, at 183 K, the ^{31}P{^{1}H} NMR spectra of **2**−**4** show an AB spin system centered at 20.5 ppm and defined by $\Delta\nu = 130$ Hz and $J_{\text{A}-\text{B}} = 219.5$ Hz, a singlet at 13.5 ppm, and an AB spin system centered at 14.7 ppm and defined by $\Delta\nu = 134$ Hz and $J_{\text{A}-\text{B}} = 217$ Hz, respectively. Figure 4 shows the ^{31}P{^{1}H} NMR spectrum of **4** at 193 K (A) and the ^{1}H NMR

spectrum in the isopropyl group region at the same temperature (B), where the six multiplets corresponding to the six inequivalent CH isopropyl groups can be clearly observed.

In conclusion, the addition of benzoic acid to the 14-valence-electron monohydride−stannyl complex $OsH(SnPhCl)(P^iPr_3)_2$ affords elongated dihydrogen derivatives, containing four- and five-coordinate tin centers. The elongated dihydrogen ligand of these compounds shows blocked rotation on the NMR time scale, whereas the hydrogen atoms undergo quantum exchange coupling. After the formation of the elongated dihydrogen ligand, a chloride−oxygen exchange takes place between the tin and osmium atoms.

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 $OsH_3(SnPh_2Cl)\{[\eta^2\text{-}CH_2{=}C(CH_3)]P^iPr_2\}(P^iPr_3)$ (**1**) was prepared as previously described.[5] Chemical shifts are referenced to residual solvent peaks (^1H and $^{13}C\{^1H\}$), external H_3PO_4 ($^{31}P\{^1H\}$), or Me_4Sn ($^{119}Sn\{^1H\}$). Coupling constants J and N ($N = J_{P-H} + J_{P'-H}$ for ^1H; $N = J_{P-C} + J_{P'-C}$ for $^{13}C\{^1H\}$) are given in hertz.

Preparation of $Os(SnPh_2Cl)(\kappa^2\text{-}O_2CPh)(\eta^2\text{-}H_2)(P^iPr_3)_2$ (2). Benzoic acid (23.5 mg) was added to a solution of **1** (150 mg, 0.19 mmol). After stirring for 3 h at room temperature, the resulting solution was filtered through Celite and was taken to dryness. Methanol caused the precipitation of a deep yellow solid, which was washed with methanol at 223 K and dried in vacuo. Yield: 98 mg (55%). Anal. Calcd for $C_{37}H_{59}ClO_2OsP_2Sn$: C, 47.16; H, 6.31. Found: C, 47.28; H, 6.01. ^1H NMR (293 K, C_7D_8): δ 8.27−6.99 (15H, Ph), 2.39 (m, 6H, PC*H*), 1.14 (dvt, $N = 12.9$, $J_{H-H} = 6.9$, 36H, CH_3), −13.02 (t, $J_{P-H} = 10.8$, 2H, OsH). ^1H NMR (203 K, hydride region): δ −12.93 (AB spin system, $\Delta\nu = 182.8$, $J_{A-B} = 242.6$). $T_{1(min)}$ (ms, OsH_2, 300 MHz, 243 K): 74 ± 1. $^{31}P\{^1H\}$ NMR (293 K, C_7D_8): δ 22.0 (s with tin satellites). $^{31}P\{^1H\}$ NMR (183 K): δ 20.5 (AB spin system, $\Delta\nu = 130$ Hz, $J_{A-B} = 219.5$). $^{13}C\{^1H\}$ NMR (293 K, C_6D_6): δ 180.0 (s, CO), 150.0, 137.4, 134.2, 132.5, 128.5, 128.3, 127.9, 127.9 (Ph), 26.3 (vt, $N = 24.1$, P*C*), 20.1 (br, *C*H_3). $^{119}Sn\{^1H\}$ NMR (293 K, C_6D_6): δ 66.4 (t, $J_{P-^{119}Sn} = 76$). MS (LDI): m/z 821 ($M^+ - O_2CPh_2$).

Preparation of $OsCl\{OC(Ph)OSn(\kappa^2\text{-}O_2CPh)Ph\}(\eta^2\text{-}H_2)(P^iPr_3)_2$ (3). A yellow solution of **2** (100 mg, 0.106 mmol) in 10 mL of toluene was stirred for 48 h at room temperature. The resulting yellow solution was filtered through Celite and dried in vacuo. Methanol was added to afford a yellow solid, which was filtered with further portions of methanol at 223 K. This solid is a mixture of isomers **2** and **3**. Complex **3** can be isolated in pure form by crystallization from the mixture of toluene/methanol at 243 K. Yield: 40 mg (40%). Anal. Calcd for $C_{37}H_{59}ClO_2OsP_2Sn{\cdot}C_7H_8$: C, 51.09; H, 6.52. Found: C, 50.99; H, 6.39. ^1H NMR (293 K, C_7D_8): δ 8.59−6.97 (15H, Ph), 2.62 (m, 6H, PC*H*$(CH_3)_2$), 1.27 (dvt, $N = 12.8$, $J_{H-H} = 6.4$, 18H, CH_3), 1.02 (dvt, N = 12, $J_{H-H} = 6$, 18H, CH_3), −12.60 (t, with tin satellites, $J_{P-H} = 11.6$, $J_{Sn-H} = 102.8$, 2H, OsH). ^1H NMR (193 K, hydride region): δ −12.40 (AB spin system, $\Delta\nu = 476$, $J_{A-B} = 303$). $T_{1(min)}$ (ms, OsH_2, 300 MHz, 243 K): 80 ± 1. $^{31}P\{^1H\}$ NMR (293 K, C_6D_6): δ 13.5 (s with tin satellites). $^{13}C\{^1H\}$ NMR (293 K, C_6D_6): δ 178.6 (s, CO), 154.8, 133.8, 132.8, 131.2, 130.9, 128.9, 128.3, 128.3 (Ph), 26.2 (vt, $N = 23.5$, P*C*), 19.7, 19.5 (both s, *C*H_3). $^{119}Sn\{^1H\}$ NMR (293 K, C_6D_6): δ 53.3 (t, $J_{P-^{119}Sn} = 100$). MS (LDI): m/z 940 ($M^+ - 2H$).

Preparation of $OsCl\{OC(Ph)OSn(\kappa^2\text{-}O_2CPh)Ph\}(\eta^2\text{-}H_2)(P^iPr_3)_2$ (4). Benzoic acid (46.3 mg, 0.38 mmol) was added to a solution of **1** (150 mg, 0.19 mmol) in toluene (10 mL). After stirring for 48 h at room temperature the resulting solution was filtered through Celite and was taken to dryness. Methanol caused the precipitation of a pale yellow solid, which was washed with methanol at 223 K and dried in vacuo. Yield: 138 mg (73%). Anal. Calcd for $C_{38}H_{59}ClO_4OsP_2Sn$: C, 46.28; H, 6.03. Found: C, 46.32; H, 6.20. ^1H NMR (293 K, CD_2Cl_2): δ 8.33−7.32 (Ph), 2.50 (m, 6H, PC*H*), 1.26−0.88 (m, 36H, CH_3), −11.86 (t, $J_{P-H} = 11.4$, 2H, OsH). $T_{1(min)}$ (ms, OsH_2, 300 MHz, 223 K): 64 ± 0.1. $^{31}P\{^1H\}$ NMR (293 K, CD_2Cl_2): δ 13.2 (s with tin satellites). $^{31}P\{^1H\}$ NMR (193 K): δ 14.7 (AB spin system, $\Delta\nu = 134$, $J_{A-B} = 217$). $^{13}C\{^1H\}$ NMR (293 K, C_6D_6): δ 178.1, 177.6 (s, CO), 154.0, 135.5, 133.1, 132.7, 131.3, 130.4, 129.7, 128.8, 128.4, 128.3, 130.8, 130.5 (Ph), 26.3 (br, P*C*), 19.7, 19.5 (both s, *C*H_3). $^{119}Sn\{^1H\}$ NMR (293 K, C_6D_6): δ −178.2 (t, $J_{P-^{119}Sn} = 120$). MS (LDI): m/z 863 ($M^+ - O_2CPh_2 - 2H$).

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Supporting Information Available: Tables of positional and displacement parameters, crystallographic data, and bond lengths and angles of complexes **3** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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