Notes

Preparation and Full Characterization of a Tetrahydride-bis(stannyl)-osmium(VI) Derivative

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Summary: The dihydride-dichloro complex $OsH_2Cl_2(P^iPr_3)_2$ (**1**) *reacts with 4.0 equiv of* $HSnPh_3$ *to afford 2.0 equiv of* $ClSnPh_3$ *and the tetrahydride-bis(stannyl)-osmium(VI) derivative* $OsH_4(SnPh_3)_2(P^iPr_3)_2$ (**2**)*, which has been characterized by X-ray diffraction analysis. DFT calculations in a model system of* **2***, in which the bulky ligands have been replaced by small models, followed by QM/MM optimizations with the real ligands have allowed the complete determination of the hydride positions and the role played by the steric effects on the experimental structure.*

Transition metal hydride compounds play a central role in modern inorganic and organometallic chemistry.[1] In particular, ruthenium- and osmium-polyhydride complexes have shown to be useful precursors for carbon−carbon and carbon−heteroatom coupling reactions.[2]

Hydride-stannyl derivatives ($HSnR_3$) undergo easy oxidative addition and reductive elimination. Furthermore, tin ligands have a strong labilizing effect on their *trans* ligands. Thus, they provide vacant coordination sites, facilitating the coordination of unsaturated organic substrates to the transition metal and subsequent migratory insertion. As a consequence, the use of transition metal tin compounds in the catalysis of organic transformations is attracting a great deal of attention.[3] Bis-stannyl complexes have been proposed as intermediates in the metal-catayzed double stannylation of 1,3-dienes, alkynes, and allenes.[4]

In an effort to add to the osmium-polyhydride complexes the advantages of tin ligands, we have recently initiated a research project centered on the preparation of osmium-stannyl compounds[5] containing a high number of hydrogen atoms bonded to the metallic center. Despite that the oxidative addition of neutral XY molecules to d^4 L_nM complexes of the platinum group metals had no precedents, we have shown that the dihydride-dichloro-osmium(IV) derivative $OsH_2Cl_2(P^iPr_3)_2$ reacts with 2 equiv of $HSnPh_3$ to afford the tetrahydride-mono(stannyl) $OsH_4Cl(SnPh_3)(P^iPr_3)_2$.[6] This tetrahydride, which is the first d^2-mono-stannyl derivative in the chemistry of the platinum group metals, allows access to other novel polyhydrides, including species reminiscent of the intermediates proposed by Murai for the insertion of olefins into aromatic *ortho*-CH bonds of ketones or imines.[7]

We find now that the reaction of $OsH_2Cl_2(P^iPr_3)_2$ (**1**) with 4.0 equiv of $HSnPh_3$ affords the tetrahydride-bis(stannyl)-osmium(VI) derivative $OsH_4(SnPh_3)_2(P^iPr_3)_2$ (**2**) and 2.0 equiv of $ClSnPh_3$.[8] This complex can also be obtained by a two-step procedure via the mono(stannyl) $OsH_4Cl(SnPh_3)(P^iPr_3)_2$ (**3** in Scheme 1).

Complex **2** is the first reported bis(stannyl)-osmium(VI) derivative. Although transition metal bis(stannyl) compounds are known, they have been stabilized with a transition metal in a low oxidation state.[9] This tetrahydride is not only the first bis(stannyl) derivative in the chemistry of osmium(VI) but also a rare example

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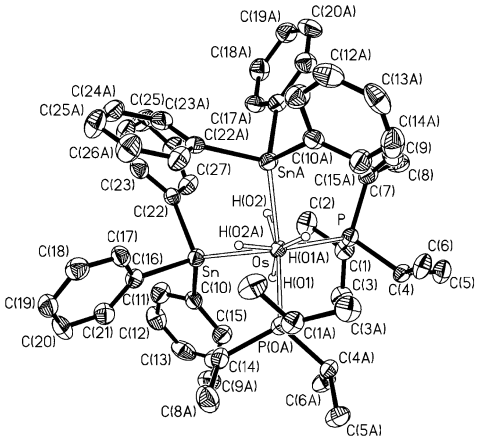
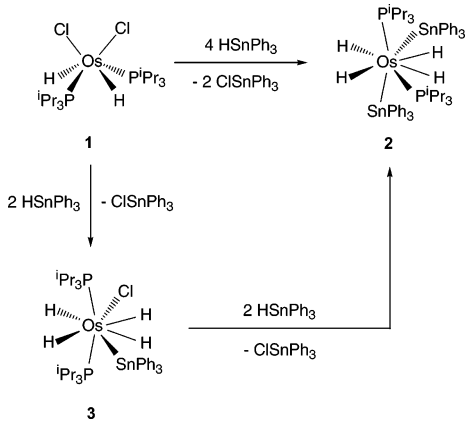


Figure 1. Molecular diagram of complex $OsH_4(SnPh_3)_2(P^iPr_3)_2$ (**2**).

Scheme 1



of a bis(stannyl) complex with the transition metal in a high oxidation state.

The new tetrahydride was isolated as a white solid in almost quantitative yield (88%) and characterized by elemental analysis, MS, IR, and ^1H, $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, and $^{119}Sn\{^1H\}$ NMR spectroscopy, and by an X-ray crystallographic study. At 173 K, the four hydride ligands were located in the difference Fourier maps and refined as isotropic atoms together with the remaining non-hydrogen atoms of the structure. A view of its molecular geometry is shown in Figure 1. Selected bond distances and angles are listed in Table 1.

The coordination geometry around the osmium atom can be rationalized as derived from a distorted dodecahedron. This dodecahedral structure is defined by two intersecting orthogonal (about 87.2°) trapezoidal planes.

Table 1. Selected Bond Distances and Angles for the Complex $OsH_4(SnPh_3)_2(P^iPr_3)_2$ (2) and Optimized Distances (Å) and Angles (deg) of $OsH_4(SnH_3)_2(PH_3)_2$ (2a, B3LYP) and $OsH_4(SnPh_3)_2(P^iPr_3)_2$ (2b, IMOMM (B3LYP:MM3))

	2	2a	2b
Os−Sn	2.6897(3)	2.724	2.771
Os−Sn(A)			2.772
Os−P	2.4234(11)	2.387	2.523
Os−P(0A)		2.386	
Os−H(01)		1.674	1.665
Os−H(01A)		1.674	1.665
Os−H(02)		1.656	1.652
Os−H(02A)		1.655	1.651
Sn−Os−Sn(A)	101.473(15)	106.095	99.402
Sn−Os−P	122.56(3)	137.592	122.824
Sn(A)−Os−P(0A)		137.809	122.895
Sn−Os−P(0A)	100.24(3)	92.349	102.712
Sn−Os−H(01)	58.5(14)	63.900	57.221
Sn−Os−H(01A)	151.2(14)	138.342	148.375
Sn−Os−H(02)	65.6(15)	70.927	66.308
Sn−Os−H(02A)	64.5(14)	62.339	66.191
P−Os−P(0A)	111.10(5)	99.114	107.715
P−Os−H(01)	78.2(15)	76.827	77.993
P−Os−H(01A)	83.6(15)	84.062	88.652
P−Os−H(02)	77.5(15)	85.568	76.124
P−Os−H(02A)	165.8(15)	158.567	167.743
C(10)−Sn−C(22)	97.13(15)		100.04
C(10)−Sn−Os	119.72(11)		118.029
H(01)−Os−H(01A)	148(3)	150.300	152.260
H(01)−Os−H(02)	87.3(19)	76.685	83.884
H(01)−Os−H(02A)	115(2)	124.572	114.142
H(02)−Os−H(02A)	96(3)	97.638	102.626

One plane contains the atoms Sn(A), H(02), H(01), and P(0A), while the other one contains the atoms Sn, H(02A), H(01A), and P. In both planes the P−Os−Sn angle is 122.56(3)°. Although similar structures have been found for the hexahydride $OsH_6(P^iPr_2Ph)_2$, the pentahydrides $[OsH_5(PHPh_2)(P^iPr_3)_2]^+$, $[OsH_5(PMe_2Ph)_3]^+$, and $OsH_5(SnClPh_2)(P^iPr_3)_2$, and the tetrahydride $OsH_4Cl(SnPh_3)(P^iPr_3)_2$, it should be mentioned that the P−Os−Sn angles in **2** are significantly smaller than the related angles in the above-mentioned polyhydrides, 155.2(1)° (P−Os−P in $OsH_6(P^iPr_2Ph)_2$),[10] 149.43(6)° ($^iPr_3P$−Os−P^iPr_3 in $[OsH_5(PHPh_2)(P^iPr_3)_2]^+$),[11] 146.2(5)° (P(11)−Os−P(20) in $[OsH_5(PMe_2Ph)_3]^+$),[12] 149.31(3)° (P−Os−P in $OsH_5(SnClPh_2)(P^iPr_3)_2$), and 145.05(7)° and 145.43(5)° (P−Os−P and Sn−Os−Cl, respectively, in $OsH_4Cl(SnPh_3)(P^iPr_3)_2$).[6] This appears to be a consequence of the steric hindrance experienced by the isopropyl groups of the phosphines and the phenyl groups of the stannyl ligands.

The Os−Sn distances (2.6897(3) Å) are similar to those found in the octahedral *trans*-stannyl complex $Os(SnPh_3)_2(CO)_4$ (2.71 Å)[13] and agree well with those reported for mononuclear osmium-stannyl derivatives (2.6−2.7 Å),[5c,h,6] while they are about 0.15 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).[14]

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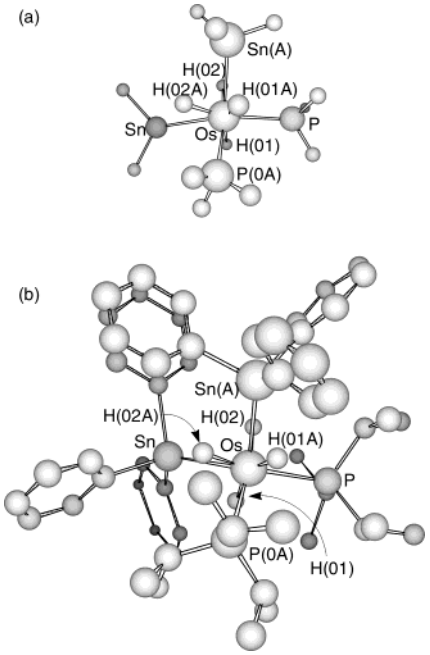

Figure 2. (a) B3LYP optimized structure of $OsH_4(SnH_3)_2(PH_3)_2$ (**2a**) and (b) IMOMM (B3LYP:MM3) optimized structure of $OsH_4(SnPh_3)_2(P^iPr_3)_2$ (**2b**).

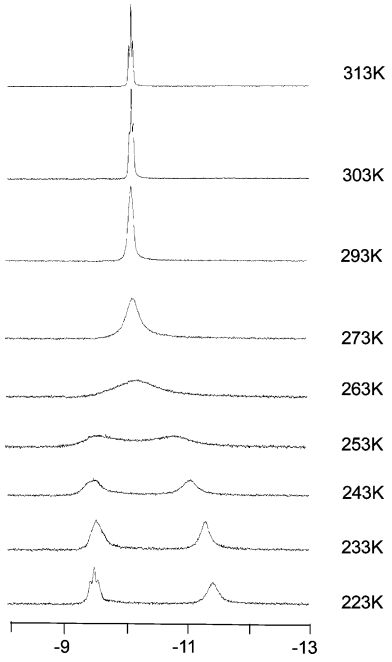

Figure 3. Variable-temperature ^1H NMR spectra (300 MHz, toluene-d_8) in the high-field region of $OsH_4(SnPh_3)_2(P^iPr_3)_2$ (**2**).

The environment of the tin atom is tetrahedral, with angles between 97.13(15)° (C(10)−Sn−C(22)) and 119.72(11)° (C(10)−Sn−Os).

The hydride positions obtained from X-ray diffraction data are, in general, imprecise.[15] However, DFT calculations have been shown to provide useful accurate data for the hydrogen positions in both classical polyhydride and dihydrogen complexes.[16] Thus, to corroborate the structure of **2**, a DFT study of the model complex $OsH_4(SnH_3)_2(PH_3)_2$ (**2a**), supplemented by QM/MM IMOMM calculations on the real complex, has been carried out.

Figure 2a shows the B3LYP optimized structure of **2a**, while Figure 2b shows the IMOMM (B3LYP:MM3) optimized structure of **2** (**2b**). Their main geometrical parameters are listed in Table 1. Both theoretical results agree well with the dodecahedral structure obtained from the X-ray diffraction analysis, and two almost perpendicular trapezoidal planes are found.

The structure of **2b** reproduces very well the structural parameters of **2**, in particular the bond angles. For instance, the P−Os−Sn angles in the trapezoidal planes are 122.895° and 122.824°, whereas the experimental value is 122.56(3)°.

The structure of **2a** points out the steric hindrance experienced by the isopropyl groups of the phosphine and the phenyl group of the stannyl ligands in **2** and **2b**. The absence of these groups in **2a** is reflected in the P−Os−Sn angles within the trapezoidal planes, which are now 137.809° and 137.592°, about 15° greater than those of **2** and **2b**.

As expected, the Os−H distances are between 1.651 and 1.674 Å, while the separation between the hydride ligands is in all cases longer than 2.066 Å. This clearly supports the tetrahydride character of **2**. Neither is there any interaction between the tin atom and the hydride ligands. The Sn−H separations are longer than 2.4 Å.

In agreement with the presence of the hydride ligands in **2**, its IR spectrum in Nujol contains two ν(Os−H) bands at 1993 and 1956 cm^{-1}. At room temperature, the $^{31}P\{^1H\}$ NMR spectrum in toluene-d_8 shows a singlet at 26.7 ppm, along with the tin satellites ($J_{P-^{119}Sn} = J_{P-^{117}Sn} = 32$ Hz). Lowering the sample temperature leads to a broadening of the resonance. However, decoalescence is not observed even at 193 K. Because the phosphine ligands in **2** are equivalent, the broadening of the resonance with the decreasing temperature appears to be related 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 phosphine and the stannyl groups. A similar behavior has been previously observed in some five-, six-, and eight-coordinate ruthenium and osmium complexes containing bulky phosphine ligands.[7,17] At 333 K under off-resonance conditions, the singlet is split into a quintuplet as a result of the P−H coupling with the four hydride ligands.

The ^1H NMR spectrum is also temperature-dependent (Figure 3). At 313 K in toluene-d_8, the spectrum shows in the hydride region a triplet at −10.05 ppm with a H−P coupling constant of 12 Hz. This observation is consistent with the operation of a thermally activated site exchange process for the hydride ligands, which proceeds at rate sufficient to lead to the single hydride resonance. Consistent with this, lowering the sample temperature leads to broadening of the resonance. Between 263 and 253 K, decoalescence occurs. At 223 K, a broad triplet at −9.44 ppm ($J_{H-P} = 19.5$ Hz) and a

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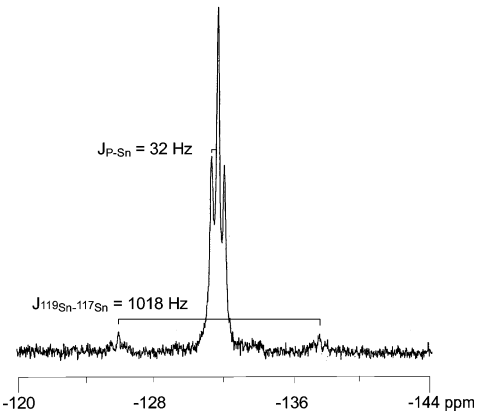

Figure 4. ^{119}Sn NMR spectrum (111.82 MHz, C_6D_6) of $OsH_4(SnPh_3)_2(P^iPr_3)_2$ (**2**).

broad resonance at −11.39 ppm are observed. The spectrum at 223 K is in agreement with the structures shown in Figures 1 and 2, which contain two different types of hydride ligands: H(01) and H(01A), and H(02) and H(02A). According to the P−Os−H(02A) (167.743°) and P(0A)−Os−H(02) (167.892°) angles, the resonance at −9.44 ppm is assigned to the hydride ligands H(02) and H(02A), while the resonance at −11.39 ppm, for which a H−P coupling constant of about 3 Hz can be estimated, is assigned to H(01) and H(01A) (P−Os−H(01) = 77.993°, P−Os−H(01A) = 85.652°, P(0A)−Os−H(01) = 85.718°, P(0A)−Os−H(01A) = 78.053°). At 263 K, the activation energy for the exchange process is estimated to be 12 kcal·mol^{-1}.

The T_1 values of the hydrogen nuclei of the OsH_4 unit were determined between 273 and 193 K. $T_{1(min)}$ values of 208 ± 5 ms for H(02) and H(02A) and 209 ± 6 ms for H(01) and H(01A) were obtained at 253 K and 300 MHz. They agree well with the tetrahydride character of **2**.

The ^{119}Sn{^{1}H} NMR spectrum in benzene-d_6 at room temperature shows a triplet at −131.7 ppm with a ^{119}Sn−P coupling constant of 32 Hz. There are satellites due to the ^{117}Sn isotope in this spectrum (Figure 4). The value of the ^{119}Sn−^{117}Sn coupling constant is 1018 Hz.

In conclusion, bis(stannyl) complexes can be stabilized not only when the transition metal is in a low oxidation state but also when it is high. We report the first example of a derivative of this latter type and its full characterization in the solid state, as well as in solution. Complex $OsH_4(SnPh_3)_2(P^iPr_3)_2$ has the typical dodecahedral structure of the eight-coordinate polyhydrides. However the heteroatom−osmium−heteroatom angles within the trapezoidal planes are notably small. This is a consequence of the steric hindrance experienced by the phosphine and stannyl ligands. In solution, the two different types of hydrides of the molecule undergo a thermally activated site exchange process. The enthalpy of activation[18] for the process is estimated to be 12 kcal·mol^{-1}.

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 starting material $OsH_2Cl_2(P^iPr_3)_2$ (**1**) was prepared by a published method.[19] Chemical shifts are referenced to residual solvent peaks (^{1}H, ^{13}C{^{1}H}), external H_3PO_4 (^{31}P{^{1}H}), or external Me_4Sn (^{119}Sn{^{1}H}). 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.

Preparation of $OsH_4(SnPh_3)_2(P^iPr_3)_2$ (2). This compound can be prepared by two methods. Method a: A suspension of **1** (200 mg, 0.34 mmol) in 10 mL of toluene was treated with triphenyltin hydride (481 mg, 1.37 mmol). An immediate color change from brown to colorless was observed. The resulting mixture was stirred for 2 min at room temperature and then evaporated to dryness. Addition of pentane affords a white solid, which was washed with pentane and dried in vacuo. Yield: 366 mg (88%). Method b: A solution of **3** (100 mg, 0.085 mmol) in 10 mL of toluene was treated with triphenyltin hydride (60 mg, 0.17 mmol). The resulting mixture was stirred for 2 min at room temperature and then evaporated to dryness. Addition of pentane affords a white solid, which was washed with pentane and dried in vacuo. Yield: 83 mg (80%). Anal. Calcd for $C_{54}H_{76}OsP_2Sn_2$: C, 53.39; H, 6.31. Found: C, 53.21; H, 6.88. IR (Nujol, cm^{-1}): ν(OsH) 1993 (m), 1956 (m). ^{1}H NMR (300 MHz, C_6D_6, 293 K): δ 7.89 (d, J_{H-H} = 6.9, 12H, Ph-H_{ortho}), 7.21 (t, J_{H-H} = 6.9, 12H, Ph-H_{meta}), 7.13 (t, J_{H-H} = 6.9, 6H, Ph-H_{para}), 1.96 (m, 6H, PC*H*), 0.94 (dvt, J_{H-H} = 6.9, N = 13.5, 36H, PCH(CH_3)$_2$), −10.06 (br, 4H, OsH). ^{1}H NMR (300 MHz, tol-d_8, 223 K, high-field region): δ −9.44 (t, J_{P-H} = 19.5, 2H, Os-H), −11.39 (br, 2H, Os-H). ^{13}C{^{1}H} NMR (75.42 MHz, C_6D_6, 293 K): δ 148.4 (s, Ph), 138.2 (s with tin satellites, J_{C-Sn} = 37, Ph), 127.5 (s, Ph), 127.3 (s, Ph), 30.5 (vt, N = 26.6, P*C*H), 20.2 (s, PCH(*C*H_3)$_2$). ^{31}P{^{1}H} NMR (121.42 MHz, C_6D_6, 293 K): δ 26.7 (s with tin satellites, J_{P-Sn}= 32). ^{119}Sn{^{1}H} NMR (111.82 MHz, C_6D_6, 293 K): δ −131.7 (t with tin satellites, J_{P-Sn} = 32, $J_{^{117}Sn-^{119}Sn}$ = 1018, $SnPh_3$). $T_{1(min)}$ (ms, OsH_4, 300 MHz, tol-d_8, 253 K): 208 ± 5 (−9.50 ppm), 209 ± 6 (−10.82 ppm). MS (FAB$^+$): m/z 1212 (M^+ − 2H).

X-ray Structure Analysis of $OsH_4(SnPh_3)_2(P^iPr_3)_2$. A yellow irregular prism suitable for X-ray diffraction analysis (0.60 × 0.20 × 0.10 mm) was mounted onto a glass fiber and transferred to a Bruker SMART APEX CCD diffractometer (T = 173.0(2) K, Mo Kα radiation, λ = 0.71073 Å). $C_{54}H_{76}OsP_2Sn_2$: M_w 1214.67, monoclinic, space group $C2/c$, a = 12.7173(13) Å, b = 20.0547(13) Å, c = 20.9584(17) Å, β = 107.547(2)°, V = 5096.5(7) Å^3, Z = 4, D_{calc} = 1.583 g cm^{-3}, F(000) = 2424, μ = 3.556 mm^{-1}; 16 921 measured reflections (2θ: 3−57°, ω scans 0.3°), 6092 unique (R_{int} = 0.0715); multiscan absorption correction applied (SADABS program), with min./max. transmission factors 0.862/0.474. Structure solved by Patterson and difference Fourier maps; refined using SHELXTL. Final agreement factors were R1 = 0.0374 (4657 observed reflections, $I > 2\sigma(I)$)) and wR2 = 0.0641; data/restraints/parameters 6092/0/281; GoF = 0.996; largest peak and hole 1.319 and −1.454 e/Å^3.

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

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(18) It is reasonable to think that the process is intramolecular. So, we assume that $\Delta S^{\ddagger} = 0$.

(19) Aracama, M.; Esteruelas, M. A.; Lahoz, F. J.; López, J. A.; Meyer, U.; Oro, L. A.; Werner, H. *Inorg. Chem.* **1991**, *30*, 288.