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Communications

Tin Trihydride as a Ligand in Osmium Complexes

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Summary: Tin trihydride $Os(SnH_3)(Tp)L(PPh_3)$ [$L = P(OMe)_3$, $P(OEt)_3$] *complexes were prepared by allowing chloro* $OsCl(Tp)L(PPh_3)$ *complexes to react first with* $SnCl_2$ *and then with* $NaBH_4$ *in ethanol. The complexes were characterized spectroscopically and by the X-ray crystal structure determination of the* $Os(SnH_3)(Tp)\{P(OMe)_3\}(PPh_3)$ *derivative. Reaction of tin trihydride complexes with* CO_2 *led to formate* $Os[SnH\{OC(H){=}O\}_2](Tp)L(PPh_3)$ *derivatives.*

Organotin compounds have been widely used as ligands in transition metal chemistry[1,2] in order to modify the properties of complexes and often to improve their catalytic activity.[3] However, despite extensive studies, no example of a stable complex[4] containing the simplest of the tin ligands, trihydride SnH_3, has ever been reported. This is somewhat surprising, as the chemistry of the EH_3 ligands is very well known[5] for carbon, the [M]-CH_3 complexes of which lie at the heart of organometallic chemistry. Some examples of [M]-SiH_3 and [M]-GeH_3 complexes have also been reported for silicon and germanium,[6] but only theoretical studies on model [M]-SnH_3 complexes are described for tin.[7]

In this communication we report the synthesis of the first transition metal complexes containing tin trihydride as a ligand, together with some reactivity studies that highlight the unprecedented insertion of CO_2 into the coordinate[8] Sn−H bond.

The reaction of chloro $OsCl(Tp)L(PPh_3)$ complexes [Tp = tris(pyrazolyl)borate; $L = P(OMe)_3$, $P(OEt)_3$] with $SnCl_2$ gives trichlorostannyl $Os(SnCl_3)(Tp)L(PPh_3)$ derivatives (**1**), in about 80% yield. Treatment of **1** with $NaBH_4$ in ethanol gives the trihydridestannyl $Os(SnH_3)(Tp)L(PPh_3)$ complexes (**2**) as white microcrystals in 70% yield (Scheme 1).

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[4] A very unstable compound, formulated as $Mn(SnH_3)(CO)_5$, was obtained from the reaction of $Na[Mn(CO)_5]$ with SnH_3Cl at −45 °C. However, the ^{119}Sn and ^{117}Sn satellites in the proton signals attributed to the SnH_3 group in the ^1H NMR spectra were not observed. See: Foster, S. P.; Mackay, K. M. *J. Organomet. Chem.* **1983**, *247*, 21−26.

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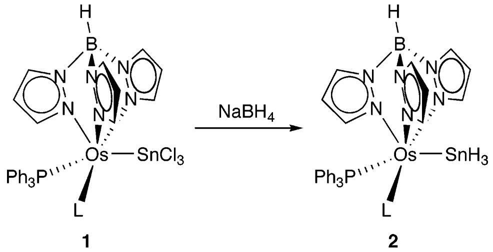
Scheme 1[a]



[a] L = $P(OMe)_3$ (**a**), $P(OEt)_3$ (**b**).

The complexes were characterized spectroscopically (IR, ^1H, ^{31}P, ^{119}Sn NMR) and by X-ray crystal structure determination[9] of $Os(SnH_3)(Tp)\{P(OMe)_3\}(PPh_3)$ (**2a**) (Figure 1). Compound **2a** crystallizes in the triclinic $P\bar{1}$ space group, with two independent molecules in the asymmetric unit. The two $Os(SnH_3)(Tp)\{P(OMe)_3\}(PPh_3)$ molecules are very similar, and Figure 1 shows the structure and numbering scheme of one of them. Osmium coordination is octahedral, with the monodentate PPh_3, $P(OMe)_3$, and SnH_3 ligands arranged in *fac* geometry at the three sites left free by the tripodal tris(pyrazolyl)borate molecule. The complex is chiral, but both enantiomers are present in the centrosymmetric crystal. Os−Sn bond distances (2.6360(5), 2.6473(5) Å) fall in the range observed for the 29 examples of compounds containing a terminal $Os{-}SnX_3$ bond reported in the crystallographic literature (2.61−2.73 Å). The Sn−H bond distances[10] range between 1.73 and 1.90 Å. Comparison of the three Os−N distances observed for tripodal ligand Tp suggests ranking the *trans* influence of PPh_3, $P(OMe)_3$, and SnH_3 molecules: the trihydridestannyl group appears to be the most effective in elongating the opposite Os−N bonds (Os−N = 2.183(5), 2.189(5) Å, respectively, for the two independent molecules), followed by $P(OMe)_3$ (2.181(5), 2.160(5) Å) and PPh_3 (2.147(5), 2.145(5) Å).

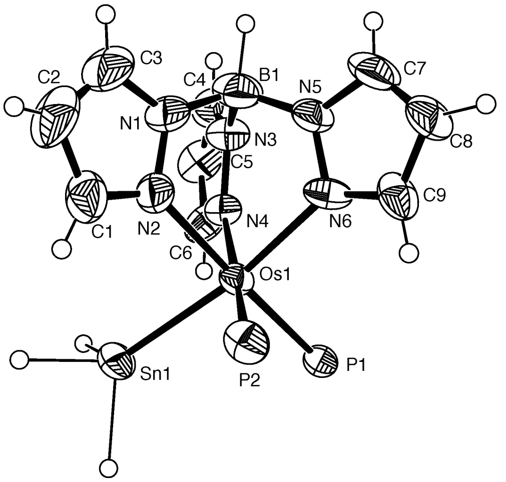


Figure 1. Perspective view of complex $Os(SnH_3)(Tp)\{P(OMe)_3\}(PPh_3)$ (**2a**), with thermal ellipsoids drawn at the 50% probability level. Phenyl (at P1) and methoxy groups (at P2) have been omitted for clarity. Coordination geometry for the two independent molecules: Os−N2 = 2.147(5)/2.145(5), Os−N4 = 2.181(5)/2.160(5), Os−N6 = 2.189(5)/2.183(5), Os−P1 = 2.315(1)/2.324(2), Os−P2 = 2.214(2)/2.212(2), Os−Sn = 2.6360(5)/2.6473(5) Å. Sn−H distances[10] range between 1.73 and 1.90 Å.

The IR spectra (KBr) of trihydridestannyl **2** complexes show two absorptions between 1761 and 1718 cm^{-1}, attributed to the ν_{SnH} of the SnH_3 ligand. In the spectra of labeled $Os(SnD_3)(Tp)\{P(OEt)_3\}(PPh_3)$ (**2b**$_1$), the two ν_{SnD} bands were observed at 1259 and 1238 cm^{-1}.

Diagnostic for the presence of tin trihydride as a ligand are both ^1H and ^{119}Sn NMR spectra. In the proton spectra, a doublet of doublets, with the characteristic satellites due to coupling with ^{119}Sn and ^{117}Sn, was observed at 2.46 (**2a**) and 2.63 ppm (**2b**) and attributed to SnH_3 protons. The ^{119}Sn NMR spectra appear as a quartet of doublets of doublets at −545.2 (**2a**) and −542.2 ppm (**2b**), due to coupling with the hydride and phosphorus nuclei, fitting the presence of the SnH_3 group.

Use of the $NaBH_4$ protocol to synthesize **2** is rare in organometallic tin chemistry,[11] which generally involves oxidative addition or nucleophilic substitution reactions to coordinate tin compounds to metal fragments.[1,2] The nature of the ancillary ligands in stabilizing $[Os]{-}SnH_3$ complexes (**2**) also seems to be crucial, since both Tp and phosphite[12] ligands are required for the synthesis of stable tin trihydride derivatives.[13]

Tin trihydride **2** complexes react with CCl_4 sequentially to give tin dihydride $[Os]{-}SnH_2Cl$ (**3**), hydride $[Os]{-}SnHCl_2$ (**4**), and trichloride $[Os]{-}SnCl_3$ (**1**) complexes (Scheme 2).

Scheme 2[a]

$$\underset{\mathbf{2}}{[Os]{-}SnH_3} \xrightarrow{CCl_4} \underset{\mathbf{3}}{[Os]{-}SnH_2Cl} \longrightarrow$$

$$\xrightarrow{CCl_4} \underset{\mathbf{4}}{[Os]{-}SnHCl_2} \xrightarrow{CCl_4} \underset{\mathbf{1}}{[Os]{-}SnCl_3}$$

[a] [Os] = $Os(Tp)L(PPh_3)$; L = $P(OMe)_3$ (**a**), $P(OEt)_3$ (**b**).

Both dihydride $Os(SnH_2Cl)(Tp)\{P(OMe)_3\}(PPh_3)$ (**3a**) and monohydride $Os(SnHCl_2)(Tp)\{P(OMe)_3\}(PPh_3)$ (**4a**) chlorostannyl derivatives were separated in pure form and characterized by standard methods. Diagnostic were the proton-coupled ^{119}Sn NMR spectra, which appear as a triplet of doublets of doublets at −274.1 ppm for dihydride **3a** and as a doublet of doublets of doublets at −307.8 ppm for monohydride **4a**. Also of interest was the shift of the tin hydride signal in the proton spectra on going from complex **2** to **4**, which moved from 2.46 (**2a**) to 5.85 (**3a**) and reached 9.22 ppm in **4a**.

The reaction with CCl_4 is classic for transition metal hydrides[14] and indicates the polyhydridic character of the SnH_3 group. Support for this hypothesis comes from the reaction with carbon dioxide, which quickly reacted with $Os(SnH_3)(Tp)L(PPh_3)$ to give tin formate $Os[SnH\{OC(H){=}O\}_2](Tp)L(PPh_3)$ derivatives (**5**), which were isolated as solids and characterized

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(8) Thermodynamic parameters for the formation of tributylformate Bu_3SnO_2CH from the reaction of Bu_3SnH with CO_2 have been reported: Klingler, R. J.; Bloom, I.; Rathke, J. W. *Organometallics* **1985**, *4*, 1893−1894.

(9) *Crystal data*: $C_{30}H_{37}BN_6O_3OsP_2Sn$ (**2a**), fw = 911.30, crystal dimensions 0.3 × 0.2 × 0.1 mm, triclinic, space group $P\bar{1}$, $Z = 4$, $a = 11.2586(8)$ Å, $b = 15.005(1)$ Å, $c = 21.336(2)$ Å, $\alpha = 81.162(1)°$, $\beta = 77.028(1)°$, $\gamma = 88.442(1)°$, $V = 3470.7(5)$ Å^3, $\rho = 1.744$ Mg m^{-3}, 14 118 unique reflections (R(int) = 0.0466), 10 201 observed ($I > 2\sigma(I)$), 14 118 data, 826 parameters, 8 restraints, R1 = 0.0377, wR2 = 0.0920 (on $I > 2\sigma(I)$), R1 = 0.0622, wR2 = 0.1040 on all data.

(10) Hydrogen atoms bonded to Sn were located on Fourier maps and constrained to have all similar Sn−H bond lengths and thermal parameters.

(11) Lappert, M. F.; McGeary, M. J.; Parish, R. V. *J. Organomet. Chem.* **1989**, *373*, 107−117.

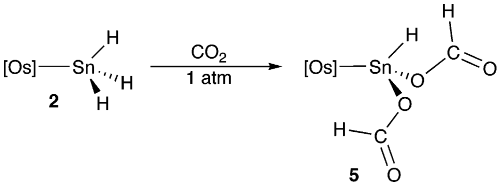
(12) The important role of phosphite ligands in the chemistry of classical and nonclassical transition metal hydrides has previously been highlighted; see: Albertin, G.; Antoniutti, S.; Bettiol, M.; Bordignon, E.; Busatto, F. *Organometallics* **1997**, *16*, 4959−4969. Albertin, G.; Antoniutti, S.; Bortoluzzi, M. *Inorg. Chem.* **2004**, *43*, 1328−1335, and references therein.

(13) Related ruthenium $Ru(SnH_3)(Tp)L(PPh_3)$ [L = $P(OMe)_3$, $P(OEt)_3$] complexes have recently been prepared in our laboratory.

(14) (a) Muetterties, E. L. *Transition Metal Hydrides*; Marcel Dekker: New York, 1971. (b) Dedieu, A. *Transition Metal Hydrides*; Wiley-VCH: New York, 1992.

(Scheme 3). The reaction proceeds with the insertion of two CO_2 molecules into two Sn−H bonds, to give the final tin hydridebis(formate) species **5**.

Scheme 3 [a]



[a] [Os] = Os(Tp)L(PPh_3); L = $P(OMe)_3$ (**a**), $P(OEt)_3$ (**b**).

Insertion of CO_2 into the M−H bond of classical hydrides is well-known[15,16] and studied as an important step of its functionalization reactions. Insertion into the tin hydride bond has been reported in only one case[8] for a free Bu_3SnH compound, so that our reaction on the [Os]-SnH_3 group is the first example of insertion of CO_2 into the coordinate Sn−H bond.[1,2,17]

Complexes **5** were isolated as white powders and characterized by spectroscopic methods. The IR spectra of bis(formate) Os[SnH{OC(H)═O}$_2$](Tp)L(PPh_3) complexes (**5**) show one strong band at 1676−1675 cm^{-1} due to ν_{SnH} and two medium absorptions at 1662−1629 cm^{-1} attributed[15,16] to the $\nu_{OCO\mathit{asym}}$ of the two η^1-formate O−C(H)═O groups. In the high-frequency region of ^1H NMR spectra, a multiplet appears at 8.99 (**5a**) and 9.60 ppm (**5b**), with the characteristic satellites of ^{119}Sn and ^{117}Sn attributed to SnH proton resonances. Two singlets at 8.21 and 7.81 (**5a**) and 8.14 and 8.01 ppm (**5b**) also appear in the spectra, which, in an HMQC experiment, were correlated with two singlets[18] at 158.2 and 157.8 (**5a**) and 167.0 and 166.2 ppm (**5b**) of the ^{13}C spectra and attributed to the resonance of the two ═CH formate groups, respectively.[15,16,19] The ^{119}Sn NMR spectra appear as a doublet of doublets of doublets at −341.5 (**5a**) and −349.5 ppm (**5b**) due to coupling with phosphorus nuclei and the hydride of the SnH{OC(H)═O}$_2$ group, fitting the proposed formulation for the complexes.

The behavior of [Os]SnH_3 complexes toward CCl_4 and CO_2 highlights the hydridic nature of the SnH_3 group and leads us to regard our Os(SnH_3)(Tp)L(PPh_3) species from two points of view, i.e., as either metal complexes containing SnH_3 as a ligand or tin polyhydride complexes stabilized by the Os(Tp)L(PPh_3) fragment.

We are currently extending experimental work to prepare other tin trihydride complexes and study the influence of the stannyl group on the properties of the metal fragments.

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Supporting Information Available: Experimental, analytical, and spectroscopic data for new compounds (PDF); crystallographic data for compound **2a** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) (a) Whittlesey, M. K.; Perutz, R. N.; Moore, M. H. *Organometallics* **1996**, *25*, 5166−5169. (b) Field, L. D.; Lawrenz, E. T.; Shaw, W. J.; Turner, P. *Inorg. Chem.* **2000**, *39*, 5632−5638, and references therein.

(17) Davies, A. G. *Organotin Chemistry*; Wiley-VCH: Weinheim, Germany, 2004.

(18) In the proton-coupled ^{13}C NMR spectra of **5a** at 203 K, two doublets appear at 158.2 and 157.8 ppm, whose J_{CH} value of about 200 Hz is characteristic for a CH formyl resonance (see ref 16).

(19) In transition metal complexes containing a formyl [M]-η^1-OC(H)═O group, a CH resonance appears between 9.32 and 7.47 ppm in ^1H NMR spectra, and a carbonyl carbon resonance typically occurs between 184 and 170 ppm in ^{13}C spectra (see ref 16b). These data strongly support the presence of η^1-formate groups in our complexes **5**.