



Communication

Synthesis of $\text{Ph}_2\text{LSn}(\mu\text{-OH})\text{Bu}_3\text{SnCl}$. Trapping of monomeric triorganotin hydroxide Ph_2LSnOH [☆]

Libor Dostál ^a, Jan Taraba ^{b,1}, Roman Jambor ^{a,*}^a Department of General and Inorganic Chemistry, Faculty of Chemical Technology, University of Pardubice, nám. Čs. legií 565, CZ-532 10 Pardubice, Czech Republic^b Department of Inorganic Chemistry, Faculty of Science, Masaryk University of Brno, Kotlarska 2, CZ-611 37 Brno, Czech Republic

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ABSTRACT

The reaction of triorganotin(IV) compound Ph_2LSnCl (**1**), ($L = 2,6\text{-}(t\text{-BuOCH}_2)_2\text{C}_6\text{H}_3$), with $(\text{Bu}_3\text{Sn})_2\text{O}$ resulted to the isolation of $\text{Ph}_2\text{LSn}(\mu\text{-OH})\text{Bu}_3\text{SnCl}$ (**2**), in which a monomeric triorganotin(IV) hydroxide Ph_2LSnOH intermolecularly coordinates Bu_3SnCl moiety. Compound **2** was characterized by combination of ^1H , ^{13}C and ^{119}Sn NMR spectroscopy, ESI/MS, elemental analysis and X-ray diffraction.

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Organotin(IV) oxides and hydroxides are well established as homogenous catalysts in various transesterification or transcarbamoylation processes [1]. Triorganotin(IV) hydroxides R_3SnOH are usually reported as the class of compounds synthesized by hydrolytic processes of corresponding halides and they can easily undergo the dehydration resulting to corresponding distannoxane species. The structures of these compounds strongly depend on the nature of R groups. Triorganotin hydroxides with relatively small R groups form infinite zig-zag chains, in which R_3SnOH moieties are associated via hydroxo bridges [2]. When bulkier groups are involved, however, R_3SnOH compounds form monomeric species but only two compounds of this type containing four-coordinated tin atom have previously been structurally characterized [3,4] (Chart 1A and B).

Recently, the simple preparation of tetraorganodistannoxane $[(L)_2\text{Sn}(\text{OH})_2\text{O}]_n$ and Sn_2 diorganotin(IV) dication $[\text{Ph}(L')\text{Sn}(\mu\text{-OH})_2\text{-Sn}(L')\text{Ph}]^{2+} 2[\text{CB}_{11}\text{H}_{12}]^-$, diorganotin hydroxides containing O,C,O-chelating ligands L ($2,6\text{-}(t\text{-BuOCH}_2)_2\text{C}_6\text{H}_3$) and L' ($2,6\text{-}(\text{MeOCH}_2)_2\text{C}_6\text{H}_3$) [5], has been reported (Chart 1C and D).

To further explore the field of potential use of O,C,O-chelating ligands in the preparation of organotin hydroxide, we focused on the synthesis of triorganotin hydroxides containing O,C,O-chelating ligands. Here we report on the isolation of $\text{Ph}_2\text{LSn}(\mu\text{-OH})$

Bu_3SnCl (**2**), where monomeric triorganotin(IV) hydroxide Ph_2LSnOH intermolecularly coordinates Bu_3SnCl .

The compound **2** was prepared by the reaction of triorganotin compound Ph_2LSnCl (**1**) [6] with $(\text{Bu}_3\text{Sn})_2\text{O}$ [7,8] (Scheme 1).

The ^{119}Sn NMR spectrum of **2** in CDCl_3 exhibited two signals at -131.8 and 62.2 ppm indicating the presence of two different tin atoms in the molecule. While the first one is shifted downfield compare to starting Ph_2LSnCl (-144.2 ppm) [6] and is diagnostic for pentacoordinated central tin atoms [9], the latter one is shifted downfield compare to the starting $(\text{Bu}_3\text{Sn})_2\text{O}$ (92.7 ppm) [10a]. The ^1H NMR spectrum showed the presence of both ligand L (broad singlet at 4.6 ppm for CH_2O groups comparable to starting compound **1** $\delta^1\text{H}(\text{CH}_2) = 4.6$ ppm) and Bu groups in mutual 1:3 integral ratio. The ^{13}C NMR spectrum of **2** revealed three sets of signals with tin satellites indicating the presence the three different L, Ph and Bu groups bonded to the central tin atom. The values of bonding angles of $\text{C}^{\text{Ph}}\text{-Sn-C}^{\text{Ph}}$ (118°) and $\text{C}^{\text{Bu}}\text{-Sn-C}^{\text{Bu}}$ (115°) calculated from $^1J(^{119}\text{Sn}, ^{13}\text{C}^{\text{Ph}}(1)) = 705$ Hz and $^1J(^{119}\text{Sn}, ^{13}\text{C}^{\text{Bu}}(1)) = 407$ Hz indicate distorted trigonal bipyramidal configuration at both tin atoms in **2** [9]. Positive mode of ESI/MS spectrum of **2** showed the presence of intense peak at $m/z = 523$ assigned to $[\text{Ph}_2\text{LSn}]^+$, fragment of triorganotin(IV) hydroxide Ph_2LSnOH . This observation indicates that the Bu_3SnCl moiety is weakly coordinated by the triorganotin(IV) hydroxide Ph_2LSnOH in compound **2**. Similar result could be also determined from ^{119}Sn NMR spectra of **2**. The value of $\delta(^{119}\text{Sn})$ 62.2 ppm shows a considerable upfield shift relative to non-coordinated Bu_3SnCl (152 ppm), but is shifted downfield compare to the values of $\delta(^{119}\text{Sn})$ found in $\text{Bu}_3\text{SnCl}^*\text{A}$ complexes [**A** = py ($+10.6$ ppm), dmsO ($+2.7$ ppm), hmpa (-35.1 ppm)] where five

[☆] L is an abbreviation for O,C,O-chelate $2,6\text{-}(t\text{-BuOCH}_2)_2\text{C}_6\text{H}_3$.

* Corresponding author. Fax: +420 466037068.

E-mail address: roman.jambor@upce.cz (R. Jambor).

¹ Fax: +420 549492443.

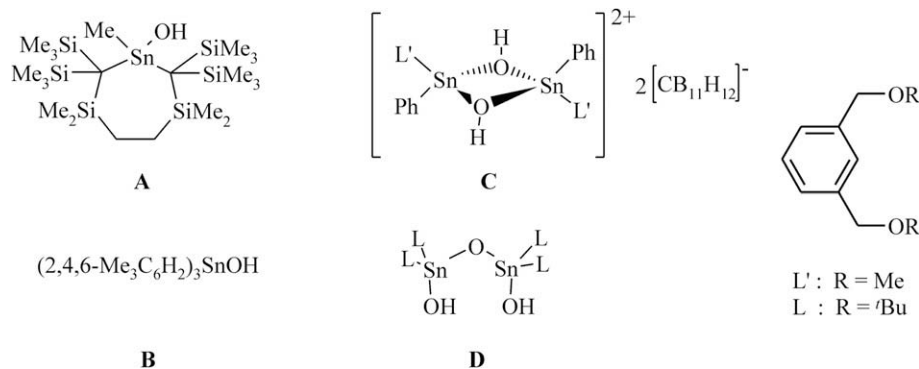
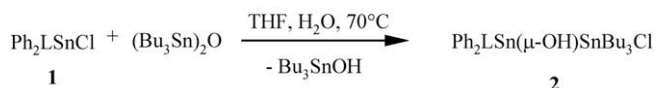


Chart 1.



Scheme 1. Preparation of compound 2.

coordinated tin atom was reported [10b]. These experimental data establish that the Ph_2LSnOH moiety coordinates Bu_3SnCl by weaker interaction than the solvent molecules like pyridine or DMSO.

The molecular structure of **2** was determined by single-crystal X-ray analysis (Fig. 1). Single crystals of **2** were obtained by slow evaporation of a hexane solution and selected bond lengths, angles and of **2** and structural parameters of related compounds are given in Table 1 [11].

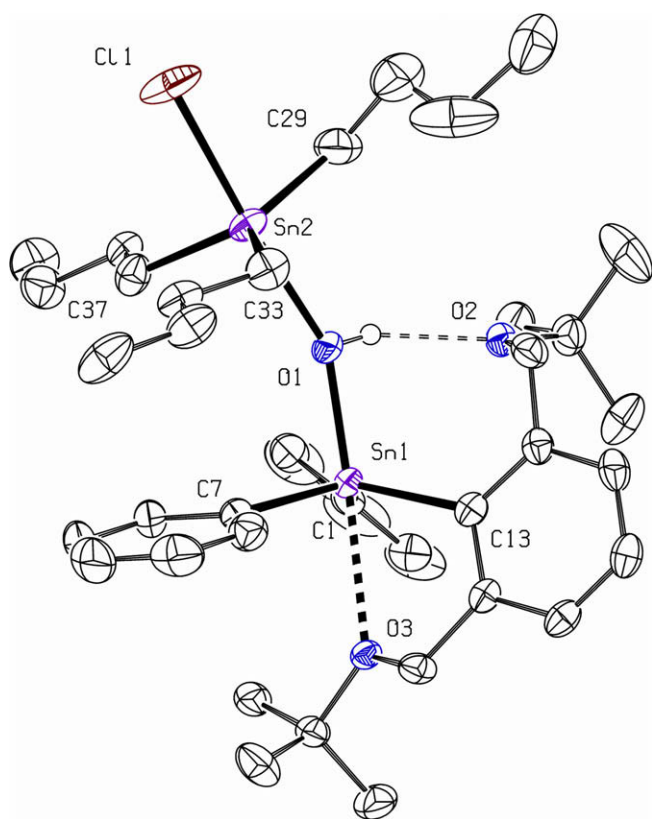


Fig. 1. General view (ORTEP) of a molecule showing 40% probability displacement ellipsoids and the atom-numbering scheme for **2**. The hydrogen atoms are omitted for clarity (expect hydrogen involved in OH group).

The molecular structure of **2** consists of two moieties Ph_2LSnOH and Bu_3SnCl that are joined by $\text{Sn}-(\mu\text{-OH})\text{-Sn}$ bridge formed by an intermolecular $\text{Sn}-\text{O}$ coordination. The shapes of coordination polyhedrons around both central tin atoms can be described as a distorted *trans*-trigonal bipyramids, with carbon atoms in equatorial positions and electronegative atoms in axial positions. The $\text{Sn}(1)$ atom of Ph_2LSnOH fragment is occupied by three carbon atoms C(1), C(7) and C(13) (involving ligand L and both Ph groups) forming equatorial plane and two oxygen atoms O(3) and O(1) (involving ligand L and hydroxyl group) in axial position with bonding angle $\text{O}(3)\text{-Sn}(1)\text{-O}(1) = 176.43(12)^\circ$. The value of bond length $\text{Sn}(1)\text{-O}(3)$ (2.624(3) Å) indicates the presence of medium strong $\text{Sn}-\text{O}$ intramolecular interaction in Ph_2LSnOH , while the second oxygen atom O(2) of ligand L is out of the primary tin coordination sphere [$\text{Sn}(1)\text{-O}(2) = 3.218(3)$ Å]. This oxygen atom O(2) and the hydrogen atom H(1) of the hydroxy group (O(1)) are, however, involved in the hydrogen-bonding interaction [$\text{O}(1)\cdots\text{O}(2)$ 2.693(5) Å, $\text{O}(1)\text{-H}(1)\cdots\text{O}(2)$ $175.68(10)^\circ$]. The bond length $\text{Sn}(1)\text{-O}(1)$ (2.068(3) Å) is comparable to the Σ_{cov} (Sn, O) = 2.066 Å [12] and clearly demonstrates the presence of covalent bond $\text{Sn}-\text{O}$ defining thus the presence of monomeric triorganotin hydroxide Ph_2LSnOH . The longer $\text{Sn}(2)\text{-O}(1)$ bond (2.342(4) Å) suggests that hydroxy group of Ph_2LSnOH is involved in coordinate dative interaction with Bu_3SnCl . The central tin atom Sn(2) of Bu_3SnCl , due to this interaction, is also in the centre of distorted trigonal bipyramid, where equatorial plane is formed by three carbon atoms (C(29), C(33), C(37)) involving Bu groups and axial positions are occupied by oxygen atom O(1) and chloride Cl(1) [$\text{O}(1)\text{-Sn}(2)\text{-Cl}(1) = 175.68(10)^\circ$ and $\text{Sn}(2)\text{-Cl}(1) = 2.5481(16)$ Å]. While simple triorganotin(IV) hydroxides Ph_3SnOH or Et_3SnOH contain two nearly same $\text{Sn}-\text{O}$ dative bonds (see Table 1), similar structural motif with one covalent $\text{Sn}-\text{O}$ (2.078 Å) and one dative $\text{Sn}-\text{O}$ bond (2.265 Å) was found in $[\text{Me}_3\text{Sn}(\mu\text{-OH})\text{SnMe}_3(\mu\text{-OH})\text{SnMe}_3]^+\text{Br}^-$ (see Table 1) [13]. This comparison of bond lengths of $\text{Sn}-\text{O}$ dative bonds in discussed compounds clearly shows that compound **2** consists of two weakly coordinated parts Ph_2LSnOH and Bu_3SnCl bonded by medium strength $\text{Sn}-\text{O}$ intermolecular coordination. In contrast, related triorganotin compound $\{[(\text{Me}_2\text{L}^{\text{CN}}\text{Sn})_2(\mu\text{-OH})]^+\text{I}^-\}$ (where L^{CN} is $\text{Me}_2\text{NCH}_2\text{C}_6\text{H}_4$), having two five coordinated tin atoms [14] and $\{[(\text{Me}_3\text{Sn})_2(\mu\text{-OH})]^+\text{Cl}^-\}$, compound with two four-coordinated trimethyl tin atoms [15] contain two nearly same $\text{Sn}-\text{O}$ dative bonds (range of 2.124–2.146 Å) similarly to simple triorganotin(IV) hydroxides.

In summary we have reported on the preparation of $\text{Ph}_2\text{LSn}(\mu\text{-OH})\text{Bu}_3\text{SnCl}$ (**2**) consisting of two weakly coordinated moieties of monomeric triorganotin(IV) hydroxide Ph_2LSnOH and Bu_3SnCl bonded by $\text{Sn}-\text{O}$ dative bond. Up to date prepared and structurally characterized compounds R_3SnOH , which adopt a structure consisting of discrete molecules, are highly crowded triorganotin

Table 1
Selected bond length (Å) and angles (°) for R_3SnOH , $[Me_3Sn(\mu-OH)SnMe_3(\mu-OH)SnMe_3]^+Br^-$ and **2**.

R_3SnOH	Sn–O	O → Sn	O–Sn–O	Sn–O–Sn	Ref.
$Ph_2LSn(\mu-OH)Bu_3SnCl$ (2)	2.068	2.342	–	149.6	This work
Et_3SnOH	2.156	2.244	177.9	145.4	[2a]
Ph_3SnOH	2.197	2.255	177.6	137.8	[2b]
$[Me_3Sn(\mu-OH)SnMe_3(\mu-OH)SnMe_3]^+Br^-$	2.078	2.265	178.8	134.4	[13]

For table of contents use only. The reaction of triorganotin(IV) compound Ph_2LSnCl (**1**), ($L = 2,6-(t-BuOCH_2)_2C_6H_3$), with $(Bu_3Sn)_2O$ resulted to the isolation of $Ph_2LSn(\mu-OH)Bu_3SnCl$ (**2**) containing monomeric triorganotin(IV) hydroxide Ph_2LSnOH that intermolecularly coordinates Bu_3SnCl moiety. Compound **2** was characterized by the help of 1H , ^{13}C and ^{119}Sn NMR spectroscopy, ESI/MS, elemental analysis and X-ray diffraction.

hydroxides. Other organotin hydroxides form hydrogen-bonded dimmers [16] or polymers containing five-coordinate tin [2b]. The synthesis of **2** is thus another example of that the use of Y,C,Y-chelating ligands can be an alternative concept for the bulky substituents substitution.

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Appendix A. Supplementary material

CCDC 695719 contains the supplementary crystallographic data for **2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2009.01.009](https://doi.org/10.1016/j.jorganchem.2009.01.009).

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- [7] 0.91 ml of $(Bu_3Sn)_2O$ (1.8 mmol) was added to THF solution of Ph_2LSnCl (1 g; 1.8 mmol) and resulting suspension was heated to 70 °C for 5 days. THF was evaporated then and oily residue was extracted to hexane (2×20 ml) and hexane was evaporated to give oily product that was crystallized by adding of 5 ml of cold pentane. White crystalline product was identified as **2** (0.79 g, 50.9%). *Characterization*: $C_{40}H_{63}ClO_3Sn_2$ MW = 864.78 g/mol, m.p. 133–137 °C; *Elemental Anal.*: Calc./found) C: 55.56/(55.98); H 7.34/(7.89). ESI/MS: m/z 523, 100% $[M-Bu_3SnCl-OH]^+$. 1H NMR ($CDCl_3$, 360 MHz): δ (ppm) 0.84 (s, 18H, CH_3), 0.89 (t, 9H, CH_2), 1.17 (m, 6H, CH_2), 1.32 (m, 6H, CH_2), 1.61 (m, 6H, CH_2), 2.61 (s, 1H, OH), 4.60 (s, 4H, CH_2), 7.29–7.38 (m, 9H, ArH), 7.73 (m, 4H, ArH). ^{13}C NMR ($CDCl_3$, 90 MHz): δ (ppm): 13.6 ($C^{Bu}(4)$), 19.7 ($C^{Bu}(1)$), $^1J(^{119}Sn,^{13}C) = 407$ Hz), 26.9 ($C^{Bu}(3)$), $^3J(^{119}Sn,^{13}C) = 75.2$ Hz), 27.2 ($OCCH_3$), 28.0 ($C^{Bu}(2)$), $^2J(^{119}Sn,^{13}C) = 24.9$ Hz), 65.8 (CH_2O), 76.3 ($OCCH_3$), 127.1 ($C^L(3,5)$), $^3J(^{119}Sn,^{13}C) = 55.3$ Hz), 128.3 ($C^{Ph}(3,5)$), $^3J(^{119}Sn,^{13}C) = 67.2$ Hz), 129.3 ($C^{Ph}(4)$), 129.6 ($C^L(4)$), 134.9 ($C^L(1)$), 135.9 ($C^{Ph}(2,6)$), $^2J(^{119}Sn,^{13}C) = 45$ Hz), 143.5 ($C^{Ph}(1)$), $^1J(^{119}Sn,^{13}C) = 705$ Hz), 147.7 ($C^L(2,6)$), $^2J(^{119}Sn,^{13}C) = 34$ Hz). ^{119}Sn NMR ($CDCl_3$): δ (ppm) 62.2; –131.8. IR (solution of CH_2Cl_2): (cm^{-1}) ν (OH) = 3468 vbr.
- [8] (a) Since the reaction of Me_3SnCl and $(Me_3Sn)_2O$ resulted to the isolation of an unusual $[(Me_3Sn)_3O]^+ Cl^-$ compound with two dimensional, graphite like supramolecular structure based upon $Sn \cdots Cl$ secondary bonds [8b] similar compound $[(Bu_3Sn)_2(Ph_2LSnO)]^+ Cl^-$ can be postulated as an intermediate of the reaction of **1** with $(Bu_3Sn)_2O$. The presence of O,C,O-chelating ligand **L** could caused high non-stability of the intermediate resulting thus to the immediate reaction with water yielding compound **2**. Alternatively, the reaction of $(Bu_3Sn)_2O$ with H_2O yielded Bu_3SnOH that reacted with Ph_2LSnCl to form compound **2**;
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- [11] Colorless crystals of **2** were obtained by slow evaporation of hexane solution of **2**. The intensity data were collected on a KUMA KM-4 CCD kappa-axis diffractometer using a graphite monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å) at 120(2) K. $C_{20}H_{31.5}O_{1.5}Sn_1$, $M = 432.37$, triclinic, space group P1, $a = 10.502(2)$, $b = 11.625(2)$, $c = 18.625(4)$, $\alpha = 104.58(3)^\circ$, $\beta = 90.75(3)^\circ$, $\gamma = 107.55(3)^\circ$, $U = 2088.2(7)$ Å³, $Z = 4$, $\rho = 1.375$ g cm^{-3} , $\mu = 1.292$ mm⁻¹, 21641 reflections collected, of which 8415 were independent [$R(int) = 0.0372$]. Final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0459$, $wR_2 = 0.1215$. The structure was solved by direct methods (Sheldrick G.M.: SHELXL-97[17] program package, University of Goettingen 1997., Sheldrick G.M.: SHELXTL V 5.1[18], Bruker AXS GmbH.) Non-hydrogen atoms were refined anisotropically while hydrogen atoms were inserted in calculated positions and isotropically refined assuming a “ride-on” model.
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