



## Organotin(IV) compounds containing N,C,O-chelating ligand



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## ABSTRACT

A set of organotin(IV) compounds containing unsymmetrical N,C,O-chelating ligands  $\{C_6H_3(CH_2OMe)_2-(CH_2NMe_2)_2-6\}^-$  (hereafter denoted as  $L^1$ ) and  $\{C_6H_3(CH_2OtBu)_2-(CH_2NMe_2)_2-6\}^-$  (hereafter denoted as  $L^2$ ) was prepared. While triorganotin(IV) chlorides  $L^{1-2}Ph_2SnCl$  (**1** for  $L^1$ , **2** for  $L^2$ ) are stable, diorganotin(IV) chloride  $L^1PhSnCl_2$  (**3**) and monoorganotin(IV) bromide  $L^1SnBr_3$  (**5**) reacts with water under elimination of HX (X = Cl, Br). The reaction of another molecule **3** or **5** with HX (X = Cl, Br) provided “stannatranane type” compounds  $[\{C_6H_3(CH_2OMe)_2-(CH_2N^+HMe_2)_2-6\}(Ph)SnCl_3]$  (**4**) and  $[\{C_6H_3(CH_2OMe)_2-(CH_2N^+HMe_2)_2-6\}SnBr_4]$  (**6**), respectively. Compounds **1–6** were characterized by multinuclear NMR spectroscopy and molecular structures of **1**, **3**, **4** and **6** were determined by X-ray diffraction analysis.

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## 1. Introduction

The field of hyper-coordinated organotin(IV) compounds is currently extensively investigated [1a–k]. The hyper-coordination of tin(IV) atom can be achieved by using of organic groups containing additional donor atom Y, that provide an intramolecular Y→Sn donor–acceptor bond [2]. Exploration in the field of such ligands resulted to the preparation of terdentate monoanionic, so-called “pincer”, ligands with general formula  $[2,6-(YCH_2)_2C_6H_3]^-$ . First organotin(IV) compound, prepared in late 1970th, contained N,C,N-chelating ligand  $\{C_6H_3(CH_2NMe_2)_2-2,6\}^-$  [3]. Afterwards, organotin(IV) compounds containing an aryldiphosphonic ester  $\{C_6H_2[P(O)(OR)_2]_2-1,3-t-Bu-5\}^-$  as O,C,O-chelating ligand were mentioned in the late 1990s [4]. Different O,C,O-chelating ligand  $\{C_6H_3(CH_2OR)_2-2,6\}^-$  has been applied for preparation of hyper-coordinated organotin(IV) [5] compounds in 2002 and other types of Y,C,Y-pincer ligands were also applied in the chemistry of tin compounds [6]. Moreover, it was demonstrated, that different Y donor atoms influence the structure, stability and reactivity of prepared organotin compounds [7]. Besides other results in the field of organotin(IV) or organotin(II) compounds, it was demonstrated that N,C,N- or O,C,O-type chelating ligands are even useful for the stabilization of organotin(I) distannynes (Fig. 1) [8].

Above mentioned examples, however, dealt with symmetrical Y,C,Y-chelating ligands, while organotin(IV) compounds bearing unsymmetrical Y,C,Y'-chelating ligand are not practically known. The only example was reported by Jurkschat, who synthesized organotin(IV) compounds containing O,C,S-chelating ligand [9].

This prompt us to prepare an unsymmetrical N,C,O-chelating ligands  $\{C_6H_3(CH_2OMe)_2-(CH_2NMe_2)_2-6\}^-$  (hereafter denoted as  $L^1$ ) and  $\{C_6H_3(CH_2OtBu)_2-(CH_2NMe_2)_2-6\}^-$  (hereafter denoted as  $L^2$ ) [10]. As a part of the comprehensive studies on the intramolecularly coordinated organotin(IV) compounds [11], we report here synthesis of triorganotin(IV) chlorides  $L^1Ph_2SnCl$  (**1**) and  $L^2Ph_2SnCl$  (**2**); diorganotin(IV) chloride  $L^1PhSnCl_2$  (**3**) and monoorganotin(IV) bromide  $L^1SnBr_3$  (**5**). Compounds **3** and **5** react with  $H_2O$  under elimination of HX (X = Cl, Br). The following reaction of another molecule **3** or **5** with HX (X = Cl, Br) provided “stannatranane type” compounds  $[\{C_6H_3(CH_2OMe)_2-(CH_2N^+HMe_2)_2-6\}(Ph)SnCl_3]$  (**4**) and  $[\{C_6H_3(CH_2OMe)_2-(CH_2N^+HMe_2)_2-6\}SnBr_4]$  (**6**), respectively. Compounds **1–6** were characterized by the multinuclear NMR spectroscopy and molecular structure of **2–4** and **6** were determined by X-ray diffraction analysis.

## 2. Result and discussion

2.1. Synthesis and characterization of triorganotin(IV) compounds  $L^{1-2}Ph_2SnCl$ 

Treatment of  $L^{1-2}Li$  with  $Ph_2SnCl_2$  provided triorganotin(IV) compounds  $L^1Ph_2SnCl$  (**1**) and  $L^2Ph_2SnCl$  (**2**) (Scheme 1). Compounds **1** and **2** are white solids soluble in polar solvents and stable on air.

Compounds **1** and **2** were studied in  $CDCl_3$  solution by the help of  $^1H$ ,  $^{13}C$  and  $^{119}Sn$  NMR spectroscopy. The  $^1H$  NMR spectrum revealed signals at  $\delta$  1.91 for  $NMe_2$  group and at 3.29 ppm for  $OMe$  group, respectively, in **1** ( $\delta$  1.30 for  $NMe_2$  and 1.83 ppm for  $OtBu$  in **2**). The  $^1H$  NMR spectrum also exhibited signals at  $\delta$  3.50 for methylene  $CH_2N$  group and at 4.94 ppm for methylene  $CH_2O$

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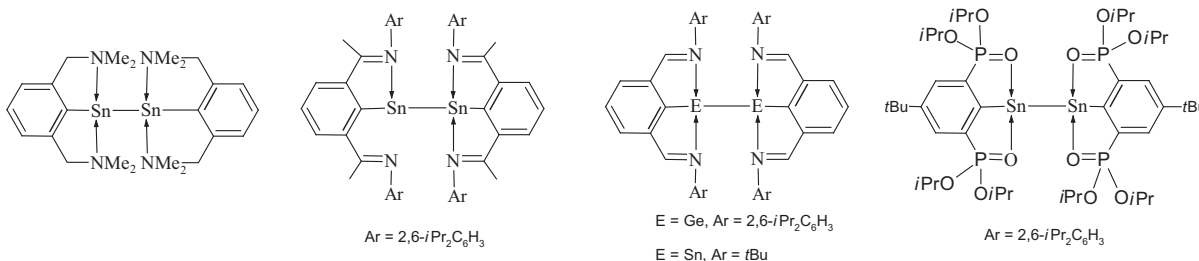
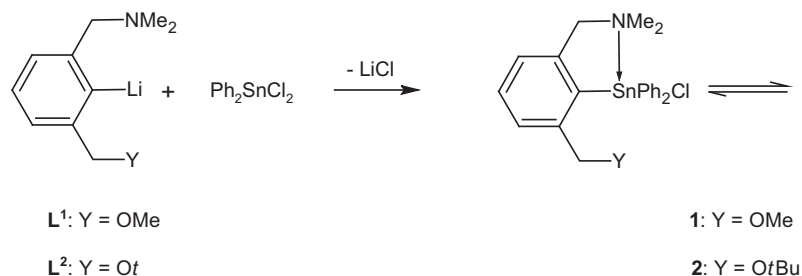


Fig. 1. Organotin(II) species stabilized by an N,C,N- and O,C,O-chelating ligands.



Scheme 1. Synthesis of triorganotin(IV) compounds **1** and **2**.

protons in **1** ( $\delta$  3.47 for  $CH_2N$  and 5.13 ppm for  $CH_2O$  in **2**). The signal of methylene  $CH_2O$  protons is shifted downfield ( $\Delta\delta = 0.48$ ) compared with those found in ligand precursor **L<sup>1</sup>H** ( $\Delta\delta = 0.70$  ppm in **2** in comparison with **L<sup>2</sup>H**). The downfield shifts of  $CH_2O$  groups indicate the presence of  $O \rightarrow Sn$  coordination in **1** and **2**. The  $^{119}Sn$  NMR spectrum shows resonance at  $\delta$   $-203.0$  ppm in **1** ( $-201.3$  ppm in **2**) that is shifted upfield ( $\Delta\delta$  158.3 ppm for **1**, and 156.6 ppm for **2**) compared with  $Ph_3SnCl$  ( $-44.7$  ppm) [12]. Values of  $\delta$  ( $^{119}Sn$ ) hint the presence of five-coordinated tin atom in **1** and **2** [12,13] and are comparable with those found in triorganotin(IV) compounds bearing C,N-chelating ligands [13]. The existence of  $O \rightarrow Sn$  interaction and the presence of five coordinated tin atom in **1** and **2** is also reflected in  $^{13}C$  NMR spectra of **1** and **2**. The values of the  $^1J(^{119}Sn, ^{13}C(1))$  and  $^1J(^{119}Sn, ^{13}C(1)_{Ph})$  coupling constants (730 and 735 Hz for **1**, 695 and 705 Hz for **2**) are higher than those found in  $Ph_3SnCl$  (614.3 Hz) [12,14]. The coordination arrangement at the tin atom is described as trigonal bipyramid in **1** and **2** based on the values of the calculated bonding angles  $C(1)-Sn-C(1)_{Ph}$  and  $C(1)_{Ph}-Sn-C(1)_{Ph}$  ( $119^\circ$ ,  $119^\circ$  (**1**);  $116^\circ$ ,  $119^\circ$  (**2**)) [15]. The presence of  $O \rightarrow Sn$  coordination in **1** and **2** is, however, in direct contrast with the strong  $N \rightarrow Sn$  coordination found in the solid state of **1** (*vide infra*) and this suggests the dynamic coordination of both donor atoms of the ligand **L<sup>1</sup>** in the solution of **1** and **2** (see Scheme 1).

The molecular structure of **1** was determined by X-ray diffraction analysis and is depicted in Fig. 2, crystallographic data are given in Table 1.

The tin atom is five coordinated with deformed *trans*-trigonal bipyramidal geometry in **1**. The equatorial plane is formed by C1, C12 and C18 carbon atoms of ligand **L<sup>1</sup>** and phenyl groups, while nitrogen atom N1 of ligand **L<sup>1</sup>** and chlorine atom Cl1 are located in the axial positions. The  $N1-Sn1$  bond distance ( $2.451(2)$  Å) indicates strong  $N \rightarrow Sn$  intramolecular coordination ( $\sum_{cov}(Sn,N) = 2.11$  Å,  $\sum_{vdw}(Sn,N) = 3.89$  Å) [16], while the  $O1-Sn1$  bond distance ( $3.293(2)$  Å) proves absence of  $O1 \rightarrow Sn1$  interaction in **1** ( $\sum_{vdw}(Sn,O) = 3.86$  Å) [16]. This hints that the **L<sup>1</sup>** ligand more resemble related C,N-chelating ligands in the solid state of **1** [13,17].

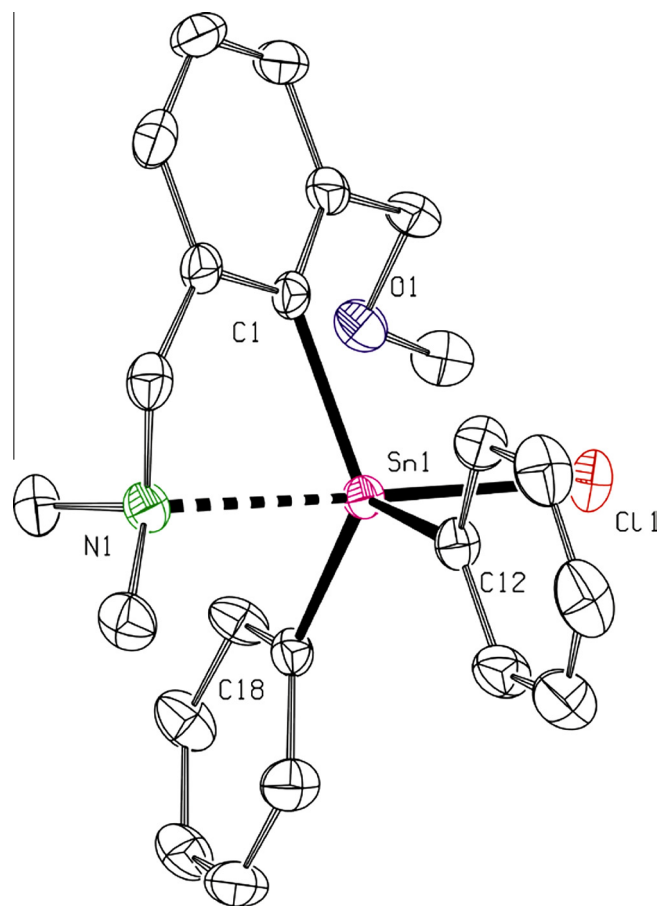


Fig. 2. ORTEP View of **1**. The thermal ellipsoids are drawn with 50% probability. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles ( $^\circ$ ):  $Sn1-N1$  2.451(2),  $Sn1-O1$  3.293(2),  $Sn1-C1$  2.149(3),  $Sn1-C12$  2.147(3),  $Sn1-C18$  2.132(3),  $Sn1-Cl1$  2.5123(8),  $N1-Sn1-Cl1$  176.93(7),  $C18-Sn1-C12$  120.63(12),  $C12-Sn1-C1$  124.63(12),  $C12-Sn1-C1$  110.98(12).

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