Available online at www.sciencedirect.com
ScienceDirect
Journal of Organometallic Chemistry 692 (2007) 908–911
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Note

Role of O,C,O-ligand in a new coordination mode of organotin compounds to 2-mercapto-1-methylimidazol. Stabilization of its thione form

Jana Martincová [a], Libor Dostál [a], Jan Taraba [b,1], Roman Jambor [a,*]

[a] Department of General and Inorganic Chemistry, 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, Kotlářská 2, CZ-611 37, Brno, Czech Republic

Received 29 June 2006; received in revised form 25 August 2006; accepted 29 September 2006
Available online 5 October 2006

Abstract

The reaction of the organotin compound $[Ph_2LSn]^+ [OTf]^-$ (**1**), ($L(O,C,O) = 2,6\text{-}(t\text{-}BuOCH_2)_2C_6H_3$), with the sodium salt Na(mimt), mimt = 1-methylimidazole-2-thiolate, resulted in the isolation of Ph_2LSn(mimt) (**2**), where the polar group (mimt) has been stabilized as the thione-tautomeric form by the triorganotin fragment Ph_2LSn. Product **2** was characterized by ^{1}H, ^{13}C and ^{119}Sn NMR and IR spectroscopy, ESI/MS, elemental analyses and X-ray diffraction.

Keywords: Organotin; Pincer ligands; S-ligands; NMR; Crystal structure

---

Organotin compounds containing various mercapto groups are extensively studied for their biological activities, most importantly as antitumor agents and their *in vitro* potency against trypanozoma cultures was demonstrated as well [1]. These compounds containing covalent Sn–S bond are also studied for industrial use, namely as stabilizers for polyvinyl chlorides [2]. An interesting class of organotin mercapto derivatives comprises those of general formula $R_3Sn(SR')$, where R′ contains a donor atom (D) capable of forming a secondary bond with tin atom [3]. The second donor atom (D) in mercapto groups is most commonly the nitrogen atom (N) and these ligands are known to possibly exist in two tautomeric thione and thiol forms (Scheme 1) [4]. While the thione form of the free ligand is more favorable and is preferred in solution based on ^{1}H NMR studies, where the presence of N–H instead of S–H has been detected, the thiol form of these polar groups can be found in the chemistry of organotin compounds resulting in the presence of the Sn–S covalent bond.

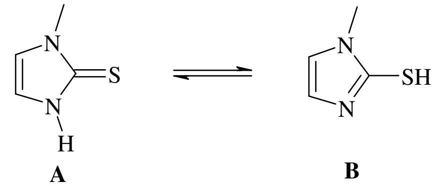
In connection with our previous studies that were focused on hypercoordinated organotin derivatives of Y,C,Y-pincer ligands containing covalent bond Sn–X, where X was a monodentate polar group that could not affect the geometry of the central tin atom [5], we decided to prepare a triorganotin compound containing 1-methylimidazole-2-thiol (Hmimt), which contains a nitrogen donor atom capable of forming an additional coordination bond Sn ← N. Here we report on the use of the triorganotin fragment Ph_2LSn containing pincer type ligand L ($L(O,C,O) = 2,6\text{-}(t\text{-}BuOCH_2)_2C_6H_3$) on the stabilization of thione-form in Ph_2LSn(mimt) (**2**) (mimt = 1-methylimidazole-2-thiolate).

The triorganotin compound $[Ph_2LSn]^+[OTf]^-$ (**1**) has been prepared according to literature [5] and stirring a solution of **1** with sodium salt Na(mimt) in dry degassed tetrahydrofuran overnight yielded a solid powder (Scheme 2) [6].

---

[*] Corresponding author. Fax: +420 466037068.
E-mail addresses: taraba@chemi.muni.cz (J. Taraba), roman.jambor@upce.cz (R. Jambor).
[1] Fax: +420 549492443.

0022-328X/$ - see front matter
doi:10.1016/j.jorganchem.2006.09.056



Scheme 1. Thione (**A**) and thiol (**B**) tautomeric forms of the mercapto ligands.

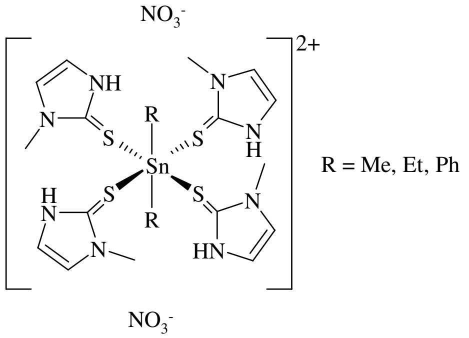


Chart 1.

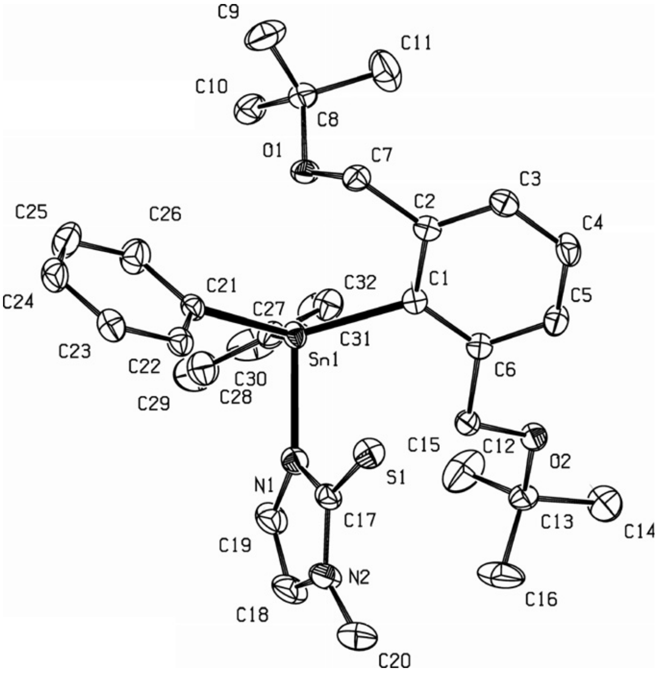


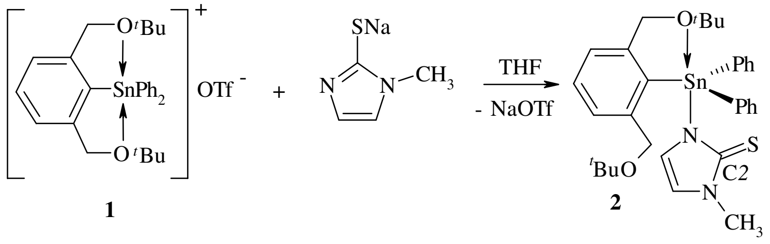
Fig. 1. General view (ORTEP) of a molecule showing 50% probability displacement ellipsoids and the atom-numbering scheme for **2**. The hydrogen atoms are omitted for clarity.

The analytical data show that the polar group (mimt) is stabilized in a thione form both in solution and solid state. The value of chemical shift C*2* in ^{13}C NMR spectroscopy is the most informative for thiol–thione tautomeric form determination [7]. The ^{13}C NMR data revealed broad signal of C*2* at 163.5 ppm for **2** that is comparable to the same signal of C*2* in free ligand (Hmimt) (δ ^{13}C(C*2*) = 160.2 ppm) existing in the thione form in solution [7]. To the best of our knowledge, such a stabilization of the thione form of this ligand has been reported in several organotin cations (δ^{13}C(C*2*) = 157.0 ppm), where free ligand (Hmimt) has been used as the S-donor ligand for organotin cations resulting in the Sn–S bond (Chart 1) [8].

However, the stabilization of the anionic polar group (mimt)$^-$ in thione form in organotin compounds resulting in the presence of Sn–N bond is unknown so far. The structurally similar compound Ph_3Sn(mimt) contains the covalent bond Sn–S indicating the presence of thiol form of (mimt)$^-$ (compare δ^{13}C(C*2*) = 138.7 ppm) [7]. The presence of thione form in **2** was also corroborated by IR spectroscopy where bands at 694 and 536 cm^{-1} assignable to σ(C═S) and π(C═S) were found [8].

Single crystals of **2** were obtained from a toluene solution at −5 °C and the molecular structure is shown in Fig. 1 [9]. The selected bond lengths, and angles of **2** and related compound Ph_3Sn(mimt) are given in Table 1.

The shape of the coordination polyhedron of **2** can be described as a distorted trigonal bipyramid, with carbon atoms in equatorial positions. One axial position is occupied by the oxygen donor atom from ligand L, while the nitrogen atom from mercapto polar group (mimt) is in the second one (found bonding angle O(1)–Sn(1)–N(1) = 168.07(8)°). The found bond length Sn(1)–O(1) (2.7875(16) Å) indicates the presence of medium strong Sn–O intramolecular interaction in **2**. Bond length Sn(1)–N(1) (2.1518(19) Å) is comparable to the Σ_{cov}(Sn, N) = 2.154 Å and clearly demonstrates the presence of covalent bond Sn–N in compound **2**. The presence of thione form of (mimt) is also corroborated by bond length C(17)–S(1) (1.696(2) Å) that is comparable to those found in organotin cations containing Hmimt in its thione form [8] and both double bonds C(17)–S(1) (1.696(2) Å) and



Scheme 2. Preparation and labeling of titled compound **2**.