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Mercapto derivatives of triorganotin Y,C,Y-pincer complexes: Role of Y,C,Y-chelating ligands in a new coordination mode of organotin compounds

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Abstract

We report the use of triorganotin fragments $R_2L^{1\text{-}2}Sn$ containing N,C,N and O,C,O-ligands $L^{1\text{-}2}$($L^1 = C_6H_3(Me_2NCH_2)_2$-2,6$^-$, $L^2 = C_6H_3(^tBuOCH_2)_2$-2,6$^-$) on stabilization of both thiol-form in $R_2L^{1\text{-}2}$Sn-2-SPy (2-SPy = pyridine-2-thiolate) and thione-form in $R_2L^{1\text{-}2}$Sn(mimt) (mimt = 1-methylimidazole-2-thiolate) of the polar groups. Treatment of ionic organotin compounds $[Me_2L^1Sn]^+[Cl]^-$ (**1**) and $[Ph_2L^2Sn]^+[OTf]^-$ (**2**) with appropriate sodium salts Na-2-SPy and Na(mimt) resulted in the isolation of Me_2L^1Sn-2-SPy (**3**), Ph_2L^2Sn-2-SPy (**4**), Me_2L^1Sn(mimt) (**5**), Ph_2L^2Sn(mimt) (**6**). While polar group 2-SPy exists in its thiol-tautomeric form in compounds **3** and **4**, the second polar group (mimt) has been stabilized as the thione-tautomeric form by triorganotin fragments $R_2L^{1\text{-}2}Sn$ in compounds **5** and **6**. The products were characterized by ^1H, ^{13}C and ^{119}Sn NMR and IR spectroscopy, ESI/MS, elemental analyses and structures of **3**, **6** were determined by X-ray diffraction study. The reactivity of compound **4** containing non-coordinated nitrogen atom of 2-SPy polar group towards CuCl and $AgNO_3$ is also reported. The reactions led to isolation of organotin compounds Ph_2L^2SnCl (**7**) and $Ph_2L^2SnNO_3$ (**8**) as the result of polar group transfer. The mechanism of this reaction has been investigated and compounds Ph_3Sn-2-SPy (**9**) and Ph_2L^2Sn-4-SPy (**10**) (4-SPy = pyridine-4-thiolate) have been prepared for this purpose.

Keywords: Organotin; Chelating ligands; NMR; Crystal structure

1. Introduction

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 too [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 a tin atom [3]. This donor atom (D) is most commonly the nitrogen atom (N) and these ligands are known to possibly exist in two tautomeric thione and thiol forms (Chart 1) [4].

In organotin compounds, at least three bonding modes between ligand SR′ and tin atom are conceivable (Chart 2) [5]. While the coordination with exo cyclic sulfur can be found in every kind of tetrahedral monomeric structures (**A**) [6], the coordination with endo cyclic nitrogen atom is not common for tin (**B**), but it is often found in zinc compounds. The N,S coordination is commonly observed in tri- or diorganotin compounds (**C**) and the coordination polyhedra of these compounds are thus intermediate between tetrahedron and trigonal bipyramid, where the strength of the Sn–N bond determines the degree of distortion [7].

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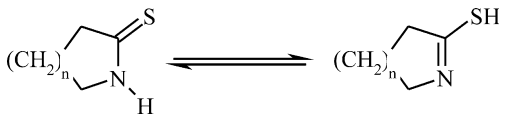


Chart 1.

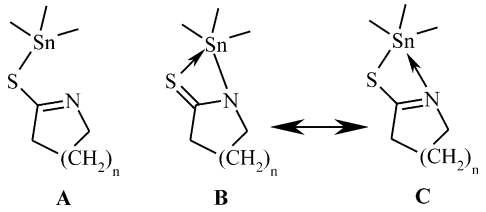


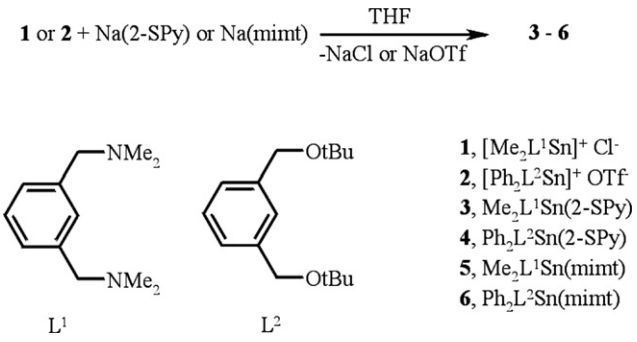
Chart 2.

In connection with our previous studies that were focused on hypercoordinated organotin derivatives of Y,C,Y-coordinating pincer-type ligands containing covalent bond Sn–X, where X was a monodentate polar group that could not affect the geometry of the central tin atom [8], we decided to prepare triorganotin compounds containing 2-mercaptopyridine (H-2-SPy) and 2-mercapto-1-methylimidazole (Hmimt). These polar groups contain a mercapto group and nitrogen donor atom capable of forming an additional coordination bond. Our preliminary results showed the possibility of stabilizing of a new thione-form of (mimt) polar group by triorganotin fragment [9]. To extend our study, we have used triorganotin fragments $R_2L^{1\text{-}2}Sn$ containing N,C,N (hereafter referred to as L^1) and O,C,O (hereafter referred to as L^2) – ligands ($L^1 = C_6H_3(Me_2NCH_2)_2\text{-}2,6^-$, $L^2 = C_6H_3(^tBuOCH_2)_2\text{-}2,6^-$) on the stabilization of both thiol-form in $R_2L^{1\text{-}2}Sn$-2-SPy (2-SPy = pyridine-2-thiolate) and thione-form in $R_2L^{1\text{-}2}Sn$-(mimt) (mimt = 1-methylimidazole-2-thiolate). The prepared compounds Me_2L^1Sn-2-SPy (**3**), Ph_2L^2Sn-2-SPy (**4**), Me_2L^1Sn(mimt) (**5**), Ph_2L^2Sn(mimt) (**6**) were characterized by ^1H, ^{13}C and ^{119}Sn NMR and IR spectroscopy, ESI/MS, elemental analyses and the structures of **3** and **6** were determined by X-ray diffraction study. The reactivity of compound **4** containing non-coordinated nitrogen atom of 2-SPy polar group towards CuCl and $AgNO_3$ is reported as well. The reactions resulted to isolation of organotin compounds Ph_2L^2SnCl (**7**) and $Ph_2L^2SnNO_3$ (**8**) as the result of polar group transfer. The mechanism of this reaction has been investigated and compounds Ph_3Sn-2-SPy (**9**) and Ph_2L^2Sn-4-SPy (**10**) (4-SPy = pyridine-4-thiolate) have been prepared for this purpose.

2. Result and discussion

2.1. Solution and solid state studies of 3–6

Compounds **3**–**6** were prepared by treatment of the ionic organotin compounds $[Me_2L^1Sn]^+[Cl]^-$ (**1**) and $[Ph_2L^2Sn]^+[OTf]^-$ (**2**) with the appropriate sodium salts Na-2-SPy and Na(mimt) (Scheme 1) [8].



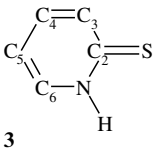
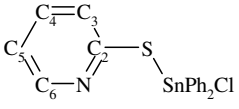
Scheme 1. Preparation of compounds **3**–**6**.

The values of $\delta(^{119}Sn)$ in **3** (−95.0 ppm), **4** (−141.9 ppm), **5** (−124.04 ppm) and **6** (−173.53 ppm) are typical for five coordinated central tin atom in molecular nonionic triorganotin compounds [10–12] (compare with the values of the ionic compounds **1** (14.5 ppm) and **2** (−25.8 ppm)) and they are shifted upfield compared to $Et_2Sn(\text{-}2\text{-}SPy)_2$ (−116.0 ppm), Ph_3Sn-2-SPy (−116.3 ppm) and Ph_3Sn-(mimt) (−112.2 ppm) [13–15]. The values of $^2J(^{119}Sn, ^1H(Me)) = 64$ Hz for **3**, 63.5 Hz for **5** and $^1J(^{119}Sn, ^{13}C(1)) = 692$ Hz for **4** and 713 Hz for **6** together with calculated bond angles C–Sn–C (115° for **3**, 119° for **4**, 115° for **5** and 120° for **6**) indicate distorted trigonal bipyramidal configuration at the tin atoms in **3**–**6** [16]. Dynamic behavior of **3**–**6** was studied by ^1H NMR spectroscopy at various temperatures (200–300 K, toluene-d_8) and showed non-equivalence of CH_2YR groups in **3**–**6** at low temperatures (decoalescence of CH_2 a CH_3 signals at 250 K for **3**, **4** and **6** and at 220 K for **5**).

Those data, however, do not predict the way in which the polar group is bonded to the organotin fragment. The ^{13}C NMR spectra and especially the value of C2 chemical shift (see Tables 1 and 2) are a very informative tool to determine, whether the polar group is stabilized in thione or thiol tautomeric form.

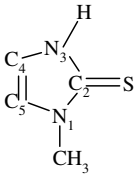
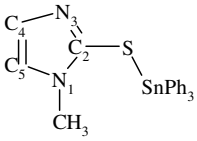
The value of $\delta(^{13}C(C2)) = 177.7$ ppm could be found when H-2-SPy is in its thione form [17], while the value of 164.2 ppm was found in organotin compound Ph_2SnCl-2-

Table 1
Selected values of $\delta(^{13}C)$ found in free ligand (existing as thione form), **3**, **4** and Ph_2SnCl-2-SPy (thiol form)

Compound/signal[a]	C(2)	C(3)	C(4)	C(5)	C(6)
	177.7	133.0	137.0	112.0	137.0
3	165.2	121.3	135.2	117.6	148.3
4	161.6	124.1	129.7	118.7	147.7
	164.2	123.7	139.7	119.5	146.2

[a] Measured in $CDCl_3$.

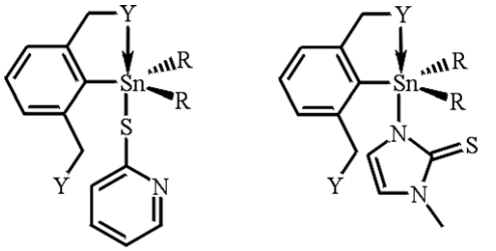
Table 2
Selected values of $\delta(^{13}C)$ found in free ligand (existing as thione form), **5**, **6** and Ph_3Sn(mimt) (thiol form) [15]

Compound/signal[a]	C(2)	C(4)	C(5)	N–CH_3
	160.2	114.0	118.7	34.0
5	162.8	118.8	118.8	34.6
6	163.5	120.2	121.4	34.8
	138.7	119.9	119.9	34.2

[a] Measured in $CDCl_3$.

SPy, where this polar group is stabilized in its thiol form (i.e. upfield shift, see Table 1) [18].

The ^{13}C NMR data revealed signal of C2 at 165.2 ppm for **3** and 161.6 ppm for **4**, i.e. very close to those found in Ph_2SnCl-2-SPy, where the polar group exists in the thiol form ($\delta^{13}C(C2) = 164.2$ ppm), and established presence of covalent bond Sn–S in compounds **3** and **4**. The structure



3. Y = NMe_2, R = Me
4. Y = O^{t}Bu, R = Ph

5. Y = NMe_2, R = Me
6. Y = O^{t}Bu, R = Ph

Fig. 1. Proposed structure of **3**–**6** in solution.

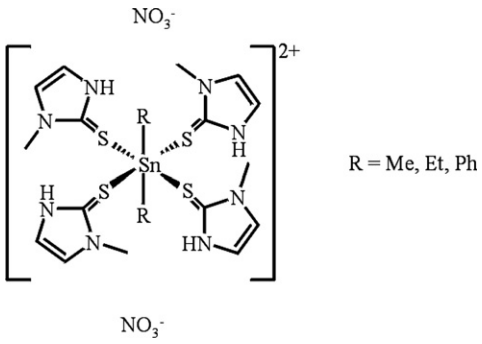


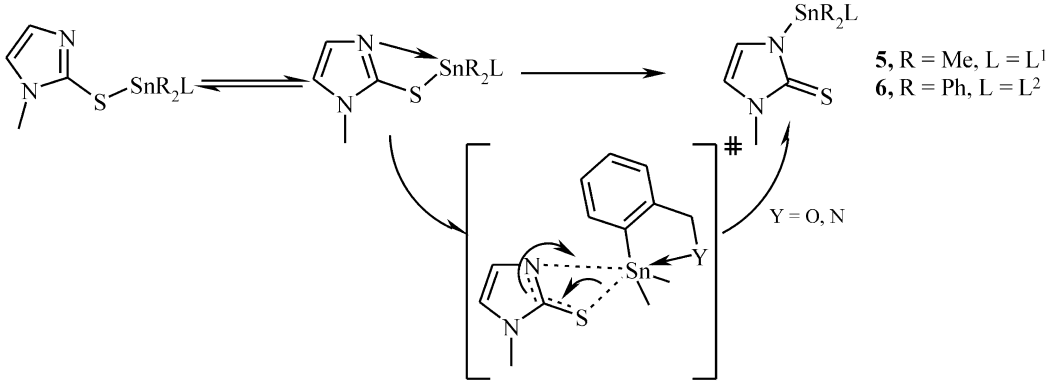
Chart 3.

of both compounds can be thus described as *trans*-trigonal bipyramid with carbon atoms in equatorial plane, one donor atom of Y,C,Y-chelating ligand and sulfur atom in axial positions (see Fig. 1).

On the other hand, the ^{13}C NMR spectra of **5** and **6** showed the polar group (mimt) is stabilized in a thione form in solution. While the value of $\delta^{13}C(2)$ 160.2 ppm indicated the presents of thione form of (mimt) in solution [15,19], the value of 138.7 ppm could be found in the case of its thiol form (i.e. upfield shift, see Table 2). The ^{13}C NMR data revealed broad signal of C2 at 162.8 ppm for **5** and 163.5 ppm for **6** that are comparable to the same signal of C2 in free ligand (Hmimt) ($\delta^{13}C(C2) = 160.2$ ppm) existing in the thione form in solution (see Table 2).

To the best of our knowledge, such a stabilization of the thione form of this ligand has been reported in several organotin cations ($\delta^{13}C(C2) = 157.0$ ppm), where a free ligand (Hmimt) has been used as the S-donor ligand for organotin cations resulting in the Sn–S bond (Chart 3) [20].

The stabilization of thione form of the anionic polar group $(mimt)^-$ by organotin compounds is unknown so far (but is usual in organozinc or thalium compounds) and results to the presence of Sn–N covalent bond in **5** and **6** (see Fig. 1). A structurally similar compound Ph_3Sn(mimt) contains covalent bond Sn–S as a result of the presence of thiol form of $(mimt)^-$ (compare $\delta^{13}C(C2) = 138.7$ ppm) [15]. The presence of thione form in **6** was also corroborated by IR spectroscopy where bands



5, R = Me, L = L^1
6, R = Ph, L = L^2

Scheme 2. Proposed formation of **5** and **6**.

at 694 cm^{-1} and 536 cm^{-1} assignable to σ(C=S) and π(C=S) were found [20]. Since the prepared organotin compounds analogously exists only as thiolato derivatives it seems to be reasonable to propose the role of Y,C,Y-chelating ligands in a new coordination mode of organotin compounds. The presence of additional Sn ← Y coordination by introducing Y,C,Y-chelating ligand may enable rearrangement of thiol to thione form (Scheme 2).

The structures of **3** and **6** have been determined by X-ray crystallographic studies (see Figs. 2, 3) and the crystallographic data are given in Table 3.

The shape of the coordination polyhedron of **3** can be described as a distorted trigonal bipyramid, with carbon atoms in equatorial positions (see Fig. 2). One axial position is occupied by the nitrogen donor atom from ligand L^1, while the sulfur atom from polar group 2-SPy is in the second one (N(1)–Sn(1)–S(1) = 169.4(2)°). Bond length Sn(1)–S(1) (2.544(3) Å) is comparable to the Σ_{cov}(Sn, S) = 2.469 Å and clearly demonstrates the presence of covalent bond Sn–S in compound **3** [21]. The presence of thiol form of 2-SPy is also corroborated by bond length S(1)–C(15) (1.761(11) Å) indicating a single bond character. The found bond lengths Sn(1)–N(1) (2.634(9) Å) and Sn(1)–N(3) (3.118(15) Å) indicate the presence of Sn–N intramolecular interactions in **3**.

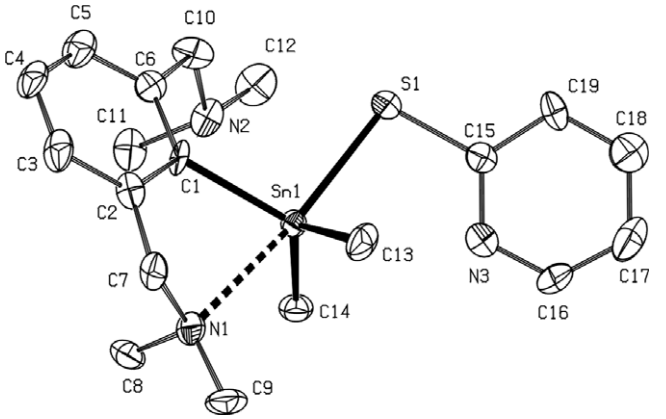


Fig. 2. General view (ORTEP) of a molecule showing 50% probability displacement ellipsoids and the atom-numbering scheme for **3**. The hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) for **3**: Sn(1)–C(1) 2.174(9), Sn(1)–C(14) 2.130(10), Sn(1)–C(13) 2.145(11), Sn(1)–N(1) 2.634(9), Sn(1)–N(2) 3.311 (9), Sn(1)–S(1) 2.544(3), S(1)–C(15) 1.761(11), N(3)–Sn(1) 3.118(11), N(1)–Sn(1)–S(1) 169.4(2), Sn(1)–S(1)–C(15) 97.5(4).

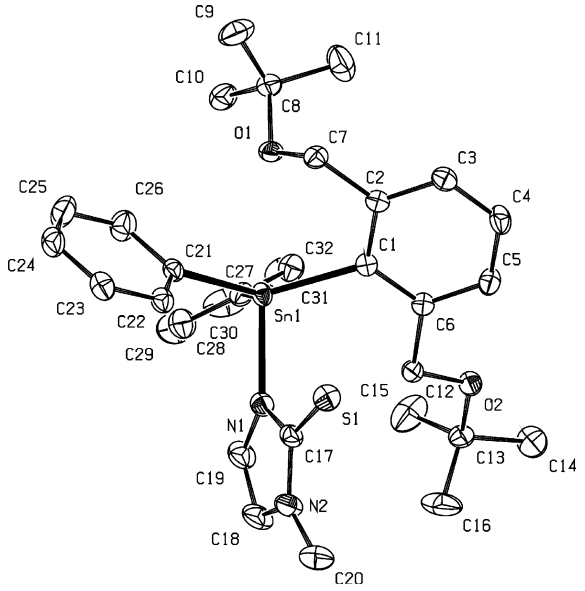


Fig. 3. General view (ORTEP) of a molecule showing 50% probability displacement ellipsoids and the atom-numbering scheme for **6**. The hydrogen atoms are omitted for clarity.

The shape of the coordination polyhedron of **6** can be described as a distorted trigonal bipyramid, with carbon atoms in equatorial positions (see Fig. 3). One axial position is occupied by the oxygen donor atom from ligand L^2, while the nitrogen atom from 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 **6**. 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 **6** [21]. 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 [20] and both double bonds C(17)–S(1) (1.696(2) Å) and C(18)–C(19) (1.340(4) Å) are well localized in **6**. There is no additional interaction between Sn and S as indicated by interatomic distance Sn(1)–S(1) (3.5989(10) Å).

The comparison of **6** with related Ph_3Sn(mimt) (C(17)–S(1) = 1.746(4) Å, Sn(1)–N(1) = 2.920(3) Å and Sn(1)–S(1) = 2.437(1) Å) also demonstrates the different coordination mode of the mercapto group (mimt) (see Table 4).

2.2. Reactivity of *4* towards CuCl and $AgNO_3$

The fact that compounds **3** and **4** contain free nitrogen atom of polar group 2-SPy led us to the idea of reacting **4** with CuCl and $AgNO_3$ with the aim to using the free nitrogen donor atom to stabilize monomeric species of CuCl and $AgNO_3$ on organotin fragment. However, both reactions resulted in the exchange of polar groups only and organotin compounds Ph_2L^2SnCl (**7**) and $Ph_2L^2SnNO_3$ (**8**) together with Cu-2-SPy and Ag-2-SPy were obtained and characterizes by ^1H, ^{13}C, ^{119}Sn NMR, IR spectroscopy, and ESI/MS (see Scheme 3, and for crystal structure of **8** see supporting information).

2.3. Mechanism study of polar group transfer

To give closer insight into the polar group transfer, we have prepared Ph_3Sn-2-SPy (**9**) and Ph_2L^2Sn-4-SPy (**10**) (see Fig. 4). Those together with **4**, enable us to study the stability of Sn–S covalent bond depending on an additional

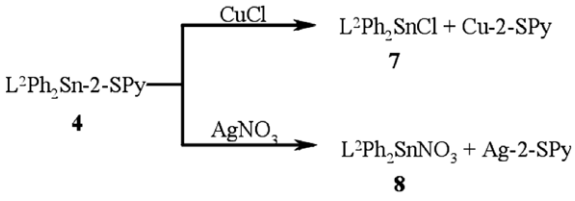
Table 3
Crystal data and structure refinement for **3** and **6**

	3	**6**
Empirical formula	$C_{17}H_{29}N_3SSn$	$C_{32}H_{40}N_2O_2SSn$
Crystal system	Orthorhombic	Triclinic
Space group	$Pca2_1$	$P1$
a (Å)	12.4890(5)	10.256(2)
b (Å)	9.4950(11)	10.471(2)
c (Å)	17.5370(15)	14.351(3)
α (°)	90.0(8)	86.78(3)
β (°)	90.0(7)	83.94(3)
γ (°)	90.0(8)	87.24(3)
Z	4	4
μ (mm^{-1})	1.330	0.934
D_x ($Mg\,m^{-3}$)	1.361	1.383
Crystal size (mm)	$0.35 \times 0.30 \times 0.15$	$0.3 \times 0.25 \times 0.20$
θ Range (°)	1–27.5	1–27.5
No. of reflections measured	13553	14411
No. of unique reflections; R_{int}	4637, 0.1109	6106, 0.0278
Final R[a] $[I > 2\sigma(I)]$	0.0739	0.027
$wR2$[a] (all data)	0.1845	0.069

[a] *Definitions:* $R(F) = \Sigma\|F_o| - \| F_c\|/\Sigma|F_o|$, $wR2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma\ (w(F_o^2)^2)]^{1/2}$, $S = [\Sigma\ (w(F_o^2 - F_c^2)^2)/(N_{reflns} - N_{params})]^{1/2}$.

Table 4
Selected bond length (Å) and angles (°) of **6** and related compound Ph_3Sn(mimt) [15]

Compound/bond length (Å), angle (°)	**6**	Ph_3Sn(mimt)
Sn(1)–N(1)	2.1518(19)	2.920(3)
Sn(1)–S(1)	3.5989(10)	2.437(1)
C(17)–S(1)	1.696(2)	1.746(4)
C(18)–C(19)	1.340(4)	1.321(9)
Sn(1)–O(1)	2.7875(16)	–
N(1)–C(17)–S(1)	127.34(17)	123.7(4)
O(1)–Sn(1)–N(1)	168.08(7)	–
O(1)–Sn(1)–S(1)	118.85(4)	–



Scheme 3. Reactivity of compound **4** toward CuCl and $AgNO_3$.

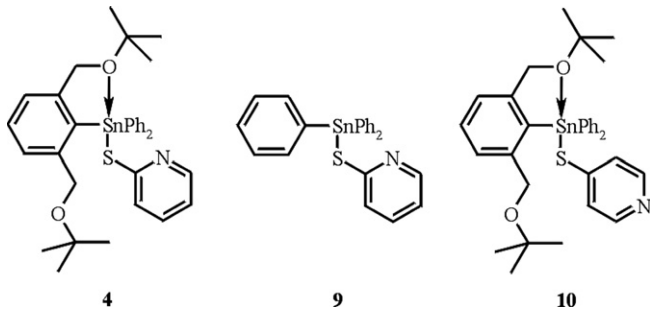


Fig. 4. Schematic drawings of compounds **4**, **9** and **10**.

three factors: (i) compound **4** contains Sn–O coordination and a free nitrogen atom in *ortho* position to Sn–S bond, (ii) compound **9** contains a nitrogen atom in *ortho* position to Sn–S bond, but is void of any Sn–O interaction, and (iii) compound **10** contains Sn–O interaction, but contains a nitrogen atom in *trans* position to Sn–S bond.

The reaction of CuCl with compounds **4**, **9** and **10**, respectively, was monitored by ^{119}Sn NMR spectroscopy. Thus, the spectra of corresponding equimolar mixtures which had been kept at room temperature for three hours are shown in Fig. 5. In the reaction of **4** with CuCl, there was the only one signal at −121.6 ppm in ^{119}Sn NMR spectrum assigned to Ph_2L^2SnCl (**7**) as the only one organotin product of the reaction (see Fig. 5a). The reaction of **9** with CuCl showed two signals at −104.6 ppm and −44.6 ppm in 3:7 ratio in ^{119}Sn NMR spectrum assigned to starting compound **9** (30%) and Ph_3SnCl (70%) (see Fig. 5b). Similarly, the ^{119}Sn NMR spectrum of reaction of **10** with CuCl revealed two signals at −107.9 and −121.6 ppm in 9:1 ratio assigned to starting compound **10** (90%) and Ph_2L^2SnCl (**7**) (10%) (see Fig. 5c).

These observations suggest the polar group transfer proceeds at a different rate in all three reactions **A**–**C**. Addition of CuCl into Sn–S bond is supposed to be the first step of the reaction followed then by cleavage of formed intermediate to give detected products of polar group transfer (see Scheme 4). The stability of proposed intermediate is the rate-determine step of the reaction. In the fastest reaction **A** (100% conversion), the presence of free N donor atom in *cis*-position enable presence of Cu–N interaction that together with Sn–O interaction can result to polarization of Sn–S and Cu–Cl bond in this intermediate. This polarization results then in fast cleavage of the original bonds together with the formation of a new Sn–Cl and Cu–S bonds. In the slowest reaction **C** (10% conversion), there is no possibility of Cu–N interac-

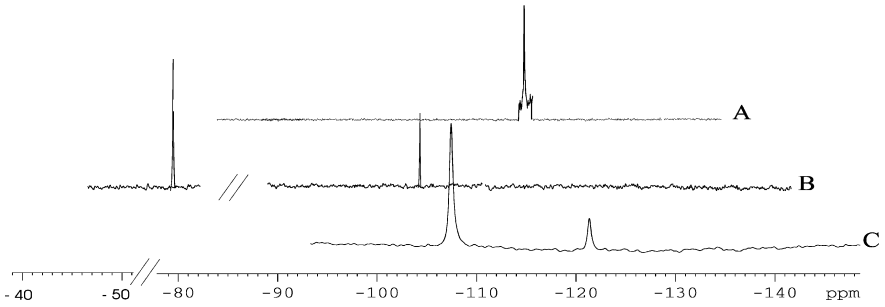
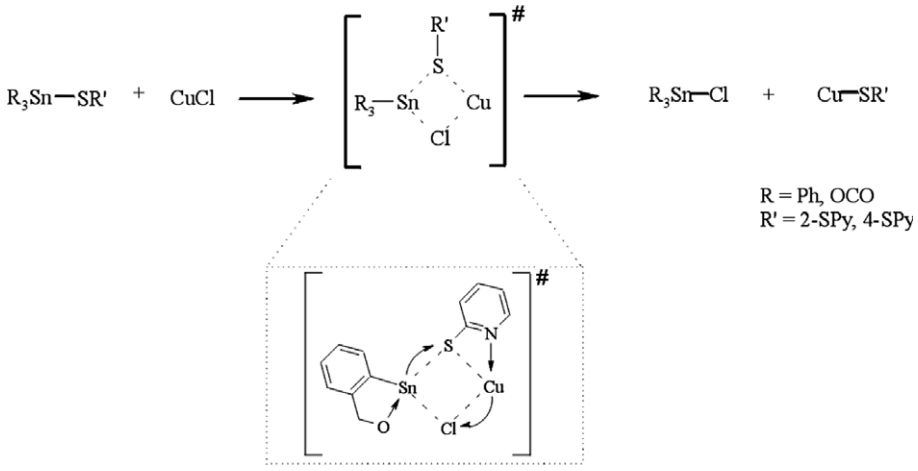


Fig. 5. The ^{119}Sn NMR spectra of reaction mixtures obtained after 3 h; **A** – reaction of **4** with CuCl, **B** – reaction of **9** with CuCl, **C** – reaction of **10** with CuCl.



Scheme 4. Proposed mechanism of polar group transfer.

tion (the N atom is in *para*-position towards Sn–S bond) and similarly there is no Sn–O interaction in reaction **B** (70% conversion).

In summary, we have reported on the preparation of triorganotin compounds containing N,C,N and O,C,O – ligands and their use for the stabilization of both thiol-form of pyridine-2-thiolate and thione-form of 1-methylimidazole-2-thiolate polar group. The polar group transfer has been demonstrated and its mechanism was studied.

3. Experimental

3.1. General methods

The starting compounds $[Me_2L^1Sn]^+[Cl]^-$ (**1**), $[Ph_2L^2Sn]^+[OTf]^-$ (**2**), Ph_2L^2SnCl (**7**) and Ph_3SnSPy (**9**) were prepared according to the literature [8,11,14]. Starting 2-mercaptopyridine, 4-mercaptopyridine, and 2-mercapto-1-methylimidazole were purchase from Sigma–Aldrich. All reactions were carried out under argon, using standard Schlenk techniques. Solvents were dried by standard methods and distilled prior to use. The reactions with silver salts were protected from light. The ^{1}H, ^{13}C, and ^{119}Sn NMR spectra were acquired on Bruker Avance500 spectrometer in $CDCl_3$ (range 300–210 K). Appropriate chemical shifts were calibrated on: ^{1}H-residual peak of $CHCl_3$ ($\delta = 7.25$ ppm), ^{13}C-residual peak of $CHCl_3$ ($\delta = 77.23$ ppm), ^{119}Sn-external tetramethylstannane ($\delta = 0.00$ ppm). Electrospray mass spectra (ESI/MS) were recorded in positive mode on an Esquire3000 ion trap analyzer (Bruker Daltonics) in the range 100–600 *m*/*z* and in the negative mode on the Platform quadrupole analyzer in the range 100–800 *m*/*z*. The samples were dissolved in acetonitrile and analyzed by direct infusion at a flow rate of 1–10 μl/min. The IR spectra (cm^{-1}) were recorded on Perkin–Elmer 684 equipment as nujol suspensions or CH_3CN solutions. For the carbons atoms assignment of polar groups see Tables 1 and 2.

3.2. Synthesis of Me_2L^1Sn-2-SPy (3)

A solution of Na(2-SPy) (0.13 g; 0.96 mmol) in 15 ml of THF was added to the solution of **1** (0.37 g; 0.96 mmol) in 20 ml of THF. The resulting mixture was stirred for 24 h at the 40 °C. The solvent was evaporated and residue was suspended in 30 ml pentane. After the filtration, filtrate was evaporated and washed with cold pentane (5 ml) to obtain **3** as yellow powder. Yield: 0.62 g (69%). M.p. 79–84 °C. *Anal.* Calc. for **Me_2L^1Sn-2-SPy** (MW 450.22): C, 50.69; H, 6.49. Found: C, 50.91; H, 6.71%. MS: *m*/*z* 110, 100% $[2\text{-SPy}]^-$, *m*/*z* 341, 100% $[M\text{-2-SPy}]^+$, ^{1}H NMR ($CDCl_3$)

δ (ppm): 0.81 (6H, s, $SnCH_3$), ($^2J(^{119}Sn, ^1H) = 64$ Hz), 2.37 (12H, s, NCH_3), 3.86 (4H, s, CH_2N), 6.97 (1H, bs, Pyridin), 7.26–7.4 (3H, m, Ar–H), 7.48 (2H, bs, 2-SPy), 8.3 (1H, bs, 2-SPy), ^{13}C NMR($CDCl_3$) δ (ppm): 0.9 ($SnCH_3$), 45.1 (NCH_3), 77.2 (CH_2N), 117.6 (*C*-SPy), 121.3 (*C*-SPy), 127.7 (*C*(3,5)), 128.4 (*C*(4)), 135.2 (*C*-SPy), 143.6 (*C*(1)), 146.3 (*C*(2,6)), 148.3 (*C*-SPy), 165.2 (*C*-SPy), $\delta(^{119}Sn)$ ppm = −95.0.

3.3. Synthesis of Ph_2L^2Sn-2-SPy (**4**)

A solution of Na(2-Spy) (78.5 mg; 0.7 mmol) in 15 ml of THF was added to the solution of **2** (473.8 mg; 0.7 mmol) in 20 ml of THF. The resulting mixture was stirred for 2 days at the room temperature. The solvent was evaporated and residue was suspended in 30 ml hexane. After the filtration, filtrate was evaporated and washed with cold pentane (5 ml) to obtain **4** as yellow powder. Yield: 345.1 mg (74%). M.p. 78–84 °C. *Anal.* Calc. for **Ph_2L^2Sn-2-SPy** (MW 632,44): C, 62.67; H, 6.22. Found: C, 62.87; H, 6.42%. ^1H NMR ($CDCl_3$) δ (ppm): 0.99 (18H, s, OCH_3), 4.62 (4H, s, CH_2O), 6.9 (1H, bs, 2-SPy), 7.40 (9H, m, Ar–H), 7.50 (2H, bs, 2-SPy), 7.73 (4H, m, Ar–H), 8.0 (1H, bs, 2-SPy), ^{13}C NMR($CDCl_3$) δ(ppm): 27.8 (OCH_3), 66.4 (CH_2O), 73.9 ($OC(CH_3)_3$), 118.7 (*C*-SPy), 124.1 (*C*-SPy), 125.9 (*C*(4)) 128.4 (*C*(3,5)), 128.5 (*C*(4′)), 128.9 (*C*(3′,5′)), 129.6 (*C*-SPy), 136.4 (*C*(2′,6′)), 136.8 (*C*(1)), ($^1J(^{119}Sn; ^{13}C) = 692$ Hz), 144.8 (*C*(1′)), 147.1 (*C*(2,6)), 147.7 (*C*-SPy), 161.6 (*C*-SPy), $\delta(^{119}Sn)$ ppm = −141.9.

3.4. Synthesis of Me_2L^1Sn(mimt) (**5**)

A solution of Na(mimt) (34 mg; 0.3 mmol) in 15 ml of THF was added to the solution of **1** (0.105 g; 0.302 mmol) in 20 ml of THF. The resulting mixture was stirred for 24 h at the 40 °C. The solvent was evaporated and residue was suspended in 40 ml of pentane/CH_2Cl_2 (3:1). After the filtration, filtrate was evaporated and washed with cold pentane (5 ml) to obtain **5** as white solid. Yield: 94.5 mg (70%). M.p. 179–185 °C. *Anal.* Calc. for **Me_2L^1Sn(mimt)** (MW 467.25): C, 47.70; H, 6.67. Found: C, 47.90; H, 6.87%. MS: *m*/*z* 113, 70% $[mimt]^-$, *m*/*z* 225, 100% $[2mimt-H]^-$, *m*/*z* 341, 100% $[M-mimt]^+$, ^1H NMR ($CDCl_3$) δ(ppm): 0.65 (6H, s, $SnCH_3$), ($^2J(^{119}Sn, ^1H) = 63$ Hz), 2.02 (12H, s, NCH_3), 3.50 (3H, s, CH_3N (mimt)), 3.57 (4H, s, CH_2N), 6.58 (1H, bs, mimt), 6.67 (1H, bs, mimt), 7.05–7.21 (3H, m, Ar–H), ^{13}C NMR ($CDCl_3$) δ(ppm): −1.1 ($SnCH_3$), 34.2 (CH_3 Im), 45.2 (NCH_3), 65.3 (CH_2N), 118.9 (*C*−mimt), 128.0 (*C*(3,5)), 128.7 (*C*(4)), 142.4 (*C*(1)), 146.0 (*C*(2.6)), 162.9 (SCN_2), δ (^{119}Sn) ppm = −124.0.

3.5. Synthesis of Ph_2L^2Sn(mimt) (**6**)

A solution of Na(mimt) (41.8 mg; 0.3 mmol) in 15 ml of THF was added to the solution of **2** (205.9 mg; 0.3 mmol) in 20 ml of THF. The resulting mixture was stirred for 2 days at room temperature. The solvent was evaporated and residue was suspended in 30 ml hexane/CH_2Cl_2 (2:1). After the filtration, filtrate was evaporated and washed with cold pentane (5 ml) to obtain **6** as white solid. Yield: 120.5 mg (59%). M.p. 175–178 °C. *Anal.* Calc. for **Ph_2L^2Sn(mimt)** (MW 649.47): C, 61.03; H, 6.52. Found: C, 61.33; H, 6.77% MS: *m*/*z* 113, 15% $[mimt]^-$, *m*/*z* 523, 60% $[M-mimt]^+$, *m*/*z* 632 $[M+H]^+$, *m*/*z* 563, 30% $[M+H-t\text{BuOH}]^+$, *m*/*z* 411, 80% $[M-mimt-2butane]^+$, ^1H NMR ($CDCl_3$) δ(ppm): 0.88 (18H, s, OCH_3), 3,45 (3H, s, NCH_3 (mimt)), 4.53 (4H, s, CH_2O), 6.59 (1H, bs, mimt), 6.63 (1H, bs, mimt), 7.40 (9H, m, Ar–H), 7.78 (4H, m, Ar–H), ^{13}C NMR ($CDCl_3$) δ(ppm): 27.4 ($OCCH_3$), 34.8 (NCH_3), 65.7 (CH_2O), 75.1 ($OC(CH_3)_3$), 120.3 (*C*−mimt), 121.5 (*C*−mimt), 126.4 (*C*(3,5)), 128.5 (*C*(3′,5′)), ($^nJ(^{119}Sn; ^{13}C) = 45{,}37$ Hz), 129.5 (*C*(4)), 129.6 (*C*(4′)), 135.9 (*C*(1)), ($^1J(^{119}Sn; ^{13}C) = 713$ Hz), 137.2 (*C*(2′,6′)), 141,2 (*C*(1′)), ($^1J(^{119}Sn; ^{13}C) = 715$ Hz), 147.3 (*C*(2,6)), 163.5 (SCN_2), δ (^{119}Sn) ppm = −173.5.

3.6. Synthesis of Ph_2L^2Sn-4-SPy (**10**)

The NaOH (0.184 g; 4.6 mmol) was added to the solution of 4-mercaptopyridine (H-4-Spy, 511 mg; 4.6 mmol) dissolved in the 10 ml of H_2O and then $TlNO_3$ (1.22 g; 4.6 mmol) was added to the same of solution after 30 min stirring. The resulting mixture was stirred for 1 h at room temperature and after the filtration the insoluble fraction was dried to obtain Tl(4-SPy) as yellow powder. Yield: 38 mg (95%). A Tl(4-SPy) (34 mg; 0.1 mmol) was added to the solution of **7** (58 mg; 0.1 mmol) in the 20 ml of CH_2Cl_2. The resulting mixture was stirred for 1 week at room temperature. After the filtration, the solvent was evaporated and washed with cold pentane (5 ml) to obtain **10** as yellow solid. Yield: 56 mg (90%). M.p. 83–88 °C. *Anal.* Calc. for **Ph_2L^2Sn-4-SPy** (MW 632,44): C, 62.67; H, 6.22. Found: C, 62.87; H, 6.42%. MS: *m*/*z* 110, 65% $[4-SPy]^-$, *m*/*z* 523, 60% $[M-4-SPy]^+$, *m*/*z* 467, 50% $[M-4-SPy-buten]^+$, *m*/*z* 411, 62% $[M-4-SPy-2buten]^+$; *m*/*z* 634, 3% $[M+H]^+$, ^1H NMR ($CDCl_3$) δ (ppm): 0.88 (18H, s, OCH_3), 4.55 (4H, s, CH_2O), 7.00 (2H, bs, 4-SPy), 7.31 (9H, m, Ar–H), 7.55 (4H, m, Ar–H), 8.01 (2H, bs, 4-SPy), ^{13}C NMR ($CDCl_3$) δ(ppm): 27.5 ($OCCH_3$), 66.2 (CH_2O), ($^nJ(^{119}Sn, ^{13}C) = 31.3$ Hz), 75.1 ($OC(CH_3)_3$), 126.7 (*C*(1)), ($^1J(^{119}Sn; ^{13}C) = 699$ Hz), 127.2 (C(3,5)), 128.7 (C(3′,5′)), 129.3 (C(4′)), 130.0 (*C*, 4−SPy), 130.1 (C(4)), 134.6 (C(1′)), ($^1J(^{119}Sn; ^{13}C) = 700$ Hz), 136.1 (C(2′,6′)), 141.7 (C(2,6)), 148.2 (*C*, 4−SPy), 148.6 (*C*, 4−SPy). δ (^{119}Sn) ppm = −107.9.

3.7. Reaction of **4** with CuCl

The CuCl (10 mg; 0,1 mmol) was added to the solution of **4** (70 mg; 0.1 mmol) in the 20 ml of THF. The resulting mixture was stirred 10 h at room temperature. The solvent was evaporated, and residue was suspended in 10 mL of CH_2Cl_2/pentane (1:1). After the filtration, filtrate was

evaporated and the residue was characterized by ^{1}H and ^{119}Sn NMR spectroscopy as **7** according to the literature data [11]. The insoluble precipitate was characterized by ^{1}H NMR and IR spectroscopy as CuSPy in accordance to data found in the literature [22].

3.8. Reaction of 4 with $AgNO_3$

A 15 ml acetone solution of **4** (70 mg; 0.1 mmol) was slowly added to the $AgNO_3$ (19 mg; 0.1 mmol) dissolved in the 20 ml of H_2O. On the interface of both phases, crystals suitable for X-ray diffraction study were grown within four days. The solution was decanted and crystalline material was characterized by ^{1}H, ^{13}C and ^{119}Sn NMR spectroscopy, ESIMS and elemental analysis as compound **8**. Structure was detected by X-ray diffraction (see Supporting information). Yield: 48 mg (75%). M.p. 140–145 °C. *Anal.* Calc. for $\mathbf{Ph_2L^2SnNO_3}$ (MW 584,28): C, 57.56; H, 6.04. Found: C, 5.76; H, 5.85%. MS: *m/z* 523, 60% $[M–NO_3]^+$, ^{1}H NMR ($CDCl_3$) δ(ppm): 0.87 (18H, s, OCH_3), 4.62 (4H, s, CH_2O), 7.43 (9H, m, Ar–H), 7.79 (4H, m, Ar–H), ^{13}C NMR ($CDCl_3$) δ(ppm): 27.4 ($OC(CH_3)_3$), 65.5 (CH_2O), 77.2 ($OC(CH_3)_3$), 127.5 (*C*(3,5)), 129.0 (*C*(3′,5′)), 130.2 (*C*(4)), 130.3 (*C*(4′)), 136.9 (*C*(2′,6′)), 142.2 (*C*(2,6)), $\delta(^{119}Sn)$ ppm = −80.3. The evaporation of solvent, the residue was characterized by IR and ^{1}H NMR spectroscopy as Ag-2-SPy in accordance to data found in the literature [23].

3.9. Crystallography studies

Colorless crystals were obtained from toluene solutions at −5 °C solutions of **3** and **6**. The intensity data for single crystal of **3** were measured on four-circle diffractometer KappaCCD with CCD area detector by monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) at 150(2) K. The crystallographic details are summarized in Table 1, and empirical absorption corrections were applied (multiscan from symmetry-related measurements). The structure was solved by the direct methods (SIR97) and refined by a full-matrix least-squares procedure based on F^2 (SHELXL 97). Hydrogen atoms were mostly localized on a difference Fourier map, however to ensure uniformity of treatment of crystal, all hydrogen were recalculated into idealized positions (riding model) and assigned temperature factors $H_{iso}(H) = 1.2\ U_{eq}$ (pivot atom) or of 1.5 U_{eq} for the methyl moiety. In the case of **3**, the main residual electron density maximum ∼1 e Å^{-3} is located about 1 Å from tin atom which is probably caused by presence of two lone electron pairs originated from nitrogen atoms. The intensity data for **6** were collected on a KUMA KM-4 CCD kappa-axis diffractometer using a graphite monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) at 260(2) K. The structure was solved by direct methods (Sheldrick G.M. SHELX-97 [24]), (Sheldrick G.M.: SHELXTL V 5.1 [25]). 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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Appendix A. Supplementary material

CCDC 632632 and 610595 contain the supplementary crystallographic data for **3** and **6**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.04.006.

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