



## Communication

## Reduction of C,N-chelated Diorganotin(IV) Dichlorides

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## ARTICLE INFO

## Article history:

Received 11 February 2010

Received in revised form

23 March 2010

Accepted 18 April 2010

Available online 24 April 2010

Dedicated to Prof. Dr. Antonín Lyčka on the occasion of his 60<sup>th</sup> birthday in recognition of his outstanding contributions to the area of organometallic and organic chemistry and NMR spectroscopy.

## Keywords:

Organotin(IV) compounds

Reduction

C,N-ligand

Distannane

## ABSTRACT

The  $L^{CN}n\text{-BuSnCl}_2$  where  $L^{CN}$  is 2-(*N,N*-dimethylaminomethyl)phenyl- as a chelating ligand was reduced by one molar equivalent of potassium to distannane  $L^{CN}n\text{-Bu(Cl)Sn-Sn(Cl)n-BuL}^{CN}$  (**3**). The same reduction of  $L^{CN}n\text{-BuSnCl}_2$  led essentially quantitatively to the stannylene  $L^{CN}n\text{-BuSn}$ . Distannane **3** can be oxidized to corresponding organotin(IV) chalcogenides ( $L^{CN}n\text{-Bu(Cl)Sn-Y-Sn(Cl)n-BuL}^{CN}$ , where Y is O, S, Se, and Te). The structure of these chalcogenides was evaluated by multinuclear NMR spectroscopy techniques and X-ray crystallographic techniques for sulfide, revealing two diastereomeric pairs with the centre of chirality at the tin atoms for all compounds. The further reduction of **1** by excess of reducing agents gave tetranuclear compound  $[L^{CN}(n\text{-Bu)SnCl}]_2\text{-Sn-}\{\text{[Sn}(n\text{-Bu)L}^{CN}\}_2(\mu\text{-Cl})\}$  (**10**) and  $L^{CN}(n\text{-Bu})_2\text{SnCl}$ . The product of reduction of **3** by  $K(\text{BEt}_3)\text{H.THF}$  is the complex **10** as well. The structure and bonding properties in **10** were conducted at DFT theory level.

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## 1. Introduction

Organotin(IV) hydrides have found extensive applications in organic syntheses which involve radical chain reactions in which the stannyl radical  $R_3\text{Sn}\cdot$  is a chain carrying intermediate [1].

Distannanes of general formula  $R_3\text{SnSnR}_3$  can be taken as being above-mentioned radical  $R_3\text{Sn}\cdot$  as well, and are also frequently studied by means of reactivity and NMR spectroscopy [2].

Our interest is mainly focused on the family of organotin(IV) compounds containing 2-[(dimethylamino)methyl]phenyl- group ( $L^{CN}$ ) or related ligands which reveal interesting structural properties [3,4] and potential use [5]. In our recent paper, we described the preparation, structure and reactivity of triorganotin(IV) cyclopentadienides, hydrides and distannanes bearing  $L^{CN}$  ligand [6].

Now we would like to report on structure and properties of analogous diorganotin(IV) distannanes containing  $L^{CN}R\text{Sn}$  moiety, where R is *n*-Bu and  $L^{CN}$ , respectively.

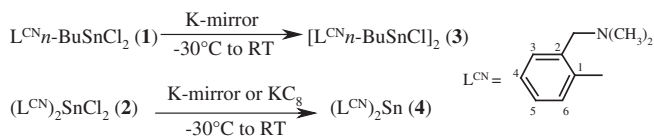
## 2. Results and discussion

Two C,N-chelated compounds  $L^{CN}n\text{-BuSnCl}_2$  (**1**) [7] and  $L^{CN}n\text{-BuSnCl}_2$  (**2**) [8] were reduced by one equivalent of potassium mirror (Scheme 1) at room temperature. The products were the distannane **3** and the stannylene **4** [9]. In the case of distannane **3**, the isolated yield is satisfactory, but the conversion to **4** is rather low. **2** and **4** are the only detected compounds in this reaction.

The  $^{119}\text{Sn}$  NMR spectrum of **3** reveals one sharp singlet at  $-88.1$  ppm ( $^1J(^{119}\text{Sn}, ^{117}\text{Sn}) = 9221$  Hz) which is typical for penta-coordinated tin(IV) compounds containing *n*-Bu and  $L^{CN}$  groups [7]. The value of coupling constant is one of the highest values determined up to now [1b,2h,2i]. For example the value of the coupling constant for the resembling intramolecularly coordinated distannane  $[\text{MeN}(\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{SnCl}]_2$  is much more smaller (6814 Hz) [10]. Two different doublets were found for  $\text{CH}_2$  groups in  $^1\text{H}$  NMR spectrum of **3**, where these are nonequivalent due to the slow exchange on the NMR time scale.

The coordination geometry of the tin atoms is trigonal bipyramidal (Fig. 1) with Cl and N atoms, from donor groups, in axial positions, similarly as in the  $L^{CN}n\text{-BuSn(Cl)-WCp}(\text{CO})_3$  [11]. On the other hand, the coordination vicinity in corresponding triorganotin(IV) distannane ( $(L^{CN}\text{Ph}_2\text{Sn})_2$ ) [6] is distorted tetrahedral due to nonexistence of Sn–N intramolecular connection.

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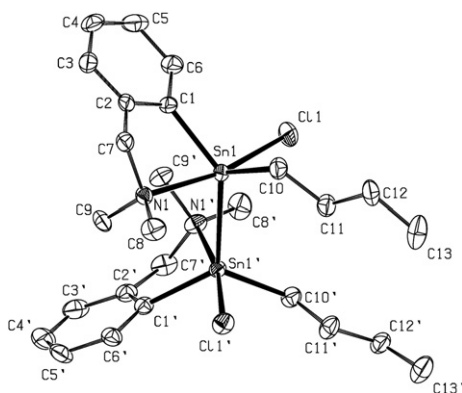
**Scheme 1.** Reduction of C,N-chelated tin(IV) dichlorides.

The distance Sn1–Sn1' in **3** is comparable with distances usually found in tri- and diorganotin(IV) distannanes [1,2,10]. The nitrogen donor atoms are coordinated to the tin atoms by a medium strong interactions (2.622(3) Å) comparable to those found in triorganotin(IV) chloride bearing the same ligand [7c]. The Sn–Cl bonds are slightly elongated using the same comparison. The N–Sn–Cl angles are approaching the value of 180°. The torsion N1–Sn1–Sn1'–N1' is 117.1(2)°.

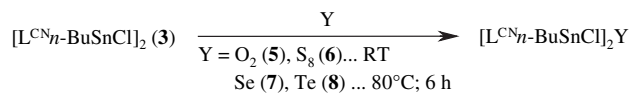
The distannane **3** can be oxidized by elemental chalcogens at different conditions (Scheme 2). These oxidations proceed similarly as was recently shown for stannylene **4** [12] yielding **5–8**. The  $^{119}\text{Sn}$  NMR spectra of all **5–8** reveal two different signals with mutually similar values. Also the two sets of signals with very complex patterns were found in  $^1\text{H}$  NMR spectra of **5–8**. This can be explained by the presence of two diastereotopic centers at the tin atoms and two pairs of diastereoisomers in solution similarly as demonstrated for analogous oxo-bridged diorganotin species bearing the same ligand (( $\text{L}^{\text{CN}}\text{RSnCl}_2$ )<sub>2</sub>O) [13] previously.

The molecular structure of **6** was determined by X-ray diffraction techniques in the solid state (Fig. 2). Two independent molecules were found in the crystal lattice. These two molecules differ only slightly, with the main deviations in the S–Sn–C(Bu) angles and the *n*-butyl chains shapes. Both tin atoms in **6** are five-coordinated with coordination geometry of distorted trigonal bipyramid where two carbon and one sulfur atoms made up each equatorial plane. The axial planes are constructed of nitrogen and chlorine atoms with nearly linear N–Sn–Cl angles. The Sn–N intramolecular connection is slightly shortened in comparison to **3**, and significantly shortened when compared to ( $\text{L}^{\text{CN}_2}\text{SnS}$ )<sub>2</sub> being 2.838(2) Å [12] probably due to a concurrency of *cis*-coordinated and rigid (S)<sub>2</sub> bridges in ( $\text{L}^{\text{CN}_2}\text{SnS}$ )<sub>2</sub>. When the same comparison is made for Sn–S distances, the slight shortening of this parameter (~0.05 Å) is seen in **6**. In **6**, both phenyl rings of the ligands are connected via a  $\pi$ – $\pi$  stacking interaction (<4 Å).

When **1** is reacted with high excess (>4 eq.) of potassium mirror, or 1.1 molar equivalent of  $\text{KC}_8$ , or two molar equivalents of lithium



**Fig. 1.** Molecular structure of **3**, ORTEP diagram, 50% probability level, hydrogen atoms are omitted for clarity. Selected interatomic distances and angles [Å, °]: Sn1 C10 2.139(5), Sn1 C1 2.148(4), Sn1 N1 2.514(4), Sn1 Cl1 2.5414(13), Sn1 Sn1' 2.8075(5), Sn1' C1' 2.151(5), Sn1' N1' 2.538(4), Sn1' C10' 2.156(5), Sn1' Cl1' 2.5087(12), N1 Sn1 Cl1 169.11(9), Cl1' Sn1' N1' 169.16(10).

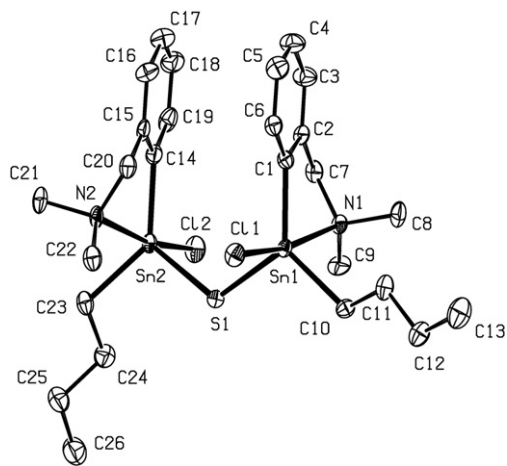


**Scheme 2.** Oxidation of C,N-chelated distannane (**3**).

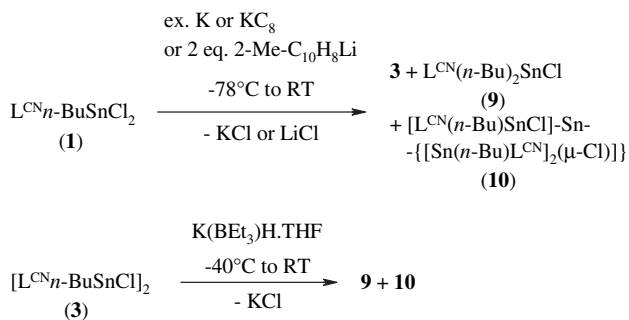
2-methylnaphthenide, compounds **9** [7] and **10** are formed as products of tin reduction and a redistribution reaction (the proposed mechanism of formation of compound **10** is given in Supporting information as Fig. S1), similarly as previously found for methyl or phenyl substituted organotin(IV) compounds [14]. The same products are formed when **3** is reacted with one molar equivalent of K(BEt<sub>3</sub>)H (Scheme 3).

Compound **10** crystallizes from hexane solution at low temperature. The  $^1\text{H}$  NMR spectrum in toluene-*d*<sub>8</sub> reveals two sets of signals at room temperature. The signals at 3.62 ppm (broad) and 2.98 ppm (broad doublet) can be attributed to benzylic protons of two ligands bonded to tin atoms (Sn1 and Sn2) connected via bridging chlorine atom Cl1 (Fig. 3). Relatively sharp singlet (3.02 ppm) is attributed to remaining benzylic protons from ligand bonded to the tin atom Sn3. The next characteristic signals are found at 8.07 (broad) and 8.55 ppm (doublet with  $^1\text{H}$ ,  $^{117/119}\text{Sn}$  coupling 72 Hz) attributable to hydrogen atoms of ligands in ortho positions to tin atoms. All these signals indicate a fast dynamic exchange on the NMR time scale. Each of broad signals at 3.62 ppm, 2.98 ppm for benzylic protons and 8.07 ppm for aromatic ones are split into two doublets at 4.35 and 2.81 ppm; 8.70 and 7.41 ppm, respectively, at 230 K, which confirm non-equivalence of two ligands bonded to tin atoms interconnected by chlorine bridging atom Cl1. The situation in aliphatic part of spectra, mainly in the region from 0.7 to 1.6 ppm is providing not an easy survey due to a non-equivalence of *n*-butyl and methyl groups at low temperature. In the  $^{119}\text{Sn}$  NMR spectrum, there is a broad signal at –114.5 ppm at the room temperature. When the temperature is decreased, the signal starts to split into two broad signals at –114.2 and –115.8 ppm with integral ratio 1:2 at 230 K which is the lowest accessible temperature due to solubility problems.

The molecular structure of **10** (Fig. 3), similarly as proposed in solution (vide supra), consists of three tin(IV) fragments

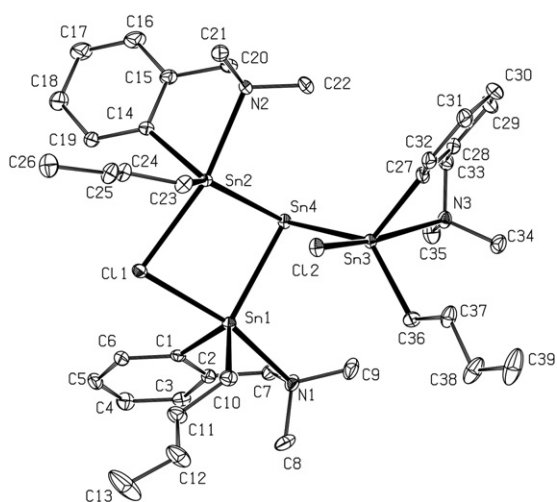


**Fig. 2.** Molecular structure of one independent molecule **6**. C<sub>6</sub>H<sub>6</sub>, ORTEP diagram, 50% probability level, solvent and hydrogen atoms are omitted for clarity. Selected interatomic distances and angles [Å, °], for the second molecule the same parameters are given in parentheses: Sn1 C1 2.107(6) (2.118(6)), Sn1 C10 2.129(6) (2.128(6)), Sn1 S1 2.3959(16) (2.3915(15)), Sn1 N1 2.436(5) (2.462(5)), Sn1 Cl1 2.5193(17) (2.4983(18)), Sn2 C14 2.118(6) (2.107(6)), Sn2 C23 2.129(6) (2.133(6)), Sn2 S1 2.3943(15) (2.4026(16)), Sn2 N2 2.468(5) (2.450(5)), Sn2 Cl2 2.4816(18) (2.5117(18)), N1 Sn1 Cl1 168.93(12) (167.83(13)), N2 Sn2 Cl2 167.21(13) (168.69(13)).

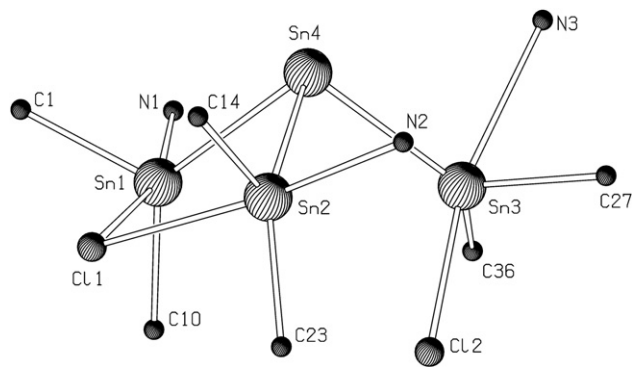
**Scheme 3.** Further reduction of C,N-chelated tin(IV) dichloride (**1**) and distannane (**3**).

interconnected (Sn–Sn 2.84 Å) via Sn4 atom in formal oxidation state +II. The coordination geometry of three tins(IV) is trigonal bipyramidal with Sn4, and carbon atoms in the equatorial planes. Atoms Sn1 and Sn2 are interconnected via chlorine atom being a symmetrical bridge forming a puckered four-membered tristanna ring. On the other hand, the Cl2 atom is terminal one and is connected to Sn3 atom with no short contact to other tin atoms. The distance Sn3–N3 is much longer than those found for the remaining two pairs of nitrogen and tin atoms which are bridged by Cl1 atom. The pyramidal shape of coordination geometry of Sn4 atom is demonstrated in Fig. 4. There is no contact between tin atoms Sn1, Sn2, and Sn3, which enables us to compare **10** with previously published compounds cyclo-[(L<sup>CN</sup><sub>2</sub>Sn)<sub>2</sub>-μ-(SnL<sup>CN</sup>)-μ-(OH)] [15], [Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>C(Me)<sub>2</sub>SnCl]<sub>3</sub>.SnCl<sub>2</sub> [16] and a triply chelated Sn(IV)–Sn(II)–Cl [17] complex which are the only proposed complexes of such type. The Sn4 atom is located 1.596 Å above the plane determined by Sn1, Sn2, and Sn3 atoms. The chlorine bridging atom is also located 0.855 Å out of Sn1–Sn2–Sn4 plane.

The structure of **10** is rather unusual. We studied electronic structure and bonding situation in **10** at DFT level, real structure was used for calculations (for details see Supporting Information). Calculated structure is in good agreement with X-ray data. Bonding situation in **10** is best described by Lewis structure (Scheme 4).



**Fig. 3.** Molecular structure of **10**, ORTEP diagram, 50% probability level, hydrogen atoms are omitted for clarity. Selected interatomic distances and angles [Å, °]: Sn4 Sn2 2.8429(8), Sn4 Sn1 2.8431(8), Sn4 Sn3 2.8445(8), Sn1 C10 2.151(9), Sn1 C1 2.165(8), Sn1 N1 2.468(7), Sn1 Cl1 2.706(2), Sn2 C14 2.152(8), Sn2 C23 2.160(8), Sn2 N2 2.444(7), Sn2 Cl1 2.733(2), Sn3 C27 2.143(9), Sn3 N3 2.696(8), Sn3 C36 2.183(9), Sn3 Cl2 2.532(2), Sn2 Sn4 Sn1 83.04(2), Sn2 Sn4 Sn3 96.06(2), Sn1 Sn4 Sn3 94.84(2), Sn1 Cl1 Sn2 87.74(7), N1 Sn1 Cl1 164.91(18), N2 Sn2 Cl1 166.71(18).

**Fig. 4.** Detail of the core of the molecular structure of **10**.

Partial atomic charges were calculated using different algorithms. It was found that central tin atom Sn4 and both chlorine atoms bears negative charges, while Sn1–Sn3 have strong positive charges. According to NBO as well as AIM analysis, bonding within Sn4 core is nonpolar covalent. Contrary, bonding of Sn1–Sn3 atoms with peripheral groups L, Bu and Cl is mostly ionic.

According to NBO analysis, Sn4 atom has three single non-polarized bonds with neighboring tin atoms and a lone pair. Sn4 is not hybridized. Only p-orbitals of Sn4 atom participate in Sn–Sn bonding, while a lone pair has strong s-character (sp<sup>0.3</sup>). This results in a narrow Sn–Sn4–Sn valance angles close to 90°. There was no evidence for any significant Sn4...Sn π-symmetry interactions found.

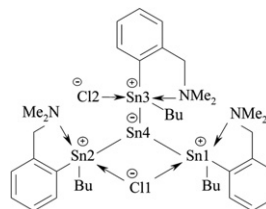
Bonding around Sn1–Sn3 strikingly differs from Sn4. Hybridization of Sn1–Sn3 atoms is sp<sup>2</sup>. These atoms participate in Sn4–Sn and Sn–C bonding with sp<sup>2</sup> hybrids. Each Sn1–Sn3 tin atom has vacant p-orbital as well. Bonding between Sn1...Cl1, Sn2...Cl1, and Sn3...Cl2 is best described as donation of a lone pair of chloride anion to vacant p-orbital of stannyl cation fragment.

### 3. Experimental

All experiments were carried out under an argon atmosphere. (N,N-dimethylaminomethyl)benzene, K(BEt<sub>3</sub>)H·THF and potassium were obtained from commercial sources (Sigma–Aldrich). Diethyl ether, THF and n-hexane were dried over and distilled from potassium–sodium alloy, degassed and stored under argon over potassium mirror. Compound **1** was prepared as published elsewhere[7].

#### 3.1. Bis-[[2-(N,N-dimethylaminomethyl)phenyl]n-butylchloro]distannane (**3**)

The K-mirror (0.93 g, 23.79 mmol) was prepared and poured over with a mixture of hexane and benzene (1:1). Afterwards, the solution of **1** (4 g, 10.50 mmol) in a mixture of hexane and benzene (1:1) was added during 15 min at –30 °C. The reaction mixture

**Scheme 4.** Lewis structure of **10**.

was stirred for one week at room temperature. Afterwards, the reaction mixture was filtered off and *vacuo* evaporated. Oily dark brown product was treated with hexane and white solid product was obtained. Yield 2.356 g (65%). M.p. 119–121 °C. Elemental analysis for C<sub>26</sub>H<sub>42</sub>Cl<sub>2</sub>N<sub>2</sub>Sn<sub>2</sub> (MW = 690.92): calculated: C 45.20%, H 6.13%, N 4.05%, found: C 45.2%, H 6.1%, N 4.1%. NMR characterization: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 K, ppm): 8.67 (d, 2H-6, <sup>3</sup>J(<sup>119</sup>Sn, <sup>1</sup>H) = 58 Hz); 7.21 (t, 2H-4); 7.09 (t, 2H-5); 6.74 (d, 2H-3); 3.04 (d, 2H-NCH<sub>2</sub>-α); 2.77 (d, 2H-NCH<sub>2</sub>-β); 2.25 (m, 4H-CH<sub>2</sub>-α); 2.13 (s, 6H-N(CH<sub>3</sub>)<sub>2</sub>′); 1.93 (s, 6H-N(CH<sub>3</sub>)<sub>2</sub>′′); 1.64 (m, 4H-CH<sub>2</sub>-β); 1.47 (m, 4H-CH<sub>2</sub>-γ); 0.94 (t, 6H-CH<sub>3</sub>). <sup>119</sup>Sn{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 300K, ppm): -88.1 (s, <sup>1</sup>J(<sup>119</sup>Sn, <sup>117</sup>Sn) = 9221 Hz). <sup>13</sup>C{<sup>1</sup>H} (C<sub>6</sub>D<sub>6</sub>, 298 K, ppm): 144.34 (s, 2C-2); 142.86 (s, 2C-1); 138.30 (s, 2C-3); 129.73 (s, 2C-5); 128.73 (s, 2C-4); 127.21 (s, 2C-6); 66.10 (s, 2C-NCH<sub>2</sub>); 46.69 (s, 4C-N(CH<sub>3</sub>)<sub>2</sub>); 29.19 (s, 2C-C-β, <sup>2</sup>J(<sup>119/117</sup>Sn(β), <sup>13</sup>C) = 31 Hz); 27.62 (s, 2C-C-γ, <sup>3</sup>J(<sup>119/117</sup>Sn(β), <sup>13</sup>C) = 94 Hz); 23.08 (s, 2C-C-α, <sup>1</sup>J(<sup>119</sup>Sn(β), <sup>13</sup>C) = 430 Hz, <sup>1</sup>J(<sup>117</sup>Sn(β), <sup>13</sup>C) = 410 Hz, <sup>2</sup>J(<sup>119/117</sup>Sn(α), <sup>13</sup>C) = 78 Hz); 14.34 (s, 2C-CH<sub>3</sub>). Crystallographic data for **3**: C<sub>26</sub>H<sub>42</sub>Cl<sub>2</sub>N<sub>2</sub>Sn<sub>2</sub>, M = 690.90, orthorhombic, Pbc<sub>a</sub>, a = 8.9398 (5), b = 18.3382(14), c = 35.399(3) Å, Z = 8, V = 5803.4(7) Å<sup>3</sup>, D<sub>c</sub> = 1.582 g cm<sup>-3</sup>, μ = 1.922 mm<sup>-1</sup>, T<sub>min</sub> = 0.412; T<sub>max</sub> = 0.607, 30,428 reflections measured (θ<sub>max</sub> = 27.5°), 6362 independent (R<sub>int</sub> = 0.0324), 5688 with I > 2σ(I), 289 parameters, S = 1.242, R<sub>1</sub>(obs. data) = 0.0439, wR<sub>2</sub>(all data) = 0.0978; max., min. residual electron density = 1.500, -1.057 eÅ<sup>-3</sup>.

### 3.2. {Bis-[[2-(N,N-dimethylaminomethyl)phenyl]n-butylchloro}tin oxide (**5**)

Synthetic air was bubbled through a solution of **3** (130 mg, 0.19 mmol) in benzene at nearly atmospheric pressure for 20 min at room temperature. The reaction mixture was *vacuo* evaporated to the half volume. A colorless solution of product **5** was obtained. In <sup>119</sup>Sn NMR spectrum signals of starting compound and product were observed. The conversion calculated from the spectra is 60%. <sup>119</sup>Sn{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 300 K, ppm): -134.5 (s); -137.5 (s), <sup>1</sup>H NMR spectrum of the inseparable mixture is very complex.

### 3.3. Bis-[[2-(N,N-dimethylaminomethyl)phenyl]n-butylchloro}tin sulfide (**6**)

The solution of **3** (151 mg, 0.22 mmol) in benzene was added during 5 min at room temperature to the suspension of S<sub>8</sub> (7 mg, 0.03 mmol). The reaction mixture was stirred for one week and afterwards filtered off and *vacuo* evaporated to the half volume. Pale yellow solution of **6** was obtained. The volume of the solvent was reduced to approximately 5 ml and the pale yellow crystals of **6** were obtained at -28 °C (yield 65%). The NMR and XRD spectroscopy shows the chirality of the product and two pairs of diastereoisomers. In <sup>1</sup>H and <sup>119</sup>Sn NMR spectra, two sets of partly differentiated signals which are related to the corresponding pairs of diastereoisomers were observed. (<sup>119</sup>Sn{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 300 K, ppm): -67.7 (s); -68.8 (s). Elemental analysis for C<sub>26</sub>H<sub>42</sub>Cl<sub>2</sub>N<sub>2</sub>SSn<sub>2</sub> (MW = 722.99): calculated: C 43.19%, H 5.86%, N 3.87%, found: C 43.2%, H 5.9%, N 3.9%. Crystallographic data for **6**: C<sub>26</sub>H<sub>42</sub>Cl<sub>2</sub>N<sub>2</sub>SSn<sub>2</sub>. C<sub>6</sub>H<sub>6</sub>, M = 801.06, triclinic, P-1, a = 9.5090(15), b = 15.415(4), c = 24.485(4) Å, α = 94.243(20), β = 95.414(14), γ = 104.26(3)°, Z = 4, V = 3445.3(12) Å<sup>3</sup>, D<sub>c</sub> = 1.544 g cm<sup>-3</sup>, μ = 1.689 mm<sup>-1</sup>, T<sub>min</sub> = 0.270; T<sub>max</sub> = 0.748, 44,483 reflections measured (θ<sub>max</sub> = 27.5°), 14,746 independent (R<sub>int</sub> = 0.0865), 11898 with I > 2σ(I), 703 parameters, S = 1.132, R<sub>1</sub>(obs. data) = 0.0592, wR<sub>2</sub>(all data) = 0.1546; max., min. residual electron density = 2.243, -2.144 eÅ<sup>-3</sup>.

### 3.4. {Bis-[[2-(N,N-dimethylaminomethyl)phenyl]n-butylchloro}tin selenide (**7**)

The solution of **3** (129 mg, 0.19 mmol) was added in one portion at room temperature to the suspension of black Se (15 mg, 0.19 mmol) in benzene. Reaction mixture was stirred at 80 °C for 6 h. After cooling down to the room temperature the reaction mixture was filtered and *vacuo* evaporated to a one half of the initial volume. A colorless solution of **7** was obtained. When the solvent was completely evaporated an oily residue reveals sufficient elemental analysis. The yield of the oily product is approximately 60%. <sup>119</sup>Sn{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 300 K, ppm): -106.5 (s); -107 (s). The <sup>1</sup>H NMR spectrum reveals very complex pattern. Elemental analysis for C<sub>26</sub>H<sub>42</sub>Cl<sub>2</sub>N<sub>2</sub>SeSn<sub>2</sub> (MW = 769.88): calculated: C 36.97%, H 4.14%, N 4.79%, found: C 37.0%, H 4.1%, N 4.8%.

### 3.5. {Bis-[[2-(N,N-dimethylaminomethyl)phenyl]n-butylchloro}tin telluride (**8**)

The solution of **3** (197 mg, 0.29 mmol) was added into one portion at room temperature to the suspension of Te (37 mg, 0.29 mmol) in benzene. Reaction mixture was stirred at 80 °C for 6 h. After cooling down to the room temperature the reaction mixture was *vacuo* evaporated to the half volume. A pale green solution of product **8** was obtained. The conversion based on the <sup>119</sup>Sn NMR spectrum pattern is essentially quantitative. <sup>119</sup>Sn{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 300 K, ppm): -195.7 (s); -203.0 (s). The <sup>1</sup>H NMR spectrum reveals very complex pattern. Elemental analysis for C<sub>26</sub>H<sub>42</sub>Cl<sub>2</sub>N<sub>2</sub>TeSn<sub>2</sub> (MW = 818.52): calculated: C 34.13%, H 3.82%, N 4.42%, found: C 34.1%, H 3.8%, N 4.4%.

### 3.6. {{Bis-[[2-(N,N-dimethylaminomethyl)phenyl]n-butylchloro}tin]-μ-chloro}[[2-(N,N-dimethylaminomethyl)phenyl]n-butylchloro}tin (**10**)

**10** can be prepared in multiple ways: from **1** in reactions with the excess of KCl<sub>8</sub> or K-mirror or in reaction with two molar equivalents of 2-Me-C<sub>10</sub>H<sub>18</sub>Li. In all reaction attempts **9** and **3** were detected as byproducts. The most convenient way to prepare **10** is the reaction of **3** with one molar equivalent of K(BEt<sub>3</sub>)H·THF: **3** (329 mg, 0.48 mmol) was dissolved in THF at -40 °C and 476 μl of K(BEt<sub>3</sub>)H·THF (c = 1 mol dm<sup>-3</sup>, 0.48 mmol) were added. The reaction mixture was stirred until it reached room temperature. Then the solvent was *vacuo* evaporated and afterwards hexane was added and soluble part was filtered off. Pale yellow single crystals of **10** were obtained from this solution at -28 °C (yield 21%). <sup>1</sup>H NMR (Tol-D<sub>8</sub>, 295 K, ppm): 8.60 (d, 1H-6, 5.5 Hz); 8.07 (br, 2H-6′,6′′); 7.14 (d, 3H-5,5′,5′′, 6.9 Hz); 7.09 (d, 3H-4,4′,4′′, 7.2 Hz); 6.76 (d, 3H-3,3′,3′′, 8.0 Hz); 3.64 (br, 2H-NCH<sub>2</sub>); 3.02 (s, 2H-NCH<sub>2</sub>′); 2.98 (d, 2H-NCH<sub>2</sub>′′); 1.93 (br-m-anisochromous protons, 6H-CH<sub>2</sub>-α); 1.75 (s, 6H-N(CH<sub>3</sub>)<sub>2</sub>); 1.72 (s, 12H-N(CH<sub>3</sub>)<sub>2</sub>′, N(CH<sub>3</sub>)<sub>2</sub>′′); 1.44 (m, 6H-CH<sub>2</sub>-β); 1.21 (m, 6H-CH<sub>2</sub>-γ); 0.98 (t, 9H-CH<sub>3</sub>). <sup>119</sup>Sn{<sup>1</sup>H} NMR (Tol-D<sub>8</sub>, 295 K, ppm): -114.5 (s). Elemental analysis for C<sub>39</sub>H<sub>63</sub>Cl<sub>2</sub>N<sub>3</sub>Sn<sub>4</sub> (MW = 1119.62): calculated: C 41.84%, H 5.67%, N 3.75%, found: C 41.8%, H 5.7%, N 3.8%. Crystallographic data for **10**: C<sub>39</sub>H<sub>63</sub>Cl<sub>2</sub>N<sub>3</sub>Sn<sub>4</sub>, M = 1119.58, monoclinic, P2<sub>1</sub>/c, a = 13.0550(14), b = 19.6227(16), c = 18.5071(13) Å, β = 101.116(8)°, Z = 4, V = 4652.1(7) Å<sup>3</sup>, D<sub>c</sub> = 1.599 g cm<sup>-3</sup>, μ = 2.265 mm<sup>-1</sup>, T<sub>min</sub> = 0.732; T<sub>max</sub> = 0.869, 37,152 reflections measured (θ<sub>max</sub> = 27.55°), 10622 independent (R<sub>int</sub> = 0.0769), 6864 with I > 2σ(I), 433 parameters, S = 1.146, R<sub>1</sub>(obs. data) = 0.0615, wR<sub>2</sub>(all data) = 0.1094; max., min. residual electron density = 1.533, -1.320 eÅ<sup>-3</sup>.

## Acknowledgements

The Pardubice group would like to thank the Grant Agency of Czech Academy of Science (KJB401550802) and the Ministry of Education of the Czech Republic (VZ 0021627501) for financial support.

## Appendix. Supplementary Information

CCDC 753965, 753966, and 753967 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Supplementary data associated with this article can be found in the online version at [10.1016/j.jorganchem.2010.04.019](https://doi.org/10.1016/j.jorganchem.2010.04.019).

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