

Communication

# Monoanionic Tin Oligomers Featuring Sn–Sn or Sn–Pb Bonds: Synthesis and Characterization of a Tris(Triheteroarylstannyl)Stannate and -Plumbate

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**Abstract:** The reaction of the lithium tris(2-pyridyl)stannate  $[\text{LiSn}(2\text{-py}^{6\text{O}t\text{Bu}})_3]$  ( $\text{py}^{6\text{O}t\text{Bu}} = \text{C}_5\text{H}_3\text{N-6-O}t\text{Bu}$ ), **1**, with the element(II) amides  $\text{E}\{\text{N}(\text{SiMe}_3)_2\}_2$  ( $\text{E} = \text{Sn, Pb}$ ) afforded complexes  $[\text{LiE}\{\text{Sn}(2\text{-py}^{6\text{O}t\text{Bu}})_3\}_3]$  for  $\text{E} = \text{Sn}$  (**2**) and  $\text{E} = \text{Pb}$  (**3**), which reveal three Sn–E bonds each. Compounds **2** and **3** have been characterized by solution NMR spectroscopy and X-ray crystallographic studies. Large  $^1J(^{119}\text{Sn}–^{119/117}\text{Sn})$  as well as  $^1J(^{207}\text{Pb}–^{119/117}\text{Sn})$  coupling constants confirm their structural integrity in solution. However, contrary to **2**, complex **3** slowly disintegrates in solution to give elemental lead and the hexaheteroarylditin  $[\text{Sn}(2\text{-py}^{6\text{O}t\text{Bu}})_3]_2$  (**4**).

**Keywords:** tin; lead; catenation; pyridyl ligands

## 1. Introduction

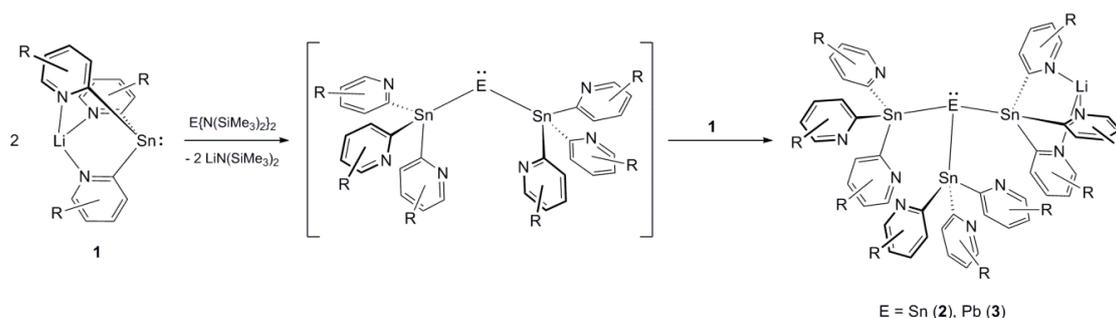
The synthesis and characterization of catenated heavier group 14 element compounds have attracted attention in recent years [1–5]. However, contrary to silicon and germanium, there are limitations for tin and lead associated with the significant decrease in element–element bond energy. Hence, homonuclear as well as heteronuclear molecules with E–E bonds become less stable when E represents tin and or lead. Moreover, within this class of compounds, discrete branched oligomers with more than one E–E bond are rare compared with their linear analogs [6–10]. It has been shown that reactions of lead(II) halides with Grignard reagents involved disproportionation processes leading to plumbates of type  $[\text{MgBr}(\text{THF})_5][\text{Pb}(\text{PbPh}_3)_3]$  [11] and  $[\text{Mg}(\text{THF})_3(\mu\text{-Cl})_3\text{Mg}(\text{THF})_3][\text{Pb}(\text{PbBp}_3)_3]$  ( $\text{Bp} = 4\text{-Biphenyl}$ ) [12]. The formation of closely related anions  $[\text{Sn}(\text{SnR}_3)_3]^-$  ( $\text{R} = \text{Me}$  or  $\text{Ph}$ ) was found as part of decomposition of corresponding stannyl anions in the presence of distannanes [13–16]. Further rare investigations included the reduction reaction of  $\text{SnPh}_4$  with elemental lithium in liquid ammonia to give  $[\text{Li}(\text{NH}_3)_4][\text{Sn}(\text{SnPh}_3)_3]$  [17] or reactions of the organotin chlorides  $\text{SnPh}_2\text{Cl}_2$  as well as  $\text{SnMe}_3\text{Cl}$  with lanthanoid metals, yielding complexes  $[\text{Yb}(\text{DME})_3\text{Cl}]_2[\text{Sn}(\text{SnPh}_3)_3]_2$  [18] and  $[\text{Ln}(\text{THF})_4[\text{Sn}(\text{SnMe}_3)_3]_2]$  ( $\text{Ln} = \text{Sm, Yb}$ ) [19]. Complete structural characterizations, however, are missing due to the very low solubility and sensitivity of all compounds reported.

Recently, conventional salt metathesis reactions have been employed for synthesis of neutral distannylstannylene species  $\text{Sn}(\text{SnAr}_3)_2$  ( $\text{Ar} = \text{C}_6\text{H}_3\text{-2,6-(O}^i\text{Pr)}_2$ ) [20] and  $\text{Sn}(\text{SnPh}_2\text{Ar}^*)_2$  ( $\text{Ar}^* = \text{C}_6\text{H}_3\text{-2,6-(Trip)}_2$ ,  $\text{Trip} = \text{C}_6\text{H}_2\text{-2,4,6-}^i\text{Pr}_3$ ) [21], bearing a divalent tin atom bonded to two triarylstannyl groups. In both cases, the catenation was implemented by a stannyl lithium derivative  $\text{LiSnAr}_3$  or  $\text{LiSnPh}_2\text{Ar}^*$ , respectively. Our studies on related triheteroaryl(II) compounds revealed a diverse reactivity. Thereby, it was found that compounds  $[\text{Li}(\text{THF})\text{Sn}(2\text{-py}^{\text{R}})_3]$  ( $\text{py}^{\text{R}} = \text{C}_5\text{H}_3\text{N-5-Me}$  or  $\text{C}_5\text{H}_3\text{N-3-Me}$ ), in which the lithium cation is well embedded within the tris(pyridyl)stannate core, can either act as a two-electron donor leading to a tin–element bond formation [22,23] or may be used for salt metathesis reactions with the lone pair of electrons at the tin(II) atom remaining available [24].

Continuing these studies, it is now shown that the reaction between the lithium tris(2-pyridyl)stannate [LiSn(2-py<sup>6*O*tBu</sup>)<sub>3</sub>] (py<sup>6*O*tBu</sup> = C<sub>5</sub>H<sub>3</sub>N-6-*O*tBu), **1**, with group 14 element(II) amides E{N(SiMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub> (E = Sn or Pb) lead to the straight formation of the lithium salts [LiSn{Sn(2-py<sup>6*O*tBu</sup>)<sub>3</sub>}<sub>3</sub>] (**2**) and [LiPb{Sn(2-py<sup>6*O*tBu</sup>)<sub>3</sub>}<sub>3</sub>] (**3**) each with the lithium cation intramolecularly coordinated by the novel tris(stannyl)metallate enabled through the unique donor functionality of the complex anion [Sn{Sn(2-py<sup>6*O*tBu</sup>)<sub>3</sub>}<sub>3</sub>]<sup>−</sup> as well as [Pb{Sn(2-py<sup>6*O*tBu</sup>)<sub>3</sub>}<sub>3</sub>]<sup>−</sup> itself.

## 2. Results

Compounds **2** and **3** have been prepared in reactions of the lithium stannate **1** upon addition of tin(II) or lead(II) amide E{N(SiMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub> (E = Sn, Pb) in a 3:1 stoichiometry (Scheme 1). The initial yellow THF solution of **1** gradually changed to a reddish-brownish solution of **2** and a green solution of **3**. The complexes were obtained as the only products in good isolated yields as colorless (**2**) as well as yellow (**3**) crystalline material upon work up and re-crystallization from toluene or benzene. It is likely that neutral E{Sn(2-py<sup>6*O*tBu</sup>)<sub>3</sub>}<sub>2</sub> was initially generated. However, this molecule, which could neither be isolated nor detected, may have then reacted further with another equiv of **1** to give the lithium complexes **2** or **3**, respectively, by virtue of a donor–acceptor interaction between two low valent group 14 element species. This may be explained with the less steric requirement of the pyridyl ligand as well as the pronounced two-electron donor ability of **1** comparable to other tris(2-pyridyl)stannates [22–24].



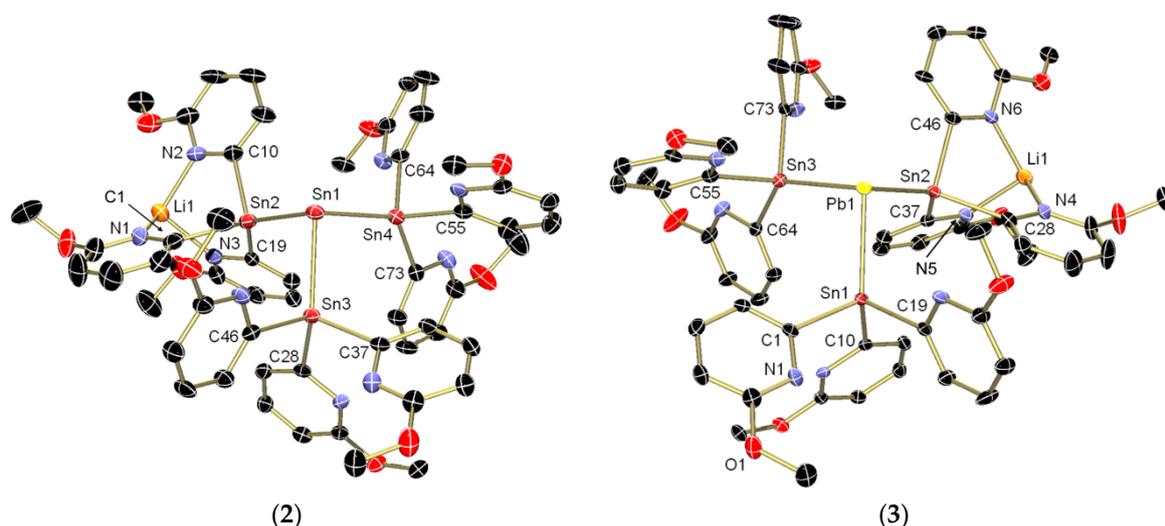
**Scheme 1.** Illustration of the possible reaction pathway to give compounds **2** and **3**; with py<sup>R</sup> = py<sup>6*O*tBu</sup> = C<sub>5</sub>H<sub>3</sub>N-6-*O*tBu.

Indeed, the molecular structures of complexes **2** and **3** (Figure 1, Table 1) imply the donation of a lithium stannate fragment to the central element(II) atom of a E{Sn(2-py<sup>6*O*tBu</sup>)<sub>3</sub>}<sub>2</sub> molecule due to the intramolecular *N*-coordination of the lithium cation by only one tris(2-pyridyl)stannyl unit in **2** and **3** as found for previously reported tris(2-pyridyl)stannate complexes [22–25]. Thus, compounds **2** and **3** can be described as zwitter-ionic complexes with a Li···Sn separation of 3.339(14) Å in **2** as well as 3.321(10) Å in **3**.

In complex **2**, the central Sn atom adopts a trigonal pyramidal geometry with Sn–Sn(1)–Sn angles of 92.52(2), 93.22(2), and 96.13(2)°. The Sn–Sn bond lengths range from 2.8127(7) to 2.8217(6) Å and lie well within the previously known range (2.811–2.836 Å) for complexes of the [Sn(SnPh<sub>3</sub>)<sub>3</sub>]<sup>−</sup> anion [16–19] but are considerably shorter than those found for the distannylstannylenes Sn(SnAr<sub>3</sub>)<sub>2</sub> (Ar = C<sub>6</sub>H<sub>3</sub>-2,6-(*O*<sup>*i*</sup>Pr)<sub>2</sub>) (2.86 Å) [20] as well as Sn(SnPh<sub>2</sub>Ar\*)<sub>2</sub> (Ar\* = C<sub>6</sub>H<sub>3</sub>-2,6-(Trip)<sub>2</sub>, Trip = C<sub>6</sub>H<sub>2</sub>-2,4,6-*i*Pr<sub>3</sub>) (2.96 Å) [21]). The geometry at Sn(2), whose interligand angles vary from 93.8(2)° to 132.5(2)°, is strikingly distorted from idealized tetrahedral geometry. This can be attributed to the binding of the lithium cation by the three pyridyl groups of this stannyl unit contrary to atoms Sn(3) and Sn(4).

Compound **3** crystallized as two structurally similar, but crystallographically independent molecules. Therefore, only one of the crystallographically independent molecules is shown in Figure 1. The molecular structure of **3** has many similarities to that of **2**. In **3**, the lead atom may also be described as trigonal pyramidal with the lone pair of electrons located at the apex. Accordingly, the Sn–Pb–Sn

angles are relatively small with values ranging from  $90.85(1)^\circ$  to  $94.49(1)^\circ$ . Similar structural features can be found in the previously reported tris(plumbyl)plumbate anions, where angles around the central lead atom average to  $93.0^\circ$  [11] and  $94.1^\circ$  [12]. The Pb–Sn bond lengths amount to 2.8743(3) and 2.8919(4) Å, and may be compared with 2.7844(4) Å in  $\text{Pb}(\text{Ar})\text{SnAr}_3$  (Ar =  $\text{C}_6\text{H}_3\text{-}2,6\text{-}(\text{O}^i\text{Pr})_2$ ) and 2.9283(4) Å in  $\text{Pb}(\text{SnAr}_3)_2$  [26].



**Figure 1.** Molecular structures of  $[\text{LiSn}\{\text{Sn}(2\text{-py}^{6\text{OtBu}})_3\}_3]$  (2) and  $[\text{LiPb}\{\text{Sn}(2\text{-py}^{6\text{OtBu}})_3\}_3]$  (3) with 30% probability ellipsoids. Hydrogen atoms and methyl groups are omitted for clarity.

**Table 1.** Selected bond lengths (Å) and bond angles ( $^\circ$ ) of compounds 2 and 3.

2		3	
Sn(1)–Sn(2)	2.8127(7)	Pb(1)–Sn(1)	2.8743(4)
Sn(1)–Sn(3)	2.8181(6)	Pb(1)–Sn(2)	2.8919(4)
Sn(1)–Sn(4)	2.8217(6)	Pb(1)–Sn(3)	2.8818(4)
Sn(2)···Li(1)	3.339(14)	Sn(2)···Li(1)	3.321(10)
Sn(2)–C <sub>ipso</sub>	2.168(7), 2.179(7), 2.184(8)	Sn(1)–C <sub>ipso</sub>	2.154(5), 2.167(6), 2.182(5)
Sn(3)–C <sub>ipso</sub>	2.161(6), 2.165(7), 2.183(6)	Sn(2)–C <sub>ipso</sub>	2.172(6), 2.183(6), 2.191(6)
Sn(4)–C <sub>ipso</sub>	2.163(6), 2.167(6), 2.172(7)	Sn(3)–C <sub>ipso</sub>	2.167(6), 2.169(5), 2.177(5)
Li(1)–N	2.024(13)–2.038(15)	Li(1)–N	1.996(11)–2.030(11)
Sn(2)–Sn(1)–Sn(3)	92.52(2)	Sn(1)–Pb(1)–Sn(2)	90.90(1)
Sn(2)–Sn(1)–Sn(4)	93.22(2)	Sn(1)–Pb(1)–Sn(3)	94.49(1)
Sn(3)–Sn(1)–Sn(4)	96.13(2)	Sn(2)–Pb(1)–Sn(3)	90.85(1)
C <sub>ipso</sub> –Sn(2)–C <sub>ipso</sub>	93.8(2), 98.9(3), 99.8(3)	C <sub>ipso</sub> –Sn(1)–C <sub>ipso</sub>	101.2(2), 103.2(2), 104.8(2)
C <sub>ipso</sub> –Sn(3)–C <sub>ipso</sub>	100.8(2), 102.8(2), 104.7(2)	C <sub>ipso</sub> –Sn(2)–C <sub>ipso</sub>	92.4(2), 98.6(2), 100.0(2)
C <sub>ipso</sub> –Sn(4)–C <sub>ipso</sub>	100.4(2), 101.2(3), 103.6(2)	C <sub>ipso</sub> –Sn(3)–C <sub>ipso</sub>	101.8(2), 103.3(2), 104.3(2)
C <sub>ipso</sub> –Sn(2)–Sn(1)	112.1(2), 114.0(2), 132.5(2)	C <sub>ipso</sub> –Sn(1)–Pb(1)	109.2(1), 112.5(1), 123.8(1)
C <sub>ipso</sub> –Sn(3)–Sn(1)	109.2(2), 112.6(2), 124.5(1)	C <sub>ipso</sub> –Sn(2)–Pb(1)	111.8(2), 113.7(2), 134.1(2)
C <sub>ipso</sub> –Sn(4)–Sn(1)	106.0(2), 113.0(2), 129.7(2)	C <sub>ipso</sub> –Sn(3)–Pb(1)	104.6(1), 107.9(1), 132.0(1)

Solution NMR spectra of both complexes in  $d_8$ -THF reveal a symmetric arrangement within the  $[\text{Sn}\{\text{Sn}(2\text{-py}^{6\text{OtBu}})_3\}_3]^-$  or  $[\text{Pb}\{\text{Sn}(2\text{-py}^{6\text{OtBu}})_3\}_3]^-$  skeleton, indicated by three chemical equivalent stannyl moieties with  $^{119}\text{Sn}$  NMR room temperature resonances at  $-151$  ppm (2) and  $-180$  ppm (3). The  $^{119}\text{Sn}$ – $^{119}/^{117}\text{Sn}$  coupling constant in compound 2 is 7050 Hz, and may be compared with scalar coupling constants found for stannylstannylene species (6240–9400 Hz) [20,27–31]. The chemical shift of the bridging tin atom in 2 appears at  $-1064$  ppm. This value is consistent with reported data for  $\text{LiSn}(\text{SnMe}_3)_3$  ( $\delta = -1062$  ppm) [14,32], but reveals a significant upfield shift by *ca.* 870 ppm compared to the three-coordinate tin(II) atom in 1 ( $\delta = -191$  ppm). The  $^{207}\text{Pb}$  NMR spectrum of 3 is characterized by one signal at  $-1643$  ppm and a  $^1J(^{207}\text{Pb}$ – $^{119}/^{117}\text{Sn})$  coupling of 14900 Hz, which is smaller than observed for the hitherto isolated stannylplumbylenes (19971–22560 Hz) [26], but

larger than determined for stannylplumbanes, e.g.,  $\text{Ph}_3\text{SnPbPh}_3$  (3469 Hz) [33,34]. The chemical shift value of the three-coordinate lead atom in **3**, however, is strikingly deviating from low field  $^{207}\text{Pb}$  resonances usually observed for triaryl plumbates, e.g., at +1063 ppm for  $\text{LiPbPh}_3$  [35] or +1020 ppm for the related  $[\text{LiPb}(2\text{-py}^{6\text{O}t\text{Bu}})_3]$  [36]. Thus, in **3**, the central lead atom is significantly more shielded according to a smaller contribution to the paramagnetic contribution term. In addition, fast fluctuation of the lithium counterion in **2** or **3** can be attributed to an upfield shifting of the  $^7\text{Li}$  NMR resonances to +0.68 ppm (**2**) and +1.08 ppm (**3**) in comparison to the parent lithium stannate **1** ( $\delta = +2.12$  ppm).

Compound **3** decomposes when stored over time in solution, yielding elemental lead, the lithiumstannate **1** and the hexaorganoditin  $[\text{Sn}(2\text{-py}^{6\text{O}t\text{Bu}})_3]_2$  (**4**). The decomposition, which was monitored by NMR spectroscopy, proceeds smoothly with the generation of less soluble crystalline **4**. Single crystals, suitable for X-ray diffraction analysis (see Supplementary Material) were isolated from the NMR tube. Compound **4** ranks into the group of hitherto known hexaorganoditin compounds as a result of an apparently inexorable cleavage of the comparably weak Sn–Pb bond. Similar to  $[\text{Sn}(2\text{-py}^{6\text{Me}})_3]_2$  [37], **4** provides further functionalities with prospective coordination characteristics due to the *N*-heteroaromatic ligand system.

Finally, the results obtained suggest the formation of the tris(stannyl)metallate complexes  $[\text{LiSn}\{\text{E}(2\text{-py}^{6\text{O}t\text{Bu}})_3\}_3]$  **2** and **3** to be favored over neutral bis(stannyl) derivatives. This may be rationalized with the following: (i) the less steric requirement of the organic substituent used, allowing further attack on E; (ii) the rapid reaction of electron rich **1**; and (iii) a stabilization of the anionic oligomers by the intramolecular coordination of the counterions. Thus, a straight route in synthesis of heavier group 14 element catenates containing more than one homonuclear or heteronuclear element–element bonds has been presented. Solution studies on **3**, however, underline the weakness of the Pb–Sn bonds in this molecule.

### 3. Experimental

All manipulations were carried out using standard Schlenk techniques under an atmosphere of dry nitrogen. THF and benzene have been distilled over sodium and stored over potassium mirror. Deuterated THF was stored over activated 4 Å molecular sieves.  $\text{Sn}\{\text{N}(\text{SiMe}_3)_2\}_2$  and  $\text{Pb}\{\text{N}(\text{SiMe}_3)_2\}_2$  were prepared according to published procedures [38].

NMR spectra have been recorded on a Bruker Avance DRX 400 spectrometer (Bruker BioSpin GmbH, Rheinstetten, Germany). The chemical shifts ( $\delta$ ) are quoted in ppm and are relative to tetramethylsilane (TMS). CHN analyses were carried out on a Vario EL III CHNS instrument (Elementar Analysensysteme GmbH, Hanau, Germany).

#### 3.1. Syntheses

**[LiSn(2-py<sup>6O<sup>t</sup>Bu</sup>)<sub>3</sub>] (1):**  $\text{SnCl}_2$  (0.76 g, 4 mmol) was added to a solution of  $\text{Li}(2\text{-py}^{6\text{O}t\text{Bu}})$  (1.88 g, 12 mmol) (generated from  $\text{LiPh}$  and 2-Br- $\text{C}_5\text{H}_3\text{N-6-O}t\text{Bu}$ ) in 30 mL of diethyl ether at 0 °C. The reaction mixture was stirred overnight at room temperature. After filtration, the residue was dissolved in toluene. Further filtration from  $\text{LiCl}$ , the removal of toluene, and the re-crystallization from THF gave yellow **1** in a total of 1.75 g (76%). Characterization: Elemental analysis (%) calcd. for  $\text{C}_{27}\text{H}_{36}\text{N}_3\text{O}_3\text{SnLi}$ ,  $\text{C}_4\text{H}_8\text{O}$ : C, 57.43; H, 6.84; N, 6.48. Found: C, 57.31; H, 6.87; N, 6.32.  $^1\text{H}$  NMR (400.1 MHz, 298 K,  $d_8$ -THF):  $\delta = 1.43$  (s, 9H,  $\text{CMe}_3$ ), 6.51 (d, 8 Hz, py), 7.29 (t, 8 Hz, py), 7.40 ppm (d, 8 Hz, py);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100.6 MHz, 298 K,  $d_8$ -THF):  $\delta = 28.5$  ( $\text{CMe}_3$ ), 78.3 ( $\text{CMe}_3$ ), 109.9 (py), 130.0 ( $^2J(^{13}\text{C}_{-119/117}\text{Sn}) = 109$  Hz, py), 135.0 ( $^3J(^{13}\text{C}_{-119/117}\text{Sn}) = 19$  Hz, py), 161.7 (py), 194.5 ppm ( $^1J(^{13}\text{C}_{-119/117}\text{Sn}) = 345$  Hz,  $\text{C}_{\text{ipso}}$ );  $^7\text{Li}$  NMR (155.5 MHz, 298 K,  $d_8$ -THF)  $\delta = 2.12$  ppm;  $^{119}\text{Sn}\{^1\text{H}\}$  NMR (149.2 MHz, 298 K,  $d_8$ -THF):  $\delta = -191$  ppm.  $^1\text{H}$  NMR (400.1 MHz, 298 K,  $\text{C}_6\text{D}_6$ ):  $\delta = 1.30$  (s, 9H,  $\text{CMe}_3$ ), 6.32 (d, 8 Hz, py), 7.01 (t, 8 Hz, py), 8.15 (d, 8 Hz, py);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100.6 MHz, 298 K,  $\text{C}_6\text{D}_6$ ):  $\delta = 27.9$  ( $\text{CMe}_3$ ), 77.8 ( $\text{CMe}_3$ ), 111.2 (py), 131.1 ( $^2J(^{13}\text{C}_{-119/117}\text{Sn}) = 134.8$  Hz, py), 134.8 ( $^3J(^{13}\text{C}_{-119/117}\text{Sn}) = 25$  Hz, py), 160.4 (py), 191.9 ppm ( $^1J(^{13}\text{C}_{-119/117}\text{Sn}) = 360$  Hz,  $\text{C}_{\text{ipso}}$ );  $^7\text{Li}$  NMR (155.5 MHz, 298 K,  $\text{C}_6\text{D}_6$ ):  $\delta = 3.78$  ppm;  $^{119}\text{Sn}\{^1\text{H}\}$  NMR (149.2 MHz, 298 K,  $\text{C}_6\text{D}_6$ ):  $\delta = -201$  ppm.

**[LiSn{Sn(2-py<sup>6OfBu</sup>)<sub>3</sub>]<sub>3</sub> (2):** To a solution of **1** (1.10 g, 19 mmol) in 10 mL of THF, Sn{N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (0.28 g, 6.3 mmol) was added at room temperature. The greenish solution was stirred for 1 h, and the solvent was then completely removed *in vacuo*. Crystallization from the concentrated toluene solution afforded colorless crystals of **2**. Yield: 0.73 g (63%). Characterization: Elemental analysis (%) calcd. for C<sub>81</sub>H<sub>108</sub>N<sub>9</sub>O<sub>9</sub>Sn<sub>4</sub>Li: C, 53.06; H, 5.94; N, 6.88. Found: C, 52.67; H, 6.02; N, 6.85. <sup>1</sup>H NMR (400.1 MHz, 298 K, *d*<sub>8</sub>-THF): δ = 1.20 (s, 9H, CMe<sub>3</sub>), 6.15 (d, 8 Hz, py), 6.78–6.84 ppm (m, py); <sup>13</sup>C{<sup>1</sup>H} NMR (100.6 MHz, 298 K, *d*<sub>8</sub>-THF): δ = 23.7 (CMe<sub>3</sub>), 76.0 (CMe<sub>3</sub>), 107.3 (py), 125.7 (<sup>2</sup>J(<sup>13</sup>C–<sup>119/117</sup>Sn) = 96 Hz, py), 133.5 (<sup>3</sup>J(<sup>13</sup>C–<sup>119/117</sup>Sn) = 36 Hz, py), 160.9 (<sup>3</sup>J(<sup>13</sup>C–<sup>119/117</sup>Sn) = 46 Hz, py), 174.8 ppm (<sup>1</sup>J(<sup>13</sup>C–<sup>119</sup>Sn) = 285 Hz, <sup>1</sup>J(<sup>13</sup>C–<sup>117</sup>Sn) = 271 Hz, <sup>2</sup>J(<sup>13</sup>C–<sup>119/117</sup>Sn) = 20 Hz, C<sub>ipso</sub>); <sup>7</sup>Li NMR (155.5 MHz, 298 K, *d*<sub>8</sub>-THF): δ = 0.68 ppm; <sup>119</sup>Sn{<sup>1</sup>H} NMR (149.2 MHz, 298 K, *d*<sub>8</sub>-THF): δ = –151 (<sup>1</sup>J(<sup>119</sup>Sn–<sup>119/117</sup>Sn) = 7050 Hz, <sup>2</sup>J(<sup>119</sup>Sn–<sup>119/117</sup>Sn) = 890 Hz, Sn(py)<sub>3</sub>), –1064 ppm (SnSn<sub>3</sub>).

**[LiPb{Sn(2-py<sup>6OfBu</sup>)<sub>3</sub>]<sub>3</sub> (3):** Crystalline **3** was prepared from **1** and Pb{N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> in a 3:1 stoichiometry as described above for the synthesis of **2**. Concentration of the benzene solution and storage at 8 °C overnight gave yellow **3** in 84% yield. Characterization: Elemental analysis (%) calcd. for C<sub>81</sub>H<sub>108</sub>N<sub>9</sub>O<sub>9</sub>Sn<sub>3</sub>PbLi: C, 50.62; H, 5.66; N, 6.56. Found: C, 49.77; H, 5.62; N, 6.34. <sup>1</sup>H NMR (400.1 MHz, 298 K, *d*<sub>8</sub>-THF): δ = 1.27 (s, 9H, CMe<sub>3</sub>), 6.20 (d, 8 Hz, py), 6.86–6.91 ppm (m, py); <sup>13</sup>C{<sup>1</sup>H} NMR (100.6 MHz, 298 K, *d*<sub>8</sub>-THF): δ = 29.3 (CMe<sub>3</sub>), 78.7 (CMe<sub>3</sub>), 110.1 (py), 128.4 (<sup>2</sup>J(<sup>13</sup>C–<sup>119/117</sup>Sn) = 95 Hz, py), 136.1 (py), 163.8 (<sup>3</sup>J(<sup>13</sup>C–<sup>119/117</sup>Sn) = 41 Hz, py), 180.0 ppm (<sup>1</sup>J(<sup>13</sup>C–<sup>119/117</sup>Sn) = 214 Hz, <sup>2</sup>J(<sup>13</sup>C–<sup>207</sup>Pb) = 78 Hz, C<sub>ipso</sub>); <sup>7</sup>Li NMR (155.5 MHz, 298 K, *d*<sub>8</sub>-THF): δ = 1.08 ppm. <sup>119</sup>Sn{<sup>1</sup>H} NMR (149.2 MHz, 298 K, *d*<sub>8</sub>-THF): δ = –180 ppm (<sup>1</sup>J(<sup>119</sup>Sn–<sup>207</sup>Pb) = 14700 Hz); <sup>207</sup>Pb{<sup>1</sup>H} NMR (83.6 MHz, 298K, *d*<sub>8</sub>-THF): δ = –1643 ppm (<sup>1</sup>J(<sup>207</sup>Pb–<sup>119/117</sup>Sn) = 14,900 Hz). <sup>1</sup>H NMR (400.1 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>): δ = 1.41 (s, 9H, CMe<sub>3</sub>), 6.42 (d, 8Hz, py), 7.00 (t, 8 Hz, py), 7.35 ppm (d, 8Hz, py); <sup>13</sup>C{<sup>1</sup>H} NMR (100.6 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>): δ = 28.7 (CMe<sub>3</sub>), 78.6 (CMe<sub>3</sub>), 111.0 (py), 136.1 (py), 162.9 (py), 178.4 ppm (C<sub>ipso</sub>); <sup>7</sup>Li NMR (155.5 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>): δ = 1.20 ppm. <sup>119</sup>Sn{<sup>1</sup>H} NMR (149.2 MHz, 298K, C<sub>6</sub>D<sub>6</sub>): δ = –161 ppm; <sup>207</sup>Pb{<sup>1</sup>H} NMR (83.6 MHz, 298K, C<sub>6</sub>D<sub>6</sub>): δ = –1738 ppm (<sup>1</sup>J(<sup>207</sup>Pb–<sup>119/117</sup>Sn) = 14,620 Hz).

**[Sn(2-py<sup>6OfBu</sup>)<sub>3</sub>]<sub>2</sub> (4):** A NMR solution of **3** in C<sub>6</sub>D<sub>6</sub> was set aside at room temperature. The color of the solution gradually changed from green to pale yellow. The formation of elemental lead was observed. After several days, the colorless crystals of **4** were grown from solution. In the <sup>119</sup>Sn{<sup>1</sup>H} NMR spectrum finally only one signal at –201 ppm was detected, according to free lithium stannate **1**. Isolated crystals of **4** were dissolved in *d*<sub>8</sub>-THF for characterization by NMR spectroscopy. Characterization: Elemental analysis (%) calcd. for C<sub>54</sub>H<sub>72</sub>N<sub>6</sub>O<sub>6</sub>Sn<sub>2</sub>: C, 56.96; H, 6.37; N, 7.38. Found: C, 56.92; H, 6.32; N, 7.28. <sup>1</sup>H NMR (400.1 MHz, 298 K, *d*<sub>8</sub>-THF): δ = 1.20 (s, 9H, CMe<sub>3</sub>), 6.37 (d, 8Hz, py), 7.03 (t, 8 Hz, py), 7.27 ppm (d, 8Hz, py); <sup>119</sup>Sn{<sup>1</sup>H} NMR (149.2 MHz, 298K, *d*<sub>8</sub>-THF): δ = –223 ppm. No <sup>119</sup>Sn–<sup>117</sup>Sn coupling could be detected.

### 3.2. X-ray Crystallography

Crystals of **2**, **3**, and **4** were removed from a Schlenk tube under a nitrogen atmosphere and covered with a layer of hydrocarbon oil. A suitable crystal was attached to a glass fiber and quickly placed in a low-temperature N<sub>2</sub> stream.

The crystallographic data were collected on a Xcalibur-S diffractometer (Rigaku Oxford Diffraction, Kent, UK) with MoK $\alpha$  radiation ( $\lambda$  = 0.71073 Å), solved by direct methods and refined by full-matrix least squares on  $F^2$  (SHELX97) [39,40] using all data. All non-hydrogen atoms are anisotropic, with H-atoms included in calculated positions (riding model). CCDC1467318 (**2**), CCDC1467319 (**3**), and CCDC1467320 (**4**) contain the supplementary crystallographic data that can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/structures](http://www.ccdc.cam.ac.uk/structures). The crystallographic data for compound **2** and **3** are given in Table 2.

**Table 2.** Crystallographic data for compounds 2 and 3.

	2	3
Formula	C <sub>81</sub> H <sub>108</sub> LiN <sub>9</sub> O <sub>9</sub> Sn <sub>4</sub>	C <sub>81</sub> H <sub>108</sub> LiN <sub>9</sub> O <sub>9</sub> PbSn <sub>3</sub>
M <sub>r</sub> (g·mol <sup>-1</sup> )	1833.46	1921.96
Cryst system	triclinic	triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	16.2901(9)	17.2766(4)
<i>b</i> (Å)	17.2775(8)	19.4489(6)
<i>c</i> (Å)	19.5167(8)	28.6285(7)
$\alpha$ (°)	103.329(4)	88.874(2)
$\beta$ (°)	101.969(4)	85.776(2)
$\gamma$ (°)	118.018(5)	65.256(3)
<i>V</i> (Å <sup>3</sup> )	4388.4(4)	8711.9(4)
<i>Z</i>	2	4
F(000)	1864	3856
<i>T</i> (K)	−180(2)	−130(2)
$\rho_{\text{calcd}}$ (g cm <sup>3</sup> )	1.388	1.465
$\mu$ (mm <sup>-1</sup> )	1.181	2.833
Reflns collected	31672	74704
Reflns unique	16052	41501
<i>R</i> <sub>int</sub>	0.0620	0.0391
Final <i>R</i> <sub>1</sub> ( <i>I</i> > 2σ( <i>I</i> ))	0.0574	0.0531
Final <i>wR</i> <sub>2</sub> ( <i>F</i> <sup>2</sup> ) (all data)	0.1172	0.1050

**Supplementary Materials:** The following are available online at [www.mdpi.com/2304-6740/4/2/19/s1](http://www.mdpi.com/2304-6740/4/2/19/s1). Figure S1: Molecular structure of compound 4. Table S1: Crystallographic data for compound 4. Figures S2–S7 contain the graphical representations of recorded NMR spectra.

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