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Novel diaminopropyl substituted organotin compounds

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Abstract

A novel synthetic pathway involving the desilylation of a tin trimethylsilyl species ($\text{Ph}_2\text{Sn}(\text{SiMe}_3)_2$) towards non-protected di(3-aminopropyl)tin dichloride ($(\text{H}_2\text{N}(\text{CH}_2)_3)_2\text{SnCl}_2$) is described. Di(3-aminopropyl)tin dichloride is then converted to the respective dicarboxylates species $(\text{H}_2\text{N}(\text{CH}_2)_3)_2\text{Sn}(\text{OCOR})_2$ employing carboxylic acids of different lengths ($\text{R} = -\text{CH}_3, -(\text{CH}_2)_{10}\text{CH}_3$). Depending on the nature of R, discrete packing effects are observed in the solid state of di(3-aminopropyl)tin dicarboxylate derivatives. All the synthesized substances were characterized by ^1H , ^{13}C and ^{119}Sn nuclear magnetic resonance (NMR) data and also single crystal X-ray analysis. These compounds are a promising class of substances for biological, pharmaceutical and technical applications.

Keywords

Organotin, diaminopropyl, ^{119}Sn NMR, single crystal X-ray diffraction, crystal packing motifs

Introduction

Until a recent contribution from this working group,¹ most of the known aminoalkyltin compounds including triphenyl- γ -*N,N*-diethylaminopropyltin² by Gilman, *N,N*-dimethylaminopropyltin³⁻⁶ by Jurkschat, and a series of aminoethyltin compounds⁷ by Weichmann displayed protected amino groups. In contrast, compounds with non-protected amino propyl side chains and functional residues at the central atom are well known for silicon and are commonly used for so-called silyl-terminated polyurethanes (STPU) in modern construction.⁸⁻¹⁶ However, much less is known concerning the heavier group 14 derivatives and their potential applications. This is in part due to the alkyl groups at the nitrogen atom being quite difficult to remove without compromising the carbon tin bond. Therefore, this class of compounds is quite limited in the chemistry at the nitrogen atom.

However, Weichmann's aminoethyltin compounds⁷ allow derivatization at the tin center as well as at the nitrogen atom. Unfortunately, these compounds undergo Grob fragmentation even at low temperatures,¹⁷ thus the practical use of these compounds is limited. Other attempts to synthesize compounds which are able to undergo reactions at the central tin atom as well as at the nitrogen atom in the side chain were described by van der Kerk¹⁸ and Smith¹⁹ but are limited to aminopropyl side chains.

Since this class of compounds should provide new applications in polymer science and catalysis as well as biological activity, we recently published the synthesis for a series of non-protected (3-aminopropyl)diethyl tin derivatives $(\text{H}_2\text{N}(\text{CH}_2)_3)\text{Et}_2\text{SnX}$ (X = halide, carboxylate) (Figure 1a) which overcome the problems associated with the compounds found in literature thus far.¹ This synthetic strategy is flexible in terms of the spacer length of the side chain and the target compounds bear functional residues at the tin atom as well as an unprotected nitrogen atom in the side chain.¹ This provided motivation for the preparation of the di(3-aminopropyl) analogues (Figure 1b). A novel synthetic pathway involving the

desilylation of a tin trimethylsilyl species ($\text{Ph}_2\text{Sn}(\text{SiMe}_3)_2$) towards di(3-aminopropyl)tin dichloride was employed. This compound was then converted to the respective tin dicarboxylate species ($\text{H}_2\text{N}(\text{CH}_2)_3)_2\text{Sn}(\text{OCOR})_2$ ($\text{R} = -\text{CH}_3, -(\text{CH}_2)_{10}\text{CH}_3$) and depending on the length of the carboxylate, discrete packing effects are observed in the solid state.

Insert Figure 1 here

Results and discussion

Synthesis

Previous reactions routes affording (3-aminopropyl)tin derivatives entailed the synthesis of organotin monohydride educts which were then deprotonated with LDA (lithium diisopropyl amide).¹ However, this route was not advantageous for the synthesis of the di(3-aminopropyl)tin derivatives due to fact that tin dihydride precursors are much more difficult to synthesize and temperature labile, partially polymerizing.²⁰ Therefore, an alternative tin educt was employed, the literature known diphenylbis(trimethylsilyl)tin, ($\text{Ph}_2\text{Sn}(\text{SiMe}_3)_2$).²¹ This stannane is more stable than the corresponding dihydrides and can be stored for long periods of time without decomposition. Diphenylbis(trimethylsilyl)tin was desilylated (Scheme 1) using a one-pot variation of the well-established cleavage of trimethylsilyl residues with KO^tBu .²²⁻²⁴

Insert Scheme 1 here

The resulting nucleophilic potassium stannides was then reacted with the electrophilic (*E*)-*N*-(3-chloropropyl)-2,2-dimethylpropan-1-imine¹ (chloroimine) undergoing a salt-elimination reaction to afford di((*E*)-*N*-(3-propyl)-2,2-dimethylpropan-1-imine)diphenyltin

(diimine) (**1**). This addition of a protecting group to the chloroimine derivative is necessary to preserve the active amino hydrogen successfully circumventing unwanted side reactions. Using this procedure, the diimine (**1**) was obtained in very good yield and purity through distillation after solvent removal and filtration of the potassium salt byproduct. The deprotection was easily achieved by using diluted aqueous solutions of HCl in equimolar amounts. Compound **1** was hydrolyzed, and the liberated aldehyde was removed together with the water under vacuum. The labile Sn–C bond remains untouched under these conditions and leads to an almost quantitative isolation of di(3-aminiumpropyl)chloridediphenyltin (**2**) as an amorphous solid (Scheme 2).

Insert Scheme 2 here

Compound **2** was then converted into di(3-aminopropyl)tin dichloride (**3**) *via* a thermally induced intramolecular protodearylation reaction (Scheme 3). A TGA/DSC-MS measurement was first conducted to establish the optimal reaction temperature in order to avoid Grob fragmentation.⁷ According to this measurement, the first phenyl ring was liberated as benzene at around 190 °C and the second phenyl ring at around 225 °C. At 260 °C, no phenyl groups were observed, however, decomposition of the target molecule begins at 240 °C. Therefore, a heating temperature of 235 °C was chosen for the preparative synthesis of (**3**). After 1 h of heating, di(3-aminopropyl)tin dichloride (**3**) was obtained as a solid and recrystallized out of methanol. Compound **3** was converted into the corresponding di(3-aminopropyl)tin diacetate ((H₂N(CH₂)₃)₂Sn(OCOCH₃)₂) (**4**) and di(3-aminopropyl)tin dilaurate ((H₂N(CH₂)₃)₂Sn(OCO(CH₂)₁₀CH₃)₂) (**5**) *via* a salt metathesis reaction with an alkaline metal carboxylate salt in methanol (Scheme 4). Compounds **4** and **5** were obtained as crystalline solids from benzene and heptane respectively.

Insert Scheme 3 here

Insert Scheme 4 here

Crystallographic Studies

Compounds **3-5** all crystallize with tin in a distorted octahedral environment displaying close Sn–N bonds from the amino propyl substituents (Table 1). These Sn–N bond lengths fall within published ranges for dative tin nitrogen interactions and similar values have been observed for a series of halide (X = F–I) and acetate (3-aminopropyl)diethyltin derivatives described by this working group.¹

Insert Table 1 here

In the case of the dichloride (**3**) (Figure 2), the compound crystallizes in a *cis* configuration, which is in contrast to all other related species summarized in Table 1 which crystallize in a *trans* configuration. The structure of **3** can be best compared to di(3-dimethylamino-1,1-dimethylpropyl)tin dichloride ((Me₂N(CH₂)₂CMe₂)₂SnCl₂)^{12,14} and di(3-dimethylaminopropyl)tin difluoride dihydrate ((Me₂N(CH₂)₃)₂SnF₂·2H₂O).²⁵ While both (Me₂N(CH₂)₂CMe₂)₂SnCl₂ and (Me₂N(CH₂)₃)₂SnF₂·2H₂O are soluble in apolar solvents, compound **3** is only soluble in polar solvents and a crystalline solid was only able to be obtained from methanol. This contrast in solubility is due to the presence of acidic protons on the amines in compound **3** which consequently allow for strong intermolecular interactions in the form of N–H···Cl (2.37(5)–2.71(5) Å) and C–H···Cl (2.94 Å) hydrogen bonds in the solid state (Figure 3). These strong interactions in the solid state were also observed in the aforementioned (3-aminopropyl)diethyltin halide and acetate derivatives.¹ The presence of

144 methyl groups on the amine of $(\text{Me}_2\text{N}(\text{CH}_2)_2\text{CMe}_2)_2\text{SnCl}_2$ and $(\text{Me}_2\text{N}(\text{CH}_2)_3)_2\text{SnF}_2 \cdot 2\text{H}_2\text{O}$
145 does not allow for any interactions in the solid state.

146
147 *Insert Figure 2 here*

148
149 *Insert Figure 3 here*

150
151 The diacetate (**4**) and dilaurate (**5**) (Figures 4 and 5) di(3-aminopropyl)tin derivatives
152 crystallize in a *trans* configuration in contrast to the dichloride (**3**). In both cases, the
153 carboxylate interacts with the central tin atom through only one oxygen atom, displaying an
154 averaged Sn–O bond length of 2.215(2) Å (Table 1). This bonding motif is also observed in
155 the (3-aminopropyl)diethyltin acetate derivative which displays a shorter Sn–O bond of
156 2.027(1) Å.¹ This shorter bond length is attributed to the lower substitution on the central tin
157 atom in this compound. In addition, **4** and **5** display the shortest Sn–N bond interactions
158 among presented compounds with 2.294(2) and 2.292(2) Å respectively. Similar to the
159 dichloride (**3**), compounds **4** and **5** show intermolecular interactions in the form of N–H···O
160 (2.09(3)–2.57(3) Å) hydrogen bonds in the solid state. However, the dichloride (**3**) (Figure 3)
161 exhibits a 3D polymeric structure in the solid state, whilst the acetate and laurate moieties
162 only allow for 2D networks to form. The diacetate (**4**) (Figure 6) and dilaurate (**5**) (Figure 7)
163 di(3-aminopropyl)tin derivatives arrange themselves to form planar sheets of
164 intermolecularly hydrogen bonded molecules. While there is a separation of the planar sheets
165 in the diacetate (**4**), the longer chains in the dilaurate (**5**) create intercalated layers exhibiting
166 discrete hydrophilic and hydrophobic regions (Figure 8). A similar type of arrangement or
167 interdigitation can also be observed in the arrangement of membrane lipids which form the

surface of all cells²⁶ and in transition metal coordination compounds with linear chain fatty acids.²⁷⁻²⁸

Insert Figure 4 here

Insert Figure 5 here

Insert Figure 6 here

Insert Figure 7 here

Insert Figure 8 here

Conclusion

We were able to extend the synthetic procedure reported for (3-aminopropyl)tin derivatives successfully to di(3-aminopropyl)tin species employing the desilylation of a tin trimethylsilyl educt ($\text{Ph}_2\text{Sn}(\text{SiMe}_3)_2$). Also, the synthesis of di(3-aminopropyl)tin dichloride *via* a thermochemical procedure similar to the already published monoamine derivatives could be demonstrated. Di(3-aminopropyl)tin dichloride was also converted into the corresponding acetate and laurate derivatives *via* a simple salt-metathesis reaction. Single crystal structure analysis reveals discrete crystal packing effects depending on the nature of the substituent on the tin central atom. While the di(3-aminopropyl)tin dichloride and diacetate derivatives display only extensive hydrogen bonding, the arrangement of the long hydrocarbon chains of the laurate moiety allows the formation of discrete hydrophilic and hydrophobic layers trough

interdigitation of the laurate alkyl chains. The synthesized compounds are highly interesting candidates for biological or catalytic applications and are currently tested for these purposes.

Experimental

Materials and Methods

All moisture and air sensitive reactions were carried out under inert atmosphere using Schlenk line techniques unless otherwise stated. Nitrogen was used as inert gas and passed through molecular-sieve 4Å and P₅O₁₀ with moisture indicator (Sicapent[®] by Merck) to remove trace water. Solvents were stored over a drying agent (lithium aluminum hydride (LDA) in case of THF, P₅O₁₀ for CH₂Cl₂ and (MeO)₂Mg for methanol) under N₂ and distilled prior to use or taken directly from an Innovative Technology[®] solvent drying system (benzene). CDCl₃ was distilled over P₅O₁₀ and stored under N₂, MeOH-d₄ was purchased water free. All chemicals were used as received from various chemical suppliers without any further purification. Diphenylbis(trimethylsilyl)tin²¹ and (*E*)-*N*-(3-chloropropyl)-2,2-dimethylpropan-1-imine¹ (chloroimine) were synthesized according to literature. All elemental analyses were performed on a Heraeus VARIO ELEMENTAR EL analyzer. Melting points were determined with a STUART SCIENTIFIC SMP 10, no temperature corrections were applied. TGA/DSC/MS measurements were conducted on a TG-DSC STA 409 TASC 414/3C/3/F connected to a QMS 403 C by a capillary coupling (both by NETZSCH). Samples were measured in an Al crucible on a Pt-sample carrier RG-2 in a temperature range of 35 °C up to 540 °C with a ramp of 10 K/min under a He flow of 200 mL/min as inert gas. The following m/z values were tracked during the experiment: 2, 12, 14, 15, 16, 17, 18, 26, 30, 35, 38, 41, 44, 51, 59, 77, 78, 119.

NMR-spectroscopy

^1H (300.22 MHz), ^{13}C (75.50 MHz) and ^{119}Sn (111.92 MHz) NMR spectra were recorded on a Mercury 300 MHz spectrometer from Varian at 25 °C. Chemical shifts are given in parts per million (ppm) relative to TMS ($\delta = 0$ ppm) regarding ^{13}C and ^1H and relative to SnMe_4 in the case of ^{119}Sn . Coupling constants (J) are reported in Hertz (Hz). For complete peak assignment, multinuclear NMR experiments were also carried out ($^1\text{H}, ^1\text{H}$ -COSY and $^1\text{H}, ^{13}\text{C}$ -HETCOR). Processing of the data was carried out using MestReNova7 (Mestrelab research).

Crystal structure determination

All crystals suitable for single crystal X-ray diffractometry were removed from a vial and immediately covered with a layer of silicone oil. A single crystal was selected, mounted on a glass rod on a copper pin, and placed in the cold N_2 stream provided by an Oxford Cryosystems cryometer. XRD data collection was performed on a Bruker APEX II diffractometer with use of Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) and a CCD area detector. Empirical absorption corrections were applied using SADABS.²⁹⁻³⁰ The structures were solved with use of either direct methods or the Patterson option in SHELXS and refined by the full-matrix least-squares procedures in SHELXL.³¹⁻³² The space group assignments and structural solutions were evaluated using PLATON.³³⁻³⁴ Non-hydrogen atoms were refined anisotropically. Hydrogen atoms bonded to amine nitrogens for all compounds were located in a difference map. All other hydrogen atoms were located in calculated positions corresponding to standard bond lengths and angles. Disorder was handled by modeling the occupancies of the individual orientations using free variables to refine the respective occupancy of the affected fragments. Disordered positions for the laurate chain in compound **5** were refined using 50/50 split positions. Table 2 contains the crystallographic data and

details of measurements and CCDC 1450038-1450040 contain the supplementary crystallographic data for compounds **3-5** respectively. CCDC 1450038-1450040 contains the supplementary crystallographic data for this paper. These data can be obtained, free of charge, via <http://www.ccdc.cam.ac.uk/products/csd/request/> (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K. (Fax: 44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk)).

Insert Table 2 here

Di((*E*)-*N*-(3-propyl)-2,2-dimethylpropan-1-imine)diphenyltin (1)

A 200 mL Schlenk tube was charged with 5.0 g (12 mmol) of diphenylbis(trimethylsilyl)tin²¹ and 100 mL THF. The solution was chilled to 0 °C and 3.0 g (26 mmol) KO^tBu were added under stirring. After 5 min, 3.9 g (24 mmol) of (*E*)-*N*-(3-chloropropyl)-2,2-dimethylpropan-1-imine¹ was added *via* a syringe and the reaction mixture stirred for another 20 min. Afterwards, the solvent was removed under vacuum and the residue suspended in 50 mL CH₂Cl₂ and filtered over Celite[®] 512. The crude product was distilled under vacuum. Bp.: 175 °C at 4x10⁻² mbar. Yield: 5.6 g (89%). ¹H NMR (CDCl₃) δ: 7.65-7.46 (m, 4H, *o*-Ph), 7.46-7.40 (s, 2H, -CH₂CH₂CH₂N=CHC(CH₃)₃), 7.40-7.25 (m, 6H, *m/p*-Ph); 3.38 (t, 4H, -CH₂CH₂CH₂N=CHC(CH₃)₃), 1.92 (m, 4H, -CH₂CH₂CH₂N=CHC(CH₃)₃), 1.25 (m, 4H, -CH₂CH₂CH₂N=CHC(CH₃)₃), 1.07 (s, 18H, -CH₂CH₂CH₂N=CHC(CH₃)₃) ppm. ¹³C NMR (CDCl₃) δ: 172.0 (2C, -CH₂CH₂CH₂N=CHC(CH₃)₃), 139.6 (2C, *i*-Ph), 136.7 (4C, *o*-Ph), 128.4 (2C, *p*-Ph), 128.2 (4C, *m*-Ph), 64.8 (2C, -CH₂CH₂CH₂N=CHC(CH₃)₃), 35.8 (2C, -CH₂CH₂CH₂N=CHC(CH₃)₃), 27.7 (2C, -CH₂CH₂CH₂N=CHC(CH₃)₃), 26.9 (6C, -CH₂CH₂CH₂N=CHC(CH₃)₃), 7.3 (2C, ¹J(¹³C-¹¹⁹Sn) = 366 Hz, ¹J(¹³C-¹¹⁷Sn) = 350 Hz, -

263 $\underline{\text{C}}\text{H}_2\text{CH}_2\text{CH}_2\text{N}=\text{CHC}(\text{CH}_3)_3$ ppm. ^{119}Sn NMR (CDCl_3) δ : -71.5 ppm. Elemental analysis
 264 (calcd.): C: 63.7% (64.0%); H: 8.0% (8.1%); N: 5.4% (5.3%).

265

266 **Di(3-aminiumpropyl)chloridediphenyltin (2)**

267 A 250 mL round bottom flask was charged with 5.0 g (9.5 mmol) of (1). 95 mL (19 mmol) of
 268 0.5 M HCl were added while stirring. Once all of the educt went into solution, the solvent
 269 was removed under vacuum at 60 °C. Mp: 178-180 °C. Yield: 4.3 g (98.3%). ^1H NMR
 270 (MeOH-d_4) δ : 7.58-7.50 (m, 4H, $^3J(^1\text{H}-^{119/117}\text{Sn}) = 46.1$ Hz, *o*-Ph), 7.42-7.34 (m, 6H, *m/p*-
 271 Ph), 2.95 (t, 4H, $^3J(^1\text{H}-^1\text{H}) = 7.47$ Hz, $-\text{CH}_2\text{CH}_2\underline{\text{C}}\text{H}_2\text{NH}_2$), 2.07-1.89 (m, 4H, $-\text{CH}_2\text{CH}_2$
 272 $\underline{\text{C}}\text{H}_2\text{CH}_2\text{CH}_2\text{NH}_2$), 1.41-1.30 (m, 4H, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$) ppm. ^{13}C NMR (MeOH-d_4) δ : 139.2
 273 (2C, *i*-Ph), 137.8 (4C, $^2J(^{13}\text{C}-^{119}\text{Sn}) = 35.2$ Hz, $^2J(^{13}\text{C}-^{117}\text{Sn}) = 33.7$ Hz, *o*-Ph), 130.1 (2C,
 274 $^4J(^{13}\text{C}-^{119/117}\text{Sn}) = 11.3$ Hz, *p*-Ph), 129.7 (4C, $^3J(^{13}\text{C}-^{119}\text{Sn}) = 48.2$ Hz, $^3J(^{13}\text{C}-^{117}\text{Sn}) = 46.1$ Hz,
 275 *m*-Ph), 44.0 (2C, $^3J(^{13}\text{C}-^{119}\text{Sn}) = 83.3$ Hz, $^3J(^{13}\text{C}-^{117}\text{Sn}) = 79.2$ Hz, $-\text{CH}_2\text{CH}_2\underline{\text{C}}\text{H}_2\text{NH}_2$), 25.9
 276 (2C, $^2J(^{13}\text{C}-^{119/117}\text{Sn}) = 16.4$ Hz, $-\text{CH}_2\underline{\text{C}}\text{H}_2\text{CH}_2\text{NH}_2$), 6.9 (2C, $^1J(^{13}\text{C}-^{119}\text{Sn}) = 362$ Hz,
 277 $^1J(^{13}\text{C}-^{117}\text{Sn}) = 347$ Hz, $-\underline{\text{C}}\text{H}_2\text{CH}_2\text{CH}_2\text{NH}_2$) ppm. ^{119}Sn NMR (MeOH-d_4) δ : -70.6 ppm.
 278 Elemental analysis (calcd.): C: 44.4% (46.8%); H: 6.0% (6.1%); N: 6.2% (6.1%).

279

280 **Di(3-aminopropyl)tin dichloride (3)**

281 A 100 mL Schlenk tube was charged with 3.5 g (7.6 mmol) of (2) and placed under vacuum
 282 in an oil bath. The oil bath was heated to 235 °C and the temperature was kept for 1 h. The oil
 283 bath was removed and the colorless product which had sublimed into the upper part of the
 284 Schlenk tube was dissolved in hot methanol, filtered through a 0.20 μm PTFE syringe filter
 285 and afterwards the solvent removed under vacuum. The crude product was recrystallized
 286 from methanol. Mp: 270-272 °C. Yield: 2.3 g (98.2%). ^1H NMR (65 °C, MeOH-d_4) δ : 3.35 (t,
 287 4H, $^3J(^1\text{H}-^1\text{H}) = 5.9$ Hz, $-\text{CH}_2\text{CH}_2\underline{\text{C}}\text{H}_2\text{NH}_2$), 2.49-2.38 (m, 4H, $^3J(^1\text{H}-^{119}\text{Sn}) = 175.2$ Hz,

288 $^3J(^1\text{H}-^{117}\text{Sn}) = 169.1 \text{ Hz}$, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$), 1.84 (t, 4H, $^3J(^1\text{H}-^1\text{H}) = 7.1 \text{ Hz}$,
 289 $^2J(^1\text{H}-^{119}\text{Sn}) = 96.2 \text{ Hz}$, $^2J(^1\text{H}-^{117}\text{Sn}) = 91.4 \text{ Hz}$, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$) ppm. ^{13}C NMR (65 °C,
 290 MeOH- d_4) δ : 41.2 (2C, $^3J(^{13}\text{C}-^{119}\text{Sn}) = 74.4 \text{ Hz}$, $^3J(^{13}\text{C}-^{117}\text{Sn}) = 71.1 \text{ Hz}$, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$),
 291 25.3 (2C, $^1J(^{13}\text{C}-^{119}\text{Sn}) = 908 \text{ Hz}$, $^1J(^{13}\text{C}-^{117}\text{Sn}) = 863 \text{ Hz}$, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$), 25.2 (2C,
 292 $^2J(^{13}\text{C}-^{119/117}\text{Sn}) = 51.3 \text{ Hz}$, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$) ppm. ^{119}Sn NMR (65 °C, MeOH- d_4) δ : -185.7
 293 ppm. Elemental analysis (calcd.): C: 23.4% (23.6%); H: 5.2% (5.3%); N: 9.1% (9.2%).

294

295 Di(3-aminopropyl)tin diacetate (4)

296 A 100 mL Schlenk tube was charged with 2.0 g (6.5 mmol) of (3) and 50 mL methanol. 1.1 g
 297 (13 mmol) sodium acetate was added to the suspension under stirring. After 5 min, the
 298 solvent was removed under vacuum, the residue suspended in 50 mL CH_2Cl_2 and filtered
 299 through a 0.20 μm PTFE syringe filter. The solvent was removed under vacuum and the
 300 crude product recrystallized from benzene. Mp: 142-143 °C. Yield: 2.2 g (96.2%). ^1H NMR
 301 (CDCl_3) δ : 3.13 (bs, 4H, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$), 2.88 (t, 4H, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$), 1.92 (s, 6H, -
 302 $\text{O}_2\text{C}(\text{CH}_3)$), 1.90-1.81 (m, 4H, $^3J(^1\text{H}-^{119/117}\text{Sn}) = 175.3 \text{ Hz}$, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$), 1.05 (t, 4H,
 303 $^3J(^1\text{H}-^1\text{H}) = 6.7 \text{ Hz}$, $^2J(^1\text{H}-^{119/117}\text{Sn}) = 100.9 \text{ Hz}$, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$) ppm. ^{13}C NMR (CDCl_3) δ :
 304 178.9 (2C, $-\text{O}_2\text{C}(\text{CH}_3)$), 40.1 (2C, $^3J(^{13}\text{C}-^{119/117}\text{Sn}) = 69.6 \text{ Hz}$, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$), 24.1 (2C,
 305 $^2J(^{13}\text{C}-^{119/117}\text{Sn}) = 53.6 \text{ Hz}$, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$), 23.6 (2C, $-\text{O}_2\text{C}(\text{CH}_3)$), 20.5 (2C, -
 306 $\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$) ppm. ^{119}Sn NMR (CDCl_3) δ : -330.2 ppm. Elemental analysis (calcd.): C:
 307 35.6% (34.0%); H: 6.1% (6.3%); N: 7.1% (7.9%).

308

309 Di(3-aminopropyl)tin dilaurate (5)

310 A 100 mL Schlenk tube was charged with 0.51 g (13 mmol) freshly cut (in dry box)
 311 potassium and 50 mL methanol. After the metal had dissolved, 2.6 g (13 mmol) lauric acid
 312 were added. After a clear solution was obtained, 2.0 g (6.5 mmol) of (3) were added. After 5

min the solvent was removed under vacuum, the residue suspended in 50 mL CH₂Cl₂ and filtered through a 0.20 µm PTFE syringe filter. The solvent was pumped down under vacuum and the product was dried under oil vacuum for 2 h at 60 °C. The crude product was recrystallized from heptane. Mp: 84-85 °C. Yield: 3.7 g (98.3%). ¹H NMR (CDCl₃) δ: 2.88 (m, 4H); 2.19 (m, 4H); 1.88 (m, 3H); 1.56 (m, 4H); 1.24 (m, 30H); 1.04 (m, 3H); 0.87 (t, 6H). ¹³C NMR (CDCl₃) δ: 181.5 (2C, -O₂C(CH₂)₁₀CH₃), 39.9 (2C, ³J(¹³C-^{119/117}Sn)= 68.2 Hz, -CH₂CH₂CH₂NH₂); 36.2; 31.9; 29.6; 29.5; 29.4; 29.4; 29.0 20.0; 23.924.1 (2C, ²J(¹³C-^{119/117}Sn)= 55 Hz, -CH₂CH₂CH₂NH₂) ; 22.7; 14.1. ¹¹⁹Sn NMR (CDCl₃) δ: -330.1. Elemental analysis (calcd.): C: 58.6% (54.1%); H: 9.9% (9.4%); N: 2.2% (4.9%).

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X = Halogen, Carboxylate

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331 **Figure 1.** **a)** Non-protected (3-aminopropyl)diethyltin¹ derivative; **b)** Non-protected di(3-aminopropyl)tin
332 derivative.

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337 **Scheme 1.** Desilylation and alkylation of diphenylbis(trimethylsilyl)tin with (*E*)-*N*-(3-chloropropyl)-2,2-
338 dimethylpropan-1-imine (chloroimine).

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343 **Scheme 2.** Deprotection of di((*E*)-*N*-(3-propyl)-2,2-dimethylpropan-1-imine)diphenyltin (diimine) (1) *via* acidic
344 hydrolysis.

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361 **Figure 2.** Crystal structure of **(3)**. Sn–N interactions highlighted by dashed bonds. All non-carbon atoms shown
362 as 30% shaded ellipsoids. Non-amino hydrogen atoms removed for clarity.

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363

364 **Figure 3.** Crystal packing diagram of (3). Sn–N, N–H...Cl and C–H...Cl interactions highlighted by dashed
365 bonds. All non-carbon atoms shown as 30% shaded ellipsoids. Hydrogen atoms not involved in intermolecular
366 interactions removed for clarity.

367

368 **Figure 4.** Crystal structure of (4). Sn–N interactions highlighted by dashed bonds. All non-carbon atoms shown
369 as 30% shaded ellipsoids. Non-amino hydrogen atoms removed for clarity.

370

371 **Figure 5.** Crystal structure of (5). Sn–N interactions highlighted by dashed bonds. All non-carbon atoms shown
372 as 30% shaded ellipsoids. Non-amino hydrogen atoms removed for clarity.

Figure 6. Crystal packing diagram of (4) displaying interactions propagated by hydrogen bonding. Sn–N and N–H···O interactions highlighted by dashed bonds. All non-carbon atoms shown as 30% shaded ellipsoids. Hydrogen atoms not involved in intermolecular interactions removed for clarity.

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381 **Figure 7.** Crystal packing diagram of (5) displaying interactions propagated by hydrogen bonding. Sn–N and
382 N–H···O interactions highlighted by dashed bonds. All non-carbon atoms shown as 30% shaded ellipsoids.
383 Hydrogen atoms not involved in intermolecular interactions removed for clarity.

Figure 8. Crystal packing diagram of (5) displaying sheet intercalation through the laurate moiety creating layers. Sn–N and N–H···O interactions highlighted by dashed bonds. All non-carbon atoms shown as 30% shaded ellipsoids. Hydrogen atoms not involved in intermolecular interactions removed for clarity.

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399 **Table 2.** Crystallographic data and details of measurements for compounds **3-5**
400 Mo K α ($\lambda=0.71073\text{\AA}$). $R_1 = \Sigma/|F_o|-|F_c|/\Sigma|F_d|$; $wR2 = [\Sigma_w(F_o^2-F_2^2)^2/\Sigma_w(F_o^2)^2]^{1/2}$

Compound	3	4	5
Formula	C ₆ H ₁₆ Cl ₂ N ₂ Sn	C ₁₀ H ₂₂ N ₂ O ₄ Sn	C ₃₀ H ₆₂ N ₂ O ₄ Sn
Fw (g mol ⁻¹)	305.80	352.98	633.50
<i>a</i> (Å)	8.193(2)	5.8127(2)	18.616(5)
<i>b</i> (Å)	6.6061(16)	7.7301(3)	8.974(2)
<i>c</i> (Å)	20.879(5)	7.8056(3)	10.391(3)
α (°)	90	75.373(2)	90
β (°)	97.559(16)	82.377(2)	99.002(10)
γ (°)	90	88.861(2)	90
<i>V</i> (Å ³)	1120.2(5)	336.33(2)	1714.6(8)
<i>Z</i>	4	1	2
Crystal size (mm)	0.10 × 0.09 × 0.03	0.12 × 0.10 × 0.09	0.10 × 0.09 × 0.07
Crystal habit	Colorless plate	Colorless plate	Colorless block
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> -1	<i>P</i> 2 ₁ / <i>c</i>
<i>d</i> _{calc} (mg/m ³)	1.813	1.743	1.714
μ (mm ⁻¹)	2.71	1.91	0.78
<i>T</i> (K)	100(2)	100(2)	100(2)
2 θ range (°)	2.8–27.1	2.7–33.1	2.5–25.5
<i>F</i> (000)	600	178	676
<i>R</i> _{int}	0.070	0.065	0.077
independent reflns	2473	2551	3022
No. of params	116	88	271
R1, wR2 (all data)	R1 = 0.0561 wR2 = 0.0644	R1 = 0.0151 wR2 = 0.0385	R1 = 0.0353 wR2 = 0.0629
R1, wR2 (>2 σ)	R1 = 0.0317 wR2 = 0.0576	R1 = 0.0151 wR2 = 0.0385	R1 = 0.0226 wR2 = 0.0553

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References

- [1] Pichler, J.; Torvisco, A.; Bottke, P.; Wilkening, M.; Uhlig, F., *Can. J. Chem.* **2014**, *92* (6), 565. doi: 10.1139/cjc-2013-0504.
- [2] Gilman, H.; Wu, T. C., *J. Am. Chem. Soc.* **1955**, *77* (12), 3228. doi: 10.1021/ja01617a024.
- [3] Jurkschat, K.; Klaus, C.; Dargatz, M.; Tzschach, A.; Meunier-Piret, J.; Mahieu, B., *Z. Anorg. Allg. Chem.* **1989**, *577* (1), 122. doi: 10.1002/zaac.19895770114.
- [4] Jurkschat, K.; Tzschach, A.; Weichmann, H.; Rajczy, P.; Mostafa, M. A.; Korecz, L.; Burger, K., *Inorg. Chim. Acta* **1991**, *179* (1), 83. doi: 10.1016/S0020-1693(00)85377-3.
- [5] Schollmeyer, D.; Hartung, H.; Klaus, C.; Jurkschat, K., *Main Group Met. Chem.* **1991**, *14*, 27.
- [6] Zickgraf, A.; Beuter, M.; Kolb, U.; Dräger, M.; Tozer, R.; Dakternieks, D.; Jurkschat, K., *Inorg. Chim. Acta* **1998**, *275–276*, 203. doi: 10.1016/S0020-1693(98)00071-1.
- [7] Weichmann, H.; Tzschach, A., *Z. Anorg. Allg. Chem.* **1979**, *458* (1), 291. doi: 10.1002/zaac.19794580139.
- [8] Akram, D.; Ahmad, S.; Sharmin, E.; Ahmad, S., *Macromol. Chem. Phys.* **2010**, *211* (4), 412. doi: 10.1002/macp.200900404.
- [9] Nomura, Y.; Sato, A.; Sato, S.; Mori, H.; Endo, T., *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45* (13), 2689. doi: 10.1002/pola.22025.
- [10] O'Connor, A. E.; Kingston, T., *J. ASTM Int.* **2004**, *1* (3). doi: 10.1520/JAI11620.
- [11] Sardon, H.; Irusta, L.; Fernández-Berridi, M. J.; Lansalot, M.; Bourgeat-Lami, E., *Polymer* **2010**, *51* (22), 5051. doi: 10.1016/j.polymer.2010.08.035.
- [12] Subramani, S.; Choi, S.-W.; Lee, J.-Y.; Kim, J. H., *Polymer* **2007**, *48* (16), 4691. doi: 10.1016/j.polymer.2007.06.023.
- [13] Subramani, S.; Lee, J. M.; Lee, J.-Y.; Kim, J. H., *Polym. Adv. Technol.* **2007**, *18* (8), 601. doi: 10.1002/pat.860.
- [14] Subramani, S.; Lee, J.-Y.; Kim, J. H.; Cheong, I. W., *Compos. Sci. Technol.* **2007**, *67* (7–8), 1561. doi: 10.1016/j.compscitech.2006.07.011.
- [15] Vega-Baudrit, J.; Sibaja-Ballesteros, M.; Vázquez, P.; Torregrosa-Maciá, R.; Miguel Martín-Martínez, J., *Int. J. Adhes. Adhes.* **2007**, *27* (6), 469. doi: 10.1016/j.ijadhadh.2006.08.001.
- [16] Xu, J.; Shi, W.; Pang, W., *Polymer* **2006**, *47* (1), 457. doi: 10.1016/j.polymer.2005.11.035.
- [17] Grob, C. A.; Schiess, P. W., *Angew. Chem.* **1967**, *79* (1), 1. doi: 10.1002/ange.19670790102.
- [18] van der Kerk, G. J. M.; Noltes, J. G.; Luijten, J. G. A., *J. Appl. Chem.* **1957**, *7* (7), 356. doi: 10.1002/jctb.5010070703.
- [19] Smith, G. Per (Beta and Gamma Substituted Alkylene)mono- and Di-Tin Compounds and the Preparation Thereof. U. S. Patent 3,332,970, 1967.
- [20] Voronkov, M. G.; Egorochkin, A. N. In *The Chemistry of Organic Germanium, Tin and Lead Compounds*, John Wiley & Sons, Ltd 2003; p 2003.
- [21] Fischer, R.; Schollmeier, T.; Schürmann, M.; Uhlig, F., *Appl. Organomet. Chem.* **2005**, *19* (4), 523. doi: 10.1002/aoc.854.
- [22] Fischer, R.; Baumgartner, J.; Marschner, C.; Uhlig, F., *Inorg. Chim. Acta* **2005**, *358* (11), 3174. doi: 10.1016/j.ica.2005.04.006.
- [23] Hlina, J.; Mechtler, C.; Wagner, H.; Baumgartner, J.; Marschner, C., *Organometallics* **2009**, *28* (14), 4065. doi: 10.1021/om900287c.
- [24] Marschner, C., *Eur. J. Inorg. Chem.* **1998**, *1998* (2), 221. doi: 10.1002/(SICI)1099-0682(199802)1998:2<221::AID-EJIC221>3.0.CO;2-G.
- [25] Pieper, N.; Klaus-Mrestani, C.; Schürmann, M.; Jurkschat, K.; Biesemans, M.; Verbruggen, I.; Martins, J. C.; Willem, R., *Organometallics* **1997**, *16* (5), 1043. doi: 10.1021/om960895h.
- [26] Slater, J. L.; Huang, C.-H., *Prog. Lipid Res.* **1988**, *27* (4), 325. doi: doi.org/10.1016/0163-7827(88)90010-0.

- 454 [27] Johnpeter, J. P.; Therrien, B., *J. Struct. Chem.* **2011**, *52* (1), 151. doi:
455 10.1134/s0022476611010203.
- 456 [28] Petrič, M.; Leban, I.; Šegedin, P., *Polyhedron* **1995**, *14* (8), 983. doi: doi.org/10.1016/0277-
457 5387(94)00362-I.
- 458 [29] Bruker *APEX2 and SAINT*, Bruker AXS Inc.: Madison, Wisconsin, USA, 2012.
- 459 [30] Blessing, R. H., *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1995**, *51* (1), 33. doi:
460 10.1107/S0108767394005726.
- 461 [31] Sheldrick, G. M., *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1990**, *46* (6), 467. doi:
462 10.1107/S0108767390000277.
- 463 [32] Sheldrick, G. M., *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, *64* (1), 112. doi:
464 10.1107/S0108767307043930.
- 465 [33] Spek, A. L., *J. Appl. Crystallogr.* **2003**, *36* (1), 7. doi: 10.1107/S0021889802022112.
- 466 [34] Spek, A. L., *Acta Crystallogr., Sect. D: Biol. Crystallogr.* **2009**, *65* (2), 148. doi:
467 10.1107/S090744490804362X.

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