

# Routes to bis(amino)tin dichlorides: exchange reactions between tin(IV) chloride and tin(II) and tin(IV) amides, and the synthesis of a cyclic bis(amino)tin dichloride from tin(IV) chloride and *N,N'*-di-tert-butyl-1,3-diaminopropane via HCl elimination

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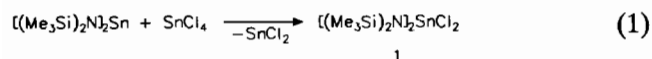
## Abstract

Monomeric non-cyclic and dimeric cyclic bis(amino)stannylenes react with tin(IV) chloride to give the corresponding bis(amino)tin dichlorides (**1**, **2**) in essentially quantitative yield. By monitoring the exchange reaction between tin(IV) chloride and tetrakis(diethylamino)tin using  $^{119}\text{Sn}$  NMR at low temperature, two intermediates (**4**, **5**) were identified as binuclear complexes in which the tin atoms are bridged by two amino groups and one chloro ligand. The equilibrated 1:1 reaction mixture finally contains mainly bis(diethylamino)tin dichloride (**3**). The reaction between *N,N'*-di-tert-butyl-1,3-diaminopropane/triethylamine (1:2) and  $\text{SnCl}_4$  affords the cyclic bis(amino)tin dichloride (**6**) via elimination of HCl. The compounds **1–6** were characterized in solution by  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{29}\text{Si}$  and  $^{119}\text{Sn}$  NMR. The solid state  $^{119}\text{Sn}$  CP/MAS NMR spectrum of compound **6** proves that its monomeric character is retained also in the crystalline state.

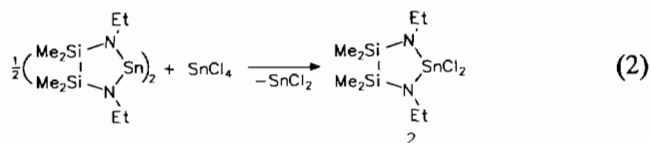
## Introduction

Although, bis(amino)tin dichlorides must be considered as useful starting materials both in inorganic and organic tin chemistry, only a few examples of these compounds are known [1]. In two cases, they have been obtained from the reaction between monomeric cyclic bis(amino)stannylenes and tin(IV) chloride [2, 3], and a non-cyclic derivative was prepared from tin(IV) chloride and *N*-lithiated hexamethyldisilazane [4].

In this work, we want to show that the target compounds are also available from a monomeric non-cyclic bis(amino)stannylenes (eqn. (1)) or from a dimeric cyclic



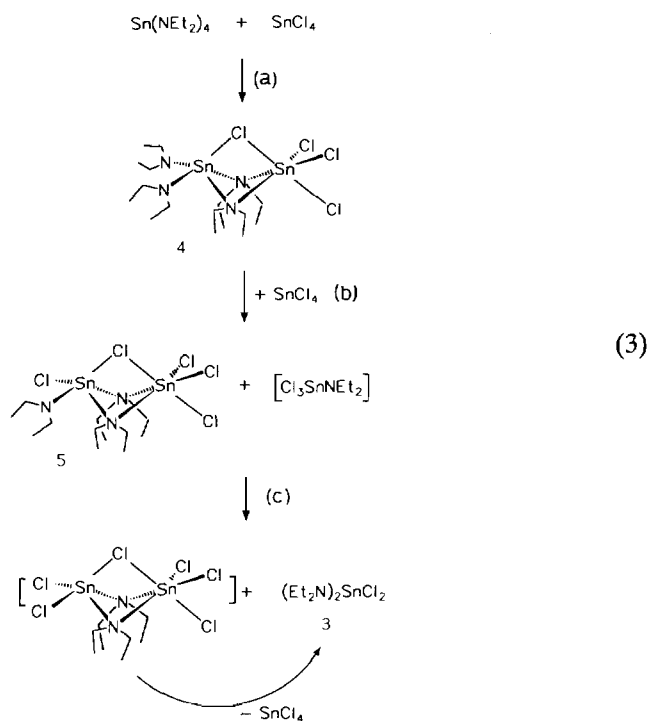
bis(amino)stannylenes (eqn. (2)). Furthermore, we have studied the exchange reaction between tin(IV)



chloride and tetrakis(diethylamino)tin (eqn. (3)) with regard to possible intermediates and to the synthesis of bis(diethylamino)tin dichloride (**3**).

All these routes require metallation or dimetallation of the respective amine either for the syntheses of the tin(II) and tin(IV) amides [1, 5, 6] or for the direct reaction of lithium amides with tin(IV) chloride [4]. In order to avoid this step, we have tested several amines in the reaction with tin(IV) chloride for preparing the desired bis(amino)tin dichlorides via HCl elimination.

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## Results and discussion

The reactions according to eqns. (1) and (2) proceed quantitatively to give the bis(amino)tin dichlorides 1 and 2 in high purity.

The exchange reaction eqn. (3) is more complex and the formation of bis(diethylamino)tin dichloride (3) as the final product is always accompanied by some decomposition and formation of small amounts of other products which have not yet been identified. However, solutions of 3 (purity >90%) in toluene, benzene or  $\text{CH}_2\text{Cl}_2$  can be prepared if the mixtures of tin(IV) chloride and tetrakis(diethylamino)tin (1:1) are allowed to reach equilibrium after several hours at room temperature. The proceeding of the exchange reaction was monitored by variable temperature  $^{119}\text{Sn}$  NMR (see Fig. 1). All NMR spectroscopic evidence points towards compound 4 (eqn. (3)) as the first intermediate in the exchange process. The  $\delta$   $^{119}\text{Sn}$  data [7] are strongly indicative of one tin atom with coordination number 6 ( $\delta^{119}\text{Sn} - 517.5$ ) and the other one with coordination number 5 ( $\delta^{119}\text{Sn} - 200.6$ ). The coordination number 5 for this tin atom requires a bridging chloro ligand in addition to the bridging diethylamino groups. If there were no bridging chloro ligand, the  $^{119}\text{Sn}$  nuclear shielding should be significantly reduced as has been found for numerous examples where the tin atom is tetra-coordinate and adjacent to an ammonium-type nitrogen [8]. The assumption of a bridging chloro ligand is also supported by the  $^{119}\text{Sn}$  resonance of the hexa-coordinate

tin atom which is shifted by >100 ppm to higher frequency with respect to complexes of the type *cis*- or *trans*- $\text{L}_2\text{SnCl}_4$  [9]. Both tin atoms belong to the same molecule as is evident from  $^{117/119}\text{Sn}$  satellites owing to  $^2J(\text{SnSn})$  (188.0 Hz). By adding more tin(IV) chloride to a solution containing 4 and 5, the  $^{119}\text{Sn}$  NMR signals for 4 vanish and  $^{119}\text{Sn}$  resonances ascribed to compound 5 grow in intensity. The position of the low-frequency signal of 5 ( $\delta^{119}\text{Sn} - 506.5$ ) is rather similar to that of 4. Therefore, we assume the analogous surrounding of this tin atom. A more pronounced change is observed for the  $^{119}\text{Sn}$  resonance at high frequency ( $\delta^{119}\text{Sn} - 250.6$ ). We interpret this as the result of an exchange of one of the terminal amino groups in 4 against a chloro ligand. Compound 5 appears to be much more

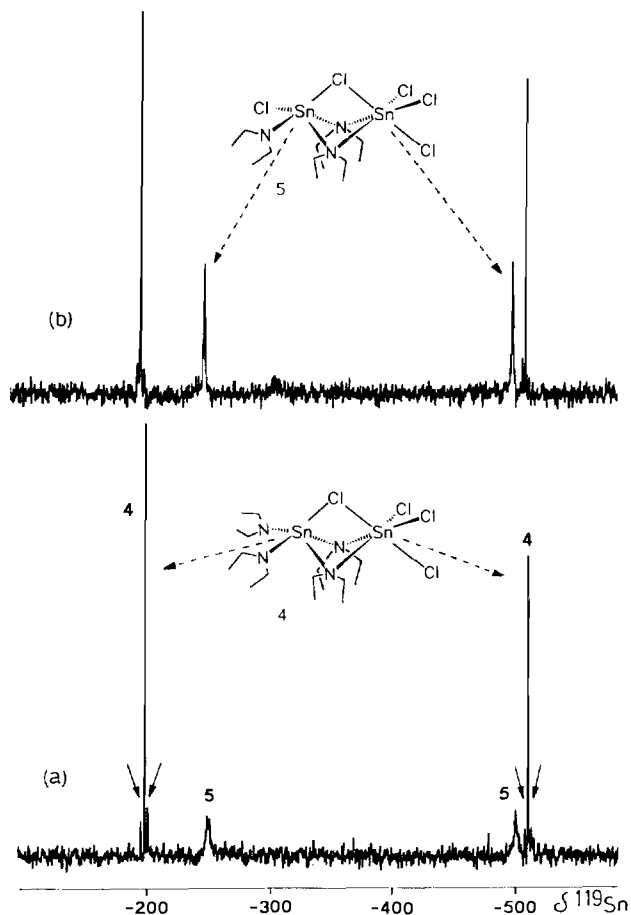
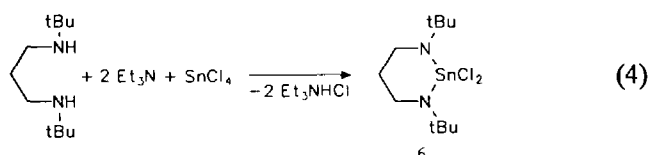


Fig. 1. 33.6 MHz  $^{119}\text{Sn}$  NMR spectra ( $^1\text{H}$  inverse gated decoupled for NOE suppression [7]), recorded for a mixture containing  $(\text{Et}_2\text{N})_4\text{Sn}$  and  $\text{SnCl}_4$  ( $\approx 1:1.8$ ) in  $\text{CD}_2\text{Cl}_2$ . The integral ratio of signals within each pair of  $^{119}\text{Sn}$  resonances is close to 1:1. (a) Spectrum recorded at  $-90^\circ\text{C}$  after mixing of the starting compounds;  $^{117/119}\text{Sn}$  satellites corresponding to  $^2J(\text{SnSn})$  (188.0 Hz) are marked by arrows. The  $^{119}\text{Sn}$  resonances for compound 4 ( $\delta^{119}\text{Sn} - 200.6$ ,  $-517.5$ ) are already sharp whereas rather broad signals appear for 5 ( $\delta^{119}\text{Sn} - 250.6$ ,  $-506.5$ ). (b) Spectrum recorded at  $-100^\circ\text{C}$ , showing the sharpening of the  $^{119}\text{Sn}$  resonances for compound 5.

labile than **4** with regard to exchange processes since the  $^{119}\text{Sn}$  resonances of **5** readily coalesce at temperatures above  $-70\text{ }^\circ\text{C}$ . It is interesting to note that no  $^{119}\text{Sn}$  resonance is observed in the range expected [7] ( $\delta^{119}\text{Sn} -100$  to  $-155$ ) for monomeric  $\text{Et}_2\text{NSnCl}_3$ . If these solutions are warmed to  $-40\text{ }^\circ\text{C}$  all  $^{119}\text{Sn}$  resonances have broadened beyond detection. At room temperature the system approaches equilibrium, and in the 1:1 mixture a  $^{119}\text{Sn}$  NMR signal ( $\delta^{119}\text{Sn} -100.1$ ,  $-30\text{ }^\circ\text{C}$ ) (in the expected range [7] for this type of surrounding of the tin atom with coordination number 4) is growing which is assigned to compound **3**.

The peculiar role of  $^{119}\text{Sn}$  NMR in this study must be emphasized. Neither  $^1\text{H}$  nor  $^{13}\text{C}$  NMR measurements, carried out parallel to the recording of  $^{119}\text{Sn}$  NMR spectra, gave any detailed information. Both  $^1\text{H}$  and  $^{13}\text{C}$  spectra showed broad resonances for the  $\text{NEt}_2$  groups, just indicative of dynamic processes which could not be resolved owing to small differences in  $^1\text{H}$  and  $^{13}\text{C}$  nuclear shielding. In contrast, the large difference in the  $^{119}\text{Sn}$  resonances enables processes which are too fast as compared to the  $^1\text{H}$  and  $^{13}\text{C}$  NMR time scale to be distinguished.

In general, reactions of tin(IV) halides with secondary amines do not afford aminotin derivatives [1, 10]. We have tried several secondary diamines in order to find out whether cyclic bis(amino)tin dichlorides can be prepared directly via HCl elimination. It turned out that reactions between tin(IV) chloride and  $N,N'$ -dialkylamino-1,2-diethanes (alkyl = Me, tert-butyl) in the presence of two equivalents of triethylamine did not give the desired product, whereas compound **6** is readily obtained if a mixture of  $N,N'$ -di-tert-butyl-1,3-diaminopropane/triethylamine (1:2) is used (eqn. (4)).



The compounds **1–6** were characterized by multinuclear NMR (see Table 1 and 'Experimental'). All NMR data indicate that the bis(amino)tin dichlorides **1**, **2**, **3**, **6** are monomers in solution. Although, we have not obtained suitable crystals of **6** for X-ray analysis as yet, a solid state  $^{119}\text{Sn}$  CP/MAS NMR spectrum (see Fig. 2) has been measured in order to glean information on the coordination number of the tin atom. The agreement between  $\delta^{119}\text{Sn}$  data for solution and solid state proves the absence of coordinative N–Sn bonds in the latter.

We have shown that there are various useful routes to bis(amino)tin dichlorides. In the case of bis(diethylamino)tin dichloride,  $^{119}\text{Sn}$  NMR proved ex-

tremely helpful in shedding some light on the reaction mechanism. Two complexes were identified in solution which must be regarded as model compounds for illustrating the  $\text{Et}_2\text{N}/\text{Cl}$  exchange. Finally, we found that the heterocyclic compound **6** is readily available, avoiding metallation and a multi-step synthesis. Therefore, it is expected that **6** becomes a useful starting material in the chemistry of bis(amino)tin chlorides.

## Experimental

All products and most starting materials are extremely sensitive to traces of moisture; carefully dried solvents and working under an atmosphere of dry nitrogen are necessary. The starting materials for compounds **1** [5], **2** [6] and **3** [13] were prepared according to literature procedures.  $N,N'$ -Di-tert-butyl-1,3-diaminopropane was obtained as described in ref. 6.

### Bis[bis(trimethylsilyl)amino]tin dichloride (**1**)

A solution of 2.2 g (5.0 mmol) of bis[bis(trimethylsilyl)amino]stannylene in 40 ml of hexane was cooled to  $-78\text{ }^\circ\text{C}$  and 1.3 g (5 mmol) of tin(IV) chloride were added dropwise with vigorous stirring. The orange colour of the solution faded and a colourless precipitate was formed. The mixture was kept for 12 h at room temperature, insoluble material ( $\text{SnCl}_2$ ) was filtered off and hexane was removed in vacuum. Compound **1** (2.6 g, 100%) was left as a colourless oil (purity  $>98\%$ , according to NMR spectra).

$^1\text{H}$  NMR (300 MHz, in  $\text{C}_6\text{D}_6$ ),  $\delta^1\text{H} = 0.29$  (s).

### 2,2-Dichloro-1,3-diethyl-4,4,5,5-tetramethyl-1,3,2,4,5-diazastannadisilacyclopentane (**2**)

Compound **2** was obtained in quantitative yield as a light yellow, oily liquid (purity  $>98\%$ , according to NMR spectra) from the dimeric cyclic stannylene, in the same way as described for **1**.

$^1\text{H}$  NMR (300 MHz, in  $\text{C}_6\text{D}_6$ ),  $\delta^1\text{H}$  [ $^J(^{119}\text{Sn}^1\text{H})$ ] = 0.10 (s) 12H, 3.05 (q) [128.0] 4H, 1.16 (t) 6H.

### Bis(diethylamino)tin dichloride (**3**)

A solution of 4.1 g (10 mmol) of tetrakis(diethylamino)tin in 30 ml of  $\text{CH}_2\text{Cl}_2$  was cooled to  $-78\text{ }^\circ\text{C}$  and a solution of 2.6 g (10 mmol) of tin(IV) chloride in 30 ml of  $\text{CH}_2\text{Cl}_2$  was added dropwise with vigorous stirring. A small amount of a colourless solid precipitated and an orange to brown colour developed. The solution was slowly warmed to room temperature and the progress of the reaction was monitored by  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{119}\text{Sn}$  NMR. After 4 h at room temperature,  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{119}\text{Sn}$  NMR spectra showed that the solution contained mainly ( $>90\%$ ) compound **3** and some other unidentified compounds. Attempts to isolate **3** led to

TABLE 1.  $^{13}\text{C}$ ,  $^{29}\text{Si}$ ,  $^{119}\text{Sn}$  NMR data<sup>a,b</sup> of the bis(amino)tin dichlorides 1–3 and 6

Compound	$\delta^{13}\text{C}$		$\delta^{29}\text{Si}$	$\delta^{119}\text{Sn}$
	(SiMe)	(NR)		
$[(\text{Me}_3\text{Si})_2\text{N}]_2\text{SnCl}_2$ (1)	5.5 <sup>c</sup> [18.0]		+9.7 [20.9]	-143.8
$[\text{Me}_2\text{SiN}(\text{Et})]_2\text{SnCl}_2$ (2)	0.1 <sup>d</sup> [22.9]	41.0, 21.7 [14.2][16.3]	-4.6 [100.4]	-100.2
$(\text{Et}_2\text{N})_2\text{SnCl}_2$ (3)		44.4, 16.4 [5.8][22.5]		-100.1 <sup>e</sup>
$\text{CH}_2[\text{CH}_2\text{N}(\text{tBu})]_2\text{SnCl}_2$ (6)		49.3, 33.8 [14.2][41.4] 57.2, 30.2 (tBu) [20.7][31.6]		-163.0 <sup>f</sup>

<sup>a</sup>In  $\text{C}_6\text{D}_6$  (10% vol./vol., at  $27 \pm 1$  °C), 3 in  $\text{CH}_2\text{Cl}_2/\text{CD}_2\text{Cl}_2$ ; coupling constants  $J(^{119}\text{Sn}^{13}\text{C})$ ,  $J(^{119}\text{Sn}^{29}\text{Si})$  in Hz ( $\pm 0.5$ ) are given in square brackets. <sup>b</sup>Chemical shifts are given with respect to external  $\text{Me}_4\text{Si}$  ( $\delta^{13}\text{C}_{\text{C}_6\text{D}_6} = 128.0$ ), ( $\delta^{29}\text{Si}$ ,  $\Xi(^{29}\text{Si}) = 19\,867\,184$  Hz) and external  $\text{Me}_4\text{Sn}$  ( $\delta^{119}\text{Sn}$ ,  $\Xi(^{119}\text{Sn}) = 37\,290\,665$  Hz). <sup>c</sup> $^1J(^{29}\text{Si}^{13}\text{C}) = 56.1$  Hz. <sup>d</sup> $^1J(^{29}\text{Si}^{13}\text{C}) = 49.0$  Hz. <sup>e</sup>At  $-30$  °C in  $\text{CD}_2\text{Cl}_2$ ;  $-90$  °C:  $\delta^{119}\text{Sn} = -93.2$ . <sup>f</sup> $\delta^{119}\text{Sn}$  (solid state) =  $-164 \pm 5$ .

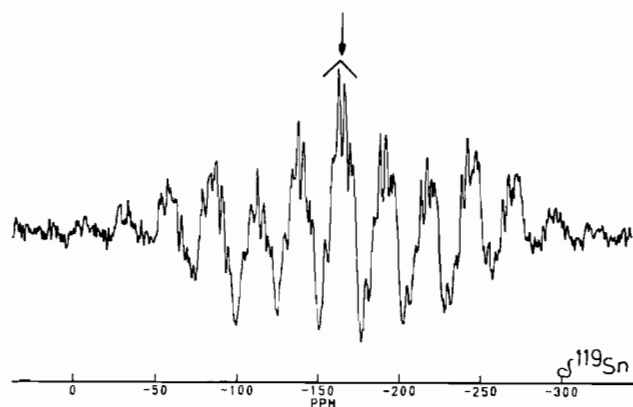


Fig. 2. 112.0 MHz solid state  $^{119}\text{Sn}$  CP/MAS NMR spectrum of compound 6 (936 scans, recycle delay 5 s, contact time 2 ms). The centre band (checked by different spinning speeds) representing the isotropic  $\delta^{119}\text{Sn}$  value ( $\delta = -164 \pm 5$ ; solid  $^1\text{Pr}_4\text{Sn}$  served as secondary external reference [11]) is indicated by an arrow; the spinning side bands indicate a chemical shift anisotropy of  $c. 400 \pm 50$  ppm. The base-line distortion is due to the experimental parameters which are required to record the broad signals. The broadening and splitting of the signals arise from the presence of two quadrupolar  $^{14}\text{N}$  and two quadrupolar  $^{35/37}\text{Cl}$  nuclei linked to tin [12].

decomposition.  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta^1\text{H}$  [ $J(^{119}\text{Sn}^1\text{H})$ ] = 3.12 (q) [75.6] 8H, 1.14 (t) 12H.

#### 1,3-Di-tert-butyl-2,2-dichloro-1,3,2-diazastannacyclohexane (6)

A mixture of 3.72 g (20 mmol) of *N,N'*-di-tert-butyl-1,3-diaminopropane and 5.52 ml (40 mmol) of triethylamine in 40 ml of hexane was stirred and cooled to  $-78$  °C. A solution of 2.36 ml (20 mmol) of tin(IV) chloride in 15 ml of hexane was added dropwise with constant stirring. After the addition, stirring was continued for 1 h at  $-78$  °C and until the mixture reached

room temperature. After filtration, all volatile material was removed *in vacuo*, leaving 6.35 g (85%) of a yellow solid which could be recrystallized from 10 ml of hexane or pentane at  $-30$  °C (m.p. 73 °C).

EI-MS (70 eV): 374  $M^+$ , 0%; 359  $M - \text{Me}^+$ , 50%; 98, 52%; 86, 100%; 57, 41%; 49, 52%.

$^1\text{H}$  NMR (300 MHz, in  $\text{C}_6\text{D}_6$ ),  $\delta^1\text{H}$  [ $^1J(^{119}\text{Sn}^1\text{H})$ ] = 2.86 (m) [120.0] 4H, 1.61 (m) 2H, 1.22 (s) 18H.

The NMR spectra of solutions have been recorded using Jeol FX 90 Q and Bruker AC 300 instruments, both equipped with multinuclear units (see Table 1 for details). A Bruker MSL 300 spectrometer served for recording the solid state  $^{119}\text{Sn}$  CP/MAS NMR spectrum (see Fig. 1 for details). Because of the sensitivity of compound 6 to traces of moisture, it was packed into an air-tight insert [14] which fitted exactly into the commercial  $\text{ZrO}_2$  rotors for the double-bearing probe-head.

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