### N-Silylaminotin Trichlorides. Synthesis and Characterisation by Multinuclear Magnetic Resonance Spectroscopy

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N-Silyl-aminotin trichlorides,  $R^1R^2N$ -SnCl<sub>3</sub> [ $R^1 = R^2 = SiMe_3$  (1a),  $R^1 = SiMe_3$ ,  $R^2 = {}^{t}Bu$  (1b),  $R^1 = SiMe_3$ ,  $R^2 = 9$ -borabicyclo[3.3.1]nonyl (1c),  $R^1R^2 = Me_2SiCH_2CH_2SiMe_2$  (1d)] were prepared by the reaction of tin tetrachloride with the respective bis(amino)plumbylenes, ( $R^1R^2N$ )<sub>2</sub>Pb 4. The analogous reactions with bis(amino)stannylenes, ( $R^1R^2N$ )<sub>2</sub>Sn 3, afforded only mixtures of the aminotin trichlorides 1 and bis(amino)tin dichlorides, ( $R^1R^2N$ )<sub>2</sub>SnCl<sub>2</sub> 2. The products were characterised by  ${}^1H$ ,  ${}^{11}B$ ,  ${}^{13}C$ ,  ${}^{15}N$ ,  ${}^{29}Si$  and  ${}^{119}Sn$  NMR spectroscopy, and the NMR data of 1 were compared with those of the corresponding N-silylamino(trimethyl)tin compounds 8.

#### Introduction

In contrast with organotin trichlorides [1, 2] aminotin trichlorides are virtually unknown [3]. In the case of sterically non-demanding amino groups this can be explained by fast exchange reactions which lead to equilibrated mixtures. However, if the amino nitrogen atom bears bulky substituents aminotin trichlorides should be accessible. In addition, the presence of an N-silyl group may help to lower the basic character of the amino groups, and by this the tendency for exchange reactions should be reduced. Aminotin trichlorides should be attractive starting materials for further transformations. Therefore, we have set out to prepare N-silylaminotin trichlorides by various methods. We have focused our attempts on the ligands **a** - **d** as representative examples. The characterisation of these new tin trichlorides in solution can be achieved by multinuclear magnetic resonance spectroscopy, since the presence of magnetically active nuclei such as <sup>1</sup>H, <sup>11</sup>B, <sup>13</sup>C, <sup>14</sup>N, <sup>15</sup>N, <sup>29</sup>Si, <sup>117</sup>Sn, <sup>119</sup>Sn provides fairly complete indirect structural data.

#### **Results and Discussion**

#### Synthesis of the aminotin trichlorides

One logical approach to the synthesis of aminotin trichlorides 1 involves the reaction of the lithium amides Li(a) - Li(d) with tin tetrachloride,  $SnCl_4$ , in a 1:1 molar ratio or with an excess of  $SnCl_4$ 



(Scheme 1). However, this procedure afforded only mixtures containing the desired products 1 along with the respective bis(amino)tin dichlorides 2 (at least 20 %) which could not be separated. Attempts to heat mixtures of 1 and 2 in the presence of an excess of SnCl<sub>4</sub> led mainly to decomposition. Therefore, it proved necessary to look for another amide transfer reagent. Potential candidates are the respective bis(amino)stannylenes 3. It is known that stannylenes of type 3 react with SnCl<sub>4</sub> (1:1) to give bis(amino)tin dichlorides and SnCl<sub>2</sub> [3, 4]. We carried out these reactions using a large excess of SnCl<sub>4</sub>; again mixtures of the aminotin trichlorides 1 and bis(amino)tin dichlorides 2 were formed. In the case of the synthesis of N-silylaminotitanium trichlorides, we showed that monomeric bis(amino)plumbylenes 4 are excellent amide transfer reagents [5]. Indeed, the analogous procedure works well also with SnCl<sub>4</sub>, and the aminotin trichlorides **1a** - **d** were obtained in high yield and high purity (Scheme 1).

In the case of the reaction of cyclic bis-(amino)stannylenes with  $SnCl_4$  one observes just the corresponding cyclic bis(amino)tin dichlo-

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Scheme 2.

rides [6]. By monitoring the reaction of the cyclic bis(amino)plumbylene **5** [7] with an excess of SnCl<sub>4</sub> using NMR spectroscopy, it proved possible to detect the non-cyclic intermediate **6** prior to ring closure to the known tin dichloride **7** and elimination of SnCl<sub>4</sub> (Scheme 2).

# *NMR* spectroscopic study of *N*-silylaminotin trichlorides

Most NMR data of **1a** - **d** and **6** are listed in Table 1 (<sup>1</sup>H NMR data are given in the experimental section). In contrast with the <sup>119</sup>Sn NMR signals which are broadened as a result of scalar <sup>119</sup>Sn-<sup>35/37</sup>Cl and <sup>119</sup>Sn-<sup>14</sup>N coupling (scalar relaxation of the second kind [8]), the <sup>15</sup>N and <sup>29</sup>Si NMR signals are extremely sharp. By using conditions close to those described for ultra-high resolution [9,10] the signal-to-noise ratio is sufficient to observe many types of weak satellite signals both in <sup>15</sup>N and <sup>29</sup>Si spectra (see Figs. 1 and 2).

### Signs of coupling constants ${}^{1}J({}^{119}Sn, {}^{15}N)$

In the case of the compounds **1**, the sign of the coupling constants  ${}^{1}J({}^{119}\text{Sn}, {}^{15}\text{N})$  cannot be determined by straightforward one- (1D) or two-dimensional (2D) double resonance experiments owing to lack of scalar  ${}^{119}\text{Sn}{}^{-1}\text{H}$  couplings and suitable polarisation transfer from  ${}^{1}\text{H}$  to tin nuclei. Therefore, the suggestion of a positive or nega-



Fig. 1. 99.4 MHz <sup>29</sup>Si NMR spectrum (INEPT, refocused with <sup>1</sup>H decoupling [21]) of  $(Me_3Si)_2N$ -SnCl<sub>3</sub> **1a** (in C<sub>6</sub>D<sub>6</sub>; 23 ± 1 °C; result of 64 transients; acquisition time 12 s; repetition time 8 s; optimised low power CPD <sup>1</sup>H decoupling; spectrometer time  $\approx 15$  min). The <sup>13</sup>C satellites are marked by open circles and the <sup>117/119</sup>Sn satellites by asterisks. The <sup>15</sup>N satellites (isotope-induced chemical shift  ${}^{1}\Delta^{14/15}N({}^{29}Si) = -13.0$  ppb) are marked by arrows.

tive sign must be based on comparison with related data. A negative sign of  ${}^{1}J({}^{119}Sn, {}^{15}N)$  has been determined experimentally for numerous trimethylstannylamines [11, 12], and this is also true for 8a, d using the same type of experiments. There are also cases where the magnitude of this coupling constant is close to zero, e.g. for 8b, where  ${}^{1}J({}^{119}Sn, {}^{15}N)$  can be either positive or negative. If the Sn-methyl groups are replaced by more electronegative substituents such as chlorine atoms, it is expected that negative contributions to the Fermi contact term become less significant and that a positive sign of  $J(^{119}\text{Sn},^{15}\text{N})$  will be the result. This is clearly shown by the data in Table 1. The amino group d causes less negative contributions to the magnitude of  ${}^{1}J({}^{119}Sn, {}^{15}N)$  in **8d** (-38.6 Hz) as compared with the bis(trimethylsilyl)amino group a in 8a (-51.6 Hz). Therefore, we find more positive contributions to  ${}^{1}J({}^{119}Sn, {}^{15}N)$  in 1d (+75.4) than in 1a (+39.3). This trend is further confirmed by the data for **8b**  $[{}^{1}J({}^{119}\text{Sn},{}^{15}\text{N})$  is small, 5.4 Hz, and can be of either sign] and 1b, where a large, most likely positive value (+90.4 Hz) of  ${}^{1}J({}^{119}Sn, {}^{15}N)$  is observed for the latter.

In the case of the trimethyltin derivatives, the magnitude of  ${}^{1}J({}^{119}\text{Sn},{}^{15}\text{N})$  can also readily be

	(Me <sub>3</sub> Si) <sub>3</sub> N	$(Me_3Si)_2NSnMe_3$	$Me_3SiN(SnMe_3)_2$	(Me <sub>3</sub> Si) <sub>2</sub> N <sup>t</sup> Bu	Me <sub>3</sub> Si( <sup>t</sup> Bu)NSnMe <sub>3</sub>
$\frac{I_{J}(^{29}\text{Si},^{15}\text{N})}{S^{29}\text{Si}}$ [Hz]	7.6	8.0	6.5	11.9	11.4
$\delta^{15}$ N	+1.8 -345.8	-356.6	+5.8 -375.4	-326.6	-1.5 -324.1



Fig. 2. 50.7 MHz <sup>15</sup>N NMR spectrum (INEPT refocused with <sup>1</sup>H decoupling [21]) of a mixture containing (Me<sub>3</sub>Si)<sub>2</sub>N-SnCl<sub>3</sub> **1a**, and [(Me<sub>3</sub>Si)<sub>2</sub>N]<sub>2</sub>SnCl<sub>2</sub> **2a** (in C<sub>6</sub>D<sub>6</sub>; 23 ± 1 °C; result of 1056 transients; acquisition time 8 s; repetition time 5 s; optimised low power CPD <sup>1</sup>H decoupling; spectrometer time  $\approx$  4 h). The <sup>29</sup>Si and <sup>117/119</sup>Sn satellites are marked by arrows and asterisks, respectively [data for **2a**:  $\delta^{15}$ N = -317.4; <sup>1</sup>J(<sup>29</sup>Si, <sup>15</sup>N) = 4.5 Hz; <sup>1</sup>J(<sup>119</sup>Sn, <sup>15</sup>N) = 39.6 Hz].

determined from the sharp <sup>15</sup>N satellites in the <sup>119</sup>Sn NMR spectra by using HEED INEPT experiments [13] (Fig. 3). This is not possible for the compounds **1** owing to broad parent and satellite signals (vide supra).

### Coupling constants <sup>1</sup>J(<sup>29</sup>Si, <sup>15</sup>N)

There is a considerable data set available for coupling constants  ${}^{1}J({}^{29}\text{Si},{}^{15}\text{N})$  of N-silylamines [14, 15], and it appears that all known values  ${}^{1}J({}^{29}\text{Si},{}^{15}\text{N})$  possess a positive sign, including the compounds **1**, where the sign was determined experimentally for **1a**, using a 2D  ${}^{15}\text{N}/{}^{1}\text{H}$  HETCOR experiments, as described for tris(trimethylsilyl)amine [12]. The comparison of  ${}^{1}J({}^{29}\text{Si},{}^{15}\text{N})$  in **1a**, **b**, **d** and **8a**, **b**, **d** shows the somewhat surprising trend that the



Fig. 3 186.5 MHz <sup>119</sup>Sn NMR spectrum (INEPT-HEED, refocused with <sup>1</sup>H decoupling [13]) of **8d** (in C<sub>6</sub>D<sub>6</sub>; 23  $\pm$  1 °C; result of 256 transients; acquisition time 8 s; repetition time 5 s; optimised low power CPD <sup>1</sup>H decoupling; spectrometer time  $\approx$  1 h). The sharp <sup>15</sup>N satellites (compare with the line width of the central signal) are indicated, and the isotope-induced chemical shift <sup>1</sup> $\Delta$ <sup>14/15</sup>N(<sup>119</sup>Sn) is obvious by inspection. The absolute negative sign of <sup>1</sup>*J*(<sup>119</sup>Sn, <sup>15</sup>N) was determined by another experiment (2D <sup>15</sup>N/<sup>1</sup>H HETCOR based on <sup>3</sup>*J*(<sup>15</sup>N, <sup>1</sup>H<sub>SnMe</sub>) [12a]).

magnitude of  ${}^{1}J({}^{29}\text{Si},{}^{15}\text{N})$  is significantly smaller for the N-silvlaminotin trichlorides 1 with respect to their trimethyltin analogues 8. Taking into account only the group electronegativity of the Me<sub>3</sub>Sn and the Cl<sub>3</sub>Sn units, one would have expected just the opposite trend. Therefore, there must be additional effects pertinent to the nature of the N-Sn bond in 1 which give rise to negative contributions to the Fermi contact term. It is suggested that such negative contributions arise from the presence of the lone pair of electrons at the nitrogen atom. As can be seen from the following examples (data taken from [12, 16, 17]), the replacement of a Me<sub>3</sub>Si by a Me<sub>3</sub>Sn group induces rather small changes in the magnitude of  ${}^{1}J({}^{29}\text{Si},{}^{15}\text{N})$  for the remaining  ${}^{29}\text{Si}$ nucleus which means that the nature of the nitrogen lone pair of electrons is not much affected, in contrast to the situation when the Cl<sub>3</sub>Sn group is present.

No	$\delta^{13}\mathbf{C}$		$\delta^{15} \mathbf{N}$	$\delta^{29}$ Si	$\delta^{119}$ Sn
	SIMe	Other			
1a	4.8		-313.6	12.7 <sup>[c,d]</sup>	-142.1
	[20.4] (56.4)		[39.3] (3.7)	[29.0]	
1b	5.6	59.4, 35.2 (N <sup><i>t</i></sup> Bu)	-269.2 <sup>[e]</sup>	9.4 <sup>[f]</sup>	-159.0
( )	[15.9] (56.6)	[25.1] [41.5] (1.9)	[90.6] (6.4)	[17.1]	
1c <sup>[g]</sup>	4.0	30.2 (broad; BCH)	n.m.	14.3	-175.8
	[] (57.2)	33.5 (CH-CH <sub>2</sub> )		[18.8]	
		22.8 (-CH <sub>2</sub> -)			
1d	2.1	9.2 (SiCH <sub>2</sub> )	-316.3	23.6	-97.3
	[< 3] (57.0)	[66.4] (56.7)	[75.4] (4.0)	[<1]	
6	5.7	59.8, 31.3 (N <sup>t</sup> Bu)	n.m.	7.4	-148.7
8a	5.7	-0.8 (SnMe <sub>3</sub> )	-356.6	2.7	55.3
	[8.7] (55.1)	[387.0]	[-51.1] (8.0)	[6.6]	
8b	6.8	1.2 (SnMe <sub>3</sub> )	-324.1	-1.5	30.8
(1-1	[6.9] (55.2)	$56.3, 35.9 (N^tBu)$	[5.4](11.4)	[20.0] &	[7.0] [18.7]
$\mathbf{8c}^{[n]}$	5.0	-0.8 (SnMe <sub>3</sub> )	$-281 (\delta^{14}N)$	4.6	39.9
	[381.0]	international and and an one	[13.2]		
		30.5 (broad) (BCH)			
		$33.9 (CH-CH_2)$			
		23.4 (-CH <sub>2</sub> -)	<b>1</b> :1		
8d	3.2	-4.4 (SnMe <sub>3</sub> )	-355.4	15.7	53.0
	[< 3] (53.2)	10.5 (SiCH <sub>2</sub> )	[-38.6] (7.7)	[<1]	
		[18.5] (56.2)			

Table 1. <sup>13</sup>C, <sup>15</sup>N, <sup>29</sup>Si and <sup>119</sup>Sn NMR data<sup>[a,b]</sup> of the N-silyl-aminotin trichlorides **1a-d** and **6**, and of corresponding trimethyltin derivatives **8a-d**.

[a] Coupling constants  $J({}^{29}\text{Si}, {}^{13}\text{C})$ and  $J({}^{29}\text{Si}, {}^{15}\text{N})$  are given in parentheses (± 0.2 Hz), and  $J({}^{119}\text{Sn}, {}^{13}\text{C})$ ,  $J({}^{119}\text{Sn}, {}^{15}\text{N})$ , and  $J({}^{119}\text{Sn}, {}^{29}\text{Si})$  in brackets (± 0.2 Hz); [b] isotope-induced chemical shifts are given in ppb; a negative sign denotes a shift of the resonance signal of the heavy isotopomer to lower frequencies; [c]  ${}^{1}\Delta^{14/15}\text{N}({}^{29}\text{Si}) = -13.0$  ppb; [d]  ${}^{1}\Delta^{12/13}\text{C}({}^{29}\text{Si}) = -1.4$  ppb; [e]  ${}^{1}\Delta^{12/13}\text{C}({}^{29}\text{Si}) = -1.4$  ppb; [f]  ${}^{1}\Delta^{12/13}\text{C}({}^{29}\text{Si}) = -1.4$  ppb; [g]  $\delta^{11}\text{B} = 60.6$ ; [h]  $\delta^{11}\text{B} = 57.2$ ; [i]  ${}^{1}\Delta^{14/15}\text{N}({}^{119}\text{Sn}) = -40.0$  ppb.

This can be interpreted by the assumption that the Cl<sub>3</sub>Sn group causes an increase in N-Si multiple bonding (and) or N-Sn multiple bonding sets in. Therefore, nitrogen magnetic shielding should be reduced owing to increased delocalisation of the nitrogen lone pair of electrons. Indeed, the <sup>15</sup>N resonance signals are shifted to higher frequencies by 43.0, 54.9 and 39.1 ppm for the pairs 8a / 1a, 8b / 1b, and 8d /1d, respectively. Interestingly, the parallel trend is found for the magnitude of the coupling constants  ${}^{1}J({}^{29}\text{Si},{}^{15}\text{N})$  which becomes smaller by 4.3, 5.0 and 3.7 Hz for the same pairs of compounds. The deshielding of the <sup>29</sup>Si nuclei in the N-silvlaminotin trichlorides **1** is also noteworthy: again the same trend emerges, now for all pairs 8/1: <sup>29</sup>Si nuclear magnetic deshielding by 10.0, 10.9, 9.7 and 7.9 ppm.

#### Experimental

Necessary precautions were observed to exclude oxygen and moisture during the synthesis and handling of all compounds. Starting materials such as the N-silylamines **a**-H, **b**-H, **d**-H, SnCl<sub>4</sub>, SnCl<sub>2</sub>, PbCl<sub>2</sub>, and BuLi in hexane (1.6 M) were commercial products and used without further purification. The N-silylamine **c**-H [18], the stannylenes **3a**, **3b** [19], **3c** [20], the plumbylenes **4a**, **4b** [19], **4c** [20], and the cyclic plumbylene **5** [7] were prepared as described.

All NMR spectra were recorded on Bruker ARX 250, AC 300 or DRX 500 spectrometers, equipped with multinuclear units and accessories for measurements at variable temperature. Chemical shifts are given with respect to Me<sub>4</sub>Si [ $\delta^{1}$ H(CHCl<sub>3</sub>/CDCl<sub>3</sub>) = 7.24, (C<sub>6</sub>D<sub>5</sub>CD<sub>2</sub>H) = 2.03;  $\delta^{13}$ C (CDCl<sub>3</sub>) = 77.0, (C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub>) = 20.4;  $\delta^{29}$ Si = 0 with  $\Xi$ <sup>(29</sup>Si) = 19.867184 MHz], BF<sub>3</sub>-OEt<sub>2</sub> [ $\delta$ <sup>11</sup>B = 0 with  $\Xi(^{11}B) = 32.083971 \text{ MHz}$ , neat MeNO<sub>2</sub>.[ $\delta^{14}N = 0$ with  $\Xi(^{14}N) = 7.226455$  MHz;  $\delta^{15}N = 0$  with  $\Xi(^{15}N) =$ 10.136767 MHz], H<sub>3</sub>PO<sub>4</sub>, 85% aq. for  $\delta^{31}P = 0$ , Me<sub>4</sub>Sn  $[\delta^{119}\text{Sn} = 0 \text{ with } \Xi^{(119}\text{Sn}) = 37.290665 \text{ MHz}], \text{ and } \text{Me}_4\text{Pb}$  $\delta^{207}$ Pb = 0 with  $\Xi(^{207}$ Pb) = 20.9205977 MHz]. Polarisation transfer experiments (INEPT, refocused with <sup>1</sup>H decoupling [21]) for recording the <sup>15</sup>N NMR spectra were optimised for the small long range coupling constants <sup>3J</sup> (<sup>15</sup>N,<sup>1</sup>H) either for Me<sub>3</sub>Si groups (ca. 1.8 Hz) or N<sup>t</sup>Bu groups (ca. 2.8 Hz). In the case of the boron compounds 1c and 8c, this technique cannot be applied since most of the <sup>15</sup>N magnetisation is lost during the pulse sequence owing to efficient scalar relaxation of the second kind [22, 8] (partially relaxed scalar <sup>15</sup>N-<sup>11</sup>B coupling).

#### Preparation of the stannylene 3d and the plumbylene 4d

A suspension of the freshly prepared amide Li(d) (300 mmol) in hexane/ether (1:1; 100 ml) was cooled to -78 °C, and SnCl<sub>2</sub> or PbCl<sub>2</sub> (150 mmol) was added in several portions while the mixture was kept stirring. After warming to room temperature, the mixture was stirred for another 30 min.; then the solvents were re-

moved in vacuo, and hexane (100 ml) was added to the residue. Insoluble material was filtered off, and hexane was removed in vacuo. The stannylene 3d was obtained as a dark-yellow, waxy solid (83%), and the plumbylene 4d as a yellow solid (88%), which liquefies at room temperature. **3d**: <sup>1</sup>H NMR (250.1 MHz; 25 °C; C<sub>6</sub>D<sub>6</sub>):  $\delta^{1}$ H = 0.27 (s, 24H, MeSi), 0.80 (s, 8H, SiCH<sub>2</sub>); <sup>13</sup>C NMR (62.8 MHz; 25 °C, C<sub>6</sub>D<sub>6</sub>):  $\delta^{13}$ C = 4.0 (SiMe), 11.4 (SiCH<sub>2</sub>); <sup>14</sup>N NMR (18.0 MHz; 25 °C; C<sub>6</sub>D<sub>6</sub>):  $\delta^{14}$ N – 237 ± 2; <sup>29</sup>Si NMR (49.7 MHz; 25 °C; C<sub>6</sub>D<sub>6</sub>):  $\delta^{29}$ Si = 13.1 [< 10]; <sup>119</sup>Sn NMR (93.3 MHz; 25 °C;  $C_6D_6$ ):  $\delta^{119}$ Sn = 798.2. 4d: <sup>1</sup>H NMR (250.1 MHz; 25 °C; C<sub>6</sub>D<sub>6</sub>):  $\delta^{1}$ H = 0.19 (s, 24H, MeSi), 0.82 (s, 8H, SiCH<sub>2</sub>); <sup>13</sup>C NMR (62.8 MHz; 25 °C, C<sub>6</sub>D<sub>6</sub>):  $\delta^{13}$ C = 3.8 (SiMe), 14.1 (SiCH<sub>2</sub>); <sup>14</sup>N NMR (18.0 MHz; 25 °C; C<sub>6</sub>D<sub>6</sub>): δ<sup>14</sup>N –185  $\pm$  2; <sup>29</sup>Si NMR (49.7 MHz; 25 °C; C<sub>6</sub>D<sub>6</sub>):  $\delta^{29}$ Si = 11.4  $[< 10]; {}^{207}\text{Pb} \text{ NMR} (52.3 \text{ MHz}; 25 \,^{\circ}\text{C}; \text{C}_6\text{D}_6): \delta^{207}\text{Pb} =$ 4962.

## Preparation of the N-silylaminotin trichlorides 1 via the plumbylenes 4

The plumbylenes 4a - 4d, respectively (5 mmol) were dissolved in pentane (25 ml) and added dropwise to a solution of SnCl<sub>4</sub> (2.6 g; 10 mmol) in pentane (10 ml) at 0  $^{\circ}$ C. The loss of the yellow colour of the plumbylene is accompanied by the precipitation of a colourless solid (PbCl<sub>2</sub>). The mixtures were allowed to warm to room temperature, and kept stirring for another 30 min. After filtration the solvent was removed in vacuo, the N-silvlaminotin trichlorides 1 were left as colourless, moisture-sensitive, waxy solids in 83-85% yield. 1a: m. p. 78 °C; <sup>1</sup>H NMR (250.1 MHz; 25 °C; C<sub>6</sub>D<sub>6</sub>):  $\delta^1 H = 0.19$  (s, 9H, MeSi). **1b**: m. p. 65 °C; <sup>1</sup>H NMR (250.1 MHz; 25 °C;  $C_6D_6$ );  $\delta^{1}$ H = 0.24 (s, 9H, MeSi); 1.21 (s, 9H, MeC). 1c: m. p. 59 °C; <sup>1</sup>H NMR (250.1 MHz; 25 °C; C<sub>6</sub>D<sub>6</sub>):  $\delta^{1}$ H = 0.19 (s, 9H, MeSi); 1.27 (m, broad, 2H, BCH), 1.41-1.80 (m, 12H, CH<sub>2</sub>CB/CH<sub>2</sub>CCB). 1d: m. p. 62 °C; <sup>1</sup>H NMR (250.1 MHz; 25 °C; C  $_{6}D_{6}$ ):  $\delta^{1}H = 0.18$  (s, 12H, MeSi; 0.80 (s,4H, CH<sub>2</sub>).

#### Reaction of an excess of plumbylenes 4 with SnCl<sub>4</sub>

Tin tetrachloride (0.26 to 1.3 g; 1 to 5 mmol) in pentane (20 ml) were added to a solution of the plumbylenes **4a** - **4d**, respectively (5 mmol) in pentane (10 ml) at 0 °C. After filtration the pentane was removed in vacuo and a mixture of the compounds **1** and **2** in 1:1 to 4:1 ratio remeined (depending on the amount of SnCl<sub>4</sub>), which could not be separated, neither by crystallisaton nor by distillation or sublimation (decomposition).

#### Reactions of stannylenes 3 with SnCl<sub>4</sub> in excess

The stannylenes **3a** - **3d**, respectively (5 mmol), were dissolved in pentane (10 ml) and the solution was cooled

to 0 °C. Then SnCl<sub>4</sub> (10, 20 or 50 mmol) dissolved in pentane (20 ml) was added dropwise to the stirred solutions. The solutions became colourless, and after warming to room temperature a white precipitate (SnCl<sub>2</sub>) was filtered off. The pentane and the excess of SnCl<sub>4</sub> were removed *in vacuo* to leave yellowish waxy solids which consisted of the compounds **1** and **2** in 1:1 to 4:1 ratio, depending on the amount of SnCl<sub>4</sub> used. These mixtures could not be separated by distillation or sublimation.

## Reactions of lithium amides Li(a) - Li(d) with $SnCl_4$ in 1:1 or smaller molar ratio

The lithium amides Li(a) - Li(d) (1 mmol) a suspensions in pentane (10 ml) were added to a solution of SnCl<sub>4</sub> (0.26 - 1.3 g; 1 - 5 mmol) in pentane (10 ml) at 0 °C. After filtration, all volatile material was removed in vacuo, leaving again a mixture of the compounds 1 and 2 in 1:2 to 4:1 ratio.

#### Reaction of the plumbylene 5 with SnCl<sub>4</sub>

A small amount (*ca.* 10 mg) of **5** was dissolved in  $C_6D_6$ in an NMR tube and cooled to 0 °C in an ice bath. Then SnCl<sub>4</sub> was injected through a syringe, and the mixture was examined by NMR: the compounds **6** and **7** (ratio  $\approx 2 : 1$ ) could be detected. After removing all volatile material in vacuum, the residue was again dissolved in  $C_6D_6$ . Compound **6** was still present in the mixture, together with **7**. After 5 h, all of **6** was converted into **7** by elimination of SnCl<sub>4</sub> which could be detected by <sup>119</sup>Sn NMR and was also found as one of the volatile materials present in this solution.

## Preparation of the trimethyltin amides 8 via salt elimination

The respective lithium amide Li(a) - Li(d) (1 mmol) was suspended in hexane (15 ml), and the suspension was cooled to -78 °C. Then Me<sub>3</sub>SnCl (1.0 mmol; 0.20 g) was added in several portions under stirring. The mixture was allowed to warm to room temperature and insoluble material was filtered off. After removing the solvent in vacuo, the compounds 8 were obtained as colourless oils (88-95% yield) which partially solidified to waxy solids. 8a: <sup>1</sup>H NMR (250.1 MHz; 25 °C;  $C_6D_6$ ):  $\delta^1H = 0.17$  (s, 18H, MeSi), 0.24 (s 9H, MeSn). 8b: <sup>1</sup>H NMR (250.1 MHz; 25 °C; C<sub>6</sub>D<sub>6</sub>):  $\delta^{1}$ H = 0.12 (s, 9H, MeSi), 0.29 (s, 9H, MeSn), 1.24 (s, 9H, MeC). 8c:<sup>1</sup>H NMR (250.1 MHz; 25 °C; C<sub>6</sub>D<sub>6</sub>):  $\delta^1$ H = 0.16 (s, 9H, MeSi), 0.25 (s, 9H, MeSn), 1.30 (m, broad, 2H, BCH), 1.35-1.78 (m, 12H, CH<sub>2</sub>CB/CH<sub>2</sub>CCB). 8d: <sup>1</sup>H NMR (250.1 MHz; 25 °C;  $C_6D_6$ ):  $\delta^1H = 0.13$ , (12H, MeSi), 0.19 (s, 9H, MeSn), 0.82 (s, 4H, CH<sub>2</sub>Si).

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