# **ORGANOMETALLICS**

# Stable Divalent Triarylstannates R<sub>3</sub>SnLi Derived from 2-[(Dimethylamino)methyl]phenyllithium and SnCl<sub>2</sub> or R<sub>2</sub>Sn

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**Supporting Information** 

**ABSTRACT:** The triarylstannate lithium compound  $[\{\kappa^1-C-(2-Me_2NCH_2C_6H_4)_2\}\{\kappa^2-C, N-(2-Me_2NCH_2C_6H_4)\}$ SnLi-(THF)<sub>2</sub>] (**3a**) was obtained in 63% yield from the reaction of 2-Me<sub>2</sub>NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Li (**1**) with SnCl<sub>2</sub> in THF. Quantitative formation of **3a** was also observed on reacting **1** with  $[\kappa^2-C, N-(2-Me_2NCH_2C_6H_4)_2Sn]$  (**2**). Removal of one THF molecule occurred when **3a** was kept in vacuo; this process afforded  $[\{\kappa^1-C-(2-Me_2NCH_2C_6H_4)\}\{\kappa^2-C, N-(2-Me_2NCH_2C_6H_4)_2\}$ -SnLi(THF)<sub>2</sub>] (**3b**). Also, THF-free (2-Me\_2NCH\_2C\_6H\_4)<sub>2</sub>}-SnLi(THF)<sub>2</sub>] (**3b**). Also, THF-free (2-Me\_2NCH\_2C\_6H\_4)<sub>3</sub>SnLi (**3c**) is likewise accessible. In the solid state (X-ray) both **3a** and **3b** are monomeric; notable structural features are the Sn– Li distances (2.860(6) and 2.72(2) Å, respectively) and the



distortion of the tetrahedral geometry at Sn in the direction of a trigonal pyramidal one. In **3a**, one of the 2-Me<sub>2</sub>NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub> anions is C-bonded to Sn, while N-coordination occurs to Li; in **3b**, two of the three 2-Me<sub>2</sub>NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub> anions are  $\kappa^2$ -C<sub>1</sub>N bonded. <sup>1</sup>H, <sup>13</sup>C, <sup>119</sup>Sn, and <sup>7</sup>Li NMR spectroscopic studies of the species **3** in *toluene* showed that both **3a** and **3b** are monomeric in solution; at temperatures below 253 K, via both the <sup>119</sup>Sn and <sup>7</sup>Li NMR spectra (toluene-*d*<sub>8</sub>), the <sup>119</sup>Sn–<sup>7</sup>Li coupling (289 Hz) is nicely resolved. The exchange of aryl groupings (vide infra) as well as between coordinated and free-NMe<sub>2</sub> substituents remains fast on the NMR time scale at 183 K. 2D <sup>1</sup>H–<sup>1</sup>H EXSY spectroscopy confirmed that the 2-Me<sub>2</sub>NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub> groups present in stannate **3b** and bisaryltin(II) **2** undergo chemical exchange. The 2D <sup>7</sup>Li–<sup>7</sup>Li EXSY spectrum points to the occurrence of chemical exchange of the lithium atoms of stannate **3b** and aryllithium **1**.

# INTRODUCTION

Stannyl metal reagents of the type " $R_3SnM$ " (M = Li, Na, K) have been known for many years and have an important role in modern organic chemistry.<sup>1</sup> In general, the R-grouping of the stannyl reagent is activated to react with organic electrophiles such as ketones, epoxides, or acid chlorides.<sup>2</sup>

In 1972 Lappert and co-workers reported the use of triorganostannate alkali metal complexes,  $[R_3Sn]M$ , as ligand transfer reagents for the synthesis of  $[Zr(\eta^5-C_5H_5)_2(Cl)-(SnPh_3)]_2^3$  and  $[Yb{Sn(CH_2Bu^t)_3}_2(THF)]$ .<sup>4</sup> The structural features of the triorganostannate anions  $[SnR_3]^-$  (R = Ph or CH<sub>2</sub>Bu<sup>t</sup>) in the respective transfer reagents were studied in more detail by elucidating the structures of both  $[Li(SnPh_3)-(pmdeta)]^5$  and  $[K{Sn(CH_2Bu^t)_3}(\eta^6-C_6H_5Me)_3]$ ,<sup>6</sup> respectively. These stannate compounds have Sn(II)–alkali metal close contacts as a common structural feature (Li–Sn 2.871(7) Å and K–Sn 3.548(3) Å).

The earliest report of a triorganostannate,  $Me_3SnNa$ , dates back to 1922.<sup>7</sup> Its synthesis involved the reaction of  $Me_3SnBr$ with metallic sodium in liquid ammonia.<sup>8</sup> Later, various alternate routes have proven successful; see Scheme 1. These protocols involve either the reduction of a triorganotin halide (i)<sup>9</sup> or a hexaorganoditin compound (iii)<sup>10,11</sup> with an alkali metal reagent. Alternate reactions involve reduction of either a

#### Scheme 1



triorganostannane with an organoalkali metal compound (ii)<sup>11</sup> or reaction of a diorganotin compound with an organoalkali metal derivative (iv).<sup>13,14</sup>

It is obvious that the latter route is restricted to diorganotin(II) compounds that are stabilized toward oligomerization (typically through Sn–Sn bond formation) either by intramolecular coordination,<sup>15</sup> by groups providing steric constraints near the tin center,<sup>16</sup> or by multiatom bonding of the organic groups to tin, as, for example, in Cp<sub>2</sub>Sn.<sup>17</sup>

In related "ate" chemistry, the formally monoanionic,  $\kappa^2$ -C,N-chelating [2-Me<sub>2</sub>NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>]<sup>-</sup> ligand has proven to be a

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Received: December 4, 2014 Published: April 1, 2015 valuable building block for the stabilization of neutral and ionic organocuprates,<sup>18</sup> organoaurates,<sup>19</sup> and organozincates.<sup>20</sup> In the latter series of "ate" compounds, R<sub>m-n</sub>M<sup>n</sup>Li, the 2- $Me_2NCH_2C_6H_4$  anion (abbreviated as R), shows a versatile Cipso-metal bonding behavior, while the amine ligand, depending on the nature of the solvent, stabilizes either the solvent-separated ion pair or the close contact pair state of the "ate" compound. In the present study, we report on the direct synthesis and structural characterization in the solid state of the arylstannate(II) compound  $[{\kappa^1-C-(2-Me_2NCH_2C_6H_4)_2}]{\kappa^2 C_{1}N-(2-Me_{2}NCH_{2}C_{6}H_{4})$  SnLi(THF)<sub>2</sub> from the reaction of the corresponding organolithium compound with tin dichloride. Additional intramolecular Li-N coordination with replacement of coordinated THF is observed, affording  $[\{\kappa^1, \ldots, \kappa^n\}$  $C-(2-Me_2NCH_2C_6H_4)$  { $\kappa^2-C_1N-(2-Me_2NCH_2C_6H_4)_2$  } SnLi-(THF)]. Interestingly, NMR studies showed that these orthochelated arylstannates exist in equilibrium with the neutral bis(aryl)tin(II) and aryllithium species (see iv in Scheme 1).

#### RESULTS AND DISCUSSION

**Synthesis Aspects.** The reaction of the diaryltin(II) compound  $(2-Me_2NCH_2C_6H_4)_2Sn$  (2) with one equivalent of  $2-Me_2NCH_2C_6H_4Li$  (1) in THF as solvent (see Scheme 2)





afforded (after workup; see Experimental Section) the pure bis-THF stannate adduct  $(2-Me_2NCH_2C_6H_4)_3SnLi(THF)_2$  (3a) as a yellow, crystalline solid. The reaction of three equivalents of  $2-Me_2NCH_2C_6H_4Li$  (1) with one equivalent of  $SnCl_2$  in THF involves a more direct route toward 3a (see Scheme 2). It is obvious that during the latter reaction 2 is likely formed as an intermediate.

One of the THF molecules in **3a** is observed to be weakly bound. When pure **3a** is kept in vacuo for 1 h, the crystalline material converts into a pale yellow, amorphous powder. The <sup>1</sup>H NMR spectrum (in toluene- $d_8$ ) of this powder confirmed the formation of  $(2-Me_2NCH_2C_6H_4)_3SnLi(THF)$  (**3b**), i.e., the loss of one THF molecule. Pure crystalline **3b** can be obtained by recrystallization from *n*-hexane (see Experimental Section). When a solution of **3b** (or **3a**) in *n*-hexane is evaporated at 50 °C to dryness at reduced pressure, a yellow, viscous material is obtained, which according to its <sup>1</sup>H NMR spectrum (toluene $d_8$ ) is devoid of any THF (see Experimental Section). This material we ascribe to [ $(2-Me_2NCH_2C_6H_4)_3SnLi$ ] (**3c**). Compounds **3a**, **3b**, and **3c** were all thereafter fully characterized by <sup>1</sup>H, <sup>13</sup>C, <sup>7</sup>Li, and <sup>119</sup>Sn NMR spectroscopy (see Experimental Section and Supporting Information).

**Structural Features of 3a and 3b in the Solid State.** The molecular geometries of both **3a** and **3b** in the solid state were established by X-ray crystal structure determinations (see data deposited at the CCDC).<sup>21,22</sup> The core structural motif of **3a** consists of a tris(aryl)stannate with the tin center in a formal 2+ oxidation state; this anionic unit is linked via a direct Li–Sn interaction to the lithium cation. This latter cation is further coordinated by two THF molecules (Figure 1). Two of the



Figure 1. Molecular geometries of 3a and 3b as found in the solid state. Some selected bond distances (A) and angles (deg) are presented in Table 1.

three 2-Me<sub>2</sub>NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub> anions are exclusively  $\sigma$ -C–Sn bonded to the tin(II) center, leaving their respective 2-Me<sub>2</sub>NCH<sub>2</sub> groupings as free, noncoordinating units. The third 2-Me<sub>2</sub>NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub> anion is bridge bonded, i.e.,  $\sigma$ -C–Sn bonded to the formal tin(II) center, while its 2-Me<sub>2</sub>NCH<sub>2</sub> substituent is intramolecularly coordinated to the Li center. The observed Sn–Li bond (2.860(6) Å) is slightly larger than the sum of the covalent radii (2.75 Å), but is in the range of that observed for the few known tris(organo)stannate(II) lithium compounds having a direct Sn–Li interaction, e.g., 2.882(7) Å in Ph<sub>3</sub>SnLi(PMDTA) (4),<sup>5</sup> 2.876(14) Å in But<sub>3</sub>SnLi(THF)<sub>3</sub> (5),<sup>23</sup> and 2.809(6) Å in [Ar\*Ph<sub>2</sub>SnLi]<sub>2</sub> (Ar\* is C<sub>6</sub>H<sub>3</sub>-2,6-Trip<sub>2</sub>; Trip is C<sub>6</sub>H<sub>2</sub>-2,4,6-Pr<sup>i</sup><sub>3</sub>) (6).<sup>14</sup>

The lithium centers in the respective tris(organo)stannates have similar, slightly distorted tetrahedral geometries, while the coordination geometries at the tin centers can be best described as being trigonal pyramidal, i.e., distorted from tetrahedral, with the three carbon atoms in the basal plane and the lithium atom approximately at the apex. For example, in Ph<sub>3</sub>SnLi(PMDTA)

Table 1. Selected Bond Distances and Angles for 3a and 3b

3a		3b	
	Distance	es (Å)	
Li-Sn	2.860(6)		2.72(2)
C(1)–Sn	2.249(3)		2.24(1)
C(2)–Sn	2.218(3)		2.206(9)
C(3)–Sn	2.221(3)		2.24(1)
N(1)–Li	2.117(7)		2.15(2)
O(1)–Li	1.949(6)		1.92(2)
O(2)–Li	1.956(7)	N(2)–Li	2.13(2)
	Angles	(deg)	
C(1)–Sn–Li	79.9(1)		89.0(5)
C(2)–Sn–Li	128.5(1)		101.3(4)
C(3)–Sn–Li	136.2(1)		158.8(5)
C(1) - Sn - C(2)	94.1(1)		93.7(4)
C(1) - Sn - C(3)	94.9(1)		99.2(5)
C(2) - Sn - C(3)	95.1(1)		97.6(4)
Sn-Li-N(1)	94.7(2)		98.2(7)
Sn-Li-O(1)	115.8(2)		120.2(8)
Sn-Li-O(2)	116.2(2)	Sn-Li-N(2)	92.2(6)
N(1)-Li-O(1)	112.9(3)		113.6(9)
N(1)-Li-O(2)	108.5(3)	N(2) -Li–O(1)	106.3(8)
O(1)-Li- $O(2)$	108.1(3)	N(1)-Li-N(2)	125.3(9)

Table	2.	Relevant	<sup>1</sup> Η,	<sup>13</sup> C,	<sup>119</sup> Sn, a	ind	<sup>7</sup> Li NMR	Data	of 2	and	3a-c	: at	298	K in	Toluene-d	8
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	$^{1}\mathrm{H}$				<sup>13</sup> C			
compound	H <sub>6</sub>	NCH <sub>2</sub>	NMe <sub>2</sub>	C <sub>1</sub>	CH <sub>2</sub>	NMe <sub>2</sub>	<sup>119</sup> Sn	<sup>7</sup> Li
2	7.88	3.52	2.14	169.7 <sup>a</sup>	68.1	45.9	143.4 <sup>b</sup>	
3a	7.82	3.68	2.03	161.8 <sup>c</sup>	68.3	45.6	$-158.1^{d}$	0.80
3b	7.87	3.67	1.97	162.1 <sup>e</sup>	68.4	45.5	$-157.9^{f}$	0.78
3b <sup>g</sup>	7.37	3.63	2.11	163.5 <sup><i>h</i></sup>	68.3	45.6	$-157.2^{i}$	0.34
3c	7.95	3.58	1.67	162.8	67.9	44.2	$-78.2^{j}$	1.53
71 (117 110 - 12 -)	1-		(117 110 - 12 - )		<i>d</i> .	al (117 110 ·	12 -> F	

 ${}^{a1}J({}^{117, 119}\text{Sn}-{}^{13}\text{C})$  393, 411 Hz.  ${}^{b}w_{1/2}$  22 Hz.  ${}^{c1}J({}^{117, 119}\text{Sn}-{}^{13}\text{C})$  220 Hz,  $w_{1/2}$  35 Hz.  ${}^{d}w_{1/2}$  460 Hz.  ${}^{e1}J({}^{117, 119}\text{Sn}-{}^{13}\text{C})$  231 Hz.  ${}^{f}w_{1/2}$  470 Hz; see Figure 2 for the  ${}^{119}\text{Sn}$  and  ${}^{7}\text{Li}$  NMR spectra at 233 K.  ${}^{g}\text{In}$  THF- $d_8$ .  ${}^{h}\text{At}$  298 K broad signal, at 248 K, sharp signal, average  ${}^{1}J({}^{117, 119}\text{Sn}-{}^{13}\text{C})$  276 Hz.  ${}^{i}w_{1/2}$  111 Hz.  ${}^{j}w_{1/2}$  725 Hz.

(4) and  $Bu_3^tSnLi(THF)_3$  (5) the (average) C-Sn-C bond angles around Sn are 96.1(2)° (4) and 102.9(5)° (5), while the respective (average) C-Sn-Li angles amount to 120.7(2)° (4) and 115.3(4)° (5).

With respect to complex **3a**, a similar such distortion toward trigonal pyramidal geometry at tin is observed, with an average C–Sn–C angle of 94.6(1)°. This value points to a low s-character of the Sn–C bond. However, due to the intra-molecular N–Li coordination of one of the dimethylamino substituents (i.e., acting as a monoanionic  $\kappa^2$ -C,N chelate), the lithium atom is pulled away from an idealized apical position. This is reflected by one very acute C–Sn–Li bond angle (79.9(1)°) that seems compensated by two larger C–Sn–Li bond angles (128.5(1)° and 136.2(1)°, respectively).

The structural motif of 3b in the solid state shows large similarities with that of 3a (see Figure 1). The main difference between these THF solvates is the replacement of one coordinating THF molecule in 3a by an intramolecular coordinating 2-dimethylamino substituent of a second aryl grouping in 3b. Most likely as a consequence of the presence of two intramolecular coordinating dimethylamino groups, the Sn-Li distance in **3b** is significantly shorter (Sn-Li 2.72(2) Å) than that found in **3a**. Also for **3b**, a distortion toward a trigonal pyramidal coordination geometry at tin is observed (the average of the C-Sn-C angles is  $96.9(4)^{\circ}$ ). Two of the C-Sn-Li angles are rather acute (C(1)- and C(2)-Sn-Liamount to  $89.0(5)^{\circ}$  and  $101.3(4)^{\circ}$ , respectively), whereas the C(3)-Sn-Li bond angle has opened up to  $158.8(5)^{\circ}$  in the direction of an almost linear C-Sn-Li arrangement with Cipso of the monodentate  $\kappa^1$ -*C*-bonded aryl formal anion.

Structural Features of 3a, 3b, and 3c in Toluene- $d_8$ . The relevant <sup>1</sup>H, <sup>13</sup>C, <sup>119</sup>Sn, and <sup>7</sup>Li NMR spectroscopic data for 2 and 3a-c are presented in Table 2.

In terms of solution behavior, a single resonance pattern is observed for the three 2-Me<sub>2</sub>NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub> groupings in both the <sup>1</sup>H and <sup>13</sup>C NMR spectra of solutions of **3a** and **3b**, respectively (toluene- $d_{8i}$  at RT; see Supporting Information). This indicates that in toluene all three organic moieties are equivalent on the NMR time scale, whereas in the solid state there is a clear difference between these three groups with one  $\kappa^2$ -C,N- and two  $\kappa^1$ -C-bonded. The observation of an average  $^{1}J(^{117,119}Sn-^{13}C)$  on  $C_{ipso}$  (220 Hz: 3a and 231 Hz: 3b) indicates that aryl exchange involves an intramolecular process with retention of the Sn-C interaction. Furthermore, the observation of a single methyl resonance for the NMe<sub>2</sub> groups indicates that fast exchange occurs between coordinated and free-NMe<sub>2</sub> functionalities. Likewise, the singlet resonance observed for the CH<sub>2</sub> protons points to the occurrence of processes involving a rapid averaging of the local geometry about Sn on the NMR time scale. Notably, in the temperature

range of 343 K down to 203 K, the <sup>1</sup>H and <sup>13</sup>C NMR spectra of 3a and 3b are virtually unchanged. At 203 K, all resonances start to broaden, and extremely broad lines result at 183 K (the lowest temperature studied). Thus, even at this low temperature limit, the exchange processes, which involve the exchange of aryl groupings (vide infra) as well as between coordinated and free-NMe<sub>2</sub> substituents, are still fast on the NMR time scale. More conclusive evidence concerning the structural features of 3a and 3b could be obtained from their <sup>1</sup>H, <sup>13</sup>C, <sup>119</sup>Sn, and <sup>7</sup>Li NMR spectra (toluene- $d_{8}$ ; at RT). The <sup>119</sup>Sn chemical shift values of both 3a (-158.1 ppm) and 3b (-157.9 ppm) are considerably upfield shifted, by about 300 ppm, as compared to the neutral bis(aryl)tin(II) compound 2 (+143.4 ppm). Note that for the Ph<sub>3</sub>Sn anion  $\delta^{119}$ Sn is -98.4 ppm,<sup>9</sup> whereas for Ph<sub>2</sub>Ar\*SnLi a  $\delta^{119}$ Sn of -117 ppm<sup>14</sup> has been reported. The <sup>119</sup>Sn resonances of 3a and 3b are rather broad  $(w_{1/2} = 460 \text{ and } 470 \text{ Hz}, \text{ respectively})$  and unresolved, a situation that could be the result of unresolved  $^1\!J$   $^7\!{\rm Li}{-}^{119}{\rm Sn}$ coupling. To our surprise, this appears to contrast the case for 3b; at temperatures below 253 K, in both the <sup>119</sup>Sn and <sup>7</sup>Li NMR spectra (toluene- $d_8$ ), this coupling is nicely resolved indeed (see Figure 2) and has a measured value of 289 Hz. This



Figure 2. <sup>119</sup>Sn and <sup>7</sup>Li NMR spectra of 3b in toluene- $d_8$  at 233 K.

value is close to the value reported for  $Bu_3^t SnLi(THF)_3$  (287 Hz)<sup>23</sup> but considerably smaller than that reported for Ph<sub>3</sub>SnLi(PMDTA) (412 Hz).<sup>5</sup> The observation of <sup>1</sup>*J* is conclusive evidence that in solution a bonding interaction between lithium and tin is present in **3b**, and most likely also in **3a**; the multiplicity of the respective <sup>119</sup>Sn and <sup>7</sup>Li resonances is further conclusive evidence for a monomeric solution structure.

As mentioned before, we obtained 3c as a mixture of products, of which we ascribe the main component (>75%) to

be THF-free "R<sub>3</sub>SnLi", of which relevant <sup>1</sup>H, <sup>13</sup>C, <sup>119</sup>Sn, and <sup>7</sup>Li NMR data are summarized in Table 2. The origin of some of the other minor components in the mixture is discussed below. Its <sup>1</sup>H and <sup>13</sup>C NMR spectra show single resonance patterns at RT and above, indicating that the three  $2-Me_2NCH_2C_6H_4$ anions in 3c are equivalent. The observed singlet NMe2-methyl proton resonance ( $\delta = 1.67$  ppm) is notable and is considerably upfield shifted as compared to those in THF-solvated 3a and **3b**. It is known<sup>24</sup> that coordination of the NMe<sub>2</sub> grouping to a metal center causes such an upfield shift. In the case of 3c, this upfield shift indicates that all three nitrogen substituents are involved in N-Li coordination in either an intra- or intermolecular sense. Furthermore, its respective  $\delta^{119}$ Sn (-78.2 ppm) and  $\delta$  <sup>7</sup>Li (1.53 ppm) are significantly different from those observed for 3a and 3b (Table 2). In particular, the latter data suggest that the structure of 3c in toluene solution must be significantly different from that of 3a or 3b.

Nature of 3a, 3b, and 3c in THF-d<sub>8</sub>. In contrast to the temperature dependence of the NMR spectra of 3a and 3b in toluene-d<sub>8</sub>, no significant changes are observed in similar spectra of solutions of both 3a and 3b in THF- $d_8$  over the whole temperature range studied (298 down to 193 K). The <sup>1</sup>H and <sup>13</sup>C NMR spectra of **3b** show a single resonance pattern for the aryl moieties. An exception is the temperature dependence of the <sup>13</sup>C<sub>inso</sub> resonance that is rather broad at RT, but at 248 K becomes a sharp line with a well-resolved average  ${}^{1}J({}^{117,119}Sn - {}^{13}C)$  coupling (276 Hz). In contrast to the temperature-dependent <sup>119</sup>Sn chemical shifts for 3a and 3b in toluene- $d_{8}$ , their respective spectra in THF- $d_8$  are rather temperature independent (see Table 2) in the temperature range from 298 K (-157.2 ppm) down to 193 K (-160.4 ppm). This might suggest that in neat THF, 3a and 3b may exist as tris-solvated species, R<sub>3</sub>SnLi(THF)<sub>3</sub>, i.e., as complexes lacking any intramolecular N-Sn coordination.

Equilibria Involving THF-Solvated and THF-Free Tris-(aryl)stannates 3. Irrespective of the batch of crystallization, the <sup>1</sup>H, <sup>119</sup>Sn, and <sup>7</sup>Li NMR spectra of toluene solutions of 3a and 3b always showed the presence of some other molecules/ materials in quite minor amounts (<2%). In the <sup>1</sup>H NMR spectra, there is invariably observed additional H(6)-resonance patterns, one at  $\delta = 7.82$  ppm (which we ascribe to the presence of minor amounts of 2) and another at  $\delta = 8.15$  ppm. This latter resonance occurs at the identical chemical shift value of the corresponding organolithium compound 1. In apolar solvents and in the presence of only small amounts of THF, this organolithium compound exists as a THF-solvated dimer  $[2-\text{Me}_2\text{NCH}_2\text{C}_6\text{H}_4\text{Li}(\text{THF})_n]_2$ .<sup>25–27</sup> Moreover, the <sup>119</sup>Sn NMR spectra of 3a and 3b showed the presence of minor amounts of 2, while the <sup>7</sup>Li NMR spectra always showed an additional resonance of low intensity at 2.3 ppm, which is very close to the known chemical shift value of pure [2-Me2NCH2C6H4Li- $(\text{THF})_n]_2$  dissolved in toluene.<sup>25,26</sup>

Combining these latter observations, the data of temperature-dependent NMR data for 3a-c and, last but not least, the knowledge that even in the solid state the THF molecules are rather weakly bonded leads us to propose the existence of the sequence of equilibria as shown in Scheme 3.

Such a series of events would explain the large temperaturedependent <sup>119</sup>Sn chemical shifts as observed (toluene- $d_8$ ) for **3a** and **3b**. At 343 K, these values are  $\delta_{Sn} = -138.1$  and -121.9ppm, respectively, while at 193 K these values rise to -172.3and -172.2 ppm, respectively. At low temperature, this equilibrium appears to lie completely to the left with, in the

Scheme 3. Equilibria Involving THF-Solvated and THF-Free Tris(aryl)stannates 3 in Toluene

	- THF		- THF		- THF	
R <sub>3</sub> SnLi(THF) <sub>3</sub>	$\rightarrow$	R <sub>3</sub> SnLi(THF) <sub>2</sub>	$\rightarrow$	R <sub>3</sub> SnLi(THF)	<del>~ ``</del>	R₃SnLi
	+ THF	3a	+ THF	3b	+ THF	3c

limiting situation, a <sup>119</sup>Sn chemical shift in the order as observed for 3a in THF- $d_8$ , i.e., as for R<sub>3</sub>SnLi(THF)<sub>3</sub>. At high temperatures, however, the equilibrium lies completely to the right-hand side with a limiting <sup>119</sup>Sn chemical shift value as observed for THF-free 3c.

A further and somewhat remarkable observation was made when a sample of 3b (toluene- $d_8$ ) was reacted with H<sub>2</sub>O. It appeared that a mixture of (2-Me<sub>2</sub>NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>SnH (6), (2- $Me_2NCH_2C_6H_4)_2Sn$  (2), and the arene  $Me_2NCH_2C_6H_5$  in approximately a 2.5:1:1 molar ratio was formed. The triaryltin hydride could be unequivocally identified by its <sup>1</sup>H NMR spectrum (see Experimental Section) with a telltale Sn-H resonance at  $\delta_{\rm H}$  = 6.83 ppm displaying typical <sup>1</sup>J(<sup>117,119</sup>Sn-<sup>1</sup>H) coupling values of 2368 and 2469 Hz, respectively. Furthermore, the H(6) resonance at  $\delta_{\rm H}$  = 7.45 ppm shows a typical  ${}^{2}J({}^{117,119}\text{Sn}-{}^{1}\text{H})$  value (52 Hz). The proton-coupled <sup>119</sup>Sn spectrum of this mixture clearly indicated the presence of 2 (single line at  $\delta_{sn}$  = 143.5 ppm), while the <sup>119</sup>Sn resonance of  $(2-Me_2NCH_2C_6H_4)_3SnH$  (6) is present at  $\delta_{Sn} = -213$  ppm with as expected a large  ${}^{1}J({}^{119}Sn-{}^{1}H)$  value of 2469 Hz, which is on the same order of magnitude as observed for Ph<sub>3</sub>SnH.<sup>28</sup>

The formation of **2** and  $Me_2NCH_2C_6H_5$  upon reaction of **3a** or **3b** with  $H_2O$  might be explained by the existence of an equilibrium between the tris(aryl)stannate, neutral bis(aryl)tin-(II) compound **2** and the aryllithium-THF species **1**, a situation as suggested in Scheme 4. Interestingly, it is the latter reaction (to the left-hand side) that we applied for the direct synthesis of **3**, as shown in Scheme **2**.

Scheme 4. Addition of H <sub>2</sub> O to a S	Sample of 3b in toluene-da
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	-	-	
R₃SnLi(THF) <sub>n</sub> <b>3</b>	<→	$R_2Sn + [RLi(THF)_n]_2$ 2 1	
H <sub>2</sub> O		H <sub>2</sub> O	
R <sub>3</sub> SnH		RH	
6		$R = 2 - Me_2 NCH_2 C_6 H_4$	

Both stannate 3 and aryllithium 1 are highly sensitive to water but will almost certainly react at different rates. Obviously, reaction of 1 is causing this equilibrium to shift to the right side, which explains the formation of equivalent amounts of 2 and the free arene  $Me_2NCH_2C_6H_5$ . The product distribution  $(2-Me_2NCH_2C_6H_4)_3SnH$  (6) versus  $(2-Me_2NCH_2C_6H_4)_2Sn$  is then dependent on (i) the rate constants of the equilibrium and (ii) the kinetics of the hydrolysis of the aryllithium species, leading to  $Me_2NCH_2C_6H_5$  versus the kinetics of the conversion of  $(2-Me_2NCH_2C_6H_4)_3SnLi(THF)$  leading to  $(2-Me_3NCH_2C_6H_4)_3SnH$ .

2D EXSY spectroscopy would be an excellent technique to study the existence of the equilibrium as shown in Scheme 4 in more detail. Unfortunately, the concentration of the components at the right side in the equilibrium mixture is too low to obtain reliable EXSY spectra. Therefore, we prepared a sample in which the concentration of **2** was enhanced by adding pure **2** to a solution of **3b**. Similarly,



Figure 3. 2D <sup>1</sup>H-<sup>1</sup>H EXSY spectra of solutions of pure 3b to which either pure R<sub>2</sub>Sn, 2, or pure RLi, 1, has been added.

another sample was prepared in which the concentration of the aryllithium component was enhanced by adding pure 2-Me<sub>2</sub>NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Li to a solution of 3b. Each sample was then studied in detail by 2D <sup>1</sup>H-<sup>1</sup>H EXSY spectroscopy, running the spectra at various temperatures and with various mixing times (see Experimental Section). The spectra of the first mixture confirmed that the 2-Me<sub>2</sub>NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub> groups present in 3b and 2 undergo chemical exchange; see Figure 3a. Similarly, the 2D EXSY spectra of the second mixture showed clearly that the 2-Me<sub>2</sub>NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub> groups present in 3b and [2- $Me_2NCH_2C_6H_4Li(THF)_n]_2$ , 1, are also chemically exchanging; see Figure 3b. This latter Li-Li exchange phenomenon was moreover corroborated by the observation of strong crosspeaks in the 2D 7Li-7Li EXSY spectrum, pointing to the occurrence of chemical exchange of the lithium atoms of 3b and 1 (see Experimental Section and Supporting Information).

These spectra, clearly displaying aryl exchange on the NMR time scale, confirm that in solutions of 3a and 3b an equilibrium exists between the stannate and the neutral tin(II) compound and the aryllithum species as suggested in Scheme 4.

# CONCLUSIONS

In this study we have demonstrated that, in addition to the synthetic methods i-iii (Scheme 1), all involving reduction of formally Sn(IV) organometallics, triaryltin lithium compounds can be directly synthesized through reaction of the corresponding, pure aryllithium compound with SnCl<sub>2</sub>. An obvious prerequisite for the success of this route is that the intermediate bisaryltin(II) species is stable against oligomerization through (irreversible) Sn-Sn bond formation. In the case of the present synthesis of stannates  $(2-Me_2NCH_2C_6H_4)_3SnLi(THF)_3$  3, it is the formation of  $bis({\kappa^2-C_1N-(2-Me_2NCH_2C_6H_4)_2}Sn(2)$  as intermediate along the synthesis route. This diaryltin compound is effectively stabilized by intramolecular Sn-N coordination (cf. refs 15a and 15e). Consequently, stannate 3 is likewise nicely available via route iv (Scheme 1), in which 2 is reacted with corresponding 2-Me<sub>2</sub>NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Li in an apolar solvent. Alternate stabilization can also be achieved when at least one of the aryl groups contains bulky ortho-substituents, as is the case for the stannate lithium compounds Ar\*3-nPhnSnLi.14

Two types of stannates are known that have distinctly different structural features both in the solid state and in solution. One type consists of separate formal  $R_3Sn$  anions and a countercation stabilized by coordination through a crown ether or polydentate ligand, e.g.,  $[Ph_3Sn][K(18-Crown-6)]$ ,<sup>9,29</sup>  $[Ph_3Sn][Ba(18-Crown-6)(HMPA)_2]$ ,<sup>11</sup>  $[Cp_3Sn][Mg-(THF)_6]$ ,<sup>13</sup> and  $[(9-fluorenyl)_3Sn][Li(THF)_4]$ .<sup>13</sup> These species

exist in solution as solvent-separated ion pairs. Another type of stannates has a direct metal to tin bond as in, for example  $Bu_3^tSnLi(THF)_3$ ,<sup>23</sup>  $Ph_3SnLi(PMDTA)$ ,<sup>5</sup> ( $Bu^tCH_2$ )<sub>3</sub>SnK-(toluene)<sub>3</sub>,<sup>6</sup> and [ $Ph_2Ar*SnLi$ ]<sub>2</sub> ( $Ar* = C_6H_3$ -2,6-Trip<sub>2</sub>; Trip =  $C_6H_2$ -2,4,6-Pr<sup>i</sup>).<sup>14</sup> They can be considered as close contact ion pairs.

Article

It is interesting to note that the coordination geometries of the tin center in the latter stannates, e.g., Ph<sub>3</sub>SnLi(PMDTA)<sup>5</sup> (4) and  $Bu_{3}^{t}SnLi(THF)_{3}^{23}$  (5) (Li–Sn distances: 4 2.817(7) and 5 2.876(14) Å), show similar distortions toward a trigonal pyramidal one (with the lone pair at the apex). This distortion of geometry has been explained in terms of enhanced pcharacter in the tin-carbon bond, caused by the differences in energy between the s and p orbitals.<sup>30</sup> As a consequence, the lone pair in R<sub>3</sub>Sn anions and the tin-lithium bond in R<sub>3</sub>SnLi species possess an enhanced s-character, i.e., the Sn hybridization that is more  $[p^3+s]$  than  $sp^3$  with the Sn s orbital being very important in the Sn-Li interaction. The resulting reduced s-character and consequently enhanced p-character in the Sn-C bonds are also reflected in the observation of a relatively small  ${}^{1}J({}^{13}C-{}^{7}Li)$  coupling in the  ${}^{13}C$  NMR spectrum of 3a (vide infra). Comparison of the structural features of 4 and 5, which can be considered as parent compounds for stannates 3a and 3b,<sup>31</sup> reveals that the intramolecular N-Sn coordination considerably affects the mutual orientation of the Sn-Li vector versus the C3-manifold interaction but has little influence on the nature of the Sn-Li (e.g., for 3a 2.860(5) Å) interaction. The variation in the C–Sn–Li bond angle of the  $\kappa^1$ -C-bonded aryl grouping  $(136.2(13)^{\circ}$  in 3a and  $158.8(5)^{\circ}$  in 3b) is another indication for the high s-character of the Sn-Li interaction.

Removal of the last THF molecule from **3b** provides **3c**, which according to NMR spectral data seems to lack a Sn–Li interaction. A likely possibility for a structure of this material is provided in Figure 4, which is inspired by the structural features of the zincate { $\kappa^2$ -*C*,*N*-(2-Me<sub>2</sub>NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)}<sub>4</sub>ZnLi<sub>2</sub> (7; see ref 20 for the structural data in the solid state, in particular the



**Figure 4.** Schematic representation of the structure in the solid state of the zincate  $[\kappa^2-C_rN-(2-Me_2NCH_2C_6H_4)]_4$ ZnLi<sub>2</sub> (7) and the proposed limiting structure of **3c**.

 $C_{ipso}$ -Li distances).<sup>33</sup> In the latter compound, each of the Li cations is four-coordinate, and this is provided by both Li–N coordination and via interaction with the  $\pi$ -electron density on (aryl) $C_{ipso}$  of the  $C_{ipso}$ -Zn bond. Application of this finding provides a limiting structure for **3c** in which the electron density of the Sn orbital with high s-character is directed away from the Sn–Li vector, consistent with the absence of any <sup>117,119</sup>Sn–<sup>7</sup>Li coupling for **3c** in toluene solution. In fact, it is suggested that interaction of the  $\pi$ -electron density on either (aryl) $C_{ipso}$  center with Li compensates for the lack of coordinating (THF) solvent molecules as present in **3a** and **3b**, cf. Scheme 3.

#### EXPERIMENTAL SECTION

All experiments were carried out under a dry, oxygen-free nitrogen atmosphere using standard Schlenk techniques. Solvents were dried and distilled prior to use. The starting material 2-[(dimethylamino)-methyl]phenyllithium (1) was prepared according to a literature procedure.<sup>25</sup> Bis{2-[(dimethylamino)methyl]phenyl}tin (2) was prepared according to a modified (vide infra) procedure reported earlier.<sup>15a</sup> Crystallographic data and refinement of the crystal structures of **3a** and **3b** were deposited at the Cambridge Crystallographic Database earlier.<sup>21,22</sup> <sup>1</sup>H, <sup>13</sup>C, <sup>119</sup>Sn, and <sup>7</sup>Li NMR spectra were recorded on 400 MHz Varian VNMRS400 and Agilent MRF400 spectrometers at ambient temperature unless otherwise stated. Chemical shifts ( $\delta$ ) are given in ppm relative to Me<sub>4</sub>Si as an internal standard (<sup>1</sup>H and <sup>13</sup>C), to Me<sub>4</sub>Sn in C<sub>6</sub>D<sub>6</sub> (<sup>119</sup>Sn), or to LiCl (<sup>7</sup>Li) in D<sub>2</sub>O (1 M) as an external standard. Coupling constants are in Hz. Complete assignments in <sup>1</sup>H and <sup>13</sup>C NMR spectra could be made from COSY and HMQC spectra.

Elemental analyses were obtained from Kolbe Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr, Germany.

(2-Me<sub>2</sub>NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>Sn (2). To a solution of 2.80 g (20 mmol) of 2-[(dimethylamino)methyl]phenyllithium in 20 mL of THF was added a solution of 1.90 g (10 mmol) of SnCl<sub>2</sub> in 15 mL of THF during 5 min, which resulted in the formation of a clear yellow solution. This mixture was stirred for 30 min, after which all volatiles were removed in vacuo. The remaining yellow solid material was extracted with 75 mL of warm (50 °C) *n*-hexane. The hexane extract was cooled to -30 °C for 12 h. The pale yellow crystalline material was isolated by decantation, washed with cold pentane, and dried in vacuo to afford pure 2 (2.5 g, 65% yield).

<sup>1</sup>H NMR (400.093 MHz, benzene-*d*<sub>6</sub>, 298 K): δ (in ppm) 7.88 (d, 1H, *H*(6)), 7.25 (t, 1H, *H*(5)), 7.15 (t, 1H, *H*(4)), 7.03 (d, 1H, *H*(3)), 3.52 (s, 2H, CH<sub>2</sub>N), 2.14 (s, 6H, N(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (100.614 MHz, benzene-*d*<sub>6</sub>, 298 K): δ (in ppm) 169.7 (*C*(1), <sup>1</sup>*J*(<sup>117, 119</sup>Sn<sup>-13</sup>C) 393, 411 Hz), 146.4 (*C*(2) <sup>2</sup>*J*(<sup>117, 119</sup>Sn<sup>-13</sup>C) 10 Hz), 136.6 (*C*(6) <sup>2</sup>*J*(<sup>117, 119</sup>Sn<sup>-13</sup>C) 29 Hz), 126.7 (*C*(3)), 126.4 (*C*(5)), 126.0 (*C*(4), 68.1 (CH<sub>2</sub>N), 45.9 (N(CH<sub>3</sub>)<sub>2</sub>, <sup>2</sup>*J*(<sup>117, 119</sup>Sn<sup>-13</sup>C) 32 Hz). <sup>119</sup>Sn NMR (149.215 MHz, benzene-*d*<sub>6</sub>, 298 K): δ (in ppm) 143.4 (*w*<sub>1/2</sub> 22 Hz).

(2-Me<sub>2</sub>NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>SnLi(THF)<sub>2</sub> (3a). To a solution of 2.15 g (15 mmol) of 2-[(dimethylamino)methyl]phenyllithium in 25 mL of THF was added a solution of 0.95 g (5 mmol) of SnCl<sub>2</sub> in 15 mL of THF during 5 min. The resulting clear yellow solution was stirred for 30 min, after which all volatiles were removed in vacuo. The remaining yellow solid material was extracted two times with 30 mL of benzene (removal of LiCl). The combined benzene extracts were evaporated at reduced pressure, affording a pale yellow, waxy solid. This crude product was recrystallized from *n*-hexane containing 5% of THF at -30 °C. The yellow crystalline material was isolated by decantation, washed with 10 mL of pentane, and dried for 5 min in vacuo to afford pure 3a (2.1 g, 63% yield).

<sup>1</sup>H NMR (400.093 MHz, toluene- $d_8$ , 298 K): δ (in ppm) 7.82 (d, 3H, H(6)), 7.31 (d, 3H, H(3)), 7.10 (t, 3H, H(4)), 6.99 (t, 3H, H(5)), 3.68 (s, 6H, CH<sub>2</sub>N), 3.42 (m, 8H, THF), 2.03 (s, 18H, N(CH<sub>3</sub>)<sub>2</sub>), 1.41 (m, 8H, THF). <sup>13</sup>C NMR (100.614 MHz, toluene- $d_8$ , 298 K): δ (in ppm) 161.8 (C(1), <sup>1</sup>J(<sup>117, 119</sup>Sn-<sup>13</sup>C) 220 Hz,  $w_{1/2}$  35 Hz), 145.9 (C(2) <sup>2</sup>J(<sup>117, 119</sup>Sn-<sup>13</sup>C) 39 Hz), 140.1 (C(6), <sup>2</sup>J(<sup>117, 119</sup>Sn-<sup>13</sup>C) 15

Hz), 128.5 (*C*(3)), 126.4 (*C*(5)), 125.5 (*C*(4)), 68.3 (*C*H<sub>2</sub>N), 68.2 (THF), 45.6 (N(*C*H<sub>3</sub>)<sub>2</sub>), 25.6 (THF). <sup>119</sup>Sn NMR (149.215 MHz, toluene-*d*<sub>6</sub>, 298 K): δ (in ppm) -158.1 ( $w_{1/2}$  460 Hz). <sup>7</sup>Li NMR (155.376 MHz toluene-*d*<sub>6</sub>, 298 K): δ (in ppm) 0.80 ( $w_{1/2}$  16 Hz). <sup>1</sup>H NMR (400.093 MHz, THF-*d*<sub>8</sub>, 248 K): δ (in ppm) 7.23 (d, 3H, H(6)), 7.19 (d, 3H, H(3)), 6.81 (t, 3H, H(4)), 6.57 (t, 3H, H(5)), 3.63 (s, 6H, *C*H<sub>2</sub>N), 3.55 (m, 8H, THF), 2.07 (s, 18H, N(*C*H<sub>3</sub>)<sub>2</sub>), 1.71 (m, 8H, THF). <sup>13</sup>C NMR (100.614 MHz, THF-*d*<sub>8</sub>, 248 K): δ (in ppm) 165.0 (*C*(1), <sup>1</sup>*J*(<sup>117</sup>, <sup>119</sup>Sn-<sup>13</sup>C) 275 Hz), 147.3 (*C*(2) <sup>2</sup>*J*(<sup>117</sup>, <sup>119</sup>Sn-<sup>13</sup>C) 37 Hz), 139.9 (*C*(6)), 126.6 (*C*(3)), 125.2 (*C*(5)), 124.6 (*C*(4)), 67.4 (*C*H<sub>2</sub>N), 68.3 (THF), 46.1 (N(*C*H<sub>3</sub>)<sub>2</sub>), 26.4 (THF). <sup>119</sup>Sn NMR (149.215 MHz, THF-*d*<sub>8</sub>, 248 K): δ (in ppm) -159.4 ( $w_{1/2}$  18 Hz). <sup>7</sup>Li NMR (155.376 MHz, THF-*d*<sub>8</sub>, 248 K): δ (in ppm) -0.10 ( $w_{1/2}$  4 Hz). Anal. Calcd for C<sub>35</sub>H<sub>52</sub>LiN<sub>3</sub>O<sub>2</sub>Sn: C 62.51, H 7.79, N 6.25. Found: C 62.37, H 7.78, N 6.21.

(2-Me<sub>2</sub>NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>SnLi(THF) (3b). Crystalline 3a (1.3 g, 2 mmol) was kept in vacuo ( $10^{-2}$  mmHg) at room temperature for 1 h, after which a pale yellow, amorphous powder was obtained. The <sup>1</sup>H NMR spectrum of this material showed the loss of one THF molecule. The crude material was recrystallized from *n*-hexane at -30 °C. The yellow crystalline material was isolated by decantation, washed with 5 mL of pentane, and dried in vacuo to afford pure 3b (0.7 g, 58% yield).

<sup>1</sup>H NMR (400.093 MHz, toluene-*d*<sub>8</sub>, 298 K): δ (in ppm) 7.87 (d, 3H, *H*(6)), 7.25 (d, 3H, *H*(3)), 7.10 (t, 3H, *H*(4)), 7.01 (t, 3H, *H*(5)), 3.67 (s, 6H, *CH*<sub>2</sub>N), 3.35 (m, 8H, THF), 1.97 (s, 18H, N(*CH*<sub>3</sub>)<sub>2</sub>), 1.36 (m, 8H, THF). <sup>13</sup>C NMR (100.614 MHz, toluene-*d*<sub>8</sub>, 298 K): δ (in ppm) 162.1 (*C*(1), <sup>1</sup>*J*(<sup>117, 119</sup>Sn<sup>-13</sup>C) 231 Hz), 145.8 (*C*(2) <sup>2</sup>*J*(<sup>117, 119</sup>Sn<sup>-13</sup>C) 37 Hz), 140.6 (*C*(6), <sup>2</sup>*J*(<sup>117, 119</sup>Sn<sup>-13</sup>C) 16 Hz), 128.8 (*C*(3)), 126.5 (*C*(5)), 125.6 (*C*(4)), 68.4 (*CH*<sub>2</sub>N), 68.3 (THF), 45.5 (N(*CH*<sub>3</sub>)<sub>2</sub>), 25.5 (THF). <sup>119</sup>Sn NMR (149.215 MHz, toluene-*d*<sub>8</sub>, 298 K): δ (in ppm) –157.9 (*w*<sub>1/2</sub> 470 Hz). <sup>7</sup>Li NMR (155.376 MHz toluene-*d*<sub>8</sub>, 298 K): δ (in ppm) 0.78 (*w*<sub>1/2</sub> 16 Hz). Anal. Calcd for C<sub>31</sub>H<sub>44</sub>LiN<sub>3</sub>OSn: C 62.02, H 7.39, N 7.00. Found: C 61.88, H 7.48, N 7.06.

(2-Me<sub>2</sub>NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>SnLi (3c). Compound 3b (500 mg, 0.83 mmol) was dissolved in 10 mL of *n*-hexane. The solvent was removed in vacuo at 323 K, yielding a yellow, very viscous material. To this material again 10 mL of *n*-hexane was added, affording a clear yellow solution, and evaporated in vacuo at 323 K. According to its <sup>1</sup>H NMR spectrum the product (3c) did not contain any THF but contained some contaminations, of which (2-Me<sub>2</sub>NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>Sn and Me<sub>2</sub>NCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub> could be identified. Due to its extreme solubility, purification by recrystallization appeared to be impossible.

<sup>1</sup>H NMR (400.093 MHz, toluene-*d*<sub>8</sub>, 298 K): δ (in ppm) 7.95 (d, 3H, *H*(6)), 7.09 (m, 9H, *H*(3), *H*(4), and *H*(5)), 3.58 (s, 6H, CH<sub>2</sub>N), 1.67 (s, 18H, N(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (100.614 MHz, toluene-*d*<sub>8</sub>, 298 K): δ (in ppm) 162.8 (*C*(1)), 147.6 (*C*(2)), 143.5 (*C*(6)), 130.3, 126.9 (*C*(3), *C*(4), and *C*(5)), 67.9 (CH<sub>2</sub>N), 44.2 (N(CH<sub>3</sub>)<sub>2</sub>). <sup>119</sup>Sn NMR (149.215 MHz, toluene-*d*<sub>8</sub>, 298 K): δ (in ppm) -78.2 (*w*<sub>1/2</sub> 725 Hz). <sup>7</sup>Li NMR (155.376 MHz, toluene-*d*<sub>8</sub>, 298 K): δ (in ppm) 1.53.

Alternative Synthesis of 3a. Pure bis{2-[(dimethylamino)methyl]phenyl}tin, 2 (770 mg, 2 mmol), and 280 mg (2 mmol) of 2-[(dimethylamino)methyl]phenyllithium (1) were mixed and dissolved in 5 mL of THF. The <sup>1</sup>H NMR spectrum of this solution showed the immediate and exclusive formation of 3. The THF was removed in vacuo at room temperature, and the remaining yellow solid material was recrystallized from 10 mL of *n*-hexane containing 5% of THF. The yellow crystalline material was isolated by decantation, washed with 5 mL of pentane, and dried in vacuo, affording 800 mg (59% yield) of pure 3a.

**Hydrolysis of 3a.** Pure **3a** (30 mg) was dissolved in 0.5 mL of benzene- $d_6$  in an NMR tube. The <sup>1</sup>H NMR spectrum of this solution showed that it contained pure **3a**. To this solution was added 10  $\mu$ L of degassed H<sub>2</sub>O, and the reaction mixture was vigorously shaken for 1 min, after which the tube contained a colorless solution and a few microdroplets of H<sub>2</sub>O. The <sup>1</sup>H NMR spectrum of this solution showed the presence of (2-Me<sub>2</sub>NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>SnH (4) (vide infra), (2-Me<sub>2</sub>NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>Sn (2), and Me<sub>2</sub>NCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub> in a 2.5:1:1 molar ratio. The presence of (2-Me<sub>2</sub>NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>Sn in the reaction mixture was confirmed by the observation of a signal at 146.5 ppm in its <sup>119</sup>Sn

NMR spectrum. In an independent experiment in which  $10 \,\mu\text{L}$  of H<sub>2</sub>O was added to 0.5 mL of a solution of pure **2**, it was shown that (2-Me<sub>2</sub>NCH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>Sn is inert toward hydrolysis for at least a few hours.

**Data Assigned to (2-Me<sub>2</sub>NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>SnH, 6. <sup>1</sup>H NMR (400.093 MHz, benzene-d\_6, 298 K): \delta (in ppm) 7.45 (d, 3H, H(6), <sup>2</sup>J(<sup>117,119</sup>Sn<sup>-1</sup>H 52 Hz), 7.08 (m, 9H, H(3), H(4), and H(5)), 6.83 (s, 1 H, SnH, <sup>1</sup>J(<sup>117,119</sup>Sn<sup>-1</sup>H) 2368, 2469 Hz), 3.33 (s, 6H, CH<sub>2</sub>N), 1.78 (s, 18H, N(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (100.614 MHz, benzene-d\_6, 298 K): \delta (in ppm) 145.8 (C(1), <sup>1</sup>J(<sup>117, 119</sup>Sn<sup>-13</sup>C) 551, 526 Hz), 145.6 (C(2), <sup>2</sup>J(<sup>117, 119</sup>Sn<sup>-13</sup>C) 24 Hz), 138.2 (C(6), <sup>2</sup>J(<sup>117, 119</sup>Sn<sup>-13</sup>C) 38 Hz), 128.3, 127.7, and 126.2 (C(3), C(4), and C(5)), 66.1 (CH<sub>2</sub>N), 44.3 (N(CH<sub>3</sub>)<sub>2</sub>). <sup>119</sup>Sn NMR (149.215 MHz, benzene-d\_6, 298 K): \delta (in ppm) –213.1 (<sup>1</sup>J(<sup>119</sup>Sn<sup>-1</sup>H 2469 Hz). (Note that the data for Ph<sub>3</sub>SnH amount to \delta\_{Sn} = -164.5 ppm with <sup>1</sup>J(<sup>119</sup>Sn<sup>-1</sup>H) 1936 Hz.)<sup>34</sup>** 

NMR Studies of a 1:1 Molar Mixture of 2 and 3b. Pure 3a (30 mg, 0.05 mmol) and 29 mg (0.075 mmol) of pure 2 were mixed in an NMR tube and dissolved in 0.5 mL of toluene- $d_8$ . <sup>1</sup>H, <sup>119</sup>Sn, and 2D EXSY (NOESY pulse sequence) NMR spectra were recorded at 298 and 333 K. Although of low intensity, obvious cross-peaks between the resonances of 2 and 3b were clearly observable in the 2D EXSY spectrum at 298 K; at higher temperatures (333 K) the intensities of these cross-peaks are even more expressed. The 2D EXSY spectra at 333 K were recorded with mixing times of 100, 400, and 800 ms, respectively.

**NMR Studies of a 1:1 Molar Mixture of 1 and 3b.** Pure 3a (30 mg, 0.05 mmol) and 5.6 mg (0.04 mmol) of pure 1 were mixed in an NMR tube and dissolved in 0.5 mL of toluene- $d_8$ . An additional 25  $\mu$ L of THF was added to obtain a clear solution. <sup>1</sup>H, <sup>7</sup>Li, and <sup>119</sup>Sn, 2D <sup>1</sup>H<sup>1</sup>H EXSY, and 2D <sup>7</sup>Li<sup>7</sup>Li EXSY (NOESY pulse sequence) NMR spectra of these solutions were studied in detail.

**X-ray Structure Determinations of 3a and 3b.** Structural data for **3a** and **3b** were deposited earlier at the CCDC (refs 21 and 22) but now were rerefined using more state-of-the-art refinement software (SHELXL2014).<sup>35</sup>

# ASSOCIATED CONTENT

# **Supporting Information**

The relevant <sup>1</sup>H, <sup>13</sup>C, <sup>119</sup>Sn, and <sup>7</sup>Li NMR spectroscopic data for **2** and **3a–c** are presented as well as a Mercury representation of the molecular structures of **3a** and **3b**. This material is available free of charge via the Internet at http:// pubs.acs.org.

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#### Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

#### Notes

The authors declare no competing financial interest.

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### DEDICATION

Dedicated to Professor Mike Lappert in honor of his excellent and inspiring contributions to the field of organometallic chemistry.

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(31) A similar structural motif to that observed in **3b** has been reported for the triarylgermyl lithium compound (2- $Me_2NC_6H_4$ )\_3GeLi(THF)<sub>2</sub> in the solid state.<sup>32</sup> In solution, however, based on variable-temperature <sup>7</sup>Li and <sup>13</sup>C NMR data, a temperature-dependent equilibrium exists between this compound and a dimer in which two Li(THF)<sub>2</sub> cationic moieties are bridging via Ge–Li bonds between two (2- $Me_2NC_6H_4$ )\_3Ge anionic groups. Also in the Si–Si linked dimer [(2- $Me_2NCH_2C_6H_4$ )\_2SiLi(THF)\_2]\_2<sup>33</sup> the two (2- $Me_2NCH_2C_6H_4$ )\_2SiLi(THF)\_2]\_2<sup>33</sup> the two (2- $Me_2NCH_2C_6H_4$ )\_2SiLi(THF)\_2 units show large structural similarities to that observed in **3a**.

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