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ARTICLE

Synthesis of Aminobismuthanes via Me_3SnCl Elimination

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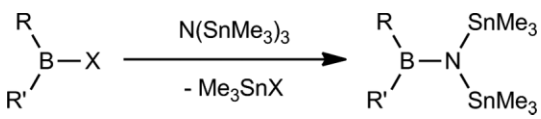
Dedicated to Professor Wolfgang Schnick on the Occasion of his 60th Bbirthday

Abstract. The synthesis of *N*-trimethylstannylamines of the type $RN(SnMe_3)H$ (stannylated anilines) with the sterically encumbered substituents *R* such as Ter [terphenyl, 2,6-bis(2,4,6-trimethylphenyl)-phenyl], Ar* [2,6-bis(diphenylmethyl)-4-methylphenyl], and Mes* (supermesityl, 2,4,6-tri-*tert*-butylphenyl) is described. These stannylated anilines were treated with $BiCl_3$ leading to the formation of $RN(H)BiCl_2$ (for *R* = Ter), $(RNH)_3Bi$ (for *R* = Mes*), and $RN(BiCl_2)_2$ (for *R* = Ar*). The synthesis and structure of the starting material $RN(SnMe_3)H$ and the new aminobismuthanes are reported.

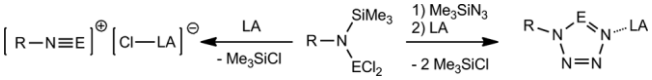
Introduction

Since the fundamental work of *Lappert* and co-workers on stannylated amines [$RR'N(SnMe_3)$; *R*, *R'* = alkyl, aryl],[1–5] there have been only a few investigations on such compounds.[6–11] Although stannylamines are interesting compounds in chemical synthesis, structural data are rare and often analytical data is limited to NMR and vibrational spectroscopic data.[8,9,11] Already in 1965, the group of *Lappert* demonstrated the potential of $(Me_3Sn)NMe_2$ as an amination agent[4] and *Nöth* et al. extensively investigated the use of $N(SnR_3)_3$ in the synthesis of nitrogen-boron compounds.[12–22] For example, the reaction of halogenated boron compounds with $N(SnMe_3)_3$ led to the formation of boron-nitrogen bonds under mild conditions via Me_3SnX (*X* = Cl, Br) elimination (Scheme 1).



Scheme 1. Nitrogen-boron bond formation via R_3SnX elimination (*X* = Cl, Br).

Because Me_3SnCl is readily eliminated from amines, *N*-trimethylstannyl anilines are considered as promising starting materials for the synthesis of low-valent inter-pnictogen compounds. Since our group is especially interested in nitrogen-rich heavy pnictogen species,[23–34] we wanted to investigate the respective stannylated compounds of the type $RN(SnMe_3)BiCl_2$ to achieve intramolecular elimination of Me_3SnCl. Previous studies revealed that the analogous silylated compounds $RN(SiMe_3)BiCl_2$ were unsuitable for the intended reaction protocol (Scheme 2).



Scheme 2. Elimination of Me_3SiCl from $RN(SiMe_3)ECl_2$ (*E* = P, As; *R* = Mes*; LA = Lewis-acid).[25,29]

The elimination of the Me_3Si group could not be facilitated,[33] in contrast to results obtained with lighter homologues, $RN(SiMe_3)ECl_2$ (*E* = P, As; *R* = Mes*).[25,29,34] Hence, we hoped that the elimination of Me_3SnCl might represent a more favorable reaction pathway.

Additionally, it was previously shown that the application of alkali metal amides can be problematic in metathesis reactions with $BiCl_3$.[32,35] This prompted us to investigate alternative pathways to achieve nitrogen–bismuth bond formation under base-free conditions and led to the idea to utilize stannylated anilines with sterically encumbered substituents as starting materials for the synthesis of amino-bismuthanes.

Several routes have been reported for the synthesis of stannylamines in the literature:

(i) The reaction of a lithium amide with Me_3SnCl (Scheme 3) is a straightforward procedure in case of secondary amines.[1] However, the synthesis turned out to be complicated for primary amines, $RN(SnMe_3)H$, due to ligand scramble as illustrated in Scheme 4, leading to the partial formation of free amine and the distannylated compound under certain conditions.[1,6,7] This process prevents the isolation of $RN(SnMe_3)H$ (*R* = small alkyl substituent),[1] whereas *Nöth* and *Storch* were able to synthesize $tBuN(SnMe_3)H$ due to the steric hindrance of the *tert*-butyl group.[7] Moreover, the formation of the distannylated species does not only depend on the steric demand of the substituent *R* but also on the presence of excessive Me_3SnCl or traces of hydrogen chloride as catalysts. Recently, the group of *Nelson* and *Kiplinger* reported

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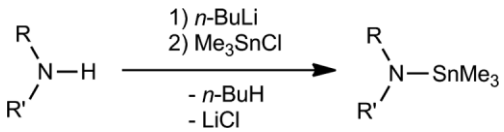
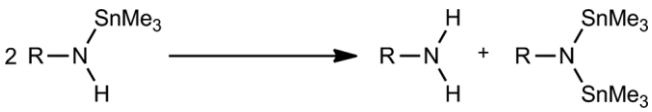
on the synthesis of Mes*N($SnMe_3$)H (Mes* = 2,4,6-tri-*tert*-butylphenyl) utilizing the potassium salt Mes*N(H)K rather than the lithium amide. The reaction of Mes*N(H)K with Me_3SnCl afforded the corresponding stannylated aniline in a clean reaction in over 80% yield. It can be assumed that the formation of the distannylated compound is suppressed by the higher reactivity of the potassium salt.[6]



Scheme 3. General synthesis of stannylated amines via lithium amides (*R* = alkyl, aryl; *R′* = alkyl, aryl, H).



Scheme 4. Formation of the free amine and the distannylated species in a ligand exchange reaction from the stannylated amine (*R* = alkyl, aryl).

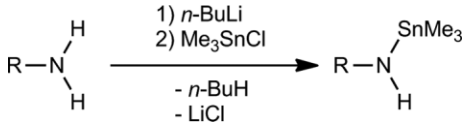
(ii) Another possible method for generating stannylated amines are transamination reactions.[1] $R_3SnNR'_2$ (*R* = alkyl, aryl; *R′* = Me) can be reacted with secondary or primary amines or even directly with ammonia, respectively, to form the stannylated amines.

(iii) An alternative synthesis of *N*-trimethylstannyl-aniline represents the reaction of phenyl azide with Me_3SnH to give PhN($SnMe_3$)H under evolution of N_2.[9] Moreover, when Me_3SnLi is used as stannylating agent instead of Me_3SnH, the reaction afforded the stannylated lithium anilide PhN($SnMe_3$)Li. Unfortunately, this reaction is limited to the phenyl-substituted derivative.[9]

Results and Discussion

Syntheses of Sterically Encumbered Stannylated Anilines of the Type RN(SnMe₃)H [R = Ter (1), Ar (2), Mes* (3)] and Synthesis of RN(SnMe₃)(SiMe₃) [R = Mes* (4)]*

To generate stannylated anilines of the type *R*N($SnMe_3$)H, we applied a synthetic protocol as shown in Scheme 5, which was successfully utilized before for PhN($SnMe_3$)H,[1,8] DippN($SnMe_3$)H (Dipp = 2,6-diisopropylphenyl),[7] and Mes*N($SnMe_3$)H.[5,6] As discussed before, the route is severely hampered by the dismutation reaction (ligand scramble) as illustrated in Scheme 4 leading to the partial formation of *R*NH_2 and *R*N($SnMe_3$)$_2$. We found that this dismutation reaction was even more pronounced when the work-up (see Supporting Information) was carried out under slightly basic conditions, for example, when a frit was used that was treated overnight with ammonia and dried at 120 °C. Only when neutralized glass ware was used under strict exclusion of moisture and oxygen it was possible to isolate compounds **1**, **2**, and **3** in ca. 25% yields (Figure 1). The purity of these species could be increased by repeated recrystallization. Interestingly, the synthesis of the silylated, stannylated aniline, Mes*N($SnMe_3$)($SiMe_3$) (**4**) was carried out without any difficulties since the starting material was a secondary amine, Mes*N($SiMe_3$)H. Hence, compound **4** could be obtained in nearly quantitative yield (96%) as a colorless solid (Figure 1).



Scheme 5. Applied synthesis of bulky stannylated amines (*R* = aryl).

Spectroscopic Characterization

Selected NMR and IR data are listed in Table 1, Table 2, and Table 3. The proton shifts of the Me_3Sn group and coupling constants were detected in the range between –0.19 and 0.29 ppm in CD_2Cl_2, –0.25 and 0.17 ppm in benzene as well as –0.28 and 0.28 in thf (Table 1), in agreement with known literature values for similar species[6–8,18] or for the known compound **3**.[6] The values are comparable to those reported for trimethylsilyl groups attached to amino moieties.[32,36] The ^{13}C NMR resonances (Table 2) of the Me_3Sn group revealed a similar trend as found for the proton resonances (Table 1), namely a small downfield shift for species **3** and **4** compared to **1** and **2** but no significant dependency on the solvent. The ^{119}Sn NMR resonances (measured in [D_6]benzene) were found between 55.0 ppm and 65.1 ppm (**1**: 55.0, **2**: 65.1, **3**: 63.7, and

Table 1. Chemical shifts (δ in ppm) and coupling constants (*J* in Hz) of the Sn(C***H***$_3$)$_3$ group in the ^1H NMR spectra of **1**, **2**, **3**, and **4**.

Compound	Solvent	δ	$^2J(^1H\text{-}^{119}Sn)$	$^2J(^1H\text{-}^{117}Sn)$
1	CD_2Cl_2	–0.28	57.8	55.3
	[D_6]benzene	–0.25	57.2	55.0
	[D_8]thf	–0.28	58.4	55.7
2	CD_2Cl_2	–0.19	56.5	53.8
	[D_6]benzene	0.03	55.9	53.6
	[D_8]thf	0.11	57.4	54.8
3	CD_2Cl_2	0.29 (0.29)[a]	55.1 (51.7)[a]	52.7
	[D_6]benzene	0.17 (0.17)[a]	54.2 (51.7)[a]	52.5
	[D_8]thf	0.24 (0.24)[a]	55.7 (51.7)[a]	53.3
4	CD_2Cl_2	0.26	53.3	51.0
	[D_6]benzene	0.27	52.7	50.4
	[D_8]thf	0.28	53.4	51.6

a) Values in parentheses are taken from Ref. [6].

Table 2. Chemical shift (δ in ppm) and *J* coupling constant (in Hz) of the Sn(***C***H$_3$)$_3$ group in the $^{13}C\{^1H\}$ NMR spectra of **1**, **2**, **3** and **4**.

Compound	Solvent	Δ	$^1J(^{13}C\text{-}^{119}Sn)$	$^1J(^{13}C\text{-}^{117}Sn)$
1	CD_2Cl_2	–4.9	386	369
	[D_6]benzene	–4.9	385	367
2	CD_2Cl_2	–4.7	386	371
	[D_6]benzene	–4.9	378	361
3	CD_2Cl_2	–2.7 (–2.9)[a]	386 (376)[a]	369
	[D_6]benzene	–2.9 (–3.2)[a]	384 (376)[a]	367
4	CD_2Cl_2	–0.6	387	370
	[D_6]benzene	–0.4	387	369

a) Values in parentheses are taken from Ref. [6].

4: 53.7 ppm), which is in the expected range for a trimethyltin group attached to an aniline nitrogen.[6,7,11]

Table 3. Selected IR and Raman data [ν(N–H) in cm^{-1}].

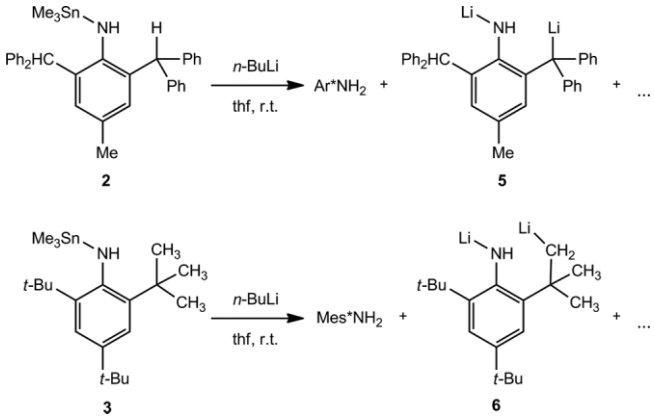
Compound	IR	Raman	Free amine[a)]
1	3321	3314	3384
2	3342	3345	3381
3	3417	3420	3444

a) Raman data, ν_{sym}(N–H).

All compounds were examined by IR and Raman spectroscopy and the characteristic vibrations ν(NH) are listed in Table 3. The IR spectra were recorded with an ATR-IR device without exclusion of air. Hence always small bands, which can be assigned to the ν_{sym}(NH) and ν_{asym}(NH) from the starting material RNH$_2$, were observed in addition to the expected bands of the products. Moreover, often a weak vibrational band at ca. 3600 cm^{-1} was observed, which is in accord to the literature values for the OH stretching vibration of Me_3SnOH.[37–39] A closer look at the hydrolysis process revealed that **3** hydrolyses much faster than compounds **1**, **2**, and **4**. To avoid hydrolysis and reaction with oxygen, Raman spectra were recorded from crystals in a sealed capillary tube under an argon atmosphere. The ν(NH) vibrations were detected as sharp bands between 3314 (**1**) and 3420 (**3**) cm^{-1} which is slightly shifted to lower wave numbers in comparison to the symmetrical stretching vibration of the corresponding free amine RNH$_2$.

Reactivity of RN(SnMe$_3$)H towards nBuLi at Ambient Temperature

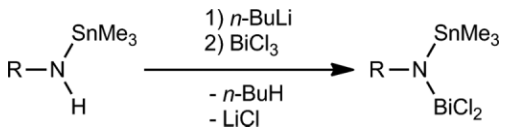
Experiments were run to determine the stability of the stannylated anilines in the presence of *n*BuLi. While all three compounds (**1**–**3**) are readily reacted with *n*BuLi, the formation of the compound RN(SnMe$_3$)Li could not be observed. For example, a solution of **2** dissolved in thf was reacted with *n*BuLi at room temperature (Scheme 6). The resulting red suspension was filtered and concentrated. At 5 °C deep red crystals were obtained, which were highly sensitive towards air and moisture. X-ray diffraction revealed the extrusion of the Me_3Sn moiety and the formation of a doubly lithiated compound **5**, which can be regarded as the di-lithium salt of Ar*NH$_2$. The connectivity of **5** was determined from a low quality data set (Scheme 6, Figure 2, vide infra). In addition, the formation of several other byproducts such as Ar*NH$_2$ were observed. This reaction clearly demonstrated the instability of the stannyl group towards *n*BuLi at ambient temperatures since the Me_3Sn group was immediately removed. Similar decomposition reactions were observed for **3**, but in this case only RNH$_2$ could be identified. It was impossible to crystallize the expected double lithiated species. However, we assume the formation of a similar double lithiated species (**6**) as illustrated in Scheme 6.



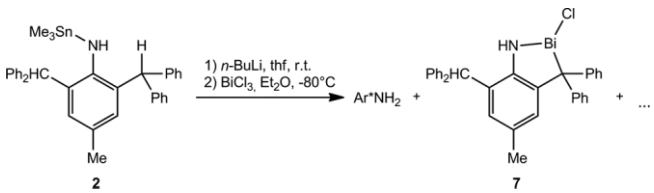
Scheme 6. Reaction of RN(SnMe$_3$)H (R = Ar* and Mes*) with *n*BuLi yielding C–H activation products.

Reaction of RN(SnMe$_3$)H (R = Ar and Mes*) with nBuLi in the Presence of BiCl$_3$*

In analogy to the silylated compounds [RN(SiMe$_3$)H],[32] first RN(SnMe$_3$)H (R = Ar* and Mes*) were treated with a slight excess of *n*BuLi solution at room temperature (Scheme 7). Upon addition to a suspension of $BiCl_3$ in Et_2O at –80 °C, the solvent was removed in vacuo. The black residue was extracted with toluene (Ar*) or *n*-hexane (Mes*), respectively. After concentration of the clear red filtrate, an orange solid immediately precipitated. Recrystallization gave single crystals of a new species in very low yields (ca. 5% yield) besides a black precipitate. It should be noted that larger amounts of RNH$_2$ were also detected. X-ray diffraction studies of the single crystals revealed, in case of Ar*N(SnMe$_3$)H (**2**), the formation of compound **7** (Scheme 8, Figure 3), which can be regarded as the formal product of the reaction of the double lithiated species **5** with $BiCl_3$ (Scheme 6 and Scheme 8).



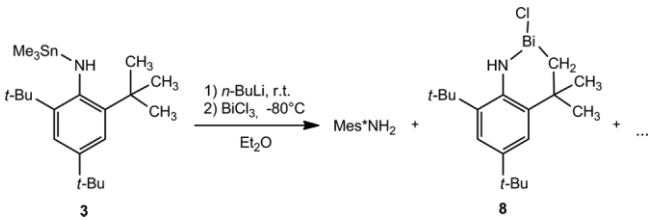
Scheme 7. Intended synthesis protocol for the generation of RN(SnMe$_3$)BiCl$_2$ in analogy to the synthesis of RN(SiMe$_3$)BiCl$_2$.



Scheme 8. Reaction of Ar*N(SnMe$_3$)H with *n*BuLi in the presence of $BiCl_3$.

Utilizing Mes*N(SnMe$_3$)H (**3**) as the starting material, X-ray analysis of the reaction product also revealed the presence of a C–H bond activation product (**8**) (Scheme 9, Figure 4). This finding indicates that also double lithiation had occurred prior to the reaction with $BiCl_3$ as depicted in Scheme 6 (bottom) displaying the lithiated *ortho* alkyl group beside the lithi-

ated amino group. Interestingly, **7** and **8** might be regarded as formal constitution isomers of a chloro-imino bismuthane *R*N=BiCl.

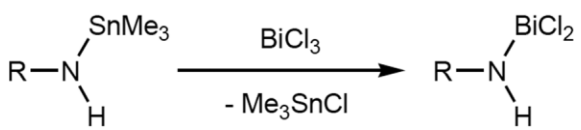


3 8

Scheme 9. Reaction of Mes*N(SnMe$_3$)H with *n*BuLi in the presence of $BiCl_3$.

Reaction of RN(SnMe$_3$)H with BiCl$_3$

Since the synthetic route via lithiated species resulted in the formation of many byproducts including C–H activation, we studied the reaction of *R*N(SnMe$_3$)H with $BiCl_3$ without an additional base. Therefore **1**, **2**, **3**, and **4** were tested with respect to their reactivity towards $BiCl_3$ (Scheme 10). As a typical reaction procedure, the compounds were mixed together as solids and transferred into an NMR tube. The reaction mixture was dissolved in [D$_8$]thf and a ^{1}H NMR spectrum was periodically measured to monitor the reaction progress. Expected products of the reaction of **1** and **3** with $BiCl_3$ were the already known compounds TerN(H)BiCl$_2$[23] or (Mes*NH)$_3$Bi,[40] which were obtained from the reaction of *R*N(H)Li and $BiCl_3$. In these cases the reaction was carried out only in an NMR tube and checked by comparison with authentic samples. Utilizing **1** as amination agent, the reaction afforded the expected products TerN(H)BiCl$_2$ and Me$_3$SnCl. When **3** was applied as amine source in a three to one stoichiometry reaction with $BiCl_3$, (Mes*NH)$_3$Bi was formed, however, only in traces. The main products were "black bismuth", Me$_3$SnCl and Mes*NH$_2$. Also traces of the lower substituted derivatives Mes*N(H)BiCl$_2$ and (Mes*NH)$_2$BiCl could be detected in situ as shown by ^{1}H NMR studies. From these results it can be concluded that the formed (Mes*NH)$_3$Bi rapidly decomposes into "black bismuth", Mes*NH$_2$, and, possibly, azo compounds.



Scheme 10. Intended reaction of *R*N(SnMe$_3$)H with $BiCl_3$ (*R* = aryl).

In contrast, the reaction of **2** with $BiCl_3$ was carried out on a preparative scale, because the expected product Ar*N(H)BiCl$_2$ was unknown in the literature. Ar*N(SnMe$_3$)H was treated with one equiv. of $BiCl_3$ in thf at ambient temperatures. However, after recrystallization from toluene, yellow crystals of Ar*N(BiCl$_2$)$_2$ (**9**) were obtained as proven by single-crystal X-ray analysis. Independent of the stoichiometry of the starting materials, the reaction of $BiCl_3$ with **2** formed always the doubly substituted product **9** (Figure 5) under release of Me$_3$SnCl and HCl. Again, Ar*NH$_2$ was also detected in significant amounts.

Compound **4** showed no reaction at all in the presence of $BiCl_3$, which can be attributed to a good steric protection by the Mes* and Me$_3$Si group. Even after three days only the resonances of **4** were observed in the ^{1}H NMR spectrum.

Structure Elucidation

X-ray quality crystals were selected in Fomblin YR-1800 perfluoroether (Alfa Aesar) at ambient temperature. The samples were cooled to 123(2) K during measurement. Selected structural data for the compounds **1**, **2**, **3**, **4**, and **10** are listed in Table 4, the molecular structures of all considered species are shown in Figure 1, Figure 2, Figure 3, Figure 4, and Figure 5.

Stannylated Species

The compounds **1**, **3** and **4** are highly soluble in common organic solvents. Generally, all stannylated anilines presented here display better solubility than their corresponding free amines. While **1** and **2** were easily crystallized from *n*-hexane or toluene at 5 °C, the crystallization of **3** and **4** was more complicated. Compounds **3** and **4** also crystallize from *n*-hexane, but no crystals suitable for structure elucidation were obtained. X-ray quality crystals of **3** and **4** were obtained from a saturated benzene solution by crystal ripening over 28 h at 35 °C to 40 °C and subsequently cooling to room temperature over 1 h. According to the literature, X-ray quality crystals of **3** can also be obtained from a saturated acetonitrile solution at –30 °C.[6]

Depending on the temperature, **1** crystallizes in two different modifications. The α-phase was obtained by crystallization at –24 °C and the β-phase by crystallization at room temperature. In both cases **1** crystallizes in the monoclinic space group $P2_1/c$. Both unit cells differ mainly in the β-angle (α-phase: 90.339(2)°; β-phase: 104.813(2)°) while the lattice parameters differ only slightly.

Compound **2** crystallizes in the orthorhombic space group *Pnma*. In the solid-state structure, the asymmetric unit contains only half a molecule, because the molecule resides on a crystallographic mirror plane along Sn1–N1–C1.

The crystal structure of **3** was recently published by *Nelson* and *Kiplinger*.[6] Although **3** was crystallized form benzene at room temperature (this work) and not from acetonitrile at –30 °C (*Nelson* and *Kiplinger*), the same modification was obtained in good agreement with our data set. Interestingly, from the reaction mixture of **3**, we were also able to isolate small amounts of single crystals of Mes*N(SnMe$_3$)$_2$ (**10**), which crystallizes in the orthorhombic space group *Pbca* with eight formula units per unit cell (Figure 1).

The sylilated and stannylated compound **4** crystallizes in the monoclinic space group $P2_1/n$ with four formula units per unit cell. Since the Me$_3$Si moiety is quite similar to the Me$_3$Sn group, both groups can occupy the same position. But due to

Table 4. Selected bond lengths /Å, angles /° and dihedral angles /° of **1**, **2**, **3**, **4**, and Mes*N($SnMe_3$)$_2$ (**10**).

	N1–Sn1	N1–C1	C1–N1–Sn1	Sn1–N1–C1–C2
1 (α-phase)	2.068(2)	1.396(2)	125.9(1)	61.3(2)
1 (β-phase)	2.067(2)	1.399(2)	127.8(2)	60.6(3)
2	2.051(4)	1.425(5)	121.6(2)	89.4(3)
3	2.053(2)	1.425(3)	126.1(2)	96.4(2)
4	2.085(5)	1.456(5)	107.3(3)	91.5(3)
10	2.060(2)	1.449(4)	120.8(2)	84.7(3)
	2.069(2)		120.7(2)	

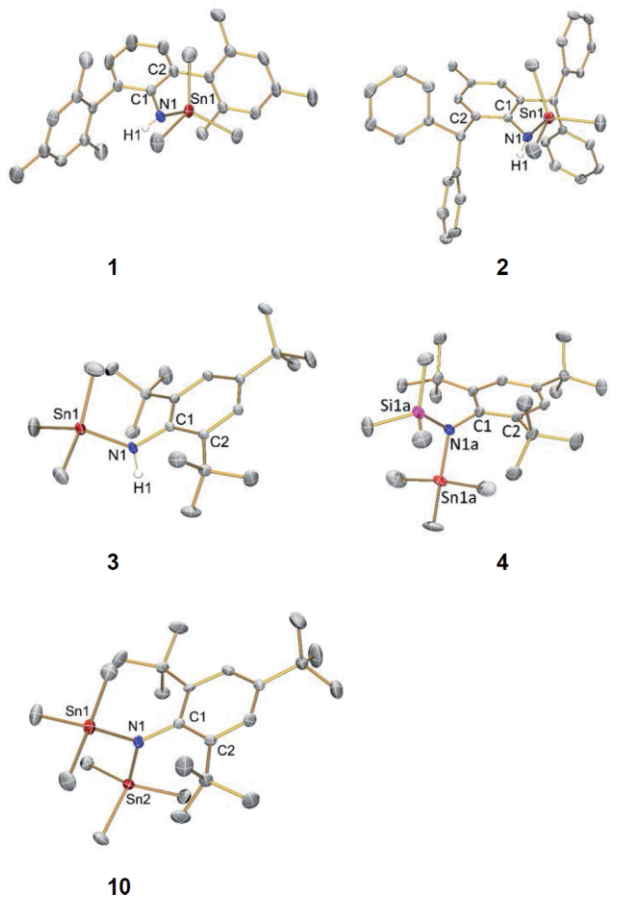


Figure 1. ORTEP drawing of the molecular structures of **1**–**4** and Mes*N($SnMe_3$)$_2$ (**10**). Thermal ellipsoids drawn with 50 % probability at 123 K. Hydrogen atoms are omitted for clarity. Selected bond lengths and angles are listed in Table 4.

the unequal bond lengths around tin and silicon, there are two different geometries of the amino functionality.

All stannylated species **1**–**3** feature a tetrahedral tin atom attached to a trigonal pyramidal nitrogen atom. This stannylated amino moiety sits inside a pocket formed by the bulky substituent (Ter, Ar*, or Mes*). In contrast, for compound **4** and Mes*N($SnMe_3$)$_2$ (**10**) an almost trigonal planar nitrogen atom was found inside the pocket, which can be best explained by a larger hyperconjugative effect of the lone pair located at the nitrogen atom with the antibonding Sn–C and Si–C orbitals. In compound **1**–**3** hyperconjugation with the hydrogen atom is more or less impossible. The N–Sn bond lengths between 2.05–2.09 Å (Table 4) are in the range of a typical polarized Sn–N single bond [cf. Σr_{cov}(Sn–N) = 2.11 Å].[41] Interestingly, the C–N bond lengths very slightly increase along **1** < **2** < **3** < **4** [from 1.396(2) to 1.456 Å, Table 4], possibly due to an increase of the steric demand of the amino moiety in combination with the steric demand of the bulky organic substituent.

CH Activation Product 5

Since the data set was rather poor due to partly decomposition of the highly sensitive compound during the crystal mounting, we want to abstain from a detailed discussion of the crystal data but do want to discuss the unusual connectivity and coordination arrangements in this molecular doubly lithiated species **5**. As depicted in Figure 2, two strongly distorted, tetrahedrally coordinated Li^+ ions are found: Li1 is bonded to the methanide carbon atom C7, whereas Li2 is coordinated by N1. Additionally, Li2 also interacts with two carbon atoms (C18, C9) of one adjacent phenyl group (η^2 mode). Furthermore, each Li^+ ion is coordinated by two thf molecules, of which one acts as bridging ligand between both Li ions (Figure 2).

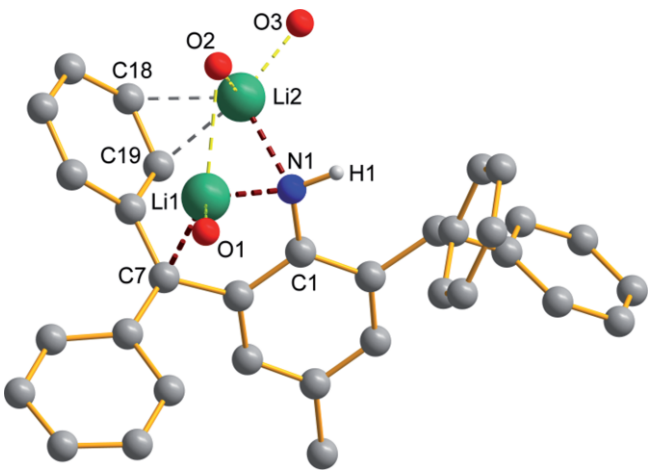


Figure 2. Ball-and-stick representation of C–H activation product **5**. Hydrogen atoms attached to C atoms and all C atoms of the heavily disordered thf molecules are omitted for clarity.

Amino-Bismuthanes

Single crystals of [**7**·$BiCl_3$]$_2$ were obtained in the reaction of Ar*N(Me_3Sn)$_3$H (**2**) with *n*BuLi after addition of $BiCl_3$

(Scheme 5 and Scheme 7). Obviously, in situ generation of doubly lithiated species **5** (Figure 2) led upon reaction with an excess of $BiCl_3$ to $[\mathbf{7}\cdot BiCl_3]_2$. Although the data set is rather poor, the connectivity could be established unequivocally (Figure 3). Neglecting the coordination of the $BiCl_3$ molecules for a moment, the molecular structure consists of a centrosymmetric dimer, which can be regarded as donor-acceptor complex between two molecules of **7** with the nitrogen lone pair as donor and the bismuth atom as acceptor atom. The Bi_2N_2 ring is planar and both Bi atoms are part of a puckered five-membered ring of which each is condensed with the four-membered Bi_2N_2 ring. Taking the interaction of this dimeric species **7** with dimeric $BiCl_3$ into account, a chain-like structure of alternating dimeric **7** and $(BiCl_3)_2$ units is observed in the crystal as depicted in Figure 3 (bottom).

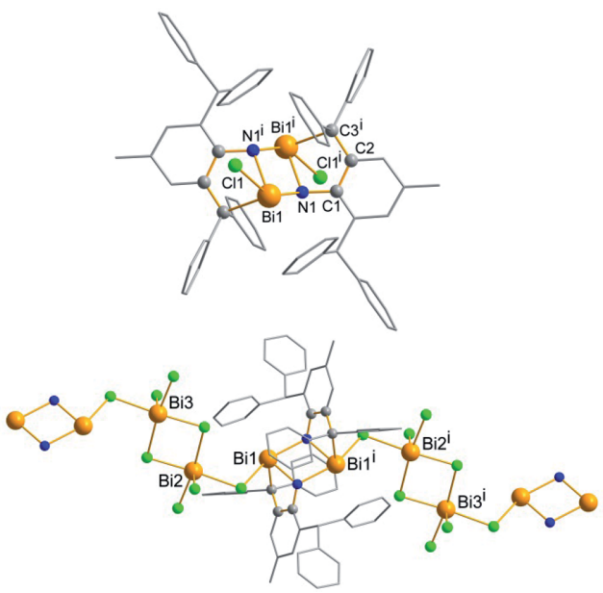


Figure 3. Top: Ball-and-stick representation of the dimeric core in $[\mathbf{7}\cdot BiCl_3]_2$ ($BiCl_3$ omitted for clarity). Bottom: Chain-like structure in $[\mathbf{7}\cdot BiCl_3]_2$. View along *a* axis.

Compound **8** crystallizes as thf diadduct in the triclinic space group $P\bar{1}$ from a saturated thf solution at 5 °C. The molecular structure consists of a centrosymmetric dimer $[\mathbf{8}]_2$ (Figure 4). The monomer **8** is the expected product of the reaction of **6** with $BiCl_3$ (Scheme 5 and Scheme 7). Monomer **8** consists of a trigonal pyramidal Bi atom, which is part of a puckered six-membered ring. The bismuth–nitrogen (2.17 Å) and the bismuth–carbon (2.18 Å) distances are in the expected range for single bonds (vide supra). Additionally, two thf molecules coordinate to the Lewis acidic Bi atom. Furthermore, the chlorine atom attached to the bismuth atom also interacts with an adjacent Lewis acidic bismuth atom of a neighboring molecule of **8**, thereby forming the centrosymmetric dimer [Bi1–Cl1 2.5940(8) Å and Bi1–Cl1' 3.5161(9) Å; cf. Σr_{cov}(Bi–Cl) = 2.50 Å[41] and Σr_{vdW}(Bi···Cl) = 3.82 Å].[42] Hence the arrangement around the Bi atom may be referred to as a [3+3] coordination.

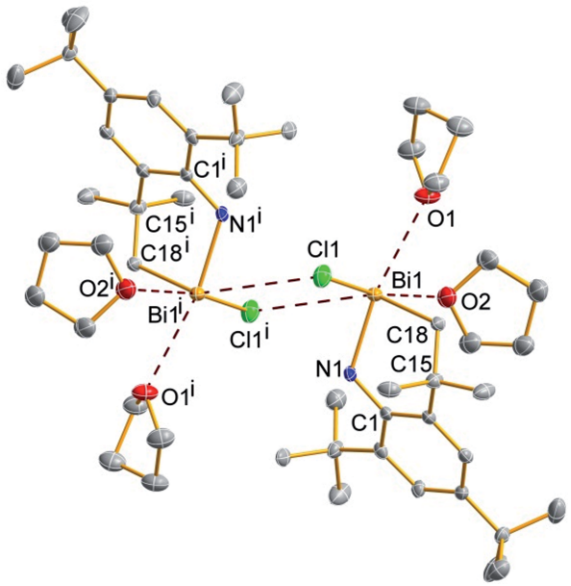


Figure 4. ORTEP drawing of the dimeric structure of **8**. Thermal ellipsoids drawn with 50 % probability at 123 K. Hydrogen atoms are omitted for clarity. Selected bond lengths /Å and angles /°: Bi1–N1 2.168(2), Bi1–C18 2.184(2), Bi1–Cl1 2.5940(8), Bi1–Cl1' 3.5161(9), Bi1–O1 2.96(2), Bi1–O2 2.75(2), Cl1–Bi1–Cl1' 81.56(2), Cl1–Bi1–O1 84.8(2), Cl1–Bi1–O2 166.5(3), O1–Bi1–O2 82.6(6), Cl1'–Bi1–O1 127.8(3), Cl1'–Bi1–O2 110.1(3), Cl1'–Bi1–N1 64.4(3), Cl1'–Bi1–C18 148.7(5).

Compound **9** crystallizes in the orthorhombic space group *Pbcn* with four molecules per unit cell. The molecular structure consists of a planar central nitrogen atom attached to two $BiCl_2$ moieties, which are twisted against each other to form a staggered conformation (Cl1–Bi1–B1'–Cl1' 97.0°). The Bi–N distance [2.150(4) Å] is in accord with a polarized single bond (Figure 5).

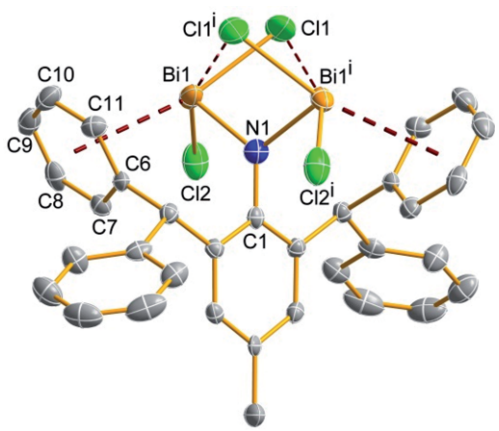


Figure 5. ORTEP drawing of the molecular structure of **9**. Thermal ellipsoids drawn with 50 % probability at 123 K. Hydrogen atoms are omitted for clarity. Selected bond lengths /Å and angles /°: Bi1–Cl1 2.526(2), Bi1–Cl2 2.504(3), Bi1–N1 2.150(4), Bi1–Bi1' 3.6151(7), Cl1–Bi1' 3.345(4), Cl2–Bi1–Cl1 95.7(1), N1–Bi1–Cl1 86.5(2), N1–Bi1–Cl2 94.8(1), C1–N1–Bi1 122.8(2), Bi1–N1–Bi1' 114.5(4).

Interestingly, there are a few secondary interactions (Figure 5): (i) The Cl1···Bi1' distance of 3.35 Å is clearly within

the sum of the van der Waals radii [Σr_{vdW}(Cl···Bi) = 3.82 Å].[42] (ii) Each bismuth atom is η^6 coordinated by one phenyl ring of the Ar* moiety. The Bi···C_{phenyl} distances are between 3.05 Å to 3.58 Å and lie well within the sum of the van der Waals radii of 3.77 Å.[42] Such intramolecular Mentschutkin type complexes[43] are already known for bismuth compounds bearing the Ar*[33,44] and the terphenyl moiety, respectively.[24,30,32] The coordination around the bismuth atom may be regarded as [3+2] coordination leading to a strongly distorted square pyramidal arrangement for the bismuth atom. A triclinic modification of **9** was also observed, but all attempts to obtain a high quality data set failed. Only the connectivity could be proven but no structure solution is given herein. The analogous antimony compound is already known and can be prepared in a metathesis reaction of $SbCl_3$ with the distannadiazane [Ar*NSn]$_2$.[44]

Conclusions

Although it is possible to synthesize the stannylated anilines of the type *R*N(SnMe$_3$)H (*R* = bulky substituent) using lithium amides, it is difficult to isolate the pure products due to ligand scrambling (dismutation) leading to *R*NH$_2$ and *R*N(SnMe$_3$)$_2$ in a side-reaction. The stannylated anilines, however, are highly reactive and cannot be transformed into the corresponding Li amides simply by adding e.g. *n*BuLi since double lithiation can occur at ambient temperatures. Often adjacent C–H bonds are attacked resulting in the formation of di-lithium salts. Upon adding $BiCl_3$, such di-lithium salts are transformed into aminobismuth species bearing five- or six-membered rings with an incorporated N–Bi moiety. Nevertheless, we could show that stannylated anilines can be used for generating interesting Bi-N compounds. Further investigations should concentrate on distannylated compounds of the type *R*N(SnMe$_3$)$_2$. Such compounds could be valuable starting materials in element-nitrogen chemistry for the introduction of a *R*N unit.

Experimental Section

General: All manipulations were carried out in oxygen- and moisture-free conditions in an argon atmosphere using standard Schlenk or dry-box techniques. Dichloromethane (deuterated) was purified according to a literature procedure,[45] dried with P_4O_{10} and CaH_2 and freshly distilled prior to use. Tetrahydrofurane (thf, [D$_8$]thf), Et$_2$O, *n*-hexane, benzene (benzene, [D$_6$]benzene), and toluene were dried with Na/benzophenone and freshly distilled prior to use.

NMR Spectroscopy: ^{1}H-, ^{13}C{^{1}H}-, ^{29}Si-INEPT- and ^{119}Sn NMR spectra were recorded with a Bruker AVANCE 250, a Bruker AVANCE 300, or a Bruker AVANCE 500. The chemical shifts were referenced to solvent signals (CD_2Cl_2: δ = ^{1}H = 5.32, δ = ^{13}C = 54.0; [D$_6$]benzene: δ = ^{1}H = 7.16, δ = ^{13}C = 128.4; [D$_8$]thf: δ = ^{1}H = 1.73 or 3.58, δ = ^{13}C = 25.4 or 67.6).[46] The NMR signals were assigned by DEPT and two-dimensional correlation spectra (HSQC and HMBC) using standard pulse sequences (standard Bruker software).

IR Spectroscopy: A Nicolet 6700 FT-IR spectrometer with a Smart Endurance ATR device was used.

Raman Spectroscopy: A LabRAM HR 800 Horiba Jobin Yvon with a High Stability BX40 Microscop (focus 1 μm) and Olympus Mplan 50 × NA 0.70 objectivs were used. A infrared laser (785 nm, 100 mW, air cooled diode laser), a red laser (633 nm, 17 mW, HeNe-laser), a green laser (532 nm, 50 mW, air cooled, doubled frequency Nd:YAG solid state laser) or a blue laser (473 nm, 20 mW, air cooled solid state laser) were used.

CHN Analyses: Analysator vario micro cube from elementar was used.

Melting points are uncorrected (*EZ*)-Melt, Stanford Research Systems). Heating-rate 20 K·min^{-1} (clearing-points are reported).

DSC: DSC 823e from Mettler-Toledo (Heating-rate 5 K·min^{-1}) was used.

Synthesis of TerN(SnMe$_3$)H (1): A 2.5 M solution of *n*BuLi in *n*-hexane (0.42 mL, 1.05 mmol) was added at 0 °C to a solution of TerNH$_2$ (0.329 g, 1.00 mmol) in ethyl ether (5 mL). The reaction mixture was warmed up to room temperature, stirred for 30 min at this temperature and a solution of Me$_3$SnCl (0.219 g, 1.10 mmol) in Et$_2$O (5 mL) was added dropwise at 0 °C. Upon warming to room temperature the reaction mixture was stirred at room temperature for 4 h. After removal of the solvent in vacuo the white residue was extracted with *n*-hexane (5 mL) and filtered through a Kieselguhr padded frit. Fractional crystallization from a concentrated *n*-hexane solution yielded 0.125 g (0.254 mmol, 25.4 %) of TerN(SnMe$_3$)H (**1**) as colorless crystals. Mp.: 93–95 °C. **EA**: calcd. (found): C 65.87 (65.355), H 7.17 (7.372), N 2.85 (2.783) %. **^{1}H NMR** (298.2 K, CD_2Cl_2, 300.13 MHz): δ = –0.28 [s, 9 H, ^2J{^{1}H-^{117}Sn} = 55.3, ^2J{^{1}H-^{119}Sn} = 57.8 Hz, Sn(C***H***$_3$)$_3$], 2.08 (s, 12 H, *o*-C***H***$_3$), 2.31 (s, 6 H, *p*-C***H***$_3$), 2.51 (broad, 1 H, N***H***), 6.68–6.96 (m, 7 H, arom. C***H***); (298.2 K, [D$_6$]benzene, 300.13 MHz): δ = –0.25 [s, 9 H, ^2J{^{1}H-^{117}Sn} = 55.0, ^2J{^{1}H-^{119}Sn} = 57.2 Hz, Sn(C***H***$_3$)$_3$], 2.22 (s, 6 H, *p*-C***H***$_3$), 2.26 (s, 12 H, *o*-C***H***$_3$), 2.80 (broad, 1 H, N***H***), 6.82–6.99 (m, 7 H, arom. C***H***); (298.2 K, [D$_8$]thf, 300.13 MHz): δ = –0.28 [s, 9 H, ^2J{^{1}H-^{117}Sn} = 55.7, ^2J{^{1}H-^{119}Sn} = 58.4 Hz, Sn(C***H***$_3$)$_3$], 2.08 (s, 12 H, *o*-C***H***$_3$), 2.28 (s, 6 H, *p*-C***H***$_3$), 2.54 (broad, 1 H, N***H***), 6.65–6.92 (m, 7 H, arom. C***H***). **^{13}C{^{1}H} NMR** (298.2 K, CD_2Cl_2, 75.5 MHz): δ = –4.9 [s, ^1J{^{13}C-^{117}Sn} = 369, ^1J{^{13}C-^{119}Sn} = 386 Hz], 20.9 (s, *o*-***C***H$_3$), 21.3 (s, *p*-***C***H$_3$), 116.8 (arom. ***C***H), 129.0 (arom. ***C***H), 129.6 (arom. ***C***), 130.0 (arom. ***C***H), 137.1 (s, arom. ***C***), 137.1 (s. arom. ***C***), 137.8 (s. arom. ***C***), 148.4 (s, arom. ***C***); (298.2 K, [D$_6$]benzene, 75.5 MHz): δ = –4.9 [s, ^1J{^{13}C-^{117}Sn} = 367, ^1J{^{13}C-^{119}Sn} = 385 Hz, Sn(***C***H$_3$)$_3$], 21.3 (s, *o*-***C***H$_3$), 21.5 (s, *p*-***C***H$_3$), 117.9 (s, arom. ***C***), 129.4 (s, arom. ***C***), 129.9 (s, arom. ***C***), 130.3 (s, arom. ***C***), 137.0 (s, arom. ***C***), 137.5 (s, arom. ***C***), 137.9 (s, arom. ***C***), 148.3 (s, arom. ***C***). **^{119}Sn NMR** (298.2 K, [D$_6$]benzene, 111.85 MHz): δ = 55.0 (s) ppm. **Raman** (laser 633 nm, accumulation time 60 s, scans 10): $\tilde{\nu}$ = 3314 (2), 3045 (2), 3013 (3), 2916 (6), 2858 (2), 2731 (1), 1610 (8), 1582 (4), 1479 (2), 1439 (2), 1378 (3), 1301 (10), 1279 (4), 1234 (1), 1199 (2), 1183 (1), 1163 (1), 1077 (3), 1003 (3), 945 (2), 850 (2), 744 (1), 641 (1), 631 (1), 575 (7), 541 (7), 517 (10), 452 (3), 399 (3), 350 (1), 327 (2), 270 (2), 217 (2) cm^{-1}. **IR** (ATR, 32 scans): ν(NH) = 3321 (w) cm^{-1}.

Synthesis of Ar*N(SnMe$_3$)H (2): A 2.5 M solution of *n*BuLi in *n*-hexane (0.42 mL, 1.05 mmol) was added dropwise at 0 °C to a solution of Ar*NH$_2$ (0.440 g, 1.00 mmol) in thf (20 mL). After the dark red reaction mixture was stirred for 30 min at room temperature, a solution of Me$_3$SnCl (0.219 g, 1.10 mmol) in thf (10 mL) was added dropwise at 0 °C. The reaction mixture was stirred for additional 2.5 h at room temperature and the solvent was removed in vacuo. The yellowish residue was extracted with toluene (15 mL) and filtered through a

Kieselguhr padded frit. A mixture of Ar*N($SnMe_3$)H (**2**) and Ar*NH_2 was obtained by fractional crystallization from a saturated toluene solution. Yield Ar*N($SnMe_3$)H (**2**): 0.153 g (0.254 mmol, 25.4 %). Mp.: 191.8 °C (decom.). **EA**: calcd. (found): C 71.78 (72.086), H 6.19 (6.023), N 2.33 (2.099) %. **^{1}H NMR** (298.2 K, CD_2Cl_2, 300.13 MHz): δ = –0.19 [s, 9 H, $^2J\{^1H\text{-}^{117}Sn\}$ = 55.9, $^2J\{^1H\text{-}^{119}Sn\}$ = 56.5 Hz, Sn(C***H***$_3$)$_3$], 2.03 (s, 3 H, *p*-C***H***$_3$), 2.16 (broad, 1 H, N***H***), 5.73 (s, 2 H, C***H***Ph$_2$), 6.47 [s, 2 H, (Ph$_2$C***H***)$_2$C$_6$***H***$_2$(CH$_3$)N(SnC$_3$H$_9$)H] 7.01–7.30 (m, 20 H, arom. C***H***); (298.2 K, [D$_6$]benzene, 300.13 MHz): δ = 0.03 [s, 9 H, $^2J\{^1H\text{-}^{117}Sn\}$ = 53.6, $^2J\{^1H\text{-}^{119}Sn\}$ = 55.9 Hz, Sn(C***H***$_3$)$_3$], 1.92 (s, 3 H, *p*-C***H***$_3$), 2.16 (broad, 1 H, N***H***), 6.02 (s, 2 H, C***H***Ph$_2$), 6.87 [s, 2 H, (Ph$_2$C***H***)$_2$C$_6$***H***$_2$(CH$_3$)N(SnC$_3$H$_9$)H], 7.01–7.25 (m, 20 H, arom. C***H***); (296.7 K, [D$_8$]thf, 300.13 MHz): δ = 0.11 [s, 9 H, $^2J\{^1H\text{-}^{117}Sn\}$ = 54.8, $^2J\{^1H\text{-}^{119}Sn\}$ = 57.4 Hz, Sn(C***H***$_3$)$_3$], 1.98 (s, 3 H, *p*-C***H***$_3$), 2.21 (broad, 1 H, N***H***), 5.84 (s, 2 H, C***H***Ph$_2$), 6.47 [s, 2 H, (Ph$_2$C***H***)$_2$C$_6$***H***$_2$(CH$_3$)N(SnC$_3$H$_9$)H], 7.01–7.24 (m, 20 H, arom. C***H***) ppm. **^{13}C{^{1}H} NMR** (298.2 K, CD_2Cl_2, 75.5 MHz): δ = –4.7 [$^1J\{^{13}C\text{-}^{117}Sn\}$ = 371, $^1J\{^{13}C\text{-}^{119}Sn\}$ = 386 Hz, Sn(***C***H$_3$)$_3$], 21.4 (s, ***C***H$_3$), 52.9 (s, ***C***HPh$_2$), 126.7 (s, arom. ***C***), 128.8 (s, arom. ***C***), 130.2 (s, arom. ***C***), 136.6 (s, arom. ***C***), 143.5 (s, arom. ***C***), 144.9 (s. arom. ***C***), 146.5 (s. arom. ***C***); (298.2 K, [D$_6$]benzene, 75.5 MHz): δ = –4.9 [s, $^1J\{^{13}C\text{-}^{117}Sn\}$ = 361, $^1J\{^{13}C\text{-}^{119}Sn\}$ = 378 Hz, Sn(***C***H$_3$)$_3$], 21.5 (s, ***C***H$_3$), 53.2 (s, ***C***HPh$_2$), 126.9 (s, arom. ***C***), 129.0 (s, arom. ***C***), 130.5 (s, arom. ***C***), 137.6 (s, arom. ***C***), 145.4 (s, arom. ***C***), 146.7 (arom. ***C***) ppm. **^{119}Sn NMR** (298.2 K, [D$_6$]benzene, 111.85 MHz): δ = 65.1 (s) ppm. **Raman** (laser: 633 nm, accumulation time: 20 s, scans: 10): $\tilde{\nu}$ = 3345 (1), 3060 (2), 3048 (3), 3041 (1), 2977 (1), 2915 (1), 2862 (1), 1599 (2), 1380 (1), 1296 (1), 1258 (2), 1237 (1), 1198 (1), 1187 (2), 1172 (2), 1157 (1), 1152 (1), 1129 (1), 1075 (1), 1032 (4), 1001 (10), 980 (2), 918 (1), 864 (1), 833 (2), 820 (1), 785 (1), 746 (1), 702 (1), 683 (19, 648 (1), 634 (1), 618 (2), 604 (1), 532 (3), 510 (6), 472 (1), 438 (1), 339 (1), 292 (1), 266 (1), 248 (1), 233 (1), 218 (1) cm^{-1}. **IR** (ATR, 32 scans): $\tilde{\nu}$ = 3342 (w), 3103 (w), 3082 (w), 3057 (w), 3022 (w), 2978 (w), 2906 (w), 2860 (w), 1597 (w), 1493 (m), 1452 (m), 1441 (m), 1391 (w), 1335 (w), 1315 (w), 1279 (w), 1257 (m), 1238 (w), 1215 (w), 1192 (w), 1176 (w), 1153 (w), 1128 (w), 1076 (w), 1032 (m), 1003 (w), 982 (w), 966 (w), 916 (w), 885 (w), 860 (w), 833 (m), 822 (w), 760 (s), 744 (m), 694 (s), 683 (s), 648 (m), 635 (m), 621 (m), 604 (s), 557 (m), 530 (s) cm^{-1}.

Synthesis of Mes*N($SnMe_3$)H (3): To a stirred solution of Mes*NH_2 (0.261 g, 1.00 mmol) in thf (5 mL) was added a 2.5 M solution of *n*BuLi in *n*-hexane (0.42 mL, 1.05 mmol) at 0 °C. The solution was stirred 30 min at room temperature and a solution of Me_3SnCl (0.219 g, 1.10 mmol) in thf (5 mL) was added at 0 °C. This reaction mixture was stirred 4 h at room temperature and afterward the solvent was removed in vacuo. The residue was extracted with *n*-hexane (5 mL) and filtered through Kieselguhr. Removal of the solvent resulted in a colorless solid. Yield: 0.10 g (0.236 mmol, 23.6 %).* X-ray quality crystals can be obtained from a saturated benzene solution. Repeated recrystallization at 45 °C from benzene yields a pure sample of Mes*N($SnMe_3$)H (**3**). Crystals of Mes*N($SnMe_3$)$_2$ were also obtained from such a reaction by fractional crystallization. Mp.: 68.9 °C (lit.: 66–67 °C).[6] **EA**: calcd. (found): C 59.45 (60.381), H 9.27 (9.466), N 3.30 % (3.366) %. **^{1}H NMR** (298.2 K, CD_2Cl_2, 300.13 MHz): δ = 0.29 [s, 9 H, $^2J\{^1H\text{-}^{117}Sn\}$ = 52.7, $^2J\{^1H\text{-}^{119}Sn\}$ = 55.1 Hz, Sn(C***H***$_3$)$_3$], 1.27 [s, 9 H, *p*-C(C***H***$_3$)$_3$], 1.46 [s, 18 H, *o*-C(C***H***$_3$)$_3$], 2.73 (broad, 1 H, NH), 7.21 (s, 2 H, arom. C***H***); (298.2 K, [D$_6$]benzene, 300.13 MHz): δ = 0.17 [s, 9 H, $^2J\{^1H\text{-}^{117}Sn\}$ = 52.5, $^2J\{^1H\text{-}^{119}Sn\}$ = 54.2 Hz, Sn(C***H***$_3$)$_3$], 1.38 [s, 9 H, *p*-C(C***H***$_3$)$_3$], 1.56 [s, 18 H, *o*-C(C***H***$_3$)$_3$], 2.67 (broad, 1 H, NH), 7.47 (s, 2 H, arom. C***H***); (298.2 K, [D$_8$]thf, 300.13 MHz): δ = 0.24 [s, 9 H, $^2J\{^1H\text{-}^{117}Sn\}$ = 53.3, $^2J\{^1H\text{-}^{119}Sn\}$ = 55.7 Hz, Sn(C***H***$_3$)$_3$], 1.25 [s, 9 H, *p*-C(C***H***$_3$)$_3$], 1.46 [s, 18 H, *o*-C(C***H***$_3$)$_3$], 2.77 (broad, 1 H, N***H***), 7.18 (s, 2 H, arom. C***H***). **^{13}C{^{1}H} NMR** (298.2 K, CD_2Cl_2, 75.5 MHz): δ = –2.7 [s, $^1J\{^{13}C\text{-}^{117}Sn\}$ = 369, $^1J\{^{13}C\text{-}^{119}Sn\}$ = 386 Hz, Sn(***C***H$_3$)$_3$], 32.0 [s, *p*-C(***C***H$_3$)$_3$], 32.4 [s, *o*-C(***C***H$_3$)$_3$], 34.8 [s, *o*-***C***(CH$_3$)$_3$], 36.4 [s, *o*-***C***(CH$_3$)$_3$], 122.7 (arom. ***C***), 140.8 (arom. ***C***), 142.4 (arom. ***C***), 148.5 (arom. ***C***); (298.2 K, [D$_6$]benzene, 75.5 MHz): δ = –2.9 [s, $^1J\{^{13}C\text{-}^{117}Sn\}$ = 367, $^1J\{^{13}C\text{-}^{119}Sn\}$ = 384 Hz, Sn(***C***H$_3$)$_3$], 32.3 [s, *p*-C(***C***H$_3$)$_3$], 32.8 [s, *o*-C(***C***H$_3$)$_3$], 35.0 [s, *p*-***C***(CH$_3$)$_3$], 36.6 [s, *o*-***C***(CH$_3$)$_3$], 122.8 (arom. ***C***), 141.4 (arom. ***C***), 143.0 (arom. ***C***), 148.4 (arom. ***C***). **^{119}Sn NMR** (298.2 K, [D$_6$]benzene, 111.85 MHz): δ = 63.7 (s) ppm. **Raman** (laser: 632 nm, accumulation time: 20 s, 10 Scans): $\tilde{\nu}$ = 3420 (1), 2960 (2), 2915 (3), 2771 (1), 2703 (1), 1600 (2), 1469 (1), 1444 (1), 1422 (1), 1388 (1), 1360 (1), 1287 (1), 1242 (1), 1194 (3), 1188 (3), 1144 (1), 1119 (1), 1022 (1), 927 (1), 829 (2), 813 (1), 756 (1), 741 (1), 644 (1), 568 (1), 537 (5), 523 (2), 508 (10), 460 (1), 338 (1), 258 (1), 201 (1) cm^{-1}. **IR** (ATR, 16 scans): ν(NH) = 3417 (w) cm^{-1}.

Synthesis of Mes*N($SiMe_3$)$SnMe_3$ (4): To a stirred solution of Mes*N($SiMe_3$)H (0.668 g, 2.00 mmol) in thf (10 mL) was added a 2.5 M *n*BuLi solution in *n*-hexane (0.84 mL, 2.10 mmol) dropwise at room temperature. After 10 min a solution of Me_3SnCl (0.409 g, 2.05 mmol) in thf (5 mL) was added dropwise at room temperature and the reaction mixture was stirred for 2 h. Afterward the solvent was removed in vacuo and the residue was extracted with *n*-hexane (7 mL). The solvent was removed again after filtration through a Kieslguhr padded frit. The resulting solid was dried in vacuo. Yield: 0.957 g (1.93 mmol, 96.4 %). X-ray quality crystals could be obtained from a saturated benzene solution at room temperature. Mp.: 80 °C. **EA**: calcd. (found): C 58.07 (58.463), H 9.54 (9.134), N 2.82 (2.594) %. **^{1}H NMR** (296.9 K, CD_2Cl_2, 300.13 MHz): δ = 0.13 [s, 9 H, $^2J\{^1H\text{-}^{29}Si\}$ = 6.2 Hz, Si(C***H***$_3$)$_3$], 0.26 [s, 9 H, $^2J\{^1H\text{-}^{117}Sn\}$ = 51.0, $^2J\{^1H\text{-}^{119}Sn\}$ = 53.3 Hz, Sn(C***H***$_3$)$_3$], 1.27 [s, 9 H, *p*-C(C***H***$_3$)$_3$], 1.47 [s, 18 H, *o*-C(C***H***$_3$)$_3$], 7.31 (s, 2 H, arom. C***H***); (298.2 K, [D$_6$]benzene, 300.13 MHz): δ = 0.27 [s, 18 H, $^2J\{^1H\text{-}^{29}Si\}$ was not observed, $^2J\{^1H\text{-}^{117}Sn\}$ = 50.4, $^2J\{^1H\text{-}^{119}Sn\}$ = 52.7 Hz, Si(C***H***$_3$)$_3$ and Sn(C***H***$_3$)$_3$], 1.32 [s, 9 H, *p*-C(C***H***$_3$)$_3$], 1.58 [s, 18 H, *o*-C(C***H***$_3$)$_3$], 7.52 (s, 2 H, arom. C***H***); (298.2 K, [D$_8$]thf, 300.13 MHz): δ = 0.13 [s, 9 H, $^2J\{^1H\text{-}^{29}Si\}$ = 6.0 Hz, Si(C***H***$_3$)$_3$], 0.28 [s, 9 H, $^2J\{^1H\text{-}^{119}Sn\}$ = 53.4, $^2J\{^1H\text{-}^{117}Sn\}$ = 51.6 Hz], 1.27 [s, 9 H, *p*-C(C***H***$_3$)$_3$], 1.49 [s, 18 H, *o*-C(C***H***$_3$)$_3$], 7.34 (s, 2 H, arom. C***H***). **^{13}C{^{1}H} NMR** (298.2 K, CD_2Cl_2, 75.5 MHz): δ = –0.6 [s, $^1J\{^{13}C\text{-}^{117}Sn\}$ = 370, $^1J\{^{13}C\text{-}^{119}Sn\}$ = 387 Hz, Sn(***C***H$_3$)$_3$], 4.7 [s, Si(***C***H$_3$)$_3$], 31.7 [s, *p*-C(***C***H$_3$)$_3$], 34.8 [s, *p*-***C***(CH$_3$)$_3$], 35.2 [s, *o*-C(***C***H$_3$)$_3$], 38.4 [s, *o*-***C***(CH$_3$)$_3$], 125.0 (s, arom. ***C***H), 143.9 (s, arom. ***C***), 146.5 (s, arom. ***C***), 148.2 (arom. ***C***); (298.2 K, [D$_6$]benzene, 75.5 MHz): δ = –0.4 [s, $^1J\{^{13}C\text{-}^{117}Sn\}$ = 369, $^1J\{^{13}C\text{-}^{119}Sn\}$ = 387 Hz, Sn(***C***H$_3$)$_3$], 5.0 [s, Si(***C***H$_3$)$_3$], 32.0 [s, *p*-C(***C***H$_3$)$_3$], 34.9 [s, *p*-***C***(CH$_3$)$_3$], 35.5 [s, *o*-C(***C***H$_3$)$_3$], 38.6 [s, *o*-***C***(CH$_3$)$_3$], 125.3 (s, arom. ***C***H), 144.2 (s, arom. ***C***), 146.5 (s, arom. C), 148.4 (s, arom. ***C***). **^{29}Si INEPT NMR** (296.8 K, CD_2Cl_2, 59.6 MHz): δ = 2.5 (m); (298.2 K, [D$_6$]benzene, 59.6 MHz): δ = 2.7 (m) ppm. **^{119}Sn{^{1}H} NMR** (298.2 K, [D$_6$]benzene, 111.85 MHz): δ = 53.7 (s) ppm. **IR** (ATR, 32 scans): $\tilde{\nu}$ = 3070 (w), 2958 (s), 2949 (2), 2904 (m), 2866 (m), 1622 (w), 1603 (w), 1551 (w), 1462 (w), 1406 (m), 1391 (m), 1360 (m), 1283 (w), 1263 (m), 1250 (s), 1221 (m), 1182 (s), 1146 (m), 1109 (m), 1020 (w), 926 (m), 914 (m), 891 (s), 837 (s), 770 (s), 756 (s), 721 (m), 702 (m), 679 (m), 656 (m), 644 (m), 623 (m), 536 (s) cm^{-1}. **Raman** (laser: 633 nm, accumulation time: 30 s, 10 scans): $\tilde{\nu}$ = 3071 (1), 2953 (3), 2905 (6), 1606 (1), 1471 (1), 1407 (1), 1285 (1), 1265 (1), 1203 (2), 1192 (3), 1148 (2), 1110 (1), 934 (1), 916 (1), 847 (1), 821 (3), 703 (2), 680 (1), 647 (1), 639 (1), 626 (2), 569 (2), 539 (3), 509 (10), 456 (1), 406 (1), 304 (1), 189 (3), 177 (3), 150 (3), 126 (4), 100 (3), 80 (4) cm^{-1}.

Supporting Information (see footnote on the first page of this article): Crystallographic details and spectra (^{1}H NMR, IR, Raman) of the stannylated anilines and experimental details for the reactions of the stannylated anilines with $BiCl_3$ and *n*-BuLi are given.

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Keywords: Aminobismuthane; Lithiation; Stannylated aniline; Synthesis; Structure elucidation

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