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Precise measurements of $^{115/117/119}$Sn NMR frequencies and first observation of isotope-induced chemical shifts $^{1}\Delta^{117/119}$Sn(^{15}N), $^{1}\Delta^{115/119}$Sn(^{15}N), and $^{2}\Delta^{117/119}$Sn(^{29}Si) in *N*-trimethylstannyl amines[☆]

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Abstract

Tris(trimethylstannyl)amine **1** and trimethylsilyl-bis(trimethylstannyl)amine **2** (both ca. 13% ^{15}N labelled) were studied by $^{115/117/119}$Sn-, ^{15}N-, and ^{29}Si NMR spectroscopy. Precise measurements of the Sn NMR frequencies of the respective Sn/^{15}N isotopomers did not reveal any appreciable primary isotope effect, in agreement with the previous results. The standard frequencies Ξ(^{119}Sn) and Ξ(^{117}Sn), determined for tetramethyltin more than 30 years ago, were found to be very accurate, and Ξ(^{115}Sn) = 32.718781 MHz was measured in this work. In the ^{15}N NMR spectra, small secondary isotope effects $^{1}\Delta^{117/119}$Sn(^{15}N) and $^{1}\Delta^{115/119}$Sn(^{15}N) could be detected for the first time, the ^{15}N nucleus in the heavier isotopomer being more shielded. In the ^{29}Si NMR spectrum of **2**, the expected isotope-induced chemical shift $^{1}\Delta^{14/15}$N(^{29}Si) is shown, and in addition the so far unknown effect over two bonds $^{2}\Delta^{117/119}$Sn(^{29}Si) is visible. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Amines; Tin; Tin–; Nitrogen–; Silicon NMR; Isotope-induced chemical shifts

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1. Introduction

Of all elements tin possesses the largest number of stable isotopes from ^{112}Sn (0.96%) to ^{124}Sn (5.94%), the most abundant being ^{120}Sn (32.85%). Tin is also unique, since there are three spin-1/2 nuclei, suitable for NMR experiments, namely ^{115}Sn (0.35%), ^{117}Sn (7.61%) and ^{119}Sn (8.58%), all of which have a receptivity for NMR experiments either close to that of ^{13}C (^{115}Sn) or larger by a factor >20 (^{117}Sn, ^{119}Sn) [1,2]. The nucleus of choice for NMR studies is normally ^{119}Sn, but ^{117}Sn NMR spectra can be measured almost with the same sensitivity, and there are applications of ^{115}Sn NMR [3]. For many tin compounds, the $^{115/117/119}$Sn resonance frequencies can in principle be determined with high accuracy, although this is not routinely done. Frequently the $^{115/117/119}$Sn resonance signals in solutions are somewhat broadened by exchange processes due to dynamic association processes, by slow molecular motion and/or by slow motion of groups attached to the tin nucleus, or by partially relaxed scalar indirect nuclear spin–spin coupling of the tin nuclei with quadrupolar nuclei

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[☆] Dedicated to Professor Graham A. Webb on the occasion of his 65th birthday.

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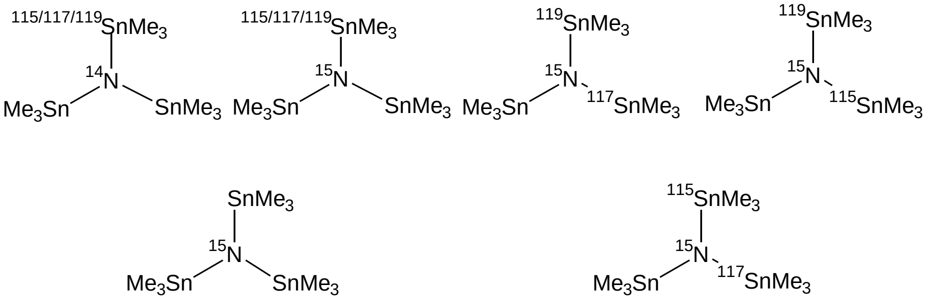

Scheme 1. Relevant isotopomers for NMR studies of tris(trimethylstannyl)amine **1**.

[1,2]. High precision $^{115/117/119}$Sn frequency measurements are available so far only for tetramethyltin, Me_4Sn [4,5], the accepted reference for Sn chemical shifts. Primary isotope effects on shielding and coupling constants involving the tin nuclei appear to be close to zero [6]. Isotope induced chemical shifts of other nuclei due to the presence of ^{115}Sn, ^{117}Sn or ^{119}Sn have not been noted. In order to get a more clear picture on these issues, we have determined the precise frequency of ^{115}Sn in Me_4Sn, and we have been looking for a suitable compound, in which there are at least three chemically equivalent tin atoms present, all linked directly to a magnetically active nucleus, for which the resonance can be observed within short time, and for which the nuclear shielding might likely to be affected by small changes in its surroundings, e.g. by the changes in the mass of the tin isotopes. The final choice was tris(trimethylstannyl)amine, $N(SnMe_3)_3$ **1**, ^{15}N labelled (ca. 13%).

2. Results and discussion

2.1. General

Starting to look for a suitable compound, we first selected tris(trimethylstannyl)methane, $HC(SnMe_3)_3$, and tetrakis(trimethylstannyl)methane, $C(SnMe_3)_4$ (see Ref. [7] for previous NMR studies). The measurements were not very successful, owing to the low natural abundance of the ^{13}C nucleus which made it difficult to record the spectra of the isotopomer containing ^{13}C/^{115}Sn within short time. Prolonged measurement times led to slight broadening of the ^{13}C resonance signal for the central carbon atom, preventing a highly accurate determination of relevant frequencies. We refrained from preparing ^{13}C labelled material, since the outcome of the measurements seemed to be doubtful, and part of the expensive preparation is not necessarily a high-yield procedure.

Considering the long transversal relaxation time of ^{15}N nuclei [8], in the absence of protons attached to nitrogen giving rise to extremely sharp ^{15}N resonances, partially ^{15}N labelled tris(trimethylstannyl)amine, $N(SnMe_3)_3$ **1**, appeared to be a better candidate. This compound is readily available by the quantitative reaction of $Me_2N{-}SnMe_3$ with ^{15}N labelled ammonia (see Section 4). Scheme 1 shows the most abundant isotopomers relevant to NMR spectroscopy of this compound (ignoring the methyl groups). Compound **1** (^{15}N labelled or unlabelled) has been repeatedly studied mainly with respect to the signs of coupling constants [9–12]. The measurements carried out in this work were aiming for precise $^{115/117/119}$Sn resonance frequencies, in order to find primary isotope effects, and for precise ^{15}N NMR frequencies in order to detect secondary isotope effects, arising from the presence of various tin isotopes. In addition to **1**, the ^{15}N labelled *N*-trimethylsilyl-*N*,*N*-bis(trimethylstannyl)amine, $Me_3Si{-}N(SnMe_3)_2$ **2**, available from **1** by the reaction with Me_3SiCl [13], was prepared and studied by tin NMR as well as by ^{15}N- and ^{29}Si NMR. A list of experimental NMR data for the compounds **1** and **2** is given in Table 1.

2.2. Tin NMR measurments

$^{115/117/119}$Sn NMR spectra were measured by the

Table 1
^{15}N-, ^{119}Sn- and ^{29}Si NMR parameters of the compounds **1** and **2**. (Compound **1** in D_8-toluene (ca. 15% v/v); compound **2** in C_6D_6 (ca. 15% v/v), both in 5 mm (OD) tubes, measured at 23 ± 1°C; accuracy of chemical shifts δ better than ±0.05 ppm (δ^{13}C ± 0.1); coupling constants $J(^{29}\mathrm{Si},X)$ are given in ( ), $J(^{119}\mathrm{Sn},X)$ in [ ], $J(^{117}\mathrm{Sn},X)$ in { }, and $J(^{115}\mathrm{Sn},X)$ in < >, with an accuracy better than ± = 0.03 Hz; data were reproduced by using three different spectrometers. Isotope induced chemical shifts $^1\Delta$ and $^2\Delta$ in ppb (±0.2); a negative sign denotes a shift to higher frequency with respect to the NMR signal of the respective lighter isotopomer)

No	δ^{13}C	δ^{15}N	δ^{119}Sn		$^1\Delta^{14/15}$N(^{119}Sn)		$^1\Delta^{115/119}$Sn(^{119}Sn)	$^1\Delta^{117/119}$Sn(^{119}Sn)	
1	− 1.1 [364.5]	− 396.2 [83.68] {79.97} <73.42>	87.8 [185.7] {170.4} <163.3>		− 38.4		− 3.2	− 1.7	
				δ^{29}Si		$^1\Delta^{14/15}$N(^{29}Si)	$^1\Delta^{28/29}$Si(^{15}N)	$^1\Delta^{117/119}$Sn(^{119}Sn)	$^2\Delta^{117/119}$Sn(^{29}Si)
2	− 1.7 (MeSn) [378.0, 4.1] 6.1 (MeSi) (54.1) [10.2]	− 375.4 [61.43] {58.70} (6.54)	64.7 [185.7] (7.55)	5.79 [7.55] {7.21}	− 46.7	− 10.5	− 2.2	− 1.0	− 0.8

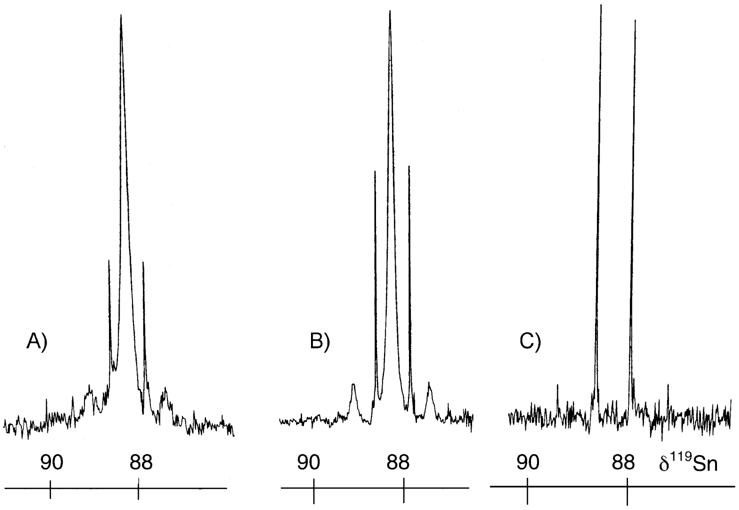

Fig. 1. 111.9 MHz ^{119}Sn NMR spectra of tris(trimethylstannyl)amine, $N(SnMe_3)_3$ **1** (labelled ca. 13% with ^{15}N), after eight transients. (A) Recorded with inverse gated ^{1}H decoupling; the dominant broad central signal represents the ^{119}Sn/^{14}N isotopomer, the broad satellites are due to the $^{119/117}$Sn/^{14}N isotopomer, the sharp doublet due to the ^{119}Sn/^{15}N isotopomer is already visible; (B) Recorded with the refocused INEPT pulse sequence and ^{1}H decoupling [14–17]; the intensity of the broad central line is already somewhat reduced due to loss of magnetisation during the refocusing delays in the pulse sequence; (C) Recorded with the INEPT-HEED pulse sequence [18], by which the magnetisation of the ^{119}Sn/^{14}N isotopomer decays to zero as a result of additional delays (two times 75 ms in the Hahn-echo extension).

refocused INEPT pulse sequence with ^{1}H decoupling [14–17]. Polarisation transfer was based on the coupling constants $^2J(\mathrm{Sn}, ^1\mathrm{H}) = 57$ Hz(^{119}Sn), 54.5 Hz (^{117}Sn) and 50.0 Hz (^{115}Sn). The effect of the presence of the quadrupolar ^{14}N nucleus on all tin NMR spectra is readily seen by the inspection of ^{119}Sn NMR spectra of **1** in Fig. 1. The 'normal' ^{1}H decoupled ^{119}Sn NMR spectrum (here recorded by inverse gated decoupling in order to suppress the negative NOE, since $\gamma(^{115/117/119}\mathrm{Sn}) < 0$) shows the dominant broad central line due to the isotopomer containing ^{14}N/^{119}Sn (Fig.1(A)). In the ^{119}Sn NMR spectrum recorded by the ^{1}H decoupled refocused INEPT pulse sequence [14–17], the intensity of the

Table 2
Experimental resonance frequencies ν(Sn) (for the ^{1}H NMR signal of Me_4Si at exact 300.13 MHz) and ratios of resonance frequencies for $^{15}N(SnMe_3)_3$ and Me_4Sn (Ξ(Sn) values with the ^{1}H NMR signal of Me_4Si at exact 100.000000 MHz)

$^{15}N(SnMe_3)$ **1**	Frequencies	δSn[a]	δSn	Frequencies	Me_4Sn
$\nu(^{119}\mathrm{Sn})$ (MHz)	111.9303013	88.78	0	37.290629	$\Xi(^{119}\mathrm{Sn})$ (MHz)[b,c]
$\nu(^{117}\mathrm{Sn})$ (MHz)	106.9525975	88.90	0	35.632256	$\Xi(^{117}\mathrm{Sn})$ (MHz)[b,c]
$\nu(^{115}\mathrm{Sn})$ (MHz)	98.2074992	88.87	0	32.718746	$\Xi(^{115}\mathrm{Sn})$ (MHz)[b,c]
	Frequency ratio			Frequency ratio	
$\nu(^{119}\mathrm{Sn})/\nu(^{117}\mathrm{Sn})$	1.046541215			1.046541642	$\Xi(^{119}\mathrm{Sn})/\Xi(^{117}\mathrm{Sn})$
$\nu(^{119}\mathrm{Sn})/\nu(^{115}\mathrm{Sn})$	1.139732731			1.139732831	$\Xi(^{119}\mathrm{Sn})/\Xi(^{115}\mathrm{Sn})$
$\nu(^{117}\mathrm{Sn})/\nu(^{115}\mathrm{Sn})$	1.089047154			1.089047117	$\Xi(^{117}\mathrm{Sn})/\Xi(^{115}\mathrm{Sn})$

[a] $\delta\mathrm{Sn} = \{[(\nu(\mathrm{Sn})/3.0013) - \Xi(\mathrm{Sn})]/\Xi(\mathrm{Sn})\}10^6$.

[b] Recently proposed [32] frequencies for Me_4Sn.

[c] Old reference frequencies (Me_4Sn + 30% C_6D_6) [$\Xi(^{119}\mathrm{Sn}) = 37.290665$ MHz [4]; $\Xi(^{117}\mathrm{Sn}) = 35.632295$ MHz [4]; $\Xi(^{115}\mathrm{Sn}) = 2.718781$ MHz (this work) give δSn values up to 1 ppm different, but are more consistent $\delta\,^{119}\mathrm{Sn} = 87.82$, $\delta^{117}\mathrm{Sn} = 87.81$ and $\delta^{115}\mathrm{Sn} = 87.83$.

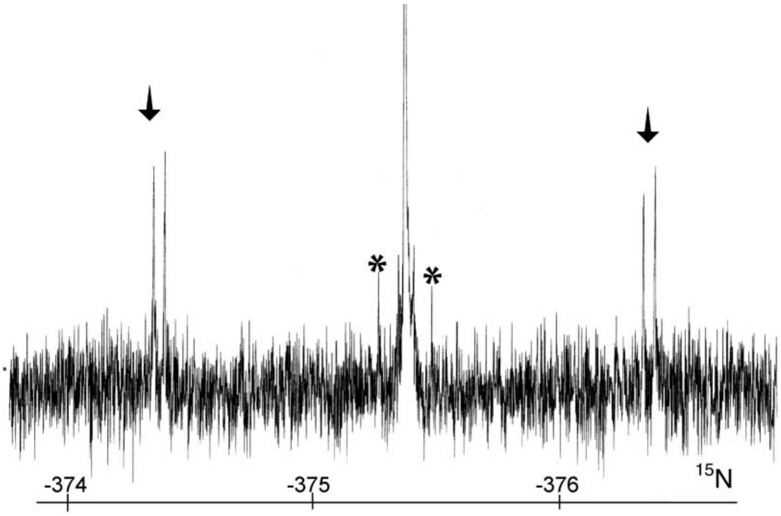

Fig. 2. 30.4 MHz ^{15}N NMR spectrum of *N*-trimethylsilyl-*N*,*N*-bis(trimethylstannyl)amine, $Me_3SiN(SnMe_3)_2$ **2** (labelled ca. 13 % with ^{15}N), after four transients. The $^{117/119}Sn$ satellites are marked by arrows and the ^{29}Si satellites by asterisks. Close to the bottom of the central line are additional satellite due to $^{15}N-^{13}C$ couplings across two bonds.

broad central line is already somewhat reduced owing to the loss of the fast decaying magnetization for the $^{14}N/^{119}Sn$ isotopomer during the pulse sequence (Fig. 1(B)). Finally, the INEPT-HEED [18] (HEED = Hahn echo extended) experiment was applied to eliminate the broad central line completely (Fig. 1(C)). The same situation applies of course to ^{117}Sn and ^{115}Sn NMR spectra. In contrast with the broad central resonance, the frequencies of the sharp doublet owing to the scalar Sn–^{15}N coupling can always be measured precisely. In agreement with the previous results [6], there is no appreciable primary isotope effect on tin nuclear shielding, as shown in Table 2 by comparison of the respective ratio of the resonance frequencies and the chemical shifts δSn with respect to Me_4Sn.

The tin NMR spectra of **2** shows the same features as those of **1**, except that there are also ^{29}Si satellites due to geminal scalar Sn–^{29}Si coupling (the number of relevant isotopomer in Scheme 1 is markedly increased by ^{29}Si if one of the $SnMe_3$ group is replaced by a $SiMe_3$ group), and the intensities of ^{117}Sn or ^{115}Sn satellites are lower than in **1**. Thus, longer measurement times were required which led to the slight broadening of all signals. Therefore, these spectra were not used to assess any isotope effects with the exception of $^{1}\Delta^{14/15}N(^{119}Sn)$ which is a large effect and the slight broadening of the lines can be tolerated.

2.3. ^{15}N NMR spectra

The refocused INEPT pulse sequence with ^{1}H decoupling was used to record the ^{15}N NMR spectra. Delays corresponding to assumed coupling constants $^{3}J(^{15}N, ^{1}H) = 1.3$ Hz for **1** and 1.8 Hz for **2** gave best results for polarisation transfer, and the ^{1}H decoupling power (^{1}H decoupling frequency offset set on resonance) was adjusted for low power selective decoupling in order to minimize the dielectric heating of the sample during the acquisition time. This is important since acquisition times of 15–20 s were necessary to collect the FID's without truncation.

In ^{15}N NMR spectra of **1**, a line width $h_{1/2} = 0.075$ Hz (after four scans) could be achieved by careful shimming of the magnet. This line width increased only to $h_{1/2'} = 0.115$ Hz after 400 transients. This made it possible to assign the $^{117/119}Sn$ satellites (easy to observe already after a single transient) as well as the ^{115}Sn satellites with high accuracy. The ^{119}Sn satellites are completely symmetric (within the experimental error) with respect to the central ^{15}N resonance signal. The ^{117}Sn satellites are shifted slightly to lower field, and this trend increases for

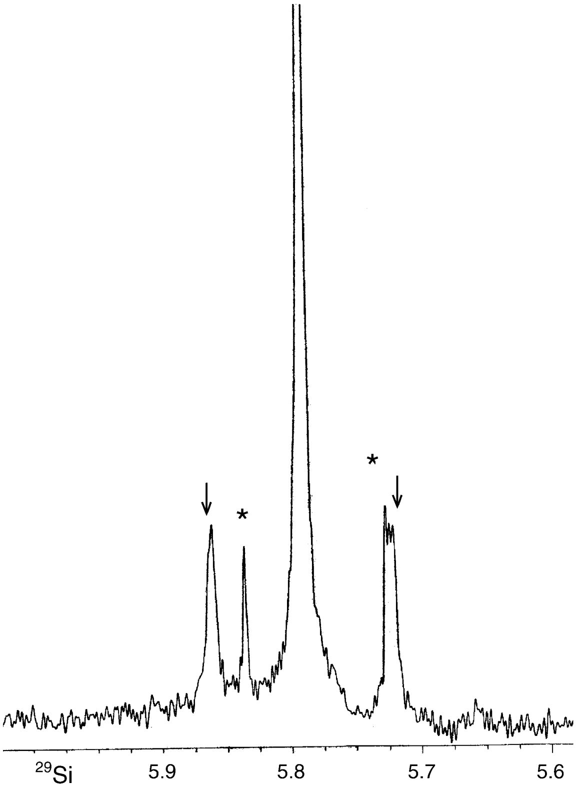

Fig. 3. 59.6 MHz ^{29}Si NMR spectrum of *N*-trimethylsilyl-*N*,*N*-bis(trimethylstannyl)amine, $Me_3SiN(SnMe_3)_2$ **2** (labelled ca. 13% with ^{15}N), after four transients. The ^{15}N satellites (asterisks) are readily assigned knowing the magnitude from the ^{15}N NMR spectrum (see Fig. 2). The $^{117/119}$Sn satellites (arrows) are resolved at the high-field side and overlap at the low-field side which indicates a small isotope-induced chemical shift $^{2}\Delta^{117/119}$Sn(^{29}Si).

the ^{115}Sn satellites (see Table 1). Clearly, this points to isotope-induced chemical shifts $^{1}\Delta^{117/119}$Sn(^{15}N) and $^{1}\Delta^{115/119}$Sn(^{15}N), observed here for the first time.

In the case of **2**, independent of the solvent D_8-toluene or C_6D_6, and also independent of the conditions (i.e. short or very long repetition delays), broadening and even splitting of the ^{15}N resonance signals were observed already after 8 or 16 transients, most likely a result of temperature dependence of the ^{15}N chemical shift. Fig. 2 shows the ^{15}N NMR spectrum of **2** after four transients where the signal is still narrow ($h_{1/2'} = 0.10$ Hz) and enables one to measure the $^{117/119}$Sn and ^{29}Si satellites with the necessary accuracy. Again, it was found that a small isotope-induce chemical shift $^{1}\Delta^{117/119}$Sn(^{15}N) exists. The measurement of the ^{29}Si satellites gives $^{1}\Delta^{28/29}$Si(^{15}N) value in the same order of magnitude as for other examples [19,20].

2.4. ^{29}Si NMR spectra

In the ^{29}Si NMR spectra of **2**, the central line is broadened owing to partially-relaxed scalar ^{29}Si–^{14}N coupling. Since the magnitude of $^{1}J(^{29}\text{Si},^{14}\text{N})$ of **2** is markedly smaller when compared with $^{1}J(^{119}\text{Sn},^{14}\text{N})$ of **1** or **2** (compare the coupling constants with ^{15}N in Table 1), the broadening is much less dramatic than in the tin NMR spectra, and isotope effects can be determined without recording ^{29}Si NMR spectra in which the central line is eliminated. This is shown in Fig. 3, where a small isotope-induced chemical shift $^{2}\Delta^{117/119}$Sn(^{29}Si) becomes evident for the first time. On the high-field side, the $^{117/119}$Sn satellites are resolved, whereas they overlap on the low-field side. The FID resolution was 0.03 Hz which excludes any artefact. The precise value of the coupling constant $^{1}J(^{29}\text{Si},^{15}\text{N})$ already determined from the ^{15}N NMR spectrum of **2** (see Fig. 2) and confirmed in this experiment (Fig. 3), allows here for the accurate determination of $^{1}\Delta^{14/15}$N(^{29}Si).

3. Conclusions

It appears that it is worthwhile to look for secondary isotope effects $^{1}\Delta^{117/119}$Sn(X) or $^{1}\Delta^{115/119}$Sn(X), in particular if the chemical shift of the X nucleus is sensitive to small changes in the surroundings. Our knowledge about isotope-induced chemical shifts is still limited, at least for heavier nuclei [21]. The present work adds some new data, which are in principle in agreement with expectations (the ^{15}N nucleus in the heavier isotopomer is better shielded). Clearly, a larger data set is required to establish such a rule firmly for the isotope effects observed here. Surprisingly, a two bond effect $^{2}\Delta^{117/119}$Sn(Si) has also been found. That means, it might be rewarding to study compounds with a stannyl group in the geminal position relative to a nucleus X in more detail than it has been done before. To the best of our knowledge, the isotope effects detected in this work represents the influence of the smallest mass difference in percent observed so far in NMR spectroscopy.

4. Experimental

4.1. General, starting materials, and NMR spectroscopy

Dimethylaminotrimethyltin, $Me_2N–SnMe_3$ [22–24] was prepared according to the literature procedure. Trimethyltin chloride was obtained by the reaction of tetramethyltin with tin tetrachloride (3:1 ratio; slow mixing without a solvent, heating to 130°C for 2 h; recrystallised from hexane). The ^{15}N-labelled starting material [^{15}N]ammonium chloride [13.6% enriched) was a commercial product (Chemotrade–Leipzig), used without further purification.

NMR spectra were measured using Bruker DRX 500, DPX 300 and ARX 250 spectrometers, all equipped for multinuclear magnetic resonance. The 90° pulses for ^{1}H, $^{117/119}$Sn, ^{29}Si and ^{15}N were calibrated for each spectrometer, using the actual samples **1** and **2** which were sealed in 5 mm tubes in order to prevent any changes in the composition. The 90° pulse for ^{115}Sn was assumed to be same as that for ^{117}Sn on each spectrometer. Digital resolution of the FIDs were in general 0.05 Hz or better. All spectra were processed with a minimum of line broadening (0.01 Hz) or without any line broadening. The conditions for measuring the NMR spectra were adjusted to correspond close to those reported for ultra-high resolution NMR [25–30].

4.2. Syntheses

4.2.1. [^{15}N]tris(trimethylstannyl)amine **1**

[^{15}N]tris(trimethylstannyl)amine **1** was obtained by the reaction of dry [^{15}N]ammonia gas (evolved from the reaction mixture of [^{15}N]ammonia chloride and an aqueous solution of NaOH) with Me_2NSnMe_3. The product **1** was purified and isolated as described [31].

4.2.2. [^{15}N]N-Trimethylsilyl-N,N-bis(trimethylstannyl)amine **2**

Treatment of [^{15}N]tris(trimethylstannyl)amine **1** with an excess of trimethylsilylchloride gave **2** as described for the non-labelled compound according to the literature procedure [13].

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