Synthesis and Structure of Tris(trialkylstannyl)- and Tris(dialkylhalostannyl)amines; Stabilization of the Sn_3N Skeleton by Intramolecular Sn−X−Sn Bridges

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Received July 4, 1995

Key Words: Tristannylamines / Tris(trialkylstannyl)amines / Tris(dialkylhalostannyl)amines / Sn−N Bond cleavage / Sn−X−Sn Intramolecular bridges

Tris(triorganylstannyl)amines $(R_2R'Sn)_3N$ (**1**, **2**) with substituents R = R′ = Me, Bu or R = Me and R′ = *i*Pr, *t*Bu are obtained by metathesis from $R_2R'SnX$ and $NaNH_2$ in liquid ammonia or by transamination of R_3SnNMe_2 with NH_3. Tris(diorganylhalostannyl)amines $(R_2XSn)_3N$ (**3**) are synthesized by stannazane cleavage of $(Me_3Sn)_3N$ (**1**) with R_2SnX_2. Information from multinuclear magnetic resonance spectra ascertain the planarity of the Sn_3N skeleton of type **2** and **3**, as well as the relationship between the coupling constants $^1J(^{119}Sn^{15}N)$ and $^2J(^{119}Sn^{117}Sn)$ and the Sn−N bond length as determined by the X-ray structure analysis of **1**, **3b** and **3r**. Compound **3b** shows an almost undistorted D_{3h} symmetry with a planar Br_3Sn_3N skeleton and SnN bond lengths of 1.99 Å, which beside those of **3a** are the shortest found so far. According to MNDO approximate and *ab initio* calculations π interactions between the lone electron pair at the N atom and empty orbitals at the Sn atoms can be excluded. Therefore, the tristannylamines discussed here have a trigonal planar nitrogen center with its lone electron pair in a *p*-type orbital. Further characteristic features of the molecular structures of typ **3** compounds are the intramolecular Sn−X−Sn bridges (X = Cl, Br, I) found in the solid state as well as in solution. The molecular geometries of the tristannylamines are supported by MS fragmentation patterns as well as by infrared and Raman spectra.

The synthetic potential of tin-nitrogen compounds has been known for a long time[1]. However, only in the last years have these compounds been used for the synthesis of other element-nitrogen compounds[2]. Investigations on the spectroscopic properties and the molecular structure of distannylamines, especially those with partially halogenated tin atoms, indicate an interesting type of bonding for this class of compounds[3]. Contradicting results about the structure of tristannylamines $(R_3Sn)_3N$ exist. Infrared spectroscopic investigations of tris(trimethylstannyl)amine **1** indicate a pyramidal Sn_3N skeleton[4]; electron diffraction in the gas phase favour a trigonal-planar arrangement of the tin atoms around the nitrogen center[5]. This geometry probably is present also with other tris(triorganylstannyl)amines **2**, which has been proven for **3a**, a molecule with a planar Cl_3Sn_3N skeleton stabilized through intramolecular Sn−Cl−Sn bridges[6]. It is especially interesting to compare the $(R_3Sn)_3N$ compounds with the lighter homologs $(R_3M)_3N$ (M = Si, Ge), which possess a planar M_3N arrangement. This has been often rationalized by the π-acceptor properties of the M atom[7]. The planar arrangement of the N atom in triisopropylamine is explained by steric "over crowding" due to the isopropyl substituents[8].

The structure of **3a** raises again the question of the type of bonding in tristannylamines. This question is important, since the extent of possible Sn-N π-interaction could be clarified. Furthermore, electronic and steric influences of the substituents on the geometry and on the hybridization at the N atom can be studied. A thorough investigation of this class of compounds was therefore necessary. Here we report on the chemistry and structure of tristannylamines with different substituents at the Sn atoms.

Synthesis

The synthesis of peralkylated tristannylamines is performed according to known procedures: transamination of stannylamines Me_3SnNMe_2 with ammonia (eq. 1)[9] and transmetallation (metathesis) of metal amides with trialkylhalogenstannanes (eq. 2)[10]. Only the methyl derivative of the three known compounds (R = R′ = Me, Et, Pr) of this class is characterized spectroscopically in more detail[11]. Peralkylated tristannylamines **2a**−**2c** with different alkyl groups at the Sn atom can be prepared with good yields according to eq. (2).

$$3\,Me_3SnNR'_2 \;+\; NH_3 \;\rightarrow\; \underset{\mathbf{1}}{(Me_3Sn)_3N} \;+\; 3\,HNR'_2 \qquad (1)$$

$$3\,R_2(R')SnX \;+\; 3\,NaNH_2 \;\rightarrow\; \underset{\mathbf{2}}{[R_2(R')Sn]_3N} \;+\; 3\,NaX \;+\; 2\,NH_3\uparrow \qquad (2)$$

	2a	2b	2c
R	Me	Me	nBu
R′	iPr	tBu	nBu

In contrast, the tris(halodiorganylstannyl)amines **3** cannot be prepared via this route. Formation of insoluble products according to eq. (2) indicate that the presumable intermediates, $R_2Sn(X)NH_2$, disproportionate to unstable $R_2Sn(NH_2)_2$ and R_2SnX_2 or condense to $(R_2SnNH)_x$. Similar results have been reported by other authors[12,13].

Compounds of type **3** can be prepared via exchange of Me_3Sn groups of **1** with dihalodiorganylstannanes R_2SnX_2 according to eq. (3). Some compounds of type **3** cannot be separated completely from the byproduct Me_3SnX neither by distillation nor by sublimation; therefore their purity and yield is not satisfactory.

$$\underset{\mathbf{1}}{(Me_3Sn)_3N} \quad + \quad 3\ R_2SnX_2 \quad \rightarrow \quad \underset{\mathbf{3}}{[R_2(X)Sn]_3N} \quad + \quad 3\ Me_3SnX \tag{3}$$

	3a	**3b**	**3c**	**3d**	**3e**	**3f**	**3g**	**3h**	**3i**	**3k**	**3l**	**3m**	**3n**	**3o**
R	Me	Me	CD_3	Me	Et	Et	iPr	iPr	nBu	nBu	Bz	Bz	Bz	Ph
X	Cl	Br	Br	I	Cl	Br	Cl	Br	Cl	Br	Cl	Br	I	Cl

According to NMR monitoring, the trans-stannylation reactions described by eq. (3) are quantitative if the tristannylamine **1** is added to the diorganyldihalostannane. When the order of addition is reversed, mixtures are produced since the intermediate mono- and dihalogenated tristannylamines of the type $(Me_3Sn)_2(R_2XSn)N$ and $(Me_3Sn)(R_2XSn)_2N$ tend to form SnN polycondensates with elimination of Me_3SnCl and Me_3SnCl_2.

Even at temperatures of approximately −70°C, compounds of type $(Me_3Sn)_2(Me_2ClSn)N$ are unstable. However, the monohalogenated tristannylamine $(Me_3Sn)_2(tBu_2ClSn)N$, **4**, can be prepared by the reaction of tBu_2SnCl_2 with $(Me_3Sn)_3N$, **1**, according to eq. (4). This compound is stable at ambient temperature in solution only as a mixture with Me_3SnCl, but can be characterized by NMR spectroscopy. After removal of Me_3SnCl via sublimation, **4** decomposes with formation of insoluble products.

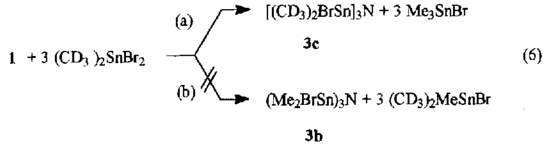
$$\underset{\mathbf{1}}{(Me_3Sn)_3N} + tBu_2SnCl_2 \rightarrow \underset{\mathbf{3p}}{(Me_3Sn)_2(tBu_2ClSn)N} \quad + \quad Me_3SnCl \tag{4}$$

To obtain pure products, compound **3a** must be synthesized at −30°C, the bromine-containing species **3b** at −60°C. The iodide **3d** can not be prepared according to eq. (3). However, **3d** can be characterized spectroscopically at ambient temperature mixed with Me_3SnI. After removal of Me_3SnI via sublimation, **3d** decomposes to form Me_2SnI_2 and an insoluble product. The halogen exchange according to eq. (5) does not give a single product even after replacing the methyl with benzyl groups; only Me_2SnI_2 can be identified in the reaction solution unambiguously. Therefore the reaction conditions depend upon the nature of the halogen substituents attached to the tin atoms in the order Cl < Br < I.

$$\underset{\mathbf{3a}}{(Me_2SnCl)_3N} + 3\ NaI \overset{Et_2O}{\not\longrightarrow} \underset{\mathbf{3d}}{(Me_2SnI)_3N} + 3\ NaCl \tag{5}$$

Decomposition of **3d** with elimination of Me_2SnI_2 can be prevented in the presence of Me_3SnI. This indicates the formation of intermolecular Sn−I−Sn bridges. This assumption is supported by the appearance of a broad ^{119}Sn-NMR signal, shifted approximately 5 ppm higher than that expected for the product. Also in this solution the signal for Me_3SnI is shifted approximately 7 ppm to lower field.

The stabilizing influence of the sterically more demanding alkyl groups such as R = *i*Pr is documented by isolation of clean **3g**, **3h** and **3r**. Intermolecular tin-halogen contacts amongst compounds **3** which could start decomposition, can be prevented by the bulky *i*Pr substituents. These results can be described either as Sn−N cleavage or alkyl-halogen exchange. Both of these reaction pathways were observed in the preparation of distannylamines[3]. Reactions according to eq. (3) proceed predominantly with Sn−N cleavage as has been shown by use of $(CD_3)_2SnX_2$ compounds (see eq. 6a).



(6)

Reactions according to eq. (6b) have been observed with distannylamines such as $2,6\text{-}iPr_2C_6H_3N(SnMe_3)_2$ because the tin−nitrogen cleavage is kinetically hindered due to the steric shielding around the N atom[3]. We assume that the course of the reaction according to eq. (6a) is in effect also during the preparation of the other compounds in this class where R ≤ *i*Pr. This is due to the comparatively low steric hindrance in **1**. Whereas the substitution of the Me_3Sn group for the iPr_2ClSn or the iPr_2BrSn group occurs without a problem, the reaction of **1** with iPr_2SnI_2 is more complex. Two iPr_2ISn groups can be introduced by trans-stannylation as shown in eq. (7); however, attempts to achieve $(iPr_2ISn)_3$ failed, but a nucleophilic Me/I exchange occurs as described by eq. (8). Obviously the cleavage of the third SnN bond is kinetically inhibited by the presence of the two bulky iPr_2ISn groups.

$$\underset{\mathbf{1}}{(Me_3Sn)_3N} \quad + \quad 2\ iPr_2SnI_2 \quad \rightarrow \quad \underset{\mathbf{3q}}{[iPr_2(I)Sn]_2N\text{-}SnMe_3} \quad + \quad 2\ Me_3SnI \tag{7}$$

$$\mathbf{3q} \quad + \quad iPr_2SnI_2 \quad \rightarrow \quad \underset{\mathbf{3r}}{[iPr_2(I)Sn]_2N\text{-}SnMe_2I} \quad + \quad iPr_2(Me)SnI \tag{8}$$

The course of reaction, shown in eq. 7 and eq. 8, which forms the bis(diisopropyliodostannyl)(dimethyliodostannyl)amine **3r**, could be elucidated by monitoring the reaction via NMR spectroscopy; **3q** was detected as an intermediate. To our knowledge, compound **3r** is the first example of a stable mixed alkylated tristannylamine with Sn−I bonds.

The synthesis of tristannylamines of the type $(Me_2RSn)_3N$ via reaction of $(Me_2ClSn)_3N$ (**3a**) with alkyllithium compounds according to eq. (9) was not successful.

$$(Me_2SnCl)_3N + 3\ RLi \not\longrightarrow (Me_2RSn)_3N \ + 3\ LiCl \tag{9}$$

This is because the alkyllithium compounds attack not only the Sn−Cl bond as expected, but also the Sn−N bond (R = Me, Bu, Ph), as evidenced by the formation of mixtures, for example, R_2Me_2Sn and Me_2RSnCl.

Thermal Stability

Tris(dialkyliodostannyl)amines with R = Me, Et and benzyl are stable only in the presence of Me_3SnI at 25 °C, while tristannylamines with SnCl- and SnBr bonds are stable even in the absence of Me_3SnX. Their solubility in methylenechloride, chloroform, toluene, benzene and petroleum ether decreases drastically after removal of the trimethylhalostannane by sublimation. The decomposition of **3a** occurs, surprisingly, with elimination of Me_3SnCl and not, as expected, with formation of Me_2SnCl_2 and is complete at 160−170 °C after 8 hours. A 0.06 M solution of **3a** in *o*-dichlorobenzene is decomposed at 120 °C after 5 days, and at the same concentration in toluene at 80 °C in 14 days. In each case approximately 65% Me_3SnCl was found. The rest was an insoluble, colourless solid. This course of reaction proves the stability of Sn−X−Sn bridges, since the elimination of Me_3SnCl hints towards methyl migration, and not halogen migration. Depending on the amount of the Me_3SnCl found, the solid could be a polycondensate of the composition $(NSnCl)_n$.

NMR Spectra

Table 1 contains selected ^1H-, ^{13}C-, ^{14}N-, ^{15}N-, and ^{119}Sn-NMR data as well as relevant coupling constants for peralkylated and halogenated tristannylamines together with some other compounds for comparison. Further NMR data can be found in the Experimental section.

Table 1. ^1H-, ^{13}C-, ^{14}N-, ^{15}N-, and ^{119}Sn-NMR data of peralkylated and halogenated tristannylamines and some other compounds for comparison (solvent: see Experimental section)

Compound	Nr	δ^1H_α [a]	^2J [b] [Hz]	^{13}C	^1J[c]	^{119}Sn	$\delta^{15}N$ (^{14}N)	^1J[d] [Hz]	^2J[e] [Hz]
$(Me_3Sn)_3N$[15]	**1**	0.16	56	-1.1	366	86.3	-396.2	-83.1	-186.7
$(Me_2i PrSn)_3N$	**2a**	0.20	48	-5.0	338	89.2	(-406)	/	207
$(Me_2t BuSn)_3N$	**2b**	0.07	49	-7.2	326	76.8	(-410)	/	242
$(Bu_3Sn)_3N$	**2c**	0.92	n.o.	14.7	360	73.0	(-401)	/	226
$(Me_2ClSn)_3N$[6]	**3a**	0.94	70	8.02	492	83.5	-335	66.4	38
$(Me_2BrSn)_3N$	**3b**	1.11	70	10.4	485	66.6	(-308)	/	43
$[(CD_3)_2BrSn]_3N$	**3c**	/	/	8.31	452	73	(-314)	/	45
$(Me_2ISn)_3N$	**3d**	1.2	66	11.1	447	24.9	/	/	67
$(Et_2ClSn)_3N$	**3c**	1.47	n.o.	18.8	466	67.7	-354	89.5	68
$(Et_2BrSn)_3N$	**3f**	1.61	n.o.	21	441	65.3	-356	102.9	62.3
$(i Pr_2ClSn)_3N$	**3g**	2.04	n.o.	31	453	29.2	/	/	94
$(i Pr_2BrSn)_3N$	**3h**	2.01	43	33	446	43.9	/	/	97
$(i Pr_2ISn_b)_2N$- Sn_aMe_2I	**3r**	2.10 1.22	n.o. 67.4	34.7 14.1	416 475	99.2[b] 15.3[a]	(-370)	164 98.8	~160 123
$(n Bu_2ClSn)_3N$	**3i**	1.61	80	27.2	447	58.1	-347	/	68
$(n Bu_2BrSn)_3N$	**3k**	1.62	n.o.	28.9	448	57.1	/	/	68.6
$(Ph_2ClSn)_3N$	**3o**	/	/	138	n.o.	-156	/	/	76
$(Bz_2SnCl)_3N$	**3l**	2.63	73.7	33.7	n.o.	-15.6	/	/	160
$(Bz_2ISn)_3N$	**3n**	2.96	95	31.9	410	-107.8	/	/	74.8
Me_3SnNMe_2[9]	**4**	0.06	55.4	-8.7	378	74.1	-383	~4	/
$(Me_3Sn)_2Nt Bu$[3,17]	**5**	0.29	54.8	-6.83	366	40.7	-326.7	-38.0	76.6
$(Me_2ClSn)_2Nt Bu$[3]	**6**	0.82	64.3	6.84	464	99.7	-289.3	60.7	~65

[a] data from $SnCH_3$ and $SnCH_2R$ only. − [b] ($^{119}Sn^1H$). − [c] ($^{119}Sn^{13}C$). − [d] ($^{119}Sn^{15}N$) sign measured only when indicated. − [e] ($^{117}Sn^{119}Sn$) sign measured only when indicated.

Substitution of a methyl group with bulky groups, like *i*Pr (**2a**) or *t*Bu (**2b**) on each of the three stannyl groups in the tristannylamine **1** leads to deshielding of the Sn nucleus. However, the ^{14}N, ^{15}N and ^{13}C nuclei are subsequently subjected to better shielding. Compound **1** has a planar Sn_3N skeleton in the gas phase[5] and in the crystalline state (see below); therefore introduction of bulky substituents R should result in longer Sn−N bonds and a change in the bond angles at the Sn atom. The better shielding of the ^{14}N, ^{15}N and ^{13}C nuclei points to an increase of the Sn−N bond length, while smaller values for the $^1J(^{119}Sn^{13}C)$ coupling constant indicate smaller Me−Sn−Me bond angles. Between the two parameters, a linear correlation exists as has been shown by several authors[14]. In addition there is a direct proportionality between the absolute value of the $|^1J(^{119}Sn^{13}C)|$ and the *s* character of the Sn−C bond. According to this correlation, the C−Sn−C angle is 106.9° for **2a** and 105.9° for **2b**[14]); compare these values to that for **1** (109.4°). These results indicate a distorted tetrahedral geometry around the Sn atoms. The crystal structure analysis of **1** is in good agreement with these estimations (see below). Especially apparent is the change in the value of the geminal coupling constant $^2J(^{119}Sn^{117}Sn)$ in **2**. The absolute value of $|^2J|$ decreases by ~50 Hz in comparison to **1**. Assuming that the sign of the coupling constant for **2** is negative as for **1**[15,16], the increase of the absolute value of the scalar coupling means a decrease of the *s* character in the Sn−N bonds[3,16]. Assuming that the hybridization of the N atoms in **2a** and **2b** is comparable to that in **1** (trigonal planar N atoms in crystal, compare below) one might think that the decrease of the scalar $^2J(^{119}Sn^{117}Sn)$ coupling indicates an elongation of the Sn−N bond which would result in a weakening of the coupling transmission. Further support for this idea comes from the large value of the corresponding $^2J(^{119}Sn^{117}Sn)$ coupling in the sterically strained $(Me_2t BuSn)_3N$, **2b**.

Exchange of a methyl group for halogens X = Cl, Br, and I on each Sn atom in **1** leads to a deshielding for the ^1H, ^{13}C, ^{14}N, and ^{15}N nuclei. The value for $\delta^{14}N/^{15}N$ lies in the region between pyramidal and planar N atoms[17]. Therefore the chemical shift does not allow an unambiguous assignment of the geometry at the N atoms in the tristannylamines **3**. The values of the coupling constants $^1J(^{119}Sn^{13}C)$ and $^2J(^{119}Sn^1H)$ in comparison with those found for **1**, **2a** and **2b** are much larger. This can be explained by the lower polarizability of the Sn atom[18] (because of the −I effect of the halogen substituent); however, the change in the geometry at this atom in solution is an alternative explanation. This trend can be seen by comparing the data of the peralkylated with the Sn-halogenated distannazanes[3] (compare **5** and **6** in Table 1). Further information on structures of type **3** can be derived from an estimation of the C−Sn−C angle with the help of $^{1}J(^{119}Sn^{13}C)$ coupling[14] which depends mainly on the *s* character of the Sn−C bond. This relationship holds especially if one or two electronegative groups are linked to the Sn atom[19]. The C−Sn−C angle for **3a** is 121.8°, for **3b** 121.5°, and therefore indicates a trigonal bipyramidal geometry at the Sn atoms. This assumption is confirmed by the molecular structures of **3a**[6] and **3b**.

The increase in shielding of the Sn atom in the halogenated tristannylamines **3** seems unusual in comparison to compounds **2**. On the other hand, the Sn nuclei in distannazanes are strongly deshielded when a methyl group is replaced with a halogen atom (compare **5** and **6**, Table 1). This indicates an increase in the coordination number of the Sn atoms in **3**. Changing from tetra- to pentacoordination at a Sn atom usually results in a 50−100 ppm highfield shift of the ^{119}Sn NMR signal[18], whereas the −I effect of the halogens and the weak donor acceptor interaction between the bridging halogen atoms X and the Sn atoms in **3** – weak in comparison to a typical adduct like $Me_3SnCl \cdot py$ – probably works in the opposite direction. The ^{119}Sn CP-MAS-NMR spectra of **3a** and **3b** show an even more pronounced high field shift of 40 and 20 ppm for the signal group as compared with that in solution. Signal assignment is impossible[20] because of perturbation of the high resolution caused by interaction of the Sn nucleus with the quadrupole nuclei ^{14}N and $^{35}Cl/^{37}Cl$ leading to additional signals.

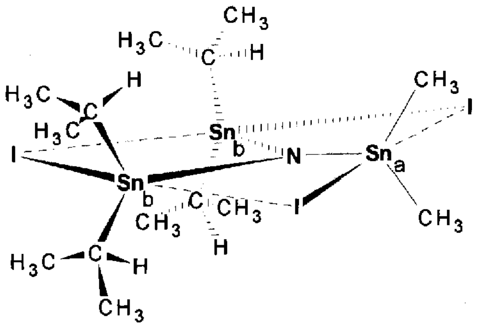
Especially striking is the large change in the geminal $^{2}J(^{119}Sn^{117}Sn)$ coupling found for partially Sn-halogenated tristannylamines **3** in comparison to peralkylated compounds **1** and **2**; $|^{2}J|$ decreases by 150 to 300 Hz. Assuming that this coupling has a negative sign as for **1**[15], a decrease in the value of the scalar coupling means an increase of the *s* character of the Sn−N bond. So far it has been assumed that this is related to an increase of the Sn−N−Sn angle[21]. The structure of the tris(trimethylstannyl)amine **1** in the gas phase, as well as the molecular structure of **1**, **3a**[6], **3b** and **3r** in the crystal always show a planar Sn_3N skeleton regardless of the substituents at the Sn atoms. For this reason and also due to steric factors, the geometry at the N atom of tristannylamines **3** should be retained; consequently, the value of the geminal $^{2}J(^{119}Sn^{117}Sn)$ coupling is largely independent of the size of the Sn−N−Sn angle. Thus the coupling constant should be the prime indicator for a change in the Sn−N bond lengths. We find small values for ^{2}J for compounds with short Sn−N lengths (for example in **3a** $^{2}J(^{119}Sn^{117}Sn)$ (−)38 Hz, d(SnN) 1.99(1) Å; or **3b** (−)43 Hz, 1.997(3) Å) and large values when long Sn−N bonds are present (for example, in **1** $^{2}J(^{119}Sn^{117}Sn)$ −186.7 Hz, d(SnN) 2.041(6) Å). This assumption is supported by comparing the value of $^{1}J(^{119/117}Sn^{15}N)$ for the peralkylated tristannylamines **1** and **2c** with **3**; **1** and **2c** have considerably smaller absolute values. The coupling constants were taken from ^{15}N-INEPT and ^{119}Sn-HEED-INEPT-NMR experiments[22]. For **1** and for a number of other mono- and distannylamine compounds, a negative sign for ^{1}J was found[15,16]. Here also, the smaller absolute values of ^{1}J (better coupling) should correspond to a larger *s* character of the covalent Sn−N bond (for example **1**, 83.1 Hz; **3a**, 66.4 Hz).

Interesting in this context is the dependence of the $^{1}J(^{119/117}Sn^{15}N)$ and $^{2}J(^{119}Sn^{117}Sn)$ coupling on the steric influence of the R substituent in compounds $(R_2XSn)_3N$ **3** while the hybridization of the Sn as well as the N atoms remain nearly unchanged. Going from R = Me to Et and *i*Pr one finds a nearly linear increase of the $|^{1}J|$ and $|^{2}J|$ values. This indicates an elongation of the Sn−N bonds − due to the increasing volume of the $R_2R'SnX$ groups − whereas their *s* character remains untouched. The dominance of the Fermi contact term − the dependence of the ^{1}J coupling with the *s* overlap in the Sn−N bond of **3**[23,16] − is thus confirmed.

This interpretation is strongly supported by NMR data of the unsymmetrically substituted tristannylamines **3r**. The assignment of the ^{119}Sn-NMR signal at 15.3 to the R_2SnI group was deduced from the ^{1}H-coupled ^{119}Sn-NMR spectrum. The recording of a ^{15}N-NMR spectrum was unsuccessful. The (Sn,N) and (Sn,Sn) coupling constants were taken from the ^{119}Sn-NMR spectrum by using the HEED-INEPT pulse sequence. The trend is confirmed that large $^{1}J(^{119/117}Sn^{15}N)$ and large $^{2}J(^{119}Sn^{117}Sn)$ coupling constants correspond to large SnN distances and vice versa. The ^{1}J coupling of the $^{117/119}Sn$ nuclei in the iPr_2ISn group with the central ^{15}N nucleus in **3r** amounts to 164 Hz, the ^{2}J coupling with the ^{117}Sn nucleus in the second iPr_2ISn is 160 Hz, and the corresponding coupling of the $^{117/119}Sn$ nuclei of the Me_2ISn group with the ^{15}N nucleus and with the ^{117}Sn nuclei is 98.8 and 123 Hz, respectively. Therefore the Sn_aN bond should be shorter than the Sn_bN bond, and both bonds should be longer than those in **3a** and **3b** (Figure 1).

The C−Sn−C angle can be estimated at 120.0° and 114.7° from the coupling constants $^{1}J(^{119}Sn_a{}^{13}C) = 475$ Hz and $^{1}J(^{119}Sn_b{}^{13}C) = 416.1$ Hz. These data indicate a molecular structure for **3r** which is similar to the geometry of crystalline **3a** and **3b**, but slightly different in respect to the SnN and SnI distances (Figure 1). The larger halfwidth of the ^{119}Sn-NMR signal at δ = 99.2 indicates a rather labile Sn−I−Sn bridge between the two Sn_b atoms in solution (for the molecular structure in the crystal, see below).

Figure 1. Proposed structure of **3r**



Whereas the steric effects of alkyl groups at Sn atoms has a large effect on the coupling constants, the replacement of halogen substituents in the order of Cl, Br, I, as exemplified for **3a**–**c**, leads only to small changes. Consequently the electronegativity of the halogen substituents have only marginal effect on the bonding situation within the Sn_3N skeleton.

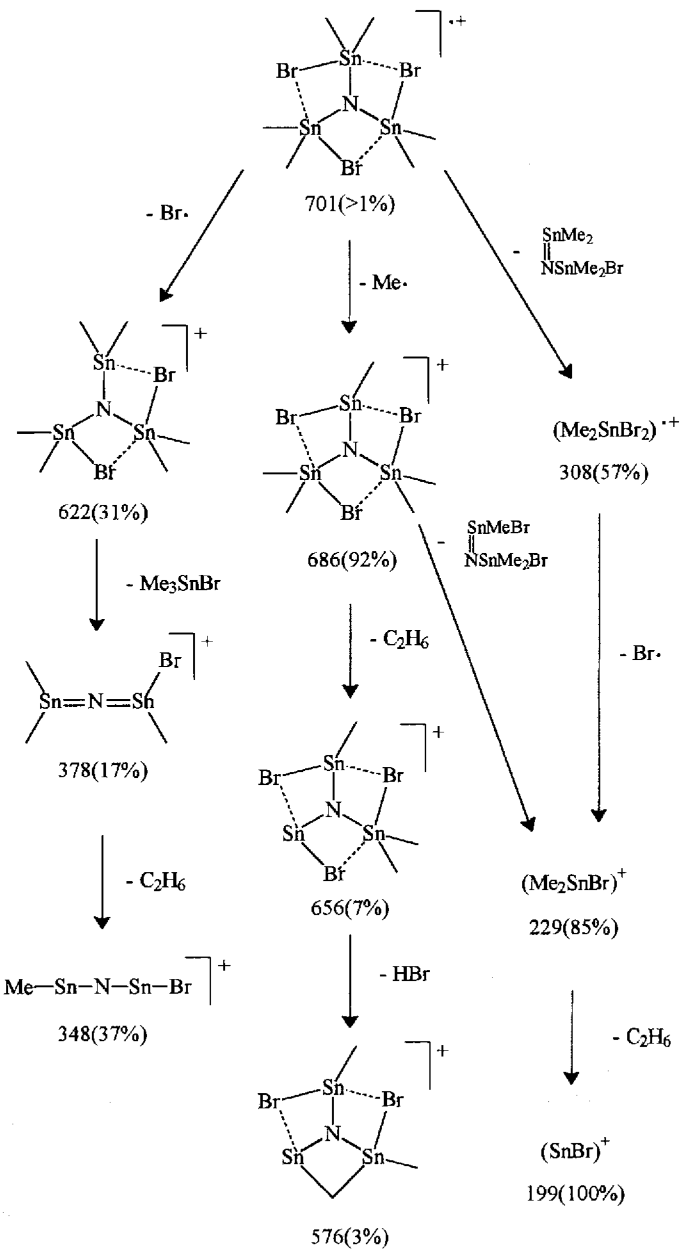
^{15}N-NMR spectra of the tristannylamines **3** could be recorded only for a few compounds because INEPT measurements require the $^3J(^{15}N,^1H)$ coupling which is difficult to measure and can be only roughly estimated. The measured ^{15}N-NMR signals are, in comparison to **1** and **2a**–**c**, shifted to lower field by 40–70 ppm. Deshielding should be explained by the −I effect of the halogens. No conclusions about the geometry at the N center can be drawn from the chemical shift of the signals because planar as well as pyramidal configurated amines could be found there[17], as has already been mentioned.

Mass Spectra

Selected molecules have been studied by mass spectrometry. Fragment ions with an occurence larger than 1% are found in the Experimental section. Measured isotope patterns correspond to the calculated ones. The fragmentation of three tristannylamines **3** at 70 eV EI, which is characteristic for this class of compounds, is summarized in Schemes 1–3.

The fragmentation paths confirm the conclusions for structure and bonding of compounds **3** as derived from the NMR spectra. The molecular ion occurs in the most cases only at low intensity which shows the weak stabilization of the positive charge of the radical cation in the molecule. The first step of fragmentation is always the cleavage of a Sn−C bond forming an ion $[M - R]^+$ of high intensity; cleavage of a Sn-halogen bond seldom occurs which is an indication of the stability of the Sn−X−Sn bridge bond even in the gas phase. The favored Sn−C bond cleavage gives rise to formation of presumed pentalene analogous bicyclic and tricyclic fragment ions of high intensity. Three ethane molecules are lost in the case of **3e** (Scheme 2). Similar fragmentation pathways are observed for the decomposition of tris(diorganylthioboryl)amines to form cations of tricyclic B−S heterocycles[2d]. In any case, the Et_2SnCl^+ ion is also found, occuring with 22% relative intensity and formed through the cleavage of a Sn−N bond. Contrary to the tristannylamines, the fragmentation of monomeric distannylamines occurs usually with cleavage of Sn−N bonds[3]. This decomposition path is also seen for the iodine substituted tristannylamines **3r**. In this compound in particular, the cleavage of Sn−X bond is not the predominant fragmentation pathway. The Me_2ISn_a groups – as was concluded from NMR data – seem to be more strongly bonded than $i\text{Pr}_2ISn_b$ groups (see Figure 1), since only $i\text{Pr}_2ISn$ groups are lost during fragmentation. All decomposition paths of Tris(diorganylhalostannyl)amines have in common the presence of Sn−X fragments as basis ions.

Scheme 1. Main fragmentation path of the tristannylamine **3b**; proposed structures of fragment ions (70 eV electron impact energy)

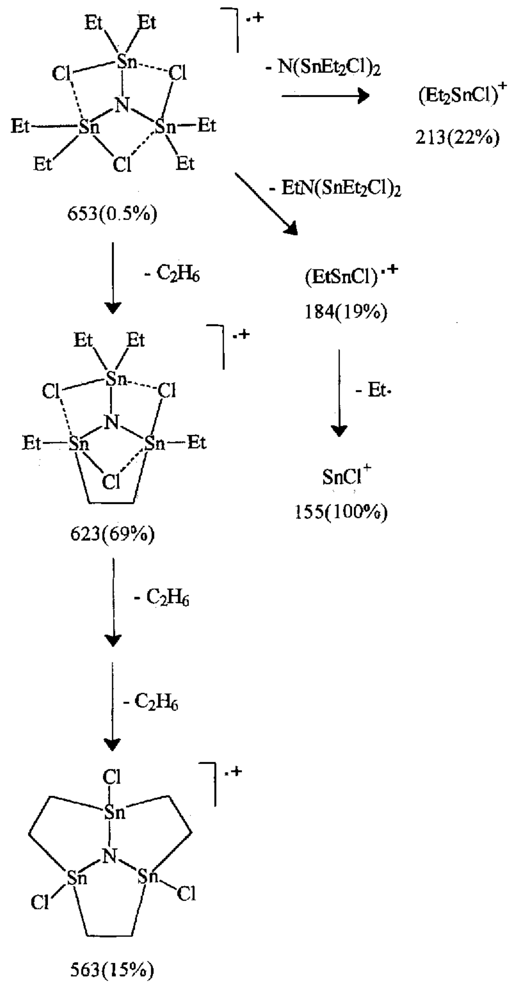


Infrared and Raman Spectra

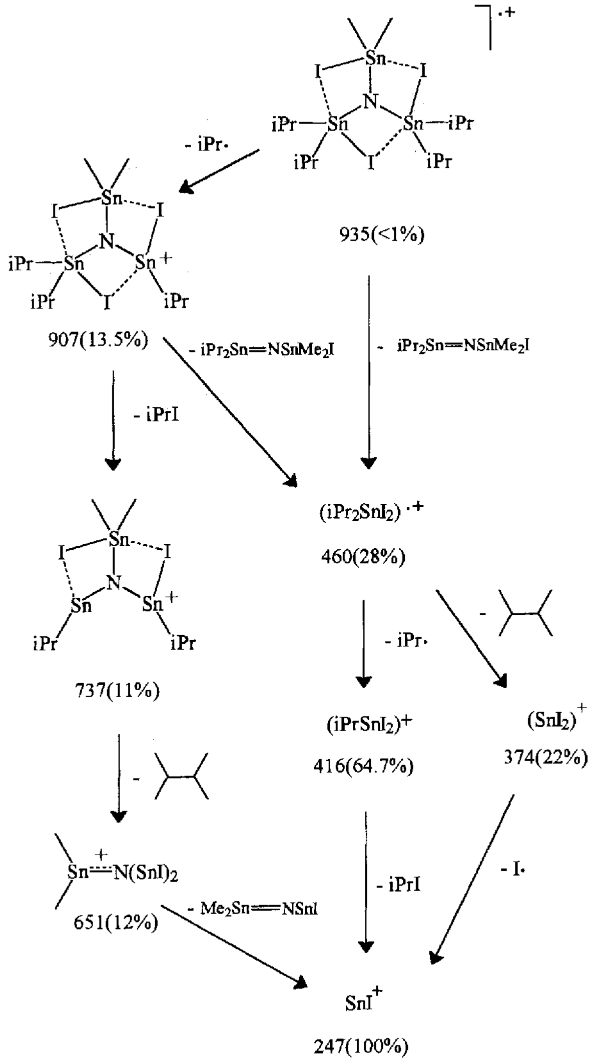
SnN compounds have already been investigated by IR spectroscopy[4,24]. However the assignment of bands for tristannylamines has been controversial.

Bands can be considered as established for $\nu_s(SnC_3)$ and $\nu_{as}(SnC_3)$ vibrations at 505 and 530 cm^{-1} of peralkylated tristannylamines[10,24]. This assignment is supported by the absence of these bands in the IR spectra of distannazanes without SnC bonds (for example, $MesN(SnCl_3)_2$[25]). Assignment of the Sn−N stretching mode has not been unambiguous so far. A band at 510 cm^{-1} has been assigned to the Sn−N stretching vibration[24]. However this region is that for a Sn−C stretching vibration. The Sn−N stretching

Scheme 2. Main fragmentation path of the tristannylamine **3e**; proposed structures of fragment ions (70 eV electron impact energy)



Scheme 3. Main fragmentation path of the tristannylamine **3r**; proposed structures of fragment ions (70 eV electron impact energy)



vibration has been assigned for an isotope-labeled aminostannane $PhNHSnMe_3$ at 843 cm^{-1}[26], the $\nu(NSn_2)$ vibration in $MeN[Sn(Cl)tBu_2]_2$ at 705 cm^{-1}[27] and that for stannylamino boranes in the range of 700–850 cm^{-1}[28]. Furthermore, Kozima et al. assigned the 710 cm^{-1} band in the IR spectrum of $(Me_3Sn)_3N$, **1**, to an antisymmetric Sn_3N stretching mode by comparing with the known Si–N frequencies. They also assumed that the symmetrical Sn_3N stretching was in the range of KCl lattice vibrations[10]. This is contrary to the results of an investigation which assigned $\nu_{as}(Sn_3N)$ to a band at 672 cm^{-1} and $\nu_s(Sn_3N)$ at 514 cm^{-1} from their IR and Raman spectra[4]. These last results cannot be confirmed by our vibrational spectroscopic analysis. Our assignments of the stretching modes for the tristannylamines **1**, **2c**, and some compounds of type **3** are summarized in Table 2. For AB_3 molecules of point symmetry group D_{3h}, three IR-active and three Raman-active vibrations can be expected.

The SnN stretching vibrations $\nu_{as}(Sn_3N)$ are assigned to wavenumbers between 740 and 700 cm^{-1}[29], the deformation vibrations $\delta(Sn_2N)$ between 680 and 590 cm^{-1}. The out of plane vibrations $\gamma(Sn_3N)$, which could be expected

Table 2. Selected IR-active vibrations of peralkylated and halogenated tristannylamines (wave numbers in cm^{-1})

compound		$\rho(CH_3)$	$\upsilon_{as}(NSn_3)$	$\delta(SnNSn)$	$\upsilon_{as}(SnC_{2/3})$	$\upsilon_s(SnC_{2/3})$	$\upsilon("Sn_2X")$
$(Me_3Sn)_3N$	**1**	762	734	675	523	502	
$(Bu_3Sn)_3N$	**2c**	/	711	682	591 ?	499 ?	
$(Me_2ClSn)_3N$	**3a**	782	734	597	554	520	289
$(Me_2BrSn)_3N$	**3b**	780	721	588	549	516	249
$[(CD_3)_2BrSn]_3N$	**3c**	739 ?	722	605	542	519	253
$(Et_2ClSn)_3N$	**3e**	/	753/677[a]	596	524[a] ?	493 ?	312
$(Et_2BrSn)_3N$	**3f**	/	736/678[a]	594	522[a] ?	490 ?	279
$(iPr_2ClSn)_3N$	**3g**	/	720	595	543 ?	481 ?	290
$(iPr_2BrSn)_3N$	**3h**	/	731[a]	593	?	503[a]	?
$(Bu_2BrSn)_3N$	**3k**	/	734/674	599			
$(Ph_2ClSn)_3N$	**3o**	/	745	?	583 ?	556 ?	
$(H_3Sn)_3N$[b]		/	728	683	/	/	/

[a] broad bands about 60–80 cm^{-1}, not resolved; assignment not save. – [b] Frequency-analysis according to geometry optimised approximate ab initio calculations with the Gaussian 92 program, Windows version, LANL1DZ basis set.

at lower frequencies, could not be detected because they are probably dominated by $\nu_{as}(SnC_{2/3})$ and $\nu_{s}(SnC_{2/3})$. These are assigned to the region of 550–520 cm^{-1} and 520–490 cm^{-1}, respectively. Coupling between SnN and SnC stretching vibrations is small. This has been confirmed by frequency analysis at the molecule $Me_3SnN(SnH_3)_2$ with geometry-optimized ab initio calculation with Gaussian 92 (LANDIDZ basis set). We assign the area of 740–790 cm^{-1} to the rocking vibration of $\rho(CH_3)$ as has been confirmed by the investigations of Dehnike et al.[29]. The assignment of the NSn_3 stretching vibration is confirmed with a frequency analysis of $(H_3Sn)_3N$ based on an ab initio calculation. The following values were calculated: $\nu_{as}(Sn_3N)$ 728 cm^{-1}, $\gamma(Sn_3N)$ 683 cm^{-1} and $\delta(Sn_2N)$ 583 cm^{-1}. To check the pyramidal configuration of the N center in **1** postulated from IR data[4], the Raman spectra of **1** and of the tristannylamine **3a** were recorded. In each case, in the area of 100–1000 cm^{-1} only one strong Raman active vibration with a shoulder at 524 cm^{-1} for **1** and 512 cm^{-1} for **3a** occurs. Thus the planarity of the Sn_3N skeleton in solution is supported by the existence of only one strong band and one weak Raman band, recognized as a shoulder. It should be mentioned, that the IR bands of C–H and C–C vibrations are not very characteristic. Typical bands of the *t*Bu and *i*Pr connected to Sn appear at approximately 1466 and 1380 cm^{-1}. For the tris(diorganylhalostannyl)amines, a strong band at 320–250 cm^{-1} is assigned to the Sn–halogen stretching vibration shifted to lower frequencies in comparison to Me_2SnCl_2. The corresponding vibrations of the pyridine adduct of the distannylamine, 2,6-$i\text{Pr}_2C_6H_3N(SnClMe_2)(SnMe_2Cl) \cdot py$ which has in the crystal a Sn–Cl–Sn bridge and not a bridged Sn–Cl bond, has been found at 329 cm^{-1} [ν(Sn–Cl–Sn)] and 435 cm^{-1} [ν(Sn–Cl)][25,30]. The shift of these bands in compounds of type **3** of approximately 140 cm^{-1} (for example, **3a** 289 cm^{-1}, **3b** 249 cm^{-1}) to lower frequencies ascertain halogen-bridge bonding also in solution.

Molecular Structures

NMR data provide convincing evidence for the planarity of the Cl_3Sn_3N skeleton in compounds of type **3**. Additionally, the structure of several tristannylamines were determined by X-ray crystallography. Figures 2, 3, and 4 show ORTEP plots of molecules **3b**, **3r** and **1**. Selected bonding parameters are listed in the legend of each figure. Compound **3r** is monoclinic like **3a**; **3r** crystallizes $P2_1/m$ with $Z = 4$; **3b** crystallizes the triclinic space group $P\bar{1}$, $Z = 2$. For each molecule of **3r**, one molecule of CH_2Cl_2 is present in the unit cell which are located in the spaces between the tristannylamine units.

The molecule **3b** shows almost perfect D_{3h} symmetry which was found also for **3a**[6]. Both molecular geometries are very similar except of small differences in the Sn–X bond lengths. Obvious deviations are evident in the structure of **3r** especially regarding the Sn–I bond lengths. The planar Br_3Sn_3N molecular skeletons of **3b** and the I_3Sn_3N skeleton of **3r** are characteristic and have been confirmed by geometry optimized AM1 calculations for halogenated tristannylamines $(H_2XSn)_3N$ with X = Cl, Br and I[6,31] (see Table 3). The sum of bond angles at the N atom of **3b** is 359.1° and 360° in **3r**.

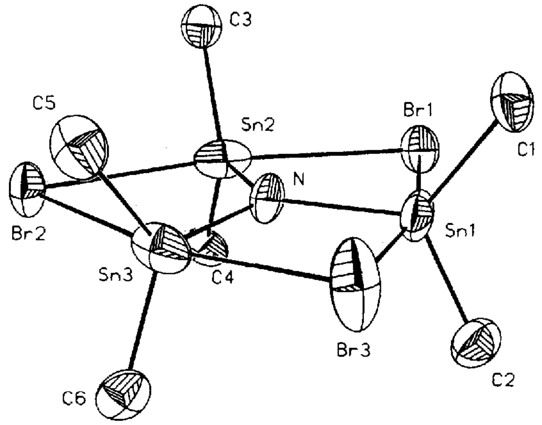


Figure 2. Molecular structure of $N[Sn(CH_3)_2Br]_3$ **3b** in ORTEP-type description. Thermal ellipsoids represent a 25% probability. Selected bond lengths [Å] (estimated standard deviations in parentheses): Sn1–N 2.002(13), Sn2–N 1.987(14), Sn3–N 2.00(2), Sn1–C1 2.08(2), Sn1–C2 2.06(2), Sn1–Br1 2.901(4), Sn1–Br3 2.861(4), Sn2–Br1 2.920(3), Sn2–Br2 2.852(3), Sn3–Br2 2.940(4), Sn3–Br3 2.855(4). – Selected bond angles [°]: Sn1–N–Sn2 120.5(7), Sn1–N–Sn3 119.1(7), Sn2–N–Sn3 119.5(7), N–Sn1–C1 120.2(8), N–Sn1–C2 117.7(8), Sn1–Br1–Sn2 73.03(7), Sn1–Br3–Sn1 74.34(9), Sn2–Br2–Sn3 73.03(8), Br1–Sn1–Br3 165.92(8), Br1–Sn2–Br2 167.65(8), C1–Sn1–C2 122.0(10)

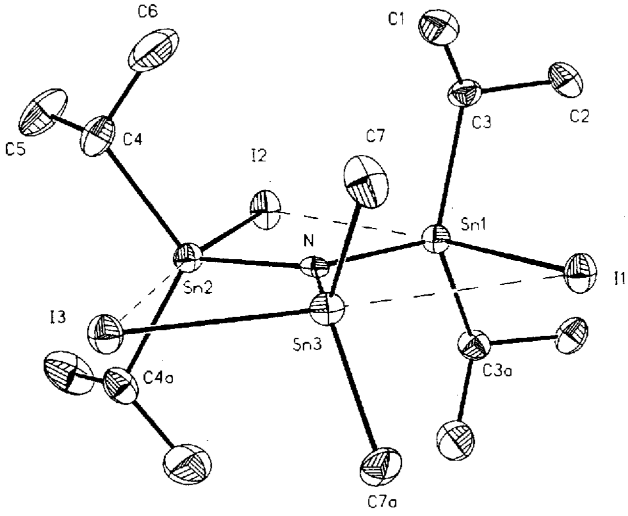
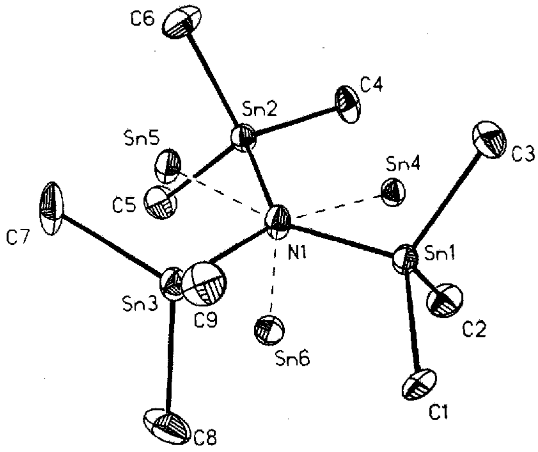


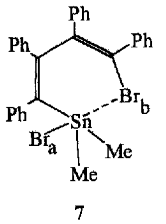
Figure 3. Molecular structure of $(i\text{Pr}_2ISn)_2NSn(CH_3)_2I$ **3r** in ORTEP-type description. Thermal ellipsoids represent a 25% probability. Selected bond lengths [Å] (estimated standard deviations in parentheses): Sn1–N 2.064(13), Sn2–N 2.02(2), Sn3–N 2.048(13), Sn1–C3(C3a) 2.170(14), Sn2–C4(C4a) 2.16(2), Sn3–C7(C7a) 2.11(2), Sn1–I1 2.830(2), Sn2–I2 2.794(2), Sn3–I3 2.807(2), Sn1–I2 3.474(2), Sn2–I3 3.565(2). – Selected bond angles [°]: Sn1–N–Sn2 121.0(6), Sn1–N–Sn3 118.1(7), Sn2–N–Sn3 121.0(6), N–Sn1–C3(C3a) 114.9(4), N–Sn2–C6(C6a) 116.4(4), C7–Sn3–C7a 120.5(10), C4–Sn2–C4a 118.5(9), Sn1–I1–Sn3 67.2, Sn1–I2–Sn2 68.1, Sn2–I3–Sn3 66.3, I1–Sn1–I2 172, I2–Sn2–I3 172.2, I1–Sn3–I3 175.3

The molecular structure of **3b** shows the intramolecular Sn–X–Sn bridges which give rise to pentacoordination of the Sn atoms which is typical for this class of compounds. The Sn–Br–Sn bridges are slightly asymmetrical with

Figure 4. Molecular structure of N[Sn(CH$_3$)$_3$]$_3$ **1** in ORTEP-type description. Thermal ellipsoids represent a 25% probability. Selected bond lengths [Å] (estimated standard deviations in parentheses): Sn1–N 2.001(7), Sn2–N 2.071(6), Sn3–N 2.037(6), Sn4–N 2.020(7), Sn5–N 2.008(7), Sn6–N 2.082(6), Sn1–C1 2.15(3), Sn1–C2 2.159(10), Sn1–C3 2.204(10), Sn2–C4 2.12(2), Sn2–C5 2.177(9), Sn2–C6 2.158(10), Sn4–C2 2.162(10), Sn4–C3 2.152(9), Sn4–C4 2.38(2). – Selected bond angles [°]: Sn1–N–Sn2 119.7(3), Sn1–N–Sn3 122.3(3), Sn2–N–Sn3 117.4(3), Sn4–N–Sn5 121.7(3), Sn4–N–Sn6 119.3(3), Sn5–N–Sn6 118.8(3), Sn1–N–Sn4 41.3(1), Sn2–N–Sn4 78.7(2), N–Sn1–C1 108.6(8), N–Sn1–C2 111.6(4), N–Sn1–C3 107.8(4), C1–Sn1–C2 107.9(8), C1–Sn1–C3 113.5(7)



alternating shorter (2.85 Å) and longer Sn–Br bond lengths (2.92 Å). In contrast, calculations predict symmetrical Sn–Br–Sn bridges[31]. However, the difference in the Sn–X bond lengths can be explained by packing effects since the crystal shows intermolecular Br–Br distances of 3.41 Å (van der Waals distance 3.9 Å[32]). The deviations from the ideal trigonal bipyramidal arrangement of substituents at the Sn atoms is much less than it is for the homologs **3a** but larger than in **3r**. For example, the I(1)–Sn(2)–I(2) angle is 172°, and the Br(1)–Sn(2)–Br(2) angle is 167.7°. The corresponding angle in **3a** is 163.7°. The Sn–Br bonds in **3b** are considerably longer (2.85–2.92 Å) than the Sn–Br bonds in nonionic pentacoordinated tin compounds (for example **7** d(SnBr$_a$) 2.504 Å)[33]. The distances between the Sn center and the equatorial bonding partners are shortened according to Bent's rule[34]. The Sn–N bond length in **3b** is approximately 2 Å which is about 0.01 Å longer than in **3a**, but still one of the shortest single bonds so far found.



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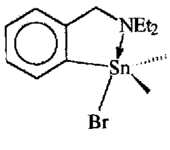

8

For comparison, the Sn–N bond length of 2,6-diisopropylphenylbis(trimethylstannyl)amine having a planar CNSn$_2$ skeleton is 2.044(3) Å[3]. The sum of the covalent radii of both elements is 2.033 Å[35]. Furthermore, the Sn–C bonds (approximately 2.08 Å) are shorter in comparison with tetracoordinated Sn compounds (2.12 Å in 2,6-*i*Pr$_2$C$_6$H$_3$N(SnMe$_2$Cl)$_2$ and 2.13 Å in **6**)[30]. The angle sum of 360° confirms the planar arrangement of substituents in the equatorial region of the Sn atom. As in **3a** "clampling action" of the Sn–X–Sn bridging bond seems to be of decisive importance for the molecular geometry. Bent's rule postulates, starting from a pentacoordinated central atom, a larger *s* proportion in the equatorial bonds. This is expressed not only in the significant decrease of the bond length, but is also reflected in the larger spin-spin coupling between the nucleii of these bonds [$^1J(^{119/117}Sn^{15}N)$, $^1J(^{119/117}Sn^{13}C)$ and $^2J(^{119}Sn^{117}Sn)$]. The agreement between the C–Sn–C angle calculated from the $^1J(^{119}Sn^{13}C)$ coupling (122°) and the angle, determined for the crystal (123°) is interesting. This supports the assumption that the structures of the tristannylamines in solution and solid state are similar. In solution the structures are probably more symmetric. Intramolecular Sn–X–Sn bridges have been described for Sn–N compounds only once so far[6]. Organotin compounds, **7** and the distannylmethane derivative CH$_2$(SnClPh$_2$)$_2$[36], have pronounced asymmetric Sn–X–Sn bridges. For the latter, the Sn–Cl bond lengths are 2.441 Å and 3.368 Å.

The molecular structure of **3r** is rather different in comparison to **3a** and **3b** except for the planarity of the X$_3$Sn$_3$N moiety. In particular, the Sn–X–Sn bridging bonds have only little importance: The Sn–I bonds (2.79–2.83 Å) are 0.1 Å longer than in tetracoordinated Sn compounds (for example IPh$_2$Sn(CH$_2$)$_4$SnPh$_2$I 2.729(3) Å[37]). Accordingly, the intramolecular Sn–I contacts with the neighbouring Sn atoms elongate to 3.47–3.57 Å. These Sn–I distances are considerably shorter than the van der Waals distances (4.08 Å)[38]. But they are too long to be effective Sn–I bridge bonds. Nevertheless these interactions result in a significant deviation of the angle at the Sn centers in the direction towards a trigonal bipyramidal arrangement of substituents. The N–Sn–I angle is only 95–96°, the I–Sn–I angle is approximately 173° and the sum of angles in the equatorial plane is 353–355°. The C7–Sn3–C7a angle of the IMe$_2$Sn group amounts to 120.5° and agrees well with the value predicted from NMR data.

The Sn–N bonds in **3r** (2.02(2)–2.06(1) Å) are considerably longer in comparison with the tristannylamines **3a** and **3b**. But they are similar to the values for **1**. This finding confirms the relationship, postulated from NMR data, that larger $^1J(^{119}Sn^{15}N)$ and $^2J(^{119}Sn^{117}Sn)$ coupling constants correlate with larger Sn–N bond lengths and vice versa. The assumption, based on NMR data, that the Sn–N bond to the IMe$_2$Sn group in **3r** is the shortest bond, is not confirmed. But this bonding parameter has a relatively large standard deviation. Therefore a detailed discussion of the structure parameters of this molecule is not useful.

In the solid state, the molecules of (Me$_3$Sn)$_3$N, **1**, are disordered. This disorder prohibits a discussion of the SnC bond lengths. All other parameters confirm the structural data of **1** in the gas phase[5] as well as the conclusions drawn from NMR data. The refinement was difficult due to the disorder, which is depicted in Figure 4. The refinement of the positions of the Sn atoms with respect to one another as free variables leads to an occupancy of 64:36. The two partially occupied positions are shifted around the C_3 axis by 41.3°. Therefore, the carbon atoms of the methyl groups which are in between two Sn positions move very close together. For this reason, the determination of the coordinates and the refinement of the occupancy factors could not be undertaken for those atoms. Consequently, the geometric addition of H atoms was not considered as sensible. The C atoms, C-1, C-4, and C-7, are found in the area swept out by the wedge formed from the Sn(64%)/N1/Sn(36%) atoms (78.8°) and each can be found in two positions. The refinement of the less occupied positions (C1a, C4a, C7a, not depicted) had to be done only isotropically.

The Sn_3N skeleton is planar as for **3a**, **3b**, and **3r**. AM1 calculations on **1** show bond lengths comparable to the experimental data, but a significant pyramidalization of the N center (see below). The Sn−N bond lengths d(SnN) = 2.04 Å correspond to single bonds, as has been found for other stannylamines[39] and correlate well with the estimation of the bond length resulting from NMR data.

Results of AM1 and Ab Initio Calculations

To recognize possible $(dp)\pi$ interactions between Sn and N atoms and to calculate approximate bonding energies, AM1 calculations (PM3 basis set) were undertaken for $(H_2XSn)_3N$ (X = F, I, Cl)[40]. AM1 calculations were performed for **1**, **3a** and **3d**[31] and, furthermore, an ab initio calculation was done (LAN1DZ basis set) for the model compound $(H_3Sn)_3N$. The calculated molecular parameters are assembled in Table 3.

Table 3. Calculated and found structure parameters of some tristannylamines

compound	Bond Length [Å]				Bond Angle [°]		
	Sn-N	Sn-C	Sn-X1	Sn-X2	Sn-N-Sn	C-Sn-N	X-Sn-X
$(Me_3Sn)_3N$ **1**[5]	2.041(6)	2.164(5)	/	/	119.5(4)	108.3(2)	/
$(Me_2ClSn)_3N$ **3a**[6]	1.988(7)	2.079(1)	2.808(1)	2.728(2)	120.0(1)	118.1(2)	163.0(1)
$(Me_2BrSn)_3N$ **3b**	1.997(3)	2.082(1)	2.919(4)	2.855(4)	119.7(2)	119.2(4)	166.2(2)
$(Me_3Sn)_3N$ **1**[a]	2.049	2.142	/	/	117.3	116.4	/
$(Me_2ClSn)_3N$ **3a**[a]	2.012	2.079	2.560	2.560	120	118.1	163.0
$(Me_2ISn)_3N$ **3d**[a]	2.041	2.162	2.813	2.813	120	120.5	171
$(Me_2FSn)_3N$[a][40]	2.022	2.163	2.973	1.955	120	118.0	87.7
$(H_3Sn)_3N$[b]	1.999	1.706	/	/	120	109.5	/

[a] Results of AM1 calculations[31]. – [b] Result of an ab initio calculation of $(H_3Sn)_3N$ with LANL1DZ-basis set.

The AM1 calculations[6] for $(H_2ClSn)_3N$ show a preference for the bridged structure with D_{3h} symmetry in comparison to the unbridged structure with C_3 symmetry. The energy difference is 104.6 kJ/mol (for comparison, the dissociation energy of the intramolecular Sn−N adduct in *o*-diethylaminomethylphenyl(bromodimethyl)stannane **8** was estimated to be 97.9 kJ/mol via dynamic NMR techniques[41]).

An AM1 calculation for **3a** determines an energy difference between bridged (D_{3h}) and unbridged (C_3) of 143.5 kJ/mol[6], corresponding to an energy gain of 36 kJ/mol per chlorine bridge.

The energy hypersurface for $(H_2ClSn)_3N$ was determined for 13 different Sn−Cl bond lengths (2.30−2.80 Å) and 10 different Sn−N−Cl angles (70−115°)[6]. The ground state is in a very shallow valley. Simultaneously elongating the Sn−Cl bond and decreasing the N−Sn−Cl angle requires an energy barrier of only <4 kJ/mol to be overcome; the geometry leans towards the bridged form with D_{3h} symmetry and without any minima in between. According to AM1 calculations the energy barrier for a rotation around the Sn−N bond is 8 kJ/mol for the unbridged form.

The bridged type isomer of **3a** has a planar NSn_3 skeleton with the free electron pair of the N atom in an orbital of *p*-type as determined by model calculations. The structural parameters of **3a** and **3b** are the same except for the Sn−X bonds (see Table 3). The *p*-type orbital position of the free electron pair at the N atom which most likely will be the same for all of the tristannylamines investigated so far, has been documented for the first time at the sterically demanding triisopropylamine (one should also mention the planar C_3N skeleton of $(F_7C_3)_3N$[42]). Planar nitrogen atoms also can be found in trisilyl- and trigermylamines according to electron diffraction experiments[7]. The configuration of the N atom of "element amines" (amino compounds with atoms from elements in the second or third period connected to the nitrogen) are usually explained by a partial double bond character. The correct geometry of **3a**, **3b** and **3d** is also derived from AM1 calculations, but a discussion of $(dp)\pi$ interactions is not sensible, since this program is not suitably parameterized. Therefore, it would be interesting to know the structure of a triplumbylamine. The planarity of the NPb_3 skeleton of such a molecule could certainly not be explained by $(dp)\pi$ interactions because of the enormous difference of the size of the Pb and N atoms.

Calculation for the molecule $(H_2FSn)_3N$ gives results (see Table 3) which are drastically different from those obtained for $(H_2ClSn)_3N$. Strong asymmetry in the Sn−F bridges makes their existence in $(H_2FSn)_3N$ unlikely. Possibly intermolecular Sn−F−Sn interactions are energetically favorable over intramolecular fluorine bridges as in the case of the corresponding alkyltin fluorides[43].

Conclusion

Our investigations of the tristannylamines show that one can describe the structure and bonding of these molecules in solution successfully and they are compatible with the structures in the crystal and the gas phase. The trigonal planar arrangement of the Sn atoms around the N centers is forced neither by $(dp)\pi$ interactions nor by sterical overcrowding. Therefore, electronic effects should explain the arrangement of substituents. New ideas to explain structures of silylamines take into account $(p\sigma)^*$ interactions[44]. The second order Jahn-Teller effect (SOJT)[45] might explain the configuration at the N atom for all NM_3 and RNM_2 compounds with M = Si, Ge, Sn and Pb, as well as alkaline and alkaline earth metals. Molecular orbital theoretical approximations lead to the assumption that the transition from planar to the pyramidal configuration at the N center is dependent on the HOMO/LUMO gap in the molecule. Glidewell deals with the problem with the help of vibrational theory[46]. The decrease of symmetry from the trigonal planar to the pyramidal surroundings (vibronic transition)[47] combined with the electron transition, occurs if the energy difference between the nonbinding orbital of the free electron pair of the N atom and the anti-bonding σ^* level in amines is less than or equal to 4 eV (for example, NF_3). An explanatory model is based on the idea that there is an electron density transfer from electropositive substituents to the M−N bond which is mainly concentrated at the N atom. The increased repulsion between the σ electrons stabilizes the planar geometry at the N atom and the presence of the free electron pair into a *p*-type orbital. Further model systems are being investigated in order to put this idea on a broader foundation.

We gratefully acknowledge the support of this research by the *Deutsche Forschungsgemeinschaft*, the *Fonds der Chemischen Industrie* and the *Chemetall mbH*. We also thank Prof. *B. Wrackmeyer* for the recording of the INEPT HEED NMR spectra and, above all, for stimulating discussions. Further more we thank Dr. *J. Kroner*, Dr. *G. Linti*, Dr. *N. Metzler*, and Dipl. Chem. *H. Schwenk* for their competent support of the solution of problems concerning the crystal structure determinations as well as for the performance of geometry optimized approximate calculations. We also thank Mr. *P. Maier* and Mr. *S. Huber* for recording many NMR spectra, Mrs. *D. Ewald* for mass spectra and Mrs. *E. Kiesewetter* for IR spectra.

Experimental

Because of the air and moisture sensitivity of most compounds and their toxic properties[48], all reactions involving organo tin compounds were performed under dry dinitrogen or argon gas in a hood. Glassware was flame-dried in vacuo. The following starting materials were prepared according to literature procedures: Me_3SnCl[49], Me_2SnCl_2[49], Me_2SnBr_2[50], $(CD_3)_2SnBr_2$ (from $(CD_3)_4Sn$[51] and BBr_3 according to lit.[52]), Me_2SnI_2[53], Et_2SnCl_2[54], Et_2SnBr_2[55], *i*Pr_3SnCl[56], *i*Pr_2SnX_2 [X = Cl[57,56], Br[56] (according to lit.[49]), I[58] (according to a modified procedure from tin and *i*PrI in BuOH)], Bu_2SnX_2 [X = Cl[59], X = Br[60]], Bz_2SnX_2 [X = Cl[61] (yield about 9%; lit.[61]: 80%), I[62] (modified procedure see below), Bz_3SnCl[59], *t*Bu_2SnCl_2[63] (yield only 33% even after optimisation of reaction conditions, lit.[63]: 57%), *i*$PrMe_2SnCl$[64] (procedure see below), *t*$BuMe_2SnCl$ (in analogy to the preparation of *i*$PrMe_2SnCl$ from Me_2SnCl_2 and *t*BuMgCl/OEt_2)[64], $N(SnMe_3)_3$[10] according to a modified procedure from $NaNH_2/NH_3/OEt_2/Me_3SnCl$[28], $(Me_2SnCl)_3N$[6]. Compounds used as supplied: $NaNH_2$, Bu_3SnCl, metalorganyls: LiMe, LiC_4H_9 and LiPh as solutions in Et_2O, hexane, or in THF. − NMR: Jeol PMX 60, Jeol FX 90 Q, Jeol EX 400 (^1H, ^{13}C), Bruker AC 300 (HEED-INEPT measurements), Bruker AC P200 and Jeol GSX 270. Standards: TMS (internal, ^1H, ^{13}C); saturated $NaNO_3$ solution (external, ^{14}N); CH_3NO_2 (external, ^{15}N); tetramethyltin (external, ^{119}Sn). When the coupling constant is stated as $^nJ(^{119(117)}Sn^mX)$ = ..., (...), the value in parentheses describes the coupling of the X nucleus with the ^{117}Sn isotopomere. The formulation $^nJ(^{119/117}Sn^mX)$, represents the coupling of both isotopomers with X, if coupling cannot be observed separately. ^{15}N-NMR measurements with the INEPT pulse sequence were successful only in few cases; variation of the $^3J(^{15}N^1H)$: 0.4 to 0.7 Hz. − Abbreviations: s = singlet, d = doublet, t = triplet, m = multiplet, mc = center of a multiplet, pd, pt, pq = pseudo doublet, -triplet, -quadruplet, br = broad, n.o.: not observed. Chemical shifts δ are given in ppm, coupling constants *J* in Hz. − MS: Varian Atlas CH-7. In all cases the calculated isotopic pattern of M^+ or, in case of very low intensity, the fragment with the highest mass could be observed. The data refer to a ionisation by electron impact at 70 eV in the sequence: *m*/*z* (%, assignment). The masses found refer to the isotopes ^1H, ^{12}C, ^{14}N, ^{35}Cl, ^{79}Br, ^{127}I, ^{120}Sn. − IR data are quoted in cm^{-1}, in most cases without CH valence frequences. − Elemental analysis: Microchemical Laboratory of the department. − X-ray Structure Analysis: Siemens P4 four circle diffractometer; $Mo_{K\alpha}$ radiation, graphite monochromator; single crystals were mounted under argon using glass capillaries; **1** was coated with perfluoro ether oil. Crystal data were determined and intensity data recorded at 213 K; program X-scan, structure solution by Patterson methods and refinement using the SHELXPLUS PC-version package and final refinement was performed using the SHELX 93 programs. All atoms except the hydrogen atoms are described with anisotropic temp. factors; all hydrogen positions were refined by using the riding model and fixed U_i. Details of the crystal structure determinations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository numbers CSD-404313 (**1**), -404312 (**3b**), -404314 (**3r**), the names of the authors, and the journal citation. When stated, "method a)", refers to the synthesis described for **3b**, method a).

Dimethylisopropyltinchloride (Modified procedure according to lit.[61]): To a suspension of Me_2SnCl_2 (35.9 g, 164 mmol) in Et_2O (350 ml) was added dropwise at 0 °C with stirring a 2.56 M solution of *i*PrMgCl in THF (65 ml, 164 mmol). Then the solvent was removed at 0 °C/13 Torr and the residue kept under reflux for 1.5 h. At 25 °C the insoluble part was separated by centrifugation and washed twice with petrol ether (100 ml each). After removal of the solvent from the solution at 25 °C/13 Torr, fractional distillation at 30 °C/10^{-3} Torr yielded 28 g of a 30:70 mixture, consisting of *i*Pr_2SnMe_2 and Me_2*i*PrSnCl. − NMR (C_6D_6): δ^1H = 0.15 [s, Sn-CH_3 (*i*Pr_2SnMe_2), $^2J(^{119(117)}Sn^1H)$ = 50 (47)], 0.34 [s, Sn-CH_3, $^2J(^{119(117)}Sn^1H)$ = 52 (49)]; δ ^{119}Sn = 4.8 (*i*Pr_2SnMe_2), lit.: 3.7[18], 154 (Me_2*i*PrSnCl), integral ratio of the Me protons: 8.5:15.5. − The fraction at 81 °C/10^{-3} Torr consists of 3.1 g (8.3%) of the pure Me_2*i*PrSnCl; it is a colourless, extremely unpleasant smelling liquid. − NMR (C_6D_6): δ^1H = 0.36 [s, 6 H, Sn-CH_3, $^2J(^{119(117)}Sn^1H)$ = 52 (49)], 1.16 [d, 6 H, C-CH_3, $^3J(^{119(117)}Sn^1H)$ = 99 (94)], 1.45 [sept., 1 H, CH_3-CH, $^2J(^{119/117}Sn^1H)$ = 67.3]; $\delta^{13}C$ = −3.47 [s, Sn-CH_3, $^1J(^{119(117)}Sn^{13}C)$ = 319 (305)], 20.0 [s, C-CH_3, $^2J(^{117/119}Sn^{13}C$ = 17], 21.83 [s, CH-CH_3, $^1J(^{119(117)}Sn^{13}C)$ = 449 (429)]; $\delta^{119}Sn$ = 155. − IR (film): 1180 (m), 1159 (w), 1096 (w), 1077 (w), 983 (m), 910 (w), 723 (s), 587 (w), 523 (s), 491 (w), 389 (w). − MS: 228 (7, M^+), 213 (6, $M^+ - CH_3$), 198 (2, $M^+ - C_2H_6$), 193 (18, $M^+ - Cl$), 185 (66, M^+ − *i*Pr), 177 (10, $M^+ - HCl$, $- CH_3$), 170 (2.5, M^+ − *i*Pr, − CH_3), 155 (20, M^+ − *i*Pr, − C_2H_6), 135 (34, $SnCH_3^+$).

Tribenzyltin Iodide (Modified procedure according to ref.[58]): Tribenzyltinchloride (19.7 g, 46 mmol) dissolved in 150 ml acetone was treated with NaI (6.9 g, 46 mmol) added in several portions. The colour of the mixture gradually turned brown-violet. After stirring overnight all insoluble material was removed by centrifugation and the clear solution was brought to dryness. The residue was recrystallized from CH_2Cl_2 at −78 °C. Yield: 21.4 g (89%). − NMR ($CDCl_3$): δ^1H = 2.91 [s, 2 H, $^2J(^{119}Sn^1H)$ = 61], 7.01 (m, 5 H).

Dibenzyltin Diiodide[59]: Tribenzyltin iodide (21.4 g, 41.1 mmol) dissolved in about 150 ml of CCl_4 was treated with iodine (10.4 g, 82.2 mmol). After stirring for 12 h at 30 °C, the solvent was removed in vacuo and the violet-coloured, slowly-solidifying residue was dissolved in CH_2Cl_2. After removal of insoluble impurities by filtration and evaporation of the solvent in vacuo the remaining material was recrystallized twice from CH_2Cl_2 at −78 °C. Yield 1.7 g (7.8%). − NMR ($CDCl_3$): $\delta^{1}H$ = 3.42 [s, 4H; $^{2}J(^{119/117}Sn^{1}H)$ = 62.7], 7.1−7.34 (m, 10H); $\delta^{13}C$ = 32.0 [$SnCH_2$-, $^{1}J(^{119/117}Sn^{13}C)$ = 284], 125.9 [*p*-C, $^{5}J(^{119/117}Sn^{13}C)$ = 31], 128.0 [*o*-C, $^{3}J(^{119(117)}Sn^{13}C)$ = 42 (37.5)], 128.9 [*m*-C, $^{4}J(^{119/117}Sn^{13}C)$ = 2.6], 136.5 (*i*-C, $^{2}J(^{119/117}Sn^{13}C$ = 59]; $\delta^{119}Sn$ = −130.6.

Tris(dimethylisopropylstannyl)amine (**2a**): To a suspension of $NaNH_2$ (0.6 g, 14.4 mmol) in 11 ml of liquid NH_3 and 2.5 ml of petroleum ether, *i*$PrMe_2SnCl$ (3.1 g, 13.4 mmol) dissolved in 5 ml of Et_2O was added slowly at −78 °C. After warming to ambient temp. and removal of the solvents at 25 °C/13 Torr, the nonvolatile residue was suspended in petroleum ether, centrifuged, and the solvent of the supernatant liquid was removed at 0 °C/10^{-3} Torr. Purification by Kugelrohr distillation (34 °C/10^{-3} Torr) yielded 0.5 ml of **2a** (0.9 g, 33%) as a pungent smelling, colourless liquid. − NMR (C_6D_6): $\delta^{1}H$ = 0.20 [s, 18H, $SnMe_2$, $^{2}J(^{119/117}Sn^{1}H)$ = 48] 1.23 [sept., 3H, Sn*CH*Me_2, $^{2}J(^{119/117}Sn^{1}H)$ = n.o.], 1.24 [(d, 18H, $CHMe^2$, $^{3}J(^{119/117}Sn^{1}H)$ = 88.9 (85.5)]; $\delta^{13}C$ = 5.04 [s, $SnMe_2$, $^{1}J(^{119(117)}Sn^{13}C)$ = 338 (327)], 20.18 [s, Sn*C*HMe_2, $^{1}J(^{119(117)}Sn^{13}C)$ = n.o.], 20.36 [s, SnCH*Me_2*, $^{3}J(^{119/117}Sn^{13}C)$ = 14.3]; $\delta^{119}Sn$ = 89.2 (s, $^{2}J(^{117}Sn^{119}Sn)$ = 207); $\delta^{14}N$: −406. − MS: 593 (5, M^+), 563 (<1, $M^+ - C_2H_6$), 401 (1, $M^+ - H_2CSn$*i*PrMe), 385 (8, M^+ − *i*$PrMe_3Sn$), 359 (100, 401 − C_3H_6), 345 (5, $387^+ - C_3H_6$), 317 (35, $359^+ - C_3H_6$), 301 (90, $317^+ - CH_4$), 285 (23, $301^+ - CH_4$), 271 (45, $301^+ - C_2H_6$), 256 (20, $271^+ - CH_3$), 194 (22, $345^+ - Me_2SnH$), 177 (8, $194^+ - NH_3$), 167 (30, 345^+ − *i*PrMeSn), 151 (35, $167^+ - NH_2$), 135 (70, $SnMe^+$). − IR (film): 1463 (m), 1420 (w), 1384 (m), 1367 (w), 1261 (w), 1200 (m), 1186 (m), 1154 (w), 1097 (w), 1081 (w), 987 (m), 917 (w), 871 (m), 770 (s), 727 (s), 601 (w), 528 (s), 494 (w), 393 (w). − $C_{15}H_{39}NSn_3$ (589.5): calcd. C 30.56, H 6.62, N 2.37; found C 31.02, H 6.73, N 2.02.

Tris(dimethyl-tert-butyl)stannylamine (**2b**): Prepared as described for compound **2a**; $NaNH_2$ (1.2 g, 28 mmol) 22 ml of liquid NH_3, 5 ml of petroleum ether, *t*$BuMe_2SnCl$ (6.8 g, 28 mmol) in 10 ml of ether. Yield: 2.5 ml of **2b** (4.3 g, 73.3%), as a colourless, pungent smelling liquid, b.p. 32 °C/10^{-3} Torr. − NMR (C_6D_6): $\delta^{1}H$ = 0.07 [s, 18H, $SnMe_2$, $^{2}J(^{119/117}Sn^{1}H)$ = 49], 1.08 [s, 27H, [*t*Bu, $^{3}J(^{119(117)}Sn^{1}H)$ = 73.5 (70.3)]; $\delta^{13}C$ = −7.18 [s, $SnMe_2$, $^{1}J(^{119(117)}Sn^{13}C)$ = 326 (304)], 25.46 [s, Sn*C*Me_3, $^{1}J(^{119(117)}Sn^{13}C)$ = 400 (376)], 29.74 [s, C(*CH_3*)$_3$, $^{2}J(^{119}Sn^{13}C)$ = 98]; $\delta^{119}Sn$ = 76.8 [s, $^{2}J(^{119}Sn^{117}Sn)$ = 242]; $\delta^{14}N$ = 410 ($h_{1/2}$ = 274 Hz). − MS: 620 (11, M^+ − 15), 429 (2, M^+ − *t*$BuMeSnCH_2$), 373 (41, 429 − C_4H_8), 357 (3, $373^+ - CH_4$), 343 (4, 373 − C_2H_6), 317 (52, $373^+ - CH_4$), 301 (40, $317^+ - CH_4$), 285 (38, $301^+ - CH_4$), 271 (26, $301^+ - C_2H_6$), 256 (10, $285^+ - C_2H_5$), 207 (28, *t*$BuMe_2Sn^+$), 165 (88, $SnMe_2NH^+$), 150 (20, $SnMe_2^+$), 135 (44, $SnMe^+$). − IR (film): 1701 (w), 1466 (s, *t*Bu), 1389 (w), 1364 (s), 1261 (w), 1190 (w), 1184 (m), 1170 (w), 715 (s), 524 (s), 505 (m). − $C_{18}H_{45}NSn_3$ (631.6): calcd. C 34.23, H 7.18, N 3.22; found C 34.23, H 6.75, N 3.50.

Tris(tributylstannyl)amine (**2c**): Prepared as described for compound **2a**; *n*Bu_3SnCl (9.3 g, 28.5 mmol) in 10 ml of ether, $NaNH_2$ (1.1 g, 28.5 mmol) in 15 ml of NH_3, 5 ml of petroleum ether. Yield 1.7 g **2c** (31%) as a viscous, slightly muddy liquid, b.p. 46 °C/10^{-3} Torr. − NMR (C_6D_6): $\delta^{1}H$ = 0.88 (t, 27H, δ-CH_3), 0.92 (t, 18H, α-CH_2), 1.37 (quint., 18H, β-CH_2), 1.56 (sext., 18H, γ-CH_2); $\delta^{13}C$: 14.1 (δ-C), 14.7 [α-C, $^{1}J(^{119/117}Sn^{13}C)$ = 360], 27.9 [β-C, $^{2}J(^{119/117}Sn^{13}C)$ = 59.1], 29.1 [γ-C, $^{3}J(^{119/117}Sn^{13}C)$ = 19.5]; $\delta^{119}Sn$ = 73.0 [$^{2}J(^{119}Sn^{117}Sn)$ = 226]; $\delta^{14/15}N$ = n.o. − MS: 887 (5, M^+), 614 (9), 596 (14, M^+ − *n*Bu_3Sn), 540 (<1, $596^+ - C_4H_8$), 539 (100, M^+ − *n*Bu_4Sn), 484 (2, $540^+ - C_4H_8$), 433 (10), 428 (65, $484^+ - C_4H_8$), 377 (1), 372 (92, $428^+ - C_4H_8$), 316 (100, $372^+ - C_4H_8$), 305 (7, M^+ − (*n*$Bu_3Sn)_2$), 291 (20, $SnBu_3^+$), 269 (84, 539/2^+), 260 (29, $316^+ - C_4H_8$), 250 (93, $H_2NSnBu_2^+$), 248 (55, $CH_2SnBu_2^+$), 241 (55), 213 (22), 199 (18), 177 (74, $SnBu^+$), 155 (26, $SnMe^+$), 120 43, Sn^+), 57 (63, *n*-Bu^+). − IR (nujol/hostaflon): 1464 (s), 1458 (s), 1416 (m), 1376 (s), 1357 (w), 1340 (m), 1291 (m), 1271 (w), 1260 (w), 1248 (w), 1192 (w), 1181 (w), 1146 (w), 1069 (s), 1048 (m), 1017 (m), 1001 (m), 960 (m), 873 (m), 861 (m), 840 (w), 796 (w), 768 (w), 743 (m), 711 [s, $\nu_{as}(NSn_3)$], 682 [s, δ(SnNSn)], 591 (s), 499 [m, $\nu_s(SnC_3)$], 451 (w), 407 (w), 390 (w), 346 (w), 334 (w), 320 (w). − $C_{36}H_{81}NSn_3$ (884.1): calcd. C 48.91, H 9.23, N 1.58; found C 49.97, H 8.95, N 2.01.

Attempt to Prepare Bis(trimethylstannyl(chlorodimethylstannyl)amine by Reaction of **1** *with Me_2SnCl_2 (Molar Ratio 1:1):* Me_2SnCl_2 (4.1 g, 18.8 mmol), dissolved in 20 ml of CH_2Cl_2, was added to a solution of **1** (9.5 g, 18 mmol) in 30 ml of CH_2Cl_2 at −78 °C with stirring. After warming to ambient temp. and removal of CH_2Cl_2 at 40 °C/720 Torr, Me_3SnCl (6.8 g, 106%) was trapped at −78 °C by keeping the residue at 25 °C/10^{-5} Torr. ^{1}H- und ^{119}Sn-NMR spectra of a sample of the viscous residue dissolved in CH_2Cl_2 showed several signals which could not be assigned. Further heating of the residue to 80 °C/10^{-5} Torr yielded additional Me_3SnCl (0.8 g). The nonvolatile material was insoluble in CH_2Cl_2, CCl_4, OEt_2, benzene, toluene, petroleum ether. It contained 7.3% Cl^-. This material was not investigated further.

Reaction of **1** *with tBu_2SnCl_2 (Molar ratio 1:1), Attempt to Prepare Bis(trimethylstannyl)(chlorodi-tert-butylstannyl)amine* (**3p**): *t*Bu_2SnCl_2 (2.6 g, 8.7 mmol) dissolved in 10 ml of CH_2Cl_2 was added dropwise at −78 °C and with stirring to a solution of **1** (4.4 g, 8.7 mmol) in 10 ml of CH_2Cl_2. After allowing the mixture slowly to attend ambient temp., a sample was checked by ^{1}H- und ^{119}Sn NMR spectroscopy. NMR (CH_2Cl_2/Tol): $\delta^{1}H$ = 0.43 [s, br, $^{2}J(^{119}Sn^{1}H)$ = 52], 0.56 (s, Me_3SnCl), 1.36 [s, *t*Bu, $^{3}J(^{119}Sn^{1}H)$ = 80]; $\delta^{119}Sn$ (measured in the invers gatet pulse mode): 85.6 (1 Sn, br, *t*BuSn), 89.6 [2 Sn, $^{2}J(^{119}Sn^{117}Sn)$ = 106], 159.7 (Me_3SnCl). Subsequently the solvent was removed in vacuo and Me_3SnCl (1.6 g, 92%) was sublimed at 25 °C/10^{-3} Torr into a cooled trap (−78 °C). The large number of not assignable signals in the ^{1}H- and ^{119}Sn-NMR spectra of the residue points to the formation of decomposition products.

Reaction of **3a** *with PhLi (Molar Ratio 1:3), Formation of Ph_2SnMe_2:* A solution of **3a** (5.6 g, 9.9 mmol) dissolved in 25 ml of Et_2O was stirred and treated dropwise at 0 °C with 14.9 ml of a 2 M PhLi solution in cyclohexane/Et_2O. After 12 h stirring at ambient temp., a filtered sample of the suspension formed contained only Ph_2SnMe_2 as shown by NMR, $\delta^{119}Sn$ = −62.0; lit.: −60[18].

Pyrolysis of Tris(chlorodimethylstannyl)amine (**3a**): a) **3a** (1.0 g, 1.8 mmol) was heated stepwise (ΔT = 10 °C) from 50 °C to 150 °C in a 5 mm NMR tube, while the selected temp. was kept constant for 90 min. No decomposition was detected by ^{1}H-NMR spectroscopy. Visable decomposition of the crystalline **3a** into a yellow oil started at ca. 160 °C with formation of Me_3SnCl {$\delta^{1}H(CH_2Cl_2)$ = 0.66 [s, $SnMe_3$, $^{2}J(^{119(117)}Sn^{1}H)$ = 58 (56)]} at the same time. After 8 h at 160−170 °C only Me_3SnCl but no **3a** could be detected in the CH_2Cl_2-soluble part of the residue (^{1}H and ^{119}Sn NMR). The colourless solid was insoluble in CH_2Cl_2, $CDCl_3$, toluene, Et_2O and THF. − b) **3a** (5.0 g, 8.8 mmol) dissolved in 150 ml of *o*-dichlorobenzene was heated to 120 °C for 5 d. The ^{1}H-NMR spectrum showed **3a** at the limit of detection in addition to five additional signals. δ^1H (o-$Cl_2C_6H_4$) = 0.61 [s, 18 H, $SnMe_3$, $^2J(^{119(117)}Sn^1H)$ = 58 (56)], 0.75 (?), 1.0 [s, SnMe, $^xJ(^{119(117)}Sn^1H)$ = 52 (49), ?], 1.13 (s, br, SnMe, $^xJ(^{119(117)}Sn^1H)$ = n.o.], 1.20 [s, Cl_2SnMe_2 ?, $^2J(^{119(117)}Sn^1H)$ = 68 (65)]; Integral ratio: 10.5:4.0:2.6:2.9:2.7. Separation of the Me_3SnCl from the solvent failed. – c) 5.0 g of **3a** in toluene was warmed up to 80 °C for 14 d. Hereafter, **3a** could not be detected. Except Me_3SnCl [ca. 1.4 g (79% refering to the ratio of **3a**) was obtained from recrystallization from a toluene solution] and traces of Me_2SnCl_2, no other products could be isolated from the solid, neither by recrystallization from CH_2Cl_2 or toluene, nor by sublimation in vacuo. δ^1H(tol) = 0.55 [s, $SnMe_3$, $^2J(^{119(117)}Sn^1H)$ = 58 (56)], 1.0 (?), 1.1 [s, Cl_2SnMe_2 ?, $^xJ(^{119(117)}Sn^1H)$ = 67 (65)], 1.3 [s, br, SnMe, $^xJ(^{119(117)}Sn^1H)$ = n.o.], 1.6 [s, br, SnMe ?, $^xJ(^{119(117)}Sn^1H)$ = n.o.]; integral ratio: 0.5:4.5:2.0:2.3:4.0.

IR-Date of Tris(chlorodimethylstannyl)amine (**3a**): IR (nujol/hostaflon): 2965 (s), 2932 (s), 2861 (m), 2845 (s), 1465 (m), 1401 (m), 1191 (m), 782 (s, $\rho(SnC_3)$, 734 [s, $\nu_{as}(NSn_3)$], 597 [w, $\delta(NSn_2)$], 554 [m, $\nu_{as}(SnC_2)$], 520 [s, $\nu_s(SnC_2)$], 290 [s, ν("SnClSn")].

Tris(bromdimethylstannyl)amine (**3b**): a) To a suspension of 6.9 g Me_2SnBr_2 (22 mmol) in 30 ml of CH_2Cl_2 at −30 °C with stirring half of a solution of 3.8 g $N(SnMe_3)_3$ **1** (7.5 mmol) dissolved in 15 ml of CH_2Cl_2 was added dropwise. The rest of this solution was added at −60 °C. After allowing the solution to slowly attain ambient temp. (12 h), the solvent was condensed at 25 °C/10^{-2} Torr into a cooled trap (−78 °C), 4.3 g of Me_3SnBr (82%) was distilled at 28 °C/10^{-2} Torr from the residue which was subsequently suspended in pentane. After removal of pentane from the residue at 25 °C/10^{-2} Torr, additional Me_3SnBr (0.5 g, ~10%) was recovered by distillation at 28 °C/10^{-2} Torr. The off-white, solid residue was recrystallized twice from CH_2Cl_2 (25°/−20 °C) to give 4.2 g of **3b** (81%) as a colourless powder, m.p. 159 °C. Single crystals suitable for X-ray structure analysis separated from a saturated solution of **3b** in petroleum ether by slow diffusion of the solvent into paraffine at ca. 25 °C. – NMR ($CDCl_3$): δ^1H = 1.1 [s, $SnMe_2$, $^2J(^{119(117)}Sn^1H)$ = 70 (65)]; δ^{13}C = 10.3 [$SnMe_2$, $^1J(^{119(117)}Sn^{13}C)$ = 485 (463)]; δ^{119}Sn = 67.0 [$^2J(^{119}Sn^{117}Sn)$ = 43]; δ^{14}N = −308. – MS: 689 (98, M^+ − Me), 622 (30, M − Br), 378 (17, M^+ − Me_3SnBr − Br), 348 (36, 378^+ − C_2H_6), 229 (100, Me_2SnBr^+), 214 (33, $Me{-}Sn{-}Br^+$), 199 (95, $SnBr^+$). – IR (nujol/hostaflon): 3276 (w), 3181 (w), 2959 (s), 2929 (s), 2856 (m), 2261 (m), 2123 (m), 1700 (w), 1463 (m), 1395 (m), 1189 (w), 925 (w), 780 (s), 721 (s), 588 (s), 549 (s), 516 (s), 249 (m). – $C_6H_{18}Br_3NSn_3$ (699.7): calcd. C 10.30, H 2.59, N 2.00, Br 34.25; found C 10.46, H 2.67, N 1.98, Br 33.93. – b) To 4.8 g Me_2SnBr_2 (15.4 mmol) dissolved in 20 ml of CH_2Cl_2, 50% of a solution of **1** (2.6 g, 5.2 mmol) in 10 ml of CH_2Cl_2 at 0 °C was added dropwise; the rest at −30 °C. The following ^{1}H-NMR signals were recorded after warming the reaction mixture to ambient temp. (numbers in brackets are the relative signal intensity): 0.43 (1), 0.5 (1.3), 0.59 (2.4), 0.69 (14), 0.81 (4), 0.84 (0.5), 1.0 (7.3), 1.25 (3), 1.3 (3), 1.7 (1). From comparison of the δ^1H and $^2J(^{119}Sn^1H)$ data with the data for **3b**, prepared according to method a), the yield of the product was estimated as 47% mixed with non identifiable species. No further workup was attempted.

Tris(bromo[D6]dimethylstannyl)amine (**3c**): Method a); **1** (1.1 g, 2.1 mmol) in 5 ml of CH_2Cl_2, [D_6]Me_2SnBr_2 (2.0 g, 6.3 mmol) in 10 ml of CH_2Cl_2. The volatile components of the reaction mixture were condensed at 25 °C/10^{-6} Torr into a cooled trap (−78 °C). After removal of CH_2Cl_2 from the trapped components at 25 °C/13 Torr, 1.5 g Me_3SnBr (97%) was distilled at 30 °C/10^{-2} Torr. Treatment of the residue with 20 ml CH_2Cl_2 afforded 1.1 g (72%) colourless crystals of **3c** at −20 °C, m.p. 172–174 °C. – NMR ($CDCl_3$): δ^{13}C = 9.50 (sept.); δ^{119}Sn = 73 [$^2J(^{119}Sn^{117}Sn)$ = 62]. – IR (nujol/-hostaflon): 783, 739, 722, 696, 605, 542, 519, 471, 253. – $C_6D_{18}Br_3NSn_3$ (718.1): calcd. C 10.04, N 1.95, Br 33.38; found C 9.86, N 1.78, Br 32.90; MS 719.

Reaction of Tris(trimethylstannyl)amine **1** *with Me_2SnI_2 (Molar Ratio 1:3):* To a suspension of **1** (2.3 g, 4.4 mmol) in 20 ml of CH_2Cl_2 was added dropwise at −60 °C a suspension of Me_2SnI_2 (5.4 g, 13.5 mmol) dissolved in 50 ml of CH_2Cl_2. After allowing the mixture to attain ambient temp. (12 h) thc ^{1}H-NMR spectrum of the yellow solution confirmed the quantitative formation of Me_3SnI. – NMR data of the mixture ($CDCl_3$): δ^1H = 0.92 [s, 27 H, Me_3SnI, $^2J(^{119}Sn^1H)$ = 57.2], Lit.[18]: 0.88 [$^2J(^{119}Sn^1H)$ = 57.2], 1.25 [s, 18 H, $SnMe_2$, $^2J(^{119/117}Sn^1H)$ = 65]; δ^{13}C = −1.6 [$SnMe_3I$, $^1J(^{119}Sn^{13}C)$ = 322], 11.0 [$SnMe_2I$, $^1J(^{119/117}Sn^{13}C)$ = 466]; δ^{119}Sn = 45.5, Me_3SnI, [lit.[65]: 38.6], 24.9 [$N(SnMe_2I)_3$?, $^2J(^{119}Sn^{117}Sn)$ = 67,], 21, br, −120 br, −154 [Me_2SnI_2, lit.[18]: −158]; intensity rates about: 5:4:1:1:0.8; δ^{14}N = −380 ($h_{1/2}$ = 18.6)]. After removal of the solvent in vacuo the solid residue turned brown while subliming Me_3SnI at 25 °C/10^{-3} Torr and dissolved only sparingly in CH_2Cl_2, toluene, Et_2O or PE. The ^{1}H-NMR spectrum of a CH_2Cl_2 solution of the nonvolatile material showed 12 signals besides that of Me_3SnI. Attempts to obtain a pure product by sublimation or recrystallization failed because of the nonvolatility of the residue in vacuo and its insolubility. No further workup was carried out.

Reaction of Tris(chlorodimethylstannyl)amine **3a** *with NaI (Molar Ratio 1:3):* **3a** (5.5 g, 9.7 mmol) dissolved in 25 ml of Et_2O was treated with NaI (4.5 g, 29.1 mmol) at room temp. After stirring of the brown solution for 2 d, the insoluble material was separated by centrifugation and the volatile components were removed in vacuo from the solution. The residue was dissolved in 20 ml of CH_2Cl_2; [NMR spectrum of a sample in CH_2Cl_2/$CDCl_3$ solution: δ^1H = 0.98 (s, SnMe), 1.10 (?), 1.28 (Me_2SnCl_2 ?), 1.64 (Me_2SnI_2) integral ratio: 1.2:0.9:0.4:4.8; δ^{119}Sn = 24.3 (very small), −156 (Me_2SnI_2, lit.: −159[25]). Me_2SnI_2 (8.1 g, 69% calcd. on the amount of NaI) was obtained by sublimation at 25 °C/10^{-5} Torr. The insoluble residue was not investigated further.

Tris(chlorodiethylstannyl)amine (**3e**): Method a); Addition of 50% of 3.4 g **1** (4.5 g, 6.7 mmol) dissolved in 15 ml of CH_2Cl_2 at 0 °C, (the rest at −30 °C) to a solution of Et_2SnCl_2 (5.0 g, 20 mmol) dissolved in 15 ml of CH_2Cl_2 was performed. After the solution had attained 25 °C, the solvent was stripped of at 10^{-3} Torr. Recrystallization of the residue twice from CH_2Cl_2 (15 ml each, 25 °C/−20 °C) gave 3.4 g of **3e** (77%) as a colourless powder, m.p. 103 °C. – NMR ($CDCl_3$): δ^1H = 1.37 [q, 12 H, $SnCH_2$, $^2J(^{119/117}Sn^1H)$ = 58], 1.47 [t, 18 H, $SnCH_2CH_3$, $^3J(^{119/117}Sn^1H)$ = 88], δ^{13}C = 9.45 [CH_2CH_3, $^2J(^{119(117)}Sn^{13}C)$ = 37 (33)], 18.8 [CH_2CH_3, $^1J(^{119(117)}Sn^{13}C)$ = 467 (446)]; δ^{119}Sn = 67.7 [$^2J(^{119}Sn^{117}Sn)$ = 69]; δ^{14}N = −348; δ^{15}N = −354 [$^1J(^{119}Sn^{15}N)$ = 89.5]. – MS: 653 (0.5, M^+), 623 (69, M^+ − C_2H_6), 593 (1, M^+ − 2 C_2H_6), 563 (15, M^+ − 3 C_2H_6), 441 (3, M^+ − Et_2SnCl), 213 (22, M^+ − $N(SnEt_2Cl)_2$), 184 (19, $EtSnCl^+$), 155 (100, $SnCl^+$). – IR (nujol/-hostaflon): 2969 (s), 2952 (s), 2928 (s), 2871 (s), 2820 (w), 2732 (w), 2148 (w), 1457 (m), 1418 (m), 1377 (m), 1233 (w), 1190 (m), 1022 (m), 960 (m), 753 (s), 677 (s), 596 (m), 524 (m), 493 (m), 312 (s). – $C_{12}H_{30}Cl_3NSn_3$ (650.6): calcd. C 22.15, H 4.65, N 2.15, Br 16.34; found C 22.46, H 4.19, N 2.15, Br 15.93.

Tris(bromodiethylstannyl)amine (**3f**): Method a); Et_2SnBr_2 (11.6 g, 34.5 mmol) dissolved in 15 ml of CH_2Cl_2; **1** (5.8 g, 11.5 mmol) dissolved in 15 ml of CH_2Cl_2, reaction temp. −30 °C. Isolation of 7.3 g Me_3SnBr (86%) at b.p. 28 °C/10^{-3} Torr, and additional 1 g Me_3SnBr within 12 h at 25 °C/10^{-5} Torr by condensation into a cooled trap. Crystallization of the residue from 10 ml of CH_2Cl_2 gave **3f** (3.84 g, 38.5%) in 24 h at −30 °C as colourless crystals, m.p. 119−121 °C. – NMR ($CDCl_3$): $\delta^{1}H$ = 1.40 [t, 18 H, CH_3, $^{3}J(^{119}Sn^{1}H)$ = n.o., 1.61 [q, 12 H, CH_2, $^{2}J(^{119}Sn^{1}H)$ = n.o.], $\delta^{13}C$ = 9.90 [$CH_2\mathit{C}H_3$, $^{2}J(^{119/117}Sn^{13}C)$ = 38.4], 20.95 [$\mathit{C}H_2CH_3$, $^{1}J(^{119(117)}Sn^{13}C)$ = 462 (441)], $\delta^{119}Sn$ = 65.3 [$^{2}J(^{119}Sn^{117}Sn)$ = 62.5], $\delta^{15}N$ = −356 [$^{1}J(^{119}Sn^{15}N)$ = 103]. – MS: 755 (32, $M^+ - C_2H_6$), 725 (2, $M^+ - 2\ C_2H_6$), 695 (5, $M^+ - 3\ C_2H_6$), 642 (9, $695^+ - C_2H_4, - C_2H_2$), 587 (2), 529 (4, $M^+ - Et_2SnBr$), 393 (1, $529^+ - C_2H_2, -$ EtBr), 335 (5, $393^+ - 2\ C_2H_6$), 257 (21, 393 − HBr), 199 (52, SnBr), 162 (10), 120 (16, Sn). – IR (nujol/hostaflon): 2966 (s), 2950 (s), 2922 (s), 2867 (s), 2815 (w), 2727 (w), 2143 (w), 1456 (s, ethyl), 1416 (s), 1376 (s), 1261 (w), 1232 (m), 1187 (s), 1020 (s), 956 (m), 736 [s, $\nu_{as}(NSn_3)$], 678 (s), 594 (m), 535 (m), 521 [s, $\nu_{as}(SnC_2)$], 490 (m), 396 (w), 279 (m, SnBr). – $C_{12}H_{30}Br_3NSn_3$ (784.18): calcd. C 18.38, H 3.86, N 1.79; found C 18.33, H 3.99, N 1.54.

Tris(chlorodiisopropylstannyl)amine (**3g**): Prepared in analogy to **3f**. **1** (0.47 g, 0.92 mmol) dissolved in 10 ml of CH_2Cl_2, $\mathit{i}Pr_2SnCl_2$ (0.76 g, 2.76 mmol) in 10 ml of CH_2Cl_2; yield **3g** (0.5 g, 73%) as colourless, cereous solid, m.p. 52 °C. – NMR ($CDCl_3$): $\delta^{1}H$ = 1.52 [d, 36 H, $^{3}J(^{119/117}Sn^{1}H)$ = 113], 2.04 [sept., 6 H, $^{2}J(^{119/117}Sn^{1}H)$ = n.o.], $\delta^{13}C$ = 20.9 [$CH(\mathit{C}H_3)_2$, $^{2}J(^{119/117}Sn^{13}C)$ = 21], 31.4 [$\mathit{C}H(CH_3)_2$, $^{1}J(^{119(117)}Sn^{13}C)$ = 453 (433)]; $\delta^{119}Sn$ = 29.2 [$^{2}J(^{119}Sn^{117}Sn)$ = 94]; $\delta^{15}N$ = n.o. – MS: 737 (M^+, <1), 694 ($M^+ -$ *i*Pr, 19) and by the loss of alkyl groups a number of peaks with overlapping patterns due to Sn isotops. – IR (nujol/hostaflon): 1463 (s), 1453 (s), 1380 (m), 1365 (m), 1198 (s), 1155 (m), 1082 (w), 1001 (m), 923 (w), 873 (m), 720 [m, $\nu_{as}(NSn_3)$], 595 (s, br), 543 (s, br), 481 (w), 409 (w), 290 [s, ν(“SnClSn”)]. – $C_{18}H_{42}Cl_3NSn_3$ (735): calcd. C 29.42, H 5.76, N 1.91; found C 29.15, H 5.43, N 1.87.

Tris(bromodiisopropylstannyl)amine (**3h**): Method a); **1** (8.9 g, 17.6 mmol) in 25 ml of CH_2Cl_2, $\mathit{i}Pr_2SnBr_2$ (19.2 g, 52.7 mmol) in 25 ml of CH_2Cl_2; yield 14.1 g of **3h** (92.4%, after two-fold recrystallization from 10 ml CH_2Cl_2) as beige-coloured needles, m.p. 83 °C. – NMR ($CDCl_3$): $\delta^{1}H$ = 1.25 [d, 36 H, $CH(C\mathit{H}_3)_2$, $^{3}J(^{119(117)}Sn^{1}H)$ = 126 (118)], 2.0 [sept., 6 H, $C\mathit{H}(CH_3)_2$, $^{2}J(^{119/117}Sn^{1}H)$ = n.o.], $\delta^{13}C$ = 21.0 [$CH(\mathit{C}H_3)_2$, $^{2}J(^{119/117}Sn^{13}C)$ = 21], 33.0 [$\mathit{C}H(CH_3)_2$, $^{1}J(^{119(117)}Sn^{13}C)$ = 446 (427)]; $\delta^{119}Sn$ = 43.9 [$^{2}J(^{119}Sn^{117}Sn)$ = 97]; $\delta^{15}N$ = n.o. – MS: 869 (<1, M^+), 826 (23, $M^+ -$ *i*Pr), and a number of peaks due to the loss of alkyl groups whose isotopic patterns could not be separated to well defined fragments. – IR (nujol/hostaflon): 1460 (s), 1403 (m), 1366 (m), 1195 (s), 1153 (s), 1087 (m), 994 (s), 970 (m), 966 (w), 921 (m), 731 [s, $\nu_{as}(NSn_3)$], 593 (m), 523 (w), 503 (m), 481 (w), 398 (m), 273 [m, ν(“SnBrSn”)]. – $C_{18}H_{42}Br_3NSn_3$ (867.8): calcd. C 24.89, H 4.88, N 1.61, Br 27.60; found C 24.27, H 4.53, N 1.81, Br 27.10.

Bis(diisopropyldiodostannyl)(dimethyliodostannyl)amine (**3r**): A solution of $\mathit{i}Pr_2SnI_2$ (20.3 g, 44.3 mmol) in 200 ml of CH_2Cl_2 was treated dropwise at −78 °C with stirring with a solution of $(Me_3Sn)_3N$ **1** (7.45 g, 14.5 mmol) in 100 ml of CH_2Cl_2. The mixture was allowed to warm slowly to ambient temp. After the reaction mixture was reduced to about 60 ml the ^{119}Sn-NMR spectrum of a sample showed four main signals at δ = 110.5 ($\mathit{i}Pr_2MeSnI$), 100.4, 36.9 (Me_3SnI, lit.: 38.6[18]), 13.8; intensity ratio ~1:2:2:1]. After removal of all CH_2Cl_2 at 0 °C/14 Torr a mixture of Me_3SnI and $\mathit{i}Pr_2MeSnI$ (9.8 g, $\delta^{119}Sn$ = 37.1 and 111.3, ratio about 2:1) was condensed at 25 °C/10^{-2} Torr into a cooled trap. Dissolving the sticky residue in 20 ml of CH_2Cl_2 yielded 7.4 g (54%) of **3r** within 2 d at −20 °C in colourless cubic shaped crystals, m.p. 40 °C, dried 12 h at 10^{-3} Torr. Crystals suitable for X-ray structure analysis were obtained when the product was dried under streaming N_2 gas. – NMR (CH_2Cl_2/C_6D_6): $\delta^{1}H$ = 1.22 [s, 6 H, $SnMe_2$, $^{2}J(^{119(117)}Sn^{1}H)$ = 67.4 (64.5)], 1.27 [d, 24 H, $CH\mathit{Me}_2$, $^{3}J(^{1}H^{1}H)$ = 7.3, $^{3}J(^{119(117)}Sn^{1}H)$ = 117.6 (112.3)], 2.10 [sept., 4 H, $C\mathit{H}Me_2$, $^{2}J(^{117/119}Sn^{1}H)$ = n.o.)], $\delta^{13}C$ (C_6D_6) = 14.1 [(s, $SnMe_2$, $^{1}J(^{119(117)}Sn^{13}C)$ = 475 (454.5)], 21.6 [$CH\mathit{Me}_2$, $^{2}J(^{119/117}Sn^{13}C)$ = 21.2], 34.7 [$\mathit{C}HMe_2$, $^{1}J(^{119(117)}Sn^{13}C)$ = 416.1 (398.1)] (calculation of the CSnC angle of the Me_2ISn group according to [14]: $\Phi(SnC_2) = 0.0874 \times |^{1}J(^{119}Sn^{13}C)| + 79.419$, $\Phi(SnC_2) = 120.9°$; calculation of the CSnC angle of the $\mathit{i}Pr_2ISn$ group $\Phi(SnC_2) = 114.7°$); $\delta^{14}N$ (C_6D_6) = 370, $^{119}Sn_a$ = 15.3 [$SnMe_2I$, $^{2}J(^{119}Sn_a{}^{117}Sn_b)$ = 120, $h_{1/2}$ = 19.6 Hz], $\delta^{119}Sn_b$ = 99.2 [$Sn\mathit{i}Pr_2I$, $^{2}J(^{119}Sn^{117}Sn)$ = 121, $h_{1/2}$ = 32 Hz], HEED-INEPT experiment: $^{1}J(^{119}Sn_a{}^{15}N)$ = 98.8, $^{2}J(^{119}Sn_a{}^{119}Sn_b)$ = n.o., $^{1}J(^{119}Sn_b{}^{15}N)$ = 164, $^{2}J(^{119}Sn_b{}^{117}Sn_b)$ ≈ 160; HE delay for $\delta^{119}Sn_a$ = 0.05 s, for $\delta^{119}Sn_b$ = 0.025 s. The ^{1}H-coupled ^{119}Sn NMR spectrum showed a septuplet pattern [$^{2}J(^{119}Sn^{1}H)$ = 66] at $\delta^{119}Sn$ 15.3, at 99.2 a coupling pattern of higher order. – MS: 950 (<1, M^+), 935 (<1, $M^+ -$ Me), 907 (13.5, $M^+ - CHMe_2$), 863 (5.5, $907^+ -$ *i*PrH), 822 (8.3, $M^+ -$ HI), 737 (11, $M^+ -$ *i*Pr, − *i*PrI), 651 (12, $737^+ - Me_2CH - CHMe_2$), 459 (28, $Me_2C^+ - Sn\mathit{i}PrI_2$), 415 (64.7, $Me_2C^+ - SnI_2$), 374 (22, SnI_2), 305 (13.5, $\mathit{i}PrI_2Sn^+$), 290 (32.5, $\mathit{i}PrISn^+$), 247 (100, SnI^+), 163 (16, $\mathit{i}PrSn^+$), 135 (10, $MeSn^+$), 120 (31, Sn^+), 43 (24, Me_2CH^+). – IR (nujol/hostaflon): 2955 (s), 2937 (s), 2919 (s), 2916 (s), 2756 (w), 2717 (w), 1456 (s), 1384 (s), 1366 (s), 1193 (s), 1151 (m), 1088 (m), 996 (s), 988 (s), 921 (m), 870 (m), 805 (s, br), 781 (s, br), 704 (ss, br [m, $\nu_{as}(NSn_3)$?], 559 (m), 544 (m), 512 (m), 501 (m), 483 (w), 443 (w), 398 (m), 266 [m, ν(SnI) ?], 221 [m, ν(SnI) ?]. – $C_{14}H_{34}I_3NSn_3$ (953.3): calcd. C 17.64, H 3.60, N 1.47; found C 17.55, H 3.59, N 1.40.

Tris(chlorodibutylstannyl)amine (**3i**): Method a); Compound **1** (5.4 g, 10.7 mmol) was dissolved in 50 ml of CH_2Cl_2; $\mathit{n}Bu_2SnCl_2$ (9.78 g, 32.1 mmol) was dissolved in 50 ml of CH_2Cl_2; temp. −30 °C during addition. The rest of Me_3SnCl was removed at 80 °C/10^{-3} Torr. The remaining light brown liquid solidified at about −25 °C. Yield: 12.3 g of **3i** (47%). – NMR (C_6D_6): $\delta^{1}H$ = 0.91 [t, 18 H, δ-$C\mathit{H}_3$, $^{5}J(^{119/117}Sn^{1}H)$ = n.o.], 1.37 [sext., 12 H, γ-$C\mathit{H}_2$, $^{4}J(^{119/117}Sn^{1}H)$ = 119], 1.61 [t, 12 H, α-$C\mathit{H}_2$, $^{2}J(^{119/117}Sn^{1}H)$ = 80], 1.83 [q, 12 H, β-$C\mathit{H}_2$, $^{3}J(^{119/117}Sn^{1}H)$ = 130]; $\delta^{13}C$ = 13.8 (s, δ-CH_3, $^{4}J(^{119/117}Sn^{13}C)$ = n.o.], 26.8 [s, β-C, $^{2}J(^{119/117}Sn^{13}C)$ = 88], 27.2 [s, α-C, $^{1}J(^{119(117)}Sn^{13}C)$ = 452 (447)], 27.9 [s, γ-C, $^{3}J(^{119/117}Sn^{13}C)$ = 190 Hz]; $\delta^{119}Sn$ = 58.1 [s, $^{2}J(^{119}Sn^{117}Sn)$ = 68]; $\delta^{15}N$ = −347 [$^{1}J(^{119}Sn^{15}N)$ = n.o.]. – MS (FAB): 822 (35, $M^+ + 1$), 765 (3, $M^+ -$ *n*Bu), 653 (15, $M^+ - \mathit{n}Bu_2ClSn$), 638 (1, $653^+ - CH_3$), 610 (4, $653^+ -$ *n*Pr), 596 (1, $653^+ -$ *n*Bu), 561 (14, $596^+ -$ Cl), 284 (23, $\mathit{n}Bu_2ClSnNH^+$), 227 (3, $284^+ -$ *n*Bu), 192 (15, $227^+ -$ Cl), 177 (2, $192^+ - CH_3$), 163 (1, $192^+ - CH_3CH_2$), 149 (5, $192^+ -$ *n*Pr), 155 (25, SnCl). – IR (film): 1415 (m), 1378 (m), 1342 (m), 1293 (m), 1181 (m), 1154 (m), 1078 (m), 1024 (m), 962 (m), 778 (m), 754 (w), 459 (w). – $C_{24}H_{54}Cl_3NSn_3$ (819.1): calcd. C 35.19, H 6.65, N 1.71; found C 34.98, H 6.71, N 1.67.

Tris(bromodibutylstannyl)amine (**3k**): Method a); **1** (7.0 g, 13.9 mmol) was dissolved in 25 ml of CH_2Cl_2, $\mathit{n}Bu_2SnBr_2$ (16.4 g, 41.8 mmol) in 30 ml of CH_2Cl_2; temp. −60 °C. The solvent was removed at −30 °C/10^{-3} Torr, 4.1 g Me_3SnBr (40%) distilled from the residual muddy liquid at 25 °C/10^{-3} Torr and 10.3 g of a mixture of $\mathit{n}Bu_2SnBr_2$ and $\mathit{n}Bu_2MeSnBr$ distilled at 50 °C/10^{-3} Torr [^{119}Sn NMR: $\mathit{n}Bu_2SnBr_2$, $\delta^{119}Sn$ ($CDCl_3$): 87, $\mathit{n}Bu_2MeSnBr$, $\delta^{119}Sn$ ($CDCl_3$) = 136]. The viscous residue contained **3k** free of impurities according to ^{119}Sn- und ^{13}C-NMR data. Yield: 3.6 g (27.0%).

− NMR ($CDCl_3$): δ^{1}H = 0.78 (t, 18 H, δ-CH_3), 1.28 (sext. 12 H, γ-CH_2), 1.49 (quint., 12 H, β-CH_2), 1.62 (t, 12 H, α-CH_2); δ^{13}C = 13.5 (δ-C), 26.2 (γ-C), 27.7 (β-C, $^{2}J(^{119/117}Sn^{13}C)$ = 32.5), 28.9 [α-CH_2, $^{1}J(^{119/117}Sn^{13}C)$ = 448]; δ^{119}Sn = 57.2 [$^{2}J(^{119}Sn^{117}Sn)$ = 68.6]; $\delta^{14}N/^{15}N$: n.o. − MS: M^+ n.o., 392 (18, $n$$Bu_2SnBr_2$), 370 (5), 335 (86, $n$$BuSnBr_2$), 327 (10, $n$$Bu_2BrSnN$), 313 (100, $n$$Bu_2BrSn$), 295 (12), 270 (100, 327^+ − nBu), 257 (53, 313^+ − C_4H_8), 249 (10), 214 (40, 270^+ − C_4H_8), 199 (95, $BrSn^+$), 177 (57, 257^+ − HBr), 135 (52, $SnMe^+$), 120 (50, Sn^+), 99 (27), 57 (72). − IR (nujol/hostaflon): 1463 (m, nBu, δ-CH), 1414 (w), 1378 (m), 1360 (w), 1342 (w), 1292 (w), 1260 (w), 1248 (w), 1221 (w), 1193 (w), 1179 (w), 1151 (w), 1076 (m), 1047 (w), 1023 (w), 1003 (w), 962 (w), 877 (m), 868 (m), 847 (w), 768 (m), 734 [s, $\nu_{as}(NSn_3)$], 700 [s, $\delta(NSn_3)$?], 674 (m), 599 (m), 535 (w), 517 (w), 454 (w), 410 (w), 391 (w), 349 (w), 303 (w).

Tris(chlorodiphenylstannyl)amine (**3o**): Method a); Compound **1** (7.94 g, 15 mmol) was dissolved in 25 ml of CH_2Cl_2; Ph_2SnCl_2 (16.2 g, 45 mmol) dissolved in 40 ml of CH_2Cl_2. A small amount of solid impurities were removed by filtration from a petroleum ether solution (15 ml) of the nonvolatile residue. Removal of Me_3SnCl from the residue at 25°C/10^{-6} Torr. Yield 3.2 g of **3o** (22%) as a viscous, light brown liquid. − NMR (C_6D_6): δ^{1}H = 6.84 (pt, 12 H), 7.3 [pq, 12 H, $^{n}J(^{119/117}Sn^{1}H)$ = 77], 7.7 (pq, 6 H); δ^{13}C = 129 [s, o-C, $^{2}J(^{119(117)}Sn^{13}C)$ = 65 (62)], 131 [s, m-C, $^{3}J(^{119/117}Sn^{13}C)$ = 13.4], 136 [(s, p-C, $^{4}J(^{119(117)}Sn^{13}C)$ = 68 (50)], 138 [s, i-C, $^{2}J(^{119(117)}Sn^{13}C)$ = n.o.]; δ^{119}Sn = 156.4, [$^{2}J(^{119}Sn^{117}Sn)$ = 76]. − MS: 906 (2, M^+ − Cl), 864 (11, M^+ − Ph), 829 (14, M^+ − PhCl), 787 (8, M^+ − 2 Ph), 632 (23, M^+ − Ph_2SnCl), 597 (55, 632^+ − Cl), 555 (53, 632^+ − Ph), 520 (42, 632^+ − PhCl), 323 (63, M^+ − 2 $SnPh_2Cl$), 288 (155, 323^+ − Cl), 246 (88, 323^+ − Ph), 206 (18.9, 323^+ − PhCl), 197 (15.3, SnPh), 155 (18, SnCl). − IR (hostaflon/nujol): 1491 (w), 1430 (s), 1398 (w), 1333 (w), 1309 (w), 1266 (w), 1207 (s), 1191 (m), 1147 (w), 1114 (w), 1093 (w), 1038 (w), 985 (w), 901 (w), 853 (w), 843 (w), 798 (s), 756 (w), 745 (s), 693 (w), 677 (w), 652 (w), 583 (m), 556 (m), 378 (s). − $C_{36}H_{30}Cl_3NSn_3$ (939.0): calcd. C 46.05, H 3.22, N 1.49, Cl 11.3; found C 45.74, H 3.12, N 1.53, Cl 10.8.

Tris(chlorodibenzylstannyl)amine (**3l**): Prepared according to the procedure for **3f**. Compound **1** (1.78 g, 3.5 mmol) dissolved in 15 ml of CH_2Cl_2; Bz_2SnCl_2 (3.8 g, 10.2 mmol) was dissolved in 10 ml of CH_2Cl_2. A colourless solid remained after evaporation of the solvent at −30°C in vacuo. Me_3SnCl was removed by sublimation at 25°C/10^{-3} Torr; the residue was dissolved in about 10 ml of CH_2Cl_2 and crystallized at −30°C. Yield: 2.6 g of **3l** (74.5%), colourless needles, m.p. 160°C. − NMR ($CDCl_3$): δ^{1}H = 2.68 [s, 12 H, −CH_2−, $^{2}J(^{119/117}Sn^{1}H)$ = 73.7], 6.98 [d, 12 H, o-H, $^{4}J(^{119/117}Sn^{1}H)$ = 25.3)], 7.09 (t, 6 H, p-H), 7.20 [d, 12 H, m-H, $^{5}J(^{119/117}Sn^{1}H)$ = 25.6]; δ^{13}C = 33.7 (CH_2), 125.4 (Ph), 128.2 (Ph), 128.5 (Ph), 137.1 (Ph); δ^{119}Sn = −15.6 [$^{2}J(^{119}Sn^{117}Sn)$ = 160]; δ^{14}N: n.o. − MS: 421 (21, M^+ − $Bz_2Sn{=}SnBz_2$), 369 (12), 337 (93, M^+ − $(Bz_2SnCl)_2N$), 302 (12, Bz_2Sn^+), 295 (29, $BzSnCl_2N^+$), 278 (23, 369^+ − Bz), 267 (9), 246 (58, 337^+ − 246), 211 (100, SnBz), 204 (11, 295^+ − Bz), 181 (96, Bz_2CH^+), 155 (100, $SnCl^+$), 120 (41, Sn^+). − IR (nujol/hostaflon): 1492 (s), 1452 (s), 1404 (m), 1383 (w), 1335 (m), 1325 (m), 1262 (m), 1207 (s), 1179 (m), 1154 (m), 1117 (m), 1103 (m), 1054 (s), 1029 (s), 999 (w), 984 (w), 964 (w), 905 (m), 838 (w), 799 (s), 758 (s), 726 [s, $\nu_{as}(NSn_3)$?], 697 (s), 619 (m), 599 (m), 585 (m), 561 (m), 549 (m), 534 (s, SnC_3), 496 (w), 453 (s), 438 (m), 405 (w), 352 (w), 334 (m), 323 (m), 296 (s), 254 (m), 235 (s), 228 (s). − $C_{42}H_{42}Cl_3NSn_3$ (1023.2): calcd. C 49.30, H 4.14, N 1.37; found C 47.73, H 4.14, N 0.91.

Attempted Synthesis of Tris(iododibenzylstannyl)amine (**3n**): To a solution of Bz_2SnI_2 (1.9 g, 3.4 mmol) in 40 ml of CH_2Cl_2 was added slowly with stirring at −78°C a solution of **1** (0.59 g, 1.16 mmol) in 10 ml of CH_2Cl_2. After warming the mixture to ambient temp. and removal of the solvent at 10^{-3} Torr the residue was dissolved in C_6D_6 and investigated by NMR spectroscopy. − NMR (C_6D_6): δ^{1}H = 0.93 [s, 18 H, $^{2}J(^{119}Sn^{1}H)$ = 57.4, Me_3SnI], 3.27 [s, 12 H, $^{2}J(^{119}Sn^{1}H)$ = 59.4], 7.3 (m, 30 H); δ^{13}C = 3.63 [Sn-C, $^{1}J(^{119}Sn^{13}C)$ = 410], 123.9 [o-C, $^{3}J(^{119}Sn^{13}C)$ = 10], 124.9 [m-C, $^{4}J(^{119}Sn^{13}C)$ = 12], 146.4 [i-C, $^{2}J(^{119}Sn^{13}C)$ = 26.9], 147.2 [p-C, $^{5}J(^{119}Sn^{13}C)$ = 19]; δ^{119}Sn = 37.6 (Me_3SnI), −107.8 [$^{2}J(^{119}Sn^{117}Sn)$ = 74.8]. After Me_3SnI was removed from the residue at 25°C/10^{-3} Torr by condensation in a cooled trap the ^{119}Sn-NMR spectrum recorded from the residue (dissolved in CH_2Cl_2) showed the signal for Bz_3SnI (−18.2) besides a variety of signals, which could not be assigned. Therefore, workup was not attempted.

X-Ray Structure Analysis: **3b**: $C_6H_{18}Br_3NSn_3$; M_r = 700.0; colourless rhombus; size 0.35 × 0.35 × 0.15 mm, triclinic; space group $P\bar{1}$, a = 6.932(3), b = 9.422(5), c = 14.944(8) Å, α = 93.47(6)°, β = 100.38(4)°, γ = 111.36(4), V = 885.6(8) $Å^3$, Z = 2, $\rho_{calcd.}$ = 2.625 g cm^{-3}; μ ($Mo_{K\alpha}$) = 10.937 mm^{-1}, $F(000)$ = 632. − Data collection: 3065 reflections in $-h$, $\pm k$, $\pm l$, measured in the range 4.68° ≤ 2Θ ≤ 48.10°; 2796 independent reflections; R_{int} = 0.0540, 1744 reflections with $F_0 > 4\sigma(F_o)$, semi-empirical absorption correction, max/min transmission: 0.113/0.068; 118 variables, R = 0.072, wR^2 = 0.159, largest difference peak: 1.14 e/$Å^3$ close to Br. − **3r**: $C_{14}H_{32}I_3NSn_3 \cdot CH_2Cl_2$; M_r = 1038.1, colourless rhombus, size 0.4 × 0.28 × 0.28 mm, monoclinic, space group $P2(1)/m$, a = 10.071(2), b = 13.618(4), c = 10.898(3) Å, β = 93.91(1)°; V = 1491.1(7) $Å^3$, Z = 2, $\rho_{calcd.}$ = 2.312 g cm^{-3}; μ($Mo_{K\alpha}$) = 5.780 mm^{-1}, $F(000)$ = 952. − Data collection: 2884 reflections in h, k, $\pm l$, measured in the range 3.74° ≤ 2Θ ≤ 50°, 2723 independent reflections, R_{int} = 0.0629, 2022 reflections with $F_o > 4\sigma(F_o)$, semi-empirical absorption correction, max/min transmission: 0.097/0.033; 138 variables, R = 0.054, wR^2 = 0.133, largest difference peak: 2.18 e/$Å^3$. − **1**: $C_9H_{27}NSn_3$; M_r = 505.4, colourless rhombus, size 0.15 × 0.15 × 0.1 mm, triclinic, space group $P\bar{1}$, a = 6.759(1), b = 9.192(1), c = 15.256(2) Å, α = 95.35(1)°, β = 97.50(1)°, γ = 109.61(1), V = 875.6(2) $Å^3$, Z = 2, $\rho_{calcd.}$ = 1.917 g cm^{-3}, μ($Mo_{K\alpha}$) = 4.219 mm^{-1}, $F(000)$ = 476. − Data collection: 4097 reflections in $\pm h$, $\pm k$, $\pm l$, measured in the range 2.72° ≤ 2Θ ≤ 52.08°, 3331 independent reflections, R_{int} = 0.0546, semi-empirical absorption correction, max/min transmission 0.770/0.460, 118 variables, R = 0.049, wR^2 = 0.114, largest difference peak: 0.61 e/$Å^3$.

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