Base-Induced Synthesis of a Tetrastannatriazabicyclo[3.1.1]heptane from Tris(dimethylchlorostannyl)amine☆

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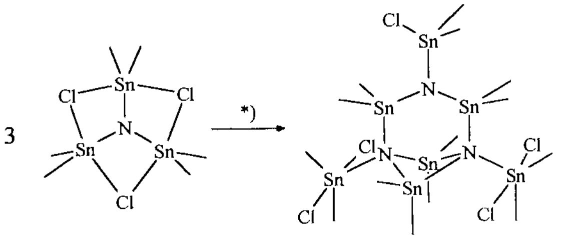
Tris(dimethylchlorostannyl)amine (**2a**) reacts with pyridine in a 3:4 molar ratio to produce the tin–nitrogen containing bicyclo[3.1.1]heptane (**3**) with elimination of the adduct $Me_2SnCl_2 \cdot 2$ py. Treatment of the distannylamine 2,6-$i$$Pr_2C_6H_3N(SnMe_2Cl)_2$ (**4**) with pyridine, however, leads to the formation of the 1:1 pyridine adduct **5** and this can be regarded as a model to explain the route to **3**. The molecular structures of **3** and **5** were determined by multinuclear magnetic resonance spectroscopy in solution, as well as by X-ray structure analysis of their crystals. Typical structural features for both compounds are intramolecular Sn–X–Sn bridges. Support for the structures comes from MS fragmentation patterns, IR spectra, and the Mössbauer spectra.

The synthetic potential of aminostannanes has been made particularly evident by the work on Sn–N cleavage reactions involving Lewis acids[1,2]. However, the behavior of tin–nitrogen compounds towards Lewis bases is almost unknown. The main reason is, obviously, the weak Lewis acid strength of the Sn atoms of triorganylstannylamines such as $(Me_3Sn)_3N$, **1**. The Lewis acidity at tin can be increased by introduction of electron-withdrawing substituents, as is the case in halogenostannylamines $(Me_2XSn)_3N$ (X = Cl: **2a**; X = Br: **2b**).

This type of tristannylamine is characterized by a planar Sn_3N skeleton as well as by intramolecular, and almost symmetrical, Sn–X–Sn bridges, emphasizing the acceptor function of its tin atoms[3]. This bonding also explains their thermal stability, whereas di- or monohalogenated tristannylamines, $Me_3Sn\ N(SnMe_2X)_2$, **2c**, and $(Me_3Sn)_2NSnMe_2X$, **2d**, are unstable at ambient temperatures[4]. The tristannylamines, **2a** and **2b**, decompose into insoluble, and as yet uncharacterized solids, after heating to 160 °C for a few hours[5]. This decomposition requires further studies since the formation of tin–nitrogen polycondensates, starting from functionalized aminostannanes, may be of particular interest with respect to preceramic materials. Insight into the decomposition pathway of the tristannylamines could be facilitated by interception of the unstable intermediates with Lewis bases. Initial information was obtained by reaction of **2a** and the distannylamine, **4**, with pyridine.

Results

Treating **2a** with pyridine in a 1:3 molar ratio in CH_2Cl_2 does not lead to the formation of the pyridine adduct, $N(SnClMe_2 \cdot py)_3$, but results in the bicyclic SnN heterocycle **3** and $Me_2SnCl_2 \cdot 2$ py. This suggests a reaction of **2a** with pyridine in a 3:4 molar ratio as shown in equation (1). The molecular structure of **3**, which has been determined by X-ray crystallography, allows us to suggest a reaction pathway for its formation which probably involves three steps (Scheme 1).



2a **3**

(1)

*) — = CH_3, + 4 py, - 2 $(CH_3)_2SnCl_2 \cdot 2$ py

The pyridine adduct **A**, assumed to be the first intermediate, decomposes by elimination of $Me_2SnCl_2 \cdot 2$ py and, probably, the formation of the iminostannane **B** [step (a)][6], stabilized by a pyridine tin interaction[7]. After dimerization of the highly reactive species **B** to the four membered heterocycle $(\mathbf{B})_2$, [step (b)], the acid base cycloadduct **C**, [step (c)] is supposedly formed by the simultaneous interactions of the nitrogen atoms of $(\mathbf{B})_2$ with two tin atoms of **2a**. Finally, the formation of the bicyclus **3** proceeds via 1,3-migration of a chlorine atom from a stannyl group of **2a**, attached to the ring nitrogen atoms of $(\mathbf{B})_2$, to the exocyclic Sn atoms of the cyclodimer.

The proposed mechanism is supported by the molecular structure of the pyridine adduct **5**. This compound is obtained by the reaction of the distannylamine **4** with pyridine according to equation (2). It corresponds to the unstable intermediate **A**.

Moreover, the synthesis of the diazadistannetidine, **7**, can be compared to the formation of the cyclodimer $(\mathbf{B})_2$ [step (a), (b) in Scheme 1]. The four membered Sn_2N_2 ring **7**[8], with *tert*-butyl groups attached to the nitrogen atoms in-

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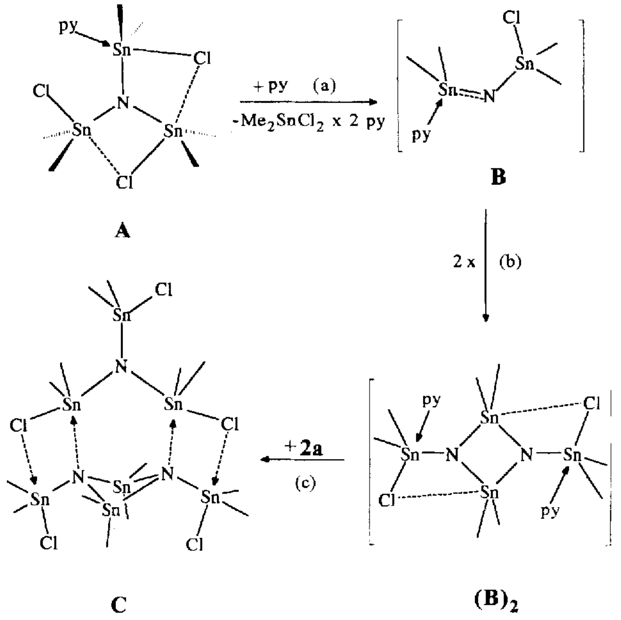
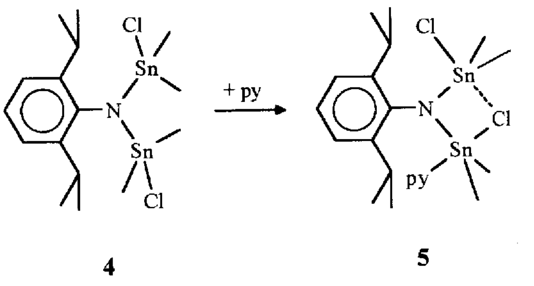
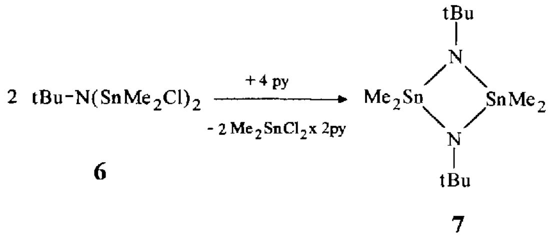
Scheme 1





(2)

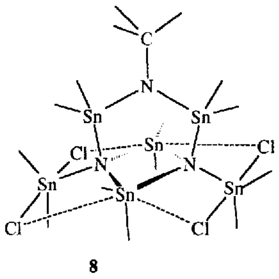


(3)

stead of Me_2ClSn groups as in **(B)**$_2$, is obtained in good yield by the reaction of the distannylamine *t*BuN$(SnMe_2Cl)_2$, **6**, with two equivalents of pyridine according to equation (3). A sample of the reaction mixture, kept at −30°C and checked by ^{119}Sn NMR, showed the signals of the pyridine adduct intermediate[9].

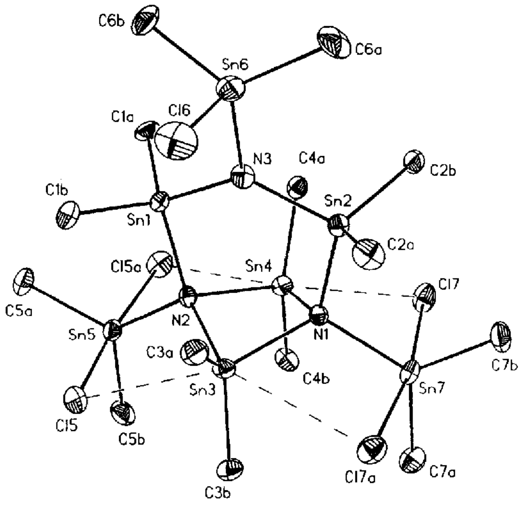
The proposed cyclodimer **(B)**$_2$ (Scheme 1) may be formed in a comparable pathway. The following cycloaddition of a N−Sn−N unit of **(B)**$_2$ with a Sn−N−Sn unit of **2a** [step (c)] is confirmed by the reaction of the diazadistannetidine **7** with **2a**, which results in a bicyclic SnN ring **8**. Its molecular structure is confirmed by its NMR spectroscopic data obtained in solution[10a]. The solid-state structure of **8** (Scheme 2) shows that a rearrangement of substituents occurs. Details will be given elsewhere.

Scheme 2



The characteristic structural features of cyclic aminostannanes and tin nitrogen adducts of stannanes with alkylamines, are combined in an ideal fashion in the molecular framework of the bicyclo[1.1.3]heptane **3** (Figure 1).

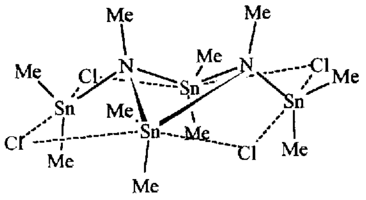
Figure 1. ORTEP plot of the molecular structure of **3**[a]



[a] Thermal ellipsoides represent 20% probability; hydrogen atoms are not shown for sake of clarity; selected bond lengths [Å] (estimated standard deviations in parentheses): N1−Sn2 2.128(8), N1−Sn3 2.189(9), N1−Sn4 2.153(8), N1−Sn7 2.134(9), N2−Sn1 2.143(9), N2−Sn3 2.172(9), N2−Sn5 2.099(8), N3−Sn1 2.027(9), N3−Sn2 2.03(1), N3−Sn6 2.042(9), Sn1−C1a 2.12(1), Sn3−C3a 2.13(1), Sn5−C5a 2.13(1), Sn6−C6a 2.12(1), Sn5−Cl5 2.631(4), Sn5−Cl5a 2.541(4), Sn6−Cl6 2.394(5), Sn7−Cl7a 2.584(3), Sn7−Cl7 2.585(4), Sn3−Sn4 3.206(1); selected bond angles [°]: Sn1−N2−Sn5 110.4(4), Sn1−N3−Sn2 130.0(5), Sn1−N3−Sn6 115.4(5), Sn2−N3−Sn6 114.5(4), Sn3−N2−Sn4 94.4(3), N2−Sn1−N3 103.0(3), N2−Sn3−N1 79.5(3), C1a−Sn1−C1b 113.0(6), C5a−Sn5−C5b 119.2(6), C6a−Sn6−C6b 122.4(7).

Its structure can be derived from the molecular skeleton of $(Me_2ClSn)_3N$, **2a**, and $[MeN(SnMe_2Cl)_2]_2$, **9**, respectively[3,8] (Scheme 3). Bond distances and angles are similar to those of **3**. The latter can be constructed by formal replacement of the *N*-methyl groups of the dimeric distannylamine **9** by the bridging $[-Me_2Sn-N(SnMe_2Cl)-SnMe_2-]$ unit of **2a**. The skeleton of **3** therefore consists of a diazadistannetidine fragment with two dimethyldichlorostannane units forming an adduct with the ring nitrogen atoms and a bridging tristannylamine fragment. One should notice the similarity of the structural features between the basal four membered stannyl substituted Sn_2N_2 ring and the analogeous structure of the dimeric distannylamine **9** shown in Scheme 3. Particularly striking are the Sn–Cl–Sn bridges leading to a hexacoordination of Sn3 and Sn4 due to the relatively close contacts with Cl5/5a and Cl7/7a, as evidenced by Sn–Cl atom distances of 3.19 Å. These are considerably shorter than the sum of the van der Waals radii [*d*(SnCl) ca. 4 Å[11]]. However, the geometry at these tin atoms deviates from an octahedron as shown by the Cl–Sn–Cl angle of 170° (in **9**: 163°). The folded skeleton of the four-membered ring in the structure of **3** is characterized by long Sn–N bonds (ca. 2.17 Å) as compared to the short exocyclic Sn–N bonds (ca. 2.11 Å). Responsible for the long Sn–N bonds in the four-membered ring unit are the tetracoordinated N atoms, which should lead to a decrease of the *s* character in these bonds, whereas the Sn–N distances in the planar diazadistannetidine, **7**, of 2.05 Å[10b] are shorter. As a consequence the Sn3–Sn4 distance in the cage compound **3** is 3.21 Å as compared to 3.076 Å in **7** [Sn–Sn: *d*(covalent) 2.80 Å[12], *d*(van der Waals) = 4.34 Å[11]].

Scheme 3

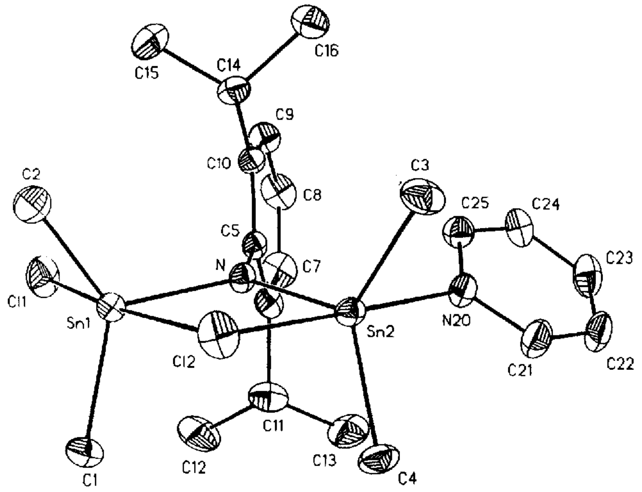


9

The bridging tristannylamine unit in **3** exhibits a skeleton different from $(Me_2SnCl)_3N$, **2a**. Though the nitrogen centre remains in a trigonal planar environment, the SnN bonds of the $Me_2Sn-N(SnClMe_2)-SnMe_2$ unit, however, are about 0.06 Å longer than those in **2a**. This is unusual because the transition from pentacoordination into tetracoordination of the tin atoms should lead to shorter SnN bonds. This could be due to a decrease in the *s* overlap of the SnN σ bonds as a result of ring strain. The tetrahedral environment of the atom Sn6 is considerably distorted, due to the interaction of atom Sn6 with the atom Cl5 of an adjacent molecule.

The structure of the distannylamine pyridine adduct **5** (Figure 2) serves as model for the proposed donor acceptor complex **A** in Scheme 1. Although the distannylamine **4** does not show Sn–X–Sn bridges[10b], the 1,3-shift of the chlorine atom Cl2 from Sn2 to Sn1 is indicated by an intramolecular Sn–Cl–Sn bridge. The central N atom is in a trigonal planar environment, while both Sn atoms show a trigonal bipyramidal configuration. The Sn1–Cl1 bond length of 2.43 Å corresponds to those of non-ionic, pentacoordinated tin compounds[13]. The Sn1–Cl2 distance of 2.88 Å in the Sn–Cl–Sn bridge, however, is considerable longer in contrast to the Sn2–Cl2 distance. This confirms, that the original tin–chlorine bond is hardly effected by the Sn–Cl–Sn bridge bond formation. The tin–nitrogen bond length of 2.43 Å between the pyridine N atom and atom Sn2 is considerably longer than in the adduct $Me_3SnCl \cdot py$ (d_{SnN}: 2.26 Å)[13]. This is possibly due to the influence of the bulky aryl group attached to the central nitrogen atom in **5**, which hinders a closer approach of the pyridine ligand to the Sn2 centre. The result also explains the stability of the adduct **5** in contrast to the lability of the adduct **A**, the proposed intermediate of the formation of the bicyclic **3**.

Figure 2. ORTEP plot of the molecular structure of **5**[a]



[a] Thermal ellipsoides represent 20% probability; hydrogen atoms are not shown for sake of clarity; selected bond lengths [Å] (estimated standard deviations in parentheses): N1–Sn1 2.052(3), N1–Sn2 2.039(3), N20–Sn2 2.426(4), Sn1–Cl1 2.431(2), Sn1–Cl2 2.876(1), Sn2–Cl2 2.590(2), Sn1–C1 2.129(5), Sn1–C2 2.112(6), Sn2–C3 2.120(5), Sn2–C4 2.134(5), N–C5 1.434(5); selected bond angles [°]: Sn1–N–Sn2 117.3(2), Sn1–N–C5 119.3(3), Sn2–N–C5 123.1(3), Cl1–Sn1–Cl2 175.1(1), N20–Sn2–Cl2 177.0(1), Sn1–Cl2–Sn2 79.3(1), C1–Sn1–C2 123.3(2), C3–Sn2–C4 127.7(2); Σ_{angle} (C1–Sn1–C2, C1–Sn1–N, C2–Sn1–N) 354°, Σ_{angle} (C3–Sn1–C4, C3–Sn2–N, C4–Sn1–N) 360°.

The low solubility of **3** in polar and nonpolar aliphatic and aromatic hyrocarbons prevented a detailed NMR investigation. The ^1H-NMR spectrum shows eight groups of proton signals. According to the symmetry of the molecule found in the crystal structure nine signals are to be expected. Obviously, two signal groups are isochronous. The exact assignment was not possible, because 2D NMR experiments failed to provide the relevant information. An unusually small $^nJ(^{119}Sn^1H)$ coupling constant of 19 Hz for the ^1H-NMR signal at δ = 1.07 is of interest, because it indicates a coupling over three or four bonds (*n* = 3, 4). As a result of the proposed isochronism only seven signals instead of nine can be detected in the ^{13}C-NMR spectrum. A remarkable deshielding of the carbon nuclei as shown by the signals at δ = 23, 32, and 53 is observed. Typical shifts for carbon nuclei of organotin halides are found at δ = 5–15[8]. The ^{119}Sn-NMR spectrum shows four signals. Taking into account the chemical shift of the tin nuclei of the dimeric distannylamine **9**, which shows similar structural features to compound **3**, the signal at δ = −116 is assigned to the Sn5/7 nuclei of the exocyclic stannyl groups, the signal at δ = −81 to the Sn3/4 nucleii of the four membered ring, the signal at δ = 1.3 to the Sn6 nuclei of the tristannylamine unit, and the signal at δ = 34.7 to the Sn1/Sn2 nuclei of the Me_2Sn groups. The considerable upfield shift of the nuclei Sn3, Sn4, Sn5, and Sn7 confirmes their penta- and hexacoordination respectively, but the NMR shift of the endocyclic tin nuclei of the tristannylamine unit indicates tetracoordination[14].

The ^{13}C-NMR spectrum of **5** shows a doubling of the signals for the ^{13}C-nuclei of the ArN- and the Me_2Sn groups, and the ^{119}Sn-NMR signal at $\delta = 95$ points to a Sn atom in a tetrahedral environment. On the other hand, the C−Sn−C angle of 121°, estimated from the $^{1}J(^{119}Sn^{13}C)$ coupling constant, indicates a coordination > 4 for the Sn atoms[15]. Taking the large half width of the ^{119}Sn-NMR signal at $\delta = 95$ into account an equilibrium between the adduct and the free distannylamine **4** seems to be present in solution. This is confirmed by a migration of the shift of about 20 ppm to high field in spectra recorded at −30°C. The spectroscopic data of the distannylamine pyridine adduct **5** therefore indicate fairly weak donor-acceptor interactions in solution.

Further information concerning structural features of the bicycloheptane derivative **3** are obtained from the data of the ^{119m}Sn Mössbauer spectra[16] of **3** in comparison to that of **2a** and Me_3SnNMe_2[17], which are collected in Table 1.

Table 1. Tin-119m Mössbauer parameters for **3**, as well as for **2a** and, for comparison, for Me_3SnNMe_2[a]

	3			**2a**			Me_3SnNMe_2[17]
δ_{IS}	1.03(2)	1.06(2)	1.29(2)	0.98(2)	1.08(2)	1.29(2)	1.16[b]
Δ_{EQ}	3.20(1)	2.45(1)	3.47(1)	2.75(1)	3.03(1)	2.99(1)	1.07
I	2	2	3	1	1	1	–

[a] δ_{IS} [mm/s]: isomer shift relative to $Ba^{119}SnO_3$, temperature of measurement of absorber and source refer to 4.2 K, half-height of the single absorptions: 0.80 mm/s, Δ_{EQ} [mm/s]: quadrupole splitting; I: relative intensity. – [b] δ_{IS} relative to SnO_2 at 25°C; temperature of absorber and source refer to 80 K; half-height of the single absorptions: 0.80 mm/s, $\delta_{IS} = 1.23$ using $^{119}Sn/Pd$ source.

The isomer shift for **2a** and **3**, as well as the quadrupole splitting, is significantly smaller than for the "classical" pentacoordinated tin complex $Me_3SnCl \cdot py$ ($\delta_{IS} = 1.43$, $\Delta_{EQ} = 3.44$ mm/s) and for $(Me_3SnCl)_n$ ($\delta_{IS} = 1.39$, $\Delta_{EQ} = 3.30$ mm/s)[18]. Both are penta-coordinated in the solid state. Smaller isomer shifts as well as smaller Δ_{EQ} are observed for tetra-coordinated Sn atoms[19]. The values of δ_{IS} and Δ_{EQ} for the tristannylamine **2a** and the bicyclus **3** indicate an environment for the tin atoms which is found half way between tetra- and pentacoordination[19]. Also, the values of the quadrupolar splitting of the tin atoms in **3** and **2a** lie half-way between those of tetracoordinated (ca. 1.0 mm/s) and pentacoordinated (ca. 3.2 mm/s) nuclei. These data definitly exclude hexacoordinated tin atoms in **3**. The line narrowing for the signals of **3** points to the presence of three different kinds of tin atoms with the ratio 2:3:3. This confirms three different kinds of coordination sites of the tin atoms in the crystal structure of **3**. In the ^{119}Sn-NMR spectrum, however, four different tin moieties can be detected in solution. In this manner it is ascertained that the deceptive equivalence of Sn6 and Sn7/5, resulting from the Mössbauer spectrum, is only due to the intermolecular Sn−Cl···Sn contacts of the molecules found in the crystal. The large isomer shift of the signal with $I = 3$ indicates a considerable deviation from the tetrahedral symmetry and a stronger participation of electronegative substituents in bonding[18]. This also leads to a larger quadrupolar splitting, which holds for the tin atoms of the three exocyclic stannyl groups. The assignment of the various tin atoms recorded in the Mössbauer spectrum is of importance, because the interpretation of the ^{119}Sn-NMR data is comparably difficult in so far as it concerns the coordination number of these atoms.

The formation of the heterobicyclic **3**, by base-induced elimination of tin halides, demonstrates the importance of N → Sn donor acceptor interactions as well as Sn−Cl−Sn bridges in the stabilization of intermediates on the way to polycondensated stannylamines. The generality of this method to the generation of polycondensation products needs to be demonstrated however.

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Experimental Section

General: All manipulations were performed under an atmosphere of dry dinitrogen. Glassware was dried prior to use by heating in vacuo. – NMR spectra were recorded on a Jeol GSX 270 (^{119}Sn) or Jeol EX 400 (^{1}H, ^{13}C) instrument; standards: TMS (internal, ^{1}H, ^{13}C), tetramethyltin (external ^{119}Sn). When the coupling constant is stated as $^{n}J(^{119(117)}Sn^{m}X) = ..., (...)$, the value in parentheses describes the coupling of the X nucleus with the ^{117}Sn isotopomer. The notation $^{n}J(^{119/117}Sn^{m}X)$ represents the coupling of both isotopomers with X, if the coupling cannot be observed separately. – IR spectra: Nujol-Hostaflon mulls between CsI plates on a Nicolet SZDX FT-IR spectrometer, data are quoted in [cm^{-1}]. – Mass spectra: Varian CH7 instrument with electron impact ionisation at 70 eV, data are given in the sequence: m/z (%, assignment). The masses found refer to the isotopes ^{1}H, ^{12}C, ^{14}N, ^{35}Cl, ^{120}Sn. – Elemental analysis: Microchemical Laboratory of the Institute. – X-ray: Siemens P4 four circle diffractometer; Mo-K_α radiation, graphite monochromator; single crystals were mounted under argon using glass capillaries. Crystal data were determined and intensity data recorded at 213 K; program X-scan, structure solution by Patterson method and refinement using the SHELX-PLUS PC-version package; final refinement was performed using the SHELX-93 programs[20]. All atoms except the hydrogen atoms are described with anisotropic temp. factors, all hydrogen positions were geometrically places [d(CH) = 0.96 Å] and refined by using the Riding model and fixed J_i. – Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100255. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: int. code +44(1223)336-033, e-mail: deposit@chemcrys.cam.ac.uk].

Starting Materials: $N(SnMe_3)_3$[21] was prepared in a modified procedure[22] from $NaNH_2/NH_3/OEt_2/Me_3SnCl$, $(Me_2SnCl)_3N$[3], 2,6-i-$Pr_2C_6H_3N(SnMe_2Cl)_2$[8].

Azastannabicyclo[3.1.1]heptane **3**: A stirred solution of $(Me_2ClSn)_3N$ (**2a**), (4.8 g, 8.4 mmol) in 25 ml of CH_2Cl_2 was treated with pyridine (2.1 ml, 2.0 g, 25.3 mmol) at 0 °C. After stirring for 24 h a muddy and yellowish precipitate had formed from which the volatile components were removed at 0 °C/10^{-2} Torr. The residue, insoluble in ether and CH_2Cl_2, was dissolved in 60 ml of boiling toluene with formation of a colourless solution. From this solution a colourless powdery solid, which separated on cooling, was removed at ambient temp. by filtration and washed with 15 ml of ether. It proved to be compound **3** (yield: 0.8 g, 21%), m.p. 133 °C. Concentration of the filtrate yielded a mixture of two kinds of crystals, consisting of **3** and $Me_2SnCl_2 \cdot 2$ py, which could be separated under the microscope. – NMR of **3**: ^{1}H ($CDCl_3$) δ = 0.88 [3 H, $^{2}J(^{119(117)}Sn^{1}H)$ = 62.6 (59.4) Hz], 0.97 (s, 3 H), 1.07 [6 H, $^{n}J(^{119(117)}Sn^{1}H)$ = 18.6 (15) Hz], 1.25 (3 H), 1.26 (3 H), (15 H), 1.44 [6 H, $^{2}J(^{117/119}Sn^{1}H)$ = 73.2 Hz], 1.53 [3 H, $^{2}J(^{119(117)}Sn^{1}H)$ = 72.0 (68.4) Hz], 2.33 (toluene, CH_3), 7.09 (toluene, C_6H_5). – ^{13}C ([D_8]toluene) δ = 11.8, 12.77, 13.84, 17.29, 22.59, 31.54, 52.79. – ^{119}Sn ([D_8]toluene): –116, –81.3, 1.4, 34.7; Sn-119m Mössbauer data see Table 1. – IR (Nujol/Hostaflon, only characteristic bands are quoted): $\tilde{\nu}$ = 790 [s, (CH_3)], 736 (w), 703 (s), 694 (w) [$\nu_{as}(Sn_2N)$], 621 [s, $\delta(Sn_2N)$], 570 [s, $\nu_{as}(C_2Sn)$], 518 (w) $\nu_s(C_2Sn)$, 473 (m), 466 [w, ν(SnCl)], 289 (m) ν(SnClSn). – MS: 1359 (<1) [M^{+}], 1324 (3) [M^{+} – Cl], 1139 (4) [M^{+} – Me_2SnCl_2], 1104 (4) [M^{+} – Cl, Me_2SnCl_2], 884 [1324 – 2 Me_2SnCl_2], 220 (100) [Me_2SnCl_2]. – $C_{21}H_{50}Cl_5N_3Sn_7$ (1352.7): calcd. C 18.65, H 3.70, N 3.11; found: C 20.05, H 3.75, N 3.05.

Pyridine Adduct **5**: A stirred solution of 2,6-$i$$Pr_2C_6H_3N$-$(SnMe_2Cl)_2$ (3.8 g, 6.9 mmol) in 25 ml of toluene was treated with pyridine (1.1 ml, 6.9 mmol). After 12 h of stirring at 25 °C, the clear solution became turbid. The mixture was then kept under reflux for 30 min. After the solution had attained ambient temp. very slowly the solution was cooled to 4 °C, **5** (3.5 g, 81%) separated in colourless crystals within 24 h. m.p. 112 °C. – NMR: ^{1}H (C_6D_6) δ = 0.50 [s, 12 H, $SnCH_3$, $^{2}J(^{119}Sn^{1}H)$ = 63.2 Hz], 1.12 [d, 12 H, $CHCH_3$, $^{3}J(^{1}H^{1}H)$ = 6.8 Hz], 3.77 [sept, 2 H, $CHCH_3$, $^{3}J(^{1}H^{1}H)$ = 6.8 Hz], 6.66 (t, 2 H, py/*m*-H), 6.99 (s, 3 H, $NC_6H_3R_2$), 8.45 (d/s, 3 H, py, *o*-H/*p*-H). – ^{13}C (C_6D_6) δ = 1.38 [1.39] {$SnCH_3$, $^{1}J(^{119/117}Sn^{13}C)$ = 478 [473] Hz, Φ(CSnC) = 121.2°[15]}, 24.7 [24.5] (CCH_3), 27.75 [27.5] (CCH_3), 123.5 (py), 123.80 [123.4] {*m*-C, $^{4}J(^{119/117}Sn^{13}C)$ = 10.5 [9.5] Hz}{, 124.71 [124.2] {*p*-C, $^{5}J(^{119/117}Sn^{13}C)$ = 12.1 [13.4] Hz}, 135.36 (py), 145.85 [145.17] (*i*-C), 146.88 [146.5] {*o*-C, $^{3}J(^{119/117}Sn^{13}C)$ = 18.9 [18.8] Hz}. – ^{119}Sn (C_6D_6) δ = 95.0 [103.3] ($h/2$ = 38 Hz). The ^{1}H-NMR spectrum recorded at –55 °C ($CDCl_3$) showed no difference compared to the spectrum recorded at 20 °C. – IR: $\tilde{\nu}$ = 795 [s, br, (CH_3)], 699 [s, $\nu_{as}(Sn_2N)$], 627 [m, $\delta(Sn_2N)$], 547 [m, $\nu_{as}(C_2Sn)$], 528, 513 [m, $\nu_s(C_2Sn)$], 435 [m, ν(SnCl)], 329, [m, $\nu(Sn_2Cl)$?], 289 [s, $\nu(Sn_2Cl)$?]. – MS: 544 (17) [M^{+} – py], 323 (2) [M^{+} – 296]. The isotopic pattern of the masses 360 to ca. 50 was identical with that of the distannylamine **4**; the ion of the pyridine adduct could not be detected. – $C_{21}H_{34}Cl_2N_2Sn$ (622.8): calcd. C 40.50, H 5.50, N 5.50; found: C 40.29, H 5.56, N 5.39.

Crystal-Structure Determinations: Compound **3**: $C_{21}H_{50}Cl_5N_3Sn_7$; M_r = 1352.7; colourless cuboids; crystal size 0.45 × 0.3 × 0.3 mm, orthorhombic, space group $P2_12_12_1$, a = 11.800(2), b = 16.078(2), c = 22.176(4) Å, V = 4207(1) Å^3, Z = 4, $_{\text{calcd.}}$ = 2.136 g cm^{-3}, μ(Mo-K_α) = 4.420 mm^{-1}, F(OOO) = 2528. – Data collection: 7972 reflections in -h, $\pm k$, $\pm l$, recorded in the range 3° $\leqslant 2\,\Theta \leqslant$ 50°; 7327 independent reflections (R_{int} = 0.0417), 6630 reflections with $F_o > 4\sigma(F_o)$, semi-empirical absorption correction, max/min transmission: 0.675/0.421, 290 variables, R = 0.0541, wR^2 = 0.1295, largest difference peak: 1.739 eÅ^{-3} close to Sn3. – Compound **5**: $C_{21}H_{34}Cl_2N_2Sn_2$; M_r = 622.8; colourless plates; crystal size 0.12 × 0.42 × 0.64 mm, orthorhombic; space group $P2_12_12_1$, a = 9.371(1), b = 14.556(3), c = 19.290(4) Å, V = 2631(1) Å^3, Z = 4, $_{\text{calcd.}}$.575 g cm^{-3}, μ(Mo-K_α) = 2.110 mm^{-1}, F(OOO) = 1236. – Data collection: 5101 reflections in -h, $\pm k$, $\pm l$, measured in the range 3.5° $\leqslant 2\,\Theta \leqslant$ 50°; 4618 independent reflections (R_{int} = 0.0178), 4206 reflections with $R_o > 4\sigma(F_o)$, semi-empirical absorption correction, max/min transmission: 0.867/0.461; 262 variables, R = 0.0294, wR^2 = 0.0708, largest difference peak: 0.385 eÅ^{-3} close to N.

☆ Dedicated to Professor *W. Siebert* on the occasion of his 60th birthday.

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