Structural Study of 2,6-Bis[(dimethylaminomethyl)phenyl]butyl Stannanes: Nonconventional Behaviour of Triorganotin(IV) Halides

Aleš Růžička,*[a] Roman Jambor,[a] Ivana Císařová,[b] and Jaroslav Holeček[a]

Abstract: The four organotin (IV) compounds ([2,6-bis(dimethylaminomethyl)phenyl](*n*-butyl)R^1R^2stannane, with $R^1 = R^2 = n$Bu (**1**), $R^1 = n$Bu, $R^2 = Cl$ (**2**), $R^1 = n$Bu, $R^2 = Br$ (**3**) and $R^1 = R^2 = Br$ (**4**)), have been prepared and their structures have been investigated in various solvents and at various temperatures (NMR). The structures of these compounds in solution are solvent- and temperature-dependent. The solid state structures of **2** and **3** were studied using CP/MAS NMR spectroscopy and X-ray diffraction techniques. The tetraorganotin compound **1** exhibits tetrahedral geometry with very weak Sn–N coordination. The dynamic process of Sn–N bond(s) association/dissociation was observed using low-temperature NMR measurements. The tin central atom in **2** and **3** is [4+2]-coordinated in toluene solutions and the NMR low-temperature measurements reveal the same dynamic behavior as for **1** in this solution, with retention of the covalent halogen–tin bond. However, this bond is dissociated in methanol solutions, yielding ionic species, where the tin atom is only [3+2]-coordinated, and the halogen atom lies outside of the primary coordination sphere of the tin atom. In addition, while the same ionic structure as in methanol was found in the whole measured temperature range in the chloroform solution of **3**, the structure of **2** varies in this solvent. In this compound, the covalent Sn–Cl bond (similar structure as in toluene solution), which is retained at room temperature in chloroform solution, is continuously dissociated with a decrease in temperature, leading to ionic bonding (a similar structure as in methanol solution). All the above-mentioned processes are reversible in all the solvents and at all temperatures. In the solid state, the covalent Sn–Cl bond is observed for **2**, while an ionic bond was found in **3**.

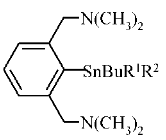
Keywords: chelates · N ligands · NMR spectrsocopy · tin

Introduction

The family of so-called hypervalent or hypercoordinated[1] organometallic compounds has been extensively studied, especially when C,Y-chelating (for example 2,6-bis[(dimethylaminomethyl)phenyl]- (N,C,N-pincer)) ligands are employed.[2, 3] To the best of our knowledge, the previous studies of organotin(IV) derivatives reveal very interesting structural[4] and biological[5] properties and enhanced reactivity.[6]

At the present time, dynamic processes have been extensively studied in solutions of the organotin(IV) derivatives of C,Y- or Y,C,Y-ligands,[3b, 6a,b, 7] to understand the properties and stereochemistry, mainly using temperature-dependent NMR spectra parameters (^{1}H and ^{119}Sn).

We described the structural behaviour of phenyltin(IV) derivatives of above-mentioned moiety in our previous papers.[8, 9] This paper describes a continuation of the investigation of *n*-butyl tin(IV) derivatives, which display interesting structural behaviour in the solid state, in solutions of different type of solvents and at different temperatures.



1: R^1, R^2= Bu
2: R^1= Bu, R^2= Cl
3: R^1= Bu, R^2= Br
4: R^1, R^2= Br

Scheme 1. Numbering of the compounds studied.

Results and Discussion

Synthetic aspects: All the compounds studied were prepared by *trans*-metallation of the appropriate lithium salt[2] by *n*-butyl tin halides. The reaction mixtures were purified by distillation in vacuo, for compounds **1** and **2**, and crystalization from a toluene/hexane mixture for **3** and **4**. The purity of the prepared compounds was corroborated by ESI-MS, ^{1}H NMR in CDCl$_3$ and elemental analysis. In contrast to the analogous

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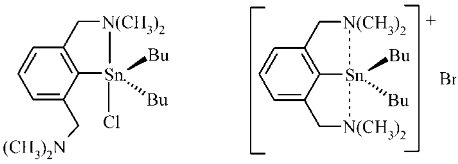
phenyl[8] compounds, which are unstable at higher temperatures, triorganotin compounds **2** and **3** are stable on the air and no such decomposition has been observed, even after refluxing of solutions of toluene for 24 h (corroborated by ^{1}H NMR spectroscopy).

Structural study: To elucidate the solution structure in the studied compounds, the conventional NMR parameters (chemical shifts of ^{1}H, ^{13}C, ^{15}N, ^{119}Sn nuclei and related coupling constants) were obtained in $CDCl_3$. Additional different temperature measurements of $\delta(^{119}\mathrm{Sn})$ and $\delta(^{1}\mathrm{H})$ in [D$_1$]chloroform, [D$_8$]toluene and [D$_4$]methanol solutions, respectively, were carried out to explain the dynamic processes. Crystalline compounds **2** and **3** were studied in the solid state using ^{13}C and ^{119}Sn CP/MAS NMR spectroscopy, DSC and X-ray diffraction techniques.

Structural study in [D]chloroform solution: The $\delta(^{119}\mathrm{Sn})$, $\delta(^{15}\mathrm{N})$, $\delta(^{13}\mathrm{C})$ and $\delta(^{1}\mathrm{H})$, as well as $J(^{119}\mathrm{Sn},^{15}\mathrm{N})$, $J(^{119}\mathrm{Sn},^{13}\mathrm{C})$ and $J(^{119}\mathrm{Sn},^{1}\mathrm{H})$ NMR parameters are well known and generally used for structural[10] elucidation and evaluation of the intramolecular interaction strength[11] in organotin(IV) chemistry. These parameters were measured in $CDCl_3$ solutions at 300 K for **1**–**4**.

The tetraorganotin compound **1** is a colorless oil. The ^{119}Sn NMR and ^{15}N NMR spectra reveal one narrow signal (-70.0 ppm, -351.2 ppm, values for Bu_3PhSn (-45 ppm)[12] and the "free" amine (-353.7 ppm),[8] respectively), while the ^{15}N NMR spectrum enables us to determine the value of $J(^{119}\mathrm{Sn},^{15}\mathrm{N}) = 9.0$ Hz. The values of $^{1}J(^{119}\mathrm{Sn},^{13}\mathrm{C})$ (356.5 and 449.4 Hz, respectively) were obtained from the ^{13}C NMR spectrum, from which the magnitude of bonding angles in solution can be predicted[10] (111.0° for C(Bu)-Sn-C(Bu)). The values of these parameters can be regarded as proof of a tetracoordinated central tin atom in this compound with very weak Sn–N intramolecular bond, and in the case of $\delta(^{119}\mathrm{Sn})$ comparable with similar compounds investigated by Jurkschat et al.,[13] where the tin substituents occupy the corners of a slightly distorted tetrahedron (these parameters are comparable with those found for analogous compound with one nitrogen donor atom, [2-(dimethylaminomethyl)phenyl](tri-*n*-butyl)stannane: -50.0 ppm, -351.9 ppm, 10.6 Hz and 109°, respectively) with similar geometry[11]).

The triorganotin compound **2** was obtained as yellowish oil, which crystallized upon standing for several weeks at -40 °C. One very broad signal ($\delta(^{119}\mathrm{Sn}) = -54.9$ ppm (nonsubstituted $PhMe_2SnCl$: 98.0 ppm)[14]) was observed in the ^{119}Sn NMR spectrum. The signal width in the ^{119}Sn (and also in the ^{1}H NMR spectra) indicates a dynamic process (fast exchange of both nitrogen atoms of the pincer ligand probably occurs, thus causing averaging of all the NMR parameters) leading us to carry out additional measurements (see below). A satellites of the central signal ($\delta(^{15}\mathrm{N}) = -347.0$ ppm) could be obtained in the ^{15}N NMR spectrum, from which the value of $J(^{119}\mathrm{Sn},^{15}\mathrm{N}) = 49.9$ Hz was calculated, demonstrating (together with $\delta(^{119}\mathrm{Sn})$ upfield shift) increasing strength of the Sn–N interaction compared with **1**. The values of $^{1}J(^{119}\mathrm{Sn},^{13}\mathrm{C})$ (491.4 and 626.3 Hz, respectively) were determined from the ^{13}C NMR spectrum. The first value enable us to calculate the C(Bu)-Sn-C(Bu) bonding angle in solution (124.0°). The values of the C(Bu)-Sn-C(Bu) bonding angle, $\delta(^{15}\mathrm{N})$, $J(^{119}\mathrm{Sn},^{15}\mathrm{N})$ and $\delta(^{119}\mathrm{Sn})$ (comparable with the values found for the triorganotin compound [2-(dimethylaminomethyl)-phenyl](di-*n*-butyl)stannyl chloride: 124°, -348.0 ppm, 68.2 Hz and -51.7 ppm) with similar geometry[11] and the upfield $\delta(^{119}\mathrm{Sn})$ value shift of 152.9 ppm compared with the unsubstituted analogue $PhMe_2SnCl$[14]) allow us to predict that the tin atom is pentacoordinated with *trans*-trigonal bipyramidal geometry with carbon atoms in the equatorial plane and one nitrogen atom and one chlorine atom in axial positions. The second nitrogen donor atom derived from the $CH_2N(CH_3)_2$ arm is outside of the tin coordination sphere in **2** (see Figure 1). Further proof of this proposed geometry of **2**



2 **3**

Figure 1. The proposed structure of compounds **2** and **3** in chloroform solution at 300 K.

Abstract in Czech: *Byla připravena sada čtyř organocíničitých sloučenin ([2,6-bis(dimethylaminomethyl)phenyl](n-butyl)-R^{1}R^{2}stannan, kde R^1 = R^2 = nBu (**1**), R^1 = nBu, R^2 = Cl (**2**), R^1 = nBu, R^2 = Br (**3**) a R^1 = R^2 = Br (**4**)). Struktura těchto sloučenin byla studována v roztocích různých rozpouštědel za různých teplot pomocí NMR spektroskopie. Struktura sloučenin **2** a **3** v tuhém stavu byla studována pomocí CP/MAS NMR spektroskopie a difrakčních technik na monokrystalickém materiálu. Tetraorganocíničitá sloučenina **1** vykazuje tetraedrickou geometrii s velice slabou donor–akceptorovou vazbou Sn–N. Při nízkoteplotním NMR měření byl pozorován dynamický proces asociace/disociace vazby Sn–N. Centralní atom cínu ve sloučeninách **2** a **3** je [4+2] koordinován v toluenovém roztoku. Nízkoteplotní NMR měření v tomto rozpouštědle odhalilo stejný dynamický proces jako v **1** se zachovanou kovalentní vazbou cín-halogen. Naproti tomu, tato vazba je disociována v methanolu, za vzniku iontových sloučenin, kde je atom cínu pouze [3+2] koordinován, a atom halogenu se nalézá mimo jeho primární koordinační sféru. Zatímco stejná struktura jako roztoku methanolu byla nalezena v celém teplotním rozsahu chloroformového roztoku sloučeniny **3**, struktura sloučeniny **2** je v roztoku tohoto rozpouštědla s teplotou proměnlivá. V této sloučenině je v chloroformovém roztoku za laboratorní teploty zachována kovalentní vazba Sn–Cl (podobná struktura jako v toluenovém roztoku). Tato vazba se snižující se teplotou kontinuálně disociuje za vzniku iontové sloučeniny (podobná struktura jako v methanolovém roztoku). Všechny výše zmíněné procesy jsou reversibilní jak z hlediska teploty, tak i podle typu použitého rozpouštědla. V pevné fázi byla pozorována kovalentní vazba Sn–Cl ve sloučenině **2**, oproti iontové vazbě přítomné ve sloučenině **3**.*

probably lies in our ^{13}C, ^{119}Sn CP/MAS and X-ray investigations (see below).

The triorganotin compound **3** is a white solid that is soluble in common organic solvents. One narrow signal ($\delta(^{119}\mathrm{Sn}) = 69.3$ ppm) has been observed in the ^{119}Sn NMR spectrum and the ^{15}N NMR spectrum also exhibits one narrow signal ($\delta(^{15}\mathrm{N}) = -347.0$ ppm). The value of the C(Bu)-Sn-C(Bu) bonding angles (117.0°) has been calculated from $^{1}J(^{119}\mathrm{Sn},^{13}\mathrm{C}) = 420.4$ Hz. The significant downfield shift of $\delta(^{119}\mathrm{Sn})$ going from **2** (-54.9 ppm) to **3** (69.3 ppm) indicates their different coordination mode and, particularly, the value of $\delta(^{119}\mathrm{Sn})$ for **3** does not seem to be a typical for pentacoordinated triorganotin compounds (compare with the same parameters for [2-(dimethylaminomethyl)phenyl](di-*n*-butyl)stannyl bromide: -44.9 ppm, -347.3 ppm, 66.1 Hz and 123°, respectively). On the other hand, such values of tin chemical shift are typical for pentacoordinated organotin(IV) C_3Sn^+ cations[15] with *trans*-trigonal bipyramidal geometry (carbon atoms form an equatorial plane), with their coordination polyhedron completed by two donor atoms (axial position). Because of this fact and the values of the calculated bonding angles, we believed compound **3** to be an organotin cation with *trans*-trigonal bipyramidal geometry (three carbons in equatorial plane and two nitrogen donor atoms in the axial position) compensated by a bromide anion (see Figure 1). Similar results have been reported in solution[3b, 9] and in solid state[4b, 16] investigations of analogous compounds and the solid state investigation of **3** has also revealed the a similar ionic structure.

The diorganotin compound **4** has been obtained as a white solid. In this compound, the tin central atom is six or more [4+2] coordinated ($\delta(^{119}\mathrm{Sn}) = -190.1$ ppm), due to two relatively strong Sn–N interactions. All the NMR spectra parameters ($^{1}J(^{119}\mathrm{Sn},^{13}\mathrm{C(Bu)}) = 581.0$ Hz and only one set of narrow signals for all the protons in the ^{1}H spectrum refer to the same structure as in the analogous N,C,N-chelating ligand containing diorganotin dihalides[2, 8] and the parameters are comparable with those found for the analogous compound with one nitrogen donor atom, [2-(dimethylaminomethyl)phenyl](*n*-butyl)dichlorostannane[11]: -104.3 ppm, 686.9 Hz and [2,6-bis(dimethylaminomethyl)phenyl](*p*-tolyl)stannyldiiodide[2]: -208.7 ppm, respectively. The structure of this compound is characterised by distorted octahedral geometry with two carbons and halogen atoms in *trans* positions thus forming an equatorial plane, and two nitrogen atoms in axial positions.

Dynamic NMR studies in [D$_8$]toluene: The ^{119}Sn NMR measurement of **1** does not exhibit any important temperature dependences in the studied range (170–360 K, see Table 1). The dynamic behaviour of **1** was studied using ^{1}H NMR spectroscopy at various temperatures (170–360 K). At room temperature, the ^{1}H NMR spectrum displays one set of sharp signals for all the protons. As the temperature is decreased, first a broadening of the CH_2 and CH_3 protons is observed, followed by decoalescence of all the protons at 190 K, which indicates, as is well known, a dissociation/association dynamic procedure[17] in **1** (see Figure 2A and B). The energy barrier ($\Delta G^{\neq}$) of the fluxional processes (calculated from the Eyring equation) is 33.6 ± 1.0 kJ mol^{-1}.

Table 1. Temperature- and solvent-dependent NMR parameters.

Cpd.[a]	Solvent	T [K]	$\delta(^{1}\mathrm{H})(\mathrm{CH_2N})$	$\delta(^{119}\mathrm{Sn})$
1	toluene	300	3.30	−71.8
		170	2.41/3.87[b]	−78.9
	chloroform	300	3.48	−70.0
		190	3.44	−75.0
	methanol	300	3.49	−70.9
		170	3.52	7.5
2	toluene	300	3.38	−76.3
		170	3.51/5.30[c]	−89.4
	chloroform	300	3.83	−54.9
		190	3.90	51.6
	methanol	300	3.89	57.9
		170	3.92	51.4
	solid state	290	[d]	−84.6
3	toluene	300	3.43	−76.3
		170	3.02/4.95[c]	−93.2
	chloroform	300	3.83	69.3
		190	3.89	51.9
	methanol	300	3.91	57.0
		170	3.93	49.8
	solid state	290	[d]	37.1
4	toluene	300	3.34	−199.1
		170	3.14	[d]
	chloroform	300	3.93	−189.6
		190	3.91	−192.2
	methanol	300	3.94	[d]
		170	3.89	[d]

[a] See Scheme 1. [b] Decoalescence at 190 K. [c] Decoalescence at 245 K. [d] Not observed.

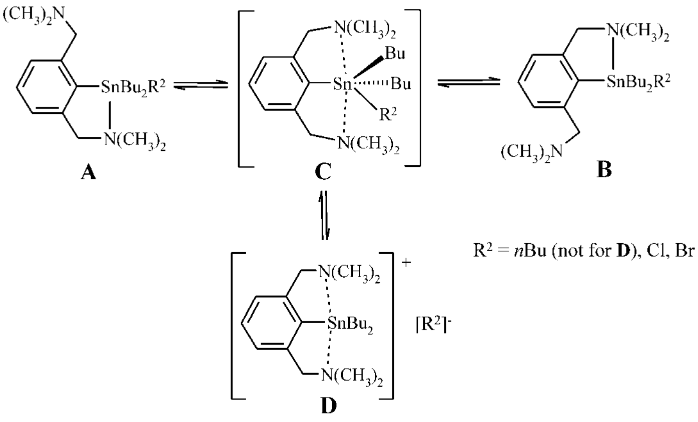


Figure 2. Proposed structural behaviour of the studied compounds.

The $\delta(^{119}\mathrm{Sn})$ values are shifted upfield with decreasing temperature (170–360 K, [D$_8$]toluene, see Table 1), thus indicating forcing of the Sn–N interaction at a lower temperature in **2** and **3**. The proton NMR spectra reveal decoalescence of the CH_2 and CH_3 protons at 245 K for both compounds (**2** and **3**), thus indicating the conformable fluxional process as for **1**. The higher activation energy of this process (43.0 ± 1.0 kJ mol^{-1}) agrees with the increased strength of the Sn–N bond in **2** and **3** compared with **1**. These results ($\delta(^{119}\mathrm{Sn})$ values and the dynamic behaviour of **2** and **3**) allow us to predict that the Sn–Cl bond remains covalent in nonpolar noncoordinating toluene solution in the whole temperature range studied.

The $\delta(^{119}Sn)$ value is rather temperature-independent (−199.1 ppm at 300 K and −202.6 ppm at 230 K) in **4**. The signals in the ^1H NMR spectra do not reveal any decoalescence in whole measured temperature range. This fact (one set of signals in ^1H NMR) only confirms the suggested structure of **4** (all atoms in the *trans* position, leading to high symmetry of this compound).

Dynamic NMR studies in [D$_4$]methanol: The signals in the ^1H NMR spectra of compound **1** are already very broad at 220 K, but do not reveal significant splitting or decoalescence. The $\delta(^{119}Sn)$ values (−70.9 ppm at 300 K and −72.9 ppm at 260 K) are similar to those found in other solvents, but the two signals (24.8 and −75.5 ppm, in integral ratio 5:1) appeared at 220 K, with only one signal (7.5 ppm) at 170 K. For comparison the chemical shift values for Bu_3PhSn in methanol going from 300 to 200 K (from −45 to −42.3 ppm) were obtained. This behaviour is different from **1**, in this solution. On the basis of these findings (the reversibility of process does not enable us to isolate the species with unusual $\delta(^{119}Sn)$), we can propose only a equilibrium with an indefinite role of the solvent. [To explain these chemical shift values, we carried out an NMR tube experiment: one to twenty molar equivalents of methanol were gradually added to a [D$_8$]toluene solution of **1** at 220 K and the ^1H and ^{119}Sn NMR spectra were measured. We observed the same values for the chemical shifts as before the addition of methanol.]

The $\delta(^{119}Sn)$ values of **2** are shifted downfield of 134.2 ppm when the solvent is changed from [D$_8$]toluene (−76.3 ppm) to [D$_4$]methanol (57.9 ppm). This signal is slightly shifted upfield with decreasing temperature (170–360 K, see Table 1). The ^1H NMR spectra reveal one set of signals, without any decoalescence, in the measured temperature range (170–300 K). The value of $\delta(^{119}Sn)$ (57.9 ppm at 300 K and 51.4 ppm at 170 K) can be explained only by the existence of an ionic structure of compound **2** with [3+2]-coordination number of the tin center (Figure 2D), with the chlorine atom outside of the primary coordination sphere of the tin central atom in methanol solution. In addition, equivalent protons (especially CH_2 and CH_3 groups) indicate, that the geometry of the organotin cation is *trans*-trigonal bipyramid with three carbons in the equatorial plane and both nitrogen atoms in the axial position, resulting in the equivalency of the $CH_2N(CH_3)_2$ arms of the "pincer" ligand in **2**.

The compound **3** has similar ^1H and ^{119}Sn NMR spectra (57.0 ppm at 300 K and 49.8 ppm at 170 K) to compound **2** in [D$_4$]methanol and the structure is also identical.

The signals in the ^1H NMR spectra of compound **4** are very broad at lower temperatures (below 220 K). No signal has been observed in whole temperature range in the ^{119}Sn NMR spectra; this is probably due to unidentified fast exchange processes in this solvent.

Dynamic NMR studies in [D$_1$]chloroform: In the ^1H NMR spectra of **1**, only broadening of the signals has been observed (decoalescence could probably be observed below the lowest measured temperature −190 K). The $\delta(^{119}Sn)$ value and widths of the signals are practically independent of temperature (−70.0 ppm at 300 K and −75.0 ppm at 190 K).

The ^{119}Sn NMR shift value of compound **2** is rather temperature-dependent. One broad signal has been obtained at 300 K (−54.9 ppm, lowering of the frequency value, compared with that measured in toluene, is probably caused by the weaker Sn–N bond(s) in chloroform solution). The chemical shift value and the signal pattern indicate, similar disymmetric structures (Figure 2A and B) as in toluene solution (see above) at this temperature. This signal is split into the three signals (−81.1, −27.0 and 53.7 ppm (integral ratio 1:1:8), respectively) at 220 K. Two of these signals can be assigned on the basis of our previous measurements[8] and findings. The broad signal $\delta(^{119}Sn) = -81.1$ ppm corresponds the intercepted fast exchange structure (Figure 2A) ([4+1]-coordinated tin center) and the narrow signal $\delta(^{119}Sn) = 53.7$ ppm corresponds to ionic structure (Figure 2D) with a [3+2] coordinated tin center, which was also observed in the solid state of the analogous compound.[15] The broad signal $\delta(^{119}Sn) = -27.0$ ppm probably corresponds to the state depicted in Figure 2C. Only one narrow signal (51.6 ppm) was observed at 190 K. In the ^1H NMR spectra the second set of aliphatic signals was already observed upon decreasing the temperature to 260 K (approx. 10% of main peaks intensity). These signals intensity is increased with a decrease in temperature. Only one set of much narrower signals (than at 260 K) with the same chemical shifts was observed at 190 K. This experiment is also proof of the proposed change over that depicted in Figure 2 (A or B → C → D) with a decrease in temperature.

In compound **3**, only one set of signals was observed for all the protons, without any change in the values of $\delta(^1H)$ and decoalescence of the signals in the ^1H NMR spectra (in the 300–200 K range). The ^{119}Sn NMR spectrum of compound **3** reveals one narrow signal in the whole temperature range. The value of the chemical shift changes only slightly with a decrease in temperature (69.3 ppm at 300 K and 54.9 ppm at 200 K, respectively). These chemical shift values and the equivalence of all the protons correspond the ionic structure of **3** (Figure 2D) with a [3+2]-coordinated tin center. The results observed for **2** and **3** corresponds well to the results for similar O,N-chelated silicon compounds.[18]

The signals in the ^1H NMR spectrum of **4** do not reveal any decoalescence and are narrower at lower temperatures (about 200 K) than at room temperature. The $\delta(^{119}Sn)$ value is shifted only slightly on a decrease in temperature (−189.6 ppm at 300 K to −192.2 ppm at 200 K). These findings indicate, that the structure of **4** is similar to that found in toluene at all temperatures in this solvent.

Solid state structure study of compounds 2 and 3: Compound **2** reveals one slightly asymmetric signal (−84.6 ppm, the ^{119}Sn chemical shift values obtained from the CP/MAS NMR spectra can be compared with those obtained in solution, the same value indicate similar structure) in the ^{119}Sn CP/MAS NMR spectrum. The chemical shift value is typical for penta-coordinated trioganotin(IV) compounds[8] and is rather independent of the temperature (−84.6 ppm at 285 K and −85.9 ppm at 210 K, respectively). The asymmetrical shape of this signal probably corresponds to the two overlapping signals with 1:2 ratio of their relative intensities as a result of residual quadrupolar coupling to ^{14}N ($I = 1$).[19] The proposed dissymmetric structure (also found in toluene and chloroform (300 K) solutions) has geometry with carbon atoms in the equatorial plane and one nitrogen atom and chlorine atom in the axial positions (see Figure 1). The second nitrogen donor atom derived from the $CH_2N(CH_3)_2$ arm lies outside of the tin coordination sphere (see Figure 1); this is also confirmed by the ^{13}C CP/MAS NMR spectral patterns, which reveal two sets of signals for the ligand aliphatic carbons. The butyl and phenyl carbons signals are broadened. The same spectral patterns and chemical shifts were observed when **2** was obtained by crystallisation from chloroform, methanol or toluene solutions, respectively. This fact is clear evidence of a compound structure that is independent of the crystallization media.

Compound **2** crystallizes in regular plates which melt at 22 °C. All attempts to determine the molecular structure using diffraction techniques were only partially successful. The crystals measured did not reveal any diffraction at 15 °C, but they exhibited weak diffraction at −70 °C. A strongly disordered structure was obtained at this temperature (crystal data in Table 2). Figure 3 depicts one of the overlapping molecules in the unit cell. The other differs not only in the position of the whole molecules, but also in the orientation of the -$N(CH_3)_2$ moiety towards the Sn atom, as the only atom preserving translation symmetry within the crystal seems to be Cl. Therefore, the only reliable information that can be obtained from structural analysis is the Sn–Cl distances (2.468(2)–2.555(2) Å), which are in the range for covalent bonds, and the confirmation that the arms bearing the nitrogen donor atoms are not equivalent and lie within two intervals (2.60(1)–2.65(1) Å and 3.12(1)–3.21(1) Å). Measurements at a lower temperatures are impracticable because of crystals in other crystal modifications are formed (inversion points corroborated by the DSC technique: exothermic; −85.1 °C, $\Delta H = -3.1\,\mathrm{J\,g^{-1}}$ and −106.3 °C, $\Delta H = -2.0\,\mathrm{J\,g^{-1}}$, endothermic; −86.6 °C, $\Delta H = 2.1\,\mathrm{J\,g^{-1}}$ and −79.3 °C, $\Delta H = 3.6\,\mathrm{J\,g^{-1}}$).

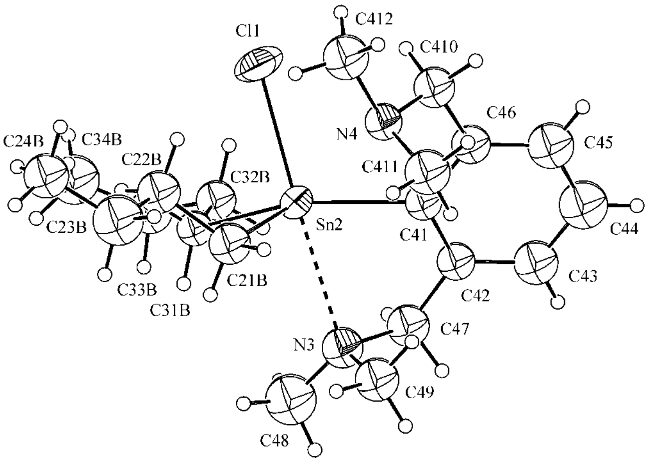


Figure 3. Molecular structure of compound **2** (ORTEP). Only one of the overlapping molecules in the unit cell of **2** is shown.

The ^{13}C CP/MAS NMR spectrum of compound **3** crystallized from chloroform at 300 K reveals one set of relatively sharp signals that, in their chemical shifts and integral ratio confirm the presence of two butyl groups and a ligand moiety. The ^{119}Sn NMR spectrum has a central signal (37.1 ppm, centre of gravity) which is split into a triplet with integral ratio of 1:4:4 and equidistant length between the subsignals ($J(^{14}\mathrm{N},^{119}\mathrm{Sn}) = 100$ Hz); the signal pattern is the result of residual quadrupolar coupling to two equivalent ^{14}N nuclei ($I = 1$)[19]), which is proof of the proposed ionic structure which is also found in the methanol and chloroform solutions (Figure 1). Two equivalent $CH_2N(CH_3)_2$ groups are connected to the tin centre through a intramolecular bond and the bromine atom lies outside of the first coordination sphere of the tin atom. This structure and this spectral pattern were found in an analogous compound (two butyls in **3** are replaced by phenyls).[8] The same spectral patterns and chemical shifts were observed when compound **3** was obtained from methanol or toluene solution, respectively. This fact is evidence of the fact that the compound structure is independent of the crystallization media.

The X-ray diffraction study on a single crystal indicates the structure of compound **3** proposed from the NMR parameters, showing the Br atom outside the tin coordination shell (Figure 4). The complex corresponds to the symmetry of the two-fold axis passing through atoms C4, C1 and Sn1, which ensures equivalent coordination of both -$CH_2N(CH_3)_2$ arms. The positions of all the atoms are well resolved except those of the end atoms of butyl groups, where the large thermal ellipsoids occupy disordered positions; however, structural elucidation using measurements at the lower temperatures are impracticable due to crystal destruction because of another crystal modification is formed (inversion points corroborated by DSC technique: exothermic; −95.6 °C, $\Delta H = -1.2\,\mathrm{J\,g^{-1}}$, endothermic; −87.4 °C, $\Delta H = 1.1\,\mathrm{J\,g^{-1}}$).

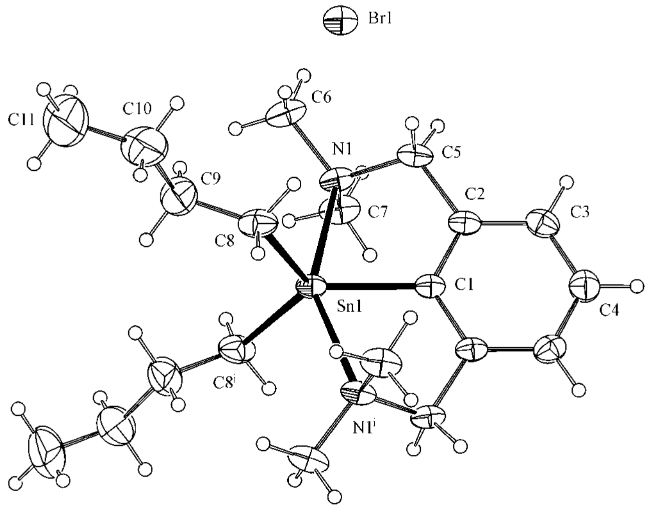


Figure 4. The molecular structure of compound **3** (ORTEP). Selected distances [Å] and angles [°]: Sn–C1 2.104(3), Sn–C8 2.141(3), Sn–N1 2.461(2), Sn–Br 5.0782(1), C1-Sn-C8 121.9(1), C1-Sn1-N1 74.74(5), C8-Sn-C8^{i} 116.1(1), N1-Sn-N1^{i} 149.5(1), C8-Sn1-N1 97.9(1), C8-Sn1-N1^{i} 98.1(1). Symmetry operation i: $0.5 - x, y, 1.5 - z$.

Concluding Remarks

A set of four organotin(IV) compounds has been prepared and characterised by conventional methods. The structures of these compounds are solvent- and rather temperature-dependent. The main NMR investigations of fluxional processes and of the structure were performed for triorganotin compounds **2** and **3**. The tin central atom in compound **2** is $[4+2]$-coordinated in toluene and chloroform solutions. As the temperature of the chloroform solution decreases, the structure of **2** becomes increasingly ionic where, at 220 K, the tin atom is only $[3+2]$-coordinated and the chlorine atom lies outside of the primary coordination sphere of the tin atom. The same structure has compound **2** in methanol.

Solutions of compound **3** in toluene have also been found to contain a structure with a $[4+2]$-coordinated tin center. On the other hand, the same ionic structure as in compound **2** was found over the whole temperature range measured in chloroform and methanol solutions of compound **3**.

All the above-mentioned processes are reversible in all the solvents and at all temperatures.

The structure of compounds **2** and **3** was also studied using solid-state NMR and diffraction techniques. Compound **2** has a structure with a $[4+1]$-coordinated tin center; in contrast, the compound **3** is ionic with $[3+2]$ coordination. The structures in the solid states of these compounds are independent of the crystallization media.

Experimental Section

General remarks: All the experiments were carried out in an argon atmosphere. 1,3-Bis(dimethylaminomethyl)benzene, *n*-butyllithium, tri-*n*-butyltin(IV) chloride, di-*n*-butyltin(IV) dichloride and di-*n*-butyltin(IV) dibromide were obtained from commercial sources (Sigma-Aldrich). Toluene, benzene, *n*-hexane, *n*-pentane and diethyl ether were dried over and distilled from sodium wire; chloroform was dried over and distilled from P_2O_5 and $LiAlH_4$. Compounds **1**–**4** were prepared by standard methods[2] (e.g. *ortho*-lithiation of the initial 1,3-bis[(dimethylamino)methyl]benzene using *n*-butyllithium in hexane solution). The organolithium salt formed was filtered off, dissolved in benzene and added to a solution of appropriate organotin(IV) halides in benzene. The reaction mixtures were evaporated in vacuo. The solid (**3** and **4**) materials formed were recrystallized from toluene to yield pure white solids. The compounds **1** and **2** were obtained after evaporation of solvents as oily materials, which were purified by distillation.

[2,6-Bis(dimethylaminomethyl)phenyl](tri-*n*-butyl)stannane (1): A solution of 2,6-bis(dimethylaminomethyl)phenyllithium (1 g, 5 mmol) in benzene (50 mL) was added dropwise to a solution of tributyltin chloride (1.64 g, 5 mmol) in benzene (50 mL) over five minutes. The reaction mixture was stirred for 20 min. and then the solvent was evaporated in vacuo. The residual yellowish oil was distilled (137–140 °C/50 Pa) to yield a colorless oil (1.75 g, 72 %). ^{1}H NMR (500.13 MHz, CDCl$_3$, 300 K): $\delta = 7.18$ (m, 3H, Ph-C(3-5)H), 3.47 (s, 4H, NCH$_2$), 2.13 (s, 12H, NCH$_3$), 1.52 (m, 6H, Bu-C(1)H$_2$), 1.38 (m, 6H, Bu-C(2)H$_2$), 1.03 (m, 6H, Bu-C(3)H$_2$), 0.94 (t, 9H, Bu-C(4)H$_3$); ^{13}C NMR (90.57 MHz, CDCl$_3$, 300 K): $\delta = 147.0$ ($^{2}J(^{119}\mathrm{Sn},^{13}\mathrm{C}) = 26.4$ Hz, Ph-C(2,6)), 143.3 ($^{1}J(^{119}\mathrm{Sn},^{13}\mathrm{C}) = 449.4$ Hz, Ph-C(1)), 128.2 ($^{3}J(^{119}\mathrm{Sn},^{13}\mathrm{C}) = 39.5$ Hz, Ph-C(3, 5)), 127.4 ($^{4}J(^{119}\mathrm{Sn},^{13}\mathrm{C}) = 9.7$ Hz, Ph-C(4)), 66.4 ($^{n}J(^{119}\mathrm{Sn},^{13}\mathrm{C}) = 18.7$ Hz, N*C*H$_2$), 45.0 (N*C*H$_3$), 29.3 ($^{2}J(^{119}\mathrm{Sn},^{13}\mathrm{C}) = 18.0$ Hz, Bu-*C*(2)H$_2$), 27.7 ($^{3}J(^{119}\mathrm{Sn},^{13}\mathrm{C}) = 68.0$ Hz, Bu-*C*(3)H$_2$), 13.6 (Bu-*C*(4)H$_3$), 12.5 ($^{1}J(^{119}\mathrm{Sn},^{13}\mathrm{C}) = 356.5$ Hz, Bu-*C*(1)H$_2$); ^{15}N NMR (36.50 MHz, CDCl$_3$, 300 K): $\delta = -351.2$ ($^{n}J(^{119}\mathrm{Sn},^{15}\mathrm{N}) = 9.0$ Hz); ^{119}Sn NMR (134.29 MHz, CDCl$_3$, 300 K): $\delta = -70.9$; ESI-MS (pos.): *m*/*z* (%): calcd for 482;
found: 425 (100) [*M* − (CH$_3$)$_3$C]$^+$, 311 (100) [*M* − (CH$_3$)$_3$C − isobutane − isobutene]$^+$, 268 (2) [*M* − (CH$_3$)$_3$C − isobutane − isobutene − CH$_3$N=CH$_2$]$^+$, 191 (11) [*M* − (CH$_3$)$_3$C − isobutane − isobutene − Sn]$^+$, 148 (6) [*M* − (CH$_3$)$_3$C − isobutane − isobutene − Sn − CH$_3$N=CH$_2$]$^+$; elemental analysis calcd (%) for $C_{24}H_{46}N_2Sn$ (481.33): C 59.89, H 9.63, N 5.82; found: C 60.0, H 9.5, N 5.9.

2,6-Bis(dimethylaminomethyl)phenyl](di-*n*-butyl)stannylchloride (2): The solution of 2,6-bis(dimethylaminomethyl)phenyllithium (1 g, 5 mmol) in benzene (50 mL) was added dropwise to solution of dibutyltin dichloride (1.52 g, 5 mmol) in benzene (50 mL) in five minutes. The reaction mixture was stirred for 20 min and then the solvent was evaporated in vacuo. The residual yellowish oil was distilled (139–142 °C/70 Pa) to give yellowish **2** (1.56 g, 68 %). White crystals were formed when the oil was left to stand at −40 °C for several weeks. M.p. 22–24 °C; ^{1}H NMR (500.13 MHz, CDCl$_3$, 300 K): $\delta = 7.19$ (t, 1H, Ph-C(4)H), 7.09 (d, 2H, Ph-C(3,5)H), 3.71 (s, 4H, NCH$_2$), 2.22 (s, 12H, NCH$_3$), 1.75 (m, 4H, Bu-C(1)H$_2$), 1.38 (m, 4H, Bu-C(2)H$_2$), 1.32 (m, 4H, Bu-C(3)H$_2$), 0.92 (t, 6H, Bu-C(4)H$_3$); ^{13}C NMR (90.57 MHz, CDCl$_3$, 300 K): $\delta = 144.2$ ($^{2}J(^{119}\mathrm{Sn},^{13}\mathrm{C}) = 36.8$ Hz, Ph-C(2, 6)), 139.5 ($^{1}J(^{119}\mathrm{Sn},^{13}\mathrm{C}) = 626.4$ Hz, Ph-C(1)), 127.2 ($^{3}J(^{119}\mathrm{Sn},^{13}\mathrm{C}) = 53.7$ Hz, Ph-C(3,5)), 128.6 (Ph-C(4)), 63.9 (N*C*H$_2$), 44.6 (N*C*H$_3$), 27.3 ($^{2}J(^{119}\mathrm{Sn},^{13}\mathrm{C}) = 28.4$ Hz, Bu-*C*(2)H$_2$), 26.2 ($^{3}J(^{119}\mathrm{Sn},^{13}\mathrm{C}) = 92.9$ Hz, Bu-*C*(3)H$_2$), 13.0 (Bu-*C*(4)H$_3$), 18.2 ($^{1}J(^{119}\mathrm{Sn},^{13}\mathrm{C}) = 491.5$ Hz, Bu-*C*(1)H$_2$); ^{15}N NMR (36.50 MHz, CDCl$_3$, 300 K): $\delta = -347.0$ ($^{n}J(^{119}\mathrm{Sn},^{15}\mathrm{N}) = 49.9$ Hz); ^{119}Sn NMR (134.29 MHz, CDCl$_3$, 300 K): $\delta = -54.9$; ^{13}C CP/MAS NMR (50.32 MHz, 300 K): $\delta = 147.4$, 145.5, 142.6, 128.8, 128.1 (phenyl carbons), 64.1 (very broad, N*C*H$_2$), 46.8, 45.9, 44.1, 43.2 (N*C*H$_3$), 29.8, 29.6, 27.8, 27.1, 22.8, 22.0, 16.0, 13.8 (butyl carbons, C(1) and C(4) are unressolved); ^{119}Sn CP/MAS NMR (74.63 MHz, 300 K): $\delta = -84.6$; ESI-MS: *m*/*z* (%): calcd for: 460; found (pos. mode): 425 (100) [*M* − Cl]$^+$, 311 (100) [*M* − Cl − isobutane − isobutene]$^+$, 268 (2) [*M* − Cl − isobutane − isobutene − CH$_3$N=CH$_2$]$^+$, 191 (15) [*M* − Cl − isobutane − isobutene − Sn]$^+$, 148 (7) [*M* − Cl − isobutane − isobutene − Sn − CH$_3$N=CH$_2$]$^+$; found (neg. mode): 35 (100) and 37 (32) [Cl]$^-$; elemental analysis calcd (%) for $C_{20}H_{37}N_2SnCl$ (459.67): C 52.26, H 8.11, N 6.09; found: C 51.9, H 8.2, N 6.0.

[2,6-Bis(dimethylaminomethyl)phenyl](di-*n*-butyl)stannylbromide (3): The solution of 2,6-bis(dimethylaminomethyl)phenyllithium (1 g, 5 mmol) in benzene (50 mL) was added dropwise to solution of dibutyltin dibromide (1.96 g, 5 mmol) in benzene (50 mL) in five minutes. The reaction mixture was stirred for 20 min and then the solvent was evaporated in vacuo. The residual white solid material was recrystallized from toluene to produce **3** as a white solid (1.44 g, 57 %); m.p. 111–113 °C; b.p. 95–100 °C (100 Pa). A single crystal suitable for x-ray analysis was obtained by vapor diffusion of hexane into the 5% solution of **3** in CH$_2$Cl$_2$. M.p. 120–122 °C; ^{1}H NMR (500.13 MHz, CDCl$_3$, 300 K): $\delta = 7.37$ (t, 1H, Ph-C(4)H), 7.20 (d, 2H, Ph-C(3, 5)H), 3.84 (s, 4H, NCH$_2$), 2.57 (s, 12H, NCH$_3$), 1.54 (m, 4H, Bu-C(1)H$_2$), 1.38 (m, 8H, Bu-C(2, 3)H$_2$), 0.87 (t, 6H, Bu-C(4)H$_3$); ^{13}C NMR (90.57 MHz, CDCl$_3$, 300 K): $\delta = 142.8$ ($^{2}J(^{119}\mathrm{Sn},^{13}\mathrm{C}) = 32.6$ Hz, Ph-C(2, 6)), 134.5 ($^{1}J(^{119}\mathrm{Sn},^{13}\mathrm{C}) = 628.0$ Hz, Ph-C(1)), 126.3 ($^{3}J(^{119}\mathrm{Sn},^{13}\mathrm{C}) = 56.2$ Hz, Ph-C(3, 5)), 131.4 (($^{4}J(^{119}\mathrm{Sn},^{13}\mathrm{C}) = 12.5$ Hz, Ph-C(4)), 64.9 (($^{n}J(^{119}\mathrm{Sn},^{13}\mathrm{C}) = 28.7$ Hz, N*C*H$_2$), 46.5 (N*C*H$_3$), 28.2 ($^{2}J(^{119}\mathrm{Sn},^{13}\mathrm{C}) = 29.8$ Hz, Bu-*C*(2)H$_2$), 26.9 ($^{3}J(^{119}\mathrm{Sn},^{13}\mathrm{C}) = 88.8$ Hz, Bu-*C*(3)H$_2$), 13.4 (Bu-*C*(4)H$_3$), 15.7 ($^{1}J(^{119}\mathrm{Sn},^{13}\mathrm{C}) = 420.4$ Hz, Bu-*C*(1)H$_2$); ^{15}N NMR (36.50 MHz, CDCl$_3$, 300 K): $\delta = -347.15$ ($^{n}J(^{119}\mathrm{Sn},^{15}\mathrm{N}) = 85.9$ Hz); ^{119}Sn NMR (134.29 MHz, CDCl$_3$, 300 K): $\delta = 69.3$; ^{13}C CP/MAS NMR (50.32 MHz, 300 K): $\delta = 144.9$, 137.2, 129.5, 126.0 (phenyl carbons), 61.0 (broad, N*C*H$_2$), 46.7, 44.0 (N*C*H$_3$), 29.9, 26.8, 15.3 (butyl carbons, C(1) and C(4) are unressolved); ^{119}Sn CP/MAS NMR (74.63 MHz, 300 K): $\delta = 37.1$; ESI-MS : *m*/*z* (%): calcd for 504; found (pos. mode): 425 (100) [*M* − Br]$^+$, found (neg. mode): 79 (100) and 81 (95) [Br]$^-$, 311 (100) [*M* − Br − isobutane − isobutene]$^+$, 268 (3) [*M* − Br − isobutane − isobutene − CH$_3$N=CH$_2$]$^+$, 191 (15) [*M* − Br − isobutane − isobutene − Sn]$^+$, 148 (7) [*M* − Br − isobutane − isobutene − Sn − CH$_3$N=CH$_2$]$^+$; elemental analysis calcd (%) for $C_{20}H_{37}N_2SnBr$ (504.12): C 47.65, H 7.40, N 5.56; found: C 47.7, H 7.3, N 5.7.

[2,6-Bis(dimethylaminomethyl)phenyl](*n*-butyl)stannyldibromide (4): A solution of 2,6-bis(dimethylaminomethyl)phenyllithium (1 g, 5 mmol) in benzene (50 mL) was added dropwise to a solution of butyltin tribromide (2.08 g, 5 mmol) in benzene (50 mL) in five minutes. The reaction mixture was stirred for 20 min and then the solvent was evaporated in vacuo. The residual solid material was recrystallized from toluene to give **4** as a white solid (1.67 g, 63 %). M.p. 235–237 °C; ^{1}H NMR (500.13 MHz, CDCl$_3$, 300 K): $\delta = 7.29$ (t, 1H, Ph-C(4)H), 7.06 (d, 2H, Ph-C(3, 5)H), 3.91 (s, 4H, NCH$_2$), 2.74 (s, 12 H, NCH$_3$), 1.92 (m, 2 H, Bu-C(1)H$_2$), 2.40 (m, 2 H, Bu-C(3)H$_2$) 1.43 (m, 2 H, Bu-C(2)H$_2$), 0.95 (t, 3 H, Bu-C(4)H$_3$); ^{13}C NMR (90.57 MHz, CDCl$_3$, 300 K): $\delta = 137.0$ ($^2J(^{119}\text{Sn},^{13}\text{C}) = 45.3$ Hz, Ph-C(2, 6)), 136.3 ($^1J(^{119}\text{Sn},^{13}\text{C})$ not observed, Ph-C(1)), 126.0 ($^3J(^{119}\text{Sn},^{13}\text{C}) = 95.2$ Hz, Ph-C(3, 5)), 130.1 (Ph-C(4)), 62.8 (($^nJ(^{119}\text{Sn},^{13}\text{C}) = 47.8$ Hz, N*C*H$_2$), 48.2 (N*C*H$_3$), 28.6 ($^2J(^{119}\text{Sn},^{13}\text{C}) = 52.6$ Hz, Bu-*C*(2)H$_2$), 25.8 ($^3J(^{119}\text{Sn},^{13}\text{C}) = 173.0$ Hz, Bu-*C*(3)H$_2$), 13.4 (Bu-*C*(4)H$_3$), 19.4 ($^1J(^{119}\text{Sn},^{13}\text{C}) = 581.0$ Hz, Bu-*C*(1)H$_2$); ^{15}N NMR (36.50 MHz, CDCl$_3$, 300 K): $\delta = -347.2$ ($^nJ(^{119}\text{Sn},^{15}\text{N})$, not observed); ^{119}Sn NMR (134.29 MHz, CDCl$_3$, 300 K): $\delta = -190.1$; ESI-MS: *m*/*z* (%): calcd for 526; found (pos. mode): 447 (100) $[M - \text{Br}]^+$, 389 (8) $[M - \text{Br} - \text{isobutane}]^+$, 367 (6) $[M - \text{Br} - \text{HBr}]^+$, 311 (24) $[M - \text{Br} - \text{HBr} - \text{isobutene}]^+$, 191 (100) $[M - \text{Br} - \text{HBr} - \text{isobutene} - \text{Sn}]^+$, 148 (79) $[M - \text{Br} - \text{HBr} - \text{isobutene} - \text{Sn} - \text{CH}_3\text{N{=}CH}_2]^+$, 132 (5) $[M - \text{Br} - \text{HBr} - \text{isobutene} - \text{Sn} - (\text{CH}_3)_3\text{N}]^+$; found (neg. mode): 79 (100) and 81 (96) $[\text{Br}]^-$; elemental analysis calcd (%) for $C_{16}H_{28}N_2SnBr_2$ (526.90): C 36.47, H 5.36, N 5.32; found: C 36.6, H 5.3, N 5.4.

NMR measurements: The solution state ^{1}H (500.13 MHz), ^{13}C (125.76 MHz), ^{119}Sn (186.50 MHz) and ^{15}N (50.65 MHz) NMR spectra of the studied compounds were measured on a Bruker Avance 500 spectrometer equipped with 5 mm broadband probe with *z* gradient and a SGI O2 computer in the temperature range of 170–360 K. The solutions were obtained by dissolving of 50 mg of each compound in 0.5 mL of deuterated solvents. The chemical shifts were calibrated relative to the signal of residual CHCl$_3$ ($\delta = 7.25$), toluene ($\delta = 2.09$) and methanol ($\delta = 3.31$), respectively, the ^{119}Sn on external tetramethylstannane ($\delta = 0.00$). The ^{13}C chemical shifts were referred to the signal of CDCl$_3$ ($\delta = 77.0$), the ^{119}Sn chemical shifts are referred to external neat tetramethylstannane ($\delta = 0.0$) and the ^{15}N chemical shifts are referred to external neat nitromethane ($\delta = 0.0$). Positive chemical shifts values denote shifts to the higher frequencies relative to the standards. The solid state ^{13}C and ^{119}Sn spectra of the studied compounds were acquired at 50.32 and 74.63 MHz, respectively, on a Bruker DSX 200 spectrometer equipped with a double-bearing CP-MAS probe. The compounds were packed in a standard 4 mm or 7 mm ZrO$_2$ rotor. The ^{13}C and ^{119}Sn Hartmann–Hahn cross-polarization match was set with adamantane and tetracyclohexyltin, respectively, using a ^{1}H 90° pulse of 4 μs. The contact time was set to 1–2 ms. Recycle delay was 10 s. The sample of **2** was measured at 280 and 210 K and sample of **3** at 300 K, respectively. In the ^{119}Sn CP/MAS NMR experiments, at least two spinning rates (4.5–9 kHz) were used to identify the isotropic chemical shift. The number of scans varied between 200 and 22000 to achieve an acceptable signal-to-noise ratio. The ^{13}C and ^{119}Sn chemical shifts were calibrated indirectly by external glycine (carbonyl signal $\delta = 176.03$) and tetracyclohexyltin ($\delta = -97.35$).

Mass spectrometry: Positive-ion electrospray ionization (ESI) mass spectra were measured on the Esquire3000 ion trap analyser (Bruker Daltonics, Bremen, Germany) in the range *m*/*z* 50–1000 and negative-ion ESI mass spectra were measured on the Platform quadrupole analyser (Micromass, UK) in the range *m*/*z* 15–600. The ion trap was tuned to yield an optimum response for *m*/*z* 500. The samples were dissolved in acetonitrile and analysed by direct infusion at a flow rate of 1 µL min^{-1}. The selected precursor ions were further analysed by MS/MS analysis with the ion trap analyser under the following conditions: isolation width *m*/*z* 8, collision amplitude 1 V for the MS/MS spectra of compounds **1**–**3** and 0.9 V for compound **4**, ion source temperature 300 °C, flow rate 4 L min^{-1} and the pressure of nitrogen 10 psi.

A typical feature of the ESI mass spectra of the studied organotin compounds is the cleavage of the most labile bond in the molecules, yielding two complementary ions, where the cationic part of the molecule can be measured in the positive-ion mode and the anionic part in the

Table 2. Crystal data and structure refinement for **2** and **3**.

Compound	**2**	**3**
empirical formula	$C_{20}H_{37}ClN_2Sn$	$C_{20}H_{37}BrN_2Sn$
F_w	459.66	504.12
T [K]	200(2)	200(2)
λ [Å]	0.71070 A	0.71070
crystal system	monoclinic	monoclinic
space group	$P2_1/c$	$P2/n$
unit cell dimensions		
a [Å]	9.1900(1)	10.1420(2)
b [Å]	13.0070(2)	11.8650(3)
c [Å]	19.3910(3)	10.5380(2)
β [°]	95.2450(7)	113.473(1)
V [Å^3]	2308.18(6)	1163.15(4)
Z	4	2
ρ_{calcd} [Mg m^{-3}]	1.323	1.439
μ [mm^{-1}]	1.227	2.820
$F(000)$	952	512
crystal size [mm^3]	0.4 × 0.3 × 0.3	0.35 × 0.3 × 0.1
θ for data collection [°]	1.89–27.5	3.4–27.5
index ranges	$-11 \leq h \leq 11$ $-16 \leq k \leq 16$ $-25 \leq l \leq 25$	$-13 \leq h \leq 13$ $-15 \leq k \leq 15$ $-13 \leq l \leq 12$
refls collected	35743	19171
max./min. transmission		0.798; 0.491
indep. refls	5214 [R(int) = 0.036]	2669 [R(int) = 0.034]
absorption correction	none	multi-scans
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/parameters	5214/1/173	2669/0/122
GoF on F^2	1.026	1.053
final R indices [$I > 2\sigma(I)$]		
$R1$	0.069	0.026
$wR2$	0.195	0.066
R indices (all data)		
$R1$	0.082	0.029
$wR2$	0.209	0.068
largest diff. peak and hole [e Å^{-3}]	0.843/ – 0.591	0.563/ – 0.551

negative-ion mode. When an Sn−halogen bond is present in the structure, then this bond is primarily cleaved and complementary ions $[M-\text{halogen}]^+$ and $[\text{halogen}]^-$ are observed in the positive-ion or negative-ion ESI mass spectra. Because of the very low masses of negative ions (m/z 79 and 81 for $[\text{Br}]^-$ and m/z 35 and 37 for $[\text{Cl}]^-$), the quadrupole analyser is used for negative-ion ESI measurements instead of the ion trap. No halogen atom is present in the structure of compound **1**, therefore, cleavage of the Sn−*n*-butyl bond occurs leading to the $[M-n\text{Bu}]^+$ ion with the same mass as for compounds **2** and **3** (m/z 425). The following MS/MS spectra of m/z 425 are identical for compounds **1**–**3**. The fragmentation pattern confirms the expected structures, because observed fragment ions can be correlated with the structures. The precursor ion is different for compound **4** (m/z 447) and hence the masses of fragment ions also differ in comparison to other studied compounds, but the fragmentation behaviour follows the similar pattern (see the Experimental Section). Typical neutral compound lost for studied compounds are isobutane, isobutene, $CH_3N{=}CH_2$, Sn and, for compound **4** also HBr and $(CH_3)_3N$. Because of the characteristic isotopic pattern of the tin atom, the fragment ions containing tin atoms can be readily recognised. All ions observed are even-electron ions, which is typical for a soft ionization technique such as ESI.

Crystallography: Selected crystallographic data for compound **3** are given in Table 2. The selected structural parameters (distances/Å and angles/°) are given in the caption to Figure 3.

CCDC-197187 (**2**) and -197188 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; (fax: (+44)1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).

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