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Quest for triorganotin(IV) compounds containing three *C*,*N*- and *N*,*C*,*N*-chelating ligands

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ABSTRACT

Three novel tetraorganotin(IV) compounds of general formula L_3SnR [where *i*) L is L^{CN} 2-(*N*,*N*-dimethylaminomethyl)phenyl- and R = *n*-Bu (**1**), Ph (**2**); and *ii*) L is L^{NCN} 2,6-bis-(*N*,*N*-dimethylaminomethyl)phenyl- with R = *n*-Bu (**3**)] were synthesized. These species were used as potential precursors for the target preparation of some triorganotin(IV) species of general formula L_3SnX [where *i*) L is L^{NCN} with X = OH (**4**), and *ii*) L is L^{CN} and X = Br (**5**), F (**5b**), Cl (**5c**)]. Several methods were applied to reach the target L_3SnX molecules including the reactions of **1** or **2** with bromine, iodine or hydrohalic acids in various media, Kocheshkov reactions or transmetallation with $HgCl_2$, but the composition of all reaction mixtures was not satisfactory towards the target. Compound **4** has the monomeric structure with OH group interacting with one of the nitrogen atoms via H-bridge. Target compound **5** was prepared by the reaction of three equivalents $L_4^{CN}Sn$ with $SnBr_4$ followed by the isolation of **5** from the reaction mixture based on different solubility of **5** in various solvents. Surprisingly, the presumably air-stable **5** can easily ionize in the air to give a novel aqua-complex $[L_3^{CN}Sn(H_2O)]^+Br^-$ (**5a**). All prepared organotin(IV) compounds bearing both L^{CN} and L^{NCN} ligands were characterized by multinuclear NMR spectroscopy and, when eligible, by the elemental analysis. In addition, the solid-state structures of **1**, **2**, **4**, **5a**, **6**, **8** and **9** were determined by the X-ray diffraction analysis.

1. Introduction

C,*N*- and *N*,*C*,*N*-chelated metal complexes attracted much attention of chemists directly after the development by van Koten in 1970 [1]. Since that time, a plethora of papers dealing with this part of chemistry appeared. The first and simple monoanionic bi- (L^{CN}) of terdentate L^{NCN}) ligands (Fig. 1) underwent a number of structural changes of their respective backbone which led in fact to the constitution of self consistent field of chemistry covering nearly all metals [2]. Although the amount of prepared and structurally characterized compounds bearing only one or two simplest or slightly modified ligands (Fig. 1) is really high (1226 structures in the Cambridge Structural Data Base), the number of complexes containing three or more ligands of this type per metal centre is rather limited.

Compounds with the central metal atom substituted by four ligands were described for Si [3], Sn [4], Nd and Gd [5] only, where for Si and Sn compounds the strictly monodentate bonding of all ligands was found (with shortest Sn–N distance 3.276 Å). For the lanthanide compounds ($L_2^{CN}M$-μ^2-$(L^{CN})_2Li$), two of the ligands are bidentately bound but the remaining two act as bridging to the lithium counter atom.

The family of the compounds having three of these ligands is from the first view a bit broader but the major part of it are compounds of groups 3, 13, 15 and lanthanides, where the stable oxidation state III suggests the formation of such species [5,6]. In the case of phosphorus, these compounds ($L_3^{CN}P$) are successfully used as *N*,*P*-chelating ligands for complexation of transition metal species [7].

On the other hand, for the rest of the metalloids and metals only limited number of examples of compounds of the $L_3^{CN}M$ type is known. The tris-chelated chromium(III) complex with pseudooctahedrally six-coordinated central metal atom is reported by Cotton [8]. Two examples of 'ate Zn–Li complexes' were reported by van Koten [9], where one of the ligands acts as *C*,*N*-chelating to the zinc atom, the second one is bridging between both metals and the last one has C–Zn covalent and Li–N coordination bond. For the central atom from the group 14 elements, where the rest of examples is found, compounds $L_3^{CN}GeH$ [10] and $L_3^{CN}SiF$ [11] were

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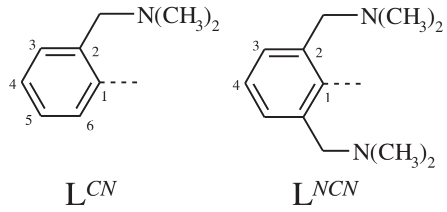


Fig. 1. Ligands used including the numbering of atoms.

described by Corriu, and L$_3^{CN}$SiH [3] by Herdtweck having dynamic behaviour in solution and only monodentately bound ligands in the solid state with M–N distances about 3 Å and thus the coordination geometry of a distorted tetrahedron. Two very last examples came from the private communication to the Cambridge Crystallographic Data Base from the van Koten's group [12], it seems these are complexes of stannylene L$_2^{CN}$Sn with L^{CN}Li. In both cases the tin atom is bonded to the three carbon atoms of ligands, nitrogen donor groups are far from tin to speculate about coordination, and one or two nitrogen donor group(s) being coordinated to the lithium atom. There is rather short Sn–Li distance (~2.7–2.83 Å) completing the coordination polyhedra of the tin atom to a deformed Ψ-trigonal bipyramid with the lithium atom in an axial position.

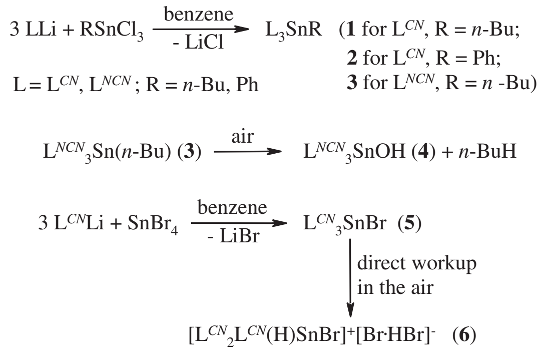
Twenty years ago (~1994) we started some synthetic work in the area of organotin(IV) compounds substituted by L^{CN} ligand(s) originally developed by van Koten and Jastrzebski [2b,13]. The main idea was to develop a methodology for structure evaluation of these hypercoordinated compounds based on various NMR spectroscopy techniques in solution. For that reason we have developed the chemistry of *n*-butyl [14] substituted compounds which enabled us to measure the spectra of all nuclei present in the molecule and to determine various coupling constants in high concentration samples. Since that time a plenty of L^{CN} and L^{NCN} substituted organotin(IV) compounds were prepared and presented by us and others [15], including the doubly [16] or quadruple [4] chelated ones. These compounds also found a potential practical use as transesterification or esterification catalysts [17], fluorinating agents [18], parts of ion selective electrodes [19] or antimycotical agents [20]. The particular use of some of these complexes in various types of catalytically driven reactions such as CO$_2$ activation to dimethyl carbonate reactions has been developed, too [21].

As side products of this investigation, the compounds of the types L$_3^{CN}$SnR and L$_3^{NCN}$SnR were prepared and investigated in order to prepare highly coordinated species, L$_3$Sn• radicals or ionic species L$_3$Sn$^-$ and L$_3$Sn$^+$ which are of current interest not only as chemical curiosities but also as heavier congeners of instable intermediates of organic compounds formation and reactivity in various types of substitution reactions.

2. Results and discussion

2.1. Synthesis and structural characterization of tetraorganotin(IV) compounds used as precursors for target triorganotin(IV) species. Hydrolysis of L$_3^{NCN}$Sn(n-Bu) (3)

As precursors for target triorganotin(IV) compounds of the L$_3$SnX type, where X = halogen, potentially trischelated complexes L$_3$SnR **1**–**3** (Scheme 1) were prepared by conversion of a slight excess of appropriate lithium salt with *n*-butyl- or phenyltin(IV) trichloride, respectively. All complexes were identified by ^{1}H and ^{119}Sn NMR spectroscopy in solution, ESI-MS spectrometry and elemental analysis. In addition the structure and composition of both **1** and **2** containing three potentially bidentate ligands, have been studied by ^{13}C and ^{15}N NMR spectroscopy in solution and X-ray diffraction techniques in the solid state. The preparation of **1** and **2** has been performed by addition of 3 equiv of L^{CN}Li to the stirred solution of RSnCl$_3$ in benzene under an argon atmosphere at approximately 10 °C. The subsequent addition of chloroform in air, led to the formation of yellowish precipitate of LiCl. Sufficiently pure crystals of **1** and **2** were obtained after evaporation of solvents and washing the solid residue by hexane in the case of **2**, and long time high dynamic vacuo evaporation in the case of **1**. In order to prepare L$_3^{CN}$SnBr, the direct reaction of 3 equiv of L^{CN}Li and SnBr$_4$ was conducted, the subsequent workup on the air gave a mixture of different species from which the compound **6** as an adduct of **5** with 2 equiv of HBr was separated in about 20% yield. When the same procedure is applied in the preparation of **3** which would contain three potentially terdentate L^{NCN} ligands, only compound **4** is obtained as a product of a hydrolysis in a moderate yield (Scheme 1). Such a hydrolysis and elimination of *n*-butane from the presumably hydrolytically stable tetraorganotin(IV) compound, known for metal-alkyl species of more electropositive metals, is for tin(IV) compounds still elusive in the literature. Compounds **3** and **5** can be obtained by described procedures under strictly inert conditions only, where **5** is still isolated in a mixture together with L$_2^{CN}$SnBr$_2$ [16a] and L$_4^{CN}$Sn [4] (see below for more details).



Scheme 1. Preparation and reactivity of L$_3$SnR (L = L^{CN}, L^{NCN}; R = *n*-Bu, Ph).

The solution state ^{1}H and ^{119}Sn NMR spectra measurements of precursors **1** and **2** in CDCl$_3$ gave surprisingly well resolved signals at room temperature, which indicate high degree of fluxionality of all ligands and enabled us to measure also the ^{13}C and ^{15}N NMR spectra at this temperature. The patterns typical for tetraorganotin(IV) compounds containing L^{CN} chelating ligands were observed for room temperature ^{1}H NMR spectra of **1** and **2**. The temperature dependent ^{1}H NMR spectra of **1** and **2** performed at −50 °C show only a broadening of all signals. In ^{119}Sn NMR spectra of these compounds, signals at −109.9 for **1** and −161.9 ppm for **2** were observed which are similar to values found for comparable tin compounds as for example −163.3 ppm for L^{CN}SnPh$_3$ [15g] and −129.6 ppm for (2-*i*-Bu-C$_6$H$_4$)SnPh$_3$ [14b], respectively. This fact could be explained by very low effect of the potentially chelating ligand or an increase of shielding by the presence of the L^{CN} ligand instead of *n*-butyl group – the comparison of δ(^{119}Sn) [14b] for L^{CN}Sn(*n*-Bu)$_3$ being −50.7 ppm, for L$_2^{CN}$Sn(*n*-Bu)$_2$ −85.3 ppm, and **1** (δ(^{119}Sn) = −109.9 ppm). On the other hand, the ^3J(^{119}Sn,^{1}H) (56.1 Hz for **1**, and 60.3 Hz for **2**) and ^1J(^{119}Sn,^{13}C) (484.9 and 480.1 Hz for **1**; 594.8 and 557.4 Hz for **2**) coupling constants, which are highly indicative for the tin coordination number value [22], are in line with previously found values for related tetraorganotin(IV) compounds [14b]. Also the values found in ^{15}N NMR spectra are almost identical with values for L^{CN}Sn(*n*-Bu)$_3$ [14a] and other tetraorganotin(IV) compounds containing one potentially chelating ligand.

Both identity and purity of all stable compounds were confirmed by ESI-MS spectrometry in the positive-ion mode. The typical feature of ESI mass spectra of early studied organotin compounds is the cleavage of the most labile bond present in the molecule – for example Sn–halogen or Sn–oxygen. Completely different behaviour is observed for samples where any labile bond is present (**1** and **2**). In the case of **2**, two series of ions are observed. First, the phenyl is cleaved and then the subsequent losses of CH_3NHCH_3 or L^{CN} ligands are observed. The second series came from protonated molecule of **2**, the subsequent losses of CH_3NHCH_3 are observed in spectra. When *n*-butyl is bound to the tin atom together with three L^{CN} ligands (**1**), the butyl together with $(CH_3)_3N$ or L^{CN} ligand together with $(CH_3)_3N$ are primarily lost.

The solid state structures of **1** (Fig. 2) and **2** (Fig. 3) were determined by crystallographic techniques. Both compounds reveal tetrahedral vicinity of the tin central atoms with average C–Sn–C angles being 109.3°, but with large discrepancies in angle values from 102.54(9) to 121.56(9)°. These can be hardly described as perfect tetrahedra. On the other hand, the influence of the pendant arms containing the nitrogen donor atoms seems to be negligible in the solid state from the point of view of observed Sn–N distances around 3 Å (as a minima). Although these distances are still in the range determined by the sum of van der Waals radii of both atoms, usually the distance over 2.8 Å is not taken into the account as an intramolecular connection.

In the case of NMR spectroscopic studies of **3**, only broad set of signals is observed in the ^{1}H NMR spectrum at room temperature. The broad signal at −135 ppm was detected in the ^{119}Sn NMR spectrum of **3** measured in C_6D_6. This value is slightly lower than for **1**, but reasonable explanation pointer is available on the basis of comparison with analogous lowering from $L^{CN}SnPh_3$ which resonates at −163.9 ppm with $L^{NCN}SnPh_3$ resonating at −201.9 ppm [15i]. A cooperative influence of more than one donor group in chelating ligands could be the reason for this phenomenon. When **3** is exposed in solution to air, the loss of signals for *n*-butyl group is observed in the ^{1}H NMR spectrum in chloroform which is indicative for the plausible formation of **4**, but the OH resonance is not visible and the rest of the signals remain broader. In the ^{119}Sn NMR spectrum of **4** in $CDCl_3$, the broad signal at −158.1 ppm is detected at room temperature. New broad set of signals was detected in ^{1}H NMR spectrum in THF-d_8 which is not resolved in the whole temperature range up to 220 K, but two new broad signals are visible in the low field part of the spectrum at such a low temperature (13.5 and 12.3 ppm). Two broad signals of relative integral intensities approximately 2:3 (−147.7 and −165.6 ppm – determined at 220 K) and close to the chemical shift values observed in chloroform were detected also in the ^{119}Sn NMR spectrum. It seems, the structure of **4** is different in chloroform and THF solution, respectively, where the formation of new species, presumably cationic one due to the extrusion of the OH$^-$ group from the tin coordination sphere, or the formation of an isomer of **4** is observed. In the ^{119}Sn NMR spectrum of the same sample recorded in $CDCl_3$ after the evaporation of THF-d_8 the same sole signal at −158.1 ppm is observed again thus indicating the reversibility of the process.

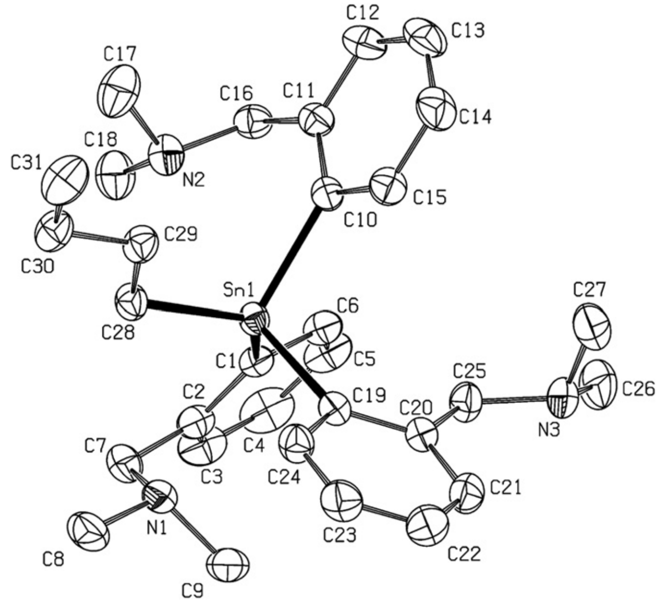


Fig. 2. Molecular structure of **1** (ORTEP view, 40% probability level). Hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Sn1 C1 2.157(2), Sn1 C10 2.179(2), Sn1 C19 2.177(2), Sn1 C28 2.145(2), Sn1 N1 3.059(2), Sn1 N2 3.173(2), Sn1 N3 4.785(2); C1 Sn1 C10 107.73(8), C1 Sn1 C19 110.26(8), C1 Sn1 C28 121.56(9), C28 Sn1 C19 105.87(9), C28 Sn1 C10 107.25(9), C10 Sn1 C19 102.54(9).

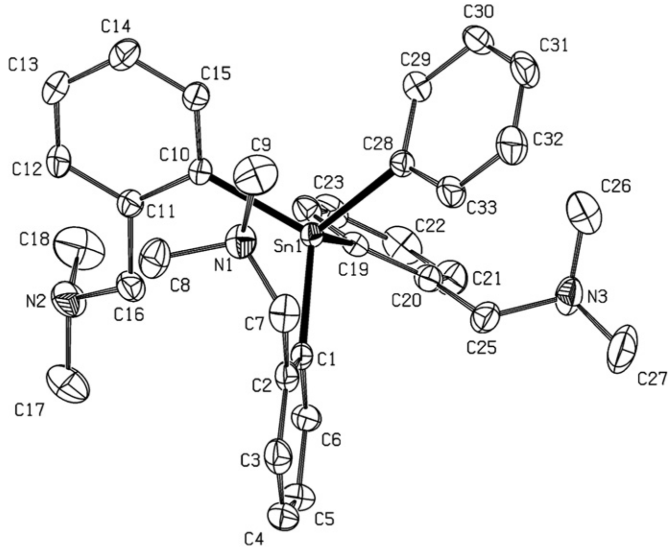


Fig. 3. Molecular structure of **2** (ORTEP view, 40% probability level). Hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Sn1 C1 2.146(3), Sn1 C10 2.149(2), Sn1 C19 2.173(3), Sn1 C28 2.135(3), Sn1 N1 2.992(3), Sn1 N2 4.787(3), Sn1 N3 4.705(3); C1 Sn1 C10 114.44(9), C1 Sn1 C19 106.38(10), C1 Sn1 C28 115.22(10), C28 Sn1 C19 103.05(10), C10 Sn1 C19 105.11(10), C28 Sn1 C10 111.30(10).

The formation of $[L_3^{NCN}Sn]^+$ fragment *e.g.* loss of the hydroxyl group is primarily observed in the positive mode of ESI-MS spectrum of **4**.

Single crystals of pure **4** grew from the neat oily **4** after standing for one week at room temperature. Its solid state structure (Fig. 4) is composed of three L^{NCN} ligands and one terminal OH moiety covalently bound to the tin atom. Although the tin coordination polyhedron could be described as even more distorted tetrahedron than in **1** or **2**, the nitrogen containing pendant arms which have any contact with the central atom play important role in stabilization of the terminal Sn–OH group by relatively strong connection performed by hydrogen bridge to the N1 atom. The Sn1–O1 distance being 1.981(2) Å lies in the range determined by values of 1.961 Å and 2.005 Å reported for only two correctly crystallographically determined structures of the tetrahedral monomeric triorganotin(IV) hydroxides [23]. In comparison to **1**, **2** and the rest of Sn–C bonds in **4**, the Sn1–C1 distance of 2.208(3) Å is significantly longer again probably due to the H-bond being situated in the same part of the molecule. The literature comparison of the structure of **4** to another Sn–OH fragment containing compounds positioned **4** to the very limited group of monomeric triorganotin(IV) hydroxides. The rest of triorganotin(IV) hydroxides

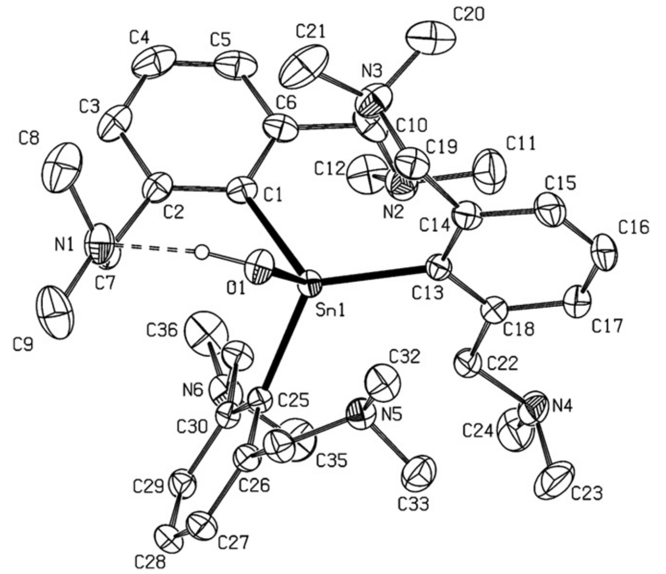


Fig. 4. Molecular structure of **4** (ORTEP view, 50% probability level). Some of the hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Sn1 O1 1.981(2), Sn1 C1 2.208(3), Sn1 C13 2.169(3), Sn1 C25 2.184(3), Sn1 N1 3.721(4), Sn1 N2 3.680(3), Sn1 N3 3.469(3), Sn1 N4 4.819(4), Sn1 N5 2.934(3), Sn1 N6 4.909(3); C1 Sn1 O1 97.40(10), O1 Sn1 C13 106.95(10), O1 Sn1 C25 102.66(10), C1 Sn1 C13 118.20(11), C1 Sn1 C25 106.63(11), C13 Sn1 C25 121.15(10). Hydrogen bonding: O1–H···N1 2.760(4) Å, 168.6°.

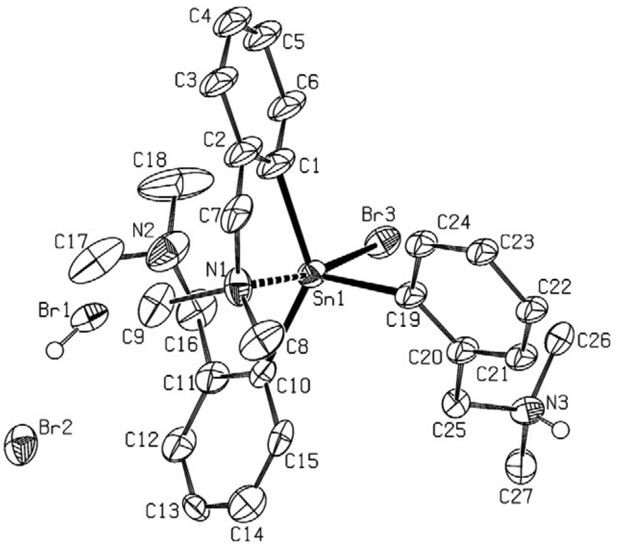


Fig. 5. Molecular structure of **6** (ORTEP view, 30% probability level). Some of hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Sn1 C1 2.155(9), Sn1 C10 2.151(10), Sn1 C19 2.146(10), Sn1 N1 2.474(8), Sn1 N2 3.310(11), Sn1 N3 4.748(7), Sn1 Br3 2.6887(12); C1 Sn1 C10 136.4(4), C1 Sn1 C19 108.5(4), C19 Sn1 C10 112.2(3), C1 Sn1 Br3 97.0(3), N1 Sn1 Br3 172.1(2). Hydrogen bonding: N3–H···Br1a 3.310(8) Å, 158.5°; Br1–H···Br2 4.107(8) Å, 144.6(2)°.

usually condensate to oxides [24a] or crystallize as dimers or polymers as in the cases of trimethyl- or triphenyltin(IV) hydroxides [25]. The target synthesis and structural characterization of **5** is described in detail in following Chapters 2.2. and 2.3.

The composition and structure of $[\mathrm{L}^{CN}_2\mathrm{L}^{CN}(\mathrm{H})\mathrm{SnBr}]^+[\mathrm{Br}\cdot\mathrm{HBr}]^-$ (**6**), as a minor product of reaction of 3 equiv of $\mathrm{L}^{CN}\mathrm{Li}$ and $\mathrm{SnBr_4}$ (which should presumably produce **5**) with a workup in the air, were studied by NMR spectroscopy in solution as well as X-ray diffraction in the solid state. Unfortunately, very low solubility (it also did not melt below 270 °C) of **6** in inert solvents such as benzene or chloroform did not allow detailed NMR studies and only broad signals at predictable positions were observed in the ^{1}H NMR spectrum in chloroform solution, no signal has been detected after a whole day measurement in the ^{119}Sn NMR spectrum.

The solid-state structure of **6** consists of tin containing fragment $[\mathrm{L}^{CN}_2\mathrm{L}^{CN}(\mathrm{H})\mathrm{SnBr}]^+$ interconnected by hydrogen bridge with $\mathrm{Br}^-\cdots\mathrm{HBr}$ fragment (Fig. 5). The coordination behaviour of the tin atom is trigonal bipyramidal with all three carbon atoms located in equatorial plane and nitrogen donor atom and one of the bromine atoms in axial positions revealing almost ideal flat interatomic angle (N1 Sn1 Br3 = 172.1(2)°).

Finally, having precursors **1**–**3**, one could start the synthesis and structural characterization of target triorganotin(IV) species bearing three potentially chelating ligands.

2.2. Preparation and structural investigation of target compounds of the L^{CN}_3SnX type (X = halogen)

We decided to use **1** and **2** for plausible formation of the target species L^{CN}_3SnX (where X = halogen, Scheme 2). The formation of triorganotin(IV) bromides is described in the literature using reaction of triarylalkyltin(IV) compounds with bromine or HBr [26]. Applying exactly the same protocol to the reaction of **1** yielded (immediate decolourization of the bromine solution) surprisingly the triorganotin(IV) compound **7** and an adduct of the *ortho*-brominated ligand with HBr (**8**) (Scheme 2). The reaction mixture was separated by crystallization of **8** from oily **7**. The composition of **7** is deduced from ^{1}H and ^{119}Sn NMR spectra patterns similar to $\mathrm{L}^{CN}_2\mathrm{Sn}(n\text{-Bu})\mathrm{Cl}$ [14a]. The $\delta(^{119}\mathrm{Sn})$ of **7** and its chlorinated analogue differs only by ca. 7 ppm.

Except of the peak attributed to the protonated **7**, the peak corresponding to the loss of bromide anion is the most intense peak observed in both positive mode ESI-MS spectra of **7** and **8**, respectively. Moreover the structure of **8** has been determined in the solid state (see Supplementary material, Figs. S1 and S2).

The next possibility for the preparation of the $\mathrm{L_3SnX}$ species is the reaction of tetraaryltin(IV) species with bromine in benzene or chloroform [27]. This procedure has been applied to **2** and half of equivalent of bromine in the air taking into the account presumably higher reactivity of the unsubstituted phenyl ring than the phenyl with the pendant arm. The reaction is rather slow with yield of about 30% after two days. When the same reaction is conducted at elevated temperature the yield increased to approximately 45%, but

$$\mathrm{L}^{CN}{}_3\mathrm{Sn}(n\text{-Bu})\ (\mathbf{1}) + \mathrm{Br_2} \xrightarrow[\text{R. T.}]{\text{DMF, air}} \mathrm{L}^{CN}{}_2\mathrm{Sn}(n\text{-Bu})\mathrm{Br}\ (\mathbf{7}) + 2\text{-}(\mathrm{Me_2NCH_2})\mathrm{C_6H_4Br{\cdot}HBr}\ (\mathbf{8})$$

$$\mathrm{L}^{CN}{}_3\mathrm{SnPh}\ (\mathbf{2}) + \mathrm{Br_2} \xrightarrow[\text{R. T.}]{\text{benzene, air}} [\mathrm{L}^{CN}{}_3\mathrm{Sn(H_2O)}]^+\mathrm{Br}^-\ (\mathbf{5a}) + \mathrm{PhBr}$$

$$\mathrm{L}^{CN}{}_3\mathrm{SnPh}\ (\mathbf{2}) + \mathrm{I_2} \xrightarrow[\text{reflux}]{\text{benzene, air}} \mathrm{L}^{CN}{}_2\mathrm{SnI_2} + \mathrm{Ph_4Sn} + \mathrm{L}^{CN}\mathrm{Ph_2SnI}$$

$$\mathrm{L}^{CN}{}_3\mathrm{SnPh}\ (\mathbf{2}) + \mathrm{HI} \xrightarrow[\text{R. T.}]{\text{benzene, air}} \mathrm{L}^{CN}{}_2\mathrm{SnPhI{\cdot}HI}\ (\mathbf{9}) + \mathrm{Me_2NCH_2C_6H_5{\cdot}HI}$$

$$\mathrm{L}^{CN}{}_3\mathrm{SnPh}\ (\mathbf{2}) + \mathrm{HF} \xrightarrow[\text{R. T.}]{\text{benzene, air}} \mathrm{L}^{CN}{}_2\mathrm{SnPhF}\ (\mathbf{5b}) + \mathrm{L}^{CN}\mathrm{H}$$

$$\mathrm{L}^{CN}{}_4\mathrm{Sn} + \mathrm{HgCl_2} \xrightarrow[\text{R. T.}]{\text{benzene, air}} \mathrm{L}^{CN}{}_2\mathrm{SnCl_2} + \mathrm{L}^{CN}{}_2\mathrm{Hg}$$

$$2\ \mathrm{L}^{CN}{}_4\mathrm{Sn} + \mathrm{HgCl_2} \xrightarrow[\text{R. T.}]{\text{THF, air}} \mathrm{L}^{CN}{}_3\mathrm{SnCl}\ (\mathbf{5c}) + \mathrm{L}^{CN}{}_2\mathrm{SnCl_2} + \mathrm{L}^{CN}{}_2\mathrm{Hg}$$

Scheme 2. Reactivity of L^{CN}_3SnR and L^{CN}_4Sn.

a mixture of products (L^{CN}_3SnBr, probably $L^{CN}_2SnPhBr$ and $L^{CN}_2SnBr_2$ [16a]) is obtained. The analogous procedure starting from L^{CN}_4Sn [4] led to the yield of about 10% of **5**. From both reactions the crystalline compound $[L^{CN}_3Sn(H_2O)]^+Br^-$ (**5a**) as an adduct of **5** with one water molecule is isolated (see Scheme 2).

The structure of **5a** (Fig. 6) consists of trigonal bipyramidal tin-containing cation which is made of three L^{CN} ligands from which one is bidentately coordinated (Sn1 N1 2.551(3) Å) and the remaining two have the hydrogen bonds to the water molecule tightly connected to the tin atom in mutual *trans* positions to the intramolecularly coordinated nitrogen atom.

Other attempts to prepare L^{CN}_3SnI (Scheme 2) by reactions of **2** with HI and I_2, respectively, were carried out. The reaction with iodine yielded $L^{CN}_2SnI_2$ [16a], $L^{CN}Ph_2SnI$ [16b], and tetraphenylstannane, as identified by NMR spectroscopy [24b] and X-ray diffraction analysis and a negligible amount of species having similar broad signals in ^1H NMR spectrum as **5a**. The iodinated analogue of **5a** is probably the minor product. The second reaction of **2** with HI yielded tin compound **9** and adduct of the free ligand with HI which was identified by NMR spectroscopy revealing similar spectrum as the protonated ligand with protic acids [28]. The structure of **9** is evaluated by ESI-MS and multinuclear NMR spectroscopy showing similar spectral patterns as other stannates bearing two L^{CN} moieties [28] and X-ray techniques on single crystalline material revealed similar structure to **6**, unfortunately the quality of crystals was not ideal and a disorder of the phenyl ring together with only isotropical displacement of two nitrogen atoms caused the publishing the data and figure in Supplementary material (Figs. S3 and S4).

The reaction of **2** with aqueous HF provided L^{CN}_2SnPhF [16c] together with free ligand $L^{CN}H$ which was confirmed by multinuclear NMR spectroscopy.

The attempt to prepare compound L^{CN}_3SnCl was based on the reaction of L^{CN}_4Sn with $HgCl_2$ (Scheme 2), but only $L^{CN}_2SnCl_2$ and L^{CN}_2Hg were detected by the help of ^1H and ^{119}Sn NMR spectra measurement and comparison with the literature data [1c,16a,b]. When 2 equiv of L^{CN}_4Sn was reacted with $HgCl_2$ in THF at room temperature, inseparable mixture of all compounds present in the residue after the previous reaction is formed together with **5c** which could be identified by the help of NMR measurements and similarity of the spectra with **5** as L^{CN}_3SnCl. Broad signals were observed in ^1H as well as in ^{119}Sn NMR spectra where signal at −190.2 ppm is attributed to **5c**.

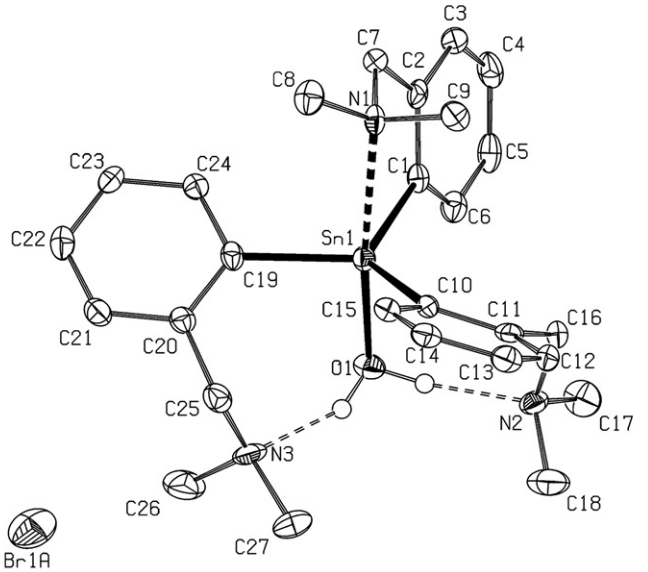


Fig. 6. Molecular structure of **5a** (ORTEP view, 50% probability level). Some of the hydrogen atoms and the non-coordinated THF molecule are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Sn1 C1 2.125(4), Sn1 C10 2.140(4), Sn1 C19 2.157(4), Sn1 N1 2.551(3), Sn1 N2 3.674(3), Sn1 N3 3.703(4), Sn1 O1 2.083(3); C1 Sn1 C10 123.80(14), C1 Sn1 C19 114.65(15), C1 Sn1 O1 98.75(13), C1 Sn1 N1 73.95(13). Hydrogen bonding: O1⋯N3 2.677(5) Å and O1⋯N2 2.814(5) Å.

On the basis of above mentioned rather unsuccessful experiments we decided to follow and reinvestigate the reaction of 3 equiv $L^{CN}Li$ with $SnBr_4$ at various conditions.

*2.3. Revisiting the synthesis and isolation of L^{CN}_3SnBr (**5**). Synthesis of L^{CN}_3SnF (**5b**). Detailed structural characterization of **5**, **5a** and **5b** in solution*

Surprisingly, all attempts for the direct synthesis of **5** from $L^{CN}Li$ and $SnBr_4$ (in a 3:1 ratio) in benzene at ambient temperature failed and the only species which was isolated from the reaction mixture was identified by ^1H and ^{119}Sn NMR spectroscopy as pure L^{CN}_4Sn ($\delta(^{119}Sn) = -145.8$ ppm in THF-d_8) [4]. Changing the reaction conditions (e.g. the use of toluene or THF instead of benzene as a solvent) or varying the reaction temperature (e.g. reflux, ambient temperature or maintaining the temperature around 0 °C) did not lead to the expected exclusive formation of the desired product as well. Unfortunately, however, even reactions of $L^{CN}_2SnBr_2$ [Ref. [16a]] and $L^{CN}SnBr_3$ [15f] with $L^{CN}Li$ (1 or 2 equiv, respectively) always resulted only in the formation of mixture of products (identified as $L^{CN}_2SnBr_2$, L^{CN}_3SnBr, and L^{CN}_4Sn [4] by ^1H and ^{119}Sn NMR spectroscopy) where the desired compound **5** was present in less than 10% yield. Due to these reasons we decided to synthesize the title compound by the so-called Kocheshkov redistribution reaction [29].

Several possible reaction pathways were thus investigated (see Scheme 3). Unfortunately, neither the reaction of L^{CN}_4Sn [4] with 1 equiv of $L^{CN}_2SnBr_2$ [16a] nor with $L^{CN}SnBr_3$ [15h] (in a 2:1 ratio) in warm toluene gave exclusively the desired compound (reaction time 3 days). Nevertheless, we observed the presence of the desired product in the reaction mixture as the major product (assay of **5** ca. 42, and 47 mol%, respectively) according to the ^1H and ^{119}Sn NMR spectroscopy ($\delta(^{119}Sn) = -201.8$ ppm in THF-d_8). The most promising thus seemed to be the reaction of 3 equiv of L^{CN}_4Sn (which can be easily prepared on a large scale) with commercially available anhydrous $SnBr_4$ in boiling toluene (mixed with ca. 25% THF by volume for better solubility of reagents, reaction time 2 days). According to the ^1H and ^{119}Sn NMR spectroscopy, the reaction mixture contains both starting reagent L^{CN}_4Sn ($\delta(^{119}Sn) = -145.8$ ppm in THF-d_8; ca. 32 mol %) and desired compound **5** ($\delta(^{119}Sn) = -201.8$ ppm in THF-d_8; ca. 64 mol%). In addition, $L^{CN}_2SnBr_2$ was formed as well ($\delta(^{119}Sn) = -271.4$ ppm in THF-d_8; ca. 4 mol%). Target species **5** can be then isolated in ca. 95% purity (with L^{CN}_4Sn being the unreactive

$$L^{CN}{}_4Sn + L^{CN}{}_2SnBr_2 \xrightarrow[\text{inert at., 3 d}]{\text{toluene, 90°C}} \underset{42\%}{L^{CN}{}_3SnBr} + \underset{29\%}{L^{CN}{}_4Sn} + \underset{29\%}{L^{CN}{}_2SnBr_2}$$

$$2\,L^{CN}{}_4Sn + L^{CN}SnBr_3 \xrightarrow[\text{inert at., 3 d}]{\text{toluene, 90°C}} \underset{47\%}{L^{CN}{}_3SnBr} + \underset{42\%}{L^{CN}{}_4Sn} + \underset{11\%}{L^{CN}{}_2SnBr_2}$$

$$3\,L^{CN}{}_4Sn + SnBr_4 \xrightarrow[\text{inert at., 3 d}]{\text{THF, R.T.}} \underset{41\%}{L^{CN}{}_3SnBr} + \underset{33\%}{L^{CN}{}_4Sn} + \underset{26\%}{L^{CN}{}_2SnBr_2}$$

$$3\,L^{CN}{}_4Sn + SnBr_4 \xrightarrow[\text{reflux, inert at., 2 d}]{\text{Toluene/THF}} \underset{64\%}{L^{CN}{}_3SnBr} + \underset{32\%}{L^{CN}{}_4Sn} + \underset{4\%}{L^{CN}{}_2SnBr_2}$$

Scheme 3. Various unsuccessful reactions studied for the plausible exclusive synthesis of **5**.

impurity) from this reaction mixture thanks to the different solubility in selected solvents (diethyl ether and chloroform) according to the procedure which is described in the Experimental part in detail. Preparation of **5** requires strictly anaerobic and anhydrous conditions otherwise formation of its adduct with water (**5a**) will occur.

L^{CN}_3SnF (**5b)** was prepared from **5** by the simple reaction with $L^{CN}(n\text{-Bu})_2SnF$ which proved to be a very effective and versatile fluorinating agent [18]. **5b** has been prepared in order to distinguish between the presence of terminal or bridging fluorine atoms by the help of multinuclear NMR spectroscopy. This can be done simply by the comparison of coupling constants ($^1J(^{119}Sn, ^{19}F)$ found for **5b** with previously reported results (see below).

Structure of **5** (95% purity) in solution was investigated by ^1H and ^{119}Sn NMR spectroscopy. ^1H NMR spectra of **5** recorded both in THF-d_8 and $CDCl_3$ showed similar patterns at ambient temperature revealing slightly broader resonances when measured in $CDCl_3$. According to the presence of only one set of signals that were unambiguously attributed to all three ligands we assume the bonding equality of these ligands. In general, the value of the $^3J(^{119}Sn, ^1H)$ satellites of the doublet of the H(6) signal in the ^1H NMR spectra is a useful tool for characterizing all *C,N*-chelated organotin compounds. Prepared **5** exhibits the coupling constant $^3J(^{119}Sn, ^1H)$ being ca. 65 Hz which is in good agreement with previously published results [14,22]. All other minor signals found in the ^1H NMR spectra were assigned to the L^{CN}_4Sn [4] species being the impurity (less than 5%). Almost pure **5b** revealed similar spectral pattern as in the case of ^1H NMR spectrum of **5** but exhibiting more narrow resonances, especially that one of the doublet of the H(6) signal when recorded in THF-d_8.

The most valuable data about the structure (i.e. the coordination geometry of the central tin atom) of **5** in solution arose from the ^{119}Sn NMR spectra. Surprisingly, according to the ^{119}Sn NMR spectrum of **5** recorded in $CDCl_3$ at ambient temperature ($\delta(^{119}Sn) = -123.8$ ppm, broad) we suggest no intramolecular N → Sn interaction and thus only four-coordinate tin centre as depicted in Fig. 7 (structural motif **A**). On the other hand, the ^{119}Sn NMR spectrum recorded at room temperature in THF-d_8 clearly shows significant upfield shift of the broad resonance up to −201.8 ppm which corresponds with five-coordinate tin atom (Fig. 7, structural motif **B**). So, based on structural data combined from ^1H and ^{119}Sn NMR spectra recorded in THF-d_8 at room temperature we assume very fast equilibrium (at least on the NMR time scale) between one coordinated and two non-coordinated pendant arms of all three potentially chelating ligands. Contrary to the situation described for **5**, we observed only one signal in each deuterated solvent (doublets with coupling constants $^1J(^{19}F, ^{119}Sn)$ being 2162 Hz, and 2251 Hz, respectively) in the ^{119}Sn NMR spectra of **5b** recorded in both $CDCl_3$ ($\delta(^{119}Sn) = -207.8$ ppm) and THF-d_8 ($\delta(^{119}Sn) = -204.8$ ppm) which indicates that the central tin atom is five-coordinated in both cases. The ^{19}F NMR spectrum of **5b** exhibited only one resonance at −196.9 ($^1J(^{119}Sn, ^{19}F) = 2236$ Hz, measured in THF-d_8) which is typical for monomeric triorganotin(IV) fluorides with terminal Sn–F bond [30]. This is the direct and unambiguous evidence of the purely covalent nature of the Sn–F bond in **5b** in solution.

Unfortunately, however, single crystals of **5** were not obtained despite several attempts to crystallize it were performed. But when crystallized from wet THF in the air we were able to isolate again single crystals of its aqua-derivative $[L^{CN}_3Sn(H_2O)]^+Br^-$ (**5a**) discussed above (see Fig. 6). ^1H NMR spectra of this species recorded both in $CDCl_3$ and THF-d_8 revealed nearly the same spectral pattern when compared to ^1H NMR spectra of anhydrous **5** (see Experimental part). The only difference is caused by the presence of the very broad resonance of the solvating water molecule ($\delta(^1H) = 5.67$ ppm) observed when measured in $CDCl_3$. Surprisingly, this signal disappeared when measuring the sample in THF-d_8. More interesting structural data were gathered from ^{119}Sn NMR spectra. Only one broad signal was observed at −185 ppm (recorded in $CDCl_3$) which is a sign of the presence of five-coordinate tin species. In general, according to our opinion, there are two possible structural motifs (presumably ionic) of this species in solution: *i)* ionic form with only one intramolecularly coordinated ligand, two non-coordinated ligands and coordinated solvating water molecule (Fig. 7, structural motif **C**), and *ii)* ionic form bearing two intramolecularly coordinated ligands, one non-coordinated ligand and the water molecule interacting with the "naked" bromide anion (Fig. 7, structural motif **D**). Unfortunately, we were not able to prove which one of the two possible forms is really present in the chloroform solution. The ^{119}Sn NMR spectrum of **5a** recorded in THF-d_8 displayed only one broad resonance at −202.0 ppm which is very close to the chemical shift value found for anhydrous **5** ($\delta(^{119}Sn) = -201.8$ ppm in THF-d_8). This could be explained by the similar, presumably ionic, structure of these species in solution. As described above in the discussion we suppose, in general, the presence of two possible species with five-coordinate tin centres (Fig. 7, structural motif **C** or **D**). In this particular case we favour the presence of the species having the **D** ionic structural motif (e.g. bearing two intramolecularly coordinated ligands, one non-coordinated ligand and the water molecule interacting with the "naked" bromide anion). All these conclusions were further supported by ^1H and ^{119}Sn VT-NMR spectroscopy measurements (*vide infra*) and solid state investigation according to the literature [31,32].

In addition, structural behaviour of anhydrous **5** (prepared under an argon atmosphere and further dried over molecular sieves) in solution was studied by VT-NMR spectroscopy in order to further elucidate its structural behaviour in solution. Decreasing the temperature to −40 °C led to the differentiation of signals of ligands forming thus quite complex spectral pattern (revealing several AX spin systems attributable to the pendant arms of ligands) in the ^1H NMR spectra (recorded in $CDCl_3$) as expected. Even more

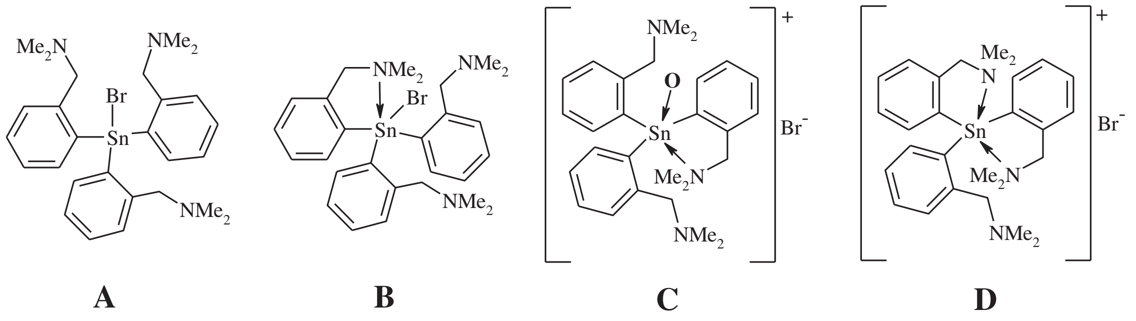


Fig. 7. Schematic drawings of four proposed structural motifs of **5** and its aqua complex **5a** (**O** = H_2O or THF in the case of **C**).

complicated was interpretation of ^{1}H VT-NMR spectra recorded in THF-d_8 at −60 °C due to the complex equilibrium among three structural motifs **A**, **B** and **C** or **D** depicted in Fig. 7 that was confirmed by the ^{119}Sn VT-NMR. Therefore, the complete assignment of all signals was not carried out. Nevertheless, it is evident that at lower temperatures the differentiation of signals of ligands (both intramolecularly coordinated and non-coordinated) occurs, too. The ^{119}Sn VT-NMR spectra measured in $CDCl_3$ exhibited always only one narrow resonance shifted several ppm upfield (for example $\delta(^{119}Sn) = -127.5$ ppm at −40 °C) relatively to the signal observed at ambient temperature ($\delta(^{119}Sn) = -123.8$ ppm) but still matching with only four-coordinate tin atom (e.g. Fig. 7, structural motif **A**). As stated *vide supra* we observed complex equilibrium among three tin-containing species (structural motifs **A**, **B** and **C** or **D** depicted in Fig. 7) in the ^{119}Sn VT-NMR spectra measured in THF-d8. This hypothesis is based on following chemical shift values found in the spectrum (recorded at −60 °C): *i)* minor signal at −125.7 ppm (structural motif **A**) corresponds with non-ionic four-coordinate tin-containing species; *ii)* first major narrow signal at −185.1 ppm (structural motif **C** or **D**) matches to presumably ionic five-coordinated tin-containing species; and *iii)* second major signal at −221.5 ppm can be attributed to the non-ionic form of **5** where the central tin atom is five-coordinated (e.g. Fig. 7, structural motif **B**). The mutual integral intensity of these two major resonances is nearly in a 1:1 ratio.

3. Conclusion

Ten novel tri- or tetraorganotin(IV) compounds were prepared and structurally characterized in the course of this work. Unfortunately, in general, we were not able to discover any reaction which would result in the exclusive formation of desired triorganotin(IV) species bearing three *C*,*N*- or *N*,*C*,*N*-chelating ligands. Only mixtures of target L_3^{CN}SnX compounds together with other organotin(IV) species were formed in all reactions studied. Nevertheless, at least in the case of **5** a viable way of preparation and isolation is described leading to 95% purity (with 5% of L_4^{CN}Sn as impurity which shall not influence the future proposed reactivity studies of **5**). Further reactivity studies of **5** (e.g. preparation of its hydride, hydroxide *etc.* derivatives) are currently in progress.

4. Experimental

4.1. General methods

4.1.1. Mass spectrometry

Positive-ion electrospray ionization (ESI) mass spectra (MS) were measured on the LCQ ion trap analyser (Thermo Fisher Scientific, Waltham, MA, USA) in the range *m*/*z* 50–1000. The samples were dissolved in acetonitrile and analysed by direct infusion at the flow rate 10 μl/min. The ESI ion source spray voltage was set to 4 kV, capillary temperature was 200 °C, capillary voltage 30 V and tube lens offset 15 V.

4.1.2. NMR spectroscopy

NMR spectra were recorded from solutions in $CDCl_3$, C_6D_6 and THF-d_8 on a Bruker Avance 500 spectrometer (equipped with *z*-gradient 5 mm probe) at frequencies 500.13 MHz for ^{1}H, 125.76 MHz for $^{13}C\{^1H\}$, and 186.50 MHz for $^{119}Sn\{^1H\}$ at 295 K. VT-NMR experiments were carried out using this spectrometer, too. The rest of NMR measurements was performed on a Bruker Avance II 400 spectrometer operating at 400.13 MHz for ^{1}H, 100.62 MHz for $^{13}C\{^1H\}$, 40.56 MHz for $^{15}N\{^1H\}$, 376.50 MHz for $^{19}F\{^1H\}$, and 149.17 MHz for $^{119}Sn\{^1H\}$ at 295 K. Solutions were obtained by dissolving of approximately 40 mg (100 mg for ^{15}N measurements) of each compound approximately in 0.6 ml of deuterated solvents. The values of ^{1}H chemical shifts were calibrated to residual signals of chloroform ($\delta(^1H) = 7.27$ ppm), benzene ($\delta(^1H) = 7.16$ ppm) or THF ($\delta(^1H) = 3.57$ ppm). The values of $^{13}C\{^1H\}$ chemical shifts were calibrated to signals of $CDCl_3$ ($\delta(^{13}C) = 77.2$ppm), $^{15}N\{^1H\}$ chemical shifts to external neat nitromethane ($\delta(^1N) = 0.0$ ppm). Values of $^{19}F\{^1H\}$ chemical shifts were calibrated to external standard CCl_3F ($\delta(^{19}F) = 0.0$ ppm). The $^{119}Sn\{^1H\}$ chemical shift values are referred to external neat tetramethylstannane ($\delta(^{119}Sn) = 0.0$ ppm). Positive chemical shift values denote shifts to the higher frequencies relative to the standards. $^{119}Sn\{^1H\}$ NMR spectra were measured using the inverse gated-decoupling mode. All $^{13}C\{^1H\}$ NMR spectra were measured using standard proton-decoupled experiment and CH and CH_3 vs. C and CH_2 were differentiated by the help of APT method – in the cases of compounds with a dynamic behaviour in solution or limited solubility no ^{13}C NMR spectra were recorded.

4.1.3. Elemental analyses

The compositional analyses were determined on the automatic analyzer EA 1108 by FISONS Instruments.

4.1.4. Crystallography

The X-ray data (Table 1) for colourless crystals of all compounds were obtained at 150 K using Oxford Cryostream low-temperature device on a Nonius KappaCCD diffractometer with MoK_α radiation ($\lambda = 0.71073$ Å), a graphite monochromator, and the ϕ and χ scan mode. Data reductions were performed with DENZO-SMN [33]. The absorption was corrected by integration methods [34]. Structures were solved by direct methods (Sir92) [35] and refined by full matrix least-square based on F^2 (SHELXL97) [36]. Hydrogen atoms were mostly localized on a difference Fourier map, however to ensure uniformity of the treatment of the crystal, all hydrogen atoms were recalculated into idealized positions (riding model) and assigned temperature factors $H_{iso}(H) = 1.2U_{eq}$(pivot atom) or of $1.5U_{eq}$ for the methyl moiety with C–H = 0.96, 0.97, and 0.93 Å for methyl, methylene and hydrogen atoms in aromatic rings, respectively. The hydrogen atoms of the OH or H_2O groups were placed according to maxima on the Fourier difference maps. Disordered non-coordinated solvents (THF or diethyl ether) were found in crystals of **6** and **5a**. Attempts were made to model this disorder or split into two positions, but were unsuccessful. PLATON/SQUEZZE [37] was used to correct the data for the presence of disordered solvent. A potential solvent volume of 2074 and 246 Å^3 was found. 1056 and 98 electrons per unit cell worth of scattering were located in the voids. The calculated stoichiometry of solvent was calculated to be twenty four additional molecules of THF and two Et_2O per unit cell.

4.2. Synthesis

All solvents and starting materials such as *n*-butyltin trichloride, phenyltin trichloride, $SnBr_4$ and dimethylbenzylamine were purchased from commercial sources (Sigma–Aldrich) and purified by vacuum distillation. 2,6-Bis(*N*,*N*-dimethylaminomethyl)benzene and appropriate lithium compounds were prepared as described elsewhere [38]. L_4^{CN}Sn [4] and L^{CN}(*n*-Bu)$_2$SnF [30] were synthesized according to procedures described in the literature. Solvents were distilled from K/Na alloy and stored over a potassium mirror under and the argon atmosphere or dried and degassed using commercial drying columns (Innovative Technology Inc., USA). Single crystals suitable for XRD analyses were obtained from corresponding saturated solutions or upon a long standing of distilled compound (**1**).

4.2.1. Preparation of L_3^{CN}Sn(n-Bu) (**1**)

The suspension of 4.2 g of L^{CN}Li (29.7 mmol) in 20 ml of benzene was added dropwise to the solution of 2.80 g (9.92 mmol) of *n*-

Table 1
Crystallographic data for **1**, **2**, **4**, **5a** and **6**.

Compound	**1**	**2**	**4**	**5a**·0.5Et$_2$O	**6**·6THF
Empirical formula	$C_{31}H_{45}N_3Sn$	$C_{33}H_{41}N_3Sn$	$C_{36}H_{58}N_6OSn$	$C_{29}H_{43}BrN_3O_{1.5}Sn$	$C_{51}H_{98}Br_3N_3O_6Sn$
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*P*-1	*P*-1	$P2_1/c$	$P2_1/c$	*C*2
a (Å)	8.9920(2)	9.2710(5)	12.7960(10)	9.1390(8)	35.1540(10)
b (Å)	11.9701(8)	9.6890(8)	22.2431(14)	24.163(2)	14.4641(6)
c (Å)	14.4119(7)	17.5859(13)	18.1280(10)	13.7750(12)	9.5970(3)
α (°)	91.120(5)	88.172(6)	90	90	90
β (°)	96.735(3)	87.961(6)	133.425(5)	108.140(6)	105.349(3)
γ (°)	99.448(4)	73.775(4)	90	90	90
Z	2	2	4	4	4
V (Å^3)	1518.43(13)	1515.41(19)	3747.3(5)	2890.7(4)	4705.7(3)
Crystal size (mm)	0.54 × 0.30 × 0.22	0.29 × 0.23 × 0.12	0.31 × 0.25 × 0.19	0.51 × 0.24 × 0.15	0.31 × 0.22 × 0.07
h;*k*;*l* range	−11,11;−15,15;−18,18	−12,12;−12,12;−22,22	−16,16;−27,28;−20,23	−11,11;−28,31;−17,17	−43,43;−17,17;−11,11
θ range/°	2.28–27.50	2.29–27.40	1.80–27.50	1.69–27.50	4.25–26.37
Reflections measured	27,702	27,630	34,561	23,919	20,009
Independent (R_{int})[a]	6875	6803	8566	6491	8143
Observed [$I > 2\sigma(I)$]	5980	5775	6572	4169	6589
Parameters refined	316	334	397	314	251
Max/min τ/e Å^{-3}	0.394/−0.472	0.447/−0.470	0.734/−0.436	0.543/−0.879	1.343/−1.344
GOF[b]	1.165	1.132	1.181	1.035	1.054
R[c]/*wR*[c]	0.0280/0.0591	0.0330/0.0594	0.0410/0.0732	0.0499/0.0838	0.0626/0.1567

[a] $R_{int} = \sum|F_o^2 - F_{o,mean}^2|/\sum F_o^2$.

[b] $S = [\sum(w(F_o^2 - F_c^2)^2)/(N_{diffr.} - N_{param.})]^{1/2}$.

[c] Weighting scheme: $w = [\sigma(F_o^2) + (w_1P)^2 + w_2P]^{-1}$, where $P = [\max(F_o^2) + 2F_c^2]$, $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$, $wR(F^2) = [\sum(w(F_o^2 - F_c^2)^2)/\sum w(F_o^2)^2]^{½}$.

BuSnCl$_3$ in 30 ml of benzene during 10 min at ∼10 °C. The reaction mixture was warmed to the room temperature and 30 ml of chloroform was added gradually. The solution was filtered in air and the white precipitate washed by 20 ml of hexanes. Volatiles were removed in high vacuo and the residue fractionally distilled up to 210°C/20 Pa; 4.30 g of pure colourless oily **1** is obtained in 75% yield. Mp 57–62 °C. ^{1}H NMR (CDCl$_3$, 400.13 MHz, 295 K, ppm): 7.52 (d, 3H, H(6), ^3J = 8.1 Hz, $^3J(^{119}$Sn, ^{1}H) = 56.1 Hz); 7.31 (d, 3H, H(3), ^3J = 8.1 Hz); 7.26 (dd, 3H, H(4), ^3J = 8.1 Hz, 8.1 Hz); 7.15 (dd, 3H, H(5), ^3J = 8.1 Hz, 8.1 Hz); 3.35 (s, 6H, NCH$_2$); 1.86 (s, 18H, N(CH$_3$)$_2$); 1.51 (m, 2H, H(*n*-Bu)); 1.36 (m, 4H, H(*n*-Bu)); 0.82 (t, 3H, H(*n*-Bu), $^3J(^1$H,^{1}H) = 7.2 Hz). ^{13}C NMR (CDCl$_3$, 100.62 MHz, 295 K, ppm): 146.0 (C(2), $^2J(^{119}$Sn,^{13}C) = 27.5 Hz); 143.2 (C(1), $^1J(^{119}$Sn,^{13}C) = 484.9 Hz); 138.2 (C(6), $^2J(^{119}$Sn,^{13}C) = 35.6 Hz); 128.1 (C(5), $^3J(^{119}$Sn,^{13}C) = 39.7 Hz); 127.9 (C(4), $^4J(^{119}$Sn,^{13}C) = 9.8 Hz); 126.1 (C(3), $^3J(^{119}$Sn,^{13}C) = 48.0 Hz); 66.2 (NCH$_2$, $^3J(^{119}$Sn,^{13}C) = 20.3 Hz); 45.1 (N(CH$_3$)$_2$); 29.0 (C(*n*-Bu), $^2J(^{119}$Sn,^{13}C) = 20.1 Hz); 27.5 (C(*n*-Bu), $^3J(^{119}$Sn,^{13}C) = 94.8 Hz); 13.7 (C(*n*-Bu), $^1J(^{119}$Sn,^{13}C) = 480.1 Hz); 13.5 (C(*n*-Bu)). ^{119}Sn NMR (CDCl$_3$, 149.17 MHz, 295 K, ppm): −109.9. ^{15}N NMR (CDCl$_3$, 40.56 MHz, 295 K, ppm): −352.2. ESI-MS: molecular weight (MW) = 578; *m*/*z* 463 [M−Bu−(CH$_3$)$_3$N]$^+$, 100%; *m*/*z* 386 [M−L^{CN}−(CH$_3$)$_3$N]$^+$, 42%; *m*/*z* 344 [L$_2^{CN}$Sn−CH$_3$N(H)CH$_3$+H]$^+$, 43%, *m*/*z* 254 [L^{CN}Sn]$^+$, 20%, *m*/*z* 224 [L$_2^{CN}$Sn−CH$_3$N(H)CH$_3$−Sn + H]$^+$, 15%, *m*/*z* 179 [L$_2^{CN}$Sn−2*CH$_3$N(H)CH$_3$−Sn + H]$^+$, 6%. Elemental analysis (%): found: C 64.6; H 7.6; N 7.4. Calcd (%) for $C_{31}H_{45}SnN_3$ (578.41): C 64.37; H 7.84; N 7.26.

4.2.2. *Preparation of L$_3^{CN}$SnPh (**2**)*

Using the same procedure as for **1** starting from 4.7 g of L^{CN}Li (33.3 mmol) and 3.35 g (11.1 mmol) of PhSnCl$_3$, 5.48 g (83%) of pure **2** was crystallized after addition of hexanes to the supernatant solution. Mp 110–112 °C. ^{1}H NMR (CDCl$_3$, 400.13 MHz, 295 K, ppm): 7.77 (d, 2H, H(*o*-Ph), ^3J = 7.2 Hz, $^3J(^{119}$Sn,^{1}H) = 60.3 Hz); 7.67 (d, 3H, H(6), ^3J = 8.2 Hz, $^3J(^{119}$Sn,^{1}H) = 55.4 Hz); 7.41–7.21 (m, 12H, H(3), H(4), H(5), H(*m*-Ph), H(*p*-Ph)); 3.43 (s, 6H, NCH$_2$); 1.67 (s, 18H, N(CH$_3$)$_2$). ^{13}C NMR (CDCl$_3$, 100.62 MHz, 295 K, ppm): 146.0 (C(2), $^2J(^{119}$Sn,^{13}C) = 29.9 Hz); 144.0 (C(*i*-Ph), $^1J(^{119}$Sn,^{13}C) = 594.8 Hz); 142.7 (C(1), $^1J(^{119}$Sn,^{13}C) = 557.4 Hz); 138.2 (C(6), $^2J(^{119}$Sn,^{13}C) = 35.6 Hz); 136.7 (C(*o*-Ph), $^2J(^{119}$Sn,^{13}C) = 37.1 Hz); 128.3 (C(5), $^3J(^{119}$Sn,^{13}C) = 43.4 Hz); 128.2 (C(4), $^4J(^{119}$Sn,^{13}C) = 10.6 Hz); 127.7 (C(*m*-Ph), $^3J(^{119}$Sn,^{13}C) = 52.7 Hz); 127.5 (C(*p*-Ph), $^4J(^{119}$Sn,^{13}C) = 11.7 Hz); 126.3 (C(3), $^3J(^{119}$Sn,^{13}C) = 52.7 Hz); 66.1 (NCH$_2$, $^3J(^{119}$Sn,^{13}C) = 22.5 Hz); 44.8 (N(CH$_3$)$_2$). ^{119}Sn NMR (CDCl$_3$, 149.17 MHz, 295 K, ppm): −161.9. ^{15}N NMR (CDCl$_3$, 40.56 MHz, 295 K, ppm): −352.0. ESI-MS: molecular weight (MW) = 599; *m*/*z* 555 [M−CH$_3$N(H)CH$_3$+H]$^+$, 48%; *m*/*z* 522 [M−Ph]$^+$, 70%; *m*/*z* 477 [M−Ph−CH$_3$N(H)CH$_3$]$^+$, 30%; *m*/*z* 465 [M−3*CH$_3$N(H)CH$_3$+H]$^+$, 30%; *m*/*z* 254 [L^{CN}Sn]$^+$, 11%. Elemental analysis: found: C 66.3; H 7.0; N 7.2. Calcd (%) for $C_{33}H_{41}SnN_3$ (598.40): C 66.24; H 6.91; N 7.02.

4.2.3. *Preparation of L$_3^{NCN}$Sn(n-Bu) (**3**)*

Using the same procedure as for **1** starting from 1.5 g of L^{NCN}Li (7.57 mmol) and 0.71 g (2.52 mmol) of *n*-BuSnCl$_3$. Then the hexanes were added, solution was filtered under argon atmosphere and 1.30 g (69%) of oily **3** was obtained after evaporation of all volatiles from filtrate in high vacuo. ^{1}H NMR (C$_6$D$_6$, 500.13 MHz, 295 K, ppm): 7.52 (broad, 6H, H(3)); 7.31 (broad, 3H, H(4)); 3.42 (broad, 12H, NCH$_2$); 1.94 (s, 36H, N(CH$_3$)$_2$); 1.31 (broad, 2H, H(*n*-Bu)); 1.18 (broad, 4H, H(*n*-Bu)); 0.86 (t, 3H, ^3J = 7.6 Hz, H(*n*-Bu)). ^{119}Sn NMR (C$_6$D$_6$, 186.50 MHz, 295 K, ppm): −135.0 (broad).

4.2.4. *Preparation of L$_3^{NCN}$SnOH (**4**)*

When 1.10 g (1.47 mmol) of oily **3** was exposed on air in benzene solution for an hour and afterwards all volatiles were removed in high vacuo, 0.88 g (85%) of viscous oily residue is gained which crystallized after one week. Mp 167–170 °C. ^{1}H NMR (CDCl$_3$, 500 MHz, 295 K) δ: 7.30 (broad, 9H, H(3), H(4)); 3.49 (broad, 12H, NCH$_2$); 1.96 (s, 36H, N(CH$_3$)$_3$); ^{119}Sn NMR (CDCl$_3$, 149.17 MHz, 295 K) δ: −158.1 (broad). ^{1}H NMR (THF-d8, 500 MHz, 295 K) δ: 7.45 (broad); 7.33 (broad); 4.0 (broad); 3.51 (broad); 2.04 (broad); ^{119}Sn NMR (THF-*d*$_8$, 149.17 MHz, 295 K) δ: −145.6 and −163.5 ppm (broad). ^{1}H NMR (THF-*d*$_8$, 500 MHz, 220 K) δ: 13.5 (broad); 12.3 (broad); 7.41 (broad); 7.36 (broad); 7.27 (broad); 5.02 (broad); 4.77 (broad); 4.11 (broad); 3.21 (broad); 3.03 (broad); 2.85 (broad); 2.55 (broad); ^{119}Sn NMR (THF-*d*$_8$, 149.17 MHz, 220 K) δ: −147.7 and −165.6 ppm ratio 2:3. ESI-MS: molecular weight (MW) = 710; *m*/*z* 693 [L$_3^{NCN}$Sn]$^+$, 100%; *m*/*z* 501 [L$_3^{NCN}$Sn−L^{NCN}H]$^+$, 4%; *m*/*z* 311 [L^{NCN}Sn]$^+$, 10%.

4.2.5. Preparation and isolation of L_3^{CN}SnBr (**5**)

L_4^{CN}Sn (4.65 g, 7.1 mmol) was reacted with anhydrous $SnBr_4$ (1.05 g, 2.4 mmol) in boiling toluene/THF mixture of solvents (75/25 mL) for two days. Afterwards the reaction mixture was filtered and the filtrate was evaporated to dryness *in vacuo*. The residue was treated with diethyl ether (2 × 10 mL per 1 g of the residue) in order to separate the insoluble $L_2^{CN}SnBr_2$. After evaporation of the clear yellowish etheric filtrate to dryness a mixture containing only **5** and L_4^{CN}Sn is obtained. This mixture was consequently treated with chloroform (1 mL of chloroform per 1 g of the mixture) and filtered. Evaporation of the filtrate *in vacuo* gave crude oily **5** which was then crystallized from dichloromethane/hexane mixture (ca 1:20 v/v) in ca. 95% purity. The overall yield usually varies in between 25 and 35% with respect to the starting amount of L_4^{CN}Sn. ^{1}H NMR (THF-d_8, 500.13 MHz, 295 K, ppm): 8.02 (br, 3H, H(6), $^3J(^{119}Sn, ^1H) \approx 65$ Hz); 7.34 (br, 3H, L^{CN}); 7.28 (br, 6H, L^{CN}); 3.61 (br, 6H, NCH_2); 1.85 (br, 18H, $N(CH_3)_2$). ^{119}Sn NMR (THF-d_8, 186.50 MHz, 295 K, ppm): −201.8 (broad). ^{119}Sn NMR (THF-d_8, 186.50 MHz, 263 K, ppm): −122.9, −182.9, and −216.7. ^{119}Sn NMR (THF-d_8, 186.50 MHz, 243 K, ppm): −124.8, −183.6, and −220.3. ^{119}Sn NMR (THF-d_8, 186.50 MHz, 213 K, ppm): −125.7, −185.1, and −221.5. ^{1}H NMR ($CDCl_3$, 500.13 MHz, 295 K, ppm): 7.80 (very broad, 3H, H(6), $^3J(^{119}Sn, ^1H)$ could not be read); 7.40 (br, 9H, L^{CN}); 3.78 (br, 6H, NCH_2); 2.13 (br, 18H, $N(CH_3)_2$). ^{119}Sn NMR ($CDCl_3$, 186.50 MHz, 295 K, ppm): −123.8 (broad). ^{119}Sn NMR ($CDCl_3$, 186.50 MHz, 243 K, ppm): −127.0. ^{119}Sn NMR ($CDCl_3$, 186.50 MHz, 233 K, ppm): −127.5. Elemental analysis was not carried out due to the limited purity of the product.

4.2.6. Crystallization of $[L_3^{CN}Sn(H_2O)]^+Br^-$ (**5a**)

5 (95% purity) was dissolved in wet THF and was left to crystallize in the air. Single crystals of pure **5a** grew on the walls of the glass tube within several days. Mp 65–67 °C. ^{1}H NMR (THF-d_8, 400.13 MHz, 295 K, ppm): 8.06 (br, 3H, H(6), $^3J(^{119}Sn, ^1H) \approx 63$ Hz); 7.37 (br, 3H, L^{CN}); 7.32 (br, 6H, L^{CN}); 3.65 (br, 6H, NCH_2); 1.90 (br, 18H, $N(CH_3)_2$); signal of solvating water molecule was not observed. ^{119}Sn NMR (THF-d_8, 149.17 MHz, 295 K, ppm): −202.0 (broad). ^{1}H NMR ($CDCl_3$, 400.13 MHz, 295 K, ppm): 7.76 (very broad, 3H, H(6), $^3J(^{119}Sn, ^1H)$ could not be read); 7.49 (br, 3H, L^{CN}); 7.41 (m, 6H, L^{CN}); 5.67 (very broad, solvating H_20); 3.83 (br, 6H, NCH_2); 2.23 (br, 18H, $N(CH_3)_2$). ^{119}Sn NMR ($CDCl_3$, 149.17 MHz, 295 K, ppm): −185.0 (broad). Elemental analysis (%): found: C, 52.0; H, 6.6; N, 6.3. Calcd. for $C_{27}H_{38}BrN_3OSn$ (619.22): C, 52.37; H, 6.19; N, 6.79.

4.2.7. Preparation of L_3^{CN}SnF (**5b**)

5 (95%, 240 mg, 0.38 mmol) was reacted with $L^{CN}(n\text{-}Bu)_2SnF$ (146 mg, 0.38 mmol) in THF for two days. Afterwards the reaction mixture was evaporated to dryness and carefully washed with cold pentane (2×3 mL) in order to remove soluble $L^{CN}(n\text{-}Bu)_2SnBr$. Nearly pure **5a** was then isolated as a yellowish oil after evaporation of volatiles *in vacuo*. Yield 158 mg (77%). ^{1}H NMR (THF-d_8, 400.13 MHz, 295 K, ppm): 8.02 (d, 3H, H(6), $^3J(^1H(5), ^1H(6)) = 9.0$ Hz, $^3J(^{119}Sn, ^1H) = 65.7$ Hz); 7.35 (m, 3H, L^{CN}); 7.30 (m, 6H, L^{CN}); 3.62 (s, 6H, NCH_2); 1.96 (s, 18H, $N(CH_3)_2$). ^{19}F NMR (THF-d_8, 376.50 MHz, 295 K, ppm): −196.9 ($^1J(^{119}Sn, ^{19}F) = 2236$ Hz). ^{119}Sn NMR (THF-d_8, 149.17 MHz, 295 K, ppm): −204.9 (broad d, $^1J(^{19}F, ^{119}Sn) = 2251$ Hz). ^{119}Sn NMR ($CDCl_3$, 149.17 MHz, 295 K, ppm): −207.8 (broad d, $^1J(^{19}F, ^{119}Sn) = 2162$ Hz). Elemental analysis was not carried out due to the limited purity of the sample.

4.2.8. Isolation of $[L_2^{CN}L^{CN}(H)SnBr]^+[BrHBr]^-$ (**6**)

6 was isolated in ca. 20% yield when complete workup of **5** was done in the air. Mp >270 °C. Due to the limited solubility of **6** in inert deuterated solvents and therefore of poor quality of recorded ^{1}H NMR spectrum the complete assignment of all signals was not carried out. ^{1}H NMR ($CDCl_3$, 500.13 MHz, 295 K, ppm): 8.38 (d, L^{CN}); 7.73 (m, L^{CN}); 7.53–7.40 (br, L^{CN}); 7.14 (d, L^{CN}); 3.30 (br, NCH_2); 4.22 (br, $N(CH_3)_2$); 2.57(br, $N(CH_3)_2$); 2.35(br, $N(CH_3)_2$); 1.90(br, $N(CH_3)_2$). No signal was observed in the ^{119}Sn NMR spectrum even after recording for one day.

4.2.9. Attempts to prepare compounds of the L_3^{CN}SnX type

By the reaction of **1** (1.7 g, 2.93 mmol) in 15 ml of DMF and 0.24 g (1.47 mmol) of bromine which was added dropwise *via* a syringe, 0.252 g (29% to **1**) of pure 2-$(Me_2NCH_2)C_6H_4Br\cdot HBr$ (**8**) was crystallized and isolated by filtration after an addition of hexanes to the supernatant solution. Mp 177–182 °C. ^{1}H NMR ($CDCl_3$, 500.13 MHz, 295 K, ppm): 11.69 (br, 1H, NH); 8.18 (d, 1H, H(6), $^3J(^1H(5), ^1H(6)) = 7.7$ Hz); 7.66 (d, 1H, H(3), ^3J(H(4), H(3) = 7.7 Hz); 7.49 (dd, 1H, H(4), $^3J = 8.1$ Hz, 8.1 Hz); 7.34 (dd, 1H, H(5), $^3J = 7.8$ Hz, 7.8 Hz); 4.49 (d, 2H, NCH_2, $^3J(^1H(NH), ^1H(NCH_2)) = 5.9$ Hz); 2.86 (d, 6H, $N(CH_3)_2$, $^3J(^1H(NH), ^1H(N(CH_3)_2) = 5.0$ Hz). ESI-MS: molecular weight (MW) = 293; *m*/*z* 214 $[M - Br]^+$, 100%; *m*/*z* 169 $[M-Br-CH_3N(H)CH_3]^+$, 5%. Elemental analysis (%): found: C, 36.9; H, 4.7; N, 4.4. Calcd. for $C_9H_{13}Br_2N$ (295.02): C, 36.64; H, 4.44; N, 4.75.

Nearly all volatiles (ca. 80%) from pale yellow filtrate were removed in high vacuo, unreacted **1** was then removed by centrifugation, and the high vacuo was applied again in order to pump off the rest of the volatiles to give 0.64 g of yellowish oil of $L_2^{CN}Sn(n\text{-}Bu)Br$ (**7**) in 42% yield to **1**. ^{1}H NMR ($CDCl_3$, 500.13 MHz, 295 K, ppm): 7.50 (d, 1H, H(6), $^3J = 7.6$ Hz, $^3J(^{119}Sn, ^1H) = 56.8$ Hz); 7.48 (d, 1H, H(6′), $^3J = 7.2$ Hz, $^3J(^{119}Sn, ^1H) = 56.0$ Hz); 7.30 (m, 1H, H(L^{CN})); 7.22–7.11 (m, 5H, H(L^{CN})); 3.32 (s, 2H, NCH_2); 3.20 (s, 2H, NCH_2'); 1.87 (s, 6H, $N(CH_3)_2$); 1.84 (s, 6H, $N(CH_3)_2'$); 1.43 (m, 2H, H(*n*-Bu)); 1.30 (m, 2H, H(*n*-Bu)); 0.85 (m, 5H, H(*n*-Bu)). ^{119}Sn NMR ($CDCl_3$, 186.50 MHz, 295 K, ppm): −125.3. ESI-MS: molecular weight (MW) = 524; *m*/*z* 525 $[M + H]^+$, 22%; *m*/*z* 445 $[M - Br]^+$, 100%; *m*/*z* 388 $[L_2^{CN}Sn]^{+\bullet}$, 21%. Elemental analysis (%): found: C, 50.6; H, 6.6; N, 5.2. Calcd. for $C_{22}H_{33}BrN_2Sn$ (524.12): C, 50.42; H, 6.35; N, 5.34.

The reaction of **2** (1.00 g, 1.67 mmol, solution in 20 ml of benzene) with I_2 (0.42 g, 1.67 mmol) in 10 ml of benzene yielded after 2 h of reflux a mixture of $L_2^{CN}SnI_2$ [16a], $L^{CN}Ph_2SnI$ [16b] and Ph_4Sn [24b] (as identified by the multinuclear NMR spectroscopy) which was not further separated.

On the other hand, the reaction of **2** (0.50 g, 0.83 mmol) with aqueous HI (57%, 120 μL, $d = 1.70$ g cm^{-3}, 0.91 mmol) in a biphase system (water/benzene) afforded a mixture of $L^{CN}H\cdot HI$ and $L_2^{CN}SnPhI\cdot HI$ (**9**). **9** was isolated by crystallization from the organic phase after separation of both phases. Very complex ^{1}H NMR spectrum was obtained when recorded in $CDCl_3$ and therefore the detailed assignment of signals was not carried out but the presence of the protonated ligand is evident (e.g. the presence of the $CH_2N(H)Me_2$ fragment). Due to the limited solubility of **9** no ^{119}Sn NMR spectra were recorded. Mp 221 °C (dec.). ESI-MS: molecular weight (MW) = 720; *m*/*z* 515 $[L_2^{CN}SnI]^+$, 25%; *m*/*z* 465 $[L_2^{CN}SnPh]^+$, 100%; *m*/*z* 134 $[L^{CN}]^+$, 18%; *m*/*z* 91 $[C_6H_5CH_2]^+$, 12%. Elemental analysis (%): found: C, 40.3; H, 4.5; N, 3.7. Calcd. for $C_{22}H_{33}BrN_2Sn$ (524.12): C, 40.09; H, 4.21; N, 3.90.

Similar reaction of **2** (0.207 g, 0.35 mmol) with aqueous HF (38%, ca. 20 mg, ∼0.40 mmol) in water/benzene biphasic system gave mixture of presumably L_2^{CN}SnPhF [16c] and free ligand L^{CN}H as the by-product which was confirmed by multinucelar NMR spectroscopy.

L_4^{CN}Sn (0.116 g, 0.18 mmol) and $HgCl_2$ (0.048 g, 0.18 mmol) were dissolved in THF and stirred overnight in the air. Afterwards the suspension thus formed was filtered and the filtrate was evaporated to dryness. The multinuclear NMR spectroscopy proved only the presence of $L_2^{CN}SnCl_2$ [16a] and L_2^{CN}Hg [1c] in the sample obtained from the evaporated filtrate. According to ^{119}Sn NMR spectroscopy no desired **5c** was formed and thus the mixture of compounds was not separated.

Similarly, the reaction of $L_4^{CN}Sn$ (0.236 mg, 0.36 mmol) and $HgCl_2$ (0.048 g, 0.18 mmol) in a 2:1 ratio was carried out. In this particular case the formation of desired **5c** was observed together with $L_2^{CN}SnCl_2$ and $L_2^{CN}Hg$ in the reaction mixture. The starting $L_4^{CN}Sn$ was identified as well (only minor assay). Although the target compound was not separated from the reaction mixture the interpretation of the ^{1}H NMR spectrum allowed assignment of all signals corresponding to **5c**. ^{1}H NMR ($CDCl_3$, 400.13 MHz, 295 K, ppm): 7.96 (br, 3H, H(6), $^3J(^{119}Sn,^1H)$ could not be read); 7.51–7.15 (m, 9H, H(L^{CN}); 3.75 (s, 6H, NCH_2); 2.00 (s, 18H, $N(CH_3)_2$). ^{119}Sn NMR ($CDCl_3$, 149.17 MHz, 295 K, ppm): −190.2 (broad). According to ^{1}H and ^{119}Sn NMR spectroscopy the mutual ratio of **5c** to $L_2^{CN}SnCl_2$ is approximately 1:1.

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Appendix A. Supplementary data

CCDC 918470–918476 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.cccdc.cam.ac.uk/data-request/cif.

Supplementary material associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jorganchem.2013.02.018.

References

[1] (a) G. van Koten, A.J. Leusink, J.G. Noltes, Inorg. Nucl. Chem. Lett. 7 (1971) 227–230;
(b) A.J. Leusink, G. van Koten, J.G. Notes, J. Organomet. Chem. 56 (1973) 379–390;
(c) A.F.M.J. van der Ploeg, C.E.M. van der Kolk, G. Van Koten, J. Organomet. Chem. 212 (1981) 283–290;
(d) G. van Koten, J.G. Notes, J. Organomet. Chem. 102 (1975) 551–563;
(e) G. van Koten, J.T.B.H. Jastrzebski, J.G. Noltes, Inorg. Chem. 16 (1977) 1782–1787.

[2] (a) D. Morales-Morales, C.M. Jensen, The Chemistry of Pincer Compounds, first ed., Elsevier Science, 2007;
(b) J.T.B.H. Jastrzebski, G. van Koten, Adv. Organomet. Chem. 35 (1993) 241–294.

[3] N. Auner, R. Probst, F. Hahn, E. Herdtweck, J. Organomet. Chem. 459 (1993) 25–41.

[4] R. Rippstein, G. Kickelbick, U. Schubert, Monatsh. Chem. 130 (1999) 385–399.

[5] A.R. Petrov, K.A. Rufanov, K. Harms, J. Sundermeyer, J. Organomet. Chem. 694 (2009) 1212–1218.

[6] (a) For example for Sc, Y, Ln see: A.L. Wayda, J.L. Atwood, W.E. Hunter Organometallics 3 (1984) 939–941;
A.R. Petrov, O. Thomas, K. Harms, K.A. Rufanov, J. Sundermeyer, J. Organomet. Chem. 695 (2010) 2738–2746;
(b) For example for B, Al, Ga see: C. Boker, M. Noltemeyer, H. Gornitzka, B.O. Kneisel, M. Teichert, R. Herbst-Irmer, A. Meller Main Group Met. Chem. 21 (1998) 565–579;
H. Schumann, T.D. Seuss, H. Hemling, Private Communication to CCDC, 1994;
M. Asakura, M. Oki, S. Toyota, Organometallics 19 (2000) 206–208;
D.K. Coggin, P.E. Fanwick, M.A. Green, Chem. Commun. (1993) 1127–1129;
H. Schumann, T.D. Seuss, O. Just, R. Weimann, H. Hemling, J. Organomet. Chem. 479 (1994) 171–186;
(c) For example for P, As, Sb, Bi see: D. Copolovici, C. Silvestru, R.A. Varga Acta Crystallogr., Sect. C 64 (2008) M37–M39;
S. Kamepalli, C.J. Carmalt, R.D. Culp, A.H. Cowley, R.A. Jones, N.C. Norman, Inorg. Chem. 35 (1996) 6179–6183;
P. Sharma, D. Castillo, N. Rosas, A. Cabrera, E. Gomez, A. Toscano, F. Lara, S. Hernandez, G. Espinosa, J. Organomet. Chem. 689 (2004) 2593–2600;
H.J. Breunig, M.G. Nema, C. Silvestru, A.P. Soran, R.A. Varga, Z. Anorg. Allg. Chem. 636 (2010) 2378–2386;
L.M. Opris, A. Silvestru, C. Silvestru, H.J. Breunig, E. Lork, Dalton Trans. (2003) 4367–4374;
A. Soran, H.J. Breunig, V. Lippolis, M. Arca, C. Silvestru, J. Organomet. Chem. 695 (2010) 850–862;
A. Schulz, A. Villinger, Organometallics 30 (2011) 284–289.

[7] For chelate containing phoshine as a ligand for transition metals: (a) H. Lang, M. Leschke, H.A. Mayer, M. Melter, C. Weber, G. Rheinwald, O. Walter, G. Huttner, Inorg. Chim. Acta 324 (2001) 266–272;
(b) A. Chandrasekaran, N.V. Timosheva, R.O. Day, R.R. Holmes, Inorg. Chem. 41 (2002) 5235–5240;
(c) H. Lang, M. Leschke, M. Melter, B. Walfort, K. Kohler, S.E. Schulz, T. Gessner, Z. Anorg. Allg. Chem. 629 (2003) 2371–2380;
(d) M. Leschke, M. Melter, B. Walfort, A. Driess, G. Huttner, H. Lang, Z. Anorg. Allg. Chem. 630 (2004) 2022–2030;
(e) V.M. Demyanovich, I.N. Shishkina, K.A. Potekhin, E.V. Balashova, Y.T. Struchkov, N.S. Zefirov, Dokl. Akad. Nauk SSSR 360 (1998) 645–648;
(f) M. Leschke, G. Rheinwald, H. Lang, Z. Anorg. Allg. Chem. 628 (2002) 2470–2477;
(g) M.A. Alonso, J.A. Casares, P. Espinet, K. Soulantica, A.G. Orpen, H. Phetmung, Inorg. Chem. 42 (2003) 3856–3864;
(h) Y. Shen, H. Pritzkow, B. Walfort, T. Rueffer, H. Lang, Acta Crystallogr., Sect. E 60 (2004) M91–M93;
(i) M. Leschke, H. Lang, M. Melter, G. Rheinwald, C. Weber, H.A. Mayer, H. Pritzkow, L. Zsolnai, A. Driess, G. Huttner, Z. Anorg. Allg. Chem. 628 (2002) 349–356;
(j) C. Chuit, R.J.P. Corriu, P. Monforte, C. Reye, J.-P. Declercq, A. Dubourg, Angew. Chem., Int. Ed. 32 (1993) 1430–1432;
(k) H. Lang, Y. Shen, T. Rueffer, B. Walfort, Inorg. Chim. Acta 361 (2008) 95–102;
(l) H. Lang, M. Leschke, G. Rheinwald, M. Melter, Inorg. Chem. Commun. 1 (1998) 254–256;
(m) M. Leschke, M. Melter, C. Weber, G. Rheinwald, H. Lang, A. Driess, G. Huttner, Z. Anorg. Allg. Chem. 627 (2001) 1199–1203;
(n) A. Rotar, A. Covaci, A. Pop, A. Silvestru, Rev. Roum. Chim. 55 (2010) 823–829.

[8] F.A. Cotton, G.N. Mott, Organometallics 1 (1982) 38–43.

[9] E. Rijnberg, J.T.B.H. Jastrzebski, J. Boersma, H. Kooijman, N. Veldman, A.L. Spek, G. van Koten, Organometallics 16 (1997) 2239–2245.

[10] C. Breliere, F. Carre, R.J.P. Corriu, G. Royo, Organometallics 7 (1988) 1006–1008.

[11] C. Breliere, F. Carre, R.J.P. Corriu, G. Royo, M.W.C. Man, Organometallics 13 (1994) 307–314.

[12] (a) H. Kooijman, A.L. Spek, G. van Koten, Private Communication to CCDC, 2007;
(b) H. Kooijman, A.L. Spek, M.E. Bruin, J.T.B.H. Jastrzebski, G. van Koten, Private Communication to CCDC, 2007.

[13] (a) G. van Koten, C.A. Schaap, J.G. Noltes, J. Organomet. Chem. 99 (1975) 157–170;
(b) G. van Koten, J.G. Noltes, J. Am. Chem. Soc. 98 (1976) 5393–5395;
(c) G. van Koten, J.T.B.H. Jastrzebski, J.G. Noltes, J. Organomet. Chem. 177 (1979) 283–292.

[14] (a) A. Růžička, V. Pejchal, J. Holeček, A. Lyčka, K. Jacob, Collect. Czech. Chem. Commun. 63 (1998) 977–989;
(b) M. Biesemans, J.C. Martins, R. Willem, A. Lyčka, A. Růžička, J. Holeček, Magn. Reson. Chem. 40 (2002) 65–69.

[15] (a) P. Švec, Z. Padělková, Z. Černošek, F. De Proft, A. Růžička, J. Organomet. Chem. 693 (2008) 2937–2941;
(b) Z. Padělková, A. Havlík, P. Švec, M.S. Nechaev, A. Růžička, J. Organomet. Chem. 695 (2010) 2651–2657;
(c) P. Švec, Z. Padělková, P. Štěpnička, A. Růžička, J. Holeček, J. Organomet. Chem. 696 (2011) 1809–1816;
(d) R.A. Varga, M. Schuermann, C. Silvestru, J. Organomet. Chem. 623 (2001) 161–167;
(e) R.A. Varga, K. Jurkschat, C. Silvestru, Eur. J. Inorg. Chem. (2008) 708–716;
(f) P. Novák, Z. Padělková, I. Císařová, L. Kolářová, A. Růžička, J. Holeček, Appl. Organomet. Chem. 20 (2006) 226–232;
(g) A. Růžička, R. Jambor, J. Brus, I. Císařová, J. Holeček, Inorg. Chim. Acta 323 (2001) 163–170.

[16] (a) P. Novák, Z. Padělková, L. Kolářová, I. Císařová, A. Růžička, J. Holeček, Appl. Organomet. Chem. 19 (2005) 1101–1108;
(b) R.A. Varga, A. Rotar, M. Schuermann, K. Jurkschat, C. Silvestru, Eur. J. Inorg. Chem. (2006) 1475–1486;
(c) P. Novák, J. Brus, I. Císařová, A. Růžička, J. Holeček, J. Fluorine Chem. 126 (2005) 1531–1538.

[17] (a) Z. Padělková, T. Weidlich, L. Kolářová, A. Eisner, I. Císařová, T.A. Zevaco, A. Růžička, J. Organomet. Chem. 692 (2007) 5633–5645;
(b) T. Weidlich, L. Dušek, B. Vystrčilová, A. Eisner, P. Švec, A. Růžička, Appl. Organomet. Chem. 26 (2012) 293–300.

[18] (a) P. Švec, P. Novák, M. Nádvorník, Z. Padělková, I. Císařová, A. Růžička, J. Holeček, J. Fluorine Chem. 128 (2007) 1390–1395;
(b) P. Švec, A. Eisner, L. Kolářová, T. Weidlich, V. Pejchal, A. Růžička, Tetrahedron Lett. 49 (2008) 6320–6323.

[19] S. Chandra, A. Růžička, P. Švec, H. Lang, Anal. Chim. Acta 577 (2006) 91–97.

[20] (a) A. Růžička, L. Dostál, R. Jambor, V. Buchta, J. Brus, I. Císařová, M. Holčapek, J. Holeček, Appl. Organomet. Chem. 16 (2002) 315–322.

[21] (a) P. Švec, Z. Padělková, A. Růžička, T. Weidlich, L. Dušek, L. Plasseraud, J. Organomet. Chem. 696 (2011) 676–686;
(b) P. Švec, R. Olejník, Z. Padělková, A. Růžička, L. Plasseraud, J. Organomet. Chem. 708 (2012) 82–87.

[22] (a) J. Holeček, M. Nádvorník, K. Handlíř, A. Lyčka, J. Organomet. Chem. 241 (1983) 177–184;
(b) T.P. Lockhart, W.F. Manders, E.M. Holts, J. Am. Chem. Soc. 108 (1986) 6611–6616.

[23] (a) H. Reuter, H. Puff, J. Organomet. Chem. 379 (1989) 223–234;
(b) H.K. Sharma, F. Cervantes-Lee, J.S. Mahmoud, K.H. Pannell, Organometallics 18 (1999) 399–403.
[24] (a) A.G. Davies, Organotin Chemistry, second ed., Wiley-VCH, Weinheim, 2004. (Chapter 12) pp. 179–202;
(b) A.G. Davies, Organotin Chemistry, second ed., Wiley-VCH, Weinheim, 2004. (Chapter 2) pp. 14–30.
[25] (a) N. Kasai, Y. Yasuda, R. Okawara, J. Organomet. Chem. 3 (1965) 172–173;
(b) A.G. Davies, S.D. Slater, Silicon, Germanium, Tin, and Lead Compounds 9 (1986) 87;
(c) C. Glidewell, D.C. Liles, Acta Crystallogr., Sect. B 34 (1978) 129–134;
(d) C. Glidewell, J.N. Low, J.A.S. Bomfim, C.A.L. Filgueiras, J.L. Wardell, Acta Crystallogr., Sect. C 58 (2002) M199–M201.
[26] (a) M. Newcomb, Y. Azuma, A.R. Courtney, Organometallics 2 (1983) 175–177;
(b) Y. Azuma, M. Newcomb, Organometallics 3 (1984) 9–14;
(c) A.N. Kashin, N.B. Ivashchenko, I.P. Beletskaya, O.A. Reutov, Metalloorg. Khim. 2 (1989) 541–547.
[27] (a) M. Gielen, K. Jurkschat, J. Organomet. Chem. 273 (1984) 303–312;
(b) R.H. Fish, B.M. Broline, J. Organomet. Chem. 159 (1978) 255–278;
(c) I. Wharf, M.G. Simard, J. Organomet. Chem. 532 (1997) 1–9.
[28] P. Švec, E. Černošková, Z. Padělková, A. Růžička, J. Holeček, J. Organomet. Chem. 695 (2010) 2475–2485.
[29] (a) K.A. Kocheshkov, Chem. Ber. 62 (1929) 996–999;
(b) K.A. Kocheshkov, Chem. Ber. 66 (1933) 1661–1665.
[30] J. Bareš, P. Novák, M. Nádvorník, R. Jambor, T. Lébl, I. Císařová, A. Růžička, J. Holeček, Organometallics 23 (2004) 2967–2971.
[31] A. Růžička, R. Jambor, I. Císařová, J. Holeček, Chem.—Eur. J. 9 (2003) 2411–2418.
[32] R. Jambor, I. Císařová, A. Růžička, J. Holeček, Acta Crystallogr., Sect. C 57 (2001) 373–374.
[33] Z. Otwinowski, W. Minor, Methods Enzymol. 276 (1997) 307–326.
[34] P. Coppens, in: F.R. Ahmed (Ed.), Crystallographic Computing, Munksgaard, Copenhagen, 1970, pp. 255–270.
[35] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, J. Appl. Crystallogr. 26 (1993) 343–350.
[36] G.M. Sheldrick, SHELXL-97, A Program for Crystal Structure Refinement, University of Göttingen, Göttingen, 1997.
[37] A.L. Spek, Acta Crystalllogr., Sect. C A46 (1990) 194–201.
[38] (a) F.N. Jones, M.F. Zinn, C.R. Hauser, J. Org. Chem. 28 (1963) 663–665;
(b) G. van Koten, J.T.B.H. Jastrzebski, J.G. Noltes, J. Organomet. Chem. 148 (1978) 233–245.