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Structural study of C,N-chelated monoorganotin(IV) halides

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Three monoorganotin(IV) compounds of general formula $L^{CN}SnX_3$, where L^{CN} is a 2-(dimethylaminomethyl)phenyl- group and X = Cl (1), Br (2) and I (3), were prepared and characterized using XRD and NMR techniques. Compound 1 reacts with moisture producing $[(L^{CN})_2HSnCl_2]^+[L^{CN}SnCl_4]^-$. Compound 3 decomposes to $(L^{CN})_2SnI_2$, SnI_2 and I_2 when heated. Compound 2 was reacted with NH_4F yielding an equilibrium of fluorine-containing species. The major products were $[L^{CN}SnF_5]^{2-}$ and $[(L^{CN}SnF_3)_2(\mu^2\text{-}F)_2]^{2-}$ (4a). When compound 2 was reacted with another fluorinating agent, $L^{CN}(n\text{-Bu})_2SnF$, an oligomeric product, $[L^{CN}SnF_2(\mu^2\text{-}F)_2]_n$, was observed. Further addition of NH_4F led to subsequent formation of 4a. The structure of fluorinated products was investigated by ^1H, ^{19}F and ^{119}Sn NMR spectroscopy. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: monoorganotin(IV); halides; N-ligand; structure

INTRODUCTION

The family of monoorganotin(IV) compounds reveals interesting structural properties[1] and potential use.[2–7] The simple alkyl halides, such as $MeSnCl_3$, are tetrahedral in the gas phase,[8] and in the crystal $MeSnCl_3$[9] and $MeSnBr_3$[10] are essentially isostructural, with near-tetrahedral molecules very weakly bridged through two of the three halogen atoms, as shown in Scheme 1(a). In $MeSnI_3$ the discrete tetrahedral molecules show no significant interaction.[11]

Although the first papers from the area of hypercoordinated organotin compounds can be found in the 1970s,[12] the monoorganotin halides with tin coordination number higher than 4 are rather rare.[13–23] To the best of our knowledge, there is only one paper dealing with synthesis and structure of a monomeric monoorganotin(IV) trifluoride, $[(2,6\text{-OMe})_2C_6H_3]_3CSnF_3$.[24] The tin atom in this compound is seven-coordinated and described by the authors as a distorted monocapped-trigonal-antiprism with Sn–F bond lengths from 1.948(7) to 1.975(6) Å and $^1J(^{119}Sn, ^{19}F)$ being 3390 Hz in chloroform solution. A limited number of structurally related zwitterionic organostannates has been reported.[25] Two monoorganotin(IV) compounds (**1, 2**) containing the 2-(dimethylaminomethyl)phenyl- group [L^{CN}, Scheme 1(b)] have been reported and NMR-characterized by our group recently,[26,27] but only limited attention has been paid to their preparation, solid-state structure and reactivity. During the course of this work a paper on the synthesis, NMR-characterization in solution as well as the crystal and molecular structures of $L^{CN}SnCl_3$ (**1**) and its DMSO adduct appeared.[28]

In this paper we report a solid-state study of $L^{CN}SnX_3$ [X = Cl (**1**), Br (**2**), I (**3**)] and their reactivity towards moisture and some fluorinating agents (Fig. 1) in order to prepare a defined monoorganotin fluoride derivative that is potentially useful for fluorination of organic compounds similarly to Gingras' salt.[29,30]

Dedicated to Assoc. Prof. Milan Nádvorník on the occassion of his 60th birthday.

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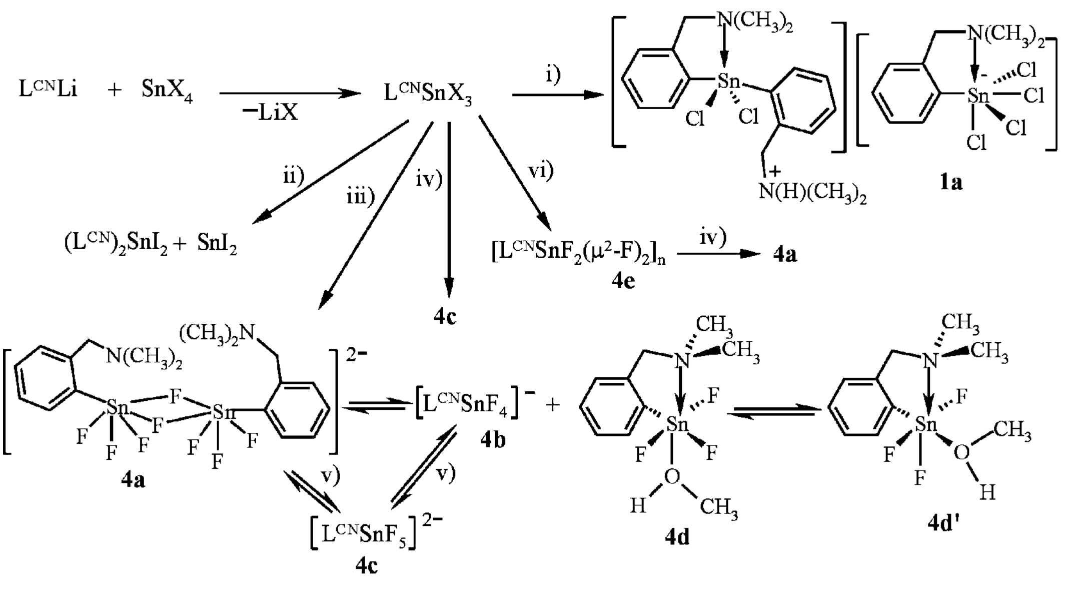
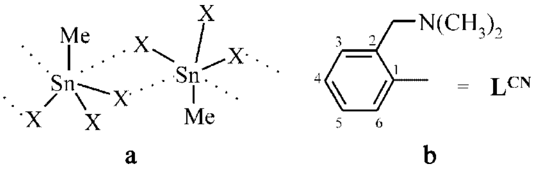


Figure 1. Studied compounds, their reactivity and proposed structures of products; X = Cl (**1**), Br (**2**), I (**3**); (i) X = Cl, air, moisture; (ii) X = I, toluene, 100 °C; (iii) X = Br, 3 equiv. NH_4F, methanol; (iv) X = Br, 3 equiv. of L^{CN} (*n* -Bu)$_2$ SnF (**5**); (v) NH_4F, methanol; (vi) 3 equiv. **5**.



Scheme 1.

RESULTS AND DISCUSSION

Compounds **1**–**3** were prepared by conversion of $L^{CN}Li$ with one molar equivalent of tin(IV) halide in relatively low yield. Such a low yield is typical for monoorganotin compounds[31] and in this specific case is probably caused by high Lewis acidity of tin atom, and thus the formation of a stannate species as unidentified by-product. The $L^{CN}I$ was detected in crude product of **3** using NMR and ESI/MS. The purity of the compounds was checked by multinuclear NMR, ESI-MS and elemental analysis. Compounds **2** and **3** are relatively stable to air and moisture and no decomposition or hydrolysis was observed after a long exposure of compounds on a watch glass under laboratory conditions. On the other hand, when **1** was slowly crystallized from a hexane–dichloromethane mixture in air, only single crystals of **1a** and SnO_2 powder were obtained. The ^{1}H and ^{119}Sn NMR of **1a** revealed the patterns and shifts very close to a 1 : 1 mixture of **1** and $(L^{CN})_2SnCl_2$,[32] but the signals were much broader and also the values of $^3J(^{119}Sn, ^1H)$ were significantly smaller. This led us to the conclusion that **1a** exists in solution in air and the presence of a moisture in an equilibrium of **1**, $(L^{CN})_2SnCl_2$ and $SnCl_4$ (as a products of phenyl group migration),[32,33] producing with moisture SnO_2 and HCl, and crystallizing as described below (Fig. 4). A similar process of phenyl group migration was observed when **3** was heated in toluene solution to 100 °C under *vacuo* for 1 min. It decomposes quantitatively to diorganotin compound $(L^{CN})_2SnI_2$[32] SnI_2 and I_2.

In ESI/MS spectra of **1**–**3** in acetonitrile solution, no molecular peaks were observed except for spectra for **2**. On the other hand, the typical ions found for all compounds are $[(L^{CN})_2SnX_2 + H]^+$ in the positive-ion and $[L^{CN}SnX_4]^-$ in the negative-ion mode. Analogous ions were found in the case of monoorganotin(IV) compounds containing O,C,O-chelating ligands,[22] and they are probably the products of a reaction of compounds with water molecule in an ion trap. This finding is supported by the fact that the spectra measured from single crystal of **1a** are identical to those of analytically pure **1**. There was no significant change in spectra patterns when dried acetonitrile was used.

The most significant parameters of NMR spectra of **1**–**3** in non-coordinating solvents like chloroform and toluene are $\delta(^{119}Sn)$ and $^3J[^{119}Sn, ^1H(6)]$. The lower ^{119}Sn chemical shifts found for the set **1**–**3** [−227.4, −408 (broad), and −944.4 ppm] in comparison to phenyl compounds $PhSnX_3$ (−61.3, −227.2 and −699.9 ppm)[34] reflect relatively strong intramolecular Sn–N connection and thus the pentacoordinated tin atom. This is supported by value of ^{119}Sn chemical shift for $PhSnCl_3$ measured in DMSO (−509.2 ppm),[34] which can be regarded as a 1 : 2 adduct with solvent, and thus the coordination number of tin atom is 6. The coupling constant in the set of **1**–**3** (132.0, 128.6 and 126.2 Hz) gives evidence on the decrease in Lewis acidity of tin atom with respect to electronegativity of X.

Compound **2** as the most stable and easily prepared compound from the studied set was treated with two different fluorinating agents in order to obtain a defined organotin fluoride. First, we mixed **2** with three molar equivalents of dried NH_4F in dichloromethane and the mixture was stirred for several days. In this mixture, four different species were observed. Based on our previous study[35] and ^{119}Sn and ^{19}F NMR spectra of the mixture, we identified two of the compounds as **4a** (for proposed structures see Fig. 1), i.e. a dinuclear species consistent with two 6-coordinated tin atoms bridged by two fluoride atoms; the coordination sphere of tin is completed by three terminal fluoride atoms and one carbon atom originating from the ligand [$\delta(^{119}Sn) = -605.5$ ppm (d of d of t); $^1J(^{119}Sn, {}^{19}F) = 2628$ and 1470 Hz], and **4c** [$\delta(^{119}Sn) = -685.0$ ppm (d of quintets); $^1J(^{119}Sn, {}^{19}F) = 2530$ and 1165 Hz]. The structure of **4c** was suggested to be identical to the complex $[L^{CN}SnF_5]^{2-}$ reported recently by us[35] and similar to complex $[PhSnF_5]^{2-}$ reported earlier by Dakternieks and Zhu.[33] On each tin *pseudo*-octahedral centre, there are one carbon and five terminal fluorine atoms, four in equatorial and one in axial positions. The logical step going from dinuclear **4a** to monomeric **4c**, complex $[L^{CN}SnF_4]^-$ (**4b**), with a presumably strong intramolecular $N \rightarrow Sn$ interaction and hence a 6-coordinated tin central atom, was unfortunately not observed in the reaction mixture. The very minor species observed in the mixture can be identified as **4d** [$\delta(^{119}Sn) = -561.4$ (d of t); $^1J(^{119}Sn, {}^{19}F) = 2670$ and 2676 Hz] and its isomer **4d′** [$\delta(^{119}Sn) = -556.0$ (d of t); $^1J(^{119}Sn, {}^{19}F) = 2673$ and 2650 Hz] similarly to suggestion of Varga *et al.*[28] with coordinated methanol as a solvent. When an excess of NH_4F (~20 equiv.) is mixed together with **2** overnight, complex $[L^{CN}SnF_5]^{2-}$ (**4c**) is observed by the NMR techniques as the major product, the minor impurities being assigned to **4a**.

Secondly, **2** was treated with one to three equivalents of $L^{CN}(n\text{-}Bu)_2SnF$ (**5**)[35,36] reported previously as a fluorinating agent. After all reactions, a nearly theoretical amount of $L^{CN}(n\text{-}Bu)_2SnBr$[26] (**6**), as the product of fluorine for bromine atom metathetical exchange, was identified as the toluene-only soluble product, which indicates a high conversion of **2** to a fluoride-containing species. In the case of a toluene-washed product (**4e**) of reaction of **2** with three equivalents of **5**, the CP/MAS NMR and ESI/MS spectra were measured. An oligomeric structure can be deduced of all the indicia: (i) positive-ion ESI/MS spectra where the highest observable tin-containing isotopic cluster was m/z 1216, which is close to the molecular weight of a tetramer, MW = 1244, and in negative-ion ESI/MS spectra the main signal m/z 330 corresponded to $[L^{CN}SnF_4]^-$; (ii) species insoluble in common organic solvents and water; and (iii) relatively high melting point in comparison to **1**–**3**. In order to explore the possibility of further complexation of fluoride ion, an excess of NH_4F in methanol was added to **4e** in an NMR tube. Based on ^1H, ^{19}F and ^{119}Sn NMR spectra parameters, the major species in solution was identified as **4a**. The rest of the very minor signals in NMR spectra belong to the same complexes as depicted in Fig. 1 (**4d** and **4e**).

Table 1. Selected structural parameters [distances (Å) and angles (deg)] for **1**–**3**

Compound/parameter	**1** (X = Cl)	**2** (X = Br)	**3** (X = I)
Sn1–C1	2.104(2)	2.128(3)	2.136(4)
Sn1–X1	2.3497(6)	2.4864(4)	2.7030(4)
Sn1–X2	2.3848(6)	2.5760(4)	2.8183(4)
Sn1–X3	2.3334(6)	2.4826(4)	2.6984(4)
Sn1–N1	2.380(2)	2.402(3)	2.436(4)
C1–Sn1–N1	77.11(9)	76.96(11)	75.95(15)
C1–Sn1–X1	134.57(7)	135.66(9)	135.38(11)
C1–Sn1–X2	101.16(7)	98.83(9)	98.75(11)
C1–Sn1–X3	114.30(7)	112.26(9)	110.57(11)
N1–Sn1–X1	86.14(6)	87.49(7)	87.89(9)
N1–Sn1–X2	175.00(6)	173.29(7)	172.79(9)
N1–Sn1–X3	88.67(6)	89.27(7)	89.73(9)
X3–Sn1–X1	107.08(3)	108.720(15)	110.641(13)
X3–Sn1–X2	96.31(3)	97.202(14)	96.774(12)
X1–Sn1–X2	91.90(2)	92.078(15)	92.693(12)

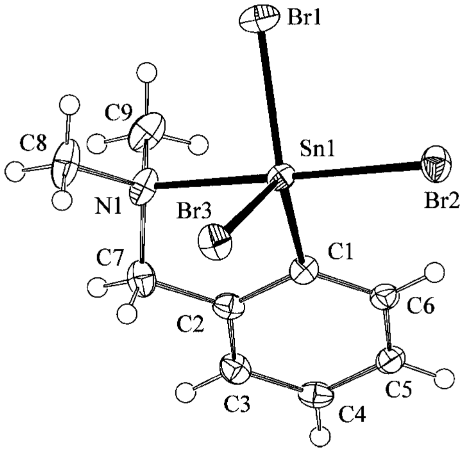


Figure 2. Molecular structure of **2**, ORTEP drawing 50% probability level.

Structural study

The coordination vicinity of central tin atom in each of **1**–**3** is distorted trigonal bipyramidal (Table 1; Fig. 2 shows an example of **2**; **1** and **3** are isostructural to **2**). The major differences are caused by different electronegativities and sizes of present halogen atoms. The Sn1–N1 and Sn1–C1 separations are slightly elongated in **3** compared with **1**. Rather similar distances can be found for each pair of equatorial Sn–X1 and Sn–X3 bonds. On the other hand, the corresponding distance for X2, which is situated *trans* to coordinated nitrogen atom, is distinct from the others in the case of iodide or bromide, respectively, and is rather comparable for chloride **1**. The nitrogen donor atoms deviate from the plane defined by the phenyl ring of the ligand from 41.61° for **1** to 43.91° for **3**; no simple explanation of this behaviour can be found as the position of nitrogen is probably affected not only by the coordination sphere of Sn, but also by intramolecular contacts X1$\cdots$H–C(9), with different strengths for **1–3** [Cl(1)$\cdots$C(9) 3.339(3) Å, Br(1)$\cdots$C(9) 3.457(3) Å, I(1)$\cdots$C(9) 3.629(5) Å, sum van der Waal's radii 3.45, 3.55, 3.68 Å for **1,2,3** respectively].

The solid-state packing of crystals under study is generally molecular, with weak C–H$\cdots$X intermolecular interactions just below the sum of van der Waal's radii (Fig. 3, thinner dashed lines). From this, crystal **1** is exceptional as the important contact is a formation of dimer by the interaction Sn–Cl$\cdots$Sn. (Fig. 3, wider dashed lines). Its prominent role is revealed by comparison of two structure determinations of **1**, one at room temperature, which has been published during the course of this work,[28] and second at 150 K, which is presented in this paper (for changes of structural parameters with temperature see Asadi *et al.*[37]). At room temperature the Cl$\cdots$Sn intermolecular distance [3.944(1) Å] is also bordering the van der Waal's sum (4.01 Å) and was disregarded as the authors emphasized the formation of the supramolecular arrangement via several week inter- and intra-molecular hydrogen-bonds to a two-dimensional framework. At 150 K the Cl$\cdots$Sn becomes significantly shorter [Sn–Cl1^{i} = 3.8596(7) Å], whereas the hydrogen distances are almost preserved. The usefulness of description of geometry of **1** as a two chlorine atoms-bridged dimer (similar to Scheme 1, Fig. 3) is further supported by chemical behaviour of **1** in comparison to **2** and **3**. The concept of a dimer of **1** allows its instability towards the moisture to be explained, as well as the proposed mechanism of this decomposition. This arrangement does not take place at either **2** or **3**, where Sn atoms are not involved in intermolecular contacts and crystal packing appears to be molecular, with hardly any intermolecular distances shorter than the sum of van der Waal's radii.

The molecular structure of **1a** is ionic (Fig. 4); the cationic one can be described as $(L^{CN})_2SnCl_2$, protonated on one of nitrogen donor atoms, and the anionic complex as $L^{CN}SnCl_4$. From the comparison of the cationic part of **1a** with $(L^{CN})_2SnCl_2$[32] it is seen that the tin atom is a distorted trigonal bipyramid, a geometry defined by two carbon (C1′ and C10′) and one chloride atoms (Cl1′) in equatorial, and one chloride (Cl2′) and nitrogen (N1′) donor atoms in axial positions. The protonated nitrogen donor group remains non-coordinated. The anion features a distorted octahedral tin atom. All Sn1–Cl and Sn1–N bond distances are elongated in comparison to **1** (see Table 1, Fig. 4).

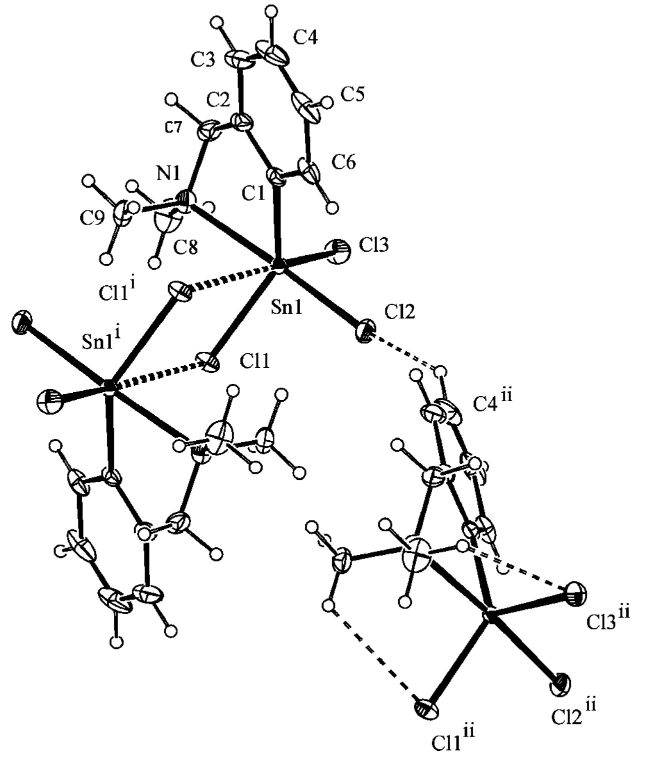


Figure 3. Hydrogen bonding (dashed lines) and short contacts Sn–Cl^{i} (wider dashed lines) in **1**. ORTEP drawing 30% probability level. Symmetry code: (i) $-x$, $-y$, $1-z$; (ii) x, $-0.5-y$, $-0.5+z$.

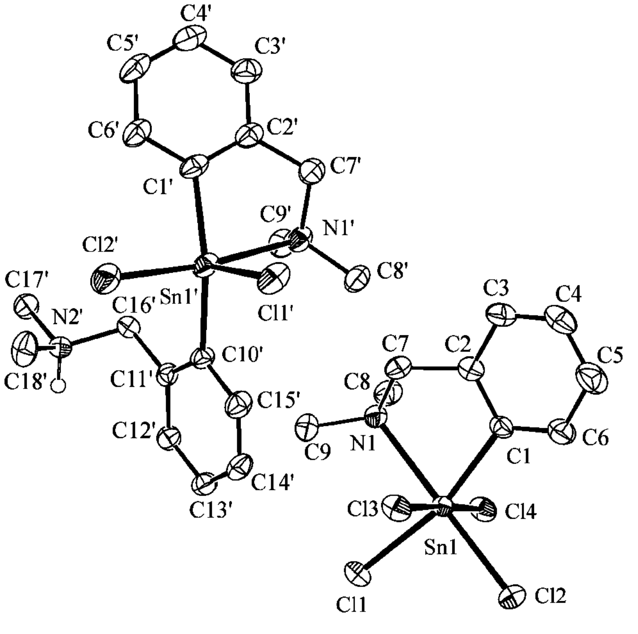


Figure 4. Molecular structure of **1a**; hydrogen atoms and the residual disordered $N(CH_3)_2$ group are omitted for clarity. ORTEP drawing 50% probability level. Selected structural parameters [distances (Å) and angles (deg)]: Sn1–C1, 2.142(3); Sn1–Cl1, 2.4004(6); Sn1–Cl2, 2.4356(6); Sn1–Cl3, 2.4669(7); Sn1–Cl4, 2.5630(6); Sn1–N1, 2.412(2); Cl2–Sn1–N1, 177.41(6); Sn1′–C1′, 2.129(3); Sn1′–C10′, 2.148(2); Sn1′–Cl2′, 2.4577(8); Sn1′–Cl1′, 2.3662(7); Sn1–N1′, 2.414(2); Cl2′–Sn1′–N1′, 173.34(5).

EXPERIMENTAL SECTION

General remarks

All experiments were carried out in an argon atmosphere. (*N*,*N*-dimethylaminomethyl)benzene, *n*-butyllithium, tin(IV) chloride, bromide and iodide, and ammonium fluoride (dried *in vacuo*) were obtained from Sigma-Aldrich. Toluene, benzene, *n*-hexane and *n*-pentane were dried over and distilled from sodium/potassium alloy, degassed and stored over a potassium mirror. Chloroform and dichloromethane were dried over and distilled from P_2O_5 and CaH_2. Compounds **2** ({2-[(*N*,*N*-dimethylaminomethyl)phenyl]}tin tribromide, MW = 491; positive-ion ESI-MS: *m*/*z* 547, $[(L^{CN})_2SnBr_2 + H]^+$, 10%; *m*/*z* 492, $[M + H]^+$, 64%; *m*/*z* 467, $[(L^{CN})_2SnBr]^+$, 16%; *m*/*z* 412, $[M - Br]^+$, 100%; *m*/*z* 350, $[L^{CN}Br + H + HL^{CN}]^+$, 10%; *m*/*z* 214, $[L^{CN}Br + H]^+$, 65%; *m*/*z* 169, $[L^{CN}Br - CH_3NHCH_3 + H]^+$, 46%; *m*/*z* 136, $[HL^{CN} + H]^+$, 79%; *m*/*z* 91, $[C_6H_5CH_2]^+$, 21%; negative-ion ESI-MS: *m*/*z* 570, $[M + Br]^-$, 100%; *m*/*z* 508–510, 9%).[26] in 68% yield and **5** ({2-[(*N*,*N*-dimethylaminomethyl)phenyl]}di(*n*-butyl)tin fluoride)[35,36] were prepared using published methods.

*{2-[(N,N-dimethylaminomethyl)phenyl]}tin(IV) trichloride (1) and complex, **1a***

This compound was prepared by similar procedure as described in Varga *et al.*[28] Yield: 0.35 g (25%). M.p. = 102–104 °C. MW = 359. Positive-ion ESI-MS: *m*/*z* 594, $[(L^{CN})_2SnCl_2 + H + HL^{CN}]^+$, 3%; *m*/*z* 459, $[(L^{CN})_2SnCl_2 + H]^+$, 84%; *m*/*z* 423, $[(L^{CN})_2SnCl]^+$, 31%; *m*/*z* 136, $[HL^{CN} + H]^+$, 100%; *m*/*z* 91, $[C_6H_5CH_2]^+$, 24%. Negative-ion ESI-MS: *m*/*z* 485, 4%; *m*/*z* 394, $[M + Cl]^-$, 100%; *m*/*z* 299, 4%. Elemental analysis (%): found: C, 30.14; H, 3.39; N, 3.88; calcd for $C_9H_{12}Cl_3NSn$ (359.25): C, 30.09; H, 3.37; N, 3.9. The analytically pure **1** was crystallized by vapour diffusion of heptane into chloroform solution on air in order to make single crystals. Small amounts of SnO_2 and single crystals of **1a** were obtained. This attempt was reproduced three times with the same result. ESI/MS spectra were the same as for **1**. ^1H NMR for **1a** ($CDCl_3$, 300 K, ppm): 8.24 [br s, 2H, H(6′)], $^3J(^{119}Sn, ^1H) = 130$ Hz; 8.12 [br s, 1H, H(6)]; $^3J(^{119}Sn, ^1H) = 102$ Hz, 7.46 [br m, 8H, H(4, 5, 4′, 5′)]; 7.19 [br m, 4H, H(3, 3′)]; 4.14 and 3.40 (AX pattern, 4H, N′CH_2); 3.84 (s, 2H, NCH_2); 2.62 [s, 6H, $N(CH_3)_2$]; 2.18 [br s, 12H, N′ $(CH_3)_2$]. $^{119}Sn\{^1H\}$ NMR ($CDCl_3$, 300 K, ppm, broad): −252.8.

*{2-[(N,N-dimethylaminomethyl)phenyl]}tin(IV) triiodide (**3**)*

As for **1**, to a solution of 1.385 g of SnI_4 (2.2 mmol) in 20 ml of benzene was dropwise added 0.31 g of $(L^{CN})Li$ (2.2 mmol) in 30 ml benzene. The pure pale yellow product was obtained by recrystallization from a mixture of dichloromethane and pentane. Yield: 0.53 g (38%); m.p.: 172–174 °C. NMR (toluene-d_8, 300 K, ppm): 7.98 [d, 1H, H(6)], $^3J[^1H(5), ^1H(6)] = 7.2$ Hz, $^3J(^{119}Sn, ^1H) = 126.2$ Hz; 7.00 [m, 2H, H(4,5)]; 6.41 [d, 1H, H(3)], $^3J[^1H(4), ^1H(3)] = 7.2$ Hz, $^3J(^{119}Sn, ^1H) = 50.7$ Hz; 2.93 (s, 2H, NCH_2); 1.74 [s, 6H, $N(CH_3)_2$]; $^{119}Sn\{^1H\}$ NMR (toluene-d_8, 300K, ppm): −944.38. MW = 635. Positive-ion ESI-MS: *m*/*z* 650, $[2^*L^{CN}I + H + HI]^+$, 3%; *m*/*z* 643, $[(L^{CN})_2SnI_2 + H]^+$, 3%; *m*/*z* 515, $[(L^{CN})_2SnI]^+$, 4%; *m*/*z* 262, $[L^{CN}I + H]^+$, 100%; *m*/*z* 217, $[L^{CN}I + H - CH_3NHCH_3]^+$, 46%. Negative-ion ESI-MS: *m*/*z* 762, $[M + I]^-$, 3%; *m*/*z* 381, $[I_3]^-$, 100%; *m*/*z* 127, $[I]^-$, 15%. Elemental analysis (%): found: C, 16.87; H, 1.98; N, 2.19, calcd for $C_9H_{12}I_3NSn$ (633.61): C, 17.06; H, 1.91; N, 2.21.

Fluoride derivates of 2

Fluoride derivatives were prepared by methods shown in Fig. 1.

To a solution of **2** (200 mg, 0.4 mmol) in dichloromethane three molar equivalents of in high *vacuo*-dried NH_4F were added and the reaction mixture was stirred for 5 days, then the solvent was removed *in vacuo*. A remaining crude solid was dissolved in methanol-d_4. ^1H NMR (CD_3OD, 300 K, ppm): 7.67 (bs), 7.36 (bs), 7.22 (bs), 3.85 (bs), 2.64 (bs). $^{19}F\{^1H\}$ NMR (methanol-d_4, 300 K, ppm): −124.6 (bs), −127.5 (bs), −136.0 (s); $^1J(^{19}F, ^{119}Sn) = 2560$ Hz, −138.8 (s); $^1J(^{19}F, ^{119}Sn) = 1100$ Hz, −144.3 (bs), −153.9 (bs), −162.0 (bs). $^{119}Sn\{^1H\}$ NMR (methanol-d_4, 300 K, ppm): −556.0 (d of t); $^1J(^{119}Sn, ^{19}F) = 2673$ and 2650 Hz, −561.4 (d of t); $^1J(^{119}Sn, ^{19}F) = 2670$ and 2676 Hz, −605.5 (d of d of t); $^1J(^{119}Sn, ^{19}F) = 2628$ and 1470 Hz, −685.0 (d of quintets); $^1J(^{119}Sn, ^{19}F) = 2530$ and 1165 Hz.

To a solution of **2** (200 mg, 0.4 mmol) in dichloromethane, 20 molar equivalents of in high *vacuo*-dried NH_4F were added and the reaction mixture was stirred overnight, then the solvent was removed *in vacuo*. A remaining crude solid was dissolved in methanol-d_4. ^1H NMR (CD_3OD, 300 K, ppm): 7.87 (bs), 7.40 (bs), 4.51 (s), 3.83 (bs), 2.85 (s), 2.63 (bs). $^{19}F\{^1H\}$ NMR (methanol-d_4, 300 K, ppm): −136.8 (s); $^1J(^{19}F, ^{119}Sn) = 2518$ Hz, −140.2 (s); $^1J(^{19}F, ^{119}Sn) = 1156$ Hz, −145.8 (bs), −154.9 (bs), −164.0 (bs). $^{119}Sn\{^1H\}$ NMR (methanol-d_4, 300 K, ppm): −606.7 (d of d of t); $^1J(^{119}Sn, ^{19}F) = 2618$ and 1476 Hz, −686.3 (d of q); $^1J(^{119}Sn, ^{19}F) = 2520$ and 1169 Hz.

To a toluene solution of **2** (100 mg, 0.2 mmol) was added **5** (235 mg, 0.61 mmol) and the reaction mixture was stirred and heated at 80 °C for 2 days. Afterwards toluene was removed by filtration and a remaining insoluble solid was washed twice with toluene in order to remove **6**. The toluene extract was evaporated to dryness and a residue was subsequently identified by NMR as pure **6**.[26] The insoluble part was suspended in methanol-d_4 and an excess of NH_4F added. M.p.: 165–168 °C. ^1H NMR (CD_3OD, 300 K, ppm): 7.7 (bs), 7.55 (bs), 7.32 (m), 7.15 (m), 3.81 (bs), 3.66 (bs), 2.93 (bs), 2.7 (bs), 2.32 (bs). ^{19}F NMR (methanol-d_4, 300 K, ppm): −139.9 (s), −148.2 (bs), −158.6 (bs), −163.4(s); $^1J(^{19}F, ^{119}Sn) = 1557$ Hz, −167.3 (bs). $^{119}Sn\{^1H\}$ NMR (methanol-d_4, 300 K, ppm): −608.4 (d of d of t); $^1J(^{119}Sn, ^{19}F) = 2630$ and 1550 Hz. MW = 311. Positive-ion ESI-MS: *m*/*z* 1216, 14%; *m*/*z* 929, 8%; *m*/*z* 791, 4%; *m*/*z* 735, 13%; *m*/*z* 623, $[2M + H]^+$, 3%; *m*/*z* 581, 13%; *m*/*z* 448, 8%; *m*/*z* 425, 4%; *m*/*z* 407, 5%; *m*/*z* 368, 6%; *m*/*z* 136, $[HL^{CN} + H]^+$,

Table 2. Crystal data and structure refinement for **1, 1a, 2** and **3**

Compound	1	1a	2	3
Empirical formula	$C_9H_{12}Cl_3NSn$	$C_{18}H_{25}Cl_2N_2Sn.C_9H_{12}Cl_4NSn$	$C_9H_{12}Br_3NSn$	$C_9H_{12}I_3NSn$
Formula weight	359.24	853.68	492.62	633.59
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P2_1/n$
Unit cell dimensions a, b, c, β (Å, deg)	9.3960(2) 8.7030(2) 15.4860(3) 92.5690(12)	9.3920(1) 35.7820(4) 9.8350(1) 97.3700(5)	6.8070(2) 15.7660(4) 12.6310(4) 102.3310(14)	7.1350(1) 16.0460(3) 13.1960(3) 102.7300(9)
Volume ($Å^3$)	1265.07(5)	3277.89(6)	1324.28(7)	1473.65(5)
Z	4	4	4	4
Density (mg/m^3) (calculated)	1.886	1.730	2.471	2.856
Absorption coefficient (mm^{-1})	2.616	2.036	10.947	7.988
$F(000)$	696	1688	912	1128
Crystal size (mm)	0.25 × 0.50 × 0.50	0.075 × 0.125 × 0.40	0.12 × 0.15 × 0.37	0.25 × 0.35 × 0.40
Refl. collected	14 720	43 799	16 743	19 238
T_{min}, T_{max}	0.288, 0.592	0.696, 0.852	0.143, 0.683	0.077, 0.188
Independent/ observed refl.[a]	2890/2759	7478/6107	3030/2580	3378/3247
R_{int}[b]	0.053	0.056	0.050	0.053
Absorption correct.	Integration	Multiscans[e]	Integration	Integration
Number of parameters	130	382	129	130
G *of* F, all data[c]	1.148	1.040	1.054	1.294
$R1$, $wR2$ [$I > 2\delta(I)$][d]	0.025, 0.063	0.027, 0.054	0.026, 0.054	0.027, 0.067
$R1$, $wR2$ (all data)	0.026, 0.065	0.041, 0.058	0.036, 0.058	0.029, 0.068
$\Delta\rho_{max}$, $\Delta\rho_{min}$ ($e/Å^3$)	0.61, −1.24	0.53, −0.83	0.55, −0.87	1.28, −1.52
CCCD deposition no.	262 112	262 115	262 113	262 114

[a] $I > 2\delta(I)$; [b] $R_{int} = \Sigma|F_o{}^2 - F_{o,mean}{}^2|/\Sigma F_o{}^2$; [c] $S = \{\Sigma[w(F_o{}^2 - F_c{}^2)^2]/(N_{diffrs} - N_{params})\}^{1/2}$. [d] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR(F^2) = \{\Sigma[w(F_o{}^2 - F_c{}^2)^2]/[\Sigma w(F_o{}^2)^2]\}^{1/2}$. [e] PLATON.

100%; m/z 91, $[C_6H_5CH_2]^+$, 85%. Negative-ion ESI-MS: m/z 448, $[L^{CN}SnF_3 + SnF_3]^-$, 4%; m/z 388, $[(L^{CN})_2Sn]^-$, 20%; m/z 330, $[M + F]^-$, 100%; m/z 177, $[SnF_3]^-$, 3%. Elemental analysis (%): found: C, 34.9; H, 3.93; N, 4.50, calcd for $C_{36}H_{48}F_{12}N_4Sn_4$ (1239.55): C, 34.88; H, 3.90; N, 4.52.

NMR spectroscopy

The solution state ^1H (500.13 MHz), $^{119}Sn\{^1H\}$ (186.50 MHz) and $^{19}F\{^1H\}$ (470.59 MHz) NMR spectra of the studied compounds were measured on a Bruker Avance 500 spectrometer equipped with 5 mm probes with z-gradient in the temperature range of 170–360 K. The solutions were obtained by dissolving 20 mg of each compound in 0.5 ml of deuterated solvents. The ^1H chemical shifts were calibrated relative to the signal of residual $CHCl_3$ ($\delta = 7.25$), toluene (2.09) and methanol ($\delta = 3.31$), respectively. The ^{119}Sn chemical shifts are referred to external neat tetramethylstannane ($\delta = 0.0$) and the ^{19}F chemical shifts are referred to external Cl_3FC ($\delta = 0.0$). Positive chemical shifts values denote shifts to the higher frequencies relative to the standards. ^{119}Sn NMR spectra were measured using the inverse gated-decoupling mode.

Mass spectrometry

Electrospray ionization (ESI) mass spectra (MS) were measured on the ion trap analyser Esquire3000 (Bruker Daltonics, Bremen, Germany) in the range m/z 50–1500. The ion trap was tuned to give an optimum response for m/z 500 or 1000. The samples were dissolved in acetonitrile and analysed by direct infusion at the flow rate 5 μl/min. The ion source temperature was 300 °C, the flow rate and the pressure of nitrogen were 4 l/min and 10 psi, respectively.

The isolation width for MS^n experiments was $m/z = 8$, and the collision amplitude (CA) was selected depending on the stability of particular fragment ion in the range 0.6–1 V.

X-ray crystallography

Single crystals of **1, 1a** and **2** were grown from ca 5% CH_2Cl_2 solution of the appropriate compound, into which hexane was charged via slow vapour diffusion or from a saturated toluene solution of **3**. Data for colourless crystals were collected at 150(2) K on a Nonius KappaCCD diffractometer using MoK_α radiation ($\lambda = 0.71073$ Å) and a graphite monochromator, so that $\theta_{max} = 27.5°$. The structures were solved by direct methods (SIR92[38]) and structure refinement was based by full-matrix least-squares technique on F^2 (SHELXL97[39]). Hydrogen atoms were mostly localized on a difference Fourier maps. However, to ensure uniformity of treatment of all models, all hydrogen atoms were recalculated into idealized positions (riding model) and assigned temperature factors $H_{iso}(H) = 1.2\ U_{eq}$ (pivot atom) or $1.5U_{eq}$ for the methyl moiety. Absorption corrections were carried on, using either a multiscan procedure (PLATON[40] or SORTAV[41]) or Gaussian integration from the crystal shape (Coppens[42]). Crystallographic data for individual structures are summarized in Table 2.

Structure solutions and refinement of **1, 2** and **3** crystals were unexceptional. The maximal residual electron density peaks are in **1, 2** and **3** located within the 1.5 Å shell from the heaviest atoms. The crystal structure of **1a** is harmed by disorder of the nitrogen arm of the $L^{CN}SnCl_4$ anion. The disordered atoms were refined anisotropically with a fixed occupancy ratio 0.6 : 0.4. The final difference maps of **1a** displayed no peaks of chemical significance (ρ_{min} in 0.6 Å from Sn1).

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