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Structure of *N*,*C*,*N*-chelated organotin(IV) fluorides

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Abstract

The set of starting tri-, di- and monoorganotin(IV) halides containing *N*,*C*,*N*-chelating ligand ($L^{NCN} = \{1,3\text{-}[(CH_3)_2NCH_2]_2C_6H_3\}^-$) has been prepared (**1**–**5**) and two compounds structurally characterized ($[L^{NCN}Ph_2Sn]^+I_3^-$ (**1c**), $L^{NCN}SnBr_3$ (**5**)) in the solid state. These compounds were reacted with KF with 18-crown-6, NH_4F or $L^{CN}nBu_2SnF$ to give derivatives containing fluorine atom(s). Triorganotin(IV) fluorides $L^{NCN}Me_2SnF$ (**2a**) and $L^{NCN}nBu_2SnF$ (**3a**) revealed monomeric structural arrangement with covalent Sn–F bond both in the coordinating and non-coordinating solvents, except the behaviour of **3a** that was ionized in the methanol solution at low temperature. The products of fluorination of $L^{NCN}SnPhCl_2$ (**4**) and **5** were described by NMR in solution as the ionic hypervalent fluorostannates or the oligomeric species reacting with chloroform, methanol or moisture to zwitterionic monomeric stannate $L^{NCN}(H)^+SnF_4^-$ (**5c**), which was confirmed by XRD analysis in the solid state.

Keywords: Organotin(IV) fluorides; *N*,*C*,*N*-ligand; Structure

1. Introduction

One of the goals in the chemistry of tri-, di- and monoorganotin(IV) compounds is to prepare and structurally characterize monomeric organotin fluorides, which are of great interest due to their ability to undergo the metathetical halide for fluoride exchange reactions with different kinds of organometallic halides [1]. The latest published application of triorganotin(IV) fluorides, namely Ph_3SnF, deals with liquid–solid phase-transfer catalyzed fluorinations of alkyl halides and sulfonates, where Ph_3SnF acts as a phase-transfer catalyst via continuous formation of lipophilic $Ph_3SnF_2^-$ anions entering organic phase in the form of potassium salt [2–4].

The structures of many tri- and a limited number of diorganotin fluorides have been determined and found to be either oligo- or polymeric with the ''rod-like'' or ''zig-zag'' F-Sn–F chains [5]. These compounds have relatively high melting points, and are rather insoluble in common organic solvents, which is a limitation in the studies of their structure and reactivity. Only a small number of compounds containing bulky ligands, e.g., $Sn[C(SiMe_2Ph)_3]Me_2F$ [6], $Sn[C(SiMe_3)_3]Ph_2F$ [6], $Sn(C_6H_2Me_3\text{-}2,4,6)_3F$ [7] and $Sn(CH_2SiMe_3)_3F$ [8], with a four-coordinated tin central atom, are monomeric with a Sn–F terminal single bond distance about 1.96Å [9].

In the case of diorganotin difluorides, only a limited number of monomeric species are known, because a whole class of these compounds tends to form insoluble polymeric chains or nets *via* intermolecular associations [10], or hypervalent complexes with excess of fluoride ion, which were studied at −100 °C by ^{19}F and ^{119}Sn NMR spectroscopy [11]. Only one purely monomeric diorganotin compound has been described in the solid state by crystallographic techniques [12]. It is a quinoline substituted dialkyltin difluoride (Fig. 1A) which was prepared by reaction of alkyltin(II) compound with tin(II) fluoride

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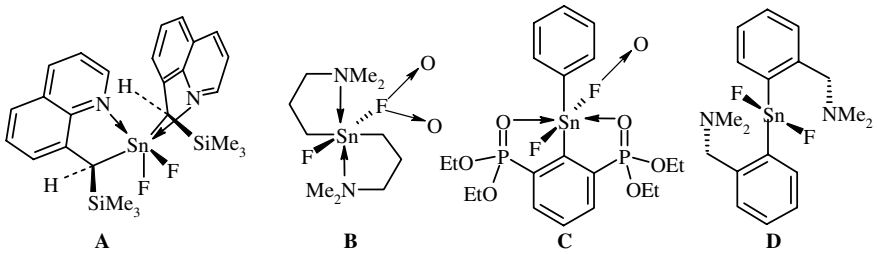


Fig. 1. Structure of monomeric diorganotin difluorides.

in boiling THF. The fluorine and nitrogen atoms occupy the equatorial plane both mutually in *cis*-fashion and carbons are in the apical positions of the distorted octahedron. There are two more compounds published aspire to appertain to this group. These compounds are monomeric in solution, but dimeric in the solid state because bridging water molecule(s) are present in their structure. Both compounds with $[(CH_3)_2N(CH_2)_3]$ [13] and {2,6-$[P(O)(OEt)_2]_2$-4-*t*-Bu-C_6H_2} [14] ligands (Fig. 1B and C), respectively, having tin in "all-*trans*" deformed octahedron coordination geometry, one of fluorine atoms from the first part of molecule being connected to the second part by one or two oxygen atom bridges.

Another two compounds as the product of rearrangements [15] or reactions of **B** with an excess of fluoride ion or amine originated from ligand quarternization [16] have been reported. The X-ray based investigations of some difluorotriorganostannates appeared as well [17,18]. Concerning monomeric monoorganotin(IV) fluoride only one monomeric compound has been prepared by reaction of tris(2,6-dimethoxyphenyl)methanol with SnF_2 in diluted H_2SO_4 providing tris(2,6-dimethoxyphenyl)methylstannyltrifluoride [19]. The tin atom in this compound is seven-coordinated and described by the authors as the distorted monocapped-trigonal-antiprism with Sn–F bond lengths from 1.948(7) to 1.975(6) Å.

Recently, we have reported triorganotin(IV) fluorides of general formula $L^{CN}R_2SnF$, where L^{CN} is $\{2\text{-}[(CH_3)_2NCH_2]C_6H_4\}^-$ and R are alkyl (Me, *n*Bu, *t*Bu) or aryl (Ph) groups of different steric bulk and electronic properties [20]. The compounds have five-coordinated tin and are able to fluorinate titanocene dichloride essentialy quantitatively. In our latest reports in this field, we reported the di- [21] (Fig. 1D) and monoorganotin(IV) [22] fluorides wearing the same ligand. These compounds are presumably tri- or tetranuclear species with rather low solubility in common organic solvents and we used them as a part of selective and sensitive carriers for fluoride ion recognition [23]. In our latest paper, we reported the structure and fluorination ability of *C*,*N*-chelated *n*-butyltin(IV) fluorides [24] towards organochlorosilanes, chlorophosphine and some metal halides.

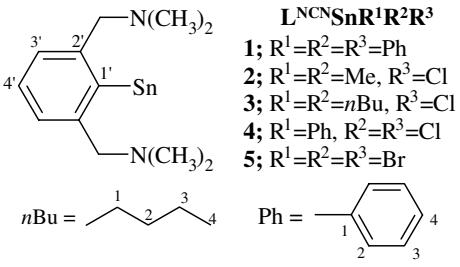
In this paper, we would like to expand our contributions [25] on the structure of *N*,*C*,*N*-chelated tri-, di- and monoorganotin(IV) halides (L^{NCN} = {1,3-$[(CH_3)_2NCH_2]_2$-C_6H_3}-) with the main focus on the structure of the respective fluorides.

2. Results and discussion

The representative group of tri-, di- and monoorganotin(IV) halides (Scheme 1) has been chosen in order to study the differences in structure of products of their fluorination by different methods (KF in biphasic system, KF with 18-crown-6, NH_4F or $L^{CN}nBu_2SnF$).

The iodo-derivative of compound **1**, **1b** ($L^{NCN}Ph_2SnI$) has been used previously for the preparation of some organotin carboxylates [26]. Applying the same synthetic procedure, we obtained **1c** only, which showed the same spectral parameters described previously for **1b**. Compound **1c** is ionic with the known structure [27] of five-coordinated stannylium ion and the triiodide takes the place of the counter anion (Fig. 2). Unfortunately, this species did not reveal reactivity towards the fluorinating agents used because of its ionic character. Fluorination of **2** by KF and 18-crown-6 in benzene yielded $L^{NCN}Me_2SnF$ (**2a**) which revealed a similar structural behaviour (e.g. five-coordinated tin atom δ (^{119}Sn) = −83.5 (d); $^1J(^{119}Sn, ^{19}F)$ = 2160 Hz) in solution as previously reported in analog $L^{CN}Me_2SnF$[20] with a five-coordinated tin centre and the dynamic exchange of nitrogen donors.

Compound **3a**, prepared in biphasic system ether/water, revealed the same structural behaviour in non-coordinating solvents as was found for **2a** with retained covalent Sn–F bond (in $CDCl_3$ at 300 K δ (^{119}Sn) = −96.0 ppm (d); $^1J(^{119}Sn, ^{19}F)$ = 2195 Hz; δ (^{119}Sn) = −107.1 ppm (d); $^1J(^{119}Sn, ^{19}F)$ = 2286 Hz; $CDCl_3$ (235 K); δ (^{119}Sn) = −107.7 ppm (d); $^1J(^{119}Sn, ^{19}F)$ = 2320 Hz; toluene-d_8,



$L^{NCN}SnR^1R^2R^3$
1; R^1=R^2=R^3=Ph
2; R^1=R^2=Me, R^3=Cl
3; R^1=R^2=*n*Bu, R^3=Cl
4; R^1=Ph, R^2=R^3=Cl
5; R^1=R^2=R^3=Br

Scheme 1.

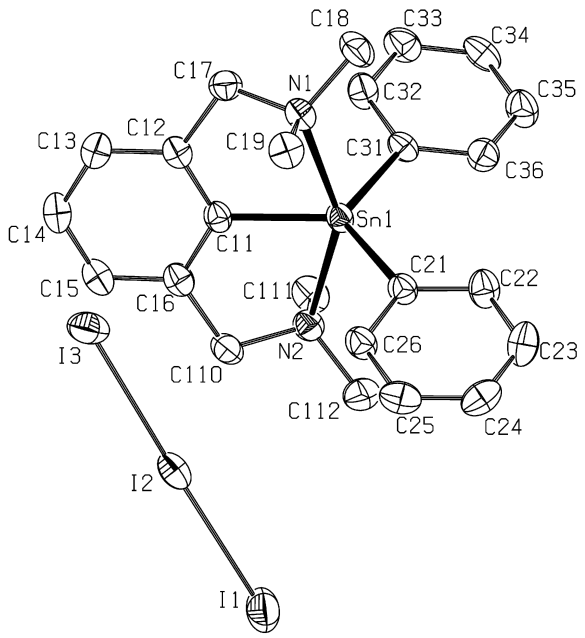


Fig. 2. Molecular structure of **1c** (ORTEP, 50% probability level). Hydrogen atoms are omitted for clarity. The selected distances (Å) and angles (°): Sn(1)–N(1) 2.417(3), Sn(1)–N(2) 2.428(3), Sn(1)–C(11) 2.092(3), Sn(1)–C(21) 2.122(3), Sn(1)–C(31) 2.121(3), I(1)–I(2) 2.8918(4), I(2)–I(3) 2.9388(4), C(11)–Sn(1)–C(31) 118.17(13), C(11)–Sn(1)–C(21) 122.93(13), C(31)–Sn(1)–C(21) 118.86(13), C(11)–Sn(1)–N(1) 75.47(12), C(31)–Sn(1)–N(1) 97.19(12), C(21)–Sn(1)–N(1) 99.28(12), C(11)–Sn(1)–N(2)-75.66(12), C(31)–Sn(1)–N(2) 98.71(12), C(21)–Sn(1)–N(2) 94.04(12), N(1)–Sn(1)–N(2) 151.00(10), C(12)–C(11)–Sn(1) 118.9(2), C(16)–C(11)–Sn(1) 119.5(3), I(1)–I(2)–I(3) 178.087(13).

(190 K)). In proton NMR spectrum measured at 290 K, only one set of broad signals for $-CH_2N$ and NMe_2 were observed, which decoalesce with the decrease in temperature ($-CH_2N$ at 280 K and $N(CH_3)_2$ at 260 K). Only negligible shift of these signals to the higher field is caused by strengthening Sn–N interaction. One sharp signal at −186.0 ppm with satellites ($^1J(^{19}F,\ ^{119}Sn) = 2150$ Hz) in ^{19}F NMR spectrum gave further evidence of monomeric structure with covalent and terminal Sn–F bond. This structural arrangement retained in the whole temperature range (300–210 K) and only a few hertz decrease in the value of $^1J(^{19}F,\ ^{119}Sn)$ is caused by shortening of interaction between the Sn and donor atoms and consequent elongation of the tin–fluorine bond. On the other hand, in methanol solution, a similar dynamic equilibrium as found for $L^{NCN}nBu_2SnCl$ or Br with the Sn–X bond ionization was observed [25a]. The dynamic process (Fig. 3) was determined on the basis of VT ^{119}Sn and ^{19}F NMR spectra in methanol. There, one singlet resonance at −165.9 ppm corresponding to the structural type depicted in Fig. 3 as type B and the broad doublet at −198.8 ppm with $^1J(^{119}Sn,\ ^{19}F) = 2294$ Hz related to the type A, as a result of dissociation of Sn–F bond at room temperature, are observed. At 260 K new singlet at +53.4 ppm appeared in the spectrum. Such downfield shift is characteristic for the process of ionization leading to the limit ionic structure C ($[(L^{NCN})Bu_2Sn]^+$) as a consequence of strengthening of Sn–N interaction and five- or better [3 + 2] coordinated tin centre. With further decrease of temperature to 200 K the only detectable signal was $\delta(^{119}Sn) = 48.8$ ppm which is due to further increase of Sn–N bond strength and an extrusion of methanol molecule from tin coordination sphere as shown in the limit structure C. In ^{19}F NMR spectra at 260 K, two broad signals, are at −149.0 ppm with $^1J(^{19}F,\ ^{119}Sn) = 2398$ Hz, corresponding to structure A, and the other at −130.0 ppm corresponding to values of free F ion, were observed. Decreasing the temperature to the limit 170 K, adjacent broad signals were detected (−131.1; −137.8; −146.2; −147.9; −150.4 at 170 K). The signal with the tin satellites observed at higher temperature (−149.0 ppm; 260 K) was getting broader and at 200 K was not detected which can be explained by Sn–F bond dissociation and ionic structure formation. The next signals at lower temperature can be explained by an interaction of 'naked' fluorine ion with the solvent molecules.

During the preparation of fluoride derivatives of diorganotin [21], a more complicated situation than triorganotin fluorides containing L^{CN} ligand was observed. Similar to Dakternieks [11], the phenyl group migration in the case of reactivity of diorganotin $L^{CN}SnPhCl_2$ was observed. This fact was assisted by the presence of $L_2^{CN}SnF_2$, $L^{CN}SnPh_2F$ in the crude product and Ph_2SnF_2 and Ph_3SnF in the insoluble part of the product detected by the solid state ^{19}F CP/MAS NMR spectra. The previously published products of fluorination of $L^{CN}SnPhCl_2$ were only slightly soluble in methanol. The structural investigation was based on ^1H, ^{119}Sn and low temperature ^{19}F NMR spectral data. Very complicated multiplets in the ^{119}Sn spectra and very broad signals in the ^{19}F NMR spectra at room temperature were found. The similar structural behaviour was assigned to the derivative **4a** by means of multinuclear NMR spectroscopy in the chloroform solution. In contrast to analogs of **4** containing L^{CN} ligand, all fluoroderivatives of **4**

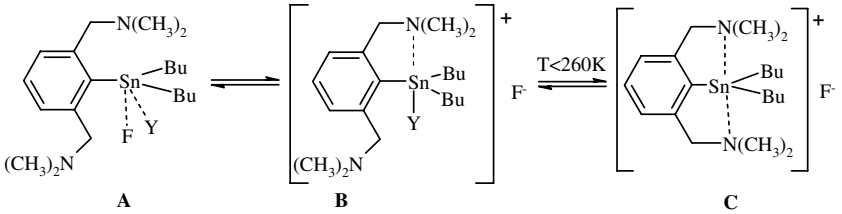


Fig. 3. Structural behaviour of **3a** in the methanol solution; Y – molecule of solvent.

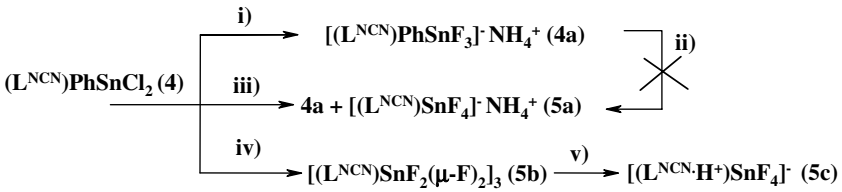


Fig. 4. The reactivity of **4** with: (i) 2 equiv. of NH_4F; (ii) excess of NH_4F; (iii) 20 equiv. of NH_4F; (iv) 2 equiv. of $L^{CN}nBu_2SnF$; (v) CH_2Cl_2/hexane.

revealed very good solubility in methanol and even in $CDCl_3$ and CD_2Cl_2.

Firstly, 2 equiv. of NH_4F in CH_2Cl_2 were added to **4** (Fig. 4) which led, according to ^{19}F and ^{119}Sn NMR spectra, to the dominant formation of **4a**. This compound reveals characteristic broadened doublet of triplet (dt) in ^{119}Sn NMR spectrum measured in methanol ($\delta(^{119}Sn) = -486.6$ ppm with $^1J(^{119}Sn, ^{19}F) = 2770$ and 2635 Hz). Similar spectral pattern and chemical shift have been observed in ^{119}Sn NMR spectrum of $[Bu_4N^+][Ph_2SnF_3^-]$ (−402 ppm; $^1J(^{119}Sn, ^{19}F) = 2310$ (d) and 2250 (t) Hz) [11] and for $[L^{CN}PhSnF_3^-]$ moiety (−484.8 ppm with $^1J(^{119}Sn, ^{19}F) = 2626$ and 2706 Hz). A triplet (−143.0 ppm; $^1J(^{19}F, ^{119}Sn) = 2581$ Hz and $^2J(^{19}F, ^{19}F) = 32$ Hz) and a doublet (−159.9 ppm; $^1J(^{19}F, ^{119}Sn) = 2745$ Hz and $^2J(^{19}F, ^{19}F) = 32$ Hz) with integral ratio 1:2 were found in ^{19}F NMR spectrum at 250 K. Further addition of NH_4F into the sample of **4a** did not lead to changes in NMR spectral patterns.

As depicted in Fig. 4, some reactions of **4** led to the formation of monoorganotin derivatives identical to those found in the case of reactivity of **5** (vide infra) as a result of previously described phenyl group migration process [21]. The reaction of **4** with 20 molar equivalents of ammonium fluoride gave the described **4a** in an equilibria with **5a** $[(L^{NCN})SnF_4]^-NH_4^+$ which are sparingly soluble in $CDCl_3$. ^{119}Sn NMR spectrum in this solvent shows the major doublet of triplet for **4a** −488.3 ppm with two comparable Sn–F couplings 2792 and 2577 Hz and the second quite complex multiplet (Fig. 7a, −601.3 ppm (ddt) $^1J(^{119}Sn, ^{19}F) \approx 2430$ Hz) which corresponds to **5a**. ^{19}F NMR spectrum at 295 K contained a couple of very broad signals and one broadened triplet at −138.6 ppm with $^1J(^{19}F, ^{119}Sn) = 2745$ Hz and $^2J(^{19}F, ^{19}F) = 32$ Hz. In the same spectrum at 220 K, some signals are sharper (−136.9 ppm with $^1J(^{19}F, ^{119}Sn) = 2752$ Hz and −165.6 ppm with $^1J(^{19}F, ^{119}Sn) = 2606$ Hz (**4a**)) but remaining signals which belonging to **5a** remained unchanged (vide infra).

After the reaction of **4** with 2 equiv. of $L^{CN}nBu_2SnF$, the toluene insoluble residue was analyzed by ESI/MS. The highest intensity isotopic peak with the highest m/z value was 1161 $[M+H]^+$ in positive ion mode which can be assigned to compound $[(L^{NCN})SnF_2(\mu\text{-}F)_2]_3$ (**5b**). In the negative ion mode, there is the main peak $m/z = 387$ which belongs to anion $[(L^{NCN})SnF_4]^-$. The trimeric organization of **5b** comes apart owing to solvent leading to the compound **5c** that will be discussed later and also ^1H, ^{19}F and ^{119}Sn NMR spectra of **5b** measured in chloroform are identical to spectra of **5c** (vide infra). Insoluble products formed by this reaction were identified to be identical with Ph_2SnF_2 and Ph_3SnF previously detected in the reactivity of $L^{CN}PhSnCl_2$ by ^{19}F CP/MAS NMR spectroscopy [21].

Compound **5** is very reactive towards the moisture and its molecular structure can be described as a distorted octahedron with nearly equivalent Sn–Br and Sn–N bonds (Fig. 5). In the case of reactivity of **5** $(L^{NCN})SnBr_3$ two synthetic pathways were used (Fig. 6).

When only 3 equiv. of NH_4F were used for fluorination of **5**, poorly soluble products in non-coordinating solvents were obtained. Although these species revealed relatively higher solubility in methanol, we were not able to identify their structures even from low temperature proton and ^{19}F NMR spectra. We can suggest the presence of partially fluorinated products making various types of oligomers through halide bridges with the increase of temperature.

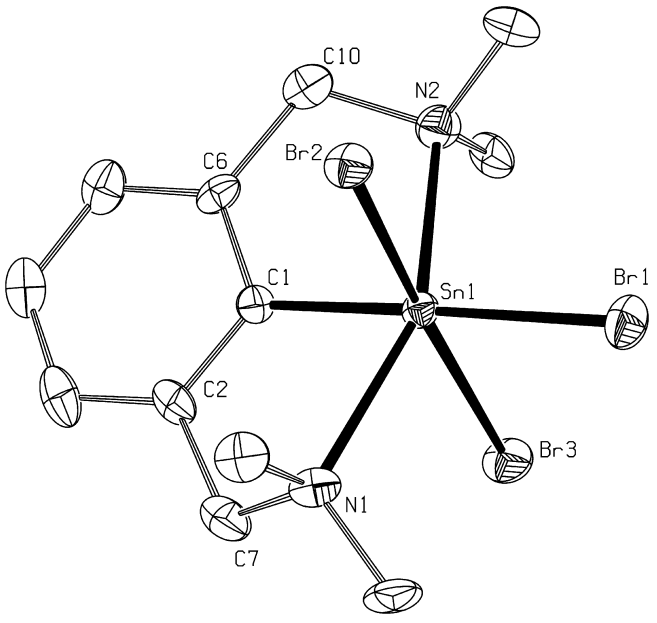


Fig. 5. Molecular structure of **5** (ORTEP, 50% probability level) Hydrogen atoms are omitted for clarity. Sn(1)–C(1) 2.034(14), Sn(1)–N(2) 2.387(13), Sn(1)–N(1) 2.400(14), Sn(1)–Br(1) 2.4977(17), Sn(1)–Br(2) 2.6488(17), Sn(1)–Br(3) 2.6589(17), C(1)–Sn(1)–N(2) 77.7(5), C(1)–Sn(1)–N(1) 77.1(5), N(2)–Sn(1)–N(1) 154.7(4), C(1)–Sn(1)–Br(1) 177.5(4), N(2)–Sn(1)–Br(1) 102.3(3), N(1)–Sn(1)–Br(1) 103.0(3), C(1)–Sn(1)–Br(2) 94.6(4), N(2)–Sn(1)–Br(2) 86.7(3), N(1)–Sn(1)–Br(2) 93.7(3), Br(1)–Sn(1)–Br(2) 87.83(6), C(1)–Sn(1)–Br(3) 89.9(4), N(2)–Sn(1)–Br(3) 95.7(3), N(1)–Sn(1)–Br(3) 85.9(3), Br(1)–Sn(1)–Br(3) 87.64(6), Br(2)–Sn(1)–Br(3) 175.25(6).

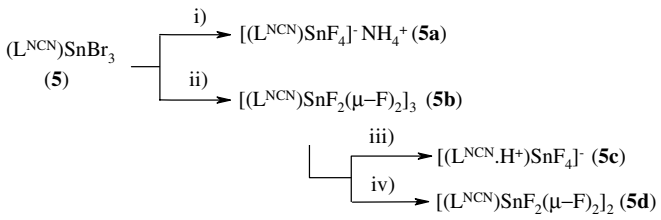


Fig. 6. The reactivity of **5**: (i) 3 equiv. of NH_4F and subsequent excess of NH_4F; (ii) 3 equiv. of $L^{CN}nBu_2SnF$; (iii) CH_2Cl_2/hexane; (iv) methanol.

This suggestion can be supported mainly by study of ^{19}F NMR spectra. At 290 K, a sharp singlet at −131.86 ppm with satellites $^1J(^{19}F, ^{119}Sn) = 2561$ Hz, which belongs to a terminal fluorine bonded to tin atom, but without any further coupling to fluorine atoms, and very broad signal in the range of −142 to −154 ppm. In this area of spectrum at 220 K eight new quite broad signals without any couplings were visible. Earlier sharp signal is getting very broad with the loss of satellites at the same conditions. At the same time, two new signals appeared at −163.6 and −167.4 ppm with $^1J(^{19}F, ^{119}Sn) \approx 1785$ Hz as is typical for bridging fluorine atoms and which is in good agreement with an oligomeric structure.

In the next reaction, an excess of NH_4F was applied which led to formation of **5a** characterized by ^{119}Sn (Fig. 7) and ^{19}F NMR spectra in methanol. ^{19}F NMR spectrum at 290 K reveals two broad signals at −143.6 and −153.2 ppm. With a decrease in temperature to 250 K, the original signal at −143.6 ppm became sharper, the tin couplings were observed ($^1J(^{19}F, ^{119}Sn) = 2529$ Hz) and the second signal disappeared. Further decrease of temperature did not change the spectral pattern (220 K: −142.9 ppm; $^1J(^{19}F, ^{119}Sn) = 2531$ Hz). The long time measurement of ^{119}Sn NMR spectrum gave an additional structural information; a unsymmetrical quintet ($\delta(^{119}Sn) = -603.5$ ppm; $^1J(^{119}Sn, ^{19}F) \approx 2300$ Hz) was observed supporting thus the description of **5a** as hypercoordinated (six-coordinated tin) ionic species where there are four nearly equivalent terminal fluorine atoms and one ligand with dynamically exchanging donor atoms.

In order to exclude ammonium fluoride from the reaction systems, previously successful $L^{CN}Bu_2SnF$ was used as a fluorinating agent. In toluene insoluble fraction (toluene filtrate contained only $L^{CN}Bu_2SnBr$) was analyzed by ESI/MS measurements. The same spectral patterns as in the case of formation of **5b** were observed. This product is insoluble in inert solvents such as toluene but dramatically reactive with, for example, $CDCl_3$ and methanol, giving **5c** as a zwiterionic product of acidic proton abstraction and further amine quarternization. The monomeric stannate structure (Fig. 8), where, one L^{NCN} ligand is bonded in bidentate fashion to the tin atom and the second arm is protonized is observed. The tin coordination octahedron is formed next by four non-equivalent Sn–F (for F1 1.983(4) Å, for F2 (*trans* to N1) 1.961(2) Å, for F3 2.030(2) Å, for F4 1.952(4) Å) bonds.

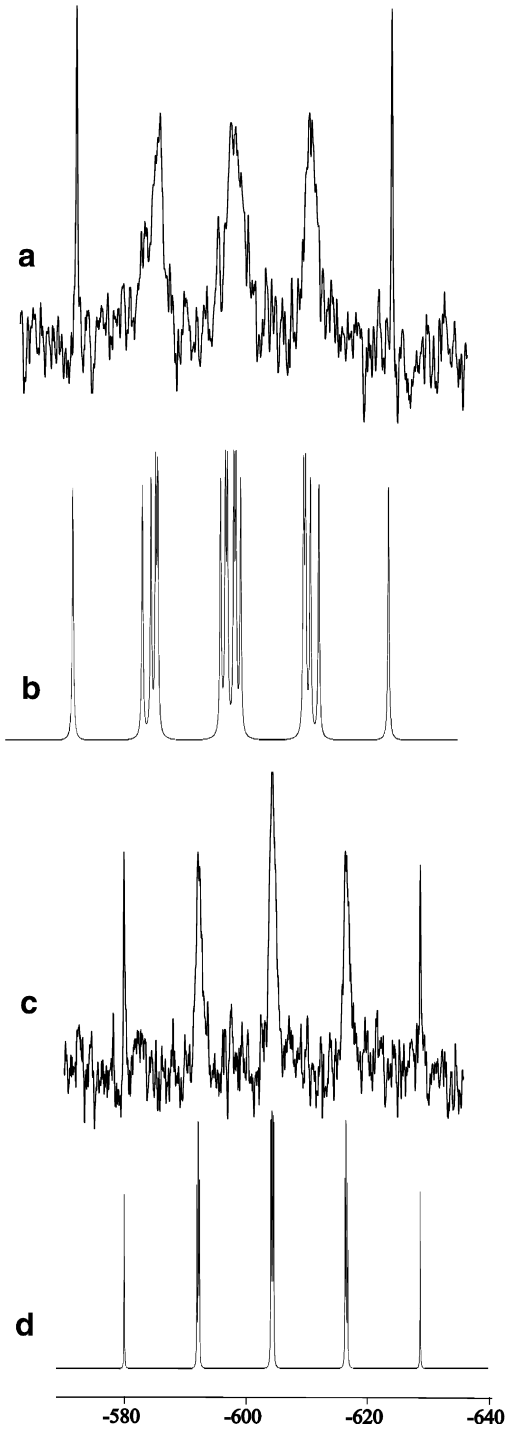


Fig. 7. ^{119}Sn NMR spectra of **5a**: (a) in chloroform, (b) simulated for $[L^{NCN}SnF_4]^-$ by gNMR 5.0 software (IVORYSOFT) using couplings from ^{19}F NMR spectrum in chloroform; (c) in methanol; (d) simulated spectrum in methanol.

The distance Sn–F1 is somewhat shorter in comparison with Sn–F2 and F4, respectively, as a product of *trans*-effect of donor amino group. Much longer elongation can be seen in the case of Sn–F3 bond due to the existence of hydrogen bonding (N2–H2···F3 (2.757(3) Å)). Similar bondlengths were found in the sole published mono-

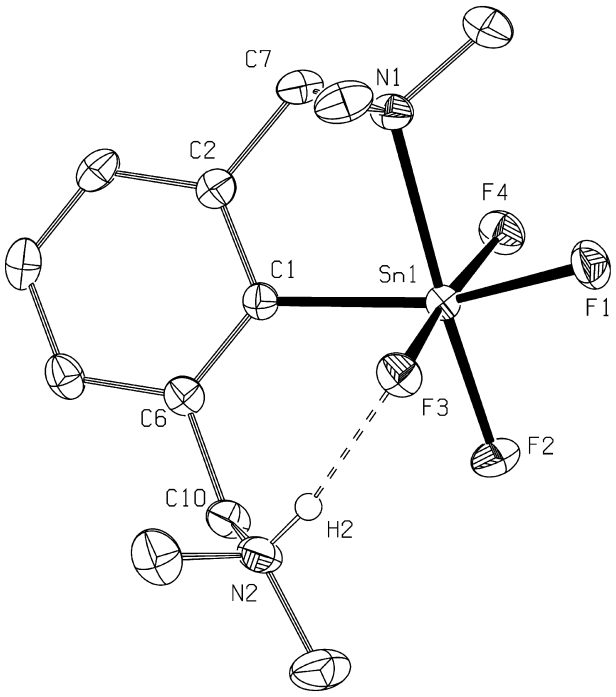


Fig. 8. Molecular structure of **5c** (ORTEP, 50% probability level). Hydrogen atoms are omitted for clarity. The selected distances (Å) and angles (°): Sn(1)–N(1) 2.325(2), Sn(1)–F(1) 1.9522(14), Sn(1)–F(2) 1.9613(14), Sn(1)–F(3) 2.0302(13), Sn(1)–F(4) 1.9835(14), Sn(1)–C(1) 2.150(2), F(1)–Sn(1)–F(2) 93.64(6), F(1)–Sn(1)–F(4) 89.24(6), F(2)–Sn(1)–F(4) 91.30(6), F(1)–Sn(1)–F(3) 85.29(6), F(2)–Sn(1)–F(3) 87.50(6), F(4)–Sn(1)–F(3) 174.31(5), F(1)–Sn(1)–C(1) 161.08(8), F(2)–Sn(1)–C(1) 103.82(8), F(4)–Sn(1)–C(1) 97.49(7), F(3)–Sn(1)–C(1) 88.19(7), F(1)–Sn(1)–N(1) 85.04(7), F(2)–Sn(1)–N(1) 174.35(7), F(4)–Sn(1)–N(1) 83.20(7), F(3)–Sn(1)–N(1) 97.84(6), C(1)–Sn(1)–N(1) 78.27(8).

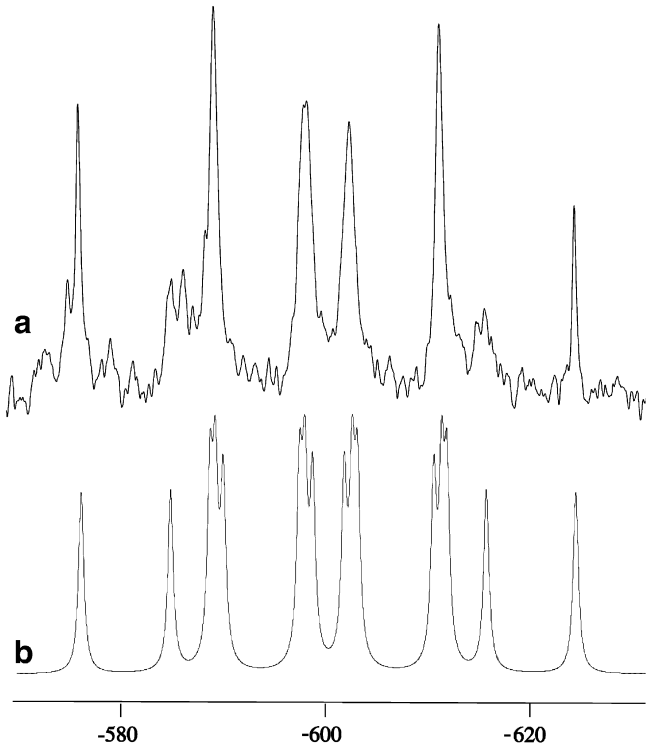


Fig. 9. ^{119}Sn NMR spectra of **5c**: (a) in chloroform; (b) simulated for $[L^{NCN}(H)^{+}Sn^{-}F_4]$ by gNMR 5.0 software (IVORYSOFT) using couplings from ^{19}F NMR spectrum in chloroform.

organotin fluoride with terminal fluorine atoms (Sn–F: 1.956; 1.948 aand 1.975 Å) [19]. The main deviation from the octahedral shape are the values of N1–Sn–F1 angle (174.36(1)°, ideally 180°) and C1–Sn–F2 (103.83(3)°, ideally 90°). Very close to this arrangement are also the hydrolysis products of chlorine and bromine analogs [25,28]. Although the hydrolysis product of **5** is dimeric the torsion angle defined by C1–C2–C7–N1 (37.01° (**5a**), 34.52° (**5**)) are similar. The distance Sn–N1 (2.325(2) Å) is the strongest reported contact Sn–N in this type of compounds; (2.386(4) and 2.400(1) Å for **5** and 2.3700(3)Å for its hydrolysis product [25c]). This structure retained in $CDCl_3$, which is supported by ^{1}H, ^{119}Sn a ^{19}F NMR spectra. In the proton spectrum of **5c** at 295 K, there is signal at 9.78 ppm assigned to R_3NH^{+} group. In aliphatic part of the spectrum, two broad signals (4.58 and 3.83 ppm) belonging to two different $-CH_2N$ groups were found, as well as another two (2.89 and 2.64 ppm) for methyl of NMe_2 groups, and these signals are not changed with lowering of the temperature. Complex multiplet (doublet of doublets of triplets – ddt (Fig. 9)) with the centre of gravity at −601.2 ppm and coupling $^{1}J(^{119}Sn, ^{19}F) \approx 2520$ Hz were visible in ^{119}Sn NMR spectrum, and this supports the non-equivalency of terminal fluorine atoms. Measured ^{19}F NMR spectrum at 290 K gave no additional information about the structure, because only one major signal at −141 ppm and two minor very broad signals at −148.5 and −161.7 ppm were found. With the lowering of the temperature to 250 K, the major signal (−141 ppm) goes broader and the remaining two signals are sharpened (−148.2 ppm with $^{1}J(^{19}F, ^{119}Sn) = 2267$ Hz and −161.8 ppm) with $^{1}J(^{19}F, ^{119}Sn) = 1593$ Hz. Further decrease in temperature led to broadening of these signals again.

A different NMR spectral pattern was found directly after dissolution of **5b** in methanol-d_4. We proposed the equilibrium of a couple of species (Fig. 10) which led after some minutes to the formation of **5c**. In ^{119}Sn NMR spectrum (295 K) two doublets of triplets at −576.8 ppm with $^{1}J(^{119}Sn, ^{19}F) = 2485$ Hz and −579.3 ppm with $^{1}J(^{119}Sn, ^{19}F) = 2670$ Hz which could be assigned to two different isomers (Fig. 10) of $[(L^{NCN})SnF_3.O(H)Me]$ type are observed. The third signal is split into a pseudoquartet of triplets (or better, doublet of triplets – dtt) at −604.9 ppm with $^{1}J(^{119}Sn, ^{19}F) = 2560$ and 1595 Hz, which could be assigned to a dinuclear **5d** $[(L^{NCN})SnF_2(\mu\text{-}F)_2]_2$, with two terminal and two bridging fluorine atoms.

^{19}F NMR spectrum at 295 K gave no useful information, because very broad and unresolved signals were obtained. These signals are much sharper at 250 K, but they are not consistent with the proposed monomeric structure of two isomers of $[(L^{NCN})SnF_3 \cdot O(H)Me]$ type. With

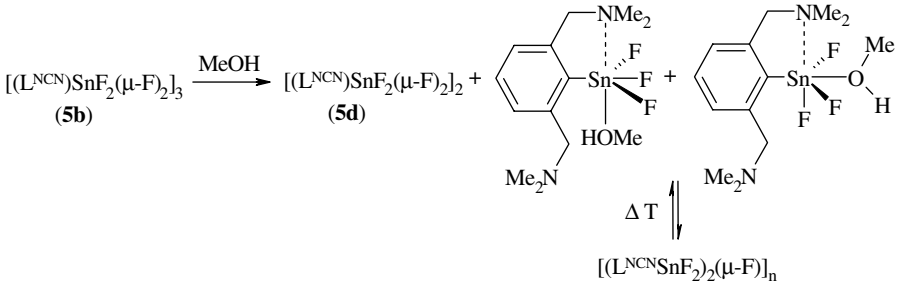


Fig. 10. Influence of solvent (CD_3OD) to structure of **5b**.

respect to the existence of two new signals at −150.7 ppm (d) with $^1J(^{119}Sn,\ ^{19}F) = 2770$ Hz, $^2J(^{19}F,\ ^{19}F) = 19.8$ Hz and −168.5 ppm (t) with $^1J(^{119}Sn,\ ^{19}F) = 1536$ Hz and $^2J(^{19}F,\ ^{19}F) = 19.8$ Hz with integral ratio 4:1 which signalize a formation of new oligomeric species of $[(L^{NCN})\text{-}SnF_2(\mu\text{-}F)]_n$ type.

3. Conclusions

The set of tri-, di- and monoorganotin(IV) halides containing *N*,*C*,*N*-chelating ligand has been prepared and structurally characterized (**1c**, **5**). These compounds were reacted with different fluorinating agents to give derivatives containing fluorine atom(s).

Triorganotin(IV) fluorides **2a** and **3a** revealed the monomeric structural arrangement with covalent Sn–F bond both in the coordinating and noncoordianting solvents, except the behaviour of **3a** which was ionized in the methanol solution at low temperature.

Good solubility in more solvents as a consequence of two chelating arms of ligand L^{NCN} in the case of fluorides originated from the compounds **4** and **5** was observed. The compounds **4a** and **5a** were described in solution as the ionic hypervalent fluorostannates. On the other hand, the oligomeric compound **5b** dissolved in chloroform or methanol providing the zwitterionic monomeric stannate **5c**. This structural arrangement was confirmed by XRD analysis in the solid state.

4. Experimental

4.1. General remarks

All experiments were carried out in an argon atmosphere or in vacuo. (*N*,*N*-dimethylaminomethyl)benzene, *n*-butyllithium, phenyltin(IV) trichloride, dibutyltin(IV) dichloride, dimethyltin(IV) dichloride, tin(IV) bromide, potassium fluoride, ammonium fluoride (dried in vacuo), 18-crown-6-ether were obtained from commercial sources (Sigma–Aldrich). Toluene, benzene, *n*-hexane, *n*-pentane were dried over and distilled from potassium alloy, degassed and stored over potassium mirror. Chloroform and dichloromethane were dried over and distilled from P_2O_5 and CaH_2. Compounds **1**–**4** and $L^{CN}nBu_2SnF$ have been prepared by procedures reported in Refs. [20,25a,25b]. Compound **5** was prepared similarly as in ref. [25c] but very strict vacuo conditions were applied. Yield: 62%; ^{1}H NMR (500.13 MHz, Toluene-d_8, 300 K, ppm): 7.06 (t, 1H, H(4′)); 6.65 (d, 2H, H(3′), $^3J(^{119}Sn,\ ^1H) = 62.7$ Hz); 3.32 (bs, 4H, NCH_2); 2.39 (bs, 12H, $N(CH_3)_2$). ^{13}C NMR (Toluene-d_8, 30 0K, ppm): 60.66, NCH_2; 46.84, NCH_3. ^{119}Sn{^{1}H} NMR (Toluene-d_8, 300 K, ppm): −601.4 (brs). The same conditions as described in Ref. [26] for preparation of **1b** yielded **1c** only with the same spectral data.

4.2. NMR spectroscopy

The NMR spectra were recorded as solutions in methanol-D_4, C_6D_6, $CDCl_3$ on a Bruker Avance 500 spectrometer (equipped with *Z*-gradient 5mm probe) at 300, 250, 220 or 170 K, ^{1}H (500.13 MHz), ^{119}Sn{^{1}H} (186.50 MHz) and ^{19}F{^{1}H} (470.53 MHz). The assignments of signals in ^{1}H spectra were made from standard 2D measurements. The solutions were obtained by dissolving of 5–40 mg of each compound in 0.5 ml of deuterated solvents. The ^{1}H chemical shifts were calibrated relative to the signal of residual $CHCl_3$ ($\delta = 7.27$) and benzene (7.16), methanol ($\delta = 3.31$), respectively, and the ^{19}F chemical shifts are referred to external Cl_3FC ($\delta = 0.0$). The ^{119}Sn chemical shifts are referred to external neat tetramethylstannane ($\delta = 0.0$). 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. ^{19}F MAS NMR spectra were measured using Bruker Avance 500 WB/US NMR spectrometer (Karlsruhe, Germany, 2003) in 2.5 ZrO_2 rotors. Magic angle spinning (MAS) frequency was 30 kHz. Intensity of excitation $B_1(^{19}F)$ field corresponds to $\omega_1/2\pi = 113.6$ kHz (length of 90° pulse is 2.2 μs). All experiments were performed at room temperature (296 K). ^{19}F chemical shift scale was calibrated using external standard KF (−130.0 ppm).

4.3. 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* 50–2000.

The sample was dissolved in dried acetonitrile or methanol and analysed by direct infusion at the flow rate 5 μl/min both in the negative- and positive-ion modes. 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/MS experiments was $F[x]$ $m/z = 8$, and the collision amplitude was 0.9 V.

4.4. X-ray crystallography

The single crystals of **1c**, **5** and **5b** were obtained from toluene (**5**) or dichlormethane solution.

Data for colorless crystals were collected at 150(1) K on a Nonius KappaCCD diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å), and graphite monochromator. The structures were solved by direct methods (SIR92 [29]). All reflections were used in the structure refinement based on F^2 by full-matrix least-squares technique (SHELXL97 [30]). Hydrogen atoms were mostly localized on a difference Fourier map, however to ensure uniformity of treatment of 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. Absorption corrections were carried on, using either multi-scans procedure (PLATON [31] or SORTAV [32]) or Gaussian integration from crystal shape (Coppens [33]). A twinned crystal of **5** reveals after solving of structure, rather high residual electron density maxima but has no chemical significance; one of atoms (C1) was refined isotropically.

Crystallographic data for **1c**: $C_{24}H_{29}N_2I_3Sn$, $M = 844.88$, monoclinic, $P21/c$, $a = 10.4230(2)$, $b = 17.3750(3)$, $c = 15.7690(3)$ Å, $\beta = 97.9620(13)°$, $Z = 4$, $V = 2828.23(9)$ Å^3, $D_{calc} = 1.984$ g cm^{-3}, $\mu = 4.191$ mm^{-1}, $T_{min} = 0.418$, $T_{max} = 0.545$; 128 617 reflections measured ($\theta_{max} = 27.5°$), 10 134 independent ($R_{int} = 0.0706$), 5736 with $I > 2\sigma(I)$, 276 parameters, $S = 1.097$, $R1$(obs. data) = 0.0306, $wR2$(all data) = 0.0741; max., min. residual electron density = 0.888, −0.959 e Å^{-3}.

Crystallographic data for **5**: $C_{12}H_{19}N_2Br_3Sn$, $M = 549.71$, monoclinic, $P21/n$, $a = 14.1760(4)$, $b = 8.4830(2)$, $c = 14.7100(4)$ Å, $\beta = 108.7860(14)°$, $Z = 4$, $V = 1674.72(8)$ Å^3, $D_{calc} = 2.180$ g cm^{-3}, $\mu = 8.670$ mm^{-1}, $T_{min} = 0.152$, $T_{max} = 0.699$; 27 954 reflections measured ($\theta_{max} = 27.5°$), 10 134 independent ($R_{int} = 0.1498$), 3781 with $I > 2\sigma(I)$, 163 parameters, $S = 1.085$, $R1$(obs. data) = 0.0829, $wR2$(all data) = 0.2596; max., min. residual electron density = 4.515, −2.591 e Å^{-3}.

Crystallographic data for **5c**: $C_{12}H_{20}N_2F_4Sn$, $M = 386.99$, monoclinic, $P21/n$, $a = 15.1340(4)$, $b = 7.3050(2)$, $c = 15.5510(4)$ Å, $\beta = 116.0381(14)°$, $Z = 4$, $V = 1544.73(7)$ Å^3, $D_{calc} = 1.664$ g cm^{-3}, $\mu = 1.685$ mm^{-1}, $T_{min} = 0.813$, $T_{max} = 0.885$; 15 798 reflections measured ($\theta_{max} = 27.5°$), 10 134 independent ($R_{int} = 0.0393$), 3086 with $I > 2\sigma(I)$, 180 parameters, $S = 1.092$, $R1$(obs. data) = 0.0250, $wR2$(all data) = 0.0563; max., min. residual electron density = 1.064, −0.775 e Å^{-3}.

4.5. {[Bis-2,6-(N,N-dimethylaminomethyl)]phenyl}dimethyltin(IV) fluoride (**2a**)

To a benzene solution of **2** (0.1 g, 0.27 mmol) in a Schlenk tube was added KF (0.27 mmol) and 18-crown-6-ether (0.02 mmol) and the reaction mixture was stirred for one week. Afterwards a white solid was formed. The filtrate was concentrated and pentane was added to give an oily product. Yield: 66 mg (68%). ^{1}H NMR (C_6D_6, 300 K, ppm): 6.87 (bs, 2H, H(3′)), 7.31 (m, 1H, H(4′)); 3.5 (bs, 4H, NCH_2); 1.76 (d, 6H, $N(CH_3)_2$); 1.34 (d, 6H, $N(CH_3)_2$); 0.49 (s, 6H, H(1)), $^2J(^{119}Sn, ^1H) = 65.1$ Hz, $^3J(^{19}F, ^1H(1)) = 7$ Hz. $^{19}F\{^1H\}$ NMR (C_6D_6, 300 K, ppm): −173.2 (s); $^1J(^{19}F, ^{119}Sn) = 2116$ Hz, $^{119}Sn\{^1H\}$ NMR (C_6D_6, 300 K, ppm): −83.5 (d); $^1J(^{119}Sn, ^{19}F) = 2160$ Hz.

4.6. {[Bis-2,6-(N,N-dimethylaminomethyl)]phenyl}di(1-butyl)tin(IV) fluoride (**3a**)

To a solution of 0.2 g of **3** (0.44 mmol) in diethylether (10 ml) was added an aqueous solution of KF (20 eq. excess). The reaction mixture was stirred for one week. Then, both phases were separated and the water phase was extracted twice with diethylether. The organic phases were brought together and dried over magnesium sulphate. After removing of volatiles, the filtrate was evaporated to dryness in vacuo to obtain the oily product. Yield: 0.164 g (82%). ^{1}H NMR (500.13 MHz, $CDCl_3$, 300 K, ppm): 7.16 (bs, 1H, H(4′)); 7.02 (bs, 2H, H(3′)); 3.55 (bs, 4H, NCH_2); 2.14 (bs, 12H, $N(CH_3)_2$); 1.66 (m, 4H, H(1)); 1.34 (m, 4H, H(2)); 1.20 (m, 4H, H(3)); 0.86 (t, 6H, H(4)). ^{13}C NMR ($CDCl_3$, 300 K, ppm): 143.1, C(2′, 6′); 140.2, $^2J(^{19}F, ^{13}C) = 38.6$ Hz, C(1′); 125.9, C(3′, 5′); 128.3, C(4′); 64.2, NCH_2; 44.8, NCH_3; 17.5, $^1J(^{119}Sn, ^{13}C) = 526.3$ Hz, $^2J(^{19}F, ^{13}C) = 11.3$ Hz, C(1); 28.1, $^2J(^{119}Sn, ^{13}C) = 26.3$ Hz, C(2); 27.2, $^3J(^{119}Sn, ^{13}C) = 87.8$ Hz, C(3); 13.6, C(4). $^{19}F\{^1H\}$ NMR ($CDCl_3$, 300 K, ppm): −186 (s); $^1J(^{19}F, ^{119}Sn) = 2150$ Hz, $^{119}Sn\{^1H\}$ NMR ($CDCl_3$, 300 K, ppm): −96.0 (d); $^1J(^{119}Sn, ^{19}F) = 2195$ Hz. ESI-MS: MW = 444. m/z (%). Positive ion mode MS: $[M-F]^+$, 425 (100). Elemental Anal. Calc. for $C_{20}H_{37}N_2FSn$ (443.22): C, 54.2; H, 8.41; N, 6.32. Found: C, 54.18; H, 8.39; N, 6.35%.

4.7. Products of fluorination of (L^{NCN})$PhSnCl_2$ (**4**) and (L^{NCN})$SnBr_3$ (**5**)

Method A. The compound **4** (100 mg, 0.21 mmol) was dissolved in 10 ml of dichloromethane and NH_4F (20 eq. excess) was added. The reaction mixture was stirred for five days. Afterwards, the soluble part was filtered off and the volatiles were vacuo removed. The product was dissolved in $CDCl_3$. ^{1}H NMR ($CDCl_3$, 300 K, ppm): 7.92 (d, 2H), $^3J(^1H(4'), ^1H(3')) = 6.5$Hz, $^3J(^{119}Sn, ^1H) = 102.84$ Hz, 7.31–7.02 (m, 8H), 4.08 (bs, 4H, NCH_2), 3.72 (bs, 4H,

NCH_2), 2.74–2.65 (m, 12H, NCH_3), 2.34–2.17 (m, 12H, NCH_3). $^{19}F\{^1H\}$ NMR ($CDCl_3$, 300 K, ppm): −138.6 (s), $^1J(^{19}F, ^{119}Sn) = 2734$ Hz, −145 (bs), −152 (bs), −155 (s), −160 (bs). $^{119}Sn\{^1H\}$ NMR ($CDCl_3$, 300 K, ppm): −488.3 (dt), $^1J(^{119}Sn, ^{19}F) = 2792$ and 2577 Hz, −601.3 (ddt), $^1J(^{119}Sn, ^{19}F) \approx 2430$ Hz.

Method B. To a toluene solution of **4** (0.145 g, 0.31 mmol) was added $L^{CN}nBu_2SnF$ (0.104 g, 0.63 mmol) and the reaction mixture was stirred and heated at 80 °C for 5 days. Afterwards, toluene was removed by filtration and the remaining insoluble solid was washed several times with toluene. The toluene extract was evaporated to dryness in vacuo and a residuum was identified by NMR spectroscopy as the chloride analogue of $L^{CN}nBu_2SnF$. The solid was investigated by ESI/MS: MW = 1161; *m/z* (%): Positive ion mode: $[(L^{NCN}SnF_4)_3 + K]^+$, 1200 (10); $[(L^{NCN}SnF_4)_3 + Na]^+$, 1184 (49); $[(L^{NCN}SnF_4)_3 + H]^+$, 1162 (11); $[M-(L^{NCN}SnF_4)+Na]^+$, 797 (100); $[M-(L^{NCN}SnF_4) + H]^+$, 775 (35); $[L^{NCN}SnF_3 + K]^+$, 407 (61); Negative ion mode: $[L^{NCN}SnF_4]^-$, 387 (100). Afterwards, the solid was dissolved in $CDCl_3$ to give. ^1H NMR ($CDCl_3$, 300 K, ppm): 9.78 (bs, NH^+), 7.42–7.11 (m), 4.58 (bs, 2H, CH_2N), 3.83 (bs, 2H, CH_2N), 2.89 (bs, 6H, NCH_3), 2.65 (bs, 6H, NCH_3). $^{19}F\{^1H\}$ NMR ($CDCl_3$, 300 K, ppm): −139 (bs), −148.6 (bs), −163.4 (bs). $^{119}Sn\{^1H\}$ NMR: ($CDCl_3$, 300 K, ppm): −604.0 (ddt), $^1J(^{119}Sn, ^{19}F) \approx 2520$ Hz.

For **5**: *Method A.* The compound **5** (0.2 g, 0.36 mmol) was dissolved in 10 ml of dichloromethane and NH_4F (20 eq. excess) was added. The reaction mixture was stirred for five days. Afterwards the soluble part was filtrated off and the volatiles were vacuo removed. The product was dissolved in CD_3OD. ^1H NMR (500.13 MHz, CD_3OD, 300 K, ppm): 7.44 (bs, 1H), 7.27 (m, 2H), 5.16 (bs, NH_4^+), 4.2 (bs, 4H, NCH_2), 2.74 (bs, 12H, NCH_3). $^{19}F\{^1H\}$ NMR (CD_3OD, 300 K, ppm): −140 to −155 (vbs). $^{119}Sn\{^1H\}$ NMR (CD_3OD, 300 K, ppm): −600.9 (pseudo-quintet), $^1J(^{119}Sn, ^{19}F) = 2308$ Hz. ESI-MS: MW = 405. Positive ion mode: *m/z* (%): $[M-NH_4F+H]^+$, 369 (100), $[L^{NCN}SnF_2]^+$, 349 (60), $[M-F-2^*HF-CH_2{=}N(CH_3)_2]$, 271 (68), $[L^{NCN}]^+$, 193 (57). Negative ion mode: $[L^{NCN}SnF_4]^-$, 387 (100).

Method B. To a toluene solution of **5** (90 mg, 0.16 mmol) was added $L^{CN}nBu_2SnF$ (190 mg, 0.48 mmol) and the reaction mixture was stirred and heated at 80 °C for 5 days. Afterwards toluene was removed by filtration and the remaining insoluble solid was washed several times with toluene. The solid was investigated by ESI/MS: MW = 1161; *m/z* (%): Positive ion mode: $[(L^{NCN}SnF_4)_3+K]^+$, 1200 (10); $[(L^{NCN}SnF_4)_3+Na]^+$, 1184 (49); $[(L^{NCN}SnF_4)_3+H]^+$, 1162 (11); $[M-(L^{NCN}SnF_4)+ Na]^+$, 797 (100); $[M-(L^{NCN}SnF_4)+H]^+$, 775 (35); $[L^{NCN}SnF_3+K]^+$, 407 (61). Negative ion mode: $[L^{NCN}SnF_4]^-$, 387 (100). Afterwards the solid was dissolved in $CDCl_3$ to give: ^1H NMR ($CDCl_3$, 300 K, ppm): 9.78 (bs, NH^+), 7.42–7.11 (m), 4.58 (bs, 2H, CH_2N), 3.83 (bs, 2H, CH_2N), 2.89 (bs, 6H, NCH_3), 2.65 (bs, 6H, NCH_3). $^{19}F\{^1H\}$ NMR ($CDCl_3$, 300 K, ppm): −141 (bs), −146.8 (bs), −161.7 (s). $^{119}Sn\{^1H\}$ NMR: ($CDCl_3$, 300 K, ppm): −601.2 (ddt), $^1J(^{119}Sn, ^{19}F) \approx 2520$ Hz. ESI-MS: MW = 388; *m/z* (%). Positive ion mode: $[M+K]^+$, 427 (49), $[M+K-HF]^+$, 407 (75), $[M-F]^+$, 369 (93), $[M-F-HF]^+$, 349 (100), $[M-F-2^*HF-CH_2{=}N(CH_3)_2]$, 271 (32), $[L^{NCN}+H]^+$, 193 (90). Negative ion mode: $[L^{NCN}SnF_4]^-$, 387 (100).

5. Supplementary material

CCDC 636307, 636308 and 636309 contain the supplementary crystallographic data for **1c**, **5** and **5c**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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