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Tri- and diorganostannates containing 2-(*N*,*N*-dimethylaminomethyl)phenyl ligand

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ABSTRACT

The *C,N*-chelated tri and diorganotin(IV) chlorides react with both protic mineral acids and carboxylic acids. The nitrogen atom of the L^{CN} ligand (where L^{CN} is 2-(dimethylaminomethyl)phenyl) is thus quarternized – protonated and new Sn–X bond (X = Cl, Br, I or the remainder of the starting acid used) is simultaneously formed. The set of zwitterionic tri and diorganostannates containing protonated 2-(dimethylaminomethyl) phenyl-moiety was prepared and structurally characterized by multinuclear NMR spectroscopy and XRD techniques. In all these cases, the intramolecular N–H···X bond is present in the molecule. Despite the central tin atom remains five-coordinated (except for the $[HL^{CN}H]^+[(n\text{-}Bu)_2SnCl(NO_3)_2]^-$) and reveals a distorted trigonal bipyramidal geometry, the ^{119}Sn NMR chemical shift values of these zwitterionic stannates are somewhat shifted to the higher field than corresponding starting *C,N*-chelated tri and diorganotin(IV) halides. Reactions of *C,N*-chelated organotin(IV) halides with various Lewis acids are also discussed.

1. Introduction

The tetraalkylstannanes react with protic acids to give triorganotin(IV) species with high yield at mild conditions. Breaking of tin–aryl bonds seems to be even much easier [1]. In the case of triorganotin(IV) halides, the well known Kocheshkov reaction is applied to prepare much polar di or monoorganotin(IV) halides with rather low selectivity and usually drastic conditions and long reaction time [2]. The reactivity of mixed alkyl-aryltin(IV) compounds with mineral acids, mainly HCl in a polar solvent, is of increasing interest due to an efficiency of products of this reaction – trichlorotin(IV) substituted solid support in transesterification processes [3] or ring opening polymerization of ε-caprolactone [4].

In previous works, we have described the product of hydrolysis of $L^{CN}SnCl_3$ (where L^{CN} is 2-(dimethylaminomethyl)phenyl) to be a product of one ligand migration, $[L^{CN}SnCl_4]^-[HL^{CN}{}_2SnCl_2]^+$, where one of the amino group of ligand was quarternized – protonated (Scheme 1A) [5]. Similar results were found by Varga and Silvestru for hydrolysis of $L^{CN}SnBr_3$ [6]. Both the hydrolytic products reveal strong intermolecular bond between NH and the halide atom from $[L^{CN}SnX_4]^-$ (X = Cl, Br) fragment. In the case of bischelating compounds (L^{NCN} is 2,6-bis(dimethylaminomethyl)phenyl), the zwitterionic species are observed from the hydrolysis of di or monoorganotin(IV) compounds (Scheme 1B) – for hydrolysis of $L^{NCN}Sn(n\text{-}Bu)Cl_2$ [7], $L^{NCN}SnF_3$[8] and $L^{NCN}SnCl_3$ [7]. On the other hand, $L^{NCN}SnBr_3$ hydrolyzes to form a dimeric structure $[HL^{NCN}SnBr_3(OH)]_2$ connected *via* OH···Br bridges (Scheme 1C) [9].

The triorganotin(IV) chlorides containing one *C,N*-chelating ligand were also hydrolyzed with an excess of sodium hydroxide [10]. The composition of the final reaction mixtures is strongly dependent on the nature of the substituents bonded to the central tin atom. The di-*n*-butyltin, dimethyltin and diphenyltin derivatives undergo an equilibrium hydroxide ↔ stannoxane (oxide), where the tin-hydroxo species react spontaneously and reversibly with atmospheric carbon dioxide to form the corresponding bridged tin alkyl-carbonates. In comparison, the diphenyl derivative hardly reacts with CO_2 and the di-*t*-butyl-substituted one does not react at all and remains as a stable tin hydroxide. Unsuccessful attempts to quarternize the nitrogen atom of the *C,N*-chelating ligand with diluted HCl and HF were also discussed there [10].

In this paper, we report on the reactivity of *C,N*-chelated tri and diorganotin(IV) species (for ^1H NMR numbering see Scheme 2) [11] towards equimolar, as well as a high excess of mineral acids. Reactivity of *C,N*-chelated organotin(IV) halides towards carboxylic acids and various Lewis acids is also discussed.

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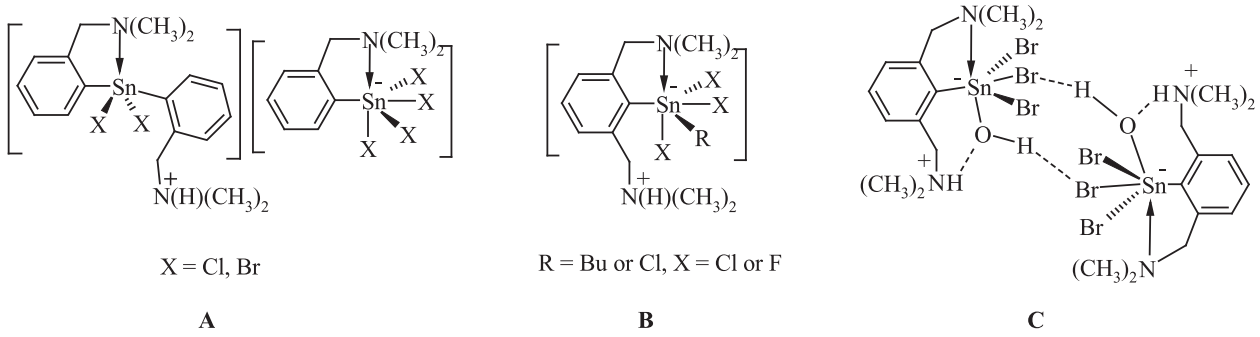


Scheme 1. Hydrolytic products of di and monoorganotin(IV) halides.

2. Results and discussion

The reactions of tri and diorganotin(IV) chlorides containing *C,N*-chelating ligand(s) with mineral as well as Lewis acids have been carried out in order to support literature results mentioned above and to prepare di or monoorganotin(IV) halides by an easier way.

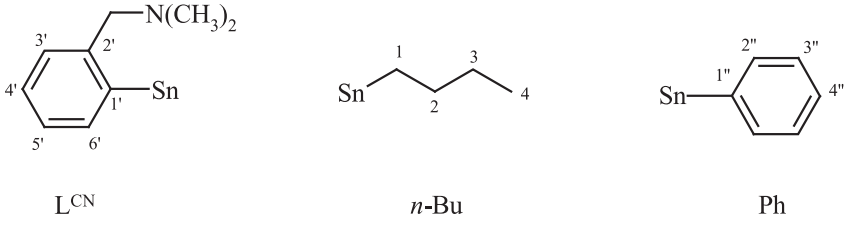
2.1. General remarks

$L^{CN}(n\text{-Bu})_2SnCl$, $L^{CN}Ph_2SnCl$, $(L^{CN})_2(n\text{-Bu})SnCl$, $L^{CN}(n\text{-Bu})SnCl_2$, $L^{CN}PhSnCl_2$ and $(L^{CN})_2SnCl_2$ were reacted with a slight excess of HCl, an excess of HBr and HI, respectively, to give corresponding zwitterionic stannates (for numbering of compounds see Scheme 3). All these reactions were carried out in the air and concentrated aqueous hydrohalic acids were used. When HCl is used, satisfactory yields (from 65% for $L^{CN}Ph_2SnCl\cdot HCl$ up to 97% for $L^{CN}(n\text{-Bu})_2SnCl\cdot HCl$; all zwitterionic stannates are scripted in the form of adducts – "substrate·acid" – for better clarity see also Scheme 3) of desired zwitterionic stannates are obtained. The situation is much more complicated when HBr or HI is used. When only 1.1 eq. of respective hydrohalic acid was reacted with appropriate substrate the formation of inseparable mixture of products was observed by multinuclear NMR spectroscopy. To pass over this problem, an excess (2.2 eq.) of hydrohalic acid needs to by applied. The stronger acid displaces HCl and simultaneous formation of two new Sn–X bonds (X = Br or I) and the protonation of the $CH_2N(CH_3)_2$ group of the *C,N*-chelating ligand proceeds. The second problem is that slow oxidation to elemental bromine or iodine occurs during the reaction time. Into the bargain, the products need to be washed with methanol to remove residual hydrohalic acid and/or elemental X_2 (X = Br or I) and subsequent recrystallization of the crude product is necessary. These operations decrease the overall yield of the reaction (for example only 47% yield in the case of $L^{CN}Ph_2SnBr\cdot HBr$). The stannates bearing the phenyl substituent are somewhat unstable in comparison with butyl-substituted stannates. In the case of $L^{CN}Ph_2SnBr\cdot HBr$, an instability of this compound in a coordinating solvent (MeOH) was observed when the sample was left for a couple of days in a closed vessel to give $L^{CN}Ph_2SnBr$ [11d]. This instability is probably a result of a concurrency of bases $-NMe_2$ and $-OMe$ and is confirmed by ^1H and ^{119}Sn NMR spectroscopy as well as XRD analysis of the single crystals.

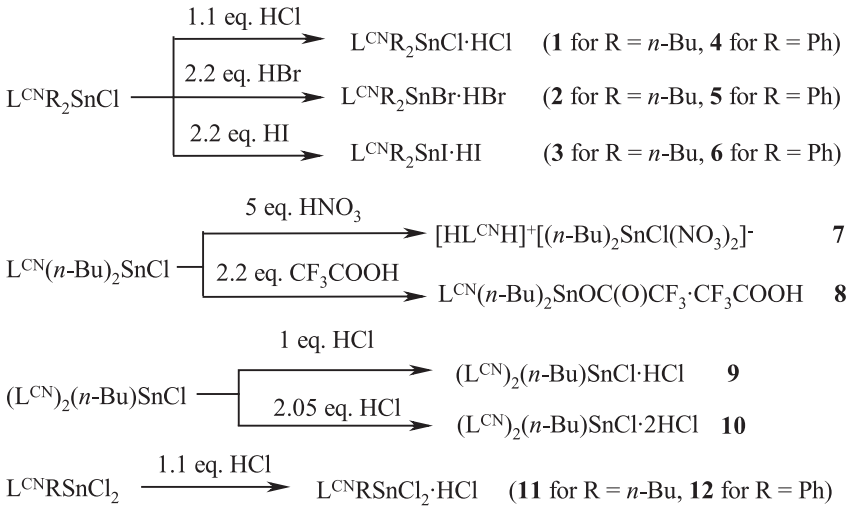
2.2. Preparation and structural characterization of zwitterionic triorganostannates

Prepared triorganostannates of the general formula $L^{CN}R_2SnX\cdot HX$ (where R = *n*-Bu or Ph, X = Cl, Br or I) were characterized by multinuclear NMR spectroscopy and XRD techniques (Fig. 1). In all these cases the central tin atom is five-coordinated and reveals distorted trigonal bipyramidal geometry. According to the Bent's rule [12], both electronegative atoms X (X = Cl, Br or I) occupy axial positions and all three carbon atoms are situated in equatorial positions, independently whether R is *n*-Bu or Ph. In the case of $L^{CN}(n\text{-Bu})_2SnX\cdot HX$ the interatomic distances Sn1–X1 (2.7292(9) Å for Cl, 2.8117(11) Å for Br and 2.9412(16) Å for I) and Sn1–X2 (2.5412(9) Å for Cl, 2.7258(11) Å for Br and 2.8929(10) Å for I) are unequal thanks to the presence of the strong intramolecular N–H···X bond. The differences in these interatomic distances decrease with increasing covalent radii [13] of X (0.1880 Å for X = Cl, 0.0859 Å for X = Br and finally 0.0483 Å for X = I). The X1–Sn1–X2 interatomic angle changes from 178.16(3)° for X = Cl to 174.39(3)° for X = Br, and is very close to the ideal flat angle. The sum of all equatorial C–Sn–C angles is 359.3° for $L^{CN}(n\text{-Bu})_2SnCl\cdot HCl$ (**1**), 359.8° for $L^{CN}(n\text{-Bu})_2SnBr\cdot HBr$ (**2**) and 359.4° for $L^{CN}(n\text{-Bu})_2SnI\cdot HI$ (**3**), respectively.

The ^1H NMR spectra of all compounds studied display typical broad signal of the NH moiety about 10.3 ppm which is within the range characteristic for this bonding array. This chemical shift is dependent on the deuterated solvent used and varies for example from 11.06 ppm (in $CDCl_3$) to 9.61 ppm (in CD_3OD) in the case of **1** (for other compounds see Table 1). The presence of the direct N–H bond causes splitting of the original singlet assigned to the CH_2N moiety to a doublet at ca. 4.3 ppm with coupling constant of about 5.2 Hz. The signal of the $N(CH_3)_2$ group is split into a doublet (with coupling constant being about 4.8 Hz) for the same reason, too. The



Scheme 2. General ^1H NMR numbering.



Scheme 3. The reactivity of *C,N*-chelated organotin(IV) chlorides and general numbering of prepared compounds.

^{1}H NMR chemical shift value of the $N(CH_3)_2$ group is strongly influenced by deuterated solvent used. When compound **1** is dissolved in $CDCl_3$, the signal of the $N(CH_3)_2$ group is found at 2.68 ppm, which is in contrast with the value found in C_6D_6 (1.67 ppm). The position and the value of the $^3J(^{119}Sn, ^1H)$ satellites of the doublet of the H(6′) signal in the ^{1}H NMR spectra is another useful tool for characterizing all *C,N*-chelated organotin compounds. Prepared triorganostannates reveal the coupling constant $^3J(^{119}Sn, ^1H)$ being between 50 Hz up to 65 Hz (see Experimental). On the other hand diorganostannates exhibit higher coupling constant $^3J(^{119}Sn, ^1H)$ within the range of 75–95 Hz, which is in good agreement with previous published results [11b–e]. The ^{119}Sn NMR chemical shift values of these zwitterionic stannates are shifted to lower frequencies than corresponding starting $L^{CN}(n\text{-Bu})_2SnX$. The trend is that $\Delta\delta$ ^{119}Sn decreases with increasing of the covalent radii of X (X = Cl, Br or I) as shown in Table 1. In addition, the ^{15}N NMR spectra of **1** were recorder in DMSO-d_6 ($\delta = -337.5$ ppm) and CD_3OD ($\delta = -336.7$ ppm). When measured without the proton decoupling the signal splits to a doublet with coupling constant $^1J(^1H, ^{15}N) = 74.6$ Hz in DMSO-d_6.

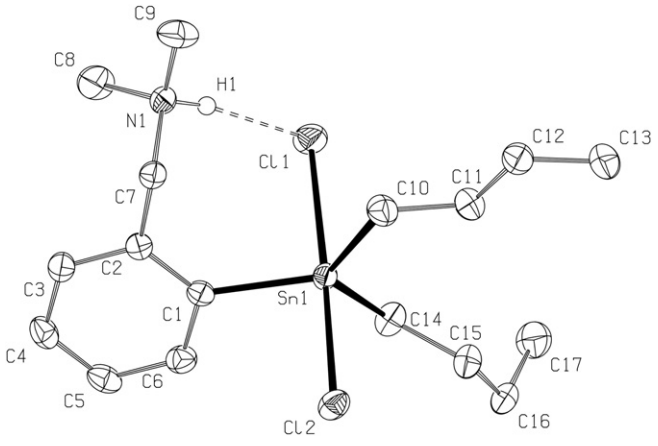


Fig. 1. Molecular structure of **1** (ORTEP view, 50% probability level). Hydrogen atoms bonded to carbon atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Sn1–Cl1 2.7292(9), Sn1–Cl2 2.5412(9), Sn1–C1 2.154(3), Sn1–C10 2.138(4), Sn1–C14 2.141(3), Cl1–Sn1–Cl2 178.16(3), Cl1–Sn1–C1 87.63(8), Cl2–Sn1–C1 90.24 (8), C1–Sn1–C10 127.92(13), C1–Sn1–C14 111.30(13), C10–Sn1–C14 120.30(16). H-bonding: N1–Cl1 3.057(2), N1–H1···I1 170.4. For **2**: Sn1–Br1 2.8117(11), Sn1–Br2 2.7258(11), Sn1–C1 2.155(7), Sn1–C10 2.142(9), Sn1–C14 2.160(8), Br1–Sn1–Br2 174.39(3), Br1–Sn1–C1 88.8(2), Br2–Sn1–C1 86.4(2), C1–Sn1–C10 115.9(3), C1–Sn1–C14 126.2(3), C10–Sn1–C14 117.7(3). H-bonding: N1–Br1 3.234(6), N1–H1···Br1 167.0. For **3**: Sn1–I1 2.9412(16), Sn1–I2 2.8929(10), Sn1–C1 2.165(9), Sn1–C10 2.152(13), Sn1–C14 2.148(10), I1–Sn1–I2 176.73(5), I1–Sn1–C1 87.3(2), I2–Sn1–C1 91.1(2), C1–Sn1–C10 122.3(4), C1–Sn1–C14 113.4(4), C10–Sn1–C14 123.7 (4). H-bonding: N1–I1 3.243(7), N1–H1···I1 174.2.

The vicinity of the central tin atom in $L^{CN}Ph_2SnCl\cdot HCl$ (**4**) (Fig. 2) reveals analogous geometry as in the case of mentioned $L^{CN}(n\text{-Bu})_2SnX\cdot HX$. The interatomic distances of Sn1–Cl1 (2.7270 (7) Å) and Sn1–Cl2 (2.5015(7) Å) are a little bit shorter than in **1** (2.7292(9) Å and 2.5412(9) Å, respectively). The Cl1–Sn1–Cl2 interatomic angle 168.76(2)° differs slightly from almost flat angle in the case of **1** (178.16(3)°) described above. This deflection is caused by the sterical hinderance of the two phenyl groups when compared with the corresponding butyl-substituted zwitterionic stannate. The sum of equatorial interatomic angles is 359.6°. Unfortunately single crystals of $L^{CN}Ph_2SnBr\cdot HBr$ (**5**) and $L^{CN}Ph_2SnI\cdot HI$ (**6**) were not obtained.

According to literature [14], a high excess of HCl (20 eq.) was used in the reaction with $L^{CN}(n\text{-Bu})_2SnCl$ in boiling methanol in order to remove the butyl group. Surprisingly no signals of $L^{CN}(n\text{-Bu})_2SnCl\cdot HCl$ as a by-product were observed in the ^{119}Sn NMR spectra. The only signal detected at −22.0 ppm can be attributed by our opinion to a $[(n\text{-Bu})_2SnCl_3]^-$ anion (controversial case is that the published chemical shift for $[(n\text{-Bu})_2SnCl_3]^-$ in the ^{119}Sn NMR spectra of a mixture with $[(n\text{-Bu})_2SnCl_2F]^-$ is −122 ppm [15]) which is compensated with the *N,N*-dimethylbenzylammonium as a counter cation. The chemical shift in the ^{119}Sn NMR spectrum is about 150 ppm lower than found for $(n\text{-Bu})_2SnCl_2$ ($\delta = 126.3$ ppm) [16]. This suggestion is also supported by the ^{1}H NMR spectra pattern. The exactly same results were obtained when gaseous HCl was bubbled through a diethyl ether solution of $L^{CN}(n\text{-Bu})_2SnCl$ for 10 min.

Since the reaction of $L^{CN}(n\text{-Bu})_2SnCl$ with only one equivalent of HNO_3 gave no reproducible results, the excess of HNO_3 was used. The reaction of $L^{CN}(n\text{-Bu})_2SnCl$ with 5 eq. of HNO_3 ended analogously by the formation of *N,N*-dimethylbenzylammonium connected by one H-bond to a counter anion of empirical formula $[(n\text{-Bu})_2SnCl(NO_3)_2]^-$ (Fig. 3). Surprisingly the Sn–Cl bond remained untouched. According to τ-descriptor, the coordination geometry of the central tin atom in the solid state can be described as a distorted square pyramidal with O1, O4, C10 and C14 atoms in the base of the pyramid and the Cl1 as the top atom. Computed τ-descriptor for five-

Table 1
Selected ^{1}H and ^{119}Sn NMR chemical shift values of prepared compounds with coupling constants of doublets in Hz in parentheses.

Compound	Solvent	NH	H(6′)	CH_2N	$N(CH_3)_2$	^{119}Sn	$\Delta\delta$ ^{119}Sn [a]
$L^{CN}(n\text{-Bu})_2SnCl\cdot HCl$	$CDCl_3$	11.06	7.84 (6.7)	3.83 (5.4)	2.68 (4.8)	−105.1	−57.6
	C_6D_6	10.81	8.11 (7.3)	3.40 (5.5)	1.67 (4.9)	−133.7	−84.5
	CD_3OD	9.61	7.69 (7.0)	4.39 (5.6)	2.87 (4.7)	−77.5/−336.7[b]	−25.5
	DMSO-d_6	10.17	7.64 (6.1)	4.36 (4.9)	2.76 (4.6)	−137.3/−337.5[b]	−80.0
$L^{CN}(n\text{-Bu})_2SnBr\cdot HBr$	$CDCl_3$	10.44	7.85 (7.2)	3.75 (4.8)	2.64 (4.8)	−94.2	−54.5
	C_6D_6	10.43	8.10 (7.3)	3.44 (5.5)	1.72 (4.9)	−125.7	−83.9
	DMSO-d_6	9.89	7.63 (5.9)	4.39 (5.5)	2.78 (4.6)	−121.1	−76.2
$L^{CN}(n\text{-Bu})_2SnI\cdot HI$	$CDCl_3$	10.14	7.67 (7.3)	4.16 (4.6)	2.75 (4.0)	−61.0	−28.1
$L^{CN}(n\text{-Bu})_2Sn(OCOCF_3)\cdot CF_3COOH$	$CDCl_3$	10.66	7.73 (7.2)	4.57 (br)	2.87 (4.6)	−130.1	−65.9
$L^{CN}Ph_2SnCl\cdot HCl$	$CDCl_3$	10.55	7.64 (6.2)	4.06 (5.2)	2.31 (5.0)	−224.9	−48.4
	DMSO-d_6	9.83	7.63 (7.3)	4.34 (5.5)	2.41 (4.7)	−252.0	−69.1
$L^{CN}Ph_2SnBr\cdot HBr$	$CDCl_3$	10.32	7.77 (7.2)	4.05 (5.1)	2.18 (4.2)	−213.8	−32.8
	DMSO-d_6	9.82	7.67 (6.5)	4.37 (5.0)	2.43 (4.5)	−238.8	−56.8
$L^{CN}Ph_2SnI\cdot HI$	$CDCl_3$	10.47	7.79 (7.6)	4.55 (6.6)	2.75 (5.1)	−298.4	−98.5
$L^{CN}(n\text{-Bu})SnCl_2\cdot HCl$	$CDCl_3$	10.28	7.61 (6.9)	4.51 (5.5)	2.82 (4.7)	−196.0	−91.7
$L^{CN}PhSnCl_2\cdot HCl$	THF-d8	10.15	7.51 (6.2)	4.60 (6.1)	2.85 (5.2)	−262.7	−82.5
$(L^{CN})_2(n\text{-Bu})SnCl\cdot HCl$	$CDCl_3$	11.80	8.22/8.16[c] (br)	4.03 (147.1)/3.39(94.4) [c]	2.53/1.64[c] (br)	−125.0	−6.9
$(L^{CN})_2(n\text{-Bu})SnCl\cdot 2HCl$	DMSO-d_6	10.77	7.84 (7.3)	4.51 (5.2)	2.72 (4.6)	−216.4	−99.4
	CD_3OD	–[d]	7.88 (6.8)	4.48 (s)	2.82 (s)	−188.6	−72.1
$[HL^{CN}H]^+[Bu_2SnCl(NO_3)_2]^-$	C_6D_6	9.16	–	3.48 (5.4)	2.03 (5.0)	−401.6	–

[a] $\Delta\delta$ ^{119}Sn are relative to corresponding *C,N*-chelated organotin halides or trifluoroacetate (e.g. $L^{CN}Ph_2SnBr\cdot HBr$ is relative to $L^{CN}Ph_2SnBr$; except of $[HL^{CN}H]^+\backslash Bu_2SnCl(NO_3)_2]^-$).
[b] ^{15}N NMR chemical shift values.
[c] Signals are split due to the presence of two unequivalent H(6′) protons and NCH_2 and $N(CH_3)_2$ groups, for details see text.
[d] Signal disappears probably due to fast D for H exchange.

coordination $\tau = (\alpha - \beta)/60 = (160.73 - 147.21)/60 = 0.23$ (extreme forms: $\tau = 0.00$ for square pyramid and 1.00 for trigonal bipyramid) [17]. The O2 and O5 atoms are 2.8492(19) Å and 2.7873(19) Å, respectively, distant from Sn1 and are within the range of the sum of van der Waals (3.58 Å) and covalent radii (2.05 Å) [13,18]. The ^{119}Sn NMR chemical shift value at −401.6 ppm matches with seven-coordinated tin which may be caused by bonding equality of both $(NO_3)^-$ groups in the solution in the NMR time scale.

Reaction of $L^{CN}(n\text{-Bu})_2SnCl$ with CF_3COOH as a strong carboxylic acid has been also studied. This involves the reaction of the $L^{CN}(n\text{-Bu})_2SnCl$ with the excess of CF_3COOH (2.2 eq.) resulting in the formation of desired $L^{CN}(n\text{-Bu})_2SnOC(O)CF_3\cdot CF_3COOH$ (**8**). The molecular structure and parameters of the multinuclear NMR spectra are similar to triorganostannates discussed *vide supra*. In addition, the ^{13}C and ^{19}F NMR spectra of this compound in $CDCl_3$ were recorded in order to evaluate the presence of the CF_3COO^- groups. There are two characteristic quartets in the ^{13}C NMR spectra, first one at 162.1 ppm (COO) with coupling constant $^{2}J(^{19}F, ^{13}C) = 41.1$ Hz and the second one at 115.9 ppm with much higher coupling constant $^{1}J(^{19}F, ^{13}C) = 288.2$ Hz (CF_3). The only one signal for both CF_3 groups was found in the ^{19}F NMR spectra at −74.7 ppm. These data indicate the equality of both CF_3COO^- substituents in solution. The second pathway for the preparation of this compound is *via* the reaction of $L^{CN}(n\text{-Bu})_2Sn(OCOCF_3)$, prepared by the reaction of $L^{CN}(n\text{-Bu})_2SnCl$ and CF_3COOAg [19], with only 1.1 eq. of

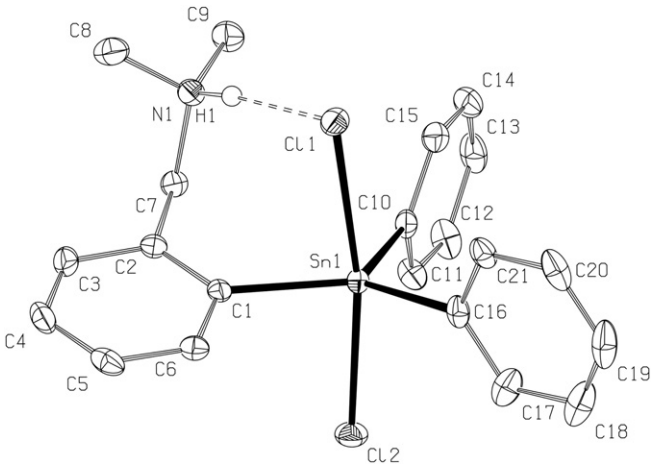


Fig. 2. Molecular structure of **4** (ORTEP view, 50% probability level). Hydrogen atoms bonded to carbon atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Sn1–Cl1 2.7270(7), Sn1–Cl2 2.5015(7), Sn1–C1 2.156(3), Sn1–C10 2.148(2), Sn1–C16 2.162(2), Cl1–Sn1–Cl2 168.76(2), Cl1–Sn1–C1 82.05(6), Cl2–Sn1–C1 87.31(7), C1–Sn1–C10 120.49(9), C1–Sn1–C16 124.73(9), C10–Sn1–C16 114.38(9). H-bonding: N1–Cl1 3.083(2), N1–H1···Cl1 172.0.

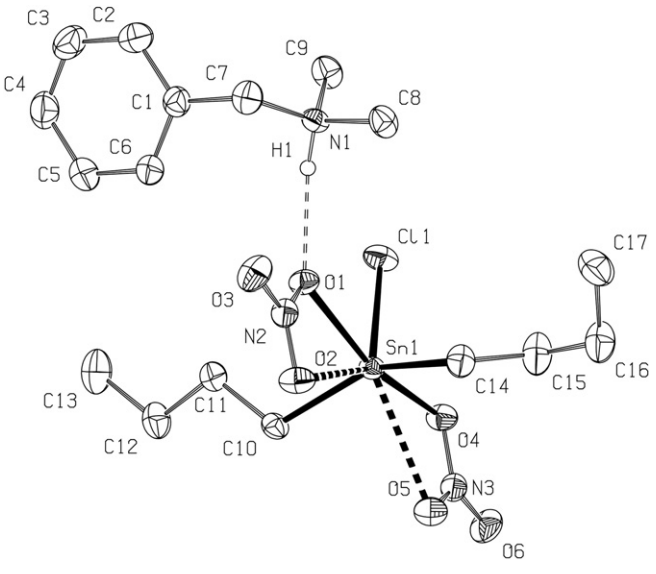


Fig. 3. Molecular structure of **7** ½C_6H_6 (ORTEP 40% probability). Benzene molecule and hydrogen atoms bonded to carbon atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Sn1–Cl1 2.4052(7), Sn1–O1 2.3108(17), Sn1–O2 2.8492(19), Sn1–O4 2.2546(17), Sn1–O5 2.7873(19), Sn1–C10 2.112(3), Sn1–C14 2.105(3), O1–Sn1–O4 160.73(7), O4–Sn1–O5 49.68(6), O1–Sn1–O5 149.58(6), O1–Sn1–Cl1 78.87(5), C10–Sn1–C14 147.21(10), Cl1–Sn1–O4 81.86(5), Cl1–Sn1–O5 131.54(4). H-bonding: N1–O1 2.893(3), N1–H1···O1 149.7.

CF_3COOH. This result is confirmed by multinuclear NMR spectroscopy. The tin atom is five-coordinated once again in the solid state and posses the geometry of distorted trigonal bipyramid (Fig. 4) with the sum of all C–Sn–C interatomic angles being practically 360° (359.99°). The interatomic angle O1–Sn1–O3 (174.62(12)°) is closed to the ideal 180° angle.

On the other hand, when weak carboxylic acids, such as PhCOOH, FcCOOH (where Fc is ferrocenyl) and picric acid, were used the reactions did not proceed at all and only starting substrates together with respective acids were identified in the reaction mixture by multinuclear NMR spectroscopy. Elevating the temperature had no effect on the reaction progress. The CF_3SO_3H and HBF_4 acids were reacted with $L^{CN}(n\text{-Bu})_2SnCl$ to give presumably ionic species. According to the ^1H and ^{119}Sn NMR spectroscopy, there is definitely no starting $L^{CN}(n\text{-Bu})_2SnCl$ in the reaction mixture. There are characteristic doublets of the protonated CH_2N and $N(CH_3)_2$ moieties but incredibly no signals of the ^+NH moieties were found around 10 ppm in the ^1H NMR spectra where expected. The only signals detected by ^{119}Sn NMR spectroscopy at 30.5 ppm (for reaction of CF_3SO_3H) and 60.0 ppm (for reaction of HBF_4) can be probably assigned to *in-situ* generated ionic tin-containing species. All these spectra were recorded in $CDCl_3$. These results were reproduced for the second time but still no single crystals have been grown from the reaction mixtures up to now.

Reaction of $L^{CN}(n\text{-Bu})_2SnF$ with HCl, HBr and HI led to the formation of HF and respective triorganotin(IV) halide. These results were confirmed by ^1H and ^{119}Sn NMR spectroscopy. Reaction of $L^{CN}(n\text{-Bu})_2SnF$ with HF is a complex process and no reproducible results were obtained despite several more reactions were carried out. The hydrofluoric acid is definitely not strong enough both to break the intramolecular Sn–N bond and to protonate the nitrogen atom of the *C,N*-ligand since no signals of the $CH_2N^+(H)(CH_3)_2$ group were observed in the ^1H NMR spectra. On the other hand, when stochiometric amounts of dihydric or trihydric acid were used (H_2SO_4 and H_3PO_4, respectively) the reaction always ended with a mixture of unidentified inseparable products, which was confirmed by ^1H and ^{119}Sn NMR spectroscopy. In some cases the formation of free *N,N*-dimethylbenzylammonium can be deduced from ^1H NMR spectra indicating some parallelism with the reaction of excess of HNO_3 with $L^{CN}(n\text{-Bu})_2SnCl$.

The last triorganostannates prepared are the $(L^{CN})_2(n\text{-Bu})SnCl\cdot HCl$ (**9**) and $(L^{CN})_2(n\text{-Bu})SnCl\cdot 2HCl$ (**10**). Unfortunately only the single crystals suitable for XRD analysis of **10** were obtained (Fig. 5). Although compound **9** was isolated as a white crystalline solid, it became oily when stored at room temperature in a glass vial. The tin atom in compound **10** in solid state is five-coordinated as in *vide supra* described zwitterionic stannates and reveals a distorted trigonal bipyramidal geometry, too. Cl1 and Cl2 atoms are placed in the axial positions with C1, C10 and C19 atoms occupying the equatorial sites. The Sn1–Cl1 (2.6423(7) Å) and Sn1–Cl2 (2.5848(6) Å) interatomic distances are not equal. The Cl1–Sn1–Cl2 interatomic angle (176.14(4)°) differs only a little from the ideal flat angle. The sum of equatorial interatomic angles C–Sn–C is 359.65°. There are two intramolecular N–H···Cl bonds in the molecule of **10**. The Cl3 atom is out of the primary coordination sphere of the tin atom (interatomic distance Sn1–Cl3 = 7.4119(6) Å). ^1H NMR spectra of both **9** and **10** exhibit characteristic signal of the NH proton at 11.80 ppm (in $CDCl_3$) and 10.77 ppm (in DMSO-d_6 due to insolubility of **10** in chloroform), respectively. The ^1H NMR spectrum of **9** is relatively complicated since two unequivalent (protonated and not protonated) ligands are present. This results in characteristic ^1H NMR pattern having two broad doublets at 4.03 ppm (CH_2N^+, $J = 147.1$ Hz) and 3.39 ppm (CH_2N, $J = 94.4$ Hz). Another two different broad signals at 2.53 ppm for $N^+(CH_3)_2$ and 1.64 ppm for $N(CH_3)_2$ groups are observed. Splitting of the signals of the protonated $CH_2N^+(H)(CH_3)_2$ moiety into doublets is not evident probably due to the dynamic character of the whole molecule. The value of ^{119}Sn NMR chemical

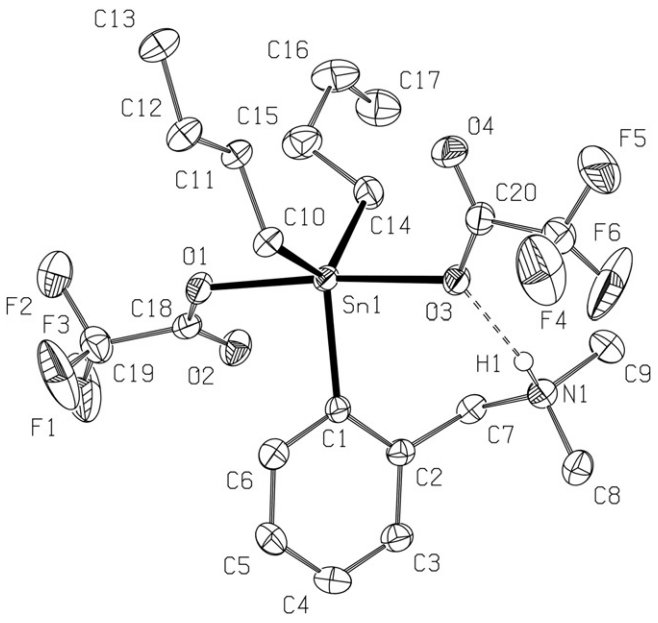


Fig. 4. Molecular structure of **8** (ORTEP view, 50% probability level). Hydrogen atoms bonded to carbon atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Sn1–O1 2.232(2), Sn1–O3 2.334(2), Sn1–C1 2.153(3), Sn1–C10 2.127(3), Sn1–C14 2.140(4), O1–Sn1–O3 174.58(8), O1–Sn1–C1 87.8(10), O3–Sn1–C1 86.69 (10), C1–Sn1–C10 113.19(12), C1–Sn1–C14 124.04(12), C10–Sn1–C14 122.77(13). H-bonding: N1–O3 2.771(3), N1–H1···O3 156.6.

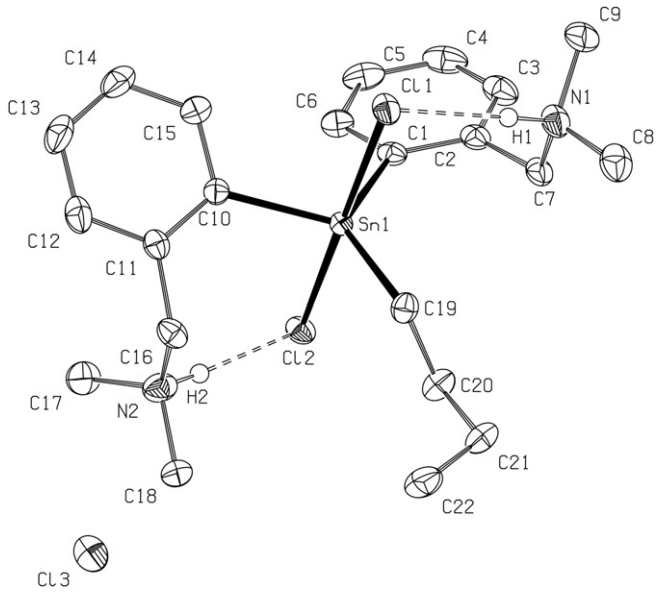


Fig. 5. Molecular structure of **10** (ORTEP view, 50% probability level). Only hydrogen atoms bonded to nitrogen atoms are depicted for clarity. Selected interatomic distances [Å] and angles [°]: Sn1–Cl1 2.6423(7), Sn1–Cl2 2.5848(6), Sn1–Cl3 7.4119(6), Sn1–C1 2.146(2), Sn1–C10 2.157(2), Sn1–C19 2.145(2), Cl1–Sn1–Cl2 176.14(4), Cl1–Sn1–C1 89.08(7), Cl1–Sn1–C10 88.18(7), Cl1–Sn1–C19 86.94(7), Cl2–Sn1–C1 87.07(7), Cl2–Sn1–C10 93.05(7), Cl2–Sn1–C19 95.57(7), C1–Sn1–C10 112.47(9), C1–Sn1–C19 126.60(9), C10–Sn1–C19 120.58(9). H-bonding: N1–Cl1 3.096(2), N2–Cl2 3.074(2), N1–H1···Cl1 172.4, N2–H2···Cl2 172.3.

shift at −125.0 ppm ($CDCl_3$) for **9** differs only by −6.9 ppm relative to $(L^{CN})_2(n\text{-Bu})SnCl$ ($\delta = -118.1$ ppm). On the other hand, there is a −99.4 ppm difference of doubly protonated **10** ($\delta = -216.4$ ppm in DMSO-d_6) relative to starting $(L^{CN})_2(n\text{-Bu})SnCl$.

2.3. Preparation and structural characterization of zwitterionic diorganostannates

In order to expand the set of prepared zwitterionic triorganostannates to diorganostannates, the reactivity of *C,N*-chelated diorganotin(IV) chlorides with hydrochloric acid was the next task. According to previous results of the reactions of $(L^{CN})_2(n\text{-Bu})SnCl$ with HCl, doubly *C,N*-chelated tin(IV) dichloride was treated with 1 eq. and 2 eq. of HCl, respectively. Unfortunately both reactions resulted in a mixture of products. Into the bargain, the products dissolve only in DMSO. In both cases the ^{1}H NMR spectra in DMSO-d_6 are complicated to be interpreted in a right way. The signal at 10.33 ppm indicates the presence of quarternized $CH_2N^+(H)(CH_3)_2$ moiety. In the ^{119}Sn NMR spectra of the reaction of $(L^{CN})_2SnCl_2$ with two equivalents of HCl the original signal of $(L^{CN})_2SnCl_2$ at −266.6 ppm in DMSO-d_6 disappears and two new signals at −434.6 and −454.1 ppm in 3:1 ratio arise. When only 1 eq. of HCl was used signals at −434.6 and −454.1 ppm were detected again, changing only the ratio of the signals to 6:1. The signal at −434.6 ppm was attributed to monoorganotin compound $L^{CN}SnCl_3$ [20] and the signal at −454.1 ppm can be thus assigned to presumably protonated species $L^{CN}SnCl_3\cdot HCl$. In summary, $(L^{CN})_2SnCl_2$ reacts with HCl to give a mixture of $L^{CN}SnCl_3$ and $L^{CN}SnCl_3\cdot HCl$ independently on stoichiometry of the reaction. Due to poor solubility in other common organic solvents no single crystals of these compounds were obtained.

The situation becomes conspicuous when $L^{CN}(n\text{-Bu})SnCl_2$ or $L^{CN}PhSnCl_2$ is used instead of $(LCN^{CN})_2SnCl_2$. Owing to the presence of only one L^{CN} ligand no mixture of products of the reaction with concentrated aqueous HCl is observed. The reactions proceed perfectly to form corresponding zwitterionic stannates which are isolated as white crystalline solids.

The coordination geometry of the central tin atom in both $L^{CN}(n\text{-Bu})SnCl_2\cdot HCl$ (**11**) (Fig. 6) and $L^{CN}PhSnCl_2\cdot HCl$ (**12**) (Fig. 7) can be evidently defined as a distorted trigonal bipyramid. The Sn–Cl interatomic distance of equatorial chlorine atom ($Sn-Cl_{eq} = 2.3740(6)$ Å) is naturally shorter when compared to

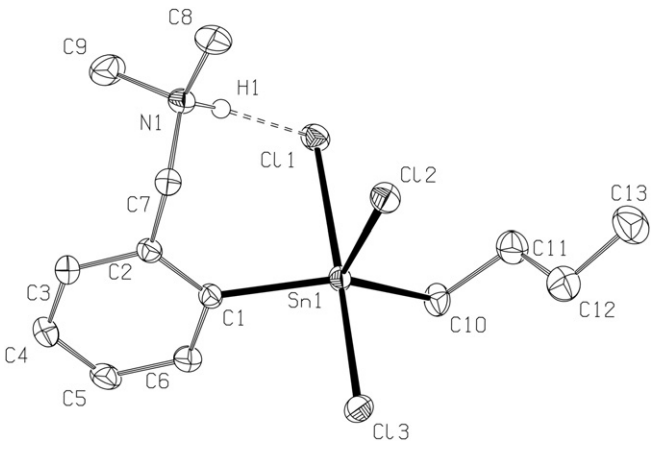


Fig. 6. Molecular structure of **11** (ORTEP view, 50% probability level). Hydrogen atoms bonded to carbon atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Sn1–Cl1 2.6596(5), Sn1–Cl2 2.3740(6), Sn1–Cl3 2.5061(6), Sn1–C1 2.1396 (19), Sn1–C10 2.136(2), Cl1–Sn1–Cl3 177.40(2), Cl1–Sn1–Cl2 86.41(2), Cl2–Sn1–Cl3 92.22(2), Cl1–Sn1–C1 86.50(5), C1–Sn1–C10 132.65(8), C1–Sn1–Cl2 115.26(5), C10–Sn1–Cl2 111.00(6). H-bonding: N1–Cl1 3.0840(18), N1–H1···Cl1 175.4.

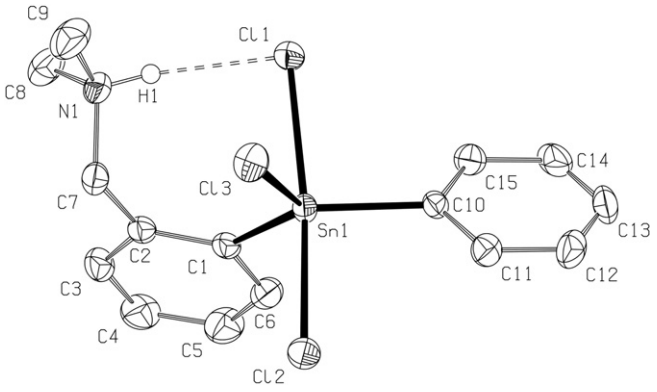


Fig. 7. Molecular structure of **12**·C_6H_6 (ORTEP view, 40% probability level). Benzene molecule and hydrogen atoms bonded to carbon atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Sn1–Cl1 2.5920(7), Sn1–Cl2 2.5019(7), Sn1–Cl3 2.3628(7), Sn1–C1 2.140(2), Sn1–C10 2.126(2), Cl1–Sn1–Cl2 173.50(2), Cl1–Sn1–Cl3 85.97(2), Cl2–Sn1–Cl3 89.29(2), Cl1–Sn1–C1 89.22(7), C1–Sn1–C10 120.63(9), C1–Sn1–Cl3 122.24(6), C10–Sn1–Cl3 117.06(7). H-bonding: N1–Cl1 3.157 (2), N1–H1···Cl1 155.5.

axial chlorines ($Sn-Cl_{ax}$ distances being 2.6596(5) Å and 2.5061 (6) Å, respectively) in **11**. The same trend is clearly seen for **12**, too ($Sn-Cl_{eq} = 2.3628(7)$ Å, $Sn-Cl_{ax}$ distances being 2.5920(7) Å and 2.5019(7) Å, respectively). The interatomic distances between axial chlorine atoms and the central tin atom are somewhat shorter or equal for both **11** and **12** when compared to corresponding interatomic distances in triorganotin stannates (Sn1–Cl1 2.7292(9) Å and Sn1–Cl2 2.5412(9) Å for **1**; Sn1–Cl1 2.7270(7) Å and Sn1–Cl2 2.5015(7) Å for **4**). The sum of interatomic angles among all atoms in the equatorial plane is 358.91° for **11** and 359.93° in the case of **12**. The corresponding values of interatomic angles Cl1–Sn1–Cl3 (177.40(2)°) for **11** and Cl1–Sn1–Cl2 (173.50(2)°) for **12**, respectively) are influenced by the sterical hinderance of the respective organic substituent and are attacking the value of ideal flat angle. This interatomic angle in **11** is very close to corresponding angle in the triorganotin zwitterionic stannate **1** (Cl1–Sn1–Cl 178.16(3)°) discussed above. Due to the presence of only one sterically hindering phenyl substituent in **12**, the value of the Cl1–Sn1–Cl2 angle (173.50(2)°) is much more closer to 180° in comparison with **4** (Cl1–Sn1–Cl2 168.76(2)°) bearing two phenyl substituents. The presence of the direct N–H bond is confirmed by ^{1}H NMR spectroscopy since signals of the NH protons and two doublets assigned to protonated CH_2N and $N(CH_3)_2$ moieties can be found in each spectra. The ^{119}Sn NMR spectra reveal shift of the signals to lower frequencies (−196.0 ppm in $CDCl_3$ for **11** and −262.7 ppm in THF-d8 for **12**) relative to starting $L^{CN}(n\text{-Bu})SnCl_2$ (−104.3 ppm in $CDCl_3$) and $L^{CN}PhSnCl_2$ (−180.2 ppm in THF-d8), respectively.

2.4. Unexpected product of reaction of triphosgene with $L^{CN}(n\text{-Bu})_2SnF$

We have reported on use of $L^{CN}(n\text{-Bu})_2SnF$ for preparation of acyl fluorides a fluoroformates from their chloride precursors recently [21]. These reactions concerned fluorination of phosgene, diphosgene as well as triphosgene. In all three latter cases the formation of COF_2 in the reaction mixture is consequently confirmed by multinuclear NMR spectroscopy as expected [21]. On the other hand, when reaction of triphosgene with six equivalents of $L^{CN}(n\text{-Bu})_2SnF$ was carried out in toluene on the air, crystals of $[HL^{CN}(n\text{-Bu})_2SnCl]_2[SiF_6]$ (**13**) as a minor by-product were isolated from the reaction mixture in 14% yield (relative to starting $L^{CN}(n\text{-Bu})_2SnF$).

The following reaction mechanism is proposed for the formation of **13** (Scheme 4): in the first step, the complete fluorination of the starting triphosgene takes place followed by the formation of the fluorophosgene that dissolves immediately in toluene. Hydrolysis of the fluorophosgene yields hydrogen fluoride that attacks the glass surface giving hexafluorosilicate acid. The hexafluorosilicate acid finally reacts with $L^{CN}(n\text{-Bu})_2SnCl$ that is still present in the reaction mixture forming thus unexpected product **13**. Unfortunately compound **13** is unstable and decomposes to $L^{CN}(n\text{-Bu})_2SnCl$, SiF_4 and hydrofluoric acid when dissolved in deuterated chloroform since ^1H and ^{119}Sn NMR spectra reveal only signals that correspond to pure $L^{CN}(n\text{-Bu})_2SnCl$. This conclusion is further supported by ^{19}F NMR spectroscopy since no signals of the hexafluorosilicate anion were found in the ^{19}F NMR spectrum. Compound **13** dissolves poorly even in C_6D_6 and therefore no NMR spectra in non-polar solvents were recorded.

The single crystals of **13** (Fig. 8) were obtained from a concentrated reaction mixture which was left for one week in a glass flask. Both Sn1 and Sn2 tin atoms reveals distorted trigonal bipyramidal geometry with nearly octahedral SiF_6^{2-} anion connecting both triorganotin(IV) moieties. The Sn1–F3 (2.485(3) Å) and Sn2–F1 (2.400(3) Å) distances are somewhat unequal. On the other hand, the Sn1–Cl1 (2.4568(18) Å) and Sn2–Cl2 (2.4785(18) Å) distances are comparable in **13**. The sum of equatorial C–Sn–C angles is represented by 357.3° and is identical for both C–Sn1–C and C–Sn2–C. The ideal octahedral geometry of the SiF_6^{2-} anion is cracked up due to the existence of two Sn–F–Si bridges lengthening thus the Si1–F1 (1.738(4) Å) and Si1–F3 (1.740(4) Å) bonds. The four remaining Si1–F bonds are about 0.08 Å shorter than Si1–F1 and Si1–F3 bonds (see Fig. 8). As shown in Fig. 8, there are also two multicentric N–H···F intramolecular bonds strongly influencing the geometry of the SiF_6^{2-} anion.

According to the literature, the free SiF_6^{2-} anion posses the O_h symmetry and the corresponding vibrational modes are: $1A_{1g}$ (R) + $1E_g$ (R) + $1F_{2g}$ (R) + $2F_{1u}$ (IR) + $1F_{2u}$ (IR). Indeed, only three characteristic bands were observed in the Raman spectra of the SiF_6^{2-} anion at around 670 (s, υ_sSi–F), 470 (w, υ_{as}Si–F) and 390 (m, δF–Si–F) cm^{-1} [22]. In the case of isolated solid complex **13** the characteristic bands were not observed since only bands situated at 338, 509 and 602 cm^{-1} were found which are closest to previously published results. This disparity may be caused by the presence multiple Si–F···H bonds. The vibrational mode of the molecule is also influenced by two Sn–F–Si bonds that crumple the symmetry of the SiF_6^{2-} anion. Other bands detected by Raman spectroscopy can be assigned to vibrations of remaining bonds in the molecule.

2.5. Reactions of C,N-chelated organotin(IV) compounds with various Lewis acids

Based on previously published results concerning reactions of $L^{CN}(n\text{-Bu})_2SnCl$ and $L^{CN}(n\text{-Bu})_2SnCp$ with $TiCl_4$ [23], further

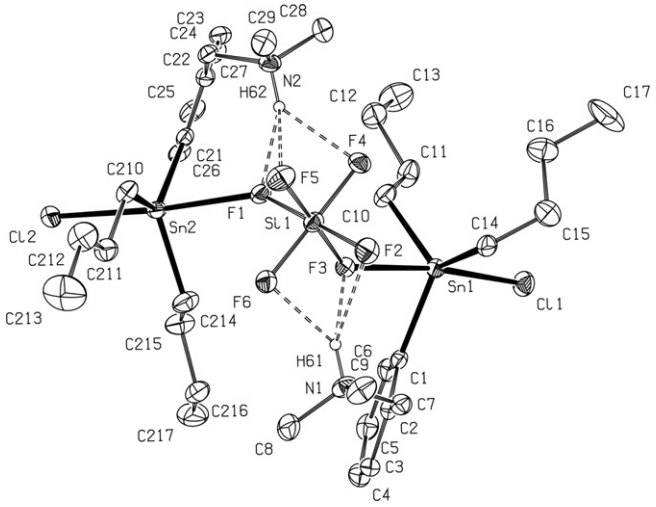
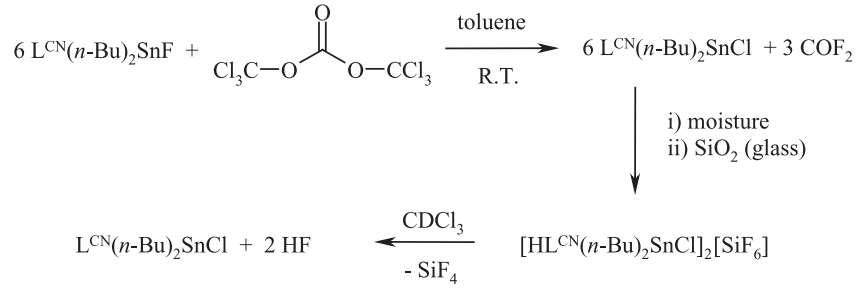


Fig. 8. Molecular structure of **13** (ORTEP view, 30% probability level). Hydrogen atoms bonded to carbon atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Sn1–Cl1 2.4568(18), Sn2–Cl2 2.4785(18), Sn1–F3 2.485(3), Sn2–F1 2.400 (3), Sn1–C1 2.150(5), Sn2–C21 2.152(6), Sn1–C10 2.135(7), Sn2–C210 2.145(7), Sn1–C14 2.148(7), Sn2–C214 2.122(7), Si1–F1 1.738(4), Si1–F2 1.654(4), Si1–F3 1.740 (4), Si1–F4 1.670(4), Si1–F5 1.647(4), Si1–F6 1.657(4), Cl1–Sn1–F3 172.75(9), Cl2–Sn2–F1 173.86(9), Cl1–Sn1–C1 92.03(16), Cl2–Sn2–C21 92.37(16), Cl1–Sn1–C10 101.3(2), Cl2–Sn2–C210 97.32(17), Cl1–Sn1–C14 99.11(17), Cl2–Sn2–C214 97.1(2), C1–Sn1–F3 81.13(17), C21–Sn2–F1 81.53(18), F1–Si1–F2 176.1(2), F3–Si1–F5 176.9 (2), F4–Si1–F6 174.0(2), Sn1–F3–Si1 140.30(18), Sn2–F1–Si1 141.96(19). H-bonding: N1–F2 3.157(6), N1–H61···F2 125.4, N1–F3 2.827(6), N1–H61···F3 155.5, N1–F6 2.836 (6), N1–H61···F6 133.3, N2–F1 2.817(6), N2–H62···F1 155.4, N2–F4 2.909(6), N2–H62···F4 135.0, N2–F5 3.233(6), N2–H62···F5 123.9.

reactivity of *C,N*-chelated organotin(IV) halides with other Lewis acids was also studied. Excess of $TiCl_4$ used in mentioned reactions led to the formation of ionic $[L^{CN}(n\text{-Bu})_2Sn]^+[Ti_2Cl_9]^-$. Unfortunately when $AlCl_3$ was used instead of $TiCl_4$ the reaction did not take place. When $L^{CN}(n\text{-Bu})_2SnCl$ was treated with $AlBr_3$ (1:1 ratio) only simple chlorine for bromine substitution occurred forming thus corresponding $L^{CN}(n\text{-Bu})_2SnBr$ which was confirmed by NMR experimental data found in literature [24]. In this particular case, $AlBr_3$ served as a common brominating agent (proven by ^1H and ^{119}Sn NMR spectroscopy). The Kocheshkov reactions of various *C,N*-chelated organotin(IV) halides with $SnCl_4$ and $SnBr_4$ were also studied. $L^{CN}(n\text{-Bu})_2SnCl$ and $L^{CN}Ph_2SnCl$ were selected as an exemplary substrates. These substrates were reacted with varying ratio of $SnCl_4$ and $SnBr_4$. The formation of mixtures of various *C,N*-chelated organotin(IV) halides and non-chelated organotin(IV) halides was observed in all cases. The assay of corresponding products in the reaction mixtures was elucidated by ^1H and ^{119}Sn NMR spectroscopy. All recorded NMR spectra were then confronted with known experimental data published in literature – for details see Experimental.



Scheme 4. Proposed sequences of reaction of $L^{CN}(n\text{-Bu})_2SnF$ with triphosgene.

2.6. Thermal stability and possible use of prepared zwitterionic triorganostannates

To test the thermal stability of prepared compounds the DSC methods were applied. **1**, **2** and **4** were heated in an open vessel 10 °C/min. In the cases of 1-butyl-substituted compounds, only a melting of solid material was observed. In the case of **4** two different reactions were detected, loss of benzene molecule led to the formation of $L^{CN}PhSnCl_2$ (proven by ^1H and ^{119}Sn NMR spectroscopy) and the second one reaction is a simple loss of HCl to give $L^{CN}Ph_2SnCl$. These two processes are in approx. molar ratio of 4:1 according to ^1H and ^{119}Sn NMR spectroscopy.

In order to explore possible use of prepared zwitterionic stannates as a well defined transferors of mineral acids to organic solvents, the attempts to deprotect 1-*N*-(4,4′-dimethoxytrityl) substituted D-(+)-biotin by **1** have been carried out. After 1 h of reaction of 1-*N*-(4,4′-dimethoxytrityl)-protected D-(+)-biotin with **1**, the unprotected D-(+)-biotin was obtained as a pure compound in DMSO extract in ~30% yield at room temperature. When the reaction mixture was refluxed for 10 min in toluene, it became turbid as the insoluble unprotected D-(+)-biotin precipitated. Essentially quantitative yield of unprotected D-(+)-biotin was obtained in 1 h by this method. All these reactions were monitored by multinuclear NMR spectroscopy and all recorded ^1H and ^{13}C NMR spectra were confronted with the Sigma–Aldrich NMR spectra library [25].

2.7. Correlations concerning the experimental data of a set of prepared triorganostannates

Based on collected experimental data for zwitterionic stannates of general formula $L^{CN}(n\text{-Bu})_2SnX{\cdot}HX$ (X = Cl, Br and I), some correlations concerning ^1H NMR chemical shift values of the NH group (in $CDCl_3$), Sn–X bond lengths, N–H···X interatomic distances, pK_A of used hydrohalic acids and chemical hardness η were studied. All correlation diagrams are available in the Supporting information. In cases of phenyl-substituted compounds, the collected experimental data were not complete due to insolubility of some products in one of solvents used in the *n*-butyl series. Furthermore, the crystal structure of some products was not determined by XRD analyses since no suitable single crystals were obtained.

Generally, one could evaluate the strength of used acid in respective solvent by the $\delta(^1H)$ value of the signal of the NH fragment in ^1H NMR spectra. There is obvious linear correlation between the ^1H NMR chemical shift values of the NH group and pK_A of used hydrohalic acids as depicted in Diagram S1. The strength of the acid used (represented by its pK_A values) influences the ^1H NMR chemical shift value of the NH moiety. The stronger the acid is more the signal of the NH moiety shifts to lower frequencies. For example, in the case of **1** ($pK_A(HCl) = -7$) the signal of the NH moiety is found at 11.06 ppm. On the other hand, for **3** ($pK_A(HI) = -10$) the signal of the NH moiety shifts to 10.14 ppm in $CDCl_3$. The second linear correlation concerns the ^1H NMR chemical shift values of the NH fragment and differences in the interatomic distances Δx (Δx = d(Sn1 − X1) − d(Sn1 − X2)) in Å. With decreasing value of Δx (from 0.1880 Å for **1** to 0.0483 Å in the case of **3**, e.g. with increasing covalent radii of the X atom) the position of the signal of the NH moiety in the ^1H NMR spectra shifts to lower frequencies (from 11.06 ppm for **1** to 10.14 ppm in the case of **3**, recorded in $CDCl_3$, Diagram S2). Similar trend is found when the ^1H NMR chemical shift values of the NH moiety and N–H···X interatomic distances in $L^{CN}(n\text{-Bu})_2SnX{\cdot}HX$ (X = Cl, Br and I) are correlated (Diagram S3). With increasing covalent radii of the X atom (e.g. with lengthening of the N–H···X bond, with softer acid character of the X atom) the more ^1H NMR chemical shift values of the NH moiety are shifted to lower frequencies. The last example of attempt to correlate chemical hardness η ($\eta = (I - A)$, where I is the ionization energy in kJ/mol and A is the electron affinity in kJ/mol of the X atom) and difference in interatomic distances Δx (Δx = d(Sn1 − X1) − d(Sn1 − X2)) for $L^{CN}(n\text{-Bu})_2SnX{\cdot}HX$ (X = Cl, Br and I) is depicted in Diagram S4. With increasing the value of η (e.g. with increasing electronegativity of the X atom) the Δx values are increasing, too.

3. Experimental

3.1. NMR spectroscopy

The NMR spectra were recorded from solutions in $CDCl_3$, benzene-d_6, DMSO-d_6, THF-d8 or CD_3OD on a Bruker Avance 500 spectrometer (equipped with *Z*-gradient 5 mm probe) at frequencies ^1H (500.13 MHz), $^{13}C\{^1H\}$ (125.76 MHz), $^{15}N\{^1H\}$ (50.65 MHz), $^{19}F\{^1H\}$ (470.57 MHz) and $^{119}Sn\{^1H\}$ (186.50 MHz) at 295 K. The solutions were obtained by dissolving of approximately 40 mg of each compound in 0.6 mL of deuterated solvents. The values of ^1H chemical shifts were calibrated to residual signals of $CDCl_3$ ($\delta(^1H) = 7.27$ ppm), benzene-d_6 ($\delta(^1H) = 7.16$ ppm), DMSO-d_6 ($\delta(^1H) = 2.54$ ppm), THF-d8 ($\delta(^1H) = 3.57$ ppm) or CD_3OD ($\delta(^1H) = 3.34$ ppm). The values of ^{13}C chemical shifts were calibrated to signals of $CDCl_3$ ($\delta(^{13}C) = 77.2$ ppm), ^{15}N chemical shifts to external neat nitromethane ($\delta(^{15}N) = 0.0$ ppm). The ^{119}Sn 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 NMR spectra were measured using the inverse gated-decoupling mode.

3.2. Crystallography

The X-ray data (Tables S1–S3, see Supporting information) 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 [26]. The absorption was corrected by integration methods [27]. Structures were solved by direct methods (Sir92) [28] and refined by full matrix least-square based on F^2 (SHELXL97) [29]. 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 $H_{iso}(H) = 1.2\ U_{eq}$(pivot atom) or of 1.5 U_{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, and 0.82 Å for N–H groups.

3.3. DSC

The calorimetric measurements were performed by Mettler DSC 12E calorimeter in perforated alumina pans using heating rate 10 °C/min in the temperature range 20–180 °C. Calorimeter was calibrated with indium and sapphire. Samples were weighted (Sartorius R 160 P) before and after DSC measurements.

3.4. Raman spectroscopy

Raman scattering measurements were carried out using an FT-spectrometer IFS-55 FRA 106 (Bruker); using the excitation line 1064 nm (Nd:YAG laser), with a Ge-detector cooled by liquid

nitrogen. A back-scattering geometry was used. Raman spectra were measured at room temperature.

3.5. Synthesis

$L^{CN}(n\text{-Bu})_2SnCl$ [11e], $L^{CN}Ph_2SnCl$ [11d], $(L^{CN})_2Sn(n\text{-Bu})Cl$ [11e], $L^{CN}(n\text{-Bu})SnCl_2$ [11c] and $L^{CN}PhSnCl_2$ [11b] were prepared according to published procedures. All solvents and both protic and Lewis acids were obtained from commercial sources (Sigma–Aldrich). Diethyl ether was used as received. All reactions were carried out in the air except for reactions of Lewis acids which were handled by standard Schlenk techniques under an argon atmosphere. Single crystals suitable for XRD analyses were obtained from corresponding solutions of products by slow evaporation of the solvent. Melting points are uncorrected.

3.6. Preparation of **1**

Aqueous HCl (35%, 121 μL, 1.37 mmol) was added to a solution of $L^{CN}(n\text{-Bu})_2SnCl$ (500 mg, 1.24 mmol) in diethyl ether (10 mL). The reaction mixture was stirred overnight. Afterwards the volatiles were removed *in vacuo* giving 530 mg of white crystalline product. Yield 97%. M.p. 92–94 °C. ^{1}H NMR ($CDCl_3$, 295 K, ppm): 11.06 (br, 1H, NH); 7.84 (d, 1H, H(6′), $^3J(^1H(5'), ^1H(6')) = 6.7$ Hz, $^3J(^{119}Sn, ^1H) = 60.1$ Hz); 7.44 (m, 1H, H(5′)); 7.30 (m, 2H, H(4′, 3′)); 3.83 (d, 2H, NCH_2, $^3J(^1H(NH), ^1H(NCH_2)) = 5.4$ Hz); 2.68 (d, 6H, $N(CH_3)_2$, $^3J(^1H(NH), ^1H(N(CH_3)_2)) = 4.8$ Hz); 1.88 (m, 4H, H(1)); 1.78 (m, 4H, H(2)); 1.46 (m, 4H, H(3)); 0.96 (t, 6H, H(4)). ^{119}Sn NMR ($CDCl_3$, 295 K, ppm): −105.1. Elemental analysis (%): found: C, 46.9; H, 6.8; N, 3.4. Calcd. for $C_{17}H_{31}Cl_2NSn$ (439.04): C, 46.51; H, 7.12; N, 3.19.

3.7. Preparation of **2**

Aqueous HBr (46%, 774 μL, 6.6 mmol) was added to a solution of $L^{CN}(n\text{-Bu})_2SnCl$ (1.210 g, 3.00 mmol) in diethyl ether (15 mL). The reaction mixture was stirred for 24 h. Afterwards the volatiles were removed *in vacuo* and the crude product was crystallized from acetonitrile giving 1.180 g of white crystalline product. Yield 81%. M.p. 117–119 °C. ^{1}H NMR ($CDCl_3$, 295 K, ppm): 10.44 (br, 1H, NH); 7.85 (d, 1H, H(6′), $^3J(^1H(5'), ^1H(6')) = 7.2$ Hz, $^3J(^{119}Sn, ^1H) = 52.3$ Hz); 7.44 (m, 1H, H(5′)); 7.30 (m, 2H, H(4′, 3′)); 3.75 (d, 2H, NCH_2, $^3J(^1H(NH), ^1H(NCH_2)) = 4.8$ Hz); 2.64 (d, 6H, $N(CH_3)_2$, $^3J(^1H(NH), ^1H(N(CH_3)_2)) = 4.8$ Hz); 1.87 (m, 4H, H(1)); 1.81 (m, 4H, H(2)); 1.44 (m, 4H, H(3)); 0.95 (t, 6H, H(4)). ^{119}Sn NMR ($CDCl_3$, 295 K, ppm): −94.2. Elemental analysis (%): found: C, 38.3; H, 6.1; N, 2.5. Calcd. for $C_{17}H_{31}Br_2NSn$ (527.94): C, 38.68; H, 5.92; N, 2.65.

3.8. Preparation of **3**

Aqueous HI (57%, 739 μL, 5.60 mmol) was added to a solution of $L^{CN}(n\text{-Bu})_2SnCl$ (1.027 g, 2.55 mmol) in diethyl ether (10 mL). The reaction mixture was stirred for 24 h. Afterwards the volatiles were removed *in vacuo*, the residue was washed with MeOH (2 × 2 mL) and the crude product was crystallized from acetonitrile giving 0.888 g of yellowish crystalline product. Yield 56%. M.p. 101–103 °C. ^{1}H NMR ($CDCl_3$, 295 K, ppm): 10.14 (br, 1H, NH); 7.67 (d, 1H, H(6′), $^3J(^1H(5'), ^1H(6')) = 7.3$ Hz, $^3J(^{119}Sn, ^1H) = 60.0$ Hz); 7.39 (m, 1H, H(5′)); 7.34 (m, 2H, H(4′, 3′)); 4.16 (d, 2H, NCH_2, $^3J(^1H(NH), ^1H(NCH_2)) = 4.6$ Hz); 2.75 (d, 6H, $N(CH_3)_2$, $^3J(^1H(NH), ^1H(N(CH_3)_2)) = 4.0$ Hz); 1.86 (m, 4H, H(1)); 1.70 (m, 4H, H(2)); 1.40 (m, 4H, H(3)); 0.90 (t, 6H, H(4)). ^{119}Sn NMR ($CDCl_3$, 295 K, ppm): −61.0. Elemental analysis (%): found: C, 33.0; H, 5.3; N, 2.2. Calcd. for $C_{17}H_{31}I_2NSn$ (621.94): C, 32.83; H, 5.02; N, 2.25.

3.9. Reaction of $L^{CN}(n\text{-Bu})_2SnCl$ with an excess of HCl

$L^{CN}(n\text{-Bu})_2SnCl$ (250 mg, 0.62 mmol) was dissolved in methanol (15 mL) and aqueous HCl (35%, 547 μL, 6.20 mmol) was added. The reaction mixture was refluxed for 1 h and the second portion of HCl (547 μL, 6.20 mmol) was added again. The reflux continued for 1 h. Afterwards the volatiles were removed *in vacuo* and the residue was extracted with $CHCl_3$. The chloroform extract was dried with Na_2SO_4 and filtered. The filtrate was reduced *in vacuo* giving 198 mg of yellow oily product. Yield 67%. ^{1}H NMR ($CDCl_3$, 295 K, ppm): 10.23 (br, 1H, NH); 7.58 (m, 2H, L^{CN} group); 7.41 (m, 3H, L^{CN} group); 4.29 (d, 2H, NCH_2, $^3J(^1H(NH), ^1H(NCH_2)) = 5.1$ Hz); 2.84 (d, 6H, $N(CH_3)_2$, $^3J(^1H(NH), ^1H(N(CH_3)_2)) = 4.6$ Hz); 1.93 (m, 4H, H(1)); 1.85 (m, 4H, H(2)); 1.40 (m, 4H, H(3)); 0.91 (t, 6H, H(4)). ^{119}Sn NMR ($CDCl_3$, 295 K, ppm): −22.0. Elemental analysis (%): found: C, 42.2; H, 7.1; N, 3.1. Calcd. for $C_{17}H_{32}Cl_3NSn$ (475.50): C, 42.90; H, 6.78; N, 2.95.

3.10. Preparation of **4**

Aqueous HCl (35%, 88 μL, 0.99 mmol) was added to a solution of $L^{CN}Ph_2SnCl$ (400 mg, 0.90 mmol) in THF (20 mL). The reaction mixture was stirred for 24 h. Formed precipitate was filtered off and the filtrate was concentrated *in vacuo* giving 281 mg of white crystalline product. Yield 65%. M.p. 148–150 °C. ^{1}H NMR (DMSO-d_6, 295 K, ppm): 9.83 (br, 1H, NH); 8.28 (d, 4H, H(2″), $^3J(^1H(3''), ^1H(2'')) = 6.7$ Hz, $^3J(^{119}Sn, ^1H) = 68.9$ Hz); 7.63 (d, 1H, H(6′), $^3J(^1H(5'), ^1H(6')) = 7.3$ Hz, $^3J(^{119}Sn, ^1H) = 56.2$ Hz); 7.57 (m, 2H, H(4″)); 7.46 (m, 5H, L^{CN} and Ph group); 7.41 (m, 4H, L^{CN} and Ph group); 4.34 (d, 2H, NCH_2, $^3J(^1H(NH), ^1H(NCH_2)) = 5.5$ Hz); 2.41 (d, 6H, $N(CH_3)_2$, $^3J(^1H(NH), ^1H(N(CH_3)_2)) = 4.7$ Hz). ^{119}Sn NMR (DMSO-d_6, 295 K, ppm): −252.0. Elemental analysis (%): found: C, 52.5; H, 5.00; N, 3.0. Calcd. for $C_{21}H_{23}Cl_2NSn$ (479.02): C, 52.66; H, 4.84; N, 2.92.

3.11. Preparation of **5**

Aqueous HBr (46%, 145 μL, 1.23 mmol) was added to a solution of $L^{CN}Ph_2SnCl$ (250 mg, 0.56 mmol) in THF (15 mL). The reaction mixture was stirred overnight. After removing the volatiles *in vacuo* the residue was washed with MeOH (2 × 5 mL) giving 140 mg of white crystalline product. Yield 47%. M.p. 152–153 °C. ^{1}H NMR ($CDCl_3$, 295 K, ppm): 10.32 (br, 1H, NH); 8.22 (d, 4H, H(2″), $^3J(^1H(3''), ^1H(2'')) = 6.6$ Hz, $^3J(^{119}Sn, ^1H) = 62.3$ Hz); 7.77 (d, 1H, H(6′), $^3J(^1H(5'), ^1H(6')) = 7.2$ Hz, $^3J(^{119}Sn, ^1H) = 58.5$ Hz); 7.67 (m, 2H, H(4″)); 7.43 (m, 5H, L^{CN} and Ph group); 7.23 (m, 4H, L^{CN} and Ph group); 4.05 (d, 2H, NCH_2, $^3J(^1H(NH), ^1H(NCH_2)) = 5.1$ Hz); 2.18 (d, 6H, $N(CH_3)_2$, $^3J(^1H(NH), ^1H(N(CH_3)_2)) = 4.2$ Hz). ^{119}Sn NMR ($CDCl_3$, 295 K, ppm): −213.8. Elemental analysis (%): found: C, 44.2; H, 4.3; N, 2.6. Calcd. for $C_{21}H_{23}Br_2NSn$ (567.92): C, 44.41; H, 4.08; N, 2.47.

3.12. Preparation of **6**

Aqueous HI (57%, 163 μL, 1.23 mmol) was added to a solution of $L^{CN}Ph_2SnCl$ (250 mg, 0.56 mmol) in THF (15 mL). The reaction mixture was stirred for 24 h. After removing the solvent *in vacuo* the residue was extracted with $CHCl_3$ (2 × 15 mL). The extract was filtered and the filtrate was concentrated in *vacuo* giving 190 mg of yellowish crystalline product. Yield 51%. M.p. 125–127 °C. ^{1}H NMR ($CDCl_3$, 295 K, ppm): 10.47 (br, 1H, NH); 8.34 (d, 4H, H(2″), $^3J(^1H(3''), ^1H(2'')) = 7.8$ Hz, $^3J(^{119}Sn, ^1H) = 69.0$ Hz)); 7.79 (d, 1H, H(6′), $^3J(^1H(5'), ^1H(6')) = 7.6$ Hz); 7.65 (m, L^{CN} and Ph group); 7.57 (m, L^{CN} and Ph group); 4.55 (d, 2H, NCH_2, $^3J(^1H(NH), ^1H(NCH_2)) = 6.6$ Hz); 2.75 (d, 6H, $N(CH_3)_2$, $^3J(^1H(NH), ^1H(N(CH_3)_2)) = 5.1$ Hz). ^{119}Sn NMR ($CDCl_3$, 295 K, ppm): −298.0. Elemental analysis (%): found: C, 38.5; H, 4.0; N, 2.5. Calcd. for $C_{21}H_{23}I_2NSn$ (661.92): C, 38.1; H, 3.5; N, 2.1.

3.13. Preparation of **7**

L^{CN}(*n*-Bu)$_2$SnCl (403 mg, 1.00 mmol) was dissolved in diethyl ether and aqueous HNO_3 (65%, 346 μL, 5.00 mmol) was added. The reaction mixture was stirred overnight. Afterwards the volatiles were removed *in vacuo* and the residue was extracted with chloroform (15 mL). The chloroform phase was dried with Na_2SO_4 and filtered. Finally the solvent was evaporated giving 365 mg of yellowish oily product. The crude product was recrystallized from benzene. Overall yield 69%. M.p. 84–85 °C. ^{1}H NMR (C_6D_6, 295 K, ppm): 9.16 (br, 1H, NH); 7.15 (m, 3H, L^{CN} group); 7.03 (m, 2H, L^{CN} group); 3.48 (d, 2H, NCH_2, $^3J(^1H(NH), ^1H(NCH_2)) = 5.4$ Hz); 2.03 (d, 6H, $N(CH_3)_2$, $^3J(^1H(NH), ^1H(N(CH_3)_2)) = 5.0$ Hz); 1.32 (m, 4H, H(1)); 1.22 (m, 4H, H(2)); 0.91 (m, 4H, H(3)); 0.76 (t, 6H, H(4)). ^{119}Sn NMR (C_6D_6, 295 K, ppm): −401.6. Elemental analysis (%): found: C, 38.5; H, 6.0; N, 8.1. Calcd. for $C_{17}H_{32}ClN_3Sn$ (528.60): C, 38.63; H, 6.10; N, 7.95.

3.14. Preparation of **8**

L^{CN}(*n*-Bu)$_2$SnCl (528 mg, 1.31 mmol) was dissolved in chloroform (15 mL) and trifluoroacetic acid (214 μL, 2.88 mmol) was added dropwise. The reaction mixture was stirred overnight. The volatiles were then evaporated giving 748 mg of yellowish oily product. Yield 96%. Single crystals were obtained from chloroform solution *via* slow evaporation of the solvent. M.p. 99–103 °C. ^{1}H NMR ($CDCl_3$, 295 K, ppm): 10.66 (br, 1H, NH); 7.73 (d, 1H, H(6′), $^3J(^1H(5'), ^1H(6')) = 7.2$ Hz, $^3J(^{119}Sn, ^1H) = 54.4$ Hz); 7.47 (t, 1H, H(5′)); 7.40 (m, 2H, H(4′, 3′)); 4.57 (br, 2H, NCH_2); 2.87 (d, 6H, $N(CH_3)_2$, $^3J(^1H(NH), ^1H(N(CH_3)_2)) = 4.6$ Hz); 1.76 (m, 4H, H(1)); 1.66 (m, 4H, H(2)); 1.45 (m, 4H, H(3)); 0.95 (t, 6H, H(4)). ^{13}C NMR ($CDCl_3$, 295 K, selected signals, ppm): 162.1 (q, OOC, $^2J(^{19}F, ^{13}C) = 41.1$ Hz); 115.9 (q, CF_3, $^1J(^{19}F, ^{13}C) = 288.2$ Hz). ^{19}F NMR ($CDCl_3$, 295 K, ppm): −74.7. ^{119}Sn NMR ($CDCl_3$, 295 K, ppm): −130.1. Elemental analysis (%): C, 42.9; H, 5.1; N, 2.2. Calcd. for $C_{21}H_{31}F_6NO_4Sn$ (594.17): C, 42.45; H, 5.26; N, 2.36.

3.15. Preparation of **9**

Aqueous HCl (35%, 92 μL, 1.04 mmol) was added to a solution of (L^{CN})$_2$(*n*-Bu)SnCl (500 mg, 1.04 mmol) in diethyl ether (15 mL). The reaction mixture was stirred overnight. Afterwards the volatiles were removed *in vacuo* and the crude oily product was crystallized from chloroform giving 408 mg of yellowish crystals. Yield 76%. M.p. 69–72 °C. ^{1}H NMR ($CDCl_3$, 295 K, ppm): 11.80 (br, 1H, NH); 8.22 and 8.16 (br, 2H, two non-equivalent H(6′)); 7.33 (m, 4H, L^{CN} groups); 7.10 (m, 2H, L^{CN} groups); 4.03 (br d, 2H, $^+NCH_2$, $J = 147.1$ Hz); 3.39 (br d, 2H, NCH_2, $J = 94.4$ Hz); 2.53 (br, 6H, $^+N(CH_3)_2$); 2.21 (m, 2H, H(1)); 1.64 (br, 8H, ($N(CH_3)_2$ and H(2)); 1.31 (m, 2H, H(3)); 0.80 (t, 3H, H(4)). ^{119}Sn NMR ($CDCl_3$, 295 K, ppm): −125.0. Elemental analysis (%): found: C, 51.0; H, 6.6; N, 5.5. Calcd. for $C_{22}H_{34}Cl_2N_2Sn$ (516.12): C, 51.20; H, 6.64; N, 5.43.

3.16. Preparation of **10**

Aqueous HCl (35%, 386 μL, 4.37 mmol) was added to a solution of (L^{CN})$_2$(*n*-Bu)SnCl (500 mg, 2.08 mmol) in diethyl ether (15 mL). The reaction mixture was stirred overnight. Afterwards the volatiles were removed *in vacuo* giving 530 mg of white crystalline product. Yield 92%. M.p. 160–161 °C. ^{1}H NMR (DMSO-d_6, 295 K, ppm): 11.90 (br, 1H, NH); 7.84 (d, 1H, H(6′), $^3J(^1H(5'), ^1H(6')) = 7.3$ Hz, $^3J(^{119}Sn, ^1H) = 77.3$ Hz); 7.70 (d, 1H, H(3′)); 7.41 (m, 2H, H(4′, 5′)); 4.51 (d, 2H, NCH_2, $^3J(^1H(NH), ^1H(NCH_2)) = 5.2$ Hz); 2.72 (d, 6H, $N(CH_3)_2$, $^3J(^1H(NH), ^1H(N(CH_3)_2)) = 4.6$ Hz); 1.89 (br, 2H, H(1)); 1.75 (br, 2H, H(2)); 1.44 (m, 2H, H(3)); 0.93 (t, 3H, H(4)). ^{119}Sn NMR (DMSO-d_6, 295 K, ppm): −216.4. Elemental analysis (%): found: C, 44.8; H, 6.3; N, 4.5. Calcd. for $C_{22}H_{36}Cl_4N_2Sn$ (589.04): C, 44.86; H, 6.16; N, 4.76.

3.17. Preparation of **11**

Aqueous HCl (35%, 127 μL, 1.44 mmol) was added to a solution of L^{CN}(*n*-Bu)$SnCl_2$ (500 mg, 1.31 mmol) in diethyl ether (10 mL). The reaction mixture was stirred overnight. Afterwards the volatiles were removed *in vacuo* giving 504 mg of white crystalline product. Yield 92%. Single crystals were obtained from THF solution *via* slow evaporation of the solvent. M.p. 137–139 °C. ^{1}H NMR ($CDCl_3$, 295 K, ppm): 10.28 (br, 1H, NH); 7.61 (d, 1H, H(6′), $^3J(^1H(5'), ^1H(6')) = 6.9$ Hz, $^3J(^{119}Sn, ^1H) = 79.6$ Hz); 7.46 (m, 2H, H(4′, 3′)); 7.18 (m, 1H, H(5′)); 4.51 (d, 2H, NCH_2, $^3J(^1H(NH), ^1H(NCH_2)) = 5.5$ Hz); 2.82 (d, 6H, $N(CH_3)_2$, $^3J(^1H(NH), ^1H(N(CH_3)_2)) = 4.7$ Hz); 2.24 (t, 2H, H(1)); 2.00 (m, 2H, H(2)); 1.53 (m, 2H, H(3)); 0.97 (t, 3H, H(4)). ^{119}Sn NMR ($CDCl_3$, 295 K, ppm): −196.0. Elemental analysis (%): found: C, 37.1; H, 5.5; N, 3.4. Calcd. for $C_{13}H_{22}Cl_3NSn$ (417.38): C, 37.41; H, 5.31; N, 3.36.

3.18. Preparation of **12**

$L^{CN}PhSnCl_2$ (501 mg, 1.25 mmol) was dissolved in THF/diethyl ether mixture (1:1, 20 mL) and aqueous HCl (35%, 122 μL, 1.38 mmol) was added. The reaction mixture was stirred overnight. Afterwards the volatiles were removed *in vacuo* and the residue was extracted with chloroform (2 × 20 mL). The extract was reduced *in vacuo* giving 396 mg of white crystalline product. Yield 73%. M.p. 134–136 °C. ^{1}H NMR (THF-d8, 295 K, ppm): 10.15 (br, 1H, NH); 8.36 (d, 2H, H(2″), $^3J(^1H(3''), ^1H(2'')) = 6.9$ Hz, $^3J(^{119}Sn, ^1H) = 92.1$ Hz); 7.51 (d, 1H, H(6′), $^3J(^1H(5'), ^1H(6')) = 6.2$ Hz, $^3J(^{119}Sn, ^1H) = 93.7$ Hz); 7.44–7.29 (m, Ph and L^{CN} groups); 4.60 (d, 2H, NCH_2, $^3J(^1H(NH), ^1H(NCH_2)) = 6.1$ Hz); 2.85 (d, 6H, $N(CH_3)_2$, $^3J(^1H(NH), ^1H(N(CH_3)_2)) = 5.2$ Hz). ^{119}Sn NMR (THF-d8, 295 K, ppm): −262.7. Elemental analysis (%): found: C, 41.0; H, 4.3; N, 3.4. Calcd. for $C_{15}H_{18}Cl_3NSn$ (437.37): C, 41.19; H, 4.15; N, 3.20.

3.19. Reaction of L^{CN}(*n*-Bu)SnF_2 with triphosgene

L^{CN}(*n*-Bu)$_2$SnF (313 mg, 0.81 mmol) was dissolved in toluene (10 mL) and triphosgene (40 mg, 0.13 mmol) was added. The reaction mixture was stirred for 1 h. Afterwards the reaction mixture was concentrated *in vacuo*. Single crystals of **13** were obtained from the concentrated reaction mixture which was left for one week in a glass flask. Yield 54 mg (14%). For NMR spectra see discussion above. Raman spectroscopy (cm^{-1}): 255, 338, 509, 602, 841, 965, 1060, 1173, 1464, 1588, 2132, 2974–2800, 3056. Elemental analysis (%): found: C, 43.2; H, 5.9; N, 2.5. Calcd. for $C_{34}H_{61}Sn_2N_2Cl_3F_6$ (956.62): C, 42.7; H, 6.6; N, 2.9.

3.20. Reaction of L^{CN}(*n*-Bu)$_2$SnCl with $SnCl_4$ (1:1 ratio)

L^{CN}(*n*-Bu)$_2$SnCl (258 mg, 0.64 mmol) was dissolved in toluene and $SnCl_4$ (168 mg, 0.64 mmol) was added in one portion at room temperature. The reaction mixture was stirred overnight. Afterwards the solvent was evaporated *in vacuo*. According to ^{1}H and ^{119}Sn NMR spectroscopy the reaction residue consisted of 1:1 mixture of (*n*-Bu)$_2SnCl_2$ [16] and $L^{CN}SnCl_3$ [20].

3.21. Reaction of L^{CN}(*n*-Bu)$_2$SnCl with $SnCl_4$ (4:1 ratio)

L^{CN}(*n*-Bu)$_2$SnCl (250 mg, 0.62 mmol) was dissolved in toluene and $SnCl_4$ (40 mg, 0.16 mmol) was added in one portion at room temperature. The reaction mixture was stirred overnight. Afterwards the solvent was evaporated *in vacuo*. According to ^{1}H and

^{119}Sn NMR spectroscopy the reaction residue consisted of ca. 1:1:1 mixture of $L^{CN}(n\text{-Bu})_2SnCl$ [11e], $(n\text{-Bu})_2SnCl_2$ [16] and $L^{CN}SnCl_3$ [20]. Essentially the same results were obtained when the reaction mixture was refluxed for 4 h in toluene.

3.22. Reaction of $L^{CN}(n\text{-Bu})_2SnCl$ with $SnBr_4$ (2:1 ratio)

$L^{CN}(n\text{-Bu})_2SnCl$ (203 mg, 0.50 mmol) was dissolved in toluene and $SnBr_4$ (111 mg, 0.25 mmol) was added in one portion at room temperature. The reaction mixture was stirred overnight. Afterwards the solvent was evaporated *in vacuo*. According to ^{1}H and ^{119}Sn NMR spectroscopy the reaction residue consisted of mixture of $L^{CN}(n\text{-Bu})_2SnBr$ as the major product [24], $(n\text{-Bu})_2Sn(Cl)Br$ [16] and $L^{CN}SnBr_3$ [11b] as minor products.

3.23. Reaction of $L^{CN}Ph_2SnCl$ with $SnCl_4$ (1:1 ratio)

$L^{CN}Ph_2SnCl$ (232 mg, 0.52 mmol) was dissolved in toluene and $SnCl_4$ (136 mg, 0.52 mmol) was added in one portion at room temperature. The reaction mixture was stirred overnight. Afterwards the solvent was evaporated *in vacuo*. According to ^{1}H and ^{119}Sn NMR spectroscopy the reaction residue consisted of 1:1 mixture of Ph_2SnCl_2 [30] and $L^{CN}SnCl_3$ [20].

3.24. Reaction of $L^{CN}Ph_2SnCl$ with $SnCl_4$ (2:1 ratio)

$L^{CN}Ph_2SnCl$ (248 mg, 0.56 mmol) was dissolved in toluene and $SnCl_4$ (73 mg, 0.28 mmol) was added in one portion at room temperature. The reaction mixture was stirred overnight. Afterwards the solvent was evaporated *in vacuo*. According to ^{1}H and ^{119}Sn NMR spectroscopy the reaction residue consisted of mixture of $L^{CN}Ph_2SnCl$ (~35%) [11d], Ph_2SnCl_2 (~20%) [30], Ph_3SnCl (~10%) [30] and $L^{CN}SnCl_3$ (~35%) [20].

3.25. Reaction of $L^{CN}Ph_2SnCl$ with $SnCl_4$ (3:1 ratio)

$L^{CN}Ph_2SnCl$ (254 mg, 0.57 mmol) was dissolved in toluene and $SnCl_4$ (50 mg, 0.19 mmol) was added in one portion at room temperature. The reaction mixture was stirred overnight. Afterwards the solvent was evaporated *in vacuo*. According to ^{1}H and ^{119}Sn NMR spectroscopy the reaction residue consisted of mixture of $L^{CN}Ph_2SnCl$ (~20%) [11d], Ph_2SnCl_2 (~30%) [30], Ph_3SnCl (~10%) [30] and $L^{CN}SnCl_3$ (~40%) [20].

3.26. Reaction of $L^{CN}Ph_2SnCl$ with $SnCl_4$ (1:3 ratio)

$L^{CN}Ph_2SnCl$ (239 mg, 0.54 mmol) was dissolved in toluene and $SnCl_4$ (422 mg, 1.62 mmol) was added in one portion at room temperature. The reaction mixture was stirred overnight. Afterwards the solvent was evaporated *in vacuo*. According to ^{1}H and ^{119}Sn NMR spectroscopy the reaction residue consisted of mixture of Ph_2SnCl_2 (~30%) [30], $PhSnCl_3$ (~30%) [30] and $L^{CN}SnCl_3$ (~40%) [20].

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Appendix A. Supporting information

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre (789986–789995). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EY, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Supporting information related to this article can be found in the online version, at doi:10.1016/j.jorganchem.2010.08.006

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