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C,N-chelated organotin(IV) trifluoroacetates. Instability of the mono- and diorganotin(IV) derivatives.

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ABSTRACT

The *C,N*-chelated tri-, di- and monoorganotin(IV) halides react with equimolar amounts of CF_3COOAg to give corresponding *C,N*-chelated organotin(IV) trifluoroacetates. The set of prepared tri-, di- and monoorganotin (IV) trifluoroacetates bearing the L^{CN} ligand (where L^{CN} is 2-(*N,N*-dimethylaminomethyl)phenyl-) was structurally characterized by X-ray diffraction analyses, multinuclear NMR and IR spectroscopy. In the case of triorganotin(IV) trifluoroacetates and $(L^{CN})_2Sn(OC(O)CF_3)_2$, no tendency to form hydrolytic products, or instability towards the moisture was observed. $L^{CN}RSn(OC(O)CF_3)_2$ (where R is *n*-Bu or Ph) and $L^{CN}Sn(OC(O)CF_3)_3$ forms upon crystallization from THF in the air mainly dinuclear complexes in which the two tin atoms are interconnected either by hydroxo-bridges or by an oxo-bridge and/or by a bridging trifluoroacetate(s). In the case of hydrolysis of $L^{CN}(n\text{-Bu})Sn(OC(O)CF_3)_2$, a zwitterionic stannate of formula $L^{CN}(n\text{-Bu})Sn(OC(O)CF_3)_2 \cdot CF_3COOH$ was isolated from the mother liquor, too. Products of hydrolysis of $L^{CN}(n\text{-Bu})Sn(OC(O)CF_3)_2$ and $L^{CN}Sn(OC(O)CF_3)_3$, and some other oxygen bridged organotin(IV) compounds containing the same ligand, were tested as possible catalysts of some transesterification reactions as well as in direct dimethyl carbonate (DMC) synthesis from CO_2 and methanol.

1. Introduction

There is a long-standing interest in chemistry and generally the structure of triorganotin(IV) esters of carboxylic acids both in academia and industry, because of known catalytic and medicinal activity [1,2]. The structural motifs of these compounds are well established and studied by X-ray diffraction techniques [3], Mössbauer spectroscopy [4] and CP/MAS NMR techniques in the solid state, and mainly by multinuclear NMR spectroscopy in solution [5]. The tin atom in these compounds is mainly four-coordinated (Scheme 1A) or five coordinated with major occurrence in the solid state. In this case, the tin atom is surrounded by three carbon atoms originated from organo substituents and two oxygen atoms from carboxylate group, whereas the carboxylate can act as a bidentate or bidentate-bridging (or anisobidentate) ligand (Scheme 1B and 1C). Scheme 1D shows another general ability of the COO group to bridge two tin atoms. Compounds where the bidentate-bridging bond fashion occurs, tend to form infinite polymeric networks in the solid state [3], which can be often fragmented into oligomeric or monomeric particles in solutions of coordinating solvents [6].

Depending on the nature of the carboxylic acid used and the stoichiometry of the reactants, several products such as monomers, dimers, tetramers, oligomeric ladders, and hexameric drums can be isolated [3,7]. Diorganotin carboxylates have been an extensively investigated class of compounds over the last several decades. The most common reaction product of a reaction between R_2SnO (or R_2SnX_2) and R'COOH (in a 1:2 ratio) is the hexacoordinate mononuclear tin dicarboxylate of formula $[R_2Sn(OOCR')_2]$, where the tin centre exists in a skewed trapezoidal geometry [8]. The same reaction, when carried out with a strict 1:1 stoichiometry of the reactants, yields tetrameric compounds $[R_2(OOCR')SnOSn(OOCR')]_2$ [3,9]. On the other hand, monoorganotin carboxylates are predominately known to exist as drum-shaped hexameric clusters [10], although a few examples of other structural types are also known [11].

There is a plenty of examples of tri- and diorganotin(IV) compounds containing the 2-(*N,N*-dimethylaminomethyl)phenyl group as a *C,N*-chelating ligand in the literature [12]. All referred compounds of this type reveal significant intramolecular contact between tin and nitrogen which is changing their properties, mainly preventing their oligo- or polymerization. This coordination bond has been proven by means of X-ray diffraction analyses and ^{119}Sn CP-MAS NMR techniques in the solid state [13], and recently by multinuclear NMR spectroscopy in solution [14].

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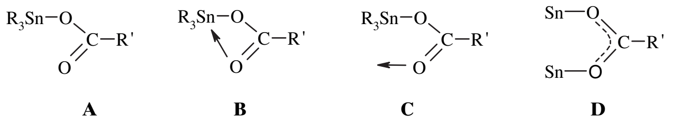


Scheme 1. Possible structural motifs for triorganotin(IV) esters of carboxylic acids.

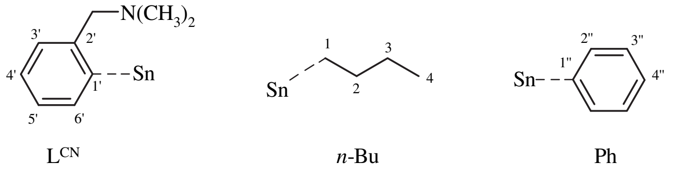
We have published recently about zwitterionic tri- and diorganostannates containing protonated 2-(*N*,*N*-dimethylaminomethyl)phenyl- moiety which were prepared by reactions of *C*,*N*-chelated organotin(IV) chlorides with various protic acids. These zwitterionic stannates were structurally characterized both by multinuclear NMR spectroscopy and X-ray diffraction techniques [15]. Promising results concerning reaction of $L^{CN}(n\text{-Bu})_2SnCl$ with CF_3COOH were also described there. Latter results led us to a concept to prepare and structurally characterize some *C*,*N*-chelated organotin (IV) trifluoroacetates since no information is related with the preparation and structural characterization of these compounds. Although a plethora of tin(IV) compounds is known, there are only two examples of organotin(IV) trifluoroacetates bearing the *N*,*C*,*N*-bischelating ligand ($L^{NCN} = [2,6\text{-}(Me_2NCH_2)_2C_6H_3]^-$) which can be directly related to the suggested compounds containing *C*,*N*-chelating ligand. These two compounds ($L^{NCN}Sn(H_2O)(OC(O)CF_3)_3$ and presumably the ionic $[L^{NCN}Ph_2Sn]^+[CF_3COO]^-$ were prepared and structurally characterized recently [16]. Other known organotin(IV) trifluoroacetates are used in glycosidation of sugar peracetates [17], as initiators of the ring-opening polymerization of ε-caprolactone [18], as precursors for AP CVD of fluorine-doped SnO_2 thin films [19] and are investigated as potential metal-based antitumor drugs [20], too.

In this paper, we report on the reactivity of various *C*,*N*-chelated tri-, di- and monoorganotin(IV) halides [21] towards CF_3COOAg (for ^1H NMR numbering see Scheme 2). The structure of products of hydrolysis of di- and monoorganotin(IV) trifluoroacetates bearing the *C*,*N*-chelating ligand is also discussed.

2. Results and discussion

2.1. General remarks

$L^{CN}(n\text{-Bu})_2SnCl$, $L^{CN}Ph_2SnCl$, $L^{CN}(n\text{-Bu})SnCl_2$, $L^{CN}PhSnCl_2$, $(L^{CN})_2SnBr_2$ and $L^{CN}SnBr_3$ reacted with equimolar amount of CF_3COOAg to give corresponding organotin(IV) trifluoroacetates (for numbering of compounds see Table 1) while attempts to prepare mixed organotin(IV) halogenides-trifluoroacetates were not carried out. All reactions were protected from exposure to light. Reactions of triorganotin(IV) chlorides and $(L^{CN})_2SnBr_2$ with CF_3COOAg were carried out in the air due to the stability of corresponding triorganotin(IV) trifluoroacetates. On the other hand, preparation of *C*,*N*-chelated di- and monoorganotin(IV) trifluoroacetates requires anhydrous THF and strictly anaerobic conditions. In the case of preparation of $L^{CN}(n\text{-Bu})_2SnOC(O)CF_3$ and $L^{CN}Ph_2SnOC(O)CF_3$ high yields (89% and 85%, respectively) are obtained, which is in contrast with the preparation of the rest of the desired products (for example only 62% yield for $(L^{CN})_2Sn(OC(O)CF_3)_2$). This is caused by low solubility of these products as well as necessary multiple filtration of the reaction mixtures in order to eliminate finely suspended silver(I) halide.



Scheme 2. General ^1H NMR numbering.

Table 1
Numbering of prepared compounds.

Compound	
$L^{CN}(n\text{-Bu})_2SnOC(O)CF_3$	**1**
$L^{CN}Ph_2SnOC(O)CF_3$	**2**
$(L^{CN})_2Sn(OC(O)CF_3)_2$	**3**
$L^{CN}(n\text{-Bu})Sn(OC(O)CF_3)_2$	**4**
$L^{CN}(n\text{-Bu})Sn(OC(O)CF_3)_2\cdot CF_3COOH$	**4a**
$[L^{CN}(n\text{-Bu})SnOC(O)CF_3]_2(\mu\text{-OH})_2$	**4b**
$L^{CN}PhSn(OC(O)CF_3)_2$	**5**
$[L^{CN}PhSnOC(O)CF_3]_2(\mu\text{-OH})(\mu\text{-OC(O)CF}_3)$	**5a**
$[L^{CN}SnOC(O)CF_3]_2(\mu\text{-O})(\mu\text{-OC(O)CF}_3)_2$	**6**

2.2. Triorganotin(IV) trifluoroacetates containing the C,N-chelating ligand

Prepared *C*,*N*-chelated triorganotin(IV) trifluoroacetates of the general formula $L^{CN}R_2SnOC(O)CF_3$ (where R = *n*-Bu (**1**) or Ph (**2**)) were characterized by multinuclear NMR spectroscopy and, in addition, by X-ray diffraction analysis in the case of **2** (Fig. 1). According to recorded multinuclear NMR spectra and X-ray diffraction analysis one can assume that the central tin atom is five-coordinated and reveals distorted trigonal bipyramidal geometry. Owing to the Bent's rule [22], both electronegative atoms X (X = N and O) 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 **2**, the interatomic distances Sn1-N1 (2.451(3) Å) and Sn1-O1 (2.187(3) Å) are similar to previously published results [23b]. The interatomic distance Sn1-O2 (3.384(3) Å) proves that the

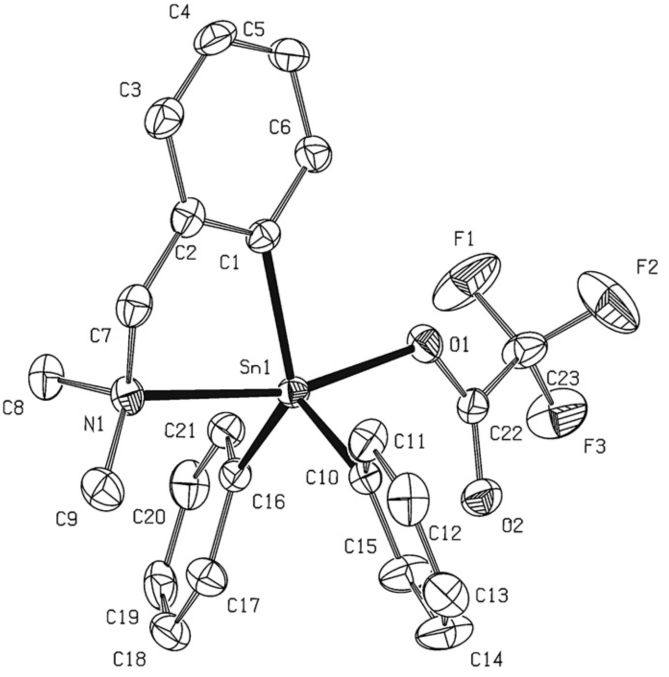


Fig. 1. Molecular structure of **2** (ORTEP view, 40% probability level). Hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Sn1-N1 2.451 (3), Sn1-O1 2.187(3), Sn1-O2 3.384(3), O1-C22 1.276(4), O2-C22 1.204(4), Sn1-C1 2.115 (3), Sn1-C10 2.123(3), Sn1-C16 2.123(3), N1-Sn1-O1 162.99(10), N1-Sn1-C1 76.24(11), O1-Sn1-C1 88.79(11), C1-Sn1-C10 116.30(13), C1-Sn1-C16 125.52(12), O1-Sn1-C10 100.94(11), O1-Sn1-C16 90.44(11), C10-Sn1-C16 117.27(13), N1-Sn1-C10 93.02(11), N1-Sn1-C16 91.77(11).

trifluoroacetate acts as a monodentate substituent. The N1-Sn1-O1 interatomic angle (162.99(10)°) differs relatively roughly from the ideal flat angle due to the sterical hindrance of the two phenyl substituents. For **2**, the sum of all equatorial C–Sn–C angles is 359.1°. The monodentate bonding fashion of the CF_3COO substituent in neat **1** and **2** is confirmed by IR (ATR) spectroscopy, too (see Experimental).

The ^1H NMR spectra of these two compounds display signals of *n*-Bu or Ph and L^{CN} moieties that are bonded to the central tin atom. The ^1H chemical shift values of the $N(CH_3)_2$ groups differs significantly for **1** ($\delta(^1H) = 2.36$ ppm in $CDCl_3$) in comparison with **2** ($\delta(^1H) = 1.88$ ppm in $CDCl_3$). On the other hand, the chemical shift values of the CH_2N moiety are nearly equivalent (3.62 ppm for **1** and 3.56 ppm for **2**). The position and the value of the $^3J(^{119}Sn, {}^1H)$ satellites of the doublet of the H(6′) signal in the ^1H NMR spectra is another useful tool for characterizing all *C,N*-chelated organotin compounds. Prepared triorganotin(IV) trifluoroacetates exhibit the coupling constant $^3J(^{119}Sn, {}^1H)$ being 58.8 Hz in the case of **1** and 60.5 Hz in the case of **2**. In contrast, diorganotin(IV) bis(trifluoroacetates) containing the L^{CN} ligand exhibit higher coupling constant $^3J(^{119}Sn, {}^1H)$ within the range of 90–110 Hz, which is in good agreement with previously published results [13,14,21]. The values of these coupling constants, as well as the $^1J(^{119}Sn, {}^{13}C)$, are naturally influenced by the *s*-electron density (e.g. *sp*^{2} vs. *sp* hybridization) on the tin atom. According to measured coupling constant $^1J(^{119}Sn, {}^{13}C) = 501.1$ Hz in **1** the interatomic angle C–Sn–C value was calculated using the empirical equation [24b] to be 124.5°. Similarly, the C–Sn–C angle in **2** was calculated to 123.3° ($^1J(^{119}Sn, {}^{13}C) = 795.3$ Hz).

The ^{13}C and ^{19}F NMR spectra of **1** and **2**, respectively, were recorded in order to elucidate the presence of the CF_3COO substituent. There are two characteristic quartets in each ^{13}C NMR spectra, first one at 160.8 ppm (160.4 ppm, respectively) (COO) with coupling constant $^2J(^{19}F, {}^{13}C) = 37.2$ Hz (37.5 Hz, respectively) and the second one at 116.3 ppm (116.0 ppm, respectively) with much higher coupling constant $^1J(^{19}F, {}^{13}C) = 291.1$ Hz (290.0 Hz, respectively) (CF_3). The signal of the CF_3 group in the ^{19}F NMR spectra was found at −74.7 ppm and −74.5 ppm, respectively. The ^{119}Sn NMR chemical shift values of these *C,N*-chelated triorganotin(IV) trifluoroacetates are shifted by 17 and 27 ppm, respectively, to lower frequencies relative to the starting $L^{CN}R_2SnCl$ (R = *n*-Bu or Ph).

2.3. Diorganotin(IV) trifluoroacetates containing the C,N-chelating ligand(s)

Another air-stable product was prepared by the reaction of $(L^{CN})_2SnBr_2$ with two equivalents of CF_3COOAg. Resulting $(L^{CN})_2Sn(OC(O)CF_3)_2$ (**3**) was isolated as a yellowish crystalline solid. The stability of this compound towards hydrolysis is probably caused by sterical hindrance of the two *C,N*-chelating ligands which protect the central tin atom from nucleophilic attack of water. The tin atom is six-coordinated with heavily distorted octahedral geometry having both carbon atoms in *trans* positions (Fig. 2). The interatomic distances Sn1-N1 (2.506(3) Å) and Sn1-N2 (2.516(4) Å) are nearly equivalent and are similar with analogous halides $(L^{CN})_2SnF_2$ (Sn1-N1 2.496(2) Å, Sn1-N2 2.597(1) Å) [25], $(L^{CN})_2SnCl_2$ (Sn1-N1 2.6179(13) Å, Sn1-N2 2.6179(13) Å) [21] or $(L^{CN})_2SnI_2$ (Sn1-N1 2.537(2) Å, Sn1-N2 2.648(2) Å) [21]. The interatomic angle N1-Sn1-N2 (106.70(12)°) is similar when compared to $(L^{CN})_2SnF_2$ (N1-Sn1-N2 104.05(4)°), $(L^{CN})_2SnCl_2$ (N1-Sn1-N2 108.47(4)°) and $(L^{CN})_2SnI_2$ (N1-Sn1-N2 103.65(7)°), too. The Sn1-O1 (2.114(3) Å) and Sn1-O3 (2.108(3) Å) interatomic distances are nearly identical and are a little bit shorter when compared to corresponding Sn–O distance in **2** (Sn1-O1 2.187(3) Å) or in bis{[2-(dimethylaminomethyl)phenyl]diphenyltin}-4-oxoheptanedioate (Sn1-O1 2.133(3) Å and Sn2-O4 2.120(3) Å) [23c]. From the X-ray diffraction analysis, it is evident that both CF_3COO substituents are bonded by the monodentate bond fashion to the tin atom (Sn1-O1 2.114(3) Å and Sn1-O2 3.416(5) Å; Sn1-O3 2.108(3) Å and Sn1-O4 3.404(5) Å). The Sn–C distances, both being 2.115(3) Å, are similar to previously published results [21].

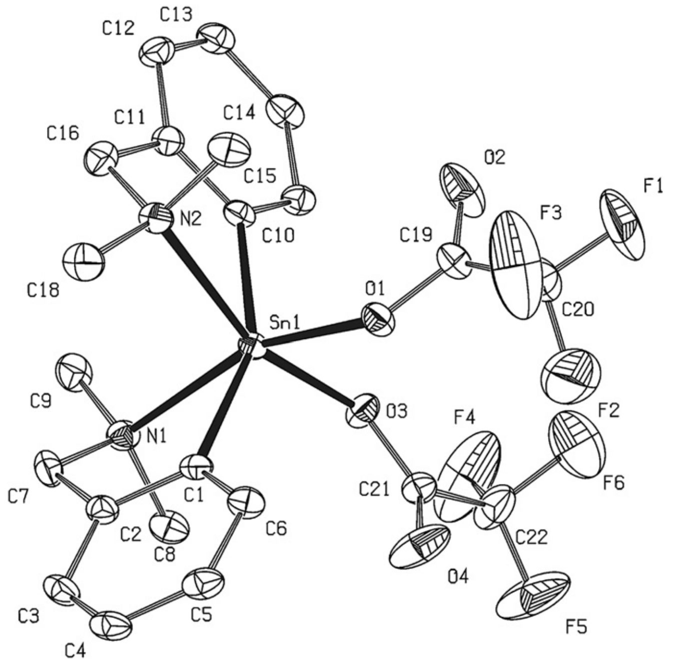


Fig. 2. Molecular structure of **3** (ORTEP view, 30% probability level). Hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Sn1-N1 2.506(3), Sn1-N2 2.516(4), Sn1-O1 2.114(3), Sn1-O2 3.416(5), Sn1-O3 2.108(3), Sn1-O4 3.404(5), O1-C19 1.275(6), O2-C19 1.219(7), O3-C21 1.270(6), O4-C21 1.188(6), Sn1-C1 2.115(3), Sn1-C10 2.115(3), N1-Sn1-O1 161.50(11), N2-Sn1-O3 161.58(12), N1-Sn1-C1 75.04(12), N2-Sn1-C10 75.09(12), N1-Sn1-N2 106.70(12), O1-Sn1-O3 85.35(12), C1-Sn1-C10 154.68(17), O1-Sn1-C1 92.36(13), O1-Sn1-C10 106.76(12), O3-Sn1-C1 106.71(15), O3-Sn1-C10 91.56(13).

Compound **3** was characterized by multinuclear NMR spectroscopy in THF-d8, too. The ^1H NMR spectra of this compound display only one signal for both CH_2N moieties at 3.74 ppm. On the other hand, the $N(CH_3)_2$ groups are unequivalent in solution since two signals at 2.31 ppm and 2.01 ppm, each with appropriate integral intensity, are present in the same ^1H NMR spectrum, which is in the strong contrast to the spectra of starting halides, where AX pattern is found for CH_2 moieties and one very broad signal for methyl groups [21]. The doublet assigned to the H(6′) is positioned at 8.15 ppm with coupling constant $^3J(^{119}Sn, {}^1H) = 97.9$ Hz. The ^{119}Sn NMR chemical shift value of this *C,N*-chelated diorganotin(IV) bis(trifluoroacetate) is found at −381.3 ppm which matches with six-coordinated tin species. The ^{13}C and ^{19}F NMR spectra were also recorded to elucidate the presence of the CF_3COO substituents. Similarly to triorganotin(IV) trifluoroacetates discussed (*vide supra*), there are two characteristic quartets in the ^{13}C NMR spectra, first one at 161.0 ppm (COO) with coupling constant $^2J(^{19}F, {}^{13}C) = 38.5$ Hz and the second one at 115.9 ppm (CF_3) with naturally higher coupling constant $^1J(^{19}F, {}^{13}C) = 282.2$ Hz. Only one signal in ^{19}F NMR spectrum at −75.0 ppm attributed to the CF_3 moiety is found. According to the ^{13}C and ^{19}F NMR spectra we suggest on the equality of both CF_3COO substituents in solution. These ^{13}C and ^{19}F NMR chemical shift values and the values of $^2J(^{19}F, {}^{13}C)$ and $^1J(^{19}F, {}^{13}C)$ are similar to discussed triorganotin(IV) trifluoroacetates.

In contrast to **3**, other two prepared diorganotin(IV) bis(trifluoroacetates), bearing only one *C,N*-chelating ligand, reveal strong tendency to hydrolyze in the presence of moisture. Despite this instability, both L^{CN}(*n*-Bu)Sn(OC(O)CF$_3$)$_2$ (**4**) and L^{CN}PhSn(OC(O)CF$_3$)$_2$ (**5**) were prepared under anhydrous conditions in argon atmosphere and characterized by multinuclear NMR spectroscopy. The ^{1}H NMR spectra of these two compounds reveal signals of both *n*-Bu or Ph and L^{CN} moieties that are bonded to the central tin atom. The ^{1}H chemical shift values of the N(CH$_3$)$_2$ groups differs only by 0.1 ppm for **4** ($\delta(^1H) = 1.82$ ppm in C_6D_6) in comparison with **5** ($\delta(^1H) = 1.72$ ppm in C_6D_6). On the other hand, the chemical shift values of the CH$_2$N moieties are significantly different (3.13 ppm for **4** and 3.48 ppm for **5**). As mentioned above, the coupling constants of the H(6′) protons $^3J(^{119}Sn, ^1H)$ are significantly higher for diorganotin(IV) species (89.9 Hz for **4** and 106.3 Hz in the case of **5**) in comparison to triorganotin(IV) species due to the higher *s*-electron density on the tin atom. The probable structural assignment for **4** comes from the ^{119}Sn NMR spectra of the compound, which gives a single resonance at −282.8 ppm, indicating the presence of only one type of tin atom. Compound **5** has a single resonance ($\delta(^{119}Sn) = -366.5$ ppm) in the ^{119}Sn NMR spectra, too. The ^{119}Sn NMR chemical shift values of these two *C,N*-chelated diorganotin (IV) bis(trifluoroacetates) are shifted to higher field relative to starting L^{CN}(*n*-Bu)SnCl$_2$ ($\delta(^{119}Sn) = -104.8$ ppm) and L^{CN}PhSnCl$_2$ ($\delta(^{119}Sn) = -164.8$ ppm). From these experimental data one could deduce that the tin atom is six-coordinated in solution in both cases with dynamic bonding fashion of both CF$_3$COO substituents (fast equilibrium between monodentately and bidentately bonded CF$_3$COO substituents). The ^{13}C and ^{19}F NMR spectra in C_6D_6 of both **4** and **5** reveal only one set of corresponding signal(s) of the CF$_3$COO moieties, indicating thus their bonding equality in solution. Multiplicity and coupling constants of the signals of CF$_3$COO moieties in these ^{13}C and ^{19}F NMR spectra are nearly the same as for **1** and **2**. The only difference is a slight shift of the $\delta(^{13}C)$ value to lower field (by ca. 2 ppm relative to **1** and **2** in the case of diorganotin(IV) bis(trifluoroacetates)) which further supports our hypothesis of the fast equilibrium between monodentately and bidentately bonded CF$_3$COO substituents in the NMR time scale. Multinuclear NMR spectra of **5** in DMSO-d6 as a coordinating solvent were also recorded. The presence of the coordinated DMSO molecule in **5** in DMSO-d6 has no effect on ^{1}H, ^{13}C and ^{19}F NMR spectra pattern but shifts the ^{119}Sn NMR chemical shift value by ca. 55 ppm relative to compound **5** to lower frequencies ($\delta(^{119}Sn) = -422.9$ ppm).

Unfortunately, compound **4** was isolated as yellowish oil which cannot be crystallized but the structure of **5**·DMSO was determined by X-ray diffraction analysis (Fig. 3). This compound was isolated from a sealed tube containing concentrated solution of **5** in dimethylsulfoxide. The strong coordination of the DMSO molecule to the tin atom (Sn1-O1 2.152(3) Å) probably prevents oligomerization or hydrolysis of the compound. The tin atom in **5**·DMSO is six-coordinated with nearly octahedral geometry having both carbon atoms mutually in *trans* positions. Oxygen atoms of CF$_3$COO substituents are mutually in *trans* position, too, as well as the nitrogen atom is in *trans* position to the oxygen atom of DMSO. The Sn1-N1 (2.389(6) Å) interatomic distance is very close to corresponding Sn–N distance in compound **2** (2.451(3) Å). The Sn1-O2 (2.201(3) Å) and Sn1-O4 (2.213(3) Å) interatomic distances for the monodentately bonded carboxylates are longer than the interatomic distance Sn1-O1 of coordinated DMSO molecule via the O1 atom. These interatomic distances between the tin atom and carboxylic oxygen atoms are even longer in comparison to corresponding distances Sn1-O1 (2.114(3) Å) and Sn1-O3 (2.108(3) Å) in **3** or Sn1-O1 (2.187(3) Å) in **2**. As well as in previous cases, both CF$_3$COO substituents are bonded monodentately to the tin atom in the solid state (Sn1-O2 2.203(4) Å and Sn1-O3 3.745(4) Å; Sn1-O4 2.213(3) Å and Sn1-O5 3.461(4) Å). The Sn–C distances, being 2.099(6) Å (Sn1-C1) and 2.145(5) Å (Sn1-C10), respectively, are comparable with previously published results [21]. The monodentate bonding fashion of the CF$_3$COO substituents in neat **3**, **4** and **5** is confirmed by IR (ATR) spectroscopy, too.

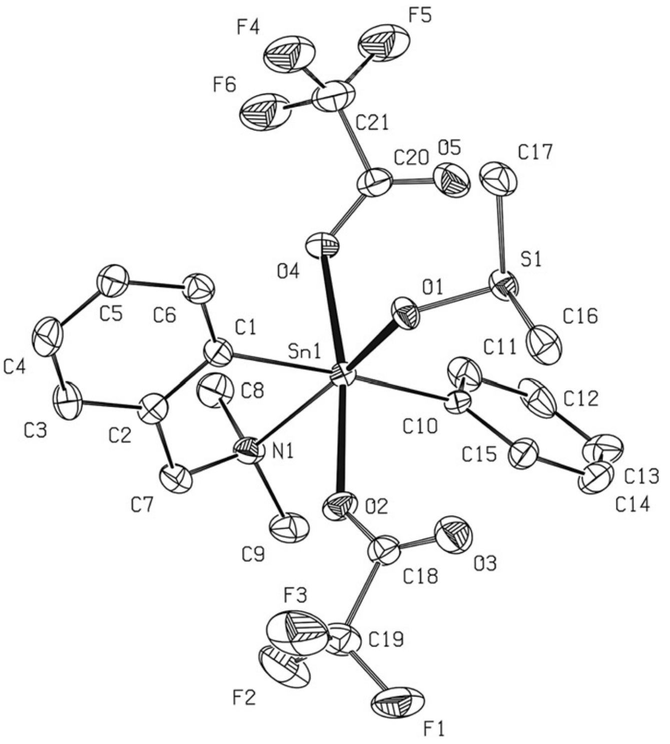


Fig. 3. Molecular structure of **5**·DMSO (ORTEP view, 40% probability level). Hydrogen atoms and one of two positions of disordered CF$_3$ group as well as a positional disorder of Ph and L^{CN} moieties are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Sn1-N1 2.389(6), Sn1-O1 2.152(3), Sn1-O2 2.201(3), Sn1-O3 3.745(4), Sn1-O4 2.213(3), Sn1-O5 3.461(4), Sn1-C1 2.099(6), Sn1-C10 2.145(5), N1-Sn1-O1 167.34(15), O2-Sn1-O4 170.35(11), N1-Sn1-C1 77.8(2), N1-Sn1-O2 78.70(16), C1-Sn1-C10 169.6(2), O1-Sn1-C1 91.19(18), O1-Sn1-C10 98.90(17), O4-Sn1-C1 84.4(2), O2-Sn1-C10 93.52(17).

2.4. Hydrolysis of instable diorganotin(IV) bis(trifluoroacetates)

Unsuccessful attempts to crystallize compound **4** under an argon atmosphere in a freezing box led to an idea to crystallize this compound from THF (0.1% H$_2$O) in the air in order to verify the expectation of its instability. In the case of **4**, the crystallization from wet THF provided two different hydrolytic products (see Scheme 3).

The first one isolated can be considered to be a zwitterionic stannate of formula L^{CN}(*n*-Bu)Sn(OC(O)CF$_3$)$_2$·CF$_3$COOH (**4a**, Fig. 4). This compound reveals structure similar to previously published zwitterionic stannates [15]. The compound bears two CF$_3$COO substituents which are monodentately bonded to the tin atom in the solid state (Sn1-O3 2.163(5) Å and Sn1-O4 2.906(7) Å; Sn1-O5 2.092(4) Å and Sn1-O6 3.108(7) Å). The third CF$_3$COO substituent is bonded to the tin atom and is also connected by a hydrogen bond (N1-H1…O2 2.833(7) Å) with the nitrogen atom of the ligand which decreases the differences in the O1-C14 (1.251(8) Å) and O2-C14 (1.216(7) Å) interatomic distances when compared with strictly monodentately acting CF$_3$COO substituent (for example O3-C21 1.270(6) Å and O4-C21 1.188(6) Å in the case of **3**). The negative charge on the tin atom is compensated by the protonated nitrogen atom possessing thus a positive charge. The central tin atom remains five-coordinated having distorted trigonal bipyramidal geometry. The Sn1-O1 (2.237(5) Å), Sn1-O3 (2.163(5) Å) and

$$4\ L^{CN}(n\text{-Bu})Sn(OC(O)CF_3)_2 + 2\ H_2O \xrightarrow[\text{air}]{\text{THF}} 2\ L^{CN}(n\text{-Bu})Sn(OC(O)CF_3)_2\cdot CF_3COOH \quad (\mathbf{4a})$$

$$+\ [L^{CN}(n\text{-Bu})SnOC(O)CF_3]_2(\mu\text{-OH})_2 \quad (\mathbf{4b})$$

Scheme 3. The hydrolysis of compound **4**.

Sn1-O5 (2.092(4) Å) interatomic distances are within the range of Sn—O distances of previously discussed **2** (Sn1-O1 2.187(3) Å), **3** (Sn1-O1 2.114(3) Å and Sn1-O3 2.108(3) Å) or in already published zwitterionic stannate $L^{CN}(n\text{-Bu})_2SnOC(O)CF_3\cdot CF_3COOH$ [15] (Sn1-O1 2.232(2) Å and Sn1-O3 2.334(2) Å). The interatomic angle O1-Sn1-O3 (161.50(19)°) differs relatively roughly from the ideal flat angle. The sum of all interatomic angles in the equatorial plane is 358.8°. There is a relatively narrow band (1728 cm^{-1}) and a very broad band with shoulders (1662 cm^{-1}) in the IR (ATR) spectrum. These bands were assigned to the ν_{as}(COO) vibration. Exactly the same situation occurs for the ν_s(COO) vibration (relatively narrow band at 1510 cm^{-1} and broadened band with shoulders at 1404 cm^{-1}). This may indicate two non-equivalent types of trifluoroacetate groups, the first one reveals the H-bond with the protonated amino group and the second one is attributed to the two monodentately bonded trifluoroacetate moieties. The characteristic vibration for N—H group was not observed probably due to the broadening of band.

The multinuclear NMR spectra in C_6D_6 of this compound reveal patterns characteristic for the *n*-butyl and protonated L^{CN} moieties [15]. Very broad signal of the NH moiety was observed at 10.25 ppm in the ^1H NMR spectra, too. The presence of only one resonance at −74.7 ppm in the ^{19}F NMR spectrum and one set of signals assigned to the CF_3COO moieties in the ^{13}C NMR spectrum (quartet for COO at 162.5 ppm, $^2J(^{19}F, ^{13}C) = 37.5$ Hz and quartet for CF_3 at 117.5 ppm, $^1J(^{19}F, ^{13}C) = 286.5$ Hz) presumes the equality of all three CF_3COO substituents in solution. The ^{119}Sn NMR chemical shift value shifts upfield to −315.3 ppm in the case of **4a** relative to starting **4** ($\delta(^{119}Sn) = -282.8$ ppm).

The second hydrolytic product isolated from the mother liquor is a centrosymmetric dimeric species of formula $[L^{CN}(n\text{-Bu})SnOC(O)CF_3]_2(\mu\text{-OH})_2$ (**4b**, Fig. 5). Tin atoms are interconnected by two hydroxo bridges forming thus four-membered rhombic planar ring (torsion angle Sn1-O1-Sn1a-O1a 0.02(12)°). The interatomic angle Sn1-O1-Sn1a (109.57(12)°) is much more wide than the O1-Sn1-O1a interatomic angle (70.43(10)°). Each tin atom is six-coordinated with roughly distorted octahedral geometry. Both CF_3COO substituents are bonded monodentately to the tin atom via O2 and O2a (both Sn1-O2 and Sn1-O2a 2.412(3) Å) atoms and the remaining O3 and O3a atoms (both Sn1-O3 and Sn1-O3a 3.692 (3) Å) are bonded to the hydroxo bridging groups (connecting the tin atoms) (O1-H1…O3 2.652(4) Å). This bond fashion again decreases the differences in the O2-C14 (1.241(4) Å) and O3-C14 (1.228(5) Å) interatomic distances when compared with strictly monodentately bonded CF_3COO substituent (for example O3-C21 1.270(6) Å and O4-C21 1.188(6) Å in the case of **3**). The Sn1-O2 (2.412(3) Å) and Sn1a-O2a, respectively, interatomic distances are identical and are apparently longer when compared with prepared compounds **2** (Sn1-O1 2.187(3) Å), **3** (2.114(3) Å) and Sn1-O3 (2.108 (3) Å) or **5**·DMSO (Sn1-O2 (2.203(4) Å) and Sn1-O4 (2.215(4) Å)) described *vide supra*. Both Sn—N interatomic distances are 2.520

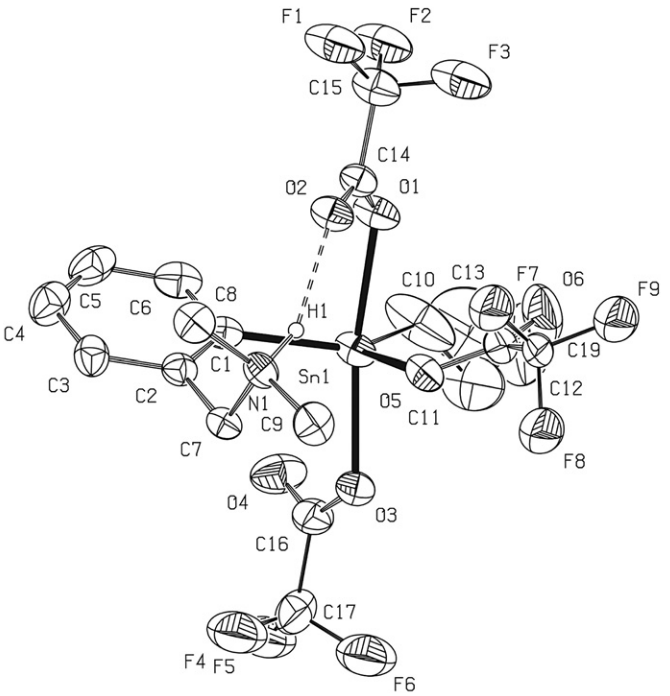


Fig. 4. Molecular structure of **4a** (ORTEP view, 30% probability level). Hydrogen atoms bonded to carbon atoms and one of the positions of disordered CF_3 groups are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Sn1-O1 2.237(5), Sn1-O2 3.474(5), Sn1-O3 2.163(5), Sn1-O4 2.906(7), Sn1-O5 2.092(4), Sn1-O6 3.108(7), Sn1-C1 2.129(7), Sn1-C10 2.072(11), O1-C14 1.251(8), O2-C14 1.216(7), O3-C16 1.262(10), O4-C16 1.205(11), O5-C18 1.261(9), O6-C18 1.204(10), O1-Sn1-O3 161.50(19), O1-Sn1-C1 88.3(2), O3-Sn1-C1 96.7(2), O1-Sn1-O5 82.21(18), O1-Sn1-C10 88.1(3), C1-Sn1-O5 109.9(2), C1-Sn1-C10 129.2(4), O5-Sn1-C10 119.7(4). H-bonding (visualized by dashed line): N1-O2 2.833(7), N1-H1…O2 155.8.

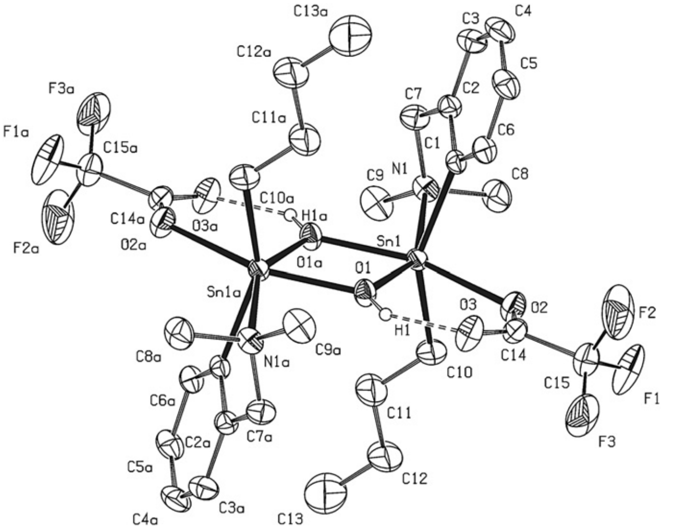


Fig. 5. Molecular structure of **4b** (ORTEP view, 30% probability level). Hydrogen atoms bonded to carbon atoms and one of the positions of disordered CF_3 groups are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Sn1-O1 2.094(3), Sn1-O1a 2.106(3), Sn1-O2 2.412(3), Sn1-O3 3.692(3), Sn1-C1 2.116(3), Sn1-N1 2.520(3), Sn1-C10 2.126(4), O2-C14 1.241(4), O3-C14 1.228(5), Sn1-O1-Sn1a 109.57(12), O1-Sn1-O1a 70.43(10), O1-Sn1-O2 80.20(9), O1a-Sn1-O2 150.63(10), N1-Sn1-C10 89.84(13), N1-Sn1-O2 125.92(9), N1-Sn1-O1 152.23(10), N1-Sn1-O1a 83.06(10), N1-Sn1-C1 74.68 (12), O1-Sn1-C1 101.55(12), O1a-Sn1-C1 100.45(11). H-bonding (visualized by dashed line): O1-O3 2.652(4), O1-H1…O3 143.8.

(3) Å. The bands attributed to ν_{as}(COO) (1666 cm^{-1}, very broad with shoulders) and ν_s(COO) (1457 and 1423 cm^{-1}, broadened bands) in the IR (ATR) spectrum predicate only about uncertain bonding fashion of the CF_3COO substituents.

The ^{1}H NMR spectrum of **4b** in THF-d8 reveals all signals of the *n*-butyl and L^{CN} moieties, the signal of bridging OH moieties was not found. The possible explanation for this is that the OH bridges may be NMR silent. According to the ^{13}C and ^{19}F NMR spectra, both CF_3COO substituents are equivalent in solution similarly as well as in the case of **4a**. There is only one resonance in the ^{119}Sn NMR spectra at −344.6 ppm proving the existence of only one tin-containing species.

On the other hand, the dinuclear product obtained by crystallization of **5** from the THF (0.1% H_2O) in the air, exhibits a new type of the bonding fashion. The two tin atoms in [L^{CN}PhSnOC(O)CF$_3$]$_2$(μ-OH)(μ-OC(O)CF$_3$) (**5a**) are interconnected by one hydroxo bridge and by one bridging trifluoroacetate substituent (interatomic distances Sn1-O1 2.119(4) Å, Sn2-O1 2.134(4) Å, Sn1-O4 2.256(4) Å and Sn2-O5 2.327(4) Å) (Fig. 6). Both tin atoms are six-coordinated with nearly octahedral geometry. Each tin atom also bears another monodentately bonded trifluoroacetate substituent (Sn1-O2 2.165(4) Å and Sn1-O3 3.467(6) Å; Sn2-O6 2.170(5) Å and Sn2-O7 3.545(5) Å), phenyl substituent and bidentately bonded L^{CN} moieties (very strong intramolecular interaction Sn1-N1 2.425(6) Å and Sn2-N2 2.465(5) Å). The nitrogen atoms are in *trans* position to oxygen atom originating from the hydroxo bridge as well as oxygen atoms of CF_3COO substituents (bridging and two monodentately bonded) are mutually in *trans* position. Both carbon atoms (from Ph and L^{CN}) are mutually in *trans* position, too. The O1 (bridging) and O3 (from the CF_3COO moiety) atoms are connected by hydrogen bond (O1-O3 2.727(7) Å). This bonding fashion decreases the differences in the O2-C16 (1.255(7) Å) and O3-C16 (1.199(10) Å) interatomic distances when compared with strictly monodentately bonded CF_3COO substituent as discussed above. The interatomic angle Sn1-O1-Sn2 (142.27(18)°) is forced out by the geometry of the whole molecule. The presence of both bridging and monodentately bonded CF_3COO substituents, in the solid state, is further supported by IR (ATR) spectroscopy. Two sets of broadened bands assigned to ν_{as}(COO) (1714 and 1684 cm^{-1}) and ν_s(COO) (1478 and 1402 cm^{-1}) were observed in the IR spectrum.

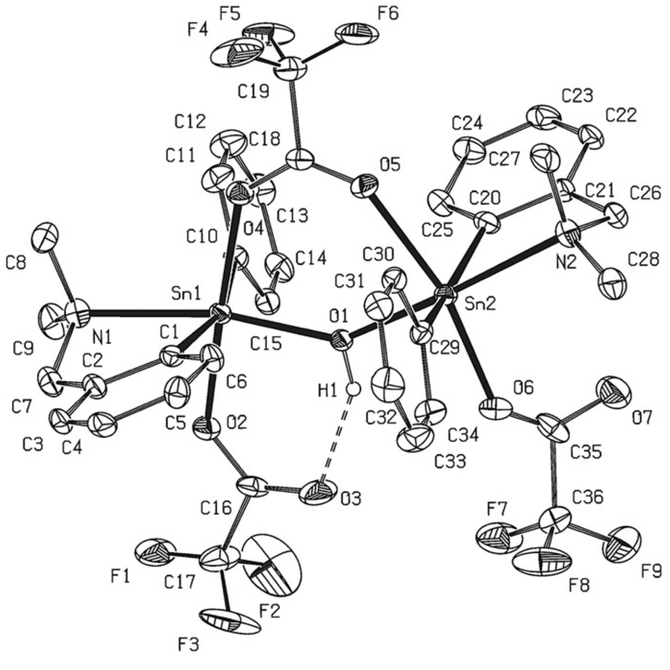


Fig. 6. Molecular structure of **5a** (ORTEP view, 30% probability level). Hydrogen atoms bonded to carbon atoms and one of the positions of disordered CF_3 groups are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Sn1-O1 2.119(4), Sn1-O2 2.165(4), Sn1-O3 3.467(6), Sn1-O4 2.256(4), Sn2-O1 2.134(4), Sn2-O5 2.327(4), Sn2-O6 2.170(5), Sn2-O7 3.545(5), Sn1-N1 2.425(6), Sn2-N2 2.465(5), Sn1-C1 2.120(6), Sn2-C20 2.126(6), Sn1-C10 2.123(6), Sn2-C29 2.115(6), O2-C16 1.255(7), O3-C16 1.199(10), O4-C18 1.247(8), O5-C18 1.224(7), O6-C35 1.120(10), O7-C35 1.233(9), Sn1-O1-Sn2 142.27(18), O1-Sn1-N1 167.76(17), O1-Sn2-N2 174.02(17), O2-Sn1-O4 177.15(13), O5-Sn2-O6 166.38(18), C1-Sn1-C10 164.0(2), C20-Sn2-C29 159.8(2), N1-Sn1-C1 76.0(2), N2-Sn2-C20 76.1(2). H-bonding (visualized by dashed line): O1-O3 2.727(7), O1-H1…O3 147.4.

Due to the very low solubility of **5a**, only ^{1}H and ^{19}F NMR spectra in THF-d8 were recorded. The ^{1}H NMR spectra pattern prove the presence of both phenyl and L^{CN} moieties. The signal of the bridging OH moiety was not found in the spectra since the signal is probably very broad. A broad multiplet is observed at −74.0 ppm in the ^{19}F NMR spectrum which is attributed to the two different CF_3COO substituents (two monodentately bonded ones and the bridging one). Compound **5a** is probably formed by the reaction of two molecules of 5 with one molecule of water giving trifluoroacetic acid as the by-product

2.5. *Instability of C,N-chelated tin(IV) tris(trifluoroacetate)*

The most complicated situation involves the preparation and structure determination of the L^{CN}Sn(OC(O)CF$_3$)$_3$. The preparation of this compound, even carried out under an argon atmosphere and anhydrous conditions, resulted in a mixture of two inseparable products (with approximate ratio of 2:3), which was confirmed by multinuclear NMR spectroscopy (in THF-d8). The ^{1}H NMR spectrum displays two sets of signals owing to the presence of two different species in the reaction mixture. The value of the coupling constants of satellites ($^3J(^{119}\text{Sn}, ^1\text{H}) = 124.1$ Hz and 118.8 Hz, respectively) of the doublet of the H(6′) signals at 7.97 ppm and 7.74 ppm respectively, matches perfectly with previously published monoorganotin (IV) species [21d]. Two broad signals assigned to CH_2N ($\delta(^1\text{H}) = 3.92$ ppm) and $N(CH_3)_2$ ($\delta(^1\text{H}) = 2.67$ ppm) are present, too. Surprisingly, only one set of signals assigned to the CF_3COO moieties was observed in the ^{13}C NMR spectrum (quartet at 158.7 ppm $^2J(^{19}\text{F}, ^{13}\text{C}) = 38.0$ Hz and quartet at 116.9 ppm $^1J(^{19}\text{F}, ^{13}\text{C}) = 285.5$ Hz) but two sets of signal belonging to L^{CN} moieties are distinct. The existence of two products in the reaction mixture is further proven by ^{19}F NMR and ^{119}Sn NMR spectroscopy since there are two signals in each NMR spectrum (−78.0 and −78.6 ppm in ^{19}F NMR spectrum and −525.8 and −544.3 ppm in ^{119}Sn NMR spectrum. The signals in ^{119}Sn NMR spectrum are shifted by ca. 110 ppm and 130 ppm, respectively, to lower frequencies relative to starting L^{CN}SnBr$_3$ ($\delta(^{119}\text{Sn}) = -413.5$ ppm). Unfortunately no single crystals were isolated from the reaction mixture up to now and therefore the real identity of these compounds still remains doubtable. Despite these complications, it is highly probable that one of the compounds is the desired L^{CN}Sn(OC(O)CF$_3$)$_3$ and the second one could be dimeric or oligomeric species.

Hence the reaction mixture was afterwards left in the air, single crystals of [L^{CN}Sn(OC(O)CF$_3$)]$_2$(μ-O)(μ-OC(O)CF$_3$)$_2$ (**6**) were obtained as a major hydrolytic product in ca. 65% yield. Compound **6** is virtually formed by the reaction of two molecules of L^{CN}Sn(OC(O)CF$_3$)$_3$ with one molecule of water giving two molecules of trifluoroacetic acid as the by-product. Both tin atoms are six-coordinated again in this dinuclear complex and are interconnected by one nearly symmetric oxo-bridge (Sn1-O1 1.939(2) Å and Sn2-O1 1.931(2) Å) and two bridging trifluoroacetates (Fig. 7). There is a difference between the O—C interatomic distances in bridging (nearly symmetric O2-C19 1.253(4) Å and O3-C19 1.240(4) Å; symmetric O4-C21 1.251(4) Å and O5-C21 1.251(4) Å) and

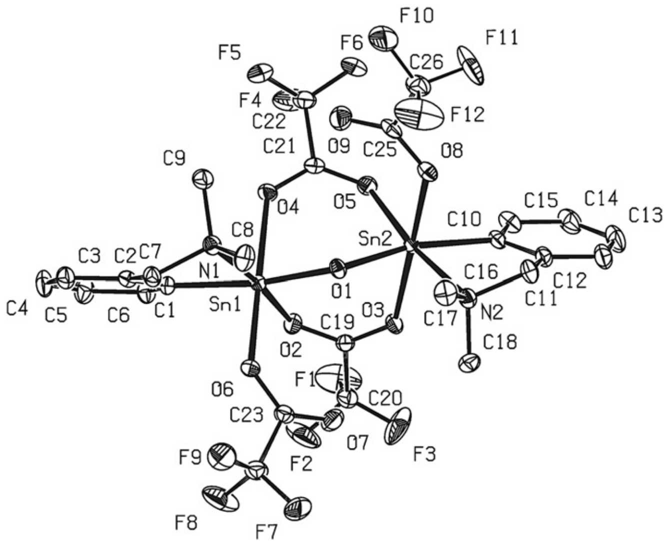


Fig. 7. Molecular structure of $\mathbf{6} \cdot C_6H_6$ (ORTEP view, 40% probability level). Benzene molecule, hydrogen atoms and one of the positions of disordered CF_3 moiety are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Sn1-O1 1.939(2), Sn2-O1 1.931(2), Sn1-O2 2.151(3), Sn1-04 2.259(2), Sn1-O6 2.107(2), Sn1-O7 3.449(4), Sn2-O3 2.281(2), Sn2-O5 2.150(2), Sn2-O8 2.118(2), Sn2-O9 3.432(3), Sn1-N1 2.275(4), Sn2-N2 2.288(4), Sn1-C1 2.104(3), Sn2-C10 2.104(4), O2-C19 1.253(4), O3-C19 1.240(4), O4-C21 1.251(4), O5-C21 1.251(4), O6-C23 1.268(4), O7-C23 1.212(5), O8-C25 1.270(5), O9-C25 1.213(5), Sn1-O1-Sn2 129.02(13), N1-Sn1-O2 173.77(11), N1-Sn1-C1 79.76(13), N2-Sn2-C10 80.54(12), N2-Sn2-O5 171.76(10), O1-Sn1-C1 170.18(12), O1-Sn2-C10 168.01(12), O4-Sn1-O6 179.06(9), O3-Sn2-O8 178.27(9), O1-Sn1-N1 91.82(11), N2-Sn2-O1 90.61(10).

monodentate (O6-C23 1.268(4) Å and O7-C23 1.212(5) Å; O8-C25 1.270(5) Å and O9-C25 1.213(5) Å) trifluoroacetate substituents. The monodentate bonding fashion of the two CF_3COO moieties is also clearly seen from the Sn–O distances (Sn1-O6 2.107(2) Å and Sn1-O7 3.449(4) Å; Sn2-O8 2.118(2) Å and Sn2-O9 3.432(3) Å). The vicinity of both tin atoms reveals slightly distorted octahedral geometry. This hydrolytic product exhibits extremely strong intramolecular interactions N→Sn (Sn1-N1 2.275(4) Å and Sn2-N2 2.288(4) Å) when compared with **4b** (both Sn–N 2.520(3) Å), **3** (Sn1-N1 2.506(3) Å and Sn1-N2 2.516(4) Å) or **5a** (Sn1-N1 2.425(6) and Sn2-N2 2.465(5) Å) discussed above. The Sn1-O1-Sn2 interatomic angle (129.02(13)°) is forced out by the presence of two bridging trifluoroacetates connecting the tin atoms, which also influences the geometry of the whole molecule. The IR (ATR) spectroscopy confirms the presence of both monodentately bonded CF_3COO and bridging CF_3COO substituents in the solid state since two sets of broadened bands attributed to $\nu_{as}(COO)$ (1719 and 1685 cm^{-1}) and $\nu_s(COO)$ (1475 and 1416 cm^{-1}) are found in the IR spectrum.

The interpretation of multinuclear NMR spectra of this dinuclear complex in THF-d8 provided rather disputable results. There are very broad signals in the aromatic region in the ^1H NMR spectrum. Two broad resonances assigned to CH_2N and $N(CH_3)_2$ moieties are the only signals in the aliphatic region of the same proton NMR spectrum. Parallel to NMR investigation of the reaction mixture containing presumably $L^{CN}Sn(OC(O)CF_3)_3$ only one set of signals of the CF_3COO groups (quartet at 161.8 ppm $^2J(^{19}F, ^{13}C) = 40.4$ Hz and quartet at 116.1 ppm $^1J(^{19}F, ^{13}C) = 289.8$ Hz) was found in the ^{13}C NMR spectrum. This indicates presumably fast equilibrium between mono- and bidentately bonded trifluoroacetates in the NMR time scale. One major broad signal at −575.5 ppm and several minor signals within the range of −500 to −750 ppm are found in the ^{119}Sn NMR spectrum. According to these interpretations it seems that the structure of **6** is somewhat instable in solution and repeated dissolution of this complex results in formation of further unidentified hydrolytic products.

2.6. *Catalytic experiments*

Due to high Lewis acidity of the tin centres in both **4b** and **6** the possible catalytic activity of these compounds was also investigated. Other oxygen bridged organotin(IV) compounds bearing the same ligand were investigated for the same purpose, too.

2.6.1. *Synthesis of Dimethyl carbonate (DMC) in supercritical carbon dioxide using $(L^{CN}(n\text{-}Bu)_2Sn)_2O$, $L^{CN}(t\text{-}Bu)_2SnOH$, $(L^{CN})_2Sn{=}O$ and organotin(IV) trifluoroacetates as pre-catalysts*

One of possible uses of the organotin(IV) compounds is their use as catalysts in the synthesis of linear carbonates from alcohols and carbon dioxide [26–28] in the presence of dehydrating reagents as well as in the production of polycarbonates via ring-opening polymerization of cyclic carbonates [29]. The use of above mentioned compounds, described recently, as well as those appeared in this paper as pre-catalysts of the synthesis of DMC in supercritical CO_2 was tested in order to evaluate the tin-containing species activity in the use of CO_2 as a cheap source of organic carbon as published elsewhere.

The reaction of $(L^{CN}(n\text{-}Bu)_2Sn)_2O$ [30] (1.190 g, 1.586 mmol) with 20 mL of methanol at 220 bar of CO_2 and 150 °C for 20 h led to the formation of 1.2 mmol of DMC. After this experiment, the volatiles were removed and the NMR spectra were recorded. The very major signal in ^{119}Sn NMR spectrum was observed at −71.4 ppm belonging to $L^{CN}(n\text{-}Bu)_2SnOH$ [30] as a product of hydrolysis of $(L^{CN}(n\text{-}Bu)_2Sn)_2O$ by water formed by reaction of methanol and CO_2. Two additional very minor signals for starting oxide and the appropriate carbonate were also detected in the same spectrum [30]. Using of the solid residue - 0.986 g (2.57 mmol, calculated for $L^{CN}(n\text{-}Bu)_2SnOH$) led to the formation of 2.31 mmol of DMC at the same conditions. The next recycling of 0.534 g (1.39 mmol, calculated to $L^{CN}(n\text{-}Bu)_2SnOH$) of solid residue gave 2.30 mmol of DMC. Then the nature of alcohols (methanol to isopropanol) was changed in order to observe the possible versatility of the catalyst but no trace of diisopropyl carbonate was observed.

Enormous increase of catalytic activity going from oxide to hydroxide led us to the idea to use the sterically hindered and stable $L^{CN}(t\text{-}Bu)_2SnOH$ for the same reaction. After one night under CO_2 at atmospheric pressure, the analysis of the tin-based residue $L^{CN}(t\text{-}Bu)_2SnOH$ by IR (ATR) showed two new strong absorptions located at 1582 and 1318 cm^{-1}, respectively. The ^{119}Sn NMR spectrum (in C_6D_6) displays a major signal (broad) at −65.9 ppm attributable to the carbonate species. In the ^{13}C NMR (in C_6D_6), the presence of a signal at 163.4 ppm confirms the formation of a CO_2-adduct complex. In the reactor (200 bar, 150 °C, 15 h, 20 mL of CH_3OH), the complex $L^{CN}(t\text{-}Bu)_2SnOH$ seems to be active for the synthesis of DMC. However, at the end of the reaction, the IR fingerprint of the tin-based residue collected does not correspond to the initial species. In fact, the 2-(*N,N*-dimethylaminomethyl)phenyl- ligand is lost during the reaction involving the formation of the known trimeric complex, $\{[OC(OSn\textit{t}\text{-}Bu_2)_2O \cdot \textit{t}\text{-}Bu_2Sn(OH)_2]$ in the reactor [26c]. This observation is confirmed by comparison between the IR and ^{119}Sn NMR spectra. Single crystals in the NMR tube using CD_3OD as deuterated solvent were also isolated. The cell parameters are strictly identical to the structure of $\{[OC(OSn\textit{t}\text{-}Bu_2)_2O \cdot \textit{t}\text{-}Bu_2Sn(OH)_2]_3 \cdot (CH_3OH)_3\}_n$.

The next experiment using $[(L^{CN})_2SnO]_n$ ($n = 1$–4) [31] (0.163 g, 0.141 mmol, yellow crystalline powder) as the catalyst precursor under pressure of CO_2 (200 bar, 150 °C) and in presence of methanol

(20 mL) was carried out. Initially, the tin-compound is completely soluble in methanol giving a solution slightly colour in yellow. After 20 h, no formation of DMC was observed. The tin-based residue was also analysed (yellowish oil) by ^{119}Sn NMR spectroscopy. Two weak signals located at −284.3 ppm (attributable to $[(L^{CN})_2Sn(OH)]_2(\mu\text{-}OH)$ and −313.3 ppm for oxo-carbonate species were observed [31b].

The reaction of **6** (0.884 g, 0.91 mmol) with 20 mL of methanol at 200 bar of CO_2 and 150 °C for 20 h led to the formation of only 0.3 mmol of DMC. The catalyst was not recycled due to its poor catalytic activity and no additional runs were carried out. When the same reaction was catalyzed by **4b** (0.922 g, 1.05 mmol) under the same conditions, somewhat higher yield of DMC was obtained (0.7 mmol).

2.6.2. Preparation of carbonates, urea derivatives and decarboxylation of resorcylic acid

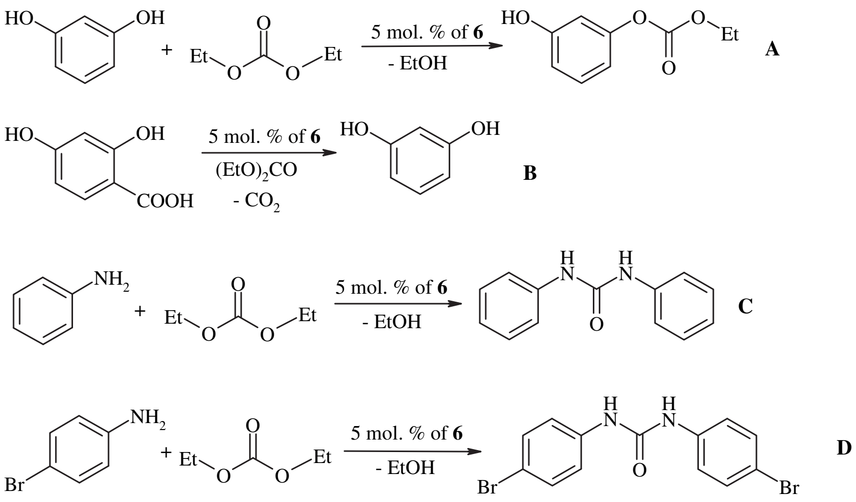
Alkylation reactions are among the key industrial/organic transformations for the production of a variety of fine and bulk chemicals [32]. In this field, particularly in the past two decades, the need for more environmentally acceptable processes has fuelled a great interest towards dialkylcarbonates ($(RO)_2C{=}O$) as innovative alkylating agents [33b]. These compounds, in fact, possess physico-chemical and reactivity features which make them appealing for general synthetic applications, including, for example, the selective alkylation of amines and phenols carried out by both linear and cyclic organic carbonates [34]. The diethyl carbonate (DEC) is a well-known non-toxic reagent and solvent that have been used for many green applications, namely the substitution of toxic reagents such as alkyl halides and phosgene for the selective alkylation and carboxyalkylation, respectively, of numerous nucleophiles [32]. The alkylation reactions of DEC with phenols normally occurred in presence of overstoichiometric amounts of base [35]. For preparation of diphenyl carbonate (DPC) from DMC and phenol various organotin(IV) compounds (such as Bu_2SnO and $Bu_2Sn(OAc)_2$) were tested [36]. The best results were obtained using minimally 1 M percent of $[Bu_2Sn(OH)(OTf)]_2$ (20.0% yield of DPC), $Bu_2SnO/CH_3C_6H_4SO_3H$ system (20.8% yield of DPC) and $[Bu_2Sn(OPh)]_4(\mu_3\text{-}O)_2/CF_3SO_3H$ system (20.4% yield of DPC) as catalysts. In all described reactions a methyl phenyl carbonate (MPC) was also obtained as a by-product in high yields (up to 40.9% in the case of $Bu_2Sn(OH)(OTf)]_2$). The plausible reaction mechanism of formation of DPC was also described in the same paper [36]. DPC was also synthesized from DEC and phenol in 1.4% yield using mixed niobium and titanium oxide catalyst with 37.6% of MPC as a by-product [37]. Other possible pathways to produce DPC are the reaction of dibutyl carbonate with phenol catalyzed by lead(II) oxide (yield 1% wt. of DPC and 21% wt. of butyl phenyl carbonate [38]) or lead(II) phenoxide (yield 62.5% wt. of DPC [39]).

Resorcylic acid can be decarboxyled at elevated temperatures (ca. 270 °C) to give pure resorcinol by treating the substrate with NaOH or KOH in satisfactory yields [40] but there is still a demand for lower temperature process.

And finally diphenyl carbonate reacts with aniline using NaOH as a catalyst to give diphenyl urea in 38% yield [41]. On the other hand, when compound **6** was used as a catalyst in related reactions described *vide infra*, no formation of by-products was observed with relatively high yields of desired products (see below). All the reactions proceeded at lower temperatures (ca. 127 °C) in comparison to reported reactions.

In general, carbamates and urea derivatives are widely encountered in the structure of biologically active compounds. These compounds are usually prepared from phosgene [42], phosgene derivatives [43] or isocyanates [44] in reaction with alcohols in the case of carbamates and amines in the case of ureas. Nevertheless, none of these methods are environmentally benign (use of toxic reagents and generation of by-products). Heterogeneous catalysis has also been reported for carbamate and urea synthesis. For example, platinum group metals have been developed to catalyze the alkoxycarbonylation of amines leading to carbamates [45] but this reaction requires the use of carbon monoxide. Only reactions of resorcinol with chloroformates were previously investigated to the best of our knowledge [46].

In the course of our studies on the use of catalysis in organic chemistry, we developed a method which allows the direct synthesis of ureas from amines and DEC. These reactions are theoretically possible to run without catalysts but in that case they are too slow to be useful in preparative scale. We have tested various organotin(IV) catalysts. Best results were obtained with compound **6** which was used as a catalyst for this reaction. Compound **6** was selected to potentially catalyze also other reactions of DEC with resorcinol (Scheme 4A), resorcylic acid (Scheme 4B), above mentioned aniline (Scheme 4C) and 4-bromoaniline (Scheme 4D). The yields of desired products are essentially quantitative in the case of reactions C and D.



Scheme 4. Selected reactions catalyzed by 5 mol % of **6** (conversion 9.2% (A), 73.5% (B), 100% (C) and 100% (D) relative to starting aromatic substrate).

3. Experimental

3.1. NMR spectroscopy

The NMR spectra were recorded from solutions in $CDCl_3$, benzene-d6, THF-d8 and DMSO-d6 on a Bruker Avance 500 spectrometer (equipped with *Z*-gradient 5 mm probe) at frequencies ^{1}H (500.13 MHz), $^{13}C\{^{1}H\}$ (125.76 MHz), $^{19}F\{^{1}H\}$ (470.57 MHz) and $^{119}Sn\{^{1}H\}$ (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 solvent. The values of ^{1}H chemical shifts were calibrated to residual signals of $CDCl_3$ (7.27 ppm), benzene-d6 ($\delta(^{1}H) = 7.16$ ppm) or THF-d8 ($\delta(^{1}H) = 3.57$ ppm). The values of ^{13}C chemical shifts were calibrated to signals of $CDCl_3$ ($\delta(^{13}C) = 77.2$ ppm), benzene-d6 ($\delta(^{13}C) = 128.4$ ppm) or THF-d8 ($\delta(^{13}C) = 67.4$ ppm). The values of ^{19}F chemical shifts were calibrated to external standard CCl_3F ($\delta(^{19}F) = 0.0$ 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 Material) 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 [47]. The absorption was corrected by integration methods [48]. Structures were solved by direct methods (Sir92) [49] and refined by full matrix least-square based on F^2 (SHELXL97) [50]. 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 $1.5U_{eq}$ for the methyl moiety with C–H = 0.96, 0.97, and 0.93 Å for methyl, methylene and hydrogen atoms in aromatic rings, respectively, and 0.82 Å for N–H and O–H groups. The molecules of **4b**, **5a** and **6**$\cdot C_6H_6$ reveal the disordered CF_3 groups, molecule of **4a** the *n*-butyl group and a positional disorder of phenyl and L^{CN} moieties is found in **5**·DMSO. All these disorders were solved by constraint and restraint options available in SHELXL97 software giving the best results in crystallographic parameters.

3.3. IR spectroscopy

IR spectra were recorded on Bruker Vector 22 spectrometer using ATR technique at ambient temperature.

3.4. Synthesis

$L^{CN}(n\text{-Bu})_2SnCl$ [14], $L^{CN}Ph_2SnCl$ [13], $L^{CN}(n\text{-Bu})SnCl_2$ [21c], $L^{CN}PhSnCl_2$ [21b], $(L^{CN})_2SnBr_2$ [21b] and $L^{CN}SnBr_3$ [21d] were prepared according to published procedures. All solvents and CF_3COOAg (98%) were obtained from commercial sources (Sigma–Aldrich). THF was dried by distillation from sodium-potassium alloy, degassed and stored over a potassium mirror. All reactions were carried out under an argon atmosphere using standard Schlenk techniques. Single crystals suitable for X-ray diffraction analyses were obtained from corresponding solutions of products by slow evaporation of the solvent in the air. Melting points are uncorrected.

3.5. Preparation of 1

$L^{CN}(n\text{-Bu})_2SnCl$ (687 mg, 1.71 mmol) was dissolved in THF (15 mL) and solution of CF_3COOAg (377 mg, 1.71 mmol) in THF (10 mL) was added. AgCl precipitated immediately. The reaction mixture was filtered and the filtration cake was washed with 10 mL of THF. Oily colourless product was isolated after removing the solvent *in vacuo*. Yield 730 mg (89%). ^{1}H NMR ($CDCl_3$, 295 K, ppm): 7.87 (d, 1H, H(6′), $^{3}J(^{1}H(5'), ^{1}H(6')) = 5.9$ Hz, $^{3}J(^{119}Sn, ^{1}H) = 58.8$ Hz); 7.30 (m, 2H, H(4′, 5′)); 7.13 (d, 1H, H(3′)); 3.62 (s, 2H, NCH_2); 2.36 (s, 6H, $N(CH_3)_2$); 1.62 (m, 4H, H(1)); 1.51 (m, 4H, H(2)); 1.41 (m, 4H, H(3)); 0.85 (t, 6H, H(4)). ^{13}C NMR ($CDCl_3$, 295 K, ppm): 160.8 (q, OCO, $^{2}J(^{19}F, ^{13}C) = 37.2$ Hz); 142.3 (C(2′), $^{2}J(^{119}Sn, ^{13}C) = 36.4$ Hz); 140.3 (C(1′), $^{1}J(^{119}Sn, ^{13}C) = 500.0$ Hz); 137.6 (C(6′), $^{2}J(^{119}Sn, ^{13}C) = 34.7$ Hz); 129.6 (C(4′)); 128.3 (C(5′), $^{3}J(^{119}Sn, ^{13}C) = 59.9$ Hz); 126.9 (C(3′), $^{3}J(^{119}Sn, ^{13}C) = 54.8$ Hz); 116.3 (q, CF_3, $^{1}J(^{19}F, ^{13}C) = 291.1$ Hz); 65.8 (CH_2N); 45.8 ($N(CH_3)_2$); 28.1 (C(2), $^{2}J(^{119}Sn, ^{13}C) = 30.8$ Hz); 27.3 (C(3), $^{3}J(^{119}Sn, ^{13}C) = 87.5$ Hz); 16.6 (C(1), $^{1}J(^{119}Sn, ^{13}C) = 501.1$ Hz); 13.7 (C(4)). ^{19}F NMR ($CDCl_3$, 295 K, ppm): −74.7. ^{119}Sn NMR ($CDCl_3$, 295 K, ppm): −64.5. IR analysis (cm^{-1}, selected bands): 1698 ($\nu_{as}(COO)$, s), 1405 ($\nu_s(COO)$, m), 1185 ($\nu(CF_3)$, vs), 1138 ($\nu(CF_3)$, vs). Elemental analysis (%): found: C, 47.7; H, 6.6; N, 2.6. Calcd. for $C_{19}H_{30}F_3NO_2Sn$ (480.14): C, 47.53; H, 6.30; N, 2.92.

3.6. Preparation of 2

$L^{CN}Ph_2SnCl$ (300 mg, 0.68 mmol) was dissolved in THF (15 mL). AgCl precipitated upon addition of a solution of CF_3COOAg (150 mg, 0.68 mmol) in THF (10 mL). The reaction mixture was filtered and the filtration cake was washed with 10 mL of THF. White crystalline product was isolated after removing the solvent *in vacuo*. Yield 300 mg (85%). M.p. 157–160 °C. ^{1}H NMR ($CDCl_3$, 295 K, ppm): 8.15 (d, 1H, H(6′), $^{3}J(^{1}H(5'), ^{1}H(6')) = 7.0$ Hz, $^{3}J(^{119}Sn, ^{1}H) = 60.5$ Hz); 7.70 (d, 4H, H(2‴), $^{3}J(^{1}H(3'''), ^{1}H(2''')) = 6.6$ Hz, $^{3}J(^{119}Sn, ^{1}H) = 61.2$ Hz); 7.44 (m, 4H, L^{CN} and Ph group); 7.38 (m, 4H, L^{CN} and Ph group); 7.19 (d, 1H, H(3′), $^{3}J(^{1}H(4'), ^{1}H(3')) = 7.5$ Hz); 3.56 (s, 2H, NCH_2); 1.88 (s, 6H, $N(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 295 K, ppm): 160.4 (q, OCO, $^{2}J(^{19}F, ^{13}C) = 37.5$ Hz); 143.0 (C(2′), $^{2}J(^{119}Sn, ^{13}C) = 38.9$ Hz); 139.1 (C(1‴), $^{1}J(^{119}Sn, ^{13}C) = 795.3$ Hz); 138.3 (C(6′), $^{2}J(^{119}Sn, ^{13}C) = 38.8$ Hz); 136.6 (C(1′), $^{1}J(^{119}Sn, ^{13}C) = 814.8$ Hz); 136.1 (C(2‴), $^{2}J(^{119}Sn, ^{13}C) = 45.3$ Hz); 130.5 (C(4′)); 130.0 (C(4‴)); 129.1 (C(3‴), $^{3}J(^{119}Sn, ^{13}C) = 69.9$ Hz); 128.7 (C(5′), $^{3}J(^{119}Sn, ^{13}C) = 68.4$ Hz); 127.5 (C(3′), $^{3}J(^{119}Sn, ^{13}C) = 64.0$ Hz); 116.0 (q, CF_3, $^{1}J(^{19}F, ^{13}C) = 290.0$ Hz); 64.9 (CH_2N); 46.0 ($N(CH_3)_2$). ^{19}F NMR ($CDCl_3$, 300 K, ppm): −74.5. ^{119}Sn NMR ($CDCl_3$, 300 K, ppm): −204.2. IR analysis (cm^{-1}, selected bands): 1684 ($\nu_{as}(COO)$, s), 1402 ($\nu_s(COO)$, m), 1179 ($\nu(CF_3)$, s), 1136 ($\nu(CF_3)$, vs). Elemental analysis (%): found: C, 53.2; H, 4.4; N, 2.6. Calcd. for $C_{23}H_{22}F_3NO_2Sn$ (520.12): C, 53.11; H, 4.26; N, 2.69.

3.7. Preparation of 3

$L^{CN})_2SnBr_2$ (608 mg, 1.11 mmol) was dissolved in THF (20 mL) and solution of CF_3COOAg (491 mg, 2.22 mmol) in THF (15 mL) was added. AgCl precipitated immediately. The reaction mixture was filtered and the filtration cake was washed with THF (10 mL). Yellowish crystalline product was isolated after removing the solvent *in vacuo*. Yield 422 mg (62%). M.p. 246–248 °C. ^{1}H NMR (THF-d8, 295 K, ppm): 8.15 (d, 2H, H(6′), $^{3}J(^{1}H(5'), ^{1}H(6')) = 6.0$ Hz, $^{3}J(^{119}Sn, ^{1}H) = 97.9$ Hz); 7.43 (m, 4H, H(4′, 5′); 7.23 (dd, 2H, H(3′), $^{3}J(^{1}H(4'), ^{1}H(3')) = 5.2$ Hz, $^{4}J(^{119}Sn, ^{1}H) = 47.0$ Hz); 3.74 (s, 4H, NCH_2); 2.31 (s, 6H, $N(CH_3)_2$); 2.01 (s, 6H, $N(CH_3)_2$). ^{13}C NMR (THF-d8, 295 K, ppm): 161.0 (q, OCO, $^{2}J(^{19}F, ^{13}C) = 38.5$ Hz); 141.8 (br, C(2′)); 139.0 (br, C(1′)); 137.2 (br, C(6′)); 131.3 (br, C(4′)); 129.1 (br, C(5′)); 128.5 (br, C(3′)); 115.9 (q, CF_3, $^{1}J(^{19}F, ^{13}C) = 282.2$ Hz); 64.7 (CH_2N); 46.6 (br, $N(CH_3)_2$). ^{19}F NMR (THF-d8, 295 K, ppm): −75.0. ^{119}Sn NMR

(THF-d8, 295 K, ppm): −381.3. IR analysis (cm^{-1}, selected bands): 1696 (ν_{as}(COO), s), 1396 (ν_s(COO), m), 1181 (ν(CF_3), vs), 1142 (ν(CF_3), vs). Elemental analysis (%): found: C, 43.0; H, 4.0; N, 4.6. Calcd. for $C_{22}H_{24}F_6N_2O_4Sn$ (613.13): C, 43.10; H, 3.95; N, 4.57.

3.8. *Preparation of **4***

L^{CN}(*n*-Bu)$SnCl_2$ (826 mg, 2.17 mmol) was dissolved in THF (20 mL) and solution of CF_3COOAg (958 mg, 4.34 mmol) in THF (20 mL) was added. AgCl precipitated immediately. The reaction mixture was filtered and the filtration cake was washed with THF (10 mL). The solvent was evaporated *in vacuo* giving yellow oil as the sole product. Yield 498 mg (78%). ^{1}H NMR (C_6D_6, 295 K, ppm): 8.00 (d, 1H, H(6′), $^{3}J(^{1}H(5'), ^{1}H(6')) = 6.3$ Hz, $^{3}J(^{119}Sn, ^{1}H) = 89.9$ Hz); 7.08 (m, 1H, H(4′)); 7.00 (t, 1H, H(5′)); 6.74 (d, 1H, H(3′)); 3.13 (s, 2H, NCH_2); 1.82 (s, 6H, $N(CH_3)_2$); 1.75 (br, 4H, H(1, 2)); 1.27 (m, 2H, H(3)); 0.84 (t, 3H, H(4)). ^{13}C NMR (C_6D_6, 295 K, ppm): 163.1 (q, OCO, $^{2}J(^{19}F, ^{13}C) = 34.5$ Hz); 140.3 (br, C(2′)); 139.0 (very broad signal, C(1′)); 135.1 (C(6′), $^{2}J(^{119}Sn, ^{13}C) = 61.4$ Hz); 128.4 (C(4′)); 127.2 (C(3′), $^{3}J(^{119}Sn, ^{13}C) = 86.2$ Hz); 116.5 (q, CF_3, $^{1}J(^{19}F, ^{13}C) = 288.8$ Hz); 63.1 (CH_2N); 44.7 ($N(CH_3)_2$); 26.9 (C(2), $^{2}J(^{119}Sn, ^{13}C) = 48.4$ Hz); 26.1 (C(3), ^{119}Sn satellites were not found); 25.5 (C(1), ^{119}Sn satellites were not found); 13.3 (C(4)); the resonance for the C(5′) atom is overlapped by the signal of C_6D_6. ^{19}F NMR (C_6D_6, 295 K, ppm): −74.5. ^{119}Sn NMR (C_6D_6, 295 K, ppm): −282.8. IR analysis (cm^{-1}, selected bands): 1666 (ν_{as}(COO), s), 1400 (ν_s(COO), m), 1180 (ν(CF_3), vs), 1132 (ν(CF_3), vs). Elemental analysis (%): found: C, 38.3; H, 4.1 N, 2.4. Calcd. for $C_{17}H_{21}F_6NO_4Sn$ (536.04): C, 38.09; H, 3.95; N, 2.61.

3.9. *Preparation of **5***

$L^{CN}PhSnCl_2$ (844 mg, 2.10 mmol) was dissolved in THF (20 mL) and solution of CF_3COOAg (930 mg, 4.20 mmol) in THF (15 mL) was added. AgCl precipitated upon addition. The reaction mixture was filtered and the filtration cake was washed with THF (10 mL). After removing the solvent *in vacuo* yellowish crystalline product was isolated. Yield 655 mg (56%). M.p. 145–147 °C. ^{1}H NMR (C_6D_6, 295 K, ppm): 8.25 (d, 1H, H(6′), $^{3}J(^{1}H(5'), ^{1}H(6')) = 6.8$ Hz, $^{3}J(^{119}Sn, ^{1}H) = 106.3$ Hz); 8.04 (d, 2H, H(2‴), $^{3}J(^{1}H(3'''), ^{1}H(2''')) = 7.0$ Hz, $^{3}J(^{119}Sn, ^{1}H) = 107.5$ Hz); 7.31 (t, 2H, H(3‴)); 7.20 (m, 2H, L^{CN} and Ph group); 7.14 (m, 1H, H(4‴)); 6.85 (d, 1H, H(3′), $^{3}J(^{1}H(4'), ^{1}H(3')) = 7.0$ Hz, $^{4}J(^{119}Sn, ^{1}H) = 106.3$ Hz); 3.48 (s, 2H, NCH_2); 1.72 (s, 6H, $N(CH_3)_2$). ^{13}C NMR (C_6D_6, 295 K, ppm): 161.7 (q, OCO, $^{2}J(^{19}F, ^{13}C) = 39.3$ Hz); 142.0 (br, C(2′)); 141.0 (br, C(1‴)); 138.9 (br, C(6′)); 137.1 (br, C(1′)); 136.0 (very broad signal, C(2‴)); 131.5 (very broad signal, C(4‴)); 130.5 (br, C(4′)); 129.9 (very broad signal, C(3‴)); 128.4 (br, C(3′)); 116.0 (q, CF_3, $^{1}J(^{19}F, ^{13}C) = 289.2$ Hz); 64.0 (CH_2N); 45.9 ($N(CH_3)_2$), the resonance for the C(5′) atom is overlapped by the very broad signal of the C(3′′) atom. ^{19}F NMR (C_6D_6, 295 K, ppm): −74.7. ^{119}Sn NMR (C_6D_6, 295 K, ppm): −366.5 (very broad signal). IR analysis (cm^{-1}, selected bands): 1685 (ν_{as}(COO), s), 1402 (ν_s(COO), m), 1182 (ν(CF_3), vs), 1144 (CF_3, s). Elemental analysis (%): found: C, 40.9; H, 3.2; N, 2.6. Calcd. for $C_{19}H_{17}F_6NO_4Sn$ (556.03): C, 41.04; H, 3.08; N, 2.52.

3.10. *Attempt to prepare $L^{CN}Sn(OC(O)CF_3)_3$*

$L^{CN}SnBr_3$ (2.150 g, 4.36 mmol) was dissolved in THF (20 mL) and solution of CF_3COOAg (2.892 g, 13.09 mmol) in THF (15 mL) was added. AgBr precipitated immediately. The reaction mixture was filtered and the filtration cake was washed with THF (2 × 10 mL). A mixture of two yellowish crystalline inseparable products resulted from the reaction residue after removing the solvent *in vacuo*. ^{1}H NMR (THF-d8, 295 K, ppm): 7.97 (d, H(6′), $^{3}J(^{1}H(5'), ^{1}H(6')) = 6.8$ Hz, $^{3}J(^{119}Sn, ^{1}H) = 124.1$ Hz); 7.74 (d, H(6′), $^{3}J(^{1}H(5'), ^{1}H(6')) = 7.0$ Hz, $^{3}J(^{119}Sn, ^{1}H) = 118.8$ Hz); 7.40 (m, 2H, L^{CN}); 7.35 (m, 1H, L^{CN}); 7.23 (m, 1H, L^{CN}); 3.92 (br, 4H, NCH_2); 2.67 (br, 6H, $N(CH_3)_2$). ^{13}C NMR (THF-d8, 295 K, ppm): 158.7 (q, OCO, $^{2}J(^{19}F, ^{13}C) = 38.0$ Hz); 138.9 (br, C(2′)); 135.6 (very broad signal, C(1′)); 134.5 (br, C(6′)); 132.0 (br, C(4′)); 130.0 (br, C(5′)); 128.7 (br, C(3′)); 116.9 (q, CF_3, $^{1}J(^{19}F, ^{13}C) = 285.5$ Hz); 63.8 (CH_2N); 63.3 (CH_2N); 46.7 ($N(CH_3)_2$); 45.9 ($N(CH_3)_2$). ^{19}F NMR (THF-d8, 295 K, ppm): −78.0; −78.6. ^{119}Sn NMR (THF-d8, 295 K, ppm): −525.8; −544.3. IR analysis (cm^{-1}, selected bands): 1719 and 1685 (ν_{as}(COO, vs), 1416 and 1370 (ν_s(COO), s), 1178 (ν(CF_3), vs), 1140 (ν(CF_3), vs).

3.11. *Isolation of **6***

Compound **6** was crystallized in the air from the THF (0.1% H_2O) solution of reaction mixture of $L^{CN}SnBr_3$ and CF_3COOAg described above. Yield 1.86 g (65%–relative to starting $L^{CN}SnBr_3$). M. p. 98–100 °C. Multinuclear NMR spectra are described in results and discussion section.

3.12. *Catalytic experiments*

General procedure for reactions of methanol with CO_2: The reaction was carried out in a 125 mL stainless steel reactor equipped with a magnetic stirrer. The reactor was purged with argon and a 20 mL solution of the appropriate tin(IV) complex in methanol was introduced by syringe. Then, CO_2 was admitted to the desired amount. The reaction temperature was controlled by an internal thermocouple. After a reaction time of 20 h the reactor was cooled down to 0 °C, pressure was gently released and the liquid phase was transferred to a Schlenk tube. Trap-to-trap distillation under *vacuum* at ambient temperature allowed separation of volatiles compounds that were quantitatively analysed by GC (DEC external standard, Fisons 8000, J&W Scientific DB-WAX 30 m capillary column, FID detector). Tin-based residue was characterized by IR and multinuclear NMR spectroscopy. Recycling experiments consisted of taking the tin-based residue for successive runs under the same experimental conditions.

General procedure for other reactions catalyzed by **6**: 1M solutions of appropriate substrate (resorcinol, resorcylic acid, aniline and 4-bromoaniline) in diethyl carbonate were prepared by dissolving 0.1 mol of the substrate in 100 mL volume of DEC.

The reaction was carried out in a 50 mL round-bottomed flask equipped with a magnetic stirrer and a reflux condenser. The outlet of the condenser was fitted to a glass tube filled with granulated charcoal. The reaction flask was immersed in an oil bath. The catalyst (compound **6**; 5 mol %) and 5 mL of 1M DEC solution of appropriate substrate (5 mmol) was added. The reaction mixture was heated to reflux for 16 h under vigorous stirring and evaporated to dryness in the next step. The 20 mg portion of the residue of reaction mixture was dissolved in DMSO-d_6. The ^{1}H NMR spectra then indicate the conversion of substrate to products (products were identified using commercially available or synthesized internal standards).

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Appendix. Supplementary material

Supplementary material associated with this article can be found in the online version, at doi:10.1016/j.jorganchem.2010.09.050.

Appendix A. Supplementary material

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre. 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).

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