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C,*N*-chelated organotin(IV) trifluoromethanesulfonates: Synthesis, characterization and preliminary studies of its catalytic activity in the direct synthesis of dimethyl carbonate from methanol and CO₂

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ABSTRACT

C,*N*-chelated tri- and diorganotin(IV) halides react with 1 or 2 mol equiv of silver trifluoromethanesulfonate (triflate, AgOTf, OTf = OSO₂CF₃) to give corresponding *C*,*N*-chelated organotin(IV) triflates. The triorganotin(IV) triflates of general formula $L^{CN}R_2SnOTf$ (R = n-Bu (1), Ph (2)) are presumably more stable towards hydrolysis than the diorganotin(IV) triflates $L^{CN}RSn(OTf)_2$ (R = n-Bu (3), Ph (4)). All prepared organotin(IV) triflates bearing the L^{CN} ligand (where L^{CN} is 2-(*N*,*N*-dimethylaminomethyl)phenyl-) were characterized by multinuclear NMR spectroscopy and elemental analysis. In addition, the structure of **3** was determined by the X-ray diffraction analysis. The catalytic activity of 1, **2** and **3** in the direct synthesis of dimethyl carbonate (DMC) from CO₂ and methanol was investigated showing promising yield of DMC in the case of reaction promoted by **1**.

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1. Introduction

Organotin(IV) trifluoromethanesulfonate (abbreviated as triflates or OTf) of general formula R_3SnOTf and $R_2Sn(OTf)_2$ (R = Me, *n*-Bu, Ph) were first reported by Schmeisser *et al.* in 1970 [1]. During the years a number of both di- and triorganotin(IV) triflates with interesting structural motifs (such as double-ladder structures) have been described [2]. These compounds are usually prepared by the reactions of organotin(IV) oxides (R_2SnO and ($R_3Sn)_2O$) with HOTf [1–3] or treating the respective organotin(IV) halide with AgOTf [1]. The most important aspects of chemistry of organotin(IV) triflates have been reviewed by Beckmann [4].

Organotin(IV) triflates can serve as useful Lewis acid catalysts for a variety of organic reactions. For example, it was found that (*n*-Bu)₂Sn(OTf)₂ can catalyze the Mukaiyama aldol reaction, in which aldehydes, ketones, and their acetals were completely discriminated [5]. The same compound also effectively mediates the Robinson annulations [6]. Recently, Otera used structurally similar organotin(IV) perfluorooctanesulfonates as catalysts for various carbon–carbon bond-forming reactions [7]. To the best of our knowledge, there are no organotin(IV) triflates bearing the L^{CN} ligand described in the literature. There are only a few studies briefly discussing the chemistry of *O*,*C*,*O*- and *N*,*C*,*N*-chelated organotin(IV) triflates [8,9]. The impulse to establish this field of chemistry was the report of Sakakura who discovered that triflate salts are very efficient catalysts in direct synthesis of dimethyl carbonate [10].

We have recently synthesized and structurally characterized novel *C*,*N*-chelated organotin(IV) trifluoroacetates [11]. The use of these species bearing the *C*,*N*-chelating ligand(s) L^{CN} (where L^{CN} is 2-(*N*,*N*-dimethylaminomethyl)phenyl-) as potential catalysts in the direct synthesis of dimethyl carbonate (DMC) from CO₂ and methanol was investigated, too.

Here we report on the preparation and structural investigation of some novel C,N-chelated organotin(IV) triflates and the use of **1**, **2** and **3** as catalyst precursors for the direct synthesis of DMC from CO₂ and methanol.

2. Results and discussion

2.1. General remarks

 $L^{CN}(n-Bu)_2SnCl$ [12b], $L^{CN}Ph_2SnCl$ [12a], $L^{CN}(n-Bu)SnCl_2$ [12b,d] and $L^{CN}PhSnCl_2$ [12c] reacted with 1 or 2 mol equiv of AgOTf in THF to give corresponding organotin(IV) triflates **1–4** (for



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numbering of compounds and NMR numbering of organic substituents bound to the central tin atom see Scheme 1) while attempts to prepare mixed organotin(IV) halides-triflates were not carried out. Preparation of C,N-chelated organotin(IV) triflates requires the use of anhydrous THF and strictly anaerobic conditions due to the presumptive sensitivity of formed products to moisture. All target products were prepared in satisfactory yields varying from 56% (for compound **4**) to 82% vield in the case of **2**. In addition, doubly C,N-chelated tin(IV) bis(triflate) and C,N-chelated tin(IV) tris(triflate) were synthesized but all attempts to study the structure of these two compounds by multinuclear solution NMR spectroscopy failed for two reasons: i) (L^{CN})₂Sn(OTf)₂ is almost insoluble even in THF- d_8 and the use of chlorinated solvents led to the exchanging of triflate ligands, ii) due to unprecedented reactivity of L^{CN}Sn(OTf)₃ no solution NMR spectra were recorded since this compound reacts readily at ambient temperature with the solvent (THF- d_8) to form unidentified polymeric products. Unfortunately, however, both compounds failed to give suitable single crystals for the X-ray diffraction analysis as well.

2.2. Solution NMR studies of 1-4

Compounds **1–4** were primarily characterized by multinuclear NMR spectroscopy in solution. Multinuclear NMR spectra of **2–4** compounds were recorded in THF- d_8 because of their limited solubility in other common organic solvents. Multinuclear NMR spectra of **1** were recorded in benzene- d_6 and, in addition, in methanol- d_4 in the air in order to check out the stability of **1** towards air moisture. Based on the data acquired from these measurements it was found that compound **1** does not react with air moisture at room temperature, because all the recorded spectral patterns remained unchanged even when measured again after one week.

The chemical shift values, integral intensities and multiplicity of each signal in the ¹H NMR spectra of **1–4** correspond well to proposed molecular structures with the respect to the number and nature of organic substituents bound to the tin atom. The value of the ³*J*(¹¹⁹Sn, ¹H) coupling constant of satellites of the doublet of the H(6') signal in the ¹H NMR spectra is a very useful tool for characterization of all *C,N*-chelated organotin(IV) compounds. Prepared triorganotin(IV) triflates exhibit the coupling constant ³*J*(¹¹⁹Sn, ¹H) of 56.1 Hz in the case of **1** and 64.8 Hz in the case of **2**. Corresponding ¹H NMR resonances of diorganotin(IV) bis(triflates) **3** and **4** reveal much higher values ³*J*(¹¹⁹Sn, ¹H) of 101.5 Hz and 113.8 Hz, respectively. This difference is in good agreement with previously published results [11,12].

The ${}^{13}C{}^{1}H$ and ${}^{19}F{}^{1}H$ NMR spectra of **1–4** were recorded in order to elucidate the presence of the OTf substituent(s). All signals in the ${}^{13}C{}^{1}H$ NMR spectra were in good agreement with expected patterns for each particular compound (see Experimental for detailed assignment of all resonances). There is one characteristic quartet in each ${}^{13}C{}^{1}H$ NMR spectra at ca. 121 ppm with coupling

constant ¹J(¹⁹F, ¹³C) \approx 319 Hz (CF₃ moiety). The resonances of the CF₃ group(s) in the ¹⁹F{¹H} NMR spectra were found as singlets at ca. –77 ppm for all prepared compounds.

The most valuable data about the structure (i.e. the coordination geometry of the tin atom) of **1–4** in solution always arose from the $^{119}Sn\{^{1}H\}$ NMR spectra. According to the $^{119}Sn\{^{1}H\}$ NMR spectrum of **1** in benzene- d_6 we suggest partial dissociation of **1** leading to the formation of an ion pair with [4+1] coordinated tin atom. The ionization is a well-known feature of organotin(IV) triflates [2,3,8,9]. The formation of the $[L^{CN}(n-Bu)_2Sn]^+$ cation has already been described for the $[L^{CN}(n-Bu)_2Sn]^+[Ti_2Cl_9]^-$ where the tin atom resonates at 69 ppm in the ¹¹⁹Sn{¹H} NMR spectrum [13]. The assumption of some degree of ionization of **1** is supported by the chemical shift value (δ (¹¹⁹Sn) = -1.0 ppm) of the only resonance found in the ¹¹⁹Sn{¹H} NMR spectrum in benzene- d_6 . The value of δ ⁽¹¹⁹Sn) is consistent with a tin atom bearing three organic substituents plus exhibiting the intramolecular N \rightarrow Sn interaction which increases the coordination number of the tin atom from 3 to 4. In other words, the resonance is shifted about 50 ppm downfield relative to the ¹¹⁹Sn{¹H} NMR chemical shift value of starting L^{CN}(*n*-Bu)₂SnCl (δ (¹¹⁹Sn) \approx -50.0 ppm) where the tin atom is pentacoordinated with a distorted trigonal-bipyramidal geometry [12b]. Similar results were deduced from the ¹¹⁹Sn{¹H} NMR spectra of **1** recorded in methanol- d_4 (broad resonance at -0.5 ppm) or THF- d_8 (-6.7 ppm). On the other hand, the Sn–O bond cannot be of purely ionic character and there should be a Sn–OTf interaction because measured chemical shifts are nearly in the middle of the range found for the covalent character in some carboxylates $(\sim -80 \text{ ppm})$ and ionic chlorotitanate [13].

Similarly, the only resonance in the ¹¹⁹Sn NMR spectrum of **2** found at – 162.8 ppm in THF- d_8 can be best attributed to the [4 + 1] coordinate tin-containing species as it is very close to the ¹¹⁹Sn{¹H} NMR chemical shift value of starting L^{CN}Ph₂SnCl (δ (¹¹⁹Sn) \approx – 176.0 ppm) where the tin atom reveals a distorted trigonalbipyramidal geometry (e.g. coordination number being 5) [12a]. The ¹¹⁹Sn{¹H} NMR chemical shifts in related diphenyltin(IV) carboxylates found at ~ –210 ppm indicate similar weakening of the Sn–OTf bond. Despite the fact that the spectrum was recorded in THF- d_8 we did not observe any coordination of the solvent to the central tin atom in the case of **2**.

In contrast to **1** and **2**, the coordination of the THF- d_8 to the tin atom in **3** and **4** was detected by the help of the ¹¹⁹Sn{¹H} NMR spectroscopy. Observed ¹¹⁹Sn{¹H} NMR chemical shift values of both **3** (δ (¹¹⁹Sn) = -350.9 ppm) and **4** (δ (¹¹⁹Sn) = -418.6 ppm) are shifted about 250 ppm to lower frequencies relative to the starting L^{CN}(*n*-Bu)SnCl₂ (δ (¹¹⁹Sn) \approx -105 ppm) [12b,d] and L^{CN}PhSnCl₂ (δ (¹¹⁹Sn) \approx -167 ppm) [12c]. Based on these facts, and according to the results of the X-ray diffraction analysis of **3** (vide Infra), it is unambiguous that the tin atom is six-coordinated with more or less distorted octahedral geometry in both **3** and **4** bearing the *C*,*N*chelating ligand, *n*-Bu/Ph substituent, two OTf moieties and finally the coordinated THF molecule.



Scheme 1. Table of prepared compounds and the NMR numbering of organic substituents.

2.3. X-ray crystal structure of 3. THF

Several attempts to crystallize all prepared compounds were made yielding only single crystals of **3** suitable for the X-ray diffraction analysis. Low-quality single crystals of **1** were obtained from its diethyl ether solution but the data collected by X-ray crystallography techniques enabled only partial determination and refinement of its molecular structure with disordered ligand and butyl groups. Nevertheless, it was found that the tin atom in **1** is definitively five-coordinate in the solid state and reveals distorted trigonal-bipyramidal geometry which is in contrast with its behaviour in the solution as discussed above (for X-ray crystallography details see Supplementary material).

Compound 3 was isolated in the form of its adduct with THF (Fig. 1). The tin atom in **3** · THF is six-coordinate with nearly octahedral geometry having both carbon atoms mutually in trans positions (C1-Sn1-C10A 174.0(3)°). Oxygen atoms of OTf substituents are mutually in *trans* position (O1–Sn1–O4 174.73(8)°), too, which means that the nitrogen atom is positioned trans to the oxygen atom of the THF molecule (N1-Sn1-O7 168.92(10)°). The Sn1-N1 (2.346(2)Å) interatomic distance reveals one of the strongest intramolecular $N \rightarrow Sn$ interaction ever reported in the solid state [for comparison see Refs. [8,9,11-14]]. All three Sn-O interatomic distances fall within the range from 2.224(2) Å (Sn1-O1) to 2.281(2) Å (Sn1-O4) which reveals a very strong $O \rightarrow Sn$ coordination of THF molecule. Thus both OTf substituents are covalently bound to the tin atom in strictly monodentate fashion which underlines the tendency of $3 \cdot \text{THF}$ to retain its monomeric covalent structure even in the solid state. The Sn-C distances, being 2.102(3) Å (Sn1–C1) and 2.124(8) Å (Sn1–C10A), respectively, are comparable with corresponding interatomic distances previously published in the literature [11–14]. Another comparison with structures of triflates [4,15] which adopt a higher nuclearity or polymeric character is not relevant here.

From another point of view the molecular structure (e.g. the geometry of the central tin atom) of 3-THF highly resembles the



Fig. 1. Molecular structure of **3**·THF (ORTEP view, 30% probability level). Hydrogen atoms as well as the disordered parts are omitted for charity. Selected interatomic distances [Å] and angles [°]: Sn1–N1 2.346(2), Sn1–O1 2.224(2), Sn1–O4 2.281(2), Sn1–O7 2.271(2), Sn1–C1 2.102(3), Sn1–C10A 2.124(8), S1–O1 1.480(2), S1–O2 1.425(3), S1–O3 1.415(3), S2–O5 1.417(3), S2–O6 1.418(3), N1–Sn1–O7 168.92(10), O1–Sn1–O4 174.73(8), C1–Sn1–C10A 174.0(3), N1–Sn1–C1 78.92(12), N1–Sn1–C10A 100.9(2), N1–Sn1–O1 87.66(8), N1–Sn1–O4 97.31(9), O1–Sn1–O7 87.27(8), O4–Sn1–O7 87.53(8), C1–Sn1–O1 88.71(10), C1–Sn1–O4 90.52(10), C1–Sn1–O7 91.12(12).

structure of L^{CN}Phce:inf>)/ce:inf>)₂·DMSO which was determined by the X-ray crystallography in one of our previous papers [11].

2.4. Catalytic experiments

During the last decades and in the quest of efficient catalysts for the direct synthesis of dimethyl carbonate (DMC) from carbon dioxide and methanol, several reports highlighted the efficiency of Ti-, Sn-, and Nb-based organometallic complexes as potential soluble active species [16]. Despite a lower activity than heterogeneous materials, molecular organometallic precursors are strongly more selective, and, in addition, they can also be considered as appropriate molecular models for calculation studies as described in recent papers [16i,17]. To the best of our knowledge, the dialkyldimethoxystannanes, $[R_2Sn(OCH_3)_2]$ (R = Me, *n*-Bu, *t*-Bu), are the best molecular candidates reported up to now in the literature [18]. However, the recorded values of $n_{\text{DMC}}/n_{\text{cat}}$ ratio (where n_{DMC} is the amount of formed DMC and n_{cat} is the amount of catalyst used in moles) which expresses their activity did not go beyond the stoichiometry. Catalytic behaviour requires the presence of dehydrating agents, or the implementation of recyclings [19]. In this context, Sakakura et al. published recently about the promoting role of triflate salts which drastically enhanced the yield of DMC [10]. In addition, Sakakura reviewed key issues of the synthesis of organic carbonates from carbon dioxide in 2009 [20].

As foreshadowed in Introduction, we have already tested the potential catalytic activity of some C,N-chelated organotin(IV) trifluoroacetates in the direct synthesis of DMC with promising results [11]. Therefore, it seemed promising to use the three organotin(IV) triflate compounds 1, 2 and 3 described in this study as catalyst precursors for the direct high-pressure carbonation of methanol (see Table 1) because of two major reasons: i) the triorganotin(IV) triflates **1** and **3** can presumably form $[L^{CN}R_2Sn]^+$ and [OTf]⁻ ions in the methanol solution at elevated temperatures increasing thus its potential catalytic activity and ii) due to the high Lewis acidity of the central tin atom in the diorganotin(IV) triflate 3 which might promote the formation of desired DMC. Interestingly, 2 and 3 appeared inefficient or very poorly active for the target reaction. In the case of **2**, the cleavage of the Sn–Ph bond was in particular observed leading to the release of benzene molecules (detected by gas chromatography). In contrast, using 1 as the catalyst precursor, an amount of DMC slightly higher than the stoichiometry ($n_{\text{DMC}}/n_{\text{cat}} = 1.15$) was detected (the detailed procedure is described in Experimental). Such activity (presumably caused by its relatively easy ionization in methanol at elevated temperatures) positions the species 1 as one of the best organometallic candidates reported so far, however we still do not fully understand the actual mechanism of the reaction. Due to the poor solubility of 4 and observed cleavage of the Sn-Ph bond in 2 during the DMC synthesis we did not employ compound 4 in the catalytic activity studies.

Further work is in progress now to improve these results by adding the water trapping agents or using other weakly

Table 1

Summary of results of direct synthesis of DMC from CO₂ and methanol using compounds **1**, **2** and **3** as catalyst precursors ($P_{(CO2)} = 200$ bar, T = 150 °C, reaction time 15 h).

Complex	Solvent	CO ₂ used (g)	n _{DMC} ^a (mmol)	n _{cat} (mmol)	$n_{\rm DMC}/n_{\rm cat}$
1	MeOH (20 mL)	32.7	2.3	2.00	1.15
2	MeOH (20 mL)	32.1	0.6	1.17	0.51
3	MeOH (20 mL)	32.0	Traces	1.17	-

^a Determined by GC using diethyl carbonate (DEC) as external standard.

coordinating anions. After the high-pressure reaction catalyzed by **1**, it is evident from the ¹¹⁹Sn{¹H} NMR spectrum that only decomposition products are present in the residue when all volatiles were evaporated *in vacuo*. Three different broad signals of various integral intensities were detected in the ¹¹⁹Sn{¹H} NMR spectrum. One of the decomposition products could be probably attributed to **1**·HOTf. This presumption is derived from similar pattern of the ¹H NMR spectrum and ¹¹⁹Sn{¹H} NMR chemical shift value (δ (¹¹⁹Sn) \approx –138 ppm) which is close to L^{CN}(*n*-Bu)₂Sn(OCOCF₃)·CF3COOH (δ (¹¹⁹Sn) \approx –130.1 ppm) [21]. The identity of other species is still uncertain.

3. Experimental

3.1. NMR spectroscopy

The NMR spectra were recorded from solutions of compounds in benzene- d_6 , THF- d_8 or methanol- d_4 on a Bruker Avance 500 spectrometer (equipped with Z-gradient 5 mm probe) at frequencies ¹H (500.13 MHz), ¹³C{¹H} (125.76 MHz), ¹⁹F{¹H} (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 ¹H chemical shifts were calibrated to residual signals of benzene- d_6 (δ (¹H) = 7.16 ppm), THF- d_8 $(\delta(^{1}H) = 3.57 \text{ ppm})$ or methanol- d_4 ($\delta(^{1}H) = 3.31 \text{ ppm}$). The values of ${}^{13}C{}^{1}H$ chemical shifts were calibrated to signals of benzene- d_6 $(\delta(^{13}C) = 128.4 \text{ ppm}), \text{ THF-}d_8 (\delta(^{13}C) = 67.4 \text{ ppm}) \text{ or methanol-}d_4$ $(\delta(^{13}C) = 49.0 \text{ ppm})$. The values of ¹⁹F chemical shifts were calibrated to external standard CCl₃F (δ (¹⁹F) = 0.0 ppm). The ¹¹⁹Sn chemical shift values are referred to external neat tetramethylstannane (δ (¹¹⁹Sn) = 0.0 ppm). Positive chemical shift values denote shifts to the higher frequencies relative to the standards. All ¹¹⁹Sn{¹H} NMR spectra were measured using the inverse gateddecoupling mode.

3.2. X-ray crystallography

Data for colourless crystal of **3** ·THF were collected on a Nonius KappaCCD diffractometer using MoK_α radiation ($\lambda = 0.71073$ Å), and graphite monochromator at 150 K. The structures were solved by direct methods (SIR92 [22]). All reflections were used in the structure refinement based on F^2 by full-matrix least-squares technique (SHELXL97 [23]). Heavy atoms were refined anisotropically. Hydrogen atoms were mostly localized on a difference Fourier map, however to ensure uniformity of treatment of crystal, all hydrogens were recalculated into idealized positions (riding model) and assigned temperature factors $H_{iso}(H) = 1.2U_{eq}$ (pivot atom) or of $1.5U_{eq}$ for the methyl moiety. Absorption corrections were carried on, using Gaussian integration from crystal shape [24]. The static positional disorder in **3** ·THF was treated by standard SHELXL procedures, where disordered carbon atoms from THF and *n*-butyl chain were split to two positions.

Selected crystallographic parameters of **3** · THF: $C_{19}H_{29}F_6NO_7S_2Sn$, MW = 680.24, triclinic, *P*-1, *a* = 9.2150(5) Å, *b* = 11.5401(10) Å, *c* = 13.1290(5) Å, α = 86.527(4)°, β = 72.105(5)°, γ = 82.766(5)°, *Z* = 2, *V* = 1317.68(14) Å³, *D_c* = 1.714 g cm⁻³, μ = 1.209 mm⁻¹, *T_{min}/ T_{max}* = 0.9042, 20,941 reflections measured (θ_{max} = 26.37°), 5335 independent (*R_{int}* = 0.0496), 4747 with *I* > 2 σ (*I*), 351 parameters, *S* = 1.077, *R*₁(obs. data) = 0.0329, *wR*₂(all data) = 0.0684; max., min. residual electron density = 0.729, -0.608 e Å⁻³.

3.3. Synthesis

 $L^{CN}(n-Bu)_2SnCl$ [12b], $L^{CN}Ph_2SnCl$ [12a], $L^{CN}(n-Bu)SnCl_2$ [12b,d], $L^{CN}PhSnCl_2$ [12c], $(L^{CN})_2SnBr_2$ [12c] and $L^{CN}SnBr_3$ [14i] were

prepared according to published procedures. All solvents and AgOTf (99%) were obtained from commercial sources (Sigma–Aldrich). Diethyl ether and THF were distilled from sodium–potassium alloy, degassed and stored over a potassium mirror. All reactions were carried out under an argon atmosphere using standard Schlenk techniques. Melting points are uncorrected.

3.3.1. Preparation of $L^{CN}(n-Bu)_2$ SnOTf (1)

L^{CN}(*n*-Bu)₂SnCl (2.013 g, 5.0 mmol) was dissolved in THF (30 mL) and solution of AgOTf (99%, 1.299 g, 5.0 mmol) in THF (30 mL) was added. AgCl precipitated immediately. The reaction mixture was filtered and the filtration cake was washed with 10 mL of THF. Oily yellowish product was obtained after removing the solvent in vacuo. The crude product was crystallized from saturated diethyl ether solution in a freezing box $(-35 \circ C)$ to give colourless crystals of **1**. Overall yield 2.01 g (78%). M.p. 63–66 °C. ¹H NMR $(C_6D_6, 295 \text{ K}, \text{ ppm})$: 8.30 (d, 1H, H(6'), ${}^3J({}^1H(5'), {}^1H(6')) = 6.8 \text{ Hz},$ ${}^{3}J({}^{119}Sn, {}^{1}H) = 56.1 \text{ Hz}); 7.15 (m, 2H, H(4', 5')); 6.96 (d, 1H, H(3'), 1H) = 56.1 \text{ Hz}); 7.15 (m, 2H, H(4', 5')); 6.96 (d, 1H, H(3'), 1H) = 56.1 \text{ Hz}); 7.15 (m, 2H, H(4', 5')); 6.96 (d, 1H, H(3'), 1H) = 56.1 \text{ Hz}); 7.15 (m, 2H, H(4', 5')); 6.96 (d, 1H, H(3'), 1H) = 56.1 \text{ Hz}); 7.15 (m, 2H, H(4', 5')); 7.15 (m, 2H, H(4', 5')); 7.15 (m, 2H) = 56.1 \text{ Hz}); 7.15 (m, 2H, H(4', 5')); 7.15 (m, 2H) = 56.1 \text{ Hz}); 7.15 (m, 2H$ ${}^{3}I({}^{1}H(4'), {}^{1}H(3')) = 7.3 \text{ Hz}); 3.17 (s, 2H, CH_2N); 1.81 (s, 6H, N(CH_3)_2);$ 1.63 (m, 4H, H(1)); 1.51-1.31 (m, 8H, H(2) and H(3)); 0.90 (t, 6H, H(4)). ¹³C{¹H} NMR (C₆D₆, 295 K, ppm): 142.7 (C(2'), ²J(¹¹⁹Sn, ¹³C) = 36.2 Hz); 139.8 (C(1'), ${}^{1}J({}^{119}Sn, {}^{13}C) = 624.5$ Hz); 138.3 (C(6'), ${}^{2}J({}^{119}Sn, {}^{13}C) = 40.7$ Hz); 130.5 (C(4')); 129.2 (C(5'), ${}^{3}J({}^{119}Sn, {}^{13}C) =$ 65.6 Hz); 127.2 (C(3'), ${}^{3}J({}^{119}Sn, {}^{13}C) = 52.5$ Hz); 121.3 (q, CF₃, ${}^{1}J({}^{19}F,$ $^{13}C) = 315.0 \text{ Hz}$; 65.9 (CH₂N); 45.8 (N(CH₃)₂); 28.5 (C(2), ²*J*(¹¹⁹Sn, ¹³C) = 35.3 \text{ Hz}; 27.7 (C(3), ³*J*(¹¹⁹Sn, ¹³C) = 92.5 \text{ Hz}); 18.2 (C(1), ¹*J*(¹¹⁹Sn, ¹³C) = 462.3 \text{ Hz}); 14.0 (C(4)). ¹⁹F¹H} NMR (C₆D₆, 295 K, ppm): -77.7. ¹¹⁹Sn{¹H} NMR (C₆D₆, 295 K, ppm): -1.0. Elemental analysis (%): found: C. 42.3: H. 6.6: N. 2.5: S. 5.5. Calcd. for C₁₈H₃₀F₃NO₃SSn (516.19): C, 41.88; H, 5.86; N, 2.71; S, 6.21.

3.3.2. Preparation of $L^{CN}Ph_2SnOTf(2)$

L^{CN}Ph₂SnCl (2.213 g, 5.0 mmol) was dissolved in THF (50 mL). AgCl precipitated immediately upon addition of a solution of AgOTf (99%, 1.299 g, 5.0 mmol) in THF (30 mL). The reaction mixture was filtered and the filtration cake was washed with 25 mL of THF. The filtrate was concentrated in vacuo until solid started to precipitate from the solution. This saturated solution was then stored at -35 °C for several days to give pure **2** as a white crystalline solid. Overall isolated yield 2.28 g (82%). M.p. 165–167 °C. ¹H NMR (C₆D₆, 295 K, ppm): 8.74 (d, 1H, H(6'), ${}^{3}J({}^{1}H(5'), {}^{1}H(6')) = 6.8 \text{ Hz}, {}^{3}J({}^{119}\text{Sn}, {}^{1}\text{H}) = 64.8 \text{ Hz}); 7.60 (d, 4H, H(2''), {}^{3}J({}^{1}H(3''), {}^{1}H(2'')) = 5.2 \text{ Hz}, {}^{3}J({}^{119}\text{Sn}, {}^{119}\text{Sn}) = 5.2 \text{ Hz}, {}^{3}J({}^{119}\text{Sn}) = 5.2 \text{ Hz}, {}^{3}J({}^{119}\text$ 1 H) = 66.9 Hz); 7.29 (t, 1H, H(5')); 7.16 (m, 7H, H(4') and H(3" and 4")); 6.80 (d, 1H, H(3'), ${}^{3}J({}^{1}H(4'), {}^{1}H(3')) = 7.6 \text{ Hz}$); 2.82 (s, 2H, NCH₂); 1.24 (s, 6H, N(CH₃)₂). ¹H NMR (THF-*d*₈, 295 K, ppm): 8.24 (br, 1H, H(6'), ${}^{3}J({}^{119}\text{Sn}, {}^{1}\text{H}) \approx 65 \text{ Hz}$); 7.73 (d, 4H, H(2''), ${}^{3}J({}^{119}\text{Sn}, {}^{1}\text{H}) \approx 65 \text{ Hz}$); 7.73 (d, 4H, H(2''), ${}^{3}J({}^{119}\text{Sn}, {}^{1}\text{H}) \approx 65.6 \text{ Hz}$); 7.46 (m, 3H, L^{CN} and Ph groups); 7.42 (m, 5H, L^{CN} and Ph groups); 7.46 (m, 3H, H(3')); 3.83 (s, 2H, NCH_2); 2.07 (s, 6H, N(CH_3)_2). {}^{13}\text{C}{}^{1}\text{H} \right) \text{NMR} (THF- d_8 , 295 K, ppm): 144.6 (C(2')); 138.8 (C(6'), ${}^{2}J({}^{119}\text{Sn}, {}^{13}\text{C}) = 51.5 \text{ Hz}$); 137.2 $(C(2''), {}^{2}I({}^{119}Sn, {}^{13}C) = 47.2 \text{ Hz}); 136.3 (br, C(1'')); 131.8 (C(4')); 131.4$ $(C(4'')); 130.1 (C(3''), {}^{3}J({}^{119}Sn, {}^{13}C) = 69.9 Hz); 129.6 (C(5')); 128.6$ $(C(3'), {}^{3}J({}^{119}Sn, {}^{13}C) = 62.4 \text{ Hz}); 121.9 (q, CF_3, {}^{1}J({}^{19}F, {}^{13}C) = 318.5 \text{ Hz});$ 65.5 (CH₂N); 46.5 (N(CH₃)₂), signal of the C(1') was not found. ¹⁹F ${^{1}H}$ NMR (THF- d_{8} , 295 K, ppm): -77.0. ${^{119}Sn}{^{1}H}$ NMR (THF- d_{8} , 295 K, ppm): -162.8. Elemental analysis (%): found: C, 48.1; H, 4.4; N, 2.2; S, 5.2. Calcd. for C₂₂H₂₂F₃NO₃SSn (556.17): C, 47.51; H, 3.99; N, 2.52; S, 5.77.

3.3.3. Preparation of $L^{CN}(n-Bu)Sn(OTf)_2 \cdot THF$ (**3** · THF)

 $L^{CN}(n-Bu)SnCl_2$ (2.514 g, 6.6 mmol) was dissolved in THF (40 mL) and solution of AgOTf (99%, 3.426 g, 13.2 mmol) in THF (30 mL) was added. AgCl precipitated immediately. The reaction mixture was filtered and the filtration cake was washed with THF (15 mL). The filtrate was concentrated *in vacuo* and stored at -35 °C. Crystals of

pure **3** ·THF grew in few days. Overall isolated yield 2.77 g (69%). M.p. 88–90 °C. ¹H NMR (THF- d_8 , 295 K, ppm): 7.70 (d, 1H, H(6'), ³*J*(¹H(5'), ¹H(6')) = 7.0 Hz, ³*J*(¹¹⁹Sn, ¹H) = 101.5 Hz); 7.42–7.34 (m, 2H, H(4') and H(5')); 7.27 (d, 1H, H(3'), ³*J*(¹H(4'), ¹H(3')) = 7.3 Hz); 4.02 (s, 2H, NCH₂); 2.65 (s, 6H, N(CH₃)₂); 2.17 (m, 2H, H(1))); 1.85 (m, 2H, H(2)); 1.45 (m, 2H, H(3)); 0.94 (t, 3H, H(4)). ¹³C{¹H} NMR (THF- d_8 , 295 K, ppm): 142.1 (C(2')); 140.9 (C(1')); 134.7 (C(6')); 132.0 (C(4')); 129.8 (C(5')); 128.6 (C(3')); 120.7 (q, CF₃, ¹*J*(¹⁹F, ¹³C) = 318.8 Hz); 64.0 (CH₂N); 46.1 (N(CH₃)₂); 32.7 (br, C(1)); 28.2 (C(2)); 26.7 (C(3)); 13.8 (C(4)); ^{*n*}*J*(¹¹⁹Sn, ¹³C) were not observed. ¹⁹F{¹H} NMR (THF- d_8 , 295 K, ppm): -76.5. ¹¹⁹Sn{¹H} NMR (THF- d_8 , 295 K, ppm): -350.9. Elemental analysis (%): found: C, 33.6; H, 4.4 N, 2.0; S, 9.5. Calcd. for C₁₉H₂₉F₆NO₇S₂Sn (680.25): C, 33.55; H, 4.30; N, 2.06; S, 9.43.

3.3.4. Preparation of $L^{CN}PhSn(OTf)_2$ (4)

L^{CN}PhSnCl₂ (0.930 g, 2.32 mmol) was dissolved in THF (40 mL) and solution of AgOTf (99%, 1.194 g, 4.64 mmol) in THF (15 mL) was added. AgCl precipitated upon mixing these solutions. The reaction mixture was filtered and the filtration cake was washed with THF (15 mL). The saturated THF solution of **4** was left for a couple of days in a freezing box $(-35 \degree C)$ to give nearly colourless crystals. Yield 0.816 g (56%). M.p. 145–147 °C. ¹H NMR (THF-*d*₈, 295 K, ppm): 7.96 (d, 2H, H(2"), ${}^{3}J({}^{1}H(3"), {}^{1}H(2")) = 7.5 \text{ Hz}, {}^{3}J({}^{119}\text{Sn}, {}^{1}\text{H}) = 110.4 \text{ Hz});$ 7.83 (d, 1H, H(6'), ${}^{3}J({}^{1}H(5'), {}^{1}\text{H}(6')) = 7.2 \text{ Hz}, {}^{3}J({}^{119}\text{Sn}, {}^{1}\text{H}) =$ 113.8 Hz); 7.55 (m, 2H, L^{CN} and Ph moieties); 7.40 (m, 3H, L^{CN} and Ph moieties); 7.30 (d, 1H, H(3'), ${}^{3}J({}^{1}H(4'), {}^{1}H(3')) = 7.2$ Hz); 3.58 (s, 2H, NCH₂); 2.47 (s, 6H, N(CH₃)₂). ¹³C{¹H} NMR (THF-*d*₈, 295 K, ppm): 141.2 (C(2')); 140.6 (C(1')); 135.7 (C(2")); 134.8 (C(6')); 132.4 (C(4')); 132.2 (C(4")); 130.6 (C(3")); 130.0 (C(5')); 128.8 (C(3')); 120.8 (q, CF_3 , ${}^{1}J({}^{19}F, {}^{13}C) = 319.7 \text{ Hz}$; 63.8 (CH_2N); 46.2 ($N(CH_3)_2$); signal of the C(1") was not found; ${}^{n}J({}^{119}Sn, {}^{13}C)$ were not observed. ${}^{19}F{}^{1}H{}$ NMR (THF-d₈, 295 K, ppm): -76.9. ¹¹⁹Sn{¹H} NMR (THF-d₈, 295 K, ppm): -418.6. Elemental analysis (%): found: C, 33.0; H, 3.0; N, 2.0; S, 9.9. Calcd. for C₁₇H₁₇F₆NO₆S₂Sn (628.14): C, 32.51; H, 2.73; N, 2.23; S, 10.21.

3.3.5. Attempt for the preparation and characterization of $(L^{CN})_2$ Sn(OTf)₂

The synthesis was carried out similarly to the preparation of **1–4** using $(L^{CN})_2$ SnBr₂ (0.547 g, 1.00 mmol) and AgOTf (99%, 0.514 g, 2.00 mmol). Due to the unexpected limited solubility in common organic solvents only ¹H NMR spectrum could be recorded but this gave us no relevant information about the structure of the title compound. Unfortunately, however, the single crystals of this species were not obtained.

3.3.6. Attempt for the preparation and characterization of $L^{CN}\text{Sn}(\text{OTf})_3$

The synthesis was carried out similarly to the preparation of **1–4** using $L^{CN}SnBr_3$ (0.493 g, 1.00 mmol) and AgOTf (99%, 0.771 g, 3.00 mmol). Due to the unprecedented reactivity of the title compound formed, no NMR spectra could be recorded since it reacts with the solvent (THF) even at room temperature to form presumably polymeric species. Unfortunately, however, the single crystals of this compound were not obtained.

3.4. Catalytic experiments

General procedure for reactions of methanol with carbon dioxide: 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 organotin(IV) triflate (**1**, **2** and **3**) in methanol was introduced by syringe. Then, CO_2 was admitted to the desired amount (see Table 1). The reaction

temperature was controlled by an internal thermocouple. After a reaction time of 15 h the reactor was cooled down to 0 °C, the 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 analyzed by GC (DEC external standard, Thermo Scientific FOCUS GC, TR-Wax 30 m capillary column, FID detector). The tin-based residue was studied by IR and multinuclear NMR spectroscopy.

4. Conclusions

Four novel organotin(IV) triflates bearing the C.N-chelating ligand were synthesized and structurally characterized in the terms of this work. It was found that triorganotin(IV) triflate **1** (which is presumably stable towards air moisture at ambient temperature) undergoes significant weakening of the Sn-OTf bond in solution which makes it effective catalyst precursor for the direct synthesis of DMC as demonstrated. On the other hand, compounds 2 and 3 did not seem to be applicable for this purpose due to reasons discussed above. Unfortunately, it was found that the catalyst precursor **1** was not able to survive the harsh reaction conditions as detected by the multinuclear NMR spectroscopy. The possibility of using of some drying agent(s) as well as the influence of the reaction time, temperature and pressure with respect to the yield of the DMC promoted by 1 is now under close investigation. Careful effort is devoted to the further identification of products of decomposition of 1 during the high-pressure synthesis of the DMC, too.

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Appendix A. Supplementary material

CCDC 863441 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.cccdc.cam.ac.uk/ data-request/cif. Supplementary data related to this article can be found in the online version, at doi:10.1016/j.jorganchem.2012.02. 022.

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