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Products of hydrolysis of *C,N*-chelated triorganotin(IV) chlorides and use of products as catalysts in transesterification reactions

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Abstract

Triorganotin(IV) chlorides containing one L^{CN} chelating ligand were hydrolyzed with an excess of sodium hydroxide. The composition of the products is strongly dependent on the nature of the organic groups bound to the tin atom. Di(*n*-butyl)tin, dimethyltin as well as the diphenyl derivative exhibits an equilibrium between hydroxide and stannoxane forms (oxide), whereas alkyltin species react spontaneously and reversibly with carbon dioxide present in the air to form carbonate species. On the other hand, diphenyl derivatives display virtually no reaction with CO_2 towards carbonates, while the di-*t*-butyl-substituted tin derivative is stable under the same experimental condition and remains as a tin hydroxide. In the case of the dimethyltin derivative, a methyl group migration was observed with displacement of one L^{CN} chelating ligand during the reaction on the air. The coordination geometry of the tin central atom(s) of all studied compounds can be described as trigonal bipyramidal with a dative bonded dimethylamino group occupying one coordination site. The catalytic activity of these compounds in transesterification reactions is generally lower compared to the systems reported in the literature, with the exception of the transesterification of ethyl acetate by cyclohexanol which displays a remarkable activity.
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1. Introduction

The chemistry of organotin(IV) oxides and/or hydroxides is well established [1]. This class of compounds, mainly diorganotin(IV) or cationic species, were used as homogenous catalysts in various types of transesterification and transcarbamoylation processes [2]. Although the first attempts to use triorganotin(IV) compounds in a catalytic process were made in the late 1960s, there is only a limited number of papers reporting on such activity [3].

The triorganotin(IV) compounds were structurally investigated mainly by help of NMR techniques in solution [4]. Triorganotin(IV) hydroxides of general formula R_3SnOH with relatively small R groups ($R_3 = Et_3$ [5], Ph_3 [6], $(PhCH_2)Me_2$ [7]) form infinite zig-zag chains, where the molecular tectons are associated via hydroxo bridges through dative bonds. Using bulkier substituent groups repress the intermolecular association [8]. The elimination of one water molecule from two molecules of hydroxide give the corresponding distannoxane species. According to the literature, the major parameter in the

structural evaluation of bis(triorganotin) oxides, also known as stannoxanes ($R_3SnOSnR_3$), is the interatomic Sn–O–Sn angle. Generally, the presence of bulkier substituent groups on tin leads to higher angle values [9]. The further reaction of these compounds with inorganic carbonates or carbon dioxide leading to organotin(IV) carbonates or organic carbonates has been reported as well [4a,10].

Recently, we have reported on monomeric triorganotin(IV) fluorides and carboxylates of general formula $L^{CN}R_2SnX$ (X = F, OOCR′), which contain one chelating L^{CN} = 2-[(CH$_3$)$_2$NCH$_2$]C$_6$H$_4$ ligand and two alkyl (Me, n-Bu, t-Bu) or aryl (Ph) groups of different steric bulk and electronic properties [11,12]. The family of organotin(IV) compounds containing the 2-(dimethylaminomethyl)phenyl-group or related ligands exhibits noteworthy structural properties [1,13]. Additionally, owing to the activation of the Sn–F bond (fluorinated tin derivatives) or Sn–O bond (carboxylated tin derivatives) in trans position to the lone electron pair of the nitrogen atom of the dimethylamino group, such compounds are very promising for applications in synthetic organic chemistry [14]. In this paper, we focused our attention on the hydrolysis' products of chlorides of general formula $L^{CN}R_2SnCl$ (where R = Me (1c), n-Bu (1a), t-Bu (1d) or Ph (1b)), investigated their structure, reactivity and, in particular, their catalytic activity in transesterification reactions.

2. Results and discussion

The reactivity of 1a–d (Fig. 1) with several molecules was studied: water, an excess of aqueous ammonia, a 1 M triethyl amine in water/benzene mixture [15], 1–10 molar equivalents of sodium hydroxide in water/benzene biphasic system, as well as diluted HCl, and HF aqueous solution. The last two screening tests were performed in order to assess the possibility to quaternize [16] the ligand's nitrogen donor atom, respectively.

Compounds 1a–d do not react with atmospheric moisture when exposed to air for two months as well as when used as suspension or solution in water. Similarly they show no reactivity with an excess of aqueous ammonia, or solubilized in a 1 M solution of triethyl amine/water in benzene and heated to 60 °C for a couple of days. Surprisingly, no quarternization of the dimethylamino group occurred when 1a–d were dissolved in a biphasic system (diethyl ether/water) and stirred for additional 2 h with 3 molar equivalents of HCl or HF at room temperature. This suggest a high stability of the tin–nitrogen bond (vide infra).

The hydrolysis of 1a–d proceeds essentially quantitatively when the appropriate compound is reacted with one or more molar equivalents of NaOH. The amount of NaOH has no significant influence on the reaction progress.

Reaction of 1b (R = Ph) with NaOH under an inert atmosphere, in a benzene/water biphasic, system yields two products in the benzene phase. The amount of products dissolved in the water phase is less than 10% of the amount dissolved in the organic one, and can be anew extracted with fresh benzene almost quantitatively. The products were identified by ^1H and ^{119}Sn (^{13}C spectra of the starting compounds and products were very similar and thus useful only in the case of carbonates (4a–c) – see below) NMR techniques (Fig. 3) as $L^{CN}Ph_2SnOH$ (2b; δ (^{119}Sn) = −187.3 ppm) and ($L^{CN}Ph_2Sn)_2O$ (3b; δ (^{119}Sn) = −173.2 ppm, $^2J(^{119}Sn, ^{119}Sn) = 417$ Hz) and directly after the reaction are in 1:1.3 molar ratio, the same ratio was observed by cryoscopic measurements in benzene under argon. The $\delta(^{119}Sn)$ values for 2b and 3b are comparable to the values found for the starting chloride compound (−175.7 ppm) [17], but upfield-shifted in comparison to analogous hexaphenyl distannoxanes (−83.1 to −75.1 ppm) [18,19]. No signal which could be attributed to a OH group was observed in the ^1H NMR spectrum of 2b, which was isolated as a pure product once
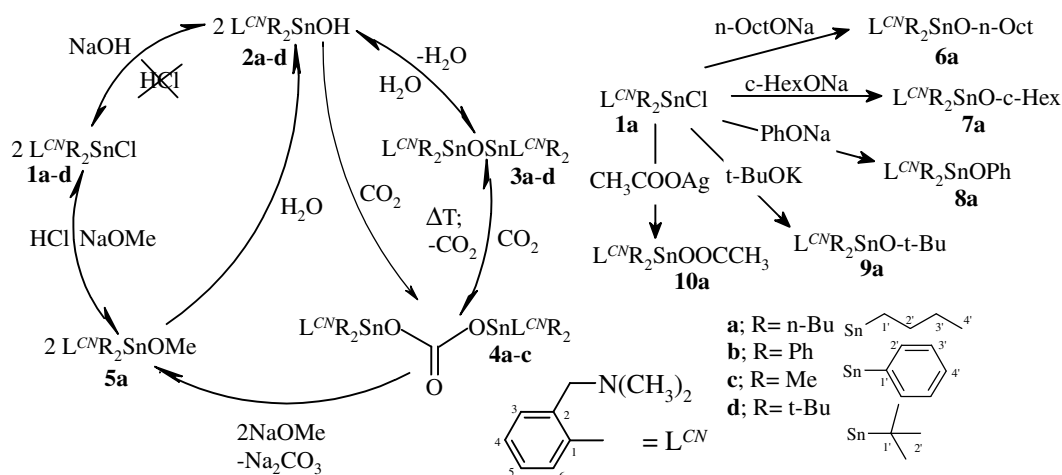

Fig. 1. Reactivity and numbering of studied compounds.

the reaction mixture has been heated to 60 °C for 3 h. It undergoes a rearrangement to form **3b** after elimination of a water molecule within a few hours, **3b** being obtained as the sole product after crystallization of the reaction mixture. The $^2J(^{119}Sn, ^{119}Sn)$ value is comparable to the value found for hexaphenyldistannoxane (437 Hz) [18]. A Sn–O–Sn angle of 134.9° for **3b** was calculated from the coupling constant value [18]. The solid state structure of **3b** was determined by XRD on a single crystal. Tin atoms display a distorted trigonal bipyramidal coordination geometry with three carbon atoms occupying the equatorial positions while the bridging oxygen and datively coordinated nitrogen atoms the axial positions. The distances Sn–O in the nearly symmetrical oxo bridge are a bit longer (1.9764(15) Å) than the ones found in compounds with four-coordinated tin atom (~1.92 Å) (Cambridge Structural Database search July 2006 [20]). The Sn–N distances (2.7785(19) and 2.7955(19) Å) are somewhat longer than those found for triorganotin(IV) derivatives bearing the same ligand (~2.5 Å) [20]. Also the sum the C–Sn–C equatorial angles (349.9° and 349.0°), the bigger torsion angles indicating the deviation of nitrogen atom from the plane of parent phenyl ring (C11–C12–C17–N11 is 40°), and the O–Sn–N angles (ca. 163°) suggest a significant weaker interaction between metallic center and the dimethylamino ligand. The Sn–O–Sn angle measured in the X-ray structure is 136.02(8)°, similar to the value found in bis(triphenylstannyl)oxide (137.3°) [21] and in agreement with the value calculated from the NMR spectrum in solution (vide supra). In comparison, the values found for this angle in the case of analogous compounds bearing o-anisyl- or o-tolyl-ligands are significantly higher (167.0° [9] and 180.0° [18]). It is worth to mention here, that a related structure of an ionic hydrolysis products of $L^{CN}Me_2SnI$ was reported very recently, $[L^{CN}Me_2Sn–(OH)–SnMe_2L^{CN}]^+I^-$, two $L^{CN}Me_2Sn$ units bridged by one single OH group forming the cation whereas the iodine acts as counter-anion [22].

Benzene solutions of **2b** and **3b** equilibrium react slowly with atmospheric CO_2 to form carbonate **4b**. Small amounts of this compound (ca 5%) were detected after 3 h at the air with both NMR and IR spectroscopies (δ (^{119}Sn) = −226.6 ppm (Fig. 2), $\delta(^{13}C(CO_3^{2-}))$ = 164.3 ppm, v_3 = 1580 cm^{-1}). Similar values were recently reported as typical for this type of carbonates [23]. Fragments characteristic for all three compounds (**2b**, **3b** and **4b**) were also detected by ESI MS measurements (Table 1, the tin isotopic clusters at 408 – $L^{CN}Ph_2Sn^+$, 832 – $(L^{CN}Ph_2Sn)_2O$ – observed only when the 'compound stability' parameter was set to 100%, 1284 – $[(L^{CN}Ph_2Sn)_3CO_3]^+$. The formation of **4b** was also observed when the toluene solution of **3b** was stirred with dry ice. The maximum yield of this reaction carried out under
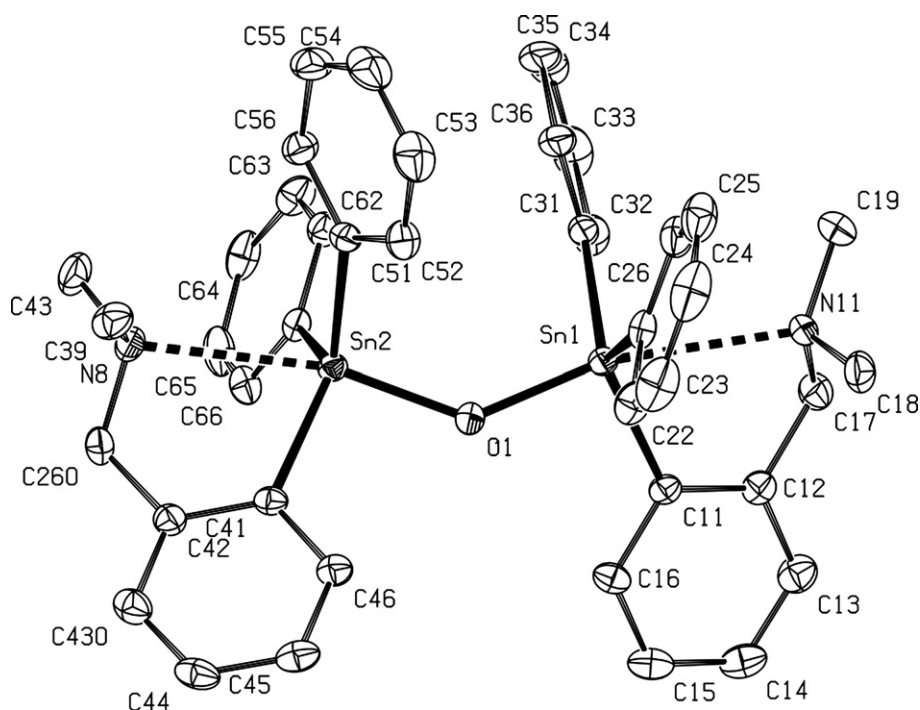

Fig. 2. The molecular structure of **3b**, ORTEP view, 50% probability level. Hydrogen atoms and the solvent are omitted for clarity. The selected distances [Å] and angles [°]: Sn(1)–N(11) 2.7785(19), Sn(2)–N(8) 2.7955(19), Sn(1)–O(1) 1.9764(15), Sn(1)–C(31) 2.132(2), Sn(1)–C(11) 2.137(2), Sn(1)–C(21) 2.142(2), Sn(2)–O(1) 1.9802(15), Sn(2)–C(51) 2.141(2), Sn(2)–C(41) 2.143(2), Sn(2)–C(61) 2.144(2), O(1)–Sn(1)–C(31) 106.28(7), O(1)–Sn(1)–C(11) 95.74(7), C(31)–Sn(1)–C(11) 118.35(8), O(1)–Sn(1)–C(21) 100.31(8), C(31)–Sn(1)–C(21) 112.91(9), C(11)–Sn(1)–C(21) 118.62(8), O(1)–Sn(2)–C(51) 102.10(7), O(1)–Sn(2)–C(41) 94.32(7), C(51)–Sn(2)–C(41) 120.15(8), O(1)–Sn(2)–C(61) 107.61(7), C(51)–Sn(2)–C(61) 109.35(8), C(41)–Sn(2)–C(61) 119.52(7), Sn(1)–O(1)–Sn(2) 136.02(8), N(11)–Sn(1)–O(1) 165.59(7), N(8)–Sn(2)–O(1) 163.32(6).

Table 1
Relative abundances of ions (in %) observed in positive-ion first-order mass spectra of hydrolysis products of **1a–d** in acetonitrile

Species[a]/ion	a		b		c		d	
	m/z	%	m/z	%	m/z	%	m/z	%
$[L^{CN}R_2Sn]^+$	368	1	408	1	284	8	368	–
$[L^{CN}R_2SnO]^+$	384	–	424	–	300	–	384	100
$[(L^{CN}R_2Sn)_2OH]^+$	753	1	833	4	585	13	792[b]	65
$[(L^{CN}R_2Sn)_2CO_3H]^+$	797	–	877	–	629	–	797	–
$[(L^{CN}R_2Sn)_3CO_3]^+$	1164	100	1284	100	912	100	1164	–

[a] Listed m/z values are related to ^{120}Sn, but centroid peaks in mass spectra are shifted by two (for two tin atoms, species $[(L^{CN}R_2Sn)_2OH]^+$ and $[(L^{CN}R_2Sn)_2CO_3H]^+$) or four (for three tin atoms, species $[(L^{CN}R_2Sn)_3CO_3]^+$) mass units.
[b] Adduct ion with acetonitrile $[Cat_2OH \cdot acetonitrile]^+$.

atmospheric CO_2 is approaching 15% which is probably connected to the steric hindrance of the ligands bound to the tin atoms.

The hydrolysis of **1a** was made under the same experimental conditions as in the case of 2b, with 0.7–10 molar equivalents of NaOH, and lead to the formation of similar products No tin-containing product was detected in the water phase. Two products were obtained from the benzene layer in analogy to the hydrolysis of **2b**: the triorganotin hydroxide **2a** ($\delta(^{119}$Sn$) = -76.3$ ppm) as major species and the distannoxane **3a** [$\delta(^{119}$Sn$) = -55.4$ ppm, $^2J(^{119}$Sn, ^{119}Sn$) = 488$ Hz; calculated angle Sn–O–Sn: 141.1°] as the minor species, its concentration increased when the mixture was left at room temperature under an argon atmosphere for a few days or was heated (60°) for a few minutes under vacuum. The $\delta(^{119}$Sn$)$ values are comparable to those of the starting chloride **1a** [26] or analogous fluoride ($\delta(^{119}$Sn$) = -77.1$ ppm) [11]. The coupling constants in **3a** $^2J(^{119}$Sn, ^{119}Sn$)$ are similar to the ones found in hexapropyl- and hexabutyl-distannoxane (447 Hz and 440 Hz) [18] which suggests a comparable Sn–O–Sn angle. The hydroxide **2a** was also observed by cryoscopic measurements directly after the reaction. Both **2a** and **3a** undergo a complete and swift reaction with CO_2 to form carbonate **4a** ($\delta(^{119}$Sn$) = -93.2$ ppm, $\delta(^{13}$C$(CO_3^{2-})) = 163.2$ ppm, $v_3 = 1571$ cm^{-1}) when left at the air. This reaction is reversible and only **3a** was observed when **4a** was heated at 100 °C for 20 min. The tin atoms geometry of this compound can be extrapolated from the ^{119}Sn chemical shifts as being a distorted trigonal bipyramid with a calculated interatomic C–Sn–C average angle of 116.5° [24]. The presence of **4a** was also confirmed by ESI MS spectrometry (tin isotopic clusters at 368 – $L^{CN}n$-Bu$_2$Sn$^+$, 1164 – $[(L^{CN}n$-Bu$_2$Sn$)_3$CO$_3]^+$). The bridged carbonato specie **4a** was also obtained when **1a** was reacted with half an equivalent of anhydrous sodium carbonate. The reverse reaction has also to be taken into account: **4a** reacts with HCl in a biphasic water/benzene system producing **1a** as the sole product. Another quantitative reaction of **4a** is the reaction with two equivalents of sodium methoxide in benzene, producing organotin methoxide **5a** ($\delta(^{119}$Sn$) = -65.6$ ppm) and sodium carbonate. This compound can be hydrolyzed with water to **2a**, or reacted with HCl diluted in benzene to form **1a** (>90%

yield) and affords surprisingly low yield of the protonated form of **2a**, $[L^{CN}(H)n$-Bu$_2$SnOH$]^+[Cl]^-$ or **1a**, $[L^{CN}(H)n$-Bu$_2$SnCl$]^+[Cl]^-$ (**1a′**, $\delta(^{119}$Sn$) = -99.4$ ppm, δ (^{1}H(NH$^+$)) = 11.44 ppm, $\delta(^1$H(NHCH$_2$)) = 3.96 ppm ($^3J(^1$H^{1}H$) = 5.9$ Hz), $\delta(^1$H(NH(CH$_3)_2)) = 2.67$ ppm ($^3J(^1$H^{1}H$) = 4.8$ Hz) in ~5% yield – not isolated). This is probably caused by the strong intramolecular Sn–N bond which should favour substitution reactions at the tin center over the quarternization of the dimethylamino moiety [25]. According to the literature [1a], the reaction of **3a** with butyl lithium in hexane yields $L^{CN}n$-Bu$_2$SnOLi (δ (^{119}Sn$) = -59.5$ ppm, $\delta(^7$Li$) = 1.08$ ppm) and $L^{CN}n$-Bu$_3$Sn ($\delta(^{119}$Sn$) = -51.2$ ppm) [26]. Also the alkoxide of $L^{CN}n$-Bu$_2$SnOR′ type (R′ = n-octyl (**6a**; $\delta(^{119}$Sn$) = -68.6$ ppm), cyclohexyl (**7a**; $\delta(^{119}$Sn$) = -69.5$ ppm), *tert*-butyl (**8a**; $\delta(^{119}$Sn$) = -75.9$ ppm)), phenolate (**9a**; $\delta(^{119}$Sn$) = -82.2$ ppm) and the acetate (**10a**; $\delta(^{119}$Sn$) = -87.1$ ppm) derivatives were prepared as described below and characterized by NMR spectroscopy.

The hydrolysis of **1d** with NaOH yields the organotin hydroxide **2d** as sole product present in the organic layer. This product was suggested from ^{1}H (singlet resonance at 2.74 ppm for OH group, that disappeared when measured in wet CDCl$_3$ or CD_3OD) and ^{119}Sn ($\delta(^{119}$Sn$) = -46.3$ ppm) NMR spectroscopy as well as with ESI-MS spectrometry (384 – $L^{CN}t$-Bu$_2$SnO$^+$) and cryoscopic measurements in benzene. This hydroxide reacts very slowly to the corresponding distannoxane (**3d**; yield 41% after 7 h in vacuo at 90 °C, $\delta(^{119}$Sn$) = -35.6$ ppm, $^2J(^{119}$Sn, ^{119}Sn$) = 852$ Hz (calculated Sn–O–Sn angle is 172.7°)) [18]. The bridged oxo-tin compound **3d** is very reactive towards air moisture to form the monomeric **2d**, but interestingly does not react with CO_2. The $\delta(^{119}$Sn$)$ values for **2d** (-46.3 ppm) and **3d** (-35.6 ppm) are within the chemical shift range found for five-coordinated tin atom, as e.g. in $L^{CN}t$-Bu$_2$SnF (-92.1 ppm) [11], and four-coordinated tin as in $[(t$-Bu$)_2$PhSn$]_2$O (53.9 ppm [18]). Hence these tin compounds can be estimated in benzene solution as species with Sn–N intramolecular interactions of intermediate strength in contrast to the starting chloride **1d** which displays a weak Sn–N interaction ($\delta(^{119}$Sn$) = 18.5$ ppm) [27]. On the other hand, the crystal structure determination of **3d** (Fig. 4) showed that no interaction between tin and nitrogen atoms is present (Sn–N
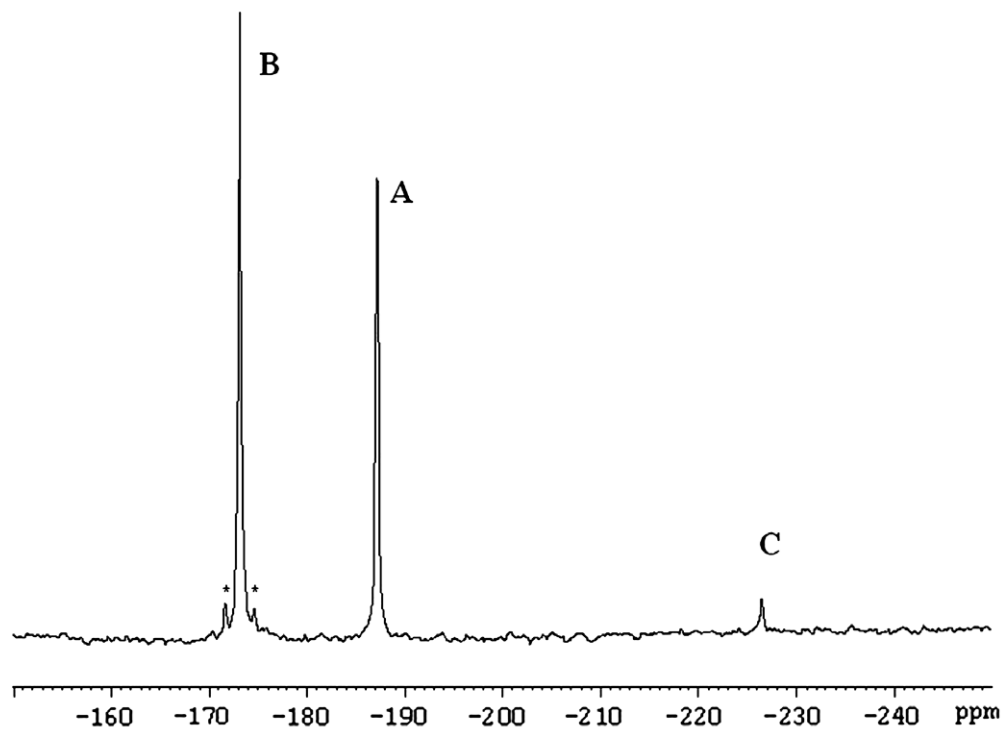
Fig. 3. ^{119}Sn NMR spectrum of **2b** (A), **3b** (B), and **4b** (C) as mixture, $^2J(^{117}$Sn, ^{119}Sn) are indicated with asterisks.
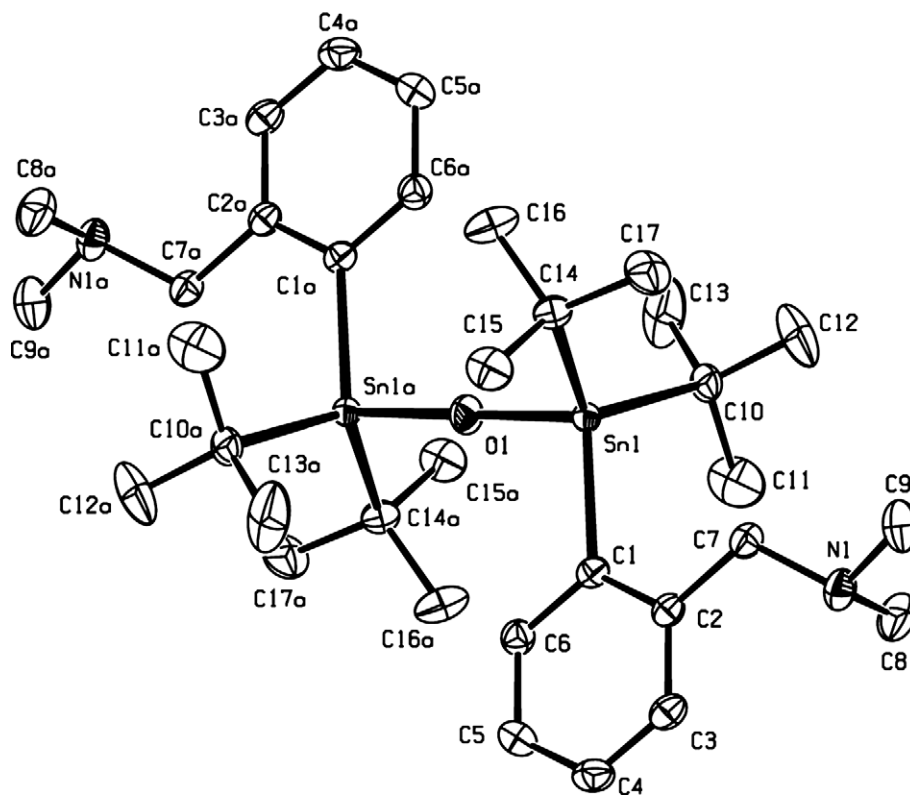

Fig. 4. The molecular structure of **3d**, ORTEP view, 50% probability level. Hydrogen atoms are omitted for clarity. The selected distances [Å] and angles [°]: Sn(1)–N(1) 4.7584(16), Sn(1)–O(1) 1.94871(13), Sn(1)–O(1) 1.94871(13), Sn(1)–C(1) 2.1645(17), Sn(1)–C(10) 2.1911(17), Sn(1)–C(14) 2.1919(18), O(1)–Sn(1)–C(1) 103.17(5), O(1)–Sn(1)–C(10) 102.84(5), C(1)–Sn(1)–C(10) 111.73(7), O(1)–Sn(1)–C(14) 104.20(5), C(1)–Sn(1)–C(14) 112.31(7), C(10)–Sn(1)–C(14) 120.25(7), Sn(1)–O(1)–Sn(1a) 180.0, N(1)–Sn(1)–O(1) 152.31(2).

4.7584(16) Å). The molecule displays a center of symmetry at O1 with a distinctive Sn1–O1–Sn2 angle of 180°. The sum of the "equatorial" C–Sn–C angles (344.3(3)°) as well as the diverse C–Sn–O1 angles, in the range 102.8–104.2°, clearly point towards a distorted tetrahedral geometry around the tin atom. This is obviously due to the presence of the sterically demanding *t*-butyl groups which has also an influence on the distance Sn–O (1.94871(13) Å) that is slightly shorter than in **3b**.

The differences in ESI/MS spectra between **a–c** and **d** (see Table 1) indicate that the sterically demanding *t*-Bu groups prevents the formation of carbonate **4d** and oxide **3d** under atmospheric carbon dioxide and that only the hydroxo compound is present.

The hydrolysis of **1c** was performed under similar conditions as described above for **1a**, **1b** or **1d** . This reaction was studied by ^1H and ^{119}Sn NMR spectroscopy. After the reaction in the air, it can be noticed that distannoxane (**3c**; $\delta(^{119}Sn) = -62.6$ ppm), hydroxide (**2c**; $\delta(^{119}Sn) = -85.9$ ppm) and carbonate (**4c**; $\delta(^{119}Sn) = -55.2$ ppm, $\delta(^{13}C(CO_3^{2-})) = 163.5$ ppm), $v_3(C=O) = 1580$ cm^{-1}) are in mutual chemical equilibrium in the organic phase. The carbonate was the only separable species observed separately in the water phase. Typical fragments were also observed in ESI MS spectrograms for these three compounds. The hydroxide/oxide molar ratio evaluated directly after the

reaction run under argon atmosphere was 1–2.6 as determined by ^{119}Sn, ^1H NMR spectroscopy and cryoscopic measurements.

In order to investigate the stability of stannoxannes potentially usable in catalytic applications, the compounds **3a**–**d** were exposed as solid samples to air for one year. The di-*n*-butyl compound **3a** exclusively yielded the carbonate **4a**, the diphenyl compound **3b** was reacting very slowly to form carbonate **4b** in 15% yield, whereas the hydroxide **2d** was detected as the main product of reactivity of di-*t*-butyl compound **3d**. The dimethyl containing species **3c** seems to be very instable yielding the carbonate **4c**, a diorganotin(IV) oxo-carbonato bridged specie $L_2^{CN}Sn(\mu-O)$-$(\mu-CO_3)SnL_2^{CN}$ [28], a stannoxane $L_2^{CN}MeSn(\mu-O)$-$SnMeL_2^{CN}$ (**11**), $(Me_3SnO)_2$ ($\sim$ 5%) [29], and other five unidentified tin-containing species ($\delta(^{119}Sn) = -86.24$, -114.42, -145.12, -149.45 and -151.19 ppm). The characterization of $(Me_3SnO)_2$ is quite remarkable, because it clearly indicates that a dimethylaminomethyl benzene ligand has been substituted by a methyl group. This reaction is an important example of phenyl–methyl ligand exchange at the tin (IV) center and is related to processes already described in the literature [15,30]. The solid state structure of $L_2^{CN}MeSn(\mu-O)SnMeL_2^{CN}$ (**11**) (Fig. 5) is similar to the structure of **3b** – trigonal bipyramidal geometry for the tin atoms with three carbon atoms in equatorial
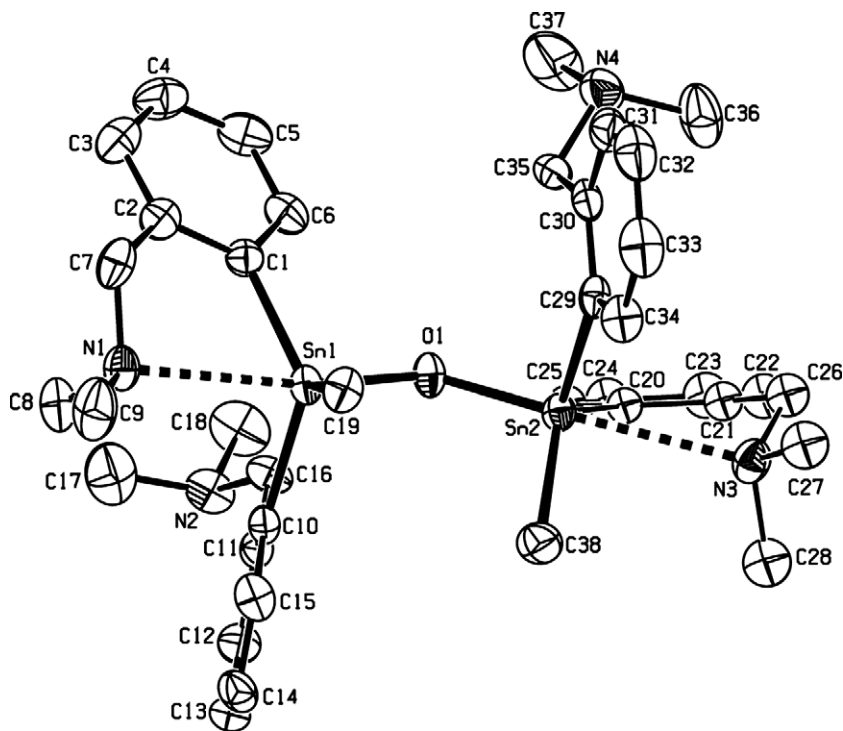

Fig. 5. The molecular structure of 11, ORTEP view, 50% probability level. Hydrogen atoms and the disordered atoms from one of the ligands are omitted for clarity. The selected distances [Å] and angles [°]: Sn(1)–N(1) 2.744(4), Sn(1)–N(2) 4.723(4), Sn(2)–N(3) 2.791(4), Sn(2)–N(4) 4.632(4), Sn(1)–O(1) 1.983(3), Sn(1)–C(19) 2.132(4), Sn(1)–C(1) 2.137(4), Sn(1)–C(10) 2.140(4), Sn(2)–O(1) 1.974(3), Sn(2)–C(20) 2.128(3), Sn(2)–C(38) 2.132(5), Sn(2)–C(29) 2.151(4), O(1)–Sn(1)–C(19) 105.06(15), O(1)–Sn(1)–C(1) 96.20(15), C(19)–Sn(1)–C(1) 119.73(17), O(1)–Sn(1)–C(10) 98.75(14), C(19)–Sn(1)–C(10) 109.80(17), C(1)–Sn(1)–C(10)–121.80(16), O(1)–Sn(2)–C(20) 97.06(12), O(1)–Sn(2)–C(38) 104.77(17), C(20)–Sn(2)–C(38) 122.88(16), O(1)–Sn(2)–C(29) 101.49(14), C(20)–Sn(2)–C(29) 115.17(14), C(38)–Sn(2)–C(29) 111.10(19), Sn(1)–O(1)–Sn(2) 129.92(16), N(1)–Sn(1)–O(1) 166.56(11), N(2)–Sn(1)–O(1) 80.38(10), N(3)–Sn(2)–O(1) 166.67(10), N(4)–Sn(2)–O(1) 78.68(11).

position and the nitrogen and bridging oxygen atoms occupying the axial ones. The N–Sn–O and Sn1–O1–Sn2 angles are also comparable to the related angles found in **3b** (166.56(11)°, 166.67(10)° and 129.92(16)°, respectively). Two non-equivalent ligands are bound to each tin atoms, one of them is bonded in a *C,N*-chelating mode with Sn–N distances 2.744(4) and 2.791(4) Å, indicating weak intramolecular bonds, and the remaining two nitrogen atoms clearly being outside the coordination sphere of the tin atom (4.723(4) and 4.632(4) Å) as found similarly in **3d**.

A typical feature found in the ESI mass spectra for this class of compounds (see Table 1) is the cleavage of the most labile bond in the molecules yielding two complementary ions, where the cationic part of the molecule can be measured in the positive-ion mode and the anionic part in the negative-ion mode.

2.1. Catalytic activity in transesterification reactions

In order to evaluate the efficiency of these tin compounds as transesterification catalysts, the catalytic activity of compounds **3a–d** was assessed using strictly the reaction procedures as described in the literature [2–4], so as to make comparison possible (Table 2, Scheme 1; for the further investigations only **3a** was selected as the most stable and efficient one).

Firstly the transesterification of ethylbutyrate with 1-heptanol according to the procedure reported by Jousseaume et al. (Scheme 1, reaction A) [2a] was carried out in order to correlate the observed activity with the nature of the tin substituents. The most active compound was the **3a** wearing *n*-butyl groups. The activity of this compound in comparison to compounds used by Jousseaume
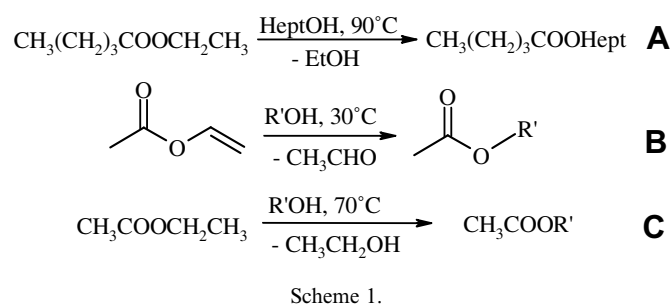
Scheme 1.

is much lower probably due to the lower Lewis acidity of the tin atom.

The same conclusion can be made in the case of reaction B (Scheme 1) developed by Otera [2b]. On the other hand, a much lower catalyst loading (0.05 or 0.5 mol% instead of originally used 1–10 mol%) was used and higher yields could be achieved in the transesterification with secondary alcohols and with phenol (from 0% [2b] to 5–17%).

The best results were obtained using Willem's [3a] process (Scheme 1, equation C), where higher yield of primary alcohol and remarkably higher (from 23% to 95.8% – run 19) yield of transesterificated secondary alcohol were observed when compared to the literature data. Interestingly, the yield of product transesterificated with more sterically hindered secondary alcohols is a bit higher than the yield obtained for primary alcohol. One can speculate here on existence of a dynamic equilibrium between **2a** (the hydroxide), **3a** (the oxide). Under reaction conditions of catalytic experiments C, in the presence of alcohols, hydroxylic protons are available (proof: the reaction mixtures show the tin alkoxides corresponding to the transesterification alcohols engaged), so these should be able, even in moisture free conditions, to establish the equilibrium between the tin oxide **3a** and the tin hydroxide **2a** after proton transfer and protolysis. In turn, it is realistic to consider that the latter tin hydroxide **2a** now exists as an equilibrium between $L^{CN}R_2SnOH$ on one hand, and the cation $L^{CN}R_2Sn^+$ and the anion OH^- on the other hand, because the intramolecular dative N–Sn bond stabilizes the triorganotin(IV) cation [31]. It is well known that Sn–X systems in which an intramolecular dative bond is present are prone to limited ionization in solution, leading sometimes even to full ionic pairs in the crystalline state. To support this idea and to generalize the trend of increasing of activity of catalyst for secondary alcohols, the reaction system A substituting *n*-heptanol for cyclohexanol has been performed but only negligible yield of cyclohexyl butyrate (0.7%) was detected.

In order to gain some information on the catalytically active species, the ^1H and ^{119}Sn NMR spectra of the reaction mixtures were eventually recorded after evaporation under high vacuum. These measurements clearly showed that in the case of successful transesterifications, the alkoxide (resp. phenoxide) derivatives (**6a–8a**) were present in

Table 2
Studied transesterification reactions

Run	Catalysis (Eq.)/R′	Catalyst/loading [mol%]	Time [h]	Yield [%]
1	A/–	**3a**/1	4	37.8
2	A/–	**3b**/1	4	11.7
3	A/–	**3c**/1	4	9.4
4	A/–	**3d**/1	4	5.3
5	B/*n*-Oct	**3a**/0.05	96	7.3
6	B/*c*-Hex	**3a**/0.05	96	9.4
7	B/Ph	**3a**/0.05	96	2.3
8	B/*n*-Oct	**3a**/0.5	24	18.2
9	B/*c*-Hex	**3a**/0.5	24	16.3
10	B/Ph	**3a**/0.5	24	4.3
11	B/*n*-Oct	**3a**/0.5	45	31.5
12	B/*c*-Hex	**3a**/0.5	45	23.8
13	B/Ph	**3a**/0.5	45	7.4
14	B/*n*-Oct	**3a**/0.5	4[a]	63.0
15	B/*c*-Hex	**3a**/0.5	4[a]	15.8
16	B/Ph	**3a**/0.5	4[a]	7.0
17	B/*n*-Oct	**3a**/0.5	8[a]	76.1
18	C/*n*-Oct	**3a**/0.5	24	92.1
19	C/*c*-Hex	**3a**/0.5	24	96.2(15)[b]

[a] Reflux.
[b] Average value of six experiments with standard error.

the solution. Considering now the unsuccessful attempts to transesterificate t-BuOH, only the acetate **10a** could be characterized as tin-containing species after the reaction run.

Another possible use of the organotin(IV) compounds is their use as catalyst in the synthesis of linear carbonates from alcohols and carbon dioxide [10,32,33] in the presence of dehydrating reagents as well as in the production of polycarbonates via ring opening polymerisation of cyclic carbonates [34]. In a first reaction screening, we investigated the reaction of the bridged tin oxo compound **3a** under high CO_2-pressure with four different substrates (phenol, ethanol, propylene oxide and cyclohexene oxide; catalyst-to-substrate molar ratio of ca. 1–1000, substrate-to-CO_2 ratio: ca. 1–2). We found that **3a**, under the chosen experimental conditions (see Section 3), immediately form a stable bridged carbonato specie **4a** which did not further react with the substrate to yield a catalytically active species. This lack of versatility is most probably due to the high thermal stability (loss of CO_2 at 257.8 °C; decomposition at 314.6 °C – determined by DTA) of the formed carbonate **4a**. More work is currently in progress to optimize the course of reactions involving bridged tin oxo complexes and carbon dioxide. This implies, for instance, the search for a suitable substrate capable of reacting with **3a** to form new intermediate tin compounds reactive towards carbon dioxide and, hopefully, also able to start a catalytic reaction implicating both CO_2 and substrate.

2.2. Concluding remarks

The triorganotin(IV) chlorides containing one N,N-(dimethylaminomethyl)benzene (L^{CN}) chelating ligand were hydrolyzed with an excess of sodium hydroxide. The composition of the final reaction mixtures is strongly dependent on the nature of the organometallic substituents on the tin atom. The di-n-butyltin, dimethyltin and diphenyltin derivatives undergo an equilibrium hydroxide↔stannoxane (oxide), where the tin hydroxo species react spontaneously and reversibly with atmospheric carbon dioxide to form the corresponding bridged tin alkyl-carbonates. In comparison, the diphenyl derivative hardly reacts with CO_2 and the di-t-butyl-substituted one does not react at all and remains as a stable tin hydroxide. The ligand exchange involving methyl group and N,N-(dimethylaminomethyl)benzene was observed when dimethyl compound **3a** was left under normal atmosphere for one year. The coordination geometry at the tin atom(s) can be in the mainly described as trigonal bipyramidal with an intramolecularly coordinated dimethylamino group as axial substituent. The catalytic activity of these compounds used in transesterification reactions is lower than the activity of the already published systems but a remarkably high activity could be noticed in the case of transesterification of ethyl acetate by cyclohexanol, when compared to previous literature data on secondary alcohols [3].

3. Experimental

3.1. NMR spectroscopy

The NMR spectra were recorded as solutions in C_6D_6, CD_2Cl_2 or toluene-d_8 on a Bruker Avance 500 spectrometer and a Varian Inova 400 spectrometer (equipped with Z-gradient 5 mm probe) at 300 K ^{1}H (500.13 MHz, 399.10 MHz), ^{119}Sn{^{1}H} (186.50 MHz) and ^{13}C{^{1}H} (125.67 MHz, 100.10 MHz) The assignments of signals in ^{1}H spectra were made from standard 2D measurements. The solutions were obtained by dissolving 40 mg of each compound in 0.5 ml of deuterated solvents. The ^{1}H chemical shifts were calibrated relative to the signal of residual $CHCl_3$ ($\delta = 7.27$) and benzene (7.16), respectively. The ^{13}C chemical shifts were calibrated relative to the signal of residual $CHCl_3$ ($\delta = 77.23$) or benzene (128.44). The ^{119}Sn chemical shifts are referred to external neat tetramethylstannane ($\delta = 0.0$). ^{119}Sn NMR spectra were measured using the inverse gated proton broad band decoupling mode.

3.2. Mass spectrometry

Positive-ion electrospray ionization (ESI) mass spectra (MS) were measured on the ion trap analyser Esquire3000 (Bruker Daltonics, Bremen, Germany) in the range m/z 50–2500. The ion trap was tuned to give an optimum response for m/z 300–1600. The samples were dissolved in acetonitrile and analysed by direct infusion at the flow rate 3 μl/min. The ion source temperature was 300 °C, the flow rate and the pressure of nitrogen were 4 L/min and 10 psi, respectively. The isolation width for MS^n experiments was $m/z = 8$, and the collision amplitude (CA) was selected depending on the stability of particular fragment ion in the range 0.6–1 V.

3.3. IR spectroscopy

IR spectra for carbonates **4a**–**c** were recorded on Perkin–Elmer 684 spectrophotometer in Nujol mulls at laboratory conditions.

3.4. DTA

Measurement was carried out in open tube on Perkin–Elmer 551 DTA-DSC equipment from 35 to 350 °C, increase 5 °C/min.

3.5. GC/MS

The samples were analysed using gas chromatograph GC 17A coupled with mass spectrometry detector QP 5050A (EI, NCI, both Shimadzu) and GC/MS solution data system (Shimadzu). The helium (grade 5.0, Linde) was used as carrier gas. Separations were performed on capillary column (30 m × 25 μm i.d.) coated with a

0.25 μm film of polymethylsiloxane (HP-5 MS). Split injection 1:200 was used. The column oven was isothermally maintained at 45 °C for 1 min and than the temperature increase for 20 °C/min to 300 °C (kept for 6.5 min) was applied. The temperature of injector was 220 °C and the temperature of interface was 230 °C. The identification of compounds was based on the comparison of their mass spectrum with the library spectrum (NIST 107 and NIST 21, Shimadzu).

3.6. X-ray crystallography

The single crystals of **3b** were grown from C_6D_6 solution in NMR tube. The suitable crystals of **3d** were obtained from THF solution at -30 °C and the crystals of $L_2^{CN}MeSn(\mu-O)SnMeL_2^{CN}$ appeared when the mixture of species resulting from the stability test (vide supra) was crystallized from dichloromethane.

Data for colourless crystals were collected at 150(1) K on a Nonius KappaCCD diffractometer using Mo K_α radiation ($\lambda = 0.71073$ Å), and graphite monochromator. The structures were solved by direct methods (SIR92 [35]). All reflections were used in the structure refinement based on F^2 by full-matrix least-squares technique (SHELXL97 [36]). Hydrogen atoms were mostly localized on a difference Fourier map, however to ensure uniformity of treatment of crystal, all hydrogen were recalculated into idealized positions (riding model) and assigned temperature factors $H_{iso}(H) = 1.2U_{eq}$ (pivot atom) or of $1.5U_{eq}$ for the methyl moiety. Absorption corrections were carried on, using either multi-scans procedure (PLATON [37] or SORTAV [38]) or Gaussian integration from crystal shape (Coppens [39]).

Crystallographic data for **3b** · C_6D_6: $C_{48}H_{50}N_2OSn_2$, $M = 908.28$, monoclinic, $P2_1$, $a = 9.80100(10)$, $b = 18.0170(2)$, $c = 12.84400(10)$ Å, $\beta = 112.2240(7)°$, $Z = 2$, $V = 2099.56(4)$ Å^3, $D_c = 1.437$ g cm^{-3}, $\mu = 1.226$ mm^{-1}, $T_{min} = 0.541$, $T_{max} = 0.799$; 26888 reflections measured ($\theta_{max} = 27.5°$), 9611 independent ($R_{int} = 0.0193$), 9455 with $I > 2\sigma(I)$, 483 parameters, $S = 1.056$, R_1(obs. data) $= 0.020$, wR_2(all data) $= 0.0467$; maximum, minimum residual electron density $= -0.667$, 0.631 e Å^{-3}.

Crystallographic data for **3d**: $C_{34}H_{60}N_2OSn_2$, $M = 750.22$, triclinic, $P\bar{1}$, $a = 9.4760(4)$, $b = 9.6350(7)$, $c = 11.6010(2)$ Å, $\alpha = 87.805(3)°$, $\beta = 69.267(4)°$, $\gamma = 67.514(4)°$, $Z = 1$, $V = 909.49(8)$ Å^3, $D_c = 1.370$ g cm^{-3}, $\mu = 1.399$ mm^{-1}, $T_{min} = 0.650$, $T_{max} = 0.763$; 13823 reflections measured ($\theta_{max} = 27.5°$), 2748 independent ($R_{int} = 0.0574$), 2171 with $I > 2\sigma(I)$, 186 parameters, $S = 1.136$, R_1(obs. data) $= 0.0178$, wR_2(all data) $= 0.0469$; maximum, minimum residual electron density $= -0.492$, 0.073 e Å^{-3}.

Crystallographic data for **11**: $C_{38}H_{54}N_4OSn_2$, $M = 820.23$, triclinic, $P\bar{1}$, $a = 12.4470(12)$, $b = 12.8750(14)$, $c = 13.3520(4)$ Å, $\alpha = 88.943(6)°$, $\beta = 89.420(5)°$, $\gamma = 63.825(7)°$, $Z = 2$, $V = 1920.0(3)$ Å^3, $D_c = 1.419$ g cm^{-3}, $\mu = 1.334$ mm^{-1}, $T_{min} = 0.714$, $T_{max} = 0.815$; 29427 reflections measured ($\theta_{max} = 27.5°$), 5877 indepen-

dent ($R_{int} = 0.0603$), 5008 with $I > 2\sigma(I)$, 353 parameters, $S = 1.088$, R_1(obs. data) $= 0.0433$, wR_2(all data) $= 0.1005$; maximum, minimum residual electron density $= -1.185$, 0.973 e Å^{-3}.

3.7. General remarks

All experiments were carried out under argon atmosphere. The alkaline metal hydroxides were separated from carbonates via Sörensen's method, or prepared via addition of alkaline metals or *n*-butyllithium to degassed water. (*N,N*-Dimethylaminomethyl)benzene, *n*-butyllithium, alcohols, phenol and diorganotin(IV) dichlorides, were obtained from commercial sources (Sigma–Aldrich), sodium methoxide was prepared from sodium metal and dried/degassed methanol. Toluene, benzene, *n*-hexane, *n*-pentane were dried over and distilled from sodium, degassed and stored under argon. Chloroform and dichloromethane were dried over and distilled from P_2O_5 and CaH_2. Compounds **1a** [26], **1b** [40], **1c** [41], and **1d** [11] were obtained by published methods.

3.8. Typical hydrolytic conditions

The appropriate triorganotin chloride **1a–d** (1 g) was stirred overnight at room temperature with sodium hydroxide (four equivalents) in 20/20 ml mixture of benzene/water under an argon atmosphere. Subsequently the phases were separated and evaporated under vacuo, there was typically no tin-containing species in the water phase. The residue from the benzene layer was extracted with benzene, washed with water, dried with sodium sulphate and then evaporated giving typically the mixture of appropriate hydroxide and oxide as colourless oil. The hydroxide/oxide equilibrium can be shifted by heating with water the hydroxide or in vacuo the oxide species.

3.9. [2-(N,N-Dimethylaminomethyl)phenyl]di-n-butyltin (IV) hydroxide (2a)

Colourless oil, yield 84%. ^{1}H NMR (500.13 MHz, CDCl$_3$, 300 K, ppm): 7.90 (d, 1H, H(6), $^3J(^1H,^1H) = 6.4$ Hz, $^3J(^1H,^{119}Sn) = 65$ Hz); 7.14 (m, 2H, H(4, 5)); 7.01 (d, 1H, H(3), $^3J(^1H,^1H) = 7.2$ Hz); 3.41 (s, 2H, NCH$_2$); 2.14 (s, 6H, N(CH$_3$)$_2$); 1.60 (m, 4H, H(1′)); 1.35 (m, 4H, H(2′)); 1.12 (m, 4H, H(3′)); 0.82 (t, 6H, H(4′), $^3J(^1H,^1H) = 7.1$ Hz); -0.20 (br s, 1H, OH). $^{119}Sn\{^1H\}$ NMR (C$_6$D$_6$, 300 K, ppm): -76.9. Elemental Anal. Calc. for C$_{17}$H$_{31}$NOSn (384.13): C, 53.16; H, 8.13; N, 3.65. Found: C, 53.2; H, 8.1; N, 3.7%.

3.10. [2-(N,N-Dimethylaminomethyl)phenyl]diphenyltin (IV) hydroxide (2b) (not isolated)

^{1}H NMR (360.13 MHz, CDCl$_3$, 300 K, ppm): 8.17 (d, 1H, H(6), $^3J(^1H,^1H) = 7.4$ Hz, $^3J(^1H,^{119}Sn) = 67.5$ Hz); 7.61 (d, 2H, H(2′), $^3J(^1H,^1H) = 7.1$ Hz, $^3J(^1H,^{119}Sn)$

= 60.0 Hz); 7.29 (m, 8H, H(4, 5, 3′, 4′)); 7.01 (d, 1H, H(3), $^3J(^1H, ^1H) = 6.4$ Hz); 3.34 (s, 2H, NCH$_2$); 1.70 (s, 6H, N(CH$_3$)$_2$). ^{119}Sn{^{1}H} NMR (134.26 MHz, CDCl$_3$, 300 K, ppm): −187.6.

3.11. [2-(N,N-Dimethylaminomethyl)phenyl]dimethyltin (IV) hydroxide (2c) (not isolated)

^{1}H NMR (500.13 MHz, CDCl$_3$, 300 K, ppm): 7.87 (br s, 1H, H(6)); 7.22 (m, 2H, H(4, 5)); 7.04 (d, 2H, H(3), $^3J(^1H, ^1H) = 6.1$ Hz); 3.57 (s, 2H, NCH$_2$); 2.26 (s, 6H, N(CH$_3$)$_2$); 0.53 (s, 3H, H(Me), $^3J(^1H, ^{119}$Sn$) = 56$ Hz). ^{119}Sn{^{1}H} NMR (186.50 MHz, CDCl$_3$, 300 K, ppm): −85.9.

3.12. [2-(N,N-Dimethylaminomethyl)phenyl]di-t-butyltin (IV) hydroxide (2d)

Colourless solid, yield 92%, m.p. 139–145 °C. ^{1}H NMR (500.13 MHz, C$_6$D$_6$, 300 K, ppm): 7.90 (br s, 1H, H(6)); 7.14 (m, 2H, H(4, 5)); 7.03 (d, 1H, H(3), $^3J(^1H, ^1H) = 6.4$ Hz); 3.28 (s, 2H, NCH$_2$); 1.94 (s, 6H, N(CH$_3$)$_2$); 1.35 (s, 18H, H(2′), $^3J(^1H, ^{119}$Sn$) = 76$ Hz); 1.70 (br s, 1H, OH, 2.74 ppm in CDCl$_3$). ^{13}C NMR (90.55 MHz, CDCl$_3$, 300 K, ppm): 145.2 (C(2), $^1J(^{119}$Sn, ^{13}C$) = 25$ Hz); 143.5 (C(1), $^1J(^{119}$Sn, ^{13}C$) = 445$ Hz); 137.2 (C(3), $^3J(^{119/117}$Sn, ^{13}C$) = 43$ Hz); 131.0 (C(6), $^2J(^{119/117}$Sn, ^{13}C$) = 38$ Hz); 128.5 (C(4), $^4J(^{119/117}$Sn, ^{13}C$) = 11$ Hz); 126.7 (C(2), $^2J(^{119/117}$Sn, ^{13}C$) = 48$ Hz); 67.3 (C(NCH$_2$), $^nJ(^{119/117}$Sn, ^{13}C$) = 17$ Hz); 45.4 (C(NCH$_3$), $^nJ(^{119/117}$Sn, ^{13}C$) = 11$ Hz); 34.0 (C(1′), $^1J(^{119}$Sn, ^{13}C$) = 442$ Hz); 30.5 (C(2′)). ^{119}Sn{^{1}H} NMR (134.30 MHz, C$_6$D$_6$, 300 K, ppm): −46.3 br s. Elemental Anal. Calc. for C$_{17}$H$_{31}$NOSn (384.13): C, 53.16; H, 8.13; N, 3.65. Found: C, 53.1; H, 8.1; N, 3.6%.

3.13. Bis{[2-(N,N-Dimethylaminomethyl)phenyl] di-n-butyltin(IV)} oxide (3a)

Colourless oil, yield 91%. ^{1}H NMR (500.13 MHz, C$_6$D$_6$, 300 K, ppm): 8.56 (d, 2H, H(6), $^3J(^1H, ^1H) = 6.2$ Hz, $^3J(^1H, ^{119}$Sn$) = 50$ Hz); 7.34 (t, 2H, H(4), $^3J(^1H, ^1H) = 6.6$ Hz); 7.23 (t, 2H, H(5), $^3J(^1H, ^1H) = 6.8$ Hz); 7.01 (d, 2H, H(3), $^3J(^1H, ^1H) = 6.9$ Hz); 3.35 (s, 4H, NCH$_2$); 2.04 (s, 12H, N(CH$_3$)$_2$); 1.97 (br s, 8H, H(1′)); 1.57 (m, 8H, H(2′)); 1.30 (m, 8H, H(3′)); 1.02 (t, 12H, H(4′), $^3J(^1H, ^1H) = 7.2$ Hz). ^{119}Sn{^{1}H} NMR (C$_6$D$_6$, 300 K, ppm): −59.3, $^2J(^{119}$Sn, ^{117}Sn$) = 498$ Hz. Elemental Anal. Calc. for C$_{34}$H$_{60}$N$_2$OSn$_2$ (750.25): C, 52.93; H, 7.61; N, 3.53. Found: C, 53.4; H, 7.5; N, 3.7%.

3.14. Bis{[2-(N,N-Dimethylaminomethyl)phenyl] diphenyltin(IV)} oxide (3b)

White powder, m.p. 170–173 °C, yield 86%. ^{1}H NMR (360.13 MHz, CDCl$_3$, 300 K, ppm): 8.45 (d, 4H, H(6),

$^3J(^1H, ^1H) = 7.3$ Hz, $^3J(^1H, ^{119}$Sn$) = 68$ Hz); 7.29 (m, 20H, H(4, 5, 2′, 3′, 4′)); 7.02 (d, 2H, H(3), $^3J(^1H, ^1H) = 6.5$ Hz); 3.19 (s, 4H, NCH$_2$); 1.52 (s, 12H, N(CH$_3$)$_2$). ^{119}Sn{^{1}H} NMR (C$_6$D$_6$, 300 K, ppm): −173.2, $^2J(^{119}$Sn, ^{117}Sn$) = 398$ Hz. Elemental Anal. Calc. for C$_{42}$H$_{44}$N$_2$OSn$_2$ (830.21): C, 60.76; H, 5.34; N, 3.37. Found: C, 60.8; H, 5.3; N, 3.4%.

3.15. Bis{[2-(N,N-Dimethylaminomethyl)phenyl] dimethyltin(IV)} oxide (3c)

Colourless oil, yield 66%. ^{1}H NMR (500.13 MHz, C$_6$D$_6$, 300 K, ppm): 7.93 (br s, 2H, H(6)); 7.28 (m, 4H, H(4, 5)); 7.09 (d, 2H, H(3), $^3J(^1H, ^1H) = 6.2$ Hz); 3.51 (s, 4H, NCH$_2$); 2.20 (s, 12H, N(CH$_3$)$_2$); 0.47 (s, 6H, H(Me), $^3J(^1H, ^{119}$Sn$) = 54$ Hz). ^{119}Sn{^{1}H} NMR (186.50 MHz, CDCl$_3$, 300 K, ppm): −61.8.

3.16. Bis{[2-(N,N-Dimethylaminomethyl)phenyl] di-t-butyltin(IV)} oxide (3d)

White powder, m.p. 165–168 °C, yield 86%. ^{1}H NMR (500.13 MHz, C$_6$D$_6$, 300 K, ppm): ^{1}H NMR (500.13 MHz, C$_6$D$_6$, 300 K, ppm): 8.27 (d, 2H, H(6)); 7.20 (m, 4H, H(4, 5)); 7.03 (d, 2H, H(3), $^3J(^1H, ^1H) = 6.2$ Hz); 3.54 (s, 4H, NCH$_2$); 2.15 (s, 12H, N(CH$_3$)$_2$); 1.51 (s, 36H, H(2′), $^3J(^1H, ^{119}$Sn$) = 77$ Hz). ^{119}Sn{^{1}H} NMR (C$_6$D$_6$, 300 K, ppm): −35.6, $^2J(^{119}$Sn, ^{117}Sn$) = 814$ Hz. Elemental Anal. Calc. for C$_{34}$H$_{60}$N$_2$OSn$_2$ (750.25): C, 54.43; H, 8.06; N, 3.73. Found: C, 54.3; H, 8.1; N, 3.7%.

3.17. Bis{[2-(N,N-Dimethylaminomethyl)phenyl] di-n-butyltin(IV)} carbonate (4a)

The neat mixture of 2a and 3a was left on the air overnight. Colourless oil, yield 100%. ^{1}H NMR (500.13 MHz, CDCl$_3$, 300 K, ppm): 7.95 (br s, 2H, H(6)); 7.20 (br s, 4H, H(4, 5)); 7.00 (br s, 2H, H(3)); 3.52 (s, 4H, NCH$_2$); 2.24 (s, 12H, N(CH$_3$)$_2$); 1.61 (br s, 8H, H(1′)); 1.32 (br s, 16H, H(2′, 3′)); 0.88 (br s, 12H, H(4′)). ^{13}C NMR (90.55 MHz, CDCl$_3$, 300 K, ppm): 163.2 (C(C=O)); 143.0 (C(2), $^2J(^{119/117}$Sn, ^{13}C$) = 37$ Hz); 142.2 (C(1), $^1J(^{119}$Sn, ^{13}C$) = 649$ Hz); 138.0 (C(3), $^3J(^{119/117}$Sn, ^{13}C$) = 30$ Hz); 126.2 (C(6), $^2J(^{119/117}$Sn, ^{13}C$) = 47$ Hz); 128.2 (C(4), $^4J(^{119/117}$Sn, ^{13}C$) = 12$ Hz); 127.2 (C(2), $^2J(^{119/117}$Sn, ^{13}C$) = 49$ Hz); 65.6 (C(NCH$_2$), $^nJ(^{119/117}$Sn, ^{13}C$) = 21$ Hz); 45.4 (C(NCH$_3$), $^nJ(^{119/117}$Sn, ^{13}C$) = 16$ Hz); 28.1 (C(2′), $^2J(^{119/117}$Sn, ^{13}C$) = 30$ Hz); 27.2 (C(3′), $^3J(^{119/117}$Sn, ^{13}C$) = 92$ Hz); 16.3 (C(1′), $^1J(^{119}$Sn, ^{13}C$) = 419$ Hz); 13.5 (C(4′)). ^{119}Sn{^{1}H} NMR (134.30 MHz, C$_6$D$_6$, 300 K, ppm): − 92.6. IR $v_{3(C=O)} = 1570$ cm^{-1}. Elemental Anal. Calc. for C$_{35}$H$_{60}$N$_2$O$_3$Sn$_2$ (794.26): C, 52.93; H, 7.61; N, 3.53. Found: C, 52.9; H, 7.6; N, 3.5%.

3.18. Bis{[2-(N,N-Dimethylaminomethyl)phenyl] diphenyltin(IV)} carbonate (4b) (not isolated)

When **3b** was left on the air overnight yielding (based on NMR techniques) 6% of **4b** in the mixture with **2b** (only characteristic parameters are given). ^{1}H NMR (360.13 MHz, CDCl$_3$, 300 K, ppm): 8.47 (d, 2H, H(6), $^3J(^1\text{H},^1\text{H}) = 7.6$ Hz, $^3J(^1\text{H},^{119}\text{Sn}) = 67$ Hz); 7.82 (d, 2H, H(2′), $^3J(^1\text{H},^1\text{H}) = 7.1$ Hz, $^3J(^1\text{H},^{119}\text{Sn}) = 61$ Hz); 3.24 (s, 4H, NCH$_2$); 1.64 (s, 12H, N(CH$_3$)$_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (90.55 MHz, CDCl$_3$, 300 K, ppm): 164.3 (CO$_3^{2-}$). $^{119}\text{Sn}\{^1\text{H}\}$ NMR (134.26 MHz, CDCl$_3$, 300 K, ppm): −226.5. IR $\nu_{3(\text{C=O})} = 1580$ cm^{-1}.

3.19. Bis{[2-(N,N-Dimethylaminomethyl)phenyl] dimethyltin(IV)} carbonate (4c)

Compound bf 4c was isolated from the water layer when the hydrolysis of **1c** was carried out on the air as yellowish oil in 12% yield. ^1H NMR (500.13 MHz, C$_6$D$_6$, 300 K, ppm): ^1H NMR (500.13 MHz, CDCl$_3$, 300 K, ppm): 8.63 (br s, 2H, H(6), $^3J(^1\text{H},^{119}\text{Sn}) = 67$ Hz); 7.24 (m, 4H, H(4, 5)); 6.99 (br s, 2H, H(3)); 3.10 (s, 4H, NCH$_2$); 1.72 (s, 12H, N(CH$_3$)$_2$); 0.67 (s, 6H, H(Me), $^3J(^1\text{H},^{119}\text{Sn}) = 66$ Hz). ^{13}C NMR (90.55 MHz, CDCl$_3$, 300 K, ppm): 163.5 (C(C=O)); 142.5 (C(2), $^2J(^{119/117}\text{Sn},^{13}\text{C}) = 39$ Hz); 140.9 (C(1), $^1J(^{119/117}\text{Sn},^{13}\text{C}) = 737$ Hz); 137.9 (C(3), $^3J(^{119/117}\text{Sn},^{13}\text{C}) = 43$ Hz); 126.2 (C(6), $^2J(^{119/117}\text{Sn},^{13}\text{C}) = 47$ Hz); 129.4 (C(4), $^4J(^{119/117}\text{Sn},^{13}\text{C}) = 13$ Hz); 126.7 (C(2), $^2J(^{119/117}\text{Sn},^{13}\text{C}) = 60$ Hz); 64.4 (C(NCH$_2$), $^nJ(^{119/117}\text{Sn},^{13}\text{C}) = 28$ Hz); 44.5 (C(NCH$_3$); − 0.2 (C(Me), $^1J(^{119}\text{Sn},^{13}\text{C}) = 433$ Hz)). $^{119}\text{Sn}\{^1\text{H}\}$ NMR (134.30 MHz, C$_6$D$_6$, 300 K, ppm): − 55.2. IR $\nu_{3(\text{C=O})} = 1580$ cm^{-1}. Elemental Anal. Calc. for C$_{23}$H$_{36}$N$_2$O$_3$Sn$_2$ (625.93): C, 44.14; H, 5.80; N, 4.48. Found: C, 44.1; H, 5.8; N, 4.5%.

When the mixture of **2c** and **3c** was left on the air overnight only 15% of material was consumed to **4c** and other minor products appeared (discussed in preparation of **11**).

3.20. [2-(N,N-Dimethylaminomethyl)phenyl] di-n-butyltin(IV) methoxide (5a)

To a solution of **1a** in benzene (0.83 g, 2 mmol in 15 ml) 10 ml of suspension of sodium methoxide in benzene (0.11 g, 2 mmol) was added. This mixture was stirred overnight at room temperature, than evaporated to dryness and washed with cold pentane. After evaporation of pentane extract pale yellow oil was obtained, yield 0.71 g, 87%. ^1H NMR (500.13 MHz, C$_6$D$_6$, 300 K, ppm): 8.43 (d, 1H, H(6), $^3J(^1\text{H},^1\text{H}) = 6.9$ Hz, $^3J(^1\text{H},^{119}\text{Sn}) = 61$ Hz); 7.30 (m, 2H, H(4, 5)); 6.92 (d, 1H, H(3), $^3J(^1\text{H},^1\text{H}) = 7.0$ Hz); 4.11 (s, 3H, OMe, $^3J(^1\text{H},^{119}\text{Sn}) = 26$ Hz); 3.03 (s, 2H, NCH$_2$); 1.79 (s, 6H, N(CH$_3$)$_2$); 1.73 (m, 4H, H(1′)); 1.42 (m, 4H, H(2′)); 1.16 (m, 4H, H(3′)); 0.92 (t, 6H, H(4′), $^3J(^1\text{H},^1\text{H}) = 6.6$ Hz). $^{119}\text{Sn}\{^1\text{H}\}$ NMR (C$_6$D$_6$, 300 K, ppm): −65.6. Elemental Anal. Calc. for C$_{18}$H$_{33}$NOSn

(398.16): C, 54.30; H, 8.35; N, 3.52. Found: C, 54.3; H, 8.4; N, 3.5%.

3.21. [2-(N,N-Dimethylaminomethyl)phenyl]di-n-butyltin (IV) 1-octyloxide (6a)

Procedure was similar as in the case of **5a**. 0.34 g (0.8 mmol) of **1a**, 1-octylONa (from 1-octanol (0.12 g, 0.8 mmol) and NaH), colourless oil, yield 0.22 g, 56%. ^1H NMR (360.13 MHz, C$_6$D$_6$, 300 K, ppm): 8.57 (d, 1H, H(6), $^3J(^1\text{H},^1\text{H}) = 7.2$ Hz, $^3J(^1\text{H},^{119}\text{Sn}) = 61$ Hz); 7.22 (m, 2H, H(4, 5)); 6.94 (d, 1H, H(3), $^3J(^1\text{H},^1\text{H}) = 7.6$ Hz); 4.25 (t, 2H, n-Oct-O); 3.15 (s, 2H, NCH$_2$); 1.86 (s, 6H, N(CH$_3$)$_2$); 1.91 (m, 4H, H(1′)); 1.49 (m, 8H, H(2′, n-Oct)); 1.36 (m, 8H, n-Oct); 1.26 (m, 4H, H(3′)); 0.99 (m, 9H, H(4′, n-Oct)). $^{119}\text{Sn}\{^1\text{H}\}$ NMR (134.29 MHz, C$_6$D$_6$, 300 K, ppm): −68.6. Elemental Anal. Calc. for C$_{25}$H$_{47}$NOSn (496.35): C, 60.05; H, 9.54; N, 2.82. Found: C, 60.5; H, 9.5; N, 2.8%.

3.22. [2-(N,N-Dimethylaminomethyl)phenyl]di-n-butyltin (IV) cyclohexyloxide (7a)

Procedure was similar as in the case of **5a**. 1.69 g (4 mmol) of **1a**, cyclohexylONa (from cyclohexanol (0.43 g, 4 mmol) and NaH), colourless oil, yield 1.31 g, 67%. ^1H NMR (360.13 MHz, C$_6$D$_6$, 300 K, ppm): 8.46 (d, 1H, H(6), $^3J(^1\text{H},^1\text{H}) = 6.8$ Hz, $^3J(^1\text{H},^{119}\text{Sn}) = 63$ Hz); 7.28 (m, 2H, H(4, 5)); 6.90 (d, 1H, H(3), $^3J(^1\text{H},^1\text{H}) = 7.3$ Hz); 3.96 (m, 1H, c-Hex-O); 3.31 (s, 2H, NCH$_2$); 2.02 (s, 6H, N(CH$_3$)$_2$); 1.93 (m, 8H, H(1′, c-Hex)); 1.49 (m, 8H, H(2′, c-Hex)); 1.26 (m, 6H, H(3′, c-Hex)); 0.99 (t, 6H, H(4′), $^3J(^1\text{H},^1\text{H}) = 6.9$ Hz). $^{119}\text{Sn}\{^1\text{H}\}$ NMR (134.29 MHz, C$_6$D$_6$, 300 K, ppm): −69.5. Elemental Anal. Calc. for C$_{23}$H$_{41}$NOSn (466.28): C, 59.25; H, 8.86; N, 3.00. Found: C, 59.3; H, 8.8; N, 3.0%.

3.23. [2-(N,N-Dimethylaminomethyl)phenyl]di-n-butyltin (IV) t-butoxide (8a)

Procedure was similar as in the case of **5a**. 0.034 g, 0.085 mmol of **1a**, 0.012 g of t-BuOK, colourless oil, yield 0.0355 g, 95%. ^1H NMR (360.14 MHz, CDCl$_3$, 300 K, ppm): 8.00 (br s, 1H, H(6)); 7.30 (m, 2H, H(4, 5)); 7.10 (d, 1H, H(3), $^3J(^1\text{H},^1\text{H}) = 7.1$ Hz); 3.48 (s, 2H, NCH$_2$); 2.27 (s, 6H, N(CH$_3$)$_2$); 1.22 (br s, 9H, t-Bu); 1.53 (m, 4H, H(1′)); 1.32 (m, 8H, H(2′, 3′)); 0.88 (t, 6H, H(4′), $^3J(^1\text{H},^1\text{H}) = 7.1$ Hz). $^{119}\text{Sn}\{^1\text{H}\}$ NMR (134.29 MHz, CDCl$_3$, 300 K, ppm): −75.9. Elemental Anal. Calc. for C$_{21}$H$_{39}$NOSn (440.24): C, 57.29; H, 8.93; N, 3.18. Found: C, 57.4; H, 8.8; N, 3.2%.

3.24. [2-(N,N-Dimethylaminomethyl)phenyl]di-n-butyltin (IV) phenoxide (9a)

Procedure was similar as in the case of **5a**. 0.10 g (0.2 mmol) of **1a**, PhONa (from phenol (0.024 g, 0.2 mmol)

and NaH), colourless oil, yield 0.0819 g, 89%. ^{1}H NMR (500.13 MHz, CDCl$_3$, 300 K, ppm): 8.07 (br s, 1H, H(6)); 7.30, 7.13 (m, 6H, H(4, 5, OPh)); 6.74 (d, 1H, H(3), $^3J(^1H, ^1H) = 6.9$ Hz); 6.63 (t, 1H, H(OPh-*para*), $^3J(^1H, ^1H) = 6.5$ Hz); 3.55 (s, 2H, NCH$_2$); 2.29 (s, 6H, N(CH$_3$)$_2$); 1.63 (m, 4H, H(1′)); 1.28 (m, 8H, H(2′, 3′)); 0.84 (t, 6H, H(4′), $^3J(^1H, ^1H) = 6.9$ Hz). ^{119}Sn{^{1}H} NMR (C$_6$D$_6$, 300 K, ppm): −82.2. Elemental Anal. Calc. for C$_{23}$H$_{35}$NOSn (460.23): C, 60.03; H, 7.67; N, 3.04. Found: C, 59.9; H, 7.9; N, 3.2%.

3.25. [2-(N,N-Dimethylaminomethyl)phenyl]di-n-butyltin (IV) acetate (10a)

Procedure was similar as in the case of **5a**. 0.12 g (0.3 mmol) of **1a**, 0.026 g of AcONa (0.3 mmol), colourless oil, yield 0.109 g, 86%. ^{1}H NMR (360.14 MHz, CDCl$_3$, 300 K, ppm): 7.86 (d, 1H, H(6), $^3J(^1H, ^1H) = 6.4$ Hz, $^3J(^1H, ^{119}Sn) = 56$ Hz); 7.26 (m, 2H, H(4, 5)); 7.07 (d, 1H, H(3), $^3J(^1H, ^1H) = 6.9$ Hz); 3.53 (s, 2H, NCH$_2$); 2.29 (s, 6H, N(CH$_3$)$_2$); 2.06 (s, 3H, OAc); 1.57 (m, 4H, H(1′)); 1.26 (m, 8H, H(2′, 3′)); 0.85 (t, 6H, H(4′), $^3J(^1H, ^1H) = 7.2$ Hz). ^{119}Sn{^{1}H} NMR (134.29 MHz, CDCl$_3$, 300 K, ppm): −87.1. Elemental Anal. Calc. for C$_{19}$H$_{33}$NO$_2$Sn (426.17): C, 53.55; H, 7.81; N, 3.29. Found: C, 53.5; H, 7.8; N, 3.3%.

3.26. Bis{bis[2-(N,N-dimethylaminomethyl)phenyl] methyltin(IV)} oxide (11)

Compound was isolated by crystallization (from dichloromethane) of the mixture obtained after standing of neat **3c** on the air for one year. Colourless crystals, m.p. 73–75 °C, yield 16%. ^{1}H NMR (500.13 MHz, C$_6$D$_6$, 300 K, ppm): 7.79 (br s, 2H, H(6), $^3J(^1H, ^{119}Sn) = 65.3$ Hz); 7.20 (m, 4H, H(4, 5)); 7.02 (m, 2H, H(3)); 3.17 (AX pattern − 78.6 Hz, 4H, NCH$_2$, $^3J(^1H, ^1H) = 12.9$ Hz); 1.86 (2 × s, 12H, N(CH$_3$)$_2$); 0.58 (s, 6H, H(CH$_3$), $^3J(^1H, ^{119}Sn) = 64.9$ Hz). ^{119}Sn{^{1}H} NMR (CDCl$_3$, 300 K, ppm): −110.3. Elemental Anal. Calc. for C$_{38}$H$_{54}$N$_2$OSn$_2$ (820.26): C, 55.64; H, 6.64; N, 6.83. Found: C, 55.6; H, 6.6; N, 6.9%.

3.27. Catalytic transesterification experiments

Catalytical transesterification attempts were performed strictly according to appropriate reference (Scheme 1; A [2a], B [2b], C [3a]) in 10 ml flasks with typically 3 ml of starting ester and exclusion of atmospheric CO$_2$. Temperature, catalyst loading and reaction time for all runs are given in Scheme 1 and Table 2. All reactions were monitored by GC/MS, ^{1}H and ^{119}Sn NMR measurements.

3.28. General procedure for autoclave experiments and HP NMR

The catalytic screening tests were performed in high pressure reactors equipped with magnetically coupled stirring systems and electrical heating mantles. Temperature

and pressure were monitored via a digital multimeter (HP 34970A) connected to a personal computer. The catalytic tests were typically conducted in 70 ml stainless steel (SS316) autoclaves equipped with standard Swagelock fittings and a separate loop made of stainless steel tubing which can be operated independently of the main reactor body. Because of the general moisture sensitivity of metal alkoxides and in order to get reproducible results, the reactors were heated at 100 °C and purged with argon prior to use. The substrates (phenol, ethanol, propylene oxide and cyclohexene oxide) were transferred into the autoclave with benzene as solvent in the case of phenol (10 g) and with trimethyl orthoacetate (20 ml) as dehydrating agent in the case of phenol and ethanol, the epoxides were used without additional solvents (20 ml). The reactor was then pressurized with CO$_2$ (60 bar) for a few minutes under stirring and afterwards weighed, the procedure was repeated until the desired substrate/CO$_2$ molar fraction was reached (ca. 1–2, 15–30 g CO$_2$). Owing to a general high Lewis acidity of tin compounds and their ability to also catalyze ring opening polymerisations, the catalyst was first dissolved under argon into ca. 3 ml of an inert solvent (benzene) and introduced into the separate loop. After establishing the communication with the epoxide/CO$_2$ mixture in the autoclave, the solution was allowed to diffuse into the reaction mixture through gravity. The test reactions were run at 100 °C under a CO$_2$-pressure ranging from 65 to 100 bar. After the reaction time, the autoclaves were cooled down to RT (water bath) and the carbon dioxide slowly (!) vented, under stirring, in a fume hood. The reaction mixtures were investigated with IR-FT and NMR spectroscopies.

Appendix A. Supplementary material

CCDC 607130, 632792 and 632793 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.09.018.

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