C,N-chelated hexaorganodistannanes, and triorganotin(IV) hydrides and cyclopentadienides

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ABSTRACT

Triorganotin(IV) hydrides and cyclopentadienides as well as hexaorganodistannanes containing the moiety L^{CN} (2-(*N,N*-dimethylaminomethyl)phenyl-) as chelating ligand and phenyl, *n*-butyl or *t*-butyl substituents were prepared and characterized by NMR and XRD. The compounds reveal trigonal bipyramidal geometry around the central tin atom except for the distannanes in which the tin atom has tetrahedral configuration. The di-*n*-butyl distannane cannot be oxidized by oxygen or heavier chalcogens and give no tin radical when irradiated by UV light or treated with the TEMPO – free radical at room temperature. $L^{CN}(t\text{-Bu})_2SnH$ undergoes reaction in solution toward the corresponding distannane. The hydrostannation reaction of $L^{CN}(n\text{-Bu})_2SnH$ with ferrocenylacetylene was investigated. The CO_2 activation by $L^{CN}(n\text{-Bu})_2SnH$ was also examined.

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1. Introduction

In recent years, the organotin(IV) hydrides have found extensive applications in organic syntheses that involve radical chain reactions in which the stannyl radical $R_3Sn^{\cdot}$ is a chain carrying intermediate [1].

Distannanes of general formula R_3SnSnR_3 can be taken as being the source of above mentioned radical $R_3Sn^{\cdot}$ as well, and are also frequently studied. The chemistry of organotin(IV) compounds where the tin atom is σ-bonded to a cyclopentadienyl moiety is also well established including, for example, studies of mixed valence tin(II) and tin(IV) compounds or stability and properties of tin(III) radicals generated by irradiation of $Bu_{4-n}Cp_nSn$. Recent studies targeted mainly onto the synthesis of tin substituted ferrocenes [2] or ferrocenophanes [3], and the use of these compounds as cyclopentadienyl group transfer agents to the transition metal center [4].

Our interest is mainly focused on the family of organotin(IV) compounds containing 2-[(dimethylamino)methyl]phenyl-group (L^{CN}) or related ligands which reveal interesting structural properties [5,6] and potential use [7]. The aim of our previous studies was to prepare tin(IV) bridged *ansa* metallocenes containing mentioned C,N-chelating ligand(s). In a recent paper, we described the unusual reactivity of bis{2-[(dimethylamino)methyl]phenyl} tin(IV) dibromide [8–13] with two equivalents of cyclopentadienyl- or fluorenyllithium in THF [14].

In the present paper, the structure, properties and preliminary reactivity studies of hydrides, cyclopentadienides and distannanes containing $L^{CN}R_2Sn$ moiety, where R is Ph, *n*-Bu and *t*-Bu are reported.

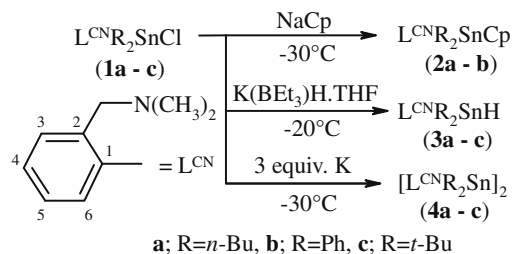## 2. Results and discussion

Reactions of starting chlorides **1a–c** with NaCp, $K(BEt_3)H\cdot THF$ and an excess of potassium provided the desired products in high yield as shown in Scheme 1. The only problematic seems to be the reaction of *t*-butyl derivative **1c** towards NaCp giving a mixture of starting material and inseparable products.

The reactions of starting chlorides **1a** and **1b** with sodium cyclopentadienide in diethyl ether gave the desired cyclopentadienides in 81% (for **2a**) and 72% (for **2b**) yield. The reaction of di-*t*-butyl derivative (**1c**) gave the mixture of inseparable products at the same conditions. In ^{1}H NMR spectra of **2a** and **2b**, a signal at 6.42 ppm ($^2J(^{119}Sn,{}^1H) = 14$ Hz) for **2a** and 6.29 ppm ($^2J(^{119}Sn,{}^1H) = 19$ Hz) for **2b**, respectively, typical for a monohapto bonded cyclopentadienyl ring, was observed [18]. Compounds **2a** and **2b** display ^{119}Sn resonances at −73.6 and −144.9 ppm, respectively,

Scheme 1.

$$L^{CN}R_2SnCl \xrightarrow[\text{-30°C}]{\text{NaCp}} L^{CN}R_2SnCp$$
(1a – c) (2a – b)

$$\xrightarrow[\text{-20°C}]{\text{K(BEt}_3\text{)H·THF}} L^{CN}R_2SnH$$
(3a – c)

$$\xrightarrow[\text{-30°C}]{\text{3 equiv. K}} [L^{CN}R_2Sn]_2$$
(4a – c)

$$\overset{3}{\underset{5}{\overset{2}{\underset{6}{\bigcirc}}}}\overset{1}{-}N(CH_3)_2 = L^{CN}$$

a; R=*n*-Bu, **b**; R=Ph, **c**; R=*t*-Bu

Scheme 1.

Table 1
Selected NMR spectra parameters

Compound type/R	$\delta(^{119}Sn)$ [ppm]/$^1J(^{119}Sn, X)$, X = ^1H for **3**; X = ^{117}Sn for **4**; X = ^{19}F for $L^{CN}R_2SnF$ [Hz]		
	n-Bu	Ph	*t*-Bu
$L^{CN}R_2SnCp^a$	−73.6 (**2a**)	−144.9 (**2b**)	–
$L^{CN}R_2SnH^a$	−113.2 (**3a**)/1668	−180.9 (**3b**)/2128	−90.0 (**3c**)/1638
$(L^{CN}R_2Sn)_2^a$	−105.7 (**4a**)/3416	−145.1 (**4b**)/5158	(**4c**)^c
$L^{CN}R_2SnF^b$	−77.1 [6]/2114	−198.6 [6]/2148	−92.1 [6]/2197
$L^{CN}R_2SnCl^b$	−51.7 (**1a**) [6]	−177.1 (**1b**) [15]	17.5 (**1c**) [16]
$L^{CN}R_2SnOH^a$	−76.9 [17]	−187.6 [17]	−46.3 [17]
$(L^{CN}R_2Sn)_2O^a$	−59.3 [17]	−173.2 (**5b**) [17]	−35.6 [17]

^{a} Measured in C_6D_6.
^{b} Measured in $CDCl_3$.
^{c} See Section 3.

Fig. 1. ORTEP plot of molecule **2b** showing 50% probability displacement ellipsoid and the atom numbering scheme. Hydrogen atoms were omitted for clarity. Selected bonding lengths (Å) and angles (°): Sn1–N1 2.7288(17), Sn1–C1 2.1427(18), Sn1–C10 2.292 (2), Sn1–C15 2.144(2), Sn1–C21 2.129(2), Sn1–C10–Cg 108.9(1), C21–Sn1–C1 116.06(7), C21–Sn1–C15 116.24(8), C1–Sn1–C15 117.39(7), C21–Sn1–C10 102.80(7), C1–Sn1–C10 100.25(8), C15–Sn1–C10 99.42(8).

in good agreement with a distorted trigonal bipyramidal configuration at the tin atom. These values are of the same order of magnitude as for the starting chlorides and related compounds (see Table 1).

Single crystals of **2b** were obtained from diethyl ether at −30 °C. The geometry of the tin atom is in agreement with the solution NMR data, with a relatively weak Sn–N intramolecular interaction (2.7288(17) Å) and a trigonal bipyramidal coordination geometry. The sum of the equatorial C–Sn–C angles is 349.69°, which demonstrates a deviation towards the tetrahedral geometry. There is a notable elongation of Sn1–C10 (2.2922(19) Å) bond, being about 0.06–0.10 Å longer than usual Sn–C_{Cp} bonds (2.19–2.23 Å) [19], likely related to the trans effect of the weakly tin coordinating Me_2N moiety. Also the Sn1–C10–Cg (as centroid of Cp ring) angle (108.95°) is smaller than expected for a non-distorted structure (ideally 125°) [19], for example for (1-(CH_3)$_3$Sn)(3-(C_6H_5)$_3$C)C_5H_4(118.0(1)°) [20].

The sigmatropic migration of the tin atom around the cyclopentadienyl ring, rapid on the proton NMR time scale, focused much attention in the past [21]. This phenomenon was also observed for **2a** and **2b**, with only some signal broadening in toluene at low temperature. At 180 K, the onset to a decoalescence, evidenced by a saddle point in the resonance, was observed at 6.81 ppm for **2a**. An estimation of the Gibbs free energy for this sigmatropic migration in **2a**, based on these data, provides 37 ± 1 kJ/mol, which is higher than for $Me_3Sn(\eta^1-C_5H_5)$, 29.7 ± 2.9 kJ/mol [19]. One might expect that the coordination of Me_2N-group to tin would increase the ionic character of Sn–Cp bond (trans effect), thus leading to the decrease in energy barrier. We assume that the observed increase is due to steric repulsion of Cp ring and phenyl group of L^{CN} ligand (Fig. 1).

The reactions yielding hydrides **3a–c** were carried out in THF solution at −40 °C. The yield in the obtained hydrides, using K(BEt₃)H·THF, is much better than reported by Vedejs, using LiAlH₄ [22]. All hydrides reveal the typical hydride ^1H NMR signal, albeit shifted to higher frequency (5.83 ppm for **3a**, 6.98 ppm for **3b**, and 6.01 ppm for **3c**) when compared, for example, to tributyltin
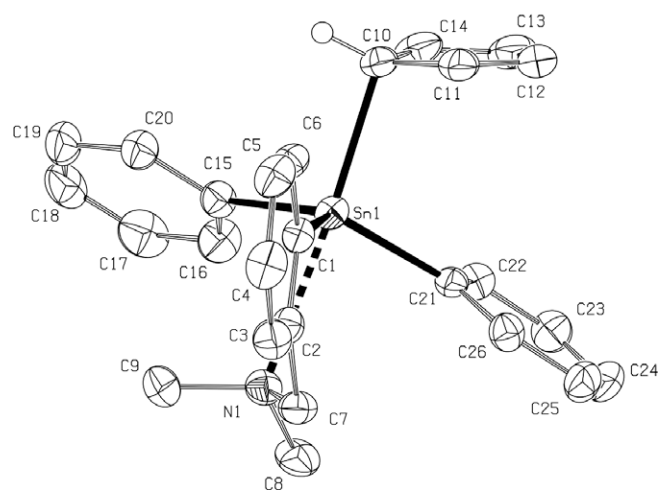
hydride (4.78 ppm) [23,24]. Another parameter characteristic for monomeric triorganotin hydrides is $^1J(^{119}Sn, ^1H)$ coupling constant, found here to be 1627 Hz for **3a**, 2128 Hz for **3b** to be compared to 1576 Hz for *n*-Bu₃SnH and 1950 Hz for Ph₃SnH [25]. The ^{119}Sn chemical shift of compound **3a** (−113.2 ppm, Table 1) is strongly shifted to low frequency field when compared to its closest analog without intramolecular donor, Bu₂PhSnH, 82 ppm [26]. In contrast, the change observed for the ^{119}Sn chemical shift of the diphenyl substituted compound **3b**, −180.9 ppm, when compared to the value for Ph₃SnH, −162.1 ppm, is rather limited. These results suggest a strong intramolecular Sn–N coordination in **3a**, but only a limited one, at most very weak, for the triaryl compound **3b**. This discrepancy can be tentatively ascribed to the larger steric strain induced by the phenyl groups. An alternative explanation could be that, since the *n*-butyl groups of **3a** are inductive releasing groups, while the phenyl groups of **3b** are inductive electron withdrawing, the hydride ligand should be much more apicophile in **3a** than in **3b**, explaining why the former tends more to five-coordination, while the latter would be rather tetrahedral. Unfortunately no crystals could be obtained for any of these hydrides, so that corroborating any of this explanation with an X-ray structure determination of **3a** and/or **3b** turned out impossible.

Further reactivity of the starting chlorides was investigated as reductors using a slight excess of potassium mirror, which yielded the corresponding hexaorganodistannanes. In the case of the *n*-butyl substituted organotin, the only product was the distannane **4a**. Compound **4a** reveals similar ^{119}Sn NMR shift value change as **3a** (−105.7 ppm), indicating relatively strong Sn–N intramolecular coordination leading to five-coordinated tin atom in this compound, unfortunately the direct proof as the ^{119}Sn NMR shift value for (Ph*n*-Bu₂Sn)₂ is not available in the literature. The $^1J(^{119}Sn, ^{117}Sn)$ coupling constant of **4a** is 3416 Hz, but in hexaorganodistannanes in general, this coupling constant can display a wide range of values from 624 to 16870 Hz [27]. The reduction of **1b** by potassium mirror was performed in a similar way as for **1a**. Even though all the processes were performed in strict moisture- and air-free conditions, two ^{119}Sn resonances (−145.1 and −172.6 ppm in integral ratio 15:1) were observed for the target compound **4b**. The high frequency resonance is assigned to the distannane because of its coupling satellites ($^1J(^{119}Sn, ^{117}Sn)$ = 5158 Hz), while the low frequency resonance arises from the distannoxane **5b** [17], which
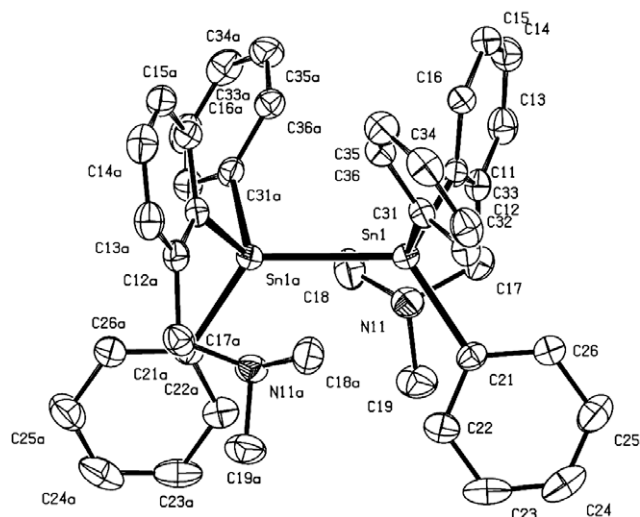
Fig. 2. ORTEP plot of molecule **4b** showing 50% probability displacement ellipsoid and the atom numbering scheme. Hydrogen atoms and the stannoxane molecule were omitted for clarity. The selected bonding lengths (Å) and angles (°): for **4b**: Sn1–Sn1a 2.8014(13), Sn1–N11 3.106(13), C21–Sn1–C11 110.53(12), C21–Sn1–C31 103.54(12), C11–Sn1–C31 103.99(12), C21–Sn1–Sn1a 122.94(9), C11–Sn1–Sn1a 111.52(8), C31–Sn1–Sn1a 101.78(8); for **5b**: Sn2–O1 1.958(3), Sn3–O1 1.976(3), Sn3–N71 2.723(3), Sn2–N41 2.789(3), O1–Sn2–C41 96.01(12), O1–Sn2–C61 98.16(13), C41–Sn2–C61 123.84(13),O1–Sn2–C51 108.75(11), C41–Sn2–C51 112.32(13), C61–Sn2–C51 113.64(13), O1–Sn3–C71 94.47(11), O1–Sn3–C91 99.90(12), C71–Sn3–C91 131.37(12), O1–Sn3–C81 101.82(12), C71–Sn3–C81 111.85(12), C91–Sn3–C81 110.16(13), Sn2–O1–Sn3 142.69(14).

is the oxidation product of **4b**. The value of ^{119}Sn NMR chemical shift of −145.1 ppm, to be compared with that of hexaphenylditin, −144 ppm [30c,d], indicates a four-coordinate tin atom without any Sn–N interaction. This matches the high reactivity of **4b** towards oxygen. A couple of crystals suitable for X-ray diffraction measurements were obtained in the NMR tube of crude product. These crystals are formed by one equivalent of distannane **4b** and two equivalents of distannoxane **5b** (Figs. 2 and 3).

The structure of **4b** consists of two symmetry equivalent tin moieties, where the tin atoms are tetrahedrally coordinated by the three phenyl carbon atoms and the adjacent tin atom. The sum of the interatomic angles C–Sn–C (318.1°), is extremely small, being 328.5° for an ideal tetrahedral configuration of the tin atom. The Sn–Sn bond distance of 2.8014(13) Å is relatively short and of the same order as the Sn–Sn distance in Me$_6$Sn$_2$ (2.78 Å) in the vapor phase, as found by gas electron diffraction, 2.763(2) Å for Ph$_6$Sn$_2$ [28] and the Sn–Sn distance (2.804(4) Å) recently observed in our group for a distannane coordinated by zirconocene [29]. The nitrogen atom is primarily not involved in the tin atom coordination sphere, given the long Sn1–N11 bond (3.106(13) Å), even

though this distance is much smaller than the sum of the Van der Waals radii. In the co-crystal of **4b**·(**5b**)$_2$ there are comparable interatomic distances for the **5b** fragment as found for the structure of **5b**·C$_6$D$_6$ [17]. The only difference is the wider Sn–O–Sn angle in the case of co-crystal **4b**·(**5b**)$_2$ caused probably by crystal packing.

2.1. Reactivity of selected compounds

In order to investigate the potential chemistry of the prepared compounds, the following reactions have been performed. Compounds **3a**, **4a** and **3b** were treated with one molar equivalent of the TEMPO – free radical at room temperature in benzene for 5 min in order to prepare the appropriate organotin radical. Similar results were obtained for the reaction of **2a** and **2b** under UV-light irradiation for 1 h under the same conditions. Unfortunately no results were obtained, in particular no tin radical could be observed using ESR.

In order to prepare chalcogen derivatives of the compounds studied, **4a** was treated with an excess of oxygen in benzene solution at room temperature for 10 min, and with one equivalent of sulfur, selenium and tellurium in benzene solution at 80 °C for 6 h. No product was observed in all reaction attempts. Under slightly more drastic conditions, the reaction of neat **4a** in molten sulfur gave exclusively (L^{CN}n-Bu$_2$Sn)$_2$S, which displays a single ^{119}Sn signal at −7.7 ppm with ^2J(^{119}Sn, ^{117}Sn) satellites of 162 Hz. This indicates tetrahedrally coordinated tin atom (about 70 ppm difference in comparison to an oxide analog (L^{CN}n-Bu$_2$Sn)$_2$O, see Table 1) and is also comparable to previously found values for triorganotin sulfides [30a,b].

To examine the possibilities of hydrostannation reactions, **3a** was heated with ferrocenylacetylene at 90 °C in a sealed NMR tube for 6 h, giving a mixture of stannylated ferrocenyl derivatives in overall 47.2% yield. For comparison, the reaction of Bu$_3$SnH with ferrocenylacetylene gave no desired product under the same conditions. The same reaction was also conducted in the presence of a catalytic amount (1 mol.%) of Pd(PPh$_3$)$_4$ at −30 °C for 30 min. Compound **3a** gave the same product as in the previous case in 23.6% yield and Bu$_3$SnH gave virtually no reaction. The yield in final stannylated vinylferrocene compound was deduced from the integral ratio of the new and well-separated doublet at 6.28 ppm, tentatively assigned to one of the vinylic protons, and the hydride signal of unreacted **3a,b**.

Activation of small molecules such as CO$_2$ is presently the object of major investigation. CO$_2$ activation by organotin(IV) species to give linear and/or cyclic organic organotin [17,31] carbonates was reported previously [32]. The use of both tin(II) and tin(IV) hydrides to produce formates as reactive species is also mentioned in the literature [33]. The reaction of **3a** with CO$_2$ gave formate L^{CN}(n-Bu)$_2$SnOC(=O)H (Scheme 2) in almost quantitative yield when the
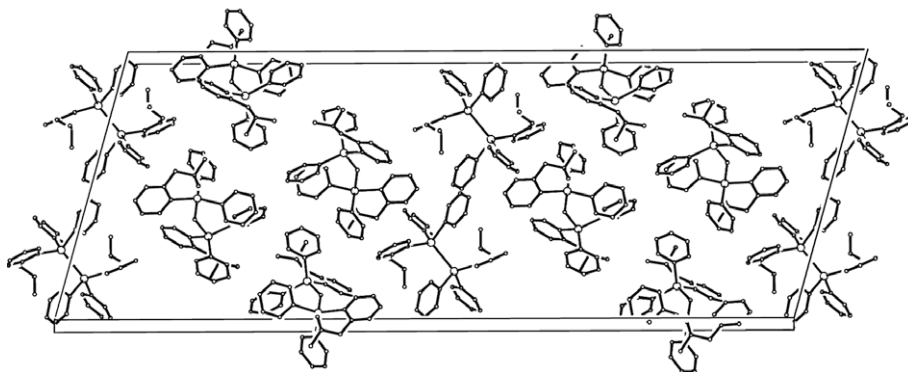

Fig. 3. View of the unit cell of **4b**·(**5b**)$_2$.

reaction was carried out in hexane. In the case of the same reaction in benzene, but with moistened CO_2, formaldehyde was obtained as a by-product, as identified by NMR and IR. $L^{CN}(n\text{-Bu})_2$SnOC(=O)H reveals, for the SnOC(=O)H moiety, a characteristic ^{1}H resonance at 8.78 ppm and a characteristic ^{13}C NMR at 168.3 ppm, in good agreement with data of Jana et al. [33a]. The single ^{119}Sn NMR resonance at −75.4 ppm indicates a monomeric, monodentate bonding mode for the formate ligand to the five-coordinated tin center as observed for analogous carboxylates [34]. Infrared spectra of the isolated product showed strong absorption bands at 1591, 1367 and 761 cm^{-1} that are assigned to the v_a, v_s and scissoring modes of the formate moiety, respectively. A similar IR pattern has been reported for related compounds R_3SnOC(=O)H (R = Me, Et, n-Pr) [35,36].

Based on ^{1}H, ^{13}C and ^{119}Sn NMR spectra $L^{CN}(n\text{-Bu})_2$SnOC(=O)Me (see Fig. 6) and $L^{CN}(n\text{-Bu})_2$SnOMe [17] are most probably the products of reaction of **3a** with CO_2 in methanol. The ^{119}Sn NMR spectrum displays two signals in ratio 100 (−46.8 ppm) to 37 (−65.8 ppm), the minor signal being assigned to the methoxide. The ^{13}C NMR spectrum of the solid product washed with benzene displays a broad resonance at 161.5 ppm assigned to the carbonate function [17,31]. The IR spectrum of isolated solid shows a broad v_a band centered at 1672 cm^{-1} indicating the presence of carboxylic ester. The strong band at 1342 cm^{-1} is assigned to the v_s mode of the OCO moiety. The absorption band gap between v_a and v_s of 330 cm^{-1} indicates a contribution of ionic form that could be explained by the presence of the asymmetric methylcarbonate unit O-bonded to the tin atom, in agreement with earlier observations for oligomeric compounds of the type $[Bu_3SnOC(=O)OR]_n$ (R = Me, i-Pr) [33a].

Another reaction at room temperature, between cyclohexene oxide and CO_2 at atmospheric pressure, in the presence of **3a**, gave, after 30 min, the cyclic carbonate, hexahydro-benzo[1,3]dioxol-2-one, with 7% yield calculated from the starting oxide amount. The ^{119}Sn NMR spectrum of the reaction mixture revealed two signals, a major one at −69.7 ppm and a minor one at −48.5 ppm which do not raise from the starting hydride **3a** but rather from the corresponding tin alcoholate [17] and the above mentioned carbonate.

To examine the possible transfer of the Cp ring from **2a** to a moiety with a transition metal atom, the reaction of **2a** in benzene with neat $TiCl_4$ in excess was investigated. In the reaction mixture, CpTiCl$_3$, $[L^{CN}(n\text{-Bu})_2\text{Sn}]^+[Ti_2Cl_9]^-$ and a minor amount of (n-Bu)$_2$SnCl$_2$ were detected in various NMR spectra. The ^{1}H NMR spectrum of $[L^{CN}(n\text{-Bu})_2\text{Sn}]^+[Ti_2Cl_9]^-$ gave a single set of broad signals, while the ^{119}Sn NMR signal at 185.6 ppm indicated a four-coordinate tin atom. This chemical shift value is about 240 ppm to higher frequency with respect to starting compound **3a** or chloride **1a**, as similarly found for tributylstannylium [37]. Such an increase is most probably caused by the ionic character of $[L^{CN}(n\text{-Bu})_2\text{Sn}]^+[Ti_2Cl_9]^-$ in benzene solution. The structure of the organotin fragment is thus composed of three carbon atoms and one intramolecularly coordinated nitrogen atom. The ionization of triorganotin compounds was observed in the case of tributyltin dodecamethyl-1-carba-closo-dodecaborate [37], tris(triisopropylphenyl)stanny-

lium tetrakis(pentafluorophenyl)borate [38] both for three-coordinated tin atom and N,C,N- or O,C,O-chelating ligands derivatives for five-coordinated tin atoms [39]. The determined crystal structure of $[L^{CN}(n\text{-Bu})_2\text{Sn}]^+[Ti_2Cl_9]^-$ revealed the same geometry for the tin atom as proposed from the solution NMR studies. Three carbon atoms are localized in the basement of the square pyramid which is capped by the nitrogen donor atom (Fig. 4). The sum of the three C–Sn–C angles is 356.5(2)°, and the Sn1–N1 distance is 2.258(4) Å, the shortest one found for a donor–acceptor Sn–N connection. $[L^{CN}(n\text{-Bu})_2\text{Sn}]^+[Ti_2Cl_9]^-$ is the first four-coordinate triorganotin(IV) ionic compound. Attempts to prepare analogous ionic species by reaction of **1a** with AgPF$_6$, AgBF$_4$, and AgSbF$_6$ failed [40]. The distance between the Sn1 atom of a molecule and the Cl2a atom from symmetry related Ti$_2$Cl$_9^-$ anion (3.1872(14) Å) is smaller than the sum of van der Waals radii (3.92 Å) (Fig. 5), indicating a contact. This anion is a common moiety stabilizing various unstable cations, as the oxonium [41], iminium [42], phosphonium [43] or thiophenium [44] ones. When **3a** is reacted with only one mole equivalent of $TiCl_4$, **1a** and CpTiCl$_3$ are detected by ^{1}H and ^{119}Sn NMR. In the case of the reaction of **3a** with a half equivalent of FeBr$_2$ in THF at room temperature, ferrocene and $L^{CN}(n\text{-Bu})_2$SnBr [12] were found as products.

Since $[L^{CN}(n\text{-Bu})_2\text{Sn}]^+[Ti_2Cl_9]^-$ is the first four-coordinated triorganotin(IV) ionic compound it was of interest to study stabilization factors by DFT methods. As can be seen from Fig. 6, in all cases, abstraction of Cl$^-$ from triorganotin compounds using two molecules of $TiCl_4$ with formation of isolated ions is an energetically unfavorable process. Free Gibbs energies of the reactions show highly positive values. However, the presence of coordination groups at tin assist ionization. The presence of one-coordination group lowers the Gibbs free energy by 125.6 kJ/mol. The cooperative effect of two-coordination groups is even higher, $\Delta\Delta G^0$ = 205.2 kJ/mol. Thus in the absence of coordination groups at tin, the isolation of stannylium ions is achieved with the use of weakly coordinating anions $[Bu_3Sn]^+[CB_{11}Me_{12}]^-$ [37], and/or by introduction of steric bulk $[(2,4,6\text{-}^i\text{PrC}_6\text{H}_2)_3\text{Sn}]^+[B(C_6F_5)_4]^-$ [38]. Further, the use of O,C,O and N,C,N monoanionic tridentate ligands allows the isolation of stannylium ions in presence of nucleophilic anions such as halogenides [39].

It should be noted that not only steric and electronic factors are responsible for the formation of ionic species. Thus, optimization of the isolated structure of $[L^{CN}(n\text{-Bu})_2\text{Sn}]^+[Ti_2Cl_9]^-$ reveals that the Sn–Cl bond distance is significantly shorter in the isolated structure (2.756 Å), than in the crystal state (3.187 Å), while it is longer
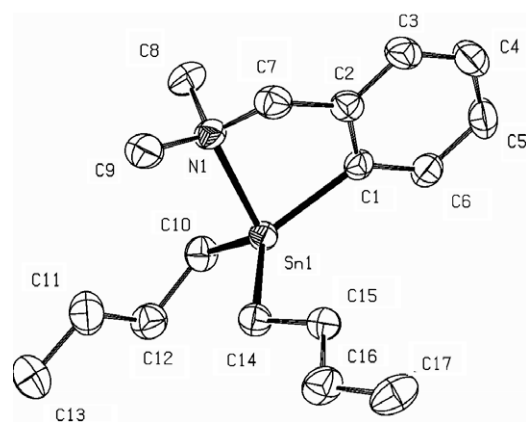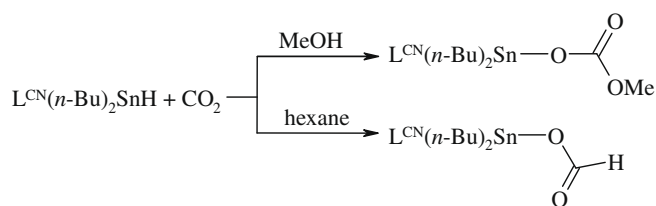

Fig. 4. ORTEP plot of the molecule $[L^{CN}(n\text{-Bu})_2\text{Sn}]^+[Ti_2Cl_9]^-$ showing 50% probability displacement ellipsoids and the atom numbering scheme. Hydrogen atoms, C$_6$D$_6$ and $[Ti_2Cl_9]^-$ were omitted for clarity. The selected bonding lengths (Å) and angles (°): Sn1–N1 2.258(4), Sn1–C1 2.121(5), Sn1–C10 2.129(5), Sn1–C14 2.152(5), C1–Sn1–C10 123.56(19), C1–Sn1–C14 114.87(19), C10–Sn1–C14 118.1(2).
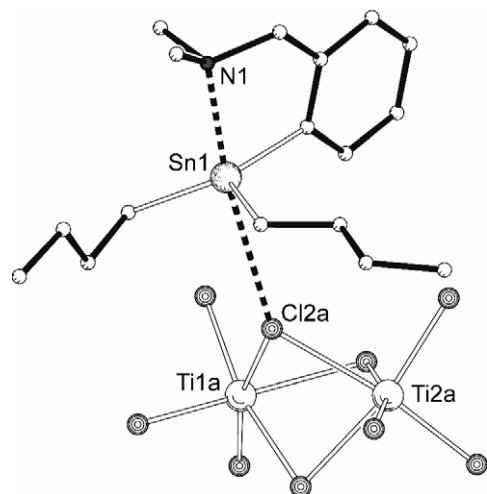

Scheme 2.

Fig. 5. View of the cationic and symmetry related anionic parts of $[L^{CN}(n\text{-}Bu)_2Sn]^+[Ti_2Cl_9]^-$ with Sn1–Cl2a interaction. Sn1–Cl2a 3.1872(14) Å, N1–Sn1–Cl2a 171.42(12)°; symmetry operator = $x, y, -1 + z$.

$\Delta G^0 = 456.4; \Delta\Delta G^0 = 0.0$

$\Delta G^0 = 330.8; \Delta\Delta G^0 = 125.6$

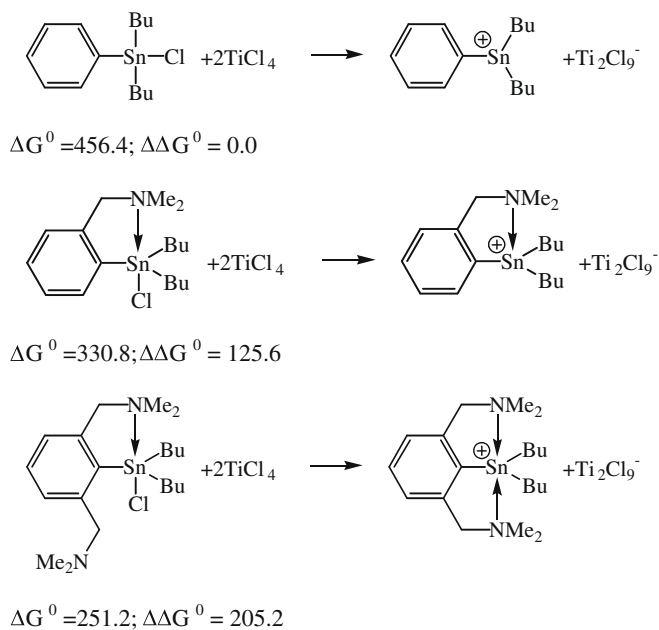$\Delta G^0 = 251.2; \Delta\Delta G^0 = 205.2$

Fig. 6. Calculated energies of Cl$^-$ abstraction from triorganotin compounds (free Gibbs energies in kcal/mol).

than the calculated Sn–Cl bond length in $L^{CN}(n\text{-Bu})_2$SnCl (2.472 Å). Thus, the crystal field effect is also of importance for the formation of tetracoordinated $L^{CN}(n\text{-Bu})_2$Sn$^+$ stannylium cation.

3. Experimental

3.1. IR spectroscopy

Infrared spectra were recorded on a FTIR Nicolet Magna 550 spectrometer, the sample being placed between KBr windows dispersed in Nujol.

3.2. Calculation procedure

All molecules were studied at the DFT level. Molecular geometries were optimized using generalized gradient-corrected func-

tional PBE [45,46]. Valence electrons were treated using TZ2P basis set. Innermost electrons of Sn, Ti, Cl, C, N atoms were emulated using effective core potentials ECP-SBKJC [47]. All calculations were made using the PRIRODA program [48].

3.3. ESR spectroscopy

The solution ESR spectra were recorded at ambient temperature at X-band ($v \sim 9.5$ GHz) using an ERS 221 spectrometer (Magnettech Berlin). A microwave power of 1 mW, sufficiently below the saturation power, was used.

3.4. NMR spectroscopy

The NMR spectra were recorded from samples in C_6D_6 solution, unless otherwise indicated, on a Bruker Avance 500 spectrometer (equipped with Z-gradient 5 mm probe) at 300 K with resonance frequencies of 500.13 MHz for ^{1}H, 186.50 MHz for ^{119}Sn$\{^1$H$\}$ and 125.67 MHz for ^{13}C$\{^1$H$\}$ nuclei. The assignments of ^{1}H resonances were achieved from standard 2D spectra. The solutions were obtained by dissolving 40 mg of each compound in 0.5 ml of C_6D_6 or CD_3OD *in vacuo* sealed tubes. The ^{1}H chemical shifts were calibrated relative to the signal of residual benzene (7.16 ppm) or methanol (4.87 ppm). The ^{13}C chemical shifts were calibrated relative to the residual benzene (128.44) or methanol (49.1 ppm) signal. 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.

3.5. X-ray crystallography

Data for the colorless crystals were collected on a Nonius KappaCCD diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å), and a graphite monochromator. The structures were solved by direct methods (SIR92 [49]). All reflections were used in the structure refinement based on F^2 by full-matrix least-squares technique (SHELXL97 [50]). Heavy atoms were refined anisotropically. The highest residual maximum in the co-crystal of **4b**·(**5b**)$_2$ is close to the tin atoms. Hydrogen atoms were localized on a difference Fourier map; however to ensure the uniformity of the treatment of the crystal, they were all recalculated into idealized positions (riding model) and were assigned temperature factors H_{iso}(H) of 1.2 U_{eq} (pivot atom) or of 1.5 U_{eq} for the methyl group. Absorption corrections were carried on, using Gaussian integration from crystal shape [51].

3.5.1. Crystallographic data for **4b**·(**5b**)$_2$

$2(C_{42}H_{44}N_2OSn_2)\cdot C_{42}H_{44}N_2Sn_2$, $M = 2474.52$, monoclinic, $C\,2/c$, $a = 55.9238(5)$, $b = 9.80601(10)$, $c = 21.1252(2)$ Å, $\beta = 105.4850(6)°$, $Z = 4$, $V = 11164.23(18)$ Å^3, $D_c = 1.472$ g cm^{-3}, 1.375 mm^{-1}, $T_{min} = 0.785$, $T_{max} = 0.910$; 81 362 reflections measured ($\theta_{max} = 27.5°$), 12 799 independent ($R_{int} = 0.0537$), 10 061 with $I > 2\sigma(I)$, 637 parameters, $S = 1.041$, R_1(obs. data) = 0.0363, wR_2(all data) = 0.0766; maximum, minimum residual electron density = 2.806, -1.518 eÅ^{-3}.

3.5.2. Crystallographic data for **2b**

$C_{26}H_{27}NSn$, $M = 472.18$, triclinic, $P\bar{1}$, $a = 8.2807(2)$, $b = 11.1968(3)$, $c = 12.1249$ Å, $\alpha = 78.5558(13)°$, $\beta = 83.3013(16)°$, $\gamma = 87.3236(16)°$, $Z = 2$, $V = 1094.02$ Å^3, $D_c = 1.433$ g cm^{-3}, $\mu = 1.178$ mm^{-1}, $T_{min} = 0.758$, $T_{max} = 0.840$; 20 385 reflections measured ($\theta_{max} = 27.5°$), 5025 independent ($R_{int} = 0.0361$), 4598 with $I > 2\sigma(I)$, 259 parameters, $S = 1.052$, R_1(obs. data) = 248, wR_2(all data) = 0.0581; maximum, minimum residual electron density = 0.799, -0.788 eÅ^{-3}.

3.5.3. Crystallographic data for $[L^{CN}(n\text{-}Bu)_2Sn]^+[Ti_2Cl_9]^-\cdot C_6D_6$

$C_{23}H_{36}Cl_9NSnTi_2$, $M = 860.07$, triclinic, $P\bar{1}$, $a = 9.6642(8)$, $b = 10.0831(6)$, $c = 10.2396(4)$ Å, $\alpha = 92.325(4)°$, $\beta = 101.151(4)°$, $\gamma = 115.512(6)°$, $Z = 1$, $V = 874.83(10)$ Å^3, $D_c = 1.633$ g cm^{-3}, 1.856 mm^{-1}, $T_{min} = 0.519$, $T_{max} = 0.650$; 16 514 reflections measured ($\theta_{max} = 27.49°$), 7427 independent ($R_{int} = 0.0564$), 6671 with $I > 2\sigma(I)$, 325 parameters, $S = 1.118$, R_1(obs. data) = 0.0385, wR_2 (all data) = 0.0849; maximum, minimum residual electron density = 0.679, -0.979 eÅ^{-3}. $R_{int} = \sum |F_o^2 - F_{o,mean}^2| / \sum F_o^2$,

$$S = \left[\sum \left(w \left(F_o^2 - F_c^2 \right)^2 \right) / (N_{diffrs} - N_{params}) \right]^{\frac{1}{2}},$$ weighting scheme: $w = \left[\sigma^2(F_o^2) + (w_1 P)^2 + w_2 P \right]^{-1}$, where $P = \left[\max \left(F_o^2 \right) + 2F_c^2 \right]$, $R(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR(F^2) = \left[\sum \left(w \left(F_o^2 - F_c^2 \right)^2 \right) \middle/ \left(\sum w(F_o^2)^2 \right) \right]^{\frac{1}{2}}$.

3.6. GC/MS

The samples were analysed using a gas chromatograph GC 17A coupled with a mass spectrometry detector QP 5050A (EI, NCI, both Shimadzu) and a GC/MS solution data system (Shimadzu). The helium (grade 5.0, Linde) was used as carrier gas. Separations were performed on a 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, subsequently, a temperature increase for 20 °C/min to 300 °C (kept for 6.5 min) was applied. The temperature of the injector was 220 °C and the temperature of the interface was 230 °C. The identification of the compounds was based on the comparison of their mass spectrum with the library spectrum (NIST 107 and NIST 21, Shimadzu).

3.7. Synthesis

All experiments were carried out under argon atmosphere. (N,N-dimethylaminomethyl)benzene, sodium cyclopentadienide (NaCp), K(BEt$_3$)H·THF and potassium were purchased (Sigma–Aldrich). Diethyl ether, THF and n-hexane were dried over and distilled from potassium-sodium alloy, degassed and stored under argon over a potassium mirror. Compounds **1a–c** were obtained by published methods [12,15,16].

3.7.1. [2-(N,N-dimethylaminomethyl)phenyl]di-n-butyltin (IV) cyclopentadienide (2a)

Compound **1a** (2.6 g, 6.5 mmol) was dissolved in diethyl ether and a solution of NaCp (0.57 g, 6.5 mmol) in diethyl ether was added dropwise during 10 min at −30 °C. The reaction mixture was stirred for 5 days. Afterwards, the reaction mixture was filtered off and the solvent was evaporated *in vacuo*. A brown oily product was obtained in 81% yield (2.3 g). ^{1}H NMR (C$_6$D$_6$, 295 K, ppm): 8.00 (d, 1H-6, ^{3}J(^{119}Sn, ^{1}H) = 50 Hz); 7.24 (m, 2H-4, 5); 7.03 (d, 1H-3); 6.42 (s, 5H-Cp, ^{2}J(^{119}Sn, ^{1}H) = 14 Hz); 3.19 (s, 2H-NCH$_2$); 1.92 (s, 6H-N(CH$_3$)$_2$); 1.62 (m, 4H-α); 1.52 (m, 4H-β); 1.40 (m, 4H-γ); 0.96 (t, 6H-δ). ^{119}Sn{^{1}H} NMR (C$_6$D$_6$, 295 K, ppm): −73.6 (s). *Anal.* Calc. for C$_{22}$H$_{35}$NSn (432.22): C, 61.14; H, 8.16; N, 3.24. Found: C, 61.1; H, 8.2; N, 3.3%.

3.7.2. [2-(N,N-dimethylaminomethyl)phenyl]di-n-butyltin (IV) hydride (3a)

Compound **1a** (1.3 g, 3.2 mmol) was dissolved in THF at −20 °C and 3.22 ml of K(BEt$_3$)H·THF ($c = 1$ mol dm^{-3}, 3.2 mmol) were added. The reaction mixture was stirred up to room temperature. Subsequently, the solvent was evaporated *in vacuo*, hexane was then added and the soluble part was filtered off. A colorless oily

product was obtained when the mother liquor was evaporated *in vacuo*. ^{1}H NMR (C$_6$D$_6$, 300 K, ppm): 7.78 (d, 1H-6, ^{3}J(^{119}Sn, ^{1}H) = 55 Hz); 7.20 (m, 2H-4, 5); 7.06 (m, 1H-3); 5.83 (s, 1H-SnH, ^{1}J(^{119}Sn, ^{1}H) = 1627 Hz); 3.25 (s, 2H-NCH$_2$); 1.99 (s, 6H-N(CH$_3$)$_2$); 1.73 (m, 4H-α); 1.47 (m, 4H-β); 1.18 (m, 4H-γ); 0.98 (t, 6H-δ). ^{119}Sn{^{1}H} NMR (C$_6$D$_6$, 300 K, ppm): −113.2 (s, ^{1}J(^{1}H, ^{119}Sn) = 1668 Hz). ^{13}C{^{1}H} (C$_6$D$_6$, 300 K, ppm): 146.0 (C-2, ^{2}J($^{119/117}$Sn, ^{13}C) = 24 Hz); 142.0 (C-1, ^{1}J(^{119}Sn, ^{13}C) = 500 Hz, ^{1}J(^{117}Sn, ^{13}C) = 477 Hz); 138.7 (C-3, ^{3}J($^{119/117}$Sn, ^{13}C) = 40 Hz); 128.8 (C-5, ^{3}J($^{119/117}$Sn, ^{13}C) = 40 Hz); 128.7 (C-4, ^{4}J($^{119/117}$Sn, ^{13}C) = 11 Hz); 127.5 (C-6, ^{2}J($^{119/117}$Sn, ^{13}C) = 51 Hz; 66.5 (C-NCH$_2$, ^{n}J($^{119/117}$Sn, ^{13}C) = 19 Hz); 44.8 (C-N(CH$_3$)$_2$); 30.8 (C-β, ^{2}J($^{119/117}$Sn, ^{13}C) = 20 Hz); 27.9 (C-γ, ^{3}J($^{119/117}$Sn, ^{13}C) = 61 Hz); 14.3 (C-δ); 11.3 (C-α, ^{1}J(^{119}Sn, ^{13}C) = 384 Hz, ^{1}J(^{117}Sn, ^{13}C) = 367 Hz). *Anal.* Calc. for C$_{17}$H$_{31}$NSn (368.13): C, 55.47; H, 8.49; N, 3.80. Found: C, 55.5; H, 8.5; N, 3.8%.

3.7.3. Bis{[2-(N,N-dimethylaminomethyl)phenyl]di-n-butyltin(IV)} (4a)

The K-mirror (0.65 g, 16.6 mmol) was prepared and poured over with hexane. Afterwards, the solution of (L^{CN})(n-Bu)$_2$SnCl (4.5 g, 11.0 mmol) in hexane was added during 15 min at −30 °C. The reaction mixture was stirred for 5 days. Afterwards, the solvent was evaporated *in vacuo*. A white oily product was obtained. Yield 3.72 g (92%). ^{1}H NMR (C$_6$D$_6$, 300 K, ppm): 7.74 (d, 2H-6, ^{3}J(^{119}Sn, ^{1}H) = 48 Hz); 7.30 (m, 4H-4, 5); 7.15 (m, 2H-3); 3.34 (s, 4H-NCH$_2$); 2.01 (s, 12H-N(CH$_3$)$_2$); 1.71 (m, 8H-α); 1.44 (br m, 16H-β, γ); 0.95 (t, 12H-δ). ^{119}Sn{^{1}H} NMR (C$_6$D$_6$, 300 K, ppm): −105.7 (s, ^{1}J(^{119}Sn, ^{117}Sn) = 3416 Hz). *Anal.* Calc. for C$_{34}$H$_{60}$N$_2$Sn$_2$ (734.25): C, 55.62; H, 8.24; N, 3.82. Found: C, 55.6; H, 8.2; N, 3.8%.

3.7.4. [2-(N,N-dimethylaminomethyl)phenyl]diphenyltin (IV) cyclopentadienide (2b)

Compound **1b** (0.80 g, 1.8 mmol) was dissolved in diethyl ether and a solution of NaCp (0.16 g, 1.8 mmol) in diethyl ether was added dropwise during 10 min at −30 °C. The reaction mixture was stirred for 5 days. Afterwards, the reaction mixture was filtered off and the solvent was evaporated *in vacuo*. A yellow crystalline product was obtained. The solid was recrystallized at −30 °C from diethyl ether to give white crystals. Yield 0.61 g (72%), m.p. 217–220 °C. ^{1}H NMR (C$_6$D$_6$, 295 K, ppm): 8.18 (d, 1H-6, ^{3}J(^{119}Sn, ^{1}H) = 64 Hz); 7.46 (m, 12H-4, 5, o, m, p); 7.14 (m, 2H-3); 6.29 (s, 5H-Cp, ^{2}J(^{119}Sn, ^{1}H) = 19 Hz); 2.99 (s, 2H-NCH$_2$); 1.27 (s, 6H-N(CH$_3$)$_2$). ^{119}Sn{^{1}H} NMR (C$_6$D$_6$, 295 K, ppm): −144.9 (s). *Anal.* Calc. for C$_{26}$H$_{27}$NSn (472.20): C, 66.13; H, 5.76; N, 2.97. Found: C, 66.2; H, 5.8; N, 3.0%.

3.7.5. [2-(N,N-dimethylaminomethyl)phenyl]diphenyltin (IV) hydride (3b)

Compound **1b** (0.54 g, 1.2 mmol) was dissolved in THF at −20 °C and 1.22 ml of K(BEt$_3$)H·THF ($c = 1$ mol dm^{-3}, 1.2 mmol) were added. The reaction mixture was stirred up to room temperature. Subsequently, the solvent was evaporated *in vacuo*, diethyl ether was then added and the soluble part was isolated by filtration. A colorless solution of the desired product was obtained. ^{1}H NMR (C$_6$D$_6$, 295 K, ppm): 7.60 (d, 1H-6, ^{3}J(^{119}Sn, ^{1}H) = 58 Hz); 7.14 (br m, 13H-3, 4, 5, o, m, p); 6.98 (s, 1H-SnH, ^{1}J(^{119}Sn, ^{1}H) = 2128 Hz); 3.15 (s, 2H-NCH$_2$); 1.66 (s, 6H-N(CH$_3$)$_2$). ^{119}Sn{^{1}H} NMR (C$_6$D$_6$, 295 K, ppm): −180.9 (s). *Anal.* Calc. for C$_{21}$H$_{23}$NSn (408.11): C, 61.80; H, 5.68; N, 3.43. Found: C, 61.8; H, 5.7; N, 3.4%.

3.7.6. Bis{[2-(N,N-dimethylaminomethyl)phenyl]diphenyltin(IV)} (4b)

The K-mirror (0.65 g, 16.6 mmol) was prepared and poured over with hexane. Afterwards, the solution of **1b** (4.9 g, 11.0 mmol) in hexane was added during 15 min at −30 °C. The reaction mixture was stirred for 5 days. Afterwards, the solvent was evaporated *in*

vacuo. The white solid product was crystallized from toluene. Yield 3.95 g (88%), m.p. 178–180 °C. ^1H NMR (C_6D_6, 300 K, ppm): 9.00 (d, 2H-6, $^3J(^{119}Sn, ^1H) = 72$ Hz); 7.67 (m, 24H-4, 5, *o, m, p*); 7.05 (d, 2H-3); 2.95 (s, 4H-NCH$_2$); 1.34 (s, 12H-N(CH$_3$)$_2$). $^{119}Sn\{^1H\}$ NMR (C_6D_6, 300 K, ppm): −145.1 (s, $^1J(^{119}Sn, ^{117}Sn) = 5158$ Hz). *Anal.* Calc. for $C_{42}H_{44}N_2Sn_2$ (814.21): C, 61.96; H, 5.45; N, 3.44. Found: C, 62.0; H, 5.5; N, 3.4%.

3.7.7. [2-(N,N-dimethylaminomethyl)phenyl]di-t-butyltin (IV) hydride (3c)

Compound **1c** (0.40 g, 1.0 mmol) was dissolved in THF and toluene at −20 °C and 989 µl of K(BEt$_3$)H·THF (*c* = 1 mol dm^{-3}, 1.0 mmol) were added. The reaction mixture was stirred up to room temperature. Subsequently, the solvent was evaporated *in vacuo*, hexane was added and the soluble part was isolated by filtration. A pale yellow solution of the product was obtained. ^1H NMR (C_6D_6, 300 K, ppm): 7.19 (m, 4H-3, 4, 5, 6); 6.01 (s, 1H-SnH, $^1J(^{119}Sn, ^1H) = 1638$ Hz); 3.28 (s, 2H-NCH$_2$); 2.06 (s, 6H-N(CH$_3$)$_2$); 1.40 (s, 18H-*t*-Bu, $^3J(^{119}Sn, ^1H) = 63$ Hz). $^{119}Sn\{^1H\}$ NMR (C_6D_6, 300 K, ppm): −90 (s). After 3 days, decomposition of product and formation of a mixture of new products, probably including distannane, were observed. $^{119}Sn\{^1H\}$ NMR (C_6D_6, 300 K, ppm): −145.5 (major, s); −4.8 (major, s); −64.0 (s); −70.0 (s); −80.0 (s).

3.7.8. [2-(N,N-dimethylaminomethyl)phenyl]di-n-butyltin(IV) sulfide

Oily **4a** (0.44 g, 0.59 mmol) was transferred into a Schlenk tube and 0.019 g of sulfur (0.59 mmol) was added in one portion. The mixture was stirred at 140 °C for 4.5 h. A part of the yellow oily product was dissolved in C_6D_6 and NMR spectra were recorded. ^1H NMR (C_6D_6, 300 K, ppm): 8.83 (d, 2H-6, $^3J(^{119}Sn, ^1H) = 58$ Hz, $^3J(^1H, ^1H) = 7.2$ Hz); 7.27 (m, 4H-4, 5); 7.01 (d, 2H-3, $^3J(^1H, ^1H) = 7.2$ Hz); 2.98 (s, 4H-NCH$_2$); 1.94 (s, 12H-N(CH$_3$)$_2$); 1.78 (m, 8H-α); 1.36 (m, 16H-β, γ); 0.93 (t, 12H-δ). $^{119}Sn\{^1H\}$ NMR (C_6D_6, 300 K, ppm): −7.7 (s, $^2J(^{119}Sn, ^{117}Sn) = 162$ Hz).

3.7.9. [L^{CN}(n-Bu)$_2$Sn]$^+$[Ti$_2$Cl$_9$]$^-$

Oily **2a** (0.05 g, 0.11 mmol) was transferred into an NMR tube, dissolved in C_6D_6 and 50 µl of TiCl$_4$ (0.45 mmol) was added in one portion. The NMR spectra were recorded. In the ^{119}Sn NMR spectrum a minor signal from (*n*-Bu)$_2$SnCl$_2$ was observed. ^1H NMR (C_6D_6, 300 K, ppm): 7.87 (d, 1H-6, $^3J(^{119}Sn, ^1H) = 49$ Hz); 7.31 (m, 4H-4, 5); 7.15 (d, 2H-3); 2.62 (s, 2H-NCH$_2$); 2.21 (s, 6H-N(CH$_3$)$_2$); 1.61 (m, 4H-α); 1.38 (m, 8H-β, γ); 1.17 (t, 6H-δ). $^{119}Sn\{^1H\}$ NMR (C_6D_6, 300 K, ppm): 185.6 (s). M.p. 98–102 °C.

3.7.10. L^{CN}(n-Bu)$_2$SnOC(=O)H

The reaction of the solution of **3a** (0.05 g, 0.13 mmol) in C_6D_6 with not dried CO_2 was carried out in an NMR tube at room temperature and under atmospheric pressure of CO_2 for 10 min. The NMR spectra were recorded. In the ^1H NMR spectrum of reaction mixture, the signal of formaldehyde was observed. The reaction was repeated in the Schlenk tube with CO_2 dried by sulfuric acid in hexane giving identical spectra and no formaldehyde. ^1H NMR (C_6D_6, 300 K, ppm): 8.78 (s, 1H-HC(=O)O−); 8.26 (d, 1H-6, $^3J(^{119}Sn, ^1H) = 48$ Hz); 7.24 (m, 2H-4, 5); 6.90 (d, 1H-3); 3.04 (s, 2H-NCH$_2$); 1.73 (s, 6H-N(CH$_3$)$_2$); 1.50 (m, 4H-α); 1.10 (m, 8H-β, γ); 0.94 (t, 6H-δ). $^{119}Sn\{^1H\}$ NMR (C_6D_6, 300 K, ppm): −75.4 (s). $^{13}C\{^1H\}$ (C_6D_6, 300 K, ppm): 168.36 (C-HC(=O)O−); 143.29 (C-2); 141.65 (C-1); 138.70 (C-3); 129.72 (C-5); 127.30 (C-6); 127.46 (C-4); 65.76 (C-NCH$_2$); 45.39 (C-N(CH$_3$)$_2$); 28.80 (C-β); 27.79 (C-γ); 14.19 (C-δ); 9.34 (C-α).

3.7.11. 3a + CO$_2$ + methanol

CO_2 was bubbled through a solution of **3a** (0.68 g, 1.78 mmol) in methanol at nearly atmospheric pressure for 30 min at room temperature. A colorless solution was obtained. The solution was evaporated and the white waxy material obtained was washed by benzene and crystallized from methanol. The obtained single crystals were destroyed during the XRD measurement. $^{119}Sn\{^1H\}$ NMR (C_6D_6, 300 K, ppm): −46.6 (s). $^{13}C\{^1H\}$ (CD$_3$OD 300 K, ppm): 161.50 (C(=O)O−); 147.05 (C-2); 142.94 (C-1); 138.22 (C-3); 130.82 (C-5); 130.24 (C-6); 127.51 (C-4); 67.82 (C-NCH$_2$); 49.67 (OMe); 45.92 (C-N(CH$_3$)$_2$); 30.59 (C-β); 28.71 (C-γ); 14.23 (C-δ); 11.14 (C-α).

3.7.12. 3a + CO$_2$ + cyclohexene oxide

The reaction of 10 ml of cyclohexene oxide (98.8 mmol) with CO_2 in presence of **3a** (0.72 g, 1.88 mmol, 1.9 mol% to cyclohexene oxide) was carried out by bubbling CO_2 at nearly atmospheric pressure for 30 min at room temperature through the mixture. Colorless solution was obtained. ^1H NMR spectrum of reaction mixture is very complex and was not analyzed. $^{119}Sn\{^1H\}$ NMR (C_6D_6, 300 K, ppm): −48.5 (s), −69.7 (s). GC/MS measurement was performed at declared conditions using starting material and product as standards to proof the course of the reaction.

Acknowledgements

Appendix A. Supplementary material

CCDC 702855, 702854 and 720158 contain the supplementary crystallographic data for **4b**·(**5b**)$_2$, **2b** and [L^{CN}(*n*-Bu)$_2$Sn]$^+$ [Ti$_2$Cl$_9$]$^-$·C_6D_6. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via <http://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.2009.04.043.

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