Dalton
Transactions

RSCPublishing

PAPER

View Article Online
View Journal | View Issue

Cite this: *Dalton Trans.*, 2013, **42**, 7660

Activation of E–Cl bonds (E = C, Si, Ge and Sn) by a *C*,*N*-chelated stannylene†‡

Zdeňka Padělková,*[a] Petr Švec,[a] Vladimír Pejchal[b] and Aleš Růžička[a]

Received 27th January 2013,
Accepted 14th March 2013

DOI: 10.1039/c3dt50278c

www.rsc.org/dalton

The reactivity of $(L^{CN})_2Sn$ (**1**) (where L^{CN} is 2-(*N*,*N*-dimethylaminomethyl)phenyl-) towards various substrates containing E–Cl bond(s) has been studied (E = C, Si, Ge and Sn). Alkyl chlorides like chloroform or dichloromethane reacts with **1** to form $(L^{CN})_2SnCl_2$ and unidentified by-products in poor yields. The reaction of benzoyl chloride with **1** at low temperature yielded a thermally unstable product $(L^{CN})_2Sn(Cl)$-$C(=O)Ph$ (**2**) which was isolated and characterized by both multinuclear NMR spectroscopy and X-ray diffraction techniques. The vicinity of the central tin atom in **2** reveals trigonal bipyramidal geometry. Attempts to oxidize **2** by dioxygen to give the corresponding organotin(IV) benzoate failed. On the other hand, the reaction of the *in situ* prepared $(L^{CN})_2Sn{=}O$ (synthesized by the reaction of **1** with dioxygen) with PhCOCl resulted in the formation of the desired organotin(IV) benzoate $(L^{CN})_2Sn(Cl)C(=O)OPh$ (**3**). The reaction of **1** with Ph_3GeCl yielded triphenylgermyl-substituted diorganotin(IV) chloride $(L^{CN})_2Sn(Cl)$-$GePh_3$ (**4**) which subsequently gave mixed diorganotin(IV) chloride-oxide $[(L^{CN})_2SnCl]_2O$ (**5**) upon loss of the $GePh_3$ moiety in the air. When the same reaction was carried out in benzene instead of chloroform a unique $[Ph_3Ge]_4[Sn_6O_8]$ cluster (**6**) was obtained. Similarly, the reaction of **1** with Ph_3SiCl provided triphenylsilyl-substituted diorganotin(IV) chloride $(L^{CN})_2Sn(Cl)SiPh_3$ (**7**) which was then oxidized to $(L^{CN})_2Sn(Cl)$-$OSiPh_3$ (**8**). The unprecedented reaction of **1** with $(n\text{-}Bu)_3SnCl$ provided the distannane $(L^{CN})_2Sn(Cl)SnBu_3$ (**9**) which could be oxidized by dioxygen to a distannoxane $(L^{CN})_2Sn(Cl)OSnBu_3$ (**10**). In addition, the solid-state structures of **3**, **5**, **6** and **8** were determined by the X-ray diffraction techniques.

1. Introduction

In early 1974, directly after its breakthrough discovery by Lappert, thermally robust higher congeners of carbenes – germylenes and stannylenes – attracted considerable attention.[1] Much attention has been paid to the oxidation reactions,[2] complexation to various transition metals[3] and photolysis.[4] The prominent reactivity issues have been studied also in the area of the oxidative addition reactions of alkyl- or arylhalides to dialkyl- or bis-amidogermylenes and stannylenes.[5] The tin halide promoted C–H bond activation as well as the addition of tin compounds to the unsaturated systems is also described but the number of papers is rather limited.[6] On the other hand, tin(II) compounds are widely used for example for ring opening polymerization of biodegradable polymers.[7] In the last few years, a renaissance of low valent germanium and tin chemistry is taking place mainly thanks to discoveries of new reactivity of low valent germanium and tin compounds by Bannaszak-Holl and Power, where the first one used Lappert germylenes and stannylenes for activation of C–H bonds in alkanes, alkenes and alkynes[8] or one-pot coupling reactions,[9] and the second one is successful in activation of various small molecules such as for example dihydrogen or ammonia.[10]

It is a well known fact that common stannylenes[5b,d] (Fig. 1A and B) or tin(II) halides[11] can undergo an oxidative addition using appropriate reagents, usually of the R–X type (R = alkyl or aryl, X = Cl, Br, I), as stated above. The proper choice of the

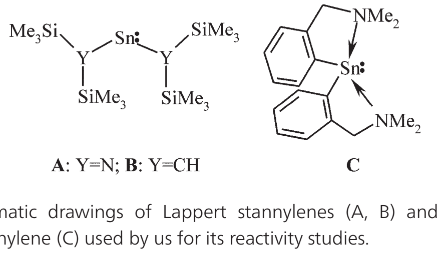


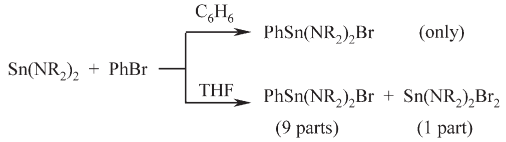
Fig. 1 Schematic drawings of Lappert stannylenes (A, B) and doubly *C*,*N*-chelated stannylene (C) used by us for its reactivity studies.

---

[a] *Department of General and Inorganic Chemistry, Faculty of Chemical Technology, University of Pardubice, Studentská 573, CZ-532 10, Pardubice, Czech Republic. E-mail: zdenka.padelkova@upce.cz; Fax: +420 466037068*
[b] *Institute of Organic Chemistry and Technology, Faculty of Chemical Technology, University of Pardubice, Studentská 573, CZ-532 10, Pardubice, Czech Republic*

† This paper is dedicated to Professor Dr Jaroslav Holeček on the occasion of his 80th birthday on February 6th 2013 and for his enormous contribution to the chemistry of coordination and organometallic compounds, NMR spectroscopy as well as to the development of his parent faculty.

‡ CCDC 921170–921174. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt50278c



Scheme 1 Solvent participation in oxidative reactions affects the formation of products (the scheme is adopted from the literature[5d]).

solvent plays a key role since different products can be thus obtained as shown in Scheme 1. An important issue of these reactions is also the possibility of oxidative coupling to give R–R species which was reported in mid-seventies of the last century.[12]

To the best of our knowledge, nobody has investigated the reactivity of the *C*,*N*-chelated stannylene **1** (Fig. 1C) towards group 14 species containing the E–X (where E = C, Si, Ge and Sn; and X = Cl, Br and I) bond(s) yet. Recently only one paper dealt with the oxidative additions of the R_nPCl_{3-n} (where n = 1–2) compounds towards the cyclic and acyclic germanium and tin heterocarbenoids.[13] The other two papers by Lappert describe[14] the reactivity of homoleptic aromatic amino-stabilized germylene and stannylene ($E\{C_6H_3(NMe_2)_2\text{-}2,6\}_2$), respectively, with $SiCl_4$, $MeSiCl_3$, XeF_2, $HgCl_2$, $TeCl_4$, dabco·$2Br_2$, I_2, or $SiMe_3N_3$. Mixed species with a direct Sn–E (where E = Si, Ge and Sn) bond are usually prepared from hydrido[15] and lithium[16] compounds or by a Wurtz type coupling[17] but the direct and clean procedure using low valent compounds is still elusive.

In this paper we explore the reactivity of coordinationally saturated bis-*C*,*N*-chelated stannylene **1** (for the numbering of the L^{CN} ligand see Fig. 2), first prepared by Angermund,[18] and try to compare it with the first Lappert V-shaped stannylenes. We have already described the *C*,*N*-chelated stannylene oxidation by chalcogenes,[19] the reactivity with azobenzene,[20] molybdenum and tungsten carbonyls[21] and Negishi reagent analogs.[22] Now we decided to investigate the reactivity of *C*,*N*-chelated stannylene (Fig. 1C) towards various E–X (where E = C, Si, Ge and Sn; X = Cl, I) bond containing species.

2. Results and discussion

2.1. Reactivity of $(L^{CN})_2Sn$ (1) towards alkyl chlorides and aryl iodide

In general, and contrary to the reactivity described for the Lappert stannylenes[1c,5] as shown in Scheme 1, rather unsuccessful results were obtained when the reactivity of **1** towards alkyl chlorides (such as CH_2Cl_2 and $(Me_3Si)_2CHCl$) and aryl iodide (9-isopropyl-6-iodopurine) was investigated. The presumed oxidative addition reactions did not proceed as one would expect, and only the slow formation of the corresponding diorganotin(IV) dihalides of the $(L^{CN})_2SnX_2$ type was confirmed by the multinuclear NMR measurements. The products of the C–C coupling reactions were probably formed as corresponding by-products but we did not even try to identify them. Identically, $(L^{CN})_2SnI_2$ was the product of the reaction of **1** with $[(Me_3Si)_2CH]_3SnI$. On the other hand, the reaction of **1** with benzoyl chloride provided novel organotin(IV) species as a product of oxidative addition when carried out at proper conditions as discussed below.

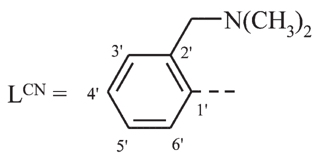


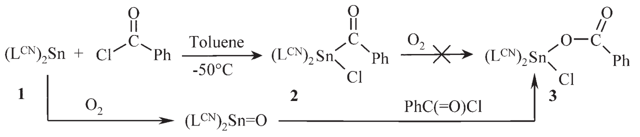
Fig. 2 Schematic drawing of the *C*,*N*-chelating ligand and the numbering of its atoms.

2.2. Reactivity of $(L^{CN})_2Sn$ (1) towards benzoyl chloride

The reaction of doubly *C*,*N*-chelated stannylene **1** with benzoyl chloride, which has been also reported to be a successful one by Lappert, was chosen for the purpose of this work as a parallel for both types of stannylenes comparison, and also due to the facile availability of both reagents. This reaction could be taken as an alternative of conventional acyl stannanes successfully used for the acylation of dienes or allylic esters.[23] Moreover, the desired product of the oxidative addition **2** can be isolated in a moderate yield of 42% (Scheme 2).

Single crystals of **2** (Fig. 3) suitable for X-ray diffraction analysis grew overnight in the NMR tube containing the saturated benzene-d6 solution of **2**. The central tin atom in **2** is five-coordinated and reveals distorted trigonal bipyramidal geometry. According to Bent's rule,[24] both electronegative atoms X (X = N and Cl) occupy axial positions while all three carbon atoms originating from organic ligands lie in the equatorial plane of the trigonal bipyramid. It is clearly seen that only one of the ligands is bidentately bound to the tin atom (the interatomic distance Sn1–N1 being 2.447(2) Å). This connection can be considered as a strong intramolecular N→Sn interaction. The second ligand behaves as a monodentate one. This conclusion is based on the corresponding Sn1–N2 interatomic distance (Sn1–N2 = 3.440(2) Å) found in the single crystal of **2**. The intramolecular N→Sn interaction causes a slight elongation of the Sn–Cl bond to 2.508(3) Å which is in line with the values found for similar *C*,*N*-chelated triorganotin(IV) chlorides.[25] The N1–Sn1–Cl1 interatomic angle being 170.88(5)° is close to the ideal straight angle.

The chemical shift values, integral intensities and multiplicity of each signal in the ^1H NMR spectrum of **2** (recorded in THF-d8) correspond well to the proposed molecular



Scheme 2 Preparation of **2** and **3** from **1**.

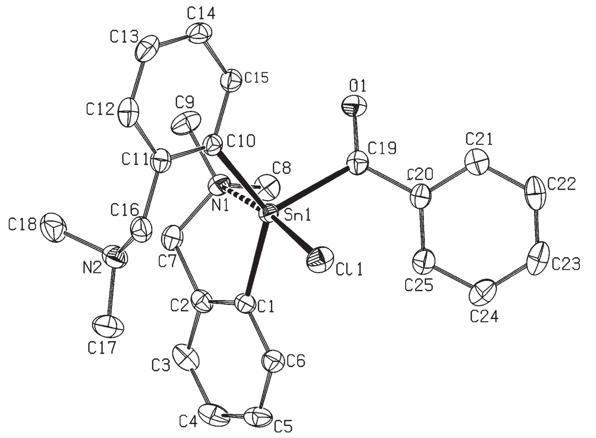


Fig. 3 Molecular structure of **2** (ORTEP presentation, 50% probability level). Hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Sn(1)–N(1) 2.447(2), Sn(1)–N(2) 3.440(2), Sn(1)–Cl(1) 2.5083(6), Sn(1)–C(1) 2.129(2), Sn(1)–C(10) 2.140(2), Sn(1)–C(19) 2.220(3), O(1)–C(19) 1.218(3); C(1)–Sn(1)–C(10) 132.28(9), C(1)–Sn(1)–C(19) 119.36(9), C(10)–Sn(1)–C(19) 106.55(9), C(1)–Sn(1)–N(1) 75.81(8), C(10)–Sn(1)–N(1) 93.35(8), C(19)–Sn(1)–N(1) 89.28(8), C(1)–Sn(1)–Cl(1) 95.30(7), C(10)–Sn(1)–Cl(1) 94.24(7), C(19)–Sn(1)–Cl(1) 93.40(7), N(1)–Sn(1)–Cl(1) 170.88(5).

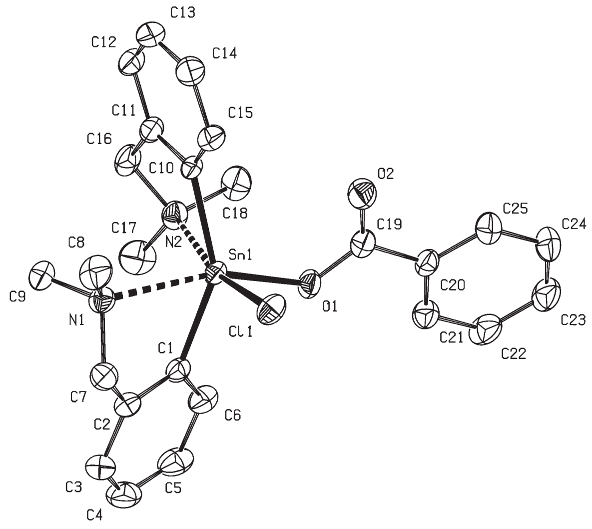


Fig. 4 Molecular structure of **3** (ORTEP presentation, 30% probability level). Hydrogen atoms and solvent molecules are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Sn(1)–N(1) 2.580(3), Sn(1)–N(2) 2.623(3), Sn(1)–O(1) 2.071(3), Sn(1)–O(2) 3.189(3), Sn(1)–Cl(1) 2.4305(10), Sn(1)–C(1) 2.124(4), Sn(1)–C(10) 2.118(4), C(19)–O(1) 1.305(5), C(19)–O(2) 1.219(6), O(1)–Sn(1)–N(1) 162.59(10), Cl(1)–Sn(1)–N2 168.75(8), O(1)–Sn(1)–C(10) 112.53(14), O(1)–Sn(1)–C(1) 92.02(17), C(10)–Sn(1)–C(1) 146.53(18), O(1)–Sn(1)–Cl(1) 90.28(8), C(10)–Sn(1)–Cl(1) 101.25(10), C(1)–Sn(1)–Cl(1) 100.01(9).

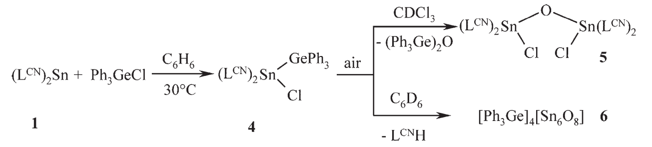
structure. In general, the value of the $^3J(^{119}Sn, ^1H)$ coupling constant of satellites of the doublet of the H(6′) signal in ^1H NMR spectra is a very useful tool for the characterization of all *C*,*N*-chelated organotin(IV) compounds.[26] The observed value of the coupling constant $^3J(^{119}Sn, ^1H)$ being 72.7 Hz in the case of **2** thus clearly matches with the typical values reported for related triorganotin(IV) species.[27] A typical AX spectral pattern of the CH_2N fragments is usually observed for doubly *C*,*N*-chelated organotin(IV) species[25b,c] in ^1H NMR spectra and **2** makes no exception (see the Experimental section). The only broad resonance ($\delta(^{119}Sn) = -319.6$ ppm) observed in the ^{119}Sn NMR spectrum of **2** lies in the range of chemical shift values found for six-coordinate organotin(IV) species in solution.[25b,c] Based on the latter finding we assume that both ligands exhibit a bidentate bonding fashion and thus the vicinity of the central tin atom in solution reveals a distorted octahedral geometry. Moreover, the ^{13}C NMR spectrum of **2** was recorded. The signal of the carbonyl fragment is significantly shifted downfield to 238 ppm. Similar chemical shift values have already been reported for compounds containing the E–C(=O)R (for example E = Al, Mo, W, Pd, Ga, Pb, As, Sb and others) moieties.[28]

Surprisingly, the air-stable diorganotin(IV) benzoate **3** could not be prepared by the oxidation of **2** by bubbling dry dioxygen into the diethyl ether/THF solution of **2**. Nevertheless, the desired organotin(IV) benzoate **3** was synthesized by the alteration of the reaction procedure (Scheme 2) which is based first on the oxidation of **1** by dioxygen and subsequent reaction of the *in situ* prepared $(L^{CN})_2Sn{=}O$[19a] with benzoyl chloride. Since suitable single crystals of **3** were obtained the structure of **3** in the solid state could be thus determined by X-ray crystallography techniques (Fig. 4). The tin atom is six-coordinated with a heavily distorted octahedral geometry having both carbon atoms in mutual *trans* positions. Contrary to **2**, where only one intramolecular N→Sn interaction was identified, in this particular case both ligands are bound bidentately to the tin atom. Nitrogen donor atoms are mutually in *cis* position and the Sn–N interatomic distances (Sn1–N1 = 2.580(3) Å, Sn1–N2 = 2.623(3) Å) reveal medium strength of the N→Sn intramolecular interaction. It is evident from the X-ray diffraction analysis that the benzoate moiety exhibits a monodentate bonding fashion with respect to the tin atom (Sn1–O1 2.071(3) Å and Sn1–O2 3.189(3) Å) which is in accordance with previously published results concerning the structure of doubly *C*,*N*-chelated diorganotin(IV) carboxylates.[29]

The ^1H NMR spectrum of **3** reveals similar spectral pattern as observed for **2** (see the Experimental section). The ^{119}Sn NMR spectrum further supports the presumable formation of **3** because the observed chemical shift value ($\delta(^{119}Sn) = -372.5$ ppm) is shifted by *ca.* 50 ppm upfield when compared to **2** (($\delta(^{119}Sn) = -319.6$ ppm)). Another proof of the formation of **3** is based on the resonance of the OC=O moiety found at 161.9 ppm in the ^{13}C NMR spectrum which is in the range typical of related organotin(IV) carboxylates.[29]

2.3. Reactivity of $(L^{CN})_2Sn$ (1) towards triphenylgermyl chloride

Reaction of **1** with Ph_3GeCl exclusively produced the triphenylgermyl-substituted doubly *C*,*N*-chelated diorganotin(IV) chloride **4** (Scheme 3) in a reasonable yield. Since we isolated no suitable single crystals of **4** this complex was characterized by multinuclear NMR spectroscopy only.



Scheme 3 Preparation of **4** and its reactivity towards air.

The ^1H NMR spectrum of **4** recorded in THF-d8 displays all resonances at predictable positions which were assigned to both L^{CN} and $-GePh_3$ substituents. The signal of the H(6′) protons is somewhat broadened but still showing a readable $^3J(^{119}Sn, ^1H)$ coupling constant of *ca.* 65 Hz which is close to the typical values observed for related *C*,*N*-chelated triorganotin(IV) species. From this point of view one could say that the $-GePh_3$ substituent affects the $^3J(^{119}Sn, ^1H)$ value in a similar way as common organic substituents do. Unequivalent CH_2N protons resonate as doublets in the AX pattern at 3.78 and 2.94 ppm, respectively. The ^{119}Sn NMR chemical shift value ($\delta(^{119}Sn) = -167.7$ ppm) of the resonance found for **4** indicates that the central tin atom is only five-coordinate in solution, reflecting thus the presence of one monodentately and one bidentately bound *C*,*N*-ligands. A very close ^{119}Sn NMR chemical shift value ($\delta(^{119}Sn) = -163.4$ ppm) was observed when the same ^{119}Sn NMR spectrum was recorded in benzene-d6 as a non-coordinating solvent. Based on these measurements we assume no coordination of the THF-d8 solvent to the tin center in **4**.

When chloroform solution of **4** is exposed to air for a long period of time the Sn–Ge bond cleaves, forming thus novel dinuclear doubly *C*,*N*-chelated organotin(IV) oxochloride **5** and a hexaphenyldigermoxane which was confirmed by both multinuclear NMR spectroscopy and X-ray diffraction analysis (Scheme 3). Single crystals of **5** were isolated within several days from the diethyl ether/THF solution stored in a freezing box (Fig. 5). The main feature of **5** is that the oxygen atom bridges two tin-containing units (with interatomic Sn–O distances being 1.961(2) and 1.963(2) Å, respectively) each bearing two *C*,*N*-chelating ligands and a terminal chlorine. A detailed investigation revealed that only one of two ligands of each tin-containing unit exhibits intramolecular N→Sn interaction (Sn1–N1 = 2.560(3) Å and Sn2–N3 = 2.607(3) Å) of a medium strength while the second one acts only as a monodentate ligand since the interatomic Sn–N distances (Sn1–N2 = 2.804(3) Å and Sn2–N4 = 2.910(3) Å) are too long to speculate about coordination. From another point of view, one could say that crystal structure of **5** is made up of two identical tin-containing trigonal bipyramidal units which share one common vertex represented by the O1 atom.

Due to the limited solubility of **5** in common organic solvents only ^1H and ^{119}Sn NMR spectra of poor quality were recorded. Nevertheless, the ^1H NMR spectrum of **5** measured in $CDCl_3$ exhibited one set of broad signals attributable to the L^{CN} ligands. A detailed interpretation further revealed the non-equivalency of the CH_2N moieties which is represented by two very broad resonances at 3.81 and 3.42 ppm, respectively, each with an integral intensity of four. The resonance observed in the ^{119}Sn NMR spectrum ($\delta(^{119}Sn) = -278.8$ ppm) can be thus attributed to **5** since this chemical shift value is close to that previously reported for doubly *C*,*N*-chelated organotin(IV) halides.[25b,c]

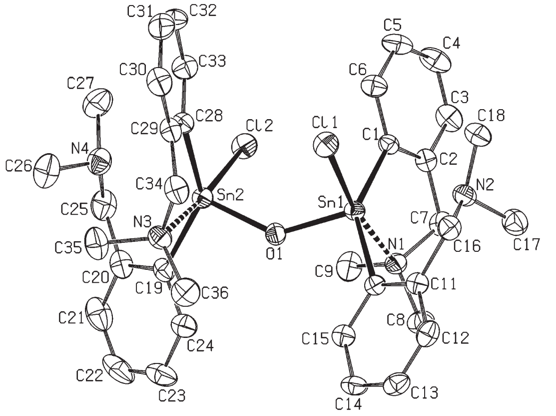


Fig. 5 Molecular structure of **5** (ORTEP presentation, 40% probability level). Hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Sn(1)–Cl(1) 2.4828(9), Sn(1)–O(1) 1.961(2), Sn(1)–C(1) 2.123(3), Sn(1)–C(10) 2.142(3), Sn(2)–Cl(2) 2.4774(9), Sn(2)–O(1) 1.963(2), Sn(2)–C(19) 2.132(3), Sn(2)–C(28) 2.119(3), Sn(1)–N(1) 2.560(3), Sn(1)–N(2) 2.804(3), Sn(2)–N(3) 2.607(3), Sn(2)–N(4) 2.910(3), O(1)–Sn(1)–C(1) 112.17(11), O(1)–Sn(1)–C(10) 97.78(11), C(1)–Sn(1)–C(10) 145.40(13), O(1)–Sn(1)–Cl(1) 96.99(7), C(1)–Sn(1)–Cl(1) 96.07(9), C(10)–Sn(1)–Cl(1) 97.10(8), O(1)–Sn(2)–C(28) 110.64(11), O(1)–Sn(2)–C(19) 100.00(11), C(28)–Sn(2)–C(19) 143.02(13), O(1)–Sn(2)–Cl(2) 96.79(7), C(28)–Sn(2)–Cl(2) 97.29(9), C(19)–Sn(2)–Cl(2) 99.18(9), Sn(1)–O(1)–Sn(2) 138.96(15), N(1)–Sn(1)–Cl(1) 169.76(6), N(3)–Sn(2)–Cl(2) 171.43(7).

On the other hand, surprisingly, if **4** is exposed to air in benzene for several days it undergoes a hydrolysis giving thus a unique germanium-substituted oxo-tin cluster and free ligand as a by-product (Scheme 3). Unequivocal proof of structure **6** was provided by crystallographic analysis of single crystals (Fig. 6). The structure of the $[Sn_6O_8]$ core (Fig. 7) is identical with that prepared by the thermally-driven self-condensation of the bis[bis(trimethylsilanolato)tin] reaction differing only in the nature of substituents ($-GePh_3$ instead of $-SiMe_3$).[30] The Sn–O (2.08 Å on average) and Sn–O(Ge) (varying from 2.32 to 2.47 Å) interatomic distances are somewhat longer than the corresponding distances found for similar clusters bearing trimethylsilyl-substituents.[30] Owing to the presence of four Ph_3Ge moieties, **6** is only sparingly soluble in common organic solvents which was a limitation for us to study the structure of **6** in solution by multinuclear NMR spectroscopy. Only the ^1H NMR spectrum of **6** was recorded revealing resonances of Ph substituents at predictable positions.

2.4. Reactivity of $(L^{CN})_2Sn$ (1) towards triphenylsilyl and trimethylsilyl chloride

Oxidative addition of Ph_3SiCl to **1** gave triphenylsilyl substituted diorganotin(IV) chloride **7** in a reasonable yield as expected (Scheme 4). Unfortunately, we were not able to isolate single crystals of sufficient quality for the X-ray diffraction analysis and thus **7** was fully characterized by multinuclear

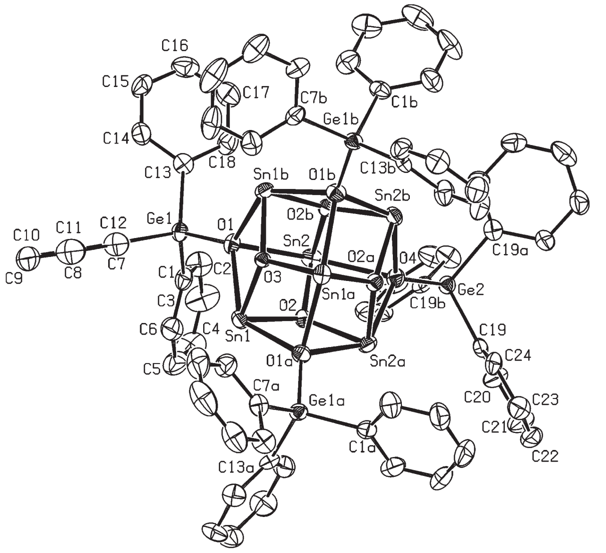


Fig. 6 Molecular structure of **6** (ORTEP presentation, 50% probability level). Hydrogen atoms are omitted for clarity. Selected interatomic distances and angles are given in Fig. 7 caption.

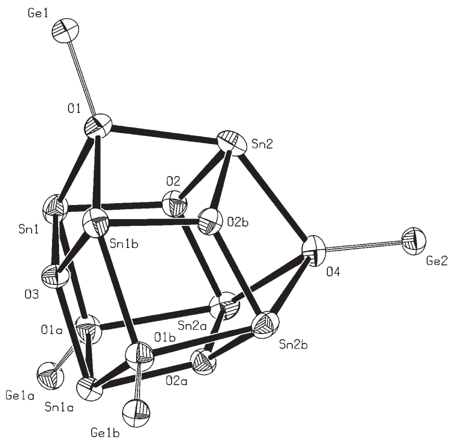
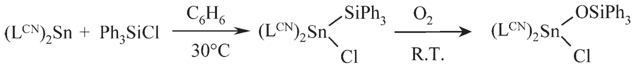


Fig. 7 Detailed ORTEP presentation (50% probability level) of the oxo-tin core of **6**. All hydrogen and carbon atoms were omitted for clarity. Selected interatomic distances [Å] and angles [°]: Sn(1)–O(1) 2.469(4), Sn(1)–O(2) 2.091(4), Sn(1)–O(3) 2.0852(12), Sn(1)–O(1a) 2.324(4), Sn(2)–O(1) 2.421(4), Sn(2)–O(2) 2.062(4), Sn(2)–O(2b) 2.079(3), Sn(2)–O(4) 2.420(3), Ge(1)–O(1) 1.787(3), Ge(2)–O(4) 1.792(5), Ge(1a)–O(1a) 1.787(4), Ge(1b)–O(1b) 1.787(3), Sn(1)–O(1)–Sn(2) 92.88(12), Sn(1)–O(3)–Sn(1a) 115.50(10), Sn(1)–O(3)–Sn(1b) 115.50(10), Sn(1)–O(1a)–Sn(1a) 94.72(14), Sn(1)–O(3)–Sn(2a) 94.74(10), Sn(1)–O(2)–Sn(2) 117.18(17), Sn(1)–O(2)–Sn(2a) 113.75(16), Sn(1)–O(2)–Sn(2) 117.18(17), O(1)–Sn(1)–O(1a) 135.31(12), O(1)–Sn(1)–O(2) 74.14(13), O(1)–Sn(1)–O(3) 73.19(8), O(1)–Sn(1)–O(1a) 135.31(12), O(1)–Sn(1b)–O(1b) 135.31(13), O(1)–Sn(1b)–O(2b) 135.31(13), O(1)–Sn(1b)–O(3) 76.39(10).



$$(L^{CN})_2Sn + Ph_3SiCl \xrightarrow[30°C]{C_6H_6} (L^{CN})_2Sn(SiPh_3)Cl \xrightarrow[R.T.]{O_2} (L^{CN})_2Sn(OSiPh_3)Cl$$

1 **7** **8**

Scheme 4 Preparation of **7** and its reactivity towards dioxygen.

NMR spectroscopy in solution only. The ^1H NMR spectrum of **7** is in accordance with its proposed structure exhibiting very broad resonances of both non-equivalent CH_2N ($\delta(^1H)$ = 4.25 and 2.80 ppm, respectively, in C_6D_6) and NMe_2 ($\delta(^1H)$ = 1.80 ppm in C_6D_6) moieties. The resonance of the H(6′) is somewhat broadened as well. The ^{13}C NMR spectrum of **7** displays somewhat broadened resonances at predictable positions. The only signal observed in the ^{119}Sn NMR spectrum of **7** was found at 210.0 ppm (measured on two different spectrometers) which is far away from the chemical shift value found for **4** ($\delta(^{119}Sn)$ = −167.7 ppm). This discrepancy has not been rationally explained yet. To further support the suggested presence of the silicon-tin bond we tried to read the $^1J(^{29}Si, {}^{119}Sn)$ value in the ^{119}Sn NMR spectrum but no silicon satellites were observed despite the long time of acquisition. The explanation for this could be that the $^1J(^{29}Si, {}^{119}Sn)$ usually exhibits a value of about 100 to 500 Hz (reported earlier in the literature for compounds containing the Si–Sn bond(s))[31] and thus it is overlapped by the relatively broad resonance of the tin atom. On the other hand, a similar chemical shift value ($\delta(^{119}Sn)$ = 192 ppm) was observed for tris(trimethylsilyl)silyl substituted tin chloride.[32] Downfield shift of the tin resonance was reported for the 1,2-dichloro-1,1,2,2-tetrakis(di-*tert*-butylmethylsilyl)distannane ($\delta(^{119}Sn)$ = 59 ppm), too.[33] To the best of our knowledge no more structurally relevant compounds have been studied by ^{119}Sn NMR spectroscopy and thus a more detailed comparison with an observed chemical shift value could not be made.

Amazingly, the analogous reaction of **1** with Me_3SiCl did not provide the target product of oxidative addition and only pure unreacted **1** was recovered from the reaction mixture. The possible explanation is that volatile Me_3SiCl slowly evaporates during the course of the reaction and thus becomes absent in the solution.

In contrast to the unsuccessful oxidation of **2**, the reaction of **7** with oxygen gave presumably novel doubly *C*,*N*-chelated diorganotin(IV) oxochloride **8** (Scheme 4). In other words, the oxygen atom inserts into the original Sn–Si bond to form **8**. This species was structurally characterized by both multinuclear NMR spectroscopy and X-ray diffraction techniques (Fig. 8). In general, the vicinity of the tin atom in doubly *C*,*N*-chelated diorganotin(IV) complexes usually exhibits a distorted octahedral geometry with *C*,*C*-transoid arrangement and **8** makes no exception. Carbon atoms of the *C*,*N*-chelating ligands are mutually in *trans* positions as well as the N2 and O1 atoms are. The intramolecular N1→Sn1 interaction (Sn(1)–N(1) = 2.582(6) Å) of medium strength causes the elongation of the Sn–Cl bond to 2.4345(16) Å as in the case of **2** or **3**. The second N→Sn intramolecular interaction is significantly weaker (Sn(1)–N(2) = 2.714(3) Å) but still influences the vicinity of the central tin atom.

The structure of **8** in solution was investigated with the help of multinuclear NMR spectroscopy, too. The ^1H NMR spectrum of **8** recorded in benzene-d6 exhibits all expected signals of both L^{CN} ligands and Ph substituents. The resonances of the H(6′) (with $^3J(^{119}Sn, {}^1H)$ being 94 Hz which is a

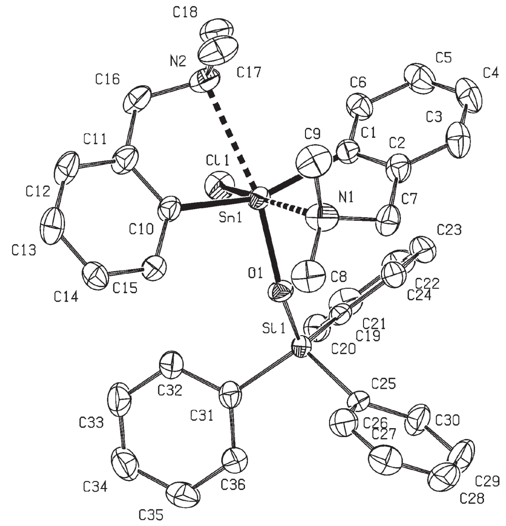


Fig. 8 Molecular structure of **8** (ORTEP presentation, 50% probability level). Hydrogen atoms are omitted for charity. Selected interatomic distances [Å] and angles [°]: Sn(1)–N(1) 2.582(6), Sn(1)–N(2) 2.714(3), Sn(1)–Cl(1) 2.4345(16), Sn(1)–N(O1) 1.999(3), Sn(1)–C(1) 2.112(5), Sn(1)–C(10) 2.127(4), Si(1)–O(1) 1.610(3), N(1)–Sn(1)–Cl(1) 168.45(12), O(1)–Sn(1)–N(2) 168.35(13), C(1)–Sn(1)–C(10) 151.11(17), Sn(1)–O(1)–Si(1) 146.39(19).

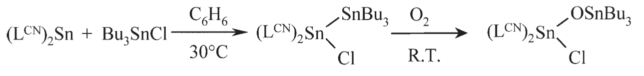
typical value for *C*,*N*-chelated diorganotin(IV) species[25,26]) and CH_2N protons (3.61 and 2.83 ppm, respectively, AX pattern) are narrow when compared to the ^1H NMR spectrum of the precursor **7**. Since the only resonance observed in the ^{119}Sn NMR spectrum is found at −355.5 ppm (in benzene-d6) it is evident that the central tin atom is six-coordinated with a distorted octahedral geometry which is in line with the solid state study. Both ligands must be thus bound bidentately to the tin atom. In addition, such a chemical shift value is close to that observed for related diorganotin(IV) species bearing two highly negative substituents.[25,26]

2.5. Reactivity of $(L^{CN})_2Sn$ (1) towards tributyltin chloride

The reaction of **1** with $(n\text{-}Bu)_3SnCl$ provided exclusively a distannane of formula $(L^{CN})_2Sn(Cl)SnBu_3$ (**9**) as a product of a Sn–Sn coupling reaction (Scheme 5). In other words, this unprecedented reaction thus led to the formation of a dinuclear complex containing the Sn–Sn single bond. **9** can be isolated as an oily product in a nearly quantitative yield and can be gently oxidized by oxygen to give distannoxane **10** similarly as described for the oxidation of **7**.

Due to the oily nature of **9** and **10** only multinuclear NMR structural characterization was employed. The ^1H NMR spectrum of **9** exhibits one set of signals attributable to L^{CN} ligands and *n*-butyl substituents. The resonance of the H(6′) proton ($\delta(^1H)$ = 8.21 ppm) is extremely broad which makes it impossible to read the $^3J(^{119}Sn, {}^1H)$ coupling constant. The non-equivalence of the CH_2N moieties is demonstrated by the presence of the AX pattern ($\delta(^1H)$ = 3.73 and 3.10 ppm, respectively) in the ^1H NMR spectrum of **9**. Two sets of signals at predictable positions were observed in the ^{13}C NMR spectrum of **9** when recorded at ambient temperature (see the Experimental section). The ^{119}Sn NMR spectrum displays two signals which were assigned to both the $(n\text{-}Bu)_3Sn$ moiety ($\delta(^{119}Sn)$ = −46.3 ppm) and the $(L^{CN})_2SnCl$ fragment (extremely broad, $\delta(^{119}Sn)$ = −133.8 ppm). The direct and unambiguous proof of the formation of the Sn–Sn bond is based on the observation of the $^1J(^{119}Sn, {}^{117/119}Sn)$ coupling constant being 4532 Hz of the resonance at −46.3 ppm. Unfortunately, the extremely broad resonance of the $(L^{CN})_2SnCl$ fragment spoiled the reading of the $^1J(^{119}Sn, {}^{117/119}Sn)$ coupling constant which should have the same value. These extremely high values of the Sn–Sn coupling constants are characteristic of the single Sn–Sn bonds.[34] According to the observed chemical shift values we assume that the tin atom in the $(n\text{-}Bu)_3Sn$ moiety is four-coordinate (as in the case of related $Bu_3SnSnBu_3$ which resonates at −80 ppm in the ^{119}Sn NMR spectrum[34a,b]). On the other hand, the tin atom in the $(L^{CN})_2SnCl$ fragment is evidently five-coordinate bearing thus one monodentately and one bidentately bound L^{CN} ligands. The direct proof of this assignment is the ^1H-^{119}Sn HMBC NMR experiment where appropriate cross-peaks were found.

The facile oxidation of **9** to **10** was carried out directly in the NMR tube containing the benzene-d6 solution of **9**. The oxidation yielded exclusively the distannoxane **10** and hexabutyldistannoxane[34b,c] as a minor product (less than 5% according to ^1H and ^{119}Sn NMR spectroscopy). Contrary to the situation described for **9** we found two sets of signals assigned to the non-equivalently bound L^{CN} ligands in the ^1H NMR spectrum of **10**. Therefore, two doublets of the H(6′) protons are found with two different ($^3J(^{119}Sn, {}^1H)$ coupling constants – one of *ca.* 114 Hz and the second being *ca.* 82 Hz. These values can be attributed to the diorganotin(IV) species as described earlier in the literature.[26b] In addition, four different doublets (3.85, 3.72, 2.96, and 2.87 ppm, respectively, all with a coupling constant of *ca.* 13 Hz), each with the integral intensity of one, are displayed for the non-equivalent protons of the CH_2N moieties. There are two sets of broad resonances assigned to the two L^{CN} ligands and one set attributed to *n*-butyl substituents in the ^{13}C NMR spectrum of **10**. This is in good agreement with the observed ^1H NMR spectral pattern. The insertion of the oxygen atom to the original Sn–Sn bond causes the downfield shift of the resonance of the Bu_3Sn moiety to 81.6 ppm. A low intense resonance attributed to the hexabutyldistannoxane is observed as well ($\delta(^{119}Sn)$ = 88.8 ppm[34b,c]) in the same region of the ^{119}Sn NMR spectrum. This species was formed as a minor product during the oxidation of **9**. On the other hand, the original resonance of the $(L^{CN})_2SnCl$ fragment observed at −133.8 ppm in the ^{119}Sn NMR spectrum of **9** moves up to the −254.3 ppm in the case of



$$(L^{CN})_2Sn + Bu_3SnCl \xrightarrow[30°C]{C_6H_6} (L^{CN})_2Sn(SnBu_3)(Cl) \xrightarrow[R.T.]{O_2} (L^{CN})_2Sn(OSnBu_3)(Cl)$$

1 **9** **10**

Scheme 5 Synthesis of a distannane **9** and its oxidation by dioxygen to **10**.

10. Based on these data we unequivocally assume the hexacoordination of this tin atom bearing two bidentately bound L^{CN} ligands. Moreover, this chemical shift value is comparable with those observed for $(L^{CN})_2SnCl_2$[25b] or **5** described above. Another direct proof of the oxygen insertion into the original Sn–Sn bond is represented by the $^2J(^{119}Sn, ^{117/119}Sn)$ coupling constants both being 435 Hz which is in line with the corresponding values reported for structurally similar compounds.[19a,b,d] According to the Lockhart equation[19e] the magnitude of Sn–O–Sn angle could be calculated to be 137.4°.

3. Conclusion

The unprecedented reactivity of the *C*,*N*-chelated stannylene **1** towards species containing the E–Cl bond(s) (E = C, Si, Ge, and Sn) has been exposed. In general, the corresponding products of oxidative additions were achieved. Unique results described in this paper thus open an up-to-date unexplored field of chemistry of stannylenes. Further reactivity studies of **1** towards other reagents containing group 14 elements, the triorganotin(IV) halides in particular, are under thorough investigation now. The mentioned Sn–Sn coupling reaction shall be a very powerful tool for accessing novel organotin(IV) compounds. Similar reactivity studies described here for **1** will follow using other available stannylenes (*e.g.* the Lappert stannylenes). Moreover, we shall pay attention to the possible use of other acyl chlorides or chloroformates instead of benzoyl chloride within the reaction of **1**.

4. Experimental

4.1. General methods

4.1.1. NMR spectroscopy. NMR spectra were recorded from solutions in $CDCl_3$, C_6D_6 and THF-d_8 on a Bruker Avance 500 spectrometer (equipped with a *z*-gradient 5 mm probe) at frequencies 500.13 MHz for ^1H, 125.76 MHz for $^{13}C\{^1H\}$, and 186.50 MHz for $^{119}Sn\{^1H\}$ at 295 K. Solutions were obtained by dissolving approximately 40 mg of each compound in 0.6 mL of a deuterated solvent. The values of ^1H chemical shifts were calibrated to residual signals of chloroform ($\delta(^1H)$ = 7.27 ppm), benzene ($\delta(^1H)$ = 7.16 ppm) or THF ($\delta(^1H)$ = 3.57 ppm). The values of $^{13}C\{^1H\}$ chemical shifts were calibrated to signals of C_6D_6 ($\delta(^{13}C)$ = 128.4 ppm) and THF-d_8 ($\delta(^{13}C)$ = 67.4 ppm); due to insufficient solubility of **4–6**, no ^{13}C NMR spectra for these compounds are reported. The $^{119}Sn\{^1H\}$ chemical shift values are referred to external neat tetramethylstannane ($\delta(^{119}Sn)$ = 0.0 ppm). Positive chemical shift values denote shifts to the higher frequencies relative to the standards. $^{119}Sn\{^1H\}$ NMR spectra were measured using the inverse gated-decoupling mode.

4.1.2. Elemental analyses. The compositional analyses were determined on the automatic analyzer EA 1108 by FISONS Instruments.

4.1.3. Crystallography. The X-ray data (Table 1) for colourless crystals of all compounds were obtained at 150 K using an Oxford Cryostream low-temperature device on a Nonius KappaCCD diffractometer with MoK_α radiation (λ = 0.71073 Å), a graphite monochromator, and the ϕ and χ scan modes. Data

Table 1 Selected crystallographic data for compounds **2**, **3**, **5**, **6** and **8**

Compound	**2**	**3**·3(C_6H_6)	**5**	**6**·2(C_6H_6)	**8**
Empirical formula	$C_{25}H_{29}ClN_2OSn$	$C_{43}H_{47}ClN_2O_2Sn$	$C_{36}H_{48}Cl_2N_4OSn_2$	$C_{84}H_{72}Ge_4O_8Sn_6$	$C_{36}H_{39}ClN_2OSiSn$
Crystal system	Monoclinic	Monoclinic	Triclinic	Hexagonal	Triclinic
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P6_3$	$P1$
a (Å)	12.7460(8)	12.6721(5)	9.5180(12)	16.0010	9.1550(6)
b (Å)	9.9541(8)	21.1300(18)	9.5810(5)	16.0010	9.4191(5)
c (Å)	18.3250(14)	16.1630(9)	23.3921(12)	17.4671(15)	11.4639(9)
α (°)	90	90	78.972(4)	90	66.266(5)
β (°)	94.748(5)	127.645(4)	81.579(6)	90	79.640(5)
γ (°)	90	90	60.585(7)	120	63.335(4)
Z	4	4	2	2	1
V (Å^3)	2317.0(3)	3426.8(4)	1820.4(3)	3873.0(4)	808.70(9)
D_c (g cm^{-3})	1.513	1.508	1.571	1.897	1.433
Crystal size (mm)	0.24 × 0.20 × 0.10	0.25 × 0.23 × 0.19	0.27 × 0.24 × 0.15	0.29 × 0.22 × 0.12	0.49 × 0.33 × 0.09
Crystal shape	Block	Block	Block	Plate	Plate
μ (mm^{-1})	1.237	0.866	1.552	3.483	0.941
F(000)	1072	1608	868	2136	358
h; *k*; *l* Range	−16, 16; −11, 12; −20, 23	−16, 16; −26, 27; −19, 20	−12, 12; −12, 12; −30, 30	−20, 17; −18, 17; −22, 22	−11, 11; −12, 11; −14, 14
θ Range (°)	2.78–27.50	1.86–27.50	1.78–27.50	2.80–27.50	1.94–27.49
Reflections measured	18 190	35 304	34 529	23 887	15 546
Independent (R_{int})[a]	5196	7488	8281	5856	6923
Observed [$I > 2\sigma(I)$]	4335	5186	5607	5053	6852
Parameters refined	271	388	406	271	379
Max/min τ (e Å^{-3})	0.668/−0.562	0.428/−0.763	0.520/−0.599	0.472/−0.786	0.684/−0.713
GOF[b]	1.079	1.159	1.046	1.063	1.055
R^c/wR^c	0.0289/0.0544	0.0413/0.0775	0.0393/0.0535	0.0341/0.0643	0.0329/0.0802

[a] $R_{int} = \Sigma|F_o^2 - F_{o,mean}^2|/\Sigma F_o^2$, [b] $S = [\Sigma(w(F_o^2 - F_c^2)^2)/(N_{diffrs} - N_{params})]^{1/2}$, [c] Weighting scheme: $w = [\sigma^2(F_o^2) + (w_1P)^2 + w_2P]^{-1}$, where $P = [\max(F_o^2) + 2F_c^2]$, $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR(F^2) = [\Sigma(w(F_o^2 - F_c^2)^2)/(\Sigma w(F_o^2)^2)]^{1/2}$.

reductions were performed with DENZO-SMN.[35] The absorption was corrected by integration methods.[36] Structures were solved by direct methods (Sir92)[37] and refined by full matrix least-square based on F^2 (SHELXL97).[38] Hydrogen atoms were mostly localized on a difference Fourier map; however, to ensure uniformity of the treatment of the crystal, all hydrogen atoms were recalculated into idealized positions (riding model) and assigned temperature factors $H_{iso}(H) = 1.2\ U_{eq}$-(pivot atom) or 1.5 U_{eq} for the methyl moiety with C–H = 0.96, 0.97, and 0.93 Å for methyl, methylene and hydrogen atoms in aromatic rings, respectively. A disordered non-coordinated solvent (benzene) was found in the structure of **6**. Attempts were made to model this disorder or split into two positions, but were unsuccessful. PLATON/SQUEZZE[39] was used to correct the data for the presence of a disordered solvent. A potential solvent volume of 528 Å^3 was found. 196 electrons per unit cell worth of scattering were located in the voids. The calculated stoichiometry of the solvent was calculated to be four additional molecules of benzene per unit cell.

4.2. Synthesis

4.2.1. General remarks. All solvents and starting materials such as $SnCl_2$, *n*-BuLi, benzoyl chloride, dimethylbenzylamine *etc.* were purchased from commercial sources (Sigma-Aldrich) and used without further purification. $(L^{CN})_2Sn$ (**1**) was synthesized according to the procedure described in the literature.[18] Solvents were distilled from a K/Na alloy and stored over a potassium mirror under an argon atmosphere or dried and degassed using a commercial drying collumn apparatus (Innovative Technology Inc., USA). Compounds **2**, **4**, **7** and **9** should be stored in a fridge or better in a freezing box in order to avoid the slow decomposition of samples which was observed even in the cases of *vacuo* sealed samples at room temperature.

4.2.2. Preparation of $(L^{CN})_2Sn(Cl)C({=}O)Ph$ (2). **1** (0.505 g, 1.30 mmol) was dissolved in toluene (10 mL) and a solution of benzoyl chloride (99%, 153 μL; 1.30 mmol) in toluene (5 mL) was added drop-wise at −50 °C. The yellow reaction mixture was then stirred for 10 minutes at room temperature. Within several minutes a yellow precipitate of the desired product sedimented. The supernatant yellow solution was removed and the yellow precipitate of **2** was dried *in vacuo*. Isolated yield was 0.288 g (42%). Single crystals of **2** suitable for the X-ray diffraction analysis grew overnight in the NMR tube containing the saturated benzene-d6 solution of **2**. M.p. 160–161 °C. ^{1}H NMR (THF-d8, 295 K, ppm): 8.34 (d, 2H, H(6′), $^3J(^1H(5'), ^1H(6')) = 6.4$ Hz, $^3J(^{119}Sn, ^1H) = 72.7$ Hz); 7.98 (d, 2H, H(*o*-Ph), $^3J(^1H(m\text{-}Ph), ^1H(o\text{-}Ph)) = 8.4$ Hz); 7.47 (m, 2H, H(5′)); 7.40–7.30 (m, 5H, H(4′ and *m*, *p*-Ph)); 7.18 (d, 2H, H(3′), $^3J(^1H(4'), ^1H(3')) = 7.2$ Hz); 3.86 (d, 2H, CH_2N, $^2J(^1H(A), ^1H(X)) \approx 13$ Hz); 3.23 (br, 2H, CH_2N); 1.92 (br, 12H, NMe_2). ^{13}C NMR (THF-d8, 295 K, ppm): 238.0 (br, C=O); 144.7 (C(2′), $^2J(^{119}Sn, ^{13}C)$ was not observed); 143.9 (C(1′), $^1J(^{119}Sn, ^{13}C)$ was not observed); 140.0 (i-Ph); 138.0 (br, C(6′)); 133.8 (C^{Ar}); 130.0 (C^{Ar}); 129.8 (C^{Ar}); 129.4 (C^{Ar}); 128.0 (C^{Ar}); 127.1 (C^{Ar}); 126.9 (C^{Ar}); 125.0 (C^{Ar}); 65.9 (br, CH_2N); 46.1 (br, $N(CH_3)_2$). ^{119}Sn NMR (THF-d8, 295 K, ppm): −319.6 (br). Elemental analysis (%): found: C 57.1; H 5.8; N 5.1. Calcd (%) for $C_{25}H_{29}ClN_2OSn$ (527.67): C 56.91; H 5.54; N 5.31.

4.2.3. Preparation of $(L^{CN})_2Sn(Cl)(OC({=}O)Ph)$ (3). **1** (0.104 g, 0.27 mmol) was dissolved in an Et_2O–THF mixture (10/10 mL) and dry dioxygen was bubbled through the solution for 30 minutes. Afterwards the benzoyl chloride (99%, 32 μL, 0.27 mmol) was added drop-wise and the reaction mixture was stirred overnight at 30 °C. The clear pale yellow reaction mixture was then concentrated. Crystals of pure **3** grew upon storing the saturated solution at −30 °C for several days. Overall isolated yield was 0.072 g (49%). **3** can be handled in the air. Single crystals of **3** grew in the NMR tube containing the C_6D_6 solution of **3**. M.p. 210–211 °C. ^{1}H NMR (C_6D_6, 295 K, ppm): 8.61 (br, 2H, H(6′), $^3J(^{119}Sn, ^1H)$ could not be read); 7.99 (d, 2H, H(*o*-Ph), $^3J(^1H(m\text{-}Ph), ^1H(o\text{-}Ph)) = 8.5$ Hz); 7.30–7.00 (m, 7H, H(4′, 5′ and *m*, *p*-Ph)); 6.90 (m, 2H, H(3′)); 3.66 (br d, 2H, CH_2N, $^2J(^1H(A), ^1H(X)) \approx 13$ Hz); 2.99 (br, 2H, CH_2N); 1.82 (br, 12H, NMe_2). ^{13}C NMR (C_6D_6, 295 K, ppm): 161.9 (OC=O); 143.6 (C(2′), $^2J(^{119}Sn, ^{13}C)$ was not observed); 136.2 (br, C(1′), $^1J(^{119}Sn, ^{13}C)$ could not be read); 135.4 (C(6′)); 134.3 (C^{Ar}); 130.2 (C^{Ar}); 129.7 (C^{Ar}); 128.8 (C^{Ar}); 128.0 (C^{Ar}); 127.4 (C^{Ar}); 126.9 (C^{Ar}); 68.0 (anisochronous CH_2N); 63.5 (anisochronous CH_2N); 46.1 (br, $N(CH_3)_2$); resonance of the i-Ph was not observed. ^{119}Sn NMR (C_6D_6, 295 K, ppm): −372.5. Elemental analysis (%): found: C 55.5; H 5.7; N 5.0. Calcd (%) for $C_{25}H_{29}ClN_2O_2Sn$ (543.67): C 55.23; H 5.38; N 5.15.

4.2.4. Preparation of $(L^{CN})_2Sn(Cl)GePh_3$ (4). **1** (0.379 g, 0.98 mmol) was dissolved in benzene (10 mL) and a benzene solution of Ph_3GeCl (99%, 0.336 g, 0.98 mmol) was added in one portion. The reaction mixture was tempered to 30 °C and stirred overnight. Afterwards the volatiles were removed *in vacuo* giving crude **4** which was washed with pentane (2 × 5 mL). Off-white crystalline **4** was then dried *in vacuo* and crystallized from toluene. Isolated yield was 0.513 g (72%). M.p. 170–173 °C. ^{1}H NMR (THF-d8, 295 K, ppm): 8.04 (br, 2H, H(6′), $^3J(^{119}Sn, ^1H) \approx 65$ Hz); 7.64 (m, 6H, H(*o*-Ph)); 7.53 (m, 2H, H(5′)); 7.24 (m, 2H, H(4′)); 7.18–7.08 (m, 11H, H(3′ and *m*, *p*-Ph)); 3.78 (br d, 2H, CH_2N, $^2J(^1H(A), ^1H(X)) \approx 13$ Hz); 2.94 (d, 2H, CH_2N, $^2J(^1H(A), ^1H(X)) \approx 13$ Hz); 1.55 (s, 12H, NMe_2). ^{119}Sn NMR (THF-d8, 295 K, ppm): −167.7. ^{119}Sn NMR (C_6D_6, 295 K, ppm): −163.4. Elemental analysis (%): found: C 59.8; H 5.7; N 3.7. Calcd (%) for $C_{36}H_{39}ClGeN_2Sn$ (726.46): C 59.52; H 5.41; N 3.86.

4.2.5. Preparation of $[(L^{CN})_2SnCl]_2O$ (5). A stirred chloroform solution of **4** was exposed to moist air for one day giving dinuclear complex **5** which was isolated by fractional crystallization from CH_2Cl_2/hexane. M.p. 250–251 °C. ^{1}H NMR ($CDCl_3$, 295 K, ppm): 8.14 (br, 4H, H(6′), $^3J(^{119}Sn, ^1H)$ could not be read); 7.36 (m, 8H, H(5′ and 4′)); 7.14 (d, 4H, H(3′), $^3J(^1H(4'), ^1H(3')) = 7.7$ Hz)); 3.81 (very broad, 4H, CH_2N); 3.42 (very broad, 4H, CH_2N); 2.09 (very broad, 24H, NMe_2). ^{119}Sn NMR ($CDCl_3$, 295 K, ppm): −278.8. Elemental analysis (%): found: C 50.5; H 5.9; N 6.3. Calcd (%) for $C_{36}H_{48}Cl_2N_4OSn_2$ (861.10): C 50.22; H 5.62; N 6.51.

4.2.6. Preparation of $[Ph_3Ge]_4[Sn_6O_8]$ (6). A stirred benzene solution of **4** was exposed to moist air for two days giving a unique oxo-tin cluster species **6** which precipitated as the most insoluble product. Single crystals of **6** were obtained from the benzene solution *via* slow evaporation of benzene at ambient temperature. M.p. 176 °C. ^{1}H NMR (C_6D_6, 295 K, ppm): 7.85 (m, 24H, H(*o*-Ph)); 7.12–7.02 (m, 36H, H(*m*, *p*-Ph)). Elemental analysis (%): found: C 42.3; H 3.1. Calcd (%) for $C_{72}H_{60}Ge_4O_8Sn_6$ (2055.76): C 42.07; H 2.94.

4.2.7. Preparation of $(L^{CN})_2Sn(Cl)SiPh_3$ (7). Synthesis of **7** was carried out similarly as for **4** starting from **1** (0.441 g, 1.14 mmol) and Ph_3SiCl (99%, 0.339 g, 1.14 mmol). Isolated yield 0.552 g (71%). ^{1}H NMR (C_6D_6, 295 K, ppm): 7.87 (br, 2H, H(6′), $^{3}J(^{119}Sn, ^{1}H)$ could not be read); 7.64 (br d, 6H, H(*o*-Ph), $^{3}J(^{1}H(m\text{-Ph}), ^{1}H(o\text{-Ph})) \approx 8$ Hz); 7.19–7.01 (m, 13H, H(L^{CN} and *m*, *p*-Ph)); 6.90 (d, 2H, H(3′), $^{3}J(^{1}H(4'), ^{1}H(3')) = 7.0$ Hz)); 4.25 (br, 2H, CH_2N); 2.80 (br, 2H, CH_2N); 1.80 (br, 12H, NMe_2). ^{13}C NMR (C_6D_6, 295 K, ppm): 146.7 (C(2′), $^{2}J(^{119}Sn, ^{13}C)$ was not observed); 143.1 (br, C(1′), $^{1}J(^{119}Sn, ^{13}C)$ could not be read); 140.6 (br, i-Ph); 138.1 (br, C(6′)); 135.6 (br, *m*-Ph); 129.5 (C^{Ar}); 129.1 (C^{Ar}); 128.5 (C^{Ar}); 128.4 (C^{Ar}); 127.4 (C^{Ar}); 127.3 (C^{Ar}); 124.9 (C^{Ar}); 68.8 (anisochronous CH_2N); 63.8 (anisochronous CH_2N); 44.7 (br, $N(CH_3)_2$). ^{119}Sn NMR (C_6D_6, 295 K, ppm): 210.0. Elemental analysis (%): found: C 63.6; H 5.9; N 4.0. Calcd (%) for $C_{36}H_{39}ClSiN_2Sn$ (681.95): C 63.41; H 5.76; N 4.11.

4.2.8. Preparation of $(L^{CN})_2Sn(Cl)OSiPh_3$ (8). Pure **8** was prepared by the bubbling of dioxygen into the benzene solution of **7** for *ca.* 30 minutes. All volatiles were then removed *in vacuo* giving essentially pure **8** which was crystallized from chloroform. M.p. 218–220 °C. ^{1}H NMR (C_6D_6, 295 K, ppm): 8.45 (d, 1H, H(6′), $^{3}J(^{1}H(5'), ^{1}H(6')) = 5.2$ Hz, $^{3}J(^{119}Sn, ^{1}H) \approx 94$ Hz); 8.44 (d, 1H, H(6′), $^{3}J(^{1}H(5'), ^{1}H(6')) = 5.2$ Hz, $^{3}J(^{119}Sn, ^{1}H) \approx 94$ Hz); 7.75 (d, 6H, H(*o*-Ph), $^{3}J(^{1}H(m\text{-Ph}), ^{1}H(o\text{-Ph})) = 8.2$ Hz); 7.34–6.99 (m, 15H, H(3′, 4′, 5′ and *m*, *p*-Ph)); 3.61 (br d, 2H, CH_2N, $^{2}J(^{1}H(A), ^{1}H(X)) \approx 13$ Hz); 2.83 (d, 2H, CH_2N, $^{2}J(^{1}H(A), ^{1}H(X)) = 13$ Hz); 1.50 (s, 12H, NMe_2). ^{13}C NMR (C_6D_6, 295 K, ppm): 143.2 (C(2′), $^{2}J(^{119}Sn, ^{13}C)$ could not be read); 143.0 (C(1′), $^{1}J(^{119}Sn, ^{13}C)$ could not be read); 140.3 (br, i-Ph); 136.7 (C(6′)); 136.1 (*o*-Ph); 135.6 (C^{Ar}); 129.9 (C^{Ar}); 129.3 (C^{Ar}); 128.9 (C^{Ar}); 128.5 (C^{Ar}); 127.6 (C^{Ar}); 127.3 (C^{Ar}); 64.5 (CH_2N); 46.1 ($N(CH_3)_2$). ^{119}Sn NMR (C_6D_6, 295 K, ppm): −355.5. Elemental analysis (%): found: C 62.2; H 5.9; N 3.9. Calcd (%) for $C_{36}H_{39}ClSiON_2Sn$ (697.95): C 61.95; H 5.63; N 4.01.

4.2.9. Preparation of $(L^{CN})_2Sn(Cl)SnBu_3$ (9). Synthesis of **9** was carried out similarly as for **4** starting from **1** (0.195 g, 0.50 mmol) and $(n\text{-Bu})_3SnCl$ (97%, 0.169 g, 0.50 mmol). Nearly pure oily **9** was obtained after evaporation of all volatiles from the reaction mixture. Isolated yield 0.552 g (88%). ^{1}H NMR (C_6D_6, 295 K, ppm): 8.21 (extremely broad, 2H, H(6′), $^{3}J(^{119}Sn, ^{1}H)$ could not be read); 7.25–7.05 (br, 6H, H(3′, 4′, 5′)); 3.73 (br, 2H, CH_2N); 3.10 (d, 2H, CH_2N, $^{2}J(^{1}H(A), ^{1}H(X)) = 13$ Hz); 1.84 (br, 12H, NMe_2); 1.70 (m, 6H, H(*n*-Bu)); 1.38 (m, 12H, H(*n*-Bu)); 0.88 (t, 9H, H(*n*-Bu), ^{3}J (^{1}H, ^{1}H) = 8.0 Hz). ^{13}C NMR (C_6D_6, 295 K, ppm): 146.2 (anisochronous C(2′), $^{2}J(^{119}Sn, ^{13}C)$ was not observed); 145.2 (br, anisochronous C(2′), $^{1}J(^{119}Sn, ^{13}C)$ could not be read); 143.6 (anisochronous C(1′), $^{2}J(^{119}Sn, ^{13}C)$ was not observed); 141.6 (br, anisochronous C(1′), $^{1}J(^{119}Sn, ^{13}C)$ could not be read); 137.6 (anisochronous C(6′)); 137.4 (anisochronous C(6′)); 129.1 (C^{Ar}); 128.9 (C^{Ar}); 128.8 (C^{Ar}); 128.3 (C^{Ar}); 127.4 (C^{Ar}); 126.7 (C^{Ar}); 65.9 (anisochronous CH_2N); 65.6 (anisochronous CH_2N); 46.0 (br, $N(CH_3)_2$, $^{3}J(^{119}Sn, ^{13}C) \approx 117$ Hz); 30.2 (*n*-Bu(C^{β}), $^{2}J(^{119}Sn, ^{13}C) = 20$ Hz); 27.7 (*n*-Bu(C^{γ}), $^{3}J(^{119}Sn, ^{13}C) = 59$ Hz); 16.0 (*n*-Bu(C^{α}), $^{1}J(^{119}Sn, ^{13}C) = 340$ Hz, $^{2}J(^{119}Sn, ^{13}C) = 197$ Hz); 13.7 (br, *n*-Bu(C^{δ})). ^{119}Sn NMR (C_6D_6, 295 K, ppm): −46.3 ($(n\text{-Bu})_3Sn$ moiety, $^{1}J(^{119}Sn, ^{117/119}) = 4532$ Hz); −133.8 (extremely broad, $(L^{CN})_2SnCl$ fragment, $^{1}J(^{119}Sn, ^{117/119}Sn)$ could not be read). Elemental analysis (%): found: C 50.8; H 7.3; N 3.9. Calcd (%) for $C_{30}H_{51}ClN_2Sn_2$ (712.59): C 50.57; H 7.21; N 3.93.

4.2.10. Conversion of 9 to $(L^{CN})_2Sn(Cl)OSnBu_3$ (10). Oxygen was passed through the NMR tube containing the benzene-d6 solution of **9** for 30 minutes resulting in the formation of oily **10**. $[(n\text{-Bu})_3Sn]_2O$ was also formed as a minor by-product (less than 5%). ^{1}H NMR (C_6D_6, 295 K, ppm): 8.39 (d, 1H, anisochronous H(6′), $^{3}J(^{1}H(5'), ^{1}H(6')) = 6.8$ Hz, $^{3}J(^{119}Sn, ^{1}H) \approx 114$ Hz); 8.24 (d, 1H, anisochronous H(6′), $^{3}J(^{1}H(5'), ^{1}H(6')) = 6.7$ Hz, $^{3}J(^{119}Sn, ^{1}H) \approx 82$ Hz); 7.25 (m, 2H, H(4′)); 7.14 (m, 2H, H(5′)); 6.92 (d, 1H, H(3′), $^{3}J(^{1}H(4'), ^{1}H(3')) = 7.1$ Hz); 6.87 (d, 1H, anisochronous H(3′), $^{3}J(^{1}H(4'), ^{1}H(3')) = 7.1$ Hz); 3.85 (d, 1H, CH_2N, $^{2}J(^{1}H(A), ^{1}H(X)) \approx 13$ Hz); 3.72 (d, 1H, CH_2N, $^{2}J(^{1}H(A), ^{1}H(X)) \approx 13$ Hz); 2.96 (d, 1H, CH_2N, $^{2}J(^{1}H(A), ^{1}H(X)) \approx 13$ Hz); 2.87 (d, 1H, CH_2N, $^{2}J(^{1}H(A), ^{1}H(X)) \approx 13$ Hz); 1.88 (br s, 12H, NMe_2); 1.61 (br m, 6H, H(*n*-Bu)); 1.33 (m, 12H, H(*n*-Bu)); 0.84 (t, 9H, H(*n*-Bu), ^{3}J (^{1}H, ^{1}H) = 8.0 Hz). ^{13}C NMR (C_6D_6, 295 K, ppm): 145.1 (br, anisochronous C(2′), $^{2}J(^{119}Sn, ^{13}C)$ was not observed); 144.4 (br, anisochronous C(2′), $^{1}J(^{119}Sn, ^{13}C)$ could not be read); 143.8 (br, anisochronous C(1′), $^{2}J(^{119}Sn, ^{13}C)$ was not observed); 142.1 (br, anisochronous C(1′), $^{1}J(^{119}Sn, ^{13}C)$ could not be read); 137.3 (br, anisochronous C(6′)); 136.5 (br, anisochronous C(6′)); 129.0 (br, C^{Ar}); 128.7 (br, C^{Ar}); 127.8 (C^{Ar}); 127.6 (br, C^{Ar}); 127.2 (br, C^{Ar}); 65.4 (br, anisochronous CH_2N); 64.7 (br, anisochronous CH_2N); 46.6 (extremely broad, $N(CH_3)_2$); 29.1 (*n*-Bu(C^{β}), $^{2}J(^{119}Sn, ^{13}C) = 20$ Hz); 28.0 (*n*-Bu(C^{γ}), $^{3}J(^{119}Sn, ^{13}C) = 61$ Hz); 17.7 (*n*-Bu(C^{α}), $^{1}J(^{119}Sn, ^{13}C) = 368$ Hz); 14.4 (*n*-Bu(C^{δ})). ^{119}Sn NMR (C_6D_6, 295 K, ppm): 81.6 ($(n\text{-Bu})_3SnO$ moiety, $^{2}J(^{119}Sn, ^{117/119}Sn) = 435$ Hz); −254.3 ($(L^{CN})_2Sn(Cl)O$ fragment, $^{2}J(^{119}Sn, ^{117/119}Sn) = 435$ Hz). Elemental analysis (%): found: C 49.8; H 7.2; N 3.9. Calcd (%) for $C_{30}H_{51}ClON_2Sn_2$ (728.59): C 49.46; H 7.06; N 3.84.

4.2.11. Reaction of 1 towards Me_3SiCl. **1** (0.097 g, 0.25 mmol) was dissolved in toluene (10 mL) and Me_3SiCl (98%, 32 μL, 0.25 mmol) was added drop-wise. The reaction mixture was stirred overnight. Multinuclear NMR spectroscopy measurements of the sample prepared from the concentrated reaction mixture revealed only the presence of unreacted **1**.[18]

4.2.12. Reaction of 1 towards CH_2Cl_2 (1 : 1). **1** (0.162 g, 0.42 mmol) was dissolved in toluene (20 mL) and dichloromethane (27 μL, 0.42 mmol) in toluene (5 mL) was added at −30 °C. The reaction mixture was then stirred overnight at ambient temperature. The clear yellow solution was concentrated in order to prepare the NMR sample. $(L^{CN})_2SnCl_2$[25b] (minor product, *ca.* 15% mol Sn) and unreacted **1**[18] (major, *ca.* 85% mol Sn) were identified as the tin-containing components of the reaction mixture with the help of multinuclear NMR spectroscopy.

4.2.13. Reaction of 1 towards CH_2Cl_2 (2 : 1). Similarly as in the case described above the reaction of **1** (0.228 g, 0.59 mmol) with dichloromethane (19 μL, 0.29 mmol) in toluene resulted in the formation of $(L^{CN})_2SnCl_2$[25b] (minor product, *ca.* 5% mol Sn). Unreacted **1**[18] (major, *ca.* 95% mol Sn) was identified as well.

4.2.14. Reaction of 1 towards 9-isopropyl-6-iodopurine. Similarly as in the case described above the reaction of **1** (0.081 g, 0.21 mmol) with 9-isopropyl-6-iodopurine (0.061 g, 0.21 mmol) in toluene yielded $(L^{CN})_2SnI_2$[25b] (*ca.* 40% mol Sn) which was confirmed by multinuclear NMR spectroscopy. Unreacted **1**[18] (*ca.* 60% mol Sn) was identified as well.

4.2.15. Reaction of 1 towards $(Me_3Si)_2CHCl$. Similarly as in the case described above, the reaction of **1** (0.090 g, 0.23 mmol) with $(Me_3Si)_2CHCl$ (97%, 0.047 g, 0.23 mmol) in toluene yielded $(L^{CN})_2SnCl_2$[25b] (minor, *ca.* 11% mol Sn) and unreacted **1**[18] (major, *ca.* 77% mol Sn) which was confirmed by the multinuclear NMR spectroscopy. In addition, unidentified tin-containing species (*ca.* 11% mol Sn) was detected with the help of multinuclear NMR spectroscopy.

4.2.16. Reaction of 1 towards $[(Me_3Si)_2CH]_3SnI$. **1** (0.078 g, 0.20 mmol) was dissolved in toluene (10 mL) and $[(Me_3Si)_2CH]_3SnI$ (0.145 g, 0.20 mmol) in toluene (10 mL) was added drop-wise. The reaction mixture was stirred overnight at ambient temperature and then filtered. Colourless filtrate contained unreacted **1**[18] (major, *ca.* 67% mol Sn) and $(L^{CN})_2SnI_2$[25b] (*ca.* 22% mol Sn) which was confirmed by multinuclear NMR spectroscopy.

Acknowledgements

The authors would like to thank the Czech Science Foundation (grant no. P207/10/P092) for the financial support of this work. Professor D. Dvořák from ICT Prague is acknowledged for the gift of the iodopurine sample.

Notes and references

1 (*a*) *The Chemistry of Organic Germanium, Tin and Lead Compounds*, ed. Z. Rappoport, Wiley VCH, Weinheim, Germany, 2003, vols. 1 and 2; (*b*) A. G. Davies, in *Organotin Chemistry*, Wiley VCH, Weinheim, Germany, 1997 & 2004; (*c*) M. F. Lappert, A. V. Protchenko, P. P. Power and A. Seeber, *Metal Amide Chemistry*, Wiley, John Wiley and Sons, Ltd, Chichester, UK, 2009, Ch. 9, pp. 263–318; (*d*) D. H. Harris and M. F. Lappert, *J. Chem. Soc., Chem. Commun.*, 1974, 895–896; (*e*) P. J. Davidson, D. H. Harris and M. F. Lappert, *J. Chem. Soc., Dalton Trans.*, 1976, 2268–2274.

2 (*a*) W.-P. Leung, W.-H. Kwok, L. T. C. Law, Z.-Y. Zhou and T. C. W. Mak, *Chem. Commun.*, 1996, 505–506; (*b*) P. Brown, M. F. Mahon and K. C. Molloy, *J. Chem. Soc., Chem. Commun.*, 1989, 1621–1622; (*c*) J. J. Schneider, J. Hagen, O. Heinemann, J. Bruckmann and C. Krüger, *Thin Solid Films*, 1997, **304**, 144–148; (*d*) Y. Matsuhashi, N. Tokitoh and R. Okazaki, *Organometallics*, 1993, **12**, 2573–2583; (*e*) N. Tokitoh, H. Suzuki, T. Matsumoto, Y. Matsuhashi, R. Okazaki and M. Goto, *J. Am. Chem. Soc.*, 1991, **113**, 7047–7049; (*f*) N. Tokitoh, Y. Matsuhashi and R. Okazaki, *Tetrahedron Lett.*, 1991, **32**, 6151–6154; (*g*) Y. Matsuhashi, N. Tokitoh, R. Okazaki, M. Goto and S. Nagase, *Organometallics*, 1993, **12**, 1351–1358; (*h*) For a review, see: N. Takeda, N. Tokitoh and R. Okazaki, *Handbook of Chalcogen Chemistry, New Perspectives in Sulfur, Selenium and Tellurium*, ed. F. Devillanova, The Royal Society of Chemistry, Cambridge, UK, 2007, Ch. 3, p. 107; (*i*) M. Saito, N. Tokitoh and R. Okazaki, *J. Am. Chem. Soc.*, 2004, **126**, 15572–15582; (*j*) N. Tokitoh, M. Saito and R. Okazaki, *J. Am. Chem. Soc.*, 1993, **115**, 2065–2066; (*k*) M. Saito, N. Tokitoh and R. Okazaki, *Organometallics*, 1996, **15**, 4531–4536.

3 (*a*) M. F. Lappert, *Silicon, Germanium, Tin and Lead Compounds*, 1986, **9**, 129–154; (*b*) M. F. Lappert and R. S. Rowe, *Coord. Chem. Rev.*, 1990, **100**, 267–292.

4 (*a*) P. J. Davidson, A. Hudson, A. M. F. Lappert and P. W. Lednor, *J. Chem. Soc., Chem. Commun.*, 1973, **21**, 829–830; (*b*) R. W. Chorley, P. B. Hitchcock and M. F. Lappert, *J. Chem. Soc., Dalton Trans.*, 1992, 1451–1452; (*c*) C. Bibal, S. Mazieres, H. Gornitzka and C. Couret, *Organometallics*, 2002, **21**, 2940–2943; (*d*) D. Kurzbach, S. L. Yao, D. Hinderberger and K. W. Klinkhammer, *Dalton Trans.*, 2010, **39**, 6449–6459; (*e*) A. Hudson, M. F. Lappert and P. W. Lednor, *J. Chem. Soc., Dalton Trans.*, 1976, 2369–2375.

5 (*a*) J. D. Cotton, P. J. Davidson and M. F. Lappert, *J. Chem. Soc., Dalton Trans.*, 1976, 2275; (*b*) M. J. S. Gynane, M. F. Lappert, S. J. Miles and P. P. Power, *J. Chem. Soc., Chem. Commun.*, 1976, 256–257; (*c*) M. J. S. Gynane, M. F. Lappert, S. J. Miles and P. P. Power, *J. Chem. Soc., Chem. Commun.*, 1978, 192–193; (*d*) M. F. Lappert, M. C. Misra, M. Onyszchuk, R. S. Rowe, P. P. Power and M. J. Slade, *J. Organomet. Chem.*, 1987, **330**, 31–46; (*e*) I. Gűmrűkçű, A. Hudson, M. F. Lappert, M. J. Slade and P. P. Power, *J. Chem. Soc., Chem. Commun.*, 1980, 776–777.

6 (*a*) L. Pu, A. D. Phillips, A. F. Richards, M. Stender, R. S. Simons, M. M. Olmstead and P. P. Power, *J. Am. Chem. Soc.*, 2003, **125**, 11626–11636; (*b*) C. Cui, M. M. Olmstead and P. P. Power, *J. Am. Chem. Soc.*, 2004, **126**, 5062–5063; (*c*) C. Cui, M. Brynda, M. M. Olmstead and P. P. Power, *J. Am. Chem. Soc.*, 2004, **126**, 6510–6511; (*d*) P. P. Power, *Appl. Organomet. Chem.*, 2005, **19**, 488–493; (*e*) C. Cui, M. M. Olmstead, C. C. Fettinger, G. H. Spikes and P. P. Power, *J. Am. Chem. Soc.*, 2005, **127**, 17530–17541.

7 (*a*) S. Dutta, W. C. Hung, B. H. Huang and C. C. Lin, *Synthetic Biodegradable Polymers*, ed. B. Rieger, A. Kunkel, G. W. Coates, R. Reichardt, E. Dinjus and T. A. Zevaco, Book Series: Advances in Polymer Science, 2012, vol. 245, pp. 219–283; (*b*) O. Coulembier, P. Degee, J. L. Hedrick and P. Dubois, *Prog. Polym. Sci.*, 2006, **31**, 723–747.

8 (*a*) K. A. Miller, J. M. Bartolin, R. M. O'Neil, R. D. Sweeder, T. M. Owens, J. W. Kampf, M. M. Banaszak Holl and N. J. Wells, *J. Am. Chem. Soc.*, 2003, **125**, 8986–8987; (*b*) A. Kavara, T. T. Boron, Z. S. Ahsan and M. M. Banaszak Holl, *Organometallics*, 2010, **29**, 5033–5039.

9 J. M. Bartolin, A. Kavara, J. W. Kampf and M. M. Banaszak Holl, *Organometallics*, 2006, **25**, 4738–4740.

10 (*a*) Y. Peng, J. D. Guo, B. D. Ellis, Z. L. Zhu, J. C. Fettinger, S. Nagase and P. P. Power, *J. Am. Chem. Soc.*, 2009, **131**, 16272–16282; (*b*) P. P. Power, *Nature*, 2010, **463**, 171–177.

11 (*a*) P. Pfeiffer and I. Keller, *Ber.*, 1904, **37**, 4618–4620; (*b*) G. Meyer, *Ber.*, 1883, **16**, 1439–1443; (*c*) A. Tchakiran, M. Lesbe and M. Lewinsohn, *Compt. Rend.*, 1936, **202**, 138–143.

12 K. D. Bos, E. J. Bulten and J. G. Notes, *J. Organomet. Chem.*, 1975, **99**, 397–405.

13 J. K. West and L. Stahl, *Organometallics*, 2012, **31**, 2042–2052.

14 (*a*) C. Drost, P. B. Hitchcock and M. F. Lappert, *J. Organomet. Chem.*, 2002, **21**, 2095–2100; (*b*) B. Hitchcock, M. F. Lappert, A. V. Protchenko and P. G. H. Uiterweerd, *Dalton Trans.*, 2009, 353–361.

15 U. Englich, I. Prass, K. Ruhlandt-Senge, T. Schollmeier and F. Uhlig, *Monatsh. Chem.*, 2002, **133**, 931–943.

16 (*a*) J. Baumgartner, R. Fischer, J. Fischer, A. Wallner and C. Marschner, *Organometallics*, 2005, **24**, 6450–6457; (*b*) J. Fischer, J. Baumgartner and C. Marschner, *Organometallics*, 2005, **24**, 1263–1268; (*c*) R. Fischer, J. Baumgartner, C. Marschner and F. Uhlig, *Inorg. Chim. Acta*, 2005, **358**, 3174–3182.

17 A. Kawachi, Y. Tanaka and K. Tamao, *J. Organomet. Chem.*, 1999, **590**, 15–24.

18 K. Angermund, K. Jonas, C. Kruger, J. L. Latten and Y.-H. Tsay, *J. Organomet. Chem.*, 1988, **353**, 17–25.

19 (*a*) Z. Padělková, M. S. Nechaev, Z. Černošek, J. Brus and A. Růžička, *Organometallics*, 2008, **27**, 5303–5308; (*b*) Z. Padělková, H. Vaňkátová, I. Císařová, M. S. Nechaev, T. A. Zevaco, O. Walter and A. Růžička, *Organometallics*, 2009, **28**, 2629–2632; (*c*) Z. Padělková, I. Císařová, M. S. Nechaev and A. Růžička, *J. Organomet. Chem.*, 2009, **694**, 2871–2874; (*d*) Z. Padělková, T. Weidlich, L. Kolářová, A. Eisner, I. Císařová, T. A. Zevaco and A. Růžicka, *J. Organomet. Chem.*, 2007, **692**, 5633–5645; (*e*) T. P. Lockhart, H. Puff, W. Schuh, H. Reuter and T. N. Mitchell, *J. Organomet. Chem.*, 1989, **366**, 61–72.

20 Z. Padělková, M. S. Nechaev, A. Lyčka, J. Holubová, T. A. Zevaco and A. Růžička, *Eur. J. Inorg. Chem.*, 2009, 2058–2061.

21 Z. Padělková, I. Císařová, K. Fejfarová, J. Holubová, A. Růžička and J. Holeček, *Collect. Czech. Chem. Commun.*, 2007, **72**, 629–636.

22 J. Bareš, P. Richard, P. Meunier, N. Pirio, Z. Padělková, Z. Černošek, I. Císařová and A. Růžička, *Organometallics*, 2009, **28**, 3105–3108.

23 (*a*) Y. Nakao, E. Shirakawa, T. Tsuchimoto and T. Hiyama, *J. Organomet. Chem.*, 2004, **689**, 3701–3721; (*b*) Y. Obora, M. Nakanishi, M. Tokunaga and Y. Tsuji, *J. Org. Chem.*, 2002, **67**, 5835–5837; (*c*) E. Shirakawa, Y. Yamamoto, Y. Nakao, T. Tsuchimoto and T. Hiyama, *Chem. Commun.*, 2001, 1926–1927; (*d*) E. Shirakawa, Y. Nakao and T. Hiyama, *Chem. Commun.*, 2001, 263–264; (*e*) E. Shirakawa, Y. Nakao, H. Yoshida and T. Hiyama, *J. Am. Chem. Soc.*, 2000, **122**, 9030–9031.

24 H. A. Bent, *J. Chem. Phys.*, 1960, **33**, 1258–1259.

25 (*a*) P. Švec, Z. Padělková, I. Císařová, A. Růžička and J. Holeček, *Main Group Met. Chem.*, 2008, **31**, 305–309; (*b*) P. Novák, Z. Padělková, L. Kolářová, I. Císařová, A. Růžička and J. Holeček, *Appl. Organomet. Chem.*, 2005, **19**, 1101–1108; (*c*) R. A. Varga, A. Rotar, M. Schuermann, K. Jurkschat and C. Silvestru, *Eur. J. Inorg. Chem.*, 2006, 1475–1486.

26 See for example: (*a*) A. Růžička, V. Pejchal, J. Holeček, A. Lyčka and K. Jacob, *Collect. Czech. Chem. Commun.*, 1998, **63**, 977–989; (*b*) M. Biesemans, J. C. Martins, R. Willem, A. Lyčka, A. Růžička and J. Holeček, *J. Magn. Reson Chem.*, 2002, **40**, 65–69.

27 For related triorganotin(IV) species bearing *C*,*N*-chelating ligand(s) see for example: (*a*) P. Švec, Z. Padělková, I. Císařová, A. Růžička and J. Holeček, *Main Group Met. Chem.*, 2008, **31**, 305–309; (*b*) J. Bareš, P. Novák, M. Nádvorník, R. Jambor, T. Lébl, I. Císařová, A. Růžička and J. Holeček, *Organometallics*, 2004, **23**, 2967–2971; (*c*) P. Švec, E. Černošková, Z. Padělková, A. Růžička and J. Holeček, *J. Organomet. Chem.*, 2010, **695**, 2475–2485; (*d*) P. Švec, R. Olejník, Z. Padělková, A. Růžička and L. Plasseraud, *J. Organomet. Chem.*, 2012, **708–709**, 82–87.

28 (*a*) R. Villazana, H. Sharma, F. Cervantes-Lee and K. H. Pannell, *Organometallics*, 1993, **12**, 4278–4279; (*b*) H. K. Sharma, F. Cervantes-Lee and K. H. Pannell, *J. Organomet. Chem.*, 1991, **409**, 321–330; (*c*) C. Jones, P. C. Junk, J. W. Steed, R. C. Thomas and T. C. Williams, *J. Chem. Soc., Dalton Trans.*, 2001, 3219–3226; (*d*) M. R. Mason, B. Song and K. Kirschbaum, *J. Am. Chem. Soc.*, 2004, **126**, 11812–11813; (*e*) I. Meana, A. C. Albéniz and P. Espinet, *Organometallics*, 2008, **27**, 4193–4198; (*f*) F. R. Kreissl, W. J. Sieber, H. Keller, J. Riede and M. Wolfgruber, *J. Organomet. Chem.*, 1987, **320**, 83–90.

29 (*a*) P. Švec, Z. Padělková, A. Růžička, T. Weidlich, L. Dušek and L. Plasseraud, *J. Organomet. Chem.*, 2011, **696**, 676–686; (*b*) P. Švec, Z. Padělková, P. Štěpnička, A. Růžička and J. Holeček, *J. Organomet. Chem.*, 2011, **696**, 1809–1816.

30 L. R. Sita, R. Xi, G. P. A. Yap, L. M. Liable-Sands and A. L. Rheingold, *J. Am. Chem. Soc.*, 1997, **119**, 756–760.

31 (*a*) R. Fischer, J. Baumgartner, C. Marschner and F. Uhlig, *Inorg. Chim. Acta*, 2005, **358**, 3174–3182; (*b*) R. Fischer and F. Uhlig, *Coord. Chem. Rev.*, 2005, **249**, 2075–2093; (*c*) R. Fischer, T. Schollmeier, M. Schürmann and F. Uhlig, *Appl. Organomet. Chem.*, 2005, **19**, 523–529.

32 S. P. Mallela, Y. Saar, S. Hill and R. A. Geanangel, *Inorg. Chem.*, 1999, **38**, 2957–2960.

33 T. Fukawa, V. Ya. Lee, M. Nakamoto and A. Sekiguchi, *J. Am. Chem. Soc.*, 2004, **126**, 11758–11759.

34 (*a*) A. G. Davies, *Organotin Chemistry*, Wiley VCH, Weinheim, 2nd edn, 2004; (*b*) B. Wrackmeyer, *Annu. Rep. NMR Spectrosc.*, 1985, **16**, 73–186; (*c*) B. Wrackmeyer, *Annu. Rep. NMR Spectrosc.*, 1999, **38**, 203–264; (*d*) K. Jurkschat, A. Tzschach, C. Mugge, J. Piret-Meunier, M. Van Meerssche, G. Van Binst, C. Wynants, M. Gielen and R. Willem, *Organometallics*, 1988, **7**, 593–603.

35 Z. Otwinowski and W. Minor, *Methods Enzymol.*, 1997, **276**, 307–326.

36 P. Coppens, in *Crystallographic Computing*, ed. F. R. Ahmed, S. R. Hall and C. P. Huber, Munksgaard, Copenhagen, 1970, pp. 255–270.

37 A. Altomare, G. Cascarano, C. Giacovazzo and A. Guagliardi, *J. Appl. Crystallogr.*, 1993, **26**, 343–350.

38 G. M. Sheldrick, *SHELXL-97, A Program for Crystal Structure Refinement*, University of Göttingen, Göttingen, 1997.

39 A. L. Spek, *Acta Crystallogr., Sect. A: Fundam. Crystallogr.*, 1990, **46**, 194–201.