



Aminostannanes and aminostannylenes containing a C,N-chelated ligand

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Dedicated to Dr. Bohumil Štíbr on the occasion of his 70th birthday in recognition of his outstanding contributions to the area of boron and organometallic chemistry.

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ABSTRACT

Aminotin(II and IV) compounds $\{[(2,6-i\text{-Pr-C}_6\text{H}_3)(\text{H})\text{N}]-\mu\text{-(Sn-Cl)}_2\}$, $\{2-[(\text{CH}_3)_2\text{NCH}_2]\text{C}_6\text{H}_4\}_2\text{Sn}[\text{N}(\text{H})(2,6-i\text{-Pr-C}_6\text{H}_3)_2]$ and $\{2-[(\text{CH}_3)_2\text{NCH}_2]\text{C}_6\text{H}_4\}_2\text{Sn}[\text{N}(2,6-i\text{-Pr-C}_6\text{H}_3)(\text{SiMe}_3)]$ were prepared by lithium halide elimination from tin halides and corresponding lithium complexes. $\{[(2,6-i\text{-Pr-C}_6\text{H}_3)(\text{H})\text{N}]\text{Li}(\mathbf{1})\}$ reacts with one half of molar equivalent of SnCl_2 to give $\{[(2,6-i\text{-Pr-C}_6\text{H}_3)(\text{H})\text{N}]-\mu\text{-(Sn-Cl)}_2\}$. The same lithium amide ($\mathbf{1}$) gave with R_3SnCl corresponding aminostannanes. Further reactions of these compounds with *n*-butyllithium gave the starting $\mathbf{1}$ and tetraorganostannanes. $\{2-[(\text{CH}_3)_2\text{NCH}_2]\text{C}_6\text{H}_4\}_2\text{SnBr}_2$ reacts with two equivalents of $\mathbf{1}$ to $\{2-[(\text{CH}_3)_2\text{NCH}_2]\text{C}_6\text{H}_4\}_2\text{Sn}[\text{N}(\text{H})(2,6-i\text{-Pr-C}_6\text{H}_3)_2]$. The dimeric heteroleptic stannylene $\{[(2,6-i\text{-Pr-C}_6\text{H}_3)(\text{SiMe}_3)\text{N}](\mu_2\text{-Cl})\text{Sn}\}_2$ reacts with $2-[(\text{CH}_3)_2\text{NCH}_2]\text{C}_6\text{H}_4\text{Li}$ to the monomeric $\{2-[(\text{CH}_3)_2\text{NCH}_2]\text{C}_6\text{H}_4\}_2\text{Sn}[\text{N}(2,6-i\text{-Pr-C}_6\text{H}_3)(\text{SiMe}_3)]$. The structure in the solid state and in solution and reactivity of products is also discussed. The unique decatin cluster has been isolated by hydrolysis of $\{[(2,6-i\text{-Pr-C}_6\text{H}_3)(\text{H})\text{N}]-\mu\text{-(Sn-Cl)}_2\}$. The structure of some compounds was also evaluated by theoretical DFT methods.

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1. Introduction

The group of aminostannanes [1] is well established and compounds with covalent Sn–N bonds, particularly compounds of Sn–NR₂ type play an interesting role in structural chemistry and they provide a route to various new types of compounds, mainly due to the high reactivity of Sn–N bond. Especially the reactivity of these compounds, where NR₂ group can act as a mild nucleophile, in substitution or addition reactions is very important. Also the products of reactions with protic acids, heterocumulenes or other singly- or doubly bonded electrophiles [2] constitute interesting groups of molecules. The structure of aminostannanes strongly depends on steric hindrance and electronic demand of tin and nitrogen substituents which is illustrated in the next paragraph. The $(\text{Me}_3\text{Sn})_3\text{N}$ [3] and $\text{ArN}(\text{SnMe}_3)_2$ [4] (Ar = 2,6-(diisopropyl)phenyl – Fig. 1) are monomeric, and $(t\text{-Bu}_2\text{SnN-}t\text{-Bu})_2$ is dimeric [5] with planar four membered ring, all of them having planar geometry at nitrogen atoms. On the other hand, in $(t\text{-Bu}_2\text{SnNH})_3$, the ring is again planar but the nitrogen atoms display a distorted pyramidal configuration. The Sn–N interatomic distances determined by GED

or XRD techniques oscillate around the value of 2.05 Å. The structure and reactivity of some stannaimines of R₂Sn = NR' type have also been investigated previously [6]. The ¹⁵N NMR parameters of above mentioned compounds were reviewed by Wrackmeyer [7].

The Sn–N donor interaction is frequently involved as a driving force to electronic and kinetic stabilization of compounds where the tin atom is present in lower [8] oxidation states. These thermally robust complexes in which amino substituents, whether bulky or not, are involved, are studied as a higher congeners of N-heterocyclic carbenes which are useful in transition metal coordination and catalysis [9].

The unusual 1,3-diaza-2,4-distannylcyclobutanide with an aromaticity bonding character within the ring has been prepared by reaction of $\{[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Sn-}\mu\text{-Cl}\}_2$ with AgOCN [10]. Similar compounds with bridging chlorine atoms [11] reveal different reactivity, and $\{[(2,6-i\text{-Pr-C}_6\text{H}_3)(\text{SiMe}_3)\text{N}](\mu_2\text{-Cl})\text{Sn}\}_2$ [12] is the only compound of this type which can be reduced to the endo Sn₁₅ cluster.

The phosphorus and arsenic analogues of amino-bridged compounds are $\text{Bu}^t_2\text{E}^{15}\text{Sn-Cl}$ (E¹⁵ = P or As) as the centrosymmetric dimers with bridging E¹⁵Bu^t₂ groups with unusually short interatomic E¹⁵–Sn distances [13].

In this paper we present the joint effect of tin atom stabilization by both bulky amino substituents and C,N-chelating ligand, used for similar purposes recently [14].

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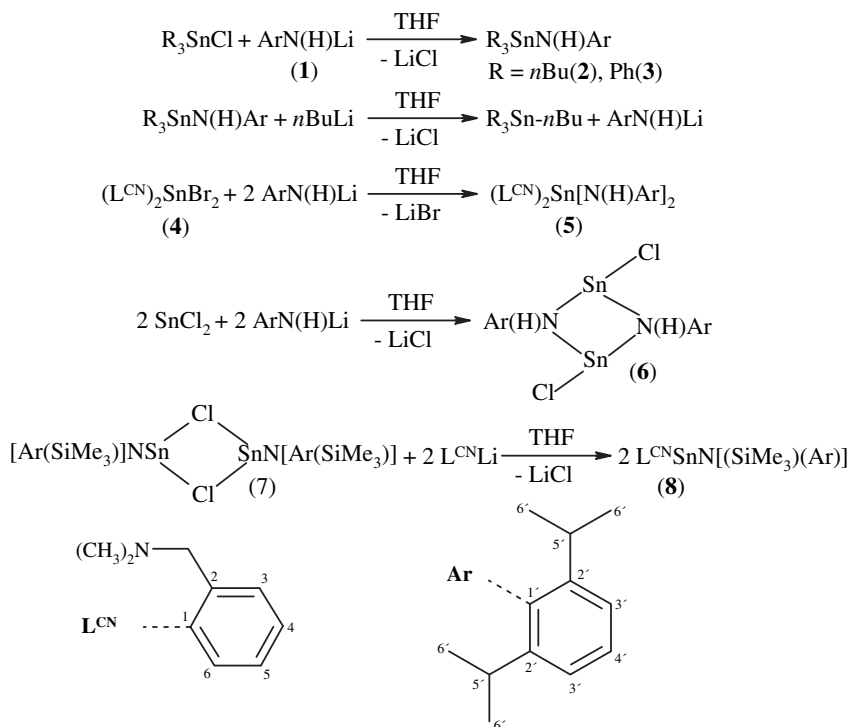


Fig. 1. Reactivity and numbering (NMR) of compounds studied.

2. Results and discussion

All the compounds mentioned in the text are sensitive to air and moisture. The reactions of [(2,6-*i*-Pr-C₆H₃)(H)N]Li (**1**) with Ph₃SnCl and *n*Bu₃SnCl (Fig. 1) yielded corresponding aminostannanes of R₃Sn[N(H)-(2,6-*i*-Pr-C₆H₃)] type (R = *n*Bu (**2**), Ph (**3**)) as yellowish oils in high yields. The trialkyltin(IV) derivative **2** as well as the triaryltin(IV) compound **3** reveal one set of rather broad signals in ¹H NMR spectra with the approximate half-height line-width about 300 Hz. Also the signals found in ¹¹⁹Sn NMR spectra are rather broad at room temperature – with the approximate half-height line-width about 650 Hz. Values of the chemical shifts of **2** and **3** are in line with previously published shifts for related aminostannanes [15]. Compounds **2** and **3** react with one equivalent of 1-butyl-lithium or with lithium diisopropylamide to give the products of transmetalation – [(2,6-*i*-Pr-C₆H₃)(H)N]Li [16] and tetraorganotin(IV) compounds at –78 °C.

Reaction of one to 2 M equivalents of [(2,6-*i*-Pr-C₆H₃)(H)N]Li (**1**) with 1 M equivalent of doubly C,N-chelated diorganotin(IV) dibromide (**4**) gives compound {2-[(CH₃)₂NCH₂]C₆H₄}₂Sn[N(H)-(2,6-*i*-Pr-C₆H₃)]₂ (**5**) essentially quantitatively. Compound **5** displays a single relatively sharp signal (half-height line-width about 80 Hz) with the chemical shift value –161.1 ppm in ¹¹⁹Sn NMR spectrum. This value is within the range for diorganotin(IV) compounds carrying C,N-chelating ligands [17]. In the ¹H NMR spectrum at room temperature, both anilate moieties are isochronous but both dimethylaminomethyl groups resonate at the same frequency. The same non-equivalence for N-aryl groups is also visible from ¹³C and ¹⁵N NMR spectra parameters where two distinct sets of signals for anilate moieties were found (Fig. 2).

On the other hand, the molecular structure determination of **5** in the solid state shows two different dimethylamino groups where the first one is medium-weakly coordinated to the tin atom (Sn1–N31 distance is 2.6987(16) Å) and the second nitrogen atom is out of the tin primary coordination sphere

(Sn1–N41 4.7880(18) Å). The tin coordination geometry is that of deformed trigonal bipyramid with the atom N31 of chelating ligand and one of the arylamino substituents (distance Sn1–N1 is 2.0971(15) Å) in axial positions. The *ipso* carbon atoms and the remaining nitrogen atom of the aniline substituents are located in equatorial positions. The distance of the plane defined by

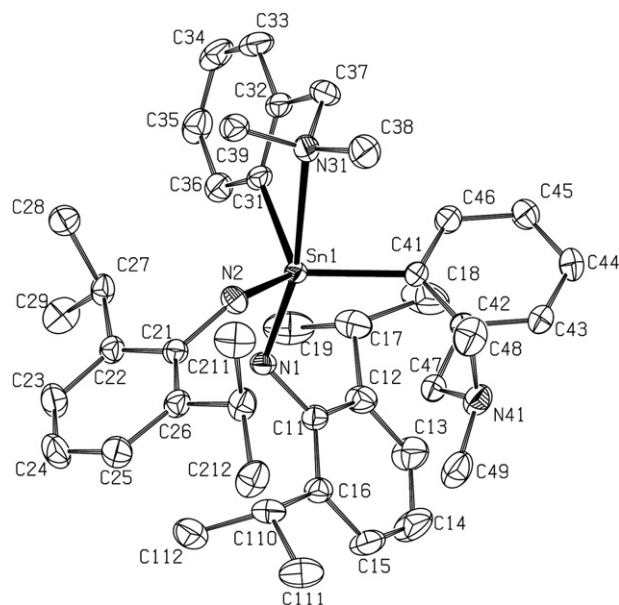


Fig. 2. The molecular structure (ORTEP 50% probability level) of **5**, hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Sn1–N1 2.0971(15), Sn1–N2 2.0680(16), Sn1–N31 2.6987(16), Sn1–N41 4.7880(18), Sn1–C31 2.1427(19), Sn1–C41 2.1511(19), N1–Sn1–N2 97.66(6), N1–Sn1–N31 167.86(6), N1–Sn1–C31 102.57(7), N2–Sn1–C31 117.60(7), N1–Sn1–C41 105.05(7), N2–Sn1–C41 122.47(7), C31–Sn1–C41 107.94(7).

these three atoms from the tin atom is 0.427(2) Å. There is significant difference between Sn–N (aryl–N1 and N2) distances caused probably by a *trans*- effect of dimethylamino group and a weak H-bridge N2–H2⋯N31 being 2.993(2)°Å and 89.3°. Heating of colorless crystals of **5** under vacuo to 160 °C, led to the formation of a dark red insoluble slurry and the elimination of the parent amine (2,6-*i*-Pr-C₆H₃NH₂ – proven by GC/MS).

The reaction of 1 M equivalent of [(2,6-*i*-Pr-C₆H₃)(H)N]Li with SnCl₂ gave compound **6** as a sole product. The white crystalline compound **6** is soluble in organic solvents and reveals instability towards air and moisture. The ¹H NMR spectrum of **6** reveals two broad signals for CH moieties of isopropyl groups at 3.62 and 2.75 ppm, respectively, indicating their non-equivalency in solution at room temperature. The remaining signals are broad and only the signal at 5.82, attributed to NH group, shows satellites due to the coupling with tin 22.3 Hz. This signal is significantly shifted to the higher value in comparison to appropriate signals found in ¹H NMR spectrum of **6** (3.34 and 3.98 ppm). In the ¹¹⁹Sn NMR spectrum, one broad signal at –29.5 ppm is found at 295K but all the attempts to find a decoalescence temperature failed. The ¹¹⁹Sn NMR chemical shift of **6** shifts to low frequency upon temperature decrease, which suggests a possible fast dynamic equilibrium between dimer **6** and its monomeric unit, decreasing the temperature favouring dimer formation. Alternatively, this can reflect the N→Sn interaction becoming increasingly strong when the temperature is lowered, which leads to increased ¹¹⁹Sn nucleus shielding. The chemical shift value is comparable to the value found for **7** [12] where the tin atom is also three coordinated and ligated by the same ligand.

The structure of **6** has been determined by X-ray diffraction. Two different polymorphs of **6** and **6'** were identified. Both polymorphs crystallize in monoclinic crystal system (see **Experimental part**) and the main differences are associated with slight changes in bond distances and interatomic angles. In the centrosymmetric polymorph, the Sn–Cl bonds are almost parallel, in the second one, the angle between the planes defined by mentioned bonds and the centroid of the ring is 8.2°. The tin atoms are bridged by nitrogen atoms forming thus a four membered diazadistanna heterocycle (Fig. 3). The Sn–N bonds in **6** and **6'** are elongated by approximately 0.2°Å in comparison to appropriate distances found in **5**, where the

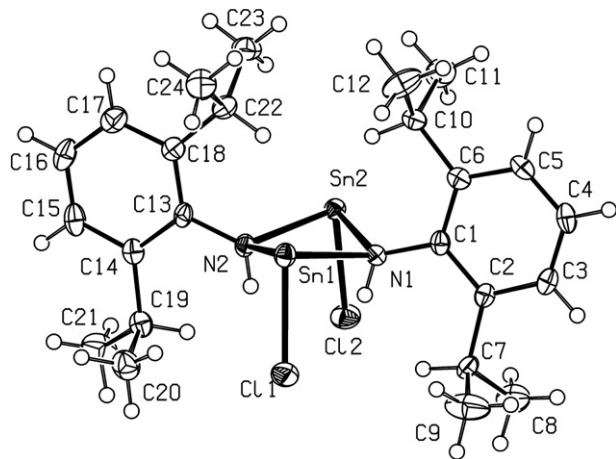


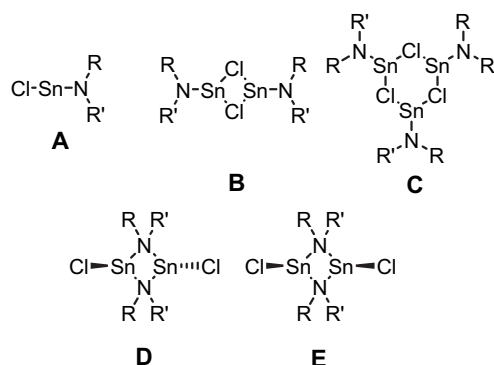
Fig. 3. The molecular structure (ORTEP 50% probability level) of **6'**. Selected interatomic distances [Å] and angles [°]; the appropriate parameters for the centrosymmetric polymorph (**5**) are given in parentheses: Sn1–N1 2.272(3) (2.243(7)), Sn1–N2 2.267(3) (2.308(6)), Sn2–N1 2.272(3), Sn2–N2 2.265(3), Sn1–Cl1 2.4401(11) (2.481(2)), Sn2–Cl2 2.4356(10), N1–Sn1–N2 76.29(11) (78.5(2)), N1–Sn1–Cl1 86.94(8) (84.42(15)), N2–Sn1–Cl1 89.84(8) (89.26(16)), N1–Sn2–N2 76.33(11), N1–Sn2–Cl2 87.28(8), N2–Sn2–Cl2 89.17(8), Sn1–N2–Sn2 100.49(12).

terminal Sn(IV)–N bonds to the same ligand are present. The Sn–N distances are almost equal in the first one polymorph but rather distinct in the centrosymmetric polymorph of **6**. The chlorine atoms lie at the same side below the Sn₂N₂ ring with Sn–Cl bond being almost perpendicular to the ring. The Sn–Cl bond lengths are similar to values found in Cambridge Crystallographic Database for typical Sn–Cl terminal bonds. The small difference in Sn–Cl distances between both polymorphs is probably caused by a slightly larger repulsion in the centrosymmetric polymorph. Surprisingly, the N–H bonds are oriented toward the same side of the Sn₂N₂ ring as the two Sn–Cl bonds. The structure of **6** can be compared to the compounds described previously in the literature. There is a number of compounds with tin(II) atoms bridged by amino ligands, some of them are oligomeric, mainly tetranuclear with a heterocubane structure [18], others having trinuclear six-membered ring arrangement [19], and the remaining ones contain two tin atoms as described mainly by Veith, Lappert or Khrustalev [20–24]. These compounds are chloro aminogermylene and aminostannylene of formulae R₂N–E¹⁴–Cl (E¹⁴ = Ge or Sn) which form dimers through the singly or doubly bridging amino ligands, with terminal chloro ligands in mutual *trans* configuration. When compared to **6**, the tin compound of Khrustalev [24], (Me₂N–Sn–Cl)₂, has an almost planar Sn₂N₂ ring and a *trans* configuration of the Sn–Cl bonds. The same orientation of Sn–Cl bonds in **5** could be explained by the discrepancy in steric bulk of the nitrogen substituents. The remaining interatomic distances and angles are similar.

Tin amido chlorides Cl–Sn–NRR' can adopt different types of structures in solid state (**Scheme 1**): chloro-bridged dimer **B** (R = R' = SiMe₃, [11]) and trimer **C** (R = SiMe₃, R' = Mes, [19]), amido bridged dimers **D** (R = R' = Me, [24]) and **E** (R = H, R' = Dipp, **5**). Monomeric structures of the type **A** are not known to date. This seems natural since steric protection of tin by bulky substituents of amido group can block the central atom only from one side while the other side is accessible for coordination by at least chlorine atom.

We performed DFT study of structures of Cl–Sn–NRR' type. Relative energies of monomers, dimers and trimers in gas phase were calculated at PBE/TZ2P level (**Table 1**). All compounds under study can adopt any type of structures **B–E**, although relative energies in respect to monomers **A** lie in a wide range. Notably, the lowest calculated energies correspond to structures found experimentally.

Compounds bearing the most bulky substituents at nitrogen adopt structures **B** and **C**, respectively. These are the only structures for which relative energies are negative. The least substituted adopts amido bridged structure **D** (–7.3 kcal/mol) with *trans*-arrangement of chlorine atoms. We suppose that chlorine atoms occupy mutual *trans*-positions to avoid steric congestion, **6–E** with



Scheme 1.

Table 1
Calculated relative Gibbs free energies of mono and oligomers of Cl–Sn–NRR' A–E (ΔG in kcal/mol in respect to one subunit, structures found experimentally in bold).

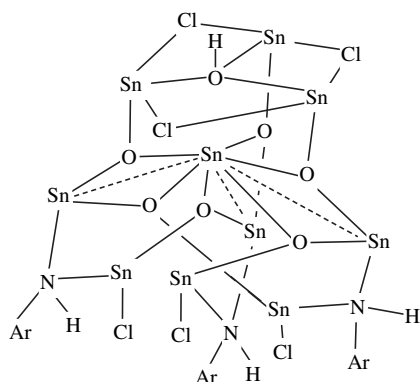
Type	R = SiMe ₃	R = SiMe ₃	R = Me	R = H
	R = SiMe ₃	R = Mes	R' = Me	R' = Dipp
A	0.0	0.0	0.0	0.0
B	–0.4	0.4	0.5	–0.5
C	0.8	–0.5	1.9	1.6
D	6.0	13.7	–7.3	–3.2
E	6.7	15.3	–5.8	–7.5

cis-arrangement of chlorides has a higher in energy (–5.8 kcal/mol). In **6** each nitrogen atom bears one bulky 2,6-diisopropylphenyl (Dipp) group, even though nitrogen to tin coordination can still occur in **6-E** (–7.5 kcal/mol). In this case, cis-arrangement of chlorides decreases steric repulsion from Dipp groups, *vide supra*. Relative energy of **6-D** is 4.3 kcal/mol higher than of **6-E**.

Notably, in the absence of steric congestion about nitrogen atom bridging by amido groups favours over bridging by chlorides. Otherwise, only chloro-bridged dimers would be formed independently from steric congestion of amido groups. Heavy steric loading of amido groups only leads to formation of weakly bound chloro-dimers. Formation of amido-dimers gains more than 7 kcal/mol in free energy, while the bridging by chlorides gains less than 1 kcal/mol.

Many reactions of compound **6** were also investigated including attempts to reduce **6** by different reagents as for example potassium, potassium graphite, lithium naphthenide etc. but only inseparable mixtures of unidentified products and reactants were obtained.

When the compound **6** was left in a freezer and the stopcock was not greased enough, the unique oxo-decatin cluster **6a** was isolated by pure luck as a single crystalline insoluble material. The attempts to prepare **6a** were made many times but we were not successful to reproduce the primary result anymore. The compound **6a** (Scheme 2 and Fig. 4) crystallizes in trigonal system and consists of ten tin, six chlorine, seven oxygen atoms and three –[N(H)(2,6-*i*-Pr-C₆H₃)] ligands. Four different types of tin atoms are present in the structure of **6a**: *i*) three atoms on the top of the cluster connected by OH group in the middle of the triangle, three chlorine and three oxygen atoms to the lower level, *ii*) the middle tin atom is associated to the remaining nine tin atoms by oxygen bridges, *iii*) the middle level is made up by three tin atoms each of which is connected by two oxygen atoms to the lower as well as upper levels and one bridging amino ligand to the lower level, *iv*) the lowest level consists of three tin



Scheme 2.

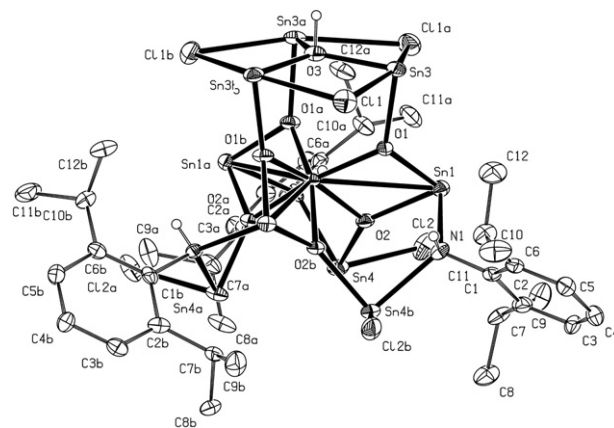


Fig. 4. The molecular structure (ORTEP 50% probability level) of **6a**, some hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Sn2–O1b 2.051(4), Sn2–O1a 2.052(4), Sn2–O1 2.052(4), Sn2–O2b 2.068(4), Sn2–O2a 2.068(4), Sn2–O2 2.069(4), Sn2–Sn1b 3.2301(6), Sn2–Sn1a 3.2310(6), Sn2–Sn1 3.2318(6), Sn3–O3 2.0822(8), Sn3–O1 2.098(4), Sn3–Cl1 2.822(2), Sn4–O2 2.090(4), Sn4–Cl2 2.455(2), Sn1–O2 2.096(4), Sn1–O1 2.106(4), Sn1–N1 2.261(5), O3–Sn3b 2.0808(8), O3–Sn3a 2.0822(8), N1–Sn4 2.253(5), Cl1a–Sn3 2.792(2), O1b–Sn2–O1a 99.68(15), O1–Sn2–O1b 99.68(15), O1–Sn2–O1a 99.64(15), O1b–Sn2–O2b 79.06(16), O1a–Sn2–O2b 165.39(16), O1–Sn2–O2b 94.91(17), O1b–Sn2–O2a 94.94(17), O1a–Sn2–O2a 79.02(16), O1a–Sn2–O2 165.32(16), O2b–Sn2–O2a 86.56(17), O1–Sn2–O2b 165.39(16), O1–Sn2–O2a 94.88(17), O1–Sn2–O2 79.00(16), O2–Sn2–O2b 86.53(17), O2–Sn2–O2a 86.53(17), Sn1b–Sn2–Sn1a 119.220(5), O3–Sn3–O1 87.6(2), O3–Sn3–Cl1a 80.85(5), O1–Sn3–Cl1a 82.38(13), O1–Sn3–Cl1 89.19(13), Cl1–Sn3–Cl1a 159.42(6), O2–Sn4–N1a 89.28(17), Sn2–O1–Sn3 125.1(2), Sn2–O1–Sn1 102.01(18), Sn3–O1–Sn1 124.3(2), Sn3b–O3–Sn3a 119.29(6).

atoms containing three terminal chlorine atoms and one bridging amino ligand connecting this level with upper tin atoms.

The interatomic distances found in **6a** are comparable to usual distances found for similar bonds in the Cambridge Crystallographic Database. The Sn–Cl distances (Table 2) are also comparable to those found in tetranuclear compound published by us very recently, where also terminal and bridging Sn–Cl bonds are present [25].

Last, the reaction of the heteroleptic aminostannylene **7**, used also by one of us for preparation of Sn₁₅ endo cluster [12], with the lithium salt of C,N-chelating ligand was investigated (Scheme 1). This reaction gave compound **8** (Fig. 5) as yellowish crystals in essentially quantitative yield.

One set of relatively narrow signals was found in ¹H NMR spectrum of **8**. In ¹¹⁹Sn NMR spectrum, there is only one sharp signal at 326.9 ppm which is between the values for homoleptic stannylenes {2-[(CH₃)₂NCH₂][C₆H₄]₂Sn (144.5 ppm) [14] and Sn[N(SiMe₃)(2,6-*i*-Pr-C₆H₃)]₂ (439.6 ppm) [26] which are formed if **8** is heated or is left for a couple of days in toluene solution. **8** can be

Table 2
Selected bond lengths [Å] for compounds **5–8**.

Compound	Sn1–N1	Sn1–N2	Sn1–Cl1
5	2.0971(15)	2.0680(16)	–
6	2.272(3) ^a	2.267(3)	2.4401(11)
	2.272(3)	2.265(3)	2.4356(10)
6'	2.243(7)	2.308(6)	2.481(2)
6a	2.261(5)	2.253(5) ^b	2.822(2) ^c , 2.455(2) ^d , 2.792(2) ^e
8	2.133(3)	2.368(3)	–

^a Two independent molecules.

^b N1–Sn4.

^c Sn3–Cl1.

^d Sn4–Cl2.

^e Cl1a–Sn3.

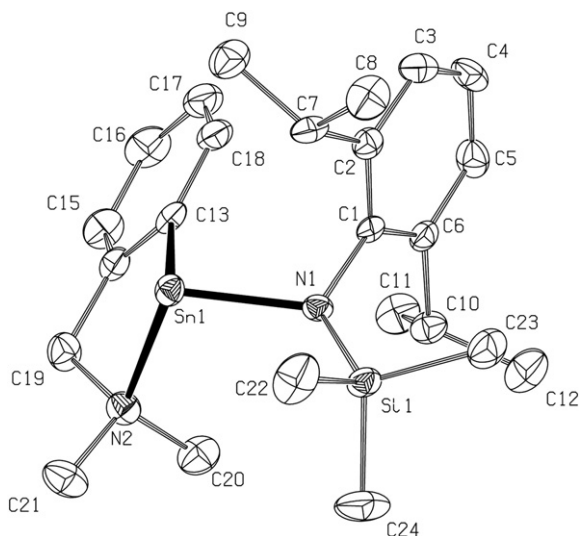


Fig. 5. The molecular structure (ORTEP 50% probability level) of **8**, hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Sn1–N1 2.133(3), Sn1–N2 2.368(3), Sn1–C13 2.205(3), Si1–N1 1.725(3), Si1–C22 1.870(4), Si1–C23 1.862(4), Si1–C24 1.863(4), N1–Sn1–N2 104.48(11), N1–Sn1–C13 97.22(12), N2–Sn1–C13 76.49(12), C1–N1–Si1 120.4(2), C1–N1–Sn1 113.7(2), Si1–N1–Sn1 121.00(15).

prepared also by mixing of stannylene $\{2-[(\text{CH}_3)_2\text{NCH}_2]\text{C}_6\text{H}_4\}_2\text{Sn}$ with $\text{Li}[\text{N}(\text{SiMe}_3)(2,6\text{-}i\text{-Pr-C}_6\text{H}_3)]$, where $2-[(\text{CH}_3)_2\text{NCH}_2]\text{C}_6\text{H}_4\text{Li}$ is isolated as a byproduct.

The polyhedral structure of **8** around the tin atom is a triangular pyramid defined by one carbon and two nitrogen atoms with nearly ideal interatomic angles around the tin atom. The distances Sn1–N1 and Sn1–C13 bond lengths are slightly higher than in **5**, because of lower oxidation state of the tin atom. On the other hand, the Sn1–N2 bond distance of 2.368(3) Å is significantly lower than in homoleptic stannylene $\{2-[(\text{CH}_3)_2\text{NCH}_2]\text{C}_6\text{H}_4\}_2\text{Sn}$ (2.516 and 2.660 Å) [14] and is the second shortest Sn–N distance found for a tin atom substituted by the $2-[(\text{CH}_3)_2\text{NCH}_2]\text{C}_6\text{H}_4$ -ligand, to be compared with 2.258 Å for cationic four-coordinated complex described previously [27].

Reactivity of interest of **8** is limited to low temperatures, because at higher temperatures, the reaction products can be formulated as resulting from the reactivity of the parent homoleptic stannylenes (for example the oxidation with chalcogens) [28] because of the decomposition of **8** to $\{2-[(\text{CH}_3)_2\text{NCH}_2]\text{C}_6\text{H}_4\}_2\text{Sn}$ and $\text{Sn}[\text{N}(\text{SiMe}_3)(2,6\text{-}i\text{-Pr-C}_6\text{H}_3)]_2$.

To conclude, we investigated both the reactivity and structure of aminotin compounds containing bulky amino as well as the C,N-chelating ligands. Both tin(IV) and tin(II) compounds were prepared including dimeric and monomeric stannylenes. Dimeric stannylene reacts with water to unique cluster.

3. Experimental

$(\text{L}^{\text{CN}})_2\text{SnBr}_2$ (**4**) [17] and $[(\text{Ar})(\text{SiMe}_3)\text{NSnCl}]_2$ (**7**) [12] were prepared according to published procedures. All solvents and starting compounds were obtained from commercial sources (Sigma–Aldrich). Toluene, THF, diethyl ether, benzene, *n*-hexane, *n*-pentane were dried over and distilled from potassium/sodium alloy with benzophenone, degassed and stored over potassium mirror under argon. Standard Schlenk techniques were used for all manipulations under an argon atmosphere.

4. Preparation of compounds studied

4.1. $(n\text{-Bu})_3\text{SnN}(\text{H})\text{Ar}$ (**2**)

$(n\text{-Bu})_3\text{SnCl}$ (1.814 g, 5.57 mmol) was dissolved in 30 mL of benzene and suspension of $\text{ArN}(\text{H})\text{Li}$ (1.021 g, 5.57 mmol) in 30 mL of benzene was added in 15 min. The reaction mixture was stirred at room temperature for 12 h. Afterwards the reaction mixture was filtered and the filtrate was evaporated *in vacuo* to dryness giving a yellow oily product. Yield 2.208 g (85%). ^1H NMR (C_6D_6 , 295 K, ppm): 7.12 (d, 2H, H(3')), 6.95 (t, 1H, H(4')), 3.32 (m, 2H, H(5')), 2.76 (s, 1H, NH), 1.58 (m, 6H, H(1')), 1.35 (m, 6H, H(2')), 1.27 (d, 12H, H(6')), 1.12 (m, 6H, H(3')), 0.97 (t, 9H, H(4')). ^{119}Sn NMR (C_6D_6 , 295 K, ppm): 40.1. Elemental analysis (%): found: C, 62.0; H, 9.9; N, 2.8; calcd for $\text{C}_{24}\text{H}_{45}\text{NSn}$ (466.32): C, 61.82; H, 9.73; N, 3.00.

4.2. $\text{Ph}_3\text{SnN}(\text{H})\text{Ar}$ (**3**)

Ph_3SnCl (1.673 g, 4.34 mmol) was dissolved in 30 mL of benzene and a suspension of $\text{ArN}(\text{H})\text{Li}$ (0.795 g, 4.34 mmol) in 30 mL of benzene was added in 15 min. The reaction mixture was stirred at room temperature for 12 h. Afterwards the reaction mixture was filtered and the filtrate was evaporated *in vacuo* to dryness giving yellow oily product. Yield 2.033 g (89%). ^1H NMR (C_6D_6 , 295 K, ppm): 7.60 (d, 6H, H(2')), 7.35 (m, 12H, H(3'), H(4')), 7.12 (d, 2H, H(3')), 6.98 (t, 1H, H(4')), 3.32 (m, 2H, H(5')), 2.72 (s, 1H, NH), 1.12 (d, 12H, H(6')). ^{119}Sn NMR (C_6D_6 , 295 K, ppm): –111.5. Elemental analysis (%): found: C, 68.7; H, 6.2; N, 2.8; calcd for $\text{C}_{30}\text{H}_{33}\text{NSn}$ (526.29): C, 68.47; H, 6.32; N, 2.66.

4.3. $(\text{L}^{\text{CN}})_2\text{Sn}[\text{N}(\text{H})\text{Ar}]_2$ (**5**)

$(\text{L}^{\text{CN}})_2\text{SnBr}_2$ (1.395 g, 2.55 mmol) was dissolved in 30 mL of diethyl ether and a solution of $\text{ArN}(\text{H})\text{Li}$ (0.935 g, 5.10 mmol) in 30 mL of diethyl ether was added dropwise at -78°C . The reaction mixture was then slowly warmed up and stirred for 1 h at room temperature. Afterwards the reaction mixture was filtered and the filtrate was evaporated *in vacuo* to dryness giving the sole product. Yield 1.811 g (96%). Single crystals of **4** were obtained from saturated diethyl ether solution at -30°C . M.p. 218–221 $^\circ\text{C}$. ^1H NMR (C_6D_6 , 295 K, ppm): 8.20 (d, 2H, H(6), $^3J(^{119}\text{Sn}, ^1\text{H}) = 72.1$ Hz), 7.28 (t, 1H, H(4)), 7.23 (m, 2H, H(3,5)), 7.15 (d, 2H, H(3)), 7.13 (d, 2H, H(3')), 6.98 (t, 1H, H(4)), 6.95 (t, 1H, H(4')), 3.98 (br, 1H, N'H), 3.49 (m, 2H, H(5)), 3.34 (br, 1H, N'H), 3.21 (s, 2H, NCH₂), 2.77 (m, 2H, H(5')), 1.93 (s, 6H, N(CH₃)₂), 1.24 (d, 24H, H(6)). ^{13}C NMR (C_6D_6 , 295 K, ppm): 141.84 (C1, $^1J(^{119}\text{Sn}, ^{13}\text{C}) = 782.5$ Hz), 137.3 (C6, $^2J(^{119}\text{Sn}, ^{13}\text{C}) = 47.7$ Hz), 129.97 (C4), 129.45 (C3), 127.68 (C5), 123.44 (C4'), 66.16 (NCH₂, $^3J(^{119}\text{Sn}, ^{13}\text{C}) = 27.6$ Hz), 45.94 (N(CH₃)₂), 29.55 (C5'), 28.5 (C5'), 24.1 (C7'), 22.8 (C7'). ^{15}N NMR (C_6D_6 , 295 K, ppm): –351.3 (CH₂N(CH₃)₂), –335.1 (NH), –330.2 (NH). ^{119}Sn NMR (C_6D_6 , 295 K, ppm): –161.1. Elemental analysis (%): found: C, 68.0; H, 8.3; N, 7.7; calcd for $\text{C}_{42}\text{H}_{60}\text{N}_4\text{Sn}$ (739.66): C, 68.20; H, 8.18; N, 7.57.

4.4. $[\text{Ar}(\text{H})\text{NSnCl}]_2$ (**6**)

A suspension of $\text{ArN}(\text{H})\text{Li}$ (0.855 g, 4.67 mmol) in 40 mL of benzene was added dropwise to suspension of SnCl_2 (0.885 g, 4.67 mmol) in 20 mL of benzene. The reaction mixture was stirred for 12 h at room temperature. The precipitate was filtered off and the filtrate was evaporated to dryness *in vacuo* giving a crude solid product. The crude product was washed twice with 20 mL of hexane giving white crystalline **6**. Yield 0.799 g (52%). M.p. 227–229 $^\circ\text{C}$. ^1H NMR (Tol-d₈, 295 K, ppm): 7.02 (d, 4H, H(3')), 6.89 (t, 2H, H(4')), 5.82 (s, 2H, NH, $^2J(^{119}\text{Sn}, ^1\text{H}) = 22.3$ Hz), 3.62 and 2.75 (br, 4H, H(5')), 1.14 (d, 24H, H(6')). ^{119}Sn VT-NMR (Tol-d₈, ppm): –22.1 (320 K), –29.5

(295 K), –47.8 (250 K), –55.2 (220 K). Elemental analysis (%): found: C, 43.8; H, 5.6; N, 4.1; calcd for C₂₄H₃₆N₂Cl₂Sn₂ (660.86): C, 43.62; H, 5.49; N, 4.24.

4.5. $L^{CN}SnN[(SiMe_3)Ar]$ (**8**)

A suspension of $L^{CN}Li$ (0.545 g, 3.86 mmol) in 30 mL of diethyl ether was added to a solution of **7** (1.555 g, 1.93 mmol) in diethyl ether (30 mL) at –30 °C in 20 min. The reaction mixture was slowly warmed up to room temperature and stirred overnight. The colour of the mixture changed from light to deep yellow. Afterwards, the reaction mixture was evaporated to dryness *in vacuo* and the solid residue was extracted with hexane (2 × 20 mL). Evaporation of volatiles from the hexane extracts gave yellowish crystalline **8**. Yield 1.029 g (54%). M.p. 44–47 °C. 1H NMR (Tol-d₈, 300 K, ppm): 7.97 (d, 1H, H(6)), $^3J(^{119}Sn, ^1H) = 62.2$ Hz, 7.36 (m, 3H, H(4, 4', 5)), 7.08 (d, 2H, H(3')), 7.01 (d, 1H, H(3)), 3.64 (m, 2H, H(5')), 3.43 (s, 2H, NCH₂), 2.34 (s, 3H, NCH₃), 2.27 (s, 3H, NCH₃), 1.42 (d, 12H, H(6')), 0.30 (s, 9H, SiMe₃). ^{119}Sn NMR (Tol-d₈, 300 K, ppm): 326.9. Elemental analysis (%): found: C, 57.7; H, 7.7; N, 5.4; calcd for C₂₄H₃₈N₂SiSn (501.36): C, 57.50; H, 7.64; N, 5.59.

4.6. NMR spectroscopy

The NMR spectra were recorded from solutions in toluene-d₈ or benzene-d₆ on a Bruker Avance 500 spectrometer (equipped with Z-gradient 5 mm probe) at frequencies 1H (500.13 MHz), $^{13}C\{^1H\}$ (125.76 MHz), $^{15}N\{^1H\}$ (50.65 MHz), and $^{119}Sn\{^1H\}$ (186.50 MHz) and at 220–320 K. The solutions were obtained by dissolving of 40 mg of each compound in 0.5 ml of deuterated solvents. The values of 1H chemical shifts were calibrated to internal standard - tetramethylsilane ($\delta(^1H) = 0.00$ ppm) or to residual signals of benzene ($\delta(^1H) = 7.16$ ppm), toluene ($\delta(^1H) = 2.09$ ppm). The values of ^{13}C chemical shifts were calibrated to signals of benzene ($\delta(^{13}C) = 128.3$ ppm), ^{15}N chemical shifts to external neat

nitromethane ($\delta(^{15}N) = 0.0$), and ^{119}Sn chemical shifts to external Me₄Sn (0.0 ppm).

4.7. Crystallography

The X-ray data (Table 3) for colorless crystals of **5**, **6**, **6'**, **6a** and **8** were obtained at 150K using Oxford Cryostream low-temperature device on a Nonius KappaCCD diffractometer with MoK α radiation ($\lambda = 0.71073$ Å), a graphite monochromator, and the φ and χ scan mode. Data reductions were performed with DENZO-SMN [29]. The absorption was corrected by integration methods [30]. Structures were solved by direct methods (Sir92) [31] and refined by full matrix least-square based on F^2 (SHELXL97) [32]. 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 $H_{iso}(H) = 1.2 U_{eq}(\text{pivot atom})$ or of $1.5 U_{eq}$ 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, 0.86 and 0.82 Å for N–H and O–H groups, respectively. There are disordered solvent benzene molecules in this structure. Attempts were made to model this disorder or split it into two positions, but were unsuccessful. PLATON/SQUEZZE [33] was used to correct the data for the presence of disordered solvent. A potential total solvent volume of 1566 Å³ was found. 569 electrons per unit cell worth of scattering were located in the voids. The calculated stoichiometry of solvent was calculated to be twelve molecules of benzene per unit cell which results in 504 electrons per unit cell.

4.8. Theoretical calculations

All calculations were conducted at the DFT level using the PBE functional [34]. Valence electrons were treated using a TZ2P basis set. Innermost electrons of Sn, Cl, C, and N atoms were emulated using effective core potentials ECP-SBKJC [35]. Calculations were made using the PRIRODA program [36].

Table 3
Crystallographic data for **5**, **6**, **6'**, **6a** and **8**.

Compound	5	6'	6	6a	8
Empirical formula	C ₄₂ H ₆₀ N ₄ Sn	C ₂₄ H ₃₆ Cl ₂ N ₂ Sn ₂	C ₅₄ H ₇₈ Cl ₂ N ₂ Sn ₂	C ₃₆ H ₅₅ Cl ₆ N ₃ O ₇ Sn ₁₀ ·C ₆ H ₆	C ₂₄ H ₃₈ N ₂ SiSn·4C ₆ H ₆
Crystal system	Monoclinic	Monoclinic	Monoclinic	Trigonal	Orthorhombic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> –3	<i>P</i> bca
<i>a</i> (Å)	11.0461(2)	23.6781(9)	24.9031(12)	17.0032(12)	15.6031(14)
<i>b</i> (Å)	19.5800(3)	9.4303(12)	8.8753(14)	17.0032(18)	16.1323(18)
<i>c</i> (Å)	19.0449(3)	12.1867(8)	36.3628(13)	22.3289(12)	19.8168(15)
β (°)	105.6781(8)	109.46(6)	133.099(9)	90, $\gamma = 120$	90
<i>Z</i>	4	4	8	2	8
<i>V</i> (Å ³)	3965.82(11)	2565.6(2)	5868.2(11)	5590.5(11)	4988.1(8)
<i>D_c</i> /g cm ^{–3}	1.239	1.711	1.584	1.303	1.335
Crystal size (mm)	0.32 × 0.30 × 0.20	0.29 × 0.15 × 0.15	0.17 × 0.15 × 0.11	0.41 × 0.31 × 0.12	0.25 × 0.14 × 0.14
Crystal shape	Colorless prism	Colorless block	Colorless plate	Colourless plate	Yellow block
μ (mm ^{–1})	0.677	2.169	1.902	2.363	1.084
<i>F</i> (000)	1560	1312	2792	2060	2080
<i>h</i> ; <i>k</i> ; <i>l</i> range	–14, 14; –25, 25; –24, 24	–29, 30; –12, 12; –15, 15	–32, 32; –11, 11; –47, 47	–22, 18; –18, 22; –29, 25	–17, 20; –16, 20; –25, 22
θ range/°	3.04; 27.51	3.12; 27.5	2.55; 27.5	2.29; 27.5	3.26; 27.5
Reflections measured	56173	16777	121477	24924	23595
– independent (<i>R_{int}</i>) ^a	9096 (0.0281)	2916 (0.1253)	13483 (0.0517)	8294 (0.1089)	5703 (0.0744)
– observed [<i>I</i> > 2 σ (<i>I</i>)]	6780	1785	10191	4869	3795
Parameters refined	445	136	595	190	253
Max/min $\Delta\rho$ /eÅ ^{–3}	0.838/–0.455	1.565/–2.698	1.069/–1.196	0.974/–1.296	1.565/–2.698
GOF ^b	1.018	1.056	1.095	0.916	1.068
<i>R</i> ^c / <i>wR</i> ^c	0.0268/0.0590	0.0646/0.1214	0.0397/0.0629	0.0531/0.1259	0.0450/0.0626

^a $R_{int} = \sum |F_o^2 - F_{o,mean}^2| / \sum F_o^2$.

^b $GOF = [\sum (w(F_o^2 - F_c^2))^2] / (N_{diffs} - N_{params})^{1/2}$ for all data.

^c $R(F) = \sum |F_o| - |F_c| / \sum |F_o|$ for observed data, $wR(F^2) = [\sum w(F_o^2 - F_c^2)^2] / (\sum w(F_o^2)^2)^{1/2}$ for all data.

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Appendix A. Supplementary material

CCDC Nos. 765424, 765420, 765421, 765423 and 765422 contain crystallographic data for the structural analysis of compound **5**, **6**, **6a** and **8**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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