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PAPER

Reactivity of lithium n-butyl amidinates towards group 14 metal(II) chlorides providing series of hetero- and homoleptic tetrylenes†

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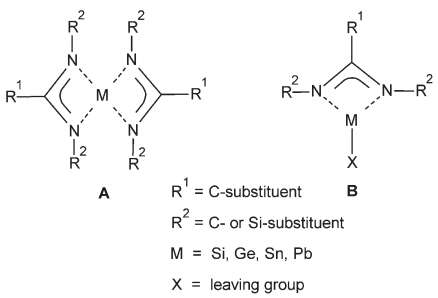
The new class of homo- and heteroleptic n-butyl-*N*,*N*′-disubstituted amidinato group 14 metal(II) complexes were prepared by salt elimination from starting lithium amidinates and metal(II) chlorides both in stoichiometric ratio 2 : 1 and 1 : 1, respectively. The target amidinates contain less bulky isopropyl or cyclohexyl as well as a sterically demanding aromatic substituent. Desired 1 : 1 Pb(II) complexes are not accessible by the described procedure. Ligand transfer from Pb to Sn is taking place if homoleptic Pb(II) compounds are reacted with $SnCl_2$. Prepared tetrylenes were characterized by ^{1}H, ^{13}C, ^{119}Sn and ^{207}Pb NMR spectroscopy in C_6D_6 or THF-d_8. X-Ray diffraction studies of one heteroleptic Ge(II) monomeric where the coordination polyhedron of the three coordinated germanium atoms is a trigonal pyramid, two different dimeric structures of heteroleptic Sn(II) complexes, one amidine hydroiodide byproduct and the oxidation product of the heteroleptic chloro Sn(II) amidinate as a tetranuclear species with two Sn(IV) and two Sn(II) atoms in central Sn_2O_2 planar ring were performed on appropriate single crystals. The dimer of one of the heteroleptic stannylenes reveals a new type of monomeric units connection, weak Sn–Cl contact and an interaction of the tin atom with delocalized N–C(C)–N system of the amidinato ligand of the second molecule.

1. Introduction

The amidinates,[1] formally *N*′,*N*-disubstituted amidoimides, have become very popular ligands especially for stabilization/specific activation of low valent metal centres of a whole periodic system, within the last decade. The f- [2] and d-element[3] complexes are frequently studied because of their catalytic activity of various processes, s-element[4] complexes as precursors for other metal complexes or reducing agents. The investigation of new p-block metal or metalloid complexes,[5,3f] especially of group 14 elements[6] is a current topic in this field. The stabilization of lower oxidation states of these elements through the formation of unsaturated four-membered diazametalla ring(s) produces interesting complexes with remarkable properties.[7] The heavier elements of group 14 metal complexes with the metal atom in a lower oxidation state are widely accepted as carbene,[8] radical[9] or alkyne[10] analogues. With a lone electron pair and a vacant π-orbital on the central atom they can be seen as Lewis amphoters. Particular attention has been paid to the reactivity of these compounds in oxidative addition reactions,[11] in activation of small molecules,[12] in use as carbene analogues for complexation[13] of transition metal complexes and in reductions to metal clusters.[14] Two types of these metal complexes with group 14 elements in the oxidation state of II (tetrylenes) are known. The first one is the homoleptic type of compounds (Scheme 1A) containing the same amidinato ligands in the molecule. To the best of our knowledge there exist no reactivity studies of these compounds. On the other hand the reactivity of the second type, heteroleptic one (Scheme 1B), where the only one amidinato unit is employed, with various reducing agents is the subject of numerous papers.[15,6g] These reduced amidinato complexes or their



Scheme 1 Homoleptic (A) and heteroleptic (B) type of tetrylene amidinates.

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†Electronic supplementary information (ESI) available: ^{13}C CP/MAS NMR spectrum and details of the coordination sphere of tin atoms of **5a**; molecular structure of $L^{Cy}HI$. CCDC 858674 (for **7**), 858678 (for **8**), 858676 (for **9**), 858677 (for **5a**) and 858675 (for $\mathbf{L^{Cy}HI{\cdot}C_6H_6}$). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt12472f

precursors can activate unsaturated systems[16,6b,6h] or small molecules.[17,15c]

This paper deals with the preparation and structural studies of n-butyl amidinato *N*′,*N*-disubstituted (formally derivatives of pentanoic acid) complexes of Ge, Sn and Pb in the oxidation state II. Only one homoleptic *N*,*N*′-diisopropyl n-butylamidinato germanium(II) complex is reported as MOCVD precursor of germanium compounds.[18] The main objective of this study is to prepare such complexes that contain a rather flexible aliphatic chain which could facilitate further reactivity studies in respect of higher solubility of products in comparison to used amidinates.

2. Results and discussion

2.1. Synthesis

The preparation of desired complexes *via* the salt elimination reactions from various lithium n-butyl amidinates[19] and $GeCl_2$·-dioxane complex (1 : 1), $SnCl_2$ and $PbCl_2$, respectively, in molar ratio 1 : 1 or 2 : 1 has been performed according to Fig. 1 in rather good yields. The preliminary attempts to prepare germanium(II) amidinates from GeI_2 as a germanium source led to the mixture of rather insoluble products from which only a minor part crystallizes the adduct of free ligand with HI ($L^{Cy}HI$, for the crystal structure see ESI†). These problems were eliminated by the use of $GeCl_2$·dioxane complex instead of GeI_2. The reactions of lithium n-butyl amidinates with $PbCl_2$ in both stoichiometric ratios 1 : 1 and 2 : 1 led to the same product, formation of homoleptic plumbylenes only. On the other hand, there is only one amidinato lead complex described until now, and in a series of related guanidinato complexes, the only reported types are a few heteroleptic complexes.[20] All reactions of lithium amidinate precursors with $PbCl_2$ have to be conducted in the dark because of the instability of lead amidinates on the light which is reflected in an elimination of elemental Pb from the solution.

Attempts to prepare heteroleptic plumbylenes from $SnCl_2$ and $L^{iPr}{}_2Pb$ (**12**) or $L^{Cy}{}_2Pb$ (**15**), respectively, were made. When **12** was stirred with equimolar amount of $SnCl_2$ in THF at room temperature for 20 min, the desired heteroleptic plumbylene was not observed but a mixture of corresponding homo- and heteroleptic stannylenes 18 : 1 has been detected with the help of ^{119}Sn NMR in solution. When the reaction time was prolonged to 4 h, the reaction mixture contains no plumbylenes but the molar ratio of corresponding homo- and heteroleptic stannylenes was 1 : 1. Surprisingly, after two days the equilibrium of the reaction was moved towards the excess of homoleptic stannylene to 3 : 1. Similar reactions of **15** with $SnCl_2$ led after 4 h to the homoleptic stannylene **14** as the sole product. After 3 days at the same conditions the ratio of homo-(**14**) and heteroleptic (**7**) stannylenes was changed to 1 : 3. The $PbCl_2$ was detected ($\delta(^{207}Pb)$ *ca.* −1730 ppm)[21] in the solid residue using ^{207}Pb MAS NMR spectroscopy after all reactions.

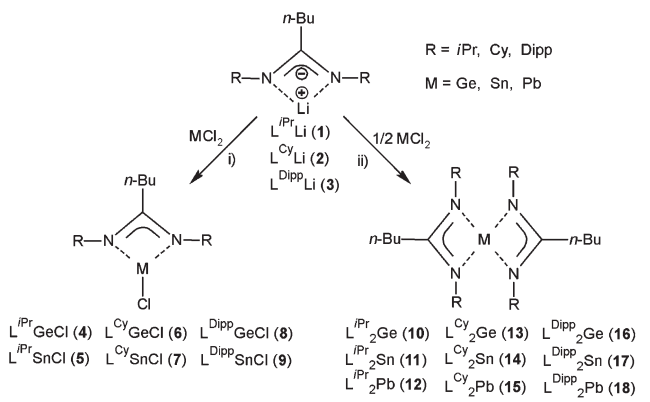


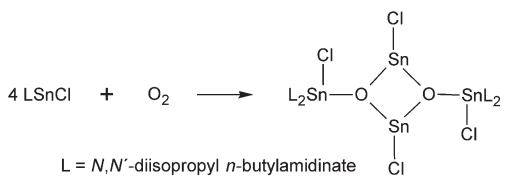
Fig. 1 Reagents and conditions: (i) Et_2O, −60 °C to RT, −LiCl; (ii) Et_2O, RT, −2LiCl (darkness in the case of Pb).

Accidentally, when the stopcock of the Schlenk tube was not sufficiently greased, the insoluble colourless crystalline material of **5a** as the oxidation product of **5** was obtained by slow diffusion of air. The process is fully reproducible and is described in the Experimental section. The formation of **5a** could be understood as the reaction of four molecules of heteroleptic stannylene **5** with a molecule of oxygen (Scheme 2). There is obvious oxidation of two tin(II) atoms to tin(IV) only. The migration of the amidinato units from tin(II) to tin(IV) atoms takes place and the formation of the central 1,3-Sn_2O_2 ring is the main structural motif of this compound (for more details of NMR and X-ray studies see below).[22] **5a** is one of the rare examples of compounds where both stable oxidation states are present[23] but the only example of a compound where low-valent tin atoms are connected together as well as with tin(IV) atoms by oxygen bridges.

2.2. NMR spectroscopic studies in solution

Compounds **4–18** were investigated by multinuclear NMR approach in solution with a view to elucidating their structural behaviour. The ^1H NMR spectra reveal one set of signals for each symmetry independent group in C_6D_6 as well as in THF-d_8, as an example of a coordinating solvent, for an aliphatic chain or ring substituted heteroleptic amidinates **4–7**, while the *N*,*N*′-cyclohexyl substituted compounds **6** and **7** show broadening of aliphatic signals. The bulky aromatic group substituted heteroleptic compounds **8**, **9** and homoleptic **16–18** have dynamic behavior in solution, and, thus, the ^1H NMR spectra are quite complex. On the other hand, from the ^1H NMR spectra of the rest of the homoleptic compounds **10–15** the deduction about the higher symmetry of compounds in solution is made on the basis of simple spectral patterns.

In the ^{13}C NMR spectra of heteroleptic compounds **4–9** the signals for the central *ipso* carbon atom are found around 176 ppm, while the lowest values of *ca.* 174 ppm are attributed to the germylenes **4** and **6** in C_6D_6 solution. For compounds **5** and **9** little decreases by 2 ppm are caused by changing of the solvent to THF-d_8 and contrasted with all ^{13}C NMR spectral



Scheme 2 Reaction route leading to **5a**.

Table 1 Selected NMR spectra parameters

Compound	Solvent	δ ($^{13}C_{ipso}$)	δ ($^{119}Sn/^{207}Pb$)
$L^{iPr}GeCl$ (**4**)	C_6D_6	174.2	—
$L^{iPr}SnCl$ (**5**)	C_6D_6	178.1	78.9
	THF-d_8	176.2	69.1
$L^{Cy}GeCl$ (**6**)	C_6D_6	174.8	—
$L^{Cy}SnCl$ (**7**)	C_6D_6	177.8	75.7
	THF-d_8	177.9	69.7
$L^{Dipp}GeCl$ (**8**)	C_6D_6	177.2	—
$L^{Dipp}SnCl$ (**9**)	C_6D_6	179.2	29.4
	THF-d_8	175.9	−124.0
$L^{iPr}{}_2Ge$ (**10**)	C_6D_6	165.8	—
$L^{iPr}{}_2Sn$ (**11**)	C_6D_6	168.2	−252.3
$L^{iPr}{}_2Pb$ (**12**)	C_6D_6	168.8	1734.8
	THF-d_8	169.5	1743.5
$L^{Cy}{}_2Ge$ (**13**)	C_6D_6	166.1	—
$L^{Cy}{}_2Sn$ (**14**)	C_6D_6	168.8	−255.3
$L^{Cy}{}_2Pb$ (**15**)	C_6D_6	168.6	1729.0
	THF-d_8	169.8	1745.6
$L^{Dipp}{}_2Ge$ (**16**)	C_6D_6	169.8	—
$L^{Dipp}{}_2Sn$ (**17**)	C_6D_6	171.7	−341.3
$L^{Dipp}{}_2Pb$ (**18**)	C_6D_6	170.4	1541.3
	THF-d_8	171.3	1540.1

parameters of the remaining heteroleptic stannylene **7** which are solvent independent. These values of the specified *ipso* carbon atom are in line with the appropriate values for known *t*-butylamidinato substituted germylene (~176 ppm)[24] and stannylene (~180 ppm).[25] The values of the same parameter of homoleptic compounds **10–18** are much lower ~168 ppm than in comparable heteroleptic compounds, all are solvent independent, and the increase in these values in the row from germylenes to plumbylenes is quite significant. The highest chemical shifts are found for bulky Dipp substituted compounds **16–18**.

^{119}Sn NMR spectroscopy, which is very significant in the investigation of coordination polyhedra of tin s,[26] has been used in studies of compounds **5**, **7**, **9**, **11**, **14** and **17**. The tin chemical shifts of all heteroleptic stannylenes except for **9** are found to be solvent independent at similar values in C_6D_6 and THF-d_8 (see Table 1). The appropriate value for Dipp substituted stannylene **9** is a bit lower (29.4 ppm) in C_6D_6, when dissolved in THF-d_8 a high field shift of *ca*. 150 ppm is observed, probably caused by increase of the coordination number of the tin atom to four. For homoleptic stannylenes **11**, **14** and **17** a direct comparison with the compounds bearing the same substituent can be made, the δ(^{119}Sn) decrease of ~350 ppm is seen for each pair of hetero- and homoleptic stannylenes. The same trend was also observed in the literature for related methyl and *t*-butyl amidinato stannylenes.[6d,25]

There is no literature comparison for ^{207}Pb NMR spectra in solution of amidinato plumbylenes **12**, **15** and **18** but it could be a generally helpful tool for further structural studies of amidinato, guanidinato and formamidinato plumbylenes in solution. The δ(^{207}Pb) around 5000 ppm are found for lead bisamides[27] where the lead coordination number is two, for four-coordinated complexes of lead(II) a decrease of the chemical shift is found (2624 ppm [28] and 1816 ppm [29]). In compounds **12**, **15** and **18** solvent independent ^{207}Pb chemical shifts were found in a similar range while for aliphatic group substituted plumbylenes **12** and **15** the ~200 ppm higher chemical shift were observed.

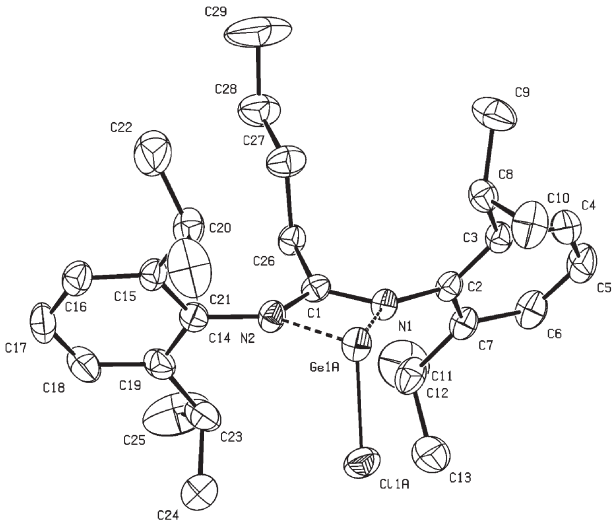


Fig. 2 Molecular structure of $L^{Dipp}GeCl$ (**8**) (ORTEP view, 50% probability level). Hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: N1–C1 1.322(5); N1–C2 1.436(4); N1–Ge1a 2.029(3); N2–C1 1.339(5); N2–C14 1.429(5); N2–Ge1a 2.019 (3); C1–C26 1.493(5); C1–Ge1a 2.475(4); Ge1a–Cl1a 2.2400(13); N1–C1–N2 108.9(3); N1–Ge1a–N2 64.69(12); C1–Ge1a–Cl1a 102.63(11); C14–C1–C2 164.1(2).

The ^{13}C and ^{119}Sn MAS NMR spectra of **5a** were measured (see ESI†), a rather simple ^{13}C NMR spectrum reveals all the carbon signals in a similar range found for **5** in solution, except of the amidinato *ipso* carbon signal which is located at 164 ppm. Surprisingly, only the signal for tin(IV) atoms is observed at −600 ppm which indicates the coordination number of the tin atoms to be six, the resonance for tin(II) remains silent.

2.3. Crystal structure determination by X-ray diffraction

For five of the compounds studied the crystal structure has been determined by means of X-ray diffraction techniques on single crystalline material. Three of the molecular structures are of heteroleptic germylene and stannylenes. The common feature of the heavier elements heteroleptic tetrylenes is an easy formation of dimeric structures either *via* chlorido or amido bridges.[29–31] On the other hand, related silylenes and germylenes tend to be monomeric.

The germanium atom in the molecular structure of **8** (Fig. 2) is three-coordinated with the coordination polyhedra of trigonal pyramid as reported for analogues of monomeric *t*-butyl/phenyl amidinatogermylenes [Dipp-NC(*t*-Bu)N-Dipp]GeCl and [*t*-Bu-NC(Ph)N-*t*-Bu]GeCl, respectively.[24,32] Based on the comparison of interatomic distances and angles in these three structures, a conclusion about the same structure is made.

On the other hand, tin atoms in amidinato or guanidinato substituted stannylenes are ready to increase their coordination number to four by an interaction with adjacent donor groups as for example halides, to form infinite chains[6d] or dimers in the solid state.[31]

Compound **9** is an asymmetric dimer in the solid state (Fig. 3). The amidinato units are nearly symmetrically bonded to the tin atoms together with one covalently bonded chlorine

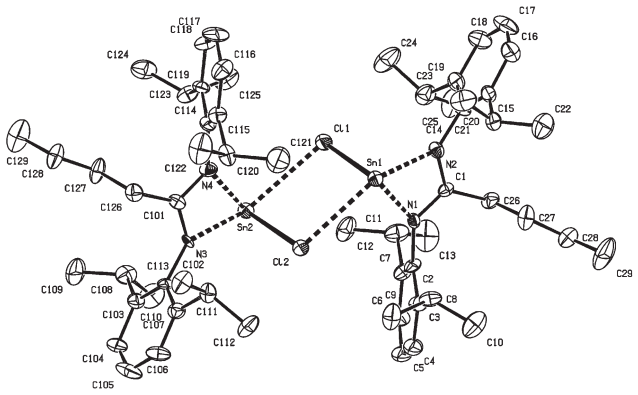


Fig. 3 Molecular structure of $[L^{Dipp}SnCl]_2$ (**9**) (ORTEP view, 50% probability level). Hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: N1–C1 1.322(11); N1–C2 1.422(12); N2–C1 1.316(12); N2–C14 1.419(13); C1–C26 1.523(13); N3–C101 1.320(12); N4–C101 1.342(12); N3–C102 1.427(12); N4–C114 1.426(12); C101–C126 1.487(13); N1–Sn1 2.192(8); N2–Sn1 2.251(9); N3–Sn2 2.248(9); N4–Sn2 2.198(8); C1–Sn1 2.662(9); C101–Sn2 2.678(9); Cl1–Sn1 2.482(2); Cl2–Sn1 2.986(3); Cl2–Sn2 2.484(2); Cl1–Sn2 3.033(3); N1–C1–N2 112.3(8); N3–C101–N4 111.1(8); C2–C1–C14 167.4(5); C102–C101–C114 166.3(5); N1–Sn1–N2 59.0(3); N4–Sn2–N3 59.2(3); C1–Sn1–Cl1 96.33(19); C101–Sn2–Cl2 96.89 (19); Sn1–Cl1–Sn2 101.98(9); Cl1–Sn1–Cl2 77.80(8).

atom. The coordination polyhedra are completed by a weak interaction with the second type of chlorine atoms. The interactions between the tin atoms and coordinated chlorine atoms Sn1–Cl2 and Sn2–Cl1 are much longer than the covalent bonds Sn–Cl but still in the range of the sum of the van der Waals radii of both atoms. The intermolecular interaction Sn–Cl in [*t*-Bu-NC(Ph)N-*t*-Bu]SnCl[6d] which forms an infinite linear chain is even weaker (3.602 Å) than the same type of connection in **9**. The rest of interatomic distances and angles is comparable with the same values found in the previously published monomeric heteroleptic amidinato stannylene [Dipp-NC(*t*-Bu)N-Dipp]SnCl.[25]

The new type of intermolecular connection is responsible for the formation of a dimer of **7**. The molecules are interconnected by one weak Sn1b–Cl1 contact and an interaction of the tin atom Sn1 with a delocalized N1c–C1b(C8b)–N1b system of the amidinato ligand of the second molecule. To the best of our knowledge, this type of interaction has not been known up until now in the chemistry of amidinato and related ligands of the main group metals. The saturation of the tin empty orbitals with π-electrons of the second amidinato unit is probably the reason for this interaction. The shape of coordination polyhedra of the tin atom in **7** is quite similar to the shape of the polyhedra in **9**.

The characteristic C1–Sn1–Cl1 angle and the covalent Sn–Cl bond distances in stannylene **7** and **9** are comparable with the same parameters in the known heteroleptic stannylenes [Dipp-NC(*t*-Bu)N-Dipp]SnCl[25] (96.64(3)°; 2.4282(6) Å) and [*t*-Bu-NC(Ph)N-*t*-Bu]SnCl[6d] (95.43(7)°; 2.4831(9) Å). On the other hand, the changing of these parameters (shortening of the bonding distance and extension of the interatomic angle) going from the discussed stannylenes to germylenes **8**, [Dipp-NC(*t*-Bu)N-Dipp]GeCl (104.61(18)°; 2.174(2) Å) and [*t*-Bu-NC(Ph)N-*t*-Bu]GeCl (100.21(5)°; 2.2572(13) Å) is caused by the difference in covalent radii of both central atoms (Fig. 3 and 4).

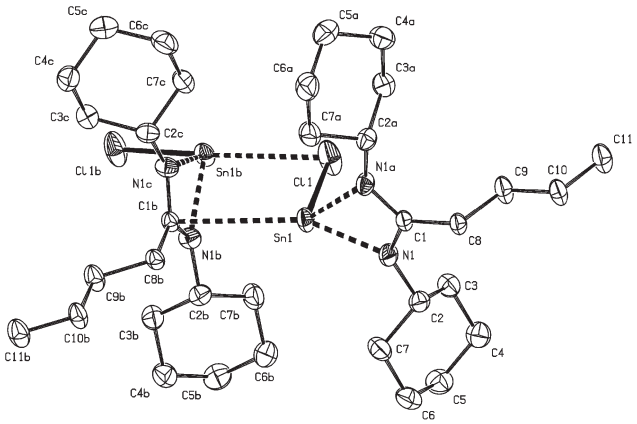


Fig. 4 Molecular structure of $L^{Cy}SnCl$ (**7**) (ORTEP view, 50% probability level). Hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: N1–C1 1.325(4); N1–C2 1.459(4); N1–Sn1 2.195(3); N1a–C1 1.325(4); N1a–C2a 1.459(4); N1a–Sn1 2.195(3); C1–Sn1 2.661(6); Sn1–Cl1 2.4823(18); C1–C8 1.506(7); Cl1–Sn1b 3.4089(19); C1b–Sn1 3.597(6); N1–C1–N1a 110.4(4); N1–Sn1–N1a 59.40(10); C1–Sn1–Cl1 96.67(13); C1–C8–C9 113.2(4); C2a–C1–C2 165.8(3); Sn1–Cl1–Sn1b 97.96(6); Sn1–C1b–Sn1b 90.32 (17).

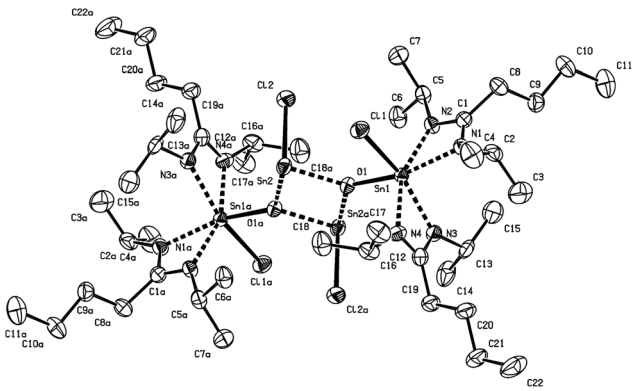


Fig. 5 Molecular structure of $\{[L^{iPr}{}_2SnCl]\text{-}\mu^2\text{-}(OSnCl)\}_2$ (**5a**) (ORTEP view, 50% probability level). Hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: N1–C1 1.322(9); N1–C2 1.456(9); N2–C1 1.340(8); N2–C5 1.467(9); C1–C8 1.516(8); N3–C12 1.338(8); N4–C12 1.339(8); N3–C13 1.482(8); N4–C16 1.475(7); C12–C19 1.339(8); N1–Sn1 2.203(5); N2–Sn1 2.141(5); N3–Sn1 2.200 (5); N4–Sn1 2.153(5); C1–Sn1 2.611(6); C12–Sn1 2.633(7); Cl1–Sn1 2.4287(17); O1–Sn1 2.028(4); O1–Sn2 2.117(5); Cl2–Sn2 2.4801(19); O1–Sn2a 2.134(3); N1–C1–N2 112.3(5); N3–C12–N4 111.0(6); C2–C1–C5 169.7(3); C13–C12–C16 169.1(4); N1–Sn1–N2 61.15(19); N4–Sn1–N3 60.93(18); C1–Sn1–Cl1 93.49(13); C12–Sn1–O1 95.05(19); C1–Sn1–C12 119.4(2); O1–Sn2–Cl2 95.35(13); O1–Sn1–Cl1 89.20 (12); Sn2–O1–Sn2a 103.00(17); Sn2–Sn2a–Cl2a 97.78(9).

The tetranuclear structure of **5a** consists of the central Sn_2O_2 planar ring where the tin atoms are in the oxidation state +II with the coordination vicinity of a trigonal pyramid. Each of the tin (Sn2, Sn2a) coordination polyhedra is constructed of two bridging oxygens, one chlorine atom at the base of the pyramid and the lone electron pair situated in an apical position. The arrangement of this fragment as well as the interatomic distances and angles (see Fig. 5) are very close to the reported compounds

Table 2 Crystallographic data for **7**, **8**, **9**, **5a** and $L^{Cy}HI{\cdot}C_6H_6$

Compound reference	$L^{Cy}SnCl$ (**7**)	$L^{Dipp}GeCl{\cdot}1/18\ Et_2O$ (**8**)	$[L^{Dipp}SnCl]_2$ (**9**)	$\{[L^{iPr}{}_2SnCl]OSnCl\}_2$ (**5a**)	$L^{Cy}HI{\cdot}C_6H_6$
Chemical formula	$C_{17}H_{31}ClN_2Sn$	$C_{29}H_{43}ClGeN_2{\cdot}1/18(C_4H_{10}O)$	$C_{58}H_{86}Cl_2N_4Sn_2$	$C_{44}H_{92}Cl_4N_8O_2Sn_4$	$C_{23}H_{39}N_2I$
Formula mass	417.58	540.05	1147.59	1381.82	470.46
Crystal system	Orthorhombic	Hexagonal	Monoclinic	Monoclinic	Monoclinic
a/Å	17.1751(9)	40.6731(2)	9.8450(10)	23.5241(9)	10.5760(9)
b/Å	12.4098(11)	40.6731(2)	28.878(2)	17.8710(11)	15.2480(6)
c/Å	8.8522(9)	9.5350(4)	10.6540(8)	16.6439(7)	15.1009(11)
α (°)	90	90	90	90	90
β (°)	90	90	104.068(7)	123.122(12)	98.247(7)
γ (°)	90	120	90	90	90
Unit cell volume/Å^3	1886.7(3)	13 660.5(7)	2938.1(4)	5860.0(3)	2410.0(3)
T/K	150(1)	150(1)	150(1)	150(1)	150(1)
Space group	$Cmc2_1$	$R\bar{3}$	$P2_1$	$C2/c$	$P2_1/c$
No. of formula units per unit cell, Z	4	18	2	4	4
Absorption coefficient, μ/mm^{-1}	1.493	1.114	0.979	1.907	1.337
No. of reflections measured	9173	31 427	27 606	47 387	17 797
No. of independent reflections	2211	6764	12 365	6389	5456
R_{int}	0.0354	0.0683	0.0982	0.0594	0.0355
Final R_1 values ($I > 2\sigma(I)$)	0.0270	0.0675	0.0707	0.0491	0.0301
Final w$R(F^2)$ values ($I > 2\sigma(I)$)	0.0554	0.1210	0.1534	0.0690	0.0571
Goodness of fit on F^2	1.127	1.076	1.075	1.188	1.139

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

$[SnCl\text{-}\mu^2\text{-}(O^tBu)]_2$[33] and $\{SnCl\text{-}\mu^2\text{-}[OCr(NMe_2)_2Cl_2(THF)]\}_2$.[34] The only difference is the larger deviation of Sn–Cl bonds from the perpendicular arrangement with the central Sn_2O_2 plane (Sn2–Sn2a–Cl2a 97.78(9)°). Two tin(IV) atoms on the periphery of the molecule are joined to two tin(II) atoms by a three-centric oxygen bridge in an alternating fashion – 0.314 Å below and above the central plane, respectively. These tin atoms (Sn1, Sn1a) are pseudo-octahedrally coordinated by two asymmetrically bonded amidinato ligands in bidentate mode, chlorine and oxygen atom. The Sn1–Cl1 bond is parallel to the central Sn_2O_2 plane and shortened in comparison to the Sn2–Cl2 bond by *ca.* 0.05 Å. The asymmetrical bonding of the amidinato units, which are mutually nearly parallel (85.47(9)°), is probably caused by the stronger *trans*-effect of oxygen and chlorine atoms, where the differences in Sn–N distances are about 0.05 Å.

Compound **5a** is the third example of the tin(IV)bisamidinato substituted complex but the mutual comparison with previously reported bisamidinato tin sulfides is not very interesting because of the highly disordered structure with a strongly polarized double tin–sulfur bond in the first case and the less electrophilic sulfur substituents of the octahedral tin atom in the other one.[35]

3. Experimental

3.1 General methods

3.1.1 NMR spectroscopy. The NMR spectra of the compounds measured were recorded from solutions in benzene-d_6 and THF-d_8 on a Bruker Avance 500 spectrometer (equipped with *Z*-gradient 5mm probe) at frequencies for ^1H (500.13 MHz), $^{13}C\{^1H\}$ (125.76 MHz), and $^{119}Sn\{^1H\}$ (186.50 MHz) at 295 K and on a Bruker Avance II 400 spectrometer operating at 400.13 MHz for ^1H, and 81.49 MHz for ^{207}Pb at 295 K. All deuterated solvents were degassed and then stored over a K-mirror under argon atmosphere. Solutions were obtained by dissolving of approximately 40 mg (100 mg for ^{207}Pb measurements) of each compound approximately in 0.5 ml of deuterated solvents. ^1H chemical shifts were calibrated to an internal standard—tetramethylsilane ($\delta(^1H) = 0.00$) or to residual signals of benzene ($\delta(^1H) = 7.16$) and THF ($\delta(^1H) = 3.58$ or 1.73). The values of ^{13}C chemical shifts were calibrated to signals of THF ($\delta(^{13}C) = 67.6$) and benzene ($\delta(^{13}C) = 128.4$). All ^{13}C NMR spectra were measured using a standard proton-decoupled experiment and CH and CH_3 *vs.* C and CH_2 were differentiated using the APT method.[36] The ^{119}Sn and ^{207}Pb chemical shifts are referred to as external neat tetramethylstannane ($\delta = 0.0$) and tetraethyllead ($\delta = 0.0$), respectively, and measured using the inverse gated proton broad band decoupling mode.

The solid state NMR spectra were measured at 11.7 T using a Bruker Avance 500 WB/US NMR spectrometer in a double-resonance 4-mm probe head. Direct-polarization MAS NMR experiments with a high-power dipolar decoupling (TPPM) and sufficiently long recycle delays (RD) were preformed to obtain quantitative NMR spectra. ^{207}Pb MAS NMR spectra were acquired at 104.52 MHz; the spinning frequency was $\omega_r/2\pi = 11$ and 13 kHz; 90° pulse width was 3 μs; recycle delay of 10 s; and the number of scans was 2048. The spectra were referenced to $Pb(NO_3)_2$ at 0.0 ppm. ^{119}Sn MAS NMR spectra were acquired at 186.49 MHz; the spinning frequency was $\omega_r/2\pi = 11$ and 13 kHz; 90° pulse width was 3 μs; a recycle delay of 15 s; and the number of scans was 8200. The ^{119}Sn chemical shifts were calibrated indirectly using tetracyclohexyl tin ($\delta = -97.35$ ppm). The ^{119}Sn NMR chemical shift was allocated approximately in the centre of gravity of the signal.

3.1.2 Elemental analyses. The compositional analyses were determined under an inert atmosphere of argon on the automatic analyzer EA 1108 by FISONS Instruments.

3.1.3 Crystallography. The X-ray data (Table 2) obtained from colourless crystals for all compounds were acquired at

150 K using an Oxford Cryostream low-temperature device on a Nonius KappaCCD diffractometer with Mo-Kα radiation (λ = 0.71073 Å), a graphite monochromator, and in the ϕ and χ scan mode. Data reductions were performed with DENZO-SMN.[37] The absorption was corrected using integration methods.[38] The structures were solved by direct methods (Sir92)[39] and refined by a full matrix least-square based on F^2 (SHELXL97).[40] Hydrogen atoms were mostly localized on a difference Fourier map, but in order to ensure uniformity of the crystal treatment, all hydrogen atoms were recalculated into idealized positions (riding model) and assigned temperature factors $H_{iso}(H)$ = $1.2U_{eq}$(pivot atom) or of $1.5U_{eq}$ for the methyl moiety with C–H = 0.96, 0.97, 0.98 and 0.93 Å for methyl, methylene, methine and hydrogen atoms in aromatic rings and 0.86 Å for N–H, respectively. The positional disorder of Ge and Cl atoms in **8** is split into two positions with approximate ratio 9 : 1 and treated by standard SHELXL97[40] procedures. Higher residual electron density in 9 was treated using several methods but no better results of refinement were obtained, this maximum gave no chemical significance.

3.2 Synthesis

All syntheses were performed using the standard Schlenk techniques under inert argon atmosphere. Solvents and reactants were purchased from commercial sources. Solvents were distilled over K/Na alloy, degassed and then stored over a K-mirror under argon atmosphere. Single crystals suitable for X-ray diffraction analyses were obtained under argon from corresponding saturated solutions of products in Et_2O or hexane cooled to −30 °C. The melting points were measured in inert perfluoroalkylether and were uncorrected. Preparations of starting lithium *N*,*N*′-di(propan-2-yl)n-butylamidinate (**1**), lithium *N*,*N*′-bis(cyclohexyl) n-butylamidinate (**2**) and lithium *N*,*N*′-bis[2,6-di(propan-2-yl) phenyl]n-butylamidinate (**3**) are reported elsewhere.[19]

General procedure of preparation of heteroleptic tetrylene amidinates L^RMCl (4–9)

To a white suspension of metal(II) chloride in Et_2O cooled down to −60 °C, one equivalent of pure starting lithium *N*,*N*′-disubstituted n-butylamidinate precursor **1–3** dissolved in Et_2O was added. The reaction mixtures were slowly heated up to room temperature and stirred overnight. After that they were filtered from forming lithium chloride and Et_2O was evaporated under vacuo to give products of heteroleptic tetrylenes **4–9** in good yields.

General procedure of preparation of homoleptic tetrylene amidinates $(L^R)_2M$ (10–18)

To a white suspension of metal(II) chloride in Et_2O at room temperature, two equivalents of pure colorless Et_2O solution of starting lithium precursor **1–3** were added (reactions with lead dichloride have to be performed in the dark because of elimination of elemental Pb). The reaction mixtures were stirred overnight, filtered from forming lithium chloride and Et_2O was evaporated under vacuo. Pure products of homoleptic tetrylenes **10–18** in good yields were obtained.

3.2.1 Preparation of *N*,*N*′-di(propan-2-yl)n-butylamidinatogermanium(II) chloride ($L^{iPr}GeCl$) (4). 0.81 g of **1** (4.2 mmol), 0.97 g of $GeCl_2$ dioxane complex (1 : 1) (4.2 mmol), 30 ml of Et_2O. 1.13 g (92%) of colourless oily matter of **4**. ^1H NMR (C_6D_6, 500 MHz, 295 K) δ: 3.41 (m, 2H, C*H*); 1.81 (t, ^3J = 7.9 Hz, 2H, α-CH_2(Bu)); 1.26 (m, 2H, β-CH_2(Bu)); 1.15 (m, 2H, γ-CH_2(Bu)); 1.02 (br s, 12H, (CH_3)$_2$); 0.93 (t, 3H, ^3J = 7.3 Hz, CH_3). ^{13}C NMR (C_6D_6, 125 MHz, 295 K) δ: 174.2 (N═*C*(Bu)–N); 46.1 (*C*H); 28.6 (α-*C*H$_2$(Bu)); 25.3 (β-*C*H$_2$(Bu)); 23.3 (br s, (*C*H$_3$)$_2$); 22.5 (γ-*C*H$_2$(Bu)); 13.5 (*C*H$_3$). Elemental Anal. Calcd (%) for $C_{11}H_{23}ClGeN_2$: C 45.34; H 7.96; N 9.61. Found: C 45.12; H 7.85; N 9.78.

3.2.2 Preparation of *N*,*N*′-di(propan-2-yl)n-butylamidinatotin(II) chloride ($L^{iPr}SnCl$) (5). 1.22 g of **1** (6.3 mmol), 1.19 g of $SnCl_2$ (6.3 mmol), 30 ml of Et_2O. 1.83 g (84%) of colourless oily matter of **5**. ^1H NMR (C_6D_6, 500 MHz, 295 K) δ: 3.57 (m, 2H, C*H*); 1.82 (t, ^3J = 8.1 Hz, 2H, α-CH_2(Bu)); 1.31 (m, 2H, β-CH_2(Bu)); 1.15 (m, 2H, γ-CH_2(Bu)); 1.00 (d, 12H, ^3J = 6.3 Hz, (CH_3)$_2$); 0.77 (t, 3H, ^3J = 7.3 Hz, CH_3). ^{13}C NMR (C_6D_6, 125 MHz, 295 K) δ: 178.1 (N═*C*(Bu)–N); 46.6 (*C*H); 29.9 (α-*C*H$_2$(Bu)); 27.4 (β-*C*H$_2$(Bu)); 26.1 ((*C*H$_3$)$_2$); 23.5 (γ-*C*H$_2$(Bu)); 14.3 (*C*H$_3$). ^{119}Sn NMR (C_6D_6, 186 MHz, 295 K) δ: 78.9. ^1H NMR (THF-d_8, 500 MHz, 295 K) δ: 3.88 (m, 2H, C*H*); 2.25 (t, ^3J = 8.0 Hz, 2H, α-CH_2(Bu)); 1.58 (m, 2H, β-CH_2(Bu)); 1.45 (m, 2H, γ-CH_2(Bu)); 1.12 (d, 12H, ^3J = 6.3 Hz, (CH_3)$_2$); 0.96 (t, 3H, ^3J = 7.3 Hz, CH_3). ^{13}C NMR (THF-d_8, 125 MHz, 295 K) δ: 176.2 (N═*C*(Bu)–N); 45.0 (*C*H); 28.5 (α-*C*H$_2$(Bu)); 25.6 (β-*C*H$_2$(Bu)); 24.2 ((*C*H$_3$)$_2$); 21.7 (γ-*C*H$_2$(Bu)); 12.4 (*C*H$_3$). ^{119}Sn NMR (THF-d_8, 186 MHz, 295 K) δ: 69.1. Elemental Anal. Calcd (%) for $C_{11}H_{23}ClN_2Sn$: C 39.15; H 6.87; N 8.30. Found: C 39.33; H 6.69; N 8.36.

3.2.3 Oxidation product of 5 – {[L^{iPr}_2SnCl]-μ^2-(OSnCl)}$_2$ (5a). After standing of 1.2 g of **5** in 50 ml of Et_2O in a not well greased Schlenk tube at −30 °C for three weeks, about 150 mg of insoluble colorless solid of **5a** has been reproducibly crystallized. Mp 112–113 °C. ^{13}C CP/MAS NMR (125 MHz, 295 K) δ: 164.1; 47.6; 44.7; 30.1; 22.0; 14.2. ^{119}Sn CP/MAS NMR (186 MHz, 295 K) δ: −598.1. Elemental Anal. Calcd (%) for $C_{44}H_{92}Cl_4N_8O_2Sn_4$: C 38.24; H 6.71; N 8.11. Found: C 38.52; H 6.39; N 8.45.

3.2.4 Preparation of *N*,*N*′-bis(cyclohexyl)n-butylamidinatogermanium(II) chloride ($L^{Cy}GeCl$) (6). 1.86 g of **2** (6.8 mmol), 1.59 g of $GeCl_2$ dioxane complex (1 : 1) (6.8 mmol), 40 ml of Et_2O. 2.29 g (90%) of white solid of **6**. Mp 97–98.5 °C. ^1H NMR (C_6D_6, 500 MHz, 295 K) δ: 3.28 (m, 2H, Cy*H*); 2.01 (t, 2H, ^3J = 8.0 Hz, α-CH_2(Bu)); 1.86 (s, 4H, Cy*H*); 1.72 (m, 4H, Cy*H*); 1.52–1.41 (m, 10H, Cy*H* + β-CH_2(Bu)); 1.27–1.06 (m, 6H, Cy*H* + γ-CH_2(Bu)); 0.85 (t, 3H, ^3J = 7.2 Hz, CH_3). ^{13}C NMR (C_6D_6, 125 MHz, 295 K) δ: 174.8 (N═*C*(Bu)–N); 54.4 (Cy); 37.0 (Cy); 29.7 (α-*C*H$_2$(Bu)); 26.1 (β-*C*H$_2$(Bu)); 26.0 (Cy); 25.7 (Cy); 23.2 (γ-*C*H$_2$(Bu)); 14.2 (*C*H$_3$). Elemental Anal. Calcd (%) for $C_{17}H_{31}ClGeN_2$: C 54.96; H 8.41; N 7.54. Found: C 55.13; H 8.63; N 7.37.

3.2.5 Preparation of *N*,*N*′-bis(cyclohexyl)n-butylamidinatotin(II) chloride ($L^{Cy}SnCl$) (7). 3.58 g of **2** (13.3 mmol), 2.51 g of $SnCl_2$ (13.3 mmol), 60 ml of Et_2O. Washed with 10 ml of pentane. 4.72 g (85%) of white solid of **7**. Mp 88.5–90.5 °C. Single crystalline material suitable for XRD analyses were obtained under argon from saturated solution of **7** in Et_2O cooled

to −30 °C. ^{1}H NMR (C_6D_6, 500 MHz, 295 K) δ: 3.31 (m, 2H, Cy*H*); 1.92 (t, 2H, ^{3}J = 8.0 Hz, α-CH_2(Bu)); 1.77 (m, 4H, Cy*H*); 1.61 (m, 4H, Cy*H*); 1.48–1.36 (m, 4H, Cy*H* + β-CH_2(Bu)); 1.25–1.01 (m, 12H, Cy*H* + γ-CH_2(Bu)); 0.77 (t, 3H, ^{3}J = 7.3 Hz, CH_3). ^{13}C NMR (C_6D_6, 125 MHz, 295 K) δ: 177.8 (N═*C*(Bu)–N); 54.3 (Cy); 36.9 (Cy); 30.2 (α-*C*H_2(Bu)); 27.4 (β-*C*H_2(Bu)); 26.1 (Cy); 25.8 (Cy); 23.4 (γ-*C*H_2(Bu)); 14.3 (*C*H_3). ^{119}Sn NMR (C_6D_6, 186 MHz, 295 K) δ: 75.7. ^{1}H NMR (THF-d_8, 500 MHz, 295 K) δ: 3.41 (m, 2H, Cy*H*); 2.19 (t, 2H, ^{3}J = 7.4 Hz, α-CH_2(Bu)); 1.64 (m, 6H, Cy*H*); 1.50 (m, 4H, Cy*H*); 1.38 (m, 2H, β-CH_2(Bu)); 1.27–1.05 (m, 12H, Cy*H* + γ-CH_2(Bu)); 0.89 (t, 3H, ^{3}J = 7.3 Hz, CH_3). ^{13}C NMR (THF-d_8, 125 MHz, 295 K) δ: 177.9 (N═*C*(Bu)–N); 54.5 (Cy); 37.0 (Cy); 30.6 (α-*C*H_2(Bu)); 27.5 (β-*C*H_2(Bu)); 26.5 (Cy); 26.1 (Cy); 23.7 (γ-*C*H_2(Bu)); 14.4 (*C*H_3). ^{119}Sn NMR (THF-d_8, 186 MHz, 295 K) δ: 69.7. Elemental Anal. Calcd (%) for $C_{17}H_{31}ClN_2Sn$: C 48.89; H 7.48; N 6.71. Found: C 48.96; H 7.25; N 6.56.

3.2.6 Preparation of *N*,*N*′-bis[2,6-di(propan-2-yl)phenyl]n-butylamidinato-germanium(II) chloride (L^{Dipp}GeCl) (8). 2.43 g of **3** (5.7 mmol), 1.32 g of $GeCl_2$ dioxane complex (1 : 1) (5.7 mmol), 50 ml of Et_2O. 2.81 g (93%) of pale yellow solid of **8**. Mp 161–162 °C. Single crystalline material suitable for XRD analyses were obtained under argon from saturated solution of **8** in Et_2O cooled to −30 °C. ^{1}H NMR (C_6D_6, 500 MHz, 295 K) δ: 7.26–7.16 (m, 6H, Ar*H*); 4.02 (m, 2H, C*H*); 3.48 (m, 2H, C*H*); 2.05 (t, ^{3}J = 8.2 Hz, 2H, α-CH_2(Bu)); 1.52 (d, ^{3}J = 6.3 Hz, 6H, (CH_3)$_2$); 1.39 (d, ^{3}J = 6.4 Hz, 6H, (CH_3)$_2$); 1.33 (d, ^{3}J = 6.6 Hz, 6H, (CH_3)$_2$); 1.29 (m, 2H, β-CH_2(Bu)); 1.21 (d, ^{3}J = 6.4 Hz, 6H, (CH_3)$_2$); 0.76 (m, 2H, γ-CH_2(Bu)); 0.50 (t, ^{3}J = 7.2 Hz, 3H, CH_3). ^{13}C NMR (C_6D_6, 125 MHz, 295 K) δ: 177.2 (N═*C*(Bu)–N); 147.2 (Ar); 144.5 (Ar); 136.8 (Ar); 127.7 (Ar); 124.9 (Ar); 124.0 (Ar); 29.8 (α-*C*H_2(Bu)); 29.0 (β-*C*H_2(Bu)); 27.1 (*C*H); 27.0 (*C*H); 23.6 ((*C*H_3)$_2$); 23.4 ((*C*H_3)$_2$); 23.1 (γ-*C*H_2(Bu)); 13.7 (*C*H_3). Elemental Anal. Calcd (%) for $C_{29}H_{43}ClGeN_2$: C 66.00; H 8.21; N 5.31. Found: C 66.22; H 8.25; N 5.12.

3.2.7 Preparation of *N*,*N*′-bis[2,6-di(propan-2-yl)phenyl]n-butylamidinatotin(II) chloride (L^{Dipp}SnCl) (9). 6.29 g of **3** (14.7 mmol), 2.79 g of $SnCl_2$ (14.7 mmol), 60 ml of Et_2O. Crystallized from hexane and Et_2O (1 : 1). 5.56 g (66%) of white solid of **9**. Mp 193–195 °C. Single crystalline material suitable for XRD analyses were obtained under argon from a saturated solution of **9** in Et_2O cooled to −30 °C. ^{1}H NMR (C_6D_6, 500 MHz, 295 K) δ: 7.10 (br s, 6H, Ar*H*); 3.98 (br s, 2H, C*H*); 3.68 (m, 1H, C*H*); 3.55 (m, 1H, C*H*); 1.91 (t, ^{3}J = 8.1 Hz, 2H, α-CH_2(Bu)); 1.28 (br s, 24H, (CH_3)$_2$); 1.15 (m, 2H, β-CH_2(Bu)); 0.60 (m, 2H, γ-CH_2(Bu)); 0.39 (t, ^{3}J = 7.3 Hz, 3H, CH_3). ^{13}C NMR (C_6D_6, 125 MHz, 295 K) δ: 179.2 (N═*C*(Bu)–N); 147.6 (Ar); 145.1 (Ar); 138.6 (Ar); 127.0 (Ar); 124.8 (Ar); 124.1 (Ar); 31.5 (α-*C*H_2(Bu)); 29.2 (br s, *C*H); 27.3 (β-*C*H_2(Bu)); 27.1 (br s, *C*H); 23.6 (br s, (*C*H_3)$_2$); 23.2 (γ-*C*H_2(Bu)); 13.7 (*C*H_3). ^{119}Sn NMR (C_6D_6, 186 MHz, 295 K) δ: 29.4. ^{1}H NMR (THF-d_8, 500 MHz, 295 K) δ: 7.15 (s, 4H, Ar*H*); 7.08 (m, 2H, Ar*H*); 3.57 (s, 2H, C*H*); 3.29 (m, 1H, C*H*); 3.17 (m, 1H, C*H*); 1.87 (t, ^{3}J = 8.4 Hz, 2H, α-CH_2(Bu)); 1.29 (d, 12H, ^{3}J = 6.9 Hz, (CH_3)$_2$); 1.24 (d, 12H, ^{3}J = 6.7 Hz, (CH_3)$_2$); 1.16 (m, 2H, β-CH_2(Bu)); 0.87 (m, 2H, γ-CH_2(Bu)); 0.52 (t, ^{3}J = 7.3 Hz, 3H, CH_3). ^{13}C NMR (THF-d_8, 125 MHz, 295 K) δ: 175.9 (N═*C*(Bu)–N); 148.2 (Ar); 145.5 (br s, Ar); 140.5 (Ar); 126.3 (Ar); 124.2 (Ar); 123.6 (Ar); 31.6 (α-*C*H_2(Bu)); 29.4 (*C*H); 29.3 (br s, *C*H); 29.1 (*C*H); 27.8 (β-*C*H_2(Bu)); 26.7 ((*C*H_3)$_2$); 24.0 ((*C*H_3)$_2$); 23.7 (γ-*C*H_2(Bu)); 13.8 (*C*H_3). ^{119}Sn NMR (THF-d_8, 186 MHz, 295 K) δ: −124.0. Elemental Anal. Calcd (%) for $C_{29}H_{43}ClN_2Sn$: C 60.70; H 7.55; N 4.88. Found: C 60.72; H 7.48; N 4.59.

3.2.8 Preparation of bis[*N*,*N*′-di(propan-2-yl)n-butyl-amidinato]germanium(II) (L^{iPr}_2Ge) (10). 1.68 g of **1** (8.8 mmol), 1.02 g of $GeCl_2$ dioxane complex (1 : 1) (4.4 mmol), 40 ml of Et_2O. 1.54 g (79%) of pale yellow oily matter of **10**. ^{1}H NMR (C_6D_6, 500 MHz, 295 K) δ: 3.70 (m, 4H, C*H*); 2.11 (t, ^{3}J = 8.1 Hz, 4H, α-CH_2(Bu)); 1.42 (m, 4H, β-CH_2(Bu)); 1.36 (d, 24H, ^{3}J = 6.5 Hz, (CH_3)$_2$); 1.21 (m, 4H, γ-CH_2(Bu)); 0.83 (t, 6H, ^{3}J = 7.3 Hz, CH_3). ^{13}C NMR (C_6D_6, 125 MHz, 295 K) δ: 165.8 (N═*C*(Bu)–N); 47.3 (*C*H); 29.7 (α-*C*H_2(Bu)); 25.4 (β-*C*H_2(Bu)); 25.2 ((*C*H_3)$_2$); 22.9 (γ-*C*H_2(Bu)); 13.6 (*C*H_3). Elemental Anal. Calcd (%) for $C_{22}H_{46}GeN_4$: C 60.15; H 10.56; N 12.75. Found: C 60.43; H 10.32; N 12.63.

3.2.9 Preparation of bis[*N*,*N*′-di(propan-2-yl)n-butyl-amidinato]tin(II) (L^{iPr}_2Sn) (11). 0.73 g of **1** (3.8 mmol), 0.36 g of $SnCl_2$ (1.9 mmol), 30 ml of Et_2O. 0.81 g (88%) of colourless oily matter of **11**. ^{1}H NMR (C_6D_6, 500 MHz, 295 K) δ: 3.77 (m, 4H, C*H*); 2.10 (t, 4H, ^{3}J = 8.1 Hz, α-CH_2(Bu)); 1.44 (m, 4H, β-CH_2(Bu)); 1.31 (d, 24H, ^{3}J = 6.5 Hz, (CH_3)$_2$); 1.24 (m, 4H, γ-CH_2(Bu)); 0.85 (t, 6H, ^{3}J = 7.3 Hz, CH_3). ^{13}C NMR (C_6D_6, 125 MHz, 295 K) δ: 168.2 (N═*C*(Bu)–N); 47.4 (*C*H); 29.8 (α-*C*H_2(Bu)); 25.8 (β-*C*H_2(Bu)); 25.7 ((*C*H_3)$_2$); 23.0 (γ-*C*H_2(Bu)); 13.7 (*C*H_3). ^{119}Sn NMR (C_6D_6, 186 MHz, 295 K) δ: −252.3. Elemental Anal. Calcd (%) for $C_{22}H_{46}N_4Sn$: C 54.44; H 9.55; N 11.54. Found: C 54.71; H 9.83; N 11.34.

3.2.10 Preparation of bis[*N*,*N*′-di(propan-2-yl)n-butyl-amidinato]lead(II) (L^{iPr}_2Pb) (12). 0.87 g of **1** (4.6 mmol), 0.63 g of $PbCl_2$ (2.3 mmol), 30 ml of Et_2O. 1.08 g (82%) of colourless oily matter of **12**. ^{1}H NMR (C_6D_6, 500 MHz, 295 K) δ: 4.53 (m, 4H, C*H*); 2.09 (t, 4H, ^{3}J = 8.1 Hz, α-CH_2(Bu)); 1.56 (m, 4H, β-CH_2(Bu)); 1.30 (m, 4H, γ-CH_2(Bu)); 1.29 (d, 24H, ^{3}J = 6.3 Hz, (CH_3)$_2$); 0.88 (t, 6H, ^{3}J = 7.3 Hz, CH_3). ^{13}C NMR (C_6D_6, 125 MHz, 295 K) δ: 168.8 (N═*C*(Bu)–N); 47.9 (*C*H); 30.7 (α-*C*H_2(Bu)); 30.0 (β-*C*H_2(Bu)); 26.7 ((*C*H_3)$_2$); 23.7 (γ-*C*H_2(Bu)); 14.1 (*C*H_3). ^{207}Pb NMR (C_6D_6, 81 MHz, 295 K) δ: 1734.8. ^{1}H NMR (THF-d_8, 500 MHz, 295 K) δ: 4.48 (m, 2H, C*H*); 2.14 (t, 4H, ^{3}J = 8.1 Hz, α-CH_2(Bu)); 1.53 (m, 4H, β-CH_2(Bu)); 1.40 (m, 4H, γ-CH_2(Bu)); 1.13 (d, 24H, ^{3}J = 6.3 Hz, (CH_3)$_2$); 0.94 (t, 6H, ^{3}J = 7.3 Hz, CH_3). ^{13}C NMR (THF-d_8, 125 MHz, 295 K) δ: 169.5 (N═*C*(Bu)–N); 48.6 (*C*H); 31.4 (α-*C*H_2(Bu)); 30.5 (β-*C*H_2(Bu)); 26.9 ((*C*H_3)$_2$); 24.4 (γ-*C*H_2(Bu)); 14.5 (*C*H_3). ^{207}Pb NMR (THF-d_8, 81 MHz, 295 K) δ: 1743.5. Elemental Anal. Calcd (%) for $C_{22}H_{46}N_4Pb$: C 46.05; H 8.08; N 9.76. Found: C 46.01; H 8.23; N 9.63.

3.2.11 Preparation of bis[*N*,*N*′-bis(cyclohexyl)n-butyl-amidinato]germanium(II) (L^{Cy}_2Ge) (13). 0.93 g of **2** (3.4 mmol), 0.39 g of $GeCl_2$ dioxane complex (1 : 1) (1.7 mmol), 30 ml of Et_2O. 0.86 g (84%) of pale yellow oily matter of **13**. ^{1}H NMR (C_6D_6, 500 MHz, 295 K) δ: 3.28 (m, 4H, Cy*H*); 2.20 (t, 4H, ^{3}J

= 7.7 Hz, α-CH_2(Bu)); 1.87–1.71 (br m, 20H, Cy*H*); 1.59–1.43 (br m, 8H, Cy*H* + β-CH_2(Bu)); 1.35–1.15 (br m, 20H, Cy*H* + γ-CH_2(Bu)); 0.85 (t, 6H, ^3J = 7.3 Hz, CH_3). ^{13}C NMR (C_6D_6, 125 MHz, 295 K) δ: 166.1 (N=*C*(Bu)–N); 56.2 (Cy); 35.7 (Cy); 30.0 (α-*C*H_2(Bu)); 26.2 (β-*C*H_2(Bu)); 25.8 (Cy); 25.1 (Cy); 22.8 (γ-*C*H_2(Bu)); 13.7 (*C*H_3). Elemental Anal. Calcd (%) for $C_{34}H_{62}GeN_4$: C 68.11; H 10.42; N 9.35. Found: C 68.03; H 10.61; N 9.58.

3.2.12 Preparation of bis[*N*,*N*′-bis(cyclohexyl)n-butyl-amidinato]tin(II) (L^{Cy}_2Sn) (14). 2.18 g of **2** (8.1 mmol), 0.76 g of $SnCl_2$ (4.0 mmol), 40 ml of Et_2O. 2.11 g (82%) of colourless oily matter of **14**. ^{1}H NMR (C_6D_6, 500 MHz, 295 K) δ: 3.38 (m, 4H, Cy*H*); 2.19 (t, 4H, ^3J = 7.8 Hz, α-CH_2(Bu)); 1.92–1.73 (br m, 20H, Cy*H*); 1.67–1.48 (br m, 8H, Cy*H* + β-CH_2(Bu)); 1.38–1.10 (br m, 20H, Cy*H* + γ-CH_2(Bu)); 0.87 (t, 6H, ^3J = 7.3 Hz, CH_3). ^{13}C NMR (C_6D_6, 125 MHz, 295 K) δ: 168.8 (N=*C*(Bu)–N); 56.6 (Cy); 36.5 (Cy); 30.2 (α-*C*H_2(Bu)); 26.3 (β-*C*H_2(Bu)); 26.0 (Cy); 25.9 (Cy); 23.1 (γ-*C*H_2(Bu)); 13.9 (*C*H_3). ^{119}Sn NMR (C_6D_6, 186 MHz, 295 K) δ: −255.3. Elemental Anal. Calcd (%) for $C_{34}H_{62}N_4Sn$: C 63.25; H 9.68; N 8.68. Found: C 63.46; H 9.52; N 8.39.

3.2.13 Preparation of bis[*N*,*N*′-bis(cyclohexyl)n-butyl-amidinato]lead(II) (L^{Cy}_2Pb) (15). 1.92 g of **2** (7.1 mmol), 0.98 g of $PbCl_2$ (3.5 mmol), 40 ml of Et_2O. 2.31 g (90%) of colourless oily matter of **15**. ^{1}H NMR (C_6D_6, 500 MHz, 295 K) δ: 4.08 (m, 4H, Cy*H*); 2.15 (t, 4H, ^3J = 8.0 Hz, α-CH_2(Bu)); 1.88–1.75 (br m, 16H, Cy*H*); 1.65–1.54 (br m, 16H, Cy*H* + β-CH_2(Bu)); 1.36–1.22 (br m, 16H, Cy*H* + γ-CH_2(Bu)); 0.89 (t, 6H, ^3J = 7.2 Hz, CH_3). ^{13}C NMR (C_6D_6, 125 MHz, 295 K) δ: 168.6 (N=*C*(Bu)–N); 56.2 (Cy); 36.9 (Cy); 30.4 (α-*C*H_2(Bu)); 29.4 (β-*C*H_2(Bu)); 26.0 (Cy); 25.8 (Cy); 23.1 (γ-*C*H_2(Bu)); 13.7 (*C*H_3). ^{207}Pb NMR (C_6D_6, 81 MHz, 295 K) δ: 1729.0. ^{1}H NMR (THF-d_8, 500 MHz, 295 K) δ: 4.01 (m, 4H, Cy*H*); 2.17 (t, 4H, ^3J = 7.7 Hz, α-CH_2(Bu)); 1.74–1.65 (br m, 18H, Cy*H*); 1.57–1.37 (br m, 16H, Cy*H* + β-CH_2(Bu)); 1.34–1.15 (br m, 14H, Cy*H* + γ-CH_2(Bu)); 0.95 (t, 6H, ^3J = 7.2 Hz, CH_3). ^{13}C NMR (THF-d_8, 125 MHz, 295 K) δ: 169.8 (N=*C*(Bu)–N); 57.4 (Cy); 37.9 (Cy); 31.5 (α-*C*H_2(Bu)); 30.4 (β-*C*H_2(Bu)); 26.9 (Cy); 26.8 (Cy); 24.2 (γ-*C*H_2(Bu)); 14.8 (*C*H_3). ^{207}Pb NMR (THF-d_8, 81 MHz, 295 K) δ: 1745.6. Elemental Anal. Calcd (%) for $C_{34}H_{62}N_4Pb$: C 55.63; H 8.51; N 7.63. Found: C 55.58; H 8.36; N 7.75.

3.2.14 Preparation of bis[*N*,*N*′-bis[2,6-di(propan-2-yl)phenyl]-n-butylamidinato]-germanium(II) (L^{Dipp}_2Ge) (16). 1.38 g of **3** (3.2 mmol), 0.37 g of $GeCl_2$ dioxane complex (1 : 1) (1.6 mmol), 30 ml of Et_2O. 1.19 g (82%) of pale yellow oily matter of **16**. ^{1}H NMR (C_6D_6, 500 MHz, 295 K) δ: 7.24–6.94 (m, 12H, Ar*H*); 3.76 (m, 4H, C*H*); 3.35 (m, 2H, C*H*); 3.22 (m, 2H, C*H*); 2.13 (s, 4H, α-CH_2(Bu)); 1.29 (m, 4H, β-CH_2(Bu)); 1.36 (s, 48H, (CH_3)$_2$); 0.80 (m, 4H, γ-CH_2(Bu)); 0.35 (t, 6H, ^3J = 7.3 Hz, CH_3). ^{13}C NMR (C_6D_6, 125 MHz, 295 K) δ: 169.8 (N=*C*(Bu)–N); 147.6 (Ar); 142.5 (Ar); 141.0 (Ar); 126.8 (Ar); 123.9 (br s, Ar); 29.3 (α-*C*H_2(Bu)); 28.8 (β-*C*H_2(Bu)); 28.4 (br s, *C*H); 23.3 (br s, (CH_3)$_2$); 22.8 (γ-*C*H_2(Bu)); 13.6 (*C*H_3). Elemental Anal. Calcd (%) for $C_{58}H_{86}GeN_4$: C 76.39; H 9.51; N 6.14. Found: C 76.58; H 9.86; N 5.88.

3.2.15 Preparation of bis[*N*,*N*′-bis[2,6-di(propan-2-yl)phenyl]-n-butylamidinato]tin(II) (L^{Dipp}_2Sn) (17). 4.61 g of **3** (10.8 mmol), 1.02 g of $SnCl_2$ (5.4 mmol), 50 ml of Et_2O. Extracted with 30 ml of hexane. 3.89 g (75%) of white solid of **17**. Mp 63–65 °C. ^{1}H NMR (C_6D_6, 500 MHz, 295 K) δ: 7.14–6.97 (br m, 12H, Ar*H*); 3.70 (s, 4H, C*H*); 3.35 (s, 2H, C*H*); 3.15 (m, 2H, C*H*); 1.86 (s, 4H, α-CH_2(Bu)); 1.48–1.11 (br m, 52H, β-CH_2(Bu) + (CH_3)$_2$); 0.48 (m, 4H, γ-CH_2(Bu)); 0.36 (t, ^3J = 7.3 Hz, 6H, CH_3). ^{13}C NMR (C_6D_6, 125 MHz, 295 K) δ: 171.7 (N=*C*(Bu)–N); 145.0 (Ar); 144.4 (Ar); 142.2 (Ar); 126.0 (Ar); 123.9 (Ar); 123.7 (Ar); 32.0 (α-*C*H_2(Bu)); 28.5 (br s, *C*H); 27.2 (β-*C*H_2(Bu)); 25.1 (br s, *C*H); 23.8 (br s, (*C*H_3)$_2$); 23.3 (γ-*C*H_2(Bu)); 13.6 (*C*H_3). ^{119}Sn NMR (C_6D_6, 186 MHz, 295 K) δ: −341.3. Elemental Anal. Calcd (%) for $C_{58}H_{86}N_4Sn$: C 72.71; H 9.05; N 5.85. Found: C 72.59; H 9.24; N 5.63.

3.2.16 Preparation of bis[*N*,*N*′-bis[2,6-di(propan-2-yl)phenyl]-n-butylamidinato]lead(II) (L^{Dipp}_2Pb) (18). 0.77 g of **3** (1.8 mmol), 0.25 g of $PbCl_2$ (0.9 mmol), 30 ml of Et_2O. 0.82 g (87%) of colourless oily matter of **18**. ^{1}H NMR (C_6D_6, 500 MHz, 295 K) δ: 7.09 (br s, 8H, Ar*H*); 7.09 (t, 4H, ^3J = 7.5 Hz, Ar*H*); 3.46 (br s, 8H, C*H*); 1.88 (s, 4H, α-CH_2(Bu)); 1.30 (br s, 48H, (CH_3)$_2$); 1.06 (m, 4H, β-CH_2(Bu)); 0.59 (m, 4H, γ-CH_2(Bu)); 0.37 (t, ^3J = 7.2 Hz, 6H, CH_3). ^{13}C NMR (C_6D_6, 125 MHz, 295 K) δ: 170.4 (N=*C*(Bu)–N); 146.9 (Ar); 142.5 (Ar); 138.6 (Ar); 124.7 (Ar); 123.4 (Ar); 123.2 (Ar); 33.9 (α-*C*H_2(Bu)); 28.0 (br s, *C*H); 26.8 (β-*C*H_2(Bu)); 23.2 (br s, (*C*H_3)$_2$); 23.0 (γ-*C*H_2(Bu)); 12.9 (*C*H_3). ^{207}Pb NMR (C_6D_6, 81 MHz, 295 K) δ: 1541.3. ^{1}H NMR (THF-d_8, 500 MHz, 295 K) δ: 7.04 (br s, 8H, Ar*H*); 6.88 (t, 4H, ^3J = 7.6 Hz, Ar*H*); 3.29 (m, 8H, C*H*); 1.69 (s, 4H, α-CH_2(Bu)); 1.21 (br s, 48H, (CH_3)$_2$); 0.92 (m, 4H, β-CH_2(Bu)); 0.67 (m, 4H, γ-CH_2(Bu)); 0.38 (t, ^3J = 7.3 Hz, 6H, CH_3). ^{13}C NMR (THF-d_8, 125 MHz, 295 K) δ: 171.3 (N=*C*(Bu)–N); 148.2 (Ar); 143.6 (Ar); 139.4 (Ar); 125.6 (Ar); 124.3 (Ar); 123.6 (Ar); 34.9 (α-*C*H_2(Bu)); 29.0 (br s, *C*H); 27.9 (β-*C*H_2(Bu)); 24.1 (γ-*C*H_2(Bu)); 23.7 (br s, *C*H); 13.6 (*C*H_3). ^{207}Pb NMR (THF-d_8, 81 MHz, 295 K) δ: 1540.1. Elemental Anal. Calcd (%) for $C_{58}H_{86}N_4Sn$: C 66.56; H 8.28; N 5.35. Found: C 66.48; H 8.12; N 5.38.

4. Conclusions

A series of homo- and heteroleptic Ge(II), Sn(II) and homoleptic Pb(II) *N*,*N*′-disubstituted n-butyl amidinates were prepared and characterized. In the solid state the heteroleptic Ge(II) amidinate is a monomer, Sn(II) amidinate with bulky Dipp substituents is a dimer *via* chlorine bridges and the cyclohexyl *N*,*N*′-disubstituted Sn(II) chloride reveals a unique dimeric structure *via* one Cl bridge and Sn to an amidinate π-system contact. Accidental but reproducible oxidation of heteroleptic Sn(II) chloride led to the tetranuclear linear complex containing two Sn(II) and two Sn(IV) atoms formed by migrations of two ligands.

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