*Dedicated to Professor Ion Grosu
on the occasion of his 65th anniversary*

HYPERCOORDINATED ORGANOTIN(IV) COMPOUNDS CONTAINING (IMINO)ARYL LIGANDS – [(*E*)-2-(2′,6′-^{i}Pr$_2$C$_6$H$_3$N=CH)C$_6$H$_4$]SnR$_2$X (R = Me, X = Cl, I; R = ^{n}Bu, X = Cl, F, Br). MOLECULAR STRUCTURES AND SUPRAMOLECULAR ASPECTS

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Five new dialkyl(iminoaryl)tin(IV) halides, [(*E*)-2-(2′,6′-^{i}Pr$_2$C$_6$H$_3$N=CH)C$_6$H$_4$]SnR$_2$X [R = Me, X = Cl (**1**), I (**2**); R = ^{n}Bu, X = Cl (**3**), F (**4**), Br (**5**)], were prepared by reacting either [(*E*)-2-(2′,6′-^{i}Pr$_2$C$_6$H$_3$N=CH)C$_6$H$_4$]MgBr with R$_2$SnCl$_2$ for **1** and **3**, or by halogen exchange reaction between the chlorides [(*E*)-2-(2′,6′-^{i}Pr$_2$C$_6$H$_3$N=CH)C$_6$H$_4$]SnR$_2$Cl with KX (X = I, F, Br) for **2**, **4** and **5**, respectively. The compounds were characterized by solution multinuclear (^{1}H, ^{13}C, ^{119}Sn) NMR spectroscopy and mass spectrometry. The crystal and molecular structure of all five compounds was established by single-crystal X-ray diffraction. The NMR data for **1**–**5** are consistent with the presence of an intramolecular N→Sn coordination which results in a trigonal bipyramidal (*C,N*)SnC$_2$X core, similar with that observed in solid state. In the crystal of **1**–**5** different supramolecular architectures, based on intermolecular X···H and C–H···π (Ar$_{centroid}$) interactions, were evidenced and discussed.
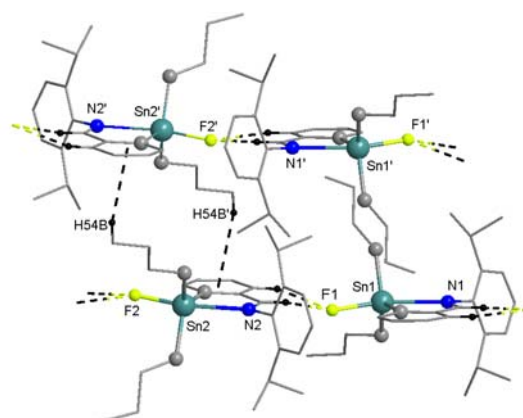
INTRODUCTION

Aromatic ligands with one or two pendant arms containing *sp^3* nitrogen as donor atom, were extensively used in last years in the organotin chemistry. Such ligands include 2-(R$_2$NCH$_2$)C$_6$H$_4$ (R = Me,[1] Et[2]), 2-(Et$_2$NCH$_2$)-4,6-^{t}Bu$_2$C$_6$H$_2$,[3] 2-[Me$_2$NCH(R)]C$_6$H$_4$ (R = Me,[4] ^{t}Bu[5]) and 2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$.[6] In addition to stabilization of unusual, low-valent species which are important from fundamental point of view, some of the organotin

compounds bearing such organic substituents were reported to exhibit biological[7] and catalytic properties.[8] By contrast, reports on organotin species containing related aromatic ligands bearing one or two pendant arms with an *sp^2* nitrogen as donor atom such as 2-(RN=CH)C$_6$H$_4$,[9] or 2,6-(RN=CMe)$_2$C$_6$H$_3$,[10] are seldom. Of particular interest is the use of di(imino)aryltin(IV) dichlorides as tectons for heterometallic coordination compounds, *e.g.* [Cl$_2$Pd{2-(2′-PyCH$_2$N=CH)C$_6$H$_4$}$_2$SnCl$_2$],[9b] or the stabilization of unusual low-valent species such as

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the distannyne [2,6-(2′,6′-^{i}Pr$_2$C$_6$H$_3$N= =CMe)$_2$C$_6$H$_3$]$_2$Sn$_2$,[10a] and the monomeric hydride [2,6-(2′,6′-^{i}Pr$_2$C$_6$H$_3$N=CMe)$_2$C$_6$H$_3$]SnH.[10a] Recently we have also reported on related bimetallic species as ClSnMe$_2$[2-C$_6$H$_4$(4-CH=N-1,1′-C$_6$H$_4$C$_6$H$_4$-4′- N=CH)-2′-C$_6$H$_4$]SnMe$_2$Cl or XSnMe$_2$[2-C$_6$H$_4$(CH= =NCH$_2$CH$_2$N=CH)-2′-C$_6$H$_4$]SnMe$_2$X (X = Cl, SCN) which might be useful as linkers for coordination polymers.[11]

We report here on the synthesis, the spectroscopic characterization in solution as well as the molecular structure of several new mixed aryl/alkyl triorganotin(IV) halides with an aromatic ligand bearing a pendant arm containing an imine function, *i.e.* [(*E*)-2-(2′,6′-^{i}Pr$_2$C$_6$H$_3$N=CH)C$_6$H$_4$]SnR$_2$X, useful starting materials for the preparation of novel triorganotin(IV) derivatives.

RESULTS

The mixed dialkyl(iminoaryl)tin(IV) chlorides, R′SnR$_2$Cl [R′ = (*E*)-2-(2′,6′-^{i}Pr$_2$C$_6$H$_3$N=CH)C$_6$H$_4$; R = Me (**1**), Bu (**3**)] were obtained by reacting the *in situ* prepared Grignard reagent *(E)*-2-(2′,6′-^{i}Pr$_2$C$_6$H$_3$N=CH)C$_6$H$_4$MgBr with R$_2$SnCl$_2$, in anhydrous THF. Halogen exchange reactions between **1** and **3** and excess of KX, carried out in CH$_2$Cl$_2$/H$_2$O mixture, afforded the isolation of the corresponding R′SnR$_2$X [R = Me, X = I (**2**); R = Bu, X = F (**4**), Br (**5**)] (Scheme 1).

R'Br + Mg $\xrightarrow{\text{THF}}$ R'MgBr $\xrightarrow{\text{R}_2\text{SnCl}_2}$ R'SnR$_2$Cl

R = Me (**1**), ^{n}Bu (**3**)

$\downarrow$ KX / CH$_2$Cl$_2$

R'SnR$_2$X

R = Me, X = I (**2**)
^{n}Bu, X = F (**4**)
^{n}Bu, X = Br (**5**)
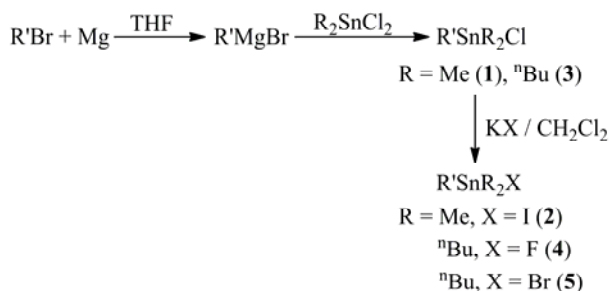
Scheme 1

Details of the preparations are given in the Experimental section. The triorganotin(IV) species were isolated as white or yellow (the iodide **2**) solids with a good solubility in chloroform. The EI mass spectra showed the [M–Me]$^+$ and [M–I]$^+$ ions as base peaks for **1** and **2**, respectively, while for compounds **3–5** the base peak was [M–Bu]$^+$.

All compounds were characterized in solution by ^{1}H, ^{13}C and ^{119}Sn NMR spectroscopy as well as ^{19}F NMR spectroscopy for compound **4**. The NMR spectra were recorded in CDCl$_3$ at room temperature and are consistent with the investigated new organotin(IV) species. The assignment of the observed ^{1}H and ^{13}C resonances for the ligand with the pendant arm was made using 2D experiments, according to the numbering scheme shown in Scheme 2.
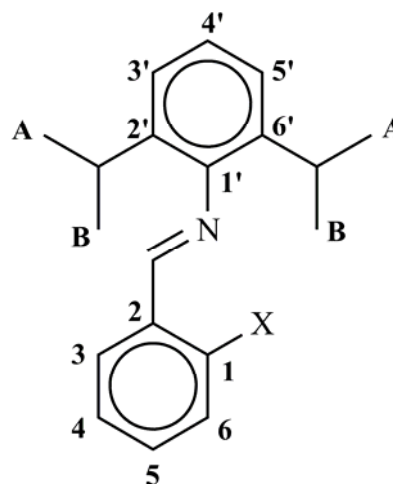
Scheme 2

The ^{1}H and ^{13}C NMR spectra for compounds **1**– **5** showed the expected resonances for the organic substituents in the alkyl as well as in the aromatic regions. For the methyl and butyl groups, respectively, attached to a metal atom in halides **1**– **5** only one set of resonances was observed. For several ^{1}H and ^{13}C resonances satellites due to tin-hydrogen and tin-carbon couplings were observed.

Single crystals of good quality were obtained for all reported organotin(IV) halides by diffusion of *n*-hexane into the methylene dichloride solution of the corresponding organometallic species. The crystal and molecular structures were established by X-ray diffraction studies. In all cases it was found that the crystals contain discrete molecules, with no unusual intermolecular distances shorter than the sum of the van der Waals radii between heavy atoms. The ORTEP-like representations of the molecular structure of halides **1–5**, with the atom numbering scheme, are depicted in Figure 1. Selected interatomic distances and bond angles are listed in Table 1. The unit cell of compound **4** contains two independent molecules (**4a** and **4b**), with very similar molecular parameters (see Table 1) and therefore only data for molecule **4a** are indicated in the subsequent discussion.
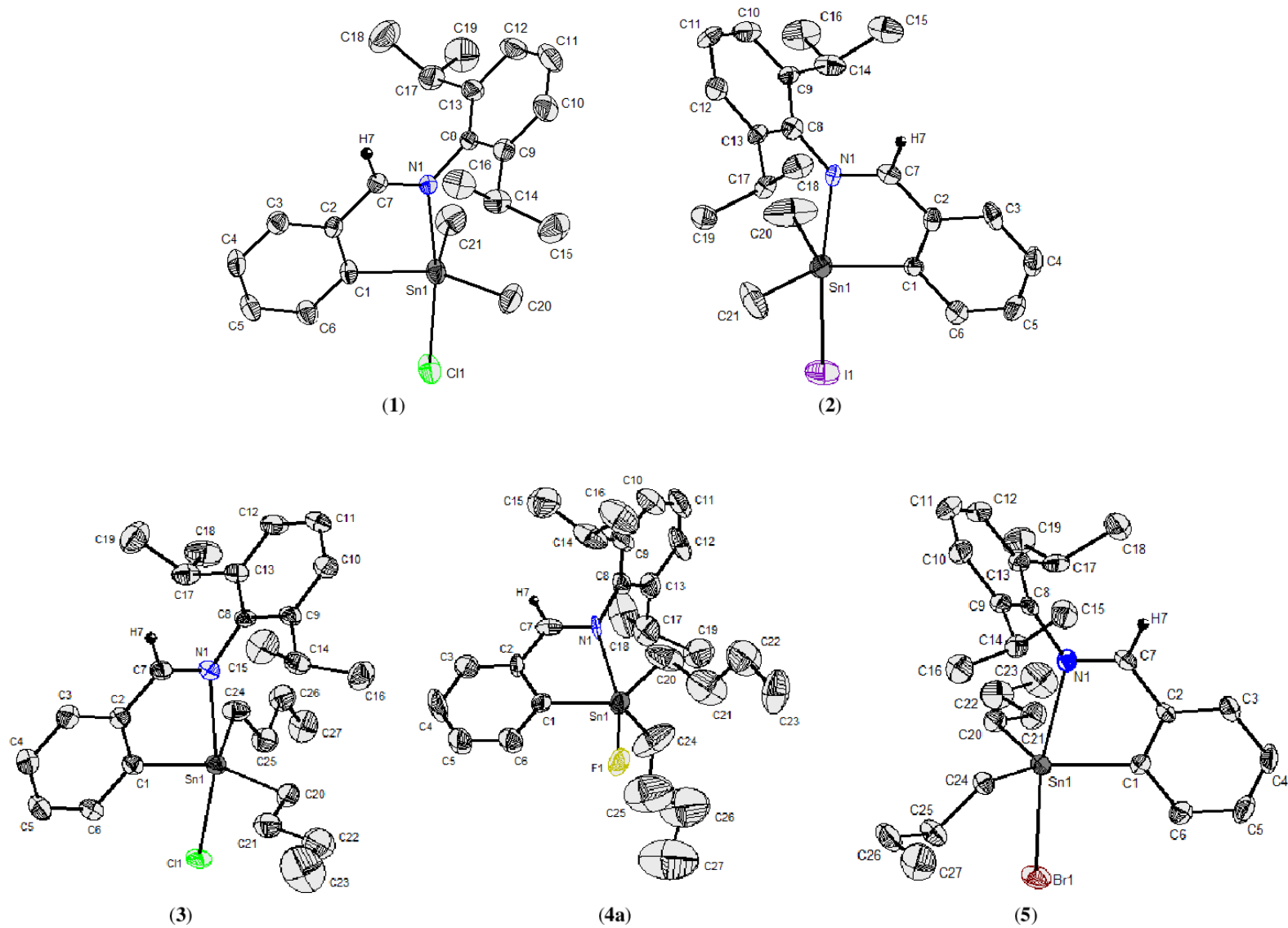
Fig. 1 – ORTEP representation at 25% probability and atom numbering scheme for RSnMe$_2$Cl (**1**), RSnMe$_2$I (**2**), RSn^{n}Bu$_2$Cl (**3**), RSn^{n}Bu$_2$F (**4**) and RSn^{n}Bu$_2$Br (**5**) [R′ = (*E*)-2-(2′,6′-^{i}Pr$_2$C$_6$H$_3$N=CH)C$_6$H$_4$]. Hydrogen atoms are omitted for clarity, except the H(7) of the imine –CH=N– group.

Table 1

Selected interatomic distances (Å) and angles (deg) for RSnMe$_2$Cl (**1**), RSnMe$_2$I (**2**), RSn^{n}Bu$_2$Cl (**3**), RSn^{n}Bu$_2$F (**4**) and RSn^{n}Bu$_2$Br (**5**) [R′ = (*E*)-2-(2′,6′-^{i}Pr$_2$C$_6$H$_3$N=CH)C$_6$H$_4$]

	1	**2**		**3**	**4a [4b]**	**5**
Sn(1)–C(1)	2.147(5)	2.135(11)	Sn(1)–C(1)	2.148(5)	2.110(13)	[Sn(2)–C(28) 2.127(13)]	2.147(7)
Sn(1)–C(20)	2.116(7)	2.08(3)	Sn(1)–C(20)	2.127(7)	2.09(2)	[Sn(2)–C(47) 2.135(19)]	2.129(7)
Sn(1)–C(21)	2.108(7)	2.12(2)	Sn(1)–C(24)	2.131(5)	2.08(3)	[Sn(2)–C(51) 2.101(15)]	2.138(7)
Sn(1)–X(1)^a	2.5055(15)	2.8344(17)	Sn(1)–X(1)^a	2.5053(14)	2.023(8)	[Sn(2)–X(2) 2.009(8)]	2.6287(10)
Sn(1)–N(1)	2.516(3)	2.487(10)	Sn(1)–N(1)	2.566(4)	2.521(11)	[Sn(2)–N(2) 2.499(9)]	2.527(5)
N(1)–C(7)	1.269(6)	1.284(16)	N(1)–C(7)	1.253(7)	1.255(16)	[N(2)–C(34) 1.244(17)]	1.262(9)
N(1)–C(8)	1.441(6)	1.442(15)	N(1)–C(8)	1.446(6)	1.450(16)	[N(2)–C(35) 1.495(17)]	1.439(9)
X(1)–Sn(1)–N(1)^a	167.51(10)	173.1(2)	X(1)–Sn(1)–N(1)^a	167.00(10)	163.9(4)	[X(2)–Sn(2)–N(2) 163.7(4)]	168.97(12)
C(1)–Sn(1)–C(20)	125.8(2)	122.1(7)	C(1)–Sn(1)–C(20)	115.2(2)	128.3(8)	[C(28)–Sn(2)–C(47) 117.0(7)]	123.8(3)
C(1)–Sn(1)–C(21)	115.5(2)	118.6(7)	C(1)–Sn(1)–C(24)	124.2(2)	113.0(8)	[C(28)–Sn(2)–C(51) 125.2(7)]	116.6(3)
C(20)–Sn(1)–C(21)	116.5(3)	116.8(9)	C(20)–Sn(1)–C(24)	116.7(2)	116.9(10)	[C(47)–Sn(2)–C(51) 115.2(9)]	116.7(3)
X(1)–Sn(1)–C(1)^a	95.43(14)	99.2(3)	X(1)–Sn(1)–C(1)^a	95.18(13)	91.8(4)	[X(2)–Sn(2)–C(28) 92.0(4)]	95.9(2)
X(1)–Sn(1)–C(20)^a	91.65(19)	91.6(6)	X(1)–Sn(1)–C(20)^a	96.91(18)	96.3(6)	[X(2)–Sn(2)–C(47) 96.7(6)]	92.3(2)
X(1)–Sn(1)–C(21)^a	98.0(2)	94.8(5)	X(1)–Sn(1)–C(24)^a	97.57(16)	95.3(7)	[X(2)–Sn(2)–C(51) 97.6(5)]	99.3(2)
N(1)–Sn(1)–C(1)	74.14(16)	74.0(4)	N(1)–Sn(1)–C(1)	72.45(16)	73.3(4)	[N(2)–Sn(2)–C(28) 72.1(4)]	73.2(2)
N(1)–Sn(1)–C(20)	89.1(2)	91.1(7)	N(1)–Sn(1)–C(20)	92.12(19)	88.5(5)	[N(2)–Sn(2)–C(47) 93.9(5)]	92.5(2)
N(1)–Sn(1)–C(21)	92.8(2)	89.7(6)	N(1)–Sn(1)–C(24)	86.60(17)	96.3(6)	[N(2)–Sn(2)–C(51) 89.0(5)]	87.4(2)
C(7)–N(1)–Sn(1)	108.0(3)	107.2(8)	C(7)–N(1)–Sn(1)	108.1(3)	107.7(8)	[C(34)–N(2)–Sn(2) 109.2(8)]	108.3(4)
C(8)–N(1)–Sn(1)	132.9(3)	133.0(7)	C(8)–N(1)–Sn(1)	132.8(3)	135.5(7)	[C(35)–N(2)–Sn(2) 131.5(7)]	131.0(4)
C(7)–N(1)–C(8)	119.1(4)	119.8(10)	C(7)–N(1)–C(8)	118.8(4)	116.5(11)	[C(34)–N(2)–C(35) 119.0(10)]	120.7(6)

^{a} X(1) = Cl (for **1**), I (for **2**), Cl (for **3**), F (for **4**) and Br (for **5**).

Table 2

Correlations between ^1H–^{119}Sn and ^{13}C–^{119}Sn coupling constants (Hz) and C–Sn–C angles (θ, °) in compounds **1–5**

Compound	^1H		^{13}C	
	$^2J(^{119}Sn^1H)$	C–Sn–C^a	$^1J(^{119}Sn^{13}C)$	C–Sn–C^b
1^c	70.6	120.5	523.7	122.7
2^c	69.0	119.0	-	-
3^d	-	-	497.5	120.4
4^d	-	-	519.0	122.3
5^d	-	-	485.7	119.4

^{a} $\theta = 0.0161|^2J|^2 - 1.32|^2J| + 133.4$;[13] ^{b} $|^1J| = 11.4\theta - 875$;[14] ^{c} For C(20)–Sn(1)–C(21) angle; ^{d} For C(20)–Sn(1)–C(24) angle.

DISCUSSION

Solution behaviour

As a general remark, the NMR data suggest that an intramolecular N→Sn coordination is present in solution as was also found in solid state (see subsequent discussion).

In solution, at room temperature, the ^{119}Sn NMR spectra for all derivatives **1–5** show one single resonance consistent with the presence of only one species. For compound **4** the ^{19}F NMR spectrum also exhibit only one singlet resonance at δ –201.8 ppm, surrounded by tin satellites ($^1J_{117SnF} = 2032$, $^1J_{119SnF} = 2127$ Hz), thus providing further support for the presence of one organotin species in solution.

The ^{119}Sn resonances appear at chemical shifts (δ –40.7, –65.8, –32.0, –65.7 and –23.4 ppm for **1–5** in CDCl$_3$, respectively) similar to those reported for the related [2-(Me$_2$NCH$_2$)C$_6$H$_4$]SnMe$_2$Cl (δ –48.7 ppm, in CH$_2$Cl$_2$/acetone-d_6)^{1e} and [2-{Me$_2$NCH$_2$CH$_2$N(Me)CH$_2$}C$_6$H$_4$]SnMe$_2$Cl (δ –45 ppm, in CDCl$_3$).[12] The magnitude of the observed ^{119}Sn chemical shifts is typical for five-coordinate triorganotin(IV) species in solution.

The ^1H and ^{13}C NMR spectra of compounds **1** and **2** exhibit a singlet resonance signal for the methyl groups bonded to tin with the corresponding tin satellites. For compounds **3–5** the butyl groups show one set of ^1H resonances which are partially overlapped by resonances of the isopropyl substituents of the imine ligand; by contrast, the corresponding ^{13}C resonances are well separated and the $^1J(^{119}Sn^{13}C)$ coupling constants could be easily observed. The C–Sn–C angles [C(20) and C(21) of the methyl groups in compounds **1** and **2**, and C(20) and C(24) of the butyl groups in compounds **3–5**] were calculated based on the relationships between $^2J(^{119}Sn,^1H)$ and $^1J(^{119}Sn,^{13}C)$ coupling constants and the C–Sn–C angle.[13,14] The obtained values (Table 2) indicate a good correlation between the structure present in solution and the trigonal bipyramidal (C,E) SnC$_2$X core with equatorial Sn–C bonds as determined in solid state, providing thus further support for the presence of the N→Sn intramolecular interaction in solution.

For all compounds **1–5** the ^1H and ^{13}C NMR spectra show one set of resonances for the substituents in *ortho* positions of the aromatic (*E*)-2-(2′,6′-^{i}Pr$_2$C$_6$H$_3$N=CH)C$_6$H$_4$ group attached to nitrogen, consistent with the presence of a species in solution for which free rotation around the C–N(=C) single bond is not restricted. The presence of two doublets for the methyl protons of the ^{i}Pr groups indicates their diastereotopic nature.

For organometallic compounds containing substituents with an imine bond the NMR spectroscopy is an excellent tool to evidence casual hydrolysis to a carbonyl-containing substituent. For compounds **1–5** both ^1H NMR ($\delta_{CH=N}$ range is 8.30-8.33 ppm) and ^{13}C NMR ($\delta_{CH=N}$ range is 168.1-168.7 ppm) spectra are indicative for the presence of only imine-containing organometallic species in solution.

Solid state structure

The dialkyl(iminoaryl)tin(IV) halides **1–5** exhibit a distorted trigonal bipyramidal (C,N)SnC$_2$X core (X = F, Cl, Br, I) [*i.e.* hypervalent (or hypercoordinated) 10-*Sn*-5 species] due to a strong intramolecular N$_{imine}$→Sn interaction (Fig. 1) [c.f. the sum of the covalent and van der Waals radii of the corresponding atoms: Σr_{cov}(Sn,N) 2.1 Å; Σr_{vdW}(Sn,N) 3.74 Å].[15] The axial positions are occupied by the nitrogen and the halide atoms [N–Sn–X 167.51(10), 173.1(2), 167.00(10), 163.9(4) and 168.97(12)° for **1**, **2**, **3**, **4a** and **5**, respectively], while the equatorial positions are occupied by carbon atoms (for

equatorial-axial C–Sn–N and C–Sn–X angles, as well as equatorial-equatorial C–Sn–C angles, see Table 1). A planar NC_3Sn chelate ring is thus formed and the tin-nitrogen distances in **1** [2.516(3) Å], **2** [2.487(10) Å], **3** [2.566(4) Å], **4a** [2.521(11) Å] and **5** [2.527(5) Å], respectively, are of the same order of magnitude as those observed for   [(*E*)-2-(4′-{MeO(O)C}C$_6$H$_4$N=CH)C$_6$H$_4$]SnMe$_2$Br [2.474(4) Å],[9d] or ClSnMe$_2$[2-C$_6$H$_4$(4-CH=N-1,1′-C$_6$H$_4$C$_6$H$_4$-4′-N=CH)-2′-C$_6$H$_4$]SnMe$_2$Cl [2.479(4) Å],[11] and the related [2-(Me$_2$NCH$_2$)C$_6$H$_4$]Me$_2$SnX [N$_{amine}$→Sn 2.509(2), 2.485(3), 2.445(3) and 2.442(4) Å for X = F, Cl, Br and I, respectively].[1c] Surprisingly, in spite of the different hybridization of the donor atom no obvious difference could be noticed, although one would expect better donor properties for a N(*sp²*) *vs* a N(*sp³*) atom, respectively. Moreover, the change of the halogen atom attached to tin atom does not result in a significant influence on the intramolecular N$_{imine}$→Sn distance.

All molecules of halides **1**–**5** contain an intramolecular C–H$_{aryl}$···X interactions involving the halogen atom and the H(6) atom of the aromatic ring [C(6)–H(6)···X 2.83 Å for **1** (X =

Cl), 3.09 Å for **2** (X = I), 2.79 Å for **3** (X = Cl), 2.52 Å for **4a** (X = F), and 2.89 Å for **5** (X = Br); c.f. Σr_{vdW}(Sn,X) 2.55, 3.01, 3.15 and 3.35 Å for X = F, Cl, Br and I, respectively].[15] A closer check of the crystal structure of all these organometallic halides revealed that while no intermolecular interactions between heavy atoms are established, several intermolecular C–H$_{CH=N}$···X and C–H···π interactions are present, thus resulting in supramolecular networks. For the chloride **1** the molecules are associated through C(7)–H(7)$_{CH=N}$···Cl(1a) (2.67 Å) interactions into chain polymers developed along the *b* axis (Fig. 2a). Such chain polymers are associated into a layer (Fig. 2b) through C–H···π (Ar$_{centroid}$) interactions [C(4)–H(4)$_{aryl}$···Ar$_{i-Pr}${C(8″)-C(13″)} 2.97 Å; γ = 12.7°; *i.e.* H···Ar$_{centroid}$ contacts shorter than 3.1 Å, with an angle γ between the normal to the aromatic ring and the line defined by the H atom and Ar$_{centroid}$ smaller than 30°].[16] Further C–H···π (Ar$_{centroid}$) interactions [C(15‴)–H(15B‴)$_{i-Pr}$···Ar{C(1)-C(6)} 2.89 Å; γ = 8.7°] connect parallel layers of molecules into a 3D supramolecular architecture (Fig. 2d).

(a)   (b)

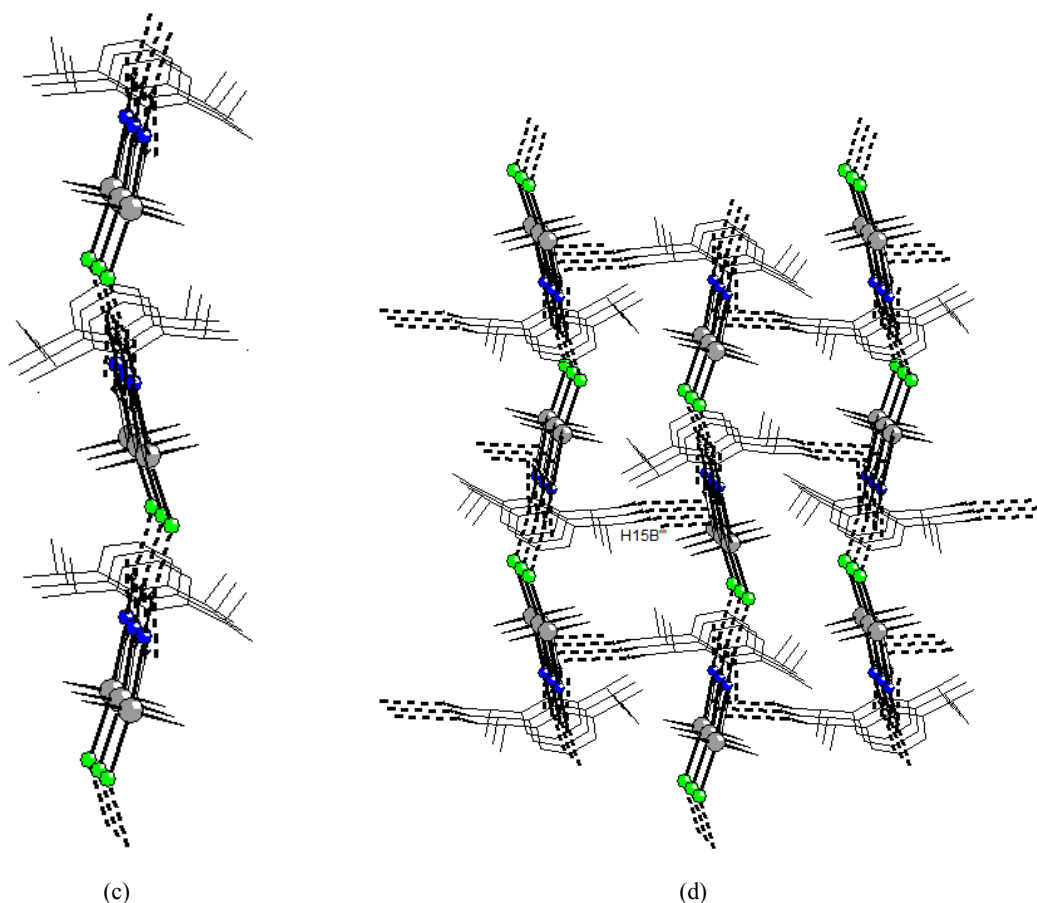(c)   (d)
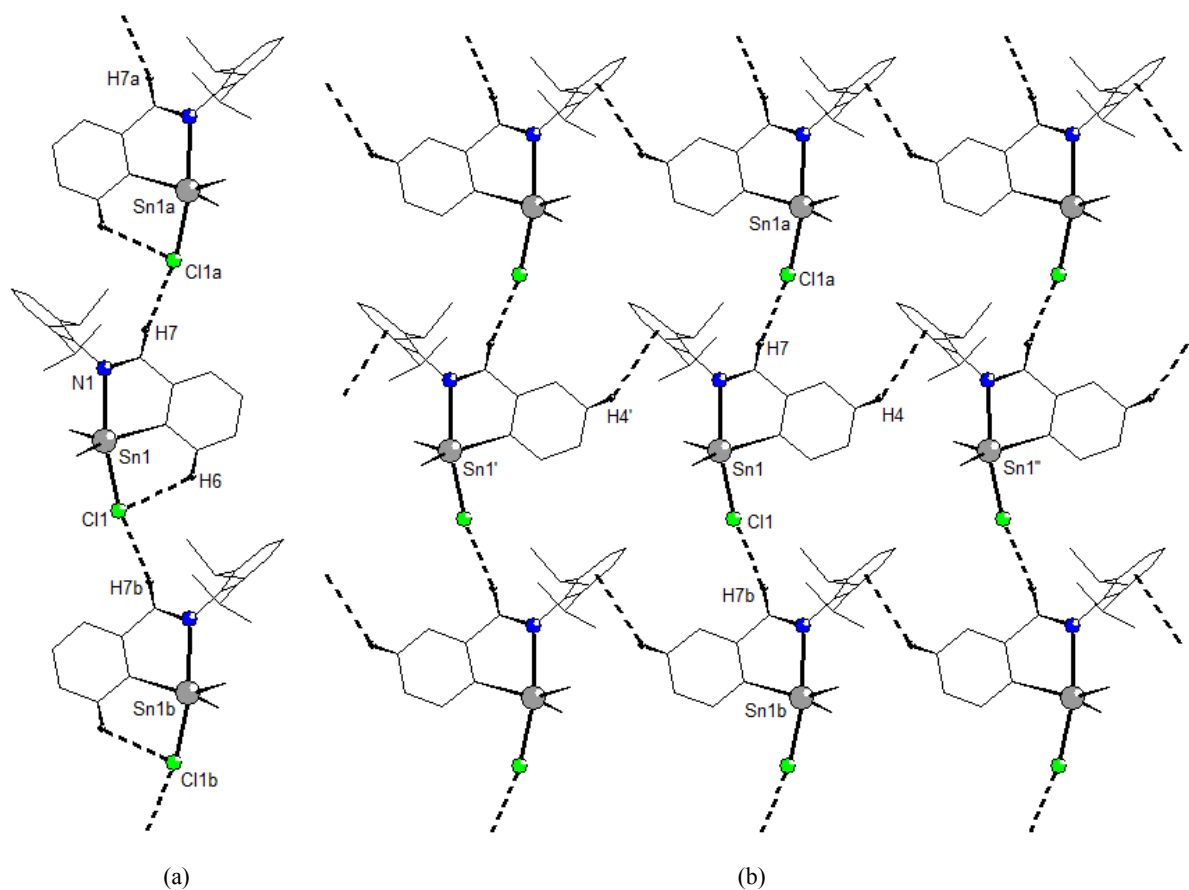
Fig. 2 – (a) View along *c* axis of a fragment of the chain polymer association based on intermolecular Cl···H$_{CH=N}$ interactions; (b) view along *c* axis of the association of the polymeric chains into a layer through inter-chains C–H$_{aryl}$···π (Ar$_{centroid}$) interactions; (c) view along *a* axis of the association of the polymeric chains into a layer; (d) view along *a* axis of the association of the layers into a 3D architecture through inter-layers C–H$_{methyl}$···π (Ar$_{centroid}$) interactions in the crystal of **1** (only hydrogens involved in intermolecular contacts and intramolecular Cl···H$_{aryl}$ interactions are shown) [symmetry equivalent atoms (*1.5–x, 0.5+y, 0.5–z*), (*1.5–x, –0.5+y, 0.5–z*), (*–1+x, y, z*), (*1+x, y, z*) and (*0.5+x, 0.5–y, 0.5+z*) are given by "a", "b", "prime", "double prime" and "triple prime", respectively].

In the crystal of the iodide **2** the molecules are connected [C(7)–H(7)$_{CH=N}$···I(1a) 3.24 Å] into similar chain polymers (Fig. 3a), which are associated into a layer (Fig. 3b) through C–H···π (Ar$_{centroid}$) interactions [C(4)–H(4)$_{aryl}$···Ar$_{i\text{-}Pr}${C(8″)-C(13″)} 2.91 Å; γ = 6.6°]. No further contacts are established between the parallel layers in the crystal of the iodide **2**.

In contrast to the chloride **1**, the molecules of the related chloride **3** are associated into chain polymers (Fig. 4a) through C(7)–H(7)$_{CH=N}$···Cl(1b) (2.86 Å), but no further interactions between such chain polymers were observed.

A different supramolecular architecture was found in the crystal of the fluoride **4**. The two independent molecules **4a** and **4b** alternate in a polymeric chain built based on several C–

H$_{CH=N}$···F [C(34)–H(34)$_{CH=N}$···F(1) 2.36 Å; C(7a)–H(7a) $_{CH=N}$···F(2) 2.33 Å] and C–H$_{aryl}$···F [C(30)–H(30)···F(1) 2.47 Å; C(3a)–H(3a)···F(2) 2.39 Å] interactions. Pairs of such chain polymers are further connected into isolated double-chain systems (Fig. 5) through C–H$_{butyl}$···π (Ar$_{centroid}$) interactions [C(54)–H(54B)$_{Me\text{-}butyl}$···Ar{C(28″)-C(33″)} 2.98 Å; γ = 7.7°] established only between molecules **4b** belonging to different chains.

Finally, a supramolecular 2D architecture could be also observed in the crystal of the bromide **5**. In contrast to the layers built in the crystals of the chloride **1** and iodide **2**, in this case similar polymeric chains (Fig. 6a) [C(7)–H(7)$_{CH=N}$···Br(1a) 3.01 Å] are associated into a layer (Fig. 6b) through further C–H···Br interactions [C(16)–H(16A)$_{i\text{-}Pr}$···Br(1a′) 3.06 Å].
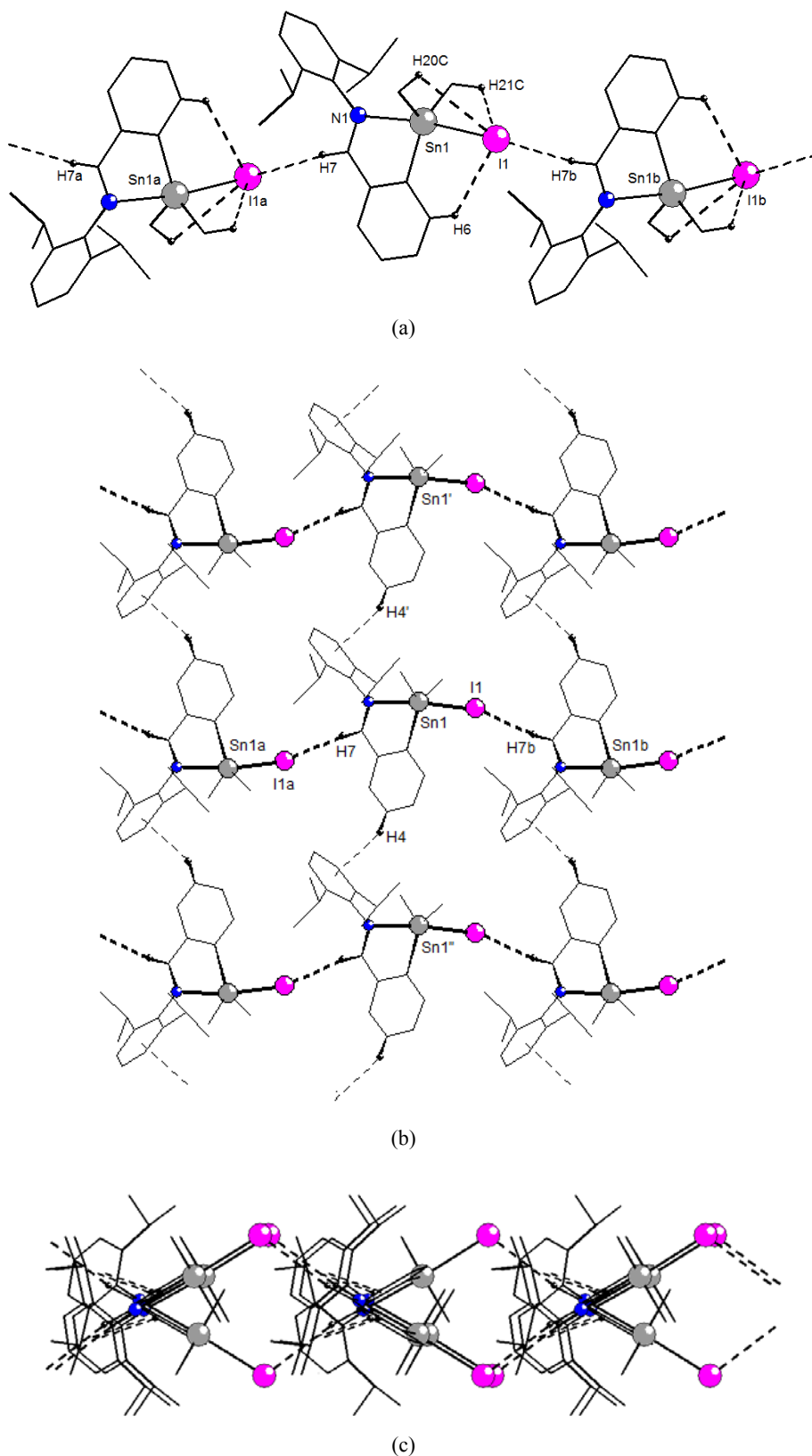
(a)

(b)

(c)

Fig. 3 – (a) View along *b* axis of a fragment of the chain polymer association based on intermolecular I···$H_{CH=N}$ interactions; (b) view along *b* axis of the association of the polymeric chains into a layer through inter-chains C–H_{aryl}···π ($Ar_{centroid}$) interactions; (c) view along *c* axis of the association of the polymeric chains into a layer in the crystal of **2** (only hydrogens involved in intermolecular contacts and intramolecular I···H_{aryl} and I···H_{methyl} interactions are shown) [symmetry equivalent atoms (–0.5+x, 1.5–y, 1–z), (0.5+x, 1.5–y, 1–z), (x, 1.5– y, –0.5+ z) and (x, 1.5– y, 0.5+ z) are given by "a", "b", "prime", and "double prime", respectively].
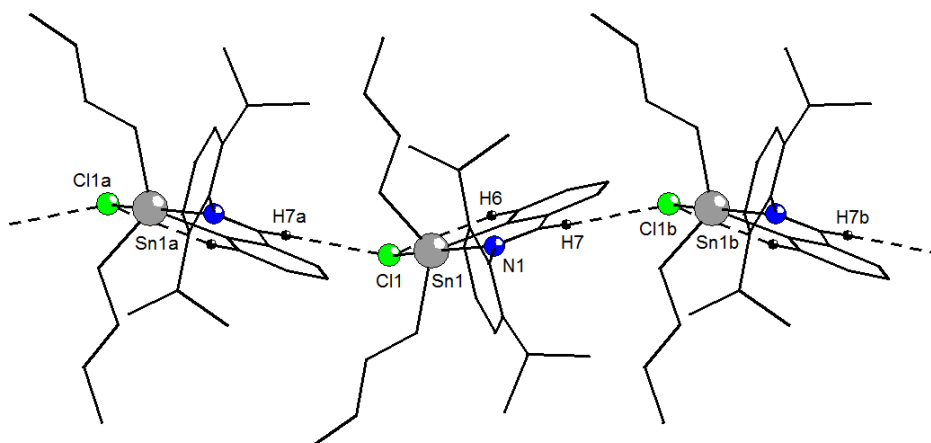
Fig. 4 – View of a fragment of the chain polymer association based on intermolecular Cl···H$_{CH=N}$ interactions in the crystal of **3** (only hydrogens involved in intramolecular Cl···H$_{aryl}$ and intermolecular Cl···H$_{CH=N}$ contacts interactions are shown) [symmetry equivalent atoms (*−0.5+x, 0.5–y, 0.5+z*) and (*0.5+x, 0.5–y, –0.5+z*) are given by "a" and "b", respectively].
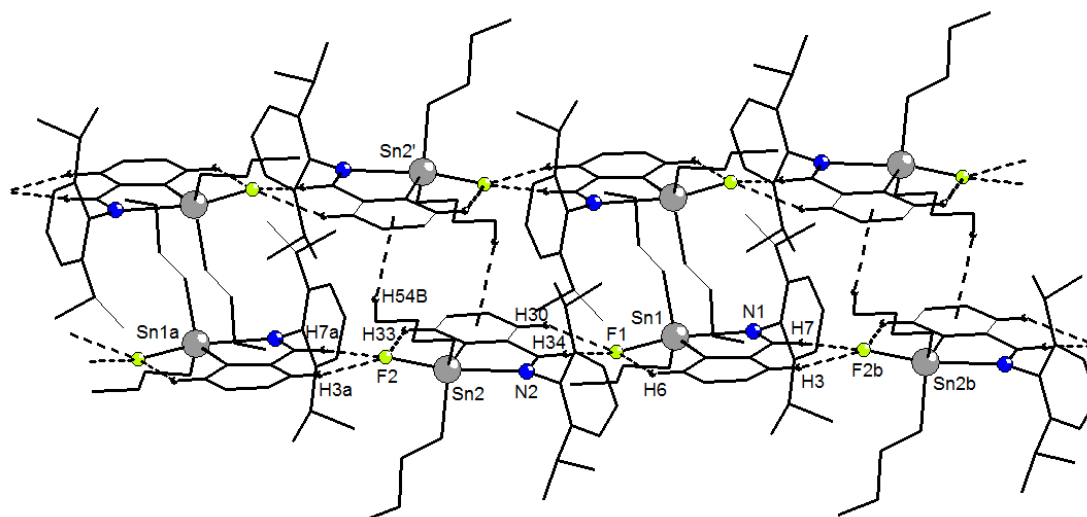

Fig. 5 – View of a fragment of the double-chain polymer association based on intermolecular F···H interactions within a chain and inter-chains C–H$_{alkyl}$···π (Ar$_{centroid}$) interactions in the crystal of **4** (only hydrogens involved in intramolecular F···H$_{aryl}$, intermolecular F···H and C–H$_{alkyl}$···π interactions are shown) [symmetry equivalent atoms (*x, y, 1+z*), (*x, y, –1+z*) and (*– x, 2– y, 2– z*) are given by "a", "b" and "prime", respectively].

EXPERIMENTAL

Most reactions and manipulations were carried out under an inert atmosphere of argon using Schlenk techniques. When appropriate, solvents were dried and freshly distilled under argon prior to use. Starting materials such as Me$_3$SnCl, Me$_2$SnCl$_2$, ^{n}Bu$_2$SnCl$_2$, KF, KBr, KI, 2-(O=CH)C$_6$H$_4$Br, 2′,6′-^{i}Pr$_2$C$_6$H$_3$NH$_2$ and Mg fillings were obtained from Aldrich or Merck, and were used as received. The organic bromide *(E)*-2-(2′,6′-^{i}Pr$_2$C$_6$H$_3$N=CH)C$_6$H$_4$Br was obtained using a procedure already described.[17] The ^{1}H, ^{13}C, ^{19}F and ^{119}Sn NMR spectra as well as 2D NMR spectra were recorded at room temperature on a VARIAN GEMINI 300S instrument, using solutions in CDCl$_3$. The ^{1}H chemical shifts are reported in δ units (ppm) relative to the residual peak of the deuterated solvent (CHCl$_3$, 7.26 ppm). The ^{13}C chemical shifts are reported in δ units (ppm) relative to the peak of the deuterated solvent (CDCl$_3$, 77.16 ppm).[18] The ^{1}H and ^{13}C resonances were assigned using 2D NMR experiments (COSY, HSQC, HMBC). The ^{19}F and ^{119}Sn chemical shifts are reported in δ

units (ppm) relative to CF$_3$COOH and Me$_4$Sn, respectively, used as external standards. The NMR spectra were processed using the *MestReC* and *MestReNova* software.[19] Mass spectra were recorded on Finnigan MAT 8200 instrument and were processed using the *MASPEC* II software.[20]

Synthesis of [(E)-2-(2′,6′-^{i}Pr$_2$C$_6$H$_3$N=CH)C$_6$H$_4$]SnMe$_2$Cl (**1**)

A solution of *(E)*-2-(2′,6′-^{i}Pr$_2$C$_6$H$_3$N=CH)C$_6$H$_4$Br (2.0 g, 5.81 mmol) in 50 mL THF was added dropwise under stirring to magnesium fillings (0.14 g, 5.83 mmol), activated with 1,2-dibromoethane (0.5 mL). The addition was completed after 0.5 h and the yellow reaction mixture was stirred for further 1.5 h under reflux. The resulted Grignard reagent was added dropwise to a solution of Me$_2$SnCl$_2$ (1.15 g, 5.23 mmol) in 20 mL THF. A yellowish precipitate was formed and the reaction mixture was stirred overnight. Then the solvent was removed under vacuum and the oily residue was stirred with hexane to give **1** as a white solid which was filtered and dried under vacuum. Yield: 1.2 g (51%). M.p. = 190-194 °C. ^{1}H NMR (300 MHz): δ 0.77 (6H, s, SnC*H*$_3$, ^{2}J$_{117SnH}$ = 67.5, ^{2}J$_{119SnH}$ =

70.6 Hz), 1.05 [6H, d, -CH(CH_3)$_2$ (A), $^3J_{HH}$ = 6.8 Hz], 1.27 [d, 6H, -CH(CH_3)$_2$ (B), $^3J_{HH}$ = 6.8 Hz], 2.71 [2H, hept, -CH(CH$_3$)$_2$, $^3J_{HH}$ = 6.8 Hz], 7.25 (m, 3H, *H*-3′-5′), 7.59 (1H, ddd, *H*-4, $^3J_{HH}$ = 7.4, $^4J_{HH}$ = 1.2 Hz), 7.65 (1H, dd, *H*-3, $^3J_{HH}$ = 7.4, $^4J_{HH}$ = 1.3 Hz), 7.74 (1H, ddd, *H*-5, $^3J_{HH}$ = 7.2, $^4J_{HH}$ = 1.6 Hz), 8.33 (1H, s, -C*H*=N-, $^4J_{SnH}$ = 9.6 Hz), 8.52 (1H, d, *H*-6, $^3J_{HH}$ = 7.3, $^3J_{SnH}$ = 64.0 Hz). ^{13}C NMR (75.5 MHz): δ 1.78 (s, SnCH$_3$, $^1J_{117SnC}$ = 500.5, $^1J_{119SnC}$ = 523.7 Hz), 22.64 [s, -CH(CH$_3$)$_2$ (B)], 26.43 [s, -CH(CH$_3$)$_2$ (A)], 28.19 [s, -

CH(CH$_3$)$_2$], 124.08 (s, *C*-3′,5′), 126.85 (s, *C*-4′), 130.10 (s, *C*-4, $^4J_{SnC}$ = 13.0 Hz), 132.56 (s, *C*-3, $^3J_{SnC}$ = 51.1 Hz), 133.74 (s, *C*-5, $^3J_{117SnC}$ = 62.1, $^3J_{119SnC}$ = 64.5 Hz), 137.94 (s, *C*-2, $^2J_{SnC}$ = 33.8 Hz), 138.36 (s, *C*-6, $^2J_{SnC}$ = 37.2 Hz), 140.01 (s, *C*-2′,6′), 142.28 (s, *C*-1, $^1J_{117SnC}$ = 655.8, $^1J_{119SnC}$ = 686.1 Hz), 144.10 (s, *C*-1′), 168.17 (s, -CH=N-, $^3J_{SnC}$ = 21.7 Hz). ^{119}Sn NMR (111.9 MHz): δ –40.7 (s). MS (EI, 70 eV, 200 ºC): *m/z* (%) 434 (100) [M–Me]$^+$, 414 (19) [M–Cl]$^+$, 264 (16) [R′]$^+$ [R′ = 2-(2′,6′-^{i}Pr$_2$C$_6$H$_3$N=CH)C$_6$H$_4$].

(a)

(b)

(c)
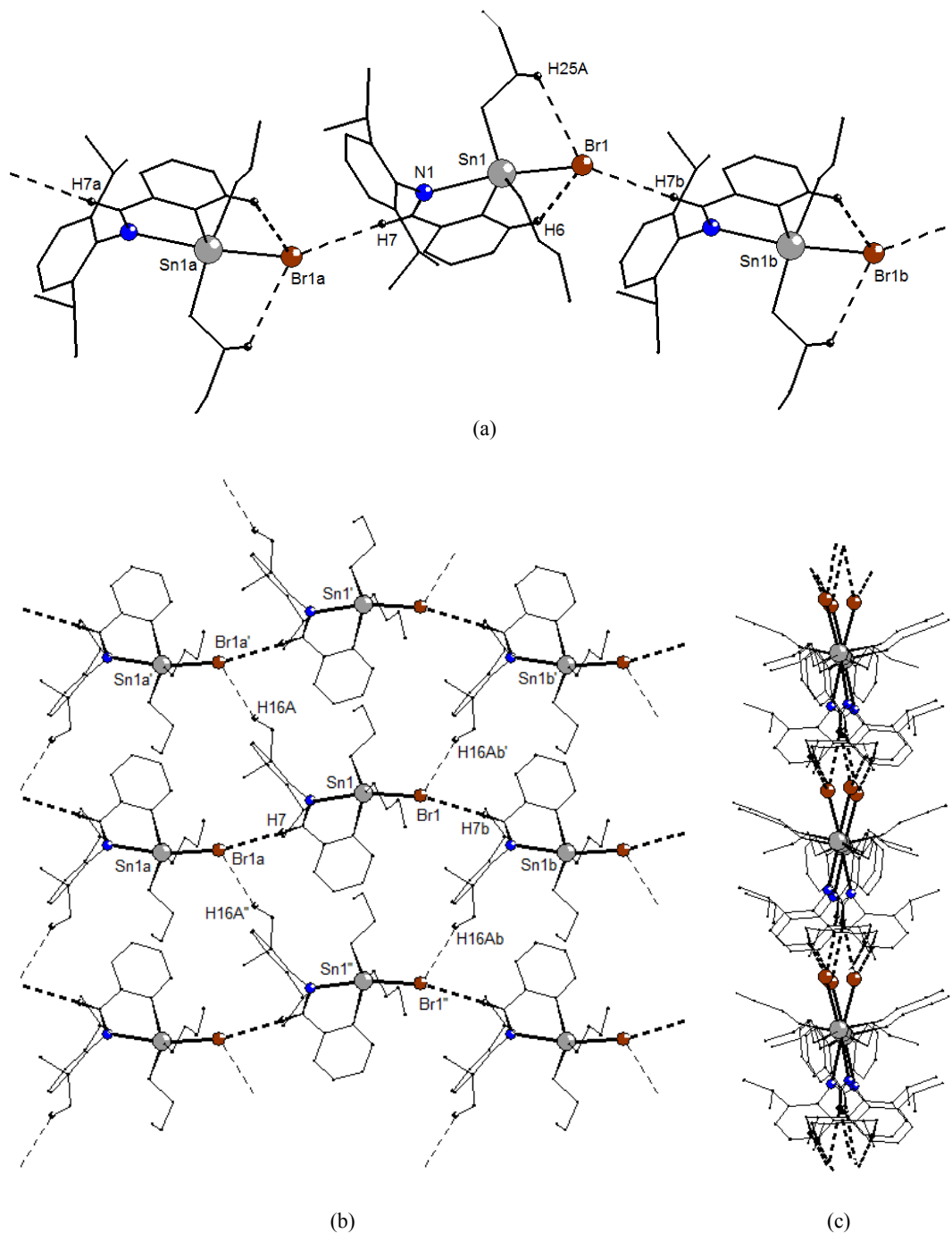
Fig. 6 – (a) View of a fragment of the chain polymer association based on intermolecular Br···H$_{CH=N}$ interactions; (b) view along *a* axis of the association of the polymeric chains into a layer through inter-chains Br···H$_{alkyl}$ interactions; (c) view along *b* axis of the association of the polymeric chains into a layer in the crystal of **5** (only hydrogens involved in intermolecular and intramolecular Br···H interactions are shown) [symmetry equivalent atoms *(0.5–x, 1–y, 0.5+z)*, *(0.5–x, 1–y, –0.5+z)*, *(0.5–x, 0.5+y, z)*, *(x, 1.5–y, 0.5+ z)*, *(x, 1.5–y, –0.5+ z)* and *(0.5–x, –0.5+ y, z)* are given by "a", "b", "prime", "a prime", "b prime" and "double prime", respectively].

Synthesis of [(E)-2-(2′,6′-ⁱPr₂C₆H₃N=CH)C₆H₄]SnMe₂I (2)

An aqueous solution of KI (0.1 g, 0.60 mmol, 500% excess) was added to a solution of **1** (0.05 g, 0.11 mmol) in 10 mL CH_2Cl_2, and the reaction mixture was stirred for 3 h at room temperature. The organic layer was separated and the aqueous phase was washed with 2 x 10 mL CH_2Cl_2. The unified organic phases were dried over anhydrous Na_2SO_4, then filtered and the solvent was removed under vacuum to give the title compound **2** as a pale yellow solid. Yield: 0.02 g (34%). M.p. = 155 °C. ^1H NMR (300 MHz): δ 1.05 (6H, s, SnCH_3, $^2J_{117SnH}$ = 66.1, $^2J_{119SnH}$ = 69.0 Hz), 1.07 [6H, d, -CH(CH_3)₂ (A), $^3J_{HH}$ = 6.6 Hz], 1.29 [d, 6H, -CH(CH_3)₂ (B), $^3J_{HH}$ = 6.7 Hz], 2.71 [2H, hept, -CH(CH₃)₂, $^3J_{HH}$ = 6.8 Hz], 7.26 (m, 3H, H-3′-5′), 7.61 (2H, m, H-3,4), 7.76 (1H, m, H-5), 8.30 (1H, s, -CH=N-, $^4J_{SnH}$ = 7.4 Hz), 8.66 (1H, d, H-6, $^3J_{HH}$ = 8.7, $^3J_{SnH}$ = 67.8 Hz). ^{13}C NMR (75.5 MHz): δ 5.23 (s, SnCH_3), 22.62 [s, -CH(CH_3)₂ (B)], 26.48 [s, -CH(CH_3)₂ (A)], 28.26 [s, -CH(CH_3)₂], 124.18 (s, C-3′,5′), 127.02 (s, C-4′), 130.38 (s, C-4), 132.67 (s, C-3), 133.75 (s, C-5), 137.73 (s, C-2), 139.70 (s, C-1), 140.23 (s, C-2′,6′), 140.87 (s, C-6), 144.02 (s, C-1′), 168.34 (s, -CH=N-). ^{119}Sn NMR (111.9 MHz): δ −65.8 (s). MS (EI, 70 eV, 200 ºC): m/z (%) 526 (15) [M–Me]⁺, 414 (100) [M–I]⁺.

Synthesis of [(E)-2-(2′,6′-ⁱPr₂C₆H₃N=CH)C₆H₄]SnⁿBu₂Cl (3)

A solution of (E)-2-(2′,6′-ⁱPr₂C₆H₃N=CH)C₆H₄Br (2.0 g, 5.81 mmol) in 50 mL THF was added dropwise under stirring to magnesium fillings (0.14 g, 5.83 mmol), activated with 1,2-dibromoethane (0.5 mL). The addition was completed after 0.5 h and the yellow reaction mixture was stirred for further 1.5 h with reflux. Then the Grignard reagent was added dropwise to a solution of ⁿBu₂SnCl₂ (1.59 g, 5.23 mmol) in 20 mL THF. A yellow precipitate was obtained and the reaction mixture was stirred overnight. Then the solvent was removed under vacuum and the oily residue was treated with hexane to give a crude solid product, which was filtered off. It was dissolved in CH_2Cl_2 and addition of n-hexane gave colourless crystals of **3** which were filtered and dried under vacuum. Yield: 1.0 g (36%). M.p. = 129-130 °C. ^1H NMR (300 MHz): δ 0.80 [6H, t, Sn(CH₂)₃CH_3, $^3J_{HH}$ = 7.2 Hz], 1.05 [6H, d, -CH(CH_3)₂ (A), $^3J_{HH}$ = 6.8 Hz], 1.29 [d, 6H, -CH(CH_3)₂ (B), $^3J_{HH}$ = 6.9 Hz], 1.20–1.73 [12H, m, Sn(CH_2)₃CH₃, overlapped by -CH(CH_3)₂ (B)], 2.76 [2H, hept, -CH(CH₃)₂, $^3J_{HH}$ = 6.8 Hz], 7.24 (m, 3H, H-3′-5′), 7.58 (2H, m, H-3,4), 7.71 (1H, ddd, H-5, $^3J_{HH}$ = 7.1, $^4J_{HH}$ = 1.6 Hz), 8.31 (1H, s, -CH=N-, $^4J_{SnH}$ = 10.3 Hz), 8.51 (1H, d, H-6, $^3J_{HH}$ = 7.2, $^3J_{SnH}$ = 57.3 Hz). ^{13}C NMR (75.5 MHz): δ 13.80 [s, Sn(CH₂)₃CH_3], 20.16 [s, SnCH_2CH₂CH₂CH₃, $^1J_{117SnC}$ = 475.4, $^1J_{119SnC}$ = 497.5 Hz], 22.78 [s, -CH(CH_3)₂ (B)], 26.39 [s, -CH(CH_3)₂ (A)], 26.89 [s, SnCH₂CH_2CH₂CH₃, $^3J_{117SnC}$ = 87.4, $^3J_{119SnC}$ = 91.4 Hz], 28.14 [s, -CH(CH_3)₂], 28.32 [s, SnCH₂CH₂CH_2CH₃, $^2J_{SnC}$ = 31.2 Hz], 124.03 (s, C-3′,5′), 126.64 (s, C-4′), 129.80 (s, C-4, $^4J_{SnC}$ = 11.7 Hz), 132.67 (s, C-3, $^3J_{SnC}$ = 46.6 Hz), 133.54 (s, C-5, $^3J_{SnC}$ = 53.9 Hz), 138.36 (s, C-2, $^2J_{SnC}$ = 29.9 Hz), 138.72 (s, C-6, $^2J_{SnC}$ = 30.8 Hz), 139.91 (s, C-2′,6′), 142.25 (s, C-1), 145.15 (s, C-1′), 168.52 (s, -CH=N-, $^3J_{SnC}$ = 14.7 Hz). ^{119}Sn NMR (111.9 MHz): δ −32.0 (s). MS (EI, 70 eV, 200 ºC): m/z (%) 498 (22) [M–Cl]⁺, 476 (100) [M–Bu]⁺, 264 (11) [R′]⁺ [R′ = 2-(2′,6′-ⁱPr₂C₆H₃N=CH)C₆H₄].

Synthesis of [(E)-2-(2′,6′-ⁱPr₂C₆H₃N=CH)C₆H₄]SnⁿBu₂F (4)

An aqueous solution of KF (0.36 g, 6.2 mmol, 500% excess) was added to a solution of **3** (0.65 g, 1.22 mmol) in 10 mL CH_2Cl_2, and the reaction mixture was stirred for 3 h at room temperature. The organic layer was separated and the aqueous phase was washed with 2 x 10 mL CH_2Cl_2. The organic layers were dried over anhydrous Na_2SO_4. The latter was filtered and the solvent was removed in vacuum to give the title compound as a white solid. Yield: 0.34 g (54%). M.p. = 125-126 °C. ^1H NMR (300 MHz): δ 0.81 [6H, t, Sn(CH₂)₃CH_3, $^3J_{HH}$ = 7.3 Hz], 1.05 [6H, d, -CH(CH_3)₂ (A), $^3J_{HH}$ = 6.8 Hz], 1.27 [d, 6H, -CH(CH_3)₂ (B), $^3J_{HH}$ = 6.8 Hz], 1.20–1.35 [8H, m, SnCH_2CH₂CH₂CH₃, overlapped by -CH(CH_3)₂ (B)], 1.50–1.65 [4H, m, SnCH₂CH_2CH₂CH₃,], 2.75 [2H, hept, -CH(CH₃)₂, $^3J_{HH}$ = 6.8 Hz], 7.20 (m, 3H, H-3′-5′), 7.53 (1H, ddd, H-4, $^3J_{HH}$ = 7.2, $^4J_{HH}$ = 1.2 Hz), 7.60 (1H, dd, H-3, $^3J_{HH}$ = 7.3, $^4J_{HH}$ = 1.0 Hz), 7.68 (1H, ddd, H-5, $^3J_{HH}$ = 7.1, $^4J_{HH}$ = 1.5 Hz), 8.25 (1H, d, H-6, $^3J_{HH}$ = 7.2, $^3J_{SnH}$ = 52.5 Hz), 8.29 (1H, s, -CH=N-, $^4J_{SnH}$ = 11.6 Hz). ^{13}C NMR (75.5 MHz): δ 13.81 [s, Sn(CH₂)₃CH_3], 17.97 [s, SnCH_2CH₂CH₂CH₃, $^2J_{FC}$ = 13.0, $^1J_{117SnC}$ = 494.7, $^1J_{119SnC}$ = 519.0 Hz], 22.76 [s, -CH(CH_3)₂ (B)], 26.30 [s, -CH(CH_3)₂ (A)], 27.05 [s, SnCH₂CH_2CH₂CH₃, $^3J_{117SnC}$ = 84.1, $^3J_{119SnC}$ = 87.2 Hz], 27.92 [s, SnCH₂CH₂CH_2CH₃, $^2J_{SnC}$ = 30.2 Hz], 28.06 [s, -CH(CH_3)₂], 123.90 (s, C-3′,5′), 126.42 (s, C-4′), 129.64 (s, C-4, $^4J_{SnC}$ = 11.6 Hz), 132.43 (s, C-3, $^3J_{SnC}$ = 47.2 Hz), 133.31 (s, C-5, $^3J_{SnC}$ = 55.5 Hz), 137.77 (d, C-6, $^3J_{FC}$ = 2.6, $^2J_{SnC}$ = 29.1 Hz), 138.49 (d, C-2, $^3J_{FC}$ = 0.7, $^2J_{SnC}$ = 32.7 Hz), 139.80 (s, C-2′,6′), 143.75 (d, C-1, $^2J_{FC}$ = 18.1 Hz), 145.37 (s, C-1′), 168.10 (s, -CH=N-, $^3J_{SnC}$ = 17.0 Hz). ^{19}F NMR (282.4 MHz): δ −201.8 (s, $^1J_{117SnF}$ = 2032, $^1J_{119SnF}$ = 2127 Hz). ^{119}Sn NMR (111.9 MHz): δ −65.7 (d, $^1J_{SnF}$ = 2127 Hz). MS (EI, 70 eV, 200 ºC): m/z (%) 498 (18) [M–F]⁺, 460 (100) [M–Bu]⁺, 384 (18) [R′M]⁺ [R′ = 2-(2′,6′-ⁱPr₂C₆H₃N=CH)C₆H₄].

Synthesis of [(E)-2-(2′,6′-ⁱPr₂C₆H₃N=CH)C₆H₄]SnⁿBu₂Br (5)

An aqueous solution of KBr (0.3 g, 2.52 mmol, 500% excess) was added to a solution of **3** (0.26 g, 0.49 mmol) in 10 mL CH_2Cl_2, and the reaction mixture was stirred for 3 h at room temperature. The organic layer was separated and the aqueous phase was washed with 2 x 10 mL CH_2Cl_2. The organic layers were dried over anhydrous Na_2SO_4. The latter was filtered and the solvent was removed in vacuum to give the title compound as a white solid. Yield: 0.1 g (35%). M.p. = 129-130 °C. ^1H NMR (300 MHz): δ 0.80 [6H, t, Sn(CH₂)₃CH_3, $^3J_{HH}$ = 7.3 Hz], 1.06 [6H, d, -CH(CH_3)₂ (A), $^3J_{HH}$ = 6.8 Hz], 1.29 [d, 6H, -CH(CH_3)₂ (B), $^3J_{HH}$ = 6.9 Hz], 1.20–1.73 [12H, m, Sn(CH_2)₃CH₃, overlapped by -CH(CH_3)₂ (B)], 2.76 [2H, hept, -CH(CH₃)₂, $^3J_{HH}$ = 6.8 Hz], 7.24 (m, 3H, H-3′-5′), 7.58 (2H, m, H-3,4), 7.71 (1H, ddd, H-5, $^3J_{HH}$ = 6.8, $^4J_{HH}$ = 2.0 Hz), 8.30 (1H, s, -CH=N-, $^4J_{SnH}$ = 10.4 Hz), 8.51 (1H, d, H-6, $^3J_{HH}$ = 7.3, $^3J_{SnH}$ = 57.1 Hz). ^{13}C NMR (75.5 MHz): δ 13.77 [s, Sn(CH₂)₃CH_3], 21.02 [s, SnCH_2CH₂CH₂CH₃, $^1J_{117SnC}$ = 464.4, $^1J_{119SnC}$ = 485.7 Hz], 22.80 [s, -CH(CH_3)₂ (B)], 26.39 [s, -CH(CH_3)₂ (A)], 26.78 [s, SnCH₂CH_2CH₂CH₃, $^3J_{117SnC}$ = 88.0, $^3J_{119SnC}$ = 91.5 Hz], 28.18 [s, -CH(CH_3)₂], 28.66 [s, SnCH₂CH₂CH_2CH₃, $^2J_{SnC}$ = 31.1 Hz], 124.07 (s, C-3′,5′), 126.72 (s, C-4′), 129.87 (s, C-4, $^4J_{SnC}$ = 11.4 Hz), 132.74 (s, C-3, $^3J_{SnC}$ = 45.7 Hz), 133.55 (s, C-5, $^3J_{SnC}$ = 56.8 Hz), 138.28 (s, C-2, $^2J_{SnC}$ = 29.0 Hz), 139.71 (s, C-6, $^2J_{SnC}$ = 32.0 Hz), 139.98 (s, C-2′,6′), 141.50 (s, C-1), 145.12 (s, C-1′), 168.67 (s, -CH=N-, $^3J_{SnC}$ = 13.9 Hz). ^{119}Sn NMR (111.9 MHz): δ −23.4 (s). MS (EI, 70 eV, 200 ºC): m/z (%) 576 (15) [M–H]⁺, 520 (100) [M–Bu]⁺, 498 (18) [M–Br]⁺, 384 (20) [R′M]⁺, 264 (10) [R′]⁺ [R′ = 2-(2′,6′-ⁱPr₂C₆H₃N=CH)C₆H₄].

	1	**2**	**3**	**4**	**5**
Molecular formula	$C_{21}H_{28}ClNSn$	$C_{21}H_{28}INSn$	$C_{27}H_{40}ClNSn$	$C_{27}H_{40}FNSn$	$C_{27}H_{40}BrNSn$
M	448.58	540.03	532.74	516.29	577.20
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Triclinic	Orthorhombic
Space group	$P2_1/n$	*Pbca*	$P2_1/n$	*P*-1	*Pbca*
Temperature (K)	297(2)	297(2)	297(2)	297(2)	297(2)
a/Å	9.2647(11)	16.266(3)	11.3098(11)	13.157(3)	17.937(3)
b/Å	16.9191(19)	14.699(3)	17.5060(17)	14.673(3)	16.820(3)
c/ Å	14.3385(18)	18.998(4)	13.9407(14)	15.149(3)	18.112(3)
α/º	90	90	90	88.726(4)	90
β/º	91.282(2)	90	90.609(2)	87.962(4)	90
γ/º	90	90	90	72.609(4)	90
V/Å^3	2247.0(5)	4542.3(16)	2760.0(5)	2788.9(10)	5464.5(14)
Z	4	8	4	4	8
D_{calc}/gcm^{-3}	1.326	1.579	1.282	1.230	1.403
F(000)	912	2112	1104	1072	2352
μ(Mo-Kα)/mm^{-1}	1.258	2.487	1.035	0.935	2.410
Crystal size (mm^3)	0.30 x 0.21 x 0.19	0.22 x 0.18 x 0.12	0.40 x 0.33 x 0.28	0.33 x 0.28 x 0.21	0.34 x 0.29 x 0.26
θ range for data collection (º)	2.41 to 25.00	2.14 to 25.00	2.14 to 25.00	1.45 to 25.00	2.00 to 25.00
Reflections collected	11644	31220	14289	26934	37674
Independent reflections	3938 [R_{int} = 0.0440]	4004 [R_{int} = 0.0964]	4857 [R_{int} = 0.0465]	9812 [R_{int} = 0.1053]	4804 [R_{int} = 0.0718]
Absorption correction	Multi-Scan[23]	Multi-Scan[23]	Multi-Scan[23]	Multi-Scan[23]	Multi-Scan[23]
Maximum and minimum transmissions	0.7960 and 0.7041	0.742 and 0.590	0.7603 and 0.6822	0.8279 and 0.7479	0.5730 and 0.4945
Data / restraints / parameters	3938 / 0 / 223	4004 / 0 / 224	4857 / 0 / 277	9812 / 96 / 553	4804 / 0 / 277
Goodness-of-fit on F^2	1.097	1.283	1.104	1.173	1.280
Final *R* indices [*I*>2σ(*I*)]	R_1 = 0.0517	R_1 = 0.1190	R_1 = 0.0569	R_1 = 0.1338	R_1 = 0.0773
	wR_2 = 0.1138	wR_2 = 0.2150	wR_2 = 0.1275	wR_2 = 0.2827	wR_2 = 0.1330
R indices (all data)	R_1 = 0.0674	R_1 = 0.1492	R_1 = 0.0763	R_1 = 0.2079	R_1 = 0.0965
	wR_2 = 0.1208	wR_2 = 0.2285	wR_2 = 0.1356	wR_2 = 0.3207	wR_2 = 0.1402
Largest difference peak and hole (e Å^{-3})	0.937 and –0.488	0.992 and – 1.260	0.719 and – 0.881	1.693 and – 1.499	0.686 and – 1.297

Crystal structure determination

Block colorless crystals of **1–5** were obtained from CH_2Cl_2/n-hexane mixture and attached on cryoloops using epoxy glue. The details of the crystal structure determination and refinement are given in Table 3. For compounds **2** and **4** the low quality of the measured crystal (and subsequently of the recorded data) resulted in a high R_1 parameter for the final structure refinement. Data collection and processing was carried on a Bruker SMART APEX system using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å), at room temperature.

The structures were refined with anisotropic thermal parameters. The hydrogen atoms were refined with a riding model and a mutual isotropic thermal parameter. For structure solving and refinement the software package SHELX-97 was used.[21] The drawings were created with the Diamond program.[22]

CONCLUSIONS

Several mixed aryl/alkyltin(IV) halides of the type $[(E)$-2-(2′,6′-^{i}Pr$_2$C$_6$H$_3$N=CH)C$_6$H$_4$]SnR$_2$X [R = Me, X = Cl (**1**), I (**2**); R = ^{n}Bu, X = Cl (**3**), F (**4**), Br (**5**)] were prepared and characterized by solution multinuclear (^{1}H, ^{13}C, ^{119}Sn) NMR spectroscopy and single-crystal X-ray diffraction. The NMR data suggest that an intramolecular N→Sn coordination is present in solution as was also evidenced in the solid state molecular structure of these (iminoaryl)tin(IV) species exhibiting a trigonal bipyramidal (C,N)SnC$_2$X core. In the crystal of these triorganotin(IV) halides there are no intermolecular interactions between heavy atoms. By contrast, 1D, 2D or 3D supramolecular networks, based on intermolecular C–H$_{CH=N}$···X and C–H···π (Ar$_{centroid}$) interactions, were evidenced for all five compounds.

Supplementary material

Crystallographic data for the structural analysis of compounds **1–5** have been deposited with the Cambridge Crystallographic Data Centre [CCDC no. 871118 (**1**), 871120 (**2**), 871121 (**3**), 871124 (**4**) and 871122 (**5**)]. Copies of the information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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