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Hypercoordinated Organotin(IV) Halides Containing 2-(Me_2NCH_2)C_6H_4 Groups: {2-(Me_2NCH_2)C_6H_4}$_2SnX_2$ (X = F, Cl, Br, I) and {2-(Me_2NCH_2)-C_6H_4}R_2SnX (R = Me, Ph; X = F, Cl, Br, I) and Their Solution Behaviour and Solid-State, Hydrogen-Bonding-Based Supramolecular Architecture

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The hypercoordinated di- and triorganotin(IV) chlorides [{2-(Me_2NCH_2)C_6H_4}$_2SnCl_2$] (**1a**) and [{2-(Me_2NCH_2)C_6H_4}-R_2SnCl] [R = Me (**2a**), Ph (**3a**)] were prepared by treating $SnCl_4$ or R_2SnCl_2 with [Li{2-(Me_2NCH_2)C_6H_4}]. Halide-exchange reactions between the organotin(IV) chlorides and the appropriate potassium halides gave [{2-(Me_2NCH_2)-C_6H_4}$_2SnX_2$] [X = F (**1b**), I (**1d**)], [{2-(Me_2NCH_2)C_6H_4}-Me_2SnX] [X = F (**2b**), Br (**2c**), I (**2d**)] and [{2-(Me_2NCH_2)-C_6H_4}Ph_2SnX] [X = F (**3b**), I (**3d**)]. Their solution behaviour was investigated by multinuclear (^1H, ^{13}C, ^{19}F and ^{119}Sn) NMR spectroscopy, including variable-temperature studies. Single-crystal X-ray diffraction analyses revealed that the strong intramolecular coordination of the nitrogen atom from the pendant CH_2NMe_2 group to tin induces chirality. The influence of the identity and the number of the halogen atoms and the organic substituents at tin is discussed in relation with the hydrogen-bonding network, which results in different supramolecular architectures in the crystal.

Introduction

Several organotin(IV) halides containing the [2-(Me_2NCH_2)C_6H_4] group or related organic ligands have been investigated so far both in solution and the solid state. Single crystal X-ray diffraction studies have revealed, in all cases, hypercoordinated structures obtained as a result of strong intramolecular N→Sn interactions.[1–27] On the basis of NMR spectroscopic data, octahedrally and trigonal bipyramidally configured tin atoms were suggested in solution for the intramolecularly coordinated diorganotin dihalides [{2-(Me_2NCH_2)C_6H_4}$_2SnX_2$] and triorganotin halides [{2-(Me_2NCH_2)C_6H_4}R_2SnX] (X = halogen), respectively. Single-crystal X-ray diffraction studies have confirmed the hypercoordinated nature of [{2-(Me_2NCH_2)C_6H_4}-Me_2SnCl] (**2a**)[17] and [{2-(Me_2NCH_2)C_6H_4}Ph_2SnX] [X = Cl (**3a′**),[20] Br (**3c**)[3]), but no crystallographic data are available for the diorganotin(IV) derivatives [{2-(Me_2-NCH_2)C_6H_4}$_2SnX_2$], and no studies on the influence of the identity and number of halogen atoms and organic substituents on the association through hydrogen bonds in the solid state have been reported. On the other hand, it has been shown previously that intramolecular coordination of the nitrogen atom to a metal atom in compounds containing a [2-(Me_2NCH_2)C_6H_4]M moiety induces chirality at the metal centre,[27–31] and therefore the crystals usually contain 1:1 mixtures of (*R*) and (*S*) isomers [with the C(1)–C(6) aromatic ring and the N(1) atom as chiral plane and pilot atom, respectively].[32] While this work was in progress the molecular structures of the fluorides [{2-(Me_2NCH_2)-C_6H_4}R_2SnF] [R = Me (**2b′**), Ph (**3b′**)], which crystallise in different space groups,[26] were reported, but no details concerning the planar chirality induced by the intramolecular N→Sn interaction and the hydrogen-bond network in the crystal were mentioned.

Here we report the synthesis and spectroscopic characterisation of some organotin(IV) halides, as well as the crystal and molecular structures of [{2-(Me_2NCH_2)-C_6H_4}$_2SnX_2$] [X = Cl (**1a**), F (**1b**), I (**1d**)], [{2-(Me_2NCH_2)-C_6H_4}Me_2SnX] [X = Cl (**2a**), F (**2b**), Br (**2c**), I (**2d**)] and [{2-(Me_2NCH_2)C_6H_4}Ph_2SnX] [X = F (**3b**), I (**3d**)]. The discussion of the solid-state structure is focused on the hydrogen-bonding-based network between the isomers, which results in different supramolecular architectures in the crystal.

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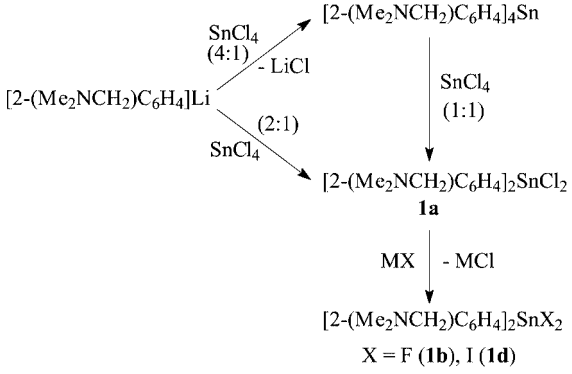
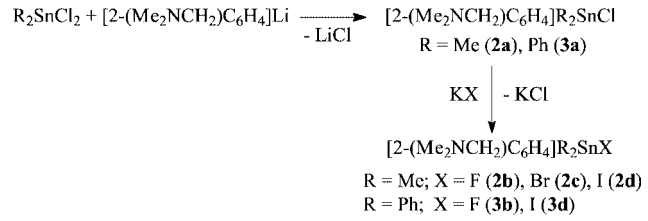
Results and Discussion

The diorganotin(IV) dihalides were prepared according to Scheme 1. The ligand-redistribution reaction between [{2-(Me_2NCH_2)C_6H_4}$_4$Sn] and $SnCl_4$ in the absence of a solvent has proved to be an excellent alternative to the direct synthesis from [Li{2-(Me_2NCH_2)C_6H_4}] and $SnCl_4$ for the preparation of **1a** as it allows a better control of the stoichiometry of the reagents. The halide-exchange reactions between the organotin(IV) chlorides and the appropriate potassium halides (Schemes 1 and 2) were performed according to a modified literature procedure[33] in a two-layer solvent system (H_2O/MeOH/CH_2Cl_2).



Scheme 1. Synthesis of compounds **1a**–**1d**.

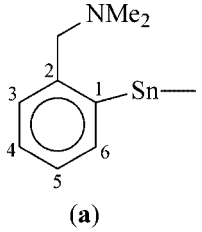


Scheme 2. Synthesis of compounds **2a**–**2d**, **3a**, **3b** and **3d**.

All compounds were isolated as air-stable, colourless, crystalline products. They are soluble in common organic solvents, such as chloroform, methylene dichloride or benzene.

Solution Behaviour

All compounds were investigated by multinuclear (^{1}H, ^{13}C, ^{119}Sn) NMR spectroscopy in solution at room temperature. For the organotin fluorides, the ^{19}F NMR spectra were also recorded.



(a)

The assignments of the ^{1}H and ^{13}C resonances according to the numbering scheme above were based on 2D experiments and tin–carbon coupling constants, and were confirmed for several compounds by simulation of the aromatic region of the ^{1}H NMR spectra using the gNMR program (see Supporting Information).

The low-temperature ^{1}H NMR spectra of the diorganotin derivatives [{2-(Me_2NCH_2)C_6H_4}$_2$$SnX_2$] [X = Cl (**1a**), F (**1b**) and I (**1d**)] are very similar (see Supporting Information) to that reported for the dibromide analogue **1c**,[6] i.e. an AB system and two singlet resonances in the aliphatic region for the diastereotopic CH_2 protons and the CH_3 groups at nitrogen, respectively. This is consistent with a *trans* arrangement of the organic ligands and a *cis* arrangement of the two coordinated nitrogen atoms and halogen atoms in solution,[6] as subsequently proved by single-crystal X-ray diffraction for compounds **1a**, **1b** and **1d** (see below). When the temperature is raised, the diorganotin dichloride **1a** and the diorganotin diiodide **1d** exhibit a similar behaviour to the diorganotin dibromide **1c**.[6,22] The two singlets for the methyl protons of the NMe_2 group coalesce at 20 °C for **1a** ($\Delta G^{\ddagger}$ = 13.8 kcal mol^{-1}) and 0 °C for **1d** ($\Delta G^{\ddagger}$ = 12.6 kcal mol^{-1}) in $CDCl_3$. This coalescence indicates that the process involving N→Sn dissociation/recoordination, with inversion at a three-coordinate nitrogen atom and rotation of the $C_{methylene}$–N bond, becomes fast on the NMR timescale. The AB pattern for the methylene protons is retained even at 60 °C, thus indicating configurational stability of the tin atom in the [{2-(Me_2NCH_2)C_6H_4}$_2$$SnX_2$] derivatives containing heavier halogens. In contrast, coalescence of both the two resonances of the NMe_2 group ($\Delta G^{\ddagger}$ = 14.2 kcal mol^{-1}) and the AB pattern of the CH_2 group ($\Delta G^{\ddagger}$ = 14.3 kcal mol^{-1}) is observed at 10 °C for the diorganotin difluoride **1b** in $CDCl_3$. This suggests that exchange of the chloride by fluoride results in a considerable decrease of the configurational stability of the tin atom in **1b** compared to **1a**. There is no indication for a *cis–trans* equilibrium in solution such as that observed for [{$Me_2N(CH_2)_3$}$_2$$SnF_2$]·2$H_2O$.[34]

The magnitudes of the ^{119}Sn chemical shifts for the diorganotin halides **1a** (s, δ = –260.7 ppm), **1b** (t, δ = –386.7 ppm) and **1d** (δ = –346.9 ppm) at room temperature are typical for six-coordinate diorganotin(IV) species in solution [cf. [{$Me_2N(CH_2)_3$}$_2$$SnF_2$]·2$H_2O$[34] ($\delta$ = –292.0 ppm in CD_2Cl_2) and [(8-$Me_2NC_{10}H_6$)$_2$$SnI_2$][11] ($\delta$ = –361.9 ppm in $C_6D_5CD_3$)]. The equivalence of the fluoride atoms in **1b** is reflected in a singlet ^{19}F resonance surrounded by tin satellites (δ = –181.5 ppm, $^1J_{F,Sn}$ = 2567/2683 Hz) and a triplet ^{119}Sn resonance (δ = –386.7 ppm, $^1J_{F,Sn}$ = 2663 Hz).

The ^{1}H and ^{13}C NMR spectra for the triorganotin halides [{2-(Me_2NCH_2)C_6H_4}Me_2SnX] [X = Cl (**2a**), F (**2b**), Br (**2c**), I (**2d**)] and [{2-(Me_2NCH_2)C_6H_4}Ph_2SnX] [X = F (**3b**), I (**3d**)] are very similar to those of benzyldimethylamine, regardless of the nature of the halogen and the other organic groups attached to tin. Two singlet resonances are observed in the aliphatic region for the methylene and the methyl protons, respectively, which is compatible either with a tetrahedral or with a pentacoordinate structure (assuming a fast conformational change of the five-membered SnC_3N nonplanar chelate ring in solution, which gives averaged ^{1}H NMR signals). The ^{13}C NMR spectrum contains two sing-

Table 1. Comparison of the solution NMR spectroscopic data for triorganotin(IV) compounds (δ in ppm, J in Hz).[a]

Compound	^{119}Sn	^{19}F
[{2-(Me_2NCH_2)C_6H_4}$_2$$SnF_2$] (**1b**)	–386.7 (t)[b]	–181.5 (s)
	($^1J_{F,Sn}$ = 2663)	($^1J_{F,Sn}$ = 2567/2683)
[{2-(Me_2NCH_2)C_6H_4}$_2$$SnCl_2$] (**1a**)	–260.7 (s)[b]	
[Ph_2SnCl_2][35]	–26.7 (s)	
[{2-(Me_2NCH_2)C_6H_4}$_2$$SnI_2$] (**1d**)	–346.9 (s)	
[Ph_2SnI_2][35]	–241.1 (s)	
[{2-(Me_2NCH_2)C_6H_4}Me_2SnF] (**2b**)[c]	–52.7 (d)	–178.4 (s)
	($^1J_{F,Sn}$ = 2039.3)	($^1J_{F,Sn}$ = 1944.2/2034.6)
[Me_2PhSnF][33]	–52.3 (t)	–137.4 (s)
	($^1J_{F,Sn}$ = 1340)	($^1J_{F,Sn}$ = 1255)
	–53.0 (t, br)[d]	–139.0 (s)[d]
	($^1J_{F,Sn}$ = 1334)	($^1J_{F,Sn}$ = 1260)
	–49.5 (t)[e]	
	($^1J_{F,Sn}$ = 1235)	
[{2-(Me_2NCH_2)C_6H_4}Me_2SnCl] (**2a**)	–48.7 (s)[b]	
[$Me_2PhSnCl$][36]	48.3 (s)	
[{2-(Me_2NCH_2)C_6H_4}Me_2SnBr] (**2c**)	–55.5 (s)	
[{2-(Me_2NCH_2)C_6H_4}Me_2SnI] (**2d**)	–72.8 (s)	
[Me_2PhSnI][37]	–17.9 (s)	
[{2-(Me_2NCH_2)C_6H_4}Ph_2SnF] (**3b**)[f]	–197.6 (d)	–182.4 (s)
	($^1J_{F,Sn}$ = 2157)	($^1J_{F,Sn}$ = 2058.3/2154.0)
[Ph_3SnF][38]	–211.9 (t)[e]	
	($^1J_{F,Sn}$ = 1530)	
[{2-(Me_2NCH_2)C_6H_4}Ph_2SnCl] (**3a**)[20]	–176.9 (s)	
[Ph_3SnCl][39]	–44.8 (s)	
[{2-(Me_2NCH_2)C_6H_4}Ph_2SnI] (**3d**)	–199.5 (s)	
[Ph_3SnI][39]	–113.4 (s)	

[a] Spectra recorded in $CDCl_3$ at room temperature. [b] In CH_2Cl_2/[D$_6$]acetone. [c] Ref.[26]: $\delta_{^{119}Sn}$ = –53.8 ppm ($^1J_{F,Sn}$ = 2023 Hz), $\delta_{^{19}F}$ = –178.8 ppm. [d] In $C_6D_5CD_3$. [e] ^{119}Sn MAS NMR spectroscopic data. [f] Ref.[26]: $\delta_{^{119}Sn}$ = –198.6 ppm ($^1J_{F,Sn}$ = 2141 Hz), $\delta_{^{19}F}$ = –182.3 ppm.

let signals for the methylene and the methyl carbon atoms, respectively, but the tin satellites are well resolved only for the former; the magnitude of the $^2J_{C,Sn}$ (ca. 28–30 Hz) couplings is consistent with the presence of an intramolecular N→Sn coordination, i.e. a trigonal bipyramidal (*C*,*N*)-C_2SnX core. The major difference noted in the ^{1}H NMR spectra of the two series of compounds is the downfield shift of the resonance for the aromatic H-6 proton, which is a result of the intramolecular interaction of this proton with the halogen atom.

The increase in the H-6 chemical shift follows the order F < Cl < Br < I (δ = 7.97, 8.17, 8.26 and 8.31 ppm for the triaryltin halides **2b**, **2a**, **2c** and **2d**, respectively). In addition to the resonances assigned to the 2-(Me_2NCH_2)C_6H_4 ligand, the ^{1}H and ^{13}C NMR spectra for the [{2-(Me_2NCH_2)-C_6H_4}R_2SnX] derivatives also contain signals corresponding to equivalent methyl and phenyl groups, respectively.

A comparison of the ^{19}F and ^{119}Sn NMR parameters for the diorganotin dihalides [{2-(Me_2NCH_2)C_6H_4}$_2$$SnX_2$] and the triorganotin halides [{2-(Me_2NCH_2)C_6H_4}R_2SnX] described in this work and the related [Ph_2SnX_2], [Me_2PhSnX] and [Ph_3SnX] derivatives is given in Table 1. The increase of the coordination number at the metal atom in solution to six and five, respectively, is supported by the upfield shift of the ^{119}Sn chemical shift in the 2-(Me_2NCH_2)C_6H_4-containing derivatives (X = Cl, Br, I) with respect to the corresponding monomeric, tetrahedral [Ph_2SnX_2], [Me_2PhSnX] and [Ph_3SnX] compounds.

In conclusion, the NMR spectroscopic data indicate that both [{2-(Me_2NCH_2)C_6H_4}$_2$$SnX_2$] and [{2-($Me_2NCH_2$)-$C_6H_4$}$R_2SnX$] compounds exhibit intramolecular N→Sn coordination in solution, which results in similar coordination geometries to those found in the solid state (see below).

Solid-State Structures

The crystal and molecular structures of **1a**, **1b**, **1b**·CH_2Cl_2, **1d**, **2a**, **2a′**, **2b**–**2d**, **3a**, **3b** and **3d** were determined by single-crystal X-ray diffraction. Crystals suitable for X-ray diffraction analysis were generally grown by solvent diffusion from dichloromethane and *n*-hexane. Crystals of the dichloromethane solvate of the diorganotin difluoride [{2-(Me_2NCH_2)C_6H_4}$_2$$SnF_2$], namely **1b**·$CH_2Cl_2$, were obtained from a CH_2Cl_2/*n*-hexane (approximately 1:3) mixture, and were measured immediately after removal from solution. The crystal was stable enough for a sufficiently good measurement, but they turned opaque within two days in the air due to loss of the crystallisation solvent, as proved by ^{1}H NMR spectroscopy. Crystals of [{2-(Me_2NCH_2)C_6H_4}$_2$$SnF_2$] (**1b**), free of crystallisation solvent, were also obtained by slow crystallisation from a CH_2Cl_2/*n*-hexane (approximately 1:5) mixture. The triorganotin chloride [{2-(Me_2NCH_2)C_6H_4}Me_2SnCl] crystallises in different forms from ethanol (**2a**; orthorhombic, space group *Pbca*) and *n*-hexane (**2a′**; orthorhombic, space group $Pna2_1$. This form has also been reported by Rippstein et al.[17] for crystals grown from $CHCl_3$). Monoclinic crystals (space group $P2_1/n$) with different unit-cell parameters were obtained for [{2-(Me_2NCH_2)C_6H_4}-Ph_2SnCl] when the compound was crystallised from tolu-

ene[20] or CH_2Cl_2/*n*-hexane (**3a**); the first form contains one molecule in the unit cell[20] while the second one contains two independent molecules. The crystals of [{2-(Me_2NCH_2)-C_6H_4}Ph_2SnF] (**3b**; monoclinic, space group $P2_1/n$, which is different from the reported space group $P2_1/c$[26]) also contain two independent molecules in the unit cell.

Selected molecular parameters are given in Tables 2, 3 and 4, and the molecular structures of representative compounds **1b** and **3d**, with the atom numbering schemes, are shown in Figures 1 and 2, respectively. The molecules of all compounds investigated in this work feature a metal atom strongly coordinated by two or one nitrogen atoms of the pendant arms *trans* to an Sn–halogen bond in diorganotin(IV) and triorganotin(IV) halides, respectively [the Sn–N distance exceeds the sum of the covalent radii for the corresponding atoms, Σ_{cov}(Sn,N) = 2.1 Å[40]]. This results in different coordination environments of the metal atom, i.e. octahedral $(C,N)_2SnX_2$ for **1a**, **1b** and **1d**, and trigonal bipyramidal $(C,N)C_2SnX$ configurations for **2a**–**2d**, **3b** and **3d**.

The $(C,N)_2SnX_2$ core in the [{2-(Me_2NCH_2)-C_6H_4}$_2SnX_2$] derivatives shows a *trans*-SnC_2 fragment, while the N and X atoms are *cis* (Figure 1). This contrasts with the molecular structure reported for the related [{$Me_2N(CH_2)_3$}$_2SnF_2$]·$2H_2O$,[34] which exhibits an all-*trans* octahedral $(C,N)_2SnX_2$ configuration. The difference in the configuration of the octahedral environment of tin is reflected in the lengthening and shortening of the Sn–F and Sn–N bond lengths, respectively, in **2b** [Sn(1)–F(1) = 1.9726(14), Sn(1)–F(2) = 1.9774(13), Sn(1)–N(1) = 2.5083(19) and Sn(1)–N(2) = 2.6064(18) Å] in comparison

Table 2. Selected bond lengths [Å] and angles [°] for [{2-(Me_2NCH_2)C_6H_4}$_2SnX_2$] compounds.

	1a[a] (X = Cl)	**1b** (X = F)	**1b**·CH_2Cl_2 (X = F)	**1d** (X = I)
Sn(1)–C(1)	2.1278(17)	2.119(2)	2.109(6)	2.142(6)
Sn(1)–C(10)		2.113(2)	2.130(5)	2.128(5)
Sn(1)–X(1)	2.4394(5)	1.9726(14)	1.988(3)	2.8371(7)
Sn(1)–X(2)		1.9774(13)	1.988(3)	2.8315(7)
Sn(1)–N(1)	2.6199(16)	2.5083(19)	2.601(5)	2.572(5)
Sn(1)–N(2)		2.6064(18)	2.469(5)	2.677(6)
C(1)–Sn(1)–C(10)	152.22(9)	154.86(8)	154.8(2)	156.3(2)
X(1)–Sn(1)–N(1)	166.25(4)	166.79(6)	168.00(16)	170.95(14)
X(2)–Sn(1)–N(2)		167.53(6)	166.83(16)	170.62(12)
C(1)–Sn(1)–N(1)	73.77(6)	74.99(7)	73.7(2)	74.3(2)
C(10)–Sn(1)–N(2)		73.54(7)	75.26(19)	73.1(2)
N(1)–Sn(1)–N(2)	108.54(7)	103.86(6)	105.40(17)	102.39(18)
X(1)–Sn(1)–X(2)	89.79(3)	89.87(7)	88.30(18)	89.55(2)

[a] C(10) = C(1a), X(2) = X(1a), N(2) = N(1a); symmetry equivalent positions (–*x*, *y*, –*z* + 1/2) are indicated by an "a".

Table 3. Selected bond lengths [Å] and angles [°] for [{2-(Me_2NCH_2)C_6H_4}Me_2SnX] compounds.

	2a[a] (X = Cl)	**2a′**[b] (X = Cl)	**2b** (X = F)	**2c** (X = Br)	**2d** (X = I)
Sn(1)–C(1)	2.129(3)	2.127(4)	2.123(3)	2.132(3)	2.135(4)
Sn(1)–C(10)	2.124(4)	2.144(5)	2.118(3)	2.110(4)	2.120(4)
Sn(1)–C(11)	2.115(4)	2.121(4)	2.120(3)	2.106(4)	2.133(5)
Sn(1)–X(1)	2.5250(16)	2.5371(9)	2.0187(17)	2.6839(5)	2.9367(5)
Sn(1)–N(1)	2.485(3)	2.488(3)	2.509(2)	2.445(3)	2.442(4)
X(1)–Sn(1)–N(1)	168.11(7)	170.79(8)	167.45(9)	168.62(7)	170.45(9)
C(1)–Sn(1)–N(1)	74.17(11)	75.55(13)	74.08(11)	74.76(12)	75.99(15)
C(1)–Sn(1)–C(10)	123.73(14)	119.92(16)	118.91(13)	124.67(16)	129.5(2)
C(1)–Sn(1)–C(11)	116.94(15)	116.13(18)	123.55(13)	116.02(17)	111.66(18)
C(10)–Sn(1)–C(11)	117.71(16)	122.55(19)	115.75(15)	118.17(19)	117.2(2)

[a] Crystals from ethanol. [b] Crystals from *n*-hexane.

Table 4. Selected bond lengths [Å] and angles [°] for [{2-(Me_2NCH_2)C_6H_4}Ph_2SnX] compounds.

	3a[a,b] (X = Cl)		**3b**[b] (X = F)		**3d** (X = I)
Sn(1)–C(1)	2.118(4)	2.134(4)	2.105(5)	2.128(5)	2.135(5)
Sn(1)–C(10)	2.130(4)	2.126(4)	2.121(4)	2.132(5)	2.132(5)
Sn(1)–C(16)	2.134(4)	2.132(4)	2.129(4)	2.132(4)	2.135(4)
Sn(1)–X(1)	2.4944(11)	2.4872(12)	2.008(3)	2.006(4)	2.8631(6)
Sn(1)–N(1)	2.538(4)	2.509(3)	2.560(4)	2.521(4)	2.496(4)
X(1)–Sn(1)–N(1)	169.73(10)	168.68(8)	167.53(14)	168.34(14)	171.56(10)
C(1)–Sn(1)–N(1)	75.46(15)	74.86(14)	74.74(17)	74.88(18)	75.36(18)
C(1)–Sn(1)–C(10)	116.85(16)	113.58(15)	117.34(18)	126.98(19)	114.09(19)
C(1)–Sn(1)–C(16)	124.23(15)	126.56(16)	122.80(17)	112.10(17)	122.55(17)
C(10)–Sn(1)–C(16)	116.28(16)	117.42(17)	117.61(18)	118.45(18)	121.29(19)

[a] Crystals from CH_2Cl_2/*n*-hexane. [b] Two independent molecules are present in the unit cell.

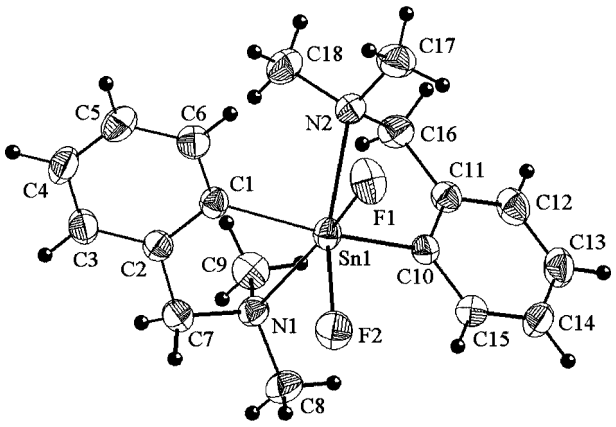


Figure 1. ORTEP representation at 50% probability and atom-numbering scheme for the isomer (R_{N1},S_{N2})-**1b**.

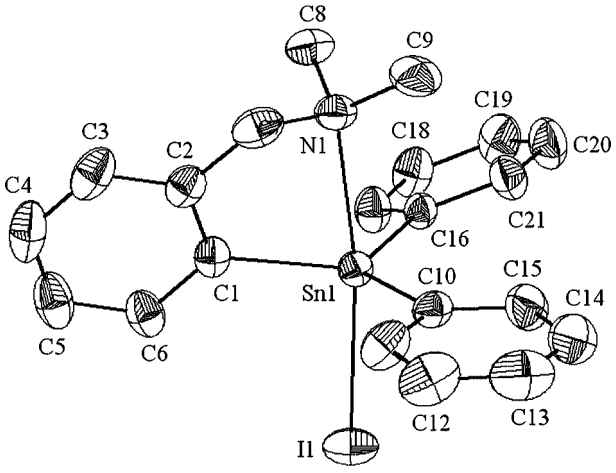


Figure 2. ORTEP representation at 30% probability and atom-numbering scheme for the isomer (*S*)-**3d**. Hydrogens have been omitted for clarity.

with [{$Me_2N(CH_2)_3$}$_2$$SnF_2$]·$2H_2O$ [Sn(1)–F(1) = 2.084(6) and Sn(1)–N(1) = 2.366(8) Å].[34]

The molecular structures of the triorganotin halides [{2-(Me_2NCH_2)C_6H_4}R_2SnX] (**2a**–**2d**, **3b** and **3d**) are very similar. One representative is shown in Figure 2. The tin–nitrogen distances are not dramatically affected by the identity of the halogen atom *trans* to the nitrogen atom. The Sn(1) atom is displaced from the equatorial plane defined by C(1), C(10) and C(16) (Figure 2) in the direction of the X(1) atom, which means that the X–Sn–C angles are larger than the N–Sn–C angles.

As a result of the intramolecular coordination of the nitrogen to the tin atom a five-membered SnC_3N ring is formed. This ring is not planar but is folded along the Sn(1)···$C_{methylene}$ axis, with the nitrogen atom lying above the best plane defined by Sn(1), C(1), C(2) and C(methylene). This induces planar chirality at the metal atom,[27–31] and all compounds reported here crystallise as racemates. The crystals of the triorganotin(IV) derivatives (**2a**, **2a′**, **2b**–**2d**, **3a**, **3a′**, **3b**, **3b′** and **3d**) contain 1:1 mixtures of (*R*) and (*S*) isomers, with the C(1)–C(6) aromatic ring and the N(1) atom as chiral plane and pilot atom, respectively.[32] The crystals of the diorganotin(IV) derivatives contain either (S_{N1},R_{N2}) and (R_{N1},S_{N2}) isomers (for **1b**) or (S_{N1},S_{N2}) and (R_{N1},R_{N2}) isomers (for **1a** and **1d**) with respect to the two chelate rings in a molecular unit. The discrete monomeric molecular units are separated by normal van der Waals distances between heavy atoms.

However, a closer check of the crystal structures revealed several intermolecular hydrogen-bonding interactions shorter than the sum of the corresponding van der Waals radii [i.e. Σ_{vdW}(F,H) ≈ 2.55, Σ_{vdW}(Cl,H) ≈ 3.0, Σ_{vdW}(Br,H) ≈ 3.15 and Σ_{vdW}(I,H) ≈ 3.35 Å].[40] This results in different supramolecular architectures that are presented in the subsequent discussion taking into account the increasing degree of association, with the common patterns summarised in Table 5 (further details are available in the Supporting Information). Thus, in the crystal of the fluoride **3b** (space group $P2_1/n$) pairs of isomers (*S*,*S* or *R*,*R*) of the two independent molecules are associated through F(1)···H(34)$_{aryl}$ contacts (2.50 Å). The short interatomic distance (2.56 Å) between the F(2) atom and a methyl hydrogen of a neighbouring dinuclear unit of the same type is at the limit of a van der Waals contact. The crystal of **3b′** (space group $P2_1/c$[26]) contains polymeric chains of (*S*) and (*R*) isomers, respectively, built through F(1)···H(17Ba)$_{methylene}$ interactions (2.37 Å). Similar polymeric chains of (*S*) and (*R*) isomers, respectively, were also found in the crystals of the triorganotin chlorides **3a**, **3a′**[20] and the triorganotin iodide **3d**. In contrast to the phenyl derivatives, the crystals of the methyl analogues **2a** (space group *Pbca*) and **2b** contains chains of alternating (*S*) and (*R*) isomers. There are no further halogen–hydrogen contacts between the parallel polymeric chains.

For compound **1b**·CH_2Cl_2, alternating (R_{N1},S_{N2})- and (S_{N1},R_{N2})-**1b** isomers are connected through F(2)···H-(7Ab)$_{methylene}$ interactions (2.52 Å) and further bridged by CH_2Cl_2 molecules [F(1)···H(19A)$_{solvent}$ = 2.37, Cl(2a)···H-(8A)$_{methyl}$ = 2.94 Å], resulting in ribbon-like chains (Figure 3), with no further inter-chain halogen–hydrogen contacts.

Polymeric chains of (*S*) and (*R*) isomers, respectively, built through I(1)···H(7Ba)$_{methylene}$ interactions (3.16 Å), are also found in the crystal of the triorganotin iodide **2d**, but in this case additional I(1)···H(10Ac)$_{Sn–methyl}$ contacts (3.29 Å) between chains of the same isomers result in a 2D supramolecular architecture. The crystal consists of layers alternating in the sequence -*R*-*R*-*S*-*S*-*R*-*R*-*S*-*S*-, with no further inter-layer contacts. The triorganotin chloride **2a′** (space group $Pna2_1$) and the triorganotin bromide **2c** also form polymeric chains, but in this case they are built from alternating (*S*) and (*R*) isomers [Cl(1)···H(8Bb)$_{N–methyl}$ = 2.81 Å for **2a′**; Br(1)···H(9Bb)$_{N–methyl}$ = 3.02 Å for **2c**]. For **2a′**, weak inter-chain contacts [Cl(1)···H(8Cc)$_{N–methyl}$ = 2.98 Å] result in a 2D network with a honeycomb motif (Figure 4, a) in which each molecule is linked to four neighbouring molecules (two isomers of a different type for the polymeric chain and two isomers of the same type for the parallel chains). For **2c**, the weak inter-chain contacts between the halogen and an aromatic hydrogen atom [Br(1)···

Table 5. Structural patterns of the hydrogen-bonding-based supramolecular architectures in the crystals of [{2-(Me_2NCH_2)C_6H_4}$_2SnX_2$] and [{2-(Me_2NCH_2)C_6H_4}R_2SnX].

Compound [R = 2-(Me_2NCH_2)C_6H_4]	Supramolecular architecture patterns	X···H [Å]		
1D architectures				
[RPh_2SnF] (**3b**)	dinuclear associations between isomers of the same type of two independent molecules; no further intermolecular contacts	intermolecular	F(1)–H(34)$_{aryl}$	2.50
[RPh_2SnF] (**3b′**)[26]	chains of (*S*) and (*R*) isomers no inter-chain contacts	intra-chain	F(1)–H(17Ba)$_{methylene}$	2.37
[RPh_2SnCl] (**3a**)	chains of (*S*) and (*R*) isomers	intra-chain	Cl(1)–H(34b)$_{aryl}$	2.88
	(with alternating independent molecules 1 and 2); no inter-chain contacts	intra-chain	Cl(2a)–H(9A)$_{methyl}$	2.92
[RPh_2SnCl] (**3a′**)[20]	chains of (*S*) and (*R*) isomers no inter-chain contacts	intra-chain	Cl(1)–H(20a)$_{aryl}$	2.89
[RPh_2SnI] (**3d**)	chains of (*S*) and (*R*) isomers no inter-chain contacts	intra-chain	I(1)–H(19a)$_{aryl}$	3.11
[RMe_2SnCl] (**2a**)	chains of alternating (*S*) and (*R*) isomers; no inter-chain contacts	intra-chain	Cl(1)–H(9Cb)$_{N–methyl}$	2.95
[RMe_2SnF] (**2b**)	chains of alternating (*S*) and (*R*) isomers;	intra-chain	F(1)–H(10Bb)$_{Sn–methyl}$	2.47
	no inter-chain contacts	intra-chain	F(1)–H(9Ab)$_{N–methyl}$	2.52
[R_2SnF_2]·CH_2Cl_2	ribbon-like chains of alternating	intra-chain	F(2)–H(7Ab)$_{methylene}$	2.52
(**1b**·CH_2Cl_2)	(R_{N1},S_{N2})- and (S_{N1},R_{N2}) isomers,	intra-chain	F(1)–H(19A)$_{solvent}$	2.37
	connected through CH_2Cl_2 molecules; no inter-chain contacts	intra-chain	Cl(2a)–H(8A)$_{methyl}$	2.94
2D Architectures				
[RMe_2SnI] (**2d**)	chains of (*S*) and (*R*) isomers	intra-chain	I(1)–H(7Ba)$_{methylene}$	3.16
	contacts between parallel chains, resulting in a layer network;	inter-chain	I(1)–H(10Ac)$_{Sn–methyl}$	3.29
	no inter-layer contacts			
[R_2SnF_2] (**1b**)	chains of (R_{N1},S_{N2}) and (S_{N1},R_{N2})	intra-chain	F(2)–H(12a)$_{aryl}$	2.38
	isomers	inter-chain	F(1)–H(7Ad)$_{methylene}$	2.47
	contacts between parallel chains, resulting in a layer network;			
	no inter-layer contacts			
[RMe_2SnCl] (**2a′**)	chain of alternating (*S*) and (*R*) isomers;	intra-chain	Cl(1)–H(8Bb)$_{N–methyl}$	2.81
	contacts between parallel chains, resulting in a layer network;	inter-chain	Cl(1)–H(8Cc)$_{N–methyl}$	2.98
	no inter-layer contacts			
[RMe_2SnBr] (**2c**)	chain of alternating (*S*) and (*R*) isomers;	intra-chain	Br(1)–H(9Bb)$_{N–methyl}$	3.02
	contacts between parallel chains, resulting in a layer network;	inter-chain	Br(1)–H(4d)$_{aryl}$	3.15
	no inter-layer contacts			
3D architectures				
[R_2SnCl_2] (**1a**)	alternating layers of (S_{N1},S_{N2}) and	intra-layer	Cl(1)–H(4a′)$_{aryl}$	2.81
	(R_{N1},R_{N2}) isomers, respectively;	inter-layer	Cl(1)–H(6f′)$_{aryl}$	2.94
	inter-layer contacts leading to a 3D supramolecular architecture			
[R_2SnI_2] (**1d**)	chain of alternating (S_{N1},S_{N2}) and	intra-chain	I(2)–H(9Ca)$_{methyl}$	3.15
	(R_{N1},R_{N2}) isomers;	inter-chain	I(2)–H(8Ac)$_{methyl}$	3.26
	contacts between parallel chains, resulting in a layer network;	inter-layer	I(1)–H(14f)$_{aryl}$	3.32
	inter-layer contacts leading to a 3D supramolecular architecture			

H(4d)$_{aryl}$ = 3.15 Å, at the limit of a van der Waals contact] lead to a different two-dimensional motif, with rings built from two molecules [(*R*)- and (*S*)-**2c** isomers] and four molecules [(*R*)-(*R*)-(*S*)-(*S*)-**2c** isomers], respectively (Figure 4, b). In both cases there are no further contacts between the parallel layers.

In contrast to **1b**·CH_2Cl_2, the crystal structure of the diorganotin difluoride **1b** consists of layers in which alternating polymeric chains of (R_{N1},S_{N2})- and (S_{N1},R_{N2})-**1b** isomers [F(2)–H(12a)$_{aryl}$ = 2.38 Å] are connected through F(1)–H(7Ad)$_{methylene}$ (2.47 Å) interactions. The overall layer network resembles that observed in the crystal of the triorganotin iodide **2d**, with both fluorine atoms being involved in weak hydrogen-bonding interactions.

Three-dimensional supramolecular architectures (Table 5) were found for the diorganotin dihalides **1a** and **1d**. Thus, in the crystal of the diorganotin diiodide **1d** there are parallel chains built from alternating (S_{N1},S_{N2}) and

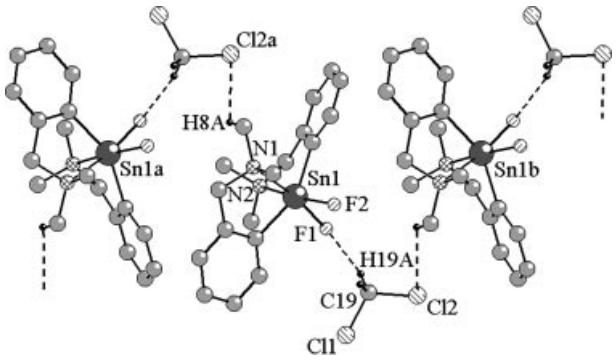


Figure 3. Polymeric associations in the crystal of compound **1b**·CH_2Cl_2 based on halogen–hydrogen contacts (only hydrogens involved in such contacts are shown) [symmetry-equivalent atoms (x, 2 – y, 0.5 + z) and (x, 2 – y, –0.5 + z) are labelled as "a" and "b"].

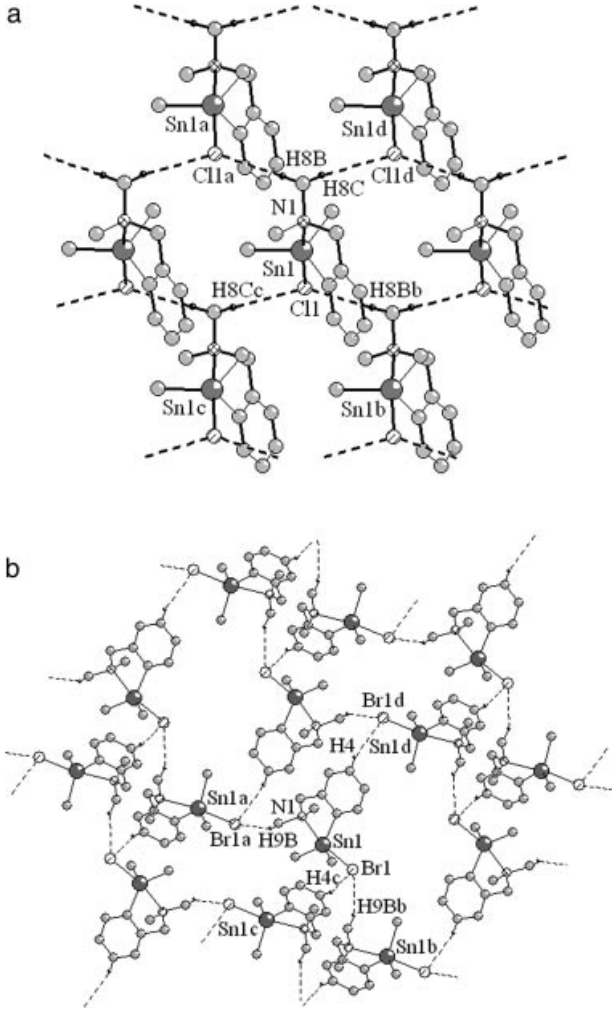


Figure 4. View of the layer network based on intermolecular hydrogen bonding (only hydrogens involved in intermolecular interactions are shown) in the crystals of (a) **2a**′ [symmetry-equivalent atoms (1.5 – x, 0.5 + y, 0.5 + z), (1.5 – x, –0.5 + y, –0.5 + z), (1.5 – x, –0.5 + y, 0.5 + z) and (1.5 – x, 0.5 + y, –0.5 + z) are labelled "a", "b", "c" and "d", respectively] and (b) **2c** [symmetry-equivalent atoms (–0.5 + x, y, 0.5 – z), (0.5 + x, y, 0.5 – z), (0.5 – x, –y, 0.5 + z) and (0.5 – x, –y, –0.5 + z) are labelled "a", "b", "c" and "d", respectively].

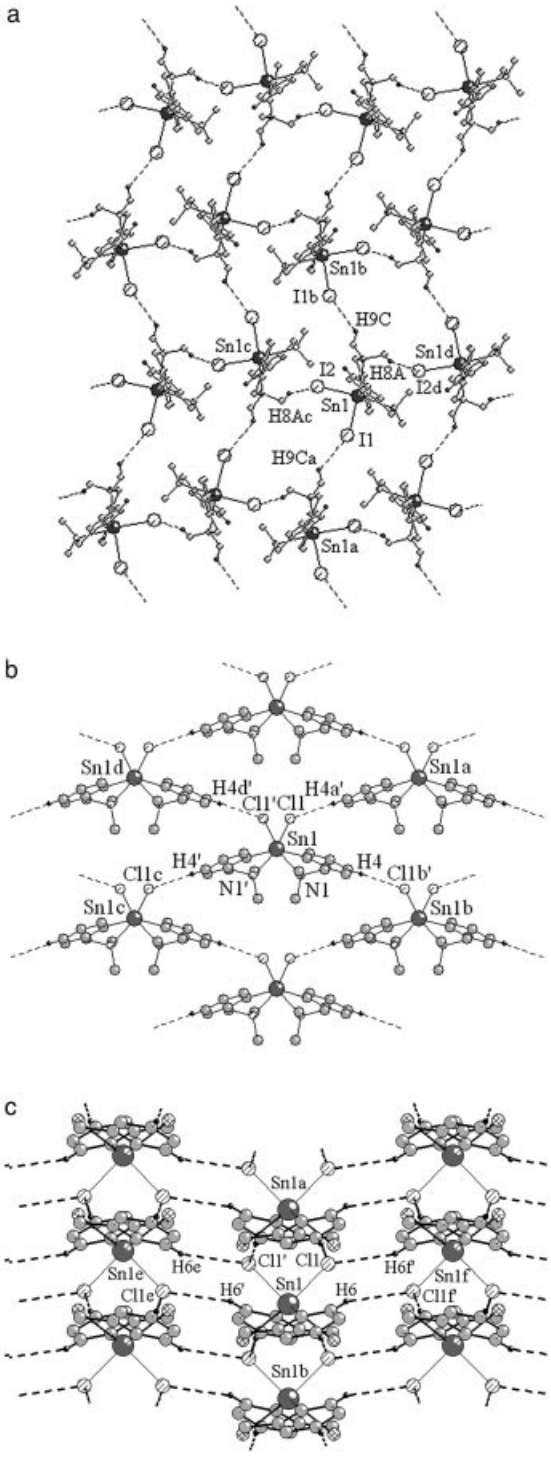


Figure 5. View of supramolecular architectures based on hydrogen bonding (only hydrogen atoms involved in intermolecular interactions are shown): (a) the layer network of (S_{N1},S_{N2}) and (R_{N1},R_{N2}) isomers in the crystal of **1d** [symmetry equivalent atoms (–0.5 + x, 1.5 – y, 0.5 + z), (0.5 + x, 1.5 – y, –0.5 + z), (0.5 – x, –0.5 + y, 1.5 – z) and (0.5 – x, 0.5 + y, 1.5 – z) are labelled as "a", "b", "c" and "d", respectively]; (b) the layer network of (S_{N1},S_{N2}) isomers in the crystal of **1a** [symmetry equivalent atoms (0.5 + x, 0.5 + y, z), (0.5 + x, –0.5 + y, z), (–0.5 + x, –0.5 + y, z) and (–0.5 + x, 0.5 + y, z) are labelled as "a", "b", "c" and "d", respectively]; (c) 3D supramolecular structure in the crystal of **1a** [symmetry equivalent atoms (–x, 1 – y, 1 – z) and (0.5 – x, 0.5 – y, –z) are labelled as "e" and "f", respectively].

(R_{N1},R_{N2}) isomers through I···H_{methyl} contacts [I(2)–H-(9Ca)$_{methyl}$ = 3.15 Å]. Inter-chain contacts [I(2)···H-(8Ac)$_{methyl}$ = 3.26 Å] result in a similar layer network to that observed for **2a′** (Figure 5, a). Additional weak, inter-layer contacts between I(1) and an aromatic proton [I(1)···H(14f)$_{aryl}$ = 3.32 Å] lead to a 3D network. By contrast, in the crystal of the diorganotin dichloride **1a** only aromatic protons are involved in hydrogen bonding. The molecules are associated into layers built of the same type of isomer [Cl(1)···H(4a′)$_{aryl}$ = 2.81 Å] (Figure 5, b) and alternating parallel layers of (S_{N1},S_{N2}) or (R_{N1},R_{N2}) isomers are bridged through weak Cl(1)···H(6f′)$_{aryl}$ (2.94 Å) interactions (Figure 5, c).

Conclusion

The hypercoordinated di- and triorganotin(IV) halides [{2-(Me_2NCH_2)C_6H_4}$_2$$SnX_2$], [{2-($Me_2NCH_2$)$C_6H_4$}-$Me_2$SnX] and [{2-($Me_2NCH_2$)$C_6H_4$}$Ph_2$SnX] (X = F, Cl, Br, I) have been prepared and their solutions investigated by multinuclear NMR spectroscopy, including variable-temperature studies. Single-crystal X-ray structure analyses have revealed that the strong intramolecular coordination of the nitrogen atom from the pendant CH_2NMe_2 group to tin induces planar chirality and the compounds crystallise as racemates. The influence of the identity and number of halogen atoms and organic substituents attached to the tin atoms is reflected in different supramolecular architectures based on hydrogen-bonding networks.

Experimental Section

General Remarks: All manipulations were carried out under argon using dried solvents freshly distilled prior to use. The ^{1}H and ^{13}C NMR spectra were recorded with Bruker Avance DRX 400 (including 2D experiments), Bruker Avance 300 and Bruker DPX 200 instruments. The ^{19}F NMR were recorded with Bruker Avance DRX 400 and Bruker DPX 300, and ^{119}Sn NMR were obtained using Bruker DPX 400 and Varian Unity 300 instruments. Variable-temperature ^{1}H NMR studies were performed with a Varian Unity 300 (compound **1a**) and a Varian Gemini 300S (compound **1b**). The chemical shifts are reported in ppm relative to the residual peak of solvent ($CHCl_3$; $\delta_{^1H}$ = 7.26, $\delta_{^{13}C}$ = 77.0 ppm for ^{1}H and ^{13}C, $CFCl_3$ for ^{19}F and neat $SnMe_4$ for ^{119}Sn). Starting materials such as $SnCl_4$, $BuSnCl_3$, Ph_2SnCl_2, Me_2SnCl_2 KX (X = F, Br, I), *N*,*N*-dimethylbenzylamine and *n*-butyllithium were commercially available. The compounds [Li{2-(Me_2NCH_2)C_6H_4}],[41] [{2-(Me_2NCH_2)C_6H_4}$_4$Sn][17] and [{2-(Me_2NCH_2)C_6H_4}Ph_2SnCl] (**3a**)[20] were prepared according to the literature methods.

Synthesis of [{2-(Me_2NCH_2)C_6H_4}$_2$$SnCl_2$] (1a). Procedure 1: A suspension of [Li{2-(Me_2NCH_2)C_6H_4}] [prepared as above from *n*BuLi in *n*-hexane (24.6 mL, 1.6 M, 20% excess) and $Me_2NCH_2C_6H_5$ (4.43 g, 32.8 mmol) in 200 mL of anhydrous *n*-hexane] in anhydrous toluene (150 mL) was added dropwise, whilst stirring, to a cooled (–78 °C) solution of $SnCl_4$ (4.27 g, 16.4 mmol) in 300 mL of toluene (300 mL). After all the suspension had been added, the reaction mixture was stirred for 1 h at –78 °C, and then allowed to reach room temperature overnight. The reaction mixture was filtered under inert atmosphere and the solvent of the filtrate was removed in vacuo. The solid residue was recrystallised from CH_2Cl_2/*n*-hexane to give 6.1 g (81%) of the title compound as colourless crystals.

Procedure 2: $SnCl_4$ (0.437 g, 1.68 mmol) was added to [{2-(Me_2NCH_2)C_6H_4}$_4$Sn] (1.1 g, 1.68 mmol) under inert atmosphere and the mixture was slowly heated whilst stirring until a homogeneous melt was obtained. The heating was maintained for 15 min and then the reaction mixture was cooled to room temperature. Recrystallisation from a CH_2Cl_2/*n*-hexane mixture (approximately 1:4) provided 1.2 g (78%) of **1a** as colourless crystals (m.p. 257–259 °C). ^{1}H NMR ($CDCl_3$, 300 MHz, 20 °C): δ = 2.22 (br. s, 12 H, NCH_3), AB spin system with δ_A = 3.37 and δ_B = 4.07 ($^2J_{H,H}$ = 14.1 Hz, 4 H, CH_2N), 7.18 (m, 2 H, 3-H), 7.41 (m, 4 H, 4,5-H), 8.22 (m, $^3J_{H,Sn}$ = 108 Hz, 2 H, 6-H) ppm. ^{1}H NMR ($CDCl_3$, 300 MHz, 60 °C): δ = 2.21 (br. s, 12 H, NCH_3), AB spin system with δ_A = 3.38 and δ_B = 4.04 (br. s, 4 H, CH_2N), 7.17 (d, $^3J_{H,H}$ = 6.9 Hz, 2 H, 3-H), 7.52 (m, 4 H, 4,5-H), 8.25 (d, $^3J_{H,H}$ = 6.3, $^3J_{H,Sn}$ = 108 Hz, 2 H, 6-H) ppm. ^{1}H NMR (300 MHz, $CDCl_3$, –60 °C): δ = 2.05 (s, $^3J_{H,Sn}$ = 39 Hz, 6 H, NCH_3), 2.55 (s, $^3J_{H,Sn}$ = 39 Hz, 6 H, NCH_3), AB spin system with δ_A = 3.39 and δ_B = 4.14 ($^2J_{H,H}$ = 14.2, $^3J_{H,Sn}$ = 39 Hz, 4 H, CH_2N), 7.19 (d, $^3J_{H,H}$ = 6.6 Hz, 2 H, 3-H), 7.41 (m, 4 H, 4,5-H), 8.19 (d, $^3J_{H,H}$ = 6.8, $^3J_{H,Sn}$ = 110 Hz, 2 H, 6-H) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz, 20 °C): δ = 46.78 (br. s, NCH_3), 63.80 (s, $^2J_{C,Sn}$ = 42.8 Hz, CH_2N), 127.85 (s, $^3J_{C,Sn}$ = 97.1/99.3 Hz, C-3), 128.18 (s, $^3J_{C,Sn}$ = 104.8/107.6 Hz, C-5), 130.16 (s, $^4J_{C,Sn}$ = 19.1 Hz, C-4), 135.47 (s, $^2J_{C,Sn}$ = 61.3 Hz, C-6), 140.79 (s, $^2J_{C,Sn}$ = 62.8 Hz, C-2; $^1J_{C,Sn}$ = 1167.1/1221.3 Hz, C-1) ppm. ^{119}Sn NMR (CH_2Cl_2/[D$_6$]acetone, 149.2 MHz, 20 °C): δ = –260.7 ppm (s). $C_{18}H_{24}Cl_2N_2Sn$ (458.00): calcd. C 47.21, H 5.28, N 6.12; found C 47.34, H 5.43, N 5.84.

Synthesis of [{2-(Me_2NCH_2)C_6H_4}$_2$$SnF_2$] (1b): Dichloromethane was added to a suspension of **1a** (0.3 g, 0.65 mmol) in MeOH (20 mL) until the solid compound dissolved. An aqueous solution of KF (0.2 g, 3.44 mmol) was then added and the mixture was stirred for 3 h at room temperature. The organic layer was separated and the water solution was washed twice with 5 mL of CH_2Cl_2. The combined organic layers were dried with anhydrous Na_2SO_4. The latter was filtered, the solvent was removed in vacuo and the obtained white solid residue was recrystallised from a CH_2Cl_2/*n*-hexane mixture to give **1b** (0.25 g, 90%; m.p. 213–215 °C). Colourless crystals suitable for single-crystal X-ray diffraction were obtained by slow crystallisation from a CH_2Cl_2/*n*-hexane (approximately 1:5) mixture. ^{1}H NMR ($CDCl_3$, 400 MHz, 20 °C): δ = 2.24 (br. s, 12 H, NCH_3), 3.66 (br. s, 4 H, CH_2N), 7.16 (m, 2 H, 3-H), 7.38 (m, 4 H, 4,5-H), 8.08 (m, $^3J_{H,Sn}$ = 92.2 Hz, 2 H, 6-H) ppm. ^{1}H NMR ($CDCl_3$, 300 MHz, 55 °C): δ = 2.24 (s, 12 H, NCH_3), 3.66 (s, 4 H, CH_2N), 7.17 (m, 2 H, 3-H), 7.39 (m, 4 H, 4,5-H), 8.09 (m, $^3J_{H,Sn}$ = 91.5 Hz, 2 H, 6-H) ppm. ^{1}H NMR ($CDCl_3$, 300 MHz, –55 °C): δ = 2.10 (s, 6 H, NCH_3), 2.42 (s, 6 H, NCH_3), AB spin system with δ_A = 3.53 and δ_B = 3.82 ($^2J_{H,H}$ = 14.3 Hz, 4 H, CH_2N), 7.17 (m, 2 H, 3-H), 7.38 (m, 4 H, 4,5-H), 8.05 (m, $^3J_{H,Sn}$ = 93.3 Hz, 2 H, 6-H) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz, 20 °C): δ = 46.09 (br. s, NCH_3), 64.10 (s, $^2J_{C,Sn}$ = 48.4 Hz, CH_2N), 127.31 (s, $^3J_{C,Sn}$ = 96.7 Hz, C-3), 127.93 (s, $^3J_{C,Sn}$ = 99.3 Hz, C-5), 129.97 (s, $^4J_{C,Sn}$ = 17.6 Hz, C-4), 136.30 (s, $^2J_{C,Sn}$ = 49.5 Hz, C-6), 139.23 (t, $^3J_{C,F}$ = 22.5 Hz, C-1), 141.04 (s, $^2J_{C,Sn}$ = 66.7 Hz, C-2) ppm. ^{19}F NMR ($CDCl_3$, 282.38 MHz, 20 °C): δ = –181.5 ppm (s, $^1J_{F,Sn}$ = 2567/2683 Hz). ^{119}Sn NMR (CH_2Cl_2/[D$_6$]acetone, 149.2 MHz, 20 °C): δ = –386.7 ppm (t, $^1J_{F,Sn}$ = 2663 Hz). $C_{18}H_{24}F_2N_2Sn$ (425.09): calcd. C 50.86, H 5.69, N 6.59; found C 50.58, H 5.33, N 6.37.

Synthesis of [{2-(Me_2NCH_2)C_6H_4}$_2$$SnI_2$] (1d): A saturated aqueous solution of NH_4I (20 mL) was added to a solution of **1a** (0.79 g,

1.73 mmol) in CH_2Cl_2 (20 mL)/EtOH (4 mL) and the reaction mixture was stirred for 10 h at room temperature. The organic layer was separated and the water solution was washed twice with 5 mL of CH_2Cl_2. The organic solution was separated and dried with anhydrous Na_2SO_4. The latter was filtered, the solvent was removed in vacuo and the solid residue was recrystallised from a CH_2Cl_2/*n*-hexane mixture to give **1d** as colourless crystals (0.66 g, 60%; m.p. 238 °C). ^{1}H NMR ($CDCl_3$, 300 MHz, 20 °C): δ = 2.23 (br. s, 12 H, NCH_3), AB spin system with δ_A = 3.19 and δ_B = 4.22 ($^2J_{H,H}$ = 12.7 Hz, 4 H, CH_2N), 7.13 (d, $^3J_{H,H}$ = 6.9 Hz, 2 H, 3-H), 7.37 (dd, $^3J_{H,H}$ = 7.4 Hz, 2 H, 4-H), 7.47 (dd, $^3J_{H,H}$ = 7.5 Hz, 2 H, 5-H), 8.19 (d, $^3J_{H,H}$ = 7.2, $^3J_{H,Sn}$ = 111.9 Hz, 2 H, 6-H) ppm. ^{1}H NMR ($CDCl_3$, 300 MHz, 50 °C): δ = 2.21 (s, $^3J_{H,Sn}$ = 39.1 Hz, 12 H, NCH_3), AB spin system with δ_A = 3.24 and δ_B = 4.16 (br. s, 4 H, CH_2N), 7.12 (d, $^3J_{H,H}$ = 7.3 Hz, 2 H, 3-H), 7.37 (dd, $^3J_{H,H}$ = 7.4 Hz, 2 H, 4-H), 7.47 (dd, $^3J_{H,H}$ = 7.5 Hz, 2 H, 5-H), 8.21 (d, $^3J_{H,H}$ = 7.3, $^3J_{H,Sn}$ = 111.9 Hz, 2 H, 6-H) ppm. ^{1}H NMR (300 MHz, $CDCl_3$, –50 °C): δ = 1.96 (s, $^3J_{H,Sn}$ = 39.2 Hz, 6 H, NCH_3), 2.63 (s, $^3J_{H,Sn}$ = 38.8 Hz, 6 H, NCH_3), AB spin system with δ_A = 3.17 and δ_B = 4.30 ($^2J_{H,H}$ = 14.2 Hz, 4 H, CH_2N), 7.13 (d, $^3J_{H,H}$ = 7.2 Hz, 2 H, 3-H), 7.37 (dd, $^3J_{H,H}$ = 7.4 Hz, 2 H, 4-H), 7.46 (dd, $^3J_{H,H}$ = 7.4 Hz, 2 H, 5-H), 8.15 (d, $^3J_{H,H}$ = 7.4, $^3J_{H,Sn}$ = 115.3 Hz, 2 H, 6-H) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz, 20 °C): δ = 46.90 (br. s, NCH_3), 62.80 (s, $^2J_{C,Sn}$ = 35.6 Hz, CH_2N), 128.02 (s, $^3J_{C,Sn}$ = 104.1 Hz, C-5), 128.22 (s, $^3J_{C,Sn}$ = 90.8 Hz, C-3), 130.29 (s, $^4J_{C,Sn}$ = 18.2 Hz, C-4), 135.73 (s, $^2J_{C,Sn}$ = 67.1 Hz, C-6), 138.17 (s, C-1), 140.51 (s, C-2) ppm. ^{119}Sn NMR ($CDCl_3$, 111.9 MHz, 20 °C): δ = –346.9 ppm (s). $C_{18}H_{24}I_2N_2Sn$ (640.90): calcd. C 33.73, H 3.77, N 4.37; found C 33.42, H 3.53, N 4.12.

Synthesis of [{2-(Me_2NCH_2)C_6H_4}Me_2SnCl] (2a): A suspension of [Li{2-(Me_2NCH_2)C_6H_4}] [prepared as above from *n*BuLi in *n*-hexane (17.6 mL, 1.6 M, 20% excess) and $Me_2NCH_2C_6H_5$ (3.18 g, 23.5 mmol) in 50 mL of anhydrous *n*-hexane] in anhydrous toluene (50 mL) was added dropwise, whilst stirring, to a cooled (–78 °C) solution of Me_2SnCl_2 (5.17 g, 23.5 mmol) in 150 mL of toluene (300 mL). After all the suspension had been added the reaction mixture was stirred for 1 h at –78 °C, and then allowed to reach room temperature overnight. The reaction mixture was filtered under inert atmosphere and the solvent was removed in vacuo. The white solid residue was recrystallised from CH_2Cl_2/*n*-hexane to give **2a** (5.2 g, 69%) as colourless crystals (m.p. 119–121 °C; ref.[12] 120–123 °C). ^{1}H NMR ($CDCl_3$, 200 MHz, 20 °C): δ = 0.73 (s, $^2J_{H,Sn}$ = 64.1/67.0 Hz, 6 H, $SnCH_3$), 2.29 (s, 6 H, NCH_3), 3.62 (s, 2 H, CH_2N), 7.12 (m, 1 H, 3-H), 7.32 (m, 2 H, 4,5-H), 8.17 (m, $^3J_{H,Sn}$ = 67.2 Hz, 1 H, 6-H) ppm. ^{13}C NMR ($CDCl_3$, 50.3 MHz, 20 °C): δ = –0.28 (s, $^1J_{C,Sn}$ = 492.4/515.4 Hz, $SnCH_3$), 45.15 (s, NCH_3), 64.78 (s, $^2J_{C,Sn}$ = 28.8 Hz, CH_2N), 126.46 (s, $^3J_{C,Sn}$ = 59.1 Hz, C-3), 127.88 (s, $^3J_{C,Sn}$ = 67.2 Hz, C-5), 129.32 (s, $^4J_{C,Sn}$ = 13.2 Hz, C-4), 137.60 (s, $^2J_{C,Sn}$ = 42.9 Hz, C-6), 140.28 (s, C-1), 141.78 (s, $^2J_{C,Sn}$ = 38.6 Hz, C-2) ppm. ^{119}Sn NMR (CH_2Cl_2/[D_6]acetone, 149.2 MHz, 20 °C): δ = –48.7 ppm (s). $C_{11}H_{18}ClNSn$ (318.41): calcd. C 41.49, H 5.70, N 4.40; found C 41.23, H 5.61, N 4.53.

Synthesis of [{2-(Me_2NCH_2)C_6H_4}Me_2SnF] (2b): Same procedure as for **1b**, using **2a** (0.25 g, 0.78 mmol) and KF (0.228 g, 3.92 mmol). Recrystallisation from CH_2Cl_2/*n*-hexane (approximately 1:3) mixture gave **2b** (0.21 g, 89%) as colourless crystals (m.p. 92–94 °C). ^{1}H NMR ($CDCl_3$, 400 MHz, 20 °C): δ = 0.56 (d, $^3J_{H,F}$ = 3.7, $^2J_{H,Sn}$ = 64.8/67.2 Hz, 6 H, $SnCH_3$), 2.28 (s, 6 H, NCH_3), 3.59 (s, 2 H, CH_2N), 7.12 (m, 1 H, 3-H), 7.32 (m, 2 H, 4,5-H), 7.97 (m, $^3J_{H,Sn}$ = 60.4 Hz, 1 H, 6-H) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz, 20 °C): δ = –3.67 (d, $^2J_{C,F}$ = 16.7, $^1J_{C,Sn}$ = 507.7/531.3 Hz, $SnCH_3$), 45.16 (s, NCH_3), 64.91 (s, $^2J_{C,Sn}$ = 30.3 Hz, CH_2N), 126.47 (s, $^3J_{C,Sn}$ = 58.3 Hz, C-3), 127.83 (s, $^3J_{C,Sn}$ = 64.6 Hz, C-5), 129.24 (s, $^4J_{C,Sn}$ = 12.8 Hz, C-4), 137.19 (s, $^2J_{C,Sn}$ = 38.2 Hz, C-6), 141.32 (d, $^3J_{C,F}$ = 21.7 Hz, C-1), 142.04 (s, $^2J_{C,Sn}$ = 39.4 Hz, C-2) ppm. ^{19}F NMR ($CDCl_3$, 376.5 MHz, 20 °C): δ = –178.4 ppm (s, $^1J_{F,Sn}$ = 1944.2/2034.6 Hz). ^{119}Sn NMR ($CDCl_3$, 111.9 MHz, 20 °C): δ = –52.7 ppm (d, $^1J_{F,Sn}$ = 2039.3 Hz). $C_{11}H_{18}FNSn$ (301.96): calcd. C 43.75, H 6.01, N 4.64; found C 43.41, H 5.79, N 4.41.

Synthesis of [{2-(Me_2NCH_2)C_6H_4}Me_2SnBr] (2c): An aqueous solution of KBr (0.93 g, 7.85 mmol) was added to a solution of **2a** (0.5 g, 1.57 mmol) in CH_2Cl_2 (30 mL) and the reaction mixture was stirred for 3 h at room temperature. The organic layer was separated and the water solution was washed twice with 10 mL of CH_2Cl_2. The organic solution was dried with anhydrous Na_2SO_4. The solvent was removed in vacuo and the obtained pale brown-red residue was recrystallised from a CH_2Cl_2/*n*-hexane mixture to give **2c** (0.52 g, 91%) [m.p. 136–138 °C (dec); ref.[2] white solid, 136–137 °C]. Colourless crystals suitable for single-crystal X-ray diffraction were obtained from a CH_2Cl_2/*n*-hexane (approximately 1:4) solution. ^{1}H NMR ($CDCl_3$, 200 MHz, 20 °C): δ = 0.87 (s, $^2J_{H,Sn}$ = 63.5/66.4 Hz, 6 H, $SnCH_3$), 2.32 (s, 6 H, NCH_3), 3.64 (s, 2 H, CH_2N), 7.12 (m, 1 H, 3-H), 7.35 (m, 2 H, 4,5-H), 8.26 (m, $^3J_{H,Sn}$ = 68.5 Hz, 1 H, 6-H) ppm. ^{13}C NMR ($CDCl_3$, 50.3 MHz, 20 °C): δ = 1.02 (s, $^1J_{C,Sn}$ = 483.1/505.1 Hz, $SnCH_3$), 45.22 (s, NCH_3), 64.74 (s, $^2J_{C,Sn}$ = 28.1 Hz, CH_2N), 126.46 (s, $^3J_{C,Sn}$ = 58.9 Hz, C-3), 127.89 (s, $^3J_{C,Sn}$ = 67.6 Hz, C-5), 129.39 (s, C-4), 138.22 (s, $^2J_{C,Sn}$ = 44.7 Hz, C-6), 139.54 (s, C-1), 141.58 (s, $^2J_{C,Sn}$ = 37 Hz, C-2). ^{119}Sn NMR ($CDCl_3$, 149.2 MHz, 20 °C): δ = –55.5 ppm (s). $C_{11}H_{18}BrNSn$ (362.86): calcd. C 36.41, H 5.00, N 3.86; found C 36.11, H 5.21, N 3.67.

Synthesis of [{2-(Me_2NCH_2)C_6H_4}Me_2SnI] (2d): Same procedure as for **1b**, using **2a** (0.2 g, 0.63 mmol) and KI (0.52 g, 3.14 mmol). Recrystallisation from a CH_2Cl_2/*n*-hexane (approximately 1:3) mixture gave **2d** (0.21 g, 82%) as pale-yellow crystals (m.p. 105–107 °C). ^{1}H NMR ($CDCl_3$, 300 MHz, 20 °C): δ = 1.05 (s, $^2J_{H,Sn}$ = 63.2/65.0 Hz, 6 H, $SnCH_3$), 2.34 (s, 6 H, NCH_3), 3.65 (s, 2 H, CH_2N), 7.11 (d, $^3J_{H,H}$ = 7.0 Hz, 1 H, 3-H), 7.35 (m, 2 H, 4,5-H), 8.30 (d, $^3J_{H,H}$ = 6.6, $^3J_{H,Sn}$ = 71.2 Hz, 1 H, 6-H) ppm. ^{13}C NMR ($CDCl_3$, 75.5 MHz, 20 °C): δ = 3.18 (s, $^1J_{C,Sn}$ = 470.1/492.0 Hz, $SnCH_3$), 45.42 (s, NCH_3), 64.84 (s, $^2J_{C,Sn}$ = 26.9 Hz, CH_2N), 126.54 (s, $^3J_{C,Sn}$ = 58.9 Hz, C-3), 128.03 (s, $^3J_{C,Sn}$ = 69.4 Hz, C-5), 129.58 (s, $^3J_{C,Sn}$ = 13.7 Hz, C-4), 138.26 (s, $^1J_{C,Sn}$ = 664.0/694.8 Hz, C-1), 139.62 (s, $^2J_{C,Sn}$ = 46.2 Hz, C-6), 141.40 (s, $^2J_{C,Sn}$ = 35.8 Hz, C-2) ppm. ^{119}Sn NMR ($CDCl_3$, 111.9 MHz, 20 °C): δ = –72.8 ppm (s). $C_{11}H_{18}INSn$ (409.87): calcd. C 32.24, H 4.43, N 3.42; found C 32.11, H 4.25, N 3.33.

Synthesis of [{2-(Me_2NCH_2)C_6H_4}Ph_2SnF] (3b): Same procedure as for **1b**, using **3a** (0.25 g, 0.56 mmol) and KF (0.164 g, 2.82 mmol). Recrystallisation from a CH_2Cl_2/*n*-hexane (approximately 1:3) mixture gave **3b** (0.21 g, 87%) as colourless crystals (m.p. 161–163 °C). ^{1}H NMR ($CDCl_3$, 400 MHz, 20 °C): δ = 1.97 (s, 6 H, NCH_3), 3.56 (s, 2 H, CH_2N), 7.20 (d, $^3J_{H,H}$ = 7.2 Hz, 1 H, 3-H), 7.44 (m, 8 H, 4,5-H + C_6H_5-*meta*,*para*), 7.72 (m, $^3J_{H,Sn}$ = 61.1 Hz, 4 H, C_6H_5-*ortho*), 8.31 (d, $^3J_{H,H}$ = 7.0, $^3J_{H,Sn}$ = 64.4 Hz, 1 H, 6-H) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz, 20 °C): δ = 45.76 (s, NCH_3), 64.82 (s, $^2J_{C,Sn}$ = 31.2 Hz, CH_2N), 127.03 (s, $^3J_{C,Sn}$ = 64.6 Hz, C-3), 128.05 (s, $^3J_{C,Sn}$ = 68.7 Hz, C-5), 128.75 (s, $^3J_{C,Sn}$ = 67.5 Hz, C_6H_5-*meta*), 129.53 (s, $^4J_{C,Sn}$ = 13.5 Hz, C_6H_5-*para*), 129.93 (s, $^4J_{C,Sn}$ = 13.1 Hz, C-4), 136.03 (s, $^2J_{C,Sn}$ = 44.8 Hz, C_6H_5-*ortho*), 138.34 (s, $^2J_{C,Sn}$ = 39.1 Hz, C-6), 140.29 (d, $^3J_{C,F}$ = 15.5 Hz, C_6H_5-*ipso*), 142.88 (s, $^2J_{C,Sn}$ = 44.3 Hz, C-2) ppm; the resonance for C-1 is overlapped by the resonance of C-6. ^{19}F NMR ($CDCl_3$, 376.5 MHz, 20 °C): δ = –182.4 ppm (s, $^1J_{F,Sn}$ = 2058.3/2154.0 Hz). ^{119}Sn NMR ($CDCl_3$,

111.9 MHz, 20 °C): δ = –197.6 ppm (d, $^1J_{F,Sn}$ = 2157 Hz). $C_{21}H_{22}FNSn$ (426.10): calcd. C 59.20, H 5.20, N 3.29; found C 58.96, H 5.05, N 3.07.

Synthesis of [{2-(Me_2NCH_2)C_6H_4}Ph_2SnI] (3d): Same procedure as for **1b**, using **3a** (0.2 g, 0.45 mmol) and KI (0.375 g, 2.26 mmol). Recrystallisation from a CH_2Cl_2/*n*-hexane (approximately 1:4) mixture gave **3d** (0.22 g, 91%) as pale-yellow crystals (m.p. 235–236 °C). ^{1}H NMR ($CDCl_3$, 300 MHz, 20 °C): δ = 1.87 (s, 6 H, NCH_3), 3.56 (s, 2 H, CH_2N), 7.18 (d, $^3J_{H,H}$ = 7.3 Hz, 1 H, 3-H), 7.40 (m, 7 H, 4-H + C_6H_5-*meta*,*para*), 7.53 (dd, $^3J_{H,H}$ = 7.5 Hz, 1 H, 5-H), 7.72 (m, $^3J_{H,Sn}$ = 65.3 Hz, 4 H, C_6H_5-*ortho*), 8.60 (d, $^3J_{H,H}$ = 7.1, $^3J_{H,Sn}$ = 75.1 Hz, 1 H, 6-H) ppm. ^{13}C NMR ($CDCl_3$, 75.4 MHz, 20 °C): δ = 45.84 (s, NCH_3), 64.64 (s, $^2J_{C,Sn}$ = 25.8 Hz, CH_2N), 127.19 (s, $^3J_{C,Sn}$ = 62.1 Hz, C-3), 128.29 (s, $^3J_{C,Sn}$ = 74.2 Hz, C-5), 128.85 (s, $^3J_{C,Sn}$ = 69.3 Hz, C_6H_5-*meta*), 129.35 (s,

Table 6. Crystallographic data for compounds **1a**, **1b**, **1b**·CH_2Cl_2 and **1d**.

	1a	**1b**	**1b**·CH_2Cl_2	**1d**
Empirical formula	$C_{18}H_{24}Cl_2N_2Sn$	$C_{18}H_{24}F_2N_2Sn$	$C_{18}H_{24}F_2N_2Sn{\cdot}CH_2Cl_2$	$C_{18}H_{24}I_2N_2Sn$
Formula mass	457.98	425.08	510.01	640.88
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	*C*2/*c*	$P2_1/n$	*Cc*	$P2_1/n$
a [Å]	16.9910(4)	9.4178(13)	12.9347(16)	10.0711(10)
b [Å]	8.0759(1)	16.101(2)	12.7973(16)	13.7642(14)
c [Å]	14.5798(4)	12.2211(17)	13.4533(17)	15.1918(15)
α [°]	90	90	90	90
β [°]	105.9252(11)	111.560(2)	102.312(2)	96.531(2)
γ [°]	90	90	90	90
V [Å^3]	1980.0(3)	1723.6(4)	2175.7(5)	2092.2(4)
Z	4	4	4	4
$D_{calcd.}$ [g cm^{-3}]	1.581	1.638	1.557	2.035
F(000)	920	856	1024	1208
Crystal size [mm]	0.25 × 0.15 × 0.13	0.40 × 0.31 × 0.18	0.32 × 0.20 × 0.10	0.44 × 0.20 × 0.20
μ(Mo-K_α) [mm^{-1}]	1.607	1.503	1.442	4.174
θ range [°]	3.79–27.45	2.19–27.10	2.26–26.37	2.00–26.37
No. of reflections collected	8700	10414	8549	16388
No. of independent reflections	2201 (R_{int} = 0.0330)	3778 (R_{int} = 0.0201)	4259 (R_{int} = 0.0349)	4274 (R_{int} = 0.0392)
No. of parameters	107	213	239	212
Absorption correction	none	multi-scan (Bruker SAINT)	multi-scan (SAINT)	multi-scan (SAINT)
R_1 [$I > 2\sigma(I)$]	0.0211	0.0240	0.0381	0.0465
wR_2	0.0452	0.0529	0.0816	0.1068
GOF on F^2	1.006	1.080	1.023	1.157
Residual electron density [e Å^{-3}]	0.370/–0.601	0.408/–0.334	0.767/–0.700	1.277/–1.382

Table 7. Crystallographic data for compounds **2a**, **2a′** and **2b**–**2d**.

	2a	**2a′**	**2b**	**2c**	**2d**
Empirical formula	$C_{11}H_{18}ClNSn$	$C_{11}H_{18}ClNSn$	$C_{11}H_{18}FNSn$	$C_{11}H_{18}BrNSn$	$C_{11}H_{18}INSn$
Formula mass	318.40	318.40	301.97	362.86	409.85
Crystal system	orthorhombic	orthorhombic	monoclinic	orthorhombic	monoclinic
Space group	*Pbca*	$Pna2_1$	$P2_1/n$	*Pbca*	$P2_1/n$
a [Å]	13.993(9)	17.155(3)	9.5956(8)	14.1705(13)	7.1685(10)
b [Å]	12.973(9)	11.2080(19)	12.7844(12)	13.0368(12)	7.5197(11)
c [Å]	14.687(10)	7.0150(12)	11.3157(10)	14.6525(14)	26.236(4)
α [°]	90	90	90	90	90
β [°]	90	90	111.521(2)	90	90.067(2)
γ [°]	90	90	90	90	90
V [Å^3]	2666(3)	1348.8(4)	1291.4(2)	2706.9(4)	1414.3(4)
Z	8	4	4	8	4
$D_{calcd.}$ [g cm^{-3}]	1.586	1.568	1.553	1.781	1.925
F(000)	1264	632	600	1408	776
Crystal size [mm]	0.13 × 0.21 × 0.23	0.42 × 0.37 × 0.17	0.24 × 0.29 × 0.53	0.25 × 0.22 × 0.17	0.37 × 0.21 × 0.08
μ(Mo-K_α) [mm^{-1}]	2.084	2.084	1.957	4.808	3.959
θ range [°]	2.55–26.37	2.17–26.37	2.4–26.4	2.54–26.37	1.55–26.37
No. of reflections collected	19522	10378	7352	20438	10856
No. of independent reflections	2716 (R_{int} = 0.0372)	2727 (R_{int} = 0.0220)	2623 (R_{int} = 0.0174)	2763 (R_{int} = 0.0362)	2876 (R_{int} = 0.0519)
No. of parameters	131	131	131	131	132
Absorption correction	multi-scan (SAINT)	multi-scan (SAINT)	multi-scan (SAINT)	multi-scan (SAINT)	multi-scan (SAINT)
R_1 [$I > 2\sigma(I)$]	0.0315	0.0217	0.0260	0.0317	0.0354
wR_2	0.0620	0.0447	0.0588	0.0715	0.0752
GOF on F^2	1.100	1.092	1.060	1.101	1.116
Residual electron density [e Å^{-3}]	0.522/–0.470	0.218/–0.408	0.476/–0.202	0.534/–0.602	0.701/–0.762

Table 8. Crystallographic data for compounds **3a**, **3b** and **3d**.

	3a	**3b**	**3d**
Empirical formula	$C_{21}H_{22}ClNSn$	$C_{21}H_{22}FNSn$	$C_{21}H_{22}INSn$
Formula mass	442.54	426.09	533.99
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a [Å]	9.2370(15)	9.2868(7)	8.8090(15)
b [Å]	24.215(4)	23.5553(17)	15.875(3)
c [Å]	17.832(3)	17.8373(13)	15.058(3)
α [°]	90	90	90
β [°]	97.558(3)	99.7480(10)	92.636(3)
γ [°]	90	90	90
V [Å^3]	3954.1(11)	3845.6(5)	2103.5(6)
Z	8	8	4
$D_{calcd.}$ [g cm^{-3}]	1.487	1.472	1.686
$F(000)$	1776	1712	1032
Crystal size [mm]	0.24 × 0.23 × 0.18	0.20 × 0.19 × 0.04	0.22 × 0.15 × 0.14
μ(Mo-K_α) [mm^{-1}]	1.429	1.339	2.684
θ range [°]	1.43–26.35	1.45–26.38	1.87–26.37
No. of reflections collected	31134	30497	16667
No. of independent reflections	8068 (R_{int} = 0.0424)	7877 (R_{int} = 0.0411)	4292 (R_{int} = 0.0438)
No. of parameters	220	437	219
Absorption correction	multi-scan (SAINT)	multi-scan (SAINT)	multi-scan (SAINT)
R_1 [$I > 2\sigma(I)$]	0.0444	0.0457	0.0425
wR_2	0.0933	0.1091	0.0830
GOF on F^2	1.195	1.026	1.058
Residual electron density [e Å^{-3}]	1.161/–0.509	2.576/–0.921	0.797/–0.874

$^4J_{C,Sn}$ = 13.7 Hz, C_6H_5-*para*), 130.20 (s, $^4J_{C,Sn}$ = 14.2 Hz, C-4), 135.18 (s, $^2J_{C,Sn}$ = 45.8 Hz, C_6H_5-*ortho*), 135.23 (s, C-1), 140.80 (s, $^2J_{C,Sn}$ = 50.3 Hz, C-6), 142.32 (s, $^2J_{C,Sn}$ = 38.4 Hz, C-2), 142.36 (s, $^1J_{C,Sn}$ = 705.1/737.9 Hz, C_6H_5-*ipso*). ^{119}Sn NMR ($CDCl_3$, 111.9 MHz, 20 °C): δ = –199.5 ppm (s). $C_{21}H_{22}INSn$ (534.01): calcd. C 47.23, H 4.15, N 2.62; found C 47.01, H 3.88, N 2.45.

X-ray Crystallographic Study: The crystal structure measurement and refinement data for **1a**, **1b**, **1b**·CH_2Cl_2, **1d**, **2a**, **2a′**, **2b**–**2d**, **3a**, **3b** and **3d** are given in Tables 6, 7 and 8. Data for **1a** were collected with a Nonius KappaCCD diffractometer (University of Dortmund) at 291 K. For all the other compounds the data were collected using a SMART APEX diffractometer ("Babes-Boyai" University) at 297 K. In both cases a graphite monochromator was used to produce a wavelength (Mo-K_α) of 0.71073 Å. The structures were solved by direct methods (full-matrix least-squares on F^2). All non-hydrogen atoms were refined with anisotropic thermal parameters. For structure solving and refinement the SHELX-97 software package was used.[42] The drawings were created with the Diamond program by Crystal Impact GbR.[43]

CCDC-231308 (for **1a**), -230620 (for **1b**), -230621 (for **1b**·CH_2Cl_2), -285103 (for **1d**), -215229 (for **2a**), -215230 (for **2a′**), -215224 (for **2b**), -230622 (for **2c**), -215380 (for **2d**), -215228 (for **3a**), -215226 (for **3b**) and -215227 (for **3d**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information Available (for details see the footnote on the first page of this article): Figure S1 (variable-temperature ^{1}H NMR spectra for **1a** and **1b**, in $CDCl_3$ solution), Figures S2–S8 (simulation of the aromatic region of the ^{1}H NMR spectra for **1a**, **1b**, **2a**–**2d** and **4b**, respectively) and Figures S9–S43 (details of the different supramolecular architectures based on hydrogen-bonding networks in the crystals of investigated compounds).

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