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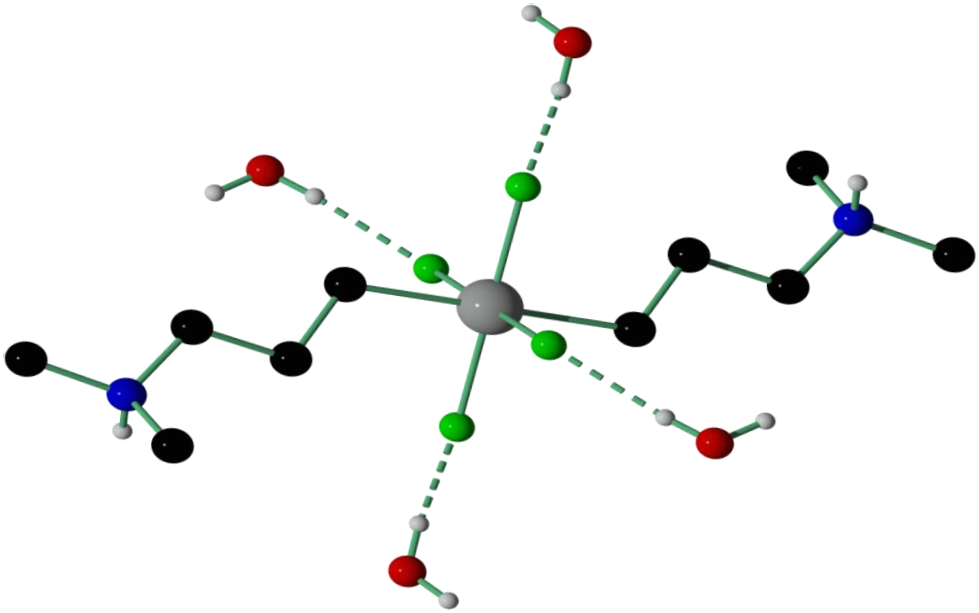
Aminopropyl-Substituted Organotin Compounds for Sensing, Detection and Removal of Fluoride Anions



Thesis presented for obtaining the degree of

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by

Dipl. Chem. Nour Alashkar

First Reviewer: Prof. Dr. Klaus Jurkschat

Second Reviewer: Prof. Dr. Sonja Herres-Pawlis

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Contents

List of Abbreviations

General abbreviations			
R	Organic group	c	Consentration
Ar	Aryl	M	Molarity
Ph	Phenyl	mL	Milliliter
Me	Methyl	t	Time
Et	Ethyl	min	Minutes
Pr	Propyl	h	Hours
An	Anthracene	T	Temperature
Bn	Benzyl	*i*	Ipso-position in aromatic ring
X	Halide	*o*	Ortho-position in aromatic ring
THF	Tetrahydrofuran	*m*	Meta-position in aromatic ring
DMSO	Dimethyl sulfoxide	*p*	Para-position in aromatic ring
eq	Equation	Calcd	Calculated
Spectroscopy			
MS	Mass spectrometry	MHz	Megaherz
ESI	Electrospray Ionization	s	Singulet
m/z	Mass per charge	d	Doublet
NMR	Nuclear magnetic resonance	t	Triplett
ppm	Parts per million	m	Multiplett
δ	Chemical shift in ppm	dd	Doublet of doublet
J	Coupling constant	IR	Infrared
υ1/2	Line width	UV	Ultra Violet
Hz	Hertz		
Molecular Structure Determination			
a, b, c	Unit cell dimensions	Z	Number of molecules in the unit cell
Å	Angström	σ	Standard deviation
α, β, γ	Unit cell angles	μ	Absorption coefficient
°	Degree	F(000)	number of electrons in the unit cell
V	Volume of the unit cell	Dc	Density

List of Abbreviation

1. General Introduction

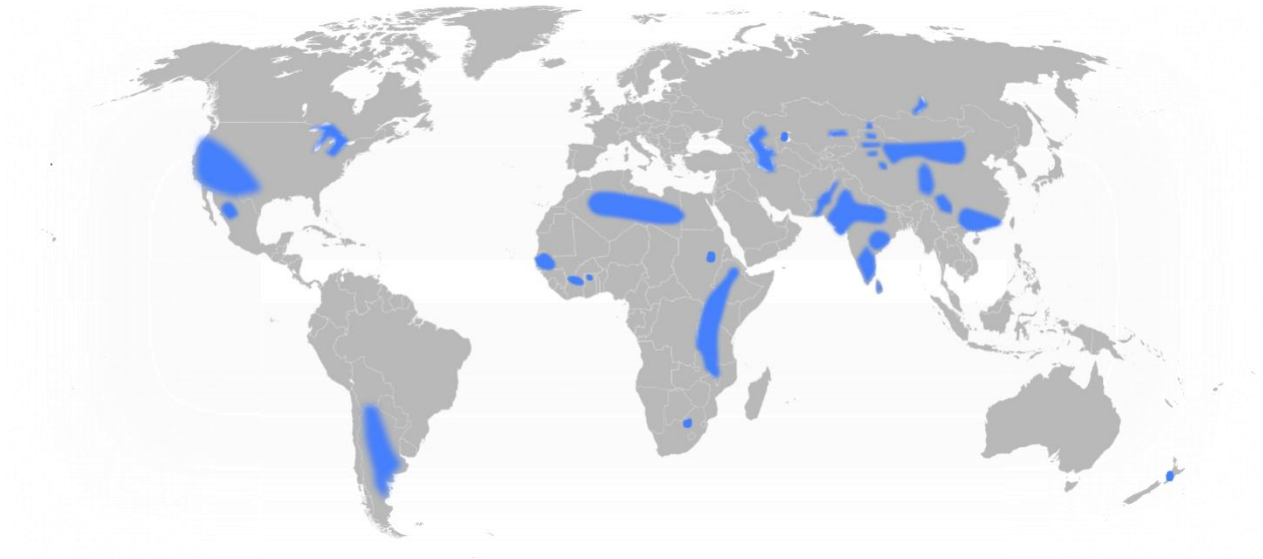
1.1 Fluoride in water

Fluorine is the lightest and most reactive element in the halogen family. It is the most electronegative element, and exists as a highly toxic pale yellow diatomic molecular gas. Fluorine is the 13th most abundant element in the earth's crust,[1] and because of the extreme reactivity of this element usually it does not exist in the nature in the elemental form (F_2),[2] but spreads in the nature in the combined form. In solution fluorine forms fluoride anions, those resemble to hydroxyl anions in terms of charge and size.

Fluorite or fluorospar (CaF_2) is a common fluoride mineral and the most widely exploited ore.[3] [4] In addition to that, natural cryolite ($AlF_3{\cdot}3NaF$) and fluorapatite ($Ca_5(PO_4)_3F$) represent economically exploitable starting materials for industry.[1]

Fluoride anions are found in nature waters at different concentrations. The high or low concentrations of these anions occur in the ground water depending on the nature of the rocks and fluoride-bearing minerals the water flows through.[3][5][6][7] Thermal waters are also rich in fluoride anions, as fluoride is commonly associated with volcanic activity and fumarolic gases.[3]

Fluoride anions are classified as one of the very few chemicals that have shown a significant effects on human health through drinking water.[3] Although fluoride anions are added to drinking water in some countries to strengthen teeth,[7][8] other countries must treat their water to remove excess amounts of fluoride anions.[9][10] These excess concentrations of fluoride anions in drinking water, that is present either naturally or from pollution, is a great challenge for these countries.



Geographical areas with high natural fluoride levels (>1.5 mg/L).[11]

According to World Health Organization (WHO) standards, fluoride anions considered beneficial in drinking water at levels of about 0.7 mg/L, but detrimental to health at concentration above 1.5 mg/L. Lack of fluoride anions in drinking water results in dental caries (Table 1).[3][6][10]

Table 1. Effect of fluoride anions concentrations in drinking water on the human health.[10]

concentration of F^- (mg/L)	Impact on health
0.0–0.5	Dental caries
0.5–1.5	promotes dental health
1.5–4.0	Dental fluorosis
4.0–10	Dental and skeletal fluorosis
>10.0	Crippling fluorosis

Given the importance of the danger excess concentrations of fluoride anions in drinking water, and its serious environmental problems, many papers and reviews are reported about the removal of excess fluoride anions from water.[3][6][12][13]

The removal techniques are very variable but can broadly classified into two categories, specifically membrane and adsorption techniques.

Membrane processes include reverse osmosis,[14] nanofiltration,[15] dialysis and electro-dialysis.[16] A wide variety of adsorbents have been studied for their use in reducing the concentration of fluoride anions in aqueous solutions. Adsorption on activated alumina is one of the successful technologies for removal of fluoride anions.[17] Other reported adsorbents are clays,[18] carbon,[19] zeolites,[20] synthetic resins[21] and biopolymer.[22]

In addition to the removal of fluoride anions from water, sensing and detection of this anion is of great importance. The challenge of fluoride binding in aquatic solutions is a result of different factors as the properties of water, in terms of polarity and hydrogen-bonding abilities, the competition of the hydroxyl group, and the high hydration energy of fluoride anion ($-\Delta H°$ = 100–110 kcal mol^{-1}) compared to other anions.

Different fluoride receptors containing variable binding sites have been reported. The most fluoride receptors reported in the literature commit the binding of fluoride anions to the hydrogen bonding interactions.[23] In addition to the hydrogen binding receptors (**I**,[24] **II**,[25] Figure 1) two other classes depend on electrostatic cation-anion interactions (**III**,[26] Figure 1) and metal-based receptors (**IV**,[27] **V**,[28] **VI**,[29] Figure 1) are reported. In comparison to the H-bonding receptors, the charged system shows higher solubility in water, and the interaction between the metal-center and the anion is stronger. In metal-based systems the fluoride binding is achieved by the use of Lewis acid-base interaction and different metal-centers used for this purpose are reported such as Zr,[30] Sn,[31] Sb[32] and UO_2.[27]

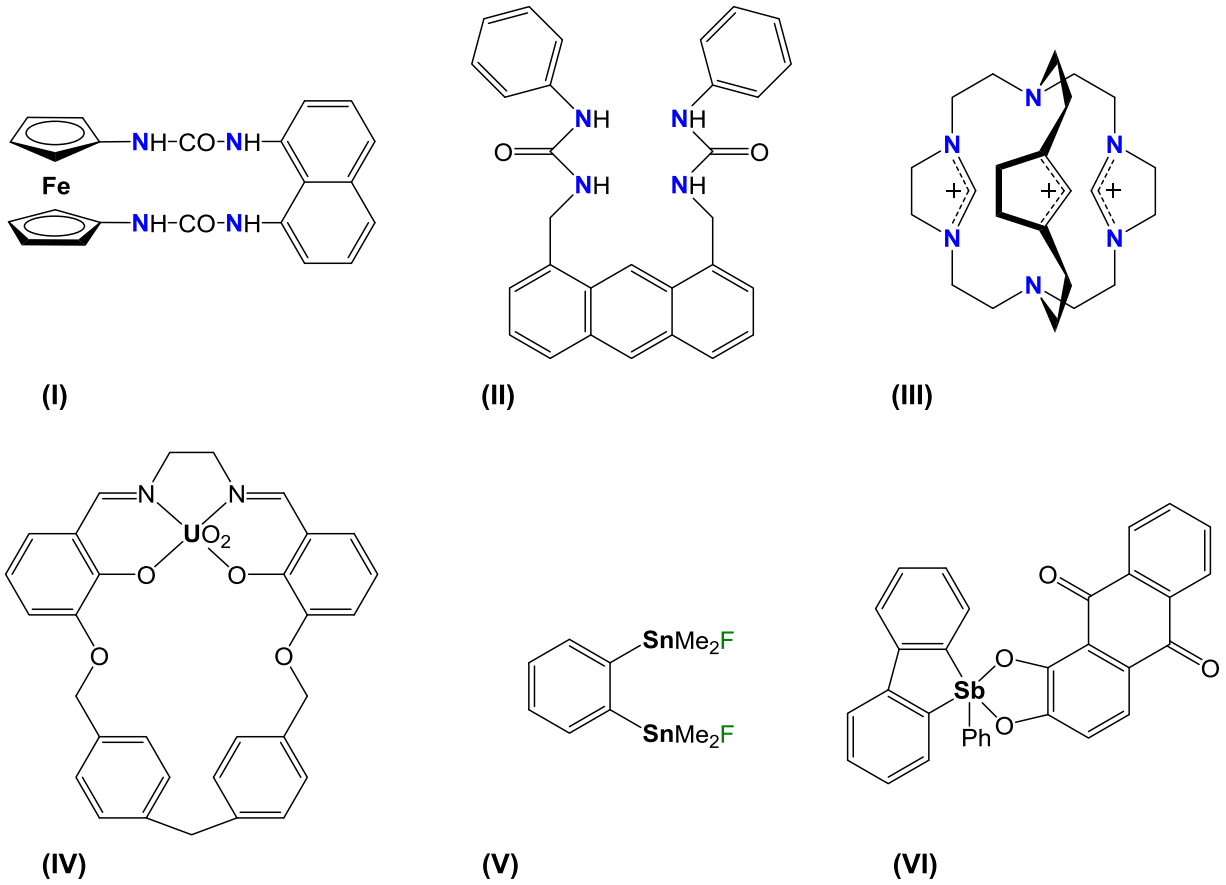


Figure 1. Different types of Fluoride receptors reported in the literature.

1.2 Organotin compounds

Tin is the 4th element of group 14 (C, Si, Ge, Sn, Pb) in the periodic table. Its most important ore is cassiterite, SnO_2, which is reduced by smelting with coal or fuel oil to tin.[33]

Organotin compounds are organic compounds containing at least on tin–carbon bond. They are classified according to the number of organic groups into mono, di, tri and tetra-organotin compounds.

Organotin compounds are used in a wide variety of applications. Triorganotin compounds find applications in agricultural biocides,[34] marine antifoulants,[35] and wood preservatives.[36] Diorganotin compounds are used as catalysis and stabilizers, whereas monoorganotin compounds are used in glass coating.[33]

Environmental fate of organotin compounds

Organotin compounds are released into the environment via several routes,[37] and their uses as agrochemicals and antifouling paints is the most important way for their occurrence in soils, sediments and water (Figure 2).[38] However, they commonly breakdown in the environment.[39] Degradation of organotin compounds accompanied with the cleavage of the tin–carbon bond may occur photolytically by UV irradiation, microbiologically by fungi or bacteria, or by chemical cleavage. [35][40]

In water, there are many factors that affect the rate of the organotin degradation, such as *p*H, turbidity, light and temperature.[41] As photolysis exceeds in clean seawaters and in surface waters, biodegradation found to be a major process in seawaters which are rich with suspended solids.[41] In comparison with water, the degradation of organotin compounds in sediment is much slower.[42] On the other hand, oxygen deficiency is shown to be an essential factor that extends the residence time of organotin compounds in sediments.[43]

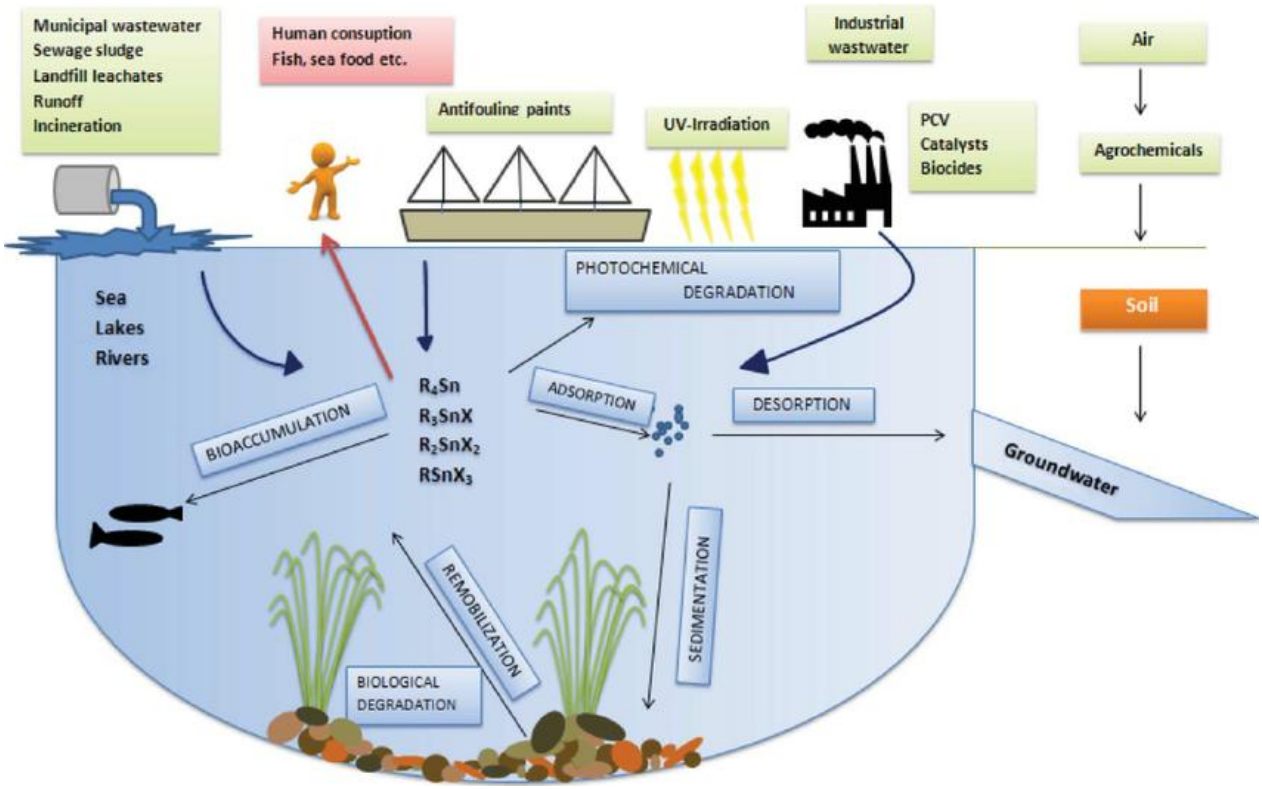


Figure 2. Environmental fate of organotin compounds. This photo was taken from *Crit. Rev. Anal. Chem*. **2013**, *43*, 35.

The idea of using organotin compounds for sensing, detection and removal of fluoride anions is based on the fact that, it can coordinate with up to three electron-donating substituents such as fluoride and other Lewis-basic anions.[33] On the other hand, fluoride anion with its relatively small ionic radius (1.47 Å) and a high charge density is classified as one of the hard bases, and therefore is expected to interact strongly with hard metal centers.[23] For the best achieving of the binding of Lewis-basic anions to organotin compounds, the tin atom should have considerable Lewis acidity.

Organotin halides R_nSnX_{4-n} (n = 1 – 3) are known to have higher Lewis acidity, in comparison with tetraorganotin compounds. The Lewis acidity increases as n decreases, and when the halide varies in the sequence I < Br < Cl. Although, the tin atoms in organotin fluorides have a high Lewis acidity, the low solubility of these compounds precluded their applications in practical fields, however.

One strategy to solubilize organotin fluorides is the employment of intramolecularly *built-in* substituents such as $Me_2N(CH_2)_3$, $ROCOCH_2CH_2$–, 2-$(Me_2NCH_2)C_6H_4$. The application of this concept for synthesizing soluble organotin fluorides has been widely used and reported (**VII**,[44] **VIII**,[45] **IX**,[46] **X**,[47] **XI**,[47] **XII**,[48] Figure 3).

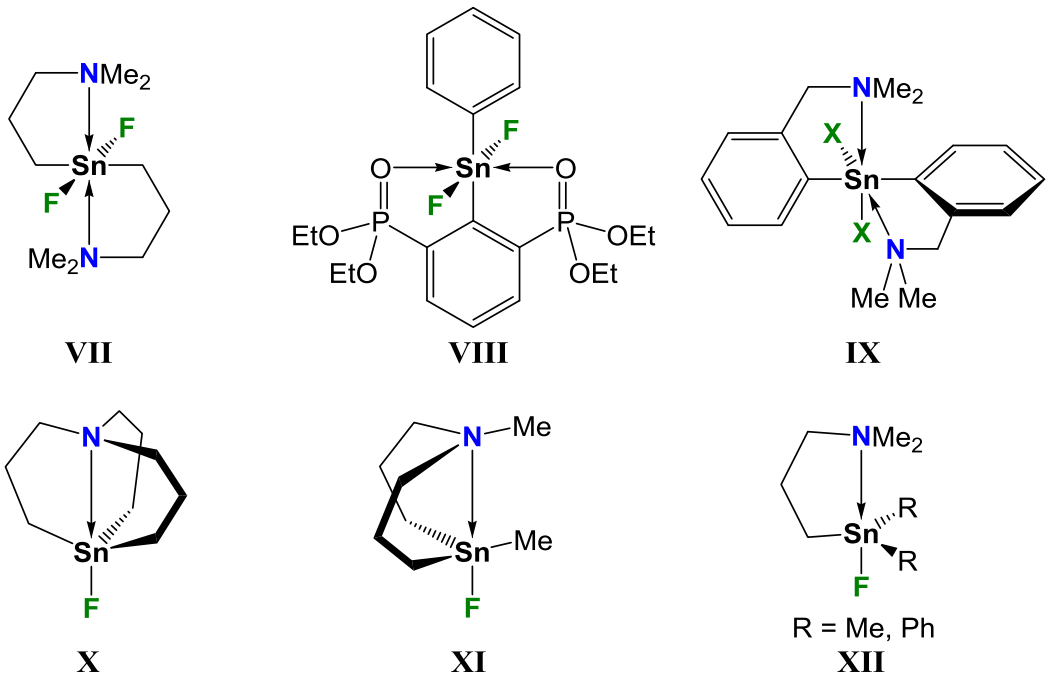


Figure 3. Organotin fluorides with N→Sn or O→Sn intramolecular interaction.

1. General Introduction

In this work the detection of fluoride anions using a series of organotin compounds containing the moiety $RR'N(CH_2)_3$ (R, R' = organic substituents) will be presented. These compounds can be classified into two types. The first type containing the intramolecularly coordinated aminopropyl-substituted organotin compounds in which the reactivity towards different halide anions, especially fluoride, took place in organic solvents. The second type dealing with organotin compound decorated with protonated aminopropyl arms, $Me_2NH(CH_2)_3$, resulted in good solubility of these organotin compounds in water.

Till now, the syntheses of organometallic compounds that are able to react selectively with fluoride anions in water is especially challenging. In chapter **4**, the water-soluble organotin compound $\{Me_2(H)N(CH_2)_3\}_2SnF_2{\cdot}2ClO_4$ is presented. Its reactivity towards fluoride anions in water in terms of selectivity, reversibility, effect of *p*H of the solution will be investigated.

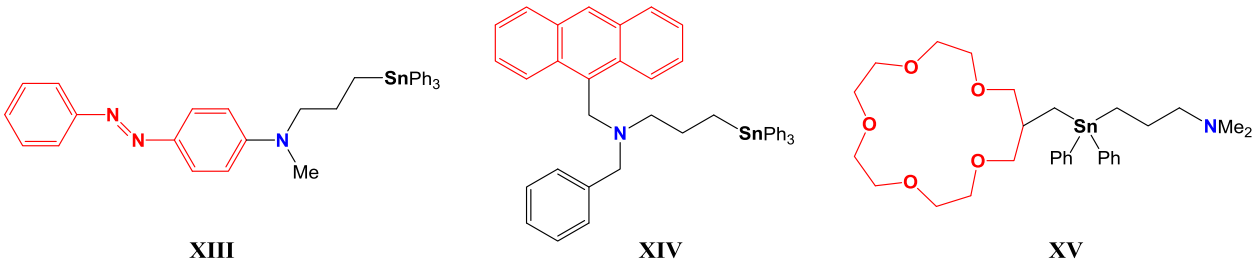
In view of the higher affinity of bicentric ditin compounds toward anions than the mononuclear organotin analogues, the syntheses of different spacer-bridged organoditin compounds are presented in the second chapter. In particular, the syntheses and structural characteristics of the organotin fluorides $\{Me_2N(CH_2)_3\}PhFSn(CH_2)_nSnFPh_2$ (n = 1, 3) will be focused on. The effect of spacing between the two tin centers on the molecular structure of the latter compounds in both solid state and solution, in addition to their ability to bind fluoride anions, will be discussed.

Attempts to use the fluorine-substituted organotin compound $\{Me_2N(CH_2)_3\}PhFSnCH_2SnFPh_2$ as an ionophore in fluoride-selective electrode will also presented.

The development of sensors for the direct detection of fluoride anions accompanied by a visually color change is an important target for real-life applications. For this purpose, attempts to design a colorimetric sensor for fluoride anions based on organotin compounds that contain a chromophoric group at the nitrogen atom (Figure 4, **XIII**), will be presented in the third Chapter. In addition to that, attempts to design a fluorescence chemosensor for sensing of fluoride anions using organotin compounds containing an azo group as a chromophore (Figure 4, **XIV**) will also be presented.

The selective recognition of fluoride salts, especially of NaF, is challenging as a result of the high lattice energy. For this purpose, the synthesis of ditopic receptor consists of the [16]-

crown-5 moiety, for the selective recognition of sodium ions, that is bound to the tin center (Figure 4, **XV**) will be presented. The selective recognition of NaF and NaI will be investigated.



XIII XIV XV

Figure 4. Tin–Nitrogen-based chemosensors.

On the other hand, designing an N/Sn-based Lewis pairs is an up-to-date research field. In the last chapter the syntheses, structural characteristic of the organotin compounds $\{Me_2N(CH_2)_3\}_2SnRX$ (R = Me, Ph; X = Cl, F) as well as their reactivity towards CH_2Cl_2 will be presented.

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2 Spacer-Bridged Organoditin Compounds and Their Reactivity toward Halide Anions

2.1 Unsymmetrical Bicentric Organotin Lewis Acids $\{Me_2N(CH_2)_3\}PhXSn(CH_2)_nSnPh_2X$ (X = F, I; n = 1, 3): Syntheses, Structures and Reactivity toward Fluoride Anion

2.1.1 INTRODUCTION

The selective complexation of anions by all sorts of host molecules remains a hot topic in contemporary chemistry. The progress made in this field is demonstrated in regular reviews.[1] Although the topic is still dominated by organic receptors, organometallic compounds also receive increasing attention in this domain.[2][3][4]

The ability of organotin halides to bind anions by the use of Lewis acid–base interaction has been widely studied.[5] The tin atoms in these compounds have considerable Lewis acidity in comparison with tetraorganotin compounds. Bicentric ditin compounds may show a higher affinity toward anions than the mononuclear organotin analogues. This is explained by their ability to form chelate complexes with the anions.[6][7]

The complexation behavior of spacer-bridged ditin compounds as bicentric Lewic acids towards different anions was intensively studied in the last years. Bis(haloorganylstanny1)alkanes of the type $[R_yX_{(3-y)}Sn]_2(CH_2)_n$ showed good results in this field, and many successful examples for their use as ionophores in ion-selective electrodes were reported.[4] An elegant example is bis(fluoro-di-*n*-octylstannyl)methane, $[(n\text{-}C_8H_{17})_2SnF]_2CH_2$,[8] **A** (Chart 1), that was synthesized previously in our research group and is commercially available as ionophore for fluoride anion selective electrode. Other examples are bis(dibromophenylstannyl)methane, $(PhSnBr_2)_2CH_2$,[9] **B** (Chart 1), which exhibits excellent selectivity towards phosphate ions, and bis(dichloroorganostannyl)methane, $\{(RCl_2Sn)_2CH_2$, R= (4-*n*-C_8H_{17}-C_6H_4)$\}$,[10] **C** (Chart 1), that was shown to be a highly selective arsenate ionophore.

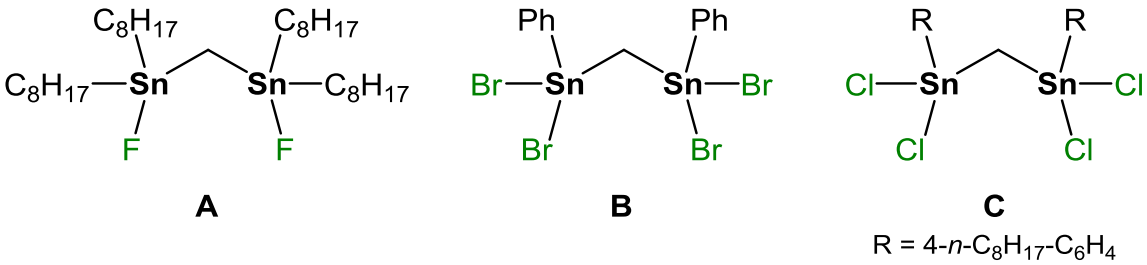


Chart 1. Selected bicentric tin-based Lewis acids having potential as anion carriers.

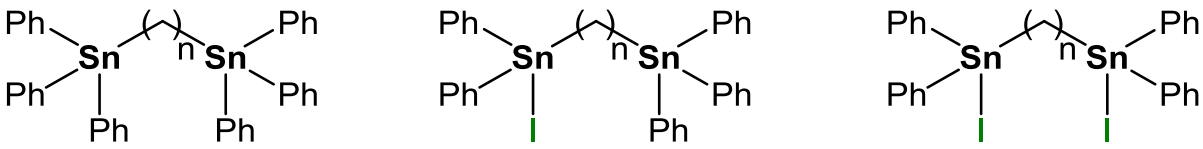
In general, the structural characteristics that determine the selectivity of organoditin compounds towards different anions are the substituent patterns at the tin atoms, as well as the distance separating the two tin centers.

Dakternieks and Jurkschat reported the complexation reactions of bis(halodiphenylstannyl)alkanes, $(Ph_2XSn)_2(CH_2)_n$; (X = I, Br, Cl, F; n = 1, 2, 3)[6] with different halide anions, and found that bis(fluorodiphenylstannyl)alkanes always preferentially chelate fluoride anions over chloride or bromide. However, the low solubility of these compounds as many other fluoridoorganotin compounds precluded their applications in practical fields. One strategy to overcome this problem and to solubilize organotin fluorides is the employment of intramolecularly coordinating *built-in* ligands such as $\{Me_2N(CH_2)_3\}$.[11]

In this work, a series of oligomethylene-bridged organodistannanes containing the ligand [3-(dimethylamino)propyl] will be presented. Furthermore, the solubility of the fluorido-substituted organotin compounds in organic solvents as well as their ability to bind fluoride anions will be investigated.

2.1.2 Syntheses of the [3-(dimethylamino)propyl]-substituted tetraorganotin compounds $\{Me_2N(CH_2)_3\}Ph_2Sn(CH_2)_nSnPh_3$ (n = 1–4)

The α-(diphenyliodostannyl)-ω-(triphenylstannyl) alkanes $Ph_2ISn(CH_2)_nSnPh_3$ (n = 1 – 4) were synthesized by the reaction of 0.85 molar equivalent of elemental iodine with the corresponding bis(triphenylstannyl)alkanes, $[Ph_3Sn]_2(CH_2)_n$, n = 1 – 4.[12][13][14][15] Each reaction mixture contains a set of three compounds, the desired compound, namely the mono iodine-substituted compound, the diiodine-substituted compound, and the starting compound (Chart 2).



1a, n = 1
2a, n = 2
3a, n = 3
4a, n = 4

1b, n = 1
2b, n = 2
3b, n = 3
4b, n = 4

1c, n = 1
2c, n = 2
3c, n = 3
4c, n = 4

Chart 2. Drawing of Compounds **1a** – **4a**, **1b – 4b** and **1c – 4c**.

Both tin atoms in the starting compounds are equivalent, and react similarly with iodine. This allowed us to take an excess of the bis(triphenylstannyl)alkanes to favor the formation of the mono iodide compounds **1b** – **4b**. Thus, these compounds were obtained in 45-60% yields as proved by ^{119}Sn NMR spectroscopy. The unreacted starting compounds could be recovered in the next steps.

As an example, the reaction of 1,3-bis(triphenylstannyl)propane, $(Ph_3SnCH_2)_2CH_2$ (**3a**),[14] with 0.85 molar equivalent of elemental iodine gave a crude reaction mixture the ^{119}Sn NMR spectrum of which indicated this mixture containing 29% **3a** (δ –103.8), 56% $Ph_2ISn(CH_2)_3SnPh_3$ (**3b**, δ –59.6, –104.0), and 15% $(IPh_2SnCH_2)_2CH_2$ (**3c**, δ –60.9) (Figure 1).

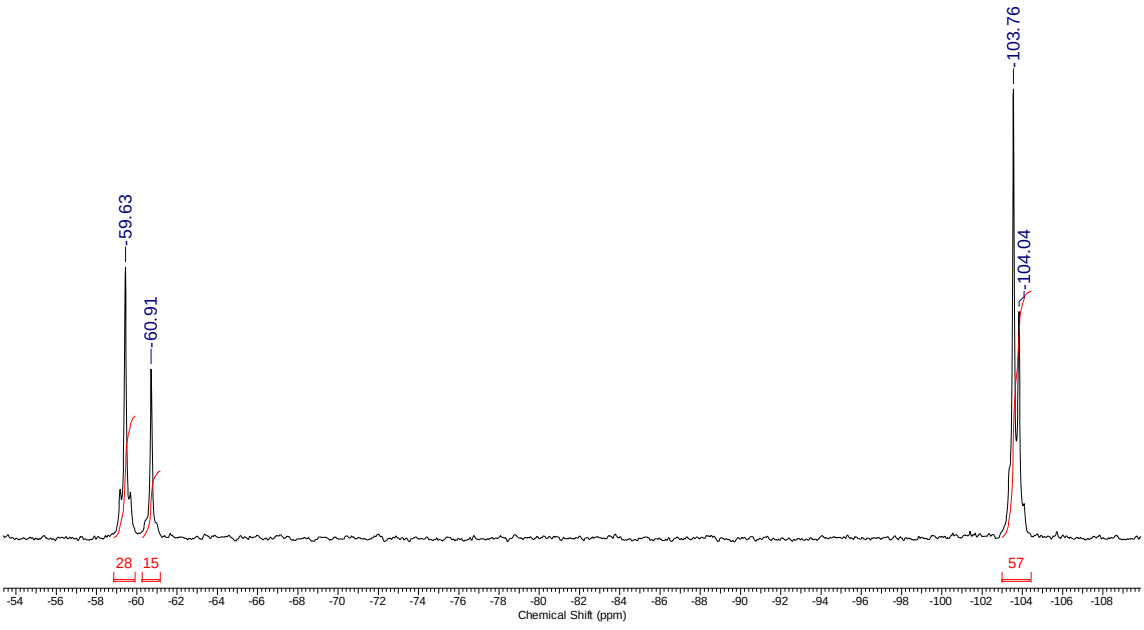
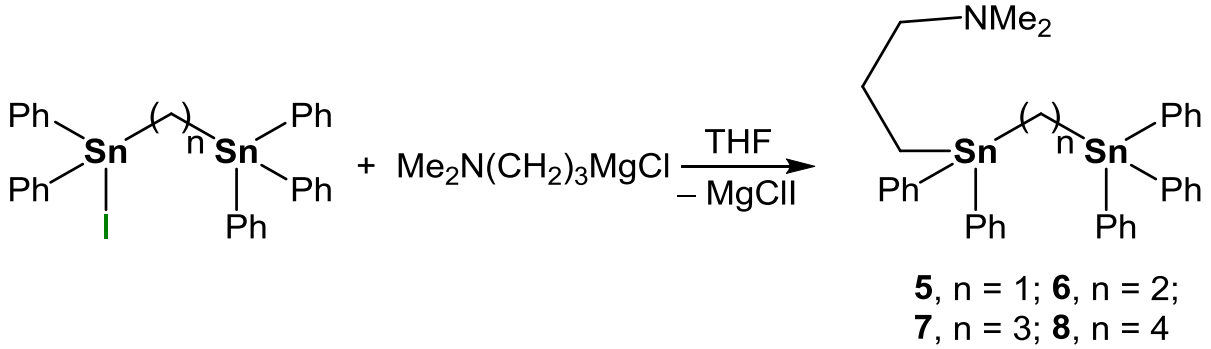


Figure 1. ^{119}Sn NMR spectrum in $CDCl_3$ of the product mixture obtained from the reaction of $(Ph_3SnCH_2)_2CH_2$ with 0.85 molar equivalent elemental iodine.

As it is known, organotin iodides are sensitive towards chromatographic conditions. This prevented the purification of compounds **1b** – **4b** by column chromatography. Furthermore, recrystallizations of these compounds from their mixtures were not successful. Therefore, these mixtures were used in the next reactions without further purification.

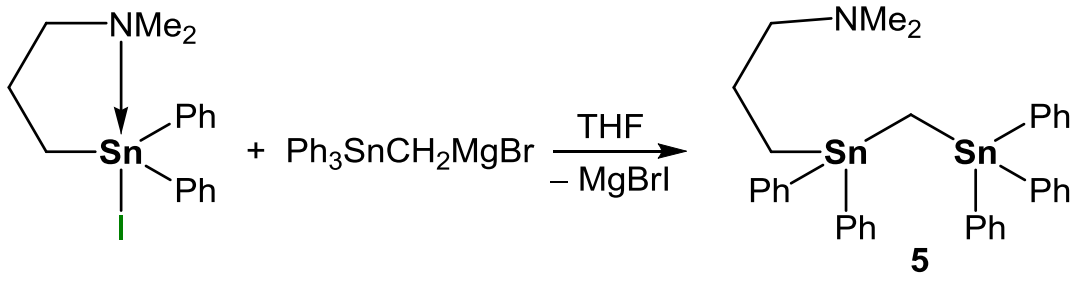
Reactions of the mixtures containing compounds **1b** – **4b** with an excess of $Me_2N(CH_2)_3MgCl$ provided the corresponding $Me_2N(CH_2)_3$-substituted organotin compounds **5** – **8**, respectively, in moderate yields (Scheme 1).



Scheme 1. Syntheses of the organotin compounds **5** – **8**.

Compounds **5** – **8** were purified by column chromatography and obtained as light yellowish oils in moderate yields. They show well solubility in common organic solvents such as CH_2Cl_2, $CHCl_3$, THF, and diethyl ether.

Compound **5** has also been synthesized in moderate yield by the reaction of the triorganotin iodide $\{Me_2N(CH_2)_3\}(Ph_2)SnI$[11] with triphenylstannylmethylmagnesium bromide, Ph_3SnCH_2MgBr,[16] in THF (Scheme 2).



Scheme 2. Alternative synthesis of compound **5**.

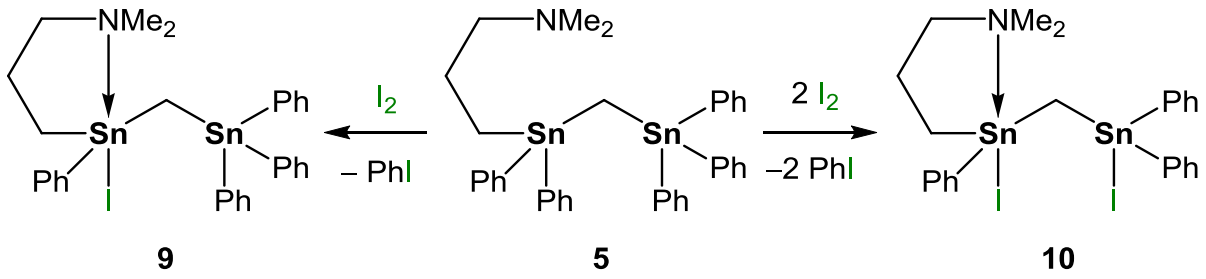
The tin atoms in compounds **1b** – **4b** and **5** – **8** are tetra-coordinated in solution as evidenced by their ^{119}Sn NMR chemical shifts. Those for the tin atoms in Ph_3Sn locate at δ –87, –103, –104, –100 for **1b** – **4b**, and at δ –77, –104, –104, –100 for **5** – **8**, respectively, being in the same order of magnitude as those in the corresponding bis(triphenylstannyl)alkanes at δ –79,[12] –104,[13] –103[14] and –100,[15] respectively, (Table 1). On the other hand, replacing one phenyl group with the [3-(dimethylamino)propyl] substituent in compounds **5** – **8** causes low-field shifts of about 28–30 ppm as chemical shifts at δ –49, –74, –75 and –72, respectively, were observed, (Table 1). The chemical shifts of the tin atoms in Ph_2ISn for compounds **1b** – **4b** at δ –52, –52, –60, and –54 are close to those reported for the corresponded bis(iododiphenylstannyl)alkanes at –68,[12] –54,[13] –61,[17] and –55,[18] respectively, (Table 1).

Table 1. ^{119}Sn NMR data for compounds **1a – 4a**, **1b – 4b**, **1c – 4c**, and **5** – **8** in $CDCl_3$.

	$Ph_3Sn(CH_2)_nSnPh_3$	$IPh_2Sn(CH_2)_nSnPh_2I$	$Ph_2ISn(CH_2)_nSnPh_3$	$Ph_2RSn(CH_2)_nSnPh_3$ R = $Me_2N(CH_2)_3$
n = 1	–79 (**1a**)	–68 (**1c**)	–52, –87 (**1b**)	–49, –77 (**5**)
n = 2	–104 (**2a**)	–54 (**2c**)	–52, –103 (**2b**)	–74, –104 (**6**)
n = 3	–103 (**3a**)	–61 (**3c**)	–60, –104 (**3b**)	–75, –104 (**7**)
n = 4	–100 (**4a**)	–55 (**4c**)	–54, –100 (**4b**)	–72, –100 (**8**)

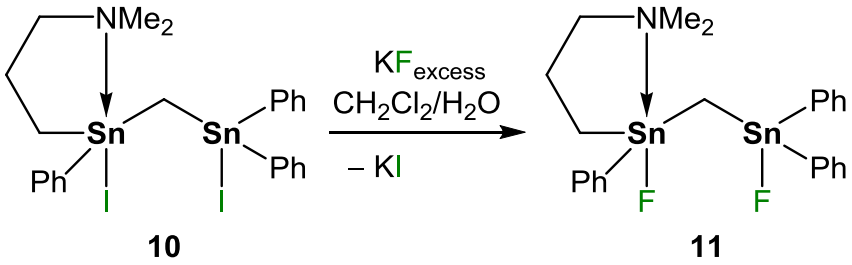
2.1.3 Syntheses of the [3-(dimethylamino)propyl]-substituted organotin halides $\{Me_2N(CH_2)_3\}Ph(X1)SnCH_2SnPh_2(X2)$ (9, X1 = I, X2 = Ph; 10, X1 = X2 = I; 11, X1 = X2 = F)

The reactions of compound **5** with one, respectively, two molar equivalents of elemental iodine in CH_2Cl_2 afforded the corresponding iodine-substituted compounds $\{Me_2N(CH_2)_3\}PhISnCH_2SnPh_3$, **9**, and $\{Me_2N(CH_2)_3\}PhISnCH_2SnPh_2I$, **10**, in good, respectively, quantitative yields (Scheme 3).



Scheme 3. Syntheses of the organotin iodide **9** and **10**.

The reaction of compound **10** with an excess of potassium fluoride, KF, in CH_2Cl_2 and water provided the triorganotin fluoride $\{Me_2N(CH_2)_3\}PhFSnCH_2SnPh_2F$, **11**, in moderate yield, (Scheme 4).



Scheme 4. Synthesis of the organotin fluoride **11**.

Compounds **9** and **10** are light yellowish solids, whereas compound **11** is a white solid. They show good solubility in $CHCl_3$, CH_2Cl_2, and acetone. They are air-stable materials.

2.1.3.1 Molecular structures of compounds 9 – 11

Single crystals of compounds **9** and **10** suitable for X-ray diffraction analysis were each obtained each by slow evaporation of the corresponding solution in CH_2Cl_2/ *n*-hexane at room temperature. Those for **11** were obtained by keeping a solution of the compound in acetone at –5°C.

Compounds **9** and **11** crystallize in the monoclinic space group *P*2(1)/c with four molecules for **9** and two molecules for **11** in the unit cell. Compound **10**, however, crystallizes in the monoclinic space group C2/c with 8 molecules in the unit cell.

The molecular structures of **9** – **11** are presented in Figures 2 – 4, selected interatomic distances and bond angles are listed in Table 2.

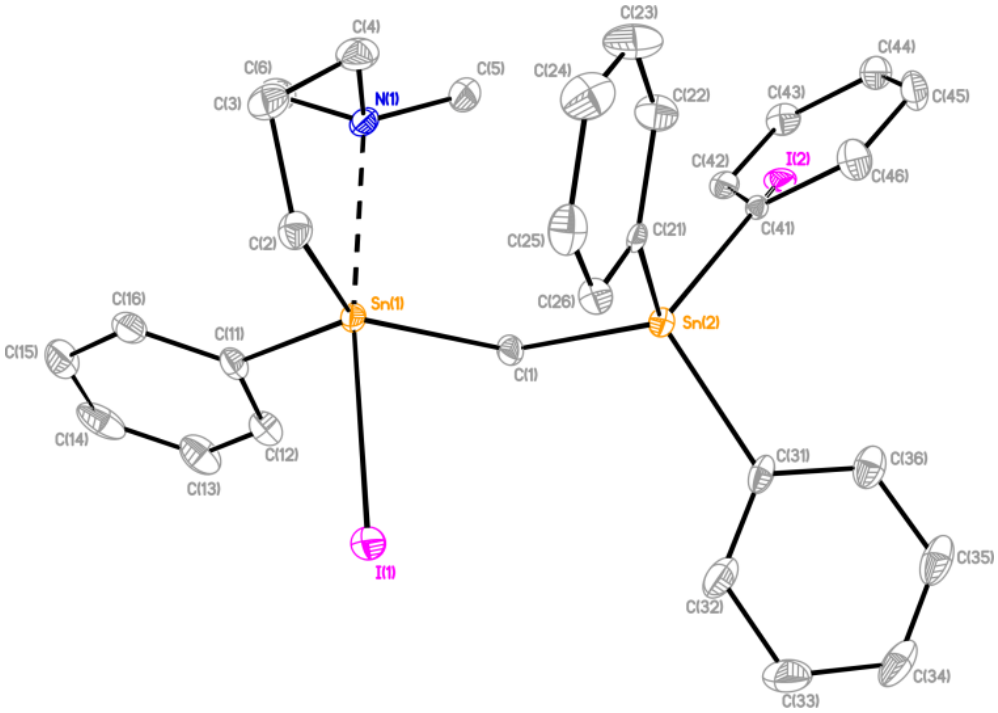


Figure 2. General view (SHELXTL) of a molecule of **9** showing 30% probability displacement ellipsoids and the crystallographic numbering scheme. There is a disorder of the phenyl ring C(41) to C(46) with iodine I(2) with a ratio of 90:10. Hydrogen atoms are omitted for clarity.

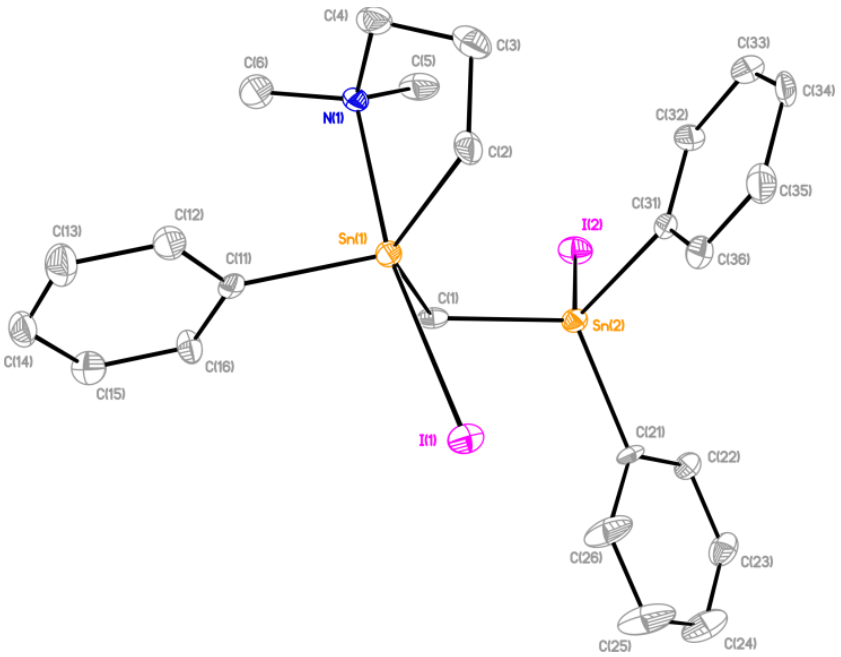


Figure 3. General view (SHELXTL) of a molecule of **10** showing 30% probability displacement ellipsoids and the crystallographic numbering scheme. Hydrogen atoms are omitted for clarity.

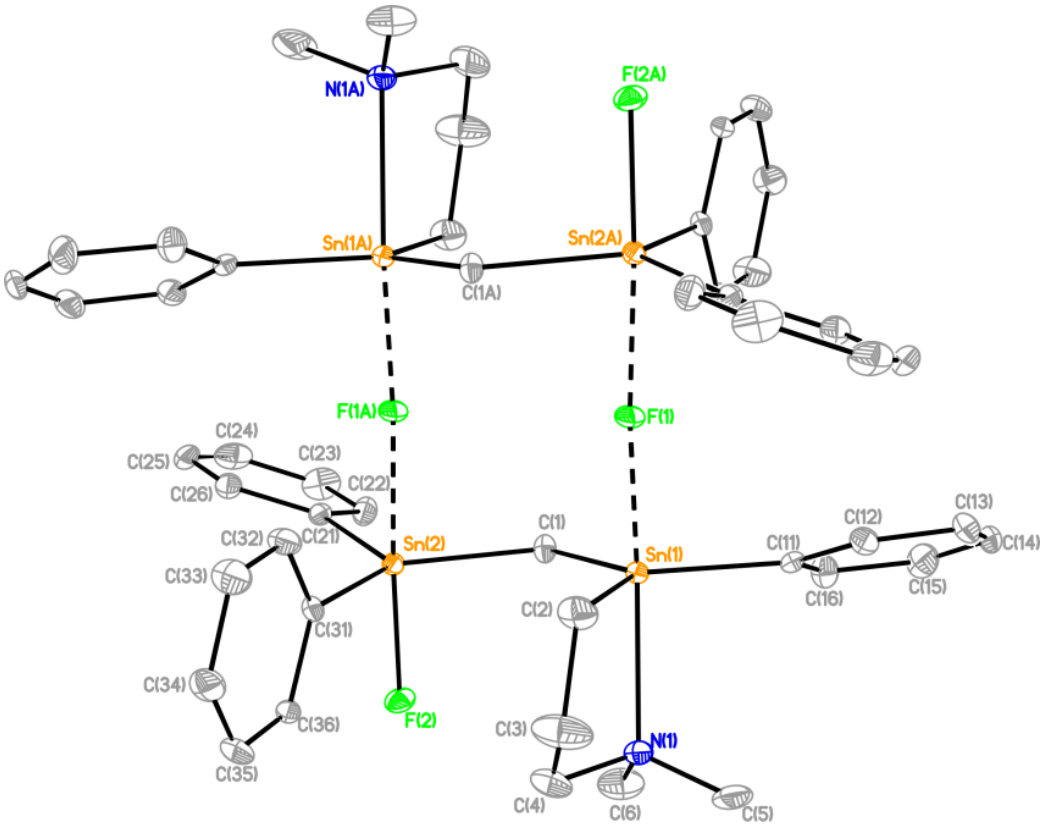


Figure 4. General view (SHELXTL) of a molecule of **11** showing 30% probability displacement ellipsoids and the crystallographic numbering scheme. Hydrogen atoms are omitted for clarity.

Table 2. Selected interatomic distances /Å and bond angles /° in $\{Me_2N(CH_2)_3\}Ph(X1)SnCH_2SnPh_2(X2)$, **9** – **11**.

	9	**10**	**11**
	X1 = I(1), X2 = C(41)	X1 = I(1), X2 = I(2)	X1 = F(1), X2 = F(2)
Sn(1)–N(1)	2.486(4)	2.433(3)	2.400(3)
Sn(1)–X(1)	2.9777(4)	2.9613(4)	2.1229(17)
Sn(2)–X(1A)			2.2291(17)
Sn(2)–X(2)	2.161(2)	2.7050(5)	2.0300(18)
Sn(1)–C(1)–Sn(2)	119.7(2)	118.54(19)	118.32(15)
N(1)–Sn(1)–X(1)	164.51(8)	169.76(9)	168.99(9)
X(2)–Sn(2)–X(1A)			176.91(8)
N(1)–Sn(1)–C(1)	91.58(15)	92.71(13)	96.19(12)

N(1)–Sn(1)–C(2)	78.78(15)	79.06(15)	79.72(13)
N(1)–Sn(1)–C(11)	96.31(15)	93.56(12)	92.85(11)
X(1)–Sn(1)–C(1)	88.56(13)	90.29(11)	91.09(11)
X(1)–Sn(1)–C(11)	98.26(12)	94.64(8)	91.28(10)
X(1)–Sn(1)–C(2)	89.76(13)	91.58(13)	89.43(11)
X(1A)–Sn(2)–C(1)			85.87(10)
X(1A)–Sn(2)–C(21)			88.54(10)
X(1A)–Sn(2)–C(31)			87.45(10)
X(2)–Sn(2)–C(1)	108.77(15)	105.47(10)	91.60(11)
X(2)–Sn(2)–C(21)	105.67(14)	104.32(9)	94.13(10)
X(2)–Sn(2)–C(31)	105.12(14)	103.77(9)	92.51(10)

The Sn1 tin atoms in compounds **9** and **10** are each pentacoordinated and exhibit a distorted trigonal-bipyramidal environment (geometric goodness $\Delta\Sigma(\theta) = 83.1°$ for 2 and 3) with C(1), C(2), and C(11) occupying the equatorial and N(1) and I(1) the axial positions. The Sn(1)–N(1) interatomic distances of 2.486(4) (**9**) and 2.433(3) (**10**) Å are shorter than the corresponding distance in compound $Me_2N(CH_2)_3SnPh_2I$ (**A**) 2.541(5) Å,[11] and longer than that in compound $Me_2N(CH_2)_3SnMe_2I$ (**B**) 2.38(1) Å.[19]

The Sn(1)–I(1) distances of 2.9777(4) (**9**) and 2.9613(4) (**10**) Å are between the corresponding distances in compounds **A** and **B** of 2.888 Å and 3.0567 Å, respectively. The N(1)–Sn(1)–I(1) angles in **9** and **10** of 164.51(8)° and 169.76(9)°, respectively, are rather close to the corresponding angles in **A** (167.9(1)°) and **B** (169.4(3)°).

The environments at Sn(2) in compounds **9** and **10** are distorted tetrahedral, with angles varying between 105.15(15)° (C(41)–Sn(2)–C(21)) and 114.07(16)° (C(21)–Sn(2)–C(31)) in **9** and between 103.77(9)° (C(31)–Sn(2)–I(2)) and 114.67(14)° (C(1)–Sn(2)–C(21)) in **10**. The distance Sn(2)–I(2) of 2.7050(5) Å in **10** is shorter than the Sn(1)–I(1) distances of 2.9777(4) and 2.9613(4) Å in **9** and **10**, respectively.

Compound **11** forms a centrosymmetric head-to-tail dimer via unsymmetrical Sn(1)−F(1)−Sn(2A) bridges at distances of 2.1229(17) and 2.2291(17) Å. These distances are

comparable with those reported for the organofluorido stannate complexes $NEt_4[CH_2(SnXPh_2)_2{\cdot}F]$ (X = F, Br, I) ranging between 2.204(2) and 2.274(5) Å.[6]

Both tin atoms in **11** are pentacoordinated and exhibit distorted trigonal-bipyramidal geometries (geometric goodness ΔΣ(θ) = 88.2° for Sn1 and 81.1° for Sn2) with the equatorial positions being occupied by carbon atoms C(1), C(2) and C(11) at Sn1, and C(1), C(21), C(31) at Sn2. The axial positions are occupied by N(1), F(1) atoms at Sn1 and F(1A), F(2) atoms at Sn2.

The Sn(1)–N(1) distance of 2.400(3) Å is considerably shorter than the sum of the Van der Waals radii of Sn and N (3.75 Å)[20]. The distances F(1)–Sn(1) and F(1A)–Sn(2) of 2.1229(17) Å and 2.2291(17) Å , respectively, are somewhat longer than those found in compounds[2-$\{(CH_3)_2NCH_2\}C_6H_4$]Me_2SnF (**C**) of 2.0384(10) Å[21] and [2- $\{(CH_3)_2NCH_2\}C_6H_4$] Ph_2SnF (**D**) of 2.0242(12) Å.[21]

The N(1)–Sn1–F1 angle of 168.99(9)° is rather similar to the corresponded angles observed in compounds **C** and **D** of 167.37(5)°[21] and 166.83(6)°[21], respectively. The N(1)–Sn(1) distance of 2.400(3) Å is shorter than the corresponding distances in compounds **C** (2.4899(14) Å),[21] and **D** (2.5294(18) Å).[21] The angles F(1A)–Sn(2)–F(2) and Sn(1)–F(1)–Sn(2A) are 176.91(8)° and 172.05(10)°, respectively.

2.1.3.2 Structures of the compounds 9 – 11 in Solution

A ^{119}Sn NMR spectrum of **9** showed two showed two equally intense resonances (total integral 90) at δ –86 and δ –92 related to Sn2, respectively, Sn1 in **9**. In addition to that, two equally intense resonances at δ –54 and δ –102 (integral 10) was observed. These two latter resonances are related to Sn2 and Sn1 in **10**, respectively.

The Sn2 atoms in **9** and **10** are four-coordinated as evidenced by their ^{119}Sn chemical shifts at δ –86 and δ –54, respectively, being close to those reported for $(Ph_3Sn)_2CH_2$ at [12] δ –79 and $(IPh_2Sn)_2CH_2$ at δ –68, respectively.[12]

On the other hand, the comparison of the ^{119}Sn NMR chemical shifts of Sn1 in the organotin iodides **9** (δ –92) and **10** (δ –102) with those for Me_2PhSnI (δ –18)[22] and {2-$(Me_2NCH_2)C_6H_4$}Me_2SnI (δ –73)[23], containing four- respectively five-coordinated tin atoms,

suggests that Sn1 in **9** and **10** are five-coordinated as a result of N→Sn intramolecular interaction. Furthermore, the ^{13}C NMR chemical shifts of the Sn*C*H$_2$CH$_2$ carbon atoms in the organotin iodides **9** and **10** at δ 19.1 and 18.7, respectively, are close to those reported for the corresponding carbon atoms in the five-coordinated organotin compound Me$_2$N(CH$_2$)$_3$SnPh$_2$I (δ 18.5 ppm).[11] This geometry in solution for **9** and **10** is similar to that found in the solid state. ESI mass spectra (positive mode) of the organotin iodides **9** and **10** showed mass clusters centered at *m*/*z* 646.1 and 696.0, respectively, which correspond to $[M - I]^+$.

A ^{119}Sn NMR spectrum of a solution of compound **11** in $CDCl_3$ at –35°C reveals a doublet of doublet resonances at δ –18 [$^1J(^{119}Sn1–^{19}F1)$ = 1168, $^3J(^{119}Sn1–^{19}F2)$ = 120 Hz, Sn1] and δ –159 [$^1J(^{119}Sn2–^{19}F2)$ = 2201, $J(^{119}Sn2–^{19}F1)$ = 560 Hz, Sn2] (Figure 5). In addition, there is a minor intense resonance at δ –52 (integral 5, not assigned). However, the chemical shift at –18 ppm is close to that reported for the pentacoordinated tin atom Sn1in Ph$_2$FSnCH$_2$*Sn*1FPh-[19]-crown-6 at δ –17.[24]

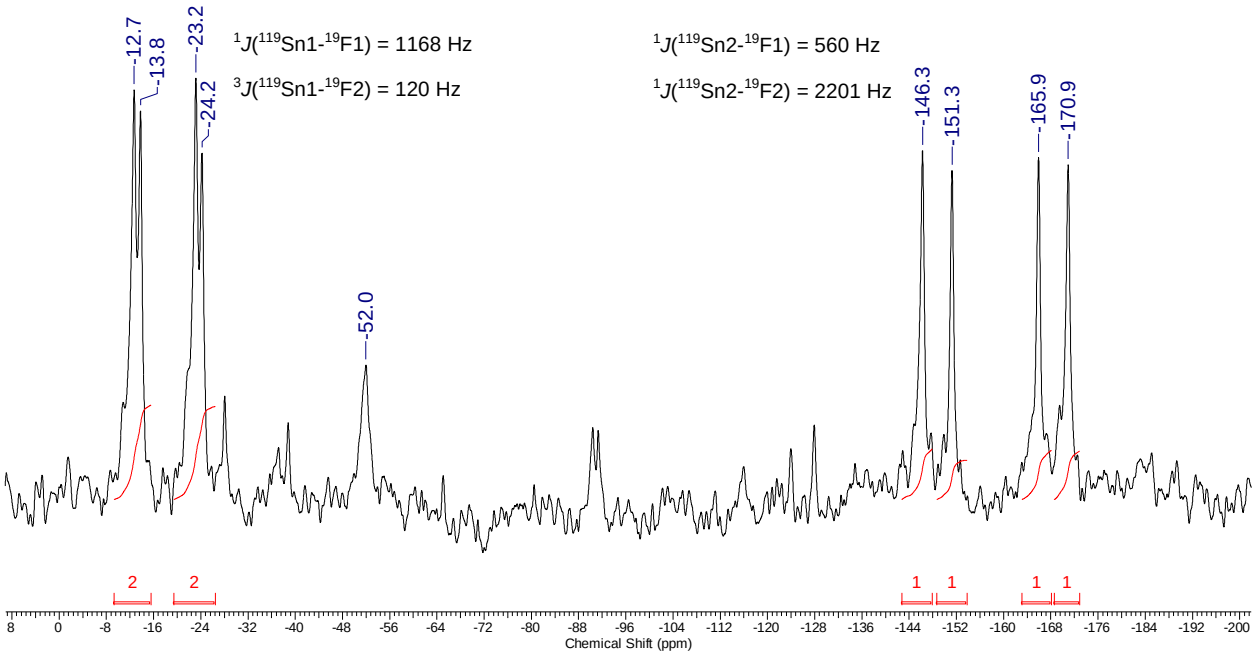


Figure 5. ^{119}Sn NMR spectrum of **11** in CD_2Cl_2 at –35°C.

Noteworthy, the chemical shift of Sn2 at –159 ppm and the coupling constant values of 560 and 2201 Hz are close to those reported for Sn2 in the compound [(Ph$_2$F^a*Sn*2CH$_2$)$_2$SnF^{b}Ph·F^b]$^-$ [Bu$_4$N]$^+$[25] of δ –159 [$^1J(^{119}Sn2–^{19}F^a)$ = 2216, $^1J(^{119}Sn2–^{19}F^b)$ = 582,

$^{3}J(^{119}Sn2–^{19}F^{b})$ = 116 Hz], F^{a} and F^{b} are assigned to the terminal and bridging fluorides, respectively.

A ^{19}F NMR spectrum at ambient temperature of the same sample showed two equally intense resonances at δ –96 ($^{1}J(^{19}F1–^{117/119}Sn1)$ = 451, 1249 Hz, F1) with a satellite-to-satellite-to-signal-to-satellite-to-satellite ratio of approximately [6:9:70:9:6] and –188 ($^{1}J(^{19}F2–^{117/119}Sn2)$ = 2187 Hz, F2) with a satellite-to-signal-to-satellite ratio of approximately [8:84:8] (Figure 6). These two chemical shifts are close to those reported for $[(Ph_2F^{a}Sn2CH_2)_2Sn1F^{b}Ph{\cdot}F^{b}]^{-}[Bu_4N]^{+}$ at δ –101 [$^{1}J(^{19}F^{b}–^{117/119}Sn1)$ = 1174/1224, $^{1}J(^{19}F^{b}–^{117/119}Sn2)$ = 573 Hz] and –182 [$^{1}J(^{19}F^{a}–^{117/119}Sn2)$ = 2163 Hz].

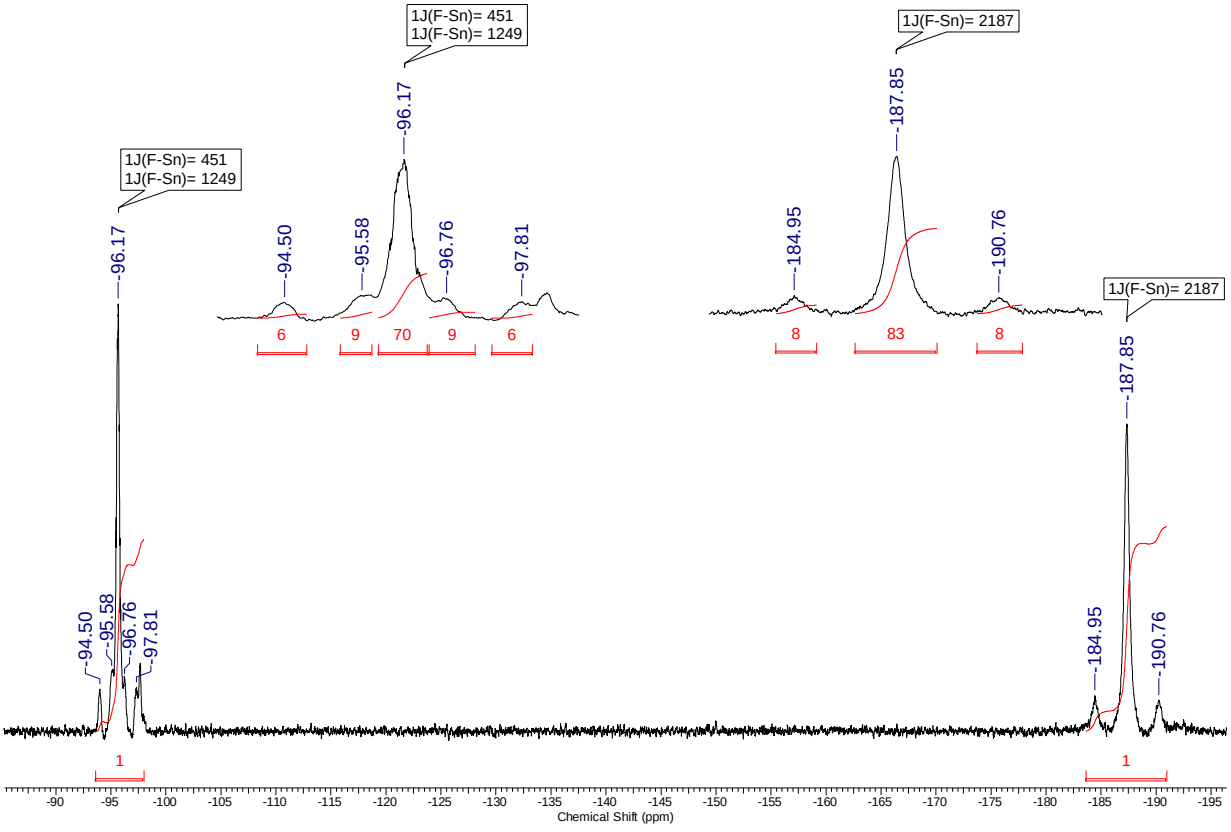


Figure 6. ^{19}F NMR spectrum of **11** in $CDCl_3$ at 22°C.

The question that has to be answered is whether compound **11** presents as a monomer or as a dimer in solution. According to a ^{1}H DOSY NMR spectrum of compound **11** shown in Figure 7, the expansion indicates two components with diffusion coefficients of $7.09{\cdot}10^{-10}$ and $7.45{\cdot}10^{-10}$ m^2/s. With the Stokes-Einstein equation, a hydrodynamic radius of 5.4–5.7 Å was calculated, which in turn indicates compound **11** being monomeric in solution.

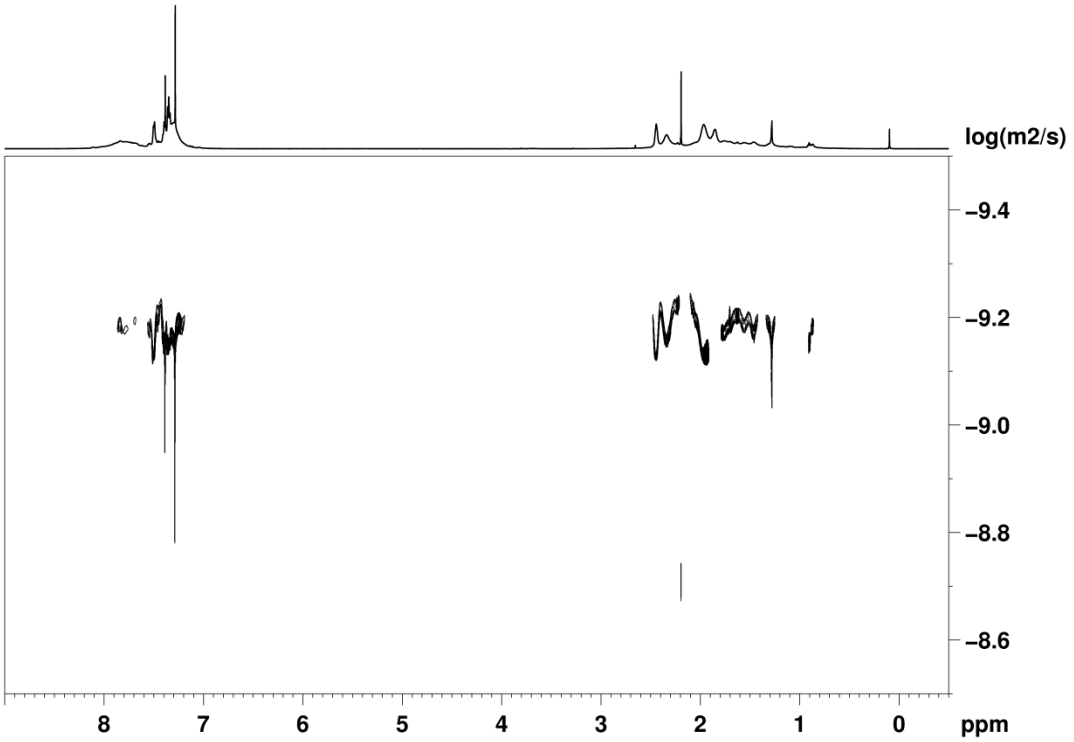


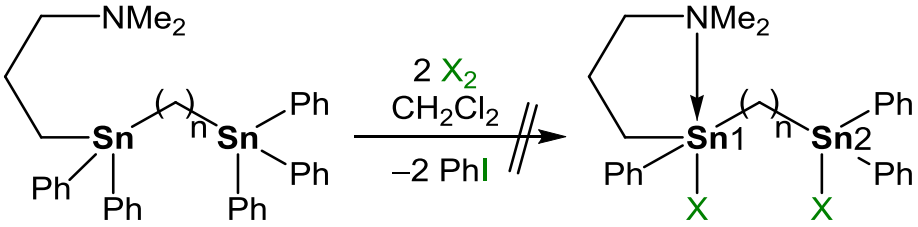
Figure 7. ^{1}H Dosy NMR spectrum of compound **11** in $CDCl_3$.

Notably, an ESI mass spectrum (positive mode) revealed, in addition to the major mass cluster centered at *m*/*z* 588.1 that is assigned to $[M - F]^+$, a rather low-intense mass cluster centered at *m*/*z* 1191.0, which fits to $[2M - 3F + 2OH]^+$. At least, this supports the idea that the formation of dimers in solution might be possible.

From variable-temperature ^{1}H NMR spectroscopy showing for both compounds **10** and **11** two equally intense resonances for the NC*H*$_3$ protons at T = −80 °C (**10**: 1.84, 2.34 ppm; **11**: 1.88, 2.24 ppm) but only one resonance at room temperature (**10**: 2.08 ppm; **11**: 1.96 ppm) it is concluded that the intramolecular N→Sn coordination is kinetically labile on the NMR time scale at room temperature but inert at T = −80 °C.

2.1.4 Attempts to synthesize [3-(dimethylamino)propyl]-substituted organoditin halides $RPhXSn(CH_2)_nSnPh_2X$ ($R = Me_2N(CH_2)_3$, n = 2, 3, 4; X = I, Br)

The course of the reactions between **6** and two molar equivalents iodine, and each of **7** and **8** with two molar equivalents bromine in attempt to synthesize the corresponding organotin halides was monitored by ^1H, ^{13}C, and ^{119}Sn NMR spectroscopy (Scheme 5).



6, n = 2
7, n = 3
8, n = 4

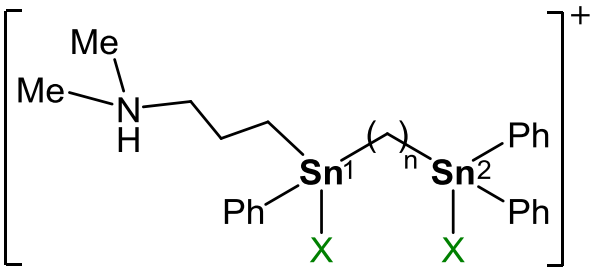
12, n = 2, X = I
13, n = 3, X = Br
14, n = 4, X = Br

Scheme 5. Attempts at synthesizing the organotin halides **12**, **13** and **14**.

In an attempt to synthesize compound **12**, two molar equivalents of iodine were added to a solution of **6** in CH_2Cl_2 at 0°C and the mixture was stirred for two days. After evaporating the solvents under reduced pressure and moderate heat (56°C) ^1H, ^{13}C, and ^{119}Sn NMR spectra were recorded. A ^{119}Sn NMR spectrum in $CDCl_3$ of the crude reaction mixture showed two signals at δ –5 (integral 38) and δ –53 ($^3J(^{119}Sn–^{117/119}Sn)$ = 2087 Hz, integral 39). these are assigned with caution to Sn1 and Sn2 in **12`**, respectively, (Chart 3). In addition, there are four minor intense resonances at δ –24 (integral 5, not assigned), –67 (integral 8, not assigned), –91 (integral 5, not assigned) and –145 (integral 5, not assigned). After 8 days a ^{119}Sn NMR spectrum of the same sample showed two major signals at δ –15 (integral 28) and –56 (integral 29). In addition, there are eight minor signals at δ –23 (integral 2), –38 (integral 2), –47 (integral 1), –60 (integral 12), –70 (integral 4), –106 (integral 6), –114 (integral 4) and –189 (integral 12).

On the other hand, a ^1H NMR spectrum of the same sample showed two signals in the field between 9–10 ppm, being in the range characteristic for $[Me_2NH]^+$ proton.

With caution, the ^{119}Sn chemical shifts at δ –91 and δ –53 could be related to Sn1 and Sn2 in **12**, as they are close to those found for the corresponding tin atoms in $\{Me_2N(CH_2)_3\}Ph(I)Sn(CH_2)_3Sn(I)Ph_2$ at δ –91 and δ –54, respectively, (Chapter 2.1.5). The hypothesis is that after the reaction of compound **6** with iodine took place the resulting compound **12** was not stable under the experimental employed conditions (heating to 60°C and pressure of $5x10^{-3}$ m bar).



12', n = 2, X = I
13', n = 3, X = Br
14', n = 4, X = Br

Chart 3. Suggested structures of the protonated compounds **12`**, **13`** and **14`**.

A similar hydrolysis behavior was observed when compound **8** was stirred with bromine (two molar equivalents) in CH_2Cl_2 in order to give compound **14**. The reaction mixture was stirred for one day, followed by evaporating the solvent and PhBr under reduced pressure and heat (56°C). A ^{119}Sn NMR spectrum in $CDCl_3$ showed two signals at δ –73 and –101 related to unreacted compound **8** with a total integral of 30. In addition, there are two major signals at δ –2 (integral 26) and –74 (integral 27), and four minor signals at δ –12 (integral 7), –27 (integral 6), –62 (integral 1), and –146 (integral 3). A ^{1}H NMR spectrum showed a broad signal between 9–10 ppm related to the $[Me_2NH]^+$ moiety.

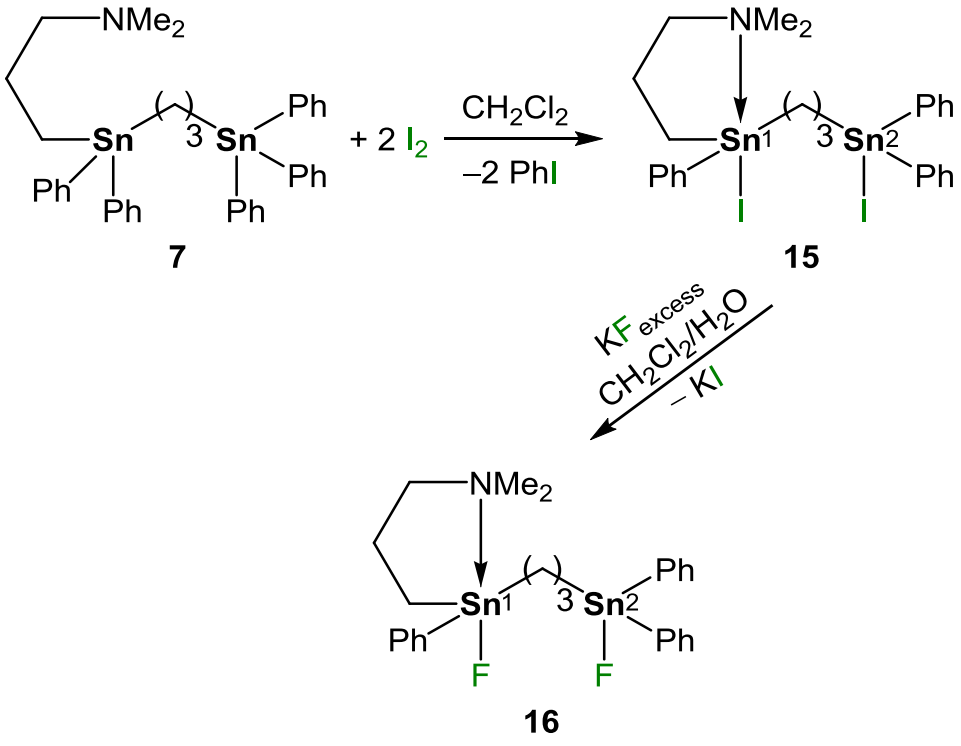
Similarly, a ^{119}Sn NMR spectrum in $CDCl_3$ of the crude product obtained from the reaction of **7** with two molar equivalents of bromine showed two signals at δ –77 and –105 (total integral 20) related to unreacted compound **7**. In addition, there were eight new signals at δ –5 (integral 1), –8 (integral 21), –15 (integral 6), –20 (integral 14), –37 (integral 8), –78 (integral 19), –114 (integral 4) and –146 (integral 4). Furthermore, in a ^{1}H NMR spectrum a broad signal between 9–10 ppm related to the $[Me_2NH]^+$ moiety was observed.

However, the reaction of compound **7** with two molar equivalents of elemental iodine gave a crude reaction mixture the ^{119}Sn NMR spectrum of which showed five resonances at δ –53 (integral 37), –58 (integral 16), –91 (integral 38), –104 (integral 3), and –169 (integral 6). In this reaction, the resulting PhI was removed in vacuo (5 x 10^{-3} m bar) and heat (45°C). Noteworthy, repeating the reaction but with removing PhI only under reduced pressure (5 x 10^{-3} m bar) without heating gave a crude reaction mixture the ^{119}Sn NMR spectrum of which showed resonances at δ –53 and –91. these are assigned to the iodine-substituted compound $\{Me_2N(CH_2)_3\}Ph(I)Sn(CH_2)_3Sn(I)Ph_2$, **15**. This experiment may prove that the set of the unsymmetrical organoditin halides **12** – **15** are sensitive to heat, that is in turn may explain the reason of decomposing these compounds as proved by NMR spectra.

The synthesis of compound **15** will be presented in the next chapter. The dimethylene- and tetramethylene-bridged organoditin compounds $\{Me_2N(CH_2)_3\}Ph_2Sn(CH_2)_nSnPh_3$ (**6**, n = 2; **8**, n = 4) were not used for further experiment. However, compound **6** was used for synthesizing $[\{Me_2NH(CH_2)_3\}Cl_2Sn(CH_2)_2SnPhCl_2{\cdot}Cl]$ that will be presented in Chapter 4.3.2.

2.1.5 Syntheses of the [3-(dimethylamino)propyl]-substituted organotin halides $\{Me_2N(CH_2)_3\}PhXSn(CH_2)_3SnPh_2X$ (15, X = I; 16, X = F).

The reaction of compound **7** with two molar equiv of elemental iodine provided a crude reaction mixture a ^{119}Sn NMR spectrum of which showed two resonances of equal integral at δ −91 ($\nu_{1/2}$ 41 Hz) and δ −54 ($\nu_{1/2}$ 96 Hz), respectively, that are assigned to the tin atoms Sn1 and Sn2 in the corresponding iodine-substituted compound $\{Me_2N(CH_2)_3\}Ph(I)Sn1(CH_2)_3Sn2(I)Ph_2$ (Scheme 6). The Sn1 atom is five-coordinate by intramolecular N→Sn interaction, as its ^{119}Sn chemical shift is close to the δ −102 measured for the pentacoordinated tin atom Sn1 in compound **10**. The Sn2 atom is four-coordinate, as its ^{119}Sn chemical shift is close to that reported for $(Ph_2ISnCH_2)_2$ (δ −54 ppm).[13] The compound $\{Me_2N(CH_2)_3\}Ph(I)Sn(CH_2)_3Sn(I)Ph_2$ was not isolated, but reacted with an excess of potassium fluoride, KF, in CH_2Cl_2/water, providing the triorganotin fluoride derivative $\{Me_2N(CH_2)_3\}Ph(F)Sn(CH_2)_3Sn(F)Ph_2$, **16**, as a white solid material in moderate yield (Scheme 6).



Scheme 6. Syntheses of the trimethylene-bridged ditin compounds **15** and **16**.

Compound **16** shows good solubility in $CHCl_3$, CH_2Cl_2 and moderate solubility in ethylacetate. Single crystals of **16** suitable for X-ray diffraction analysis were obtained by recrystallisation from its solution in ethylacetate at 4°C.

2.1.5.1 Molecular structure of compound 16

Compound **16** crystallize in the monoclinic space group *P*2(1)/c with four molecules per unit cell. The molecular structure of **16** is presented in Figure 8, selected interatomic distances and bond angles are listed in Table 3.

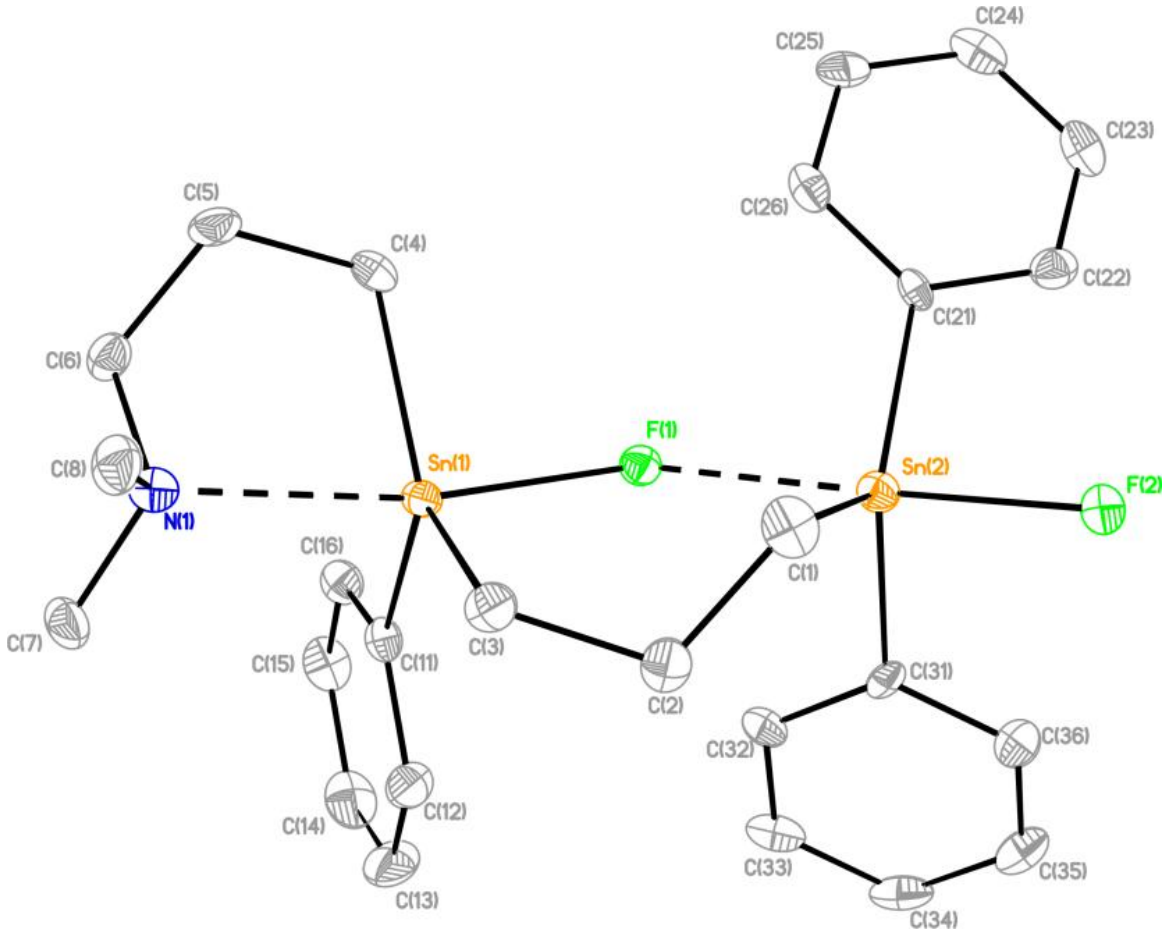


Figure 8. General view (SHELXTL) of a molecule of **16** showing 30% probability displacement ellipsoids and the crystallographic numbering scheme. Hydrogen atoms are omitted for clarity.

Table 3. Selected interatomic distances /Å and bond angles /° in **16**.

Sn(1)–N(1)	2.407(3)	F(1)–Sn(1)–N(1)	169.46(11)
Sn(1)–F(1)	2.1266(19)	C(11)–Sn(1)–N(1)	93.18(11)
Sn(2)–F(1)	2.240(2)	C(3)–Sn(1)–F(1)	94.26(12)
Sn(2)–F(2)	2.027(2)	C(4)–Sn(1)–F(1)	89.91(12)
Sn(1)–C(3)	2.113(4)	C(4)–Sn(1)–N(1)	79.59(14)
Sn(2)–C(1)	2.126(3)	Sn(1)–F(1)–Sn(2)	137.68(10)
Sn(1)–C(4)	2.126(4)	F(2)–Sn(2)–F(1)	177.27(9)
Sn(1)–C(11)	2.131(2)	F(2)–Sn(2)–C(1)	94.24(13)
Sn(2)–C(21)	2.137(2)	F(2)–Sn(2)–C(21)	91.90(10
Sn(2)–C(31)	2.159(2)	C(1)–Sn(2)–F(1)	84.05(13)

Compound **16** is a monomer in the solid state with F1→Sn2 intramolecular coordination giving a six membered ring of half chair conformation (Figure 9).[26] Both the Sn1 and Sn2 atoms are pentacoordinated and exhibit distorted trigonal bipyramidal geometries (geometric goodness ΔΣ(θ) = 85.1° for Sn1 and 79.4° for Sn2) with the equatorial positions being occupied by three carbon atoms [C(3), C(4), C(11) in Sn1 and C(1), C(21), C(31) in Sn2]. The axial positions are occupied by N(1) and F(1) atoms in Sn1 and by F(1) and F(2) atoms in Sn2.

The Sn(1)–N(1) interatomic distance of 2.407(3) Å is similar to 2.400(3) Å for the corresponding distance in [{$Me_2N(CH_2)_3$}PhFSn(CH_2)SnFPh_2], **11**, that are longer than the sum of the covalent radii of Sn and N (2.15 Å),[27] but is considerably less than the sum of the Van der Waals radii (3.75 Å).[20]

The distances F(1)–Sn(1), F(1)–Sn(2) and F(2)–Sn(2) of 2.1266(19) Å, 2.240(2) Å and 2.027(2) Å are close to 2.1229(17) Å , 2.2291(17) Å and 2.0300(18) Å for the corresponding distances in **11**, respectively. The N(1)–Sn(1)–(F1) (169.46(11)°) and F(1)–Sn(2)–F(2) (177.27(9)°) angles are rather close to the angles observed in **11** of 168.99(9)° and 176.91(8)°, respectively.

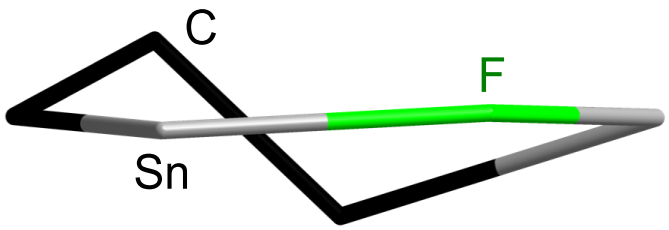


Figure 9. The molecular structure of compound **16**. All atoms bound to the six-membered ring are omitted for clarity.

2.1.5.2 Structure of compound 16 in solution

A ^{119}Sn NMR spectrum at room temperature of compound **16** in $CDCl_3$ reveals a doublet resonance at δ –48 ($^{1}J(^{119}Sn1–^{19}F1)$ = 1680 Hz, Sn1) and a doublet of doublet resonance at δ –191 ($^{1}J(^{119}Sn2–^{19}F2)$ = 2030, 960 Hz, Sn2) (Figure 10). In addition to these resonances with a total integral ratio of 98, one signal at δ –71 (integral 2) was observed, which, however, was not assigned.

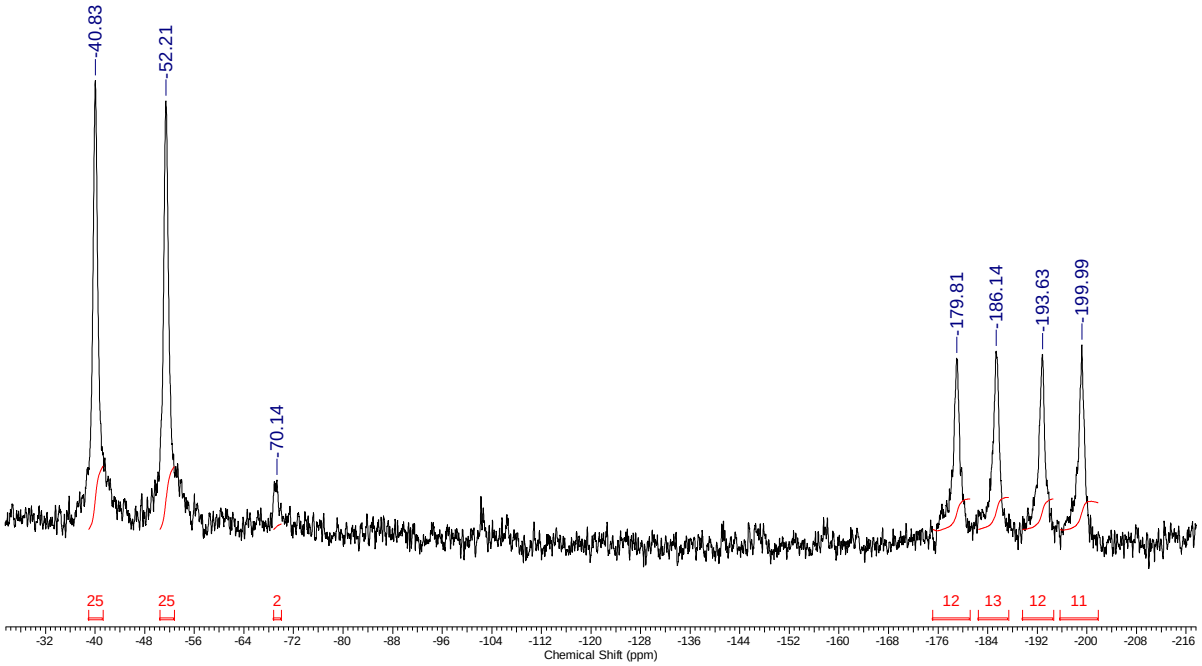


Figure 10. ^{119}Sn NMR spectrum of **16** in $CDCl_3$.

A ^{19}F NMR spectrum of **16** in $CDCl_3$ at room temperature showed two broad resonances of 1:1 integral ratio at δ –145 [$\nu_{1/2}$ 183 Hz, $^{1}J(^{19}F1–^{117/119}Sn1)$ = 1688, 927 Hz, F1] and δ –177 [$\nu_{1/2}$ 387 Hz, $^{1}J(^{19}F2–^{117/119}Sn2)$ = 2097 Hz, F2] (Figure 11).

These two chemical shifts are close to δ –140 [$^{1}J(^{119}Sn–^{19}Fb)$ = 1250 Hz] and δ –169 [$^{1}J(^{119}Sn–^{19}F)$ = 2042 Hz] reported for $[ClPh_2Sn(CH_2)_3SnPh_2F{\cdot}F]^-$[6] and to δ –139 [$^{1}J(^{119}Sn–^{19}Fb)$ = 1264 Hz], and –165 [$^{1}J(^{119}Sn–^{19}F)$ = 2030 Hz] reported for $[FPh_2Sn(CH_2)_3SnPh_2F{\cdot}F]^-$[6] (resulted from the reaction of $(ClPh_2SnCH_2)_2CH_2$ with two, respectively, three molar equivalents of fluoride ions).

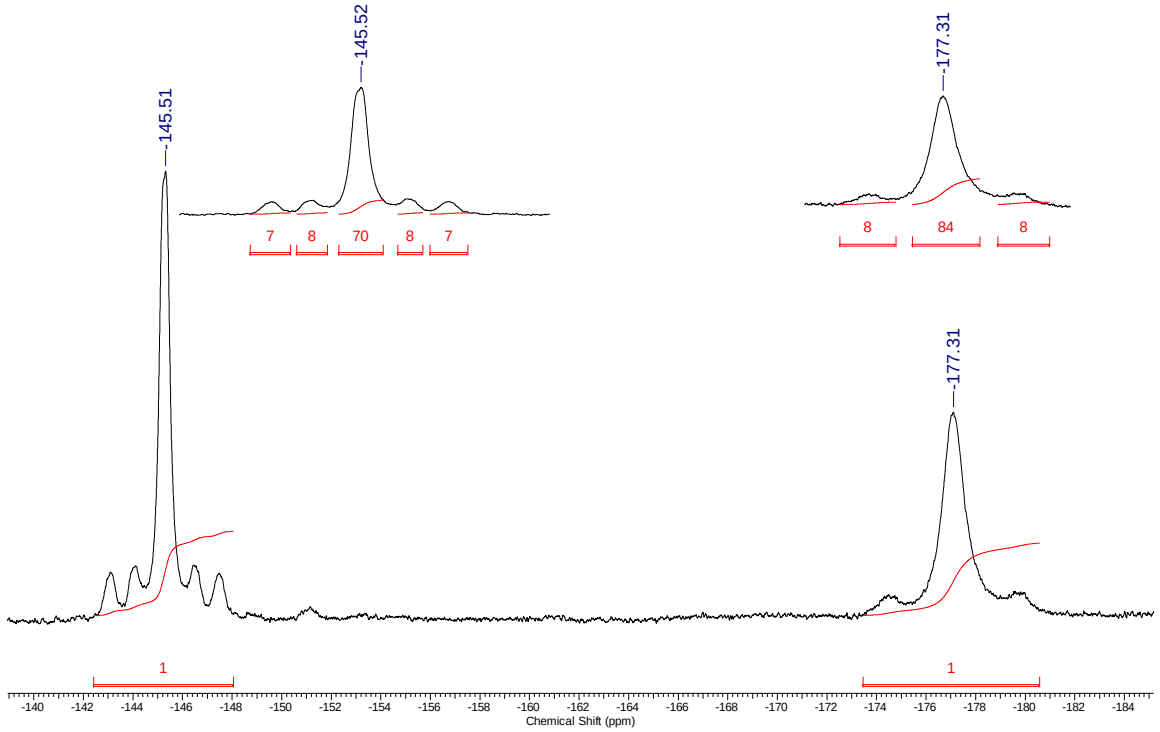


Figure 11. ^{19}F NMR spectrum of **16** in $CDCl_3$.

An ESI mass spectrum (positive mode) of the organotin fluoride **16** showed a mass cluster centered at *m*/*z* 632.2 that is assigned to $[M - 2F + 2OH + H]^+$. There is no mass cluster containing four tin atoms, which supports that compound **16** is monomeric in solution.

2.1.6 Complexation behavior of 11 and 16 towards fluoride anions

The reaction of compounds **11** and **16** with fluride anion (as $Et_4NF{\cdot}2H_2O$) in CD_2Cl_2 solution was examined.

A ^{119}Sn spectrum at –65°C showed a doublet resonance at δ –60 [$^1J(^{119}Sn1–^{19}F)$ = 1899 Hz] that is assigned to Sn1 and a triplet resonance at δ –252 [$^1J(^{119}Sn2–^{19}F)$ = 1907 Hz] for Sn2 (Figure 12). The latter signal is close to the triplet resonance at δ –244 [$^1J(^{119}Sn–^{19}F)$ = 1840 Hz] measured at –100°C for the anion $[F_2Ph_2Sn)_2CH_2]^{2-}$.[6]

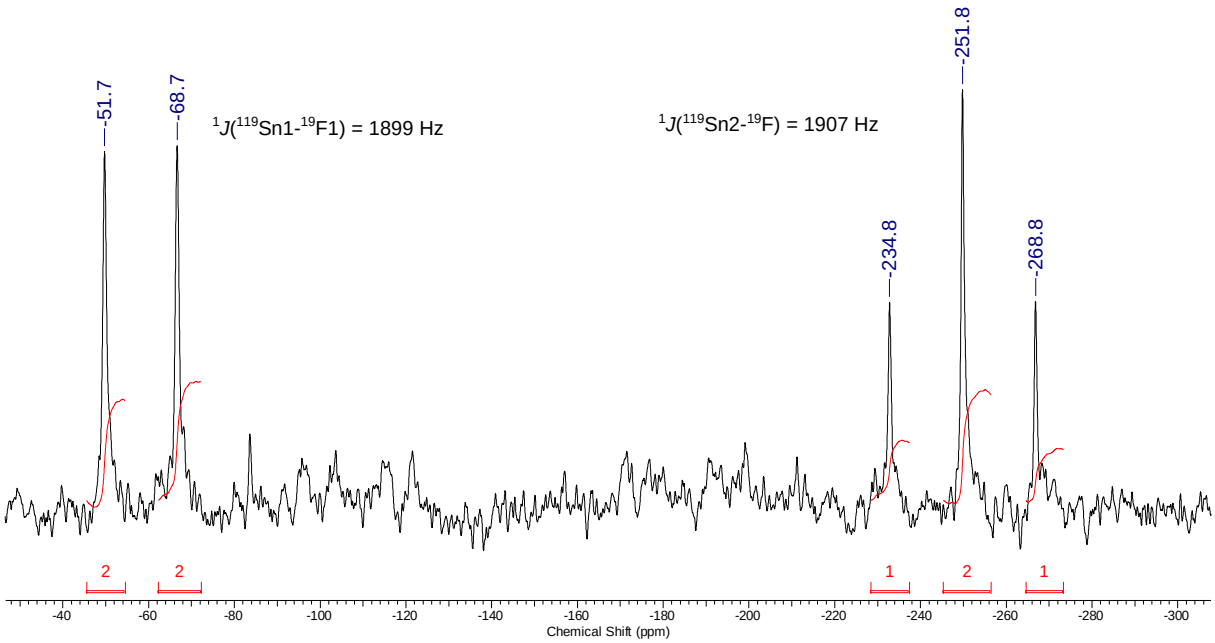


Figure 12. ^{119}Sn NMR spectrum of $[\mathbf{11}{\cdot}F]^-[Et_4N]^+$ at –65°C in CD_2Cl_2.

A ^{19}F NMR spectrum of the same sample at –60°C showed two resonances of 2:1 integral ratio at δ –140 [$^1J(^{19}F–^{117/119}Sn2)$ = 1833/1895 Hz] assigned to F2 and δ –141 [$^1J(^{19}F–^{117/119}Sn1)$ = 1854 Hz] assigned to F1 (Figure 13). These chemical shifts are close to δ –142 [$^1J(^{19}F–^{119}Sn1)$ = 1840 Hz] reported of $[F_2Ph_2Sn)_2CH_2]^{2-}$ at –100°C.[6]

In addition to these two resonances with total integral ratio 45, four uncertain signals were observed at δ –93 (integral 12), –163 (integral 16), –167 (integral 19) and –181 (integral 8). With caution, these signals might originate from products formed by hydrolysis reactions. The latter are facilitated by the presence in compound **11** of the dimethylaminopropyl moiety acting as a base.

This view gets support from an ESI-mass spectrum (negative mode) revealing a major mass cluster centered at *m/z* 719.1 that fits with [**11** + OH + MeCN + 3H$_2$O]$^-$.

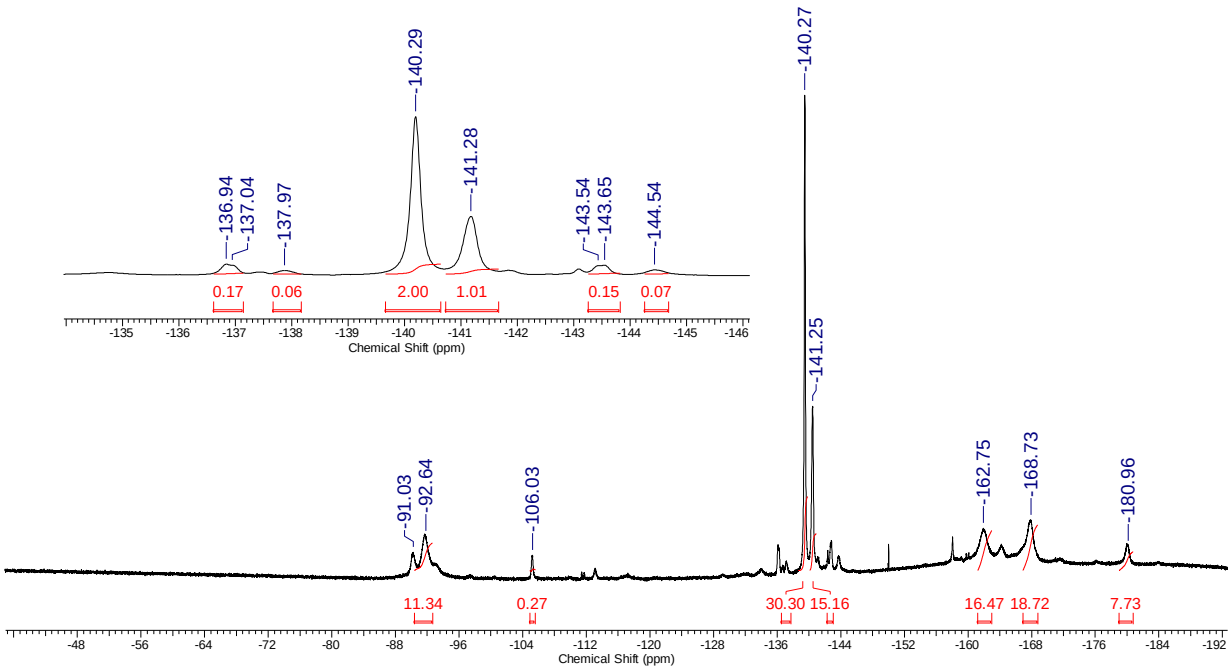


Figure 13. $^{19}F\{^1H\}$ NMR spectrum in CD_2Cl_2 at T = –65°C of compound **11** to which had been added one molar equiv $NEt_4F{\cdot}2H_2O$. The resonances in the cutout section refer to $[NEt_4][\mathbf{11}{\cdot}F]$.

A ^{l19}Sn NMR spectrum at −80 °C of a solution of compound **16** to which had been added 1 molar equiv of $NEt_4F{\cdot}2H_2O$ showed a doublet resonance at δ −47 (d, $^1J(^{119}Sn–^{19}F)$ = 1566 Hz, integral 30, SnFPh, **16**) and a doublet of doublet resonance at δ −203 ($^1J(^{119}Sn–^{19}F)$ = 2067, 941 Hz, integral 32, $SnFPh_2$, **16**). In addition, there are minor intense resonances at δ −86 (d, $^1J(^{119}Sn–^{19}F)$ = 1957 Hz, integral 12, Sn1, $NEt_4[\mathbf{16}{\cdot}F]$), δ −88 (d, $^1J(^{119}Sn–^{19}F)$ = 1973 Hz), integral 13, not assigned), δ −203 (dd, $^1J(^{119}Sn–^{19}F)$ = 2067, 941 Hz, integral 32, $SnFPh_2$, **16**), δ −222 (3%), δ −226 (integral 4, not assigned), δ −235 (integral 2, not assigned), and δ −270 (Sn2, $NEt_4[\mathbf{16}{\cdot}F]$).

A ^{19}F NMR spectrum at −80 °C of the same sample showed two doublet resonances at δ −143 ($^1J(^{19}F–^{117/119}Sn)$ = 1124, 1498/ 1564 Hz), $^2J(^{19}F–^{19}F)$ = 83 Hz, integral 31, SnFPh, **16**) and δ −174 ($^1J(^{19}F–^{117/119}Sn)$ = 1976/2070 Hz), $^2J(^{19}F–^{19}F)$ = 83 Hz, integral 29, $SnFPh_2$, **16**). In addition there are minor intense resonances at δ −154 (integral 14, F2, $NEt_4[\mathbf{16}{\cdot}F]$), δ −158

(integral 7, F1, NEt_4[**16**·F]), δ −159 (integral 8, not assigned), δ −162 (integral 2, not assigned), and δ −169 (integral 9, not assigned).

A ^{119}Sn NMR spectrum at −80 °C of a solution of compound **16** to which had been added 2 molar equivalent of $NEt_4F{\cdot}2H_2O$ showed a doublet resonance at δ −86 ($^1J(^{119}Sn{-}^{19}F)$ = 1957 Hz, integral 40, Sn1, NEt_4[**16**·F]) and a triplet at δ −271 ($^1J(^{119}Sn{-}^{19}F)$ = 1888 Hz, integral 40, Sn2, NEt_4[**16**·F]). In addition there are minor intense resonances at δ −47 (d, $^1J(^{119}Sn{-}^{19}F)$ = 1563 Hz, integral 5, SnFPh, **16**), δ −88 (d, $^1J(^{119}Sn{-}^{19}F)$ = 1973 Hz, integral 7, not assigned), and δ −203 (dd, $^1J(^{119}Sn{-}^{19}F)$ = 2067, 941 Hz, integral 7, $SnFPh_2$, **16**) (Figure 14).

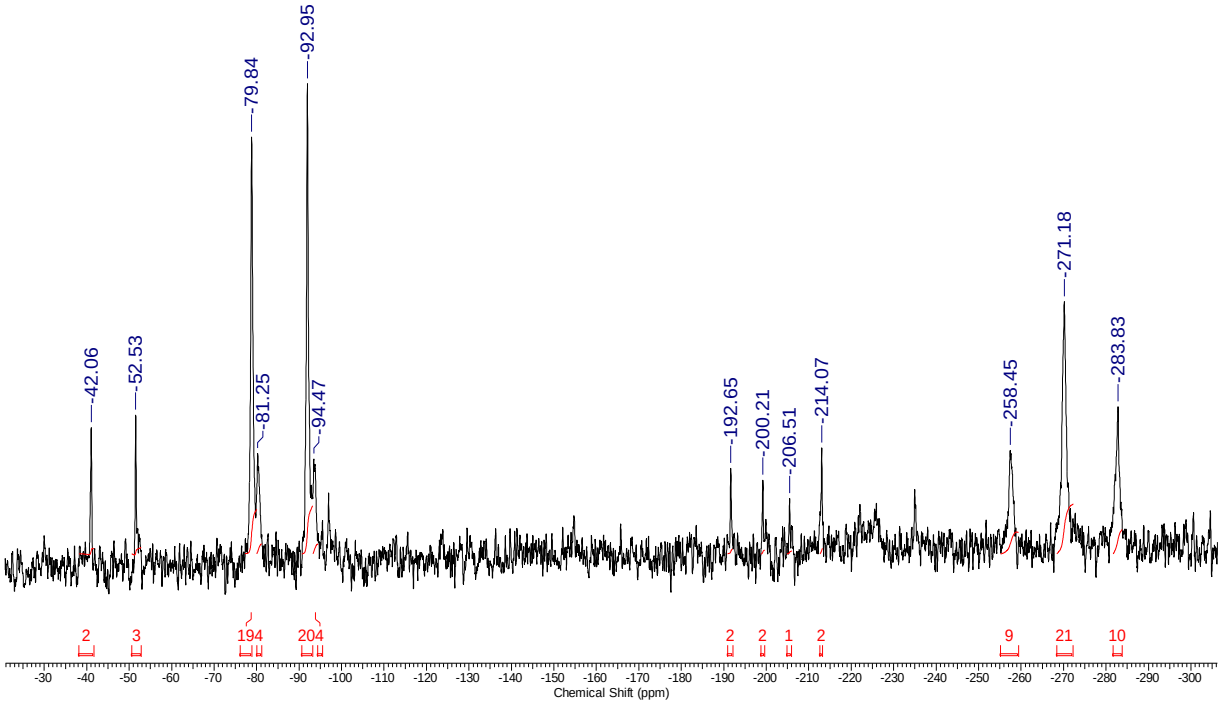


Figure 14. ^{119}Sn NMR spectrum (in CD_2Cl_2) at T = –80°C of compound **16** to which had been added two molar equivalents $NEt_4F{\cdot}2H_2O$.

A ^{19}F NMR spectrum at −80 °C of the same sample showed two resonances with a 2:1 ratio (total integral 69) at δ −154 (integral 46, F2, NEt_4[**16**·F]) and δ −158 (integral 23, F1, [NEt_4][**16**·F]). In addition there are minor intense resonances at δ −143 (d, integral 5, SnFPh, 7), δ −151 (integral 5, not assigned), δ −156 (integral 6, not assigned), δ −160 (integral 6, not assigned), δ −169 (integral 5, not assigned), and δ −174 (d, integral 5, $SnFPh_2$, **16**) (Figure 15). No resonances were observed in the ^{119}Sn NMR spectra at ambient temperature.

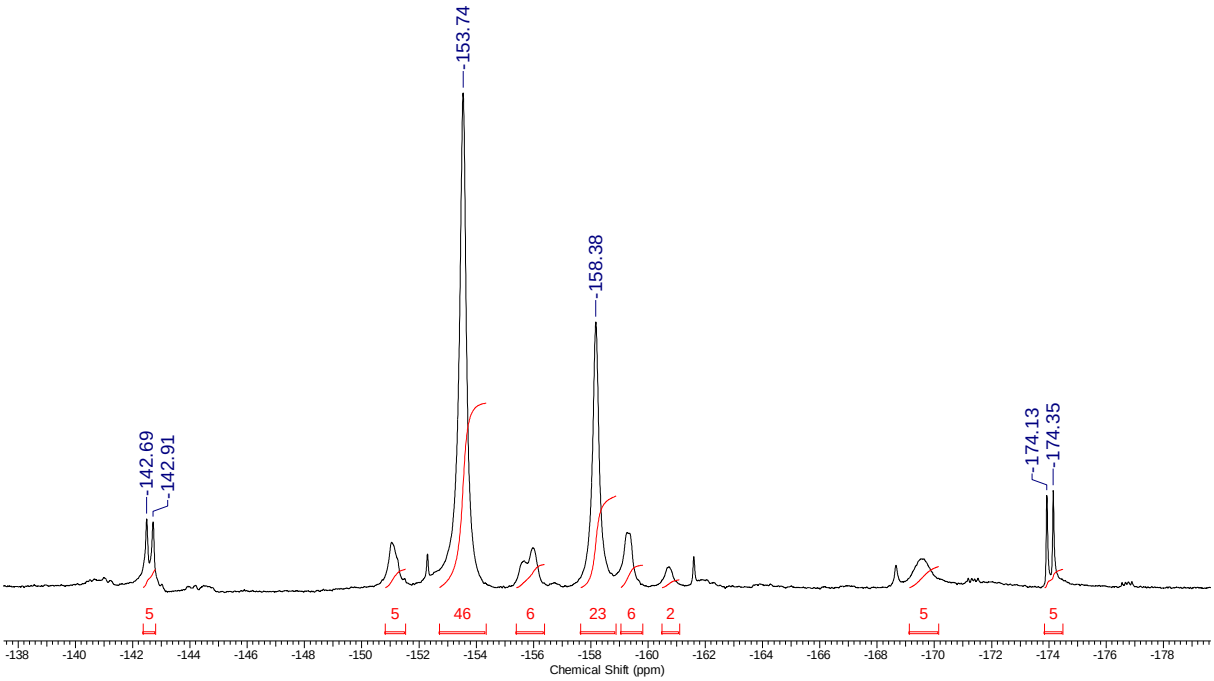
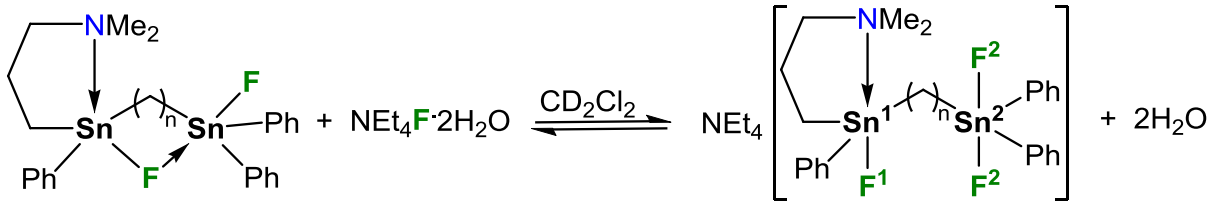


Figure 15. ^{19}F NMR spectrum (CD_2Cl_2) at T = –80°C of compound **16** to which had been added two molar equivalents $NEt_4F{\cdot}2H_2O$.

The ^{119}Sn and ^{19}F NMR data are consistent with the equilibrium shown in Scheme 7. It is fast on the ^{19}F and ^{119}Sn NMR time scales at room temperature but slow at low temperature. For the methylene-bridged compound **11** (n = 1) this equilibrium is on the side of the organostannate complex NEt_4[**11**·F] by addition of 1 molar equivalent of fluoride anion only, while 2 molar equivalent of fluoride anion is needed to cause formation of NEt_4[**16**·F]. The results indicate the six-membered ring involving the intramolecular Sn−F→Sn coordination in **16** to be more stable against fluoride anion attack than the four-membered ring in **11**.



NEt_4[**11**·F], n = 1; NEt_4[**16**·F], n = 3

Scheme 7. Reactions of $\{Me_2N(CH_2)_3\}Ph(F)Sn(CH_2)_nSn(F)Ph_2$ (**11**, n =1; **16**, n = 3) with $NEt_4F{\cdot}2H_2O$.

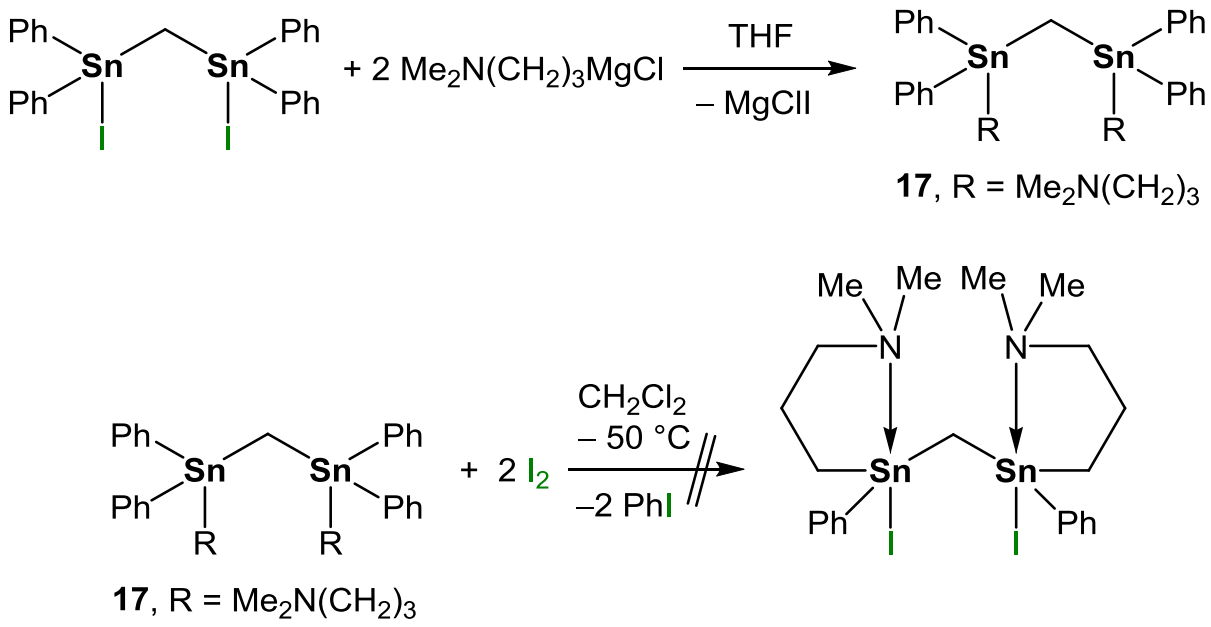
Applying compound **11** as an ionophore for fluoride selective electrode represents a further aim in this field that will be discussed in Chapter 2.3.3.

2.1.7 Synthesis of bis[(dimethylaminopropyl)diphenylstannyl]methane, $[\{Me_2N(CH_2)_3\}Ph_2Sn]_2CH_2$, 17

The reaction of bis(diphenyliodidostannyl)methane, $(Ph_2ISn)_2CH_2$,[12] with two molar equivalents of $Me_2N(CH_2)_3MgCl$ provided the corresponding $Me_2N(CH_2)_3$-substituted organotin compound $[\{Me_2N(CH_2)_3\}Ph_2Sn]_2CH_2$, **17**, in quantitative yield, (Scheme 8). Compound **17** is obtained as light yellowish oil and shows good solubility in common organic solvents such as THF, $CHCl_3$, and CH_2Cl_2.

The tin atoms in **17** are equivalent.They are tetracoordinated as it is evidenced by their ^{119}Sn NMR chemical shift at δ –48, measured in $CDCl_3$, that is similar to δ –49 measured for the corresponding tin atom Sn1 in $[\{Me_2N(CH_2)_3\}Ph_2Sn^1CH_2SnPh_3]$, **5**.

Attempts to synthesize the corresponding iodine-substituted organotin compound $[\{Me_2N(CH_2)_3\}PhISn]_2CH_2$ by the reaction of **17** with two molar equivalents of elemental iodine failed, (Scheme 8).



Scheme 8. Synthesis of the tetraorganoditin compound **17**.

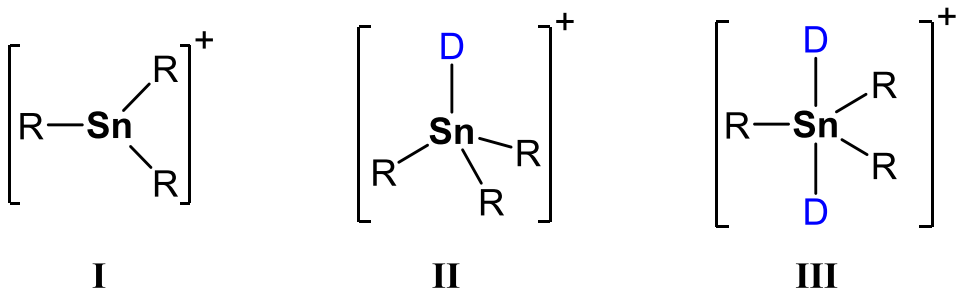
The crude reaction mixture showed poor solubility in $CDCl_3$ and C_6D_6. a ^{119}Sn NMR spectrum of which measured in acetone-d_6 showed seven resonances located at δ –83 (8%), –103 (21%), –110 (29%), –123 (16%), –134 (12%), –157 (5%) and –199 (9%). The chemical shift at δ –103 is close to that measured for Sn1 in $\{Me_2N(CH_2)_3\}PhISn^1CH_2Sn^2Ph_2I$, **10**, at δ –102, and could be assigned with caution to the iodine-substituted organotin compound $[\{Me_2N(CH_2)_3\}PhISn]_2CH_2$.

One possibility to explain this result may be, with caution, that the desired compound $[\{Me_2N(CH_2)_3\}PhISn]_2CH_2$ was not stable under the conditions of removing PhI (heat 56°C and pressure of 5 x 10^{-3} m bar) and suffered decomposing. This is similar to the behavior of the unsymmetrical organoditin halides $RPhXSn(CH_2)_nSnPh_2X$ (R = $Me_2N(CH_2)_3$, n = 2, 3, 4; X = I, Br) **12** – **15** those were unstable towards heating under reduced pressure (5 X 10^{-3} m bar).

The compound $[\{Me_2N(CH_2)_3\}PhISn]_2CH_2$ could not be isolated from the crude mixture.

2.1.8 Synthesis of the [3-(dimethylamino)propyl]-substituted organoditin cation

Organotin (IV) cations are of great interest as they play an important role in catalytic applications.[28] [29] [30] [31] One possibility to stabilize organotin cations is by the use of organotin compounds containing chelating ligands. The most common type of organotin cations are the pentacoordinate triorganotin cations that are usually stabilized by two N→Sn or O→Sn intramolecular interactions (Chart 4, **III**). The compound $[L(n\text{-}Bu)_2Sn]^+[Ti_2Cl_9]^-$, where L = (2-(N,N-dimethylaminomethyl)phenyl),[32] is the first example of a four coordinate triorganotin (IV) ionic compound, type **II** in Chart 4.



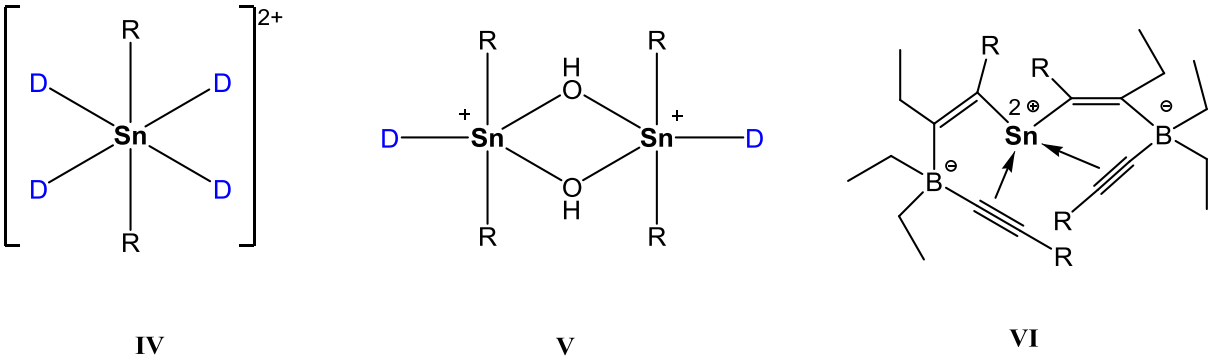
I **II** **III**

R = organic substituent; D = donor substituent

Chart 4. Three types of triorganotin cations.

However, the enhanced Lewis acidity at the tin atoms in mono- and diorganotin cations in comparison with triorganotin cations, which in turn results in improvment in the expected catalytic activity, causes a great interest to prepare mono- and diorganotin cations.

There are many examples of monomeric diorganotin cations in which the tin atoms are stabilized by four donor ligands[33] [34] [35] (Chart 5, **IV**). Dimeric diorganotin cations having the $Sn(OH)_2Sn$ four-membered ring usually contain coordinated molecules of water as a consequence of hydrolysis[36] (Chart 5, **V**). One example of monomeric non-solvated diorganotin cations is presented in Chart 5 (**VI**), where the tin atom is intramolecularly stabilized by π-coordination of two alkyne moieties.[37]



IV **V** **VI**

R = organic substituent; **D** = donor substituent

Chart 5. Diorganotin dications.

In our research group we have reported the first examples of crown ether intramolecularly encapsulating mono- and diorganotin dications. Compounds $[HOSnCH_2([16]crown\text{-}5)]^{2+}(Y)_2$ (Y = ClO_4; CF_3SO_3)[38] are the first examples of a monomeric monoorganotin(IV) dication, whereas $[PhSnCH_2([16]crown\text{-}5)]^{2+}(ClO_4)_2$[38] is an example for a diorganotin(IV) dication (Chart 6).

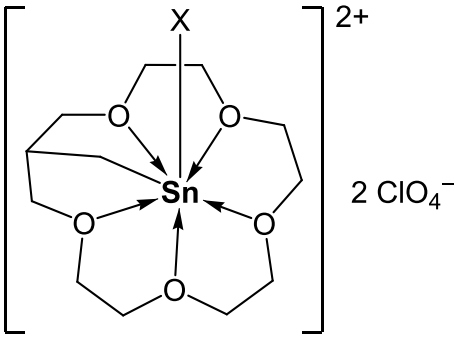
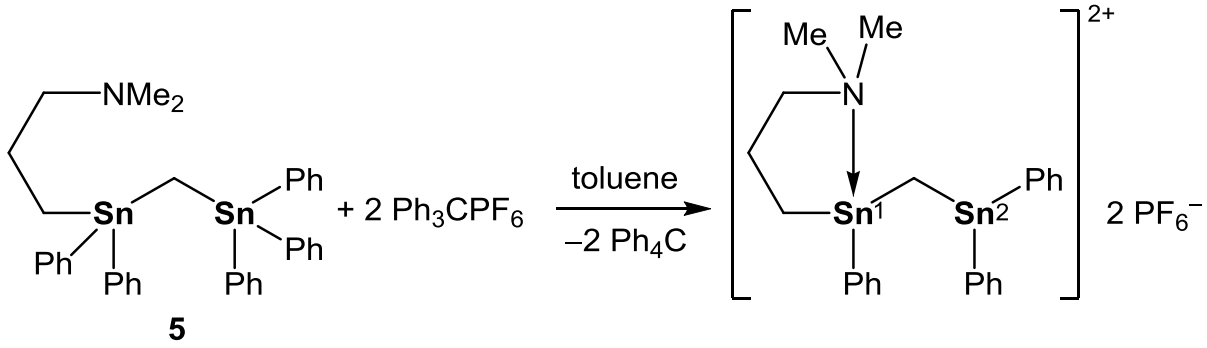


Chart 6. Crown ether substituted-mono- and diorganotin dications (X = OH, Ph).

Preparing organotin cations based on our compound {[$Me_2N(CH_2)_3$]$Ph_2Sn(CH_2)SnPh_3$}, **5**, is of great interest as the two tin atoms in this compound are not equivalent.

However, the reaction of **5** with one molar equivalent of $Ph_3C^+PF_6^-$ in toluene gave a white precipitate that was filtered and washed twice with dry CH_2Cl_2. A ^1H NMR spectrum of this compound in CD_3CN showed that the integration of the phenyl groups corresponds with 15H, in contrast to 25H found in **5**. This result enhances the possibility of the reaction of **5** with $Ph_3C^+PF_6^-$ in a ratio of 1:2 resulted in forming two molar of Ph_4C (Scheme 9).

The elemental analysis of the resulting precipitate agrees with the ratio 1:2 with two phenyl groups are less. Also the ESI MS spectrum corresponds with this result as a mass cluster in the positive mode centered at *m/z* 586.1 related to $C_{24}H_{30}NOSn_2^+$ was observed. The formula of $C_{24}H_{30}NOSn_2^+$ could be assigned with caution to $[R(OH)SnCH_2SnPh_3]^+$ or $[RPhSnCH_2Sn(OH)Ph_2]^+$ (R = $Me_2N(CH_2)_3$).

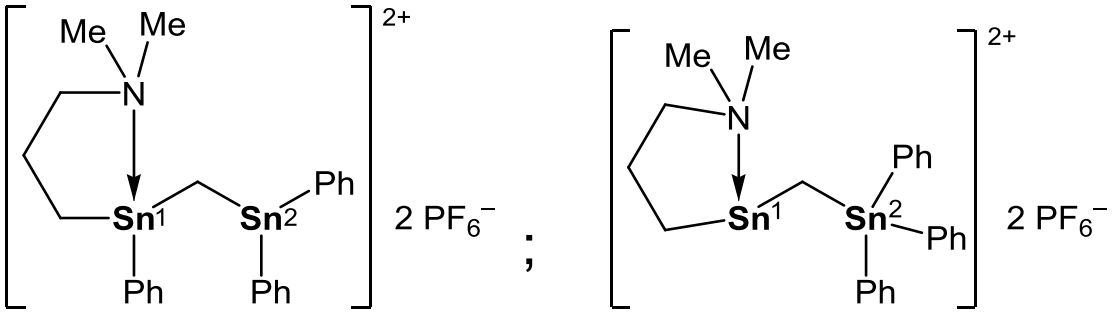


Scheme 9. The reaction of compound **5** with Ph_3CPF_6.

Depending on the data mentioned above and the reported examples of different types of organotin cations, there are two possible structures of this cationic organotin compound. (i) The compound is an organoditin dication with the first tin atom Sn1 bound to the $Me_2N(CH_2)_3$ substituent, is four coordinate triorganotin cation with N→Sn intramolecular coordination (Chart 4, type **II**). The second tin atom Sn2 is a tricoordinate stannylium cation (Chart 4, type **I**), containing two phenyl groups (Chart 7, **VII**). (ii) The Sn1 in this compound is a diorganotin dication with N→Sn intramolecular coordination, whereas the second tin atom Sn2 is tetraorganotin containing three phenyl groups (Chart 7, **VIII**).

The latter alternative is weak, because relating to the known examples for diorganotin dications these type of cations are stabilized usually by more than one coordinating ligands.

In the suggested structure **VIII** (Chart 7) there is only one N→Sn coordination and the possibility of having more coordinating molecules such as water or solvents is inconsistent with the elemental analysis.



VII **VIII**

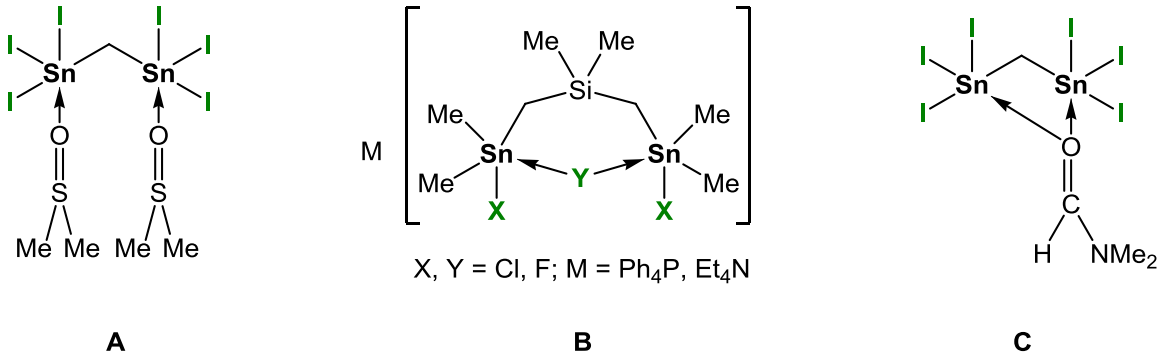
Chart 7. Suggested structures of the organotin dication obtained.

2.2 Spacer-bridged Ditin Compounds. Syntheses, Structures and Reactivity

2.2.1 Introduction

Spacer-bridged ditin compounds are of great interest as they show good affinity towards different anions. Oligo alkylene-bridged organoditin compounds, in which the two tin atoms are separated by $–(CH_2)_n–$ (n = 1,2,3,4,8), show good affinity towards Lewis bases and neutral donor molecules.[39][6][40][41] Interestingly, the tin atoms in these compounds can exhibit different modes of coordination not only as bicentric but also as monocentric or polycentric.

For example, α,ω-bis(trichlorostannyl)alkanes act towards halide anions as bis(monodentate) Lewis acids without any evidence for the ditin acting as a chelate (type **A**, Figure 16).[41] Differently, bis(triiodostannyl)methane chelates DMF giving the corresponding adduct even when reacted with two equivalents of DMF (**C**, Figure 16). However, it reacts with one or two molar equivalents DMSO giving only the adduct $(I_3Sn)_2CH_2 \cdot 2DMSO$ (**A**, Figure 16).[42]



A **B** **C**

Figure 16. Different coordination types of spacer-bridged organoditin compounds.

Similarly to oligo alkylene-bridged organoditin compounds, silicon-containing spacers are of great interest for the synthesis of bi- and multicentric organotin Lewis acids.

Recently, our research group reported the syntheses of bis(trimethylstannylmethyl)dimethylsilane, $(Me_3SnCH_2)_2Si(CH_3)_2$, and derivatives.[3] These compounds proved to be able to form fluoride and chloride complexes in which the two tin centers act as bicentric Lewis acid (**B**, Figure 16).

In continuation to this study, here will be presented the syntheses of organoditin compounds separated by one silicon and two carbon atoms of the type $(Ph_3SnCH_2)_2SiMe_2$ and its halogen-derivatives. Also will be presented is the ability of these halogen-substituted compounds to chelate halide anions.

2.2.2 Syntheses of the tetraorganoditin compound $(Ph_3SnCH_2)_2SiMe_2$, 18, and its mono- di and triorganotin halides derivatives

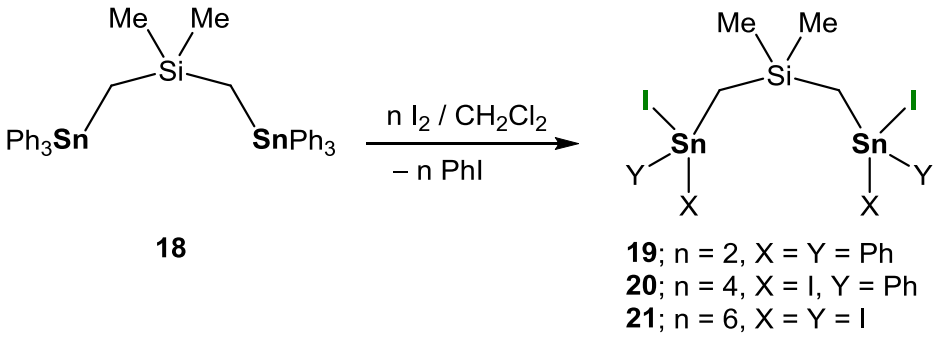
The reaction of two molar equivalents sodium triphenylstannide, Ph_3SnNa, with bis(chloromethyl)dimethylsilane, $Me_2Si(CH_2Cl)_2$, in THF gave the tetraorganotin compound $(Ph_3SnCH_2)_2SiMe_2$, **18**, as slightly yellowish oil in very good yield (eq. 1).

$$2Ph_3SnNa + Me_2Si(CH_2Cl)_2 \xrightarrow[-\ 2\ NaCl]{THF,\ -78\ °C} \underset{\mathbf{18}}{(Ph_3SnCH_2)_2SiMe_2} \qquad (1)$$

Compound **18** was synthesized previously in our research group by the reaction of $Me_2Si(CH_2MgCl)_2$ with Ph_3SnCl,[43][44] However, it was not completely characterized and the complexation of its halogen-derivatives with halide anions was not studied.

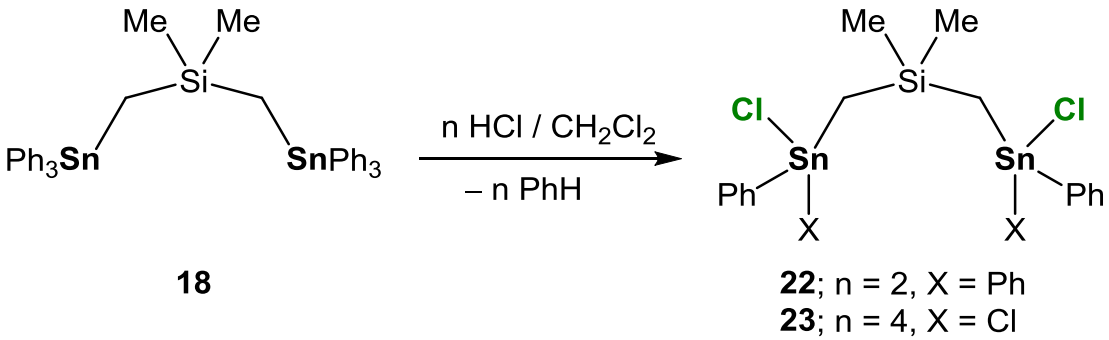
Treatment of compound **18** with two, four and six equivalents elemental iodine afforded the corresponding iodine-substituted compounds $(IPh_2SnCH_2)_2SiMe_2$, **19**, $(I_2PhSnCH_2)_2SiMe_2$, **20**, and $(I_3SnCH_2)_2SiMe_2$, **21**, respectively, in quantitative yields, (Scheme 10).

Compounds **19** and **20** were obtained as colorless and yellowish oils, respectively, whereas compound **21** was obtained as dark green oil. Compounds **18** – **21** show good solubility in $CHCl_3$, and CH_2Cl_2.



Scheme 10. Syntheses of the organotin iodides **18** – **21**.

Similarly, the reaction of compound **18** with two, respectively, four equivalents HCl afforded the corresponding chlorine-substituted compounds $(ClPh_2SnCH_2)_2SiMe_2$, **22**, and $(Cl_2PhSnCH_2)_2SiMe_2$, **23**, as yellowish oils in quantitative yields, (Scheme 11).



Scheme 11. Syntheses of the organotin chlorides **22** and **23**.

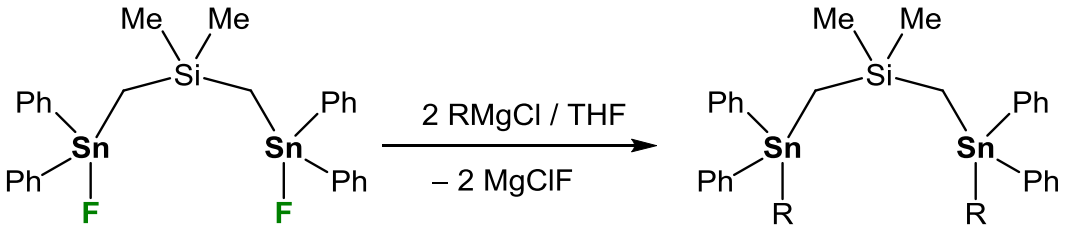
Compounds **22** and **23** show good solubility in common organic solvents such as $CHCl_3$, CH_2Cl_2 and acetone.

The reaction of compound **19** with excess of KF gave the corresponding fluorine-substituted derivative $(FPh_2SnCH_2)_2SiMe_2$, **24**, as amorphous solid material (eq. 2). Compound **24** is poorly soluble in common organic solvents. Compounds **19** and **24** were synthesized before in our research group, However, they were not completely characterized.[43][44]

$$(IPh_2SnCH_2)_2SiMe_2 \xrightarrow[-KI]{KF/\ water,\ CH_2Cl_2} (FPh_2SnCH_2)_2SiMe_2 \qquad \text{(eq. 2)}$$

19 **24**

The reaction of two molar equivalents of the Grignard reagent $Me_2N(CH_2)_3MgCl$ with compound **24** afforded the corresponded compound $[Me_2N(CH_2)_3Ph_2SnCH_2]_2SiMe_2$, **25**, in good yield as yellowish oil, (Scheme 12). Compound **25** shows good solubility in common organic solvents such as $CHCl_3$, CH_2Cl_2, and THF.



24 **25**; R = $Me_2N(CH_2)_3$

Scheme 12. Syntheses of the organotin compound **25**.

Structures in solution

Both tin atoms in each of the organotin compounds **18** – **23** are equivalent on the ^{1}H, ^{13}C, and ^{119}Sn NMR time scales. This was proved by their NMR spectra that showed single ^{1}H and ^{13}C NMR resonances for the $SnCH_2Si$ moiety as well as one singlet ^{119}Sn NMR resonance. In addition to that, the tin atoms in these compounds are tetracoordinated as evidence by their ^{119}Sn NMR chemical. That is for compound **21** at –750 ppm which is in the range between –622 and –835 ppm reported for the tetracoordinated organotin compounds $(I_3Sn)_2(CH_2)_3$ and $(I_3Sn)_2CH_2$, respectively.[42]

The chemical shifts of the organotin compounds **18**, **19**, **20** and **22** at δ –90, δ –65, δ –219 and δ 26 (Table 4) are comparable with those reported for $(Ph_3Sn)_2CH_2$,[12] $(Ph_2ISn)_2CH_2$,[12] $(PhI_2Sn)_2(CH_2)_2$,[13] $(Ph_2ClSn)_2CH_2$,[12] at δ –79, δ –68, δ –169, δ 20, respectively.

A ^{119}Sn NMR spectrum of compound **25** in $CDCl_3$ showed a single resonance at δ –60. This chemical shift is close to that found for the analogous tin atom Sn^1 in $Me_2N(CH_2)_3Ph_2Sn^1CH_2SnPh_3$ at δ –49. The ^{13}C NMR chemical shift of the $SnCH_2C$ moiety at δ 9.1 ($^{1}J(^{13}C–^{117/119}Sn)$ = 363/380 Hz) is close to that found for the corresponding carbon atom in $Me_2N(CH_2)_3Ph_2Sn^1CH_2SnPh_3$ at δ 9.0 ($^{1}J(^{13}C–^{117/119}Sn)$ = 373/391 Hz).

Table 4. Selected NMR data of compounds **18** – **23** measured in $CDCl_3$ solutions.

	$SnCH_2Si$		δ ^{29}Si	δ ^{119}Sn
	δ ^{13}C	δ ^{1}H		
	$^{1}J(^{13}C–^{117/119}Sn)$ Hz	$^{2}J(^{1}H–^{117/119}Sn)$ Hz		
$(Ph_3SnCH_2)_2SiMe_2$ (**18**)	–3.2 (265/277)	0.54 (75.2/77.6)	6.2	–90
$(Me_3SnCH_2)_2SiMe_2$[3]	–2.3 (239/249)	–0.25 (71)	4.9	5
$(IPh_2SnCH_2)_2SiMe_2$ (**19**)	3.5 (253/267)	1.03 (78.0/81.1)	6.7	–65
$(I_2PhSnCH_2)_2SiMe_2$ (**20**)	12.6 (260/271)	1.55 (86.8/90.6)	6.8	–219
$(I_3SnCH_2)_2SiMe_2$ (**21**)	19.8 (283/296)	2.27 (103.2/107.7)	8.3	–750
$(ClPh_2SnCH_2)_2SiMe_2$ (**22**)	3.1 (314/318)	0.79 (77.2/80.5)	6.1	26
$(ClMe_2SnCH_2)_2SiMe_2$[3]	5.4 (260/272)	0.39	4.2	163
$(Cl_2PhSnCH_2)_2SiMe_2$ (**23**)	10.4 (350/367)	1.22 (89.5/92.2)	5.9	52

The ^{1}H NMR spectra of the organotin compounds **19** – **23** showed that the chemical shifts of the methylene protons are lower field shifted, in comparison with that for the parent compound **18** (δ 0.54), and increases in the sequence **22**, **19**, **23**, **20**, **21**. The $^{2}J(^{1}H–^{117/119}Sn)$ coupling constant for the methylene protons increases as the Lewis acidity of the tin atom increases and the largest value was observed for the organotin triiodide **21** (103.2/107.7 Hz).

In the ^{13}C NMR spectra of compounds **19** – **23** low-field shifts of the methylene carbon chemical shifts, in comparison with that of **18**, were observed. These increase with the sequence **19**, **22**, **23**, **24** and **21**. The largest value of the $^{1}J(^{13}C–^{117/119}Sn)$ coupling constant for the methylene carbon was observed for the diorganotin dichloride **23** (350/367 Hz). The $^{1}J(^{13}C–^{117/119}Sn)$ coupling constant for $(ClPh_2SnCH_2)_2SiMe_2$, **22**, (314/318 Hz) is bigger than that reported for the analogous compound $(ClMe_2SnCH_2)_2SiMe_2$ (260/272 Hz).[3]

The electrospray ionization mass spectra (ESI MS, positive mode) of the triorganotin halides **19** and **22** showed a mass cluster centered at *m*/*z* 649.0 that fits exactly with $[(Ph_2SnCH_2)_2SiMe_2{\cdot}OH]^+$. In the negative mode of compound **22** two mass clusters centered

at *m*/*z* 640.9 and 736.9 related respectively to [**22** – Cl – Ph + 3OH]$^-$ and [**22** + OH + H_2O]$^-$ were observed. The ESI MS spectrum of compound **6** (positive mode) showed a mass cluster centered at *m*/*z* 564.9 that fits exactly with [**23** – 2Cl + OH]$^+$. In the negative mode a major mass cluster centered at *m*/*z* 654.7 [**23** + OH + H_2O]$^-$ and a mass cluster centered at *m*/*z* 598.8 [**23** – 2Cl + 3OH]$^-$ were observed.

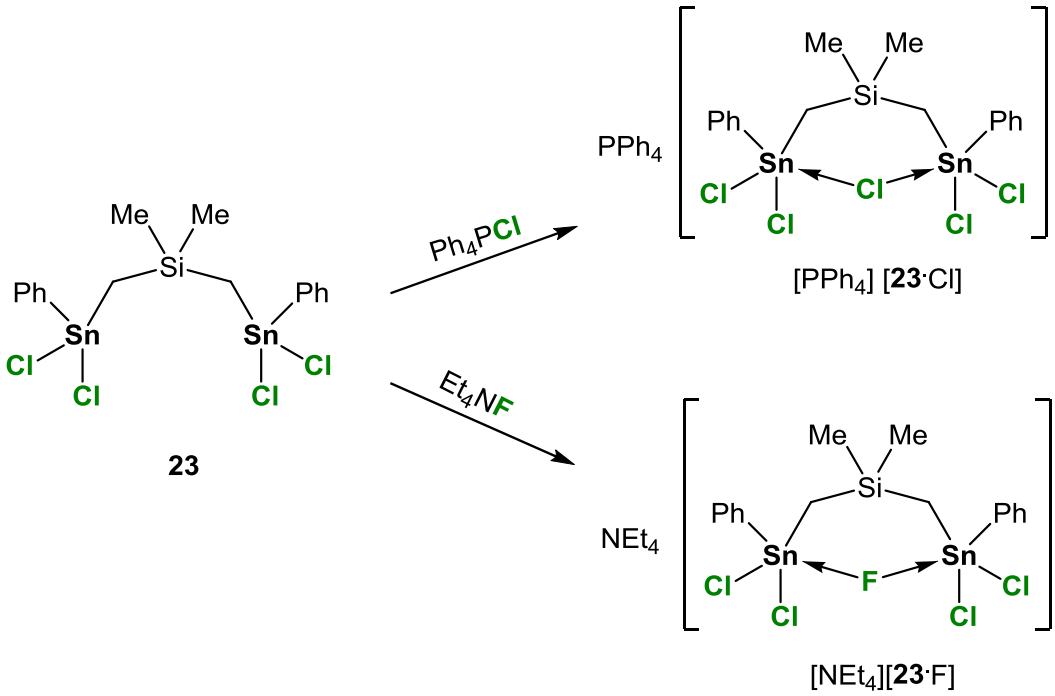
2.2.3 Complexation behavior of compounds 23 and 24 towards fluoride and chloride anions

The complexation behavior of compounds **23** and **24** have been studied in solution by ^{119}Sn, ^{19}F, ^{13}C, ^{1}H NMR spectroscopy and electrospray ionization mass spectrometry.

A ^{119}Sn NMR spectrum at ambient temperature of a solution of compound **23** in $CDCl_3$ to which had been added one molar equivalent of tetraphenylphosphonium chloride, Ph_4PCl, showed one resonance at δ –119. This chemical shift is 171 ppm low-frequency shifted with respect to **23** (δ 52). This is consistent with the formation of the 1:1 complex [PPh_4][**23**·Cl] with the chloride anion chelated by two tin atoms forming a six-membered ring, (Scheme 13).

The complexation of the chloride anion is supported by the ^{1}H and ^{13}C NMR spectra. In a ^{1}H NMR spectrum of the complex [PPh_4][**23**·Cl] the signal of the SiCH_2Sn protons, with respect to the ^{1}H NMR chemical shift of pure **23** in $CDCl_3$, is low-frequency shifted by 0.2 ppm. Furthermore, the $^{2}J(^{1}H–^{117/119}Sn)$ for these protons were changed from 89.5/92.2 Hz in **23** to 101.7/104.3 Hz in the complex [PPh_4][**23**·Cl].

A ^{13}C NMR spectrum of the same sample showed, in comparison with the ^{13}C NMR spectrum of pure **23**, that the signal of the SiCH_2Sn carbon atom is shifted by 10.5 ppm to low field.



Scheme 13. Syntheses of the halide complexes [PPh_4][**23**·Cl] and [NEt_4][**23**·F].

A ^{119}Sn NMR spectrum of a solution of compound **23** in $CDCl_3$ to which had been added 1 molar equivalent of tetraethylammonium fluoride dihydrate, $Et_4NF{\cdot}2H_2O$, showed a doublet resonance at δ –172 ($^{1}J(^{119}Sn–^{19}F)$ = 1558 Hz). A ^{19}F NMR spectrum of the same sample showed a resonance at δ–86 ($^{1}J(^{19}F–^{117/119}Sn)$ = 1556 Hz). These data are consistent with the formation of the 1:1 complex [NEt_4][**23**·F] (Scheme 13). In a ^{1}H NMR spectrum of the same sample the signal of the SiCH_2Sn protons was shifted from 1.22 ppm with $^{2}J(^{1}H–^{117/119}Sn)$ = 89.5/92.2 Hz in pure **23** to 1.12 ppm with $^{2}J(^{1}H–^{117/119}Sn)$ = 114.2/115.6 Hz. A ^{13}C NMR spectrum of the same sample showed that the signal of SiCH_2Sn carbon atom is low-field shifted by 7.6 ppm in comparison with a ^{13}C NMR spectrum of pure **23**.

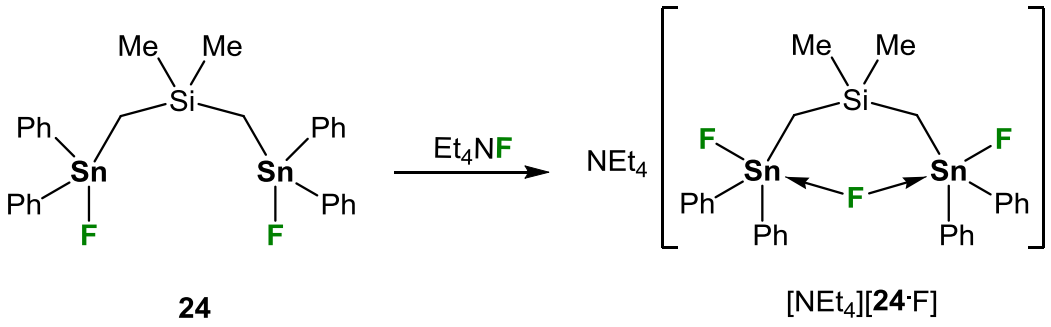
The electrospray ionization mass spectra (negative mode) of the halide complexes [**23**·Cl][Ph_4P] and [NEt_4][**23**·F] showed a mass cluster centered at *m/z* 600.8 that fits with [**23** – Cl + O]$^-$. In the negative mode of [NEt_4][**23**·F] a major mass cluster centered at *m/z* 636.8 related to [**23** + OH]$^-$ was observed.

A ^{119}Sn NMR spectrum of a solution of compound **24** in $CDCl_3$ at ambient temperature to which had been added 1 molar equivalent of tetraethylammonium fluoride dihydrate,

$Et_4NF{\cdot}2H_2O$, showed a doublet of doublet resonance at δ–215 ($^1J(^{119}Sn–^{19}F)$ = 1558 Hz). This chemical shift is similar to δ–215 reported for the complex $[(Ph_2FSnCH_2)_2CH_2{\cdot}F]^-$.[6]

A ^{19}F NMR spectrum of the same sample showed two signals at δ–129 ($^1J(^{19}F–^{117/119}Sn)$ = 1308 Hz, signal a) and δ –159 ($^1J(^{19}F–^{117/119}Sn)$ = 1955 Hz, signal b), signals a and b are assigned to the bridging and terminal fluorine atoms, respectively. These two signals are close to those reported for the complex $[(Ph_2F^aSnCH_2)_2CH_2.F^b]^-$ at δ–139 ($^1J(^{19}F^b–^{117/119}Sn)$ = 1264 Hz) and –165 ($^1J(^{19}F^a–^{117/119}Sn)$ = 2030 Hz).

These data are consistent with the formation of the 1:1 complex $[NEt_4]$[**24**·F] with the fluoride anion chelated by two tin atoms forming a six-membered ring, (Scheme 14). Till now, all attempts to get single crystals of compounds $[PPh_4]$[**23**·Cl], $[NEt_4]$[**23**·F] and $[NEt_4]$[**24**·F] failed.



24 [NEt4][**24**·F]

Scheme 14. Synthesis of the halide complex $[NEt_4]$[**24**·F].

2.2.4 Synthesis of bis(triiodostannyl)butane, $I_3Sn(CH_2)_4SnI_3$, 27.

As it is known, increasing the number of halides attached to the tin atom appears to increase significantly the Lewis acidity of the organotin compound. Alkylidene-bridged ditin hexaiodides $I_3Sn(CH_2)_nSnI_3$ (n = 1, 3) were synthesized in our research group some years ago by the cleavage of all phenyl groups in $Ph_3Sn(CH_2)_nSnPh_3$ (n = 1, 3) species.[42]

In a similar way, the reaction of bis(triphenylstannyl)butane, $Ph_3Sn(CH_2)_4SnPh_3$, with six molar equivalents of elemental iodine gave the corresponded hexaiodine-substituted organotin compound $I_3Sn(CH_2)_4SnI_3$, **27**, in almost quantitative yield. Compound **27** was obtained as yellowish solid, and shows good solubility in CH_2Cl_2 and $CHCl_3$.

On the other hand, an attempt to synthesize bis(triiodostannyl)ethane, $I_3Sn(CH_2)_2SnI_3$, by treatment of bis(triphenylstannyl)ethane, $Ph_3Sn(CH_2)_2SnPh_3$, with six molar equivalents of elemental iodine was not successful. The resulting solid compound showed poor solubility in CH_2Cl_2 and $CHCl_3$, and the elemental analysis does not agree with the proposed structure.

2.2.4.1 Molecular structure of compound 27

Single crystals suitable for X-ray diffraction analysis were obtained from a solution of **27** in $CHCl_3$ at –5°C. Compound **27** crystallizes in the orthorhombic space group P b c a with four molecules in the unit cell. The molecular structure of **27** is presented in Figure 17, selected interatomic distances and bond angles are listed in Table 5.

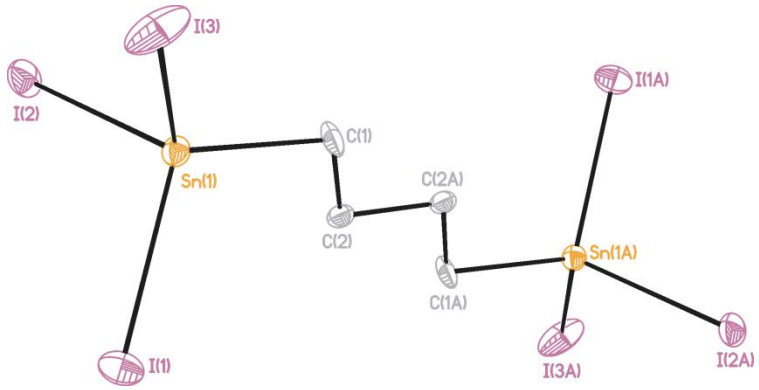


Figure 17. General view (SHELXTL) of a molecule of **27** showing 30% probability displacement ellipsoids and the crystallographic numbering scheme.

Table 5. Selected interatomic distances /Å and angles /° in **27**.

Sn(1)–C(1)	2.132(7)	C(1)–Sn(1)–I(2)	111.6(2)
Sn(1)–I(3)	2.6554(8)	C(1)–Sn(1)–I(1)	111.1(2)
Sn(1)–I(2)	2.6621(8)	I(3)–Sn(1)–I(2)	107.71(3)
Sn(1)–I(1)	2.6686(7)	I(1)–Sn(1)–I(3)	107.79(3)
C(1)–Sn(1)–I(3)	113.2(2)	I(2)–Sn(1)–I(1)	105.14(2)

The compound can be viewed as being centrosymmetric, as one half of the molecule comprises the crystallographic asymmetric unit and the other half is generated by an inversion center.

The tin atom is tetracoordinated and exhibits distorted tetrahedral environment with angles varying between 105.14(2)° (I2–Sn1–I1) and 113.2(2)° (C1–Sn1–I3). The Sn(1)–I distances are in the range between 2.6554(8) Å (Sn(1)–I(3)) and 2.6686(7) Å (Sn(1)–I(1)) being similar to the corresponded distances found in $I_3SnCH_2SnI_3$ (2.6535(10) – 2.6683(11) Å) and $I_3Sn(CH_2)_3SnI_3$, **26**, (2.6667(8) – 2.6862(9) Å).[42]

2.2.4.2 Structure of compound 27 in solution

A ^{119}Sn NMR spectrum of **27** in $CDCl_3$ showed one signal at δ –613. That is close to δ –622 (in CD_2Cl_2) reported for the analogous compound $I_3Sn(CH_2)_3SnI_3$. In a ^{13}C NMR spectrum two signals related to $SnCH_2\mathit{C}H_2$ and $Sn\mathit{C}H_2$ were observed at δ 28.1 ($^2J(^{13}C–^{117/119}Sn)$ = 126/131 Hz) and δ 30.7 ($^1J(^{13}C–^{117/119}Sn)$ = 440/459 Hz), respectively. These two chemical shifts are similar to the corresponding ones found in $I_3Sn(CH_2)_3SnI_3$ at δ 26.2 and δ 30.2, respectively.[42]

A ^{1}H NMR spectrum of the same sample showed two signals at δ 1.88 and δ 2.64 assigned to $SnCH_2\mathit{C}H_2$ and $Sn\mathit{C}H_2$, respectively, that are close to those reported for $I_3Sn(CH_2)_3SnI_3$ at δ 1.98 and δ 2.67.[42]

2.2.5 The complexation behavior of hexaiodidoditin compounds $(I_3SnCH_2)_2SiMe_2$, 21, $I_3Sn(CH_2)_3SnI_3$, 26, and $I_3Sn(CH_2)_4SnI_3$, 27, towards halide anions

The complexation behavior of compounds **21**, **26** and **27** have been studied in solution by ^{1}H, ^{13}C and ^{119}Sn NMR spectroscopy.

The reactions of one molar equivalent of $I_3Sn(CH_2)_3SnI_3$, **26**, with each of one molar equivalent of Ph_4PCl, Ph_4PBr and Ph_4PI, separately, were carried out in $CDCl_3$. The ^{119}Sn NMR spectra showed resonances at –732, –754, –771 ppm, related to the halide complexes $[PPh_4][\mathbf{26}\cdot Cl]$, $[PPh_4][\mathbf{26}\cdot Br]$ and $[PPh_4][\mathbf{26}\cdot I]$, respectively (Table 6). These chemical shifts are 93, 115 and 132 ppm high field shifted in comparison with the parent compound **26** (δ –639). In a ^{13}C NMR spectra the chemical shifts of the Sn*C*H_2 are located at 36.4, 36.7 and 34.9 ppm for $[PPh_4][\mathbf{26}\cdot Cl]$, $[PPh_4][\mathbf{26}\cdot Br]$ and $[PPh_4][\mathbf{26}\cdot I]$, respectively. These are 6.3, 6.6 and 4.8 ppm higher frequency shifted as compared to **26** (δ 30.1).

In a similar manner, the reactions of $(I_3SnCH_2)_2SiMe_2$, **21**, with each one molar equivalent of Ph_4PCl, Ph_4PBr and Ph_4PI, separately, cause high-field shifts in ^{119}Sn NMR spectra of 67, 77 and 111 ppm, respectively. The corresponding chemical shifts are located at –817, –827 and –861 ppm (Table 6).

In the ^{13}C NMR spectra the signals of Si*C*H_2Sn were about 4.6 ± 0.7 ppm low-field shifted in comparison to **21** (δ 19.8). These signals for $[PPh_4][\mathbf{21}\cdot Cl]$, $[PPh_4][\mathbf{21}\cdot Br]$ and $[PPh_4][\mathbf{21}\cdot I]$ are located at 25.1, 25.1 and 23.7 ppm, respectively.

The complexation study of $I_3Sn(CH_2)_4SnI_3$, **27**, was not carried with halide anions but rather with thiocyanate anion. This is because, on hand, the complexation studies of organotin compounds with halide anions were intensively studied by us and many others. On the other hand, the distance between the two tin centers in **27** is predictable to be suitable for binding thiocyanate anions, as proved by the electrochemical studies of analogues organotin compounds.[4]

For this purpose, compound **27** was stirred with one molar equivalent of KSCN for two days at room temperature. A ^{119}Sn NMR spectrum showed only one signal related to unreacted compound **27** and no reaction was observed.

Table 6. Selected NMR data measured in $CDCl_3$ solutions for the organotin compounds **21**, **26, 27** and their halide complexes.

	δ ^{13}C (Sn–CH_2)	δ ^{29}Si	δ ^{119}Sn
$(I_3SnCH_2)_2SiMe_2$ (**21**)	19.8	8.3	–750
[PPh_4][**21**·Cl]	25.1	7.0	–817
[PPh_4][**21**·Br]	25.1	7.2	–827
[PPh_4][**21**·I]	23.7	7.8	–861
$I_3Sn(CH_2)_3SnI_3$ (**26**)	30.1		–639
$I_3Sn(CH_2)_4SnI_3$ (**27**)	30.7		–613
[PPh_4][**26**·Cl]	36.4		–732
[PPh_4][**26**·Br]	36.7		–754
[PPh_4][**26**·I]	34.9		–771

Increasing the reactivity of the thiocyanate anion by complexing the potassium ion using 18–crown–6 resulted in changing the color of the solution from pale yellow to dark red. A ^{119}Sn NMR spectrum of the reaction mixture after stirring for two hours showed one signal at δ –660 being 47 ppm high field shifted in comparison to **27** (δ –613).

Recrystallization by the slow evaporation of the reaction mixture in $CHCl_3$ afforded single crystals of the polymer $(K^{\cdot}18–crown–6)^{\cdot}I_3$ suitable for X-ray diffraction analysis.

Interestingly, the same behavior was observed by the other halide adducts. The yellow color of the adducts solutions [PPh_4][**21**·Cl], [PPh_4][**21**·Br], [PPh_4][**21**·I], [PPh_4][**26**·Cl], [PPh_4][**26**·Br] and [PPh_4][**26**·I] in $CDCl_3$ turned to dark red.

Recrystallization of these adducts by the evaporations of their solutions in $CHCl_3$ gave in all the cases single crystals of $[Ph_4P^{\cdot}I_3]$ suitable for X-ray diffraction analysis. In addition to that, yellowish precipitates were failed from these solutions after few days. These were not isolated.

Further studies were carried out for the reaction of $I_3SnCH_2SnI_3$ with one molar equivalent of Ph_4PCl in $CDCl_3$. In this case the reaction was faster than the other complexation reactions mentioned above as the red color of the solution was observed in few minutes. Furthermore, after three hours a yellowish precipitate was observed followed by appearing of new crystals of $[Ph_4P^{\cdot}I_3]$ from the red solution. Washing the precipitate many times with CH_3CN solution resulted in a yellow compound that is poorly soluble in common organic solvents. The elemental analysis of this compound showed Anal. Found (%) C 3.2, H 2.0.

2.3Anion Selective Electrodes Based on Organotin Compounds

2.3.1 INTRODUCTION

According to the guidance of the World Health Organization, fluoride selective electrode is one of the successful and widely used tool for the quantification of fluoride anions in foodstuffs, biological and environmental fields.[46] This highlighted the major role of the ion selective electrodes (ISEs) as an essential tool for the detection of different ions, in little concentrations and in different environmental areas. This could return to the excellent characteristics of (ISEs) as the reasonable selectivity, easy preparation, relatively fast response, sensitivity over a wide concentration range, and low cost.

The widely used fluoride selective electrode is the lanthanum fluoride electrode in which the sensing element is a crystal of lanthanum fluoride LaF_3 doped with europium fluoride (EuF_2).[47] Many other fluoride selective electrodes depending on polymeric membrane electrodes are reported such as gallium(III) Schiff base complexes,[48] uranyl salophen receptors,[49] aluminum(III) complexes,[50] scandium(III) complex[51] and organotin compounds.[52]

The Lewis acidity of the tin centers in organotin compounds gives advantage for binding Lewis-basic anions. On the other side, the structure characteristics of the organotin ionophores plays a major role on the potentiometric selectivity towards different anions, in terms of the distance between the tin centers (in multicentric organotin compounds), the electronegativity of the inorganic substituents and the steric hindrance of the organic substituents. Designing of bicentric organotin compounds with different characteristic structures enabled them to reach a wide range of anions such as the most hydrophilic anions, phosphate, and the smallest anions, Fluoride.

2. Spacer-Bridged Organoditin Compounds

A set of organotin compounds was synthesized in our research group and their employment as ionophores for ion selective electrodes was reported.

These studies showed that bis(chlorodiphenylstannyl)methane, $(Ph_2ClSn)_2CH_2$, (Chart 8, **A**) is a highly selective ionophore for fluoride anions.[4] On the other hand, replacing one phenyl group by a second chlorine atom at each tin atom gave a higher response towards phosphate anions, and the optimal selectivity towards phosphate anions was obtained by using $(PhBr_2Sn)_2CH_2$ as an ionophore.[9]

The effect of the organic substituents on the selectivity as a result of the steric hindrance is particularly evident by replacing the phenyl group in $(PhCl_2Sn)_2CH_2$ (Chart 8, **B**) with the organic substituent 4-*n*-octyl-phenyl giving $\{Cl_2(4\text{-}n\text{-}C_8H_{17}\text{-}C_6H_4)Sn_2\}_2CH_2$ (Chart 8, **C**) that is an excellent carrier for arsenate selective electrode.[10]

An improvement on fluoride selective electrode was reported by using the organic substituents *n*-octyl and *n*-dodycyl instead of the phenyl groups. The corresponding ionophore $(R_2FSn)_2CH_2$ (Chart 8, **D**) showed increased life time of the electrode, in comparison with the ionophore $(Ph_2ClSn)_2CH_2$, with retaining the high selectivity towards fluoride anions.[8]

Lang and co-workers reported a new type of ionophores for fluoride selective electrode depending on oligomeric diorganotin difluorides $((C_6H_4(CH_2NMe_2)\text{–}2)PhSnF_2)_n$ (n = 3–4) containing a C,N- chelating ligand. This ionophore showed a detection limit of 7.9×10^{-7} M enabling the use of this electrode for the determination of fluoride anions in drinking mineral water.[52]

Inspired by the work of *Lang*, who used an oligomeric organotin ionophore with C,N-chelating ligand, and by our previous ionophore $(R_2FSn)_2CH_2$ (R = *n*-octyl or *n*-dodycyl), the use of $[\{Me_2N(CH_2)_3\}PhFSn(CH_2)SnFPh_2]$ as an ionophore for fluoride selective electrode is encouraging. This ionophore is characteristic as methylene-bridged organoditin fluoride with intramolecular N→Sn coordination, as well as, it has a dimeric structure in the solid state.

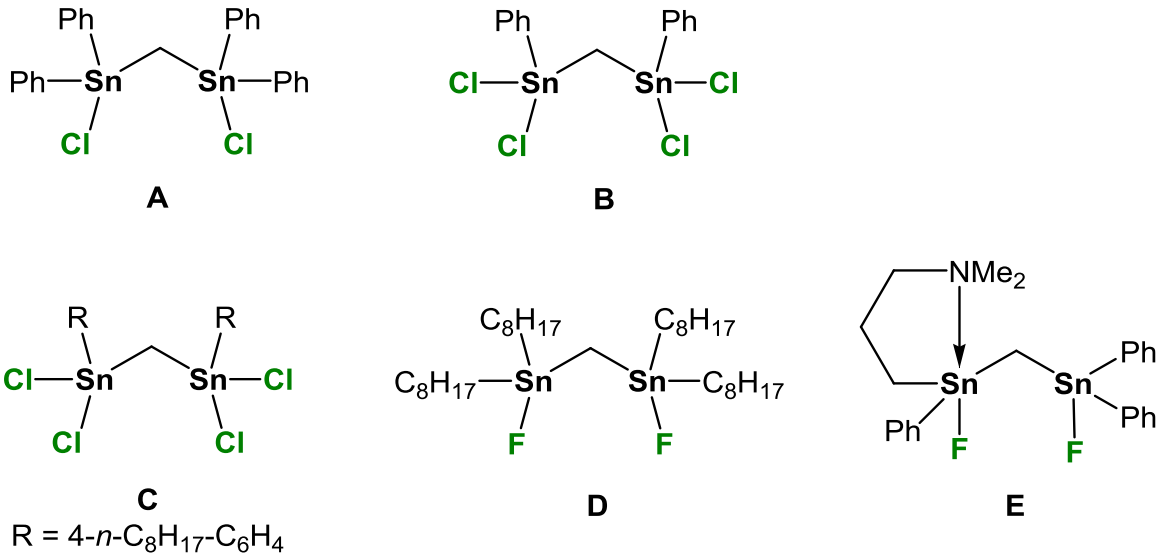


Chart 8. Organotin compounds **A** – **D** as ionophores for anion selective electrodes reported in the literature, and the proposed ionophore **E**.

In a continuation of our systematic studies on fluoride selective electrodes here will be presented the employment of the organotin fluoride [{$Me_2N(CH_2)_3$}$PhFSnCH_2SnFPh_2$] as an ionophore-based sensor. The synthesis, characteristic structure and reactivity of this compound towards fluoride anions are reported in chapter 2.1.3.

2.3.2 Principles of ion selective electrodes

Ion-selective electrode is a sensor that converts the activity of a specific ion in solution into an electrical potential. For the electrochemical circuit of an ISE measurement the ISE and the reference electrode should connect to a selective millivolt meter and immerse in an aqueous solution containing the ions to be measured. When the target ions in solution diffuse through from the high concentration side to the lower concentration side a potential difference is developed across the ISE membrane (Figure 18). The voltage is theoretically dependent on the logarithm of the ionic activity, according to the Nernst equation (eq. 1).

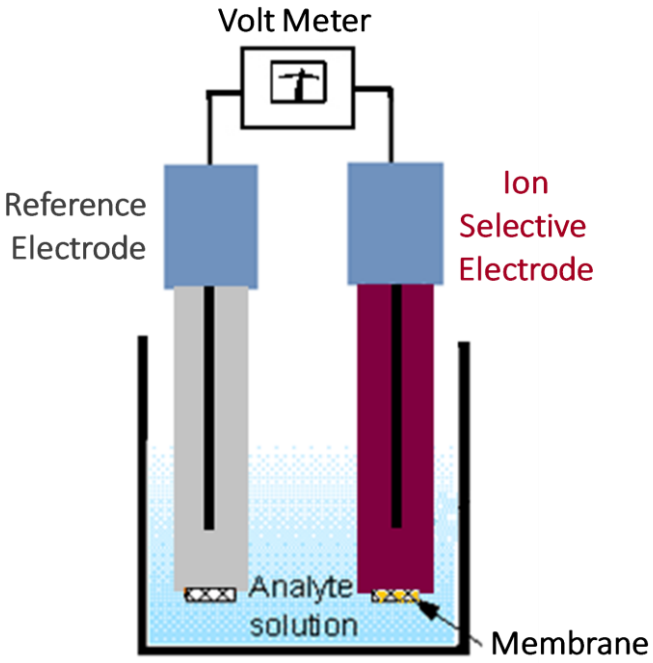


Figure 18. Electrochemical cell used for potentiometric measurements.

For the real membrane electrode systems the additional contributions to the total measured activity, resulted from the interfering ions in the solution, have to be considered. Therefore, an extension to the Nernst equation with the interference effects are commonly described by Nikolsky-Eisenman equation (eq. 2).[53]

$$E = E^{\circ} + \frac{2.303 \cdot RT}{zF} \log a \qquad \text{eq.1}$$

$$E = E^{\circ} + \frac{2.303 \cdot RT}{z_A F} \log \left[a_A + \mathrm{K}_{\mathrm{A,B}}^{\mathrm{pot}} \, (a_B)^{\frac{zA}{zB}} + \mathrm{K}_{\mathrm{A,C}}^{\mathrm{pot}} \, (a_C)^{\frac{zA}{zC}} + \ldots \right] \qquad \text{eq.2}$$

E is the experimentally observed potential of the cell (in V); *E*° is the cell potential at standard conditions; *R* is the gas constant and is equal to 8.314510 J K^{-1} mol^{-1}; *T* is the temperature (in K); *F* is the Faraday constant and is equal to 9.6485 x 10^4 C mol^{-1}; *a* is the activity of the ion, A is the analyzed ion, B and C are the interfering ions; $\mathrm{K}_{\mathrm{A,B}}^{\mathrm{pot}}$ and $\mathrm{K}_{\mathrm{A,C}}^{\mathrm{pot}}$ are the potentiometric selectivity coefficient for the ions B and C, respectively, with respect to the primary ion A; *z* is the charge number.[54]

From this equation it is clear that the measured potential is linearly dependent on the logarithm of the activity of the target ion in solution, and the ISE response to the primary

ion A is more selective than the interfering ion B only when $K_{A,B}^{pot}$ is smaller than 1. The factor 2.303RT/F has a theoretical value of 59.16 mV (at 25°C).[54]

2.3.3 The organotin fluoride [{$Me_2N(CH_2)_3$}PhFSnCH_2SnFPh_2], 11, as an ionophore in fluoride selective electrode

2.3.4 Experimental section.

Tetrahydrofuran (THF) was doubly distilled before use. Polyvinyl chloride (PVC), bis(2-ethylhexyl) sebacate (DOS) and sodium fluoride (NaF) were commercially available, and they were used without further purification.

2.3.5 Membrane preparation.

For the membrane construction (PVC) was used as a membrane matrix and (DOS) as a plasticizer. A mixture of the organotin compound **11** (2 mg), PVC (33 mg) and DOS (65 mg) were dissolved in THF (1.5 mL) and the resultant solution was poured into a glass ring. The glass ring was covered with a glass beaker to ensure a slow evaporation of the solvent. After allowing the solvent to evaporate overnight circular pieces (diameter 7 mm) of the membranes were cut off and mounted in the electrode body.

2.3.6 Electrode preparation and the measurement conditions.

The electrode containing the membrane was filled with a solution of potassium chloride (10^{-2} M) as an internal solution. Ag/AgCl electrode was used as a reference electrode and filled with the same solution of potassium chloride (10^{-2} M). The measure cell was filled with 100 mL of the buffer solution 2-(N-morpholino)ethanesulfonic acid (10^{-3} M) and the temperature was kept on 25°C. The potential changes observed towards the concentration of fluoride anions (as NaF) are summarized below; the resulting calibration curve of the ion selective electrode is presented in Figure 19.

E (mv)	–log (F^-)
113.6167	7
113.0457	6
110.3471	5
102.4212	4
90.8460	3
65.0747	2
32.5960	1

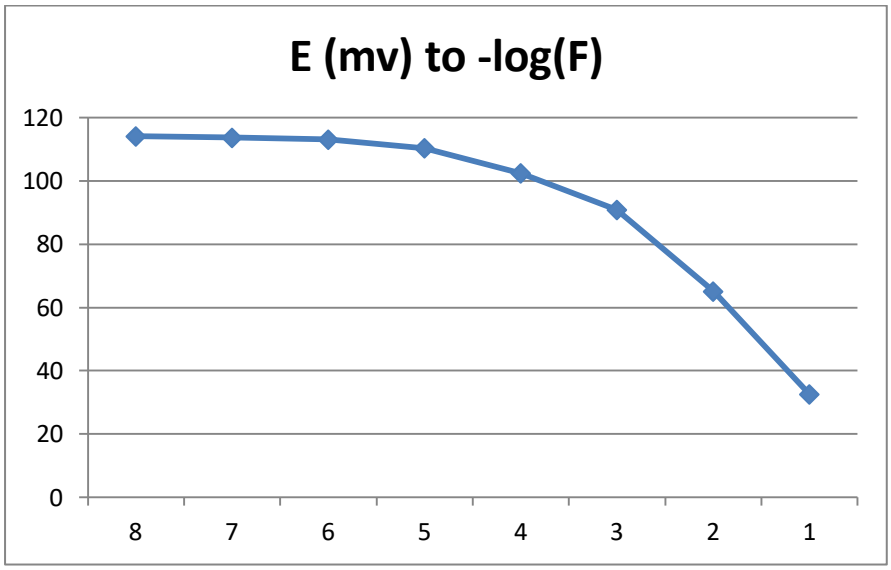


Figure 19. Calibration curve of the ISE based on organotin compound **11**.

The studied electrode showed a good response for fluoride anions with detection limits of 10^{-4} to 10^{-5} as proved by repeating the measurements several times. These values are comparable to those reported for the published fluoride selective electrodes based on gallium(III) Schiff base complexes ($6.5x10^{-5}$),[48] uranyl salophen receptors ($3.0x10^{-4}$)[49] and aluminum complexes ($4x10^{-5}$).[55] However, the slope of the calibration curve is about –32 mV/–log[F^-] that is smaller as the theoretical sensitivity value for monovalent anions of –59.16 mV/–log[anion].

One possibility to improve the sensitivity (slope) to fluoride anion may be achieved by trying to use different plasticizers. Many papers reported that a change in the slope curve is observed by using different plasticizers as the plasticizer used has a rather significant effect and influences the potentiometric properties of the ion selective membrane.[52][4][56]

It was planned to study the effect of the different plasticizers used in the membrane composition on the sensitivity slope, as well as the selectivity of the proposed electrode towards fluoride anions. However, these studies could not be carried out within the given time frame as a result of a technical defect in the electrode measuring system.

2.4 CONCLUSION

A series of unsymmetrical substituted space-bridged organoditin compounds containing the [3-(dimethylamino)propyl] moiety was synthesized and characterized. Some of the corresponding organotin halides are not stable, and suffer hydrolysis accompanied with protonation of the amine group, as proved by NMR spectroscopy in the attempts to synthesize compounds **12** – **14**. On the other hand, the iodine-substituted organotin compounds **10** and **15** were synthesized. Their fluorido-substituted analogous (compound **11**, respectively, **16**) are synthesized and characterized. They show N→Sn intramolecular interaction both in solution and solid state. This interaction results in better solubility of the organotin fluorides **11** and **16** in common organic solvents with respect to the analogous compounds $Ph_2FSn(CH_2)_nSnPh_2F$ (n = 1, 3) lacking an *intramolecularly* coordinating substituent. Compound **11** is monomeric in solution and shows an intramolecular F→Sn coordination that is kinetically inert at low temperature on the ^{19}F and ^{119}Sn NMR time scales. Upon crystallization, it dimerizes as a result of *intermolecular* F→Sn coordination.

Upon addition to compound **11** of fluoride anion, as $NEt_4F{\cdot}2H_2O$, in CD_2Cl_2 solution, the salt NEt_4[**11**·F] containing an organostannate anion is formed. The same holds for compound **16** giving the salt NEt_4[**16**·F]. Based on NMR data, the intramolecular N→Sn coordination is retained and the incoming fluoride anion does not bridge the two tin centers but is bound to the diphenyl-substituted tin atom only. In contrast to compound **11**, the trimethylene-bridged ditin compound **16** is monomeric both in solution and in the solid state stabilized by intramolecular N→Sn and F→Sn coordination. The structural difference between **11** and **16** is likely the higher ring strain in a four-membered compared to a six-membered ring.

A series of $CH_2SiMe_2CH_2$-bridged ditin compounds was synthesized and completely characterized, their ability to complex halide anions were investigated by NMR spectroscopy and electrosoray mass spectrometry. In the case of bis(triiodostannylmethyl)dimethylsilane, **21**, the halide complexes [PPh_4][**21**·Cl], [PPh_4][**21**·Br] and [PPh_4][**21**·I] seem to be not stable as the tetraphenylphosphonium triiodide was obtained in all these cases. Crystals of the polymer $(K^{\cdot}18\text{–crown–}6)^{\cdot}I_3$ were obtained by the reaction of tetramethylene-bridged hexaiodidoditin compound **27** with KSCN in presence of 18–crown–6.

2.5 EXPERIMENTAL SECTION

All solvents were dried and purified according to standard procedures and freshly distilled prior to use. $Me_2N(CH_2)_3Cl$,[11] $\{Me_2N(CH_2)_3\}(Ph_2)SnI$,[11] Ph_3SnCH_2Br,[16] $(Ph_3Sn)_2CH_2$,[12] $(Ph_3SnCH_2)_2$,[13] $(Ph_3SnCH_2)_2CH_2$,[14] $Ph_3Sn(CH_2)_4SnPh_3$[15], $I_3Sn(CH_2)_3SnI_3$[42] were synthesized according to literature methods. $[Me_2N(CH_2)_3Cl]^{\cdot}HCl$, triphenylcarbenium hexafluorophosphate, tetraethylammonium fluoride, tetraphenylphosphonium chloride, tetraphenylphosphonium bromide, tetraphenylphosphonium iodide, tetraethylammonium fluoride were commercially available, and they were used without further purification. Bruker DPX–300, DRX–400 and AVIII–500 spectrometers were used to obtain ^1H, ^{13}C, ^{19}F, and ^{119}Sn NMR spectra. Solution ^1H, ^{13}C, ^{19}F, ^{29}Si and ^{119}Sn NMR chemical shifts are given in ppm and were referenced to Me_4Si (^1H, ^{13}C, ^{29}Si), $CFCl_3$ (^{19}F), and Me_4Sn (^{119}Sn). Elemental analyses were performed on a LECO–CHNS–932 analyzer. The electrospray mass spectra were recorded with a Thermoquest–Finnigan instrument, using CH_3CN, MeOH or CH_2Cl_2 as the mobile phase.

The DOSY (diffusion ordered spectroscopy) measurement was performed with a pulse sequence using double stimulated echo for convection compensation and LED and bipolar gradient pulses for diffusion (A. Jerschow & N. Mueller, J. Magn. Reson. A 123, 222-225 (1996), A. Jerschow & N. Mueller, J. Magn. Reson. A 125, 372-375 (1997)). The measurements were executed with a 600 MHz NMR spectrometer AVANCE-III HD equipped with a 5mm helium cooled BBFO probe from Bruker BioSpin GmbH (Rheinstetten, Germany). Thirty-two different gradient strengths varying between 3 and 95 % of the maximum strength of 53 G/cm were used. Thirty-two scans per gradient strength were acquired with 16 kB data points of the FID (acquisition time of 0.97 s) and a relaxation delay of 1.5 s. *Crystallography*. Intensity data for all crystals were collected on a XcaliburS CCD diffractometer (Oxford Diffraction) using Mo-Kα radiation at 110 K. The structures were solved with direct methods using SHELXS-97 and refinements were carried out against F^2 by using SHELXL-2014.[57]

General procedure for synthesizing the compounds 5 – 8.

Elemental iodine was added in small portions under ice-cooling to a stirred solution of $Ph_3Sn(CH_2)_nSnPh_3$, where n = 1 – 4, in CH_2Cl_2 (200 mL). The reaction mixture was stirred

overnight. The solvent and the iodobenzene were removed in vacue. The residue contains a mixture of three compounds, that refers as mixture **A**, the unreacted compound, the monoiodo compound $Ph_2ISn(CH_2)_nSnPh_3$, and $Ph_2ISn(CH_2)_nSnIPh_2$. To a solution of the mixture A in THF (150 mL) was added the Grignard reagent prepared from $Me_2N(CH_2)_3Cl$ and magnesium turnings in THF (40 mL). After the completion of the addition the mixture was stirred overnight at room temperature. The mixture was then heated at reflux for three hours before it was cooled to room temperature. THF was distilled off under reduced pressure, then cold water (100 mL) was added, and the mixture was extracted three times with 70 mL of dichloromethane. The combined organic phases were dried with $MgSO_4$ and the solvents evaporated in vacuo to give the crude product. The residue was purified by column chromatography on silica gel using CH_2Cl_2 to separate the unreacted $Ph_3Sn(CH_2)_nSnPh_3$ compound, then using acetone to separate the target compound as yellow oil.

Synthesis of [{$Me_2N(CH_2)_3$}$Ph_2SnCH_2SnPh_3$] (5).

The first method: A solution of Ph_3SnCH_2MgBr, prepared from Ph_3SnCH_2Br, (2.00 g, 4.51 mmol) and magnesium (0.11g, 4.51 mmol) in THF (50 mL) was added dropwise to a stirred solution of $Me_2N(CH_2)_3Ph_2SnI$ (1.97 g, 4.05 mmol) in THF (60 mL) for a period of 1 h. After the addition had been completed, the reaction mixture was heated at reflux overnight and then cooled to room temperature. THF was distilled off under reduced pressure, then cold water (60 mL) was added, and the mixture was extracted three times with 50 mL of dichloromethane. The combined organic phases were dried with $MgSO_4$ and the solvents evaporated in vacuo to give the crude product. It was purified by column chromatography (SiO_2, *n*-hexane:Ethylacetate 5:1, Ethanol) to yield 1.24 g (38%) as a yellow oil.

The second method: As described above in the general procedure using Iodine (1.66 g, 6.55 mmol), $Ph_3SnCH_2SnPh_3$ (5.50 g, 7.70 mmol), $Me_2N(CH_2)_3Cl$ (0.95 g, 7.77mmol), and Mg (0.19 g, 8.16 mmol) giving compound **5** (1.42 g, 30%).

^{1}H NMR (400.13 MHz, $CDCl_3$): δ 1.02 (s, $^2J(^1H–^{117/119}Sn)$ = 60.7 Hz, 2H, Sn–CH_2–Sn), 1.24 (t, 2H, Sn–CH_2), 1.84 (m, 2H, Sn–CH_2–CH_2), 2.26 (s, 6H, N(CH_3)$_2$), 2.30 (t, 2H, CH_2–N), 7.39–7.69 (25H, Ph). **^{13}C{^{1}H} NMR** (100.63 MHz, $CDCl_3$): δ –17.3 ($^1J(^{13}C–^{117/119}Sn)$ = 252/262 Hz, Sn–

*C*H$_2$–Sn), 9.0 (^1J(^{13}C–$^{117/119}$Sn) = 373/391 Hz, Sn–*C*H$_2$), 24.1 (^2J(^{13}C–$^{117/119}$Sn) = 19 Hz, Sn–CH$_2$–*C*H$_2$), 45.2 N(*C*H$_3$)$_2$, 63.0 (^3J(^{13}C–$^{117/119}$Sn) = 70 Hz, *C*H$_2$–N), 128.1 (^3J(^{13}C–$^{117/119}$Sn) = 47 Hz, SnPh$_2$, C$_m$), 128.2 (^3J(^{13}C–$^{117/119}$Sn) = 50 Hz, SnPh$_3$, C$_m$), 128.4 (SnPh$_2$, C$_P$), 128.7 (^4J(^{13}C–$^{117/119}$Sn) = 12 Hz, SnPh$_3$, C$_P$), 136.4 (^2J(^{13}C–$^{117/119}$Sn) = 36 Hz, SnPh$_2$, C$_o$), 136.7 (^2J(^{13}C–$^{117/119}$Sn) = 38 Hz, SnPh$_3$, C$_o$) 139.3 (^1J(^{13}C–$^{117/119}$Sn) = 488/510 Hz, ^3J(^{13}C–$^{117/119}$Sn) = 9 Hz, SnPh$_3$, C$_i$), 140.4 (^1J(^{13}C–$^{117/119}$Sn) = 448/468 Hz,^3J(^{13}C–$^{117/119}$Sn) = 13 Hz, SnPh$_2$, C$_i$). **^{119}Sn{^{1}H} NMR** (111.92 MHz, CDCl$_3$): δ –49 (^2J(^{119}Sn–$^{117/119}$Sn) = 236 Hz, SnPh$_2$), –77 (^2J(^{119}Sn–$^{117/119}$Sn) = 232 Hz, SnPh$_3$). Anal. Calcd (%) for C$_{36}$H$_{39}$NSn$_2$ (723.09): C 59.79, H 5.44, N 1.94. Found: C 60.0, H 5.6, N 1.6.

Synthesis of [{Me$_2$N(CH$_2$)$_3$}Ph$_2$Sn(CH$_2$)$_2$SnPh$_3$] (6).

As described above in the general procedure using Iodine (2.96 g, 11.67 mmol), Ph$_3$Sn(CH$_2$)$_2$SnPh$_3$ (10.00 g, 13.73 mmol), Me$_2$N(CH$_2$)$_3$Cl (1.56 g, 12.85 mmol), and Mg (0.34 g, 14.14 mmol) giving compound **6** (2.9 g, 36%).

^{1}H NMR (300.13 MHz, CDCl$_3$): δ 1.26 (t, ^2J(^{1}H – $^{117/119}$Sn) = 51.2 Hz, 2H, Sn–C*H*$_2$), 1.76 (t, 2H, Sn–C*H*$_2$–CH$_2$–Sn), 1.79 (t, 2H, Sn–CH$_2$–C*H*$_2$–Sn), 2.08 (m, 2H, Sn–CH$_2$–C*H*$_2$), 2.55 (s, 6H, N(C*H*$_3$)$_2$), 2.91 (t, 2H, C*H*$_2$–N), 7.38–7.57 (25H, Ph). **^{13}C{^{1}H} NMR** (100.63 MHz, CDCl$_3$): δ 6.2 (Sn–*C*H$_2$), 7.1 (Sn–*C*H$_2$–CH$_2$–Sn), 7.4 (Sn–CH$_2$–*C*H$_2$–Sn), 21.4 (^2J(^{13}C–$^{117/119}$Sn) = 16 Hz, Sn–CH$_2$–*C*H$_2$), 42.7 N(*C*H$_3$)$_2$, 60.6 (^3J(^{13}C–$^{117/119}$Sn) = 27 Hz, *C*H$_2$–N), 128.5 (^3J(^{13}C–$^{117/119}$Sn) = 47 Hz, SnPh$_3$, C$_m$), 128.7 (^3J(^{13}C–$^{117/119}$Sn) = 45 Hz, SnPh$_2$, C$_m$), 128.9 (^4J(^{13}C–$^{117/119}$Sn) = 10 Hz, SnPh$_3$, C$_P$), 129.0 (^4J(^{13}C–^{119}Sn) = 10 Hz, SnPh$_2$, C$_P$), 136.8 (^2J(^{13}C–$^{117/119}$Sn) = 33 Hz, SnPh$_2$, C$_o$), 137.1 (^2J(^{13}C–$^{117/119}$Sn) = 33 Hz, SnPh$_3$, C$_o$) 138.2 (SnPh$_2$, C$_i$), 138.5 (SnPh$_3$, C$_i$). **^{119}Sn{^{1}H} NMR** (111.92 MHz, CDCl$_3$): δ –74 (^3J(^{119}Sn–$^{117/119}$Sn) = 1088/1287 Hz, SnPh$_2$), –104 (^3J(^{119}Sn–$^{117/119}$Sn) = 1088/1285 Hz, SnPh$_3$).

Synthesis of [{Me$_2$N(CH$_2$)$_3$}Ph$_2$Sn(CH$_2$)$_3$SnPh$_3$] (7).

As described above in the general procedure using Iodine (2.91 g, 11.45 mmol), Ph$_3$Sn(CH$_2$)$_3$SnPh$_3$ (10.00 g, 13.47 mmol), Me$_2$N(CH$_2$)$_3$Cl (1.39 g, 11.45 mmol), and Mg (0.3 g, 12.6 mmol) giving compound **7** (2.41 g, 28%).

^{1}H NMR (400.13 MHz, $CDCl_3$): δ 1.20 (t, 2H, SnCH_2), 1.51 (t, 2H, CH_2SnCH_2(CH_2)$_2$Sn), 1.66 (t, 2H, Sn(CH_2)$_2$CH_2Sn), 2–2.15 (m, 4H, 2H $SnCH_2CH_2$ + 2H $SnCH_2CH_2CH_2Sn$), 2.59 (s, 6H, N(CH_3)$_2$), 2.95 (t, 2H, CH_2N), 7.34–7.63 (25H, Ph). **^{13}C{^{1}H} NMR** (100.63 MHz, $CDCl_3$): δ 6.2 (^{1}J(^{13}C–$^{117/119}$Sn) = 319/333 Hz, Sn–CH_2(L)), 15.5 (^{1}J(^{13}C–$^{117/119}$Sn) = 352/368 Hz, SnCH_2), 15.9 (^{1}J(^{13}C–$^{117/119}$Sn) = 382 Hz, SnCH_2), 21.1 (^{2}J(^{13}C–$^{117/119}$Sn) = 15 Hz, $SnCH_2CH_2CH_2Sn$), 24.1 (^{2}J(^{13}C–$^{117/119}$Sn) = 20 Hz, $SnCH_2CH_2$), 42.5 N(CH_3)$_2$, 60.3 (^{3}J(^{13}C–$^{117/119}$Sn) = 67 Hz, CH_2N), 128.2 ($SnPh_3$, C_m), 128.4 ($SnPh_2$, C_m), 128.6 ($SnPh_3$, C_p), 128.7 ($SnPh_2$, C_p), 136.5 (^{2}J(^{13}C–$^{117/119}$Sn) = 35 Hz, $SnPh_2$, C_o), 136.7 (^{2}J(^{13}C–$^{117/119}$Sn) = 35 Hz, $SnPh_3$, C_o) 138.1 ($SnPh_2$, C_i), 138.5 ($SnPh_3$, C_i). **^{119}Sn{^{1}H} NMR** (111.92 MHz, $CDCl_3$): δ –76 ($Sn$$Ph_2$), –104 ($Sn$$Ph_3$). Anal. Calcd (%) for $C_{38}H_{43}NSn_2$ (751.19): C 60.76, H 5.77, N 1.86. Found: C 60.0, H 5.9, N 1.8. **Electrospray MS**: m/z (%) positive mode: 674.1 (58, $[M - Ph]^+$), 752.2 (2, $[M + H]^+$).

Synthesis of [{$Me_2N(CH_2)_3$}$Ph_2Sn(CH_2)_4SnPh_3$] (8).

As described above in the general procedure using Iodine (1.49 g, 7.64 mmol), $Ph_3Sn(CH_2)_4SnPh_3$ (6.80 g, 8.99 mmol), $Me_2N(CH_2)_3Cl$ (0.93 g, 7.64 mmol), and Mg (0.19 g, 8.0 mmol) giving compound **8** (2.10 g, 36%).

^{1}H NMR (400.13 MHz, $CDCl_3$): δ 1.27 (t, 2H, Sn–CH_2 (L)), 1.36 (t, 2H, CH_2–Sn–CH_2–(CH_2)$_3$–Sn), 1.59 (t, 2H, Sn–(CH_2)$_3$–CH_2–Sn), 1.75–1.89 (m, 6H, 2H Sn–CH_2–CH_2(L)+ 4H Sn–CH_2–(CH_2)$_2$–CH_2–Sn)), 2.22 (s, 6H, N(CH_3)$_2$), 2.32 (t, 2H, CH_2–N), 7.36–7.65 (25H, Ph). **^{13}C{^{1}H} NMR** (100.63 MHz, $CDCl_3$): δ 7.6 (^{1}J(^{13}C–$^{117/119}$Sn) = 350/365 Hz, Sn–CH_2(L)), 9.9 (^{1}J(^{13}C–$^{117/119}$Sn) = 352/369 Hz, Sn–CH_2(Butyl)), 10.5 (^{1}J(^{13}C–$^{117/119}$Sn) = 375/393 Hz, Sn–CH_2(Butyl)), 24.4 (^{2}J(^{13}C–$^{117/119}$Sn) = 19 Hz, Sn–CH_2–CH_2(L)), 31.2 (^{3}J(^{13}C–$^{117/119}$Sn) = 60 Hz, Sn–CH_2–CH_2(Butyl)), 31.4 (^{3}J(^{13}C–$^{117/119}$Sn) = 68 Hz, Sn–CH_2–CH_2(Butyl)), 45.3 N(CH_3)$_2$, 63.3 (^{3}J(^{13}C–$^{117/119}$Sn) = 64 Hz, CH_2–N), 128.2 (^{3}J(^{13}C–$^{117/119}$Sn) = 45 Hz, $SnPh_2$, C_m), 128.4 (^{3}J(^{13}C–$^{117/119}$Sn) = 47 Hz, $SnPh_3$, C_m), 128.7 (^{4}J(^{13}C–$^{117/119}$Sn) = 11 Hz, $SnPh_3$ + $SnPh_2$, C_P), 136.7 (^{2}J(^{13}C–$^{117/119}$Sn) = 33 Hz, $SnPh_2$, C_o), 136.9 (^{2}J(^{13}C–$^{117/119}$Sn) = 35 Hz, $SnPh_3$, C_o) 138.9 ($SnPh_2$, C_i), 139.9 ($SnPh_3$, C_i). **^{119}Sn{^{1}H} NMR** (111.92 MHz, $CDCl_3$): δ –72 ($SnPh_2$), –100 ($SnPh_3$). Anal. Calcd (%) for $C_{39}H_{45}NSn_2$ (765.17): C 61.22, H 5.93, N 1.83. Found: C 60.6, H 6.0, N 1.8.

Synthesis of [{$Me_2N(CH_2)_3$}PhISnCH_2SnPh_3] (9).

Elemental iodine (35 mg, 0.41 mmol) was added in small portions and under ice cooling to a stirred solution of **5** (100 mg, 0.41 mmol) in CH_2Cl_2 (20mL). Stirring was continued while warming to room temperature overnight. The solvent and the iodobenzene were removed in vacuo to afford 86 mg (80%) of **9** as a slightly yellow solid. Single crystals of **9** suitable for X-ray diffraction analysis were obtained by slow evaporation of a solution of the compound in CH_2Cl_2/ *n*-hexane.

^{1}H NMR (499.79 MHz, $CDCl_3$): δ 1.20–1.65 (Complex pattern, 6H, Sn–CH_2–Sn + Sn–CH_2 + Sn–CH_2–CH_2), 1.92 (s, 6H, N(CH_3)$_2$), 2.16 (t, 2H, CH_2–N), 7.34–7.88 (20H, Ph). **^{13}C{^{1}H} NMR** (125.68 MHz, $CDCl_3$): δ –5.2 (^1J(^{13}C–$^{117/119}$Sn) = 281/295 Hz, Sn–CH_2–Sn), 19.1 (Sn–CH_2), 21.9 (^2J(^{13}C–$^{117/119}$Sn) = 35 Hz, Sn–CH_2–CH_2), 46.3 (N(CH_3)$_2$), 61.1 (CH_2–N), 128.4 (^3J(^{13}C–$^{117/119}$Sn) = 51 Hz, SnIPh + $SnPh_3$, C_m), 128.8 (SnIPh, C_P), 128.9 (^4J (^{13}C–$^{117/119}$Sn) = 11 Hz, $SnPh_3$, C_P), 134.1(SnIPh, C_o), 137.1 (^2J(^{13}C–$^{117/119}$Sn) = 38 Hz, $SnPh_3$, C_o), 139.1 (^1J(^{13}C–$^{117/119}$Sn) = 497/520, $SnPh_3$, C_i), 144.5 (SnIPh, C_i). **^{119}Sn{^{1}H} NMR** (111.92 MHz, $CDCl_3$): δ –54 (5%), –86 (40%, $SnPh_3$), –92 (50%, SnIPh), –102 (5%). **Electrospray MS**: m/z (%) positive mode: 646.1 (100, $[M - I]^+$), 614.1 (40, $[M - I - 2Ph + 2OH + MeOH + 3H_2O]^+$), (1, $[M + H]^+$), negative mode: 127.0 (100, I^-), 380.8 (17, I_3^-).

Synthesis of [{$Me_2N(CH_2)_3$}PhISnCH_2SnIPh_2] (10).

Elemental iodine (0.91 g, 3.60 mmol) was added in small portions and under ice cooling to a stirred solution of **5** (1.3 g, 1.80 mmol) in CH_2Cl_2 (70mL). Stirring was continued while warming to room temperature overnight. The solvent and the iodobenzene were removed in vacuo to afford 1.4 g (95%) of **10** as a slightly yellow solid (mp 163-165). Single crystals of **10** suitable for X-ray diffraction analysis were obtained by slow evaporation of a solution of the compound in CH_2Cl_2/ *n*-hexane.

^{1}H NMR (400.13 MHz, $CDCl_3$): δ 1.30–1.65 (m, 4H, Sn–CH_2–Sn + Sn–CH_2), 2.09 (8H, N(CH_3)$_2$ + Sn–CH_2–CH_2), 2.36 (t, 2H, CH_2–N), 7.36–7.92 (15H, Ph). **^{13}C{^{1}H} NMR** (100.63 MHz, $CDCl_3$): δ 7.1 (Sn–CH_2–Sn), 18.7 (Sn–CH_2), 21.7 (^2J(^{13}C–$^{117/119}$Sn) = 33 Hz, Sn–CH_2–CH_2), 46.3 (N(CH_3)$_2$), 61.1 (CH_2–N), 128.5 (^3J(^{13}C–$^{117/119}$Sn) = 56 Hz, $SnIPh_2$, C_m), 128.6 (^3J(^{13}C–$^{117/119}$Sn) = 60 Hz, SnIPh, C_m), 129.3 ($SnIPh_2$, C_P), 129.8 (^4J(^{13}C–$^{117/119}$Sn) = 14 Hz, SnIPh, C_P), 134.3 ($SnIPh_2$, C_o),

136.6 ($^2J(^{13}C–^{117/119}Sn)$ = 51 Hz, SnIPh, C_o) 137.2 (SnIPh, C_i), 138.2 ($SnIPh_2$, C_i). **$^{119}Sn\{^1H\}$ NMR** (111.92 MHz, $CDCl_3$): δ –54 ($SnIPh_2$), –102 (SnIPh). Anal. Calcd (%) for $C_{24}H_{29}I_2NSn_2$ (822.72): C 35.04, H 3.55, N 1.70.Found: C 35.2, H 3.6, N 1.5. **Electrospray MS**: m/z (%) positive mode: 614.1 (100, $[M – 2I – Ph + 2OH + MeOH + 3H_2O]^+$), negative mode: 380.7 (100, I_3^-), 126.9 (64, I^-).

Synthesis of [{$Me_2N(CH_2)_3$}PhFSn(CH_2)$SnFPh_2$] (11).

A solution of **10** (1.0 g, 1.22 mmol) in CH_2Cl_2 (30 mL) was mixed with a solution of KF (71 mg, 12.15 mmol) in water (30 mL).The biphasic mixture was stirred at room temperature for 8 days. The organic phase was then separated and dried over $MgSO_4$. Removing the solvent in vacuo afford a yellow solid. This solid was dissolved in acetone, and the solution was cooled at –5 °C for several days to give 400 mg (53%) of pure **11** as a white solid (mp 168-170 °C). Single crystals of **11** suitable for X-ray diffraction analysis were obtained by slow evaporation of a solution of the compound in acetone at –5°C.

^1H NMR (300.13 MHz, CD_2Cl_2, –64°C): δ 0.86–2.23 (complex pattern, 14H), 6.80–7.86 (15H, Ph). **$^{13}C\{^1H\}$ NMR** (125.68 MHz, $CDCl_3$): δ 9.9 (Sn–*C*H_2–Sn), 21.5 (Sn–*C*H_2), 30.8 (Sn–CH_2–*C*H_2), 46.2 (N(*C*H_3)$_2$), 61.7 (*C*H_2–N), 128.0 ($^3J(^{13}C–^{117/119}Sn)$ = 65 Hz, SnFPh, C_m), 128.6 ($^3J(^{13}C–^{117/119}Sn)$ = 56 Hz, $SnFPh_2$, C_m), 128.8 (SnFPh, C_P), 129.6 ($SnFPh_2$, C_P), 135.1 (SnFPh, C_o), 136.2 ($SnFPh_2$, C_o) 140.2 (SnFPh, C_i), 142.7 ($SnFPh_2$, C_i). **$^{19}F\{^1H\}$ NMR** (282.36 MHz, $CDCl_3$): δ –95 ($^1J(^{19}F–^{119}Sn)$ = 1039 Hz, SnFPh), –185 ($^1J(^{19}F–^{119}Sn)$ = 2221 Hz, $SnFPh_2$). **$^{119}Sn\{^1H\}$ NMR** (111.89 MHz, $CDCl_3$, –35°C): δ –18 (dd, $^1J(^{119}Sn–^{19}F)$ = 1168 Hz, $^3J(^{119}Sn–^{19}F)$ = 120 Hz, SnFPh), –159 (dd, $^1J(^{119}Sn–^{19}F)$ = 2201 Hz, $^3J(^{119}Sn–^{19}F)$ = 560 Hz $SnFPh_2$). Anal. Calcd (%) for $C_{24}H_{29}F_2NSn_2$ (606.91): C 47.50, H 4.82, N 2.31. Found: C 47.2, H 5.0, N 2.0. **Electrospray MS**: m/z (%) positive mode: 614.1 (100, $[M – 2F – Ph + 2OH + MeOH + 3H_2O]^+$), 306.6 (24, $[M – 2F – Ph + 2OH + H + MeOH + 3H_2O]^{2+}$), negative mode 588.1 (100), 626.1 (18, $[M + F]^-$).

Reaction of {$Me_2N(CH_2)_3$}Ph(F)$SnCH_2$Sn(F)Ph_2 (11) with one molar equivalent. of $NEt_4F·2H_2O$.

Compound **11** (70 mg, 0.12 mmol) and tetraethylammoniumfluoride dihydrate (21 mg, 0.12 mmol) were refluxed in CD_2Cl_2 for 5 min. From this solution NMR spectra were recorded.

^{19}F{^{1}H} NMR (282.36 MHz, CD_2Cl_2, –60°C): δ –93(12%), δ –140 (30%, $^{1}J(^{19}F–^{117/119}Sn)$ = 1833/1895 Hz, 2F, SnF_2Ph), –141 (15%, $^{1}J(^{19}F–^{117/119}Sn)$ = 1854 Hz, SnFPh), –163 (16%), –167(19%), –181(8%). **^{119}Sn{^{1}H} NMR** (111.89 MHz, CD_2Cl_2, –65°C): δ –60 (d, $^{1}J(^{119}Sn–^{19}F)$ = 1899 Hz, SnFPh), –252 (t, $^{1}J(^{119}Sn–^{19}F)$ = 1907 Hz, SnF_2Ph). **Electrospray MS**: m/z (%) positive mode: 130.2 (100, Et_4N^+), 614.1 (10, $[M – Et_4N – 2F – Ph + 2OH + MeOH + 3H_2O]^+$), negative mode: 719.1 (100, $[M – Et_4N – F + OH + 3H_2O + MeCN]^–$).

Synthesis of $\{Me_2N(CH_2)_3\}PhFSn(CH_2)_3SnFPh_2$ (16).

Elemental iodine (0.300 g, 1.20 mmol) was added in small portions and under ice cooling to a stirred solution of **7** (0.450 g, 0.60 mmol) in CH_2Cl_2 (30mL). Stirring was continued while warming to room temperature overnight. The solvent and iodobenzene were removed in vacuo to afford $\{Me_2N(CH_2)_3\}Ph(I)Sn(CH_2)_3Sn(I)Ph_2$ as yellow oil that was used for the next reaction without further purification. **^{119}Sn{^{1}H} NMR** ($CDCl_3$, 149.26 MHz): δ –54 (*Sn*IPh_2), –91 ($\{Me_2N(CH_2)_3\}$*Sn*IPh). A solution of $\{Me_2N(CH_2)_3\}Ph(I)Sn$-$(CH_2)_3Sn(I)Ph_2$ (0.300 g, 0.35 mmol) in CH_2Cl_2 (10 mL) was mixed with a solution of KF (0.200 g, 3.53 mmol) in water (15 mL). The biphasic mixture was stirred at room temperature for 3 days. The organic phase was then separated and dried over $MgSO_4$. Removing the solvent in vacuo afforded a white solid. This solid was dissolved in ethyl acetate, and the solution was cooled at –5 °C for several days to give 0.100 g (45%) of **7** as a white solid (mp 142-144 °C). Single crystals of **7** suitable for X-ray diffraction analysis were obtained by slow evaporation of a solution of the compound in ethyl acetate at 4°C.

^{1}H NMR (300.13 MHz, $CDCl_3$): δ 1–2.7 (complex pattern, 18H), 6.90–7.86 (15H, Ph). **^{13}C{^{1}H} NMR** (75.48 MHz, $CDCl_3$): δ 10.2 (Sn–*C*H_2), 10.5 (Sn*C*H_2), 18.5 (Sn*C*H_2), 21.4 ($^{2}J(^{13}C–^{117/119}Sn)$ = 29 Hz, $SnCH_2CH_2$), 22.1 ($SnCH_2CH_2CH_2Sn$), 45.8 N(CH_3)$_2$, 61.6 (CH_2N), 127.6 ($SnFPh_2$, C_m), 128.3 (SnFPh, C_m), 128.7 ($SnFPh_2$, C_p), 129.5 (SnFPh, C_p), 135.2 (SnFPh, C_o), 136.3 ($SnFPh_2$, C_o) 136.9 (SnFPh, C_i), 137.3 ($SnFPh_2$, C_i). **^{19}F{^{1}H} NMR** (376.61 MHz, $CDCl_3$): δ –146 ($\nu_{1/2}$ 183 Hz, $^{1}J(^{19}F–^{117/119}Sn)$ = 1688, 927 Hz, Sn*F*Ph), –177 ($\nu_{1/2}$ 387 Hz, $^{1}J(^{19}F–^{117/119}Sn)$ = 2097 Hz, Sn*F*Ph_2). **^{119}Sn{^{1}H} NMR** (149.26 MHz, $CDCl_3$): δ –47 (d, $^{1}J(^{119}Sn–^{19}F)$ = 1698 Hz, *Sn*FPh), –190 (dd, $^{1}J(^{119}Sn–^{19}F)$ = 2062, 950 Hz, $SnFPh_2$). Anal. Calcd (%) for $C_{26}H_{33}F_2NSn_2{\cdot}CH_2Cl_2$ (719.90): C 45.05, H 4.90, N 1.95. Found: C 45.5, H 5.2, N 2.0. **Electrospray MS**: m/z (%) positive mode: 632.2 (5, $[M – 2F + 2OH + H]^+$).

Reaction of $\{Me_2N(CH_2)_3\}Ph(F)Sn(CH_2)_3Sn(F)Ph_2$ (16) with one molar equivalent of $NEt_4F{\cdot}2H_2O$.

Compound **16** (0.040 g, 0.06 mmol) and tetraethylammonium fluoride dihydrate (0.012 g, 0.06 mmol) were mixed in CD_2Cl_2 and stirred for 5 min.

$^{19}F\{^1H\}$ NMR (376.6 MHz, CD_2Cl_2, –80°C): δ –143 (31%, d, $^1J(^{19}F–^{117/119}Sn)$ = 1124, 1498/1564 Hz), $^2J(^{19}F–^{19}F)$ = 83 Hz, Sn*F*Ph, **16**), –154 (14%, SnF_2Ph_2, [NEt_4][**16**$^{\cdot}$F]), –158 (7%, Sn*F*Ph, [NEt_4][**16**$^{\cdot}$F]), –159 (8%), –162 (2%), –169 (9%), –174 (29%, d, $^1J(^{19}F–^{117/119}Sn)$ = 1976/2070 Hz), $^2J(^{19}F–^{19}F)$ = 83 Hz, Sn*F*Ph_2, **16**). **$^{119}Sn\{^1H\}$ NMR** (149.26 MHz, CD_2Cl_2, –80°C): δ –47 (30%, d, $^1J(^{119}Sn–^{19}F)$ = 1566 Hz, *Sn*FPh, **16**), –86 (12%, d, $^1J(^{119}Sn–^{19}F)$ = 1957 Hz, *Sn*FPh, [NEt_4][**16**$^{\cdot}$F]), –88 (13%, d, $^1J(^{119}Sn–^{19}F)$ = 1973 Hz), – 203 (32%, dd, $^1J(^{119}Sn–^{19}F)$ = 2067, 941 Hz, *Sn*FPh_2, **16**), –222 (3%), –226 (4%), –235 (2%), –270 (*Sn*F_2Ph_2, [NEt_4][**16**$^{\cdot}$F]).

Reaction of $\{Me_2N(CH_2)_3\}Ph(F)Sn(CH_2)_3Sn(F)Ph_2$ (16) with two molar equivalent of $NEt_4F{\cdot}2H_2O$.

Compound **16** (0.035 g, 0.06 mmol) and tetraethylammonium fluoride dihydrate (0.020 g, 0.11 mmol) were mixed in CD_2Cl_2 and stirred for 5 min.

$^{19}F\{^1H\}$ NMR (376.6 MHz, CD_2Cl_2, –80°C): δ –143 (5%, d, Sn*F*Ph, **16**), –151 (5%), –154 (46%, SnF_2Ph_2, [NEt_4][**16**$^{\cdot}$F]), –156 (6%), –158 (23%, Sn*F*Ph, [NEt_4][**16**$^{\cdot}$F]), –160 (6%), –169 (5%), –174 (5%, d, Sn*F*Ph_2, **16**). **$^{119}Sn\{^1H\}$ NMR** (149.26 MHz, CD_2Cl_2, –80°C): δ –47 (5%, d, $^1J(^{119}Sn–^{19}F)$ = 1563 Hz, *Sn*FPh, **16**), –86 (40%, d, $^1J(^{119}Sn–^{19}F)$ = 1957 Hz, *Sn*FPh, [NEt_4][**16**$^{\cdot}$F]), –88 (8%, d, $^1J(^{119}Sn–^{19}F)$ = 1973 Hz), – 203 (7%, dd, $^1J(^{119}Sn–^{19}F)$ = 2067, 941 Hz, *Sn*FPh_2, **16**), –271 (40%, t, $^1J(^{119}Sn–^{19}F)$ = 1888 Hz, *Sn*F_2Ph_2, [NEt_4][**16**$^{\cdot}$F]).

Synthesis of $[\{Me_2N(CH_2)_3\}Ph_2Sn]_2CH_2$ (17).

To a solution of $(IPh_2Sn)_2CH_2$ (2.0 g, 2.50 mmol) in THF (60 mL) was added the Gringard reagent prepared from $Me_2N(CH_2)_3Cl$ (0.6 g, 5.0 mmol) and magnesium (0.2 mg, 5.0 mmol) in THF (20 mL). After the completion of the addition the mixture was stirred overnight at room temperature. The mixture was then heated at reflux for three hours before it was cooled to room temperature. THF was distilled off under reduced pressure, then cold water

(100 mL) was added, and the mixture was extracted three times with 70 mL of dichloromethane. The combined organic phases were dried with $MgSO_4$ and the solvents evaporated in vacuo to give (1.5 g, 83%) of **17** as yellow oil.

^{1}H NMR (400.13 MHz, $CDCl_3$): δ 0.59 (s, $^2J(^1H–^{117/119}Sn)$ = 60.7 Hz, 2H, Sn–CH_2–Sn), 1.05 (t, 4H, Sn–CH_2), 1.67 (m, 4H, Sn–CH_2–CH_2), 2.13 (s, 12H, N(CH_3)$_2$), 2.19 (t, 4H, CH_2–N), 7.21–7.50 (20H, Ph). **^{13}C{^{1}H} NMR** (100.63 MHz, $CDCl_3$): δ –17.9 ($^1J(^{13}C–^{117/119}Sn)$ = 257/267 Hz, Sn–*C*H_2–Sn), 8.8 ($^1J(^{13}C–^{117/119}Sn)$ = 365/389 Hz, Sn–*C*H_2), 23.6 ($^2J(^{13}C–^{117/119}Sn)$ = 18 Hz, Sn–CH_2–*C*H_2), 44.7 N(*C*H_3)$_2$, 62.6 ($^3J(^{13}C–^{117/119}Sn)$ = 71 Hz, *C*H_2–N), 128.2 ($^3J(^{13}C–^{117/119}Sn)$ = 47 Hz, C_m), 128.5 (C_P), 136.5 ($^2J(^{13}C–^{117/119}Sn)$ = 35 Hz, C_o), 140.5 ($^1J(^{13}C–^{117/119}Sn)$ = 466 Hz, $^3J(^{13}C–^{117/119}Sn)$ = 12 Hz, C_i). **^{119}Sn{^{1}H} NMR** (111.92 MHz, $CDCl_3$): δ –48 ($^2J(^{119}Sn–^{117/119}Sn)$ = 232 Hz).

Reaction of [{$Me_2N(CH_2)_3$}$Ph_2SnCH_2SnPh_3$], 5, with $Ph_3C^+PF_6^-$.

Ph_3CPF_6 (32 mg, 0.08 mmol) was added to a stirred solution of **5** (60 mg, 0.08 mmol) in toluene (10 mL). The suspension was stirred for 3 days. After that the solid was filtered off and washed with two portions of CH_2Cl_2 (10 mL) to give a white solid (33 mg, 92%).

^{1}H NMR (400.13 MHz, CD_3CN): δ 1.20 (b, 2H, Sn–CH_2–Sn), 1.72 (b, 2H, Sn–CH_2), 2.33–2.79 (complex pattern, 8H, Sn–CH_2–CH_2 + N(CH_3)$_2$), 3.65 (t, 2H, CH_2–N), 7.25–7.69 (15H, Ph). **^{19}F{^{1}H} NMR** (282.37 MHz, CD_3CN): δ –72 (d, $^1J(^{19}F–^{31}P)$ = 707 Hz). **^{31}P{^{1}H} NMR** (121.48, C_6D_6): δ –144 (sep, $^1J(^{19}F–^{31}P)$ = 711 Hz). Anal. Calcd (%) for $C_{24}H_{29}F_{12}NP_2Sn_2$ (858.8): C 33.56, H 3.40, N 1.63. Found: C 33.1, H 3.6, N 1.7. **Electrospray MS**: m/z (%) positive mode: 586.1 (100, $C_{24}H_{30}NOSn_2^+$, $[Me_2N(CH_2)_3(OH)SnCH_2SnPh_3]^+$), negative mode: 145.1 (100, PF_6^-).

Synthesis of bis(triphenylstannylmethyl)dimethylsilane, $(Ph_3SnCH_2)_2SiMe_2$ (18).

To a suspension of hexaphenyldistannane (8.20 g, 10.8 mmol) in THF (130mL) was added metallic sodium (0.53 g, 22.6 mmol) and a catalytic amount of naphthalene. The mixture was stirred at room temperature for two days. Then it was added to a solution of $Me_2Si(CH_2Cl)_2$ (1.50 g, 9.7 mmol) in THF (75mL) at –70°C. The brown mixture was stirred at room temperature for one day before THF was distilled off under reduced pressure. Cold water (100 mL) was added, and the mixture was extracted three times with 75 mL of

dichloromethane. The combined organic phases were dried with $MgSO_4$, filtered, and the solvents evaporated in vacuo to give compound **18** (7.2 g**,** 85%) as slightly yellowish oil, which was solidified after two days (mp 91-92 °C).

^{1}H NMR (300.13 MHz, $CDCl_3$): δ –0.07 (s, 6H, Me_2Si), 0.46 (s, 4H, $^2J(^1H–^{117/119}Sn)$ = 75.4/77.6 Hz, SiCH_2Sn), 7.28–7.60 (m, 30H, Ar–*H*). **^{13}C{^{1}H} NMR** (125.68 MHz, $CDCl_3$): δ –3.2 ($^1J(^{13}C–^{29}Si)$ = 23 Hz, $^1J(^{13}C–^{117/119}Sn)$ = 265/277 Hz, SiCH_2Sn), 2.8 ($^1J(^{13}C–^{29}Si)$ = 52 Hz, $^3J(^{13}C–^{117/119}Sn)$ = 13 Hz, Me_2Si), 128.4 ($^3J(^{13}C–^{117/119}Sn)$ = 50 Hz, C_m), 128.7 ($^4J(^{13}C–^{117/119}Sn)$ = 11 Hz, C_p), 136.9 ($^2J(^{13}C–^{117/119}Sn)$ = 37 Hz, C_o), 139.7 ($^1J(^{13}C–^{117/119}Sn)$ = 479/501 Hz, C_i). **^{29}Si{^{1}H} NMR** (59.63 MHz, $CDCl_3$): δ 6.2 ($^2J(^{29}Si–^{117/119}Sn)$ = 23 Hz). **^{119}Sn{^{1}H} NMR** (111.92 MHz, $CDCl_3$): δ –90.

Synthesis of bis(diphenyliodostannylmethyl)dimethylsilane, $(IPh_2SnCH_2)_2SiMe_2$ (19).

Elemental iodine (1.90 g, 7.6 mmol) was added in portions at 0 °C to a solution of (**18**) (3.00 g, 3.8 mmol) in CH_2Cl_2 (150 mL) and the mixture was allowed to reach room temperature and stirred overnight. Removing of the solvent and iodobenzene in vacuo gave (3.30 g, 98%) of (**19**) as colorless oil.

^{1}H NMR (500.13, $CDCl_3$): δ 0.21 (s, 6H, Me_2Si), 1.03 (s, 4H, $^2J(^1H–^{117/119}Sn)$ = 78.0 /81.1 Hz, SiCH_2Sn), 7.42–7.72 (m, 20H, Ar–*H*). **^{13}C{^{1}H} NMR** (125.77, $CDCl_3$): δ 2.5 ($^1J(^{13}C–^{29}Si)$ = 53 Hz, $^3J(^{13}C–^{117/119}Sn)$ = 16 Hz, Me_2Si), 3.5 ($^1J(^{13}C–^{117/119}Sn)$ = 253/267 Hz, $^1J(^{13}C–^{29}Si)$ = 47 Hz, $^3J(^{13}C–^{117/119}Sn)$ = 27 Hz, SiCH_2Sn), 128.8 ($^3J(^{13}C–^{117/119}Sn)$ = 60 Hz, C_m), 129.9 ($^4J(^{13}C–^{117/119}Sn)$ = 13 Hz, C_p), 135.7 ($^2J(^{13}C–^{117/119}Sn)$ = 49 Hz, C_o), 137.8 ($^1J(^{13}C–^{117\119}Sn)$ = 514\540 Hz, C_i). **^{29}Si{^{1}H} NMR** (59.63, $CDCl_3$): δ 6.7 ($^2J(^{29}Si–^{117/119}Sn)$ = 27 Hz). **^{119}Sn{^{1}H} NMR** (111.91, $CDCl_3$): δ –65 ($^1J(^{119}Sn–^{13}C_{CH2})$ = 266 Hz, $^1J(^{119}Sn–^{13}C_{Ph})$ = 537 Hz). Anal. Calcd (%) for $C_{28}H_{30}I_2SiSn_2$ (885.86): C 38.0, H 3.41. Found: C 38.4, H 3.4. **Electrospray MS**: *m/z* (%), positive mode, 663.1 (100, [**19** – 2I – Ph + 2OH + KOH + H_2O]$^+$), 649.0 (35, [**19** – 2I + OH]$^+$), negative mode, 127.0 (25, I^-).

Synthesis of bis(phenyldiiodostannylmethyl)dimethylsilane, $(I_2PhSnCH_2)_2SiMe_2$ (20).

Elemental iodine (0.3 g, 1.0 mmol) was added in portions at 0 °C to a solution of (**18**) (0.2 g, 0.3 mmol) in CH_2Cl_2 (30 mL) and the mixture was allowed to reach room temperature and

stirred overnight. Removing of the solvent and iodobenzene in vacuo gave (0.2 g, 96%) of (**20**) as yellow oil.

^{1}H NMR (500.13, $CDCl_3$): δ 0.34 (s, 6H, *Me*$_2$Si), 1.55 (s, 4H, $^{2}J(^{1}H–^{117/119}Sn)$ = 86.8 /90.6 Hz, Si*C*H$_2$Sn), 7.41–7.70 (m, 10H, Ar–*H*). **^{13}C{^{1}H} NMR** (125.77, $CDCl_3$): δ 2.1 ($^{1}J(^{13}C–^{29}Si)$ = 54 Hz, $^{3}J(^{13}C–^{117/119}Sn)$ = 21 Hz, *Me*$_2$Si), 12.6 ($^{1}J(^{13}C–^{117/119}Sn)$ = 260/271 Hz, $^{3}J(^{13}C–^{117/119}Sn)$ = 34 Hz, Si*C*H$_2$Sn), 129.1 ($^{3}J(^{13}C–^{117/119}Sn)$ = 78 Hz, C_m), 131.1 ($^{4}J(^{13}C–^{117/119}Sn)$ = 15 Hz, C_p), 134.1 ($^{2}J(^{13}C–^{117/119}Sn)$ = 62 Hz, C_o), 137.0 (C_i). **^{29}Si{^{1}H} NMR** (59.63, $CDCl_3$): δ 6.8 ($^{2}J(^{29}Si–^{117/119}Sn)$ = 33 Hz). **^{119}Sn{^{1}H} NMR** (111.91, $CDCl_3$): δ –219. Anal. Calcd (%) for $C_{16}H_{20}I_4SiSn_2$ (985.46): C 19.50, H 2.05. Found: C 20.3, H 2.3.

Synthesis of bis(triiodostannylmethyl)dimethylsilane, $(I_3SnCH_2)_2SiMe_2$ (21).

Elemental iodine (0.8 g, 2.9 mmol) was added in portions at 0 °C to a solution of (**18**) (0.4 g, 0.5 mmol) in CH_2Cl_2 (40 mL), the stirring was continued for 4 weeks at room temperature. Removing of the solvent and iodobenzene in vacuo gave (0.5 g, 92%) of (**21)** as dark green oil.

^{1}H NMR (400.13, $CDCl_3$): δ 0.55 (s, 6H, *Me*$_2$Si), 2.27 (s, 4H, $^{2}J(^{1}H–^{117/119}Sn)$ = 103.2 /107.7 Hz, Si*C*H$_2$Sn). **^{13}C{^{1}H} NMR** (100.63, $CDCl_3$): δ 1.4 ($^{1}J(^{13}C–^{29}Si)$ = 55 Hz, $^{3}J(^{13}C–^{117/119}Sn)$ = 26 Hz, *Me*$_2$Si), 19.8 ($^{1}J(^{13}C–^{117/119}Sn)$ = 283/296 Hz, $^{3}J(^{13}C–^{117/119}Sn)$ = 46 Hz, Si*C*H$_2$Sn). **^{29}Si{^{1}H} NMR** (59.63, $CDCl_3$): δ 8.3 ($^{2}J(^{29}Si–^{117/119}Sn)$ = 44 Hz). **^{119}Sn{^{1}H} NMR** (111.91, $CDCl_3$): δ –750. Anal. Calcd (%) for $C_5H_{12}Cl_2I_6SiSn_2$ $(I_3SnCH_2)_2SiMe_2 \cdot CH_2Cl_2$ (1169.98): C 5.13, H 1.03. Found: C 5.1, H 1.1. **Electrospray MS**: *m/z* (%), negative mode, 380.8 (100, I_3^-), 127.0 (50, I^-).

Synthesis of bis(diphenylchloridostannylmethyl)dimethylsilane, $(ClPh_2SnCH_2)_2SiMe_2$ (22).

To a solution of **18** (0.35 g, 0.45 mmol) in CH_2Cl_2 (25 mL) was added a solution of hydrogen chloride (1.0 M in diethyl ether, 32 mg, 0.89 mmol) in one portion at 0 °C and the mixture was stirred for 30 min at the same temperature. Then the mixture was stirred overnight at ambient temperature. Evaporation of the solvent and the benzene gave compound **22** (0.29 mg, 95%) as slightly yellow oil.

^{1}H NMR (300.13 MHz, $CDCl_3$): δ –0.20 (s, 6H, Me_2Si), 0.79 (s, 4H, $^{2}J(^{1}H–^{117/119}Sn)$ = 77.2/80.5 Hz, $SiCH_2Sn$), 7.39 – 7.71 (m, 20H, Ar–*H*). **^{13}C{^{1}H} NMR** (75.47 MHz, $CDCl_3$): δ 2.5 ($^{3}J(^{13}C–^{117/119}Sn)$ = 17 Hz, Me_2Si), 3.1 (($^{1}J(^{13}C–^{117/119}Sn)$ = 314/318 Hz, $SiCH_2Sn$), 128.9 ($^{3}J(^{13}C–^{117/119}Sn)$ = 61 Hz, C_m), 130.1 ($^{4}J(^{13}C–^{117/119}Sn)$ = 13 Hz, C_p), 135.5 ($^{2}J(^{13}C–^{117/119}Sn)$ = 51 Hz, C_o), 139.4, C_i). **^{29}Si{^{1}H} NMR** (59.63 MHz, $CDCl_3$): δ 6.1 ($^{2}J(^{29}Si–^{117/119}Sn)$ = 29 Hz). **^{119}Sn{^{1}H} NMR** (111.92 MHz, $CDCl_3$): δ 26. **Electrospray MS**: *m/z* (%), negative mode, 460.9 (30, [**22** – Cl – Ph + 3OH]$^{-}$.

Synthesis of bis(phenyldichloridostannylmethyl)dimethylsilane, $(Cl_2PhSnCH_2)_2SiMe_2$ (23).

To a solution of **18** (0.30 g, 0.38 mmol) in CH_2Cl_2 (15 mL) was added a solution of hydrogen chloride (1.0 M in diethyl ether, 56 mg, 1.53 mmol) in one portion at 0 °C and the mixture was stirred for 30 min at the same temperature. Then the mixture was stirred overnight at ambient temperature. Evaporation of the solvent and the benzene gave compound **23** (0.23 mg, 97%) as yellow oil.

^{1}H NMR (500.13, $CDCl_3$): δ 0.46 (s, 6H, Me_2Si), 1.22 (s, 4H, $^{2}J(^{1}H–^{117/119}Sn)$ = 89.5 /92.2 Hz, $SiCH_2Sn$), 7.46–7.78 (m, 10H, Ar–*H*). **^{13}C{^{1}H} NMR** (125.77, $CDCl_3$): δ 2.1 ($^{1}J(^{13}C–^{29}Si)$ = 54 Hz, $^{3}J(^{13}C–^{117/119}Sn)$ = 24 Hz, Me_2Si), 10.4 ($^{1}J(^{13}C–^{117/119}Sn)$ = 350/367 Hz, $^{3}J(^{13}C–^{117/119}Sn)$ = 30 Hz, $SiCH_2Sn$), 129.6 ($^{3}J(^{13}C–^{117/119}Sn)$ = 82/85 Hz, C_m), 131.6 ($^{4}J(^{13}C–^{117/119}Sn)$ = 17 Hz, C_p), 134.3 ($^{2}J(^{13}C–^{117/119}Sn)$ = 66 Hz, C_o), 139.4 ($^{1}J(^{13}C–^{117/119}Sn)$ = 720/752 Hz, C_i). **^{29}Si{^{1}H} NMR** (59.63, $CDCl_3$): δ 5.9 ($^{2}J(^{29}Si–^{117/119}Sn)$ = 42 Hz). **^{119}Sn{^{1}H} NMR** (111.91, $CDCl_3$): δ 52. Anal. Calcd (%) for $(Cl_2PhSnCH_2)_2SiMe_2 \cdot CH_2Cl_2$ $C_{17}H_{22}Cl_6SiSn_2$ (704,57): C 29.0, H 3.15. Found: C 29.4, H 3.7. **Electrospray MS**: *m/z* (%), positive mode, 564.9 (78, [**23** – 2Cl + OH]$^{+}$), negative mode, 654.7 (100, [**23** + OH + H_2O]$^{-}$), 598.8 (40, [**23** – 2Cl + 3OH]$^{-}$).

Synthesis of bis(diphenylfluoridostannylmethyl)dimethylsilane, $(FPh_2SnCH_2)_2SiMe_2$ (24).

To a solution of $(IPh_2SnCH_2)_2SiMe_2$ (3.00 g, 3.4 mmol) in CH_2Cl_2 (25 mL) was added a solution of KF (1.90 g, 34 mmol) in water (20 mL) with stirring for three days. The colourless precipitate formed was filtered off, washed with water, Acetone, and diethylether, and then dried to give (1.80 g, 79%) of **24** as a colourless amorphous solid.

Synthesis of $[Me_2N(CH_2)_3Ph_2SnCH_2]_2SiMe_2$ (25).

A solution of $Me_2N(CH_2)_3MgCl$, prepared from $Me_2(CH_2)_3Cl$ (1.35 g, 11.10 mmol) and magnesium (0.28 g, 11.32 mmol) in THF (40 mL) was added dropwise to a suspension of $(FPh_2SnCH_2)_2SiMe_2$ (1.49 g, 2.22 mmol) in THF (60 mL) during a period of 1 h. After the addition had been completed, the reaction mixture was heated at reflux overnight and then cooled to room temperature. THF was distilled off under reduced pressure, then cold water (80 mL) was added, and the mixture was extracted three times with 50 mL of dichloromethane. The combined organic phases were dried with $MgSO_4$ and the solvents evaporated in vacuo to give (1.43 g, 80%) of **25** as colorless oil.

^{1}H NMR (400.13 MHz, $CDCl_3$): δ –0.07 (s, 6H, *Me*$_2$Si), 0.19 (s, 4H, $^2J(^1H–^{117/119}Sn)$ = 71.8/74.8 Hz, SiC*H*$_2$Sn), 1.23 (t, 4H, Sn–C*H*$_2$), 1.74 (m, 4H, Sn–CH$_2$–C*H*$_2$), 2.15 (s, 12H, N(CH$_3$)$_2$), 2.22 (t, 4H, C*H*$_2$–N), 7.33–7.60 (m, 20H, Ar–*H*). **^{13}C{^{1}H} NMR** (100.63 MHz, $CDCl_3$): δ –3.8 ($^1J(^{13}C–^{29}Si)$ = 21 Hz, $^1J(^{13}C–^{117/119}Sn)$ = 241/252 Hz, Si*C*H$_2$Sn), 2.7 ($^1J(^{13}C–^{29}Si)$ = 52 Hz, $^3J(^{13}C–^{117/119}Sn)$ = 12 Hz, *Me*$_2$Si), 9.1 ($^1J(^{13}C–^{117/119}Sn)$ = 363/ 380 Hz, Sn–CH$_2$), 24.5 ($^2J(^{13}C–^{117/119}Sn)$ = 19 Hz, Sn–CH$_2$–*C*H$_2$), 45.5 N(CH$_3$)$_2$, 63.5 ($^3J(^{13}C–^{117/119}Sn)$ = 67 Hz, CH$_2$–N), 128.1 ($^3J(^{13}C–^{117/119}Sn)$ = 45 Hz, C_m), 128.4 ($^4J(^{13}C–^{117/119}Sn)$ = 11 Hz, C_p), 136.6 ($^2J(^{13}C–^{117/119}Sn)$ = 35 Hz, C_o), 140.6 ($^1J(^{13}C–^{117/119}Sn)$ = 438/459 Hz, C_i). **^{29}Si{^{1}H} NMR** (59.63 MHz, $CDCl_3$): δ 5.8 ($^2J(^{29}Si–^{117/119}Sn)$ = 22 Hz). **^{119}Sn{^{1}H} NMR** (111.92 MHz, $CDCl_3$): δ –60.

Synthesis of bis(triiodostannyl)butane, $I_3Sn(CH_2)_4SnI_3$, (27).

Elemental iodine (3.02 g, 11.90 mmol) was added in portions at 0 °C to a solution of $Ph_3Sn(CH_2)_4SnPh_3$ (1.50 g, 1.98 mmol) in CH_2Cl_2 (mL), the stirring was continued for 4 weeks at room temperature. Removing of the solvent and iodobenzene in vacuo followed by washing with Et_2O gave (1.25 g, 60%) of **27** as light yellowish solid (mp 136-137 °C). Single crystals of **27** suitable for X-ray diffraction analysis were obtained by standing a solution of the compound in $CDCl_3$ at –5°C.

^{1}H NMR (300.13, $CDCl_3$): δ 1.88 (m, 4H, $^3J(^1H–^{117/119}Sn)$ = 139.8 Hz, C–C*H*$_2$–C*H*$_2$–C), 2.64 (t, 4H, $^1J(^1H–^{117/119}Sn)$ = 58.18 Hz, Sn–C*H*$_2$). **^{13}C{^{1}H} NMR** (75.47, $CDCl_3$): δ 28.1 ($^2J(^{13}C–^{117/119}Sn)$ = 126/131 Hz, C–*C*H$_2$–*C*H$_2$–C), 30.7 ($^1J(^{13}C–^{117/119}Sn)$ = 440/459 Hz, *C*H$_2$Sn). **^{119}Sn{^{1}H} NMR**

(111.91, $CDCl_3$): δ –613. Anal. Calcd (%) for $C_4H_8I_6Sn_2$ (1055.3): C 4.6, H 0.8. Found: C 4.8, H 0.8.

Complexation Studies

Synthesis of the complex [PPh_4][21·Cl]

Tetraphenylphosphonium chloride (24 mg, 0.06 mmol) was added to a solution of **21** (70 mg, 0.06 mmol) in $CDCl_3$ (0.6 mL) and the mixture was stirred for 5 min.

^{1}H NMR (300.13 MHz, $CDCl_3$): δ 0.52 (s, 6H, *Me*$_2$Si), 2.40 (s, 4H, $^2J(^1H–^{117/119}Sn)$ = 113.4 Hz, SiC*H*$_2$Sn), 7.59– 7.95 (20H, *Ph*$_4$P). **^{13}C{^{1}H} NMR** (75.47 MHz, $CDCl_3$): δ 1.23 ($^1J(^{13}C–^{29}Si)$ = 34 Hz, *Me*$_2$Si), 25.1 (Si*C*H$_2$Sn), 117.2 ($^1J(^{13}C–^{31}P)$ = 90 Hz, Ph_4P, C_i), 130.8 ($^3J(^{13}C–^{31}P)$ = 12 Hz, Ph_4P, C_m), 134.3 ($^2J(^{13}C–^{31}P)$ = 10 Hz, Ph_4P, C_o), 135.8 ($^4J(^{13}C–^{31}P)$ = 4 Hz, Ph_4P, C_p). **^{29}Si{^{1}H} NMR** (59.63 MHz, $CDCl_3$): δ 7.0 ($^2J(^{29}Si–^{117/119}Sn)$ = 53 Hz). **^{31}P{^{1}H} NMR** (121.49 MHz, $CDCl_3$): δ 24. **^{119}Sn{^{1}H} NMR** (111.91 MHz, $CDCl_3$): δ –817. **Electrospray MS**: *m/z* (%), positive mode, 339.1 (100, $[PPh_4]^+$), negative mode, 380.7 (100, $[I_3]^-$), 168.0 (23, $[I{\cdot}CH_3CN]^-$), 127.0 (22, $[I]^-$).

Synthesis of the complex [PPh_4][21·Br]

Tetraphenylphosphonium bromide (23 mg, 0.06 mmol) was added to a solution of **21** (60 mg, 0.06 mmol) in $CDCl_3$ (0.6 mL) and the mixture was stirred for 5 min.

^{1}H NMR (300.13 MHz, $CDCl_3$): δ 0.53 (s, 6H, *Me*$_2$Si), 2.46 (s, 4H, $^2J(^1H–^{117/119}Sn)$ = 112.9 Hz, SiC*H*$_2$Sn), 7.60–7.95 (20H, *Ph*$_4$P). **^{13}C{^{1}H} NMR** (75.47 MHz, $CDCl_3$): δ 1.24 ($^1J(^{13}C–^{29}Si)$ = 33 Hz, *Me*$_2$Si), 25.1 (Si*C*H$_2$Sn), 117.2 ($^1J(^{13}C–^{31}P)$ = 89 Hz, Ph_4P, C_i), 130.8 ($^3J(^{13}C–^{31}P)$ = 13 Hz, Ph_4P, C_m), 134.3 ($^2J(^{13}C–^{31}P)$ = 10 Hz, Ph_4P, C_o), 135.8 ($^4J(^{13}C–^{31}P)$ = 3 Hz, Ph_4P, C_p). **^{29}Si{^{1}H} NMR** (59.63 MHz, $CDCl_3$): δ 7.2 ($^2J(^{29}Si–^{117/119}Sn)$ = 51 Hz). **^{31}P{^{1}H} NMR** (121.49 MHz, $CDCl_3$): δ 24. **^{119}Sn{^{1}H} NMR** (111.91 MHz, $CDCl_3$): δ –827.

Synthesis of the complex [PPh_4][21·I]

Tetraphenylphosphonium iodide (26 mg, 0.06 mmol) was added to a solution of **21** (60 mg, 0.06 mmol) in $CDCl_3$ (0.6 mL) and the mixture was stirred for 5 min.

^{1}H NMR (300.13 MHz, $CDCl_3$): δ 0.54 (s, 6H, *Me*$_2$Si), 2.50 (s, 4H, $^{2}J(^{1}H–^{117/119}Sn)$ = 110.1 Hz, SiC*H*$_2$Sn), 7.59–7.94 (20H, *Ph*$_4$P). **^{13}C{^{1}H} NMR** (75.47 MHz, $CDCl_3$): δ 1.18 (*Me*$_2$Si), 23.7 (Si*C*H$_2$Sn), 117.2 ($^{1}J(^{13}C–^{31}P)$ = 90 Hz, Ph_4P, C_i), 130.8 ($^{3}J(^{13}C–^{31}P)$ = 13 Hz, Ph_4P, C_m), 134.3 ($^{2}J(^{13}C–^{31}P)$ = 10 Hz, Ph_4P, C_o), 135.7 ($^{4}J(^{13}C–^{31}P)$ = 3 Hz, Ph_4P, C_p). **^{29}Si{^{1}H} NMR** (59.63 MHz, $CDCl_3$): δ 7.8 ($^{2}J(^{29}Si–^{117/119}Sn)$ = 49 Hz). **^{31}P{^{1}H} NMR** (121.49 MHz, $CDCl_3$): δ 24. **^{119}Sn{^{1}H} NMR** (111.91 MHz, $CDCl_3$): δ –861.

Synthesis of the complex [PPh$_4$][23·Cl]

Tetraphenylphosphonium chloride (30 mg, 0.08 mmol) was added to a solution of **23** (50 mg, 0.08 mmol) in $CDCl_3$ (0.6 mL) and the mixture was stirred for 5 min. In the next day Hexane was added, and the reaction mixture was slowly evaporated to yield the complex [PPh_4][**23**·Cl] (79 mg, 98%) as light yellow oil.

^{1}H NMR (300.13 MHz, $CDCl_3$): δ 0.42 (s, 6H, *Me*$_2$Si), 1.42 (s, 4H, $^{2}J(^{1}H–^{117/119}Sn)$ = 101.7 /104.3 Hz, SiC*H*$_2$Sn), 7.25–8.22 (complex pattern, 30H, Ph). **^{13}C{^{1}H} NMR** (75.47 MHz, $CDCl_3$): δ 1.9 ($^{1}J(^{13}C–^{29}Si)$ = 43 Hz, *Me*$_2$Si), 20.9 (Si*C*H$_2$Sn), 117.2 ($^{1}J(^{13}C–^{31}P)$ = 90 Hz, Ph_4P, C_i), 128.1 ($^{3}J(^{13}C–^{117/119}Sn)$ = 89/92 Hz, C_m), 129.4 ($^{4}J(^{13}C–^{117/119}Sn)$ = 19 Hz, C_p), 130.7 ($^{3}J(^{13}C–^{31}P)$ = 13 Hz, Ph_4P, C_m), 134.2 ($^{2}J(^{13}C–^{31}P)$ = 10 Hz, Ph_4P, C_o), 135.5 ($^{2}J(^{13}C–^{117/119}Sn)$ = 68 Hz, C_o), 135.7 ($^{4}J(^{13}C–^{31}P)$ = 4 Hz, Ph_4P, C_p), 145.9 (C_i). **^{29}Si{^{1}H} NMR** (59.63 MHz, $CDCl_3$): δ 3.3 ($^{2}J(^{29}Si–^{117/119}Sn)$ = 62 Hz). **^{31}P{^{1}H} NMR** (121.49 MHz, $CDCl_3$): δ 24. **^{119}Sn{^{1}H} NMR** (111.91 MHz, $CDCl_3$): δ –119. **Electrospray MS**: *m/z* (%), positive mode, 339.1 (100, $[PPh_4]^+$), negative mode, 600.1 (100, [**23** – Cl + O]$^-$).

Synthesis of the complex [NEt$_4$][23·F]

Tetraethylammonium fluoride dihydrate (12 mg, 0.06 mmol) was added to a solution of **23** (40 mg, 0.06 mmol) in $CDCl_3$ (0.6 mL) and the mixture was stirred for 5 min. In the next day Hexane was added, and the reaction mixture was slowly evaporated to yield the complex [**23**·F][Et_4N] (42 mg, 83%) as yellow oil.

^{1}H NMR (300.13 MHz, $CDCl_3$): δ 0.30 (s, 6H, *Me*$_2$Si), 1.01 (t, 12H, CH_3 (Et_4N)), 1.12 (s, 4H, $^{2}J(^{1}H–^{117/119}Sn)$ = 114.2 /115.6 Hz, SiC*H*$_2$Sn), 2.87 (q, 8H, CH_2 (Et_4N)), 7.30–8.22 (m, 10H, Ar–

H). **^{13}C{^{1}H} NMR** (75.47 MHz, $CDCl_3$): δ 2.2 ($^{1}J(^{13}C–^{29}Si)$ = 43 Hz, Me_2Si), 7.4 (CH_3 (Et_4N)), 18.0 ($SiCH_2Sn$), 52.3 (CH_2 (Et_4N)), 128.3 ($^{3}J(^{13}C–^{117/119}Sn)$ = 92 Hz, C_m), 129.8 (C_p), 135.9 ($^{2}J(^{13}C–^{117/119}Sn)$ = 70 Hz, C_o), 145.3 (C_i). **^{19}F{^{1}H} NMR** (282.40 MHz, $CDCl_3$): δ –86 (s, $^{1}J(^{19}F–^{117/119}Sn)$ = 1556 Hz). **^{29}Si{^{1}H} NMR** (59.63 MHz, $CDCl_3$): δ 3.4 ($^{2}J(^{29}Si–^{117/119}Sn)$ = 54 Hz). **^{119}Sn{^{1}H} NMR** (111.91 MHz, $CDCl_3$): δ –172 (d, $^{1}J(^{119}Sn–^{19}F)$ = 1558 Hz). **Electrospray MS**: *m/z* (%), positive mode, 130.2 (100, $[NEt_4]^+$), negative mode, 636.8 (100, [**23** + OH]$^-$), 600.1 (32,[**23** – Cl + O]$^-$).

Synthesis of the complex [NEt_4][24·F]

Tetraethylammonium fluoride dihydrate (17 mg, 0.09 mmol) was added to a solution of **24** (60 mg, 0.09 mmol) in $CDCl_3$ (0.6 mL) and the mixture was stirred for 5 min. In the next day Hexane was added, and the reaction mixture was slowly evaporated to yield the complex [NEt_4][**24**·F] (61 mg, 83%) as yellow oil.

^{1}H NMR (300.13 MHz, $CDCl_3$): δ 0.00 (s, 6H, Me_2Si), 0.19 (s, 4H, $SiCH_2Sn$), 0.57 (t, 12H, CH_3 (Et_4N)), 2.28 (q, 8H, CH_2 (Et_4N)), 7.15– 7.85 (m, 20H, Ar–*H*). **^{13}C{^{1}H} NMR** (75.47 MHz, $CDCl_3$): δ 2.9 ($^{1}J(^{13}C–^{29}Si)$ = 33 Hz, Me_2Si), 4.9 ($SiCH_2Sn$), 6.8 (CH_3 (Et_4N)), 51.4 (CH_2 (Et_4N)), 127.5 ($^{3}J(^{13}C–^{117/119}Sn)$ = 65 Hz, C_m), 128.0 (C_p), 136.7 ($^{2}J(^{13}C–^{117/119}Sn)$ = 49 Hz, C_o), 147.4 (C_i). **^{18}F{^{1}H} NMR** (282.40 MHz, $CDCl_3$): δ –159 (s, $^{1}J(^{19}F–^{117/119}Sn)$ = 1955 Hz), –129 (s, $^{1}J(^{19}F–^{117/119}Sn)$ = 1308 Hz). **^{29}Si{^{1}H} NMR** (59.63 MHz, $CDCl_3$): δ 4.4 ($^{2}J(^{29}Si–^{117/119}Sn)$ = 36 Hz). **^{119}Sn{^{1}H} NMR** (111.91, $CDCl_3$): δ –215 (dd, $^{1}J(^{119}Sn–^{19}F)$ = 1558 Hz).

Synthesis of the complex [PPh_4][26·Cl]

Tetraphenylphosphonium chloride (25 mg, 0.07 mmol) was added to a solution of **26** (70 mg, 0.07 mmol) in $CDCl_3$ (0.6 mL) and the mixture was stirred for 5 min.

^{1}H NMR (300.13 MHz, $CDCl_3$): δ 2.0 (m, 2H, C–CH_2–C), 2.80 (t, 4H, $^{2}J(^{1}H–^{117/119}Sn)$ = 65.5 Hz, Sn–CH_2), 7.59–7.95 (20H, Ph_4P). **^{13}C{^{1}H} NMR** (75.47 MHz, $CDCl_3$): δ 25.3 (C–CH_2–C), 36.4 (Sn–CH_2), 117.2 ($^{1}J(^{13}C–^{31}P)$ = 89 Hz, Ph_4P, C_i), 130.8 ($^{3}J(^{13}C–^{31}P)$ = 13 Hz, Ph_4P, C_m), 134.3 ($^{2}J(^{13}C–^{31}P)$ = 10 Hz, Ph_4P, C_o), 135.8 ($^{4}J(^{13}C–^{31}P)$ = 3 Hz, Ph_4P, C_p). **^{31}P{^{1}H} NMR** (121.49 MHz, $CDCl_3$): δ 24. **^{119}Sn{^{1}H} NMR** (111.91 MHz, $CDCl_3$): δ –732.

Synthesis of the complex [PPh_4][26·Br]

Tetraphenylphosphonium bromide (28 mg, 0.06 mmol) was added to a solution of **26** (70 mg, 0.06 mmol) in $CDCl_3$ (0.6 mL) and the mixture was stirred for 5 min.

^{1}H NMR (300.13 MHz, $CDCl_3$): δ 1.98 (m, 2H, C–C*H*$_2$–C), 2.85 (t, 4H, ^2J(^{1}H–$^{117/119}$Sn) = 63.7 Hz, Sn–C*H*$_2$), 7.59–7.95 (20H, *Ph*$_4$P). **^{13}C{^{1}H} NMR** (75.47 MHz, $CDCl_3$): δ 25.3 (C–*C*H$_2$–C), 36.7 (Sn–*C*H$_2$), 117.2 (^1J(^{13}C–^{31}P) = 89 Hz, Ph_4P, C_i), 130.8 (^3J(^{13}C–^{31}P) = 12 Hz, Ph_4P, C_m), 134.3 (^2J(^{13}C–^{31}P) = 10 Hz, Ph_4P, C_o), 135.8 (^4J(^{13}C–^{31}P) = 3 Hz, Ph_4P, C_p). **^{31}P{^{1}H} NMR** (121.49 MHz, $CDCl_3$): δ 24. **^{119}Sn{^{1}H} NMR** (111.91, $CDCl_3$): δ –754.

Synthesis of the complex [PPh_4][26·I]

Tetraphenylphosphonium iodide (31 mg, 0.07 mmol) was added to a solution of **26** (70 mg, 0.07 mmol) in $CDCl_3$ (0.6 mL) and the mixture was stirred for 5 min.

^{1}H NMR (400.13 MHz, $CDCl_3$): δ 1.91 (m, 2H, C–C*H*$_2$–C), 2.89 (t, 4H, ^2J(^{1}H–$^{117/119}$Sn) = 65.5 Hz, Sn–C*H*$_2$), 7.60–7.95 (20H, *Ph*$_4$P). **^{13}C{^{1}H} NMR** (75.47 MHz, $CDCl_3$): δ 25.7 (C–*C*H$_2$–C), 34.9 (Sn–*C*H$_2$), 117.2 (^1J(^{13}C–^{31}P) = 90 Hz, Ph_4P, C_i), 130.9 (^3J(^{13}C–^{31}P) = 13 Hz, Ph_4P, C_m), 134.3 (^2J(^{13}C–^{31}P) = 10 Hz, Ph_4P, C_o), 135.8 (^4J(^{13}C–^{31}P) = 3 Hz, Ph_4P, C_p). **^{31}P{^{1}H} NMR** (121.49 MHz, $CDCl_3$): δ 24. **^{119}Sn{^{1}H} NMR** (111.91 MHz, $CDCl_3$): δ–771.

In situ reaction of 27 with KSCN and 18–crown–6 in $CDCl_3$

To a solution of **27** (60 mg, 0.06 mmol) in $CDCl_3$ (3 mL) was added KSCN (6 mg, 0.06 mmol) and 18–crown–6 (17 mg, 0.06 mmol). The mixture was stirred for two hours, and the yellow color of the solution was turned to red.

^{119}Sn{^{1}H} NMR (111.91 MHz, $CDCl_3$): δ–660.

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3 Tin–Nitrogen-Based Chemosensors for Detection of Fluoride Anions

3.1 Attempt to Design a Colorimetric Fluoride Sensor Using Azobenzene-Substituted Organotin Compound

3.1.1 INTRODUCTION

Developing of selective and sensitive methods for the detection of fluoride anions is of great interest.[1][2] That is return to the importance of fluoride anions in different biological, pharmacological and environmental fields. Ion selective electrodes proved to give satisfied results with selective detection and quantitative fluoride analysis.[3][4][5] However, there is still a big requirement to develop highly selective, sensitive and rapid methods for detection of fluoride anions in environmental samples.[6]

Colorimetric sensors showed good results in the detection of fluoride anions, in which the sensing is usually accompanied with visible color-change.[2] Many successful examples of organic azo compounds for sensing of fluoride anions are reported whereas the examples of organoelement azo dyes are still limited.

Boronic acid-substituted azobenzenes showed good results in the field of the saccharide colorimetric sensing.[7] For examples, a clear color change from orange to red upon addition of sugar is achieved depending on boron-nitrogen (B–N) interaction between two molecules (**A**, Figure 1).[8] A large color change upon saccharide addition from purple to red is reported as a result of the intramolecular B–N interaction between the boronic acid moiety and the nitrogen of the aniline moiety (**B**, Figure 1).[9]

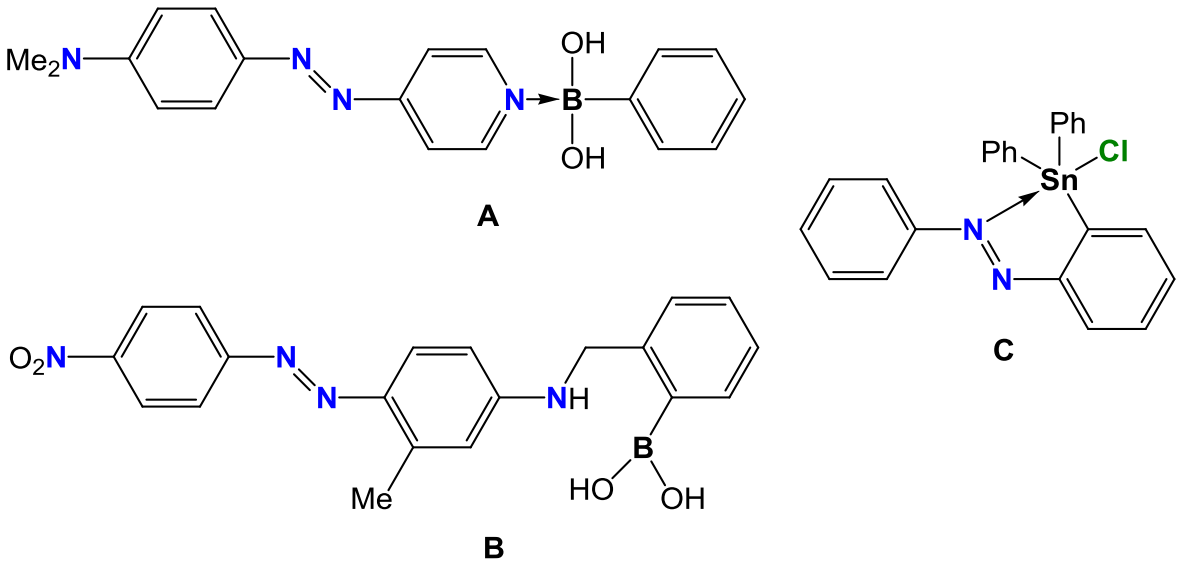


Figure 1. Different azo compounds reported in the literatures.

A similar intramolecular interaction is widely studied in organotin compounds bearing nitrogen-containing donor moieties. The tin atoms in these compounds should have sufficient Lewis acidity enabling it to form intramolecular N–Sn interaction.[10][11][12] Furthermore, the binding of fluoride anions to this type of compounds is also studied.[3][13][14]

For these reasons, applying the same principle used for colorimetric sugar sensing by the N→B intramolecular interaction could be of great interest for designing organotin substituted azobenzenes. The N–Sn interaction in these receptors could be responsible for the color change upon the reaction with fluoride anions. These organotin compounds could find applications in the field of developing colorimetric sensors for detection of fluoride anions.

The first example of pentacoordinated organotin compound with N→Sn intramolecular coordination of the nitrogen in the azo group with the tin atom was reported for the yellow-orange compound {(2-C_6H_4N=NPh)Sn(Ph)Cl_2} (**C**, Figure 1).[15] However, this compound had not been studied as colorimetric sensor for fluoride anions.

Here will be reported the syntheses of organotin compounds containing azobenzenes, the ability of these compounds to form intramolecular N→Sn interaction, as well as, the possibility to use them as colorimetric sensors for detection of fluoride anions will be tested.

Inspired by the design of compound **B** (Figure 1) who showed satisfied results in the field of colorimetric sensing of sugar with a Nitrogen–Boron interaction based system, here will be presented the attempt to design organotin-based sensor for colorimetric detection of fluoride anions (Chart 1). Upon the reaction with fluoride anion, the intramolecular N→Sn interaction will be broken and a color change is to be expected.

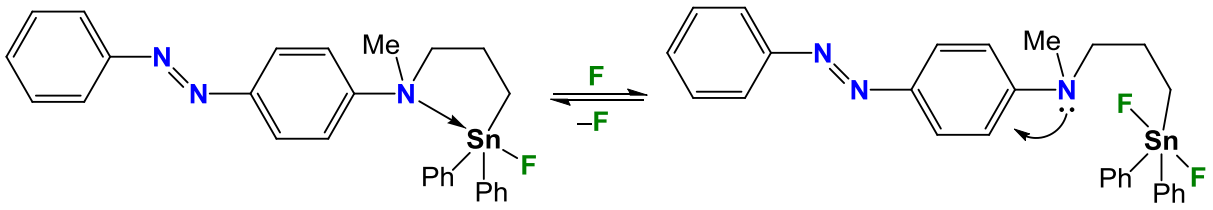


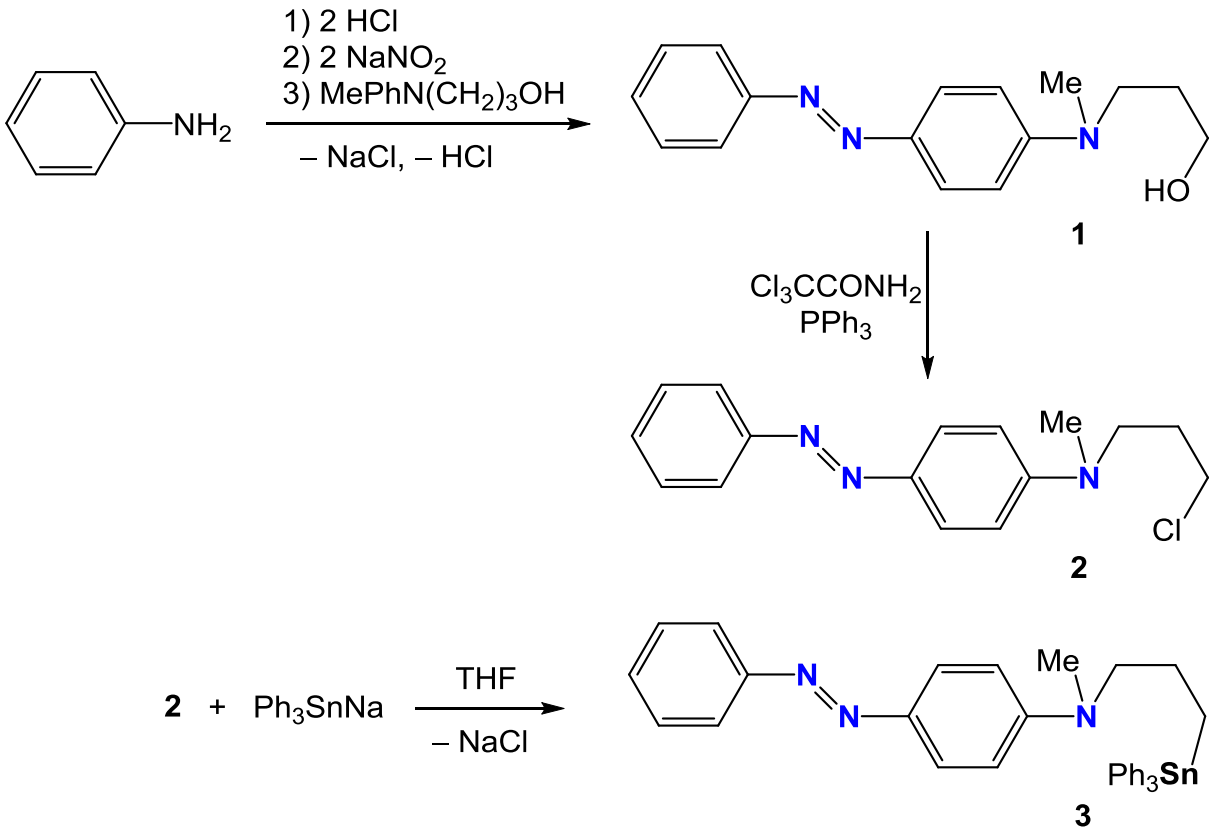
Chart 1. The proposed mechanism of the organotin-based sensor for fluoride anion.

3.1.2 Syntheses of the organotin compounds {(PhN=NC$_6$H$_4$)(Me)N(CH$_2$)$_3$}SnPh$_n$X$_{3-n}$ (n = 0, 1, 2, 3; X = F, Cl, I)

The reaction of aniline with 3-N-methylanilino-1-propanol,[16] Ph(Me)N(CH$_2$)$_3$OH, gave the corresponded azo dye (PhN=NC$_6$H$_4$)(Me)N(CH$_2$)$_3$OH, **1**, in quantitative yield as red oil (Scheme 1). Chlorination of the OH group in compound **1** was achieved by using a combination of PPh$_3$ and Cl$_3$CCONH$_2$ as the reagent system[17] affording (PhN=NC$_6$H$_4$)(Me)N(CH$_2$)$_3$Cl, **2**, in good yield as red oil (Scheme 1).

Compounds **1** and **2** showed good solubility in common organic solvents such as CH$_2$Cl$_2$, CHCl$_3$ and acetone.

The reaction of **2** with Ph$_3$SnNa in THF gave the tetraorganotin compound {(PhN=NC$_6$H$_4$)(Me)N(CH$_2$)$_3$}SnPh$_3$, **3**, in quantitative yield as red waxy oil (Scheme 1). Compound **3** showed good solubility in common organic solvents such as CH$_2$Cl$_2$, CHCl$_3$ and THF.

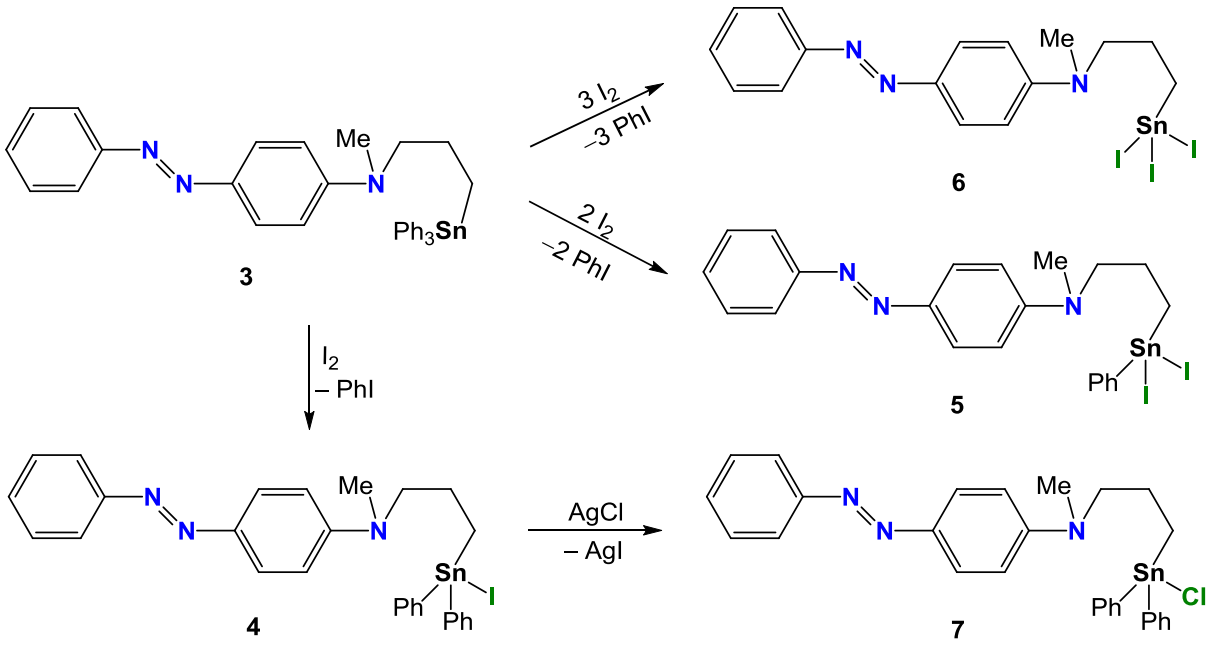


Scheme 1. Syntheses of the compounds **1** – **3** containing azo group.

The reaction of the tetraorganotin compound **3** with one molar equivalent elemental iodine gave the corresponding iodine-substituted triorganotin compound {(PhN=NC$_6$H$_4$)(Me)N(CH$_2$)$_3$}SnPh$_2$I, **4**, in almost quantitative yield. Similarly, treatment of the tetraorganotin compound **3** with two, respectively, three molar equivalents of elemental iodine gave the corresponding compounds {(PhN=NC$_6$H$_4$)(Me)N(CH$_2$)$_3$}SnPhI$_2$, **5**, and {(PhN=NC$_6$H$_4$)(Me)N(CH$_2$)$_3$}SnI$_3$, **6**, in almost quantitative, respectively, good yields (Scheme 2). Compounds **4** and **5** were obtained as red waxy oil, whereas compound **6** was obtained as oil that solidified after few days.

The reaction of the triorganotin iodide **4** with an excess silver chloride, AgCl, in acetonitrile provided the chlorine-substituted triorganotin {(PhN=NC$_6$H$_4$)(Me)N(CH$_2$)$_3$}SnPh$_2$Cl, **7**, as red oil in quantitative yield (Scheme 2).

Compounds **4**, **5** and **7** showed good solubility in common organic solvents such as CH$_2$Cl$_2$, CHCl$_3$, THF and acetone, whereas the organotin triiodide **6** showed poor solubility in organic solvents.



Scheme 2. Syntheses of the organotin compounds **4** – **7**.

3.1.3 Structures in solution

A ^{119}Sn NMR spectrum of a solution of the tetraorganotin compound **3** in $CDCl_3$ showed one signal at δ –100. This chemical shift is close to those reported for the tetracoordinated tin atoms in Ph_3SnMe[18] and $Me_2N(CH_2)_3SnPh_3$[19] at δ –92 and δ –102, respectively. This suggested that the tin atom in **3** is tetracoordinated in solution. A ^{13}C NMR spectrum of the same sample showed a chemical shift with $^{117/119}$Sn coupling satellites at δ 7.6 (^1J(^{13}C–$^{117/119}$Sn) = 366/384 Hz) related to the Sn*C*H_2 carbon atom. In addition to that, a chemical shift at δ 138.3 (^1J(^{13}C–$^{117/119}$Sn) = 470/492 Hz) assigned to the Sn–C_{ipso} was observed. These two chemical shifts are close to those reported for the corresponding carbon atoms in $Me_2N(CH_2)_3SnPh_3$ at δ 8.3 (^1J(^{119}Sn–^{13}C) = 399 Hz) and δ 139.1 (^1J(^{119}Sn–^{13}C) = 487 Hz), respectively.[19] A ^{1}H NMR spectrum of the same sample showed one signal for the Sn*C*H_2 protons at δ 1.65 (^2J(^{1}H–$^{117/119}$Sn) = 55.9 Hz).

The ^{13}C NMR spectra of the organotin iodides **4** and **5** showed that the signals of the Sn*C*H_2 carbon atoms are low field shifted by 5.9 and 14.6 ppm, respectively, with respect to the parent compound **3**.

Interestingly, the coupling satellites ^1J(^{13}C–$^{117/119}$Sn) of 389 Hz for the Sn*C*H_2 carbon atom in **4** is close to that found in the tetraorganotin compound **3** of 366/384 Hz and is characteristic

for tetracoordinated environment of the tin atom in solution. This configuration was proved also by comparing the ^{13}C chemical shift of the Sn*C*H_2 carbon atom in **4** at δ 13.4 with the corresponding one in the pentacoordinate organotin compound $Me_2N(CH_2)_3SnPh_2I$ at δ 18.5 ($^1J(^{13}C–^{117/119}Sn)$ = 526 Hz).[19]

For comparison, the diorganotin diiodide $Me_2N(CH_2)_3SnPhI_2$ was synthesized. A ^{13}C NMR spectrum showed that the signal of the Sn*C*H_2 carbon atom in $Me_2N(CH_2)_3SnPhI_2$ (δ 28.6) is low field shifted by 6.5 ppm with respect to the diorganotin diiodide **5** (δ 22.1).

In the ^1H NMR spectra of the tri- diorganotin iodides **4** and **5** the signals for the Sn*CH*$_2$ protons were observed at δ 1.78 ($^2J(^1H–^{117/119}Sn)$ = 52.5 Hz) and δ 2.11 ($^2J(^1H–^{117/119}Sn)$ = 55.2 Hz), respectively. These values of the coupling satellites are close to that of 55.9 Hz found for the tetraorganotin compound **3**. Indeed, these values fall in the range characteristic of tetracoordinated organotin compounds.

The tetracoordinated environment of the tin atoms in compounds **4** and **5** were also proved by the ^{119}Sn NMR spectra. That for compound **4** in $CDCl_3$ solution showed one signal at δ –56. This chemical shift is close to those reported for the triorganotin iodides $(IPh_2Sn)_2CH_2$ and Ph_2MeSnI at δ –68,[20] but much smaller than that reported for the pentacoordinated triorganotin iodide $Me_2N(CH_2)_3SnPh_2I$ containing N→Sn intramolecular coordination at δ –168.[19] Furthermore, a ^{119}Sn NMR spectrum of compound **5** in $CDCl_3$ solution showed one signal at δ –165. This chemical shift is close to that reported for $(I_2PhSn)_2(CH_2)_2$ at δ –169,[21] on hand, but much smaller than that reported for the pentacoordinated triorganotin iodide $Me_2N(CH_2)_3SnPhI_2$ at δ –274. In the case of the organotin triiodide **6** the low solubility of this compound in CD_3CN and $CDCl_3$ solutions prevented its characterization by NMR spectra.

Although replacing the iodine atom in the triorganotin iodide **4** with the highly electronegative chlorine atom increases the Lewis acidity of the tin atom and enhances the ability to form N→Sn intramolecular coordination, no evidence of the pentacoordinated structure for compound **7** in solution was observed, as proved by NMR spectroscopy.

A ^{119}Sn NMR spectrum of a solution of **7** in $CDCl_3$ showed one signal at δ +10. This chemical shift is 146 ppm lower field shifted in comparison to that reported for the pentacoordinated organotin $Me_2N(CH_2)_3SnPh_2Cl$ (δ –146).[19] On the other hand, this chemical shift is close to

those reported for tetracoordinated triorganotin chlorides as $(ClPh_2Sn)_2CH_2$,[20] $(ClPh_2Sn)_2(CH_2)_2$[21] and $(ClPh_2Sn)_2(CH_2)_3$[22] at δ 20, +2, +7, respectively.

In a ^{13}C NMR spectrum of the same sample a chemical shift of the Sn*C*H_2 carbon atom at δ 14.1 ($^1J(^{13}C–^{117/119}Sn)$ = 415/424 Hz) was observed. In spite of this chemical shift being close to that reported for the pentacoordinated organotin $Me_2N(CH_2)_3SnPh_2Cl$ (δ 14.4), but there is a big difference in the coupling values $^1J(^{13}C–^{117/119}Sn)$ that in the case of $Me_2N(CH_2)_3SnPh_2Cl$ is 586 Hz.[19] In a ^1H NMR spectrum of **7** a signal for the SnC*H*$_2$ protons at δ 1.72 ($^2J(^1H–^{117/119}Sn)$ = 55.6 Hz) was observed. This coupling satellite is close to that found for the tetraorganotin compound **3** of 55.9 Hz and smaller than those reported for the triorganotin chlorides $(ClPh_2Sn)_2CH_2$[20] and $(ClPh_2Sn)_2(CH_2)_2$[21] of 64.6 and 67.2 Hz, respectively.

Attempts to synthesize the triorganotin fluoride by the reaction of the triorganotin iodide **4** with one molar equivalent tetraethylammonium fluoride, Et_4NF, in $CDCl_3$ solution resulted in formation of a brownish precipitate. This precipitate consists of the triorganotin fluoride $\{(PhN{=}NC_6H_4)(Me)N(CH_2)_3\}SnPh_2F$, **8**, as proved by elemental analysis. Apparently it has no intramolecular N→Sn coordination as a result of it is poor solubility in common organic solvents that is characteristic for organotin fluorides in general. However, as it is known, fluoridoorganotin compounds having intramolecular coordination show usually good solubility in organic solvents.[19] [23] [24]

Addition of a second molar equivalent of tetraethylammonium fluoride, Et_4NF, in $CDCl_3$ solution resulted in solubilizing the system. However, no resonances were observed in the ^{119}Sn and ^{19}F NMR spectra as they were measured at room temperature. In a ^1H NMR spectrum a signal of the SnC*H*$_2$ protons at δ 1.09 was observed. This signal is high field shifted by 0.56 ppm and 0.69 ppm with respect to compounds **3** and **4**, respectively. In a ^{13}C NMR spectrum of the same sample a signal of the Sn*C*H_2 carbon atom without coupling satellites $^1J(^{13}C–^{117/119}Sn)$ at δ 17.0 was observed.

This chemical shift is low field shifted with 9.4 ppm and 3.63 ppm with respect to those of compounds **3** and **4**, respectively. This change in the chemical shifts could be attributed to the formation of the adduct $[NEt_4]^+[\{(PhN{=}NC_6H_4)(Me)N(CH_2)_3\}SnPh_2F{\cdot}F]^-$.

The ESI MS spectra of the triorganotin halides {(PhN=NC_6H_4)(Me)N(CH_2)$_3$}$SnPh_2X$ (**4**, X = I; **7**, X = Cl) showed two mass clusters related to [**M** – X]$^+$ and [**M** + H]$^+$. In the ESI MS spectrum (positive mode) of the diorganotin diiodide **5** a mass cluster centered at *m/z* 704.0 was observed that fits exactly with [**5** + H]$^+$.

3.2 Attempt to Synthesize Tin–Nitrogen-Based Fluoresence Chemosensor for Sensing Fluoride anions

3.2.1 INTRODUCTION

Sensing and recognition of fluoride anions are of great interest. Many examples of fluoresence chemosensors of different types dealing with the detection of fluoride anions are reported.[25][26][27][28] *Yang* and co-workers reported an example of a rapid fluoride anion sensor in aqueous solution **A** (Figure 2).[29] This type of sensors depends on the cleavage of a Si–O bond during the reaction with fluoride anions. In addition to the Si–O bond cleavage, many examples have been reported dealing with the cleavage of Si–C bond for sensing of fluoride anions.[30][31] In such reactions the formation of Si–F bonds as a result of the cleavage of Si–O or Si–C bonds takes place, based on the large differences among the dissociation energies of Si–C, Si–O bonds (69, 103, respectively) on one side and that of Si–F bond (141 kcal/ mol) on the other side. Compound **B** (Figure 2)[32] is an example of fluorescence sensors that depends on removing of the trimethylsillyl substituents during the reaction with fluoride anions.

The fluorescence chemosensors which depends on the interaction between fluoride anions and Lewis acids is one of the important types used in selective fluoride sensor.[33][34] *Gabba*i and co-workers presented two types of fluoride sensors based on organoantimony(V) compounds. The triflate salt of 9-anthryltriphenylstibonium ion **C** (Figure 2)[35] reacts with fluoride anions in parts per million of concentrations accompanied with fluorescence turn-on response. In addition to that, the Lewis acidic organostiboranes containing the ligand (1,2-dihydroxyanthraquinone) **D** (Figure 2)[36] proved to be able to detect fluoride anions at ppm concentrations with fluorescence turn-on response.

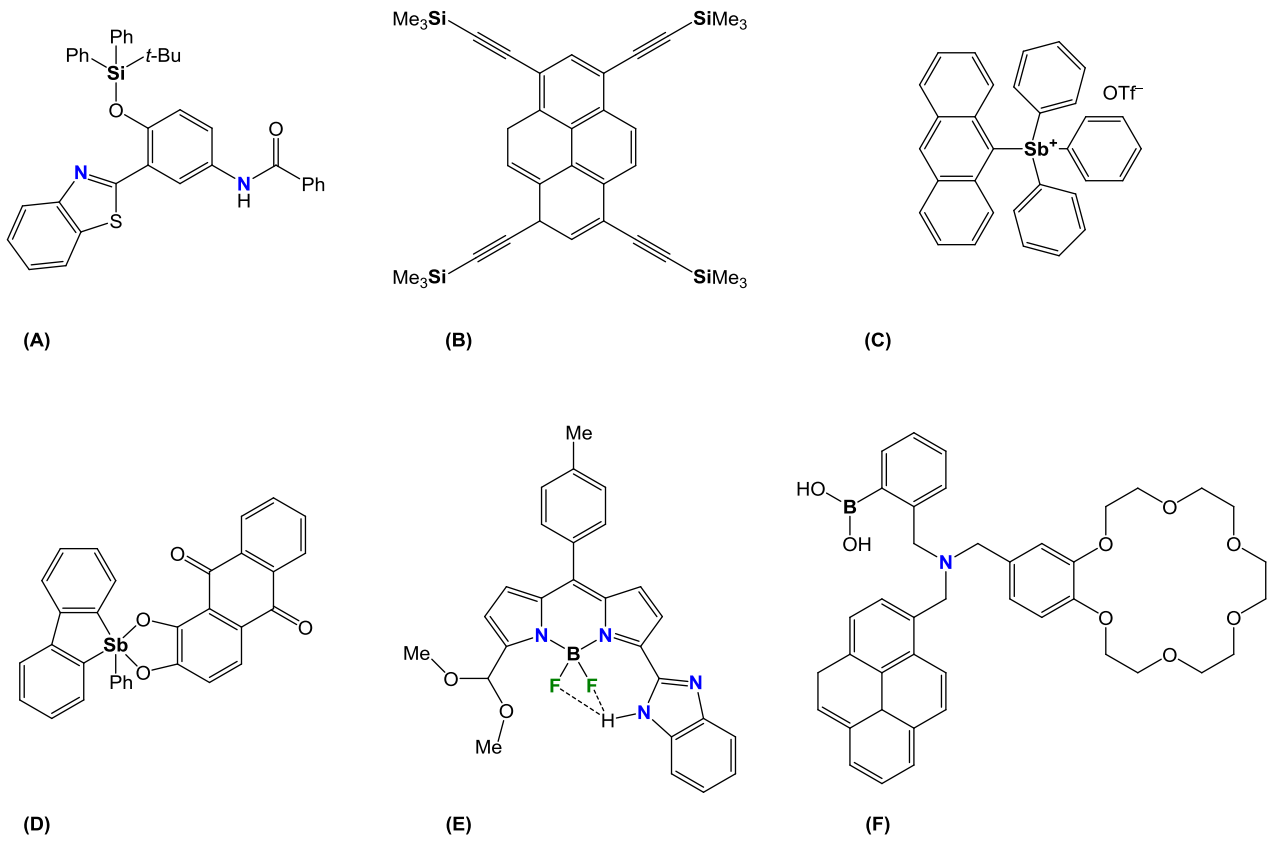
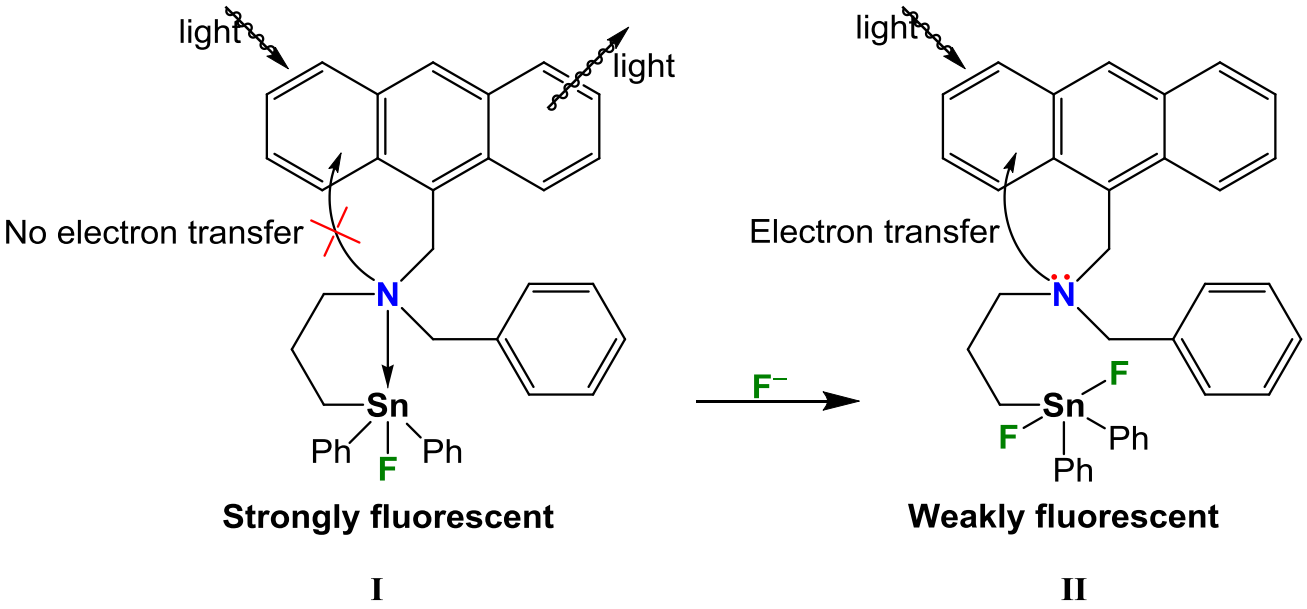


Figure 2. Fluoresence chemosensors for detection of fluoride anions reported in literature.

Sensing of fluoride anions by boron-based chemosensors is widely studied. In these sensors the changes in the electronic properties of the boron substituents during the reaction with fluoride anions is used for designing this type of receptors.[37][38] Many successful examples are reported in this field.[39] [40] *Ravikanth* and co-workers reported a novel example of boron dipyrromethene-based chemosensor **E** (Figure 2)[41] that reacts selectively and reversibility with fluoride anions. Furthermore, *James* and co-workers reported a ditopic fluorescent sensor for detecting potassium fluoride **F** (Figure 2) using crown ether-substituted boronate compound.[42]

Differently to sensing of fluoride anions, *Shinkai* and co-workers reported a saccharide receptor containing boronic acid group incorporates a fluorescent anthracene moiety.[43] This type of sensors classified in photoinduced electron transphere (PET) fluorescent sensors. The format fluorophore–spacer–receptor is the characteristic system of the PET sensors.[44]

Inspired by the work of *Shinkai*, who showed a fluorescence turn-on response for saccharide using boron–nitrogen-based sensors,[43][45] here is reported the attempt to synthesize tin–nitrogen- based sensor containing anthracene moiety for the detection of fluoride anions. This chemosensor depends on the Lewis acidity of the tin atom (receptor) to bind fluoride anions. It is supposed theoretically that the N→Sn interaction will be weak upon the reaction with fluoride anions, and the lone pair electrons of the amine will quench the fluorescence of the anthracene (fluorophore) causing the fluorescence turn-off response (**II**, Scheme 3).



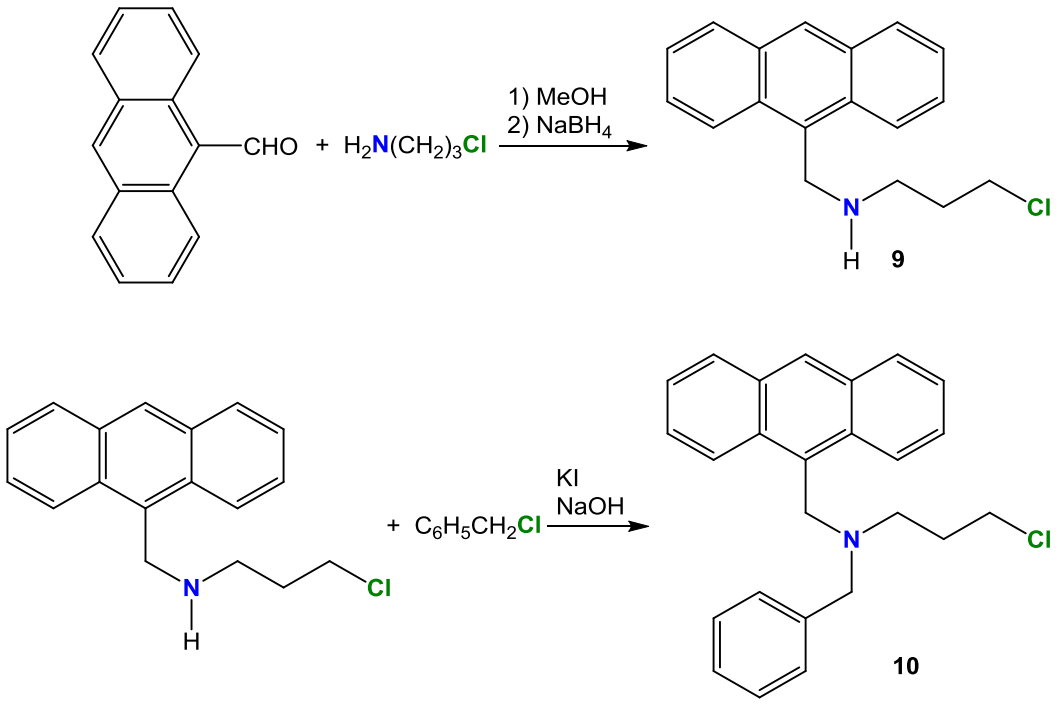
Scheme 3. Supposed Sn–N-based chemosensor with PET system for the detection of fluoride anions.

For this purpose, it will be presented the syntheses of amine-substituted organotin compounds in which the nitrogen atom is bound to chromophoric groups.

3.2.2 Syntheses of the tetraorganotin compound $\{(AnCH_2)(Bn)N(CH_2)_3\}SnPh_3$, 11, and its iodine-derivative $\{(AnCH_2)(Bn)N(CH_2)_3\}SnPh_2I$, 12.

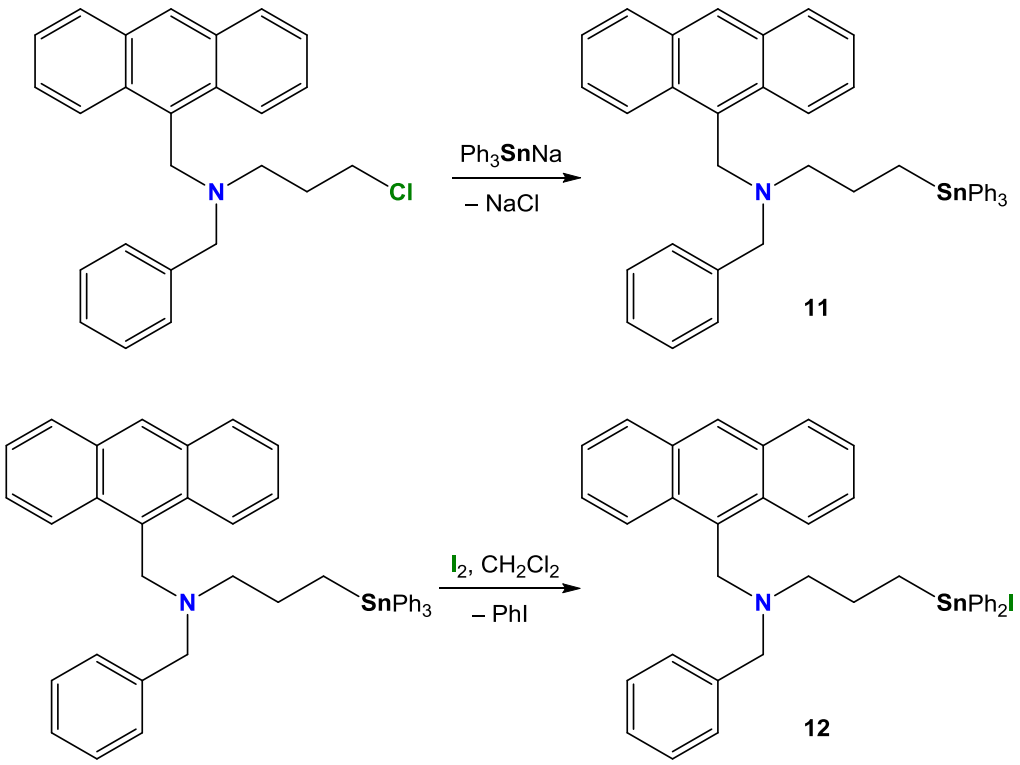
The reaction of 9-anthracene carboxaldehyde with 3-chloropropylamine, $H_2N(CH_2)_3Cl$, in MeOH followed by the reaction with sodium borohydride gave N-(anthracen-9-ylmethyl)-3-chloropropan-1-amine, An-CH_2-$NH(CH_2)_3Cl$, **9**, in quantitative yield (Scheme 4).[46]

Compound **9** was obtained as yellowish green oil and it shows good solubility in common organic solvents such as CH_2Cl_2, $CHCl_3$, and MeOH. The reaction of **9** with benzyl chloride, $C_6H_5CH_2Cl$, in acetonitrile and CH_2Cl_2 in presences of KI and NaOH gave N-(anthracen-9-ylmethyl)-N-benzyl-3-chloropropan-1-amine, $(AnCH_2)(Bn)N(CH_2)_3Cl$, **10** in good yield, (Scheme 4). Compound **10** was obtained as pale yellow solid, and shows good solubility in common organic solvents such as $CHCl_3$, diethylether but moderate solubility in ethanol.



Scheme 4. Syntheses of compounds **9** and **10**.

The reaction of **10** with Ph_3SnNa in THF gave the tetraorganotin compound $\{(AnCH_2)(Bn)N(CH_2)_3\}SnPh_3$, **11**, in low yield as slightly yellow solid (Scheme 5). Compound **11** shows good solublity in common organic solvents such as CH_2Cl_2, $CHCl_3$ and THF, but poor solubility in ethanol.



Scheme 5. Syntheses of the organotin compounds **11** and **12**.

Treatment of the tetraorganotin compound **11** with one molar equivalent iodine gave the triorganotin iodide, {(AnCH$_2$)(Bn)N(CH$_2$)$_3$}SnPh$_2$I, **12**, in good yield as pale yellow solid (Scheme 5). Compound **12** shows good solubility in ethanol, moderate solubility in CHCl$_3$, and poor solubility in CH$_3$CN and diethylether.

3.2.3 Molecular structure of compound 11

Single crystals suitable for X-ray structure determination were obtained by slow evaporation of a solution of **11** in CHCl$_3$ and ethanol at room temperature. Compound **11** crystallizeD in the triclinic space group *P*–1 with two molecules in the unit cell. The molecular structure of **11** is presented in Figure 3, selected interatomic distances and bond angles are listed in Table 1.

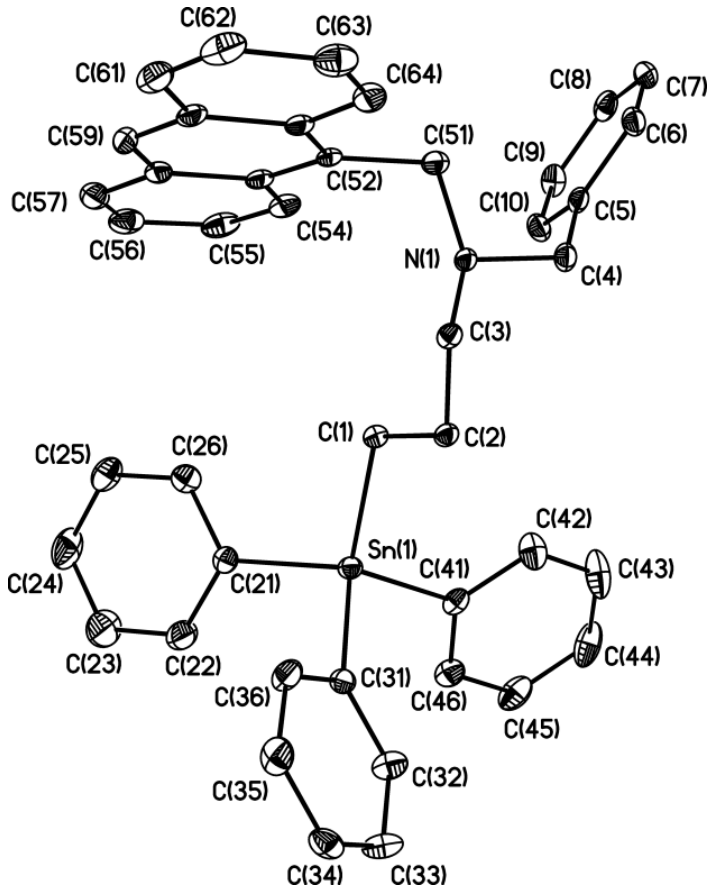


Figure 3. General view (SHELXTL) of a molecule of **11** showing 30% probability displacement ellipsoids and the crystallographic numbering scheme.

Table 1. Selected interatomic bonds /Å and bond angles /° in **11**.

Sn(1)–C(1)	2.134(2)	C(1)–Sn(1)–C(21)	108.06(8)
Sn(1)–C(21)	2.137(2)	C(1)–Sn(1)–C(41)	110.71(8)
Sn(1)–C(41)	2.140(2)	C(21)–Sn(1)–C(41)	111.78(8)
Sn(1)–C(31)	2.147(2)	C(21)–Sn(1)–C(31)	108.44(8)
N(1)–C(3)	1.464(2)	C(41)–Sn(1)–C(31)	105.89(8)
N(1)–C(51)	1.471(3)	C(3)–N(1)–C(4)	110.80(15)
C(4)–C(5)	1.511(3)	C(3)–N(1)–C(51)	113.21(16)
C(51)–C(52)	1.518(3)	C(4)–N(1)–C(51)	109.86(16)

The tin atom in **11** is tetracoordinated and exhibits a distorted tetrahedral environment with angles varying between 105.89(8)° (C(41)–Sn(1)–C(31)) and 111.98(8)° (C(1)–Sn(1)–C(31)). The (Sn–C_{Ph}) distances range between 2.137(2) Å (Sn(1)–C(21)) and 2.147(2) Å (Sn(1)–C(31)), which is comparable with the Sn–C_{Ph} distances measured for the tetraorganotin compound $[Ph_3Sn(CH_2)_3NMe_2H]Cl{\cdot}H_2O$[19] (2.131(3) – 2.148(3) Å).

3.2.4 Structures of compounds 11 and 12 in solution

A ^{13}C NMR spectrum of a solution of compound **11** in $CDCl_3$ showed a chemical shift at δ 8.2 ($^1J(^{13}C–^{117/119}Sn)$ = 377/396 Hz) assigned to the Sn*C*H_2 carbon atom. In addition to that, a chemical shift at δ 138.8 ($^1J(^{13}C–^{117/119}Sn)$ = 462/483 Hz) assigned to the SnC_{ipso} was observed. These two chemical shifts are close to those reported for the corresponding carbon atoms in $Me_2N(CH_2)_3SnPh_3$ at δ 8.3 ($^1J(^{119}Sn–^{13}C)$ = 399 Hz) and δ 139.1 ($^1J(^{119}Sn–^{13}C)$ = 487 Hz), respectively.[19] A ^{13}C NMR spectrum of compound **12** showed downfield shift for the Sn*C*H_2 carbon atom ($\Delta\delta$ = 5.9) with respect to **11**.

A ^{119}Sn NMR spectrum of the tetraorganotin compound **11** showed a signal at δ –99. This chemical shift is close to those reported for the tetracoordinated tin atom in Ph_3SnMe[18] and $Me_2N(CH_2)_3SnPh_3$[19] at δ –92 and δ –102, respectively.

A ^{119}Sn NMR spectrum of the iodine-substituted organotin compound **12** showed a major resonance at δ –51 (v 243 Hz, integral 93). In addition two minor resonances at δ –114 (integral 3, Ph_3SnI) and –130 (integral 4, Ph_4Sn) were observed. The comparison of the ^{119}Sn NMR chemical shifts of the organotin iodide **12** (δ –51) measured in $CDCl_3$ with those for $MePh_2SnI$ (δ –68)[20] and $Me_2N(CH_2)_3SnPh_2I$ (δ –168),[19] containing 4- respectively 5-coordinated tin atoms, suggests that the tin atom in **12** is 4-coordinated with no N→Sn interaction. This could probably be attributed to the Lewis acidity of the tin atom being not high enough to form the N→Sn interaction.

However, the broadness of the signal of compound **12** (v 243 Hz) may give an idea about the intramolecular N→Sn interaction that is kinetically labile on the NMR time scale at room temperature. Therefore, a ^{119}Sn NMR spectrum at low temperature may prove the presence of the N→Sn interaction or not.

Attempts to recrystallize compound **12** from its different solutions were not successful. Surprisingly, after few days a ^{119}Sn NMR spectrum showed, in addition to the resonance of compound **12** at δ –51 (integral 40), new resonances at δ –109 (integral 7, not assigned) –114 (integral 18), –130 (integral 4), –170 (integral 22) –189 (integral 9, not assigned). The resonances at δ –114, –130 and –170 are assigned with caution to Ph_3SnI, $SnPh_4$ and $Me_2N(CH_2)_3SnPh_2I$ (Figure 4). A ^{1}H NMR spectrum of the same sample showed new resonances in the region between 9–10 ppm related to the protonated ammonium group $(-CH_2)_3N^+(H)$. All these data indicate that compound **12** suffers hydrolysis reaction accompanied with protonation of the amine group. Indeed, this happened when the compound left at room temperature under air or in solutions of different solvents (in attempt to get single crystals).

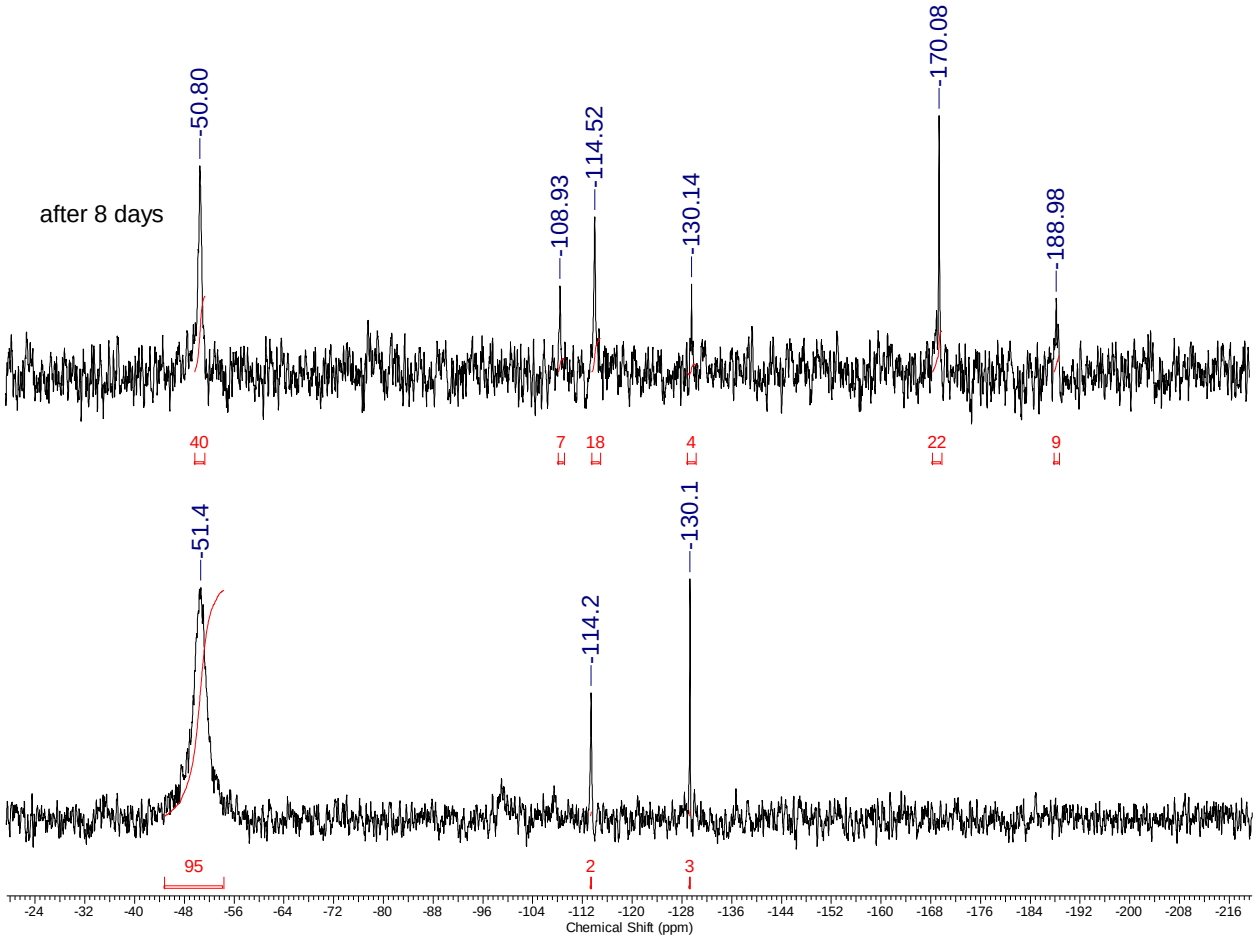


Figure 4. ^{119}Sn NMR spectra of compound **12** in $CDCl_3$ showing instability of this compound as new signals were observed after 8 days.

It was planned to synthesize the desired chemosensor, the triorganotin fluoride $\{(AnCH_2)(Bn)N(CH_2)_3\}SnPh_2F$, by the reaction of compound **12** with KF. However, this reaction could not be performed because of the instability of compound **12** under non-inert conditions.

3.3 Organotin-Substituted Crown Ether as Ditopic Receptors for Sodium Halides

3.3.1 INTRODUCTION

The design of molecular hosts for selective recognition of fluoride anions is a rather popular topic that is manifested by numerous publications and reviews.[1][2][47] These molecules should have enough energy to be able to separate the fluoride anions from its counterion to achieve the desired binding. However, the recognition of fluoride anions in sodium fluoride salt is challenging as a result of the high lattice energy of 913 kJ mol^{-1}.[48] The most common strategy employed to compensate for the high lattice energy of sodium fluoride salt is the formation of the ditopic complexes by heteroditopic receptors. In these receptors the cation and anion are bound as a separated pair. In addition, theses ditopic receptors might have possible applications as salt extraction, salt solubilization, and membrane transport agents.[1]

In this field, it seems to be not surprising that many ion-pair receptors are designed by crown-ether-like moieties for the recognition of the sodium ions. On the other hand, Lewis acidic organoelement centers proved to be efficient in the recognition of fluoride anions and many successful examples are reported.[49] [50] [35]

In our research group a set of organotin-substituted crown ethers as ditopic receptors for potassium fluoride and sodium fluoride have been tested, and only few of them were able to achieve this purpose (Figure 5).[51][52] However, many organotin-substituted crown ethers have proved to be capable to bind sodium and potassium anions but failed to bind the fluoride anions. This could be attributed to the Lewis acidity of the tin atoms in these compounds that is although not enough to bind fluoride anions, however, it is able to bind other halides or anions like SCN.[51][53][54][55]

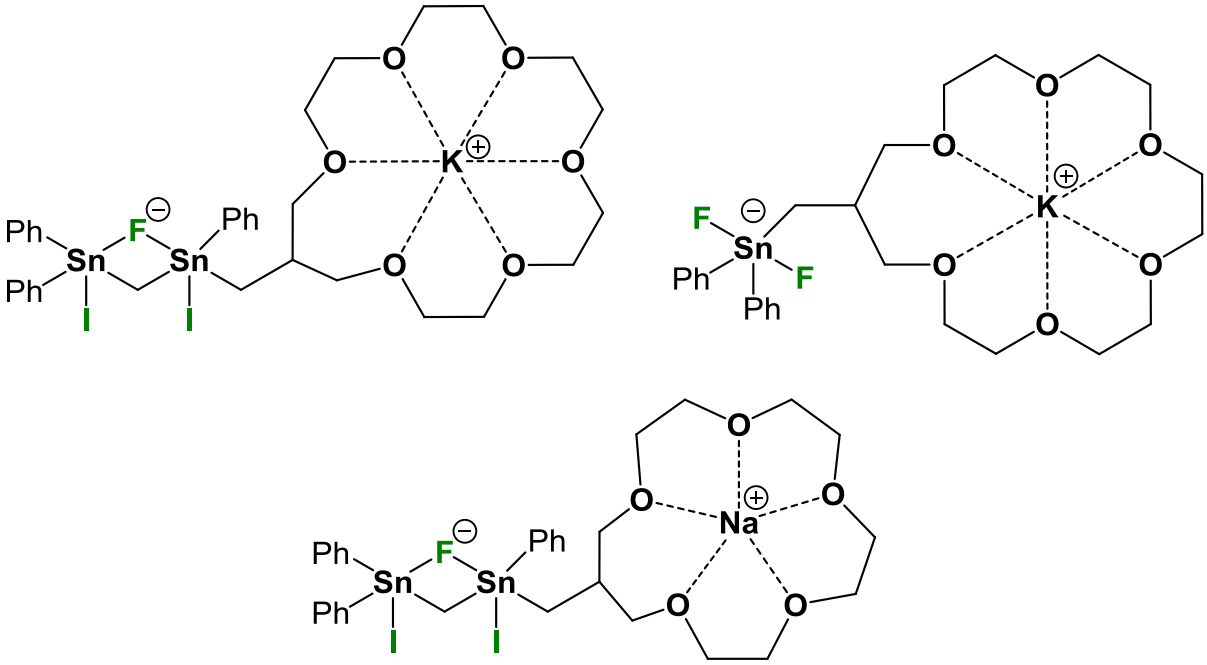


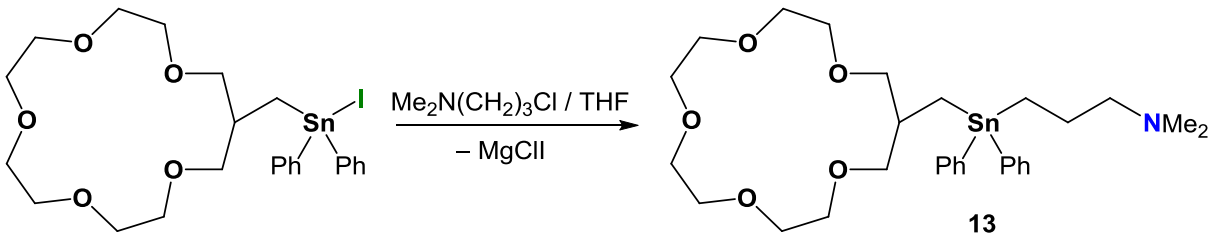
Figure 5. Organotin-substituted crown ethers as ditopic receptors for fluoride salts reported in the literature.[51][52]

In continuation of our systematic studies on organotin-substituted crown ethers here will be presented the synthesis of a heteroditopic receptor consisting of the [16]-crown-5 moiety, for the selective recognition of sodium ions, and 3-dimethylaminopropyl substituted organotin for the binding of the anions. The tin atom in this compound is bound to the $Me_2N(CH_2)_3$ moiety that is able to form intramolecular N→Sn interaction. Furthermore, the 16-crown-5 moiety has been chosen as its diameter cavity of (*d* 1.70 – 2.20 Å) is appropriate for the encapsulation of sodium ion (*d* 1.91 Å).[56] The capability of this receptor to selective binding of sodium fluoride and sodium iodide will be tested.

3.3.2 Synthesis of the tetraorganostannyl-substituted crown ether {$Me_2N(CH_2)_3$}(Ph_2)$SnCH_2$-[16]-crown-5, 13.

The reaction of the iodine-substituted triorganotin, Ph_2ISnCH_2-[16]-crown-5,[53] with excess of $Me_2N(CH_2)_3MgCl$ in THF, provided the tetraorganotin compound {$Me_2N(CH_2)_3$}(Ph_2)$SnCH_2$-[16]-crown-5, **13**, in good yield as yellowish oil.

Compound **13** shows good solubility in common organic solvents such as CH_2Cl_2, $CHCl_3$, THF, and diethyl ether (Scheme 6).



Scheme 6. Synthesis of the tetraorganotin compound **13**.

A ^{119}Sn NMR spectrum of **13** in $CDCl_3$ solution showed that the tin atom is tetracoordinated as evidenced by its chemical shift at δ –79. That is close to those reported for the tetracoordinated organotin compounds Ph_2SnMe_2[57], $Ph_2Sn(CH_2$-[13]-crown-4$)_2$,[54] and $Ph_2Sn(CH_2$-[16]-crown-5$)_2$[54] at δ –60, –78, –82, respectively. A ^{13}C NMR spectrum of **13** showed two signals with $^{117/119}$Sn satellites related to the Sn*C*H_2 and C1 carbon atoms at δ 8.3 ($^1J(^{13}C–^{117/119}Sn)$ = 362/380 Hz) and δ 10.7 ($^1J(^{13}C–^{117/119}Sn)$ = 377/397 Hz), respevtively, (for numbering see Chart 2). This chemical shift at δ 10.7 is close to that reported for the tetraorganotin compound Ph_3SnCH_2-[19]-crown-6 at δ 11.4 ($^1J(^{13}C–^{117/119}Sn)$ = 398/417 Hz).[51]

In the ESI MS spectrum of **13** (positive mode) a major mass cluster centered at *m/z* 530.2 assigned to $[\{Me_2N(CH_2)_3\}(Ph)SnCH_2$-[16]-crown-5$]^+$ was observed.

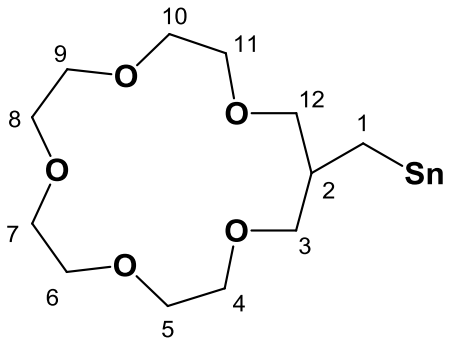


Chart 2. Numbering scheme of the crown ether ring.

3.3.3 Synthesis of the diorganotin-substituted crown ether ([{Me_2(H)N(CH_2)$_3$}(OH)ISnCH_2-[16]-crown-5]·I), 14.

A ^{119}Sn NMR spectrum of the reaction of the tetraorganotin compound **13** with two molar equivalents of elemental iodine showed one signal at δ –163 (in $CDCl_3$ and CD_3CN).

This chemical shift is close to that reported for Me_2SnI_2 at δ –159 indicating ostensibly that there is no intramolecular N→Sn or O→Sn coordination found in solution.

However, the tin atom in $\{Me_2N(CH_2)_3\}(I_2)SnCH_2$-[16]-crown-5 has a high Lewis acidity enabling it to form one or two intramolecular O→Sn coordination with the neighboring oxygen atoms in the crown ether moiety. For examples, the analogues diorganodiiodidostannanes $I_2Sn(CH_2$-[16]-crown-$5)_2$ and $I_2Sn(CH_2$-[13]-crown-$4)_2$ at δ –220 and –226 (in CD_3CN),[54] and those for the tin atoms Sn^a in $Ph_2ISnCH_2Sn^a(I)_2CH_2$-[19]-crown-6 and $Ph_2ISnCH_2Sn^a(I)_2CH_2$-[13]-crown-4 at δ –272 and –252 (in $CDCl_3$) all show intramolecular O→Sn coordination.[58]

In a ^{1}H NMR spectrum of the same sample a broad signal at δ 9.5, that is located in the region characteristic for N*H* proton, was observed.

This probably suggests that the chemical shift at δ –163 is not related to the structure $\{Me_2N(CH_2)_3\}(I_2)SnCH_2$-[16]-crown-5.

One possibility is that after the reaction of compound **13** with elemental iodine the resulted compound $\{Me_2N(CH_2)_3\}(I_2)SnCH_2$-[16]-crown-5 was hydrolyzed by air moisture and gave the compound ($[\{Me_2(H)N(CH_2)_3\}(OH)ISnCH_2$-[16]-crown-5]·I), **14**, containing an ammonium function (Scheme 7). This proposal was proved by the presences of the OH group at 3066 cm^{-1} in the IR spectrum, on one hand.

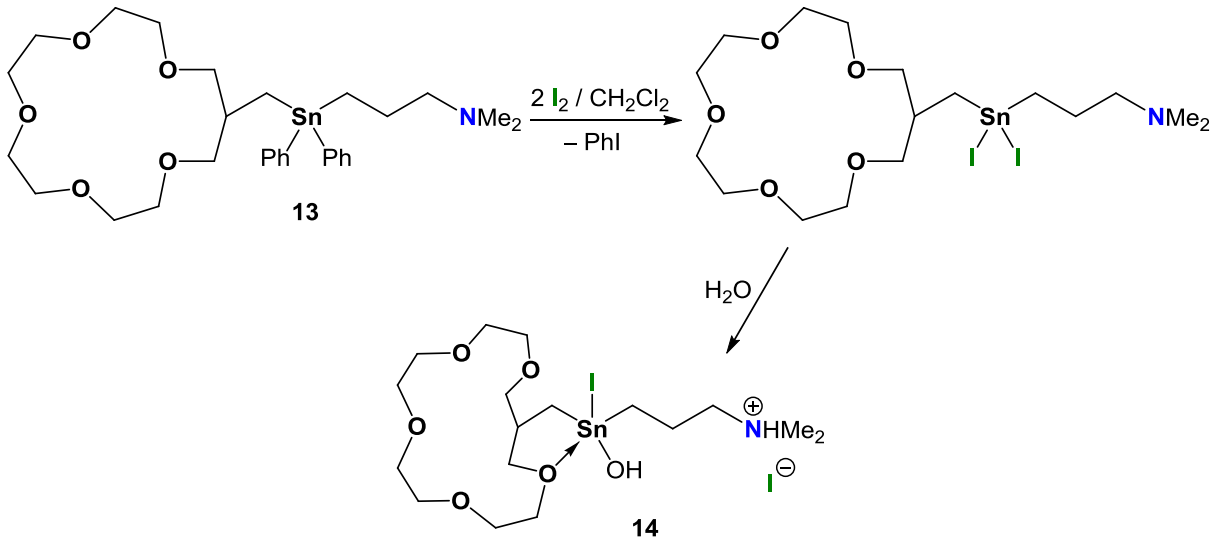
On the other hand, the chemical shift in a ^{119}Sn NMR spectrum at δ –163 is consistent with this structure where the tin atom is involved in intramolecular O→Sn coordination. It is low-frequency shifted in comparison with those reported for the pentacoordinated tin atoms in $Me_3SiCH_2(Ph)ISnCH_2$-[19]-crown-6, Ph_2ISnCH_2*Sn*$(Ph)ICH_2$-[19]-crown-6 and Ph_3SnCH_2–*Sn*$(Ph)ICH_2$-[13]-crown-4 at δ –70, –87 and –85, respectively.[58]

A ^{13}C NMR spectrum of **14** in $CDCl_3$ solution showed that the chemical shifts of the Sn*C*H_2 and C1 carbon atoms are low-field shifted by 18.0 and 23.7 ppm, respectively, with respect to those found in **13**.

In addition to the broad signal found at δ 9.53 in a ^{1}H NMR spectrum of **14** (in $CDCl_3$), a doublet signal of $(CH_3)_2N^+$ protons at δ 2.94 ($^3J(^1H–^1H)$ = 5.12 Hz) was observed. This signal was found at δ 2.84 ($^3J(^1H–^1H)$ = 5.12 Hz) in CD_3CN (Figure 7), and the chemical shift of the N*H* proton was observed at δ 7.40.

The ESI-MS spectrum of compound **14** showed in the positive mode a major mass cluster centered at *m/z* 488.1 that is assigned to $[\{Me_2NH(CH_2)_3\}(OH)_2SnCH_2\text{-}[16]\text{-crown-5}]^+$.

Compound **14** was obtained as red viscous oil. It shows good solubility in polar solvents such as acetone and acetonitrile and moderate solubility in $CHCl_3$, CH_2Cl_2. Attempts to recrystallize compound **14** from its solution in acetone/diethyl ether afforded Single crystals of $[\{Me_2(H)N(CH_2)_3\}(I_3)SnCH_2\text{-}[16]\text{-crown-5}]$, **15**, suitable for X-ray diffraction analysis.

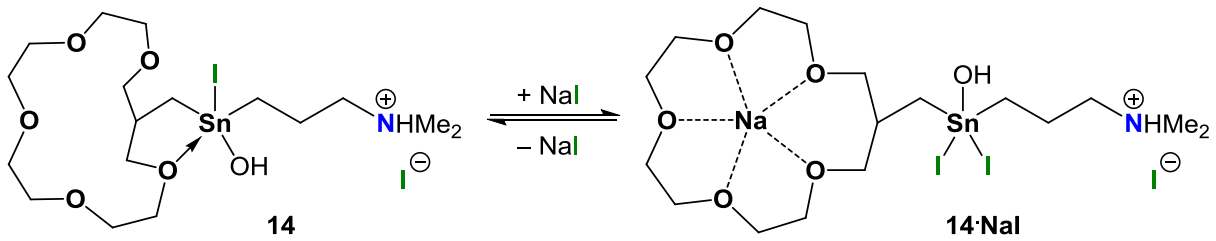


Scheme 7. Synthesis of the organotin compound **14**.

3.3.4 Complexation studies of compound 14 toward sodium iodide and sodium fluoride

A ^{119}Sn NMR spectrum of a solution of **14** to which had been added one molar equivalent of NaI in CD_3CN showed one resonance at δ –184. This chemical shift is displaced by $\Delta\delta$ 22 to high field with respect to the resonance of **14** in CD_3CN (δ –162) (Figure 6).

This change of the direction and magnitude of the chemical shift of the ^{119}Sn NMR resonance indicates that the iodide anion is probably bound to the Lewis-acidic tin atom, (Scheme 8).



Scheme 8. Synthesis of the ditopic complex **14**·NaI.

The value of Δδ 22 in the ^{119}Sn NMR spectrum is close to Δδ 29 and Δδ 27 reported for the reaction of diorganotin diiodide $I_2PhSnCH_2$-19-crown-6 (δ –254, CD_3CN) with potassium iodide, KI, (δ –283, CD_3CN) and sodium iodide, NaI, (δ –281, CD_3CN), respectively.[58]

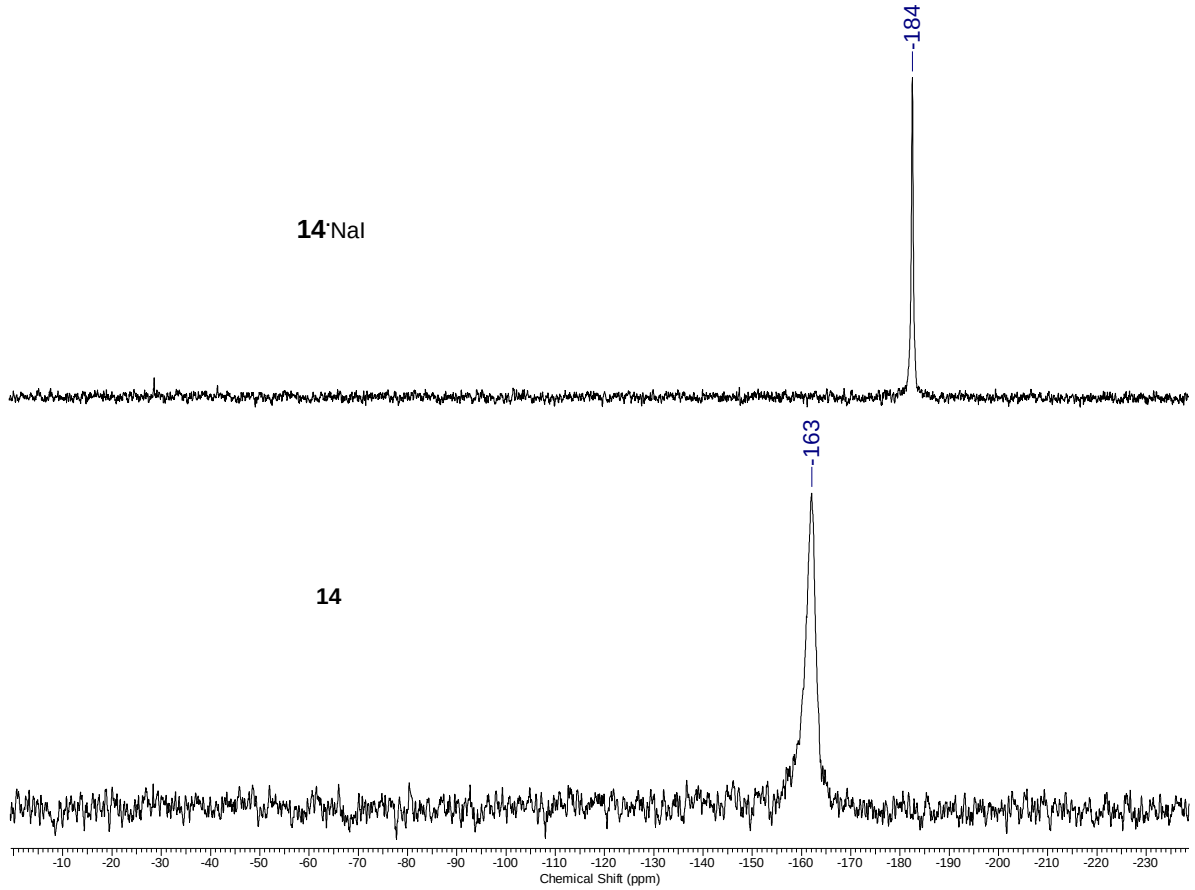


Figure 6. ^{119}Sn NMR spectra of **14** and **14**·NaI in CD_3CN.

The complexation of the sodium ion is supported by the ^{1}H and ^{13}C NMR spectra. In a ^{1}H NMR spectrum of (**14** + NaI) in CD_3CN, the doublet of H1 and multiplet of H2, with respect to the ^{1}H NMR chemical shift of **14** in CD_3CN, are low-field shifted by 0.22 and 0.14 ppm,

respectively. Furthermore, the complex pattern for the crown ether protons was narrowed to a smaller region in comparison with those of **14** (Figure 7).

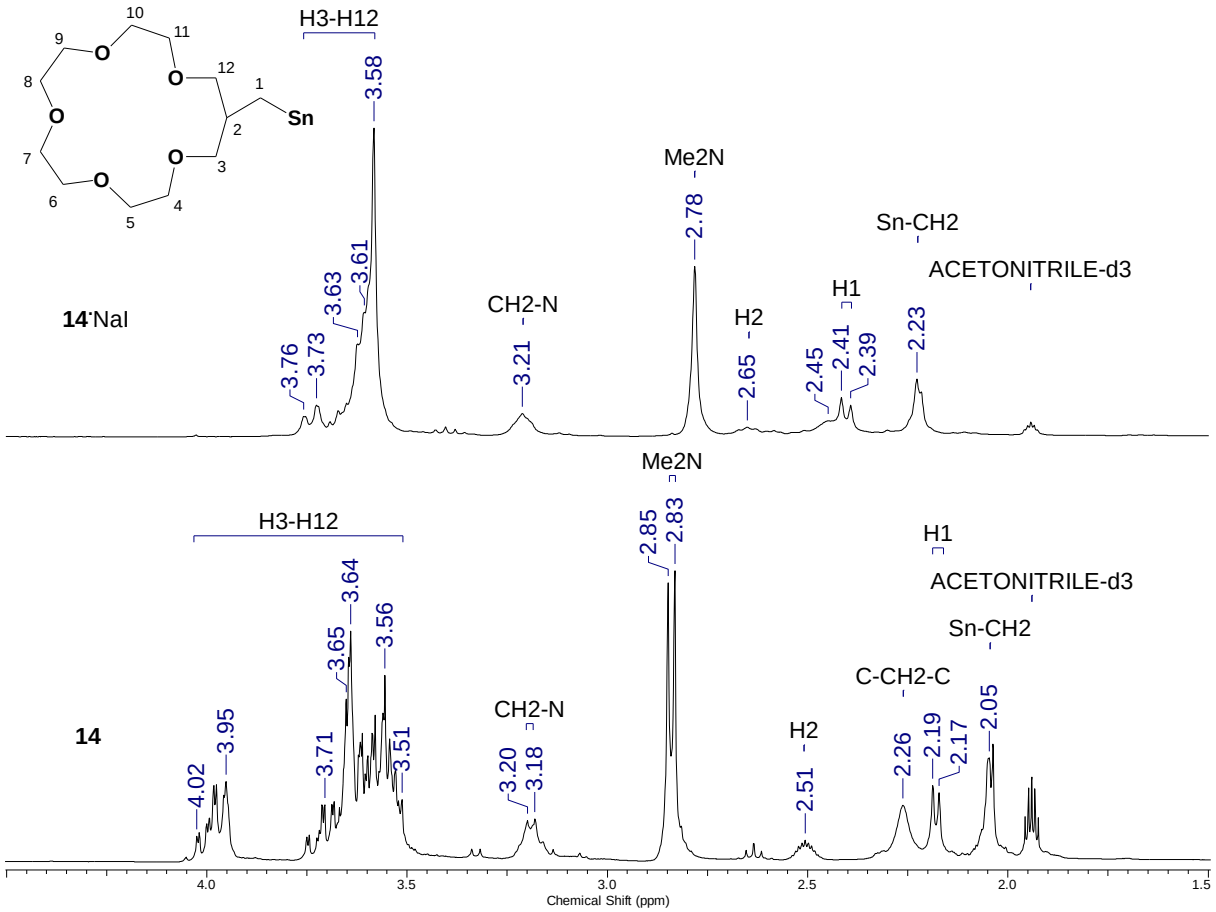


Figure 7. Expansion of the signals assigned to **14** and **14**·NaI in ^{1}H NMR spectra in CD_3CN.

A ^{13}C NMR spectrum of the same sample showed, in comparison with a ^{13}C NMR spectrum of **14**, the signal of the C1 and C2 carbon atoms moved by 2.6 and 1.3 ppm to low and high field, respectively, and the signal of the C3/C12 carbon atom is low-field shifted by 2.28 ppm. Also those of the C4–C11 crown ether carbon atoms are low field shifted, their four carbon atom signals were found between δ 69.9 and δ 72.3 in compound **14** whereas were found between δ 69.6 and 71.1 by the addition of the salt (Figure 8).

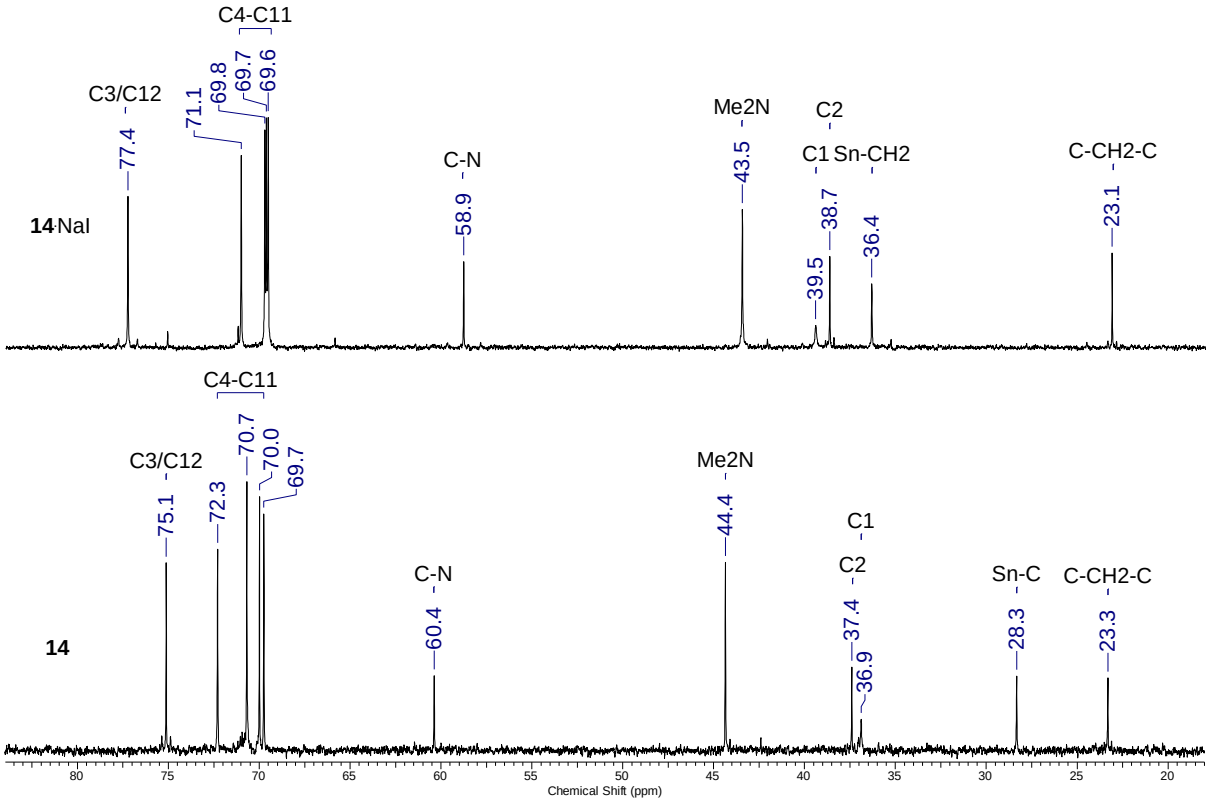


Figure 8. ^{13}C NMR spectra of **14** and **14**·NaI in CD_3CN.

The ESI MS spectrum supports the formation of the ditopic complex **14**·NaI in solution. In the positive mode a mass cluster centered at *m/z* 638.0 was observed that corresponds to $[\{Me_2NH(CH_2)_3\}(OH)_2ISnCH_2\text{-}[16]\text{-crown-}5\cdot Na]^+$.

No reaction takes place by mixing compound **14** with one molar equivalent of sodium fluoride in CH_2Cl_2 with stirring for two days. This can be attributed to the Lewis acidity of the tin atom being not high enough to overcome the high lattice energy of NaF (913 KJ/mol).[48]

3.3.5 Molecular structure of $[\{Me_2(H)N(CH_2)_3\}(I_3)SnCH_2\text{-}[16]\text{-crown-}5]$, 15.

Compound **15** crystallizes in the triclinic space group *P*–1 with two molecules per unit cell. The molecular structure of **15** is presented in Figure 9, selected interatomic distances and bond angles are listed in Table 1.

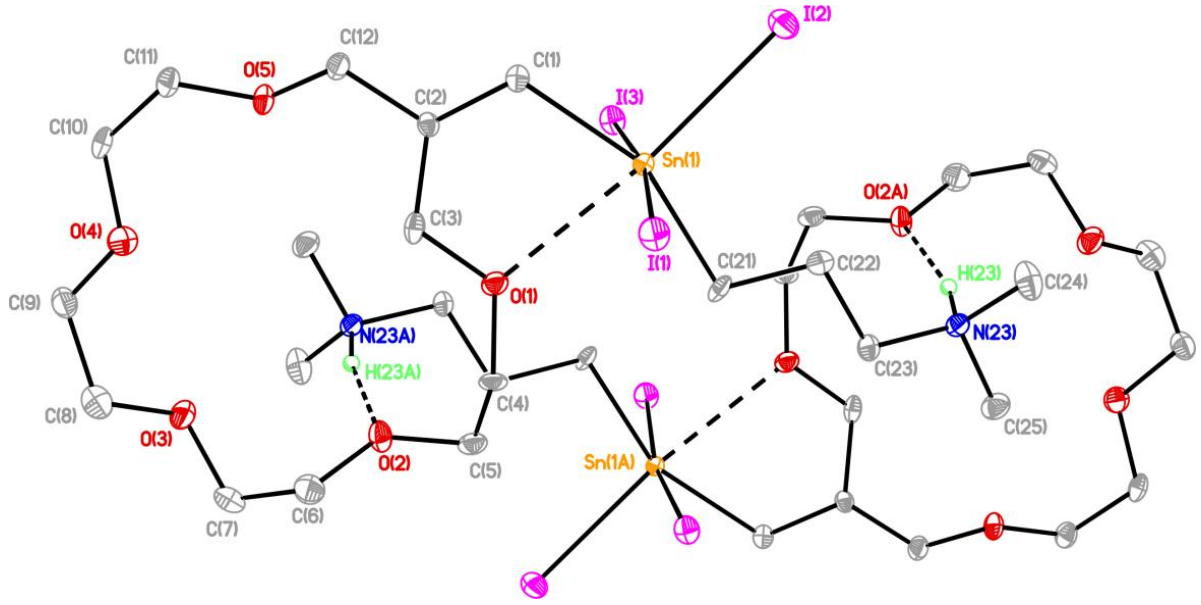


Figure 9. General view (SHELXTL) of a molecule of **15** showing 30% probability displacement ellipsoids and the crystallographic numbering scheme. Compound **15** is a centrosymmetric head-to-tail dimer realized by incorporation via hydrogen bridges of the ammonium moiety into the crown ether.

Table 1. Selected interatomic distances /Å and bond angles /° for **15**.

Sn(1)–I(1)	2.9284(5)	I(2)–Sn(1)–I(3)	91.750(17)
Sn(1)–I(2)	2.7436(6)	C(1)–Sn(1)–I(1)	91.59(13)
Sn(1)–I(3)	3.0035(5)	C(1)–Sn(1)–I(2)	99.81(15)
Sn(1)–O(1)	2.6741(4)	C(1)–Sn(1)–I(3)	86.47(13)
O(2)–H(23A)	1.9540(8)	I(1)–Sn(1)–I(3)	171.956(19)
N(23)–H(23)	0.87(5)	C(21)–Sn(1)–I(1)	91.10(13)
O(1)–Sn(1)–I(2)	173.561(88)	C(21)–Sn(1)–I(2)	104.11(15)
I(2)–Sn(1)–I(1)	96.274(18)	C(21)–Sn(1)–I(3)	87.48(14)

The tin atom in **15** is hexacoordinated and adopts a distorted octahedral environment, with O(1) and I(2) being respectively above and below the equatorial plane formed by I(1), C (1), C(21) and I(3). The O(1)–Sn(1)–I(2) angle of 173.56° is close to the ideal value of 180°. The intramolecular Sn(1)–O(1) distance of 2.6741(4) Å is longer than both Sn–O interactions reported for the octahedral tin atom in compound $PhI_2SnCH_2Sn(I)_2CH_2$-[13]-crown-4 of 2.497(3) and 2.639(3)°.[59] It is also longer than that found for the pentacoordinated tin atom in I_3SnCH_2-[13]-crown-4 of 2.416(2) Å.[59] The Sn(1)–I distances of 2.9284(5) (Sn(1)–I(1)), and 3.0035(5) (Sn(1)–I(3)) are both above the sum of the covalent radii of Sn and I (2.77 Å),[48] whereas the distance (Sn(1)–I(2)) of 2.7436(6) Å is in this range.

A ^{1}H NMR spectrum of compound **15** in $CDCl_3$ showed a broad signal of the NH proton at δ 8.17. For the $(CH_3)_2N^+$ protons a broad singlet signal at δ 2.84 was observed. In a ^{13}C NMR spectrum of the same sample two signals related to the $SnCH_2$ and C1 carbon atoms at δ 25.9 ($^1J(^{13}C–^{117/119}Sn)$ = 613 Hz) and δ 34.5 ($^1J(^{13}C–^{117/119}Sn)$ = 632/660 Hz), respectively, were observed. The chemical shift of 34.5 is similar to that found for the corresponding carbon atom in I_3SnCH_2-[19]-crown-6 at δ 34.4 ($^1J(^{13}C–^{117/119}Sn)$ = 566/593 Hz). The latter compound is hexacoordinated with two O→Sn interactions. On the other hand, these coupling constants of $^1J(^{13}C–^{117/119}Sn)$ in **15** are close to 593 Hz reported for I_3SnCH_2-[19]-crown-6. This indicates that the six-coordinated environment of the tin atom in **15** found in the solid state is retained in solution. No signal was observed in a ^{119}Sn NMR spectrum of **15** (in CD_3CN or $CDCl_3$) measured at ambient temperature.

3.4 CONCLUSION

From an inspection of the NMR data we conclude that the organotin iodides **4** and **5** show no intramolecular N→Sn coordination. The tin atoms in these compounds have a tetracoordinated environment. In addition, no color-change was observed between them and the tetraorganotin compound **3**. The same behavior was observed even with replacing the iodine atom in compound **4** with the higher electronegative chlorine atom. The organotin chloride **7** with the high Lewis aciditc tin atom shows a tetrahedral environment and no evidence for a N→Sn intramolecular coordination in solution was observed. Attempts to synthesize the corresponding triorganotin fluoride resulted in formation of a precipitate showing rather poor solubility. This is in contrast to fluoridoorganotin compounds having intramolecular coordination which show usually good solubility in organic solvents. one question remains to be answered: why these organotin halides with relatively high Lewis acidity tin atoms could not form the intramolecular N→Sn coordination, similarly to other organotin compounds containing the potential intramolecular donor $Me_2N(CH_2)_3$– substituent. This could be attributed probably to the resonance of the –(CH_3)N– moiety with the ring of the azo group that is in turn prevents the lone pair electrons of the nitrogen atom to form the N→Sn interaction. Another possibility is the Lewis acidity in the studied organotin compounds is still not high enough to achieve the intramolecular N→Sn interaction. Another issue is the steric hindrance.

The tetraorganotin compound $[(AnCH_2)(Bn)N(CH_2)_3]SnPh_3$ (An = anthracenyl), **11**, incorporating anthracene moiety was synthesized and completely characterized. Its design fits with the ''photoinduced electron transphere'' type of fluorescent sensors, with the format fluorophore–spacer–receptor. The high Lewis-acidity of the tin atom in this sensor is necessary for its role as a receptor. Therefore, the iodine-substituted triorganotin compound **12** was synthesized and characterized. No evidence on the presence of the intramolecular N→Sn coordination was obtained from a ^{119}Sn NMR spectrum at room temperature. Moreover, NMR studies indicate that compound **12** is not stable towards the room moisture and suffered hydrolysis reactions accompanied with protonation of the amino group.

In fact, compound **12** is a straightforward example for a Frustrated Lewis pair (FLP). This could be the reason for its easy hydrolysis.

Consequently, the instability of compound **12** prevented the synthesis of the triorganotin fluoride $[(AnCH_2)(Bn)N(CH_2)_3]SnPh_2F$, that was proposed to be studied as a chemosensor for the detection of fluoride anions.

The tetraorganostannyl-substituted crown ether-5 (**13**) was synthesized and characterized. The functionalization of the tin atom with iodine, accompanied with hydrolysis reaction by air moisture, resulted in compound **14** containing an ammonium moiety. Addition of NaI salt to compound **14** resulted in the ditopic complex **14**·NaI with the sodium ion being complexed by the crown ether ring and the iodide coordinated at the tin atom. The formation in solution of the complex **14**·NaI was proved by ^{1}H, ^{13}C and ^{119}Sn NMR spectroscopy and electrospray ionization mass spectrometry. On the other hand, compound **14** showed no reaction with NaF as proved by NMR spectroscopy. This could be attributed to the Lewis acidity of the tin atom being not high enough to compensate the lattice energy of sodium fluoride.

3.5 EXPERIMENTAL SECTION

All solvents were dried and purified according to standard procedures and freshly distilled prior to use. 3-N-methylanilino-1-propanol,[14] Ph_2ISnCH_2-[16]-crown-5,[53] $Me_2N(CH_2)_3Cl$[19] were synthesized according to literature methods. Hexaphenyldistannane, Aniline, triphenylphosphonium PPh_3, the chlorination agent Cl_3CCONH_2, tetraethylammonium fluoride, $\{Me_2N(CH_2)_3Cl\}$·HCl, 9-Anthraldehyde, $NaBH_4$, and benzyl chloride were commercially available and they were used without further purification. Bruker DPX–300 and DRX–400 spectrometers were used to obtain ^{1}H, ^{13}C, ^{19}F, and ^{119}Sn NMR spectra. Solution ^{1}H, ^{13}C, ^{19}F, and ^{119}Sn NMR chemical shifts are given in ppm and were referenced to Me_4Si (^{1}H, ^{13}C), $CFCl_3$ (^{19}F), and Me_4Sn (^{119}Sn). Elemental analyses were performed on a LECO–CHNS–932 analyzer. Elemental analyses were performed on a LECO–CHNS–932 analyzer. The electrospray mass spectra were recorded with a Thermoquest–Finnigan instrument, using CH_3CN, MeOH or CH_2Cl_2 as the mobile phase.

Synthesis of $Ph(Me)N(CH_2)_3OH$

A mixture of 3-chloro-1-propanol (10.0 g, 105.77 mmol), N-methylaniline (11.3 g, 105.77 mmol), KI (0.6 g, 3.6 mmol) and K_2CO_3 (14.6 g, 105.77 mmol) in butanol (70mL) was stirred at reflux for 7 days under argon. After that the mixture was stirred at room temperature followed by filtration of the suspended salts. Evaporation of the solvent gave yellowish oil that was distilled in vacuo (120°C, $9x10^{-3}$) yielding (11.78 g, 67%) of 3-*N*-methylanilino-1-propanol as yellow oil.

^{1}H NMR (300.13 MHz, $CDCl_3$): δ 1.86 (m, 2H, CH_2–CH_2), 2.49 (s, 1H, OH), 2.96 (s, 3H, N(CH_3)), 3.47 (t, 2H, OH–CH_2), 3.74 (t, 2H, CH_2–N), 6.76–7.30 (5H, Ph). **^{13}C{^{1}H} NMR** (75.48 MHz, $CDCl_3$): 29.8 (CH_2–*C*H_2), 38.9 N(*C*H_3), 49.6 (OH–*C*H_2), 59.9 (*C*H_2–N). Anal. Calcd (%) for $C_{10}H_{15}NO$ (165.24): C 72.7, H 9.2, N 8.5. Found: C 72.6, H 9.4, N 8.5.

Synthesis of $(PhN{=}NC_6H_4)(Me)N(CH_2)_3OH$ (1).

Aniline (1.487 g, 15.9 mmol) was dissolved in HCl (50 mL, 1.7 M) and the solution was kept at 0 °C. To this solution was added $NaNO_2$ (1.097 g) with stirring for 15 minutes. The resulting diazonium salt was added dropwise at 0 °C to a solution of $Ph(Me)N(CH_2)_3OH$ (2.000 g, 15.9 mmol) in HCl (75 mL, 0.4 M) followed by neutralizing the solution to *p*H 5-6 using sodium acetate. The stirring was continued for 2 hours. The resulting aqueous solution was extracted with Et_2O (3 X 100 ml). The organic extracts were combined and dried over $MgSO_4$. The solvent was removed in vacuo giving compound **1** as red oil (3.28 g, 76%).

^{1}H NMR (300.13 MHz, $CDCl_3$): δ 1.88 (m, 2H, CH_2–CH_2), 3.08 (s, 3H, N(CH_3)), 3.59 (t, 2H, OH–CH_2), 3.73 (t, 2H, CH_2–N), 6.79 (d, 2H, Ph), 7.40–7.91 (7H, Ph). **^{13}C{^{1}H} NMR** (75.48 MHz, $CDCl_3$): 29.4 (CH_2–*C*H_2), 38.3 N(*C*H_3), 49.9 (OH–*C*H_2), 60.7 (*C*H_2–N), 111.9 (Ar), 122.0 (Ar), 125.5 (Ar), 128.9 (Ar), 129.4 (Ar), 143.5 (Ar), 151.3 (Ar), 152.4 (Ar). Anal. Calcd (%) for $C_{16}H_{19}N_3O$ (269.35): C 71.35, H 7.11, N 15.60. Found: C 71.4, H 7.3, N 15.2.

Synthesis of $(PhN{=}NC_6H_4)(Me)N(CH_2)_3Cl$ (2).

To a stirred solution of **1** (4.00 g, 14.9 mmol) and PPh_3 (4.87 g, 18.6 mmol) in dry CH_2Cl_2 (75 mL) was added Cl_3CCONH_2 (3.02 g, 0.5 mmol) under argon atmosphere. The mixture was heated at reflux for three hours, then stirred at room temperature for two days. After that

the reaction was quenched with cold water, and the organic phase was dried over $MgSO_4$. Removing the solvent in vacuo gave a crude compound that was purified by column chromatography using (SiO_2, toluene) giving compound **2** as red oil (2.48 g, 58%).

^{1}H NMR (400.13 MHz, $CDCl_3$): δ 2.08 (m, 2H, CH_2–CH_2), 3.06 (s, 3H, N(CH_3)), 3.60 (t, 4H, Cl–CH_2 + CH_2–N), 6.79 (d, 2H, Ph), 7.39–7.91 (7H, Ph). **^{13}C{^{1}H} NMR** (100.14 MHz, $CDCl_3$): 29.8 (CH_2–CH_2), 38.6 N(CH_3), 42.4 (Cl–CH_2), 49.3 (CH_2–N), 111.2 (Ar), 122.1 (Ar), 124.9 (Ar), 128.8 (Ar), 129.3 (Ar), 143.5 (Ar), 151.0 (Ar), 153.0 (Ar). Anal. Calcd (%) for $C_{16}H_{18}ClN_3$ (287.79): C 66.78, H 6.30, N 14.60. Found: C 66.8, H 6.3, N 14.6.

Synthesis of {(PhN=NC$_6$H$_4$)(Me)N(CH$_2$)$_3$}SnPh$_3$ (3).

To a suspension of hexaphenyldistannane (7.00 g, 3.9 mmol) in THF (75mL) were added metallic sodium (0.18 g, 7.7 mmol) and a catalytic amount of naphthalene. The mixture was stirred at room temperature for two days. The latter mixture was added at –70°C to a solution of **2** (2.30 g, 7.7 mmol) in THF (50mL). The brown mixture was stirred at room temperature for 1 day and then heated at reflux for 2h. THF was distilled off under reduced pressure, then cold water (100 mL) was added, and the mixture was extracted three times each with 75 mL of CH_2Cl_2. The combined organic phases were dried with $MgSO_4$ and the solvent was evaporated in vacuo to give compound **3** (4.64 g, 98%) as red viscous oil.

^{1}H NMR (400.13 MHz, $CDCl_3$): δ 1.65 (t, ^2J(^{1}H–$^{117/119}$Sn) = 55.9 Hz, 2H, Sn–CH_2), 2.10 (m, 2H, Sn–CH_2–CH_2), 2.99 (s, 3H, N(CH_3)), 3.46 (t, 2H, CH_2–N), 6.68 (d, 2H, Ar), 7.42–7.93 (complex pattern, 22H, Ar). **^{13}C{^{1}H} NMR** (100.63 MHz, $CDCl_3$): δ 7.6 (^1J(^{13}C–$^{117/119}$Sn) = 366/384 Hz, Sn–CH_2), 23.7 (^2J(^{13}C–$^{117/119}$Sn) = 20 Hz, Sn–CH_2–CH_2), 38.4 N(CH_3), 55.9 (^3J(^{13}C–$^{117/119}$Sn) = 68 Hz, CH_2–N), 111.2, 122.1, 125.0, 128.6 (^3J(^{13}C–$^{117/119}$Sn) = 48 Hz, $SnPh_2$, C$_m$), 128.9. 129.0 (^4J(^{13}C–$^{117/119}$Sn) = 11 Hz, $SnPh_3$, C$_p$), 129.2, 136.9 (^2J(^{13}C–$^{117/119}$Sn) = 36 Hz, $SnPh_3$, C$_o$), 138.3 (^1J(^{13}C–$^{117/119}$Sn) = 470/492 Hz, $SnPh_3$, C$_i$), 143.4, 151.3, 153.2. **^{119}Sn{^{1}H} NMR** (111.92 MHz, $CDCl_3$): δ –100. Anal. Calcd (%) for $C_{34}H_{33}N_3Sn$ (602.37): C 67.79, H 5.52, N 6.98. Found: C 67.9, H 5.6, N 6.6.

Synthesis of {(PhN=NC$_6$H$_4$)(Me)N(CH$_2$)$_3$}SnPh$_2$I (4).

Elemental iodine (0.38 g, 1.49 mmol) was added in small portions and under ice cooling to a stirred solution of **3** (0.90 g, 1.49 mmol) in CH_2Cl_2 (70mL). Stirring was continued while warming to room temperature overnight. The solvent and the iodobenzene were removed in vacuo to afford 0.94 g (96%) of **4** as viscous red oil.

^{1}H NMR (400.13 MHz, $CDCl_3$): δ 1.78 (t, $^2J(^1H–^{117/119}Sn)$ = 52.5 Hz, 2H, Sn–CH_2), 2.12 (m, $^3J(^1H–^{117/119}Sn)$ = 69.3 Hz, 2H, Sn–CH$_2$–CH_2), 3.03 (s, 3H, N(CH_3)), 3.49 (t, 2H, CH_2–N), 6.72 (d, 2H, Ar), 7.41–7.91 (complex pattern, 17H, Ar). **^{13}C{^{1}H} NMR** (100.63 MHz, $CDCl_3$): δ 13.4 ($^1J(^{13}C–^{117/119}Sn)$ = 389 Hz, Sn–*C*H$_2$), 24.1 (Sn–CH$_2$–*C*H$_2$), 38.6 N(*C*H$_3$), 55.0 (*C*H$_2$–N), 111.4 (Ar), 122.1(Ar), 125.1(Ar), 128.8 (Ar), 128.9 (SnPh$_2$, C$_m$), 129.3 (Ar). 130.1 ($^4J(^{13}C–^{117/119}Sn)$ = 14 Hz, SnPh$_2$, C$_p$), 135.9 ($^2J(^{13}C–^{117/119}Sn)$ = 46 Hz, SnPh$_2$, C$_o$), 136.7 (SnPh$_2$, C$_i$), 143.5 (Ar), 151.2 (Ar), 153.1 (Ar). **^{119}Sn{^{1}H} NMR** (111.92 MHz, $CDCl_3$): δ –56. Anal. Calcd (%) for $C_{28}H_{28}IN_3Sn$ (652.17): C 51.57, H 4.33, N 6.44. Found: C 50.9, H 4.4, N 6.4. **Electrospray MS**: m/z (%) positive mode: 526.1 (75, $[M – I]^+$), 654.1 (18, $[M + H]^+$), negative mode: 127.0 (100, $I^–$), 380.7 (18, $I_3^–$).

Synthesis of {(PhN=NC$_6$H$_4$)(Me)N(CH$_2$)$_3$}SnPhI$_2$ (5).

Elemental iodine (0.34 g, 1.33 mmol) was added in small portions and under ice cooling to a stirred solution of **3** (0.40 g, 0.66 mmol) in CH_2Cl_2 (70mL). Stirring was continued while warming to room temperature overnight. The solvent and the iodobenzene were removed in vacuo to afford 0.43 g (93%) of **5** as viscous red oil.

^{1}H NMR (400.13 MHz, $CDCl_3$): δ 2.11 (m, 4H, ($^2J(^1H–^{117/119}Sn)$ = 55.2 Hz, Sn–CH_2) + Sn–CH$_2$–CH_2, 3.08 (s, 3H, N(CH_3)), 3.56 (t, 2H, CH_2–N), 6.77 (d, 2H, Ar), 7.38–7.91 (complex pattern, 13H, Ar). **^{13}C{^{1}H} NMR** (100.63 MHz, $CDCl_3$): δ 22.1 (Sn–*C*H$_2$), 24.6 (Sn–CH$_2$–*C*H$_2$), 38.9 N(*C*H$_3$), 54.2 (*C*H$_2$–N), 111.9 (Ar), 121.9 (Ar), 125.6 (Ar), 128.8 (Ar), 128.9 (SnPh$_2$, C$_m$), 129.2 (Ar), 129.4 (Ar), 131.1 ($^4J(^{13}C–^{117/119}Sn)$ = 16 Hz, SnPh$_2$, C$_p$), 134.4 ($^2J(^{13}C–^{117/119}Sn)$ = 45 Hz, SnPh$_2$, C$_o$), 136.4 (SnPh$_2$, C$_i$), 143.3 (Ar), 151.7 (Ar), 152.2 (Ar). **^{119}Sn{^{1}H} NMR** (111.92 MHz, $CDCl_3$): δ –163. Anal. Calcd (%) for $C_{22}H_{23}I_2N_3Sn$ (701.97): C 37.64, H 3.30, N 5.99. Found: C 36.1, H 3.4, N 5.6. **Electrospray MS**: m/z (%) positive mode: 704.0 (25, [**M** + H]$^+$), negative mode: 127.7 (100, $I^–$), 380.9 (12, $I_3^–$).

Synthesis of {(PhN=NC$_6$H$_4$)(Me)N(CH$_2$)$_3$}SnI$_3$ (6).

Elemental iodine (0.38 g, 1.49 mmol) was added in small portions and under ice cooling to a stirred solution of **3** (0.30 g, 0.45 mmol) in CH_2Cl_2 (70mL). Stirring was continued while warming to room temperature overnight. The precipitate was separated and dried affording 0.34 g (90%) of **6** as viscous red oil that solidified after few days.

Synthesis of {(PhN=NC$_6$H$_4$)(Me)N(CH$_2$)$_3$}SnPh$_2$Cl (7).

To a solution of **4** (0.08 g, 0.12 mmol) in CH_3CN (20 mL) was added silver chloride, AgCl (0.18 g, 0.12 mmol). The resulting mixture was stirred at room temperature and in the dark for 14 days. After the AgI formed had been removed by filtration the solvent was evaporated in vacuo to afford (0.63 mg, 91%) of **7** as red oil.

^{1}H NMR (300.13 MHz, $CDCl_3$): δ 1.72 (t, $^2J(^1H–^{117/119}Sn)$ = 55.6 Hz, 2H, Sn–CH_2), 2.17 (m, $^3J(^1H–^{117/119}Sn)$ = 71.0 Hz, 2H, Sn–CH$_2$–CH_2), 3.01 (s, 3H, N(CH_3)), 3.49 (t, 2H, CH_2–N), 6.72 (d, 2H, Ar), 7.39–7.91 (complex pattern, 17H, Ar). **^{13}C{^{1}H} NMR** (75.47 MHz, $CDCl_3$): δ 14.1 ($^1J(^{13}C–^{117/119}Sn)$ = 415/424 Hz, Sn–*C*H$_2$), 22.9 ($^2J(^{13}C–^{117/119}Sn)$ = 27 Hz, Sn–CH$_2$–*C*H$_2$), 38.6 N(*C*H$_3$), 55.2 ($^3J(^{13}C–^{117/119}Sn)$ = 78 Hz, *C*H$_2$–N), 111.5 (Ar), 122.1 (Ar), 125.0 (Ar), 128.9 (Ar), 129.0 ($^3J(^{13}C–^{117/119}Sn)$ = 58/61 Hz, SnPh$_2$, C$_m$), 130.3 ($^4J(^{13}C–^{117/119}Sn)$ = 13 Hz, SnPh$_2$, C$_p$), 135.7 ($^2J(^{13}C–^{117/119}Sn)$ = 49 Hz, SnPh$_2$, C$_o$), 138.4 ($^1J(^{13}C–^{117/119}Sn)$ = 559 Hz, SnPh$_2$, C$_i$), 143.5 (Ar) , 151.3 (Ar), 153.1 (Ar). **^{119}Sn{^{1}H} NMR** (111.92 MHz, $CDCl_3$): δ 10. **Electrospray MS**: m/z (%) positive mode: 526.1 (25, $[M – Cl]^+$), 562.1 (40, $[M + H]^+$).

Synthesis of {(PhN=NC$_6$H$_4$)(Me)N(CH$_2$)$_3$}SnPh$_2$F (8).

To a solution of **4** (62 mg, 0.095 mmol) in $CHCl_3$ (5 mL) was added $Et_4NF{\cdot}2H_2O$ (18 mg, 0.095 mmol). The mixture was stirred for one day, followed by filtration of the formed precipitate. The precipitate was washed with water and CH_2Cl_2 and dried in vacuo affording (0.44 mg, 82%) of [(PhN=NC$_6$H$_4$)(Me)N(CH$_2$)$_3$]SnPh$_2$F·H$_2$O as brownish solid that is not soluble in organic solvents.

Anal. Calcd (%) for $C_{28}H_{30}FN_3OSn{\cdot}H_2O$ (562.3): C 59.81, H 5.38, N 7.47. Found: C 60.0, H 5.3, N 7.2.

Reaction of {(PhN=NC$_6$H$_4$)(Me)N(CH$_2$)$_3$}SnPh$_2$I with two molar equivalents Et$_4$NF·2H$_2$O

To a solution of **4** (60 mg, 0.092 mmol) in $CDCl_3$ (0.6 mL) was added $Et_4NF{\cdot}2H_2O$ (34 mg, 0.184 mmol). The mixture was stirred for 1 hour.

^{1}H NMR (400.13 MHz, $CDCl_3$): δ 0.96 (t, Et_4N), 1.09 (t, 2H, Sn–CH_2), 1.86 (m, 2H, Sn–CH_2–CH_2), 2.79 (s, 3H, N(CH_3)), 2.87 (q, Et_4N), 3.15 (t, 2H, CH_2–N), 6.54 (d, 2H, Ar), 7.18–7.83 (complex pattern, 17H, Ar). **^{13}C{^{1}H} NMR** (100.63 MHz, $CDCl_3$): δ 7.36 (Et_4N), 17.03 (Sn–CH_2), 22.9 (Sn–CH_2–CH_2), 38.2 N(CH_3), 52.2 (Et_4N), 55.6 (CH_2–N), 110.9 (Ar), 121.8 (Ar), 124.9 (Ar), 127.5 (Ar), 128.1 (Ar), 128.6 (Ar), 136.6 (Ar), 142.6 (Ar), 146.4 (Ar) , 151.4 (Ar), 152.9 (Ar).

Synthesis of AnCH$_2$NH(CH$_2$)$_3$Cl (9).

3-chloropropylamine hydrochloride (7.0 g, 53.8 mmol) was solubilized in methanol (160 mL) and neutralized with sodium hydroxide (2.15 g, 53.8 mmol). After stirring two hours 9-Anthraldehyde (11.02 g, 53.4 mmol) was added under argon and the stirring was continued overnight. At the next day $NaBH_4$ (16.18 g, 427.5 mmol) was added in small portions at 0°C. The reaction mixture was stirred for 3h at room temperature and then concentrated under reduced pressure. Water (250 mL) was added carefully under ice cooling and the aqueous layer was extracted with CH_2Cl_2 (3 X 200 mL). The combined organic phases were dried with $MgSO_4$ and the solvents evaporated in vacuo to give **9** as yellow-green oil (14.8 g, 97%).

^{1}H NMR (499.79 MHz, $CDCl_3$): δ 1.47 (s, 1H, N*H*), 2.02 (m, 2H, C–CH_2–C), 3.04 (t, 2H, N–CH_2), 3.68 (t, 2H, Cl–CH_2), 4.71 (s, 2H, An–CH_2–N), 7.53 (t, 2H, An), 7.61 (t, 2H, An), 8.35 (d, ^3J(^{1}H–^{1}H) = 8.39 Hz, 2H, An), 8.38 (s, 1H, An), 8.41 (d, ^3J(^{1}H–^{1}H) = 5.04 Hz, 2H, An). **^{13}C{^{1}H} NMR** (125.68 MHz, $CDCl_3$): δ 32.7 (C–CH_2–C), 42.9 (Cl–CH_2), 45.6 (N–CH_2), 47.0 (An–CH_2–N), 123.9 (An), 124.7 (An), 125.8 (An), 126.9 (An), 128.9 (An), 130.0 (An), 131.3 (An).

Synthesis of (AnCH$_2$)(Bn)N(CH$_2$)$_3$Cl (10).

To a solution of **9** (10.0 g, 35.2 mmol) in CH_3CN (500mL) and CH_2Cl_2 (150mL) were added NaOH (1.41 g, 35.2 mmol), KI (2.92 g, 17.6 mmol), and benzyl chloride (4.46 g, 35.2 mmol) under inert condition. The suspension was heated at reflux for 5 h and then filtered to remove the inorganic salts. After evaporation of the solvents the residue was recrystallized from hot ethanol to give (8.1 g, 61%) of **10** as pale yellow solid (mp 88-89 °C).

^{1}H NMR (400.13 MHz, $CDCl_3$): δ 1.89 (m, 2H, C–CH_2–C), 2.67 (t, 2H, N–CH_2), 3.28 (t, 2H, Cl–CH_2), 3.68 (s, 2H, Ph–CH_2–N), 4.53 (s, 2H, An–CH_2–N), 7.29 (m, 5H, Ar), 7.49 (m, 4H, Ar), 8.01 (d, $^{3}J(^{1}H–^{1}H)$ = 7.27 Hz, 2H, An), 8.39 (s, 1H, An), 8.41 (s, 2H, An). **^{13}C{^{1}H} NMR** (100.63 MHz, $CDCl_3$): δ 30.6 (C–*C*H_2–C), 43.1 (Cl–*C*H_2), 51.0 (N–*C*H_2 + An–*C*H_2–N), 59.2 (Ph–*C*H_2–N), 124.8 (An), 125.0 (An), 125.5 (An), 127.0 (Ph), 127.5 (An), 128.1 (Ph), 129.0 (An), 129.2 (Ph), 130.0 (An), 131.3 (An), 139.4 (Ph). Anal. Calcd (%) for $C_{25}H_{24}ClN$ (373.92): C 80.3, H 6.5, N 3.8. Found: C 79.0, H 6.5, N 3.7. **Electrospray MS**: m/z (%) positive mode: 374.2 (100, $[M + H]^+$).

Synthesis of {(AnCH$_2$)(Bn)N(CH$_2$)$_3$}SnPh$_3$ (11).

To a suspension of hexaphenyldistannane (3.0 g, 4.3 mmol) in THF (75mL) were added sodium (0.20 g, 8.6 mmol) and a catalytic amount of naphthalene. The mixture was stirred at room temperature for two days. The latter mixture was added at –70°C to a solution of **10** (3.0 g, 8.1 mmol) in THF (50mL). The brown mixture was stirred at room temperature for 1 day then heated at reflux for 2h. THF was distilled off under reduced pressure, then cold water (100 mL) was added, and the mixture was extracted three times each with 75 mL of CH_2Cl_2. The combined organic phases were dried with $MgSO_4$ and the solvent was evaporated in vacuo to give the crude product. This was purified by column chromatography (SiO_2, *iso*-hexane) to give compound **11** (0.70 g, 12%) as slightly yellow solid (mp 119-121 °C). Single crystals of **11** suitable for X-ray diffraction analysis were grown from a solution in $CHCl_3$ and ethanol.

^{1}H NMR (400.13 MHz, $CDCl_3$): δ 1.45 (t, 2H, Sn–CH_2), 2.15 (m, 2H, Sn–CH_2–CH_2), 2.78 (t, 2H, N–CH_2), 3.75 (s, 2H, Ph–CH_2–N), 4.64 (s, 2H, An–CH_2–N), 7.40–7.73 (24H, Ar), 8.14 (d, $^{3}J(^{1}H–^{1}H)$ = 6.78 Hz, 2H, An), 8.52 (s, 1H, An), 8.63 (d, $^{3}J(^{1}H–^{1}H)$ = 6.02 Hz, 2H, An). **^{13}C{^{1}H} NMR** (100.63 MHz, $CDCl_3$): δ 8.2 ($^{1}J(^{13}C–^{117/119}Sn)$ = 377/396 Hz, Sn–CH_2), 24.0 ($^{2}J(^{13}C–^{117/119}Sn)$ = 19 Hz, C–*C*H_2–C), 50.9 (An–*C*H_2–N), 57.9 ($^{3}J(^{13}C–^{117/119}Sn)$ = 71 Hz, N–*C*H_2), 58.8 (Ph–*C*H_2–N), 124.7 (An), 125.1 (An), 125.3 (An), 126.7 (Ph), 127.3 (An), 127.9 (Ph), 128.4 ($SnPh_3$, C_m), 128.7 ($SnPh_3$, C_p), 128.9 (Ph), 129.0 (An), 130.5 (An), 131.3 (An), 136.9 ($^{2}J(^{13}C–^{117/119}Sn)$ = 35 Hz, $SnPh_3$, C_o), 138.8 ($^{1}J(^{13}C–^{117/119}Sn)$ = 462/483 Hz, $SnPh_3$, C_i).139.8 (Ph). **^{119}Sn{^{1}H} NMR** (111.92 MHz, $CDCl_3$): δ –99. Anal. Calcd (%) for $C_{43}H_{39}NSn$ (688.49): C 75.0, H 5.7, N 2.0. Found: C 75.1, H 5.7, N 2.0.

Synthesis of {(AnCH$_2$)(Bn)N(CH$_2$)$_3$}SnPh$_2$I (12).

Elemental iodine (156 mg, 0.614 mmol) was added in small portions and under ice cooling to a stirred solution of **11** (423 mg, 0.614 mmol) in CH_2Cl_2 (50 mL). Stirring was continued overnight while warming to room temperature. The solvent and the iodobenzene were removed in vacuo to give **12** (276 mg, 61%) as pale yellow solid.

^{1}H NMR (500.13 MHz, $CDCl_3$): δ 1.46 (t, 2H, Sn–C*H*$_2$), 1.97 (m, 2H, Sn–CH$_2$–C*H*$_2$), 2.65 (t, 2H, N–C*H*$_2$), 3.70 (s, 2H, Ph–C*H*$_2$–N), 4.56 (s, 2H, An–C*H*$_2$–N), 7.30–7.71 (19H, Ar), 8.00 (d, ^3J(^{1}H–^{1}H) = 5.74 Hz, 2H, An), 8.41 (s, 3H, An). **^{13}C{^{1}H} NMR** (125.77 MHz, $CDCl_3$): δ 14.1 (Sn–*C*H$_2$), 24.2 (C–*C*H$_2$–C), 50.9 (An–*C*H$_2$–N), 56.5 (N–*C*H$_2$), 59.0 (Ph–*C*H$_2$–N), 124.8 (Ar), 125.5 (Ar), 128.2 (Ar), 128.6 (Ar), 128.8 (Ar), 129.0 (Ar), 129.3 (Ar), 129.9 (Ar), 131.3 (Ar), 131.4 (Ar), 136.0 (Ar), 137.2 (Ar). **^{119}Sn{^{1}H} NMR** (111.92 MHz, $CDCl_3$): δ –51 (93%, **12**), –114 (3%, $SnPh_3I$), –130 (4%, $SnPh_4$). Anal. Calcd (%) for $C_{37}H_{34}INSn$ (738.30): C 60.2, H 4.6, N 1.9. Found: C 60.6, H 4.7, N 1.9. **Electrospray MS**: m/z (%) positive mode: 191.1 (100, [An–CH$_2$]$^+$), 648.2 (40, [M – I + 2H$_2$O]$^+$), negative mode: 127.0 (100, I$^-$), 380.8 (30, I$_3^-$).

The partial assignments of the ^{1}H and ^{13}C NMR data for the crown ether moiety refer to the numbering scheme in Chart 2.

Synthesis of [{Me$_2$N(CH$_2$)$_3$}(Ph$_2$)SnCH$_2$-[16]-crown-5] (13).

To a solution of Ph$_2$ISnCH$_2$-[16]-crown-5[53] (1.25 g, 1.93 mmol) in THF (45 mL) was added the Grignard reagent prepared from Me$_2$N(CH$_2$)$_3$Cl[19] (0.47 g, 3.86 mmol) and magnesium turnings (98 mg, 4.06 mmol) in THF (15 mL). After the completion of the addition the mixture was heated at reflux for three hours before it was cooled to room temperature. THF was distilled off under reduced pressure, then cold water (60 mL) was added, and the mixture was extracted three times with (40 mL) of CH_2Cl_2. The combined organic phases were dried with $MgSO_4$ and the solvents evaporated in vacuo to give (1.01 g, 86%) of **13** as yellowish oil.

^{1}H NMR (400.13 MHz, $CDCl_3$): δ 1.22 (complex pattern, 3H, ^2J(^{1}H–$^{117/119}$Sn) = 49/64 Hz, Sn–C*H*$_2$ + H1), 1.89 (m, 2H, Sn–CH$_2$–C*H*$_2$), 2.16 (m, 1H, H2), 2.31 (s, 6H, N(C*H*$_3$)$_2$), 2.52 (t, 2H, C*H*$_2$–N), 3.33-3.75 (complex pattern, 20H, CH$_2$–O–CH$_2$), 7.28–7.60 (m, 10H, Ph). **^{13}C{^{1}H} NMR** (100.63 MHz, $CDCl_3$): δ 8.3 (^1J(^{13}C–$^{117/119}$Sn) = 362/380 Hz, Sn–*C*H$_2$), 10.7 (^1J(^{13}C–$^{117/119}$Sn) =

377/397 Hz, C1), 23.2 ($^2J(^{13}C–^{117/119}Sn)$ = 18 Hz, Sn–CH_2–CH_2), 37.1 (C2), 44.3 N(CH_3)$_2$, 62.3 ($^3J(^{13}C–^{117/119}Sn)$ = 65/69 Hz, CH_2–N), 69.5-70.7 (C4-C11), 74.3 ($^3J(^{13}C–^{117/119}Sn)$ = 47 Hz, C3/C12), 128.1 ($^3J(^{13}C–^{117/119}Sn)$ = 45 Hz, $SnPh_2$, C_m), 128.2 ($^4J(^{13}C–^{117/119}Sn)$ = 11 Hz, $SnPh_2$, C_p), 136.5 ($^2J(^{13}C–^{117/119}Sn)$ = 34 Hz, $SnPh_2$, C_o), 141.1 ($^1J(^{13}C–^{117/119}Sn)$ = 434 Hz, $SnPh_2$, C_i). **^{119}Sn{^{1}H} NMR** (111.92 MHz, $CDCl_3$): δ –79. **Electrospray MS**: m/z (%) positive mode: 530.2 (100, [{$Me_2N(CH_2)_3$}(Ph)$SnCH_2$-[16]-crown-5]$^+$).

Synthesis of ([{Me_2(H)N$(CH_2)_3$}(OH)I$SnCH_2$-[16]-crown-5]·I) (14).

Elemental iodine (419 mg, 1.56 mmol) was added in small portions and under ice cooling to a stirred solution of **13** (500 mg, 0.82 mmol) in CH_2Cl_2 (20 mL). Stirring was continued while warming to room temperature overnight. The solvent and the iodobenzene were removed in vacuo to afford 0.56 g (82%) of **14** as viscous red oil.

^{1}H NMR (300.13 MHz, $CDCl_3$): δ 2.07 (t, 2H, Sn–CH_2), 2.23 (d, 2H, $^3J(^1H–^1H)$ = 4.8 Hz, H1), 2.34 (m, 2H, Sn–CH_2–CH_2), 2.49 (m, 1H, H2), 2.94 (d, $^3J(^1H–^1H)$ = 5.12 Hz, 6H, N(CH_3)$_2$), 3.34 (t, 2H, CH_2–N), 3.57-4.05 (complex pattern, 20H, CH_2–O–CH_2), 9.53 (s, ^{1}H, NH). **^{13}C{^{1}H} NMR** (75.48 MHz, $CDCl_3$): δ 22.6 (Sn–CH_2–CH_2), 26.3 (Sn–CH_2), 34.4 (C1), 36.8 (C2), 43.6 N(CH_3)$_2$, 58.8 (CH_2–N), 59.6-71.1 (C4-C11), 74.6 (C3/C12). **^{119}Sn{^{1}H} NMR** (111.92 MHz, $CDCl_3$): δ –163.

^{1}H NMR (300.13 MHz, CD_3CN): δ 2.05 (t, 2H, Sn–CH_2), 2.18 (d, $^3J(^1H–^1H)$ = 4.76 Hz, 2H, H1), 2.26 (m, 2H, Sn–CH_2–CH_2), 2.51 (m, 1H, H1), 2.84 (d, $^3J(^1H–^1H)$ = 5.12 Hz, 6H, N(CH_3)$_2$), 3.19 (t, 2H, CH_2–N), 3.51-4.02 (complex pattern, 20H, CH_2–O–CH_2), 7.40 (s, 1H, NH). **^{13}C{^{1}H} NMR** (75.47 MHz, CD_3CN): δ 23.3 ($^2J(^{13}C–^{117/119}Sn)$ = 31 Hz, Sn–CH_2–CH_2), 28.3 (Sn–CH_2), 36.9 (C1), 37.4 (C2), 44.4 N(CH_3)$_2$, 60.4 (CH_2–N), 69.8-72.3 (C4-C11), 75.1 ($^3J(^{13}C–^{117/119}Sn)$ = 36 Hz, C3/C12). **^{119}Sn{^{1}H} NMR** (111.92 MHz, CD_3CN): δ –163. **Electrospray MS**: m/z (%) positive mode: 488.1 (100, [{$Me_2NH(CH_2)_3$}$(OH)_2SnCH_2$-[16]-crown-5]$^+$), negative mode: 126.9 (100, I^-).

Synthesis of the ditopic complex [{Me_2(H)N$(CH_2)_3$}$(I_3)SnCH_2$-[16]-crown-5]·NaI (14·NaI**).**

NaI (30 mg, 0.2 mmol) was added to a solution of **14** (167 mg, 0.2 mmol) in CD_3CN and the mixture was stirred for 10 minutes. From this solution, NMR spectra were recorded.

^{1}H NMR (300.13 MHz, CD_3CN): δ 2.23 (t, 2H, Sn–CH_2), 2.40 (d, $^{3}J(^{1}H–^{1}H)$ = 6.9 Hz, 2H, (H1)), 2.45 (m, 2H, Sn–CH_2–CH_2), 2.65 (m, 1H, H1), 2.78 (s, 6H, N(CH_3)$_2$), 3.21 (t, 2H, CH_2–N), 3.52-3.76 (complex pattern, 20H, CH_2–O–CH_2), 8.62 (bs, 1H, NH). **^{13}C{^{1}H} NMR** (75.47 MHz, CD_3CN): δ 23.1 ($^{2}J(^{13}C–^{117/119}Sn)$ = 36 Hz, Sn–CH_2–*C*H_2), 36.4 (Sn–*C*H_2), 38.7 ($^{2}J(^{13}C–^{117/119}Sn)$ = 36 Hz, C2), 39.5 ($^{1}J(^{13}C–^{117/119}Sn)$ = 385/401 Hz, C1), 43.5 N(*C*H_3)$_2$, 58.9 (*C*H_2–N), 69.6-71.1 (C4-C11), 77.4 ($^{3}J(^{13}C–^{117/119}Sn)$ = 79 Hz, C3/C12). **^{119}Sn{^{1}H} NMR** (111.92 MHz, CD_3CN): δ –184. **Electrospray MS**: m/z (%) positive mode: 730.0 (28, [{$Me_2NH(CH_2)_3$}$(OH)_2$ISnCH_2-[16]-crown-5·Na]$^{+}$, 638.0 (5, [{$Me_2N(CH_2)_3$}I_2SnCH_2-[16]-crown-5·Na]$^{+}$, negative mode: 380.8 (100, I_3^-), 127.0 (26, I^-).

Synthesis of [{Me_2(H)N$(CH_2)_3$}(I_3)SnCH_2-[16]-crown-5] (15).

Recrystallization of compound **14** from its solution in acetone/diethyl ether afforded single crystals of **15** suitable for X-ray diffraction analysis.

^{1}H NMR (400.13 MHz, $CDCl_3$): δ 1.92 (complex pattern, 4H, Sn–CH_2 + Sn–CH_2–CH_2), 2.05 (d, 2H, $^{3}J(^{1}H–^{1}H)$ = 3.0 Hz, H1), 2.44 (m, 1H, H2), 2.84 (6H, N(CH_3)$_2$), 3.17 (t, 2H, CH_2–N), 3.36-3.87 (complex pattern, 20H, CH_2–O–CH_2), 8.17 (s, 1H, NH). **^{13}C{^{1}H} NMR** (100.63 MHz, $CDCl_3$): δ 21.3 (Sn–CH_2–*C*H_2), 25.9 ($^{1}J(^{13}C–^{117/119}Sn)$ = 613 Hz, Sn–*C*H_2), 34.5 ($^{1}J(^{13}C–^{117/119}Sn)$ = 632/660 Hz, C1), 35.6 ($^{2}J(^{13}C–^{117/119}Sn)$ = 54 Hz, C2), 43.6 N(*C*H_3)$_2$, 59.0 ($^{3}J(^{13}C–^{117/119}Sn)$ = 152 Hz, *C*H_2–N), 58.0-70.5 (C4-C11), 73.7 (C3/C12). **^{119}Sn{^{1}H} NMR** (111.92 MHz, $CDCl_3$): no signal. Anal. Calcd (%) for $C_{17}H_{36}I_3NO_5Sn$ (833.90): C 24.5, H 4.4, N 1.7. Found: C 24.1, H 4.3, N 1.4.

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4 Water-Soluble Organotin Compounds and Their Reactivity towards Fluoride Anions in Water

4.1 Fluoride Anion Recognition in Water By The Water Soluble Organotin Receptor $\{[Me_2NH(CH_2)_3]_2SnF_2\}\cdot 2ClO_4$

4.1.1 INTRODUCTION

Receptors that bind fluoride anions by the use of Lewis acid–base interaction have been widely studied.[1][2][3][4] Many examples dealing with fluoride binding in non-polar solvents are reported, whereas achieving this in water is still challenging. The strong competitive nature of water and its properties in terms of polarity and H-bonding abilities, in addition to the high hydration enthalpy of fluoride ($\Delta H° = -504$ kJ.mol^{-1}), are responsible for the difficulties in designing fluoride receptors that operate in water.

Boron-based fluoride receptors are among the most prominent compounds in this field.[5] Cationic boron compounds developed by *Gabbai* and co-workers enable sensing of fluoride ions below the maximum contaminant level in pure water (4 ppm).[6] The phosphonium borane **A** (Figure 1) is a recent and distinctive example. However, the practical application of these cationic boranes is limited as some of them suffer slow decomposition in aqueous media, in addition to a fluorescence turn-off response that is accompanied with the anion binding.[7]

Trembleau and co-workers reported a water soluble triarylborane-based receptor that is able to bind fluoride in water (**B**, Figure 1). A drawback of this receptor is that the binding of fluoride anion was abolished at pH 6.5 which precludes its application in acidic water.[8]

A highly selective sensor that reacts with fluoride anions in water in part per million concentrations was recently reported by *Gabbai* and co-workers. This sensor is based on stibinium cation **C** (Figure 1) and it is especially useful for analytical applications as the fluoride binding is accompanied with a fluorescence turn-on response.[7]

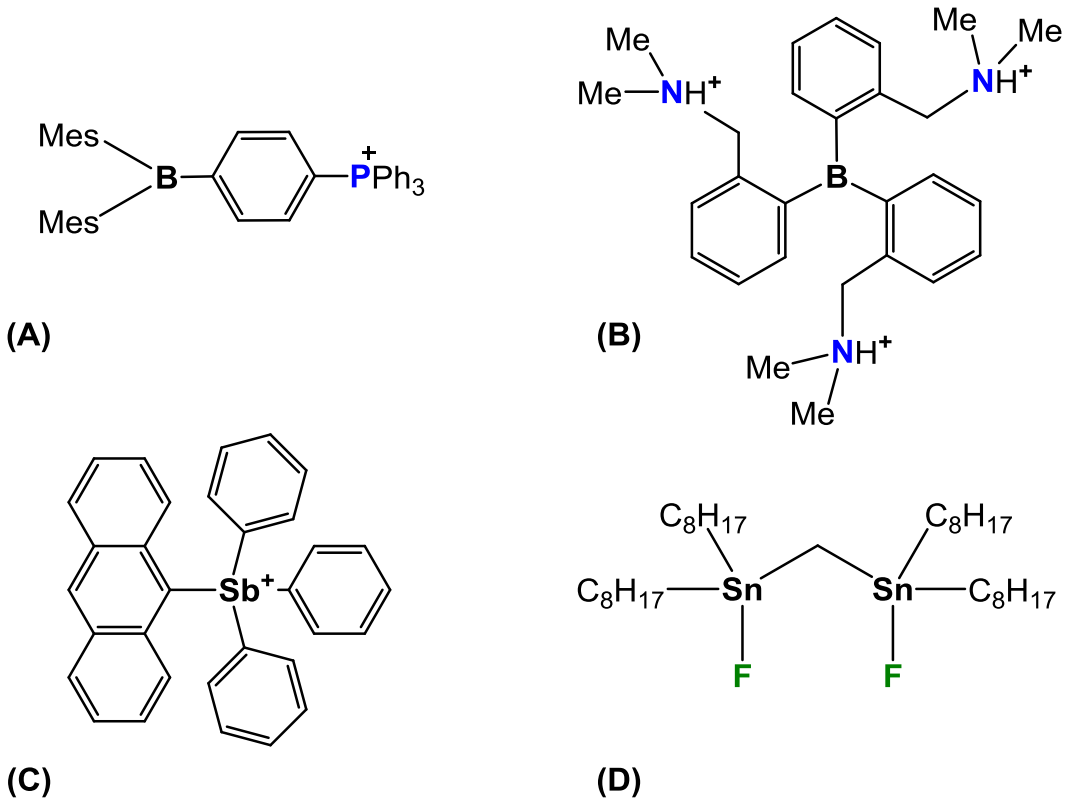


Figure 1. Fluoride receptors reported in literature.

Organotin based receptors achieved good results when fluoride binding is required in organic solvents.[9] [10] [11] In fact, some of them were studied as ionophores for fluoride ion selective electrodes. An example is bis(fluoro-di-*n*-octylstannyl)methane **D** (Figure 1), that is commercially available for this purpose.[12] Nevertheless, tin-based receptors that work in aqueous media are still missing. This could be attributed to the fact that the tin atom should have relatively high Lewis acidity to bind fluoride anions. This is achieved usually by functionalization of the tin atom with electron withdrawing substituents such as halogen atoms. On the one hand, the tin atom in organotin halides is electrophilic enough to undergo strong interactions with fluoride anions, but on the other hand, these compounds are not stable in water and suffer hydrolysis.

An example for a water-soluble organotin compounds is bis[3-(dimethylamino)propyl]difluorostannane.[13] This compound was synthesized in our research group some years ago. Although it showed good reactivity toward fluoride anions in organic solvents, it is not able to bind fluoride anions in water. We have extended the work with this

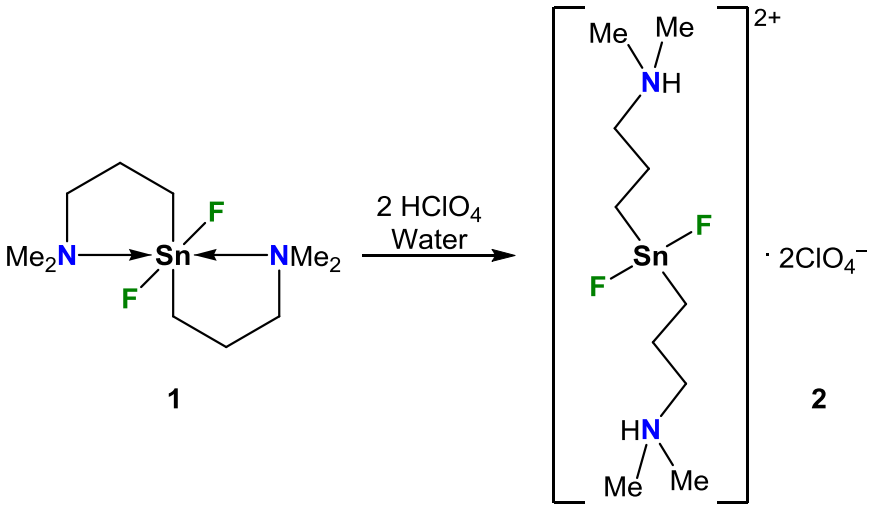
compound trying to achieve our goal in designing an organotin based receptor that is able to selectively capture fluoride anions in water.

Herein, is presented the synthesis of the water-soluble diorganotin difluoride $\{[Me_2NH(CH_2)_3]_2SnF_2\}\cdot 2ClO_4$, **2**, and its fluoride binding properties, selectivity, as well as reversibility. The effect of the *p*H of the solution on this fluoride receptor is also discussed. In addition, a set of water soluble organotin compounds, containing dimethylene-$(CH_2)_2SiMe_2$- space bridged organoditin compounds, are reported.

4.1.2 Syntheses and structures in solution of diorganotin fluorides

The reaction of bis[3(dimethylamino)propyl]dichlorostannane $[Me_2N(CH_2)_3]_2SnCl_2$ with potassium fluoride in CH_2Cl_2 gave bis[3(dimethylamino)propyl]difluorostannane dihydrate, $[\{Me_2N(CH_2)_3\}_2SnF_2\cdot 2H_2O]$, **1**, in good yield. Compound **1** has been reported before by *Jurkschat* and co-workers[13] by the reaction of $\{Me_2N(CH_2)_3\}_2SnR_2$ (R = Me; Ph) with Pr_3SnF. Compound **1** shows good solubility in $CHCl_3$, CH_2Cl_2 and also in water.

The reaction of **1** with two molar equivalent of perchloric acid, $HClO_4$, resulted in protonation of the nitrogen atoms giving the corresponding adduct $[\{Me_2NH(CH_2)_3\}_2SnF_2]\cdot 2ClO_4$, **2**, in almost quantitative yield (Scheme 1).



Scheme 1. Synthesis of the organotin compound **2**.

Compound **2** is a white solid that shows good solubility in water but is moderate soluble in acetone and acetonitrile and poorly soluble in dichloromethane, ethanol and diethyl ether. Till now, all attempts to get single crystals of compound **2** suitable for X-ray diffraction analysis failed.

A ^{119}Sn NMR spectrum of **2** in acetone-d_6 at ambient temperature showed a broad signal at δ –340 ($v_{1/2}$ = 206 Hz) without $^{1}J(^{119}Sn–^{19}F)$ couplings satellites. The ^{19}F NMR spectra of **2** in D_2O and acetone-d_6 showed signals at δ –141 and –145, respectively (Table 1). The chemical shift in D_2O is 18 ppm at higher field shifted in comparison with that measured for **1** in D_2O at –123 ppm.

The ^{1}H NMR spectra of **2** were recorded in different solvents. They showed that the chemical shifts of the N*H* proton depend on the deuterated solvent used. It varies from 7.57 ppm (in CD_3CN) to 8.58 ppm (in acetone-d_6). No signal for the N*H* proton was found in D_2O.

In D_2O, the NCH_3 protons of **2** showed a single resonance at 2.82 ppm. This resonance is shifted by 0.34 ppm to lower field in comparison with that measured for **1** (2.48 ppm in D_2O, Figure 2). In CD_3CN and acetone-d_6 solutions, the NCH_3 protons appear as doublet resonances at 2.86 ppm ($^{3}J(^{1}H–^{1}H)$ = 4.76 Hz) and 3.00 ppm ($^{3}J(^{1}H–^{1}H)$ = 4.39 Hz), respectively.

Noteworthy, the coupling constants $^{2}J(^{1}H–^{119}Sn)$ of the SnCH_2 protons in compound **2** are about 95 Hz (in CD_3CN) and 105 Hz (in acetone-d_6 and D_2O) (Table 1). These values are characteristic for hexacoordinated organotin(IV) compounds, and a little bigger than the corresponding coupling constants measured for the hexacoordinated organotin compound **1** (90 Hz in D_2O, 94 Hz in CD_2Cl_2 at –60°C).[13]

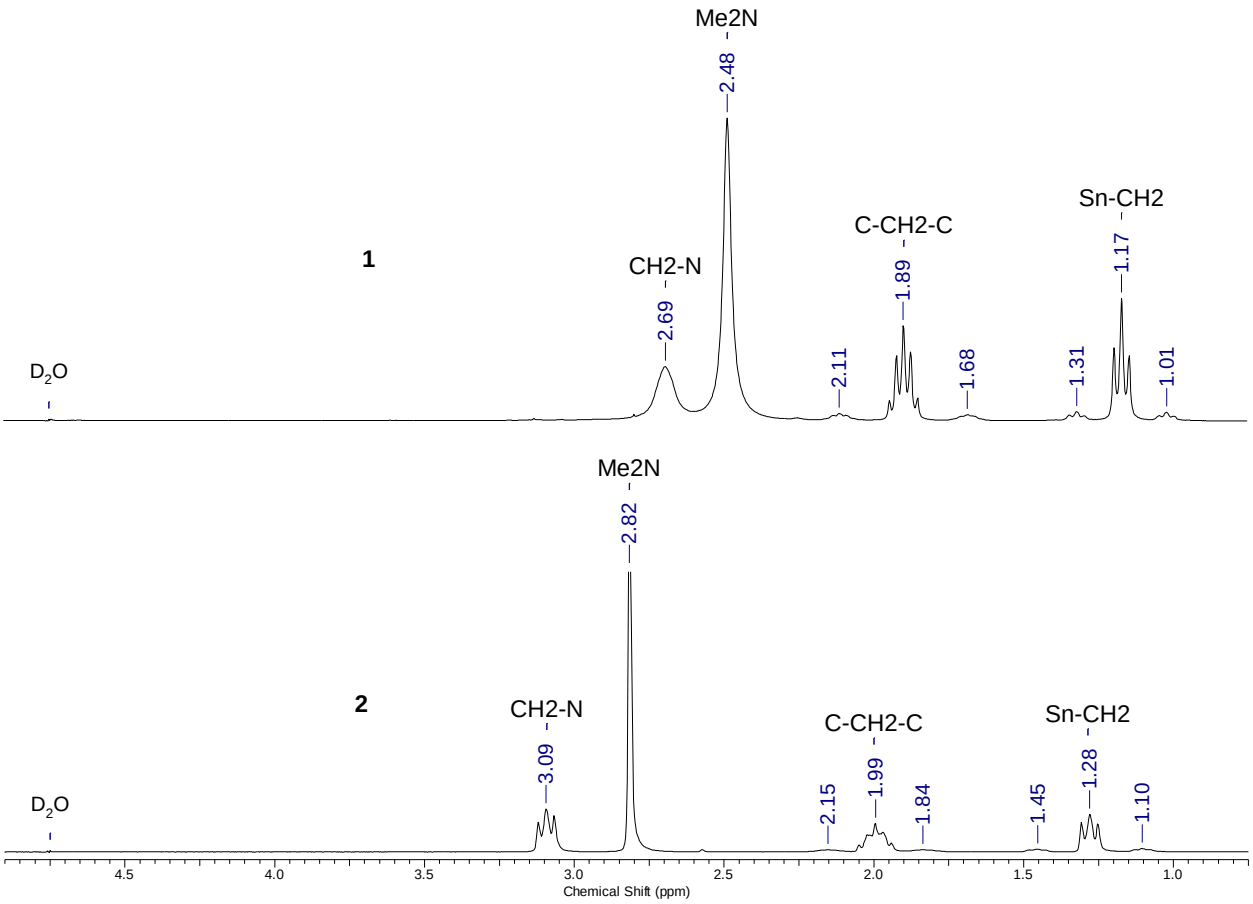


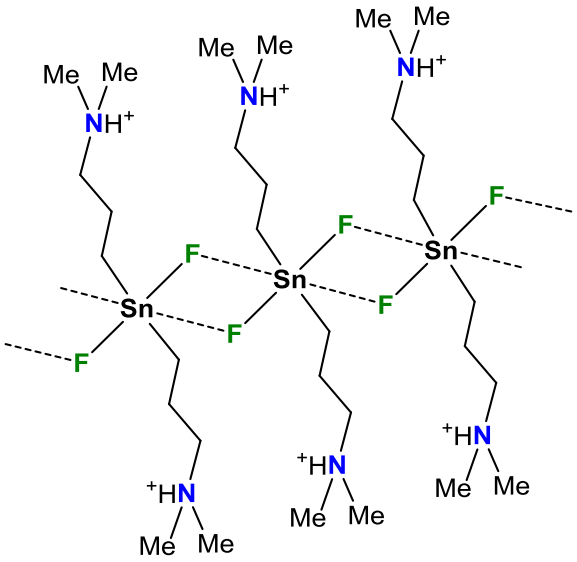
Figure 2. ^{1}H NMR spectra of **1** and **2** in D_2O.

The ^{13}C NMR spectra of **2** were recorded in D_2O and acetone-d_6 solutions. They showed upfield shifts for the Sn*C*H$_2$ carbon atom ($\Delta\delta$ = 6.2 ppm (D_2O), $\Delta\delta$ = 7.3 ppm (acetone-d_6)) with respect to compound **1** (in D_2O). Moreover, the coupling constant $^{1}J(^{13}C–^{119}Sn)$ of 977 Hz (**2** in D_2O) is a little bigger than that of 907 Hz for **1** (in D_2O), being in the range characteristic for hexacoordinated organotin(IV) compounds. A remarkable feature in the ^{13}C NMR spectrum of **2** in D_2O is that the coupling constant $^{3}J(^{13}C–^{117/119}Sn)$ of 165 Hz is bigger than that of 102 Hz found for **1** (in D_2O). These data reveal the tin atom in **2** to be hexacoordinated in solution.

As it is known, most diorganotin difluorides, R_2SnF_2, have polymeric structures with an octahedral environment around the tin atoms, and are solids that melt or decompose at higher temperatures. Taking into account that compound **2** decomposes at 250°C, on the one hand, and based on the NMR discussions which propose a hexacoordinated structure

for this compound, on the other hand, we suggest that compound **2** may have a polymeric structure in the solid state.

This structure is probably similar to that reported for dimethyltin difluoride. *Schlemper* and *Hamilton* determined the structure of dimethyltin difluoride, Me_2SnF_2, consisting of an infinite two-dimensional network of tin atoms that are connected together via bridging fluoride anions.[14] The tin atoms show octahedral environment with four bridging fluoride anions occupying the equatorial positions and with the methyl groups above and below the plane completing the octahedral coordination of the tin atom. We suggest with caution that $[\{Me_2NH(CH_2)_3\}_2SnF_2]^{2+}$ has a polymeric structure similar to that of Me_2SnF_2 (Scheme 2).



Scheme 2. The suggested structure of $[\{Me_2NH(CH_2)_3\}_2SnF_2]^{2+}$.

The perchlorate anion has been widely used in the past as non-coordinating (or weakly coordinating) counterion supporting cationic organometallic complexes. There are abundant examples of cationic organotin complexes containing perchlorate anions,[15][16] whereas organotin compounds with coordinated perchlorate anion are rare.[17] In our case, in the absence of X-ray crystal data, we are unable to indicate the nature of the two ClO_4^- anions. However, depending on the polymeric structure proposed for the cation $[\{Me_2NH(CH_2)_3\}_2SnF_2]^{2+}$ (Scheme 2), we suggest the perchlorate anions being non-coordinating.

Interestingly, in contrast to compound **1**, compound **2** shows good reactivity towards fluoride anions in water. In fact, it is able to react with fluoride anions in water as their sodium and potassium salts (NaF and KF). Remarkably, only in the case of the reaction with KF a white precipitate was formed immediately. This is likely to be $KClO_4$ that is known to have low solubility in water.

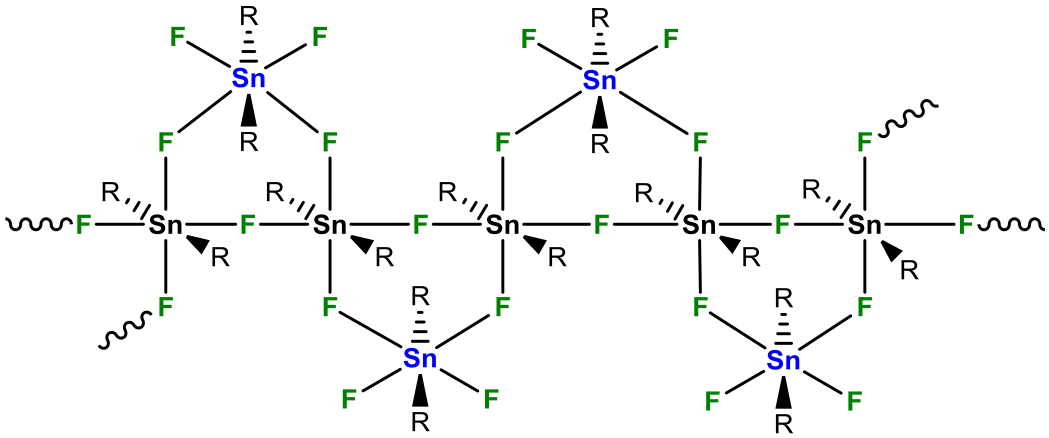
The reaction in water of compound **2** with fluoride anions in different molar ratios was studied. The ^{1}H and ^{13}C NMR spectra of a solution of **2** in D_2O to which had been added 1 molar equivalent of potassium fluoride showed similar chemical shifts to those reported for **2** in D_2O. In a ^{1}H NMR spectrum a $^{2}J(^{1}H–^{119}Sn)$ coupling for the SnCH_2 protons of 110 Hz was observed. This value is close to that measured for **2** of 105 Hz. In a ^{13}C NMR spectrum a coupling $^{1}J(^{13}C–^{119}Sn)$ of 1101/1053 Hz for SnCH_2 carbon was observed. These two coupling constants are characteristic for hexacoordinated organotin compounds and support the octahedral environment around the tin atom.

In a ^{119}Sn NMR spectrum of the same sample measured at room temperature no signal was observed. A ^{19}F NMR spectrum at room temperature showed a singlet resonance at –133 ppm without $^{1}J(^{19}F–^{119}Sn)$ satellites was observed. This chemical shift is 9 ppm lower field shifted in comparison with that measured for **2**.

Surprisingly, the elemental analysis of the reaction product did not agree with the reaction ratio compound **2** : KF (1 : 1) but with the formula $\{[Me_2(H)N(CH_2)_3]_4Sn_2F_5{\cdot}(ClO_4)_3\}{\cdot}3H_2O$ (**3**).

Therefore, it was necessary to verify firstly the reaction of compound **2** with 0.5 molar equiv of KF in D_2O. The NMR spectra showed similar chemical shifts to those recorded for the same reactants with 1:1 ratio.

With caution and in analogy to the structure of $[Me_4Sn_2F_5]^-$,[18] the suggested structure of $(R_4Sn_2F_5{\cdot}(ClO_4)_3$, R = $\{Me_2(H)N(CH_2)_3\}$), **3**, consists of the ions $R_2SnF_3^-$ interconnected to each other by R_2SnF_2 units, (Scheme 3). All the tin atoms are hexacoordinated with fluorine atoms (two bridging and one terminal) are all occupying the equatorial positions whereas the two organic groups $\{Me_2(H)N(CH_2)_3\}$ present in the axial positions. This octahedral coordination of the tin atoms corresponds with the results found in NMR discussion.

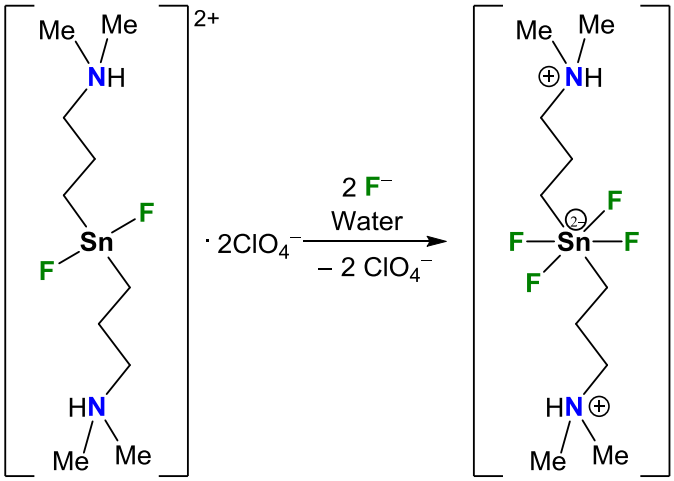


Scheme 3. The suggested structure for the cationic part of compound **3**.

Different examples of diorganotrifluorostannates were reported.[19][20] Dimethyltrifluorostannate species resulting from the reactions of dimethyltindifluoride with fluoride anions have been isolated in the solid state. Two polymeric structures are reported for the compounds $K[Me_2SnF_3]$[21] and $[Et_4N][Me_4Sn_2F_5]$.[18] The latter resulted from the addition of tetraethylammonium fluoride to Me_2SnF_2 and its solid-state structure is described as a polymeric $[Me_2SnF_3]^-$ anion involving "syndiotactical" bridging Me_2SnF_2 units. Noteworthy, the chemical shift in a ^{19}F NMR spectrum of $[Me_4Sn_2F_5]^-$ at –138 ppm (in CD_3CN) is close to that of compound **3** at –133 ppm (in D_2O).

Compound 3 was isolated as a white solid. It shows good solubility in water and low solubility in organic solvents.

The reaction of compound **2** with two molar equivalents of fluoride anions (as NaF or KF) gave $[\{Me_2N(H)(CH_2)_3\}_2SnF_4]$, **4**, quantitatively as a white solid, (Scheme 4) .



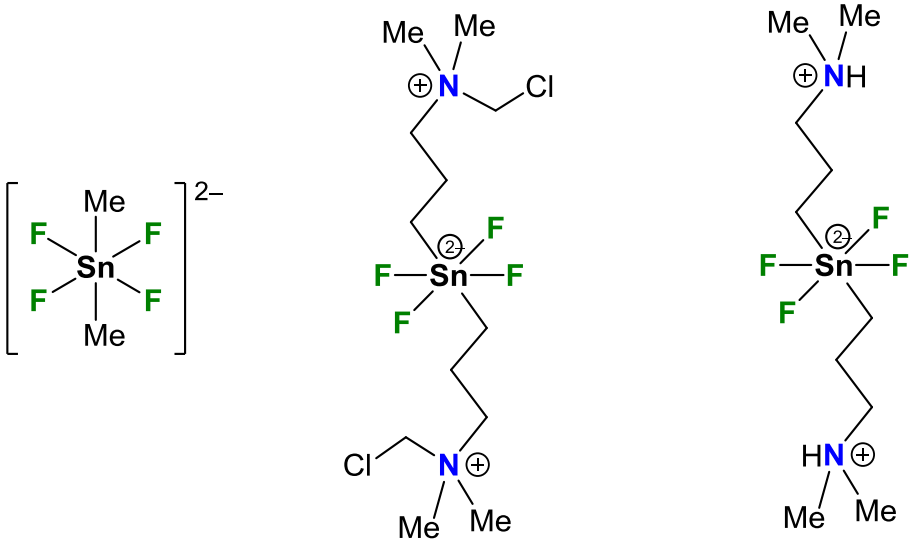
2 **4**

Scheme 4. Synthesis of the organotin compound **4**.

The ^{1}H and ^{13}C NMR spectra of a solution of compound **4** in D_2O showed no remarkable changes in comparison with those recorded for **2** in D_2O. The coupling constant $^{2}J(^{1}H–^{119}Sn)$ of the $SnCH_2$ protons in **4** are about 110 Hz (when KF was used) and 120 Hz (when NaF was used in a higher concentration). These values are in the range characteristic for hexacoordinated organotin (IV) compounds. In ^{13}C NMR spectrum the coupling constants $^{3}J(^{13}C–^{117/119}Sn)$ of 145 Hz and 159 Hz (when KF and NaF were used, respectively) are close to the coupling of 164 Hz found in **2** (in D_2O). A ^{19}F NMR spectrum of a solution of **4** in D_2O showed a singlet resonance at δ –125 without coupling satellites $^{1}J(^{19}F–^{119}Sn)$. This resonance is 17 ppm low-field shifted in comparison with that measured for **2**. It is close to that measured for **1** in D_2O at –123 ppm, and to that reported for the complex salt $K_2[Me_2SnF_4]\cdot 2H_2O$ in D_2O at –122 ppm.[22] The crystal structure of the latter is characterized by the anion $[Me_2SnF_4]^{2-}$ in which the tin atom adopts a slightly distorted octahedral environment, with the methyl groups in *trans* position (Scheme 5).

A ^{119}Sn NMR spectrum of **4** in D_2O showed one signal at –412 ppm with no coupling involving fluorine was observed. This chemical shift is 72 ppm higher field shifted in comparison with that measured for **2** in acetone-d_6. Similar chemical shifts have been observed for $[\{Me_2N(CH_2Cl)(CH_2)_3\}_2SnF_4\cdot 4H_2O]$ in ^{119}Sn NMR (–455 ppm) and ^{19}F NMR spectra (–128 ppm) measured in CD_3OD, (Table 1). The tin atom in $[\{Me_2N(CH_2Cl)(CH_2)_3\}_2SnF_4\cdot 4H_2O]$[23] shows an octahedral environment with the carbon atoms in *trans* positions (Scheme 5).

With caution, we suggest that compound **4** shows a similar structure to both $K_2\{(CH_3)_2SnF_4\}\cdot 2H_2O$[22] and $[\{Me_2N(CH_2Cl)(CH_2)_3\}_2SnF_4]\cdot 4H_2O$[23] where the tin atom adopts octahedral environment and the carbon atoms are in *trans* positions (Scheme 5).



Scheme 5. The proposed monomeric structure of compound **4** (on the right). The structures of $[\{Me_2N(CH_2Cl)(CH_2)_3\}_2SnF_4]$ and $[Me_2SnF_4]^{2-}$.

Compound **4** is a white solid that shows good solubility in water but are not well soluble in common organic solvents such as CH_2Cl_2, ethanol, and diethyl ether.

The electrospray ionization mass spectra (ESI MS, positive mode) of compounds **2** and **3** in water-acitonitrile solution showed a major mass cluster centered at *m*/z = 309.1 that is assigned to $[\{Me_2N(CH_2)_3\}_2SnOH]^+$. For compound **4** a mass cluster centered at *m*/z = 311.0 was found that is assigned to $[\{Me_2N(CH_2)_3\}_2SnF]^+$. In the negative mode a mass cluster centered at *m*/z = 507.0 was found for both compounds **2** and **3**. It corresponds with the anion $[\{Me_2N(CH_2)_3\}_2SnOH(ClO_4)_2]^-$ (Figure 3).

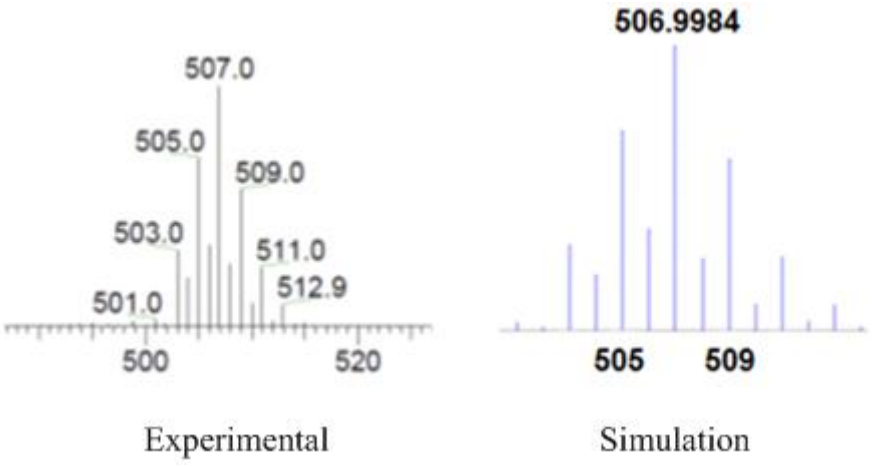


Figure 3. Experimental (from ESI MS) and simulated mass cluster for the anion $[\{Me_2N(CH_2)_3\}_2SnOH(ClO_4)_2]^-$.

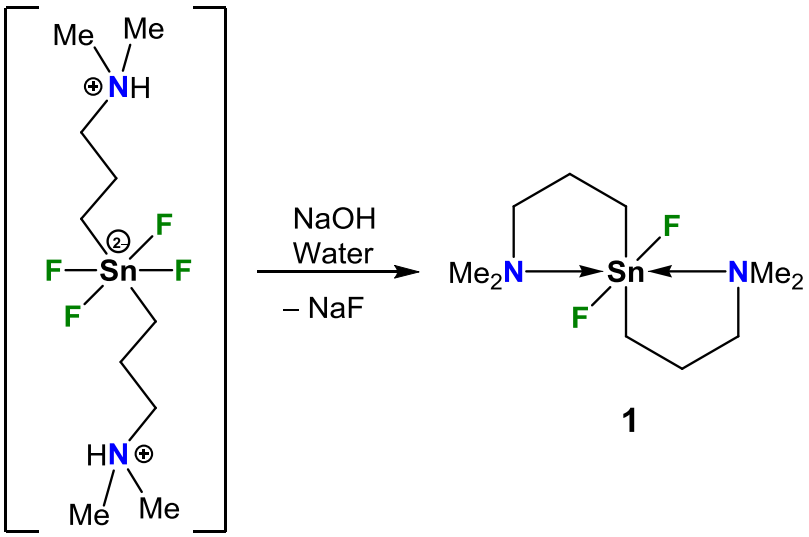
Table 1. Selected NMR data for compounds **1–4**.

		Sn–CH_2		Me_2N	δ
	Solvent	$^2J(^1H–^{117/119}Sn)$	$^1J(^{13}C–^{117/119}Sn)$	$\delta\,^1H$	^{19}F
1	CD_2Cl_2	94	1010/1060	2.35	–121
	D_2O	90	907	2.48	–123
2	D_2O	105	977	2.84	–141
	$C_3D_6O_2$	105		2.99/3.01	–145
	CD_3CN	95		2.85/2.87	
3	D_2O	110	1101/1053	2.85	–133
$[Et_4N][Me_4Sn_2F_5]$[18]	CD_3CN				–138
4	D_2O	120	1102 /1153	2.91	–125
$\{[Me_2N(CH_2Cl)(CH_2)_3]_2SnF_4\}$[23]	CD_3OD			3.23	–128
$K_2[(CH_3)_2SnF_4]\cdot 2H_2O$[22]	D_2O	99/103	937/980		–122

Coupling constants are given in Hz.

4.1.3 Studying the effect of solution *p*H on the behavior of [{$Me_2N(H)(CH_2)_3$}$_2SnF_4$]

To verify the effect of solution *p*H on the structure of [{$Me_2N(H)(CH_2)_3$}$_2SnF_4$], **4**, a few drops of aqueous NaOH solution were added to the NMR tube of compound **4** in D_2O. The experiment showed, as it is expected, that only compound **1** was identified in the NMR spectra. This could be demonstrated as under basic conditions, where pH>8, compound **4** undergoes deprotonation of the ammonium function. This reaction is accompanied by losing fluoride anions forming a neutral structure referred to compound **1**, (Scheme 6).



4 **1**

Scheme 6. The reaction of the organotin compound **4** with NaOH.

This means, that the reversibility of binding/releasing fluoride anions depends on the *p*H of the solution.

This is very important especially for most of practical purposes. Thus, a reusable feature of fluoride receptor is verified as deprotonation of compound [{$Me_2(H)N(CH_2)_3$}$_2SnF_4$}, **4**, takes place in basic solutions coincide with forming compound {$Me_2N(CH_2)_3$}$_2SnF_2$, **1**, which is in turn easily to be further separated from other fluoride salts, NaF or KF, using extraction by dichloromethane as a solvent (Figure 4).

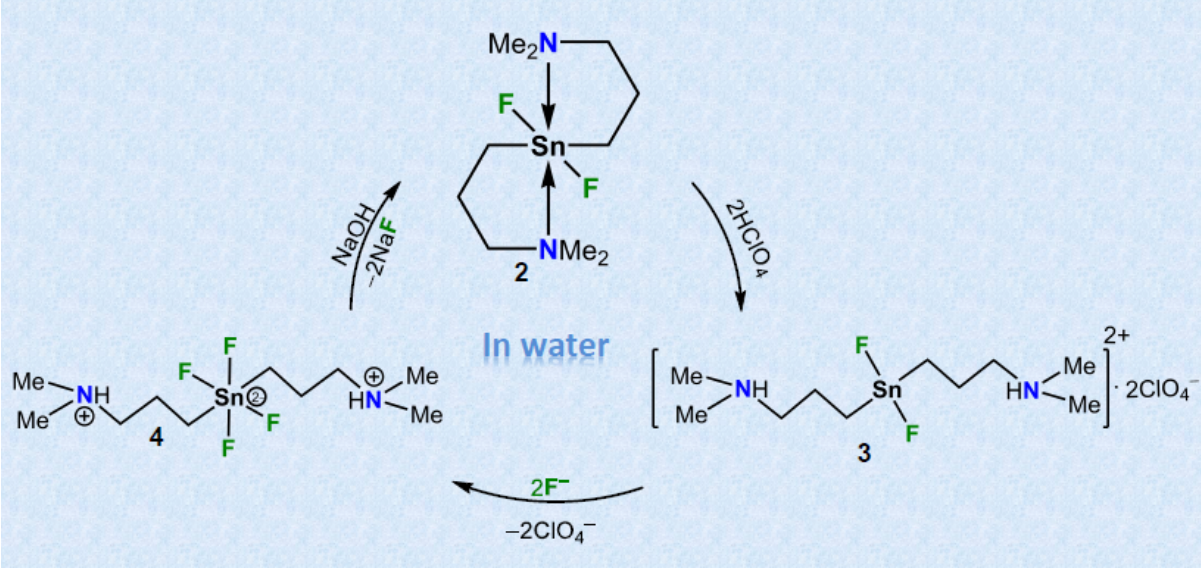


Figure 4. [{$Me_2(H)N(CH_2)_3$}$_2$$SnF_2$·$2ClO_4$] as a fluoride receptor in water.

4.1.4 Studying the selectivity of compound {$Me_2NH(CH_2)_3$}$_2$$SnF_2$·$2ClO_4$, 2, towards fluoride anions

NMR measurements were used for studying the selectivity of compound **2** towards different anions. For this purpose, fluoride, chloride, bromide, iodide anions were chosen as studied anions, and were used as their sodium salts. The reaction of **2** with two molecular equivalents of these salts was carried out in D_2O, and the resulting mixture was monitored by ^{1}H, ^{13}C and ^{19}F NMR spectroscopy.

The NMR spectra ensure that compound **2** is remarkably selective to fluoride anions and does not show any response to the other inorganic anions as compound **4** was identified in the solution (Figure 5).

To expand the selectivity study, a further reaction was done using potassium salt instead of the sodium ones, taking into account that the driving force for this reaction is the expected precipitation of $KClO_4$ that causes stronger attack on the tin atom by the counterion for the potassium. However, when KCl was added to compound **2** in D_2O, the reactions did not proceed at all and only compound **2** was identified in the solution by NMR spectroscopy.

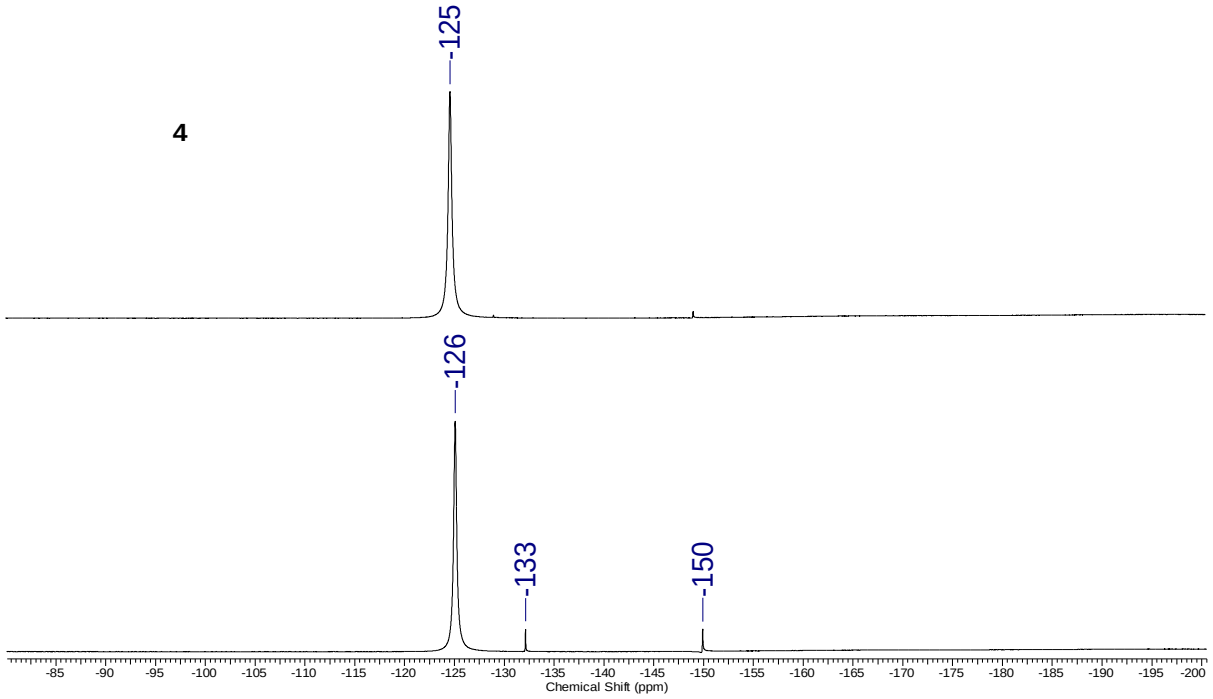


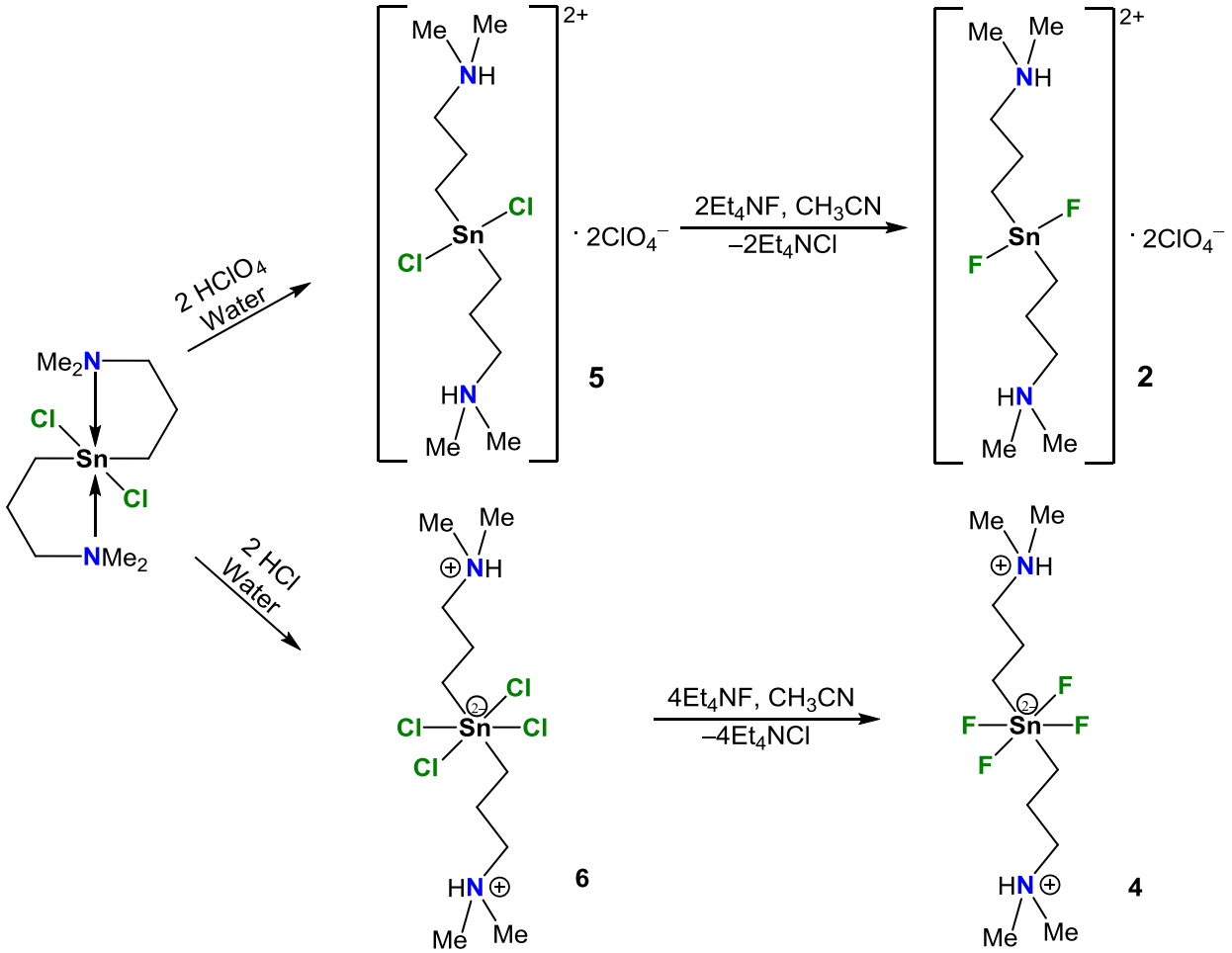
Figure 5. ^{19}F NMR spectra in D_2O of compound **4** (above) and of a solution of the reaction mixture of compound **2** with two molar equivalents of each of F, Cl, Br and I anions (below).

All the experiments shown above ensure that only fluoride anions are able to react with compound **2** in water. This selectivity is also a prerequisite for a real application as the receptor should be able to bind fluoride anions in real samples in the presence of other anions.

4.2 Another method for the syntheses of the diorganotin fluorides [$R_2SnF_2 \cdot 2ClO_4$], 2, and R_2SnF_4, 4, (R =$Me_2(H)N(CH_2)_3$)

4.2.1 Syntheses of the diorganotin compounds [$\{Me_2(H)N(CH_2)_3\}_2SnCl_2 \cdot 2ClO_4$], 5, and $\{Me_2(H)N(CH_2)_3\}_2SnCl_4$, 6.

The reaction of the diorganotin dichloride $[Me_2N(CH_2)_3]_2SnCl_2$ with two molar equivalents $HClO_4$ in water gave the adduct [$\{Me_2(H)N(CH_2)_3\}_2SnCl_2 \cdot 2ClO_4$], **5**, in quantitative yield. Furthermore, the reaction of compound **5** with two molar equivalents tetraethylammonium fluoride, $Et_4NF \cdot 2H_2O$, in CH_3CN gave the compound [$\{Me_2(H)N(CH_2)_3\}_2SnF_2 \cdot 2ClO_4$], **2**, in quantitative yield (Scheme 7).



Scheme 7. Syntheses of the diorganotin chlorides **5** and **6** and the diorganotin fluorides **2** and **4**.

Similarly, the reaction of $[Me_2N(CH_2)_3]_2SnCl_2$ with two molar equivalents HCl in water gave the diorganotin tetrachloride $\{Me_2(H)N(CH_2)_3\}_2SnCl_4$, **6**, in quantitative yield. The reaction of compound **6** with four molar equivalents $Et_4NF{\cdot}2H_2O$ in CH_3CN gave the corresponding compound $\{Me_2(H)N(CH_2)_3\}_2SnF_4$, **4**, in quantitative yield (Scheme 7).

Compounds **5** and **6** were obtained as white solids and show good solubility in water but poor solubility in organic solvents. Compound **5** shows moderate solubility in acetonitrile. Single crystals of compounds **5** and **6** suitable for X-ray diffraction analyses were each obtained by slow evaporation of the corresponding solution in water at room temperature. Those for **4** were obtained from its solution in acetonitrile.

4.2.2 Molecular structures of compounds 4 – 6

Both compounds **4** and **5** crystallized in the triclinic space group *P*–1, whereas compound **6** crystallized in the monoclinic space group $P2_1/n$. The molecular structures of **4** – **6** are presented in Figures 6 – 8, selected interatomic distances and angles are listed in Table 2.

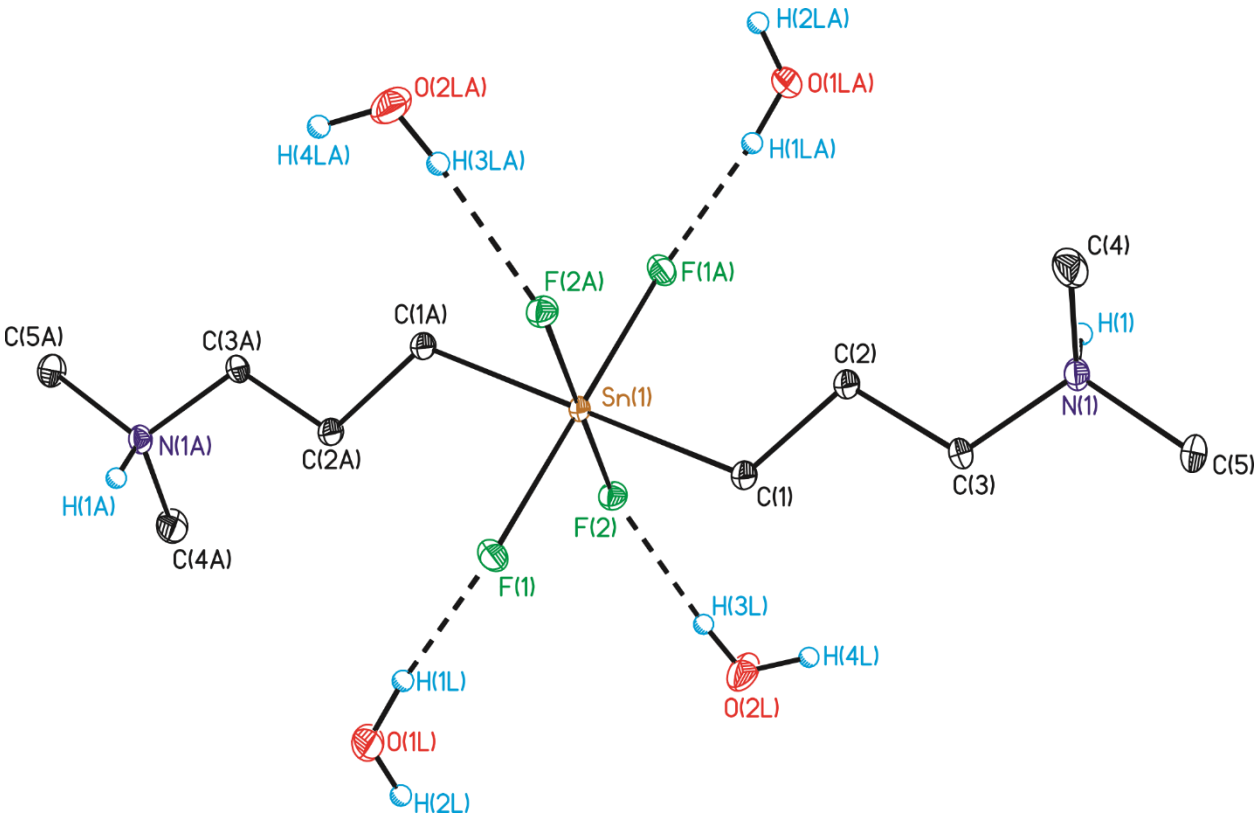


Figure 6. General view (SHELXTL) of a molecule of **4** as its tetraaqua solvate **4**·$4H_2O$, showing 30% probability displacement ellipsoids and the crystallographic numbering scheme.

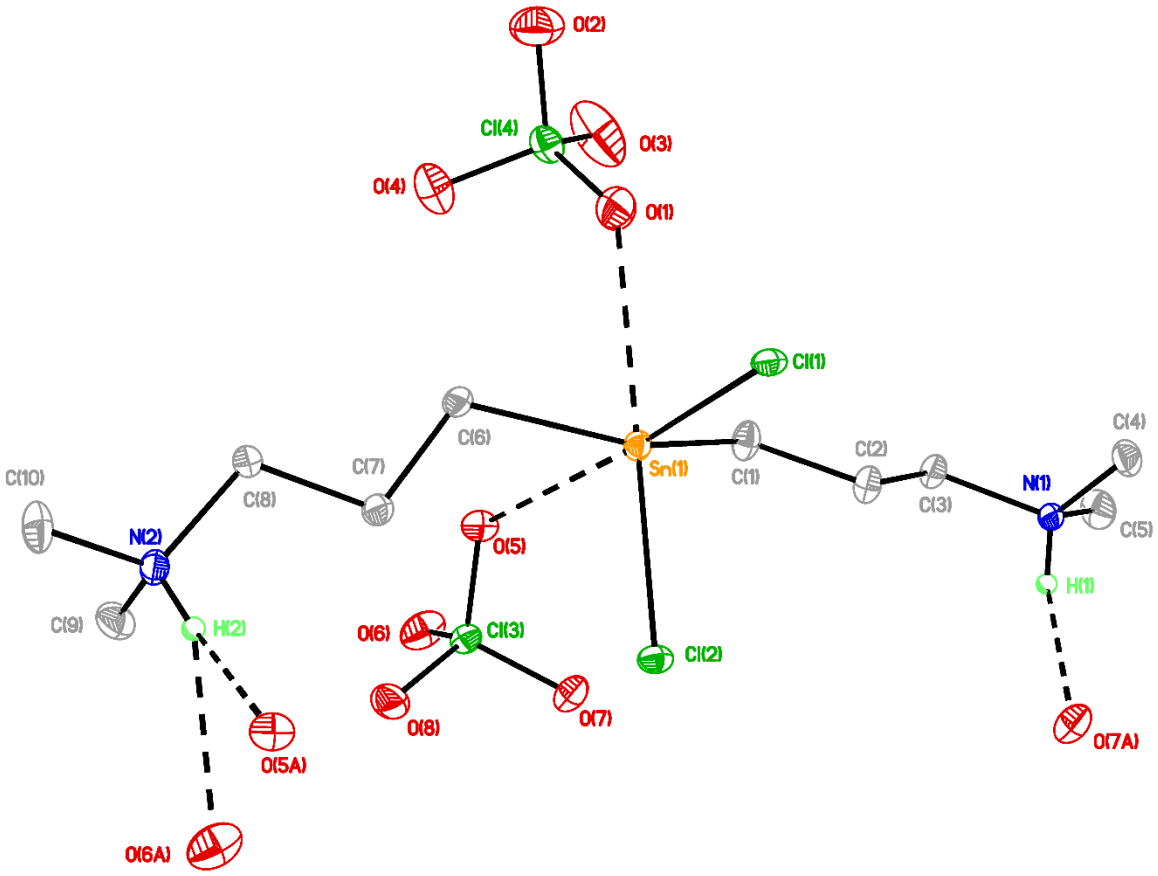


Figure 7. General view (SHELXTL) of a molecule of **5** showing 30% probability displacement ellipsoids and the crystallographic numbering scheme.

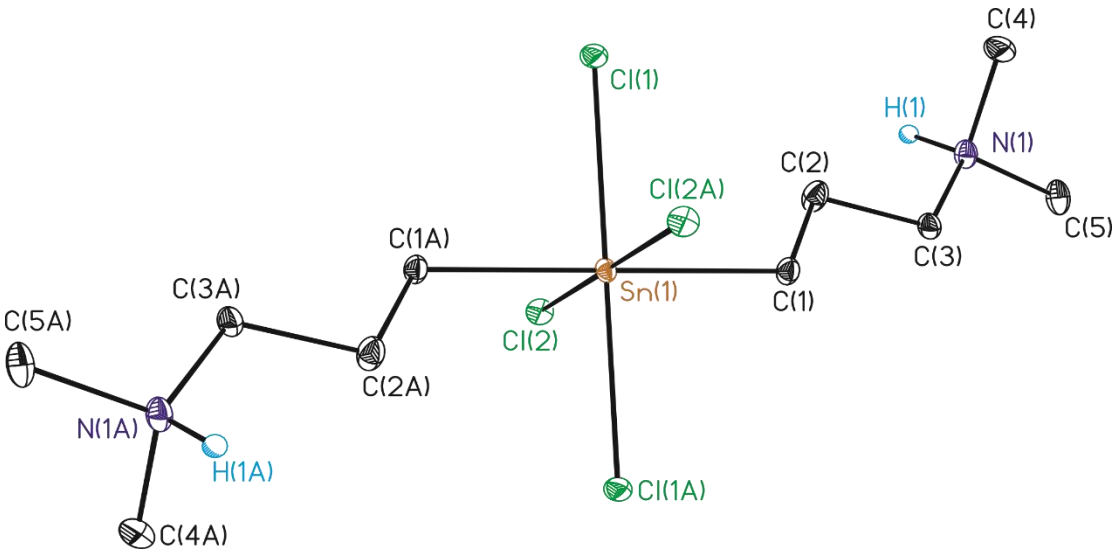


Figure 8. General view (SHELXTL) of a molecule of **6** showing 30% probability displacement ellipsoids and the crystallographic numbering scheme.

Table 2. Selected interatomic distances /Å and bond angles /° in $\{Me_2HN(CH_2)_3\}_2(X_2)Sn{\cdot}Y_2$, **4** – **6**.

	4 X = Y = F	**5** X = Cl, Y = ClO_4	**6** X = Y = Cl
Sn(1)–X(1)	2.0827(13)	2.4119(8)	2.6074(8)
Sn(1)–X(2)	2.0827(13)	2.4234(8)	2.6074(8)
Sn(1)–Y(1)	2.1172(13)	2.757(3)	2.6260(7)
Sn(1)–Y(2)	2.1172(13)	3.051(3)	2.6260(7)
C(1)–Sn(1)–X(1)	87.99(7)	103.08(10)	90.82(10)
C(1)–Sn(1)–X(2)	92.01(7)	99.46(11)	89.18(10)
C(1)–Sn(1)–Y(1)	89.66(7)		89.57(9)
C(1)–Sn(1)–Y(2)	90.34(7)		90.43(9)
X(1)–Sn(1)– X(2)	180.0	97.73(3)	180.0

The tin atoms in compounds **4** and **6** exhibit distorted octahedral geometries with two carbon and two halogen atoms in the equatorial positions and the other two halogen atoms in the axial positions. The structures are centrosymmetric, as one half of the molecule comprises the crystallographic asymmetric unit and the other half is generated by an inversion center.

The carbon atoms in compounds **4** and **6** are in the *trans* position with C(1)–Sn(1)–C(1A) of 180.0°. The Sn(1)–F distances in **4** of 2.0827(13) (F(1)) and 2.1172(13) Å (F(2)) are between the corresponding distances in compound $K_2\{(CH_3)_2SnF_4\}{\cdot}2H_2O$ of 2.064(14) – 2.135(2) Å. The F(1)–Sn(1)–F(1A) and F(2)–Sn(1)–F(2A) are 180.0°. The F–Sn(1)–C angles are close to 90° and ranging from 87.99(7)° (F(1)–Sn(1)–C(1)) to 92.01(7)° (F(1A)–Sn(1)–C(1)). Compound **4** is crystallized with four molecules of water.

In compound **6** the Sn(1)–Cl distances are 2.6074(8) Å (Cl(1)) and 2.6260(7) Å (Cl(2)). The Cl(1)–Sn(1)–Cl(1A) and Cl(2)–Sn(1)–Cl(2A) are 180.0°. The C–Sn(1)–Cl angles are close to 90° and range between 89.18(10)° (C(1)–Sn(1)–Cl(1A)) and 90.43(9)° (C(1)–Sn(1)–Cl(2A)).

The Sn atom in the perchlorate complex **5** can be characterized as being [4+2]-coordinated with O(1) and O(5) approaching the tin atom via tetrahedral faces formed by O(5), C(1), Cl(1) and C(6). The distances Sn(1)–O(1) and Sn(1)–O(5) are 2.757(3) Å and 3.051(3) Å, respectively. These values are bigger than that reported for the organostannylene complex [4-*t*-Bu-2,6-{P(O)(O*i*-Pr)$_2$}$_2$C$_6$H$_2$(ClO$_4$)SnCr(CO)$_5$] of 2.170(3) Å,[17] but are smaller than the sum of the van der Waals radii of oxygen and tin (3.80 Å).[24]

The Sn(1)–Cl distances of 2.4119(8) Å and 2.4234(8) (for Cl(1) and Cl(2), respectively) are smaller than those found in the octahedral **6** of 2.6074(8) Å and 2.6260(7) Å. The angles O(1)–Sn(1)–Cl(2) and O(5)–Sn(1)–Cl(1) are 177.65(8)° and 176.37(5)°, respectively.

4.2.3 Structures of compounds 5 and 6 in solution

A ^{119}Sn NMR spectrum of the diorganotin perchlorate complex **5** in D_2O showed one signal at δ –310 (Figure 9). This chemical shift is close to that measured for the diorganodin difluorides [{Me$_2$(H)N(CH$_2$)$_3$}$_2$SnF$_2$·2ClO$_4$]·H$_2$O, **2**, in acetone-d6 at δ –340 ($\nu_{1/2}$ = 206 Hz) indicating a hexacoordinated environment of the tin atom in **5**.

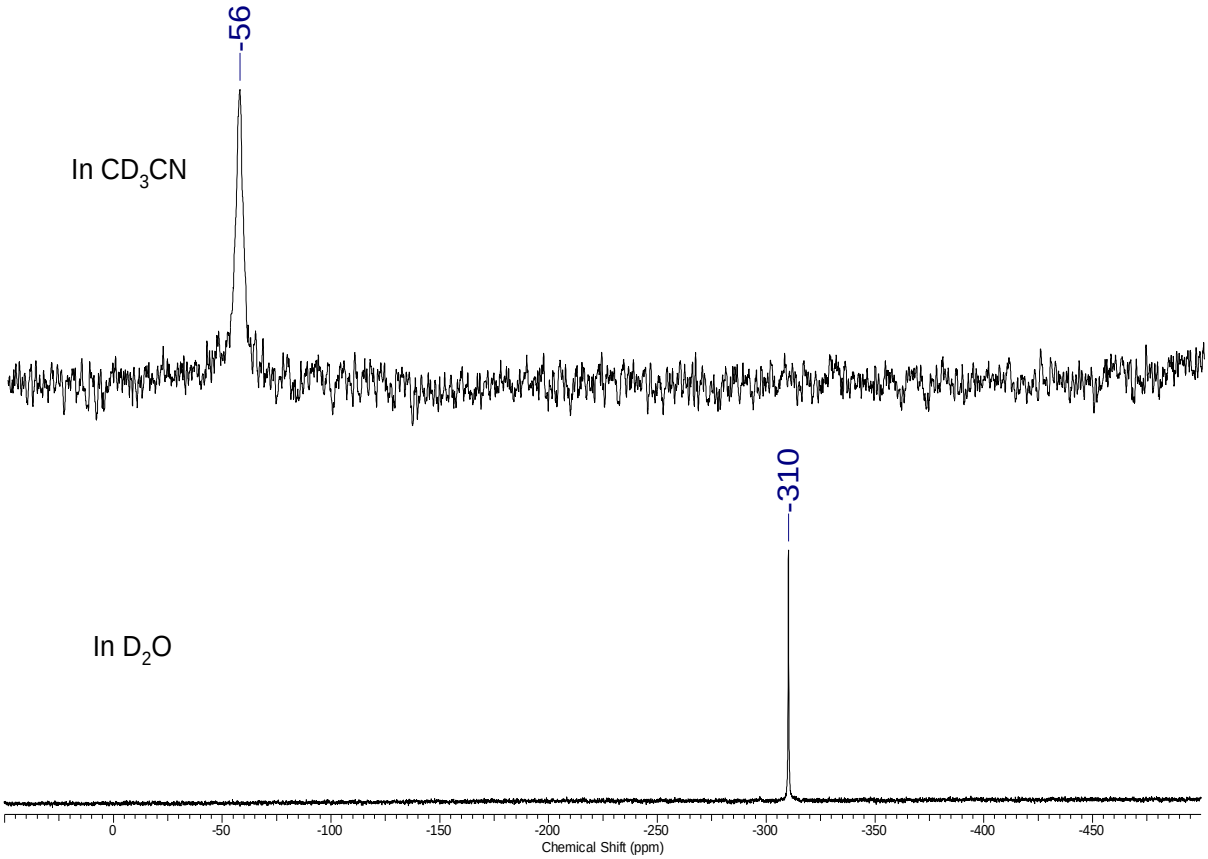


Figure 9. ^{119}Sn NMR spectra of **5** in CD_3CN and D_2O.

That was proved also by ^{1}H and ^{13}C NMR spectra. A ^{1}H NMR spectrum of **5** in D_2O showed one signal for SnCH_2 protons at δ 1.58 ($^{2}J(^{1}H–^{119}Sn)$ = 104 Hz). This coupling constant is close to that found for the corresponding protons in **2** of 105 Hz. In a ^{13}C NMR spectrum of the same sample one signal at δ 29.9 ($^{1}J(^{13}C–^{119}Sn)$ = 959/1003) relating to SnCH_2 carbon atom was observed. This value of the coupling constant is close to 977 Hz found for the corresponding carbon atom in the hexacoordinated organotin compound **2** (in D_2O). This situation is achieved by replacing the weak interaction ClO_4→Sn, found in the solid state, by the interaction of the water molecules used as a solvent. However, changing the solvent to CD_3CN caused in the ^{119}Sn NMR spectrum an upfield shift of 254 ppm of the chemical shift (δ –56) in comparison to that of **5** in D_2O.

In ^{1}H NMR spectrum, the resonance of the NCH_3 protons, found at δ 2.87 in D_2O, appears as a doublet resonance at δ 2.84 ($^{3}J(^{1}H–^{1}H)$ = 5.38 Hz), Figure 10. In addition, a broad resonance at δ 7.26 relating to N*H* proton was observed. The coupling constants of the $SnCH_2$ moiety of ($^{2}J(^{1}H–^{119}Sn)$ = 78 Hz) and $^{1}J(^{13}C–^{119}Sn)$ = 682) are distinctly smaller than those found in D_2O.

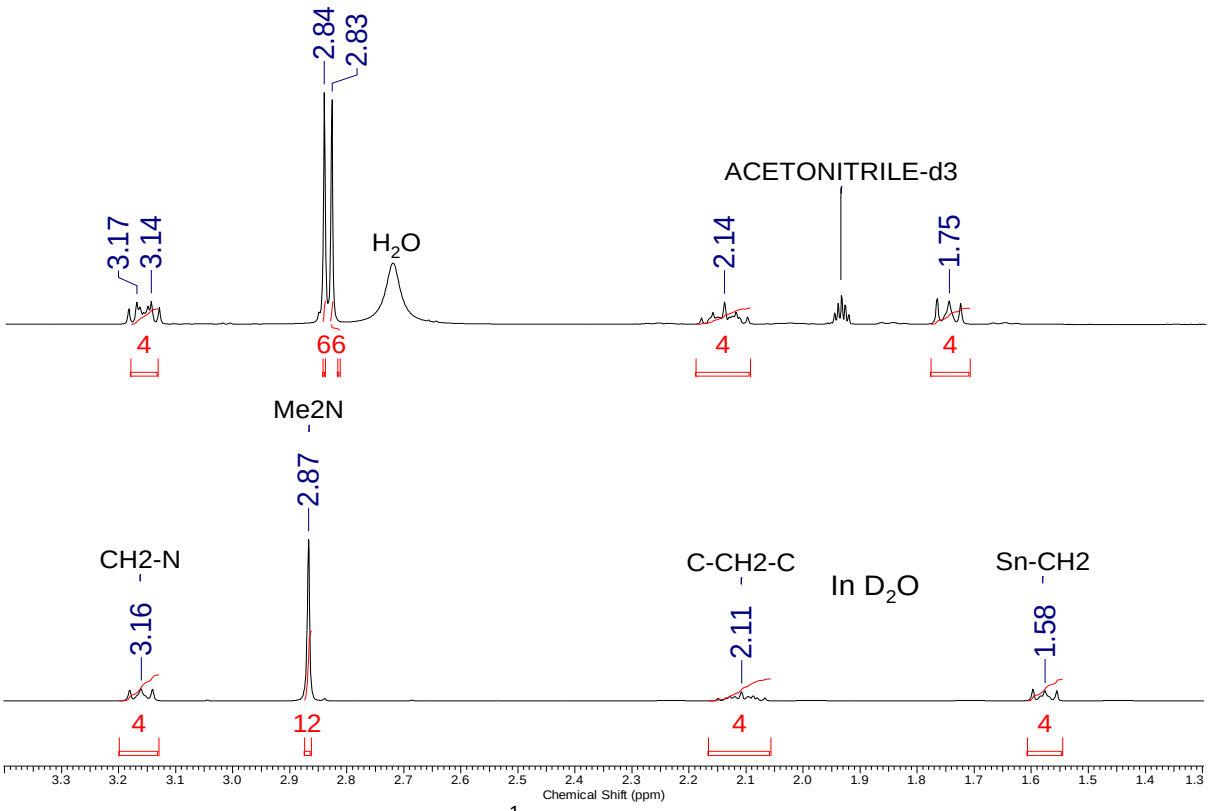


Figure 10. Expansion of the signals in ^{1}H NMR spectra of compound **5** measured in CD_3CN (400.25 Hz) and D_2O (400.25 Hz).

A ^{119}Sn NMR spectrum of compound **6** in D_2O showed one resonance at δ –282. In a ^{13}C NMR spectrum a resonance at δ 31.0 ($^1J(^{13}C–^{119}Sn)$ = 938/976 Hz) assigned to the Sn*C*H_2 carbon atom was observed. This chemical shift is similar to those found for the corresponding carbon atoms in **5** at δ 29.9 ($^1J(^{13}C–^{119}Sn)$ = 959/1003) and in the hexacoordinated organotin compound $\{Me_2N(CH_2)_3\}_2SnCl_2$ at δ 31 ($^1J(^{13}C–^{119}Sn)$ = 922 Hz). In a ^{1}H NMR spectrum of the same sample a chemical shift of the SnC*H*$_2$ protons at δ 1.60 ($^2J(^1H–^{119}Sn)$ = 102 Hz) was observed. This coupling value is characteristic for hexacoordinated organotin compounds. Therefore, the hexacoordinated environment found for compound **6** in the solid state is retained in solution.

Noteworthy, the ^{19}F and ^{119}Sn NMR spectra of $\{Me_2(H)N(CH_2)_3\}_2SnF_4$, **4**, showed concentration dependence. A ^{19}F NMR spectrum of **4** (30 mg) in D_2O showed a resonance at **–**133 ppm. This resonance was shifted to –126 ppm by increasing the concentration to 60 mg. In a ^{119}Sn NMR spectrum the chemical shift observed at –379 ppm for a solution of **4** (30 mg) in D_2O was shifted to –405 ppm by increasing the concentration to 60 mg. However, no $^1J(^{119}Sn–^{19}F)$ couplings satellites were observed in all cases. It was planned to do solid-state ^{119}Sn NMR measurements for the organotin compounds **2** – **6**, but these studies could not be carried out within the given time frame.

The electrospray ionization mass spectra (ESI MS, positive mode) of compounds **5** and **6** in water-acitonitrile solution showed two mass clusters centered at *m*/z = 309.1 and 327.1. These two clusters are assigned to $[\{Me_2N(CH_2)_3\}_2SnOH]^+$ and $[\{Me_2N(CH_2)_3\}_2SnCl]^+$, respectively.

4.3 The Water-soluble spacer-bridged ditin compounds $[\{Me_2NH(CH_2)_3\}Cl_3SnCH_2]_2SiMe_2$ and $[\{Me_2NH(CH_2)_3\}Cl_2Sn(CH_2)_2SnPhCl_2{\cdot}Cl]$

The syntheses of the organoditin compounds separated by silicon-based spacer $(CH_2)_2SiMe_2$ have been discussed in Chapter 2.2. In addition, the dimethylene-bridged organoditin compound $\{Me_2N(CH_2)_3\}Ph_2Sn(CH_2)_2SnPh_3$ has been presented in Chapter 2.1.

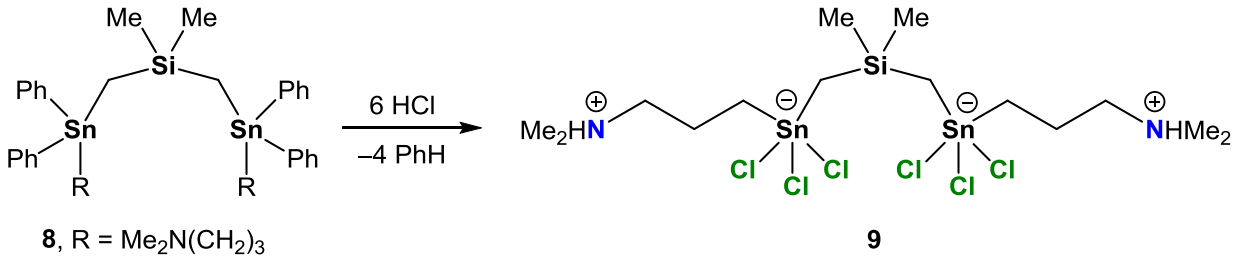
Herein will be reported the syntheses of the water soluble spacer-bridged organoditin compounds $\{[Me_2NH(CH_2)_3]Cl_3SnCH_2\}_2SiMe_2$ and $[\{Me_2NH(CH_2)_3\}Cl_2Sn(CH_2)_2SnPhCl_2{\cdot}Cl]$ decorated with $\{Me_2NH(CH_2)_3\}$ substituents. The ability of the latter compound to react with fluoride anion in water will also be discussed.

4.3.1 Synthesis of the organoditin compound $\{[Me_2NH(CH_2)_3]–Cl_3SnCH_2\}_2SiMe_2$

The reaction of two molar equivalents of the Grignard reagent $Me_2N(CH_2)_3MgCl$ with compound **7** afforded the corresponding compound $\{Me_2N(CH_2)_3Ph_2SnCH_2\}_2SiMe_2$, **8**, in good yield as yellowish oil. Compound **8** shows good solubility in common organic solvents such as $CHCl_3$, CH_2Cl_2, and THF. The compounds **7** and **8** were also reported in Chapter 2.2.2. A ^{119}Sn NMR spectrum of compound **8** in $CDCl_3$ showed a single resonance at δ –60. This chemical shift is close to that found for the analogous tin atom Sn1 in compound $Me_2N(CH_2)_3Ph_2Sn^1CH_2SnPh_3$ at δ –49. The ^{13}C NMR chemical shift of the Sn*C*H$_2$C carbon atom at δ 9.1 ($^1J(^{13}C–^{117/119}Sn)$ = 363/380 Hz) is close to that found for the corresponding carbon atom in $Me_2N(CH_2)_3Ph_2Sn^1CH_2SnPh_3$ at δ 9.0 ($^1J(^{13}C–^{117/119}Sn)$ = 373/391 Hz). In a ^{1}H NMR spectrum a single resonance for the N(C*H*$_3$)$_2$ protons located at 2.15 ppm was observed.

The reaction of compound **8** with six molar equivalents HCl caused protonation of the amine groups in addition to the cleavage of two phenyl groups at each tin atom giving the

corresponding zwitterionic compound {[$Me_2NH(CH_2)_3$]Cl_3SnCH_2}$_2SiMe_2$, **9**, in quantitative yield (Scheme 8).



8, R = $Me_2N(CH_2)_3$ **9**

Scheme 8. Syntheses of the organoditin compound **9**.

Compound **9** was obtained as white solid and showed good solubility in polar solvents such as H_2O, CH_3CN, and acetone, whereas it is poor soluble in CH_2Cl_2 and $CHCl_3$. So far, all attempts to get single crystals of **9** failed.

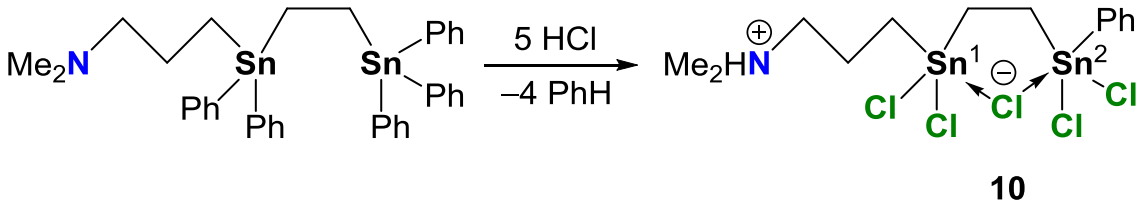
A ^{119}Sn NMR spectrum of compound **9** in D_2O showed one resonance at δ –204. This chemical shift is significantly higher field-shifted than those reported for diorganotin dichlorides. In fact, it is even more high field shifted than the signal found for the adduct [PPh_4][($Cl_2PhSnCH_2$)$_2SiMe_2$·Cl] at δ –119. This data reveal the tin atoms in compound **9** to be hexacoordinated.

Furthermore, in a ^{1}H NMR spectrum of the same sample a chemical shift at δ 0.92 (^2J(^{1}H–$^{117/119}$Sn) = 118.6 Hz) related to the SnCH_2Si protons was observed. This value is close to that found for the SnCH_2C protons in $Me_2NH(CH_2)_3SnCl_4$ of 101.6 Hz and characteristic of hexacoordinated organotin compounds. The chemical shift of the N(CH_3)$_2$ protons of 2.82 ppm is 0.67 ppm low-field shifted in comparison with that found for **8** at 2.15 ppm (in $CDCl_3$).

The NMR data reveal the tin atoms in compound **9** to be hexacoordinated. Very likely, this is achieved by double chloride bridges, or coordinating of water molecules.

4.3.2 Synthesis of the water-soluble dimethylene-bridged organoditin compound [{$Me_2NH(CH_2)_3$}$Cl_2Sn(CH_2)_2SnPhCl_2 \cdot Cl$]

The reaction of {$Me_2N(CH_2)_3$}$Ph_2Sn(CH_2)_2SnPh_3$ (Chapter 2.1.2) with five molar equivalents HCl caused protonation of the amine groups in addition to the acid cleavage of two phenyl groups at each tin atom, giving the corresponding zwitterionic compound [{$Me_2NH(CH_2)_3$}$Cl_2Sn(CH_2)_2SnPhCl_2 \cdot Cl$], **10**, in quantitative yield as a white solid, (Scheme 9).



10

Scheme 9. Synthesis of the organoditin compound **10**.

Compound **10** shows good solubility in polar solvents as H_2O, CH_3CN and CH_3OH, but poor solubility in $CHCl_3$ and CH_2Cl_2. So far, all attempts to get single crystals of **10** failed.

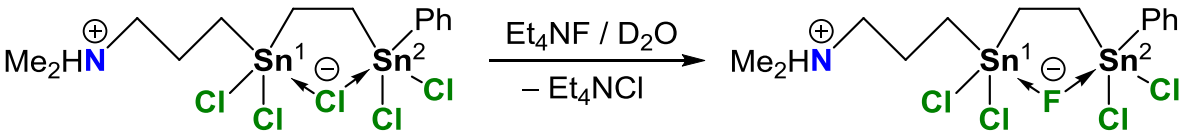
Structure in Solution

A ^{119}Sn NMR spectrum of compound **10** in D_2O showed two resonances at δ –296 and δ –380 related to Sn1 and Sn2 (Scheme 9), respectively. These two resonances shifted to δ –122 and δ –182 when CD_3CN was used as a solvent. These are 48 and 78 ppm high-field shifted in comparison to those found for [$Me_2N(CH_2)_3$]$Ph_2Sn(CH_2)_2SnPh_3$ at δ –74 and δ –104 (in $CDCl_3$). The tin atoms in **10** are pentacoordinated as evidence by their ^{119}Sn NMR chemical shifts. These are significantly bigger than those reported for the tetracoordinate diorganotin dichloride Et_2SnCl_2[25] and Ph_2SnCl_2[25] at 128 and –27 ppm (in $CDCl_3$), respectively. However, they are comparable to those reported for pentacoordinated organotin complexes $[Et_2SnCl_3]^-$[25] and $[^nPr_2SnCl_3]^-$[25] at –103 and –112 ppm (in $CDCl_3$), respectively.

The significant differences of the ^{119}Sn NMR chemical shifts for **10** measured in water could be related with caution to hexacoordinated tin atoms as result of the coordination of water molecules.

The reaction of **10** with one molar equivalent of Et_4NF in D_2O was studied by ^{1}H, ^{13}C, ^{19}F, ^{119}Sn NMR spectroscopy.

A ^{119}Sn NMR spectrum in D_2O of the resulting mixture showed two signals at –318 and –399 ppm. These two chemical shifts are 22 and 19 ppm high field shifted in comparison to those for Sn1 and Sn2 found for **10** in D_2O. A ^{19}F NMR spectrum of the same sample showed one signal at –141 ppm without coupling $^{1}J(^{19}F–^{117/119}Sn)$. This chemical shift is close to –155 ppm reported for the adduct $[(Ph_2ClSnCH_2)_2{\cdot}F]^-$ measured in $CDCl_3$. With caution, this data is consistent with the formation of the compound $[\{Me_2NH(CH_2)_3\}Cl_2Sn(CH_2)_2SnPhCl_2{\cdot}F]$, **11**, (Scheme 10).

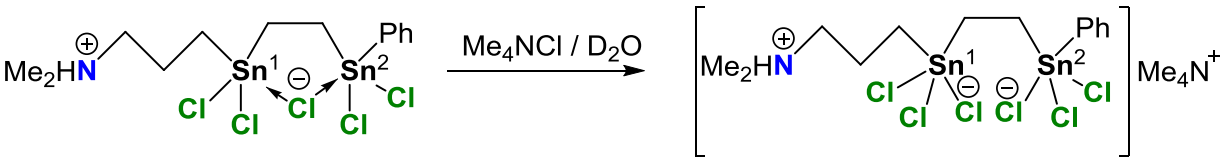


10 **11**

Scheme 10. Synthesis of the zwitterionic compound **11**.

In an effort to prove that replacing the chloride anion with fluoride ones took place in **11**, we investigated the reaction of compound **10** with chloride anion. The reaction of $[\{Me_2NH(CH_2)_3\}Cl_2Sn(CH_2)_2SnPhCl_2{\cdot}Cl]$ with one molar equivalent of Me_4NCl in D_2O resulted in formation of $[\{Me_2NH(CH_2)_3\}Cl_3Sn(CH_2)_2SnPhCl_3{\cdot}Me_4N]$, **12**, (Scheme 11).

A ^{119}Sn NMR spectrum of **12** in D_2O showed two signals at –287 and –369 ppm, related to Sn1 and Sn2, respectively. The absence of these two chemical shifts in the ^{119}Sn NMR spectrum of **11** supports the structure of **11**.



10 **12**

Scheme 11. Synthesis of compound **12**.

An ESI mass spectrum (positive mode) of compound **10** revealed, in addition to the major mass cluster centered at *m*/*z* = 515.9 that is assigned to [**10** – 4C + 3OHl]$^+$, a rather mass cluster centered at *m*/*z* = 571.9, which corresponds to [**10** – Cl]$^+$. In the negative mode, a major mass cluster centered at *m*/*z* = 605.8 was observed. That fits exactly with [**10** – H]$^-$.

For the organotin compound **11**, the ESI mass spectrum (positive mode) showed a mass cluster centered at *m*/*z* = 360.1 which corresponds with $[Me_2N(CH_2)_3SnPh_2]^+$.

In the ESI mass spectra (positive mode) of compound **12** a major mass cluster centered at *m*/*z* = 300.0 was observed. That fits with $[Me_2NH(CH_2)_3Sn(OH)_2Ph]^+$. The negative mode spectrum showed a major mass cluster centered at *m*/*z* = 387.9 which corresponds to $[Me_2N(CH_2)_3SnPhCl_3]^-$.

4.4 CONCLUSION

A set of hexacoordinated diorganotin compounds was synthesized and characterized in both solid state and solution. They show good solubility in water. The diorganotin difluoride $[\{Me_2(H)N(CH_2)_3\}_2SnF_2{\cdot}2ClO_4]$, **2**, showed reactivity towards fluoride anions as NaF or KF in water giving the zwitterionic organotin compound $[\{Me_2N(H)(CH_2)_3\}_2SnF_4]$, **4**.

The NMR studies showed that compound **2** is an ideal fluoride receptor as it is inert to other inorganic species that might also be present in the same solution. Furthermore, this receptor shows fast response, and it can easily be regenerated.

The water-soluble spacer bridged ditin compounds containing protonated ammonium groups $[\{Me_2NH(CH_2)_3\}Cl_2Sn(CH_2)]^+{}_2SiMe_2{\cdot}2Cl^-$, **9**, and $[\{Me_2NH(CH_2)_3\}Cl_2Sn(CH_2)_2SnPhCl_2{\cdot}Cl]$, **10**, were synthesized and characterized. The latter showed good ability to bind fluoride anion in water.

4.5 EXPERIMENTAL SECTION

Bis(3-(dimethylamino)propyl)tin dichloride, $\{Me_2N(CH_2)_3\}_2SnCl_2$,[13] was synthesized according to literature method. Perchloric acid, potassium fluoride, sodium fluoride, tetraethyl ammonium fluoride and tetramethylammonium chloride were commercially available, and they were used without further purification. Bruker DPX–300, DRX–400 and AVIII–500 spectrometers were used to obtain ^1H, ^{13}C, ^{19}F, and ^{119}Sn NMR spectra. Solution ^1H, ^{13}C, ^{29}Si, ^{19}F, and ^{119}Sn NMR chemical shifts are given in ppm and were referenced to Me_4Si (^1H, ^{13}C, ^{29}Si), $CFCl_3$ (^{19}F), and Me_4Sn (^{119}Sn). Elemental analyses were performed on a LECO–CHNS–932 analyzer. The electrospray mass spectra were recorded with a Thermoquest–Finnigan instrument. The mixture CH_3CN/H_2O (1:4) was used as the mobile phase.

Warning! Although we have encountered no problems during our studies, metal perchlorates are potentially explosive.

Synthesis of bis[3-(dimethylamino)propyl]tin difluoride $\{Me_2N(CH_2)_3\}_2SnF_2{\cdot}2H_2O$ (1).

To a suspention of bis(3-(dimethylamino)propyl)tin dichloride $[Me_2N(CH_2)_3]_2SnCl_2$ (3.00 g, 8.29 mmol) in CH_2Cl_2 (70 mL) was added potassium fluoride, KF (1.20 g, 20.72 mmol), and the mixture was stirred at room temperature for 10 days. After that the suspension was filtered and CH_2Cl_2 was evaporated in vacuo to give 2.18 g (72%) of **1**.

^{1}H NMR (300.13 MHz, D_2O): δ 1.17 (t, $^2J(^1H–^{117/119}Sn)$ = 90.0 Hz, 4H, Sn–CH_2), 1.89 (m, $^3J(^1H–^{117/119}Sn)$ = 128.8 Hz, 4H, Sn–CH_2–CH_2), 2.48 (s, 12H, N(CH_3)$_2$), 2.69 (t, 2H, CH_2–N). **^{13}C{^{1}H} NMR** (75.47 MHz, D_2O): δ 17.3 ($^1J(^{13}C–^{117/119}Sn)$ = 907 Hz, Sn–CH_2), 20.0 (Sn–CH_2–CH_2, $^2J(^{13}C–^{117/119}Sn)$ = 42 Hz), 43.7 N(CH_3)$_2$, 59.7 ($^3J(^{13}C–^{117/119}Sn)$ = 102 Hz, CH_2–N). **^{19}F{^{1}H} NMR** (282.40 MHz, D_2O): δ –123. **^{119}Sn{^{1}H} NMR** (111.92 MHz, D_2O): no signal. Anal. Calcd (%) for $C_{10}H_{28}F_2N_2O_2Sn$ (365.1): C 32.90, H 7.73, N 7.67. Found: C 32.9, H 7.6, N 7.7.

Synthesis of $[\{Me_2(H)N(CH_2)_3\}_2SnF_2{\cdot}2ClO_4]{\cdot}H_2O$ (2).

To a solution of **1** (1.50 g, 4.11 mmol) in water (20 mL) was added perchloric acid (1.38 g, 8.22 mmol) (60%). The solution was stirred for 1 hour, and then water was evaporated giving 2.13 g (98%) of **2** as white solid of mp 250 °C (dec.).

^{1}H NMR (300.13 MHz, D_2O): δ 1.28 (t, $^2J(^1H–^{117/119}Sn)$ = 104.7 Hz, 4H, Sn–CH_2), 1.99 (m, $^3J(^1H–^{117/119}Sn)$ = 95.1 Hz, 4H, Sn–CH_2–CH_2), 2.82 (s, 12H, N(CH_3)$_2$), 3.09 (t, 2H, CH_2–N). **^{1}H NMR** (300.13 MHz, CD_3CN): δ 1.49 (t, $^2J(^1H–^{117/119}Sn)$ = 95.1 Hz, 4H, Sn–CH_2), 2.06 (m, $^3J(^1H–^{117/119}Sn)$ = 79.0 Hz, 4H, Sn–CH_2–CH_2), 2.86 (d, $^3J(^1H–^1H)$ = 4.76 Hz, 12H, N(CH_3)$_2$), 3.15 (t, 4H, CH_2–N), 7.57 (b, 2H, *H*N(CH_3)$_2$). **^{1}H NMR** (300.13 MHz, C_3D_6O): δ 1.57 (t, $^2J(^1H–^{117/119}Sn)$ = 104.7 Hz, 4H, Sn–CH_2), 2.21 (m, $^3J(^1H–^{117/119}Sn)$ = 92.2 Hz, 4H, Sn–CH_2–CH_2), 3.00 (d, $^3J(^1H–^1H)$ = 4.39 Hz, 12H, N(CH_3)$_2$), 3.30 (t, 4H, CH_2–N), 8.6 (b, 2H, *H*N(CH_3)$_2$). **^{13}C{^{1}H} NMR** (100.63 MHz, C_3D_6O): δ 19.9 (Sn–CH_2–CH_2, $^2J(^{13}C–^{117/119}Sn)$ = 37 Hz), 24.6 (Sn–CH_2), 42.9 N(CH_3)$_2$, 59.8 (CH_2–N). **^{13}C{^{1}H} NMR** (75.47 MHz, D_2O): δ 19.7 (Sn–CH_2–CH_2, $^2J(^{13}C–^{117/119}Sn)$ = 33 Hz), 23.5 ($^1J(^{13}C–^{117/119}Sn)$ = 977 Hz, Sn–CH_2), 42.5 N(CH_3)$_2$, 59.6 (CH_2–N, $^3J(^{13}C–^{117/119}Sn)$ = 165 Hz).**^{19}F{^{1}H} NMR** (D_2O, 282.40 MHz): δ –141. **^{19}F{^{1}H} NMR** (282.40 MHz, C_3D_6O): δ –145. **^{119}Sn{^{1}H} NMR** (111.92 MHz, D_2O): no signal. **^{119}Sn{^{1}H} NMR** (111.92 MHz, C_3D_6O): δ –340. Anal. Calcd (%) for $C_{10}H_{28}Cl_2F_2N_2O_9Sn$ (547.9): C 21.92, H 5.15, N 5.11. Found: C 22.2, H 5.1,

N 5.2. **Electrospray MS**: m/z (%), positive mode, 309.1 (100, $[\{Me_2N(CH_2)_3\}_2SnOH]^+$), negative mode, 99.1 (100, $[ClO_4]^-$), 507.0 (18, [**2** – H_2O – 2F – 2H + OH]$^-$).

Synthesis of $[\{Me_2(H)N(CH_2)_3\}_4Sn_2F_5{\cdot}(ClO_4)_3]{\cdot}3H_2O$ (3).

To a solution of **2** (60 mg, 0.11 mmol) in D_2O was added KF (6.6 mg, 0.11 mmol) with stirring. A white precipitate of $KClO_4$ was formed immediately. Filtration and slow evaporation of the solvent afford **3** as white solid of mp 218-220 °C.

^{1}H NMR (300.13 MHz, D_2O): δ 1.25 (t, $^2J(^1H–^{117/119}Sn)$ = 109.8 Hz, 4H, Sn–CH_2), 2.05 (m, $^3J(^1H–^{117/119}Sn)$ = 98.1 Hz, 4H, Sn–CH_2–CH_2), 2.87 (s, 12H, N(CH_3)$_2$), 3.15 (t, 2H, CH_2–N). **^{13}C{^{1}H} NMR** (75.47 MHz , D_2O): δ 19.9 ($^2J(^{13}C–^{117/119}Sn)$ = 35 Hz, Sn–CH_2–CH_2), 22.7 ($^1J(^{13}C–^{117/119}Sn)$ = 1101/1053 Hz, Sn–CH_2), 42.6 ($^1J(^{13}C–^{15}N)$ = 140 Hz, N(CH_3)$_2$), 59.9 ($^3J(^{13}C–^{117/119}Sn)$ = 156 Hz, CH_2–N). **^{19}F{^{1}H} NMR** (188.29 MHz, D_2O): δ –133. Anal. Calcd (%) for $C_{20}H_{58}Cl_3F_5N_4O_{15}Sn_2$ (1033.46): C 23.24, H 5.66, N 5.42. Found: C 23.2, H 5.7, N 5.4. **Electrospray MS**: m/z (%), positive mode, 309.1 (100, $[\{Me_2N(CH_2)_3\}_2SnOH]^+$), negative mode, 99.1 (100, $[ClO_4]^-$), 507.0 (20, [**3** –2H – 3F + OH + ClO_4]$^-$).

Reaction of $\{Me_2(H)N(CH_2)_3\}_2SnF_2{\cdot}2ClO_4$ (2) with 0.5 KF.

To a solution of **2** (100 mg, 0.18 mmol) in D_2O was added KF (5.5 mg, 0.09 mmol) with stirring. A white precipitate of $KClO_4$ was formed immediately. Filtration and slow evaporation of the solvent afford **3** as a white solid.

^{1}H NMR (300.13 MHz, D_2O): δ 1.26 (t, $^2J(^1H–^{117/119}Sn)$ = 105.6 Hz, 4H, Sn–CH_2), 2.00 (m, $^3J(^1H–^{117/119}Sn)$ = 96.4 Hz, 4H, Sn–CH_2–CH_2), 2.82 (s, 12H, N(CH_3)$_2$), 3.12 (t, 2H, CH_2–N). **^{13}C{^{1}H} NMR** (75.47 MHz, D_2O): δ 19.8 ($^2J(^{13}C–^{117/119}Sn)$ = 35 Hz, Sn–CH_2–CH_2), 23.2 ($^1J(^{13}C–^{117/119}Sn)$ = 980/1027 Hz, Sn–CH_2), 42.6 ($^1J(^{13}C–^{15}N)$ = 139 Hz, N(CH_3)$_2$), 59.7 ($^3J(^{13}C–^{117/119}Sn)$ = 161 Hz, CH_2–N). **^{19}F{^{1}H} NMR** (282.4 MHz, D_2O): δ –136.

Synthesis of [{$Me_2(H)N(CH_2)_3$}$_2$$SnF_4$] (4).

Method 1: To a solution of **2** (60 mg, 0.11 mmol) in D_2O was added KF (13 mg, 0.22 mmol) with stirring. A white precipitate of $KClO_4$ was formed immediately. Filtration and slow evaporation of the solvent afford **4** as a white solid.

^{1}H NMR (300.13 MHz, D_2O): δ 1.27 (t, $^2J(^1H–^{117/119}Sn)$ = 109.8 Hz, 4H, Sn–CH_2), 2.11 (m, $^3J(^1H–^{117/119}Sn)$ = 101.7 Hz, 4H, Sn–CH_2–CH_2), 2.91 (s, 12H, N(CH_3)$_2$), 3.18 (t, 2H, CH_2–N). **^{13}C{^{1}H} NMR** (100.33 MHz, D_2O): δ 20.5 ($^2J(^{13}C–^{117/119}Sn)$ = 36 Hz, Sn–CH_2–*C*H_2), 22.1 (Sn–*C*H_2), 43.1 N(*C*H_3)$_2$, 60.5 ($^3J(^{13}C–^{117/119}Sn)$ = 145 Hz, *C*H_2–N). **^{19}F{^{1}H} NMR** (188.29 MHz, D_2O): δ –125. **^{119}Sn{^{1}H} NMR** (111.92 MHz, D_2O): no signal. **Electrospray MS**: m/z (%), positive mode, 311.0 (100, [{$Me_2N(CH_2)_3$}$_2$SnF]$^+$), 331.1 (90, [**4** – 2F – H]$^+$). Attempts to recrystallize compound **4** gave single crystals that were not suitable for X-ray diffraction analysis of {[$Me_2(H)N(CH_2)_3$]$_2$$SnF_3$·$H_2O$·$ClO_4$} (mp 80-82 °C). Anal. Calcd (%) for $C_{10}H_{28}ClF_3N_2O_5Sn$ (469.49): C 25.69, H 6.04, N 5.99. Found: C 25.4, H 6.2, N 5.7.

Method 2: To a solution of **2** (101 mg, 0.19 mmol) in D_2O was added NaF (16 mg, 0.38 mmol) of. The solution was stirred for 10 min. From this solution, NMR data were recorded.

^{1}H NMR (200.13 MHz, D_2O): δ 1.16 (t, $^2J(^1H–^{117/119}Sn)$ = 119.6 Hz, 4H, Sn–CH_2), 2.04 (m, $^3J(^1H–^{117/119}Sn)$ = 100.5/ 104.8 Hz, 4H, Sn–CH_2–CH_2), 2.88 (s, 12H, N(CH_3)$_2$), 3.15 (t, 2H, CH_2–N). **^{13}C{^{1}H} NMR** (100.33 MHz, D_2O): δ 20.7 ($^2J(^{13}C–^{117/119}Sn)$ = 37 Hz, Sn–CH_2–*C*H_2), 23.6 ($^1J(^{13}C–^{117/119}Sn)$ = 1102 /1153 Hz, Sn–CH_2), 43.1 N(CH_3)$_2$, 60.6 ($^3J(^{13}C–^{117/119}Sn)$ = 160 Hz, *C*H_2–N). **^{19}F{^{1}H} NMR** (188.29 MHz, D_2O): δ –125. **^{119}Sn{^{1}H} NMR** (111.92 MHz, D_2O): δ –412.

Selectivity studies.

To a solution of NaF (10 mg, 0.24 mmol), NaCl (14 mg, 0.24 mmol), NaBr (24 mg, 0.24 mmol), and NaI (36 mg, 0.24 mmol) in D_2O (0.6 mL) was added **2** (63 mg, 0.12 mmol.) The reaction mixture was stirred for 10 min. From this solution, NMR data were recorded.

^{1}H NMR (300.13 MHz, D_2O): δ 1.26 (t, $^2J(^1H–^{117/119}Sn)$ = 106.9 Hz, 4H, Sn–CH_2), 2.08 (m, $^3J(^1H–^{117/119}Sn)$ = 96.6 Hz, 4H, Sn–CH_2–CH_2), 2.91 (s, 12H, N(CH_3)$_2$), 3.17 (t, 2H, CH_2–N). **^{13}C{^{1}H}** NMR (75.47 MHz, D_2O): δ 20.2 ($^2J(^{13}C–^{117/119}Sn)$ = 35 Hz, Sn–CH_2–*C*H_2), 21.8 (Sn–*C*H_2),

43.1 N(CH_3)$_2$, 60.2 (^3J(^{13}C–$^{117/119}$Sn) = 154 Hz, CH_2–N). **^{19}F{^{1}H} NMR** (282.40 MHz, D_2O): δ –126 (97%), –133 (1%), –150 (2%).

Synthesis of [{Me$_2$(H)N(CH$_2$)$_3$}$_2$SnCl$_2$·2ClO$_4$] (5).

To a solution of {Me$_2$N(CH$_2$)$_3$}$_2$SnCl$_2$ (150 mg, 0.414 mmol) in water (5 mL) was added $HClO_4$ (139 mg, 60% solution). The solution was stirred for 5 hours followed by evaporation of water to yield **5** (229 mg, 98%) as a white solid material (mp. 182-184).

^{1}H NMR (400.25 MHz, D_2O): δ 1.58 (t, ^2J(^{1}H–$^{117/119}$Sn) = 103.7 Hz, 4H, Sn–CH_2), 2.11 (m, 4H, Sn–CH$_2$–CH_2), 2.87 (s, 12H, N(CH_3)$_2$), 3.16 (t, 2H, CH_2–N). **^{13}C{^{1}H} NMR** (100.64 MHz, D_2O): δ 20.3 (Sn–CH$_2$–CH_2, ^2J(^{13}C–$^{117/119}$Sn) = 35 Hz), 29.9 (^1J(^{13}C–$^{117/119}$Sn) = 959/1003 Hz, Sn–CH_2), 42.7 N(CH_3)$_2$, 59.3 (^3J(^{13}C–$^{117/119}$Sn) = 189 Hz, CH_2–N). **^{119}Sn{^{1}H} NMR** (149.26 MHz, D_2O): δ –310. **^{1}H NMR** (400.25 MHz, CD_3CN): δ 1.75 (t, ^2J(^{1}H–$^{117/119}$Sn) = 78.3 Hz, 4H, Sn–CH_2), 2.14 (m, 4H, Sn–CH$_2$–CH_2), 2.84 (d, (^3J(^{1}H–^{1}H) = 5.38 Hz), 12H, N(CH_3)$_2$), 3.16 (t, 2H, CH_2–N). **^{13}C{^{1}H} NMR** (100.64 MHz, CD_3CN): δ 21.7 (Sn–CH$_2$–CH_2), 29.1 (^1J(^{13}C–$^{117/119}$Sn) = 682 Hz, Sn–CH_2), 44.4 N(CH_3)$_2$, 60.9 (^3J(^{13}C–$^{117/119}$Sn) = 146 Hz, CH_2–N). **^{119}Sn{^{1}H} NMR** (149.26 MHz, CD_3CN): δ –56. Anal. Calcd (%) for $C_{10}H_{26}Cl_4N_2O_8Sn{\cdot}H_2O$ (562.8): C 20.68, H 4.86, N 4.82. Found: C 20.5, H 4.6, N 4.9. **Electrospray MS**: m/z (%), positive mode, 206.1 (34, [Sn(OH)$_3$ + 2H$_2$O]$^+$), 309.1 (10, [{Me$_2$N(CH$_2$)$_3$}$_2$SnOH]$^+$), 327.1 (4, [{Me$_2$N(CH$_2$)$_3$}$_2$SnCl]$^+$), negative mode, 99.1 (100, [ClO$_4$]$^-$).

Synthesis of [{Me$_2$(H)N(CH$_2$)$_3$}$_2$SnCl$_4$] (6).

To a solution of {Me$_2$N(CH$_2$)$_3$}$_2$SnCl$_2$ (150 mg, 0.414 mmol) in water (5 mL) was added HCl (31 mg, 37% solution). The solution was stirred for 5 hours followed by evaporation of water to yield **6** (173 mg, 96%) as a white solid material.

^{1}H NMR (500.08 MHz, D_2O): δ 1.55 (t, ^2J(^{1}H–$^{117/119}$Sn) = 101.6 Hz, 4H, Sn–CH_2), 2.08 (m, 4H, Sn–CH$_2$–CH_2), 2.82 (s, 12H, N(CH_3)$_2$), 3.13 (t, 2H, CH_2–N). **^{13}C{^{1}H} NMR** (125.75 MHz, D_2O): δ 20.5 (Sn–CH$_2$–CH_2, ^2J(^{13}C–$^{117/119}$Sn) = 35 Hz), 31.0 (^1J(^{13}C–$^{117/119}$Sn) = 928/976 Hz, Sn–CH_2), 42.6 N(CH_3)$_2$, 59.2 (^3J(^{13}C–$^{117/119}$Sn) = 175/181 Hz, CH_2–N). **^{119}Sn{^{1}H} NMR** (149.26 MHz, D_2O): δ –282. Anal. Calcd (%) for $C_{10}H_{26}Cl_4N_2Sn$ (434.84): C 27.62, H 6.03, N 6.44. Found: C 27.5, H

5.8, N 6.5. **Electrospray MS**: m/z (%), positive mode, 327.1 (90, $[\{Me_2N(CH_2)_3\}_2SnCl]^+$), 309.1 (78, $[\{Me_2N(CH_2)_3\}_2SnOH]^+$), 206.0 (40, $[Sn(OH)_3 + 2H_2O]^+$).

Reaction of 5 with two molar equiv $Et_4NF{\cdot}2H_2O$.

To a solution of $[\{Me_2NH(CH_2)_3\}_2SnCl_2]{\cdot}2ClO_4$, **5**, (40 mg, 0.07 mmol) in CH_3CN (10 mL) was added $Et_4NF{\cdot}2H_2O$ (26 mg, 0.14 mmol). A white precipitate was formed during stirring the solution for 5 hours. The precipitate was filtered, washed twice with CH_3CN and dried in vacuo to yield $[\{Me_2NH(CH_2)_3\}_2SnF_2]{\cdot}2ClO_4$, **2**, (35 mg, 92%) as a white solid material.

^{1}H NMR (400.25 MHz, D_2O): δ 1.23 (CH_3–CH_2N), 1.38 (t, 4H, Sn–CH_2), 2.05 (m, 4H, Sn–CH_2–CH_2), 2.86 (s, 12H, $N(CH_3)_2$), 3.14 (t, 2H, CH_2–N), 3.23 (CH_3–CH_2N). **^{13}C{^{1}H} NMR** (100.64 MHz, D_2O): δ 6.5 (CH_3–CH_2N), 19.9 (Sn–CH_2–CH_2), 25.7 (Sn–CH_2), 42.7 $N(CH_3)_2$, 51.9 (CH_3–CH_2N), 59.6 (CH_2–N). **^{19}F{^{1}H} NMR** (D_2O, 376.61 MHz): δ –144. **^{119}Sn{^{1}H} NMR** (149.26 MHz, D_2O): –359.

Reaction of 6 with four molar equiv $Et_4NF{\cdot}2H_2O$.

To a solution of $\{Me_2NH(CH_2)_3\}_2SnCl_4$, **6**, (110 mg, 0.25 mmol) in CH_3CN (12 mL) was added $Et_4NF{\cdot}2H_2O$ (187 mg, 1.01 mmol). A white precipitate was formed during stirring the solution for 5 hours. The precipitate was filtered, washed twice with CH_3CN and dried in vacuo to yield **4** (88 mg, 94%) as a white solid compound (mp. 128.2-129.2).

NMR spectra of a solution of **4** (40 mg) in D_2O. **^{1}H NMR** (400.25 MHz, D_2O): δ 1.24 (t, $^2J(^1H–^{117/119}Sn)$ = 111.9 Hz, 4H, Sn–CH_2), 2.02 (m, $^3J(^1H–^{117/119}Sn)$ = 99.4 Hz, 4H, Sn–CH_2–CH_2), 2.84 (s, 12H, $N(CH_3)_2$), 3.12 (t, 2H, CH_2–N). **^{13}C{^{1}H} NMR** (100.64 MHz, D_2O): δ 20.0 (Sn–CH_2–CH_2), 23.6 (Sn–CH_2), 42.6 $N(CH_3)_2$, 59.9 (CH_2–N). **^{19}F{^{1}H} NMR** (376.61 MHz, D_2O): δ –130 (3%, unresolved), –133 (97%). **^{119}Sn{^{1}H} NMR** (111.92 MHz, D_2O): –379.

NMR spectra of a solution of **4** (80 mg) in D_2O. **^{19}F{^{1}H} NMR** (376.61 MHz, D_2O): δ –126 (96%), –130 (4%, unresolved). **^{119}Sn{^{1}H} NMR** (111.92 MHz, D_2O): –405. Anal. Calcd (%) for $C_{10}H_{26}F_4N_2Sn{\cdot}3H_2O$ (423.08): C 28.39, H 7.62, N 6.62. Found: C 28.8, H 7.8, N 6.9.

Synthesis of {[$Me_2NH(CH_2)_3$]$Cl_3Sn(CH_2)$}$_2SiMe_2$ (9).

To a solution of **8** (0.7 g, 0.87 mmol) in CH_2Cl_2 (30 mL) was added a solution of hydrogen chloride (1.0 M in diethyl ether, 190 mg, 5.22 mmol) in one portion at 0 °C and the mixture was stirred for 30 min. at the same temperature. The mixture was then stirred overnight at ambient temperature. In the next day a white precipitate was formed. The precipitate was separated and washed three times with CH_2Cl_2 (20 mL) affording after drying in vacuo (566 mg, 90%) of compound **9** as a white solid.

^{1}H NMR (300.13 MHz, D_2O): δ 0.21 (s, 6H, Me_2Si), 0.92 (s, 4H, $^2J(^1H–^{117/119}Sn)$ = 118.6 Hz, SiCH_2Sn), 1.53 (t, 4H, $^3J(^1H–^{117/119}Sn)$ = 94.4 Hz, Sn–CH_2), 2.07 (m, 4H, Sn–CH_2–CH_2), 2.82 (s, 12H, $N(CH_3)_2$), 3.12 (t, 4H, CH_2–N). **^{13}C{^{1}H} NMR** (75.47 MHz, D_2O): δ 0.9 ($^1J(^{13}C–^{29}Si)$ = 40 Hz, Me_2Si), 17.3 (SiCH_2Sn), 20.1 (Sn–CH_2), 28.5 (Sn–CH_2–CH_2), 42.6 $N(CH_3)_2$, 59.3 (CH_2–N). **^{29}Si{^{1}H} NMR** (59.63 MHz, D_2O): δ 2.1 ($^2J(^{29}Si–^{117/119}Sn)$ = 54 Hz). **^{119}Sn{^{1}H} NMR** (111.92 MHz, D_2O): δ –204. Anal. Calcd (%) for $C_{14}H_{36}Cl_6N_2SiSn_2$ (710.66): C 23.7, H 5.1, N 3.9.Found: C 23.9, H 5.4, N 4.1. **Electrospray MS**: *m/z* (%), positive mode, 601.0 (100, [**9** – Cl]$^+$), 547.0 (70, [**9** – 4Cl +3OH] $^+$), negative mode, 672.9 (100, [**9** – 2HCl + Cl]$^-$).

Synthesis of {[$Me_2NH(CH_2)_3$]$Cl_2Sn(CH_2)_2SnPhCl_2$·Cl}·2H_2O (10).

To a solution of **4** (0.5 g, 0.68 mmol) in CH_2Cl_2 (25 mL) was added a solution of hydrogen chloride (1.0 M in diethyl ether, 124 mg, 3.39 mmol) in one portion at 0 °C with stirring for 30 min. then the mixture was stirred overnight at ambient temperature. In the next day a white precipitate from the orange solution was formed, the precipitate was separated and washed three times with CH_2Cl_2 (20 mL) affording after drying in vacuo compound **5** (350 mg, 85%) as a white solid m.p. 137- 138° C.

^{1}H NMR (300.13 MHz, D_2O): δ 1.55 (t, $^2J(^1H–^{117/119}Sn)$ = 97.3 Hz, 2H, Sn–CH_2), 2.07 (m, 2H, Sn–CH_2–CH_2), 2.15–2.16 (b, 4H, Sn–CH_2–CH_2–Sn), 2.80 (s, 6H, $N(CH_3)_2$), 3.11 (t, 2H, CH_2–N), 7.39- 7.75 (5H, Ph). **^{13}C{^{1}H} NMR** (75.47 MHz, D_2O): δ 20.5 ($^2J(^{13}C–^{117/119}Sn)$ = 34 Hz, Sn–CH_2–CH_2), 30.3 (Sn–CH_2), 31.2 (Sn–CH_2–CH_2–Sn), 31.9 (Sn–CH_2–CH_2–Sn), 42.7 $N(CH_3)_2$, 59.3 ($^3J(^{13}C–^{117/119}Sn)$ = 29 Hz, CH_2–N), 128.5 ($^3J(^{13}C–^{119}Sn)$ = 108 Hz, Ph, C_m), 129.9 (Ph, C_p), 134.4 ($^2J(^{13}C–^{119}Sn)$ = 68 Hz, Ph, C_o), 148.5 (Ph, C_i). **^{119}Sn{^{1}H} NMR** (111.92 MHz, D_2O): δ –296 ($SnCl_2$), –380 ($SnPhCl_2$).

^{1}H NMR (300.13 MHz, CD_3CN): δ 1.89 (t, $^{2}J(^{1}H–^{117/119}Sn)$ = 84.9 Hz, 2H, Sn–CH_2), 2.23 (m, 2H, Sn–CH_2–CH_2), 2.42–2.44 (b, 2H, Sn–CH_2–CH_2–Sn), 2.52– 2.54 (b, 2H, Sn–CH_2–CH_2–Sn), 2.76 (d, $^{3}J(^{1}H–^{1}H)$ = 5.12 Hz, 6H, $N(CH_3)_2$), 3.15– 3.17 (t, 2H, CH_2–N), 7.36–7.97 (5H, Ph).

^{13}C{^{1}H} NMR (75.47 MHz, CD_3CN): δ 22.5 ($^{2}J(^{13}C–^{117/119}Sn)$ = 38 Hz, Sn–CH_2–*C*H_2), 34.9 (Sn–CH_2), 36.5 (Sn–*C*H_2–CH_2–Sn), 37.5 (Sn–CH_2–*C*H_2–Sn), 44.4 $N(CH_3)_2$, 60.9 ($^{3}J(^{13}C–^{117/119}Sn)$ = 48 Hz, CH_2–N), 129.3 ($^{3}J(^{13}C–^{117}Sn)$ = 92 Hz, $^{3}J(^{13}C–^{119}Sn)$ = 96 Hz, Ph, C_m), 130.6 ($^{4}J(^{13}C–^{119}Sn)$ = 20 Hz, Ph, C_p), 136.6 ($^{2}J(^{13}C–^{119}Sn)$ = 64 Hz, Ph, C_o), 150.6 (Ph, C_i). **^{119}Sn {^{1}H} NMR** (111.92 MHz, CD_3CN): δ –122 ($SnCl_2$), –182 ($SnPhCl_2$). Anal. Calcd (%) for $C_{13}H_{26}Cl_5NO_2Sn_2$ (643.0): C 24.28, H 4.08, N 2.18. Found: C 23.9, H 3.6, N 2.3. **Electrospray MS**: m/z (%), positive mode, 515.9 (100, [**10** – 4Cl + 3OH]$^{+}$), 571.9 (20, [**10** – Cl]$^{+}$), negative mode, 605.8 (100, [**10** – H]$^{-}$).

Reaction of 10 with Me_4NCl.

To a solution of **10** (55 mg, 0.09 mmol) in D_2O (0.6mL) was added Me_4NCl (10 mg, 0.09 mmol). The solution was stirred for 5 minutes. NMR spectra were recorded.

^{1}H NMR (300.13 MHz, D_2O): δ 1.58 (t, $^{2}J(^{1}H–^{117/119}Sn)$ = 96.6 Hz, 2H, Sn–CH_2), 2.10 (m, 2H, Sn–CH_2–CH_2), 2.19–2.20 (b, 4H, Sn–CH_2–CH_2–Sn), 2.81 (s, 6H, $N(CH_3)_2$), 3.08 (s, Me_4N), 3.12 (t, 2H, CH_2–N), 7.40– 7.78 (5H, Ph). **^{13}C{1H} NMR** (75.47 MHz, D_2O): δ 20.6 ($^{2}J(^{13}C–^{117/119}Sn)$ = 36 Hz, Sn–CH_2–*C*H_2), 31.0 ($^{1}J(^{13}C–^{117/119}Sn)$ = 307 Hz, Sn–*C*H_2), 32.5 (Sn–*C*H_2–CH_2–Sn), 32.8 (Sn–CH_2–*C*H_2–Sn), 42.7 $N(CH_3)_2$, 55.19 Me_4N, 59.3 ($^{3}J(^{13}C–^{117/119}Sn)$ = 38 Hz, *C*H_2–N), 128.5 ($^{3}J(^{13}C–^{119}Sn)$ = 106 Hz, Ph, C_m), 129.8 (Ph, C_p), 134.4 ($^{2}J(^{13}C–^{119}Sn)$ = 69 Hz, Ph, C_o), 149.3 (Ph, C_i). **^{119}Sn{^{1}H} NMR** (111.92 MHz, D_2O): δ –287 ($SnCl_2$), –369 ($SnPhCl_2$). **Electrospray MS**: m/z (%), positive mode, 300.0 (100, [$Me_2NH(CH_2)_3Sn(OH)_2Ph$]$^{+}$), negative mode, 387.9 (100, [$Me_2N(CH_2)_3SnPhCl_3$]$^{-}$).

Reaction of 10 with $Et_4NF{\cdot}2H_2O$.

To a solution of **10** (50 mg, 0.08 mmol) in D_2O (0.6 mL) was added $Et_4NF.2H_2O$ (15 mg, 0.08 mmol). The solution was stirred for 5 minutes. NMR spectra were recorded.

^{1}H NMR (300.13 MHz, D_2O): δ 1.18 (t, 12H, (CH_3CH_2)$_4$N), 1.52 (t, $^{2}J(^{1}H–^{117/119}Sn)$ = 99.5 Hz, 2H, Sn–CH_2), 2.06 (m, 2H, Sn–CH_2–CH_2), 2.11–2.12 (b, 4H, Sn–CH_2–CH_2–Sn), 2.80 (s, 6H, $N(CH_3)_2$), 3.13 (t, 2H, CH_2–N), 3.16 (q, 8H, (CH_3CH_2)$_4$N), 7.40–7.75 (5H, Ph). **^{13}C{^{1}H} NMR**

(D_2O, 75.47 MHz): δ 6.5 (CH$_3$CH$_2$)$_4$N, 20.6 (Sn–CH$_2$–CH$_2$), 28.8 (Sn–CH$_2$), 29.6 (Sn–CH$_2$–CH$_2$–Sn), 30.3 (Sn–CH$_2$–CH$_2$–Sn), 42.6 N(CH$_3$)$_2$, 51.8 (CH$_3$$CH_2$)$_4$N, 59.4 ($^3J$(^{13}C–$^{117/119}$Sn) = 84 Hz, CH$_2$–N), 128.5 (^3J(^{13}C–^{119}Sn) = 106 Hz, Ph, C$_m$), 129.8 (Ph, C$_p$), 134.4 (^2J(^{13}C–^{119}Sn) = 69 Hz, Ph, C$_o$), 147.9 (Ph, C$_i$). **^{19}F{^{1}H} NMR** (282.40 MHz, D_2O): δ –141. **^{119}Sn{^{1}H} NMR** (111.92 MHz, D_2O): δ –318 ($SnCl_2$), –399 ($SnPhCl_2$). **Electrospray MS**: m/z (%), positive mode, 360.1 (25, [Me$_2$N(CH$_2$)$_3$SnPh$_2$]$^+$).

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5. Ionic and non-Ionic $Me_2N(CH_2)_3$-Substituted Triorganotin Halides and The Reactivity of Related N/Sn-based Lewis Pairs towards CH_2Cl_2

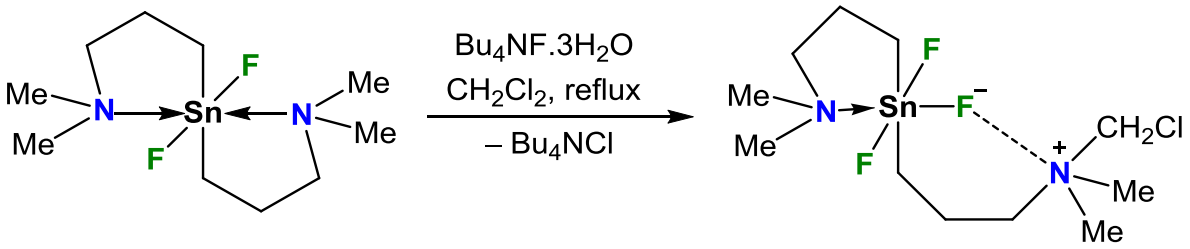
5.1 INTRODUCTION

Activation of small molecules by the use of the so called Frustrated Lewis Pairs (FLPs) is of great interest and widely studied in the last years. Frustrated Lewis Pairs are compounds containing Lewis acids and Lewis bases that cannot combine to form adducts as a result of steric hindrance. Because of that, these systems are very reactive and potentially useful for activation of small molecules such as H_2, CO_2, CO, O_2, NO, SO_2.[1]

Many examples have been reported based on phosphorus/boron, and nitrogen/boron systems.[2][3][4] Between them the implementation of bulky amines as Lewis basic components showed satisfying results in the field of FLPs, taking into account that they are generally air stable and inexpensive.[1]

In the last few years many metal-based Lewis acids used as FLPs have been reported. Cationic zirconocene-phosphinoaryloxide complexes have shown good results in heterolytic cleavage of H_2, activation of CO_2, alkenes, alkynes and aldehydes, and the ring-opening of THF.[5] In addition, a phosphorus/aluminum-based frustrated Lewis pair has proved to be an alternative strategy for the reduction of CO_2, and for selective hydrogen transfer.[6][7][8]

Jurkschat and coworkers have reported that $[\{Me_2N(CH_2)_3\}_2SnF_3]^-Bu_4N^+$ showed enhanced reactivity towards CH_2Cl_2 giving the zwitterionic compound $[\{Me_2(ClCH_2)N^+(CH_2)_3\}\{Me_2N(CH_2)_3\}SnF_3^-]\cdot H_2O$ (Scheme 1).[9]



Scheme 1. Synthesis of the zwitterionic $\{[Me_2(ClCH_2)N^+(CH_2)_3][Me_2N(CH_2)_3]SnF_3^-\}\cdot H_2O$ reported in literature.[9]

Continuing the study in this research is of great interest, as it highlights the new type of N/Sn-based Lewis pairs. Here will be presented the syntheses and characteristic of the zwitterionic triorganostannates $[\{Me_2(ClCH_2)N(CH_2)_3\}\{Me_2N(CH_2)_3\}SnRXCl]$ (R = Me, Ph; X = Cl, F) as a result of the enhanced reactivity of the halidotriorganotin compounds $[Me_2N(CH_2)_3]_2SnRX$ towards CH_2Cl_2.

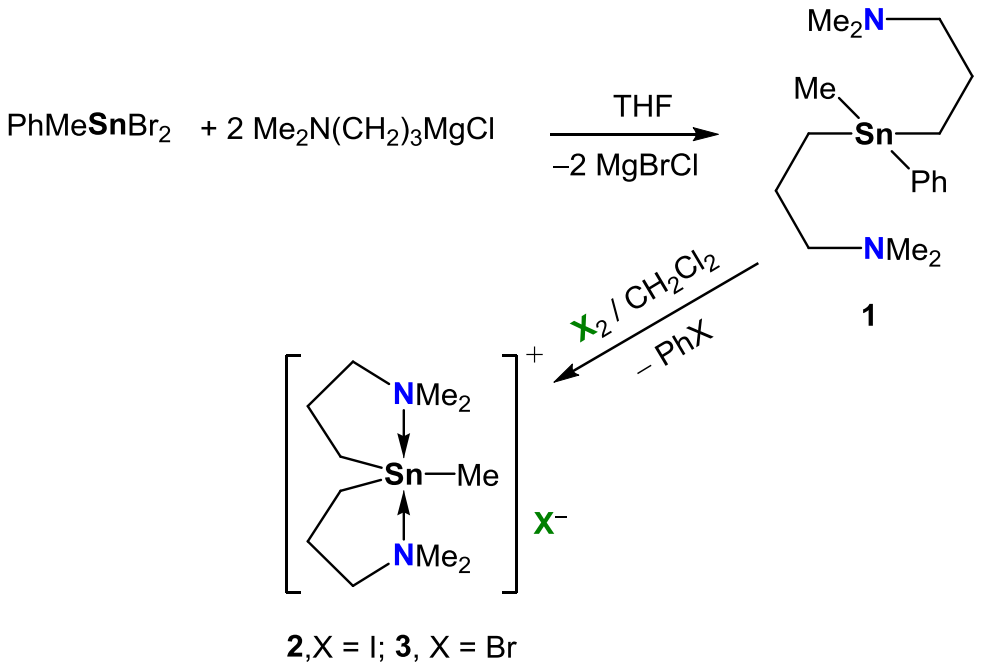
5.2 Syntheses of the triorganotin cations $[\{Me_2N(CH_2)_3\}_2SnMeX]$ (X = I, Br, ClO_4, SCN)

The reaction of methylphenyltin dibromide, $PhMeSnBr_2$,[10] with the Grignard reagent $Me_2N(CH_2)_3MgCl$ in THF gave $\{Me_2N(CH_2)_3\}_2SnMePh$, **1**, in a very good yield, (Scheme 2).

The reaction of compound **1** with one molar equivalent of elemental iodine in CH_2Cl_2 afforded the corresponding triorganotin iodide $[\{Me_2N(CH_2)_3\}_2SnMe]I$, **2**, in quantitative yield, (Scheme 2).

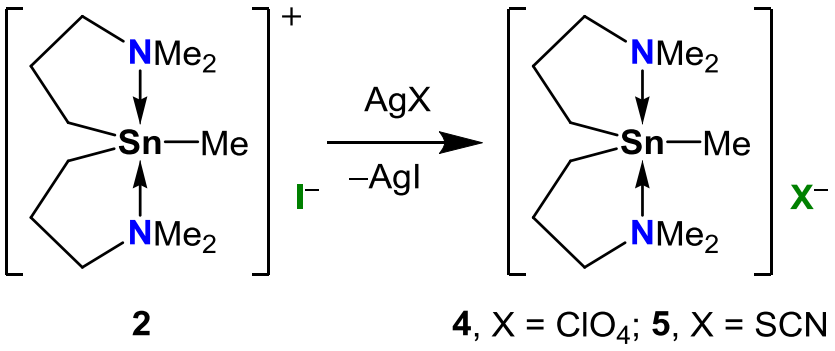
Compounds **1** and **2** were obtained as yellowish oil, respectively, yellow crystalline solid. They show good solubility in common organic solvents such as $CHCl_3$, CH_2Cl_2, and THF. Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of a solution of **2** in a mixture of acetone and ethyl acetate at room temperature.

The reaction of compound **1** with one molar equivalent bromine in CH_2Cl_2 afforded the corresponding triorganotin bromide $[\{Me_2N(CH_2)_3\}_2SnMe]Br$, **3**, in good yield, (Scheme 2).



Scheme 2. Syntheses of the organotin cations **2** and **3**.

The reaction of **2** with one molar equivalent of silver perchlorate, $AgClO_4$, provided the triorganotin cation $[\{Me_2N(CH_2)_3\}_2SnMe]ClO_4$, **4**, in very good yield, (Scheme 2). Similarly, treatment of **2** with one molar equivalent of silver thiocyanate, AgSCN, afforded the triorganotin thiocyanate $[\{Me_2N(CH_2)_3\}_2SnMe]SCN$, **5**, in very good yield as dark yellow oil, (Scheme 2). Compounds **2**–**5** show good solubility in water and common organic solvents such as CH_2Cl_2, acetone, and CH_3CN. The attempt to recrystallize compound **4** from its solution in CH_2Cl_2/*n*-hexane gave single crystals of $\{Me_2N(CH_2)_3\}_2SnMe(Ag_2I_3)$, **4a**, suitable for the X-ray diffraction analysis.



Scheme 2. Syntheses of the triorganotin cations **4** and **5**.

5.3 Molecular structure of compounds 2 and 4a

Compound **2** crystallized in the orthorhombic space group Pbca with eight molecules in the unit cell. Compound **4a** crystallized in the monoclinic space group *P*21/n with four molecules in the unit cell. The molecular structures of **2** and **4a** are presented in Figure 1 and Figure 2, respectively. Selected interatomic distances and angles are listed in Table 1.

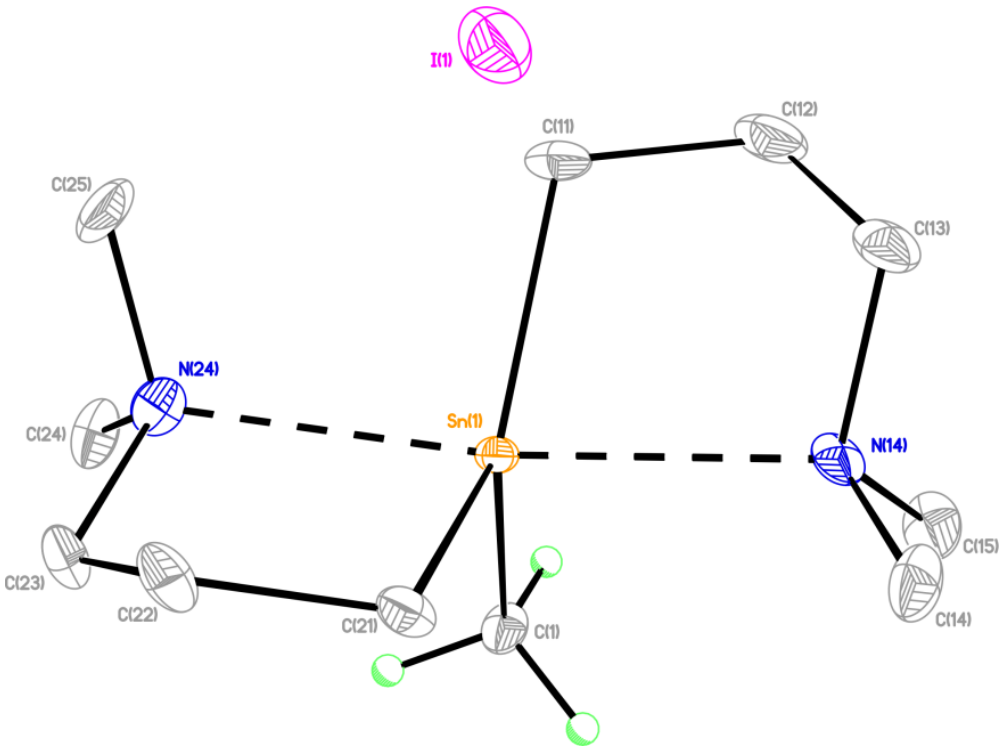


Figure 1. General view (SHELXTL) of a molecule of **2** showing 30% probability displacement ellipsoids and the crystallographic numbering scheme.

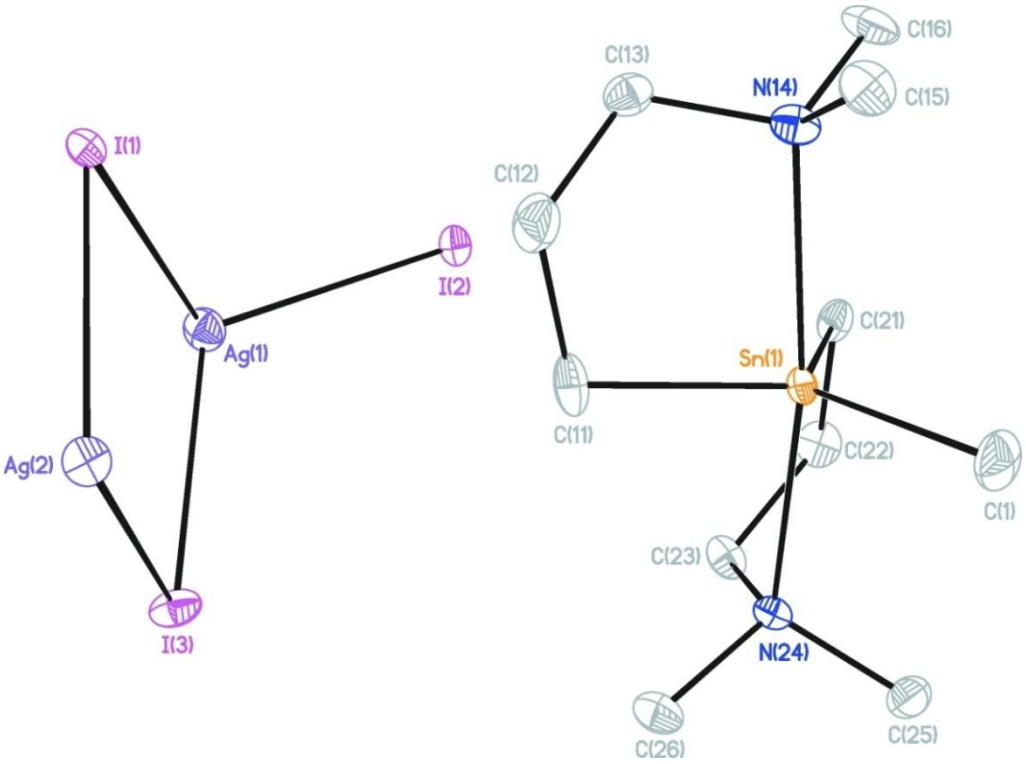


Figure 2. General view (SHELXTL) of a molecule of **4a** showing 30% probability displacement ellipsoids and the crystallographic numbering scheme.

The anion in compound **4a** presents as 1D polymer in the solid state as a result of I–Ag interactions (Figure 3). This has been reported before for different counter cations.

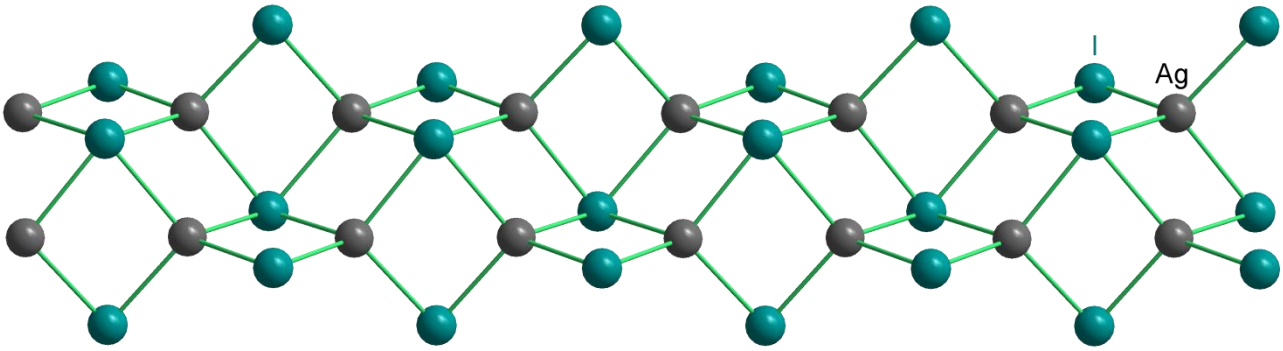


Figure 3. The polymeric structure of Ag_2I_3.

Table 1. Selected interatomic distances /Å and bond angles /° in **2** and **4a**.

	2	**4a**
Sn(1)–C(1)	2.109(6)	2.127(5)
Sn(1)–C(21)	2.130(6)	2.141(5)
Sn(1)–C(11)	2.148(6)	2.138(5)
Sn(1)–N(14)	2.377(6)	2.380(5)
Sn(1)–N(24)	2.399(6)	2.384(4)
Sn(1)–I(1)	4.5294(7)	
C(1)–Sn(1)–C(21)	112.1(3)	121.1(2)
C(1)–Sn(1)–C(11)	118.9(3)	120.3(2)
C(1)–Sn(1)–N(14)	97.0(2)	96.0(2)
C(1)–Sn(1)–N(24)	94.6(2)	95.0(2)
C(11)–Sn(1)–C(21)	129.0(3)	118.62(19)
C(11)–Sn(1)–N(14)	80.9(2)	81.6(2)
C(11)–Sn(1)–N(24)	93.3(2)	93.5(2)
C(21)–Sn(1)–N(24)	80.5(2)	81.60(18)
C(21)–Sn(1)–N(14)	95.3(2)	92.15(18)
N(14)–Sn(1)–N(24)	168.47(18)	169.03(13)

The triorganotin iodide **2** consists of an intramolecularly coordinated triorganotin cation and an iodide anion with the distance Sn(1)–I(1) of 4.529 Å. This distance is close to the corresponding distance in compound [{$Me_2N(CH_2)_3$}$_2$SnPh]I of 4.457(1) Å[11] and larger than the sum of the van der Waals radii of tin (2.2 Å) and iodine (2.15 Å).[12]

The tin atom in compound **2** is pentacoordinated and exhibits a distorted trigonal-bipyramidal environment (geometrical parameter τ = 0.66)[13] with the carbon atoms C(1), C(11), and C(21)

occupying the equatorial positions and the nitrogen atoms N(14) and N(24) occupying the axial positions (geometric goodness $\Delta\Sigma(\vartheta)$ = 86.8°).

The intramolecular N–Sn distances of 2.377(6) Å (Sn(1)–N(14)) and 2.399(6) Å (Sn(1)–N(24)) are a little smaller than the corresponding distances in [{$Me_2N(CH_2)_3$}$_2$SnPh]I of 2.392(4) and 2.401(4) Å.[11] The N(14)–Sn(1)–N(24) in **2** of 168.47(18) is slightly smaller than the corresponding angel in [{$Me_2N(CH_2)_3$}$_2$SnPh]I of 174.6(2)°.[11]

The intramolecular Sn(1)–N(14) distance of 2.380(5) Å in **4a** is similar to that found for Sn(1)–N(24) (2.384(4) Å). These two distances are in the range between the two N–Sn distances found in **2**.

Structures in solution

A ^{119}Sn NMR spectrum of a solution of {$Me_2N(CH_2)_3$}$_2$SnMePh, **1**, in $CDCl_3$ showed one signal at δ –34. This chemical shift is close to that reported for the tetraorganotin compound Me_3SnPh at δ –31.[14] A ^{13}C NMR spectrum showed two resonances with $^{117/119}$Sn coupling satellites at δ –12.1 ($^1J(^{13}C–^{117/119}Sn)$ = 308/323 Hz) and δ 7.5 ($^1J(^{13}C–^{117/119}Sn)$ = 345/362 Hz) related to the Sn*C*H$_3$ and Sn*C*H$_2$ carbon atoms, respectively.

In a ^{119}Sn NMR spectrum of the reaction mixture obtained from the reaction of **1** with two molar equivalent elemental iodine (in $CDCl_3$) two signals were observed. A major signal at δ +51 (integral 94) for [{$Me_2N(CH_2)_3$}$_2$SnMe]I, **2**, and a minor signal at δ –7 (integral 6) assigned to [{$Me_2N(CH_2)_3$}$_2$SnPh]I. The chemical shift of **2** (δ +51) is in a good agreement with those of the analogous pentacoordinated triorganotin cations [$Bu_2Sn(NCN)$][X] (NCN = [$C_6H_3(CH_2NMe_2)_2$-2,6]$^-$, X = BPh_4 (δ +57) and X = CF_3SO_3 (δ +60)).[15]

Changing the solvent plays no role in the coordination environment of the tin atom in compound **2**. A ^{119}Sn NMR spectrum of **2** in D_2O at room temperature showed a similar chemical shift at +50.

A ^{1}H NMR spectrum of compound **2** in $CDCl_3$ at room temperature showed one signal for the SnC*H*$_3$ protons at δ 0.59 ($^2J(^1H–^{117/119}Sn)$ = 52.3 Hz). However, two equally intense resonances for the N(C*H*$_3$)$_2$ protons at δ 2.33 and δ 2.38 were observed as result of their diastereotopism. In addition, splitting of the signals of the methylene resonances SnC*H*$_2$ and SnCH$_2$C*H*$_2$ was also observed (Figure 4). The data indicate the intramolecular N→Sn coordinations to be kinetically inert on the ^{1}H NMR time scale at room temperature.

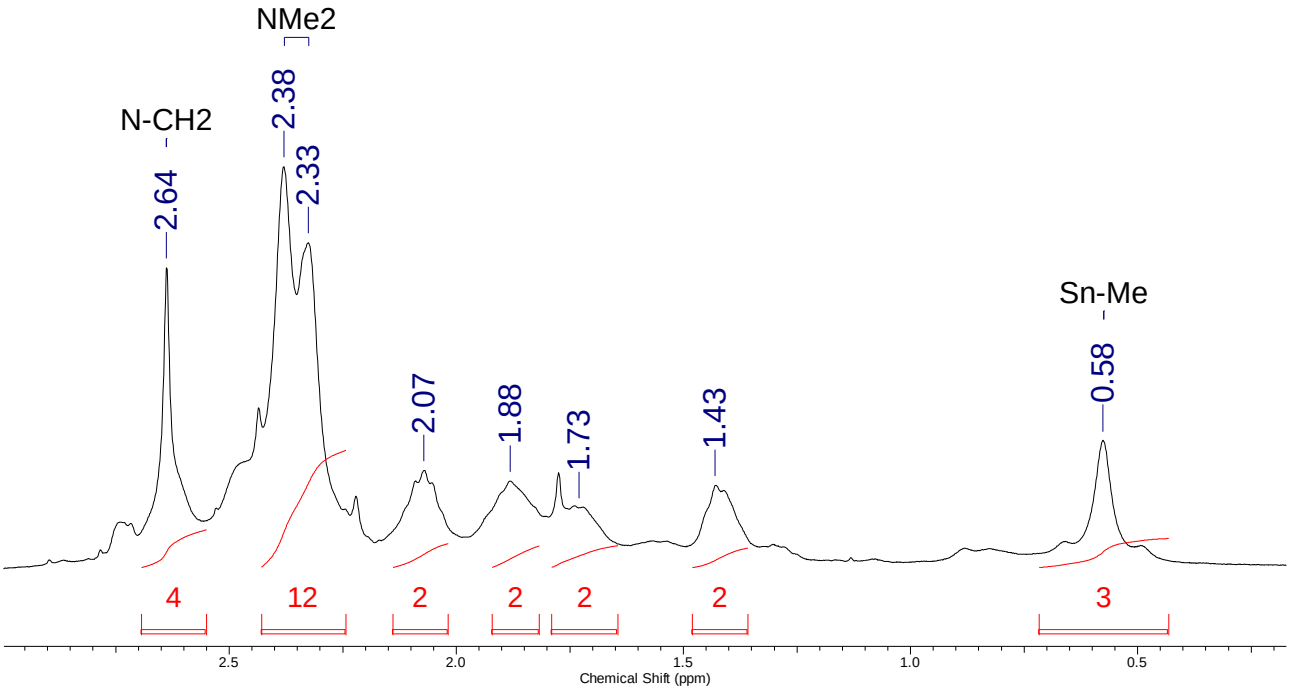


Figure 4. Expansion of ^{1}H NMR signals of compound **2** measured in $CDCl_3$ (300.13, 295 K).

Replacing the phenyl group in [{$Me_2N(CH_2)_3$}$_2$SnPh]I with the methyl one did not result in big changes in the chemical shifts of the carbon atoms in {$Me_2N(CH_2)_3$} moiety, as observed in the ^{13}C NMR spectrum of **2**. The coupling constant $^{1}J(^{13}C–^{117/119}Sn)$ for the SnCH_2 carbon atom of 461/481 Hz is in the range characteristic for pentacoordinated organotin(IV) compounds. In fact, it is a little smaller than the corresponding one in [{$Me_2N(CH_2)_3$}$_2$SnPh]I of 490/518 Hz, but much bigger than that found for the tetraorganotin compound **1** of 345/362 Hz. Two signals of the N(CH_3)$_2$ carbons at δ 46.3 and 46.8 are also observed. These two signals are close to those found for the corresponding carbon atoms in [{$Me_2N(CH_2)_3$}$_2$SnPh]I at δ δ 46.4 and 46.9.

These NMR data confirm that the pentacoordinate environment of the triorganotin cation **2** found in the solid state is retained in solution.

As it is expected, the set of organotin compounds **3** – **5** is also pentacoordinated, with two intramolecular N→Sn coordinations, as evidenced by their ^{119}Sn NMR chemical shifts. Those at δ +51, +53, +51 for **3**, **4**, and **5**, respectively, are similar to that of **2** at δ +51 indicating that compounds **2** – **5** are iso-structural.

In the case of the reaction of {$Me_2N(CH_2)_3$}$_2$SnMePh, **1**, with two molar equivalents bromine the triorganotin bromide [{$Me_2N(CH_2)_3$}$_2$SnPh]Br was resulted as a byproduct.

A ^{119}Sn NMR spectrum of the reaction mixture showed a major resonance at δ +51 (integral 56) for [{$Me_2N(CH_2)_3$}$_2$SnMe]Br, **3**, and two resonances at δ –8 (integral 26) assigned to [{$Me_2N(CH_2)_3$}$_2$SnPh]Br[16] and δ –151 (integral 18) assigned with caution to [$Me_2N(CH_2)_3$]$_2$$SnBr_2$.

In the ESI MS spectra (positive mode) of compounds **2**, **3** and **5** the same major mass cluster centered at *m*/z 307.1 that fits exactly with [{$Me_2N(CH_2)_3$}$_2$SnMe]$^+$ was found. This mass cluster was observed also in the ESI MS spectra (positive mode) of compound **4** with 46% relative abundance. The major mass cluster found for **4** is centered at *m*/z 369.1 that is assigned with caution to [{$Me_2N(CH_2)_3$}$_2$SnMe + CO_2 + H_2O]$^+$ (Figure 5).

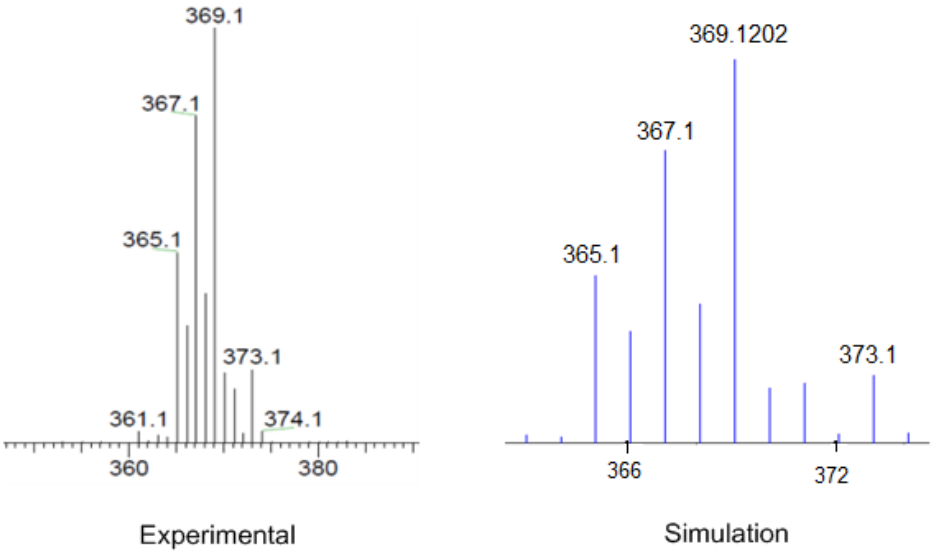
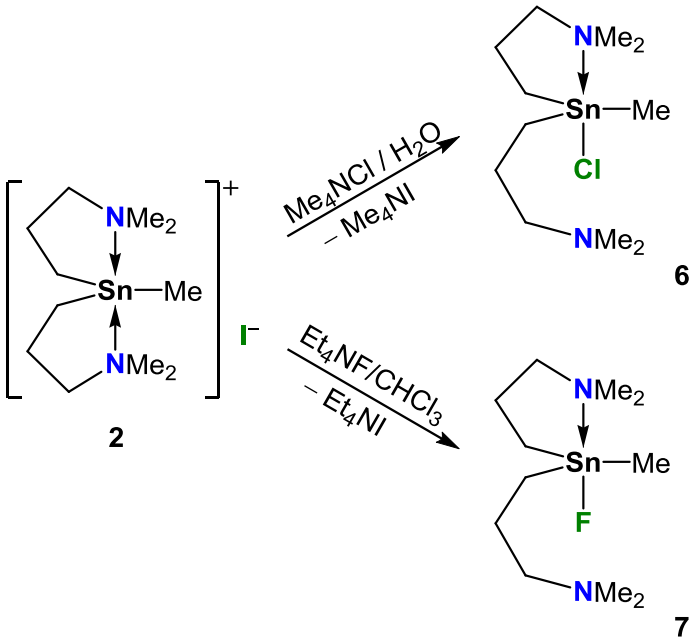


Figure 5. Experimental (from ESI MS) and simulated mass cluster for the cation [{$Me_2N(CH_2)_3$}$_2$SnMe + CO_2 + H_2O]$^+$.

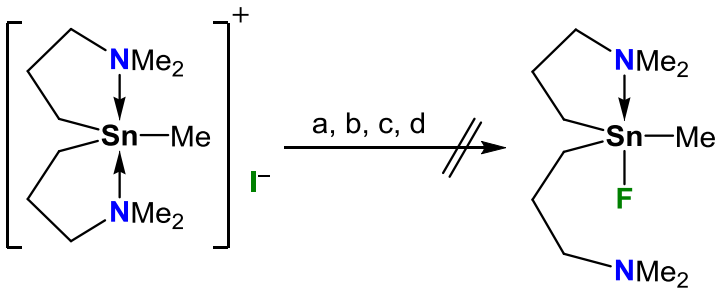
5.4 Syntheses of the non-ionic pentacoordinated triorganotin compounds $\{Me_2N(CH_2)_3\}_2SnRX$, (R = Me, Ph; X = Cl, F)

The reactions of the ionic organotin iodide **2** each with chloride or fluoride anions gave the corresponding non-ionic triorganotin compounds $\{Me_2N(CH_2)_3\}_2SnMeCl$, **6**, and $\{Me_2N(CH_2)_3\}_2SnMeF$, **7**, respectively, (Scheme 3). They were obtained as yellowish oils, and show good solubility in common organic solvents such as $CHCl_3$, CH_2Cl_2 but are poorly soluble in water.



Scheme 3. Syntheses of the non-ionic organotin compounds **6** and **7**.

Interestingly, the fluorine-substituted organotin compound **7** resulted only when the reaction between compound **2** and fluoride anions took place in $CHCl_3$ solution. No reactions happened when the polar solvents H_2O, CH_3CN, or the mixture (CH_2Cl_2+ H_2O) was used (Scheme 4).



2 **7**

a) Reaction with Et_4NF in D_2O; b) reaction with Et_4NF in CD_3OD; c) Compound **2** in DCM, Et_4NF in distilled water, stirring 3 days; d) Compound **2** in DCM, KF in distilled water, stirring 10 days.

Scheme 4. Attempts to synthesize compound **7** using different solvents.

A ^{119}Sn NMR spectrum of compound **6** in $CDCl_3$ solution showed a significant upfield shift for the tin atom (δ = –3, $\Delta\delta$ = 54 ppm) with respect to the triorganotin cation **2**. This chemical shift at δ –3 exhibits considerable high-field shift with respect to the tetracoordinated chlorine-substituted triorganotin Me_3SnCl (δ 164)[17] [18] and Bu_3SnCl (δ 141).[19] Moreover, it is comparable with those reported for pentacoordinated chlorine-substituted triorganotin compounds such as $MeN\{(CH_2)_3\}_2SnClMe$ (δ +4)[20] and $Ph_2P(O)(CH_2)_2SnClMe_2$ (δ +11).[21] A ^{13}C NMR spectrum showed a resonance at δ 15.9 ($^1J(^{13}C–^{117/119}Sn)$ = 486 Hz) assigned to the $SnCH_2$ carbon atom. This chemical shift is similar to that reported for the corresponding carbon atom in $\{Me_2N(CH_2)_3\}_3SnCl$ at δ 15.5 ($^1J(^{13}C–^{117/119}Sn)$ = 462 Hz), with the tin atom being pentacoordinated ($\delta\,^{119}Sn$ = +2).[22]

These NMR data prove the non-ionic nature of compound **6** and favor a similar structure to that found for the analogous $\{Me_2N(CH_2)_3\}_2SnPhCl$[22] with only one N→Sn intramolecular coordination.

A ^{119}Sn NMR spectrum of a solution of compound **7** in $CDCl_3$ at room temperature reveals a doublet resonance at δ –2 ($^1J(^{119}Sn–^{19}F)$ = 1947 Hz), Figure 6. This chemical shift is close to that reported for the fluorine-substituted organotin compound $Me_2N(CH_2)_3SnFMe_2$ at δ +1 ($^1J(^{119}Sn–^{19}F)$ = 1900 Hz).[20] On the other hand, the $^1J(^{119}Sn–^{19}F)$ satellites value of 1947 Hz in **7** is close to those reported for $Ph_2(O)PCH_2CH_2SnFMe_2$ (1976 Hz)[21] and $Ph_2(S)PCH_2CH_2SnFMe_2$ (1940 Hz).[21] The latter compounds are pentacoordinated organotin compounds containing intramolecular coordination.

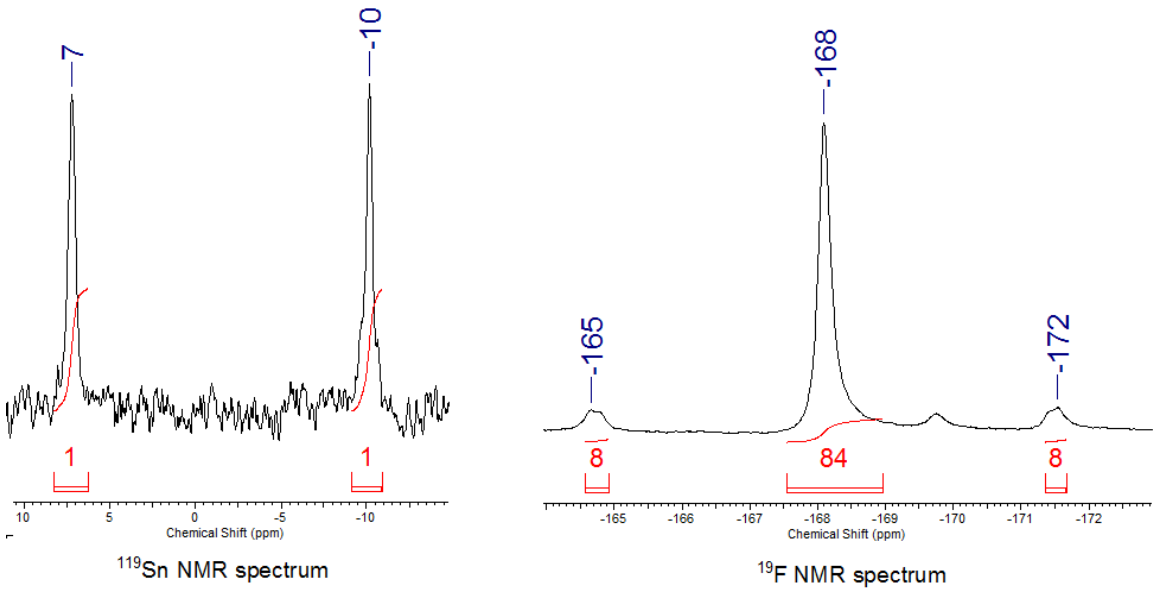


Figure 6. Expansion of the signals related to compound **7** in $^{119}Sn\{^{1}H\}$ NMR spectrum (111.92 MHz) and $^{19}F\{^{1}H\}$ NMR spectrum (282.37 MHz) measured in $CDCl_3$.

A ^{19}F NMR spectrum of the same sample showed one resonance at δ –168 ($^{1}J(^{19}F–^{117/119}Sn)$ = 1939 Hz), Figure 6. This chemical shift is comparable with those reported for the intramolecular coordinating organotin fluorides $Ph_2(O)PCH_2CH_2SnFMe_2$ (δ –169),[21] $N((CH_2)_3)_3SnF{\cdot}H_2O$ (δ –166)[20] and $MeN\{(CH_2)_3\}_2SnFMe{\cdot}H_2O$ (δ –163).[20] In a ^{13}C NMR spectrum the signals of the $SnCH_3$ and $SnCH_2$ carbon atoms at δ –3.5 and δ 12.9, respectively, were observed without $^{1}J(^{13}C–^{119}Sn)$ satellites. These chemical shifts are close to those reported for the corresponding carbon atoms in $MeN\{(CH_2)_3\}_2SnFMe{\cdot}H_2O$ (in C_6D_6) at δ –4.7 ($SnCH_3$) and δ 12.1 ($SnCH_2$, ($^{1}J(^{119}Sn–^{13}C)$ = 523 Hz)).[20]

In a ^{1}H NMR spectrum the chemical shift of the $SnCH_3$ protons at δ 0.39 ($^{2}J(^{1}H–^{117/119}Sn)$ = 59.6 Hz) (Figure 7) is similar to that reported for the corresponding protons in $MeN\{(CH_2)_3\}_2SnFMe{\cdot}H_2O$ at δ 0.34 ($^{2}J(^{119}Sn–^{1}H)$ = 61.8 Hz).[20]

The NMR data discussed above for the fluorine-substituted organotin compound **7** confirm the pentacoordinated environment of the tin atom with one intramolecular N→Sn coordination. No duplication of the $N(CH_3)_2$ and methylene resonances were observed in ^{1}H and ^{13}C NMR spectra at room temperature. This indicates that the intramolecular N→Sn coordination is kinetically labile on the NMR time scale at this temperature.

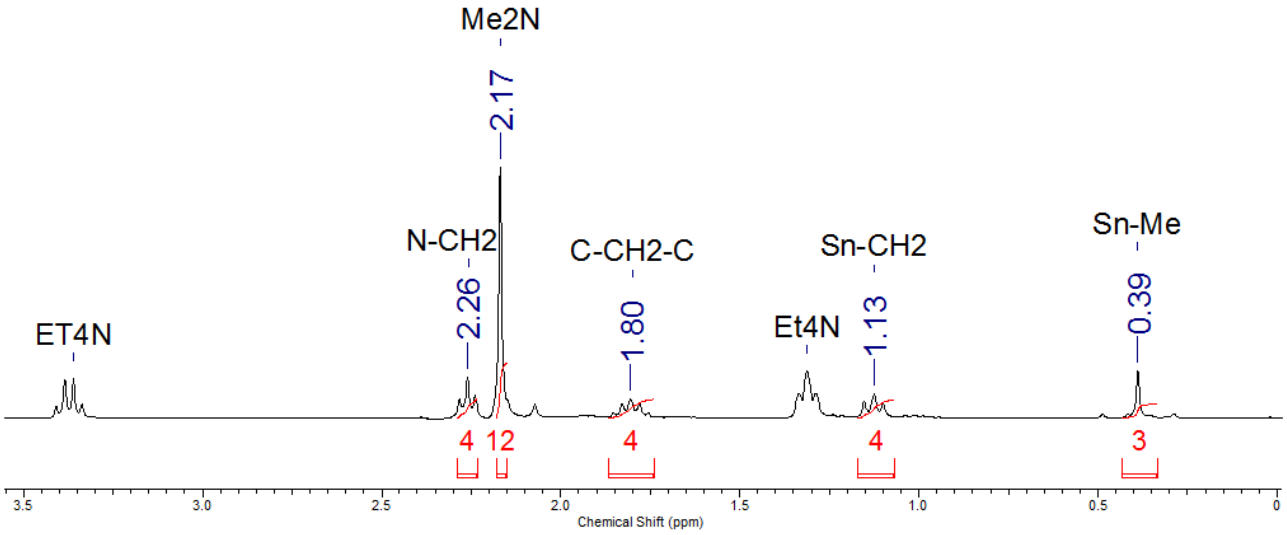


Figure 7. Expansion of the ^{1}H NMR spectrum (300.13 MHz, 295 K) of the crude reaction product of **2** and Et_4NF providing compound **7** and Et_4NI (measured in $CDCl_3$).

For comparison purposes, the fluorine-substituted organotin compound $\{Me_2N(CH_2)_3\}_2SnPhF$, **8**, was synthesized by the reaction of $[\{Me_2N(CH_2)_3\}_2SnPh]I$ with one molar equivalent $Et_4NF{\cdot}2H_2O$. A ^{119}Sn NMR spectrum of $\{Me_2N(CH_2)_3\}_2SnPhF$ in $CDCl_3$ solution at room temperature showed a doublet resonance at δ –79 ($^{1}J(^{119}Sn–^{19}F)$ = 2013 Hz), Figure 8. A ^{19}F NMR spectrum showed one resonance at δ –169 ($^{1}J(^{19}F–^{117/119}Sn)$ = 1784/2006 Hz)(Figure 8) that is close to that found for **7** at δ –168 ($^{1}J(^{19}F–^{117/119}Sn)$ = 1939 Hz).

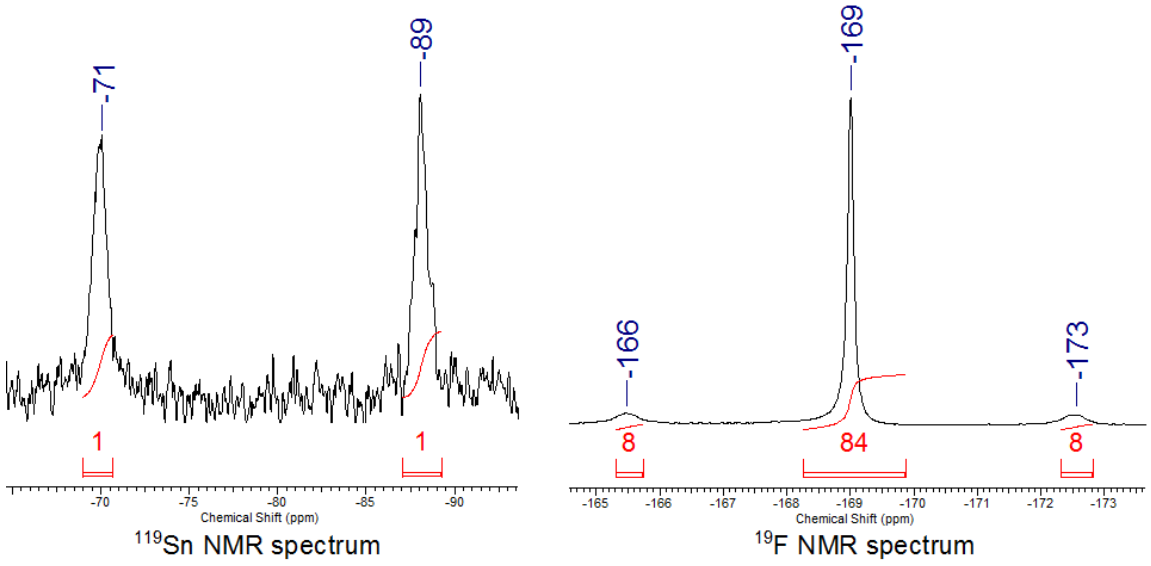


Figure 8. Expansion of the signals related to compound **8** in $^{119}Sn\{^{1}H\}$ NMR spectrum (111.92 MHz) and $^{19}F\{^{1}H\}$ NMR spectrum (282.36 MHz) measured in $CDCl_3$.

In the ESI MS spectra (positive mode) of compounds **6** and **7** a major mass cluster centered at *m*/z 307.1 that fits exactly with $[\{Me_2N(CH_2)_3\}_2SnMe]^+$ was observed. In the case of compound **8** (positive mode) a major mass cluster centered at *m*/z 369.1 that fits exactly with $[\{Me_2N(CH_2)_3\}_2SnPh]^+$ was found.

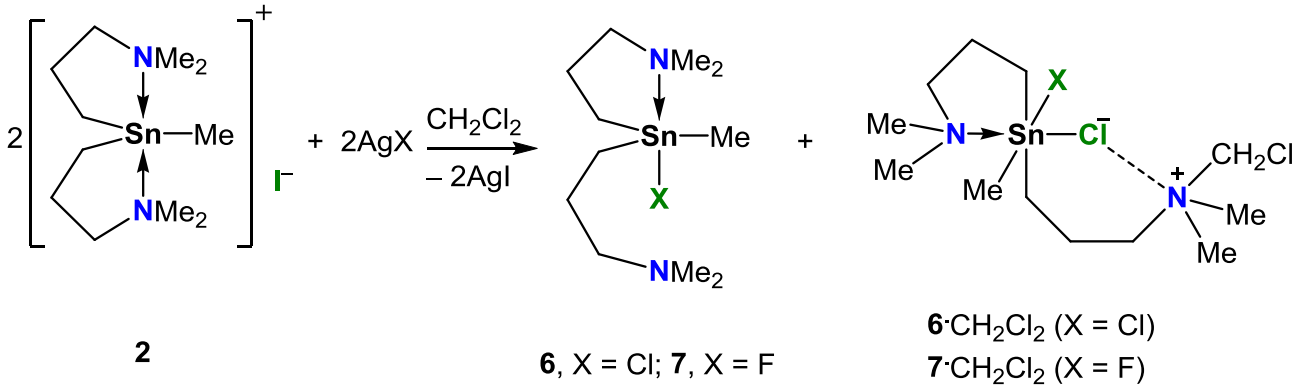
In fact, the set of the tetraorganotin halides **2**, **3**, **6** and **7** containing two (dimethylamino)propyl arms capable for N→Sn intramolecular coordination are structurally different depending on the substituted halide. In the case of the compounds **2** and **3** they are salt-like structures with a triorganotin cation containing two intramolecular N→Sn coordinations. Replacing the bromide and iodide anions with the smaller sized and higher electronegative fluoride and chloride ones resulted in the non-ionic structure with only one N→Sn intramolecular coordination.

Furthermore, the pentacoordinated structure of the organotin compounds **6** – **8** having two (dimethylamino)propyl arms with only one N→Sn intramolecular coordination fits perfectly with the design of frustrated Lewis pair (FLPs) systems. Thus, the non-interaction N···Sn in these compounds found between Lewis acid (Sn) and Lewis base (N) present in the same molecule but are not able to combine together. In contrast to the usual system found in FLPs, in the case of the organotin compounds **6** – **8** the steric hindrance is not the reason of the non-interaction between the Lewis acid and the Lewis base.

5.5 Reactivity of the organotin compounds 6 – 8 toward CH_2Cl_2 and the resulting zwitterionic triorganostannates $\{\{Me_2(ClCH_2)N(CH_2)_3\}\{Me_2N(CH_2)_3\}SnRXCl\}$ (R = Me, Ph; X = Cl, F)

The reaction of the triorganotin iodide **2** with AgCl in CH_2Cl_2/CH_3CN solution resulted in the chlorine-substituted triorganotin $\{Me_2N(CH_2)_3\}_2SnMeCl$, **6**. This reacted slowly with CH_2Cl_2 providing $[\{Me_2(ClCH_2)N(CH_2)_3\}\{Me_2N(CH_2)_3\}SnMeCl_2]$, referred as **6**·$CH_2Cl_2$ (Scheme 5) containing one quaternized nitrogen atom.

Due to the similarity in the structures and properties of compounds **6** and **7**, the same behavior was observed when compound **2** was reacted with AgF in CH_2Cl_2/CH_3CN solution. The resulting fluorine-substituted organotin compound $[Me_2N(CH_2)_3]_2SnMeF$, **7**, reacted slowly with CH_2Cl_2 giving $[\{Me_2(ClCH_2)N(CH_2)_3\}\{Me_2N(CH_2)_3\}SnMeFCl]$, **7**·$CH_2Cl_2$, (Scheme 5).



Scheme 5. Reactions of compounds **6** and **7** with CH_2Cl_2.

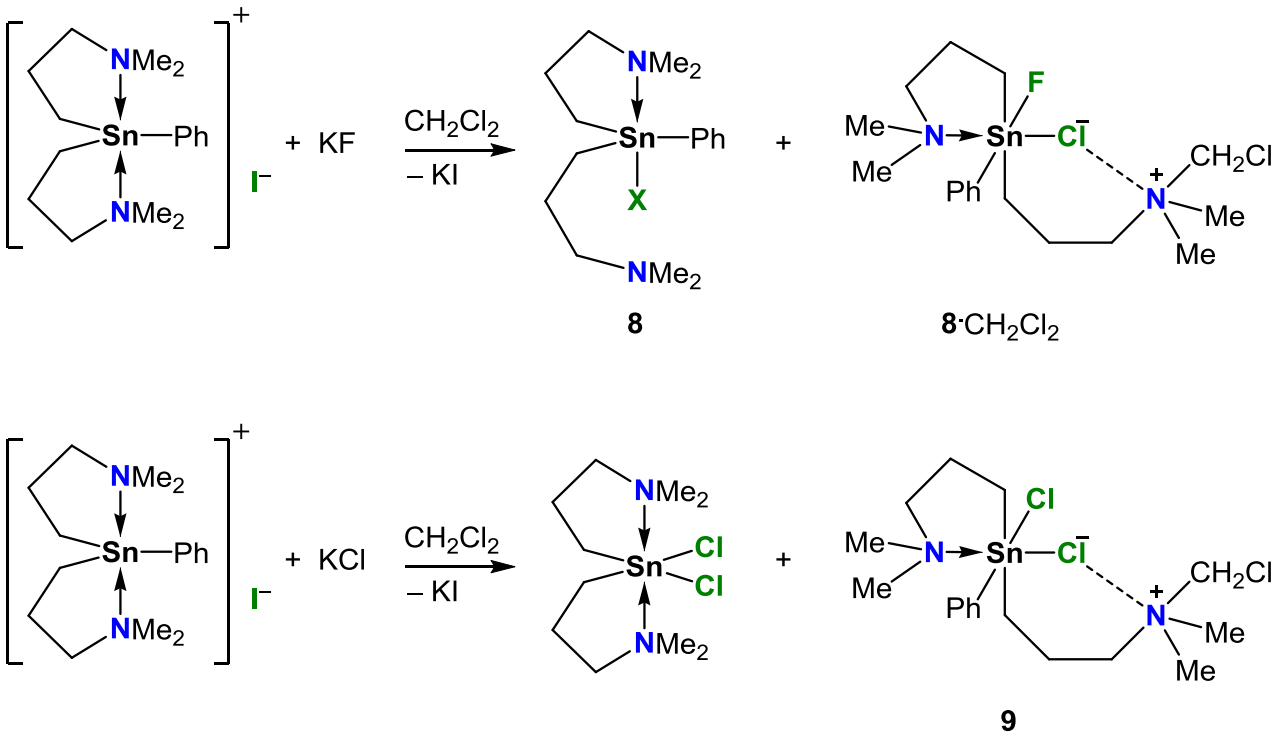
Compounds **6**·CH_2Cl_2 and **7**·CH_2Cl_2 could not be isolated, and all attempts to crystallize them from their different solutions failed.

A ^{119}Sn NMR spectrum in $CDCl_3$ of the crude reaction mixture obtained from the reaction of compound **2** with AgCl in CH_2Cl_2 showed two resonances at δ –2 assigned to compound **6** (integral 76) and δ –12 assigned to **6**·CH_2Cl_2 (integral 24). A ^{119}Sn NMR spectrum of the same sample after 4 months, when left in CH_2Cl_2 without stirring, showed three resonances at δ –3 (integral 43, **6**), δ –12 (integral 52, **6**·CH_2Cl_2) and δ –182 (integral 5) assigned to $\{[Me_2N(CH_2)_3]_2SnCl_2\}$.[22]

In a similar way, a ^{119}Sn NMR spectrum in $CDCl_3$ solution of the crude reaction mixture obtained from the reaction of **2** with AgF in CH_2Cl_2 showed after 5 days two doublet resonances at δ –2 ($^1J(^{119}Sn–^{19}F)$ = 1947 Hz) assigned to compound **7** and δ –18 ($^1J(^{119}Sn – ^{19}F)$ = 1916 Hz) assigned to compound **7**·CH_2Cl_2. A ^{19}F NMR spectrum of the same sample showed three major resonances at δ –168 ($^1J(^{19}F–^{117/119}Sn)$ = 1896 Hz) (integral 52, **7**), δ –162 ($^1J(^{19}F–^{119}Sn)$ = 1939 Hz) (integral 30, **7**·CH_2Cl_2) and δ –126 (integral 13) assigned to $\{[Me_2N(CH_2)_3]_2SnF_2\}$.[9]

Replacing the methyl group in compound **2** with the phenyl group gave similar results during the reactions with chloride and fluoride anions in CH_2Cl_2 solutions. The reaction of $[\{Me_2N(CH_2)_3\}_2SnPh]I$[11] with KF in CH_2Cl_2 gave the fluorine-substituted triorganotin $[\{Me_2N(CH_2)_3\}_2SnPhF]$, **8**. Compound **8** subsequently gave by the reaction with CH_2Cl_2 the zwitterion compound $[\{Me_2(ClCH_2)N(CH_2)_3\}\{Me_2N(CH_2)_3\}SnPhFCl]$, **8**·$CH_2Cl_2$ (Scheme 6).

Noteworthy, the reaction of $[\{Me_2N(CH_2)_3\}_2SnPh]I$[11] with KCl in CH_2Cl_2 gave a mixture of $[\{Me_2N(CH_2)_3\}_2SnCl_2]$ and $[\{Me_2(ClCH_2)N(CH_2)_3\}\{Me_2N(CH_2)_3\}SnPhCl_2]$, **9**, (Scheme 6). The latter resulted from the reaction of $\{Me_2N(CH_2)_3\}_2SnPhCl$[22] with CH_2Cl_2.



Scheme 6. The reaction of $[\{Me_2N(CH_2)_3\}_2SnPh]I$ with KF and KCl in CH_2Cl_2.

A ^{119}Sn NMR spectrum in $CDCl_3$ solution of the crude reaction mixture obtained from the reaction of $[\{Me_2N(CH_2)_3\}_2SnPh]I$[11] with KF in CH_2Cl_2 showed after 3 weeks three resonances. One resonance at δ –7 is related to the unreacted compound $[\{Me_2N(CH_2)_3\}_2SnPh]I$ (integral 20) and two doublets at δ –80 (integral 23, ($^1J(^{119}Sn–^{19}F)$ = 2030 Hz)), δ –89 (integral 57, ($^1J(^{119}Sn–^{19}F)$ = 2024 Hz)) are assigned to **8** and **8**·CH_2Cl_2, respectively, (Figure 9). In a ^{19}F NMR spectrum of the same sample two resonances at δ –168 ($^1J(^{19}F–^{117/119}Sn)$ = 1784/2006 Hz) assigned to **8**, and δ –164 ($^1J(^{19}F–^{117/119}Sn)$ = 1948/2005 Hz) corresponding to compound **8**·CH_2Cl were observed.

In the case of the reaction of $[\{Me_2N(CH_2)_3\}_2SnPh]I$[11] with KCl in CH_2Cl_2 for 12 days, a ^{119}Sn NMR spectrum in $CDCl_3$ showed two resonances at δ –7 (integral 91) related to unreacted compound $[\{Me_2N(CH_2)_3\}_2SnPh]I$ and δ –77 (integral 9) assigned to compound **9**. Interestingly, no resonance related to the triorganotin chloride $\{Me_2N(CH_2)_3\}_2SnPhCl$ (δ –50)[22] was observed in the ^{119}Sn NMR spectrum, even after stirring the reaction mixture for further three weeks. However, a ^{119}Sn NMR spectrum showed after one month three resonances. One at δ –7 (integral 53) related to unreacted compound $[\{Me_2N(CH_2)_3\}_2SnPh]I$, δ –77 (integral 35) assigned to **9** and δ –182 (integral 12) related to $\{[Me_2N(CH_2)_3]_2SnCl_2\}$.[23]

The compounds {[$Me_2N(CH_2)_3]_2SnCl_2$} and {[$Me_2N(CH_2)_3]_2SnF_2$} were found in the NMR spectra as byproducts. These two compounds could be formed as a result of the cleavage of the Sn–C_{Ph} and Sn–C_{Me} bonds by HX. The latter resulted probably in course of the hydrolysis, while the N→Sn interaction competes with the Sn–X bond results in weaker Sn–X bonds. These could suffer hydrolysis in contact with air-moisture giving HX.

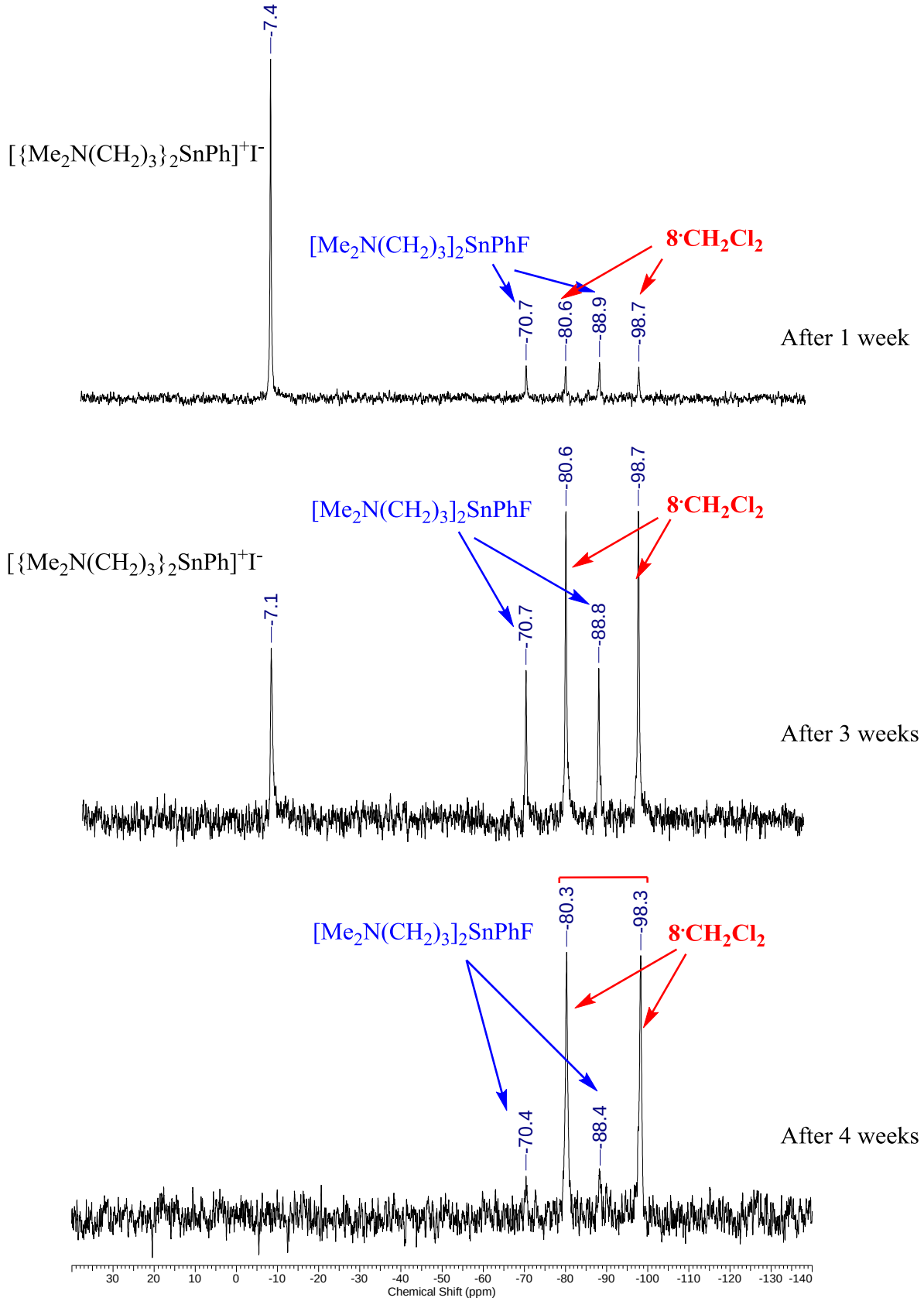


Figure 9. A ^{119}Sn NMR spectra in $CDCl_3$ for the reaction of $[\{Me_2N(CH_2)_3\}_2SnPh]^+ I^-$ with KF in CH_2Cl_2 during four weeks.

In general, the ^{119}Sn NMR resonances of the zwitterionic triorganostannates show upfield shifts (**6**·CH_2Cl_2, $\Delta\delta$ = –9; **7**·CH_2Cl_2, $\Delta\delta$ = –16; **8**·CH_2Cl_2, $\Delta\delta$ = –9; **9**, $\Delta\delta$ = –27 ppm) with respect to the corresponding triorganotin halides **6**, **7**, **8** and {[$Me_2N(CH_2)_3]_2$}SnPhCl, respectively, (Table 2). These differences are close to that reported for the zwitterionic triorganostannate $(L^{CN})_2$(*n*-Bu)SnCl·HCl (δ –125) that differs by –7 ppm with respect to $(L^{CN})_2$(*n*-Bu)SnCl (δ –118) (L^{CN} is 2-(dimethylaminomethyl)phenyl)).[24] These small differences in the chemical shifts of the tin atoms are evidence for pentacoordinated environment for compounds **6**·CH_2Cl, **7**·CH_2Cl, **8**·CH_2Cl and **9** in solution similarly to their parent compounds **6**, **7**, **8** and {[$Me_2N(CH_2)_3]_2$}SnPhCl,[22] respectively.

Table 2. ^{119}Sn and ^{19}F NMR of selected organotin compounds.

	^{119}Sn	^{19}F	$^1J(^{119}Sn–^{19}F)$ Hz
6	–3		
6·CH_2Cl_2	–12		
7	–2	–168	1947
7·CH_2Cl_2	–18	–162	1916
8	–80	–168	2030
8·CH_2Cl_2	–89	–164	2024
$[Me_2N(CH_2)_3]_2SnPhCl$[22]	–50		
9	–77		
$[Me_2N(CH_2)_3]_2SnCl_2$[22]	–182		
$[Me_2N(CH_2)_3]_2SnF_2$[9]	–292	–121	2782

The formula of the zwitterionic compounds **6**·CH_2Cl, **7**·CH_2Cl, **8**·CH_2Cl and **9** are clearly proved by ^{1}H and ^{13}C NMR spectra. The ^{13}C NMR spectra showed that the resonances of the –*C*H_2Cl carbon atom in compounds **6**·CH_2Cl_2, **7**·CH_2Cl_2, **8**·CH_2Cl_2 and **9** are at δ 69.3, δ 68.9, δ 69.1 and δ 69.2, respectively, (Table 3). These chemical shifts are similar to that found for the corresponding carbon atom in {$[Me_2(ClCH_2)N^+(CH_2)_3][Me_2N(CH_2)_3]SnF_3^-$}·$H_2O$ at δ 69.1.[9]

On the other hand, the chemical shifts of the –C*H*$_2$Cl protons in compounds **6**·CH_2Cl_2, **7**·CH_2Cl_2, **8**·CH_2Cl_2 and **9** at *δ* 5.68, *δ* 5.57, *δ* 5.49 and *δ* 5.56, respectively, are close to that reported for the corresponding protons in {[$Me_2(ClCH_2)N^+(CH_2)_3$][$Me_2N(CH_2)_3$]SnF_3^-}·H_2O at *δ* 5.25,[9] (Table 3).

The resonances in the ^1H and ^{13}C spectra of the NCH_2 and NCH_3 moieties in the ligand containing the quaternized nitrogen atom are low field shifted with respect to those in the coordinating ligand.[9][24]

In ^{13}C NMR spectra the chemical shifts of the $^+NCH_3$ carbon atom are moved to lower field by 3.3, 3.5, 3.2 and 3.0 ppm for compounds **6**·CH_2Cl_2, **7**·CH_2Cl_2, **8**·CH_2Cl_2 and **9**, respectively, with respect to the corresponding carbon atom in the (CH_3)$_2$N(CH$_2$)$_3$– ligand (Table 3). Similarly, the chemical shifts of the $^+NCH_2$ carbon atom for compounds **6**·CH_2Cl_2, **7**·CH_2Cl_2, **8**·CH_2Cl_2 and **9** are low field shifted by 3.3, 3.3, 3.9 and 3.6 ppm, respectively, with respect to the carbon atom in the NCH_2 moiety.

In the ^1H NMR spectra, the resonances of the $^+NCH_3$ protons for compounds **6**·CH_2Cl_2, **7**·CH_2Cl_2, **8**·CH_2Cl_2 and **9** are low field shifted by 1.20, 1.14, 0.86 and 0.72 ppm, respectively, with respect to the corresponding protons in NCH_3 moiety of the other ligand (Table 3).

Table 3. Selected ^1H and ^{13}C NMR of compounds **6**·CH_2Cl, **7**·CH_2Cl, **8**·CH_2Cl and **9**.

	–CH_2Cl		–$N^+(CH_3)_2CH_2Cl$		–$N(CH_3)_2$	
	^1H	^{13}C	^1H	^{13}C	^1H	^{13}C
[$Me_2N(CH_2)_3$]$_2SnF_2$[9]	5.25	70.0	3.22	49.9	2.38	45.6
6·CH_2Cl_2	5.68	69.3	3.33	49.3	2.13	45.9
7·CH_2Cl_2	5.57	68.9	3.42	49.2	2.28	45.7
8·CH_2Cl_2	5.49	69.1	3.31	49.4	2.45	46.2
9	5.56	69.2	3.33	49.3	2.61	46.3

The NMR data discussed above showed that the triorganotin halides **6**, **7**, **8** and $[Me_2N(CH_2)_3]_2SnPhCl$ react with CH_2Cl_2 giving the corresponding zwitterionic triorganostannates. Nevertheless, these reactions are somewhat slow as it takes about one month for completion (Figure 9).

The electrospray ionization mass spectra (ESI MS) support the formation of the zwitterionic organotin compounds. In the ESI MS spectra (positive mode) of compounds **8**·CH_2Cl_2 and **9** a major mass cluster centered at *m/z* 369.1 that corresponds unambiguously to $[\{Me_2N(CH_2)_3\}_2SnPh]^+$ was observed. In addition to that, a mass clusters centered at *m/z* 453.1 assigned to $[\{Me_2(ClCH_2)N(CH_2)_3\}\{Me_2N(CH_2)_3\}SnPhCl]^+$ was observed. In the case of compound **8**·CH_2Cl_2 two mass clusters centered at *m/z* 437.1 and 545.0 were also observed. These two mass clusters are assigned to $[\{Me_2(ClCH_2)N(CH_2)_3\}\{Me_2N(CH_2)_3\}SnPhX]^+$, X = F and I, respectively (Figure 10). In the ESI MS spectrum of compound **7**·CH_2Cl_2 (positive mode) a mass cluster centered at *m/z* 391.1 assigned to $[\{Me_2(ClCH_2)N(CH_2)_3\}\{Me_2N(CH_2)_3\}Sn(OH)Me\cdot H_2O]^+$ was observed.

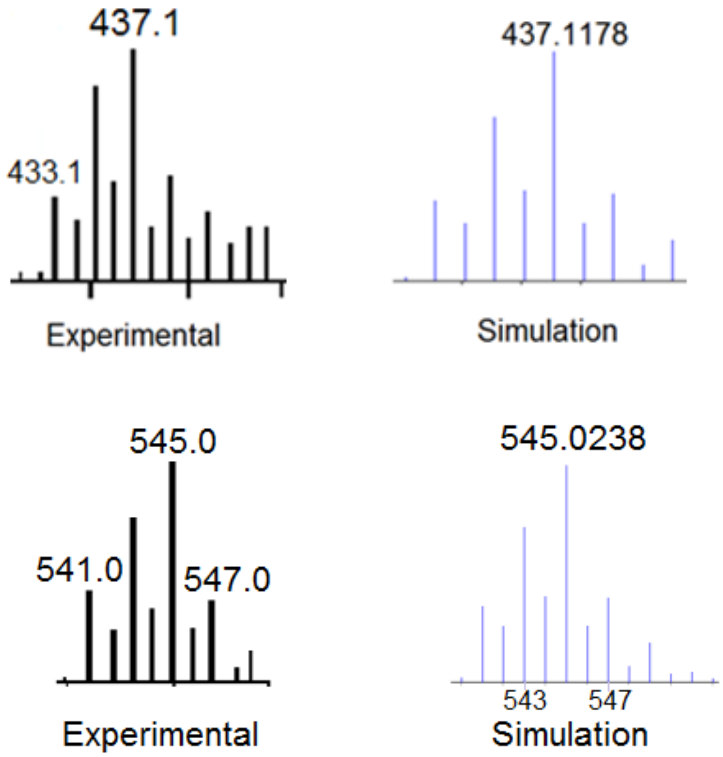


Figure 10. Experimental (from ESI MS) and simulated mass clusters for the cations $[\{Me_2(ClCH_2)N(CH_2)_3\}\{Me_2N(CH_2)_3\}SnPhF]^+$ (above) and $[\{Me_2(ClCH_2)N(CH_2)_3\}\{Me_2N(CH_2)_3\}SnPhI]^+$ (below).

5.6 DFT-Theoretical Calculation on [{$Me_2N(CH_2)_3$}$_2$SnMe]I (2)

The DFT calculation was performed by Prof. Vito Lippolis. Theoretical calculations were carried out at DFT level with the mPW1PW functional on the closed-shell compound **2** and the derivatives featuring X = Cl (**6**) and Br (**3**) in place of the iodide. Ahlrichs pVDZ BS's were chosen for C, H, and N, while for Sn and halogen species the LANL2DZ(d,p) BS's with ECP were adopted. The optimized structures of all compounds were verified by a vibrational analysis.

In order to ascertain the role of the methyl group directly bound to the Sn atom on the Sn–X bond, the same type of calculations were carried out on the hypothetical species ({$Me_2N(CH_2)_3$}$_2$SnPhCl, {$Me_2N(CH_2)_3$}$_2$SnPhBr and {$Me_2N(CH_2)_3$}$_2$SnPhI) featuring a phenyl group bound to the Sn center. In addition, the calculations were extended by fully replacing all methyl groups with phenyl substituents in the model compounds {$Ph_2N(CH_2)_3$}$_2$SnPhCl, {$Ph_2N(CH_2)_3$}$_2$SnPhBr and {$Ph_2N(CH_2)_3$}$_2$SnPhI.

Table 4 summarizes some selected bond distances for all the considered species. Both in the series {$Me_2N(CH_2)_3$}$_2$SnMeCl – {$Me_2N(CH_2)_3$}$_2$SnMeI and {$Me_2N(CH_2)_3$}$_2$SnPhCl – {$Me_2N(CH_2)_3$}$_2$SnPhI, the coordination geometry at the Sn center is close to the experimental one, with strong Sn–N interactions. This defines a pseudo square-pyramidal geometry around the metal, completed by the halogen species to give a very distorted pseudo-octahedral coordination (Figure 11).

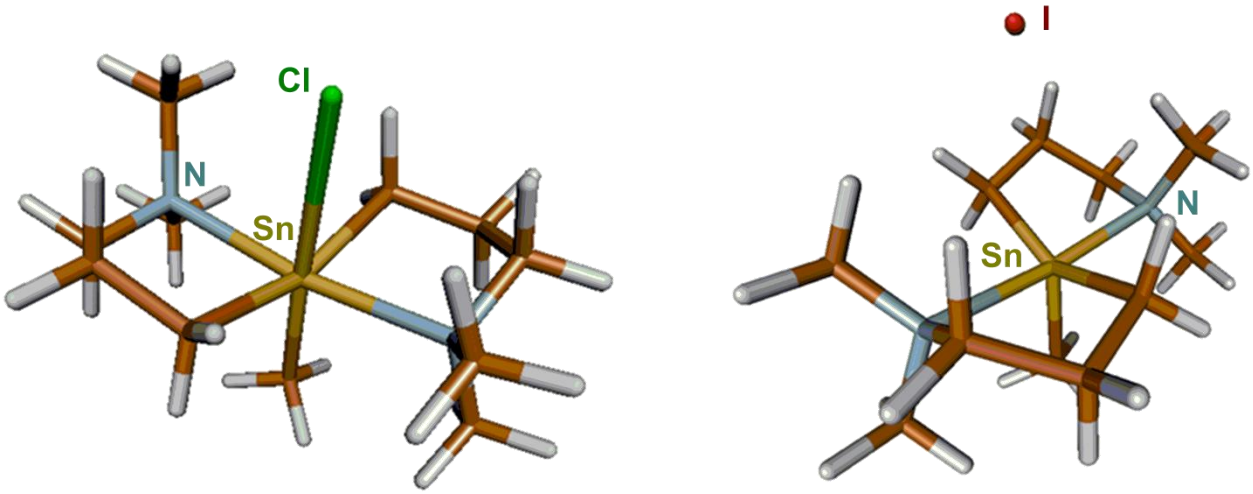


Figure 11. Stick drawing of the compounds {$Me_2N(CH_2)_3$}$_2$SnMeCl (left) and {$Me_2N(CH_2)_3$}$_2$SnMeI (right) optimized at DFT level.

Table 5. Selected optimised bond distances (Å), natural charges Q, and Wiberg bond indexes (WBI) for complex [{$Me_2N(CH_2)_3$}$_2$SnMe]I, referred as L_2SnMeI, and derivatives featuring different halogen species X and groups R directly bound to the Sn center.

	L_2SnMeCl	**L_2SnMeBr**	**L_2SnMeI**	**L_2SnPhCl**	**L_2SnPhBr**	**L_2SnPhI**
Sn–N	2.468	2.466	2.451	2.453	2.454	2.446
	2.441	2.442	2.440	2.430	2.432	2.430
Sn–X	2.837	3.201	3.745	2.824	3.148	3.651
Sn–R	2.203	2.188	2.170	2.220	2.204	2.179
$Sn–CH_2$	2.167	2.161	2.154	2.168	2.162	2.154
	2.167	2.160	2.152	2.167	2.162	2.153
X–Sn–R	175.28	175.01	174.64	176.76	176.69	176.28
R^a	1.18	1.23	1.35	1.17	1.21	1.32
Q_{Sn}	2.189	2.167	2.186	2.212	2.184	2.206
Q_X	–0.735	–0.744	–0.799	–0.728	–0.726	–0.773
Q_N	–0.628	–0.630	–0.636	–0.631	–0.632	–0.636
	–0.632	–0.634	–0.638	–0.636	–0.637	–0.640
$WBI_{Sn–X}$	0.328	0.293	0.195	0.339	0.324	0.241

R^a Ratio between the calculated Sn–X distance and the sum of covalent radii of Sn and X.

Notably, although the optimized Sn···I distance in {$Me_2N(CH_2)_3$}$_2$SnMeI is shorter than that determined by X-ray diffraction (Table 5), it is nonetheless longer than the sum of covalent radii. It should be also considered that in the solid state the iodide anion is involved in short contacts with two C–H protons of neighboring molecular units, thus contributing to further decrease the interaction with the Sn atom.

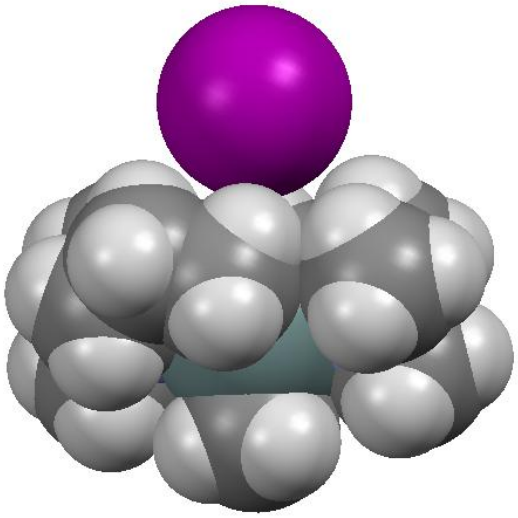


Figure 12. Space fill view of $\{Me_2N(CH_2)_3\}_2SnMeI$ from structural data.

Table 5. Selected interatomic distances /Å of the compound $\{Me_2N(CH_2)_3\}_2SnMeI$ from DFT calculation and experimental data.

	DFT calculation	Experimental
Sn–N	2.451	2.377(6)
	2.440	2.399(6)
Sn–I	3.745	4.5294(7)
$Sn–CH_2$	2.154	2.130(6)
	2.152	2.148(6)
Sn–Me	2.170	2.109(6)

The ratio R between the optimized Sn–X bond lengths and the sum of the corresponding covalent radii ($r_{Sn}+r_X$) assumes the values 1.18, 1.23 and 1.35 for X = Cl, Br, and I, respectively, in the series $\{Me_2N(CH_2)_3\}_2SnMeCl$ – $\{Me_2N(CH_2)_3\}_2SnMeI$ and 1.17, 1.21, and 1.23 in $\{Me_2N(CH_2)_3\}_2SnPhCl$, $\{[Me_2N(CH_2)_3]_2\}SnPhBr$, and $\{Me_2N(CH_2)_3\}_2SnPhI$, respectively. Accordingly, the natural charges QX on the halogen species, calculated at the optimized geometries for each species, are always more negative than –0.7 e and further decrease on passing from chlorine to iodine, indicating a

progressively increased ionic character of the Sn···X interaction. The replacement of R = Me with R = Ph, results in slightly shorter Sn···X distances. The same trends on passing from X = Cl to I and R = Me to Ph are testified by the corresponding Wiberg bond indexes (WBI's), in the range 0.2-0.33, which indicate a weak bond decreasing with the electronegativity of the halogen species.

The entity of the non-eletrostatic component of the Sn···X interaction can be evaluated by the analysis of the second order perturbation theory analysis of the Fock matrix in the NBO basis, which shows that the halide anion interacts with the three Sn–C antibonding sigma-type natural orbitals with an energy strongly decreasing on passing from $\{Me_2N(CH_2)_3\}_2SnMeCl$ to $\{Me_2N(CH_2)_3\}_2SnMeI$ (54.5, 38.7, and 2.1 kcal mol^{-1}, respectively).

The decrease in the Sn···X interaction on passing from X = Cl to I, which follows an opposite trend with respect to what expected on the basis of the electronegativity of the halogen species, might be related to the hindrance of crowding at the metal center. In Figure 12, a space fill drawing of $\{[Me_2N(CH_2)_3]_2\}SnMeI$ is depicted, showing that the large iodide anion is prevented to get further close to the tin atom by the hindrance of the methyl groups. On reducing the size of the halide anion, it is allowed to get closer to the tin center, establishing the partially covalent interaction described above.

Peculiar is the effect of the substitution of the methyl groups in the ligand with phenyl substituents in the series $\{Ph_2N(CH_2)_3\}_2SnPhCl$ – $\{Ph_2N(CH_2)_3\}_2SnPhI$. In fact, the resulting complexes show completely different geometries as compared to those calculated for $\{Me_2N(CH_2)_3\}_2SnMeCl$ $\{Ph_2N(CH_2)_3\}_2SnPhCl$, $\{Me_2N(CH_2)_3\}_2SnPhCl$ – $\{Me_2N(CH_2)_3\}_2SnPhI$, and determined structurally for $\{Me_2N(CH_2)_3\}_2SnMeI$. Due to the much less donor ability of the N-atoms, the Sn centers in $\{Ph_2N(CH_2)_3\}_2SnPhCl$ and $\{Ph_2N(CH_2)_3\}_2SnPhBr$ show tetrahedral coordination geometries at the tin centers accomplished by the halogen species, the two C-atoms and the phenyl R groups (Figure 13).

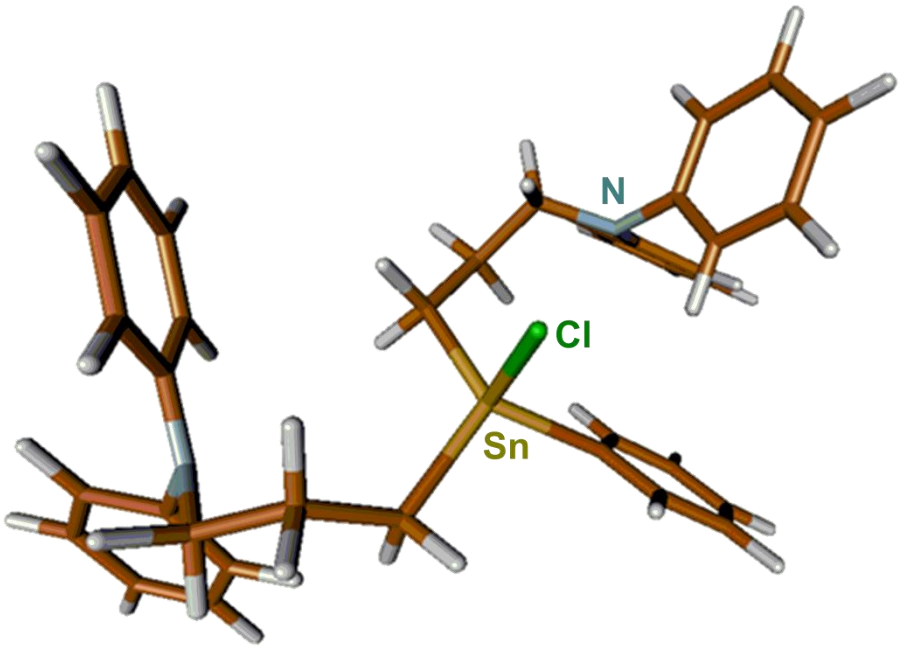


Figure 13. Stick drawing of the compound $\{Ph_2N(CH_2)_3\}_2SnPhCl$ optimized at DFT level.

As obvious in these cases the tin–halogen distances are very close to the sum of the corresponding covalent radii and follow the expected trend increasing along the series (Sn–X = 2.395 and 2.555 for X = Cl and Br, respectively; R = 0.99).

On the contrary $\{Ph_2N(CH_2)_3\}_2SnPhI$ adopts a distorted trigonal bipyramid geometry, with the N atoms on the axial positions (Sn–N = 2.555 and 3.002 Å) and the three C-atoms on the equatorial positions (Sn–CH_2 = 2.125 and 2.133; Sn–Ph = 2.137Å). In this compound, the I anion is not bonded (Sn···I = 4.61 Å), acting only as a counter-ion (QI = –0.87e).

5.7 CONCLUSION

A series of triorganotin compounds of the type $\{Me_2N(CH_2)_3\}_2SnRX$, R = Me, Ph; X = electronegative substituent} were synthesized and characterized. These compounds can be classified into two groups, triorganostannilium salts $[\{Me_2N(CH_2)_3\}_2SnMe]^+X^-$ (X = I, Br, ClO_4, SCN), **2** – **5**, and triorganotin halides ($\{Me_2N(CH_2)_3\}_2SnRX$, R = Me, Ph; X = Cl, F), **6** – **8**. These compounds are pentacoordinated in solution as proved by NMR. Compound **2** is also pentacoordinated in the solid state. The DFT calculations showed that the optimized Sn···I distance in compound **2** is shorter than that determined by X-ray diffraction, but it is nonetheless longer than the sum of covalent radii.

In the set of the triorganostannilium salts the cationic part $[\{Me_2N(CH_2)_3\}_2SnMe]^+$ contains two inramolecular N→Sn coordinations, and the Sn···anion distances are bigger than the sum of the covalent radii. That explains the salt-like character of these compounds and their good solubility in water. Changing the anions to Cl^- or F^- ones resulted in non-ionic structure of the corresponding compounds. This could be attributed to the small size of these two anions and their high electronegativity enabling them to avoid the hindrance of the methyl group and forming Sn–X short bond.

The triorganotin compounds **6**, **7**, **8** and $\{Me_2N(CH_2)_3\}_2PhSnCl$ showed good reactivity towords CH_2Cl_2 giving the set of zwitterionic triorganostannates with one quaternized nitrogen atom $[\{Me_2(ClCH_2)N(CH_2)_3\}\{Me_2N(CH_2)_3\}SnRX]^+ Cl^-$, R = Me, Ph; X = Cl, F.

5.8 EXPERIMENTAL SECTION

All solvents were dried and purified according to standard procedures and freshly distilled prior to use. $Me_2N(CH_2)_3Cl$[22] and $PhMeSnBr_2$[10] were synthesized according to literature methods. $\{Me_2N(CH_2)_3Cl\}\cdot HCl$, tetraphenylphosphonium chloride, silver fluoride, potassium chloride, potassium fluoride and tetraethylammonium fluoride were commercially available, and they were used without further purification. Bruker DPX–300 and DRX–400 spectrometers were used to obtain ^1H, ^{13}C, ^{19}F, and ^{119}Sn NMR spectra. Solution ^1H, ^{13}C, ^{19}F, and ^{119}Sn NMR chemical shifts are given in ppm and were referenced to Me_4Si (^1H, ^{13}C), $CFCl_3$ (^{19}F), and Me_4Sn (^{119}Sn). Elemental analyses were performed on a LECO–CHNS–932

analyzer. The electrospray mass spectra were recorded with a Thermoquest–Finnigan instrument, using CH_3CN, MeOH or CH_2Cl_2 as the mobile phase.

Synthesis of $\{Me_2N(CH_2)_3\}_2SnMePh$ (1).

The Grignard reagent $Me_2N(CH_2)_3MgCl$ prepared from $Me_2N(CH_2)_3Cl$ (15 g, 123 mmol) and magnesium turnings (3.00 g, 123 mmol) in 70 mL of THF was added dropwise to a mechanically stirred solution of $PhMeSnBr_2$[10] (22.8 g, 62 mmol) in 100 mL of THF. After the addition had been completed, the reaction mixture was heated at reflux overnight and then allowed to cool to room temperature. The THF was distilled off under reduced pressure. Then cold water was added, and the mixture was extracted three times with CH_2Cl_2. The combined organic phases were dried with $MgSO_4$ and the solvents evaporated in vacuo to give (72%) of compound (**1**) as yellowish oil.

^{1}H NMR (400.13 MHz, $CDCl_3$): δ 0.26 (s, $^2J(^1H–^{117/119}Sn)$ = 49.7/51.7 Hz, 3H, Sn–CH_3), 1.01 (t, 4H, Sn–CH_2), 1.70 (m, 4H, Sn–CH_2–CH_2), 2.16 (s, 12H, N(CH_3)$_2$), 2.22 (t, 4H, CH_2–N), 7.28–7.48 (5H, Ph). **^{13}C{^{1}H} NMR** (100.63 MHz, $CDCl_3$): δ –11.9 ($^1J(^{13}C–^{117/119}Sn)$ = 309/323 Hz, Sn–CH_3), 7.7 ($^1J(^{13}C–^{117/119}Sn)$ = 345/361 Hz, Sn–CH_2), 24.6 ($^2J(^{13}C–^{117/119}Sn)$ = 19 Hz, Sn–CH_2–CH_2), 45.5 N(CH_3)$_2$, 63.5 ($^3J(^{13}C–^{117/119}Sn)$ = 61 Hz, CH_2–N), 127.8 ($^3J(^{13}C–^{117/119}Sn)$= 43 Hz, C_m), 127.9 ($^4J(^{13}C–^{117/119}Sn)$ = 58 Hz, C_p), 136.0 ($^2J(^{13}C–^{117/119}Sn)$ = 33 Hz, C_o), 141.7 (C_i). **^{119}Sn{^{1}H} NMR** (111.92 MHz, $CDCl_3$): δ –34.

Synthesis of $\{Me_2N(CH_2)_3\}_2SnMeI$ (2).

Elemental iodine (1.99 g, 7.83 mmol) was added in small portions at –40°C to a stirred solution of (**1**) (3.00 g, 7.83 mmol) in CH_2Cl_2. The solvent and iodobenzene were removed under reduced pressure. The residue was recrystallized from acetone/ethyl acetate to afford (2.5 g, 75%) of (**2**) as yellow crystalline solid (mp. 171-172 °C).

^{1}H NMR (300.13 MHz, $CDCl_3$): δ 0.59 (s, $^2J(^1H–^{117/119}Sn)$ = 52.3 Hz, 3H, Sn–CH_3), 1.54–2.12 (8H, Sn–CH_2–CH_2), 2.33 (s, 6H, N(CH_3)$_2$), 2.38 (s, 6H, N(CH_3)$_2$), 2.48–2.67 (4H, CH_2–N). **^{13}C{^{1}H} NMR** (75.48 MHz, $CDCl_3$): δ –4.2 ($^1J(^{13}C–^{117/119}Sn)$ = 355 Hz, Sn–CH_3), 12.4 ($^1J(^{13}C–^{117/119}Sn)$ = 461/481 Hz, Sn–CH_2), 21.9 ($^2J(^{13}C–^{117/119}Sn)$ = 31 Hz, Sn–CH_2–CH_2), 46.3 N(CH_3)$_2$, 46.8 N(CH_3)$_2$, 61.9 ($^3J(^{13}C–^{117/119}Sn)$ = 55 Hz, CH_2–N). **^{119}Sn{^{1}H} NMR** (111.92 MHz, $CDCl_3$): δ 51.

^{1}H NMR (300.13 MHz, D_2O): δ 0.44 (s, $^{2}J(^{1}H–^{117/119}Sn)$ = 58.5 Hz, 3H, Sn–CH_3), 1.26 (bs, 4H, Sn–CH_2), 1.82 (m, 4H, Sn–CH_2–CH_2), 2.25 (s, 12H, N(CH_3)$_2$), 2.44 (bs, 4H, CH_2–N). **^{13}C{^{1}H} NMR** (75.48 MHz, D_2O): δ –5.8 (Sn–*C*H_3), 10.4 (Sn–*C*H_2), 21.3 ($^{2}J(^{13}C–^{117/119}Sn)$ = 28 Hz, Sn–CH_2–*C*H_2), 45.0 (N(*C*H_3)$_2$), 61.4 ($^{3}J(^{13}C–^{117/119}Sn)$ = 62 Hz, *C*H_2–N). **^{119}Sn{^{1}H} NMR** (111.92 MHz, D_2O): δ 50. **Electrospray MS**: m/z (%), positive mode: 307.1 (100, $[\{Me_2N(CH_2)_3\}_2SnMe]^+$); negative mode: 127.0 (100, $[I]^-$). Anal. Calcd (%) for $C_{11}H_{27}IN_2Sn$ (432.97): C 30.5, H 6.3, N 6.5. Found: C 30.8, H 6.4, N 6.4.

Synthesis of $\{Me_2N(CH_2)_3\}_2SnMeBr$ (3).

Over a period of three hours, a solution of bromine (0.59 g, 3.75 mmol) in CH_2Cl_2 (50 mL) was added dropwise at –50°C to a solution of (**1**) (1.44 g, 3.75 mmol) in CH_2Cl_2 (50 mL). After 2 hours the mixture allowed to reach room temperature and stirred overnight at ambient temperature. The solvent and bromobenzene were extensively removed in vacuo to give of crude product as yellow oil.

^{1}H NMR (300.13 MHz, $CDCl_3$): δ 0.59 (s, $^{2}J(^{1}H–^{117/119}Sn)$ = 52.3 Hz, 3H, Sn–CH_3), 1.54–2.12 (8H, Sn–CH_2–CH_2), 2.35 (s, 6H, N(CH_3)$_2$), 2.40 (s, 6H, N(CH_3)$_2$), 2.48–2.67 (bs, 4H, CH_2–N). **^{13}C{^{1}H} NMR** (75.48 MHz, $CDCl_3$): δ –4.2 ($^{1}J(^{13}C–^{117/119}Sn)$ = 355 Hz, Sn–*C*H_3), 12.4 ($^{1}J(^{13}C–^{117/119}Sn)$ = 461/481 Hz, Sn–*C*H_2), 21.9 ($^{2}J(^{13}C–^{117/119}Sn)$ = 31 Hz, Sn–CH_2–*C*H_2), 46.3 N(*C*H_3)$_2$, 46.7 (N(*C*H_3)$_2$), 61.9 ($^{3}J(^{13}C–^{117/119}Sn)$ = 55 Hz, *C*H_2–N). **^{119}Sn{^{1}H} NMR** (111.92 MHz, $CDCl_3$,): δ 51 (56%, $\{Me_2N(CH_2)_3\}_2SnMeBr$), –8 (26%, $\{Me_2N(CH_2)_3\}_2SnPhBr$), –151 (18%, $\{Me_2N(CH_2)_3\}_2SnBr_2$). **Electrospray MS**: m/z (%), positive mode: 307.1 (100, $[\{Me_2N(CH_2)_3\}_2SnMe]^+$); negative mode: 79.1 (100, $[Br]^-$).

Synthesis of $\{Me_2N(CH_2)_3\}_2SnMe(ClO_4)$ (4).

To a solution of (**2**) (0.12 g, 0.28 mmol) in CH_2Cl_2 (20 mL) was added $AgClO_4$ (0.57 g, 0.35 mmol). The reaction mixture was stirred at room temperature in darkness for 2 days, followed by filtration of the AgI formed. Removing the solvent in vacuo gave (0.10 g, 89%) of (**4**) as white oil.

^{1}H NMR (500.13 MHz, $CDCl_3$): δ 0.59 (s, $^{2}J(^{1}H–^{117/119}Sn)$ = 53.5 Hz, 3H, Sn–CH_3), 1.41 (t, 4H, Sn–CH_2), 1.57 (t, 4H, Sn–CH_2) 1.88 (m, 4H, Sn–CH_2–CH_2), 2.05 (m, 4H, Sn–CH_2–CH_2), 2.33 (s, 12H, N(CH_3)$_2$), 2.48 (t, 4H, CH_2–N), 2.55 (t, 4H, CH_2–N). **^{13}C{^{1}H} NMR** (125.77 MHz, $CDCl_3$): δ –4.9 (Sn–CH$_3$), 11.1 ($^{1}J(^{13}C–^{117/119}Sn)$ = 482/495 Hz, Sn–CH$_2$), 21.8 ($^{2}J(^{13}C–^{117/119}Sn)$ = 27 Hz, Sn–CH$_2$–CH$_2$), 45.9 (N(CH$_3$)$_2$), 46.3 (N(CH$_3$)$_2$), 61.8 ($^{3}J(^{13}C–^{117/119}Sn)$ = 56 Hz, CH$_2$–N). **^{119}Sn{^{1}H} NMR** (111.92 MHz, $CDCl_3$): δ 53. **Electrospray MS**: m/z (%), positive mode: 369.1 (100, $[\{Me_2N(CH_2)_3\}_2SnMe + CO_2 + H_2O]^+$), 307.1 (46, $[\{Me_2N(CH_2)_3\}_2SnMe]^+$); negative mode: 99.1 (100, $[ClO_4]^-$).

Synthesis of $\{Me_2N(CH_2)_3\}_2SnMe(SCN)$ (5).

To a solution of (**2**) (0.10 g, 0.231 mmol) in CH_2Cl_2 (20 mL) was added AgSCN (0.042 g, 0.254 mmol). The reaction mixture was stirred at room temperature in darkness for 2 days, followed by filtration of the formed AgI and the non-reacted AgSCN. Removing the solvent in vacuo gave (0.075 g, 89%) of **5** as dark yellow oil.

^{1}H NMR (400.13 MHz, $CDCl_3$): δ 0.60 (s, $^{2}J(^{1}H–^{117/119}Sn)$ = 54.2 Hz, 3H, Sn–CH_3), 1.49 (bs, 4H, Sn–CH_2), 1.97 (bs, 4H, Sn–CH_2–CH_2), 2.33 (s, 12H, N(CH_3)$_2$), 2.51 (bs, 4H, CH_2–N). **^{13}C{^{1}H} NMR** (100.63 MHz, $CDCl_3$): δ –4.8 (Sn–CH$_3$), 9.3 (SCN), 11.5 (Sn–CH$_2$), 21.9 ($^{2}J(^{13}C–^{117/119}Sn)$ = 31 Hz, Sn–CH_2–CH_2), 46.1 (N(CH$_3$)$_2$), 61.9 ($^{3}J(^{13}C–^{117/119}Sn)$ = 57 Hz, CH$_2$–N). **^{119}Sn{^{1}H} NMR** (111.92 MHz, $CDCl_3$): δ 51. **Electrospray MS**: m/z (%), positive mode: 307.1 (100, $[\{Me_2N(CH_2)_3\}_2SnMe]^+$); negative mode: 38.3 (100, $[SCN]^-$).

Synthesis of $\{Me_2N(CH_2)_3\}_2SnMeCl$ (6).

To a solution of (**2**) (0.08 g, 0.185 mmol) in H_2O (20 mL) was added Me_4NCl (0.02 g, 0.185 mmol). The reaction mixture was stirred at room temperature for 3 days. Evaporation of water gave a yellow oil that was washed three times with water (each of 2 mL) followed by removing the solvent in vacuo gave (0.05 g, 80%) of **6** as yellow oil.

^{1}H NMR (400.25 MHz, $CDCl_3$): δ 0.61 (s, $^{2}J(^{1}H–^{117/119}Sn)$ = 56.7/59.2 Hz, 3H, Sn–CH_3), 1.35 (t, $^{2}J(^{1}H–^{117/119}Sn)$ = 67.5 Hz, 4H, Sn–CH_2), 1.90 (m, $^{3}J(^{1}H–^{117/119}Sn)$ = 85.1 Hz, 4H, Sn–CH_2–CH_2), 2.24 (s, 12H, N(CH_3)$_2$), 2.36 (t, 4H, CH_2–N). **^{13}C{^{1}H} NMR** (100.64 MHz, $CDCl_3$): δ –0.55 (Sn–

*C*H$_3$), 15.9 (^1J(^{13}C–$^{117/119}$Sn) = 486 Hz, Sn–*C*H$_2$), 22.9 (^2J(^{13}C–$^{117/119}$Sn) = 29 Hz, Sn–CH$_2$–*C*H$_2$), 45.7 (N(*C*H$_3$)$_2$), 62.5 (^3J(^{13}C–$^{117/119}$Sn) = 68 Hz, *C*H$_2$–N). **^{119}Sn{^{1}H} NMR** (149.26 MHz, CDCl$_3$): δ 2 ($v_{1/2}$ = 546 Hz). Anal. Calcd (%) for {Me$_2$N(CH$_2$)$_3$}$_2$SnMeCl·H$_2$O $C_{11}H_{29}ClN_2OSn$ (360.10): C 36.8, H 8.1, N 7.8. Found: C 37.4, H 7.8, N 7.7. **Electrospray MS**: m/z (%), positive mode: 307.1 (100, [{Me$_2$N(CH$_2$)$_3$}$_2$SnMe]$^+$).

The reaction of {Me$_2$N(CH$_2$)$_3$}$_2$MeSnI with Ph$_4$PCl.

A solution of tetraphenylphosphonium chloride (Ph$_4$PCl) (0.05g (50 mg), 0.14 mmol) and compound **2** (0.06 mg, 0.14 mmol) in CDCl$_3$ was stirred for 1 day at room temperature before ^{119}Sn NMR spectrum was recorded.

^{119}Sn{^{1}H} NMR (111.92 MHz, CDCl$_3$): δ 50 (55%, **2**), δ: –3 (45%, **6**).

Synthesis of {Me$_2$N(CH$_2$)$_3$}$_2$SnMeF (7).

Compound (**2**) (60 mg, 0.139 mmol), and Et$_4$NF·2H$_2$O (26 mg, 0.139 mmol) were heated at reflux in CDCl$_3$ for 5 min. From this solution NMR spectra were recorded.

^{1}H NMR (400.13 MHz, CDCl$_3$): δ 0.39 (s, ^2J(^{1}H–$^{117/119}$Sn) = 59.6 Hz, 3H, Sn–C*H*$_3$), 1.13 (t, 4H, Sn–C*H*$_2$), 1.31 (t, 12H, (C*H*$_3$–CH$_2$)$_4$NF), 1.80 (m, 4H, Sn–CH$_2$–C*H*$_2$), 2.17 (s, 12H, N(C*H*$_3$)$_2$), 2.26 (t, 4H, C*H*$_2$–N), 3.37 (q, 8H, (CH$_3$–C*H*$_2$)$_4$NF). **^{13}C{^{1}H} NMR** (100.63 MHz, CDCl$_3$): δ –3.4 (Sn–C*H*$_3$), 12.9 (Sn–C*H*$_2$), 22.7 (^2J(^{13}C–$^{117/119}$Sn) = 26 Hz, Sn–CH$_2$–*C*H$_2$), 45.6 (N(*C*H$_3$)$_2$), 62.5 (^3J(^{13}C–$^{117/119}$Sn) = 67 Hz, *C*H$_2$–N). **^{19}F{^{1}H} NMR** (282.36 MHz; CDCl$_3$): δ –168 (^1J(^{19}F–$^{117/119}$Sn) = 1939 Hz. **^{119}Sn{^{1}H} NMR** (111.92 MHz, CDCl$_3$): δ –2 (d, ^1J(^{119}Sn–^{19}F) = 1947 Hz). **Electrospray MS**: m/z (%), positive mode: 307.1 (100, [{Me$_2$N(CH$_2$)$_3$}$_2$SnMe]$^+$).

The reaction of {Me$_2$N(CH$_2$)$_3$}$_2$MeSnI with AgCl in CH$_2$Cl$_2$.

To a solution of **2** (0.15 g, 0.35 mmol) in CH$_2$Cl$_2$ (20 mL) and CH$_3$CN (5 mL) was added AgCl (0.05 g, 0.35 mmol). The reaction mixture was stirred at room temperature in darkness for 4 days, followed by filtration of the AgI formed. Removing the solvents in vacuo gave 0.85g of crude products as slightly yellow oil. These crude products were left in CH$_2$Cl$_2$ solution for further 4 months without stirring.

^{1}H NMR (300.13 MHz, $CDCl_3$): δ 0.60 (s, 3H, Sn–CH_3, **6**·CH_2Cl), 0.67 (s, 3H, Sn–CH_3, **6**), 1.21 (t, 2H, N^+~Sn–CH_2, **6**·CH_2Cl), 1.34 (t, 4H, Sn–CH_2, **6**), 1.45 (t, 2H, N~Sn–CH_2, **6**·CH_2Cl), 1.93 (m, 6H, N–CH_2–CH_2, **6** and **6**·CH_2Cl), 2.07 (m, 2H, N^+–CH_2–CH_2, **6**·CH_2Cl), 2.28 (s, 6H, N(CH_3)$_2$, **6**·CH_2Cl), 2.32 (s, 12H, N(CH_3)$_2$, **6**), 2.38 (t, 2H, CH_2–N, **6**·CH_2Cl), 2.46 (t, 4H, CH_2–N, **6**), 3.42 (s, 6H, N^+(CH_3)$_2$, **6**·CH_2Cl), 3.51 (t, 2H, CH_2–N^+, **6**·CH_2Cl), 5.68 (s, 2H, CH_2Cl). **^{13}C{^{1}H} NMR** (75.47 MHz, $CDCl_3$): δ –0.8 (Sn–*C*H_3, **6**), 0.6 (Sn–*C*H_3, **6**·CH_2Cl), 13.3 (N^+~Sn–*C*H_2, **6**·CH_2Cl), 15.1 (Sn–*C*H_2, **6**), 16.0 (N~Sn–CH_2, **6**·CH_2Cl), 19.4 (N^+–CH_2–*C*H_2, **6**·CH_2Cl), 21.6 (N–CH_2–*C*H_2, **6**·CH_2Cl), 22.3 (^{2}J(^{13}C–$^{117/119}$Sn) = 28 Hz, N–CH_2–*C*H_2, **6**), 45.4 (N(*C*H_3)$_2$, **6**), 45.9 (N(*C*H_3)$_2$, **6**·CH_2Cl), 49.3 (N^+(*C*H_3)$_2$, **6**·CH_2Cl), 61.9 (*C*H_2–N, **6**·CH_2Cl), 62.0 (*C*H_2–N, **6**), 65.2 (*C*H_2–N^+, **6**·CH_2Cl), 69.3 (*C*H_2Cl). **^{119}Sn{^{1}H} NMR** (111.92 MHz, $CDCl_3$): δ –3 (43%, **6**), –12 (52%, **6**·CH_2Cl), – 182 (5%, $\{Me_2N(CH_2)_3\}_2SnCl_2$).

The reaction of $\{Me_2N(CH_2)_3\}_2MeSnI$ with fluoride anions in CH_2Cl_2.

Method A. To a solution of (**2**) (0.15 g, 0.35 mmol) in CH_2Cl_2 (10 mL) and CH_3CN (5 mL) was added excess of AgF (0.05 g, 0.39 mmol). The reaction mixture was stirred at room temperature in darkness for 5 days, followed by filtration of the formed AgI and the non-reacted AgF. The resulting crude product was obtained as yellow oil.

Method B. To a solution of (**2**) (0.12 g, 0.28 mmol) in CH_2Cl_2 (10 mL) was added excess KF (0.03 g, 0.52 mmol). The reaction mixture was stirred at room temperature for 3 days followed by filtration of the KI formed and the non-reacted KF. Removing the solvent in vacuo gave a yellow oil.

^{1}H NMR (300.13 MHz, $CDCl_3$): δ 0.33 (s, ^{2}J(^{1}H–$^{117/119}$Sn) = 59.3 Hz, 3H, Sn–CH_3, **7**·CH_2Cl), 0.39 (s, ^{2}J(^{1}H–$^{117/119}$Sn) = 61.5 Hz, 3H, Sn–CH_3, **7**), 0.99 (t, 2H, N~Sn–CH_2, **7**·CH_2Cl), 1.07 (t, 4H, Sn–CH_2, **7**), 1.17 (t, 2H, N^+~Sn–CH_2, **7**·CH_2Cl), 1.61 (m, 2H, N–CH_2–CH_2, **7**·CH_2Cl), 1.74 (m, 4H, N–CH_2–CH_2, **7**), 1.88 (m, 2H, N^+–CH_2–CH_2, **7**·CH_2Cl), 2.11 (s, 12H, N(CH_3)$_2$, **7**), 2.13 (s, 6H, N(CH_3)$_2$, **7**·CH_2Cl), 2.21 (t, 4H, CH_2–N, **7**), 2.49 (t, 2H, CH_2–N, **7**·CH_2Cl), 3.33 (s, 6H, N^+(CH_3)$_2$, **7**·CH_2Cl), 3.48 (t, 2H, CH_2–N^+, **7**·CH_2Cl), 5.57 (s, 2H, CH_2Cl). **^{13}C{^{1}H} NMR** (75.48 MHz, $CDCl_3$): δ –3.5 (Sn–*C*H_3, **7**), –3.0 (Sn–*C*H_3, **7**·CH_2Cl), 11.5 (N^+~Sn–*C*H_2, **7**·CH_2Cl), 11.8 (N~Sn–*C*H_2, **7**·CH_2Cl), 12.9 (Sn–*C*H_2, **7**), 18.7 (N^+–CH_2–*CH*$_2$, **7**·CH_2Cl), 21.0 (N–CH_2–*CH*$_2$, **7**·CH_2Cl), 22.5 (^{2}J(^{13}C–$^{117/119}$Sn) = 26 Hz, (N–CH_2–*CH*$_2$, **7**), 45.5 (N(*C*H_3)$_2$, **7**), 45.7 (N(*C*H_3)$_2$, **7**·CH_2Cl), 49.2

($N^+(CH_3)_2$, **7**·CH_2Cl), 61.6 (CH_2–N, **7**·CH_2Cl), 62.3 ($^3J(^{13}C–^{117/119}Sn)$ = 67 Hz, CH_2–N, **7**), 64.9 ($CH_2–N^+$, **7**·CH_2Cl), 68.9 (CH_2Cl). **^{19}F {^{1}H}NMR** (282.36 MHz, $CDCl_3$): δ –167 ($^1J(^{19}F–^{117/119}Sn)$ = 1896 Hz, **7**), –162 ($^1J(^{19}F–^{117/119}Sn)$ = 1939 Hz, **7**·CH_2Cl), –126 $\{Me_2N(CH_2)_3\}_2SnF_2$. **^{119}Sn{^{1}H} NMR** (111.92 MHz, $CDCl_3$): δ –2 (d, $^1J(^{119}Sn–^{19}F)$ = 1945 Hz, **7**), –18 (d, $^1J(^{119}Sn–^{19}F)$ = 1916 Hz, **7**·CH_2Cl). **Electrospray MS**: m/z (%), positive mode: 307.1 (100, $[\{Me_2N(CH_2)_3\}_2SnMe]^+$), 391.1 (2, $[\{Me_2(ClCH_2)N(CH_2)_3\}\{Me_2N(CH_2)_3\}Sn(OH)Me\cdot H_2O]^+$)

The reaction of $\{Me_2N(CH_2)_3\}_2SnPhI$ with KF in CH_2Cl_2.

To a solution of $\{Me_2N(CH_2)_3\}_2SnPhI$ (0.4 g, 0.808 mmol) in CH_2Cl_2 (20 mL) was added excess KF (0.47 g, 8.08 mmol). The reaction mixture was stirred at room temperature for 4 weeks, followed by filtration of the KI formed and the non-reacted KF. Removing the solvent in vacuo gave yellow oil.

^{1}H NMR (400.13 MHz, $CDCl_3$): δ 1.02 (t, 4H, Sn–CH_2, **8**), 1.44 (t, 4H, N~Sn–CH_2 + N^+~Sn–CH_2, **8**·CH_2Cl)), 1.79–2.12 (complex pattern, 6H, N–CH_2–CH_2 + N^+–CH_2–CH_2, **8** + **8**·CH_2Cl), 2.03 (s, 6H, $N(CH_3)_2$, **8**), 2.21 (t, 2H, CH_2–N, **8**) 2.45 (s, 6H, $N(CH_3)_2$, **8**·CH_2Cl), 2.56 (t, 2H, CH_2–N, **8**·CH_2Cl), 3.31 (s, 6H, $N^+(CH_3)_2$, **8**·CH_2Cl), 3.83 (t, 2H, $CH_2–N^+$, **8**·CH_2Cl), 5.50 (s, 2H, CH_2Cl, **8**·CH_2Cl), 7.31–7.56 (5H, Ph). **^{13}C{^{1}H} NMR** (100.63 MHz, $CDCl_3$): δ 9.9 (N^+~Sn–CH_2), 10.1 (N~Sn–CH_2), 18.9 (N^+–CH_2–CH_2), 21.1 (N–CH_2–CH_2), 46.2 ($N(CH_3)_2$), 49.4 ($N^+(CH_3)_2$), 61.4 (CH_2–N), 65.3 ($CH_2–N^+$), 69.1 (CH_2Cl), 128.7 ($^3J(^{13}C–^{117/119}Sn)$ = 58 Hz, C_m), 129.2 (C_p), 135.2 ($^1J(^{13}C–^{117/119}Sn)$ = 43 Hz, C_o), 141.9 (C_i). **^{19}F{^{1}H} NMR** (282.36 MHz, $CDCl_3$): δ –168 (12%, $\{Me_2N(CH_2)_3\}_2PhSnF$), –164 (76%, $^1J(^{19}F–^{117/119}Sn)$ = 1948/2005 Hz, **8**·CH_2Cl), –126 (12%, $\{Me_2N(CH_2)_3\}_2SnF_2$). **^{119}Sn{^{1}H} NMR** (111.92 MHz, $CDCl_3$): δ –80 (10%, d, $^1J(^{119}Sn–^{19}F)$ = 2030 Hz, $\{Me_2N(CH_2)_3\}_2SnPhF$), –89 (90%, d, $^1J(^{119}Sn–^{19}F)$ = 2024 Hz, **8**·CH_2Cl). **Electrospray MS**: m/z (%), positive mode: 369.1 (100, $[\{Me_2N(CH_2)_3\}_2SnPh]^+$), 437.1 (2, $[\{Me_2(ClCH_2)N(CH_2)_3\}\{Me_2N(CH_2)_3\}SnPhF]^+$), 453.1 (1, $[\{Me_2(ClCH_2)N(CH_2)_3\}\{Me_2N(CH_2)_3\}$-$SnPhCl]^+$), 545.0 (5, $[\{Me_2(ClCH_2)N(CH_2)_3\}\{Me_2N$-$(CH_2)_3\}SnPhI]^+$).

The reaction of $\{Me_2N(CH_2)_3\}_2PhSnI$ with KCl in CH_2Cl_2.

To a solution of $\{Me_2N(CH_2)_3\}_2SnPhI$ (113 mg, 0.23 mmol) in CH_2Cl_2 (20 mL) was added excess KCl (170 mg, 2.3 mmol). The reaction mixture was stirred at room temperature for one month, followed by filtration of the KI formed and the non-reacted KCl. Removing the solvent in vacuo gave the crude product as yellow oil.

^{1}H NMR (400.13 MHz, $CDCl_3$): δ 1.18 (complex pattern, 4H, N~Sn–CH_2 + N^+~Sn–CH_2, **9**), 1.46–1.67 (m, 4H, N–CH_2–CH_2 + N^+–CH_2–CH_2, **9**), 1.97 (t, 4H, Sn–CH_2, $\{Me_2N(CH_2)_3\}_2PhSnI$), 2.06 (m, 4H, N–CH_2–CH_2, $\{Me_2N(CH_2)_3\}_2PhSnI$) 2.10 (s, 12H, N(CH_3)$_2$, $\{Me_2N(CH_2)_3\}_2PhSnI$), 2.28 (t, 2H, CH_2–N, $\{Me_2N(CH_2)_3\}_2PhSnI$) 2.61 (s, 6H, N(CH_3)$_2$, **9**), 3.21 (t, 2H, CH_2–N, **9**), 3.33 (s, 6H, N^+(CH_3)$_2$, **9**), 3.84 (t, 2H, CH_2–N^+, **9**), 5.50 (s, 2H, CH_2Cl, **9**), 7.31–7.56 (5H, Ph). **^{13}C{^{1}H} NMR** (100.63 MHz, $CDCl_3$): δ 11.39 (Sn–*C*H_2, $\{Me_2N(CH_2)_3\}_2PhSnI$) 13.9 (N^+~Sn–*C*H_2, **9**), 15.0 (N~Sn–*C*H_2, **9**), 19.4 (N–CH_2–*C*H_2, $\{Me_2N(CH_2)_3\}_2PhSnCl_2$), 21.0 ($N^+$–$CH_2$–*C*$H_2$, **9**), 21.3 (N–$CH_2$–*C*$H_2$, **9**), 21.8 (N–$CH_2$–*C*$H_2$, $\{Me_2N(CH_2)_3\}_2PhSnI$), 30.8 (Sn–*C*H_2, $\{Me_2N(CH_2)_3\}_2PhSnCl_2$), 46.3 (N(*C*$H_3$)$_2$, **9** + $\{Me_2N(CH_2)_3\}_2PhSnI$), 47.1 (N(*C*H_3)$_2$, $\{Me_2N(CH_2)_3\}_2PhSnCl_2$), 49.3 ($N^+$(*C*$H_3$)$_2$, **9**), 59.3 (*C*$H_2$–N, $\{Me_2N(CH_2)_3\}_2PhSnCl_2$), 61.3 (*C*$H_2$–N, $\{Me_2N(CH_2)_3\}_2PhSnI$), 61.5 (*C*H_2–N, **9**), 65.1 (*C*H_2–N^+, **9**), 69.2 (*C*H_2Cl), 128.6 (C_m), 129.1 (C_p), 134.9 (C_o), 142.5 (C_i). **^{119}Sn{^{1}H} NMR** (111.92 MHz, $CDCl_3$): δ –7 (53%, $\{Me_2N(CH_2)_3\}_2SnPhI$), –77 (35%, $\{Me_2(ClCH_2)N(CH_2)_3\}\{Me_2N(CH_2)_3\}SnPhCl_2$), –182 (12%, $\{Me_2N(CH_2)_3\}_2SnCl_2$). **Electrospray MS**: *m/z* (%), positive mode: 369.1 (100, $[\{Me_2N(CH_2)_3\}_2SnPh]^+$), 453.1 (5, $[\{Me_2(ClCH_2)N(CH_2)_3\}\{Me_2N(CH_2)_3\}SnPhCl]^+$).

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6. Summary

The aim of this work was the sensing and detection of fluoride anions in both organic solvents and water using organotin compounds. For this purpose the syntheses, structures and characterization of, on the one hand, intramolecularly coordinated organotin compounds containing the RR`N$(CH_2)_3$ moiety (R, R`= organic substituent); and the water soluble organotin compounds decorated with ($Me_2NH(CH_2)_3$) arms, on the other hand, were reported.

Bicentric ditin compounds may show a higher affinity toward anions than the mononuclear organotin analogues. In order to evaluate the effect of spacing between the tin centers on the molecular structures and selectivity towards fluoride anion, a series of spacer-bridged ditin compounds were synthesized and characterized (see chapter 2).

The organotin fluorides **11** and **16** were synthesized and completely characterized. The X-ray diffraction analysis showed that compound **11** is a head-to-tail dimer whereas compound **16** is a monomer (Chart 1). In solution, both **11** and **16** are monomeric, as proved by ^{1}H DOSY NMR for **11**.

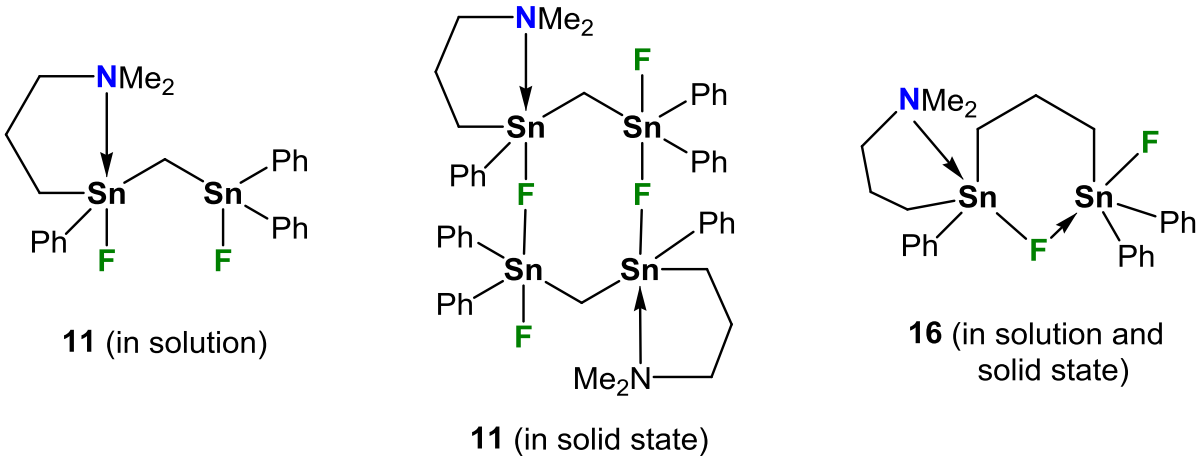


Chart 1. The structures of the triorganotin fluorides **11** and **16** in solution and solid state.

The reactivity of compounds **11** and **16** toward fluoride anion in CD_2Cl_2 solutions providing the salts NEt_4[**11**·F] and NEt_4[**16**·F], respectively, have been investigated by variable temperature ^{19}F and ^{119}Sn spectroscopy. On the basis of NMR data the intramolecular N→Sn

coordination is retained and the incoming fluoride anion does not bridge the two tin centers but is bound to the diphenyl-substituted tin atom only.

The organotin fluorides **11** and **16** are of great interest as they showed that:

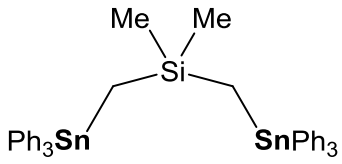
i. The *intramolecular* N→Sn coordination in **11** and **16** results in a much better solubility in common organic solvents with respect to the corresponding compounds $Ph_2FSn(CH_2)_nSnPh_2F$ (n = 1, 3) lacking an intramolecularly coordinating substituent.

ii. The *intermolecular* F→Sn coordination of compound **11** resulted in a *dimiric* structure in the solid state differently to that reported for the analogues organostannate anion $[(Ph_2FSn)_2CH_2{\cdot}F]^-$ and the complex $[(Ph_2ClSn)_2CH_2{\cdot}(Me_2N)_3P{=}O]$ having monomeric structures.

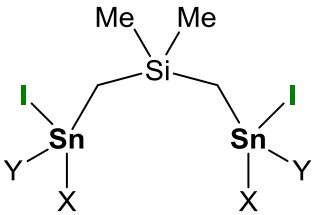
iii. Remarkably, the number of the methylene groups separating the two tin centers in **11** and **16** greatly influences the structures of these compounds. In the solid state they are monomeric (**16**) or dimeric (**11**). In solution, the six-membered ring in **16** is more stable against fluoride anion attack than the four-membered ring in **11**.

Using compound **11** as an ionophore in fluoride-selective electrode showed good response for fluoride anions with detection limits of 10^{-4} to 10^{-5}. However, the slope of the calibration curve was about –32 mV/–log[F^-] that is smaller than the theoretical sensitivity value for monovalent anions of –59.16 mV/–log[anion]. Better results in this field may be obtained by using other plasticizers in the electrode membrane.

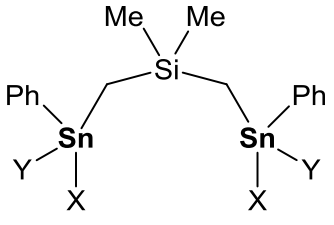
Also reported in Chapter 2 is the synthesis of the symmetrical spacer-bridged tetraorganoditin compound $(Ph_3SnCH_2)_2SiMe_2$ **18** and its halogen-substituted derivatives **19** – **24** (Chart 2).



18



19; X = Y = Ph
20; X = I, Y = Ph
21; X = Y = I



22; X = Ph, Y = Cl
23; X = Y = Cl
24; X = Ph, Y = F

Chart 2. Structures of the organoditin compounds **18** – **24**.

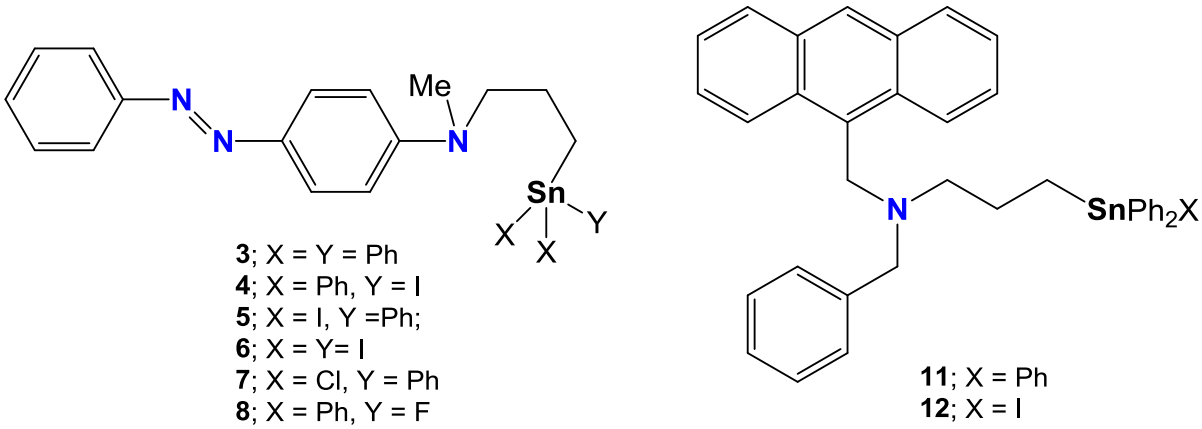
6. Summary

Compounds **18**, **19** and **24** were synthesized previously in our research group. The complexation studies of compounds **23** and **24** toward chloride and fluoride anions gave the corresponding complexes [PPh_4][**23**·Cl] , [NEt_4][**23**·F] and [NEt_4][**24**·F]. The identify of these complexes were confirmed by NMR spectroscopy and electrospray mass spectrometry.

The development of sensors for the direct detection of fluoride anions, in which the sensing is accompanied with a color-change, is an important target for real-life applications. For this purpose, designing of chemosensors based on organotin compounds containing azo or anthracene moieties as a chromophoric group were presented in the third chapter.

The tetraorganotin compounds **3** and **11** containing azo, respectively, anthracene moiety (Chart 3) were synthesized by multi-step reactions and characterized by NMR spectroscopy, elemental analysis and also by X-ray diffraction analysis in the case of **11**.

The functionalization of the tin atom in compound **3** with halogen atoms provided a set of organotin halides **4** – **8** (Chart 3).



3; X = Y = Ph
4; X = Ph, Y = I
5; X = I, Y =Ph;
6; X = Y= I
7; X = Cl, Y = Ph
8; X = Ph, Y = F

11; X = Ph
12; X = I

Chart 3. Structures of the organotin compounds **3** – **8** and **11** – **12**.

Noteworthy, no intramolecular N→Sn coordination was found for the organotin halides **4**, **5**, **7** and **8**, as proved by NMR spectroscopy. Notably, the fluorine-substituted organotin compound **8** showed low solubility in common organic solvents similarly to non-coordinated organotin fluorides. This could be attributed probably to the lone pair electrons of the amino group that contribute the resonance with the phenyl and azo groups preventing it to form the N→Sn interaction.

On the other hand, the reaction of compound **11** with elemental iodine provided the corresponding iodine-substituted organotin derivative **12** (Chart 3). Compound **12** showed to be unstable in air moisture as proved by NMR spectroscopy.

Also reported in the third chapter is the synthesis of a ditopic receptor consists of the [16]-crown-5 moiety bound to the tin center for the selective recognition of sodium ions. The organotin compound **14** (Chart 4) was synthesized and characterized.

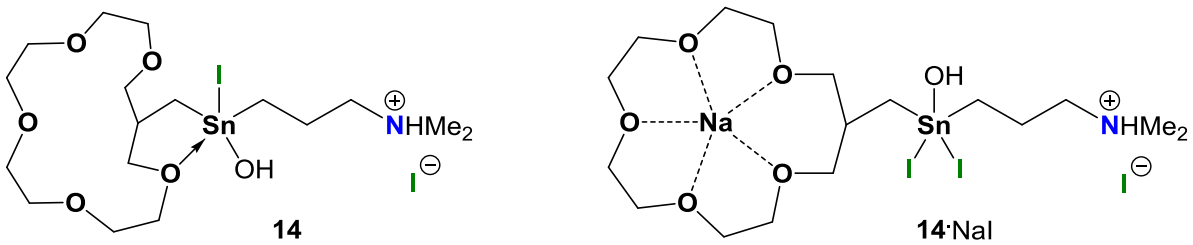


Chart 4. Structures of the organotin compound **14** and the complex **14**·NaI.

The ability of this receptor to complex ditopically the sodium salts NaF and NaI was investigated. It showed the ability to bind NaI giving the corresponding complex **14**·NaI (Chart 4), as proved by multinuclear NMR spectroscopy and electrospray mass spectrometry. However, it showed no reactivity towards NaF.

In the fourth chapter a set of water-soluble diorganotin compounds were synthesized and characterized (Chart 5).

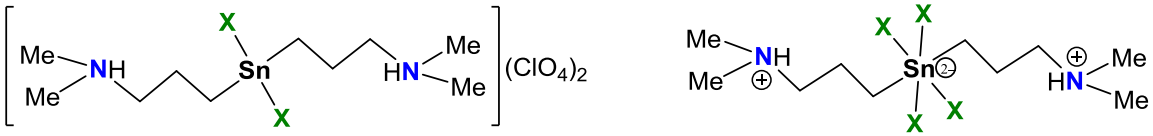


Chart 5. Schematic drawing of the water-soluble diorganotin compounds **2** and **4** – **6**.

The novel diorganotin difluoride **2** showed to be an ideal fluoride receptor as proved by NMR spectrometry.

The studies showed that:

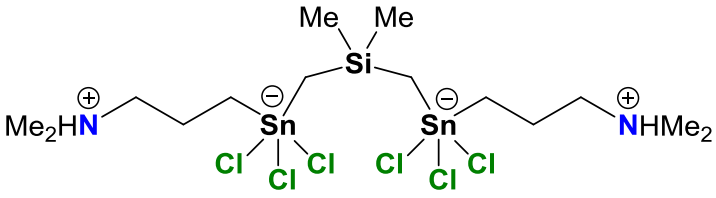
i) It is able to react with fluoride anions in water outperforming the strong competitive nature of OH^- anions.

ii) It showed selectivity to fluoride anions over other halide anions.

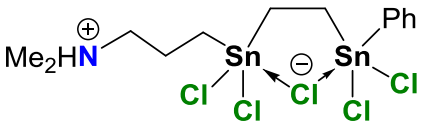
iii) It is effective in acidic conditions, whereas the ammonium moieties suffer deprotonation in basic solutions (*p*H > 8).

IV) The regeneration of this receptor can easily be achieved which is important for environmental aspects.

Also reported in this chapter are the water-soluble spacer bridged ditin compound **9** and **10** decorated with $\{Me_2NH(CH_2)_3\}$ arms (Chart 6). In compound **9** the two tin centers are separated by the $Me_2Si(CH_2)_2$ moiety, whereas compound **10** is an unsymmetrical dimethylene-bridged organoditin derivative. The latter showed good ability to bind fluoride anions in water.



9



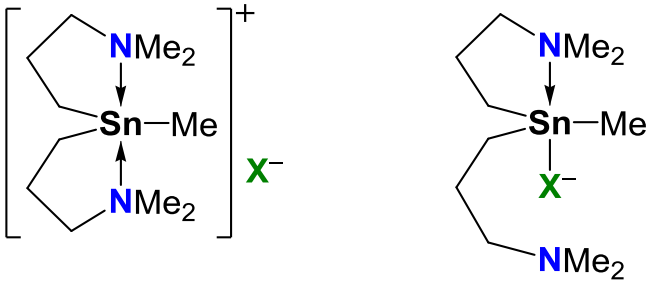
10

Chart 6. Structures of the water-soluble organoditin compounds **9** and **10**.

In the last chapter, two types of organotin compounds with the general structure ($\{Me_2N(CH_2)_3\}_2SnRX$, R = Me, Ph; X = electronegative substituent) were synthesized and characterized. The first type is represented by the triorganostannylium salts **2** – **5** (Chart 7) where the cationic part $[\{Me_2N(CH_2)_3\}_2SnMe]^+$ contains two inramolecular N→Sn coordinations, and the Sn···X distances are bigger than the sum of the covalent radii. This resulted in a salt-like character of these compounds and good solubility in water. The second type is represented by the triorganotin compounds **6** and **7** (Chart 7).

The triorganotin compounds **6** and **7** behave as N/Sn-based Frustrated Lewis Pairs (FLPs) towards CH_2Cl_2 giving the zwitterionic triorganostannates $[\{Me_2(ClCH_2)N(CH_2)_3\}\{Me_2N(CH_2)_3\}SnMeX]^+Cl^-$, (X = Cl, F) containing one quaternized

nitrogen atom (Chart 7), as proved by NMR spectroscopy and electrospray mass spectrometry.



2, X = I; **3**, X = Br
4, X = ClO_4
5, X = SCN

6, X = Cl
7, X = F

Chart 7. Ionic and non-ionic organotin compounds **2** – **7**.

To some extent, this resembles the concept of FLPs where the Lewis acid (Sn) and Lewis base (N) present in the same molecule but are not able to combine together. In contrast to the usual system found in FLPs, in the case of the organotin compounds **6** and **7** the steric hindrance is not the reason of that.

Such kind of receptors show activity towards small molecules is a highlighted and up-to-date topic. Future works can be devoted in this field is testing the reactivity of compounds **6** and **7** towards other fluorinated and chlorinated solvents.

7. Zusammenfassung

Das Ziel dieser Arbeit war die Synthese neuartiger Zinnverbindungen und ihre Anwendung zur selektiven Erkennung von Fluorid-Anionen in sowohl Wasser als auch organischen Lösungen. Charakteristisch für diese Verbindungen ist, dass sie diorganoaminopropyl-Substituenten des Typs RR`N$(CH_2)_3$ Rest (R, R` = organischer Substituent) enthalten. Die Wasserlöslichkeit wird durch Protonierung des Stickstoffatoms erreicht.

Bizentrische Dizinnverbindungen zeigen generell eine höhere Affinität zu Anionen als die einkernigen Organozinnanaloga. Um den Einfluss des Abstands zwischen den Zinnatomen auf die Molekülstruktur und die Selektivität gegen Fluorid-Anion zu bewerten, wurde eine Reihe von verbrückten Dizinnverbindungen synthetisiert und charakterisiert (Kapitel 2).

Die Organozinnfluoride **11** und **16** wurden synthetisiert und vollständig charakterisiert. Die Einkristallröntgenstrukturanalyse zeigt, dass die Verbindung **11** ein Dimer ist, während Verbindung **16** als Monomer vorliegt (Abbildung 1). In Lösung sind beide Verbindungen monomer.

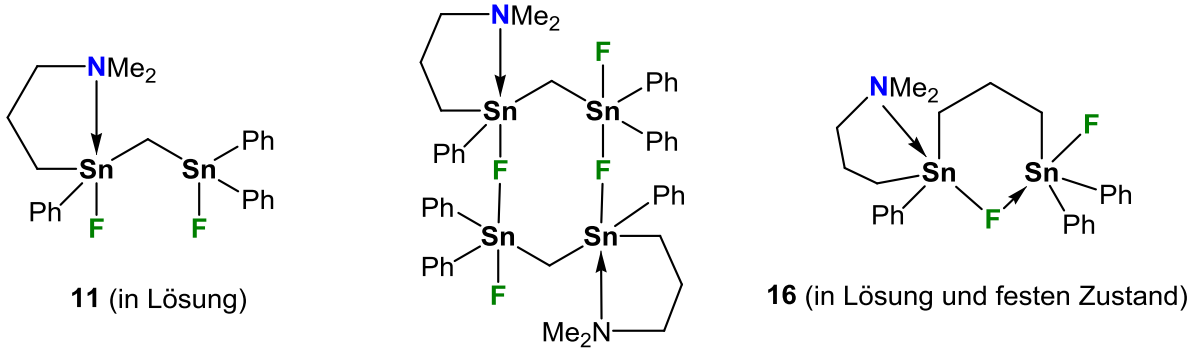


Abbildung 1. Schematische Darstellung der Strukturen der Triorganozinnfluoride **11** und **16** (Kapitel 2) in Lösung und im Festkörper.

Die Reaktionen von **11** bzw. **16** mit Fluorid-Anion (als Et_4NF) in CD_2Cl_2 führten zur Bildung der Komplexe NEt_4[**11**·F] und NEt_4[**16**·F]. Die Reaktionsmischungen wurden mithilfe der ^{19}F und ^{119}Sn NMR Spektroskopie bei verschiedenen Temperaturen untersucht. Die NMR-Daten zeigten, dass die intramolekulare N→Sn Koordination beibehalten wurde. Das Fluorid-Anion

überbrückte die Zinnzentren nicht, sondern es greift nur an dem diphenyl-substituierten Zinnatom an.

Die Organozinnfluoride **11** und **16** sind von Interesse, da sie zeigen dass

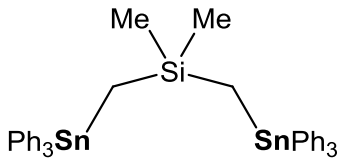
i) die intramolekulare N→Sn Koordination in **11** und **16** eine bessere Löslichkeit in gängigen organischen Lösungsmitteln im Vergleich zu $Ph_2FSn(CH_2)_nSnPh_2F$ (n = 1, 3) ergibt,

ii) die intermolekulare F→Sn Koordination der Verbindung **11** zu dimerer Struktur im festen Zustand führt, während das Organostannatanion $[(Ph_2FSn)_2CH_2{\cdot}F]^-$ und der Komplex $[(Ph_2ClSn)_2CH_2{\cdot}(Me_2N)_3P{=}O]$ monomere Strukturen zeigen und

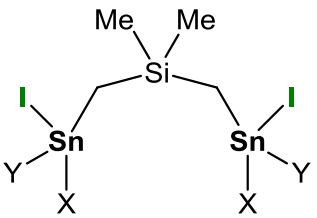
iii) die Anzahl der Methylengruppen, die die Zinnzentren in **11** und **16** trennen, deutlich die Strukturen dieser Verbindungen beeinflussen. In festem Zustand ist die Verbindung **16** monomer und die Verbindung **11** dimer. In Lösung ist der sechsgliedrige Ring in **16** stabiler gegen dem Angriff von Fluorid-Anionen als der viergliedrigen Ring in **11**.

Untersuchungen zur Eignung der Verbindung **11** als Ionophor in ionenselektiven Elektroden zeigten hohe Sensitivität gegenüber Fluorid-Anionen mit einem Nachweislimit von 10^{-4} M. Die Steigung der Kalibrationskurve von –32 mV/log[F] ist kleiner als der theoretische Wert der Sensitivität für einwertige Anionen von –59.16 mV/log[Anion]. Bessere Ergebnisse in diesem Bereich könnten durch Verwendung von anderen Plastifiziermitteln in der Elektrodenmembran erhalten werden.

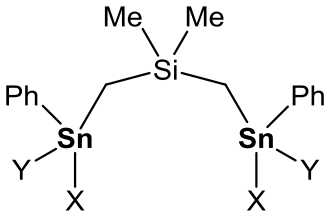
In Kapitel 2 werden die Synthesen der symmetrisch verbrückten Organodizinnverbindung $(Ph_3SnCH_2)_2SiMe_2$ **18** und ihrer Halogen-Derivate **19** – **24** beschrieben (Abbildung 2).



18



19; X = Y = Ph
20; X = I, Y = Ph
21; X = Y = I



22; X = Ph, Y = Cl
23; X = Y = Cl
24; X = Ph, Y = F

Abbildung 2. Die Organodizinnverbindungen **18** – **24** (Kapitel 2).

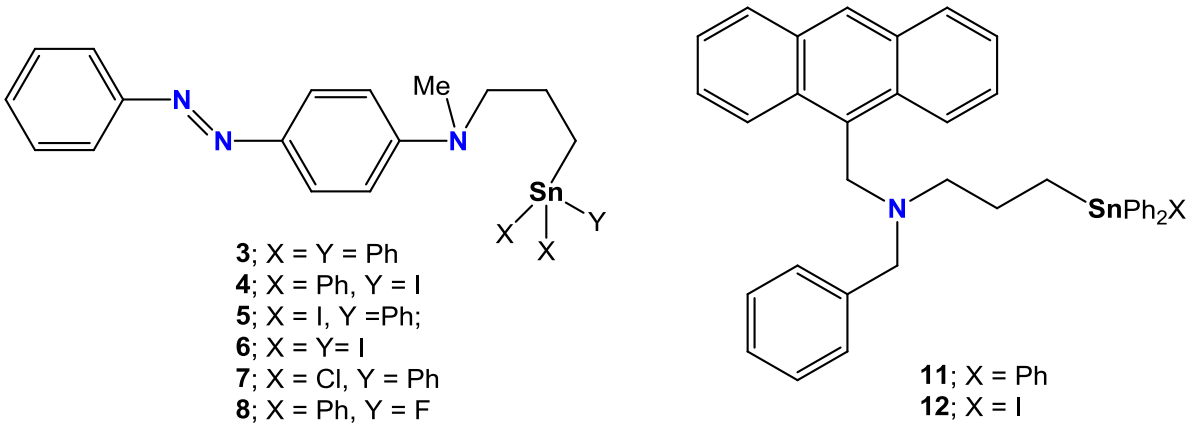
Die Verbindungen **18**, **19** und **24** wurden bereits in der Arbeitsgruppe von *Prof. Jurkschat* synthetisiert. Die Reaktionen von **23** und **24** mit Chlorid- und Fluorid-Anionen ergaben die

entsprechenden Komplexe [PPh_4][**23**·Cl], [NEt_4][**23**·F] und [NEt_4][**24**·F]. Die Strukturen dieser Komplexe wurden durch NMR-Spektroskopie und ESI-Massenspektrometrie bestätigt.

Die Entwicklung von Sensoren für die direkte Detektion von Fluorid-Anionen, bei denen die Komplexierung von Fluorid-Anionen durch Farbänderung zu erkennen ist, ist ein wichtiges Ziel für die realen Anwendungen in der Praxis. Zu diesem Zweck wurden Organozinnverbindungen, die Azo- oder Anthracen-Einheiten als chromophore Gruppen enthalten, dargestellt (Kapitel 3). Diese besitzen Potential für die Entwicklung von Rezeptoren, bei denen die Komplexierung von Anionen durch Farbänderungen mit dem bloßen Auge erkennbar ist.

Die Tetraorganozinnverbindungen **3** und **11** (Abbildung 3) wurden durch Mehrstufensynthesen dargestellt und durch NMR-Spektroskopie, Elementaranalyse und im Fall von **11** auch durch Röntgenstrukturanalyse charakterisiert.

Die Organozinnhalogenide **4** – **8** wurden durch Halogenierung der Organozinnverbindung **3** synthetisiert (Abbildung 3).



3; X = Y = Ph
4; X = Ph, Y = I
5; X = I, Y =Ph;
6; X = Y= I
7; X = Cl, Y = Ph
8; X = Ph, Y = F

11; X = Ph
12; X = I

Abbildung 3. Die Organozinnverbindungen **3** – **8** und **11** – **12** (Kapitel 3).

Bemerkenswert ist, dass keine intramolekulare N→Sn Koordination in den Organozinnhalogeniden **4**, **5**, **7** und **8** vorliegt. Das wurde durch NMR-Spektroskopie nachgewiesen. Das Organozinnfluorid **8** zeigt eine geringe Löslichkeit in den gängigen organischen Lösungsmitteln ähnlich zu den Organozinnfluoriden, die keine intramolekulare Koordination enthalten, wie z. B. Ph_3SnF.

7. Zusammenfassung

Die Reaktion von Verbindung **11** mit elementarem Iod ergab die entsprechende Iod-substituierte Organozinnverbindung **12** (Abbildung 3). Verbindung **12** unterliegt an feuchter Luft Hydrolyse.

Ebenfalls im dritten Kapitel wird die Synthese eines ditopen Rezeptors für die selektive Erkennung von Natriumionen berichtet. Der Rezeptor beseht aus der [16]-Krone-5-Einheit, die an dem Zinnzentrum gebunden ist. Die Organozinnverbindung **14** (Abbildung 4) wurde synthetisiert und charakterisiert.

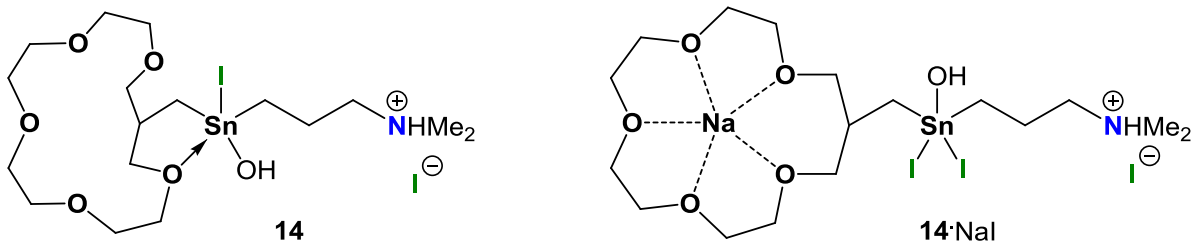
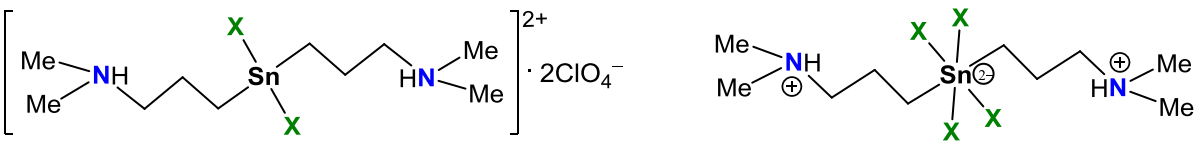


Abbildung 4. Die Organozinnverbindung **14** und der Komplex **14**·NaI(Kapitel 3).

Die Fähigkeit dieses Rezeptors zur Komplexierung von Natriumsalzen (NaF und NaI) wurde untersucht. Die Reaktion von **14** mit NaI ergab den Komplex **14**·NaI (Abbildung 4), wie es durch NMR-Spektroskopie und ESI-Massenspektrometrie nachgewiesen wurde. Die Verbindung **14** zeigte allerdings keine Reaktivität gegenüber NaF.

Im vierten Kapitel wird eine Reihe von wasserlöslichen Organozinnverbindungen vorgestellt (Abbildung 5).



2, X = F
5, X = Cl

4, X = F
6, X = Cl

Abbildung 5. Die wasserlöslichen Organozinnverbindungen **2** und **4** – **6** (Kapitel 4).

Das Organozinndifluorid **2** ist ein idealer Fluorid-Rezeptor, wie es durch NMR-Spektroskopie nachgewiesen wurde.

Die Untersuchungen zeigten, dass Verbindung **2**

i) mit Fluorid-Anionen im wässrigen Milieu reagiert, und der Konkurrenz gegenüber OH-Anionen standhält,

ii) Selektivität zu Fluorid-Anionen über andere Halogenid-Anionen zeigt,

iii) unter sauren Bedingungen wirksam ist und

iv) leicht zu regenerieren ist, was für Umweltaspekte von Bedeutung ist.

In Kapitel 4 werden außerdem die wasserlöslichen verbrückten Organozinnverbindungen **9** und **10** beschrieben (Abbildung 6). Die beiden Zinnzentren in Verbindung **9** sind durch $Me_2Si(CH_2)_2$-Einheit verbrückt. Die Verbindung **10** ist hingegen eine unsymmetrische dimethylen-verbrückte Organodizinnverbindung. Verbindung **10** zeigt eine hohe Affinität gegenüber Fluorid-Anionen im Wasser.

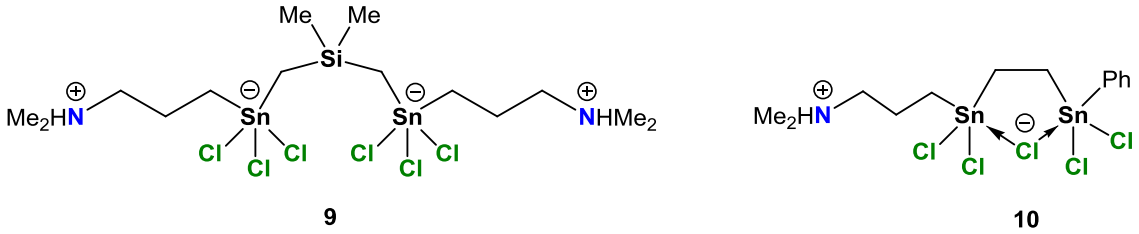
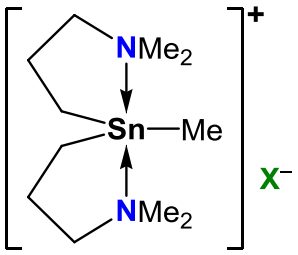


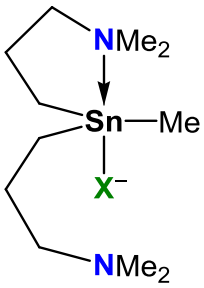
Abbildung 6. Die wasserlöslichen Organozinnverbindungen **9** und **10** (Kapitel 4).

Im letzten Kapitel werden zwei Arten von Organozinnverbindungen mit der allgemeinen Formel ($\{Me_2N(CH_2)_3\}_2SnRX$, R = Me, Ph; X = elektronegative Substituent) synthetisiert und vollständig charakterisiert (Abbildung 7). Zum ersten Typ gehören die Triorganozinnverbindungen **2** – **5**, die zwei intramolekularen N→Sn Koordination enthalten, und in Folge einen großen Sn···X Abstand zeigen. Auf Grund der salzartigen Strukturen sind die Verbindungen wasserlöslich. In der Verbindungen **6** und **7**, die zum zweiten Typ gehören, liegt nur eine intramolekulare N→Sn Koordination vor, und die Verbindungen zeigen keine salzartige Struktur.

Die Organozinnverbindungen **6** und **7** verhalten sich als N/Sn-basierte Lewis-Paare gegenüber CH_2Cl_2. Die Reaktionen mit CH_2Cl_2 lieferten die zwitterionischen Triorganostannate $[\{Me_2(ClCH_2)N(CH_2)_3\}\{Me_2N(CH_2)_3\}SnMeX]^+Cl^-$, (X = Cl, F), die durch NMR-Spektroskopie und ESI-Massenspektrometrie charakterisiert wurden.



2, X = I
3, X = Br
4, X = ClO_4
5, X = SCN



6, X = Cl
7, X = F

Abbindung 7. Die Organozinnverbindungen **2** – **7** (Kapitel 5).

Eine solche Art von Verbindungen, die Aktivität gegenüber kleinen Molekülen zeigen, ist ein Thema höchster Aktualität. Die Untersuchung der Reaktivität von Verbindungen **6** und **7** gegenüber verschiedenen chlorierten- und fluorierten Lösungsmitteln ist von großem Interesse.

8. Appendix

Crystallographic Data and Structure Refinements

Intensity data for all crystals were collected on a XcaliburS CCD diffractometer (Oxford Diffraction) using Mo-Kα radiation at 110 K. The structures were solved with direct methods using SHELXS-97 and refinements were carried out against F^2 by using SHELXL-2014.[1] The C–H hydrogen atoms were positioned with idealized geometry and refined using a riding model. All non-hydrogen atoms were refined using anisotropic displacement parameters.

Structural Data Chapter 2

The data of the organotin iodides $\{Me_2N(CH_2)_3\}PhISnCH_2SnPh_3$ (**9**) and $\{Me_2N(CH_2)_3\}PhISnCH_2SnPh_2I$ (**10**) are summarized in Table A1. Parts of compound **9** are affected by substitutional disorder, the same site is occupied by the phenyl group C(41)-C(46) in 90 % of unit cells and by iodide I(2) in 10 % of unit cells. This disorder was refined by a split model over two positions, their occupancies were allowed to refine freely to yield 0.89527: 0.10473 and then restrained to integer values 0.9:0.1.

The data of the organotin compounds $\{Me_2N(CH_2)_3\}PhFSnCH_2SnPh_2F$ (**11**), $\{Me_2N(CH_2)_3\}PhFSn(CH_2)_3SnPh_2F$ (**16**) and $I_3Sn(CH_2)_4SnI_3$ (**27**) are summarized in Table A2.

References

(1) (a) Sheldrick, G. M. *Acta Crystallogr.* **2008**, A64, 112–122; (b) Sheldrick, G. M. *Acta Crystallogr.* **2015**, *C71*, 3–8.

8. Appendix

Table A1. Crystal data and structure refinements of $\{Me_2N(CH_2)_3\}PhISnCH_2SnPh_3$ (**9**) and $\{Me_2N(CH_2)_3\}PhISnCH_2SnPh_2I$ (**10**) presented in Chapter 1.

	9	**10**
Empirical formula	$C_{29.40}H_{33.50}I_{1.10}NSn_2$	$C_{24}H_{29}I_2NSn_2$
Formula weight	777.84	822.66
Temperature / K	173(2)	173(2)
Wavelength /°A	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
space group	P2(1)/c	C 2/c
a /°A	10.3926(4)	9.9414(4)
b /°A	11.7904(4)	18.3814(9)
c /°A	23.7767(8)	29.2432(11)
α /°	90	90
β /°	99.430(4)	94.694(4)
γ /°	90	90
Volume /A^3	2874.06(18)	5325.9(4)
Z	4	8
Dc /$g.cm^{-3}$	1.798	2.052
Absorption coefficient /mm^{-1}	2.937	4.205
F(000)	1501	3088
Crystal size /mm	0.38 x 0.30 x 0.10	0.09 x 0.07 x 0.06
Range for data collection /°	2.415 to 25.499	2.216 to 25.498
Reflections collected	22890	29933
Independent reflections	5346	4957
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	5346 / 6 / 307	4957 / 0 / 228
Goodness-of-fit on F^2	0.833	0.802
Final R indices [$I>2\sigma(I)$]	R1 = 0.0291, wR2 = 0.0586	R1 = 0.0253, wR2 = 0.0347
R indices (all data)	R1 = 0.0478, wR2 = 0.0614	R1 = 0.0552, wR2 = 0.0362
Largest diff. peak and hole / $e.A^{-3}$	0.942 and -0.671	1.151 and -0.696

8. Appendix

Table A2. Crystal data and structure refinements of $\{Me_2N(CH_2)_3\}Ph(F)SnCH_2SnPh_2F$ (**11**), $\{Me_2N(CH_2)_3\}Ph(F)Sn(CH_2)_3SnPh_2F$ (**16**) and $I_3Sn(CH_2)_4SnI_3$ (**27**) presented in Chapter 1.

	11	**16**	**27**
Empirical formula	$C_{48}H_{58}F_4N_2Sn_4$	$C_{26}H_{33}F_2NSn_2$	$C_4H_8I_6Sn_2$
Formula weight	1213.72	634.91	1054.88
Temperature / K	173(2)	173(2)	173(2)
Wavelength /°A	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Orthorhombic
space group	P2(1)/n	P2(1)/c	P b c a
a /°A	12.5326(6)	16.8757(9)	11.6554(7)
b /°A	11.0605(5)	7.9337(4)	12.1008(6)
c /°A	16.8003(8)	18.9274(13)	13.4625(6)
α /°	90	90	90
β /°	94.893(4)	95.777(6)	90
γ /°	90	90	90
Volume /A^3	2320.32(19)	2521.3(3)	1898.75(17)
Z	2	4	4
Dc /$g.cm^{-3}$	1.737	1.673	3.690
Absorption coefficient /mm^{-1}	2.178	2.009	12.356
F(000)	1192	1256	1800
Crystal size /mm	0.24 x 0.19 x 0.08	0.18 x 0.12 x 0.06	0.28 x 0.24 x 0.13
Range for data collection /°	2.116 to 25.500	2.163 to 25.498	2.86 to 25.48
Reflections collected	17084	12746	6732
Independent reflections	4325	4695	1769
Refinement method	Full-matrix least squares on F^2	Full-matrix least squares on F^2	Full-matrix least squares on F^2
Data / restraints / parameters	4325 / 0 / 264	4695 / 0 / 246	1769 / 0 / 55
Goodness-of-fit on F^2	0.904	0.803	0.964
Final R indices [I>2σ(I)]	R1 = 0.0236, wR2 = 0.0494	R1 = 0.0318, wR2 = 0.0374	R1 = 0.0311, wR2 = 0.0663
R indices (all data)	R1 = 0.0364, wR2 = 0.0505	R1 = 0.0678, wR2 = 0.0390	R1 = 0.0455, wR2 = 0.0688
Largest diff. peak and hole / $e.A^{-3}$	0.859 and -0.558	0.976 and -0.671	0.814 and -1.634

Table A3. Crystal data and structure refinements of {($AnCH_2$)(Bn)N(CH_2)$_3$}$SnPh_3$ (**11**) and [{Me_2(H)N(CH_2)$_3$}(I_3)$SnCH_2$-[16]-crown-5] (**15**) presented in Chapter 3.

	11	**15**
Empirical formula	$C_{43}H_{39}NSn$	$C_{17}H_{36}I_3NO_5Sn$
Formula weight	688.44	833.86
Temperature / K	173(2)	173(2)
Wavelength /°A	0.71073	0.71073
Crystal system	Triclinic	Triclinic
space group	P-1	P-1
a /°A	9.6550(5)	10.9141(6)
b /°A	13.9411(7)	11.5964(8)
c /°A	14.4716(9)	12.0215(7)
α /°	115.306(5)	61.509(6)
β /°	102.671(5)	74.472(5)
γ /°	90.303(4)	86.370(5)
Volume /A^3	1707.22(16)	1284.69(16)
Z	2	2
Dc /g.cm^{-3}	1.339	2.156
Absorption coefficient /mm^{-1}	0.779	4.624
F(000)	708	788
Crystal size /mm	0.35 x 0.35 x 0.23	0.15 x 0.12 x 0.04
Range for data collection /°	2.37 to 25.50	2.38 to 25.50
Reflections collected	12292	11529
Independent reflections	6360	4792
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	6360 / 0 / 406	4792 / 6 / 250
Goodness-of-fit on F^2	1.127	0.807
Final R indices [I>2σ(I)]	R1 = 0.0268, wR2 = 0.0577	R1 = 0.0295, wR2 = 0.0519
R indices (all data)	R1 = 0.0304, wR2 = 0.0594	R1 = 0.0551, wR2 = 0.0541
Largest diff. peak and hole / e.A^{-3}	0.338 and -0.384	0.936 and -1.044

Table A3. Crystal data and structure refinements of [{$Me_2(H)N(CH_2)_3$}$_2SnF_4$]·$4H_2O$ (**4**), [{$Me_2(H)N(CH_2)_3$}$_2SnCl_2$·$2ClO_4$] (**5**) and [{$Me_2(H)N(CH_2)_3$}$_2SnCl_4$] (**6**) presented in Chapter 4.

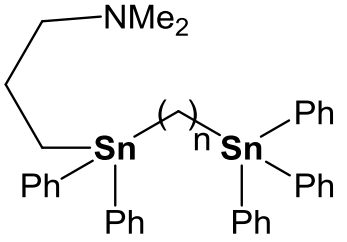
	4	**5**	**6**
Empirical formula	$C_{10}H_{34}F_4N_2O_4Sn$	$C_{10}H_{26}Cl_4N_2O_8Sn$	$C_5H_{13}Cl_2NSn_{0.50}$
Formula weight	441.08	562.82	217.41
Temperature / K	173(2)	173(2)	173(2)
Wavelength /°A	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Monoclinic
space group	P-1	P-1	$P2_1/c$
a /°A	7.1502(3)	6.8036(3)	7.3880(3)
b /°A	7.6933(5)	11.1345(6)	10.8420(4)
c /°A	8.8164(4)	14.1806(7)	11.0781(5)
α /°	73.116(5)	98.377(4)	90
β /°	80.352(4)	90.336(3)	107.514(4)
γ /°	79.359(4)	93.875(4)	90
Volume /°A^3	452.73(4)	1060.22(9)	846.23(6)
Z	1	2	4
Dc /$g.cm^{-3}$	1.618	1.763	1.706
Absorption coefficient /mm^{-1}	1.463	1.745	2.125
F(000)	226	564	436
Crystal size /mm	0.494 x 0.285 x 0.267	0.324 x 0.114 x 0.051	0.215 x 0.125 x 0.085
Range for data collection /°	2.796 to 27.491	2.180 to 25.999	2.953 to 27.497
Reflections collected	7064	17718	6389
Independent reflections	2077	4181	1944
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F2	Full-matrix least-squares on F2
Data / restraints / Parameters	2077 / 5 / 118	4181 / 0 / 238	1944 / 1 / 85
Goodness-of-fit on F^2	1.338	1.096	1.293
Final R indices [I>2σ(I)]	R1 = 0.0165, wR2 = 0.0467	R1 = 0.0302, wR2 = 0.0833	R1 = 0.0273, wR2 = 0.0830
R indices (all data)	R1 = 0.0176, wR2 = 0.0635	R1 = 0.0331, wR2 = 0.0854	R1 = 0.0324, wR2 = 0.0852
Largest diff. peak and hole / e.A^{-3}	0.781 and −0.569	1.381 and −0.766	0.948 and −0.601

Table A5. Crystal data and structure refinements of [{$Me_2(N(CH_2)_3\}_2SnMe]I$ (**2**) and [{$Me_2N(CH_2)_3\}_2SnMe]Ag_2I_3$ (**4a**) presented in Chapter 5.

	2	**4a**
Empirical formula	$C_{11}H_{27}IN_2Sn$	$C_{11}H_{27}Ag_2I_3N_2Sn$
Formula weight	432.94	902.48
Temperature / K	173(2)	173(2)
Wavelength /°A	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic
space group	Pbca	$P2_1/n$
a /°A	14.3124(4)	14.4812(6)
b /°A	14.3124(4)	7.3056(3)
c /°A	15.3835(7)	20.2619(8)
α /°	90	90
β /°	90	96.597(4)
γ /°	90	90
Volume /°A^3	3151.23(19)	2129.39(15)
Z	8	4
Dc /g.cm^{-3}	1.825	2.815
Absorption coefficient /mm^{-1}	3.560	7.327
F(000)	1680	1640
Crystal size /mm	0.45 x 0.11 x 0.10	0.43 x 0.11 x 0.10
Range for data collection /°	2.41 to 25.49	2.02 to 25.50
Reflections collected	19127	8416
Independent reflections	2920	3955
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	2920 / 0 / 141	3955 / 0 / 172
Goodness-of-fit on F^2	0.884	0.986
Final R indices [$I>2\sigma(I)$]	R1 = 0.0438, wR2 = 0.1009	R1 = 0.0265, wR2 = 0.0609
R indices (all data)	R1 = 0.0666, wR2 = 0.1103	R1 = 0.0349, wR2 = 0.0623
Largest diff. peak and hole / e.A^{-3}	0.985 and −1.565	0.910 and −1.517

9. List of New Compounds

Chapter 2.



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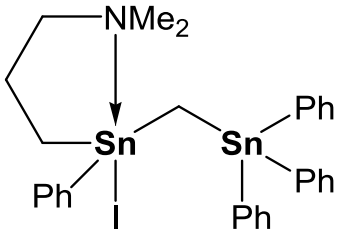
7, n = 3; **8**, n = 4



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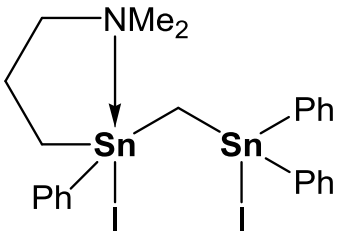

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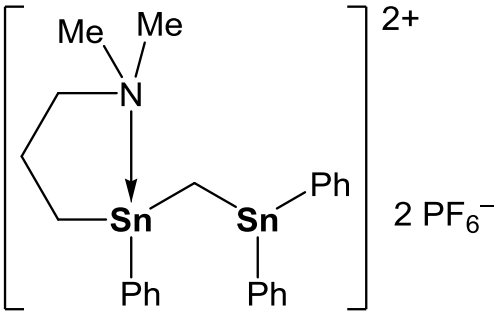

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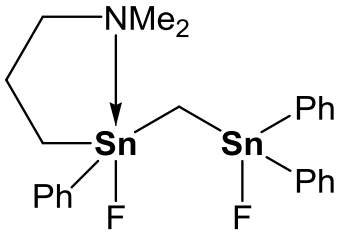

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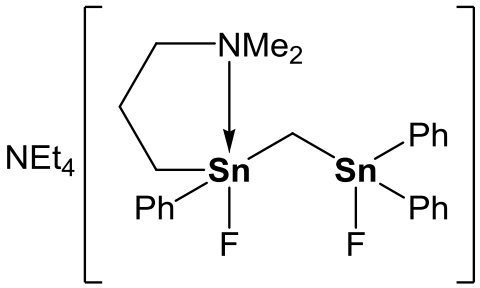
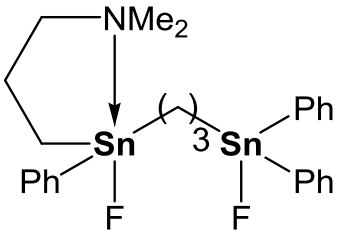


NEt_4[**11**·F]



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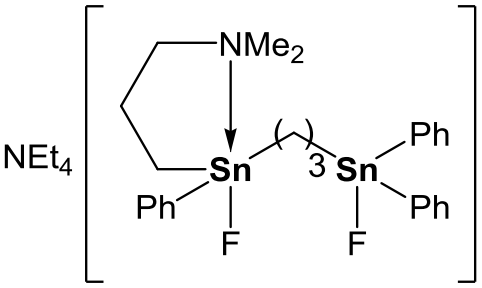

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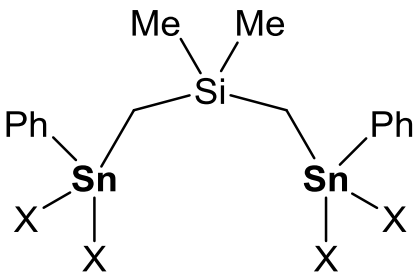
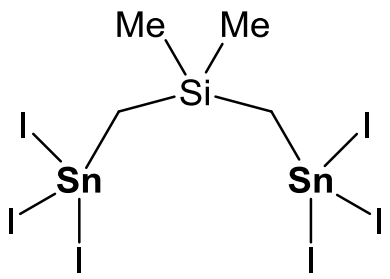


20; X = I
23; X = Cl



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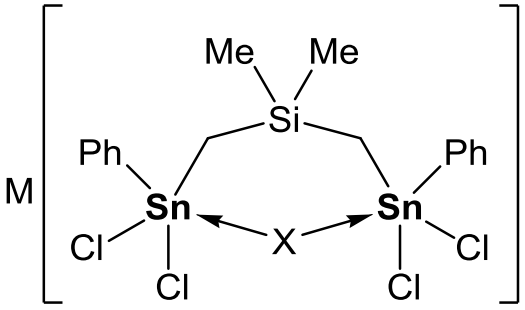
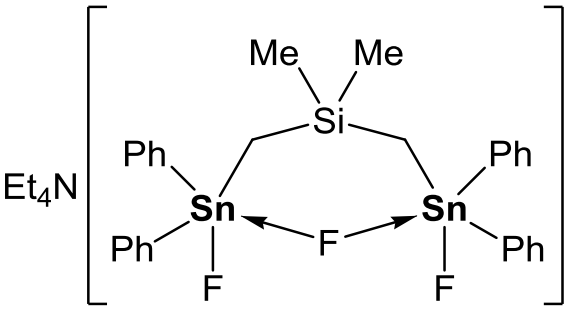
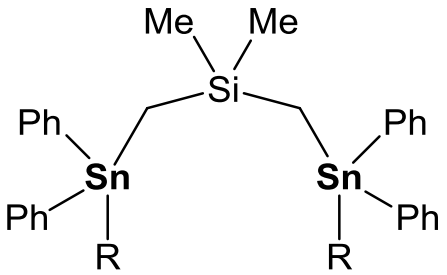


[PPh_4][**23**·Cl]; M = Ph_4P, X = Cl

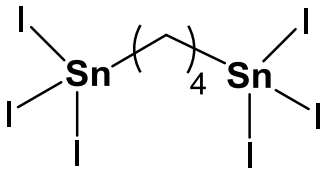
[NEt_4][**23**·F]; M = Et_4N, X = F



[NEt_4][**24**·F]



25; R = $Me_2N(CH_2)_3$



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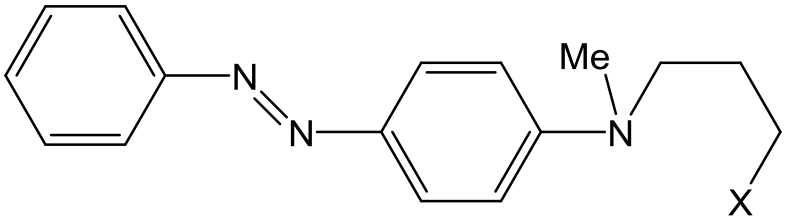
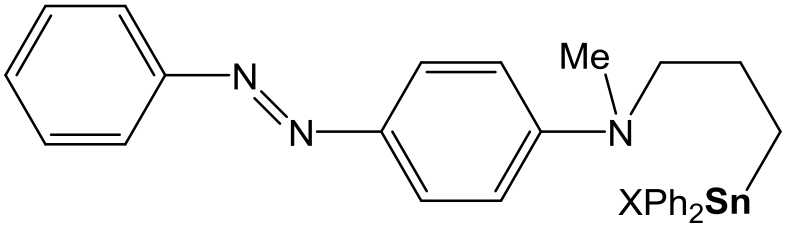
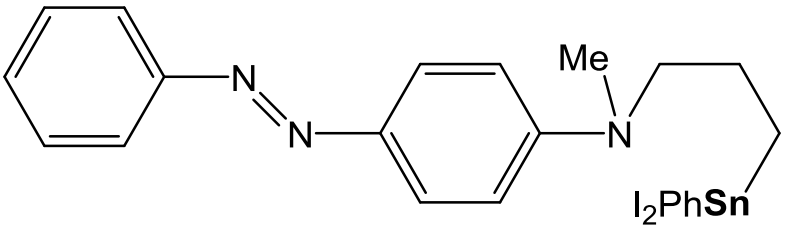
Chapter 3.



1; X = OH
2; X = Cl



3; X = Ph
4; X = I
7; X = Cl
8; X = F



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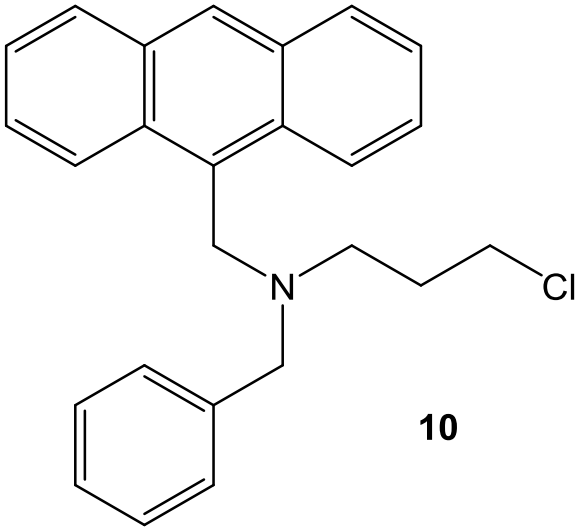

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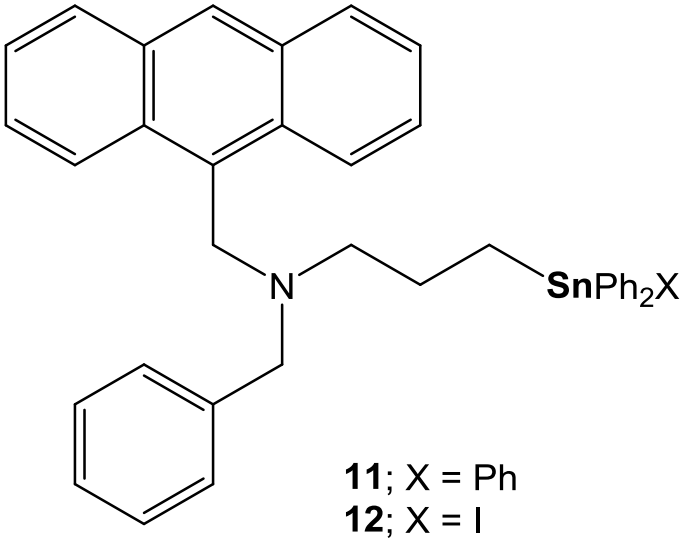
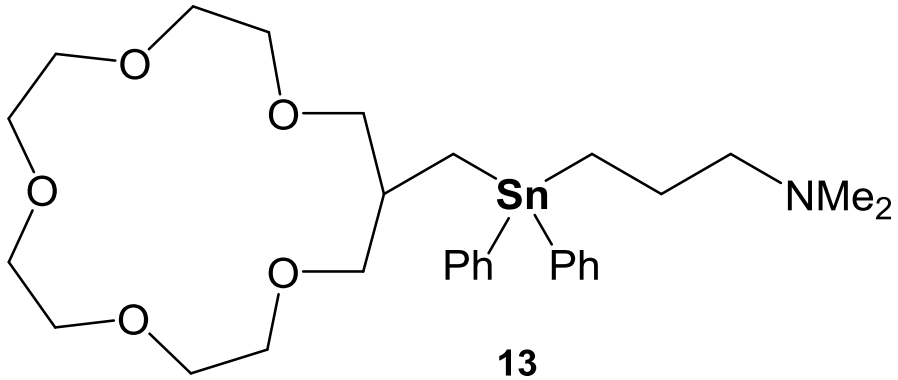


11; X = Ph
12; X = I



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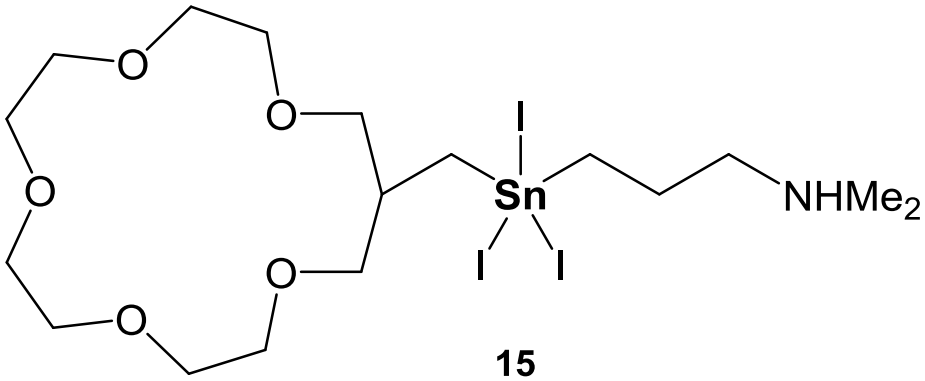

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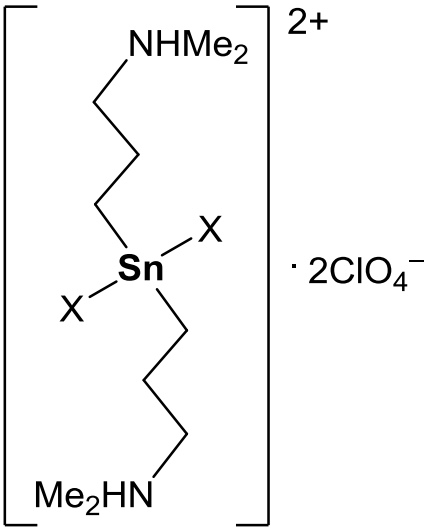
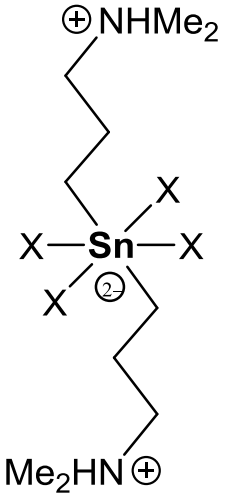
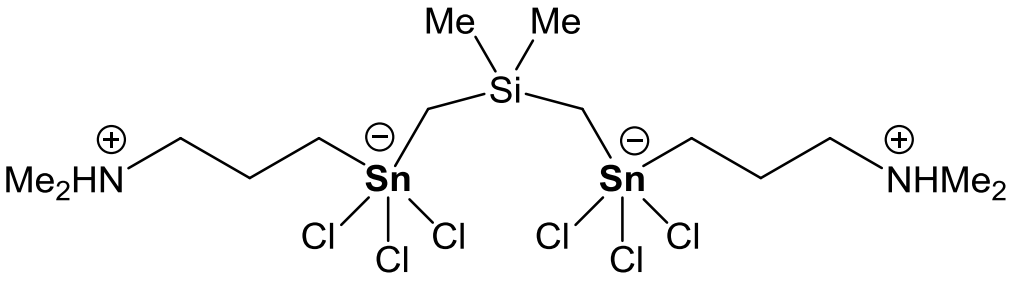
Chapter 4.



2; X = F
5; X = Cl



4; X = F
6; X = Cl



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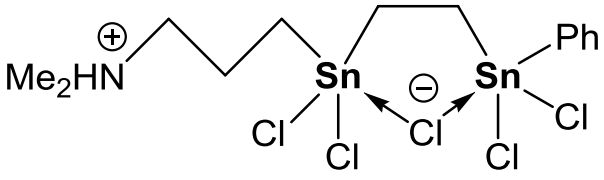

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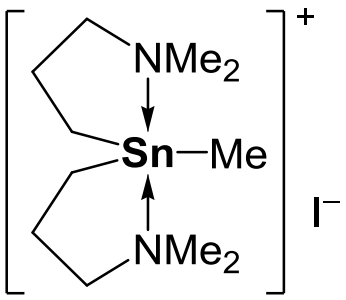
Chapter 5.



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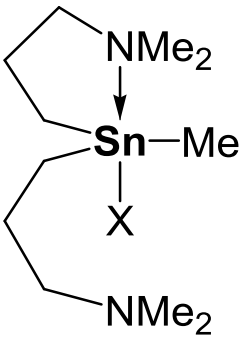

6; X = Cl
7; X = F

CURRICULUM VITAE

Personal Informations

Name	Nour Alashkar
Address	Kuntzestr. 87; 44225 Dortmund
Birthdate	01.01.1983
Birthplace	Damascus-Syria
Nationality	Syrian
Marital status	Married and have two Daughters

Education

02.2016 – 08.2016	Scientific Assistant at TU Dortmund, Germany.
01.2010 – 01.2014	PhD under the supervision of Prof. Dr. K. Jurkschat, TU Dortmund, Germany.
02.2009 – 11.2009	Research Project in the Working Group of Prof. Dr. K. Jurkschat, TU Dortmund, Germany.
07.2008 – 12.2008	Research Project in the Working Group of Prof. Dr. M. Spiteller, TU Dortmund, Germany.
08.2006 – 03.2008	Scientific Assistant at the Department of Chemistry, Damascus University, Syria.
09.2004 – 12.2005	Diploma of Science in Chemistry, Damascus University, Syria.
09.2000 – 07.2004	Bachelor of Science in Chemistry, Damascus University, Syria.
09.1994 – 07.2000	Secondary School, Damascus, Syria.
09.1988 – 07.1994	Primary School, Damascus, Syria.

Publications

"Unsymmetrical Bicentric Organotin Lewis Acids $\{Me_2N(CH_2)_3\}$-$Ph(X)Sn(CH_2)_nSnPh_2X$ (X = F, I; n = 1, 3): Syntheses and Structures" N. Alashkar, C. Dietz, S. Baba Haj, W. Hiller, K. Jurkschat, *Organometallics*, **2016**, *35*, 2738-2746.

Erklärung

Hiermit erkläre ich, dass ich die vorliegende Arbeit selbständig und nur unter der Verwendung der angegebenen Mittel angefertigt habe.

Dortmund, den 20.10.2016