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Cluj-Napoca, ROMANIA

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Department of Chemistry

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PROGRESS IN ORGANOMETALLIC CHEMISTRY OF TIN(IV) AND LEAD(II)

PhD Thesis Abstract

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Scientific advisor: **Prof. Dr. Cristian SILVESTRU**

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General introduction

Tin and lead have been mentioned in the early books of the Old Testament and they are two of the oldest metals known to humanity. Their Latin names *stannum* and *plumbum* gave the chemical symbols of these elements – Sn and Pb. Glazing pottery was one of the first uses of lead in the ancient Egypt (7000-5000 B.C.), while Romans used lead for plumbing or water pipes. The first appearance of tin dates back to the Bronze Age (3500-3200 B.C.) when some bronze weapon and tools containing 10-15% Sn alloy with Cu have been found at Ur.

Tin and lead present two common oxidation states Sn(II), Sn(IV) and Pb(II), Pb(IV), respectively. The Sn(II) state usually needs the 5*p* orbitals for bonding, while the non-bonding pair of electrons is left in the 5s state. Compounds SnX_2 (the stannylenes) adopt an X–Sn–X angle of about 90-100°. The electron-withdrawing effect of the ligands is an alternative to increase the stability of Sn(II) compounds (*e.g.* $:SnCl_2$, $:SnF_2$), together with the bulkiness of the ligands which can stop further ligation [*e.g.* $Sn[N(SiMe_3)_2]_2$]; otherwise, oxidation readily occurs to the Sn(IV) state. In Sn(IV) derivatives, the metal center is sp^3 hybridized with a tetrahedral geometry.

Pb(II) is the most common form of lead in the environment, but Pb(IV) derivatives are also known (*e.g.* $PbEt_4$ was used as gasoline additive). The presence of the $6s^2$ lone pair and the relativistic splitting of the 6*p* orbitals generate a range of intriguing electronic as well as structural effects. The so-called “inert pair effect” observed for lead is the main reason of the primary tendency of lead to form inorganic Pb(II) over Pb(IV) species.

The first industrial use of an organotin derivative was patented by Standard Oil Development Co. for the use of tetraalkyltin compounds as stabilizers of transformer oils, in 1932. In the same period, organotin compounds have been used as heat stabilizers in PVC industry, catalytic agents (in the formation of urethane foams, silicon rubbers, or esterification) or as biocidal derivatives.

The potential structural correlations between solution and solid state behavior of organotin and -lead compounds require various investigation methods. NMR spectroscopy and single crystal X-Ray diffraction are two of the compulsory tools in order to characterize these organometallic complexes.

PART 1.

Synthesis, reactivity and structural characterisation of new organotin(IV) compounds with organic ligands that exhibit coordination abilities

1.1. Literature review

Hypervalent [or hypercoordinated] organotin(IV) compounds have been known since 1963, when Hulme investigated the trimethyltin chloride/pyridine adduct, [Me3SnCl(Py)], by single-crystal X-ray diffraction and he identified the first pentacoordinated tin atom in a molecule.

The first chapter of the present thesis consists of a detailed literature study of hypervalent organotin(IV) compounds with a double-bounded intramolecularly coordinating nitrogen, –C=N→Sn. This will be followed by a literature survey about organotin(IV) heterometallic complexes and then the original contribution part.

1.2. Objectives

The main topic of the first part of present work was the design, synthesis and structural investigation of some organotin(IV) species containing organic moieties able to act as donor groups for transition metals.

Compounds of the type $RSnPh_nX_{3-n}$ (n = 1-3) containing R = $2\text{-}[(CH_2O)_2CH]C_6H_4$ fragment will be synthetized, as they are important starting materials in the chemistry of tin which is intended to be developed.

An essential step, will be the preparation and investigation of organotin(IV) compounds bearing the $2\text{-}(O{=}CH)C_6H_4$ moiety. They will be used to obtain new (imino)aryltin(IV) compounds containing an intramolecularly coordinating sp^2-nitrogen atom to the metal center.

The synthesis and characterization of some new bimetallic complexes containing at least one organotin(IV) fragment will be also studied.

1.3. Original contributions

Derivatives with –C=N– bond are known for 40 year, but most of these compounds have this motif as part of an oxazoline fragment.

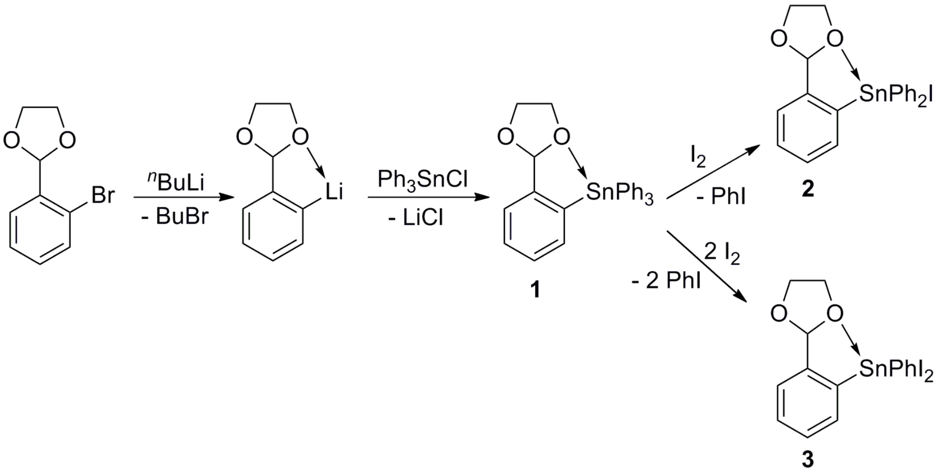
Organotin(IV) species with imine pendant-arm ligands can be obtained by condensation reactions between organotin(IV) precursors, containing a substituent on the metal with at least one benzaldehyde group, and an appropriate amine, in various conditions.

In order to obtain the desired organotin(IV) reagent containing an aldehyde fragment, the starting 2-bromobenzaldehyde reagent must be protected with an acetal group. The resulting dioxolane derivative is stable to basic nucleophiles (Mg, ^{n}BuLi), so it can be easy lithiated with nBuLi. Lithiation followed by a salt metathesis reaction with different organotin(IV) halides ends up with the isolation of the required starting materials. Deprotection of the dioxolane group can be achieved by hydrolysis in an acidic environment, and the resulting species are used further in condensation reactions to get compounds with C=N double bond.

1.3.1. Protected organotin(IV) compounds containing 2-[$(CH_2O)_2CH$]C_6H_4 moiety

Compounds [2-{$(CH_2O)_2CH$}C_6H_4]$SnPh_3$ (**1**), [2-{$(CH_2O)_2CH$}C_6H_4]$SnPh_2I$ (**2**) and [2-{$(CH_2O)_2CH$}C_6H_4]$SnPhI_2$ (**3**) have been prepared according to the reaction scheme shown below (Scheme 1). The starting organic ligand, 2-(2-bromophenyl)-1,3-dioxolane was obtained according to a literature protocol, by reaction of the commercially available 2-bromobenzaldehyde with 1 equivalent of ethylene glycol, using 4-$MeC_6H_4SO_3H$ as catalyst. Lithiation of 2-(2-bromophenyl)-1,3-dioxolane with ^{n}BuLi in dry hexane, under an inert argon atmosphere, using a slight excess of ^{n}BuLi, affords the lithiated intermediate, which was reacted further with 1 equivalent of Ph_3SnCl in toluene to give **1** in a 82% yield.

Compound **1** was isolated as a white solid, non-sensitive to hydrolysis and it was reacted with elemental iodine in different ratios, to yield organotin(IV) compounds **2** and **3**, respectively. Both iodide species are white to pale yellow solids, air and moisture stable at room temperature.



Scheme 1.

The NMR spectra of compounds **1**-**3** were recorded in CDCl$_3$, at room temperature, on either 400 or 600 MHz spectrometers.

Similar patterns can be noticed for all these 3 compounds in the aliphatic region of the ^{1}H NMR spectra: one singlet resonance signal corresponding to the H$_7$ hydrogen (δ range = 5.77-5.95 ppm) and a AA'XX' spin system between δ = 3.5 - 4 ppm for the H$_8$ hydrogens of the 1,3-dioxolane ring (Figure 1).

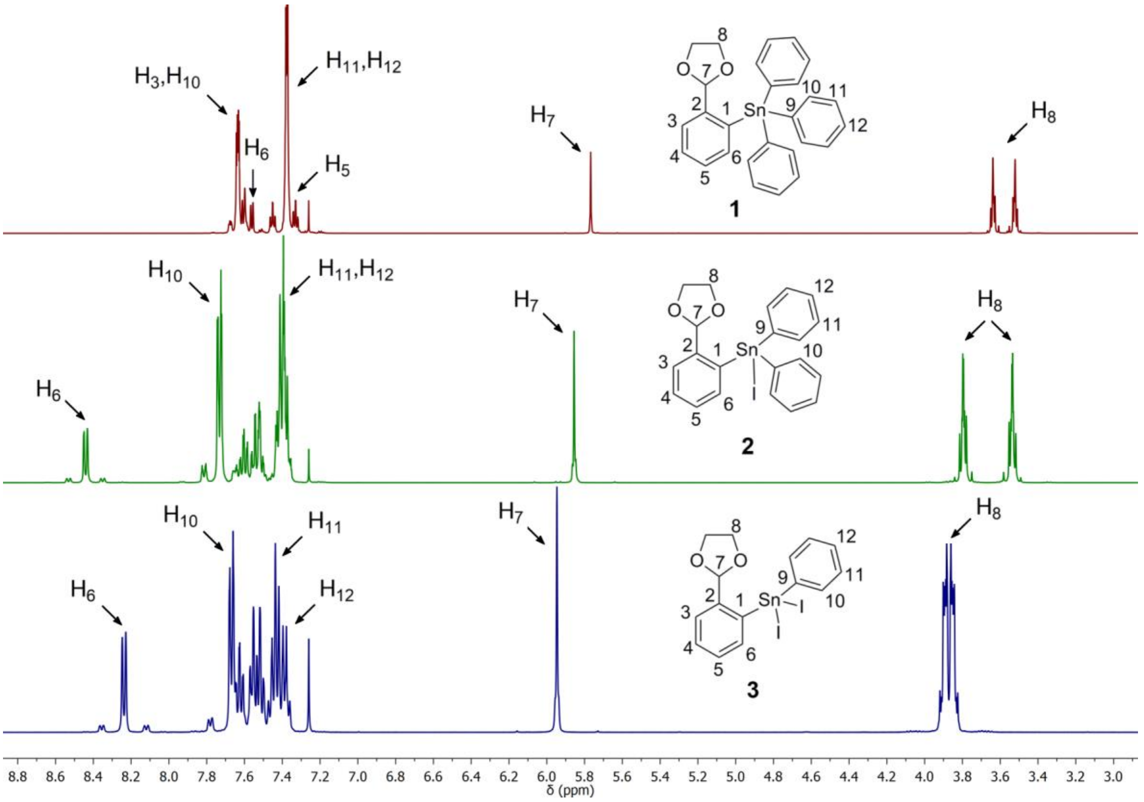


Figure 1. Stacked ^{1}H NMR spectra (CDCl$_3$, 20 °C) for compounds **1** (red), **2** (green) and **3** (blue).

The ^{119}Sn NMR chemical shift for **1** (δ = –131.24 ppm) compares very well with other tetraaryltin(IV) species reported in the literature: Ph_4Sn (δ = –128.1 ppm),[108] (3-anis)$_4$Sn (δ = –125.1 ppm)[109] or (4-$CF_3C_6H_4$)$_4$Sn (δ = –134.0 ppm).[109] This value indicates a tetracoordinated tin atom in solution, without any O→Sn intramolecular coordination. The long acquisition time of the ^{119}Sn NMR spectrum for **1**, together with a well concentrated sample, allows the observation of ^{13}C satellites (Figure 2).

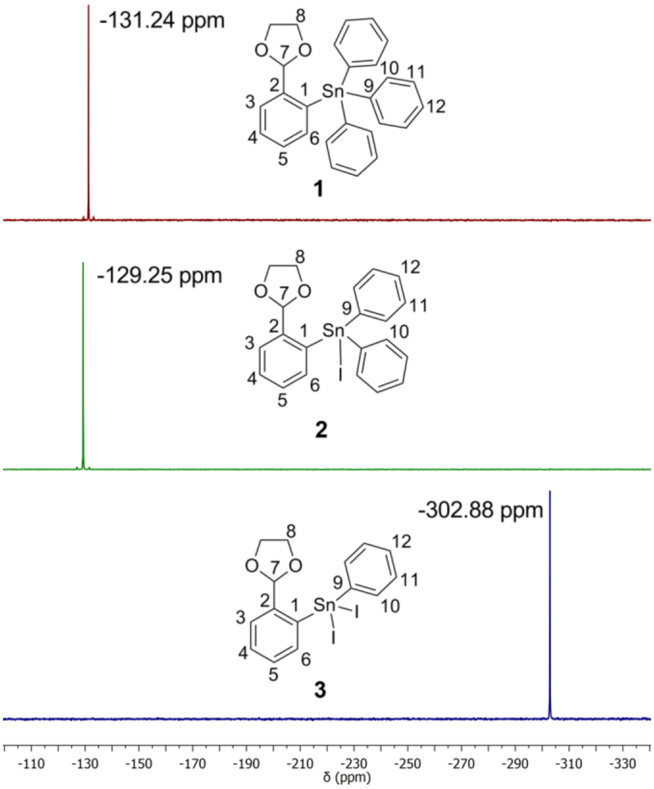


Figure 2. Stacked ^{119}Sn NMR spectra ($CDCl_3$, 149.2 MHz) for compounds **1** (red), **2** (green) and **3** (blue).

Substitution of a phenyl group from **1** with an iodine, does not bring a significant change in ^{119}Sn NMR spectra of **2**. However, a second iodine bounded to tin center comes with an important upfield shift in the ^{119}Sn NMR resonance of **3**. The chemical shift of **3** (δ = –302.88 ppm) match with that for [2-(Me_2NCH_2)C_6H_4]$SnPhI_2$ (δ = –337.4 ppm),[30] and it is upfield shifted compared with that reported for Ph_2SnI_2 (δ = –243.8 ppm)[110] suggesting the presence of intramolecular O→Sn coordination in solution and a five-coordinated tin center.

The high-resolution mass spectra of compounds containing the 2-phenyl-1,3-dioxolane fragment were recorded using atmospheric-pressure chemical ionization technique. The APCI(+) spectrum of **1** contains the molecular peak at *m/z* 501.08867

(6.25%) $[M+H^+]$, while the base peak (*m/z* 379.01498) can be assigned to the $[\{2\text{-}(O{=}CH)C_6H_4\}SnPh_2+H^+]$ fragment. In the HR-MS spectrum of **2** the base peak (*m/z* 423.02611) can be assigned to the $[[2\text{-}\{(CH_2O)_2CH\}C_6H_4]SnPh_2^+]$ fragment. The molecular peak can also be observed at *m/z* 550.94684 (2.48%).

The APCI(+) spectrum of **3** also confirms the purity of the compound as the molecular peak *m/z* 600.81864 (8.57%) $[M+H^+]$ can be noticed. $[M–I^+]$ fragment can be assigned for the base peak at *m/z* 472.90580.

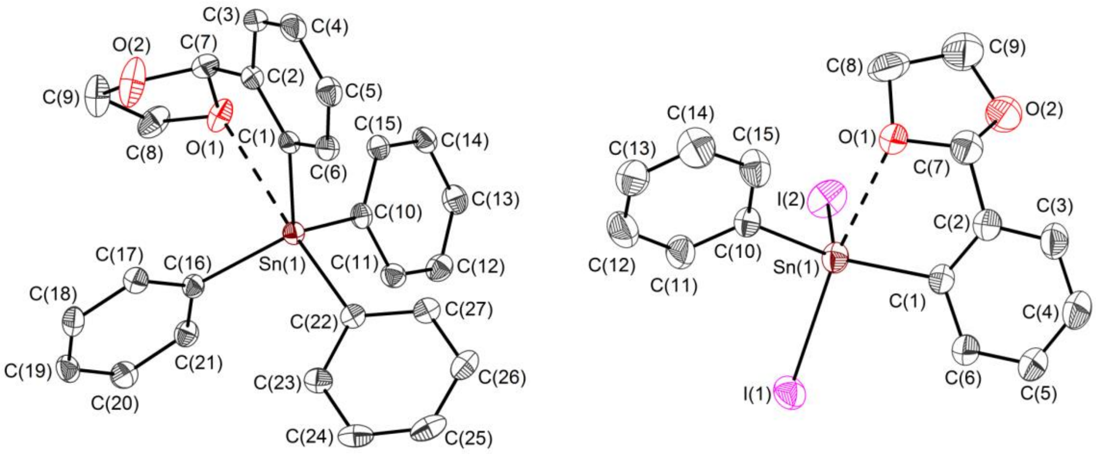


Figure 3. ORTEP drawings of $pR_{O(1)}R_{C(7)}$-**1** (*left*) and **3** (*right*) showing 30% probability displacement ellipsoids and the atom numbering scheme.

The molecular structures of compounds **1** (Figure 3, *left*), **2** (Figure 4) and **3** (Figure 3, *right*) reveal some common features:

a) the tin atom is involved in a distorted trigonal bipyramidal coordination geometry, due to the intramolecular coordination of one oxygen atom from the 1,3-dioxolane ring to the metal center; in order to confirm this geometry, a closer look at the τ_5 value should be considered. The τ_5 parameter is defined as the ratio $(\beta-\alpha)/60°$, $\beta>\alpha$, where β and α are the two greatest angles at the coordination center. If the τ_5 value is closer to 0, the structure might be described as square pyramidal, whereas if this value is closer to 1, the correct description is a trigonal bipyramid. When the τ_5 value is exactly 0 or 1, then the structure can be treated as an ideal one, but in most examples this is not the case;[111]
b) This intramolecularly coordinated oxygen atom, led to the isolation of organotin(IV) species with an increased coordination number at the metal center, *i.e.* from four to five;

c) These derivatives can be seen as *10*-Sn-*5* species (following the *N*-X-*L* nomenclature system, where N is the number of electrons in the valence shell of a central atom X with L ligands directly bonded to it).[112]

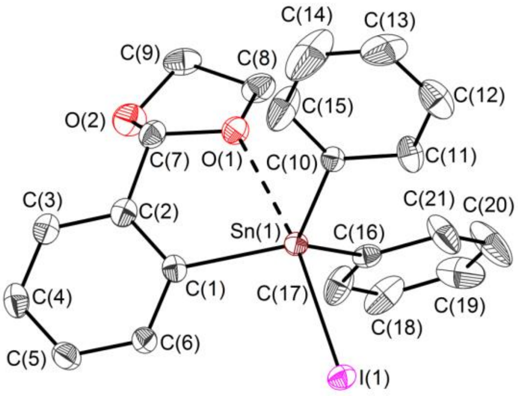
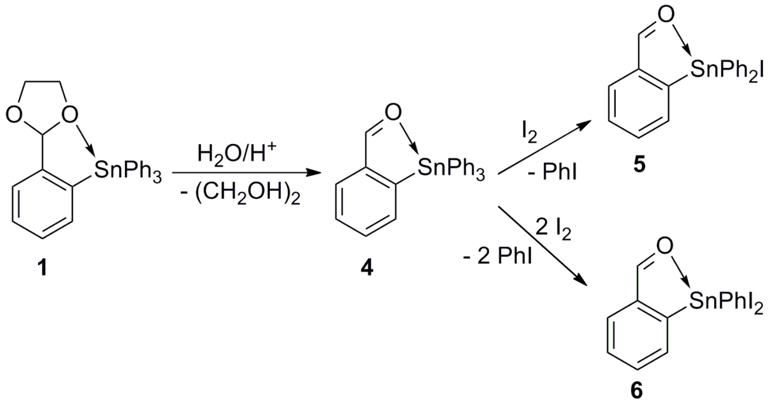


Figure 4. ORTEP drawing of $pR_{O(1)}S_{C(7)}$-**2a** showing 30% probability displacement ellipsoids and the atom numbering scheme.

1.3.2. Organotin(IV) species containing the 2-(O=CH)C6H4 fragment and aldol condensation products

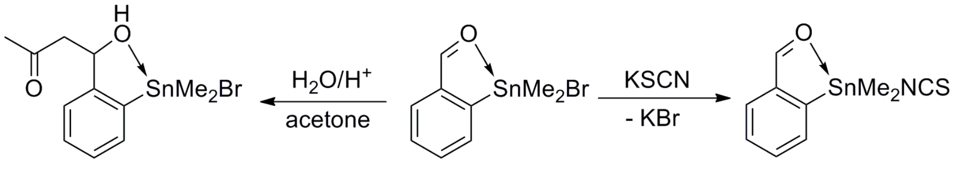
Compound [2-(O=CH)C_6H_4]$SnPh_3$ (**4**) was prepared by deprotection of the carbonyl function from [2-{$(CH_2O)_2CH$}C_6H_4]$SnPh_3$ (**1**), following an adapted literature protocol, used for mercury,[116] selenium,[117] or tin-containing species (Scheme 2).[67] Compound **4** was isolated as an air and moisture stable white powder.



Scheme 2. Synthesis of compounds **4**-**6**.

Treatment of **4** with different equivalents of elemental iodine allows the preparation of [2-(O=CH)C_6H_4]$SnPh_2I$ (**5**) and [2-(O=CH)C_6H_4]$SnPhI_2$ (**6**) in very good yields. The iodine derivatives are air and moisture stable and they are white (**5**) or pale yellow solids (**6**).

Deprotection of $[2\text{-}\{(CH_2O)_2CH\}C_6H_4]SnR_2X$ type derivatives (R = Me, Ph; X = Br, Cl) in acetone can give also aldol condensation products if the reaction time is excessively extended (Scheme 3).



8 **7**

Scheme 3. Synthesis of compounds **7** and **8**.

An anion exchange reaction was made from $[2\text{-}(O{=}CH)C_6H_4]SnMe_2Br$[67] with excess KSCN to give compound $[2\text{-}(O{=}CH)C_6H_4]SnMe_2NCS$ (**7**) as a white solid. If the same starting material is stirred for 48 h at room temperature in acetone with a small quantity of *p*-TsOH the condensation product $[2\text{-}\{CH_3C({=}O)CH_2(OH)CH\}C_6H_4]SnMe_2Br$ (**8**) can be obtained. Compound $[2\text{-}\{CH_3C({=}O)CH_2(OH)CH\}C_6H_4]SnPh_2Cl$ (**9**) was synthetized in a similar fashion starting from $[2\text{-}(O{=}CH)C_6H_4]SnPh_2Cl$ (prepared from **5** and NH_4Cl).

The presence of the carbonyl fragment O=CH- in compounds **4**-**7** can also be observed in the IR spectra. The carbonyl stretching vibration band, $\nu_{C=O}$, appears usually between 1710-1685 cm^{-1} if the C=O group is bonded to an aromatic moiety. The specific IR absorption band for the benzaldehyde is at 1696 cm^{-1}.[118]

Two strong peaks can be noticed at 1702 and 1675 cm^{-1} in the IR spectrum of compound **4**. For compound **5** the specific band was observed at 1643 cm^{-1}, while for **6** the peak was found at 1630 cm^{-1}. The $\nu_{C=O}$ stretching vibration bands for **5** and **6** are in agreement with a strong intramolecular coordination in the organotin(IV) species, they being shifted to lower values compared with the wavelength magnitude of benzaldehyde.

The solution behavior of the compounds **4**-**9** was monitored by NMR spectroscopy. The assignment of the ^1H and ^{13}C chemical shifts was made using 2D NMR correlation experiments (COSY, HSQC, HMBC).

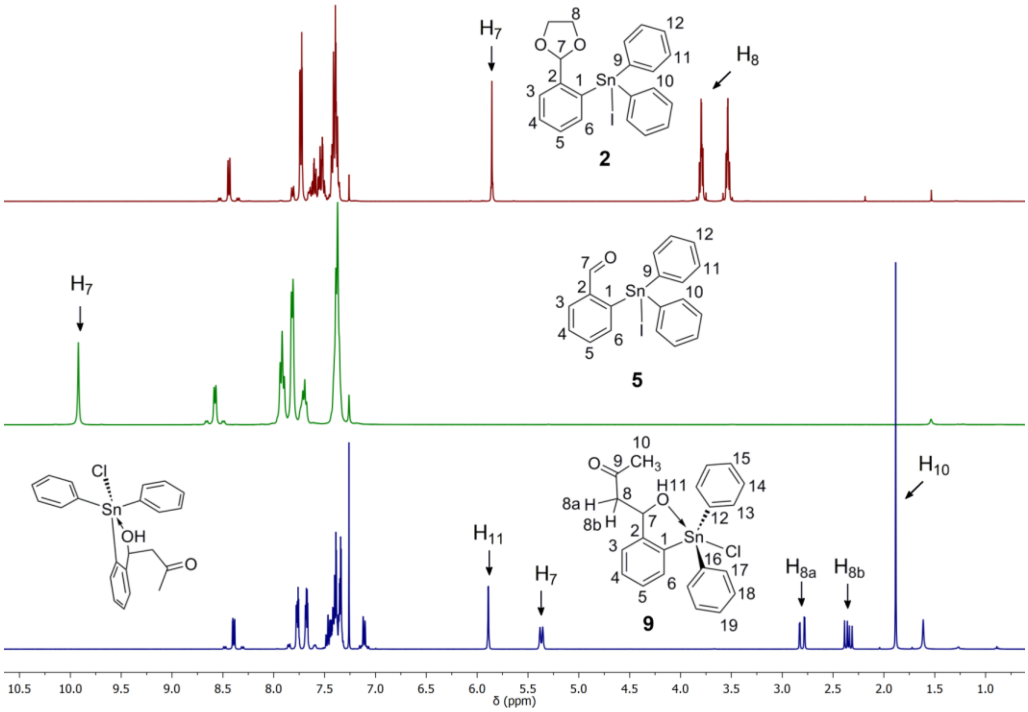


Figure 5. Stacked ^{1}H NMR spectra ($CDCl_3$, 20 °C) for compounds **2** (red), **5** (green) and **9** (blue).

The NMR spectra of compounds **4**-**9** were recorded in $CDCl_3$ at room temperature on either 400 or 600 MHz spectrometers. Hybridization change of the C_7 atom from *sp*^{3} (acetal fragment) to *sp*^{2} (aldehyde fragment) has a significant variation in the chemical shift, both in ^{1}H and ^{13}C NMR spectra. The resonance signals for H_7 are downfield shifted compared to the starting protected derivatives. All the expected resonance signals can be observed in the ^{1}H NMR spectrum of **5** (Figure 5).

The most deshielded singlet resonance signal in the ^{1}H NMR of **5** can be assigned to the H_7 hydrogen of the carbonyl function. This resonance is no longer visible in the ^{1}H NMR spectrum of **9**. A doublet resonance signal at 5.37 ppm (due to the H-H coupling with H_{8b} hydrogen) is corresponding to the H_7 hydrogen. The two hydrogen atoms (H_{8a}, H_{8b}) together with H_7 generate an AMX spin system. The pendant arm in **9** does not show any fluxional behavior in solution, either due to a strong O→Sn intramolecular interaction or due to its bulkiness which does not allow free rotation around the C(2)-C(7) bond. This is highlighted by the presence of two sets of resonances (both in the ^{1}H and ^{13}C NMR spectra) for the two different phenyl groups bounded to tin atom, one being on the same side with the pendant arm, while the other has a distinct environment.

^{1}H and ^{13}C NMR spectra of **4** and **6** present similar features: the resonance signals for H_7 are around 10 ppm as expected for the hydrogen of a carbonyl group. ^{1}H NMR spectrum of **6** is better resolved compared with the one for **4** with a triphenyltin moiety, which give 2 multiplets for 5 hydrogens (Figure 6, *left*). The signal corresponding for H_6 has also a significant shift in **6** (8.39 ppm) related to its starting material **4** (7.76 ppm). This downfield shift is a consequence of the 2 iodine atoms bonded to the metal center which change its Lewis acidity.

No uncommon aspects could be noticed in the ^{13}C NMR spectra of **4** and **6** (Figure 6, *right*). The resonances corresponding to C_7 are around 195 ppm, while the remaining aromatic signals are dispersed between 128 and 142 ppm.

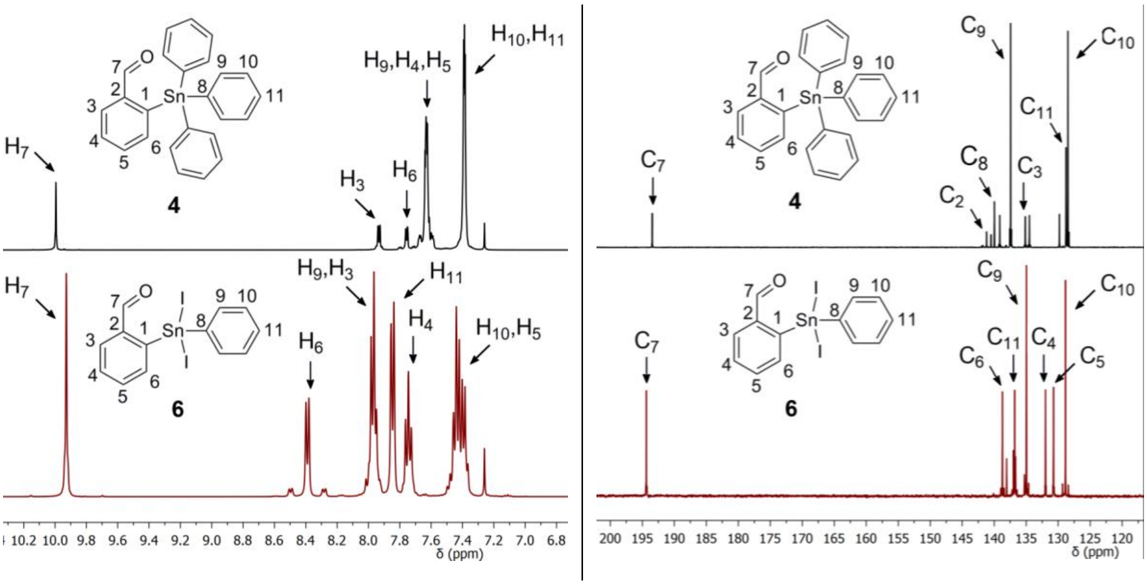


Figure 6. Stacked ^{1}H (*left*) and ^{13}C NMR (*right*) spectra ($CDCl_3$, 20 °C) for compounds **4** (black) and **6** (red).

Each ^{119}Sn NMR spectrum of compounds **4**-**9** shows a single resonance signal confirming the presence of one organotin(IV) species in solution (Figure 7). The same chemical behavior as for the protected precursors, can be noticed for compounds **4**-**6**, where a second iodine atom bound to the metal center brings a significant upfield shift in the ^{119}Sn NMR resonance of **6** (–312.74 ppm) compared with the chemical shift for **5** (–118.25 ppm). Due to a ^{119}Sn-^{14}N coupling the ^{119}Sn NMR resonance for **7** appears as a triplet ($^1J_{SnN}$ = 136.7 Hz), highlighting that the NCS ligand is attached by nitrogen to the tin atom. A similar behavior was observed in other organotin(IV) species containing the 2-(Me_2NCH_2)C_6H_4 fragment.[28] This great affinity of tin for nitrogen, nominate organotin(IV) pseudohalides to be used as potential spacers in coordination chemistry of transition metals with affinity for soft chalcogens (S, Se).

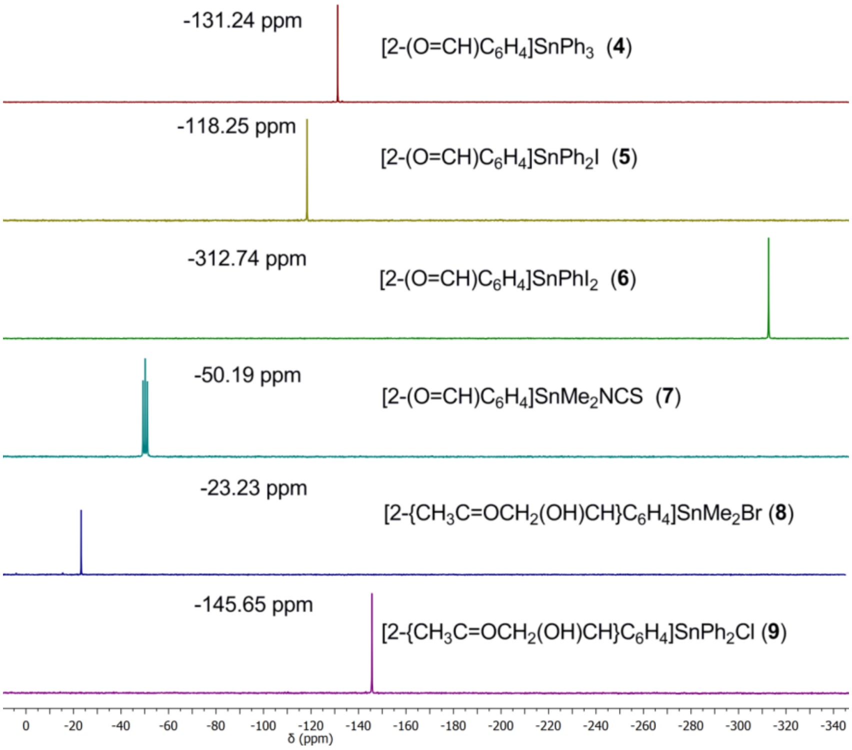


Figure 7. ^{119}Sn NMR stacked spectra ($CDCl_3$, 149.2 MHz) for compounds **4**-**9**.

The chemical shifts for compounds **7** and **8** match very well with those observed for $[2-(Me_2NCH_2)C_6H_4]SnMe_2Br$[31] (δ = –55.5 ppm), $[2-(Me_2NCH_2)C_6H_4]SnMe_2NCS$ (δ = –95.9t, $^1J_{SnN}$ = 139.4 Hz) or $[2-(O=CH)C_6H_4]SnMe_2Br$ (δ = 4.1 ppm) and are consistent with a penta-coordinated tin atom in solution.

Crystals of **5** and **9** contain two distinct molecules (indicated by **a** and **b**) in the asymmetric units with slightly differences in some interatomic distances and angles. Some common aspects have to be mentioned about the molecular structures of **5**, **6** and **9** (Figure 8): all these compounds are *10*-Sn-*5* species with a penta-coordinated tin atom due to a strong intramolecular O→Sn interaction, leading to a distorted trigonal bypiramidal coordination geometry. A halogen atom is always *trans* to the intramolecularly coordinated oxygen atom and they occupy the axial positions of the trigonal bipyramidal geometry.

When a second iodine atom is replacing one phenyl group at the tin atom, the geometry around the metal center in **6** becomes more distorted as the angles between the equatorial positions are between 107.4(2)° and 131.8(3)°, pretty far from the ideal 120° value.

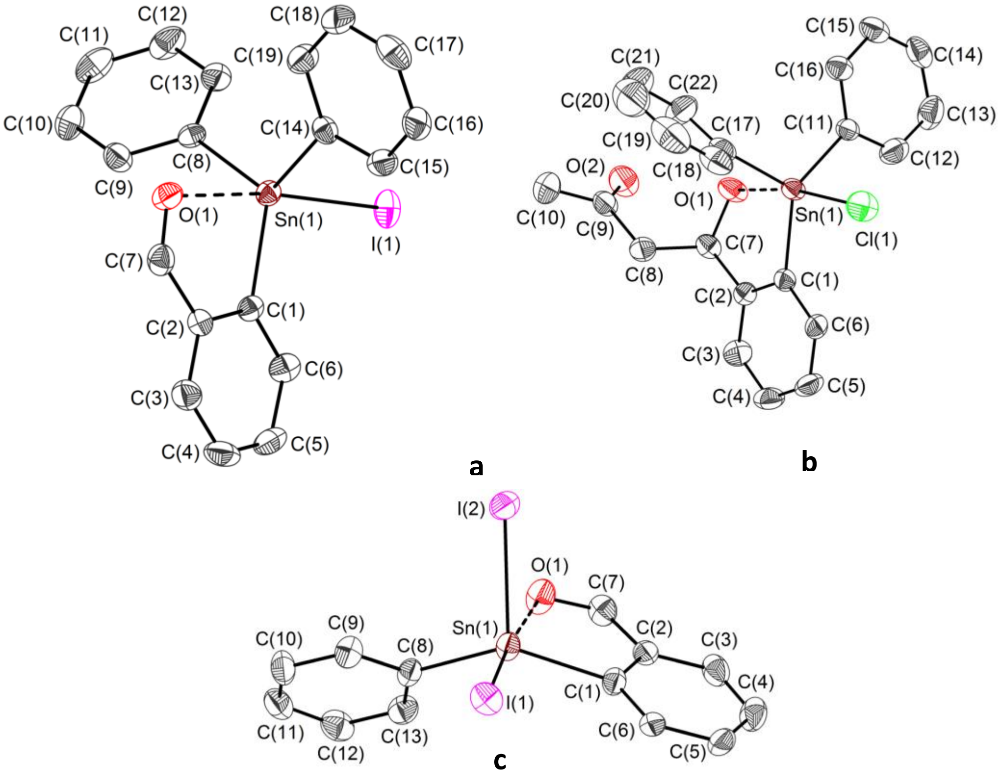


Figure 8. ORTEP drawings of **5a** (a), p$S_{O(1)}$-$R_{C(7)}$-**9a** (b) and *C*-**6** isomer (c) showing 30% probability displacement ellipsoids and the atom numbering scheme (hydrogen atoms were omitted for clarity).

Crystal of **7** contains two distinct molecules in the asymmetric unit. A distorted trigonal bypiramidal geometry [τ_5 = 0.83 (**7a**), 0.80 (**7b**) and 0.83 (**8**)] can be observed in the molecular structures of **7a**, **7b** and **8**. The equatorial sites are occupied by three carbon atoms with the equatorial angles between 116.4° and 121.1°, very close to the ideal value of 120° (Figure 9).

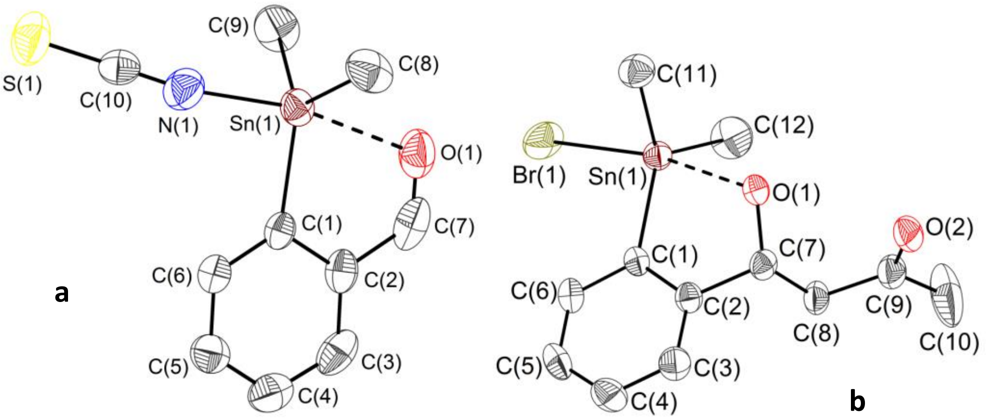
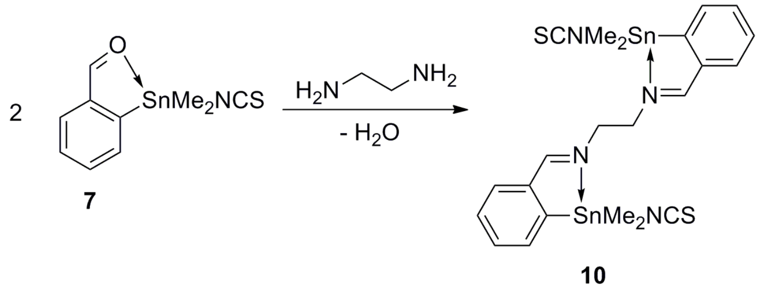


Figure 9. ORTEP drawings of **7a** (a) and p$S_{O(1)}$-$R_{C(7)}$-**8** (b), showing 30% probability displacement ellipsoids and the atom numbering scheme.

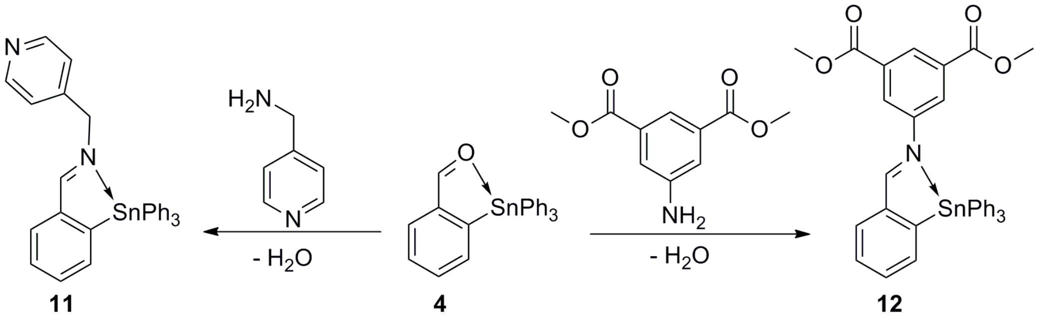
1.3.3. Organotin(IV) compounds with –C=N– bonds

Compounds **10**-**12** were synthesized by condensation reactions between organotin(IV) species bearing the 2-(O=CH)C_6H_4 moiety and different amines in the required molar ratios.



Scheme 4. Synthesis of **10**.

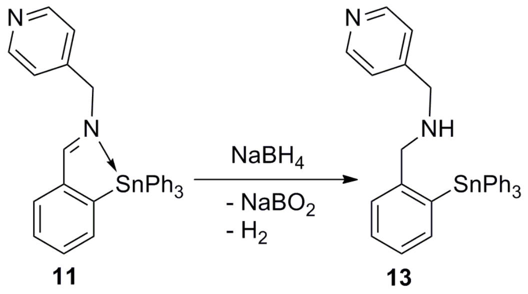
Compound (SCN)$SnMe_2$[2-C_6H_4(CH=NCH_2CH_2N=CH)-2'-C_6H_4]Me_2Sn(NCS) (**10**) was obtained by mixing 2 equivalents of **7** with 1 equivalent of ethylenediamine without a solvent or catalyst, just by heating the reaction mixture until a clear melt was obtained (Scheme 4). The temperature was maintained for 10 minutes and the resulting water was removed by vacuum to give, practically, a total conversion of the reagents to the imino compound, as the ^{1}H NMR spectra of the crude product shown.



Scheme 5. Synthesis of **11** and **12**.

In a similar fashion, compounds [2-(4'-PyCH_2N=CH)C_6H_4]$SnPh_3$ (**11**) and [2-(3',5'-$(MeOOC)_2C_6H_3$N=CH)C_6H_4]$SnPh_3$ (**12**) were obtained in excellent yields starting from deprotected derivative **4** and the corresponding amines in a 1:1 molar ratio (Scheme 5).

Reduction of **11** was also achieved after the treatment of the imino(aryl)tin(IV) derivative with an excess of $NaBH_4$ in THF to give [2-(4'-PyCH_2NHCH_2)C_6H_4]$SnPh_3$ (**13**) in a good yield (Scheme 6). The reaction steps had to be repeated, as the conversion after the first workup was just 60%



Scheme 6. Synthesis of **13**.

High-resolution mass spectra of organotin(IV) compounds **10**-**13** were recorded using atmospheric-pressure chemical ionization technique in order to confirm the identity of the products. MeCN was the solvent used for compounds **10** and **12**, while for compounds **11** and **13** a mixture of solvents has been used due to the low solubility in the usual MS solvents (MeOH+CHCl$_3$ for **11** and MeCN+CH$_2$Cl$_2$ for **13**). The APCI(+) spectrum of **10** shows a peak at *m/z* 591.98898 (93.48%) [M–SCN$^+$], while the base peak *m/*z 369.04111 was assigned to the [M–(SCN)$_2$–CH$_3$$^+$] fragment. The molecular peak for **11** can be noticed at *m/*z 547.12062 (15.79%) and the base peak (*m/*z 469.07343) is assigned to the [M–Ph$^+$] fragment. No molecular peak can be detected in the HR-MS spectrum of **12**, but the base peak at *m/*z 570.07211 is corresponding to the [M–Ph$^+$] fragment. A similar fragmentation pattern was observed also for **13** when the same [M–Ph$^+$] fragment is found at *m/*z 471.08632, while the molecular peak appears at *m/*z 549.13326 (66.98%).

For the compounds containing imino moieties, IR spectra have confirmed the presence of the C=N bond in the molecule. The stretching vibration band characteristic for the carbon-nitrogen double bond appears in the 1690-1520 cm^{-1} range.[118] Indeed, medium to strong absorption bands corresponding to the imino group were observed at 1632 cm^{-1} for **10**, 1645 cm^{-1} for **11**, and 1634 cm^{-1} for **12**. A sharp medium absorption band can be noticed at 3307 cm^{-1} in the IR spectrum of **13**, which is typical for the stretching vibration of the N–H bond of a secondary amine.

The solution behavior of organotin(IV) species **10**-**13** was investigated by NMR spectroscopy. These spectra were recorded in CDCl$_3$ or DMSO-d$_6$ and the assignment of the ^{1}H and ^{13}C chemical shifts was made using two-dimensional NMR experiments together with the coupling constants of the tin satellites (if they were visible).

Due to the poor solubility in $CDCl_3$, the NMR experiments for compound **10** were recorded in DMSO-d_6. However, just the ^1H and ^{13}C NMR experiments gave satisfactory results, whereas for the ^{119}Sn NMR, no resonance could be found.

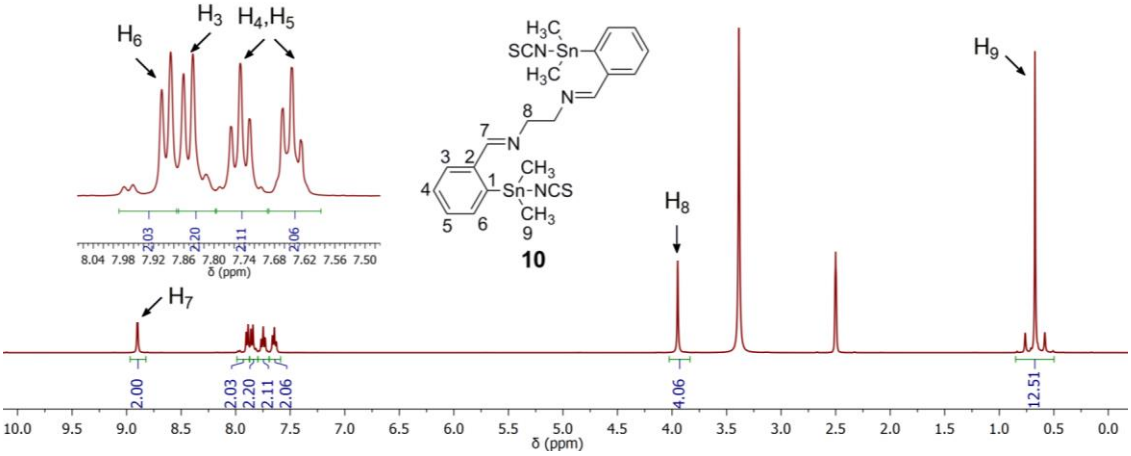


Figure 10. ^1H NMR spectrum (DMSO-d_6, 20 °C) of **10**.

All the expected resonance signals are visible in the ^1H NMR spectrum of **10** (Figure 10). The resonance signal around δ = 9 ppm was assigned for the imino hydrogen H_7 and this chemical shift is in agreement with the characteristic magnitude for such type of hydrogens.

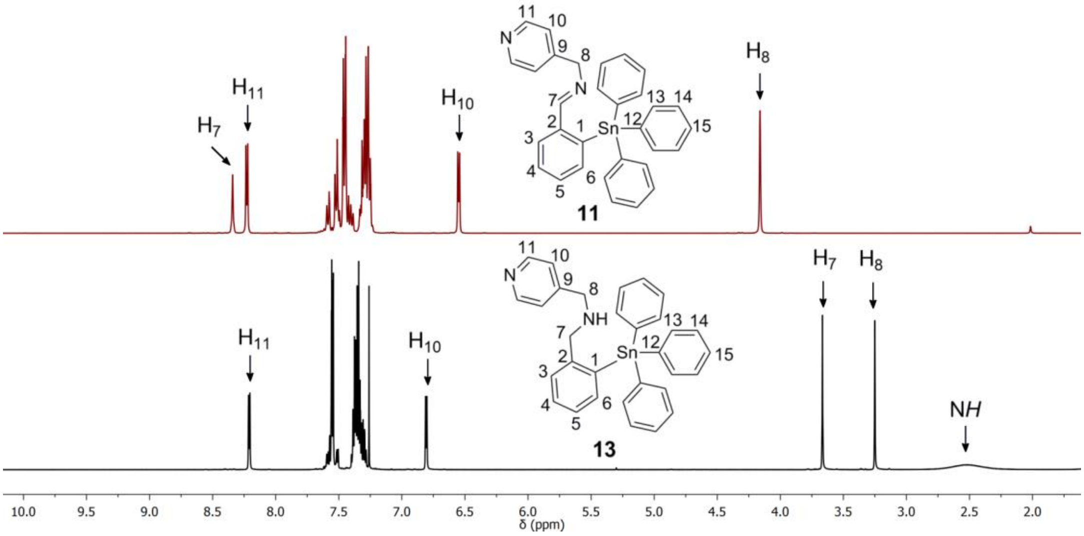


Figure 11. Stacked ^1H NMR spectra ($CDCl_3$, 20 °C) of compounds **11** (red) and **13** (black), only the significant resonances are indicated.

The conversion of the imine derivative **11** to amine complex **13** can be easy monitored by ^1H NMR, as the hybridization changes which took place are clearly observed in the ^1H NMR of **13** (Figure 11).

Each of the compounds **11**-**13** present one resonance signal in ^{119}Sn NMR (Figure 12), while for complex **10** no resonance could be detected due to the poor solubility of the compound, as mentioned before.

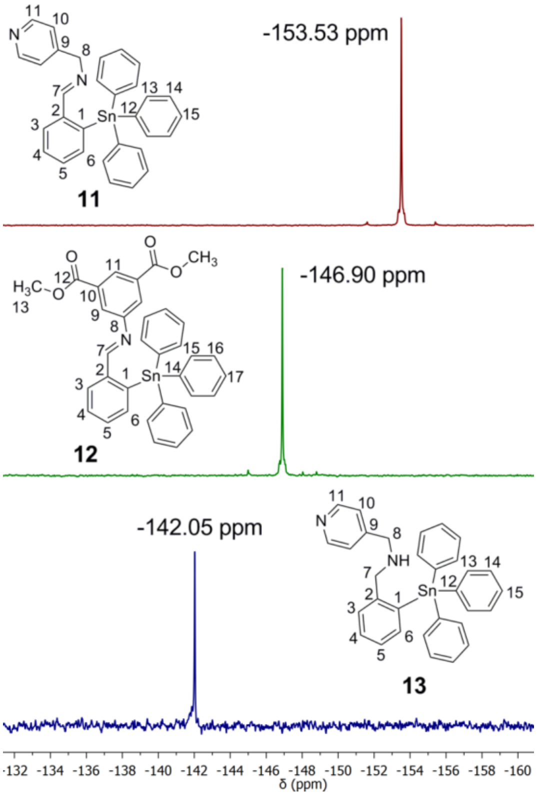


Figure 12. Stacked ^{119}Sn NMR spectra ($CDCl_3$, 20 °C) of compounds **11** (red), **12** (green) and **13** (blue).

The molecular structures of compounds **10**-**13** (Figures 13-14) reveal penta-coordinated tin cores as a result of intramolecular N→Sn coordination.

The strength of these contacts can fluctuate with respect to the moiety attached to tin in *trans* position to the nitrogen atom from the pendant arm (-NCS or Ph, in this particular case), while the hybridization of the pendant arm nitrogen atom must also be considered.

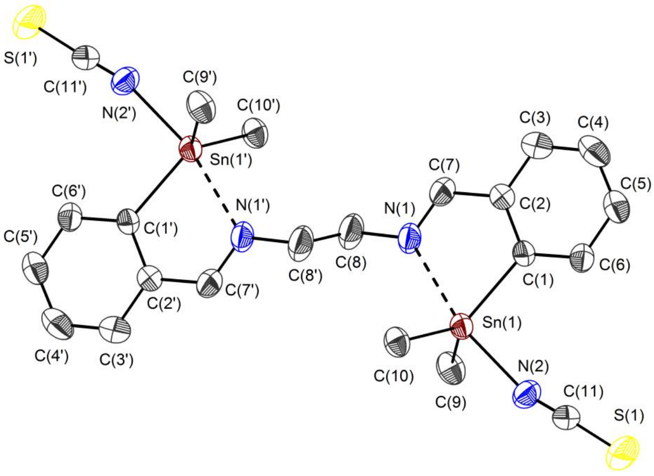


Figure 13. ORTEP drawings of **10** showing 30% probability displacement ellipsoids and the atom numbering scheme.

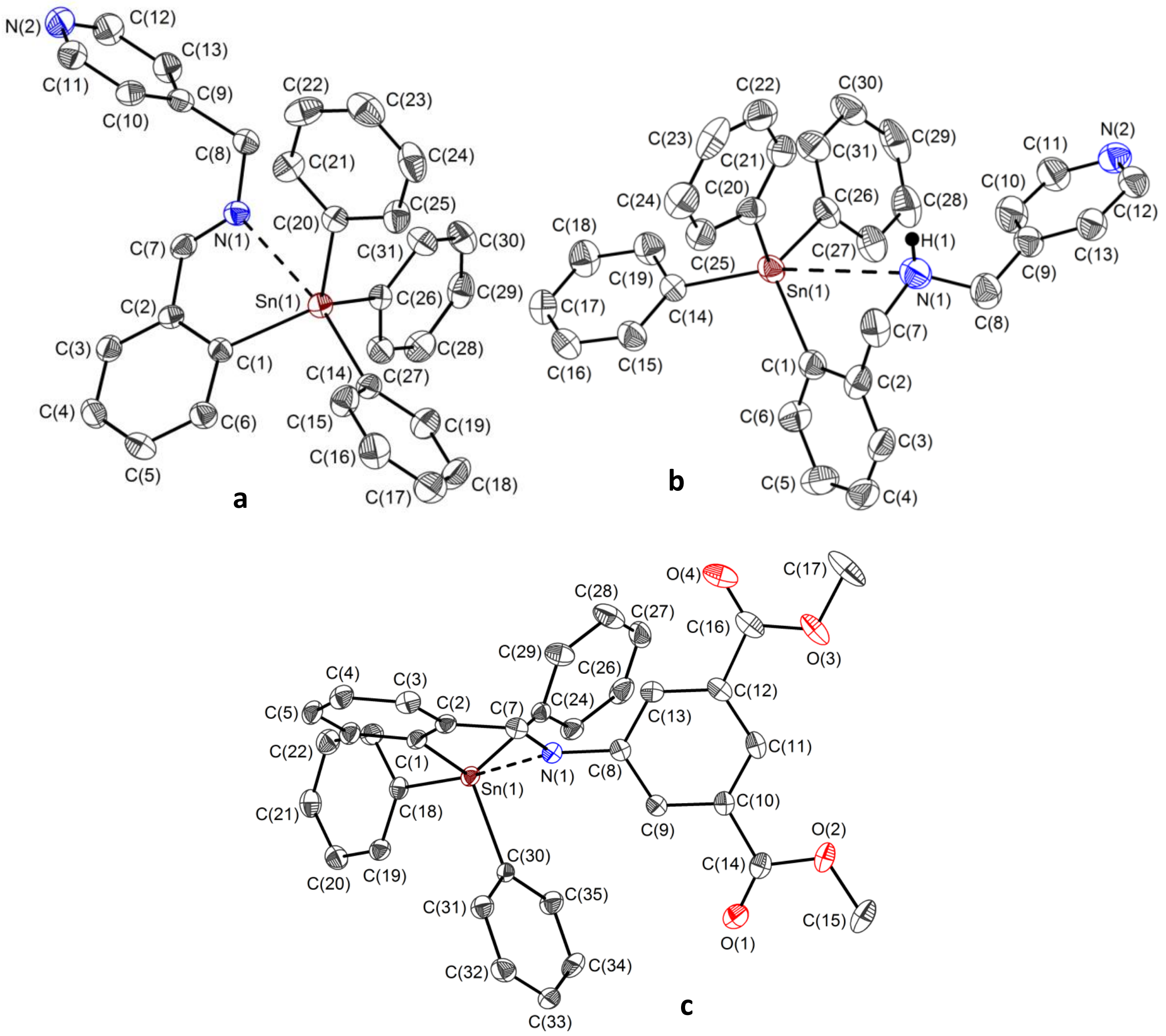
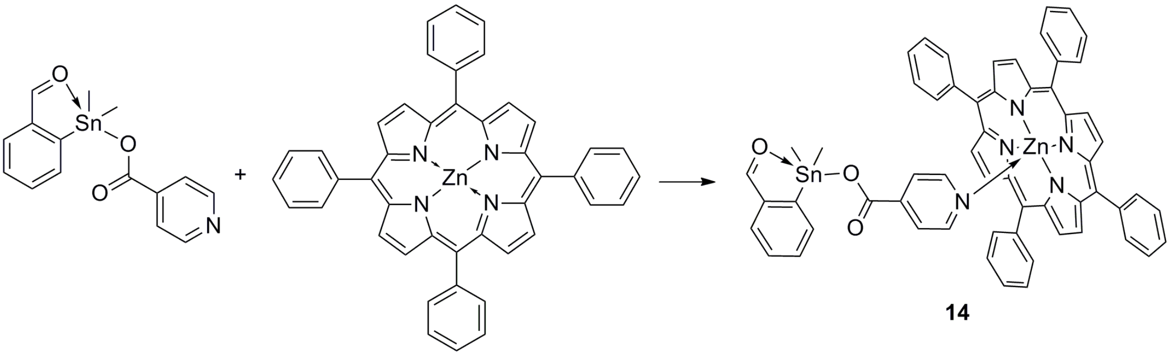


Figure 14. ORTEP drawings of **11** (a) **13** (b) and **12** (c) showing 30% probability displacement ellipsoids and the atom numbering scheme.

The N→Sn contact in **10** [2.398(4) Å] is stronger than in the other species containing triphenyltin moiety, *i.e.* 2.759(2) Å for **11** and 2.792(2) Å for **12**, but similar with those found in analogue species, *e.g.*: [2-(2'-$PyCH_2N=CH)C_6H_4]SnMe_2Br$ [2.387(3) Å], [2-(4'-$PyCH_2N=CH)C_6H_4]SnMe_2Br$ [2.376(4) Å], or [2-{4'-{MeO(O)C}$C_6H_4N=CH\}C_6H_4]$-$SnMe_2Br$ [2.474(4) Å]. These data suggest that the phenyl group *trans* to the donor atom weakens the N_{imine}→Sn intramolecular interaction, compared with a halide or a pseudo-halide fragment in a similar position.

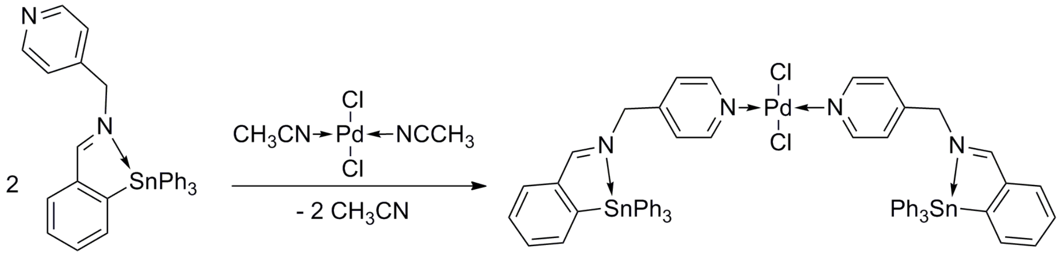
1.3.4. Heterobimetallic complexes with organotin(IV) ligands

Treatment of [2-(O=CH)$C_6H_4]Me_2SnO(O)CC_5H_4N$-4,[123] with ZnTPP in CH_2Cl_2 followed by hexane addition, allows the isolation of [{2-(O=CH)$C_6H_4\}Me_2SnO(O)CC_5H_4N$-4]ZnTTP (**14**) as deep purple crystals (Scheme 7). Adding more equivalents of the organotin(IV) ligand does not change the outcome.



Scheme 7. Synthesis of complex **14**.

The addition of two equivalents of [2-(4'-$PyCH_2N=CH)C_6H_4]SnPh_3$ (**11**) to one equivalent of $PdCl_2(CH_3CN)_2$ in $CHCl_3$ led to the formation of complex [{2-(4'-$PyCH_2N=CH)C_6H_4\}SnPh_3]_2PdCl_2$ (**15**) as a yellow powder, not very sensitive to moisture (Scheme 8).



11

15

Scheme 8. Synthesis of complex **15**.

HR-MS APCI(+) analysis (in MeCN + CH_2Cl_2) was performed for complex **15** and the fragmentation pattern was similar with that observed for the starting organotin(IV) compound **11**. No molecular peak could be noticed, but the peak corresponding to organotin(IV) ligand was observed at *m/z* 547.11743 (14.27%). The base peak (*m/z* 469.07059) was found to be the organotin(IV) ligand without a phenyl group [R-Ph$^+$]. The purity of the heterometallic complex **15** was also confirmed by elemental analysis [$C_{62}H_{52}Cl_2N_4PdSn_2$ (MW = 1267.85): C, 58.73; H, 4.13; N, 4.42 Found: C, 58.77; H, 4.08; N, 3.80].

Infrared spectroscopy of **14** highlights the stretching vibrations of the C=O double bonds, both for carbonyl and carboxyl groups, with two sharp bands at 1591 cm^{-1} and 1651 cm^{-1}, respectively. For complex **15** the C=N stretching vibration could be observed at 1647 cm^{-1}, as typical for such type of vibration.

The solution behavior of the heterometallic species **14** and **15** was investigated by NMR spectroscopy. The NMR spectra were recorded in $CDCl_3$ and the assignment of the ^1H and ^{13}C chemical shifts was made using two-dimensional NMR experiments together with the coupling constants of the tin satellites (where they were visible).

The ^1H NMR spectrum of **14** reveals one set of resonances for each organic fragment in the molecule, as expected. A significant upfield shift was observed for all the resonances corresponding to the organotin(IV) moiety in **14** with respect to the starting compound.

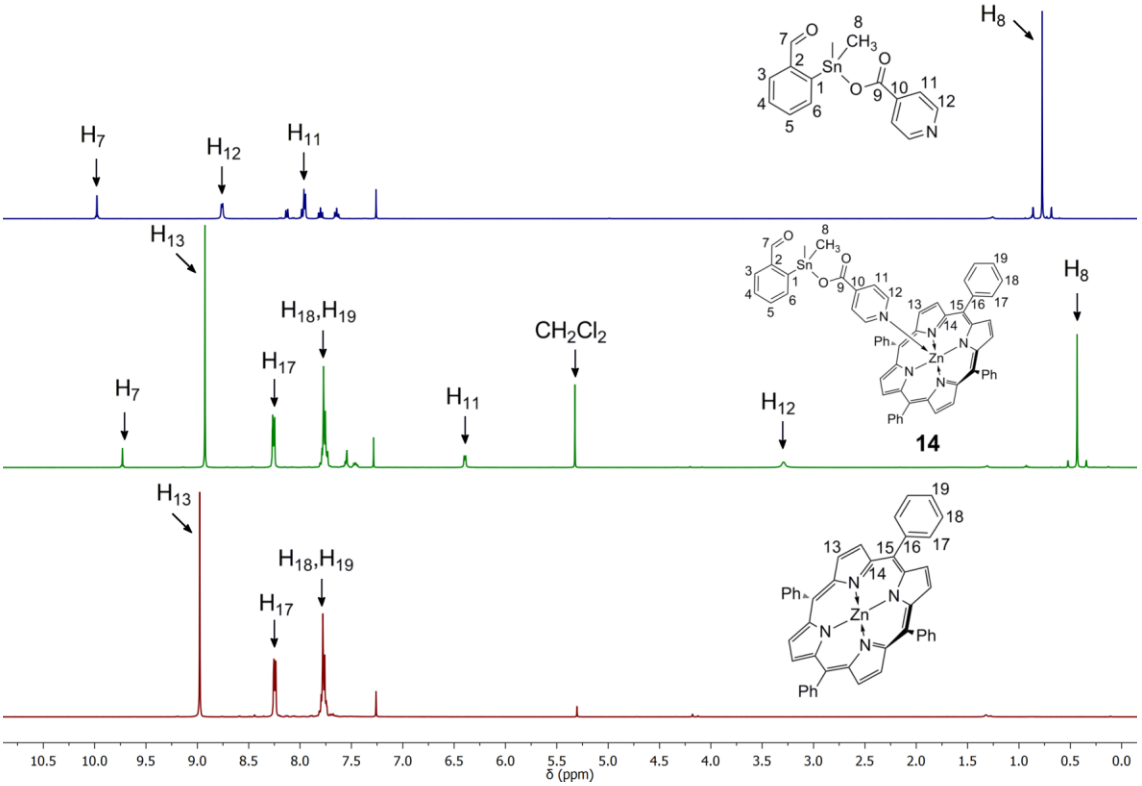


Figure 15. Stacked ^{1}H NMR spectra ($CDCl_3$, 20 °C) of [2-(O=CH)C_6H_4]$Me_2SnO(O)CC_5H_4N$-4 (blue), complex **14** (green) and ZnTPP (red).

The most important change was in the case of hydrogens H_{11} and H_{12} from the pyridyl group which is directly bounded to the zinc center (Figure 15). The resonance for H_{12} has been shifted from δ = 8.76 ppm in the free organotin(IV) precursor to δ = 3.27 ppm in **14**, while H_{11} was detected at δ = 6.37 ppm in **14**, shifted from δ = 7.95 ppm in **11**. These chemical shifts are consistent with other pyridine-ZnTPP systems reported in the literature.[124] Methyl hydrogens H_8 in **14** appear as a singlet resonance signal surrounded by tin satellites at δ = 0.41 ppm, compared to δ = 0.77 ppm in the free ligand.

Only one resonance signal could be noticed in the ^{119}Sn NMR spectra of each of complexes **14** and **15** suggesting the presence of a unique species in solution. The values of the ^{119}Sn NMR chemical shifts in **14** (δ = –19.23 ppm) and **15** (δ = –150.23 ppm) are slightly distinct compared with those of the organotin(IV) precursors.

Single-crystals of good quality have been obtained by slow diffusion of hexane into a CH_2Cl_2 solution of **14** or into a $CHCl_3$ solution of **15**, respectively. The X-Ray diffraction studies were carried out at 150 K in order to get better diffraction data. However, for complex **15** some disorder was observed for one phenyl fragment.

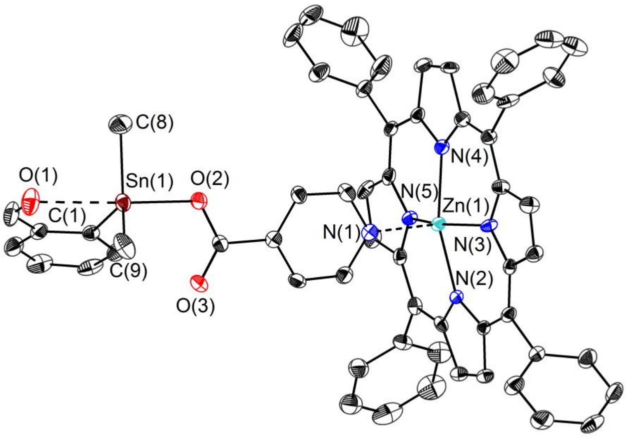


Figure 16. ORTEP drawings of **14** showing 30% probability displacement ellipsoids (only significant atoms were labeled).

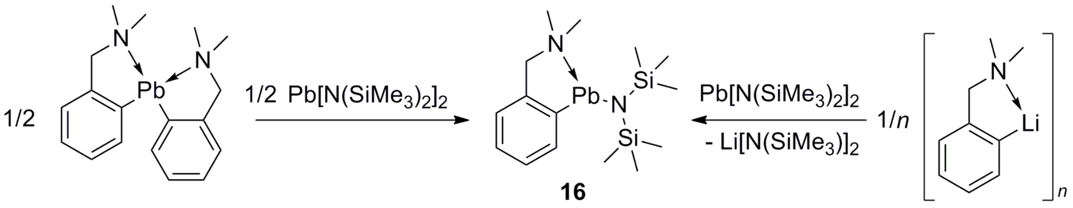
The molecular structure of compound **14** was investigated by X-Ray diffraction and the formation of the complex was confirmed. Compound **14** crystalizes with a dichloromethane molecule in the unit cell. Two pentacoordinated distinct metallic centers could be found in the molecule of **14** (Figure 16): the tin atom adopts a distorted trigonal bipyramidal coordination geometry due to a strong O→Sn intramolecular coordination, while the zinc center is involved in a distorted square pyramidal geometry. Four nitrogen atoms from the porphyrinic system set up the base of the pyramid, with the zinc center out of the best plane created by these four nitrogen atoms by 0.35 Å towards the coordinating isonicotinate. The interatomic distances between zinc atom and the porphyrin nitrogen atoms range between 2.087(6) Å and 2.093(5) Å, while the apical Zn(1)–N(1) is 2.162(4) Å, as typical for a ZnTPP system.

PART 2

Synthesis and structural characterization of new homo- and heteroleptic lead(II) species

2.3.1. Lead(II) complexes

Compound $[2\text{-}(Me_2NCH_2)C_6H_4]Pb[N(SiMe_3)_2]$ (**16**) was obtained in a very good yield by treating overnight one equivalent of $[2\text{-}(Me_2NCH_2)C_6H_4]_2Pb$[156] with one equivalent of $Pb[N(SiMe_3)_2]_2$ (Scheme 9), in Et_2O at room temperature.



Scheme 9. Synthesis of complex **16**.

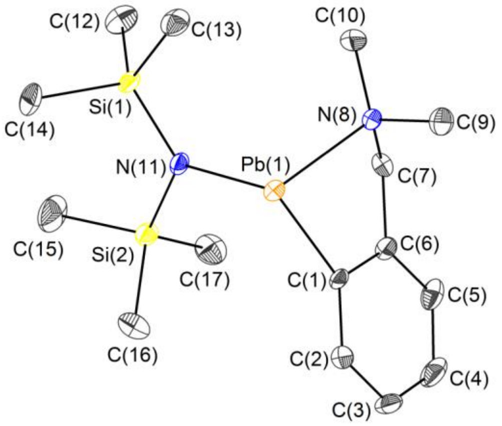
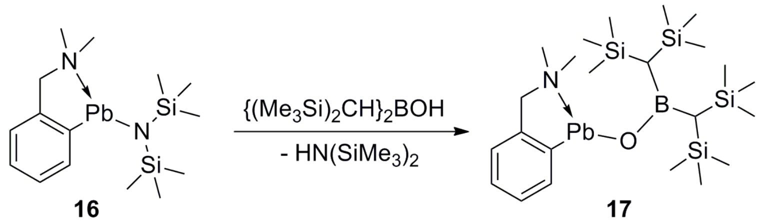


Figure 17. ORTEP drawing of S_NS_{Pb}-**16** isomer showing 50% probability displacement ellipsoids and the atom numbering scheme (hydrogen atoms were omitted for clarity).

Lead atom in **16** is 3-coordinate with a distorted pyramidal geometry having the surrounding angles in the range 73.25(1)-99.02(1)° (Figure 17). The Pb(1)–N(8) intramolecular interaction of the N_{amine} in the pendant arm is stronger in **16** (2.490(3) Å) than in the 4-coordinate $[2\text{-}(Me_2NCH_2)C_6H_4]_2Pb$ [2.616(3)–2.727(3) Å],[156] but the Pb–C interatomic distances in the two complexes are similar.

Three different singlet resonance signals can be observed, as expected, in the aliphatic region of ^{1}H NMR spectrum for complex **16**, while four well-resolved resonances (2 doublets and 2 triplets) can be distinguish in the aromatic region. In ^{207}Pb NMR spectrum of **16** a single resonance was detected at δ = 2595 ppm, close to the value for the starting diaryllead(II) complex, δ = 2624 ppm.[156]

In our pursuit for a new class of lead(II) alkoxides, more specifically, boroxides, complex **16** was reacted with a very bulky borinic acid $[(Me_3Si)_2CH]_2BOH$[197] which was considered a suitable candidate to avoid the tendency of regular alkoxides to form lead(II) oxo-clusters. Indeed, when **16** was treated with $[(Me_3Si)_2CH]_2BOH$ in Et_2O, at room temperature, the heteroleptic aryllead(II) boryloxide $[2-(Me_2NCH_2)C_6H_4]Pb[OB\{CH(SiMe_3)_2\}_2]$ (**17**) was isolated in a moderate yield (Scheme 10).[198]



Scheme 10. Synthesis of **17**.

Complex **17** was obtained as a very air- and moisture-sensitive colourless solid and crystalized from a concentrated pentane solution at –40 °C. The complex displays a resonance at δ = 48.1 ppm in the ^{11}B NMR spectrum, which is shielded by ca. 5 ppm compared to the starting borinic acid. In the ^{207}Pb NMR spectrum, a single resonance was detected at δ = 3095 ppm.

The composition and structure of **17** were validated by single-crystal X-ray diffraction analysis (Figure 18) to reveal the same 3-coordinate Pb atom as in **16**. The Pb(1)–N(8) and Pb(1)–C(1) interatomic distances match very well with those found in **16**, while the angles around the metal center are significantly altered compared to those found in the structure of the amido precursor **16**.

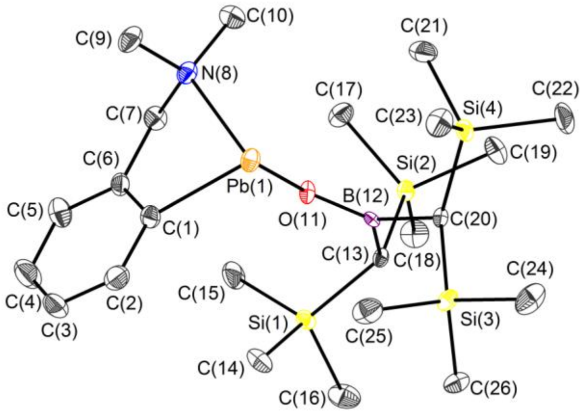
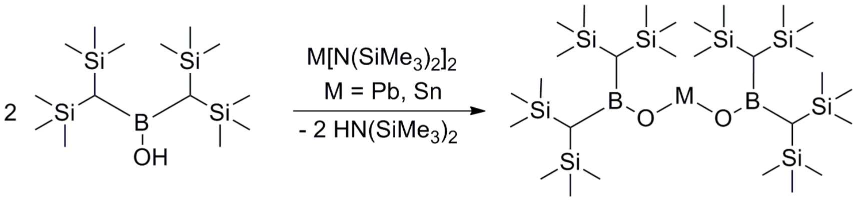


Figure 18. ORTEP drawing of R_NR_{Pb}-**17** isomer showing 50% probability displacement ellipsoids and the atom numbering scheme (hydrogen atoms were omitted for clarity).

Following simple protocols, complex Pb[OB{CH(SiMe$_3$)$_2$}$_2$]$_2$ (**18**) and its tin congener Sn[OB{CH(SiMe$_3$)$_2$}$_2$]$_2$ (**19**) were synthesized by treating M[N(SiMe$_3$)$_2$]$_2$ (M = Pb, Sn) with 2 equivalents of borinic acid [(Me$_3$Si)$_2$CH]$_2$BOH at room temperature (Scheme 11).



M = Pb **18**
M = Sn **19**

Scheme 11. Synthesis of homoleptic boroxides **18** and **19.**

Complex **18** was isolated in an excellent yield as a very pale yellow, air-sensitive solid, after removal of the volatiles. Its purity and molecular structure were established after spectroscopic and crystallographic investigations. It shows good solubility in common organic solvents, including aromatic and aliphatic hydrocarbons and crystalizes from pentane as big-block colorless crystals. Complex **18** is the first known lead(II) boroxide.[199] In a similar fashion, complex **19** was obtained in a very good yield and crystalized as colorless plates.

The NMR spectroscopic data were recorded in C_6D_6 for both complexes, but due to the simplicity of the organic ligand, the ^{1}H and ^{13}C spectra will not be displayed, as only two resonances for each of the complexes are observed as expected. The ^{11}B NMR spectrum of **18**, reveals a single resonance at δ = 53.5 ppm, which is very close to the resonance observed for [(Me$_3$Si)$_2$CH]$_2$BOH in the same solvent (δ = 53.3 ppm), but shifted with ca 5 ppm compared with that of the heteroleptic complex **17** (δ = 48.1 ppm). In its ^{207}Pb NMR spectrum, compound **18** displays a very sharp resonance at δ = 1808 ppm.

The two molecular structures of **18** and **19** are isomorphous and both display monometallic species with a two-coordinate metal center (Figure 19).

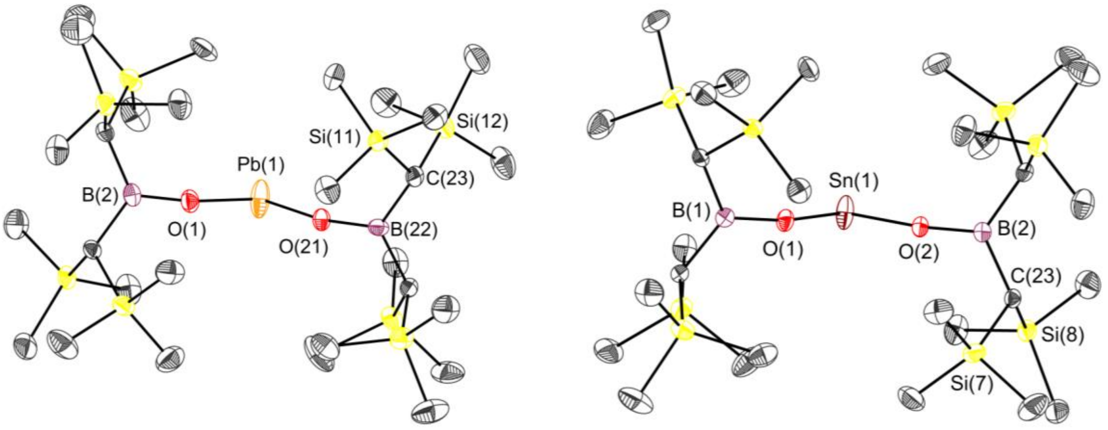


Figure 19. ORTEP drawings of **18** (*left*) and **19** (*right*) showing 50% probability displacement ellipsoids (hydrogen atoms were omitted for clarity).

The Pb(1)–O(1) and Pb(1)–O(21) interatomic distances of 2.067(6) and 2.089(5) Å are significantly shorter than in the bis-alkoxo complexes $[\mathrm{Pb}(\mu\text{-O}^i\mathrm{Pr})_2]_\infty$ [2.210(3)–2.522(2) Å][137b] and $[\mathrm{Pb}\{(\mu\text{-O}^t\mathrm{Bu})_2]_3$ [2.17(1)–2.55(1) Å],[142] or in the amido-alkoxide $[\mathrm{Pb}\{\mathrm{N}(\mathrm{SiMe}_3)_2\}(\mu\text{-O}^i\mathrm{Pr})]_2$ [2.289(9) Å][137b] and in the amido-siloxide $[\mathrm{Pb}\{\mathrm{N}(\mathrm{SiMe}_3)_2\}(\mu\text{-OSiMe}_3)]_2$ [2.276(8)–2.291(8) Å].[138]

Attempts to prepare a homoleptic lead(II) bis-alkoxide by treatment of the electron-poor hexafluoroisopropanol, $(\mathrm{CF}_3)_2\mathrm{CHOH}$, with $\mathrm{Pb}[\mathrm{N}(\mathrm{SiMe}_3)_2]_2$ in pentane only yield the oxocluster $[\mathrm{Pb}_4(\mu^4\text{-O})\{\mu\text{-OCH}(\mathrm{CF}_3)_2\}_5\{\mu^3\text{-OCH}(\mathrm{CF}_3)_2\}]$ (**20**). Other Pb(II) complexes containing this alkoxide moiety were reported in the past, *e.g.* the dimethylaminopyridine adduct $[\mathrm{Pb}\{\mu\text{-OCH}(\mathrm{CF}_3)_2\}\{\mathrm{OCH}(\mathrm{CF}_3)_2\}(\mathrm{DMAP})]_2$ or the salt $[\mathrm{Me}_2\mathrm{NH}_2]_2[\mathrm{Pb}_2\{\mu\text{-OCH}(\mathrm{CF}_3)_2\}_2\{\mathrm{OCH}(\mathrm{CF}_3)_2\}_4]$,[147] and the heterometallic species $[\mathrm{Li}_2\mathrm{Pb}_2\{\mu\text{-OCH}(\mathrm{CF}_3)_2\}_4\{\mu^3\text{-OCH}(\mathrm{CF}_3)_2\}_2]$.[148]

The ^{1}H and ^{19}F NMR spectra of **20** clearly indicate the presence of a single species in solution. A nice heptet signal (δ = 4.82 ppm) was detected in ^{1}H NMR spectrum of **20** ($^3J_{\mathrm{HF}}$ = 6 Hz), while the ^{19}F NMR shown a sharp resonance at δ = –75.46 ppm.

However, when the single-crystals were investigated by X-Ray diffraction analysis, two types of $(CF_3)_2CHO^-$ groups were observed in the molecular structure of the oxocluster **20**, giving a *C*s symmetry to the Pb_4O_7 core (Figure 20).

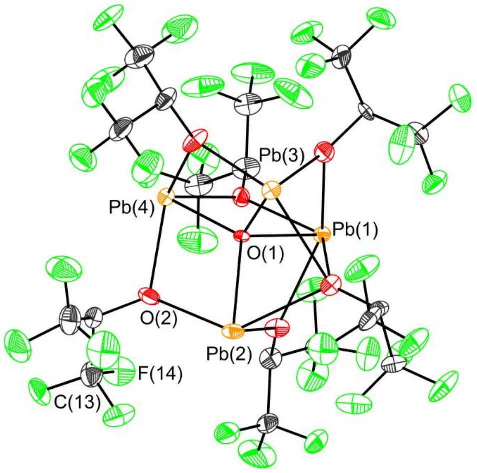
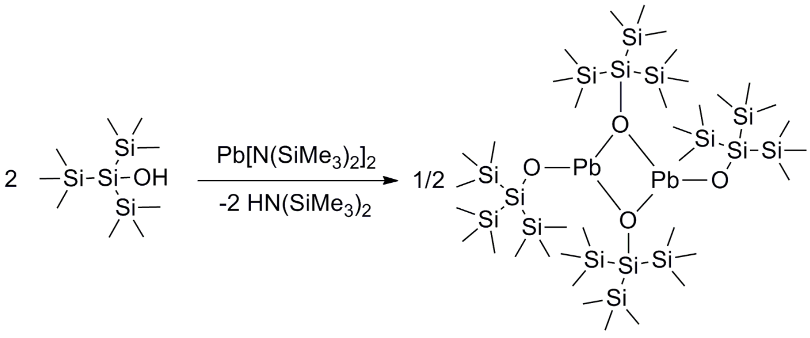


Figure 20. ORTEP drawing of **20** showing 50% probability displacement ellipsoids (hydrogen atoms were omitted for clarity).

The structure of compound **20** compares well with the adamantane-like $[Pb_4(\mu^4\text{-}O)(\mu\text{-}OSiPh_3)_6]$[154] and $[Pb_4(\mu^4\text{-}O)(\mu\text{-}O^tBu)_6]$,[144] but one of the $(CF_3)_2CHO^-$ ligands displays a μ^3-binding mode, while the remaining 5 fragments are each bridging just two Pb atoms.

On the way to get the first homoleptic lead(II) bis-siloxide, the perfect candidate to generate the desired complex was finally found. Indeed, reaction of $Pb[N(SiMe_3)_2]_2$ with 2 equivalents of $(Me_3Si)_3SiOH$ in Et_2O afforded the expected homoleptic complex $[Pb\{\mu\text{-}OSi(SiMe_3)_3\}\{OSi(SiMe_3)_3\}]_2$ (**21**) as a dimer, without formation of an oxocluster (Scheme 12).



21

Scheme 12. Synthesis of complex **21**.

The ^1H NMR of the complex shown a slightly broad singlet resonance at $\delta = 0.38$ ppm, while a broad resonance could be detected in the ^{207}Pb NMR spectrum at $\delta = 1349$ ppm.

The molecular structure of **21** was established after a single-crystal X-ray diffraction analysis. An unusual bent of the four-member ring is observed in the dimeric structure of **21** (Figure 21), similar with that found in the molecular structure of [Sn(μ-$OSiPh_3$)($OSiPh_3$)]$_2$.[200]

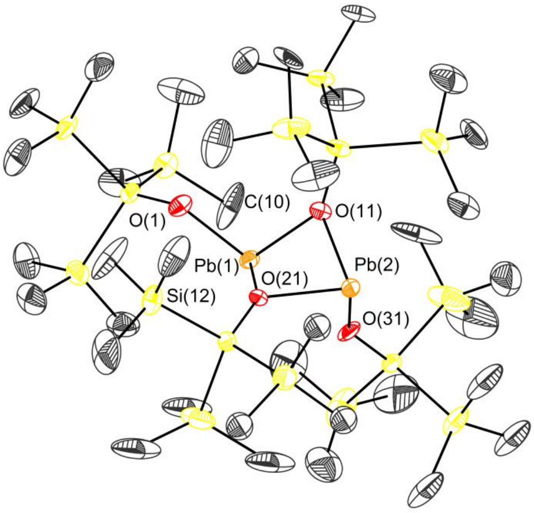
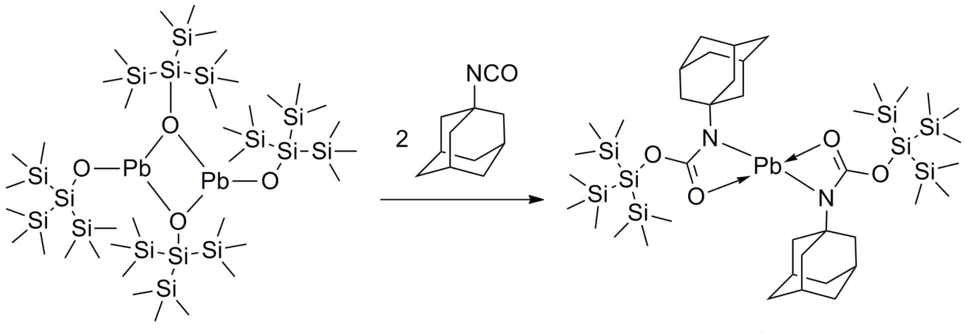


Figure 21. ORTEP drawing of **21** showing 50% probability displacement ellipsoids (hydrogen atoms were omitted for clarity).

This folding of the four-member core may be a result of a weak interaction between O(31) and Pb(1) [O(31)···Pb(1) = 2.997(9) Å]. Both metallic centers are involved in trigonal pyramidal coordination geometry.

The reactivity of **21** towards various functionalities, for instance, isocyanate, carbodiimide, CO_2 or CS_2 is expected to be similar with that of other lead(II) alkoxides.[151] When complex **21** was reacted with 1-adamantyl isocyanate in a 1:2 molar ratio, the expected carbamate Pb[N(Ad)C(O)OSi($SiMe_3$)$_3$]$_2$ (**22**) was formed (Scheme 13).

The reaction was performed in Et_2O overnight and after the work-up, compound **22** was isolated as an off-white solid in good yield. Recrystallization from a petroleum ether/ Et_2O mixture at –5 °C affords suitable crystals for X-Ray diffraction analysis. Even after successive recrystallizations, some traces of unreacted 1-adamantyl isocyanate could be detected in the ^1H and ^{13}C NMR spectra of **22**.



21 **22**

Scheme 13. Synthesis of **22**.

Nevertheless, the ^{29}Si NMR spectrum of the complex displays just two resonances as expected for the 2 different types of silicon atoms present in the molecule, while a unique broad resonance was detected in the ^{207}Pb NMR spectrum of **22** (δ = 929.4 ppm).

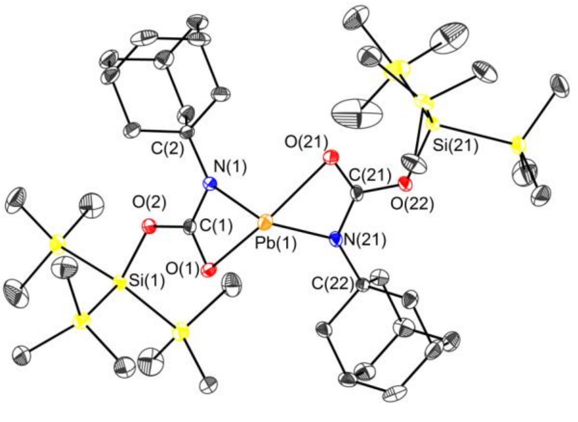
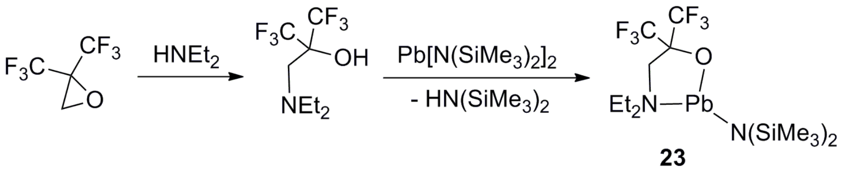


Figure 22. ORTEP drawing of **22** showing 50% probability displacement ellipsoids (hydrogen atoms were omitted for clarity).

The lead(II) complex **22** is a nice example of hemidirected coordination[18] where the 6*s* electron pair is stereochemically active taking the apical position in the square pyramidal geometry (Figure 22). The N–Pb interatomic distances [Pb(1)–N(1) = 2.289(2) Å, Pb(1)–N(21) = 2.293(2) Å] are slightly shorter than in the heteroleptic carbamate (BDI)Pb[N(Ph)C(O)O^{i}Pr] [Pb–N = 2.340(4) Å].[151]

Treatment of 2-$Et_2NCH_2C(CF_3)_2OH$ with 1 equivalent of $Pb[N(SiMe_3)_2]_2$ in Et_2O gave the mononuclear amido complex $Pb[OC(CF_3)_2CH_2NEt_2][N(SiMe_3)_2]$ (**23**) as a pale yellow crystalline solid (Scheme 14). Complex **23** shows good solubility in all common organic solvents, including aliphatic hydrocarbons and is one of the few examples of heteroleptic alkoxide/amide lead(II) species.[137]



Scheme 14. Synthesis of complex **23**.

The molecular structure of **23** is presented in Figure 23. It displays a tricoordinated lead(II) atom with a distorted trigonal pyramidal geometry. The Pb(1)–N(1) and Pb(1)–N(2) interatomic distances are comparable with those found in [2-(Me_2NCH_2)C_6H_4]Pb[N($SiMe_3$)$_2$] [2.490(3) and 2.249(3) Å]. The three angles surrounding the metal center are significantly deflected from the ideal value of 90° which is typical for three-coordinate Pb(II) atoms, showing some contribution of empty p_z orbital to the lone pair of electrons in **23**.

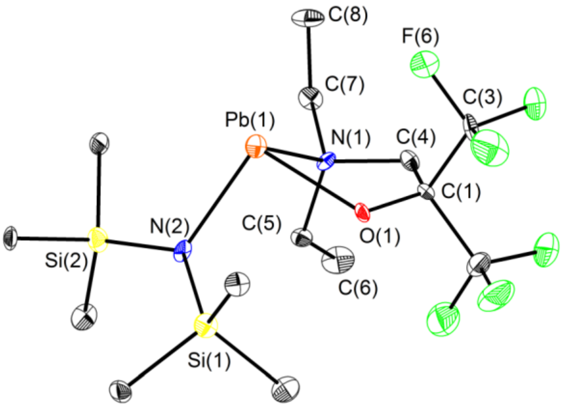
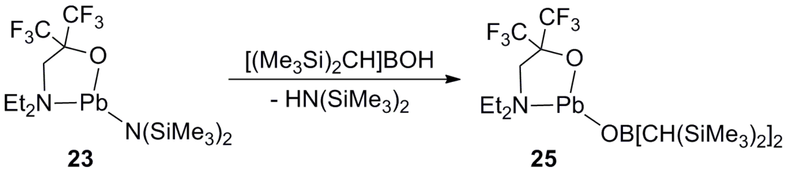


Figure 23. ORTEP drawing of **23** showing 50% probability displacement ellipsoids (hydrogen atoms were omitted for clarity).

Complex Pb[OC(CF_3)$_2$$CH_2$$NEt_2$]$_2$ (**24**) was obtained in an almost quantitative yield by reacting Pb[N($SiMe_3$)$_2$]$_2$ and 2-$Et_2NCH_2C(CF_3)_2OH$ in 1 : 2 molar ratio. ^{19}F NMR spectrum of **24** displays a broad resonance at δ = –77.1 ppm, while in ^{207}Pb NMR spectrum, a sharp singlet was observed at δ = 1187 ppm. The molecular structure of **24** was confirmed by single-crystal X-Ray diffraction studies. It presents a tetracoordinated lead atom in a hemi-directed tetrahedral geometry.[204] The Pb–N and Pb–O interatomic distances in **24** are close to those in **23**. No intermolecular contacts were found in the crystal of **24**.

Complex **23** reacts with an equimolar amount of the borinic acid [(Me_3Si)$_2$CH]$_2$BOH to generate the heteroleptic Pb[OC(CF_3)$_2$$CH_2$$NEt_2$][OB{CH($SiMe_3$)$_2$}$_2$] (**25**) (Scheme 15). This complex was isolated as a white solid with excellent solubility in most of the organic solvents.



Scheme 15.

The room temperature ^{19}F NMR spectrum of **25** in C_6D_6 shows a singlet at $\delta = -77.1$ ppm, completed by satellites due to coupling with the metal ($^4J_{FPb}$ = 125 Hz); traces of **24** and an unknown impurity (singlet at $\delta = -73.2$ ppm, with satellites presenting a coupling constant of 252 Hz to a nucleus whose natural abundancy, ca. 30–40%, does not match that of ^{207}Pb, 22.6%; this impurity was also at times detected in variable quantities in the ^{19}F NMR data for **23** and **24**) are also visible.

Colourless single crystals of **25** from different sets were investigated by X-ray diffraction analysis and even after several attempts, two sets of analogous site occupancies were found, with one (82%) far preponderant over the other (18%). Only the main site is displayed in Figure 24.

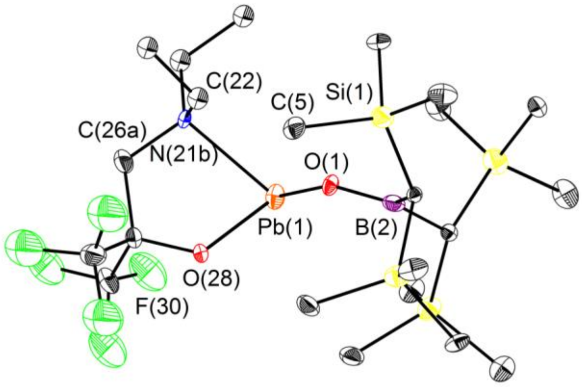


Figure 24. ORTEP drawing of **25** showing 50% probability displacement ellipsoids [only the main component (82% site occupancy) is depicted] (hydrogen atoms were omitted for clarity).

The Pb(1)–O(28) bond length in **25** [2.181(4) Å] is comparable to that in **23** [2.194(7) Å], while the Pb(1)–N$_{amine}$ interatomic distance is shorter in **25** than in **23** [2.448(4) vs. 2.550(8) Å

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