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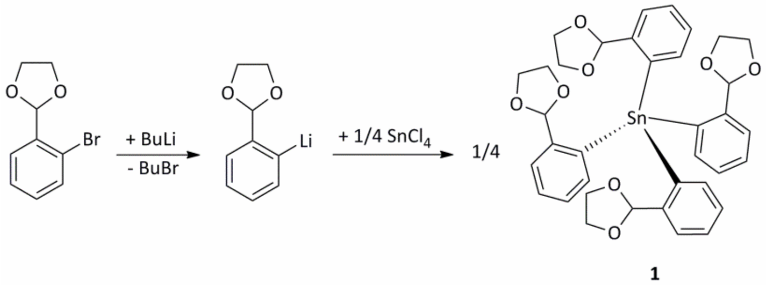
Keywords: tin; synthesis; hypervalent; X-ray diffraction; NMR spectroscopy; CVD.

1.3. Original contributions

1.3.A. Organotin(IV) compounds containing the 2-[$(CH_2O)_2CH$]C_6H_4 fragment

The syntheses of the organotin(IV) compounds **1**-**6** have been carried out according to the reaction schemes shown below. The starting material, 2-(2-bromophenyl)-1,3-dioxolane, was prepared by reacting one equivalent of 2-$BrC_6H_4CH=O$ with one equivalent of $HOCH_2CH_2OH$ in the presence of 4-$MeC_6H_4SO_3H$ as the catalyst (according to the literature procedures, but using different solvents) in order to protect the O=CH– group of the 2-bromo-benzaldehyde derivative.[83]

All compounds were synthesised using two methods, *via* the *o*-lithiated product and the Grignard reagent of 2-(2-bromophenyl)-1,3-dioxolane. However, it was found that compounds **1** and **4** were obtained to higher purity and better yields using the *o*-lithiated product as a starting material, while compounds **2**, **3**, **5**, and **6** give better yields via the Grignard reagent synthesis.

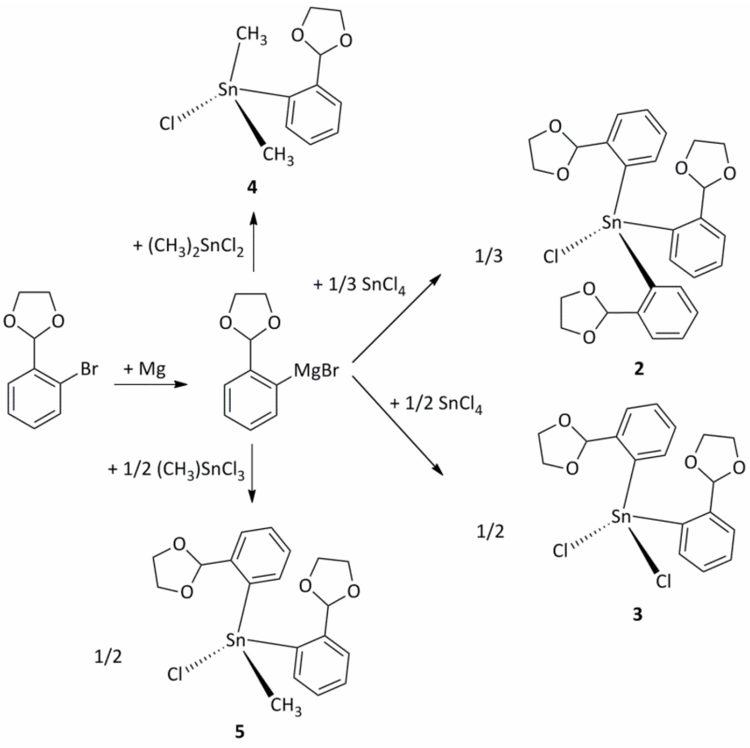


1

Scheme 15

Lithiation of the protected 2-bromobenzaldehyde with BuLi, under an inert atmosphere, in dry hexane, in a 1:1 ratio afforded the *o*-lithiated product which was further used in reactions with $SnCl_4$. By reacting one equivalent of *o*-lithiated 2-phenyl-1,3-dioxolane with $SnCl_4$, at room temperature under an inert atmosphere, in a 4:1 molar ratio, compound **1** was obtained (Scheme 15).

The organotin(IV) derivatives **2**, **3**, **4** and **5** were prepared from the Grignard reagent obtained by reacting 2-(2-bromophenyl)-1,3-dioxolane with magnesium under an inert atmosphere, in dry Et_2O. The obtained Grignard reagent was further reacted at room temperature under an inert atmosphere with $SnCl_4$ in a 3:1 molar ratio to obtain compound **2**, while compound **3** was obtained at -78°C under an inert atmosphere by reacting the Grignard reagent with $SnCl_4$ in a 2:1 molar ratio. Compound **4** was obtained by reacting one equivalent of Grignard reagent with one equivalent of $(CH_3)_2SnCl_2$ at -78°C under an inert atmosphere, while compound **5** was synthesized at room temperature under an inert atmosphere by reacting the Grignard reagent with $(CH_3)SnCl_3$ in a 2:1 molar ratio (Scheme 16).



Scheme 16

The ^1H NMR spectrum of compound **1** was measured in $CDCl_3$ and it exhibits in the aliphatic region a multiplet resonance corresponding to the H_8 protons and a singlet resonances signal corresponding to the H_7 proton from the 1,3-dioxale ring. The aromatic region shows the expected resonance signals, two triplets for H_4 and H_5 protons and two doublets for H_3 and H_6 protons (Figure 13).

The ^1H NMR spectra of **2** and **3** were measured and compared to the ^1H NMR spectrum of **1**: in the aliphatic region, the H_8 protons appear as a multiplet resonance signal in the ^1H NMR spectrum of **2** while in the ^1H NMR spectrum of **3** they appear as a singlet resonance signal. A singlet resonance signal can be observed in both ^1H NMR spectra for H_7 protons from the 1,3-dioxale ring. In the aromatic region, a multiplet resonance signal for H_4 and H_5 protons together with two doublet resonance signals for H_3 and H_6 protons are present in the ^1H NMR spectrum of compound **2** and a multiplet resonance signal for H_3, H_4 and H_5 protons and a doublet resonance signal for the H_6 protons in the ^1H NMR spectrum of compound **3**. The resonance signals in the ^1H NMR spectra of compounds **2** and **3** are shifted downfield compared to the ^1H NMR spectrum of **1**, because in both **2** and **3** the tin atom is bonded to chlorine atoms which are more electronegative than the carbon atom from the 2-phenyl-1,3-dioxolane ligand

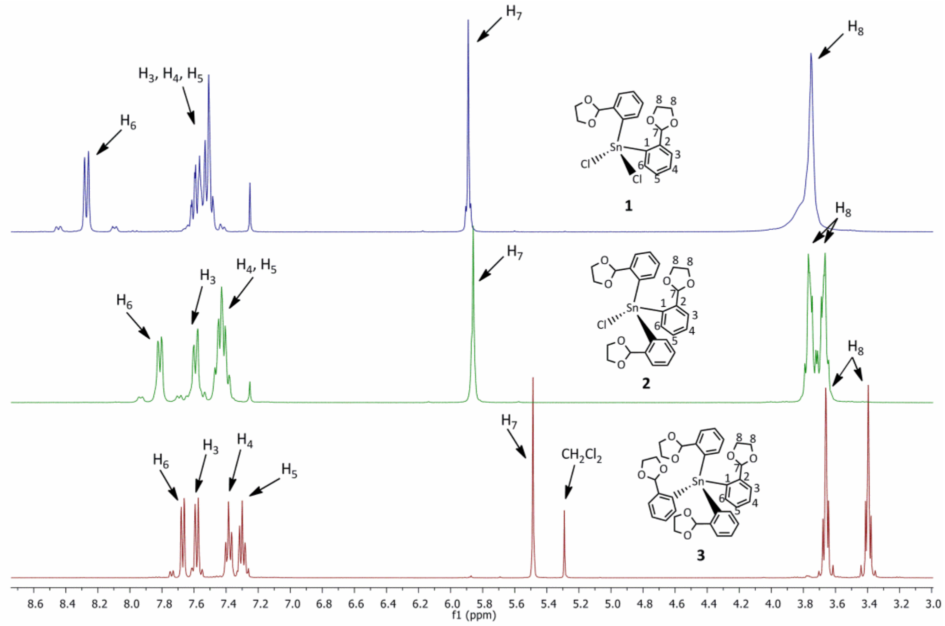


Figure 13. Stacked ^{1}H NMR spectra ($CDCl_3$, 300.1 MHz) for complexes **1** (red), **2** (green) and **3** (blue)

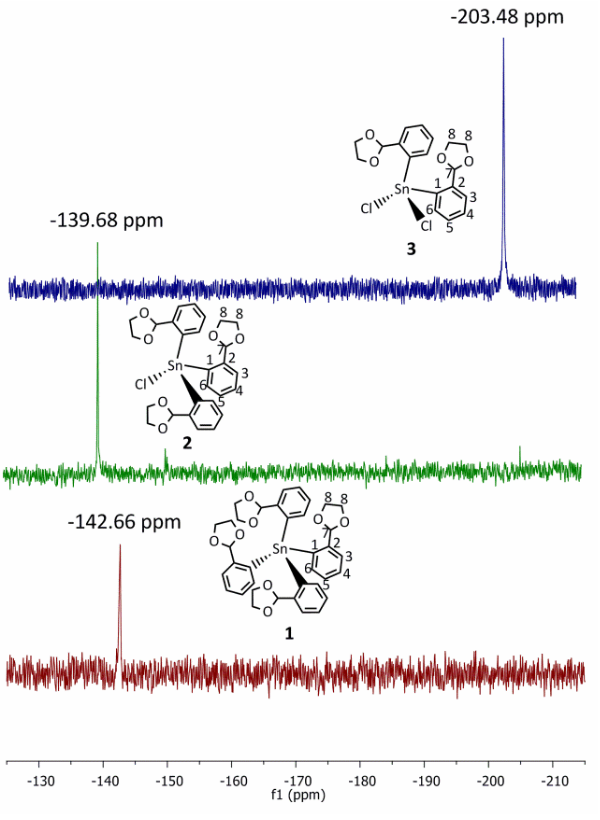


Figure 15. Stacked ^{119}Sn NMR spectra ($CDCl_3$, 111.9 MHz) for complexes **1** (red), **2** (green) and **3** (blue)

The ^{119}Sn chemical shift for compound **1** was compared to literature data for the *p*-substituted derivative.[84] The small difference in chemical shifts (-142.66 ppm for **1** and -126.5 ppm for the *p*-substituted derivative) denotes that the tin centre in compound **1** is tetracoordinated in solution. The ^{119}Sn NMR spectrum of compound **2** shows a resonance signal at -139.68 ppm, the chemical shift reflecting a similar environment of the tin atom to that of compound **1**. A small chemical shift difference is observed, due to the replacement of a 2-phenyl-1,3-dioxolane ligand with a chlorine atom and an increased Lewis acid character of the tin atom. A greater chemical shift difference is observed in the case of compound **3**. A resonance signal at -203.48 ppm in the ^{119}Sn NMR spectrum suggests that the tin atom is hexacoordinated in solution. This information is supported by the pair of tin satellites ($^{2}J_{SnH}$ 9.1 MHz) observed for the H_7 resonance signal in the ^{1}H NMR spectrum (Figure 15).

The ^{1}H NMR spectra of compounds $[2\text{-}\{(CH_2O)_2CH\}C_6H_4]SnMe_2Cl$ (**4**) and $[2\text{-}\{(CH_2O)_2CH\}C_6H_4]_2SnMeCl$ (**5**) contain in the aliphatic region a singlet resonance peak for the methyl groups bonded to the tin atom with the corresponding tin satellites (0.78 ppm with $^{2}J_{SnH}$ 64/67 Hz for **4** and 0.99 ppm with $^{2}J_{SnH}$ 68.5 Hz for **5**) and one singlet resonance signal corresponding to the H_7 protons from the 1,3-dioxale ring(5.88 ppm with $^{4}J_{SnH}$ 7.9 Hz for **4** and 5.87 ppm with $^{4}J_{SnH}$ 7 Hz for **5**). The signal for the H_8 protons appears as a singlet at 4.10 ppm in the ^{1}H NMR spectrum of **4**, while for compound **5** it appears as a multiplet due to the AA'XX' system. In the aromatic region of the ^{1}H NMR spectrum of **4**, the resonance signals for the H_3, H_4 and H_5 hydrogen atoms from the aromatic ring are overlaid and appear as a multiplet while the resonance signal for the H_6 proton appears as a doublet. In the aromatic region of the ^{1}H NMR spectrum of compound **5**, two sets of resonance signals for the aromatic protons are observed. This suggests that the two organic groups are non-equivalent. The non-equivalence is attributed to the presence of one O→Sn intramolecular interaction in solutions (Figure 18).

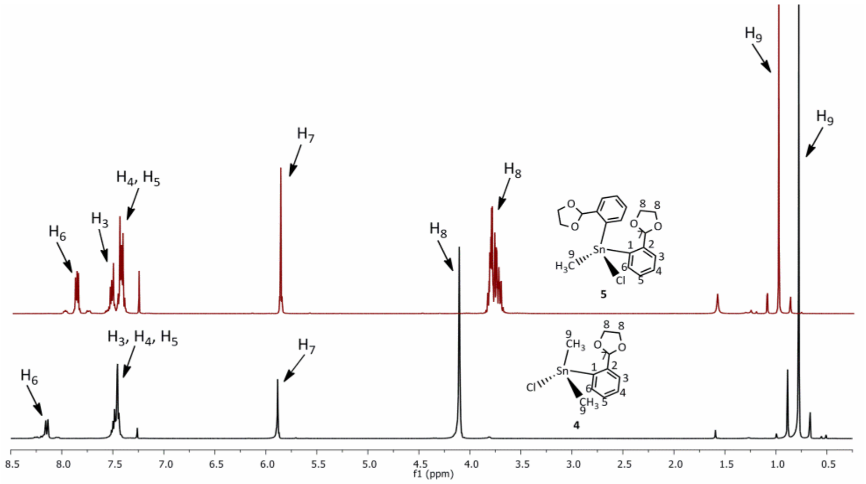
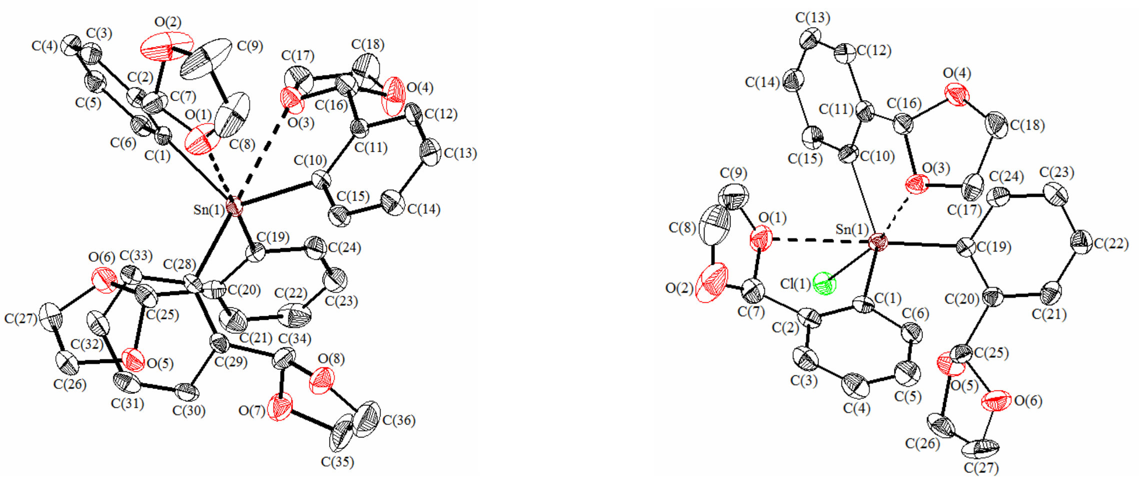


Figure 18. Stacked ^{1}H NMR spectra ($CDCl_3$, 300.1 MHz) for derivatives $[2\text{-}\{(CH_2O)_2CH\}C_6H_4]SnMe_2Cl$ (**4**) (black) and $[2\text{-}\{(CH_2O)_2CH\}C_6H_4]_2SnMeCl$ (**5**) (red)

Single crystals suitable for X-ray diffraction studies were obtained by slow diffusion of *n*-hexane into CH_2Cl_2 solutions of **1**, **2**, **3** and **5**, and *n*-hexane for **4**.



a **b**

Figure 21. ORTEP representation of the molecular structure of **1** (**a**) and **2** (**b**) showing 30% probability displacement ellipsoids and the atom numbering scheme

The molecular structures of compounds **1**-**3** show some common trends: *i)* in all three cases the tin atom has a distorted bicapped tetrahedral coordination geometry, the distortion being caused by the intramolecular coordination of the oxygen atoms from the organic ligands and the steric impediments imposed by the ligands, *ii)* two are coordinated intramolecularly to the metal centre, resulting in organotin(IV) species that have an increased coordination number at the tin atom from four to six, *iii)* all three compounds are hypervalent 12-Sn-6 species, the N–X–L nomenclature system has been previously described in the literature: the number of electrons, N, in the valence shell about a central atom X with L ligands directly bonded to it.

The molecular structure of compound **5** with the atom numbering scheme is shown in Figure 29.

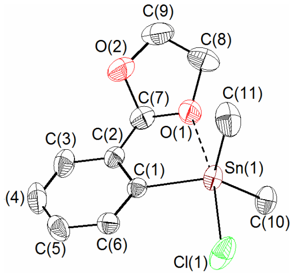


Figure 29. ORTEP representation of the molecular structure of $[2\text{-}\{(CH_2O)_2CH\}C_6H_4]SnMe_2Cl$ (**4**) showing 30% probability displacement ellipsoids and the atom numbering scheme

In compound **4**, the tin atom is pentacoordinated with a distorted trigonal bipyramidal geometry, due to the strong intramolecular O→Sn interaction with the O(1) oxygen atom from the 1,3-dioxale ring [Sn(1)–O(1) = 2.49(4) Å]. Due to the coordination of O(1) atom to the tin atom, C(7) carbon atom behaves as a chiral centre, with both $R_{\mathrm{C(7)}}$ and $S_{\mathrm{C(7)}}$ isomers present in the crystal. The Sn(1)C(1)C(2)C(7)O(1) ring is folded along the Sn(1)···$\mathrm{C_{methine}}$ axis, with a dihedral angle of 8.3° and the O(1) oxygen atom 0.14 Å out from the best plane of the rest of the atoms. The folding of the five-membered ring induces planar chirality at the tin atom. In the crystal of compound **5**, both $S_{\mathrm{O(1)}}$ and $R_{\mathrm{O(1)}}$ isomers can be observed.

The molecular structure of compound **5** with the atom numbering scheme is shown in Figure 31a The molecular structure of compound **5** contains a hexacoordinated tin atom with a distorted bicapped tetrahedral geometry due to two strong O→Sn interactions [Sn(1)···O(1) 2.60(2) Å and Sn(1)···O(3) 2.86(3) Å]. The magnitude of the angles around the tin atom is in the range between 99.5(9)-133.7(1)°. The most obvious deviation from the ideal value of 109.23° is observed for the C(1)–Sn(1)–C(10) angle of 133.7(1)°. This deviation is caused by the position of the two intramolecularly coordinated oxygen atoms in a *trans* position to the chlorine atom causing an angle opening because of their bulkiness (Figure 31b).

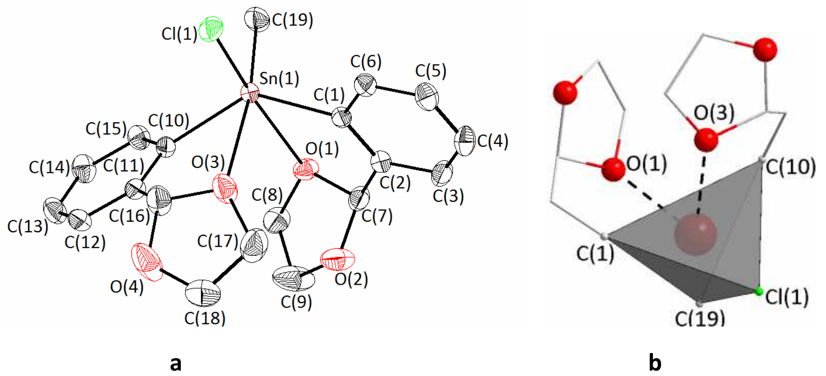
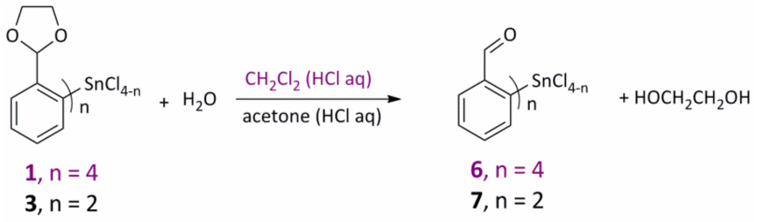


Figure 31. ORTEP representation of the molecular structure of $[2\text{-}\{(CH_2O)_2CH\}C_6H_4]_2SnMeCl$ (**5**) showing 30% probability displacement ellipsoids and the atom numbering scheme (**a**) and view of the bicapped tetrahedron $(C,O)_2SnCCl$ core (**b**)

Two five-membered SnC_3O rings are formed due to the O→Sn interactions. The rings are not planar but fold along the Sn(1)···$\mathrm{C_{methyne}}$ axis. The Sn(1)C(1)C(2)C(7)O(3) ring forms a SnC_3/SnCO dihedral angle of 18.9° and has the O(1) atom 0.32 Å out from the best plane of the rest of the atoms, while Sn(1)C(10)C(11)C(17)O(3) ring forms a SnC_3/SnCO dihedral angle of 29.7° with the O(3) atom 0.55 Å out from the best plane of the rest of the atoms. The folding of the five membered rings induce planar chirality at the metal centre and in the crystal of compound of **5** both *R* and *S* isomers are present. As a result, the polymeric chains contain a 1:1 mixture of alternating $R_{\mathrm{O(1)}}R_{\mathrm{(O3)}}R_{\mathrm{C(7)}}R_{\mathrm{C(16)}}$ and $S_{\mathrm{O(1)}}S_{\mathrm{(O3)}}S_{\mathrm{C(7)}}S_{\mathrm{C(16)}}$ isomers.

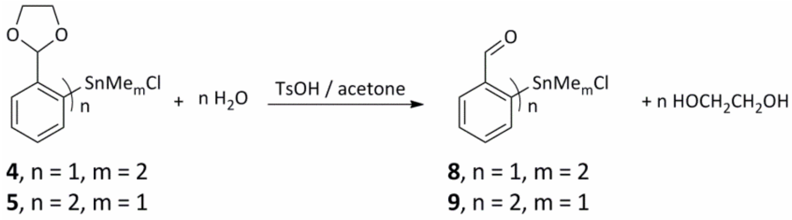
1.3.B. Organotin(IV) compounds containing the 2-(O=CH)-C_6H_4 fragment

Compounds [2-(O=CH)-C_6H_4]$_4$Sn (**6**), [2-(O=CH)-C_6H_4]$_2$SnCl_2 (**7**), [2-(O=CH)-C_6H_4]SnMe$_2$Cl (**8**) and [2-(O=CH)-C_6H_4]$_2$SnMeCl (**9**) were prepared by deprotection of the carbonyl function of the organic fragments from compounds [2-{(CH_2O)$_2$CH}C_6H_4]$_4$Sn (**1**), [2-{(CH_2O)$_2$CH}C_6H_4]$_2$SnCl_2 (**3**), [2-{(CH_2O)$_2$CH}C_6H_4]SnMe$_2$Cl (**4**) and [2-{(CH_2O)$_2$CH}C_6H_4]$_2$SnMeCl (**5**), respectively, following modified synthesis procedures used for mercury and selenium containing compounds.[16,89]



Scheme 17

Removing the protecting acetal group was achieved by hydrolysis in CH_2Cl_2 for compound **6** and in the polar solvent acetone for compounds **7** and **8** using an aqueous solution of HCl as catalyst. The reaction mixture was heated until all CH_2Cl_2 and acetone evaporated and compounds **6**, **7** and **8** precipitated as white solids (Scheme 17).



Scheme 19

Acetone solutions of compounds **4** and **5** were treated with *p*-toluene sulfonic acid as catalyst in order to remove the protecting acetal group and obtain compounds **8** and **9**, respectively. The reactions were performed at ambient temperature (Scheme 19).

Compounds **6**-**9** were used without any further purification. By comparing the procedures used to remove the protecting acetal group with the literature ones, it was observed that higher yields were obtained using the modified procedures. Moreover, it avoided the time consuming purification by chromatography over aluminium oxide, repeated recrystallisation[22e] and lengthy reflux[16,22].

The ^{1}H NMR and ^{13}C NMR spectra are very useful to monitor the formation of compounds **6**-**9** by removal of the protecting acetal group of compounds **1**-**5**. The formation of the aldehyde group is achieved when the corresponding carbon atom changes its hybridisation from *sp*^{3} (acetal group) to *sp*^{2} (aldehyde group). This change has a great effect on the chemical shift of the aldehydic carbon and hydrogen atoms that show an upfield shift compared to the starting materials.

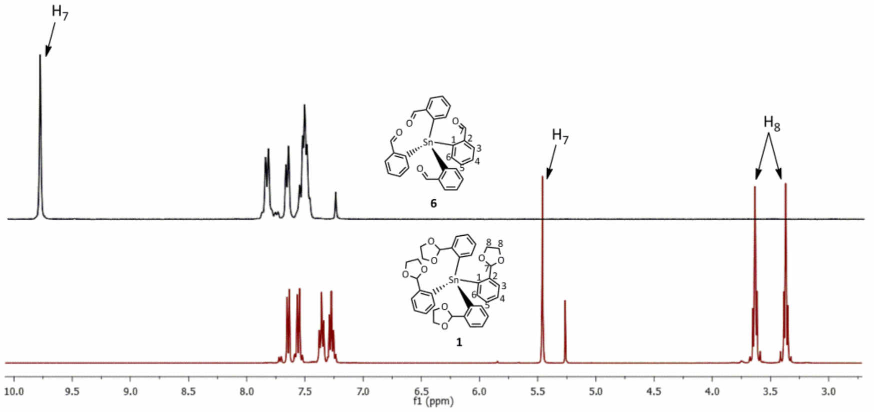


Figure 33. Stacked ^{1}H NMR spectra ($CDCl_3$, 300.1 MHz) for complexes **1** (red) and **6** (black)

The aromatic region of the ^{1}H NMR spectrum of **6** shows a multiplet resonance signal which corresponds to H_5 and H_4 protons, a doublet resonance for the H_6 hydrogen atom surrounded by tin satellites ($^{4}J_{SnH}$ 51.2/53 Hz) can be seen at 7.67 ppm as well as a doublet resonance for H_3 at 7.85 ppm with the corresponding tin satellites ($^{3}J_{SnH}$ 24.4 Hz). The last signal, a singlet resonance signal corresponds to H_7 proton from the aldehyde group. In the ^{13}C NMR spectrum all the expected resonance signals are present, six singlet resonance signals corresponding to the six types of carbon atoms from the phenyl ring and a singlet resonance signal corresponding to the carbon atom from the aldehyde group (Figure 33).

By comparing the ^{1}H NMR spectrum of compound **6** with the ^{1}H NMR spectrum of compound **1**, it can be observed that the multiplet resonance signal corresponding to the hydrogen atoms from the two $–CH_2–$ groups from the 1,3-dioxale ring in **1** disappears in ^{1}H NMR spectrum of compound **6**. The formation of the aldehyde group has a great effect on the chemical shifts of both corresponding hydrogen and carbon atoms, due to the change of hybridization on the carbon from the carbonyl group from *sp*^{3} to *sp*^{2}. Therefore, the resonance signal of the proton from the acetal moiety in compound **1** appears at 5.49 ppm, while the resonance signal of the aldehyde proton in compound **6** is shifted to 9.80 ppm (Figure 31). The same effect can be observed in the ^{13}C NMR spectra. The signal of the aldehyde carbon atom is shifted from 104.17 ppm in compound **1** to 193.53 ppm in compound **6** (Figure 34).

The ^{119}Sn resonance signal for compound **6** can not be observed at room temperature. The resonances signal is extremely broad and not visible in direct ^{119}Sn detection due to the rapid quadrupolar relaxation of the four ^{17}O nucleus present in the vicinity of the tin atom.[90]

Recording the ^{119}NMR spectrum at lower temperatures, a resonance signal appears at -129.20 ppm. Slower relaxation of the ^{17}O nucleus determined by low temperatures permits the ^{119}Sn resonance signal to become visible (Figure 35).

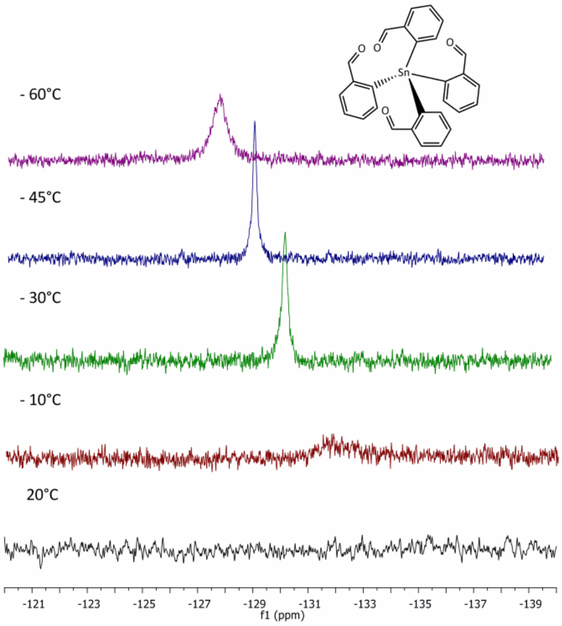
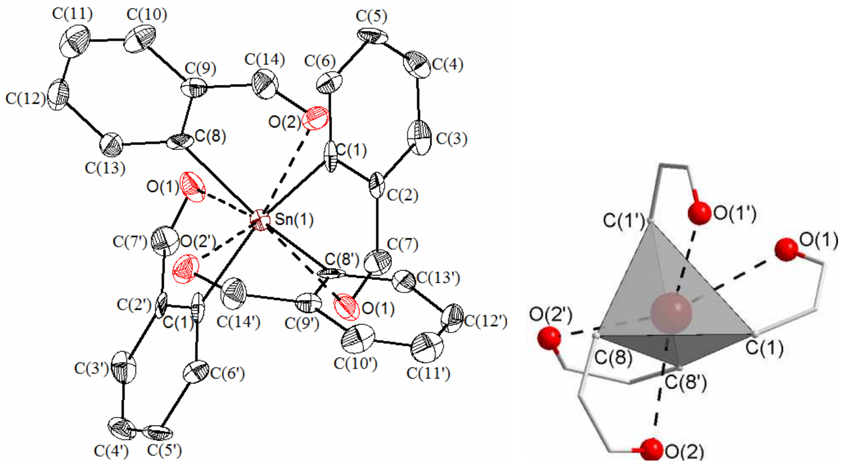


Figure 35. Variable-temperature ^{119}Sn NMR ($CDCl_3$, 111.9 MHz) spectra of **6**

The molecular unit of compound **6** features a metal centre coordinated by the oxygens of the benzaldehyde fragments (Figure 41a), with an average value for the O→Sn distance of 3.01 Å, $\Sigma r_{vdW}(Sn, O) = 3.7$ Å, $\Sigma r_{cov}(Sn, O) = 2.13$ Å.[x] The geometry around the tin atom is distorted tetracapped tetrahedron, with all four oxygen atoms, from the four organic ligands coordinating to the tin (Figure 41b), resulting in a hypervalent 16-Sn-8 species.

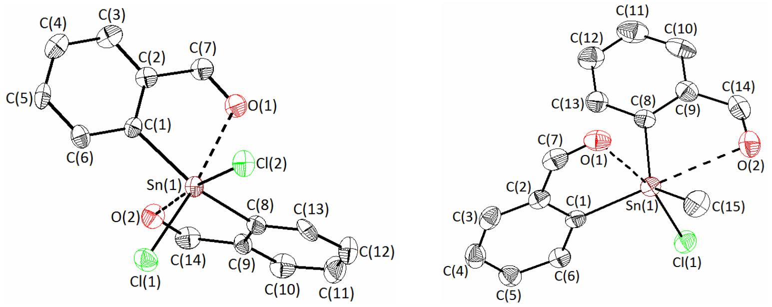


a b

Figure 41. ORTEP representation of the molecular structure of [2-(O=CH)-C_6H_4]$_4$Sn (**6**) showing 30% probability displacement ellipsoids with the atom numbering scheme (**a**) and view of the bicapped tetrahedron (*C,O*)$_4$Sn core (**b**)

Compound **6** is the first example of an octacoordinated tetraorganotin(IV) compound. The coordination is obtained by using all the benzaldehyde groups as a pendant arm ligand. The previously reported octacoordinated tin(IV) compounds[92] were obtained using inorganic ligands to increase the coordination number at the metal centre.

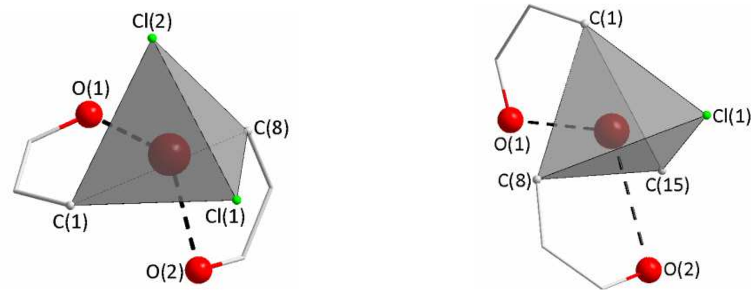
In the molecule of compound **7** (Figure 43a) and compound **9** (Figure 43b), both benzaldehyde groups act as a chelating ligand, having the oxygen atoms coordinated to the tin centre [Sn(1)···O(1) = 2.4(7) Å, Sn(1)···O(2) = 2.5(7) Å in compound **7** and Sn(1)···O(1) = 2.54(4) Å, Sn(1)···O(2) = 2.87(4) Å in compound **9**]. The strength of the O→Sn interaction is stronger, comparing to compound **6**, due to the decrease in steric impediments imposed by the ligands.



a b

Figure 43. ORTEP representation of the molecular structure of [2-(O=CH)-C_6H_4]$_2$SnCl2 (**7**) (**a**) and [2-(O=CH)-C_6H_4]$_2$SnMeCl (**9**) (**b**) showing 30% probability displacement ellipsoids with the atom numbering scheme

The geometry around the tin atom is distorted bicapped tetrahedral in both compounds **7** and **9** (Figure 44). Like in compound **3**, the C(1)–Sn(1)–C(8) angle of 143.9(4)° has a considerable deviation from the ideal value of 109.23°, due to the two intramolecularly coordinated oxygen atoms that determine the angle opening. The resulting five-membered SnC_3O rings in **7** are almost planar, with the Sn(1)C(1)C(2)C(7)/Sn(1)C(7)O(1) dihedral angle of 0.63° and the Sn(1)C(8)C(9)C(14)/Sn(1)C(14)O(2) dihedral angle of 1.4°. The oxygen atoms are out from the best plane of the rest of the atoms by O(1) 0.02 Å and O(2) 0.016 Å, respectively. Compound **9** shows similar features, with Sn(1)C(1)C(2)C(7)/Sn(1)C(7)O(1) dihedral angle of 3° and the Sn(1)C(8)C(9)C(14)/Sn(1)C(14)O(2) dihedral angle of 0.85°, while the oxygen atoms are: O(1) by 0.05 Å and O(2) by 0.02 Å out from the best plane of the rest of the atoms, resulting in basically planar SnC_3O rings.

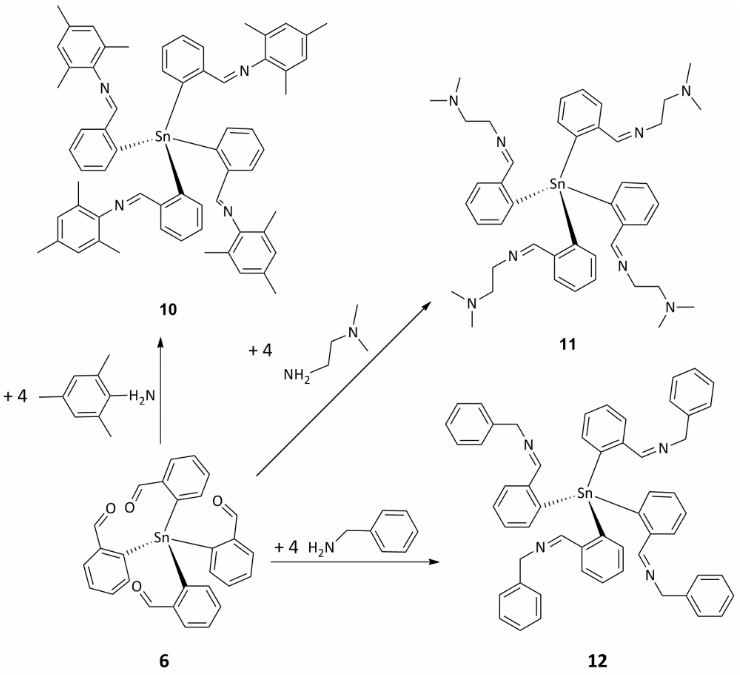


a **b**

Figure 44. View of the bicapped tetrahedron (*C,O*)$_2$SnCl$_2$ core of **7** (**a**) and (*C,O*)$_2$SnCCl core of **9** (**b**)

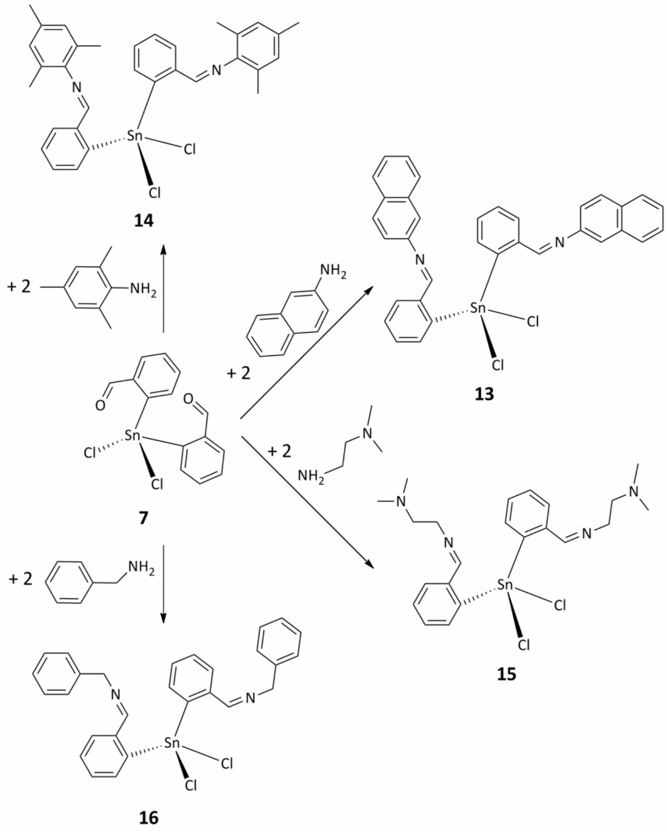
1.3.C. Organotin(IV) compounds containing the –C=N– bond

Compounds **10**-**16** were prepared by condensation reactions between organotin(IV) compounds containing the 2-(O=CH)-C_6H_4 group and different amines in the corresponding molar ratios.



Scheme 20

The condensation reactions for compounds **10**-**12** were first carried out in presence of solvent, catalyst and reflux conditions, to give good to moderate yields after long reaction times (Scheme 20). The condensation reactions for compounds **11** and **12** were carried out in refluxing toluene, using TsOH as catalyst and anhydrous Na_2SO_4 to remove the water from the reaction mixture. For compound **10**, the reaction in refluxing toluene, using anhydrous Na_2SO_4, in the presence or absence of TsOH catalyst, did not give the desired condensation product. The unreacted [2-(O=CH)-C_6H_4]$_4$Sn (**6**) was quantitatively recovered. The condensation reaction to obtain compound **10** was carried out in acetotonitrile, using anhydrous Na_2SO_4 but without TsOH as a catalyst. Compound **10**-**12** precipitated upon cooling the hot reaction mixtures.



Scheme 21

The same reactions as the ones shown in Scheme 20 and the condensation reactions to obtain compounds **13**-**16** were performed by mixing the reagents in a 1:4 and a 1:2 molar ratio, without solvent or catalyst, only by heating until a clear melt was obtained (Scheme 21). After maintaining the temperature for 5 minutes, the resulting water was removed by vacuum and a total conversion of the reagent to the iminic compounds was obtained, as revealed by ^{1}H NMR spectra of the crude product. This synthetic method represents a very good and green alternative to the ones reported so far in the literature, to obtain derivatives with C=N bonds from an aldehyde and an amine.

Conversely, the ^{1}H NMR spectrum of compound **14** shows in the aliphatic region three single resonance signals in a 1:1:1 ratio, corresponding to the methyl groups bonded to the aromatic ring. The aromatic region exhibits different resonances for the two aromatic protons of the aromatic ring bonded to the nitrogen atom, together with the resonance signals for the hydrogen atoms bonded to the tin atom and the resonance signal for the H_7 protons (Figure 48).

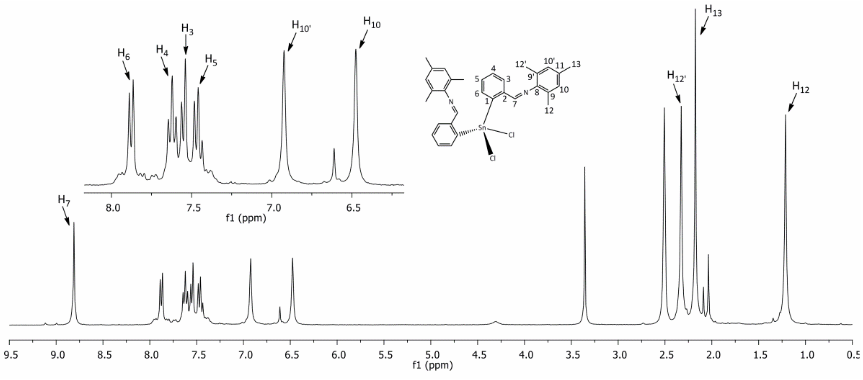


Figure 48. ^1H NMR spectra ($CDCl_3$, 300.1 MHz) for compound $[2-\{CH=N-2,4,6-(CH_3)_3C_6H_2\}C_6H_4]_2SnCl_2$ (**14**)

The presence of three different signals in the aliphatic region of the ^1H and ^{13}C NMR spectra for each methyl groups, suggests a different environment for the methyl groups. These results together with the chemical shift of the resonance signal from the ^{119}Sn NMR spectrum (-295.91 ppm), suggests that the tin atom from compound **14** is hexacoordinated in solution (Figure 49). The non-equivalence of the protons and carbon atoms from the aromatic ring bonded to the nitrogen atom is given by the intramolecular N→Sn interactions between the organic ligands and the tin atom. This coordination interaction obstructs the free rotation around N–C bond.

The ^1H NMR spectrum of compound **11** exhibits in the aliphatic region three resonance signals corresponding to the three types of protons, two triplets corresponding to C_8 and C_9 protons at 2.84 and 1.87 ppm, respectively and one singlet for the H_{10} hydrogen atoms of the methyl groups at 1.98 ppm. The aromatic region contains all expected resonance signals, with a doublet for H_6 of the phenyl ring at 7.66 ppm and singlet resonance signal for the H_7 proton found at 8.15 ppm (Figure 50).

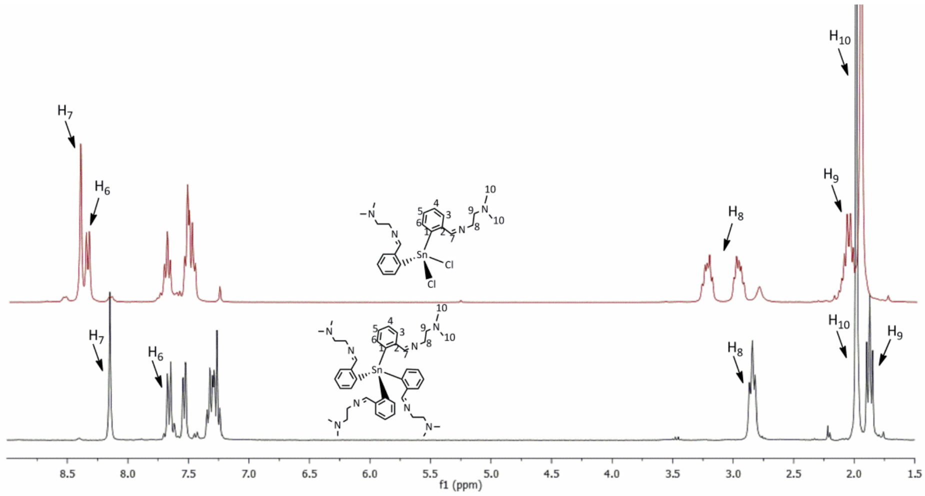


Figure 50. Stacked ^1H NMR spectra ($CDCl_3$, 300.1 MHz) for complexes $[2\text{-}\{CH{=}NCH_2CH_2N(CH_3)_2\}C_6H_4]_4Sn$ (**11**) (black) and $[2\text{-}\{CH{=}NC_2H_4N(CH_3)_2\}C_6H_4]_2SnCl_2$ (**15**) (red)

2.3.A.Tin(II) oxo-clusters

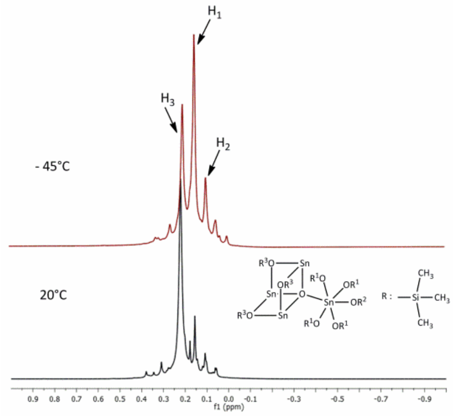


Figure 89. Variable-temperature ^1H NMR ($CDCl_3$, 99.35 MHz) spectra of **18**

The solution behaviour of $Sn_4O(OSiMe_3)_8$ (**18**) was studied by multinuclear NMR spectroscopy. At room temperature, in the aliphatic region of the ^1H and ^{13}C NMR spectra of compound **18**, the signal resonances for the methyl groups appear to be broad. A low temperature ^1H NMR experiment was performed in order to obtain better resolved resonances (Figure 89).

The molecular structure of $Sn_4O(OSiMe_3)_8$ (**18**) is shown in Figure 93. Compound **18** forms a cluster that contains three Sn(II) atoms and one Sn(IV) atom. Two of the Sn(II) atoms, Sn(2) and Sn(3), are pentacoordinated with a distorted *pseudo*-octahedral geometry around the tin atom with one position empty. The distortion of the *pseudo*-octahedral coordination geometry around the tin atoms is best reflected in the O−Sn−O bond angles [O−Sn(2)−O

65.9(1)–102.6(1)° and O–Sn(3)–O 58.0(1)–108.7(8)°]. The third Sn(II) atom has a distorted tetrahedral geometry with the O–Sn–O angles situated between the 76.9(2)-99.0(1)°. All three tin atoms have two covalent bonds with oxygen atoms from the –$OSiMe_3$ group and atoms Sn(2) and Sn(3) present three O→Sn intramolecular coordination with other three –$OSiMe_3$ group while Sn(4) forms two such O→Sn intramolecular coordinations. In all cases, the empty position is occupied by the pair of lone electrons.

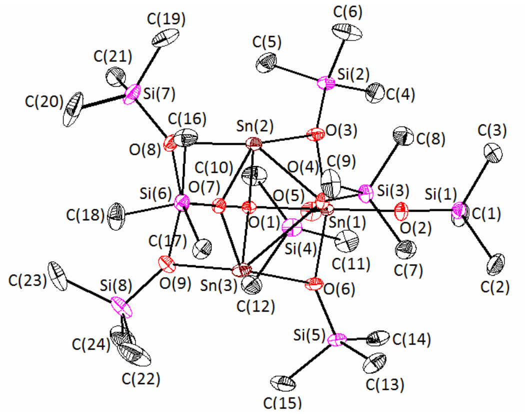


Figure 93. ORTEP representation of the molecular structure of $Sn_4O(OSiMe_3)_8$ (**18**) showing 30% probability displacement ellipsoids and the atom numbering scheme

The forth tin atom from the molecule is a Sn(IV) atom. Sn(1) is a hexacoordinated tin centre with a distorted octahedral geometry due to two intramolecular interactions with two –$OSiMe_3$ groups. The trans positions are occupied by –$OSiMe_3$ groups that form with the tin atom O–Sn(1)–O angles in the 157.2(1)-163.8(2)° range, while the cis O–Sn(1)–O angles are found between 70.2(1)-103.4(2)° values.

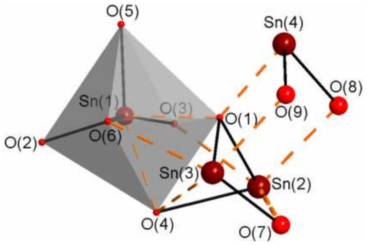


Figure 94. View of the octahedral coordination geometry around Sn(1) in compound **18**

Thermal characterisation of a chemical compounds is important for the control of the reaction process as well as in determining the properties of the resulting materials. The thermogravimetirc curves show the change of residual weight with temperature.

Thermogravimetric analysis (TGA) was carried out for the complexes **17**-**19** under controlled temperature, in nitrogen atmosphere.

Attempts to grow Sn_3N_4 films in the given conditions were unsuccessful. No depositions in the given conditions were obtained for compound **20** at temperatures below 450°C of the substrate. At 450°C a mixed deposition of SnO and metallic tin was obtained (Figure 121).

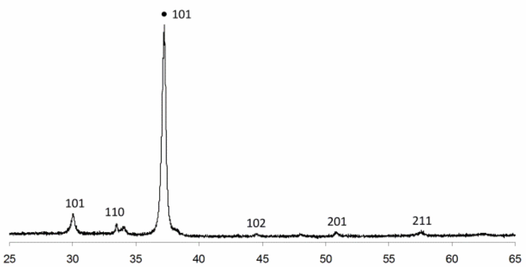


Figure 122. X-ray diffraction pattern of the film deposited on glass using **20** as precursor at a temperature of 450°C, indexation is consistent with mixed tetragonal SnO and tetragonal Sn, lines marked with • correspond to tetragonal Sn

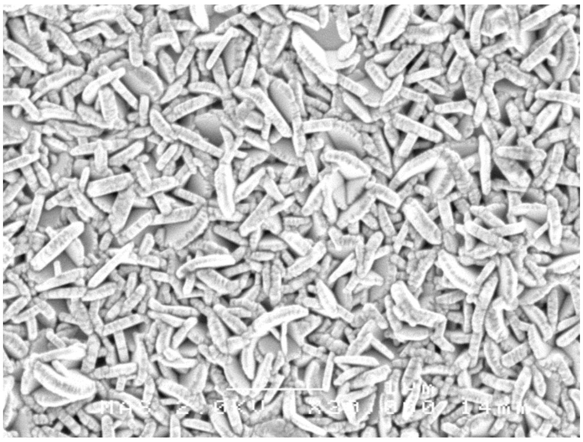
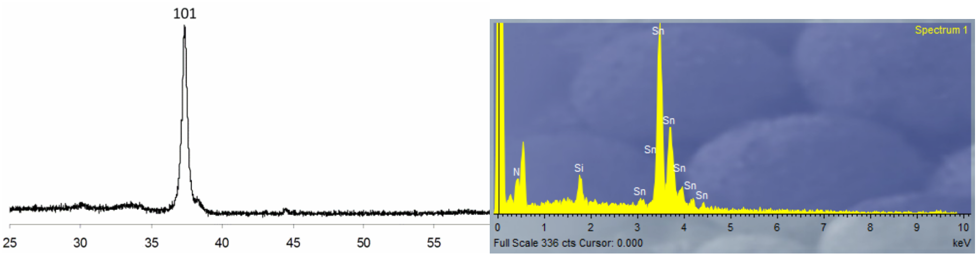


Figure 121. SEM of the film deposited from **20** on glass, at 450°C

The PXRD established the formation of a mixture of tetragonal SnO and tetragonal Sn (Figure 122). Similar studies were reported in the literature.[161] The described studies suggest that Sn_3N_4 decomposes into elements at 400°C. The presence of small amounts of SnO in the film obtained at 450°C can be caused by different reasons. During the deposition of metallic tin film, due to the decomposition of Sn_3N_4, oxygen might have gotten in the reactor by accident and small amounts of the metallic tin were oxidised to SnO. A more common explanation, encountered in the literature as well is that if the experiments are ran using N_2 or Ar as carrier gases, oxidation of the precursor may occur. To prevent this from happening an enriched carrier gas with NH_3 can be used. Another reason for the oxidation of the precursor can be the use of solvents needed to prepare the solution for DLICVD, solvents that may contain H_2O or O_2.

From this stage, by rising the temperatures, the depositions are of metallic tin (Figure 124). PXRD establishes the formation of tetragonal Sn and the presence of metallic tin is confirmed by EDX analysis (Figure 123).



a **b**

Figure 123. X-ray diffraction pattern of the film deposited on glass using **20** as precursor at a temperature of 500°C, indexation is consistent with tetragonal Sn (**a**) and and the corresponding EDX of the film (**b**)

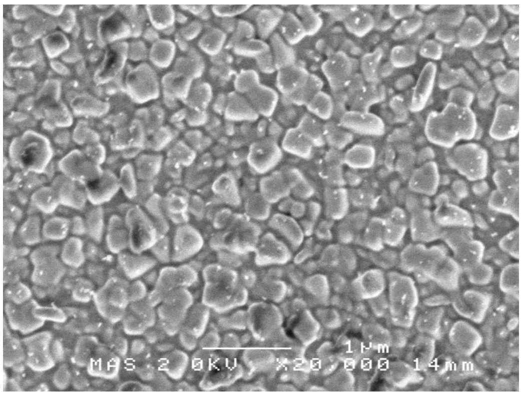


Figure 124. SEM of the film deposited from **20** on glass, at 500°C

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