A Comparative Assessment of the Effect of the Lewis Acidity of the Central Tin Atom on Intramolecular Coordination of (3-Methoxypropyl)stannanes

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The recently studied set of (3-methoxypropyl)stannanes of general formula R_xSnCl_{4-x} [R = $(CH_2)_3OCH_3$, x = 4 (**1**), x = 3 (**2**), x = 2 (**3**) and x = 1 (**4**)] is extended with two new sets of (3-methoxypropyl)stannanes of general formula $RPh_{3-x}SnCl_x$ [x = 0 (**5**), x = 1 (**6**) and x = 2 (**7**)] and $RSn(S_2CNEt_2)_{3-x}Cl_x$ [x = 0 (**8**), x = 1 (**9**) and x = 2 (**10**)]. The molecular structures of **6**, **7**, **9** and **10** in the solid state were determined by X-ray diffraction. In compounds **6** and **7**, the 3-methoxypropyl ligand forms a C,O-chelate and the tin atom is coordinated as a distorted trigonal bipyramid with the oxygen and one chlorine atom in the axial positions. Compounds **9** and **10** are hexacoordinate with a distorted octahedral ligand arrangement. While the 3-methoxypropyl ligand in **10** also forms a C,O-chelate, the oxygen atom in **9** is not coordinated to the central tin atom. The structures in a non-coordinating ($CDCl_3$) and a coordinating solvent ([D_6]DMSO) were studied by multinuclear ^{1}H, ^{13}C and ^{119}Sn NMR spectroscopy. It is proposed that the structures found in the solid state are retained upon dissolution in $CDCl_3$. Compounds **5**, **8** and **9** also preserve their structures in [D_6]DMSO. On the other hand, an equilibrium, in which one or more molecules of solvent enter the coordination sphere of the central tin atom and cleave the oxastannacycle, is established in [D_6]DMSO solutions of **6**, **7** and **10**. A comparison of the $J_{^1H,^{119}Sn}$ coupling constants obtained from 1D ^{1}H,^{119}Sn HMQC and 2D ^{1}H,^{119}Sn J-HMBC spectra and the $J_{^{13}C,^{119}Sn}$ coupling constants derived from conventional 1D ^{13}C NMR spectra shows that the best indicator of the O→Sn donor–acceptor interaction in 3-methoxypropylstannanes is the $^3J_{^{13}C,^{119}Sn}$ value.

Introduction

Organotin complexes containing C,Y-chelating ligands (i.e. organic substituents with a donor atom Y at a position where it is capable of intramolecular donor–acceptor interaction with the central metal atom) have been known for about thirty years.[1] Nevertheless, their manifold structures are still being intensively studied. Complexes of both transition and main-group metals are the subject of these studies. There are a number of reports detailing organostannanes containing either aromatic pincer-type ligands[2] or alkyl ligands substituted by a Lewis-basic heteroatom Y in a position enabling formation of five- or even six-membered heterostannacycles.[3]

Recently, we reported the synthesis and structures of the first set of (3-methoxypropyl)stannanes of the general formula R_xSnCl_{4-x} [R = $(CH_2)_3OCH_3$, x = 4 (**1**), x = 3 (**2**), x = 2 (**3**) and x = 1 (**4**)], which were studied for their considerable water solubility and appreciable in vitro trypanocidal activity.[4] We showed that the 3-methoxypropyl group can be bonded either as a monodentate ligand (Scheme 1, **A**) or as a bidentate C,O-chelating ligand (Scheme 1, **B**), and that this is dependent on the Lewis acidity of the central tin atom. However, the ^{119}Sn chemical shift gives unambiguous evidence for an O→Sn donor–acceptor interaction only if no other potentially bidentate ligand, such as a carboxylate group, is present in the coordination sphere. Moreover, even for R_4Sn (**1**), where the 3-methoxypropyl ligands do not form a chelate, all protons display ^{1}H-^{119}Sn HMQC correlations.[5] Therefore, the existence of the correlation itself cannot prove the existence of the oxastannacycle, and to distinguish between these two bonding modes (Scheme 1) in solution is a crucial issue of structural research.

In the case of the monodentate 3-methoxypropyl group (Scheme 1, **A**), there is only one scalar coupling pathway, that through the covalent bonds of the 3-methoxypropyl chain. On the other hand, if the oxastannacycle is closed (Scheme 1, **B**) there are two scalar coupling pathways − through the covalent bonds and through the coordinative O→Sn bond − which could be reflected in the magnitude of the $J_{^1H,^{119}Sn}$ and $J_{^{13}C,^{119}Sn}$ coupling constants.[5,6] The long-range $^{6+3}J_{^1H,^{119}Sn}$ coupling constants of 0.52, 1.86 and 2.24 Hz obtained for **1**, **3** and **4**, respectively, show that this parameter increases with the strength of the O→Sn interac-

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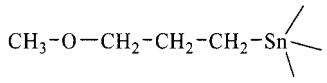
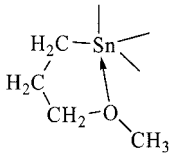


A



B

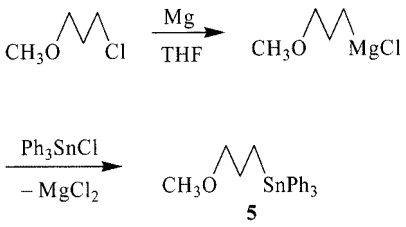
Scheme 1.

tion.[4] Since this limited set of results does not allow us to draw any final conclusion, two more sets of (3-methoxypropyl)stannanes were prepared. In the first set, of general formula $RPh_{3-x}SnCl_x$ [x = 0 (**5**), x = 1 (**6**) and x = 2 (**7**)], there is only one 3-methoxypropyl group in the coordination sphere and the Lewis acidity of the central tin atom is varied by substitution of phenyl groups by chlorine atoms. The latter set, of general formula $RSn(S_2CNEt_2)_{3-x}Cl_x$ [x = 0 (**8**), x = 1 (**9**) and x = 2 (**10**)], is composed of monorganotin compounds and variation of the Lewis acidity of tin is achieved by changing the number of chlorine atoms and strongly chelating *N*,*N*-diethyldithiocarbamate groups in the coordination sphere. These complexes were studied by X-ray diffraction, ^{13}C and ^{119}Sn CP/MAS NMR spectroscopy in the solid state and multinuclear ^{1}H, ^{13}C and ^{119}Sn NMR spectroscopy in solution in non-coordinating ($CDCl_3$) and coordinating ([D_6]DMSO) solvent. The obtained parameters are compared and are discussed with the aim of finding an indicator of the strength of the O→Sn donor–acceptor interaction.

Results and Discussion

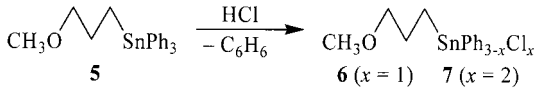
Syntheses

(3-Methoxypropyl)triphenylstannane (**5**) was synthesised as shown in Scheme 2. Treatment of chlorotriphenylstannane with excess (3-methoxypropyl)magnesium chloride, which was previously prepared from 1-chloro-3-methoxypropane and magnesium chips in THF, provided tetraorganostannane **5**, which was isolated as a white powder in a yield of 85% with respect to Ph_3SnCl.



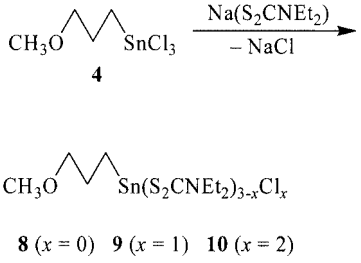
Scheme 2.

Chloro(3-methoxypropyl)phenylstannanes **6** and **7** were prepared from **5** by stepwise cleavage of phenyl groups upon treatment with HCl in $CHCl_3$ at room temperature (Scheme 3). The reaction proceeded selectively and both compounds were obtained as white crystals in yields of over 95%.



Scheme 3.

Treatment of **4** with an appropriate stoichiometric amount of sodium *N*,*N*-diethyldithiocarbamate in acetone at room temperature afforded carbamate complexes **8**, **9** and **10** (Scheme 4) as white or yellowish crystals in yields of 80, 83 and 59%, respectively.



Scheme 4.

Solid-State Structures

In the case of **5**, isolation of a single crystal suitable for X-ray crystal structure determination was unsuccessful. However, considering that **5** is a tetraorganotin compound, any coordination of oxygen to tin and consequent increase of its coordination number above four can be easily excluded, and thus it can be assumed that the structure is close to tetrahedral as in the majority of tetraorganotin compounds.[7]

The molecular structures of **6** and **7**, as determined by X-ray diffraction, are shown in Figures 1 and 2, respectively. Selected bond lengths and angles are given in Table 1.

Both complexes consist of discrete molecules with a structure that is very like that of **4**.[4] The central tin atom is coordinated as a distorted trigonal-bipyramid with the oxygen atom and one chlorine atom in the axial positions [Cl–Sn–O: 170.37(4)° and 172.6(1)°] (Figure 1). Compound **6** has a rather symmetrical equatorial plane containing two carbons of phenyl groups and one carbon of the 3-methoxypropyl group [C–Sn–C: 122.67(11)°, 119.48(11)°, 111.56(10)°]. However, the phenyl rings have different orientations: while one lies practically within the equatorial plane [C10–C5–Sn–C1: 4.2(3)°] the second one is oriented nearly along the axis of the trigonal bipyramid [C12–C11–Sn–O: –10.8(2)°]. This means that the tin atom is a stereocentre and **6** is chiral in the solid state. This asymmetry is also revealed in the ^{13}C CP/MAS NMR spectrum, where twelve signals are observed in the aromatic region. For compound

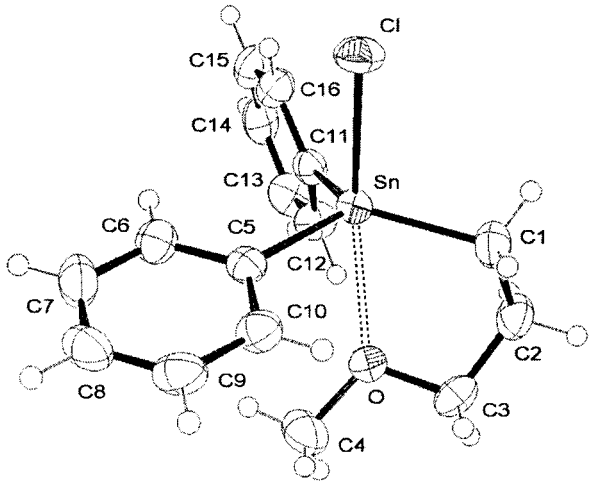


Figure 1. Solid-state structure of **6**.

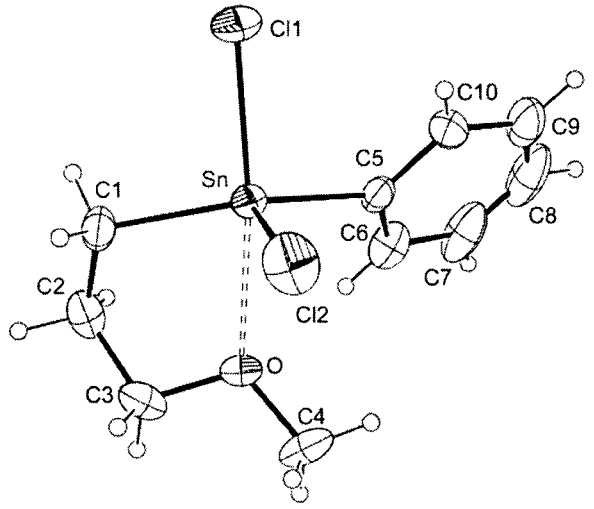


Figure 2. Solid-state structure of **7**.

7 (Figure 2), one phenyl group is replaced by the second chlorine atom and, consequently, the equatorial plane is less symmetrical [C–Sn–C: 140.2(2)°]. However, **7** still lacks a mirror plane and an inversion centre and therefore it is also chiral. The unit cells in crystals of both compounds consist of pairs of enantiomers, and thus **6** and **7** are racemates. The sum of angles in the equatorial plane of **6** and **7** (353.71° and 354.1°, respectively) is considerably smaller then 360° because both coordination polyhedra have the whole equatorial plane tilted towards the oxygen atom in a similar fashion to **4**.

In the case of **7**, the *trans* influence of the coordinated oxygen atom of the 3-methoxypropyl group causes the apical chlorine atom to have a slightly weaker bond to the central tin atom [Sn–Cl1: 2.425(2) Å] than the corresponding equatorial one [Sn–Cl2: 2.365(2) Å]. An analogous phenomenon is observed for compound **4**, where the Sn–Cl distance for the axial chlorine atom is 2.3904(12) Å while the distances for the equatorial bonds are 2.3317(14) and 2.3274(12) Å.[4] Although the structures of **6**, **7** and **4** are very similar, they differ markedly in the strength of the O→Sn coordination [Sn–O: 2.5505(18), 2.461(4) and 2.394(3) Å, respectively], which increases with the number of chlorine atoms in the coordination sphere, i.e. with the Lewis acidity of the central tin atom. Nevertheless, all the Sn–O bonds are slightly shorter than those found in **3** [Sn–O: 2.559(4) and 2.556(4) Å], where both oxygen atoms are coordinated to tin in a *cis* configuration.[4]

The crystal structure of $[RSn(S_2CNEt_2)_3]$ (**8**) was published recently.[8] An Sn–O intramolecular interaction is precluded [Sn–O: 5.427(1) Å] in this complex because of the penchant of dithiocarbamate to chelate tin and the steric crowding, given that the tin is already seven-coordinate. Thus, the 3-methoxypropyl group is bonded to tin only through carbon as a monodentate ligand and the structure is very close to those of other monorganotin tris(*N*,*N*-diethyldithiocarbamate) complexes such as $[MeSn(S_2CNEt_2)_3]$, $[BuSn(S_2CNEt_2)_3]$ and $[PhSn(S_2CNEt_2)_3]$.[9,10]

The molecular structures of the next two carbamate complexes in the set, $[RSn(S_2CNEt_2)_2Cl]$ (**9**) and $[RSn(S_2CNEt_2)Cl_2]$ (**10**), determined by X-ray diffraction, are shown in Figures 3 and 4, respectively. Selected bond lengths and angles are given in Table 2.

Complexes **9** and **10** also exist as discrete molecules. However, in contrast to previously discussed compounds, the tin atoms are hexacoordinate with a distorted octahedral ligand arrangement. The crystal structure of **9** resembles those of other monoorganotin complexes with two dithiocarbamate ligands and a chlorine atom in the coordination sphere, such as $[PhSn(S_2CNEt_2)_2Cl]$[11] and $[(MeO_2CCH_2CH_2)Sn(S_2CNMe_2)_2Cl]$.[12] The central tin atom is coordinated by four sulfur atoms from two bidentate dithiocarbamate ligands, the carbon atom of the 3-methoxypropyl substituent and the chlorine atom; the latter donor atoms are mutually *cis* [C11–Sn–Cl: 93.3(2)°]. The deviation of the coordination polyhedron from the ideal octahedral

Table 1. Selected bond lengths [Å] and angles [°] for compound **6** and **7**.

6				**7**			
Sn–O	2.5505(18)	Sn–C5	2.122(3)	Sn–O	2.461(4)	Sn–C1	2.126(6)
Sn–Cl	2.4412(8)	Sn–C11	2.139(2)	Sn–Cl1	2.425 (2)	Sn–C5	2.120(5)
Sn–C1	2.139(3)			Sn–Cl2	2.365(2)		
Cl–Sn–O	170.37(4)	C1–Sn–C5	122.67(11)	Cl1–Sn–O	172.6(1)	C1–Sn–C5	140.2(2)
Cl–Sn–C1	98.94(8)	C1–Sn–C11	119.48(11)	Cl1–Sn–C1	98.3(2)	C1–Sn–Cl2	108.0 (2)
Cl–Sn–C5	97.28(7)	C5–Sn–C11	111.56(10)	Cl1–Sn–C5	97.1(2)	C5–Sn–Cl2	105.9 (2)
Cl–Sn–C11	98.87(7)	C1–Sn–O	73.34(9)	Cl1–Sn–Cl2	97.85(9)	C1–Sn–O	74.9(2)

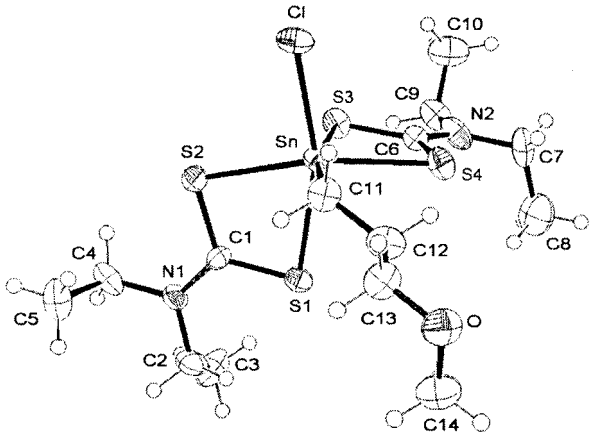


Figure 3. Solid-state structure of **9**.

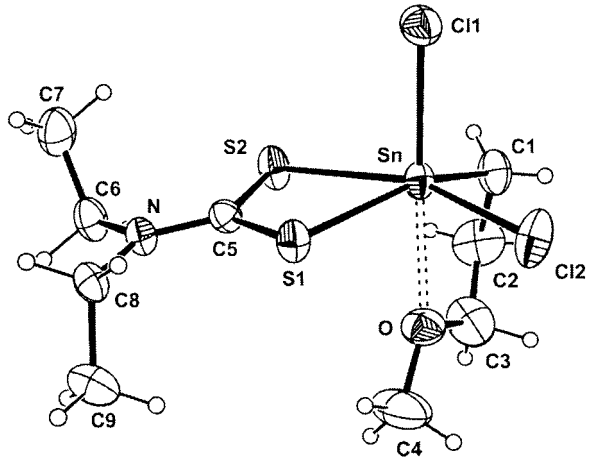


Figure 4. Solid-state structure of **10**.

geometry is especially apparent for the angles S2–Sn–S4, Cl–Sn–S1 and C11–Sn–S3, which are 153.86(6)°, 161.82(6)° and 166.2(2), respectively, instead of 180°. This distortion of the geometry is constrained by the small bite angles [S1–Sn–S2: 69.98(6)°, S3–Sn–S4: 69.86(6)°] of the dithiocarbamate ligands, which are typical for organotin dithiocarbamates.[10] The two dithiocarbamate groups are not equivalent, as becomes evident in the ^{13}C CP/MAS NMR spectrum (Figure 5), where four sets of signals for ethyl groups and two signals for the CS_2 group are observed. Nevertheless, they form unusually symmetrical chelates [Sn–S: 2.5658(18), 2.5980(19), 2.5693(19) and 2.615(2) Å].

The Sn–C [2.167(7) Å] and Sn–Cl [2.468(2) Å] bonds are longer than those of chloro(3-methoxypropyl)phenylstannanes **6** and **7**, and this can be ascribed to the lower Lewis acidity of the tin atom. On the other hand, the average Sn–S distance in **9** [2.587(15) Å] is considerably shorter than the comparable distance of 2.680(5) Å found for **8**,[8] which is a result of the higher Lewis acidity of the central tin atom caused by replacement of one dithiocarbamate ligand by chloride. In spite of this increased Lewis acidity, the oxygen atom of the 3-methoxypropyl group is not coordinated to tin as in **8**.

In the case of **10**, the distorted octahedral neighbourhood of the tin atom is composed of two chlorine atoms in mutual *cis* positions [Cl–Sn–Cl: 94.82(4)°], a four-membered chelate ring of the bidentate dithiocarbamate ligand and a five-membered chelate ring of the 3-methoxypropyl ligand arising from coordination of oxygen to tin. Thus, the molecular structure of **10** is very close to that of [(MeO$_2$CCH$_2$CH$_2$)Sn(S$_2$CNMe$_2$)Cl$_2$], where the ester carbonyl oxygen is also coordinated to tin.[13] Similarly to other organotin dithiocarbamate complexes, the dithiocarbamate ligand is bonded asymmetrically [Sn–S: 2.4728(10) and 2.6405(10) Å], with a typically small bite angle of 70.27(3)°, which is in part responsible for the distortion of the octahedral geometry.[10] The second most apparent deviation from an ideal octahedron is the bite angle of the 3-methoxypropyl ligand [C–Sn–O: 74.60(13)°]. In the solid-state structure of **10**, the ethyl groups are also non-equivalent and, consequently, the molecule lacks a mirror plane and inversion centre (Figure 4). In the ^{13}C CP/MAS NMR spectrum this is not shown for the CH_3 groups, and two signals were found only for the CH_2 groups. The unit cell in the crystal structure of **10** consist of a pair of enantiomers and thus it is also a racemate.

There is a considerable difference between the Sn–Cl distances [Sn–Cl: 2.4128(11) and 2.4309(10) Å] due to the different *trans* influence of sulfur and oxygen. Nevertheless, both distances are shorter than those found in **9** due to the higher Lewis acidity of the central tin atom in **10**. This is also demonstrated by the average Sn–S bond length of 2.557 Å, which is slightly shorter than that of **9** [2.587(15) Å] and **8** [2.680(5) Å]. Considering that the Sn–O bond length in **10** [2.475(3) Å] is longer than that of **4** and **7** [Sn–O: 2.394(3) and 2.461(4) Å, respectively], but shorter than that of **3** and **6** [Sn–O: 2.559(4), 2.556(4) and 2.5505(18) Å, respectively], it can be concluded that the

Table 2. Selected bond lengths [Å] and angles [°] for compounds **9** and **10**.

9				**10**			
Sn–S1	2.615(2)	Sn–O	5.560(6)	Sn–O	2.475(3)	Sn–S1	2.4728(10)
Sn–S2	2.5693(19)	Sn–Cl	2.468(2)	Sn–Cl1	2.4128(11)	Sn–S2	2.6405(10)
Sn–S3	2.5658(18)	Sn–C11	2.167(7)	Sn–Cl2	2.4309(10)	Sn–C1	2.138(3)
Sn–S4	2.5980(19)						
Cl–Sn–S1	161.82(6)	C11–Sn–Cl	93.3(2)	Cl1–Sn–Cl2	94.82(4)	S1–Sn–S2	70.27(3)
C11–Sn–S3	166.2(2)	C11–Sn–S4	96.41(9)	Cl1–Sn–C1	102.51(12)	S2–Sn–C1	95.71(11)
S2–Sn–S4	153.86(6)	C11–Sn–S2	103.3(2)	Cl1–Sn–S1	97.82(4)	C1–Sn–Cl2	100.65(11)
S1–Sn–S2	69.98(6)	S2–Sn–S3	90.30(6)	Cl1–Sn–S2	95.72(4)	Cl2–Sn–S1	89.33(4)
S3–Sn–S4	69.86(6)			Cl1–Sn–O	177.07(7)	C1–Sn–O	74.60(13)

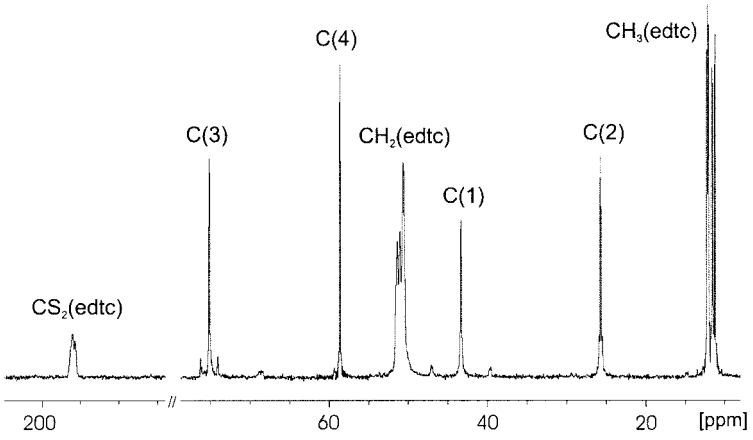


Figure 5. ^{13}C CP/MAS NMR spectrum of [RSn(S_2CNEt_2)$_2$Cl] (**9**) (edtc = *N*,*N*-diethyldithiocarbamate).

Lewis acidity of the central tin atom in **10** is in-between the Lewis acidities of the tin atoms in these compounds.

NMR Spectroscopy and Structures in Solution

The (3-methoxypropyl)stannanes were fully characterised in $CDCl_3$ solution by ^{1}H and ^{13}C NMR spectroscopy; the values of the ^{1}H and ^{13}C chemical shifts for **5**–**7**, **9** and **10** are given in the Experimental Section. The parameters for the other compounds have been published elsewhere.[4,8] In order to evaluate solution structures both in non-coordinating and coordinating solvents, ^{119}Sn NMR spectra were measured in $CDCl_3$ and [D_6]DMSO and also in the solid state. The values of the ^{119}Sn chemical shifts are summarised in Table 3. The coordinative behaviour of the 3-methoxypropyl ligand will be discussed in light of the $J_{^1H,^{119}Sn}$ coupling constants obtained from 1D ^{1}H,^{119}Sn HMQC and 2D ^{1}H,^{119}Sn J-HMBC NMR spectra[5] (Table 4) and $J_{^{13}C,^{119}Sn}$ values derived from conventional 1D ^{13}C NMR spectra (Table 5). The numbering used for the hydrogen and carbon atoms is given in Scheme 5.

Table 3. ^{119}Sn chemical shifts [ppm] for (3-methoxypropyl)stannanes in the solid state, $CDCl_3$ and [D_6]DMSO.

Compound	δ_{Sn} (solid state)	δ_{Sn} ($CDCl_3$)	δ_{Sn} ([D_6]DMSO)
1[4]	[a]	–4.3	–1.2
2[4]	[a]	49.0	27.4
3[4]	–133[d]	–108.6	–170.5
4[4]	–157	–138.5	–445.6
5	[c]	–99.6	–97.6
6	–82.4[d]	–79.5	–137.3
7	–121.7	–83.0	–281.1
8[8]	–828.3, –832.0	–774.2	–769.5
9	–593.9[d]	–582.1	–575.4
10	–405.6	–392.4	–470.3, –575.2[b]

[a] Oily substance. [b] Two signals observed due to the dynamic equilibrium discussed in the text. [c] Not measured. [d] Splitting due to the interaction of ^{119}Sn nuclei with one or two $^{35/37}$Cl spins observed according to ref.[14]

Table 4. $^nJ_{^1H,^{119}Sn}$ coupling constants [Hz] for selected protons in (3-methoxypropyl)stannanes.

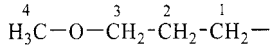
Compound	H1[a] $n = 2$	H2[a] $n = 3$	H3[b] $n = 4$	H4[b] $n = 6$
1[4]	51.2	47.8	[c]	0.52
2[4]	60.8	86.2	1.31	[d]
3[4]	95.9	195.8	7.73	1.86
4[4]	104.9	254.2	5.07	2.24
5	56.8	65.6	< 0.5	< 0.5
6	76.8	134.5	5.12	1.32
7	86.6	169.3	5.65	1.73
8[8]	107.3	151.8	< 1.5	1.06
9	102.0	153.9	5.41	2.46
10	105.2	283.1	7.84	3.24

[a] Obtained from the 1D ^{1}H,^{119}Sn HMQC spectra. [b] Obtained from the 2D ^{1}H,^{119}Sn J-HMBC NMR spectra. [c] Not obtained due to an overlap. [d] Not obtained probably due to the existence of the fast dynamic equilibrium discussed in the text.

Table 5. $^nJ_{^{13}C,^{119}Sn}$ coupling constants for selected carbons in (3-methoxypropyl)stannanes.

Compound	Solvent	C1 $n = 1$	C2 $n = 2$	C3 $n = 3$
1[4]	$CDCl_3$	324.5	18.6	59.3
	[D_6]DMSO	325.3	19.3	52.3
2[4]	$CDCl_3$	434.6	26.5	55.7
	[D_6]DMSO	456.5	27.2	65.2
3[4]	$CDCl_3$	731.6	42.7	34.0
	[D_6]DMSO	840.4	44.7	95.1
4[4]	$CDCl_3$	845,2	67.0	79.3
	[D_6]DMSO	[a]	62.5	229.6
5	$CDCl_3$	404.9	21.6	56.3
	[D_6]DMSO	412.4	23.2	53.4
6	$CDCl_3$	539.8	31.1	25.5
	[D_6]DMSO	[a]	31.3	78.3
7	$CDCl_3$	640.9	40.8	43.5
	[D_6]DMSO	1028.0	53.7	104.7
8[8]	$CDCl_3$	1005.2	61.8	247.8
	[D_6]DMSO	1008.0	62.2	239.6
9	$CDCl_3$	960.5	54.5	223.9
	[D_6]DMSO	[b]	54.4	211.6
10	$CDCl_3$	985.9	71.9	75.2
	[D_6]DMSO	[a]	56.6	216.0

[a] Not obtained probably due to the existence of the dynamic equilibrium discussed in the text. [b] Not obtained due to an overlap.



Scheme 5.

Although complex **7** (Figure 2) is chiral in the solid state, the inequivalency of the CH_2 hydrogen atoms is not seen in the 500 MHz ^1H NMR spectra of $CDCl_3$ solutions. On the other hand, there are only moderate differences between the ^{119}Sn chemical shifts in $CDCl_3$ solution and in the solid state (Table 3). Even the largest difference (57.2 ppm), found for **8,** is still far from that corresponding to a change of coordination number[14,15] and is probably caused only by crystal-packing forces. Therefore, it can be assumed that the structures found in the solid state are retained upon dissolution in $CDCl_3$.

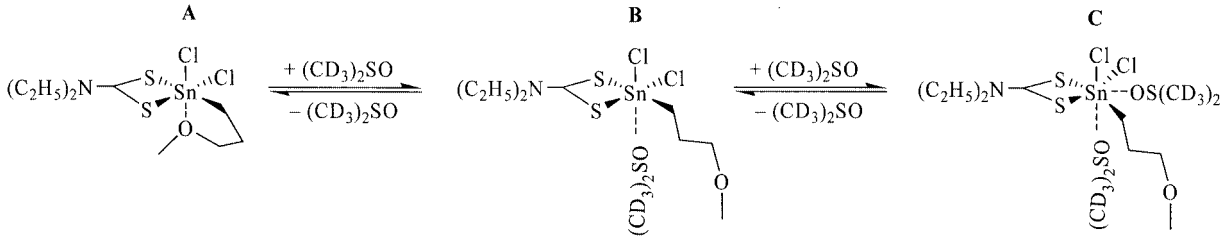
The non-equivalence of the ethyl groups in **9** and **10** found in the solid-state structures (Figures 3 and 4) and in ^{13}C CP/MAS spectra disappears in solution due to a free rotation of the C–N bonds and was not observed even in [D_8]toluene at 180 K.

In the case of compounds **1**, **5**, **8** and **9**, where the 3-methoxypropyl group is bonded to the central tin atom only through carbon, the ^{119}Sn resonances in [D_6]DMSO are only slightly shifted to higher frequency with respect to those in $CDCl_3$ (Table 3). This shows that these compounds preserve their structures even in a strongly coordinating solvent such as [D_6]DMSO. On the other hand, the remaining compounds, i.e. those where the chelate ring of the 3-methoxypropyl ligand is closed in the solid state and in $CDCl_3$ solution, have ^{119}Sn resonances in [D_6]DMSO that are more or less shifted to lower frequency. This shows that the dynamic equilibrium already described in our previous paper[4] is established in which one or more molecules of solvent enter the coordination sphere of the central tin atom and cleave the oxastannacycle.

While only one broad ^{119}Sn resonance was observed in most cases, there is one broad resonance (δ = –470.3 ppm) and one sharp resonance (δ = –575.2 ppm) in the ^{119}Sn NMR spectrum of **10**. This likely indicates that an equilibrium of at least three species is established in [D_6]DMSO solution of **10** (Scheme 6). The broad signal with a chemical shift of δ = –470.3 ppm probably arises due to the equilibrium between hexacoordinate species **A** and **B**, which is fast on the NMR timescale. The difference between the chemical shifts of the observed resonances is 105 ppm (19.5 kHz) and therefore the sharp resonance at δ = –575.2 ppm could be assigned to heptacoordinate complex **C**, which is in a slow exchange regime on the NMR timescale.

The values of the $^2J_{^1H,^{119}Sn}$ coupling constants obtained for proton H1 (Table 4) clearly show that this parameter is mainly influenced by the number of polar groups (Cl, Et_2NCS_2) bonded to the central tin atom, and by the coordination number, and therefore do not bring any information about the O→Sn coordination. Comparison of $^3J_{^1H,^{119}Sn}$ coupling constants found for proton H2 in heptacoordinate and hexacoordinate compounds **8**, **9** and **10** (151.8, 153.9 and 283.1 Hz, respectively) denote that the closure of the oxastannacycle results in a considerable increase of this parameter. However, the 3-methoxypropyl group in pentacoordinate compounds **6** and **7** also forms a chelate but the values of the $^3J_{^1H,^{119}Sn}$ coupling constants observed for proton H2 (134.5 and 169.3 Hz) are similar to those in **8** and **9**, where the oxygen is not coordinated to tin, while another pentacoordinate compound with a chelating 3-methoxypropyl group (**4**) has this parameter almost two times higher (254.2 Hz). Thus, it is evident that $^3J_{^1H,^{119}Sn}$ coupling constants are also still strongly influenced by the coordination environment of the central tin atom and it is impossible to use this parameter to evaluate the coordinative behaviour of the 3-methoxypropyl ligand. Surprisingly, the changes of long-range $^4J_{^1H,^{119}Sn}$ coupling constants obtained for proton H3 (Table 4) do not exhibit any trend that could enable conclusions to be drawn about the coordination of oxygen to tin.

For the methoxy group of tetraorganotin compound **5**, it was impossible to obtain the exact value of the long-range $^6J_{^1H,^{119}Sn}$ coupling constant, but the trace of the sine modulation obtained from an $^1H,^{119}Sn$ J-HMBC experiment enabled us to estimate that the value is lower than 0.5 Hz. On the other hand, the values of this parameter in **6** and **7** (1.32 and 1.73 Hz, respectively) are considerably higher and increase with the strength of donor–acceptor bonding between the oxygen atom of the 3-methoxypropyl ligand and the central tin atom [Sn–O: 2.5505(18) and 2.461(4) Å, respectively] but they are still smaller than that of **4** (2.24 Hz), where the closure of the oxastannacycle is even more firm [Sn–O: 2.394(3) Å]. Thus, it seems that the long-range $^6J_{^1H,^{119}Sn}$ coupling constants of proton H4 reflect the strength of the O→Sn coordinative bond and the conclusions made on the basis of the values obtained for the first



Scheme 6.

set of (3-methoxypropyl)stannanes (**1**–**4**) are confirmed.[4] However, all dithiocarbamate complexes **8**, **9** and **10** have rather large long-range $^{6}J_{^{1}H,^{119}Sn}$ coupling constants (1.06, 2.46 and 3.24 Hz, respectively) for proton H4 even though the 3-methoxypropyl ligand forms a chelate only in the last one. Moreover, the value of 3.24 Hz obtained for **10** is significantly higher than that for **4** (2.24 Hz), where the O→Sn donor–acceptor interaction is stronger [Sn–O: 2.475(3) and 2.394(3) Å, respectively]. Thus, it is evident that this long-range coupling constant is also markedly dependent on the neighbourhood of the central tin atom and is also not very useful as an indicator of intermolecular donor–acceptor interactions.

The values of the $^{1}J_{^{13}C,^{119}Sn}$ and $^{2}J_{^{13}C,^{119}Sn}$ coupling constants obtained for carbons C1 and C2, respectively (Table 5), are influenced especially by the neighbourhood of the central tin atom and no effect of the coordinative behaviour of the 3-methoxypropyl ligand is apparent. In our previous paper,[4] we remarked that the compounds with an oxastannacycle of a 3-methoxypropyl ligand (**3** and **4**) have values of $^{3}J_{^{13}C,^{119}Sn}$ for carbon C3 lower than the corresponding values for 1-butyltin. This also holds true for new compounds **6**, **7** and **10** (Table 5). As in **3**, compound **6** has $^{3}J_{^{13}C,^{119}Sn}$ lower than $^{2}J_{^{13}C,^{119}Sn}$ (i.e., opposite to the trend usually observed for 1-butylstannanes).[15] It has been suggested that this phenomenon is caused by the sum of two scalar coupling pathway contributions − through the covalent bonds of the 3-methoxypropyl chain and through the coordinative O→Sn bond − of opposite signs. In [D_6]-DMSO solutions of **3**, **4**, **6**, **7** and **10**, the $^{3}J_{^{13}C,^{119}Sn}$ coupling constants increase by between 53 and 150 Hz (Table 5). This considerable change can be ascribed to the cleavage of the oxastannacycle because of the equilibrium discussed above in which the donor oxygen atom of the 3-methoxypropyl substituent is replaced by the stronger Lewis base [D_6]DMSO. On the contrary, compounds **1**, **5**, **8** and **9**, where the 3-methoxypropyl ligand does not form a chelate and which do not change structures upon dissolution in [D_6]DMSO, have values of this parameter in [D_6]DMSO even slightly lower than in $CDCl_3$ (Table 5). Thus, $^{3}J_{^{13}C,^{119}Sn}$ coupling constants seem to be a useful indicator of the strength of the O→Sn donor–acceptor interaction in (3-methoxypropyl)stannanes.

Experimental Section

General: THF was distilled from sodium benzophenone ketyl. $CHCl_3$ was distilled from P_2O_5. Other solvents were used without purification. The solution of HCl in $CHCl_3$ was prepared by absorption of dry gaseous HCl which was obtained by dropwise addition of hydrochloric acid into concentrated sulfuric acid. Mg chips, 1,2-dibromomethane, chlorotriphenylstannane and sodium *N*,*N*-diethyldithiocarbamate trihydrate were obtained from commercial sources. Preparation of 1-chloro-3-methoxypropane, tetrakis(3-methoxypropyl)stannane (**1**), chlorotris(3-methoxypropyl)-stannane (**2**), dichlorobis(3-methoxypropyl)stannane (**3**) and trichloro(3-methoxypropyl)stannane (**4**) has been described elsewhere.[4]

Microanalyses (C, H, N, S, Cl) were carried out using a Fison EA 1108 instrument in the Microanalytical Laboratory at the University of Pardubice.

Synthesis of (3-Methoxypropyl)triphenylstannane RPh_3Sn (5): A solution of 1-chloro-3-methoxypropane (3.00 g, 27.63 mmol) in THF (6 mL) was added to Mg chips (0.83 g, 34.14 mmol) which were previously activated by I_2 vapours. About 20% of the solution was added at once and the reaction was started by addition of 2 drops of 1,2-dibromethane. The rest of the solution was added dropwise in order to maintain the reflux. Then, the reaction mixture was refluxed for a further hour. After cooling to –50 °C, a solution of chlorotriphenylstannane (7.18 g, 18.63 mmol) in THF (6 mL) was added dropwise and the reaction mixture was then refluxed for 8 h. After cooling to room temperature, the reaction mixture was filtered and water (40 mL) was added. The mixture was extracted with diethyl ether (3 × 20 mL). The organic part was separated, dried with anhydrous Na_2SO_4 and the solvents were removed by rotary evaporation. The residue was recrystallised from $CHCl_3$/hexane solution and **1** (6.56 g, yield 85%) was obtained as white crystals, m.p. 49–51 °C. ^{1}H NMR ($CDCl_3$, 25 °C): δ = 1.84 (m, 2 H, $SnCH_2CH_2$), 2.31 (m, 2 H, $SnCH_2CH_2$), 3.17 (s, 3 H, OCH_3), 3.38 (t, $^{3}J_{HH}$ = 6.5 Hz, 2 H, CH_2OCH_3), 7.37 (m, 9 H, *m*-Ph, *p*-Ph), 7.56 (m, 6 H, *o*-Ph) ppm. ^{13}C NMR ($CDCl_3$, 25 °C): δ = 7.32 ($SnCH_2$), 26.4 ($SnCH_2CH_2$), 58.1 (OCH_3), 75.0 (CH_2OCH_3), 128.3 (*m*-Ph), 128.6 (*p*-Ph), 136.9 (*o*-Ph), 139.2 (*i*-Ph) ppm. $C_{22}H_{24}OSn$ (423.14): calcd. C 62.45, H 5.72; found C 62.25, H 5.53.

Synthesis of Chloro(3-methoxypropyl)phenylstannanes $RPh_{3-x}SnCl_x$ 6 and 7: A solution of HCl in dry $CHCl_3$ [10 mL (0.169 M) for **6**; 19 mL (0.169 M) for **7**] was added to **1** (0.5 g, 1.20 mmol) and the mixture was stirred at room temperature for 2 d. The solvent was then removed by rotary evaporation. The residue was recrystallised from $CHCl_3$/hexane solution.

Chloro(3-methoxypropyl)diphenylstannane (6): Yield: 0.43 g (96%), white crystals, m.p. 93–95 °C. ^{1}H ($CDCl_3$, 25 °C): δ = 1.79 (m, 2 H, $SnCH_2$), 2.15 (m, 2 H, $SnCH_2CH_2$), 2.96 (s, 3 H, OCH_3), 3.53 (t, $^{3}J_{HH}$ = 6.0 Hz, 2 H, CH_2OCH_3), 7.41 (m, 2 H, *p*-Ph), 7.43 (m, 4 H, *m*-Ph), 7.71 (m, 4 H, *o*-Ph) ppm. ^{13}C NMR ($CDCl_3$, 25 °C): δ = 14.7 ($SnCH_2$), 25.3 ($SnCH_2CH_2$), 73.0 (CH_2OCH_3), 128.6 (*m*-Ph), 129.2 (*p*-Ph), 135.6 (*o*-Ph), 140.4 (*i*-Ph) ppm. $C_{16}H_{19}ClOSn$ (381.48): calcd. C 50.38, H 5.02, Cl 9.29; found C 49.95, H 4.89, Cl 9.01.

Dichloro(3-methoxypropyl)phenylstannane (7): Yield: 0.42 g (98%), white crystals, m.p. 99–101 °C. ^{1}H ($CDCl_3$, 25 °C): δ = 1.96 (m, 2 H, $SnCH_2$), 2.19 (m, 2 H, $SnCH_2CH_2$), 3.29 (s, 3 H, OCH_3), 3.61 (t, $^{3}J_{HH}$ = 5.4 Hz, 2 H, CH_2OCH_3), 7.45 (m, 1 H, *p*-Ph), 7.64 (m, 2 H, *m*-Ph), 7.80 (m, 2 H, *o*-Ph) ppm. ^{13}C NMR ($CDCl_3$, 25 °C): δ = 22.2 ($SnCH_2$), 24.9 ($SnCH_2CH_2$), 58.5 (OCH_3), 71.7 (CH_2OCH_3), 129.0 (*m*-Ph), 130.6 (*p*-Ph), 134.8 (*o*-Ph), 141.0 (*i*-Ph) ppm. $C_{10}H_{14}Cl_2OSn$ (339.83): calcd. C 35.35, H 4.15, Cl 20.87; found C 35.03, H 3.95, Cl 20.63.

Synthesis of (3-Methoxypropyl)stannyl *N*,*N*-Diethyldithiocarbamates $RSn(S_2CNEt_2)_{3-x}Cl_x$ (8–10): A mixture of **4** (0.5 g, 1.67 mmol) and sodium *N*,*N*-diethyldithiocarbamate [1.19 g (5.29 mmol) for **8**; 0.76 g (3.37 mmol) for **9**; 0.38 g (1.69 mmol) for **10**] in acetone (10 mL) was stirred at room temperature for 2 h. The reaction mixture was then filtered and the solvent was removed by rotary evaporation. The residue was recrystallised from $CHCl_3$/hexane solution.

(3-Methoxypropyl)stannyl Tris(*N*,*N*-diethyldithiocarbamate) (8): Yield: 0.86 g (80%), yellowish crystals, m.p. 92–93 °C (for further characterisation of **8** see ref.[8]).

Table 6. Experimental details for the X-ray crystal structure determination of **6**, **7**, **9** and **10**.

	6	**7**	**9**	**10**
Empirical formula	$C_{16}H_{19}ClOSn$	$C_{10}H_{14}Cl_2OSn$	$C_{14}H_{29}ClN_2OS_4Sn$	$C_9H_{19}Cl_2NOS_2Sn$
Formula mass	381.45	339.80	523.83	410.96
Crystal system	monoclinic	monoclinic	triclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$ (no. 2)	$P2_1/c$
a [Å]	9.6368(19)	9.4591(5)	10.416(3)	8.0136(18)
b [Å]	17.639(4)	8.3341(16)	10.670(3)	14.738(4)
c [Å]	9.786(2)	16.5793(10)	11.849(3)	13.858(5)
α [°]	90	90	93.39(3)	90
β [°]	99.87(2)	93.126(6)	114.34(3)	100.42(3)
γ [°]	90.00	90.00	107.15(3)	90.00
V [Å^3]	1638.9(6)	1305.1(3)	1121.5(7)	1609.7(8)
Z	4	4	2	4
D_c [g cm^{-3}]	1.546	1.729	1.551	1.696
μ [mm^{-1}]	1.712	2.336	1.635	2.161
T [K]	223	297	223	203
Reflections collected	11464	4609	7914	6382
Independent reflections	2759 (R_{int} = 0.047)	2122 (R_{int} = 0.069)	3658 (R_{int} = 0.102)	2838 (R_{int} = 0.046)
Goodness of fit	1.007	1.113	1.130	1.066
R_1, wR_2 [$I > 2\sigma(I)$]	0.022, 0.055	0.056, 0.156	0.050, 0.152	0.024, 0.061
R_1, wR_2 (all data)	0.028, 0.058	0.063, 0.172	0.054, 0.166	0.028, 0.065

Chloro(3-methoxypropyl)stannyl Bis(*N*,*N*-diethyldithiocarbamate) (9): Yield: 0.72 g (83%), yellowish crystals, m.p. 66–69 °C. ^{1}H (CDCl$_3$, 25 °C): δ = 1.28 (t, $^3J_{HH}$ = 6.9 Hz, 12 H, CH$_2$C*H*$_3$), 1.83–1.96 (m, 4 H, SnC*H*$_2$C*H*$_2$), 3.28 (s, 3 H, OC*H*$_3$), 3.38 (t, $^3J_{HH}$ = 5.8 Hz, 2 H, C*H*$_2$OCH$_3$), 3.69 (q, $^3J_{HH}$ = 6.9 Hz, 8 H, NC*H*$_2$) ppm. ^{13}C NMR (CDCl$_3$, 25 °C): δ = 11.7 (CH$_2$*C*H$_3$), 25.9 (SnCH$_2$*C*H$_2$), 42.4 (Sn*C*H$_2$), 50.7 (N*C*H$_2$), 58.1 (O*C*H$_3$), 73.8 (*C*H$_2$OCH$_3$), 196.8 (N*C*S$_2$) ppm. $C_{14}H_{29}ClN_2OS_4Sn$ (523.82): calcd. C 32.10, H 5.58, Cl 6.77, N 5.35, S 24.48 ; found C 31.93, H 5.35, Cl 6.43, N 5.03, S 24.35.

Dichloro(3-methoxypropyl)stannyl *N*,*N*-Diethyldithiocarbamate (10): Yield: 0.40 g (59%), white crystals, m.p. 135–136 °C. ^{1}H (CDCl$_3$, 25 °C): δ = 1.35 (t, $^3J_{HH}$ = 7.1 Hz, 6 H, CH$_2$C*H*$_3$), 1.77 (m, 2 H, SnC*H*$_2$), 2.19 (m, 2 H, SnCH$_2$C*H*$_2$), 3.67 (t, $^3J_{HH}$ = 6.0 Hz, 2 H, C*H*$_2$OCH$_3$), 3.72 (q, $^3J_{HH}$ = 7.1 Hz, 4 H, NC*H*$_2$), 3.74 (s, 3 H, OC*H*$_3$) ppm. ^{13}C NMR (CDCl$_3$, 25 °C): δ = 11.7 (CH$_2$*C*H$_3$), 24.1 (SnCH$_2$*C*H$_2$), 35.2 (Sn*C*H$_2$), 51.7 (N*C*H$_2$), 58.6 (O*C*H$_3$), 71.4 (*C*H$_2$OCH$_3$), 192.8 (N*C*S$_2$) ppm. $C_9H_{19}Cl_2NOS_2Sn$ (411.00): calcd. C 26.3, H 4.66, Cl 17.25, N 3.41, S 15.60; found C 26.11, H 4.53, Cl 17.19, N 3.32, S 15.52.

NMR Spectroscopy: ^{1}H, ^{13}C and ^{119}Sn NMR spectra were recorded in a 5-mm tuneable probe with a Bruker AMX 360 (^{1}H: 360.14 MHz; ^{13}C: 90.57 MHz; ^{119}Sn: 134.28 MHz) or a Bruker AVANCE 500 spectrometer (^{1}H: 500.13 MHz; ^{13}C: 125.77 MHz; ^{119}Sn: 186.48 MHz). ^{1}H and ^{13}C chemical shifts are given in ppm with respect to Me$_4$Si, and ^{119}Sn chemical shifts with respect to Me$_4$Sn. The gradient-assisted 1D ^{1}H,^{119}Sn HMQC and 2D ^{1}H,^{119}Sn J-HMBC spectra were recorded as explained elsewhere,[5] with the Bruker AVANCE 500 spectrometer. ^{13}C and ^{119}Sn CP/MAS NMR spectra were recorded with a Bruker AVANCE 500 spectrometer equipped with a double-bearing CP/MAS probe at room temperature. The ^{119}Sn chemical shifts were calibrated indirectly to tetracyclohexyltin (δ = –97.35 ppm) and were allocated approximately to the centre of gravity of the signals.

X-ray Crystallography: Single crystals were prepared by diffusion of hexane into CHCl$_3$ solutions of the complexes. The diffraction experiments were carried out using Mo-K_α radiation (λ = 0.71073 Å) on a Stoe IPDS (for **6** and **9**) or a Stoe STADI (for **7** and **10**) diffractometer. The structures were solved by direct methods (SHELXS-86)[16] and refined by full-matrix least-squares on F^2 (SHELXL-97)[17] with anisotropic displacement parameters for all non-H atoms. Hydrogen atoms were placed in calculated positions and refined according to the riding model (Table 6).

CCDC-238979 (for **10**), -238980 (for **7**), -238981 (for **9**) and -238982 (for **6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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