

Comparative assessment of weak intramolecular coordinations at tin in functionalized mono-organotin trichlorides and mono-organotrialkynyltins by multinuclear solution NMR

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Abstract

The intramolecular coordination behaviors of $\text{MeOOC}(\text{CH}_2)_2\text{SnCl}_3$ and $\text{MeOOC}(\text{CH}_2)_2\text{Sn}(\text{C}\equiv\text{C}-\text{Ph})_3$ are compared, using multinuclear NMR, including ^1H – ^{119}Sn -HMQC spectroscopy. While $\text{MeOOC}(\text{CH}_2)_2\text{SnCl}_3$ exhibits intramolecular coordination to tin in solution, through the carbonyl oxygen, unlike $\text{CH}_3\text{COO}(\text{CH}_2)_3\text{SnCl}_3$ which coordinates through the alkoxy oxygen, no firm evidence could be obtained for the existence of such an interaction in $\text{MeOOC}(\text{CH}_2)_2\text{Sn}(\text{C}\equiv\text{C}-\text{Ph})_3$. This is ascribed to the lower electronegativity of an alkynyl group, as compared to a chlorine atom, a result which is, however, in contrast with the fact that hydroxy-functionalized vinyl SnPh_3 compounds are known from literature to exhibit such weak intramolecular coordinations. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Intramolecular coordination; Multinuclear solution NMR; Tin

1. Introduction

Mono-organotin trichlorides are of interest as precursors of tin containing organic–inorganic hybrid materials and clusters [1–6]. The presence of a functional group on the carbon chain influences their stability because of its coordination to tin, dependent on its nature, the chain length and the solvent [7–15]. ω -(Trichlorostannyl)alkyl acetates $(\text{CH}_3\text{COO}(\text{CH}_2)_n\text{SnCl}_3, n=3-5, \text{ respectively compounds } \mathbf{1-3})$ in solution [7] are fast equilibrium mixtures of a monomer with intramolecular coordination and an oligomer with intermolecular coordination. The C4 ester [16], **2**, is a cyclodimer in the solid state, with coordination from the carbonyl oxygen to tin. In the solution mixture in

dynamic equilibrium, the monomeric form of the C3 ester **1**, with the alkoxy oxygen coordinating to tin, is predominant, independently of the concentration, while by contrast, the oligomeric form predominates increasingly upon concentration increase for the C4/C5 esters **2** and **3** [7]. In $\text{ROOC}(\text{CH}_2)_2\text{SnCl}_3$ esters [11–14], the carbonyl oxygen coordinates intramolecularly to tin, in the crystalline state ($\text{R} = \text{Me}$ [11], compound **4**; $\text{R} = i\text{-Pr}$ [12]) as well as in CH_2Cl_2 [13].

On the other hand, mild hydrolysis of functionalized mono-organotrialkynyltin compounds, $\text{RSn}(\text{C}\equiv\text{CR}')_3$, is a convenient route to functionalized mono-organotin oxides [17,18], because it by-passes the tricky route through the more unstable organotin trichlorides and trialkoxides [1]. This enables a more optimal control of the hydrolysis conditions [17,18]. Determining whether the tin atom in $\text{RSn}(\text{C}\equiv\text{CR}')_3$ compounds, with R containing a Lewis base, has still sufficient Lewis acidity to enable an intramolecular coordination should allow the

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understanding of their higher stability as compared to mono-organotin trichlorides [17,18]. Such a weak coordination is plausible, vinyltriphenyltin compounds of the type $\text{HO-CRR}'\text{-CH=CH-SnPh}_3$ exhibiting such an interaction [19–25].

This report presents a study of the coordination behavior in CD_2Cl_2 solution of $\text{CH}_3\text{OOC}(\text{CH}_2)_2\text{-Sn}(\text{C}\equiv\text{CPh})_3$, **5**, a novel derivative for which no crystals suitable for X-ray diffraction studies, were obtained. Our analysis [7,15] uses ^1H , ^{13}C , ^{119}Sn [26–28], ^{17}O 1D-NMR [29], gradient assisted [30–34] ^1H – ^{119}Sn [35–37] Heteronuclear Multiple Quantum Correlation (HMQC) [38,39] as well as IR spectroscopy. The NMR studies were performed on both compounds **4** and **5** in parallel, taking the well-known [11–14] intramolecular CD_2Cl_2 solution coordination behavior of **4** as a reference. The possible existence of a $p\pi\text{-}d\pi$ interaction between a vinylic group and a tin atom is also addressed for 4-pentenyltin trichloride (**10**) and 5-hexenyltin trichloride (**11**), the NMR and coordination characteristics of which are compared with those of compounds **1**–**3**.

2. Experimental section

2.1. General

All reactions were carried out under a dry nitrogen atmosphere. Petroleum ether, THF and toluene were distilled from sodium benzophenone ketyl prior to use. Diisopropylamine was distilled on KOH. Acetonitrile and dichloromethane were distilled on CaH_2 . Tin tetrachloride was distilled before use. **6**, **7** [40] and **8** [41] (see Table 2) were prepared from the corresponding trichlorides according to established procedures. Compound **9** [42] was obtained by transmetalation of tetrakis(phenylethynyl)tin with *t*-butylmagnesium chloride.

2.2. Synthesis of

[2-(methoxycarbonyl)ethyl]tris(phenylethynyl)tin, **5**

In a three-necked flask at 0°C , a solution of 10 ml of butyllithium (2.5 M, 25 mmol) was added to phenylacetylene (2.58 g, 25.2 mmol) in degassed toluene (the use of undegassed toluene resulted in the formation of some [2-(butoxycarbonyl)ethyl]tris(phenylethynyl)tin). After 20 min at room temperature, the lithium reagent was added dropwise to a solution of [2-(methoxycarbonyl)ethyl]trichlorotin [9] (2.28 g, 7.2 mmol) in 30 ml of dry degassed toluene at -78°C . After 3 h the mixture was allowed to reach room temperature, stirred for one additional hour and filtered on dry MgSO_4 under nitrogen. The solvents were evaporated at room temperature under high vacuum and the product chromatographed on dry Florisil with dichloromethane as a solvent: yield 59%; m.p. 66°C .

2.3. Synthesis of hex-5-enyltrichlorotin, **10**

To a solution of diisopropylamine (5.0 g, 50 mmol) in 40 ml of THF, 20 ml of butyllithium in hexane (2.5 M, 50 mmol) were added at 0°C . After 5 min, tricyclohexylstannane [1] (14.8 g, 40 mmol) in 25 ml of THF was added, followed after 15 min by 1-bromohex-5-ene (8.0 g, 50 mmol). The solution was stirred for 2 h at room temperature. Subsequently, it was hydrolyzed, decanted and dried with MgSO_4 . After evaporation of the solvents, the compound was distilled in a Kugelrohr apparatus: yield 61%; b.p. 110°C (0.001 mm). Tin tetrachloride (10.4 g, 40 mmol) was added slowly to a solution of hex-5-enyltricyclohexyltin (10.8 g, 24 mmol) in 40 ml of petroleum ether. After 30 min at 50°C , 140 ml of petroleum ether and 120 ml of acetonitrile were added and the mixture stirred for 3 h at room temperature. After decantation, the acetonitrile phase was washed three times with 100 ml of petroleum ether. After evaporation of the solvent, the product was distilled in a Kugelrohr apparatus: yield 27%; b.p. 90°C (0.001 mm).

2.4. Synthesis of pent-4-enyltrichlorotin, **11**

Pent-4-enyltrichlorotin **11** was prepared as **10** from the corresponding pent-4-enyltricyclohexyltin; yield 33%; b.p. 90°C (0.001 mm).

2.5. IR spectroscopy

IR spectra in CCl_4 were recorded on a Perkin Elmer Paragon 1000 apparatus.

2.6. NMR experiments

The samples were prepared by dissolving 10 or 100 mg of **4**, 15 or 135 mg of **5**, in 500 μl of CD_2Cl_2 , 20 or 100 mg of **10**, **11** and **12** in 500 μl of C_6D_6 . The solutions were prepared in vacuo under moisture free conditions with dichloromethane- d_2 from freshly opened ampules, into NMR tubes which were subsequently sealed. All ^1H -, ^{13}C -, ^{119}Sn - and ^{17}O -NMR spectra were recorded at 303 K, unless otherwise indicated, on a Bruker AMX500 spectrometer as previously described [7,15,34,35,43,44]. Chemical shifts were referenced to the residual solvent peak and converted to the standard Me_4Si scale by adding 5.32 and 53.8 ppm for ^1H and ^{13}C nuclei. For ^{119}Sn chemical shifts, $\Xi = 37.290665$ MHz [45,46] was used. ^{17}O chemical shifts were referenced to external deionised water at 313 K. The ^{17}O -NMR spectrum of **4** was recorded in CD_2Cl_2 at 303 K from a solution containing ca. 200 mg sample per 0.5 ml of solvent. Under such conditions, no signal was obtained for **5**. Accordingly, the ^{17}O -NMR spectrum of **5** was recorded in C_6D_6 at 343 K from a

solution with similar concentration. For the purpose of comparison, the ^{17}O -NMR spectrum of methyl butyrate was recorded in CD_2Cl_2 at 303 K. The gradient pulsed proton detected 1D ^1H - ^{119}Sn -HMQC correlation spectra were acquired as illustrated recently [7,15,34,37].

3. Results and discussion

Organotrialkynyltins were obtained by phenylethynylation [40,41] of the corresponding trichlorides with phenylethynyllithium, except **9** which could not be prepared by this method as the corresponding *t*-butyltrichlorotin decomposes in tin dichloride and *t*-butyl chloride [47]. The latter compound **9** was obtained by transmetallation of tetrakis(phenylethynyl)tin with *t*-butylmagnesium chloride [42].

The NMR data obtained from CD_2Cl_2 solutions of **4** and **5** are given in Table 1. Being essentially concentration independent—unless otherwise specified—only the NMR parameters from the diluted solutions are given (see Section 2). The ^{119}Sn chemical shift of **4** changes to low frequency by only 2 ppm upon a 10-fold concentration increase, indicating essentially the absence of any intermolecular coordination, unlike the C4/C5 esters **2** and **3** [7]. The NMR data of **4** confirm the structure previously proposed from IR data in solution and X-ray data in the crystalline state (Scheme 1) [11–14].

Though the coordinations of **1** and **4** are strikingly different, this difference can be rationalized in terms of the formation of a stable, almost planar, five-membered ring, upon intramolecular coordination. Coordination from the carbonyl oxygen in **1** would require the formation of a seven-membered ring, the higher flexibility of which destabilizes the intramolecular coordination, as demonstrated earlier [7]. For analogous reasons, intramolecular coordination is not favoured in **2** and **3**, explaining that cyclodimerization with involvement of the carbonyl oxygen is preferred [7]. The two different structures are in full agreement with the non-observation, for **4**, of a ^1H - ^{119}Sn -HMQC correlation peak between the OCH_3 ^1H and the ^{119}Sn resonances, in contrast with the existence of an intense correlation between the OCH_2 ^1H and the ^{119}Sn resonances of **1** [7].

Unlike **4**, none of the NMR data of **5** as such indicate any possibility of coordination. This specially holds true for ^{17}O -NMR data. The significant low frequency shift of the ^{17}O carbonyl resonance of **4** by -29 ppm, coupled to essentially a negligible change of its ^{17}O methoxy resonance by $+4$ ppm with respect to methyl butyrate confirms the intramolecular carbonyl oxygen coordination. It is well recognized that interactions of oxygen lone pairs cause a low frequency shift of the ^{17}O resonance [48,49] when the determinant electron density increase at the oxygen atom is domi-

nated by π -charge transfers [50], while pure σ -electron density increases induce high frequency ^{17}O shifts [49,51]. By contrast, the very similar ^{17}O chemical shifts of **5** (356 and 135 ppm) as compared to those of methyl butyrate taken as a reference (352 and 137 ppm) do not support the existence of an intramolecular donor–acceptor interaction in **5**. It should be outlined, however, that the ^{17}O data of **5** refer to a higher temperature (348 K) than for **4** (303 K), because, unlike **4**, no ^{17}O -NMR signal is visible at room temperature for **5**, maybe just because of an exchange phenomenon involving reversible formation and dissociation of the $\text{C}=\text{O} \rightarrow \text{Sn}$ interaction in **5**.

Table 1
NMR data of $(\text{PhC}\equiv\text{C})_3\text{SnCH}_2\text{CH}_2\text{COOCH}_3$ (**5**) and $\text{Cl}_3\text{SnCH}_2\text{CH}_2\text{COOCH}_3$ (**4**) in CD_2Cl_2 at 303 K^a

Compound	$(\text{PhC}\equiv\text{C})_3\text{SnCH}_2\text{CH}_2\text{COOCH}_3$ (5) ^b	$\text{Cl}_3\text{SnCH}_2\text{CH}_2\text{COOCH}_3$ (4) ^c
^{13}C		
$\text{CH}_2(\alpha)$	11.5; $^1J(^{13}\text{C}-^{119}/^{117}\text{Sn}) = 695/665$	25.0; $^1J(^{13}\text{C}-^{119}/^{117}\text{Sn}) = 835/798$
$\text{CH}_2(\beta)$	29.6; $^2J(^{13}\text{C}-^{119}/^{117}\text{Sn}) \approx 41^{\text{d}}$	28.1; $^2J(^{13}\text{C}-^{119}/^{117}\text{Sn}) = 72/69$
$\text{C}=\text{O}$	176.0	182.0
OCH_3	52.6	56.1
$\text{Cl}\equiv$	89.4; $^1J(^{13}\text{C}-^{119}/^{117}\text{Sn}) = 833/796$	—
$\text{C}2\equiv$	109.2; $^2J(^{13}\text{C}-^{119}/^{117}\text{Sn}) = 169/161$	—
C_{ipso}	123.1; $^3J(^{13}\text{C}-^{119}/^{117}\text{Sn}) \approx 18^{\text{d}}$	—
C_{ortho}	132.5	—
C_{meta}	128.7	—
C_{para}	129.3	—
^{119}Sn	-257.4	-115.0
^1H		
$\text{CH}_2(\alpha)$	1.64; $^2J(^1\text{H}-^{119}\text{Sn}) \approx 82^{\text{e}}$	2.26; $^2J(^1\text{H}-^{119}\text{Sn}) \approx 109^{\text{e}}$
$\text{CH}_2(\beta)$	2.89; $^3J(^1\text{H}-^{119}\text{Sn}) \approx 132^{\text{e}}$	2.94; $^3J(^1\text{H}-^{119}\text{Sn}) \approx 198^{\text{e}}$
OCH_3	3.77	3.98
H_{ortho}	7.54	—
$\text{H}_{\text{meta+para}}$	7.36	—
$^{17}\text{O}^{\text{f}}$		
$\text{C}=\text{O}$	(352) ^{g,h} 356 ⁱ	323 ^g
OCH_3	(137) ^{g,h} 135 ⁱ	141 ^g

^a Chemical shifts referencing as in Section 2. Coupling constants in Hz.

^b 15 mg/0.5 ml.

^c 10 mg/0.5 ml.

^d Unresolved $^nJ(^{13}\text{C}-^{119}\text{Sn})$ and $^nJ(^{13}\text{C}-^{117}\text{Sn})$ coupling constants.

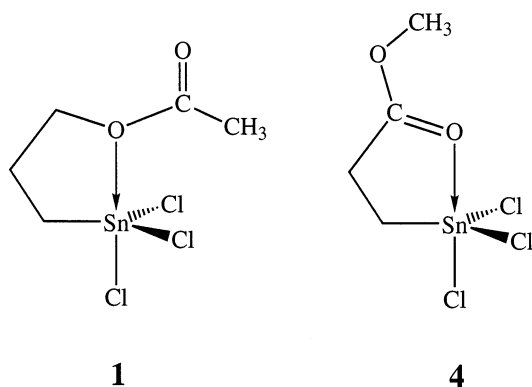
^e $^nJ(^1\text{H}-^{119}\text{Sn})$ coupling constants in Hz (in brackets), as determined from 1D ^1H - ^{119}Sn -HMQC spectra.

^f With respect to water.

^g Concentration: ca. 200 mg/0.5 ml CD_2Cl_2 .

^h ^{17}O chemical shifts of methyl butyrate in CD_2Cl_2 at 303 K: $\text{C}=\text{O}$ 352; OCH_3 137.

ⁱ From a C_6D_6 solution at 348 K.



Scheme 1.

The IR data lie essentially in the same line. While **4** displays a solution $\nu(\text{C}=\text{O})$ stretch frequency at 1660 cm^{-1} [13], **5** exhibits its $\nu(\text{C}=\text{O})$ stretch at 1729 cm^{-1} (with some shoulder at 1740 cm^{-1}), comparable to those of simple non-stannylated esters like methyl acetate, around 1740 cm^{-1} [13], and to that of methyl butyrate at 1742 cm^{-1} , determined here for comparison.

As **4**, the 1D ^1H – ^{119}Sn -HMQC spectrum of **5** displays only correlation signals with the ^{119}Sn resonance at the level of both CH_2 ^1H resonances, no such correlation being observed for the OCH_3 resonance, even with very long HMQC preparation periods [38,39].

Also the $^2J(^1\text{H}$ – $^{119}\text{Sn})$ and $^3J(^1\text{H}$ – $^{119}\text{Sn})$ coupling constants are significantly larger in **4** than in **5**, in agreement with a higher degree of five-coordination in **4** than in **5**.

In order to further assess the possible existence of an intramolecular $\text{C}=\text{O} \rightarrow \text{Sn}$ interaction in **5**, we compared its NMR data with those of four other mono-organotris(phenylethynyl)tin compounds [40–42] where such an interaction cannot be observed because of the absence of a functional group in the organic moiety R. Table 2 gives a summary of the most relevant data. Despite some dispersion in the $^1J(^{13}\text{C}$ – $^{119/117}\text{Sn})(\text{C sp}^3)$ coupling constant values (R group), it appears that the value of **5** is significantly higher than that of the four other non-functionalized $(\text{PhC}\equiv\text{C})_3\text{SnR}$ compounds **6**–**9**. This holds especially true upon comparison of compounds **5** and **7**, which are most isostructural and thus best comparable in this respect. In parallel, the ^{119}Sn resonance of **5** is low frequency-shifted by 15 to 25 ppm with respect to those of compounds **6**–**9**. Taken together, this data comparison favours the existence of a very weak intramolecular $\text{C}=\text{O} \rightarrow \text{Sn}$ interaction in **5**. Thus, this indicates that the absence of evidence in the ^{17}O -NMR data of **5** might well be related to the temperature effect discussed above. On the other hand, the $^1J(^{13}\text{C}$ – $^{119/117}\text{Sn})(\text{C}\equiv)$ coupling constant value does not appear

to be a useful structure indicator to further evidence this proposal.

The multinuclear NMR data for 4-pentenyltin trichloride (**10**) and 5-hexenyltin trichloride (**11**) are given in Table 3. Though slightly more sensitive to the concentration (especially for the ^1H α - CH_2 resonances showing a high frequency shift of 0.1–0.2 ppm upon 5-fold concentration increase), no informative concentration effects on the ^1H - and ^{13}C -NMR parameters are observed. Henceforth, as in Table 1, only diluted solution ^1H - and ^{13}C -NMR data are provided in Table 3, also because these are most relevant for the assessment of the existence of an intramolecular $\text{p}\pi$ – $\text{d}\pi$ interaction from the double $\text{C}=\text{C}$ bond to tin. For ^{119}Sn -NMR, however, the data are provided at two concentrations. The ^1H -, ^{13}C - and ^{119}Sn -NMR data for hexyltin trichloride (**12**) are provided for comparison.

Comparing the ^1H - and ^{13}C -NMR data of $\text{Cl}_3\text{Sn}(\text{CH}_2)_3\text{CH}=\text{CH}_2$ (**10**) and $\text{Cl}_3\text{Sn}(\text{CH}_2)_4\text{CH}=\text{CH}_2$ (**11**) with those of $\text{Cl}_3\text{Sn}(\text{CH}_2)_5\text{CH}_3$ (**12**), reveals the total absence of any evidence for the existence of an intramolecular coordination from the $\text{CH}=\text{CH}_2$ moiety to tin, at the level of α - CH_2 and β - CH_2 ^1H and ^{13}C chemical shifts as well as the $^nJ(^1\text{H}$ – $^{119}\text{Sn})$ and $^nJ(^{13}\text{C}$ – $^{119/117}\text{Sn})$ coupling constants. The ^{119}Sn -NMR chemical shifts lead to the same conclusion, despite the lack of self-consistency in the slight concentration dependence they display, in the alkenyltin trichlorides **10** and **11**, as well as hexyltin trichloride **12** and butyltin trichloride [15]. We have no explanation to this apparently disparate concentration effect in both the alkyl- and alkenyltin trichlorides, but they are both slight and obviously unrelated to intramolecular coordination from a functionality in the R group, whatsoever.

1D ^1H – ^{119}Sn -HMQC experiments reveal the existence of correlations between the ^{119}Sn resonance and the ^1H resonance of all the protons of the 4-pentenyl chain of **10**, including the vinylic ones. In the case of **11**, the terminal vinylic CH_2 protons do not exhibit a correlation, but the vinylic CH and all methylene protons of the 5-hexenyl chain do. This indicates that correlations between the ^{119}Sn resonance are observable up to the ε -protons, albeit with an intensity decrease, at a given constant HMQC preparation time, as the distance from the tin atom increases, indicating that in **10** and **11** correlations are observable up to $^6J(^1\text{H}$ – $^{119}\text{Sn})$ couplings. For comparison, for **12**, such correlations are observed only up to the δ -protons ($^5J(^1\text{H}$ – $^{119}\text{Sn})$ couplings) [7]. These results should be interpreted with care. Indeed the observability of such remote couplings in **10** and **11** are traced to a better transmission of long range couplings through the carbon chain due to the presence of the sp^2 carbons of the double $\text{C}=\text{C}$ bond of **10** and **11**, not present in **12**,

Table 2

Comparison of NMR data of $(\text{PhC}\equiv\text{C})_3\text{SnCH}_2\text{CH}_2\text{COOCH}_3$ (**5**) with those of other $(\text{PhC}\equiv\text{C})_3\text{SnR}$ compounds

Compound	$\delta^{119}\text{Sn}$	$^1J(^{13}\text{C}-^{119/117}\text{Sn})(\text{C sp}^3)$	$^1J(^{13}\text{C}-^{119/117}\text{Sn})(\text{C}\equiv)$
$(\text{PhC}\equiv\text{C})_3\text{SnCH}_2\text{CH}_2\text{COOCH}_3$ (5)	–257.4	695/665	833/796
$(\text{PhC}\equiv\text{C})_3\text{SnCH}_3$ (6)	–239.0	625/598	849/814
$(\text{PhC}\equiv\text{C})_3\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ (7)	–242.0	633/605	780/746
$(\text{PhC}\equiv\text{C})_3\text{SnCH}(\text{CH}_3)_2$ (8)	–235.5	669/639	731/698
$(\text{PhC}\equiv\text{C})_3\text{SnC}(\text{CH}_3)_3$ (9)	–232.9	^a	709/679

^a Not observed.

and not to an effective $p\pi$ – $d\pi$ interaction. Three pieces of evidence disfavour the latter interpretation. First, while plausible in **10** it is not in **11**, because only the CH protons and not the CH_2 protons of the vinyl group do exhibit a correlation. Second, while the correlations first decrease but again increase in intensity as the alkyl chain of the C4/C5 esters **2** and **3** is traversed [7], these correlation intensities decrease through the alkyl chain of the alkenyltin trichlorides **10** and **11**. Third, no other NMR data favour the presence of a $p\pi$ – $d\pi$ interaction, as evidenced by a comparison of the

NMR data of **10** and **11** on the one hand, **12** on the other hand (see Table 3).

4. Conclusion

For mono-organotin trichlorides with an ester functional group, it can be concluded that the carbonyl oxygen rather than the alkoxy oxygen of an ester function is the preferred intramolecular coordination site, provided the donor–acceptor interaction leads to a stable ring, e.g. a five-membered one. Only if larger rings, which are more destabilized by thermal flexibility, are generated from the intramolecular coordination with the carbonyl oxygen, does the molecule favour the alkoxy oxygen coordination from the ester function, in order to give rise to a more rigid and planar stable five-membered ring. Unlike mono-organotin trichlorides with ester functions, which generate intramolecular donor–acceptor interactions from the carbonyl oxygen to tin, the corresponding mono-organotrialkynyltin can generate at most a much weaker interaction between the functional group and the tin atom, with an unspecified coordination mode, if any. In comparison with chlorine atoms, the electronegative effect of the alkynyl groups is not strong enough to induce on the metal an electronic deficiency which would be balanced by inter- or intramolecular coordination. To some extent the absence of a marked donor–acceptor interaction in such functionalized mono-organotrialkynyltin compounds is surprising, as it is well established that functionalized vinyltriphenyltin compounds of the type $\text{HO-CRR}'\text{-CH=CH-SnPh}_3$ (R and R' alkyl groups) do exhibit a weak intramolecular donor–acceptor interaction, despite the lower electronegativity of the phenyl group, as compared to the alkynyl group [19–25]; this in turn confirms the stronger donor capacity of the hydroxy function, with respect to the ester function, as demonstrated recently in comparative investigations on intramolecular coordinations in $\text{HO-(CH}_2)_n\text{SnCl}_3$ [15] and $\text{CH}_3\text{COO-(CH}_2)_n\text{SnCl}_3$ [7] derivatives. Finally, unlike trichlorostannylesters, corresponding trichlorostannyl olefins cannot interact intramolecularly with tin, thus ruling out the possible existence of a $p\pi$ – $d\pi$ interaction.

Table 3

NMR data of $\text{Cl}_3\text{Sn}(\text{CH}_2)_3\text{CH=CH}_2$ (**10**), $\text{Cl}_3\text{Sn}(\text{CH}_2)_4\text{CH=CH}_2$ (**11**) and $\text{Cl}_3\text{Sn}(\text{CH}_2)_5\text{CH}_3$ (**12**) in C_6D_6 at 303 K^a

Compound	10 ^b	11 ^b	12 ^b
¹³ C			
C(α)	31.3 [659/628] ^c	31.7 [643/615] ^c	32.2 [648/620] ^c
C(β)	23.7 [58] ^d	24.1 [59] ^d	24.6 [59] ^d
C(γ)	35.5 [116] ^e	31.3 [121] ^e	31.9 [115] ^e
C(δ)	135.9	32.8	30.9
C(ϵ)	117.4	137.5	22.4
C(ϕ)	–	115.5	14.0
¹ H			
C(α)	1.17 [87] ^f	1.16 [87] ^f	1.19 [87] ^f
C(β)	1.21 [202] ^g	1.16 [195] ^g	1.19 [190] ^g
C(γ)	1.61	0.99	1.08
C(δ)	5.32	1.66	0.92
C(ϵ)	4.90, 4.86	5.52	0.92
C(ϕ)	–	4.91, 4.89	0.79
¹¹⁹ Sn			
100 mg/0.5 ml	–9	+6	–3 (–2) ^h
20 mg/0.5 ml	0	+7	+5 (+1) ^h

^a Chemical shifts referencing as in Section 2. Coupling constants in Hz.^b Concentration: 20 mg/0.5 ml.^c $^1J(^{13}\text{C}-^{119}\text{Sn})$ and $^1J(^{13}\text{C}-^{117}\text{Sn})$ coupling constants.^d Unresolved $^2J(^{13}\text{C}-^{119}\text{Sn})$ and $^2J(^{13}\text{C}-^{117}\text{Sn})$ coupling constants.^e Unresolved $^3J(^{13}\text{C}-^{119}\text{Sn})$ and $^3J(^{13}\text{C}-^{117}\text{Sn})$ coupling constants.^f $^2J(^1\text{H}-^{119}\text{Sn})$ coupling constants as determined from 1D ^1H – ^{119}Sn -HMQC spectra.^g $^2J(^1\text{H}-^{119}\text{Sn})$ coupling constants as determined from 1D ^1H – ^{119}Sn -HMQC spectra.^h ^{119}Sn chemical shifts of BuSnCl_3 given for comparison [15].

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