Inorganica Chimica Acta, 150 (1988) 287–291

^{119}Sn and ^{13}C NMR Study of some Trivinyltin(IV) Compounds and their Complexes

K. HANDLÍŘ, J. HOLEČEK*, M. NÁDVORNÍK, S. M. TELEB**
General and Inorganic Chemistry Department, Institute of Chemical Technology, 532 10 Pardubice, Czechoslovakia
and A. LYČKA*
Research Institute of Organic Syntheses, 532 18 Pardubice-Rybitví, Czechoslovakia

(Received November 24, 1987; revised May 3, 1988)

Abstract

The ^{119}Sn and ^{13}C NMR spectra of ten trivinyltin(IV) compounds in solutions of non-coordinating (deuteriochloroform, trideuterionitromethane) and coordinating (hexadeuteriodimethyl sulphoxide) solvents have been studied. From $\delta(^{119}$Sn) chemical shifts and $^1J(^{119}$Sn, ^{13}C) coupling constants an evaluation of the coordination number of the central tin atom and the shape of coordination polyhedra around the tin atom has been carried out. Various effects on the $\delta(^{13}$C) chemical shifts of both carbon atoms of the vinyl group are also discussed.

Introduction

In our previous papers [1–5] we manifested the possibility of the evaluation of the shape of coordination polyhedra of the tin atom in organotin(IV) compounds and their complexes from their ^{13}C and ^{119}Sn NMR spectra. In refs. 1–3 the dependence of $\delta(^{119}$Sn) chemical shifts and $^1J(^{119}$Sn, ^{13}C) coupling constants on the coordination number of the central tin atom and the geometrical arrangement of organic substituents around the tin atom were reported for tri-n-butyl, triphenyl- and tribenzyltin(IV) compounds. In this paper we describe the study of the relation between the ^{13}C and ^{119}Sn NMR spectra of trivinyltin(IV) compounds and their structures. The choice of the studied compounds aimed to cover all the basic structural types of coordination polyhedra of triorganotin(IV) compounds and also a maximal range of the values of $\delta(^{119}$Sn) chemical shifts and $^1J(^{119}$Sn, ^{13}C) coupling constants in this group of compounds. NMR spectra of the trivinyltin(IV) compounds were studied in solutions of a non-coordinating solvent (deuteriochloroform), a weakly coordinating solvent (trideuterionitromethane) and a coordinating solvent (hexadeuteriodimethyl sulphoxide).

Results

All the studied trivinyltin(IV) compounds and their ^{119}Sn and ^{13}C NMR spectral parameters are summarized in Table I.

$\delta(^{119}$Sn) Chemical Shifts

The values of the chemical shift $\delta(^{119}$Sn) of the studied compounds lie within a relatively broad range from -52.8 ppm for trivinyltin(IV) chloride (compound **2**) in deuteriochloroform up to -258.5 ppm for trivinyltin(IV) benzoate (compound **6**) in hexadeuteriodimethyl sulphoxide. Similar to the other triorganotin(IV) compounds the values of the $\delta(^{119}$Sn) chemical shifts of trivinyltin(IV) compounds depend in the first place on the magnitude of the coordination number of the central tin atom and on the type of ligands bonded to this atom. The effect of both these factors in triorganotin(IV) compounds of the type R_3SnX has similar results, *i.e.* the magnitude and the direction of the shift in $\delta(^{119}$Sn) are almost the same when comparing analogous compounds which differ only in the type of the organic substituent R. An evidence for this statement can be found in good linear correlations [6] between $\delta(^{119}$Sn) chemical shifts of triorganotin(IV) compounds with different organic substituents. The slopes of the linear correlations do not differ too much from the value of one (organic substituents affect mainly the intersection of these linear functions).

The values of $\delta(^{119}$Sn) of trivinyltin(IV) compounds are very close to those of analogous triphenyltin(IV) compounds. In comparison with tribenzyl- and especially with tri-n-butyltin(IV) compounds the values of $\delta(^{119}$Sn) chemical shifts of analogous trivinyltin(IV) compounds are significantly shifted upfield. The mutual relation between the $\delta(^{119}$Sn) chemical shift of trivinyl- and $\delta(^{119}$Sn) of other

---

*Authors to whom correspondence should be addressed.

**Permanent address: Chemistry Department, Faculty of Science, Zagazig University, Zagazig, Egypt.

0020-1693/88/$3.50

TABLE I. ^{13}C and ^{119}Sn NMR Data of Trivinyltin(IV) Compounds

No.	Compound[a]	Solvent[a]	$\delta(^{119}Sn)$ (ppm)	$\delta(^{13}C)$ (ppm)		$^1J(^{119}Sn, ^{13}C)$ [b] (Hz)
				C(1)	C(2)	
1	Vi_3SnSBu	$CDCl_3$ [c]	−73.8	134.99	136.76	539.0
		dmso-d_6 [d]	−99.5	136.82	135.72	570.1
2	Vi_3SnCl	$CDCl_3$	−52.8	134.70	138.06	587.2
		dmso-d_6	−215.5	142.27	134.90	778.1
3	Vi_3SnBr	$CDCl_3$	−72.1	134.01	138.02	575.0
		dmso-d_6	−210.1	142.14	135.07	760.5
4	Vi_3SnI	$CDCl_3$	−132.0	133.75	138.02	552.4
		dmso-d_6	−206.3	141.07	135.95	754.4
5	$Vi_3SnOCOMe$	$CDCl_3$ [e]	−123.5	135.91	137.67	628.6
		dmso-d_6 [f]	−257.6	141.70	134.15	800.8
6	$Vi_3SnOCOPh$	$CDCl_3$ [g]	−117.9	135.79	137.82	627.0
		dmso-d_6 [h]	−258.5	141.59	134.38	803.7
7	$Et_4N^+Vi_3SnCl_2^-$	CD_3NO_2 [i]	−251.5	147.04	133.00	805.9
8	Vi_3Sn·edtc	$CDCl_3$ [j]	−202.1	140.01	134.86	587.6
9	Vi_3Sn·txin	$CDCl_3$ [k]	−168.3	142.83	138.20	587.4
10	Vi_3Sn·oxin	CH_3OH	−192.5	[l]	[l]	[l]

[a] Abbreviations: Me = methyl, Et = ethyl, Bu = n-butyl, Vi = vinyl, Ph = phenyl, dmso-d_6 = hexadeuteriodimethyl sulphoxide, edtc = *N,N*-diethyldithiocarbamate, oxin = oxinate, txin = thiooxinate. [b] $^2J(^{119}Sn, ^{13}C)$ coupling constants were not found. [c–k] Other $\delta(^{13}C)$: [c] 36.60(C-1), 26.65(C-2), 21.53(C-3), 13.41(CH_3); $^1J(^{119}Sn, ^{13}C)$ = 26.3 Hz, $^2J(^{119}Sn, ^{13}C)$ = 15.0 Hz. [d] 36.15(C-1), 25.85(C-2), 21.01(C-3), 13.24(CH_3); $^1J(^{119}Sn, ^{13}C)$ = 34.4 Hz. [e] 177.74(COO), 20.78(CH_3). [f] 174.84(COO), 22.98(CH_3). [g] 173.34(COO), 134.12(i), 130.30(o), 126.11(m), 132.60(p). [h] 171.50(COO), 130.48(i), 129.51(o), 128.22(m), 131.81(p). [i] 52.70(NCH_2), 7.11(CH_3). [j] 195.35(CS_2), 49.91(CH_2), 11.83(CH_3). [k] 146.35, 143.23, 138.16, 138.02, 130.09, 128.91, 126.99, 123.04, 121.09; $^2J(^{119}Sn, ^{13}C)$(vinyl) = 8.9 Hz. [l] Not found – see 'Experimental'.

TABLE II. Parameters of Linear Correlation of Eqns. (1) and (2)

Equation	R	*a*	*b*	*N* [a]	*r* [b]
(1)	Ph	0.84 ± 0.05	−24.43 ± 8.94	8	0.988
(1)	Bz	1.00 ± 0.05	−106.22 ± 5.62	10	0.989
(1)	n-Bu	1.18 ± 0.09	−239.29 ± 7.94	9	0.980
(2)	Ph	0.96 ± 0.02	1.06 ± 12.82	8	0.999
(2)	Bz	1.29 ± 0.06	208.86 ± 21.61	10	0.993
(2)	n-Bu	1.58 ± 0.07	51.74 ± 13.14	9	0.992

[a] Number of experimental data. [b] Correlation coefficient.

triorganotin(IV) compounds can be expressed as (1) where R = phenyl-, benzyl-, and n-butyl, respectively.

$$\delta(^{119}Sn)(Vi_3Sn) = a \times \delta(^{119}Sn)(R_3Sn) + b \qquad (1)$$

The values of slopes *a* and intersections *b* from eqn. (1) are given in Table II. The values of $\delta(^{119}Sn)$ of triphenyl-, tribenzyl- and tri-n-butyltin(IV) compounds for the correlation (1) have been taken from our papers [1–3].

Chemical shifts $\delta(^{119}Sn)$ of the compounds **1**–**6** in a non-coordinating solvent (deuteriochloroform) lie in the range from −52.8 to −133.0 ppm, *i.e.* in the distinctly downfield range in comparison with the value of $\delta(^{119}Sn)$ for tetravinylstannane (−160.3 [7]). The above range can be considered as a characteristic one of simple trivinyltin(IV) compounds Vi_3SnX (X is a polar substituent) with a pesudotetrahedral arrangement of Sn–C and Sn–X bonds around the central tin atom. On the opposite side chemical shifts $\delta(^{119}Sn)$ of the compounds **2**–**6** in the coordinating solvent (hexadeuteriodimethyl sulphoxide), the complex anion $Vi_3SnCl_2^-$ in the compound **7** (in the solution of weakly coordinating solvent trideuterionitromethane) and the compounds **8**–**10** in deuteriochloroform are positioned in the significantly upfield range from −168.3 to −258.5 ppm. This substantial increase in the $\delta(^{119}Sn)$ values is characteristic for the formation of triorganotin(IV) compounds with a five-coordinate central tin atom, *i.e.* for the formation of complexes of Vi_3SnX compounds with one molecule of the coordinating solvent (L) or for the presence of a chelate ring as a consequence of the bidentate function of the oxinate, thiooxinate or diethyldithiocarbamate ligands in the complex **8**–**10**. A relatively small upfield shift in $\delta(^{119}Sn)$ for compound **1** observed under the described change of the character of solvents reveals the well-known small tendency of organotin(IV) thiolates towards the formation of complexes [5]. The determined value of $\delta(^{119}Sn)$ for compound **1** in the solution of hexadeuteriodimethyl sulphoxide (−99.5 ppm) can be considered as a weighted mean of the $\delta(^{119}Sn)$ value of the tetrahedral molecule Vi_3SnSBu (−73.8 ppm) and the unknown $\delta(^{119}Sn)$ value of its complex $Vi_3SnSBu \cdot (dmso\text{-}d_6)$.

Coupling Constants $^1J(^{119}Sn, ^{13}C)$

According to the values of the coupling constants $^1J(^{119}Sn, ^{13}C)$ the studied compounds can be divided into two groups. In the first one with the value of $^1J(^{119}Sn, ^{13}C)$ from 539.0 to 628.6 Hz there are all the compounds with a pseudotetrahedral coordination around the central tin atom and the five-coordinate chelate complexes of **8** and **9**. In the second one with higher values of $^1J(^{119}Sn, ^{13}C)$ ranging from 754.4 to 805.5 Hz there are all other compounds with a five-coordinate central tin atom. As in the case of the $\delta(^{119}Sn)$ chemical shift we can find here fair linear correlations between the values of $^1J(^{119}Sn, ^{13}C)$ of trivinyltin(IV) compounds and those of analogous triorganotin(IV) compounds of R_3SnX or $R_3SnS \cdot L$ (R = n-Bu, Bz, Ph) [1–3], which can be expressed as (2)

$$^1J(^{119}Sn, ^{13}C)(Vi_3Sn) = a \times {}^1J(^{119}Sn, ^{13}C)(R_3Sn) + b \qquad (2)$$

The calculated parameters a and b are given in Table II. It is worth mentioning that the magnitude of the slope of the relation (2) between $^1J(^{119}Sn, ^{13}C)$ of trivinyl- and triphenyltin(IV) compounds is close to 1.00 and that for the other two types of compounds (tribenzyl- and tri-n-butyltin(IV)) the relations are close to the theoretical value of 1.33. In this way relation (2) reflects a dominant effect of the different s-electron character of hybrid orbitals of carbon atoms C(1) of the compared compounds on magnitude of the $^1J(^{119}Sn, ^{13}C)$ coupling constants. The intersection of the mutual dependence of $^1J(^{119}Sn, ^{13}C)$ values between trivinyl- and triphenyltin(IV) compounds is practically equal to zero. The Sn–C bond character in both series of the compounds is similar. The values of intersection of the other two relations (with tribenzyl- and tri-n-butyltin(IV) compounds) reflect the specificities of Sn–C bonds in the compared series of compounds (σ–π conjugation, π-polarization etc.) as discussed in our previous papers [3, 5, 8].

Chemical Shifts $\delta(^{13}C)$

The values of $\delta(^{13}C)$ chemical shifts of both atoms in the vinyl groups of the studied compounds lie within the range 133.0 to 147.04 ppm. In comparison to the value of $\delta(^{13}C)$ of ethylene molecule (123.3 ppm [9]) the values of $\delta(^{13}C)$ of both carbon atoms for all the compounds under study are shifted markedly downfield. As in the case of the $\delta(^{119}Sn)$ chemical shift the values of $\delta(^{13}C)$ can also be used for an evaluation of the coordination number of the central tin atom in trivinyltin(IV) compounds. The compound with a four-coordinate central tin atom (compounds **1**–**6** in deuteriochloroform) possess the values of $\delta(^{13}C)$ of the C(1) carbon atom within the range 133.75 to 135.91 ppm, while for five-coordinate complexes $Vi_3SnX \cdot L$ (compounds **1**–**6** in hexadeuteriodimethyl sulphoxide), complex **7** and the chelates **8** and **9** they range from 140.01 to 147.64 ppm. A rather smaller difference has been found in the values of $\delta(^{13}C)$ of the C(2) carbon atom between both these types of coordination of the central tin atom.

Discussion

Applying all the criteria for $\delta(^{119}Sn)$ and $^1J(^{119}Sn, ^{13}C)$ simultaneously, we can divide the studied trivinyltin(IV) compounds into the three following groups

(a) The compounds with lower values of $\delta(^{119}Sn)$ and $^1J(^{119}Sn, ^{13}C)$ (−52.8 to −132.0 ppm and 539.0–628.6 Hz, respectively). This type of compound corresponds to monomeric molecules of simple trivinyltin(IV) compounds Vi_3SnX with a pseudotetrahedral geometry (see for example refs. 10 and 11) of coordination around the central tin atom with the sp^3-hybrid orbitals of the tin atom used for the formation of bonds with four bonding partners.

(b) Compounds with higher values of $\delta(^{119}Sn)$ and $^1J(^{119}Sn, ^{13}C)$ (−206.3 to −258.5 ppm and 754.4 to 805.9 Hz, respectively). This group covers $Vi_3SnX \cdot L$ type complexes where, due to the validity of the Bent rule [12], the five bonding partners of the central tin atom form a *trans*-trigonal bipyramidal arrangement around the tin atom. Three vinyl groups in this arrangement are situated in the equatorial plane while the polar groups X and the donor atom of the ligand L are placed in axial positions. For the formation of Sn–C(1) bonds the tin atom uses three sp^2-hybrid orbitals, the remaining p-orbital of the tin atom forms with proper orbitals of the polar group X and the donor atom of the ligand L a three-centre bond of the linear type [13].

(c) Compounds with a higher value of $\delta(^{119}Sn)$ (−168.3 to −202.1 ppm, respectively) but a lower value of $^1J(^{119}Sn, ^{13}C)$ (~587 Hz). In this group are compounds **8** and **9** with a distorted trigonal-bipyramidal geometry of bonding partners around the central tin atom with a forced *cis*-arrangement of donor centers being parts of a chelate ring. Thus the bidentate ligand with its donor atoms occupies one axial and one equatorial position. The tin atom can be used for bonding sp^3-hybrid orbitals from which three orbitals form Sn–C(1) bonds with sp^2-hybrid orbitals of the C(1) carbon atoms of the vinyl groups and the fourth orbital forms a bent-type three-center bond with donor atoms of the bidentate ligand L [13].

A more detail analysis of chemical shifts $\delta(^{13}C)$ and their changes in the set of the studied compounds is difficult due to the effect of several factors on their magnitude some of which have an opposite influence. Nevertheless we are convinced that even in this case we can make a few useful comparisons

(a) The internal chemical shift $\Delta\delta$ [9] defined as the difference in chemical shifts of (^{13}C) of both carbon atoms of the vinyl group, *i.e.* $\delta(^{13}C(1)) - \delta(^{13}C(2))$, can be considered as an extension of the polarization of the double bond in the vinyl group. All the four-coordinate compounds given in Table I (compounds **1**–**6**) reveal a negative value of this quantity, whereas five-coordinate compounds possess a positive value. This effect, caused most probably by an influence of the dipole of the rest of molecule or complex on the π-electron system of the vinyl group (π-polarization), results in the first case in the shift of π-electron density towards the C(1) atom, while in the second case of five-coordinated compounds the shift is in an opposite direction towards the C(2) atom [14].

(b) The chemical shift $\delta(^{13}C)$ of the C(1) atom in monosubstituted ethenes manifests first of all changes in its σ-electron density [15]. In accordance with this statement the values of $\delta(^{13}C)$ of the C(1) atom are generally shifted downfield with increasing electronegativity of the substituents on the vinyl group (the rest of the molecule or complex without one vinyl group), *i.e.* with increasing s-electron character of the Sn–C bond [16]. This effect is appreciable especially in the case of change in the coordination number of the central tin atom. We are convinced that in compounds with the same coordination of the central tin atom this effect of σ-electron density (σ-induction) is to a great extent overlapped by the π-inductive effects described above.

(c) σ-electron density on the C(2) carbon atom is only slightly influenced by the inductive effect of the rest of the molecule. The main role here is played by changes in the π-electron density [15, 16]. In accordance with the value of $\Delta\delta$ (see above), *i.e.* with the direction of the shift in π-electron density, the values of $\delta(^{13}C)$ of the C(2) atom are shifted somewhat upfield in compounds with a five-coordinate tin atom when compared with compounds with a four-coordinate tin atom. The rest of the molecule linked with the vinyl group is a stronger π-donor (a weaker π-acceptor) in the case of the five-coordinate tin atom than the groupings containing the four-coordinate tin atom.

Similar changes in electron density on vinyl substituents can be observed also for divinyltin(IV) compounds [5]. Due to the presence of a higher number of polar substituents in simple compounds and a higher number of ligands in the coordination sphere of the central tin atom of complexes the observed effects are more pronounced in divinyltin(IV) compounds and, therefore, the shifts in the values of $\delta(^{13}C)$ of both carbon atoms are much larger in both directions.

Experimental

The compounds **2**, **3** and **4** were prepared by published methods [16]. The other compounds were prepared by conversion of trivinyltin(IV) chloride with corresponding sodium salts (compounds **1**, **7**–**9**) or silver salts (compounds **5** and **6**) according to the procedures described for analogous organotin(IV) compounds [17–21]. Analytical and physical data of compounds **1** and **5**–**9** are given in Table III. Trivinyltin(IV) oxinate (compound **10**) was characterized only by the value of chemical shift $\delta(^{119}Sn)$, which was determined by the measurement of the ^{119}Sn NMR spectrum of the filtrate immediately after the reaction of sodium oxinate with trivinyltin(IV) chloride in a methanol solution. The NMR spectrum revealed only one signal with $\delta(^{119}Sn)$ equal to −192.5 corresponding to compound **10**. This compound disproportionates, either by standing or by

TABLE III. Analytical Data and Melting (Boiling) Points of Trivinyltin(IV) Compounds

Compound[a]	Weight: found (calc.) (%)				Melting (boiling) point (°C)
	C	H	Sn	Other	
1	42.22 (41.56)	6.13 (6.28)	39.97 (41.07)	11.58 S (11.09)	(104/400 Pa)
5	36.92 (37.11)	4.38 (4.67)	46.01 (45.84)		160–161[b]
6	48.92 (48.65)	4.56 (4.40)	36.73 (36.98)		250
7	41.53 (41.93)	7.24 (7.29)	30.02 (29.60)	3.28 N (3.49) 17.82 Cl (17.68)	117–119
8	38.24 (37.96)	5.62 (5.50)	33.86 (34.10)	18.18 S (18.42) 3.90 N (4.02)	63–66
9	50.48 (50.04)	4.11 (4.20)	33.04 (32.97)	8.70 S (8.91) 3.96 N (3.89)	109–111

[a] See Table I. [b] Melting point 159–160 and 161–162 °C [10–11].

heating or under attempts to isolate it, giving the compounds Vi_4Sn and $Vi_2Sn\cdot(oxin)_2$. These products were identified also by ^{119}Sn NMR spectral measurement giving the signals with $\delta(^{119}Sn)$ 164.0 ppm (Vi_4Sn) and −391.6 ppm ($Vi_2Sn\cdot(oxin)_2$) [5]. This disproportionation also precluded the measurement of the ^{13}C NMR spectrum of compound **10**.

The ^{119}Sn and ^{13}C NMR spectra were measured at 37.14 and 25.047 MHz, respectively, on a Jeol spectrometer JNM-FX 100 at 300 K. Chemical shifts $\delta(^{119}Sn)$ are related to external neat tetramethylstannane ($\delta = 0.0$), $\delta(^{13}C)$ to the corresponding solvent signal and converted to the δ-scale: deuteriochloroform (77.00 pm), trideuterionitromethane (62.60 ppm), hexadeuteriodimethyl sulphoxide (39.60 ppm). Positive values denote downfield shift. A more detailed description of the experimental conditions is given in refs. 1 and 2.

References

1 M. Nádvorník, J. Holeček, K. Handlíř and A. Lyčka, *J. Organomet. Chem., 275,* 43 (1984).
2 J. Holeček, M. Nádvorník, K. Handlíř and A. Lyčka, *J. Organomet. Chem., 241,* 177 (1983).
3 A. Lyčka, J. Jirman, A. Koloničný and J. Holeček, *J. Organomet. Chem., 333,* 305 (1987).
4 J. Holeček, M. Nádvorník, K. Handlíř and A. Lyčka, *J. Organomet. Chem., 315,* 299 (1986).
5 J. Holeček, K. Handlíř, M. Nádvorník, S. M. Teleb and A. Lyčka, *J. Organomet. Chem., 339,* 61 (1988).
6 J. Holeček, K. Handlíř, M. Nádvorník, A. Lyčka and R. Wagener, *Proc. Xth Conf. Coord. Chem.*, June 4, 1985, Smolenice, Bratislava, Czechoslovakia; *Chem. Abstr., 105,* 226833x (1986).
7 B. Wrackmeyer, *Ann. Rep. NMR Spectrosc., 16,* 73 (1985), and refs. therein.
8 J. Holeček, A. Lyčka, K. Handlíř and M. Nádvorník, *Collect. Czech. Chem. Commun., 53,* 571 (1988).
9 J. Schraml, *Collect. Czech. Chem. Commun., 41,* 3063 (1976).
10 V. Peruzzo, G. Plazzogna and G. Tagliavini, *J. Organomet. Chem., 24,* 347 (1970).
11 V. Peruzzo, G. Tagliavini and R. E. Hester, *J. Organomet. Chem., 56,* 185 (1973).
12 H. A. Bent, *Chem. Rev., 61,* 275 (1961).
13 R. Okawara and M. Wada, in F. G. A. Stone and R. West (eds.), 'Advances in Organometallic Chemistry', Vol. 5, Academic Press, New York/London, 1967, p. 144.
14 A. G. Nagy, *J. Organomet. Chem., 291,* 335 (1985).
15 G. Miyajima, K. Takahashiara and K. Nishimoto, *Org. Magn. Reson., 6,* 413 (1974).
16 E. Vincent, L. Verdonck, L. Naessens and G. P. Van der Kellen, *J. Organomet. Chem., 277,* 235 (1984).
17 E. W. Abel and D. B. Brandy, *J. Chem. Soc.,* 1192 (1965).
18 R. Barbieri, N. Bertazzi, C. Tomarchio and R. H. Herber, *J. Organomet. Chem., 84,* 39 (1975).
19 D. V. Naik and C. Curran, *J. Organomet. Chem., 81,* 177 (1974).
20 D. Blake, G. E. Coates and J. M. Tate, *J. Chem. Soc.,* 756 (1961).
21 H. C. Clark and R. J. Ruddephatt, in A. G. McDiarmid (ed.), 'Organometallic Compounds of the Group IV Elements', Vol. 2, Part 11, Dekker, New York, 1972, p. 71.