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^{13}C AND ^{119}Sn NMR STUDY OF SOME FOUR- AND FIVE-COORDINATE TRIPHENYLTIN(IV) COMPOUNDS

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Summary

The ^{13}C and ^{119}Sn NMR spectra of four- and five-coordinate triphenyltin(IV) compounds have been examined. The chemical shifts $\delta(^{119}\text{Sn})$ and the coupling constants $^1J(^{119}\text{Sn}-^{13}\text{C})$ depend markedly on the coordination number of the tin atom and on the geometry of the coordination sphere. The chemical shifts and the coupling constants $^1J(^{119}\text{Sn}-^{13}\text{C})$ for four-coordinate compounds are in the range -40 to -120 ppm and 550-660 Hz, respectively. The $\delta(^{119}\text{Sn})$ values for five-coordinate compounds (trigonal bipyramid arrangement) are in the range -180 to -260 ppm. The $^1J(^{119}\text{Sn}-^{13}\text{C})$ values for the compounds with three phenyl groups in the equatorial plane and the other ligands in axial positions (*trans*) are in the range 750–850 Hz. The chelate compounds with two phenyl groups in the equatorial plane and the third in the axial position and the two donor atoms of chelating ligand in equatorial and axial positions, respectively, have the coupling constants in the range 600–660 Hz. The NMR spectra are discussed in terms of a three-centre molecular orbital model.

Introduction

The use of NMR spectroscopy in the study of the structures of organotin compounds has increased in the last years. The data obtained from these studies have not yet been systematically compiled, but it is possible to compare the results obtained from the NMR spectra of the organotin(IV) compounds with those from other methods and to reach some conclusions about the structures of the compounds. In most cases only the chemical shifts $\delta(^{119}\text{Sn})$ were derived from the NMR spectra. More significant results can be obtained when other NMR parameters are also determined including the chemical shifts of other atoms (^{1}H, ^{13}C) and especially the coupling constants $^1J(^{119}\text{Sn}-^{13}\text{C})$ and $^2J(^{119}\text{Sn}-^1\text{H})$, respectively [1]. Such com-

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plete measurements are rare in the literature. For the triphenyltin(IV) compounds and the coordination compounds formed by these species with various donor-type compounds such complete NMR studies have been described in only a few cases [2,3].

In this paper we report the study of the ^{13}C and ^{119}Sn NMR spectra of some triphenyltin(IV) compounds, including coordination compounds involving monodentate ($Ph_3SnX \cdot L$) and bidentate (Ph_3SnL^2) ligands. The structures of all the compounds studied in the solid state (and in most cases also in solution) have been published. We tried to study all the possible structural types which can be formed by the triphenyltin(IV) compounds.

Experimental

All the compounds (see Tables 1 and 2) were prepared by published methods [2,4–11]. Solvents were purified by standard methods.

NMR spectra were measured on the JEOL spectrometer JNM-FX 100 equipped with multinuclear tunable probe and operating at 25.047 MHz (^{13}C); 37.14 MHz (^{119}Sn); 7.19 MHz (^{14}N); 40.32 MHz (^{31}P) and 93.71 MHz (^{19}F) in pulse mode with Fourier transform. The solutions were placed in 10 mm (o.d.) NMR tubes and the deuterated solvents were used as internal locks. The chemical shifts were measured with digital resolution of 1.22 Hz (^{13}C, ± 0.05 ppm), 3.70 Hz (^{119}Sn, ± 0.1 ppm), 0.73 Hz (^{14}N, ± 0.1 ppm; ^{31}P, ± 0.02 ppm; ^{19}F, ± 0.01 ppm) relative to internal $(CH_3)_4Si(^{13}C)$, external $(CH_3)_4Sn(^{119}Sn)$, external $CH_3NO_2(^{14}N)$, external 85% $H_3PO_4(^{31}P)$ and external $CF_3COOH(^{19}F)$ respectively. Positive values of the shifts are to downfield.

The coupling constants $^nJ(^{119}Sn-^{13}C)$ were obtained from the ^{13}C NMR spectra measured with digital resolution of 0.61 Hz. The assignment of the chemical shifts $\delta(^{13}C)$ was carried out in the same way as reported in ref. 2. The other signals were assigned on the basis of proton-coupled spectra.

Results

The chemical shifts and the coupling constants of most of the studied compounds showed no concentration dependence within experimental error. The only exception was for $Ph_3SnX \cdot L$ (compounds Nos. 15–21 in Tables 1 and 2), where e.g. at concentrations of 0.1, 0.2, 0.45 and 1.0 mol l^{-1} of the compound No. 15 in $CDCl_3$ solution at 300 K the values of $\delta(^{119}Sn)$ were −110.4, −143.7, −185.4 and −206.0, respectively. Such concentration dependence is due to dissociation, and the values of the NMR parameters increase asymptotically toward a final value with increasing concentration of compounds or the ligands. These final (maximal) values of NMR parameters are given in Tables 1 and 2, together with the conditions under which they were obtained. With some compounds we were not able to reach these steady conditions, in spite of the fact that these compounds are known in the solid state (Ph_3Sn acetylacetonate, the compounds of Ph_3SnCl with 2,2′-bipyridyl or 1,10-phenantroline). For the compounds with a low solubility in CD_3Cl the measure-

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TABLE 1

^{119}Sn NMR PARAMETERS OF TRIPHENYLTIN(IV) COMPOUNDS

No.	Compound	Concentration (mol l^{-1})	Solvent	Temperature (K)	δ(^{119}Sn) (ppm)	^nJ(^{119}Sn ^{13}C) (Hz)			
						$n = 1$	$n = 2$	$n = 3$	$n = 4$
1	Ph_4Sn	saturated solution	$CDCl_3$	298	−128.1	[b]	38.1	52.8	11.7
2	Ph_3SnCl [a]	0.65	$CDCl_3$	298	−44.7	614.3	50.0	64.5	13.4
3	Ph_3SnBr [a]	0.58	$CDCl_3$	298	−59.8	595.0	49.7	63.7	13.9
4	Ph_3SnI [a]	0.52	$CDCl_3$	298	−112.8	567.6	49.4	63.0	13.6
5	Ph_3SnOH [a]	0.68	$CDCl_3$	298	−82.5	[b]	[b]	[b]	[b]
6	$(Ph_3Sn)_2O$ [c]				−80.6				
7	$(Ph_3Sn)_2S$ [c,d]	neat liquid			−48.7	566.4	43.9	58.6	
8	Ph_3SnSPr-n [d]				[e]	551.0	42.7	56.2	
9	$Ph_3SnOCOPh$	0.56	$CDCl_3$	300	−109.9	648.4	48.8	64.4	13.6
10	$Ph_3SnOCOCF_3$	0.48	$CDCl_3$	300	−64.4	638.7	49.3	65.4	13.6
11	$Ph_3SnOCOC_6H_4NH_2$-p	0.55	$CDCl_3$	300	−122.6	650.4	48.8	64.4	12.7
12	$Ph_3SnOCOC_6H_4NH_2$-o	0.41	$CDCl_3$	300	−116.8	650.4	48.8	64.4	12.7
13	$Ph_3Sn \cdot$oxin	0.52	$CDCl_3$	300	−190.1	663.1	47.8	62.5	12.7
14	$Ph_3Sn \cdot$edtc [f]	0.43	$CDCl_3$	300	−189.8	604.2	47.6	62.3	13.4
15	$Ph_3SnCl \cdot$hmpa [g]	0.41	$CDCl_3$/hmpa 1/1 (v/v)	300	−238.9	839.8	48.8	73.2	17.1
16	$Ph_3SnBr \cdot$hmpa	0.28	$CDCl_3$/hmpa 3/2 (v/v)	300	−239.6	822.2	48.8	72.3	21.5
17	$Ph_3SnCl \cdot$dmso [h]	0.28	dmso-d_6	300	−226.8	810.6	47.9	71.3	14.6
18	$Ph_3SnBr \cdot$dmso	0.31	dmso-d_6	300	−228.4	793.0	47.9	70.3	14.6
19	$Ph_3SnI \cdot$dmso	0.28	dmso-d_6	370	−228.5	775.4	47.9	70.3	14.6
20	$Ph_3SnCl \cdot$py [i]	0.35	py	330	−203.5	783.2	45.9	70.3	14.6
21	$Ph_3SnBr \cdot$py	0.34	py	300	−224.5	781.2	46.9	70.3	14.6
22	$Ph_3SnI \cdot$py	0.35	py	300	−236.6	754.0	45.9	69.3	14.6
23	$Et_4N^+[Ph_3SnCl_2]^-$	0.62	CD_3NO_2	300	−257.2	847.2	50.0	73.2	14.6
24	$Et_4N^+[Ph_3SnBr_2]^-$	0.26	CD_3NO_2	300	−239.6	788.4	47.6	72.0	14.6
		0.15	dmso-d_6	330	231.5	798.4	47.6	70.8	16.0

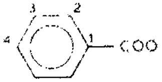
[a] Ref. 2. [b] Not measured. [c] Ref. 12. [d] Ref. 3. [e] For Ph_3SnSR values of (^{119}Sn) ranging from −47 to −84 ppm have been reported (ref. 13). [f] N,N'-Diethyldithiocarbamate. [g] Hexamethylphosphoramide. [h] Dimethylsulfoxide. [i] Pyridine.

TABLE 2

^{13}C NMR CHEMICAL SHIFTS AND OTHER NMR PARAMETERS OF TRIPHENYLTIN(IV) COMPOUNDS

Compound [a]	$\delta(^{13}C)$ of phenyl groups Ph_3Sn (ppm)				Other chemical shifts (ppm) and coupling constants (Hz)
	ipso	*ortho*	*meta*	*para*	
1	138.0	137.21	128.61	129.08	
2 [b]	137.1	136.0	129.0	130.4	
3 [b]	136.9	136.0	129.0	130.3	
4 [b]	136.2	136.2	128.9	130.1	
5 [b]	140.4	136.4	128.5	129.4	
7 [c]	139.1	136.6	128.6	129.4	
8 [c]	137.7	136.6	128.8	129.5	
9	138.24	136.81	128.81	130.86	$\delta(^{13}C)$: 172.79(CO), 130.37(C(1)), 130.06(C(2)), 128.07(C(3)), 132.59(C(4)) [d]
10	135.95	136.73	129.32	131.00	$\delta(^{13}C)$: 161.53(CO), 115.37(CF_3); $\delta(^{19}F)$: 4.43; $J(^{19}F-^{13}C)$: 287.6(^1J), 40.0(^2J)
11	138.79	136.80	128.73	129.87	$\delta(^{13}C)$: 173.02(CO), 119.18(C(1)), 132.63(C(2)), 113.44(C(3)), 150.84(C(4)) [d]
12	138.71	136.80	128.77	129.98	$\delta(^{13}C)$: 174.31(CO), 111.07(C(1)) [d], 150.48(CNH_2), 134.11, 133.06, 116.34, 116.14
13	145.03	136.06	128.22	128.69	$\delta(^{13}C)$: 155.99, 144.24, 138.32, 137.93, 129.51, 128.00, 121.24, 114.00, 113.53
14	142.54	136.50	128.31	128.85	$\delta(^{13}C)$: 50.44(CH_2), 12.05(CH_3)
15	143.13	133.92	125.49	126.07	$\delta(^{13}C)$: 34.43(CH_3); $\delta(^{31}P)$: 24.60
16	142.85	133.49	125.14	125.73	$\delta(^{13}C)$: 34.06(CH_3); $\delta(^{31}P)$: 24.05
17	143.81	136.05	128.49	129.11	
18	143.84	136.05	128.53	129.15	
19	141.85	135.54	128.25	129.03	
20	143.31	137.03	129.15	129.78	
21	143.80	137.14	129.27	129.85	
22	143.00	137.07	129.35	129.97	
23	147.49	135.84	126.68	127.22	$\delta(^{13}C)$: 51.00(CH_2), 5.48(CH_3); $\delta(^{14}N)$: −316.7
24	146.37	135.69	126.87	127.41	$\delta(^{13}C)$: 51.10(CH_2), 5.49(CH_3); $\delta(^{14}N)$: −317.0
	144.51 [a]	136.13	128.33	128.92	$\delta(^{13}C)$: 51.42(CH_2), 7.24(CH_3); $\delta(^{14}N)$: −315.7

[a] See Table 1. [b] Ref. 2. [c] Ref. 3. [d]



ments of NMR parameters were carried out at higher temperatures or in more polar solvents. These changes in measurements conditions were chosen carefully to avoid changes in the compositions of the original solutions.

The results of NMR measurements are summarized in Tables 1 and 2. In Table 1 are given the values of chemical shifts $\delta(^{119}Sn)$, and coupling constants of tin atoms with carbon atoms of the phenyl groups $^{n}J(^{119}Sn-^{13}C)$ for $n = 1$–4. Table 2 shows the values of the chemical shifts $\delta(^{13}C)$ of the carbon atoms of the phenyl groups and other NMR parameters. Both the tables include some relevant data from other recent studies [2,3,12].

The chemical shifts $\delta(^{119}Sn)$ of the compounds examined vary over a wide range, from -44.7 ppm for Ph_3SnCl up to -257.2 ppm for the Ph_3SnCl_2 anion. On the basis of the values of $\delta(^{119}Sn)$ the compounds can be divided into two groups. The first includes compounds with chemical shifts in the range -40 to -120 ppm and the second those with shifts from -180 to -260 ppm. The compounds having lower chemical shifts (Nos. 1–12) are known to form tetrahedral molecules with a four-coordinate tin atom in the solid state (or at least in a solution) [14,15]. The compounds with higher $\delta(^{119}Sn)$ values (Nos. 13–27) involve molecules with trigonal-pyramid geometry around the five-coordinate tin atom [10,11,14-18]. This observation seems to be fairly general, because with a few exceptions it is valid for all the organotin(IV) compounds described in the literature [1–3,16,19,20]. The exceptions relate to compounds which are in the five-coordinate state as solids, but dissociate in solution to give four-coordinate species. Depending on the nature of the compounds and the experimental conditions we can therefore expect the presence of the both structural types in solution (especially concentrated ones). The simultaneous presence of both the forms should result in a concentration dependence of $\delta(^{119}Sn)$ or in values of $\delta(^{119}Sn)$ between both the boundary cases [19]. The anomalous value of $\delta(^{119}Sn)$ obtained for ethyltriphenyltin dithiocarboxylate (-192.4 ppm [21]) is assumed to arise from the intermolecular interaction of a lone electron pair of the sulphur atom with the valence orbitals of the tin atom.

Small differences between both the groups of triphenyltin(IV) compounds can be found also in the values of the chemical shifts $\delta(^{13}C)$ of the carbon atoms in the *ipso*-positions of the phenyl groups. The values for the five-coordinate tin compounds are shifted downfield from those for four-coordinate compounds. It thus seems probable that the Sn–C(phenyl) bond becomes more polar with increasing coordination of tin atom, as observed in the study of infrared spectra $Ph_3SnX_2^-$ ($X = Cl$, Br) compounds [17].

The coupling constants $^{n}J(^{119}Sn-^{13}C)$, especially the values of $^{1}J(^{119}Sn-^{13}C)$, can again be used to assign compounds to two groups. Values of $^{1}J(^{119}Sn-^{13}C)$ of 550–660 Hz were obtained for the four-coordinate compounds (Nos. 1–12) and two five-coordinate compounds (Nos. 13 and 14). The other five-coordinate compounds (Nos. 15–24) have $^{1}J(^{119}Sn-^{13}C)$ values of 750–850 Hz. Similar trends can be seen for the other coupling constants $^{n}J(^{119}Sn-^{13}C)$ ($n = 2$–4).

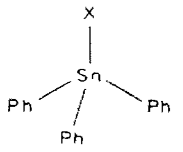
Discussion

On the basis of the values of the chemical shifts $\delta(^{119}Sn)$ and the coupling constants $^{1}J(^{119}Sn-^{13}C)$ it is possible to divide the triphenyltin(IV) compounds into three groups having different structural arrangements of the triorganotin(IV) group:

a) Compounds with lower δ(^{119}Sn) values (−40 to −120 ppm) and lower ^{1}J(^{119}Sn–^{13}C) values (550–660 Hz). These form monomer molecules of Ph_3SnX type with four-coordinate tin and tetrahedral arrangement of Ph and X substituents (structural type I).

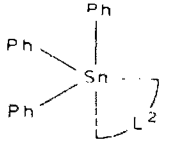
b) Compounds with higher δ(^{119}Sn) values (−180 to −200 ppm) and lower ^{1}J(^{119}Sn–^{13}C) values (600–660 Hz). These are characterized by having trigonal bipyramidal geometry of Ph_3SnL^2 (L^2 being the bidentate ligand) around the five-coordinate tin atom with two phenyl groups occupying the equatorial positions and the third one the axial position. Donor atoms of the L^2 ligand occupy the remaining equatorial and axial positions (*cis*-trigonal bipyramidal geometry, structural type II).

c) Compounds with higher δ(^{119}Sn) values (−200 to −260 ppm) and higher ^{1}J(^{119}Sn–^{13}C) values (750–850 Hz) with trigonal bipyramidal geometry of the substituents and ligands $Ph_3SnX \cdot L$ (L is a monodentate ligand) with a five-coordinate tin atom. Three phenyl groups lie in equatorial positions, the substituent X and the ligand L are in axial positions (*trans*-trigonal bipyramidal geometry, structural type III).



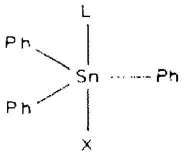
Ph_3SnX

structural type I
four coordinate
tetrahedron



Ph_3SnL^2

structural type II
five-coordinate
cis-trigonal
bipyramid



$Ph_3SnX.L$

structural type III
five-coordinate
trans-trigonal
bipyramid

Other possible structural arrangements, namely a trigonal bipyramid with the bidentate ligand L^2 occupying two equatorial positions or arrangements derived from the octahedral configuration, have not yet been unambiguously demonstrated and their existance is uncertain [22–25].

As the contribution of 5*d* orbitals to the bonding in organotin compounds is very low [26,27], it is possible to explain the above suggested structural arrangements by assuming the participation of 5*s* and 5*p* orbitals on the chemical bonding. The bonding in tetrahedral Ph_3SnX compounds can be confidently interpreted in terms of four hybrid sp^3 orbitals. For the description of the bonding in the five-coordinate compounds we can use the "three-centre orbital" model [27]. According to this model the sp^3 hybrid orbitals of the central tin atom are involved in bonding in structures of type II in such a way that three of them form the bonds with carbon atoms of phenyl groups. The fourth sp^3 orbital participates in the bonding with two donor centres of the bidentate ligand using the three-centre molecular orbital of the bent type. In the structural type III three Sn–C(phenyl) bonds are formed by sp^2 hybrid orbitals, whereas the remaining 5*p* orbital participates in bonding with the substituent X and ligand L using the three-centre molecular orbital of the linear type.

Chemical shifts δ(^{119}Sn)

The precise interpretation of the chemical shifts δ(^{119}Sn) of the compounds studied is very difficult due to their complex nature and their dependence on various factors. Nevertheless, for a group of compounds of similar composition, such as those we have studied, the shifts seem to depend mainly on the total electron density on the central tin atom. The tetrahedral molecules of the Ph_3SnX compounds (Nos. 2–12) have the values δ(^{119}Sn) shifted downfield (−44.7 to −122.6 ppm) compared with that for the tetraphenyltin (compound No. 1, δ(^{119}Sn) = −128.1 ppm). Such a shift can be explained qualitatively in terms of a decrease in the electron density on the central tin atom caused by the polar substituent. The interaction of the donor atom with valence orbitals of the tin atom during the formation of the five-coordinate tin compounds results in an increase in the electron density on the tin atom and thus in an appreciable upfield shift in δ(^{119}Sn) values (−189.8 to −257.2 ppm). Although it is not possible to regard the δ(^{119}Sn) values as unambiguous indicators of the coordination number at tin, we can probably consider δ(^{119}Sn) values of triphenyltin(IV) compounds lower than −120 ppm as typical of the four-coordinate compounds and those above −180 ppm as typical of the five-coordinate compounds.

Coupling constants $^1J(^{119}Sn-^{13}C)$

The value of the coupling constant, reflecting spin-spin coupling of neighbouring atoms joined by a simple bond, depends mainly on the magnitude of the Fermi-contact term. In the case when none of the participating bonding atoms have a lone electron pair, the ^1J values are directly proportional to the *s*-character of their hybrid orbitals [28]. Therefore the triphenyltin(IV) compounds (sp^2 hybrid carbon orbital) have higher ^1J values than analogous trialkyltin (sp^3 hybrid orbital) compounds [3]. For the same reason and in accordance with Bent's rule, in all the compounds with a Ph_3Sn–halogen bond the $^1J(^{119}Sn-^{13}C)$ values decrease in the order Cl > Br > I. The proportion of *s*-character in the tin hybrid orbitals provides a satisfactory explanation of the obtained $^1J(^{119}Sn-^{13}C)$ values of the triphenyltin(IV) compounds of the suggested structural types. The $Ph_3SnX \cdot L$ compounds (structural type III) have the highest ^1J values (750–850 Hz), in a good agreement with the high *s*-character of the tin bonding orbitals (sp^2). In Ph_3SnX (structural type I) and Ph_3SnL^2 (structural type II) the sp^3 orbitals are involved in the bonding and thus the ^1J values are substantially lower (550–660 Hz). We can assume that the *s*-character of the sp^3 hybrid orbitals in Sn–C (phenyl) bonds will, because of the presence of two polar groups, be rather higher in compounds of the structural type II than in the compounds of the structural type I. Thus we can expect to find higher mean values of ^1J in type II compounds than in type I compounds.

The results show that the values of the chemical shift δ(^{119}Sn) and the coupling constant $^1J(^{119}Sn-^{13}C)$ can be used as sensitive probes for characterization of the structures of triphenyltin(IV) compounds in solution.

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