^{119}Sn NMR Studies of Triorganostannane Dithiocarboxylates*

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The tin-119 NMR data of a series of triarylstannane dithiocarboxylic esters and dithiocarboxylato complexes are reported. Although four-coordinate in is present in all cases, the chemical shifts span the range of δ –120 to –260 ppm (upfield of tetramethyltin) with the dithiocarboxylate anion marking the high-field barrier (δ –261 ppm). The dithiocarboxylic moiety represents a high diamagnetic increment and gives rise to δ(^{119}Sn) shifts in the region of five-coordinate aryltin compounds. Complexation of the dithiocarboxylate anion or the dithioesters causes a downfield coordination shift due to the higher asymmetry of charge distribution at the tin nucleus. Rhenium complexes usually show more extended coordination effects than manganese. Small coordination shifts are induced by the presence of strong σ-donors or by monocoordination of the dithiocarboxylate ligand. The marked substituent influence involves relatively large $^4J(^{119}Sn-^{31}P)$ coupling constants in complexes with phosphorus ligands.

Introduction

Tin-element bonds may be attacked by suitable electrophilic and nucleophilic reagents, the more electropositive tin usually forming a bond with the nucleophilic pole of the substituent. The access to α-(thio)carbonyl derivatives and related compounds requires an inversion of the polarity of the tin-element bond. The syntheses of a few α-carbonyl [2, 3] and α-carbamoyl tin compounds [4] (*cf.* also ref. [5]) were accomplished by reaction of stannyl anions with the appropriate acyl halides. In contrast, unsuccessful attempts of a nucleophilic addition of organotin anions to heteroallenes have been reported [6–8].

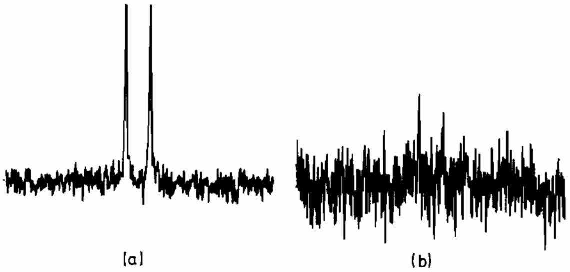
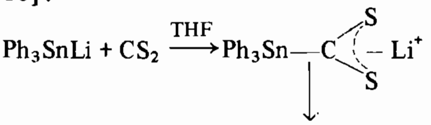


Fig. 1. Comparison of the ^{119}Sn NMR spectra of *fac*-$PPh_3(CO)_3ReS_2CSnPh_3$ (*33*) recorded by DEPT techniques (a) and proton noise-decoupled (b) for the same period. DEPT parameters: repetition time 4s, $^3J(^{119}Sn-^1H)$ = 83 Hz, θ = $0.134 \cdot P_{180}$.

We were able to demonstrate the unique character of carbon disulfide as the (hitherto) only heteroallene rendering the formation of a Sn–C bond [9, 10].



$$Ph_3SnLi + CS_2 \xrightarrow{THF} Ph_3Sn{-}C\overset{S}{\underset{S}{\langle}}{-}Li^+ \qquad (I)$$

$Ph_3SnCS_2Li\cdot 2$ Dioxane (*II*)

Ph_3SnCS_2R (*III*)

$Ph_3SnCS_2ML_n$ (*IV*)

The resulting stannanedithiocarboxylates *I* are stabilized as dioxane adducts *II*, alkylesters *III* or metalcarbonyl complexes *IV*. We collected the ^{119}Sn NMR data of selected compounds to get a compre-

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*Part VII of 'Nucleophilic Addition of Triorganotin Anions to Carbon Disulfide'; for Part VI see ref. [1].

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hensive picture of the new substance class and to arrange the obtained parameters into the order of known tin-chemical shifts.

Experimental

For the synthesis of the compounds described in this paper see refs. [11–15]. The ^{119}Sn NMR spectra were recorded with the Bruker multinuclear spectrometer WP80DS with pulse programmer ($CDCl_3$ solution, int. tetramethyltin standard, T = 304 K, 10 mm ϕ sample tube; resonance frequency 29.8 MHz). All coupling constants are given in absolute amounts. The recording time is considerably reduced by application of the DEPT (Distortionless Enhancement by Polarisation Transfer) pulse sequence using the ^3J(Sn–H) coupling with the *ortho* protons of triaryltin compounds; it is sufficient to approximate ^3J(Sn–H) for about ±20% [16]. For phenyltin compounds in general, the values of the lag time between all pulses lie in the interval of 8 and 5 ms, which corresponds to ^3J(Sn–H) of 60–90 Hz. The length of the θ pulse depends on the number of the *ortho* protons present; for triphenyltin compounds, it is given by $\theta = 0.134 \cdot P_{180}$ (P_{180}: length of the 180° decoupler pulse). For n protons, $\theta = 1/\pi \cdot \arcsin(n^{-0.5}) \cdot P_{180}$ is obtained [17]. In Fig. 1, a comparison between two spectra of *fac*-$PPh_3(CO)_3ReS_2CSnPh_3$ (*33*) is depicted which were recorded by DEPT techniques (a) and by normal proton noise-decoupling (b), with the same recording time for both.

Results and Discussion

Principally, the chemical shift of a NMR active nucleus can be described by a diamagnetic, a paramagnetic and a special term (indirect interaction, mesomeric and anisotropic effects *etc.*):

$$\sigma = \sigma^d + \sigma^p + \sigma'$$

σ^d and σ^p have opposite signs where σ^p corresponds to a deshielding (low-field shift). For heavy atoms, the paramagnetic contribution σ^p is dominant, for which Jameson and Gutowsky [18–20] have developed the simplified expression:

$$\sigma^p = \frac{2e^2h^2}{3m^2c^2\Delta E} \cdot (\langle r^{-3}\rangle_{np} \cdot Q_{np} + \langle r^{-3}\rangle_{nd} \cdot Q_{nd})$$

$$(\mathrm{Sn}: n = 5)$$

where ΔE is the average excitation energy, $\langle r^{-3}\rangle_{np}$, $\langle r^{-3}\rangle_{nd}$ are average reciprocal cubes of *p, d* valence electron-nucleus distances; Q_{np}, Q_{nd} are effective nuclear charges (amount of the asymmetric charge distribution of the *p, d* valence orbitals).

TABLE I. Selected ^{119}Sn NMR Shifts of Four-Coordinate Organotin Compounds with $\delta < 0$.

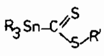
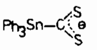
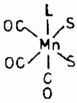
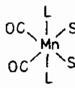
Compound	δ	Ref.
$(CH_3)_4Sn$	0	
$(C_6H_5CH_2)_4Sn$	−36	[22]
$(C_6H_5)_4Sn$	−128.1	[23]
$(CH_2{=}CH)_4Sn$	−157.4	[22]
$(HC{\equiv}C)_4Sn$	−279	[22]
Ph_3SnCl	−44.7	[23]
$(Ph_3Sn)_2S$	−48.7	[22]
Ph_3SnBr	−59.8	[23]
$(Ph_3Sn)_2O$	−80.6	[23]
Ph_3SnOH	−80.6	[23]
Ph_3SnCH_3	−98	[24]
$Ph_3SnC_2H_5$	−111.1	[24]
Ph_3SnI	−112.8	[23]
Ph_3SnCH_2I	−121.7	[24]
Ph_3SnCH_2Cl	−133.2	[24]
Ph_3SnH	−164 ± 5	[22]
Me_3SnH	−104.5	[22]
Me_3SnLi	−183	[22]

σ^p is inversely proportional to the excitation energy ΔE which can be considered as approximately constant within a given series of structurally related compounds; the same holds for $\langle r^{-3}\rangle_{np,nd}$. Q_{np} represents a measure of the charge distribution in the 5*p* orbitals of tin which is directly connected with the electronegativity of the neighboured atoms (equal distribution: $Q_{5p} \rightarrow 0$). The Q_{5d} term may be neglected for tetra-coordinate tin compounds. The Q_{5p} term increases with growing differences in the electronegativity of the four substituents. For example, a deshielding in the series R_3SnI–R_3SnBr–R_3SnCl and the typical u-shaped curve $\sigma = f(n)$ in $R_{4-n}SnX_n$ are observed.

The participation of 5*d* orbitals and its influence on the Q_{5d} term is more difficult to explain. Generally, it induces a decrease of Q_{5d} and, therefore, causes a highfield shift. This factor is dominant in tin compounds with higher coordination numbers than four. On the other hand, the diamagnetic shift (especially with trigonal-bipyramidal configuration) is also consistent with an increase of the *s* contribution in the equatorial sp^2 hybride orbital where the p_z orbital forms a three-centre bond with the axial ligands [21].

Four-coordinate organotin compounds with three or four Sn–C bonds and mainly unsaturated substituents show a highfield shift relative to tetramethyltin [20, 22]. Nearly all δ values lie in the range of 0 to −280 ppm (see Table I). The strong anisotropic effect of the alkynyl groups induces a highfield shift

TABLE II. $^{119}Sn\{^1H\}$ NMR Data of Triorganostannane Dithiocarboxylates ($CDCl_3$ sol., int. Standard Tetramethyltin). Coordination Shifts $\Delta\delta = \delta(\text{Complex}) - \delta(\text{Ligand})$; in Parentheses: Reference Compound. Abbreviations: To = Tolyl, Bz = Benzyl, Cp = η^5-Cyclopentadienyl, Cy = Cyclohexyl.

Compound Type	Formula (Nr.)	δ [ppm] ($^4J_{SnP}$ [Hz])	$\Delta\delta$	Remarks
Dithioesters	$Ph_3SnCSSMe$ (*1*)	-192.4^a		$^a\ ^1J_{SnC}$ 549
	$Ph_3SnCSSEt$ (*2*)	-194.7^b		$^b\ ^1J_{SnC}$ 546
 1–7	$Ph_3SnCSS(i\text{-}Pr)$ (*3*)	−196.8		
	$Ph_3SnCSS(allyl)$ (*4*)	−192.4		
	$[Ph_3SnCSS(CH_2)_2]_2$ (*5*)	−193.1		
	$(o\text{-}To)_3SnCSSMe$ (*6*)	−170.7		
	$(p\text{-}To)_3SnCSSMe$ (*7*)	−183.5		
Dithioester Complexes	$Ph_3SnCSSMe\cdot W(CO)_5$ (*8*)	−148	44.4 (*1*)	
	$Ph_3SnCSSEt\cdot W(CO)_5$ (*9*)	−149.6	45.1 (*2*)	
$R_3SnCSSR'\cdot W(CO)_5$ 8–14	$Ph_3SnCSS(i\text{-}Pr)\cdot W(CO)_5$ (*10*)	−151.7	45.1 (*3*)	
	$Ph_3SnCSS(allyl)\cdot W(CO)_5$ (*11*)	−148.3	44.1 (*4*)	
	$[Ph_3SnCSS(CH_2)_2\cdot W(CO)_5]_2$ (*12*)	−149.9	43.2 (*5*)	
	$(o\text{-}To)_3SnCSSMe\cdot W(CO)_5$ (*13*)	−125.6	45.1 (*6*)	
	$(p\text{-}To)_3SnCSSMe\cdot W(CO)_5$ (*14*)	−140.2	43.3 (*7*)	
$R_3SnCSSR'\cdot M(CO)_2Cp$ (M=Mn,Re) 15–19	$Ph_3SnCSSMe\cdot Mn(CO)_2Cp$ (*15*)	−118	74.4 (*1*)	
	$Ph_3SnCSSEt\cdot Mn(CO)_2Cp$ (*16*)	−130.7	64.0 (*2*)	
	$Ph_3SnCSS(allyl)\cdot Mn(CO)_2Cp$ (*17*)	−165.1	27.3 (*4*)	
	$(o\text{-}To)_3SnCSSMe\cdot Mn(CO)_2Cp$ (*18*)	−142.1	28.6 (*6*)	
	$Ph_3SnCSSMe\cdot Re(CO)_2Cp$ (*19*)	-126.3^c	66.1 (*1*)	^{c}low intensity
	$Ph_3SnCSSMe\cdot Re_2(CO)_9$ (*20*)	−130.7	61.7 (*1*)	
Dithiocarboxylate  21	$Ph_3SnCS_2Li\cdot 2Dioxane$ (*21*)^d	−261		$^d CD_3CN$ sol.
Manganese Complexes	L = CO (*22*)	−194.9	66.1 (*21*)	
 22–27	$L = PPh_3$ (*23*)	−208.5d (36.6)	52.5 (*21*)	
	$L = AsPh_3$ (*24*)	−207.5	53.5 (*21*)	
	$L = SbPh_3$ (*25*)	−205.3	55.7 (*21*)	
	$L = P(OMe)_3$ (*26*)	−209.3d (51.3)	51.7 (*21*)	
	$L = PCy_3{}^e$ (*27*)	−247.4d (31.7)	13.6 (*21*)	^{e}facial
 29–30	$L = PCy_3{}^f$ (*28*)	−254d ?^{c}	(7) (*21*)	^{f}meridional
	$L = P(OPh)_3$ (*29*)	−219br	42 (*21*)	
	$L = P(OMe)_3$ (*30*)	−219.9t (51)	41.1 (*21*)	
Rhenium Complexes	$(CO)_4ReS_2CSnBz_3$ (*31*)	−73.3	187.7 (*21*)	
	$(CO)_4ReS_2CSnPh_3$ (*32*)	−155.7	105.3 (*21*)	
	fac-$PPh_3(CO)_3ReS_2CSnPh_3$ (*33*)	−163.9d (22)	97.1 (*21*)	
	cis-$PPh_3(CO)_4ReSC(S)SnPh_3$ (*34*)^g	−211.4d (10.7)	49.6 (*21*)	^{g}monocoord.
	$(CO)_5ReSC(S)SnPh_3$ (*35*)^g	$(-203)^h$	$(58)^h$ (*21*)	^{h}estimated

to −279 ppm in tetraethynyltin. In contrast, four-coordinate alkyltin compounds give positive δ shifts with the exception of trialkyltin hydrides and alkali derivatives. Recent investigations on triphenyltin compounds showed an interval of −40 to −120 ppm for four-coordinate and −180 to −260 ppm for five-coordinate tin [23].

It is difficult to predict the shift range to be expected for triaryltin dithiocarboxylates, since very few data are known for $Ph_3Sn{-}C$ compounds and α-functional $Ph_3Sn{-}C(X)$ derivatives. As a whole, the range of 0 to −300 ppm seems to be reasonable because the coordination number four is obligatory.

The results given in Table II show that the free and coordinated aromatic stannanedithioesters and stannanedithiocarboxylato complexes have tin-119 shifts which are generally highfield with respect to triphenyltin halides. In most cases, $\delta(^{119}Sn)$ is still more negative than in triphenyltin hydride (−164 ppm) and reaches the usual range of five-coordinate tin compounds [23]. The diamagnetic shift of the triorganotin halides in the order Cl–Br–I may be explained by the different inductive effect (reduced Q_{5p} term) and a 'back-bonding' effect by participation of *d* orbitals (decrease of Q_{5d} term) as well [20]. Since the aryltin dithiocarboxylates with four Sn–C bonds are expected to reveal smaller differences in the polarity of the substituents than triphenyltin iodide, the observed highfield shift is consequent. Functionalisation of the α-alkyl group usually causes a stronger shielding of tin as is evident from the comparison of Ph_3SnCH_2I and Ph_3SnCH_2Cl with Ph_3SnCH_3 and $Ph_3SnCH_2CH_3$ (Table I). The $Ph_3SnCS_2^-$ anion (*21*) marks the highfield barrier of the resonance range due to its negative charge, and is comparable with $[Ph_3SnCl_2]^-$ (−257.2 ppm) [23].

The structural analogy of the dithioester $Ph_3SnCSSMe$ (*1*) with tetraphenyltin [11] suggests a similar point-charge model. The additional shielding compared to Ph_4Sn could be explained by a stronger $(d\text{–}p)\pi$ interaction between tin and the dithiocarboxylic unit but the molecular structure of the ester *1* reveals no shortening of the Sn–C single-bond distance (d = 214 ± 1 pm). Also, no intermolecular association or 'through-space' interaction between tin and the two sulfur atoms (d = 323 pm) has been detected. The direct coupling constant $^1J(^{119}Sn\text{–}^{13}C)$ of *1* and *2* (*ca.* 550 Hz) lies unequivocally in the range of four-coordinate tin compounds [23–25]. The anisotropic effect of the dithiocarboxylic group should rather induce a deshielding of the ^{119}Sn signal as the tin atom is located outside of the anisotropy cone (paramagnetic shift range). It is possible that the *s* share of the three tin-aryl bonds is increased by re-hybridisation to such an extent that a considerable highfield shift results [24]. The de-shielding of the tris(*o*-tolyl)tin ester *6* compared to the triphenyltin esters *1–5* is astonishing, since *6* is expected to give a diamagnetic shift due to the *'ortho'* effect. The tris(*p*-tolyl)tin ester *7* adopts an intermediate position.

The complexation of the esters leads to an increase of the asymmetry of the charge distribution at the tin nucleus (increase of Q_{5p}), and the ^{119}Sn signal shifts to lower field due to the greater σ^P share. In the fairly stable tungsten complexes *8–14*, the coordination shift is constant within a narrow range (Δδ 43 to 45 ppm) independent of the alkylester involved. The labile $(\eta^5\text{-}C_5H_5)M(CO)_2$ complexes (M = Mn, Re) reveal much larger differences. In the methyl- and ethylester complexes *15, 16* (Mn) and *19, 20* (Re), higher coordination shifts are observed than in the tungsten complexes, but *17* and *18* show unexpectedly small shifts which are not easy to explain.

The coordination of the anionic triphenylstannane dithiocarboxylate ligand *21* causes a downfield shift of about 40–70 ppm in the manganese chelate complexes *22–30*. The maximum value is observed in the unsubstituted complex *22*. CO substitution with Vb element donor ligands induces an increase of σ charge density at the transition metal which leads to a smaller coordination shift of the stannanedithiocarboxylate ligand. In the monosubstituted complexes *23–26*, the difference between the ligands concerned is rather small (Δδ 51.7 to 55.7 ppm), exhibiting a slight de-shielding in the order $PPh_3\text{–}AsPh_3\text{–}SbPh_3$. Much lower coordination shifts are observed in the isomeric complexes *27, 28* with the stronger basic tricyclohexylphosphine ligand, which nearly reach the value of the anion *21*. The signal of the *mer* isomer *28* could not be assigned unequivocally due to low intensity.

As expected, the *trans*-bis(phosphite) complexes *29, 30* reveal a smaller coordination shift (Δδ 41–42 ppm) than the monophosphite complex *26*. This diamagnetic influence of rather remote nuclei seems to be inductive and additive. The corresponding bis(triphenylelement) complexes could not be recorded due to their low stability in solution [15]. The considerable substituent effect is also expressed by the relatively large $^4J(^{119}Sn\text{–}^{31}P)$ coupling constants of the phosphine and phosphite complexes.

The rhenium complexes *31–34* in general show more extended coordination shifts; the difference amounts to 40–45 ppm in isotypic compounds like *22/32* and *23/33*. The maximum value is observed in $Bz_3SnCS_2Re(CO)_4$ (*31*) with Δδ 187.7 ppm. Apparently the greater atomic radius of rhenium allows a larger charge transfer and contributes to a de-shielding of $\delta(^{119}Sn)$. Similarly, the $^4J(Sn\text{–}P)$ couplings are smaller than in the corresponding manganese complexes.

The coordination shift of the mono-coordinate complex *34* is only half of that of the chelate complex *33* due to the incomplete charge transfer. Thus, the ^{119}Sn NMR signal may be used as a probe for the coordinative ability of the stannanedithiocarboxylate ligand. Unfortunately, no signals were obtained for monocoordinate manganese complexes [15] due to the large linewidth.

Conclusion

The results show that the ^{119}Sn chemical shifts of all recorded stannanedithiocarboxylates (with the exception of the tribenzyltin compound *31*) lie between δ −118 and −261 ppm. With few exceptions, the signals are observed highfield of tetraphenyltin (δ −128.1) and belong to the highest tin-119 shifts known for SnC_4 compounds [20]. The dithiocarboxylic moiety represents a considerable diamagnetic increment which causes shifts into the range of pentacoordinate organotin compounds. In stannanedithiocarboxylato complexes, $\delta(^{119}Sn)$ operates as a sensitive probe for the σ donating ability of the ligands and is closely related to coordination, substituent influence and complex stability.

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