Studies on *C*-heterocyclic tin compounds. The synthesis and spectral characterization of some thienyl tetraorganotin(IV) compounds

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Abstract

The synthesis of a series of tetraorganotin(IV) compounds containing selectively the 2-thienyl, 3-thienyl, 5-methyl-2-thienyl, 5-t-butyl-2-thienyl, 4-methyl-2-thienyl and 3-(2-pyridyl)-2-thienyl groups [L], of formula $R_{4-n}Sn[L]_n$ (R = Ph, *p*-tolyl, Me, cyclopentyl, cyclohexyl; $n = 1$–4) is reported. Features of structural interest deduced from ^{119m}Sn Mössbauer and NMR (^{13}C and ^{119}Sn modes) spectra are considered.

Introduction

A great deal of work has been reported on the synthesis and structural characterization of carbocyclic tin(IV) compounds [1–5], but there is relatively little information on heterocyclic organotin compounds in which the heterocyclic group is linked to tin directly through the ring carbon. The paucity of such compounds can be attributed to the lability of the Sn–C bond to the heterocycle [6], which severely limits the scope of routine methods of synthesis.

Our continuing interest in the biological properties of triorganotin compounds prompted us to investigate *C*-heterocyclic tin compounds as possible biocidal materials, and in this paper we describe the synthesis and characterization of some tetraorganotins containing one or more thiophene or substituted thiophene groups. Although tetrakis(2-thienyl)tin(IV), the first isolated *C*-heterocyclic tin compound, was reported some sixty years ago [7], only about three dozen reports have since then appeared in the chemical and patent literature on thienyltin(IV) compounds [8].

Experimental

Chemicals

The following commercial chemicals of reagent-grade quality were used in the synthesis: n-BuLi (15% in hexane), PhLi (1 *M* in hexane), thiophene, 2-methylthiophene, 3-methylthiophene, 3-bromothiophene and 2-(3-thienyl)pyridine.

Established methods were used to prepare the following: 2-bromothiophene [9] (b_{13} 40–42°C), 3-thenylbromide [10] ($b_{0.12}$ 50°C), 2-iodothiophene [11] (b_{18} 75–78°C), 2-thenylchloride [12] (b_{17} 73–75°C), 2-t-butylthiophene [13] (b_{760} 165°C), di-(p-tolyl)tin(IV) dichloride [14] (m.p. 48–49°C), tri(p-tolyl)tin(IV) chloride [15] (m.p. 98–99°C), di(p-tolyl)tin(IV) dibromide [16] (m.p. 72–73°C), diphenyltin(IV) dichloride [17] (m.p. 41–42°C), diphenyltin(IV) dibromide [18] (m.p. 39°C), phenyltin(IV) trichloride [19] (b_2 114°C), di(1-naphthyl)tin(IV) dichloride [20] (m.p. 134–136°C), tri(1-naphthyl)tin(IV) chloride [20] (m.p. 205–207°C), chlorodimethyltin(IV) acetate [21] (m.p. 185–187°C), chlorodibutyltin(IV) acetate [22] (m.p. 61–62°C), chloro(N,N-dimethyldithiocarbamato) dimethyltin(IV) [23] (m.p. 138–140°C), dichlorodiacetylacetonate tin(IV) [24] (m.p. 206–207°C), 2-chloromercurithiophene [25] (m.p. 180–181°C), tricyclohexyltin(IV) chloride [26] (m.p. 125–127°C), tricyclopentyltin(IV) chloride [27] (m.p. 40–42°C) and tris(p-chlorophenyl)tin(IV) chloride [28] (m.p. 109–110°C).

Tetrakis(2-thienyl)tin(IV)

Method A. To a ethereal solution of (2-thienyl)magnesium bromide, prepared from 3.9 g (0.16 mol) Mg and 15 ml (0.15 mol) 2-bromothiophene, was added dropwise with stirring, 4 ml SnCl$_4$ (0.034 mol) in 10 ml anhydrous benzene. The mixture was refluxed for 2 h then filtered, and the filtrate hydrolysed with dilute HCl. The organic phase was separated, dried over anhydrous calcium chloride and concentrated. 12 g (78% yield) of white needle-shaped crystals of the product were obtained.

Method B. To an ice-chilled, well-stirred solution of 12 ml (0.144 mol) of thiophene in 100 ml anhydrous ether was added dropwise 96 ml of a 15% n-BuLi solution in hexane under nitrogen. The mixture was stirred at room temperature for 2 h, and a benzene solution of 4.2 ml (0.036 mol) SnCl$_4$ was then added dropwise with cooling. The mixture was subsequently refluxed for 4 h, hydrolysed with aqueous NH$_4$Cl, and worked-up as described in method A, to yield 10 g of product (65% yield).

Method C. 2-Thienyllithium was prepared as in method B from 3.2 ml (0.04 mol) thiophene and 27 ml of n-BuLi (15% in hexane). The solution was then cooled to −70°C in a dry ice-acetone bath and 3.5 g (9 mmol) of Sn(acac)$_2$Cl$_2$ in 100 ml dry ether was added dropwise. The resulting yellow solution was allowed to warm to room temperature, and stirred for 2 h. TLC analysis of the mixture showed the presence of only tetraorganotin compound. The solution was filtered, and the filtrate concentrated to give a yellow liquid. This was chromatographed on a column of activated alumina with hexane as eluant. Concentration of the eluate yielded 3.5 g (77%) of product.

A reverse addition of 2-thienyllithium to Sn(acac)$_2$Cl$_2$ at −70°C yielded only 1.7 g (38%) of the product, and significant amounts of di- and triorganotins were present in the reaction mixture.

Bis(2-thienyl)diphenyltin(IV)

Method A. Dry ether (100 ml) was placed in a three-necked flask fitted with a condenser and a dropping funnel. The air was swept out of the reaction vessel with oxygen-free nitrogen and a steady flow of the dry gas was maintained throughout the reaction. 24 ml of n-BuLi (15% in hexane) was introduced into the flask. 3 ml (0.037 mol) thiophene diluted with an equal volume of anhydrous ether was added dropwise through the dropping funnel at $0\,^\circ$C and the mixture was then stirred for 1 h at room temperature. It was then cooled to $0\,^\circ$C and a solution of 5 g Ph_2SnCl_2 (0.014 mol) in 100 ml of dry ether was added dropwise. The mixture was refluxed for 2 h, after which TLC analysis indicated that reaction was complete. The mixture was filtered through silica gel 60 and concentrated to yield a white solid, which was recrystallised from $CHCl_3$. Yield: 4 g (89%).

Method B. 2-Thienylmagnesium bromide was prepared from 2.3 g (0.09 mol) Mg and 10 ml (0.09 mol) 2-bromothiophene in anhydrous ether and after 2 h reflux was transferred to a dropping funnel under dry nitrogen. The dropping funnel was fitted to a three-necked flask containing a suspension of 13 g (0.09 mol) of CuBr in 100 ml dry ether. With the suspension cooled to $0\,^\circ$C and flushed with nitrogen gas, the Grignard reagent was added dropwise. A straw-colored precipitate formed initially, and turned intense yellow upon addition of 14 ml of quinoline. To this quinoline-stabilised 2-thienylcopper reagent cooled to $-30\,^\circ$C was added a solution of 27.6 g (0.08 mol) Ph_2SnCl_2 in 50 ml dry ether. The mixture was allowed to warm up to $0\,^\circ$C and stirred for 2 h. The CuCl formed was filtered and the filtrate concentrated. TLC analysis showed the filtrate to consist of a mixture of di- and tetra-organotins. The whole mixture was chromatographed on a silica gel 60 column with CCl_4 and later $CHCl_3$ as the eluants. 11 g of the tetraorganotin product was obtained from the CCl_4 eluate. Concentration of the $CHCl_3$ fraction yielded 5 g of unchanged Ph_2SnCl_2.

Bis(2-thienyl)dimethyltin(IV)

This was prepared from 2-thienylmagnesium bromide and Me_2SnCl_2 as outlined for the diphenyltin derivative. Concentration of the filtrate, followed by vacuum distillation yielded the product in 52% yield (b_1 126°C). Use of $Me_2SnCl(OAc)$ in place of Me_2SnCl_2 gave a lower yield (32%).

Tris(2-thienyl)phenyltin(IV)

2-Lithiothiophene was prepared as previously described from 3 ml (0.036 mol) thiophene and 23.5 ml n-BuLi (15% in hexane), and to the solution at room temperature was added 3.6 g (0.01 mol) of $PhSnCl_3$ in 50 ml dry ether. After 4 h stirring the LiCl was filtered off, and the filtrate concentrated under reduced pressure to leave a yellow residue. This was recrystallised from a hexane/CCl_4 mixture to give the product as a white solid (4 g) in 89% yield.

A list of reagents and conditions used for the preparation of the various thienyltins is given in Table 1. Their physical and analytical data are given in Table 2.

Microanalyses were performed by the Microanalytical Service, University College, London. The ^{119}Sn NMR spectra were recorded on a JEOL-FX60Q instrument operating at 22.24 MHz under nuclear Overhauser suppressed conditions [29]. Field frequency lock was to external D_2O. ^{1}H and ^{13}C NMR spectra (Tables 3–5) were

Table 1

Synthesis of some thienyltin(IV) compounds

Compound	Reagents	Conditions	Yield [a] (%)
$(2\text{-}C_4H_3S)_4Sn$	$(2\text{-}C_4H_3S)MgBr/SnCl_4$	reflux 2 h	78
	$(2\text{-}C_4H_3S)Li/SnCl_4$	reflux 4 h	65
	$(2\text{-}C_4H_3S)MgBr/Sn(acac)_2Cl_2$	$-70\,^\circ C$, reverse addn.	44 [b]
	$(2\text{-}C_4H_3S)MgBr/Sn(acac)_2Cl_2$	reflux 2 h	53 [b]
	$(2\text{-}C_4H_3S)Li/Sn(acac)_2Cl_2$	$-70\,^\circ C$, then stir (2 h, rt)	77 [b]
	$(2\text{-}C_4H_3S)Li/Sn(acac)_2Cl_2$	$-70\,^\circ C$, reverse addn.	38 [b]
	$(2\text{-}C_4H_3S)Cu/Sn(acac)_2Cl_2$	$-70\,^\circ C$, then stir (4 h, rt)	45 [b]
	$(2\text{-}C_4H_3S)HgCl/Sn(acac)_2Cl_2/DMF$	reflux 72 h	0
$(2\text{-}C_4H_3S)_3SnPh$	$(2\text{-}C_4H_3S)Li/PhSnCl_3$	stir (4 h, rt)	89
$(4\text{-}Me\text{-}2\text{-}C_4H_2S)_3$- SnPh	$(3\text{-}MeC_4H_3S)/n\text{-}BuLi/PhSnCl_3$	stir (4 h, rt)	67
$(5\text{-}Me\text{-}2\text{-}C_4H_2S)_3$- SnPh	$(2\text{-}MeC_4H_3S)/n\text{-}BuLi/PhSnCl_3$	stir (4 h, rt)	78
$(2\text{-}C_4H_3S)_2SnPh_2$	$(2\text{-}C_4H_3S)Li/Ph_2SnCl_2$	stir (2 h, $0\,^\circ C$), hydrolysis	65
	$(2\text{-}C_4H_3S)Li/Ph_2SnCl_2$	stir (2 h, $0\,^\circ C$)	89
	$(2\text{-}C_4H_3S)Li/Ph_2SnBr_2$	$-70\,^\circ C$, then stir (2 h, $0\,^\circ C$)	75
	$(2\text{-}C_4H_3S)MgBr/Ph_2SnCl_2$	stir (2 h, $0\,^\circ C$)	59
	$(2\text{-}C_4H_3S)MgI/Ph_2SnBr_2$	stir (4 h, $-70\,^\circ C$)	46
	$(2\text{-}C_4H_3S)Cu/Ph_2SnCl_2/$ quinoline	$-30\,^\circ C$, then stir (2 h, $0\,^\circ C$)	55 [b]
$(2\text{-}C_4H_3S)_2Sn\text{-}$ (p-tolyl)$_2$	$(2\text{-}C_4H_3S)MgBr/(p\text{-tolyl})_2SnCl_2$	reflux 2 h	92
	$(2\text{-}C_4H_3S)Li/(p\text{-tolyl})_2SnCl_2$	reflux 2 h	95
$(3\text{-}C_4H_3S)_2SnPh_2$	$(3\text{-}C_4H_3S)Li/Ph_2SnCl_2$	$-70\,^\circ C$, then stir (5 h, rt)	82
	$(3\text{-}BrC_4H_3S)/EtMgBr/Ph_2SnCl_2$	reflux overnight	trace
$(3\text{-}C_4H_3S)_2Sn\text{-}$ (p-tolyl)$_2$	$(3\text{-}C_4H_3S)Li/(p\text{-tolyl})_2SnCl_2$	$-70\,^\circ C$, then stir (overnight, rt)	57
$(C_4H_3S\text{-}3\text{-}CH_2)_2$- SnPh$_2$	$(C_4H_3S\text{-}3\text{-}CH_2MgBr)/Ph_2SnCl_2$	reflux 12 h	65
$(4\text{-}Me\text{-}2\text{-}C_4H_2S)_2$- SnPh$_2$	$(3\text{-}MeC_4H_3S)/PhLi/Ph_2SnCl_2$	reflux 3 h	79
	$(3\text{-}MeC_4H_3S)/n\text{-}BuLi/Ph_2SnCl_2$	reflux 3 h	92
	$(3\text{-}Me\text{-}2\text{-}C_4H_2SCu)/Ph_2SnCl_2$	$-70\,^\circ C$, then stir (2 h, $0\,^\circ C$)	71
$(4\text{-}Me\text{-}2\text{-}C_4H_2S)_2$- Sn($p$-tolyl)$_2$	$(3\text{-}MeC_4H_3S)/n\text{-}BuLi/$ (p-Tolyl)$_2SnCl_2$	reflux 3 h	85
$(5\text{-}Me\text{-}2\text{-}C_4H_2S)_2$- SnPh$_2$	$(2\text{-}MeC_4H_3S)/n\text{-}BuLi/Ph_2SnCl_2$	stir (overnight, rt)	87
$(5\text{-}Me\text{-}2\text{-}C_4H_2S)_2$- Sn($p$-tolyl)$_2$	$(2\text{-}MeC_4H_3S)/n\text{-}BuLi(p\text{-tolyl})_2SnCl_2$	reflux 3 h	88
$(5\text{-}t\text{-}Bu\text{-}2\text{-}C_4H_2S)_2$- SnPh$_2$	$(2\text{-}t\text{-}BuC_4H_3S)/n\text{-}BuLi/Ph_2SnBr_2$	stir (2 h, rt)	42
$(2\text{-}C_4H_3S)SnPh_3$	$(2\text{-}C_4H_3S)Li/Ph_3SnCl$	stir (2 h, rt)	81
$(2\text{-}C_4H_3S)Sn\text{-}$ (p-tolyl)$_3$	$(2\text{-}C_4H_3S)Li/(p\text{-tolyl})_3SnCl$	stir (3 h, rt)	80
$(4\text{-}Me\text{-}2\text{-}C_4H_2S)\text{-}$ SnPh$_3$	$(3\text{-}MeC_4H_3S)/n\text{-}BuLi/Ph_3SnCl$	stir (2 h, rt)	50
$(5\text{-}Me\text{-}2\text{-}C_4H_2)\text{-}$ SnPh$_3$	$(2\text{-}MeC_4H_3S)/n\text{-}BuLi/Ph_3SnCl$	stir (2 h, rt)	45
$(4\text{-}Me\text{-}2\text{-}C_4H_2S)_2$- Sn(1-$C_{10}H_7)_2$	$(3\text{-}MeC_4H_3S)/n\text{-}BuLi/$ $(1\text{-}C_{10}H_7)_2SnCl_2$	reflux 2 h	79
	$(3\text{-}MeC_4H_3S)/PhLi/(1\text{-}C_{10}H_7)_2SnCl_2$	reflux 4 h	71
$(2\text{-}C_4H_3S)_2SnMe_2$	$(2\text{-}C_4H_3S)MgBr/Me_2SnCl_2$	reflux 2 h	52
	$(2\text{-}C_4H_3S)MgBr/Me_2SnCl(OAc)$	stir (2 h, rt)	32 [b]
$(5\text{-}Me\text{-}2\text{-}C_4H_2S)_2$- Sn(octyl)$_2$	$(2\text{-}MeC_4H_3S)/n\text{-}BuLi/octyl_2SnCl_2$	stir (4 h, rt)	40

[a] Yield based on organotin reagent used. [b] Yield based on thiophene.

Table 2

Analytical data for thienyltin(IV) compounds

Compound	m.p./b.p. (°C)	Analyses (Found (calc) (%))		
		C	H	S
(2-C₄H₃S)₄Sn	152–153	42.32 (42.48)	2.77 (2.65)	27.9 (28.3)
(2-C₄H₃S)₃SnPh	168–170	47.86 (48.43)	3.15 (3.14)	21.4 (21.5)
(4-Me-2-C₄H₂S)₃SnPh	85– 87	51.44 (51.85)	4.13 (4.12)	19.9 (19.8)
(5-Me-2-C₄H₂S)₃SnPh	80– 81	52.93 (51.85)	4.17 (4.12)	18.3 (19.8)
(2-C₄H₃S)₂SnPh₂	207–210	54.62 (54.80)	3.85 (3.65)	14.9 (14.6)
(2-C₄H₃S)₂Sn(p-tolyl)₂	104–107	56.33 (56.65)	4.50 (4.29)	13.8 (13.1)
(3-C₄H₃S)₂SnPh₂	225–227	54.78 (54.79)	3.64 (3.65)	14.3 (14.6)
(3-C₄H₃S)₂Sn(p-tolyl)₂	149–151	56.67 (56.65)	4.42 (4.29)	13.3 (13.7)
(C₄H₃S-3-CH₂)₂SnPh₂ ᵃ	93– 94	56.01 (56.65)	4.50 (4.29)	13.6 (13.1)
(4-Me-2-C₄H₂S)₂SnPh₂	105–107	56.25 (56.65)	4.73 (4.29)	12.1 (13.1)
(4-Me-2-C₄H₂S)₂Sn(p-tolyl)₂	145–147	57.69 (58.30)	4.90 (4.29)	12.8 (12.9)
(5-Me-2-C₄H₂S)₂SnPh₂	135–137	56.19 (56.65)	4.26 (4.29)	13.6 (13.7)
(5-Me-2-C₄H₂S)₂Sn(p-tolyl)₂	115–117	58.42 (58.30)	5.27 (4.86)	13.0 (13.0)
(5-t-Bu-2-C₄H₂S)₂SnPh₂	107–109	60.92 (61.09)	5.90 (5.80)	11.8 (11.6)
(2-C₄H₃S)SnPh₃	208–211	61.44 (61.11)	4.21 (4.17)	6.86 (7.41)
(2-C₄H₃S)Sn(p-tolyl)₃	208–210	63.34 (63.02)	4.57 (5.04)	6.57 (6.72)
(4-Me-2-C₄H₂S)SnPh₃	143–145	61.71 (61.85)	4.50 (4.48)	6.95 (7.17)
(5-Me-2-C₄H₂S)SnPh₃	153–155	61.52 (61.85)	4.45 (4.48)	6.75 (7.17)
(4-Me-2-C₄H₂S)₂Sn(1-C₁₀H₇)₂ ᵇ	149–150	63.71 (63.38)	4.25 (4.23)	11.2 (11.3)
(2-C₄H₃S)₂SnMe₂	126 (1 mmHg)	38.14 (38.22)	3.94 (3.82)	19.8 (20.3)

ᵃ (C₄H₃S-3-CH₂) = 3-thenyl. ᵇ (1-C₁₀H₇) = 1-naphthyl.

recorded on a JEOL JNM-PX 100 spectrometer operating at 99.55 MHz for ¹H NMR and 25.00 MHz for ¹³C. The complete proton decoupling irradiation mode was used to secure the ¹³C spectra in CDCl₃ (Tables 4 and 5), with the solvent functioning also as internal lock. The chemical shift assignments were confirmed in three cases (Table 6) by use of off-resonance decoupling. All spectra were recorded at ambient temperatures using concentrated solutions for ¹³C NMR and specified concentrations (Table 7) for ¹¹⁹Sn NMR. ¹¹⁹ᵐSn Mössbauer spectra (Table 8) were

recorded at 80 K using a constant-acceleration microprocessor spectrometer as described previously [30].

Results and discussion

Synthesis

The majority of the compounds were prepared by the organolithium method, except for tetrakis(2-thienyl)tin(IV), bis(2-thienyl)diphenyltin(IV) and bis(4-methyl-2-thienyl)diphenyltin(IV), where alternative synthetic methods were explored (Table 1). The reaction of 2-thienylmagnesium bromide, 2-thienyllithium and 2-thienyl-copper with the respective diorganotin dichlorides in 2/1 stoichiometry gave tetraorganotins in comparable yields. The reaction of $SnCl_2(acac)_2$ with 2-thienyl-lithium in 1/2 ratio proceeded by cleavage of both Sn–O and Sn–Cl bonds to form tetrakis(2-thienyl)tin. Rather surprisingly, the reaction of $SnCl_2(acac)_2$ with a milder reagent such as 2-thienylmagnesium bromide or 2-thienylcopper also gave the tetraorganotin compound as the sole product. The apparent failure of 2-thienyl-mercuric chloride to react with $SnCl_2(acac)_2$ may be attributed to the stronger C–Hg bond. The use of different organotin halides did not appreciably affect the nature or yields of the products, as can be seen from Table 1.

Low temperature ($-70\,^\circ C$) was necessary for the successful preparation of bis(3-thienyl)diphenyltin. An attempt to prepare 3-thienylGrignard by the entrainment method using EtMgBr and 3-bromothiophene was unsuccessful, since subsequent addition of Ph_2SnCl_2 to this system yielded diethyldiphenyltin(IV). Bis(3-thienyl)diphenyltin was obtained in high yield from 3-thenylmagnesium bromide and Ph_2SnCl_2. There was no detectable contamination by bis(3-methyl-2-thienyl)di-phenyltin, arising from a priori light-induced allylic rearrangement [31] of the 3-thenyl bromide precursor used in the Grignard synthesis. An attempt was made to prepare 2-thenyl derivatives of organotins from 2-thenyl chloride via the Grignard pathway, but unlike in the reaction for the 3-thenyl analogues, the main reaction was a coupling reaction which yielded 1,2-dithienylethane.

The directing effect of the methyl group on the metallations of 2- and 3-methyl-thiophene was demonstrated in the preparation of the corresponding bis(5-methyl-2-thienyl)diaryltin and bis(4-methyl-2-thienyl)diaryltin compounds. 3-Methyl-thiophene is metallated predominantly in the 5-position because of the inductive effect ($+I$) of the methyl group which tends to increase the electron density at the 2-position, making the proton at this position less acidic than in the 5-position. Although it has been reported [32] that lithiation of 3-methylthiophene by PhLi leads to a high yield of 3-methyl-2-lithiothiophene, we did not observe this, since when the lithiated product in our reaction was treated with Ph_3SnCl both (4-methyl-2-thienyl)triphenyltin and (3-methyl-2-thienyl)triphenyltin were obtained, with the former in larger amount. Whereas (4-methyl-2-thienyl)triphenyltin could be prepared cleanly, the di- and mono-phenyltin analogues showed additional resonances in their tin-119 NMR spectra (Table 7). Although the formation of isomeric products during the lithiation step cannot be discounted, it is conceivable that redistribution reactions may occur with these compounds in solution. Curiously, only two ^{119}Sn resonances were seen for bis(4-methyl-2-thienyl)di(p-tolyl)tin and the 1-naphthyltin analogue, the high field resonances in each case being dominant ($> 80\%$).

The syntheses of $R_3Sn(3\text{-pyridyl-2-thienyl})$ derivatives [33] (R = Ph, $p\text{-MeC}_6H_4$, $p\text{-ClC}_6H_4$, cyclo-C_5H_9, cyclo-C_6H_{11}) and $Ph_2Sn(3\text{-pyridyl-2-thienyl})_2$ [34] have been previously reported along with their physico-chemical data. These preparations gave high yields, presumably on account of the facile directed lithiation of 2-(3-thienyl)pyridine and the equally facile subsequent transmetallation reaction with the appropriate organotin(IV) halide. These compounds are discussed in this paper from the standpoint of their spectral properties (particularly ^{13}C NMR) in comparison with those for other thienyltetraorganotins (see below).

Spectral studies

Spectral characterizations of the compounds synthesized involved [119m]Sn Mössbauer and NMR (^{13}C and [119]Sn modes) techniques. Proton NMR chemical shifts for the aryl and heteroaryl ring hydrogens were found in the region 6–8 ppm (Table 3), but the complexity of the spectra, coupled with their poor resolution, precluded assignments. The ^{13}C spectra, however, proved to be more amenable to analysis and the spectral parameters are tabulated in Tables 4 and 5. The influence of a 3-pyridyl substituent on the ^{13}C chemical shifts of the tin-bound thienyl ring and on the coordination state of the tin atom is qualitatively different from those in cases where the substituents in the thienyl ring are alkyl groups, and will be discussed separately.

When attention is given first to thienyl and alkyl-substituted thienyltin derivatives, it can be seen for the R_3SnL series (L = 2-thienyl) that, relative to Me_3SnL,

Table 3

Proton NMR chemical shifts [a] for thienyltin(IV) compounds

Compound	δ (ppm, rel. to TMS)
$(2\text{-}C_4H_3S)_4Sn$	7.03–7.83(m)
$(2\text{-}C_4H_3S)_3SnPh$	7.26–7.78(m)
$(4\text{-Me-}2\text{-}C_4H_2S)_3SnPh$	2.30(s, 9H), 6.80–7.70(m, 11H)
$(5\text{-Me-}2\text{-}C_4H_2S)_3SnPh$	2.65(s, 9H), 6.90–7.80(m, 11H)
$(2\text{-}C_4H_3S)_2SnPh_2$	7.25–7.65(m)
$(2\text{-}C_4H_3S)_2Sn(p\text{-tolyl})_2$	2.33(s, 6H), 7.05–7.70(m, 14H)
$(3\text{-}C_4H_3S)_2SnPh_2$	7.20–7.47(m)
$(3\text{-}C_4H_3S)_2Sn(p\text{-tolyl})_2$	2.30(s, 6H), 7.00–7.47(m, 14H)
$(C_4H_3S\text{-}3\text{-CH}_2)_2SnPh_2$	2.24(s, 4H), 7.09–7.64(m, 16H)
$(4\text{-Me-}2\text{-}C_4H_2S)_2SnPh_2$	2.30(s, 6H), 7.00–7.50(m, 14H)
$(4\text{-Me-}2\text{-}C_4H_2S)_2Sn(p\text{-tolyl})_2$	2.30(s, 6H), 2.50(s, 6H), 6.75–7.45(m, 12H)
$(5\text{-Me-}2\text{-}C_4H_2S)_2SnPh_2$	2.51(s, 6H), 6.70–7.50(m, 14H)
$(5\text{-Me-}2\text{-}C_4H_2S)_2Sn(p\text{-tolyl})_2$	2.30(s, 6H), 2.50(s, 6H), 6.75–7.45(m, 12H)
$(5\text{-t-Bu-}2\text{-}C_4H_2S)_2SnPh_2$	1.54(s, 18H), 7.25–7.82(m, 14H)
$(2\text{-}C_4H_3S)SnPh_3$	7.22–7.73(m)
$(2\text{-}C_4H_3S)Sn(p\text{-tolyl})_3$	2.46(s, 9H), 7.05–7.58(m, 15H)
$(4\text{-Me-}2\text{-}C_4H_2S)SnPh_3$	2.40(s, 3H), 7.07–7.83(m, 17H)
$(5\text{-Me-}2\text{-}C_4H_2S)SnPh_3$	2.52(s, 3H), 6.75–8.05(m, 17H)
$(4\text{-Me-}2\text{-}C_4H_2S)_2Sn(1\text{-}C_{10}H_7)_2$	2.20(s, 6H), 7.10–7.95(m, 18H)
$(2\text{-}C_4H_3S)_2SnMe_2$	0.50(s, 6H), 6.90–7.32(m, 6H)
$(5\text{-Me-}2\text{-}C_4H_2S)_2Sn(octyl)_2$	0.85–1.18(m, 34H), 2.47(s, 6H), 6.75–7.25(m, 4H)

[a] In concentrated $CDCl_3$ solution.

Table 4

^{13}C NMR data ^{a,b}

Compound	Thienyl resonances (ppm)					Aryl resonances (ppm)				
	C(2)	C(3)	C(4)	C(5)	CH$_3$-L	C$_{ipso}$	C$_{ortho}$	C$_{meta}$	C$_{para}$	CH$_3$-Ar
LH	125.8	127.6	127.6	125.8	—					
LMe	139.1	126.6	124.9	122.8	15.0					
LBr	112.0	129.6	127.4	126.8	—					
LSnMe$_3$ ^{d}	136.7	135.0	130.8	128.0	—					
LSnPh$_3$	132.4	137.1	128.3	132.1	—	137.4	137.7	128.8	129.4	—
	^{c}	(39.0)	(19.5)	(44.2)		^{c}	(33.1)	(53.7)	(11.0)	
L$_2$SnPh$_2$	131.8	137.5	132.3	128.3		137.0	136.8	128.8	129.7	—
	^{c}	(37.8)	(22.0)	(57.3)		(501.7)	(44.0)	(56.2)	(13.4)	
L$_3$SnPh	131.7	137.6	132.5	128.3		136.7	136.5	128.9	129.9	—
	^{c}	(41.5)	(24.4)	(58.6)		(615.5)	(46.4)	(61.0)	(12.1)	
L$_4$Sn	131.6	138.2	133.1	128.6						
	(647)	(45.7)	(28.4)	(65.9)						
(4-MeL)SnPh$_3$	131.3	137.0	132.6	127.8	15.1	136.3	139.8	128.7	129.3	—
	^{c}	(39.1)	^{c}	(17.1)		(571.0)	(34.2)	(53.7)	(12.7)	
(4-MeL)$_2$SnPh$_2$	139.2	136.9	131.0	128.0	15.2	136.6	139.9	128.8	129.6	—
	^{c}	(41.9)	(25.5)	^{c}		^{c}	(35.5)	(58.4)	(12.7)	
(5-MeL)SnPh$_3$	130.3	137.0	127.0	146.9	15.2	136.3	137.8	128.7	129.3	—
	^{c}	(39.1)	(48.8)	(20.8)		(463.9)	(31.7)	(53.7)	(12.2)	
(5-MeL)$_2$SnPh$_2$	129.9	136.7	127.0	147.1	15.1	137.4	137.8	128.8	129.5	—
	^{c}	(41.5)	(52.5)	(20.8)		(549.3)	(34.2)	(58.6)	(10.4)	

(5-MeL)₃SnPh	130.0 –[e]	136.5 (40.3)	127.0 (56.2)	147.3 (23.2)	15.2	136.7 –[e]	137.9 (37.8)	128.8 (59.8)	129.7 (<10)	—
LSn(p-tolyl)₃	133.8 –[e]	137.2 (38.8)	129.5 (54.2)	131.8 (20.6)	—	134.5 (536.9)	136.9 (41.7)	129.4 (52.0)	138.8 (11.7)	21.5
L₂Sn(p-tolyl)₂	133.2 –[e]	136.7 (42.2)	128.3 (52.0)	132.1 (21.1)	⋯	136.9 –[e]	139.6 (43.6)	129.7 (63.2)	137.4 –[e]	21.5
L₂SnMe₂	134.9 –[e]	136.0 (35.5)	131.4 (20.9)	128.1 (51.6)	—					
(4-MeL)₂Sn(p-tolyl)₂	132.8 –[e]	136.8 (43.8)	133.6 –[e]	127.8 (19.0)	15.1	139.2 –[e]	139.8 (35.6)	129.7 (60.9)	139.5 –[e]	21.5
(4-MeL)₂Sn(1-C₁₀H₇)₂	139.2	140.3	134.2	126.4	15.2					
(5-MeL)₂Sn(p-tolyl)₂	130.4 –[e]	136.7 (46.4)	126.9 (52.6)	146.9 (19.7)	15.1	136.9 (568.8)	137.7 (34.2)	129.5 (59.8)	139.2 (14.7)	21.5
(5-MeL)₂Sn(octyl)₂	132.6 –[c]	136.4 (29.0)	126.8 (44.3)	145.9 (15.3)	15.0					
(5-t-BuL)₂SnPh₂	124.9 –[e]	136.5 (36.6)	123.0 (52.5)	164.9 –[e]	—	137.6 –[e]	136.8 (41.5)	128.7 –[e]	129.4 (15.9)	—
L'₂SnPh₂	133.9 (58.0)	133.7 (546.4)	133.0 (58.6)	126.0 (60.8)	—	137.9 (499.5)	136.9 (39.0)	128.7 (54.2)	129.3 (12.4)	—
L'₂Sn(p-tolyl)₂	133.8 (59.8)	134.0 –[e]	133.1 (57.6)	125.9 (63.2)	—	137.0 (417.6)	136.8 (41.0)	129.5 (56.4)	139.2 (9.2)	21.5
L''₂SnPh₂	130.9 (29.3)	146.9 (35.2)	132.1 (27.8)	127.0 –[e]	—	137.4 (577.1)	136.8 (43.2)	128.7 (58.6)	129.4 (12.5)	—

[a] In concentrated CDCl₃ solution. [b] Error in chemical shift data, ±0.2 ppm; coupling constants (in parentheses) reported are for $^nJ(^{119}\text{Sn}-^{13}\text{C})$. [c] L = 2-thienyl; L' = 3-thienyl; L'' = 3-thienyl. [d] Data quoted from ref. 47. [e] Coupling constants cannot be estimated from spectra.

the signals from the *ipso*-carbons (C(2)) of Ph_3SnL (**2**) and (p-tolyl)$_3$SnL (**3**) are shifted upfield by ca. 4 and 3 ppm, respectively, while those from the other thienyl carbons are shifted downfield, with the *ortho* (C(3)) and *para* (C(5)) atoms perceptibly more than the *meta* (C(4)). Introduction of a 5-methyl substituent in the thienyl ring in **2** leads to an upfield shift of ca. 2 ppm for C(2), and a marked downfield shift of ca. 15 ppm for C(5). The chemical shift of C(3) is unchanged, but C(4) suffers a small upfield shift. Similarly, the introduction of a 4-methyl substituent in **2** results in a slight (ca. 1 ppm) upfield shift of C(2), but the C(4) and C(5) atoms are deshielded and shielded, respectively, by ca. 4 ppm. Again, the C(3) atom is insensitive to the presence of the methyl substituent. If the ^{13}C chemical shifts are assumed to reflect changes in the electron density at carbon, the charge pattern in the above compounds corresponds to a π-polarization [35–38] rather than the conjugative mechanism which has been suggested for the Me_nSnL_{4-n} system [39]. Consistent with this is the near identity of the ^{119}Sn chemical shifts for **2** and its 4- and 5-methylthienyl derivatives (Table 7). Any direct resonance interaction between the heteroaryl ligand and tin would be expected to be enhanced by alkyl substitution in the ring, with a corresponding influence on $\delta(^{119}Sn)$.

The π-polarization of the heteroaryl ring is seen as a response to the substituent dipole, Sn^{δ}–R^{δ}: the greater the electronegativity of the R group (Ph > p-tolyl > Me), the greater the electropositive character of the tin atom and, consequently, the larger the perturbation. The π-system of thiophene is considered to be polarized as a whole, as indicated schematically, and provides a rationalization for the larger
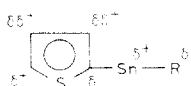
deshielding of C(5) in $Ph_3Sn(5-MeL)$ relative to that of C(4) in $Ph_3Sn(4-MeL)$. However, the observation in both derivatives of the upfield shift of the carbon atom *ortho* to the methyl substituent indicates some degree of localized polarization of the C=C unit between C(4) and C(5). This is also evident in the compounds $Ph_2Sn(5-RL)_2$ (R = Me, t-Bu), where the greater inductive effect of the t-butyl group leads to enhanced shieldings of the C(2) and C(4) atoms, and of deshielding of the C(5) atom. Although an alternative explanation involving a hyperconjugative mechanism is conceivable, the negligible shift of the C(3) atoms in both compounds suggests this to be less likely.

The chemically shift changes in the series (p-tolyl)$_2$SnL'$_2$, where L' = 2-thienyl, 4-Me-2-thienyl and 5-Me-2-thienyl, closely parallel the observations in the Ph_3Sn series (Table 4), suggesting that the presence of the additional heteroaryl group at tin exerts little influence on the carbon electron densities on either ring. This also appears to be the case for the series, $Ph_nSn(5-MeL)_{4-n}$ (n = 1–3) (Table 4). However, increasing heteroaryl substitution at tin leads to a progressive shielding of the tin atom. This is well illustrated in the $Ph_nSn(5-MeL)_{4-n}$ series; $\delta(^{119}Sn)$: −136.7 (n = 3), −143.6 (n = 2) and −150.1 (n = 1) ppm. Whereas in the Me_nSnL_{4-n} compounds this feature was ascribed to a rise in p_π–d_π interaction [39], we consider the monotonic trend in $\delta(^{119}Sn)$ to be simply an artefact of the polarizability of the thienyl rings and their additive contributions to tin shielding. A parallel may be drawn to the trends in the ^{119}Sn chemical shifts of organotin hydrides, which have been interpreted in terms of the effect of substituent polarizability on the paramagnetic term and tin shielding [40].

Table 5

^{13}C NMR data ^{a,b,c}

Compound	C_i (C_α)	C_o (C_β)	C_m (C_γ)	C_p (C_δ)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)
[3-(2-py)-2-C$_4$H$_2$S]Sn(p-tolyl)$_3$	137.2 (647.5)	136.9 (41.7)	128.9 (56.4)	137.8 (11.7)	141.3 $-^d$	147.4 $-^d$	133.9 (29.0)	125.5 (45.5)	152.4	121.7	138.6	118.9	148.0
[3-(2-py)-2-C$_4$H$_2$S]SnPh$_3$	137.3 (726.6)	136.8 (39.6)	128.0 (43.2)	128.2 (11.7)	137.3 $-^d$	147.4 $-^d$	134.2 (32.2)	125.5 (45.4)	152.1	121.7	142.3	118.8	147.7
[3-(2-py)-2-C$_4$H$_2$S]Sn(p-ClC$_6$H$_4$)$_3$	138.2 (786.2)	137.9 (45.3)	128.4 (57.3)	129.3 $-^d$	134.8 $-^d$	147.6 $-^d$	135.0 (39.3)	125.5 (49.6)	152.0	122.2	139.9	119.1	151.8
[3-(2-py)-2-C$_4$H$_2$S]Sn(cyclo-C$_5$H$_9$)$_3$	27.1 (396.7)	31.2 (14.7)	26.3 (57.4)		147.2 $-^d$	140.4 $-^d$	131.7 (15.9)	126.3 (31.7)	154.4	121.0	136.6	119.8	148.3
[3-(2-py)-2-C$_4$H$_2$S]Sn(cyclo-C$_6$H$_{11}$)$_3$	30.3 (374.8)	27.2 (<7)	29.5 (62.3)	32.2 (15.9)	147.5 $-^d$	139.2 $-^d$	131.7 (13.4)	126.5 (31.7)	154.6	120.9	136.5	119.8	148.2
[3-(2-py)-2-C$_4$H$_2$S]$_2$SnPh$_2$	135.5 (794.9)	136.3 (43.2)	127.6 (56.6)	137.1 (<10)	144.9 $-^d$	145.7 $-^d$	132.2 (32.2)	124.9 (50.8)	152.3	121.3	146.5	118.7	147.6
2-(3-thienyl)pyridine					125.2	141.3	122.6	125.3	152.2	120.7	135.4	118.9	148.4

^{a} In concentrated CDCl$_3$ solution. ^{b} i (ipso), o (ortho), m (meta), p (para) refer to aryl carbon atoms; α, β, γ, δ refer to carbon atoms of the cycloalkyl ring; C(2)–C(10) refer to carbon atoms of the heterocyclic moiety (see Figs. 1 and 2). ^{c} Error in chemical shift data, ±0.2 ppm; coupling constants (in parentheses) reported are for $^nJ(^{119}\mathrm{Sn}-^{13}\mathrm{C})$. ^{d} Coupling constants cannot be estimated from data.

317

Table 6

Comparison of ^{13}C chemical shift data (ppm) for complete decoupling (COM) and off-resonance (OFR) spectra of selected thienyltin(IV) compounds [a,b]

Ph$_3$Sn(4-MeL)			Ph$_2$Sn(5-MeL)$_2$			(cyclo-C$_5$H$_9$)$_3$Sn(3-pyL)		
	COM	OFR		COM	OFR		COM	OFR
C$_i$	136.3	136.3	C$_i$	137.4	137.4	C(2)	147.2	147.3
C$_o$	139.8	141.3	C$_o$	137.8	139.4	C(3)	140.4	140.4
		137.5			136.3			
C$_m$	128.7	130.3	C$_m$	128.8	130.3	C(4)	131.7	133.7
		127.2			127.1			130.1
C$_p$	129.3	130.9	C$_p$	129.5	131.0	C(5)	126.3	128.0
		127.8			127.9			124.8
C(2)	131.3	131.3	C(2)	129.9	129.9	C(6)	154.4	154.6
C(3)	137.0	138.6	C(3)	136.7	138.3	C(7)	121.0	121.8
		135.5			135.2			118.4
C(4)	132.6	132.5	C(4)	127.0	128.6	C(8)	136.6	138.4
					125.5			135.1
C(5)	127.8	129.5	C(5)	147.1	147.1	C(9)	119.8	121.6
		126.1						118.4
						C(10)	148.3	150.2
								146.6
						C$_\alpha$	27.1	25.2
								29.7
						C$_\beta$	31.2	32.8
								31.2
								29.8
						C$_\gamma$	26.3	27.9
								26.4
								25.0

[a] L = 2-thienyl. [b] See footnote b. Tables 4 and 5 for carbon numbering scheme.

A further point of interest concerns the ^{119}Sn–^{13}C(aryl) one-bond coupling constants derived for the few cases noted in Table 4. Particularly noteworthy are the large changes in $^1J(^{119}$Sn–^{13}C) in going from Ph$_2$SnL$_2$ to PhSnL$_3$, and from Ph$_3$Sn(5-MeL) to Ph$_2$Sn(5-MeL)$_2$. For tin, the main contribution to spin coupling is thought to arise from the Fermi contact interaction [41]. However, as the number of the polar heteroaryl rings attached to tin increases, the effective nuclear charge of the tin atom and hence $\psi_{5s}(O)^2$, the value of the s-electronic wave function at the nucleus, will increase, leading to an increase in the magnitude of coupling constants involving tin. There will also be an effect due to the diversion of s-character into bonds involving less electronegative phenyl groups [42], and this will increase the relevant couplings, as is seen to be the case.

The ^{119m}Sn Mössbauer data for the compounds are listed in Table 8. It is well known that for tetrahedral organotin(IV) compounds, the isomer shifts show little variation with bond polarity [43]. This is observed to be the case for the compounds

Table 7

^{119}Sn chemical shifts for thienyltin(IV) compounds

Compound	Concentration [a]	$\delta(^{119}$Sn) (ppm) [b]
(2-C$_4$H$_3$S)$_4$Sn	7 [c]	−147.0 [d]
(2-C$_4$H$_3$S)$_3$SnPh	15.4	−144.5
(4-Me-2-C$_4$H$_2$S)$_3$SnPh [e]	5.4	−142.2 (7%), −143.2 (15%),
		−146.9 (10%), −148.5 (24%),
		−152.8 (29%), −157.7 (15%)
(5-Me-2-C$_4$H$_2$S)$_3$SnPh	7.7	−150.1
(2-C$_4$H$_3$S)$_2$SnPh$_2$	8.7	−140.8
(2-C$_4$H$_3$S)$_2$Sn(p-tolyl)$_2$	4.7	−138.0
(3-C$_4$H$_3$S)$_2$SnPh$_2$	6.7	−148.8
(3-C$_4$H$_3$S)$_2$Sn(p-tolyl)$_2$	6.7	−146.3
(C$_4$H$_3$S-3-CH$_2$)$_2$SnPh$_2$	20	−151.4
(4-Me-2-C$_4$H$_2$S)$_2$SnPh$_2$ [e]	13.3	−143.0 (36%), −146.8 (23%)
		−148.4 (21%), −152.0 (17%)
(4-Me-2-C$_4$H$_2$S)$_2$Sn(p-tolyl)$_2$ [e]	10	−140.1 (89%), −143.9 (11%)
(5-Me-2-C$_4$H$_2$S)$_2$SnPh$_2$	25	−143.6
(5-Me-2-C$_4$H$_2$S)$_2$Sn(p-tolyl)$_2$	6.7	−140.5
(5-t-Bu-2-C$_4$H$_2$S)$_2$SnPh$_2$	6.2	−142.2
(2-C$_4$H$_3$S)	15.4	−135.5
(2-C$_4$H$_3$S)Sn(p-tolyl)$_3$	4.7	−134.6
(4-Me-2-C$_4$H$_2$S)SnPh$_3$	5.4	−136.5
(5-Me-2-C$_4$H$_2$S)SnPh$_3$	7.7	−136.7
(4-Me-2-C$_4$H$_2$S)$_2$Sn(1-C$_{10}$H$_7$)$_2$ [e]	13.3	−134.1 (80%), −140.0 (20%)
(2-C$_4$H$_3$S)$_2$SnMe$_2$	26.7	−26.7
(5-Me-2-C$_4$H$_2$S)$_2$Sn(octyl)$_2$	36.7	−76.5
[3-(2-py)-2-C$_4$H$_2$S]SnPh$_3$	6.2	−181.6
[3-(2-py)-2-C$_4$H$_2$S]Sn(p-tolyl)$_3$	8.0	−176.3
[3-(2-py)-2-C$_4$H$_2$S]Sn(p-ClC$_6$H$_4$)$_3$	6.2	−180.0
[3-(2-py)-2-C$_4$H$_2$S]Sn(cyclo-C$_5$H$_9$)$_3$	26.7	−57.8
[3-(2-py)-2-C$_4$H$_2$S]Sn(cyclo-C$_6$H$_{11}$)$_3$	8.5	−105.9
[3-(2-py)-2-C$_4$H$_2$S]$_2$SnPh$_2$	6.7	−245.5

[a] w/w % in CDCl$_3$ as solvent. [b] Relative to Me$_4$Sn. [c] Concentration in w/v %. [d] Ref. 48. [e] Multiple tin signals were observed in solution with intensities as indicated in parentheses.

studied here. The variations in Sn–C bond polarities also appear to be not significant enough to give rise to quadrupole split doublet spectra for the thienyl- and alkylated thienyltins. It is pertinent to note here that major variations of quadrupole splittings (QS) which are observed arise from structural rather than bonding changes [43] and, indeed, the presence of a 3-pyridyl substituent on the thienyl ring leads, via intramolecular N → Sn coordination, to the observation of QS for this class of organotin compounds (Table 8). Although the Mössbauer literature on tetraorganotins contains many anomalies of resolvable and non-resolvable spectra [44], it is significant that only compounds containing the pyridyl substituent display partially-resolved spectra among the thienyltins listed in Table 8. Equally noteworthy for the compounds containing the 3-pyridyl ligand are their ^{119}Sn chemical shifts (Table 7) and one-bond couplings involving the aryl and cycloalkyl moieties (Table 5). The ^{119}Sn signals occur at significantly higher fields relative to those for the thienyl- and alkyl-substituted thienyltins, indicative of the higher-than-four coordination status of tin in these compounds, and this is further supported by the enhanced values of $^1J(^{119}$Sn–^{13}C$_{ipso})$ observed for (p-tolyl)$_3$Sn(3-

Table 8

^{119m}Sn Mössbauer data ^{a} for thienyltin(IV) compounds at 80 K

Compound	IS ^{b} (mm s^{-1})	QS (mm s^{-1})
(2-C$_4$H$_3$S)$_4$Sn	1.20	0
(2-C$_4$H$_3$S)$_3$SnPh	1.08	0
(4-Me-2-C$_4$H$_2$S)$_3$SnPh	1.08	0
(5-Me-2-C$_4$H$_2$S)$_3$SnPh	1.07	0
(2-C$_4$H$_3$S)$_2$SnPh$_2$	1.12	0
(2-C$_4$H$_3$S)$_2$Sn(p-tolyl)$_2$	1.10	0
(3-C$_4$H$_3$S)$_2$SnPh$_2$	1.15	0
(3-C$_4$H$_3$S)$_2$Sn(p-tolyl)$_2$	1.15	0
(C$_4$H$_3$S-3-CH$_2$)$_2$SnPh$_2$	1.11	0
(4-Me-2-C$_4$H$_2$S)$_2$SnPh$_2$	1.15	0
(4-Me-2-C$_4$H$_2$S)$_2$Sn(p-tolyl)$_2$	1.07	0
(5-Me-2-C$_4$H$_2$S)$_2$SnPh$_2$	1.13	0
(5-Me-2-C$_4$H$_2$S)$_2$Sn(p-tolyl)$_2$	1.12	0
(5-t-Bu-2-C$_4$H$_2$S)$_2$SnPh$_2$	1.12	0
(2-C$_4$H$_3$S)SnPh$_3$	1.16	0
(2-C$_4$H$_3$S)Sn(p-tolyl)$_3$	1.21	0
(4-Me-2-C$_4$H$_2$S)SnPh$_3$	1.16	0
(5-Me-2-C$_4$H$_2$S)SnPh$_3$	1.15	0
(4-Me-2-C$_4$H$_2$S)$_2$Sn(1-C$_{10}$H$_7$)$_2$	1.12	0
(2-C$_4$H$_3$S)$_2$SnMe$_2$	1.13	0
[3-(2-py)-2-C$_4$H$_2$S]SnPh$_3$ ^{c}	1.11	0.63
[3-(2-py)-2-C$_4$H$_2$S]Sn(p-tolyl)$_3$ ^{c}	1.07	0.57
[3-(2-py)-2-C$_4$H$_2$S]Sn(p-ClC$_6$H$_4$)$_3$ ^{c}	1.13	0.59
[3-(2-py)-2-C$_4$H$_2$S]Sn(cyclo-C$_5$H$_9$)$_3$ ^{c}	1.29	0.92
[3-(2-py)-2-C$_4$H$_2$S]Sn(cyclo-C$_6$H$_{11}$)$_3$ ^{c}	1.35	0.96
[3-(2-py)-2-C$_4$H$_2$S]$_2$SnPh$_2$ ^{c}	1.03	0.73

^{a} Error ± 0.05 mm s^{-1}. ^{b} Relative to CaSnO$_3$ or BaSnO$_3$. ^{c} py = pyridyl.

pyL) and Ph$_2$Sn(3-pyL)$_2$ relative to those for corresponding unsubstituted thienyl-tin compounds (Table 5). We recently reported the X-ray crystal structures of two of these compounds, viz. (p-tolyl)$_3$Sn(3-pyL) [33] and Ph$_2$Sn(3-pyL)$_2$ [34]; the latter has a unique 6-coordinated structure (Fig. 1) and the former a pseudo-pentacoordinate tin environment, as illustrated schematically in Fig. 2.

The ^{13}C chemical shift data on the compounds containing the 3-pyridyl substituent are given in Table 5. For the series, [(p-ZC$_6$H$_4$)$_3$Sn(3-pyL)] (Z = H, Me, Cl)
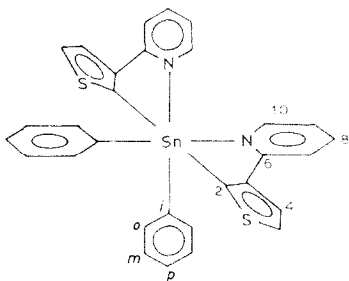
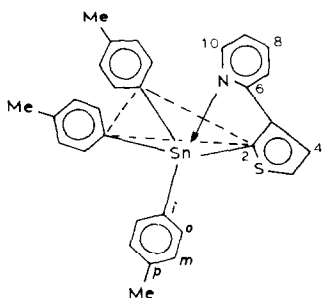Fig. 1. Bis[3-(2-pyridyl)-2-thienyl-C,N]diphenyltin(IV).

Fig. 2. [3-(2-Pyridyl)-2-thienyl-C,N]tri(p-tolyl)tin(IV).

the chemical shift of the *ipso*-carbon (C(2)) is the most sensitive: the shift to high fields follows the sequence p-Me < H < p-Cl. The trends in the aryl carbon shifts, however, appear to be erratic but, surprisingly, the $^1J(^{119}Sn-^{13}C_{aryl})$ values also follow the sequence p-Me < H < p-Cl. This is contrary to the order expected for decreasing s-character in the Sn–aryl bonds with increasing electronegativity of the aryl groups [42], but is readily rationalised in terms of increased coordination at tin [33,45,46] by the proximate pyridyl group, with increasing electronegativity of the aryl group. A comparison between Ph$_3$Sn(3-pyL) and Ph$_2$Sn(3-pyL)$_2$ indicates that while the C$_{ipso}$ and C$_{para}$ atoms of the phenyl rings are shielded and deshielded, respectively, to a greater extent in the latter, the corresponding trends involving C(2) and C(5) of the thienyl rings are in the opposite sense. These trends somewhat parallel those observed between Ph$_3$Sn(5-MeL) and Ph$_2$Sn(5-MeL)$_2$ (Table 4). The C(3) atom carrying the pyridyl substituent is shifted downfield to 147.4 ppm in Ph$_3$Sn(3-pyL) and 145.7 ppm in Ph$_2$Sn(3-pyL)$_2$ relative to 137.1 ppm in Ph$_3$SnL. There is also a relative deshielding of the C(2) and C(4) atoms, but the C(5) atoms are shielded. Seemingly, the presence of the pyridyl substituent leads to an uneven response of the π-polarization of thiophene compared to that in the unsubstituted and alkyl-substituted thienyltins. Although the reasons for this are not entirely clear, we note that varying extents of pyridyl coordination at tin are observed in solution for this class of compounds.

Acknowledgements

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