Journal of Organometallic Chemistry, 251 (1983) 45–52
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

HETEROARYLTIN COMPOUNDS. THE CHEMISTRY AND ^{119}Sn MÖSSBAUER SPECTROSCOPY OF SOME 3-THIENYLTIN HALIDES, AND A COMPARISON WITH 2-THIENYL AND 2-FURYL ANALOGUES

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(Received January 31st, 1983)

Summary

The preparation of a range of (3-thienyl)tin halides, $(3\text{-}C_4H_3S)_nSnX_{4-n}$ ($n = 2$ or 3; X = Cl, Br or I), and some complexes with donor ligands, is described. Mössbauer spectroscopy indicates that the halides have unassociated, tetrahedral, structures. The related 2-thienyl- (and 2-furyl-) tin halides have also been prepared and characterised by Mössbauer spectroscopy, but are much less stable.

Introduction

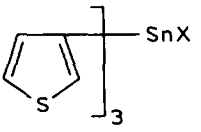
Apart from various symmetrical and unsymmetrical tetraorganostannanes [1], very little is known of the chemistry of tin compounds bearing a heteroaryl group directly linked to tin via a carbon atom of the heterocyclic ring. In view of the great variety of heterocyclic ring systems, and the established biological activity of organotin compounds of the types R_3SnX [2], together with the recent interest in complexes of diorganotin compounds, R_2SnX_2, as possible antitumour agents [3], we have commenced an exploration of the preparation, structures and properties of heteroarylorganotin compounds of the above types. In this paper we describe the chemistry of some 3-thienyltin derivatives, together with a preliminary report of related 2-thienyl and 2-furyl systems. Prior to this study, as far as we are aware, the only reported examples of compounds of these types are di(2-thienyl)tin dichloride [4], (prepared by a redistribution reaction between tetra(2-thienyl)tin and stannic chloride and characterised by conversion to related tetraorganostannanes $R_2Sn(C_4H_3S\text{-}2)_2$) and di(2-thienyl)tin diiodide [5] (prepared by a direct synthesis

0022-328X/83/$03.00

from metallic tin and 2-iodothiophen and characterised by replacement of the iodines by a series of chelating anionic ligands).

Results and discussion

The tri(3-thienyl)tin halides (I, X = Cl, Br, I) were obtained by the redistribution reactions of tetra(3-thienyl)tin (3 mol) with the appropriate stannic halide (1 mol). Whereas the reactions with stannic chloride and bromide were conducted in the absence of a solvent at ~ 150°C and were complete in a relatively short time, (ca. 1–2 h), the reaction with stannic iodide proceded more slowly. At the prevailing temperature, sublimation of stannic iodide proved to be a problem, and hence the conversion was carried out under prolonged reflux in toluene solution. The resulting triorganotin halides were purified by recrystallisation and isolated as air-stable, analytically pure solids. Of the three halides, the iodide appeared to have the lowest thermal stability, there being some evidence of decomposition on recrystallisation.



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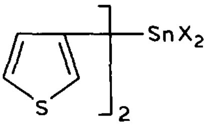


(II)

The Mössbauer spectra of the solids (recorded at 80 K) all show quadrupole-split doublets without line broadening, with parameters similar to those of the related phenyltin halides (Table 1, Fig. 1). The magnitude of the quadrupole splitting (and of the Herber ratio Δ/δ [6]) are indicative of four coordination at tin, and hence it would seem that these compounds are not associated to any significant extent in the solid state, e.g. as a result of intermolecular interactions between the thienyl sulphur of one ring system and the tin atom of another molecule. We are currently carrying out X-ray studies of the chloride and bromide of the above series in order to clarify this point. Comparison of the Mössbauer data for these compounds with that for the related phenyltin halides reveals that both the isomer shift and the quadrupole

TABLE 1

MÖSSBAUER DATA FOR TRI(3-THIENYL)TIN HALIDES AND RELATED COMPOUNDS

	Isomer shift, [a] δ (mm/s ± 0.02)	Quadrupole splitting, Δ (mm/s ± 0.02)
$(3\text{-}C_4H_3S)_3SnCl$	1.21	2.29
$(3\text{-}C_4H_3S)_3SnBr$	1.25	2.08
$(3\text{-}C_4H_3S)_3SnI$	1.29	2.02
$(3\text{-}C_4H_3S)_3SnCl \cdot Ph_3PO$	1.18	3.08
$(3\text{-}C_4H_3S)_3SnBr \cdot Ph_3PO$	1.21	3.03
Ph_3SnCl	1.37	2.45 [6]
Ph_3SnBr	1.37	2.46
Ph_3SnI	1.41	2.05 [10]

[a] Relative to $BaSnO_3$.

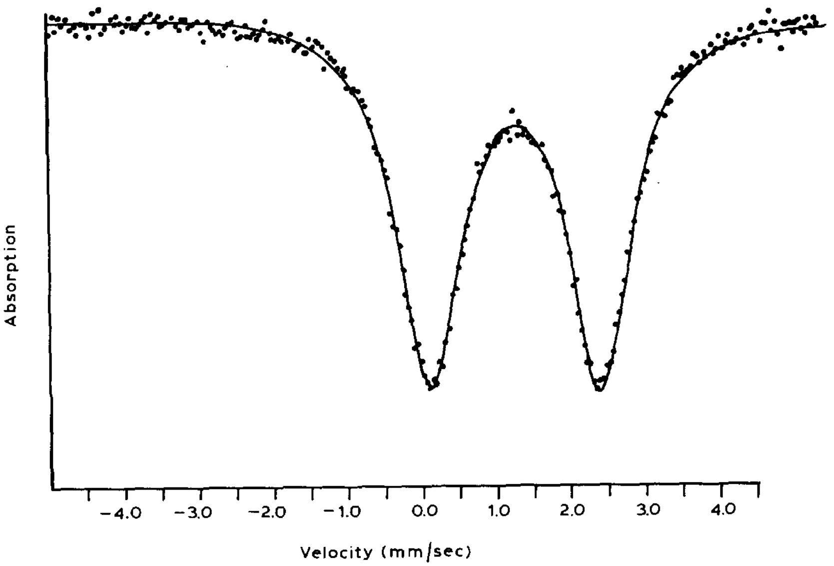


Fig. 1. Mössbauer spectrum of Tri(3-thienyl)tin chloride at 80 K.

splitting of the 3-thienyl derivatives are lower than those of the phenyl analogues. The reduction in isomer shift implies a reduction in *s*-electron density at tin, indicating that the 3-thienyl substituent is more electron-withdrawing than phenyl.

Treatment of the chloride (I, X = Cl) with an excess of *p*-tolylmagnesium bromide in ether gave the expected tri(3-thienyl)(*p*-tolyl)stannane. Both the chloride and bromide readily formed insoluble 1:1 complexes on treatment with equimolar amounts of triphenylphosphine oxide in toluene solution. Coordination of the phosphoryl oxygen is indicated by a significant reduction in the P=O infrared stretching frequency, compared with that of the free ligand, as observed for the related complex of triphenyltin chloride [7]. The Mössbauer parameters of the complexes (Table 1) are very similar to those reported for the triphenylphosphine oxide complexes of triphenyltin chloride and bromide, for which trigonal bipyramidal structures involving equatorial phenyl groups have been assumed on the basis of partial quadrupole splitting (p.q.s.) calculations [8,9].

The diorganotin dihalides (II, X = Cl or Br) have also been obtained by redistribution reactions of equimolar quantities of tetra(3-thienyl)tin with stannic halides. Both chloride and bromide were liquids which we were unable to crystallise. The related iodo derivative was obtained by direct synthesis from metallic tin and 3-iodothiophen, in the presence of pyridine hydrochloride as catalyst, according to the procedure reported by Gopinathan [5] for the synthesis of the related 2-thienyl analogue. After heating the reactants together at 150°C for several hours, the reaction mixture was distilled under reduced pressure to give a mixture of a mobile yellow oil, and a crystalline solid. A red solid, almost certainly stannic iodide, was also observed on the wall of the condenser. TLC of the distillate indicated that it consisted of two components, one of which was tetra(3-thienyl)tin and the other the diorganotin dihalide, the latter giving a characteristic blue colouration on spraying with catechol violet. The Mössbauer spectrum of this mixture showed an asymmetric

TABLE 2

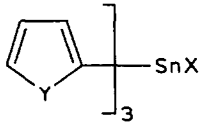
MÖSSBAUER DATA FOR DI(3-THIENYL)TIN DIHALIDES AND RELATED COMPOUNDS

	Isomer shift, δ (mm/s $\pm$ 0.02) [a]	Quadrupole splitting, Δ (mm/s $\pm$ 0.02)
$(3\text{-}C_4H_3S)_2SnCl_2$	1.23	2.55
$(3\text{-}C_4H_3S)_2SnBr_2$	1.30	2.30
$(3\text{-}C_4H_3S)_2SnI_2$	1.29	2.01
$(3\text{-}C_4H_3S)_2SnCl_2 \cdot$ bipy	0.86	2.00
$(3\text{-}C_4H_3S)_2SnBr_2 \cdot$ bipy	1.22	3.26
Ph_2SnCl_2	1.34	2.89 [10]
Ph_2SnBr_2	1.43	2.54 [12]
Ph_2SnI_2	1.51	2.38 [12]

[a] Relative to $BaSnO_3$.

doublet, consistent with the presence of a mixture of di(3-thienyl)tin diiodide and tetra(3-thienyl)tin.

The Mössbauer spectra of the diorganotin dihalides (Table 2) reveal the expected quadrupole-split doublets, and the magnitude of the quadrupole-splitting is indicative of four coordinated tin, in unassociated, discrete, molecules. As for the related tri(3-thienyl)tin halides, the values of both the isomer shift and quadrupole splitting parameters are smaller than for those of the related diphenyltin dihalides, again consistent with the greater electron-withdrawing effect of the 3-thienyl group compared to phenyl. Both the dichloride and the dibromide were characterised by formation of 1:1 complexes with 2,2′-bipyridyl on treatment of the dihalide with an equimolar amount of 2,2′-bipyridyl in toluene solution. Mössbauer data for the complexes (Table 2) are consistent with a *cis*-octahedral structure for the dichloro complex and a distorted *trans*-octahedral structure for the dibromo complex, by analogy with Mössbauer data for related complexes [11]. As expected, treatment of the di(3-thienyl)tin dichloride with *p*-tolylmagnesium bromide in ether gave di(3-thienyl)di(*p*-tolyl)tin, as a stable solid.



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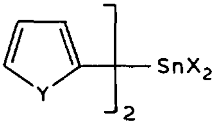

(IV)

We have also made a study of the preparation and properties of related 2-furyl- and 2-thienyl organotin compounds (III, IV, Y = O or S, X = Cl, Br or I), and now present our initial findings. The triorganotin halides were all obtained by the redistribution reactions of tetra-(2-heteroaryl)stannanes with the appropriate stannic halide. Without exception, these compounds have been found to be unstable, readily decomposing on attempted recrystallisation, or even on standing at room temperature. Traces of moisture readily cause their decomposition to stannic oxide. We have, however, obtained the Mössbauer spectra of these compounds immediately following their formation, and the parameters are presented in Table 3. All the spectra consist

TABLE 3

MÖSSBAUER DATA FOR 2-FURYL- AND 2-THIENYL-TIN HALIDES

	Isomer shift, δ (mm/s$\pm$0.02) [a]	Quadrupole splitting, Δ (mm/s$\pm$0.02)
(i) R_3SnX		
$(2\text{-}C_4H_3O)_3SnCl$	1.14	2.14
$(2\text{-}C_4H_3O)_3SnBr$	1.17	2.19
$(2\text{-}C_4H_3O)_3SnI$	1.23	1.84
$(2\text{-}C_4H_3S)_3SnCl$	1.13	1.99
$(2\text{-}C_4H_3S)_3SnBr$	1.18	1.99
$(2\text{-}C_4H_3S)_3SnI$	1.20	1.77
(ii) R_2SnX_2		
$(2\text{-}C_4H_3O)_2SnCl_2$	1.10	2.09
$(2\text{-}C_4H_3O)_2SnBr_2$	1.17	1.80
$(2\text{-}C_4H_3O)_2SnI_2$	1.34	1.42
$(2\text{-}C_4H_3S)_2SnCl_2$	1.14	2.06
$(2\text{-}C_4H_3S)_2SnBr_2$	1.21	1.96
$(2\text{-}C_4H_3S)_2SnI_2$	1.26	1.84

[a] Relative to $BaSnO_3$.

of a quadrupole-split doublet, the magnitude of the splitting indicating that the tin atom is four coordinate, as for the above 3-thienyl derivatives. Again, there is no evidence of intermolecular association leading to an increase in coordination number at tin. The related diorganotin dihalides have also been obtained by redistribution reactions, and were found to be similarly unstable. Of the dihalides, di(2-thienyl)tin diiodide was also prepared by the direct synthesis from tin metal and 2-iodothiophen, as described by Gopinathan. In our hands, distillation of the reaction mixture under reduced pressure gave, (as in the case of the 3-thienyl derivative), a mixture of tetra(2-thienyl)tin and the dihalide. The formation of tetra(2-thienyl)tin in this reaction was not reported by Gopinathan [5], and it would seem that the di(heteroaryl)tin diiodides are unstable and disproportionate on distillation. Indeed, attempts to purify other di(2-heteroaryl)tin halides by distillation under reduced pressure have also met with little success, the Mössbauer spectra of the distillates being of poorer quality than those of the initial reaction mixtures. The Mössbauer spectra of the di(2-heteroaryl)tin dihalides exhibit the expected quadrupole-split doublets, the magnitude of the splitting again being consistent with a four coordinate, unassociated structure (Table 3).

A comparison of Mössbauer isomer shifts for related compounds in Tables 1–3 indicates that the electron-withdrawing properties of the organic groups attached to tin appear to increase in the order phenyl < 3-thienyl < 2-thienyl ⩽ 2-furyl. This trend is also apparent in the case of the tetra(heteroaryl)stannanes (Table 4). In an earlier publication [13], we have considered the factors responsible for the significant decrease in the isomer shifts of tetra(2-furyl)- and -(2-thienyl)-stannanes compared to tetraphenyltin and related substituted arylstannanes, and concluded that the dominant factor is the electron-withdrawing effect of the heteroatoms. There would seem to be little tendency for such "π-excessive" heteroaromatic ring systems to be

TABLE 4

MÖSSBAUER DATA FOR TETRAHETEROARYLSTANNANES

Ar_4Sn	Isomer shift, δ (mm/s ± 0.02) [a]
Ar = 2-Furyl	1.06
Ar = 2-Thienyl	1.10
Ar = 3-Thienyl	1.16
Ar = Phenyl	1.26

[a] Relative to $BaSnO_3$.

involved in $p_\pi \rightarrow d_\pi$ interactions with the tin atom. A similar pattern is evident from studies of the reactivity of a wide range of compounds of the main Group V elements [14].

The instability of the 2-heteroarylorganotin halides is presumably due to the ease with which they undergo protodestannylation reactions, a reflection of the tendency of furan and thiophen to undergo electrophilic substitution in the 2-position with great ease [15]. The increased stability of the 3-thienyl derivatives is again consistent with this point of view.

Our studies of the chemistry of heteroarylorganotin compounds are continuing, and attempts to characterise the unstable 2-heteroarylorganotin halides by complex formation are currently in hand, and meeting with some success.

Experimental

All of the reactions described were carried out under an inert atmosphere of nitrogen or argon. Tetra(2-furyl)tin, tetra(2-thienyl)tin and tetra(3-thienyl)tin were prepared as described previously [16]. ^{119}Sn Mössbauer spectra were obtained using a constant acceleration spectrometer. A 15 mCi $Ba^{119}SnO_3$ source was used at room temperature, and the samples were sealed in perspex discs and cooled to 80 K using a continuous flow nitrogen cryostat and helium exchange gas. The Mössbauer hyperfine parameters were obtained from computer least-squares fits to the spectra, using Lorentzian line shapes. ^1H NMR spectra were recorded at 80 MHz using a Brüker WP80 SY FT spectrometer, using TMS as internal standard.

Compounds were prepared as follows:

Tri(3-thienyl)tin chloride. Tetra(3-thienyl)tin (1.0 g, 2.2×10^{-3} mol) and stannic chloride (0.08 cm^3, 7.81×10^{-4} mol) were heated together with stirring at an oil bath temperature of 120°C for 1 h. The product crystallised on cooling, and was recrystallised from hexane-toluene. m.p. 103–104.5°C. Anal. Found: C, 35.75; H, 2.15; S, 23.95. $C_{12}H_9ClS_3Sn$ calcd.: C, 35.70; H, 2.25; S, 23.85%.

Tri(3-thienyl)tin bromide. Tetra(3-thienyl)tin (0.75 g, 1.66×10^{-3} mol) and stannic bromide (0.24 g, 5.48×10^{-4} mol) were heated together with stirring at an oil bath temperature of 170°C for 1 h. On cooling, the crude product was recrystallised from hexane-toluene. m.p. 115°C. Anal. Found: C, 32.30; H, 2.15; S, 21.15. $C_{12}H_9BrS_3Sn$ calcd.: C, 32.15; H, 2.05; S, 21.45%.

Tri(3-thienyl)tin iodide. Tetra(3-thienyl)tin (1.0 g, 2.2×10^{-3} mol) and stannic iodide (0.46 g, 7.34×10^{-4} mol) were heated together in toluene (7.5 cm^3) under reflux for 3 days. The colour of the solution gradually changed from orange to yellow. TLC indicated that some unreacted tetra(3-thienyl)tin was still present. On cooling, crystals were deposited, which were filtered off and extracted with hot chloroform. Evaporation of the chloroform extracts gave a solid which was recrystallised from hexane-toluene. m.p. 127–128°C. Anal. Found: C, 29.35; H, 1.80; S, 19.90; I, 25.75. $C_{12}H_9IS_3Sn$ calcd.: C, 29.10; H, 1.85; S, 19.45; I, 25.65%.

Triphenylphosphine oxide complexes of tri(3-thienyl)tin halides. A solution of the tri(3-thienyl)tin halide in toluene was treated in the cold with stirring with an equimolar amount of triphenylphosphine oxide, also dissolved in toluene. The following complexes crystallised from the solutions:

(a) Tri(3-thienyl)tin chloride · Ph_3PO, m.p. 142–144°C. Anal. Found: C, 53.00; H, 3.60; Cl, 5.00. $C_{30}H_{24}ClOPS_3Sn$ calcd.: C, 52.85; H, 3.55; Cl, 5.20%. Infra-red (Nujol mull): 1145 and 1122 cm^{-1} (coordinated P=O),

(b) Tri(3-thienyl)tin bromide · Ph_3PO, m.p. 137–140°C. Anal. Found: C, 49.65; H, 3.35; S, 13.40. $C_{30}H_{24}BrOPS_3Sn$ calcd.: C, 49.60; H, 3.35; S, 13.25%. IR (Nujol mull): 1140 and 1119 cm^{-1} (coordinated P=O).

Tri(3-thienyl)(p-tolyl)stannane. Tri(3-thienyl)tin chloride (0.68 g, 1.69×10^{-3} mol) was dissolved in dry THF (5 cm^3) and treated with a solution of the Grignard reagent prepared from *p*-bromotoluene (0.56 g, 3.39×10^{-3} mol) and magnesium (0.1 g, 4.12×10^{-3} mol) in THF (8 cm^3). The resulting reaction mixture was stirred overnight, and then hydrolysed with aqueous ammonium chloride. The organic layer was separated, dried, and evaporated. The residue was recrystallised from isopropanol to give crystals, m.p. 119–121°C. Anal. Found: C, 49.50; H, 3.45; S, 20.95. $C_{19}H_{16}S_3Sn$ calcd.: C, 49.7; H, 3.50; S, 20.95%. ^1H NMR ($CDCl_3$): δ 7.1–7.9, (m, 13 ArH); 2.35 (s, 3H) ppm.

Di(3-thienyl)tin dichloride-2,2′-bipyridyl complex. Tetra(3-thienyl)tin (1.0 g, 2.22×10^{-3} mol) and stannic chloride (0.25 cm^3, 2.22×10^{-3} mol) were heated together with stirring at an oil bath temperature of 85°C for 1.5 h. The resulting liquid was dissolved in a mixture of chloroform and toluene (1/1 v/v), to which was added with stirring a similar solution of 2,2′-bipyridyl (0.69 g). The resulting solution rapidly deposited a white solid, which was filtered, washed with toluene and dried. m.p. 242°C. Anal. Found: C, 42.60; H, 2.80; N, 5.25. $C_{18}H_{14}Cl_2N_2S_2Sn$ calcd.: C, 42.20; H, 2.75; N, 5.45%.

Di(3-thienyl)tin dibromide-2,2′-bipyridyl complex. Tetra(3-thienyl)tin (1.0 g, 2.22×10^{-3} mol) and stannic bromide (0.97 g, 2.21×10^{-3} mol) were heated together with stirring at an oil bath temperature of 90°C for 2 h. The resulting liquid was dissolved in toluene and treated with a toluene solution of 2,2′-bipyridyl (1.38 g) to give the complex, m.p. 253°C (decomp.). Anal. Found: C, 35.65; H, 2.30; N, 4.45. $C_{18}H_{14}Br_2N_2S_2Sn$ calcd.: C, 35.95; H, 2.35; N, 4.65%.

Di(3-thienyl)tin diiodide. A mixture of 3-iodothiophen, (10 g, 4.76×10^{-2} mol), alkali-washed, powdered tin (2.82 g, 2.38×10^{-2} mol) and pyridine hydrochloride (0.06 g) was heated together under nitrogen with stirring overnight at an oil bath temperature of 150°C. The resulting deep yellow liquid was distilled under reduced pressure to give a fraction, b.p. 200–220°C at 0.05 mmHg, which crystallised on cooling. TLC analysis indicated the presence of both tetra(3-thienyl)tin and a diorganotin dihalide. The Mössbauer spectrum of the mixture was also indicative of the presence of tetra(3-thienyl)tin, and the parameters for di(3-thienyl)tin diiodide were obtained from computer fits to the combined data.

Di(3-thienyl)(di-p-tolyl)stannane. Di(3-thienyl)tin dichloride (from the reaction of tetra(3-thienyl)tin (1.0 g, 2.22 × 10^{-3} mol) and stannic chloride (0.25 cm^3, 2.17 × 10^{-3} mol)), dissolved in THF (8 cm^3) was treated with the Grignard reagent derived from *p*-bromotoluene (1.48 g, 8.65 × 10^{-3} mol) and magnesium (0.25 g, 1.03 × 10^{-2} mol) in THF (10 cm^3), and the resulting mixture stirred overnight. Treatment of the reaction mixture with aqueous ammonium chloride solution gave a white solid, which was dissolved by the addition of chloroform. Separation of the organic layer, followed by drying over anhydrous magnesium sulphate, and evaporation gave the stannane, m.p. 148–150°C, ex. isopropanol. Anal.: C, 56.3; H, 4.35; S, 13.85. $C_{22}H_{20}S_2Sn$ calcd.: C, 56.55; H, 4.30; S, 13.70%. ^1H NMR ($CDCl_3$): δ 7.1–7.9, (m, 14 Ar H); 2.35, (s, 6H) ppm.

Preparation of 2-thienyl- and 2-furyl-tin halides. These were prepared by the redistribution reactions between the tetra(2-heteroaryl)stannane and the appropriate stannic halide, under conditions similar to those used as described above for the preparation of the (3-thienyl)tin halides. Di(2-thienyl)tin diiodide was also prepared as described by Gopinathan [5]. Immediately following their preparation, the compounds were sealed in perspex discs, and the Mössbauer spectra recorded at 80 K. Attempts to purify these compounds by recrystallisation were unsuccessful.

Acknowledgements

The International Tin Research Council, London, is thanked for permission to publish this paper. D. Jane Derbyshire thanks SERC and the International Tin Research Institute for a CASE studentship.

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