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Organotin Biocides

XIII *. *C*-Triorganostannylimidazoles, -benzoxazoles and -benzothiazoles

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Abstract

The synthesis, spectroscopic characterisation, and reactivity of a series of triorganotin imidazoles, benzothiazoles and benzoxazoles $R_3Sn(Het)$ (R = Me, Bu, Ph) are described. The structure of 2-(triphenylstannyl)benzothiazole has been determined by crystallographic methods. Space group: Triclinic, $P\bar{1}$; a 9.501(1), b 10.172(2), c 13.231(2) Å, α 67.93(2) Å, β 70.46(1), γ 69.71(1)°, U 1082.8 Å^3, $F(000) = 484$, μ(Mo-K_α) 11.74 cm^{-1}, $R = 0.0719$ for 2264 reflections with $I > 3\sigma I$. The geometry at the tin is tetrahedral. Bond angles at tin are used to discuss the reactivity and Mössbauer spectra of these species.

Introduction

Despite many attempts to induce a synergistic enhancement in the biocidal activity of triorganotin compounds by the incorporation of an ancilliary ligand with complementary properties, little impact has been made in increasing the performance of these species over that of the simple, commercially available organotins e.g. $Ph_3SnO_2CCH_3$, Cy_3SnOH or $(Bu_3Sn)_2O$ [1]. The non-hydrocarbon ligand in R_3SnX does not generally influence the biocidal activity of the molecule directly, but does have a role in determining the stereochemistry about the metal which in some cases e.g. when chelating ligands are present, can diminish activity [2]. In general though, the biological performance of triorganotin compounds is independent of X and thus it is almost certain that this ligand is hydrolysed from tin at an early stage in its environmental cycle. The approach which we have recently suggested [3] and which we detail in this the first of a series of papers, is to combine

* This paper is dedicated to the late Prof. J.J. Zuckerman in recognition of his important contributions to organometallic chemistry.

the active ligand into the R_3Sn part of the molecule, reasoning that the Sn–C bond will outlive Sn–O,N,S bonds under aqueous conditions. Thus, compounds of generic form R_2R^1SnX, where R is an organic group commonly associated with active organotins i.e. Bu, Ph, Cy, R^1 the ligand of complementary activity and X is a synthetically convenient ligand e.g. halide, carboxylate become the species of interest.

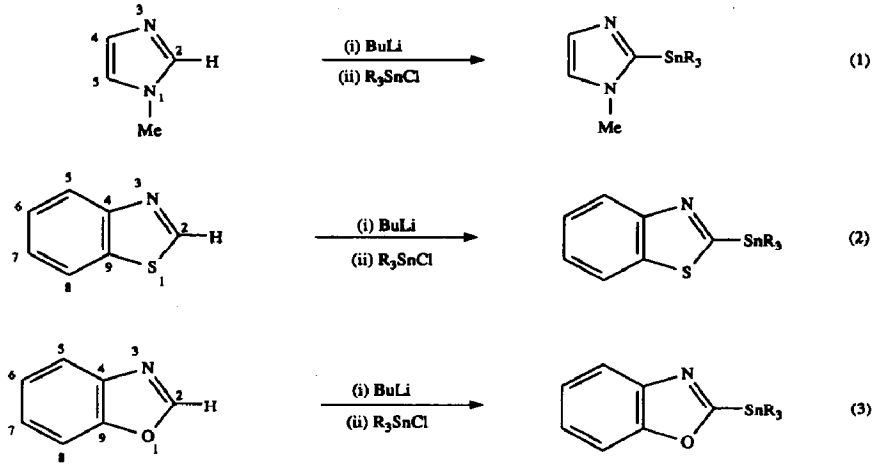
Imidazoles, oxazoles and thiazoles are well known for their biological properties [4], and we have previously reported the synthesis and biocidal evaluation of a series of triorganotin derivatives of 2-mercapto-benzimidazoles, -oxazoles and -thiazoles [5]. The synthesis of related C-triorganostannyl derivatives of *N*-methylimidazole (HN–MeI), benzothiazole (HBtz) and benzoxazole (HBox) which we report herein complements this work and expands previous reports of these systems [6–10] to include full spectral characterisation and reactivity studies.

Results and discussion

2-Triorganostannyl heterocycles (1-methylimidazole, benzothiazole and benzoxazole) have been synthesised by the reaction of 2-lithio heterocycles with triorganotin chlorides (eq. 1–3).

This follows the route most commonly used by other authors [6–8,10] although 2-(alkylsulfonyl)benzothiazole can also be reduced with Bu_3SnH to yield 2-(tributylstannyl)benzothiazole [9]. The products are sensitive to atmospheric moisture, unusually so for tetraorganotins, and only the triphenyltin compounds are stable for any length of time in the open air.

All of the compounds studied are unambiguously characterised by their spectral properties. The mass spectra contain parent ions in all cases, and follow the well established trend for organotins of being dominated by even-electron ions (Table 1) [11]. ^{1}H NMR data specify the site of metallation as C(2) both by the disappearance of resonances due to the C(2) proton in the parent heterocycles (δ 7.41, 8.94, 7.46 for HN-MeI, HBtz and HBox respectively) and, in the case of 1-methylimidazole, by the retention of signals due to the C(4,5) protons as doublets in the stannylated product. ^1J(Sn–C) and ^2J(Sn–C–H) couplings can be used to confirm the tetra-



Formule 1

Table 1

70 eV mass spectral data [a]

Compound	$R_3SnL^{+\cdot}$	R_2SnL^+	$RSnL^{+\cdot}$	SnL^+	R_3Sn^+	$R_2Sn^{+\cdot}$	RSn^+
Me_3Sn(N–MeI)	246(33)	231(88)	216(9)	201(100)	165(38)	150(18)	135(43)
Bu_3Sn(N–MeI)	372(31)	314(30)	–	201(17)	291(98)	234(40)	177(29)
Ph_3Sn(N–MeI)	432(7)	355(17)	278(27)	201(19)	351(19)	–	197(60)
Me_3SnBtz	299(42)	284(55)	269(8)	254(10)	165(36)	150(14)	135(88)
Bu_3SnBtz	426(58)	368(36)	311(9)	254(14)	291(28)	234(10)	177(15)
Ph_3SnBtz	485(68)	408(49)	331(19)	254(12)	351(66)	–	197(97)

[a] Relative intensities in parentheses.

hedral coordination at the metal using the equations developed by Lockhart, Manders and Zuckerman [12,13] for methyltin compounds (eq. 4, 5) or the modified version of eq. 5 for butyltin compounds of Holeček et al. (eq. 6) [14], where

$$\theta = 0.0161[^2J]^2 - 1.32[^2J] + 133.4 \quad (4)$$

$$[^1J] = 11.4\theta - 875 \quad (5)$$

$$[^1J] = (9.99 \pm 0.73)\theta - (746 \pm 100) \quad (6)$$

C–Sn–C(θ) is the angle between the carbon atoms of the alkyl groups about the metal. Evaluation of these equations for the four trialkyltin compounds studied gives internally consistent results (Table 2), the calculated angles lying in the range 108.0–111.1°. These findings are entirely in keeping with a tetrahedral geometry about tin.

Similarly, ^{119}Sn chemical shifts are at considerably lower field than occur in tetraorganotins which show enhanced coordination at tin e.g. bis[3-(2-pyridyl)-2-thienyl-*C*,*N*]diphenyltin, $\delta(^{119}Sn)$ −245.5 ppm [15], although examples of this latter class are remarkably scarce.

With the exception of Ph_3Sn(N–MeI) all the compounds studied exhibit doublet Mössbauer spectra reflecting the polarity imbalance in the differing Sn–C bonds (Table 3). From the magnitude of the measured quadrupole splittings (ΔE) the relative polarities of the Sn–R bond can be estimated as: R = Me, Bu < Ph, N-MeI < Btz ~ Box.

Table 2

Selected ^{1}H, ^{13}C, ^{119}Sn NMR data for triorganotin heterocycles

Compound	$^1J(^{119}Sn–^{13}C)$ [a]	$^2J(^{119}Sn–C–^1H)$ [a]	C–Sn–C°	$\delta(^{119}Sn)$ [b,c]
Me_3Sn(N-MeI)	359.1	57.6	110.8 [d], 108.2 [e]	−48.2
Bu_3Sn(N-MeI)	362.3		110.9 [f], –	−66.7
Ph_3Sn(N-MeI)				−175.7
Me_3SnBtz	356.2	56.6	110.3 [d], 108.0 [e]	−28.6
Bu_3SnBtz	364.2		111.1 [f], –	−41.9
Ph_3SnBtz				−165.9
Ph_3SnBox				−174.3

[a] Hz. [b] ppm with respect to Me_4Sn. [c] $CDCl_3$ solutions. [d] Using eq. 5. [e] Using eq. 4. [f] Using eq. 6.

Table 3

^{119}Sn Mössbauer data (78 K) for triorganotin heterocycles

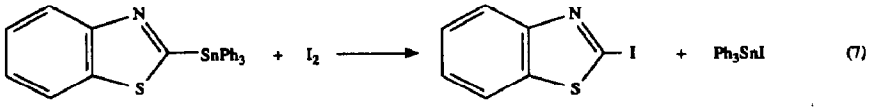
Compound	δ(mm s^{-1}) [a]	ΔE(mm s^{-1})	Γ(mm s^{-1}) [b]
Me_3Sn(N–MeI)	1.19	0.75	0.88, 0.87
Bu_3Sn(N–MeI)	1.28	0.77	0.98, 0.76
Ph_3Sn(N–MeI)	1.22	0.46	0.87, 0.80
Me_3SnBtz	1.28	1.13	0.99, 0.88
Bu_3SnBtz	1.32	1.20	0.94, 0.97
Ph_3SnBtz	1.25	0.81	1.02, 1.08
Ph_3SnBox	1.19	0.80	0.90, 0.90

[a] $\pm$0.02 mm s^{-1}. [b] Full width at half height.

The trends in isomer shifts for this series can also be used to corroborate this ordering, although the rationale is more complex than usually applied. The isomer shift reflects the *s*-electron density at tin which in turn depends on the electronegativity of the ligands bonded to the metal. Thus, in R_3SnX for common X, triphenyltin compounds show lower isomer shifts than trialkyltin species, the former having lower *s*-electron density at tin due to the greater electron-withdrawing power (electronegativity) of Ph over alkyl. It might therefore be anticipated that for common R the isomer shift would decrease for increasing electronegativity of X i.e. R_3Sn(Btz) would have lower isomer shifts than R_3Sn(N–MeI). In fact, the opposite occurs. We rationalise this observation as follows. The electrons at tin rehybridise according to the scheme of Bent [16] to produce sp^3 orbitals rich in *p*-character for bonding to X (R^1 in the current case) and concommitantly higher in *s*-character for bonding to R. It is this rehybridisation which generates a measurable electric field gradient and hence quadrupole splitting at tin. In doing so, the *s*-density is concentrated in the less polar Sn–C bonds which, being more covalent, afford tin a greater share of the electron density. Thus, while the magnitude of the isomer shift still follows the order Bu > Me > Ph for the R_3Sn part of the molecule it simultaneously increases as the electronegativity of X (R^1) increases. A similar trend has been reported though not commented upon for the series R_3SnR^1 (R = Me, Ph; R^1 = Ph, py, pyNO) for which the electronegativity series proposed in Me < Ph < py ~ pyNO although, for example, the isomer shift of Me_3SnPh is less than that for Me_3Snpy, $Me_3SnpyNO$ [17]. However, in both the series described above the variation in isomer shifts is close to the stated experimental error so the significance of these trends should not be overemphasised. Furthermore, the logic we have applied above would explain many of the so-called "anomalous" trends in organotin isomer shifts which do not follow the generally held effect of ligand electronegativities e.g. Ph_3SnBr 1.33 mm s^{-1}; Ph_2SnBr_2 1.43 mm s^{-1} [18]. On a cautious note, however, it must be remembered that both electronegativity of ligands and the coordination number of the Mössbauer atom will influence the isomer shift, and the effect of the former can only be evaluated with confidence if the latter is held constant. For the title compounds, which are all unambiguously tetrahedral at tin, this is so, but in many cases, for example Me_3SnX (X = F, Cl, Br, I), the effects of largely unquantifiable changes in intermolecular interactions cannot be ignored.

In order to generate triorganotin compounds from the tetraorganotins described above we have investigated both halogen cleavage and redistribution reactions of

the R_3SnR^1 compounds. With either Br_2 or I_2 the heterocyclic group is cleaved from tin in preference to either Me, Bu or Ph. Typically:



(7)

The ease with which the Sn–C(heterocycle) bond is cleaved is also reflected in the aerobic sensitivity of the tetraorganotins, which decompose to an organotin hydroxide (oxide) and the parent heterocycle, for example eq. 8.

$$Me_3Sn(N\text{–}MeI) \rightarrow Me_3SnOH + HN\text{–}MeI \quad (8)$$

In general, the stability of compounds studied follows the sequences R = Ph > Bu > Me and benzothiazole ~ benzoxazole > *N*-methylimidazole.

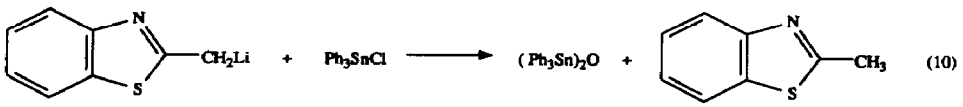
The lability of the heterocycle can, however, be utilised in redistribution reactions with other organotin halides. For example, when Ph_3SnBtz and Ph_2SnCl_2 are heated together as neat materials for 2 h at 110 °C, ^{119}Sn NMR analysis of the resulting mixture (saturated solution, $CDCl_3$) shows no resonances due to starting materials. Instead, a resonance at −46.9 ppm assigned to Ph_3SnCl appears along with a new resonance at −310.0 ppm which is probably due to the mixed triorganotin chloride.

$$Ph_3SnBtz + Ph_2SnCl_2 \xrightarrow{110\,^\circ C/2\,h} Ph_3SnCl + Ph_2Sn(Btz)Cl \quad (9)$$

We have been unable to separate the mixed triorganotin chloride from the reaction in pure form, but Ph_3SnCl has been unambiguously confirmed as one reaction product. In the case of a parallel reaction using $Bu_3Sn(N\text{–}MeI)$ the final reaction mixture is extremely moisture sensitive, behavior that would be expected for $Bu_2(N\text{–}MeI)SnCl$ extrapolated from that of the less Lewis acidic $Bu_3Sn(N\text{–}MeI)$.

Other workers have reported the cleavage of the Sn–heterocycle bond by acid chlorides as a means of synthesising new 2-ketoheterocycles [19].

In an effort to redirect the site of halogen cleavage (eq. 7) we have attempted to synthesise compounds of type $Ph_3Sn(CH_2)_n(Het)$ ($n = 1, 2$). From the chemical point of view the heterocycle becomes part of an alkyl group bonded to tin which may direct the cleavage preferrentially to the Sn–Ph bond. From the biocidal standpoint, when $n = 2$ the molecules now contain a potential ethylene precursor, the latter being a well known plant growth hormone [20]. When 2-(lithiomethyl)benzothiazole and Ph_3SnCl are reacted (eq. 10) the only identifiable products are $(Ph_3Sn)_2O$ and 2-methylbenzothiazole.

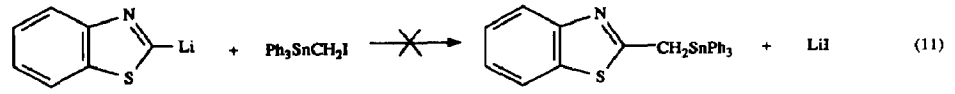


(10)

While the latter may be unreacted starting material the fate of the tin suggests that the desired product is formed but is hydrolysed during the experimental work-up (re-crystallisation) which was carried out under aerobic conditions. That 2-(triphenylstannylmethyl)benzothiazole is extremely moisture sensitive is perhaps not surprising since the probable leaving anion, $BtzCH_2^-$, has a large number of

resonance structures and is related to benzothiazole in the same way as benzyl and phenyl moieties.

More complex reactions take place when the target molecules are approached via C–C bond formation (eq. 11, 12).



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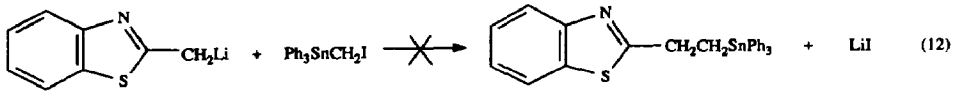
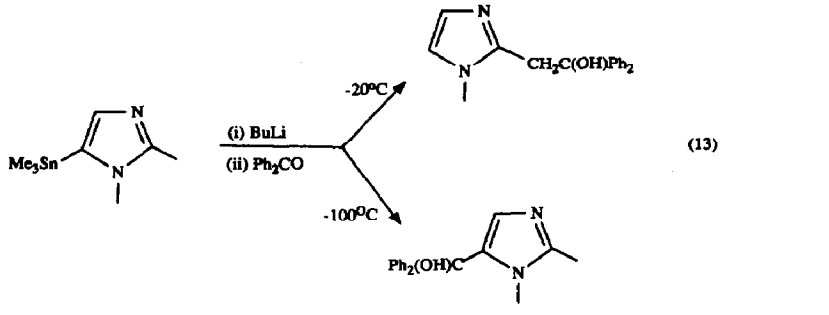


(12)

Both reactions generate a complex mixture of products according to analysis by TLC, from which we have only been able to identify $Ph_3SnSnPh_3$ and 1,2-dibenzothiazolylethane with certainty. In each case, the lithiated reagent is produced at $-78\,^{\circ}C$ and 2-lithiobenzothiazole is reported to be unstable above $-35\,^{\circ}C$ [21]. However, 2-(lithiomethyl)benzothiazole at least is known to have a low nucleophilicity towards halogenated carbon [22] and it is plausible that in both cases no reaction occurs until the mixture is warmed towards room temperature, whereupon the instability of the reagents becomes a factor. We tentatively suggest the types of scrambling reactions shown in Scheme 1 to account for the reaction products isolated.

There is literature precedent for the temperature dependence of reactions of this type, for example eq. 13 [8]. An alternative approach to the synthesis of the target species is the hydrostannylation of suitable vinyl- or allylsubstituted heterocycles (eq. 14).



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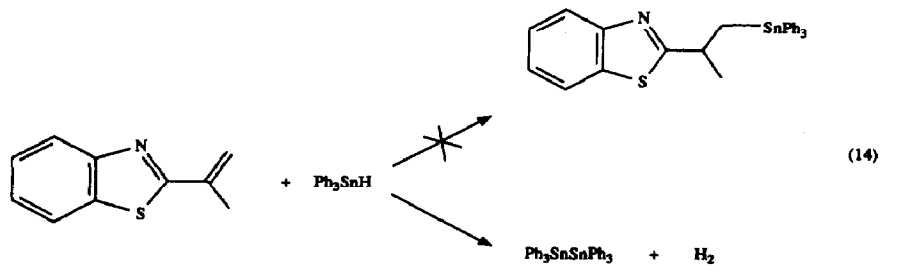

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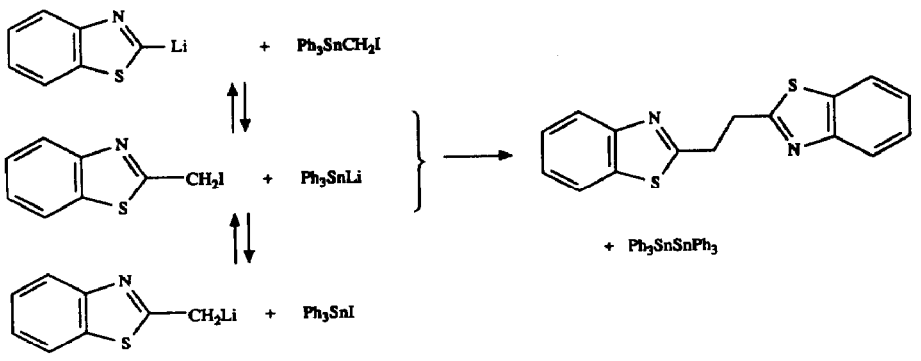

Scheme 1

However in this case, and in similar reactions involving triphenyltin hydride with *N*-allylbenzimidazole, *N*-allylimidazole, and *N*-vinylimidazole, the heterocycle acts as a base and simply promotes the coupling of Ph_3Sn units to $Ph_3SnSnPh_3$ with loss of H_2 in a reaction sequence that is well precedented in organotin chemistry [23]. The competition between hydrostannylation of the double bond and formation of di-tin species is controlled, in part, by the basic strength of the substrate. In future reports in this series we will detail more successful applications of this approach to the synthesis of *C*-organostannyl heterocycles.

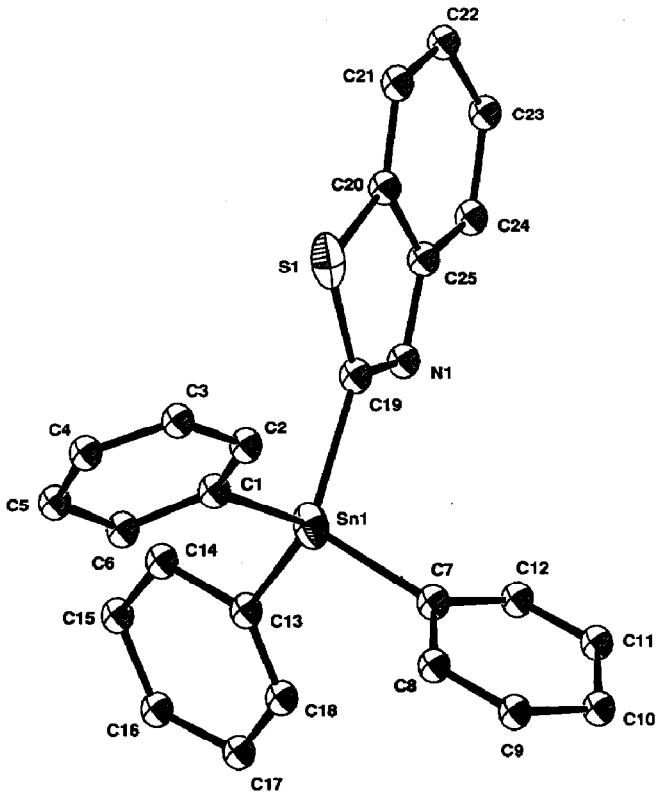

Fig. 1. The asymmetric unit of 2-(triphenylstannyl)benzothiazole showing atomic labelling.

The structure of 2-(triphenylstannyl)benzothiazole

The structure of 2-(triphenylstannyl)benzothiazole, determined crystallographically, is shown in Fig. 1 with the expected tetrahedral geometry about the metal. We were interested in rationalising the origins of the observed Mössbauer quadrupole splittings and the regiospecificity of the halogen cleavage reactions by comparison of the respective Sn–C(phenyl) and Sn–C(benzothiazole) bond parameters. However, the Sn–C bonds are equal in length within the error of the experiment. More illuminating are the trends in bond angles, in which those angles involving the heterocycle carbon [C(19)] are always smaller than those involving only the phenyl groups, although some overlap of the two ranges occurs using the 3σ criterion. This observation is in keeping with the proposed enhanced electronegativity of the heterocycle and concomitant rehybridisation of bonding electrons on tin to enrich the *p*-character of the Sn–C(benzothiazole) bonds.

Conclusions

Air sensitive 2-triorganostannyl-1-methylimidazoles, benzothiazoles and benzoxazoles have been synthesised. The heterocyclic group is easily cleaved from the metal by moisture and by halogens, or in redistribution reactions with organotin halides.

Experimental

Spectra were recorded on the following instruments: V.G. 70-70E (mass spectra), JEOL GX270 (^{1}H, ^{13}C NMR), JEOL GX400 (^{119}Sn NMR). Details of our Mössbauer spectrometer and related procedures are given elsewhere [24]. NMR spectra were recorded as saturated $CDCl_3$ solutions at room temperature. Spectral assignments are referenced to the numbering schemes of equations 1–3. Analyses for C, H and N were carried out by conventional means, but no rigorous attempts were made to maintain totally anaerobic experimental conditions.

2-Methylimidazole, benzothiazole, 2-methylbenzothiazole, benzoxazole and *N*-vinylimidazole were of commercial origin (Aldrich) and were purified by distillation prior to use. *N*-allylimidazole and *N*-allylbenzothiazole were prepared by refluxing the parent heterocycle with NaOH followed by addition of allyl bromide. Products were purified by distillation. Triphenylstannylmethyliodide was prepared by literature methods [25]. All reactions were carried out under a nitrogen atmosphere using pre-dried solvents.

Synthesis of 2-(trimethylstannyl)-1-methylimidazole

To a solution of 1-methylimidazole (3.28 g, 40 mmol) in freshly distilled THF (50 ml), cooled to $-10\,^\circ$C, was added a solution of n-butyllithium (40 mmol) in hexane (25 ml) over a period of 1 h. The solution was maintained at $-10\,^\circ$C and stirred for a further hour. Subsequently, a solution of trimethyltin chloride (40 mmol) in diethyl ether (50 ml) was added via syringe, also over a 1 h period, and the mixture allowed to warm to ambient temperature. The solution was filtered using a conventional Schlenk apparatus, the solvents removed under reduced pressure and the product isolated by distillation. Yield 10.79 g 73%, b.p. 84–86 °C/0.5 mm Hg (lit: [6] 109 °C/5.0 mm Hg). Anal., Found: C, 33.3; H, 5.5; N, 10.8. $C_7H_{14}N_2Sn$ calcd.:

C, 34.3; H, 5.8; N, 11.4%. ^{1}H NMR: 0.14 (s, 9H, Me_3Sn), 3.41 (s, 3H, NMe), 6.72 (d, 1H, C^5H), 6.89 (d, 1H, C^4H). ^{13}C NMR: 152.8 (C^2), 129.9 (C^4), 121.6 (C^5), 33.6 (NCH_3), −9.4 (CH_3Sn).

Other compounds prepared by a similar route are:

2-(Tributylstannyl)-1-methylimidazole. Yield 71%, b.p. 145–146 °C/0.05 mm Hg. Anal: Found: C, 49.2; H, 8.1; N, 6.1. $C_{16}H_{32}N_2Sn$ calcd.: C, 51.8; H, 8.7; N, 7.5%. ^{1}H NMR: 0.6–0.7 (m, 27H, Bu_3Sn), 3.60 (s, 3H, NMe), 6.92 (d, 1H, C^5H), 7.12 (d, 1H, C^4H). ^{13}C NMR: 154.0 (C^2), 130.7 (C^4), 121.9 (C^5), 34.3 (NCH_3), 10.1, 27.0, 28.8, 13.4 ($SnCH_2CH_2CH_2CH_3$, respectively).

2-(Triphenylstannyl)-1-methylimidazole. Yield 62%, m.p. 89–90 °C. Anal.: Found: C, 60.6; H, 4.6; N, 6.0. $C_{22}H_{20}N_2Sn$ calcd.: C, 61.2; H, 4.7; N, 6.5%. ^{1}H NMR: 3.51 (s, 3H, NMe), 6.77 (d, 1H, C^5H), 6.99 (d, 1H, C^4H), 7.2–7.8 (m, 15H, Ph_3Sn). ^{13}C NMR: 150.9 (C^2), 129.2 (C^4), 121.9 (C^5), 33.9 (NCH_3), 140.9, 136.7, 128.8, 129.7 (C_6H_5Sn, *i,o,m,p* respectively).

2-(Trimethylstannyl)benzothiazole. Preparation of 2-lithiobenzothiazole was performed at −78 °C. Yield 64%, b.p. 96–98 °C/0.8 mm (Lit: [6] 74 °C/0.1 mmHg). Anal.: Found: C, 41.6; H, 4.4; N, 5.4. $C_{10}H_{13}NSSn$ calcd.: C, 40.3; H, 4.4; N, 4.5%. ^{1}H NMR: 0.63 (s, 9H, Me_3Sn), 7.25–8.3 (m, 4H, C^5H–C^8H). ^{13}C NMR: 155.6 (C^2), 149.7 (C^4), 136.2 (C^9), 125.4 (C^6), 124.3 (C^7), 123.1 (C^5), 121.2 (C^8), −9.5 (CH_3Sn).

2-(Tributylstannyl)benzothiazole. Yield 80%, b.p. 179 °C/1.0 mm Hg. Anal.: Found: C, 52.5; H, 7.3; N, 3.3. $C_{19}H_{31}NSSn$ calcd.: C, 53.8; H, 7.4; N, 2.9%. ^{1}H NMR: 0.73–1.57 (m, 27H, Bu_3Sn), 7.20–7.33 (m, 2H, C^6H, C^7H), 7.81 (d, 1H, C^8H), 8.06 (d, 1H, C^5H). ^{13}C NMR: 155.9 (C^2), 153.5 (C^4), 136.1 (C^9), 125.1 (C^6), 124.1 (C^7), 122.6 (C^5), 121.6 (C^8), 11.0, 27.0, 28.7, 13.5 ($SnCH_2CH_2CH_2CH_3$ respectively).

2-(Triphenylstannyl)benzothiazole. Yield 81%, m.p. 118.5 °C. Anal.: Found: C, 62.2; H, 3.9; N, 2.7. $C_{25}H_{19}NSSn$ calcd.: C, 62.0; H, 4.0; N, 2.9%. ^{1}H NMR: 7.36–7.51 (m, 17H, Ph_3Sn, C^6H, C^7H), 7.95 (d, 1H, C^8H), 8.25 (d, 1H, C^5H). ^{13}C NMR: 156.1 (C^2), 140.5 (C^4), 136.4 (C^9), 125.6 (C^6), 124.9 (C^7), 123.4 (C^5), 121.4 (C^8), 139.5, 137.1, 128.8, 129.7 (C_6H_5Sn, *i,o,m,p* respectively).

2-(Triphenylstannyl)benzoxazole. Preparation of 2-lithiobenzoxazole was carried out at −110 °C. Yield 78%, m.p. 87–88 °C. Anal.: Found: C, 63.9; H, 4.0; N, 2.8. $C_{25}H_{19}OSSn$ calcd.: C, 64.1; H, 4.1; N, 3.0%. ^{1}H NMR: 7.05–7.75 (m, 19H, Ph_3Sn, C^5H–C^8H). ^{13}C NMR: 172.7 (C^2), 152.3 (C^9), 137.4 (C^4), 125.0 (C^6), 123.8 (C^7), 120.2 (C^5), 110.6 (C^8), 137.0, 136.7, 128.9, 129.8 (C_6H_5Sn, *i,o,m,p* respectively).

Iondination of 2-(triphenylstannyl)benzothiazole

Iodine (0.19 g, 0.7 mmol) in CCl_4 (50 ml) was added over a period of 1 h at room temperature to a solution of 2-(triphenylstannyl)benzothiazole (0.36 g, 0.7 mmol) in petroleum ether. The solution was stirred for a further 1 hour during which time the colouration due to iodine had disappeared. The solvents were removed under reduced pressure and the resulting oil redissolved in hot 80–100 °C petroleum ether, filtered and allowed to cool. White prisms, identified as Ph_3SnI (m.p. 120–121 °C, lit. [26]: 121 °C). Anal.: Found: C, 45.0; H, 3.3. $C_{18}H_{15}SnI$ calcd.: C, 45.3; H, 3.2%, and brown needles proving to be 2-iodobenzothiazole (m.p. 78–80 °C; Anal.: C, 31.8; H, 1.49; N, 5.3. C_7H_4INS calc.: C, 32.2; H, 1.54; N, 5.4%; *m/e* 134, Btz; 127 I), co-crystallised.

Table 4

Final atomic coordinates for 2-(triphenylstannyl)benzothiazole

Atom	x	y	z	U_{iso} or U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Sn1	0.38815(11)	0.24743(12)	0.33034(8)	0.044(1)	0.072(1)	0.052(1)	−0.022(1)	−0.014(1)	−0.019(1)
S1	0.38624(5)	0.58348(5)	0.13499(3)	0.076(3)	0.086(3)	0.071(3)	−0.011(2)	−0.025(2)	−0.040(2)
N1	0.1708(13)	0.4615(13)	0.1771(9)	0.061(3)					
C1	0.5654(16)	0.3054(16)	0.3589(11)	0.055(4)					
C2	0.6974(17)	0.3219(17)	0.2767(13)	0.069(4)					
C3	0.8184(20)	0.3537(20)	0.2972(15)	0.083(5)					
C4	0.8057(20)	0.3567(19)	0.4016(14)	0.081(5)					
C5	0.6795(20)	0.3294(20)	0.4857(15)	0.085(5)					
C6	0.5578(17)	0.3038(17)	0.4652(12)	0.063(4)					
C7	0.4645(15)	0.0687(15)	0.2607(11)	0.051(3)					
C8	0.5982(17)	−0.0339(17)	0.2752(12)	0.063(4)					
C9	0.6472(19)	−0.1484(19)	0.2289(13)	0.075(4)					
C10	0.5596(20)	−0.1615(22)	0.1698(15)	0.088(5)					
C11	0.4275(21)	−0.0553(21)	0.1536(15)	0.091(5)					
C12	0.3764(19)	0.0618(19)	0.1990(13)	0.074(4)					
C13	0.2070(14)	0.2136(15)	0.4778(10)	0.048(3)					
C14	0.1378(16)	0.3182(17)	0.5336(12)	0.060(4)					
C15	0.0215(17)	0.2939(18)	0.6305(13)	0.068(4)					
C16	−0.0284(18)	0.1728(18)	0.6692(13)	0.071(4)					
C17	0.0377(19)	0.0637(20)	0.6145(14)	0.081(5)					
C18	0.1562(17)	0.0873(17)	0.5173(12)	0.063(4)					
C19	0.2959(15)	0.4389(15)	0.2056(1)	0.050(3)					
C20	0.2441(16)	0.6760(17)	0.0621(12)	0.060(4)					
C21	0.2248(20)	0.8122(19)	−0.0159(14)	0.079(5)					
C22	0.978(21)	0.8650(23)	−0.0597(16)	0.091(5)					
C23	−0.0045(20)	0.7832(20)	−0.0294(14)	0.080(5)					
C24	0.0101(20)	0.6432(20)	0.0499(14)	0.080(5)					
C25	0.1376(16)	0.5876(16)	0.0969(11)	0.056(4)					

In a similar experiment using bromine in placed of iodine, crystalline Ph_3SnBr (0.69 g, 80%; m.p. 120°C, lit. [26]: 121–122°C); Anal.: Found: C, 49.8; H, 3.3. $C_{18}H_{15}SnBr$ calcd.: C, 50.3; H, 3.5%) was separated from a brown oily residue whose ^1H and ^{13}C NMR spectra show only resonances due to a benzothiazole unit and is presumably 2-bromobenzothiazole.

Attempted synthesis of 2-(triphenylstannylmethyl)benzothiazole using 2-(lithiomethyl) benzothiazole

To a stirred solution of 2-methylbenzothiazole (2.98 g, 20 mmol) in diethyl ether at −78°C was added a solution of n-butyllithium (20 mmol) in hexane (10 ml). The mixture was stirred for 30 min during which time a yellow colouration had developed. Triphenyltin chloride (7.70 g, 20 mmol) in THF (50 ml) was added dropwise over a 10 min period with no change in the colour of the solution. The solution was warmed to room temperature, during which time a dark orange colouration had developed, before the solvents were removed under reduced pressure. Petroleum ether (40 ml) was then added and the solution filtered on a Schlenk apparatus to remove precipitated LiCl. TLC analysis (silica plates, 1/1 ethyl acetate/80–100 petroleum ether) of this solution showed it to be a complex mixture comprising of primarily 2-methylbenzothiazole and bis(triphenyltin)oxide. The tin containing product was isolated by crystallisation under aerobic conditions (4.21 g, 59%; m.p. 118°, lit [26]: 118°C).

Attempted synthesis of 2-(triphenylstannylmethyl)benzothiazole using triphenylstannylmethyliodide

A solution of 2-lithiobenzothiazole (2.58 mmol) in diethyl ether was prepared at −78°C from n-butyllithium and benzothiazole following the methods described previously. To this solution was added a solution of triphenylstannylmethyliodide (1.22 g, 2.58 mmol) in THF (5 ml) over a 10 min period. The solution was stirred at −78°C for 1 h with no visible reaction occuring before warming to room temperature, whereupon the solution turned dark red. The solvents were removed under reduced pressure and the residue redisolved in 1/3 cyclohexane/ethyl acetate (60 ml). The resulting solution was washed with water (3 × 5 ml), separated and the organic layer dried over $MgSO_4$. After solvent removal, $Ph_3SnSnPh_3$ (0.91 g, 50%; m.p. 235°C, lit. [26] 237°C) could be crystallised from petroleum ether and subsequently 1,2-dibenzothiazolylethane (0.25 g, 65%; m.p. 134–135°C, lit. [27]: 137.5–138°C) by crystallisation from ethyl acetate.

Attempted synthesis of 1-(triphenylstannyl)-2-benzothiazolylethane

Following a similar procedure to that described above but using 2-(lithiomethyl)benzothiazole (13 mmol) and triphenylstannylmethyliodide (12.5 mmol) in THF (50 ml) yielded $Ph_3SnSnPh_3$ (3.17 g, 72%) identified by spectroscopic comparison with an authentic sample. TLC analysis of the final reaction solution showed the presence of 1,2-dibenzothiazolylethane as the other major product although no attempt was made to isolate this material.

Attempted synthesis of 1-(triphenylstannyl)-2-benzothiazolylpropane

Triphenyltin hydride (3.50 g, 10 mmol) and 2-benzothiazolylpropene (1.75 g, 10 mmol) were stirred together under nitrogen at 80°C for 5 h during which time a gas

Table 5

Selected bond distances (pm) and angles (°) for 2-(triphenylstannyl)benzothiazole

Sn1–Cl	214(1)	C1–Sn1–C7	115.8(5)
Sn1–C7	214(1)	C1–Sn1–C13	111.0(5)
Sn1–C13	214(1)	C7–Sn1–C13	111.1(5)
Sn1–C19	216(1)		
		C19–Sn1–C1	104.1(5)
C19–S1	176(1)	C19–Sn1–C7	106.1(5)
C19–N1	129(2)	C19–Sn1–C13	108.1(5)
S1–C20	172(2)		
N1–C25	134(2)	Sn1–C19–S1	121.7(7)
		Sn1–C19–N1	125.0(10)
		S1–C19–N1	113.0(10)
		C19–S1–C20	90.0(7)
		C19–N1–C25	114.0(10)

was evolved. The flask and its contents were allowed to cool and the resulting solid recrystallised from 60–80 °C petroleum ether to yield $Ph_3SnSnPh_3$ (3.31 g, 92%) as a white crystalline solid. Anal: Found: C, 61.6; H, 4.3. $C_{36}H_{30}Sn_2$ calcd.: C, 61.8; H, 4.3%. NMR: $^1J(^{119}Sn–^{119}Sn)$: 4278 Hz.

Under similar conditions Ph_3SnH reacted with *N*-allylbenzimidazole, *N*-allylimidazole and *N*-vinylimidazole to also yield $Ph_3SnSnPh_3$.

The crystal structure of 2-(triphenylstannyl)benzothiazole

Crystal data: Triclinic, $P\bar{1}$, $Z = 2$, a 9.501(1), b 10.172(2), c 13.231(2) Å, α 67.93(2), β 70.46(1), γ 69.71(1)°, U 1082.8 Å^3, D_{calc} 1.485 g cm^{-3}, $F(000) = 484$, μ(Mo-K_α) 11.74 cm^{-1}.

Data were collected at room temperature on a Hilger and Watts Y290 four-circle diffractometer in the range $2 < \theta < 22°$. 2834 reflections were collected of which 2264 were unique and had $I > 3\sigma(I)$. Data were corrected for Lorentz and polarisation effects but not absorption. The structure was solved by conventional Patterson and Fourier methods and refined using the SHELX [28] suite of programs. The Sn and S atoms were refined anisotropically, all other atoms isotropically. Hydrogen atoms were included at calculated positions (fixed U 0.05 Å^2). The final difference Fourier map showed residual electron density of 0.61 eÅ^{-3} around the tin atoms as the only remaining feature. Final maximum shift/esd was 0.007 for Sn1 x/a. Final $R = 0.0719$ for unit weights.

The asymmetric unit, with atomic labelling, is shown in Fig. 1. Final atomic coordinates are given in Table 4, final selected bond distances and angles in Table 5. Full listings of this latter data and thermal parameters are available from the authors upon request.

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