C-, *N*- and *C,N*-Organostannyl Tetrazoles: Synthesis, Characterisation and Reactivity†

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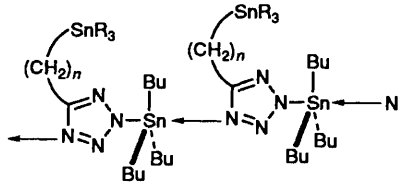
Open-chain *C,N*-organostannyl tetrazoles, $R_2R'Sn(CH_2)_nCN_4SnBu_3$ (n = 2 or 3, R_2R' = Ph_3; n = 2, R_2R' = Bu_2Ph), have been synthesised by a [3 + 2] cycloaddition reaction between $R_3Sn(CH_2)_nCN$ and $SnBu_3(N_3)$. Prolonged heating of the reaction mixture yields the novel bicyclic species *C,N*-$R_2Sn(CH_2)_nCN_4$ (n = 2 or 3, R = Ph; n = 2, R = Bu). The reaction chemistry of both classes of compound has been studied, along with a reinvestigation of the parent 5-organo(*N*-triorganostannyl)tetrazoles $RCN_4SnR'_3$, by ^{13}C and ^{119}Sn NMR spectroscopy. The crystal structure of 2,2-diphenyl-1,7,8,9-tetraaza-2-stannabicyclo[4.3.0]nona-6,8-diene has also been determined.

We have previously detailed our interest in the synthesis of *C*-organostannyl heterocycles as a possible approach to new biocidally active organotin compounds, in which the organotin and heterocycle moieties are linked through carbon rather than the conventional attachment through the heteroatom of the ring.[1–4] Such an approach has not been without its drawbacks, in as much as the tin and heterocycle need, in general, to be separated by at least two methylene units for the attachment to become aerobically stable. Thus, *C*-R_3Sn-substituted heterocycles (benzothiazole, benzoxazole, *N*-methylimidazole) all decompose on standing in air to $SnR_3(OH)$ or $(R_3Sn)_2O$ and heterocycle.[1] Furthermore, our synthetic strategies to date have all centred on construction of the Sn–$(CH_2)_n$X (X = heterocycle) linkage, starting from a preformed heterocycle. In this paper we describe an alternative strategy in which a precursor $R_3Sn(CH_2)_nX$ compound (n = 2 or 3) is transformed into the desired product *via* heterocycle construction based around the functional group X. The particular reaction is the well known [3 + 2] cycloaddition reaction between a nitrile (*i.e.* X = CN) and an organotin azide to yield *N*-organostannyl tetrazoles. Such species were first reported in 1971 by Sisido *et al.*,[5] followed some time later by an appreciation of their ability to direct the site of *N*-alkylation of tetrazoles to the N(1) position of the heterocycle.[6] The polymeric nature of the organotin tetrazoles was mentioned in these reports, a structural supposition based largely on concentration-dependent viscosity measurements[5] and subsequent variable temperature ^1H NMR spectroscopy.[7] In this paper we report on the structure and reaction chemistry of products generated from the interaction of $R_3Sn(CH_2)_nCN$ and $SnR'_3(N_3)$, and in addition include some further comments on the structure of the parent organotin tetrazoles, $RCN_4SnR'_3$, themselves.

Results and Discussion

Synthesis and Reaction Chemistry.—Heating equivalent amounts of $Ph_3Sn(CH_2)_nCN$ (n = 2 **1** or 3 **2**), prepared by the hydrostannation of $CH_2{=}CH(CH_2)_mCN$ ($m = n - 2$) with $SnPh_3H$, and $SnBu_3(N_3)$ in the absence of solvent at 130–140 °C for 3 h yielded $Ph_3Sn(CH_2)_nCN_4SnBu_3$ (n = 2 **3** or 3 **4**). The reaction can be conveniently followed by the disappearance of bands in the IR spectrum due to ν(CN) and ν(N_3) at *ca.* 2250 and 2060 cm^{-1}, respectively. The products are viscous oils, which could not be vacuum distilled or chromatographed without decomposition. The presence of two tin sites in these species is clear from the ^{119}Sn NMR spectra, which show resonances at δ *ca.* −101 and −43 due to Ph_3Sn and Bu_3Sn respectively. The chemical shift for the aryltin site is typical of such a species in a tetrahedral environment (*e.g.* $SnEtPh_3$, δ −111),[8] however the low-frequency shift of the second resonance when compared with, for example, $SnBu_3Cl$ (δ 143), suggests that the co-ordination number at the metal in the Bu_3Sn moiety is greater than four. These inferences are borne out in the Mössbauer spectra of compounds **3** and **4**, which show both a singlet (Ph_3SnCH_2) and a doublet (quadrupole splitting, q.s. = 3.45, 3.54 mm s^{-1}, respectively), the latter indicating a trigonal-bipyramidal *trans*-N_2SnBu_3 co-ordination for the *N*-bound tin.[9] The only way such a co-ordination sphere can occur is through intermolecular N:→Sn interactions, a tendency supported by earlier physical measurements[5,7] and our concentration-dependent NMR experiments reported below. The most likely structure for **3** and **4** is shown in **I** (R = Ph).



I

When either compound **1** or **2** is treated with $SnBu_3(N_3)$ at 140 °C for 21 h, or **3** or **4** heated alone under the same conditions, a second cyclisation process occurs with the elimination of $SnBu_3Ph$, yielding **5** and **6** (Scheme 1). The latter are white, crystalline, polymeric solids (see below) which are readily separated from the by-product, $SnBu_3Ph$, by washing with diethyl ether. They are only sparingly soluble in common organic solvents, and were recrystallised from boiling MeOH–CS_2. Interestingly, while CS_2 readily inserts into the Sn–N bonds of organotin amines to yield dithiocarbamates,[10] no such insertion was observed with **5** or **6**. The ^{119}Sn NMR spectra of

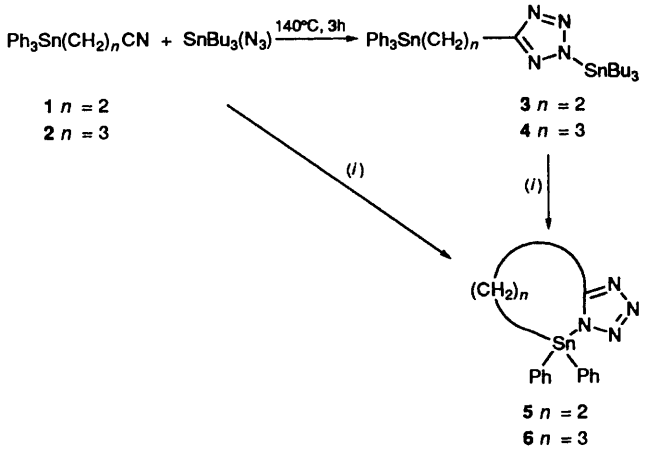
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.
Non-SI units employed = mmHg ≈ 133 Pa.

compounds **5** and **6** show only one tin environment at δ −196, −224, respectively. These low-frequency resonances suggest a co-ordination number of greater than four for the tin even in solution, though the need to use dimethyl sulfoxide (dmso) as solvent leaves ambiguous the nature of the solution species, *i.e.* dmso adduct or polymer. However, the ^{119}Sn chemical shift of $Bu_2Sn(CH_2)_2CN_4$ **14** in $CHCl_3$ (δ −84) is also to low frequency of, for example, four-co-ordinated $SnBu_3(NMe_2)$ (δ 36),[8] suggesting an inherent polymeric character for these bicyclic compounds. This fact is endorsed by the Mössbauer spectra of **5**, **6** and **14** (q.s. = 3.26–3.48 mm s^{-1}) which are consistent with a five-co-ordinate *trans*-N_2SnCR_2 arrangement.[9]

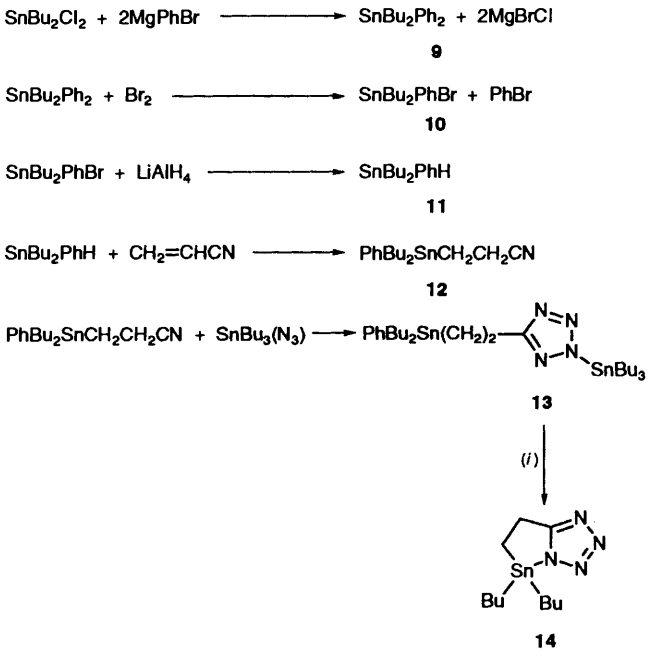
Two other routes, related to that in Scheme 1, also yield bicyclic products (Scheme 2). When $BrPh_2Sn(CH_2)_3CN$ **7**, from selective bromination of $Ph_3Sn(CH_2)_3CN$, is heated with $SnBu_3(N_3)$, compound **6** along with $SnBu_3Br$ are formed in > 95% yield in 5 min. It would appear that by including a good leaving group on the precursor organotin the formation of **6** from a monocylic intermediate analogous to **4** by nucleophilic attack of the ring nitrogen on the pendant electrophile ($BrPh_2Sn$) is enhanced. It is possible that the first step in this reaction is azide for bromine exchange, followed by an intramolecular [3 + 2] cycloaddition which generates both heterocycles of **6** simultaneously. Indeed, if $BrPh_2Sn(CH_2)_2CN$ **8** is heated for 30 min with NaN_3 in refluxing light petroleum (b.p. 60–80 °C), **5** is precipitated without isolation of the presumed intermediate $(N_3)Ph_2Sn(CH_2)_2CN$.

Furthermore, attempts to prepare the dibutyltin analogue of compound **5**, **14**, from $Bu_3Sn(CH_2)_2CN$ and $SnBu_3(N_3)$ proved unsuccessful, presumably because the reaction requires cleavage of an Sn–Bu linkage (Bu_4Sn as by-product) which is relatively unfavourable. We have, however, synthesised **14** by a route which involves addition of the unsymmetrical tin hydride **11** to acrylonitrile generating a precursor **12** containing a better leaving group on tin (Scheme 3). Compound **13**, as with **3** and **4** discussed previously, shows two tin sites in its Mössbauer spectrum (q.s. = 0.00, 3.53 mm s^{-1}) corresponding to the tetrahedral $PhBu_2SnCH_2$ and trigonal-bipyramidal *trans*-N_2SnBu_3 moieties respectively, **I** (R_3Sn = $PhBu_2Sn$).

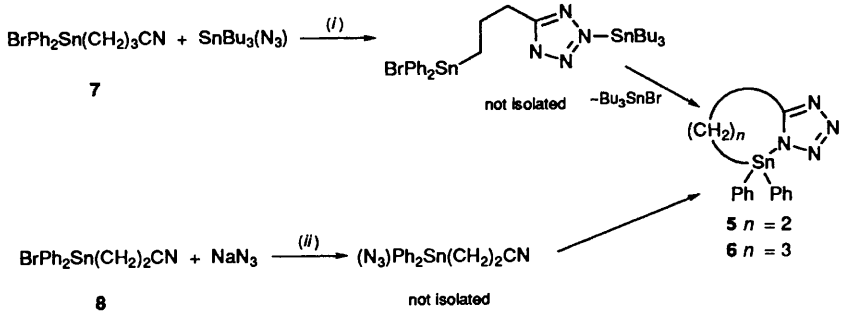
The reaction chemistry of both the mono- and bi-cyclic organotin tetrazoles is shown in Scheme 4. When compound **3** was treated with aqueous HCl in either diethyl ether (−30 °C) or methanol (room temperature), cleavage of both the Sn–N and one of the Sn–Ph bonds results to give **15**. The same product was also formed when a suspension of **5** in boiling methanol was treated with aqueous HCl, breaking the endocyclic Sn–N bond and generating new SnCl and NH units. This latter methodology has also allowed the synthesis of $ClBu_2Sn(CH_2)_2CN_4H$ **16**. Both **15** and **16** clearly show ν(N–H) (3150 cm^{-1}) and δ(NH) (*ca.* 14.35, br; *cf.* 13.95, br for HCN_4H) resulting from Sn–N bond cleavage. Structurally, the Mössbauer q.s. data for these two compounds (3.32, 3.42 mm s^{-1}) imply a *trans*-N(Cl)SnR_3 co-ordination sphere, but this may arise from either intramolecular chelation (**II**) or intermolecular bridging (**III**). We have recently published the structure of $SnPh_2[(CH_2)_2C_5H_4N\text{-}2](S_2CNMe_2)$ which adopts a structure analogous to **II** and exhibits a smaller Mössbauer q.s. (2.55 mm s^{-1}), though the q.s. data for $SnPh_2Br[(CH_2)_2C_5H_4N\text{-}2]$ are probably more representative and show a more comparable value (2.98 mm s^{-1}).[4] Compound **16** is soluble in $CDCl_3$, as is chelated $SnPh_2Br[(CH_2)_2C_5H_4N\text{-}2]$, and has δ($^{119}Sn$) at 14.2, significantly to low frequency from four-co-ordinate $SnBu_3Cl$ (δ 143). This also implies a five-co-ordinate tin, possibly as in structure **II** since the structure is retained in solution. However, **15** is only soluble in co-ordinating solvents *e.g.* dmso and tetrahydrofuran (thf),



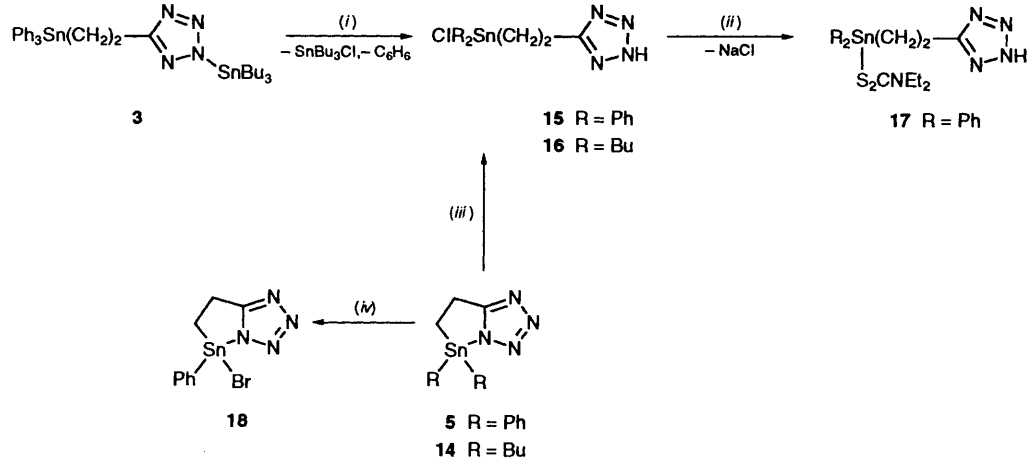
Scheme 1 (*i*) 140 °C, 21 h, $-SnBu_3Ph$



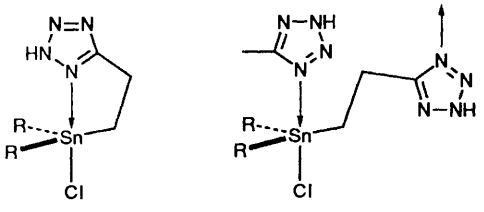
Scheme 3 (*i*) 170 °C, 12 h, $-SnBu_3Ph$



Scheme 2 (*i*) 140 °C, 5 min; (*ii*) light petroleum, 60 °C, 30 min



Scheme 4 (*i*) HCl(aq), Et_2O, −30 °C or HCl(aq), MeOH, room temperature: (*ii*) $Na[S_2CNEt_2]$; (*iii*) HCl(aq), MeOH, reflux; (*iv*) R = Ph, Br_2, $CHCl_3$, $-C_6H_5Br$



II III

probably due to the formation of a five-co-ordinated 1 : 1 adduct with the solvent (δ −162.3). The general insolubility of **15** is, therefore, more in keeping with the polymeric arrangement **III**. No definitive delineation between the two alternative structures is thus possible from the available data.

The compound $ClPh_2Sn(CH_2)_2CN_4H$ **15** can be used as the precursor for a family of compounds $LPh_2Sn(CH_2)_2CN_4H$ in much the way that we have previously used $SnPh_2Br[(CH_2)_2C_5H_4N\text{-}2]$.[4] Thus, **15** reacted with $Na[S_2CNEt_2]$ to yield the dithiocarbamate derivative **17**. This compound has a q.s. of 3.27 mm s^{-1} indicating a five-co-ordinate tin, and the similarity of this parameter to that of the chloride from which it is formed suggests a consistent structural pattern, namely *trans*-$N(S)SnR_3$. Moreover, the low solubility of this species even in co-ordinating solvents suggests a bridging role for the tetrazole. While a bridging role for the dithiocarbamate cannot be excluded, there is no precedent for such a mode in tin chemistry.

An entry into the synthesis of functionalised derivatives of the bicyclic species **5** can be found *via* the brominated derivative **18**, formed by bromodephenylation of **5** with Br_2. No reaction was observed in the analogous chemistry with molecular iodine. Compound **18** is also of exceedingly low solubility, but the Mössbauer q.s. data (3.30 mm s^{-1}) indicate that a five-co-ordinate metal centre is retained.

Structure of 2,2-*Diphenyl*-1,7,8,9-*tetraaza*-2-*stannabicyclo*-[4.3.0]*nona*-6,8-*diene* **6**.—The asymmetric unit of compound **6** is shown in Fig. 1 and consists of two independent molecules. The architecture of the two molecules is the same within experimental error, so for brevity the following discussion highlights only the molecule centred on Sn(1). The bicyclic nature of the product is confirmed, as is the *trans*-N_2SnC_3 co-ordination sphere at tin, brought about by intermolecular co-ordination from the nitrogen N(4′) of a neighbouring molecule. This intermolecular co-ordination is extremely strong, based upon the equality of the two Sn–N interactions [Sn(1)–N(1) 234(1), Sn(1)–N(4′) 239(1) pm], the resulting near linearity of the N(1)–Sn–N(4′) moiety [173.8(5)°] and the sum of the equatorial angles about tin involving C(1), C(7) and C(13) (360.0°). The Sn–N bonds are comparable with those found in $SnMe_3(N_3)$ (239 pm)[11] and tricyclohexyl(1,2,4-triazolyl)tin (229, 235 pm),[12] both of which contain a five-co-ordinated tin in a *trans*-N_2SnC_3 environment.

The tetrazole ring is planar (maximum deviation from least-squares plane: 1.1 pm), with C(15) (5.1 pm) and C(13) (−7.5 pm) approaching coplanarity with this ring. Atom Sn(1) (−44.5 pm) and to a greater extent C(14) (73.0 pm) deviate from this plane, such that the conformation of the six-membered SnC_4N heterocycle is difficult to describe though it loosely approaches an envelope arrangement (Fig. 2). Although the estimated standard deviations (e.s.d.s) in the bond lengths associated with the tetrazole ring are relatively high (±2 pm) it is noteworthy that the formal N(2)=N(3) double bond (126 pm) errs on the shorter side of that in 5-bromotetrazole (129 pm)[13] despite the interaction of neighbouring N(1) to tin.

The bicyclic nature of compound **6** makes it an analogue of 1,5-substituted tetrazoles such as pentamethylenetetrazole **19**, a central nervous system stimulant marketed as metrazole. It forms strong complexes with Lewis acids *e.g.* **19**·ICl[14] and it is interesting that both **6** and **19** utilise the more sterically hindered N^4 site for adduct formation. The situation is not, however, always as clearly resolved, for example in its dimeric 2:1 adduct with $AgNO_3$, both N^3 and N^4 of **19** co-ordinate to silver, though the shorter bonds are to N^4.[15] Nonetheless, it has been previously postulated that simple 5-organo(*N*-triorganostannyl)tetrazoles have tin bound to the N^2 site, with the polymeric character of these species originating from intermolecular co-ordination *via* N^4.[5,7] Both the structure of **6** described herein and the NMR data presented below support this latter conjecture.

The lattice structure of compound **6** is shown in Fig. 3. The intermolecular Sn–N(4′) interactions generate a one-dimensional polymeric arrangement with chains running parallel to *b*. There are no significant interactions between adjacent chains.

Carbon-13 *and* ^{119}Sn *NMR Study of* N-*Organotin Tetrazoles*.—In view of the conversion of compounds **3**, **4** into **5**, **6** discussed earlier it was of interest to consider further the structural nature of the *N*-bound organotin, since it clearly plays a role in promoting the intramolecular nucleophilic attack of N^1 on the pendant electrophile, given the generally poor nucleophilic character of tetrazole nitrogens.[16] In addition, the elimination of $SnBu_3Ph$ suggests that the Bu_3Sn moiety must come in close proximity to the Ph_3Sn fragment, an event which seems difficult (except in an intermolecular fashion) if the former

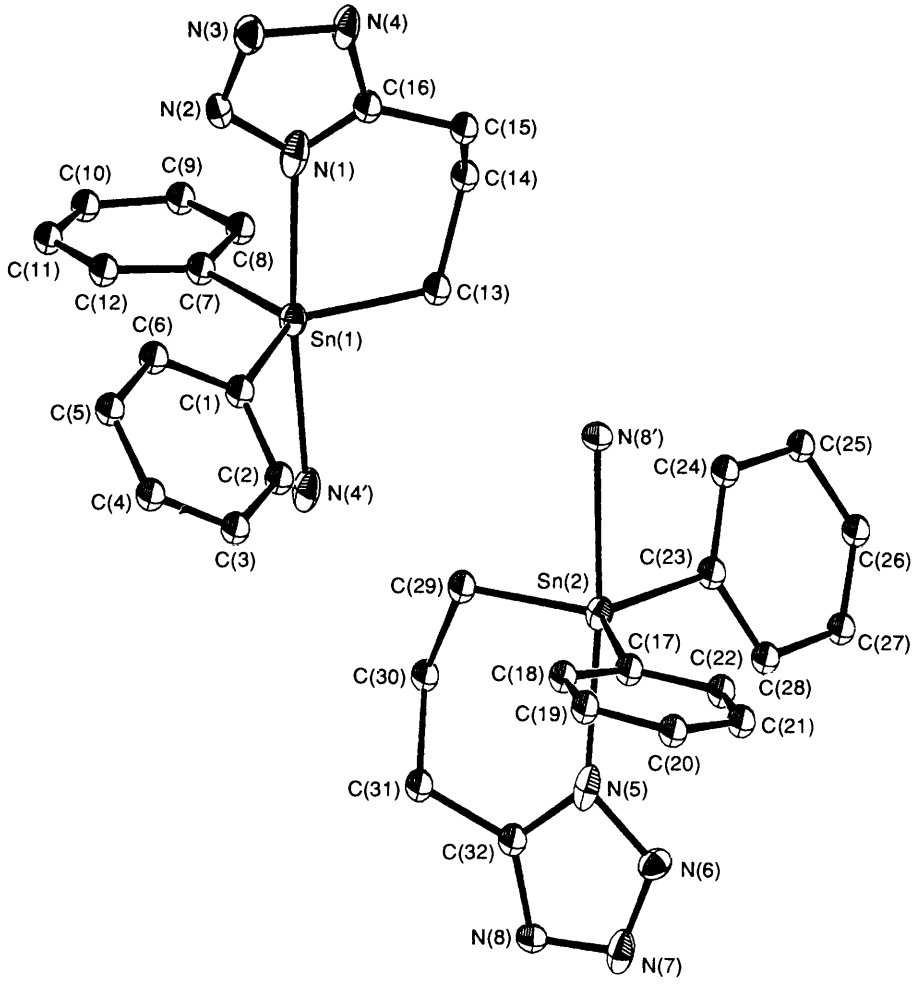


Fig. 1 The asymmetric unit of compound **6** (two independent molecules) showing the atomic labelling scheme used in the text and Tables. Thermal ellipsoids are at the 30% probability level

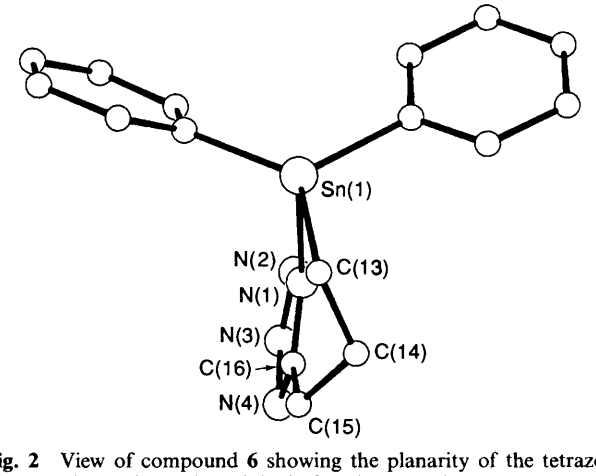
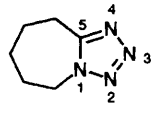


Fig. 2 View of compound **6** showing the planarity of the tetrazole ring and the conformation of the SnC_4N heterocycle



19

is bound to N^2, as suggested by earlier workers.[5,7] We have therefore re-examined simple 5-organo(*N*-triorganostannyl)-tetrazoles in order to gain a clearer insight into the **3**, **4** ⟶ **5**, **6** transformation. Our attempts to identify the binding site of the tin using X-ray crystallography have been thwarted by crystal twinning, and of the available literature data only the structure of $[(PhMe_2Si)_3C]Me_2SiN_4CMe$ is sufficiently closely related to the present case to act as a guide. In this compound, despite suffering from problems of disorder, the silicon is unambiguously attached to N^2 of the tetrazole, though the presence of the bulky $(PhMe_2Si)_3C$ ligand may make this an unrepresentative compound.[17] Moreover, the relatively low Lewis acidity of silicon (in conjunction with the bulky ligand) rules out any intermolecular interactions, in contrast with the chemistry at tin.

The polymeric character of $RCN_4SnR'_3$ is clearly demonstrated by the ^{13}C NMR data in Fig. 4, which shows the variation in $^1J(^{13}C–^{119}Sn)$ with concentration for RCN_4SnBu_3 (R = Me **20** or Ph **21**). The value of ^1J is a reflection of the angle C–Sn–C (θ),[18,19] which increases from 109 to 120° as the co-ordination number at tin increases from four to five with the onset of polymerisation (assuming equatorial R groups) (Scheme 5). Typically, ^1J values greater than 400 Hz would indicate an expansion of the tin co-ordination sphere to at least some degree, and using the relationship derived by Holecek and Lycka[19] we estimate ^1J extremes for four- and five-co-ordinate Bu_3Sn as 343 and 453 Hz, respectively, though limitations in the *J vs.* θ relationship give some latitude to these values. Fig. 4 thus clearly vindicates earlier viscosity measurements in assuming that 5-organo(*N*-triorganostannyl)tetrazoles are co-ordination polymers. Moreover, it is clear from the two profiles shown in Fig. 4 that intermolecular interactions are more readily attained when the 5-substituent is small (**20**). The implication of this

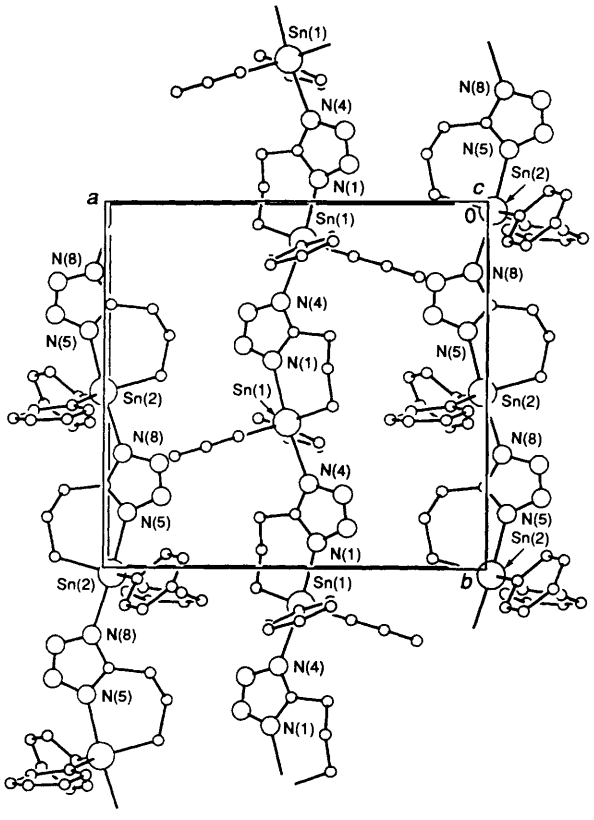


Fig. 3 The unit cell of compound **6** viewed perpendicular to the *ab* plane

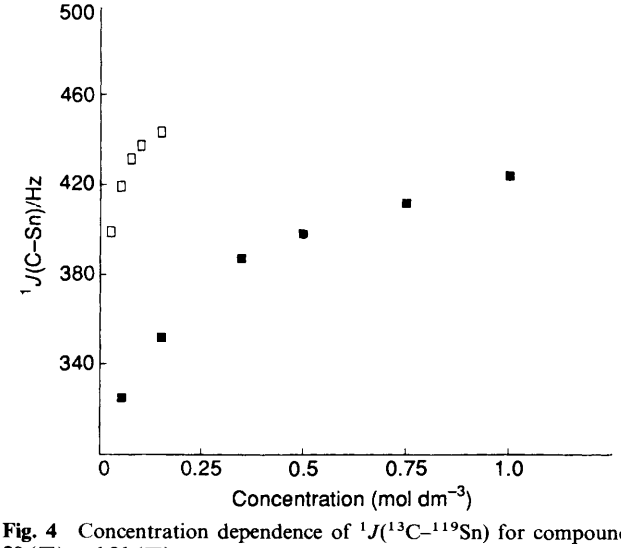
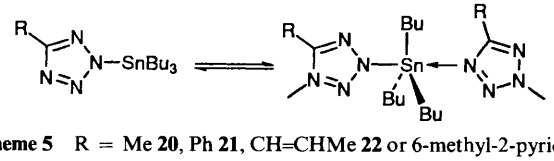


Fig. 4 Concentration dependence of $^1J(^{13}C-^{119}Sn)$ for compounds **20** (□) and **21** (■)



Scheme 5 R = Me **20**, Ph **21**, CH=CHMe **22** or 6-methyl-2-pyridyl **23**

is that the more hindered N^1 (or N^4) site is used for the intermolecular bond, as seen in compound **6**. This, at least in part, confirms the earlier postulate of Kozima *et al.*[7] on the structure of organotin tetrazoles, which placed tin covalently bound to N^3 and intermolecularly bridged through N^1 (an N^2, N^4 binding combination is identical).

The temperature dependence of the ^{119}Sn chemical shift for four 5-organo(*N*-tributylstannyl)tetrazoles **20–23** is shown in

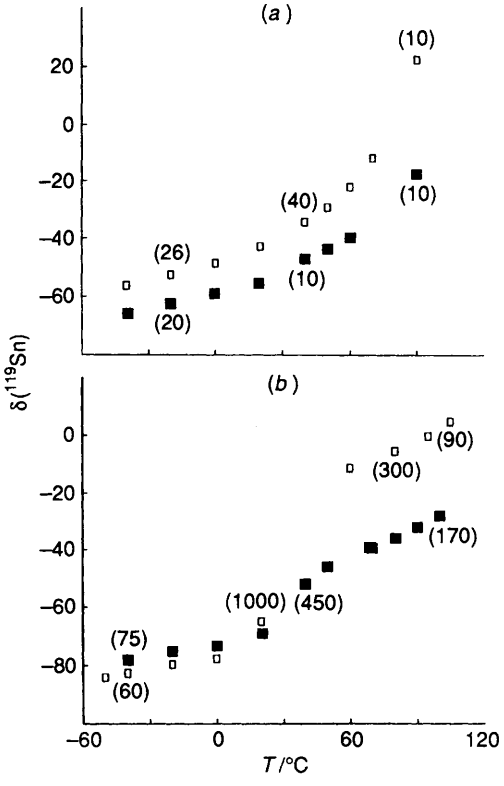
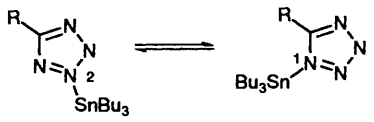


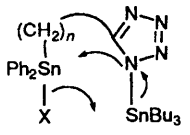
Fig. 5 Temperature dependence of $\delta(^{119}Sn)$ for (*a*) compounds **21** (□), **23** (■) and (*b*) **20** (□), **22** (■). Figures in parentheses adjacent to a symbol are the spectral linewidths (Hz)

Fig. 5. This indicates somewhat different behaviour for the 5-aryl compounds **21**, **23** [Fig. 5(*a*)] compared to the 5-alkyl or -alkenyl compounds **20**, **22** [Fig. 5(*b*)]. At −40 °C all four species have chemical shifts typical of five-co-ordinate tin, though it is consistent with the concentration-dependent ^{13}C NMR results above that the lower-frequency shifts (*i.e.* arising from a more significant proportion of five-co-ordinate polymer) are associated with the derivatives less sterically hindered at N^4 (δ −83, −78 *vs.* −56, −66 ppm for **20**, **22**, **21** and **23**, respectively). As the temperature is raised, the chemical shifts for **21** and **23** increase smoothly to δ 22 and −18, respectively. These values, particularly that for **21**, approach the shift value for four-co-ordinate $SnBu_3(NEt_2)$ (δ 36).[8] The presence of a second donor functionality in **23** may be obscuring the trend to some extent, but in both cases it is clear that the polymer–monomer equilibrium moves significantly in favour of the latter with increasing temperature. For **20** and **22** the chemical shift values increase smoothly between −40 and 20 °C, where a rapid shift to high frequency is observed (more so for **20** than **22**) before a slower increase resumes at > 60 °C. This shift in the resonance position to high frequency is associated with a significant broadening of the resonances such that for **20** no spectrum could be observed in the 20–70 °C regime (spectral linewidths are shown in parentheses in Fig. 5). No similar line broadening was observed for **21** and **23**. The ^1J coupling measured in the ^{13}C NMR spectrum of **20** at 100 °C (437 Hz) indicates that the compound is still largely five-co-ordinate at this temperature and concentration (0.6 mol dm^{-3} in toluene), therefore the origin of the high-frequency shift and line broadening must lie elsewhere. We suggest that in addition to a small movement in the polymer–monomer equilibrium towards the low-co-ordinate species (accounting for the small shifts to high frequency at temperatures below 0 and above 70 °C) these two tetrazoles, which are less hindered at N^4, are fluxional at temperatures greater than *ca.* 20 °C, such that the tin can access both N^1 and N^2 positions (Scheme 6).

The relative hindering of N^1 and N^4 in the 5-aryl derivatives



Scheme 6



IV

21 and **23** accounts for both the more rapid break-up of the polymer on heating (weaker intermolecular interactions) and the lack of fluxionality in these systems in the temperature regime studied. Fluxional behaviour has been noted previously for certain platinum tetrazoles,[20] while older quantum-mechanical calculations have shown that N^1 and N^2 binding is essentially energetically equivalent.[21]

The fluxional nature of organotin tetrazoles provides a viable explanation for the formation of the bicyclic tetrazoles **5** and **6**. It is worth comment that previous workers have reported that N^2-bound organotin groups promote the nucleophilic character of N^4. For example, 1-methyl-5-organotetrazoles predominate as products of the reaction of 5-RCN_4SnBu_3-2 with methyl iodide.[6] However, assuming that the formation of **5** and **6** takes place *via* a concerted, intramolecular process involving **IV** as a transition state then the fluxional nature of the precursors becomes central to the process. The problem is, however, complicated by the high extent of polymeric character of the organotin tetrazoles, such that the possibility that the process is intermolecular cannot be excluded.

Experimental

Spectra were recorded on the following instruments: JEOL GX270 (^1H, ^{13}C NMR), FX60Q and GX400 (^{119}Sn NMR), Perkin-Elmer 599B (IR). The NMR spectra were recorded in $CDCl_3$ unless indicated otherwise. Details of our Mössbauer spectrometer and related procedures are given elsewhere.[22] The compounds $SnBu_3(N_3)$,[23] $Ph_3Sn(CH_2)_nCN$ (n = 2 **1** or 3 **2**)[24] and $SnBu_2Ph_2$[25] were prepared by literature methods. But-2-enenitrile was obtained from Aldrich as a mixture of *E* and *Z* isomers.

Syntheses.—2-(*Tributylstannyl*)-5-[2-(*triphenylstannyl*)*ethyl*]*tetrazole* **3**. Tributyltin azide (1.80 g, 5.4 mmol) and (2-cyanoethyl)triphenylstannane (2.20 g, 5.4 mmol) were heated for 3 h at 130 °C. The reaction was monitored by the disappearance of IR bands attributable to ν(CN) and $\nu(N_3)$ at 2250 and 2060 cm^{-1}, respectively. After allowing the residue to cool, the oil was dissolved in cold light petroleum (b.p. 60–80 °C) and filtered to remove any residual traces of (2-cyanoethyl)triphenylstannane. The solvent was evaporated from the filtrate, to leave the product as a clear viscous oil (3.89 g, 97%), which was in an analytically pure form. The oil could not be vacuum distilled or chromatographed without decomposition [Found (Calc. for $C_{33}H_{46}N_4Sn_2$): C, 53.7 (53.8); H, 6.40 (6.30); N, 6.90 (7.60)%]. NMR: ^1H, δ 0.68–1.45 (m, 27 H, C_4H_9Sn), 2.55 (t, 2 H, $SnCH_2CH_2$), 3.01 (t, 2 H, $SnCH_2$) and 7.26–7.60 (m, 15 H, C_6H_5Sn); ^{13}C, δ 9.4 ($SnCH_2$), 18.0, 28.0, 27.3, 13.6 ($C^{1-4}H_9Sn$), 26.8 ($SnCH_2CH_2$), 138.9, 136.9, 128.7, 129.3 ($C_{i,o,m,p}H_5Sn$) and 163.2 (CN_4); ^{119}Sn, δ −43.2 (Bu_3Sn) and −101.1 (Ph_3Sn). Mössbauer: isomer shift, i.s. = 1.40, q.s. = 3.45 (Bu_3Sn); i.s. = 1.27, q.s. = 0.00 mm s^{-1} (Ph_3Sn).

2-(*Tributylstannyl*)-5-[3-(*triphenylstannyl*)*propyl*]*tetrazole* **4**. This compound was prepared in a manner analogous to that for **3**, by heating equimolar quantities of $SnBu_3(N_3)$ and (3-cyanopropyl)triphenylstannane at 140 °C for 3 h. The product, a clear viscous oil, was produced in near quantitative yield [Found (Calc. for $C_{34}H_{48}N_4Sn_2$): C, 53.9 (54.4); H, 6.20 (6.45); N, 7.30 (7.45)%]. NMR: ^1H, δ 0.68–1.45 (m, 27 H, C_4H_9Sn), 1.70–2.00 (m, 4 H, $SnCH_2CH_2CH_2$), 2.28 (t, 2 H, $SnCH_2$) and 7.58–7.20 (m, 15 H, C_6H_5Sn); ^{13}C, δ 16.8 ($SnCH_2$), 18.2, 28.1, 27.0, 13.7 ($C^{1-4}H_9Sn$), 23.1 ($SnCH_2CH_2$), 25.9 ($SnCH_2CH_2CH_2$), 138.4, 136.8, 128.4, 129.1 ($C_{i,o,m,p}H_5Sn$) and 161.5 (CN_4); ^{119}Sn, δ −55.2 (Bu_3Sn) and −102.2 (Ph_3Sn). Mössbauer: i.s. = 1.42, q.s. = 3.54 (Bu_3Sn); i.s. = 1.26, q.s. = 0.00 mm s^{-1} (Ph_3Sn).

2,2-*Diphenyl*-1,6,7,8-*tetraaza*-2-*stannabicyclo*[3.3.0]*octa*-5,7-*diene* **5**. *Method* (*a*). Compound **3** (3.00 g, 4.1 mmol) was heated with stirring at 130 °C for 21 h, during which time the reaction mixture solidified. The residue was washed with diethyl ether (4 × 50 cm^3), and the pure product obtained by recrystallising the undissolved solid from boiling MeOH–CS_2 (10:1, 200 cm^3), yield 0.84 g (83%), m.p. 290–295 °C. Evaporation of the ether washings yielded $SnBu_3Ph$, which was purified by vacuum distillation (115 °C, 0.3 mmHg), yield 1.47 g (97%) [Found (Calc. for $C_{15}H_{14}N_4Sn$): C, 48.3 (48.8); H, 3.95 (3.80); N, 15.20 (15.20)%]. NMR [$(CD_3)_2SO$]: ^1H, δ 2.20 (m, 2 H, $SnCH_2CH_2$), 3.23 (m, 2 H, $SnCH_2$) and 7.30–7.80 (m, 10 H, C_6H_5Sn); ^{13}C, δ 14.9 ($SnCH_2$), 19.2 ($SnCH_2CH_2$), 140.7, 136.1, 128.2, 129.7 ($C_{i,o,m,p}H_5Sn$) and 166.1 (CN_4); ^{119}Sn, δ −195.9. Mössbauer: i.s. = 1.32, q.s. = 3.28 mm s^{-1}.

Method (*b*). Bromo(2-cyanoethyl)diphenylstannane (1.5 g, 3.68 mmol) was dissolved in ethyl acetate (50 cm^3) and placed in a separating funnel (500 cm^3). Sodium azide (0.24 g, 3.68 mmol) was dissolved in distilled water (50 cm^3) and added to the funnel. The mixture was shaken for 20 min, the organic layer separated and dried (anhydrous $MgSO_4$) and the solvent evaporated *in vacuo*. Recrystallisation of the solid so obtained from light petroleum (b.p. 60–80 °C) resulted in the formation of compound **5** (0.92 g, 67%), rather than $(N_3)Ph_2Sn(CH_2)_2CN$.

2,2-*Diphenyl*-1,7,8,9-*tetraaza*-2-*stannabicyclo*[4.3.0]*nona*-6,8-*diene* **6**. *Method* (*a*). Following the procedure outlined above for compound **5**, **6** was produced by heating **4** at 140 °C for 24 h. Recrystallisation from MeOH–CS_2 (10:1) yielded the product as white needles (0.64 g, 76%), m.p. 310 °C (decomp.); $SnBu_3Ph$ was also obtained as a by-product (0.69 g, 85%) [Found (Calc. for $C_{16}H_{16}N_4Sn$): C, 50.2 (50.2); H, 4.35 (4.20); N, 14.60 (14.60)%]. NMR [$(CD_3)_2SO$]: ^1H, δ 1.90 (m, 2 H, $SnCH_2CH_2CH_2$), 2.15 (m, 2 H, $SnCH_2CH_2$), 2.94 (m, 2 H, $SnCH_2$) and 7.30–7.80 (m, 10 H, C_6H_5Sn); ^{13}C, δ 16.8 ($SnCH_2$), 23.7 ($SnCH_2CH_2$), 25.1 ($SnCH_2CH_2CH_2$), 141.3, 136.3, 128.6, 129.4 ($C_{i,o,m,p}H_5Sn$) and 160.9 (CN_4); ^{119}Sn, δ −224.3. Mössbauer: i.s. = 1.29, q.s. = 3.26 mm s^{-1}.

Method (*b*). Bromo(3-cyanopropyl)diphenylstannane (0.48 g, 1.1 mmol) and $SnBu_3(N_3)$ (0.37 g, 1.1 mmol) were heated at 140 °C for 5 min, during which time the mixture had solidified. The solid **6** was purified by washing with diethyl ether (4 × 50 cm^3); $SnBu_3Br$ (0.39 g, 96%) was obtained from the washings after solvent evaporation and subsequent vacuum distillation of the crude material.

Bromo(3-*cyanopropyl*)*diphenylstannane* **7**. (3-Cyanopropyl)-triphenylstannane **2** (0.90 g, 2.15 mmol) was dissolved in light petroleum (b.p. 60–80 °C) (100 cm^3) and bromine (0.34 g, 2.13 mmol), dissolved in the same solvent (50 cm^3), added dropwise with stirring. When the colouration due to the halogen had disappeared (*ca.* 30 min) the volatiles were removed *in vacuo* leaving the product **7** which was used immediately without further purification.

Bromo(2-*cyanoethyl*)*diphenylstannane* **8**. This was prepared by the method given above for compound **7**, from equimolar quantities of **1** and Br_2.

Bromodibutylphenylstannane **10**. Using the same methodology as for compound **7** above, **10** was prepared from dibutyldiphenylstannane[25] (23.00 g, 59 mmol) and bromine

(9.43 g, 59 mmol) in chloroform (total volume 250 cm^3). After solvent evaporation, the residue was vacuum distilled to give bromobenzene (8.71 g, 94%) and the desired product (17.22 g, 74%), b.p. 182 °C (0.3 mmHg), as a colourless oil [Found (Calc. for $C_{14}H_{23}BrSn$): C, 43.0 (43.1); H, 5.65 (5.95)%]. ^1H NMR: δ 0.81–1.76 (m, 18 H, C_4H_9Sn) and 7.24–7.70 (m, 5 H, C_6H_5Sn).

Dibutylphenylstannane **11**. A solution of compound **10** (17.22 g, 44 mmol) in dry diethyl ether (100 cm^3) was added dropwise to a suspension of $LiAlH_4$ (1.74 g, 44 mmol) in the same solvent (80 cm^3), under an atmosphere of dinitrogen gas. When addition was complete the mixture was refluxed for 2.5 h, after which time quinol (0.25 g) and water (10 cm^3) were cautiously added to decompose any residual $LiAlH_4$. The mixture was rapidly filtered, the filtrate concentrated by solvent evaporation *in vacuo*, and the residual yellow oil distilled to give **11** as a colourless oil (9.21 g, 67%), b.p. 175 °C (1.0 mmHg) [Found (Calc. for $C_{14}H_{24}Sn$): C, 54.1 (54.1); H, 7.75 (7.75)%]. ^1H NMR: 0.76–1.77 (m, 18 H, C_4H_9Sn), 7.15 (s, 1 H, SnH) and 7.14–7.70 (m, 5 H, C_6H_5Sn). IR: ν(Sn–H) 1835 cm^{-1}.

Dibutyl(2-cyanoethyl)phenylstannane **12**. Compound **11** (5.0 g, 16 mmol) and acrylonitrile (1.70 g, 32 mmol) were stirred together under an atmosphere of dinitrogen at 80 °C for 7.5 h. The flask was then cooled to 40 °C and stirring continued for 12 h, after which time the IR band due to ν(Sn–H) at 1850 cm^{-1} had disappeared. The excess of acrylonitrile was evaporated under reduced pressure, and the resulting oil vacuum distilled to give the product (3.81 g, 65%), b.p. 194 °C (0.3 mmHg) [Found (Calc. for $C_{17}H_{27}NSn$): C, 56.2 (56.1); H, 7.55 (7.45); N, 3.80 (3.85)%]. NMR: ^1H, δ 0.81–1.76 (m, 18 H, C_4H_9Sn), 1.85 (t, 2 H, $SnCH_2CH_2$), 2.62 (t, 2 H, $SnCH_2$) and 7.33–7.64 (m, 5 H, C_6H_5Sn); ^{13}C, δ 9.5 ($SnCH_2$), 14.7 ($SnCH_2CH_2$), 18.1, 28.9, 27.2, 13.6 ($C^{1-4}H_9Sn$), 139.3, 136.3, 128.3, 128.7 ($C_{i,o,m,p}H_5Sn$) (CN_4 too weak to be observed); ^{119}Sn, δ −41.0. Mössbauer: i.s. = 1.31, q.s. = 0.00 mm s^{-1}. IR: ν(CN) 2260 cm^{-1}.

5-[2-(*Dibutylphenylstannyl)ethyl*]-2-(*tributylstannyl)tetrazole* **13**. The compound $SnBu_3(N_3)$ (3.19 g, 9.6 mmol) and **12** (3.50 g, 9.6 mmol) were stirred for 2 h at 104 °C to give **13** as a yellowish, viscous oil (6.68 g, 99%) which could not be purified by distillation or chromatography without decomposition [Found (Calc. for $C_{29}H_{54}N_4Sn_2$): C, 49.8 (50.0); H, 7.70 (7.80); N, 8.10 (8.05)%]. NMR: ^1H, δ 0.86–1.64 (m, 45 H, C_4H_9Sn), 2.53 (t, 2 H, $SnCH_2CH_2$), 3.09 (t, 2 H, $SnCH_2$) and 7.34–7.64 (m, 5 H, C_6H_5Sn); ^{13}C, δ 5.0 ($SnCH_2$), 9.6 ($SnCH_2CH_2$), 14.6, 28.8, 27.2, 13.5 ($C^{1-4}H_9Sn$, unresolved), 136.9, 136.3, 128.3, 128.6 ($C_{i,o,m,p}H_5Sn$) and 161.3 (CN_4); ^{119}Sn, δ −41.0 (Bu_2PhSn) and −43.8 (Bu_3Sn). Mössbauer: i.s. = 1.45, q.s. = 3.53 (Bu_3Sn); i.s. = 1.34, q.s. = 0.00 mm s^{-1} (Bu_2PhSn).

2,2-*Dibutyl*-1,6,7,8-*tetraaza*-2-*stannabicyclo*[3.3.0]*octa*-5,7-*diene* **14**. Compound **13** was heated at 170 °C for 12 h. After allowing the flask to cool the remaining oil was washed with light petroleum (b.p. 60–80 °C) (10 × 10 cm^3). After evaporation of the washings, $SnBu_3Ph$ was isolated by vacuum distillation (2.20 g, 64%), b.p. 110 °C (0.3 mmHg). The residue remaining after washing was maintained under dynamic vacuum with mild warming for 48 h, during which time the material solidified (2.77 g, 90%), m.p. 42–47 °C. The product did not recrystallise cleanly, nor could it be vacuum distilled [Found (Calc. for $C_{11}H_{22}N_4Sn$): C, 40.02 (40.15); H, 6.70 (6.75); N, 17.25 (17.00)%]. NMR: ^1H, δ 0.68–1.54 (m, 18 H, C_4H_9Sn), 1.96 (t, 2 H, $SnCH_2CH_2$) and 3.21 (t, 2 H, $SnCH_2$); ^{13}C, δ 13.3 ($SnCH_2$), 19.5 ($SnCH_2CH_2$), 17.6, 27.8, 27.6, 13.3 ($C^{1-4}H_9Sn$) and 160.8 (CN_4); ^{119}Sn, δ −83.5. Mössbauer: i.s. = 1.43, q.s. = 3.48 mm s^{-1}.

5-[2-(*Chlorodiphenylstannyl)ethyl*]*tetrazole* **15**. *Method* (*a*). Compound **5** (1.00 g, 2.7 mmol) was suspended in boiling methanol (30 cm^3) and aqueous HCl (2.8 mmol) added dropwise over 5 min, during which time the suspension became clear. Stirring was continued for 10 min and the solution allowed to cool slowly to 0 °C. The product crystallised as white needles (0.98 g, 89%), m.p. 157 °C [Found (Calc. for $C_{15}H_{15}ClN_4Sn$): C, 44.7 (44.4); H, 3.80 (3.70); N, 13.95 (13.80)%]. NMR [$(CD_3)_2SO$]: δ 2.03 (m, 2 H, $SnCH_2CH_2$), 3.41 (t, 2 H, $SnCH_2$), 7.30–7.90 (m, 10 H, C_6H_5Sn) and 14.35 (br s, 1 H, NH); ^{13}C, δ 18.7 ($SnCH_2$), 19.5 ($SnCH_2CH_2$), 143.5, 135.8, 128.2, 128.8 ($C_{i,o,m,p}H_5Sn$) and 158.2 (CN_4); ^{119}Sn, δ −162.3. Mössbauer: i.s. = 1.39, q.s. = 3.32 mm s^{-1}. IR: ν(NH) 3150 cm^{-1}.

Method (*b*). Compound **3** (3.64 g, 4.9 mmol) and aqueous HCl (4.9 mmol) were dissolved in methanol (50 cm^3) and stirred at room temperature for 1 h. The solvent was evaporated under reduced pressure and the resulting oil triturated with diethyl ether (10 cm^3), precipitating a white solid which was filtered off. Recrystallisation from methanol yielded pure **15** (0.84 g, 85%); $SnBu_3Cl$ was isolated from the ether-soluble filtrate. The procedure was also modified by using dry diethyl ether as solvent, and adding hydrogen chloride in gaseous form to **3** at −30 °C. The same products were obtained in similar yields.

5-[2-(*Dibutylchlorostannyl)ethyl*]*tetrazole* **16**. This was prepared as for compound **15**, method (*a*). The product precipitated without the need for trituration. Recrystallisation from methanol yielded the pure product as a white powder (41%), m.p. 57 °C [Found (Calc. for $C_{11}H_{23}ClN_4Sn$): C, 36.7 (36.2); H, 6.20 (6.35); N, 15.25 (15.35)%]. NMR: ^1H, δ 0.85–1.70 (m, 18 H, C_4H_9Sn), 1.90 (t, 2 H, $SnCH_2CH_2$), 3.41 (t, 2 H, $SnCH_2$) and 14.37 (br s, 1 H, NH); ^{13}C, δ 13.3 ($SnCH_2$), 19.5 ($SnCH_2CH_2$), 17.6, 27.8, 27.6, 13.3 ($C^{1-4}H_9Sn$) and 160.8 (CN_4); ^{119}Sn, δ 14.2. Mössbauer: i.s. = 1.46, q.s. = 3.42 mm s^{-1}. IR: ν(NH) 3150 cm^{-1}.

5-{2-[(*Diethyldithiocarbamato)diphenylstannyl*]*ethyl*}*tetrazole* **17**. Compound **15** (0.32 g, 0.79 mmol) was dissolved in chloroform–thf (1:1, 50 cm^3) and solid sodium diethyldithiocarbamate (0.18 g, 0.79 mmol) added in small portions. The mixture was stirred at reflux for 2 h, the solution cooled, reduced in volume to dryness and the residue recrystallised from ethyl acetate–acetone (1:1). The product crystallised as white florets (0.12 g, 29%), m.p. 163 °C [Found (Calc. for $C_{20}H_{25}N_4S_2Sn$): C, 46.9 (46.3); H, 4.25 (4.85); N, 13.75 (13.50)%]. NMR [$(CD_3)_2SO$]: ^1H, δ 1.23 (t, 6 H, CH_3CH_2) 1.55 (q, 4 H, CH_3CH_2), 2.06 (t, 2 H, $SnCH_2CH_2$), 3.33 (t, 2 H, $SnCH_2$), 7.26–7.87 (m, 10 H, C_6H_5Sn) and 14.23 (br s, 1 H, NH); ^{13}C, δ 12.1 (CH_3), 14.5 ($SnCH_2$), 20.1 ($SnCH_2CH_2$), 48.5 (CH_3CH_2), 142.4, 135.7, 128.3, 128.9 ($C_{i,o,m,p}H_5Sn$), 159.2 (CN_4) and 201.8 (CS_2); ^{119}Sn, δ −204.3. Mössbauer: i.s. = 1.28, q.s. = 3.27 mm s^{-1}. IR: ν(NH) 3050 cm^{-1}.

2-*Bromo*-2-*phenyl*-1,6,7,8-*tetraaza*-2-*stannabicyclo*[3.3.0]-*octa*-5,7-*diene* **18**. Compound **5** (1.0 g, 2.7 mmol) was suspended in chloroform (50 cm^3) and bromine (0.43 g, 2.7 mmol) in chloroform (20 cm^3) added dropwise. The colouration due to the halogen slowly faded, with the formation of a white suspension. The solvent was distilled *in vacuo*, and the tacky residue pumped under dynamic vacuum to remove residual volatiles (PhBr). The remaining white solid (0.92 g, 92%), m.p. 125 °C (decomp), was insoluble in common organic solvents [Found (Calc. for $C_9H_9BrN_4Sn$): C, 30.4 (29.1); H, 3.00 (2.45); N, 14.35 (15.05)%]. Compound not soluble enough for NMR spectroscopy. Mössbauer: i.s. = 1.39, q.s. = 3.30 mm s^{-1}.

5-*Methyl*-2-(*tributylstannyl)tetrazole* **20**. This was prepared following the method of ref. 5 [Found (Calc. for $C_{14}H_{30}N_4Sn$): C, 45.0 (45.1); H, 8.00 (8.10); N, 15.05 (15.00)%]. NMR: ^1H, δ 0.74–1.24 (m, 27 H, C_4H_9Sn) and 2.45 (s, 3 H, CH_3); ^{13}C, δ 11.2 (CH_3), 18.4, 28.5, 27.4, 13.9 ($C^{1-4}H_9Sn$) and 157.9 (CN_4); ^{119}Sn, δ −74.9. Mössbauer: i.s. = 1.23, q.s. = 3.45 mm s^{-1}.

5-*Phenyl*-2-(*tributylstannyl)tetrazole* **21**. This was prepared following the method of ref. 5 [Found (Calc. for $C_{19}H_{32}N_4Sn$): C, 52.1 (52.5); H, 7.00 (7.40); N, 13.00 (12.90)%]. NMR: ^1H, δ 0.68–1.32 (m, 27 H, C_4H_9Sn) and 7.21–7.84 (m, 5 H, C_6H_5); ^{13}C, δ 18.3, 28.4, 27.3, 13.9 ($C^{1-4}H_9Sn$), 137.1, 136.5, 128.2, 129.7 ($C_{i,o,m,p}H_5$) and 159.1 (CN_4); ^{119}Sn, δ −40.7. Mössbauer: i.s. = 1.22, q.s. = 3.23 mm s^{-1}.

5-(*Prop*-1-*enyl*)-2-(*tributylstannyl)tetrazole* **22**. This was pre-

Table 1 Fractional atomic coordinates (Å × 10^4) for compound **6**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Sn(1)	−5 198.4(5)	1 034.3(7)	2 388.0(4)	Sn(2)	130.5(5)	192.8(7)	7 387.4(5)
C(1)	−5 155(8)	1 172(9)	3 627(6)	C(17)	957(8)	−570(12)	8 622(7)
C(2)	−4 369(9)	1 592(12)	4 233(8)	C(18)	534(11)	−708(14)	9 213(9)
C(3)	−4 379(12)	1 705(13)	5 049(8)	C(19)	1 057(16)	−979(19)	10 011(10)
C(4)	−5 199(14)	1 450(15)	5 228(9)	C(20)	2 019(17)	−1 066(19)	10 241(10)
C(5)	−5 978(12)	1 045(15)	4 652(9)	C(21)	2 480(12)	−994(18)	9 685(11)
C(6)	−5 957(9)	915(10)	3 844(7)	C(22)	1 957(9)	−715(16)	8 870(9)
C(7)	−6 498(8)	1 430(10)	1 434(6)	C(23)	828(8)	−324(9)	6 472(6)
C(8)	−6 502(11)	1 423(12)	628(8)	C(24)	526(11)	−1 056(13)	5 858(8)
C(9)	−7 353(13)	1 699(15)	−35(8)	C(25)	981(13)	−1 143(14)	5 269(8)
C(10)	−8 174(12)	1 971(15)	123(9)	C(26)	1 751(11)	−518(16)	5 309(8)
C(11)	−8 178(10)	2 005(14)	911(10)	C(27)	2 036(11)	176(17)	5 885(9)
C(12)	−7 350(9)	1 688(13)	1 573(8)	C(28)	1 580(9)	306(15)	6 479(8)
C(13)	−4 031(9)	574(9)	1 982(8)	C(29)	−1 363(8)	229(11)	7 073(8)
C(14)	−4 130(10)	−432(13)	1 565(9)	C(30)	−1 602(8)	1 359(12)	6 852(7)
C(15)	−4 102(9)	−1 342(11)	2 122(9)	C(31)	−1 153(8)	2 079(12)	7 521(8)
C(16)	−0 5019(7)	−0 1451(10)	0 2324(6)	C(32)	−70(7)	2 222(10)	7 669(6)
N(1)	−5 591(6)	−677(9)	2 352(5)	N(5)	520(7)	1 507(9)	7 668(5)
N(2)	−6 371(7)	−1 088(11)	2 526(6)	N(6)	1 425(7)	1 922(10)	7 851(6)
N(3)	−6 263(7)	−2 025(10)	2 614(6)	N(7)	1 357(7)	2 857(11)	7 945(6)
N(4)	−5 390(6)	−2 275(9)	2 493(5)	N(8)	394(7)	3 098(8)	7 835(5)

Table 2 Selected intramolecular bond lengths (pm) and angles (°) for compound **6**

Sn(1)–N(1)	234(1)	C(15)–C(16)	149(2)
Sn(1)–C(1)	211(1)	C(16)–N(1)	133(2)
Sn(1)–C(7)	211(1)	C(16)–N(4)	129(2)
Sn(1)–C(13)	213(1)	N(1)–N(2)	139(2)
Sn(1)–N(4′)	239(1)	N(2)–N(3)	126(2)
C(13)–C(14)	150(2)	N(3)–N(4)	139(2)
C(14)–C(15)	153(2)		
Sn(2)–N(5)	234(1)	C(31)–C(32)	152(2)
Sn(2)–C(17)	211(1)	C(32)–N(5)	128(2)
Sn(2)–C(23)	214(1)	C(32)–N(8)	133(2)
Sn(2)–C(29)	213(1)	N(5)–N(6)	136(1)
Sn(2)–N(8′)	238(1)	N(6)–N(7)	126(2)
C(29)–C(30)	156(2)	N(7)–N(8)	139(1)
C(30)–C(31)	147(2)		
C(1)–Sn(1)–C(7)	118.4(5)	Sn(1)–C(13)–C(14)	116.9(9)
C(1)–Sn(1)–C(13)	126.6(4)	C(13)–C(14)–C(15)	115(1)
C(7)–Sn(1)–C(13)	115.0(5)	C(14)–C(15)–C(16)	112(1)
C(1)–Sn(1)–N(1)	92.0(4)	C(15)–C(16)–N(1)	123(1)
C(1)–Sn(1)–N(4′)	86.6(5)	C(15)–C(16)–N(4)	127(1)
C(7)–Sn(1)–N(1)	94.2(4)	N(1)–C(16)–N(4)	109(1)
C(7)–Sn(1)–N(4′)	91.9(5)	C(16)–N(1)–N(2)	106(1)
C(13)–Sn(1)–N(1)	85.8(4)	N(1)–N(2)–N(3)	110(1)
C(13)–Sn(1)–N(4′)	90.0(5)	N(2)–N(3)–N(4)	108(1)
N(1)–Sn(1)–N(4′)	173.8(5)	N(3)–N(4)–C(16)	108(1)
C(17)–Sn(2)–C(23)	117.7(6)	Sn(2)–C(29)–C(30)	116.1(8)
C(17)–Sn(2)–C(29)	120.3(5)	C(29)–C(30)–C(31)	116(1)
C(23)–Sn(2)–C(29)	121.9(5)	C(30)–C(31)–C(32)	112(1)
C(19)–Sn(2)–N(5)	90.4(5)	C(31)–C(32)–N(5)	124(1)
C(17)–Sn(2)–N(8′)	88.6(6)	C(31)–C(32)–N(8)	125(1)
C(23)–Sn(2)–N(5)	95.0(4)	N(5)–C(32)–N(8)	111(1)
C(23)–Sn(2)–N(8′)	90.5(5)	C(32)–N(5)–N(6)	107(1)
C(29)–Sn(2)–N(5)	87.4(4)	N(5)–N(6)–N(7)	108(1)
C(29)–Sn(2)–N(8′)	88.1(5)	N(6)–N(7)–N(8)	109(1)
N(5)–Sn(2)–N(8′)	174.1(5)	N(7)–N(8)–C(32)	104(1)

pared using the methodology of ref. 5, by heating $SnBu_3(N_3)$ and but-2-enenitrile at 100 °C for 4 h. Vacuum distillation of the crude product yielded pure compound **22** (45%), b.p. 224 °C (0.3 mmHg) [Found (Calc. for $C_{16}H_{32}N_4Sn$): C, 47.9 (48.1); H, 8.10 (8.10); N, 14.45 (14.05)%]. NMR: ^{1}H, δ 0.68–1.27 (m, 27 H, C_4H_9Sn), 1.70 (s, 3 H, CH_3), 5.90 (m, 1 H, CH) and 6.70 (d, 1 H, CH); ^{13}C, δ 18.5, 28.0, 26.8, 13.4 ($C^{1-4}H_9Sn$) and 160.5 (CN_4); ^{119}Sn, δ −65.4. Mössbauer: i.s. = 1.23, q.s. = 3.44 mm s^{-1}.

5-(6-*Methyl*-2-*pyridyl*)-2-(*tributylstannyl*)*tetrazole* **23**. This was prepared using the methodology of ref. 5, by heating $SnBu_3(N_3)$ and 2-cyano-6-methylpyridine at 120 °C for 2 h. Recrystallisation from acetonitrile yielded pure compound **23** as white needles (71%), m.p. 217 °C [Found (Calc. for $C_{19}H_{33}N_5Sn$): C, 50.7 (50.7); H, 7.35 (7.40); N, 15.55 (15.55)%]. NMR: ^{1}H, δ 0.81–1.76 (m, 27 H, C_4H_9Sn), 2.7 (s, 3 H, CH_3) and 7.25–8.14 (m, 3 H, C_5H_3N); ^{13}C, δ 18.4, 28.6, 27.5, 13.8 ($C^{1-4}H_9Sn$), 24.0 (CH_3), 157.8, 124.0, 137.2, 120.0, 146.3 (C^{2-6} of pyridyl) and 160.5 (CN_4); ^{119}Sn, δ −55.5. Mössbauer: i.s. = 1.49, q.s. = 3.69 mm s^{-1}.

X-Ray Crystallography for Compound **6**.—*Crystal data*. $C_{16}H_{16}N_4Sn$, M = 383.0, monoclinic, space group $P2_1/c$, a = 14.544(3), b = 13.267(7), c = 17.147(4) Å, β = 109.63(1)°, Z = 8 (two molecules per asymmetric unit), U = 3116.4 Å^3, D_c = 1.63 g cm^{-3}, λ(Mo-Kα) = 0.710 69 Å, μ(Mo-Kα) = 15.01 cm^{-1}, F(000) = 1520.

Crystals were grown by slow crystallisation from MeOH–CS_2 (10:1); one of approximate dimensions 0.38 × 0.20 × 0.20 mm was used for data collection. Data were collected in the range 2 < θ < 22° (h 0–15, k 0–14, l −18 to 18) at room temperature on a Hilger and Watts Y290 automatic four-circle diffractometer. Unit-cell dimensions were based on 12 accurately centred reflections with θ > 15°. A monitor reflection measured at 75 min intervals showed no systematic decay in intensity. 4365 Reflections were collected, of which 3384 were unique and of these 2844 were considered as observed [I > 3σ(I)]. Data were corrected for Lorentz and polarisation effects, and also for absorption (maximum, minimum transmission factors 1.09 and 0.95).[26] The structure was solved by conventional Patterson and Fourier methods.[27,28] Structure factors were taken from the usual sources.[29–31] In the refinement procedure the atoms were treated as two independent blocks, corresponding to the two molecules of the asymmetric unit. In the final cycles of refinement all the non-hydrogen atoms were treated anisotropically, save for C(16) which behaved unacceptably and was restrained to isotropic behaviour. Hydrogen atoms were included at fixed, calculated positions (C–H 96 pm), and refined with a common isotropic thermal parameter (0.098 Å^2). Final R = 0.0484 for unit weights and 191 or 187 variable parameters (for the two blocks, respectively), maximum shift/e.s.d. = 0.017, residual electron-density maxima and minima 0.36, −0.50 e Å^{-3}, respectively.

Final fractional atomic coordinates are given in Table 1, with selected bond distances and angles in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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