Sterically Hindered Organotin Compounds. Part 1. Synthesis and Reaction Chemistry of Tris(trimethylsilyl)methyltin(IV) Derivatives. *X*-Ray Crystal Structures of $Sn(CH_2Ph)_2[C(SiMe_3)_3](OSiMe_3)$ and $Sn(CH_2Ph)_2[C(SiMe_3)_3]$-$[CH_2CH{=}C(SiMe_3)_2]$†

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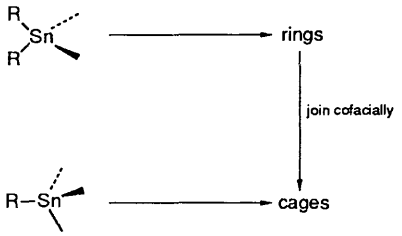
Halogen cleavage reactions of SnR_nPh_{4-n} have been explored as routes to sterically hindered organotin halides SnR_nX_{4-n} [R = hindered alkyl group: Pr^i, CH_2CMe_2Ph, or $C(SiMe_3)_3$; $n = 1$ or 2]. While the method works well for simple alkyl groups reaction of X_2 (X = Cl or Br) with $Sn[C(SiMe_3)_3]Ph_3$ usually forms $Sn[C(SiMe_3)_3]PhX_2$. The compound $Sn[C(SiMe_3)_3]X_3$ can be formed when $FeBr_3$ is added as catalyst. Reaction of $Sn(CH_2Ph)_2[C(SiMe_3)_3]Cl$ with Br_2 yields $Sn(CH_2C_6H_4Br\text{-}p)_2[C(SiMe_3)_3]Br$, while the same compound in reaction with aqueous HBr yields both $Sn(CH_2Ph)_2[C(SiMe_3)_3](OSiMe_3)$ and $Sn(CH_2Ph)_2[C(SiMe_3)_3][CH_2CH{=}C(SiMe_3)_2]$. The identity of the latter two compounds has been confirmed by *X*-ray crystallography.

While host-guest chemistry is currently enjoying a period of intense research activity, comparatively little attention has been focused on the development of new host materials[1] in contrast to the plethora of studies centred on the inclusion of organic, inorganic, and organometallic species into known porous solids.[2–4] Our interest in the solid-state chemistry of organotin compounds, built up in part through attempts to develop Mössbauer spectroscopy as a structural probe of lattice as well as molecular structure,[5] is currently targeted towards the controlled synthesis of new porous solids containing metallic elements.

The methodology we are following has three components. First, the controlled synthesis of ring and cage compounds of both defined and tailorable size. The cofacial fusion of rings can be used as a route to new cages, while the cages themselves will be the macromolecular building blocks for the novel porous solids. Stages two and three require the introduction of functional groups onto the periphery of the cage, and the subsequent linking of cages into a three dimensional network. Pore size will be determined by the way cages link through a limited number of bridging groups (functionalities). This philosophy has been described recently by others, notably the elegant synthesis of ruthenium-based building blocks by Fagan *et al.*[6]

In our work, di- and mono-organotin species act as the precursors to ring and cage compounds, respectively (see below). Recent work by Holmes[7] and by Puff and Reuter[8] has demonstrated the wealth of diverse cage structures that can be developed from mono-organotin precursors. These compounds, usually the products of the controlled hydrolysis of organotin halides but also more rationally from organostannoic acids, complement well characterised tin–sulphur cages of adamantane structure[9] and less well authenticated tin(IV) cubanes such as $(PhSnP)_4$.[10] We have focused on two aspects of organotin chemistry that we hope will enable the controlled assembly of new organometallic cages. First, we aim to use sterically hindered organotin halides as synthetic precursors, a strategy which has already proved fruitful in, for example, the isolation of oligomeric di-organotin oxides.[11] Secondly, we aim to combine the tendency of tin–sulphur compounds to form cages (see above) with the generally polymeric nature of organotin oxides,[12] to form mixed organotin–oxide–sulphides in which both intra- and inter-molecular linkages are fostered. We have recently reported the first synthesis of a four-membered 1,3-oxathia-2,4-distannetane ring system.[13] In this paper we report our work on the synthesis of highly hindered monoalkyltin halides, primarily those containing the bulky ligand tris(trimethylsilyl)methyl $[C(SiMe_3)_3]$ which we propose to use in future aspects of cage construction.[14]



Results and Discussion

The most commonly adopted preparation of organotin halides is the Kocheskov redistribution of a tetraorganotin and tin(IV) chloride,[15] in a stoicheiometry designed to maximise the yield of either tri-, di-, or mono-organotin product. The tetraorganotin can itself be synthesised from an excess of Grignard reagent and $SnCl_4$, thereby eliminating products which are less than fully alkylated. However, the synthesis of organotin halides which incorporate sterically demanding hydrocarbon groups is complicated by the difficulty in synthesising SnR_4 *cleanly and in good yield*, due to the steric congestion in compounds of this type, The compound $SnPr^i_4$ is obtained in 61% yield by the above method,[16] but increasing the steric bulk to even the modestly hindered $Sn(CH_2CMe_2Ph)_4$ reduces this yield dramatically.[17] In such cases, and in reactions involving stoicheiometric addition of carbanion to $SnCl_4$, a variety of

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† Dibenzyl(trimethylsiloxy)[tris(trimethylsilyl)methyl]stannane and 3-{dibenzyl[tris(trimethylsilyl)methyl]stannyl}-1,1-bis(trimethylsilyl)prop-1-ene respectively.

Supplementary data available (No. SUP 56784, 10 pp.): complete spectroscopic data (i.r., n.m.r., Mössbauer, and mass spectra) for the organotin compounds. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

products is obtained, from which isolation of a single, pure product is often difficult or of low yield. Equations (1)—(3) exemplify these situations.[16,17]

$$\mathrm{LiPr^i(excess) + SnCl_4 \longrightarrow \underset{(61\%)}{SnPr^i_4}} \quad (1)$$

$$\mathrm{Mg(CH_2CMe_2Ph)Br(excess) + SnCl_4 \longrightarrow \underset{(8\%)}{Sn(CH_2CMe_2Ph)_4} + \underset{(44\%)}{Sn(CH_2CMe_2Ph)_3Cl}} \quad (2)$$

$$\mathrm{3LiPr^i + SnCl_4 \longrightarrow SnPr^i_4 + SnPr^i_2Cl_2 + SnPr^iCl_3} \quad (3)$$

(approximately equal amounts)

The stoicheiometric reaction of carbanion and tin(IV) halide is, however, not without its merits in synthesising hindered organotin halides, provided that one partially alkylated product is dominant, either due to steric factors and/or the instability of other reaction products. This is most clearly evident in the reaction of 2 equivalents of $\mathrm{MgBu^tCl}$ with $\mathrm{SnCl_4}$, to yield $\mathrm{SnBu^t_2Cl_2}$ cleanly if in only 36% yield[18] (similar results were obtained using $\mathrm{LiBu^t}$[16]). The steric crowding in $\mathrm{SnBu^t_3Cl}$ on the one hand and the instability of $\mathrm{SnBu^tCl_3}$ with respect to disproportionation into $\mathrm{SnCl_2}$ and $\mathrm{Bu^tCl}$ on the other,[19] clearly influence the success of this synthesis.

Selective Halogen Cleavage Reactions.—We have found that selective halogen cleavage from an accessible tetraorganotin is a preferred route to many hindered alkyltin halides. Thus, a phenyltin halide is used as reaction precursor, in which the aryl groups are used to restrict the number of hindered alkyl groups which can be introduced into the molecule, whilst affording a sterically realisable intermediate by virtue of the planarity of the aryl groups and the presence of only a limited number of bulky alkyl moieties. Selective halogen cleavage of the more labile phenyl groups from this tetraorganotin is essentially quantitative, and after removal of aryl halides *in vacuo* the required hindered organotin halide remains, often analytically pure before purification and in good yield. The general methodology is shown in equations (4) and (5) (X = halogen, usually Br;

$$\mathrm{SnPh_{4-\mathit{n}}X_\mathit{n} + MgRX(excess) \longrightarrow SnPh_{4-\mathit{n}}R_\mathit{n} + \mathit{n}\,MgX_2} \quad (4)$$

$$\mathrm{SnPh_{4-\mathit{n}}R_\mathit{n} + (4-\mathit{n})\,X_2 \longrightarrow SnR_\mathit{n}X_{4-\mathit{n}} + (4-\mathit{n})\,PhX} \quad (5)$$

n = 1 or 2). Using this reaction sequence, we have synthesised $\mathrm{SnPr^i_2Br_2}$, $\mathrm{SnPr^iBr_3}$, and $\mathrm{Sn(CH_2CMe_2Ph)_2Br_2}$ in overall yields based upon $\mathrm{SnPh_{4-\mathit{n}}X_\mathit{n}}$ of 78, 75, and 45% respectively.

Direct Synthesis of $\mathrm{Sn[C(SiMe_3)_3]X_3}$ (X = *halogen*).—We were attracted to the tris(trimethylsilyl)methyl group as a suitably bulky entity for both stabilising and solubilising mono-organotin cages. A limited number of reports of organotin compounds containing this ligand have appeared,[20–23] one of which[20] describes the synthesis of $\mathrm{Sn[C(SiMe_3)_3]X_3}$ (X = Cl or Br) by both halogen cleavage of $\mathrm{Sn[C(SiMe_3)_3]R_3}$ and 1:1 reaction of carbanion and $\mathrm{SnCl_4}$, although the spectra reported raise questions concerning the efficiency of the syntheses and the nature of the products.

Molecular models indicate that compounds containing two (or more) $\mathrm{C(SiMe_3)_3}$ ligands bound to tin will suffer severe steric crowding, to the extent that substitution of halide in $\mathrm{SnCl_4}$ by the carbanion of $\mathrm{CH(SiMe_3)_3}$ should not readily proceed beyond a single halogen. However, although Glockling *et al.*[20] have reported the synthesis of an analytically pure sample of $\mathrm{Sn[C(SiMe_3)_3]Cl_3}$ by this method, the presence of three resonances in the ^{1}H n.m.r. spectrum of the product suggests that the synthesis is not without its complications. In our hands, 1:1 reaction of $\mathrm{Li[C(SiMe_3)_3]}$ with anhydrous $\mathrm{SnBr_4}$ yields a white crystalline product which exhibits three signals in both the ^{1}H and ^{13}C n.m.r. spectra and which can, after repeated recrystallisation, be separated into two components each of *ca.* 90% purity by n.m.r. analysis. Each compound shows only one major peak in both the respective n.m.r. spectra indicating only one type of $\mathrm{C(SiMe_3)_3}$ group. Tin-119 n.m.r. (δ −236.9 p.p.m.) and Mössbauer spectroscopies [isomer shift (i.s.) = 1.36, quadrupole splitting (q.s.) = 1.55 mm s^{-1}] identify one product as the desired $\mathrm{Sn[C(SiMe_3)_3]Br_3}$, while the other does not contain tin and is almost certainly $\mathrm{C(SiMe_3)_3Br}$ from its elemental analysis [equation (6)]. The origin of $\mathrm{C(SiMe_3)_3Br}$ as a reaction product could come either from lithium–bromine exchange between the reactants, or by reductive elimination from $\mathrm{Sn[C(SiMe_3)_3]Br_3}$ in a manner analogous to that described above for $\mathrm{SnBu^tCl_3}$. We have made no attempt to establish the formation of $\mathrm{SnBr_2}$ as a reaction product, although it is entirely possible that this compound was present in the inorganic residues removed during work-up of the reaction.

$$\mathrm{CH(SiMe_3)_3 \xrightarrow[(\mathit{ii})\ SnBr_4]{(\mathit{i})\ LiMe} Sn[C(SiMe_3)_3]Br_3 + C(SiMe_3)_3Br} \quad (6)$$

The nature and fate of the third, very minor product which gives rise to the remaining n.m.r. signal in the crude product mixture has not been ascertained.

Halogen Cleavage Reactions of $\mathrm{Sn[C(SiMe_3)_3]Ph_3}$.—Given the success of other selective halogen cleavage reactions as a route to hindered organotin halides as described above, and the complexity of the direct synthesis of $\mathrm{Sn[C(SiMe_3)_3]Br_3}$ outlined previously, we have sought to prepare the latter *via* $\mathrm{Sn[C(SiMe_3)_3]Ph_3}$. This tetraorganotin is easily prepared by the method of Glockling *et al.*[20] [equation (7)], though we find that significant amounts of $\mathrm{Sn_2Ph_6}$ are also formed in the reaction, presumably through initial *trans*-metallation of the organolithium reagent followed by coupling between $\mathrm{SnPh_3Cl}$ and $\mathrm{LiSnPh_3}$. In practice, we found it better to react this mixture further, separating secondary reaction products at a later stage. Cleavage of $\mathrm{Sn[C(SiMe_3)_3]Ph_3}$ by 3 equivalents of $\mathrm{Br_2}$ however, yields only $\mathrm{Sn[C(SiMe_3)_3]PhBr_2}$, and even using the smaller, more reactive halogen, chlorine, still only yielded the dihalide [equation (8), X = Cl or Br], though others have successfully completed the cleavage sequence on an n.m.r. scale.[20] Some success in completing the cleavage of aryl groups from tin was achieved when $\mathrm{FeBr_3}$ was added as catalyst, although the reaction was poorly reproducible at a 3.4 mmol scale, and was never successful when larger quantities of reagent were used. This reaction is further complicated by the choice of solvent. In an early reaction, $\mathrm{CCl_4}$ was used to dilute the added bromine, and the reaction products were found to contain a mix of combinations of Cl/Br trihalides [equation (9)]. The

$$\mathrm{CH(SiMe_3)_3 \xrightarrow[(\mathit{ii})\ SnPh_3Cl]{(\mathit{i})\ LiMe} Sn[C(SiMe_3)_3]Ph_3 + Ph_3SnSnPh_3 + LiCl} \quad (7)$$

$$\mathrm{Sn[C(SiMe_3)_3]Ph_3 + 2\,X_2 \longrightarrow Sn[C(SiMe_3)_3]PhX_2 + 2\,PhX} \quad (8)$$

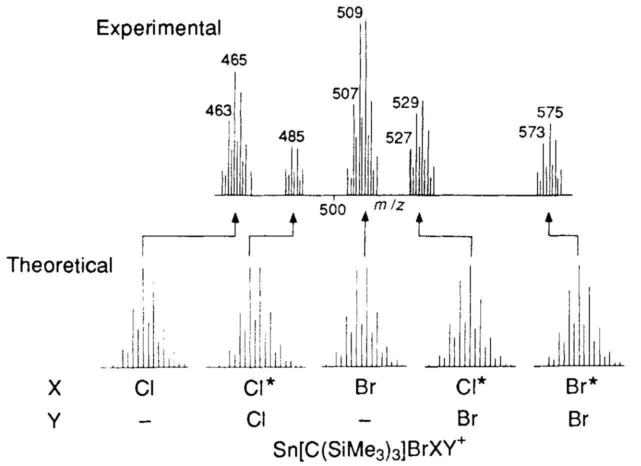


Figure 1. Comparison of theoretical and observed high mass fragment abundances in the electron-impact (e.i.) mass spectrum of the mixture resulting from Br_2 cleavage of $Sn[C(SiMe_3)_3]Ph_3$ in the presence of $FeBr_3$ and CCl_4. * $M - CH_3$

$$\mathrm{Sn[C(SiMe_3)_3]Ph_3 + 3Br_2 \xrightarrow{FeBr_3-CCl_4} \underset{\delta(^{119}Sn)\ -237.1}{Sn[C(SiMe_3)_3]Br_3} + \underset{\delta(^{119}Sn)\ -167.9}{Sn[C(SiMe_3)_3]Br_2Cl} + \underset{\delta(^{119}Sn)\ -100.5}{Sn[C(SiMe_3)_3]BrCl_2}} \quad (9)$$

compound $Sn[C(SiMe_3)_3]Br_3$ was identified by comparison of its ^{119}Sn chemical shift with that of an authentic sample (see above). The geometric progression in chemical shifts for the remaining spectral resonances strongly suggests a series of systematic substitutions within a common molecular type, and the mixed halide nature resulting from these substitutions is further confirmed by the isotopic abundances of high mass fragments in the mass spectrum of the mixture (Figure 1). Chemical analysis of the mixture agrees well with a weighted combination of the three components (49 : 41 : 10 for the tri-, di-, and mono-bromide, respectively) based upon ^{119}Sn spectral intensities and assuming identical relaxation times.

The compounds $Sn[C(SiMe_3)_3]X_3$ (X = Ph, Cl, or Br) have been reported previously,[20] but are fully characterised by spectroscopic methods for the first time in this paper.

Halogen Cleavage Reactions of $Sn(CH_2Ph)_2[C(SiMe_3)_3]Cl$.—In order to improve the efficiency of the synthesis of $Sn[C(SiMe_3)_3]X_3$ by selective halogen cleavage from $Sn[C(SiMe_3)_3]R_3$ we have investigated the reaction of halogens with benzyl-substituted tin compounds. We reasoned that while the benzyl moiety is known to be a good leaving group from tin with similar reactivity to Ph,[24] the relief in steric crowding about the central metal arising from the introduction of flexible methylene groups into the ligands would enhance the facility for total cleavage of labile hydrocarbons. The compound $Sn(CH_2Ph)_2[C(SiMe_3)_3]Cl$ was synthesised from the 1:1 reaction of $[C(SiMe_3)_3]^-$ and $Sn(CH_2Ph)_2Cl_2$ [equation (10)].

$$\mathrm{CH(SiMe_3)_3 \xrightarrow[(ii)\ Sn(CH_2Ph)_2Cl_2]{(i)\ LiMe} Sn(CH_2Ph)_2[C(SiMe_3)_3]Cl + LiCl} \quad (10)$$

In the product, the methylene protons of the benzyl groups appear as an AB quartet with calculated chemical shifts of δ 2.83 and 2.89, and J = 12 Hz.

When $Sn(CH_2Ph)_2[C(SiMe_3)_3]Cl$ was treated with an excess of Br_2, remarkably, no cleavage of benzyl groups occurred. Instead, the aromatic rings were substituted in the *para* position, along with halogen exchange between bromine and chlorine at tin [equation (11), X = Cl or Br]. In the substituted

$$\mathrm{Sn(CH_2Ph)_2[C(SiMe_3)_3]Cl + Br_2(excess) \longrightarrow Sn(CH_2C_6H_4Br\text{-}\mathit{p})_2[C(SiMe_3)_3]Br + 2\,HX} \quad (11)$$

product, the methylene protons remain as an AB quartet (δ 2.69 and 2.75, J = 12 Hz), while the aromatic protons simplify to two doublets specifying a *para*-substituted system.

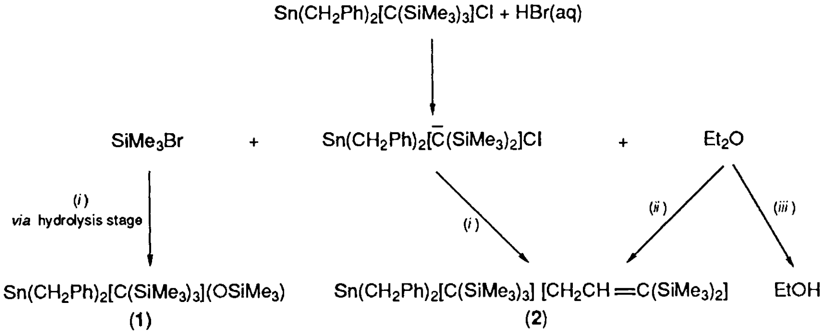
Electrophilic substitution in benzyltin compounds is known to be enhanced by σ–π conjugation between Sn–C and C=C bonds, with enhancement at a maximum when the dihedral angle between the two components is 90°,[25] albeit that MNDO calculations suggest that at this dihedral angle the energy of the molecule is lowered primarily from a reduction in steric hindrance about the double bond, with only a small contribution from σ–π conjugation.[26] It is of interest, however, to observe that despite the steric congestion in molecules containing the $C(SiMe_3)_3$ ligand which can induce angular distortions away from this ideal {see below, torsional angles involving the propenyl moiety in $Sn(CH_2Ph)_2[C(SiMe_3)_3][CH_2CH{=}C(SiMe_3)_2]$ (**2**)} the dihedral angles between Sn–C and Ph–CH_2 in the Sn–CH_2Ph parts of both $Sn(CH_2Ph)_2[C(SiMe_3)_3](OSiMe_3)$ (**1**) and (**2**) lie in the range 96.3—85.1°. This conjugation makes the R_3SnCH_2 group a better donor than either Me or OMe[27] and *ortho-*, *para*-directing by stabilisation of the intermediate carbonium ion.[28,29] It is clear that in the bromination of $Sn(CH_2Ph)_2[C(SiMe_3)_3]Cl$ steric hindrance within the molecule not only directs the incoming electrophile towards the *para* position exclusively, but also prevents the subsequent nucleophile (Br^-) from reaching the tin (and hence the normal cleavage reaction at the Sn–C bond), thus requiring the proton to be eliminated. It is somewhat contradictory then that Cl/Br exchange at tin accompanies the electrophilic substitution reaction. We can only surmise that the nucleophilic attack at the *para* position of the aromatic ring is much faster than at tin, and that halide exchange is a kinetically much slower process.

It has also been noted that reaction of Br_2 with $Sn(CH_2CMe_2Ph)_4$ does not lead to cleavage of any tin–carbon bonds, and that some bromination of the aromatic rings occurs, but no reaction products were isolated and characterised.[17]

As molecular bromine only results in electrophilic attack at the periphery of the molecule, it was decided to compare the use of aqueous HBr, in the hope that this would promote nucleophilic attack of halide ion at the metal. However, this proved not to be the case, though the reaction course is unique in the products it generates. In addition to some unreacted starting material, two other products [(**1**) and (**2**)] were isolated from the reaction mixture [equation (12)]. Both products have

$$\mathrm{Sn(CH_2Ph)_2[C(SiMe_3)_3]Cl + HBr \xrightarrow{Et_2O-H_2O} \underset{\mathbf{(1)}}{Sn(CH_2Ph)_2[C(SiMe_3)_3](OSiMe_3)} + \underset{\mathbf{(2)}}{Sn(CH_2Ph)_2[C(SiMe_3)_3][CH_2CH{=}C(SiMe_3)_2]}} \quad (12)$$

been identified spectroscopically and confirmed by subsequent crystallographic analysis. Compound (**1**) has the expected ^1H and ^{13}C n.m.r. spectrum, though for reasons which are not clear the methylenic protons now appear to be equivalent. In the ^{29}Si n.m.r. spectrum, two signals (δ 6.4 and −1.2 p.p.m.) are observed, both of which are accompanied by unresolved $^{117,119}Sn$ satelites (58.0 and 36.7 Hz), while the i.r. spectrum contains a strong band at 980 cm^{-1} typical of a non-bridging



Scheme. (*i*) + $Sn(CH_2Ph)_2[C(SiMe_3)_3]Cl$, (*ii*) C_2 unit extruded from Et_2O, (*iii*) elimination from Et_2O

Table 1. Crystallographic data for compounds (**1**) and (**2**)

	(**1**)	(**2**)
Crystal system	Monoclinic	Triclinic
Formula	$C_{27}H_{50}OSi_4Sn$	$C_{33}H_{62}Si_5Sn$
M	621.8	718.1
Space group	$P2_1/a$	$P\bar{1}$
Z	4	2
a/Å	17.037(3)	9.478(3)
b/Å	11.566(2)	12.932(3)
c/Å	18.423(4)	17.512(4)
α/°	90.0	98.07(1)
β/°	112.06(2)	98.26(2)
γ/°	90.0	103.39(2)
U/Å^3	3 364.8	2 032.5
D_c/g cm^{-3}	1.23	1.17
F(000)	1 552	760
λ(Mo-K_α)/Å	0.710 69	0.710 69
μ(Mo-K_α)/cm^{-1}	8.73	7.20
Crystal dimensions/mm	0.2 × 0.4 × 0.2	0.25 × 0.25 × 0.3
2θ range/°	4—44	4—44
Data collected	*h*, *k*, ±*l*	*h*, ±*k*, ±*l*
Total data	4 627	5 165
Unique data, $I > 3\sigma(I)$	2 699	3 395
Final *R*	6.85^a	8.43
Final *R*′	6.85	8.37^b
Max. shift/e.s.d.	0.002	0.03
Residual density (max., min.)/e Å^{-3}	0.36, −0.37	0.76, −0.46

^{a} Unit weights. ^{b} $w = 6.4789/[\sigma^2(F) + 0.0002(F)^2]$.

Sn–O–Si system.[30] For compound (**2**), discussion of the relevant spectroscopic data is confined to the newly formed propenyl fragment, data for the remainder of the molecule not requiring detailed analysis. The ^{1}H n.m.r. contains signals due to the two $SiMe_3$ groups attached to C(13) of the prop-1-enyl chain (δ 0.07 and 0.12), and mutually coupled signals (*J* 7.9 Hz) for the protons on C(12) (δ 6.56, t) and C(11) (δ 2.19, d). In the ^{13}C n.m.r. spectrum, signals due to C(12) and C(13) appear at δ 154.6 and 141.4 p.p.m. respectively, though surprisingly the signal due to fully substituted C(13) is almost as intense (66%) as that of protonated C(12). This is in contrast to the general observation that in related systems special pulse delays are required in the n.m.r. experiment to counteract the poor relaxation of bis-silylated olefinic carbon nuclei.[31] It is also curious that the long range ^{117,119}Sn couplings to these two carbon nuclei (^2J or ^3J) are identical.

We can, at present, only speculate on the mechanism of this unique C–C bond forming reaction. It is clear that either or both of Et_2O and H_2O are required in the reaction, as repetition of the reaction using dry HCl in CH_2Cl_2 over a 2 h period only regenerates starting materials from the work-up. An analysis of the origin of the molecular fragments present in the two final products is shown in the Scheme, though no chronology of assembly or reaction mechanism is intentionally implied. At present we favour a mechanism which involves initial nucleophilic attack by Br^- at the silicon atoms at the periphery of the molecule. This would yield $SiMe_3Br$ which, when co-hydrolysed with the starting material, will yield compound (**1**). Peripheral Br^- attack on silicon will also generate this bis-trimethylsilylated C_1 fragment which ultimately terminates the newly formed propenyl unit. As the only C_2 species involved in the reaction comes from the solvent, diethyl ether, it would seem reasonable to ascribe this as the source of the remainder of the propenyl unit in compound (**2**). Ethanol is suggested as the fate of the remainder of the solvent molecule, although we have no evidence to confirm its formation. If these suppositions are correct, then the reaction not only represents a new type of C–C bond forming reaction, but implies the facile, room-temperature cleavage of Et_2O, presumably *via* co-ordination to the Lewis acidic tin. Further comment on this reaction awaits future studies.

Crystal Structures of Compounds (**1**) *and* (**2**).—Crystallographic data for compounds (**1**) and (**2**) are given in Table 1. The structure of compound (**1**) is shown in Figure 2, along with the atomic labelling scheme used in the text. Atomic co-ordinates and pertinent bond distances and angles are given in Tables 2 and 3, respectively. The molecule has a distorted tetrahedral geometry about tin, with the two phenyl groups and the trimethylsiloxy group bending away from the hindered $C(SiMe_3)_3$ ligand *via* either the CH_2 or O units which separate them from tin. The molecule thus has something of a piano-stool appearance. The Sn–O and Si–O bond lengths are 193(1) and 163(1) pm, respectively while the Si–O–Sn angle is 159.2(7)°.

Very few structures are available in the literature for direct comparison. Harrison *et al.*[32] have reported preliminary data for $SnPh_3(OSiPh_3)$, though disorder precluded full structural analysis. However, in the corresponding lead compound the Si–O bond is 187(3) pm, with the Pb–O bond 201(3) pm, while the angle at oxygen is significantly different at 142(1)°.[32] Similarly, in another report, structural data for $[SnMe_2(OSiMe_3)]_2O$ are confined to the Sn–O–Sn part of the molecule.[33]

The molecular structure of compound (**2**) is shown in Figure 3, with atomic co-ordinates given in Table 4 and selected bond distances and angles in Table 5. The geometry about tin is that of a distorted tetrahedron, while the overall appearance of the structure is similar to that of compound (**1**) where again three of the groups bend away from the bulky $C(SiMe_3)_3$ unit. In particular, however, the structure confirms the construction of a propenyl unit bonded to tin. The C(12)–C(13) bond of 135(2) pm is typical of a C=C linkage, while the C(11)–C(12) bond [147(2) pm] also suggests some double bond character. With-

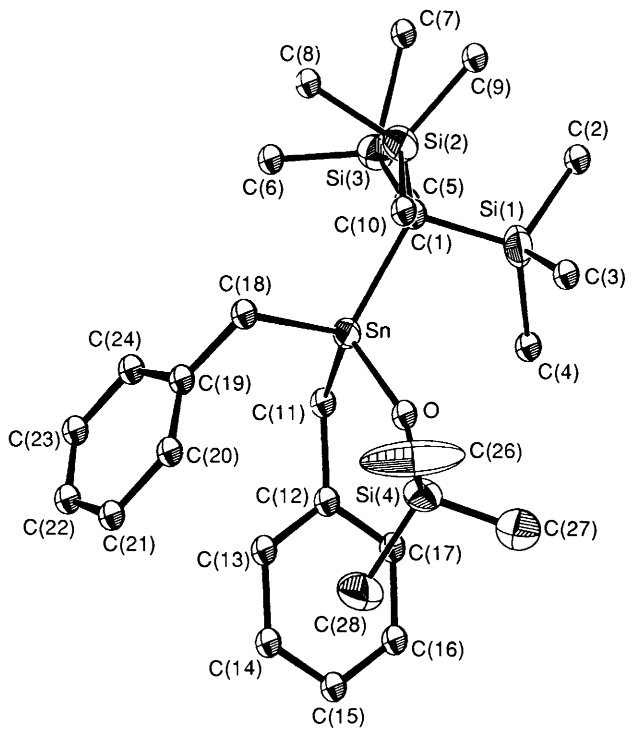


Figure 2. The molecular structure of $Sn(CH_2Ph)_2[C(SiMe_3)_3](OSiMe_3)$, showing the atom labelling scheme used in the text. Ellipsoid surfaces are of 27% probability

Table 2. Fractional atomic co-ordinates for compound (**1**) with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
Sn	0.004 21(6)	0.041 27(8)	0.220 10(6)
Si(1)	0.183 8(3)	0.067 6(4)	0.374 2(3)
Si(2)	0.037 8(3)	0.243 3(4)	0.357 4(3)
Si(3)	0.132 9(3)	0.259 9(4)	0.242 6(3)
Si(4)	−0.047 0(4)	−0.205 4(4)	0.303 9(3)
O	−0.005 0(7)	−0.093 0(9)	0.278 9(7)
C(1)	0.094 4(8)	0.156 8(12)	0.302 7(8)
C(2)	0.283 7(11)	0.150 9(17)	0.422 7(11)
C(3)	0.156 2(11)	0.001 0(16)	0.455 0(11)
C(4)	0.213 5(11)	−0.056 3(16)	0.322 8(11)
C(5)	0.184 1(11)	0.394 9(15)	0.296 2(11)
C(6)	0.047 0(10)	0.302 9(15)	0.148 5(10)
C(7)	0.213 1(11)	0.191 1(17)	0.205 6(11)
C(8)	−0.030 6(11)	0.363 7(15)	0.297 5(10)
C(9)	0.113 2(11)	0.313 3(16)	0.447 4(10)
C(10)	−0.034 4(10)	0.150 2(14)	0.388 5(10)
C(11)	0.040 4(9)	−0.023 5(13)	0.126 7(9)
C(12)	0.019 2(9)	−0.147 4(13)	0.105 9(9)
C(13)	−0.059 4(9)	−0.178 6(13)	0.051 9(9)
C(14)	−0.078 5(11)	−0.294 6(15)	0.033 1(10)
C(15)	−0.019 5(10)	−0.379 1(16)	0.065 5(10)
C(16)	0.057 6(11)	−0.349 3(17)	0.117 6(11)
C(17)	0.079 1(10)	−0.234 2(14)	0.138 1(10)
C(18)	−0.123 8(9)	0.109 2(15)	0.173 9(10)
C(19)	−0.177 7(8)	0.060 4(12)	0.094 1(8)
C(20)	−0.234 2(10)	−0.026 4(15)	0.089 0(10)
C(21)	−0.285 6(11)	−0.075 7(16)	0.015 9(11)
C(22)	−0.279 0(12)	−0.029 2(19)	−0.047 0(12)
C(23)	−0.226 7(11)	0.055 3(17)	−0.047 1(11)
C(24)	−0.175 7(10)	0.102 6(14)	0.022 6(10)
C(25)	−0.110 5(12)	−0.292 0(16)	0.217 6(11)
C(26)	−0.112 4(22)	−0.163 7(22)	0.354 6(20)
C(27)	0.033 7(19)	−0.293 4(21)	0.368 2(15)

Table 3. Bond lengths (pm) and angles (°) for compound (**1**) with e.s.d.s in parentheses

Sn–C(1)	217(1)	Sn–C(11)	217(2)
Sn–C(18)	217(2)	Si(1)–C(1)	190(1)
Si(1)–C(2)	187(2)	Si(1)–C(3)	189(2)
Si(1)–C(4)	189(2)	Si(2)–C(1)	192(1)
Si(2)–C(8)	188(2)	Si(2)–C(9)	186(2)
Si(2)–C(10)	188(2)	Si(3)–C(1)	190(2)
Si(3)–C(5)	188(2)	Si(3)–C(6)	187(2)
Si(3)–C(7)	191(2)	Si(4)–O	163(1)
Si(4)–C(25)	185(2)	Sn–O	193(1)
Si(4)–C(27)	176(2)	Si(4)–C(26)	177(2)
C(1)–Sn–O	106.7(5)	C(11)–Sn–Si(3)	89.5(4)
C(18)–Sn–O	103.3(6)	C(11)–Sn–O	105.9(5)
C(18)–Sn–C(1)	113.3(6)	C(18)–Sn–C(11)	111.0(6)
Si(4)–O–Sn(1)	159.2(7)	C(12)–C(11)–Sn	115(1)
C(19)–C(18)–Sn	113(1)		

Table 4. Fractional atomic co-ordinates for compound (**2**) with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Sn	0.250 66(12)	0.140 57(8)	0.218 36(6)
Si(1)	0.134 9(9)	−0.128 7(5)	0.193 9(4)
Si(2)	0.226 2(8)	−0.001 5(5)	0.363 5(4)
Si(3)	−0.064 4(9)	0.008 8(6)	0.260 4(6)
Si(4)	0.725 9(5)	0.461 9(4)	0.404 3(3)
Si(5)	0.476 9(6)	0.557 7(4)	0.312 3(3)
C(1)	0.330 5(24)	−0.164 3(17)	0.226 1(16)
C(2)	0.131 1(22)	−0.117 7(15)	0.090 7(9)
C(3)	−0.001 5(23)	−0.252 6(13)	0.200 8(13)
C(4)	0.165 5(33)	0.107 5(17)	0.438 9(11)
C(5)	0.170 4(26)	−0.129 6(15)	0.401 1(11)
C(6)	0.419 7(24)	0.046 0(17)	0.384 9(12)
C(7)	−0.083 2(22)	0.145 4(15)	0.280 6(13)
C(8)	−0.165 3(25)	−0.073 9(17)	0.324 9(14)
C(9)	−0.184 8(21)	−0.051 6(20)	0.151 8(13)
C(10)	0.130 1(17)	−0.002 3(11)	0.263 1(8)
C(11)	0.294 3(17)	0.295 0(10)	0.298 8(9)
C(12)	0.445 1(18)	0.339 9(11)	0.341 8(8)
C(13)	0.536 8(18)	0.439 2(12)	0.349 5(8)
C(14)	0.762 3(25)	0.556 4(16)	0.498 7(11)
C(15)	0.758 9(25)	0.334 6(15)	0.430 9(13)
C(16)	0.861 3(24)	0.508 5(21)	0.343 7(13)
C(17)	0.527 7(25)	0.570 2(18)	0.214 5(11)
C(18)	0.567 5(25)	0.685 9(14)	0.381 6(13)
C(19)	0.276 1(21)	0.551 1(15)	0.302 7(14)
C(20)	0.469 2(18)	0.121 0(14)	0.194 4(10)
C(21)	0.516 2(19)	0.179 6(14)	0.131 6(10)
C(22)	0.487 8(22)	0.127 2(16)	0.056 2(11)
C(23)	0.532 9(22)	0.180 1(16)	−0.004 8(12)
C(24)	0.605 0(23)	0.287 2(16)	0.012 9(12)
C(25)	0.632 4(24)	0.341 4(18)	0.087 0(12)
C(26)	0.594 3(22)	0.289 9(15)	0.148 8(12)
C(27)	0.119 8(21)	0.152 2(13)	0.106 8(8)
C(28)	0.129 7(19)	0.267 1(13)	0.093 4(9)
C(29)	0.036 7(23)	0.320 7(15)	0.117 1(10)
C(30)	0.042 1(25)	0.428 1(17)	0.103 1(12)
C(31)	0.143 8(24)	0.473 3(18)	0.063 2(12)
C(32)	0.236 7(27)	0.420 8(18)	0.038 7(13)
C(33)	0.242 0(23)	0.315 9(16)	0.052 6(11)

in the propenyl moiety, C(11)—C(13), Si(4), and Si(5) are essentially co-planar (maximum out-of-plane deviation = 2.8 pm), and except for the C(11)–C(12)–C(13) angle [130(1)°] all other angles in this part of the molecule are unexceptional.

Five other allylic tin compounds have been reported for comparison. In $SnPh_3(CH_2CH{=}CH_2)$[34] the C–C bond lengths within the propenyl unit are 126(3) and 137(3) pm, both

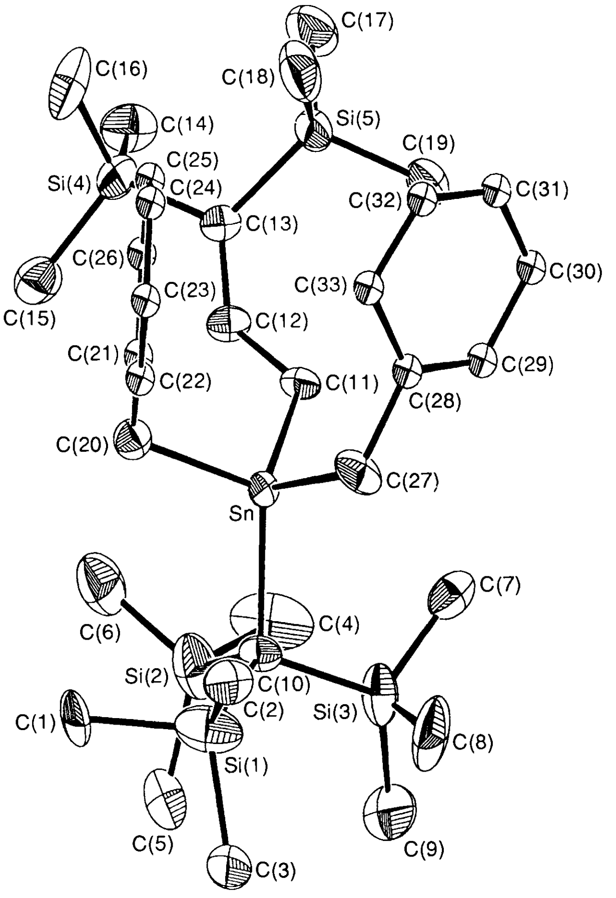


Figure 3. The molecular structure of $Sn(CH_2Ph)_2[C(SiMe_3)_3][CH_2CH{=}C(SiMe_3)_2]$, showing the atom labelling scheme used in the text. Ellipsoid surfaces are of 27% probability

Table 5. Bond lengths (pm) and angles (°) for compound (**2**) with e.s.d.s in parentheses

Sn–C(10)	224(1)	Sn–C(11)	219(1)
Sn–C(20)	224(2)	Sn–C(27)	221(1)
Si(1)–C(1)	205(2)	Si(1)–C(2)	183(2)
Si(1)–C(3)	184(2)	Si(1)–C(10)	189(1)
Si(2)–C(4)	202(2)	Si(2)–C(5)	186(2)
Si(2)–C(6)	179(2)	Si(2)–C(10)	185(2)
Si(3)–C(7)	181(2)	Si(3)–C(8)	187(2)
Si(3)–C(9)	202(2)	Si(3)–C(10)	190(2)
Si(4)–C(13)	185(2)	Si(4)–C(14)	185(2)
Si(4)–C(15)	185(2)	Si(4)–C(16)	182(2)
Si(5)–C(13)	192(2)	Si(5)–C(17)	187(2)
Si(5)–C(18)	186(2)	Si(5)–C(19)	185(2)
C(11)–C(12)	147(2)	C(12)–C(13)	135(2)

C(11)–Sn–C(10)	114.5(5)	C(20)–Sn–C(10)	110.7(6)
C(20)–Sn–C(11)	106.4(6)	C(27)–Sn–C(10)	108.9(6)
C(27)–Sn–C(11)	108.2(6)	C(27)–Sn–C(20)	107.8(6)
C(12)–C(11)–Sn	116(1)	C(13)–C(12)–C(11)	130(1)
Si(5)–C(13)–Si(4)	119.4(8)	C(12)–C(13)–Si(4)	117(1)
C(12)–C(13)–Si(5)	123(1)	C(21)–C(20)–Sn	112(1)
C(28)–C(27)–Sn	115(1)		

considerably shorter than in (**2**), while in cyclopent-2-enyltriphenyltin[35] the analogous bonds are 135(4) and 152(4) pm, both of which are comparable with compound (**2**). The bond shortening in the former case is ascribed to σ(Sn–C)—π conjugation, which is near the theoretical maximum for such an interaction[25] based upon the torsional angle between tin and the plane of the propenyl unit of either 108 or 97° depending on which of two conformers within the asymmetric unit is chosen. Analogous architectural features are apparent in 2-methylallyltriphenyltin.[36] While similar torsional angles occur in the cycloalkene derivative (111 and 92°) the authors suggest that shortening of bonds within the allylic portion of the cyclopentenyl ring by σ(Sn–C)—π conjugation is resisted in this case by increasing ring strain. However, as the ring size increases (C_6 to C_7) σ—π conjugation re-establishes itself.[37] In the case of compound (**2**), the relevant torsional angle is 130.5°, thereby reducing any σ(Sn–C)—π conjugation and resulting in normal bond lengths within the propenyl moiety. Steric factors in the molecule as a whole are the most likely cause for the observed torsional angle differences between (**2**) and the related compounds discussed.

Experimental

Spectra were recorded on the following instruments: VG 70-70E (mass spectra), JEOL GX270 (^{1}H, ^{13}C n.m.r.), JEOL GX400 (^{119}Sn n.m.r.), Perkin-Elmer 599B (i.r.). Details of the Mössbauer spectrometer and related procedures are given elsewhere.[38] N.m.r. spectra were recorded as $CDCl_3$ solutions unless stated otherwise. Chemical shifts (in p.p.m.) are relative to $SiMe_4$ (^{1}H, ^{13}C, and ^{29}Si) or $SnMe_4$ (^{119}Sn). Full spectral data, including i.r. and more detailed n.m.r. couplings are available as supplementary data (SUP56784).

Tris(trimethylsilyl)methane was prepared by the method of Merker and Scott.[39]

Syntheses.—Di-isopropyldiphenyltin, $SnPh_2Pr^i_2$. To a solution of isopropylmagnesium bromide (424 mmol) in diethyl ether (1.5 l) was added a solution of diphenyltin dichloride (145 mmol) in diethyl ether (400 cm^3). The resulting mixture was stirred for a further 2 h after addition was complete. After decomposition of the excess Grignard, inorganic salts were filtered off, the ether layer separated and dried over sodium sulphate and finally the solvent removed *in vacuo* to leave a pale yellow oil. The crude product was purified by distillation (108° C/0.2 mmHg, *ca.* 27 Pa) yielding 43.9 g (84%) of the desired product (Found: C, 60.30; H, 6.95. $C_{18}H_{24}Sn$ requires C, 60.20; H, 6.75%). N.m.r.: ^{1}H, δ 1.45 (d, 12 H, Me_2CH), 1.87 (m, 2 H, $\mathrm{Me_2C}\mathit{H}$), 7.31 and 7.49 (m, 10 H, Ph); ^3J(Me–^{117,119}Sn) 69.6, 72.9; ^{13}C, δ 15.53 ($\mathrm{Me_2}\mathit{C}\mathrm{H}$), 21.90 ($\mathit{Me}_2$CH), 128.21, 128.37, 137.35, and 139.54 p.p.m. (Ph); ^1J(CH–^{117,119}Sn) 362, 388, ^2J(Me–^{117,119}Sn) 15 Hz (unresolved); ^{119}Sn, δ −80.8 p.p.m. ^{119}Sn Mössbauer: i.s. 1.38 mm s^{-1}. Mass spectrum (e.i.): *m*/*z* 317 [$M - C_3H_7$], 275, 197, and 120.

Bis(*2-methyl-2-phenylpropyl*)*diphenyltin*, $SnPh_2(CH_2CMe_2Ph)$. In a similar manner to di-isopropyldiphenyltin above, the compound was prepared from 2-methyl-2-phenylpropylmagnesium bromide (89 mmol) and diphenyltin dichloride (29 mmol) in diethyl ether (total volume 600 cm^3). The solution was heated at reflux for 2 h to ensure complete reaction. The crude product, a pale yellow oil (11.2 g, 72%) did not distill at an oil-bath temperature of 235 °C at 0.3 mmHg (≈39 Pa) pressure, and was used without purification in further reactions (Found: C, 71.70; H, 6.85. $C_{32}H_{36}Sn$ requires C, 71.25; H, 6.75%). N.m.r.: ^{1}H, δ 1.23 (s, 12 H, $\mathrm{Ph}\mathit{Me}_2$C), 1.54 (s, 4 H, CH_2), and 7.16 (m, 20 H, Ph); ^2J(CH_2–^{117,119}Sn) 52.8 (unresolved); ^{13}C, δ 31.59 (CH_2), 32.73, 37.85 ($\mathrm{Ph}\mathit{Me}_2$C), 125.17, 125.39, 127.83, 127.96, 136.58, 141.42, and 150.82 p.p.m. (Ph and C*Ph*); ^1J(CH_2–^{117,119}Sn) 348, 364, ^3J(Me–^{117,119}Sn) 37.5 and 17.6 Hz (unresolved); ^{119}Sn, δ −97.5 p.p.m. ^{119}Sn Mössbauer: i.s. 1.34 mm s^{-1}. Mass spectrum (e.i.): *m*/*z* 463 [M − Ph], 407 [$M - CH_2CMe_2Ph$], 352, 133, and 119.

Di-isopropyltin dibromide, $SnPr^i_2Br_2$. A solution of bromine

(37.39 g, 234 mmol) in chloroform (200 cm^3) was added to a stirred solution of di-isopropyldiphenyltin (42.67 g, 117 mmol), also in chloroform (200 cm^3) at room temperature. Stirring was continued for a total of 18 h, during which time the colouration due to bromine had disappeared. The solvent was removed *in vacuo* to leave a pale orange oil. Fractional distillation [0.18 mmHg ($\approx$24 Pa)] yielded first phenyl bromide then di-isopropyltin dibromide (b.p. 46—48 °C; 39.8 g, 93%) (Found: C, 19.90; H, 3.95. $C_6H_{14}Br_2Sn$ requires C, 19.75; H, 3.85%). N.m.r.: ^1H, δ 1.46 (d, 12 H, Me_2CH) and 2.31 (m, 2 H, Me_2CH); $^3J(Me-^{117,119}Sn)$ 124.3, 130.0 Hz; ^{13}C, δ 20.33 (Me_2CH) and 31.37 p.p.m. (Me_2CH); ^{119}Sn, δ 95.2 p.p.m. ^{119}Sn Mössbauer: i.s. 1.69 mm s^{-1}; q.s. 3.41 mm s^{-1}. Mass spectrum (e.i.): *m/z* 364 [*M*], 321 [$M - C_3H_7$], 285 [*M* − Br], 242, 199, and 120.

Bis(2-methyl-2-phenylpropyl)tin dibromide, $Sn(CH_2CMe_2Ph)_2Br_2$. By a similar procedure, bis(2-methyl-2-phenylpropyl)diphenyltin (16.30 g, 30 mmol) and bromine (9.75 g, 61 mmol) were stirred in chloroform (150 cm^3) for 6 h, to yield the product (10.1 g, 62%) as an analytically pure oil which could not be distilled under vacuum using an oil-bath (Found: C, 43.80; H, 4.85. $C_{20}H_{26}Br_2Sn$ requires C, 44.10; H, 4.80%). N.m.r.: ^1H, δ 1.38 (s, 12 H, PhMe_2C), 1.96 (s, 4 H, CH_2), and 7.26 (m, 10 H, Ph); $^2J(CH_2-^{117,119}Sn)$ 53.1 (unresolved); ^{13}C, δ 31.66 and 38.44 (PhMe_2C), 47.13 (CH_2), 125.01, 126.43, 128.61, and 148.88 p.p.m. (Ph); $^1J(CH_2-^{117,119}Sn)$ 380, 395, $^3J(Me-^{117,119}Sn)$ 35 and 25 Hz (unresolved); ^{119}Sn, δ 22.8 p.p.m. ^{119}Sn Mössbauer: i.s. 1.54 mm s^{-1}, q.s. 2.72 mm s^{-1}. Mass spectrum (e.i.): *m/z* 465 [*M* − Br], 411 [$M - CH_2CMe_2Ph$], and 133.

Isopropyltriphenyltin, $SnPh_3Pr^i$. Triphenyltin chloride (40.09 g, 104 mmol) in dry tetrahydrofuran (thf) (120 cm^3) was added dropwise to a room-temperature suspension of ultrasound-cleaned lithium shot (3.60 g, 519 mmol) also in thf (120 cm^3). After stirring for 20 h any remaining lithium was removed by anaerobic filtration through a glass wool plug. The dark green solution of $LiSnPh_3$ was then added to a solution of isopropyl bromide (12.79 g, 104 mmol) in thf (120 cm^3) at room temperature and the mixture stirred for a further 3 h, during which time the solution darkened in colour. After removal of the solvent *in vacuo*, the resulting black oil was partitioned between a diethyl ether–water mixture, the ether layer separated and dried (anhydrous sodium sulphate), from which an off-white solid resulted after evaporation of the solvent. The crude material was recrystallised from chloroform–ethanol to yield 33.4 g (82%) of product (m.p. 81—82 °C) (Found: C, 64.30; H, 5.60. $C_{21}H_{22}Sn$ requires C, 64.15; H, 5.65%). N.m.r.: ^1H, δ 1.45 (d, 6 H, Me_2CH), 2.07 (m, 1 H, Me_2CH), and 7.32 and 7.54 (m, 15 H, Ph); $^3J(Me-^{117,119}Sn)$ 77.5, 80.2; ^{13}C, δ 16.74 (Me_2CH), 21.73 (Me_2CH), 128.44, 128.77, 137.36, and 138.82 p.p.m. (Ph); $^2J(Me-^{117,119}Sn)$ 17.6 Hz (unresolved); ^{119}Sn, δ −105.1 p.p.m. ^{119}Sn Mössbauer: i.s. 1.22 mm s^{-1}.

Isopropyltin tribromide, $SnPr^iBr_3$. Bromine (115 mmol) and isopropyltriphenyltin (38 mmol) reacted in a manner similar to that previously described, yielded the required product (14.0 g, 91%) as an oil [b.p. 43 °C at 0.3 mmHg ($\approx$39 Pa)] (Found: C, 9.20; H, 1.80. $C_3H_7Br_3Sn$ requires C, 9.00; H, 1.75%). N.m.r.: ^1H, δ 1.48 (d, 6 H, Me_2CH) and 2.88 (m, 1 H, Me_2CH); $^3J(Me-^{117,119}Sn)$ 215.9, 230.5; ^{13}C, δ 19.82 (Me_2CH) and 41.78 p.p.m. (Me_2CH); $^2J(Me-^{117,119}Sn)$ 41.9 Hz (unresolved); ^{119}Sn, δ −115.3 p.p.m. ^{119}Sn Mössbauer: i.s. 1.41 mm s^{-1}, q.s. 1.81 mm s^{-1}.

Triphenyl[tris(trimethylsilyl)methyl]tin, $Sn[C(SiMe_3)_3]Ph_3$. Tris(trimethylsilyl)methyl-lithium was prepared by the method of Aiube and Eaborn.[40] Triphenyltin chloride (8.48 g, 22 mmol) in dry thf (40 cm^3) was added dropwise *via* a syringe to a stirred solution of $Li[C(SiMe_3)_3]$ (25 mmol), and the whole mixture maintained under an atmosphere of dinitrogen gas. The reaction was stirred at room temperature for 15 h, then at reflux for a further 7 h, after which time solvent removal *in vacuo* yielded an orange oil. Trituration with ethanol generated an off-white solid, which was recrystallised from acetonitrile (4.2 g, 34%; m.p. 184 °C) (Found: C, 58.10; H, 7.45. $C_{28}H_{42}Si_3Sn$ requires C, 57.85; H, 7.30%). N.m.r.: ^1H, δ 0.25 (s, 27 H, $SiMe_3$), 7.31 and 7.66 (m, 15 H, Ph); $^2J(Me-^{29}Si)$ 6.2; ^{13}C, δ 6.10 ($SiMe_3$), 128.25, 128.54, 137.95, and 141.61 p.p.m. (Ph); $^3J(Me-^{117,119}Sn)$ 15.4 (unresolved), $^1J(Me-^{29}Si)$ 50.7; ^{119}Sn, δ −98.4 p.p.m.; $^2J(Sn-^{29}Si)$ 39.6 Hz. ^{119}Sn Mössbauer: i.s. 1.23 mm s^{-1}.

Phenyl[tris(trimethylsilyl)methyl]tin dibromide, $Sn[C(SiMe_3)_3]PhBr_2$. The compound $Sn[C(SiMe_3)_3]Ph_3$ (1.00 g, 1.7 mmol) and bromine (0.83 g, 5.2 mmol) were allowed to react in the usual manner. After 17 h stirring, the solution still maintained a strong colouration due to bromine. After evaporation of the solvent, the remaining red-brown slurry was washed with hexane to yield a solid, which was then purified by recrystallisation from acetonitrile to leave the required compound as a white crystalline solid (0.46 g, 45%; m.p. 191 °C) (Found: C, 33.00; H, 5.70. $C_{16}H_{32}Br_2Si_3Sn$ requires C, 32.75; H, 5.70%). N.m.r.: ^1H, δ 0.42 (s, 27 H, $SiMe_3$), 7.45 and 7.83 (m, 5 H, Ph); ^{13}C, δ 5.10 ($SiMe_3$), 23.09 (SiCSn), 129.06, 130.58, 134.77, and 143.30 p.p.m. (Ph); $^3J(Me-^{117,119}Sn)$ 26.5, $^1J(Me-^{29}Si)$ 52.9; ^{119}Sn, δ −39.5; ^{29}Si, δ 0.7 p.p.m.; $^2J(Si-^{119}Sn)$ 51.8 Hz. ^{119}Sn Mössbauer: i.s. 1.45 mm s^{-1}, q.s. 2.42 mm s^{-1}.

Phenyl[tris(trimethylsilyl)methyl]tin dichloride, $Sn[C(SiMe_3)_3]PhCl_2$. Chlorine gas was bubbled through a stirred solution containing $Sn[C(SiMe_3)_3]Ph_3$ (6.21 g) contaminated with Sn_2Ph_6 (1:1.8) in carbon tetrachloride (40 cm^3). The solution changed from yellow to red to off-white and finally back to yellow during the 3 h period of the reaction. Dinitrogen gas was then bubbled through the solution to remove any excess chlorine. Recrystallisation from methanol–ethanol of the solids remaining after solvent removal yielded colourless, needle-shaped crystals (1.35 g, 81%; m.p. 150—152 °C) (Found: C, 37.90; H, 6.55. $C_{16}H_{32}Cl_2Si_3Sn$ requires C, 38.55; H, 6.45%). N.m.r.: ^1H, δ 0.41 (s, 27 H, $SiMe_3$), 7.49 and 7.82 (m, 5 H, Ph); ^{13}C, δ 4.99 ($SiMe_3$), 32.89 (SiCSn), 129.29, 130.78, 134.67, and 143.40 p.p.m. (Ph); $^3J(Me-^{117,119}Sn)$ 26.5 (unresolved), $^1J(Me-^{29}Si)$ 72.7 Hz; ^{119}Sn, δ 17.1 p.p.m. ^{119}Sn Mössbauer: i.s. 1.36 mm s^{-1}, q.s. 2.42 mm s^{-1}.

[Tris(trimethylsilyl)methyl]tin tribromide, $Sn[C(SiMe_3)_3]Br_3$. *Method* 1. A solution of bromine (0.93 g, 5.8 mmol) in bromoform (20 cm^3) was added to a stirred slurry of $Sn[C(SiMe_3)_3]Ph_3$ (1.11 g, 1.9 mmol) and iron tribromide (0.7 g) in the same solvent (30 cm^3). After stirring for 15 h the dark brown solution was poured onto ice and extracted with bromoform. The combined bromoform washings were dried (anhydrous sodium sulphate), the solvent distilled *in vacuo* and the remaining brown slurry recrystallised from ethanol to yield a white crystalline solid (0.65 g, 58%) (Found: C, 20.85; H, 4.75. $C_{10}H_{27}Br_3Si_3Sn$ requires C, 20.35; H, 4.60%). N.m.r. (C_6D_6 solution): ^1H, δ 0.45 (s, 27 H, $SiMe_3$); ^{13}C, δ 5.02 p.p.m. ($SiMe_3$); $^3J(Me-^{117,119}Sn)$ 37.5 (unresolved), $^1J(Me-^{29}Si)$ 50.7 Hz; ^{119}Sn, δ −236.8 p.p.m. ^{119}Sn Mössbauer: i.s. 1.39 mm s^{-1}, q.s. 1.56 mm s^{-1}. Mass spectrum (e.i.): *m/z* 575 [*M* − Me], 509 [*M* − Br], 297, 231, 217, 201, and 143.

Method 2. The salt $Li[C(SiMe_3)_3]$[40] (17 mmol) in dry thf (45 cm^3) was added dropwise to a stirred solution of anhydrous tin(IV) bromide (6.80 g, 16 mmol) in dry light petroleum (b.p. 60—80 °C) maintained under an atmosphere of dinitrogen gas. A yellow oily residue formed, and the mixture was stirred for 15 h followed by heating at reflux for a further 2 h. After cooling and solvent evaporation, the remaining orange oil was triturated with ethanol, and the solid produced recrystallised from acetonitrile. Repeated recrystallisation from the same solvent yielded two distinct species. The first was identified as $Sn[C(SiMe_3)_3]Br_3$ (^{119}Sn n.m.r.: δ −236.9 p.p.m., ^{119}Sn

Mössbauer: i.s. 1.36 mm s^{-1}, q.s. 1.55 mm s^{-1}) though the compound could not be obtained analytically pure. The second product did not produce a ^{119}Sn n.m.r. resonance, but the singlet ^{1}H (δ 0.34) and ^{13}C n.m.r. spectra (δ 2.55 p.p.m.; the quaternary carbon resonance is often not observed due to poor relaxation), the latter showing coupling to ^{29}Si of magnitude suggestive of one-bond coupling (53 Hz), both indicate the presence of the $C(SiMe_3)_3$ group. On the basis of analytical data, we have assigned this compound to be $C(SiMe_3)_3Br$ (Found: C, 37.00; H, 8.85. $C_{10}H_{27}BrSi_3$ requires C, 38.55; H, 8.75%).

Other [*tris*(*trimethylsilyl*)*methyl*]*tin trihalides.* When carbon tetrachloride was used as solvent in Method 1 above, the reaction product isolated was a mixture of $Sn[C(SiMe_3)_3]Br_3$, $Sn[C(SiMe_3)_3]Br_2Cl$, and $Sn[C(SiMe_3)_3]BrCl_2$ [Found: C, 21.55; H, 5.10. Calculated value based upon ^{119}Sn n.m.r. resonance integrals (10% $C_{10}H_{27}BrCl_2Si_3Sn$, 41% $C_{10}H_{27}Br_2ClSi_3Sn$, and 49% $C_{10}H_{27}Br_3Si_3Sn$); C, 21.40; H, 4.85%]. ^{119}Sn N.m.r.: δ −100.5 {$Sn[C(SiMe_3)_3]BrCl_2$}, −167.9 {$Sn[C(SiMe_3)_3]Br_2Cl$}, and −237.1 p.p.m. {$Sn[C(SiMe_3)_3]Br_3$} (see text for discussion).

Dibenzyl[*tris*(*trimethylsilyl*)*methyl*]*tin chloride*, $Sn(CH_2Ph)_2[C(SiMe_3)_3]Cl$. A solution of dibenzyltin dichloride (7.20 g, 19 mmol) in thf (40 cm^3) was added to a solution of $Li[C(SiMe_3)_3]$ (22 mmol) in thf (45 cm^3) maintained under an atmosphere of dinitrogen gas. During addition, the dark yellow colour of the organolithium solution was discharged. The reaction was refluxed gently for 15 h, the mixture cooled and the solvent removed *in vacuo*. The cloudy yellow oil which remained was partitioned between a chloroform–water mixture, the organic layer separated and dried (anhydrous sodium sulphate) and the solvent again removed to leave a clear yellow oil. Trituration with ethanol followed by recrystallisation from chloroform–acetonitrile yielded first a purely organic material containing benzyl groups which was not analysed further, then a second crystalline product (4.85 g, 41%; m.p. 132—134 °C) identified as the required compound (Found: C, 50.70; H, 7.50. $C_{24}H_{41}ClSi_3Sn$ requires C, 50.75; H, 7.30%). N.m.r.: ^{1}H, δ 0.42 (s, 27 H, $SiMe_3$), 2.85 (q, 4 H, CH_2), 6.88 and 7.16 (m, 10 H, Ph); ^{13}C, δ 5.19 ($SiMe_3$), 12.62 (SiCSn), 30.94 (CH_2), 124.75, 128.22, 128.54, and 137.91 p.p.m. (Ph); $^{1}J(CH_2-^{117,119}Sn)$ 290.8, 304.0, $^{3}J(Me-^{117,119}Sn)$ 19.8 (unresolved), $^{1}J(Me-^{29}Si)$ 50.7 Hz; ^{119}Sn, δ 69.0 p.p.m. ^{119}Sn Mössbauer: i.s. 1.08 mm s^{-1}, q.s. 2.18 mm s^{-1}.

Di(p-*bromobenzyl*)[*tris*(*trimethylsilyl*)*methyl*]*tin bromide*, $Sn(CH_2C_6H_4Br\text{-}p)_2[C(SiMe_3)_3]Br$. Addition of a chloroform solution (10 cm^3) of bromine (0.79 g, 4.9 mmol) to a solution of $Sn(CH_2Ph)_2[C(SiMe_3)_3]Cl$ (1.4 g, 2.5 mmol) in the same solvent (10 cm^3) was followed by stirring for 15 h at room temperature and 8 h at solvent reflux. After *in vacuo* solvent removal, the remaining tan solid was recrystallised from ethanol–chloroform to yield a white crystalline product (1.57 g, 82%; m.p. 173 °C) (Found: C, 37.10; H, 5.40. $C_{24}H_{39}Br_3Si_3Sn$ requires C, 37.45; H, 5.10%). N.m.r.: ^{1}H, δ 0.30 (s, 27 H, $SiMe_3$), 2.74 (q, 4 H, CH_2), 6.57 and 7.16 (m, 8 H, C_6H_4); ^{13}C, δ 5.29 ($SiMe_3$), 12.70 (SiCSn), 30.49 (CH_2), 118.55, 129.97, 131.23, and 137.20 p.p.m. (C_6H_4); $^{1}J(CH_2-^{117,119}Sn)$ 275.5, 286.5 Hz; ^{119}Sn, δ 54.3 p.p.m. ^{119}Sn Mössbauer: i.s. 1.50 mm s^{-1}, q.s. 2.20 mm s^{-1}.

Dibenzyl(*trimethylsiloxy*)[*tris*(*trimethylsilyl*)*methyl*]*stannane* $Sn(CH_2Ph)_2[C(SiMe_3)_3](OSiMe_3)$ (**1**) *and* 3-{*dibenzyl*[*tris*(*trimethylsilyl*)*methyl*]*stannyl*}-1,1-*bis*(*trimethylsilyl*)*prop*-1-*ene* $Sn(CH_2Ph)_2[C(SiMe_3)_3][CH_2CH{=}C(SiMe_3)_2]$ (**2**). A solution of HBr (1.37 g, 17 mmol) in water (20 cm^3) was added dropwise, at room temperature, to a stirred solution of $Sn(CH_2Ph)_2[C(SiMe_3)_3]Cl$ (3.20 g, 5.6 mmol) in diethyl ether (50 cm^3). After stirring for 18 h, the two-phase system was separated and the combined ether washings dried (anhydrous sodium sulphate). After removal of the ether *in vacuo*, the remaining yellow oil was recrystallised from chloroform–acetonitrile to yield an off-white solid. A second recrystallisation from the same solvent system yielded first compound (**1**) (m.p. 117 °C), then (**2**) (m.p. 98—99 °C), along with a minimal amount of starting material. Each of the solid fractions was then purified further by additional recrystallisation. (**1**) (Found: C, 52.20; H, 8.25. $C_{27}H_{50}OSi_4Sn$ requires C, 52.15; H, 8.10%). N.m.r.: ^{1}H, δ −0.17 (s, 9 H, Me_3SiO), 0.37 (s, 27 H, $SiMe_3$), 2.71 (s, 4 H, CH_2), 6.90 and 7.16 (m, 10 H, Ph); $^{2}J(CH_2-^{117,119}Sn)$ 67.8, 71.1 Hz; ^{13}C, δ 3.47 (Me_3SiO), 5.38 (Me_3SiC), 11.36 (SiCSn), 30.62 (CH_2), 124.45, 128.44, 128.54, and 139.24 p.p.m. (Ph); $^{1}J(CH_2-^{117,119}Sn)$ 321.7, 334.9; ^{119}Sn, δ −10.2; ^{29}Si, δ −1.2 (Me_3SiC) and 6.4 p.p.m. (Me_3SiO); $^{2}J(SiC-^{117,119}Sn)$ 36.7 (unresolved), $^{2}J(SiO-^{117,119}Sn)$ 58.0 Hz (unresolved). ^{119}Sn Mössbauer: i.s. 1.24 mm s^{-1}, q.s. 1.42 mm s^{-1}. I.r. 980 cm^{-1} [ν(Sn–O–Si)].

(**2**) (Found: C,55.25; H, 8.90. $C_{33}H_{62}Si_5Sn$ requires C, 55.20; H, 8.70%). N.m.r.: ^{1}H, δ 0.07 and 0.12 [s, 18 H, $(Me_3Si)_2C{=}C$], 0.36 (s, 27 H, $SiMe_3$), 2.19 (d, 2 H, $C{=}CHCH_2Sn$; J = 7.9), 2.64 (q, 4 H, $PhCH_2Sn$), 6.56 (t, 1 H, $C{=}CHCH_2$; J = 7.9), 6.76 and 7.09 (m, 10 H, Ph); $^{2}J(C{=}CHCH_2-^{117,119}Sn)$ 61.6, 63.9; ^{13}C, δ 0.97 and 2.27 ($Me_3SiC{=}C$), 5.93 (Me_3SiC), 24.49 ($PhCH_2$), 25.17 ($C{=}CHCH_2$), 123.90, 128.18, 128.54, and 138.66 (Ph), 141.38 [$(Me_3Si)_2C{=}CH$], and 154.55 p.p.m. ($C{=}CHCH_2$); $^{1}J(PhCH_2-^{117,119}Sn)$ 248.0, 257.8; $^{1}J(CHCH_2-^{117,119}Sn)$ 266.7, 271.1; $^{2}J(CHCH_2-^{117,119}Sn)$ 37.4 (unresolved); $^{3}J(C{=}CHCH_2-^{117,119}Sn)$ 37.4 (unresolved); ^{119}Sn, δ −30.9 p.p.m.; ^{29}Si, δ −10.0 [*trans*-$Me_3Si(C{=}CH)$], −1.8 [*cis*-$Me_3SiC{=}CH$], −0.9 p.p.m. [$(Me_3Si)_3C$]; $^{2}J(Me_3SiC-^{117,119}Sn)$ 30.5 Hz (unresolved). ^{119}Sn Mössbauer: i.s. 1.40 mm s^{-1}, q.s. 0.39 mm s^{-1}. Mass spectrum (chemical ionisation): m/z 703 [$M - CH_3$], 627 [$M - CH_2Ph$], 533 [$M - CH_2CH{=}C(SiMe_3)_2$], 457, 217, and 201.

X-*Ray Crystal Structures of Dibenzyl*(*trimethylsiloxy*)[*tris*(*trimethylsilyl*)*methyl*]*stannane* (**1**) *and* 3-{*dibenzyl*[*tris*(*trimethylsilyl*)*methyl*]*stannyl*}-1,1-*bis*(*trimethylsilyl*)*prop*-1-*ene* (**2**).—Crystals of both compounds were obtained by recrystallisation of the crude reaction mixture in $CHCl_3$–CH_3CN, from which the two compounds separate sequentially. In both cases crystals were mounted on glass fibres for data collection.

Crystallographic data for the two compounds are given in Table 1. Both data sets were collected at room temperature on a Hilger and Watts Y290 automatic four-circle diffractometer. Data were corrected for Lorentz and polarisation effects but not absorption. No decay in the intensity of the monitor reflections was noted in either case. In both cases the structure was solved using a combination of Patterson (SHELX 86)[41] and Fourier methods, and refined by full-matrix least squares (SHELX 76).[42] Tin and silicon atoms were refined anisotropically in both structures. Carbon atoms were refined isotropically except for C(25)—C(27) of (**1**) and C(1)—C(20) and C(27) of (**2**) which were refined anisotropically. Hydrogen atoms were included at calculated positions [d(C–H) 108 pm] with a common thermal parameter (0.05 Å^2). Atomic scattering factors were taken from the usual sources.[43–45]

Additional data available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond distances and angles for both structures.

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