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Organotin compounds containing a bulky $(Me_3Si)_3C$ or related ligand. Crystal structures of $\{(Me_3Si)_3CMe(O_2NO)Sn\}_2O$, $(PhMe_2Si)_3CSnMeCl_2$ and $(PhMe_2Si)_3CSnCl_3$

Salih S. Al-Juaid, Mustafa Al-Rawi, Colin Eaborn, Peter B. Hitchcock, J. David Smith *

School of Chemistry, Physics and Environmental Science, University of Sussex, Brighton BN1 9QJ, UK

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Abstract

Some compounds having very bulky ligands, mainly $(Me_3Si)_3C$ (denoted by Tsi) or $(PhMe_2Si)_3C$ (denoted by Tpsi), attached to functional tin centres have been studied. Treatment of $TsiSnR_2Cl$, R = Me or Ph, with one equivalent of ICl gave the corresponding chloride $TsiSnRCl_2$, and use of an excess of ICl gave $TsiSnCl_3$ in both cases. Reaction of either chloride with one equivalent of Br_2 gave the dibromide $TsiSnRBr_2$; when an excess of Br_2 was used $TsiSnMe_2Cl$ still gave the dibromide but $TsiSiPh_2Cl$ gave the tribromide $TsiSnBr_3$. Reaction of $TsiSnMe_2Br$ with AgSCN or Ag_2O gave $TsiSnMe_2NCS$ and $(TsiSnMe_2)_2O$, respectively, but when the crude product from the reaction of $TsiSnMeBr_2$ with $AgNO_3$ was recrystallized from MeOH the nitrato–oxide $\{TsiMe(O_2NO)Sn\}_2O$ was obtained. In a seemingly previously unreported type of reaction, the alkoxide $TsiSnMe_2OEt$ reacted with ICl, Br_2, or I_2 to give $TsiSnMe_2X$, X = Cl, Br, or I, respectively, and Bu_3SnOEt likewise reacted with ICl to give Bu_3SnCl. The chlorides $TsiSnMe_2Cl$ and $TsiSnMeCl_2$ gave the hydrides $TsiSnMe_2H$ and $TsiSnMeH_2$ on treatment with $LiAlH_4$, but in the case of $TpsiSnMe_2Cl$ the Tpsi–Sn bond was cleaved to give TpsiH. The compound $(Me_3Si)_2C(SnMe_2Ph)(SiMe_2Cl)$ reacted with a 1 M proportion of $AgBF_4$ in CH_2Cl_2 with cleavage of the Sn–Ph bond to give the difluoride $(Me_3Si)_2C(SnMe_2F)(SiMe_2F)$. The crystal structures of the monomeric compounds $\{TsiMe(O_2NO)Sn\}_2O$, $TpsiSnMeCl_2$ and $TpsiSnCl_3$ are reported; $\{TsiMe(O_2NO)Sn\}_2O$ provides the first example of unidentate bonding of an NO_3 group to four-coordinate tin. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Crystal structure; Silicon; Tin; Trisyl; Tris(trimethylsilyl)methyl; Tris(dimethylphenylsilyl)methyl

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1. Introduction

There have been many fruitful studies of compounds in which the very bulky $(Me_3Si)C$ or a related ligand is attached to a functional silicon centre but only a few, and mainly rather limited, analogous studies of compounds containing a functional tin centre [1–7]. In an extension of earlier reports [5–7] we now describe the preparation and reactions of some new tin derivatives, mainly bearing the ligand $(Me_3Si)_3C$ (denoted by Tsi) or $(PhMe_2Si)_3C$ (denoted by Tpsi), and present the crystal structures of $\{TsiMe(O_2NO)Sn\}_2O$ **1**, $TpsiSnMeCl_2$ **2** and $TpsiSnCl_3$ **3**.

Tsi = $(Me_3Si)_3C$ Tpsi = $(PhMe_2Si)_3C$

$\{TsiMe(O_2NO)Sn\}_2O$ **1** $TpsiSnMeCl_2$ **2**

$TpsiSnCl_3$ **3**.

2. Results and discussion

2.1. Preparation of organotin halides and their reactions with ICl, Br_2 or I_2

The trichloride $TpsiSnCl_3$ was obtained from TpsiLi and $SnCl_4$ but it was accompanied by a substantial amount of TpsiCl. Treatment of $TsiSnMe_2Cl$ or $TsiSnPh_2Cl$ with a 1 M proportion of ICl in CH_2Cl_2 for

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* Corresponding author. Tel.: +44 1 273 678124; fax: +44 1 273 677196.

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30 min at room temperature gave the corresponding dichloride in good yield (Eq. (1)) and when an excess of ICl was used the trichloride was obtained (Eq. (2)).

$$\mathrm{TsiSnR_2Cl + ICl\ (1\ equiv.)} \rightarrow \mathrm{TsiSnRCl_2\ (R = Me\ or\ Ph)} \quad (1)$$

$$\mathrm{TsiSnR_2Cl + ICl\ (excess)} \rightarrow \mathrm{TsiSnCl_3\ (R = Me\ or\ Ph)} \quad (2)$$

The analogous reaction of $\mathrm{TsiSnMe_2Cl}$ or $\mathrm{TsiSnPh_2Cl}$ with a 1 M proportion of Br_2 gave the dibromide in each case (Eq. (3)); we suggest that the initial reaction is to give the monobromide $\mathrm{TsiSnR_2Br}$ and BrCl and that the latter then cleaves an Sn–R bond.

$$\mathrm{TsiSnR_2Cl + Br_2\ (1\ equiv.)} \rightarrow \mathrm{TsiSnRBr_2\ (R = Me\ or\ Ph)} \quad (3)$$

When an excess of Br_2 was used, $\mathrm{TsiSnMe_2Cl}$ still gave only the dibromide, indicating that Br_2 is less reactive than ICl in cleavage of the Sn–Me bond, but $\mathrm{TsiSnPh_2Cl}$ gave the tribromide $\mathrm{TsiSnBr_3}$, reflecting the higher reactivity of the Sn–Ph bond towards electrophiles.

No reaction occurred between $\mathrm{TsiSnMe_2Cl}$ and I_2 in CCl_4 for 18 h at room temperature or 4 h under reflux, or between $\mathrm{TsiSnPh_2Cl}$ and I_2 in CH_2Cl_2 for 18 h at room temperature.

2.2. Reactions with silver salts

Treatment of $\mathrm{TsiSnCl_3}$ with an excess of $AgBF_4$ in CH_2Cl_2 gave the expected trifluoride $\mathrm{TsiSnF_3}$ in high yield, and reaction of $\mathrm{TpsiSnMe_2Cl}$ with $AgNO_3$ gave the expected nitrate $\mathrm{TpsiSnMe_2ONO_2}$. The chloride $\mathrm{TpsiSnMe_2Cl}$ did not react with AgSCN in acetone during 48 h at room temperature, but when the bromide $\mathrm{TpsiSnMe_2Br}$ was used formation of the isothiocyanate $\mathrm{TsiSnMe_2NCS}$ was complete within 1 h (Eq. (4)) [7]. Reaction of the bromide with Ag_2O in CH_2Cl_2 for 24 h at room temperature gave the oxide in good yield (Eq. (5)).

$$\mathrm{TpsiSnMe_2Br + AgSCN} \rightarrow \mathrm{TpsiSnMe_2NCS} \quad (4)$$

$$\mathrm{TpsiSnMe_2Br + Ag_2O} \rightarrow \mathrm{(TpsiSnMe_2)_2O} \quad (5)$$

An unexpected outcome was observed when the product of the reaction of the dibromide $\mathrm{TsiSnMeBr_2}$ with $AgNO_3$ was, without isolation, recrystallized from MeOH, the compound obtained, in 87% yield, being the nitrato–oxide $\mathrm{\{Tsi(Me)(O_2NO)Sn\}_2O}$, which was identified by an X-ray diffraction study (see later). Presumably this was obtained by hydrolysis of the initially formed dinitrate $\mathrm{TsiSnMe(ONO_2)_2}$ by water in the MeOH, which was not dried before use. The nitrato–oxide $\mathrm{\{Ph_2(O_2NO)Sn\}_2O}$ was shown some years ago to be formed when $\mathrm{Ph_2SnI_2}$ was treated with $AgNO_3$ in acetone or when a solution of $\mathrm{Ph_2Sn(NO_3)_2}$ in $CHCl_3$ was boiled with exposure to the air [8].

2.3. The alkoxides TpsiSnMe$_2$OR (R = Me, Et)

The ethoxide $\mathrm{TpsiSnMe_2OEt}$ was unexpectedly obtained, in high yield, when the product of the reaction of TpsiLi with $\mathrm{Me_2SnCl_2}$, presumably $\mathrm{TpsiSnMe_2Cl}$, was recrystallized from boiling EtOH, the boiling lasting only 10 min. In contrast, reaction of $\mathrm{TpsiSnMe_2Cl}$ with MeOH under reflux was slow, 4 days being required for completion of the reaction. This large difference between the rates of reaction in MeOH and EtOH is puzzling, since it seems much too large to be attributed to the difference of ca. 13°C between the boiling points of the solvents. There could have been some LiOH present in the initial crude product as a result of hydrolysis of residual TpsiLi during work-up, but the amount of this (and hence of LiOEt formed from it in EtOH) could not have been sufficient to use up more than say 10% of the chloride.

An interesting, and apparently novel, reaction was observed when the ethoxide was treated with ICl in CH_2Cl_2, the chloride being readily formed (Eq. (6)). Corresponding reactions were found to take place with Br_2 and even I_2 (Eq. (7)).

$$\mathrm{TpsiSnMe_2OEt + ICl} \rightarrow \mathrm{TpsiSnMe_2Cl\ (+EtOI?)} \quad (6)$$

$$\mathrm{TpsiSnMe_2OEt + X_2} \rightarrow \mathrm{TpsiSnMe_2X\ (+EtOX?)\ (X = Br, I)} \quad (7)$$

When an excess of ICl or Br_2 was used an Sn–Me bond was cleaved, to give $\mathrm{TpsiSnMeCl_2}$ or $\mathrm{TpsiSnMeBr_2}$, respectively. However only the monoiodo compound was obtained when a large excess of I_2 was used.

This type of reaction has not, as far as we can ascertain, been observed previously for organotin alkoxides. That it is probably general was confirmed by formation of $\mathrm{Bu_3SnCl}$ from $\mathrm{Bu_3SnOEt}$ and ICl. It could possibly find application for in situ generation of (unstable) alkyl hypohalites ROX, which are useful intermediates in organic synthesis [9].

2.4. Reactions of chlorides with LiAlH$_4$

Reduction of the bromides $\mathrm{TsiSnMe_2Br}$ and $\mathrm{TsiSnMeBr_2}$ with $LiAlH_4$ was shown previously to give the corresponding hydrides $\mathrm{TsiSnMe_2H}$ and $\mathrm{TsiSnMeH_2}$ [1]. We found that the chlorides $\mathrm{TsiSnRCl_2}$ (R = Me, Ph) behaved analogously to give the expected dihydrides in high yield (Eq. (8)), but $\mathrm{TpsiSnMe_2Cl}$ gave only the cleavage product TpsiH (Eq. (9)).

$$\mathrm{TsiSnRCl_2 + LiAlH_4} \rightarrow \mathrm{TsiSnRH_2\ (R = Me, Ph)} \quad (8)$$

$$\text{TpsiSnMe}_2\text{Cl} + \text{LiAlH}_4 \rightarrow \text{TpsiH} \ (+ \text{Me}_2\text{SnH}_2?) \qquad (9)$$

2.5. The compounds $(Me_3Si)_2C(SnPh_3)_2$, $(Me_3Si)_2C(SnMe_2Ph)_2$, $(Me_3Si)_2C(SnMe_2Ph)SiMe_2Cl$ and $(Me_3Si)_2C(SnMe_2F)SiMe_2F$

An attempt to obtain the compound $(Me_3Si)_2C(SnPh_3)_2$ by treatment of $(Me_3Si)_2CCl_2$ with Ph_3SnLi yielded $(Me_3Si)_2CH(SnPh_3)$ in 10% yield and $Ph_3SnSnPh_3$ as the main product. However, the related compound $(Me_3Si)_2C(SnMe_2Ph)_2$ was made by treatment of $(Me_3Si)_2C(SnMe_2Cl)_2$ with phenyllithium. This compound was used to provide a route (see Eqs. (10a) and (10b)) to the chloride $(Me_3Si)_2C(SnMe_2Ph)SiMe_2Cl$ which was required in order to find out whether migration of the Ph group might accompany replacement of the Cl atom by fluorine upon reaction with $AgBF_4$. (Migration of Me groups was previously observed in the reactions of the iodide $(Me_3Si)_2C(SnMe_3)SiMe_2I$ with silver salts, including $AgBF_4$ in CH_2Cl_2, which gave exclusively the rearranged $(Me_3Si)_3CSnMe_2F$ [10].) The compound $(Me_3Si)_2C(SnMe_2Ph)_2$ was treated with one equivalent of MeLi in Et_2O–THF to give $(Me_3Si)_2C(SnMe_2Ph)Li$. Addition of Me_2SiCl_2 to the solution of the latter then gave $(Me_3Si)_2C(SnMe_2Ph)SiMe_2Cl$ in good yield.

$$(\text{Me}_3\text{Si})_2\text{C}(\text{SnMe}_2\text{Ph})_2 + \text{MeLi} \rightarrow (\text{Me}_3\text{Si})_2\text{C}(\text{SnMe}_2\text{Ph})\text{Li} \qquad (10a)$$

$$(\text{Me}_3\text{Si})_2\text{C}(\text{SnMe}_2\text{Ph})\text{Li} + \text{Me}_2\text{SiCl}_2 \rightarrow (\text{Me}_3\text{Si})_2\text{C}(\text{SnMe}_2\text{Ph})(\text{SiMe}_2\text{Cl}) \qquad (10b)$$

When the latter chloride was treated with a 1 M proportion of $AgBF_4$ in CH_2Cl_2 there was no reaction for 24 h at room temperature, but when the mixture was heated under reflux for 20 min reaction was complete. However, the product, isolated in 96% yield, was the difluoride $(Me_3Si)_2C(SnMe_2F)SiMe_2F$ (Eq. (11)).

$$(\text{Me}_3\text{Si})_2\text{C}(\text{SnMe}_2\text{Ph})(\text{SiMe}_2\text{Cl}) + \text{AgBF}_4 \rightarrow (\text{Me}_3\text{Si})_2\text{C}(\text{SnMe}_2\text{F})(\text{SiMe}_2\text{F}) \qquad (11)$$

It is noteworthy that each $AgBF_4$ molecule supplies two F atoms. Since Si–Cl bonds are much less reactive than Si–I bonds towards silver salts in compounds of this general type, we assume that the initial reaction involves attack at the Sn–Ph bond to give $(Me_3Si)_2C(SnMe_2F)(SiMe_2Cl)$ and (unstable) AgPh with liberation of BF_3, and that the latter then brings about fluorination at Si. It is likely that the F atom in $(Me_3Si)_2C(SnMe_2F)(SiMe_2Cl)$ provides anchimeric assistance to abstraction of Cl^- by Ag^+. (Compare such assistance from F atoms in compounds of the type $(Me_3Si)_2C(SiMe_2F)(SiMe_2X)$ [11].)

2.6. Crystal structures

2.6.1. $\{TsiMe(ONO_2)Sn\}_2O$, **1**

The crystal of **1** was found to contain molecules of C_2 symmetry, disordered about the Sn–O–Sn linkage, as shown in Fig. 1A, with site occupancies of 0.72 and 0.28. The disorder affects the accuracy of the geometrical data, especially for the Tsi group. The molecular structure of the major configuration is shown in Fig. 1B, and the selected bond lengths and angles shown in Table 1 refer only to this configuration. The main features are that: (a) the compound is monomeric (there could in principle have been intermolecular SnON(O)O...Sn coordination to give a polymer, as is the case for corresponding Cl...Sn interaction in the chloride–oxide $(Me_2ClSn)_2O$ [12]); (b) the Tsi groups are in a *trans* disposition with respect to the Sn–O–Sn linkage; and (c) the NO_3 ligand is bonded through only one O atom.

Crystal structures of tin(IV) nitrate and several organotin nitrates have been reported [13]. In all but one case the nitrato groups are bound in a bidentate fashion, though sometimes very unsymmetrically; for example, whereas in $Sn(ONO_2)_4$ the two Sn–O bonds to each NO_3 group are identical within the experimental

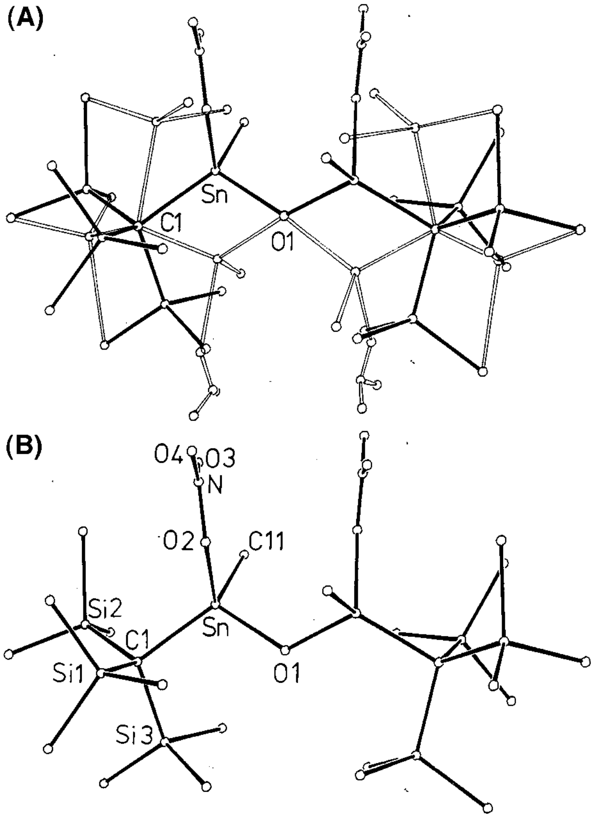

Fig. 1. (A) Structure of $\{TsiMe(O_2NO)Sn\}_2O$, **1**, showing the disorder about the Sn–O–Sn linkage. Occupancies: filled bonds 0.72, open bonds, 0.28. (B) Structure showing the numbering scheme for the major configuration.

Table 1
Selected bond lengths (Å) and angles (°), with estimated standard deviations in parentheses, for $\{(Me_3Si)_3CMe(O_2NO)Sn\}_2O$, **1**

Sn–O(1)	1.975(4)	Sn–O(2)	2.109(10)
Sn–C(1)	2.120(11)	Sn–C(11)	2.142(14)
Si–C(1) mean	1.928(10)	Si–Me mean	1.923(12)
O(2)–N	1.25(2)	O(3)–N	1.21(2)
O(4)–N	1.15(2)		
O(1)–Sn–O(2)	93.1(4)	O(1)–Sn–C(1)	111.2(4)
O(1)–Sn–C(11)	109.1(4)	O(2)–Sn–C(1)	104.5(4)
O(2)–Sn–C(11)	111.3(5)	C(1)–Sn–C(11)	123.3(5)
C(1)–Si–Me mean	111.1(6)	Me–Si–Me mean	107.7(9)
Si–C(1)–Si mean	111.0(6)	Sn–O–Sn	127.5(5)
Sn–O(2)–N	125(1)	O(2)–N–O(3)	115(1)
O(2)–N–O(4)	117(2)	O(2)–N–O(4)	128(2)
Sn–C(1)–Si(1)	111.6(5)	Sn–C(1)–Si(2)	108.0(5)
Sn–C(1)–Si(3)	104.1(5)		

uncertainty [14], in $TpsiSnMe_2ONO_2$ one O atom is strongly bound at a distance of 2.095(5) Å from Sn, and another interacts only weakly at a distance of 2.929(8) Å (which is still 0.8 Å below the sum of the relevant van der Waals radii) [7]. The exception is provided by the compound $Me_2Sn(OH)(ONO_2)$, which crystallizes as a dimer in which intramolecular O–Sn coordination makes the Sn atoms five-coordinate [15], this possibly inhibiting bidentate coordination of the NO_3 group. Thus as far as we are aware **1** represents the only example of monodentate coordination of this group to a four-coordinate Sn centre.

Relevant details of the structure of **1** are as follows. (a) The Sn–O(2) bond length, 2.109(10) Å, is the same as that of the main O–Sn bond in $TpsiSnMe_2ONO_2$. (b) The Sn–O–N angle, 125(1)°, is significantly larger than the corresponding angle for the stronger O–Sn bond in $TpsiSnMe_2ONO_2$, 116.6(4) Å, confirming that in the latter there is a definite secondary O...Sn interaction that draws the N atom over towards the Sn. (c) There is a planar geometry at the N atom, the sum of the O–N–O angles being 360°. (d) The Sn–O–Sn angle, 127.5(5)°, is significantly smaller than that in $(Ph_3Sn)_2O$, 137(3)°, in which the tin atoms are also four-coordinate [16]. (e) There is substantial deviation from ideal tetrahedral geometry at Sn, probably as a consequence of the large size of the Tsi ligand; the C–Sn–O angles vary from 104 to 111°, the C–Sn–C angle, 123°, is wide, and the O–Sn–O angle, 93°, narrow.

2.6.2. *$TpsiSnMeCl_2$, **2***

This compound was shown to be monomeric in the solid with the tin four-coordinate (see Fig. 2), unlike the great majority of diorganotin dichlorides, which form polymeric chains (though Ph_2SnCl_2 is probably monomeric [17]). There was found to be disorder involving one of the Cl groups and the Me group on Sn, the site labelled Cl(2) being occupied by Cl and C atoms in 64/36 ratio and the site labelled C(26) correspondingly having Cl and C in 36/64 ratio. Selected bond lengths and angles are shown in Table 2. The Sn–Cl(1) bond length, 2.353(3) Å, is slightly shorter than that (2.380(3) Å) in the monomeric $\{(Me_3Si)_2CH\}_3SnCl$ [18], in which the Sn atom is four coordinate and shows almost perfect tetrahedral geometry. The only other noteworthy feature is that the bulk of the Tpsi group causes the Cl and Me ligands on Sn to draw together, the Cl(1)–Sn–Cl(2), C(26)–Sn–Cl(1) and C(26)–Sn–Cl(2) angles being 98.5(1), 103.6(2) and 107.2(2)°, respectively, with correspondingly large C(1)–Sn–Cl(1), C(1)–Sn–Cl(2), and C(1)–Sn–C(26) angles of 112.2(2), 113.7(2) and 119.3(3)°, respectively.

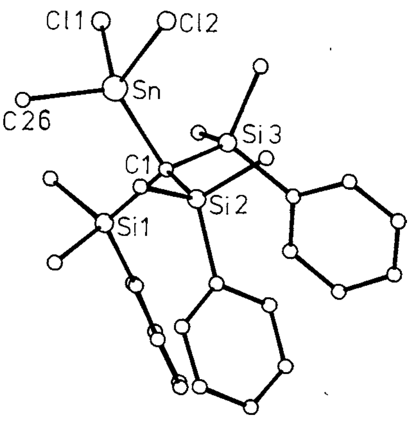

Fig. 2. Molecular structure of $TpsiSnMeCl_2$, **2**.

The torsion angles about Si–C bonds show that the three $SiMe_2Ph$ groups have the same configurations

Table 2
Selected bond distances (Å) and angles (°) in $(PhMe_2Si)_3CSnMeCl_2$, **2**, and $(PhMe_2Si)_3CSnCl_3$, **3**, with estimated standard deviations in parentheses

	2	**3**
Sn–Cl(1)	2.353(3)	2.317(4)
Sn–Cl(2)	2.312(4)	
Sn–C(26)	2.225(6)	
Sn–C(1)	2.173(7)	2.16(2)
Si–C(Ph) mean	1.879(8)	1.858(10)
Si–C(Me) mean	1.879(9)	1.854(12)
Cl(1)–Sn–Cl(2)	98.5(1)	100.6(1)
Cl–Sn–C(1) mean	113.0(2)	117.3(1)
Cl(1)–Sn–C(26)	103.6(2)	
Cl(2)–Sn–C(26)	107.2(2)	
C(1)–Sn–C(26)	119.3(3)	
C(1)–Si–C mean	112.9(4)	111.8(5)
C–Si–C mean	105.8(4)	107.0(5)
Sn–C(1)–Si mean	104.2(3)	103.6(4)
Si–C(1)–Si mean	114.2(4)	114.7(4)

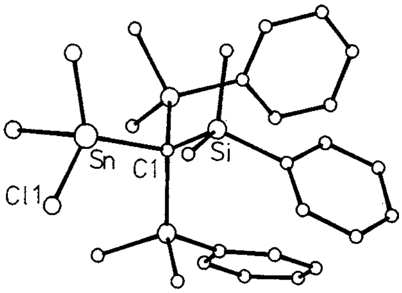

Fig. 3. Molecular structure of $TpsiSnCl_3$, **3**.

with respect to the substituents at the central carbon atom, so that the $C(SiMe_2Ph)_3$ group has the propeller-like symmetry found in TpsiH [19], $TpsiBF_2OH$ [20] and $[TpsiBH_3]^-$ [21]. (The Tpsi group in $TpsiSnMe_2ONO_2$ has lower symmetry [7].) The largest groups, Ph and $SnMe_2Cl$, are staggered about the C – Si bonds but the torsion angles are twisted from the ideal 180° to 156–160° by repulsions between methyl groups attached to adjacent silicon atoms in 1,3-positions. Such distortions have been observed in all Tpsi derivatives studied so far.

2.6.3. *$TpsiSnCl_3$*, *3*

An X-ray diffraction study of this trihalide seemed likely to be of interest since there appears to be no previous report on the structure of a simple organotin trihalide of the type $RSnCl_3$. The structure was derived from a set of strong sharp reflections and solved in a centrosymmetrical trigonal space group with two independent monomers in the asymmetric unit, one in a general position and the other on the three-fold axis. The molecules, each with C_3 symmetry, are stacked in chains with their principal axes parallel to *c*. Those in one chain point in one direction, those in the second chain point in the opposite direction, and those in the third chain point randomly in either direction. If data on additional broad reflections are included the structure can be indexed on the basis of a larger unit cell with the same *c* axis. The data suggest that over limited regions within the crystal the molecules in the third chain are ordered and these regions give the weak broad X-ray reflections. The strong sharp reflections arise from the disordered regions. The molecular structure is shown in Fig. 3 and the bond lengths and angles for the undisordered molecule are given in Table 2. Those of the other molecule are not significantly different. The values are very similar to those in $TpsiSnMeCl_2$ and so are not discussed further. The propeller-like configuration of the Tpsi group is reflected in the trigonal symmetry of the lattice. The compound $TpsiSiCl_3$ has an almost identical structure with similar lattice disorder. It is possible that it should have been refined in $P\bar{3}$ (See experimental section) not $P3$ as reported [22].

3. Experimental

All reactions involving organo-lithium or -magnesium compounds were carried out under dry argon. Solvents were carefullly dried by standard methods. Solutions of MeLi in Et_2O and BuLi in hexane were purchased from Aldrich.

The IR spectra were recorded with a Perkin-Elmer 1720 FTIR Spectrometer. EI or, where indicated, FAB mass spectra were obtained at 70 eV on a Kratos MS 80RF or MS25 spectrometer; *m/z* values refer to ions containing ^{120}Sn. The suggested ion assignments are not intended to indicate fragmentation routes but they provide further evidence that compounds containing the Tpsi group give prominent ions at *m/z* 325, 309, 263 and 175 [5]. The NMR spectra were recorded with a Brüker AC 250 spectrometer, for ^1H at 250.13 MHz, for ^{13}C at 62.85 MHz, and for ^{29}Si at 49.69 MHz (reference $SiMe_4$), for ^{19}F at 75.42 MHz (reference $CFCl_3$), and for ^{119}Sn at 93.3 MHz (reference $SnMe_4$). Coupling constants involving ^{117}Sn and ^{119}Sn are separately indicated when satellites were clearly resolved; otherwise only one value without the Sn mass mumber is given.

The starting materials TsiLi [23] and TpsiLi [24] were prepared in situ by metallation of TsiH orTpsiH with methyllithium in boiling THF. Metallation was 90–98% within 1 h. A few drops of Me_3SiOMe were added to destroy any unchanged methyllithium before the solution was used. The compounds $TsiSiR_2Cl$, R = Me or Ph, were made as described previously [5]. Several compounds described here have been synthesised previously by other methods. Their identities were established by C, H analysis and multinuclear NMR spectroscopy. We have given details only when substantial new information, e.g. about coupling constants, has been obtained.

3.1. *Reaction of $(Me_3Si)_3CSnMe_2Cl$ with ICl*

A solution of ICl (2.5 mmol) in CCl_4 was added dropwise to a solution of $(Me_3Si)_3CSnMe_2Cl$ (1.0 g, 2.4 mmol) in CCl_4. Monitoring by ^1H NMR spectroscopy showed that the reaction was complete within 30 min. The solvent was then removed to leave a white solid, which was recrystallised from hexane to give dichloro(methyl){tris(trimethylsilyl)methyl}stannane (1.0 g, 98%), m.p. 344 °C (lit. [1], 320°C). δ(H) ($CDCl_3$) 0.37 (27H, s, ^2J(HSi) 6.4 Hz, ^1J(HC) 118.6 Hz, $SiMe_3$), 1.23 ppm (3H, s, $^2J(H^{117}Sn)$ 60 Hz, $^2J(H^{119}Sn)$ 62 Hz, MeSn). δ(C) ($CDCl_3$) 4.6 (s, ^3J(CSn) 26.8 Hz, ^1J(CSi) 52.1 Hz, Me_3Si), 12.6 (s, ^1J(CSn) 455 Hz, MeSn) 19.9 (s, CSi_3). δ(Si) ($CDCl_3$): 0.15. δ(Sn) ($CDCl_3$): 95.8, *m/z*: (421 (35%, M–Me), 221 (100, M–Me–Me_3SnCl), 201 (55, M–Me–Me_2SnCl_2), 73 (45 Me_3Si), 59 (10, Me_2HSi).

3.2. Reaction of $(Me_3Si)_3CSnMe_2Cl$ with an excess of ICl

A solution of ICl (6.0 mmol) in CCl_4 (1.0 M) was added dropwise to a solution of $(Me_3Si)_3CSnMe_2Cl$ (1.0 g, 2.4 mmol) in CCl_4 (10 cm^3) and the mixture was stirred for 1 h. The solvent was removed to leave a white solid, which was recrystallised from hexane to give trichloro{tris(trimethylsilyl)methyl}stannane (1.0 g, 99%), m.p. 315°C (dec.), (lit. [1], 290°C, dec.). δ(H) ($CDCl_3$): 0.41 (s, ^2J(HSi) 6.4 Hz, Me_3Si); δ(C) NMR ($CDCl_3$): 4.4 (s, ^1J(CSi) 52.6 ^3J(CSn) 37.9 Hz, Me), 32.3 (s, ^1J(CSn) 113 ^1J(CSi) 25.5 Hz, $SnMe_2$). δ(Si) ($CDCl_3$): 1.4. δ(Sn) ($CDCl_3$): −36.4 (s), *m*/*z*: 441 (20%, M–Me), 221 (80, M–Me–Me_2SnCl_2), 201 (55, M–Me–$MeSnCl_3$), 73 (10, Me_3Si), 59 (30, Me_2HSi), 45 (15%, MeH_2Si).

3.3. Reaction of $(Me_3Si)_3CSnMe_2Cl$ with Br_2

A solution of Br_2 (2.5 mmol) in CCl_4 (2.5 cm^3) was added with stirring to a solution of $(Me_3Si)_3CSnMe_2Cl$ (1.0 g, 2.4 mmol) in CCl_4 (20 cm^3). The reaction was monitored by ^{1}HMR spectroscopy and found to be complete after 30 min. The solvent was removed to leave a white solid which was recrystallised from hexane and shown to be dibromo(methyl){tris(trimethylsilyl)methyl}stannane (1.1 g, 87%), m.p. 290°C (dec.), (lit. [1], 318°C, dec.). δ(Si) ($CDCl_3$) 0.45 (s). δ(Sn) ($CDCl_3$): + 18.8, *m*/*z* 509 (20%, M–Me), 445 (33, M–Br), 376 (20), 307 (18, M–Me_2SiBr–HBr), 201 (30), 73 (70).

3.4. Reaction of $(Me_3Si)_3CSnMeBr_2$ with $AgNO_3$

A solution of $(Me_3Si)_3CSnMeBr_2$ (2.0 g, 3.8 mmol) in CH_2Cl_2 (20 cm^3) was added to a solution of $AgNO_3$ (1.34 g, 7.8 mmol) in CH_2Cl_2 (20 cm^3). The mixture was stirred for 7 h with protection from light, then filtered through charcoal. The solvent was removed under reduced pressure to leave a white solid, which was recrystallised from MeOH to give bis{methyl(nitrato){tris(trimethylsilyl)methyl}tin) oxide (2.9 g, 87%), m.p. 187–189°C. Anal. found: C, 31.1; H 6.9. $C_{22}H_{60}N_2O_7Si_6Sn_2$. Calc.: C 30.3; H 6.9%. δ(H) ($CDCl_3$): 0.27 (6H, s, MeSn), 0.34 (54H, s, Me_3Si). δ(C) ($CDCl_3$): 4.7 (Me_3Si), 4.9 (MeSn). δ(Si) ($CDCl_3$): − 0.22. δ(Sn) ($CDCl_3$): 81.5, *m*/*z* 857 (10%, M–Me), 808 (10), 733 (30), 381 (80), 201 (70), 73 (100).

3.5. Reaction of $(Me_3Si)_3CSnMe_2Cl$ with an excess of Br_2

An excess of a 1 M solution of Br_2 in CCl_4 (10 mmol) was added to $(Me_3Si)_3CSnMe_2Cl$ (1.00 g, 2.40 mmol) in CCl_4 (20 cm^3). The mixture was stirred for 24 h then the solvent was removed to leave a white solid, which was recrystallised from hexane to give dibromo(methyl){tris(trimethylsilyl)methyl}stannane, (1.2 g, 95%), m.p. 290°C (dec.). The C, H analysis and ^{1}H NMR spectra were identical to those of $(Me_3Si)_3CSnMeBr_2$ described above.

3.6. Attempted reaction between I_2 and $(Me_3Si)_3CSnMe_2Cl$

A 1 M solution of I_2 in CCl_4 (10 cm^3) was added dropwise with stirring to $(Me_3Si)_3CSnMe_2Cl$ (1.0 g, 2.4 mmol) in CCl_4 (10 cm^3) and the mixture was stirred overnight. No change was detected by ^{1}H NMR spectroscopy, and so the mixture was heated under reflux for 4 h and then allowed to cool. Evaporation of the solvent under reduced pressure gave unchanged $(Me_3Si)_3CSnMe_2Cl$ (0.9 g, 90%), m.p. 337°C.

3.7. Reaction of $(Me_3Si)_3CSnMeCl_2$ with $LiAlH_4$

A solution of $LiAlH_4$ (0.38 g, 10 mmol) in THF (10 cm^3) was added dropwise with stirring under nitrogen to a solution of $(Me_3Si)_3CSnMeCl_2$ (2.0 g, 4.5 mmol) in THF (20 cm^3). The mixture was stirred for 5 min, the solvent removed under vacuum, and the residue extracted with hexane. The hexane was evaporated from the extract and the residue was recrystallised from hexane to give a white solid identified as methyl{tris(trimethylsilyl)methyl}stannane (1.5 g, 90%), m.p. 211°C (dec.). IR ν(SnH) (KBr) 1839 cm^{-1}, δ(H) ($CDCl_3$): δ 0.22 (27H, s, ^2J(HSi) 6.2 Hz, Me_3Si), 0.31 (3H, s, MeSn), and 5.04 (q, 2H, ^3J(HH) 2.4 Hz, ^1J($H^{119}Sn$) 1817 Hz, ^1J($H^{117}Sn$) 1737 Hz, SnH_2). δ(C) (C_6D_6): − 8.45 (s, MeSn)), 4.22 (s, ^3J(CSn) 18.6 Hz, Me_3Si). δ(Si) (C_6D_6): δ 0.1 (s, Me_3Si); δ(Sn) (C_6D_6): −206.8 (t of q, ^1J (^{119}SnH) 1817, ^2J (SnH) 54.3Hz), *m*/*z* (CI NH_3): 353 (85%, M–Me), 217 (50), 187 (100, M–Me_3SnH–Me), 129 (40, $Me_2SiCH{=}SiMe_2$), 73 (90, Me_3Si).

When a sample of the product (0.10 g, 0.27 mmol) was placed in an NMR tube and CH_2Cl_2 (2 cm^3) was added the ^{1}H NMR spectrum was found to be identical with that of $(Me_3Si)_3CSnMeCl_2$, and addition of an authentic sample of the the latter only enhanced the signals.

3.8. Reaction of $(Me_3Si)_3CSnPh_2Cl$ with ICl

A solution of ICl (1.9 mmol, 1.9 cm^3) in CCl_4 was added dropwise to a solution of $(Me_3Si)_3CSnPh_2Cl$ (1.0 g, 1.8 mmol) in CCl_4 (10 cm^3) at room temperature and the mixture was stirred for a further 3 h. The solvent was then pumped away and the residue recrystallised from hexane to give dichloro(phenyl){tris(trimethylsilyl)methyl}stannane (0.8 g, 88%), m.p. 162°C. Anal.

found: C, 38.0; H, 6.3. $C_{16}H_{32}Cl_2Si_3Sn$ calc: C, 38.6; H, 6.4%. δ(H) ($CDCl_3$): 0.40 (27H, s, Me_3Si), 7.4–7.8 (5H, m, Ph). δ(C) ($CDCl_3$): 4.95 (^3J(CSn) 27.6 Hz, Me_3Si), 129.3 (C_3) 129.9 (C_4), 134.7 (C_2), 143.4 (C_1). δ(Si) ($CDCl_3$), 0.4 (s, ^1J(SiC) 53 Hz). δ(Sn) ($CDCl_3$): + 10.2, *m/z* 483 (100%, M–Me), 448 (60, M–HCl–Me), 279 (30), 247 (35), 201 (35), 149 (40), 73 (50, Me_3Si), 58 (25, Me_2Si), 45 (15, MeH_2Si).

3.9. Reaction of $(Me_3Si)_3CSnPh_2Cl$ with an excess of ICl

A solution of ICl (20 mmol) in CCl_4 (20 cm^3) was added to a solution of $(Me_3Si)_3CSnPh_2Cl$ (1.0 g, 1.8 mmol) in CCl_4 (10 cm^3), and the mixture was stirred overnight. The solvent was removed to leave a white solid, which was recrystallised from hexane to give white cube-like crystals of trichloro{tris(trimethyl)silyl) methyl}stannane (0.8 g, 96%), m.p. 315°C (dec.) with spectra identical with those given above for this compound.

3.10. Reaction of $(Me_3Si)_3CSnPh_2Cl$ with Br_2

A solution of Br_2 (2.0 mmol) in CCl_4 (2.0 cm^3) was added dropwise to a solution of $(Me_3Si)_3CSnPh_2Cl$ (1.0 g, 1.8 mmol) in CCl_4 (10 cm^3) and the mixture stirred for 1 h. The solvent was then removed and the white solid recrystallised from hexane to give dibromo(phenyl){tris(trimethylsilyl)methyl}stannane, (0.9 g, 85%), m.p. 241°C.

Anal. found: C, 32.8; H, 5.3. $C_{16}H_{32}Br_2Si_3Sn$. Calc: C, 32.8; H, 5.5%. δ(H) ($CDCl_3$): 0.40 (27H, s, Me_3Si), 7.45–7.85 (5H, m, Ph). δ(C) ($CDCl_3$): 5.0 (s, ^3J(CSn) 27.3 Hz, Me_3Si), 129.0 (C_3), 130.6 (C_2), 134.8 (C_4), 143.3 (C_1). δ(Si) ($CDCl_3$): 0.7. δ(Sn) ($CDCl_3$): − 38.3. *m/z* 571 (25%, M–Me), 507 (70, M–Br), 492(60), 427(70), 327(30), 307(70), 201(50), 136(80), 73 (100).

3.11. Reaction of $(Me_3Si)_3CSnPh_2Cl$ with an excess of Br_2

A solution of Br_2 (10.0 mmol) in CCl_4 (10.0 cm^3) was added dropwise to a solution of $(Me_3Si)_3CSnPh_2Cl$ (1.0 g, 1.8 mmol) in CCl_4 (20 cm^3). The mixture was stirred for 6 h and the solvent then removed to leave a white solid, which was recrystallised from hexane to give tribromo{tris(trimethylsilyl)methyl}stannane, (0.9 g, 91%), m.p. 290°C (dec.). δ(C) ($CDCl_3$) 4.6 (^1J(CSi) 52.6, ^3J(CSn) 38.4 Hz, Me_3Si). δ(Si) ($CDCl_3$): 1.7 (s). δ(Sn) ($CDCl_3$) − 236 ppm. *m/z* 573 (40%, M–Me), 509 (48, M–Br), 265 (60, M–Me–Me_2SnBr_2), 201 (85, M–Me–$MeSnBr_3$), 136(95), 73 (100), 43 (90).

3.12. Reaction of $(Me_3Si)_3CSnPh_2Cl$ with I_2

A solution of I_2 (20 mmol) in CCl_4 (20 cm^3) was added to a solution of $(Me_3Si)_3CSnPh_2Cl$ [5] (1.0 g, 1.8 mmol) in CCl_4 (10 cm^3) and the mixture was stirred overnight. The solvent was then removed to leave a white solid which was shown by its analysis and ^{1}H NMR spectrum to be unchanged starting material, chloro(diphenyl){tris(trimethylsilyl)methyl}stannane (0.90 g, 88%), m.p. 203 (Lit. [4] 208°C), with NMR spectra which agreed with those obtained previously [5].

3.13. Reaction of $(Me_3Si)_3CSnPhCl_2$ with $LiAlH_4$

A solution of $LiAlH_4$ (4.2 mmol) in THF (10 cm^3) was added to a solution of $(Me_3Si)_3CSnPhCl_2$ (1.0 g, 2.0 mmol) in THF (10 cm^3) under nitrogen. When the addition was complete the solvent was removed, the residue extracted with dry hexane, and the extract filtered and evaporated to leave a white solid, which was recrystallised from hexane to give phenyl{tris(trimethylsilyl)methyl}stannane, (0.81 g, 94%), m.p. 138°C (dec.). IR (Nujol) ν(Sn–H) 1840 cm^{-1}. (Because of difficulties in combusting the compound a satisfactory analysis could not be obtained.) δ(H) (C_6H_6): 0.25 (27H, s, $^2J(^1HSi)$ 6.2 Hz, Me_3Si), 5.9 (2H, s, $^1J(H^{119}Sn)$ 1865 Hz, $^1J(H^{117}Sn)$ 1782 Hz, SnH_2) 7.05–7.83 (m, 5H, Ph). δ(C) (C_6H_6): 4.4 (Me_3Si), 128.8, 129.2, 138.5 (Ph). δ(Si) (C_6H_6) 0.36. δ(Sn) (C_6H_6) − 193. *m/z* 415 (30, M–Me), 337 (25, M–Me–PhH), 247 (30), 217 (100), 187 (55), 129 (40), 73 (60). When a sample was dissolved in CH_2Cl_2 in an NMR tube the ^{1}H NMR spectrum was found to be identical with that of $(Me_3Si)_3CSnPhCl_2$, and addition of an authentic sample of the latter only enhanced the signals.

3.14. Preparation of $(Me_3Si)_3CSnF_3$

A solution of $(Me_3Si)_3CSnCl_3$ (2.0 g, 4.4 mmol) in CH_2Cl_2 (20 cm^3) was added dropwise during 10 min to a solution of $AgBF_4$ (1.0 g, 5.1 mmol) in CH_2Cl_2 (10 cm^3). The mixture was stirred for 3 h with protection from light then filtered. The solvent was removed from the filtrate to leave a white solid which was recrystallised from hexane to give trifluoro{tris(trimethylsilyl)methyl}stannane (1.7 g, 94%), m.p. 211°C (dec.). Found: C, 29.4; H, 6.9. $C_{10}H_{27}F_3Si_3Sn$. Calc.: C, 29.6; H, 6.6%. δ(H) (C_6D_6) 0.26. δ(C) (C_6D_6): 4.4 (^3J(CSn) 37.5 Hz, Me_3Si). δ(Si) (C_6D_6) 1.0. δ(Sn) (C_6D_6): − 33.0 δ(F) (C_6D_6) − 145.1 (J(FSn) 3458 Hz). *m/z* 393 (10%, M–Me), 217 (30), 201 (50), 165 (90), 129 (15), 85 (30), 73 (100).

3.15. Preparation of $(Me_2PhSi)_3CSnMe_2OEt$

A solution of Me_2SnCl_2 (9.5 g, 43 mmol) in 1:1 THF/Et_2O (20 cm^3) was added dropwise to a solution of $(Me_2PhSi)_3CLi$ (43 mmol) in THF (30 cm^3) during 10 min at room temperature. The mixture was heated under reflux for 10 min and the solvent then removed. The pale yellow residue was extracted into CH_2Cl_2 (50 cm^3), the extract was filtered, and the solvent was removed. The residue was dissolved in boiling EtOH and the solution was allowed to cool to room temperature to give white crystals of ethoxy(dimethyl){tris(dimethylphenylsilyl)methyl}stannane, (20 g, 76%), m.p 130°C. Anal. found: C, 56.2: H, 7.1. $C_{29}H_{44}OSi_3Sn$. Calc.: C, 56.9; H, 7.2%. δ(H) (CD_2Cl_2) 0.57 (18H, s, Me_2Si), 0.59 (6H, s, Me_2Sn), 1.24 (t, CH_3CH_2O), 3.81 (q, CH_2O), 6.97–7.3 (15H, m, Ph). δ(C) (CD_2Cl_2): 4.8 (Me_2Si), 4.9 (Me_2Sn), 21.0 (CH_3CH_2O), 60.5 (CH_2O), 129.0 (C_4), 127.7 (C_3), 136.2 (C_2), 141(C_1). δ(Si) (CD_2Cl_2): -5.94. δ(Sn) (CD_2Cl_2) 92.7. *m/z* 597 (20%, M–Me), 551 (40, M–EtOH–Me), 402 (20, M–Me_3SnOEt), 309 (40) 250 (20), 197 (35), 165 (25), 135 (100), 73 (30).

3.16. Reaction of $(Me_2PhSi)_3CSnMe_2OEt$ with ICl

A solution of ICl (3.3 mmol) in CCl_4 was added dropwise to a solution of $(Me_2PhSi)_3CSnMe_2OEt$ (2.0 g, 3.2 mmol) in CCl_4 (10 cm^3), and the mixture was stirred for 1 h. The solvent was then removed to leave a white solid, which was recrystallised from hexane (10 cm^3) to give chloro(dimethyl){tris(dimethylphenylsilyl)methyl}stannane. (1.9 g, 96%), m.p. 188°C. (Lit. [5] 186°C). δ(Si) -5.7. The C, H analysis and ^{1}H, ^{13}C and ^{119}Sn NMR spectra were identical with those reported previously [5].

3.17. Reaction of $(Me_2PhSi)_3CSnMe_2OEt$ with an excess of ICl

A solution of ICl (10 mmol) in CCl_4 was added to a solution of $(Me_2PhSi)_3CSnMe_2OEt$ (2.0 g, 3.3 mmol) in CCl_4 (10 cm^3), and the mixture was stirred for 3 h. The solvent was then removed to leave a white solid, which was recrystallised from hexane to give dichloro(methyl){tris(dimethylphenylsilyl)methyl}stannane (1.9 g, 95%), m.p. 182°C. δ(H) ($CDCl_3$): 0.76 (18H, s, Me_2Si), 1.18 (3H, s, ^2J(HSn) 63.4 Hz, MeSn), 6.89–7.36 (15H, m, Ph). δ(C) ($CDCl_3$): 4.6 (Me_2Si), 15.0 (MeSn), 127.7 (C_3), 129.4 (C_4), 135.8 (C_2), 138.1 (C_1). δ(Si) ($CDCl_3$): -5.5. δ(Sn) ($CDCl_3$): 75.7. *m/z* 622 (5%, M), 607 (5, M–Me), 571 (10, M–HCl–Me), 452 (10, M–$Me_2PhSiCl$), 437 (5, M–$Me_2PhSiCl$–Me), 309, 237 (10), 197 (20), 175 (40), 135 (100), 73 (50), 43 (30).

In an attempt to displace a further Me group from tin the experiment was repeated but with the mixture heated under reflux. A complex mixture of products was obtained and not further investigated.

3.18. Reaction of $(Me_2PhSi)_3CSnMe_2OEt$ with Br_2 in 2/1 molar ratio

A solution of Br_2 (1.63 mmol) in CCl_4 was added dropwise to a solution of $(Me_2PhSi)_3CSnMe_2OEt$ (2.0 g, 3.2 mmol) in CCl_4 (10 cm^3) and the mixture was stirred for 1 h. The solvent was then pumped off to leave a white solid, which was recrystallised from hexane (10 cm^3) to give bromo(dimethyl){tris(dimethylphenylsilyl)methyl}stannane (1.9 g, 91%), m.p. 186°C. Anal. found: C, 50.2; H, 6.2. $C_{27}H_{39}BrSi_3Sn$. Calc.: C, 50.15; H, 6.0%. δ(H) ($CDCl_3$): 0.70 (18H, s, Me_2Si), 0.96 (6H, s, ^2J(HSn) 56 Hz, Me_2Sn), 6.81–7.3 (15H, m, Ph). δ(C) ($CDCl_3$): 4.7, ^1J(CSi) 52.9, ^3J(CSn) 14 Hz) Me_2Si), 8.5, (^1J(CSn) 363 Hz, Me_2Sn), 127.6 (C_3), 129.0 (C_4), 135.7 (C_2), 139.5 (^1J(CSi) 33.4 Hz, C_1). δ(Si) ($CDCl_3$): -5.7. δ(Sn) ($CDCl_3$): 82. *m/z* 631 (12%, M–Me), 551 (40, M–Me–HBr), 402 (30 M–Me_3SnBr), 340 (5, M–$Me_2PhSnBr$), 309 (60), 197 (10), 175 (15), 135 (100), 73 (20).

3.19. Reaction of $(Me_2PhSi)_3CSnMe_2OEt$ with an excess of Br_2

A solution of Br_2 (10.0 mmol) in CCl_4 (10.0 cm^3) was added to a solution of $(Me_2PhSi)_3CSnMe_2OEt$ (2.0 g, 3.2 mmol) in CCl_4 (10 cm^3). The mixture was stirred for 3 h and the reaction monitored by ^{1}H NMR spectroscopy. The solvent was then removed to leave a white solid, which was recrystallised from hexane (10 cm^3) to yield dibromo(methyl){tris(dimethylphenylsilyl)methyl}stannane (2 g, 87%), m.p. 211°C. Anal. found: C, 43.2; H, 5.0. $C_{26}H_{36}Br_2Si_3Sn$. Calc.: C, 43.8; H, 5.0%. δ(H) ($CDCl_3$): 0.83 (18H, s, Me_2Si), 1.55 (3H, s, ^2J(HSn) 56.7 Hz, MeSn), 6.8–7.37 (15H, m, Ph). δ(C) ($CDCl_3$): 4.7 (^3J(CSn) 16.3 Hz, ^1J(CSi) 53.2 Hz, Me_2Si), 17.0 (J(CSn) 425 Hz, Me_2Sn), 127.8 (C_3), 129.4 (C_4), 135.9 (C_2), 138.3 (^1J(CSn) 50 Hz, C_1). δ(Si) ($CDCl_3$): -5.4. δ(Sn) ($CDCl_3$): -7.5. *m/z* 710 (10%, M), 695 (10, M–Me), 633 (10, M–Ph), 615 (90, M–Me–HBr), 537 (50, M–Br–MeBr), 402 (40, M–Me–Me_2SnBr_2), 309 (75), 197 (70, PhSn), 135 (100, Me_2PhSi), 73 (85, Me_3Si), 43 (97, MeSi).

3.20. Reaction of $(Me_2PhSi)_3CSnMe_2OEt$ with an excess of I_2

A solution of I_2 (10.0 mmol) in CCl_4 (10 cm^3) was added to a solution of $(Me_2PhSi)_3CSnMe_2OEt$ (0.90 g, 1.46 mmol) in CCl_4 (10 cm^3) and the mixture was stirred for 3 h. The solvent was removed to leave a white solid, which was recrystallised from hexane (10 cm^3) to give iododimethyl{tris(dimethylphenylsilyl}methyl}stannane (0.92 g, 90%), m.p. 187°C. Anal. found; C, 46.8; H, 5.9. $C_{27}H_{39}ISi_3Sn$. Calc.: C, 46.6; H, 5.6%. δ(H) ($CDCl_3$) 0.73 (s, 18H, Me_2Si), 1.2 (s, 6H, ^2J(HSn) 51 Hz, Me_2Sn), 6.70–7.4 (m, 15H, Ph). δ(C) ($CDCl_3$): 4.8 (Me_2Si), 9.25 (^1J(CSn) 351 Hz, Me_2Sn,), 127.5 (C_3), 128.9 (C_4), 135.7 (C_2), 139 7 (C_1). δ(Si) ($CDCl_3$): -5.7. δ(Sn) ($CDCl_3$): -8.9. *m/z* 679 (3, M–Me), 567 (40, M–I), 551 (20, M–Me–HI), 489 (25, M–Ph–HI), 402 (50, M–Me_3SnI), 340 15, M–Me_2PhSnI), 325 (80), 309 (90), 263 (25), 247 (45), 197 (50), 175 (47), 135 (100), 78 (95), 43 (100).

3.21. $(Me_2PhSi)_3CSnMe_2ONO_2$ and $(Me_2PhSi)_3CSnMe_2NCS$

The preparations of these compounds were described previously [7].

3.22. Reaction of $(Me_2PhSi)_3CSnMe_2Br$ with Ag_2O

A solution of $(Me_2PhSi)_3CSnMe_2Br$ (2.0 g, 3.0 mmol) in CH_2Cl_2 (15 cm^3) was added to a suspension of Ag_2O (1.00 g, 4.3 mmol) in CH_2Cl_2 (10 cm^3) and the mixture was stirred in an open vessel for 24 h. The solvent was then removed to leave a white solid, which was recrystallised from hexane (10 cm^3) and found to be bis[-dimethyl{tris(dimethylphenylsilyl)methyl}]tin oxide (1.6 g, 92%), m.p. 222°C. Anal. found: C, 56.6; H, 6.9. $C_{54}H_{78}OSi_6Sn_2$. Calc.: C, 56.3; H, 6.8%. δ(H) ($CDCl_3$): 0.69 (36H, s, Me_2Si), 0.82 (12H, s, Me_2Sn), 6.6–7.3 (30H, m, Ph). δ(C) ($CDCl_3$): 4.7 (^1J(CSi) 53 Hz, ^3J(CSn) 15 Hz, Me_2Si), 5.2 ($^1J(C^{117}Sn)$ 388, $^1J(C^{119}Sn)$ 406 Hz, Me_2Sn), 127.4 (C_3), 128.4 (C_4), 135.6 (C_2), 140.1 (^1J (CSi) 21 Hz, C_1). δ(Si) ($CDCl_3$): -5.9. δ(Sn) ($CDCl_3$) 74.6. *m/z* 567 (20%, $(Me_2PhSi)_3CSnMe_2 = R$), 489 (25, R–PhH), 309 (40, R–Me_4Sn–PhH), 247 (25, R–Me_3SnPh–PhH), 227 (25, Me_2PhSn), 197 (25, PhSn), 154 (70, Ph_2), 91 (70, $C_6H_5CH_2$), 77 (55, Ph), 73 (50, Me_3Si).

3.23. Reaction of $(Me_2PhSi)_3CSnMe_2Cl$ with $LiAlH_4$

A solution of $(Me_2PhSi)_3CSnMe_2Cl$ (2.0 g, 3.3 mmol) in dry THF (10 cm^3) was added to a solution of $LiAlH_4$ (0.15 g, 3.9 mmol) in THF (10 cm^3) under nitrogen, and the mixture was stirred for 1 h. The solvent was then removed and the residue extracted with anhydrous toluene. The toluene was evaporated from the extract and the residue was recrystallised from hexane and shown to be tris(dimethylphenylsilyl)methane, $(Me_2PhSi)_3CH$, (1.2 g, 87%), m.p. 103°C (lit. [19], 105°C). ^{1}H NMR (C_6D_6): 0.25 (18H, s, Me_2Si), 0.53 (1H, s, CH), 7.1–7.3 (15H, m, Ph) (see ref. [19] for shifts in CCl_4). δ(C) (C_6D_6): 1.77 (s, ^1J(CSi) 53.5 Hz, Me_2Si), 0.45 (s, CH), 128.4 (C_3), 128.7 (C_4), 133.6 (C_2), 142.1 (C_1). δ(Si) (C_6D_6): -4 3.

3.24. Reaction of $(Me_2PhSi)_3CSnMe_2Cl$ with MeOH

A solution of $(Me_2PhSi)_3CSnMe_2Cl$ (2.0 g, 3.3 mmol) in MeOH (20 cm^3) was heated under reflux. The progress of the reaction was monitored by ^{1}H NMR spectroscopy and after 4 days the solvent was removed to give methoxydimethyl{tris(dimethylphenylsilyl)methyl}stannane, $(Me_2PhSi)_3CSnMe_2OMe$, (1.9 g, 96%), m.p. 132°C. Anal. found: C, 56.1; H, 7.2. $C_{28}H_{42}OSi_3Sn$. Calc.: C, 56.3; H, 7.0%. δ(H) ($CDCl_3$) 0.63 (18H, s, Me_2Si), 0.66 (6H, s, Me_2Sn), 3.7 (3H, s, ^3J (HSn) 41 Hz, OMe), 7.0–7.37 (15H, m, Ph). δ(C) ($CDCl_3$) 4.5 (Me_2Si), 4.7 (Me_2Sn), 52.8 (OMe), 127.3 (C_3), 128.6 (C_4), 135.6 (C_2), 140.2 (C_1). δ(Si) ($CDCl_3$): -5.9. δ(Sn) ($CDCl_3$): 92.6. *m/z* 583 (25%, M–Me), 551 (40, M–Me–MeOH), 521 (10, M–Ph), 505 (10, M–Ph–MeH), 489 (5, M–Ph–MeOH), 403 (12, M–Me–Me_4Sn), 341 (30, M–Ph–Me_4Sn), 309 (45), 279 (30, M–Ph–Me_3PhSn), 227 (20, Me_2PhSn), 197 (30, PhSn), 175 (25), 151 (35, Me_3PhSi), 135 (100, Me_2PhSi), 73 (40, Me_3Si), 43 (25, MeSi).

3.25. Reaction of $(Me_2PhSi)_3CLi$ with $SnCl_4$ in THF

A solution of $(Me_2PhSi)_3CLi$ (12.0 mmol) in THF (30 cm^3) was added dropwise with stirring during 20 min to a suspension of $SnCl_4$ (3.1 g, 12.0 mmol) in THF (25 cm^3) at 0°C. The mixture was stirred for 1 h at room temperature, the solvent then removed, and the residue extracted with CH_2Cl_2 (30 cm^3). The solvent was evaporated from the extract and the residue recrystallised from hexane (50 cm^3) to give trichloro{tris(dimethylphenylsilyl)methyl}stannane (2.0 g, 25%), m.p. 222°C. Anal. found: C, 46.5; H, 5.3%. $C_{25}H_{33}Cl_3Si_3Sn$. Calc.: C, 46.7; H, 5.1%. δ(H) ($CDCl_3$): 0.84 (18H, s, ^2J (HSi) 6.2 Hz, Me_2Si), 7.0–7.6 (15H, m, Ph). δ(C) ($CDCl_3$) 4.7 (s, ^3J(CSn), 14.7 Hz, Me_2Si), 127.8 (C_3), 129.7 (C_4), 135.9 (C_2), 136.6 (C_1). δ(Si) ($CDCl_3$): -5.0. δ(Sn) ($CDCl_3$): -56.5. *m/z* 627 (2%, M–Me), 591 (3, M–Me–HCl), 402 (30, M–$MeSnCl_3$), 325 (25, M–Ph–$MeSnCl_3$), 309 (40), 197 (30),, 175 (25), 135 (100), 105 (30), 73 (30), 43 (30). A second product began to crystallise out after 3 h as colourless needles and was identified as chloro{tris(dimethylphenylsilyl)}methane, $(Me_2PhSi)_3CCl$ (2.5 g, 46%), m.p. 199°C.(lit. [25] 201°C) Anal. found: C, 66.6; H, 7.4. $C_{25}H_{33}ClSi_3$. Calc.: C, 66.4; H, 7.3%. The ^{1}H, ^{13}C and ^{29}Si NMR and mass spectra were identical with those recorded previously [26].

3.26. Preparation of Bu_3SnOEt

Sodium (0.15 g, 6.5 mmol) was cautiously dissolved in anhydrous EtOH (10 cm^3) and a solution of Bu_3SnCl (2.0 g, 6.1 mmol) in EtOH (10 cm^3) was added. The mixture was stirred for 2 h, the solvent then removed, and the residue distilled at 90°C / 0.1 mmHg (Lit. 92°/0.1 mm [27]) to give tributyl(ethoxy)tin, Bu_3SnOEt, (1.9 g, 93%). δ(Sn) (CCl_4–$CDCl_3$ 1:1) 106. The only value given in the literature for comparison is δ 86 [28], but this is for the neat liquid which is known to be highly associated. Shifts of 90–130 have been reported for trialkylalkoxytins in halogenated or hydrocarbon solvents [29].

3.27. Reaction of Bu_3SnOEt with ICl

A solution of ICl (0.49 g, 3.0 mmol) in CCl_4 (20 cm^3) was added dropwise during 10 min to a stirred solution of Bu_3SnOEt (1.9 g, 2.97 mmol) in CCl_4 (10 cm^3). The mixture was stirred for a further 5 min, after which the ^{1}H NMR spectrum showed that reaction was complete. The solvent was removed and the residue distilled at 108–111 °C/20 mmHg to give tributylchlorostannane, Bu_3SnCl, (0.9 g, 93%). δ(Sn) NMR (CCl_4-20% $CDCl_3$): 154.2. When an authentic sample of Bu_3SnCl was added, the signal was enhanced.

3.28. Reaction of $(Me_3Si)_2CCl_2$ with two equivalents of Ph_3SnLi

A solution of $(Me_3Si)_2CCl_2$ (5 g, 21.9 mmol), in THF (20 cm^3) was added dropwise with stirring during 20 min to a solution of Ph_3SnLi [30] (43.8 mmol) in THF (50 cm^3) at 0°C. The mixture was stirred for 3 h, the solvent then removed and the solid residue recrystallised from light petroleum (b.p. 60–80 °C). Initially bis(trimethylsilyl)(triphenylstannyl)methane separated (1.2 g, 10.7%),. m.p. 96°C. Anal. found: C, 59.0; H, 6.65. $C_{25}H_{34}Si_2Sn$. Calc.: C, 58.8; H, 6.7%. δ(H) (C_6D_6): 0.13 (18H, s, Me_3Si), 0.39 (1H, s, CH), 7.0–7.7 (15H, m, Ph). δ(C) (C_6D_6) 0.59 (CH), 3.6 (Me_3Si), 128.8 (C_3), 129.1 (C_4), 137.6 (C_2), 141.4 (C_1). δ(Si) (C_6D_6) 1.5. δ(Sn) (C_6D_6) 2.1. m/z 495 (3%, M–Me), 433 (8, M–Ph), 351(3, Ph_3Sn),197 (10 PhSn) 167 (50), 151 (100), 135 (20), 73 (30), 43 (15). A second crop of crystals proved to be hexaphenylditin (12 g, 71%), m.p. 225 °C (lit. 229.5–231°C [30,31]).

3.29. Preparation of $(Me_3Si)_2C(SnMe_2Ph)_2$ [32]

A solution of PhLi (8.5 mmol) in Et_2O (10 cm^3) was added dropwise to a stirred solution of $(Me_3Si)_2C(SnMe_2Cl)_2$ [5] (2.0 g 3.8 mmol) in THF (20 cm^3) at room temperature. The mixture was stirred for 1 h and then treated with a few drops of MeOH to destroy the residual PhLi. The solvent was removed and the residue was extracted into CH_2Cl_2 (50 cm^3). The extract was filtered, the solvent was pumped away from the extract and the white residue was recrystallised from MeOH to give $(Me_3Si)_2C(SnMe_2Ph)_2$ (1.80 g, 78%) m.p. 115°C. Anal. found: C, 41.6; H, 7.5 $C_{23}H_{40}Si_2Sn_2$. Calc.: C, 41.2; H, 7.8%. δ(H) (CH_2Cl_2) 0.16 (18H, s, Me_3Si), 0.5 (12H, s, Me_2Sn ^2J(SnH) 49.5 Hz), 7.21–7.58 (10H, m, Ph). δ(C) ($CDCl_3/CH_2Cl_2$) -3.1 (^1J(CSn) 329 Hz $SnMe_2$), 5.2 (^3J(CSn) 15.9 Hz, $SiMe_3$), 127.8(C_3) 128.1(C_4), 136.6 (C_2), 143.7(C_1). δ(Sn) ($CDCl_3/CH_2Cl_2$) -19.2. m/z 597 (30%, M–Me), 535 (5, M–Ph), 385 (M–$PhMe_2Sn$), 255(20), 227(20, $PhMe_2Sn$), 193(20), 165(20), 135(100), 73(95).

3.30. Preparation of $(Me_3Si)_2C(SnMe_2Ph)Li$

A 1.3 M solution of MeLi in Et_2O (3.8 cm^3) was added dropwise to a solution of $(Me_3Si)_2C(SnMe_2Ph)_2$ (3.0 g, 4.9 mmol) in THF (20 cm^3), and the mixture was stirred at room temperature for 10 min, after which the reaction was complete. (This was shown by adding a sample (0.5 cm^3) of the mixture to Me_3SiCl (2 cm^3), replacing the solvent by CH_2Cl_2 and recording the ^{1}H NMR spectrum, in which the ratio of the integrals of the Me_3Si-signals from $(Me_3Si)_3CSnMe_2Ph$ and $(Me_3Si)_2C(SnMe_2Ph)_2$ was $> 97/3$.) A few drops of Me_3SiOMe were added to destroy any residual methyllithium before the solution was used.

3.31. Reaction of $(Me_3Si)_2C(SnMe_2Ph)Li$ with Me_2SiCl_2

A solution of $(Me_3Si)_2C(SnMe_2Ph)Li$ (4.9 mmol) in THF (20 cm^3) was added dropwise with stirring to a solution of Me_2SiCl_2 (0.64 g, 5.0 mmol) in THF (10 cm^3). The mixture was stirred for a further 10 min and the solvent then removed. The residue was extracted with CH_2Cl_2 (20 cm^3), the solvent evaporated from the extract, and the residue recrystallised from hexane (10 cm^3) to give needle-like crystals of {(chlorodimethylsilyl)bis(trimethylsilyl)methyl}dimethylphenylstannane, (1.8 g, 76%), m.p. 136°C. Anal found: C, 42.7; H, 7.35. $C_{17}H_{35}ClSi_3Sn$ Calc: C, 42.7; H, 7.3%. δ(H) ($CDCl_3$): 0.26 (18H, s, ^2J(HSi) 6.2 Hz, Me_3Si), 0.53 (s, 6H, ^2J(HSi) 6.5 Hz, Me_2Si), 0.59 (s, 6H, ^2J(HSn) 50.6 Hz, Me_2Sn), 7.31–7.72 (5H, m, Ph). δ(C) ($CDCl_3$): -2.5 (^1J(CSn) 353 Hz, Me_2Sn); 5.0, (^1J(CSi) 51.7 Hz, Me_3Si), 8.5 (Me_2Si), 127.9 (C_3), 128.3 (C_4) 136.9 (C_2), 143.2 ^1J(CSn) 470 Hz, (C_1). δ(Si) ($CDCl_3$): -0.6 (Me_3Si), 27.9 (Me_2Si). δ(Sn) ($CDCl_3$): -33.4. m/z 463 (28%, M–Me), 427 (22, M–Me–HCl), 263 (40, $Me_2Si{=}C(SiMe_3)SiMePh$), 248 (15), 227 (15), 201 (100, $Me_2Si{=}C(SiMe_3)SiMe_2$), 135 (10), 73 (60), 58 (10).

3.32. Reaction of $(Me_3Si)_2C(SnMe_2Ph)(SiMe_2Cl)$ with $AgBF_4$

A solution of $(Me_3Si)_2C(SnMe_2Ph)(SiMe_2Cl)$ (0.50 g, 1.05 mmol) in CH_2Cl_2 (10 cm^3) was added in one portion to $AgBF_4$ (0.2 g, 1.03 mmol) in CH_2Cl_2 (10 cm^3) and the mixture was stirred for 24 h. The ^1H NMR spectrum showed that only the starting material was present. The mixture was heated under reflux for 20 min and then filtered. The solvent was removed from the filtrate and the residue recrystallised from hexane (10 cm^3) to give fluoro{(fluorodimethylsilyl)bis(trimethylsilyl)methyl}dimethylstannane (90.4 g, 96%), m.p. 198°C. Anal. found: C, 32.9; H, 7.6. $C_{11}H_{30}F_2Si_3Sn$. Calc.: C, 32.7; H, 7.4%. δ(H) ($CDCl_3$): 0.25 (18H, s, ^2J(HSi) 6.1 Hz, Me_3Si), 0.43 (6H, d, ^3J(HF) 7.5 Hz, Me_2Si), 0.70 (d, 6H, ^3J(HF) 3.8 Hz, ^2J(HSn) 55 Hz, Me_2Sn,). δ(C) ($CDCl_3$): 4.1 (Me_3Si), 4.3 (Me_2Si), 4.5 (Me_2Sn). δ(Si) ($CDCl_3$): -1.9 (d, ^3J(SiF) 4.9 Hz, Me_3Si)., -28.4 (d, ^1J(SiF) 281 Hz, $SiMe_2F$). δ(Sn) ($CDCl_3$): 146.8 (dd, ^1J(SnF) 2376 Hz, ^3J(SnF) 65.5 Hz). δ(F) ($CDCl_3$): -140.4 (sept, ^3J(FH) 7.5 Hz, ^1J(FSi) 283 Hz, SiF), -204.7 (sept unresolved, ^1J ($F^{119}Sn$) 2379 ^1J($F^{117}Sn$) 2272 Hz, ^2J(FC) 65 Hz, SnF). m/z 389 (40%, M–Me), 209 (100, M–Me_4Sn–Me), 165 (35, Me_3Sn), 135 (17, MeSn), 73 (35, Me_3Si).

4. Crystal structure determinations

4.1. $[\{(Me_3Si)_3C\}Me(O_2NO)Sn]_2O$, **1**

Crystal data: $C_{22}H_{60}N_2O_7Si_6Sn_2$, monoclinic, $C2/c$, $M = 870.7$, $a = 14.397(9)$, $b = 10.599(4)$, $c = 26.798(28)$ Å, $\beta = 93.29(7)°$, $U = 4082.3$ Å^3, $Z = 4$, $D_c = 1.41$ g cm^{-3}, $F(000) = 1784$, monochromated Mo-K_α radiation, $\lambda = 0.71069$ Å, $\mu = 14.34$ cm^{-1}.

A crystal of dimensions 0.43 × 0.15 × 0.2 mm was used for data collection at 21°C on an Enraf-Nonius CAD-4 diffractometer. A total of 3944 reflections with $+h +k \pm l$ and $2 < \theta < 25°$ were measured by a $\theta/2\theta$ scan. Corrections were made for Lorentz and polarization effects. There was no decay during data collection. After averaging of equivalent reflections ($R_{int} = 0.025$) there were 3804 unique relections of which 2584 with $|F^2| > 3\sigma(F^2)$ were used in the refinement, where $\sigma(F^2) = [\sigma^2(I) + (0.04I)^2]^{1/2}/L_p$.

The SHELXS-86 program (Patterson method) was used to locate the Sn atom, and difference maps were used to find the remaining non-hydrogen atoms, which were refined by full-matrix least squares with anisotropic factors except for O(2a), O(3a), O(4a), N(a), C(8a), C(10a) and C(11a), which were left isotropic. The hydrogen atoms were omitted. The final parameters were $R = 0.074$, $R' = 0.096$, observed reflections = 2584, $w = \sigma(F)^{-2}$.

The molecule had two different orientations with occupancies 0.72 and 0.28.

4.2. $TpsiSnMeCl_2$, **2**

Crystal data: $C_{26}H_{36}Cl_2Si_3Sn$, monoclinic, $P2_1/c$, $M = 622.4$, $a = 11.151(5)$, $b = 17.766(6)$, $c = 15.074(7)$ Å, $\beta = 95.38(3)°$, $U = 2972.9$ Å^3, $Z = 4$, $D_c = 1.4$ g cm^{-3}, $F(000) = 1272$, monochromated Mo-K_α radiation, $\lambda = 0.71069$ Å, $\mu = 11.7$ cm^{-1}.

A crystal of dimensions 0.20 × 0.35 × 0.20 mm was used for data collection at 21°C on an Enraf-Nonius CAD-4 diffractometer. A total of 5686 reflections with $h\ k \pm l$ and $2 < \theta < 25°$ were measured by a $\theta/2\theta$ scan with scan width $\Delta\theta = (0.8 + 0.35 \tan \theta)°$ and a maximum scan time of 1 min. Corrections were made for Lorentz and polarization effects and for absorption using DIFABS (max 1.22, min 0.72). 2846 reflections with $|F^2| > \sigma(F^2)$ were used in the refinement, where $\sigma(F^2) = [\sigma^2(I) + (0.04I)^2]^{1/2}/L_p$.

The heavy atom routines of the SHELX-86 program were used to locate non-hydrogen atoms which were all refined by full-matrix least squares with anisotropic thermal parameters using programs from the Enraf-Nonius SDP package. The Cl and Me groups of the $SnMeCl_2$ entity showed evidence of disorder, and a refinement of occupancies suggested that the site labelled Cl(2) was in fact 0.64Cl and 0.36C while the site C(26) was 0.36Cl and 0.64C, and appropriate average scattering factors were used. The H atoms of the Tpsi group were fixed at calculated positions with $U_{iso} = 1.3U_{eq}$ for the atoms to which they were bonded. The H atoms on C(26) were omitted. The final parameters were $R = 0.061$, $R' = 0.056$, $s = 1.4$, number of variables = 289, number of observed reflections = 2846, $w = \sigma^{-2}(F)$, $\Sigma w(|F_o| - |F_c|)^2$ minimized, $(\Delta/\sigma)_{max} = 0.02$, $(\Delta\rho)_{max,min} = 0.54, -0.46$ e Å^{-3}

4.3. $TpsiSnCl_3$ **3**

Crystal data: $C_{25}H_{33}Cl_3Si_3Sn$, trigonal $P\bar{3}$, $a = 14.910(4)$, $c = 11.321(3)$ Å, $U = 2179.6$ Å^3, $Z = 3$, $D_c = 1.50$ g cm^{-3}, $F(000) = 978$. Monochromated Mo-K_α radiation, $\lambda = 0.71069$ Å, $\mu = 12.9$ cm^{-1}. Reflections from a crystal 0.2 × 0.2 × 0.2 mm were indexed on the basis of the trigonal cell above; weaker reflections with a different profile could be indexed with a larger cell with the same c axis and $a = 25.81$ Å. 4032 relections with h, $\pm k$, l and $2 < \theta < 25°$ were measured and 1514 with $|F|^2 > 3\sigma(F^2)$ were used. By direct methods (SHELXS-86) in space group $P3$ three independent molecules, two ordered and one disordered, were located. The space group was changed to $P\bar{3}$ with one molecule disordered across an inversion centre and the other in a general positon. All the atoms were refined by full matrix least squares with anisotropic temperature factors except for C(1), C(1a), C(3a) and C(8a) which were isotropic. Hydrogen atoms in molecule 1 were at calculated postions (C–H 0.95Å) and $B_{iso} = 1.3B_{eq}$ for the adjacent atom and those in molecule 2 were omitted. Refinement converged at $R = 0.067$, $R' = 0.089$.

5. Supplementary data

For all structures, hydrogen atom coordinates, anisotropic thermal parameters, and complete lists of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

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