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Synthesis and properties of some crowded organotin compounds *

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Abstract

The preparations of the compounds $(Me_3Si)_3CSnMe_2X$ (X = Cl, Br, I, CN, NCS, O_2CMe, O_2CCF_3, O_3SMe, or NO_3), $(Me_3Si)_3CSnPh_2X$ (X = Cl or Br), and $(Me_2PhSi)_3CSnMe_2X$ (X = Me, Cl, Br, or I) are described. Treatment of $(Me_2PhSi)_3CSnMe_2Cl$ with one equivalent of MeLi gives $(Me_2PhSi)_3CSnMe_3$, but with additional MeLi $(Me_2PhSi)_3CLi$ is formed. The compound $(Me_3Si)_2C(SnMe_3)_2$ is obtained by reaction of $(Me_3Si)_2CCl_2$ with either one or two equivalents of Me_3SnLi, and on treatment with MeLi gives the useful reagent $(Me_3Si)_2(Me_3Sn)CLi$. The latter reacts with Me_2SiCl_2 and to give $(Me_3Si)_2(Me_3Sn)C(SiMe_2Cl)$ and with Me_2SiHCl to give $(Me_3Si)_2(Me_3Sn)C(SiMe_2H)$, which reacts with a one molar proportion of Br_2 to give $(Me_3Si)_2(Me_3Sn)C(SiMe_2Br)$, and with a two molar proportion of Br_2 to give $(Me_3Si)_2C(SnMe_2Br)(SiMe_2Br)$. Reaction of $(Me_3Si)_2C(SnMe_3)_2$ with two equivalents of ICl or Br_2 gives the dihalides $(Me_3Si)_2C(SnMe_2X)_2$ (X = Cl or Br), and reaction of $(Me_3Si)_2C(SnMe_2Br)(SiMe_2Br)$ with PhLi gives $(Me_3Si)_2C(SnMe_2Ph)(SiMe_2Br)$.

Introduction

Studies of compounds in which the very bulky $(Me_3Si)_3C$ group (the 'trisyl' group, frequently denoted below by the symbol Tsi) is attached to a functional silicon centre, as in compounds of the type $TsiSiR_2X$, have revealed much novel chemistry [1,2]. In contrast, compounds with the trisyl group attached to the larger tin atom have so far shown few unusual properties [3–8].

The first such tin compound reported was $TsiSnMe_3$, obtained by treatment of TsiLi with Me_3SnCl [3]. (It was later also prepared by another, more complex, route [4].) A wide range of trisyl-tin derivatives was subsequently made by Glockling and

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* Dedicated to Professor E.O. Fischer on the occasion of his 70th birthday.

his co-workers, who noted that the Tsi–Sn bond is unusually inert but that cleavage of other Sn–C bonds in their compounds could be readily brought about, to give a large number of new products [6–8]. Among these were some interesting 8-hydroxyquinoline (HOX) derivatives, $TsiSnR_n(OX)_{3-n}$ (R = Me or Ph; $n = 1$ or 2), and in a surprising reaction these were found to lose an Me_3Si group in refluxing ethanol [8].

We describe below the results of some further studies on trisyl-tin compounds and some related species.

Results and discussion

Reactions of TsiLi with R_2SnCl_2 (R = Me or Ph) were used to give the compounds $TsiSnR_2Cl$ (cf. ref. 5). The related lithium reagent $(Me_2PhSi)_3CLi$ was used analogously with Me_2SnCl_2.

$$(Me_2PhSi)_3CLi + Me_2SnCl_2 \rightarrow (Me_2PhSi)_3CSnMe_2Cl$$

The chloride $TsiSnMe_2Cl$ was found to undergo metathetical reactions with salts in refluxing acetone:

$$TsiSnMe_2Cl + MX \rightarrow TsiSnMe_2X + MCl$$

(MX = LiBr, NaI, or KSCN)

The insolubility of MCl in the acetone is no doubt in some cases (e.g. in reaction with NaI) an important factor in driving the reactions to completion. Treatment of the $TsiSnMe_2Cl$ with NaOH in H_2O/EtOH gave the oxide $(TsiSnMe_2)_2O$.

The related chlorides $TsiSnPh_2Cl$ and $(Me_2PhSi)_3CSnMe_2Cl$ were shown to undergo similar reactions with salts:

$$TsiSnPh_2Cl + LiBr \rightarrow TsiSnPh_2Br$$

$$(Me_2PhSi)_3CSnMe_2Cl + NaX \rightarrow (Me_2PhSi)_3CSnMe_2X$$

(X = Br or I).

We confirmed that $TsiSnMe_2Cl$ reacted with MeLi to give $TsiSnMe_3$ (cf. ref. 6). The related chloride $(Me_2PhSi)_3CSnMe_2Cl$ behaved analogously when a one molar proportion of MeLi was used, but with an excess of MeLi the product after work-up was $(Me_2PhSi)_3CH$, isolated in 85% yield. Presumably the excess of MeLi cleaves the $C–SnMe_3$ bond in the initially formed $(Me_2PhSi)_3CSnMe_3$, a reaction facilitated by the substantial stability of the $(Me_2PhSi)_3C^-$ anion (cf. that of $(Me_3Si)_3C^-$ [9]).

$$\begin{array}{ccc} (Me_2PhSi)_3CSnMe_2Cl + MeLi & \rightarrow & (Me_2PhSi)_3CSnMe_3 \\ & & \downarrow MeLi \\ (Me_2PhSi)_3CH & \xleftarrow{MeOH} & (Me_2PhSi)_3CLi + Me_4Sn \end{array}$$

In contrast to $TsiSiMe_2Cl$, the tin chloride $TsiSnMe_2Cl$ was found to react readily with some silver salts:

$$TsiSnMe_2Cl + AgX \rightarrow TsiSnMe_2X$$

($X = O_2CMe$, O_2CCF_3, or O_3SCF_3)

The chloride did not react with AgCN, but the corresponding iodide did:

$$TsiSnMe_2I + AgCN \rightarrow TsiSnMe_2CN$$

Reaction of the iodide with $AgNO_3$ likewise gave the corresponding nitrate. The reactions of the chlorides $TsiSnMe_2Cl$, $TsiSnPh_2Cl$, and $(Me_2PhSi)_3CSnMe_2Cl$ with $AgBF_4$, apparently to give initially the corresponding tin tetrafluoroborates, and hence fluorides, have been described previously [10].

Reactions of the oxide $(TsiSnMe_2)_2O$ with mineral or organic acids HX gave, as expected, the corresponding species $TsiSnMe_2X$:

$$(TsiSnMe_2)_2O + HX \rightarrow TsiSnMe_2X$$

$$(X = Cl, F, O_2CMe, NO_3, O_3SMe).$$

More interesting results were obtained in a study of the bis-tin compound $(Me_3Si)_2C(SnMe_3)_2$ and its derivatives. This compound was, unexpectedly, the sole product from the reaction of $(Me_3Si)_2CCl_2$ with either a one or two molar proportion of Me_3SnLi in THF whatever the order of addition, and it is evident that the intermediate $(Me_3Si)_2(Me_3Sn)CCl$ is markedly more reactive than $(Me_3Si)_2CCl_2$ towards Me_3SnLi. We suggest that this observation is related to that by Prezzavento and Kuivila that Me_3SnCH_2Cl is ca. 1100 times as reactive as CH_2Cl_2 in the substitution reactions with Me_3SnLi in THF to give $(Me_3Sn)_2CH_2$ and Me_3SnCH_2Cl, respectively [11].

The compound $(Me_3Si)_2C(SnMe_3)_2$ was previously prepared by Seyferth and his colleagues by a more complex route [4]. The discovery of the simple preparation described above is of importance because the compound gives the reagent $(Me_3Si)_2(Me_3Sn)CLi$ on treatment with MeLi in THF:

$$(Me_3Si)_2C(SnMe_3)_2 + MeLi \rightarrow (Me_3Si)_2(Me_3Sn)CLi$$

The lithium reagent can be used to attach the ligand $(Me_3Si)_2(Me_3Sn)C$ to a range of metal centres, and this ligand is of special interest in being a close analogue of the trisyl ligand but containing reactive Sn–Me bonds as a potential source of functionality.

The identity and utility of the reagent $(Me_3Si)_2(Me_3Sn)CLi$ were confirmed by the following reactions:

$$(Me_3Si)_2(Me_3Sn)CLi + H_2O \rightarrow (Me_3Si)_2(Me_3Sn)CH$$

$$(Me_3Si)_2(Me_3Sn)CLi + Me_3SiCl \rightarrow (Me_3Si)_3(Me_3Sn)C$$

$$(Me_3Si)_2(Me_3Sn)CLi + Me_2SiCl_2 \rightarrow (Me_3Si)_2(Me_3Sn)C(SiMe_2Cl)$$

$$(Me_3Si)_2(Me_3Sn)CLi + Me_2HSiCl \rightarrow (Me_3Si)_2(Me_3Sn)C(SiMe_2H)$$

The silicon hydride $(Me_3Si)_2(Me_3Sn)C(SiMe_2H)$ reacted readily with a one molar proportion of bromine to give the bromide $(Me_3Si)_2(Me_3Sn)C(SiMe_2Br)$, and when additional bromine was used the subsequent cleavage of an Sn–Me bond gave $(Me_3Si)_2C(SnMe_2Br)(SiMe_2Br)$. The iodide $(Me_3Si)_2C(Me_3Sn)(SiMe_2I)$ was obtained, though not pure, from $(Me_3Si)_2(Me_3Sn)C(SiMe_2H)$ and ICl. Treatment of $(Me_3Si)_2C(SnMe_2Br)(SiMe_2Br)$ with a one molar proportion of PhLi resulted in exclusive substitution at tin to give $(Me_3Si)_2C(SnMe_2Ph)(SiMe_2Br)$.

The bis-tin compound $(Me_3Si)_2C(SnMe_3)_2$ reacted with an excess of ICl or Br_2 to give the dihalide $(Me_3Si)_2C(SnMe_2X)_2$ ($X = Cl$ or Br). When a one molar proportion of ICl or Br_2 was used the monohalides $(Me_3Si)_2C(SnMe_3)(SnMe_2X)$

(X = Cl or Br) were formed as the major products, along with some $(Me_3Si)_2C(SnMe_2X)_2$ and unchanged $(Me_3Si)_2C(SnMe_3)_2$.

Reaction of $(Me_3Si)_2C(SnMe_2Cl)_2$ with a two molar proportion of MeLi gave the expected product:

$$(Me_3Si)_2C(SnMe_2Cl)_2 + 2MeLi \rightarrow (Me_3Si)_2C(SnMe_3)_2$$

The reactions of the compounds $(Me_3Si)_2C(SnMe_3)(SiMe_2I)$ with silver salts, which involve migration of an Me group from Sn to Si, will be described elsewhere. (For a preliminary report see ref. 12.)

NMR and Mass Spectra

The NMR and EI mass spectral data, given in the Experimental section, require little comment. Chemical shifts and coupling constants are as expected from available data for related species [13], with the ^{119}Sn resonances for the compounds $TsiSnMe_2X$ and $(Me_2PhSi)_3CSnMe_2X$ (X = halogen) moving to higher field as the electronegativity of the halogen decreases. The ^{119}Sn NMR spectrum of $TsiSnMe_2NCS$, like that of $(cyclohexyl)_3SnNCS$ [14], shows a well-resolved triplet arising from $^{119}Sn-^{14}N$ coupling. The mass spectra of the compounds $TsiSnMe_2X$ (X = Me, Cl, Br, I, SCN, CO_2Me, CO_2CF_3, SO_3Me, or NO_3) show that the initial fragmentation is by loss of Me or X; for $(Me_3Si)_2C(SnMe_3)(SiMe_2X)$ (X = H, F, Cl, Br, or Me) initial loss of Me is more common than loss of X. Thereafter, $SnMe_3X$ is eliminated, apparently to give the cation $[Me_2SiC(SiMe_3)SiMe_2]^+$ (or an isomer), which is often the base peak. Elimination of $SiMe_4$ or $SiMe_3X$ seems to be less important. Likewise the compounds $(Me_2PhSi)_3CSnR_2X$ (R = Me or Ph, X = halogen) lose Me or Ph, and then HX or $SnMe_3X$. The prominent ions at m/z 325 ($[Me_2Si{=}C(SiMe_2Ph)(SiMePh]^+$), 309 (by elimination of MeH from the ion at m/z 325), 263 ($[Me_2Si{=}C(SiMe_2Ph)SiMe_2]^+$), and 135 ($[SiMe_2Ph]^+$) are characteristic of organometallic compounds containing the $(Me_2PhSi)_3C$ group.

Experimental

General

Reactions involving simple chlorosilanes, lithium metal, organolithium reagents, or silver salts were carried out under dry nitrogen. All solvents were dried by standard methods.

Sealed capillary tubes were used for determination of melting points above 300 °C.

Spectra

The ^1H NMR spectra were recorded on a Perkin–Elmer R32 spectrometer at 90 MHz with solutions in CH_2Cl_2 (except where otherwise stated) containing Me_4Si as internal standard. The ^{13}C spectra (at 90.7 MHz, relative to external Me_4Si), and ^{119}Sn spectra (at 134.1 MHz, relative to external Me_4Sn) were recorded with solutions in $CDCl_3/CH_2Cl_2$ unless otherwise stated, on a Bruker WM 360 spectrometer.

The IR spectra were determined with Nujol mulls between NaCl plates or as KBr discs.

Mass spectra were recorded at 70 eV, usually by electron impact, but where indicated by positive chemical ionization (CI) with NH_3 as ionizing gas; m/z values for chlorine-, bromine-, or tin-containing ions refer to the ^{35}Cl, ^{79}Br, and ^{120}Sn isotopes, and the reported abundances should be multiplied by 1.3, 2, and 3, respectively, to reflect the relevant total abundances.

Reagents

$(Me_3Si)_3CLi$ was prepared as previously described [15]; a few drops of Me_3SiOMe were added to destroy any residual MeLi. $(Me_2PhSi)_3CLi$ was prepared from $(Me_2PhSi)_3CH$ as previously described [16], but the progress of the metallation was monitored by treatment of samples with Me_2HSiCl in the way Me_3SiCl was used to monitor formation of TsiLi [15].

Reactions of TsiLi with Organotin Halides

(a) A solution of TsiLi (50 mmol) in THF (30 cm^3) was added with stirring during 0.5 h to a solution of Me_2SnCl_2 (12.0 g, 55 mmol) in a 1/3 THF/Et_2O mixture (50 cm^3) at room temperature. The mixture was refluxed for 1 h and the solvent then removed. The residue was extracted with CH_2Cl_2, the extract was filtered and evaporated, and the residue recrystallized from MeOH to give $(Me_3Si)_3C(SnMe_2Cl)$ (15.6 g, 75%), m.p. 337 °C (lit. [6] 332 °C (decomp.) (Found: C, 34.7; H, 8.0. $C_{12}H_{33}ClSi_3Sn$ calc.: C, 34.7; H, 8.0%); δ(H) 0.39 (27H, s, $SiMe_3$) and 0.79 (6H, Me_2Sn; $^2J(^1H-^{119}Sn)$ 55 Hz); δ(C) ($CDCl_3/CH_2Cl_2$) + 4.8 (s, Me_3Si) and + 5.4 (s, Me_2Sn); δ(Sn) ($CDCl_3/CH_2Cl_2$) + 133.8 ppm; m/z 401 (30%, $[M-Me]^+$), 221 (10, $[M-Me_4Sn-Me]^+$), 201 (100, $[M-Me_3SnCl-Me]^+$), 165 (10, $[Me_3Sn]^+$), 73 (95, $[Me_3Si]^+$), 59 (25, $[Me_2HSi]^+$), and 45 (20, $[MeH_2Si]^+$); m/z (CI) 401 (40%), 381 (10, $[M-Cl]^+$), 201 (100).

(b) A similar procedure starting with Ph_2SnCl_2 gave $(Me_3Si)_3CSnPh_2Cl$ (40%), m.p. 203 °C (lit. [5], 155–156 °C) (Found: C, 48.4; H, 6.5; $C_{22}H_{37}ClSi_3Sn$: C, 49.0, H, 6.9%); δ(H) 0.34 (27H, s, Me_3Si) and 7.85–8.00 (10H, m, Ph); δ(C) ($CDCl_3/CH_2Cl_2$) 5.3 (s, $^3J(^{13}C-^{119}Sn)$ 20.5 Hz, $SiMe_3$), 14.9 (s, quat. C, $^1J(^{13}C-^{29}Si)$ 29.3 Hz, $^1J(^{13}C-^{119}Sn)$ 103.3 Hz), 128.6 (s C(3) of Ph), $^3J(^{13}C-^{119}Sn)$ 60.3 Hz), 129.3 (s, C(4) of Ph); $^4J(^{13}C-^{119}Sn)$ 13.7 Hz), 135.9 (s, C(2) of Ph; $^2J(^{13}C-^{119}Sn)$ 58.6 Hz), and 142.9 (s, C(1) of Ph, $^1J(^{13}C-^{119}Sn)$ 535 Hz); δ(Sn) ($CDCl_3/CH_2Cl_2$) − 5.5 ppm (s); m/z 525 (15%), $[M-Me]^+$), 489 (35, $[M-HCl-Me]^+$), 325 (10), 309 (20), 289 (30), 263 (60, $[M-Me_2PhSnCl-Me]^+$), 247 (31), 216 (30), 201 (90, $[M-Me_2PhSnCl-Me]^+$), 197 (25), 175 (25), 135 (30), 70 (100), 59 (15), and 45 (10).

Reaction of $(Me_2PhSi)_3CLi$ with Me_2SnCl_2

A solution of $(Me_2PhSi)_3CLi$ (9.5 mmol) in THF (20 cm^3) was added dropwise with stirring to a solution of Me_2SnCl_2 (2.7 g, 12.3 mmol) in 1/1 THF/Et_2O (40 cm^3). The mixture was refluxed for 0.5 h, then work up as described in experiment (a) above gave $(Me_2PhSi)_3C(SnMe_2Cl)$ (4.5 g, 80%), m.p. 186 °C (Found: C, 53.7; H, 6.6; $C_{27}H_{39}ClSi_3Sn$ calc.: 53.9; H, 6.5%); δ(H) 0.61 (18H, s, $SiMe_2$), and 0.74 (6H, $^2J(^1(H-^{119}Sn)$ 54 Hz, Me_2Sn), and 6.70–7.43 (15H, m, Ph); δ(C) 4.55 $^3J(^{13}C-^{119}Sn)$ 51.7 Hz, Me_2Si), 7.8 (Me_2Sn), 11.8 (s, quat. C), 127. 4 (s, C(3), of Ph), 128.8 (s, C(4) of Ph), 125.6 (s, C(2) of Ph), and 139.5 (s, C(1) of Ph); δ(Sn) 115.9 (s);

m/z 587 (10%, $[M-\text{Me}]^+$), 551 (40, $[M-\text{HCl}-\text{Me}]^+$), 402 (5), 340 (5), 325 (35, $[M-\text{Me}_3\text{SnCl}-\text{Ph}]^+$), 309 (55), 263 (20), 247 (20), 207 (50), 197 (30), 175 (30), 165 (22), 135 (100, $[\text{Me}_2\text{PhSi}]^+$), 73 (50), 59 (5), and 45 (15).

Reactions of $TsiSnMe_2Cl$ and $(Me_2PhSi)_3CSnMe_2Cl$ with MeLi

(a) A solution of MeLi (1.50 mmol) in Et_2O (1.5 cm^3) was added to a stirred solution of $TsiSnMe_2Cl$ (0.50 g, 1.20 mmol) in THF (5 cm^3). The mixture was stirred for 0.5 h, the solvent evaporated off, and the residue extracted with CH_2Cl_2. The extract was filtered and then evaporated to leave $TsiSnMe_3$, m.p. 350 °C (lit. [3], 354–356 °C); δ(H) 0.19 (27H, s, Me_3Si) and 0.26 (9H, Me_3Sn, $^2J(^1\text{H}-^{119}\text{Sn})$ 49.4 Hz); δ(C) -2.2 (s, $^1J(^{13}\text{C}-^{119}\text{Sn})$ 328, Me_3Sn); δ(Sn) 5.4 ppm; *m/z* 381 (40%, $[M-\text{Me}]^+$), 201 (100, $[\text{M}-\text{Me}_4\text{Sn}-\text{Me}]^+$), 165 (10), 73 (90), 59 (14), and 45 (10).

(b) A solution of MeLi (0.90 mmol) in Et_2O (1 cm^3) was added dropwise from a syringe during 5 min to a solution of $(Me_2PhSi)_3C(SnMe_2Cl)$ (0.50 g, 0.83 mmol) in THF (5 cm^3) at room temperature. The mixture was stirred for 1 h and the solvent then evaporated off. The residue was extracted with CH_2Cl_2 (20 cm^3), the extract was filtered, and the solvent removed to give $(Me_2PhSi)_3C(SnMe_3)$ (0.44 g, 90%), m.p. 181°C (Found: C, 57.5; H, 7.4. $C_{28}H_{42}Si_3Sn$ calc.: C, 57.7; H, 7.2%); δ(H) 0.61 (18H, s, Me_2Si), 0.55 (9H, Me_3Sn, $^2J(^1\text{H}-^{119}\text{Sn})$ 47.7 Hz), and 6.69–7.46 (15H, m, Ph); δ(C) 0.5 ($^1J(^{13}\text{C}-^{119}\text{Sn})$ 330 Hz, Me_3Sn), 4.7 (Me_2Si), 127.1 (C(3) of Ph) 128.3 (C(4) of Ph), 135.5 (C(2) of Ph), and 141.1 ppm (C(1) of Ph); δ(Sn) 3.7 ppm.

(c) A solution of MeLi (30 mmol) in Et_2O (3 cm^3) was added dropwise to a stirred solution of $(Me_2PhSi)_3C(SnMe_2Cl)$ (0.50 g, 0.83 mmol) in THF (5 cm^3) and the mixture was stirred at room temperature for 0.5 h. The excess of MeLi was destroyed by careful addition of a little MeOH in THF, and the solvent was then evaporated and the residue extracted with CH_2Cl_2. The extract was filtered and the solvent evaporated to leave a solid, which was identified as $(Me_2PhSi)_3CH$ (0.30 g, 85%) by comparison of its ^{1}H NMR and mass spectra with those of an authentic sample.

Reaction of $TsiSnMe_3$ with ICl

A solution of ICl (1.32 mmol) in CCl_4 (13 cm^3) was added dropwise during 0.5 h to a stirred solution of $TsiSnMe_3$ (0.50 g, 1.26 mmol) in 1/4 CH_2Cl_2/CCl_4 (20 cm^3) at room temperature. The progress of the reaction was monitored by ^{1}H NMR spectroscopy, and when the organometallic starting material had been completely consumed the solvent was removed under reduced pressure and the pink residue kept under vacuum for 3 h. The white solid obtained (0.52 g, 98%) was identified as $TsiSnMe_2Cl$ by comparison of its ^{1}H NMR, ^{119}Sn NMR, and mass spectra with those of an authentic sample.

Reactions of $TsiSnMe_2Cl$ with alkali metal salts

(a) A mixture of $TsiSnMe_2Cl$ (0.50 g, 1.20 mmol), LiBr (0.50 g), and 1/1 THF/acetone (40 cm^3) was heated under reflux for 1 h. The solvent was then removed under vacuum and the residue extracted with CH_2Cl_2. The extract was filtered and evaporated to leave $TsiSnMe_2Br$ (0.52 g, 95%). m.p. 353°C (lit. [6] 318°C) (Found: C, 30.8; H, 6.9. $C_{12}H_{33}BrSi_3Sn$ calc.: C, 31.2; H, 7.1%); δ(H) 0.29 (27H, s, $SiMe_3$) and 0.88 (6H, $^2J(^1\text{H}-^{119}\text{Sn})$ 53.5 Hz, Me_2Sn); δ(C) 4.9 ($SiMe_3$) and

5.9 ppm (Me_2Sn); δ(Sn) 100.1 ppm; *m/z* 445 (70%, $[M - Me]^+$), 381 (25, $[M - Br]^+$), 265 (10), 201 (100, $[M - Me_3SnBr - Me]^+$), 165 (20), 73 (50), 59 (20), and 45 (20).

(b) A similar procedure but with NaI (0.50 g) and with acetone alone as solvent, and with sublimation (160 °C at 1 mmHg) of the product gave $TsiSnMe_2I$ (0.58 g, 95%), m.p. 354 °C (lit. [6], 332 °C (decomp)) (Found: C, 28.2; H, 6.6. $C_{12}H_{33}ISi_3Sn$ calc: C, 28.3; H, 6.5%); δ(H) 0.32 (27H, s, $SiMe_3$) and 1.02 (6H, $^2J(^1H-^{119}Sn)$ 50.4 Hz, Me_2Sn); δ(C) 5.0 (Me_3Si) and 6.25 ppm (Me_2Sn); δ(Sn) 7.8 ppm; *m/z* 493 (70%, $[M - Me]^+$), 381 (80, $[M - I]^+$), 313 (15), 277 (10), 201 (100), 185 (30), 165 (20), 73 (60), 59 (10), and 45 (10).

(c) The procedure described under (a) but starting from KSCN (0.50 g) and with acetone alone as solvent gave $TsiSnMe_2NCS$ (0.50 g, 93%), m.p. 324 °C (Found: C, 35.7; H, 7.6; N, 2.7. $C_{13}H_{33}NSSi_3Sn$: C, 35.5; H, 7.5; N, 3.2%); δ(H) 0.28 (27H, s, Me_3Si) and 0.72 (6H, $^2J(^1H-^{119}Sn)$ 54.5, Me_2Sn); δ(C) ($CDCl_3$) 4.5 ($SiMe_3$), 6.0 ($SnMe_2$), and 144 (SCN) ppm; δ(Sn) ($CDCl_3$) 62 ppm (t, $^1J(^{14}N-^{119}Sn)$ 117 Hz); ν(NCS) (KBr) 2020(st); *m/z* 424 (25%, $[M - Me]^+$), 381 (40, $[M - NCS]^+$), 244 (25), 201 (100), 185 (20), 165 (15), 73 (70), 59 (5), and 45 (5).

(d) The procedure described under (c) but with NaO_2CMe (0.50 g) gave $TsiSnMe_2O_2CMe$, m.p. 255 °C (decomp) (Found: C, 38.2; H, 8.2. $C_{14}H_{36}O_2Si_3Sn$ calcd.; C, 38.3; H 8.1%); δ(H) 0.24 (27H, s, Me_3Si), 0.73 (6H, s, $^2J(^1H - ^{119}Sn)$, 55.8 Hz, Me_2Sn), and 1.96 (3H, s, O_2CMe); δ(C) ($CDCl_3$) 4.5 ($SnMe_2$), 4.6 ($SiMe_3$), 49.5 ($O_2C\mathit{Me}$), and 175.0 ppm (CO); δ(Sn) ($CDCl_3$) 101.1 ppm; *m/z* 425 (55, $[M - Me]^+$), 381 (40, $[M - O_2CMe]^+$), 245 (45), 209 (85), 201 (100), 187 (25), 165 (35), 73 (60), 59 (5), and 45 (5).

Conversion of $TsiSnMe_2Cl$ into $(TsiSnMe_2)_2O$

Aqueous NaOH (6.0 cm^3 of 1*M* solution; 6.0 mmol) was added to a solution of $TsiSnMe_2Cl$ (0.50 g, 1.20 mmol) in acetone (50 cm^3) and the mixture was refluxed for 6 h. The solvent was then removed on a rotary evaporator and the residue extracted with CH_2Cl_2. The extract was filtered and evaporated, and the residue was recrystallized from MeOH to give $(TsiSnMe_2)_2O$ (0.37 g, 80%) (Found: C, 36.9; H, 8.6. $C_{24}H_{66}OSi_6Sn_2$ calc.: C, 37.0; H, 8.5%); δ(H) 0.23 (54H, s, Me_3Si) and 0.49 (12H, $^2J(^1H-^{119}Sn)$ 52.2 Hz, Me_2Sn); *m/z* 397 (20%, $[TsiSnMe_2O]^+$), 381 (30, $[TsiSnMe_2]^+$, 216 (60), 201 (85), 165 (75), 73 (100), 59 (60), and 45 (45); *m/z* (CI) 397 (20%), 381 (100).

Reactions of $TsiSnPh_2Cl$ and $(Me_2PhSi)_3C(SnMe_2Cl)$ with alkali metal salts

(a) A mixture of $TsiSnPh_2Cl$ (0.50 g) and LiBr 10.5 g, excess) in 1/1 THF/acetone (50 cm^3) was heated under reflux for 1 h, the solvent removed under reduced pressure, and the residue extracted with CH_2Cl_2. The extract was filtered and the solvent evaporated to leave $TsiSnPh_2Br$ (0.51 g, 95%), m.p. 208 °C, δ(H) 0.36 (27H, s, Me_3Si) and 7.31–7.83 (10H, m, Ph); δ(C) 5.4 (Me_2Si), 128.0 (C(3) of Ph), 129.3 (C(4) of Ph), 126.2 (C(2) of Ph), and 142 ppm (C(1) of Ph); δ(Sn) − 16.8 ppm.

(b) A similar procedure but starting with $(Me_2PhSi)_3C(SnMe_2Cl)$ gave $(Me_2PhSi)_3C(SnMe_2Br)$ (95%), m.p. 185 °C (Found: C, 49.7; H, 6.3. $C_{27}H_{39}BrSi_3Sn$ calc.: C, 50.1; H, 6.0%); δ(H) 0.67 (18H, s, Me_2Si), 0.93 (6H, $^2J(^1H-^{119}Sn)$ 53.2 Hz, Me_2Sn) and 6.78–7.46 (15 H, m, Ph); δ(C) 4.86 (Me_2Si), 8.70 (Me_2Sn), 127.6 (C(3) of Ph), 129.0 (C(4)), 135.8 (C(2)), and 139.7 ppm (C(1)); δ(Sn) 84.3; *m/z* 631 (10% $[M-\text{Me}]^+$), 551 (50, $[M-\text{HBr}-\text{Me}]^+$), 402 (20, $[M-\text{Me}_3\text{SnBr}]^+$), 340 (5, $[M-\text{Me}_2\text{PhSnBr}]^+$), 325 (20, $[M-\text{Me}_2\text{PhSnBr}-\text{Me}]^+$), 197 (15), 175 (25), 165 (5), 135 (100), 73 (40), 59 (5) and 45 (5).

(c) A similar procedure to that described under (b) but starting with NaI gave $(\text{Me}_2\text{PhSi})_3\text{C}(\text{SnMe}_2\text{I})$, m.p. 189 °C (Found: C, 46.7; H, 5.7. $\text{C}_{27}\text{H}_{39}\text{ISi}_3\text{Sn}$ calc.: C, 46.7; H, 5.6%); δ(H) 0.68 (18 H, s, Me_2Si), 1.16 (6H, Me_2Sn, $^2J(^1\text{H}-^{119}\text{Sn})$ 49.5 Hz), and 6.46–7.21 (15H, m, Ph); δ(C) 4.7 (Me_2Si); 9.2 (Me_2Sn), 127.4 (C(3) of Ph), 128.8 (C(4)), 135.6 (C(2)) and 139.6 ppm (C(1)); δ(Sn) −5.1 ppm; *m/z* 679 (1%, $[M-\text{Me}]^+$), 550 (25, $[M-\text{HI}-\text{Me}]^+$), 402 (10, $[M-\text{Me}_3\text{SnI}]^+$), 340 (5, $[M-\text{Me}_2\text{PhSnI}]^+$), 325 (30, $[M-\text{Me}_2\text{PhSnI}-\text{Me}]^+$), 309 (60), 263 (20), 197 (30), 175 (25), 165 (10), 135 (100), 73 (30), 59 (5), and 45 (5).

Reactions of $\text{TsiSnMe}_2\text{I}$ with silver salts

(a) A mixture of $\text{TsiSiMe}_2\text{I}$ (0.50 g, 0.98 mmol), AgNO_3 (0.20 g, 1.20 mmol), and CH_2Cl_2 (20 cm^3) was stirred at room temperature for 3 h with protection from light then filtered through charcoal (previously washed with CH_2Cl_2). The filtrate was evaporated to leave $\text{TsiSnMe}_2\text{ONO}_2$ (0.40 g, 93%), m.p. 276 °C (decomp.) (Found: C, 32.9; H, 7.6; N, 2.9. $\text{C}_{12}\text{H}_{33}\text{NO}_3\text{Si}_3\text{Sn}$ calc.: C, 32.6; H, 7.4; N, 3.2%); δ(H) 0.29 (27H, s, SiMe_3) and 0.93 (6H, $^2J(^1\text{H}-^{119}\text{Sn})$ 57.8 Hz, Me_2Sn); δ(C) 4.8 (Me_3Si) and 5.1 (Me_2Sn); δ(Sn) (CDCl_3) 160.5 ppm; ν(NO_3)(Nujol) 1540 cm^{-1} (st); *m/z* 401 (10%, $[M-\text{CNO}]^+$), 382 (10, $[M-\text{MeNO}_2]^+$), 367 (20, $[M-\text{MeNO}_2-\text{Me}]^+$), 267 (15), 201 (90, $[M-\text{Me}_3\text{SnNO}_3-\text{Me}]^+$), 165 (30), 147 (40, $[\text{Me}_3\text{SiOSiMe}_2]^+$), 73 (100), and 59 (20).

(b) The procedure described under (a) but starting with AgCN (1.5 mmol) gave $\text{TsiSnMe}_2\text{CN}$ (0.46 g, 95%), m.p. 313°C (Found: C, 38.5; H, 8.3; N, 3.4. $\text{C}_{13}\text{H}_{33}\text{NSi}_3\text{Sn}$: C, 38.3; H, 8.1; N, 3.4%); δ(H) 0.28 (27H, s, Me_3Si) and 0.67 (6H, $^2J(^1\text{H}-^{119}\text{Sn})$ 54.0 Hz, Me_2Sn); δ(C) (CDCl_3) −0.81 (Me_2Sn), 4.62 (Me_3Si), and 128.0 ppm (CN); δ(Sn) (CDCl_3) −58 ppm; *m/z* 392 (35%, $[M-\text{Me}]^+$), 212 (20), 201 (100, $[M-\text{Me}_3\text{SnCN}-\text{Me}]^+$), 165 (20), 73 (98), 59 (25), and 45 (20).

(c) The same procedure but starting with AgO_2CMe (1.5 mmol) gave exclusively $\text{TsiSnMe}_2\text{O}_2\text{CMe}$, with properties identical with those described above.

(d) The same procedure but starting from AgO_2CCF_3 gave $\text{TsiSnMe}_2\text{O}_2\text{CCF}_3$ (0.56 g, 95%), m.p. 227 °C (decomp.); δ(H) 0.24 (27H, s, SiMe_3) and 0.84 (6H, s, $^2J(^1\text{H}-^{119}\text{Sn})$ 53.1 Hz, Me_2Sn); δ(C) (CDCl_3) 4.5 (SiMe_3) and 6.5 ppm (Me_2Sn); δ(Sn) (CDCl_3) 156.6 p.p.m.; *m/z* 479 (25%, $[M-\text{Me}]^+$), 381 (5, $[M-\text{O}_2\text{CCF}_3]^+$), 205 (30), 201 (30, $[M-\text{Me}_3\text{SnO}_2\text{CCF}_3-\text{Me}]^+$), 165 (15), 73 (100), 59 (20), 45 (15), and 28 (40, $[\text{CO}]^+$).

(e) The same procedure but starting from AgO_3SCF_3 (1.4 mmol) gave $\text{TsiSnMe}_2\text{O}_3\text{SCF}_3$ (0.62 g, 98%), m.p. 231°C (decomp.) (Found: C, 30, 1; H, 6.4. $\text{C}_{13}\text{H}_{27}\text{F}_3\text{O}_3\text{SSi}_3\text{Sn}$ calc.: C, 29.4; H, 6.2%); δ(H) 0.29 (27H, s, Me_3Si) and 1.02 (6H, $^2J(^1\text{H}-^{119}\text{Sn})$ 52.2 Hz, Me_2Sn); δ(Sn) (CDCl_3) 232 ppm; ν(SO_3) (KBr) 1359 (st), 1195 (st); m/z 515 (10%, $[M-\text{Me}]^+$), 445 (20), 401 (10), 381 (10, $[M-\text{O}_3\text{SCF}_3]^+$), 335 (5), 205 (20), 201 (100, $[M-\text{Me}_3\text{SnO}_3\text{SCF}_3-\text{Me}]^+$), 165 (10), 73 (98), 59 (25) and 45 (25).

Reactions of $(\text{TsiSnMe}_2)_2\text{O}$ with acids

(a) A solution of the oxide (0.50 g) in MeCO_2H (5 cm^3) was kept at 60 °C for 15 min then evaporated under reduced pressure. The residue was kept under vacuum for several hours then shown to be $TsiSnMe_2O_2CMe$ (0.56 g, 98%) with properties identical to those described earlier.

(b) Methanesulphonic acid (1 cm^3) was added to a solution of the oxide (0.50 g) in acetone (30 cm^3), the mixture stirred for 30 min at room temperature, and the volatile material removed under reduced pressure. The residue was shaken with several portions of H_2O (total 30 cm^3) then filtered off, washed with MeOH, dried under vacuum, and shown to be $TsiSnMe_2O_3SMe$ (0.46 g, 75%), m.p. 257 °C (decomp.) (Found: C, 32.7; H, 7.5. $C_{13}H_{36}O_3SSi_3Sn$ calc.: C, 32.9; H, 7.6%); δ(H) 0.25 (27H, s, Me_3Si), 0.92 (6H, $^2J(^1H-^{119}Sn)$ 51.3 Hz, Me_2Sn), and 2.81 (3H, s, O_3SMe); δ(Sn) ($CDCl_3$) 173.3 ppm; m/z 461 (30, $[M-Me]^+$), 381 (10, $[M-SO_3-Me]^+$), 281 (95, $[M-Me_4Sn-Me]^+$), 245 (40, $[Me_2SnO_3SMe]^+$), 201 (95, $[M-Me_3SnO_3SMe-Me]^+$), 165 (30), 73 (100), 59 (40), and 45 (40).

(c) A solution of the oxide (0.20 g) in acetone (20 cm^3) was treated with a mixture (3 cm^3) of concentrated hydrochloric acid and an equal volume of water. The mixture was stirred at 60 °C for 15 min, then shaken with a mixture of CH_2Cl_2 (30 cm^3) and H_2O (30 cm^3). The organic layer was separated, washed, and evaporated, to give $TsiSnMe_2Cl$ (0.20 g, 95%) with properties identical to those described earlier.

(d) A solution of the oxide (2.0 g) in acetone (50 cm^3) was stirred for 1 h with 35% aqueous HF (2 cm^3) in a polythene vessel then solid Na_2CO_3 was added in small portions to remove the HF. The solvent was removed under vacuum and the residue extracted with CH_2Cl_2. The extract was filtered and evaporated to leave $TsiSnMe_2F$ (1.95 g, 94%) with properties identical to those of an authentic sample [12].

(e) A solution of the oxide (0.50 g) in acetone (30 cm^3) was stirred for 15 min with a 1/1 mixture (2 cm^3) of water and concentrated nitric acid. Work-up as in (c) above gave $TsiSnMe_2ONO_2$ (0.54 g, 93%) with properties identical to those of an authentic sample.

Preparation of $(Me_3Si)_2C(SnMe_3)_2$

A solution of $(Me_3Si)_2CCl_2$ (12.0 g, 52.4 mmol) in THF (15 cm^3) was added dropwise during 30 min to a stirred solution of Me_3SnLi [17] (110 mmol) in THF at 0 °C. The mixture was stirred for 1 h and the solvent then removed under reduced pressure. The residue was extracted with CH_2Cl and the extract was filtered then evaporated. The residue was recrystallized from MeOH to give $(Me_3Si)_2C(SnMe_3)_2$ (14.9 g, 76%), m.p. 372 °C (lit. [4], > 360 °C) (Found: C, 32.4; H, 7.0. $C_{13}H_{36}Si_2Sn_2$ calc.: C, 32.0; H, 7.4%); δ(H) 0.08 (18H, s, Me_3Si) and 0.17 (18H, $^2J(^1H-^{119}Sn)$ 50.8 Hz, Me_3Sn); δ(C) −2.9 (Me_3Sn, $^1J(^{13}C-^{119}Sn)$ 325 Hz) and 5.0 ppm (Me_3Si); δ(Si) 0.96 ppm ($^2J(^{29}Si-^{119}Sn)$ 33.2 Hz); δ(Sn) ($CDCl_3$) 16.2 ($^1J(^{13}C-^{119}Sn)$ 325 Hz, $^2J(^{117}Sn-^{119}Sn)$ 351 Hz, $^2J(^{29}Si-^{119}Sn)$ 33.5 Hz, $^3J(^{13}C-^{119}Sn)$ 16.3 Hz); m/z 473 (15%, $[M-Me]^+$), 323 (5), 263 (5), 193 (15), 165 (15), 135 (15), 73 (100), 59 (15), and 45 (15).

The same product was formed (and no $(Me_3Si)_2C(SnMe_3)Cl$ was detected) when the reagents were used in 1/1 molar ratio and the order of addition reversed.

Reactions of $(Me_3Si)_2C(SnMe_3)_2$ with halogens

(a) A solution of 0.1 *M* ICl in CCl_4 (25 cm^3, 2.5 mmol) was added dropwise with stirring to a solution of $(Me_3Si)_2C(SnMe_3)_2$ (0.50 g, 1.02 mmol) in CCl_4 (20 cm^3).

The progress of the reaction was monitored by ^{1}H NMR spectroscopy, and when the starting material had been completely consumed the solvent was removed rapidly under reduced pressure. The residue was kept under vacuum for 3 h until the pink colour had disappeared, and then shown to be $(Me_3Si)_2C(SnMe_2Cl)_2$ (0.53 g, 98%), m.p. 315 °C (lit. [4] 303.5–305 °C); δ(H) 0.28 (18H, s, Me_3Si) and 0.82 (12H, Me_2Sn), $^2J(^1H-^{119}Sn)$ 56.7 Hz); δ(Sn) 138 ppm.

(b) The procedure described in (a) but starting from Br_2 gave $(Me_3Si)_2C(SnMe_2Br)_2$ (98%), m.p. 324 °C (Found: C, 21.1; H, 4.7. $C_{11}H_{30}Br_2Si_2Sn_2$ calc.: C, 21.4; H, 4.6%); δ(H) 0.30 (18H, s, Me_3Si) and 0.99 (12 H, $^2J(^1H-^{119}Sn)$ 47.7 Hz, Me_2Sn); δ(C) 4.77 $^3J(^1H-^{119}Sn)$ 19.5 Hz, Me_3Si) and 5.67 ($^1J(^{13}C-^{119}Sn)$ 372.6 Hz, Me_2Sn); δ(Sn) 106; m/z 601 (45, $[M-Me]^+$), 535 (10, $[M-Br]^+$), 308 (10, $[M-Me_2SnBr_2]^+$), 257 (25), 201 (40), 193 (70), 165 (10), 135 (20), 73 (100), 59 (50), and 45 (26).

(c) When a solution containing I_2 (30 mmol) and $(Me_3Si)_2C(SnMe_3)_2$ (1.02 mmol) in CCl_4 (50 cm^3) was stirred at room temperature for 3 h there was no change in the ^{1}H NMR spectrum.

Reactions of $(Me_3Si)_2C(SnMe_2Cl)_2$ with MeLi

A solution of MeLi (2.0 mmol) in Et_2O (4 cm^3) was added dropwise during 5 min to a solution of $(Me_2Si)_2C(SnMe_2Cl)_2$ (0.50 g, 0.95 mmol) in Et_2O (10 cm^3) at room temperature. The mixture was stirred for 30 min and then a few drops of Me_3SiOMe were added to remove any residual MeLi. The solvent was removed and the residue extracted with CH_2Cl_2. The extract was filtered, then evaporated to give $(Me_3Si)_2C(SnMe_3)_2$ (0.44 g, 95%), with properties identical to those of an authentic sample.

Generation and reactions of $(Me_3Si)_2(SnMe_3)CLi$

A solution of MeLi (5 mmol) in Et_2O (10 cm^3) was added dropwise with stirring to a solution of $(Me_3Si)_2C(SnMe_3)_2$ (2.0 g, 4.1 mmol) in THF (25 cm^3) at room temperature. The solution rapidly turned yellow. The Et_2O was distilled off, the mixture kept under gentle reflux, and the extent of metallation determined from time to time by removing a small sample (0.3 cm^3), adding an excess of Me_3SiCl (1.5 cm^3) to it, then determining the relative proportions of starting material and $TsiSnMe_3$ by ^{1}H NMR spectroscopy. The metallation was 90–95% complete within 1 h, and the volatile material was removed under vacuum (mainly to remove Me_4Sn) and fresh THF (20 cm^3), then added, followed by a few drops of Me_3SiOMe to destroy any residual MeLi. Solutions thus made were used for the reactions described below. The solution gave a ^{6}Li signal at δ -0.07 (broad), a ^{7}Li signal at $+0.27$ (relative to external aqueous $LiNO_3$), and a ^{119}Sn signal at $+1.7$ ppm.

(b) A solution of $(Me_3Si)_2(Me_3Sn)CLi$ made from $(Me_3Si)_2C(SnMe_3)_2$ (4.1 mmol) in THF (20 cm^3) as described in (a) was added dropwise with stirring during 20 min to a solution of Me_3SiCl (0.54 g, 5.0 mmol) in Et_2O (30 cm^3). The mixture was subsequently stirred for 30 min and the solvent then removed under reduced pressure. The residue was extracted with CH_2Cl_2, and the extract filtered then evaporated. The residue was recrystallized from MeOH to give $TsiSnMe_3$ (1.5 g, 84%), m.p. 352 °C (lit. [4], 354–356 °C). Its NMR (^{1}H, ^{13}C, and ^{119}Sn) and mass spectra were identical with those described earlier.

(c) A solution in THF (20 cm^3) of $(Me_3Si)_2(Me_3Sn)CLi$ made from $(Me_3Si)_2C(SnMe_3)_2$ (2.0 mmol) was treated dropwise with stirring with H_2O (0.5 cm^3). The solvent was removed under pressure and the oily residue was extracted with CH_2Cl_2. The extract was filtered and the solvent removed to give an oil which was judged to be $(Me_3Si)_2(Me_3Sn)CH$ (0.63 g, 95%); δ(H) − 0.65 (1H, s, CH), 0.06 (18H, s, Me_3Si), and 0.16 (9H, $^2J(^1H-^{119}Sn)$ 51.3 Hz, Me_3Sn); δ(Sn) ($CDCl_3$) 5.0 ppm; *m/z* 309 (10%, $[M-Me]^+$), 165 (15, $[Me_3Sn]^+$), 135 (10), 129 (90, $[M-Me_4Sn-Me]^+$), 73 (100), 59 (45), and 45 (35).

(d) The procedure described in (b), but with Me_2SiCl_2 in place of Me_3SiCl, gave $(Me_3Si)_2(Me_3Sn)C(SiMe_2Cl)$ (75%), m.p. 346 °C (Found: C, 34.5; H, 8.0. $C_{12}H_{33}ClSi_3Sn$ calc.: C, 34.6; H, 7.9%); δ(H) 0.26 (18H, s, Me_3Si), 0.37 (9H, $^2J(^1H-^{119}Sn)$ 50.7 Hz, Me_3Sn) and 0.57 (6H, s, Me_2Si); δ(C) ($CDCl_3$) − 2.02 (Me_3Sn), 4.90 (Me_3Si), and 8.7 ppm (Me_2Si); δ(Sn) 6.0 ppm; *m/z* 401 (20, $[M-Me]^+$), 201 (100), 165 (5), 73 (50) and 45 (5).

(e) The procedure described under (b), but with Me_2HSiCl in place of Me_3SiCl, gave $(Me_3Si)_2(Me_3Sn)C(SiMe_2H)$ (1.1 g, 60%), m.p. 321° C (Found: C, 38.0; H, 8.9. $C_{12}H_{34}Si_3Sn$ calc.: C, 37.8; H, 8.9%); δ(H) 0.16 (18H, s, Me_3Si), 0.17 (6H, d, $^3J(^1H-^1H)$ 4 Hz, Me_2Si), and 0.25 (9H, s, Me_3Sn); δ(C) ($CDCl_3$) − 3.61 ($^1J(^{13}C-^{119}Sn)$ 331.3, Me_3Sn), 1.32 (Me_2Si), and 4.0 ppm (s, Me_3Si); δ(Sn) ($CDCl_3$) 9.3; *m/z* 367 (35 $[M-Me]^+$), 201 (100), 73 (50), 59 (15), and 45 (10).

Reactions of $(Me_3Si)_2(Me_3Sn)C(SiMe_2H)$ with Br_2 and ICl

(a) An 0.10 *M* solution of Br_2 in CCl_4 (26 cm^3, 2.6 mmol) was added dropwise with stirring at room temperature to a solution of $(Me_3Si)_2(Me_3Sn)C(SiMe_2H)$ (0.50 g, 1.30 mmol) in CH_2Cl_2 (30 cm^3). The bromine colour disappeared immediately on each addition until all the bromine solution had been added, when a faint colour persisted. The solution was stirred for 1 h to allow HBr to escape, then the solvent was evaporated off under reduced pressure. The residual solid was kept under high vacuum for several hours then shown to be $(Me_3Si)_2C(SnMe_2Br)(SiMe_2Br)$ (0.69 g, 100%), m.p. 353 °C (Found: C, 25.0; H, 5.8. $C_{11}H_{30}Br_2Si_3Sn$ calc.: C, 25.1; H, 5.7%); δ(H) (CH_2Sl_2) 0.42 (18H, s, Me_3Si), 0.89 (6H, s, Me_2Si), and 1.05 (6H, $^2J(^1H-^{119}Sn)$ 47.8 Hz, Me_2Sn); δ(C) 4.5 (Me_3Si), 6.6 (Me_2Si), and 9.2 ($^2J(^{13}C-^{119}Sn)$ 20 Hz, Me_2BrSn); δ(Sn) 79.2 ppm; *m/z* 509 (20%, $[M-Me]^+$), 265 (30, $[M-Me_3SnBr-Me]^+$), 216 (15, $[M-Me_2SnBr_2]^+$), 201 (100, $[M-Me_2SnBr_2-Me]^+$), 185 (15), and 73 (55).

(b) An 0.10 *M* solution of Br_2 in CH_2Cl_2 (5.2 cm^3, 0.52 mmol) was added dropwise with stirring at room temperature to a solution of $(Me_3Si)_2(Me_3Sn)C(SiMe_2H)$ (0.20 g, 0.52 mmol). The progress of the reaction was monitored during the addition by ^1H NMR spectroscopy, and this showed that starting material had been completely consumed when the addition was complete. The mixture was stirred for 1 h, the solvent then removed under reduced pressure, and the residue kept under high vacuum for some hours then shown to be $(Me_3Si)_2(Me_3Sn)C(SiMe_2Br)$ (0.23 3g, 95%), m.p. 356 °C (Found: C, 31.0; H, 7.5. $C_{12}H_{33}BrSi_3Sn$ calcd.: C, 31.2; H, 7.2%); δ(H) 0.35 (18H, s, Me_3Si), 0.43 (9H, $^2J(^1H-^{119}Sn)$ 53.5 Hz, Me_3Sn), and 0.81 (6H, s, Me_2Si); δ(C) − 2.08 (Me_3Sn), 4.67 (Me_3Si), and 9.57 (Me_2Si); δ(Sn) 7.4 ppm; *m/z* 445 (10%, $[M-Me]^+$), 201 (100), 185 (60), 165 (30), and 45 (25).

(c) An 0.10 *M* solution of ICl in CCl_4 (5.2 cm^3, 0.52 mmol, was added dropwise during 45 min to a solution $(Me_3Si)_2(Me_3Sn)C(SiMe_2H)$ (0.20 g, 0.52 mmol) at room temperature, and the progress of the reaction was monitored by ^{1}H NMR spectroscopy. When the addition was complete all the starting material had been consumed. The solution was stirred for 1 h then evaporated under reduced pressure, and the residue was recrystallized from pentane to give $(Me_3Si)_2(Me_3Sn)C(SiMe_2I)$ (0.17 g, 60%), m.p. 183° C (decomp.) (Found: C, 29.0; H, 6.5. $C_{12}H_{33}ISi_3Sn$ calcd.: C, 28.3; H, 6.1%); δ(H) 0.28 (18H, s, Me_3Si), 0.37 (9H, $^2J(^1H-^{119}Sn)$ 51.2 Hz, Me_3Sn), and 0.98 (6H, s, Me_2Si); m/z 493 (15%, $[M - Me]^+$), 381 (40, $[M - I]^+$), 365 (5), 216 (5), 201 (100), 185 (10), 165 (10), 73 (90), 59 (15), and 45 (10).

Reaction of $(Me_3Si)_2C(SnMe_2Br)(SiMe_2Br)$ *with PhLi*

A solution of PhLi (2.00 mmol) in Et_2O (2.5 cm^3) was added dropwise to a stirred solution of $(Me_3Si)_2C(SnMe_2Br)(SiMe_2Br)$ (0.50 g, 0.95 mmol) in THF (15 cm^3) at room temperature. The stirring was continued for 30 min, and a little MeOH in THF added cautiously to destroy any residual PhLi. The solvent was removed under reduced pressure and the residue extracted with CH_2Cl_2. The extract was filtered and the solvent removed to leave $(Me_3Si)_2C(SnMe_2Ph)(SiMe_2Br)$ (0.49 g, 95%), m.p. 286° C (Found: C, 38.9; H, 6.8. $C_{17}H_{35}BrSi_3Sn$ calc.: C, 39.0; H, 6.7%); δ(H) 0.27 (18H, s, Me_3Si), 0.65 (6H, $^2J(^1H-^{119}Sn)$ 47.7 Hz, Me_2Sn), 0.73 (6H, s, Me_2Si), and 7.24–7.80 (5H, m, Ph); $\delta(C) - 2.3$ (Me_2Sn), 4.9 (Me_3Si), 9.5 (Me_2Si); 127.0 (C(3) of Ph), 128.2 (C(4)), 136.8 (C(2)), and 143.1 (C(1)), 143.1 (C(1)); $\delta(Sn) - 30.9$ ppm; m/z 507 (15% $[M - Me]^+$), 427 (15, $[M - Ph]^+$), 263 (20), 216 (50), 201 (95), 216 (50), 201 (95), 135 (20), and 73 (100); m/z (+CI) 507 (60%), 443 (35, $[M\text{-}Ph]^+$), 427 (25), 263 (30), 216 (65), 201 (100), and 73 (45).

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