

A bulky tris(trisilyl) methyl ligand incorporating a donor sulfur atom: some $(\text{Me}_3\text{Si})_2(\text{PhSMe}_2\text{Si})\text{CSnMe}_2\text{X}$ compounds

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Abstract

Reaction of $(\text{Me}_3\text{Si})_2(\text{PhSMe}_2\text{Si})\text{CCl}$ with BuLi at low temperature gave the organolithium reagent $(\text{Me}_3\text{Si})_2(\text{PhSMe}_2\text{Si})\text{CLi}$, which was treated with Me_3SnCl to give $(\text{Me}_3\text{Si})_2(\text{PhSMe}_2\text{Si})\text{CSnMe}_3$. Reaction of the latter with a one or two molar proportion of iodine gave the monoiodide $(\text{Me}_3\text{Si})_2(\text{PhSMe}_2\text{Si})\text{CSnMe}_2\text{I}$ and the diiodide $(\text{Me}_3\text{Si})_2(\text{IME}_2\text{Si})\text{CSnMe}_2\text{I}$ respectively. The corresponding reaction with even a one molar proportion of bromine gave mainly the dibromide $(\text{Me}_3\text{Si})_2(\text{BrMe}_2\text{Si})\text{CSnMe}_2\text{Br}$. Treatment of the monoiodide with an excess of AgCN in CDCl_3 gave $(\text{Me}_3\text{Si})_2(\text{PhSMe}_2\text{Si})\text{CSnMe}_2\text{CN}$, but similar treatment with AgBF_4 gave mainly the difluoride $(\text{Me}_3\text{Si})_2(\text{FMe}_2\text{Si})\text{CSnMe}_2\text{F}$. Hydrolysis of the diiodide gave the mixed diol $(\text{Me}_3\text{Si})_2(\text{HOMe}_2\text{Si})\text{CSnMe}_2\text{OH}$.

Keywords: Tin; Lithium; Silicon; Bulky ligand

1. Introduction

Attachment of the very bulky ligands $(\text{Me}_3\text{Si})_3\text{C}$ and $(\text{PhMe}_2\text{Si})_3\text{C}$ to a range of metals has allowed isolation of many novel species [1]. More recently attention has been focused on related ligands in which an Me group on one or more of the SiMe_3 groups has been replaced by a group having the potential to coordinate intra- or intermolecularly to the metal to which the ligand is attached; e.g. $(\text{MeOSiMe}_2\text{Si})_3\text{C}$ [2], $(\text{Me}_3\text{Si})_2(\text{MeOMe}_2\text{Si})\text{C}$ [1d,e], and $(\text{Me}_2\text{NMe}_2\text{Si})_3\text{C}$ [3]. In the present work we have made an initial exploration of the applicability of the sulfur-containing ligand $(\text{Me}_3\text{Si})_2(\text{PhSMe}_2\text{Si})\text{C}$ by attaching it to tin.

2. Results and discussion

The reagent we used to attach the ligand to tin, $(\text{Me}_3\text{Si})_2(\text{PhSMe}_2\text{Si})\text{CLi}$, was first made by Wiberg and colleagues some years ago [4], and we obtained it

by a similar route. In this the compound $(\text{Me}_3\text{Si})_2(\text{BrMe}_2\text{Si})\text{CCl}$ [5] was treated with LiSPh in tetrahydrofuran (THF) to give $(\text{Me}_3\text{Si})_2(\text{PhSMe}_2\text{Si})\text{CCl}$, and the latter was metallated with BuLi in THF–Et₂O–pentane–hexane at -110°C to give $(\text{Me}_3\text{Si})_2(\text{PhSMe}_2\text{Si})\text{CLi}$. Treatment of this in situ with Me_3SnCl gave the expected $(\text{Me}_3\text{Si})_2(\text{PhSMe}_2\text{Si})\text{CSnMe}_3$. We attempted to determine the solid state structure of this compound to see if there was any intra- or intermolecular coordination of the sulfur atom to tin, but although seemingly good crystals were obtained they gave only weak diffraction, perhaps because of the pseudo-spherical nature of the molecule.

Similar treatment of $(\text{Me}_3\text{Si})_2(\text{PhSMe}_2\text{Si})\text{CLi}$ with Me_2SnCl_2 gave only a very low yield of $(\text{Me}_3\text{Si})_2(\text{PhSMe}_2\text{Si})\text{CSnMe}_2\text{Cl}$, but the corresponding iodide $(\text{Me}_3\text{Si})_2(\text{PhSMe}_2\text{Si})\text{CSnMe}_2\text{I}$ was obtained in good yield by reaction of $(\text{Me}_3\text{Si})_2(\text{PhSMe}_2\text{Si})\text{CSnMe}_3$ with a one molar proportion of I_2 (see Scheme 1). When a two molar proportion of I_2 was used the Si–SPh bond was also cleaved to give the diiodide $(\text{Me}_3\text{Si})_2(\text{IME}_2\text{Si})\text{CSnMe}_2\text{I}$, and the corresponding dibromide was the only product isolated even when only a one molar proportion of Br_2 was used at low temperature; the

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dibromide was made previously by reaction of $(\text{Me}_3\text{Si})_2(\text{HMe}_2\text{Si})\text{CSnMe}_3$ with a two molar proportion of Br_2 [6].

The cleavage of the Si–SPh bond by I_2 could itself have value in synthesis since it could possibly be used to convert other $(\text{Me}_3\text{Si})_2(\text{PhSMe}_2\text{Si})\text{C}$ –metal species into the corresponding $(\text{Me}_3\text{Si})_2(\text{IME}_2\text{Si})\text{C}$ –metal derivatives. The same products could in principle be made by treatment of the more readily available $(\text{Me}_3\text{Si})_2(\text{HMe}_2\text{Si})\text{C}$ –metal compounds with I_2 (compare the preparation in this way of $\{(\text{Me}_3\text{Si})_2(\text{IME}_2\text{Si})\text{C}\}_2\text{Hg}$ from $\{(\text{Me}_3\text{Si})_2(\text{HMe}_2\text{Si})\text{C}\}_2\text{Hg}$ [7]), but the HI generated might sometimes cause problems, whereas the PhSI presumably formed from cleavage of Si–SPh bonds is likely to be relatively inert.

Reaction of the iodide $(\text{Me}_3\text{Si})_2(\text{PhSMe}_2\text{Si})\text{CSnMe}_2\text{I}$ with an excess of AgCN in CDCl_3 gave a single product that was judged to be the expected cyanide $(\text{Me}_3\text{Si})_2(\text{PhSMe}_2\text{Si})\text{CSnMe}_2\text{CN}$. When an excess of AgBF_4 was used, however, the greatly dominant product was the difluoride $(\text{Me}_3\text{Si})_2(\text{FMe}_2\text{Si})\text{CSnMe}_2\text{F}$, though a small amount of $(\text{Me}_3\text{Si})_2(\text{PhSMe}_2\text{Si})\text{CSnMe}_2\text{F}$ was apparently also formed.

The diiodide was readily hydrolysed by water in THF to give the diol $(\text{Me}_3\text{Si})_2(\text{HOMe}_2\text{Si})\text{CSnMe}_2\text{OH}$. We expected this to have an interesting hydrogen-bonded structure, but although seemingly good crystals were obtained from both toluene and methylcyclohexane, they gave only weak diffraction.

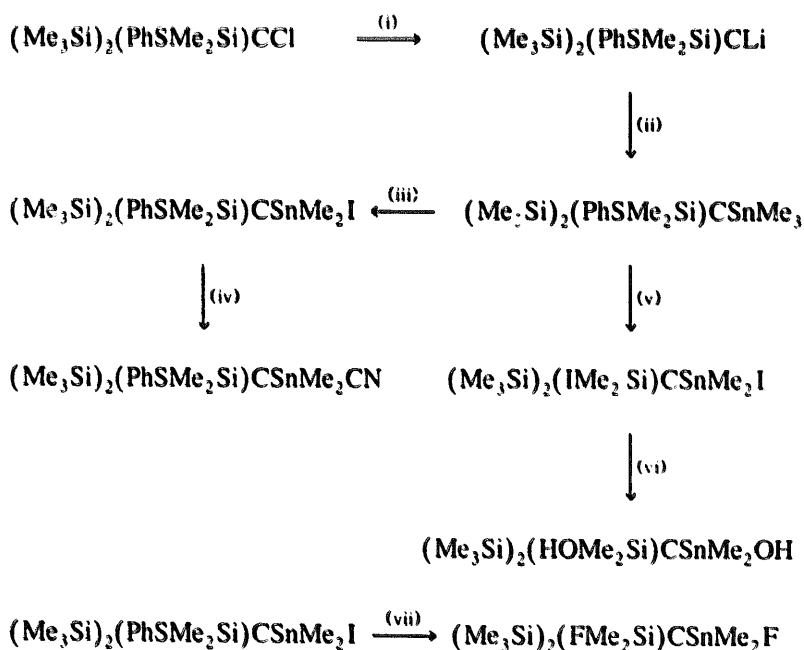
This pilot study has prepared the way for studies of the properties of compounds in which the ligand $(\text{Me}_3\text{Si})_2(\text{PhSMe}_2\text{Si})\text{C}$ is attached to a range of other metals.

3. Experimental

Reactions were carried out under Ar in carefully dried solvents. The following NMR spectrometers were used: for ^1H , Bruker WM360; for ^{13}C (at 62.85 MHz), ^{29}Si (at 49.70 MHz) and ^{119}Sn (at 93.3 Mz), Bruker AC P250; the solvent was CDCl_3 . Mass spectra were obtained by electron impact at 70 eV unless otherwise stated; only main peaks used for characterization are reported.

3.1. Preparation of $(\text{Me}_3\text{Si})_2(\text{PhSMe}_2\text{Si})\text{CCl}$

A 2.5 M solution of BuLi in hexane (13.2 cm^3 ; 33 mmol) was diluted with THF (30 cm^3) then cooled to 0°C and added dropwise during 30 min to a stirred solution of PhSH (3.6 cm^3 , 35 mmol) in THF (50 cm^3) maintained at 0°C . The mixture was stirred at 0°C for a further 1 h and then allowed to warm to room temperature. A solution of $(\text{Me}_3\text{Si})_2(\text{BrMe}_2\text{Si})\text{CCl}$ [5] (7.5 g, 22.7 mmol) in THF (30 cm^3), cooled to 0°C , was added dropwise with stirring. The mixture was stirred overnight and the solvent was then removed under reduced pressure to leave an oil, which was extracted with pentane (80 cm^3). The extract was filtered and the solvent removed to leave an oil. Heptane (30 cm^3) was added (to precipitate traces of LiBr) and the solution was set aside overnight then filtered. Removal of the solvent left $(\text{Me}_3\text{Si})_2(\text{PhSMe}_2\text{Si})\text{CCl}$ (7.5 g, 95%) as a pale yellow oil (which when cooled gave a solid of m.p. ca -5°C). Anal. Found: C, 50.0; H, 8.1; Cl, 9.8; S, 9.0; Si, 23.0. $\text{C}_{15}\text{H}_{29}\text{ClSi}_3$, Calc.: C, 49.9; H, 8.1; Cl, 9.8; S, 8.9; Si, 23.3%. $\delta(\text{H})$ 0.33 (18H, s, SiMe_3), 0.36 (6H, s,



Scheme 1. Reagents: (i) BuLi in THF–Et₂O–pentane–hexane at -110°C ; (ii) Me_3SnCl ; (iii) I_2 , one molar proportion; (iv) AgCN; (v) I_2 , two molar proportion; (vi) H_2O ; (vii) AgBF_4 .

SiMe₂), 7.28–7.5 (5H, m, Ph). *m/z* 360 (M), 345 (M–Me), 325 (M–Cl).

3.2. Preparation of (Me₃Si)₂(PhSMe₂Si)CSnMe₂Cl

A 2.5 M solution of BuLi in hexane (3.5 cm³, 8.7 mmol), cooled to –80°C, was added dropwise with stirring to a solution of (Me₃Si)₂(PhSMe₂Si)CCl (3.0 g, 8.3 mmol) in a mixture of THF (50 cm³), Et₂O (2.5 cm³) and pentane (2.5 cm³) maintained at –110°C. The mixture was stirred for a further 1 h at –110°C then allowed to warm to –85°C, and a solution of Me₂SnCl₂ (1.81 g, 8.3 mmol) in THF (15 cm³), cooled to –80°C, was added dropwise with stirring. The stirred mixture was subsequently allowed to warm to room temperature overnight and the solvent was then removed to leave an oily solid. This was extracted with pentane (10 cm³) and the extract filtered. Removal of the solvent left a residue, which was washed with a small amount of cold pentane to leave solid (Me₃Si)₂(PhSMe₂Si)CSnMe₂Cl (0.22 g, 5%). δ(H) 0.38 (18H, s, SiMe₃), 0.43 (6H, s, SiMe₂), 1.00 (6H, s, SnMe₂), ²*J*(HSn) 55 Hz, 7.23–7.43 (5H, m, Ph). δ(C) 5.0 (SiMe₃), 5.4 (SiMe₂), 7.2 (SnMe₂), 4.8 (quat. C), 126.6–135.7 (Ph). δ(Si) 0.39 (SiMe₃), 16.2 (SiMe₂). δ(¹¹⁹Sn) 96.8. *m/z* 495 (M–Me), 475 (M–Cl), 401 (M–SPh).

3.3. Preparation of (Me₃Si)₂(PhSMe₂Si)CSnMe₃

A 2.5 M solution of BuLi in hexane (3.6 cm³, 9.0 mmol), cooled to –80°C, was added dropwise with stirring to a solution of (Me₃Si)₂(PhSMe₂Si)CCl (3.0 g, 8.3 mmol) in a mixture of THF (35 cm³), Et₂O (3 cm³) and pentane (3 cm³) maintained at –110°C. The mixture was stirred for a further 2 h at –110°C then a solution of Me₃SnCl (3.0 g, 15 mmol) in THF (10 cm³), cooled to –80°C, was added dropwise with stirring, the temperature being maintained at –110°C. The stirred mixture was kept at –110°C for a further 1 h then allowed to warm to room temperature overnight. The solvent was then removed to leave a solid, which was extracted with pentane (40 cm³). The extract was filtered and the solvent removed to leave a solid, which was kept under vacuum for 3 h then recrystallized from pentane at –30°C to give (Me₃Si)₂(PhSMe₂Si)CSnMe₃ (3.3 g, 80%), m.p. 49–50°C. δ(H) 0.30 (18H, s, SiMe₃), 0.31 (6H, s, SiMe₂), 0.39 (9H, s, SnMe₃), 7.23–7.43 (5H, m, Ph). δ(C) –0.7 (quat. C), –1.5 (¹*J*(¹³C¹¹⁹Sn) 377 Hz, ²*J*(CSn) 52 Hz, SnMe₃), 5.3 (SiMe₃), 5.2 (SiMe₂), 128–136 (Ph). δ(Si) –0.2 (²*J*(SiSn) 34 Hz, SiMe₃), 16.3 (²*J*(SiSn) 35 Hz, SiMe₂). δ(¹¹⁹Sn) 6.3. *m/z* 475 (M–Me), 381 (M–SPh), 325 (M–SnMe₃).

Seemingly good quality crystals were obtained from toluene at –30°C, but they gave only weak diffraction.

3.4. Preparation of (Me₃Si)₂(PhSMe₂Si)CSnMe₂I

Solid iodine (0.52 g, 2.0 mmol) was added at room temperature to a solution of (Me₃Si)₂(PhSMe₂Si)CSnMe₃ (1.0 g, 2.0 mmol) in a mixture of CH₂Cl₂ (20 cm³) and CHCl₃ (20 cm³) and the mixture was heated under gentle reflux with protection from light for 2.5 h, after which the ¹H NMR spectrum indicated that the substrate had been converted into essentially a single product. Removal of the solvent left a pale yellow solid, which was recrystallized from heptane at –30°C to give the white (Me₃Si)₂(PhSMe₂Si)CSnMe₂I (1.0 g, 81%), m.p. 40–41°C. δ(H) 0.41 (18H, s, SiMe₃), 0.43 (6H, s, SiMe₂), 1.26 (6H, s, SnMe₂), 7.26–7.52 (5H, m, Ph). δ(Si) 0.7 (SiMe₃) and –21.9 (SiMe₂). δ(Sn) –12.7. *m/z* 602 (M), 587 (M–Me), 493 (M–SPh), 475 (M–I).

3.5. Preparation of (Me₃Si)₂(IMe₂Si)CSnMe₂I

Solid iodine (0.51 g, 2.0 mmol) was added at room temperature to a solution of (Me₃Si)₂(PhSMe₂Si)CSnMe₃ (0.50 g, 1.0 mmol) in a mixture of CH₂Cl₂ (20 cm³) and CHCl₃ (20 cm³) and the mixture was heated under gentle reflux for 6 h with protection from light. Removal of the solvent left a pale yellow solid, which was kept under vacuum for 2 h and then judged to be (Me₃Si)₂(IMe₂Si)CSnMe₂I (0.50 g, 83%). δ(H) 0.42 (18H, s, SiMe₃), 1.12 (6H, s, SiMe₂), 1.26 (6H, s, SnMe₂). *m/z* 605 (M–Me), 493 (M–I).

3.6. Preparation of (Me₃Si)₂(HOMe₂Si)CSnMe₂OH

Water (2 cm³) was added to a solution of (Me₃Si)₂(IMe₂Si)CSnMe₂I (0.50 g, 0.80 mmol) in THF (15 cm³) and the mixture was stirred at room temperature for 16 h. The solvent was removed and the solid residue extracted with pentane (40 cm³). The extract was dried (Na₂SO₄) and filtered, and the filtrate was evaporated to leave a white solid, which was recrystallized from toluene at –30°C to give the white (Me₃Si)₂(HOMe₂Si)CSnMe₂OH (0.25 g, 78%), m.p. 210–212°C. δ(H) 0.31 (18H, s, SiMe₃), 0.39 (6H, s, SiMe₂), 1.06 (6H, s, SnMe₂), 3.96 (2H, br, OH). δ(Sn) 0.75. IR (Nujol) ν(OH) 3668 and 3531s cm^{–1}. *m/z* (positive FAB, Xenon) (m-nitrobenzyl alcohol) 401 (M + 1), 383 (M–OH), 366 (M–2OH).

Seemingly good crystals were obtained from methylcyclohexane at –6°C, as well as from toluene, but all those examined gave only weak diffraction.

3.7. Reaction of (Me₃Si)₂(PhSMe₂Si)CSnMe₃ with bromine

A 1.0 M solution of Br₂ in CCl₄ (0.40 cm³, 0.40 mmol) was diluted with CH₂Cl₂ (10 cm³), cooled to

–80°C, and added dropwise with stirring to a solution of $(\text{Me}_3\text{Si})_2(\text{PhSMe}_2\text{Si})\text{CSnMe}_3$ (0.20 g, 0.40 mmol) in CH_2Cl_2 (10 cm^3) maintained at –80°C and protected from light. The mixture was stirred for a further 1 h at –80°C then the solvent was removed under vacuum at –30°C. The solid residue was sublimed at 90°C/0.2 Torr to give a white solid, which was crystallized from pentane to give $(\text{Me}_3\text{Si})_2(\text{BrMe}_2\text{Si})\text{CSnMe}_2\text{Br}$. $\delta(\text{H})$ 0.39 (18H, s, SiMe_3), 0.86 (6H, s, SiMe_2), 1.03 (6H, s, SnMe_2). m/z 509 (M–Me), 445 (M–Br).

A similar result was obtained when the reaction was carried out at 0°C.

3.8. Reaction of $(\text{Me}_3\text{Si})_2(\text{PhSMe}_2\text{Si})\text{CSnMe}_2\text{I}$ with AgBF_4

A solution of $(\text{Me}_3\text{Si})_2(\text{PhSMe}_2\text{Si})\text{CSnMe}_2\text{I}$ (0.015 g, 0.02 mmol) in CDCl_3 (0.5 cm^3) was added to an excess of AgBF_4 (ca. 0.1 g) in an NMR tube protected from light. The mixture was left at room temperature overnight and then filtered to remove the yellow AgI . The ^1H NMR spectrum of the filtrate revealed that only ca. 5% of the substrate remained and that two products had been formed, the major one apparently being the difluoride $(\text{Me}_3\text{Si})_2(\text{FMe}_2\text{Si})\text{CSnMe}_2\text{F}$. $\delta(\text{H})$ 0.27 (18H, s, SiMe_3), 0.43 (6H, d, $^3J(\text{HF})$ 7.4 Hz, SiMe_2F), 0.71 (6H, d, $^3J(\text{HF})$ 3.9 Hz, SnMe_2). $\delta(\text{Sn})$ 149 (d, $^1J(^{19}\text{F}^{119}\text{Sn})$ 2435 Hz. m/z 404 (M), 389 (M–Me), 220 (M– SnMe_2F), 216 (M– Me_2SnF_2). There were additional small peaks in the mass spectrum at 494 (M), 479 (M–Me), etc. that could possibly be attributed to $(\text{Me}_3\text{Si})_3(\text{PhSMe}_2\text{Si})\text{CSnMe}_2\text{F}$.

3.9. Reaction of $(\text{Me}_3\text{Si})_2(\text{PhSMe}_2\text{Si})\text{CSnMe}_2\text{I}$ with AgCN

A solution of $(\text{Me}_3\text{Si})_2(\text{PhSMe}_2\text{Si})\text{CSnMe}_2\text{I}$ (0.015 g, 0.02 mmol) in CDCl_3 (0.5 cm^3) was added to an excess of AgCN (ca. 0.1 g) in an NMR tube protected from light. The mixture was left at room temperature

overnight and then filtered. The ^1H NMR spectrum of the filtrate revealed that only ca. 5% of the substrate remained and that a single product had been formed, and this was judged to be $(\text{Me}_3\text{Si})_2(\text{PhSMe}_2\text{Si})\text{CSnMe}_2\text{CN}$. $\delta(\text{H})$ 0.39 (18H, s, SiMe_3), 0.41 (6H, s, SiMe_2), 0.86 (6H, s, $^2J(\text{HSn})$ 48 Hz, SnMe_2), 7.3–7.5, Ph). m/z 475 (M–CN), 392 (M–SPh), 367 (M–Me–SPh).

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