

New cyclic stannyloligosilanes

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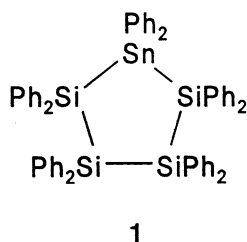
Abstract

The synthesis of new cyclic stannyloligosilanes $[R_2Sn(SiMe_2)_n]$ (**2a**, $n = 5$, $R = Ph$; **2b**, $n = 5$, $R = Me$; **3a**, $n = 6$, $R = Ph$; **3b**, $n = 6$, $R = Me$) is reported. The compounds are fully characterised by mass spectrometry and NMR spectroscopy and in the case of **2a** also by X-ray analysis. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Cyclic stannylsilanes; ^{29}Si -, ^{119}Sn -NMR spectroscopy; Crystal structure

1. Introduction

Cyclic silanes are well known as reagents in organometallic chemistry and material science [1]. However, to the best of our knowledge, only one cyclic organostannylsilane, i.e. decaphenylcyclostannatetrasilane **1**, is known [2].

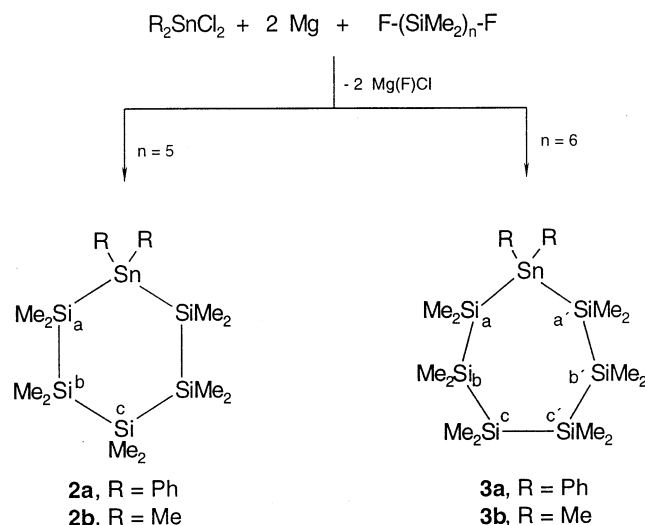


In a previous paper, we reported an Si–Sn-coupling reaction from triorganochlorostannanes with monofluorosilanes and magnesium [3]. Here we describe first results on reactions of α,ω -difluorosilanes with diorganodichlorostannanes and magnesium to form the cyclic monostannylsilanes **2a**, **2b**, **3a**, **3b** in moderate yields (Scheme 1).

The 1,2,3,4,5-pentasila-6-stanna-cyclohexanes **2a**, **b** and the 1,2,3,4,5,6-hexasila-7-stanna-cycloheptanes **3a**,

b are colourless, crystalline compounds. They are stable on air for hours and soluble in common organic solvents such as acetone, *n*-alkanes and ethers. The ^{29}Si - and ^{119}Sn -NMR data are given in Table 1. The molecular structure of **2a** is shown in Fig. 1.

Crystal data and structure solution of **2a**: $C_{22}H_{40}Si_5Sn$, $M = 563.68$, orthorhombic, *Pbca*, $a = 14.853(1)$, $b = 13.686(1)$, $c = 30.555(1)$ Å, $V = 6211.2(6)$



Scheme 1. Synthesis of cyclic stannyloligosilanes **2** and **3**.

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Table 1

 ^{119}Sn - and ^{29}Si -NMR data for **2a**, **b** and **3a**, **b** (δ [ppm] and $^xJ_{\text{Si-119/117Sn}}$ [Hz])

^{119}Si -NMR			^{29}Sn -NMR				
	Si_a	$^1J_{\text{Si-119/117Sn}}$	Si_b	$^2J_{\text{Si-119/117Sn}}$	Si_c	$^3J_{\text{Si-119/117Sn}}$	
2a ^a	−223.05	−34.9	368/350	−38.4	99/94	−41.5	24
2b	−242.6	−38.8	387/370	−39.2	93/88	−42.1	— ^b
3a	−224.1	−34.4	370/354	−38.7	94/90	−41.4	30
3b ^c	−243.6	−38.5	390/373	−39.1	92/88	−41.5	— ^b

^a $^1J(\text{Si}_a\text{--Si}_b)$ 61.3 Hz; $^2J(\text{Si}_a\text{--Si}_c)$ 9.8 Hz; $^1J(\text{Si}_b\text{--Si}_c)$ 62.5 Hz.^b Not found.^c $^1J(\text{Si}_a\text{--Si}_b)$ 60.3 Hz; $^2J(\text{Si}_a\text{--Si}_c)$ 9.2 Hz; $^1J(\text{Si}_b\text{--Si}_c)$ 61.6 Hz; $^2J(\text{Si}_b\text{--Si}_c)$ 8.9 Hz.

$\text{\AA}^3$, $Z = 8$, $D_{\text{calc.}} = 1.206 \text{ g cm}^{-3}$; $(\text{Mo--K}\alpha) = 0.71069 \text{ \AA}$, $F(000) = 2336$, $T = 291(1) \text{ K}$. The data were collected to a maximum θ of 20.84° with 360 frames via ω -rotation ($\Delta/\omega = 1^\circ$) two times 10 s per frame on a NONIUS KappaCCD diffractometer. The structure was solved by direct methods SIR92 [6] and refined by full-matrix least squares calculations using all measured F^2 data and SHELXL93 [7]. All non-H atoms were refined anisotropically. The H atoms were placed in geometrically calculated positions and refined with common isotropic temperature factors ($\text{C--H}_{\text{aryl}}$ 0.93 $\text{\AA}$, U_{iso} 0.135(7) $\text{\AA}^2$; $\text{C--H}_{\text{alkyl}}$ 0.96 $\text{\AA}$, U_{iso} 0.154(4) $\text{\AA}^2$). $R_1 = 0.0245$ for 1964 [$I > 2(I)$] and $wR_2 = 0.0564$ for 3206 independent reflections. The maximum and minimum residual electron densities were 0.334 and $-0.167 \text{ e \AA}^{-3}$. Full details have been deposited with the Cambridge Crystallographic Data Centre and are also available in CIF format from the author.

Preliminary investigations show that 1,3-difluoro-hexamethyltrisilane and 1,4-difluoro-octamethyltetrasilane, respectively, react with R_2SnCl_2 under formation of cyclic stannylsilanes with more than one tin atom.

2. Experimental

All syntheses were carried out using Schlenk-techniques to exclude oxygen and moisture. Solvents were dried by known methods. α,ω -difluorooligosilanes were obtained from dichloro- or dibromooligosilanes [4] and $[\text{Bu}_4\text{N}][\text{Ph}_3\text{SnF}_2]$ [3,5].

2.1. General procedure

In a typical reaction one equivalent α,ω -difluorooligosilane, one equivalent R_2SnCl_2 and three equivalents Mg (50% excess) are stirred in THF at room temperature. After a few hours the mixture turns to green–black indicating the start of the reaction. Stirring is continued for 5–8 days. After removing the solvent in vacuo, the residue is extracted with *n*-hexane or CH_2Cl_2 . The solvents are removed in vacuo. The

crude product is purified by recrystallisation or Kugelrohr distillation.

2.1.1. 6,6-diphenyl-decamethyl-1,2,3,4,5-pentasila-6-stanna-cyclohexane **2a**

Starting materials: 2.09 g (6 mmol) $\text{F--}(\text{SiMe}_2)_5\text{--F}$, 2.17 g (6 mmol) Ph_2SnCl_2 . For **2a** the residue is extracted with hexane. The crude product is purified by recrystallisation with acetone to afford the product in a yield of 1.35 g (40%). m.p. $180\text{--}182^\circ\text{C}$.

MS(EI): m/e 564 [M^+], 487 [$\text{PhSn}(\text{SiMe}_2)_5^+$], 429 [$\text{PhSn}(\text{SiMe}_2)_4^+$], 414 [$\text{PhSn}(\text{SiMe}_2)_3\text{SiMe}^+$], 352 [$\text{Sn}(\text{SiMe}_2)_4^+$], 294 [$\text{Sn}(\text{SiMe}_2)_3^+$]. $^1\text{H-NMR}$ [ppm]: 7.15 (m, 10H, $2 \times \text{Ph}$); 0.31 (s, 12H, Si_aMe); $^3J_{\text{Sn--H}} = 33.2/31.9 \text{ Hz}$; 0.07 (s, 18H, Si_bMe , Si_cMe). Found: C 46.85, H 7.14. $\text{C}_{22}\text{H}_{40}\text{Si}_5\text{Sn}$. Calc.: C 47.3, H 7.8.

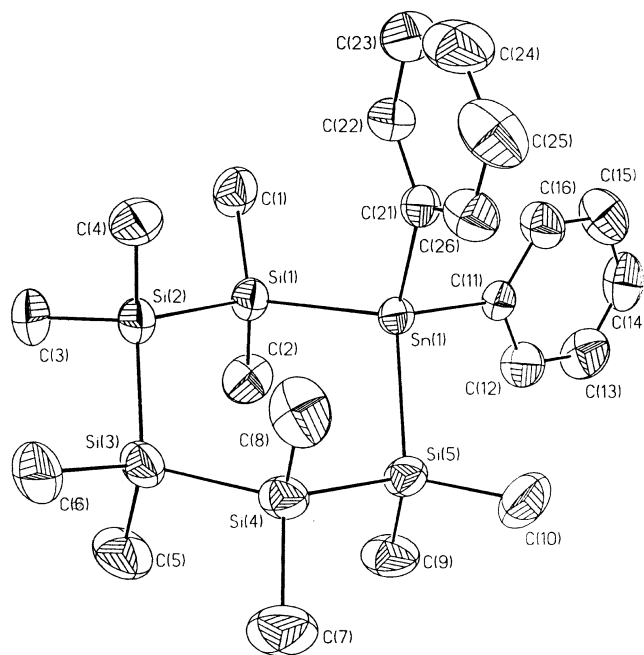


Fig. 1. General view of a molecule of (**1**) showing 30% probability displacement ellipsoids and atom numbering (SHELXTL-PLUS) [8]. Important parameters: $\text{Sn--Si}(1)$ 2.5670(13), $\text{Sn--Si}(5)$ 2.5701(13), $\text{Sn--C}(21)$ 2.136(5), $\text{Sn--C}(11)$ 2.156(4), $\text{Si}(1)\text{--Sn--Si}(5)$ 108.45(13), $\text{Si}(5)\text{--Sn--C}(21)$ 112.5(2), $\text{Si}(1)\text{--Sn--C}(21)$ 110.9(2).

2.1.2. Dodecamethyl-1,2,3,4,5-pentasil-6-stanna-cyclohexane **2b**

Starting materials: 1.96 g (5.95 mmol) F–(SiMe₂)₅–F, 1.13 g (5.95 mmol) Me₂SnCl₂. For **2b** the residue is extracted with hexane. The crude product is purified by recrystallisation with ether to afford the product in a yield of 1.17 g (45%). m.p. 120–123°C.

MS(EI): *m/e* 439 [M⁺], 424 [MeSn(SiMe₂)₅⁺], 367 [MeSn(SiMe₂)₄⁺], 352 [Sn(SiMe₂)₄⁺], 294 [Sn(SiMe₂)₃⁺]. ¹H-NMR [ppm]: 0.28 (s, 12H, Si_aMe); ³J_{Sn-H} = 34/32.4 Hz; 0.15 (s, 6H, SnMe); 0.06 (s, 18H, Si_bMe, Si_cMe). Found: C 32.29, H 8.26. C₁₂H₃₆Si₅Sn. Calc.: C 33.1, H 8.42.

2.1.3. 7,7-diphenyl-dodecamethyl-1,2,3,4,5,6-hexasil-7-stanna-cycloheptane **3a**

Starting materials: 4.7 g (12.1 mmol) F–(SiMe₂)₆–F, 4.16 g (12.1 mmol) Ph₂SnCl₂.

For **3a** the residue is extracted with hexane. The crude product is purified by recrystallisation in *n*-hexane. Yield 2.41 g (32%). m.p. 131–133°C.

MS(EI): *m/z* 622 [M⁺], 564 [Ph₂Sn(SiMe₂)₅⁺], 549 [Ph₂Sn(Si₅Me₉)⁺], 491 [Ph₂SnSi₄Me₇⁺], 428 [PhSn(SiMe₂)₄⁺], 352 [SnSi₄Me₈⁺], 348 [(SiMe₂)₆⁺], 309 [SnSi₃Me₇], 73 [SiMe₃⁺]. ¹H-NMR [ppm]: 7.29 (m, 10H, 2xPh); 0.36 (s, 12H, Si_aMe); ³J_{Sn-H} = 32.5/30.9 Hz; 0.08 (s, 12H, Si_bMe); –0.13 (s, 12H, Si_cMe). Found: C 46.34, H 7.45. C₂₄H₄₆Si₆Sn. Calc.: C 45.6, H 7.7.

2.1.4. Tetradecamethyl-1,2,3,4,5,6-hexasil-7-stanna-cycloheptane **3b**

Following the general procedure 3.32 g (8.57 mmol) F–(SiMe₂)₆–F, 1.88 g (8.57 mmol) Me₂SnCl₂ and 0.62 g (25.7 mmol) Mg (50% excess) are stirred in 150 ml THF at room temperature for 7 days. The residue is purified by Kugelrohr distillation. We received 0.64 g (15% yield) of a colourless solid **3b** with m.p. 92–98°C.

MS(EI): *m/z* 498 [M⁺], 483 [MeSn(SiMe₂)₆⁺], 425

[MeSn(SiMe₂)₅⁺], 367 [MeSn(SiMe₂)₄⁺], 348 [(SiMe₂)₆⁺], 335 [SnSi₄Me₇⁺], 290 [(SiMe₂)₅⁺], 232 [(SiMe₂)₄⁺], 131 [Me₃Si₂Me₂⁺], 73 [Me₃Si⁺]. ¹H-NMR [ppm]: 0.23 (s, 12H, Si_aMe); ³J_{Sn-H} = 35/33.3 Hz; 0.12 (s, 6H, SnMe); –0.07 (s, 24H, Si_bMe, Si_cMe). Found: C 33.76, H 8.50. C₁₄H₄₂Si₆Sn. Calc.: C 33.15, H 8.2.

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