ELSEVIER

Journal of Organometallic Chemistry 556 (1998) 165–167

Journal of Organo metallic Chemistry

New cyclic stannyloligosilanes

C. Kayser, R. Klassen, M. Schürmann, F. Uhlig *

Anorganische Chemie II, Universität Dortmund, Otto-Hahn-Straße 6, D-44221, Dortmund, Germany

Received 2 October 1997; received in revised form 17 November 1997

Abstract

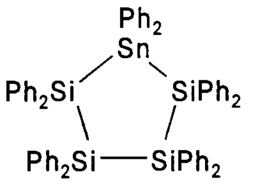
The synthesis of new cyclic stannyloligosilanes $[R_2Sn(SiMe_2)_n]$ (**2a**, $n = 5$, R = Ph; **2b**, $n = 5$, R = Me; **3a**, $n = 6$, R = Ph; **3b**, $n = 6$, R = Me) is reported. The compounds are fully characterised by mass spectrometry and NMR spectroscopy and in the case of **2a** also by X-ray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

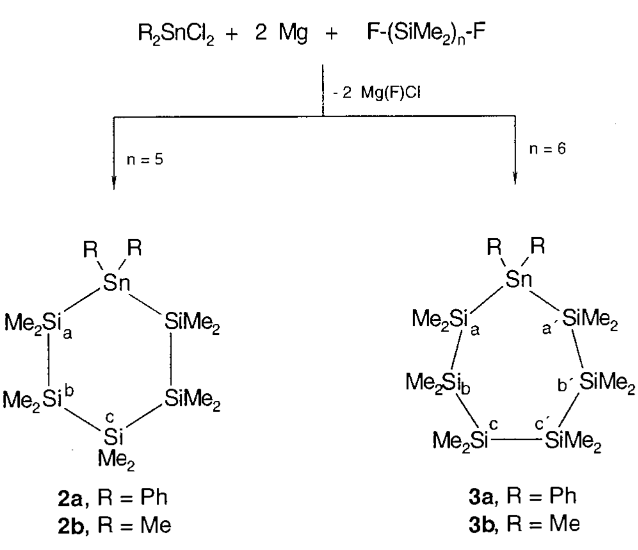


1

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**.

---

* Corresponding author. Fax: + 49 231 7553797.

PII S0022-328X(97)00755-9

Table 1
^{119}Sn- and ^{29}Si-NMR data for **2a**, **b** and **3a**, **b** (δ [ppm] and $^{x}J_{\text{Si-119/117Sn}}$ [Hz])

	^{119}Si-NMR			^{29}Sn-NMR			
		Si_a	$^{1}J_{\text{Si-119/117Sn}}$	Si_b	$^{2}J_{\text{Si-119/117Sn}}$	Si_c	$^{3}J_{\text{Si-119/117Sn}}$
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] $^{1}J(Si_a–Si_b)$ 61.3 Hz; $^{2}J(Si_a–Si_c)$ 9.8 Hz; $^{1}J(Si_b–Si_c)$ 62.5 Hz.

[b] Not found.

[c] $^{1}J(Si_a–Si_b)$ 60.3 Hz; $^{2}J(Si_a–Si_c)$ 9.2 Hz; $^{1}J(Si_b–Si_c)$ 61.6 Hz; $^{2}J(Si_b–Si_c)$ 8.9 H.

Å^3, $Z = 8$, $D_{\text{calc.}} = 1.206$ g cm^{-3}; (Mo–K$_\alpha$) = 0.71069 Å, $F(000) = 2336$, $T = 291(1)$ K. The data were collected to a maximum θ of 20.84° with 360 frames via ω-rotation ($\Delta/\omega = 1°$) 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 (C–H$_{\text{aryl}}$ 0.93 Å, U_{iso} 0.135(7) Å^3; C–H$_{\text{alkyl}}$ 0.96 Å, U_{iso} 0.154(4) Å^3). $R_1 = 0.0245$ 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 e Å^{-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 [Bu$_4$N][Ph$_3$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) F–(SiMe$_2$)$_5$–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. 180–182°C.

MS(EI): m/e 564 [M$^+$], 487 [PhSn(SiMe$_2$)$_5^+$], 429 [PhSn(SiMe$_2$)$_4^+$], 414 [PhSn(SiMe$_2$)$_3$SiMe$^+$], 352 [Sn (SiMe$_2$)$_4^+$], 294 [Sn(SiMe$_2$)$_3^+$]. ^{1}H-NMR [ppm]: 7.15 (m, 10H, 2 × Ph); 0.31 (s, 12H, Si$_a$Me); $^3J_{\text{Sn-H}} = 33.2/31.9$ Hz; 0.07 (s, 18H, Si$_b$Me, Si$_c$Me). Found: C 46.85, H 7.14. $C_{22}H_{40}Si_5Sn$. Calc.: C 47.3, H 7.8.

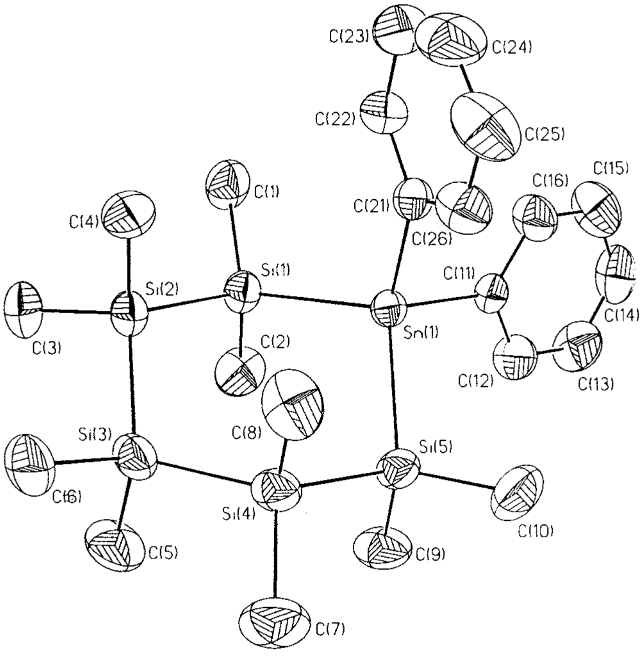


Fig. 1. General view of a molecule of (**1**) showing 30% probability displacement ellipsoids and atom numbering (SHELXTL-PLUS) [8]. Important parameters: Sn–Si(1) 2.5670(13), Sn–Si(5) 2.5701(13), Sn–C(21) 2.136(5), Sn–C(11) 2.156(4), Si(1)–Sn–Si(5) 108.45(13), Si(5)–Sn–C(21) 112.5(2), Si(1)–Sn–C(21)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

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

Starting materials: 1.96 g (5.95 mmol) F–$(SiMe_2)_5$–F, 1.13 g (5.95 mmol) Me_2SnCl_2. 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 [$MeSn(SiMe_2)_5^+$], 367 [$MeSn(SiMe_2)_4^+$], 352 [$Sn(SiMe_2)_4^+$], 294 [$Sn(SiMe_2)_3^+$]. ^{1}H-NMR [ppm]: 0.28 (s, 12H, Si_aMe); $^3J_{Sn\text{-}H} = 34/32.4$ Hz; 0.15 (s, 6H, SnMe); 0.06 (s, 18H, Si_bMe, Si_cMe). Found: C 32.29, H 8.26. $C_{12}H_{36}Si_5Sn$. Calc.: C 33.1, H 8.42.

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

Starting materials: 4.7 g (12.1 mmol) F–$(SiMe_2)_6$–F, 4.16 g (12.1 mmol) Ph_2SnCl_2.

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

MS(EI): *m*/*z* 622 [M^+], 564 [$Ph_2Sn(SiMe_2)_5^+$], 549 [$Ph_2Sn(Si_5Me_9)^+$], 491 [$Ph_2SnSi_4Me_7^+$], 428 [$PhSn(SiMe_2)_4^+$], 352 [$SnSi_4Me_8^+$], 348 [$(SiMe_2)_6^+$], 309 [$SnSi_3Me_7$], 73 [$SiMe_3^+$]. ^{1}H-NMR [ppm]: 7.29 (m, 10H, 2xPh); 0.36 (s, 12H, Si_aMe); $^3J_{Sn\text{-}H} = 32.5/30.9$ Hz; 0.08 (s, 12H, Si_bMe); −0.13 (s, 12H, Si_cMe). Found: C 46.34, H 7.45. $C_{24}H_{46}Si_6Sn$. Calc.: C 45.6, H 7.7.

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

Following the general procedure 3.32 g (8.57 mmol) F–$(SiMe_2)_6$–F, 1.88 g (8.57 mmol) Me_2SnCl_2 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 [$MeSn(SiMe_2)_6^+$], 425 [$MeSn(SiMe_2)_5^+$], 367 [$MeSn(SiMe_2)_4^+$], 348 [$(SiMe_2)_6^+$], 335 [$SnSi_4Me_7^+$], 290 [$(SiMe_2)_5^+$], 232 [$(SiMe_2)_4^+$], 131 [$Me_3Si_2Me_2^+$], 73 [Me_3Si^+]. ^{1}H-NMR [ppm]: 0.23 (s, 12H, Si_aMe); $^3J_{Sn\text{-}H} = 35/33.3$ Hz; 0.12 (s, 6H, SnMe); −0.07 (s, 24H, Si_bMe, Si_cMe). Found: C 33.76, H 8.50. $C_{14}H_{42}Si_6Sn$. Calc.: C 33.15, H 8.2.

Acknowledgements

The authors thank the Deutsche Forschungsgemeinschaft for financial support (DFG-project Uh74-3) and the ASV-innovative Chemie GmbH (Bitterfeld) for the generous gift of silanes. We are also grateful to Professor Dr. K. Jurkschat (Universität Dortmund/Germany) for supporting this investigation.

References

[1] (a) E. Hengge, R. Janoschek, Chem. Rev. 95 (1995) 1443. (b) R. West, in S. Patai, Z. Rappaport (Eds.), The Chemistry of Organic Silicon Compounds, Wiley Interscience, NY, Ch. 19, 1989. (c) P. Kochs, in: H.R. Kricheldorf (Ed.), Silicon in polymer synthesis, Springer, Berlin, Heidelberg, Ch. 4, 1996.

[2] E. Hengge, U. Brychy, M. Chem. 95 (1966) 1309.

[3] R. Hummeltenberg, K. Jurkschat, F. Uhlig, Phosphorus, Sulfur and Silicon (1997) in press.

[4] H. Gilman, R.L. Harell, J. Organomet. Chem. 14 (1966) 317.

[5] M. Gingras, Tetrahedron Lett. 132 (50) (1991) 7381–7384.

[6] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M.C. Burla, G. Polidori, M. Camalli, SIR92—a program for automatic solution of crystal structures by direc methods, J. Appl. Crystallogr. 27 (1994) 435.

[7] G.M. Sheldrick, SHELXL93, Program for Crystal Structure Refinement, University of Göttingen, Germany, 1993.

[8] G.M. Sheldrick, SHELXTL-PLUS. Release 3.4 for Nicolet R3m/V crystallographic system. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data. Nicolet Instrument Corporation, Madison, Wisconsin, USA, 1987.