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Journal of Organometallic Chemistry 585 (1999) 211–214
Journal of Organo metallic Chemistry

Novel Si–Sn ring systems with distanna and tristanna moieties

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Received 27 January 1999; received in revised form 26 March 1999

Abstract

The synthesis of new cyclic stannaoligosilanes **9**, **10** and **11** with a bridging tin–tin unit $[(^t\mathrm{Bu}_2\mathrm{Sn})_2(\mathrm{SiMe}_2)_n$, $n = 2$, **9**; $n = 3$; **10**; $n = 4$, **11**] or an Sn_3 moiety $[(^t\mathrm{Bu}_2\mathrm{Sn})_3(\mathrm{SiMe}_2)_2]$ (**12**) are reported. All compounds are fully characterised by NMR, mass spectroscopy and elemental analysis. The structure of the five-membered ring **10** is determined by X-ray crystallography. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Cyclic stannasilanes; Crystal structure; ^{29}Si-NMR; ^{119}Sn-NMR

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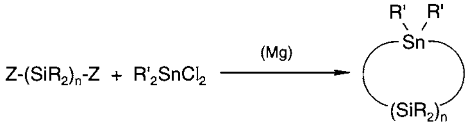
1. Introduction

A large number of reports concerning cyclic silanes of the type $(\mathrm{R_2Si})_n$ have appeared in literature. However, only a few studies have focused on cyclic silicon compounds containing the heavier elements of Group 14 [1–3]. In the last decades just two contributions about cyclic stannaoligosilanes have appeared in literature [2,3], which is surprising since they are potential precursors for ring opening polymerisation (ROP). A five-membered ring with one tin atom in the cyclic unit is obtained by a Wurtz-type reaction of dilithio octaphenyltetrasilane with diphenyldichlorostannane (Scheme 1) [2]. However, the steric requirement of phenyl substituents at the tin and silicon atoms make **1** unsuitable for ROP. Similar effects have been reported for perphenylated cyclic silanes [4]. We recently reported on the synthesis of six- and seven-membered rings **2**–**5** with one tin atom, available by reacting α,ω-difluorosilanes with diorganodichlorostannanes and magnesium (Scheme 1) [3].



R = R′ = Ph; n = 4; Z = Li; **1**
R = R′ = Me; n = 5; Z = F; **2**
R = Me; R′ = Ph; n = 5; Z = F; **3**
R = R′ = Me; n = 6; Z = F; **4**
R = Me; R′ = Ph; n = 6; Z = F; **5**

Scheme 1. Formation of cyclic compounds with one tin atom in the monocyclic skeleton.

Herein, we describe the first synthesis of cyclic stannaoligosilanes with more than one tin atom in a monocyclic unit. These investigations are based on the previously reported synthesis of dihalogen substituted stannylsilanes **6**–**8** by this group [5].

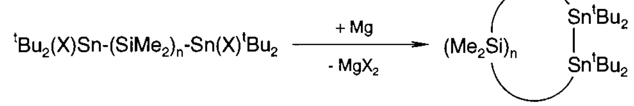
$^t\mathrm{Bu}_2(\mathrm{X})\mathrm{Sn}{-}(\mathrm{SiMe}_2)_n{-}\mathrm{Sn}(\mathrm{X})^t\mathrm{Bu}_2$

6, X = Br; $n = 2$
7, X = Br; $n = 3$
8, X = Cl; $n = 4$

2. Synthesis and discussion

Stannaoligosilanes **9**–**11** with bridging tin–tin units are available by intramolecular Wurtz coupling of compounds **6**–**8** ($n = 2$, 3, 4) in the presence of magnesium (Eq. (1)).

(1)



X = Cl, Br

9, n = 2
10, n = 3
11, n = 4

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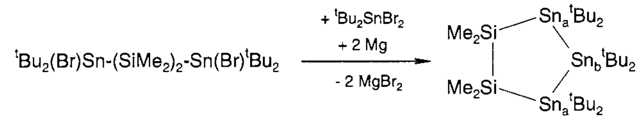
PII: S0022-328X(99)00212-0

Table 1
^{29}Si- and ^{119}Sn-NMR data of compounds **9**–**12**

Compound	δ (^{119}Sn) (ppm)	$^{1}J(^{119}\text{Sn}-^{117}\text{Sn})$ (Hz)	δ (^{29}Si) (ppm)	$^{x}J(^{119/117}\text{Sn}-^{29}\text{Si})$ (Hz)
9	−19.4	40	−11.4	^{1}J: 226/216; ^{2+3}J: 261/249
10	−98.5	65	−33.9	^{1}J: 217/207; ^{2}J: 66
			−37.4	^{2}J: 67
11	−99.7	191	−34.0	^{1}J: 214/204; ^{2}J: 54
			−38.1	^{2}J: 89; ^{3}J: 12
12	−28.2 (Sn$_b$)	762/725	−30.8	^{1}J: 206/196; ^{2}J: 62
	−95.3 (Sn$_a$)	727; ^{2}J: 226		

Contrary to the 'one pot' synthesis described in Scheme 1, the reaction pathway illustrated in Eq. (1) allows the synthesis of derivatives with ring sizes smaller than six. The first four-membered cyclic stannylsilane **9** is obtained by reacting **6** with magnesium. The treatment of **7** with magnesium yields the five-membered ring **10**, while the six-membered ring **11** is the result of the reaction of **8** with magnesium. The yields vary between 70 and 90% and no soluble byproducts are observed. **10** and **11** are colourless, crystalline solids; the four-membered ring **9** is a highly viscous oil. In sharp contrast to the high reactivity of the non-cyclic starting materials **6**–**8**, the ring systems are stable against water and **10**–**11** also are stable against air over hours. As a result of the higher ring strain, the four-membered ring **9** reacts rapidly with oxygen forming products which are nearly insoluble in common organic solvents. ^{29}Si- and ^{119}Sn-NMR data of **9**–**11** are summarized in Table 1. The value of the $^{1}J_{\text{Sn}-\text{Sn}}$ coupling constants in **9**–**11** can be clearly correlated with increasing ring strain, with smaller ring sizes displaying in smaller coupling constants. The most significant difference is observed by comparing the six-membered **11** to the five-membered ring **10**, with a decrease of the coupling constants from 195 to 65 Hz. In contrast, the $J_{\text{Si}-\text{Sn}}$ coupling constants display no significant correlation with the ring size. Fig. 1 illustrates the molecular structure of compound **10**; selected structural parameter are listed in Table 2. Due to the steric presence of the *tert.*butyl groups, Sn–Sn (283.8(1) pm) and Sn–Si (259.7(1)–261.4(1) pm) bond lengths are significantly longer (between 2 and 5 pm) than in mono- and bicyclic six-membered stannaoligosilanes carrying phenyl substituents at the tin centers [3,6]. The high ring strain of **10** is evidenced by the narrow Si–Sn–Sn bond angles (99.05(2) and 99.62(2)°). Long Sn–Sn bond lengths and narrow bond angles have also been reported for Sn–Sn compounds with a similar degree of ring strain [7].

Stannasilane **12** displaying a Sn$_3$ moiety is available by a cross-coupling of α,ω-distannyloligosilane **6** with di-^{t}butyldibromostannane and magnesium (Eq. (2)) in about 45–50% yield.



6 **12**

(2)

Byproducts of the reaction are polymeric stannanes and the four-membered ring **9**. In contrast to **9**, compound **12** is stable in air for hours and can be separated from the reaction mixture by oxidation of the byproducts and selective crystallisation. ^{29}Si- and ^{119}Sn-NMR data of **12** are also listed in Table 1. The ^{119}Sn-NMR values of **12** show a large difference in chemical shift (−28.2(Sn$_b$); −95.3(Sn$_a$) with an AM system for the ^{1}J (^{119}Sn–^{119}Sn) satellites; see Eq. (2) and Table 1) for the central Sn and the two adjacent tin atoms. The connection of Sn$_a$ and Sn$_b$ is independently confirmed by a ^{119}Sn–^{119}Sn-COSY NMR experiment [11].

Reactions of α,ω-distannyloligosilanes with larger Si-units (^{t}Bu$_2$Sn(X)–(SiMe$_2$)$_n$–Sn(X)^{t}Bu$_2$; $n = 5$, 6) and magnesium do not lead to homogenous products as mentioned above for $n = 2$, 3 or 4. This project is currently under intense investigation and will be disseminated at a later time.

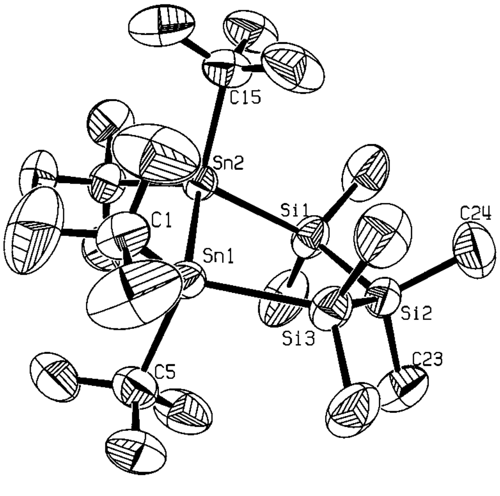


Fig. 1. Molecular structure of **10**, showing 30% probability displacement ellipsoids and numbering of selected atoms (ORTEP3). For selected parameters see Table 2.

Table 2
Selected parameters of the molecular structure of **10**

Atoms	Distance (Å)	Atoms	Angle (°)
Sn(1)–Sn(2)	2.8381(3)	C(1)–Sn(1)–C(5)	110.3(1)
Sn(1)–Si(3)	2.5974(9)	C(1)–Sn(1)–Si(3)	111.6(1)
Sn(1)–C(5)	2.231(3)	Si(3)–Sn(1)–Sn(2)	99.62(2)
Si(1)–Si(2)	2.362(1)	Si(1)–Sn(2)–Sn(1)	99.05(2)
Si(2)–Si(3)	2.363(1)	Si(2)–Si(1)–Sn(2)	108.12(4)
Si(2)–C(23)	1.880(4)	C(23)–Si(2)–C(24)	106.2(2)

3. Experimental

All experiments were carried out under an Argon or Nitrogen atmosphere using Schlenk techniques. Solvents were dried by common methods. α,ω-bis (di-^{t}butylhalogenostannyl)oligosilanes were obtained according to literature procedures [5].

3.1. General procedure

One equivalent of α,ω-bis(di-^{t}butylhalogenostannyl)oligosilane and two equivalents of Mg (100% excess) are stirred in 200 ml THF at room temperature. During the reaction the mixture becomes greyish–black within minutes (X = Br) or hours (X = Cl). After 10 h (X = Br) or 1 day (X = Cl) the solvent is evaporated in vacuo and 200 ml of dry hexane is added. Filtration (G3) yields a clear solution from which the hexane is removed under reduced pressure. The crude product is further purified by adsorptive filtration using silica gel 60 as stationary phase.

3.1.1. *3,3,4,4-Tetra-^{t}butyl-1,1,2,2-tetramethyl-1,2-disila-3,4-distannacyclobutane* ***9***

Starting materials: 3.7 g (5 mmol) ^{t}Bu$_2$(Br)Sn–(SiMe$_2$)$_2$–Sn(Br)^{t}Bu$_2$, 0.3 g (12 mmol) Mg. Adsorptive filtration of the crude product using hexane as mobile phase yields 2.5 g (84%) of a highly viscous oil.

MS (EI): m/e 582 [M^+], 525 [$M^+-{}^t$Bu], 468 [$M^+-2{}^t$Bu], 411 [$M^+-3{}^t$Bu], 411 [$M^+-4{}^t$Bu]; ^{1}H-NMR (ppm): 0.39 (12H, Sn–SiMe_2, ^3J($^{119/117}$Sn–^{1}H: 22 Hz), 1.32 (s, 36H, Sn–^{t}Bu, ^3J($^{119/117}$Sn–^{1}H): 60 Hz); ^{13}C-NMR (ppm): −2.6 (4C, Sn–SiMe_2, ^2J($^{119/117}$Sn–^{13}C): 42 Hz, ^3J($^{119/117}$Sn–^{13}C): 11 Hz), 31.1 (4C, Sn–CMe$_3$, ^1J($^{119/117}$Sn–^{13}C): 204/194 Hz, ^2J($^{119/117}$Sn–^{13}C): 58 Hz), 34.1 (12C, Sn–CMe_3, ^2J($^{119/117}$Sn–^{13}C): 74 Hz, ^3J($^{119/}$117Sn–^{13}C): 12 Hz). No satisfactory elemental analysis could be obtained.

3.1.2. *4,4,5,5-Tetra-^{t}butyl-1,1,2,2,3,3-hexamethyl-1,2,3-trisila-4,5-distannacyclopentane* ***10***

Starting materials: 4.8 g (6 mmol) ^{t}Bu$_2$(Br)Sn–(SiMe$_2$)$_3$–Sn(Br)^{t}Bu$_2$, 0.3 g (12 mmol) Mg. Adsorptive filtration of the crude product using hexane as mobile phase yields 3.15 g (82%) of colourless crystals, m.p. 112°C.

MS (EI): m/e 640 [M^+], 586 [$M^+-{}^t$Bu], 527 [$M^+-2{}^t$Bu], 469 [$M^+-3{}^t$Bu], 411 [$M^+-4{}^t$Bu]; ^{1}H-NMR (ppm): 0.14 (s, 6H, Sn–Si–SiMe_2), 0.35 (s, 12H, Sn–SiMe_2, ^3J($^{119/117}$Sn–^{1}H): 22.6 Hz), 1.34 (s, 36H, Sn–^{t}Bu, ^3J($^{119/117}$Sn–^{1}H): 60.7/58.2 Hz); ^{13}C-NMR (ppm): −5.3 (2C, Sn–Si–SiMe_2, ^3J($^{119/117}$Sn–^{13}C): 10.7 Hz), −1.6 (4C, Sn–SiMe_2, ^2J($^{119/117}$Sn–^{13}C): 35.0 Hz, ^3J($^{119/}$117Sn–^{13}C): 11.7 Hz), 30.5 (4C, Sn–CMe$_3$, ^1J($^{119/}$117Sn–^{13}C): 230/224 Hz, ^2J($^{119/117}$Sn–^{13}C): 12.6 Hz), 34.7 (12C, Sn–CMe_3); Found: C, 41.7; H, 9.2. $C_{22}H_{56}Si_3Sn_2$. Calc.: C, 41.3; H, 8.45%.

Crystal data and structure solution and refinement of **10**: colourless crystals of $C_{22}H_{56}Si_3Sn_2$, $M_r = 640.30$, orthorhombic in $P2_12_12_1$, $a = 11.808(1)$, $b = 15.814(1)$, $c = 17.398(1)$ Å, $V = 3248.8(4)$ Å^3, $Z = 4$, $D_x = 1.309$ g cm^{-3}, $F(000) = 1312$, λ(Mo–K$_\alpha$) = 0.71069 Å, $m = 1.654$ mm^{-1}, $T = 291(1)$ K, final $R = 0.0197$ for 5291 unique observed [$F = 4.0\sigma(F)$] diffractometer data. The data collection covered almost the whole sphere of reciprocal space with 360 frames via ω-rotation ($\Delta/\omega = 1°$) at twice 20 s per frame on a Nonius Kappa CCD diffractometer with a completeness to $\theta_{\max}$ (25.67°) of 95.4%. The structure was solved by direct methods (SHELXS97 [8]) and successive difference Fourier syntheses. Refinement applied full-matrix least-squares methods (SHELXL97 [9]). The absolute configuration of **10** was confirmed by refinement of the Flack [10] parameter −0.031(15). The hydrogen atoms were placed in geometrically calculated positions using a riding model and were refined with common isotropic temperature factors (C–H$_{\text{prim.}}$ 0.96 Å, U$_{iso}$ 0.135(2) Å^2). Maximum and minimum residual electron densities were 0.224 and −0.349 e Å^{-3}.

3.1.3. *5,5,6,6-Tetra-^{t}butyl-1,1,2,2,3,3,4,4-octamethyl-1,2,3,4-tetrasila-5,6-distannacyclohexane* ***11***

Starting materials: 4.6 g (6 mmol) ^{t}Bu$_2$(Cl)Sn–(SiMe$_2$)$_4$–Sn(Cl)^{t}Bu$_2$, 0.3 g (12 mmol) Mg. Adsorptive filtration of the crude product using hexane as mobile phase yields 3.19 g (76%) of a colourless solid, m.p. 151°C.

MS (EI): m/e 698 [M^+], 641 [$M^+-{}^t$Bu], 584 [$M^+-2{}^t$Bu], 526 [$M^+-3{}^t$Bu], 470 [$M^+-4{}^t$Bu]; ^{1}H-NMR (ppm): 0.15 (s, 12H, Sn–Si–SiMe_2), 0.39 (s, 12H, Sn–SiMe_2, ^3J($^{119/117}$Sn–^{1}H): 22.8 Hz), 1.35 (s, 36H, Sn–^{t}Bu, ^3J($^{119/117}$Sn–^{1}H): 60.2/57.7 Hz); ^{13}C-NMR (ppm): −5.1 (4C, Sn–Si–SiMe_2, ^3J($^{119/117}$Sn–^{13}C): 11.7 Hz), −1.1 (4C, Sn–SiMe_2, ^2J($^{119/117}$Sn–^{13}C): 35.0 Hz, ^3J($^{119/}$117Sn–^{13}C): 10.7 Hz), 30.5 (4C, Sn–CMe$_3$, ^1J($^{119/}$117Sn–^{13}C): 226/216 Hz, ^2J($^{119/117}$Sn–^{13}C): 11.7

Hz), 35.0 (12C, Sn–C*Me*$_3$); Found: C, 41.5; H, 8.9. $C_{24}H_{60}Si_4Sn_2$. Calc.: C, 41.3; H, 8.7%.

3.1.4. 3,3,4,4,5,5-Hexa-^{t}butyl-1,1,2,2-tetramethyl-1,2-disila-3,4,5-tristannacyclopentane ***12***

Starting materials: 3.7 g (5 mmol) ^{t}Bu$_2$(Br)Sn–(SiMe$_2$)$_2$–Sn(Br)^{t}Bu$_2$, 1.96 g (5 mmol) ^{t}Bu$_2$SnBr$_2$, 0.5 g (20 mmol) Mg. Adsorptive filtration of the crude product using hexane as mobile phase yields 3.4 g (84%) of a colourless solid.

MS (EI): m/e 815 [M^+], 758 [$M^+ - {}^t$Bu], 702 [$M^+ - 2{}^t$Bu], 644 [$M^+ - 3{}^t$Bu], 587 [$M^+ - 4{}^t$Bu]; ^{13}C-NMR (ppm): 0.0 (4C, Sn–Si*Me*$_2$, $^2J(^{119/117}$Sn–^{13}C): 30 Hz, $^3J(^{119/117}$Sn–^{13}C: 10 Hz), 31.6 (4C, Si–Sn–*C*Me$_3$, $^1J(^{119/}$117Sn–^{13}C): 228/216 Hz), 31.1 (2C, Sn–Sn–*C*Me$_3$, $^1J(^{119/117}$Sn–^{13}C, $^2J(^{119/117}$Sn–^{13}C): 14 Hz), 33.0 (18C, Sn–C*Me*$_3$).

4. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 113641 for compound **10**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit:ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

The authors thank the Deutsche Forschungsgemeinschaft for financial support (DFG-project Uh74-3) and the Sivento Chemie, Rheinfelden, for the generous donation of silanes. We are also grateful to Professor Dr K. Jurkschat, University of Dortmund, for supporting these investigations.

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