Journal of Organometallic Chemistry 694 (2009) 4209–4215

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Functionalized tetrastannacyclobutanes, Part I

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ARTICLE INFO

Article history:
Received 8 April 2009
Received in revised form 3 September 2009
Accepted 4 September 2009
Available online 12 September 2009

Keywords:
Organostannanes
Mono functionalised ring systems

ABSTRACT

The reaction of di^{t}butyldichlorostannane with 5 equivalents of magnesium leads to 1,1,2,2,3,3,4-hepta-^{t}butyl-4-(chloromagnesio)-tetrastannacyclobutane **1**. A mechanism of this reaction is proposed. **1** is structurally characterized by 1D and 2D ^{119}Sn NMR experiments. New monofunctionalised four membered cyclostannanes could be obtained by derivatisation of **1**. X-Ray analysis of 1,1,2,2,3,3,4-hepta-^{t}butyl-4-methyl-tetrastannacyclobutane **2** and 1,1,2,2,3,3,4-hepta-^{t}butyl-4-chlorpropyl-tetrastannacyclobutane **5** show bent ring systems with folding angles about 157°.

1. Introduction

A large variety of alkyl and aryl substituted four-membered tin-rings is known in the literature. Neumann and Fu [1] described different types of perphenanthryl substituted cyclostannanes, among them octa-phenanthryltetrastannacyclobutane. Puff et al. [2] were the first who fully characterized octa-^{t}butyl- and octa-^{t}amyltetrastannacyclobutane in 1986. Also octa-methyl- [3] and octa-phenyltetrastannacyclobutane [4] were postulated, although their structures have never been proven by X-ray analysis.

Ring systems with silicon containing substituents like octakis-((trimethylsilyl)-methyl)-tetrastannacyclobutane [5] were also reported (Fig. 1).

However, functionalised tetrastannacyclobutanes are scarcely known. Mallela et al. reported on the synthesis and structure of tetra-chloro-tetrakis-(tris-(trimethylsilyl)-silyl)tetrastannacyclobutane [6] and tetra-chloro-tetrakis-(tris-(trimethylsilyl)-germyl) tetrastannacyclobutane [7]. Bromo-heptakis-(2,6-diethylphenyl)-[8] and heptakis-(2,6-diethylphenyl)-tetrastannacyclobutane [9] have been the only known mono-functionalised tetrastannacyclobutanes so far. A possible mechanism of the formation of heptakis-(2,6-diethylphenyl)-tetrastannacyclobutane by using hexakis-(2,6-diethylphenyl)-cyclotristannane as a starting material was described, postulating an anionic monofunctionalised four-membered tin ring as an intermediate (Fig. 2).

For a couple of years our group has dealt with the formation of Si–Sn ring systems containing a larger number of tin atoms than silicon atoms in the ring skeleton. [10] We report on the formation of monofunctionalised four-membered tin ring systems and attempts for derivatisation reactions.

2. Results and discussion

The formation of 1,1,2,2,3,3,4-hepta-^{t}butyl-4-(chloromagnesio)-tetrastannacyclobutane **1** was observed by the reaction of 1,4-dichloro-octa-^{t}butyltetrastannane with magnesium. However, using di-^{t}butyldichlorostannane as a starting material also leads to derivate **1**. An ^{119}Sn NMR investigation on this second reaction pathway was performed, taking an NMR-sample every hour. This investigation showed that compound **1** was formed in a reaction cascade (Fig. 3).

In a first step (A) two monostannanes are coupled with magnesium to form tetra-^{t}butyldichlordistannane. The distannane is completely transformed into a yellow precipitate which has been identified as octa-^{t}butyltetrastannacyclobutane (B). Finally the dark red solution is formed containing **1** as a major product (Table 1, step C).

A possible mechanism for the last step of the reaction is shown in Fig. 4. A Grignard reagent present in the reaction mixture abstracts a hydrogen atom from one of the ^{t}butyl-groups on the tin ring forming isobutane and isobutene. Simultaneously a magnesium–tin function is established.

This reaction mechanism is supported by a head space analysis of the gas phase above the reaction mixture, displaying the formation of a 1:1-ratio of isobutane and isobutene.

We cannot decide yet whether this Grignard reagent is a Grignard type tin compound which decomposes afterwards forming butane and a tin(II) derivative of ^{t}BuMgCl as shown in Fig. 4. Anyway the presence of Grignard reagents is necessary. This was

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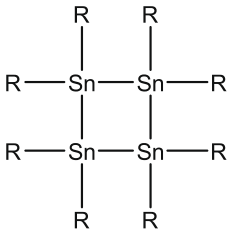
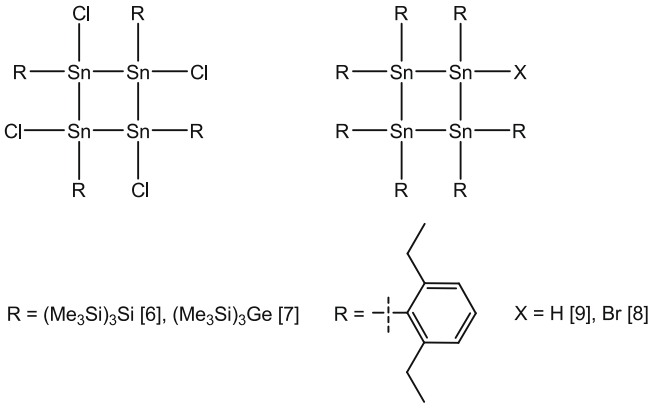
doi:10.1016/j.jorganchem.2009.09.004



R= ^{t}Bu [2], ^{t}Amyl [2], Phen [1], Me_3SiH_2C [5], Me [3], Ph [4]

Fig. 1. Various octa-alkyltetrastannacyclobutane reported in literature.



R = $(Me_3Si)_3Si$ [6], $(Me_3Si)_3Ge$ [7] R = X = H [9], Br [8]

Fig. 2. Different kinds of functionalised tetrastannacyclobutanes.

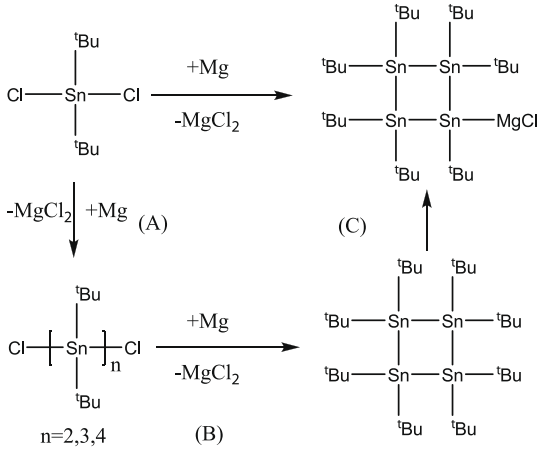


Fig. 3. Reaction path leading to **1**.

Table 1
^{119}Sn NMR signals.

Time (h)	$^{t}Bu_2SnCl_2$ (56 ppm) (%)	$^{t}Bu_4Sn_2Cl_2$ (112 ppm) (%)	$^{t}Bu_8Sn_4$ (80 ppm)	$^{t}Bu_7Sn_4MgCl$ (180 ppm, 75 ppm, −6.0 ppm) (%)
0	100	0	0%	0
1	100	0	0%	0
2	60	40	0%	0
3	0	0	Yellow precipitation	0*
4	0	0	Yellow precipitation	0*
5	0	0	0%	80*
6	0	0	0%	90*

* Minor sideproducts that could not be identified are not mentioned.

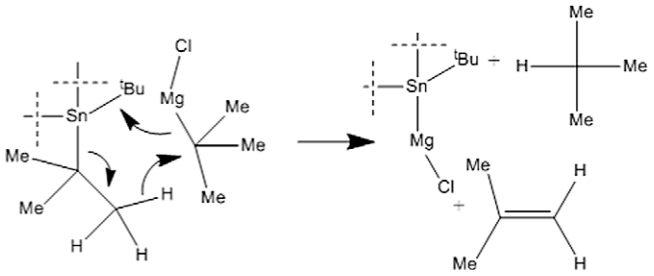


Fig. 4. Mechanism for the formation of **1** with octa-^{t}butyltetrastannacyclobutane as starting material.

proven by stirring octa-^{t}butyltetrastannacyclobutane over night in the presence of magnesium and ^{t}butylmagnesium-chloride also resulting in product **1**, whereas the same mixture without ^{t}butylmagnesiumchloride did not react at all.

The structure of **1**, the four-membered tin ring with magnesium bounded to Sn(1), was proven on the basis of 1D and 2D ^{119}Sn NMR experiments performed on compound **1** and its derivatives.

The ^{119}Sn NMR spectrum of this compound provides three signals in the ratio 1:2:1 each with the characteristic pattern of ^{119}Sn–$^{119/117}$Sn coupling constants forming a pair of satellites. The satellites of the ^{119}Sn–^{117}Sn coupling constant are centralised symmetrically around the central line while satellites of ^{119}Sn–^{119}Sn are not [11,12] yielding an AB-type spectra. Fortunately, the magnitude of the unsymmetrical ^{119}Sn–^{119}Sn coupling constants can be calculated $(J(^{119}Sn–^{119}Sn)/J(^{119}Sn–^{117}Sn) = \gamma(^{119}Sn)/\gamma(^{117}Sn) \sim 1.046$ [11]). Signals of our compounds have two pairs of satellites in the ^{119}Sn spectra coming from the one- and two-bond interactions only ^{119}Sn(2)–^{119}Sn(4) satellites are missing in the spectra of all derivatives as a consequence of the cyclic structure (Table 2, Fig. 5). If Sn(2) and Sn(4) are both ^{119}Sn isotopes, the resulting structure is then symmetric and both atoms form one line. The values of $^{1}J(^{119}Sn(1)–^{119/117}Sn(2,4))$ vary significantly due to the substituents on Sn(1). Almost 7000 Hz in **1** indicates the presence of magnesium as similarly large values were found in alkali-substituted distannanes only [13].

2D ^{1}H–^{119}Sn correlation experiments confirmed two nonequivalent ^{t}butyl groups connected to Sn(2,4) and two more connected to Sn(3) atom ($^{3}J(^{1}H–^{119}Sn) \sim 40$ Hz) while Sn(1) has only one ^{t}butyl group ($^{3}J(^{1}H–^{119}Sn) \sim 27$ Hz).

In order to confirm the nature of the product 1,1,2,2,3,3,4-hepta-^{t}butyl-4-(chloromagnesio)-tetrastannacyclobutane **1** also by reactivity several derivatisation reactions were undertaken. Alkylation with dimethylsulfate or alkylbromides leads to the corresponding 1,1,2,2,3,3,4-hepta-^{t}butyl-4-alkyltetrastannacyclobutanes (methyl: **2**, ethyl: **3**, propyl: **4**, (3-chloro)-propyl: **5**). Single crystals out of 1,1,2,2,3,3,4-hepta-^{t}butyl-4-methyltetrastannacyclobutane **2** and 1,1,2,2,3,3,4-hepta-^{t}butyl-4-chloropropyltetrastannacyclobutane **5** could be grown by recrystallisation from THF. (see Section 2.1).

Furthermore **1** could be converted into 1-chloro-1,2,2,3,3,4,4-hepta-^{t}butyltetrastannacyclobutane **6** by using chloroform as a reagent.

1 also reacts with sulfur and tellurium forming corresponding tristannadichalcogen compounds (Fig. 5) which were identified by ^{119}Sn NMR [14]. These compounds were already described by Puff et al. performing similar reaction with octa-^{t}butyltetrastannacyclobutane (Fig. 6) [15].

2.1. Discussion of the crystal structures

Hepta-^{t}butyl-methyltetrastannacyclobutane **2** crystallizes in the triclinic space group $P\bar{1}$ with three independent molecules ($Z = 6$) in the asymmetric unit of the unit cell. The three indepen-

Table 2
^{119}Sn NMR data; chemical shifts and coupling constants in hepta-^{t}butyltetrastannacyclobutane derivatives.

Compound	δ ^{119}Sn			$^{1}J(^{119}Sn–^{119/117}Sn)$		$^{2}J(^{119}Sn–^{119/117}Sn)$	
	Sn(1)	Sn(2,4)	Sn(3)	Sn(1)–Sn(2)	Sn(2)–Sn(3)	Sn(1)–Sn(3)	Sn(2)–Sn(4)*
1	−6	75	180	6810/6500	4150/3966	1640/1564	n.r.
2	−49	63	93	645/615	995/950	1940/1850	1430
3	−19	63	96	775/740	1040/990	1880/1790	1460
4	−29	58	94	759/727	1024/979	1831/1773	1476
5	−26	62	96	809/762	982/938	1906/1869	1417
6	236	102	82	1920/1835	1111/1052	2045/1952	867

* only $^{2}J(^{119}Sn–^{117}Sn)$, see text.

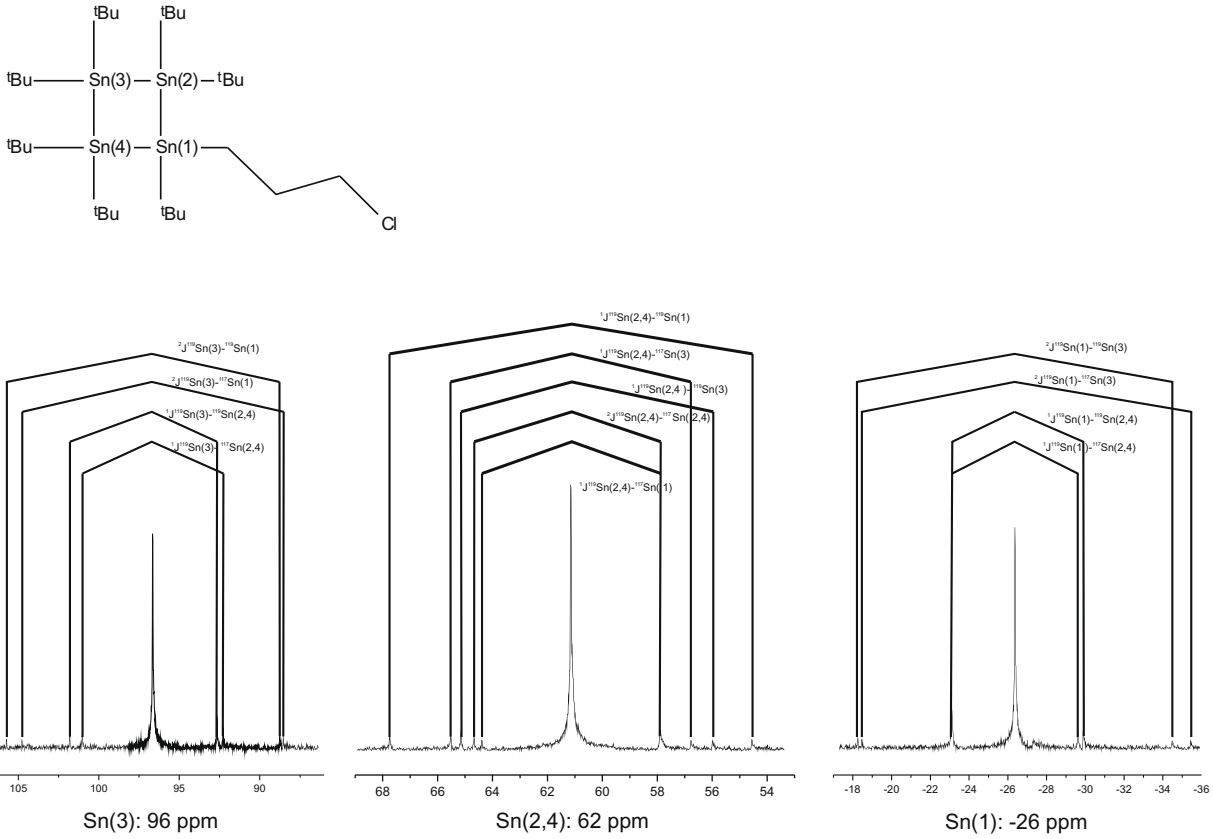


Fig. 5. ^{119}Sn NMR spectra of the chloropropyl-substituted cyclotetrastannnane **5** (δ in ppm, measured in $CDCl_3$).

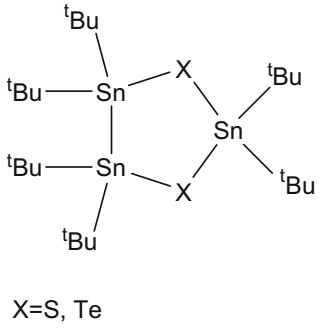


Fig. 6. Tristannadichalcogen cyclopentanes.

dent molecules exhibit almost identical structural features for the four-membered tin-rings. Discrepancies in structural features are arising almost exclusively from packing modes of the ^{t}butyl groups where different rotation angles result in crystallographically independent molecules. Tin–tin bond lengths in **2** range from 2.8107(3) to 2.8834(3) Å and therefore fall within the range of typical Sn–Sn bond distances. The shorter distances of about 2.820 Å are observed for bonds connecting the sterically less crowded methyl-substituted tin centers with their neighboring atoms. Slightly longer distances of about 2.883 Å are found for the remaining two bonds completing the tin based tetragon. Tin–carbon distances connecting the methyl group with the tin center are considerably shorter (2.178(3)–2.180(3) Å) than the remaining Sn–C bond lengths connecting the ^{t}butyl-groups with the tin centers. These distances are found in a range from 2.204(3) to 2.241(4) Å. Again steric interaction between the bulky ^{t}butyl on one hand and the less demanding methyl group on the other hand provides an explanation for this trend.

The endo-cyclic Sn–Sn–Sn angles are all found close to 90° with values between 86.333(9)° and 92.757(10)°. Generally, larger angles are observed for the methyl-substituted tin center leaving the more crowded centers with more acute angles (Fig. 7).

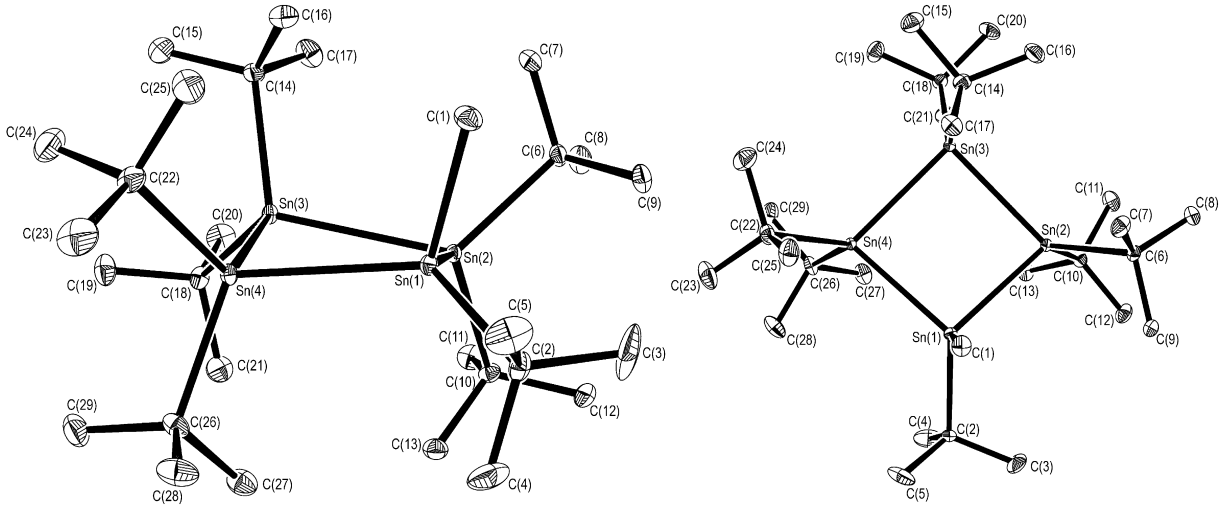


Fig. 7. Crystal structure of **2** at 30% level of propability (hydrogen atoms omitted for clarity) selected bond lengths [Å] and angles [°] for **2**: Sn(1)–C(1) 2.178(3), Sn(1)–C(2) 2.206(3), Sn(1)–Sn(4) 2.8127(3), Sn(1)–Sn(2) 2.8194(3), Sn(2)–Sn(3) 2.8788(3), Sn(3)–Sn(4) 2.8838(3), Sn(4)–Sn(1)–Sn(2) 92.369(10), Sn(1)–Sn(2)–Sn(3) 87.033(9), Sn(2)–Sn(3)–Sn(4) 89.694(9), Sn(1)–Sn(4)–Sn(3) 87.063(9), C(1)–Sn(1)–C(2) 101.61(14).

1,1,2,2,3,3,4-hepta-^{t}butyl-4-chloropropyltetrastannacyclobutane **5** crystallizes in the monoclinic space group $P2(1)/n$ with four symmetry related molecules in the unit cell. The structural features of **5** are similar to those of **2**. Tin–tin bonding distances range between 2.8321(4) Å to 2.8923(4) Å with Sn(1)–Sn(2) and Sn(1)–Sn(4) distances being shorter at about 2.83 Å and the remaining Sn(3)–Sn(2) and Sn(3)–Sn(4) distances longer with values around 2.89 Å. For the distance between Sn(1) and C(1) 2.199(4) Å and between Sn(1) and C(4) 2.209(4) Å were observed. The somewhat longer Sn–C bonding in **5** between Sn(1) to Sn(2) and Sn(4) as well as between Sn(1) to C(1) in comparison to **2** is attributed to the incomparison to the methyl-group sterically more demanding chloropropyl-group. Similar to **2**, endocyclic angles close to 90° are observed, again with somewhat larger angles around the chloropropyl bearing tin atom (91.962(11)°) and smaller angles for the sterically more hindered tin centers (min. 86.656(19)°) (Fig. 8).

However the most striking structural difference between **2** and **5** and octa-^{t}butyltetrastannacyclobutane [2] are folding angles of 157.09°–158.71 (**2**) and 156.64° (**5**) for the four-membered tin-rings in sharp contrast to the planar four-membered ring for octa-^{t}butyltetrastannacyclobutane. A similar planar arrangement was found earlier in $[(Me_3Si)CH_2]_8Sn_4$, whereas puckered rings were found in a variety of four-membered tin-rings. An overview over structural data for **2**, **5** and similar structures is given in Table 3.

The distance between Sn(1) and Cl(1) is 5.970 Å and the average distance between Sn(1) and the H atom on the ^{t}butyl-group is 3.97 Å. This clearly displays that the chlorine on the alkyl-chain is not shielded by the ^{t}butyl-groups. However 1,3-dichlorpropane does not bridge two four-membered tin-rings while reacting with a surplus of 1,1,2,2,3,3,4-hepta-^{t}butyl-4-(chloromagnesio)-tetrastannacyclobutane **1**. Simulation of the sterical demand of the substituents of 1,1,2,2,3,3,4-hepta-^{t}butyl-4-chloroalkyl-tetrastannacyclobutane displayed clearly, that the carbon chain must consist of at least 5 CH_2-groups to avoid the interference of ^{t}butyl-groups of the two four-membered tin-rings. For the same reasons the dimeric structure of **1,** consisting of two four-membered rings on the Magnesium, appears very unlikely (Fig. 9).

Single crystals of the ethyl (**3**) and propyl (**4**) substituted molecules could be isolated from THF (**3**,**4**) and toluene(**3**) solution. However due to high disorder of the ^{t}butyl groups none of these crystals gave reliable structures. So far one can suspect the disorder

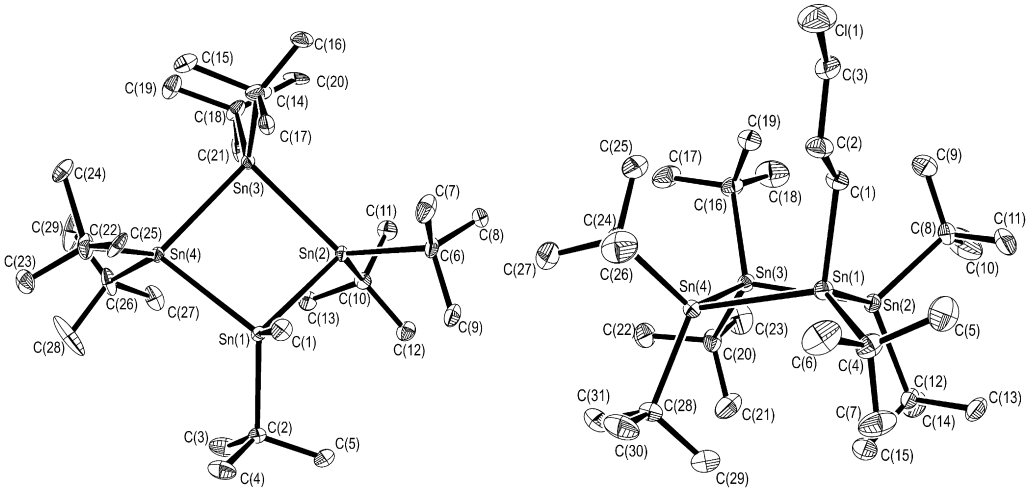


Fig. 8. Crystal structure of **5** at 50% level of propability (hydrogen atoms omitted for clarity) selected bond lengths [Å] and angles [°] for **5**: Sn(1)–Sn(2) 2.8424(4), Sn(1)–Sn(4) 2.8321(4), Sn(2)–Sn(3) 2.8923(4), Sn(3)–Sn(4) 2.8877(4), Sn(1)–C(1) 2.199(4), Sn(4)–Sn(1)–Sn(2) 91.962(11), Sn(1)–Sn(2)–Sn(3) 86.656(10), Sn(4)–Sn(3)–Sn(2) 89.818(10), Sn(1)–Sn(4)–Sn(3) 86.938(10), C(1)–Sn(1)–C(4) 105.36(15).

Table 3
Structural data of different substituted tetrastannacyclobutanes with respect to Fig. 8.

Compound			Sn–Sn distances [Å]	Sn–Sn–Sn angles [°]	Folding angle ω [°]	References
R	R′	R″				
^{t}Bu$_7$MeSn$_4$ **2**			2.811	86.33	157.09–158.71	This work
^{t}Bu	^{t}Bu	Me	2.884	92.76		
^{t}Bu$_7$(ClCH$_2$CH$_2$CH$_2$)Sn$_4$ **5**			2.832	91.96–86.66	156.64	This work
^{t}Bu	^{t}Bu	3-Cl-Propyl	2.892			
^{t}Bu$_8$Sn$_4$			2.887	89.87–90.13	180	[2]
^{t}Bu	^{t}Bu	^{t}Bu				
(1,1-Me$_2$Prop)$_8$Sn$_4$			2.814 – 2.924	88.85 – 89.34	160.07	[2]
1,1-Me$_2$Prop	1,1-Me$_2$Prop	1,1-Me$_2$Prop				
[(Me$_3$Si)$_3$Si]$_4$Cl$_4$Sn$_4$			2.803–2.915	88.14–90.37	161.45	[6]
(Me$_3$Si)$_3$Si	Cl	Cl				
[(Me$_3$Si)CH$_2$]$_8$Sn$_4$			2.829–2.834	89.96–90.04	180	[5]
(Me$_3$Si)CH$_2$	(Me$_3$Si)CH$_2$	(Me$_3$Si)CH$_2$				
[2,6-Et$_2$-C$_6$H$_3$]$_7$BrSn$_4$			2.818–2.931	87.54–92.91	155.40	[8]
2,6-Et$_2$-C$_6$H$_3$	2,6-Et$_2$-C$_6$H$_3$	Br				
[H$_3$C$_6$-2,6-(CH^{t}Bu)$_2$]$_4$Sn$_4$			2.583	88.22	151.55	
[2,6-Et$_2$-C$_6$H$_3$]$_9$Bu bicyclo[2.2.0]Sn$_8$			2.831 – 2.909	84.67 – 93.44	171.79/175.56	[23]

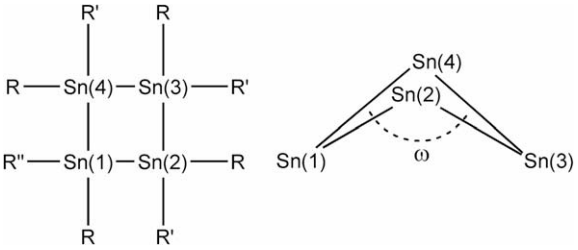


Fig. 9. Definition of the folding angle ω.

might be due to the high crystallization velocity of these compounds. In these cases the molecular packing doesn't really matter in which direction the ethyl and propyl group assembly as they can interact in all directions in the same way by weak van-der-Waals-interactions.

3. Experimental details

All reactions were carried out under an inert nitrogen atmosphere. Solvents were dried using an INNOVATIVE TECHNOLOGIES column solvent purification system [16]. All chemicals were used as received from several different chemical suppliers.

NMR spectra were measured on a Varian Mercury 300 spectrometer (operating at 300.2 MHz for ^{1}H, 111.96 MHz for ^{119}Sn and 75.5 for ^{13}C NMR measurements) using standard 5 mm broad band probe. 2D experiments like the gHSQC pulse sequence [17] were adapted to ^{119}Sn nucleus. The polarization transfer experiments were optimized by using the INEPT pulse sequence [18]. The ^{119}Sn chemical shifts are given relative to ^{t}Bu$_2$SnCl$_2$ (53 ppm). Samples for ^{119}Sn spectra were either dissolved in deuterated solvents or in cases of reaction samples and THF solutions measured with a D_2O capillary in order to provide an external standard. NMR shifts were referenced to solvent residual peaks. In order to eliminate the temperature dependence of chemical shifts, spectra were recorded at 25 °C and samples were allowed to equilibrate thermally for 10 min.

The completeness of reactions was usually controlled by NMR spectroscopy.

XRD data collection was performed with a BRUKER-AXS KAPPA8 APEX II CCD diffractometer using graphite monochromated Mo Kα radiation (0.71073 Å). Absorption corrections were performed using SADABS [19,20]. The structures were solved with direct methods and the non-hydrogen atoms were refined anisotropically (full-matrix least squares on F^2) [21,22]. All non-hydrogen atoms were refined employing anisotropic displacement parameters. Hydrogen atoms were located in calculated positions to correspond to standard bond lengths and angles. Crystallographic data for **2** and **5** are given in Table 4. More detailed information on all structures is supplied in the Supporting Information.

Table 4
Selected X-ray Crystallographic Data for Compounds **2** and **5.**

Identification code	Methyl (**2**)	Chlorpropyl (**5**)
Empirical formula	C29 H66 Sn4	C31 H69 Cl Sn4
Formula weight	889.58	952.18
Temperature (K)	100(2)	193(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2(1)/n$
Unit cell dimensions	a = 17.1953(7) Å b = 17.4677(15) Å c = 21.5922(9) Å α = 105.242(2) β = 111.8510(10)° γ = 99.053(2)°.	a = 11.2394(4) Å b = 16.9307(7) Å c = 21.6409(9) Å α = 90° β = 100.670(2)° γ = 90°
Volume (Å^3)	5567.0(6)	4046.9(3)
Z	6	4
Density (calculated) (Mg/m^3)	1.592	1.564
Absorption coefficient (mm^{-1})	2.674	2.522
F(0 0 0)	2640	1892
Crystal size (mm^3)	0.60 × 0.43 × 0.28	0.25 × 0.20 × 0.10
θ range for data collection (°)	1.26–30.00	1.54–23.57
Index ranges	$-24 \leqslant h \leqslant 24$, $-23 \leqslant k \leqslant 24$, $-30 \leqslant l \leqslant 30$	$-12 \leqslant h \leqslant 12$, $-18 \leqslant k \leqslant 18$, $-24 \leqslant l \leqslant 24$
Reflections collected	128359	121428
Independent reflections (R_{int})	32387 (0.0340)	5953 (0.0864)
Completeness to theta = 28.26° (%)	99.7	98.7
Absorption correction	SADABS multi-scan	SADABS multi-scan
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	32387/0/958	5953/0/346
Goodness-of-fit (GOF) on F_2	1.087	1.059
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0363, wR_2 = 0.0848	R_1 = 0.0227, wR_2 = 0.0402
R indices (all data)	R_1 = 0.0482, wR_2 = 0.0958	R_1 = 0.0364, wR_2 = 0.0457
Largest diff. peak and hole (e Å^{-3})	3.119 and −1.607	0.401 and −0.433

Table 5
Headspace analyses Parameters.

Level	Rate (C/min)	final Temp. (°C)	final time (min)
1	70.00	100	3.00
2	10.00	200	20.00
3	0.00	200	

Elemental analyses were performed with a Heraeus VARIO ELEMENTAR EL analyzer.

Head space analysis: GC: HP 5890 SERIES II; first column: length: 30 m, inner diameter: 0.53, film thickness: 1.8 μm, GS-Q, J8 W scientific; second column: length: 30 m, inner diameter: 0.25, film thickness: 0.25 μm, ZB-FFAP, Zebron;

Column preassure: 50 hPa

Oven program: Initial Temperature: 40 °C; initial time: 10.00 min; run time: 43.86 min (Table 5).

MS: HP 5951A; mode: TIC (total ion chrom.); *m/z* = 10–100;

3.1. Preparation of 1,1,2,2,3,3,4-hepta-^{t}butyl-4-(chloromagnesio) tetrastannacyclobutane **1**

1,4-di-chloro-1,1,2,2,3,3,4,4-octa-^{t}butyltetrastannane (2 g, 2 mmol) were dissolved in 100 mL THF in a 250 ml flask. 1 g (41 mmol) magnesium was added. The reaction was stirred 24 h at 30 °C. It was separated from the magnesium with a cannula.

3.2. First alternative synthesis of **1**

Dichlorodi^{t}butylstannane (5 g, 16 mmol) was dissolved in 100 mL THF in a 250 mL flask. 3.8 g (160 mmol) Magnesium was added. The solution was stirred for 20 hours at 30 °C. Subsequently the solution was separated from magnesium with a cannula.

3.3. Second alternative synthesis of **1**

Octa-^{t}butyltetrastannacyclobutane (0.5 g, mmol) and Magnesium was placed in a flask. 5 mL of dry THF and 0.1 mL of ^{t}butylchloride were added with a syringe. In order to start the reaction 0.1 mL of $Br_2C_2H_4$ were added. The reaction was stirred over night. A dark read solution was obtained containing the product **1**.

^{1}H NMR (299.948 MHz, D_2O): δ = 1.39–1.54 ppm [m, 63 H]

^{13}C {^{1}H} NMR (75.50 MHz, D_2O): δ = 28.23 ppm [s, 1 Cq], 32.72 ppm [s, 1 Cq], 30.84 ppm [s, 1 Cq], 29.49 ppm [s, 1 Cq], 29.85 ppm [s, 1 Cq], 35.21 ppm [s, 3 C], 34.97 ppm [s, 3 C], 36.03 ppm [s, 3 C], 35.70 ppm [s, 3 C], 29.85 ppm [s, 3 C].

^{119}SN {^{1}H} NMR (111.96 MHz, D_2O): δ = +180 ppm [s, 1 Sn(3), $^1J(^{119}Sn(3)–^{119}/^{117}Sn(2,4))$ = 4150/3966 Hz, $^2J(^{119}Sn(3)–^{119}/^{117}Sn(1))$ = 1640/1564 Hz], 75 ppm [s, 2 Sn(2,4), $^1J(^{119}Sn(2,4)–^{119/117}Sn(3))$ = 4155/3966 Hz, $^1J(^{119}Sn(2,4)–^{119/117}Sn(1))$ = 6810/6500 Hz], −6 ppm [s, 1 Sn(1), $^1J(^{119}Sn(1)–^{119/117}Sn(2,4))$ = 6810/6500 Hz, $^2J(^{119}Sn(1)–^{119/117}Sn(3))$ = 1640/1564 Hz].

3.4. Syntheses of 2, 3, 4, 5 and 6

To a solution of **1** the reagent (**2**: Me_2SO_4; **3**: bromoethane; **4**: 1-chloropropane; **5**: 1,3-dichloropropane; **6**: $CHCl_3$) was added in surplus. THF was removed and to the remaining solid pentane was added. The solution was filtered and pentane was removed.

The yield determined by 119Sn NMR spectroscopy was >70% for each product, after unoptimised recrystallisation yields between 10 and 20% were observed.

3.4.1. Compound **2**

1,1,2,2,3,3,4-hepta-^{t}butyl-4-methyltetrastannacyclobutane

Mp: 194 °C

^{1}H NMR (299.948 MHz, $CDCl_3$): δ = 0.59 ppm [s, 3 H, $^2J(^1H–^{119/117}Sn(1))$ = 15.0 Hz, $^3J(^1H–^{119/117}Sn(2,4))$ = 30.9 Hz], 1.42–1.55 ppm [m, 63 H]

^{13}C {^{1}H} NMR (75.50 MHz, $CDCl_3$): δ = −10.83 ppm [s, 1 C_4, $^1J(^{13}C–^{119/117}Sn(1))$ = 66.8 Hz, $^2J(^{13}C–^{119/117}Sn(2,4))$ = 22.4 Hz], 37.18 ppm [s, 1 C_q, $^1J(^{13}C–^{119/117}Sn)$ = n.obs.], 37.56 ppm [s, 2 C_q], 39.55 ppm [s, 1 C_q], 34.66–35.09 ppm [m, 21 C].

^{119}Sn {^{1}H} NMR (111.96 MHz, $CDCl_3$): δ = 93 ppm [s, 1 Sn(3), $^1J(^{119}Sn(3)–^{119/117}Sn(2,4))$ = 995/950 Hz, $^2J(^{119}Sn(3)–^{119/117}Sn(1))$ = 1940/1850 Hz], 63 ppm [s, 2 Sn(2,4), $^1J(^{119}Sn(2,4)–^{119/117}Sn(3))$ = 995/950 Hz, $^1J(^{119}Sn(2,4)–^{119/117}Sn(1))$ = 645/615 Hz, $^2J(^{119}Sn(2,4)–^{117}Sn(2,4))$ = 1430 Hz], −49 ppm [s, 1 Sn(1), $^1J(^{119}Sn(1)–^{119/117}Sn(2,4))$ = 645/615 Hz, $^2J(^{119}Sn(1)–^{119/117}Sn(3))$ = 1940/1850 Hz].

CHN analysis: Found: C, 40.06; H, 7.52%; $C_{29}H_{66}Sn_4$ (MM: 889.53 g mol^{-1}) requires: C, 39.16%; H, 8.01%;

Yield: according to NMR: 72%after recrystalisation: 0.55 g; 15%

3.4.2. Compound 3

1,1,2,2,3,3,4-hepta-^{t}butyl-4-ethyltetrastannacyclobutane

Decomp.:190 °C

^{1}H NMR (299.948 MHz, CDCl3): δ = 1.20–1.53 ppm [m, 68 H]

^{13}C {^{1}H} NMR (75.50 MHz, $CDCl_3$): δ = 4.59 ppm [s, 1 C, $^1J(^{13}C–^{119/117}Sn(1))$ = 29.5/28.3 Hz, $^2J(^{13}C–^{119/117}Sn(2,4))$ = 2.8 Hz], 14.75 ppm [s, 1 C, $^2J(^{13}C–^{119/117}Sn(1))$ = 12.0 Hz], 36.64 ppm [s, 2 C_q, $^1J(^{13}C–^{119/117}Sn(2,4))$ = 3.9 Hz], 36.74 ppm [s, C_q], 34.2–35.2 ppm [m, 21 C].

^{119}SN {^{1}H} NMR (111.96 MHz, $CDCl_3$): δ = 96 ppm [s, 1 Sn(3), $^1J(^{119}Sn(3)–^{119/117}Sn(2,4))$ = 1040/990 Hz, $^2J(^{119}Sn(3)–^{119/117}Sn(1))$ = 1530/1460 Hz], 63 ppm [s, 2 Sn(2,4), $^1J(^{119}Sn(2,4)–^{119/117}Sn(3))$ = 1040/990 Hz, $^1J(^{119}Sn(2,4)–^{119/117}Sn(1))$ = 775/740 Hz, $^2J(^{119}Sn(2,4)–^{117}Sn(2,4))$ = 1790 Hz], −19 ppm [s, 1 Sn(1), $^1J(^{119}Sn$ $(1)–^{119/117}Sn(2,4))$ = 775/740 Hz, $^2J(^{119}Sn(1)–^{119/117}Sn(3))$ = 1530/1460 Hz].

CHN analysis: Found: C, 39.76; H, 7.53%; $C_{30}H_{68}Sn_4$ (MM: 903.71 g mol^{-1}) requires: C, 39.87%; H, 7,36%;

Yield: according to NMR: 74%after recrystalisation: 0.45 g; 12%

3.4.3. Compound 4

1,1,2,2,3,3,4-hepta-^{t}butyl-4-propyltetrastannacyclobutane

Decomp.: 198 °C

^{1}H NMR (299.948 MHz, $CDCl_3$): δ = 1.39–1.54 ppm [m, 63 H]

^{13}C {^{1}H} NMR (75.50 MHz, $CDCl_3$): δ = 48.6 ppm [s, 1 C], 37.1 ppm [s, 1 C], 31.9 ppm [s, 1 C], 33.6–35.2 ppm [m, 28 C].

^{119}SN {^{1}H} NMR (111.96 MHz, $CDCl_3$): δ = +94 ppm [s, 1 Sn(3), $^1J(^{119}Sn(3)–^{119/117}Sn(2,4))$ = 1021/1009 Hz, $^2J(^{119}Sn(3)–^{117}Sn(1))$ = 1831 Hz], 58 ppm [s, 2 Sn(2,4), $^1J(^{119}Sn(2,4)–^{119/117}Sn(3))$ = 1024/979 Hz, $^1J(^{119}Sn(2,4)–^{119/117}Sn(1))$ = 759/727 Hz, $^2J(^{119}Sn$ $(2,4)–^{117}Sn(2,4))$ = 1476], −29 ppm [s, 1 Sn(1), $^1J(^{119}Sn(1)–^{119/117}Sn(2,4))$ = 759/727 Hz, $^2J(^{119}Sn(1)–^{117}Sn(3))$ = 1773 Hz].

CHN analysis: Found: C, 39.81; H, 7.50%; $C_{31}H_{70}Sn_4$ (MM: 917.738 g mol^{-1}) requires: C, 40.57%; H, 7.69%;

Yield: according to NMR: 78%after recrystalisation: 0.38 g; 10%

3.4.4. Compound 5

1,1,2,2,3,3,4-hepta-^{t}butyl-4-chloropropyltetrastannacyclobutane

Mp: 92 °C

^{1}H NMR (299.948 MHz, $CDCl_3$): δ = 1.23–1.56 ppm [m, 63 H]

^{13}C {1H} NMR (75.50 MHz, $CDCl_3$): δ = ppm [s, 1 C], ppm [s, 1 C], ppm [s, 2 C], 29.9–35.2 ppm [m, 28 C].

^{119}Sn {^{1}H} NMR (111.96 MHz, $CDCl_3$): δ = +96 ppm [s, 1 Sn(3), $^1J(^{119}Sn(3)–^{119/117}Sn(2,4))$ = 982/938 Hz, $^2J(^{119}Sn(3)–^{117}Sn(1))$ = 1906 Hz], 62 ppm [s, 2 Sn(2,4), $^1J(^{119}Sn(2,4)–^{117}Sn(3))$ = 939 Hz, $^1J(^{119}Sn(2,4)–^{119/117}Sn(1))$ = 809/763 Hz, $^2J(^{119}Sn(2,4)–^{117}Sn(2,4))$ = 1417], −26 ppm [s, 1 Sn(1), $^1J(^{119}Sn(1)–^{119/117}Sn(2,4))$ = 795/762 Hz, $^2J(^{119}Sn(1)–^{117}Sn(3))$ = 1869 Hz].

CHN analysis: Found: C, 39.80; H, 7.30%; $C_{31}H_{69}ClSn_4$ (MM: 952.18 g mol^{-1}) requires: C, 39.10%; H, 7.30%;

Yield: according to NMR: 74%after recrystalisation: 0.63 g; 16%

3.4.5. Compound 6

1-Chloro-1,2,2,3,3,4,4-hepta-^{t}butyltetrastannacyclobutane

^{1}H NMR (299.948 MHz, $CDCl_3$): δ = 1.46–1.51 ppm [m, 63 H]

^{13}C {^{1}H} NMR (75.50 MHz, $CDCl_3$): δ = 42. 08 ppm [s, 1 C_q], 37.30 ppm [s, 1 C_q], 41.07 ppm [s, 1 C_q], 34.71 ppm [s, 3 C], 35.17 ppm [s, 3 C], 31.33 ppm [s, 3 C].

^{119}Sn {^{1}H} NMR (111.96 MHz, $CDCl_3$): δ = 82 ppm [s, 1 Sn(3), $^{1}J(^{119}Sn(3)–^{119/117}Sn(2,4))$ = 1920/ 1835 Hz, $^{2}J(^{119}Sn(3)–^{119/117}Sn(1))$ = 2045/1952 Hz], 102 ppm [s, 2 Sn(2,4), $^{1}J(^{119}Sn$ (2,4)–$^{119/117}Sn(3))$ = 1920/1835 Hz, $^{1}J(^{119}Sn(2,4)–^{119/117}Sn(1))$ = 1110/1057 Hz, $^{2}J(^{119}Sn(2,4)–^{117}Sn(2,4))$ = 857 Hz], +236 ppm [s, 1 Sn(1), $^{1}J(^{119}Sn(1)–^{119/117}Sn(2,4))$ = 1110/1057 Hz, $^{2}J(^{119}Sn(1)–^{119/117}Sn(3))$ = 2045/1952 Hz].

Yield: according to NMR: 71%

Acknowledgments

The financial support of this work by fForte-Wissenschaftlerinnenkolleg FreChe Materie is acknowledged. We are also grateful to Dr. Dipl. Ing. A. Ranz for performing the head-space-analysis.

Appendix A. Supplementary material

CCDC 723247 and 723248 contain the supplementary crystallographic data for **2** and **5**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.09.004.

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