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

Marie-Luise Lechner [a,*], Katharina Fürpaß [a], Jan Sykora [b], Roland C. Fischer [a], Jörg Albering [c], Frank Uhlig [a]

[a] *Institute of Inorganic Chemistry, Graz University of Technology, Stremayrgasse 16/IV, A-8010 Graz, Austria*
[b] *Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic, Rozvojova 2, CZ-165 02 Prague 6, Suchdol, Czech Republic*
[c] *Institute of Chemistry and Technology of Materials, Graz University of Technology, Stremayrgasse 16/IV, A-8010 Graz, Austria*

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

---

[*] Corresponding author.
E-mail address: marie-luise.lechner@tugraz.at (M.-L. Lechner).

0022-328X/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2009.09.004

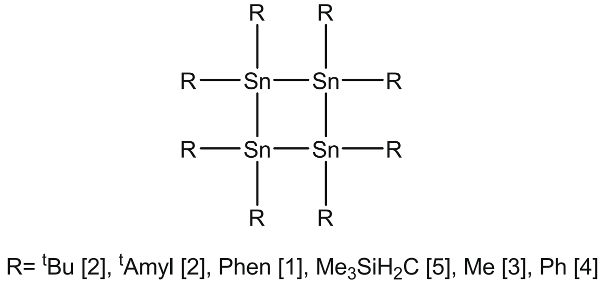

Fig. 1. Various octa-alkyltetrastannacyclobutane reported in literature.

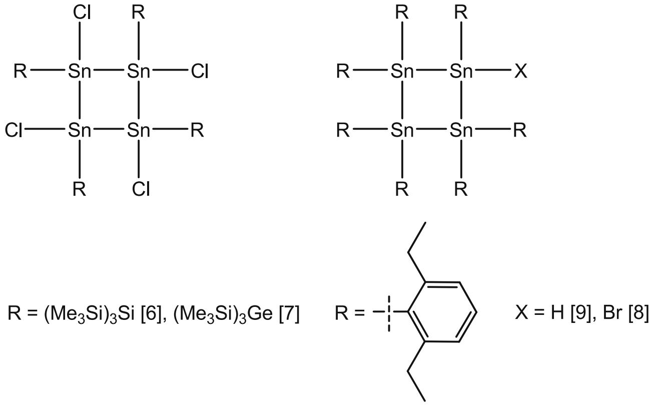

Fig. 2. Different kinds of functionalised tetrastannacyclobutanes.

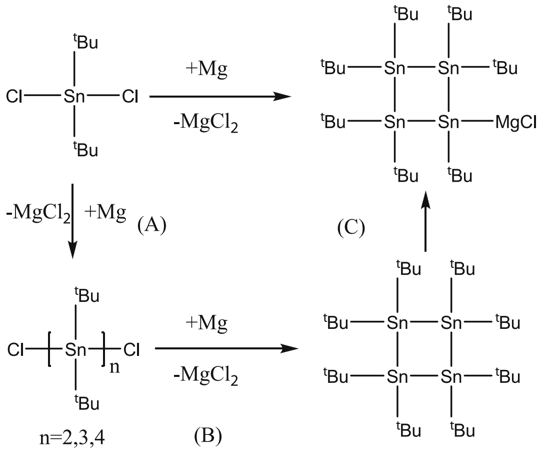

Fig. 3. Reaction path leading to **1**.

Table 1
^{119}Sn NMR signals.

Time (h)	^{t}Bu$_2$SnCl$_2$ (56 ppm) (%)	^{t}Bu$_4$Sn$_2$Cl$_2$ (112 ppm) (%)	^{t}Bu$_8$Sn$_4$ (80 ppm)	^{t}Bu$_7$Sn$_4$MgCl (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.

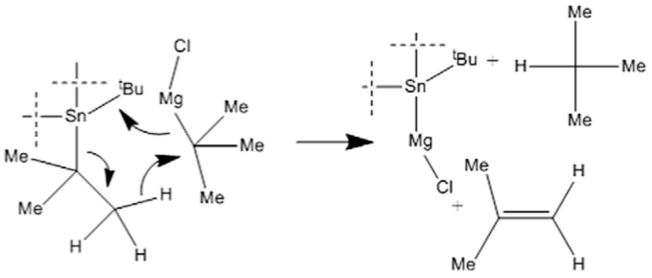

Fig. 4. Mechanism for the formation of **1** with octa-^{t}butyltetrastannacyclobutane as starting material.

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-