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## NEWS ABOUT FOUR-MEMBERED RINGS IN THE CHEMISTRY OF ORGANOSILICON, -GERMANIUM, AND -TIN COMPOUNDS

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# NEWS ABOUT FOUR-MEMBERED RINGS IN THE CHEMISTRY OF ORGANOSILICON, -GERMANIUM, AND -TIN COMPOUNDS

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The synthesis of the cyclic tin-modified silanes **1–6** are described by the reaction of  ${}^tBu_2SnCl_2$  with different dichloromono- and -disilanes in the presence of magnesium. Reacting dimethyldichlorosilane with diphenyldichlorosilane and magnesium yielded the 1,1-dimethylhexaphenylcyclotetrasilane **8** in reasonably good yields.

Keywords: Cyclotetrasilanes; four-membered rings; germanium; silicon; tin

In the last few years we reported on the syntheses of novel open chain, monocyclic and cage-like Si—Sn compounds.<sup>1–4</sup> One of the most successful reaction pathways toward the preparation of such derivatives is the reaction of halosilanes with chlorostannanes in the presence of magnesium. The first step of these reactions should be the formation of a Grignard-type tin compound. We describe here the evidence of the formation of such Grignard-type analogues as well as the synthesis of the resulting four-membered rings (1–4) and the formation of a novel cyclotetrasilane (7).

We thank the Graz University of Technology (Austria), the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie (Germany) for financial support. Also, we are grateful to ASV-innovative Chemie GmbH (Bitterfeld) for placing chemicals at our disposal. We also thank Prof. Dr. K. Jurkschat (Dortmund University) for support.

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### **RESULTS AND DISCUSSION**

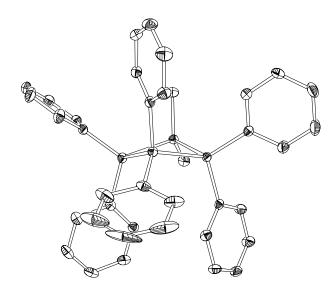
The cyclic tin-modified silanes **1** and **2** are synthesized by the reaction of  ${}^{t}Bu_{2}SnCl_{2}$  with Me<sub>2</sub>SiCl<sub>2</sub> or Cl-SiMe<sub>2</sub>-SiMe<sub>2</sub>-Cl in the presence of magnesium in yields between 80% and 90%.

The use of  $MeSi(H)Cl_2$  instead of the  $Me_2SiCl_2$  resulted a mixture of four- (3) and six-membered (4) rings, meanwhile the reaction of  $H_2SiCl_2$  leads exclusively to the six-membered ring 5.

This result is due to the smaller steric demand of the hydrido substituted dichlorosilanes in comparison to the Me<sub>2</sub>SiCl<sub>2</sub> and is provable by thermodynamic calculations. However, the use of dimethyldichlorogermane (Me<sub>2</sub>GeCl<sub>2</sub>) instead of the dichlorosilanes leads to the fourmembered ring **6** containing germanium instead of the silicon in the ring skeleton. In extension of this work, the reaction of the diorganochlorosilanes Ph<sub>2</sub>SiCl<sub>2</sub> and Me<sub>2</sub>SiCl<sub>2</sub> in the presence of magnesium was investigated, yielding a cyclic silane with a ring size of four (**7**).

By-products are polymeric silanes and the 1,3-dichlorohexaphenyltrisilane 8 besides a number of unidentified chlorosilanes with an overall yield of  $\sim\!20\%$ . In contrast to the four-membered rings 1 and 2 the yield of the 1,1-dimethylhexaphenylcyclotetrasilane 7 is with around 10–20% significant smaller. However, that is what can be expected by a Wurtz-type reaction and should be because the formation of Grignard-type tin compounds is much more favored and much more selective compared with those of silanes.

By-products are polymeric silanes and a large variety of chlorosubstituted oligosilanes. All compounds are characterized by state-ofthe-art analytical methods. As an example the x-ray structure of the cyclotetrasilane **7** is shown in Figure 1.



**FIGURE 1** Molecular structure of the  $Si_4$  ring **7** (selected bond length: Si-Si: 237.2(1)-238.0(1) pm;  $Si-C_{Me}: 188.9(3)-189.6(3)$  pm;  $Si-C_{Ph}: 187.7(3)-188.9(3)$  pm).

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