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## New Silicon and Tin Containing Ring and Cage Compounds - Syntheses and Reactivity

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## NEW SILICON AND TIN CONTAINING RING AND CAGE COMPOUNDS -

### SYNTHESES AND REACTIVITY

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The syntheses of new stannyloligosilanes starting from dichlorodi-organostannanes ( $R_2SnCl_2$ ) and  $\alpha,\omega$ -difluoromethyloligosilanes with magnesium are described. Depending on the molar ratio of reactants and substituents R, cyclic or acyclic compounds are formed.

X-ray structure of **4b** and reactivity of the cyclic stannylsilanes are also reported.

Keywords: stannanes, oligosilanes, tin-silicon derivatives

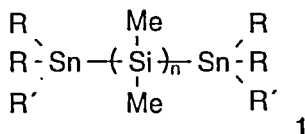
### INTRODUCTION

Only little is known about compounds with more than one silicon-tin-bond, especially for cyclic stannyloligosilanes<sup>[1]</sup>, which is in contrast to their importance as potential starting materials for ring opening polymerisations or production of defined surfaces.

## Results and Discussion

The target molecules were not uniformly accessible by conventional metathesis reactions between chlorosilanes and alkali stannides; often distannanes and polysilanes were isolated as byproducts. A new access route to compounds containing a Si-Sn moiety, developed in our laboratory<sup>[2]</sup>, involving the reaction between magnesium, organo-tin chlorides and fluorosilanes allows the isolation of the target molecules in good yields and purity.

Application of these synthetic routes allowed the isolation of the chain (1), ring (2-4) and cage (5) compounds shown below (fig. 1-3). The reactions critically depend on the stoichiometry of the starting materials, the concentration of the reactands and the nature of the organic substituents at tin.



<i>R</i>	<i>R'</i>	<i>n</i>	yields(%)
Me	Me	1, 3, 4, 6	40 - 75
Ph	Ph	1, 2, 3, 4, 6	50 - 70
Ph	H	1, 2, 5, 6	40 - 80
Bu	H	2, 3	20 - 40

FIGURE 1 oligosilane chains with 2 terminal triorganotin groups (1)

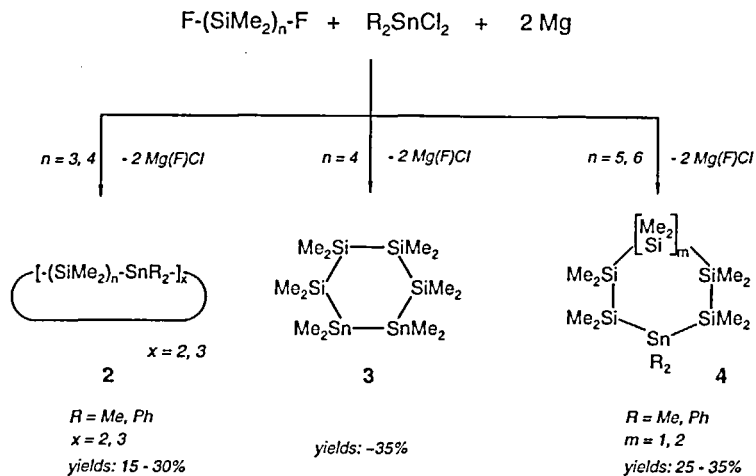


FIGURE 2 Cyclic stannyloligosilanes 2 - 4

The reaction of the 1,4 difluorocyclohexasilane with dimethyldichlorosilane and magnesium results in formation of the expected product 5, the bicycloheptane 6 is not observed.

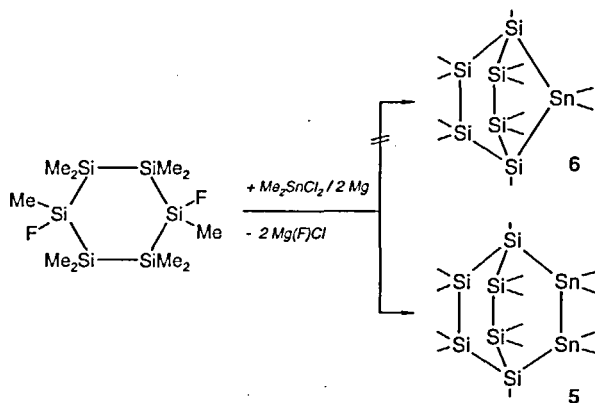
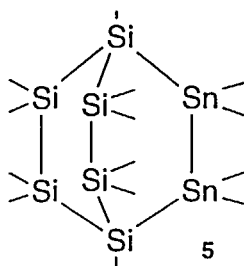


FIGURE 3 Reaction to the bicyclooctane 5

**5** is the first example of a compound exclusively containing silicon and tin in the bicyclic skeleton. Figure 4 displays selected  $^{29}\text{Si}$  and  $^{119}\text{Sn}$  NMR data for this species.



1, 2, 2, 3, 3, 3, 4, 5, 5, 6, 6, 7, 7, 8, 8 - tetradecamethyl -

1, 2, 3, 4, 5, 6 - hexasila- 7, 8 - distanna-bicyclo[2.2.2]octane

· colourless, crystalline solid

· yield: 40 - 45 %

· NMR:  $^{119}\text{Sn}$ : -227,5 ppm ( $^1J_{\text{Sn-Sn}} = 1501 \text{ Hz}$ ),

$^{29}\text{Si}$ : -80,9 ppm ( $^1J_{\text{Si-Sn}} = 243/232 \text{ Hz}$ ;  $^2J_{\text{Si-Sn}} = 93,5/89,5 \text{ Hz}$ ); -37,6 ppm

FIGURE 4 NMR data of compound **5**

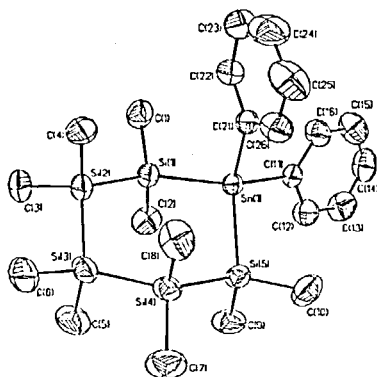


FIGURE 5 Molecular structure of **4b**

The cyclic stannyloligosilanes reacts with oxygen to polymeric stannanes and siloxane compounds.

With various synthetic strategies in hand we are now able to synthesize a wide variety of Si-Sn-containing compounds.

### Acknowledgments

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