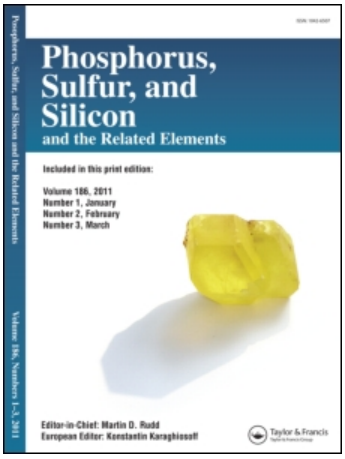

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NEW SILICON AND TIN CONTAINING RING AND CAGE COMPOUNDS -

SYNTHESES AND REACTIVITY

U. HERMANN, I. PRASS, F. UHLIG*
Department of Inorganic Chemistry II, Dortmund University,
Otto-Hahn-Str. 6, D-44221 Dortmund, Germany

The syntheses of new stannyloligosilanes starting from dichlorodiorganostannanes (R_2SnCl_2) and α,ω-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 dervatives

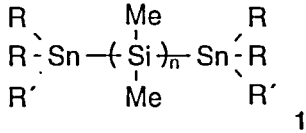
INTRODUCTION

Only little is known about compounds with more than one silicon-tin-bond, especially for cyclic stannyloligosilanes[1], 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 rections 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[2], 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.



1

R	*R'*	*n*	*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 triorganotingroups (1)

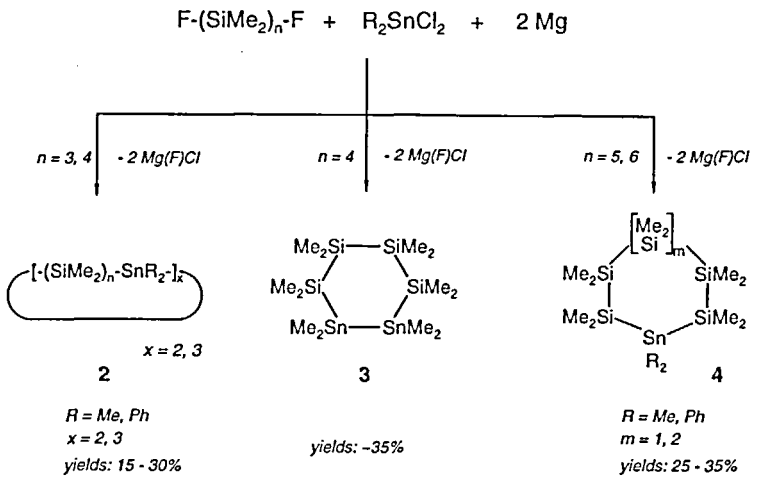


FIGURE 2 Cyclic stannyloligosilanes **2 - 4**

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.

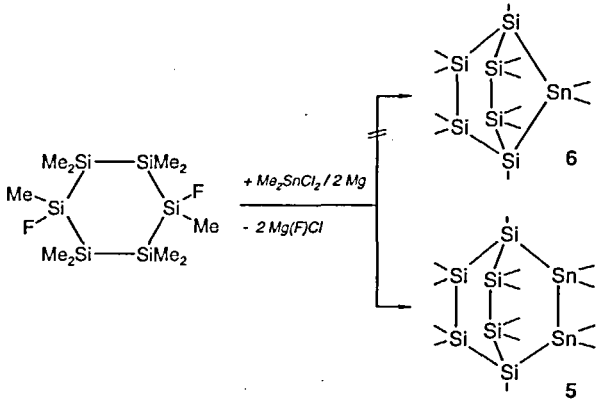
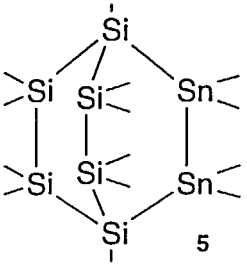


FIGURE 3 Reaction to the bicyclooctane **5**

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



5

1, 2, 2, 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}Sn: -227,5 ppm ($^{1}J_{Sn\text{-}Sn}$ = 1501 Hz),*

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

FIGURE 4 NMR data of compound **5**

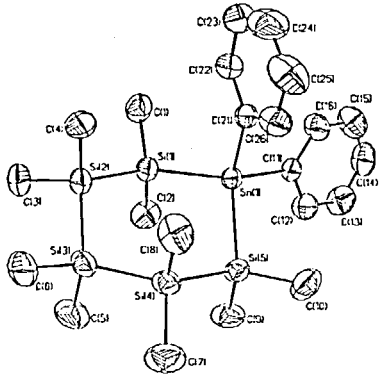


FIGURE 5 Molecular structure of **4b**

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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