Synthesis of Methoxy Substituted Polysilanes

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Recently our group introduced a convenient synthetic method to obtain tris(trimethoxysilyl)silanides (**1**) deriving from dodecamethoxyneopentasilane. This anion represents a new interesting building block for defined silicon-frameworks, as it undergoes a straightforward reaction with dichlorosilanes and dichlorodisilanes (**Scheme 1**).



**Scheme 1.** Reaction of dodecamethoxyneopentasilane with KO*t*Bu and Si2Cl2(CH3)41 or SiCl2H2 to the respective polysilane chains.

Furthermore, the synthesis of polysilane ring molecules was investigated. As seen in **Scheme 2** compound **2** can undergo a reaction with a suitable electrophile to achieve the cyclohexasilane **5**.



**Scheme 2.** Reaction of **2** with KO*t*Bu and [Si2Cl2(CH3)4] to form the cyclohexasilane **5**.

Additionally, transition metals as electrophiles were investigated to form heterocyclic molecules, which can be utilized for dehydrogenative coupling of hydrosilanes. Therefore, **2** reacts straightforward with two equivalents of KO*t*Bu to form the respective dianion which reacts to the compounds **6** - **8** as shown in **Scheme 3**.



**Scheme 3.** Reaction of **2** with KO*t*Bu and [MCl2Cp2] (M = Ti, Zr, Hf) to form the respective heterocyclic polysilane.

The dehydrogenative coupling of hydrosilanes is an important research task. Moreover, up to now no efficient catalytic system was developed, which has a high activity, as well as a high group tolerance. Therefore, compounds **6** - **8** were investigated. The formation of different oligomers/polymers was successfully achieved for SiPhH3, SiPh2H2, as well as for SiEt2H2. The obtained oligomeric/polymeric compounds were detected by NMR spectroscopy, GC-MS and GPC analysis and offer high molecular masses for SiPhH3 and SiEt2H2. Small oligomers were obtained with SiPh2H2.

(1) T. Lainer, M. Leypold, C. Kugler, R. C. Fischer, M. Haas. Front Cover: Dodecamethoxyneopentasilane as a New Building Block for Defined Silicon Frameworks. *EurJIC.* **2021**, *6*, 526−533. DOI: 10.1002/ejic.202100020