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# Polysilyldianions - Synthesis and Reactivity

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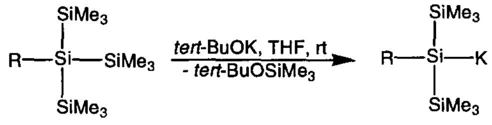
**Abstract:** Reaction of α,ω-bis[tris(trimethylsilyl)silyl]alkanes with one equivalent of potassium *tert*-butoxide resulted in clean formation of mono-potassium silyl anions. Addition of another equivalent of the transmetallating agent led to the formation of the di-potassium compounds. Partial hydrolysis of the di-potassium compounds induced an intramolecular reaction yielding a cyclic silyl potassium compound.

## Introduction

Recently, we have reported the facile conversion of tetrakis(trimethylsilyl)silane to tris(trimethylsilyl)silyl potassium upon treatment with potassium *tert*-butoxide (Scheme 1) [1]. This constitutes an interesting alternative to the well known tris(trimethylsilyl)silyl lithium reagent introduced by *Gilman* some 35 years ago [2]. In the meantime we were able to show that this approach represents a general synthetic method to a wide array of polysilyl potassium compounds [1, 3].



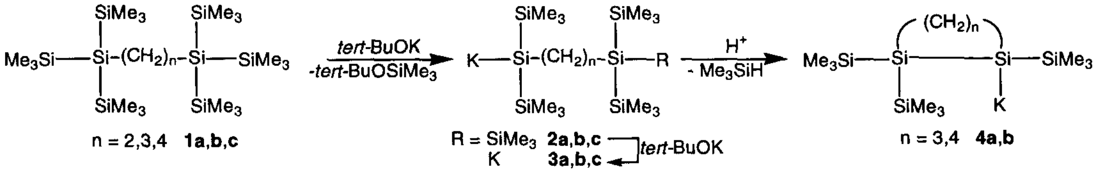
R = $SiMe_3$, $Si(SiMe_3)_3$, $Si(i\text{-}Pr)_3$, Me, Et, Ph

**Scheme 1:** General approach to polysilyl potassium compounds

First attempts towards the synthesis of bis(silylpotassium) compounds proved to be difficult [4] due to the high reactivity of the obtained compounds. In order to separate the two charged silicon atoms we set out to study the use of α,ω-bis[tris(trimethylsilyl)silyl]alkanes [5] as precursors for bis(silylpotassium) compounds.

## Results and discussion

The synthesis of the starting materials could be achieved by reaction of two equivalents of tris(trimethylsilyl)silyl potassium with the respective α,ω-ditosylalkanes (**1a,b,c**). Treatment with potassium *tert*-butoxide in THF in all cases led to clean replacement of one trimethylsilyl group by potassium (**2a,b,c**). Compounds with more than two methylene groups (**1b,c**) reacted with a second equivalent of the transmetalating reagent, though slowly, even at room temperature forming the dipotassium compounds (**3b,c**). Reaction of **1a**, however, required heating in a sealed glass tube to 60°C for several days to eventually form the dianionic species (**3a**) [6].



**Scheme 2:** Formation of mono and di-potassium compounds

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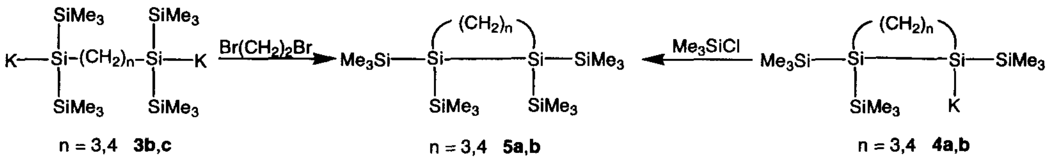
After prolonged reaction, sometimes, a new product was formed as indicated by $^{29}$Si-NMR and GC-MS. This product, which is also a silyl potassium species, contains a newly formed Si-Si bond and has a cyclic structure (**4a,b**). We found that the formation of the latter was caused by partial hydrolysis of the strongly basic di-potassium compound. We assume that once the Si-H bond is formed, the now more electrophilic silicon is attacked by the remaining silylanion and formation of the cyclic product along with trimethylsilane is accomplished. Careful addition of one equivalent of water to a solution of the di-potassium product led to the quantitative formation of the cyclic Si-K species. $S_N2$ type displacement of hydride should lead to the formation of a compound with four trimethylsilyl groups (**5a,b**). We assume that this compound might be only formed as an intermediate. The hydride ion which acts as a leaving group is instantaneously attacking a trimethylsilyl group thus forming trimethylsilane and **4a,b**, respectively. This two step process may also proceed in a concerted manner similarly to a mechanism proposed by Corriu et al. for the attack of potassium hydride on hydrosilanes [7].

Treatment of the dianions (**3a,b,c**) with excess water or cyclopentadiene gave, as expected, the dihydrodisilanes. Reaction with trimethylchlorosilane formed the starting material. Treatment of **3b,c** with ethyl bromide gave besides the expected dialkylated product also cyclic products **4a,b** [5], respectively. We attribute the formation of the latter to metal halogen exchange reaction of one Si-K moiety followed by immediate intramolecular nucleophilic attack of the second silylanion onto the newly formed silylbromide. The same products **5a,b** can be obtained almost quantitatively by reaction of **3b,c**, respectively, with 1,2-dibromoethane. Alternatively also reaction of **4a,b**, respectively, with trimethylchlorosilane leads to the same products. (Scheme 3)



**Scheme 3:** Cyclisation of silyldianions

Currently we are investigating the potential of these silyldianions with respect to their potential as polymer precursors, bidentate protecting groups, masked functionality and ligands in organometallic chemistry.

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## Notes and references:

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[6] Selected $^{29}$Si-NMR shifts of the central silicon atoms (in ppm against TMS): **1a** (-76.5), **1b** (-83.0), **1c** (-81.4), **2a** -80.1, -102.4), **2b** (-84.0, -116.0), **3b** (-118.1), **4a** (-63.4, -113.5).

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