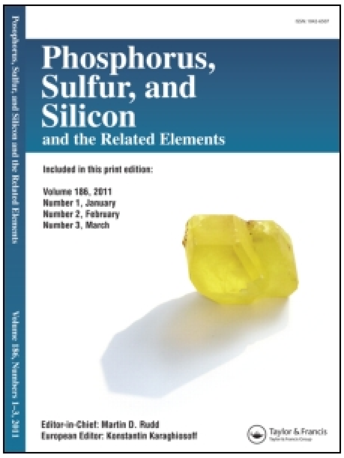

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Cyclosilylanions from Dianionic Precursors

CHRISTOPH MARSCHNER and CHRISTIAN MECHTLER

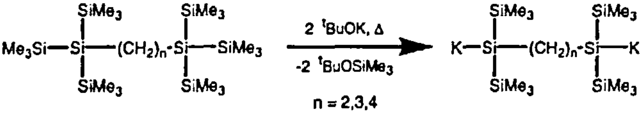
Institute for Inorganic Chemistry, Technical University Graz, Stremayrgasse 16, A-8010 Graz, Austria

Oligosilylanions can easily be prepared by cleavage of a Si-$SiMe_3$ bond with ^tBuOK in THF, if the central silicon is stabilized by at least two -SiR_3 or phenyl substituents [1]. Use of α,ω-alkylidene bridged oligosilanes leads to formation of silyldianions [2]. Reaction of the dipotassium compounds with equimolar amounts of water results in loss of trimethylsilane accompanied by formation of cyclic silylanions.

Keywords: oligosilanes; silylanions; potassium silanides

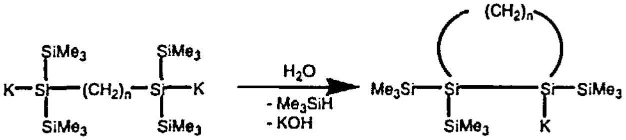
RESULTS AND DISCUSSION

α,ω-Alkylidene bridged bis(tris(trimethylsilyl)silanes) can be prepared quite easily by reacting the respective α,ω-alkylditosylates with tris(trimethylsilyl)silyl potassium. Reaction of the resulting oligosilanes with two equivalents of potassium *tert*-butoxide in THF leads to formation of alkylidene bridged silyldianions (Scheme 1).



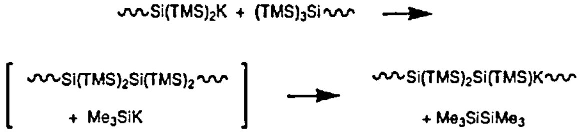
Scheme 1: Synthesis of oligosilyldianions

In some cases, we found that during the reaction considerable amounts of a second silyl potassium compound were formed. This could be proved both by ^{29}Si NMR spectroscopy and GC-MS (after quench with ethyl bromide or H^+). Addition of exactly one equivalent of water gave the second product - a cyclic silylanion -exclusively in an almost quantitative reaction (Scheme 2).



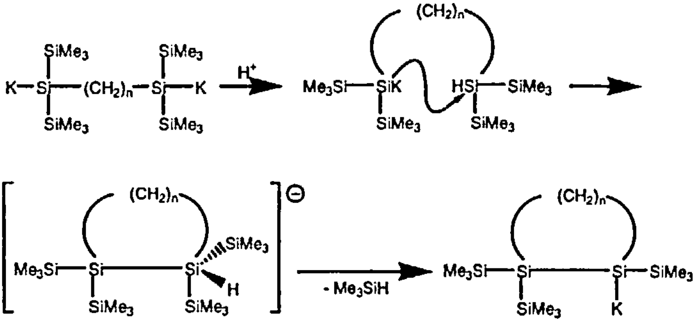
Scheme 2: Formation of cyclic silylanions

An initial mechanistic interpretation considered an intramolecular attack of a silyl potassium moiety at the tris(trimethylsilyl)silyl end of the monoanion. This should lead to the formation of hexamethyldisilane, which could be found neither by NMR spectroscopy nor GC-MS (Scheme 3). This hypothesis also contradicted to the fact that ring formation could be only observed upon addition of at least two equivalents of potassium *tert*-butoxide and proceeded on the expense of the dianion.



Scheme 3: Hypothetical ring formation from monoanion

A more likely mechanism is shown in Scheme 4. One of the silyl potassium moieties is hydrolyzed and thus susceptible to intramolecular attack which is accompanied by loss of trimethylsilane. The latter could be identified by ^{29}Si-NMR spectroscopy. It is not clear, whether a concerted or a two step mechanism is operative in the reaction, but a pentacoordinate transition state seems reasonable for silicon and is very similar to that proposed by Corriu et al. for the attack of KH on a silicon hydride.[3]



Scheme 4: Mechanism of ring closure

Ring closure can be observed for n=3 and 4, although it is favored for the 5-membered ring.

Further derivatization was successful with H^+, ethyl bromide and $MgBr_2$, yielding the silylmagnesiumbromide [4].

^{29}Si-NMR shifts of the Si-K and Si-MgBr ring for n=3

	R-Si$^{\bullet}$M(TMS)-Si	R-Si$^{\bullet}$(TMS)$_2$Si	SiMe$_3$
M=K	-113.5	-63.4	-8.0; -12.7; -13.1
M=MgBr	-99.8	-66.7	-10.0; -12.1; -12.8

CONCLUSIONS

The key step of the ring formation, that is loss of Me_3SiH and formation of the Si-SiK moiety, should also occur in an intermolecular manner. Although all reactions were carried out in concentrated solution, no significant amounts of oligomers could be observed. This could be due to the ring size as well as thermodynamic (entropic) reasons. Despite of its limitations, the method represents a facile route towards anionic silacarbacycles.

Acknowledgment

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