Pergamon

Tetrahedron Letters 39 (1998) 3193–3196

TETRAHEDRON
LETTERS

Bis[bis(methylthio)lithiomethyl]dimethylsilanes: A Useful Reagent for the Synthesis of Polysilacarbacycles *via* Disilylation

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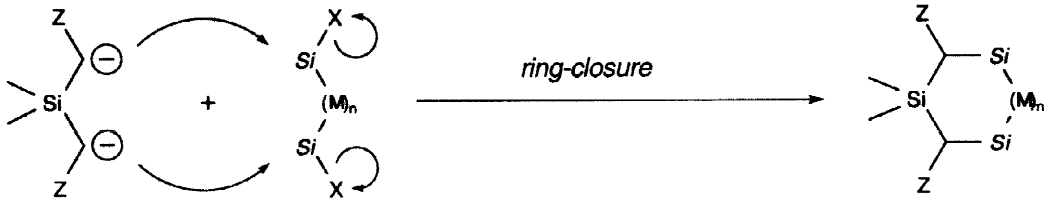
Received 24 January 1998; revised 19 February 1998; accepted 20 February 1998

Abstract: Bis[bis(methylthio)lithiomethyl]dimethylsilane was generated from bis[bis(methylthio)-methyl]dimethylsilane by deprotonation with *t*-BuLi in THF and allowed to react with various dichloro(poly)silanes to give the corresponding 4- to 7-membered polysilacarbacycles in moderate to good yields. The methylthio groups in the cyclized products were readily removed by radical reduction with Bu_3SnH. © 1998 Elsevier Science Ltd. All rights reserved.

Polysilacarbacycles, cycloalkanes containing one or more silicon atoms in the ring, have been receiving increasing attention as target molecules or precursors in the fields of polymers, ceramics, and functional materials as well as in hypervalent silicon chemistry. For example, 1,3-disilacyclobutanes are converted into polycarbosilanes by ring-opening polymerization,[1] and silacyclohexanes are shown to behave as a mesogen of liquid crystals,[2] while hexafluoro-1,3,5-trisilacyclohexane[3] and pentafluoro-1,4-disilacyclohexane anions[4] are demonstrated to capture a fluoride ion. However, a general synthetic method for polysilacarbacycles, applicable to a variety of ring sizes and substitution patterns, is lacking.[5] We report here the ring-closure reaction of an α,α'-dimetalated silane with a bis(electrophile) is a powerful strategy[6] for such ring construction (Scheme 1).



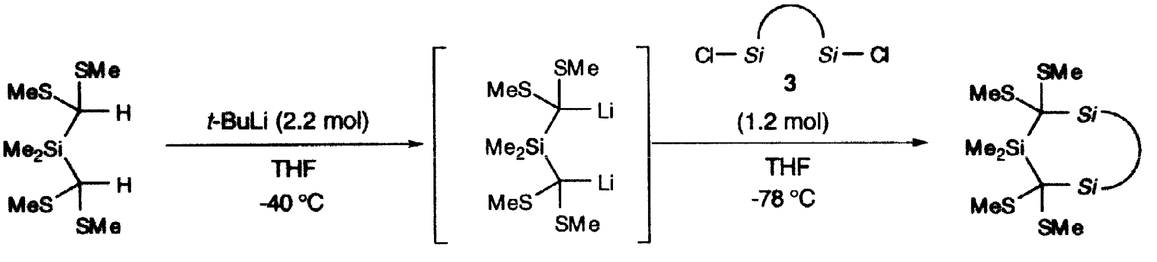
Scheme 1

The precedents of α,α'-dilithiated silanes are bis(lithiomethyl)diorganosilanes (Z = H)[7] and dimethylbis(lithiophenylmethyl)silane (Z = Ph).[8] Although the reactions of the ones (Z = H) with Me_3SiCl or Bu_3SnCl and of the ones (Z = Ph) with Me_2SiCl_2 or Me_2GeCl_2 give the corresponding products in moderate to good yields, the ones (Z = H) reportedly react with R_2SiCl_2, Me_2GeCl_2, or Cp_2TiCl_2 to give the cyclized products in *low to moderate* yields. In connection with our research concerning the base-induced cyclization of

PII: S0040-4039(98)00457-2

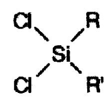
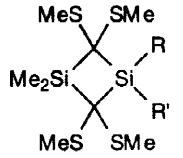
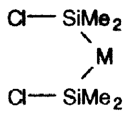
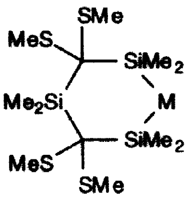
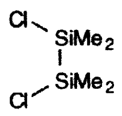
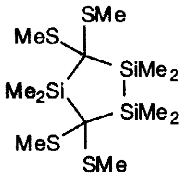
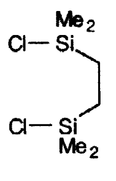
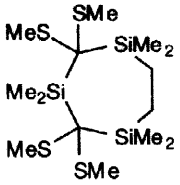
bis(alkylthio)(chloromethyldimethylsilyl)methane,[9] we became interested in bis[bis(alkylthio)lithiomethyl] diorganosilanes (Z = $(SR)_2$).[10] Thus, we envisaged that the introduction of two sulfenyl groups at both α- and α'-positions would stabilize the dianion[11] and allow us to achieve the ring formation effectively. In addition, sulfenyl groups are readily available, removable, and usable in further transformation of the products.[12] We report here that bis[bis(methylthio)lithiomethyl]dimethylsilane (**2**), generated from bis[bis(methylthio)methyl] dimethylsilane (**1**) with *t*-BuLi in THF, reacts with various bifunctional chlorosilanes **3** to give the corresponding 4- to 7-membered polysilacarbacycles **4** in *moderate to good* yields.

Treatment of **1**[13] (1 mol) with *t*-BuLi (2.2 mol) in THF at -40 ℃ followed by the addition of a solution of chlorosilane **3** (1.2 mol) in THF at -78 ℃ and warming the reaction mixture up to room temperature gave the cyclized product **4**.[14] The results are summarized in Table 1.



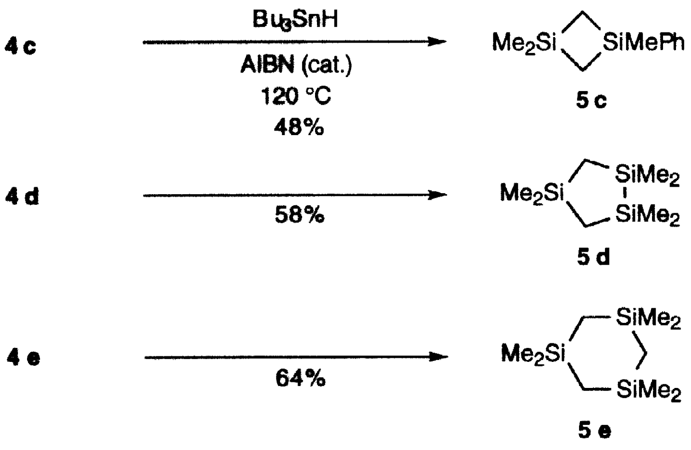
1 **2** **4**

Table 1. Dianionic ring formation of **4** *via* double silylation of **2**

Entry	Chlorosilane **3**	**4** (yield)	Entry	Chlorosilane **3**	**4** (yield)
					
1	**3a** : R = R' = Me	**4a** (72%)	5	**3e**: M = CH_2	**4e** (67%)
2	**3b**: R = R' = n-C_6H_{13}	**4b** (60%)	6	**3f** : M = O	**4f** (66%)
3	**3c**: R = Me, R' = Ph	**4c** (51%)	7	**3g** : M = $SiMe_2$	**4g** (31%)
4	 **3d**	 **4d** (75%)	8	 **3h**	 **4h** (38%)

With dichlorodiorganosilanes **3a-c**, four-membered silanes **4a-c** were produced in 72%, 60%, and 51% yield, respectively (entries 1-3). The yields are generally higher than those obtained with bis(lithiomethyl)-dimethylsilane (24%)[7b] or bis(lithiomethyl)diphenylsilane (46%),[7d] and, thus, it is apparent that the sulfenyl groups in 1,3-dianion **2** are the key to the success of the dianionic ring formation. Silylation of **1** with **3d** gave successfully 1,3,4-trisilacyclopentane **4d** whose structure was definitely confirmed by X-ray analysis (entry 4). Six-membered rings **4e-g** also were prepared in a similar way, although the yield of **4g** was low (entries 5-7). Silicon-silicon and silicon-oxygen bonds were found to tolerate the basic conditions. The introduction of dimethylsilylene, methylene, or oxygen into the 4-position of 1,3,5-trisilacyclohexane derivatives could be effected simply by changing the bis(electrophile) employed. Finally, the formation of seven-membered compound **4h** resulted in relatively low yield, comparable to **4g** (entry 8).

Desulfurization of the obtained cyclic silanes **4c-e** can be effected by reduction with tributyltin hydride to give the corresponding parent silanes **5c-e** as illustrated in Scheme 2.[15]



Scheme 2

In summary, we have demonstrated that bis[bis(methylthio)lithiomethyl]dimethylsilane is a novel and useful reagent for the synthesis of polysilacarbacycles through the dianionic ring-closure strategy. The stabilization of the α,α'-dilithiated silane by two sulfenyl groups which can be easily introduced and removed plays a key role in the double silylation. The present method can provide various types of carbacyclic silanes by the proper choice of a bis(electrophile). Further transformation of the cyclized products to functional materials is in progress.

Acknowledgment: The present work was partially supported by a Grant-in-Aid (No. 07405042) for Scientific Research from The Ministry of Education, Science, Sports and Culture and a Grant-in-Aid for "Research for the Future" Program (96R11601) from The Japan Society of the Promotion of Science. We thank Shin-Etsu Chemical Co. Ltd. for the generous gifts of organosilicon compounds.

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