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

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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 Bu₃SnH. © 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-trisilacyclohexane³ and pentafluoro-1,4-disilacyclohexane anions⁴ 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 strategy⁶ for such ring construction (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 Me₃SiCl or Bu₃SnCl and of the ones (Z = Ph) with Me₂SiCl₂ or Me₂GeCl₂ give the corresponding products in moderate to good yields, the ones (Z = H) reportedly react with R₂SiCl₂, Me₂GeCl₂, or Cp₂TiCl₂ to give the cyclized products in *low to moderate* yields. In connection with our research concerning the base-induced cyclization of

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 dianion¹¹ 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 °C followed by the addition of a solution of chlorosilane 3 (1.2 mol) in THF at -78 °C and warming the reaction mixture up to room temperature gave the cyclized product 4.¹⁴ The results are summarized in Table 1.



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

Entry	Chlorosilane 3	4 (yield)	Entry	Chlorosilane 3	4 (yield)
	a, R a ^{Si} R	MeS SMe Me ₂ Si Si MeS SMe		CI — SIMe ₂ M CI — SIMe ₂	SMe MeS Me ₂ Si MeS SMe
1	3a:R=R'=Me	4a (72%)	5	3 e: M = CH ₂	4e (67%)
2	3b:R=R'= <i>n</i> -C ₆ H ₁₃	4 b (60%)	6	3f:M=O	4f (66%)
3	3 c: R ≃ Me, R' = Ph	4 c (51%)	7	3g : M = SiMe ₂	4g (31%)
4	Cl∖_ siMe₂ cl∕ ^{SiMe} ₂	MeS Me2Si Me2Si SiMe2 SiMe2	8	CI-Si CI-Si Me ₂	MeS Me2Si MeS SMe
	3 d	4 d (75%)		3 h	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. Silvlation 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





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.

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- 13. Bis[bis(methylthio)lithiomethyl]dimethylsilane (1) was prepared by silylation of bis(methylthio)methyllithium with dichlorodimethylsilane in THF at -78 °C in 81% yield.
- 14. A general procedure for the silylation of 1: To a solution of 1 (1.0 mmol) in THF (2 mL) was added a solution of *t*-BuLi (1.51M in pentane, 1.46 mL, 2.2 mmol) at -40 °C. After 3 h, the reaction mixture was cooled to -78 °C followed by the addition of a solution of chlorosilane (1.2 mmol) in THF (1.2 mL). The resulting solution was allowed to warm up to room temperature and quenched with sat. NH₄Cl aq. The aqueous layer was extracted (3 times) with a mixture of ethyl acetate and dichloromethane. The combined organic layer was dried over anhydrous magnesium sulfate and concentrated in vacuo. The residue was purified by silica gel column chromatography to give product 4.
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