Stable Halodilithiosilanes: Synthesis and Reactivity of $TsiXSiLi_2$ (X = Br and Cl)

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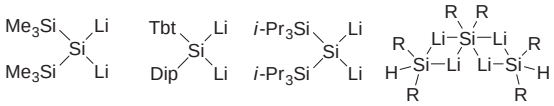
The stable bromodilithiosilane at room temperature was synthesized in 86% yield by the reduction of the corresponding tribromo[tris(trimethylsilyl)methyl]silane with lithium naphthalenide.

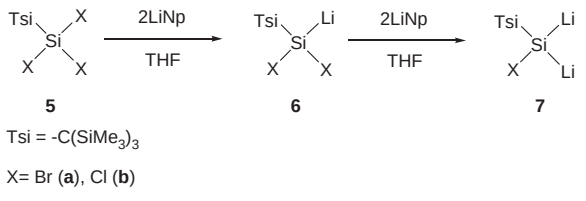
Since the first tetraphenylsilole dianion was reported by Joo et al.,[1] the structures and chemical properties of silole dianions and their analogues have been an area of great interest.[2,3] However, although acyclic 1,1-dilithiosilanes (R_2SiLi_2) are useful for the synthesis of a variety of doubly bonded derivatives containing Group 14 elements and also various silacyclic ring compounds,[4,5] far less attention has been devoted to them. To date, there have been only a few reports on acyclic geminal dilithiosilanes. In 1990, Lagow et al. reported the first dilithiosilane, bis(trimethylsilyl)dilithiosilane (**1**), generated by the pyrolysis of tris(trimethylsilyl)silyllithium·THF at 140–150 °C, which was identified only by trapping experiments.[6] Recently, aryl-substituted $Tbt(Dip)SiLi_2$ {Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl, Dip = 2,6-diisopropylphenyl} (**2**) synthesized by the reductive dehalogenation of a dibromosilane, $Tbt(Dip)SiBr_2$ at −78 °C was reported by Tokitoh, et al.[7] The first dilithiosilane isolated as a crystal, $(i\text{-}Pr_3Si)_2SiLi_2$ (**3**), was reported in 1999 by Sekiguchi and co-workers.[5] Very recently, Apeloig et al. reported the first unsolvated aggregates of the *gem*-dilithiosilane, $[(R_2SiLi_2)(R_2HSiLi)_2]$ [R = SiMe*t*-Bu_2] (**4**), containing a hexacoordinated silicon atom with an $\{R_2SiLi_4\}$ core (Chart 1).[8]

We have been interested in the syntheses of functional halosilylenoids, stable at room temperature, via the reduction of trihalosilanes bearing a bulky substituent like the tris(trimethylsilyl)methyl (Tsi = trisyl = $C(SiMe_3)_3$) group.[9] As a part of this research, we examined the further reduction of bromosilylenoid **6**[9] with lithium naphthalenide (LiNp). In this paper, we wish to report the synthesis and reactivity with electrophiles of the first functional halodilithiosilanes, **7a** and **7b**, synthesized by the reductive dehalogenation of $TsiSiX_3$ (X = Br (**5a**) and X = Cl (**5b**)) with 4 equiv of LiNp (Scheme 1). Tribromo[tris(trimethylsilyl)methyl]silane (**5a**) containing the bulky Tsi group to stabilize a bromodilithiosilane **7a** kinetically[10,11] was prepared in high yield.[12] To a THF solution of **5a** (2.0 g, 0.004 mol) at −78 °C, 4.2 equiv of LiNp diluted in THF was added using cannula technique within

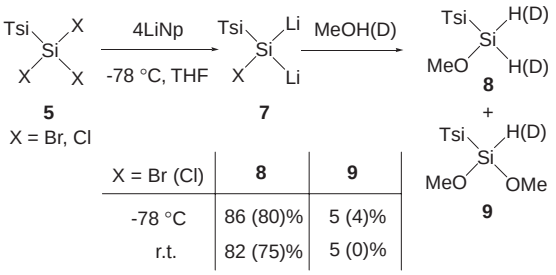


1[6] **2**[7] **3**[5] **4**[8]

Chart 1.



Scheme 1.



X = Br (Cl)	8	9
-78 °C	86 (80)%	5 (4)%
r.t.	82 (75)%	5 (0)%

Scheme 2.

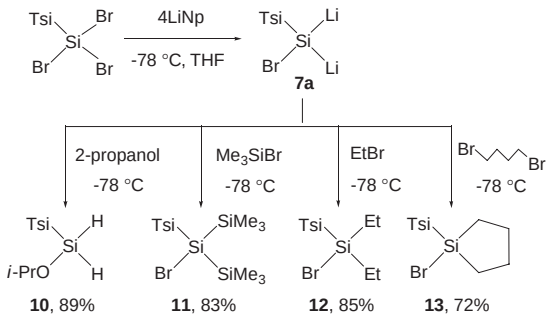
5 min. Trapping with MeOH followed by gas chromatography was used to monitor the reaction process.

After 3 h at −78 °C, all the starting material was consumed and a dark green solution was obtained, indicating that the reaction was complete. To the resulting dark green solution an excess of MeOH(D) cooled to −78 °C was added, whereupon the solution rapidly became light yellow. From the reaction mixture of trisylmethoxysilane (**8**)[13] and trisyldimethoxysilane (**9**)[9] were obtained in 86 and 5% (GC yields) (Scheme 2).

After the reduction of **5a** was completed as described above, the reaction mixture was slowly warmed to room temperature and then kept at that temperature for 12 h. The dark green color of the solution did not change during this time. Treatment of the solution with excess MeOH at 25 °C gave the trapping products **8** and **9** in 82 and 5% yield, which strongly indicates that **7a** is stable in the condensed phase at room temperature (Scheme 2). This particular stability of **7a** might be originated from the intra- and inter-molecular interactions between Li atoms, halogens, and THF solvents, and might prevent the α-elimination of lithium halide.[14]

Chlorodilithiosilane **7b** was also synthesized from the reduction of **5b** with 4.2 equiv of LiNp using a procedure similar to that for the synthesis of **7a** (Schemes 1 and 2). We observed through trapping reaction of **7b** at 25 °C that **7b** was also stable at room temperature (Scheme 2).

These results show that **7** and **6** synthesized from the reduction of **5** with LiNp were trapped by MeOH(D) and then methanolysis of the resulting hydridohalosilane took place to give the products **8** and **9**, respectively. These results also imply



Scheme 3.

that trihalosilanes **5** are initially reduced with 2 equiv of LiNp to lead to the corresponding halosilylenoids **6**, which are known to be stable under these reaction conditions[9] and then are further reduced by another 2 equiv of LiNp leading to halodilithiosilanes **7**.

The ^{29}Si NMR resonances[15] of **7a** and **7b** at $-70\,^{\circ}$C ($27\,^{\circ}$C) appeared at -106 (-108) and -110 ppm, respectively. These resonances show downfield shifts from -282 ppm of bis(silyl)-dilithiosilane **3**.[5] This difference might be due to the inductive effects between tris(trimethylsilyl)methyl and silyl substituents, and the difference may also imply that **7** might have silylenoid character due to weak complexation of Tsi(Li)Si: with lithium halide.[9,16] For comparison, the resonances of the known silole dianions appeared at far downfield between 29 and 70 ppm,[2b,2c,3a,3c] due to their aromaticity.

To investigate the reactivity of bromodilithiosilane **7a**, bimolecular reactions with various electrophiles, 2-propanol, bromotrimethylsilane, bromoethane, and 1,4-dibromobutane were carried out to give the corresponding products **10**–**13**[17] (Scheme 3). Reaction with excess 2-propanol at $-78\,^{\circ}$C yielded product **10** in 89% yield, formed by the same mechanism as described for **8**. Reaction with bromotrimethylsilane gave **11** (83%). **11** was expected as a trimethylsilylation product of **7a**. Reaction of **7a** with ethyl bromide gave a doubly ethylated product **12** (85%). Reaction with 1,4-dibromobutane gave bromosilacyclopentane **13** in 72% yield. These results show that halodilithiosilane **7** is potentially useful for the synthesis of new types of silacyclic ring compounds, especially those having functional groups.

The halodilithiosilanes are formally lithium lithiosilylenoids which might have their electrophilic property.[9,18] For clarifying this possibility, we examined the reactions of **7a** with methyllithium or mesityllithium as a nucleophile. But we observed that **7a** did not react with MeLi (MeLi/TMEDA) or MesLi to give the corresponding products. After the reaction mixtures were stirred for 6 h, MeOH-trapping was carried out to get only the product **8**, as obtained from the trapping of bromodilithiosilane with MeOH. In comparison with our previous work, the reaction of TsiMesSiLiBr·$MgBr_2$, having more bulkyl mesityl substituent than trisylbromodilithiosilane with *n*-BuLi gave nucleophilic reaction product.[9c] This comparison strongly indicates that the silicon center has high electron density due to its dianion character, which is consistent with the negative value of ^{29}Si NMR resonance.

Stable halodilithiosilanes should lead to novel silicon chemistry because of their high synthetic potential and might also be a promising precursor for silynes and disilynes. Efforts are currently underway to elucidate their synthetic usefulness, especially for doubly and triply bonded derivatives containing silicon atoms.

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15 Using on inner 5 mm (or 3 mm) NMR tube containing about 0.10 M (4.0 mmol/40 mL of THF) of **7a** and **7b** respectively, which was dipped into the solution of acetone-d_6 in on outer 10 mm (or 5 mm) NMR tube, ^{29}Si NMR experiments were carried out. Experimental details are given in the Supporting Information.
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