

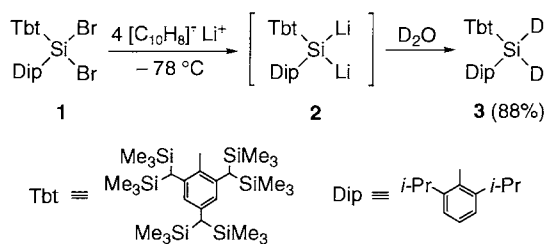
Generation and Reactions of an Overcrowded Diaryldilithiosilane

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Exhaustive reduction of dibromo(2,6-diisopropylphenyl)-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}silane with excess amount of lithium naphthalenide (more than 4 molar amounts) in tetrahydrofuran at -78°C gave the corresponding dilithiosilane, the effective formation of which was confirmed by the trapping experiments with a variety of electrophiles. The diaryldilithiosilane thus generated was found to be stable at -78°C but undergo an intramolecular proton abstraction to give the lithium-migrated dilithiosilane.¹

Although the reduction of dihalosilanes with two molar amounts of alkali metal or lithium naphthalenide is known to be a useful synthetic method for polysilanes,² cyclic oligosilanes,³ disilenes⁴ or silylenes,⁵ the formation of dimetallosilanes ($\text{RR}'\text{SiM}_2$) by the reduction of dihalosilanes is very rare except for the recent reports on the syntheses of silole dianions from the corresponding dihalosiloles.⁶ Recently, West *et al.* reported that the silole dianion they isolated was not dilithiated at the silicon center in the solid state but had a unique structure where one lithium was attached to the silicon center but the other one onto the silole ring.^{6c} A sole example of a stable dilithiosilane is bis(trimethylsilyl)dilithiosilane generated by the disproportionation of tris(trimethylsilyl)silyllithium at 140°C in the solid state reported by Lagow *et al.*^{7,8}

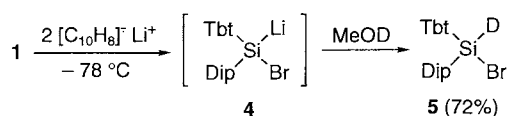


Scheme 1.

In the course of our study on the kinetic stabilization of highly reactive, low-coordinated organosilicon compounds we became interested in the reduction of dihalosilanes bearing extremely bulky substituents. Here, we wish to report a novel generation of a diaryldilithiosilane by the reductive debromination of an overcrowded dibromosilane using lithium naphthalenide together with some reactions of the resulting dilithiosilane with electrophiles.

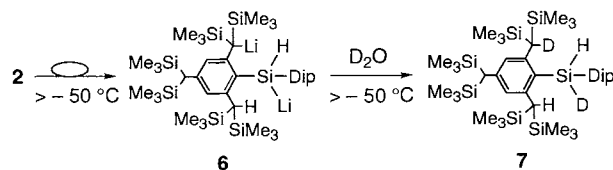
When a dibromosilane [$\text{Tbt}(\text{Dip})\text{SiBr}_2$ (**1**)] bearing two bulky aromatic substituents, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl and 2,6-diisopropylphenyl (denoted as Tbt and Dip, respectively), was treated with 5 molar amounts⁹ of lithium naphthalenide in THF at -78°C , a dark green solution was obtained. The reaction mixture was stirred for 1 h at this

temperature and then treated with excess D_2O to afford $\text{Tbt}(\text{Dip})\text{SiD}_2$ **3** (88%, D-content 92%; Scheme 1), the formation of which strongly indicates that dibromosilane **1** was exhaustively reduced with lithium naphthalenide to give the corresponding dilithiosilane, $\text{Tbt}(\text{Dip})\text{SiLi}_2$ (**2**).



Scheme 2.

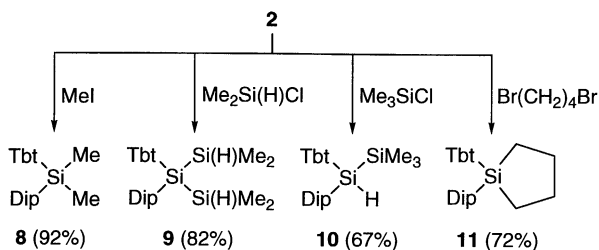
On the other hand, the treatment of dibromosilane **1** with 2.2 molar amounts of lithium naphthalenide in THF at -78°C followed by the addition of MeOD (10 molar amounts) gave the bromodeuteriosilane **5** as a main product together with a small amount of dideuteriosilane **3** (Scheme 2). These results suggest that dibromosilane **1** is initially reduced with two molar amounts of lithium naphthalenide to give bromolithiosilane **4**, which does not undergo α -elimination of lithium bromide giving the corresponding silylene $\text{Tbt}(\text{Dip})\text{Si}$: or intermolecular substitution reaction leading to oligo- or poly-silanes but survives at -78°C and is further reduced by excess lithium naphthalenide giving **2**. In other words, the steric protection with bulky substituents might invest the intermediate **4** with enough stability and lifetime to be converted into the dilithiosilane **2**. It should be noted that this is the first example of the formation of a dilithiosilane by the reductive dehalogenation of a dihalosilane.



Scheme 3.

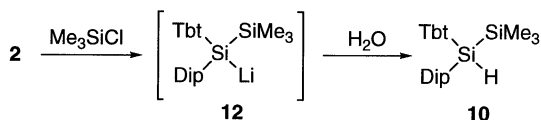
Next, we examined the thermal stability of dilithiosilane **2**. When the THF solution of **2**, prepared at -78°C as mentioned above, was kept at -50°C for 30 min and then treated with D_2O , a mixture of two deuterated silanes, $\text{Tbt}(\text{Dip})\text{SiD}_2$ **3** and **7**, was obtained ($3 : 7 = 2 : 3$ as judged by $^1\text{H-NMR}$). The formation of compound **7** can be most likely interpreted in terms of the intramolecular proton abstraction of dilithiosilane **2** leading to a lithium-migrated dilithiated compound **6** at -50°C (Scheme 3). The lithium-migration was found to be completed at -25°C for 30 min and the $^1\text{H-NMR}$ spectrum of the reaction mixture showed only signals attributable to **7**. Therefore, we used the

dilithiosilane **2** at $-78\text{ }^{\circ}\text{C}$ for the following reactions with electrophiles. Dilithiosilane **2** was allowed to react with iodomethane to give Tbt(Dip)SiMe₂ (**8**) in 92% yield.¹⁰ Treatment of **2** with chlorodimethylsilane also gave the corresponding trisilane **9** in a good yield, while the reaction of **2** with chlorotrimethylsilane did not afford the expected bisilylated product but gave only the mono-silylated product, Tbt(Dip)Si(H)SiMe₂ (**10**) (Scheme 4).



Scheme 4.

The formation of **10** indicates that **2** readily undergoes the first silylation with chlorotrimethylsilane to give the silyllithium **12** but further silylation might be suppressed by the extreme steric hindrance caused by the three bulky substituents, Tbt, Dip and Me₃Si groups (Scheme 5).¹¹



Scheme 5.

Furthermore, dilithiosilane **2** was found to react readily with 1,4-dibromobutane as a bifunctional electrophile, giving silacyclopentane **11** in 72% yield (Scheme 4).¹² It should be noted that dilithiosilane **2** underwent a ready 1:1 bimolecular reaction with 1,4-dibromobutane to produce **11** as a main product together with a small amount of an oligomeric product resulting from intermolecular reactions. The successful preparation of **11** suggests that the Tbt(Dip)SiLi₂ is potentially useful not only in the synthesis of a new type of cyclic silicon compounds but also in the systematic synthesis of silicon-containing double-bond species such as silenes, unsymmetrical disilenes, and related other metallasilenes. In the hope of further applications in the synthesis of novel organosilicon compounds, reactions of dilithiosilane **2** with other bifunctional electrophiles are currently in progress.

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References and Notes

- Parts of this work have already been presented at the 74th Annual Meeting of Chemical Society of Japan, March 1998, Kyoto (Abstract No. 3A2 35) and the 76th Annual Meeting of Chemical Society of Japan, March 1999, Yokohama (Abstract No. 3B5 33).
- a) D. Miller and J. Michl, *Chem. Rev.*, **89**, 1359 (1989). b) R. West, in "Comprehensive Organometallic Chemistry," ed by E. W. Abel, F. G. A. Stone, and G. Wilkinson, Pergamon Press, New York (1995) Vol. 2, Chapter 3, p77 and references cited therein.
- For examples, see the following references. (R₂Si)₃: a) S. Masamune, Y. Hanazawa, S. Murakami, T. Bally, and J. F. Blount, *J. Am. Chem. Soc.*, **104**, 1150 (1982). b) A. Schäfer, M. Weidenbruch, K. Peters, and H. G. von Schnering, *Angew. Chem., Int. Ed. Engl.*, **23**, 302 (1984). c) H. Matsumoto, A. Sakamoto, and Y. Nagai, *J. Chem. Soc., Chem. Commun.*, **1986**, 1768. (R₂Si)₄: d) M. Biernbaum and R. West, *J. Organomet. Chem.*, **131**, 179 (1977). (R₂Si)₅: e) C. W. Carlson and R. West, *Organometallics*, **2**, 1792 (1983). f) A. Katti, C. W. Carlson, and R. West, *J. Organomet. Chem.*, **271**, 353 (1984). (R₂Si)₆: g) C. A. Burkhard, *J. Am. Chem. Soc.*, **71**, 963 (1949).
- a) H. Watanabe, K. Takeuchi, N. Fukawa, M. Kato, M. Goto, and Y. Nagai, *Chem. Lett.*, **1987**, 1341. b) S. Masamune, Y. Eriyama, and T. Kawase, *Angew. Chem., Int. Ed. Engl.*, **26**, 584 (1987). c) N. Tokitoh, H. Suzuki, R. Okazaki, and K. Ogawa, *J. Am. Chem. Soc.*, **115**, 10428 (1993). d) M. Kira, T. Maruyama, C. Kabuto, K. Ebata, and H. Sakurai, *Angew. Chem., Int. Ed. Engl.*, **33**, 1489 (1994).
- a) M. Denk, R. Lennon, R. Hayashi, R. West, A. V. Belyakov, H. P. Verne, A. Haaland, M. Wagner, and N. Metzler, *J. Am. Chem. Soc.*, **116**, 2691 (1994). b) M. Denk, J. C. Green, N. Metzler, and M. Wangner, *J. Chem. Soc., Dalton. Trans.*, **1994**, 2405. c) B. Gehrhus, M. F. Lappert, J. Heinicke, R. Boese, and D. Bläser, *J. Chem. Soc., Chem. Commun.*, **1995**, 1931. d) K. Sakamoto, S. Tsutsui, H. Sakurai, and M. Kira, *Bull. Chem. Soc. Jpn.*, **70**, 253 (1997).
- a) W.-C. Joo, J.-H. Hong, S.-B. Choi, H.-E. Son, and C. H. Kim, *J. Organomet. Chem.*, **391**, 27 (1990). b) J.-H. Hong and P. Boudjouk, *J. Am. Chem. Soc.*, **115**, 5883 (1993). c) J.-H. Hong, P. Boudjouk, and S. Castellino, *Organometallics*, **13**, 3387 (1994). d) U. Bankwitz, H. Sohn, D. R. Powell, and R. West, *J. Organomet. Chem.*, **499**, C7 (1995). e) R. West, H. Sohn, U. Bankwitz, J. Calabrese, Y. Apeloig, and T. Müller, *J. Am. Chem. Soc.*, **117**, 11608 (1995). f) W. P. Freeman, T. D. Tilly, G. P. A. Yap, and A. L. Rheingold, *Angew. Chem., Int. Ed. Engl.*, **35**, 882 (1996). g) T. Wakahara and W. Ando, *Chem. Lett.*, **1997**, 1179.
- S. K. Mehrotra, H. Kawa, J. R. Baran, Jr., M. M. Ludvig, and R. J. Lagow, *J. Am. Chem. Soc.*, **112**, 9003 (1990).
- Recently, Sekiguchi *et al.* reported a preparation of [(*i*-Pr)₃Si]₂SiLi₂ by the reduction of 1,1-bis(triisopropylsilyl)-2,3-bis(trimethylsilyl)-1-silacyclopentene with lithium and its X-ray crystallographic analysis; S. Yamaguchi, M. Nanjo, M. Ichinohe, and A. Sekiguchi at the 76th Annual Meeting of Chemical Society of Japan, March 1999, Yokohama (Abstract No. 3B5 34). The same bulky bisilyl-substituted dilithiosilane has been independently prepared by a different synthetic method, *i. e.*, the lithium-mercury exchange reaction of [(*t*-BuHg)Si(*i*-Pr)₃]₂Hg; Y. Apeloig, private communication.
- Although 4 molar amounts of lithium naphthalenide is theoretically necessary to reduce **1**, optimization of the reaction conditions revealed that the highest yield was attained when 5 molar amounts of the reagent was used.
- 8**: ¹H NMR (270 MHz, CDCl₃) δ 0.00 (27H, br s), 0.04 (27H, s), 0.80 (6H, s), 1.14 (6H, d, *J* = 6.6 Hz), 1.17 (6H, d, *J* = 6.6 Hz), 1.33 (1H, s), 2.20 (2H, br s), 3.31 (2H, sept, *J* = 6.6 Hz), 6.26 (1H, br s), 6.37 (1H, br s), 7.12 (2H, d, *J* = 7.6 Hz), 7.25 (1H, t, *J* = 7.6 Hz). ¹³C NMR (68 MHz, CDCl₃) δ 1.0 (q), 2.0 (q), 2.3 (q), 10.0 (q), 24.2 (q), 26.5 (q), 27.7 (d), 30.2 (d), 32.3 (d), 123.3 (d), 124.0 (d), 128.4 (d), 129.1 (d), 130.4 (s), 137.8 (s), 143.0 (s), 151.3 (s), 154.5 (s); ²⁹Si NMR (53 MHz, CDCl₃) δ -15.2, 1.7. Anal. Calcd for C₄₁H₈₂Si₂: C, 63.81; H, 10.71. Found: C, 64.00; H, 10.46.
- The severe steric hindrance in the lithiosilane **12** was confirmed by the ¹H NMR spectrum of its hydrolysis product **10**. The ¹H NMR spectrum of **10** shows four broad methyl signals and a couple of septets attributable to the *ortho* SiMe₃ groups on Tbt and the *i*-Pr groups on Dip, respectively. The broadening of signals here observed can be interpreted in terms of the slow rotation of substituents due to the severe congestion around the central silicon atom. **10**: ¹H NMR (270 MHz, CDCl₃): δ -0.12 (9H, br s, SiMe₃), -0.09 (9H, br s, SiMe₃), 0.05 (9H + 3H, s, SiMe₃), 0.15 (9H, br s, SiMe₃), 0.18 (9H, br s, SiMe₃), 0.20 (9H, s, SiMe₃), 0.66 (3H, d *J* = 6.5 Hz, CH₃ of *i*-Pr), 1.12 (3H, d, *J* = 6.5 Hz, CH₃ of *i*-Pr), 1.24 (3H, d, *J* = 6.8 Hz, CH₃ of *i*-Pr), 1.29 (1H, s, CH of Tbt), 1.45 (3H, d, *J* = 6.8 Hz, CH₃ of *i*-Pr), 2.20 (1H, s, CH of Tbt), 2.25 (1H, br s, CH of Tbt), 2.64 (1H, sept, *J* = 6.8 Hz, CH of *i*-Pr), 3.64 (1H, sept, *J* = 6.8 Hz, CH of *i*-Pr), 5.28 (1H, s, SiH), 6.37 (1H, br s, CH of Tbt), 6.49 (1H, br s, CH of Tbt), 7.01 (1H, d, *J* = 7.3 Hz CH of Dip), 7.19 (1H, t, *J* = 7.6 Hz, CH of Dip), 7.26 (1H, d, *J* = 7.6 Hz, CH of Dip).
- 11**: ¹H NMR (500 MHz, CDCl₃): δ -0.05 (18H, s), 0.05 (36H, s), 1.08 (6H, d, *J* = 6.6 Hz), 1.13 (6H, d, *J* = 6.6 Hz), 1.28 (1H, s), 1.32 - 1.43 (4H, m), 1.83 (2H, br s), 1.93 (2H, br s), 1.95 (1H, s), 2.04 (1H, s), 3.36 (2H, sept, *J* = 6.4 Hz), 6.23 (1H, br s), 6.41 (1H, br s), 7.11 (2H, d, *J* = 7.7 Hz), 7.24 (1H, t, *J* = 7.7 Hz); ¹³C NMR (125 MHz, CDCl₃): δ 1.1 (q), 2.2 (q), 22.7 (t), 24.5 (q), 27.0 (d), 27.2 (d), 27.3 (q), 27.4 (t), 30.1 (d), 33.3 (d), 123.1 (d), 124.1 (d), 128.8 (d), 129.0 (d), 130.9 (s), 139.3 (s), 142.9 (s), 151.4 (s), 153.9 (s); ²⁹Si NMR (53 MHz, CDCl₃): δ -2.4, 1.7, 2.1 (br).