Reactivity of Bromodilithiosilane to Naphthalene and Anthracene

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Summary: Bromodilithiosilane, **1**, *reacted with naphthalene at 110 °C to give the silacyclopropane derivative* **2**, *which reacted with MeOH(D), MeI, and* Me_3SiCl *to yield* **3**, **4**, *and* **5** *in 84%, 82%, and 85% yields, respectively.* **1** *also reacted with anthracene at −30 °C to give the lithio-silanorbornadiene derivatives, which were trapped by i-PrOH to yield* **6** *and* **7** *as colorless crystals in 27% and 54%. These results show an important synthetic application of a 1,1-dilithiosilane bearing a halogen atom, which differs from those of known 1,1-dilithiosilanes.*

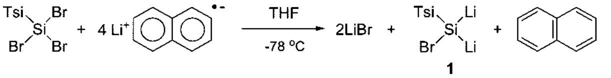
Introduction

Lithium derivatives of group 14 elements have been known for many decades.[1] Although 1,1-dilithiosilanes (R_2SiLi_2) are useful reagents for the synthesis of organosilicon species, little attention has been given to them due to the difficulties involved in doing their syntheses. Consequently, only a few 1,1-dilithiosilanes have been reported,[2] namely, the formation of novel silicon compounds derived from 1,1-dilithiosilanes, such as the formation of silastannene ($>\mathrm{Si}{=}\mathrm{Sn}<$);[3] the allenic species of main group elements ($>\mathrm{Si}\,\underline{\cdot\cdot}\,\mathrm{M}\,\underline{\cdot\cdot}\,\mathrm{Si}<$, M = Ga, In);[4] tetrasila-1,3-butadiene ($>\mathrm{Si}{=}\mathrm{Si}{-}\mathrm{Si}{=}\mathrm{Si}<$);[5] and silaborene ($>\mathrm{Si}{=}\mathrm{B}{-}$).[6] Also Tokitoh et al. reported silacyclopropabenzene, synthesized by the reaction of Tbt(Dip)$SiLi_2$ (Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl; Dip = 2,6-diiospropylphenyl) with *o*-dibromobenzene.[7] However, at this time, no investigation on the reaction of 1,1-dilithiosilanes (R_2SiLi_2) with naphthalene and anthracene has yet appeared.

Recently, we reported the first functional dilithiosilanes having a halogen substituent, $TsiSiXLi_2$ (Tsi = $(Me_3Si)_3C$, X = Cl, Br) stable at room temperature.[8] These species should have reactivities different from those of known 1,1-dilithiosilanes because of their halogen functionality. In this note, we report the novel products of the reaction of $TsiSiBrLi_2$ with naphthalene and anthracene.

Results and Discussion

Tribromo[tris(trimethylsilyl)methyl]silane, containing the bulky Tsi group to stabilize bromodilithiosilane **1**, kinetically was prepared in high yield.[9] A 4.2 equiv of LiNp (lithium naphthalenide) diluted in THF was added to a THF solution of $TsiSiBr_3$ (1.996 g, 0.004 mol) at −78 °C. After stirring for 3 h at −78 °C, all of the starting reactants were consumed to give bromodilithiosilane (eq 1).[8] THF was removed by vacuum evaporation at room temperature, and then toluene was added to the resulting residue. When the reaction mixture of **1** was warmed up to the reflux temperature, the new species **2** was formed (eq 2), which reacted with MeOH(D) to give **3** in 84% yield and with MeI and Me_3SiCl to give a methylated product **4** and a silylated product **5** in 82% and 85% (GC yield), respectively (eq 3). These trapping results strongly support that species **2** should be formed.



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(1)

Two plausible mechanisms for the formation of **2** are shown in Scheme 1. The first one begins with 1,2-addition reaction of

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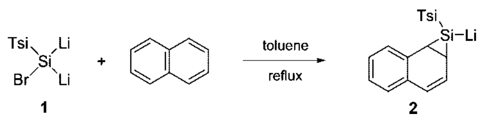

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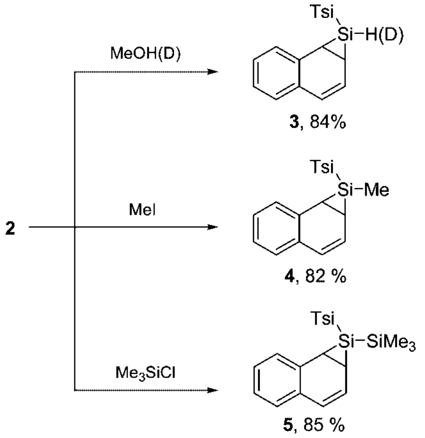


(3)

bromodilithiosilane. Bromodilithiosilane reacts with naphthalene at toluene reflux temperature to give the 1,2-addition adduct and then an intramolucular cyclization takes place to yield **2**. This intramolecular cyclization reaction due to the Br substituent on the silicon atom seems to be a unique property of bromodilithiosilane, which can be distinguished from other 1,1-dilithiosilanes.[2] The other one might be a silylene-mediated addition pathway,[10] because a silylene, Li(Tsi)Si: could be generated via the α-elimination[11] of bromodilithiosilane. To clarify this possibility, the trapping experiment to trap the silylene was carried out in the presence of Et$_3$SiH, which did not react with bromodilithiosilane. When the reaction mixture containing excess Et$_3$SiH was warmed up to reflux temperature for 1 h, MeOH was added. From this trapping experiment, we did not observe any product related to the trapping agent. The only product was **3**. We also carried out the trapping experiment using bistrimethylsilylacetylene as a trapping agent in a manner similar to that described above. But we observed that only product **3** was formed. These results suggest that bromodilithiosilane did not undergo α-elimination to generate the corresponding silylene at the reaction conditions.

To examine the reactivity of **1** to anthracene (Scheme 2), we carried out the reaction of TsiSiBr$_3$ with 4.2 equiv LiAn (lithium anthracenide) instead of LiNp. After adding LiAn to the THF solution of TsiSiBr$_3$, the reaction mixture was stirred for 2 h at −78 °C. When the resulting deep green solution was added to an excess of *i*-PrOH, it rapidly became light yellow. From the reaction mixture, only the trapping product of **1**, TsiSiH$_2$(O^{i}Pr), was obtained. After completing the reduction of TsiSiBr$_3$ to give **1** as described above, the reaction mixture was slowly warmed to −30 °C, where the reaction of **1** with anthracene began to take place, and was held at that temperature for 1 h. The deep green color of the solution changed to dark brown. Treatment of the reaction mixture with an excess of *i*-PrOH at −30 °C gave the trapping products **6** and **7** in 27% and 54% yields, respectively. In comparison with naphthalene, anthracene reacted with **1** at a lower temperature because of the lower resonance stabilization of anthracene than that of naphthalene.[12] In order to investigate the thermal effect on this reaction, the reaction mixture was warmed to room temperature and then treated with *i*-PrOH to yield only **7** in 78% yield. Interestingly, even when the solution was cooled back to −30 °C, only **7** was obtained from the *i*-PrOH trapping condition, indicating that the formation of **6** and **7** was not reversible.

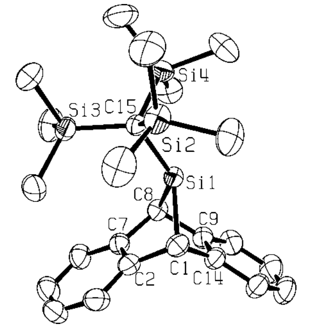
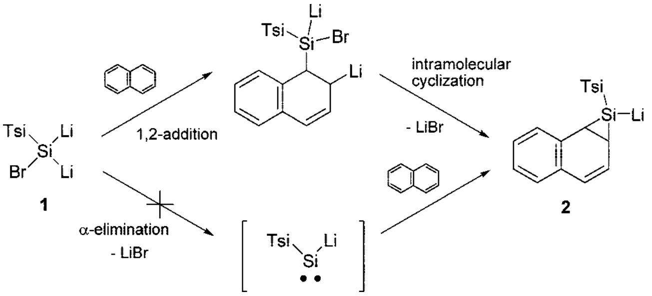


Figure 1. ORTEP drawing of **6**, shown with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Si1−C1 = 1.9434(12), Si1−C8 = 1.9361(11), Si1−C15 = 1.8804(11); C1−Si1−C8 = 80.49(5), C1−Si1−C15 = 126.46(5), C8−Si1−C15 = 125.83(5), C2−C1−C14 = 105.74, C7−C8−C9 = 106.57(9).

Scheme 1. Plausible Mechanisms for the Formation of 2



Through flash column chromatography, **6** and **7** were isolated and obtained as colorless crystals by recrystallization from *n*-hexane. Compounds **6** and **7** were characterized by NMR, GC/MS, EA, and HRMS. The ^{29}Si NMR chemical shifts of central Si atoms of **6** and **7** appeared at 45.0 and 75.5 ppm, respectively. The ^{29}Si resonance of **7** is more deshielded than those for other silanorbornadiene derivatives (70.1−37.7 ppm).[13]

The structures of **6** and **7** were characterized by X-ray crystallography (Figures 1 and 2). Si−C bond lengths around the central silicon (Si1) are longer than the typical Si−C single bond (<1.86 Å).[14] The angle between two aromatic planes in the anthracene moiety of **6** and **7** is 118.6 and 124.5°, respectively. The smaller angle of **6** implies that **6** is a more hindered structure than that of **7** due to the bulky Tsi substituent.

Plausible mechanisms for the formation of **6** and **7** may be that the process begins by forming the reactive species **a**, via 1,4-addition of Si−Li bond of **1** to the most highly reactive 9,10-positions of anthracene (Scheme 3). Species **a** then proceeds through a LiBr elimination intramolecularly to yield species **c**, which could be trapped by *i*-PrOH to give the product **6**. The formation of species **d** is distinctive and occurs a bit differently.

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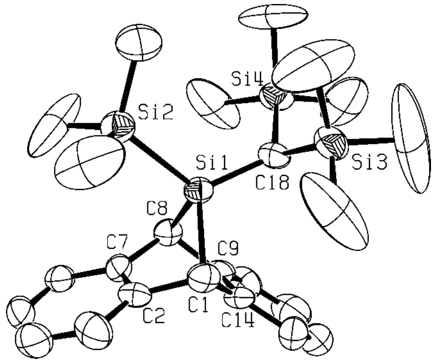

Figure 2. ORTEP drawing of **7**, shown with thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): C1−Si1 = 1.953(8), C8−Si1 = 1.939(8), C18−Si1 = 1.835 (9), Si1−Si2 = 2.405(4); C1−Si1−C8 = 78.7(4), C8−Si1−C18 = 114.1(4), C8−Si1−Si2 = 112.7(3), C1−Si1−C18 = 112.8(4), C1−Si1−Si2 = 114.2(3), C7−C8−C9 = 108.1(7), C2−C1−C14 = 108.2(7).

Species **d** could be formed through either of two reaction pathways: (1) the 1,2-migration of Li, followed by LiBr elimination to give **d** (**a** → **b** → **d**); or (2) after LiBr elimination, the 1,2-migration of Li (**a** → **c** → **d**).[15] The most important feature of these reaction pathways is the 1,2-migration of Li and the trimethylsilyl substituent. To the best of our knowledge, there is no previous example of the synchronous 1,2-migration of Li and the trimethylsilyl substituent. Because of the inductive effect, the driving force for the migration of Li might be the stability of the anion site, which is favorable to the center of a carbon atom enclosed by three silyl substituents rather than to the silicon atom with one silyl substituent.

Conclusions

In summary, the reactions of bromdilithiosilane, **1**, with naphthalene and anthracene gave 1,2- and 1,4-addition products in high yield, respectively. These results show an important synthetic application of a 1,1-dilithiosilane bearing a halogen atom, which differs from those of known 1,1-dilithiosilanes.

Experimental Details

General Comments. In all reactions in which air-sensitive chemicals were used, the reagents and solvents were dried prior to use. THF was distilled from Na/Ph_2CO. Other starting materials were purchased as reagent grade and used without further purification. Glassware was flame-dried under nitrogen or argon flushing prior to use. All manipulations were performed using standard Schlenk techniques under a nitrogen or argon atmosphere. ^{1}H NMR, ^{13}C NMR, and ^{29}Si NMR spectra were recorded on a Bruker Avance II$^+$ BBO 400 MHz S1 spectrometer in $CDCl_3$ with tetramethylsilane (TMS).

Analyses of product mixtures were accomplished using an HP 5890 II Plus instrument with FID (HP-5, 30 m column) with dried decane as an internal standard. Mass spectra were recorded on a low-resolution (Agilent Technologies GC/MS: 6890N, 5973N mass selective detector) EI mass spectrometer and a high-resolution Autospec M363 series instrument. Elemental analysis was performed on Flash EA 1112 series (CE Instruments/ThermoQuest Italia.). The preparation of bromodilithiosilane, **1**, was reported in a previous paper.[8]

X-ray Crystallography. Suitable crystals of **6** and **7** for X-ray crystallography were grown in *n*-hexane. The diffraction data for **6** and **7** were collected on a Bruker APEX II CCD area detector diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The reflection data were collected as multiscan frames with 0.5 °/frame and an exposure time of 5 s/frame. The APEX II program package was used for the determination of cell parameters, data collection, reduction, and absorption correction. The structures of the compounds were solved by direct methods and refined by full-matrix least-squares methods with the SHELXTL program package with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were placed at their geometrically calculated positions and refined as riding on the corresponding carbon atoms with isotropic thermal parameters. For **6**, final refinement based on the reflections with $I > 2\sigma(I)$ converged at $R1 = 0.0479$, $wR2 = 0.1262$, and GOF = 1.001, and for **7**, $R1 = 0.0883$, $wR2 = 0.2119$, and GOF = 0.997.

Synthesis of 3, 4, and 5. Naphthalene (2.176 g, 0.017 mol) dissolved in THF (40 mL) was added to Li (0.132 g, 0.019 mol) at room temperature. After the mixture had been stirred for 3 h, LiNp was obtained as a dark green solution. LiNp in THF was added slowly to $TsiSiBr_3$ (2.0 g, 0.004 mol) in THF (40 mL) at −78 °C using a cannula technique within 5 min. The solution was stirred for 3 h at the same temperature, and bromodilithiosilanes, **1**, was formed. The reaction mixture was slowly warmed to room temperature, and then the solvent was evaporated under reduced pressure. To the resulting viscous dark brown oil after evaporation, dried *n*-hexane (50 mL) was added, and then the precipitated species were removed by filtration. From the filtrate, *n*-hexane was removed under reduced pressure to give a dark brown oil containing **1**. To the dark brown oil, dried toluene (50 mL) was added and then stirred for 1 h at reflux temperature. The color of the solution turned from dark brown to light brown containing LiBr as a precipitate. Thereafter, MeOH(D) (3.2 mL, 0.080 mol) was added to the reaction mixture to give compound **3** (84%, GC yield). To remove LiBr, 50 mL of *n*-hexane was added and filtered to get the LiBr-free filtrate. From the filtrate, solvents were removed using a rotary evaporator, and then naphthalene was sublimed under vacuum. The crude material was purified by silica gel chromatography (*n*-hexane) to afford **3** as a white powder in 56% yield (0.87 g, 0.002 mol), which was characterized by NMR, GC/MS, EA, and HRMS.

Spectral data for **3**: White solid (mp = 71−73 °C). ^{1}H NMR (400 MHz, chloroform-*d*): δ 0.31 (s, 27H), 2.41 (d, J = 8.00, 2H), 3.32 (s, 1H), 6.45 (d, J = 7.03, 1H), 6.93 (dd, J = 1.51, 6.83, 1H), 7.15−7.17 (m, 2H), 7.26−7.30 (m, 2H). ^{13}C NMR (100 MHz, chloroform-*d*): δ 3.71 ($C(Si(CH_3)_3)_3$), 4.25 ($C(Si(CH_3)_3)_3$), 23.0, 44.7 (*C*H), 125.4, 125.6, 126.9, 130.4, 142.7, 153.7 (-*C*H=C). 143.6, 144.2 (ipso-*C*). ^{29}Si NMR (79.5 MHz, chloroform-*d*): δ −2.2 ($C(Si(CH_3)_3)_3$), 21.2 (*Si*-H). GC/MS: *m/z* (%) 388 (M$^+$, 68.9), 373 (100), 285 (33.3), 273 (29.8), 201 (95.5), 73 (50.9). HRMS: $C_{20}H_{36}Si_4$ 388.1894 (calcd), 388.1896 (found). Anal. Calcd for $C_{20}H_{36}Si_4$: C, 61.78; H, 9.33. Found: C, 61.75; H, 9.25.

Spectral data for deuterated **3**: GC/MS: *m/z* (%) 389 (M$^+$, 25.5), 374 (24.6), 259 (100), 201 (22.6), 185 (23.0), 73 (39.3).

The product mixture was trapped by MeI (5.0 mL, 0.080 mol) and Me_3SiCl (10 mL, 0.080 mol), in a manner similar to that described above, to give compounds **4** (82%, GC yield) and **5** (85%, GC yield), respectively. We carried out the workup procedures in a manner similar to that used in the MeOH(D) trapping experiments described above. The crude material was purified by silica gel chromatography (*n*-hexane) to afford **4** and **5** as colorless oils in

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(15) One of reviewers pointed out that intermediate **a**, if **a** lost LiBr, would form a silylene, which undergoes a 1,2-silyl migration to form a silene[16] and then subsequent cyclization of the lithium species onto the silene would form anion species, **d**. To clarify this assumption, after completing the reduction of $TsiSiBr_3$ to give **1** as described above, excess Et_3SiH was added into the reaction mixture at−78 °C. When the reaction mixture was slowly warmed up to room temperature, the corresponding silylene-trapped product was not obtained, which strongly supports that the silylene pathway could not be involved.

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52% yield (0.84 g, 0.002 mol) and 54% yield (1.03 g, 0.002 mol), respectively. Compounds **4** and **5** were characterized by NMR, GC/MS, EA, and HRMS.

Spectral data for **4**: ^{1}H NMR (400 MHz, chloroform-*d*): δ 0.08 (s, 9H), 0.18 (s, 9H), 0.23 (s, 9H), 0.26 (s, 3H), 2.09 (t, J = 8.52, 1H), 2.70 (d, J = 12.76, 1H), 6.42 (t, J = 9.90, 1H), 6.55 (d, J = 10.96, 1H), 7.01−7.04 (m, 4H). ^{13}C NMR (100 MHz, chloroform-*d*): δ 1.04, 5.32, 5.52 (C(Si(CH$_3$)$_3$)$_3$), 4.58 (SiCH$_3$), 5.80 (C(Si(CH$_3$)$_3$)$_3$), 23.4, 28.5 (CH), 124.5, 125.8, 126.4, 127.9 128.0, 129.0 (-CH=C). 137.3, 137.8 (ipso-C). ^{29}Si NMR (79.5 MHz, chloroform-*d*): δ −5.10, −2.77, 3.55 (C(Si(CH$_3$)$_3$)$_3$), 28.0 (SiCH$_3$). GC/MS: *m*/*z* (%) 402 (M$^+$, 53.7), 387 (27.5), 259 (100), 201 (54.1), 185 (39.6), 73 (61.3). HRMS: $C_{21}H_{38}Si_4$ 402.2051 (calcd), 402.2052 (found). Anal. Calcd for $C_{21}H_{38}Si_4$: C, 66.61; H, 9.51. Found: C, 66.63; H, 9.45.

Spectral data for **5**: ^{1}H NMR (400 MHz, chloroform-*d*): δ 0.19 (s, 9H), 0.24 (s, 27H), 2.36 (dd, J = 2.06, 13.30, 1H), 2.74 (d, J = 13.24, 1H), 5.85 (td, J = 1.63, 15.56, 1H), 6.76 (d, J = 7.76, 1H), 6.88−7.05 (m, 4H). ^{13}C NMR (100 MHz, chloroform-*d*): δ −1.89 (C(Si(CH$_3$)$_3$)$_3$), −0.05(SiSi(CH$_3$)$_3$), 5.62 (C(Si(CH$_3$)$_3$)$_3$), 22.68, 31.62 (CH), 124.1, 125.4, 125.8, 127.9, 130.3, 130.5 (-CH=C). 137.2, 140.8 (ipso-C). ^{29}Si NMR (79.5 MHz, chloroform-*d*): δ −4.31 (Si(CH$_3$)$_3$), −1.57 (C(Si(CH$_3$)$_3$)$_3$), 3.24 (SiSi(CH$_3$)$_3$). GC/MS: *m*/*z* (%) 460 (M$^+$, 20.9), 445 (8.1), 357 (37.5), 259 (60.2), 259 (60.2), 73 (100). HRMS: $C_{23}H_{44}Si_5$ 460.2289 (calcd), 460.2290 (found). Anal. Calcd for $C_{23}H_{44}Si_5$: C, 61.78; H, 9.33. Found: C, 61.77; H, 9.39.

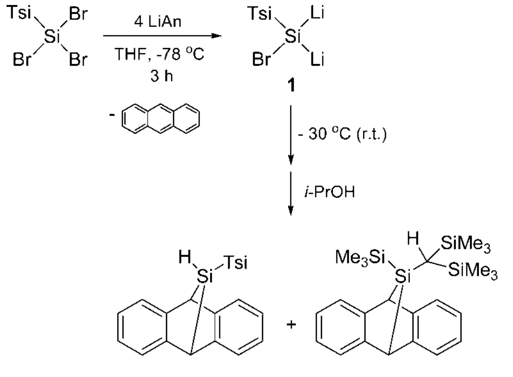
Synthesis of 6 and 7. Anthracene (3.0 g, 0.017 mol) dissolved in THF (40 mL) was added to Li (0.132 g, 0.019 mol) at room temperature. After the mixture was stirred for 3 h, LiAn was obtained as a dark blue solution. When TsiSiBr$_3$ (2.0 g, 0.004 mol) was reduced by LiAn for 3 h at −78 °C, the dark blue color changed to dark brown. Then the reaction mixture was slowly warmed to −30 °C and then kept at that temperature for 1 h. The color of the solution turned from dark brown to light brown, containing LiBr as a precipitate. The treatment of the solution with excess *i*-PrOH at −30 °C gave the trapping products **6** and **7** in 27% and 54% GC yields, respectively. After the addition of *n*-hexane (50 mL) into the resulting reaction mixture, precipitated species were removed by filtration. From the filtrate, solvents were removed using a rotary evaporator. The crude material was separated by silica gel chromatography (*n*-hexane) to give **6** and **7** as white powders, which were recrystallized from *n*-hexane to give colorless crystals **6** and **7**, respectively. Compounds **6** and **7** were characterized by NMR, GC/MS, EA, HRMS, and X-ray single crystallography.

After reducing TsiSiBr$_3$ (2.0 g, 0.004 mol) with LiAn in a manner similar to that described above, the reaction mixture was slowly warmed to room temperature and then kept at that temperature for 3 h. The color of the solution turned from dark brown to light brown, containing a white solid. The treatment of the solution with excess *i*-PrOH at room temperature gave only **7** in 78% GC yield.

Spectral data for **6**: Colorless crystals (mp = 203−205 °C). ^{1}H NMR (500 MHz, chloroform-*d*): δ 0.10 (s, 27H), 3.94 (s, 2H), 4.03 (s, 1H), 7.01−7.06 (m, 4H), 7.32−7.33 (m, 4H). ^{13}C NMR (120 MHz, chloroform-*d*): δ 3.96 (C(Si(CH$_3$)$_3$)$_3$), 8.32 (C(Si(CH$_3$)$_3$)$_3$), 47.0 (CH), 122.5, 123.9, 124.7, 125.4 (-CH=C), 144.5, 145.8 (ipso-C). ^{29}Si NMR (79.5 MHz, chloroform-*d*): δ −1.4 (C(Si(CH$_3$)$_3$)$_3$), 45.0 (Si-H). GC/MS: *m*/*z* (%) 438 (M$^+$, 16.0), 423 (8.9), 260 (73.8), 245 (32.0), 201 (69.2), 187 (100), 178 (49.4), 73 (34.0). HRMS: $C_{24}H_{38}Si_4$ 438.2051 (calcd), 438.2052 (found). Anal. Calcd for $C_{24}H_{38}Si_4$: C, 65.68; H, 8.73. Found: C, 65.61; H, 8.74.

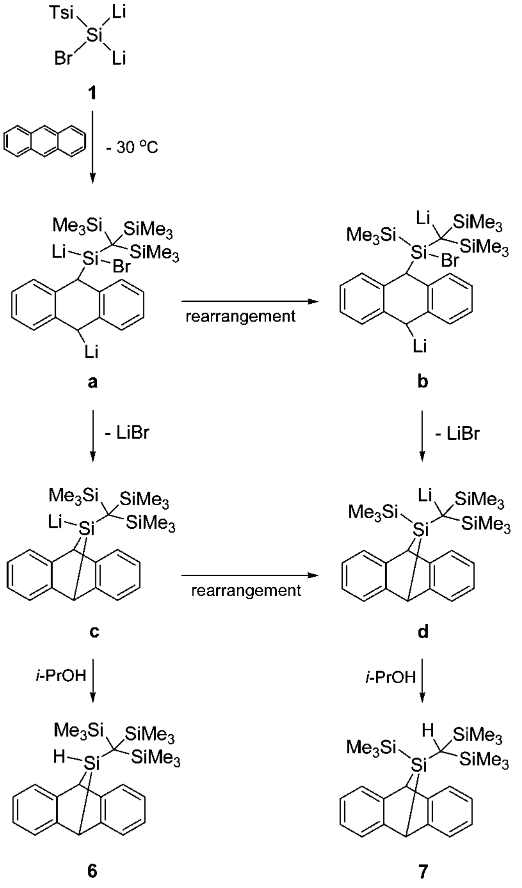
Spectral data for **7**: Colorless crystals (mp = 144−146 °C). ^{1}H NMR (500 MHz, chloroform-*d*): δ −0.07 (s, 9H), 0.05 (s, CH), 0.16 (s, 18H), 3.82 (s, 2H), 7.61−7.37 (m, 8H). ^{13}C NMR (120 MHz, chloroform-*d*): δ −0.31 (Si−Si(CH$_3$)$_3$), 3.17 (CH(Si(CH$_3$)$_2$), 4.12 (CH(Si(CH$_3$)$_2$), 48.9 (CH), 123.3(× 2), 124.1, 124.7 (-CH=C). 145.0, 146.0 (ipso-C). ^{29}Si NMR (79.5 MHz, chloroform-d): δ −11.3 (Si-SiMe$_3$), −0.65 (C(Si(CH$_3$)$_3$)$_2$), 75.5 (Si-SiMe$_3$). GC/MS: *m*/*z* (%) 438 (M$^+$, 26.6), 423 (9.8), 365 (13.5), 260 (20.1), 245 (12.6), 178 (92.0), 129 (100), 73 (55.6). HRMS: $C_{24}H_{38}Si_4$ 438.2051 (calcd), 438.2050 (found). Anal. Calcd for $C_{24}H_{38}Si_4$: C, 65.68; H, 8.73. Found: C, 65.69; H, 8.68.

Scheme 2. Reaction of Bromodilithiosilane, 1, with Anthracene



6, 27% (0%) **7**, 54% (78%)

Scheme 3. Plausible Mechanisms for the Formation of 6 and 7



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Supporting Information Available: Crystallographic information files (CIF) of compounds **6** and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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