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UNEXPECTED FORMATION OF DIHYDROBENZOSILOLE DERIVATIVE *VIA* THE INTRAMOLECULAR CYCLIZATION IN THE REACTION OF OVERCROWDED DICHLOROMETHYLSILANE WITH ARYLLITHIUM[#]

Takahiro Sasamori,* Eiko Mieda, and Norihiro Tokitoh*

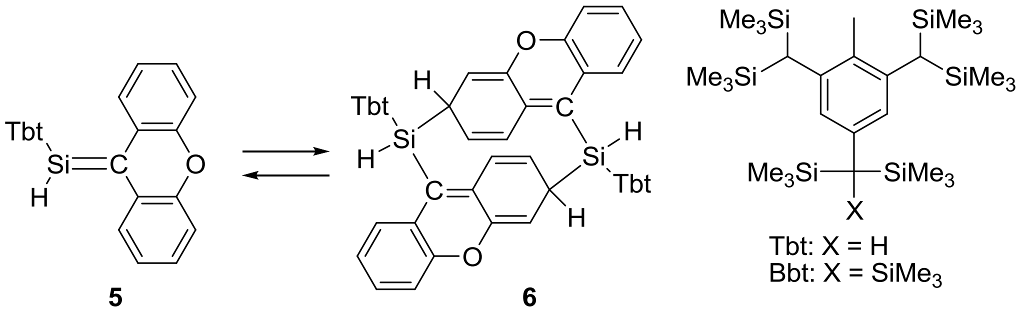
Author's address and e-mail address: Institute for Chemical Research, Kyoto University, Gokasho, Uji, Kyoto 611-0011, JAPAN
sasamori@boc.kuicr.kyoto-u.ac.jp, tokitoh@boc.kuicr.kyoto-u.ac.jp

Abstract – The reaction of overcrowded aryldichloromethylsilane **1** bearing a 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl (Bbt) group with an excess amount of XylLi or MesLi (Xyl = 2,6-xylyl, Mes = mesityl) unexpectedly afforded the corresponding dihydrobenzosilole derivative **2** together with silyl-migrated olefin **3**. The generation of **2** in this reaction is most likely interpreted in terms of intermediacy of 1,2-dihydro-2-chlorosilene **4**.

Dedicated to Prof. Dr. Albert Eschenmoser on the occasion of his 85th birthday.

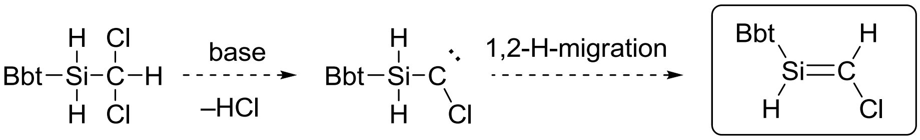
There has been much interest in low-coordinated species of heavier group 14 elements such as silylenes ($R_2Si:$), silenes ($R_2Si=CR_2$), and disilenes ($R_2Si=SiR_2$).[1] Generally, such species are too reactive to be synthesized and isolated as stable, monomeric compounds, but they can be isolated as stable species when they are well kinetically stabilized with using bulky substituents. Since these species are highly active toward addition reaction even in the case that they are well protected by the bulky substituents, they are good building blocks of heterocyclic compounds containing heavier group 14 elements. From this point of view, low-coordinated organosilicon compounds bearing a reactive site such as an Si–H bond or a halogen atom should be a potentially good precursor of heterocyclic compounds bearing further reactive site. Thus, we have focused our interest on silenes (Si=C) bearing a reactive site such as an Si–H, Si–Cl, or C–Cl bond. From this point of view, we have reported the synthesis of 1-hydrosilene derivative **5**, which underwent slow dimerization giving the corresponding [6+6] dimer **6**.[2] In this paper, we present the attempted synthesis of 1,2-dihydro-2-chlorosilene derivative **4** bearing

2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl (Bbt) group as a steric protection group by the expected intramolecular migration of a hydrogen atom of chlorodihydrosilylcarbene **7**. As a result, the reactions of Bbt-substituted dichloromethyldihydrosilane **1** with ArLi (Ar = Xyl, Mes; Xyl = 2,6-xylyl, Mes = mesityl) resulted in the unexpected formation of cyclic products, dihydrobenzosiloles **2**.



5 **6**

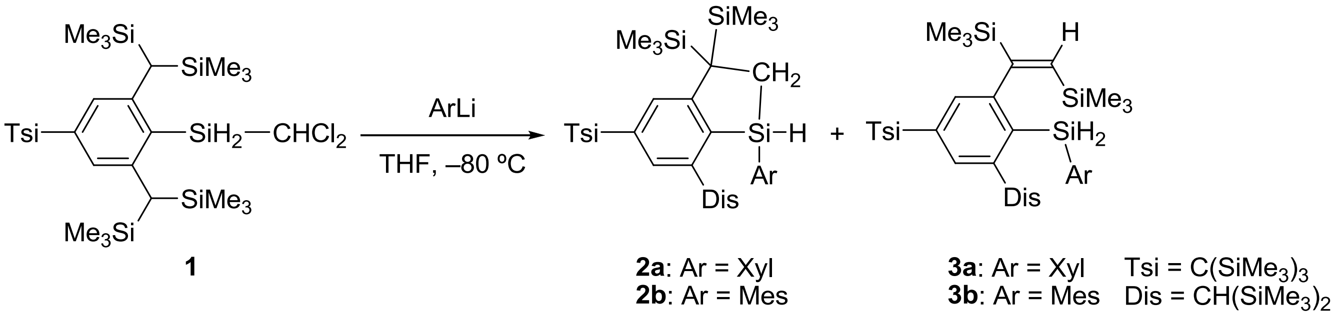
Scheme 1



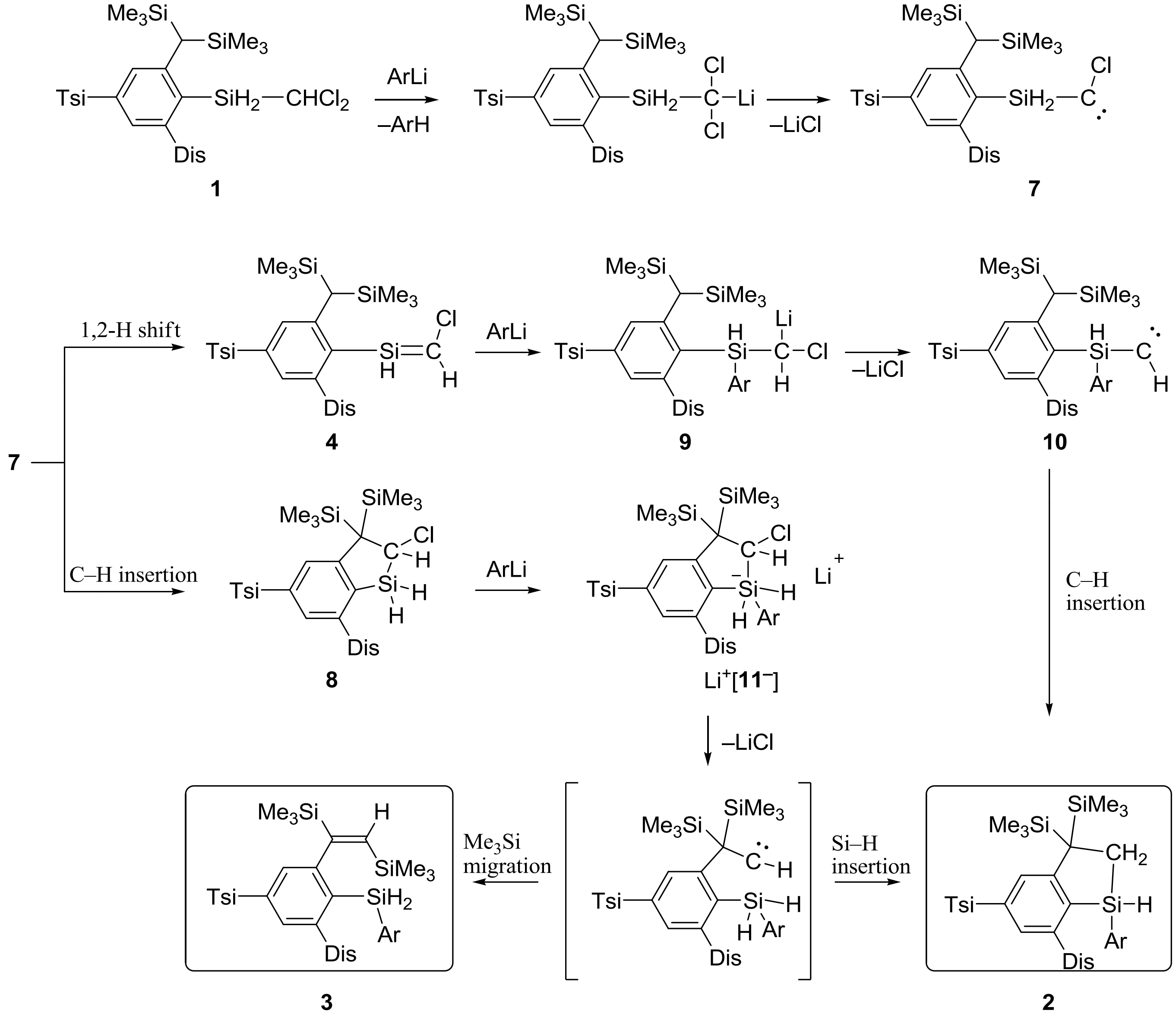
1 **7** **4**

Scheme 2

When BbtSiH$_3$ (657 mg, 1.00 mmol)[3] was treated with Cl$_3$COONa (1.85 g, 10 mmol) in toluene in the presence of 18-crown-6 (27.4 mg, 0.100 mmol) and heated under the reflux conditions, dichloromethyldihydrosilane **1** was obtained as colorless crystals in 87% yield (641 mg, 0.868 mmol).[4] The structure of **1** was definitively characterized by the spectroscopic and X-ray crystallographic analyses as shown in Figure 1(a).[5] It was shown that it has a space around the Si–C moiety enough to react with external reagents, even though the Bbt group is very bulky and may suppress the self dimerization of the resulting molecules. Compound **1** was treated with an excess amount (2.5 eq.) of XylLi as a base in THF at –80 ºC in the expectation of generating chlorosilylcarbene **7**, which further undergoes intramolecular 1,2-hydrogen shift giving 2-chloro-1,2-dihydrosilene **4**.[6,7] However, instead of expected silene **4**, dihydrobenzosilole **2a** (20%) and olefin **3a** (20%) were isolated as stable crystalline compounds.[8] In the case of using MesLi instead of XylLi under the same conditions, similar products of **2b** and **3b** were obtained in 32 and 16% yields, respectively (estimated by ^{1}H NMR spectrum).[9] The obtained products, **2a,b** and **3a,b**, were characterized by the spectroscopic analysis, and the molecular structures of **2a** and **3a** were revealed by the X-ray crystallographic analysis (Figure 1).[5] Unexpected product **2a** is a unique, overcrowded dihydrobenzosilole derivative bearing trimethylsilyl groups.



Scheme 3. Reaction of **1** with an excess amount of ArLi (Ar = Xyl, Mes)



Scheme 4. Plausible mechanism for the formation of **2** and **3**

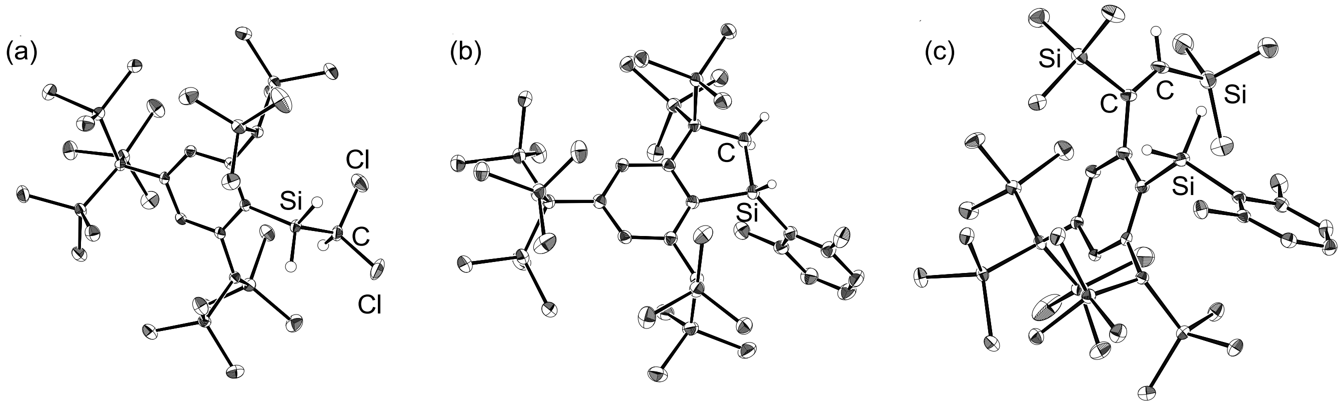


Figure 1. Molecular structures of compounds **1** (a), **2a** (b), and **3a** (c). Displacement ellipsoids were drawn at the 30% probability level[5]

The formation of compounds **2a,b** and **3a,b** is interesting and important from the viewpoints of the reactivity of extremely hindered chlorosilylcarbene **7** and a unique synthetic method for a dihydrobenzosilole derivative, although the detailed reaction mechanism leading to the formation of **2** and **3** is unclear at present. The plausible reaction mechanism for the formation of **2** and **3** is shown in Scheme 4. At the first stage of the reaction of **1** with ArLi (Ar = Mes or Xyl), deprotonation reaction would possibly occur at the CH moiety of the $CHCl_2$ unit of **1** to afford chlorosilylcarbene **7**.[6,7] Attempted intermolecular trapping reaction of **7** using an excess amount of 2,3-dimethyl-1,3-butadiene was unsuccessful, indicating the intramolecular rearrangement reaction of **7** would proceed faster than the intermolecular reaction. Simply thinking, two types of intramolecular rearrangement may be possible for carbene **7**, i. e., the 1,2-hydrogen shift to afford expected silene **4** and the C–H insertion at the benzyl position of the Bbt group giving **8**.[6,7] Since the obtained products, **2** and **3**, were found to have an additional aryl group (Mes or Xyl) on the ring silicon atom, excess ArLi would react with the reactive intermediate **4** or **8**. In the path through silene **4**, ArLi would attack the silicon atom of the Si=C moiety giving carbenoid **9** due to the following reason.[7] The LUMO of silene **4** exhibits large contribution of the p-orbital of the Si atom on the basis of the results of theoretical calculations on model compound **4'** (Figure 2).[10] In addition, the resulting anionic species of **9** would be stabilized by the α-effect of a silicon atom. Carbenoid **9** thus generated would readily afford silylcarbene **10** along with the elimination of LiCl, and then silylcarbene **10** would undergo intramolecular cyclization *via* the C–H insertion at the benzyl position of the Bbt group to give compound **2**. Thus, the formation of compound **2** is interpreted in terms of the intermediacy of silene **4**. Although the formation of compound **3** cannot be reasonably explained by the reaction mechanism *via* **4**, detailed theoretical calculations on the model molecules[10] having 2,6-$[(CH(SiMe_3)_2]_2$-C_6H_3 group instead of the Bbt group suggested another reaction mechanism for the formation of both **2** and **3**. Since the LUMO of dihydrobenzosilole **8**, which consists of a π orbital containing an Si moiety with Si–H σ* orbital, would lie in relatively low energy (that of model compound **8’** is computed as –0.59 eV), ArLi can attack **8** at the Si atom to give the corresponding silicate (Figure 2). In the theoretical calculations, silicate **11’**$^-$ (model compound of **11**$^-$) was optimized as a local minimum, indicating that silicate **11**$^-$ can exist as a meta-stable species (Figure 3). Two pseudo-rotational isomers of silicate **11’** $^-$ were found as the optimized structures, **11’A**$^-$ (trigonal bipyramidal structure; H, C(Cl): axial, aryl groups and H: equatrial) and **11’B**$^-$ (pseudo pyramidal), which would be transformed to each other *via* pseudo-rotation due to the small energy difference (0.57 kcal/mol). When a Li$^+$ was located around each Cl atom (2.20 Å from the Cl atom) of **11’A**$^-$ and **11’B**$^-$, their structural optimization resulted in the structures of products **2’** and **3’**, respectively, along with the elimination of LiCl without energy-barrier (Figure 4).[11] That is, Li$^+$[**11**$^-$] generated by the reaction of **8** with ArLi would undergo elimination of LiCl followed by the Si–H insertion and 1,2-migration of the SiMe$_3$ group to give **2** and **3**, respectively. Although the reaction mechanism for the formation of **2** and **3** is unclear at present, these theoretical investigations indicated that silene **4** and/or dihydrobenzosilole **8** generated from chlorosilylcarbene **7** would be a key intermediate in this reaction. Especially, it is of great interest that the possible reaction pathway *via* the intermediacy of silicate species of Li$^+$[**11**$^-$] giving **2** and **3** was suggested by theoretical calculations.

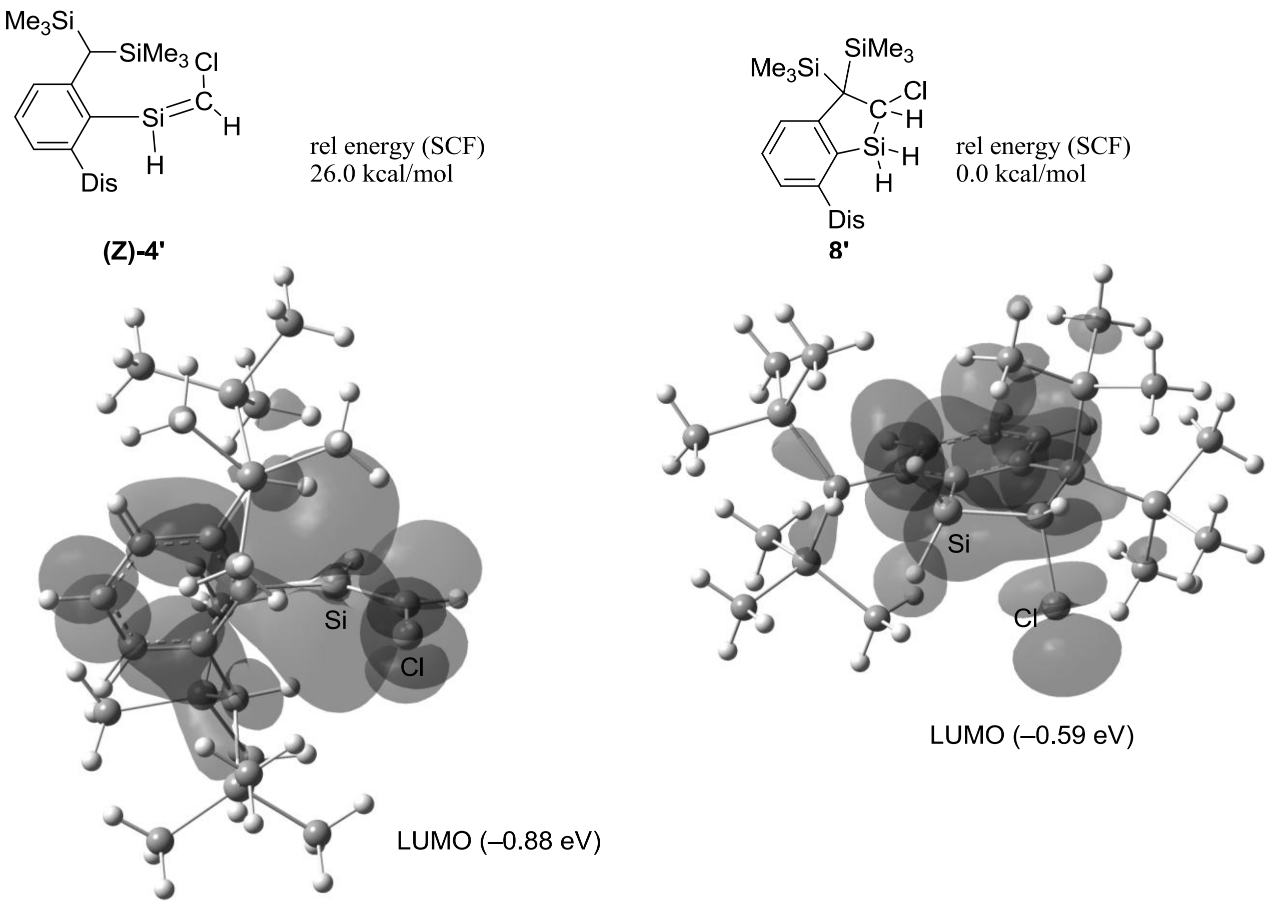
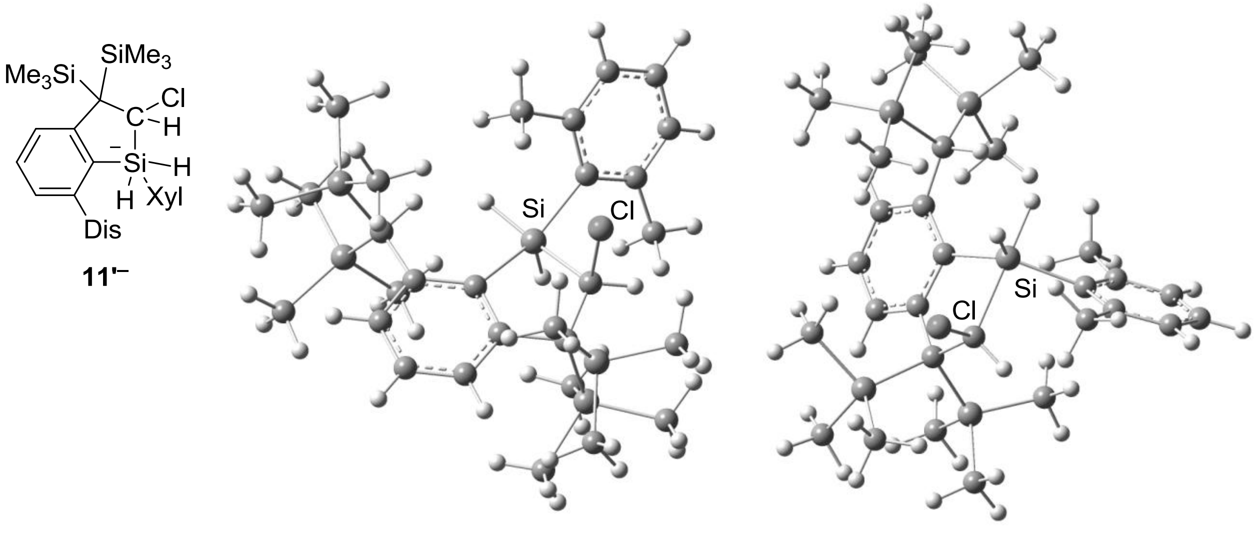


Figure 2. LUMO of compounds **4’** and **8’**



11'A⁻
optimized structure
relative energy (SCF): 0.0 kcal/mol

11'B⁻
optimized structure
relative energy (SCF): 0.57 kcal/mol

Figure 3. Optimized structures of **11'**$^-$

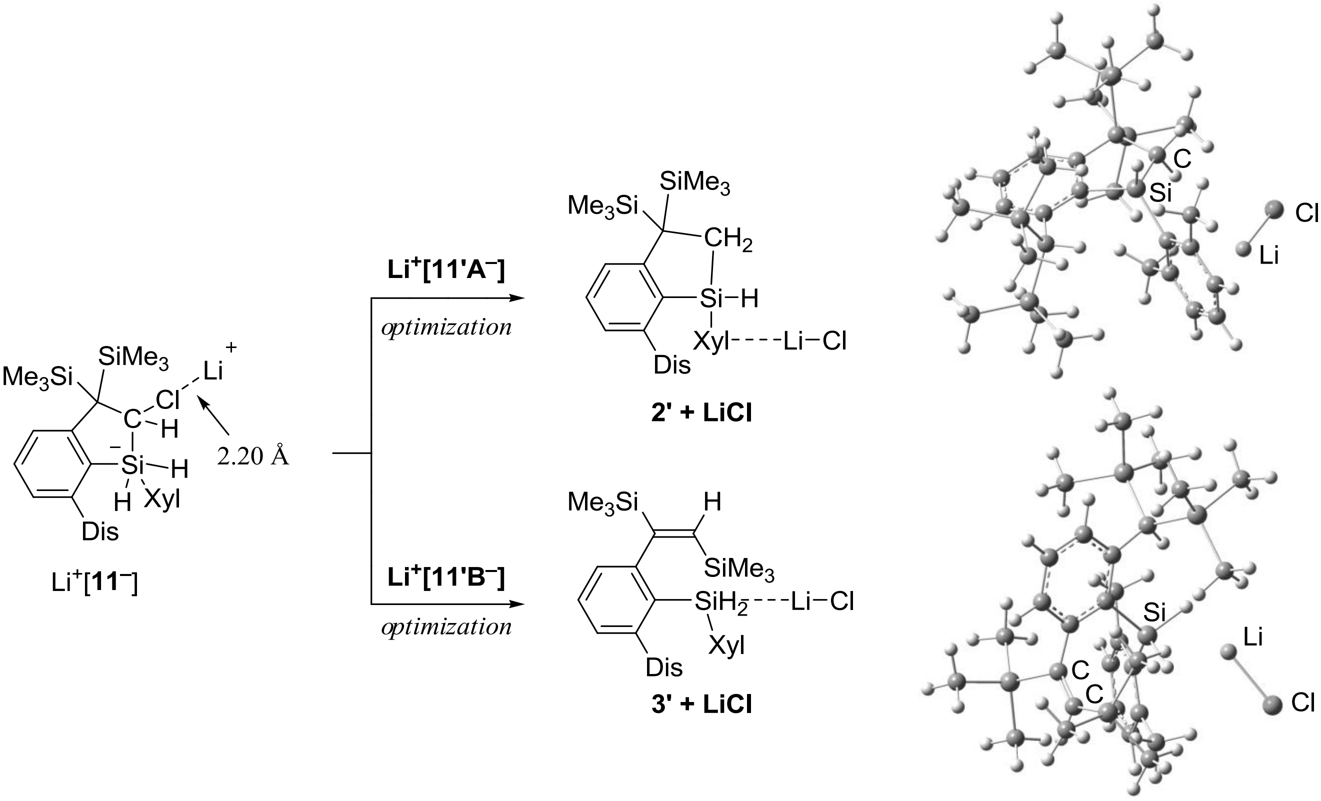


Figure 4. Structural optimization of silicate **11'**$^-$ in the presence of Li^+

In the expectation of obtaining **4** and/or **8**, the reaction of **1** (50.3 mg, 0.068 mmol) with an equimolar amount of MesLi was examined. As a result, a complicated mixture containing a small amount of **1** was obtained, indicating the possible intermediates would be highly reactive under these conditions. The crude mixture was subjected to column chromatography (SiO_2, *n*-hexane) to give starting material **1** (11.5 mg, 15.5 μmol, 22%) together with some unidentifiable products.[12]

In summary, a unique heterocyclic compound, dihydrobenzosilole **2**, was unexpectedly obtained together with olefin **3** by the reaction of **1** with an excess amount of ArLi (Ar = Mes or Xyl). Although we have examined the reaction of **1** with an equimolar amount of MesLi in the expectation of obtaining possible intermediates, it was unsuccessful and no useful information was obtained for the formation of **2** and **3**. Theoretical calculations using model compounds indicated that the possible key intermediates would be silene **4** and/or silicate $\mathbf{11}^{-}$. This unique reactivity of **1** is of great importance in view of the construction of novel Si-containing heterocyclic compounds.

ACKNOWLEDGEMENTS

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REFERENCES (AND NOTES)

1. For reviews, see: A. G. Brook and M. A. Brook, *Adv. Organomet. Chem.*, 1996, **39**, 71; J. Escudié, C. Couret, and H. Ranaivonjatovo, *Coordin Chem Rev.*, 1998, **180**, 565; T. L. Morkin and W. J. Leigh, *Acc. Chem. Res.*, 2001, **34**, 129; L. E. Gusel'nikov, *Coord. Chem. Rev.*, 2003, **244**, 149; H. Ottosson and P. G. Steel, *Chem.-Eur. J.*, 2006, **12**, 1576; M. Kira and T. Iwamoto, *Adv. Organomet. Chem.*, 2006, **54**, 73; P. Jutzi, *Angew. Chem. Int. Ed.*, 2000, **39**, 3797; R. Okazaki and R. West, *Adv. Organomet. Chem.*, 1996, **39**, 231; Y. Mizuhata, T. Sasamori, and N. Tokitoh, *Chem. Rev.*, 2009, **109**, 3479.
2. S. Ozaki, T. Sasamori, and N. Tokitoh, *Organometallics*, 2008, **27**, 2163.
3. N. Tokitoh, K. Wakita, T. Matsumoto, T. Sasamori, R. Okazaki, N. Takagi, M. Kimura, and S. Nagase, *J. Chin. Chem. Soc.*, 2008, **55**, 487.
4. Experimental procedures and chemical data: To a toluene solution (3 ml) of $BbtSiH_3$ (1.00 mmol, 655.6 mg) and 18-crown-6 ether (27.4 mg, 0.104 mmol) was added Cl_3COONa (1.85 g, 10.0 mmol) and the mixture was refluxed for 6 h. After cooling at room temperature, benzene was added to the reaction mixture. The resulting suspension was filtered through Celite® and the solvent was removed. The residue was separated by wet column chromatography (*n*-hexane) to afford **1** (641 mg, 0.868

mmol, 87%). **1**: mp 154.9 °C (decomp.), IR (neat), ν (Si-H) 2181 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.76 (s, 2H), 5.49 (t, *J* = 3 Hz, 1H), 4.84 (d, *J* = 3 Hz, 2H), 2.07 (s, 2H), 0.25 (s, 27H), 0.07 (s, 36H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.60 (s), 148.98 (s), 126.22 (d), 123.80 (s), 59.26 (d), 32.09 (d), 22.99 (s), 5.48 (q), 1.38 (q). ^{29}Si NMR (59 MHz, $CDCl_3$) δ 2.00, 0.85, –30.37. HRMS(FAB) *m/z* calcd for $C_{31}H_{70}Si_8{}^{35}Cl_2$ (M^+): 736.3009, found: 736.3009. Anal. Calcd for $C_{31}H_{70}Si_8Cl_2$: C, 50.42; H, 9.55. Found: C, 50.17; H, 9.57.

5. X-Ray crystallographic data for **1** ($C_{31}H_{70}Cl_2Si_8$): M = 738.49, *T* = 103(2) K, monoclinic, $P2_1/n$ (no.14), $a = 9.579(3)$ Å, $b = 36.546(11)$ Å, $c = 12.922(4)$ Å, $\beta = 102.943(3)$°, $V = 4409(2)$ Å^3, $Z = 4$, $D_{calc} = 1.113$ g cm^{-3}, $\mu = 0.384$ mm^{-1}, λ = 0.71070 Å, $2\theta_{max} = 51.0$, 35196 measured reflections, 8166 independent reflections ($R_{int} = 0.0499$), 399 refined parameters, GOF = 1.140, $R_1 = 0.0455$ and $wR_2 = 0.0969$ [$I>2\sigma(I)$], $R_1 = 0.0574$ and $wR_2 = 0.1029$ [for all data], largest diff. peak and hole 0.443 and -0.327 e.Å^{-3}. X-Ray crystallographic data for **2a** ($C_{39}H_{78}Si_8$): M = 771.73, *T* = 103(2) K, monoclinic, P–1 (no.2), $a = 12.6047(5)$ Å, $b = 13.5218(6)$ Å, $c = 16.5215(13)$ Å, $\alpha = 96.538(2)$°, $\beta = 102.503(3)$°, $\gamma = 117.019(3)$°, $V = 2375.0(2)$ Å^3, $Z = 2$, $D_{calc} = 1.079$ g cm^{-3}, $\mu = 0.251$ mm^{-1}, λ = 0.71069 Å, $2\theta_{max} = 51.0$, 20766 measured reflections, 8786 independent reflections ($R_{int} = 0.0583$), 451 refined parameters, GOF = 1.022, $R_1 = 0.0556$ and $wR_2 = 0.1317$ [$I>2\sigma(I)$], $R_1 = 0.0893$ and $wR_2 = 0.1506$ [for all data], largest diff. peak and hole 0.516 and -0.361 e.Å^{-3}. X-Ray crystallographic data for **3a** ($C_{39}H_{78}Si_8$): M = 771.73, *T* = 103(2) K, monoclinic, $P2_1/n$ (no.14), $a = 12.3778(2)$ Å, $b = 16.9921(3)$ Å, $c = 22.7508(4)$ Å, $\beta = 92.7957(9)$°, $V = 4779.36(14)$ Å^3, $Z = 4$, $D_{calc} = 1.073$ g cm^{-3}, $\mu = 0.249$ mm^{-1}, λ = 0.71069 Å, $2\theta_{max} = 50.0$, 40306 measured reflections, 8411 independent reflections ($R_{int} = 0.0684$), 474 refined parameters (36 restraints), GOF = 1.078, $R_1 = 0.0569$ and $wR_2 = 0.1249$ [$I>2\sigma(I)$], $R_1 = 0.0824$ and $wR_2 = 0.1405$ [for all data], largest diff. peak and hole 0.969 and -0.328 e.Å^{-3}. Crystallographic data (excluding structure factors) for the structures of **1**, **2a**, and **3a** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 780078-780080. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; E-mail: deposit@ccdc.cam.ac.uk.). The intensity data were collected on a Rigaku/MSC Mercury CCD diffractometer. The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELXL-97).

6. K. Schmohl, T. Gross, H. Reinke, and H. Oehme, *Z. Anorg. Allg. Chem.*, 2000, **626**, 1100; K. Schmohl, H. Reinke, and H. Oehme, *Z. Anorg. Allg. Chem.*, 2001, **627**, 2619.

7. M. Mickoleit, K. Schmohl, R. Kempe, and H. Oehme, *Angew. Chem. Int. Ed.* 2000, **39**, 1610; U.

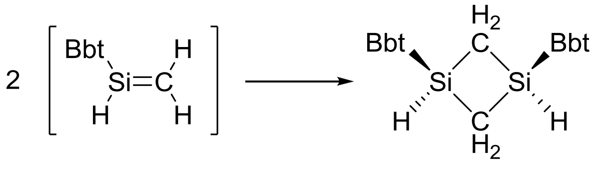
Bäumer, H. Reinke, and H. Oehme, *J. Organomet. Chem.*, 2006, **691**, 229.

8. Experimental procedures and chemical data: To a THF solution (1 mL) of **1** (73.4 mg, 0.10 mmol) was added 2,6-dimethylphenyllithium (0.30M in THF, 0.845 mL, 0.25 mmol) at –80 °C. After stirring at the same temperature for 1 h, the reaction mixture was allowed to warm up to room temperature. The solvent was evaporated under reduced pressure and hexane was added to the residue. Insoluble inorganic salts were removed by filtration through Celite®. Purification by GPLC and PTLC afforded **2a** (15.2 mg, 0.020 mmol, 20%), **3a** (15.6 mg, 0.020 mmol, 20 %). **2a**: mp 159.0 °C (decomp.) ^{1}H NMR (300MHz, $CDCl_3$) δ 7.16 (t, J = 6 Hz, 1H), 7.04 (d, J = 6 Hz, 1H), 6.88 (d, J = 6 Hz, 1H), 6.80 (s, 1H), 6.68 (s, 1H), 5.64 (dd, ^{1}J = 6 Hz, ^{3}J = 3 Hz, 1H, SiH), 2.66 (s, 3H), 2.13 (s, 3H), 1.53(dd, ^{2}J = 15 Hz, ^{3}J = 6 Hz, 1H), 1.42 (s, 1H), 1.30 (dd, ^{2}J = 15 Hz, ^{3}J = 3 Hz, 1H), 0.24 (s, 27H), 0.18 (s, 9H), 0.06 (s, 9H), 0.01 (s, 9H), –0.33 (s, 9H). ^{13}C NMR (75MHz, $CDCl_3$) δ 159.25 (s), 149.55 (s), 147.43 (s), 145.92 (s), 145.72 (s), 132.67 (s), 132.52 (s), 130.33 (d), 128.77 (d), 128.29 (d), 126.66 (d), 124.45 (d), 33.50 (d), 32.41 (s), 26.66 (q), 25.55 (q), 22.46 (s), 13.96 (t), 5.78 (q), 1.80 (q), 1.77 (q), 1.30 (q), 0.82(q). ^{29}Si NMR (60 MHz, $CDCl_3$) δ 8.15, 4.35, 2.66, 0.95, 0.72, –16.9. HRMS (FAB) *m/z*: Calcd for $C_{39}H_{78}Si_8$ ([M$^+$]) 770.4258, found 770.4265. **3a**: mp 217.6 °C (decomp.) ^{1}H NMR (300MHz, $CDCl_3$) δ 7.17 (t, J = 7.5 Hz, 1H), 6.98 (d, J = 7.5 Hz, 2H), 6.80 (d, J = 2.1 Hz, 1H), 6.68 (d, J = 2.1 Hz, 1H), 6.26 (s, 1H), 4.97 (d, J = 3 Hz, 1H, SiH), 4.90 (d, J = 3 Hz, 1H, SiH), 2.46 (s, 6H), 1.97 (s, 1H), 0.23 (s, 27H), 0.05 (s, 9H), –0.07 (s, 9H), –0.11 (s, 9H), –0.12 (s, 9H). ^{13}C NMR (75MHz, $CDCl_3$) δ 167.47 (s), 154.10 (s), 151.45 (s), 144.85 (s), 144.49 (s), 144.27 (d), 133.20 (s), 129.67 (d), 127.89 (d), 127.65 (d), 126.45 (d), 122.14 (s), 29.02 (d), 25.24 (q), 4.95 (q), 1.53 (q), 1.31 (q), 0.00 (q), –0.49 (q). ^{29}Si NMR (60 MHz, $CDCl_3$) δ 1.96, 1.86, 0.80, –5.32, –9.04, –56.7. HRMS (APPI/TOF) *m/z*: Calcd for $C_{36}H_{69}Si_7$ ([M$^+$–$SiMe_3$]) 697.3779, found 695.3766.

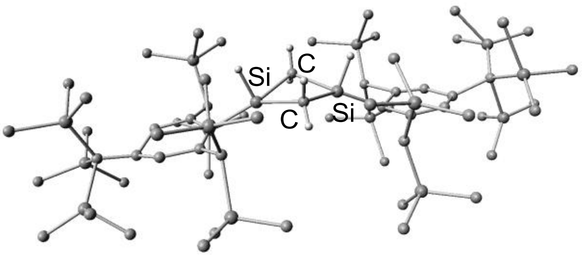
9. Experimental procedures and chemical data: To a THF solution (1 mL) of **1** (74.0 mg, 0.10 mmol) was added MesLi (0.125M in THF, 2.0 mL, 0.25 mmol) at -80 °C. After stirring at the same temperature for 1 h, the reaction mixture was allowed to warm up to room temperature. The solvent was evaporated under reduced pressure and hexane was added to the residue. Insoluble inorganic salts were removed by filtration through Celite®. Purification by GPLC and PTLC afforded mixture of **2b** and **3b**. (37.7 mg, 32 % of **2b** and 16 % of **3b** as judged by ^{1}H NMR spectrum). **2b**: mp 228.0 °C (decomp.) ^{1}H NMR (300MHz, $CDCl_3$) δ 6.87 (s, 1H), 6.79 (d, J = 1.6 Hz, 1H), 6.72 (s, 1H), 6.67 (d, J = 1.6 Hz, 1H), 5.61 (dd, ^{1}J = 6 Hz, ^{3}J = 3.5 Hz, 1H, SiH), 2.62 (s, 3H), 2.23 (s, 3H), 2.09 (s, 3H), 1.51 (dd, ^{2}J = 15 Hz, ^{3}J = 6.9 Hz, 1H), 1.44 (s, 1H), 1.27 (dd, ^{2}J = 15 Hz, ^{3}J = 3.5 Hz, 1H), 0.23 (s, 27H), 0.17 (s, 9H), 0.05 (s, 9H), 0.01 (s, 9H), –0.33 (s, 9H).

HRMS(FAB) *m/z*: Calcd for $C_{40}H_{80}Si_8$ ($[M^+]$) 784.4414, found 784.4415. ^{29}Si NMR (60 MHz, $CDCl_3$) δ 8.07, 4.29, 2.60, 0.95, 0.70, –16.7. **3b**: mp 192.8 °C (decomp.) ^{1}H NMR (300MHz, $CDCl_3$) δ 6.87 (s, 1H), 6.79 (d, *J* = 1.6 Hz, 1H), 6.72 (s, 1H), 6.67 (d, *J* = 1.6 Hz, 1H), 4.95 (d, *J* = 2.4 Hz, 1H, SiH), 4.87 (d, *J* = 2.4 Hz, 1H, SiH), 2.42 (s, 6H), 2.24 (s, 3H), 1.99 (s, 1H), 0.23 (s, 27H), 0.05 (s, 9H), –0.08 (s, 9H), –0.12 (s, 9H), –0.13 (s, 9H). ^{29}Si NMR (60 MHz, $CDCl_3$) δ 1.91, 1.84, 0.78, –5.39, –9.10, –56.6. HRMS(FAB) *m/z*: Calcd for $C_{40}H_{80}Si_8$ ($[M^+]$) 784.4414, found 784.4427.

10. All of the theoretical calculations described in this paper were performed at the B3LYP/6-31G(d) level using Gaussian 03 program. Since the calculations using real molecules related to our work using extremely large substituents cost extremely long time, model compounds bearing 2,6-$[(CH(SiMe_3)_2]_2$-C_6H_3 group instead of the Bbt group were used and Xyl group was chosen as Ar group for the calculations.
11. At present, the transition state was not found in the calculations of IRC and detailed structural optimization. Accordingly, it can be thought that these isomerization reactions would proceed without energy-barrier. However, the possibility of the existence of the transition state with very small energy-barrier cannot be completely excluded at this stage.
12. It was found that one of the unidentified products is silene-dimer **12** on the basis of the preliminary results of the X-ray crystallographic analysis of a single crystal obtained by the recrystallization of the mixture of unidentified products. Accordingly, another reaction pathway giving **2** and **3** *via* silene **13** may be taken into account in the reaction of **1** with ArLi. The data set of **12** was collected at beamline BL38B1 (Spring-8 Japan).



13 **12**



Hydrogen atoms other than those on the Si–C–Si–C four-membered ring systems were omitted for clarity.

molecular structure of **12**