Syntheses and Reactivities of Stable Halosilylenoids, $(Tsi)X_2SiLi$ ($Tsi = C(SiMe_3)_3$, $X = Br, Cl$)

Myong Euy Lee,*[a] Hyeon Mo Cho,[a] Young Mook Lim,[a] Jin Kyong Choi,[a] Chang Hee Park,[a] Seong Eun Jeong,[a] and Uk Lee[b]

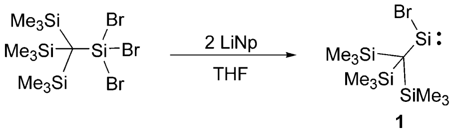
Abstract: Halosilylenoids, stable at room temperature $(Tsi)X_2SiLi$ ($Tsi = C(SiMe_3)_3$, $X = Br, Cl$), were synthesized from the reaction of $TsiSiX_3$ with lithium naphthalenide. Bromosilylenoid reacted with *t*BuOH and MeI both at −78 °C and at room temperature to give $(Tsi)HSiBr_2$ and $(Tsi)MeSiBr_2$, respectively, in high yields; this clearly shows its nucleophilicity. In the reaction of bromosilylenoid with methanol, 2-propanol, and 2,3-dimethyl-1,3-butadiene, the corresponding products, $(Tsi)HSi(OMe)_2$, (Tsi)HSi(O*i*Pr)Br, and bromo(Tsi)silacyclopent-3-ene, were obtained in high yields; this demonstrates its amphiphilic property, as if bromosilylene would be trapped. Chlorosilylenoid also exhibited both nucleophilic and amphiphilic properties. The ^{29}Si chemical shifts for $(Tsi)Br_2SiLi$, $(Tsi)Br_2SiK$, and $(Tsi)Cl_2SiLi$ were 106, 70, and 87 ppm, respectively.

Keywords: amphiphiles • NMR spectroscopy • silanes • silylenoids

Introduction

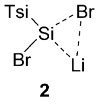
Silylenoid (R_2SiMX), a compound in which an electropositive metal (M) and a leaving group (X, usually halogen) are bound to the same silicon atom, has been postulated as an intermediate in the reduction of dihalosilanes to synthesize silylenes[1] or polysilanes.[2] In contrast to extensive experimental studies on carbenoids,[3] there are only a few experimental reports on silylenoids.[4,5] In 1995, Tamao and Kawachi reported the first experimental aspects of silylenoid chemistry. They studied $(tBuO)Ph_2SiLi$, which underwent bimolecular self-condensation at 0 °C.[6] In 1999, they focused on amine-coordinated silylenoid.[7] Tokitoh et al. reported that Tbt(Dip)SiLiBr (Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl, Dip = 2,6-diisopropylphenyl), as an intermediate, was generated in the reduction of the overcrowded dibromosilane with lithiumnaphthalenide.[8] However, no clear evidence for a stable alkylsilylenoid at room temperature has yet been reported.

Recently we reported the generation of stable bromosilylene (**1**) from the reduction of $(Tsi)SiBr_3$ ($Tsi = C(SiMe_3)_3$) with LiNp (lithium naphthalenide), but the result on its structure remained to be discussed (Scheme 1).[9]



Scheme 1. Reduction of $(Tsi)SiBr_3$.

Quite recently Wiberg and co-workers proposed that **1** might actually be a very weak LiBr adduct with Tsi(bromo)-silylene;[10] this implies the formation of a silylenoid species (**2**). In our efforts to elucidate this study, we have obtained experimental results confirming the structure of **2** in accord with the proposal above. We report here clear evidence that **1** was actually the silylenoid **2**; we also report on the synthesis of a stable chlorosilylenoid (**3**), as well as their reactivities.



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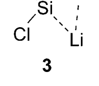

3

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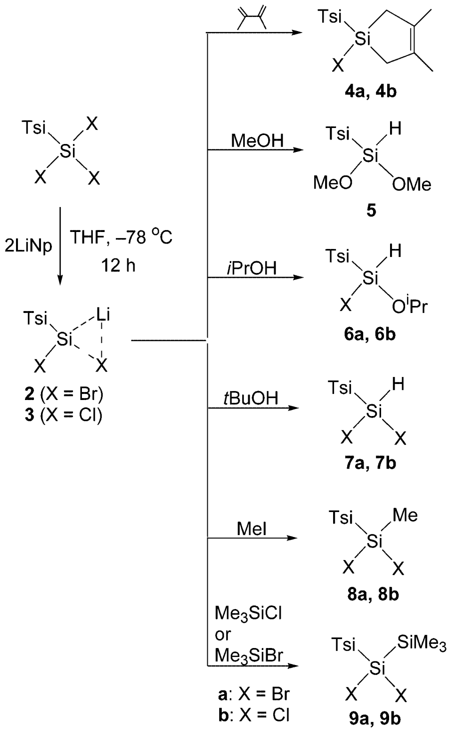
Results and Discussion

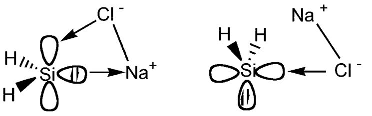
Bromosilylenoid **2** was synthesized by the reduction of tribromo(Tsi)silane with two equivalents of LiNp or KC$_8$. The bromosilylenoid-trapping products **4a**, **5**, and **6a** were formed from the reaction of **2** with an excess of 2,3-dimethyl-1,3-butadiene, MeOH, and 2-propanol, respectively.[9] These results confirm the ambiphilicity of silylenoid **2**, which is a typical property of silylenoid. In a similar manner, the reaction of **2** with an excess of *t*BuOH and MeI were carried out at −78 °C or room temperature to produce dibromo[tris(trimethylsilyl)methyl]silane (**7a**) and methyldibromo[tris(trimethylsilyl)methyl]silane (**8a**), respectively, in high yields (Scheme 2). These results show the nucleophilicity of **2** and a steric effect high enough not to form the expected product, Br(O*t*Bu)(Tsi)SiH.



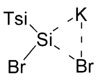
Scheme 2. Reactivities of halosilylenoids, **2** and **3** (**9a** was not obtained).

The two trapping products, **6a** and **7a**, obtained from the reaction of **2** with *i*PrOH and *t*BuOH imply that the reaction starts with the nucleophilic substitution reaction of **2**, followed by a substitution reaction of LiO*i*Pr. The reaction of **2** with 2,3-dimethyl-1,3-butadiene proceeded by either: 1) a silacyclopropane intermediate generated by the silylenoid addition into one of the double bonds in butadiene to give the corresponding β-lithiated silane, followed by an intramolecular nucleophilic attack of the anionic carbon to the silicon atom or 2) the allylic rearrangement of the corresponding β-lithiated silane to place the lithium atom on the terminal methylene carbon. There is no example of the reaction of a stable silylenoid with 2,3-dimethyl-1,3-butadiene, although discussions about the mechanism based on the one-pot reaction of dihalosilane, alkali metal, and 2,3-dimethyl-1,3-butadiene have been reported.[1]

Bromosilylenoid **2** did not react with triethylsilane. After the addition of an excess of triethylsilane to the dark orange solution of **2**, an excess of *i*PrOH was added to the reaction mixture; this only gave **6a**. These results strongly indicate that **2** is not a free silylene, a THF-solvated silylene, or a Br-bridged silylene dimer, as suggested in the previous report,[9] but a LiBr adduct with Tsi(bromo)silylene, which is a silylenoid species based on its reactivities shown above. Quite recently Flock and Dransfeld elucidated the solution structure of **2** by ab initio/NMR calculations, in accord with our experimental results.[11] This is the first example of the reactivity studies on the stable silylenoid at room temperature and it should be noted that the functionalized silylenoid has high synthetic potential. The ^{29}Si chemical shift for **2** from the reaction of tribromo(Tsi)silane and LiNp was 106 ppm, which was very different from the negative silicon resonances of simple anionic silicon compounds.[12] Although the substituents are different, the ^{29}Si resonance for nitrogen-substituted silyl anion, [Li{{Si(SiMe$_3$)$_3$}Si{(NCH$_2t$Bu)$_2$C$_6$H$_4$-1,2}}(thf)$_2$], was observed at 60 ppm,[13] which was the most deshielded silyl mono-anion known up to this time. The deshielding of **2** might be due to electron withdrawal by the bromine substituents and/or the association between Li and Br, which is explained below. The recent theoretical investigation of isomeric structures of H$_2$SiNaCl show that two basic structures have Na–Cl interactions and no classical tetrahedral structures.[5b,14] It was also reported in carbenoid chemistry that metal (lithium) coordinates with halogen atom and assists in the ionization of the halogen, thereby forming a carbon (cation)–halogen (anion) ion pair.[15]



The ^{29}Si chemical shift for **10** synthesized from the reaction of tribromo(Tsi)silane with two equivalents of KC$_8$ is 70 ppm at −60 °C; this also supports the assignment that compound **2** is the silylenoid species. Compound **10**, (Tsi)Br$_2$SiK, was less stable than **2**, as expected. Compound **10** slowly decomposed even at −40 °C, monitored by ^{29}Si NMR spectroscopy and by an analysis of MeOH-trapped products of the reaction mixture using gas chromatography.



10

Trichloro[tris(trimethylsilyl)methyl]silane[16] was reduced with two equivalents of LiNp or LDBB[17] (lithium di-*tert*-butylbiphenylide) at −78 °C in THF. The color of the solution slowly changed from dark green to brown. After stirring for 12 h all the starting material was consumed indicating the reaction was completed. In the case of using LDBB as a reducing reagent, the reaction was completed within one hour as bluish green changed to brown. To that solution, an excess of 2,3-dimethyl-1,3-butadiene cooled to −78 °C was added, whereupon the solution became light yellow. From the reaction mixture we obtained chloro(Tsi)silacyclopentene (**4b**) in 75 % isolated yield (Scheme 2). After the reduction of trichloro[tris(trimethylsilyl)methyl]silane was completed as described above, the reaction mixture was slowly warmed to room temperature; the brown color of the solution was slowly discharged as the temperature was increased. Adding an excess of 2,3-dimethyl-1,3-butadiene at room temperature gave compound **4b** in 17 % isolated yield. By using an excess of 2-propanol as a trapping agent, the corresponding halosilylenoid-trapping adduct, chloro(-isopropoxy)[tris(trimethylsilyl)methyl]silane (**6b**), was obtained in 64 % yield at −78 °C and in 11 % yield at room temperature. Similarly, the reaction of **3** with methanol gave dimethoxy[tris(trimethylsilyl)methyl]silane[18] (**5**) in 64 % yield at −78 °C and in 15 % yield at room temperature. The reaction mechanisms of **3** with trapping agents seem to be the stepwise pathways described in bromosilylenoid chemistry. It was found that the decomposition of **3** was slowly initiated at about −30 °C, even though **3** was moderately stable at room temperature, based on results monitored by an analysis of MeOH-trapped products of the reaction mixture using gas chromatography. Chlorosilylenoid **3** did not react with triethylsilane below −30 °C.

The ^{29}Si NMR spectrum of the reduction mixture containing **3** showed a gradual appearance of resonance due to central silicon atom at 87 ppm at −70 °C. The X-ray structure of **4b** is shown in Figure 1 and crystallographic data are given in Table 1. All atoms except a quaternary carbon in Tsi group appeared to be disordered, with two possible orientations in nearly equal probability ratio. The two C(1)-Si(1)-C(7) and C(7)-Si(1)-C(6) angles are somewhat large (119.8(3)° and 119.6(3)°) partially due to the bulkiness of Tsi group. The C(7)-Si(1)-Cl angle is 111.5(2)° and the C(6)-Si(1)-C(1) is 94.8(3)°. The silicon–carbon bond lengths around Si(1) are nearly same (1.877–1.879 Å).

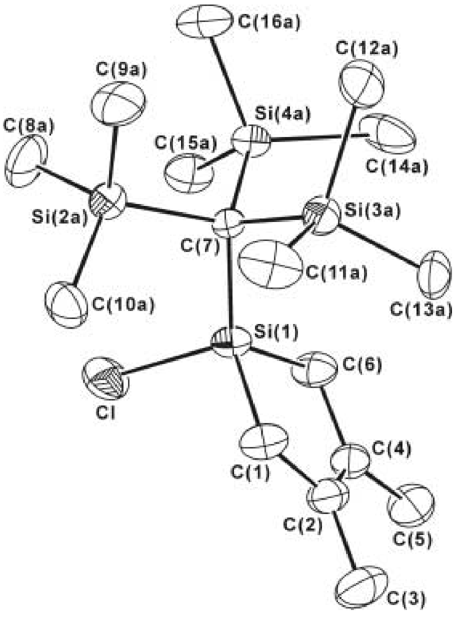


Figure 1. ORTEP[19] drawing of **4b**, showing with 30 % thermal ellipsoids. H atoms are omitted for clarity.

Table 1. Crystal data and structure refinement for **4b**.

formula	$C_{16}H_{37}ClSi_4$
M_r [g mol^{-1}]	377.27
cryst size [mm^3]	0.50 × 0.25 × 0.13
crystal color habit	colorless plate
crystal system	monoclinic
space group	*C*2/*c* (no. 15)
a [Å]	30.589(9)
b [Å]	13.173(3)
c [Å]	11.838(4)
β [°]	105.26(2)
V [Å^3]	4602(2)
Z	8
ρ_{calcd} [g cm^{-3}]	1.089
μ [mm^{-1}]	0.369
F (000)	1648
T [K]	298(2)
λ [Å]	0.71069
2θ range [°]	1.69–26.46
reflections collected	4764
data/parameters	4764/218
goodness-of-fit on F^2	1.120
final R indices [$I > 2\sigma(I)$]	R_1[a] = 0.0922, wR_2[b] = 0.1721
largest different peak/hole [e Å^{-3}]	0.41/−0.30

[a] $R = \Sigma[|F_o| - |F_c|]/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (0.0663P)^2 + 13.1160P]$, where $P = (F_o^2 + 2F_c^2)/3$.

In a similar manner, the reactions of **3** with an excess of *t*BuOH, MeI, and $XSiMe_3$ (X = Cl, Br) were performed at −78 °C to afford dichloro[tris(trimethylsilyl)methyl]silane (**7b**), methyldichloro[tris(trimethylsilyl)methyl]silane (**8b**) and trimethylsilyldichloro[tris(trimethylsilyl)methyl]silane (**9b**), respectively, in high yields. These results show that chlorosilylenoid **3** exhibits an amphiphilic property, as does bromosilylenoid **2**.

Experimental Section

In all reactions where 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 in reagent grade and used without further purification. Glassware was flame-dried under nitrogen or argon flushing prior to use. Experiments were performed under nitrogen or argon atmosphere. ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded on a Bruker AMX 500 NMR spectrometer and referenced to residual protons of the solvent with chemical shifts or silicon atom of tetramethylsilane. Analyses of product mixtures were accomplished by using a HP 5890 II with FID (HP-1, 15 m column) with dried decane as an internal standard. Mass spectra were recorded on a low resolution Shimadzu GCMS QP-2000A mass spectrometer and a high-resolution VG ANALITICLA 70-VSEQ mass spectrometer. Preparative gel permeation chromatography (GPLC) was performed by LC-10 with JAI gel AJ1H +2H columns with chloroform as solvent.

Synthesis of 4a: Naphthalene (1.28 g, 10 mmol) in THF (15 mL) was added to Li (0.08 g, 12 mmol) in at room temperature. After the mixture was stirred for 3 h, and LiNp was obtained as dark blue solution. LiNp in THF was added slowly to $TsiSiBr_3$ (2.0 g, 4.0 mmol) in THF (25 mL) at −78 °C. The solution was stirred for 12 h at that temperature. 2,3-Dimethyl-1,3-butadiene (5.0 mL, 44 mmol), cooled to −78 °C, was added rapidly to reaction mixture, after which the solution was stirred for 3 h. After addition of *n*-hexane at room temperature, the resulting mixture was washed with water. Volatiles were distilled under vacuum and naphthalene was removed by sublimation. The crude product was purified by GPLC with recycling to afford **4a** as colorless oil (1.2 g, 74 %). ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 0.32$ (s, 27 H), 1.63 (s, 4 H), 1.93 (br, 3 H), 2.14 ppm (br, 3 H); ^{13}C NMR ($CDCl_3$, 63 MHz): $\delta = 3.0$ ($SiMe_3$), 18.3 ($SiCH_2C$), 25.1 (CCH_3), 129.9 ppm (C=C); ^{29}Si NMR (99 MHz, C_6D_6): $\delta = -8.0$, -0.8 ppm; MS: *m*/*z* (%): 420 (12) [M^+], 405 (20), 267 (74), 73 (100); HRMS calcd for $C_{16}H_{37}BrSi_4$: 420.1156; found: 420.1153; elemental analysis calcd (%) for $C_{16}H_{37}BrSi_4$: C 45.57, H 8.84; found: C 45.54, H 8.81.

Using a procedure similar to that described for the trapping reaction for **2**, when the reduction mixture of $TsiSiBr_3$ with LiNp at −78 °C was slowly warmed to 25 °C, and kept at that temperature for 2 h, and then followed by addition of 2,3-dimethyl-1,3-butadiene to the mixture, compound **4a** was obtained.

Synthesis of 5: By a method similar to that used for **4a**, compound **5** was synthesized by the reaction of **2** or **3** with an excess of MeOH. Compound **5** was obtained as white solid (0.80 g, 62 %). M.p. 220–222 °C; ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 0.19$ (s, 27 H), 3.56 (s, 6 H), 4.51 ppm (s, H); ^{13}C NMR ($CDCl_3$, 63 MHz): $\delta = 4.04$ ($SiMe_3$), 52.1 ppm (OMe); MS: *m*/*z* (%): 322 (9) [M^+], 307 (53), 217 (100); HRMS calcd for $C_{12}H_{34}O_2Si_4$: 307.1341 [M^+-15]; found: 307.1398; elemental analysis calcd (%) for $C_{12}H_{34}Br_2Si_4$: C 44.66, H 10.62; found: C 44.67, H 10.62.

Synthesis of 6a: By a method similar to that used for **4a**, this compound was synthesized by the reaction of **2** with an excess of 2-propanol. Compound **6a** was obtained as colorless oil (1.1 g, 71 %). ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 0.29$ (s, 27 H), 1.23–1.26 (dd, 6 H), 4.30 (m, H), 5.56 ppm (s, H); ^{13}C NMR ($CDCl_3$, 63 MHz): $\delta = 4.57$ ($SiMe_3$), 4.99 ($C(SiMe_3)_3$), 24.74, 25.33 ($OCH(CH_3)_2$), 68.68 ppm ($OCH(CH_3)_2$); MS: *m*/*z* (%): 383 (9) [M^+-15], 341 (17), 261 (100), 187 (25), 173 (16), 73 (32); HRMS calcd for $C_{13}H_{35}OBrSi_4$: 383.0714 [M^+-15]; found: 383.0710; elemental analysis calcd (%) for $C_{13}H_{35}OBrSi_4$: C 39.07, H 8.83; found: C 39.02, H 8.81.

Syntheses of 7a and Br(O*t*Bu)(Tsi)SiH: LiNp (9.0 mmol) in THF (15 mL) was added slowly to $TsiSiBr_3$ (2.0 g, 4.0 mmol) in THF (25 mL) at −78 °C. The solution was stirred for 12 h at that temperature. *t*BuOH (5.0 mL, 52 mmol) cooled to −78 °C was added rapidly to the reaction mixture, and the solution was stirred for 1 h. After addition of *n*-hexane at room temperature, the resulting mixture was washed with water. Volatiles were distilled under vacuum and naphthalene was removed by sublimation. The crude product was purified by GPLC with recycling to afford **7a** (1.26 g) in 75 % yield as colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 0.37$ (s, 27 H), 5.62 ppm (s, 1 H); ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta = 4.25$ ppm ($SiMe_3$); MS: *m*/*z* (%): 405 (100) [M^+-15], 317 (11), 253 (36), 129 (34), 73 (85); elemental analysis calcd (%) for $C_{10}H_{28}Br_2Si_4$: C 28.56, H 6.71; found: C 28.51, H 6.68.

By using a procedure similar to that described above, after the reduction mixture was slowly warmed to room temperature, addition of *t*BuOH to the mixture gave compound **7a**. On the other hand, the reaction mixture was warmed to about 50 °C to give Br(O*t*Bu)(Tsi)SiH (0.86 g) in 52 % yield as colorless oil. The crude product was purified by GPLC.

Br(O*t*Bu)(Tsi)SiH: ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 0.29$ (s, 27 H), 1.41 (s, 9 H), 5.63 ppm (s, H); ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta = 4.50$ ($SiMe_3$), 30.95 ($C(CH_3)_3$), 62.65 ppm ($C(CH_3)_3$); MS: *m*/*z* (%): 397 (2) [M^+-15], 341 (62), 261 (100), 187 (25), 73 (75); elemental analysis calcd (%) for $C_{14}H_{37}BrOSi_4$: C 40.65, H 9.01; found: C 40.69, H 9.04.

Synthesis of 8a: MeI (3.5 mL, 56 mmol) was added rapidly to the reaction mixture of **2** in THF (40 mL) at −78 °C, the solution was stirred for 1 h. After addition of *n*-hexane at room temperature, the resulting mixture was washed with water. Volatiles were distilled under vacuum and naphthalene was removed by sublimation. The crude product was purified by GPLC with recycling to afford **8a** (1.3 g) in 74 % yield as colorless crystals. A similar experiment at room temperature also gave compound **8a**. M.p. >300 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 0.39$ (s, 27 H), 1.31 ppm (s, 3 H); ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta = 5.03$ ($SiMe_3$), 16.07 ppm (SiMe); MS: *m*/*z* (%): 419 (90) [M^+-15], 331 (17), 267 (46), 201 (7), 73 (100); elemental analysis calcd (%) for $C_{11}H_{30}Br_2Si_4$: C 30.41, H 6.96; found: C 30.46, H 7.00.

Reaction of $TsiSiBr_3$ with KC_8: KC_8[20] (10 mmol) in THF (20 mL) was added to $TsiSiBr_3$ (2.0 g, 4.0 mmol) in THF (25 mL) at −78 °C. After the solution was stirred for 3 h at −78 °C, the precipitate was removed by filtration, and the filtrate was transferred into a 5 mm NMR tube cooled to −78 °C. The 5 mm NMR tube was dipped into [D$_6$]acetone in 10 mm a NMR tube and then ^{29}Si NMR experiment for **10** was carried out. The reaction of **10** with an excess of 2,3-dimethyl-1,3-butadiene, MeOH, and 2-propanol gave **4a** in 90 % yield (GC yield), **5** in 91 % yield (GC yield), and **6a** in 87 % yield (GC yield), respectively.

Generation of 3: LiNp (9.0 mmol) in THF (15 mL) was added to $TsiSiCl_3$ (1.5 g, 4.1 mmol) in THF (25 mL) at −78 °C. The solution was stirred for 12 h (2 h in the case of using LDBB as reducing agent) at −78 °C to give **3**. In similar manners as described above, ^{29}Si NMR experiment for **3** prepared from the reduction $TsiSiCl_3$ with LDBB was carried out.

Synthesis of 4b: 2,3-Dimethyl-1,3-butadiene (5.0 mL, 44 mmol), cooled to −78 °C, was added rapidly to the reaction mixture of **3** in THF (40 mL), and the solution was stirred for 1 h. After addition of *n*-hexane at room temperature, the resulting mixture was washed with water. Volatiles were distilled under vacuum and naphthalene was removed by sublimation. The crude product was purified by GPLC to give **4b** in 75 % yield (1.16 g) as colorless crystals. M.p. >300 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 0.27$ (s, 27 H), 1.53 (s, 4 H) 1.72 (br, 3 H), 1.73 ppm (br, 3 H); ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta = 2.77$ ($SiMe_3$), 17.25 ($SiCH_2$), 24.47 (CCH_3), 128.00 ppm (C=C); MS: *m*/*z* (%): 376 (38) [M^+], 361 (54), 221 (65), 73 (100); elemental analysis calcd (%) for $C_{16}H_{37}ClSi_4$: C 50.94, H 9.89; found: C 50.95, H 9.87.

Synthesis of 6b: This compound was prepared by the same method as **4b** except that an excess of 2-propanol used instead of 2,3-dimethyl-1,3-butadiene. A colorless oil was obtained in 64 % yield (0.93 g). ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 0.27$ (s, 27 H), 1.17–1.19 (dd, 6 H), 4.23 (m, 1 H), 5.29 ppm (s, 1 H); ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta = 4.07$ ($SiMe_3$), 24.51, 25.07 ($CHCH_3$), 67.84 ppm ($CHCH_3$); MS: *m*/*z* (%): 339 (30) [M^+-15], 261 (100), 187 (21), 73 (40); elemental analysis calcd (%) for $C_{13}H_{35}ClOSi_4$: C 43.96, H 9.93; found: C 43.98, H 9.92.

Synthesis of 7b: Compound **7b**[21] was prepared by the same method used for **4b**, except that an excess of *t*BuOH used instead of 2,3-dimethyl-1,3-butadiene. The crude product was purified by GPLC with recycling. A colorless oil was obtained in 61 % yield (0.83 g). ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 0.31$ (s, 27 H), 5.40 pm (s, 1 H); ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta = 4.22$ pm ($SiMe_3$); MS: *m*/*z* (%): 315 (100) [M^+-15], 228 (3), 207 (62), 129 (30), 73 (75); elemental analysis calcd (%) for $C_{10}H_{28}Cl_2Si_4$: C 36.22, H 8.51; found: C 36.17, H 8.50.

Synthesis of 8b: Compound **8b**[16] was prepared by a method similar to that used for **4b**, except that an excess of MeI used instead of 2,3-dimethyl-1,3-butadiene. The crude product was purified by GPLC with recycling. A colorless oil was obtained in 65 % yield (0.92 g). ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 0.35$ (s, 27 H), 0.97 ppm (s, 3 H); ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta = 4.77$ ($C(SiCH_3)_3$), 12.80 ppm ($SiCH_3$); MS: *m*/*z* (%): 329 (84) [M^+-15], 241 (16) 221 (76), 205 (11), 73 (100); elemental analysis calcd (%) for $C_{11}H_{30}Cl_2Si_4$: C 38.23, H 8.75; found: C 38.19, H 8.70.

Synthesis of 9b: This compound was prepared by the same method as **4b** except that an excess of trimethylchlorosilane used instead of 2,3-dimethyl-1,3-butadiene. A colorless oil was obtained in 77 % yield (0.93 g). The reaction of **3** and an excess of trimethylbromosilane also gave **9b** (92 %, ^{1}H NMR yield). ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 0.32$ (s, 9 H), 0.34 ppm (s, 27 H); ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta = 0.20$ ($SiSiCH_3$), 5.28 ppm ($C(Si(CH_3)_3)$); MS: *m*/*z* (%): 387 (8) [M^+-15], 294 (13), 279 (16), 221 (100), 201 (29), 73 (43); elemental analysis calcd (%) for $C_{13}H_{36}Cl_2Si_5$: C 38.67, H 8.99; found: C 38.62, H 8.95.

X-ray crystallography: A single crystal was used for data collections on a STOE STADI4 four-circles-diffractometer with graphite monochromatic $Mo_{K\alpha}$ radiation at room temperature. Cell parameters and an orientation matrix for data collections were obtained from least-squares refinement, using the 36 reflections in $19.0 < 2\theta < 21.5$. Intensities were collected $\omega - 2\theta$ scan technique. During data collection three standard reflections were measured every hour and showed no significant. The intensity data were collected for Lorentz and polarization effect, and absorption correction was not applied. The structure was solved by direct method (SHELXS-97[22]) and refined by full-matrix least-squares methods

(SHELXL-97[22]). All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were inserted at calculated positions, with C–H distances of 0.96 Å and treated as riding atoms with constrained isotropic displacement parameters [$U_{iso}(H) = 1.2\,U_{eq}(C)$].

All atoms in the Tsi group, such as Si(2a)-Si(4b), C(8a)-C(16b), and H(8a)-H(16f) in the molecule appeared to be disordered and were refined as Si(*n*a):Si(*n*b) (*n* = 2,3,4), C(*n*a):C(*n*b) (*n* = 8–16), and H*n*(a,b,c):H*n*(d,e,f) (*n* = 8–16) is 0.51: 0.49 ratio. The ratio was controlled from the second free variable of the FVAR instruction. Atoms of Si*n*(a,b) (*n* = 2–4), C*m*(a,b) (*m* = 8–16), and H(*mL*) (*m* = 8–16, *L* = a–f) were refined under the FVAR, PART, EXYZ (only C atoms), and EADP (only C atoms) conditions, and H atoms of C*m*(a, b) (*m* = 8–6) were independently generated by PART condition. The disordered structure of **4b** was shown in Supporting Information. CCDC-210603 (**4b**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.uk).

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