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A Stable Magnesium Bromosilylenoid: Transmetalation of a Lithium Bromosilylenoid by Magnesium Bromide

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The reaction of lithium bromosilylenoid with MesLi at −10 °C followed by addition of $MgBr_2$ gave lithium mesitylsilylenoid as a complex with magnesium bromide that was transmetalated by $MgBr_2$ at 45 °C in THF to give magnesium silylenoid as a weak $MgBr_2$ complex of trisylmesitylsilylene. A new magnesium mesitylsilylenoid species was stable at reflux temperature in THF and *n*-hexane and showed amphiphilic properties in the reaction with 2-propanol, water, and ^{n}BuLi, respectively.

Introduction

Silylenoids, R_2SiMX, compounds in which an electropositive metal (M, usually alkali metal) and a leaving group (X, usually halogen) are bound to the same silicon atom, have been postulated as key intermediates in the reduction of dihalosilanes to synthesize silylenes[1] or polysilanes.[2] The experimental aspects of a few novel silylenoids, $Ph_2Si(O^tBu)Li$,[3] Tbt(Dip)SiLiBr[4] (Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl; Dip = 2,6-diisopropylphenyl), aminonaphthylphenylsilylenoid,[5] $(Mes)_2Si(SMes)$-Li,[6] and $(R_3Si)_2SiFLi$,[7] have been reported.[8,9]

Recently we reported the stable silylenoids $(Tsi)X_2SiLi$ (Tsi = trisyl = $C(SiMe_3)_3$, X = Br, Cl) at room temperature synthesized from the reduction of $TsiSiX_3$ with lithium naphthalenide (LiNp) or C_8K.[10] In their reactions, these species showed amphiphilic properties. Toward 2-propanol and 2,3-dimethyl-1,3-butadiene they behaved as halosilylenes, but in reactions with ^{t}BuOH and MeI they behaved as nucleophiles. This indicated that they are not free silylenes but LiBr adducts with halosilylenes, *halosilylenoid species*. Ab initio/NMR calculations for the solution structure of bromosilylenoid **1** by Flock and Dransfeld supported these experimental results.[11]

To date, most silylenoids are limited only to alkali metals such as Li, Na, and K; there are only a few reports on magnesium silylenoids inferred as reaction intermediates.[5] Herein, we describe the synthesis and reactivity of a magnesium mesitylsilylenoid, **4**, stable up to 65 °C, synthesized through the transmetalation with $MgBr_2$ of lithium mesitylbromosilylenoid, **2**, at THF reflux temperature (Scheme 1). This work provides the first example of a new stable magnesium silylenoid.

Results and Discussion

Bromotrisylsilylenoid, **1**, was produced by the reduction of tribromotrisylsilane with 2 equiv of LiNp. To the reaction mixture of **1** at −78 °C was added 1 equiv of MesLi diluted in diethyl ether. No reaction took place at that temperature; the trapping experiment using 2-propanol yielded only the corresponding bromosilylenoid-trapping adduct, **5** (Scheme 1).[10] When the reaction mixture was slowly warmed to −10 °C, the reaction of **1** with MesLi took place and was complete to give Mes(Tsi)SiLiBr, **2**, within 1 h. Species **2** was slowly decomposed at that temperature and trapped by 2-propanol to give the corresponding product, **6**, which shows the nucleophilic property of **2**. Interestingly when anhydrous $MgBr_2$ diluted in diethyl ether was added into the reaction mixture, the species **2** became stable up to room temperature,[12] which appears to form a complex with magnesium bromide, **3**. Species **3** was also

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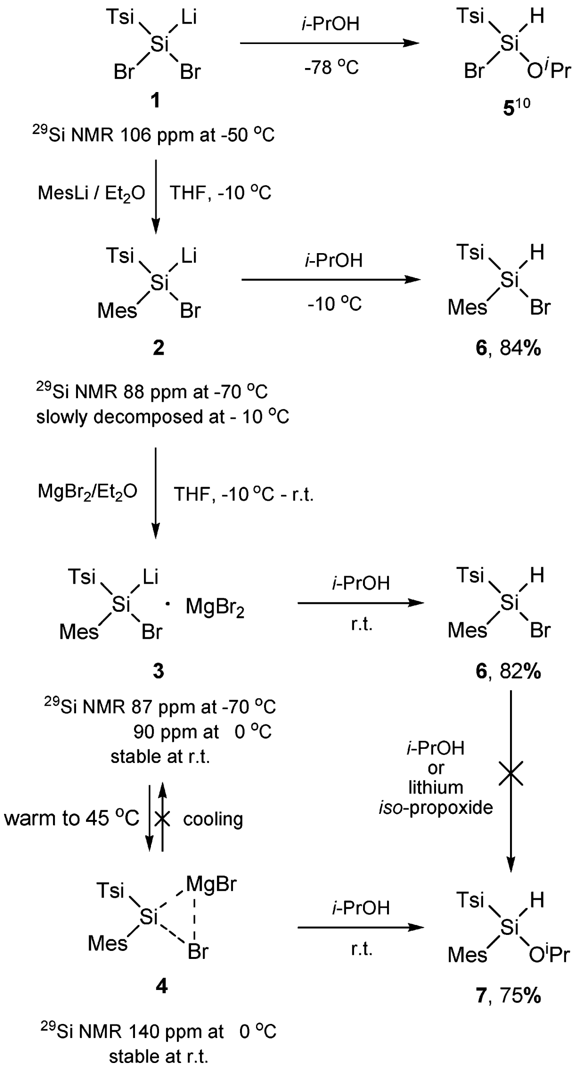
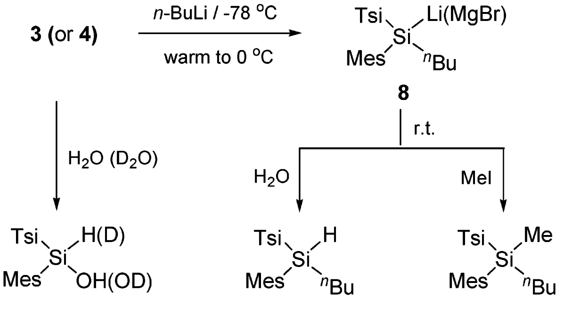
Scheme 1. Syntheses and Reactivities of 2, 3, and 4



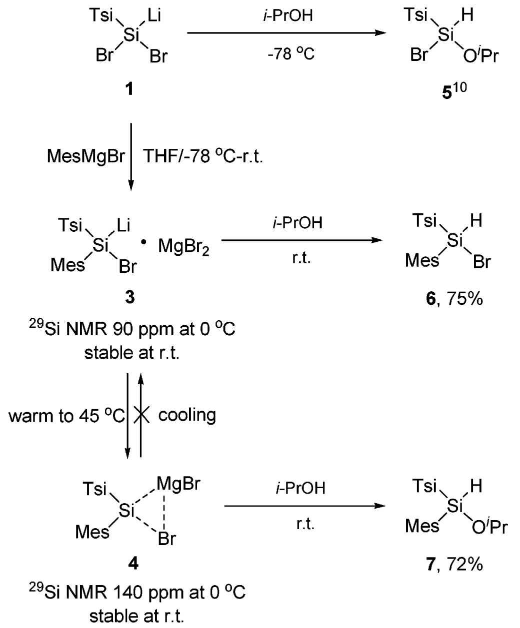
Scheme 2. Reactions of 3 or 4 with ^{n}BuLi



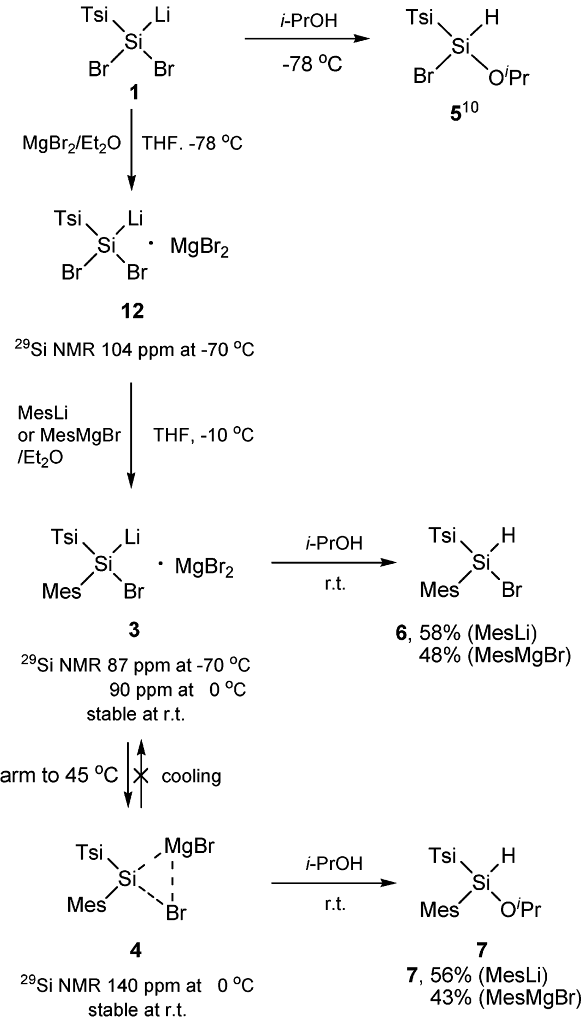
trapped by 2-propanol to yield the same product as that of **2**. When **3** was treated with H_2O and D_2O, **9** and deuterated **9** were obtained, respectively (Scheme 2). The butylation of **3** with 1 equiv of ^{n}BuLi diluted to 1.6 M in hexane yielded butylmesityltrisylsilylmagnesium bromide, **8**, which was trapped by H_2O and MeI to give the corresponding products, **10** and **11**, respectively (Scheme 2). This result shows clearly the electrophilic reactivity of **3** as well. On the basis of the results above, **3** is seen to be an amphiphilic silylenoid species.

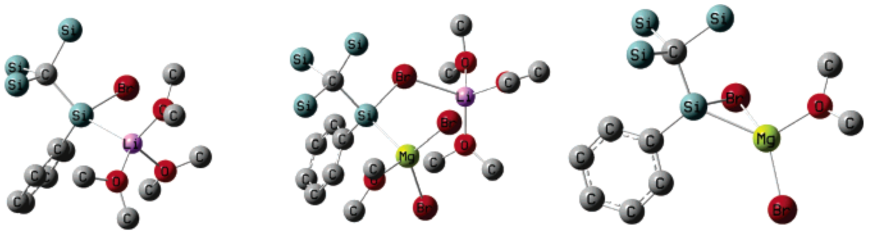
When the reaction mixture of **3** was warmed to about 45 °C in order to investigate the thermal stability of **3**, the new species **4** was formed, which reacted with 2-propanol to give isopropoxymesityltrisylsilane, **7** (Scheme 1). Although the solution was cooled back to 0 °C, the addition of 2-propanol yielded only **7**, which indicated that the formation of **4** is not reversible. The hydrolysis and butylation of **4** afforded **9**, **10**, and **11**, respectively, the same as the reactions of **3** (Scheme 2). **4** was

Scheme 3. Reaction of 1 with MesMgBr



Scheme 4. Syntheses and Reactions of 2, 3, and 4 in a Reverse Way





δ ≅ 84 ppm

2'

δ ≅ 92 ppm

3'

δ ≅ 139 ppm

4'

Figure 1. Structures and ^{29}Si NMR chemical shifts of **2′**, **3′**, and **4′** calculated by the GIAO-B3LYP/6-31G(d)//B3LYP/6-31G(d) method. (Hydrogen atoms were omitted for clarity.)

stable at reflux temperature in THF and *n*-hexane and at room temperature in toluene (however, **4** decomposed in refluxing toluene).[13] Note that **6** did not react with water, 2-propanol, and lithium isopropoxide (to give **7**); these facts indicate that **4** is a weak $MgBr_2$ complex of silylene, (Tsi)MesSi:, as shown in Scheme 1.

The ^{29}Si NMR chemical shifts[14] of **2**, **3**, and **4** were 88 ppm at −70 °C, 87 ppm at −70 °C (90 ppm at 0 °C), and 140 ppm at 0 °C, respectively, very far from the negative silicon resonances of simple silicon anions.[15] The ^{29}Si resonances were similar to that of bromosilylenoid (106 ppm)[10] and fluorosilylenoid (107 ppm),[7] but different from those of $Ph_2Si(O^tBu)Li$[3] (11 ppm) and $Ph_2Si(NEt_2)Li$[16] (19 ppm). These downfield ^{29}Si signals imply that silylenoids **2**, **3**, and **4** might be weak LiBr and $MgBr_2$ adducts with mesityltrisylsilylene, respectively. The difference of ^{29}Si NMR chemical shifts between **2**, **3**, and **4** can be deduced by comparison with the chemical shifts of $(Me_3Si)_3SiLi(THF)_3$ (^{29}Si NMR −190.7 ppm)[17] and $(Me_3Si)_3SiMgBr(THF)_2$ (−168.7 ppm).[18]

To verify the role of $MgBr_2$, we carried out the reaction of bromosilylenoid **1** with 1 equiv of MesMgBr (diluted to 1.0 M in diethyl ether) instead of MesLi, which produced $MgBr_2$ in the reaction mixture by salt elimination. When the reaction mixture of bromosilylenoid **1** with MesMgBr was slowly warmed to −10 °C, lithium mesitylsilylenoid complexed with $MgBr_2$ was obtained. Lithium mesitylsilylenoid complexed with $MgBr_2$ showed the same reaction properties and ^{29}Si NMR chemical shifts as those of **3** (Scheme 3). When this reaction mixture was warmed to about 45 °C, a new species was formed that has the same reactivity toward 2-propanol and ^{29}Si NMR chemical shift as those of **4**.

We also carried out the reactions in a reverse way; to the reaction mixture of lithium bromosilylenoid, **1**, was added $MgBr_2$, and then reactions with MesLi and MesMgBr were carried out as shown in Scheme 1 (Scheme 4). From these reactions we obtained exactly the same results as those shown in Scheme 1 and the same ^{29}Si NMR data as well. The results of Schemes 1, 3, and 4 show that $MgBr_2$ acts as a stabilizing reagent of lithium mesitylsilylenoid **2** by a complexation as well as a transmetalating reagent of lithium mesitylsilylenoid **3** at 45 °C.

To understand the different reactivities and a very large difference in the chemical shifts of ^{29}Si NMR between **3** and **4**, some preliminary quantum chemical calculations have been carried out. The simplified molecular geometries, Tsi(H)PhSi−LiBr, **2′**, Tsi(H)PhSi−LiBr·$MgBr_2$, **3′**, and Tsi(H)PhSi−$MgBr_2$, **4′** (Tsi(H) stands for $(H_3Si)_3C$, Ph instead of mesityl)), for **2**, **3**, and **4** are optimized at the hybrid density functional B3LYP/6-31+G(d) level of theory,[19a] with no symmetry constraint, by using the Gaussian-03 program package[19b] (Figure 1). The chemical shifts, $\delta^{29}Si_{calc}$, of the analogues are calculated by using the GIAO-B3LYP/6-31+G(d) method at their optimized geometry considering the solvent effects using dimethyl ether instead of THF. The calculated values of the analogues ($\delta^{29}Si_{calc} = 84.0, 92.0, 139.0$ ppm) are close to the experimental NMR chemical shifts ($\delta^{29}Si_{exp} = 88, 90, 140$ ppm).

These results are not sufficient yet to be solid evidence for the identity of the three real molecules, but the consistency shown in the comparison between the calculated and experimental NMR chemical shifts is a noticeable one. On the basis of these calculations, one can suggest that in the case of the lithium derivatives **2′** and **3′** their solution structures indeed correspond to the silylenoids **2** and **3**, respectively, but in the case of the magnesium derivative **4′** the real structure would be better described as a weak $MgBr_2$ complex of Tsi(Mes)Si: silylene, **4**. The silylene contribution to the structure **4** is more important, which gives rise to the significant deshielding of the central Si nucleus compared to that in **3**. This would also explain the strikingly different reactivity of both **3** and **4** toward 2-propanol; **3** reacts as a typical silylenoid, whereas the reactivity of **4** corresponds to that of silylene (or a silylene complex) like an insertion reaction.

Interestingly, the ^{1}H and ^{13}C NMR spectra of **7**, **9**, **10**, and **11** showed three signals of equal intensity due to the methyl groups of Tsi. This implies that the bulky Tsi group prevents free rotation about the Si (center)−C (in Tsi) bonds even at room temperature in a condensed phase. When the solution of **11** and $CDCl_3$ in the NMR tube was warmed to 65 °C, the two resonances of the *ortho*-methyl of the mesityl group were collapsed, but three resonances of the methyl groups of Tsi were still distinguishable.[20]

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[13] Several attempts to recrystallize **4** through solvent exchange have failed.

[14] Using a 5 mm (i.d.) NMR tube containing about 0.10 M (4.0 mmol/40 mL of THF) of silylenoid **2**, **3**, and **4**, respectively, which was dipped into the solution of acetone-d_6 in a 10 mm (o.d.) NMR tube, ^{29}Si NMR experiments were carried out.

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The reactions of **1** with 1 equiv of MeLi and MeMgBr diluted in diethyl ether were also carried out, respectively, by a method similar to that used for the synthesis of **2**. When both of the reaction mixtures were treated with 2-propanol at room temperature, dimethyltrisylsilane, **13**,[21] and **1**-trapping product, **5** (ratio of **13** and **5**, 1:1), were obtained. On using 2 equiv of MeLi and MeMgBr, dimethyltrisylsilane was formed quantitatively. These results strongly suggest that dimethyltrisylsilane might be produced via the double methylation of **1** and then the reaction of dimethyltrisylsilyllithium with 2-propanol. The smaller sized methyl group was not enough to stabilize the corresponding methyltrisylsilylenoid so that a double methylation took place.

Conclusions

In summary, the reaction of **1** with MesLi at −10 °C followed by addition of $MgBr_2$ gave lithium mesitylsilylenoid as a complex with magnesium bromide that was transmetalated by $MgBr_2$ at 45 °C in THF to give magnesium silylenoid as a weak $MgBr_2$ complex of trisylmesitylsilylene. A new magnesium mesitylsilylenoid species was stable at reflux temperature in THF and *n*-hexane and showed amphiphilic properties in the reaction with 2-propanol, water, and ^nBuLi, respectively. This is the first stable magnesium silylenoid and methodologically the first case of the formation of a metallosilylenoid from a metallosilylenoid through a transmetalation reaction.[18]

These reactions of **1** with two kinds of aryl- and alkyllithium (or Grignard) reagents, MesLi (or MesMgBr) and MeLi (or MeMgBr), demonstrated one of the important synthetic applications of a halosilylenoid.

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. ^1H, ^{13}C, and ^{29}Si NMR spectra were recorded on a Bruker AMX 500 NMR or DPX 400 NMR spectrometer. The chemical shifts were referenced to internal $CDCl_3$ (^1H and ^{13}C) or external Me_4Si (^{29}Si). Analyses of product mixtures were accomplished 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. The preparation of bromosilylenoid **1** was reported in a previous paper.[10]

Synthesis of 2−7 and 9. Naphthalene (1.28 g, 10 mmol) dissolved in THF (40 mL) was added to Li (0.08 g, 12 mmol) at room temperature. After the mixture had been stirred for 3 h, LiNp was obtained as dark blue solution. LiNp in THF was added slowly to $TsiSiBr_3$ (2.0 g, 4.0 mmol) in THF (20 mL) at −78 °C. The solution was stirred for 12 h at that temperature. MesLi was prepared by the reaction of 2-bromomesitylene (0.6 mL, 4.0 mmol) with ^nBuLi (3.2 mL, 8.0 mmol) in diethyl ether (50 mL). The reaction mixture was stirred for about 12 h at room temperature. The precipitated MesLi was washed with *n*-hexane by filtration. After the precipitated MesLi diluted to 20 mL in diethyl ether was added rapidly to the reaction mixture at −78 °C, the solution was stirred for 1 h at that temperature. When the reaction mixture of **1** with MesLi was slowly warmed to −10 °C, silylenoid **2** was formed. The solution was allowed to reach −10 °C, and then an excess of 2-propanol was added. After addition of *n*-hexane at room temperature, precipitated compounds were removed by filtration, and the resulting mixture was washed with water and volatiles were distilled under vacuum. The crude product was purified by GPLC with recycling to afford **6** as a white powder (mp = 114−115 °C) in 84% yield (1.54 g). In a manner similar to that described above, we obtained **9** as a colorless oil in 58% yield (0.92 g) using an excess of water.

The reaction of 1,2-dibromoethane (0.34 mL, 4.0 mmol) with Mg turnings (0.1 g, 4.0 mmol) in diethyl ether (50 mL) gave magnesium bromide. The volatiles were distilled off under vacuum to get $MgBr_2$ as white powder. After $MgBr_2$ diluted in diethyl ether (20 mL) was added to the reaction mixture of **2** at −78 °C, the solution was warmed to room temperature and then an excess of 2-propanol was added to get **6** in 82% yields. When the solution was warmed up to 45 °C, **4** began to form giving **7** as trapping product by 2-propanol. After stirring for 2 h at 45 °C, the reaction was completed to yield **7** as colorless oil in 75% yield (1.31 g).

Spectral data for 6: ^1H NMR ($CDCl_3$, 500 MHz): δ 0.32 (s, 27H, $SiMe_3$), 2.27 (s, 3H, CH_3 in mesityl), 2.56 (s, 3H, CH_3 in mesityl), 2.63 (s, 3H, CH_3 in mesityl), 5.85 (s, 1H, Si-H), 6.81 (s, 1H, aryl-H), 6.86 (s, 1H, aryl-H). ^{13}C NMR ($CDCl_3$, 125 MHz): 5.54 ($C(SiCH_3)_3$), 21.04, 25.24, 27.54 (CH_3 in mesityl), 129.13, 130.09, 131.68, 140.536, 143.89, 144.22 (aryl). MS: *m*/*z* (relative intensity): 443 ($M^+ - 15$, 100), 371 (64.6), 291 (83.3), 187 (75.0), 120 (18.1), 73 (97.7). HRMS: $C_{18}H_{36}BrSi_4$ 443.1077 ($M^+ - 15$ calcd), 443.1072 (found). Anal. Calcd for $C_{19}H_{39}BrSi_4$: C, 49.64; H, 8.55. Found: C, 49.60; H, 8.51.

Spectral data for 7: ^1H NMR ($CDCl_3$, 500 MHz): δ −0.07 (s, 9H, $SiMe_3$), 0.21 (s, 9H, $SiMe_3$), 0.23 (s, 9H, $SiMe_3$), 1.09, 1.22 (d, $J = 6.0$ Hz, 6H, $OCH(CH_3)_2$), 2.24 (s, 3H, CH_3 in mesityl), 2.48 (s, 6H, CH_3 in mesityl), 4.08 (m, 1H, $OCH(CH_3)_2$), 6.74 (s, 2H, aryl-H); the Si-H proton was not identified. ^{13}C NMR ($CDCl_3$, 125 MHz): 1.22, 3.27, 4.12 ($C(SiCH_3)_3$), 20.92, 25.29 (CH_3 in mesityl), 25.47, 26.23 ($OCH(CH_3)_2$), 66.69 ($OCH(CH_3)_2$), 129.95, 131.70, 135.68, 138.54, 143.39 (aryl). MS: *m*/*z* (relative intensity) 423 ($M^+ - 15$, 2.1), 365 (36.2), 323 (29.4), 307 (6.9), 261 (10.4), 203 (100), 73 (16.7). HRMS: $C_{21}H_{43}OSi_4$ 423.2391 ($M^+ - 15$ calcd), 423.2391 (found). Anal. Calcd for $C_{22}H_{46}OSi_4$: C, 60.20; H, 10.56. Found: C, 60.05; H, 10.51.

Spectral data for 9: ^1H NMR ($CDCl_3$, 500 MHz): δ −0.75 (s, 9H, $SiMe_3$), −0.46 (s, 9H, $SiMe_3$), 0.18 (s, 9H, $SiMe_3$), 2.25 (s, 3H, CH_3 in mesityl), 2.48 (s, 6H, CH_3 in mesityl), 5.45 (d, $J = 6.6$ Hz, 1H, Si-H), 6.75 (s, 2H, aryl-H); the Si-OH proton was not identified. ^{13}C NMR ($CDCl_3$, 125 MHz): 5.71 ($C(SiCH_3)_3$), 21.06, 23.50 (CH_3 in mesityl), 128.76, 129.88, 138.91, 143.106, 144.46, 145.63 (aryl). MS: *m*/*z* (relative intensity) 381 ($M^+ - 15$, 100), 276 (37.5), 261 (59.6), 203 (33.3), 177 (43.8), 73 (34.2). HRMS: $C_{18}H_{37}OSi_4$ 381.1921 ($M^+ - 15$ calcd), 381.1912 (found). Anal. Calcd for $C_{19}H_{40}OSi_4$: C, 57.50; H, 10.16; O, 4.03. Found: C, 57.51; H, 10.08; O,4.02. Spectral data for TsiMesSi(OD)D: MS: *m*/*z* (relative intensity) 383 ($M^+ - 15$, 100), 278 (33.8), 263 (41.9), 204 (20.8), 177 (43.8), 73 (33.3).

Synthesis of 8, 10, and 11. ^nBuLi (2.5 mL) diluted to 1.6 M in hexane was added to the reaction mixture of **3** in THF (60 mL) at

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(20) To the best of our knowledge, there was no example in which the ^1H and ^{13}C NMR of the three methyl groups of Tsi were separated at room temperature. Lickiss and co-workers found that the ^1H and ^{13}C NMR spectra of $(Tsi)SiCl_3$ and the ^1H NMR spectrum of $(Tsi)SiBr_3$ showed three signals for the Tsi group only at low temperature (ca. 206 K). Avent, A. G.; Bott, S. G.; Ladd, J. A.; Lickiss, P. D.; Pidcock, A. *J. Organomet. Chem.* **1992**, *427*, 9. Sakurai and co-workers reported that the ^1H NMR spectrum of (Tsi)(Mes)FSiOEt showed a singlet resonance due to the Tsi group. Nakadaira, Y.; Oharu, K.; Sakurai, H. *J. Organomet. Chem.* **1986**, *309*, 247.

(21) Eaborn, C.; Kowalewska, A.; Smith, J. D.; Stańczyk, W. A. *J. Organomet. Chem.* **2001**, *640*, 29.

−78 °C. After the mixture had been stirred for 2 h, the reaction mixture of **3** with ^{n}BuLi was slowly warmed to 0 °C, and **8** was formed. The solution was treated with an excess of water to give **10** (64%, GC yield), which was separated by column chlomatography as a colorless oil. In a manner similar to that described above, the reaction mixture of **3** with ^{n}BuLi (2.5 mL) was warmed to 0 °C, and **8** was formed. The solution was allowed to warm to room temperature, and then an excess of MeI was added. After addition of *n*-hexane at room temperature, precipitated compounds were removed by filtration, the resulting mixture was washed with water, and volatiles were distilled under vacuum. The crude product was purified by GPLC with recycling to afford **11** as a colorless oil in 58% yield (1.0 g).

Spectral data for 10: ^{1}H NMR ($CDCl_3$, 400 MHz): δ −0.10 (s, 9H, $SiMe_3$), 0.12 (s, 9H, $SiMe_3$), 0.19 (s, 9H, $SiMe_3$), 0.90−0.94 (m, 3H, CH_3 in *n*-butyl), 1.35−1.46 (m, 6H, CH_2 in *n*-butyl), 2.23 (s, 3H, CH_3 in mesityl), 2.42 (s, 6H, CH_3 in mesityl), 6.74 (s, 2H, aryl-H); the Si-H proton was not identified. ^{13}C NMR ($CDCl_3$, 100 MHz): 1.03, 3.00, 3.42 ($C(Si\mathit{C}H_3)_3$), 2.03 ($\mathit{C}(SiMe_3)_3$), 13.30, 20.36, 22.02, 26.87 (*n*-butyl), 25.23 (*o*-CH_3 in mesityl), 28.63 (*p*-CH_3 in mesityl), 128.87, 134.47, 136.35, 142.78 (aryl). MS: *m*/*z* (relative intensity) 421 (M^+ − 15, 7.9), 363 (93.8), 307 (100), 291 (14.6), 173 (12.5), 73 (23.3). HRMS: $C_{22}H_{45}Si_4$ 421.2598 (M^+ − 15 calcd), 421.2598 (found). Anal. Calcd for $C_{23}H_{48}Si_4$: C, 63.22; H, 11.07. Found: C, 63.20; H, 11.02.

Spectral data for 11: ^{1}H NMR ($CDCl_3$, 500 MHz): δ −0.11 (s, 9H, $SiMe_3$), 0.17 (s, 9H, $SiMe_3$), 0.20 (s, 9H, $SiMe_3$), 0.87−1.00 (m, 3H, CH_3 in *n*-butyl) 1.16−1.37 (m, 6H, CH_2 in *n*-butyl), 1.48 (s, 3H, CH_3), 2.28 (s, 3H, CH_3 in mesityl), 2.49 (s, 3H, CH_3 in mesityl) 2.53 (s, 3H, CH_3 in mesityl) 6.84 (s, 2H, aryl-H); the Si-H proton was not identified. ^{13}C NMR ($CDCl_3$, 125 MHz): 2.37, 3.21, 4.12 ($C(Si\mathit{C}H_3)_3$), 4.76 ($\mathit{C}(SiMe_3)_3$), 14.04, 17.74, 20.72, 21.23 (*n*-butyl), 25.16 ($SiCH_3$), 27.51 (*o*-CH_3 in mesityl), 28.59 (*p*-CH_3 in mesityl), 128.87, 130.18, 134.27, 138.06, 145.19, 145.56 (aryl). MS: *m*/*z* (relative intensity) 435 (M^+ − 15, 2.2), 377 (100), 321 (27.4), 177 (32.1), 73 (32.1). HRMS: $C_{23}H_{47}Si_4$ 435.2755 (M^+ − 15 calcd), 435.2755 (found). Anal. Calcd for $C_{24}H_{50}Si_4$: C, 63.92; H, 11.17. Found: C, 63.88; H, 11.16.

Reaction of Bromosilylenoid 1 with MesMgBr. After MesMgBr (4.0 mL) diluted to 1.0 M in diethyl ether was added rapidly to the reaction mixture of **1** at −78 °C, the solution was stirred for 2 h at that temperature. When the reaction mixture of **1** with MesMgBr was slowly warmed to −10 °C, silylenoid **3** was formed. The reaction of silylenoid **3** with 2-propanol gave compound **6** in 75% yield. When the reaction mixture of **3** was warmed to 45 °C, **4** began to form. After stirring for 2 h at 45 °C, the reaction was complete. In the reaction of **4** with 2-propanol, compound **7** was obtained in 72% yield.

Syntheses and Reactions of 2, 3, and 4 in a Reverse Way. To the reaction mixture of **1**, the newly prepared $MgBr_2$ (4.0 mmol) diluted to 20 mL was added at −78 °C. When the solution was stirred for 0.5 h at that temperature, compound **12** was formed. The reaction mixture of **12** was treated with MesLi (4.0 mmol) diluted to 20 mL for 1 h at −78 °C. The solution was slowly warmed to −10 °C, and silylenoid **3** was formed. After 2 h, the reaction of silylenoid **3** with 2-propanol gave compound **6** in 58% yield. When the reaction mixture of **3** was warmed to 45 °C, **4** began to form. After stirring for 2 h at 45 °C, the reaction was complete. In the reaction of **4** with 2 propanol, compound **7** was obtained in 56% yield. In a manner similar to that described above, MesMgBr was used instead of MesLi. In this reaction, **6** and **7** was obtained in 48% and 43% yields, respectively.

Reaction of Bromosilylenoid with MeLi (or MeMgBr). One equivalent of MeLi (2.7 mL) diluted to 1.5 M in diethyl ether or 1 equiv of MeMgBr (1.3 mL) diluted to 3.0 M in diethyl ether was added rapidly to the reaction mixture of **1** at −78 °C. The resulting solution was slowly warmed to room temperature. The solution was stirred for 1 h at that temperature and then trapped by 2-propanol to give dimethyltrisylsilane **13** and **5** (**1**-trapping product) (1:1 mixture). On using 2 equiv of MeLi or MeMgBr, compound **13** was formed quantitatively.

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Supporting Information Available: ^{29}Si NMR spectrum of **2**, **3**, **4**, and **12**, calculated structures of **2′**, **3′**, and **4′**, and full list of authors of ref 19b. These materials are available free of charge via the Internet at http://pubs.acs.org.

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