Preparation of Sulfur-Substituted Silyllithiums and Their Thermal Degradation to Silylenes

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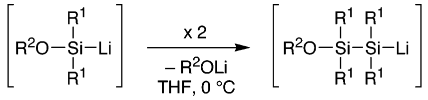
Sulfur-substituted silyllithiums were prepared for the first time, and their thermal stability was investigated. [(Mesitylthio)dimesitylsilyl]lithium (**4**) was prepared by a tin−lithium exchange reaction of the corresponding silylstannane (**6**) in THF at −78 °C in a quantitative yield. [Bis(mesitylthio)mesitylsilyl]lithium (**5**) was prepared by reductive cleavage of one of the Si−S bonds of tris(mesitylthio)mesitylsilane (**8**) in THF at −50 °C in 79% yield. The silyllithiums **4** and **5** underwent α-elimination of lithium mesitylthiolate to afford the corresponding silylenes, which were trapped in situ with triethylsilane, 2,3-dimethylbutadiene, or diphenylacetylene. To reveal the thermal lability of the sulfur-substituted silyllithiums in comparison with the organolithium counterparts, the electronic states of the model compounds $CH_3-S-SiH_2^-$ and $CH_3-S-CH_2^-$ were theoretically analyzed by ab initio calculations at the MP2/6-31+G** level.

Introduction

The importance of silicon-reactive intermediates has increased both in organosilicon chemistry and in organic synthesis.[1] Among a variety of silicon-reactive intermediates from hexacoordinate silicates to divalent silylenes, silyl anions[2] could be attractive species, in light of the fruitful progress in the corresponding carbanion chemistry.[3] In the past decade we have investigated the novel α-heteroatom-substituted silyl anions[2,4] $(X)_n R_{3-n}Si^-M^+$ and developed the [(amino)silyl]lithiums **1** ($X = NR'_2$, $M = Li$, $n = 1, 2$)[5] and the [(alkoxy)silyl]lithiums **2** ($X = OR'$, $M = Li$, $n = 1, 2$)[6] (Chart 1). These silyllithiums can be categorized into two types, in terms of the stability and reactivity. The [(amino)silyl]lithiums **1** are typical stable silyl anions and react only with electrophiles (type I).[5a] In contrast, the [(alkoxy)silyl]lithiums **2** behave as silylenoids,[6a] silicon analogues of carbenoids,[7] exhibiting ambiphilic character (type II, non-α-eliminative silylenoid). The characteristic reaction is the self-condensation of (*tert*-butoxydiphenylsilyl)lithium (**2a**), in which the "nucleophilic" silylenoid reacts with the "electrophilic" silylenoid in an S_N2 fashion, giving the (2-*tert*-butoxydisilanyl)lithium species **3a** in THF at 0 °C in 56% yield (eq 1).[6a,c,8] Because of its bimolecular process, the self-condensation is inhibited by a steric protection around the silicon center: the mesityl derivative **2b** (mesityl = 2,4,6-

Chart 1

$(R'_2N)_nR_{3-n}Si-Li$	$(R'O)_nR_{3-n}Si-Li$	$(R'S)_nR_{3-n}Si-Li$
1 (n = 1, 2) typical silyl anions **(Type I)**	**2** (n = 1, 2) non-α-eliminative silylenoids **(Type II)**	**4** (n = 1), **5** (n = 2) α-eliminative silylenoids **(Type III)**



(1)

2a: R¹= Ph; R² = *t*-Bu
2b: R¹= Mes; R² = Ph

3a: R¹= Ph; R² = *t*-Bu; 56%
3b: R¹= Mes; R² = Ph; 0%

Mes = 2,4,6-trimethylphenyl

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(8) Marschner et al. postulated a similar self-condensation reaction of a [(fluoro)silyl]potassium compound for the formation of [2-(fluoro)-disilanyl]potassium.[4j]

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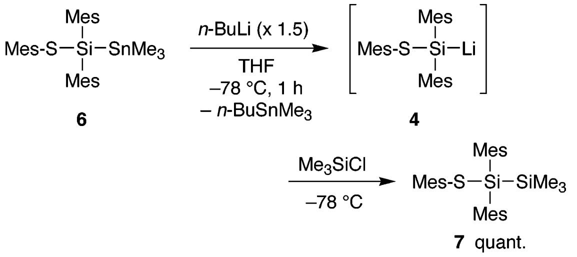
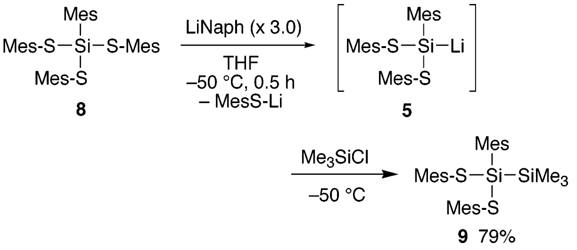
Scheme 1. Preparation of 4 and Trapping with Me_3SiCl



Scheme 2. Preparation of 5 and Trapping with Me_3SiCl



trimethylphenyl) can survive at 0 °C without the self-condensation (eq 1).[9] It is noteworthy that both **2a** and **2b** do not undergo unimolecular α-elimination to afford the corresponding silylenes.

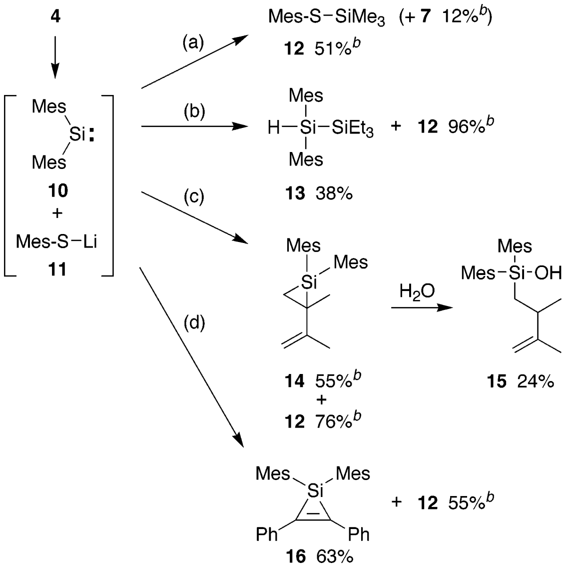
We disclose here the first example of the sulfur-substituted silyllithiums **4** and **5**. We have found that these species belong to a novel type of functionalized silyllithiums, which undergo thermal degradation to release silylenes (type III, α-eliminative silylenoid). The thermal lability of the sulfur-substituted silyllithiums is compared by the aid of ab initio calculation with the carbanion counterparts stabilized by sulfur substituents.

Results and Discussion

Experimental Study. The [(mesitylthio)silyl]lithium compound **4** was prepared by a tin−lithium exchange reaction[5a,6a] of the silylstannane **6** with *n*-BuLi (1.5 molar amounts) in THF at −78 °C, as shown in Scheme 1. The silyllithium **4** was trapped with chlorotrimethylsilane to give the corresponding disilane **7** in quantitative yield. The ^{29}Si NMR resonance of **4** in THF at −80 °C appeared at δ 7.6,[10] being shifted downfield from that of **6** (δ −7.5). The downfield shift observed here is consistent with the behavior observed in the cases of the [(amino)silyl]lithiums[5b] **1** and the [(alkoxy)silyl]lithiums[6a] **2**, which indicates that the mesitylthio group in **4** functions as an electron-withdrawing group as do the amino groups in **1** and the alkoxy groups in **2**.

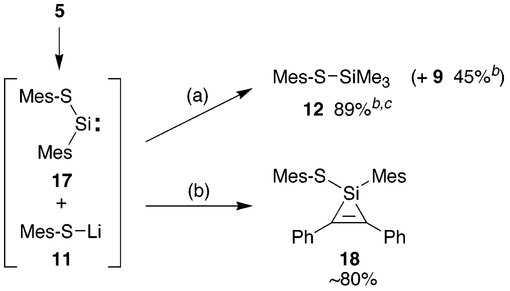
[Bis(mesitylthio)silyl]lithium **5** was next prepared by reductive cleavage[11] of the Si−S bond of the tris(mesitylthio)silane **8** with lithium naphthalenide (3 molar amounts) in THF at −50 °C, as shown in Scheme 2. The silyllithium **5** was trapped with chlorotrimethylsilane, and the corresponding disilane **9** was obtained in 79% yield. To our knowledge, this is the first example of silyl anion synthesis by reductive cleavage of a silicon−chalcogen bond.[12] The ^{29}Si resonance of **5** in THF at −50 °C appeared at δ 37.4,[10] which was shifted downfield from that of **8** (δ 11.8) and also that of the monofunctionalized silyllithium **4**.

Scheme 3. Thermal Degradation of 4[a]



[a] Conditions: (a) (i) 0 °C, 6 h, (ii) Me_3SiCl; (b) (i) Et_3SiH (×5), THF, −78 °C, (ii) −78 to 0 °C, 2.5 h, (iii) 0 °C, 15 h, (iv) Me_3SiCl; (c) (i) 2,3-dimethylbutadiene (×5), THF, −78 °C, (ii) 0 °C, 6 h, (iii) Me_3SiCl; (d) (i) PhC≡CPh (×10), THF, -78 °C, (ii) 0 °C, 6 h, (iii) Me_3SiCl. [b] The yields were determined by ^{1}H NMR analysis.

Scheme 4. Thermal Degradation of 5[a]



[a] Conditions: (a) (i) 0 °C, 2 h, (ii) Me_3SiCl; (b) (i) PhC≡CPh (×10), THF, −50 °C to room temperature, overnight, (ii) Me_3SiCl. [b] The yields were based on ^{1}H NMR analysis. [c] Based on the two MesS groups.

In contrast to the high thermal stability of the bulky aryloxy analogue **2b** mentioned above, ready thermal degradation of **4** and **5** is characteristic of the sulfur-substituted silyllithiums, as seen from the results summarized in Schemes 3 and 4, respectively. Thus, the mono(mesitylthio) derivative **4** underwent α-elimination at 0 °C to release dimesitylsilylene[13] (**10**) and lithium

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[9] Kawachi, A.; Minamimoto, T.; Tamao, K. Unpublished results.

[10] The ^{29}Si−^{7}Li scalar couplings were not observed.

[11] The silyl anion synthesis by reductive cleavage of the Si−Cl bond was established by our group.[6c]

[12] Synthesis of α-thio carbanions by reductive cleavage of a C−S bond has been established; see for example: (a) Cohen, T.; Sherbine, J. P.; Matz, J. R.; Hutchins, R. R.; McHenry, B. M.; Willey, P. R. *J. Am. Chem. Soc.* **1984**, *106*, 3245. (b) Deng, K.; Bensari, A.; Cohen, T. *J. Am. Chem. Soc.* **2002**, *124*, 12106.

[13] (a) Gasper, P. P.; West, R. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, U.K., 1998; Vol. 2, pp 2463−2568. (b) West, R.; Fink, M. J.; Michl, J. *Science* **1981**, *214*, 1343. (c) Fink, M. J.; Michalczyk, M. J.; Haller, K. J.; West, R.; Michl, J. *Organometallics* **1984**, *3*, 793. The ^{29}Si NMR shift of tetramesityldisilene was reported to be δ 63.6 in toluene-d_8. (d) Zhang, S.; Conlin, R. T. *J. Am. Chem. Soc.* **1991**, *113*, 4272. (e) Ohshita, J.; Honda, N.; Nada, K.; Iida, T.; Mihara, T.; Matsuo, Y.; Kunai, A.; Naka, A.; Ishikawa, M. *Organometallics* **2003**, *22*, 2436.

mesitylthiolate (**11**). After 6 h (or 2 h) at 0 °C, the thiolate **11** was captured by chlorotrimethylsilane as **12** in 51% (44% after 2 h) yield and the unchanged silyllithium **4** as **7** in 12% (38% after 2 h) yield. The silylene **10** was trapped with triethylsilane, 2,3-dimethylbutadiene, and diphenylacetylene to give, respectively, the corresponding insertion product **13**,[13c] the kinetic-controlled[14] [1 + 2] adduct **14**[13d] (and its hydrolyzed product **15**), and the [1 + 2] adduct **16**, together with **12**.

It is also noteworthy that, in the presence of 12-crown-4 (2 molar amounts), **4** was stable even at 0 °C for 2 h to be trapped as **7** in 81% yield, as was observed in the (alkoxy)silyllithium species **2**.[6a] This crown ether effect is ascribed to the formation of a solvent-separated ion pair, and the results suggest that the interaction between the lithium cation and the leaving group plays a key role in the α-elimination as well as in the self-condensation, as theoretically demonstrated by our previous work.[6d]

The bis(mesitylthio) derivative **5** also decomposed around 0 °C to release the lithium thiolate **11**, as shown in Scheme 4. At 0 °C for 2 h, chlorotrimethylsilane captured the unchanged silyllithium **5** as **9** in 45% yield and the thiolate **11** as **12** in 89% yield (based on the two MesS groups). While attempted trapping experiments of the expected sulfur-substituted silylene[13,15] **17** with triethylsilane or 2,3-dimethylbutadiene were unsuccessful, diphenylacetylene afforded the corresponding silirene **18** (ca. 80%). Although the isolation of **18** has not yet been successful, the NMR analysis of the reaction mixture supported the structure of **18**: the ^{29}Si resonance appears at δ −87.2 and the ^{13}C NMR resonance of the olefinic carbons appears at δ 157.3, which are close to the values of **16** (δ(^{29}Si) −111.0 and δ(^{13}C) 152.2)[13e] and those of other reported silirenes[16] having organic substituents on the silicon atom.

Several points have still remained to be solved by further study, which include the reactivity difference between **10** and **17** toward triethylsilane or 2,3-dimethylbutadiene and the fate of the silylenes **10** and **17** in the absence of trapping agents. For the former point, as pointed out in the literature,[15b] the electrophilicity of the sulfur-substituted silylene **17** may be reduced by the π donation from the nonbonding electrons on the sulfur to the vacant p orbital on the silicon, resulting in the decreased reactivity. It should also be mentioned here that an alternative route to **18**, via addition of the silyllithium **5** to acetylene and subsequent 1,3-elimination,[17] cannot be ruled out at the present time. For the latter point, the remaining butyllithium, lithium naphthalenide, and/or resulting lithium thiolate and the coordinating solvent THF[18] might have caused several unknown reactions rather than the simple dimerization of **10** or **17** forming the corresponding disilene; for example, the ^{29}Si NMR spectrum of the reaction mixture containing the silyllithium **4** at 0 °C showed more than 10 peaks between δ 50 and δ −40.

Theoretical Study. The thermal lability of the sulfur-substituted silyllithiums **4** and **5** is remarkable when it is compared to the stability of the organolithium counterparts.[19] It has been experimentally[19f,g,h] and theoretically[20] revealed that sulfur-substituted carbanions $CR_3SCH_2^-$ prefer an antiperiplanar arrangement of the electron pair on the anionic carbon (n_C) and the $S-CR_3$ bond, where the delocalization of the electron pair into the $\sigma^*(S-CR_3)$ orbital is maximized ($n_C \rightarrow \sigma^*$ negative hyperconjugation). The negative hyperconjugation results in the shortening of the $S-CH_2^-$ bond due to the partial double-bond character and the lengthening of the $S-CR_3$ bond due to the acceptance of the electrons in its σ^* orbital. Hence, the degree of the $n_C \rightarrow \sigma^*$ negative hyperconjugation can be estimated from the lengths of the $S-CH_2^-$ and $S-CR_3$ bonds, and this could be applied to the sulfur-substituted silyl anions. Thus, we calculated the models of the silyl anion $CH_3SSiH_2^-$ (**19**) and the neutral CH_3SSiH_3 (**20**) and, as a comparison, their carbon counterparts $CH_3SCH_2^-$ (**21**) and CH_3SCH_3 (**22**) at the MP2/6-31+G** level.[21]

Figure 1 plots the $S-CH_3$ bond length (Å) vs the torsion angle θ (deg) and also plots the relative energy (kcal/mol) vs θ in the optimized structures of **19** and **21**: the angle θ is defined as the angle between the electron pair (n_C or n_{Si}) and the $S-CH_3$ bond.[22] The $S-CH_3$ bond length in the carbanion **21** changes greatly,

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(14) (a) Takeda, N.; Suzuki, H.; Tokitoh, N.; Okazaki, R. *J. Am. Chem. Soc.* **1997**, *119*, 1456. (b) Takeda, N.; Tokitoh, N.; Okazaki, R. *Chem. Lett.* **2000**, 622.

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(17) For a recent example of 1,3-cycloelimination: Norsikian, S.; Marek, I.; Klein, S.; Poisson, J.-F.; Normant, J. F. *Chem. Eur. J.* **1999**, *5*, 2055 and references therein.

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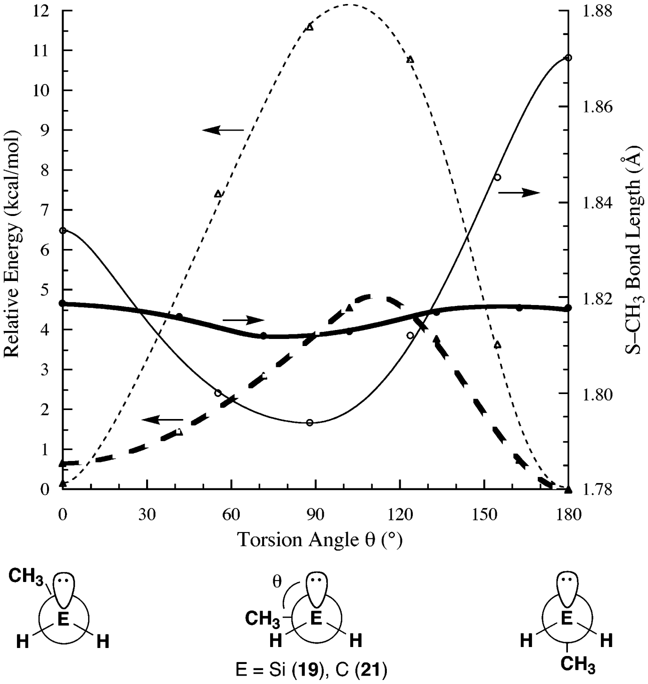

Figure 1. Plots for the S−CH$_3$ bond length (solid lines) and the relative energy (dashed lines) vs the torsion angle θ in the optimized structures of $CH_3-S-SiH_2^-$ (**19**) (bold lines) and $CH_3-S-CH_2^-$ (**21**) (plain lines) (MP2/6-31+G**).

depending on the θ value, and becomes longest (1.870 Å) in the anti conformer ($\theta = 180°$). This value is longer than that in the neutral molecule **22** (1.803 Å). In contrast to this, the S−CH$_3$ bond length in the silyl anion **19** scarcely changes, and the value in the anti conformer (1.818 Å) is shorter than that in the neutral molecule **20** (1.823 Å). In a similar manner, Figure 2 plots the E^--S bond length (E = C, Si; Å) and the relative energy (kcal/mol) vs the corresponding θ (deg) in **19** and **21**. The C^--S bond length in **21** also varies depending on the θ value and becomes shortest (1.718 Å) in the anti conformer. It is also shorter than that in the neutral molecule (1.803 Å). On the other hand, the Si^--S bond length in **19** exhibits little change. Even the shortest value (2.239 Å) in the anti conformer is longer than that in the neutral molecule (2.128 Å). Thus, the effective $n_{Si} \rightarrow \sigma^*$ negative hyperconjugation cannot be observed in **19**. It is plausible that the negative charge on the silicon is difficult to delocalize, due to the high s character[5b] of the electron pair on the silicon and also to the Si−S bond being longer than the C−S bond.

The electronic states of **19** and **21** were revealed by Muliken atomic charge analysis and natural bond orbital (NBO) analysis.[21] Figure 3 shows the isosurfaces of the charge density distribution[23] obtained by Mulliken atomic charge analysis of **19** and **21**. It is found that the isosurface on **19** is remarkably diminished along the Si^--S bond, whereas that on **21** is distributed throughout the molecule. In agreement with this, the NBO analysis showed that the Si^--S bond in **19** accepts a higher degree of contribution of the sulfur atom in comparison to the silicon atom (Si, 23.9%; S, 76.1%) and the electron pair on the anionic silicon has a high s

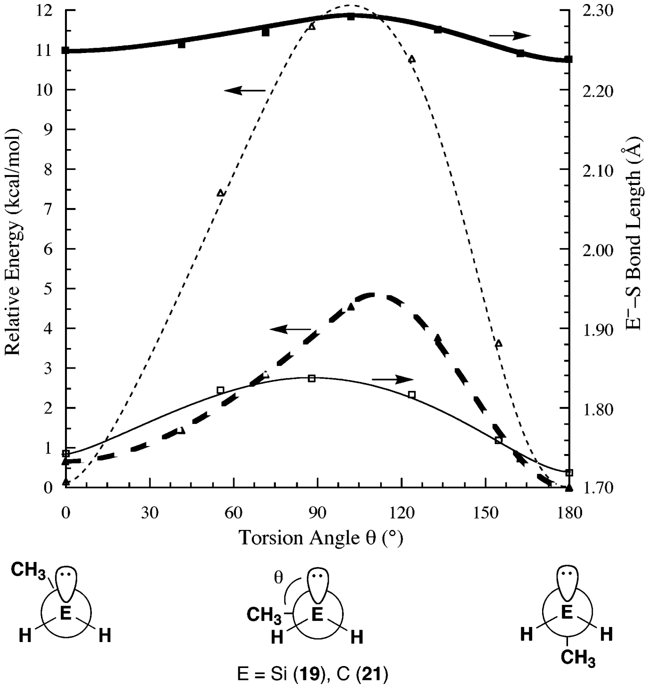

Figure 2. Plots for the E^--S bond length (E = C, Si) (solid lines) and the relative energy (dashed lines) vs the torsion angle θ in the optimized structures of $CH_3-S-SiH_2^-$ (**19**) (bold lines) and $CH_3-S-CH_2^-$ (**21**) (plain lines) (MP2/6-31+G**).

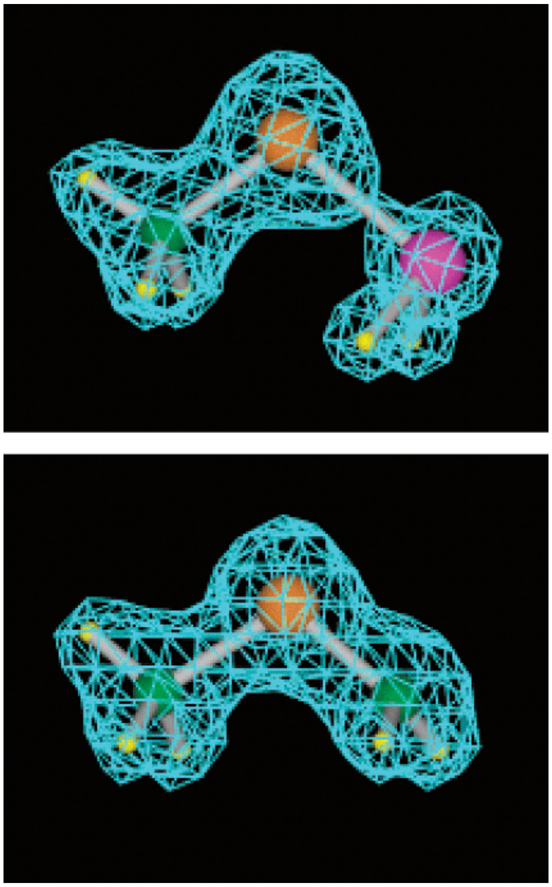

Figure 3. Isosurfaces of the charge density distribution of **19** (top) and **21** (bottom) (MP2/6-31+G**) defined by 0.0800 e/au^3: H, yellow; C, green; Si, purple; S, orange.

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(22) The relationship between the torsion angle vs the S−CH$_3$ bond length and the relative energy in $CH_3-S-CH_2^-$ was already theoretically investigated by Wiberg et al.[20d] Our calculation of $CH_3-S-CH_2^-$ is almost in agreement with theirs.

(23) The isosurface was visualized by MolStudio R3.1, NEC Corp., Japan.

character (s, 54.24%; p, 45.76%), while the C$^-$–S bond in **21** accepts a similar degree of contributions of the anionic carbon and the sulfur atom (C, 48.2%; S, 51.2%) and the electron pair on the anionic carbon has a high p character (s, 6.74%; p, 93.22%; d, 0.004%).

Energies for the isodesmic reactions in eqs 2 and 3 were also calculated (MP2/6-31+G**). The sulfur-

$$\underset{\mathbf{20}}{CH_3SSiH_3} + SiH_3^- \rightleftharpoons \underset{\mathbf{19}}{CH_3SSiH_2^-} + SiH_4 \quad (2)$$

$$\underset{\mathbf{22}}{CH_3SCH_3} + CH_3^- \rightleftharpoons \underset{\mathbf{21}}{CH_3SCH_2^-} + CH_4 \quad (3)$$

substituted silyl anion **18** (the anti conformer) is stabilized compared to the parent silyl anion SiH_3^- ($\Delta H = -12.09$ kcal/mol; eq 2), and the carbanion counterpart **20** (the anti conformer) is stabilized compared to CH_3^- ($\Delta H = -36.44$ kcal/mol; eq 3). The stability of **19** can be attributed only to the inductive effect of the electronegative sulfur atom, whereas that of **21** is due to the $n_C \rightarrow \sigma^*$ negative hyperconjugation in addition to the inductive effect.

In conclusion, we have prepared the mono(mesitylthio) and bis(mesitylthio) silyllithiums and disclosed their thermal degradation. They are categorized as "α-eliminative silylenoids" which readily release the corresponding silylenes.[24] Such behavior is in remarkable contrast to that of the sulfur-stabilized carbanions.

Experimental Section

^{1}H (270 MHz), ^{13}C (67.9 MHz), and ^{29}Si (53.7 MHz) NMR spectra were recorded on a JEOL EX-270 spectrometer. ^{1}H (300 MHz) and ^{13}C (75.4 MHz) NMR spectra were recorded on a Varian Mercury 300 spectrometer. ^{1}H and ^{13}C chemical shifts were referenced to internal benzene-d_6 (^{1}H, δ 7.200 ppm; ^{13}C, δ 128.0 ppm) and $CDCl_3$ (^{13}C, δ 77.00 ppm). ^{29}Si chemical shifts were referenced to external tetramethylsilane (δ 0 ppm). Mass spectra were measured at 70 eV on a JEOL JMS-DX300 mass spectrometer. Melting points were measured with a Yanaco-MP-S3 apparatus and were uncorrected. Elemental analyses were performed at the Microanalysis Division of the Institute for Chemical Research, Kyoto University. Analytical samples were purified by recycling reverse-phase liquid chromatography or recrystallization. Recycling reverse-phase liquid chromatography was performed with a JAI LC-908 instrument equipped with JAIGEL-ODS S-343-15 and P-15 columns. Reverse-phase column chromatography was performed using a Wakogel LP-40C18 (particle size; 20–40 μm) (Wako Pure Chemical Industries). Reverse-phase thin-layer chromatography was performed on plates of RP-18 F_{254}s (Merck). Column chromatography on silica gel was performed using Kieselgel 60 (70–230 mesh) (Merck). Thin-layer chromatography was performed on plates of silica gel 60F-254 (Merck).

Trimethylchlorostannane was prepared by disproportionation between tetramethylstannane and dimethyldichlorostannane:[25] the latter was kindly donated by Nitto Kasei Co. Dimesitylchlorosilane[26] and mesityltrichlorosilane[13c] were prepared in a manner similar to the procedures in the literature. Chlorotrimethylsilane was treated with small pieces of sodium under a nitrogen atmosphere to remove dissolved HCl, and the supernatant was used. Silicon tetrachloride and *n*-BuLi in hexane were purchased from Wako Pure Chemical Industries and used as received. Granular lithium was purchased from Chemetall Gesellschaft. Triethylsilane, 12-crown-4, and 2,3-dimethylbutadiene were purchased from Aldrich and dried over molecular sieves 4A prior to use. Diphenylacetylene was purchased from Tokyo Kasei Kogyo Co. Ltd. and used as received. Carbon tetrachloride was distilled under a nitrogen atmosphere over calcium hydride. THF was distilled under a nitrogen atmosphere over sodium benzophenone ketyl. Hexane was distilled under a nitrogen atmosphere over sodium. All reactions were carried out under an inert atmosphere.

Synthesis of [(Mesitylthio)dimesitylsilyl]trimethylstannane (6). (1) (Chlorodimesitylsilyl)trimethylstannane was prepared in the same manner as previously reported,[27] but the purification at each step was skipped, as described below. (i) (Trimethylstannyl)lithium was prepared from trimethylchlorostannane (8.11 g, 40.7 mmol) with granular lithium (1.11 g, 160 mmol) in THF (40 mL) by the literature method.[28] The resulting green solution was used in the next step without titration after removal of the unreacted lithium. (ii) The prepared solution of (trimethylstannyl)lithium was added dropwise to a solution of dimesitylchlorosilane (11.1 g, 36.6 mmol) in THF (40 mL) at −78 °C over 0.5 h. The reaction mixture was stirred at −78 °C for 1 h and warmed to ambient temperature. The solvent was evaporated, and the residue was diluted with dry hexane (ca. 50 mL) and filtered. The filtrate was concentrated to afford (dimesitylsilyl)trimethylstannane as a crude oil (16.3 g). The residue was used in the next step without further purification. (iii) The crude (dimesitylsilyl)-trimethylstannane (16.3 g) in carbon tetrachloride (50 mL) was refluxed for 66 h. The reaction mixture was concentrated in vacuo to give (chlorodimesitylsilyl)trimethylstannane as a crude oil (16.7 g). The residue was used in the next step without further purification.

(2) A solution of *n*-BuLi in hexane (1.66 M, 22.2 mL, 36.9 mmol) was added to a solution of mesitylthiol (5.62 g, 36.9 mmol) in THF (35 mL) at 0 °C, and the reaction mixture was stirred for 3 h at 0 °C. The resulting solution of lithium mesitylthiolate was added dropwise to a solution of the prepared (chlorodimesitylsilyl)trimethylstannane (16.7 g) in THF (35 mL) at 0 °C over 0.5 h. The reaction mixture was warmed to room temperature and stirred at that temperature for 10 h. The solvents were then removed with an evaporator, the residue was diluted with dry hexane (ca. 50 mL), and this mixture was filtered. The filtrate was concentrated in vacuo to afford a pale yellow solid. The solid was washed with dry CH_3CN (50 mL) with vigorous stirring and filtered. The solid on the filter paper was dried in vacuo to give **6** (14.5 g, 68% overall yield based on dimesitylchlorosilane) as a white solid, which was confirmed to be pure by ^{1}H NMR analysis. Recrystallization of the solid from hexane provided colorless crystals of **6** (8.23 g, 39% yield). Mp: 144.5–145.0 °C dec. ^{1}H NMR (C_6D_6): δ 0.28 (s, $^2J_{Sn-H} = 46.8$ and 45.0 Hz, 9H), 2.06 (s, 3H), 2.11 (s, 6H), 2.33 (s, 6H), 2.41 (s, 12H), 6.71 (s, 4H), 6.73 (s, 2H). ^{13}C NMR (C_6D_6): δ −6.69 ($^1J_{Sn-C} = 3.85$ and 3.68 Hz), 20.90, 21.08, 23.12, 25.62, 129.63, 130.18, 134.30, 137.62, 139.67, 143.81, 144.56, 145.75. ^{29}Si NMR (THF-d_8): δ −5.96. MS: *m/e* 582 (M^+, 0.41), 580 ($M^+ - 2$, 0.38), 567 ($M^+ -$ Me, 0.76), 565 ($M^+ - 2 -$ Me, 0.58), 463 ($M^+ -$ Mes, 0.21), 461 ($M^+ - 2 -$ Mes, 0.17), 431 ($M^+ -$ MesS, 0.20), 417 ($M^+ - SnMe_3$, 100). Anal. Calcd for $C_{30}H_{42}SiSSn$: C, 61.96; H, 7.28. Found: C, 62.11; H, 7.36.

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[24] The sulfur-substituted germyl- and stannyllithiums $(BuS)_2$-$[(Me_3Si)_3C]MLi(thf)_3$ (M = Ge, Sn), which are monomeric with the BuS bridges between M and the lithium, are stable at room temperature; see: (a) Borisova, I. V.; Eaborn, C.; Hill, M. S.; Khrustalev, V. N.; Kuznetzova, M. G.; Smith, J. D.; Ustynyuk, Y. A.; Lunin, V. V.; Zemlyansky, N. N. *Organometallics* **2002**, *21*, 4005. Examples of other stable sulfur-substituted germyl anions and stannyl anions: (b) Kersting, B.; Krebs, B. *Inorg. Chem.* **1994**, *33*, 3886. (c) Dean, P. A. W.; Vittal, J. J.; Payne, N. C. *Can. J. Chem.* **1985**, *63*, 394.

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Preparation of [(Mesitylthio)dimesitylsilyl]lithium (4) and Trapping as 1-(Mesitylthio)-1,1-dimesityl-2,2,2-trimethyldisilane (7). A solution of *n*-BuLi in hexane (1.56 M, 0.48 mL, 0.75 mmol) was added dropwise to a solution of **6** (290 mg, 0.50 mmol) in THF (2.0 mL) at −78 °C, and the reaction mixture was stirred for 1 h, affording a yellowish orange solution of **4**. Chlorotrimethylsilane (0.10 mL, 0.83 mmol) was then added to the solution at −78 °C, and the reaction mixture was stirred for a further 10 min and then warmed to room temperature. The solvents were removed with an evaporator, and the residue was diluted with hexane (ca. 10 mL) and this solution was filtered. The filtrate was concentrated in vacuo to afford a white solid. The yield of **7** was estimated to be 100% by ^{1}H NMR analysis (C_6D_6) of the solid using anisole as an internal standard. The solid was then washed with dry CH_3CN (3 mL) with vigorous stirring and filtered. The solid on the filter paper was washed with dry CH_3CN (1 mL × 2) and dried in vacuo to give pure **7** (214 mg, 87% yield) as a white solid. The purity was confirmed by elemental analysis. Further purification of **7** was performed by recrystallization from hexane. Mp: 123.0−124.0 °C dec. ^{1}H NMR (C_6D_6): δ 0.38 (s, 9H), 2.03 (s, 3H), 2.10 (s, 6H), 2.42 (s, 6H), 2.45 (s, 12H), 6.64 (s, 2H), 6.67 (s, 4H). ^{13}C NMR (C_6D_6): δ 0.70, 20.94, 21.14, 23.77, 25.67, 128.89, 129.53, 133.45, 136.36, 138.56, 143.58, 143.84 (2C). MS: *m/e* 490 (M^+, 15), 475 ($M^+ - Me$, 6), 417 ($M^+ - SiMe_3$, 100), 371 ($M^+ - Mes$, 17), 339 ($M^+ - MesS$, 36), 266 (21), 119 (Mes^+, 18), 73 (Me_3Si^+, 18). Anal. Calcd. for $C_{30}H_{42}Si_2S$: C, 73.40; H, 8.62. Found: C, 73.19; H, 8.64.

NMR Study of 4. A solution of **4** in THF was directly subjected to a ^{29}Si NMR measurement, being referenced to external tetramethylsilane (0 ppm). Although the spectrometer was unlocked during the acquisition, the field was stable and no significant field shift was observed. ^{29}Si NMR (THF, 193 K): δ −5.96.

Study on the Stability of 4. A solution of **4** in THF, which was prepared as above from **6** (290 mg, 0.50 mmol) and *n*-BuLi in hexane (1.63 M, 0.47 mL, 0.75 mmol) in THF (2.0 mL) at −78 °C, was warmed to 0 °C and stirred for a further 6 h at that temperature. Chlorotrimethylsilane (0.11 mL, 0.9 mmol) was then added to the solution at 0 °C, and the mixture was warmed to room temperature. The solvents were removed with an evaporator, and the residue was diluted with hexane (ca. 10 mL) and filtered. The filtrate was concentrated in vacuo. The yields of **7** and **12** were estimated to be 12% and 51%, respectively, by ^{1}H NMR analysis (C_6D_6) of the residue using anisole as an internal standard. The authentic sample of **12** was independently prepared by the reaction of **11**, which was prepared from mesitylthiol and *n*-BuLi in THF, with chlorotrimethylsilane.

Effect of 12-Crown-4 on the Stability of 4. A solution of 12-crown-4 (0.16 mL, 0.96 mmol) in THF (0.5 mL) was added at −78 °C to a solution of **4** in THF, which was prepared as above from **6** (233 mg, 0.40 mmol) and *n*-BuLi in hexane (1.66 M, 0.36 mL, 0.60 mmol) in THF (2.0 mL). The mixture was vigorously stirred for 10 min at the same temperature and then warmed to 0 °C and stirred for a further 2 h at that temperature. Chlorotrimethylsilane (0.09 mL, 0.7 mmol) was then added to the solution at 0 °C, and the mixture was warmed to room temperature. The solvents were removed with an evaporator, and the residue was diluted with hexane (ca. 10 mL) and filtered. The filtrate was concentrated in vacuo to afford a white solid. The yield of **7** was estimated to be 81% by ^{1}H NMR analysis (C_6D_6) of the solid using anisole as an internal standard. The solid was then washed with dry CH_3CN (4 mL) and filtered. The solid on the filter paper was washed with dry CH_3CN (1 mL × 2) and dried in vacuo to give pure **7** (125 mg, 64% yield) as a white solid.

Trapping Experiment of Silylene 10 with Triethylsilane: Formation of 1,1-Dimesityl-2,2,2-triethyldisilane (13). Triethylsilane (0.32 mL, 2.0 mmol) was added at −78 °C to a solution of **4** in THF, which was prepared as described above from **6** (233 mg, 0.40 mmol) and *n*-BuLi in hexane (1.66 M, 0.36 mL, 0.60 mmol) in THF (2.0 mL). The mixture was stirred for 20 min at the same temperature and warmed to 0 °C over 2.5 h and stirred for a further 15 h at that temperature. Chlorotrimethylsilane (0.09 mL, 0.7 mmol) was then added to the solution at 0 °C, and the mixture was warmed to room temperature. The solvents were removed with an evaporator, and the residue was diluted with hexane (ca. 10 mL) and the solution was filtered. The filtrate was concentrated in vacuo. The residue was subjected to column chromatography on silica gel (25 mL) and eluted with hexane/AcOEt (10/1) to give **13** (59 mg, 38% yield) ($R_f = 0.3$) as a colorless oil. The spectra were identical with those reported in the literature.[13c] ^{1}H NMR ($CDCl_3$): δ 0.82 (t, $J = 7.0$ Hz, 9H), 0.94 (q, $J = 7.0$ Hz, 6H), 2.23 (s, 6H), 2.35 (s, 12H), 5.15 (s, 1H), 6.78 (s, 4H). ^{13}C NMR ($CDCl_3$): δ 4.70, 8.33, 21.10, 24.39, 128.29, 130.96, 138.02, 144.25. ^{29}Si NMR ($CDCl_3$): δ −4.6, −59.8.

Trapping Experiment of Silylene 10 with 2,3-Dimethylbutadiene: Formation of 1,1-Dimesityl-2-methyl-2-isopropenylsilirane (14) and (2,3-Dimethyl-2-butenyl)dimesitylsilanol (15). 2,3-Dimethylbutadiene (0.23 mL, 2.0 mmol) was added at −78 °C to a solution of **4** in THF, which was prepared as above from **6** (233 mg, 0.40 mmol) and *n*-BuLi in hexane (1.56 M, 0.39 mL, 0.60 mmol) in THF (2.0 mL). The mixture was stirred for 5 min at the same temperature, warmed to 0 °C, and stirred for a further 6 h at that temperature. Chlorotrimethylsilane (0.15 mL, 1.2 mmol) was then added to the solution at 0 °C, and the mixture was warmed to room temperature. The procedure was followed by either step a or step b, as described below.

(a) After the solvent was removed, C_6D_6 (or $CDCl_3$) was added to dissolve the residue. For estimation of the yields of **12** (76%) and **14** (55%) by ^{1}H NMR analysis, anisole was added to the C_6D_6 solution as an internal standard. The solution was subjected to ^{1}H and ^{29}Si NMR analysis. The obtained spectra were found to be identical with those of **14** reported in the literature.[13d] ^{1}H NMR ($CDCl_3$): δ 1.29 (s, 3H), 1.57 (m, 2H), 2.23 (br, 3H), 2.41 (s, 6H), 2.53 (s, 6H), 2.59 (s, 6H), 4.45 (d, $J = 1.5$ Hz, 1H), 4.53 (m, 1H), 6.77 (s, 2H), 6.83 (s, 2H). ^{1}H NMR (C_6D_6): δ 1.50 (s, 3H), 1.78 (m, 2H), 1.85 (s, 3H), 2.08 (s, 3h), 2.13 (s, 3H), 2.65 (s, 6H), 2.66 (s, 6H), 4.80 (m, 1H), 4.82 (m, 1H), 6.73 (s, 2H), 6.77 (s, 2H). ^{29}Si NMR ($CDCl_3$): δ −74.1.

(b) The solvents were removed with an evaporator, and the residue was diluted with hexane (ca. 5 mL) and filtered. The filtrate was concentrated in vacuo. The residue was subjected to column chromatography on silica gel (20 mL) with hexane as eluent and subsequent reverse-phase column chromatography (20 mL) with CH_3CN as eluent to give the hydrolyzed product **15** (34 mg, 24% yield) ($R_f = 0.5$) as a colorless oil. ^{1}H NMR (C_6D_6): δ 1.53 (s, 3H), 1.59 (s, 3H), 1.67 (s, 3H), 1.68 (s, 1H), 2.15 (s, 6H), 2.32 (s, 2H), 2.43 (s, 12H), 6.75 (s, 2H). ^{13}C NMR ($CDCl_3$): δ 20.71, 21.06, 21.14, 21.23, 23.55, 23.69, 29.06, 30.46, 123.99, 124.44, 129.10, 129.13, 133.65, 138.70, 143.30, 144.04. ^{29}Si NMR ($CDCl_3$): δ −3.5. MS: *m/e* 366 (M^+, 9.5), 283 (Mes_2SiOH, 100), 265 (14). Anal. Calcd for $C_{24}H_{34}OSi$: C 78.63; H, 9.35. Found: C, 78.40; H, 9.31.

Trapping Experiment of Silylene 10 with Diphenylacetylene: Formation of 1,1-Dimesityl-2,3-diphenylsilirene (16). Diphenylacetylene (713 mg, 4.0 mmol) in THF (3.0 mL) was added at −78 °C to a solution of **4** in THF, which was prepared as above from **6** (233 mg, 0.40 mmol) and *n*-BuLi in hexane (1.56 M, 0.39 mL, 0.60 mmol) in THF (2.0 mL). The mixture was stirred for 10 min at the same temperature, warmed to 0 °C, and stirred for a further 6 h at that temperature. Chlorotrimethylsilane (0.090 mL, 0.72 mmol) was then added to the solution at 0 °C, and the mixture was warmed to room temperature. The solvents were removed with an evaporator. The yield of **12** was estimated to be 55% by a ^{1}H NMR analysis of the residue in C_6D_6 using anisole as an internal standard. After the deuterated solvent was removed, the residue was diluted with hexane (10 mL) and filtered. The filtrate was concentrated in vacuo. The residue was subjected to column chromatography on silica gel (50 mL) and eluted with hexane to give **16** (112 mg, 63% yield) ($R_f = 0.10$) as a white solid. The obtained spectra were found to be identical with those of **16** reported in the literature.[13e] ^{1}H NMR ($CDCl_3$): δ 2.25 (6H, s), 2.42 (12H, s), 6.80 (4H, s), 7.24−7.28 (1H, m), 7.33−7.36 (2H, m), 7.54−7.56 (2H, m). ^{13}C NMR ($CDCl_3$): δ 21.28, 24.19, 127.42, 128.06, 128.63, 131.84, 134.74, 139.03, 143.97, 152.22. ^{29}Si NMR ($CDCl_3$): δ −111.0.

Preparation of Tris(mesitylthio)mesitylsilane (8). A solution of *n*-BuLi in hexane (1.60 M, 97.6 mL, 158 mmol) was added dropwise to a solution of mesitylthiol (24.1 g, 158 mmol) in THF (150 mL) over 30 min at 0 °C, and the reaction mixture was stirred for 3 h at the same temperature. The resulting solution of lithium mesitylthiolate was added to a solution of mesityltrichlorosilane (12.2 g, 48.0 mmol) in THF (120 mL) over 2 h at −78 °C. The reaction mixture was stirred for a further 1 h at −78 °C and warmed to 0 °C and then to ambient temperature. The solvents were removed with an evaporator, and the residue was diluted with hexane (ca. 200 mL) and the solution was filtered. The filtrate was concentrated in vacuo. The obtained white solid was recrystallized from hexane to afford **8** (16.9 g, 58% yield) as colorless crystals. Mp: 152.7−154.0 °C. ^{1}H NMR (C_6D_6): δ 1.94 (s, 3H), 2.03 (s, 9H), 2.54 (s, 18H), 2.61 (s, 9H), 6.55 (s, 2H), 6.69 (s, 6H). ^{13}C NMR (C_6D_6): δ 21.03, 23.94, 25.67, 127.65, 128.36, 129.25, 129.78, 137.15, 140.18, 143.21, 144.47. ^{29}Si NMR (THF-d_8): δ 11.8. MS: *m*/*e* 600 (M^+, 1) 449 (M^+ − MesS, 59), 297 (11), 151 ($MesS^+$, 100). Anal. Calcd for $C_{36}H_{44}SiS_3$: C, 71.93; H, 7.38. Found: C, 71.63; H, 7.41.

Preparation of [Bis(mesitylthio)mesitylsilyl]lithium (5) and Trapping as 1,1-Bis(mesitylthio)-1-mesityl-2,2,2-trimethyldisilane (9). (1) Lithium (14 mg, 2.0 mmol) and naphthalene (256 mg, 2.0 mmol) were stirred in THF (4.0 mL) for 4 h at room temperature, resulting in a dark green solution of lithium naphthalenide. After being diluted with THF (2.0 mL), the solution was cooled to −50 °C. (2) A solution of **8** (403 mg, 0.67 mmol) in THF (2.0 mL) was added dropwise to the prepared lithium naphthalenide solution at −50 °C, and the reaction mixture was stirred at that temperature for 0.5 h to afford the solution of the silyllithium **5**. Chlorotrimethylsilane (0.28 mL, 2.2 mmol) was then added to the solution of **5** at −50 °C. After being stirred for 15 min at that temperature, the reaction mixture was warmed to room temperature. The solvents were removed with an evaporator, and the residue was diluted with hexane (ca. 3 mL) and filtered under an inert atmosphere. The filtrate was concentrated in vacuo to give the residue, from which the regenerated naphthalene was removed by sublimation (40−60 °C/0.4 mmHg). The yield of **9** was estimated to be 79% by a ^{1}H NMR analysis (C_6D_6) of the residue using anisole as an internal standard. Volatile byproducts were removed by bulb-to-bulb distillation (220−270 °C (bath temperature)/0.4 mmHg). The residue was dissolved in hexane (1 mL) and the solution was cooled to −78 °C for a while to afford colorless crystals. After the supernatant was removed with a syringe, the crystals was dried in vacuo to afford pure **9**. Mp: 75.4−76.5 °C. ^{1}H NMR (C_6D_6): δ 0.45 (s, 9H), 2.02 (s, 3H), 2.05 (s, 6H), 2.35 (s, 6H), 2.50 (s, 12H), 6.63 (s, 2H), 6.72 (s, 4H). ^{13}C NMR (THF-d_8): δ 1.44, 20.92, 21.01, 23.56, 25.66, 129.17, 129.36, 129.68, 132.54, 137, 23, 140.01, 143.10, 143.83. ^{29}Si NMR (THF-d_8): δ −6.5, 5.9. MS: *m*/*e* 522 (M^+, 8), 507 (M^+ − Me, 6), 449 (M^+ − $SiMe_3$, 11), 371 (M^+ − MesS, 100), 298 (34), 251 (15), 177 (37), 151 ($MesS^+$, 16), 119 (Mes, 37), 73 (Me_3Si, 17). Anal. Calcd for $C_{30}H_{42}Si_2S_2$: C, 68.90; H, 8.09. Found: C, 68.60; H, 8.08.

NMR Study of 5. A solution of **5** in THF was directly subjected to a ^{29}Si NMR measurement, being referenced to external tetramethylsilane (0 ppm). Although the spectrometer was unlocked during the acquisition, the field was stable and no significant field shift was observed. ^{29}Si NMR (THF, 223 K): δ −37.4.

Trapping Experiment of Silylene 17 with Diphenylacetylene: Formation of 1-Mesityl-1-(mesitylthio)-2,3-diphenylsilirene (18). (1) A THF solution of lithium naphthalenide was prepared from lithium (1.5 mg, 2.1 mmol) and naphthalene (273 mg, 2.1 mmol) in THF (4.0 mL). (2) A solution of **8** (427 mg, 0.71 mmol) in THF (2.0 mL) was added dropwise to the prepared lithium naphthalenide solution at −50 °C, and the reaction mixture was stirred at that temperature for 0.5 h to give a solution of **5**. A solution of diphenylacetylene (1.26 g, 7.1 mmol) in THF (2.0 mL) was then added to the solution of **5** at −50 °C, and the reaction mixture was warmed to ambient temperature. After 17 h, chlorotrimethylsilane (0.3 mL, 2.3 mmol) was added to the solution at room temperature. The solvents were removed with an evaporator, and the residue was diluted with hexane (ca. 10 mL) and filtered under an inert atmosphere. The filtrate was concentrated in vacuo. After (mesitylthio)trimethylsilane (**12**) and diphenylacetylene were removed by bulb-to-bulb distillation (130−180 °C (bath temperature)/0.5 mmHg), the crude silirene **18** (280 mg) was obtained as a residue. Attempted crystallization of the residue from pentane, hexane, and toluene resulted in the decomposition of **18**. ^{1}H NMR (C_6D_6): δ 1.99 (s, 3H), 2.13 (s, 3H), 2.60 (s, 6H), 2.89 (s, 6H), 6.68 (s, 2H), 6.76 (s, 2H), 7.06−7.10 (m, 4H), 7.13−7.18 (m, 6H). ^{13}C NMR (THF-d_8): δ 21.06, 21.49, 23.43, 24.72, 128.28, 128.35, 128.61, 128.88, 128.93, 129.06, 129.55, 135.44, 137.57, 141.12, 143.19, 144.05, 157.28. ^{29}Si NMR (THF-d_8): δ −87.3. MS: *m*/*e* 476 (M^+, 57), 354 (21), 325 (M^+ − MesS, 24), 296 (93), 178 (100), 151 (MesS, 14), 147 (21), 119 (Mes, 71), 105 (20), 91 (25).

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