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The First Stable Methyl-Substituted Disilene: Synthesis, Crystal Structure, and Regiospecific MeLi Addition

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Summary: The reductive debromination of 3,3-dibromo-1,1,5,5-tetra-tert-butyl-2,4-bis(di-tert-butylmethylsilyl)-1,2,4,5-tetramethylpentasilane, $[(^t\mathrm{Bu}_2\mathrm{MeSi})_2\mathrm{MeSi}]_2\mathrm{SiBr}_2$ *(**1**), gave (E)-*$[(^t\mathrm{Bu}_2\mathrm{MeSi})_2\mathrm{MeSi}](^t\mathrm{Bu}_2\mathrm{MeSi})\mathrm{Si{=}SiMe}(\mathrm{SiMe}^t\mathrm{Bu}_2)$ *(**3**), which is the first methyl-substituted isolable disilene, and its structure was determined by X-ray crystallography. The regioselective addition of a methyl anion to the* $\mathrm{Si{=}Si}$ *bond in **3** took place to give the solvent-separated silyl anion species tetrakis(tetrahydrofuran)lithium(I) 1,1,5,5-tetra-tert-butyl-2,3-bis(di-tert-butylmethylsilyl)-1,2,4,4,5-pentamethylpentasilan-3-ide (**4**).*

After the isolation of the first stable silicon−silicon doubly bonded compound, tetramesityldisilene, by West et al. in 1981,[1] more than 30 examples of stable disilenes have been synthesized using bulky protecting groups.[2−4] Reductive coupling of 1,1-dihalosilanes is one of the most convenient methods for the synthesis of stable disilenes and has been widely applied for the preparation of both acyclic and cyclic $\mathrm{Si{=}Si}$ doubly bonded compounds. However, the reductive dehalogenation of 1,1-dihalosilanes bearing sufficiently large substituents does not lead to the intermolecular coupling of the resulting silylenes.[5] We have carried out the reductive debromination of dibromosilane **1** with a new bulky $(^t\mathrm{Bu}_2\mathrm{MeSi})_2\mathrm{MeSi}$ group and succeeded in isolating a new disilene formed via a silylsilylene to disilene rearrangement, (*E*)-$[(^t\mathrm{Bu}_2\mathrm{MeSi})_2\mathrm{MeSi}](^t\mathrm{Bu}_2\mathrm{MeSi})\mathrm{Si{=}SiMe}(\mathrm{SiMe}^t\mathrm{Bu}_2)$ (**3**), which is the first example of a stable disilene with a small methyl group bound to an sp^2 silicon atom.[6] Herein, we report the synthesis and structure of **3** and the regiospecific addition of methyl anion to the $\mathrm{Si{=}Si}$ bond of **3**.

3,3-Dibromo-1,1,5,5-tetra-*tert*-butyl-2,4-bis(di-*tert*-butylmethylsilyl)-1,2,4,5-tetramethylpentasilane (**1**) was treated with 2 equiv of KC_8 in dry oxygen-free THF, giving the *E* isomer of the methyl-substituted disilene **3** as red cubic crystals in 71% yield (Scheme 1).[7] The

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[1] West, R.; Fink, M. J.; Michl, J. *Science* **1981**, *214*, 1343.

[2] For recent reviews on metallenes and dimetallenes of group 14 elements, see: (a) Baines, K. M.; Stibbs, W. G. *Adv. Organomet. Chem.* **1996**, *39*, 275. (b) Okazaki, R.; West, R. *Adv. Organomet. Chem.* **1996**, *39*, 231. (c) Kaftory, M.; Kapon, M.; Botoshansky, M. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, U.K., 1998; Vol. 2, Part 1, Chapter 5. (d) Weidenbruch, M. *Eur. J. Inorg. Chem.* **1999**, 373. (e) Power, P. P. *Chem. Rev.* **1999**, *99*, 3463. (f) Escudié, J.; Ranaivonjatovo, H. *Adv. Organomet. Chem.* **1999**, *44*, 113. (g) Weidenbruch, M. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, U.K., 2001; Vol. 3, Chapter 5.

[3] For a review on three-membered cyclic disilenes, see: Sekiguchi, A.; Lee, V. Ya. *Chem. Rev.* **2003**, *103*, 1429.

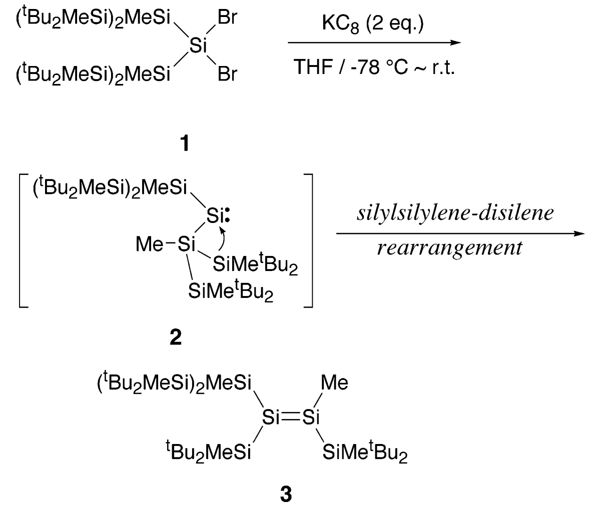
[4] (a) Sekiguchi, A.; Ichinohe, M.; Yamaguchi, S. *J. Am. Chem. Soc.* **1999**, *121*, 10231. (b) Ichinohe, M.; Arai, Y.; Sekiguchi, A.; Takagi, N.; Nagase, S. *Organometallics* **2001**, *20*, 4141. (c) Sekiguchi, A.; Izumi, R.; Lee, V. Ya.; Ichinohe, M. *J. Am. Chem. Soc.* **2002**, *124*, 14822.

[5] (a) Denk, M.; Lennon, R.; Hayashi, R.; West, R.; Belyakov, A. V.; Verne, H. P.; Haaland, A.; Wagner, M.; Metzler, N. *J. Am. Chem. Soc.* **1994**, *116*, 2691. (b) Denk, M.; Green, J. C.; Metzler, N.; Wagner, M. *J. Chem. Soc., Dalton Trans.* **1994**, 2405. (c) Gehrhus, B.; Lappert, M. F.; Heinicke, J.; Boese, R.; Bläser, D. *J. Chem. Soc., Chem. Commun.* **1995**, 1931. (d) Heinicke, J.; Opera, A.; Kindermann, M. K.; Karbati, T.; Nyulászi, L.; Veszprémi, T. *Chem. Eur. J.* **1998**, *4*, 541. (e) Kira, M.; Ishida, S.; Iwamoto, T.; Kabuto, C. *J. Am. Chem. Soc.* **1999**, *121*, 9722. (f) Lee, G.-H.; West. R.; Müller, T. *J. Am. Chem. Soc.* **2003**, *125*, 8114.

[6] The crystal structure of the stable dimethyl-substituted silene $\mathrm{Me_2Si{=}C(SiMe_3)(SiMe^tBu_2)}$ was reported; see: Wiberg, N.; Wagner, G.; Riede, J.; Müller, G. *Organometallics* **1987**, *6*, 32.

10.1021/om030571a CCC: $25.00

Scheme 1



structure of **3** with an *E* configuration at the Si=Si bond was finally determined by X-ray crystallography.[8,9] The ^{1}H NMR spectrum of **3** shows five singlets for methyl protons at 0.39, 0.44, 0.48, 0.94, and 1.37 ppm and four singlets for *tert*-butyl protons at 1.13, 1.23, 1.25, and 1.26 ppm. The signal at 1.37 ppm is assignable to the protons of the methyl group attached to an sp^2 silicon atom, which is low-field shifted relative to that of a normal methyl group on a silicon atom, probably due to the deshielding effect of the Si=Si bond. Six signals were observed in the ^{29}Si NMR spectrum. The low-field signals (103.8 and 158.9 ppm) are attributed to the sp^2 Si atoms: the Si atom with the two silyl substituents at 103.8 ppm and the Si atom with the methyl and silyl substituents at 158.9 ppm. The *E* isomer of **3** was formed exclusively.

The ORTEP drawing of **3** shows that the largest group, (^{t}Bu$_2$MeSi)$_2$MeSi, and the smallest group, methyl, are arranged in a *cis* fashion at the Si=Si double bond (Figure 1). The geometry of the Si=Si bond is not planar but is twisted by 29.0°, as determined by the angles between the planes of Si1–Si3–Si6 and Si2–Si7–C1. The sp^2 Si atoms are nearly planar; the sum of the bond angles around the Si1 and Si2 atoms are 359.81(2) and 359.51(2)°, respectively. The Si1–Si2 double-bond length is 2.1984(5) Å, which is normal (2.138–2.289 Å).[2c,10] The Si2–C1 bond length of 1.8955(14) Å is slightly stretched compared with the Si–CH$_3$ bond length of 1.84 Å.[2c] The bond angle of Si1–Si2–Si7 (137.55(2)°) is larger than those of Si1–Si2–C1 (113.21(5)°) and Si7–Si2–C1 (108.75(5)°), due to the difference in steric bulkiness of the substituents.

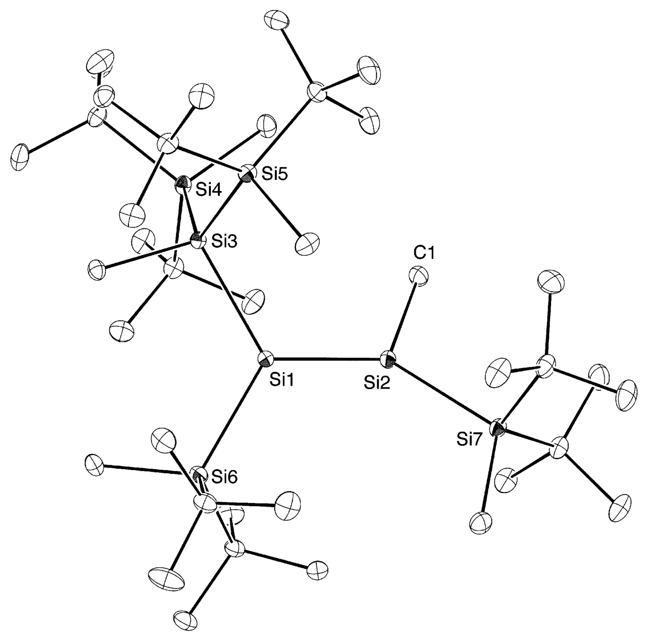


Figure 1. Molecular structure of **3** with thermal ellipsoids drawn at the 30% level (hydrogen atoms are omitted for clarity). Selected bond lengths (Å): Si1–Si2 = 2.1984(5), Si1–Si3 = 2.4083(5), Si1–Si6 = 2.3852(5), Si2–Si7 = 2.3837(5), Si2–C1 = 1.8955(14). Selected bond angles (deg): Si2–Si1–Si3 = 118.80(2), Si2–Si1–Si6 = 120.84(2), Si3–Si1–Si6 = 120.167(19), Si1–Si2–Si7 = 137.55(2), Si1–Si2–C1 = 113.21(5), Si7–Si2–C1 = 108.75(5).

A plausible formation mechanism of **3** is shown in Scheme 1. Debromination by two-electron reduction of **1** would result in the formation of silylene intermediate **2**, whose dimerization to form the disilene [(^{t}Bu$_2$MeSi)$_2$MeSi]$_2$Si=Si[SiMe(SiMe^{t}Bu$_2$)$_2$]$_2$ is prevented by the two bulky (^{t}Bu$_2$MeSi)$_2$MeSi groups. Instead of the dimerization of **2**, facile intramolecular ^{t}Bu$_2$MeSi group migration to the silylene center occurred to give **3**.[11] The silylsilylene to disilene rearrangement via the 1,2-migration of a trimethylsilyl group is a known process, forming a transient disilene that has been trapped by anthracene.[11b,d] The 1,2-silyl migration of disilanylsilylene to silyldisilene is reported to be much faster than the corresponding 1,2-methyl migration.[12] However, when the reaction was carried out in the presence of triethylsilane, which is a well-known silylene trapping reagent, no formation of the trapping product of the

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(7) Procedure for the synthesis of **3**: to a mixture of dibromide **1** (3.00 g, 3.3 mmol) and KC$_8$ (988 mg, 7.3 mmol) was added dry oxygen-free THF (30 mL) by vacuum transfer, and then the reaction mixture was warmed from –78 °C to room temperature with stirring. The solvent was replaced by hexane, and then the reaction mixture was filtered to remove the resulting potassium salt and graphite. The hexane solution was concentrated to ca. 3 mL and recrystallized at –30 °C to give **3** as red cubic crystals in 71% yield. Mp 150–152 °C dec. ^{1}H NMR (C_6D_6, δ): 0.39 (s, 3 H), 0.44 (s, 3 H), 0.48 (s, 6 H), 0.94 (s, 3 H), 1.13 (s, 18 H), 1.23 (s, 18 H), 1.25 (s, 18 H), 1.26 (s, 18 H), 1.37 (s, 3 H). ^{13}C NMR (C_6D_6, δ): –4.4, –2.4, –1.8, 3.3, 14.1, 21.8, 22.8, 23.7, 24.2, 30.0, 30.8, 31.2, 31.4. ^{29}Si NMR (C_6D_6, δ): –51.7, 12.2, 14.9, 25.2, 103.8, 158.9. MS (EI, 70 eV): *m/e* (%) 743 (M$^+$, 11), 728 (M$^+$ – Me), 686 (M$^+$ – ^{t}Bu). HRMS: *m/z* calcd for $C_{38}H_{90}Si_7$ 742.5427, found 742.5433. UV–vis (hexane): λ_{max}/nm (ϵ) 234 (25 700), 318 (1700), 429 (7100). All ^{1}H and ^{29}Si NMR signals were assigned by ^{1}H–^{29}Si HMQC spectroscopy.

(8) Crystal data of **3**: $C_{38}H_{90}Si_7$, fw = 743.73, monoclinic, space group $P2_1/c$, a = 12.9870(3) Å, b = 32.2930(7) Å, c = 11.8790(2) Å, β = 101.7830(10)°, V = 4876.94 (17) Å^3, Z = 4, d_{calcd} = 1.013 g cm^{-3}, temperature 120 K, R = 0.0372 ($I > 2\sigma(I)$), R_w = 0.1093 (all data), GOF = 1.027.

(9) One of the reviewers has pointed out the role of the silyl substitents in the stabilization of silicon doubly bonded compounds; however, in our case the more important factor is steric protection. Our isolable methyl-substituted disilene has two bulky ^{t}Bu$_2$MeSi groups and one extremely bulky (^{t}Bu$_2$MeSi)$_2$MeSi substituent, which kinetically stabilize the Si=Si bond.

(10) Schmedake, T. A.; Haaf, M.; Apeloig, Y.; Müller, T.; Bukalov, S.; West, R. *J. Am. Chem. Soc.* **1999**, *121*, 9479.

(11) For the silylsilylene-to-disilene rearrangement, see: (a) Wulff, W. D.; Goure, W. F.; Barton, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 6236. (b) Sakurai, H.; Nakadaira, Y.; Sakaba, H. *J. Am. Chem. Soc.* **1982**, *104*, 6156. (c) Krogh-Jespersen, K. *Chem. Phys. Lett.* **1982**, *93*, 327. (d) Sakurai, H.; Nakadaira, Y.; Sakaba, H. *Organometallics* **1983**, *2*, 1484. (e) Boo, B. H.; Gaspar, P. P. *Organometallics* **1986**, *5*, 698. (f) Gordon, M. S.; Truong, T. N.; Bonderson, E. K. *J. Am. Chem. Soc.* **1986**, *108*, 1421. (g) Gaspar, P. P.; Boo, B. H.; Svoboda, D. L. *J. Phys. Chem.* **1987**, *91*, 5011.

(12) Nagase, S.; Kudo, T. *Organometallics* **1984**, *3*, 1320.

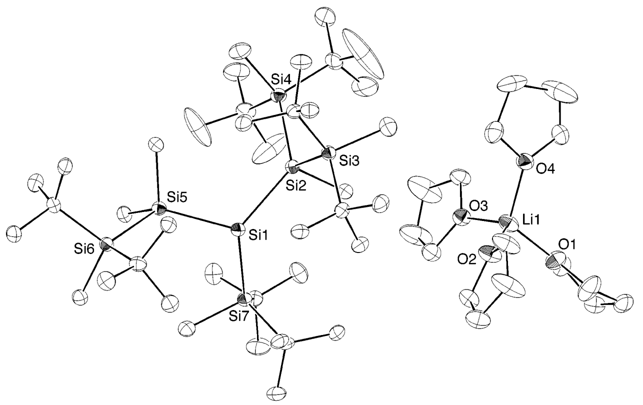
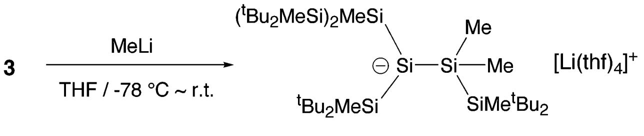


Figure 2. Molecular structure of **4** with thermal ellipsoids drawn at the 30% level (hydrogen atoms are omitted for clarity). Selected bond lengths (Å): Si1−Si2 = 2.438(2), Si1−Si5 = 2.376(2), Si1−Si7 = 2.398(2), Si2−Si3 = 2.466(2), Si2−Si4 = 2.503(2), Si5−Si6 = 2.422(2). Selected bond angles (deg): Si2−Si1−Si5 = 115.34(8), Si2−Si1−Si7 = 120.47(9), Si5−Si1−Si7 = 106.49(8).

Scheme 2



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intermediate silylene **2** was observed, due to the facile intramolecular migration of the ^{t}Bu$_2$MeSi group.

The reaction of disilenes with organometallic compounds such as organolithiums is rare,[13] and we have carried out the reaction of **3** with MeLi. Disilene **3** was reacted with MeLi in THF, and the regioselective addition of a methyl anion to the Si═Si bond occurred to give tetrakis(tetrahydrofuran)lithium(I) 1,1,5,5-tetra-*tert*-butyl-2,3-bis(di-*tert*-butylmethylsilyl)-1,2,4,4,5-pentamethylpentasilan-3-ide (**4**) in 89% yield (Scheme 2).[14] The solvent-separated ion pair structure in the solid state of **4** was determined by X-ray crystallography (Figure 2).[15,16] The formation of the solvent-separated ion pair is undoubtedly the result of steric shielding of the silicon bearing two extremely bulky silyl groups. The stability of the resulting anion also plays an important role in the regioselectivity of addition of the methyl anion.[16] The polarity of the asymmetrically substituted Si═Si bond in **3** induced by the difference in electronegativity of the substituents (silyl vs methyl groups) also supports the observed regioselectivity.[4b]

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Supporting Information Available: Tables giving details of the X-ray structure determination, fractional atomic coordinates, anisotropic thermal parameters, bond lengths, and bond angles and figures giving thermal ellipsoid plots for **3** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[13] Kira, M.; Iwamoto, T. *J. Organomet. Chem.* **2000**, *611*, 236.

[14] Procedure for the synthesis of **4**: to a mixture of the disilene **3** (50 mg, 0.067 mmol) and MeLi powder (3.3 mg, 0.15 mmol) was added dry oxygen-free THF (1 mL) by vacuum transfer, and then the reaction mixture was stirred at room temperature for 1 h. The solvent was evaporated to give the lithium salt of **4** (45.7 mg) as ruby crystals in 89% yield. Any NMR spectra were impossible to obtain, due to the very low solubility of **4** in benzene, toluene, and even tetrahydrofuran.

[15] Crystal data of **4**: $C_{55}H_{125}LiO_4Si_7$, fw = 1054.12, monoclinic, space group Pn, $a = 11.5160(16)$ Å, $b = 13.4850(11)$ Å, $c = 21.632(3)$ Å, $\beta = 96.276(7)°$, $V = 3339.2(7)$ Å^3, $Z = 2$, $d_{\mathrm{calcd}} = 1.048$ g cm^{-3}, temperature 120 K, $R = 0.0682$ ($I > 2\sigma(I)$), $R_w = 0.1845$ (all data), GOF = 1.052.

[16] Recently, the solvent-separated ion pair structures of silyl anions have been reported; see: (a) Jenkins, D. M.; Teng, W.; Englich, U.; Stone, D.; Ruhlandt-Senge, K. *Organometallics* **2001**, *20*, 4600. (b) Nakamoto, M.; Fukawa, T.; Lee, V. Ya.; Sekiguchi, A. *J. Am. Chem. Soc.* **2002**, *124*, 15160.