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Electronic Supplementary Information

# The formation of a 1,4-disilabenzene and its isomerization into a disilabenzvalene derivative

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## 1. General Remarks.

All manipulations were carried out under an argon atmosphere using either Schlenk line techniques or glove boxes. All solvents were purified by standard methods and/or the Ultimate Solvent System, Glass Contour Company.<sup>S1</sup> Trace amounts of water and oxygen remaining in the solvents were thoroughly removed by bulb-to-bulb distillation from potassium mirror prior to use. <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si NMR spectra were measured on a JEOL ECS-400 (<sup>1</sup>H: 400 MHz, <sup>13</sup>C: 101 MHz) or on a JEOL AL-300 spectrometer (<sup>1</sup>H: 300 MHz, <sup>13</sup>C: 75 MHz, <sup>29</sup>Si: 59 MHz). A signal arising from residual C<sub>6</sub>D<sub>5</sub>H (7.15 ppm) in the C<sub>6</sub>D<sub>6</sub> (mas used as the internal standard for the <sup>1</sup>H NMR spectra, while that of C<sub>6</sub>D<sub>6</sub> (128.0 ppm) was used for the <sup>13</sup>C NMR spectra, and external SiMe<sub>4</sub> (0.0 ppm) for the <sup>29</sup>Si NMR spectra. High-resolution mass spectra (HRMS) were obtained from a Bruker micrOTOF focus-Kci mass spectrometer (DART). All melting points were determined on a Büchi Melting Point Apparatus M-565 and are uncorrected. TbbSi=SiTbb (Tbb = 2,6-[CH(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>-4-*t*Bu-C<sub>6</sub>H<sub>2</sub>) was prepared according to literature procedures. <sup>S2</sup>

#### 2. Experimental Details.

#### Synthesis of 1,2-Tbb<sub>2</sub>-disilabenzvalene (3):

A solution of 1,2-Tbb<sub>2</sub>-disilyne 1 (15.0 mg, 15.7 mol) in hexane (0.2 mL) was treated with 3-hexyne (2.8 mg, 34.1 µmol, 2 equiv.) at room temperature for 20 min, and then the color of the yellow solution changed to light orange. After removal of residual 3-hexyne and hexane under reduced pressure and the addition of C<sub>6</sub>D<sub>6</sub>, the reaction mixture was exposed to LED light (commercial indoor illumination, Panasonic, LDL40S, 400-650 nm) at room temperature. After 20 min, the quantitative formation of 1,4-disilabenzvalene **3** was observed by <sup>1</sup>H NMR and the recrystallization from hexane afforded **3** as colorless crystals (16.2 mg, 14.5 µmol, 92%). **3**: colorless crystals, mp 144.4 °C (dec); <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) δ 0.25 (s, 36H, CH(SiMe<sub>3</sub>)<sub>2</sub>), 0.32 (s, 36H, CH(SiMe\_3)<sub>2</sub>), 0.86 (t, 6H, J = 7.5 Hz, CH<sub>2</sub>CH<sub>3</sub>), 1.35 (s, 18H, C(Me)<sub>3</sub>), 1.42 (t, 6H, J = 7.5 Hz, CH<sub>2</sub>CH<sub>3</sub>), 2.24 (q, 4H, J = 7.5 Hz, CH<sub>2</sub>CH<sub>3</sub>), 2.67 (q, 4H, J = 7.5 Hz, CH<sub>2</sub>CH<sub>3</sub>), 2.76 (s, 4H, CHSi), 7.00 (s, 4H, ArH); <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) δ 1.81 (q), 2.46 (q), 13.26 (q), 18.56 (q), 24.44 (t), 26.18 (t), 31.01 (d), 31.21 (q), 34.47 (s), 50.39 (s), 122.72 (d), 125.37 (s), 151.27 (s), 152.67 (s), 157.74 (s); <sup>29</sup>Si NMR (119 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) δ -85.06 (Si-C=C), 1.85 (SiMe<sub>3</sub>), 3.44 (SiMe<sub>3</sub>). MS (DART-TOF, positive mode): m/z calcd for C<sub>60</sub>H<sub>119</sub>Si<sub>10</sub> 1119.7004 ([M+H]<sup>+</sup>), found 1119.7033  $([M+H]^+).$ 

### **Reaction of disilyne 1 with 3-hexyne at room temperature:**

A solution of 1,2-Tbb<sub>2</sub>-disilyne **1** (17.0 mg, 17.8 mol) in hexane (0.2 mL) was treated with 3-hexyne (3.8 mg, 36.5 µmol, 2 equiv.) at room temperature for 3 min, and then the color of the yellow solution changed to light orange. After removal of residual 3-hexyne and hexane under reduced pressure, the formation of 1,4-disilabenzene **2** and 1,4-disilabenzvalene **3** was observed by <sup>1</sup>H NMR spectroscopy. Judging from the <sup>1</sup>H NMR spectra, the ratio of **2** and **3** was estimated in 1 : 3, respectively. The spectral data shown here were obtained by the subtraction of those of **3** from the observed spectra. **2**: <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K)  $\delta$  0.20 (s, 72H, CH(Si*Me*<sub>3</sub>)<sub>2</sub>), 1.31 (t, 12H, *J* = 7.5 Hz, CH<sub>2</sub>CH<sub>3</sub>), 1.36 (s, 18H, C(*Me*)<sub>3</sub>), 2.73 (s, 4H, CHSi), 2.99 (q, 8H, *J* = 7.2 Hz, CH<sub>2</sub>CH<sub>3</sub>), 7.01 (s, 4H, Ar*H*); <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K)  $\delta$  1.72 (q), 18.02 (q),

27.69 (t), 31.26 (q), 32.35 (d), 34.52 (s), 122.18 (d), 151.14 (s), 151.65 (s), 152.27 (s), 157.17 (s); <sup>29</sup>Si NMR (59 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K)  $\delta$  2.54 (*Si*Me<sub>3</sub>), 62.56 (*Si*–C=C). UV–vis (*n*-hexane)  $\lambda_{max}$  (nm,  $\varepsilon$ ) = 423 (16,000).

# Reaction of disilyne 1 with 3-hexyne at -78 °C:

In a *J*-Young NMR tube, a solution of 1,2-Tbb<sub>2</sub>-disilyne **1** (14.7 mg, 16.4  $\mu$ mol) in hexane (0.3 mL) was degassed. Subsequently, an excess of 3-hexyne (*ca*. 0.1 mL) was appended to the degassed solution by trap-to-trap method at -78 °C. After stirring for 10 min at -78 °C and removal of residual 3-hexyne and hexane under reduced pressure, the formation of 1,4-disilabenzene **2** and 1,4-disilabenzvalene **3** was observed by <sup>1</sup>H NMR spectroscopy. Judging from the <sup>1</sup>H NMR spectra, the ratio of **2** and **3** was estimated in 1 : 2, respectively.

# The generation of disilacyclohexadiene 5:

In a J-Young NMR tube, a solution of 1,2-Tbb2-disilyne 1 (17.2 mg, 18.0 µmol) in hexane (0.3 mL) was degassed. Subsequently, an excess of 3-hexyne (ca. 0.1 mL) was appended to the degassed solution by trap-to-trap method at -78 °C. After stirring for 1 hour at -78 °C, the reaction mixture was allowed to warm to 0 °C during 30 min. After warming to room temperature and removal of residual 3-hexyne and hexane under reduced pressure, the exposition of the reaction mixture to the air furnished the formation of 1,4-disilabenzvalene 3 (53% yield as judged by <sup>1</sup>H NMR spectrum) and disilacyclohexadiene 5 (47% yield as judged by <sup>1</sup>H NMR spectrum). Recrystallization of the mixture afforded only a few pieces of the single crystals of 5 for X-ray crystallographic analysis. The spectral data shown here were obtained by the subtraction of those of **3** from the observed spectra. **5**: <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) δ 0.20 (s, 18H, CH(SiMe<sub>3</sub>)<sub>2</sub>), 0.26 (s, 18H, CH(SiMe<sub>3</sub>)<sub>2</sub>), 0.27 (s, 18H, CH(SiMe<sub>3</sub>)<sub>2</sub>), 0.30 (s, 18H, CH(SiMe<sub>3</sub>)<sub>2</sub>), 1.16–1.38 (m, 30H, C(Me)<sub>3</sub>+CH<sub>2</sub>CH<sub>3</sub>), 2.07 (s, 1H, CHSi), 2.47–2.63 (m, 9H, CH<sub>2</sub>CH<sub>3</sub> + CHSi), 2.74 (s, 1H, CHSi), 5.43 (s, 1H, SiOH), 6.89–7.00 (m, 4H, ArH). MS (DART-TOF, positive mode): m/z calcd for  $C_{60}H_{119}O_2Si_{10}$  1151.6903 ([M+H]<sup>+</sup>), found 1151.6896 ([M+H]<sup>+</sup>).

## **Reaction of disilyne 1 with diphenylacetylene at room temperature:**

In a *J*-Young NMR tube, a solution of 1,2-Tbb<sub>2</sub>-disilyne **1** (7.5 mg, 7.8 µmol) in hexane (0.5 mL) was treated with diphenylacetylene (2.8 mg, 15.7 µmol, 2 equiv) for 10 min, and then the color of the yellow solution changed to light orange. The mixture was recrystallized from hexane to afford **6** as air-stable colorless crystals in 40% yield (3.5 mg, 3.1 µmol). **6**: colorless crystals, mp 104.9–105.9 °C; <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K)  $\delta$  –0.07 (s, 9H, CH(Si*Me*<sub>3</sub>)<sub>2</sub>), 0.04 (s, 9H, CH(Si*Me*<sub>3</sub>)<sub>2</sub>), 0.05 (s, 9H, CH(Si*Me*<sub>3</sub>)<sub>2</sub>), 0.29 (s, 9H, CH(Si*Me*<sub>3</sub>)<sub>2</sub>), 0.32 (s, 9H, CH(Si*Me*<sub>3</sub>)<sub>2</sub>), 0.34 (s, 9H, CH(Si*Me*<sub>3</sub>)<sub>2</sub>), 0.36 (s, 9H, CH(Si*Me*<sub>3</sub>)<sub>2</sub>), 0.37 (s, 9H, CH(Si*Me*<sub>3</sub>)<sub>2</sub>), 1.32 (s, 9H, C(*Me*)<sub>3</sub>), 1.35 (s, 9H, C(*Me*)<sub>3</sub>), 1.81 (s, 1H, C*H*Si), 2.60 (s, 1H, C*H*Si), 2.75 (s, 1H, C*H*Si), 6.51 (s, 1H, *J* = 1.2 Hz, Si*H*), 6.77–7.06 (m, 9H, Ph*H*+Ar*H*), 7.26–7.30 (m, 2H, Ph*H*), 7.40–7.43 (m, 3H, Ph*H*). MS (DART-TOF, positive mode): *m/z* calcd for C<sub>62</sub>H<sub>109</sub>Si<sub>10</sub> 1133.6222 ([M+H]<sup>+</sup>), found 1133.6161 ([M+H]<sup>+</sup>).

\*  ${}^{13}C/{}^{29}Si$  NMR spectra of **6** could not measured due to its insufficient supply.



Figure S1. <sup>1</sup>H NMR spectrum of **3** in  $C_6D_6$ .



Figure S2. <sup>13</sup>C NMR spectrum of 3 in  $C_6D_6$ .



Figure S3. <sup>29</sup>Si NMR spectrum of 3 in C<sub>6</sub>D<sub>6</sub>.



Figure S4. <sup>1</sup>H NMR spectrum of 2 and 3 from the reaction of disilyne 1 with 3-hexyne at room temperature (in  $C_6D_6$ ).



**Figure S5**. <sup>13</sup>C NMR spectrum of **2** and **3** from the reaction of disilyne **1** with 3-hexyne at room temperature (in  $C_6D_6$ ).



Figure S6. <sup>29</sup>Si NMR spectrum of **2** and **3** from the reaction of disilyne **1** with 3-hexyne at room temperature (in  $C_6D_6$ ).



Figure S7. <sup>1</sup>H NMR spectrum of 2 and 3 from the reaction of disilyne 1 with 3-hexyne at -78 °C (in C<sub>6</sub>D<sub>6</sub>).



**Figure S8**. <sup>1</sup>H NMR spectrum of **3** and **5** from the reaction of disilyne **1** with 3-hexyne at -78 °C (in C<sub>6</sub>D<sub>6</sub>, area shown: 1.9–7.5 ppm).



Figure S9. <sup>1</sup>H NMR spectrum of 6 in C<sub>6</sub>D<sub>6</sub>.



Figure S10. UV-vis spectra of 2 and 3 in hexane at room temperature.

# 3. X-Ray Crystallographic Analysis.

Single crystals of  $[3 \cdot 0.5(C_6H_{14})]$ , **5**, and  $[6 \cdot 0.5(C_6H_{14})]$  were obtained from recrystallization in *n*-hexane at room temperature. Intensity data for  $[3 \cdot 0.5(C_6H_{14})]$  and  $[6 \cdot 0.5(C_6H_{14})]$  were collected on a RIGAKU Saturn70 CCD(system) with VariMax Mo Optics using Mo-K $\alpha$  radiation ( $\lambda = 0.71075$  Å), while that for **5** was collected at the BL40XU beamline of SPring-8 (2017B1726, 2017B1179, 2017B1193, 2018A1167, 2018B1668, 2018B1179) on a large cylindrical camera using synchrotron radiation ( $\lambda =$ 0.78255 Å). The structures were solved using a direct method (SHELXT<sup>S3</sup>) and refined by a full-matrix least-squares method on  $F^2$  for all reflections using the programs of SHELXL-2014.<sup>S4</sup> All hydrogen atoms were placed using AFIX instructions, while all other atoms were refined anisotropically. The reflection data for **4** were insufficient due to its low quality of the single crystals. Supplementary crystallographic data were deposited at the Cambridge Crystallographic Data Centre (CCDC) under the numbers CCDC-1905119-1905121, respectively, and can be obtained free of charge from www.ccdc.cam.ac.uk/data\_request.cif.



**Figure S11.** Molecular structure of  $[3 \cdot 0.5(C_6H_{14})]$  (ORTEP drawing; thermal ellipsoids set at 50% probability). Hydrogen atoms and solvent are omitted for clarity.



**Figure S12.** Molecular structure of **5** (ORTEP drawing; thermal ellipsoids set at 50% probability). The minor parts of disordered moieties, hydrogen atoms other than the OH moiety, and the solvent molecules are omitted for clarity. Crystallographic data for **5**:  $C_{60}H_{118}O_2Si_{10}$ , FW 1152.44, crystal size  $0.02 \times 0.01 \times 0.01 \text{ mm}^3$ , -183 °C,  $\lambda = 0.78255 \text{ Å}$ , triclinic, P-1 (#2), a = 17.4581(11) Å, b = 19.3720(4) Å, c = 23.8816(10) Å,  $\alpha = 75.400(3)^\circ$ ,  $\beta = 86.427(4)^\circ$ ,  $\alpha = 69.949(4)^\circ$ , V = 7339.6 (6) Å<sup>3</sup>, Z = 4,  $D_{calcd} = 1.043 \text{ g} \cdot \text{cm}^{-3}$ ,  $\mu = 0.214 \text{ mm}^{-1}$ ,  $\theta_{max} = 25.5^\circ$ , refl./param. = 19593/1267, GOF = 1.234, Completeness = 95.6\%,  $R_1 [I > 2\sigma(I)] = 0.1639$ , w $R_2$  (all data) = 0.5098, largest diff. peak and hole 1.312 and -0.758 e.Å^{-3}. CCDC-1905120.



**Figure S13.** Molecular structure of **6** (ORTEP drawing; thermal ellipsoids set at 50% probability). The hydrogen atoms and the solvent molecules are omitted for clarity. Crystallographic data for  $[6 \cdot 0.5(C_6H_{14})]$ : C<sub>65</sub>H<sub>115</sub>Si<sub>10</sub>, FW 1177.46, crystal size  $0.08 \times 0.03 \times 0.02 \text{ mm}^3$ , -170 °C,  $\lambda = 0.71073 \text{ Å}$ , monoclinic,  $P2_1/n$  (#14), a = 12.9911(3) Å, b = 38.3496(6) Å, c = 14.8258(3) Å,  $\beta = 93.937(2)^\circ$ , V = 7368.8(3) Å<sup>3</sup>, Z = 4,  $D_{calcd} = 1.061 \text{ g cm}^{-3}$ ,  $\mu = 0.213 \text{ mm}^{-1}$ ,  $\theta_{max} = 26.0^\circ$ , refl./param. = 14413/763, GOF = 1.026, Completeness = 99.8%,  $R_1 [I > 2\sigma(I)] = 0.0452$ , w $R_2$  (all data) = 0.1012, largest diff. peak and hole 0.664 and -0.293 e.Å^{-3}. CCDC-1905121.

# 4. Computational calculations.

All calculations were carried out using the *Gaussian 09* (Revision E.01) program package.<sup>85</sup> Geometry optimizations and vibrational frequencies were calculated in the gas phase, at the theoretical level indicated in the main text.

# 5. References

- S1) A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen and F. J. Timmers, Organometallics, 1996, 15, 1518–1520.
- S2) T. Sugahara, J.-D. Guo, T. Sasamori, Y. Karatsu, Y. Furukawa, A. E. Ferao, S. Nagase, N. Tokitoh, *Bull. Chem. Soc. Jpn.*, 2016, 89, 1375–1384.
- S3) G. M. Sheldrick, *Acta Cryst.*, 2008, A64, 112–122.
- S4) G. M. Sheldrick, *Acta Cryst.*, 2015, A71, 3–8.
- Gaussian 09, Revision E.01, Frisch, M. J., Trucks, G. W., Schlegel, H. B., S5) Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Scalmani, G., Barone, V., Mennucci, B. G., Petersson, A., Nakatsuji, H., Caricato, M., Li, X., Hratchian, H. P., Izmaylov, A. F., Bloino, J., Zheng, G., Sonnenberg, J. L., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Vreven, T., Montgomery, Jr., J. A., Peralta, J. E., Ogliaro, F., Bearpark, M., Heyd, J. J., Brothers, E., Kudin, K. N., Staroverov, V. N., Keith, T., Kobayashi, R., Normand, J., Raghavachari, K., Rendell, A., Burant, J. C., Iyengar, S. S., Tomasi, J., Cossi, M., Rega, N., Millam, J. M., Klene, M., Knox, J. E., Cross, J. B., Bakken, V., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R. E., Yazyev, O., Austin, A. J., Cammi, R., Pomelli, C., Ochterski, J. W., Martin, R. L., Morokuma, K., Zakrzewski, V. G., Voth, G. A., Salvador, P., Dannenberg, J. J., Dapprich, S., Daniels, A. D., Farkas, O., Foresman, J. B., Ortiz, J. V., Cioslowski, J. & Fox, D. J. Gaussian, Inc., Wallingford CT, 2013.