Silyl-Substituted 1,4-Disila(Dewar benzene): New Synthesis and Unexpected Insertion of CO into the Si−Si Bond To Form a Disilyl Ketone

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*Summary: The silyl-substituted 1,4-disila(Dewar benzene) (**1**) was synthesized by the reduction of the corresponding dichloride **2** with 2.2 equiv of KC_8 in THF. The irradiation of **1** with light of wavelength $\lambda > 320$ nm in THF under a CO atmosphere produced the cyclic disilyl ketone **3** by the insertion of CO into the central Si−Si bond, whereas the photolysis of **1** in cyclohexane-d_{12} afforded the silyl-substituted 2,5-disilabenzvalene **4** by intramolecular isomerization.*

The chemistry of aromatic compounds containing silicon atoms has attracted considerable interest in recent decades.[1] Recently, Tokitoh and co-workers presented the synthesis, structure, and aromaticity of various monosilaaromatic compounds, such as silabenzene,[2] silanaphthalenes,[3] and 9-silaanthracene.[4] In contrast, disila aromatics have never been isolated as stable compounds, although there are some reports of the direct observation by UV/vis spectroscopy of the parent 1,4-disilabenzene in a frozen Ar matrix[5] and of the chemical trapping of intermediate 1,4-disilabenzenes with MeOH or acetylene derivatives.[6] Moreover, Ando et al. have characterized 1,4-disila(Dewar benzene) and 2,5-disilabenzvalene, i.e., valence isomers of 1,4-disilabenzene, by isomerizations of bis(silacyclopropene).[7] A theoretical study of the valence isomerization of 1,4-disila(Dewar benzene) has been recently reported.[8] Despite its very interesting reactivity and the highly strained structure, the chemistry of 1,4-disila(Dewar benzene) derivatives is very limited, due to synthetic difficulties. Here, we report a new simple synthetic method for silyl-substituted 1,4-disila(Dewar benzene) (**1**) together with its unique photochemical reactions to form a rare example of a stable cyclic disilyl ketone (**3**) in the presence of CO and the silyl-substituted 2,5-disilabenzvalene (**4**) by intramolecular isomerization, respectively.

The starting material, 1,4-*anti*-bis(di-*tert*-butylmethylsilyl)-1,4-dichloro-2,3,5,6-tetraethyl-1,4-disilacyclohexa-2,5-diene (**2**),[9] was readily prepared by treatment of 1,1,4,4-tetrachloro-2,3,5,6-tetraethyl-1,4-disilacyclohexa-2,5-diene[10] with $^t\mathrm{Bu_2MeSiNa}$ (2.2 equiv) in THF (Scheme 1). Because of the steric repulsion, only the anti isomer was formed. The reduction of dichloride **2** with KC_8 (2.2 equiv) in THF at 0 °C resulted in the formation of 1,4-bis(di-*tert*-butylmethylsilyl)-2,3,5,6-tetraethyl-1,4-disilabicyclo[2.2.0]hexa-2,5-diene (**1**), which was isolated as pale yellow crystals in 70% yield.[9]

The molecular structure of **1** was unambiguously determined by mass spectrometry, NMR spectra, and X-ray crystallographic analysis. In the ^{29}Si NMR spectrum of **1**, two signals were observed at −26.3 and 11.0 ppm, which were assigned to the skeletal and the substituent Si atoms, respectively. The UV spectrum of **1** in 3-methylpentane shows an absorption band with a maximum at 335 nm (ϵ 3000), which is assigned to the $\sigma-\sigma^*$ transition of the Si−Si bonds. Figure 1 shows an ORTEP drawing of **1** together with selected bond lengths and angles.[11] There are two crystallographically independent molecules of **1** in the unit cell, and both molecular structures are almost identical. The central Si−Si bond lengths (2.2908(15) and 2.2969(15) Å) are slightly longer than those of methyl-substituted 1,4-disila(Dewar benzene) (2.244−2.248 Å)[7] and of the calculated parent compound (2.282 Å).[12] The dihedral angles between the two disilacyclobutene rings in **1** are 109.4° for Si1−Si2−C2−C1/Si1−Si2−C3−C4 and 110.8°

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[9] For the experimental procedures and spectral data of **1**−**4**, see the Supporting Information.

[10] Kang, S. H.; Han, J. S.; Lee, M. E.; Yoo, B. R.; Jung, I. N. *Organometallics* **2003**, *22*, 2551.

[11] Crystal data for **1** at 120 K: $C_{30}H_{62}Si_4$, MW = 535.16, monoclinic, space group $P2_1/c$, $Z = 8$, $a = 16.5790(16)$ Å, $b = 9.7770(10)$ Å, $c = 42.188(2)$ Å, $\beta = 95.1200(6)°$, $V = 6811.1(10)$ Å^3, $D_{calcd} = 1.044$ g cm^{-3}, $2\theta_{max} = 50.00°$, R1 ($I > 2\sigma(I)$) = 0.0669, wR2 (all data) = 0.2019 for 10 937 reflections and 649 parameters, GOF = 1.063.

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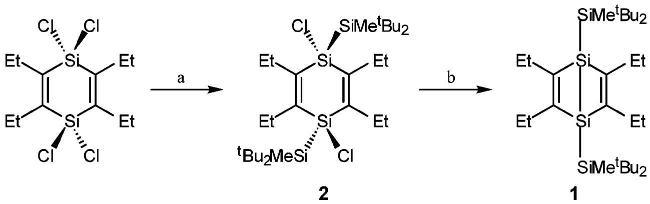
10.1021/om050261n CCC: \$30.25

Scheme 1[a]



[a] Reaction conditions: (a) ^{t}Bu$_2$MeSiNa (2.2 equiv), THF, room temperature, 25%; (b) KC_8 (2.2 equiv), THF, room temperature, 70%.

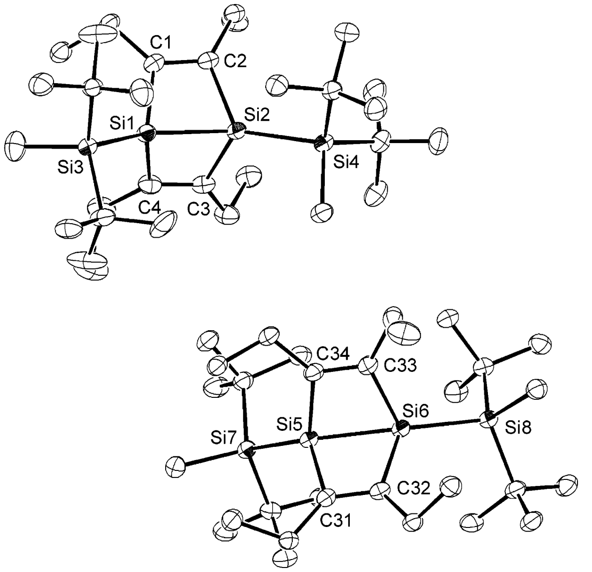
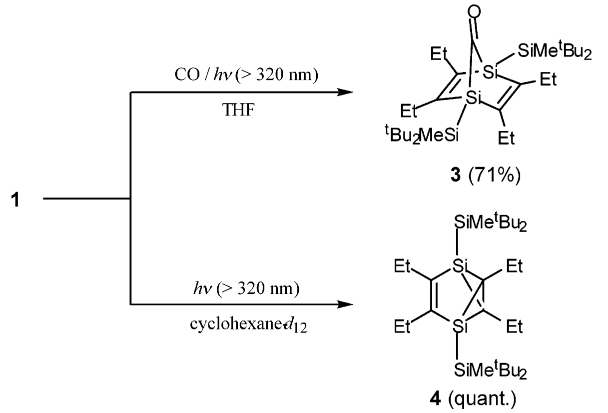


Figure 1. ORTEP drawing of 1,4-disila(Dewar benzene) **1** (30% thermal ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Si1–Si2 = 2.2908(15), Si1–Si3 = 2.3798(16), Si2–Si4 = 2.3764(16), Si1–C1 = 1.921(4), Si1–C4 = 1.909(4), Si2–C2 = 1.928(4), Si2–C3 = 1.935(4), C1–C2 = 1.356(6), C3–C4 = 1.356(6), Si5–Si6 = 2.2969(15), Si5–Si7 = 2.3807(15), Si6–Si8 = 2.3797(15), Si5–C31 = 1.926(4), Si5–C34 = 1.932(4), Si6–C32 = 1.941(4), Si6–C33 = 1.925(4), C31–C32 = 1.353(5), C33–C34 = 1.349(6), Selected bond angles (deg): Si3–Si1–Si2 = 142.82(6), Si3–Si1–C1 = 122.52(13), Si3–Si1–C4 = 122.17(14), Si4–Si2–Si1 = 138.21(6), Si4–Si2–C2 = 123.80(13), Si4–Si2–C3 = 123.08(13), Si7–Si5–Si6 = 140.67(6), Si7–Si5–C31 = 123.06(13), Si7–Si5–C34 = 122.19(13), Si8–Si6–Si5 = 144.28(6), Si8–Si6–C32 = 123.63(12), Si8–Si6–C33 = 118.91(13).

for Si5–Si6–C33–C34/Si5–Si6–C32–C31; thus, compound **1** is more folded than the reported Dewar benzene derivatives (115.9–123.3°),[13] probably due to the steric influence of the introduction of bulky ^{t}Bu$_2$MeSi groups. Although only one example of the molecular structure of a 1,4-disila(Dewar benzene) derivative has so far been determined by X-ray crystallography,[7] this is the first example of a Dewar benzene derivative with silyl substituents at the 1,4-positions.

The reactivity of **1** is quite interesting, owing to the inherently strained Si–Si bond. We have found an unexpected insertion reaction of CO into the strained Si–Si bond of **1**. Thus, photolysis of **1** in THF with light of wavelength $\lambda > 320$ nm under a CO atmosphere for 1 h proceeded efficiently, and 1,4-bis(di-*tert*-butylmethylsilyl)-2,3,5,6-tetraethyl-1,4-disilabicyclo[2.2.1]hepta-2,5-dien-7-one (**3**)[9] was produced as the sole product, which was isolated as pale yellow crystals in 71% yield after purification by gel permeation chromatography (Scheme 2). No reaction occurred without irradiation. Although the preparation and reactivity of disilyl ketones have precedents, their structures are poorly understood, due to their instability and the limited number of compounds.[14] Compound **3** is the first example of a cyclic disilyl ketone, which is relatively stable toward air, moisture, and light, in contrast to other reported acyl silanes and disilyl ketones. The ^{13}C NMR chemical shift of the carbonyl carbon of **3** (δ 260.3 ppm) is shifted downfield from those of the usual ketones (δ 197–220 ppm)[15] and acyl silanes (δ 230–240 ppm).[16] In the IR spectrum, the C=O stretching frequency for **3** (1673 cm^{-1}) was observed at lower wavenumber compared with those of the normal aliphatic ketones (ca. 1715 cm^{-1})[15] and the disilyl ketone $(PhMe_2Si)_2C{=}O$ (1690 cm^{-1}).[14e]

Scheme 2



The molecular structure of **3** was finally determined by X-ray crystallographic analysis, as shown in Figure 2.[17] The C1–O1 bond length (1.199(2) Å) is somewhat shortened in comparison with that of $(PhMe_2Si)_2C{=}O$ (1.218(6) Å)[14e] and is similar to those of norbornadienone derivatives (1.192(3)–1.197(2) Å).[18] The Si1–C1 and Si2–C1 bond lengths (1.9730(17) and 1.9807(16) Å) attached to the C=O bond in **3** are significantly elongated by 4.7% compared with those of other Si–C bonds (Si1–C2, Si1–C5, Si2–C3, and Si2–C4) attached to C=C bonds (1.8847(15)–1.8906(15) Å).

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(17) Crystal data for **3** at 120 K: $C_{31}H_{62}OSi_4$, MW = 563.17, monoclinic, space group $P2_1/c$, $Z = 4$, $a = 8.8570(4)$ Å, $b = 25.9730(9)$ Å, $c = 15.8440(6)$ Å, $\beta = 104.6070(5)°$, $V = 3527.0(2)$ Å^3, $D_{\mathrm{calcd}} = 1.061$ g cm^{-3}, $2\theta_{\max} = 55.96°$, R1 ($I > 2\sigma(I)$) = 0.0436, wR2 (all data) = 0.1254 for 8053 reflections and 427 parameters, GOF = 1.029.

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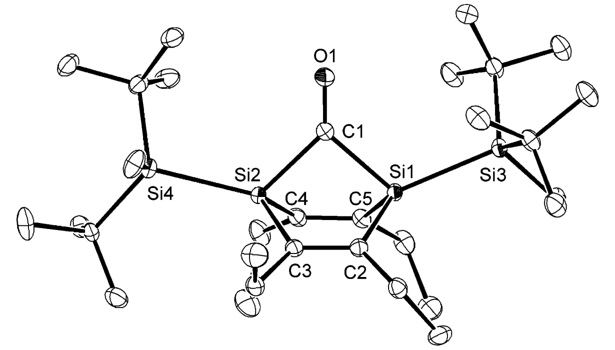
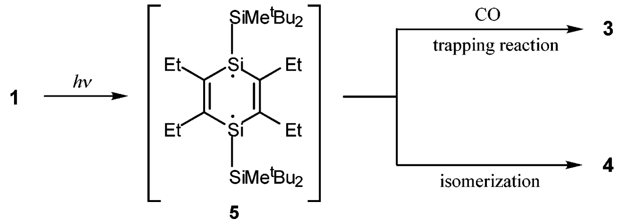


Figure 2. ORTEP drawing of disilyl ketone **3** (30% thermal ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): C1−O1 = 1.199(2), Si1−C1 = 1.9730(17), Si2−C1 = 1.9807(16), Si1−Si3 = 2.3919(5), Si2−Si4 = 2.3874(6), Si1−C2 = 1.8906(15), Si1−C5 = 1.8847(15), Si2−C3 = 1.8902(16), Si2−C4 = 1.8873(17), C2−C3 = 1.362(2), C4−C5 = 1.360(2), Selected bond angles (deg): Si1−C1−Si2 = 93.26(7), Si1−C1−O1 = 132.22(13), Si2−C1−O1 = 134.39(13), C1−Si1−Si3 = 115.48(5), C1−Si2−Si4 = 120.06(5).

On the other hand, the irradiation of a cyclohexane-d_{12} solution of **1** in a sealed NMR tube with light of wavelength $\lambda > 320$ nm for 6 h in the absence of CO resulted in the formation of the corresponding valence isomer 2,5-bis(di-*tert*-butylmethylsilyl)-1,3,4,6-tetraethyl-2,5-disilabenzvalene (**4**)[9] in quantitative yield (Scheme 2). The skeletal Si atoms in **4** are characteristically upfield shifted, appearing at −100.3 ppm in the ^{29}Si NMR spectrum.

Scheme 3



The formation of **3** and **4** can be reasonably explained by the initial formation of the biradical species **5** by the photolytic cleavage of the strained central Si−Si bond in **1**, followed by an effective trapping reaction with CO to produce **3** or the slow intramolecular isomerization to **4** in the absence of CO, respectively (Scheme 3). Thus, we have demonstrated here the first example of an unprecedented CO insertion into the strained Si−Si bond without any catalysts, leading to a disilyl ketone under very mild conditions.

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Supporting Information Available: Text giving experimental procedures of **1**−**4** and tables giving crystallographic data, including atomic positional and thermal parameters, for **1** and **3**; crystallographic data are also available in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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