

1,4-Disila(Dewar-benzene) and 1,4-Disilabenzene: Valence Isomerization of Bis(alkylsilacyclopropenyl)s

Yoshio Kabe, Kenichi Ohkubo, Hitomi Ishikawa, and Wataru Ando*

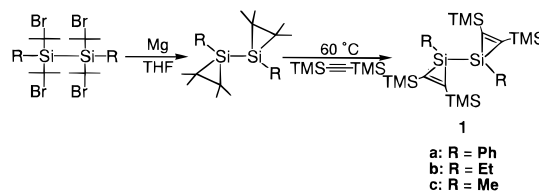
Department of Chemistry, University of Tsukuba
Tsukuba, Ibaraki 305-8571, Japan

Received August 19, 1999

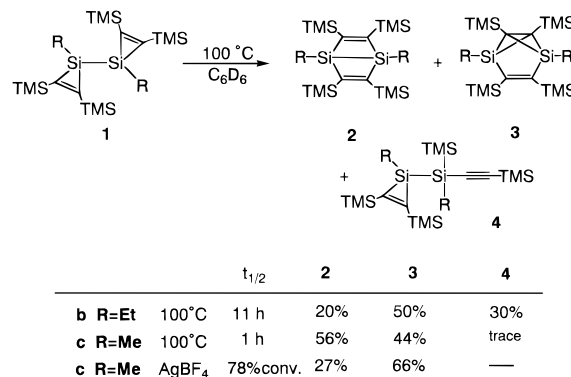
Although the explosive development of research on synthesis of silabenzene and other silabenzenoids has been stimulated from the discussion of sila-aromaticity,^{1,2} little is known of the valence isomers of silabenzene. Recently stable bis(silirane) and bis(silirene) (**1a**) have been synthesized by the simple debromination of tetrakis(2-bromoisopropyl)disilane.³ The fact that siliranes readily liberate olefin to give silylene led us believe that the bis(silirene) would be a suitable source of either valence isomers of disilabenzene or disilyne. Now we report that alkyl-substituted bis(silirene) produces the first 1,4-disila(Dewar-benzene)s (**2b**, **c**), one of which (**2c**) undergoes photochemical valence isomerization to the 1,4-disilabenzene intermediate (**9c**) under extremely mild solution conditions.

According to a previously published procedure,^{3,4} diethyl- and dimethyldisilacyclopropenyl (**1b,c**) were prepared in 58% and 43% yields, respectively, by heating bis(silacyclopropane)s in bis(trimethylsilyl)acetylene (Scheme 1). All spectroscopic data⁵ of **1b** and **1c** confirmed the structures; especially indicative are the high-field resonances of ²⁹Si NMR, characteristic of bis(silacyclopropene) ring silicons (−135.7 and −141.3 ppm for **1b** and **1c**, respectively). Thermolysis of **1c** was conducted in a degassed sealed tube at 100 °C in C₆D₆ monitored by ¹H, ¹³C, and ²⁹Si NMR spectroscopy using cyclohexane as internal standard until all the starting material was consumed. The ¹H NMR spectra of the resulting solution was comprised of three new SiMe₃ (0.15, 0.23, and 0.26 ppm) and two SiMe resonances (0.68 and 0.75 ppm). The single molecular formulas based on mass spectra (M⁺ − Me; 411) require that the products of **1c** consist of two valence

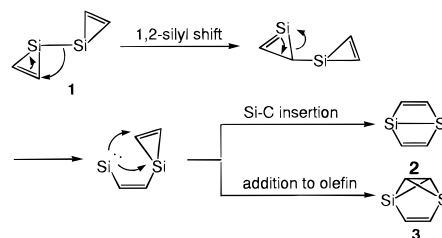
Scheme 1



Scheme 2



Scheme 3



isomers **2c** and **3c** in 56% and 44% NMR yields (Scheme 2). The presence of 2,5-dimethyldisilabenzvalene (**3c**) is assigned based on two SiMe₃ (0.15 and 0.23 ppm) and one SiMe proton resonance (0.68 ppm) as well as olefinic carbon (182.9 ppm) resonance in the ¹³C NMR and silirane ring silicon (−57.4 ppm) resonances in the ²⁹Si NMR along with the known spectra and chemical stability of the 2,5-diphenyl derivative (**3a**) (0.08 and 0.20 ppm for SiMe₃ proton resonances and 182.8 and −61.9 ppm for olefinic carbon and silirene ring silicon resonances).³ Therefore the other isomer, assigned one SiMe₃ (0.26 ppm) and one SiMe resonance (0.75 ppm), can be represented by the 1,4-disila(Dewar-benzene) (**2c**) or 1,4-disilabenzene structure. The chemical behavior of compound **2c** is incompatible with the latter structure when compared with the known chemistry of 1,4-disilabenzene.^{2n-p} The reaction mixture (**2c** and **3c**) was exposed in oxygen to provide the corresponding oxo derivative (**5c**) quantitatively (Scheme 4).⁶ On one occasion isomerically pure crystals were successfully grown from the thermolysis mixture (**2c** and **3c**) and a butterfly structure of **2c** was obtained by X-ray analysis (Figure 1).⁶ The central Si–Si bond length (2.244–2.248 Å) is substantially shorter than that of monocyclic 1,2-disilacyclobutenes (2.344–2.359 Å).^{7a,b} This short value is even smaller than those of disilacyclopropane (2.272 Å),^{7c} whose high reactivity is interpreted in terms of π-character of the Si–Si σ bond.

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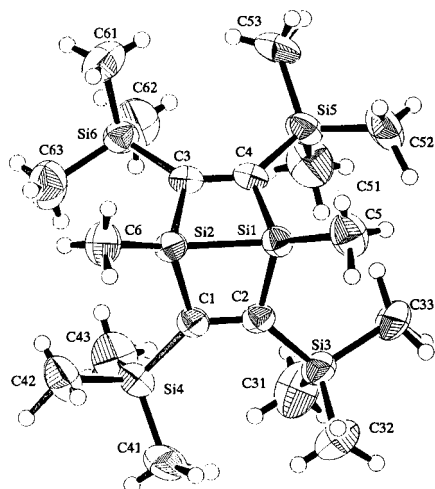
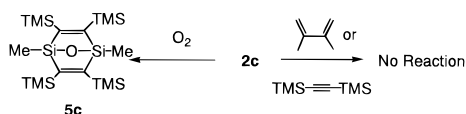


Figure 1. ORTEP drawing of **2c**. One of two independent molecules in the asymmetric unit is shown.

Scheme 4



A silver(I)-catalyzed isomerization of **1c** also takes place to give **2c** and **3c** in 27% and 66% NMR yields with 78% consumption of starting material (Scheme 2). Similarly the thermolysis of the ethyl derivative (**1b**) also resulted in the formation of **2b** and **3b** in 20% and 50% NMR yields. The low yields of these two products are due to another competing reaction taking place, which corresponds to a 1,2-terminal silyl shift to afford ethynyl disilane (**4b**)^{8a} in 30% NMR yield. The intermediate could be a vinyl silylene which is formed by a preceded 1,2-silyl shift and subsequent isomerization (Scheme 3).^{8b} Since the thermolysis of the **2c** and **3c** mixture caused only decomposition of **2c**, no valence isomerization between **2c** and **3c** occurs. This leads to the conclusion that the vinyl silylene species is a common intermediate for both 1,4-disila(Dewar-benzene) (**2**) and 2,5-disilabenzvalene (**3**) via intramolecular silylene addition and insertion to silirene.

Thermal stability toward addition of dimethylbutadiene as well as trimethylsilylacetylene was demonstrated (Scheme 4). On the other hand, without trapping reagents, upon photolysis in C_6D_6 **2c** was converted into **6c** quantitatively (Scheme 5). The structural assignment of **6c** was hampered by incorporation of C_6D_6 units, which was first disclosed by careful TOF- and FD-mass spectral analyses (M^+ 936; $[(Me_3Si)_4C_4Si_2Me_2]_2 C_6D_6$). Finally, an accumulation of more than 16 thousand ^{13}C NMR measurements established that a deuterated cyclohexene ring exists in the molecule based on three triplet resonances at 22.1 ($J_{CD} = 19$ Hz),

(6) Suitable crystals were obtained by recrystallization from hexane at -20 °C in a glovebox. Crystal data for **2c**: $C_{18}H_{22}Si_6$ M 427.04, triclinic with $a = 10.5224(6)$ Å, $b = 15.627(2)$ Å, $c = 17.7265(13)$ Å, $\alpha = 102.596(7)^\circ$, $\beta = 90.0195(5)^\circ$, $\gamma = 89.998(6)^\circ$, $V = 2844.6(4)$ Å³, space group $P1$, $Z = 4$, $\rho_{calc} = 0.99$ g cm⁻³. Crystal data for **5c**: $C_{18}H_{22}Si_6O$ M 443.04, triclinic with $a = 10.1856(10)$ Å, $b = 12.0125(8)$ Å, $c = 13.0143(10)$ Å, $\alpha = 103.671(6)^\circ$, $\beta = 92.809(7)^\circ$, $\gamma = 111.622(7)^\circ$, $V = 1422.0(3)$ Å³, space group $P1$, $Z = 2$, $\rho_{calc} = 1.035$ g cm⁻³. The 5846 and 3207 independent reflections [$2\theta < 50^\circ$]; $[F_o^2] > 3\sigma[F_o^2]$] were measured on an Enraf-Nonius CAD4 diffractometer using Mo $K\alpha$ irradiation and an ω - 2θ scan. The structures were solved by direct methods and all non-hydrogen atoms were refined anisotropically to $R = 0.054$ ($R_w = 0.064$) and $R = 0.057$ ($R_w = 0.064$).

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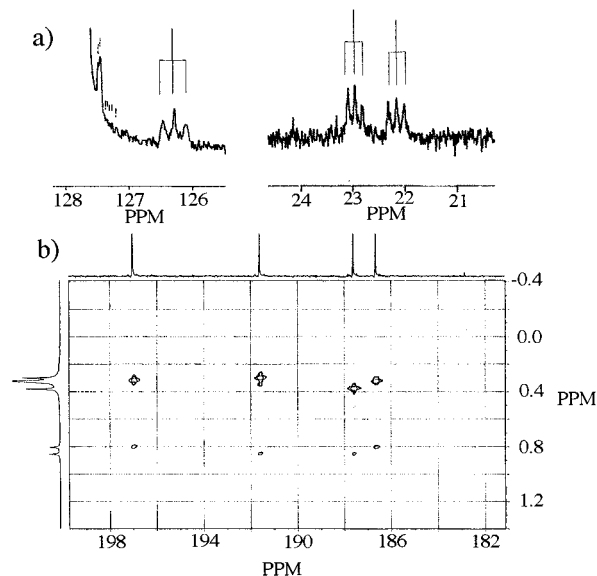
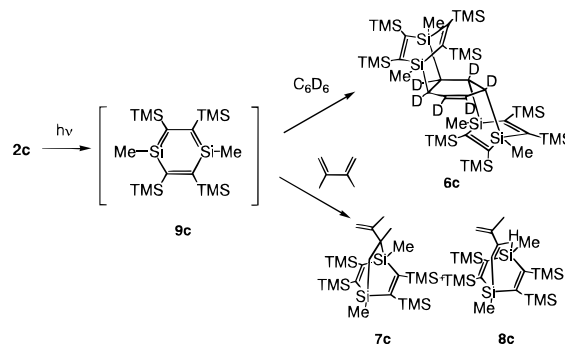


Figure 2. (a) ^{13}C NMR selected regions of **6c** and (b) C,H COLOC spectrum of **6c**.

Scheme 5



22.9 ($J_{CD} = 16$ Hz), and 126.3 ($J_{CD} = 22$ Hz) ppm, respectively (Figure 2a). The 1H , ^{13}C , and ^{29}Si NMR spectra showed the presence of four nonequivalent $SiMe_3$ and two nonequivalent $SiMe$ groups and as well as four olefinic carbons, which is consistent with the unique symmetry expressed in **6c**.⁵ The C,H COLOC long-range couplings between $SiMe$ protons and olefinic carbons support the structural integrity of 1,4-disilacyclohexadiene units (Figure 2b). Owing to steric repulsion, only the trans-anti orientation of 1,4-disilacyclohexadienes units in **6c** was possible. These arguments lead to the conclusion that the proposed structure of **6c** possesses a screw-like structure with C_2 symmetry. Photolysis of the mixture in the presence of 10 equiv of 2,3-dimethylbutadiene afforded adducts **7c** and **8c**⁵ in 41% and 35% yield after recovery of **3c** (Scheme 5).

The formation of **6c** and **7c** clearly accounts for mild photochemical valence isomerization of 1,4-disila(Dewar-benzene) (**2c**) to 1,4-disilabenzene intermediate (**9c**), which undergoes [4+2] cycloaddition toward C_6D_6 and butadiene, respectively. It is now under investigation based on theoretical calculation whether **8c** is responsible for the excited biradical species of 1,4-disilabenzene in this reaction.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research on Priority Area (No. 11120206) from the Ministry of Education, Science Sports and Culture, Japan and Japan Chemical Innovation Institute (JCII). The authors are also grateful for the skillful FD- and TOF-mass measurement of Sumitomo Chemical Industries Co. Ltd. and for the kind help of Dow Corning Asia Ltd.

Supporting Information Available: Detailed information on the spectroscopic data of all new compounds and X-ray crystal analysis of **2c** and **5c** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA9930061