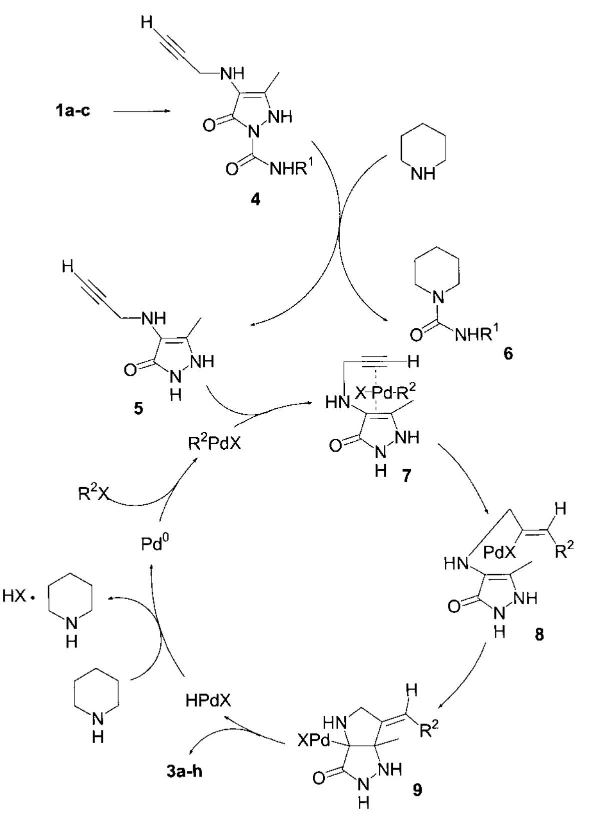

Scheme 2. A plausible catalytic cycle for the formation of **3**.

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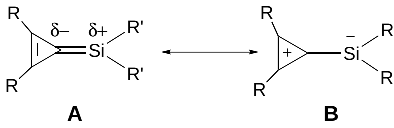
The First Isolable 4-Silatriafulvene**

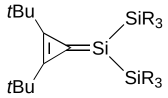
Kenkichi Sakamoto,* Jun Ogasawara, Yoshihiro Kon, Tatsuya Sunagawa, Chizuko Kabuto, and Mitsuo Kira*

Among various silicon–carbon doubly bonded compounds (silaethenes),[1] 4-silatriafulvenes have attracted much attention because of their unique electronic properties;[2,3] the intrinsic polarity of the Si=C bond in 4-silatriafulvene (**A**) is expected to be reduced by the significant contribution of resonance structure **B** (Scheme 1).

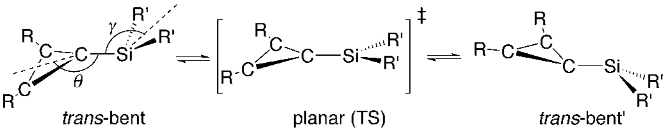


Scheme 1.

We recently generated the first 4-silatriafulvene derivative, 1,2-di-*tert*-butyl-4,4-bis(trimethylsilyl)-4-silatriafulvene (**1a**),[2] as a reactive intermediate and demonstrated that **1a** is much less reactive toward *tert*-butyl alcohol than is usual for silaethenes and isomerizes to the corresponding silacyclobutadiene at high temperatures. Theoretical calculations for 4-silatriafulvene derivatives have predicted the fluxional nature of the 4-silatriafulvene skeletons, which are not planar around the Si=C bond but *trans*-bent, with large bend angles and an energy difference of only 1.0 kcal mol^{-1} between the *trans*-bent and planar structures at the MP2/6-311++G**+ZPE level (Scheme 2).[3d]



1a, $SiR_3 = SiMe_3$
1b, $SiR_3 = SiMe_2tBu$



Scheme 2. Skeletal inversion of silatriafulvene.

Although Schumann et al. have reported the isolation of stable 4-germa-, 4-stanna-, and 4-plumbatriafulvenes,[4] no stable 4-silatriafluvene has been synthesized to date.[5] By use of bulky *tert*-butyldimethylsilyl groups instead of trimethylsilyl groups in **1a**, we synthesized the first stable 4-silatria-

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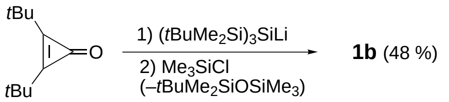
[*] Prof. K. Sakamoto,[+] Dr. J. Ogasawara, Y. Kon,
T. Sunagawa, Dr. C. Kabuto, Prof. M. Kira
Department of Chemistry,
Graduate School of Science
Tohoku University, Aoba-ku, Sendai 980-8578 (Japan)
Fax (+81) 22-217-6589
E-mail: mkira@si.chem.tohoku.ac.jp

[+] Concurrent office:
Photodynamics Research Center
The Institute of Physical and Chemical Research (RIKEN)
519-1399 Aoba, Aramaki, Aoba-ku, Sendai 980-0845 (Japan)

[**] This work was supported by the Japanese Ministry of Education, Culture, Sports, Science, and Technology [Grant-in-Aid for Scientific Research (B) No. 11440185].

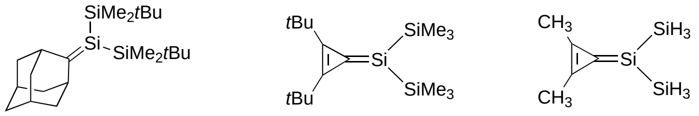
fulvene, 1,2-di-*tert*-butyl-4,4-bis(*tert*-butyldimethylsilyl)-4-silatriafulvene (**1b**), and revealed its structural characteristics by NMR and UV spectroscopic studies and X-ray crystallography. The addition of methanol to **1b** occurred with unusual regioselectivity compared with the corresponding reactions of common silaethenes.

The sila-Peterson reaction[6, 7] of di-*tert*-butylcyclopropenone with tris(*tert*-butyldimethylsilyl)silyllithium successfully gave the corresponding silatriafulvene **1b** as yellow crystals (48 % yield) [Eq. (1)].[8] Although **1b** was extremely sensitive to air and moisture, neither decomposition nor dimerization took place for several months at room temperature in an inert atmosphere.



(1)

In good accord with the unique electronic structure of 4-silatriafulvene, in the NMR spectrum, the resonance signal of the unsaturated ^{29}Si nucleus in **1b** in [D$_6$]benzene appeared at an extraordinarily high field $\delta_{Si} = -71.9$, which is 122 ppm higher than that of bis(*tert*-butyldimethylsilyl)adamantylidenesilane (**2**; Scheme 3; $\delta_{Si} = +50$)[6b]. The position of the observed ^{29}Si resonance signal is in good agreement with that of the unsaturated silicon atom in a model silatriafulvene **1c** ($\delta_{Si} = -68.7$) calculated at the bent equilibrium structure, by using the GIAO method at the HF/6-31G*//MP2/6-31G* level. The remarkable upfield shift is the result of the less polar nature of the Si=C bond caused by the significant contribution of resonance structure **B** (Scheme 1) in **1b**, compared with **2** and other common silaethenes.[9]



2 **1c** **1d**

Scheme 3.

The molecular structure of **1b**, determined by X-ray crystallography, was not consistent with the predicted bent form.[12] As shown in Figure 1, **1b** in the solid state has an almost planar skeleton with bond alternation; all the skeletal carbon and silicon atoms are located almost in a plane with bend angles θ and γ of 166.1° and 170.9°, respectively,[13] and the unsaturated silicon-carbon bond length is 1.755 Å, which is close to that of *tert*-butyldimethylsilyl(trimethylsilyl)-adamantylidenesilane (1.741 Å).[6b] The X-ray structure of **1b** does not resemble the optimized bent structure but the planar transition structure of the model silatriafulvene **1c** (Scheme 3). The discrepancy between the X-ray structure and the theoretical equilibrium structure is explained by the packing force in the crystal, which is larger than the very small energy required for the deformation of the bent structure to the planar structure.

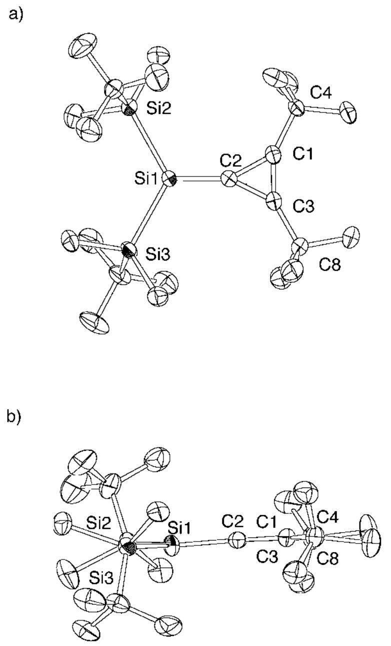
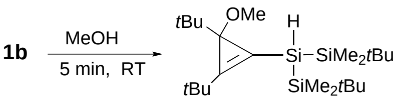


Figure 1. ORTEP drawings of **1b**. a) Top view, b) side view. Hydrogen atoms are omitted for clarity. The thermal ellipsoids are set at the 50% level. Selected bond lengths [Å] and bond angles [°]: Si1-Si2, 2.3335(8); Si1-Si3 2.3420(7), Si1-C2 1.755(2), C1-C2 1.450(3), C1-C3 1.309(3), C1-C4 1.496(3), C2-C3 1.447(3), C3-C8 1.497(3); Si2-Si1-Si3 120.21(3), Si2-Si1-C2 119.65(7), Si3-Si1-C2 119.71(7), C2-C1-C3 63.1(1), C2-C1-C4 144.6(2), C3-C1-C4 152.2(2), Si1-C2-C1 152.0(2), Si1-C2-C3 154.1(2), C1-C2-C3 53.7(1), C1-C3-C2 63.2(1), C1-C3-C8 150.6(2), C2-C3-C8 146.1(2).

The fluxional character of 4-silatriafulvene (Scheme 2) was, as predicted by theoretical calculations, evidenced by the significant temperature dependence in the ^{29}Si NMR and UV spectra of **1b**. The $\delta_{Si} = -73.7$ signal of **1b** at 298 K shifted to $\delta_{Si} = -77.0$ at 190 K in [D$_8$]THF, and the UV absorption maximum (λ_{max}) that appeared at 352 nm ($\varepsilon = 16000$) in 3-methylpentane at 298 K was blue-shifted and its intensity increased by lowering the temperature; λ_{max} reached 344 nm with $\varepsilon = 33000$ at 77 K. The GIAO calculations for the planar and bent structures of **1c** have shown that the δ_{Si} values are -68.7 and -61.2, respectively, at the HF/6-31G*//MP2/6-31G* level.[3g] CIS calculations have revealed that the $\pi-\pi^*$ transition band for the planar structure of **1d** should appear at 310 nm with an oscillator strength f of 0.065, while that for the bent structure should appear at 303 nm with an f of 0.346.[3g] The temperature dependence observed in the ^{29}Si NMR and UV spectra of **1b** is consistent with the idea that, at high temperature, the structure of **1b** fluctuates around the planar structure with large bending amplitudes, but at low temperature, **1b** freezes to the bent equilibrium structure.

While silatriafulvene **1b** did not react appreciably with *tert*-butyl alcohol over a couple of days at room temperature,[14] **1b** reacts with methanol instantaneously at room temperature to give **3** in 73 % yield [Eq. (2)].[15] Interestingly, the regioselec-



3 (73 %)

(2)

tivity was completely opposite to that for the alcohol addition to common silaethenes, which indicates the significant contribution of the resonance form **B** in **1b** (Scheme 1); the OH hydrogen and methoxy groups of methanol were bonded to the unsaturated silicon atom and a ring carbon atom in **1b**, respectively.[16]

Received: December 14, 2001 [Z18381]

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[8] **1b**: Yellow crystals; m.p. 95 °C (decomp.); ^{1}H NMR (300 MHz, [D$_6$]benzene, TMS): $\delta = 0.47$ (s, 12H), 1.16 (s, 18H), 1.17 (s, 18H); ^{13}C NMR (75 MHz, [D$_6$]benzene, TMS): $\delta = 0.2$, 19.6, 28.5, 28.6, 32.9, 157.0 (C=C), 159.9 (Si=C, $^1J_{\mathrm{Si,C}} = 66$ Hz); ^{29}Si NMR (59 MHz, [D$_6$]benzene, TMS): $\delta = -71.9$ (Si=C, $^1J_{\mathrm{Si,C}} = 66$ Hz), 1.7 (Si*t*BuMe$_2$); HRMS calcd for $C_{23}H_{48}Si_3$ 408.3064 found 408.3060.

[9] Typical δ_{Si} values for (Me$_3$SiO)(Ad)C=Si(SiMe$_3$)$_2$ (Ad = adamantyl) and (Me$_3$Si)(*t*BuMe$_2$Si)C=SiMe$_2$ are +42 and +144, respectively.[10] Recently, negative δ_{Si} values for the unsaturated silicon nuclei have been found in 1-aza-3-silaallene ($\delta_{\mathrm{Si}} = -57$)[11] and hexaphenylsilacalicene ($\delta_{\mathrm{Si}} = -28$),[5] with rather less polar Si–C double bonds.

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[12] Recrystallization of **1b** from heptane gave single crystals suitable for X-ray structural analysis. X-ray analysis of **1b**: $M_{\mathrm{F}} = C_{23}H_{48}Si_3$, $M_{\mathrm{W}} = 408.89$, monoclinic, space group $P21/c$, $a = 11.0141(8)$, $b = 17.9026(9)$, $c = 14.210(3)$ Å, $\beta = 91.173(2)°$, $V = 2801.4(7)$ Å^3, $Z = 4$, $\rho_{\mathrm{calcd}} = 0.969$ g cm^{-3}, $\mu(\mathrm{Mo}_{K\alpha}) = 1.75$ cm^{-1}. The reflection intensities were collected on a Rigaku/MSC Mercury CCD diffractometer (50 kV, 40 mA) with graphite monochromated Mo$_{K\alpha}$ radiation ($\lambda = 0.71069$ Å) at 150 K. The structure was solved by direct methods, by using SIR-92, and refined by full-matrix least-squares analysis on *F*. A total of 6392 reflections were measured, and of these, 4509 reflections [$F_o > 3.00\sigma(F_o)$] were used in refinement: $R = 0.041$, $Rw = 0.044$. CCDC-175782 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

[13] The bend angles θ and γ are defined as the angles between the three-membered-ring plane and the Si(unsaturated)–C bond, and between the R$_2$Si plane and the Si(unsaturated)–C bond, respectively (Scheme 2). Theoretical bend angles θ and γ for **1c** in the bent structure are 171.8 and 141.5°, respectively.[3g]

[14] The reaction of **1b** with *tert*-butyl alcohol in hexane under reflux afforded the alcohol adducts of the corresponding silacyclobutadiene as expected.[2] Details will be reported elsewhere.

[15] **3**: a colorless oil; ^{1}H NMR (300 MHz, C$_6$D$_6$): $\delta = 0.21$ (s, 3H), 0.25 (s × 2, 6H), 0.27 (s, 3H), 1.00 (s × 2, 18H), 1.18 (s, 9H), 1.22 (s, 9H), 3.02 (s, 3H), 4.24 (s, 1H); ^{13}C NMR (75 MHz, C$_6$D$_6$): $\delta = -2.92$, −2.87, −2.60, −2.41, 18.51, 18.59, 27.65, 29.41, 30.51, 32.73, 38.09, 53.95, 76.42, 115.25, 156.53; ^{29}Si NMR (59 MHz, C$_6$D$_6$): $\delta = -90.24$ (d, $^1J(\mathrm{Si,H}) = 155$ Hz), −1.92, −1.43; MS (70 eV) *m*/*z* (%) 425 ($M^+ - 15$, 6), 259 (6), 147 (100), 115 (6).

[16] Similar inverted regioselectivity has been observed for a silacalicene by West et al.[5]

Aldolase-Catalyzed Asymmetric Synthesis of Novel Pyranose Synthons as a New Entry to Heterocycles and Epothilones**

Junjie Liu and Chi-Huey Wong*

The enzyme 2-deoxyribose-5-phosphate aldolase (DERA, EC 4.1.2.4), a Schiff base forming type I class aldolase, catalyzes the reversible aldol reaction of acetaldehyde and D-glyceraldehyde 3-phosphate (G3P) to form D-2-deoxyribose-5-phosphate (DRP).[1] The enzyme has been overexpressed in *Escherichia coli*, and its structure and catalytic mechanism have been determined at the atomic level.[2]

DERA accepts a broad range of acceptor and donor aldehydes in addition to the natural substrates.[1] An interesting transformation is the sequential asymmetric aldol addition reaction of three achiral aldehydes to form pyranoses with two new stereogenic centers (Scheme 1 A).[3] In this sequential reaction, the first aldol product acts as a substrate for the second aldol reaction to give an enantiomerically pure 3,5-

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[*] Prof. Dr. C.-H. Wong, J. Liu
Department of Chemistry and the Skaggs Institute for Chemical Biology
The Scripps Research Institute, La Jolla, CA 92037 (USA)
Fax:(+1) 858-784-2409
E-mail: wong@scripps.edu

[**] This work was supported by the NIH GH44154. We thank Dr. G.-J. Shen for the preparation of 2-deoxyribose-5-phosphate aldolase (DERA) and Dr. D.-H. Huang and Dr. L. B. Pasternack for NMR assistance.

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