Novel Stable Silenes via a Sila-Peterson-type Reaction. Molecular Structure and Reactivity

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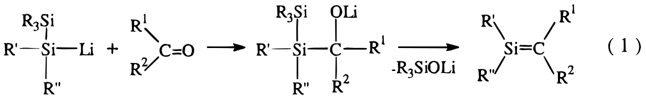
The first stable silene was synthesized only in 1981[1] after decades of intensive unsuccessful attempts.[2] Despite intensive recent research, the study of silenes is still in its infancy.[2] For example, only two methods for the synthesis of stable silenes are currently known[1,3] and the X-ray structures of only 2 silenes, $(Me_3Si)_2Si{=}C(OSiMe_3)Ad$ (**1**)[4] and $Me_2Si{=}C(SiMe_3)SiMe(t\text{-}Bu)_2$ (**2**),[5] have so far been determined. More recently West et al. reported the first X-ray structure of a 1-silaallene, $R_2Si{=}C{=}CR_2$.[6] We report here an important new synthetic method for preparing stable silenes having a novel substitution pattern and report the X-ray structure for one of these silenes.

We[7a] and others[7b] have reported recently that transient silenes can be synthesized via a sila-Peterson-type reaction (eq 1). For

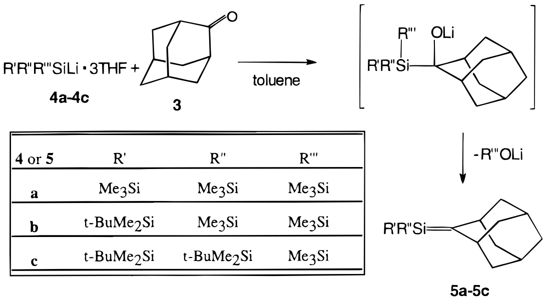


$$R'-\underset{R''}{\overset{R_3Si}{Si}}-Li + {}^{R^1}_{R^2}\!>C{=}O \longrightarrow R'-\underset{R''}{\overset{R_3Si}{Si}}-\underset{R^2}{\overset{OLi}{C}}-R^1 \xrightarrow[-R_3SiOLi]{} {}^{R'}_{R''}\!>Si{=}C<^{R^1}_{R^2} \qquad (1)$$

example, adamantanone (**3**) reacts in toluene with $(Me_3Si)_3SiLi\cdot 3THF$ (**4a**) to produce $Ad{=}Si(SiMe_3)_2$ (**5a**), where Ad = 2-adamantyl, (see Scheme 1).[7a] However, **5a** dimerized instantaneously.[7a] We assumed that increase in the steric bulk around the silene would lead to a stable isolable silene. This required the synthesis of unknown silyl anions with bulky R′ and R″ groups (eq 1). This goal was successfully achieved with the synthesis of $(t\text{-}BuMe_2Si)(Me_3Si)_2SiLi\cdot 3THF$ (**4b**) and $(t\text{-}BuMe_2Si)_2(Me_3Si)SiLi\cdot 3THF$ (**4c**).[8]

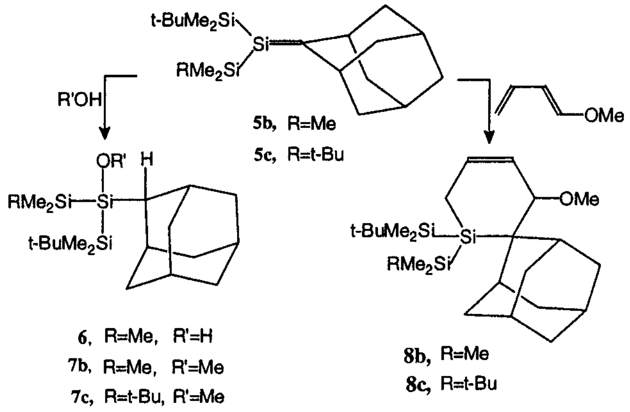
Indeed, reaction of adamantanone with **4b** or with **4c** leads in excellent yields to the novel stable silenes **5b** and **5c** (Scheme 1), respectively.[9] Compound **5a**, which can be formed in the reaction of **4b** with **3** by elimination of $t\text{-}BuMe_2SiOLi$, was not detected. The silenes **5b** and **5c** were fully characterized by their ^1H, ^{13}C, and ^{29}Si NMR spectra,[10] as well as by trapping experiments, and for **5b** also by X-ray analysis.

Scheme 1



4 or 5	R'	R''	R'''
a	Me_3Si	Me_3Si	Me_3Si
b	$t\text{-}BuMe_2Si$	Me_3Si	Me_3Si
c	$t\text{-}BuMe_2Si$	$t\text{-}BuMe_2Si$	Me_3Si

Scheme 2



The NMR of **5b** is consistent with that of other silenes; the sp^2 Si absorbs at 51.7 ppm, silenes of type **1** exhibited resonances in the range of 41.4−54.3 ppm,[11,12a] and the sp^2 C shows a signal at 196.8 ppm, ca. 15 ppm upfield than in **1**.[11,12b] Compound **5b** exhibits a strong UV band with a maximum at 322 nm, a wavelength significantly longer than in $H_2Si{=}CH_2$ (258 nm), $MeHSi{=}CH_2$ (260 nm), or in $Me_2Si{=}CH_2$ (244 nm) but similar to that of **1** (339 nm).[13] Ab initio calculations for model compounds suggest that the batochromic shifts in **1** and **5b** are due to the silyl substitution at the sp^2 silicon.

Compounds **5b** and **5c** are stable in toluene solution for more than 6 months at room temperature, even in the presence of equimolar amounts of $Me_3SiOLi + 3THF$. On the other hand, they react rapidly at room temperature with various other reagents (Scheme 2) (e.g., **5b** reacts with water to give the silanol **6** (X-ray structure is available); **5b** and **5c** react with methanol to produce **7b** and **7c**, respectively, and with 1-methoxybutadiene to produce the expected[7a] Diels−Alder products **8b** and **8c**, respectively).[14]

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[1] Brook, A. G.; Abdesaken, F.; Gutekunst, B.; Gutekunst, G.; Kallury, R. K. M. *J. Chem. Soc., Chem. Commun.* **1981**, 191.

[2] For a review, see: Raabe, G.; Michl, J. In *The Chemistry of Organosilicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, 1989; Chapter 17.

[3] Wiberg, N.; Wagner, G. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 1005.

[4] Brook, A. G.; Nyburg, S. C.; Abdesaken, F.; Gutekunst, B.; Gutekunst, G.; Kallury, R. K. M. R.; Poon, Y. C.; Chang, Y.; Wong-Ng, W. *J. Am. Chem. Soc.* **1982**, *104*, 5668.

[5] Wiberg, N.; Wagner, G.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 229.

[6] Miracle, G. I.; Ball, J. L.; Powell, D. R.; West, R. *J. Am. Chem. Soc.* **1993**, *115*, 11598.

[7] (a) Bravo-Zhivotovskii, D.; Braude, V.; Stanger, A.; Kapon, M.; Apeloig, Y. *Organometallics* **1992**, *11*, 2326; (b) For example, see: Luderer, F.; Reinke, H.; Oehme, H. *Chem. Ber.* **1996**, *129*, 15 and references therein.

[8] Compounds **4b**,**c** were synthesized by the reaction of MeLi with $(t\text{-}BuSiMe_2)Si(SiMe_3)_3$ or with $(t\text{-}BuSiMe_2)_2Si(SiMe_3)_2$, respectively.

[9] The following standard procedure is for **5b**: 3.0 g (5.9 mmol) of **4b** in 30 mL of dry toluene was placed in a Schlenk flask under vacuum, and 0.83 g (5.7 mmol) of **3** in 10 mL of dry toluene was added. The reaction mixture was stirred overnight at room tempterature (complete conversion was detected by NMR), the toluene was removed, and 50 mL of dry pentane was added. The mixture was cooled to −78 °C, and after 24 h white crystals of Me_3SiOLi were separated. The solution was concentrated to 5 mL, and at −5 °C colorless crystals of **5b**, suitable for X-ray analysis, were formed.

[10] For **5b**: ^1H NMR (C_6D_6) δ 0.18 (6H, s, $t\text{-}BuMe_2Si$), 0.26 (9H, s, Me_3Si), 0.96 (9H, s, *t*-Bu), 1.62−1.94 (12 H, m, Ad), 3.2 (2H, m, $CHC{=}Si$); ^{13}C NMR (C_6D_6) δ −2.13 ($t\text{-}BuMe_2Si$), 2.45 (Me_3Si), 18.4 (Me_3C), 27.49 (Me_3C), 29.15, 38.24, 41.91, 42.10, 42.55 (Ad), 196.84 ($C{=}Si$); ^{29}Si NMR (C_6D_6) δ −14.5 (Me_3Si), 1.0 ($t\text{-}BuMe_2Si$), 51.7 ($Si{=}C$); UV (pentane) 322 nm, $\epsilon = 6300$. For **5c**: ^1H NMR (C_6D_6) δ 0.25 (12 H, s, $t\text{-}BuMe_2Si$), 1.01 (18H, s, *t*-Bu), 1.62−1.94 (12H, m, Ad), 3.2 (2H, m, $CHC{=}Si$); ^{13}C NMR (C_6D_6) δ −1.8 ($t\text{-}BuMe_2Si$), 18.7 (Me_3C), 25.7 (Me_3C), 27.7, 29.1, 38.3, 41.9, 42.3 (Ad), 198.2 ($C{=}Si$); ^{29}Si NMR (C_6D_6) δ 0.5 ($t\text{-}BuMe_2Si$), 49.7 ($Si{=}C$).

[11] Gutekunst, G.; Brook, A. G. *J. Organomet. Chem.* **1982**, *225*, 1.

[12] (a) $\delta(^{29}Si)$ in **2** is 144.2 ppm. See: Wiberg, N.; Wagner, G. *Chem. Ber.* **1986**, *119*, 1467. (b) Similar upfield shifts were found in olefins when a methyl was substituted by a $OSiMe_3$ group (e.g., C_1 in 1-(trimethylsiloxy)-hexene and in 1-methylhexene absorbs at 150.2 and 134.0 ppm, respectively).

[13] Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419−507.

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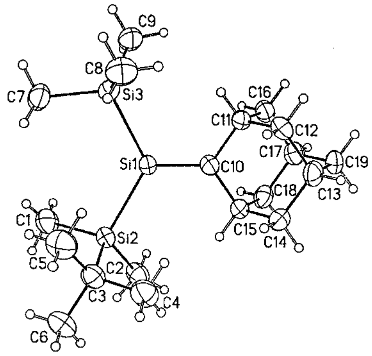

Figure 1. ORTEP diagram of **5b**. Selected bond lengths (Å) and bond angles (deg): Si(1)−C(10), 1.741(2); Si(1)−Si(2), 2.339(1); Si(1)−Si(3), 2.434; Si(2)−C(3), 1.904(2); Si(3)−C(7), 1.872(2); C(3)−C(4), 1.529(3); C(10)−C(11), 1.515(2); C(10)−C(15), 1.520(3); C(11)−C(12), 1.535(3); Si(2)−Si(1)−Si(3), 122.9(1); Si(2)−Si(1)−C(10), 119.7(1); Si(3)−Si(1)−C(10), 117.2(1); Si(1)−Si(2)−C(1), 109.1(1); Si(1)−Si(2)−C(2), 112.7(1); Si(1)−Si(2)−C(3), 108.9(1); Si(1)−Si(3)−C(7), 110.3(1); Si(1)−Si(3)−C(8), 109.2(1); Si(1)−Si(3)−C(9), 111.7(1); Si(1)−C(10)−C(11), 123.9(1); Si(1)−C(10)−C(15), 125.4(1); C(11)−C(10)−C(15), 110.6(1).

The X-ray structure of **5b** shown in Figure 1[15] exhibits an essentially planar arrangement around the C═Si bond with a small twisting of 4.6° around the C═Si bond.[16] The C═Si bond length in **5b** is 1.741 Å, intermediate between that in **2** (1.702 Å[5]) or in $Me_2Si{=}CH_2$ (1.692 Å[17]) and in **1** (1.764 Å[4]). Ab initio[18] calculations show that the relatively long *r*(C═Si) in **5b** is not due to the steric bulk of the substituents. Thus, the calculated (at 6-31G*) *r*(C═Si) in **5b** of 1.734 Å, which is in good agreement with experiment, is only by 0.005 Å longer than in the strain-free $Me_2C{=}Si(SiH_3)_2$ (1.729 Å at 6-31G*[19]). Furthermore, the calculations show that the elongation of *r*(C═Si) in **5b** is due to the electronic effects of the substituents,[20] and it is contributed to a similar degree by the silyl and the methyl substituents. The much shorter calculated *r*(C═Si) in $Me_2Si{=}C(SiH_3)_2$ of 1.722 Å at MP2/6-31G* (1.703 Å at 6-31G*, 1.702 Å experimental in **2**) demonstrates the importance of the substitution pattern of the silene, and calculations show that it is connected to the silene polarity.[20a] Thus, $Me_2C{=}Si(SiH_3)_2$ (a model for **5b**) is relatively nonpolar while $Me_2Si{=}C(SiH_3)_2$ and $Me_2C{=}SiMe_2$ are strongly polarized. The calculated Mulliken charges for the C═Si atoms (total and π charges, respectively) are the following (at RHF/6-31G*): $H_2Si{=}CH_2$, Si(+0.46, +0.17), C(−0.65, −0.15); $Me_2Si{=}CMe_2$, Si(+0.69, +0.16), C(−0.24, −0.14); **5b**, Si(−0.11, −0.02), C(−0.14, +0.03); $Me_2C{=}Si(SiH_3)_2$, Si(−0.01, −0.04), C(−0.16, +0.05). We believe that the relatively nonpolar C═Si bond in silenes of type **5** contributes significantly to their kinetic stability (the same applies to **1**[20a]).

Why is **5b** so dramatically more stable toward dimerization than **5a**? Shielding of the C═Si π bond by the *tert*-butyl group ($\angle C_3Si_2Si_1C_{10} = 89.1°$, Figure 1) is probably not the main reason since attack can occur from the side of the π bond which is shielded only by a methyl group, as in **5a** which dimerizes instantaneously.[7a] MMX force field calculations[21] reveal that the dramatic difference in reactivity between **5b** and **5a** probably results from differences in steric congestion in their dimerization transition states. Thus, the steric strain that is created on going from the silene to the head-to-head dimer (Δ)[7a] is by 28.2 kcal/mol larger for **5b** than for **5a**.[22] These calculations also predict that Δ for Ad═Si(SiMe$_3$)(*i*-PrSiMe$_2$) is 15.7 kcal/mol higher than for **5a**, suggesting that the former may also be a kinetically stable silene. In contrast, Ad═Si(SiMe$_3$)(SiMe$_2$Et) is expected to dimerize spontaneously, as does **5a**,[7a] because Δ for the former silene is by only 3.5 kcal/mol larger than for **5a**.

We have also found that the Peterson-type reaction can be extended to produce stable germenes;[23] thus, reaction of adamantanone with (*t*-BuMe$_2$Si)(Me$_3$Si)$_2$GeLi·3THF produces the stable germene Ad═Ge(SiMe$_3$)(*t*-BuSiMe$_2$) which was characterized by NMR spectroscopy and trapping experiments. Further studies to probe the scope of the sila-Peterson reaction and the chemistry of the resulting stable silenes are in progress.

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Supporting Information Available: Preparative procedures and spectroscopic data for **4b**, **4c**, (Me$_3$Si)$_3$Si(*t*-BuSiMe$_2$), (Me$_3$Si)$_2$Si(*t*-BuSiMe$_2$)$_2$, (*t*-BuMe$_2$Si)(Me$_3$Si)$_2$GeLi·3THF, trapping products of **5b** and **5c** (**6**, **7b**, **7c**, **8b**, Ad═Ge(SiMe$_3$)(*t*-BuSiMe$_2$)), and for its Diels−Alder adduct with butadiene and tables of bond lengths and bond angles, anisotropic displacement parameters, and hydrogen atom coordinates and thermal parameters for **5b** (12 pages). See any current masthead page for ordering and Internet access instructions.

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(14) The isomeric regioisomers were not detected. A single [2 + 2] product, resulting from addition of the C═Si bond to the unsubstituted end of 1-methoxybutadiene with the silicon bonded to C_4 of butadiene was also obtained in 20−30% yield.

(15) X-ray structure determination of $C_{19}H_{38}Si_3$ (MW = 350.8): crystal dimensions 0.20 × 0.15 × 0.12 mm^3, colorless, Siemens P4 diffractometer, Mo Kα radiation, $T = 140$ K, monoclinic, $a = 11.666(2)$, $b = 12.780(4)$, and $c = 14.849(4)$ Å, $\beta = 91.02(2)°$, $V = 2220(3)$ Å^3; $Z = 4$, $d_{cell} = 1.049$ mg/m^3, space group $P2_1/n$ (No. 14), 3369 reflections collected, 2891 unique intensities ($R_{merg} = 0.01$), $2\theta_{max} = 45°$, 2570 reflections observed ($F_0 \geq 4\sigma(F)$), structure solution with direct methods (SHELXS) and refinement on *F* with 216 parameters riding groups for all hydrogen atoms; (common isotropic *U* values for each group) $R = 0.0315$, $R_w = 0.0384$, $s = 1.01$, $w^{-1} = \sigma^2(F_0 + 0.0018F_0^2)$.

(16) In **1** and **2** the twisting around the C═Si bond is 14.6° and 1.6°, respectively.

(17) Gutowsky, H. S.; Chen, J.; Hajduk, P. J.; Keen, J. D.; Chuang, C.; Emilsson, T. J. *Am. Chem. Soc.* **1991**, *113*, 4747.

(18) GAUSSIAN 94, Revision C.2; Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Rahvavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Oritz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian, Inc.: Pittsburgh, PA, 1995.

(19) 1.754 Å at MP2/6-31G* and 1.752 Å at MP4(SDQ)/6-31G* were obtained. The experimental *r*(C═Si) of 1.741 Å is intermediate between the RHF and the correlated values.

(20) This was pointed out also for other silenes; see: (a) Apeloig, Y.; Karni, M. *J. Chem. Soc., Chem. Commun.* **1984**, 768. Apeloig, Y.; Karni, M. *J. Am. Chem. Soc.* **1984**, *106*, 6676. (b) e.g., in $(H_3Si)_2Si{=}C(CH_3)OSiH_3$ (a model for **1**) *r*(C═Si) is calculated to be 1.743 Å (at RHF/6-31G*), by 0.05 Å longer than in $H_2Si{=}CH_2$, indicating that the bulky substituents in **1** have a relatively small effect on *r*(C═Si).

(21) The program used was PCMODEL version 3.2 by Serena Software (containing parameters for sp^2 Si: Brook, A. G.; Gajewski, J. J. *Heteroat. Chem.* **1990**, *1*, 57).

(22) The reliability of these calculations is supported by the good agreement between the calculated (MMX) and the experimental structures of **5b** and of the head-to-head dimer of **5a**.

(23) For application of this reaction to the synthesis of transient germenes, see: Bravo-Zhivotovskii, D.; Zharov, I.; Kapon, M.; Apeloig, Y. *J. Chem. Soc., Chem. Commun.* **1995**, 1625.