Reactions of a Cyclotrisilane with Alkynes: Synthesis and First Crystal Structure of 1,2-Disilacyclobut-3-enes

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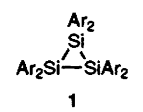
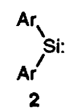
1,2-Disilacyclobut-3-enes are synthesized quantitatively from cyclotrisilane **1** and alkynes; the solid-state structure of **4d** is determined by single-crystal X-ray diffraction.

Much interest has been focussed on the chemistry of small-ring compounds containing silicon as a heteroatom during the last two decades.[1] Addition of silylenes to multiple bonds[2] or insertion of these reactive intermediates into strained cyclic compounds proved to be convenient methods for the synthesis of strained carbocyclic silanes.[3] We showed recently that treatment of the cyclotrisilane **1** with 3 equivalents of alkynes yields the corresponding silacyclopropenes **3a–d**[4] under mild thermal conditions without any byproduct. We now report that the same reaction under slightly different conditions gives exclusively 1,2-disilacyclobutenes.†

Addition of phenylacetylene or pent-1-yne (1.5 equiv.) to a solution of **1** in toluene or C_6D_6 yielded spectroscopically pure 1,2-disilacyclobutenes **4a** and **4b** respectively.‡ Although 1,2-disilacyclobutenes are known to be formed by [2 + 2] cycloaddition of stable disilenes to alkynes,[5,6] an analogous reaction of disilene **5**[7] to form **4a** or **4b** can be excluded: monitoring the reaction by ^1H NMR spectroscopy showed the initial formation of silacyclopropenes **3a** and **3b**. Further insertion of **2**[7] into a Si–C bond of the silacyclopropenes did not take place until all of the alkyne was transformed into silacyclopropene. Thus, **4a** and **4b** are formed by a two-step addition–insertion sequence of silylene **2** to the alkynes *via* the silacyclopropenes. Compounds **4b–d** were synthesized by direct reaction of **1** with 3 equivalents of silacyclopropenes **3b–d** using an analogous procedure. We consider the high strain of silacyclopropenes to be responsible for the insertion into the Si–C σ bond. Although insertion of a third silylene unit into the Si–Si bond of less bulky substituted 1,2-disilacyclobutenes has been achieved under forcing conditions,[3b] 1,2-disilacyclobutenes **4a–d** and excess of cyclotrisilane **1** did not react at 60 °C at all; even traces of the expected 1,2,3-trisilacyclopentene remained undetectable by ^1H NMR spectroscopy and prolonged reaction times had no effect.

The 1,2-disilacyclobutenes **4a–d** were mainly characterized by NMR spectroscopy. Whereas the silacyclopropenes **3a–d** show typical ^{29}Si NMR shifts up to δ −110,[4] the signals of **4a–d** are observed in the region δ +5 to −15. On the other hand, the ^1H NMR signals of the vinylic proton of the 1,2-disilacyclobutenes **4a–c** were shifted considerably to high field (*ca.* 1 ppm) in comparison to the silacyclopropenes **3a–c**, in which the vinylic proton shows a characteristic low-field signal ranging from δ 8.6 to 10.1.[4] Compounds **4a–d** turned out to be very sensitive towards air and moisture, in good agreement with the well-known fact that oxygen inserts quickly into Si–Si σ bonds of highly strained silaheterocycles.[8] Thus, the results of combustion analysis of 1,2-disilacyclobutenes reflected an elemental composition that was in good agreement with that of the oxygenated products **6a–d**. For a full characterization, 1,2-disilacyclobutenes **4a–d** were transformed into the corresponding cyclic disiloxanes **6a–d** by exposure to air or water.[9]


1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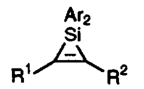
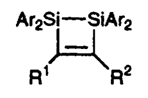
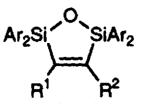

3a–d


4a–d

$Ar_2Si{=}SiAr_2$
5


6a–d

Ar = 2-(Me_2NCH_2)C_6H_4
a; R^1 = Ph, R^2 = H
b; R^1 = Pr^n, R^2 = H
c; R = Me_3Si, R^2 = H
d; R^1R^2 = –$[CH_2]_6$–

Although the first 1,2-disilacyclobutene was synthesized in 1973,[10] no solid-state structural details of these compounds could be obtained so far, whereas X-ray analysis results of 1,2-digerma-[11] and 1,2-distanna-cyclobut-3-enes[12] have been reported. We were able to grow single crystals of **4d** suitable for X-ray diffraction, and now we report the first crystal structure of a 1,2-disilacyclobut-3-ene (Fig. 1).§

The four-membered Si_2C_2 ring of **4d** is almost planar (mean deviation: 1.42 pm). The angle between this ring and the plane defined by C(1)–C(2)–C(3)–C(8) (mean deviation: 0.55 pm) is 3.7°. The distance C(1)–C(2) is 135.7 pm, showing no significant difference from the length of the C–C double bond found in cyclobutene (133 pm).[13] Similary, the lengths of the Si–Si bond as well as the Si–C bonds of the four-membered ring are comparable to normal Si–Si and Si–C distances.[14]

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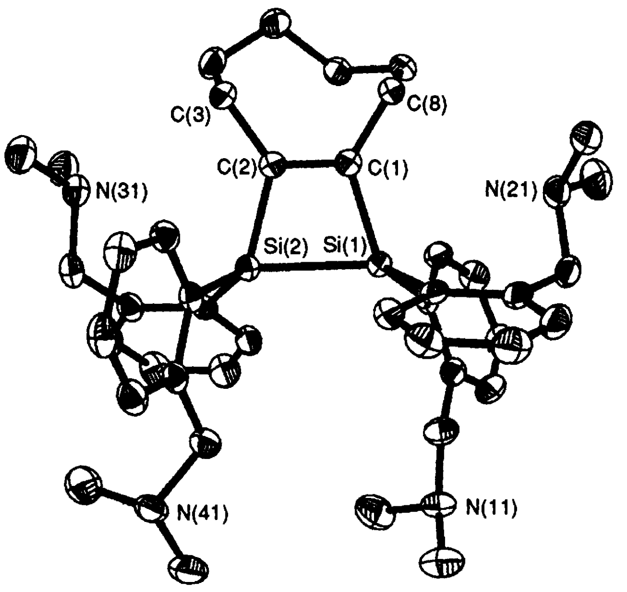

Fig. 1 The crystal structure of **4d**, with thermal ellipsoids at 50% probability level. Selected bond lengths (pm) and angles (°): Si(1)–Si(2) 235.9(3), Si(1)–C(1) 188.2(2), Si(2)–C(2) 188.1(2), C(1)–C(2) 135.7(3); C(1)–Si(1)–Si(2) 74.4(1), C(2)–Si(2)–Si(1) 74.7(1), C(2)–C(1)–Si(1) 105.7(2), C(1)–C(2)–Si(2) 105.2(1).

Footnotes

† All reactions leading to 1,2-disilacyclobut-3-enes resulted in quantitative (100%) formation of the ^{1}H NMR spectroscopically pure 4-membered ring system. **4a–c**: we were not able to purify these by distillation or crystallization; therefore, we state that these compounds were obtained in 100% yield (by weight) with purity >98% (determined by ^{1}H NMR). **4d**: from the spectroscopically pure crude product, crystals for X-ray diffraction were obtained in an isolated yield of 53%. Isolated yields of **6a–d** (based on amount of cyclotrisilane **1** without isolation of intermediates **4a–d**): **6a** 71%; **6b** 59%; **6c** 52%; **6d** 100%.

‡ Synthesis of 1,2-disilacyclobutenes (typical procedure): to a solution of **1** in C_6D_6 or toluene the alkyne (1.5 equiv.) was added. The solution was heated at 55 °C for 10 h to give spectroscopically pure 1,2-disilacyclobut-3-ene. Similarly, to a solution of freshly prepared silacyclopropenes **3b–d** in C_6D_6 or toluene, **1** (0.33 equiv.) was added. The solution was heated at 60 °C for 4 h to give spectroscopically pure 1,2-disilacyclobutenes **4b–d**. Colourless single crystals of **4d** suitable for X-ray structure determination were obtained from *n*-hexane.

9,9,10,10-Tetrakis[2-(dimethylaminomethyl)phenyl]-9,10-disilabicyclo[6.2.0]dec-1(8)-ene **4d**, mp 100 °C (decomp.); ^{1}H NMR (250 MHz, C_6D_6): δ 1.60–1.77 (m, 8 H, 3-, 4-, 5-, 6-CH_2), 1.96 (s, 24 H, NMe_2), 2.89 (br dd, ^3J 6 Hz, 4 H, 2-, 7-CH_2), 3.31, 3.43 (AB, ^2J 14 Hz, 8 H, CH_2N), 7.01 (dt, ^3J 7, ^4J 1 Hz, 4 H, Ar-H), 7.16–7.23 (m, 4 H, Ar-H), 7.59 (d, ^3J 7 Hz, 4 H, Ar-H), 7.56 (dd, ^3J 7 Hz, ^4J 1 Hz, 4 H, Ar-H); ^{13}C NMR (62.9 MHz, C_6D_6) δ 26.8, 29.5, 31.3 (C-2, -3, -4, -5, -6, -7), 45.6 (NMe_2), 64.9 (NCH_2), 128.8 (Ar-C), 129.4 (Ar-C), 126.6 (Ar-C), 137.4 (Ar-C), 145.8 (quat.-C), 145.8 (quat.-C), 172.3 (C-1, -8); ^{29}Si NMR (59.6 MHz, C_6D_6) δ −5.3; MS (EI, 70 eV): *m/v* (rel. int.) 700 (M^+, 23), 656 ($M^+ - Me$, 34), 642 ($M^+ - CH_2NMe_2$, 100), 566 ($M^+ - Ar$, 34), 296 ($SiAr_2^+$, 36), 281 ($SiAr_2^+ - Me$, 36), 58 ($CH_2NMe_2^+$, 41); HRMS: calcd for $C_{44}H_{60}N_4Si_2$, 700.4357; found, 700.4356.

§ *Crystal data* for **4d** (−120 °C): $C_{44}H_{60}N_4Si_2$, $M = 701.1$, triclinic, space group $P\bar{1}$, $a = 1243.7(11)$, $b = 1366.5(14)$, $c = 1368.1(13)$ pm, $\alpha = 92.20(6)$, $\beta = 101.03(5)$, $\gamma = 116.88(5)°$, $U = 2.015(3)$ nm^3, $Z = 2$, $D_c = 1.156$ Mg m^{-3}, $\mu = 0.123$ mm^{-1}, $F(000) = 760$, 5290 measured reflections, 5276 independent, of which 5275 were employed in the refinement of 460 parameters, $2\theta_{max} = 45°$. Data of **4d** were collected on a Stoe-Siemens-AED four-circle-diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 71.073$ pm). The structure was solved by direct methods.[15] All non-hydrogen atoms were refined anisotropically.[16] A riding model starting from calculated positions was employed for the hydrogen atoms. An extinction correction was employed $\{F_c^* = kF_c[1 + 0.001_x F_c^2\lambda^3/\sin 2\theta]^{-1/4}$ with $x = 0.0054(6)\}$. The structure was refined against F^2 with a weighting scheme $w^{-1} = \sigma^2(F_o^2) + (0.0274P)^2 + 1.270P$, with $P = (f_o^2 + 2F_c^2)/3$, $R1 = 0.032$ ($F > 4\sigma F$) and $wR2 = 0.077$ (all data), max. residual density: 261 e nm^{-3}, ($R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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