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 ^{1}H 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 ^{1}H 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 ^{1}H 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]

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] Similarly, 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]

1

2

3a–d

4a–d

$Ar_2Si=SiAr_2$

5

6a–d
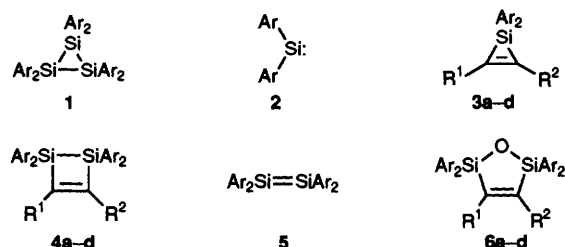
Ar = 2-(Me$_2$NCH$_2$)C$_6$H$_4$
a: R[1] = Ph, R[2] = H
b: R[1] = Pr^n, R[2] = H
c: R = Me$_3$Si, R[2] = H
d: R[1]R[2] = –[CH$_2$]$_6$–

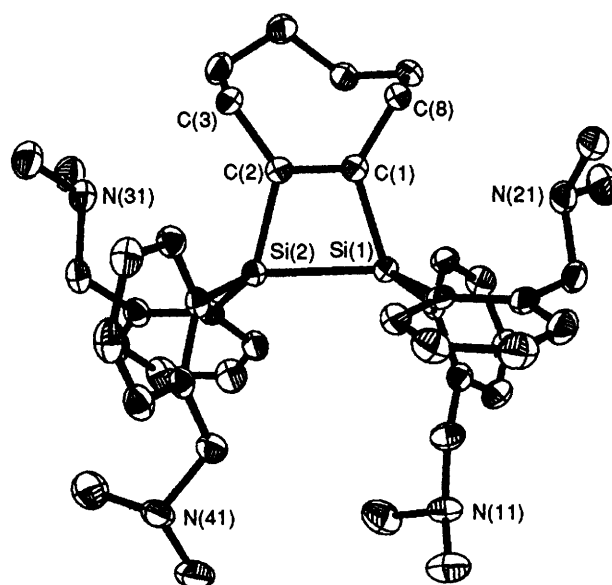Fig. 1 The crystal structure of 4d, with thermal ellipsoids at 50% probability level. Selected bond lengths (pm) and angles (°): Si(1)–Si(2) 235.9(3), Si(1)–C(1) 188.2(2), Si(2)–C(2) 188.1(2), C(1)–C(2) 135.7(3); C(1)–Si(1)–Si(2) 74.4(1), C(2)–Si(2)–Si(1) 74.7(1), C(2)–C(1)–Si(1) 105.7(2), C(1)–C(2)–Si(2) 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, α = 92.20(6), β = 101.03(5), γ = 116.88(5)°, U = 2.015(3) nm^3, Z = 2, D_c = 1.156 Mg m^{-3}, μ = 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 (λ = 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 $\{F_c{}^* = kF_c[1 + 0.001_xF_c{}^2\lambda^3/\sin2\theta]^{-1/4}$ 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 para-

meters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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