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# A Stable Disilacyclopropane: [1 + 2] Cycloaddition of the Silylene Si[(NCH$_2$Bu$^t$)$_2$C$_6$H$_4$-1,2] with a Silene

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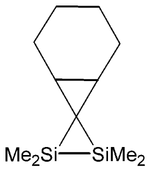
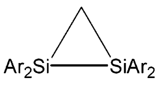
*Summary: The [1 + 2] cycloaddition of a "free" silylene, namely the bis(amino)silylene Si[(NCH$_2$Bu$^t$)$_2$C$_6$H$_4$-1,2] (**1**), with an in situ generated silene afforded the stable disilacyclopropane **2**: the molecular structure of **2** is supported by NMR spectroscopic data and confirmed by a single X-ray diffraction analysis.*

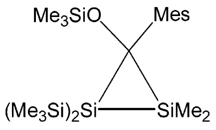
As early as 1976 the first evidence of the formation of a disilacyclopropane in solution was reported by Seyferth and Duncan by treatment of 1-chloro-2-(bromonorcaranyl)tetramethyldisilane with LiBu$^n$. The resulting 1,1,2,2-tetramethyl-3-norcaranylidene-1,2-disilacyclopropane (**A**) was not stable at ambient temperature but could be trapped with MeOH.[1] It is surprising that up to now only three other disilacyclopropanes have been isolated (**B** and **C**),[2−4] only one of which was characterized by X-ray crystallographic analysis (**B** with Ar = *o*-Xyl).[2] Other compounds containing the SiSiC ring fragment are the disilacyclopropanmethylene species **D**[5] and the disilacyclopropanimine **E**.[6]



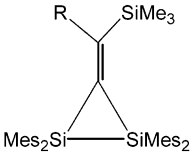
**A**



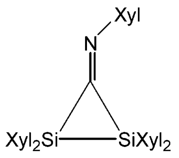
**B** Ar = Mes, *o*-Xyl



**C**



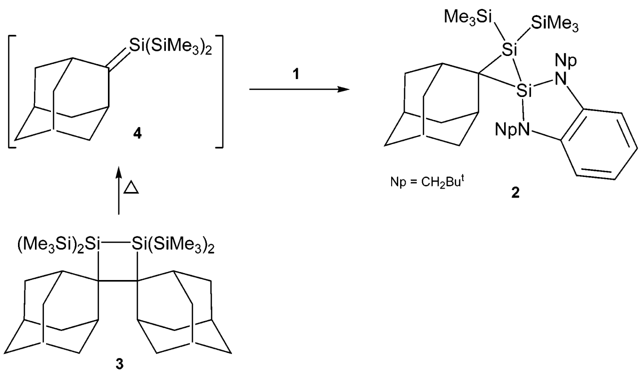
**D** R = Ph, SiMe$_3$



**E**

In this communication we report the addition of a "free" silylene, namely the thermally stable Si[(NCH$_2$-Bu$^t$)$_2$C$_6$H$_4$-1,2] (**1**),[7] to a Si−C double bond to afford the stable disilacyclopropane **2**.

**Scheme 1**



The readily available transient silene **4** can be obtained in situ by thermolysis of the 1,2-disilacyclobutane **3**.[8] Thus, by treatment of **3** with **1** in refluxing benzene for 2 days the disilirane **2** was obtained in 82% yield (Scheme 1).[9] No reaction was observed between **3** and **1** at ambient temperature.

The structure of **2** has been elucidated by an X-ray crystallographic determination and consists of two independent molecules; only one is shown and discussed (Figure 1).[10] The Si(1)−Si(2) bond length of 2.2749(10) Å in the disilirane ring is relatively short compared to Si−Si single bonds (average 2.358 Å)[11] but is in the same range which was observed for the Si−Si bond in **B** (2.272(2) Å).[2] In comparison the Si−Si bond distance in the SiSiC ring containing a methylene (**D**) or imine fragment (**E**) is somewhat longer (2.327(2) Å (**D**)[5] or

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(9) Experimental data for **2**: a solution of **1** (1.27 mmol, 0.35 g) in benzene (20 mL) was added to a solution of **3** (0.63 mmol, 0.39 g) in benzene (20 mL), and the mixture was refluxed for 48 h. The solvent was removed, and the remaining solid was crystallized from hexane at −25 °C to yield the yellow crystalline **2** (0.61 g, 82%); mp 139−141 °C. $^1$H NMR (300 MHz, C$_6$D$_6$): $\delta$ 0.42 (s, SiMe$_3$, 18 H), 1.03 (s, Bu$^t$, 18 H), 1.58−1.97 (m, adamantyl, 14 H), 3.25, 3.29, 3.35, and 3.51 (AB type, 4 H, CH$_2$) and 6.86 (br s, Ph, 4 H). $^{13}$C{$^1$H} NMR (75.48 MHz, C$_6$D$_6$): $\delta$ 3.7 (SiMe$_3$), 29.2 (C*Me*$_3$), 36.1 (*C*Me$_3$), 28.0, 29.5, and 31.5 (CH adamanyl), 37.2, 38.0 and 39.5 (CH$_2$-adamantyl), 31.5 (C$_q$ adamantyl), 53.3 (CH$_2$), 111.0, 117.7, and 139.8 (phenyl). $^{29}$Si{$^1$H} NMR (99.33 MHz, C$_6$D$_6$): $\delta$ −86.9 (NNSi), −10.3 (SiMe$_3$) and 0.9 (*Si*SiMe$_3$). MS: *m/z* 584 (M$^+$). Anal. Calcd for C$_{32}$H$_{58}$N$_2$Si$_4$: C, 65.9; H, 10.02; N, 4.8. Found: C, 65.9; H, 10.12; N, 4.74.

(10) Crystal data for **2**: C$_{32}$H$_{58}$N$_2$Si$_4$, $M_r$ = 583.16, specimen 0.2 × 0.15 × 0.05 mm$^3$, monoclinic, space group $P2_1/n$ (No. 14), $a$ = 18.9066(3) Å, $b$ = 18.7310(3) Å, $c$ = 22.4504(3) Å, $\beta$ = 114.720(1), $U$ = 7222.0(2) Å$^3$, $Z$ = 8, $\mu$ = 0.19 mm$^{-1}$, $T$ = 223(2) K, 9904 unique reflections collected, R1 = 0.045 for 7223 reflections with $I > 2\sigma(I)$, wR2 = 0.188 for all reflections. Data collection: KappaCCD, full-matrix least-squares refinement on $F^2$, SHELX-97.

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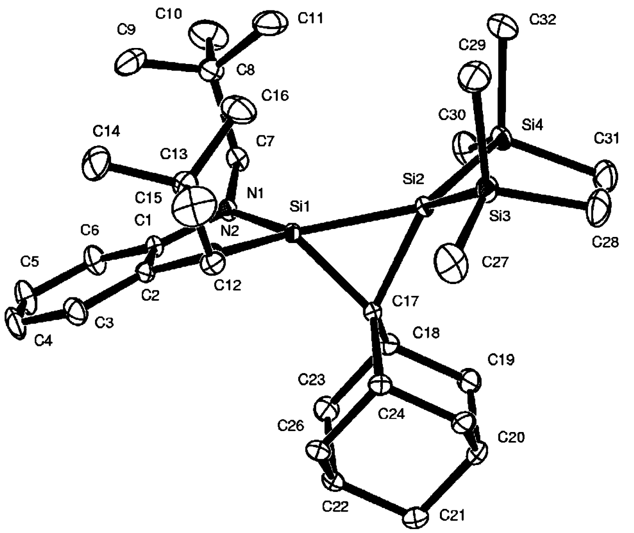

**Figure 1.** Molecular structure of **2**. Selected bond lengths (Å) and angles (deg) (two independent molecules, only one shown): Si(1)−Si(2) = 2.2749(10), Si(1)−C(17) = 1.879(3), Si(2)−C(17) = 1.980(3), Si(1)−N(1) = 1.732(2), Si(1)−N(2) = 1.742(2), Si(2)−Si(3) = 2.3726(12), Si(2)−Si(4) = 2.3650(12); Si(1)−C(17)−Si(2) = 72.2(10), Si(1)−Si(2)−C(17) = 51.84(8), Si(2)−Si(1)−C(17) = 55.96(8), N(1)−Si(1)−N(2) = 92.33(11), Si(4)−Si(2)−Si(3) = 123.49(4).

2.328(3) Å (**E**)[6]). The environment at the Si atoms shows little pyramidalization. The sums of bond angles at Si(1) and Si(2) are 357.76 and 354.99°, respectively, with Si(1) being 0.783 Å out of the Si(2)Si(3)Si(4) plane and Si(2) being 0.459 Å out of the N(1)N(2)Si(1) plane.

The $^{29}$Si NMR signal at $\delta$ −86.9 for the $N_2Si$ silicon is particularly highly shielded and can be compared to the even more shielded $(Me_3Si)_2$*Si* silicon of **C** ($\delta$ −118.5)[4] and the less shielded silicons in **B** ($\delta$ −65.97, Ar = Mes),[3] **D** ($\delta$ −48.5, R = Ph),[5] and **C** ($\delta$ −35.6, $SiMe_2$).[4] Unusual, however, is the downfield-shifted $^{29}$Si resonance of the $(Me_3Si)_2$*Si* silicon in **2** at $\delta$ 0.9, which could be attributed to the influence of the nitrogen substitution at Si(1).

Previous strategies for the synthesis of SiSiC three-membered-ring structures involved (i) cyclization via a Grignard-type reaction (**A**),[1] (ii) addition of $Mes_2Si$ to a 1-silapropadiene (both photolytically generated) (**C**),[5] (iii) addition of a carbene equivalent $(CH_2N_2)$[2,3] or carbene-like carbon compound (isonitrile)[6] to a Si−Si double bond (**B** or **C**), and (iv) the addition of a transient silylene to a Si−C double bond (**C**).[4] However, strategy iii could also proceed via 1,3-dipolar cycloaddition of the diazomethane with subsequent loss of nitrogen, as in the case of reactions of disilenes with azides,[12] and for strategy iv the reaction of a "free" silylene with the silene could not be established; **C** could also have been formed by reaction of the silirane used as the silylene precursor and the silene.[4]

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**Supporting Information Available:** Tables giving X-ray data for **2**; these data are also available as a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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