

Silylene reactions with 1,7-octadiene-3,5-diynes: evidence for the intermediate formation of a bis(silaethene)[☆]

Detlev Ostendorf, Wolfgang Saak, Detlev Haase, Manfred Weidenbruch *

Fachbereich Chemie der Universität Oldenburg, Carl-von-Ossietzky-Straße 9-11, D-26111 Oldenburg, Germany

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Dedicated to Professor Oleg M. Nefedov on the occasion of his 70th birthday

Abstract

Treatment of 1,4-bis(cyclohexen-1-yl)buta-1,3-diyne with di-*tert*-butylsilylene (**1**) furnishes the acetylene-linked bis(2-silacyclobutene) derivative **9**, presumably via a two-fold [2 + 2] cycloaddition reaction of the bis(silaethene) intermediate to the endocyclic double bonds of the cyclohexene rings. However, a similar reaction of **1** with the sterically more encumbered 1,7-octadiene-3,5-diyne **10** yields the 2,5-disilabicyclo[2.2.0]hexa-1(6),3-diene **12**, formed by rearrangement of the two-fold [1 + 2] cycloaddition product of **1** to the C/C triple bonds of **10**. The structures of **9** and **12** have been determined by X-ray crystallography. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Silicon; Silylene; Dienes; Silacyclobutene

1. Introduction

Silylenes (SiR₂) bearing bulky substituents R undergo smooth addition reactions with numerous multiple bond systems to furnish three-membered ring compounds that can often be isolated in spite of their high degrees of ring strain [2]. For example, di-*tert*-butylsilylene (**1**), which can be generated readily by photolysis of hexa-*tert*-butylcyclotrisilane [3,4], reacts with 2,2,7,7-tetramethylocta-3,5-diyne to afford the isolable bis(silacyclopentene) **2**; under renewed irradiation the latter product undergoes rearrangement to yield the 2,5-disilabicyclo[2.2.0]hexa-1(6),3-diene **3** [5] (Scheme 1).

The reactions of germynes with 1,3-diynes proceed differently. Treatment of the diarylgermylene **4**, formed by dissociation of the digermene Ar₂Ge=GeAr₂ [6] in solution [7], with phenyl- or *n*-butyl-substituted 1,3-diynes furnished the acetylene-coupled bis(germaethenes) **5**

as the first examples of a molecule with conjugated Ge=C double bonds [8]. We have now addressed the question if analogous compounds with conjugated Si=C double bonds could be isolated, or at least be detected by indirect means, through the use of suitable substituents on the 1,3-diynes.

2. Results and discussion

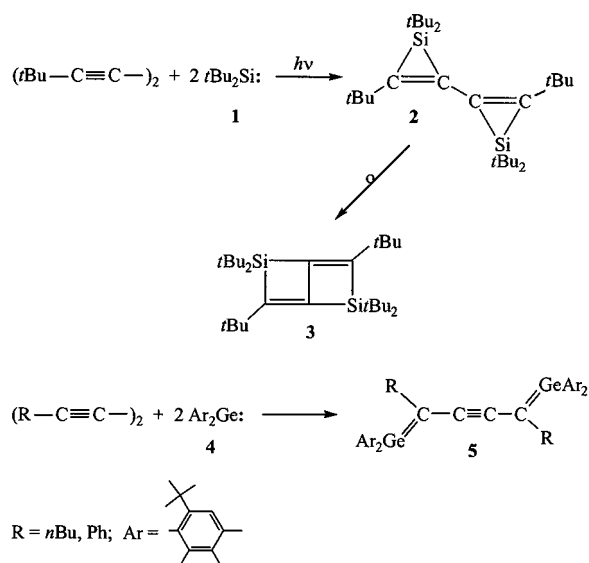
We chose the 1,4-bis(cyclohex-1-enyl)-substituted compound **6** as the diyne component because the endocyclic double bonds may have the potential to stabilise a possible acetylene-linked bis(silaethene) through intramolecular [2 + 2] cycloaddition processes (Scheme 2).

The reaction of **6** with photochemically generated **1** did indeed result in the isolation of colourless crystals in a yield of 73%; the analytical data were indicative of a 2:1 adduct of compounds **1** and **6**. The ¹³C-NMR spectrum contained signals for both olefinic and acetylenic carbon atoms thus excluding the existence of the double [2 + 1] cycloadduct **7**. However, it did not

[☆] See Ref. [1].

* Corresponding author. Fax: +49-441-7983352.

E-mail address: manfred.weidenbruch@uni-oldenburg.de (M. Weidenbruch).



allow a differentiation between the two feasible molecules **8** and **9**. The ^{29}Si -NMR spectrum containing a sharp signal at 19.4 ppm is more useful. This chemical shift value is in the typical range for silacyclobutenes and permits a distinction from the silaethenes that give ^{29}Si -NMR signals at markedly lower field [9].

An X-ray crystallographic analysis (Fig. 1) not only confirmed the constitution of **9**, but also revealed some interesting features. The molecule of **9** possesses a C_2 axis passing through the middle of the C–C triple bond. The central C_4 chain is not linear but displays C(2)–C(1)–C(1a) angles of 172.3° . The *cis*-orientation of the two silacyclobutene rings to each other is also worthy of note. The lengths of the C–C single, double, and triple bonds have values typical for a conjugated system.

Like all other currently known additions of silylenes to di- and oligoynes [5,10,11], the reaction sequence probably begins with the formation of the cycloadduct **7**. Subsequent opening of the Si–C bonds would then lead to the intermediate **8** which, in this case, does not

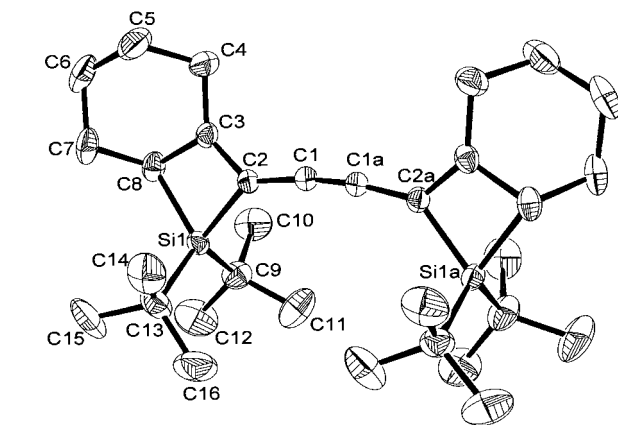
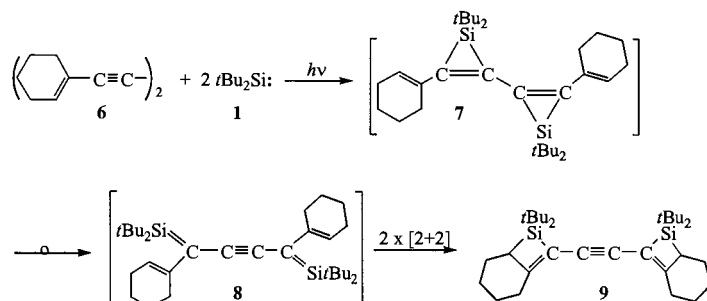


Fig. 1. Molecular structure of **9** in the crystal (hydrogen atoms omitted). Ellipsoids are drawn at 50% probability. Selected bond lengths (pm) and angles ($^\circ$): C(1)–C(1a) 121.1(3), C(1)–C(2) 141.0(2), C(2)–C(3) 135.6(2), C(2)–Si(1) 187.5(2), C(3)–C(8) 152.4(2), C(8)–Si(1) 191.3(2), C(2)–C(1)–C(1a) 172.3(1), C(2)–Si(1)–C(8) 76.2(1), Si(1)–C(2)–C(3) 90.9(1), C(2)–C(3)–C(8) 108.4(1), C(3)–C(8)–Si(1) 84.6(1).

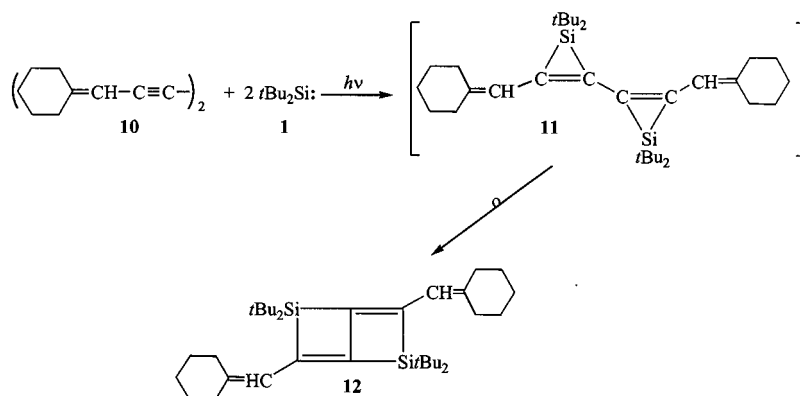
react further to afford a bicyclic product of the type **3** but rather undergoes two-fold [2 + 2] cycloadditions with the double bonds of the cyclohexene rings to furnish the isolated product **9** (Scheme 3).

For the purpose of making this intramolecular [2 + 2] cycloaddition less easy and thus, perhaps, to effect stabilisation of an acetylene-linked bis(silaethene) of the type **8**, we also allowed the octa-1,7-diene-3,5-diyne **10**, in which the terminal C=C double bonds are sterically more shielded than those in compound **6**, to react with the silylene **1**. Work-up of this reaction mixture resulted in the isolation of colourless crystals in 29% yield; the analytical data of these crystals were again indicative for a 2:1 adduct of **1** and **10**. The ^{29}Si -NMR spectrum containing only one signal at 39.0 ppm and the ^{13}C -NMR spectrum showing four signals for olefinic C atoms were in good harmony with those recorded previously for other bicyclic systems of the type **3**.

The X-ray crystallographic analysis (Fig. 2) confirmed the assumption based on the spectral data that compound **12** had been formed. Similar to other compounds of this type, **12** also possesses a crystallographic



Scheme 2.



Scheme 3.

centre of inversion at the middle of the C(1)–C(1a) bond. In spite of the presence of the bulky *tert*-butyl groups, the Si–C bond lengths are not appreciably lengthened.

It would seem that, in each case, the reactions of silylenes with 1,3-diyne proceed through the [2 + 1] cycloadducts which can subsequently be converted into molecules of the type **8**. The results presented here illustrate that even small differences in the spatial requirements of the olefinic substituents are sufficient to direct the next step of the reaction towards products of the type **9** or **12**. It is still not understood why the reactions of germlyenes lead to stable, isolable compounds of the type **5**, whereas the intermediate formation of analogous species in the silylene reactions can only be demonstrated indirectly. A possible reason is the larger polarity, and thus higher reactivity, of the Si=C double bond resulting from the differing electronegativities of silicon and germanium [12].

3. Experimental

3.1. General procedure

All reactions were performed in oven-dried glassware under an atmosphere of dry argon. Photolyses were carried out at room temperature by using a high-pressure mercury immersion lamp (Heraeus TQ 150).

The ¹H- and ¹³C-NMR spectra were obtained on a Bruker ARX 500 spectrometer using C₆H₆-d₆ as solvent. The ²⁹Si-NMR spectra were recorded on a Bruker AMX 300 spectrometer. IR spectra were taken on a Bio-Rad FTS-7 spectrometer. The mass spectra were recorded on a Finnigan-MAT 212 spectrometer. Elemental analyses were performed by Analytische Laboratorien, D-51789 Lindlar, Germany.

1-[4-(1-Cyclohexen-1-yl)-1,3-butadiynyl]-1-cyclohexene [13], (6-cyclohexylidene-2,4-hexadiynylidene)-cyclohexane [13,14], the Hay-catalyst [15] and the cyclo-

trisilane [3] were prepared according to the literature procedures.

3.2. 8-[[7,7-Bis(1,1-dimethylethyl)-7-silabicyclo[4.2.0]oct-8-en-8-yl]ethynyl]-7,7-bis(1,1-dimethylethyl)-7-silabicyclo[4.2.0]oct-8-ene (**9**)

A solution of the cyclotrisilane (0.55 g, 1.3 mmol) and diyne **6** (0.14 g, 0.67 mmol) in *n*-hexane (80 ml) was irradiated for 4 h at room temperature. The solvent was distilled off in vacuo and the residue redissolved in 5 ml of toluene. Cooling of the solution for several days at –30°C yielded 0.24 g (73%) of colourless crystals of **9**, m.p. 174–176°C. ¹H-NMR (500 MHz, 298 K, C₆H₆-d₆, δ ppm): 1.15 (s, 18H, *t*-Bu), 1.21 (s, 18H, *t*-Bu), 1.17–1.35 (m, 4H, CH₂), 1.57–1.63 (m, 4H, CH₂), 1.65–1.73 (m, 4H, CH₂), 1.80 (m, 2H, CH₂), 1.91 (m, 2H, CH₂), 2.94 (dd, 2H, 6H). ¹³C-NMR (125 MHz, 298

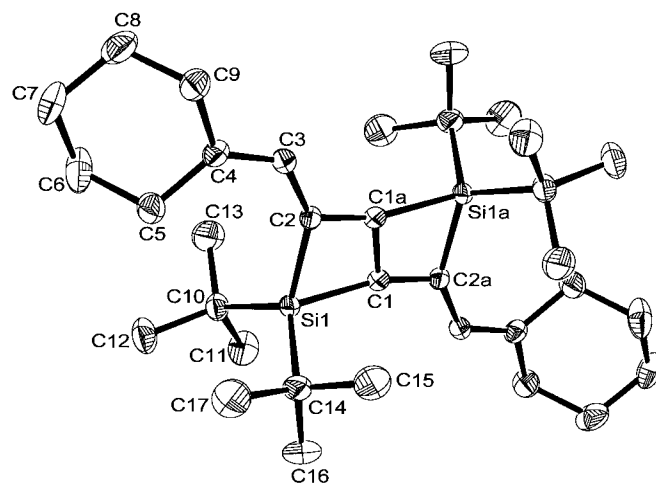


Fig. 2. Molecular structure of **12** in the crystal (hydrogen atoms omitted). Ellipsoids are drawn at 50% probability. Selected bond lengths (pm) and angles (°): C(2)–Si(1) 190.20(15), C(1)–Si(1) 188.66(15), C(2)–C(1a) 136.8(2), C(1)–C(1a) 148.0(3), C(1)–Si(1)–C(2) 75.48(6), Si(1)–C(2)–C(1a) 89.08(10), C(2)–C(1a)–C(1) 108.95(15), C(1a)–C(1)–Si(1) 86.46(12).

Table 1
Crystallographic data for **9** and **12**

	9	12
Empirical formula	C ₃₂ H ₅₄ Si ₂	C ₃₄ H ₅₈ Si ₂
Molar mass	494.93	522.98
Unit cell dimensions		
<i>a</i> (pm)	1311.74(5)	1105.50(4)
<i>b</i> (pm)	4740.4(2)	1798.92(9)
<i>c</i> (pm)	1025.5(4)	840.91(7)
β (°)	90	96.543(7)
<i>V</i> ($\times 10^6$) (pm ³)	6376(3)	1661.43(17)
<i>Z</i>	8	2
<i>D</i> _{calc} (g cm ⁻³)	1.031	1.045
Crystal system	Orthorhombic	Monoclinic
Space group	<i>Fdd2</i>	<i>P2₁/c</i>
Crystal dimensions (mm ³)	0.41 \times 0.40 \times 0.32	0.50 \times 0.24 \times 0.11
2 θ _{max} (°)	52	52
No. of reflections	12 266	12 194
No. of unique reflections	3098	3023
No. of observed reflections	2762	2061
[<i>I</i> > 2 σ (<i>I</i>)]		
Lin. abs. coefficient (mm ⁻¹)	0.128	0.126
No. of parameters	154	163
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.0315	0.0336
<i>wR</i> ₂ (all data)	0.0785	0.0780
Goodness-of-fit on <i>F</i> ²	0.978	0.861

K, C₆H₆-*d*₆, δ ppm): 20.78 (C_q, *t*-Bu), 21.17 (C_q, *t*-Bu), 26.90 (C_s, CH₂), 27.26 (C_s, CH₂), 28.25 (C_p, *t*-Bu), 29.00 (C_s, CH₂), 29.40 (C_p, *t*-Bu), 31.27 (C_s, CH₂), 31.31 (C_t, C-6), 91.59 (C_q, C \equiv C), 120.08 (C_q, C-8), 168.88 (C_q, C-1). (C_p, C_s, C_t, and C_q refer to primary, secondary, tertiary, and quaternary carbon atoms, respectively); ²⁹Si-NMR (59.6 MHz, 298 K, C₆H₆-*d*₆, δ ppm): 19.39; MS (CI-isobutane) *m/z*: 494 (100%) [M – H]⁺; IR (KBr, cm⁻¹) ν : 1602, 1558. Anal. Found: C, 77.47; H, 11.17. Calc. for C₃₂H₅₄Si₂ (494.95): C, 77.66; H, 11.00%.

3.3. 3,6-Bis(cyclohexylidenemethyl)-2,2,5,5-tetrakis-(1,1-dimethylethyl)-2,5-disilabicyclo[2.2.0]hexa-1(6),3-diene (**12**)

A solution of the cyclotrisilane (1.02 g, 2.4 mmol) and diyne **10** (0.28 g, 1.2 mmol) in *n*-hexane (80 ml) was irradiated for 6 h at room temperature. The solvent was distilled off in vacuo and the residue redissolved in 5 ml of toluene. Cooling of the solution for several days at –30°C afforded 0.18 g (29%) colourless crystals of **12**, m.p. 240–243°C. ¹H-NMR (500 MHz, 298 K, C₆H₆-*d*₆, δ ppm): 1.25 (s, 36H, *t*-Bu), 1.38–1.46 (m, 8H, CH₂), 1.48–1.52 (m, 4H, CH₂), 2.15 (m, 4H, CH₂), 2.35 (m, 4H, CH₂), 6.29 (s, 2H, CH). ¹³C-NMR (125 MHz, 298 K, C₆H₆-*d*₆, δ ppm): 21.20 (C_q, *t*-Bu), 26.93 (C_s, CH₂), 28.33 (C_s, CH₂), 28.83 (C_s, CH₂), 29.04 (C_p, *t*-Bu), 31.03 (C_s, CH₂), 37.85 (C_s, CH₂), 125.65 (C_t, C=CH), 142.48 (C_q, C=CH), 149.75 (C_q, C=C), 178.47

(C_q, C=C); ²⁹Si-NMR (59.6 MHz, 298 K, C₆H₆-*d*₆, δ ppm): 39.03; MS (CI-isobutane) *m/z*: 523 (100%) [M⁺]; IR (KBr, cm⁻¹) ν : 1622. Anal. Found: C, 77.80; H, 11.00. Calc. for C₃₄H₅₈Si₂ (523.00): C, 78.08; H, 11.12%.

3.4. X-ray structure analyses of **9** and **12**

Crystal data and numerical data of the structure determinations are given in Table 1. In each case, the crystal was mounted in an inert oil. Data collection was performed at 193(2) K on a Stoe IPDS area-detector using graphite-monochromated Mo–K α radiation.

The structures were solved by direct phase determination and refined by full-matrix least-squares techniques against *F*² with the SHELXL-97 program system [16]. Hydrogen atoms were placed in the calculated positions, and all other atoms were refined anisotropically (Section 4).

4. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre CCDC nos. 151 868 (**9**) and 151 869 (**12**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@cam.ac.uk or www:http://ccdc.cam.ac.uk).

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