

# Synthesis, structure, and photoluminescence of organosilicon based compounds containing stilbene, butadiene or styrene subunits

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## Abstract

Seven silicon based model compounds that contain stilbene, butadiene or styrene subunits with different molecular structures were synthesized and characterized by NMR spectroscopy and single crystal X-ray crystallography. The UV–Vis absorption and photoluminescence spectra were measured in THF solution as well as in the solid state. The interpretation of the spectra reveals that the absorption and emission properties of the compounds originate from the stilbene or butadiene molecular subunits. This investigation provides basic information about the influence of silicon groups, molecular structures and substituents at silicon to absorption and emission properties in organic compounds. Furthermore, due to the functionality of the phenylethynyl substituents at silicon, these compounds may serve as optical active tools and precursors for the introduction of interesting physical properties into new materials for different applications. © 2008 Published by Elsevier B.V.

*Keywords:* Silacyclobutenes; Siloles; Fluorescence; Silanes

## 1. Introduction

Organic electroluminescent devices based on organic or organometallic frameworks which are generally composed of thin multilayers of hole-transporting, emissive, and electron-transporting materials that are sandwiched between two electrodes [1,2], have received much attention because of their possible application as new display materials [3]. To achieve a full color display, the three basic color components, red, green, and blue, are required. Red and green emitters for organic electroluminescent devices have become readily available but efficient organic or organometallic blue emitters are still very rare.

During the investigation of a series of silacyclobutene compounds, it was found that 2,3-diphenyl-4-neopentyl-1-silacyclobut-2-enes (**1**) show an intense blue photoluminescence upon excitation with UV light. It has been demonstrated that the exocyclic substituents R at the silicon

atom of **1** affect both the intensities and the wavelengths of the photoluminescence [4]. In an extension of these studies, a broad range of differently substituted cyclic and acyclic organo silicon compounds (**2–8**), generally containing stilbene, stilbene vinyllogue or styrene subunits (Fig. 1), were synthesized and characterized by multinuclear NMR spectroscopy and X-ray diffraction analysis. Their UV–Vis and photoluminescence spectra were recorded to demonstrate their optoelectronic properties and to qualitatively determine the influence of substituents and of the molecular structure on the phenomena. Our work is principally aimed to provide basic information for the synthesis of new adjustable photoluminescent materials.

## 2. Results and discussion

### 2.1. Synthesis of the model compounds 2–8

The 1,1-dichlorosilanes **9**, **10**, and **12** were synthesized according to the literature [5]. Reaction of these starting materials with two mole equivalents of the Grignard reagent  $\text{PhC}\equiv\text{CMgBr}$  [6] at room temperature resulted in the

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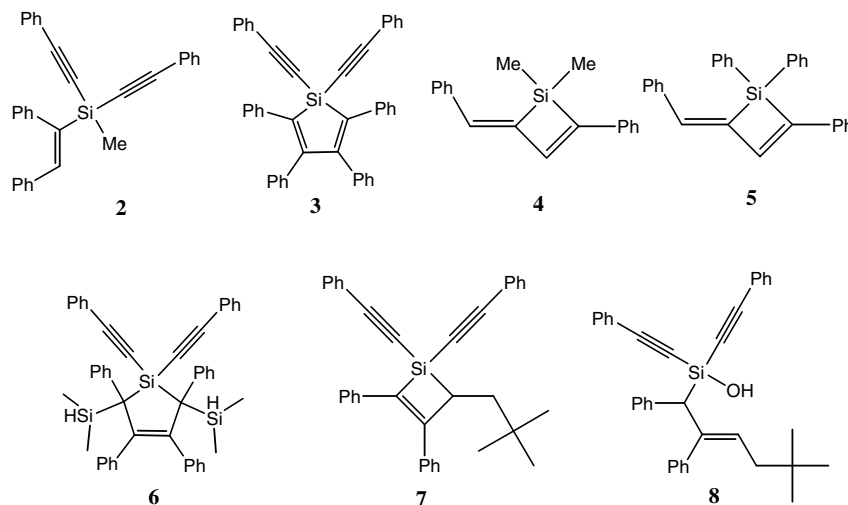


Fig. 1. Organosilicon based model compounds containing stilbene, stilbene vinylogue or styrene subunits.

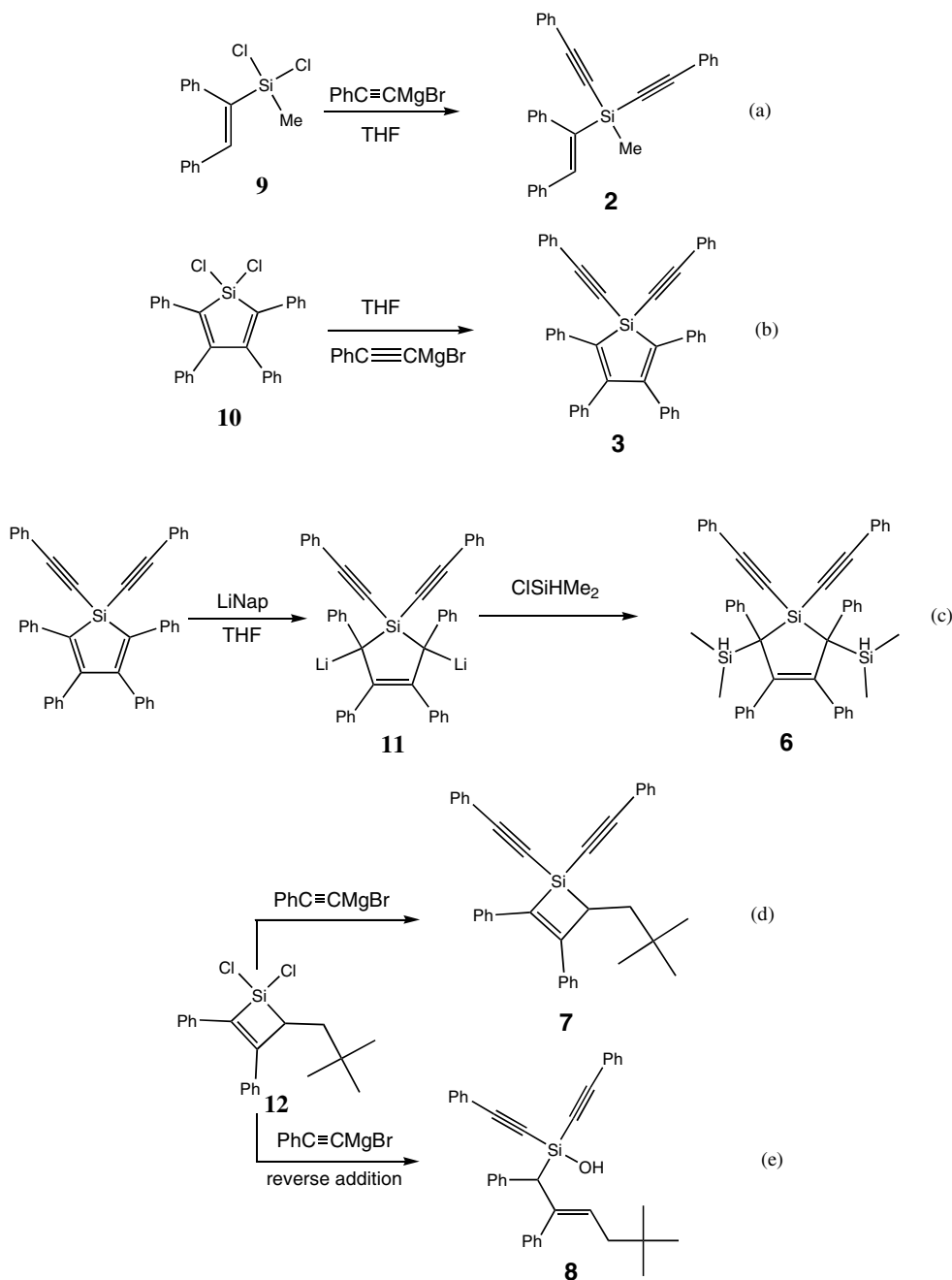
isolation of **2**, **3**, and **7** as stable crystalline compounds in 84%, 73%, and 68% yields, respectively (Scheme 1a, b, and d). The use of the less active phenylethynyl-magnesium bromide reagent instead of phenylethynyl lithium is essential to obtain the bis(phenylethynyl)silanes **2**, **3**, and **7** in high yields, since the cyclic and acyclic ethylenic moieties of the starting compounds react with the lithium organometallic to form addition products with the carbon–carbon double bond [7]. The product formation from the reaction of dichlorosilacyclobutene **12** with  $\text{PhC}\equiv\text{CMgBr}$  (reaction (e) and (d), Scheme 1) is strongly controlled by the reaction conditions: (i) addition of the Grignard reagent to a solution of **12** in THF gave the expected cyclic substitution product **7** [5e], while (ii) the reverse addition of **12** to the Grignard reagent with subsequent hydrolytic work up resulted in the isolation of the linear compound **8**, arising from cleavage of the ring silicon–carbon bond and a substitution of two chlorine atoms at silicon. The reaction pathway forming **8** is still under investigation. The silacyclobutenes **4** and **5** were synthesized according to literature procedures [8]. In an attempt to synthesize a spiro-silole in an intramolecular cyclisation reaction of diethynylsilane **3** with lithium naphthalenide ( $\text{LiNp}$ ) [9], we obtained a complex product mixture, which was successively treated with dimethylchlorosilane to quench the remaining  $\text{LiNp}$  and other lithiated species. According to thin layer chromatography investigations, the resulting mixture contains more than ten different compounds. After chromatographic separation on a silica gel column, pure colorless crystals of **6** were obtained in about 7% isolated yield. The formation of **6** is suggested to proceed via dilithiated intermediate **11** as shown in reaction (c). All attempts to trap **11** with the more bulky trimethylchlorosilane failed: the reaction solution remained blue colored, and after hydrolytic work up no silicon-substituted compound was obtained. This is apparently caused by the steric requirements of the trimethylsilyl group and the space constraints strongly influenced by the phenyl substituents at the  $\alpha$ -carbon atoms of the silole skeleton.

## 2.2. Crystal structures of **2**, **3**, **6**, and **8**

The unequivocal characterization of compounds **2**, **3**, **6**, **7**, and **8** was achieved by means of elemental analysis and standard NMR spectroscopic techniques, the data are given in Section 3. The molecular structures were further confirmed by the results of single-crystal X-ray analyses of **2**, **3**, **6**, and **8**. ORTEP drawings of the diffraction studies are depicted in Figs. 2–5. Cell dimensions, data collection and refined parameters are given in Table 1, selected bond distances and angles are added to Figs. 2–5.

The phenyl groups of the stilbene subunit in acyclic compound **2** (Fig. 2) adopt a *cis*-configuration. The dihedral angles between the mean planes of the ethenyl and the phenyl rings at the stilbene moiety are  $12.7^\circ$  and  $78.4^\circ$ , respectively. The coordination around silicon is a rather perfect tetrahedron with longest Si–C(1) (Si–Csp<sup>2</sup>), 1.870 Å, and shortest Si–C(5) (Si–Csp), 1.831 Å, distances. The angles of the sp carbon atoms adjacent to the phenyl rings are closer to linearity ( $179.5^\circ$ ,  $175.7^\circ$ ) than the angles at the C atoms bonded to Si ( $169.3^\circ$ ,  $170.6^\circ$ ). In compound **3** (Fig. 3), the silole ring is planar (rmsd 0.026 Å) and the four phenyl rings at the silole ring exhibit a propeller-like arrangement. The geometry of the silole ring is in the normal range [10] and the Si–C(1) and Si–C(4) (Si–Csp<sup>2</sup>) bond lengths are longer than those found for the Si–C(5) and Si–C(7) (Si–Csp) bonds, which is similar to compound **2**. Each phenyl ring connecting to the acetylene subunits or to the C(1) atom in compound **3** is disordered in two positions.

The coordination around the ring silicon atom in **6** (Fig. 4) is a slightly distorted tetrahedron with the Si–C(5) and Si–C(7) distances of 1.8203 and 1.8289 Å, respectively, which are shorter than Si–C(1) (1.8924 Å) and Si–C(4) (1.8943 Å). The two  $\text{Me}_2\text{SiH}$ – groups are at the same side of the silole ring (*cis*-configuration) with a similar environment. The silicon containing central ring shows an envelope conformation with the four carbon atoms in a common plane (rmsd 0.013 Å) and the Si atom



Scheme 1.

deviating by 0.729 Å from this plane to the same side as the two  $\text{Me}_2\text{SiH}$  groups, about 0.1 Å further than in the similar 2,5-substituted dihydrosiloles reported by Choi [11]. That causes a small bond angle at C(1) and C(4) ( $\text{Si}-\text{C}(4)-\text{C}(3) = 96.29^\circ$ ,  $\text{Si}-\text{C}(1)-\text{C}(2) = 97.17^\circ$ ).

In the acyclic compound **8** (Fig. 5), the coordination around the silicon atom is a distorted tetrahedron. The C(1)–C(2) and C(2)–C(3) distances are 1.499 and 1.318 Å, respectively. From this it is concluded that, simultaneously to the ring-opening reaction of the silacyclobutene, the double bond shifts from C(1)–C(2) to C(2)–C(3) and the former stilbene subunit is disintegrated. The phenyl and the neo-

pentyl group are in a *cis*-arrangement with the dihedral angle,  $114.7^\circ$ , between the ethenyl plane and phenyl ring.

### 2.3. UV–Vis absorption and fluorescence spectra

The absorption spectra of the model compounds **2–8** in THF as solvent are shown in Fig. 6. The absorption maxima and their extinction coefficients were extracted from the spectra and are listed in Table 2, which also contains the data for the pure organic compounds *cis*-stilbene (**13**) and 1,4-diphenyl-*trans-trans*-buta-1,3-diene (DPB, **14**) for comparison.

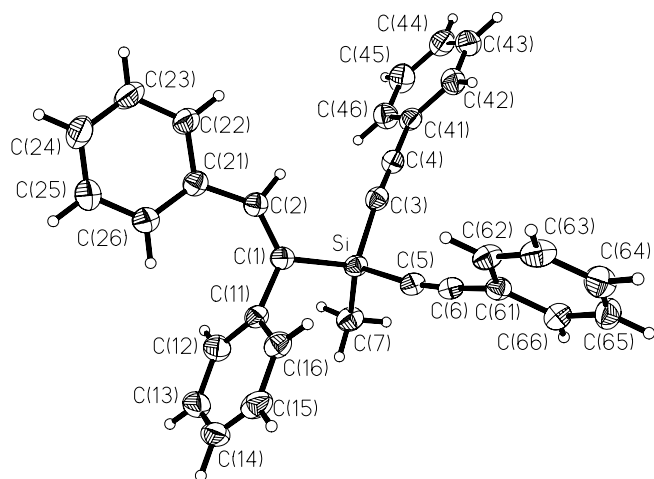


Fig. 2. Molecular structure of **2**. Ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and angles (°): Si–C(1) 1.8703(19), Si–C(3) 1.832(2), Si–C(5) 1.831(2), Si–C(7) 1.852(2), C(1)–C(2) 1.345(2), C(3)–C(4) 1.204(3), C(5)–C(6) 1.206(3), C(1)–C(11) 1.498(3), C(2)–C(21) 1.475(3), C(4)–C(41) 1.444(3), C(6)–C(61) 1.438(2), C(1)–Si–C(3) 111.17(8), C(1)–Si–C(5) 107.67(8), C(1)–Si–C(7) 109.77(9), C(3)–Si–C(5) 107.62(9), C(3)–Si–C(7) 106.79(9), C(5)–Si–C(7) 113.84(9), Si–C(3)–C(4) 169.33(18), Si–C(5)–C(6) 170.63(16), Si–C(1)–C(2) 119.72(14), C(11)–C(1)–C(2) 126.73(17), C(1)–C(2)–C(21) 132.99(18).

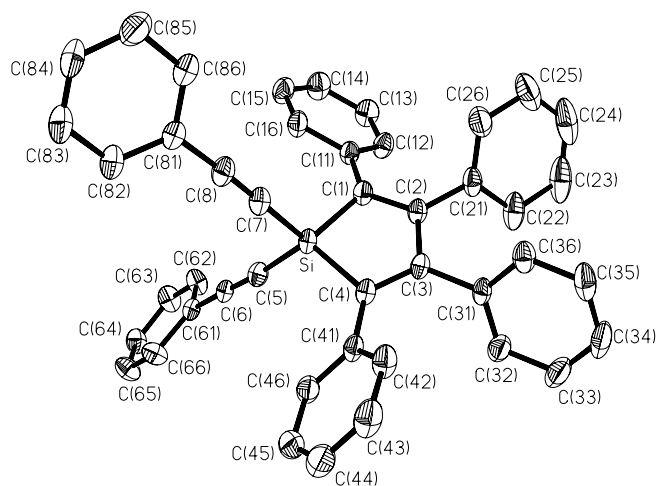


Fig. 3. Molecular structure of **3**. Ellipsoids are drawn at 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Si–C(1) 1.857(2), Si–C(4) 1.8590(19), Si–C(5) 1.814(2), Si–C(7) 1.819(2), C(1)–C(2) 1.360(3), C(2)–C(3) 1.507(3), C(3)–C(4) 1.354(3), C(5)–C(6) 1.220(4), C(7)–C(8) 1.198(3), C(5)–Si–C(7) 106.25(9), C(5)–Si–C(1) 113.45(10), C(7)–Si–C(1) 113.28(10), C(5)–Si–C(4) 117.55(10), C(7)–Si–C(4) 112.20(9), C(1)–Si–C(4) 94.09(9), C(2)–C(1)–Si 106.19(14), C(1)–C(2)–C(3) 116.51(17), C(4)–C(3)–C(2) 116.58(16), C(3)–C(4)–Si 106.32(14).

Going from *cis*-stilbene **13** to the stilbene-containing silico compounds **2**, **6**, and **7**, the long wavelength absorption maxima exhibit a blue shift of 11–27 nm and an increase of the extinction coefficient  $\epsilon$ . In contrast, a small red shift of 6–8 nm and a decrease of  $\epsilon$  is detected starting from DPB **14** to the DPB-containing silacyclobutenes **4** and **5**. The  $\pi$ -conjugated compounds **3**, **4**, and **5** display a marked

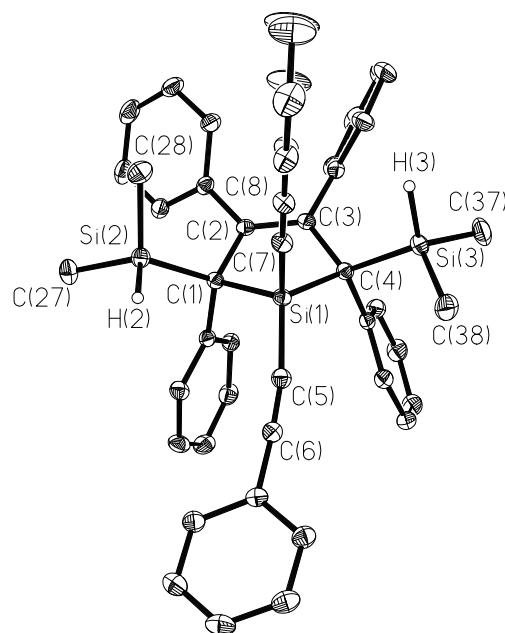


Fig. 4. Molecular structure of **6**. Ellipsoids are drawn at 30% probability. Hydrogen atoms on carbon atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Si(1)–C(5) 1.8203(17), Si(1)–C(7) 1.8289(18), Si(1)–C(1) 1.8924(16), Si(1)–C(4) 1.8943(17), C(1)–C(2) 1.538(2), C(2)–C(3) 1.360(2), C(3)–C(4) 1.554(2), Si(2)–C(1) 1.9241(16), Si(2)–C(27) 1.866(2), Si(2)–C(28) 1.868(2), Si(2)–H(2) 1.400(19), Si(3)–C(4) 1.9219(16), Si(3)–C(38) 1.860(2), Si(3)–C(37) 1.864(2), Si(3)–H(3) 1.433(18), C(5)–Si(1)–C(7) 105.14(8), C(5)–Si(1)–C(1) 113.88(7), C(7)–Si(1)–C(1) 111.58(7), C(5)–Si(1)–C(4) 121.23(8), C(7)–Si(1)–C(4) 107.96(7), C(1)–Si(1)–C(4) 96.95(7), C(27)–Si(2)–C(28) 108.27(10), C(27)–Si(2)–C(1) 114.61(8), C(28)–Si(2)–C(1) 113.17(8), C(27)–Si(2)–H(2) 106.8(8), C(28)–Si(2)–H(2) 108.0(8), C(1)–Si(2)–H(2) 105.6(8), C(38)–Si(3)–C(37) 109.01(11), C(38)–Si(3)–C(4) 110.28(8), C(37)–Si(3)–C(4) 111.03(9), C(38)–Si(3)–H(3) 107.5(7), C(37)–Si(3)–H(3) 108.4(7), C(4)–Si(3)–H(3) 110.5(8), C(21)–C(1)–Si(1) 106.21(10), C(3)–C(2)–C(1) 118.84(14), C(2)–C(3)–C(4) 118.10(14), C(3)–C(4)–Si(3) 117.88(10), Si(1)–C(1)–Si(2) 109.96(8), C(2)–C(1)–Si(2) 114.42(11), C(21)–C(1)–Si(2) 112.95(11), C(2)–C(1)–Si(1) 97.17(10), Si(1)–C(4)–Si(3) 110.74(8), C(51)–C(4)–Si(3) 103.98(10), C(3)–C(4)–Si(3) 117.88(10), C(3)–C(4)–Si(1) 96.29(10).

red shift of 70–123 nm in their long wavelength absorption compared with compounds **2**, **6**, and **7** with no endocyclic  $\pi$ -bond, which coincides with the literature [12].

Although the longest wavelength absorption is similar between 1,2,3,4-tetraphenylbuta-1,3-diene (330 nm) [13] and 1,4-diphenylbuta-1,3-diene (330 nm), their silyl-substituted compounds (**3**, **4**, **5**) have quite different UV–Vis bands: an exceptionally large red shift is observed for silole **3**. This is attributed to the particularly low-lying LUMO in **3**, which results from the orbital interaction between the  $\sigma^*$  orbital of exocyclic silicon–carbon bonds at the silole and the  $\pi^*$ -orbital of the butadiene fragment, namely  $\sigma^*-\pi^*$  conjugation [14,15]. No significant difference in the absorption spectra between the acyclic compound **2** and the cyclic silacyclobutene **7** is observed. Surprisingly, the absorption of both acyclic compounds **2** and **8** is very similar with respect to their maxima as well as in their vibrational structures: this indicates that they should have similar electronic

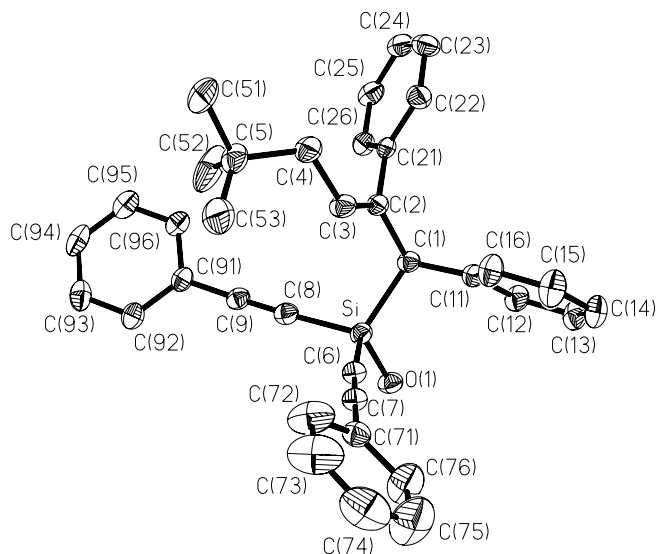


Fig. 5. Molecular structure of **8**. Ellipsoids are drawn at 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Si–O(1) 1.599(3), Si–C(6) 1.790(4), Si–C(8) 1.7960(4), Si–C(1) 1.847(4), C(1)–C(2) 1.499(5), C(2)–C(3) 1.318(5), C(3)–C(4) 1.474(5), O(1)–Si–C(6) 106.22(17), O(1)–Si–C(8) 109.50(17), C(6)–Si–C(8) 108.58(17), O(1)–Si–C(1) 111.30(16), C(6)–Si–C(1) 112.30, C(8)–Si–C(1) 108.86(17), C(2)–C(1)–Si 114.8(2), C(3)–C(2)–C(1) 122.7(3), C(2)–C(3)–C(4) 126.8(4), C(3)–C(2)–C(21) 122.3(3), C(21)–C(2)–C(1) 114.9(3), C(11)–C(1)–C(2) 114.5(3), C(11)–C(1)–Si 110.0(2).

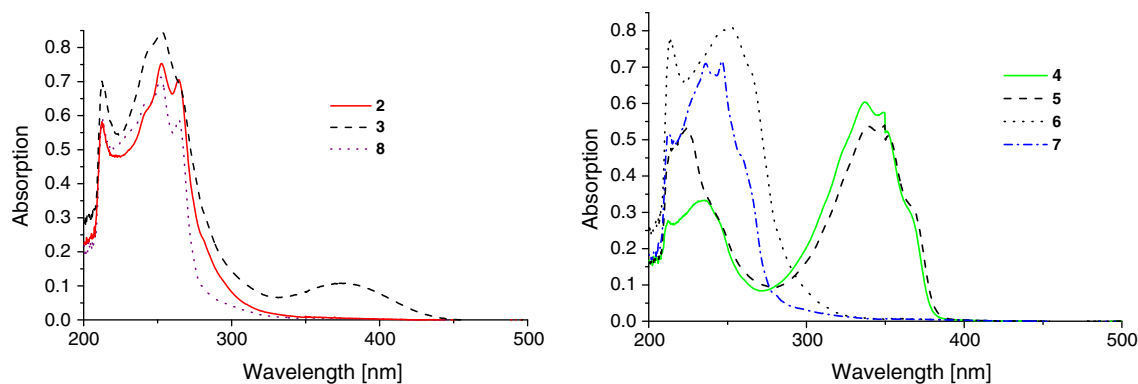
HOMO and LUMO levels, although their molecular structures are quite different. The longest wavelength absorption bands for these unsaturated organosilicon compounds **2–8** are probably caused by the  $\pi \rightarrow \pi^*$  transition in the stilbene, styrene and butadiene subunits [16].

As illustrated in Fig. 7, the excitation maxima of compounds **2–7** in THF solution are similar to their absorption spectra, except the fact that the excitation spectrum of silacyclobutene **7** is significantly broadened and red-shifted by about 40 nm. The reason for this phenomenon is still under investigation. Due to the weakness of the emission maximum of **8** (Fig. 9), its excitation spectrum cannot be measured.

The emission spectra of compounds **2–8** were recorded at room temperature using an excitation range from 261 to 388 nm in both the solid state as well as in THF solution (Figs. 8 and 9). The fluorescence data are summarized in Table 2, which also contains those data for *cis*-stilbene and DPB for comparison. It is suggested that the fluorescence of **2**, **6**, and **7** probably arises from the stilbene subunits, while that of compounds **4** and **5** may originate from the stilbene's vinylogue moieties. This is concluded because they show nearby emission maxima, similar vibrational structures and a similar variation of emission comparing the spectra with those of stilbene **13** and its vinylogue

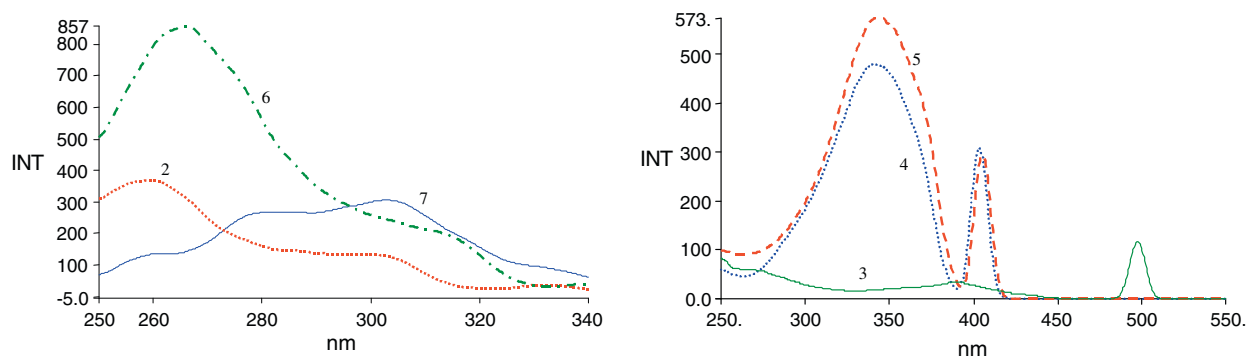
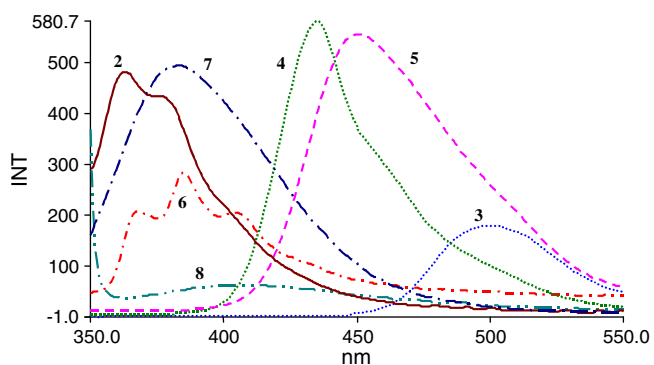
Table 1  
Crystal data, experimental conditions, and summary of structure refinement for **2**, **3**, **6**, and **8**

	<b>2</b>	<b>3</b>	<b>6</b>	<b>8</b>
Empirical formula	C <sub>31</sub> H <sub>24</sub> Si	C <sub>44</sub> H <sub>30</sub> Si	C <sub>48</sub> H <sub>44</sub> Si <sub>3</sub>	C <sub>36</sub> H <sub>34</sub> OSi
Formula weight	424.59	586.77	705.10	510.72
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Temperature (K)	173(2)	173(2)	173(2)	173(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	<i>P</i> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> (Å)	9.6440(6)	9.9080(10)	21.075(2)	10.2138(2)
<i>b</i> (Å)	5.9815(4)	18.361(2)	10.1733(8)	10.4353(2)
<i>c</i> (Å)	21.2240(10)	18.544(2)	19.836(2)	14.6600(3)
$\alpha$ (°)	90	90	90	86.750(2)
$\beta$ (°)	102.369(4)	101.148(6)	109.380(10)	71.698(2)
$\gamma$ (°)	90	90	90	73.538(2)
<i>V</i> (Å <sup>3</sup> )	1195.90(12)	3309.9(6)	4011.9(6)	1421.78(5)
<i>Z</i>	2	4	4	2
<i>D</i> <sub>calcd</sub> (Mg/m <sup>3</sup> )	1.179	1.178	1.167	1.193
$\mu$ (mm <sup>-1</sup> )	0.114	0.101	0.150	0.109
<i>F</i> (000)	448	1232	1496	544
Crystal size (mm <sup>3</sup> )	0.40 × 0.30 × 0.20	0.50 × 0.20 × 0.20	0.70 × 0.30 × 0.20	0.66 × 0.56 × 0.12
$\theta$ Range (°)	1.96–28.87	1.58–29.42	2.05–28.95	2.04–25.03
Index ranges	–12 ≤ <i>h</i> ≤ 12, –7 ≤ <i>k</i> ≤ 7, –28 ≤ <i>l</i> ≤ 26	–11 ≤ <i>h</i> ≤ 12, –24 ≤ <i>k</i> ≤ 22, –24 ≤ <i>l</i> ≤ 25	–27 ≤ <i>h</i> ≤ 28, –13 ≤ <i>k</i> ≤ 13, –25 ≤ <i>l</i> ≤ 26	–12 ≤ <i>h</i> ≤ 12, –12 ≤ <i>k</i> ≤ 12, –17 ≤ <i>l</i> ≤ 17
Reflections collected	20,608	53,189	60,860	14,859
Independent reflections [ <i>R</i> <sub>int</sub> ]	5432 [0.0393]	7905 [0.0524]	9401 [0.0400]	4975 [0.0565]
Data/restraints/parameters	5432/1/289	7905/9/580	9401/0/468	4975/0/347
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.054	1.016	1.039	1.048
Final <i>R</i> indices	<i>R</i> <sub>1</sub> = 0.0403	<i>R</i> <sub>1</sub> = 0.0590	<i>R</i> <sub>1</sub> = 0.0472	<i>R</i> <sub>1</sub> = 0.0871
[ <i>I</i> > 2σ( <i>I</i> )]	<i>wR</i> <sub>2</sub> = 0.0837	<i>wR</i> <sub>2</sub> = 0.1369	<i>wR</i> <sub>2</sub> = 0.1034	<i>wR</i> <sub>2</sub> = 0.2154
Largest difference in peak and hole (e Å <sup>-3</sup> )	0.173 and –0.248	0.447 and –0.271	0.309 and –0.291	0.801 and –0.651

Fig. 6. UV-Vis absorption spectra of **2–8** in THF ( $10^{-5}$  M).Table 2  
Absorption and Emission Data of Compounds **2–8** and **13–14**

Compounds	UV		Fluorescence (solid) $\lambda_{\max}$ (nm)	Fluorescence (THF) $\lambda_{\max}$ (nm)	Stokes' shifts (nm)	quantum yield $\Phi^a$
	$\lambda_{\max}$ (nm)	$\epsilon (\times 10^4) (\text{L} \cdot \text{mol}^{-1} \text{cm}^{-1})$				
<b>2</b>	264, 253	7.05, 7.53	363	370	106	0.0037
<b>3</b>	374, 253	1.01, 7.83	500	495	121	0.0017
<b>4</b>	337	4.37	435	411	74	0.0077
<b>5</b>	339	4.08	450	406	57	0.012
<b>6</b>	251	7.12	385	380	127	0.0046
<b>7</b>	246, 235	7.03, 6.97	384	370	124	0.058
<b>8</b>	264, 252	4.60, 5.27	–	–	–	–
<b>13</b>	278	2.00	–	353	74	0.014
<b>14</b>	331	6.82	428	379	48	0.028

<sup>a</sup> The PL quantum yields in THF ( $1 \times 10^{-6} \sim 1 \times 10^{-5}$  M) were measured in comparison to quinine sulfate (ca.  $1 \times 10^{-5}$  M) in 0.10 M  $\text{H}_2\text{SO}_4$  as standard [22].

Fig. 7. Photoluminescence excitation spectra of **2–7** in THF solution.Fig. 8. Photoluminescence emission spectra of **2–8** (solid state).

DPB **14**, respectively. The absence of an emission band in the styrene-containing compound **8** further supports this suggestion. The emission of silole **3** has been attributed to the  $\pi$  system within the silole ring by Yamaguchi et al. [14].

The emission  $\lambda_{\max}$  of compounds **2–8** is not affected by an increasing concentration of the silanes in solutions from  $1.0 \times 10^{-5}$  to  $1.0 \times 10^{-3}$  M. When the excitation wavelengths are within the absorption band of the compounds, a variation of the wavelength of the excitation light has also only little influence on the fluorescence  $\lambda_{\max}$ . These optical properties are similar to those found for stilbene and DPB [17].

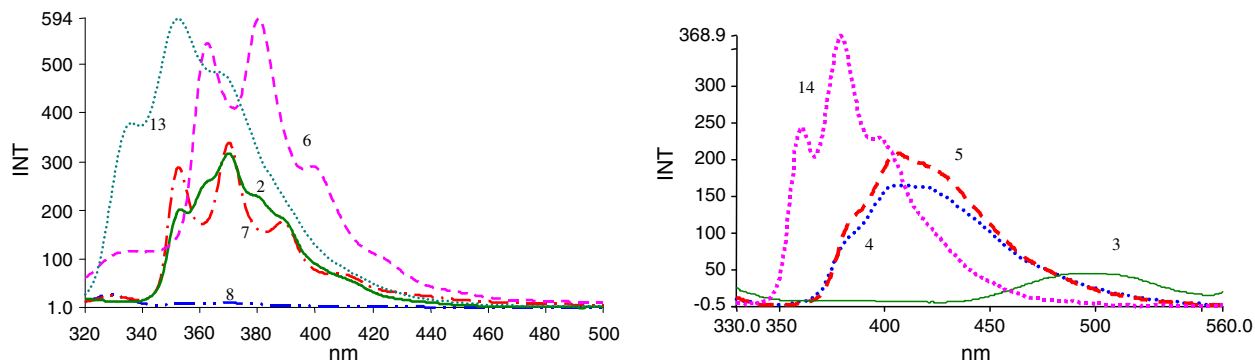


Fig. 9. Photoluminescence emission spectra of **2–8**, **13–14** in THF solution.

As shown in Figs. 8 and 9, and Table 2, there is a considerable change in the fluorescence maxima  $\lambda_{\max}$  (363–500 nm), the Stokes' shifts (57–27 nm), and the quantum yields  $\Phi$  (0.0017–0.058) of compounds **2–8** in the solid state as well as in THF solution. This indicates that the fluorescence properties of the silicon organics are obviously affected by the  $\pi$ -conjugation within the carbon moieties, the influence of the substituents at silicon, and by configurational features and the topology of the molecules. Mostly the fluorescence is detected at slightly lower wavelength in the solid state than in THF solution; an exception is found for compound **2**, in which a 7 nm blue shift is detected going from THF solution to the solid state. It appears as a general trend that the emission maxima in the silicon based compounds **2**, **4–7** occur at longer wavelengths compared to those in the corresponding pure organic compounds **13** and **14**, respectively. The emission maximum of silole **3** is particularly red-shifted. This is probably due to the  $\sigma^*-\pi^*$  conjugation between the  $\sigma^*$  orbital of the two-exocyclic  $\sigma$ -bonds with the ring silicon and the  $\pi^*$  orbital of the butadiene moiety of the silole [15]. As shown in Figs. 7–9, the photoluminescence excitation and emission spectra between the silicon methyl substituted benzylidenesilacyclobutene **4** and its phenyl substituted analogue **5** are quite similar. But the fluorescence data listed in Table 2 reveal differences in  $\lambda_{\max}$ , the Stokes' shifts, and the quantum yields  $\Phi$ . This confirms the fact that substitution at silicon will slightly affect the fluorescence behavior of organosilanes. Thus, a different substitution pattern at silicon can easily be used to finely adjust the fluorescence properties of an organosilane, a fact which has been extensively investigated in previous papers [4] as well as was found by Tamao [15].

The Stokes' shifts of the stilbene-containing compounds **2**, **3**, **6**, and **7** are much larger than those of the butadiene-containing derivatives **4** and **5**, with a maximum value of 127 nm for silacyclopentene **6** and a minimum of 57 nm for benzylidenesilacyclobutene **5**. The quantum yields  $\Phi$  of compounds **2–8** indicate their fluorescent emissions to be very weak. A comparison with  $\Phi$  of the pure organic compounds **13** and **14** shows that the introduction of silicon atoms tends to decrease the quantum yield. Referring

to *cis*-stilbene **13**, an exception is found for silacyclobutene **7**, in which a fourfold increase of the quantum yield is detected. The emission of silole **3** around 500 nm is further weak and broad, especially in THF solution, which agrees with the general properties of this class of compounds, reported by Tamao [18].

In conclusion and as expected, the fluorescence properties of the organosilicon compounds **2–8** are originated by the  $\pi$  system of the stilbene or its vinylogue subunits (DPB). The presence of silicon causes a red shift of the fluorescence  $\lambda_{\max}$ , an increase of the Stokes' shifts as well as a trend to decrease the quantum yields.  $\pi$ -Conjugated structural moieties cause both the absorption and emission  $\lambda_{\max}$  to be markedly red-shifted. The desired optical properties can be tailored by an appropriate choice of substituents at the silicon atom and the structural configuration of the molecule. Nevertheless, the unusual optical properties of silacyclobutene **7** need further investigation, currently being performed in our group.

This study provides fundamental information upon the influence of silicon atoms to the photoluminescence of organic compounds. As a tool it might help to reasonably predict the optical properties of a compound or material by introduction of silicon/substituent arrangements into the  $\pi$  system of fluorescent active materials such as PPV and its derivatives. Moreover, compounds **2** and **3**, and **6–8**, containing phenylethynyl substituents at the silicon center, are excellent precursors for intramolecular cyclisation reactions to silacyclobutenes [8] as well as for addition [19], condensation [20], and hydrosilylation reactions [21]. Thus, on the basic knowledge provided, a broad variety of photoluminescent compounds or materials might be available by well established synthetic routes.

### 3. Experimental

#### 3.1. General procedures

Unless otherwise noted, all starting materials are commercially available and are used without further purification. All reactions involving organometallic compounds

were carried out under a positive pressure of argon using standard Schlenk techniques. THF was refluxed and distilled from Na/K alloy and benzophenone under an argon atmosphere. The chromatographic separations were carried out at room temperature under ambient atmosphere. All starting materials were purchased from Fluka.  $\text{PhC}\equiv\text{CMgBr}$  was prepared by reaction of  $\text{PhC}\equiv\text{CH}$  with  $\text{EtMgBr}$  (1 M, THF solution), the latter was obtained by reaction of Mg with EtBr in THF. The dichlorosilanes **9**, **10**, and **12** were synthesized according to literature procedures [5].

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were measured on a Bruker AM 250 (250 MHz for  $^1\text{H}$  and 62.9 MHz for  $^{13}\text{C}$ ) spectrometer and  $^{29}\text{Si}$  NMR on a Bruker DPX 250 (49.7 MHz) spectrometer with chloroform-*d* as solvent at room temperature. Chemical shifts are reported in  $\delta$  [ppm] with reference relative to the  $\text{CDCl}_3$  peak for  $^{13}\text{C}$  and TMS peak for  $^1\text{H}$  and  $^{29}\text{Si}$ . UV–Vis and fluorescence spectra were obtained from a CARY-1 UV–Vis spectrophotometer and a Perkin–Elmer LS 50B luminescence spectrometer, respectively. Microanalyses were performed by the Organisch-Chemisches Institut der J. W. Goethe-Universität Frankfurt am Main.

### 3.2. Synthesis of **2**

$\text{PhC}\equiv\text{CMgBr}$  (50 mmol, 1.0 M THF solution, 50 mL) was added dropwise to a solution of **9** (6.8 g, 23.2 mmol) in THF (20 mL) in a 100 mL Schlenk flask. The reaction mixture was stirred at room temperature for 1 h, then treated with ice. The resulting mixture was extracted with diethyl ether ( $3 \times 100$  mL) and washed with water and brine. The extract was dried over  $\text{MgSO}_4$  and then evaporated *in vacuo* to give a colorless oil. Recrystallization from *n*-pentane at  $-18^\circ\text{C}$  yielded colorless crystals of **2** (8.3 g, 19.5 mmol) in 84%.  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.54\text{--}7.04$  (m, 20H, *Ph*), 0.52 (s, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (62.9 MHz,  $\text{CDCl}_3$ ):  $\delta = 141.30, 140.55, 139.74, 136.87, 132.13, 129.77, 128.98, 128.62, 128.22, 127.93, 127.61, 126.32, 122.57, 107.77, 88.88, -1.02$ .  $^{29}\text{Si}$  NMR (49.7 MHz,  $\text{CDCl}_3$ ):  $\delta = -42.3$ . Anal. Calc. for  $\text{C}_{31}\text{H}_{24}\text{Si}$ : C, 87.69; H, 5.70. Found: C, 87.27; H, 5.80%.

Compounds **3** and **7** were prepared analogous to the procedure described for **2**, using 1,1-dichloro-2,3-diphenyl-4-neopentyl-1-silacyclobut-2-ene and 1,1-dichloro-2,3,4,5-tetraphenylsilole instead of **9** as starting material.

### 3.3. Analysis of **3**

Isolated as yellow crystals after recrystallization from acetone, 73% yield.  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.51\text{--}6.89$  (m, 30H, *Ph*).  $^{13}\text{C}$  NMR (62.9 MHz,  $\text{CDCl}_3$ ):  $\delta = 156.59, 138.43, 137.87, 135.01, 132.40, 129.68, 129.54, 129.28, 128.21, 127.90, 127.61, 126.68, 126.21, 122.27, 108.61, 85.72$ .  $^{29}\text{Si}$  NMR (49.7 MHz,  $\text{CDCl}_3$ ):  $\delta = -49.13$ . Anal. Calc. for  $\text{C}_{44}\text{H}_{30}\text{Si}$ : C, 90.06; H, 5.15. Found: C, 89.62; H, 5.19%.

### 3.4. Analysis of **7**

Isolated as white needle crystalline material from the mother liquor, 86% yield.  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.55\text{--}7.07$  (m, 20H, *Ph*), 2.63 (dd, 1H,  $\text{CH}$ ,  $^3J = 12.4$  Hz,  $^3J = 4.4$  Hz), 1.60 (dd, 1H,  $\text{CH}_2$ ,  $^3J = 12.8$  Hz,  $^2J = 13.9$  Hz), 1.46 (dd, 1H,  $\text{CH}_2$ ,  $^3J = 4.4$  Hz,  $^2J = 13.5$  Hz), 0.96 (s, 9H,  $\text{C}(\text{CH}_3)_3$ ).  $^{13}\text{C}$  NMR (62.9 MHz,  $\text{CDCl}_3$ ):  $\delta = 159.35, 141.39, 136.52, 136.45, 132.32, 132.17, 129.24, 128.33, 128.25, 128.20, 128.09, 127.93, 126.85, 122.41, 122.11, 109.21, 108.34, 87.56, 87.37, 40.92, 31.62, 30.99, 29.68$ .  $^{29}\text{Si}$  NMR (49.7 MHz,  $\text{CDCl}_3$ ):  $\delta = -47.37$ . Anal. Calc. for  $\text{C}_{36}\text{H}_{32}\text{Si}$ : C, 87.75; H, 6.55. Found: C, 87.51; H, 6.66%.

### 3.5. Synthesis of **6**

A mixture of lithium granular (110 mg, 15.8 mmol) and naphthalene (2.03 g, 15.8 mmol) in 50 mL of THF was stirred at room temperature under argon for 5 h to form a deep green solution of lithium naphthalenide (LiNp). Then the solution was cooled to  $-77^\circ\text{C}$  and a THF (10 mL) solution of **3** (2 g, 3.4 mmol) was added dropwise over a period of 1 h. After stirring for 0.5 h, dimethylchlorosilane (2.2 mL, 20.3 mmol) was added. The mixture was stirred and warmed to room temperature to give a yellow solution. The solvent was removed under vacuum and the residue was extracted with hexane. The hexane solution was evaporated and the resulting mixture was subjected to a column chromatography on silica gel ( $R_f = 0.49$ , hexane:ethyl acetate = 20:1) to give crystalline **6** (0.16 g, 0.23 mmol) in 6.8% yield.  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.67\text{--}6.81$  (m, 30H, *Ph*), 4.64 (m, 2H,  $\text{SiH}$ ,  $^3J = 21.4$  Hz,  $^1J_{\text{Si-H}} = 194.0$  Hz), 0.28 (d, 6H,  $\text{SiCH}_3$ ,  $^3J = 3.7$  Hz),  $-0.37$  (d, 6H,  $\text{SiCH}_3$ ,  $^3J = 3.7$  Hz).  $^{13}\text{C}$  NMR (62.9 MHz,  $\text{CDCl}_3$ ):  $\delta = 146.63, 141.76, 141.50, 131.99, 130.96, 129.15, 129.07, 128.79, 128.40, 128.25, 127.04, 126.34, 123.72, 123.00, 122.57, 110.67, 107.81, 89.97, 89.74, 38.01, -2.12, -3.97$ .  $^{29}\text{Si}$  NMR (49.7 MHz,  $\text{CDCl}_3$ ):  $\delta = -33.74$  ( $\text{SiCPh}$ ),  $-11.48$  ( $\text{HSiMe}_2$ ). Anal. Calc. for  $\text{C}_{48}\text{H}_{44}\text{Si}_3$ : C, 81.76; H, 6.29. Found: C, 81.65; H, 6.31%.

### 3.6. Synthesis of **8**

A THF solution of 1,1-dichloro-2,3-diphenyl-4-neopentyl-1-silacyclobut-2-ene **12** (9.1 g, 25.2 mmol, 70 mL THF) was added within 2 h dropwise to a solution of  $\text{PhC}\equiv\text{CMgBr}$  (50 mmol, 160 mL THF). After stirring for 10 h, the mixture was treated with 6% HCl aqueous solution, then extracted with ether ( $3 \times 100$  mL). The extract was washed with brine, dried over  $\text{MgSO}_4$ , filtered, and evaporated. The residue was dissolved in 200 mL of *n*-pentane and concentrated to 50 mL. The solution was allowed to stand at  $4^\circ\text{C}$  for 1 week. Colorless crystals (8.75 g, 17.1 mmol) were achieved in 68% yield.  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.54\text{--}7.04$  (m, 20H, *Ph*), 6.35 (t, 1H,  $=\text{CH}$ ,  $^3J = 7.4$  Hz), 3.48 (s, 1H,  $\text{SiCH}$ ), 2.33 (s, 1H,



SiOH), 1.94 (d, 2H,  $\text{CH}_2$ ,  $^3J = 7.2$  Hz), 0.89 (s, 9H,  $\text{C}(\text{CH}_3)_3$ ).  $^{13}\text{C}$  NMR (62.9 MHz,  $\text{CDCl}_3$ ):  $\delta = 143.02$ , 139.74, 138.78, 132.17, 129.24, 129.07, 128.37, 128.19, 127.81, 126.24, 125.77, 122.01, 106.81, 106.48, 89.22, 89.15, 47.96, 43.39, 31.44, 29.46.  $^{29}\text{Si}$  NMR (49.7 MHz,  $\text{CDCl}_3$ ):  $\delta = -44.32$ . Anal. Calc. for  $\text{C}_{36}\text{H}_{34}\text{OSi}$ : C, 84.66; H, 6.71. Found: C, 84.34; H, 6.73%.

### 3.7. X-ray structure determination

Suitable single crystals for X-ray analysis of **2** were grown from a concentrated mixed solution of ethyl acetate and hexane. Crystals of **3** and **6** were obtained from evaporating a hexane and ethyl acetate solution of the samples under ambient conditions, respectively. Crystals of **8** were obtained from a concentrated pentane solution. Details on machine parameters, crystal data, data collection and refinement are given in Table 1.

### 4. Supplementary material

CCDC 187018, 187016, 187017, and 187015 contain the supplementary crystallographic data for **2**, **3**, **6**, and **8**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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