## A Novel Route to Stable Silacyclopropenes - First Synthesis of Silacyclopropenes bearing Vinylic Hydrogen

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Abstract: Starting from easily accessible cyclotrisilane 1, stable silacyclopropenes 3a - e are obtained in high yield. Their NMR spectroscopic data indicate appreciable charge delocalization throughout the three membered ring system.

Since the first synthesis of a stable silacyclopropene in 1976 by Gaspar and Conlin,<sup>1</sup> two major synthetic pathways to this interesting class of compounds have been established: Addition of thermally, photolytically or catalytically generated diarylsilanediyls to disubstituted alkynes resulted in the formation of stable silacyclopropenes.<sup>1,2,3</sup> Although convincing evidence for silacyclopropenes as intermediates was provided using terminal alkynes, only rearranged or trapping products were isolated.<sup>4</sup> A second synthetic pathway<sup>3,5</sup> involving the photolysis of alkynyldisilanes gave silacyclopropenes, which were surprisingly stable towards moisture and air.<sup>3</sup> In this communication we wish to describe a new route to this ring system. Our method allows for the first time the isolation of silacyclopropenes bearing hydrogen at vinylic carbon.



Scheme 1. Ar = 2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>; a:  $R^1 - R^2 = (CH_2)_6$ ; b:  $R^1 = R^2 = Me_3Si$ ; c:  $R^1 = R^2 = Ph$ ; d:  $R^1 = n-C_3H_7$ ,  $R^2 = H$ ; e:  $R^1 = Me_3Si$ ,  $R^2 = H$ ; f:  $R^1 = Ph$ ,  $R^2 = H$ 

Recently,<sup>6</sup> we reported the synthesis of cyclotrisilane 1, whose 2-(dimethylaminomethyl)phenyl substituent was first introduced by Corriu<sup>7</sup> into the chemistry of hypervalent silicon compounds. 1 showed an unprecedented reactivity: In a thermal reaction the three diarylsilanediyl subunits were transferred to various substrates such as benzil or bipyridine, thus acting as a synthetic equivalent for a diarylsilanediyl. However, the

occurrence of free diarylsilanediyl Ar<sub>2</sub>Si: (Ar = 2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>) in these reactions seemed to be less likely. In addition, we have now observed, that 1 also transfers its diarylsilanediyl units to a variety of monoand disubstituted alkynes thereby forming the silacyclopropene ring system. As shown in Scheme 1, aliphatic, aromatic and silylsubstituted alkynes could be used in this reaction. Stirring of 1 with an excess of alkynes 2a -2e for 4 hours at 50°C in toluene resulted in the quantitative conversion of 1 into silacyclopropenes 3a - 3e, which were obtained as spectroscopically pure oils after removal of excess alkyne in vacuo. Due to their extreme sensitivity towards moisture, the silacyclopropenes were identified mainly by NMR spectroscopy (Table 1) and subsequent reactions (vide infra).

The <sup>29</sup>Si chemical shifts of **3a** - **f**, which fell into the high field region between -106 and -116 ppm.<sup>8</sup> were of highly diagnostic value for proving the proposed silacyclopropene structure. The extreme shielding of the silicon nucleus in **3a** - **f** is known for other silacyclopropenes,<sup>2,9</sup> however, a satisfactory explanation of this phenomenon is still unavailable. The <sup>13</sup>C resonances of vinylic carbon atoms in **3a** - **f** were generally shifted to lower field in comparison with cyclopropenes.<sup>10</sup> More pronounced were the chemical shifts of vinylic hydrogen in **3d** - **f**, which showed an appreciable deshielding up to shifts lower than 10 ppm. We felt that these NMR spectroscopic results might be best explained by delocalization of the  $\pi$  electrons of the double bonds into an empty orbital at silicon.<sup>11</sup> The magnitude of the vinylic <sup>13</sup>C - <sup>1</sup>H coupling constants in **3d** and **3e**<sup>12</sup> was unexpectedly small in comparison to values higher than 220 Hz found in cyclopropenes<sup>13</sup> and resembled those observed for vinylic and aromatic protons.

	<sup>1</sup> H-NMR <sup>a</sup>	<sup>13</sup> C-NMR <sup>a</sup>	<sup>29</sup> Si-NMR <sup>a</sup>
3a		δ = 167.7 (s; C-2, C-3)	δ = -106.6
36		δ = 195.45 (s;C-2, C-3)	$\delta = -115.9,$ -13.7 (SiMe <sub>3</sub> )
3c		$\delta = 164.71$ (s;C-2, C-3)	δ = -107.4
3d	δ = 8.60 (3-Η)	δ = 147.8 (d; C-3, <sup>1</sup> J <sub>C-H</sub> = 166 Hz), 180.5 (s; C-2)	δ = -106.3
3e	$\delta = 10.13 (3-H, {}^{2}J_{Si-H} = 10 Hz)$	δ = 175.2 (d; C-3, <sup>1</sup> J <sub>C-H</sub> = 171 Hz), 189.2 (s; C-2)	$\delta = -113.1,$ -14.5 (SiMe <sub>3</sub> )
3f	$\delta = 8.80 (3-H, {}^{2}J_{Si-H} = 10 Hz)$	b	δ = -107.8
6	δ = 7.49 (3-Η)	δ = 161.98 (s; C-2)	δ = -33.0

Table 1. Selected NMR Data of 3a - f and 6

<sup>a</sup> Solvent: C<sub>6</sub>D<sub>6</sub>; Reference: Me<sub>4</sub>Si <sup>b</sup> Not determined

With excess phenylacetylene (2f), the 1:2-adduct 4 was obtained, whose *trans*-configuration at the double bond was unambiguously proved by the vicinal coupling constant (19 Hz) between vinylic hydrogens. Using less than one equivalent of 2f per silanediyle unit of 1 resulted in the formation of a mixture of 1, 4 and 3f, which reacted upon further treatment with 2f to afford 4 as main product, thus establishing 3f as the precursor of 4. This observation was in accordance with results of Seyferth, <sup>14</sup> who reported an analogous reaction of a stable silacyclopropene with 2f. The formation of 3f in the course of this reaction was further evidenced by its characteristic <sup>29</sup>Si- and <sup>1</sup>H-NMR spectroscopic data (Table 1); in addition, it could be trapped from the reaction mixture by hydrolytic workup leading to the isolation of silanol 5.



The silacyclopropene structure of 3a - f could be further corroborated by subsequent reactions typical for this class of compounds. Treatment of 3e with catalytic amounts of  $(Ph_3P)_2PdCl_2$  yielded, with high regioselectivity, the 1,4-disilacyclohexa-2,5-diene 6, which was fully characterized by its spectroscopic and analytical data. The possible isomeric structure  $7^{15}$  was excluded by the observation of only *one* signal in the <sup>29</sup>Si-NMR spectrum. The Pd-catalyzed reaction of **3e** with **2f** gave the silacyclopentadiene **8**.<sup>16</sup>

In conclusion, we have shown that cyclotrisilane 1 is a useful precursor for silacyclopropenes. It allows the first synthesis of stable proton substituted silacyclopropenes, which have a great synthetic potential. In addition, the NMR data of 3a - f provides further evidence for the long discussed electron delocalization in silacyclopropenes.

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