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Reactions of a cyclotrisilane with styrene derivatives and diarylacetylenes—evidence for nucleophilic silylenes

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Abstract—Silaindanes were obtained by reaction of hexakis[2-(dimethylaminomethyl)phenyl]cyclotrisilane (**3**) with 3 equiv. of various styrenes. Analogous treatment of **3** with *p*-methoxystryrene yielded a mixture of the corresponding silaindane and a 2:1 adduct between bis[2-(dimethylaminomethyl)phenyl]silylene (**4**) and the styrene. Competition experiments show that the addition rate of **4** to the triple bond of diarylacetylenes is accelerated by electron-withdrawing substituents. The reaction constant ($\rho=+0.85\pm0.21$) indicates that **4** acts as a nucleophile in these reactions. The rate determining step in these reactions of cyclotrisilane **3** is the formation of silylene **4**. The rate constant for this first order process was determined to be $(6.3\pm0.4)\times10^{-4}$ s^{-1} at 60°C.

1. Introduction

It is well known that silylenes have a singlet ground state.[1] Due to the simultaneous presence of a free electron pair in a σ-orbital as well as an energetically low-lying unoccupied orbital of π-symmetry, these reactive compounds are a priori ambiphilic and may react either as an electrophile or as a nucleophile towards appropriate substrates. In general, the electrophilic character of silylenes appears to dominate their reactivity. Thus, e.g. the insertion of silylenes into heteroatom–hydrogen,[2] carbon–halogen[3] or silicon–fluorine bonds[4] occurs via initial formation of a silylene–Lewis base complex, i.e. the silylene is acting as a Lewis acid. Similarly, addition reactions of Me_2Si to C–C multiple bonds proceed, in accordance with the results of ab initio calculations,[5a] via an initial electrophilic phase, in which the LUMO of the silylene interacts with the π-electron system of the double or triple bond.[5b] In contrast, the stable silylenes **1**[6] and **2**[7] are nucleophilic species. In the case of **2**, it was suggested that its reduced electrophilicity may be due to a substantial back-donation of the lone pair at the nitrogen centres into the empty p-orbital located at silicon. Consequently, this silylene is less vulnerable to the attack of Lewis bases and the nucleophilic character of **2** becomes more pronounced.[8] An alternative approach to a nucleophilic silylene may be the coordination of a Lewis base to the silylene.[1,9] Due to the overlap of the unoccupied p-orbital with the lone pair of the Lewis base the electrophilicity of the resulting silylene–Lewis base complex or silaylide may be significantly suppressed in comparison to that of the free silylene, thus making the silylene–Lewis base complex a nucleophilic species.

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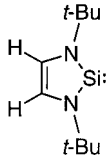
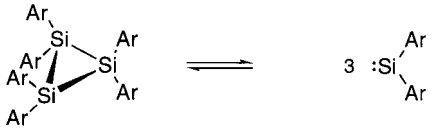


2

During the last years, we have shown that cyclotrisilane **3** reacts thermally under cleavage of all three Si–Si bonds to give the corresponding silylenes **4** as reactive, synthetically useful intermediates.[10a,b] We propose that the unprecedented reactivity of this and other[10c] cyclotrisilanes is founded on an underlying equilibrium between these cyclotrisilanes and their ring-forming silylene subunits (Scheme 1), which is facilitated by the thermodynamic stabilization of the formed silylenes by intramolecular coordination of the silicon centre by one or two NMe_2 substituents.[11] This coordination may result in a silylene with reduced electrophilic and enhanced nucleophilic character (vide supra). To obtain more insight into the electronic properties of chelated silylenes, we investigated the reactivity of **3** towards a variety of styrene and diphenylacetylene derivatives.



3 **4**

Scheme 1. Ar=2-(Me_2NCH_2)C_6H_4.

Keywords: cycloadditions; kinetics; silicon and compounds.

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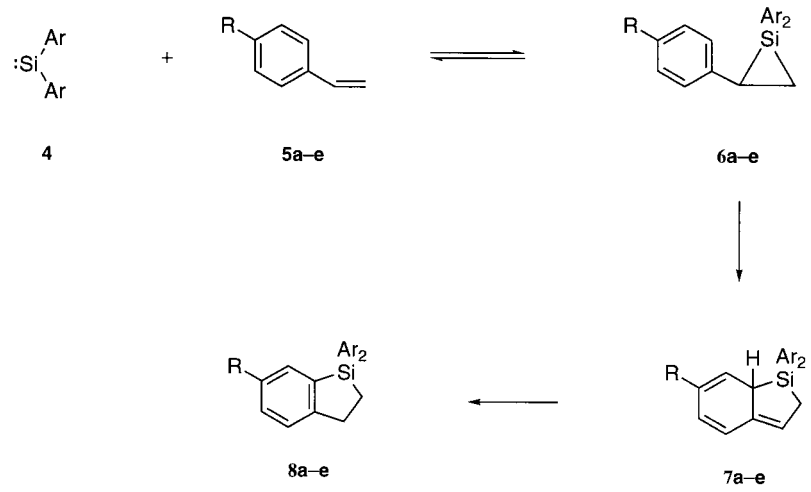
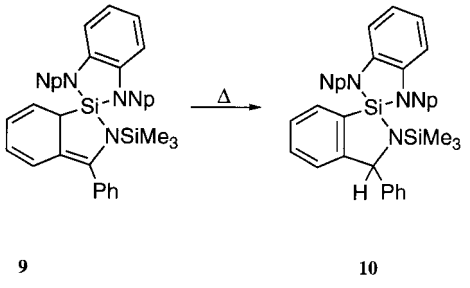


Scheme 2. Ar=2-$(Me_2NCH_2)C_6H_4$; **a**: R=H; **b**: R=CO_2Me; **c**: R=OCOMe; **d**: R=Me; **e**: R=OMe.

2. Results and Discussion

2.1. Synthetic studies

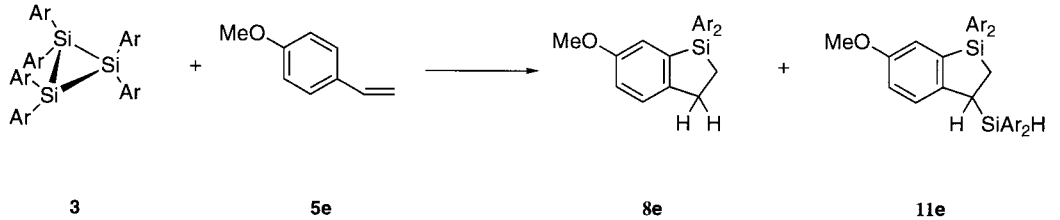
Cyclotrisilane **3** reacts with 3 equiv. of styrene (**5a**) via silylene **4** under clean formation of silaindane **8a** (Scheme 2).[10a] Thermally unstable silacyclopropane **6a** was identified by means of ^1H NMR spectroscopy as the initial product, which subsequently rearranges to **8a**, presumably via the intermediate **7a**. The likely involvement of **7a** as a reaction intermediate was later supported by the observation that the reaction of a stable silylene with $Ph_2C{=}NSiMe_3$ yielded an analogous bicyclic system **9**, which, in contrast to **7a**, can be isolated and undergoes rearomatization to **10** at room temperature only over a period of weeks (Scheme 3).[12] Similarly, silaindanes **8b–d** were formed cleanly and isolated in yields of 34–63%, when **3** was treated with 3 equiv. of the *para*-substituted styrenes **5b–d**. On the other hand, treatment of **3** with 3 equiv. of donor-substituted styrene **5e** under analogous conditions yielded a 1:2 mixture of silaindane **8e** and **11e**, which results from the reaction of two silylenes with one styrene (Scheme 4). The formation of an analogous 2:1 product was recently reported to occur on treating a stable silylene with an imine.[12] Changing the relative amounts of the starting materials affected the composition of the product mixture: When a 1:1.5 ratio of cyclotrisilane **3** and styrene **5e** was used (i.e. two silylenes **4** are available per one styrene molecule), a 1:4 mixture of **8e** and **11e** was formed, whereas the use of a tenfold excess of **5e** (referring to **4**) resulted in a 5:1 ratio of **8e** and **11e**. Careful ^1H NMR spectroscopic re-examination of the crude products of the reactions of **3** with 3 equiv. of **5a–d** revealed that with **5d** small amounts of an analogous 2:1 product were formed; in the case of the less electron-rich styrenes **5a–c** the corresponding silaindanes were the only spectroscopically identified and isolated products.



9 10

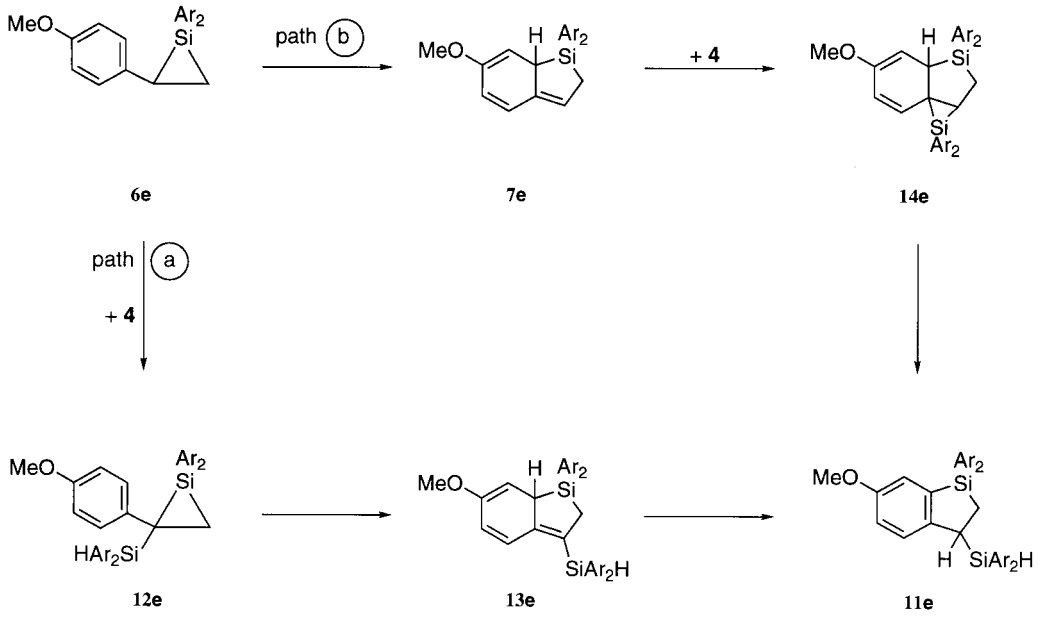
Scheme 3. Np=*t*-$BuCH_2$.

The mechanistic pathway to **11e** is not clear. A control experiment showed that **11e** does not result from an insertion reaction of silylene **4** into the C–H bond of silaindane **8e**: No **11e** is formed on treating an isolated sample of **8e** with silylene-precursor **3**. Thus, the intermediates **6e** or **7e** are possible candidates to react with a second silylene **4** (Scheme 5). Path a features the regiospecific insertion of a silylene **4** into a benzylic C–H bond of silacyclopropane **6e** to give **12e**, followed by a [1,3] silicon and a [1,3] hydrogen shift. This mechanism requires that the concentration of silacyclopropane **6e** is high enough to allow a substantial competition between the bimolecular insertion reaction (**6e**+**4**→**12e**) and the unimolecular rearrangement, which leads to **7e**. This necessary prerequisite is met as the lifetime



3 5e 8e 11e

Scheme 4. Reaction of cyclotrisilane **3** with styrene **5e**; Ar=2-$(Me_2NCH_2)C_6H_4$.



Scheme 5. Mechanistic pathways to **11e**; Ar=2-$(Me_2NCH_2)C_6H_4$.

of the intermediate silacyclopropane under the reaction conditions was found to be greatly influenced by the electronic nature of the substituent R at the *para* position of the aryl ring: The more electron-donating the group R, the longer-lived the silacyclopropane **6**. This becomes evident from the compositions of the reaction mixtures, which were determined by means of ^{1}H NMR spectroscopy after the first half-life period of the reaction (Table 1). Only starting materials and final product **8b** were detected when using the electron-poor styrene **5b**, i.e. silacyclopropane **6b** rearranges faster than it is formed by addition of silylene **4** to styrene **5b**. In contrast, 28% of silacyclopropane **6e** were present after the first half-life period of the reaction of **3** with electron-rich styrene **5e**. However, it has to be mentioned that the intermolecular, thermal insertion of a silylene into a C–H bond, the first step of pathway *a*, is not very likely in view of the fact that such processes are exceedingly rare.[1] An alternative mechanism *b* (Scheme 5) features the reaction with a second silylene at the stage of **7e** to yield **14e**. Ring opening and rearomatization eventually gives **11e**. The crucial requirement of this mechanistic pathway is a sufficiently long lifetime of intermediate **7e** so that the addition of highly reactive silylene **4** to the double bond of **7e** can compete successfully with the isomerization of **7e** to silaindane **8e**.

Table 1. Treatment of **3** with *para*-substituted styrenes: composition of the reaction mixture after the first half-life period

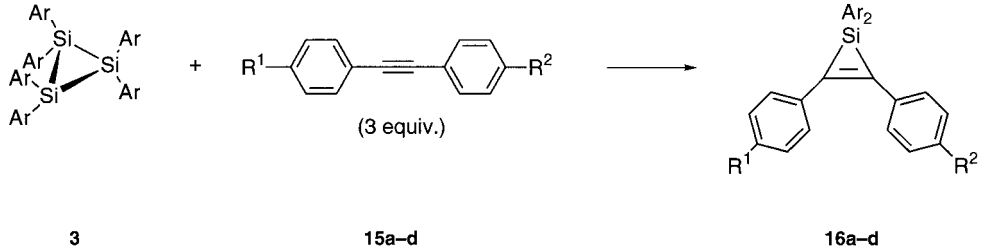
R	**3** (%)	**6** (%)	**8** (%)
H (**a**)	55	12	33
CO_2Me (**b**)	50	0	50
OCOMe (**c**)	55	19	20
Me (**d**)	49	21	26
OMe (**e**)[a]	49	28	2

[a] The mixture contains significant amounts of **11e**.

In contrast, reaction of cyclotrisilane **3** with 3 equiv. of tolane (**15a**) proceeds under clean formation of silacyclopropene **16a** (Scheme 6).[10b] Similar results were obtained using the *para*-substituted diphenylacetylenes **15b–d** as substrates: No matter, whether R was an electron-donating or withdrawing substituent, silacyclopropenes **16a–d** are formed exclusively. It is notable that no reaction occurred with the carbonyl bond of **16b** and **16c**, though the reaction of **3** with the C=O bond of ketones is well known.[13]

2.2. Kinetic and competition studies

The clean reaction of **3** with diarylacetylenes, in which the electron density of the C–C triple bond can be fine-tuned by introduction of electron-withdrawing or donating substituents in the *para* position of the aromatic ring, offers an excellent possibility to obtain more information on the



Scheme 6. Ar=2-$(Me_2NCH_2)C_6H_4$; **a**: R^1=R^2=H; **b**: R^1=CO_2Et, R^2=CO_2Me; **c**: R^1=H, R^2=CO_2Et; **d**: R^1=R^2=OMe.

Table 2. Product ratio of silacyclopropenes formed in the reaction of **3** with substituted diphenylacetylenes at 60°C

Competing diphenylacetylenes	$\sigma_p(R^1)+\sigma_p(R^2)$[a]	$\mathbf{16}_{R^1R^2}/\mathbf{16a}$
15b, **15a**	0.90	3/1
15c, **15a**	0.45	2/1
15d, **15a**	−0.54	1/3

[a] Hammett σ_p values for substituents R^1 and R^2 are taken from Ref. 14.

Table 3. Product ratio of silaindanes formed in the reaction of **3** with substituted styrenes at 60°C

Competing styrenes	σ_p[a]	$\mathbf{8}_R/\mathbf{8a}$
5b, **5a**	0.45	1/0
5d, **5a**	−0.17	9/1
5e, **5a**	−0.27	0/1

[a] Hammett σ_p values are taken from Ref. 14.

philicity of silylene **4** by means of a Hammett study. The competition experiments were performed in an NMR tube at 60°C containing a solution of **3** and an excess of a 1:1 mixture of the two respective diarylacetylenes in C_6D_6. The relative reactivity of the competing substrates towards silylene **4** can be deduced directly from the ^{1}H NMR spectroscopically determined product ratio, provided that the reactions obey a rate law of first order, i.e. an essentially constant alkyne ratio is maintained during the course of the reaction. Due to the limited solubility of the diarylacetylenes in C_6D_6 only 5 equiv. of each substrate, referring to **4**, could be used in these competition experiments However, a pseudo first order kinetics analysis appears to be justified since the product ratio at half-time of the reaction did not differ significantly from that determined after total consumption of starting material **3**.

Table 2 lists the ratios of the rate constants of the reaction of **4** with four different diarylacetylenes. As can be seen from Fig. 1, the logarithms of the relative rate constants correlate well (correlation coefficient: 0.997) with the sum of the σ_p values of the *para*-substituents.[14] The reaction constant ρ was calculated to be $+0.85\pm0.21$.[15] The positive sign of ρ indicates that the transition state of the cycloaddition reaction is stabilised by electron-withdrawing substituents and thus provides evidence for the nucleophilicity of silylene **4**. Moreover, the magnitude of $\rho=+0.85$ compares well with that of the reaction of cycloheptatrienylidene, a nucleophilic carbene, with styrenes ($\rho=+1.05\pm0.05$).[16]

In addition, we determined the consumption rate of **3** in its reactions with diarylacetylenes by monitoring the intensity

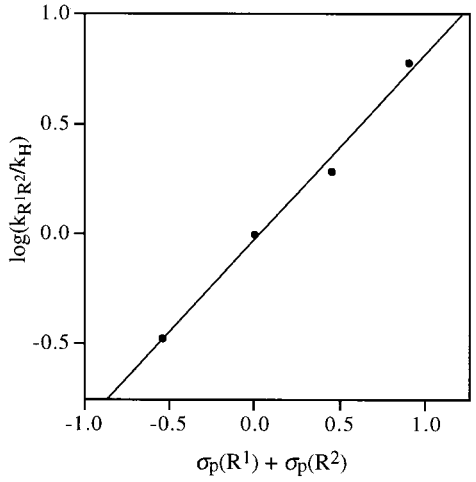


Figure 1. Plot of $\log(k_{R^1R^2}/k_H)$ of the reaction of **3** with **15a–d** at 60°C vs the sum of the substituent constants $\sigma_p(R^1)$ and $\sigma_p(R^2)$.

Table 4. Rate constants for the reaction of **3** with substituted styrenes and diphenylacetylenes at 60°C

Substrate	k (10^{-4} s^{-1})
15a	6.3
15b	6.3
15c	6.2
5a	6.3
5b	6.4
5c	6.7
5d	6.3
5e	6.1

of the ^{1}H NMR signal of the NMe_2 protons of the cyclotrisilane. All these reactions obey a rate law of first order in cylotrisilane and the observed rates are identical within the error margins for all diarylacetylenes (Table 4). This observation is in good agreement with the assumption that a cyclotrisilane–silylene equilibrium precedes the actual addition of the silylene to the triple bond and indicates that the release of silylenes **4** from cyclotrisilane **3** is the slowest and thus rate-determining step of the overall reaction. Moreover, the same decay rate of the cyclotrisilane was measured for the reactions of **3** with all styrenes (Table 4); i.e. the generation of silylenes from the cyclotrisilane again is the slowest step of the overall reaction sequence. In summary, the dissociation rate of **3** into three silylenes **4** was determined in these experiments to be $(6.3\pm0.4)\times10^{-4}$ s^{-1} at 60°C.

A competition study of the reaction of **3** with styrenes **5a–d** is of no use for determining the relative rate of the addition of silylene **4** to these styrenes because the formation of the silacyclopropanes **6a–d** from **4** and **5a–d** is a reversible process.[10a] Therefore, the product ratio determined at the end of this multi-step reaction, which leads eventually to the formation of stable silaindanes **8a–d** (Scheme 2), does not necessarily reflect the ratio of the rate constants of the addition of **4** to the styrenes under investigation, but instead may be controlled by the relative kinetic stabilities of the respective silacyclopropanes towards silylene extrusion and rearrangement to **7**. Orienting experiments indeed revealed unexpectedly high product ratios in these competition reactions (Table 3) and therefore were not used to calculate the ρ value of the cycloaddition reaction.

3. Experimental

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AM 250 (^{1}H NMR, 250 MHz; ^{13}C NMR, 62.9 MHz), a Bruker AMX 300 (^{1}H NMR: 300 MHz; ^{13}C NMR: 75.5 MHz) and a Varian VXR 500 (^{1}H NMR, 500 MHz;

^{13}C NMR, 125.7 MHz). C_q, CH, CH_2 and CH_3 were determined using the DEPT or APT pulse sequence. ^{29}Si NMR spectra were recorded on a Bruker AMX 300 (59.6 MHz) or a Varian XL 500 (99.3 MHz) using a refocused INEPT pulse sequence or performing a direct acquisition. Chemical shifts refer to $\delta_{TMS}=0.0$. Mass spectra were recorded on a Varian MAT 311 A. High resolution mass spectra were determined with a Varian MAT 311 A, using preselected ion peak matching at R~10 000 to be within ±2 ppm of the exact mass. FAB mass spectra were obtained by using an *ortho*-nitrophenyl octyl ether (NPOE) matrix. Elemental analyses were performed at Mikroanalytisches Labor der Georg-August-Universität Göttingen.

All manipulations of air and moisture sensitive compounds were carried out under an inert argon atmosphere using carefully dried glassware. Ethereal solvents, hexane and C_6D_6 used were dried by refluxing over sodium benzophenone ketyl and distilled immediately before use; $CDCl_3$ was dried using molecular sieve (4 Å).

3.1. 1,1-Bis[2′-(dimethylaminomethyl)phenyl]-6-methoxycarbonyl-1-silaindane (8b)

A solution of 500 mg (0.56 mmol) of **3** and 272 mg (1.67 mmol) of **5b** in 15 mL of toluene was stirred at 60°C. The ^1H NMR spectrum indicated the quantitative conversion of cyclotrisilane **3** into silaindane **8b** after 20 h. The solvent was removed in vacuo, 20 mL of Et_2O were added to the solid residue and the resulting suspension was filtered. The filtrate was concentrated in vacuo and 486 mg (63%) of **8b** were obtained on cooling to −15°C as colourless crystals (mp 131°C). Anal. Calcd for $C_{28}H_{34}N_2O_2Si$ (458.68): C, 73.32; H, 7.47. Found: C, 74.14; H, 7.80.[17] ^1H NMR (C_6D_6): δ=1.50 (t, ^3J=7 Hz, 2H, 2-H), 1.78 (s, 12H, NMe_2), 3.03–3.28 (m, 6H, CH_2N, 3-H), 3.51 (s, 3H, OMe), 7.00–7.30 (m, 6H, ar H), 7.84 (d, ^3J=7 Hz, 2H, ar H), 8.26 (dd, ^3J=8 Hz, ^4J=2 Hz, 2H, 5-H), 9.09 (s, 1H, 7-H). ^{13}C NMR (C_6D_6): δ=13.7 (C-2), 32.3 (C-3), 44.9 (NMe_2), 51.3 (OMe) 65.2 (CH_2N), 126.3 (ar CH), 127.1 (ar CH), 129.2 (ar CH), 129.4 (ar CH), 130.6 (ar CH), 136.0 (ar C_q), 136.6 (ar CH), 137.7 (ar CH), 140.4 (ar C_q), 145.7 (ar C_q), 159.9 (ar C_q), 167.5 (C=O). ^{29}Si NMR (C_6D_6): δ=+1.3. MS (EI), *m/z* (%): 458 (<1) [M^+], 398 (7) [M^+−COOMe−H], 324 (100) [M^+−Ar], 134 (6) [Ar^+]. $C_{28}H_{34}N_2O_2Si$ (458.2389): correct HRMS.

3.2. 6-Acetoxy-1,1-bis[2′-(dimethylaminomethyl)-phenyl]-1-silaindane (8c)

A solution of 507 mg (0.57 mmol) of **3** and 262 μL (1.71 mmol) of *p*-acetoxystyrene (**5c**) in 10 mL of toluene was stirred for 15 h at 50°C. According to the ^1H NMR spectrum, **3** was totally consumed after this period of time under formation of **8c** and minor amounts of other, unknown products. The solvent was removed in vacuo and the residue was suspended in 10 mL of Et_2O. The resulting suspension was filtered and concentrated in vacuo. Storing the solution at +3°C overnight yielded 269 mg (34%) of **8c** as colourless crystals (mp 76–79°C). Anal. Calcd for $C_{28}H_{34}N_2O_2Si$ (458.68): C, 73.32; H, 7.47. Found C, 74.56; H, 7.74.[17] ^1H NMR ($CDCl_3$): δ=1.56 (t, ^3J=7 Hz, 2H, 2-H), 1.79 (s, 12H, NMe_2), 2.26 (s, 3H, CH_3CO_2), 3.04–3.29 (m, 6H, CH_2N, 3-H), 6.98 (dd, ^3J=8 Hz, ^4J=2 Hz, 1H, 5-H), 7.09–7.40 (m, 7H, ar H), 7.44 (d, ^4J=2 Hz, 1H, 7-H), 7.60–7.73 (m, 2H, ar H). ^{13}C NMR ($CDCl_3$): δ=13.4 (C-2), 21.2 (CH_3CO_2) 31.1 (C-3), 45.0 (NMe_2), 64.7 (CH_2N), 122.0 (ar CH), 126.5 (ar CH), 126.8 (ar CH), 128.7 (ar CH), 128.9 (ar CH), 134.4 (ar C_q), 136.1 (ar CH), 141.5 (ar C_q), 145.2 (ar C_q), 148.5 (ar C_q), 151.3 (ar C_q), 169.7 (C=O). ^{29}Si NMR (C_6D_6): δ=+2.1. MS (EI), *m/z* (%): 458 (<1) [M^+], 433 (1) [M^+−CH_3], 414 (1) [M^+−NMe_2], 400 (4) [M^+−CH_2NMe_2], 324 (100) [M^+−Ar]. $C_{28}H_{34}N_2O_2Si$ (458.2389): correct HRMS.

3.3. 1,1-Bis[2′-(dimethylaminomethyl)phenyl]-6-methyl-1-silaindane (8d)

A solution of 500 mg (0.56 mmol) of **3** and 1.11 mL (8.43 mmol) of *p*-methylstyrene (**5d**) in 20 mL of toluene was stirred for 24 h at 60°C. According to the ^1H NMR spectrum **3** was totally consumed under formation of **8d** as major product, which was slightly contaminated by an impurity of unknown structure. The solvent was removed in vacuo and 10 mL of hexane were added. The suspension was filtered and the filtrate was concentrated in vacuo. On cooling to −30°C 172 mg (34%) of analytically pure **8d** were obtained as colourless crystals (mp 130–131°C). Anal. Calcd for $C_{27}H_{34}N_2Si$ (414.67): C, 78.21; H, 8.26; N, 6.76. Found C, 78.42; H, 8.33; N, 6.74. ^1H NMR ($CDCl_3$): δ=1.53 (t, ^3J=7 Hz, 2H, 2-H), 1.84 (s, 12H, NMe_2), 2.32 (s, 3H, Me), 3.17 (t, ^3J=7 Hz, 2H, 3-H), 3.20 (s, 4H, CH_2N), 7.10–7.40 (m, 8H, ar H), 7.59 (s, 1H, 7-H), 7.69 (d, ^3J=6 Hz, 2H, ar H). ^{13}C NMR ($CDCl_3$): δ=13.2 (C-2), 21.3 (Me), 31.2 (C-3), 45.1 (NMe_2), 64.8 (CH_2N), 125.7 (ar CH), 126.4 (ar CH), 128.6 (ar CH), 128.9 (ar CH), 130.0 (ar CH), 134.2 (ar C_q), 135.1 (ar CH), 136.1 (ar CH), 136.1 (ar C_q), 139.1 (ar C_q), 145.3 (ar C_q), 151.5 (ar C_q). ^{29}Si NMR ($CDCl_3$): δ=+1.9. MS (EI), *m/z* (%): 414 (1) [M^+], 356 (5) [M^+−CH_2NMe_2], 280 (100) [M^+−Ar], 134 (4) [Ar^+], 58 (9) [$CH_2NMe_2^+$].

3.4. Reaction of 3 with 3 equiv. of 5d

A solution of 50 mg (56 μmol) of **3** and 22 μL (0.17 mmol) of *p*-methylstyrene (**5d**) in 0.4 mL of C_6D_6 was heated for 4 h at 75°C. According to the ^1H NMR spectrum **3** was totally consumed under formation of a 9:1 mixture of **8d** and 1,1-bis[2′-(dimethylaminomethyl)phenyl]-3-{bis[2″-(dimethylaminomethyl)phenyl]silyl}-6-methyl-1-silaindane (**11d**). The tentative assignment of the proton signals of **11d**, which is based on the ^1H NMR data of **11e** (vide infra), is incomplete due to severe overlap of the signals of **8d** and **11d**. ^1H NMR (C_6D_6): δ=1.67 (s, 6H, NMe_2), 1.85 (s, 6H, NMe_2), 1.87 (s, 6H, NMe_2), 2.05 (s, 6H, NMe_2), 3.87 (m, 1H, 3-H), 5.30 (d, ^3J not determined, 1H, SiH), 8.20 (m, 1H, ar H).

3.4.1. 1,1-Bis[2′-(dimethylaminomethyl)phenyl]-6-methoxy-1-silaindane (8e). A solution of 200 mg (0.22 mmol) of **3** and 0.90 mL (6.8 mmol) of *p*-methoxystyrene (**5e**) in 5 mL of toluene was stirred for 18 h at 60°C. According to the ^1H NMR spectrum **3** was totally consumed under formation of a 5:1 mixture of **8e** and **11e**. The solvent was removed in vacuo and the residue was further purified by column chromatography on silica gel (solvent: hexane/NEt_3

95:5; R_f (**8e**)=0.31; 205 mg (71%)). Recrystallization from pentane at −30°C gave 161 mg (56%) of **8e** as colourless crystals (mp 122–125°C). Anal. Calcd for $C_{27}H_{34}N_2OSi$ (430.66): C, 75.30; H, 7.96. Found C, 76.21; H, 8.40.[17] ^{1}H NMR (C_6D_6): δ=1.59 (t, ^3J=7 Hz, 2H, 2-H), 1.75 (s, 12H, NMe_2), 3.18 (s, 4H, CH_2N), 3.23 (t, ^3J=7 Hz, 2H, 3-H), 3.47 (s, 3H, OMe), 6.98 (dd, ^3J=8 Hz, ^4J=3 Hz, 1H, ar H), 7.04–7.32 (m, 7H, ar H), 7.72 (d, ^4J=3 Hz, 1H, 7-H), 7.89 (dd, ^3J=7 Hz, ^4J=2 Hz, 2H, ar H). ^{13}C NMR ($CDCl_3$): δ=13.5 (C-2), 30.7 (C-3), 45.1 (NMe_2), 55.3 (OMe), 64.7 (CH_2N), 115.6 (ar CH), 118.8 (ar CH), 126.4 (ar CH), 126.6 (ar CH), 128.6 (ar CH), 128.9 (ar CH), 135.9 (ar C_q), 136.1 (ar CH), 140.8 (ar C_q), 145.2 (ar C_q), 146.1 (ar C_q), 157.4 (C-6). ^{29}Si NMR (C_6D_6): δ=+2.9. MS (EI), *m/z* (%): 430 (2) [M^+], 472 (3) [$M^+-CH_2NMe_2$], 296 (100) [Ar_2Si^+], 134 (4) [Ar^+]. $C_{27}H_{34}N_2OSi$ (430.2440): correct HRMS.

When a solution of 300 mg (0.34 mmol) of **3** and 135 μL (1.01 mmol) of **5e** in 8 mL of toluene was heated for 20 h at 60°C, the ^{1}H NMR spectrum showed the complete conversion of **3** into a 1:2 mixture of **8e** and **11e**.

3.4.2. 1,1-Bis[2′-(dimethylaminomethyl)phenyl]-3-{bis[2″-(dimethylaminomethyl)phenyl]silyl}-6-methoxy-1-silaindane(11e). A solution of 516 mg (0.58 mmol) of **3** and 116 μL (0.87 mmol) of *p*-methoxystyrene in 10 mL of toluene was stirred for 15 h at 50°C. According to the ^{1}H NMR spectrum **3** was totally consumed under formation of a 4:1 mixture of **11e** and **8e**. The solvent was removed in vacuo and 10 mL of hexane were added to the residue. The resulting suspension was filtered, the solvent was removed in vacuo and 165 mg (26%) of analytically pure **11e** were obtained in form of colourless crystals (mp 120–122°C) by recrystallization of the residue from 10 mL of Et_2O at −30°C. Anal. Calcd for $C_{45}H_{58}N_4OSi_2$ (727.15): C, 74.33; H 8.04. Found C, 74.42; H 8.20. ^{1}H NMR (C_6D_6, additional ^{1}H, ^{1}H-COSY, 300 MHz): δ=1.66 (s, 6H, NMe_2), 1.84 (s, 6H, NMe_2), 1.86 (s, 6H, NMe_2), 1.88 (m, 1H, 2-H), 2.02 (s, 6H, NMe_2), 2.03 (m, 1H, 2-H), 3.04–3.50 (m, 8H, CH_2N), 3.40 (s, 3H, OMe), 3.70–3.90 (m, 1H, 3-H), 5.32 (d, ^3J=4 Hz (dd, $^1J_{SiH}$=209 Hz), 1H, SiH), 6.78 (dd, ^3J=8 Hz, ^4J=3 Hz, 1H, ar H), 6.90–7.50 (m, 13H, ar H), 7.63 (d, ^3J=6 Hz, 1H, ar H), 7.70–7.90 (m, 3H, ar H), 8.12–8.30 (m, 1H, ar H). ^{13}C NMR ($CDCl_3$): δ=16.2 (s (d, $^1J_{SiC}$= 59 Hz), C-2), 29.2 (s (d, $^1J_{SiC}$=52 Hz), C-3), 44.7 (NMe_2), 44.9 (NMe_2), 45.0 (NMe_2), 45.1 (NMe_2), 55.3 (OMe), 64.2 (CH_2N), 64.3 (CH_2N), 64.5 (CH_2N), 64.8 (CH_2N), 115.5 (ar CH), 118.9 (ar CH), 125.7 (ar CH), 126.1 (ar CH), 126.4 (ar CH), 126.7 (ar CH), 128.1 (ar CH), 128.2 (ar CH), 128.3 (ar CH), 128.5 (ar CH), 128.6 (ar CH), 128.7 (ar CH), 128.8 (ar CH), 128.9 (ar CH), 134.5 (ar C_q), 135.6 (ar CH), 135.7 (ar C_q), 136.1 (ar C_q), 136.3 (ar CH), 136.4 (ar C_q), 137.1 (ar CH), 137.4 (ar CH), 140.6 (ar C_q), 144.8 (ar C_q), 145.0 (ar C_q), 145.5 (ar C_q), 145.8 (ar C_q), 148.8 (ar C_q), 156.7 (C-6). ^{29}Si NMR (C_6D_6): δ=+2.2 (Si-1), −22.2 (d, $^1J_{SiH}$=209 Hz, $HSiAr_2$). MS (EI), *m/z* (%): 725 (<1) [M^+-H], 682 (<1) [M^+-NMe_2], 592 (3) [M^+-Ar], 429 (<1) [$M^+-HSiAr_2$], 297 (100) [$HSiAr_2^+$].

3.5. Treatment of silaindane 8e with cyclotrisilane 3

A solution of 87 mg (0.20 mmol) of **8e** and 60 mg (0.067 mmol) of **3** in 0.4 mL of C_6D_6 was heated for 24 h at 65°C. The ^{1}H NMR spectroscopic analysis of the reaction mixture showed unchanged **8e** as main component besides small amounts of unidentified products. Neither starting material **3** nor silaindane **11e** could be detected.

3.5.1. 1,1-Bis[2′-(dimethylaminomethyl)phenyl]-2-(4″-ethyloxycarbonyl)phenyl-3-(4‴-methyloxycarbonyl)-phenyl-1-silacyclopropene (16b). A solution of 53 mg (0.06 mmol) of **3** and 55 mg (0.18 mmol) of **15b** in 0.4 mL of C_6D_6 was heated for 4 h at 60°C. The solvent was removed in vacuo and 108 mg (100%) of **16b** were obtained as a yellow solid (mp 57–58°C). ^{1}H NMR (C_6D_6): δ=1.03 (t, ^3J=7 Hz, 3H, CH_2CH_3), 1.87 (s, 12H, NMe_2), 3.29 (s, 4H, CH_2N), 3.51 (s, 3H, CO_2CH_3), 4.14 (q, ^3J=7 Hz, 2H, OCH_2), 7.00–7.40 (m, 6H, ar H), 7.55, 8.15 (AX system, ^3J=8 Hz, 8H, ar H), 7.89 (d, ^3J=7 Hz, 2H, ar H). ^{13}C NMR (C_6D_6): δ=14.3 (CH_2CH_3), 45.4 (NMe_2), 51.5 (CO_2CH_3), 60.6 (OCH_2), 63.9 (CH_2N), 127.1 (ar CH), 127.5 (ar CH), 127.6 (ar CH), 127.7 (ar C_q), 128.5 (ar C_q), 128.9 (ar C_q), 129.5 (ar CH), 130.2 (ar CH), 136.2 (ar CH), 137.2 (ar C_q), 144.1 (ar C_q), 144.2 (ar C_q), 166.2 (C═C), 166.6 (C═C), 168.0 (br s, 2×C═O). ^{29}Si NMR (C_6D_6): δ=−107.9. MS (EI), *m/z* (%): 604 (13) [M^+], 560 (18) [M^+-NMe_2], 559 (23) [M^+-NMe_2-H], 546 (20) [$M^+-CH_2Me_2$], 295 (100) [$M^+-H_{16}C_{18}O_4-H$], 279 (56) [$M^+-Ar-C_2H_5$].

3.5.2. 1,1-Bis[2′-(dimethylaminomethyl)phenyl]-2-[(4″-ethyloxycarbonyl)phenyl]-3-phenyl-1-silacyclopropene (16c). A solution of 100 mg (0.11 mmol) of **3** and 84 mg (0.34 mmol) of **15c** in 0.4 mL of C_6D_6 was heated for 3.5 h at 70°C. The solvent was removed in vacuo leaving behind 184 mg (100%) of **16c** as a yellowish, ^{1}H NMR spectroscopically pure oil. ^{1}H NMR (C_6D_6): δ=1.01 (t, ^3J=7 Hz, 3H, CH_2CH_3), 1.87 (s, 12H, NMe_2), 3.25, 3.32 (AB system, ^2J=14 Hz, 4H, CH_2N), 4.13 (q, ^3J=7 Hz, 2H, OCH_2), 7.00–7.30 (m, 9H, ar H), 7.60, 8.20 (AX system, ^3J=8 Hz, 4H, ar H), 7.68 (dd, ^3J=7 Hz, ^4J=1 Hz, 2H, ar H), 7.96 (d, ^3J=7 Hz, 2H, ar H). ^{13}C NMR (C_6D_6): δ=14.3 (CH_3), 45.3 (NMe_2), 60.5 (CH_2O), 63.9 (CH_2N), 127.0 (ar CH), 127.1 (ar CH), 127.4 (ar CH), 127.5 (ar CH), 128.4 (ar C_q), 2×128.6 (ar CH), 129.3 (ar CH), 130.1 (ar CH), 136.3 (ar CH), 137.4 (ar C_q), 138.5 (ar C_q), 144.2 (ar C_q), 145.3 (ar C_q), 164.4 (br s, C-3), 166.2 (C═O), 177.0 (br. s, C-2). ^{29}Si NMR (C_6D_6): δ=−107.9. MS (FAB, positive mode), *m/z* (%): 569 (100) [$M^+ + H_2O + H$], 551 (54) [$M^+ + H$].

3.5.3. 1,1-Bis[2′-(dimethylaminomethyl)phenyl]-2,3-bis-(4″-methoxyphenyl)-1-silacyclopropene (16d). A solution of 65 mg (0.07 mmol) of **3** and 52 mg (0.21 mmol) of **15d** in 0.4 mL of C_6D_6 was heated for 4 h at 75°C. The solvent was removed in vacuo and 117 mg (100%) of **16d** were obtained as a yellowish, ^{1}H NMR spectroscopically pure oil. ^{1}H NMR (C_6D_6): δ=1.95 (s, 12H, NMe_2), 3.33 (s, 6H, OMe), 3.35 (s, 4H, CH_2N), 6.84, 7.77 (AX system, ^3J=9 Hz, 8H, ar H), 7.10–7.22 (m, 6H, ar H), 8.07 (d, ^3J=7 Hz, 2H, ar H). ^{13}C NMR (C_6D_6): δ=45.4 (NMe_2), 54.8 (OMe), 64.1 (CH_2N), 114.1 (ar CH), 126.9 (ar CH), 127.6 (ar CH), 129.1 (ar CH), 130.1 (ar CH), 131.9 (ar C_q), 136.6 (ar CH), 137.9 (ar C_q), 144.6 (ar C_q), 159.0 (ar C_q), 161.1 (C═C). ^{29}Si NMR (C_6D_6): δ=−107.0. MS (FAB, positive mode), *m/z* (%): 553 (100) [$M^+ + H_2O + H$], 535 (68) [$M^+ + H$].

3.6. Competition experiments of diarylacetylenes with 3

A solution of 10 mg (11 μmol) of **3**, 15 equiv. of diphenylacetylene and 15 equiv. of the respective *para*-substituted diphenylacetylene in 0.4 mL of C_6D_6 was heated for 4 h at 60°C; 13 mg (15 μmol) of **3** were used for the competition experiment with **15a** and **15d**. The ratio of the formed silacyclopropenes (see Table 2) was determined by means of ^{1}H NMR spectroscopy.

3.7. Competition experiments of styrenes with 3

A solution of 25 mg (28 μmol) of **3**, 24 equiv. of styrene and 24 equiv. of the respective substituted styrene in 0.4 mL of C_6D_6 was heated for 4 h to 60 C; 27 equiv. of each styrene were used for the competition experiment with **5a** and **5b**. The ratio of the formed silaindanes (see Table 3) was determined by means of ^{1}H NMR spectroscopy.

3.8. General procedure for the determination of the decomposition rate of 3 at 333 K in the presence of substituted styrenes and diphenylacetylenes

A stock solution of **3** with c_o=1.12 mol/L in C_6D_6 was prepared by dissolving 500 mg (5.62 mmol) of **3** in approximately 5 mL of C_6D_6 (overall volume: 5.00 mL). Approximately 30 mg of polydimethylsiloxane (PMS) were added as internal integration standard.

For the individual experiment 500 μL of the standard solution were transferred into an NMR tube and 0.169 mmol (3 equiv.) of the respective styrene or acetylene were added at 0°C. The samples were introduced into the NMR probe which was pre-heated to 60°C. After an equilibration period of 4 min ^{1}H NMR spectra were recorded in intervals of 2 to 5 min. The concentration of **3** in the reaction mixture was obtained by determining the intensity of the singlet of the NMe_2 groups of **3** relative to that of the singlet at δ=0.27 of the integration standard PMS. All reactions showed a linear concentration-time relationship. The rate constants (see Table 4) were obtained by a first order kinetic analysis.

In addition, the composition of the reaction mixtures after the first half-life period was determined from these runs by means of ^{1}H NMR spectroscopy (Table 2).

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