Small Rings, 93[‡]

1,2,3,4-Tetra-*tert*-butyl-4-trimethylsilyl-4-sila-2-cyclobuten-1-yl: A Quantum Mechanical and ESR Study

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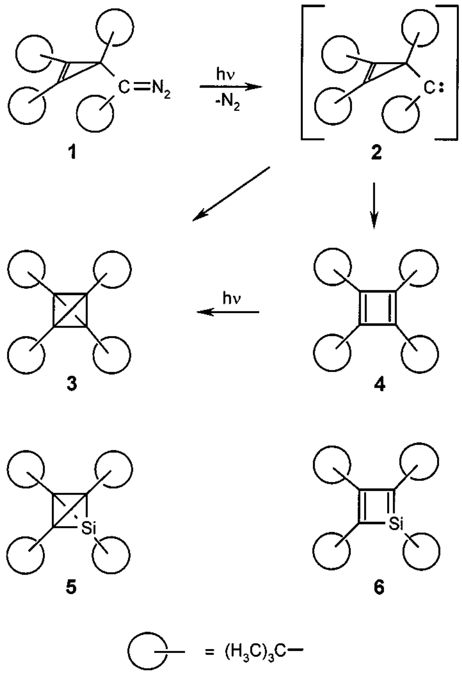
Trisilane **7** has been synthesized as a potential photochemical precursor of tetra-*tert*-butylsilatetrahedrane (**5**) and/or tetra-*tert*-butylsilacyclobutadiene (**6**). Astonishingly, only one Si,Si bond is broken upon irradiation of **7** and the silacyclobutenyl radical **9** can be identified as the reaction product. The structure of radical **9**, which in the absence of oxygen is persistent even at room temperature, has been elucidated by comparison of its experimental and calculated ESR spectra.

Introduction

In a previous report on the synthesis and properties of tetra-*tert*-butyltetrahedrane (**3**) and tetra-*tert*-butylcyclobutadiene (**4**),[1] the corresponding sila derivatives **5** and **6** were envisaged as worthwhile goals for forthcoming studies. The methodology for their preparation stems from experience gained in synthesizing **3** and **4**, which was achieved starting from the cyclopropenyldiazomethane **1**.[2] Photochemical nitrogen elimination from **1** leads to carbene **2**. This intermediate cannot be detected since it undergoes rapid ring-expansion to cyclobutadiene **4** or is directly converted to tetrahedrane **3** through a cheletropic cycloaddition of the carbenic center to the double bond of the three-membered ring.[2] Another route to **3** involves cross-addition of the double bonds in **4** upon photochemical excitation.[1]

This cyclopropenylcarbinyl route, which has hitherto been successfully exploited in the synthesis of several other alkyl-,[3] silyl-,[4] and germyl-substituted[5] analogs of **3** and **4**, was also envisaged as being feasible with one carbon in the ring skeleton replaced by a silicon atom. Thus, we initiated a project directed towards the preparation of **5** and **6**.[6]

According to calculations (B3LYP/6-31G*) on the C_3H_4Si energy hypersurface,[7,8] the parent silacyclobutadiene, cyclopropenylsilylene, and silatetrahedrane are 47.8, 54.7, and 71.2 kcal mol^{-1}, respectively, higher in energy than the global minimum, 2-methyl-1-silacyclopropenylidene. This order of relative energies is in agreement with calculations carried out previously by Gordon et al.[9]



Neither silatetrahedrane nor silacyclobutadiene could be isolated in a matrix at 10 K.[8] This encouraged us to look for the kinetically stabilized derivatives **5** and **6**.[10]

Synthesis of the Persistent Radical 9

In the silicon series, it is not possible to start from a diazo compound akin to **1**. If one wants to generate silylene **10**, it is adequate to start with trisilane **7**.[6] Irradiation of **7** in cyclohexane at room temperature at a wavelength of 254 nm generates a yellow solution showing an absorption maximum at $\lambda_{max} = 476$ nm. At first, we believed that the compound responsible for the yellow color might be silylene **10**. However, it turned out that the absorption maximum is in fact due to silacyclobutenyl radical **9**. The structure of **9** was established on the basis of its ESR spectrum (see below) and the results of trapping experiments. Radical **9** is

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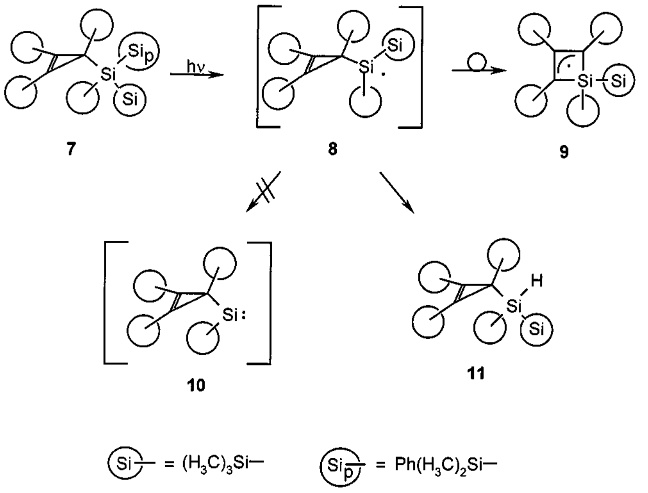
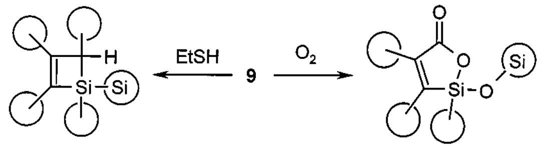
persistent provided that no oxygen is present. Even after two years the ESR spectrum of the yellow solution of **9** could still be measured.



Exposure to oxygen results in immediate quenching of the yellow color of a solution of **9** and lactone **13** can be isolated as the reaction product. A much better structural proof than the transformation of **9** into **13** is the more straightforward reaction of **9** with ethanethiol. This reagent transfers a hydrogen atom to **9** and one diastereomer of cyclobutene **12** can be isolated.



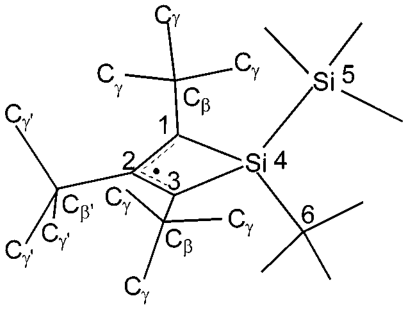
How is radical **9** formed? Clearly, irradiation of **7** does not initiate an extrusion yielding silylene **10** and finally **5** or **6**.[10] Instead, a homolytic cleavage of the Si–SiMe$_2$Ph bond occurs.[11] The initially formed radical **8** then rearranges to the more stable cyclobutenyl radical **9**.

Direct experimental proof may be obtained for the intermediacy of monoradical **8**. Thus, when the irradiation of trisilane **7** is carried out on a preparative scale, the main reaction product is disilane **11**, which can be isolated in 62% yield together with 9% of lactone **13**. The cyclopropyl derivative **11** has to be regarded as the product of a combination of **8** with a hydrogen atom, which is split off from the solvent or from a *tert*-butyl group of one of the dissolved molecules.

The observation of **9** is consistent with the results of Fink et al.,[10c] who detected triplet diradicals similar to monoradical **9** as intermediates during the dimerization of aryl tri-*tert*-butylsilacyclobutadienes.

Structure of Radical 9

In order to gain further insight into the structure of radical **9**, we performed quantum mechanical calculations. The geometry was optimized using the semiempirical AM1[12] and ab initio UHF/3-21G* methods without any symmetry restrictions. Both calculations led to a comparable geometry, in good accord with the C_s symmetry of **9**. Averaged values of bond lengths, bond angles, and dihedral angles are compared in Figure 1. In view of the good agreement, we will limit the description of the geometry of **9** to the data obtained using the UHF/3-21G* procedure. The C(1)–C(2) and C(2)–C(3) distances of 1.456 Å are typical for a delocalized π system. All carbon–silicon bond lengths are similar and are analogous to those calculated for the closed-shell silacyclobutane (1.931 Å).[13] The same holds for the Si(4)–Si(5) distance of 2.387 Å. Typical Si–Si bond lengths lie between 2.33 and 2.39 Å.[14] The C(1)–C(2)–C(3) bond angle of ca. 103° illustrates the bending of the three allylic π centres. As a consequence, the C(1)–Si(4)–C(3) angle at the Si corner of the silacyclobutane measures 74.5°. The central silacyclobutane moiety is only marginally displaced from a planar arrangement. The Si(4) atom is bent out of the C(1)–C(2)–C(3) plane [towards C(6)] by 8.1°.



	AM1	UHF/3-21G*
C(1)–C(2)	1.429 Å	1.456 Å
Si(4)–C(1)	1.883 Å	1.886 Å
Si(4)–C(6)	1.846 Å	1.925 Å
Si(4)–Si(5)	2.508 Å	2.387 Å
C(1)C(2)C(3)	103.4°	103.2°
C(1)Si(4)C(3)	73.1°	74.5°
C(6)Si(4)Si(5)	115.4°	111.9°
C(1)C(2)C(3)Si(4)	9.6°	8.1°

Figure 1. Geometrical parameters of **9**

The SOMO of **9** closely resembles that of the allyl radical. Based on the above geometries, the hyperfine coupling constants (hfc) were determined by single-point density functional theory calculations[15–18] at the unrestricted level of theory using the B3LYP functional[19] (Table 1).

ESR Spectrum of Radical 9

A very good agreement between the experimental and simulated ESR spectra was achieved when the ESR signals were attributed to a superposition of five spectral components (Figure 2). The most intense component is a central 19-line pattern indicative of an interaction between the unpaired electron and 18 equivalent protons with a ^1H hyperfine coupling constant of 0.037 mT. Thus, this coupling constant can be assigned to the 18 equivalent γ protons of the *tert*-butyl groups at C(1) and C(3). This assignment is in very good accord with the calculated values (Table 1). The outermost components have the same line pattern as the central signal with a relative intensity of ca. 2.2%. This corresponds to hyperfine coupling with a ^{13}C nucleus (m_s = 1/2; hfc = 2.560 mT) present in two equivalent positions of **9** (the natural abundance of ^{13}C is 1.1%). The simulation for the next doublet, which is spaced by 1.495 mT and is ca. twice as intense as the outermost lines, reveals a 4.7% intensity relative to the central feature and matches the natural abundance of the ^{29}Si nucleus (4.7%). The main problem was the analysis of the doublet of satellite lines seen closest to the central multiplet. Two possibilities were considered: (i) coupling with one type of nucleus (*either* ^{29}Si *or* ^{13}C) or (ii) interaction with two nuclei, ^{29}Si *and* ^{13}C, leading to overlapping satellite lines. No satisfactory agreement could be obtained when only one ^{29}Si [Si(5)] nucleus or six equivalent ^{13}C nuclei (Cγ) were taken into account. The best fit was achieved for two components with rather similar ^{13}C hfcs: one with a ^{13}C hfc of 0.692 mT stemming from the interaction with six equivalent nuclei (6.6%) and one with a ^{13}C hfc of 0.656 mT (2.2%). Although the 3:1 intensity ratio of these two components has to be utilized for a successful simulation, a 5% shift in the ^{13}C hfcs does not significantly alter the correlation between the experimental and simulated spectra.

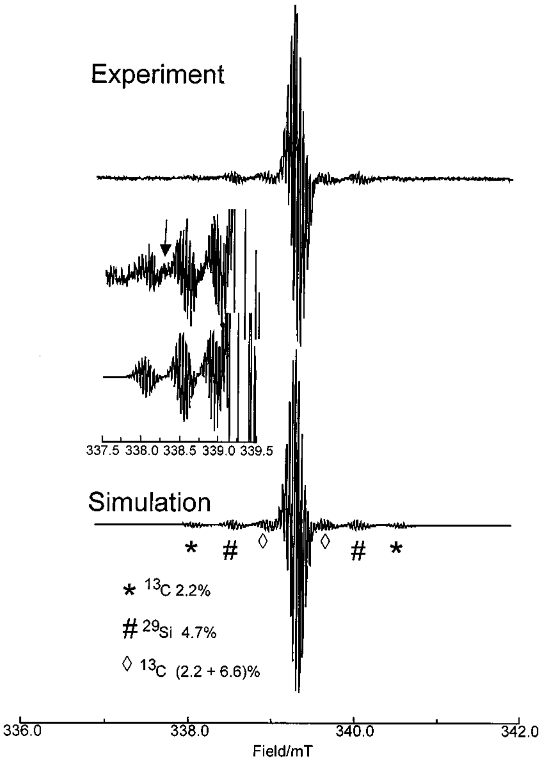


Figure 2. Experimental and simulated (WINSIM) ESR spectra of **9**; the inset shows the satellite lines in the flanks of the main central signal on an expanded scale; the numbers below the simulated spectrum indicate the relative percentages of satellite lines with respect to the whole integrated spectrum; the arrow in the inset indicates the position at which a signal attributable to hyperfine coupling with C(2) could be present

The inset in Figure 2 shows that an additional low-intensity ESR line may be present between the two outermost satellite lines. This would be consistent with the ^{13}C hfc calculated for C(2) (Table 1). However, because of the low intensity of this line (one ^{13}C nucleus, i.e. 1.1%), an unambiguous simulation is not possible.

The hyperfine data derived from the experimental ESR spectrum are in satisfying accord with the calculated data (Table 1). The assignment of the ^{1}H hfc of 0.037 mT to the 18 equivalent H$_{\gamma}$ is as straightforward as that of the prominent ^{13}C hfc of 2.56 mT to the equivalent C(1) and C(3) nuclei of the allylic moiety. A similar ^{1}H hfc of 0.027 mT has previously been found for the radical cation of cyclobutadiene **4**.[20] The predicted ^{29}Si hfc value for Si(4) in **9** of –1.299 mT (–1.194 mT; here, the values based on the ab initio geometry given in the text are followed by those based on AM1 geometry in parentheses) is closely matched by the corresponding experimental value of 1.495 mT.

Even the close similarity between the ^{13}C hfcs of six and two equivalent nuclei is convincingly accounted for by the calculations. The ^{13}C hfc of the two equivalent C$_{\beta}$ nuclei is predicted to be –0.656 mT (–0.630 mT) and that of the six equivalent C$_{\gamma}$ +0.661 mT (+0.798 mT); this is mirrored by experimental values of 0.656 and 0.692 mT, respectively. The opposite signs of the latter two ^{13}C hfcs imply two different paradigms of spin delocalization. Whereas the spin transfer to C$_{\beta}$ proceeds through spin polarization,[21] thus leading to an excess of β spin (negative coupling constant), the spin population detected at C$_{\gamma}$ is transferred by C,C hyperconjugation inducing an excess of α spin.

Application of the ENDOR technique[22] revealed a pair of broad peaks corresponding to the ^{1}H hfc of 0.037 mT and presumably some smaller ^{1}H hfcs not resolved in the ESR signal. Attempts to determine the hfcs stemming from the ^{13}C and ^{29}Si nuclei by ENDOR were unsuccessful. All the remaining calculated hfcs irrelevant for a clear-cut identification are included in Table 1.

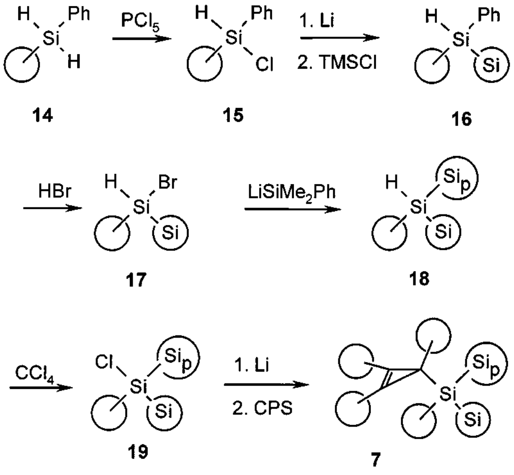
Synthesis of Precursor 7

Starting from *tert*-butylphenylsilane **14**,[23,24] precursor **7** was synthesized as outlined in Scheme 1. Chlorination of **14** was performed using PCl$_5$ in CCl$_4$.[24] Treatment of chlorosilane **15** with lithium in THF and subsequent addition of trimethylchlorosilane to the resulting silyl anion yielded disilane **16**.[24] In order to remove the phenyl group, **16** was stirred with liquid HBr at –78 °C. Trisilane **18** could be obtained by reaction of **17** with the dimethylphenylsilyl anion, which was prepared from chlorodimethylphenylsilane and lithium. Transformation of **18** into **19** was readily achieved by stirring in CCl$_4$ at 50 °C for 20 h. Finally, the cyclopropenyl substituent was introduced by treating chlorotrisilane **19** with lithium and adding the thus generated anion solution to a suspension of tri-*tert*-butylcyclopropenylium tetrafluoroborate in THF in a dropwise fashion. The product was purified by preparative TLC and recrystallization.

Table 1. Calculated and experimental hyperfine coupling constants (hfcs) attributed to **9**

Nucleus	Calcd. hfcs [mT] UB3LYP/6-31G*//UHF/3-21G*	Calcd. hfcs [mT] UB3LYP/6-31G*//AM1	Experimental hfcs [mT][a]
C(1), C(3)	+3.258	+2.961	2.560
Si(4)	−1.299	−1.194	1.495
C_{γ}	+0.661[b]	+0.798[b]	0.692
C_{β}	−0.656	−0.630	0.656
H_{γ}	+0.038[b]	+0.047[b]	0.037
C(2)	−1.851	−1.601	
$C_{\beta'}$	+0.154	+0.134	
C–Si(4)	+0.099	+0.048	
$C_{\gamma'}$	−0.164	−0.156	
$(C\mathrm{H}_3)_3\mathrm{C{-}Si(4)}$	+0.003	−0.006	
$(C\mathrm{H}_3)_3\mathrm{Si{-}Si(4)}$	+0.009	+0.015	
Si(5)	−0.026	−0.022	
$H_{\gamma'}$	+0.004[b]	−0.007[b]	
$(\mathrm{C}H_3)_3\mathrm{C{-}Si(4)}$	+0.014[b]	+0.001[b]	
$(\mathrm{C}H_3)_3\mathrm{Si{-}Si(4)}$	+0.002[b]	+0.004[b]	

[a] Determined by simulation (WINSIM). – [b] Values averaged over all rotationally different protons or ^{13}C nuclei.



CPS = Tri-*tert*-butylcyclopropenylium tetrafluoroborate

Scheme 1. Synthesis of trisilane **7** starting from monosilane **14**

Conclusions

The structure of radical **9** follows from the reaction with ethanethiol, which generates the silacyclobutene **12**. This is further supported by computational analysis of the ESR spectrum of the radical. In contrast to the parent cyclobutenyl/bicyclobut-2-yl radical, where the monocyclic structure is preferred to the 1,3-bridged bicyclic form,[25] the "corset effect" caused by the bulky groups should favor the spherical bicyclic isomer of **9**. Nevertheless, the calculated geometry of **9** is almost planar, in contrast to the related *tert*-butylated cyclobutenylium cations, in which the folding of the ring is much more marked.[26] The allyl-type radical **9** profits from 1,3-bridging to a lesser extent than would a comparable cation, but is stabilized by the Si centre.[27] Moreover, the voluminous *tert*-butyl and trimethylsilyl substituents impart a high kinetic stability to **9**.

Experimental Section

General: All reactions were carried out under dry argon. Solvents were dried using standard techniques. All glassware was thoroughly oven-dried at 130 °C prior to use. – NMR: Bruker AM 400 or AC 200. – IR: Bruker IFS 25. – MS: Varian MAT 111 or Varian MAT 311 A. – A Carlo–Erba Fractovap 2900 gas chromatograph with flame ionization detector and a 10 m × 0.3 mm column coated with silicon phase OV 101 was used for analytical gas chromatography. – Preparative thin-layer chromatography was performed on plates (20 × 20 cm) coated with silica gel or aluminum oxide (60 PF_{254}, Merck).

ESR Experiment: A degassed solution of **7** (0.2 mg, 0.4 µmol) in *n*-hexane (1 mL) ($4\cdot10^{-4}$ mol L^{-1}) was sealed in an ESR sample tube and irradiated for 5 min at a wavelength of 254 nm. ESR spectra were recorded on a Varian E9 or a Bruker ESP 300 spectrometer. The latter instrument was also used for ENDOR measurements.

The ESR spectral simulations were performed using the freeware program WINSIM.[28]

***tert*-Butylchlorophenylsilane (15):** A solution of *tert*-butylphenylsilane (**14**) (26 g, 0.158 mol) in CCl_4 (20 mL) was added dropwise to a suspension of PCl_5 (34 g, 0.163 mol) in CCl_4 (150 mL) at 0 °C. After stirring for 2 h at room temperature, the solvent was evaporated in vacuo. In order to remove the salts, the residue was taken-up in petroleum ether and this solution was filtered under argon atmosphere. Distillation of the filtrate using a Vigreux column (93–95 °C/15 Torr) yielded 23.9 g (76%) of a colorless liquid. – IR (film): $\tilde{\nu}$ = 2960 cm^{-1} (CH), 2160 (SiH), 1460 (*t*Bu), 1360 (*t*Bu), 1120, 830, 820, 740, 700. – ^{1}H NMR ($CDCl_3$): δ = 1.02 (s, 9 H, *t*Bu), 4.96 (s, 1 H, SiH), 7.3–7.8 (m, 5 H, Ph). – ^{13}C NMR ($CDCl_3$): δ = 19.4 [Si*C*(CH_3)$_3$], 25.3 [C(*C*H_3)$_3$], 128.0/130.8/131.4/134.4 (Ph). – MS (70 eV); *m*/*z* (%): 198 (98) [M^+], 183 (4), 155 (43), 141 (100), 120 (12), 105 (51). – HRMS: calcd. for $C_{10}H_{15}SiCl$ (M^+) 198.0632; found 198.0684.

1-*tert*-Butyl-2,2,2-trimethyl-1-phenyldisilane (16): At room temperature, a solution of **15** (30 g, 0.15 mol) in THF (40 mL) was added to lithium (5.0 g, 0.72 mol) in THF (350 mL) over a period of 1 h. In order to ensure complete formation of the silyl anion, the mixture was stirred for a further 10 h. The resulting brown solution was then added to chlorotrimethylsilane (19 g, 0.175 mol) in THF

(80 mL) over a period of 3 h at 0 °C. After stirring for a further 2 h, the mixture was subjected to aqueous work-up. Removal of the solvent and vacuum distillation (Vigreux column; 73–75 °C/1 Torr) yielded 27.5 g (80%) of **16**. – IR (film): ṽ = 2960 cm^{-1} (CH), 2080 (SiH), 1250, 835, 765, 715, 700. – ^1H NMR ($CDCl_3$): δ = 0.13 (s, 9 H, $SiMe_3$), 0.98 (s, 9 H, *t*Bu), 3.91 (s, 1 H, SiH), 7.23–7.56 (m, 5 H, Ph). – ^{13}C NMR ($CDCl_3$): δ = 0.0 ($SiMe_3$), 18.8 [$Si\textit{C}(CH_3)_3$], 29.0 [$C(\textit{C}H_3)_3$], 127.7/128.6/135.8/136.1 (Ph). – MS (70 eV); *m*/*z* (%): 236 (29) [M^+], 179 (90), 135 (88), 121 (63), 105 (76), 83 (100), 73 (96), 59 (33). – HRMS: calcd. for $C_{13}H_{24}Si_2$ (M^+) 236.1416; found 236.1407.

1-Bromo-1-*tert*-butyl-2,2,2-trimethyldisilane (17): HBr (ca. 40 mL) was condensed onto phenyldisilane **16** (27 g, 114 mmol) at –196 °C. After allowing the mixture to warm to –78 °C, stirring was continued for two days and then the excess HBr was evaporated at room temperature. Subsequent distillation furnished 25.5 g (94%) of bromodisilane **17** as a colorless liquid, b.p. 82 °C/22 Torr. – IR (film): ṽ = 2970 cm^{-1} (CH), 2120 (SiH), 1480, 1470 (*t*Bu), 1370, 1255 ($SiMe_3$), 845 ($SiMe_3$), 780, 720. – ^1H NMR ($CDCl_3$): δ = 0.27 (s, 9 H, $SiMe_3$), 1.10 (s, 9 H, *t*Bu), 4.15 (s, 1 H, SiH). – ^{13}C NMR ($CDCl_3$): δ = –1.9 ($SiMe_3$), 24.4 [$Si\textit{C}(CH_3)_3$], 25.4 [$C(\textit{C}H_3)_3$]. – MS (70 eV); *m*/*z* (%): 240 (13) [M^+], 238 (12), 183 (6), 181 (6), 73 (100). – HRMS: calcd. for $C_7H_{19}BrSi_2$ (M^+) 240.0225; found 240.0245.

2-*tert*-Butyl-1,1,3,3,3-pentamethyl-1-phenyltrisilane (18): The dimethylphenylsilyl anion was generated by stirring chlorodimethylphenylsilane (14.5 g, 85 mmol) with lithium pellets (2.0 g, 288 mmol) in THF (200 mL) for 24 h at room temperature. After removal of the remaining lithium, this solution was added dropwise to bromodisilane **17** (20.5 g, 85.7 mmol) in THF (100 mL) over a period of 24 h at –78 °C. The resulting mixture was stirred for a further 24 h at room temperature and then subjected to aqueous work-up. Distillation in vacuo (68–70 °C/0.01 Torr) furnished 18.3 g (73%) of trisilane **18**. – IR (film): ṽ = 3080 cm^{-1} (CH, Ph), 2960 (CH), 2060 (SiH), 1475, 1470 (*t*Bu), 1435 (SiPh), 1370, 1250 ($SiMe_3$), 1110, 860 ($SiMe_3$), 840, 815, 765, 735, 705. – ^1H NMR ($CDCl_3$): δ = 0.05 (s, 9 H, $SiMe_3$), 0.45 (s, 6 H, $SiMe_2Ph$), 0.99 (s, 9 H, *t*Bu), 3.22 (s, 1 H, SiH), 7.28–7.52 (m, 5 H, Ph). – ^{13}C NMR ($CDCl_3$): δ = –0.3/–0.7 (diastereotopic $SiMe_2Ph$), 1.1 ($SiMe_3$), 19.5 [$Si\textit{C}(CH_3)_3$], 31.5 [$C(\textit{C}H_3)_3$], 127.7/128.4/134.0/140.9 (Ph). – MS (70 eV); *m*/*z* (%): 294 (4) [M^+], 279 (30), 237 (33), 220 (63), 164 (47), 135 (60), 73 (100). – HRMS: calcd. for $C_{11}H_{21}Si_3$ (M^+ – *t*Bu) 237.0951; found 237.0901.

2-*tert*-Butyl-2-chloro-1,1,3,3,3-pentamethyl-1-phenyltrisilane (19): In order to prepare chlorotrisilane **19**, trisilane **18** (1.38 g, 4.7 mmol) was dissolved in tetrachloromethane (10 mL) and the resulting solution was stirred at 50 °C. After 20 h, the reaction was complete and all volatile materials were removed in vacuo. The remaining colorless liquid (b.p. 100–105 °C/0.04 Torr) was used without further purification. – IR (film): ṽ = 3070 cm^{-1} (CH, Ph), 2950 (CH), 1470, 1460 (*t*Bu), 1430 (SiPh), 1400, 1360, 1250 ($SiMe_3$), 1120, 1110, 1070, 840, 815, 790, 735, 700. – ^1H NMR ($CDCl_3$): δ = 0.08 (s, 9 H, $SiMe_3$), 0.49/0.50 (2 s, 2 × 3 H, diastereotopic $SiMe_2Ph$), 0.96 (s, 9 H, *t*Bu), 7.32–7.56 (m, 5 H, Ph). – ^{13}C NMR ($CDCl_3$): δ = –2.2/–2.1 (diastereotopic $SiMe_2Ph$), –0.5 ($SiMe_3$), 23.1 [$Si\textit{C}(CH_3)_3$] 28.0 [$C(\textit{C}H_3)_3$], 127.9/129.0/134.2/138.3 (Ph). – MS (70 eV); *m*/*z* (%): 328 (8) [M^+], 313 (4), 271 (9), 220 (59), 164 (49), 135 (100), 73 (100). – HRMS: calcd. for $C_{11}H_{20}ClSi_3$ (M^+ – *t*Bu) 271.0560; found 271.0573.

2-*tert*-Butyl-2-(tri-*tert*-butylcyclopropenyl)-1,1,3,3,3-pentamethyl-1-phenyltrisilane (7): A solution of chlorotrisilane **19** (6.9 g, 21 mmol) in THF (90 mL) was cooled to –78 °C, whereupon lithium (380 mg, 55 mmol) was added. After stirring for a further 20 h, the brown solution of the anion was added to a suspension of tri-*tert*-butylcyclopropenylium tetrafluoroborate (6.5 g, 22 mmol) in THF (100 mL) at –78 °C in 5 mL aliquots over a period of 6 h. The resulting mixture was then stirred for a further 24 h and subsequently allowed to slowly warm to room temperature. After aqueous work-up and removal of the solvents, the crude product was purified by recrystallization from acetone followed by TLC (SiO_2, petroleum ether, 30:50). A second recrystallization from acetone gave 4.9 g (47%) of pure cyclopropenyltrisilane **7** as a colorless solid, m.p. 135 °C. – IR (neat): ṽ = 3075 cm^{-1} (CH, Ph), 2970 (CH), 1805 (C=C), 1475 (*t*Bu), 1430 (SiPh), 1390, 1360 (Si*t*Bu), 1245 ($SiMe_3$), 1215, 1100, 830 ($SiMe_3$), 810, 735, 700. – ^1H NMR ($CDCl_3$): δ = 0.30 (s, 9 H, $SiMe_3$), 0.62 (s, 6 H, $SiMe_2Ph$), 0.85/1.09/1.21/1.32 (4 s, 4 × 9 H, 4 × *t*Bu), 7.22–7.61 (m, 5 H, Ph). – ^{13}C NMR ($CDCl_3$): δ = 4.3/4.4 (diastereotopic $SiMe_2Ph$), 5.7 ($SiMe_3$), 23.1 [$Si\textit{C}(CH_3)_3$], 31.5/31.7/32.6/33.1 [$C(\textit{C}H_3)_3$], 32.1/38.5/38.9 [$\textit{C}(CH_3)_3$], 129.6/130.2 (C=C), 127.2/127.8/135.1/143.8 (Ph). – MS (70 eV); *m*/*z* (%): 443 (3) [M^+ – *t*Bu], 207 (100), 135 (16), 73 (27), 57 (46). – HRMS: calcd. for $C_{26}H_{47}Si_3$ (M^+ – *t*Bu) 443.2987; found 443.2997.

2-*tert*-Butyl-2-(1,2,3-tri-*tert*-butylcyclopropenyl)-1,1,1-trimethyldisilane (11): A degassed solution of silane **7** (310 mg, 0.62 mmol) in methylcyclohexane (14 mL) was irradiated for 4 h at a wavelength of 254 nm. The yellow color of **9** that had developed vanished upon exposure to oxygen. After removal of the solvent, the crude product was purified by TLC (SiO_2, petroleum ether, 30:50). From the first band, 140 mg (62%) of pure cyclopropenyldisilane **11** was isolated as a colorless solid, m.p. 68 °C. – IR (film): ṽ = 2970–2860 cm^{-1} (CH), 2090 (SiH), 1835 (C=C), 1480 (*t*Bu), 1465, 1395, 1365, 1250, 860, 835, 770, 730. – ^1H NMR (C_6D_6): δ = 0.50 (s, 9 H, $SiMe_3$), 1.12/1.30/1.36/1.40 (4 s, 4 × 9 H, 4 × *t*Bu), 3.48 (s, 1 H, SiH). – ^{13}C NMR (C_6D_6): δ = 7.8 ($SiMe_3$), 21.6 [$Si\textit{C}(CH_3)_3$], 31.2/31.4/32.1/32.2 [$C(\textit{C}H_3)_3$], 31.7/31.9/36.5/37.9 [$\textit{C}(CH_3)_3$ + bridgehead], 128.9/129.8 (C=C). – MS (70 eV); *m*/*z* (%): 351 (5) [M^+], 309 (6), 207 (100), 73 (43), 57 (41), 41 (22). – HRMS: calcd. for $C_{21}H_{43}Si_2$ (M^+) 351.2903; found 351.2879.

2,3,4-Tri-*tert*-butyl-4-trimethylsiloxyl-4-oxa-5-silacyclopent-2-en-1-one (13): The TLC separation described above for the isolation of **11** was followed by a second TLC (Al_2O_3, petroleum ether, 30:50) of the residue remaining after evaporation of the solvent from the other fractions. The yield of **13** was 9%. – IR (neat): ṽ = 2958 cm^{-1} (CH), 1744 (C=O), 1581 (C=C), 1474 (*t*Bu), 1393, 1364 (Si*t*Bu), 1254 ($SiMe_3$), 1187, 1063 (SiO), 848 ($SiMe_3$). – ^1H NMR ($CDCl_3$): δ = 0.13 (s, 9 H, $SiMe_3$), 1.00 (s, 9 H, Si*t*Bu), 1.36 (s, 9 H, 2-*t*Bu), 1.41 (s, 9 H, 3-*t*Bu). – ^{13}C NMR ($CDCl_3$): δ = 1.45 ($SiMe_3$), 18.6 [$Si\textit{C}(CH_3)_3$], 26.5 [$SiC(\textit{C}H_3)_3$], 31.8/33.4 [$C(\textit{C}H_3)_3$], 34.3/37.0 [$\textit{C}(CH_3)_3$], 155.2/161.3 (C=C), 168.0 (C=O). – ^{29}Si NMR ($CDCl_3$): δ = –17.3 ($SiMe_3$), 13.5 (ring). – MS (70 eV); *m*/*z* (%): 356 (22) [M^+], 341 (21), 313 (15), 299 (19), 215 (30), 133 (90), 73 (28), 57 (100). – HRMS: calcd. for $C_{18}H_{36}Si_2O_3$ (M^+) 356.2203; found 356.2192.

1,2,3,4-Tetra-*tert*-butyl-3-trimethylsilyl-3-silacyclobut-1-ene (12): A solution of **7** (268 mg, 0.53 mmol) in methylcyclohexane (20 mL) was irradiated for 2.5 h at room temperature with light of wavelength 254 nm. Addition of ethanethiol (0.5 mL) caused the solution to turn colorless. After removal of the solvents, purification of the residue by TLC (SiO_2, pentane) yielded a mixture of the H-silanes **11** and **12**. Subsequent preparative HPLC (Lichrosorb RP-18, Merck) furnished pure silacyclobutene **12** (5%) as a colorless solid, m.p. 70 °C. – IR (neat): ṽ = 3023 cm^{-1} (CH), 1517 (C=

C), 1466 (*t*Bu), 1387, 1360 (Si*t*Bu), 1245 ($SiMe_3$), 1103, 1009, 850 ($SiMe_3$). – ^1H NMR ($CDCl_3$): $\delta = 0.27$ (s, 9 H, $SiMe_3$), 1.03/1.06/1.20/1.24 (4 s, 4×9 H, $4 \times$ *t*Bu), 2.08 (s, 1 H, CH). – ^{13}C NMR ($CDCl_3$): $\delta = 3.4$ ($SiMe_3$), 21.7 [$Si\mathit{C}(CH_3)_3$], 30.1/31.4/32.8/33.1 [$C(\mathit{C}H_3)_3$], 31.9/33.8/37.4 [$\mathit{C}(CH_3)_3$], 49.9 [C(4)], 161.2/164.4 (C=C). – MS (70 eV); *m*/*z* (%): 366 (2.4) [M^+], 351 (3), 309 (73), 293 (37), 240 (20), 171 (12), 73 (100), 57 (61). – HRMS: calcd. for $C_{22}H_{46}Si_2$ (M^+) 366.3138; found 366.3186.

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