The different modes of decomposition of hexa-t-butylcyclotrisilane [☆],[1]

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Abstract

On heating, hexa-t-butylcyclotrisilane (1) undergoes decomposition, presumably by way of Si–Si bond homolysis, isobutene elimination, 1,2-hydrogen shift, and subsequent ene-reactions, to furnish 1,1,2,3,3,7,7,8,9,9-deca-t-butyl-5-methylene-1,2,3,7,8,9-hexasilanonane; the structure of this product has been confirmed by NMR study and X-ray diffraction. However, photolysis of 1 proceeds through tetra-t-butyldisilene which dimerizes with loss of isobutene to produce the highly strained hepta-t-butylcyclotetrasilane (10) in low yield. X-ray crystal structure analysis of this compound reveals a slightly folded four-membered ring with two very long (253.8(4) pm) Si–Si bonds.

Keywords: Silicon; Silanes; Decomposition reactions; X-ray crystallography

1. Introduction

The cyclotrisilanes, which have only been known since 1982 [2], are of considerable interest not only on account of their strained ring system but also because they, like the acyclic trisilanes [3], provide a general access to the aryl- and silyl-substituted disilenes, $R_2Si=SiR_2$ [4,5]. Although stable tetraalkyldisilenes cannot be obtained by this route, the hexaalkylcyclotrisilanes also constitute the entry point to an interesting and rich area of chemistry, as illustrated in Scheme 1 for the example of hexa-t-butylcyclotrisilane (1) [6].

Photolysis of 1 proceeds with concomitant cleavage of two Si–Si bonds to generate short-lived di-t-butylsilylene and marginally stable tetra-t-butyldisilene (9) which undergo [2 + 1]- and [2 + 2]-cycloaddition reactions, respectively, with unsaturated compounds to furnish compounds of the types 3 and 4 or subsequent products derived therefrom [7]. However, thermal reac-

tions of 1 occur with cleavage of only one Si–Si bond and, depending on the nature of the reaction partner, give rise to either acyclic trisilanes or ring-expanded trisiletanes 2.

The question of how the decomposition reactions proceed in the absence of trapping reagents had not been addressed previously. Hence, we have investigated the photolysis and thermolysis of 1 under just these conditions and report here on the nature and possible routes of formation of the identified products.

2. Results and discussion

When 1 is heated at 185°C in a sealed tube, a pale red viscous oil is obtained from which a colorless, homogeneous solid can be isolated by fractional crystallization. A complete NMR analysis including two-dimensional NMR spectra clearly indicates that this product is a 4-methylene-1,2,3,7,8,9-hexasilanonane 8 (Scheme 2). Accordingly, three signals are observed in the ^{29}Si NMR spectrum and two of them exhibit $^1J(^{29}Si,\ ^1H)$ coupling. The J-modulated ^{13}C NMR spectrum as well as H,C COSY experiments demonstrate the presence of two aliphatic CH_2 groups, one quaternary
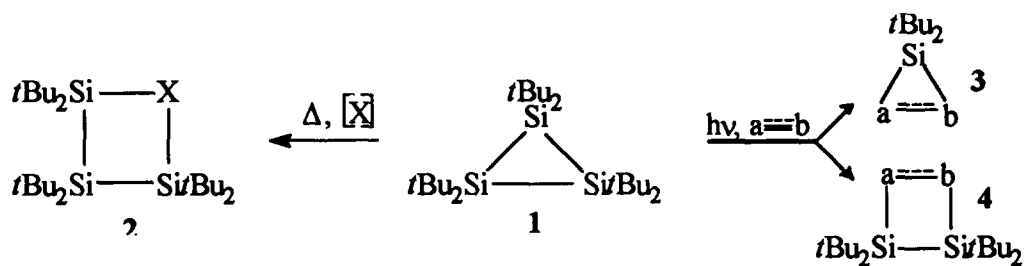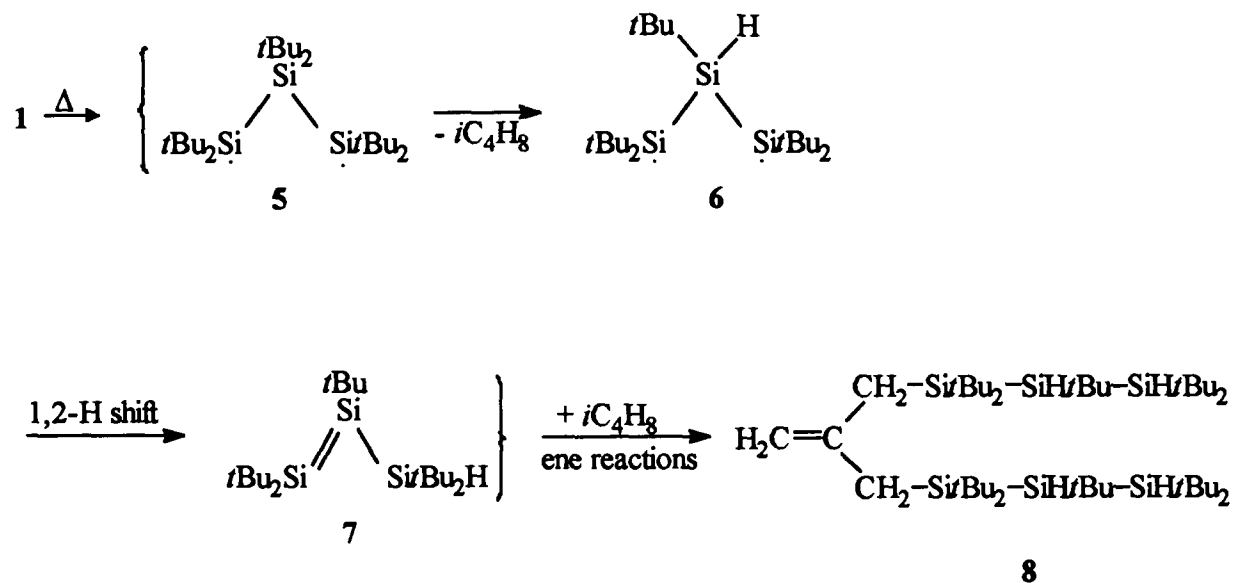
Scheme 1.

Scheme 2.

olefinic C atom, and a CH_2=C< group. The primary carbon atoms of the diastereotopic t-butyl groups at the silicon atoms 1,3,7, and 9 as well as those of the t-butyl groups at the chiral silicon atoms 2 and 8 appear as separate signals; in the case of the quaternary C atoms and in the proton spectrum two of these signals respectively occur together.

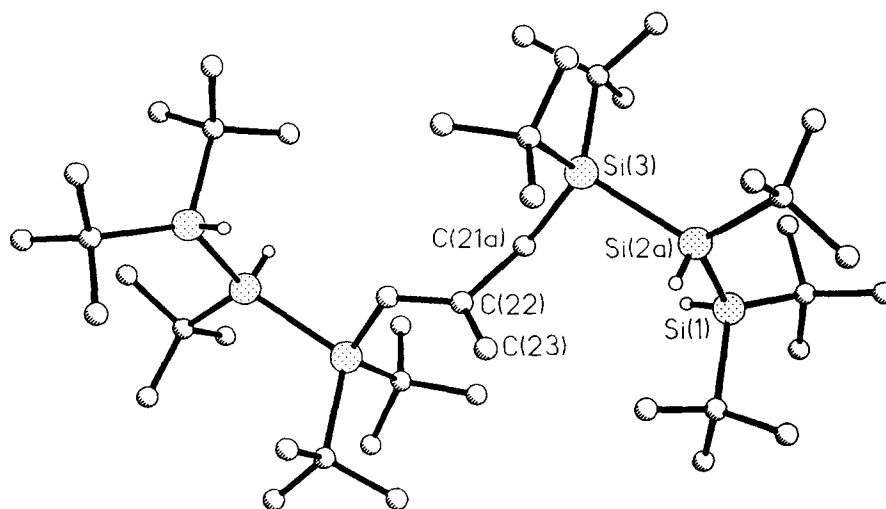The X-ray crystal structure analysis of **8** (Fig. 1,

Fig. 1. Molecular structure of **8** in the crystal (C-hydrogen atoms omitted).

Table 1

Atomic parameters ($\times 10^4$) and equivalent isotropic displacement coefficients ($pm^2 \times 10^{-1}$) for **8**

	x/a	y/b	z/c	U_{eq} [a]
Si(1) [b]	849(1)	−2540(1)	−3281(1)	57(1)
C(1a)	1214(1)	−2556(1)	−4917(1)	106(5)
C(2a)	2014(1)	−1496(1)	−5464(1)	165(8)
C(3a)	1967(1)	−3745(1)	−5425(1)	104(3)
C(4a)	−90(1)	−2239(1)	−5221(1)	160(8)
C(1b)	1585(1)	−2524(1)	−5040(1)	63(3)
C(2b)	2971(1)	−2198(1)	−5464(1)	106(4)
C(3b)	1605(1)	−3819(1)	−5328(1)	104(3)
C(4b)	712(1)	−1581(1)	−5674(1)	93(4)
C(5a)	−463(1)	−3596(1)	−2141(1)	84(3)
C(6a)	−572(1)	−3437(1)	−861(1)	139(6)
C(7a)	−1790(1)	−3154(1)	−2386(1)	193(11)
C(8a)	−41(1)	−4964(1)	−2312(1)	139(8)
C(5b)	−595(1)	−3351(1)	−2665(1)	64(2)
C(6b)	−1273(1)	−2915(1)	−1447(1)	97(4)
C(7b)	−1527(1)	−2989(1)	−3449(1)	103(4)
C(8b)	−223(1)	−4759(1)	−2510(1)	101(5)
Si(2a)	2289(3)	−2983(2)	−2047(2)	40(1)
C(9a)	3857(3)	−4204(2)	−2519(2)	73(2)
C(10a)	3389(3)	−5225(2)	−2929(2)	93(4)
C(11a)	4308(3)	−4728(2)	−1407(2)	113(5)
C(12a)	4998(3)	−3735(2)	−3509(2)	109(5)
Si(2b)	2715(3)	−2709(3)	−2614(3)	63(1)
C(9b)	3771(3)	−4303(3)	−2449(3)	73(2)
C(10b)	3720(3)	−5027(3)	−3412(3)	82(3)
C(11b)	3356(3)	−5068(3)	−1230(3)	116(5)
C(12b)	5166(3)	−4047(3)	−2678(3)	119(5)
Si(3)	2483(1)	−1106(1)	−1381(1)	54(1)
C(13a)	3763(1)	18(1)	−2566(1)	67(3)
C(14a)	3193(1)	582(1)	−3603(1)	92(4)
C(15a)	5111(1)	−721(1)	−3041(1)	106(4)
C(16a)	3893(1)	1055(1)	−1933(1)	79(3)
C(13b)	3141(1)	130(1)	−2507(1)	63(2)
C(14b)	2194(1)	584(1)	−3269(1)	80(3)
C(15b)	4465(1)	−403(1)	−3287(1)	91(4)
C(16b)	3308(1)	1218(1)	−1962(1)	101(4)
C(17a)	3209(1)	−1521(1)	−22(1)	48(2)
C(18a)	4698(1)	−1727(1)	−490(1)	63(2)
C(19a)	2773(1)	−408(1)	678(1)	70(2)
C(20a)	2755(1)	−2675(1)	797(1)	72(3)
C(17b)	2881(1)	−1596(1)	105(1)	70(3)
C(18b)	4281(1)	−2262(1)	−70(1)	93(4)
C(19b)	2661(1)	−538(1)	847(1)	70(2)
C(20b)	1929(1)	−2512(1)	758(1)	94(4)
C(21a)	687(1)	−410(1)	−907(1)	75(4)
C(21b)	801(1)	−274(1)	−1165(1)	90(5)
C(22)	−239(8)	−784(8)	546(7)	47(2)
C(23)	−414(10)	1931(10)	977(10)	65(3)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

[b] Si(1) and Si(3) occupy the same positions in all isomers.

Table 2

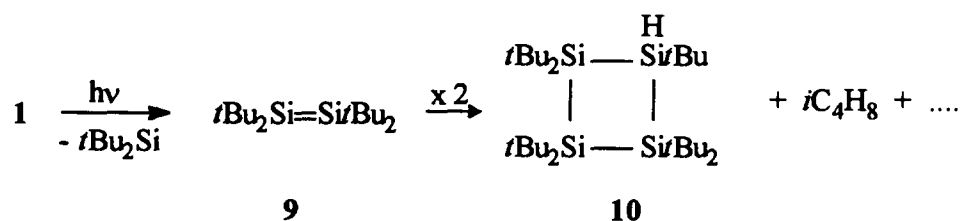Selected bond lengths (pm) and bond angles (deg) (standard deviations) for **8**

Si(1)–Si(2a)	237.3(3)	Si(1)–Si(2b)	240.1(3)
Si(2a)–Si(3)	243.6(3)	Si(2b)–Si(3)	244.5(3)
Si(1)–Si(2a)–Si(3)	110.4(1)	Si(1)–Si(2b)–Si(3)	111.1(1)

Tables 1 and 2) not only confirms the proposed structure but also, in agreement with the proton NMR spectrum of the measured crystal, indicates the existence of all three stereoisomers in the solid state. This is apparent from the disorder in which the R- and the S-configurated silicon atoms 2 and 8 each take up different positions with an occupation density of 50%.

The following rationale for the formation of the unusual thermolysis product **8** seems reasonable and is supported by indirect evidence. The reaction sequence presumably commences with the homolysis of one Si–Si bond in **1** with formation of **5**; this is also the possible first step in the generation of acyclic trisilanes [8] and the ring-expansion products **2** from **1** [9]. The intermediate **6**, formed after elimination of isobutene, then undergoes a 1,2-hydrogen shift to furnish the silyldisilene **7**. Subsequent ene reactions of **7** with the previously cleaved isobutene finally gives rise to the hexasilanonane **8**. The Si=N double bonds of silanimines exhibit a similar behavior and also take part in corresponding ene reactions with isobutene [10,11].

The thermolysis reaction proceeds more or less uniformly whereas, in contrast, the photolysis reaction with light with wavelengths > 300 nm gives rise to a mixture of products containing both t-Bu–Si and H–Si bonds (Scheme 3). Hepta-t-butylcyclotetrasilane **10** was isolated from this mixture by fractional crystallization and its constitution elucidated from the NMR data.

The yield of **10** is low for two reasons. First, only a small proportion of **1** is cleaved at the start of the reaction. This is in agreement with matrix photolysis experiments on **1** [12] which show that although di-t-butylsilylene and tetra-t-butyldisilene **9** are indeed formed by cleavage of two Si–Si bonds they at first remain together in a sort of cage compound and can only be separated when suitable trapping reagents are present. The actual formation of **10** can also be observed when the silylene, but not the disilene **9**, is trapped by cycloaddition to, for example, C=C double

$$1 \xrightarrow[- \, tBu_2Si]{h\nu} tBu_2Si{=}SitBu_2 \xrightarrow{x\,2} \begin{array}{c} H \\ tBu_2Si{-\!\!\!-\!\!\!-}SitBu \\ | \quad\quad | \\ tBu_2Si{-\!\!\!-\!\!\!-}SitBu_2 \end{array} + iC_4H_8 + \ldots$$

9   **10**

Scheme 3.

Table 3

Atomic parameters ($\times 10^4$) and equivalent isotropic displacement coefficients ($pm^2 \times 10^{-1}$) for **10**

	x / a	y / b	z / c	U_{eq} [a]
Si(1)	0	2162(2)	2500	38(1)
Si(2)	1477(2)	1157(2)	2500	43(1)
Si(3)	0	290(3)	2787(3)	43(2)
C(1)	0	2842(7)	3510(9)	86(6)
C(2)	0	2459(10)	4405(8)	126(8)
C(3a)	1451(20)	3171(12)	3512(14)	110(7)
C(3b)	733(18)	3500(12)	3455(15)	110(7)
C(4)	2420(8)	1097(5)	3507(6)	78(4)
C(5a)	1480(16)	883(11)	4356(12)	81(6)
C(5b)	2057(23)	1108(14)	4370(18)	122(9)
C(6a)	2895(17)	1883(10)	3751(13)	79(5)
C(6b)	3468(21)	1558(13)	3433(15)	112(7)
C(7a)	3344(24)	631(16)	3504(19)	142(11)
C(7b)	2979(17)	240(10)	3557(12)	78(6)
C(8)	0	−737(9)	2500	76(7)
C(9)	0	−927(16)	1503(20)	97(9)
C(10)	−1054(20)	−1077(12)	3036(13)	117(7)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

bonds [13]. With increasing photolysis duration, the proportion of **10** increases at the cost of **1** but also concomitant fragmentation of **10** commences with the result that higher yields are not possible.

The formation of **10** presumably occurs by the cyclodimerization of two molecules of the disilene **9**. Since the formation of octa-t-butylcyclotetrasilane would necessitate the widening of the endocyclic angle from 60° in **1** to about 90°, the resultant strong interactions between the H-atoms of neighboring t-butyl groups would render this process extremely unfavorable; thus,

dimerization of **9** to **10** can only occur with the simultaneous elimination of isobutene. Di-t-butylsilylene, which is formed together with **9**, is known to be unstable and isomerizes to a silirane and other products [14].

The X-ray structure analysis of **10** (Fig. 2) reveals that there is still considerable strain in the four-membered ring in spite of the replacement of a t-Bu–Si bond by an H–Si bond. This strain is reflected in the bond lengths Si(1)–Si(2) and Si(1)–Si(2a) of 253.8(4) pm; these are currently the longest Si–Si bonds observed in a cyclooligosilane and are presumably the reason for the photolytic instability of **10**. In contrast, the Si–Si bonds to the SiHt-Bu groups are only marginally lengthened. The ring is slightly folded, with an angle of 16° between the planes defined by the atoms Si(2)–Si(3)–Si(2a) and Si(2a)–Si(1)–Si(2).

3. Experimental details

3.1. General procedures

All reactions were carried out in oven-dried glassware under dry argon. Photolyses were carried out by using a low-pressure mercury immersion lamp or a high pressure mercury lamp with pyrex filter.

The ^1H and ^{13}C NMR spectra were obtained on a Bruker AM 300 spectrometer, whereas the ^{29}Si NMR spectra were recorded on a Bruker AMX 300 spectrometer using C_6D_6 as solvent. The H,C-COSY experiment was performed on a Bruker AM 500 spectrometer. IR spectra were recorded on a Bio-Rad FTS-7 spectrome-
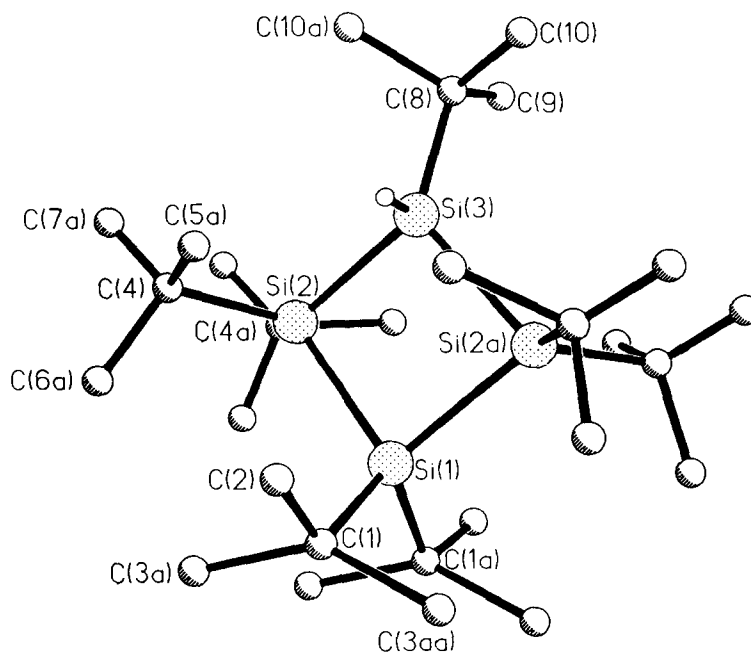

Fig. 2. Molecular structure of **10** in the crystal (C-hydrogen atoms omitted).

ter. Mass spectra were recorded on a Varian-MAT instrument (CI, isobutane) or on an Olda-1 time-of-flight instrument (plasma desorption). UV–vis spectra were recorded on a Shimadzu UV-260 spectrometer. Elemental analyses were performed by Analytische Laboratorien, D-51647 Gummersbach, Germany.

3.1. Formation of 1,1,2,3,3,7,7,8,9,9-deca-t-butyl-5-methylene-1,2,3,7,8,9-hexasilanonane (8)

In a sealed tube compound **1** (0.446 g, 1.04 mmol) was heated at 185°C for 80 min. The resulting reddish viscous oil was dissolved in n-hexane/ethyl acetate and recrystallized from these solvents to yield 0.209 g (50%) **8**: colorless solid; m.p. 175–178°C. ^{1}H NMR: δ 1.26 (s, 18H); 1.28 (s, 18H) 1.37 (s, 36H); 1.38 (s, 18H); 2.22–2.46 (4 m, 4H, $\rangle CH_2$); 3.97 (s, 2H, SiH); 4.09 (s, 2H, SiH); 5.26 (s, broad, 2H; $=CH_2$). ^{13}C NMR: δ 20.77 (C_q); 21.58 (C_q); 22.90 (C_q); 23.31 (C_q); 28.98 ($\rangle CH_2$); 31.31 (C_p); 31.37 (C_p); 31.59 (C_p); 32.12 (C_p); 34.10 (C_p); 114.70 ($=CH_2$); 146.04 (C_q), C_p and C_q refer to primary and quaternary carbon atoms, respectively. ^{29}Si NMR: $\delta - 45.78$ (d, ^1J(Si,H) = 147 Hz); 7.51 (d, ^1J(Si,H) = 174 Hz); 14.74 (s). IR (cm^{-1}): v (SiH) 2093(m), 2058(s); v(C=C) 1628(w). MS (plasma desorption, negative ions): $m/z = 797$ (M$^-$); 742 (M$^-$ – t-Bu). Found: C, 65,31; H, 12.55%. $C_{44}H_{100}Si_6$ (797.79) calc.: C, 66.24; H, 12.63%.

Similarly, heating of **1** dissolved in naphthalene at 185°C for 2.5 h also gave **8**. Since the cyclotrisilane **1** sublimes at this temperature, the reaction could not be performed in nonsealed tubes.

3.2. Formation of hepta-t-butylcyclotetrasilane (10)

A solution of 0.442 g (1.04 mmol) **1** in 100 ml n-hexane was irradiated for 6 h. After 1 h the solution turned orange–brown and became decolorized at the end of the irradiation. Concentration of the solution to 10 ml and cooling at – 25°C gave 0.028 g (11%) **10**: colorless solid; mp 100°C (decomposition). ^{1}H NMR: δ 1.32 (s, 9H); 1.41 (s, 18H); 1.44 (s, 9H); 1.46 (s, 9H); 1.47 (s, 18H); 4.12 (s, 1H, SiH). ^{13}C NMR: δ 22.47 (C_q); 24.09 (C_q); 25.28 (C_q); 25.50 (C_q); 28.23 (C_q); 32.27 (C_p); 33.34 (C_p); 34.62 (C_p); 34.92 (C_q); 36.13 (C_p). ^{29}Si NMR (D$_8$-toluene): δ – 36.18 (d, broad, ^1J(Si, H) = 137 Hz); 31.57 (s, broad); 41.72 (s, broad). IR (cm^{-1}): v (SiH) 2060. MS (CI, isobutane): m/z 513

Table 4
Selected bond lengths (pm) and angles (deg) (standard deviations) for **10**

Si(1)–Si(2)	253.8(4)	Si(1)–Si(2a)	253.8(4)
Si(2)–Si(3)	241.0(4)	Si(2)–Si(3a)	241.0(4)
Si(2)–Si(1)–Si(2a)	89.3(2)	Si(1)–Si(2)–Si(3)	86.6(1)
Si(2)–Si(3)–Si(2a)	95.5(2)	Si(1)–Si(2a)–Si(3)	86.6(1)

Table 5
Crystallographic data for **8** and **10** [a]

	8	10
Empirical formula	$C_{44}H_{100}Si_6$	$C_{28}H_{63}Si_4$
Molar weight (g mol^{-1})	799.78	512.16
a (pm)	1094.4(1)	1207.6(1)
b (pm)	1116.5(1)	1797.2(1)
c (pm)	1197.4(1)	1542.6(1)
α (deg)	79.84(1)	
β (deg)	72.37(1)	
γ (deg)	78.99(1)	
V ($\times 10^6$ pm^3)	1357.7(2)	3347.9(4)
Z	1	4
D_{calc} (g cm^{-1})	0.976	1.016
Crystal system	triclinic	orthorhombic
Space group	$P\bar{1}$	$Cmcm$
Crystal size (mm)	1.0×0.7×0.5	0.7×0.5×0.1
Data collection mode	ω–2θ–scan	ω–2θ–scan
$2\theta_{max}$ (deg)	50	50
Number of reflections	5026	1672
Number of unique reflections	4753	1616
Number of reflections $F > 3\sigma(F)$	4748	988
Linear abs. coefficient (mm^{-1})	0.179	0.178
$R(R_w)$	0.109 [b]	0.104(0.119)
Largest difference peak and hole (e nm^{-3})	926	650
	–420	–410

[a] Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, upon quoting the depository number CSD 58831.
[b] $wR2$ 0.279.

(M$^+$, 5%); 546 (M$^+$ – t-Bu, 12%). UV–vis: λ_{max} (nm) (ε) 210 (27500); 235 sh (13200); 268 sh (3100); 315 (760). Found: C, 65.38; H, 12.41%. $C_{28}H_{64}Si_4$ (513.17); calc.: C, 65.54; H, 12.57%.

In order to demonstrate the photolability of **10**, 8 mg of the compound were dissolved in d$_6$-benzene and irradiated. ^{1}H and ^{13}C NMR spectral monitoring of the reaction mixture showed that 30% of the four-membered ring substrate had decomposed after 0.5 h and 80% after 1 h. We have not yet been able to identify the resulting products.

3.3. X-ray structure analyses of 8 and 10

Selected bond lengths and angles for **10** are given in Table 4 with crystal data and numerical details of the structure determinations shown in Table 5. Crystals of **8** were grown by slow evaporation of the solvent from a solution in ethyl acetate. Crystals of **10** were obtained by cooling a solution in n-hexane to – 50°C. In each case the crystal was mounted in a thin-walled glass capillary. Data collection was performed on a Siemens STOE AED2 diffractometer using graphite-monochromated Mo-Kα radiation.

The structures were solved by direct phase determination using the Siemens SHELXTL PLUS and SHELXL-93

program systems and refined by full-matrix least squares techniques. Hydrogen atoms were placed in the calculated positions, and all other atoms were refined anisotropically.

Compound **8** forms mixed crystals, the unit cell of which contains all three diastereomers. Two of these isomeres proved to be indistinguishable. The refinement of the structure of **8** was also performed in space group *P*1. Despite a resulting better *R* value, this calculation was not reliable according to strong correlations.

In spite of the disorder of the t-butyl groups in **8** and **10** and of the silicon atoms 2 and 8 in **8** with the consequently high *R* values, the definition of the skeleton atoms is good and of acceptable accuracy.

Acknowledgment

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