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The reactivity of tetramesityldisilene with epoxides: dependence of product distributions on steric and structural characteristics of the epoxide [1]

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Abstract

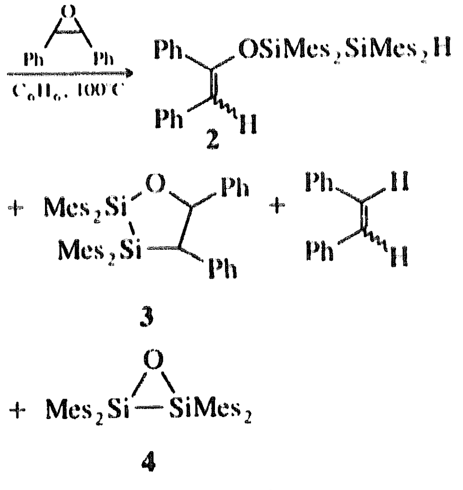
Mono- and 1,1-disubstituted epoxides react with tetramesityldisilene (**1**) to give disilyl enol ethers (**5**) five-membered rings (**6**) and the products of epoxide deoxygenation, alkenes and 1,1,2,2-tetramesityl-3-oxa-1,2-disilacyclopropane (**4**). Adducts **5** and **6** are formed with complete regioselectivity, suggesting involvement of an epoxide ring-opened intermediate. Product ratios vary systematically with a dependence on the steric properties of the epoxide. Single crystal X-ray diffraction results are given for **6a** and **6g**, the five-membered ring products derived from propylene and cyclohexene oxides.

Keywords: Disilene; Epoxide; Silyl enol ether; Crystal structure; Steric effects; Group 14; Cycloaddition

1. Introduction

In two previous publications we described the reactions of tetramesityldisilene (**1**) with cyclohexene oxide [1] and *cis*- and *trans*-stilbene oxides [2]. The unexpected major products, disilyl enol ethers (**2**) and five-membered ring formal insertion products (**3**) (observed only from stilbene oxides) were accompanied by the expected products of epoxide deoxygenation, alkenes and the known 1,1,2,2-tetramesityl-3-oxa-1,2-disilacyclopropane (**4**) [3] (Eq. (1)). The stereochemical outcome of the stilbene oxide reactions showed that **2** and **3** were generated from an epoxide ring-opened intermediate, as might be expected from the reaction of an epoxide with an electrophile [4].

1



(1)

Mes = 2,4,6-trimethylphenyl

Since the above reactions provide only three examples, it seemed wise to broaden the focus of the reaction and to test its applicability to other simple epoxides. In so doing, it was also of interest to define the effects of steric factors and substituent patterns on product distributions. To this end the reactions of **1** with a series of mono-substituted epoxides and a pair of 1,1-disubstituted compounds were investigated. The reaction is general for all epoxides studied, giving products analogous to those from stilbene oxides. Adduct formation

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[1] Dedicated to Professor Robert Corriu, an outstanding leader in organosilicon chemistry.

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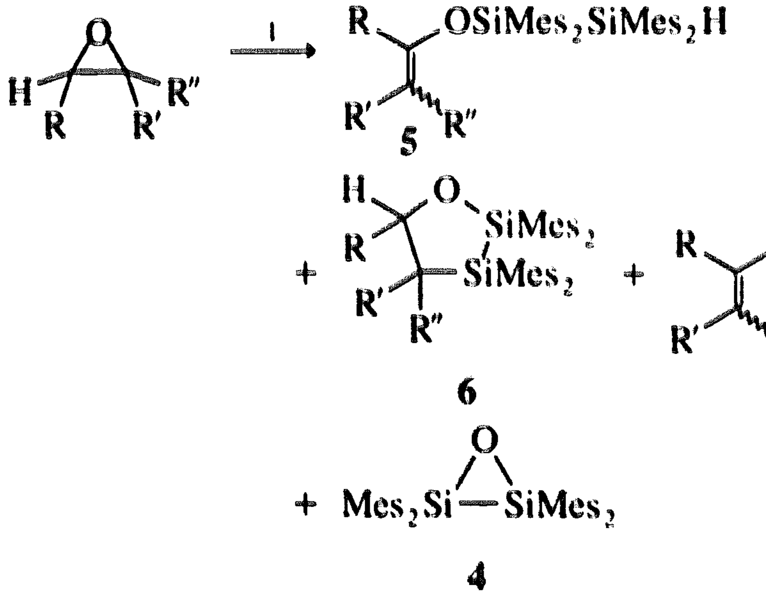
was completely regioselective, again indicative of formation of stabilized intermediates. As might be predicted considering the significant bulk at the silicons, steric properties of the epoxide can drastically influence product distributions, leading in some cases to very high stereo- and chemoselectivity.

The cyclohexene oxide reaction was also reinvestigated to see if a 5,6-fused ring compound analogous to **3** was also formed. Insertion product **6g** was, indeed, isolated, although in low yield.

2. Results and discussion

2.1. *Reactions of 1 with epoxides: yields and determination of product ratios*

The reactions of **1** with the epoxides listed in Table 1 were conducted at 85°C in benzene using 1.5 equivalents of epoxide. As shown in Eq. (2), products analogous to those obtained from the stilbene oxide reactions were observed, including disilyl enol ethers (**5**) five-membered ring insertion products (**6**) and products from epoxide deoxygenation, alkene and oxadisilacyclopropane (**4**). Compounds **5** and **6** were formed with complete regioselectivity, with the epoxide substituents occupying only positions β to oxygen in the products. As can be seen from the results of NMR-scale reactions in benzene-d_6 (Table 1), product ratios are highly variable depending on epoxide substitution.



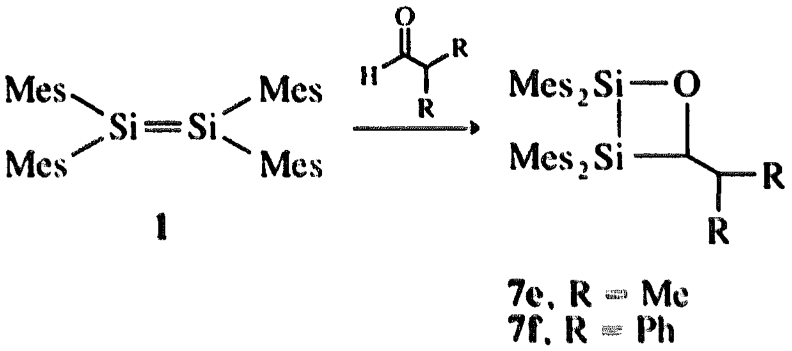
(2)

While integration of the ^{1}H NMR spectra from the NMR-scale reactions allowed a determination of the ratios of **5** and **6** as well as the relative amounts of the higher boiling alkene products (from epoxides c, f, and g), a similar quantitation of the remaining product alkenes would be less reliable. All are relatively low boiling liquids or gases at room temperature. Furthermore, in all but the isobutylene oxide case the aromatic and methyl regions were very complex, making integration of the peaks from **4** impossible.

Instead, quantitation of the deoxygenation process from epoxides a, b and d was accomplished by integration of the INEPT ^{29}Si NMR spectra using the -O-*Si*-Si- peak of the E enol ethers and the resonance of **4** at −26.8 ppm [3]. The reliability of the method as a quantitative estimate was proven for a series of standardized samples containing mixtures of **4** and enol ethers (**5**) (isolated from preparative-scale reactions). The integrated ratios in the ^{29}Si spectra agreed reasonably well with the ratios as determined by ^{1}H NMR [5].

Semi-preparative (100 mg of disilene) and preparative (600–1200 mg of disilene) scale reactions were also conducted under similar conditions. Products in the former runs were isolated by preparative thin-layer chromatography (TLC), while in the latter flash chromatography was used to separate disilene–epoxide adducts from the side products (mainly from hydrolysis of **1** and **4**), followed by selective crystallizations from the **5**/**6** mixtures. Isolated yields are given in Table 1.

Very small amounts (less than 2%) of the four-membered rings (**7**) were observed in the reactions of epoxides e and f. Their identities were confirmed by comparison of their NMR data with authentic samples generated by treating **1** with the appropriate aldehyde (Eq. (3)) [6].



(3)

2.2. *Product characterizations*

Ample quantities of pure enol ethers and five-membered rings could generally be obtained from large-scale reactions by a combination of chromatography and crystallization. E/Z enol ether mixtures from reactions of epoxides a–c were separated either by crystallization (**5b**) or silver nitrate–silica gel chromatography [7] (**5a** and purification of **E5c**). Compound **Z5c** was generated in larger quantities by photoisomerization of **E5c** (λ = 350 nm) and was purified by recrystallization.

Identifications of **5a–f** were based on a comparison of their spectroscopic data (Table 2) with that for **5g**, for which confirming X-ray data has been obtained [1]. The enol ether structure was supported by the C1–C2 bond length of 1.320(6) Å in **5g**, clearly a carbon–carbon double bond.

Several features of the NMR and IR spectra of **5g** were characteristic of **5** in general. Two distinct mesityl groups and a silyl hydride peak, which invariably appeared at 5.6–5.7 ppm, were apparent in the ^{1}H spectra. Observation of the ^{29}Si satellites, with coupling constants near −180 Hz, confirmed the latter assignments [8]. Vinyl ^{13}C signals, assigned using the DEPT 90 pulse sequence, showed the double bond polarization typical of enol ethers [9]. The β vinyl carbons were significantly shielded relative to normal olefinic carbons, while the α carbons were shifted well downfield. Coupled INEPT ^{29}Si spectra allowed assignment of the two signals of each compound and revealed that, as expected [10], the silicon α to oxygen was considerably deshielded compared with the β silicon. Inspection of data **5a–c** also shows that the α silicon of the Z isomers is consistently downfield of that of the E isomers, by 2.5–3.5 ppm, while the chemical shift of the β silicon is nearly constant. Infrared data also supported the assignments, clearly indicating an Si–H stretch for each compound with a strong absorption near 2100 cm^{-1} and a carbon–carbon double bond stretch in the range 1630–1680 cm^{-1}.

As is characteristic of β mono-substituted and unsubstituted enol ethers [9a,11], **5a–d** display a large chemical shift difference between the two vinyl protons, with the proton α to oxygen deshielded relative to the β proton. Stereochemical assignments were based on the observation that, for *cis/trans* isomeric pairs of alkenes, vinyl proton–proton coupling constants are generally larger in the *trans* isomers than in the *cis* ones [12] and, for a number of *cis/trans* trimethyl silyl enol ethers [11], the *trans* vinyl protons appear at lower field than the corresponding *cis* vinyl protons.

As with the enol ethers, compounds **6** were characterized using a combination of X-ray diffraction and NMR data (Table 3). Suitable X-ray crystals of both **6a** and **6g** were obtained; thermal ellipsoid drawings are presented in Figs. 1(a) and 2, and data is given in Tables 4–6. Although the crystals (and thus the X-ray results) were of limited quality [13], certain characteristic features can be noted besides a confirmation of the general structures. Both exhibit somewhat elongated silicon–silicon bonds in the 2.41–2.45 Å range (compared with a typical silicon–silicon single bond length of 2.34 Å), and both five-membered rings adopt a slightly distorted envelope conformation (Figs. 1(b) and 3). In addition **6g** has a *cis* 5/6 ring fusion with the six-membered ring in a chair conformation.

In the ^{1}H NMR spectra of **6**, signals at 4–5 ppm (Table 3) were assigned to the protons α to oxygen. For **6e** and **6g**, they appeared as broad singlets, and for **6a–d** as a pair of doublets of doublets, due to germinal coupling and vicinal coupling to the ring methine proton. For all compounds the mesityl aromatic and methyl regions contained broadened peaks, indicative of hindered rotation resulting from steric congestion. The ^{13}C spectra gave characteristic *C*–O peaks at 65–80 ppm, confirmed with DEPT experiments as methylene carbons for **6a–e** and a methine for **6g**.

2.3. Discussion of product ratios

From Table 1 it is clear that the product ratios vary considerably, but in a systematic way. Inspection of the results from the mono-substituted epoxides (epoxides a–d) reveals a very clear increase in the ratio of **5**/**6** as well as in the **E5**/**Z5** ratio [14] as the epoxide substituent gets larger. With the exception of the **5**/**6** ratio for R′ = Ph, the present trend agrees qualitatively with the spatial requirements of R′ based on measured *A* values, the free energy differences between R′ in equatorial and axial positions on a cyclohexane ring [15]. The order of increasing equatorial preference is Me < ^{i}Pr < Ph < ^{t}Bu.

This trend is consistent with the mechanistic conclusions drawn from the stilbene oxide results, namely that formation of **5** and **6** involves an epoxide ring-opened intermediate (in agreement with the regioselectivities of the present study), (**8**) (Scheme 1), and that proton abstraction to give **5** is intramolecular [2]. As the size of the substituent on the carbocation increases, the ability of the bulky silicon center to close the five-membered ring decreases. This is most clearly demonstrated by comparing the case of R′ = Me, where only a 2 : 1 **5**/**6**

Table 1
Crude product ratios by NMR and isolated yields of **5** and **6** for reactions of Mes$_4$Si$_2$ with epoxides

R	R′	R″		Product ratios by NMR			Isolated yields [a]	
				5/**6** [b]	**5**, E/Z	**5**/**4** (A) or **5**/alkene (B) [b]	**5**	**6**
H	Me	H	(a)	2.3	1.3	6 (A)	44	19
H	^{i}Pr	H	(b)	4.8	2.4	4 (A)	45	11
H	Ph	H	(c)	3.5	8	6 (B)	57	20
H	^{t}Bu	H	(d)	12	16 [c]	4 (A)	33 [d]	< 5
H	Me	Me	(e)	7	—	2.4 (A) [e]	42	15
H	Ph	Ph	(f)	**5** only	—	2 (B)	43	—
(CH$_2$)$_4$		H	(g)	4.7	—	3 (A,B)	33 [f]	

[a] Products were separated by preparative TLC from semi-preparative scale runs unless otherwise noted. [b] For epoxides a–d ratios correspond to (**E5** + **Z5**)/product. [c] A pair of doublets at 6.05 and 4.23 ppm in the ^{1}H NMR of the crude reaction mixture was assigned as **Z5d** which was not otherwise isolated or characterized. [d] Isolated by crystallization from preparative-scale reaction. [e] Ratio estimated by integration of **5** against **4** in the ^{1}H NMR. [f] Isolated by preparative TLC as a mixture of **5g** and **6g** in a ratio of 5 : 1.

Table 2
Selected NMR (ppm) and IR (cm^{-1}) data for **5**

	Vinyl ^1H ($J_{vinyl-vinyl}$, Hz)	Vinyl ^{13}C	^{29}Si (J_{Si-H}, Hz) [a]	IR ν_{Si-H}, $\nu_{C=C}$
E5a	6.26 5.19 (12.0)	141.2 105.2	−1.93 −56.68 (−179.4)	2128 1665
Z5a	6.16 4.43 (6.0)	140.1 103.2	0.61 −56.76 (−179.4)	2124 1659
E5b	6.26 5.21 (12.0)	139.4 118.6	−1.6 −56.8 (−180.1) (^2J = 11.6)	2128 1657
Z5b	6.06 4.29 (6.0)	137.6 118.0	1.1 −56.97 (−178.9)	[b]
E5c	[c] 6.37 (12.5)	142.9 113.1	0.96 −56.4 (−180.9)	2133 1645
Z5c	6.37 5.22 (6.9)	141.4 109.7	4.4 −56.3 (−180.2) (^2J = 12.5)	2137 1640
E5d	6.25 5.35 (12.1)	138.8 122.5	−1.2 −56.8 (−180.2)	2132 1657
Z5d	6.05 4.23 (7.5)	[b]	[b]	[b]
5e	6.09	135.2 116.7	−0.5 −56.7 (−179.9)	2135 1679
5f	[c]	140.4 124.8	3.9 −56.9 (−179.4)	2129 1628
5g	4.64	150.6 104.1	−8.4 −56.7 (−178.2)	2132 1664

[a] $^1J_{Si-H}$ unless otherwise noted. Coupling constants were determined by observation of the ^{29}Si satellites in the ^1H NMR spectra or from coupled ^{29}Si spectra. The signs of J_{Si-H} were not determined, but were assumed to be negative for ^1J and positive for ^2J (see Ref. [8]). *Si*–H signals are upfield. [b] Data not available. [c] Peaks were not observed presumably because of overlap with aromatic signals.

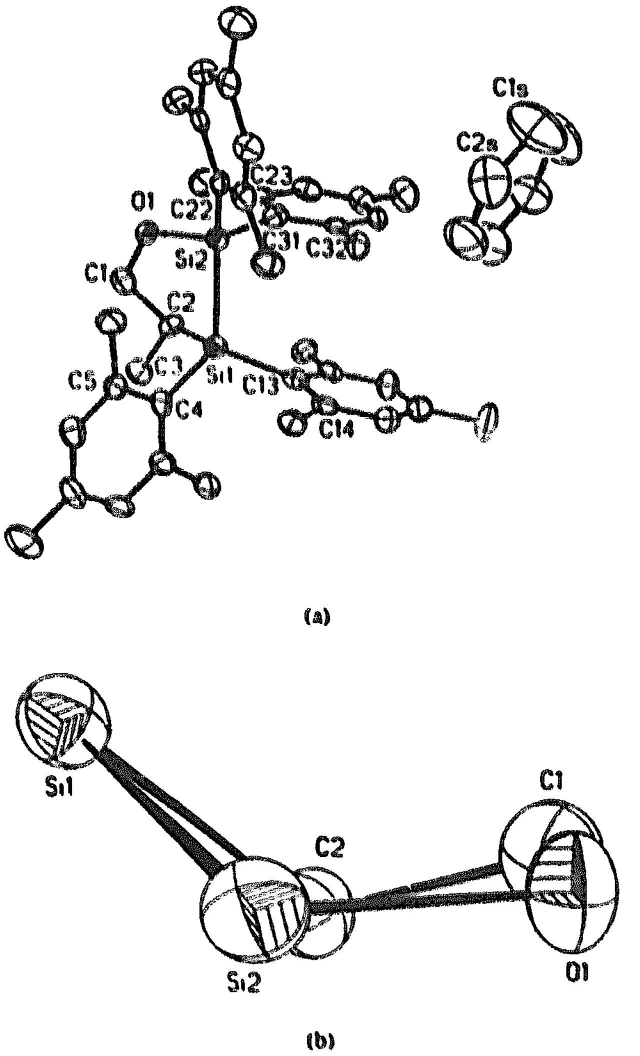
ratio was observed, with that of R′ = ^{t}Bu, where adduct formation is nearly completely selective for enol ether.

Applying the transition state model introduced for intramolecular proton abstraction to give **5** (Fig. 4) [2], it is clear that for large R′ groups enol ether formation should be highly E selective. Steric interactions between

Table 3
Selected NMR (ppm) data for **6**: ^1H, ^{13}C and ^{29}Si resonances of the central ring

	^1H (^2J or ^3J, Hz) [a]	^{13}C	^{29}Si
6a	4.31 (−10.4, 7.1) 3.78 (12.7, −10.4)	72.1 30.5	4.3 −18.7
6b	4.62 (−10.2, 6.5) 4.18 (12.6, −10.1) 2.70 (12.6, 6.5, 1.6)	65.4 41.2	3.4 −22.7
6c	4.61 (−10.5, 6.5) 4.42 (12.8, −10.5) 4.13 (12.8, 6.5)	71.2 44.8	4.4 −19.9
6d	4.76 (−10.3, 7.4) 4.40 (12.5, −10.3) 2.97 (12.5, 7.4)	68.5 47.9	6.4 −22.6
6e	3.93	80.3 33.4	8.2 −5.4
6g	4.41	72.5 33.3	4.3 −3.2

[a] The sign of the methylene ^2J was not measured, but was assumed to be negative. See L.M. Jackman and S. Sternhell, *Applications of Nuclear Magnetic Resonance in Organic Chemistry*; Pergamon Press, New York, 1969, p. 270.



(a)

(b)

Fig. 1. (a) Thermal ellipsoid drawing of **6a** · benzene. Bond distances (Å) and angles (deg) of the central ring: Si(1)–Si(2), 2.407(3); Si(1)–C(2), 1.924(7); Si(2)–O(1), 1.662(5); O(1)–C(1), 1.441(8); C(1)–C(2), 1.535(9); C(2)–Si(1)–Si(2), 83.0(2); O(1)–Si(2)–Si(1), 91.8(2); C(1)–O(1)–Si(2), 118.6(4); O(1)–C(1)–C(2), 113.9(6); C(1)–C(2)–Si(1), 103.7(5). (b) Conformation of the central ring with torsional angle Si(2)–O(1)–C(1)–C(2) −17.8(8)°.

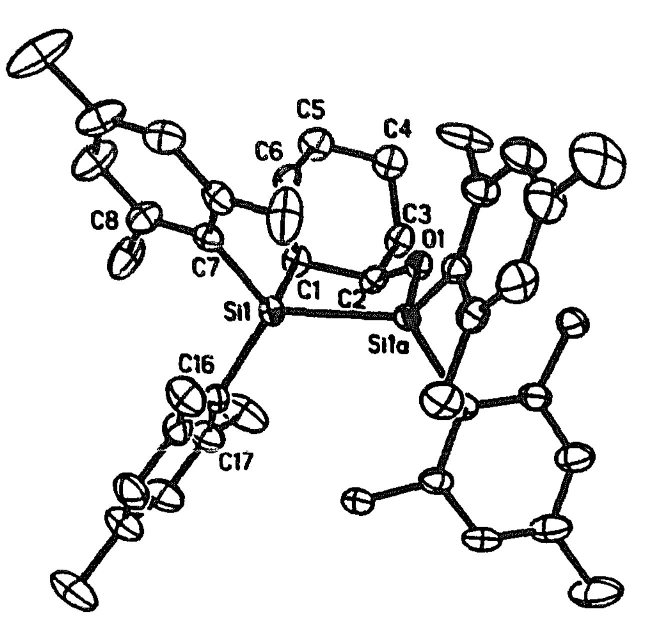


Fig. 2. Thermal ellipsoid drawing of **6g**. Bond distances (Å) and angles (deg) of the central ring: Si(1)–Si(1)′, 2.461(3); O(1)–Si(1)′, 1.601(11); Si(1)–C(1), 1.99(2); O(1)–C(2), 1.438(11); C(1)–C(2), 1.54(2); C(1)–Si(1)–Si(1)′, 86.8(6); O(1)–Si(1)′–Si(1), 91.2(5); C(2)–O(1)–Si(1)′, 116.0(10); O(1)–C(2)–C(1), 109.3(10); C(2)–C(1)–Si(1), 106.6(10).

the epoxide substituent and the mesityl rings would inhibit Z enol ether formation. In fact, the energy of transition state A of Fig. 4 should be little affected by the increasing size of R′, clearly making it the lowest energy pathway for adduct formation from bulky mono-substituted epoxides.

While the **E5c/Z5c** ratio fits into the trend defined by the mono-alkyl substituted epoxides based on *A* values, the **5/6** ratio does not. This may be a reflection of conjugation between the phenyl group and the sp^2 center of the intermediate. The effective size of the epoxide substituent would thus be reduced, since the approach of the bulky silicon center would be perpendicular to the plane of the phenyl ring. Independent evidence for the importance of conjugation is provided by the time for complete reaction of **1** with styrene oxide, which took less than 1 h, vs. that for the mono-alkyl substituted epoxides, which required several days. In a very qualitative way, this suggests that epoxide

Table 4
Summary of crystal data collection for **6a** and **6g**

	6a	**6g**
Empirical formula	$C_{45}H_{56}OSi_2$	$C_{42}H_{54}OSi_2$
Formula weight	669.1	631.0
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$C2/c$
a (Å)	15.431(4)	11.120(13)
b (Å)	13.975(5)	20.834(3)
c (Å)	17.861(6)	16.495(6)
α (deg)	90	90
β (deg)	94.56(2)	107.29(7)
γ (deg)	90	90
V (Å^3)	3840(2)	3649(5)
Z	4	4
d_{calc} (g cm^{-3})	1.157	1.149
Crystal size (mm^3)	0.2 × 0.2 × 0.1	0.6 × 0.3 × 0.3
Abs. coeff. (mm^{-1})	0.126	1.102
F(000)	1448	1368
T (°C)	−100(2)	−160(2)
2θ range (deg)	3.4–45.0	4.0–114.0
Scan type	θ–2θ	ω
Scan speed (deg min^{-1})	4.0–60.0	2.0–4.0
Scan range ω (deg)	1.16	0.90
Index ranges	$0 \leq h \leq 16$	$0 \leq h \leq 12$
	$0 \leq k \leq 15$	$0 \leq k \leq 22$
	$-19 \leq l \leq 19$	$-17 \leq l \leq 17$ + Friedel
No. of reflections collected	5245	5197
No. of independent reflections	5025 (R_{int} = 11.1%)	2461 (R_{int} = 4.3%)
No. of observed data $I > 2\sigma(I)$	2471	2135
Final R (observed data) (%)	8.03	6.48
Final wR (all data) (%)	22.55	17.38
Goodness of fit	1.069	1.090
Largest and mean Δ/σ	−1.337/0.027	0.006/0.001
Data-to-parameter ratio	11.2	10.5
Largest difference peak/hole (e Å^{-3})	0.380/−0.352	0.510/−0.43

Table 5
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **6a**

Atom	x	y	z	U_{eq} [a]
Si(1)	7506(1)	−355(2)	9230(1)	25(1)
Si(2)	8412(1)	1010(1)	9031(1)	24(1)
O(1)	9071(3)	749(3)	9785(3)	27(1)
C(1)	8770(5)	96(6)	10332(4)	34(2)
C(2)	7780(4)	−42(5)	10271(4)	26(2)
C(3)	7567(5)	−754(5)	10883(4)	35(2)
C(4)	7863(5)	−1660(5)	9183(4)	26(2)
C(5)	8690(5)	−1961(5)	8986(4)	27(2)
C(6)	8910(5)	−2919(6)	9026(4)	35(2)
C(7)	8365(5)	−3616(6)	9259(4)	34(2)
C(8)	7548(5)	−3314(5)	9446(4)	34(2)
C(9)	7291(5)	−2362(5)	9411(4)	30(2)
C(10)	9350(5)	−1279(6)	8718(4)	36(2)
C(11)	8638(6)	−4648(6)	9321(5)	54(3)
C(12)	6372(5)	−2162(6)	9615(5)	38(2)
C(13)	6371(4)	−178(5)	8755(4)	24(2)
C(14)	6179(5)	−570(5)	8036(4)	26(2)
C(15)	5405(5)	−315(5)	7608(4)	29(2)
C(16)	4807(5)	318(6)	7882(4)	34(2)
C(17)	4997(5)	668(6)	8603(4)	33(2)
C(18)	5746(5)	436(5)	9041(4)	29(2)
C(19)	6736(5)	−1289(5)	7676(4)	33(2)
C(20)	4000(5)	591(7)	7406(5)	58(3)
C(21)	5835(5)	835(5)	9829(4)	32(2)
C(22)	9152(4)	1370(5)	8278(4)	24(2)
C(23)	9091(4)	1036(5)	7538(4)	27(2)
C(24)	9625(5)	1399(5)	7017(4)	31(2)
C(25)	10244(5)	2099(6)	7193(5)	33(2)
C(26)	10321(5)	2422(6)	7930(4)	35(2)
C(27)	9786(5)	2086(5)	8457(4)	25(2)
C(28)	8448(5)	274(5)	7256(4)	36(2)
C(29)	10799(5)	2534(6)	6619(4)	44(2)
C(30)	9898(5)	2555(6)	9215(4)	39(2)
C(31)	7670(5)	2062(5)	9209(4)	26(2)
C(32)	7013(4)	2297(5)	8651(4)	25(2)
C(33)	6370(5)	2958(5)	8768(4)	29(2)
C(34)	6362(5)	3448(5)	9447(5)	36(2)
C(35)	7025(5)	3263(5)	9976(5)	35(2)
C(36)	7673(5)	2586(3)	9895(4)	28(2)
C(37)	6976(5)	1817(5)	7881(4)	30(2)
C(38)	5656(5)	4155(6)	9577(5)	51(2)
C(39)	8325(5)	2463(6)	10557(4)	38(2)
C(1S)	8655(8)	1576(8)	2634(6)	85(4)
C(2S)	8855(6)	605(7)	2722(5)	56(3)
C(3S)	8461(6)	125(7)	3246(6)	62(3)
C(4S)	7873(6)	555(7)	3674(6)	59(3)
C(5S)	7682(6)	1484(7)	3594(5)	49(2)
C(6S)	8076(8)	2000(8)	3071(6)	82(4)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

ring-opening is most likely the rate-determining step for the epoxide series a–d, and that stabilization of the developing cation is important in the transition state and presumably in the intermediate.

Isobutylene oxide, like some of the bulkier monosubstituted epoxides, showed a drop off in the amount of **6**, exhibiting a **5**/**6** ratio more comparable with that of the iso-propyl substituted epoxide than with the

Table 6
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **6g** [a]

Atom	x	y	z	U_{eq}
Si(1)	8842(1)	867(1)	2307(1)	21(1)
C(1)	8947(20)	−89(7)	2316(13)	22(4)
C(2)	10300(8)	−263(3)	2839(4)	24(2)
C(3)	10604(7)	−973(3)	2816(5)	31(2)
C(4)	10329(7)	−1218(3)	1904(5)	36(2)
C(5)	8990(7)	−1076(3)	1405(5)	37(2)
C(6)	8704(6)	−354(3)	1403(4)	26(2)
O(1)	11176(14)	108(5)	2543(9)	22(2)
C(7)	7809(3)	1030(2)	1171(2)	24(1)
C(8)	6588(3)	759(2)	935(2)	33(1)
C(9)	5802(4)	831(2)	115(2)	46(1)
C(10)	6141(4)	1179(2)	−498(2)	44(1)
C(11)	7314(4)	1452(2)	−267(2)	34(1)
C(12)	8147(3)	1387(2)	547(2)	28(1)
C(13)	6047(4)	413(2)	1559(2)	48(1)
C(14)	5242(5)	1271(3)	−1378(3)	75(2)
C(15)	9378(4)	1738(2)	719(3)	54(1)
C(16)	7995(3)	1253(2)	3027(2)	24(1)
C(17)	7696(3)	941(2)	3704(2)	34(1)
C(18)	7006(4)	1260(2)	4155(2)	43(1)
C(19)	6577(4)	1882(2)	3971(3)	44(1)
C(20)	6902(4)	2191(2)	3330(2)	40(1)
C(21)	7604(3)	1901(2)	2866(2)	29(1)
C(22)	8092(5)	260(2)	3973(3)	35(1)
C(23)	5813(5)	2218(2)	4471(3)	66(1)
C(24)	7952(4)	2308(2)	2216(2)	38(1)

[a] The Si_2Mes_4 unit sits on a two-fold crystallographic axis with the oxygen and cyclohexyl ring disordered 1 : 1.

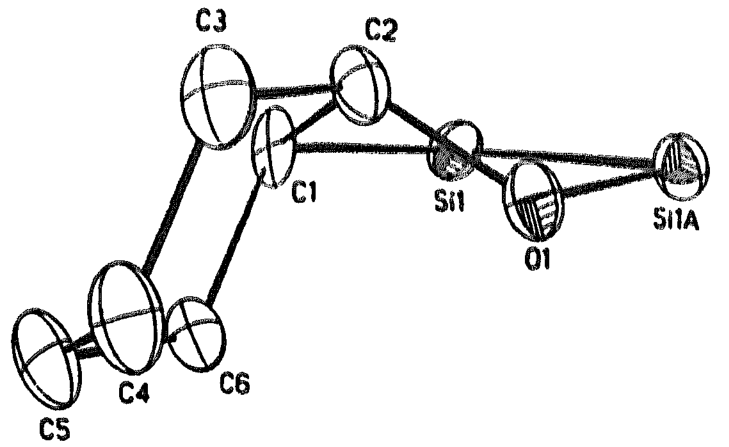
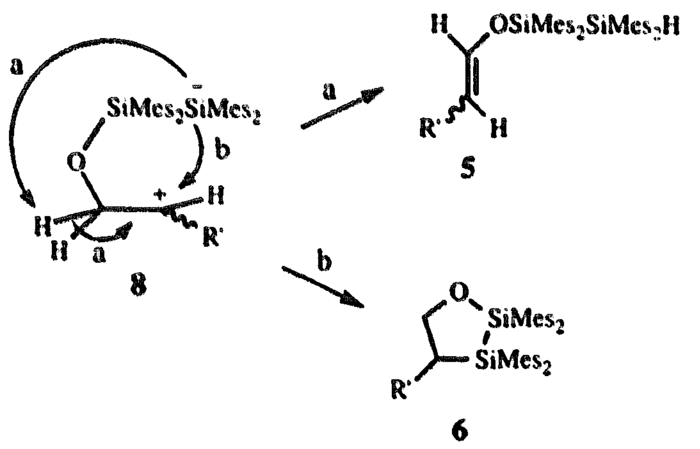


Fig. 3. Conformations of the five- and six-membered rings of **6g** with torsional angle C(1)–Si(1)–Si(1)′–O(1) + 8.7(1.5)°.



Scheme 1.

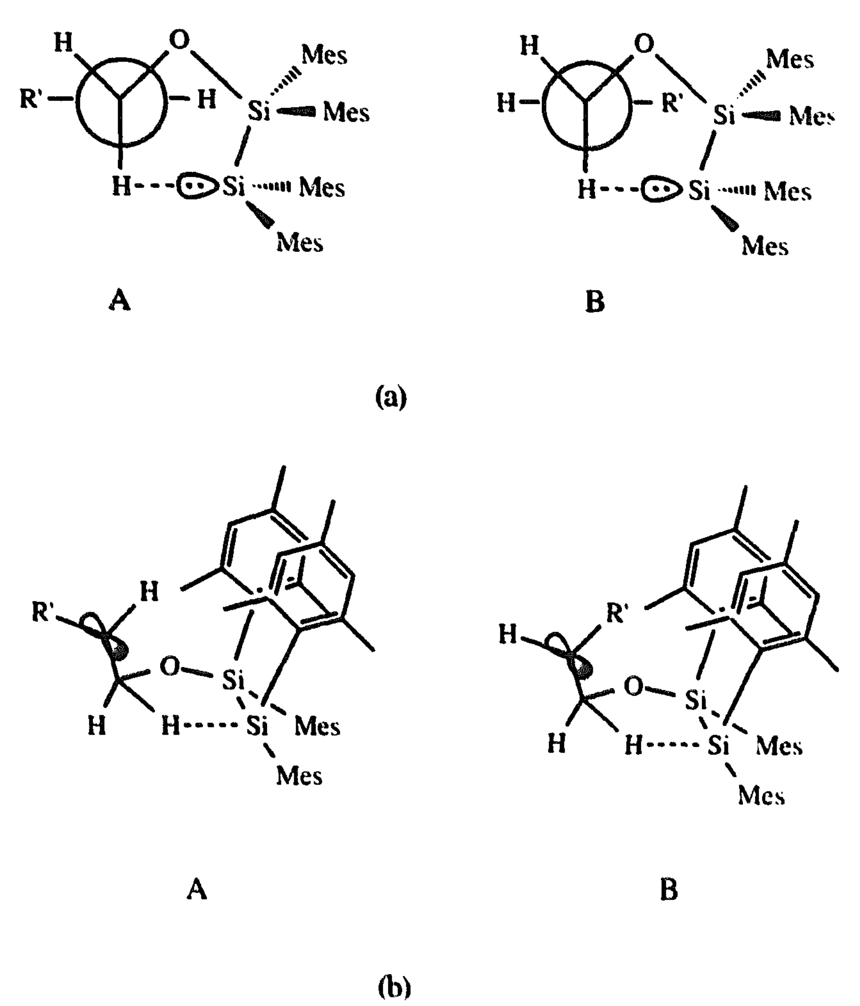


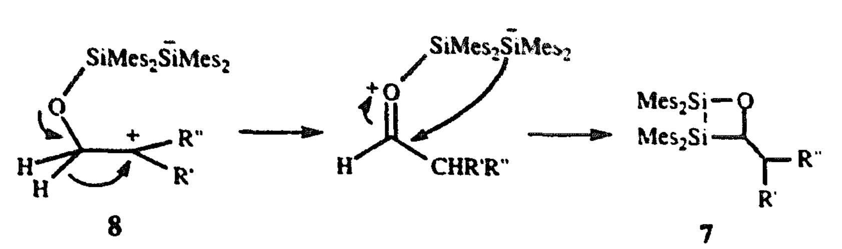
Fig. 4. Transition state models for formation of 5.

tert-butyl substituted one. A similar reactivity trend was observed for S_N2 displacement at alkyl bromides. Because of relative steric requirements, iso-propylbromide was more reactive than neo-pentylbromide towards backside attack, and was similar in reactivity to iso-butylbromide [16].

1,1-Diphenylethylene oxide gave complete chemoselectivity for enol ether formation (considering adduct formation only). Again, sterics likely dictate adduct distribution since the benzhydryl center might be expected to be the most hindered for five-membered ring closure.

The cyclohexene oxide 5/6 ratio is comparable with that from the iso-propyl substituted epoxide. A similar steric analysis is unwarranted here, since the rates of reactions of cyclohexyl compounds are known to depend not only on sterics but also on changes in ring angles and their effects on torsional strain [17].

As can be seen from Table 1, the deoxygenation pathway represents an important, although not dominant, reaction mode. Little variation was observed in the product ratios within the mono-substituted epoxide series, but an increase in deoxygenation was noted for epoxides e–g. Because of the estimative nature of the deoxygenation ratios and the uncertainty regarding the immediate precursor to deoxygenation products, it is difficult to draw any conclusions about the mechanism of oxygen abstraction. The data was included mainly for the sake of completeness and for future analysis.



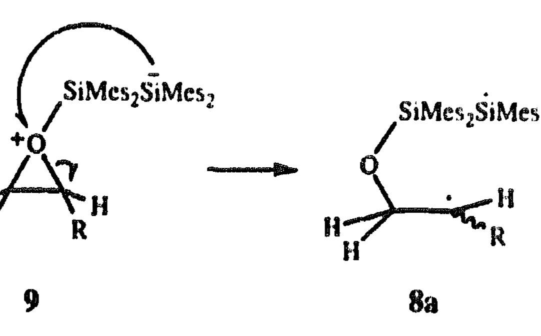
Scheme 2.

2.4. Formation of 7 and alternate precursor to 5 and 6

Recall that for the 1,1-disubstituted epoxides very small amounts of four-membered ring products 7 were observed. Since the epoxides do not thermally undergo rearrangement to carbonyl compounds at the reaction temperature, a most likely pathway for four-ring formation is by hydride migration from intermediate 8 before a final ring closure (Scheme 2). The 1,2-shift is a known pinacolic rearrangement that epoxides exhibit, usually under acidic conditions, and is normally rationalized with a cationic intermediate [4,18].

Considering the minute yields of 7 from reactions of epoxides e and f, the rearrangement process, in practical terms, is nearly non-existent for the epoxide–disilene reactions in general. Such an outcome could be used as evidence against a dipolar intermediate, and hence in favor of a pathway involving a diradical, (**8a**) (Scheme 3).

A similar argument has been used to support a radical pathway in many transition metal–epoxide reactions [19,20]. These are normally explained by an initial coordination of the metal and epoxide followed by a one electron oxidation of the metal. The resulting carbon–oxygen bond homolysis gives rise to a carbon-centered radical [20]. In the present case an initial coordination of **1** to the epoxide would likely induce a polarization of the disilene π electrons, giving the terminal silicon significant silyl anion character (Scheme 3). Complex **9** may then be viewed as a single electron donor/acceptor system. Silyl anions are known single electron transfer agents [21], and although stilbene oxides have a high oxidation potential [22], interaction with the Lewis acid could facilitate their reduction. A classic demonstration of this latter point is the drastic decrease in the reduction potential of 1,4-diazines upon complexation with electrophiles [23]. The resulting di-



Scheme 3.

radical **8a** could then give products via two common radical–radical reactions, disproportionation to give **5** and combination to give **6**.

Since the present results do not allow a conclusive choice between the two pathways, more work must be done to resolve this issue.

3. Experimental section

3.1. General procedures

All solvents for reactions of tetramesityldisilene (**1**) were distilled from sodium benzophenone ketyl under nitrogen and degassed prior to use. The disilene was prepared by the literature method [24]. Propylene, isobutylene, cyclohexene and styrene oxides were commercial products. The first three were distilled and dried over sodium sulfate before use, while styrene oxide was used without further purification. 3-Methyl- and 3,3-dimethyl-1,2-epoxybutanes (epoxides b and d) were made from the corresponding alkenes by oxidation with *m*-chloroperoxybenzoic acid using the simplified procedure of Pasto and Combo [25]. 1,1-Diphenylethylene oxide was prepared by the method of Corey and Chaykovsky [26]. ^{1}H and ^{13}C NMR spectra were referenced to the residual solvent resonances which were calibrated against tetramethylsilane. ^{13}C assignments were confirmed using DEPT pulse sequences. ^{29}Si NMR spectra were referenced to external tetramethylsilane. ^{29}Si data on **5**, **6a** and **7e** were obtained with INEPT pulse sequences, while for **6b–g** straight acquisition with inverse-gated decoupling was used. $^1J_{Si-H}$ values for **5** were determined by observation of the ^{29}Si satellites in the ^{1}H NMR spectra, or from coupled INEPT ^{29}Si spectra.

3.2. Reactions of 1 with epoxides, general procedures

All reactions were carried out under an inert atmosphere. Three different scaled reactions were conducted for each epoxide, categorized below for individual epoxides as (a) semi-preparative (100–200 mg, 0.15–0.30 mmol of **1** · 2THF/1.5 equiv. of epoxide/25 ml of benzene/reflux) to determine practical isolated yields of compounds **5** and **6**, (b) preparative (600–1200 mg, 0.9–1.8 mmol of **1** · 2THF/ca. 3 equiv. of epoxide/25 ml of benzene at reflux) to generate bulk quantities of products for characterization, and (c) NMR (15 mg, 0.022 mmol of **1** · 2THF/1 ml of a 0.04 M stock solution of epoxide, 1.8 equiv. in benzene-d_6 in sealed NMR tubes/85°C) to determine product ratios unaffected by losses incurred during isolation. Semi-preparative work-up consisted of concentration in vacuo followed by preparative TLC on 20 × 20 cm^2 commercial preparative plates (Whatman, 60 Å, 1000 μm thickness) with elution in 3% diethyl ether in hexanes. Only yields of **5** and **6** are reported. Disilene hydrolysis product generally made up 10–20% of the product mixture, while HOSiMes$_2$OSiMes$_2$H, the hydrolysis product of **4** [27], was 5–10%. The general order of elution from highest R_f to lowest was **5**, **6**, HOSiMes$_2$SiMes$_2$H, HOSiMes$_2$OSiMes$_2$H. The **5g**/**6g** mixture eluted ahead of the hydrolysis products but did not separate by TLC. In general, preparative work-up consisted of concentration in vacuo, flash chromatography to isolate the **5**/**6** mixtures (elution with 1% diethyl ether in hexanes) and selective crystallization and/or preparative TLC. Ratios of **5** to **6** for the NMR scale reactions were determined by integration of the ^{1}H spectra. Determination of the amounts of deoxygenation was accomplished either by integration of **5** (E isomer for epoxide reactions a, b, and d) vs. **4** in the ^{29}Si NMR spectra (method A) or by integration of the alkene resonances in the ^{1}H spectra (method B). For epoxides a–d, the reported **5**/**6** and **5**/(**4** or alkene) ratios correspond to (**E5** + **Z5**)/product.

3.3. Reaction of 1 with propylene oxide

(a) From the semi-preparative scale run (200 mg of **1** · 2THF), 77.6 mg (44.4%) of a 1.5 : 1 **E5a** to **Z5a** mixture and 33 mg (18.9%) of **6a** were isolated. (b) Preparative TLC was used to separate **5** and **6** isolated from the preparative-scale reaction. The E and Z isomers of **5a** were quantitatively separated by chromatography on a 5 × 20 cm^2 preparative plate containing 10% w/w silver nitrate in silica gel (MN Kieselgel G/UV 254) eluted in 5% diethyl ether in hexanes. The E isomer, which had a higher R_f, was recrystallized from hexanes as a colorless solid. ^{1}H NMR (C_6D_6, 200 MHz): δ 6.73, 6.66 (2 s, 8 H, mesityl H); 6.26 (dq, *J* = 12.0, 1.0 Hz, 1 H, α vinyl H); 5.65 (s, 1 H, Si–H); 5.19 (dq, *J* = 12.0, 6.8 Hz, 1 H, β vinyl H); 2.42, 2.34 (2 s, 24 H, *o*-methyl H); 2.10, 2.06 (2s, 12 H, *p*-methyl H); 1.39 (dd, *J* = 6.8, 1.0 Hz, 3 H, vinyl methyl H). ^{13}C NMR (C_6D_6, 125.76 MHz): δ 145.9, 145.3 (aromatic C); 141.2 (α vinyl C); 139.9, 139.2, 132.7, 131.5, 130.3, 129.5 (aromatic C); 105.2 (β vinyl C); 24.9, 24.4 (*o*-methyl C); 21.6, 21.5 (*p*-methyl C); 12.9 (vinyl methyl C). ^{29}Si NMR (C_6D_6, 53.67 MHz): δ −1.93; −54.68 (J_{Si-H} = −179.4 Hz). MS (EI) for $C_{39}H_{50}OSi_2$: calculated *m/e* 590.3400, found 590.3374. IR (cm^{-1}, Nujol): 2128.3 (Si–H); 1665.4, 1601.8. M.p.: 191–193°C.

Z5a was recrystallized from hexanes as a colorless solid. ^{1}H NMR (C_6D_6, 300 MHz): δ 6.72, 6.66 (2 s, 4 H each, mesityl H); 6.16 (dq, *J* = 6.1, 1.6 Hz, 1 H, α vinyl H); 5.64 (s, 1 H, Si–H); 4.43 (dq, *J* = 6.8, 6.0 Hz, 1 H, β vinyl H); 2.39, 2.34 (2 s, 24 H, *o*-methyl H); 2.10, 2.06 (2 s, 12 H, *p*-methyl H); 1.77 (dd, *J* = 6.8, 1.6 Hz, 3 H, vinyl methyl H). ^{13}C (C_6D_6, 125.76 MHz):

δ 145.4 144.9 (aromatic C); 140.1 (α vinyl C); 139.4, 138.8, 132.0, 130.9, 129.7, 128.8 (aromatic C); 103.2 (β vinyl C); 24.6, 24.1 (*o*-methyl C) 21.1, 21.0 (*p*-methyl C); 10.5 (vinyl methyl C). ^{29}Si NMR (C_6D_6, 53.67 MHz): δ 0.61; −56.76 ($J_{Si-H} = -179.4$ Hz). MS (EI) for $C_{39}H_{50}OSi_2$: calculated *m/e* 590.3400, found 590.3388. IR (cm^{-1}, Nujol): 2124.5 (Si–H); 1658.7, 1601.8. M.p.: 239–243°C.

6a was recrystallized from benzene as a colorless solid. ^{1}H NMR (C_6D_6, 200 MHz): δ 6.74 (s, 4 H, mesithyl H); 6.60 (s, 2 H, mesityl H); 4.31 (dd, $J = -10.4, 7.1$ Hz, 1 H, methylene H); 3.78 (dd, $J = 12.7, -10.4$ Hz, 1 H, methylene H); 2.83 (s, 6 H, *o*-methyl H); 2.63 (m, 1 H, five-ring methine H); 2.40 (br s, 6 H, *o*-methyl H); 2.08, 2.06 (2 s, 18 H, *p*- *o*-methyl H); 0.95 (d, $J = 6.9$ Hz, 3 H, five-ring methyl H). ^{13}C (C_6D_6, 125.76 MHz): δ 145.1. 144.9, 144.8, 139.5, 139.2, 138.8, 138.5, 134.5, 134.2, 132.5, 132.4, 130.2, 130.0, 129.6, 128.8 (aromatic C); 72.1 (methylene C); 30.5 (methine C); 26.6, 26.1, 25.7 (*o*-methyl C); 21.6, 21.5, 21.4 (*p*-methyl C); 13.8 (five-ring methyl C). ^{29}Si NMR (C_6D_6, 53.67 MHz): δ 4.34; −18.66. MS (EI) for $C_{39}H_{50}OSi_2$ (M^+-H): calculated *m/e* 589.3322, found 589.3318. M.p.: 115–120°C.

(c) The ratio of **E5a** to **Z5a** to **6a** was 1.3 : 1 : 1, while the ratio of **5** to **4** was estimated at 6 : 1 by method A.

*3.4. Reaction of **1** with 3-methyl-1,2-epoxybutane*

(a) From the semi-preparative scale run (160 mg, 0.24 mmol of **1** · 2THF), 66.6 mg (44.9%) of a 2.5 : 1 **E5b** to **Z5b** mixture and 15.8 mg (10.6%) of **6b** were isolated. (b) Preparative TLC was used to separate **5** and **6** isolated from the preparative-scale reaction. Several crops of **5b** enriched in the E isomer were obtained by recrystallization of the E/Z mixture from hexanes. Two subsequent recrystallizations provided pure **E5b** as a colorless solid. ^{1}H NMR (C_6D_6, 300 MHz): δ 6.73, 6.66 (2 s, 4 H each, mesityl H); 6.26 (d, $J = 12.0$ Hz, 1 H, α vinyl H); 5.65 (s, 1 H, Si–H); 5.21 (dd, $J = 12.0, 8.0$ Hz, 1 H,. β vinyl H); 2.43 (br s, *o*-methyl H); 2.34 (s, 12 H, *o*-methyl H); 2.10, 2.06 (2 s, 12 H, *p*-methyl H); 0.93 (d, $J = 6.8$ Hz, 6 H, iso-propyl methyl H). ^{13}C NMR (C_6D_6, 125.76 MHz): δ145.9, 145.3, 139.9 (aromatic C); 139.3 (α vinyl C); 139.2, 132.7, 131.5, 130.2, 129.5 (aromatic C); 118.6 (β vinyl C); 28.1 (iso-propyl methine C); 24.9, 24.6, 24.5 (*o*-methyl C, iso-propyl methyl C); 21.6, 21.5 (*p*-methyl C). ^{29}Si NMR (C_6D_6 99.36 MHz): δ −1.60 ($J_{Si-H} = 11.6$ Hz); −56.80 ($J_{Si-H} = -180.1$ Hz). MS (EI) for $C_{41}H_{54}OSi_2$: calculated *m/e* 618.3713, found 618.3696. IR (cm^{-1}, Nujol): 2127.6 (Si-H); 1657.0, 1603.9. MP: 187–188°C. Anal. Found: C, 79.20; H, 8.77. $C_{41}H_{54}OSi_2$ Calc.: C, 79.55; H, 8.79%.

The mother liquor from the first recrystallization was concentrated, and the residue recrystallized from diethyl ether to give a mixture enriched (ca. 80%) in **Z5b**. ^{1}H NMR (C_6D_6, 300 MHz): δ 6.72, 6.66 (2 s, mesityl H); 6.06 (d, $J = 6.0$ Hz, 1 H, α vinyl H); 5.64 (s, $J_{Si-H} = -178.9$ Hz, 1 H, Si–H); 4.29 (dd, $J = 9.8, 6.0$ Hz, 1 H, β vinyl H); 3.17 (m, 1 H, iso-propyl methine H); 2.41 (br s, *o*-methyl H); 2.34 (s, *o*-methyl H); 2.08, 2.07 (2 s, *p*-methyl H); 1.06 (d, $J = 6.5$ Hz, 6 H, iso-propyl methyl H). ^{13}C NMR (C_6D_6, 125.76 MHz): δ 145.9, 145.3, 139.7, 139.3 (aromatic C); 137.6 (α vinyl C); 132.6, 131.5, 130.3, 129.5 (aromatic C); 118.0 (β vinyl C); 25.1 (iso-propyl methine C); 24.6, 24.5, 24.4 (*o*-methyl C, iso-propyl methyl C); 21.6, 21.5 (*p*-methyl C). ^{29}Si NMR (C_6D_6, 99.36 MHz): δ 1.1; −56.97.

Compound **6b** was recrystallized from hexanes as a colorless solid. ^{1}H NMR (C_6D_6, 200 MHz): δ 6.74, 6.60 (2 br s, mesityl H); 4.62 (dd, $J = -10.2, 6.5$ Hz, 1 H, methylene H); 4.18 (dd, $J = 12.6, -10.1$ Hz, 1 H, methylene H); 2.83 (br s, *o*-methyl H); 2.70 (ddd, $J = 12.6, 6.5, 1.6$ Hz, five-ring methine H); 2.49 (sept d, $J = 6.8, 1.6$ Hz, iso-propyl methine H); 2.09, 2.08, 2.06, 2.06 (4 s, *p*-methyl H); 1.09 (d, $J = 6.8$ Hz, 3 H, iso-propyl methyl H); 0.42 (d, $J = 6.8$ Hz, 3 H, iso-propyl methyl H). ^{13}C ($CDCl_3$, 125.76 MHz): δ 144.8, 139.5, 139.2, 138.9, 138.3, 134.5, 134.4, 134.2, 132.6, 132.5, 130.1, 129.9 (aromatic C); 65.4 (methylene C); 41.2 (five-ring methine C); 29.1 (iso-propyl methine C); 26.6, 26.0 (*o*-methyl C); 21.9, 21.8, 21.7 (*p*-methyl C); 18.7 (iso-propyl methyl C). ^{29}Si NMR (C_6D_6, 99.36 MHz): δ 3.42; −22.73. MS (EI) for $C_{41}H_{54}OSi_2$: calculated *m/e* 618.3713, found 618.3713. M.p.: 231–232°C.

(c) The ratio of **E5b** to **Z5b** to **6b** was 3.4 : 1.4 : 1, while the ratio of **5** to **4** was estimated at 4 : 1 by method A.

*3.5. Reaction of **1** with styrene oxide*

All reactions were protected from light. (a) From the semi-preparative scale run (100 mg, 0.15 mmol of **1** · 2THF), 55.4 mg (56.6%) of a 9 : 1 **E5c** to **Z5c** mixture and 20 mg (20.4%) of **6c** were isolated. (b) **6c** crystallized from a diethyl ether solution of **5**/**6**, isolated from the preparative run. A second recrystallization from diethyl ether gave pure **6c** as a white powder. ^{1}H NMR (C_6D_6, 300 MHz): δ 6.98–6.26 (m, 13 H, aromatic H); 4.61 (dd, $J = -10.5, 6.5$ Hz, 1 H, methylene H); 4.42 (dd, $J = 12.8, -10.5$ Hz, 1 H, methylene H); 4.13 (dd, $J = 12.8, 6.5$ Hz, 1 H, five-ring methine H); 3.06, 2.83, 2.13, 2.12, 2.10, 2.09, 2.04, 1.65, 1.62 (4 br s, 5 sharp s, 34 H, methyl H). ^{13}C ($CDCl_3$, 75.40 MHz): δ 145.2, 144.8, 141.5, 139.7, 139.4, 138.6, 134.0, 133.7, 133.5, 131.8, 130.1, 129.9, 129.3, 128.5, 126.1 (aromatic C); 71.2 (methylene C); 44.8 (five-ring methine C); 26.2, 26.0 (*o*-methyl C); 21.9, 21.8, 21.6 (*p*-methyl C). ^{29}Si NMR (C_6D_6, 99.36 MHz): δ 4.40; -19.90. MS (EI) for $C_{44}H_{52}OSi_2$: calculated *m/e* 652.3557, found 652.3543. M.p.: 268–270°C.

The mother liquor from the recrystallization was concentrated, and **5c** was isolated by preparative TLC. A sample enriched in the E isomer (94%) was obtained by silver nitrate–silica gel chromatography (same procedure as for **5a** separation). Attempts to crystallize **E5c** were unsuccessful. ^{1}H NMR (C_6D_6, 300 MHz): δ 7.13 (m, phenyl H); 7.10–6.84 (m, 4 H, aromatic H, β vinyl H); 6.71, 6.65 (2 s, 4 H each, mesityl H); 6.37 (d, $J = 12.5$ Hz, 1 H, β vinyl H); 5.69 (s, $J_{Si-H} = -180.9$ Hz, 1 H, Si–H); 2.41, 2.34 (2 s, 24 H, *o*-methyl H); 2.10, 2.05 (2 s, 12 H, *p*-methyl H). ^{13}C NMR (C_6D_6, 75.40 MHz): δ 145.9, 145.3 (aromatic C); 142.9 (α vinyl C); 140.2, 139.4, 137.6, 132.2, 131.1, 130.3, 129.6, 129.4, 126.4, 126.0 (aromatic C); 113.1 (β vinyl C); 24.9, 24.6 (*o*-methyl C); 21.6, 21.5 (*p*-methyl C). ^{29}Si NMR (C_6D_6, 99.36 MHz): δ 0.96; -56.40. MS (EI) for $C_{44}H_{52}OSi_2$: calculated *m/e* 652.3557, found 652.3568. IR (cm^{-1}, Nujol): 2133.1 (Si–H); 1645.2, 1603.7.

A benzene-d_6 solution of **E5c** (ca. 50 mg in 2.5 ml of solvent) was photolyzed with light of $\lambda = 350$ nm and monitored by ^{1}H NMR for generation of the Z isomer. After 40 h, a photostationary state was reached with a Z to E ratio of 3:1. The solution was concentrated to dryness, and the residue taken up in diethyl ether from which solid **Z5c** formed as a white powder. ^{1}H NMR (C_6D_6, 300 MHz): δ 7.74 (d, $J = 8$ Hz, 2 H, phenyl H); 7.25 (t, $J = 8$ Hz, 1 H, phenyl H); 7.12 (t, phenyl H); 6.72, 6.65 (2s, 4 H each, mesityl H); 6.37 (d, $J = 6.9$ Hz, 1 H, α vinyl H); 5.69 (s, $J_{Si-H} = -180.2$ Hz, 1 H, Si–H); 5.22 (d, $J = 6.9$ Hz, 1 H, β vinyl H); 2.34, 2.32 (2 s, 24 H, *o*-methyl H); 2.11, 2.06 (2 s, 12 H, *p*-methyl H). ^{13}C NMR (C_6D_6, 125.76 MHz): δ 145.9, 145.5 (aromatic C); 141.4 (α vinyl C); 140.2, 139.4, 136.5, 132.2, 131.0, 130.3, 130.3, 129.6, 129.6, 126.6 (aromatic C); 109.7 (β vinyl C); 25.4, 24.9 (*o*-methyl C); 21.6, 21.5 (*p*-methyl C). ^{29}Si NMR (C_6D_6, 99.36 MHz): δ 4.39; -56.34. MS (EI) for $C_{44}H_{52}OSi_2$: calculated *m/e* 652.3557, found 652.3544. IR (cm^{-1}, Nujol): 2137.0 (Si–H); 1640.4, 1602.8. M.p.: 216–221°C.

(c) The ratio of **E5c** to **Z5c** to **6c** was 8:1:2.6, while the ratio of **5** to styrene (method B) was estimated at 6:1.

*3.6. Reaction of **1** with 3,3-dimethyl-1,2-epoxybutane*

(b) 380 mg (33.4%) of **E5d** crystallized from a hexane solution of **5**/**6**, isolated form the preparative run (1200 mg, 1.8 mmol of **1** · 2THF. ^{1}H NMR (C_6D_6, 300 MHz): δ 6.74, 6.66 (2 s, 4 H each, mesityl H); 6.25 (d, $J = 12.1$ Hz, 1 H, α vinyl H); 5.65 (s, 1 H, Si–H); 5.35 (d, $J = 12.1$ Hz, 1 H, β vinyl H); 2.43, 2.34 (2 s, 24 H, *o*-methyl H); 2.10, 2.05 (2 s, 12 H, *p*-methyl H); 0.97 (s, 9 H, tert-butyl H). ^{13}C NMR (C_6D_6, 75.40 MHz): δ 145.9, 145.3, 139.4, 139.2 (aromatic C); 138.8 (α vinyl C); 132.7, 131.5, 130.2, 129.5 (aromatic C); 122.5 (β vinyl C); 31.4 (tert-butyl quaternary C); 31.2 (tert-butyl methyl C); 24.9, 24.4 (*o*-methyl C); 21.6, 21.5 (*p*-methyl C). ^{29}Si NMR (C_6D_6, 99.36 MHz): δ -1.24; -56.76 ($J_{Si-H} = -180.2$ Hz). MS (EI) for $C_{42}H_{56}OSi_2$: calculated *m/e* 632.3870, found 632.3874. IR (cm^{-1}, Nujol): 2132.1 (Si–H); 1656.7, 1603.7. M.p.: 197–199°C. Anal. Found: C, 79.40; H, 8.78. $C_{42}H_{56}OSi_2$ Calc.: C, 79.68; H, 8.92%.

Compound **6d**, which was isolated by preparative TLC on the mother liquor from recrystallization, was further purified by preparative gel permeation chromatography. Attempts at crystallization were unsuccessful. ^{1}H NMR (C_6D_6, 300 MHz): δ 6.76, 6.70, 6.66, 6.42 (4 br s, 8 H, mesityl H); 4.76 (dd, $J = -10.3$, 7.4 Hz, 1 H, methylene H); 4.40 (dd, $J = 12.5$, -10.3 Hz, 1 H, methylene H); 2.97 (dd, $J = 12.5$, 7.4 Hz, 1 H, five-ring methine H); 2.77, 2.71 (2 s, 9 H, three *o*-methyl groups); 2.40, 2.34 (2 s, 6 H, two *o*-methyl groups); 2.10, 2.06, 2.05, 2.04 (4 s, 21 H, three *o*-methyl groups, four *p*-methyl groups); 0.93 (s, 9 H, tert-butyl H). ^{13}C NMR (C_6D_6, 125.76 MHz): δ 146.5, 146.0, 144.4, 143.9, 139.2, 139.0, 138.9, 137.8, 136.0, 135.5, 134.5, 133.6, 131.1, 130.1, 130.4 (aromatic C); 68.5 (methylene C); 47.9 (five-ring methine C); 34.5 (tert-butyl quaternary C); 31.8 (tert-butyl methyl C); 27.3, 27.0, 26.9, 23.9 (*o*-methyl C); 21.5, 21.4, 21.2 (*p*-methyl C). ^{29}Si NMR (C_6D_6, 99.36 MHz): δ 6.43; -22.65. MS (EI) for $C_{42}H_{56}OSi_2$ ($M^+ - H$): calculated *m/e* 631.3791, found 631.3797.

Z5d was observed only in the NMR-scale reaction. It was not isolated.

(c) The ratio of **E5d** to **Z5d** to **6d** was 16.5:1:1.5, while the ratio of **5** to **4** was estimated at 4:1 by method A.

*3.7. Reaction of **1** with isobutylene oxide*

(a) From the semi-preparative scale run (100 mg, 0.15 mmol of **1** · 2THF), 37.9 mg (41.8%) of **5e** and 16.2 mg (17.9%) of a 6:1 mixture of **6e** and **7e** were isolated. (b) **5e** crystallized as a colorless solid from a hexane solution of **5**/**6**, isolated from the preparative run. ^{1}H NMR (C_6D_6, 300 MHz): δ 6.73, 6.67 (2 s, 8 H, mesityl H); 6.09 (s, 1 H, vinyl H); 5.65 (s, $J_{Si-H} = -179.9$ Hz, 1 H, Si–H); 2.40, 2.35 (2 s, 24 H, *o*-methyl H); 2.10, 2.06 (2 s, 12 H, *p*-methyl H); 1.81 (s, 3 H, vinyl methyl H); 1.43 (s, 3 H, vinyl methyl H). ^{13}C NMR (C_6D_6, 125.76 MHz): δ 146.0, 145.4, 139.9 139.2 (aromatic C); 135.3 (α vinyl C); 132.9, 131.6, 130.2, 129.5 (aromatic C); 111.7 (β vinyl C); 25.1, 24.6 (*o*-methyl C); 21.6, 21.5 (*p*-methyl C); 20.2, 16.9

(vinyl methyl C). ^{29}Si NMR (C_6D_6, 99.36 MHz): δ −0.47; −56.73. MS (EI) for $C_{40}H_{52}OSi_2$: calculated m/e 604.3557, found 604.3544. IR (cm^{-1}, Nujol): 2135.4 (Si–H); 1679.2, 1602.0. M.p.: 236–241°C.

Compound **6e**, which was isolated by preparative TLC on the mother liquor from recrystallization, was further purified by crystallization from hexanes to give a white powder. ^{1}H NMR (C_6D_6, 300 MHz): δ 6.69, 6.65 (2 s, 8 H, mesityl H); 3.93 (s, 1 H, methylene H); 2.52, 2.28 (2 s, 24 H, *o*-methyl H); 2.08 (s, 12 H, *p*-methyl H); 1.22 (s, 6 H, five-ring methyl H). ^{13}C NMR (C_6D_6, 125.76 MHz): δ 144.7, 138.7, 138.5, 137.6, 137.3, 129.6 (aromatic C); 80.3 (methylene C); 33.4 (five-ring quaternary C); 27.2, 26.3, 25.2 (*o*-methyl C, five-ring methyl C); 21.5, 21.4 (*p*-methyl C). ^{29}Si NMR (C_6D_6, 99.36 MHz): δ 8.24; −5.35. MS (EI) for $C_{40}H_{52}OSi_2$: calculated m/e 604.3557, found 604.3533.

(c) The ratio of **5e** to **6e** was 7 : 1, while the ratio of **5** to **4** was estimated at 2.4 : 1 by integration of the ^{1}H NMR.

3.8. Reaction of 1 with 1,1-diphenylethylene oxide

(a) From the semi-preparative scale run (50 mg, 0.074 mmol of **1** · 2THF), 23 mg (42.7%) of **5f** and 4.4 mg (33.0%) of diphenylethylene were isolated. (b) **5f**, isolated from the preparative run, was recrystallized once from diethyl ether and a second time from hexanes to give colorless crystals. ^{1}H NMR (C_6D_6, 300 MHz): δ 7.48 (m, 2 H, phenyl H); 7.22 (m, 4 H, phenyl H); 6.90 (m, 5 H, phenyl H, α vinyl H); 6.67, 6.63 (2 s, 8 H, mesityl H); 5.63 (s, $J_{Si-H} = -179.4$ Hz, 1 H, Si–H); 2.33, 2.21 (2 s, 24 H, *o*-methyl H); 2.07, 2.04 (2 s, 12 H, *p*-methyl H). ^{13}C NMR (C_6D_6, 125.76 MHz): δ 145.8, 145.4, 142.1 (aromatic C); 140.4 (α vinyl C); 140.1, 139.5, 139.4, 132.5, 131.7, 131.2, 130.2, 129.4, 129.1, 128.8, 127.9, 127.4, 126.8 (aromatic C); 124.8 (β vinyl C); 25.1, 24.7 (*o*-methyl C); 21.6, 21.5 (*p*-methyl C). ^{29}Si NMR (C_6D_6, 99.36 MHz): δ 3.92; −56.92. MS (EI) for $C_{50}H_{56}OSi_2$: calculated m/e 728.3870, found 728.3860. IR (cm^{-1}, Nujol): 2129.0 (Si–H); 1627.6, 1600.6. M.p.: 194–196°C. Anal. Found: C, 82.56; H, 7.80. $C_{50}H_{56}OSi_2$ Calc.: C, 82.36; H, 7.74%.

Compound **7f** was isolated in very small quantities by preparative TLC. For independent synthesis and full characterization see Ref. [2].

(c) The ratio of **5f** to diphenylethylene was estimated at 2 : 1 by method B. Compound **7f** was barely visible in the ^{1}H NMR; no integration was done.

3.9. Reaction of 1 which cyclohexene oxide

(a) From the semi-preparative scale run (100 mg, 0.15 mmol of **1** · 2THF), 31 mg (32.8%) of a 5 : 1 mixture of **5g** and **6g** was isolated. (b) **6g** crystallized as a white solid from a hexane solution of **5**/**6**, isolated from the preparative run. ^{1}H NMR (C_6D_6, 300 MHz): δ 6.78, 6.60 (2 s, 8 H, mesityl H); 4.41 (br s, 1 H, *H*–C–O); 2.76, 2.35 (2 br s, methyl H); 2.15, 2.14, 2.12, 2.03, 2.00 (5 s, methyl H); 1.67–1.06 (m, 7 H, cyclohexyl H). ^{13}C NMR ($CDCl_3$, 62.90 MHz): δ 144.8, 139.5, 139.1, 138.7, 138.5, 138.4, 136.7, 136.1, 135.3, 130.1, 129.1 (aromatic C); 72.5 (*C*–O); 34.6 (methylene C); 33.3 (*C*–C–O methine C); 29.0, 26.1 (methylene C); 26.0, 25.9 (*o*-methyl C); 21.9, 21.8, 21.7 (*p*-methyl C); 21.3 (methylene C). ^{29}Si NMR (C_6D_6, 99.36 MHz): δ 4.30; −3.25. MS (EI) for $C_{42}H_{54}OSi_2$: calculated m/e 630.3713, found 630.3658.

The mother liquor was concentrated, and the residue taken up in diethyl ether from which **5g** crystallized as a colorless solid. ^{1}H NMR (C_6D_6, 300 MHz): δ 6.74, 6.67 (2 s, 4 H each, mesityl H); 5.63 (s, 1 H, Si–H); 4.64 (m, 1 H, vinyl H); 2.43, 2.32 (2 s, 24 H, *o*-methyl H); 2.13, 2.11, 2.08 (2 s, m, 14 H, *p*-methyl H, aliphatic H); 1.82, 1.52, 1.37 (3 m, 6 H), aliphatic H). ^{13}C NMR (C_6D_6, 75.40 MHz): δ 150.6 (α vinyl C); 146.0, 145.1, 139.6, 139.1, 134.6, 132.0, 130.2, 129.4 (aromatic C); 104.1 (β vinyl C); 30.6 (methylene C); 25.2 (*o*-methyl C); 24.9 (methylene C); 24.7 (*o*-methyl C); 24.3, 23.2 (methylene C); 21.6, 21.5 (*p*-methyl C). ^{29}Si NMR (C_6D_6, 53.67 MHz): δ −8.36; −56.67 ($J_{Si-H} = -178.2$ Hz). MS (EI) for $C_{42}H_{54}OSi_2$ ($M^+ -$ H): calculated m/e 629.3635, found 629.3621. IR (cm^{-1}, Nujol): 2132.2 (Si–H); 1664.5, 1603.7. M.p.: 213–219°C. Anal. Found: C, 79.67; H, 8.74. $C_{42}H_{54}OSi2$ Calc.: C, 79.94; H, 8.62%.

(c) The ratio of **5g** to **6g** was 4.7 : 1, while the ratios of **5g** to cyclohexene (method B) and **5g** to **4** (method A) were estimated at 3 : 1.

3.10. Synthesis of 4-iso-propyl-1,1,2,2-tetramesityl-3-oxa-1,2-disilacyclobutane (7e)

Compound **1** · 2THF (400 mg, 0.60 mmol) was added to a solution of ca. 80 mg of isobutyraldehyde (1.1 mmol, 1.85 equiv.) in 20 ml of hexanes, and the mixture was swirled at room temperature for ca. 1 min. The resulting colorless solution was concentrated in vacuo. Recrystallization of the residue from hexanes gave 270 mg (74.5%) of **7e** as a colorless solid. ^{1}H NMR (C_6D_6, 300 MHz): δ 6.74, 6.70, 6.57, 6.54 (4 s, 8 H, mesityl H); 4.84 (d, $J = 8.2$ Hz, 1 H, four-ring methine H); 2.76 (s, 6 H, *o*-methyl H); 2.44, 2.37, 2.32, 2.21, 2.11, 2.06, 2.04, 2.01 (7 s, m, six *o*-methyl groups, four *p*-methyl groups, iso-propyl methine H); 1.22 (d, $J = 6.4$ Hz, 3 H, iso-propyl methyl H); 0.91 (d, $J = 6.1$ Hz, 3 H, iso-propyl methyl H). ^{13}C NMR (C_6D_6, 125.76 MHz): δ 145.6, 144.8, 144.6, 143.1, 139.7, 139.6, 139.1, 138.8, 135.9, 134.9, 133.7, 132.0, 130.0, 129.8, 129.7, 129.6, (aromatic C); 85.2 (four-ring methine C); 34.7 (iso-propyl methine C); 26.9, 26.0, 25.0, 23.2, 21.6, 21.5, 21.4, 20.8 (methyl C). ^{29}Si NMR (C_6D_6, 99.36 MHz): δ 18.21; 14.36. MS (EI) for $C_{40}H_{52}OSi_2$: calculated m/e 604.3557, found 604.3555. M.p.: 161–165°C. Anal. Found: C, 79.64; H, 8.40. $C_{40}H_{52}OSi_2$ Calc.: C, 79.41; H, 8.66%.

3.11. Ratios of 2 to 4 by ^{29}Si NMR, standard samples

A standard sample was prepared by addition of 2 mg of **4**, 7–15 mg of a selected enol ether and 1 ml of benzene-d_6 to an NMR tube under an inert atmosphere. The tube was sealed, and its contents heated to 80°C until **4** had completely dissolved. The sample was then cooled, and spectra taken at 25°C. The INEPT ^{29}Si spectra were obtained using parameters for polarization transfer from the mesityl *ortho* methyl protons. For a signal to noise ratio of 6–10:1 for **4**, 8000–9000 scans were generally required. The integrated ratios of **5** to **4** were determined for **E5b**, **E5d** (two different ratios), **5e**, and **5g** with the following results, given as ^{1}H ratio/^{29}Si ratio: **E5b**, 2.4/2.7; **E5d**(1), 2.6/2.3; **E5d**(2), 9.8/8.8; **5e**, 3/3; **5g**, 4.4/4.3. The H–Si–*Si*–O peak was integrated against the single resonance of **4** at −26.8 ppm [3] in the ^{29}Si spectra. In the ^{1}H spectrum the mesityl aromatic signal of **4** at 6.61 ppm was integrated against the vinyl proton(s) of **5**.

3.12. X-ray structure determinations

X-ray crystallographic analyses were performed on a Siemens P4 diffractometer equipped with a graphite crystal monochromator. Mo Kα radiation (λ = 0.71073 Å) was used for **6a** and Cu Kα (λ = 1.54178 Å) for **6g**. Suitable crystals of **6a** were grown from benzene at 25°C, and obtained as the benzene solvate **6a** · benzene. Those of **6g** were obtained from *n*-hexane at −5°C. The orientation matrices and unit cell parameters were determined by the least-squares fitting of 25–36 centered reflections ($9° \leq \theta \leq 12°$ for **6a**, and $10° \leq \theta \leq 45°$ for **6g**). Intensities of three standard reflections were monitored every 50 or 100 reflections, with a maximum variation of 0.04–0.051. Both structures were solved using the SHELXS-86 program [28]. The non-hydrogen atoms were refined anistropically using the SHELXL-93 program [29] by full-matrix least-squares analysis on F^2. The applied weighting scheme for both structures was $w^{-1} = \sigma^2 F_o^2 + (xP)^2 + yP$, where $x = 0.0748$ and $y = 0.00$ for **6a**, and $x = 0.0721$ and $y = 14.0397$ for **6g** and $P = (F_o^2 + 2F_c^2)/3$ [29]. An extinction correction was applied to structure **6a** with the form $F_c^* = kF_c[1 + 0.001\chi F_c^2\lambda^3/\sin(2\theta)]^{-1/4}$ [30], with $\chi = 0.004(1)$. The positions of the hydrogen atoms were calculated by idealized geometry and refined using a riding model. Neutral atom scattering factors were taken from Ref. [31]. The Si_2Mes_4 unit of **6g** sits on a crystallographic two-fold axis with the oxygen and cyclohexyl ring disordered 1:1. Complete lists of bond lengths and angles, and tables of hydrogen coordinates and anisotropic displacement parameters have been deposited at the Cambridge Crystallographic Data Centre.

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