

Decomposition of bis(silyldiazomethyl) polysilanes: formation of polysilabicyclo[1.m.n]alkane derivatives [☆]

Wataru Ando ^{*}, Mitsuru Sugiyama, Tomohisa Suzuki, Chikako Kato, Yusuke Arakawa,
 Yoshio Kabe

Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305, Japan

Received 25 January 1995; in revised form 31 March 1995

Abstract

The photolysis of bis(trimethylsilyldiazomethyl)disilane (**4a**) in tert-butyl alcohol provided the tert-butyl alcohol adducts **5**, **6**, **7**, **8** and **9**. The structures of these products revealed the stepwise formation of asymmetric silenes as intermediates. Gas-phase pyrolysis of **4a** and subsequent reaction with methanol and 4-methyl-1,2,4-triazoline-3,5-dione yielded the compounds **13** and **14**, which are derived from the 1,4-disilabutadiene intermediate (**16**) rather than 1,2-disilacyclobutene (**15**). The photolysis and thermolysis of bis(dimethylphenylsilyl-diazomethyl)trisilane (**4b**) afforded **21b**, **22b**, **23b** and **24b**. Formation of compound **21b** is attributed to the head-to-tail [2 + 2]cycloaddition of 1,5-disila-1,4-pentadiene (**26b**), while that of **23b**, **22b** and **24b** is attributed to head-to-head [2 + 2]cycloaddition of **26b** followed by reactions with tert-butyl alcohol and oxygen. Photolysis and pyrolysis of bis(trimethylsilyldiazomethyl)trisilane (**4c**) and bis(dimethylphenylsilyldiazomethyl)tetrasilane (**4d**) gave **29**, **30** and **21d**, which is consistent with an alternative mechanism, i.e. [2 + 3]silene-diazo cycloaddition.

Keywords: Silicon; Silene; Diazo

1. Introduction

Disilanyl carbenes (**2**) generated by photolysis or thermolysis of disilanyl diazomethane (**1**) form silenes (**3**) by trimethylsilyl migration from a silicon atom to the carbene center (Scheme 1). The silyl carbene-to-silene rearrangement has proved to be a convenient route to a variety of functionalized silenes such as silaarenes [1], silaacylate [2] and silaenone [3]. Our preliminary paper [4] reported that bis(silyldiazomethyl)trisilane (**4b**) gave either trisilabicyclo[1.1.1]pentane (**21b**) and/or trisilabicyclo[2.1.0]pentane (**23b**), depending on the mode of decomposition, through 1,5-disila-1,4-pentadiene (**26b**) as intermediate. Thus, bis(silyldiazomethyl)polysilane could be a good precursor for “bissilene” as well as polysilabicyclo[1.m.n]alkane derivatives. In the present paper we describe full details

of the thermal and photochemical reaction of bis(silyldiazomethyl)polysilane compounds (**4a–d**) with varying of polysilane chain lengths.

2. Results and discussion

2.1. Synthesis of bis(trimethylsilyldiazomethyl)polysilanes

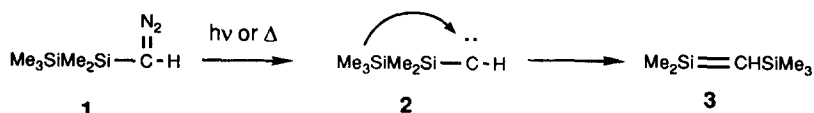
The bis(silyldiazomethyl)polysilanes were prepared by lithiation of silyl diazomethane followed by coupling with the corresponding dichloropolysilanes (Scheme 2). IR spectra of compounds **4a–d** showed a 2040–2044 cm⁻¹ absorption, attributed to diazo groups.

2.2. Decomposition of bis(silyldiazomethyl)disilane (**4a**)

Photolysis of **4a** in the presence of tert-butyl alcohol with a high pressure mercury lamp gave rise to one mole of the tert-butyl alcohol adducts (**5–7**) and two moles of tert-butyl alcohol adducts (**8**, **9**) in 2%, 12%, 12% and 58% (combined yield of **8** and **9**) yield,

[☆] Dedicated to Professor Hideki Sakurai upon his formal retirement from Tohoku University and in honor of his contribution to organometallic chemistry and silicon chemistry.

^{*} Corresponding author.

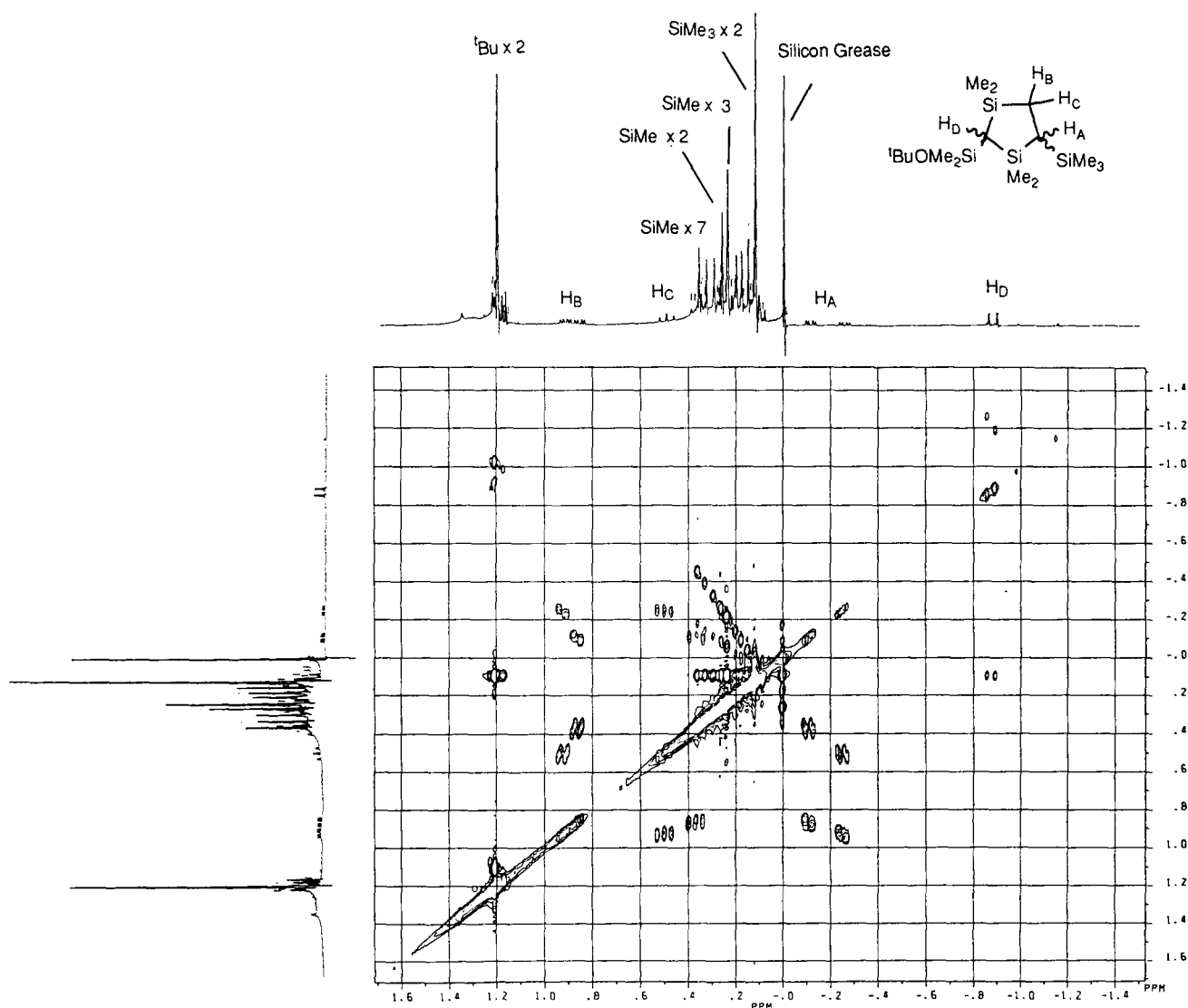


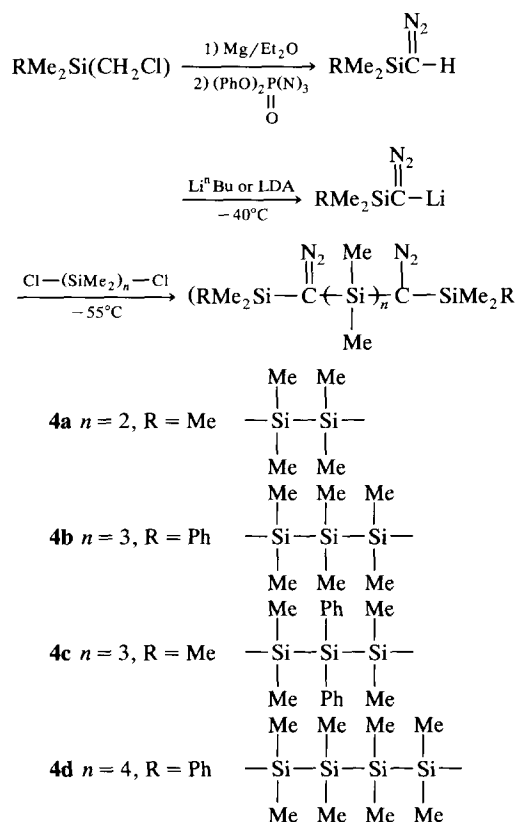
Scheme 1.

respectively. In the ^1H NMR spectra of **5** and **6**, the presence of chiral carbons was attributed to four diastereotopic SiMe_2 moieties. IR absorptions appeared at 2048 cm^{-1} ($\text{C}=\text{N}_2$) and 2210 cm^{-1} ($\text{N}=\text{C}=\text{N}$). In the ^1H NMR spectrum of **7**, the diastereotopic SiMe_2 displays twelve resonances, which indicates the presence of *cis* and *trans* isomers. The C–H COSY spectrum of **7** shows the methylene carbons with cross peaks at H_B and H_C . From the H–H COSY spectrum of **7**, methine and methylene protons may be classified as a pair of

isolated protons (H_D , singlet) and other spin-relaying groups (H_A , H_B and H_C , dd, dd and t) as shown in Fig. 1.

In theory two molecules of tert-butyl alcohol adducts having two chiral carbons in each molecule allow the existence of two and four diastereomers. However, ^1H and ^{13}C NMR spectra of **8** show 12-diastereotopic SiMe_2 signals along with double and quartet proton coupling of the CHMe signals, which confirms the proposed structure. The structure of **9** was elucidated by

Fig. 1. H–H COSY spectrum of **7**.



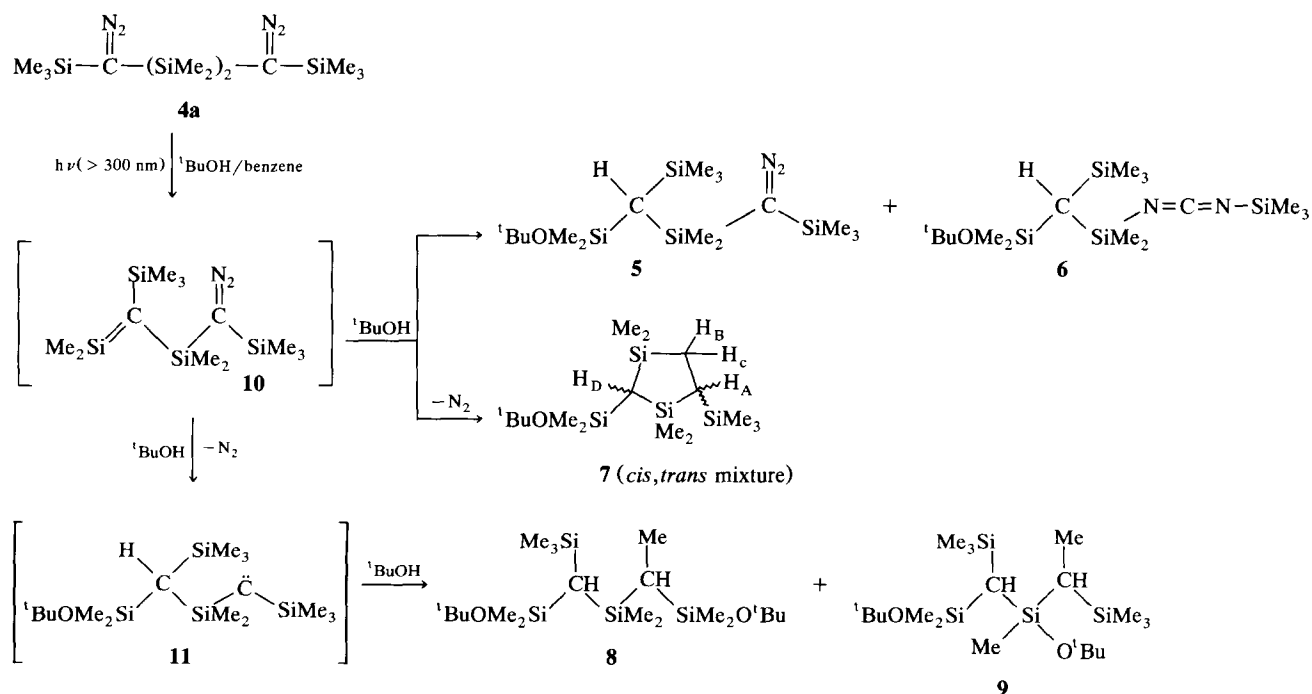
Scheme 2.

its having the same molecular weight as **8** with eight resonances for the methine and tert-butoxy groups in the ^1H NMR spectrum. From these results, it seems likely that a dimethylsilanyl group migration followed by

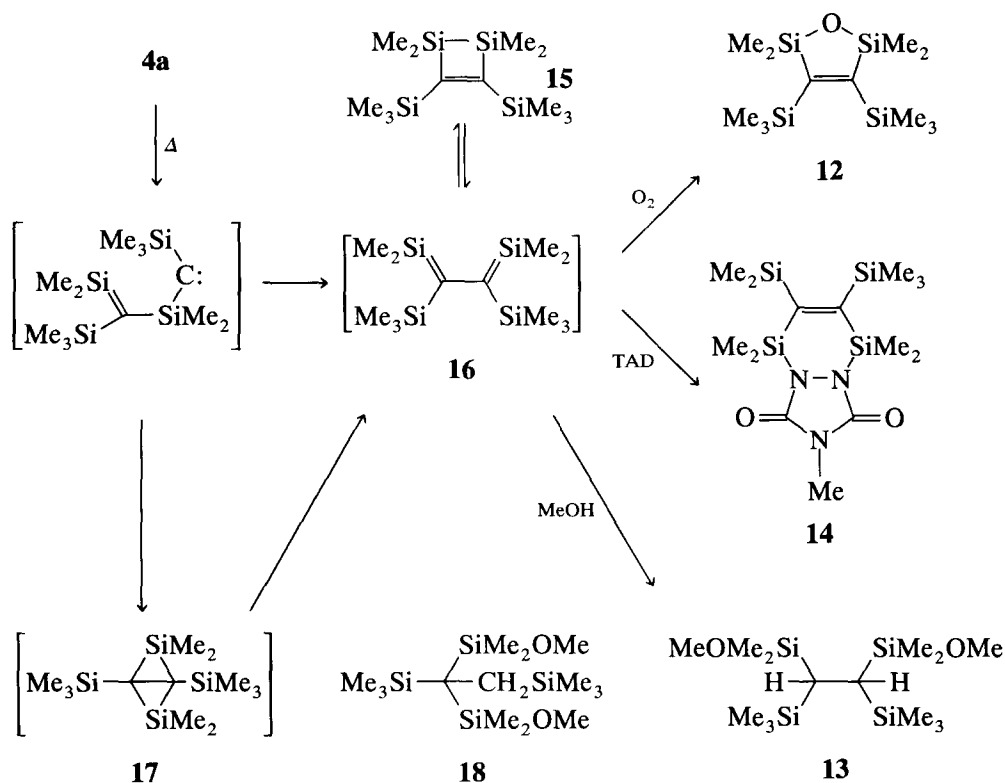
successive methyl migrations to the carbene center (**4a**, **10** and **11**) takes place (Scheme 3). This result was unexpected.

In order to maximize the chance of intramolecular reactions of bissilenes, the gas-phase pyrolysis of compound **4a** was carried out at 450°C under reduced pressure (Scheme 4). Treatment of pyrolysate with methanol and 4-methyl-1,2,4-triazoline-3,5-dione (TAD) yielded compounds **12**, **13** and **14**. The formation of compounds **12** and **14** may be understood in terms of oxygen and TAD insertion into a Si–Si bond of 1,2-disilacyclobutene (**15**).

1,2-Disilacyclobutenes have been prepared by the reaction of transient tetramethyldisilene with acetylene [5a,b] or silylene insertion into silacyclopentene [5c] and the high reactivity of the Si–Si bond has been described in the literature. The methanol adduct **13** was clearly derived from the intermediate 1,4-disilabutadiene (**16**). Thermal interconversion between 1,2-disilacyclobutene (**15**) and 1,4-disilabutadiene (**16**) was proposed by Barton and Kilgour [6]. The possibility that disilabicyclo[1.1.0]butane (**17**) is the primary product may be excluded because compound **17** has been synthesized by different route and its methanolysis product verified to have an unsymmetrical structure (**18**) [7]. By contrast it is interesting to note that pyrolysis of bisphenyldiazomethylsilane (**4e**) afford only disilacyclobutene (**19**), even after treatment of the pyrolysate with methanol, indicating that the terminal phenyl groups lead to carbene–carbene coupling. However, decomposition of bisacyldiazomethylsilane (**4f**) is reported to undergo silene–carbene coupling to yield 3,7-diox-



Scheme 3.

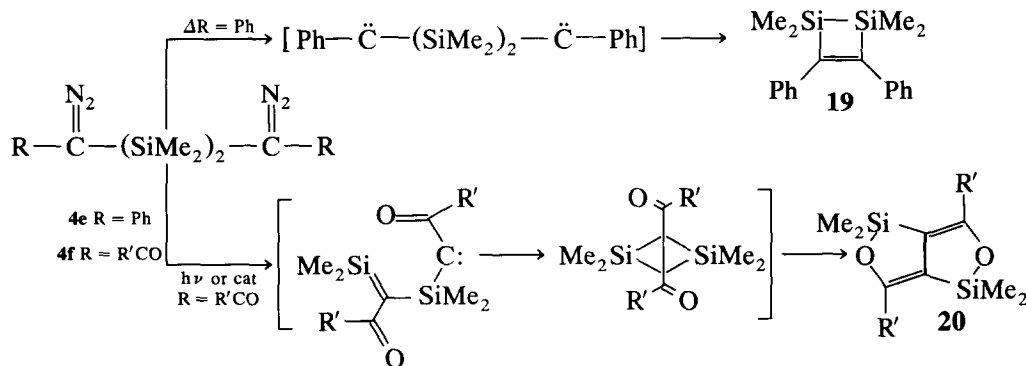


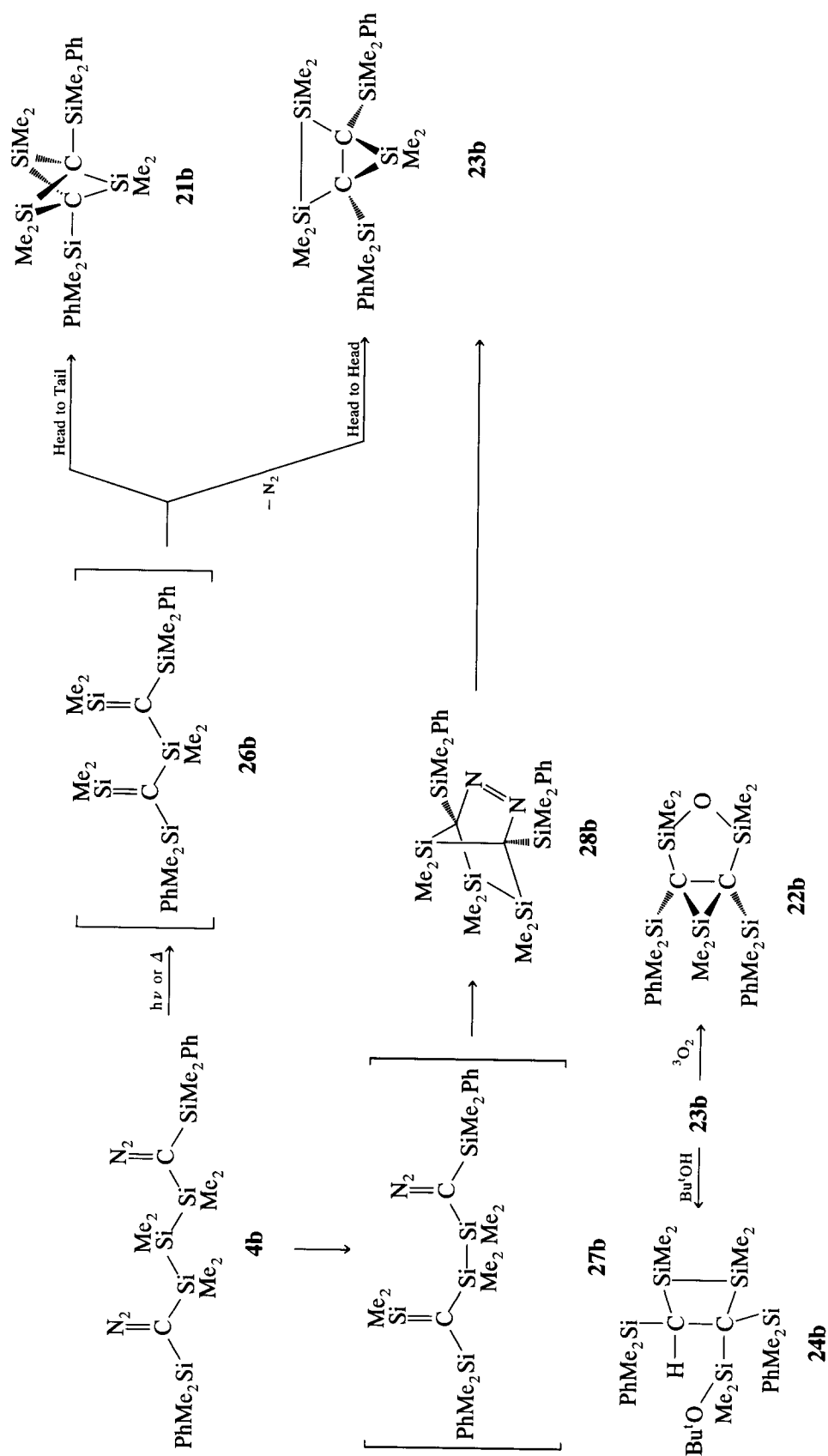
2,6-disilabicyclo [3.3.0]-oxa-4,8-dienes (**20**) [8] (Scheme 5).

2.3. Decomposition of bis(dimethylphenylsilyl- and trimethylsilyldiazomethyl)trisilane (**4b,c**) [4]

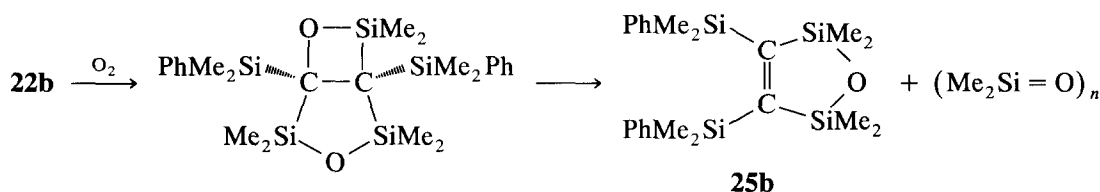
Photolysis of **4b** in cyclohexane with high pressure mercury lamps yielded mainly polymeric products, but the formation of trisilabicyclo[1.1.1]pentane **21b** and **22b** formed in 1% and 6% yield, respectively, was interesting [4]. Photolysis of **4b** in cyclohexane- d_{12} revealed the existence of **23b** which is easily polymerized at room temperature, but may be trapped by oxygen or tert-butyl alcohol to give **22b** or **24b**, respectively (Scheme 6). The silirane moiety of **22b** was

gradually oxidized by oxygen to give the corresponding olefin (**25b**) (Scheme 7), whereas pyrolysis of **4b** gave **21b** as the sole volatile product. In previous paper [4], we suggested bissilene (i.e. 1,5-disilapentadiene (**26b**)) as a common intermediate in the formation of **21b** and **23b**. Although transient silene is known to dimerize in head-to-tail fashion [9], **23b** was assumed to be derived from head-to-head [2 + 2]cycloaddition of **26b**, whereas the formation of **23b** implies that the bicycloazo compound (**28b**) is an intermediate in the intramolecular [2 + 3]cycloaddition of diazosilene (**27b**). To investigate this mechanism, a photochemical reaction of bis(silyldiazomethyl)trisilane (**4c**) was carried out, since the two reaction above lead to the same product (**23b**) so long as the two silyldiazomethyl groups are linked





Scheme 6.



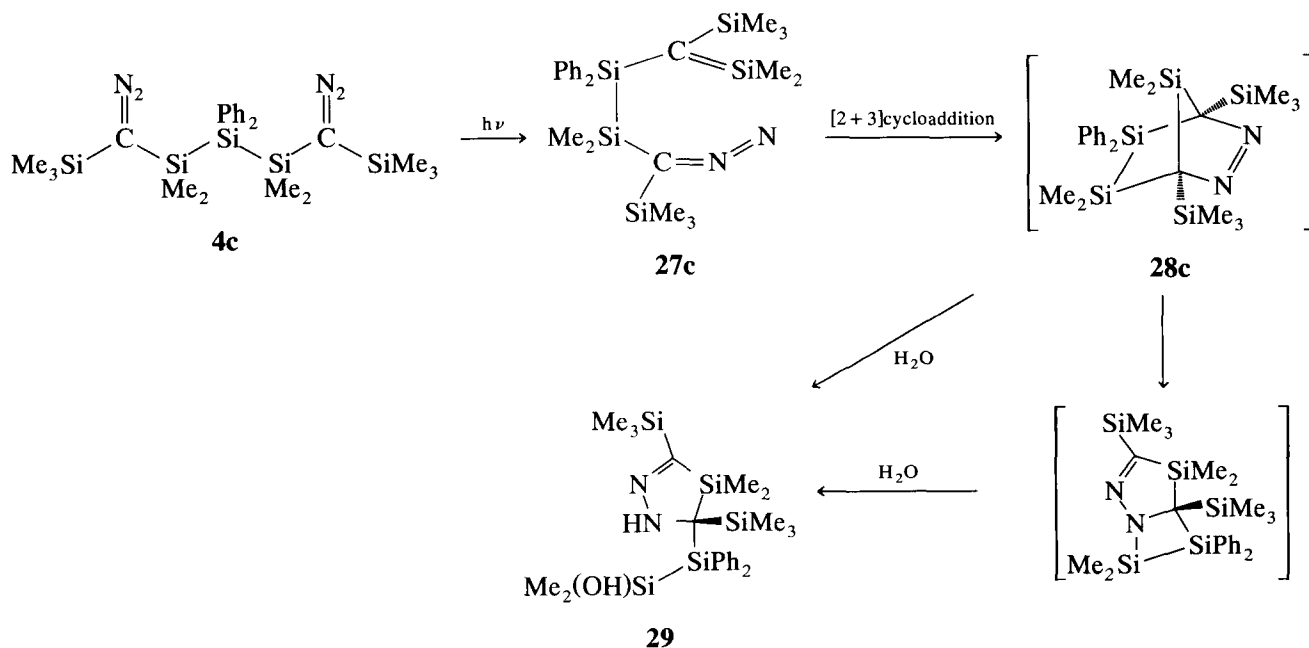
Scheme 7.

with the 1,1,2,2,3,3-hexamethyltrisilanylene unit (**4b**). Introduction of 2,2-diphenyl-1,1,3,3-tetramethyltrisilanylene units (**4c**) may be used to distinguish between the two reaction mechanisms since the location of diphenylsilanylene unit in the products will be different. A solution of **4c** in cyclohexane was irradiated for 4 h with a high pressure mercury lamp at $0^\circ C$. After removal of the solvent, the residue was separated by preparative HPLC, however subsequent recrystallization did not give bicyclic compounds such as **21b** and **23b** but rather the five-membered heterocycle (**29**) in 11% yield (Scheme 8). Analysis of **29** by 1H , ^{13}C and ^{29}Si NMR spectroscopy showed that the molecule had no planes of symmetry and X-ray analysis finally established the structures shown in Fig. 2. Compound **29** is evidently the product of hydrolysis of the bicyclic azo compound (**28c**), itself formed by intramolecular [2 + 3]cycloaddition of diazosilene (**27c**).

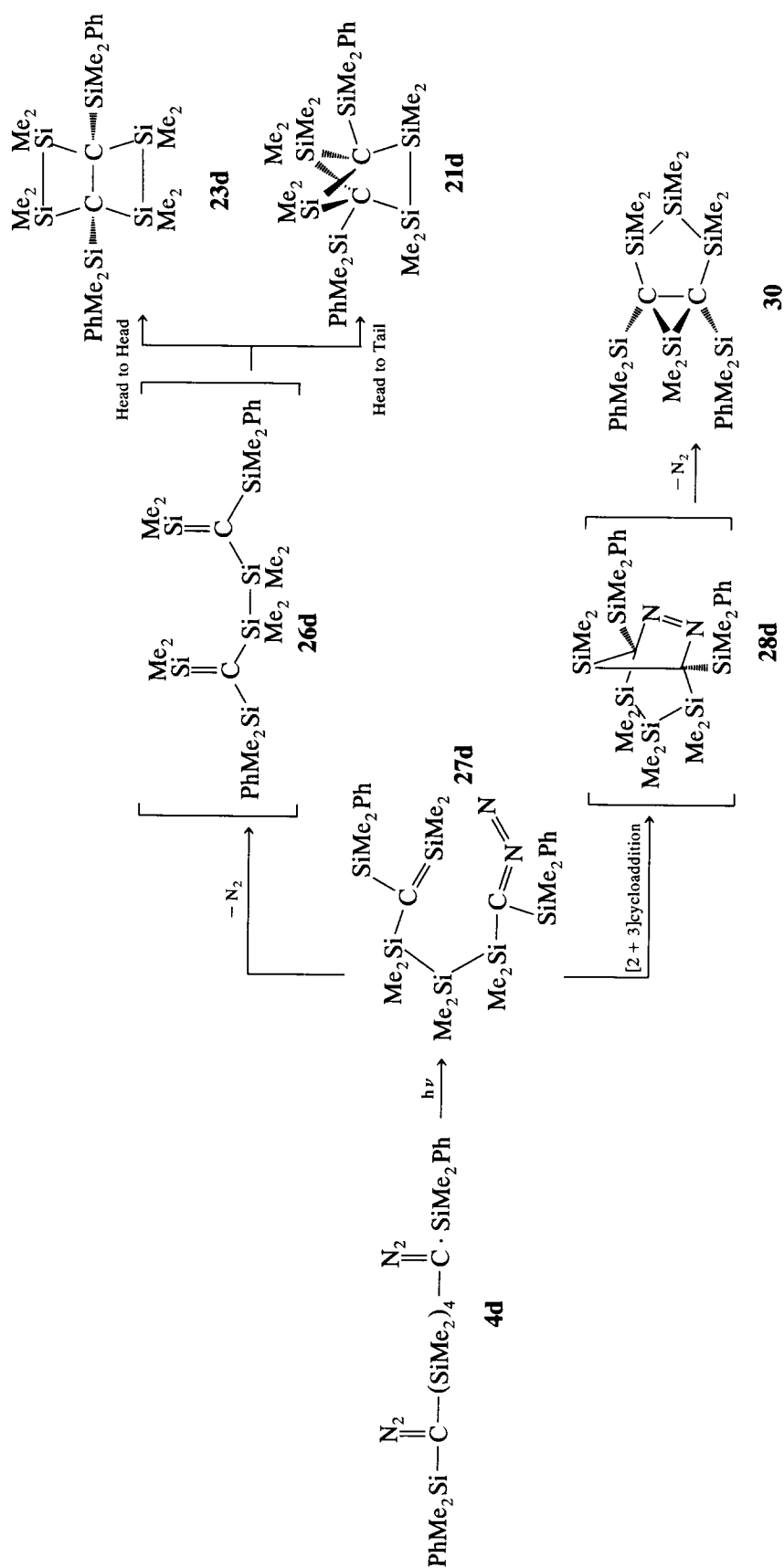
2.4. Decomposition of bis(dimethylphenylsilyldiazomethyl)tetrasilane (**4d**)

Photolysis of **4d** under the above conditions gave rise to tetrasilabicyclo[3.1.0]hexane (**30**) in 25% yield

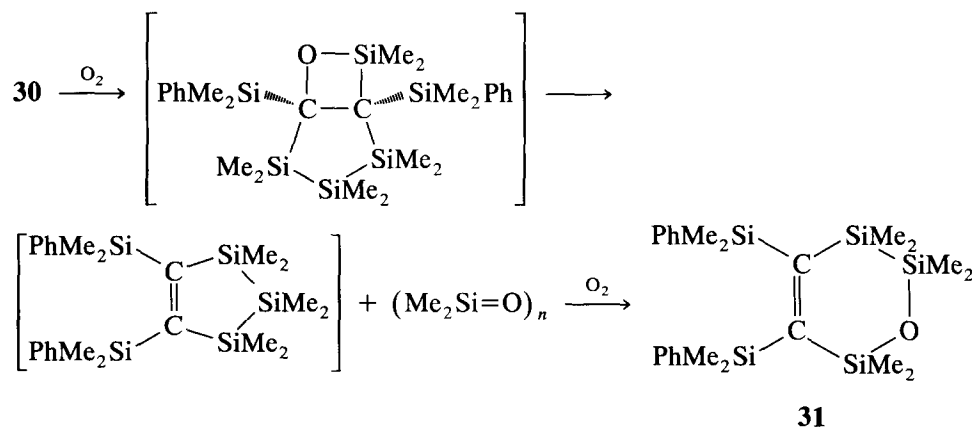
(Scheme 9). The three possible ring frameworks tetrasilabicyclo[2.1.1]hexane (**21d**), tetrasilabicyclo[2.2.0]hexane (**23d**) and tetrasilabicyclo[3.1.0]hexane (**30**) should exhibit four (4:4:2:2), three (4:4:4) and eight (2:2:2:2:1:1:1:1) SiMe resonances in their respective 1H NMR spectra, based on their molecular symmetry. Indeed, compound **30** showed eight SiMe resonances in the 1H NMR spectrum and four resonances in the ^{29}Si NMR spectrum in which the highest-field signal at -54.1 ppm is characteristic of a silirane ring silicon. X-ray analysis confirmed the structure of **30** shown in Fig. 3. Interestingly, compound **30** was regarded as one of the most stable silirane bearing methyl substituents on a silicon atom. However, under prolonged exposure to air **30** decomposed to give the corresponding olefin (**31**) [10] (Scheme 10). Thus, compound **30** is derived from nitrogen extrusion of the bicyclic azo compound (**28d**) and there is no need to invoke the head-to-head [2 + 2]cycloaddition of 1,6-disila-1,5-hexadiene (**26d**) to give tetrasilabicyclo[2.2.0]hexane (**23d**), at least for photochemical reactions. Flow pyrolysis of **4d** at $500^\circ C$ gave tetrasilabicyclo[2.1.1]hexane (**21d**) in 9% yield, the 1H NMR spectrum of which contains four SiMe resonances. There was no indication that tetrasilabicyclo-



Scheme 8.



Scheme 9.



Scheme 10.

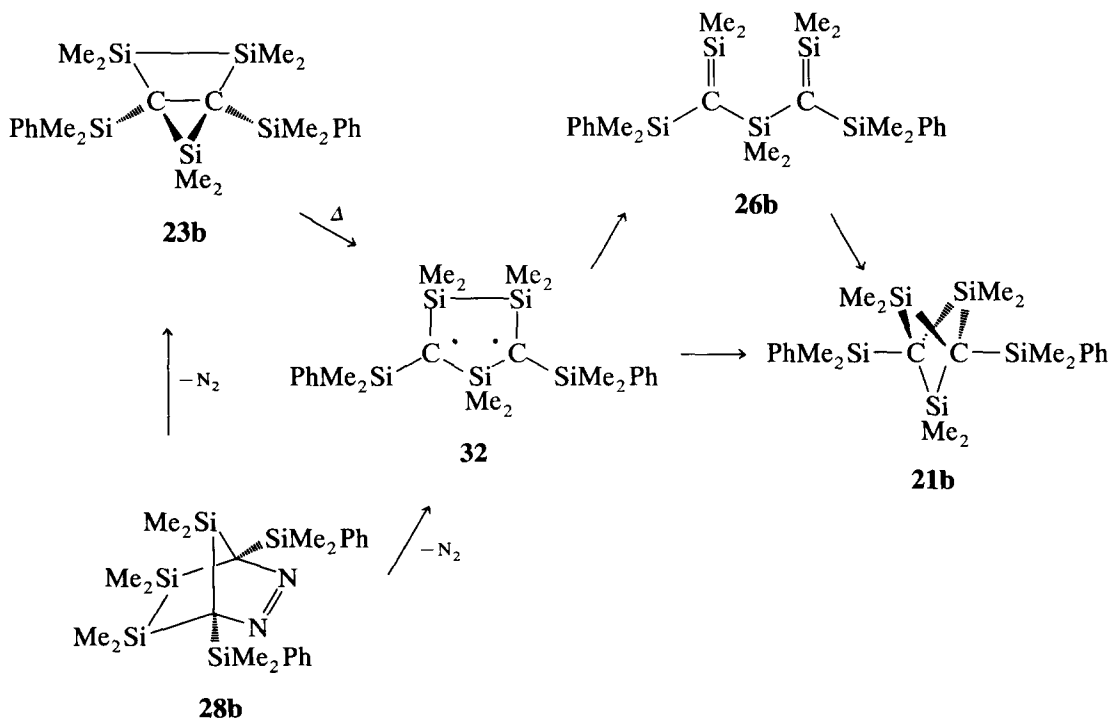
[2.2.0]hexane (**23d**) was present among the pyrolytic products.

In conclusion, it is clear that photochemical decomposition of bis(silyldiazomethyl)polysilane produces one silene group followed by [2 + 3] silene–diazo cycloaddition, while thermal decomposition gives two silenes which then undergo [2 + 2] silene–silene cycloaddition in a head-to-tail (not head-to-head) fashion. Lastly, as mentioned above, photolysis of **4b** also afforded a minute quantity of trisilabicyclo[1.1.1]pentane (**21b**). Therefore, it is proposed that, even under photochemical conditions, a unique rearrangement may occur in trisilabicyclo[2.1.0]pentane (**23b**) and/or bicycloazo compounds (**28b**) to **21b** through the biradical (**32**) and/or bisilene (**26b**) as intermediates, (Scheme 11).

3. Experimental details

3.1. General data

All reactions were carried out under argon. NMR spectra were recorded on a JEOL FX-90Q, FX-100 or a Bruker AC-400, AM-500 spectrometer. UV spectra were carried out on a Shimadzu UV 365 spectrometer. Mass spectra were obtained on Shimadzu GCMS-QP2000A and JEOL SX102A mass spectrometers. A LC-08 gel permeation chromatograph (Japan Analytical Ind. Co., Ltd.) with a JAIGEL-1H column (20Ø × 60 mm × 2) was used for preparative HPLC. All melting points are given uncorrected.



Scheme 11.

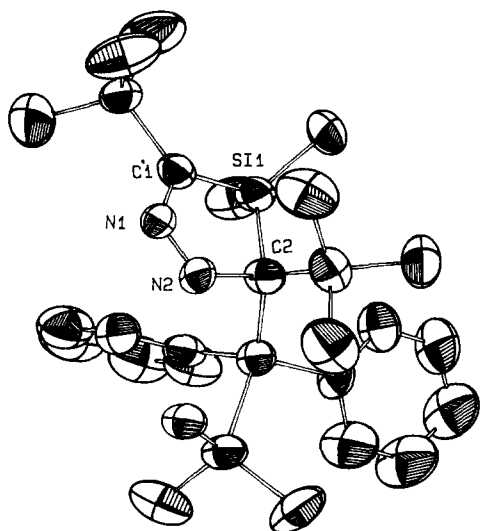


Fig. 2. ORTEP drawing of **29**. Since two independent molecules are present in the symmetric unit, two values are given for each bond distance (Å) and angles (°): Si(1)–C(1) 1.87(1)–1.89(1); Si(1)–C(2), 1.90(1)–1.94(1); N(1)–N(2), 1.33(1)–1.34(1); N(1)–C(1), 1.31(1)–1.31(2); N(2)–C(2), 1.50(2)–1.53(1); C(1)–Si(1)–C(2), 90.4(6)–91.1(5); N(2)–N(1)–C(1), 118(1); N(1)–N(2)–C(2), 118.9(8)–119.1(7); Si(1)–C(1)–N(1), 109.8(9)–110.5(9); Si(1)–C(2)–N(2), 100.0(8)–101.8(8).

3.2. Materials

$\text{Me}_3\text{SiCHN}_2$ [11], $\text{PhMe}_2\text{SiCHN}_2$ [11], $(\text{PhO})_2\text{PON}_3$ (DPPA) [12], $\text{Cl}(\text{SiMe}_2)_2\text{Cl}$ [13] and $\text{Cl}(\text{SiMe}_2)_3\text{Cl}$ [14] were prepared by published procedures. All solvents and reagents were purified by standard procedures. $\text{Cl}(\text{SiMe}_2)_4\text{Cl}$ (61–68°C/0.1 mmHg) was prepared by Na–K coupling of $\text{PhSiMe}_2\text{SiMe}_2\text{Cl}$ (52% yield) and subsequent dephenylation with $\text{HCl}/\text{AlCl}_3\text{--CHCl}_3$

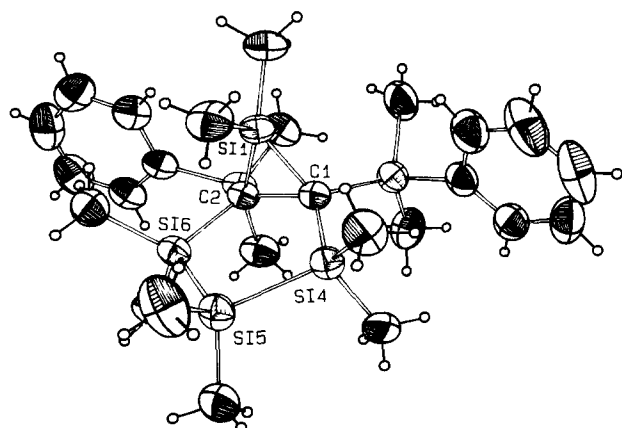


Fig. 3. ORTEP drawing of **30**. Selected bond lengths (Å) and angles (°): Si(1)–C(1) 1.832(4); Si(1)–C(2), 1.843(4); C(1)–C(2), 1.686(5); C(1)–Si(4), 1.916(4); C(2)–Si(6), 1.920(4); Si(4)–Si(5), 2.337(2); Si(5)–Si(6), 2.331(2); C(1)–Si(1)–C(2), 54.6(2); C(1)–C(2)–Si(1), 62.4(2); C(2)–C(1)–Si(1), 63.0(2); Si(1)–C(1)–Si(4), 116.9(2); Si(1)–C(2)–Si(6), 111.9(2); C(1)–Si(4)–Si(5), 105.9(1); Si(4)–Si(5)–Si(6), 94.59(6); C(2)–Si(6)–Si(5), 104.6(1).

(85% yield). $\text{PhMe}_2\text{SiMe}_2\text{SiCl}$ was prepared by reaction of 1.0 equiv. of PhMgCl with $\text{Cl}(\text{SiMe}_2)_2\text{Cl}$ (74% yield). $\text{ClSiMe}_2\text{SiPh}_2\text{SiMe}_2\text{Cl}$ (122–129°C/0.022 mmHg) was prepared by B.P.O. chlorination of $\text{HSiMe}_2\text{SiPh}_2\text{SiMe}_2\text{H}$ (84% yield), which was obtained by Mg/MgBr₂ coupling of HSiMe_2Cl and Ph_2SiCl_2 (54% yield).

3.3. General procedures for preparation of bis(silyldiazomethyl)polysilanes

Lithium silyldiazomethanes ($\text{LiC}(\text{N}_2)\text{SiMe}_2\text{R}$, R = Me or Ph) were prepared by adding lithium diisopropylamide (LDA) or BuLi in ether to a solution of silyldiazomethane ($\text{RMe}_2\text{SiCHN}_2$, R = Me or Ph) in ether. A solution of dichloropolysilanes in ether was added to a solution of the $\text{LiC}(\text{N}_2)\text{SiMe}_2\text{R}$ at low temperature and the mixture allowed to reach room temperature overnight. The reaction mixture was poured into ice water, neutralized with saturated NH_4Cl solution and extracted with ether. The ethereal solution was dried over sodium sulfate and concentrated. The residual yellow oil was either distilled or purified by preparative HPLC.

3.3.1. Preparation of 1,2-bis(trimethylsilyldiazomethyl)-1,1,2,2-tetramethyldisilane (**4a**)

$\text{Me}_3\text{SiCHN}_2$ (5.1 g, 45 mmol) in 15 ml ether was lithiated with 28 ml of BuⁿLi (1.6 M, 45 mmol) at –100°C. Then 4.1 g of $\text{Cl}(\text{SiMe}_2)_2\text{Cl}$ in 46 ml ether was introduced and the mixture was worked up as described above. Distillation of the residual oil gave 4.53 g (58%) of **4a**. For **4a**: yellow oil; b.p. 73–77°C/4 mmHg; ¹H NMR (90 MHz, CDCl_3) δ 0.21 (18H, s), 0.31 (12H, s); ¹³C NMR (25.5 MHz, CDCl_3) δ –2.10 (q), –0.11 (q), 15.6 (s); ²⁹Si NMR (18 MHz, C_6D_6) δ –15.49 (s), 1.65 (s); MS, m/z 342 (M^+); Exact mass m/z Found 342.1492, Calc. for $\text{C}_{12}\text{H}_{34}\text{N}_4\text{Si}_4$ 342.1548; IR (NaCl) $\nu(\text{C}=\text{N}_2)$ 2025 cm^{-1} .

3.3.2. Preparation of 1,3-bis(dimethylphenylsilyldiazomethyl)-1,1,2,2,3,3-hexamethyltrisilane (**4b**)

$\text{PhMe}_2\text{SiCHN}_2$ (3.50 g, 19.9 mmol) in 15 ml ether was lithiated at –40°C with LDA prepared by treatment of 12.3 ml of BuⁿLi (1.62 M, 19.9 ml) in 20 ml ether with 3.35 ml (23.9 mmol) of Pr_2NH in 25 ml ether at –78°C. Then 2.44 g (9.95 mmol) of $\text{Cl}(\text{SiMe}_2)_3\text{Cl}$ in 25 ml ether was introduced at –55°C and the mixture was worked up as described above. Purification of the residual oil by preparative HPLC gave 2.92 g (56%) of **4b**. For **4b**: yellow oil; ¹H NMR (500 MHz, C_6D_6) δ 0.17 (s, 12H), 0.26 (s, 6H), 0.36 (s, 12H), 7.17–7.27 (m, 6H), 7.49–7.54 (m, 4H); ¹³C NMR (125 MHz, C_6D_6) δ –5.60 (q), –1.57 (q × 2), 16.12 (s), 128.20 (d), 129.78 (d), 134.15 (d), 136.01 (s); ²⁹Si NMR (18 MHz, C_6D_6) δ –43.7, –11.6, –3.5; MS m/z 524 (M^+); Exact mass m/z Found 524.2110,

Calc. for $C_{24}H_{40}N_4Si_5$ 524.2099; UV(n-hexane) λ_{max} nm (ϵ) 259 (8600), 373 (140); IR (NaCl) $\nu(C=N_2)$ 2042 cm^{-1} .

3.3.3. Preparation of 1,3-bis(trimethylsilyldiazomethyl)-1,1,3,3-tetramethyl-2,2-diphenyltrisilane (4c)

3.0 g (26.3 mmol) of Me_3SiCHN_2 in 20 ml ether was lithiated at $-40^\circ C$ with LDA which was prepared by treatment of 18 ml Bu^iLi (1.5 M, 27.1 mmol) in 30 ml ether with 4.43 ml (31.6 mmol) of Pr_2^iNH in 30 ml ether at $-78^\circ C$. Then 4.88 g (13.2 mmol) of $ClSiMe_2SiPh_2SiMe_2Cl$ in 30 ml ether was introduced at $-55^\circ C$ and the mixture was worked up as described above. Purification of the residual oil by preparative HPLC gave 6.03 g (87%) of **4c**. For **4c**: yellow oil; 1H NMR (90 MHz, C_6D_6) δ -0.03 (s, 18H), 0.43 (s, 12H), 7.1 – 7.3 (m, 6H), 7.7 – 7.9 (m, 4H); ^{13}C NMR (22.5 MHz, C_6D_6) δ -0.25 (q), -0.18 (q), 16.96 (s), 128.49 (d), 129.15 (d), 134.59 (d), 136.62 (s); ^{29}Si NMR (18 MHz, C_6D_6) δ -40.52 , -13.39 , 1.82 ; MS m/z 524 (M^+); Exact mass m/z Found 524.2069, Calc. for $C_{24}H_{40}N_4Si_5$ 524.2099; UV (cyclohexane) λ_{max} nm (ϵ) 258 (15600), 375 (62); IR (NaCl) $\nu(C=N_2)$ 2040 cm^{-1} .

3.3.4. Preparation of 1,4-bis(dimethylphenylsilyldiazomethyl)-1,1,2,2,3,3,4,4-octamethyltetrasilane (4d)

$PhMe_2SiCHN_2$ (3.5 g, 19.1 mmol) in 15 ml ether was lithiated with LDA (prepared as in Section 3.3.2) at $-40^\circ C$. Then 3.02 g (9.95 mmol) of $Cl(SiMe_2)_4Cl$ in 25 ml ether was introduced at $-55^\circ C$ and the mixture was worked up as described above. Purification of the residual oil by preparative HPLC gave 5.23 g (95%) of **4d**. For **4d**: pale yellow oil; 1H NMR (90 MHz, C_6D_6) δ 0.17 (s, 12H), 0.29 (s, 12H), 0.38 (s, 12H), 7.1 – 7.6 (m, 10H); ^{13}C NMR (22.5 MHz, C_6D_6) δ -5.04 (q), -1.55 (q), -1.28 (q), 16.37 (s), 128.22 (d), 129.78 (d), 134.15 (d), 136.06 (s); ^{29}Si NMR (18 MHz, C_6D_6) δ -42.55 , -11.14 , -4.00 ; MS, m/z 582 (M^+); Exact mass m/z Found 582.2345, Calc. for $C_{26}H_{46}N_4Si_6$ 582.2338; UV (hexane) λ_{max} (ϵ) 252 (15000), 369 (130); IR (NaCl) $\nu(C=N_2)$ 2042 cm^{-1} .

3.3.5. Preparation of 1,2-bisphenyl-1,1,2,2-tetramethyldisilane (4e)

To a mixture of phenyldiazomethane [15] (6.51 g, 55 mmol) and $Cl(SiMe_2)_2Cl$ (5.0 g, 27 mmol) in 100 ml of ether was added LDA at $-78^\circ C$ prepared by treatment of 76 ml of $BuLi$ (1.55 M, 118 ml) in 40 ml ether with 20 ml (141 mmol) of Pr^iNH in 70 ml of ether at $-78^\circ C$. Then reaction mixture was allowed to warm to room temperature overnight and worked up as described above. Purification of the residual oil by preparative HPLC gave 1.15 g (12%) of **4e**. For **4e**: yellow oil; 1H NMR (500 MHz, C_6D_6) δ 0.23 (s, 12H), 6.85 (t, 2H), 6.88 (d, 4H), 7.09 – 7.11 (m, 4H); ^{13}C NMR (125 MHz, C_6D_6) δ -2.91 (q), 41.06 (s), 123.28 (d), 124.00 (d),

129.33 (d), 133.66 (s); ^{29}Si (18 MHz, C_6D_6) δ 19.61 ; MS m/z 350 (M^+); Exact mass m/z found 350.1390, Calc. for $C_{18}H_{32}N_4Si_2$ 350.1383; IR (NaCl) $\nu(C=N_2)$ 2038 cm^{-1} .

3.4. Photolysis of 4a in tert-butyl alcohol

A solution of **4a** (346 mg, 1 mmol), tert-butyl alcohol (4.5 ml) and benzene (1.5 ml) were irradiated in a Pyrex tube with a high pressure mercury lamp until N_2 evolution had ceased. Separation of the reaction mixture by preparative GPC (8 mm $\times$ 1 m glass column packed with 10% SF-96 on Celite 545) gave **5**, **6**, **7** and a mixture of **8** and **9**. The mixture of **8** and **9** was further separated by preparative HPLC (eluent $CHCl_3$) for structural analyses. Yields were determined by GPC (using an internal standard) as 2%, 12%, 12% and 58% of **2**, **6**, **7** and the mixture of **8** and **9**, respectively. For **5**: 1H NMR (500 MHz, C_6D_6) δ -0.38 (s, 1H), 0.20 (s, 9H), 0.33 (s, 9H + 3H), 0.36 (s, 3H), 0.40 (s, 3H), 0.44 (s, 3H), 1.21 (s, 9H); ^{13}C NMR (125 MHz, C_6D_6) δ -1.16 (q, $SiMe_3$), 1.21 (q, $SiMe$), 2.00 (q, $SiMe_3$), 2.32 (q, $SiMe$), 4.80 (q, $SiMe$), 5.17 (q, $SiMe$), 5.47 (d), 17.85 (s), 31.12 (q), 72.12 (s); ^{29}Si NMR (18 MHz, C_6D_6) δ -21.39 , -0.48 , 0.75 , 6.10 ; MS, m/z 373 ($M^+ - Me$); Exact mass Found m/z 373.1977, Calc. for $C_{15}H_{27}N_2OSi_4$ 373.1982; IR (NaCl) $\nu(C=N_2)$ 2048 $\nu(Si-O-C)$ 1044, 1015 cm^{-1} . For **6**: 1H NMR (500 MHz, C_6D_6) δ -0.36 (s, 1H), 0.21 (s, 9H), 0.35 (s, 9H + 3H), 0.36 (s, 3H), 0.40 (s, 3H), 0.44 (s, 3H), 1.21 (s, 9H); ^{13}C NMR (125 MHz, C_6D_6) δ 0.33 (q, $SiMe_3$), 1.96 (q, $SiMe_3$), 3.00 (q, $SiMe$), 3.40 (q, $SiMe$), 4.66 (q, $SiMe$), 4.70 (q, $SiMe$), 8.64 (d), 31.23 (q), 71.95 (s), 123.22 (s); ^{29}Si NMR (18 MHz, C_6D_6) δ -21.39 , -2.95 , -1.23 , 6.03 ; MS, m/z 373 ($M^+ - Me$); Exact mass Found m/z 373.1978, Calc. for $C_{15}H_{33}N_2OSi_4$ 373.1981; IR (NaCl) $\nu(N=C=N)$ 2210 $\nu(Si-O-C)$ 1021 cm^{-1} . For **7**: 1H NMR (500 MHz, C_6D_6) δ -0.89 (s, 1H), -0.86 (s, 1H), -0.25 (dd, 1H, $J_{AB} = 6.0$ Hz, $J_{AC} = 14.5$ Hz), -0.11 (dd, 1H, $J_{AB} = 5.3$ Hz, $J_{AC} = 14.5$ Hz), 0.12 (s, 18H), 0.13 (s, 3H), 0.15 (s, 3H), 0.18 (s, 3H), 0.20 (s, 3H), 0.24 (s, 9H), 0.26 (s, 6H), 0.29 (s, 3H), 0.33 (s, 3H), 0.36 (s, 3H), 0.37 (t, 1H, $J_{AC} = J_{BC} = 14.5$ Hz), 0.50 (t, 1H, $J_{AC} = J_{BC} = 14.5$ Hz), 0.86 (dd, 1H, $J_{AB} = 5.3$ Hz, $J_{BC} = 14.5$ Hz), 0.92 (dd, 1H, $J_{AB} = 5.3$ Hz, $J_{BC} = 14.5$ Hz), 1.247 (s, 9H), 1.249 (s, 9H); ^{13}C NMR (125 MHz, C_6D_6) δ -2.28 (q, $SiMe$), -1.63 (q, $SiMe_3$), -1.57 (q, $SiMe$), -1.55 (q, $SiMe_3$), -0.15 (q, $SiMe$), -0.11 (q, $SiMe$), 0.54 (q, $SiMe$), 1.30 (q, $SiMe$), 1.31 (q, $SiMe$), 1.41 (q, $SiMe$), 1.60 (q, $SiMe$), 4.42 (q, $SiMe \times 2$), 4.46 (q, $SiMe$), 6.00 (d), 6.72 (d), 11.05 (d), 12.39 (t), 12.56 (d), 13.52 (t), 31.06 (q), 31.24 (q), 71.30 (s); ^{29}Si NMR (18 MHz, C_6D_6) δ 2.54 , 3.02 , 5.07 , 5.28 , 13.44 , 13.71 , 15.22 , 16.60 ; MS, m/z 360 (M^+); Exact mass m/z Found 360.2143, Calc. for $C_{16}H_{40}OSi_4$ 360.2155; IR

(NaCl) $\nu(\text{Si-O-C})$ 1046, 1023 cm^{-1} . For **8**: ^1H NMR (500 MHz, C_6D_6) δ -0.12 (s, 1H), -0.05 (s, 1H), 0.23 (s, 6H), 0.257 (s, 3H), 0.26 (s, 3H), 0.31 (s, 9H), 0.32 (s, 9H), 0.346 (s, 6H), 0.354 (s, 3H), 0.357 (s, 6H), 0.38 (s, 3H), 0.42 (s, 3H), 0.45 (s, 3H), 1.08 (d, 3H, $J_{\text{AB}} = 7.62$ Hz), 1.086 (d, 3H, $J_{\text{A'B'}} = 7.52$ Hz), 1.20 (bs, 36H), two CH (quartet) protons were hidden in 0.3–0.45 ppm; ^{13}C NMR (125 MHz, C_6D_6) δ 0.78 (q, SiMe), 1.00 (q, SiMe), 1.95 (q, SiMe $\times$ 2), 1.98 (q, SiMe $\times$ 2), 2.81 (q, SiMe), 2.84 (q, SiMe), 3.72 (q, SiMe₃), 3.87 (q, SiMe₃), 5.29 (d), 5.50 (d), 6.30 (q, SiMe), 6.45 (q, SiMe), 6.48 (q, SiMe), 6.56 (q, SiMe), 9.65 (q, Me), 9.72 (q, Me), 9.90 (d), 9.99 (d), 32.17 (q), 72.35 (s), 72.86 (s), 72.89 (s); ^{29}Si NMR (18 MHz, C_6D_6) δ -1.26, -0.71, 6.54, 9.34; MS, m/z 419 ($\text{M}^+ - \text{Me}$); Exact mass m/z Found 419.2677, Calc. for $\text{C}_{19}\text{H}_{47}\text{O}_2\text{Si}_4$ 419.2654; IR (NaCl) $\nu(\text{Si-O-C})$ 1044, 1021 cm^{-1} . For **9**: ^1H NMR (500 MHz, C_6D_6) δ -0.32, -0.13, -0.12, 0.20–0.51 (m), 0.60, 0.61, 0.87, 0.89, 0.90, 1.08, 1.09, 1.13–1.33 (m); ^{13}C NMR (125 MHz, C_6D_6) δ 0.61 (q), 0.40 (q), 0.95 (q), 3.19 (q), 3.38 (q), 3.61 (q), 3.84 (q), 3.91 (q), 4.06 (q), 4.28 (q), 4.59 (q), 5.79 (q), 5.80 (q), 6.29 (q), 6.48 (q), 6.52 (q), 6.58 (q), 6.77 (q), 7.20 (q), 9.77 (d), 10.37 (d), 10.80 (d), 10.86 (d), 11.0 (d), 11.25 (d), 11.90 (d), 12.14 (d), 32.17 (q), 32.21 (q), 32.24 (q), 32.28 (q), 32.41 (q), 32.60 (q), 32.65 (q), 32.70 (q), 73.14 (s), 73.16 (s), 73.23 (s), 73.30 (s), 73.38 (s), 73.44 (s), 73.48 (s), 73.54 (s); ^{29}Si NMR (18 MHz, C_6D_6) δ -7.85, -7.41, -7.09, -5.88, -3.41, -2.75, 0.28, 0.38. IR (NaCl) $\nu(\text{Si-O-C})$ 1042, 1019 cm^{-1} .

3.5. Vacuum pyrolysis of **4a** with methanol

Pyrolysis of **4a** was performed at ca. 450°C in a vertical vacuum pyrolysis (1 mmHg) apparatus which consisted of a 50 cm $\times$ 1 cm Pyrex tube packed with Pyrex tip (28 cm height). The upper end of the tube was equipped with a rubber septum and the bottom end was connected to a vacuum outlet and a receiver containing 4.5 ml of methanol cooled with liquid nitrogen. A solution of **4a** (274 mg, 0.8 mmol) in 65 ml hexane was introduced into the heated Pyrex tube under reduced pressure by syringe through the septum. The pyrolysate was trapped in a receiver and allowed to warm to room temperature. Separation of the reaction mixture by preparative HPLC gave **12** and mixture of *dl*- and *meso*-isomers of **13**. Yields were determined by GPC (using an internal standard) as 13% and 33% of **12** and **13** (1:1 mixture of two diastereomers), respectively. For **12**: white crystals, m.p. 61–63°C; ^1H NMR (500 MHz, C_6D_6) δ 0.28 (s, 18H), 0.36 (s, 12H); ^{13}C NMR (125 MHz, C_6D_6) δ 2.52 (q), 2.69 (q), 188.78 (s); ^{29}Si NMR (18 MHz, C_6D_6) δ -12.74, 19.0; MS, m/z 302 (M^+); Exact mass m/z Found 302.1399, Calc. for $\text{C}_{12}\text{H}_{30}\text{OSi}_4$ 302.1374; IR (CCl_4) $\nu(\text{Si-O-Si})$ 930

cm^{-1} . For **13**: colorless oil; ^1H NMR (500 MHz, C_6D_6) δ 0.26 (s, 36H), 0.290 (s, 6H), 0.293 (s, 6H), 0.37 (bs, 12H), 0.50 (s, 2H), 0.61 (s, 2H), 3.29 (s, 6H), 3.32 (s, 6H); ^{13}C NMR (125 MHz, C_6D_6) δ 0.25 (q), 1.77 (q), 12.57 (d), 49.16 (q); ^{29}Si NMR (18 MHz, C_6D_6) δ 3.29, 16.87; MS, m/z 355 ($\text{M}^+ - \text{Me}$); Exact mass m/z Found 335.1683, Calc. for $\text{C}_{13}\text{H}_{35}\text{O}_2\text{Si}_4$ 335.1713; IR (CCl_4) $\nu(\text{Si-O-Si})$ 930 cm^{-1} .

3.6. Flow pyrolysis of **4a** with *N*-methyl triazolidione

A solution of **4a** (70 mg, 0.2 mmol) in 50 ml hexane was introduced by syringe through the septum into the heated (470°C) Pyrex tube (see above) under flowing dinitrogen. The dinitrogen flow was ca. 20 ml min^{-1} ; the receiver contained *N*-methyl triazolidione (92.4 mg, 0.8 mmol) in 3 ml benzene and was cooled with a dry ice. The pyrolysate was trapped in the receiver and allowed to warm to room temperature. Separation of the reaction mixture by preparative GPC (8 mm $\times$ 1 m glass column packed with 10% SF-96 on Celite 545) gave **14**. The yield was determined by GPC (using an internal standard) as 10%. For **14**: waxy solid; ^1H NMR (500 MHz, C_6D_6) δ 0.33 (s, 18H), 0.65 (s, 12H), 2.85 (s, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 1.35 (q), 3.87 (q), 24.91 (q), 157.63 (s), 187.27 (s); ^{29}Si NMR (18 MHz, C_6D_6) δ -1.37, -10.98; MS, m/z 399 (M^+); Exact mass m/z Found 399.1643, Calc. for $\text{C}_{15}\text{H}_{33}\text{N}_3\text{O}_2\text{Si}_4$ 399.1649; IR (CCl_4) $\nu(\text{C=O})$ 1742, 1723, 1717, $\nu(\text{Si-N})$ 1114, 884 cm^{-1} .

3.7. Photolysis of **4b** in cyclohexane

A solution of **4b** (560 mg, 1.07 mmol) and cyclohexane 15 ml was degassed and sealed in Pyrex tube. After irradiation with a high pressure mercury lamp using a glass filter (cut off < 350 nm) for 4 h, separation of the reaction mixture by preparative HPLC (eluent toluene) gave 6.7 mg (1%) of **21b** and 29.3 mg (6%) of **22b**. **21b** was gradually oxidized in air to give **25b**. For **21b**: colorless crystals; m.p. 128–129°C; ^1H NMR (500 MHz, C_6D_6) δ 0.29 (s, 12H), 0.30 (s, 18H), 7.16–7.25 (m, 6H), 7.45–7.50 (m, 4H); ^{13}C NMR (125 MHz, C_6D_6) δ 0.11 (q), 7.36 (q), 43.23 (s), 126.70 (d), 127.95 (d), 133.35 (d), 142.01 (s); ^{29}Si NMR (18 MHz, C_6D_6) δ -15.65, -3.95; MS, m/z 453 ($\text{M}^+ - \text{Me}$); Exact mass m/z Found 468.1952, Calc. for $\text{C}_{24}\text{H}_{40}\text{Si}_5$ 468.1976. For **22b**: colorless crystals; m.p. 128–132°C; ^1H NMR (500 MHz, C_6D_6) δ -0.32 (s, 6H), 0.26 (s, 3H), 0.34 (s, 6H), 0.37 (s, 3H), 0.39 (s, 6H), 0.60 (s, 6H), 7.15–7.24 (m, 6H), 7.53–7.59 (m, 4H); ^{13}C NMR (125 MHz, C_6D_6) δ -1.16 (q), -0.90 (q), 1.49 (q), 2.01 (s), 2.25 (q), 4.42 (q), 5.63 (q), 127.95 (d), 129.12 (d), 134.79 (d), 141.53 (s); ^{29}Si NMR (80 MHz, C_6D_6) δ -44.31, -6.08, 20.91; MS, m/z 484 (M^+); Exact mass m/z Found 484.1880, Calc. for $\text{C}_{24}\text{H}_{40}\text{OSi}_5$

484.1923. For **25b**: colorless oil; ^1H NMR (500 MHz, C_6D_6) δ 0.23 (s, 12H), 0.34 (s, 12H), 7.19–7.27 (m, 6H), 7.43–7.49 (m, 4H); ^{13}C NMR (125 MHz, C_6D_6) δ 1.27 (q), 2.00 (q), 128.04 (d), 129.27 (d), 134.62 (d), 140.29 (d), 189.20 (s); MS, m/z 426 (M^+); Exact mass m/z Found 426.1720, Calc. for $\text{C}_{22}\text{H}_{34}\text{OSi}_4$ 426.1687.

3.8. Photolysis of **4b** in cyclohexane- d_{12}

A solution of **4b** (25.4 mg, 0.048 mmol) in cyclohexane- d_{12} (0.4 ml) was degassed and sealed in a Pyrex NMR tube. After irradiation with a high pressure mercury lamp using glass filter (cut off < 350 nm) for 4 h, ^1H NMR measurement at room temperature detected **23b** with estimated half-life $t_{1/2} = 99$ min. ^{29}Si NMR measurement at -55°C also detected **23b**. For **23b**: ^1H NMR (500 MHz, cyclohexane- d_{12} , 25°C) δ -0.238 (s, 6H), 0.293 (s, 6H), 0.322 (s, 6H), 0.460 (s, 3H, silirane SiMe), 0.556 (s, 3H, silirane SiMe), 0.579 (s, 6H), 7.1–7.6 (m, 10H); ^{29}Si NMR (18 MHz, n-hexane- d_{14} , -55°C) δ -54.1 (silirane), -21.77 ($\text{SiMe}_2\text{SiMe}_2$), -5.8 (SiMe_2Ph).

3.9. Reaction of **23b** with *tert*-butyl alcohol

A solution **4b** (300 mg, 0.57 mmol) and cyclohexane (15 ml) was degassed and sealed in Pyrex tube. After irradiation at 0°C with a high pressure mercury lamp using glass filter (cut off < 350 nm) for 2 h, excess *tert*-butyl alcohol was introduced and the mixture allowed to stand overnight. Separation of the reaction mixture by preparative HPLC (eluent toluene) gave 14.2 mg (5%) of **24b**. For **24b**: colorless oil; *cis/trans* = 51/49 mixture; ^1H NMR (500 MHz, C_6D_6) δ *trans*-**24b**, 0.123 (brs, 6H), 0.165 (brs, 6H), 0.301 (s, 6H), 0.581 (brs, 6H), 0.599 (s, 1H), 0.621 (s, 6H), 1.145 (s, 9H), 7.16–7.30 (m, 6H), 7.66–7.68 (m, 4H), *cis*-**24b**, 0.165 (s, 1H), 0.195 (s, 6H), 0.375 (s, 6H), 0.466 (s, 6H), 0.502 (s, 6H), 0.596 (s, 6H), 1.199 (s, 9H), 7.16–7.30 (m, 6H), 7.57–7.63 (m, 4H); ^{29}Si NMR (18 MHz, C_6D_6) δ -4.9 , -4.4 , 0.1, 0.8, 6.3, 6.6; MS, m/e 542 (M^+); Exact mass m/z Found 542.2680, Calc. for $\text{C}_{28}\text{H}_{50}\text{OSi}_5$ 542.2708.

3.10. Photolysis of **4c** in cyclohexane

A solution of **4c** (338 mg, 0.643 mmol) and cyclohexane 15 ml was degassed and sealed in Pyrex tube. After irradiation at 0°C with a high pressure mercury lamp using glass filter (cut off < 350 nm) for 4 h, separation of reaction mixture by preparative HPLC gave 35.2 mg (11%) of **29**. For **29**: colorless crystals, m.p. $131\text{--}132^\circ\text{C}$; ^1H NMR (400 MHz, C_6D_6) δ -0.15 (s, 9H), 0.18 (s, 3H), 0.21 (s, 3H), 0.33 (s, 9H), 0.40 (s, 3H), 0.56 (s, 3H), 7.20–7.23 (m, 6H), 7.57–7.61 (m,

2H), 7.65–7.69 (m, 2H); ^{13}C NMR (100 MHz, C_6D_6) δ -0.36 (q), 0.82 (q), 2.38 (q), 3.88 (q), 4.22 (q), 4.74 (q), 14.28 (s), 127.88 (d), 128.42 (d), 129.17 (d), 129.65 (d), 135.87 (d), 136.84 (d), 137.04 (s), 138.11 (s), 223.28 (s); ^{29}Si NMR (80 MHz, C_6D_6) δ -23.74 , -6.37 , 1.32, 13.93, 21.48; Exact mass m/z Found 514.2133, Calc. for $\text{C}_{24}\text{H}_{42}\text{N}_2\text{OSi}_5$ 514.2143.

3.11. Photolysis of **4d** in cyclohexane

A solution of **4d** (370 mg, 0.63 mmol) and cyclohexane 10 ml was degassed and sealed in a Pyrex tube. After irradiation with a high pressure mercury lamp using a glass filter (cut off < 350 nm) for 10 h, separation of the reaction mixture by silica gel column chromatography and TLC gave 82.3 mg (25%) of **30**. **30** was gradually oxidized in air to give **31**. For **30**: colorless crystals, m.p. $123\text{--}124^\circ\text{C}$; ^1H NMR (400 MHz, C_6D_6) δ -0.02 (s, 6H), 0.19 (s, 3H), 0.20 (s, 3H), 0.29 (s, 3H), 0.49 (s, 3H), 0.50 (s, 6H), 0.52 (s, 6H), 0.64 (s, 6H), 7.27–7.36 (m, 6H), 7.71–7.74 (m, 4H); ^{13}C NMR (100 MHz, C_6D_6) δ -7.37 (q), -5.78 (q), 0.07 (q), 0.71 (q), 1.76 (q), 3.63 (q), 4.21 (q), 7.19 (q), 11.41 (s), 127.59 (d), 128.83 (d), 135.22 (d), 142.85 (s); ^{29}Si NMR (80 MHz, C_6D_6) δ -54.10 , -42.14 , -4.90 , -3.41 ; MS m/z 526 (M^+); E.A. calc. for $\text{C}_{26}\text{H}_{46}\text{Si}_6$ C: 59.24 H: 8.80%. found C: 59.10, H: 8.65%. For **31**: colorless oil; ^1H NMR (500 MHz, C_6D_6) δ 0.20 (s, 6H), 0.34 (s, 6H), 0.38 (s, 6H), 0.52 (s, 6H), 0.53 (s, 6H), 7.27–7.31 (m, 6H), 7.54–7.63 (m, 4H); ^{13}C NMR (125 MHz, C_6D_6) δ 1.26 (q), 2.16 (q), 3.30 (q), 3.45 (q), 4.40 (q), 128.06 (d), 128.19 (d), 128.77 (d), 128.99 (d), 133.64 (d), 134.66 (d), 141.96 (s), 142.49 (s), 190.32 (s), 196.00 (s); ^{29}Si NMR (80 MHz, C_6D_6) δ -36.21 , -15.56 , -12.83 , -5.83 , 8.62; MS m/z 484 (M^+); Exact mass m/z Found, 484.1951 Calc. for $\text{C}_{24}\text{H}_{40}\text{OSi}_5$ 484.1926.

3.12. Flow pyrolysis of **4d**

A solution of **4d** (100 mg, 0.17 mmol) in 50 ml hexane was introduced by syringe through a septum into the heated (500°C) Pyrex tube (see above) under flowing dinitrogen. The pyrolysate was trapped in a receiver and cooled with dry ice. Separation of reaction mixture by preparative HPLC (eluent toluene) gave 14.9 mg (9%) of **21d**. For **21d**: colorless crystals m.p. $118\text{--}119^\circ\text{C}$; ^1H NMR (500 MHz, C_6D_6) δ 0.15 (s, 12H), 1.36 (s, 6H), 0.47 (s, 12H), 0.53 (s, 6H), 7.27–7.32 (m, 6H), 7.55–7.68 (m, 4H); ^{13}C NMR (125 MHz, C_6D_6) δ 1.82 (q), 2.12 (q), 5.82 (q), 7.71 (q), 19.18 (s), 128.29 (d), 128.53 (d), 133.56 (d), 142.17 (s); ^{29}Si NMR (80 MHz, C_6D_6) δ -19.99 , -8.69 , 3.12; MS m/z 526 (M^+); Exact mass m/z Found 526.2239, Calc. for $\text{C}_{26}\text{H}_{46}\text{Si}_6$ 526.2215.

3.13. Flow pyrolysis of **4e** with methanol

A solution of **4e** (100 mg, 0.29 mmol) in 20 ml hexane was introduced by syringe through the septum into the heated (480–510°C) Pyrex tube (see above) under flowing argon (20 ml min⁻¹). The pyrolysate was trapped with methanol in a receiver cooled with dry ice bath. Separation of reaction mixture by preparative GLC (8 mm × 1 m, glass column packed with 10% SF-96 on Celite 545) gave **19** in 19% yield. **19** was rapidly oxidized in air to give the corresponding siloxane. For **19**: ¹H NMR (500 MHz, CDCl₃) δ 0.34 (s, 12H), 6.9–7.2 (m, 10H); ¹³C NMR (125 MHz, CDCl₃) δ 0.59 (q), 125.89 (d), 127.73 (d), 128.14 (d), 140.71 (s), 158.77 (s); ²⁹Si NMR (90 MHz, CDCl₃) δ 15.8; MS *m/z* 294 (M⁺); Exact mass *m/z* Found 294.1238, Calc. for C₁₈H₂₂Si₂ 294.1260.

3.14. X-ray structure determination of **29** and **30**

Suitable crystals were obtained by recrystallization from hexane and benzene. **29**: C₂₄H₄₂Si₅N₂O, *M* = 515.05, triclinic with *a* = 13.468(7), *b* = 13.467(7), *c* = 20.512(11) Å, α = 101.22(3), β = 100.18(3), γ = 115.73(2)°, *V* = 3140.3 Å³, space group *P*-1, *Z* = 4, ρ_{calc} = 1.09 g cm⁻³, 4607 reflections, *R* = 0.089 (*R*_w = 0.108). **30**: C₂₆H₄₆Si₆, *M* = 527.17, triclinic with *a* = 9.331(3), *b* = 10.914(3), *c* = 15.834(4) Å, α = 92.43(2), β = 100.82(1), γ = 94.98(2)°, *V* = 1575.1 Å³, space group *P*-1, *Z* = 2, ρ_{calc} = 1.11 g cm⁻³, 3429 reflections, *R* = 0.044 (*R*_w = 0.046). The independent reflections [*2θ* ≤ 50°; |*F*o²| > 3σ |*F*o²|] were measured on an Enraf-Nonius CAD4 diffractometer using Mo-Kα irradiation and ω – 2θ scan. The structure were solved by direct methods, all nonhydrogen atoms were refined anisotropically and hydrogen atoms were refined with fixed thermal parameters. Atomic coordinates and thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

Acknowledgments

The authors are grateful to Shin-Etsu Chemical Co. Ltd. for their gifts of chlorosilanes. This work was

supported by a Grant-in-Aid for Scientific Research for Ministry of Education, Science and Culture of Japan.

References and notes

- [1] (a) A. Sekiguchi, H. Tanikawa and W. Ando, *Organometallics*, 3 (1985) 584; (b) G. Markel and W. Schlosser, *Angew. Chem. Int. Ed. Engl.*, 27 (1988) 963.
- [2] A. Sekiguchi, T. Sato and W. Ando, *Organometallics*, 6 (1987) 2337.
- [3] (a) A. Sekiguchi and W. Ando, *J. Am. Chem. Soc.*, 106 (1984) 1486; (b) G. Maas, K. Schneider and W. Ando, *J. Chem. Soc. Chem. Commun.*, (1988) 72; (c) K. Schneider, B. Daucher, A. Fronda and G. Maas, *Chem. Ber.*, 123 (1990) 589.
- [4] W. Ando, H. Yoshida, K. Kurishima and M. Sugiyama, *J. Am. Chem. Soc.*, 113 (1991) 7790.
- [5] (a) W.H. Atwell and J.G. Uhlmann, *J. Organomet. Chem.*, 52 (1973) C21; (b) H. Sakurai, T. Kobayashi and Y. Nakadaira, *J. Organomet. Chem.*, 162 (1978) C43; (c) D. Seyferth, D.C. Annarelli and S.C. Vick, *J. Organomet. Chem.*, 272 (1984) 123.
- [6] (a) T.J. Barton and J.A. Kilgour, *J. Am. Chem. Soc.*, 96 (1974) 7150; (b) idem, 98 (1976) 7746.
- [7] G. Fritz, E. Wartanessian, E. Mateen, W. Honle and H.G. von Schnering, *Z. Anorg. Allg. Chem.*, 475 (1981) 87.
- [8] G. Maas and A. Fronda, *J. Organomet. Chem.*, 398 (1990) 229.
- [9] Unlike the head-to-tail dimerization observed in transient silenes which produces 1,3-disilacyclobutane, stable silenes dimerize in a head-to-head fashion to form 1,2-disilacyclobutane: (a) A.G. Brook, S.C. Nyburg, W.F. Reynolds, Y.C. Poon, Y.-M. Chang and J.-S. Lee, *J. Am. Chem. Soc.*, 101 (1979) 6750; (b) M. Ishikawa, T. Fuchikami, M. Kumada, T. Higuchi and S. Miyamoto, *J. Am. Chem. Soc.*, 101 (1979) 1348; (c) J. Ohshita, Y. Masaoka and M. Ishikawa, *Organometallics*, 10 (1991) 3775; (d) D. Bravo-Zhivotovskii, V. Braude, A. Stanger, M. Kapon and Y. Apeloig, *Organometallics*, 11 (1992) 2326. For ab initio calculations: (e) E.T. Seidl, R.S. Grev and H.F. Schaefer III, *J. Am. Chem. Soc.*, 114 (1992) 3643; (f) F. Bernardi, A. Bottoni, M. Olivucci, M.A. Robb and A. Venturini, *J. Am. Chem. Soc.*, 115 (1993) 3322.
- [10] T.J. Barton and E.A. Kline, *J. Organomet. Chem.*, 42 (1972) C21.
- [11] T. Shioiri, T. Aoyama and S. Mori, *Organic Synthesis*, 68 (1989) 1.
- [12] T. Shioiri and S. Yamada, *Organic Synthesis*, 62 (1984) 187.
- [13] H. Sakurai K. Tominaga, T. Watanabe and M. Kumada, *Tetrahedron Lett.*, 45 (1966) 5493.
- [14] M. Ishikawa, M. Kumada and H. Sakurai, *J. Organomet. Chem.*, 23 (1970) 63.
- [15] X. Creary, *Organic Synthesis*, 64 (1985) 207.