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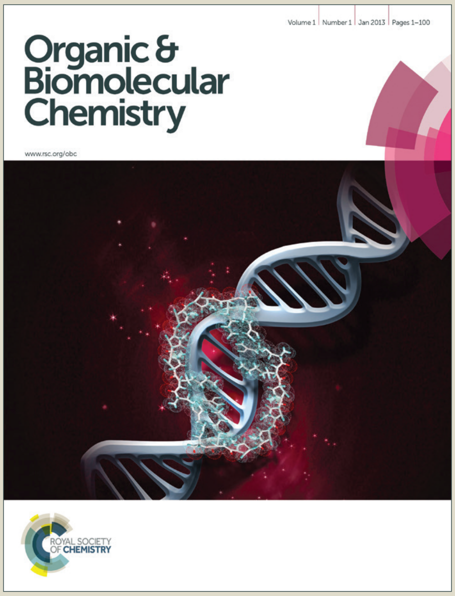

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ARTICLE TYPE

Elusive 2*H*-1,2-Oxasiletes Through Reactions of an Isolable Dialkylsilylene with Diazocarbonyl Compounds

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The reactions of isolable dialkysilylene **1** with 2-diazo-1,2-diphenylethanone and ethyl 2-diazo-2-phenylacetate gave elusive silacycles, 2*H*-1,2-oxasiletes **2** and **3**, respectively, in high yields. Because these reactions occur at low temperatures of ca. -30 °C, initial complexation of the silylene to the carbonyl oxygen of the diazocarbonyl compounds is suggested to trigger the dinitrogen elimination followed by the cyclization. In contrast, six-membered cyclic diazo compound **8** and 1-sila-2,3-diazabicyclo[3.3.0]oct-3-ene **10** were obtained in good yields by the reaction of **1** with less reactive ethyl 2-diazo-3-oxo-3-phenylpropanoate **7** and trimethylsilyldiazomethane **9**. Molecular structures of **2**, **3**, **8** and **10** were determined by X-ray crystallography.

Introduction

In recent two decades, a number of studies have been devoted to explore the reactions of silylenes, silicon divalent compounds, with a variety of organic unsaturated species including alkenes, alkynes, carbonyl compounds, nitriles and imines.[1] These reactions are not only helpful to understand the bonding and chemical properties of silylenes, but also synthetically useful to construct various novel silacycles which are difficult to be obtained by conventional routes.[1,2]

During the course of our studies of the reactions of an isolable dialkylsilylene, 2,2,5,5-tetrakis(trimethylsilyl)silacyclopentane-1,1-diyl **1** (Chart 1),[3,4] we have found that silylene **1** reacts with various diazo compounds to give different types of products depending on substituents. Most remarkably, elusive 2*H*-1,2-oxasiletes **2** and **3** are obtained as thermally stable compounds by the reactions of **1** with diazocarbonyl compounds. Though the first 2*H*-1,2-oxasilete **4** was characterized by NMR spectroscopy in solution by Sekiguchi and Ando,[5] **4** was found to be thermally unstable to prevent its isolation as a pure substance. The reactions are quite interesting because thermal,[6] photochemical,[7] or activation with transition metal catalysts[8,9] is usually required to eliminate dinitrogen from diazocarbonyl compounds; no dinitrogen release of the compounds by main-group element compounds has been reported.

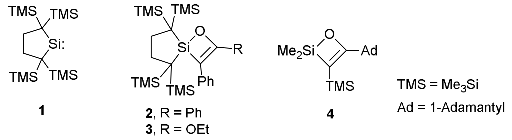
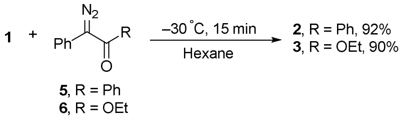


Chart 1. Structural formulae of **1-4**.

Results and discussion

When **1** was treated with an equimolar amount of 2-diazo-1,2-diphenylethanone (**5**) and ethyl 2-diazo-2-phenylacetate (**6**) in hexane at –30 °C, the orange yellow color of **1** turned to pale yellow within 15 minutes. Usual work-up gave 2*H*-1,2-oxasiletes **2** and **3**, respectively, in more than 90 % yields as colorless crystals (Eq 1).



(1)

2*H*-1,2-Oxasiletes **2** and **3** were characterized by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopic studies in $CDCl_3$. Typically, in the ^{1}H NMR spectrum of **2**, two singlets due to two types of trimethylsilyl protons appeared at 0.01 and 0.11 ppm with the 1:1 intensity ratio, indicating the asymmetric structure of **2**; similarly, two trimethylsilyl protons appeared at 0.34 and 0.39 ppm for **3**. The ^{29}Si NMR spectra of **2** and **3** showed three resonances assignable to two different trimethylsilyl silicon and a ring silicon nuclei at 1.9, 4.2, and 52.2 ppm for **2** and 2.0, 3.9, and 42.2 ppm for **3**. The unsaturated ^{13}C signals in the four-membered ring appeared at 162.0 and 116.2 ppm for **2** and at 162.2 and 81.7 ppm for **3**, which are comparable with 185.3 and 103.3 ppm for **4**.[5]

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† *Electronic supplementary information (ESI) available: NMR spectra and X-ray crystallographic data of* ***2, 3, 8*** *and* ***11****. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b0xx00000x.*

Single crystals of **2** and **3** suitable for X-ray crystallography were obtained by slowly evaporating the hexane solution of these silacycles. The perspective drawings of the molecular structures of **2** and **3** determined by the X-ray analysis are given in Figures 1 and 2. In both **2** and **3**, the ring silicon atom (Si1) adopts distorted tetrahedral geometry. The distance of Si1-O1 in **2** and **3** is 1.728(2) Å and 1.745(3) Å, respectively, which are in the nomal range of Si-O bond lengths. The four-membered ring is perfectly planar, with the sum of the inner angles of 360.0°. The C17-C18 distance is 1.350(3) Å and 1.348(5) Å for **2** and **3**, indicating the double bond character between C17 and C18 atoms.

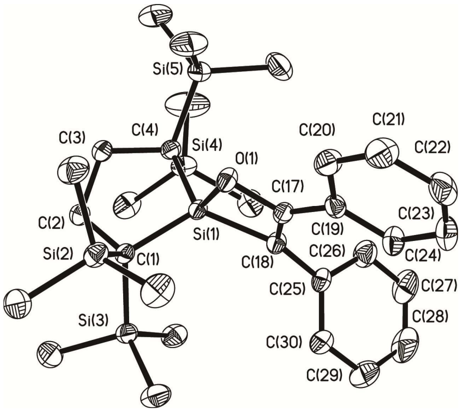


Figure 1. ORTEP drawing of **2**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 30% probability level. Selected bond lengths (Å) and angles (°): Si1-O1=1.7276(19), Si1-C18=1.880(2), Si1-C1=1.884(2), Si1-C4=1.892(2), O1-C17=1.404(2), C17-C18=1.350(3), C17-C19=1.474(3), C18-C25=1.486(3), O1-Si1-C18=76.75(9), O1-Si1-C1=110.74(10), C18-Si1-C1=124.66(11), O1-Si1-C4=111.87(9), C1-Si1-C4=100.80(10), C17-O1-Si1=89.36(11), C18-C17-O1=109.03(17), C18-C17-C19=135.67(19), C17-C18-C25=127.51(19), C17-C18-Si1=84.85(14), C25-C18-Si1=147.64(16).

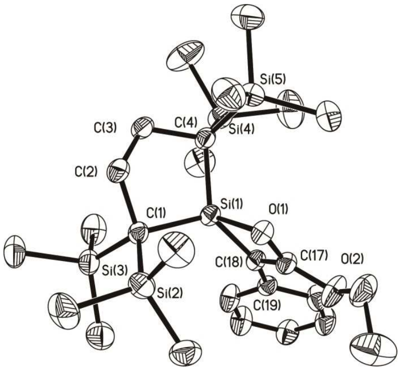
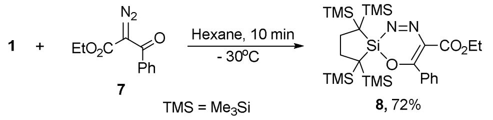


Figure 2. ORTEP drawing of **3**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 30% probability level. Selected bond lengths (Å) and angles (°): Si1-O1=1.745(3), Si1-C18=1.855(4), Si1-C4=1.881(4), Si1-C1=1.890(4), C19-C18=1.457(5), C18-C17=1.348(5), C17-O2=1.325(4), C17-O1=1.370(4), O1-Si1-C18=77.18(13), O1-Si1-C4=110.54(14), O1-Si1-C1=109.61(13), C4-Si1-C1=101.60(15), C17-C18-C19=126.6(3), C17-C18-Si1=83.8(2), O2-C17-C18=129.8(3), O2-C17-O1=118.7(3), C18-C17-O1=111.5(3), C17-O1-Si1=87.5(2).

In contrast to **4** reported by Sekiguchi and Ando,[5] compounds **2** and **3** are thermally very stable and intact after heating at 120 °C in $CDCl_3$ in a sealed NMR tube for more than 2 h. No reaction occurs when **2** and **3** are mixed with methanol.

A similar reaction of **1** with electron-withdrawing ethoxycarbonyl-substituted diazoketone **7** afforded a cyclic adduct without releasing dinitrogen. Thus, when **1** was treated with an equimolar amount of **7** in hexane at –30 ˚C，the colour of the mixture changed from orange yellow to green within 10 min. Usual work-up gave formal [1+5]-cycloadduct **8** in a good yield (Eq 2).



(2)

The molecular structure of **8** determined using X-ray crystallography is shown in Figure 3 with pertinent structural parameters. The six-membered SiN_2C_2O ring of **8** is nearly planar. The N=N and C=C bond lengths of **8** [1.269(2) Å and 1.362(2)Å] are in the range of their localized double bond lengths.

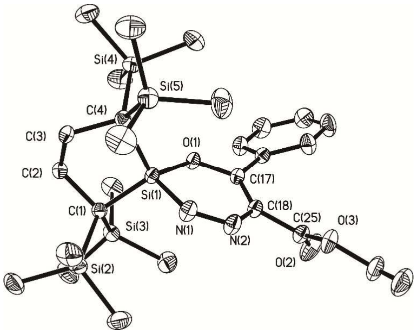
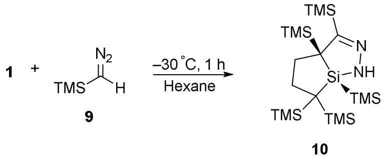


Figure 3. ORTEP drawing of **8**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 30% probability level. Selected bond lengths (Å) and angles (°): Si1-O1=1.6967(12), Si1-N1=1.7635(16), Si1-C1=1.8654(18), Si1-C4=1.8682(17), N1-N2=1.269(2), N2-C18=1.421(2), O1-C17=1.3482(19), C17-C18=1.362(2), O1-Si1-N1=101.55(7), C1-Si1-C4=102.46(7), N2-N1-Si1=124.28(12), N1-N2-C18=121.74(15), C17-O1-Si1=124.50(10), O1-C17-C18=121.05(15), C17-C18-N2=125.57(15).

When trimethyldiazomethane (**9**), a diazoalkane with no carbonyl substituent, was treated with **1** under similar reaction conditions, rather unusual 1-sila-2,3-diazabicyclo[3.3.0]oct-3-ene **10** was obtained in a good yield (Eq 3). The structure of **10** was confirmed by NMR spectroscopic studies and finally by X-ray crystallography.



(3)

Molecular structure of **10** determined by X-ray crystallography is shown in Figure 4, confirming its bicylo[3.3.0]octene ring structure. The Si-N bond lengh of **10** [1.743(2) Å] is shorter than thoses of the reported 1,3-diaza-2-siloles [1.777(3) and 1.79(3) Å][10] and 1,4-diaza-2-siloles [1.757(3) Å].[11] While the C=N bond lengh of **10** [1.284(3) Å] is similar to those of the related compounds.[10,11] The N2-Si1-C4 plane of **10** is almost perpendicular to the C1-Si1-C4 plane with a dihedral angle of 83.9°.

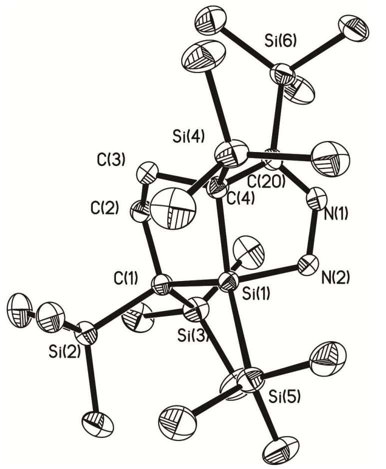


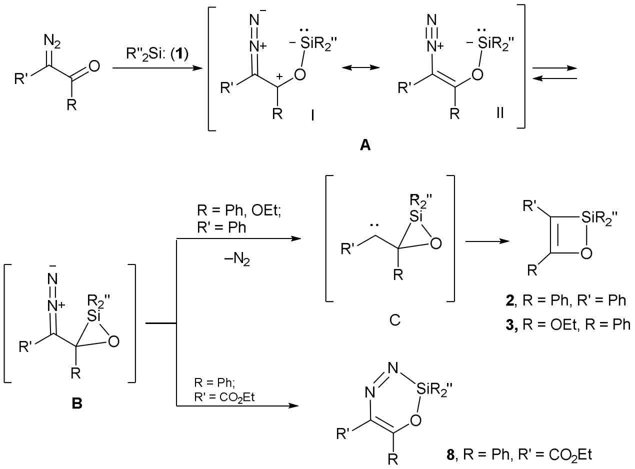
Figure 4. ORTEP drawing of **10**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 30% probability level. Selected bond lengths (Å) and angles (°): Si1-N2=1.743(2), Si1-C4=1.918(2), Si1-C1=1.932(2), N1-N2=1.413(2), C20 -N1=1.284(3), N2-Si1-C4=89.26(10), C4-Si1-C1=96.11(10), C20-N1-N2=113.52(18), N1-N2-Si1=113.14(14), C2-C1-Si1=101.85(13), Si3-C1-Si1=112.33(12), C3-C2-C1=110.93(17), C2-C3-C4=108.45(19), C20-C4-C3=111.95(17), C20-C4-Si1=100.35(14), C3-C4-Si1=103.01(14), Si4-C4-Si1=117.29(11), N1-C20-C4=118.02(18).

The reactions of dialkylsilylene **1** with a variety of diazo compounds give diverse types of products depending on the substituents as shown above. It would be worth to discuss here the mechanistic aspects of these reactions, while the complete picture of the mechanisms still remains open.

Very limited studies on the reactions of silylenes with diazo compounds have been reported. Driess et al.[12] have recently found that the reaction of an isolable cyclic diaminosilylene with diphenyldiazomethane gives rather unusual diiminylsilane adduct. Roesky, Stalke, et al.[13] have reported the reaction of a base-coordinate aminochlorosilylene with trimethylsilyldiazomethane affords a cyclic dimer of the silylene-diazoalkane adduct without release of dinitrogen. No straightforward dinitrogen release has been observed in these cases.

As shown in Scheme 1,[14] facile dinitrogen release from **5** and **6** may occur via the initial approach of **1** to the carbonyl oxygen of the diazocarbonyl compounds giving complex **A** followed by the cyclization to afford silaoxacyclopropane intermediate **B**.[15] A silacyclopropyl group in **B** is electron-donating probably due to σ(SiC)-π conjugation, accelerating the dinitrogen release from **B** to afford the corresponding carbene **C**. 1,2-Silyl migration of **C** may give **2** and **3**.[16] Direct nucleophlic attack of the silyl anion of complex **A** at the diazo carbon will be possible but improbable because the carbon is sp^2 hybridized.

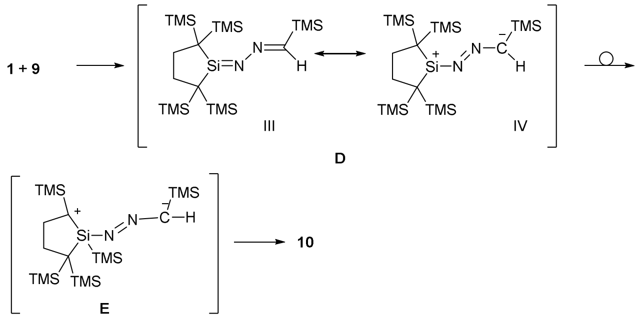
On the other hand, **8** with ethoxycarbonyl group as R' may give a similar silaoxacyclopropane by the reaction with **1** but the enhanced contribution of the resonance forms II due to electron-withdrawing effects of CO_2Et substituent may hamper the release of dinitrogen from the complex and allow the silyl anion to approach to the terminal nitrogen of the diazo group giving **8** (Scheme 1).



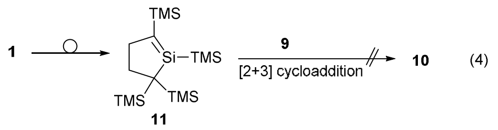
Scheme 1. Possible reaction pathways for the formation of **2** and **3**.

The ring structure of **8** remained intact when **8** was heated at 60 °C, while heating of **8** at 120 °C for 4 h gave a complex mixture. The results suggest that similar cyclic diazo compounds would not be involved in the formation of **2** and **3** by the reactions of **1** with **5** and **6**.

The reaction of silylene **1** with **9** is unusually accompanied by 1,2-trimethylsilyl migration of the silylene moiety. A plausible mechanism for the reaction is proposed as shown in Scheme 2: Because silaimine intermediate **D** has a significant contribution of a polar resonance form **IV**, the silylene silicon of the intermediate will be positively charged to prompt the 1,2-trimethylsilyl migration from carbon to silicon giving a 1,5-zwitterionic intermediate **E**. Intramolecular cyclization of **E** would give the final product **10**. A similar 1,2-silyl migration has been proposed to occur during the reactions of **1** with diarylimines with an electron-withdrawing aryl group on nitrogen.[19] Because thermal isomerization of **1** into the corresponding silaethene **11** is known to occur at rt,[3,20] **10** may be formed via the [2+3]-cycloaddition between **11** and **9** as a 1,3-dipole for the formation of **10**. However, the latter mechanism is unlikely because no reaction occurred when a mixture of silathene **11** and silyldiazomethane **9** was kept at room temperature for 5 h (Eq 4).



Scheme 2. A plausible reaction pathway for the reaction of **1** with **9**.



In sumamry, silylene **1** reacts with 2-diazo-1,2-

diphenylethanone **5** and ethyl 2-diazo-2-phenylacetate **6** at low temperatures to give stable new-type silacycles, 2*H*-1,2-oxasiletes **2** and **3**, respectively. The reaction constitutes the first dinitrogen release from diazo compounds activated by heavy main-group element reagents. In contrast, the reactions of **1** with diazoketone **7** and diazoalkane **9** afforded unique cyclic compounds **8** and **10**, respectively, without releasing dinitrogen. The origin of the difference in the reaction pathways between the reactions of **1** with **5** (and **6**) and **7** remains open but may be attributed to the difference in the basicity of the keto-carbonyl groups. Further works including theoretical studies will be needed to elucidate the detailed reaction mechanisms.

Experimental section

Reagents and Instruments

All synthetic experiments were performed under argon or nitrogen in a standard vacuum system unless otherwise noted. Tetrahydrofuran (THF), hexane, and toluene were distilled from sodium-benzophenone. ^{1}H (400 MHz), ^{13}C (100 MHz), and ^{29}Si (80 MHz) spectra were recorded with TMS as an internal standard on a BRUKER AV-400 MHz instrument. MS were measured with a Trance 2000 DSQ mass spectrometer. High-resolution MS were measured on a Thermo Scientific LTQ Orbitrap XL spectrometer. Melting points were uncorrected. Dialkylsilylene **1** was prepared according to the literature procedures.[3] Dialkylsilylene **1** and other air-sensitive materials were handled in an MBraun glovebox. All products were purified by flash chromatography or GPC (LC-9101, Japan Analytical Industry Co. Ltd).

The general reactions of dialkylsilylene 1 with 2-diazo-1,2-diphenylethanone 3 and ethyl 2-diazo-2-phenylacetate 4.

A hexane solution of 2-diazo-1,2-diphenylethanone or ethyl 2-diazo-2-phenylacetate (0.2 mmol) was added to silylene **1** (75 mg, 0.2 mmol) in hexane (10 mL) at - 30 ^{o}C. The reaction mixture was stirred for half an hour at the same temperature. Then the reaction mixture was allowed to gradually warm to rt over 1 h. After the removal of the solvent under reduced pressure, the residual was purified by a silica gel column chromatography to give **2** and **3** as a white solid.

2: White solid (104.3 mg, 92%); mp:156-159℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.33 (m, 2H), 7.19 – 7.08 (m, 8H), 2.08-1.95 (m, 4H), 0.11 (s, 18H), 0.00 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0, 137.3, 132.4, 129.6, 129.3, 128.3, 127.9, 127.5, 125.7, 116.8, 32.1, 12.3, 3.7, 2.9; ^{29}Si NMR (80 MHz, $CDCl_3$) δ 52.2, 4.2, 1.9; HRMS *m/z* $[M+H]^+$ Calcd for $C_{30}H_{51}OSi_5$: 567.2781 Found: 567.2768.

3: White solid (96.1 mg, 90%); mp:115-117℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.0 Hz, 2H), 7.35 (t, *J* = 8.0 Hz, 2H), 7.07 (t, *J* = 8.0 Hz, 1H), 4.12 (q, 2H), 2.17 – 2.00 (m, 4H), 1.08 (t, 3H), 0.39 (s, 18H), 0.34 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.2, 135.9, 128.3, 127.8, 123.3, 81.7, 63.5, 31.7, 15.2, 10.9, 3.6, 3.2 ^{29}Si NMR (80 MHz, C_6D_6) δ 42.7, 3.9, 2.0; HRMS *m/z* $[M+H]^+$ Calcd for $C_{26}H_{51}O_2Si_5$: 535.2730 Found: 535.2700.

Thermal reactions of 2 and 3 and reactions of 2 and 3 with methanol.

When a solution of **2** (or **3**) in $CDCl_3$ was heated at 120 °C in a sealed NMR tube, no reaction took place as evidenced by the NMR spectra.

A mixture of 2*H*-1,2-oxasiletes **2** (or **3**) (10 mg), CD_3Cl (1 mL), and two drops of methanol in an NMR tube was shaken at room temperature for 30 min. No difference was observed in the ^{1}H-NMR spectra of before and after the reaction.

The reaction of silylene 1 with 2-diazo-3-oxo-3-phenylpropanoate 7

A hexane solution of 2-diazo-3-oxo-3-phenylpropanoate (0.2 mmol) was added to silylene **1** (75 mg, 0.2 mmol) in hexane (10 mL) at –30 ^{o}C. The reaction mixture was stirred for 15 min at the same temperature. Then the reaction mixture was allowed to gradually warm to rt over 0.5 h. The solvent was removed under vacuum. The residue was dissolved in hexane. Green crystals of **8** were obtained by keeping the solution at –20 $^\circ$C for one week.

8: Green solid (85 mg, 72%); mp:154-157 °C (decomp.); ^{1}H NMR (500 MHz, C_6D_6) δ 7.73 – 7.59 (m, 2H), 7.07 – 7.01 (m, 3H), 4.09 (q, *J* = 8.0 Hz, 2H), 2.03-2.25 (m, 4H), 0.86 (t, *J* = 8.0 Hz, 3H), 0.28 (s, 16H), 0.12 (s, 16H); ^{13}C NMR (126 MHz, C_6D_6) δ 167.0, 143.8, 135.5, 134.2, 130.9, 129.6, 128.1, 60.6, 32.2 15.2, 13.6, 3.5, 3.3; ^{29}Si NMR (99 MHz, C_6D_6) δ 6.7, 2.76, 2.78; HRMS *m/z* $[M+H]^+$ Calcd for $C_{30}H_{51}OSi_5$: 591.2741 Found: 591.2736.

The reaction of silylene 1 with trimethylsilyldiazomethane 9

A hexane solution of trimethylsilyldiazomethane **9** (0.2 mmol) was added to a hexane solution of silylene **1** (75 mg, 0.2 mmol) at –30 °C. The reaction mixture was stirred for 1 h at the same temperature. Then the reaction mixture was allowed to gradually warm to rt over 1 h. After removal of the solvent under reduced pressure, the residue was purified by a silica gel column chromatography to give **10** as a white solid.

10: White solid (67.6 mg, 70%); mp:137-142 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.98 (s, 1H), 2.48-2.51 (m, 1H), 2.09-2.12 (m, 1H), 1.55-1.76 (m, 2H), 0.29 (s, 10H), 0.22 (s, 9H), 0.12 (d, *J* = 8.9 Hz, 18H), 0.06 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.3, 47.6, 35.4, 33.8, 20.1, 2.9, 2.2, 2.1, 1.4, 0.3. ^{29}Si NMR (99 MHz, $CDCl_3$) δ 22.5, 1.8, -0.1, -0.6, -6.9, -18.3. HRMS *m/z* $[M+H]^+$ Calcd for $C_{30}H_{51}OSi_5$: 487.2662 Found: 487.2659.

X-ray Analysis

Single crystals of **2**, **3, 8** and **10** suitable for X-ray analysis were obtained by the recrystallization from hexane. The X-ray diffraction data were collected on a Bruker Smart Apex CCD diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) using the ω-2θ scan mode. The structure was solved by direct methods and refined on F2 by full-matrix least-squares methods using SHELX-2000.[21] All the structural data are deposited with CCDC. The reference numbers are: 1056197 (**2**), 1056194 (**3**), 1063129 (**8**), and 1405300 (**10**).

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Notes and references

1 For recent reviews on silylenes and their reactions, see: (a) M. Driess and H. Grützmacher, *Angew. Chem., Int. Ed.*, 1996, **36**, 828. (b) J. Barrau and R. Ghassoub, *Coord. Chem. Rev.*, 1998, **178**, 593. (c) P. Jutzi and N. Burford, *Chem. Rev.*, 1999, **99**, 969. (d) P. P. Gaspar and R. West, *The Chemistry of Organic Silicon Compounds*, eds. Z. Rappoport and Y. Apeloig, New York, John Wiley & Sons 1998, vol. 2, part 3, Ch. 43, 2463. (e) N. Tokitoh and R. Okazaki, *Coord. Chem. Rev.*, 2000, **210**, 251. (f) M. Weidenbruch, *J. Organomet. Chem.*, 2002, 646, 39. (g) M. Weidenbruch, *Organometallics*, 2003, **22**, 4348. (h) N. J. Hill and R. West, *J. Organomet. Chem.*, 2004, **689**, 4165. (i) Y. Mizuhata, T. Sasamori and N. Tokitoh, *Chem. Rev.*, 2009, **109**, 3479. (j) W. H. Atwell, *Organometallics* 2009, **28**, 3573. (k) S. Yao, Y. Xiong and M. Driess, *Organometallics*, 2011, **30**, 1748. (l) M. Asay, C. Jones and M. Driess, *Chem. Rev.*, 2011, **111**, 354. (m) S. Yao and M. Driess, *Acc. Chem. Res.*, 2012, **45**, 276. (n) S. Sen, S. Khan, S. Nagendran and H. W. Roesky, *Acc. Chem. Res.*, 2012, **45**, 578. (o) M. Driess, *Nat. Chem.*, 2012, **4**, 525. (p) S. S. Sen, S. Khan, S. P. Samuel and H. W. Roesky, *Chem. Sci.*, 2012, **3**, 659-682.

2 (a) W. Ando and Y. Kabe, In *The Chemistry of Organic Silicon Compounds*, Z. Rappoport and Y. Apeloig, (Eds.); Wiley: Chichester, UK, 1998; p. 2401. (b) R. Azhakar, H. W. Roesky, R. S. Ghadwal, J. J. Holstein and B. Dittrich, *Dalton Trans.* 2012, **41**, 19601.

3 M. Kira, S. Ishida, T. Iwamoto and C. Kabuto, *J. Am. Chem. Soc.*, 1999, **121**, 9722.

4 For reviews on silylene **1**, see: (a) M. Kira, *J. Organomet. Chem.*, 2004, **689**, 4475. (b) M. Kira, S. Ishida and T. Iwamoto, *Chem. Rec.*, 2004, **4**, 243. (c) M. Kira, T. Iwamoto and S. Ishida, *Bull. Chem. Soc. Jpn.*, 2007, **80**, 258. (d) M. Kira, *Chem. Commun.*, 2010, 2893. (e) M. Kira, *J. Chem. Sci.*, 2012, **124**, 1205.

5 A. Sekiguchi and W. Ando, *J. Am. Chem. Soc.*, 1984, **106**, 1486.

6 (a) L. Benati, D. Nanni and P. Spagnolo, *J. Chem. Soc., Perkin Trans. 1*, 1997, **4**, 457-461. (b) L. L. Rodina, J. J. Medvedev, O. S. Galkina and V. A. Nikolaev, *Eur. J. Org. Chem.* 2014, **14**, 2993. (c) M. C. Perez-Aguilar and C. Valdes, *Angew. Chem., Int. Ed.*, 2013, **52**, 7219. (d) A. Kaupang and T. Bonge-Hansen, *Beilstein J. Org. Chem*, 2013, **9**, 1407.

7 (a) V. A. Nikolaev, V. V. Shevchenko, M. S. Platz and N. N. Khimich, *Russ. J. Org. Chem.* 2006, **42**, 815. (b) T. Kopke, M. Pink and J. M. Zaleski, *J. Am. Chem. Soc.*, 2008, **1030**, 15864. (c) A. J. P. Mortimer, J. R. H, Plet, O. A. Obasanjo, N. Kaltsoyannis and M. J. Porter, *Org. Biomol. Chem.* 2012, **10**, 8616. (d) M. R. Smith, A. J. Blake C. J. Hayes, M. F. G. Stevens and C. J. Moody, *J. Org. Chem.* 2014, **74**, 9372.

8 For reviews, see: (a) M. P. Doyle, *Chem. Rev.,* 1986, **96**, 919. (b) M. P. Doyle and D. C. Forbes, *Chem. Rev.,* 1998, **98**, 911. (c) R. H. Grubbs, *Handbook of Metathesis*; Wiley-VCH: Weinheim, Germany, 2003. (d)T. Trnka and R. H. Grubbs, *Acc. Chem. Res.*, 2001, **34**, 18. (e) R. R. Schrock, *Angew. Chem., Int. Ed.*, 2006, **45**, 3748.

9 (a) G. Du, B. Andrioletti, E. Rose and L. W. Woo, *Organometallics*, 2002, **21**, 4490. (b) W. Kirmse, *Angew. Chem., Int. Ed.*, 2003, **42**, 1088. (c) R. H. Grubbs, *Angew. Chem., Int. Ed.*, 2006, **45**, 3760. (d) D. Marcoux and A. B. Charette, *Angew. Chem., Int. Ed.*, 2008, **47**, 10155. (e) M. Czyzewski, J. Bower, M. Box, H. Ottosson and P. G. Steel, *Chem. Sci.,* 2011, **2**, 2367.

10 (a) P. Jutzi; D. Eikenberg; B. Neumann and H. G. Stammler, *Organometallics* 1996, **15***,* 3659. (b) M.Weidenbruch; P. Will and K. Peters, *Z. Anorg. Allg. Chem.* 1996, **622**, 1811.

11 L. L. Wang, W. F. Chen, Z. F. Li, X. –Q. Xiao, G. Q. Lai, X. P. Liu, Z. Xu and M. Kira, *Chem. Commun*., 2013, 9776.

12 Y. Xiong, S. L. Yao and M. Driess, *Chem. Eur. J.,* 2009, 8542.

13 A. Jana, S. S. Sen, H. W. Roesky, C. Schulzke, S. Dutta and S. K. Pati, *Angew. Chem., Int. Ed.*, 2009, **48**, 4246.

14 We thank an anonymous reviewer for suggesting the mechanisms shown in Scheme 1.

15 Formation of silaoxacyclopropanes by the reactions of silylenes with carbonyl compounds is a well known process. See: S. Ishida, T. Iwamoto and M. Kira, *Organometallics*, 2010, **29**, 5526, and references cited therein.

16 The process will occur easily because it constitutes a well-known cyclopropylcarbene-to-cyclobutene rearrangement[17] involving facile 1,2-silyl migration from saturated carbon to carbene center.[18]

17 (a) L. Friedman and H. Shechter, *J. Am. Chem. Soc.*, 1960, **82**, 1002. (b) W. J. Barton, M. R. DeCamp, M. E. Hendrick, J. M. Jones, R. H. Levin and M. B. Sohn, in *Carbenes*, eds. J. M. Jones and R. A. Moss, J. Wiley & Sons, New York, 1973, vol. 1, Chapter 1..

18 (a) X. Creary and Y.-X. Wang, *Tetrahedron Lett.*, 1989, **30**, 2493. (b) X. Creary and Y.-X. Wang, *J. Org. Chem.*, 1994, **59**, 1604. (c) M. Trommer, W. Sander, C.-H. Ottosson and D. Cremer, *Angew. Chem. Int. Ed. Engl.* 1995, **34**, 929. See also: M. Kira and T. Iwamoto, in *The Chemistry of Organic Silicon Compounds*, eds. Z. Rappoport and Y. Apeloig, John-Wiley, Chichester, 2001, vol. 3, pp. 853.

19 (b) W. F. Chen, L. L.Wang, Z. F. Li, A. Q. Lin, G. Q. Lai, X. X. Xiao, Y. Deng and M. Kira, *Dalton Trans.,* 2013, **42**, 1872.

20 S. Ishida, T. Iwamoto and M. Kira, *Organometallics* 2009, **28**, 919.

21 (a) C. L. Picou, E. D. Stevens, M. Shah and J. H. Boyer, *Acta Crystallogr. Sect. C* 1990, **46**, 1148. (b) SMART, SAINT, SADABS and SHELXTL, Bruker AXS Inc., Madison, 2000.