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The chemical behavior of the silaoxine $C_{22}H_{34}OSi_3$ and silaazetidine $C_{25}H_{43}NSi_4$ towards CO_2

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Abstract: When 4,4a-dihydro-3,3-dimethyl-1-phenyl-4,4-bis(trimethylsilyl)-*3H*-2-oxa-3-sila-naphthaline (silaoxine $C_{22}H_{34}OSi_3$ (**3**); orthorhombic, space group $Pna2_1$, $Z = 4$) was thermolized in a CO_2 atmosphere, the corresponding oxasilacyclobutane (silaoxetane) **5** was quantitatively formed. The [2+2] cycloreversion of the silaoxetane **5** occurred at temperatures higher than 120°C to give exclusively $Ph_2C{=}C(SiMe_3)_2$ and $(Me_2SiO)_n$. Single crystals of $Ph_2C{=}C(SiMe_3)_2$ (**6**; monoclinic, space group $C2/c$, $Z = 8$) were isolated from this reaction. When the azasilacyclobutane (silaazetidine) $C_{25}H_{43}NSi_4$ (**4**; monoclinic, space group $P2_1/n$, $Z = 4$) was reacted with an excess of CO_2 at 100°C an unknown intermediate was formed along with the benzophenonimine $Ph_2C{=}N(SiMe_3)$. The NMR resonances of this intermediate indicates the formation of the β-silalactone (silaoxetanone) $C_{10}H_{24}O_2Si_3$ (**7**). At temperatures higher than 120°C the silaoxetanone **7** decomposed to give $(Me_3Si)_2C{=}C{=}O$ and $(Me_2SiO)_n$, respectively.

Keywords: carbon dioxide; silene; X-ray structure analysis.

1 Introduction

In the past decade the reactivity of frustrated Lewis pairs (FLPs) [1, 2] towards small molecules such as dihydrogen [3, 4] or carbon dioxide [5, 6] has been extensively studied. Previously we have reported that the phosphinoborane **1** (phosphaboradibenzofulvene; Fig. 1) reacts fast with H_2 [7]. In addition to the reaction of **1** with gaseous H_2, the compound **1** reacts also with acetonitrile, benzophenone, and 2,3-dimethylbutadiene [7].

The structural analogy of phosphinoboranes $R_2B{=}PR_2$ and isoelectronic Wiberg-type silenes (Fig. 2) evidently implies that the π bonds in phosphinoboranes [8] are similar to those in silenes [9–12].

The parent Wiberg-type silene $Me_2Si{=}C(SiMe_3)_2$ (**2**) could be conveniently generated either by retro Diels-Alder reaction from the silaoxine **3** or by [2+2] cycloreversion from the silaazetidine **4** (see Scheme 1 and footnote[1]) [9, 10, 13–16]. It should also be noted that the reactivity of the Brook-type is distinguished significantly from that of the Wiberg-type silenes [9, 10, 17, 18].

Following the approaches of Wiberg we synthesized the silaoxine **3** [14] and the silaazetidine **4** [15] to make a comparison of the reaction behavior of Wiberg-type silenes with that of the related phosphinoboranes. As an example we have investigated the reactions of **3** and **4** with carbon dioxide. In addition we present here the structure of the silaoxine **3**, the silaazetidine **4,** and the olefin $Ph_2C{=}C(SiMe_3)_2$. The latter one was obtained from the silaoxetane **5** by [2+2] cycloreversion.

2 Results and discussion

As noticed above heating of the silaoxine **3** to a temperature higher than 100°C leads to the formation of the silene **2** along with benzophenone (cf. Scheme 1). However, when the silaoxine **3** was thermolized in a CO_2 atmosphere, the silaoxetane **5** was quantitatively formed at this temperature. In this case the Lewis acid CO_2 solely catalyzed the rearrangement of the silaoxine **3** to the silaoxetane **5**, as depicted in Scheme 2 (see footnote[2]). This implies that the [2+2] cycloadduct of **2** with $Ph_2C{=}O$ is apparently more stable than that with CO_2.

At a temperature higher than 120°C the [2+2] cycloreversion of the silaoxetane **5** occurred to give exclusively $Ph_2C{=}C(SiMe_3)_2$ and $(Me_2SiO)_n$ (see Scheme 2). Single crystals of the olefin **6** were isolated from this reaction.

When the silaazetidine **4** was treated with an excess of CO_2 at 100°C an unknown intermediate was formed along with the benzophenonimine $Ph_2C{=}N(SiMe_3)$. The

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[1] For the reactivity of silaazetidines, see ref. [13].

[2] Rearrangement of **3** to **5** also takes place in the presence of Me_3SiCl see ref. [14].

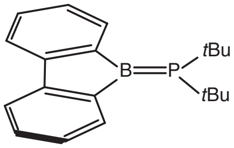

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Fig. 1: Phosphaboradibenzofulvene **1**.

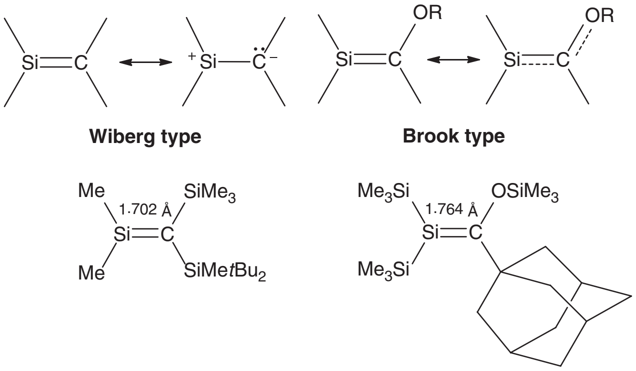
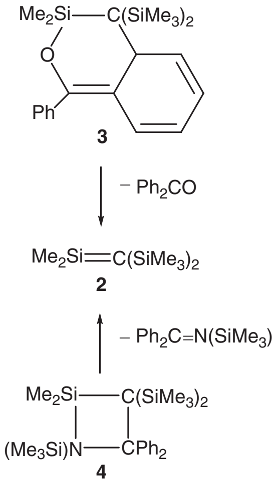
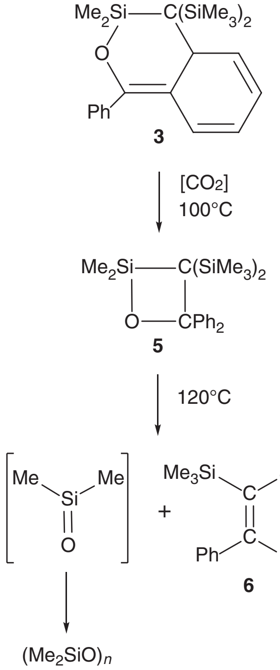


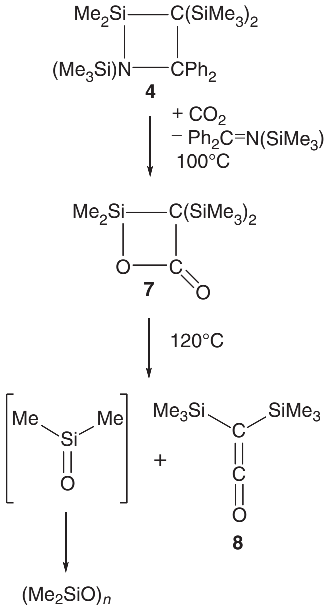
Fig. 2: Wiberg-type and Brook-type silenes.



Scheme 1: Synthesis of the silene $Me_2Si{=}C(SiMe_3)_2$ (**2**) by cycloreversion of **3** and **4** at 100°C.



Scheme 2: Thermolysis of the silaoxine **3** in the presence of CO_2.



Scheme 3: Reaction of the silaazetidine **4** with CO_2.

NMR resonances of this intermediate indicates the formation of silaoxetanone **7**. This reaction reveals that the parent Wiberg-type silene **2** which was generated from the silaazetidine **4**, activates carbon dioxide. Unfortunately, we were not able to isolate **7**. As also shown in Scheme 3, the silaoxetanone **7** decomposed at higher temperatures to give the literature-known bis(trimethylsilyl)ketene **8** [19, 20] and $(Me_2SiO)_n$ (see Scheme 3).

The silaoxine **3** crystallizes in the orthorhombic space group $Pna2_1$ as a racemate. Fig. 3 represents the structure of one of two enantiomers (selected bond lengths are reported in the caption of Fig. 3) and indicates a central C_4OSi heterocycle with an annelated C_6 ring. The C_4OSi heterocycle in **3** adopts a screw-chair conformation and reveals a dihedral angle with the attached phenyl ring of 36.1(1)° (atoms used to define the ring planes: Si(1), O(1), C(1), C(2), C(7), C(8), and C(81), C(82), C(83), C(84),

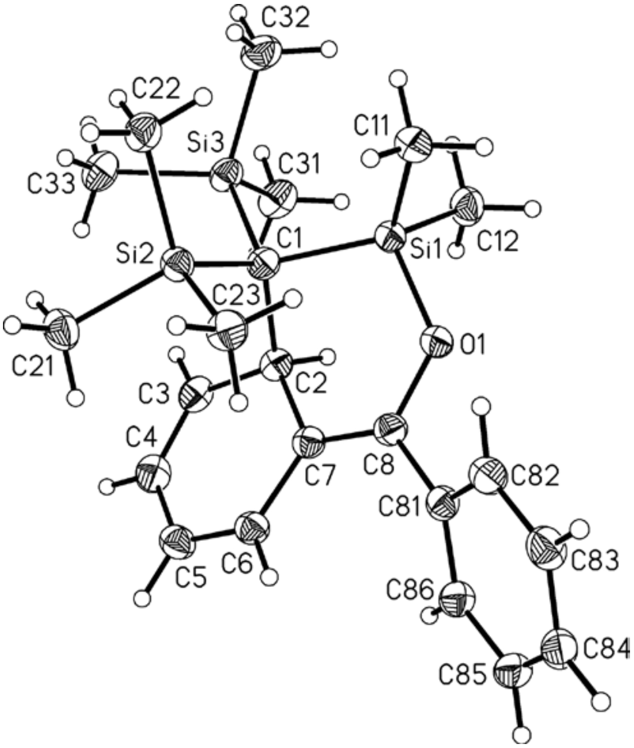


Fig. 3: Solid-state structure of one enantiomer of the silaoxine **3**. Selected bond lengths (Å) and bond angles (deg): O(1)–C(8) 1.369(2), O(1)–Si(1) 1.677(1), Si(1)–C(11) 1.859(2), Si(1)–C(12) 1.862(2), Si(1)–C(1) 1.887(2), C(1)–C(2) 1.612(2), C(1)–Si(2) 1.914(2), C(1)–Si(3) 1.917(2), Si(2)–C(21) 1.879(2), Si(2)–C(23) 1.882(2), Si(2)–C(22) 1.898(2), C(2)–C(3) 1.517(2), C(2)–C(7) 1.533(2), Si(3)–C(31) 1.884(2), Si(3)–C(33) 1.887(2), C(3)–C(4) 1.333(3), C(4)–C(5) 1.448(3), C(5)–C(6) 1.349(2), C(6)–C(7) 1.448(2), C(7)–C(8) 1.365(2), C(8)–C(81) 1.475(2); C(8)–O(1)–Si(1) 127.2(1), O(1)–Si(1)–C(11) 106.0(1), O(1)–Si(1)–C(12) 102.7(1), C(11)–Si(1)–C(12) 107.7(1), O(1)–Si(1)–C(1) 105.2(1), C(11)–Si(1)–C(1) 116.9(1), C(12)–Si(1)–C(1) 116.8(1), C(2)–C(1)–Si(1) 100.5(1), C(2)–C(1)–Si(2) 112.6(1), Si(1)–C(1)–Si(2) 111.6(1), C(2)–C(1)–Si(3) 111.9(1), Si(1)–C(1)–Si(3) 108.4(1), Si(2)–C(1)–Si(3) 111.4(1), C(3)–C(2)–C(7) 112.1(1), C(3)–C(2)–C(1) 114.3(1), C(7)–C(2)–C(1) 113.0(1), C(3)–C(4)–C(5) 121.3(2), C(6)–C(5)–C(4) 120.4(2), C(5)–C(6)–C(7) 122.3(2), C(8)–C(7)–C(6) 121.1(2), C(8)–C(7)–C(2) 119.3(2), C(6)–C(7)–C(2) 119.5(1), C(7)–C(8)–O(1) 120.9(2).

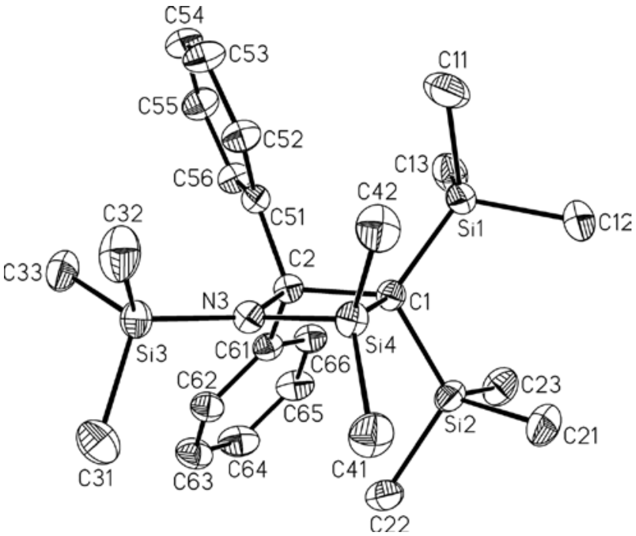


Fig. 4: Molecular structure of the silaazetidine **4** in the solid state. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): C(1)–C(2) 1.647(2), C(1)–Si(4) 1.909(1), C(1)–Si(1) 1.917(1), C(1)–Si(2) 1.933(1), C(2)–N(3) 1.501(1), C(2)–C(61) 1.533(2), C(2)–C(51) 1.553(2), N(3)–Si(4) 1.734(1), N(3)–Si(3) 1.740(1), Si(4)–C(42) 1.875(1), Si(4)–C(41) 1.878(2), Si(1)–C(12) 1.875(2), Si(1)–C(13) 1.882(2), Si(1)–C(11) 1.882(2); C(2)–C(1)–Si(4) 84.4(1), C(2)–C(1)–Si(1) 118.2(1), Si(4)–C(1)–Si(1) 120.5(1), C(2)–C(1)–Si(2) 117.7(1), Si(4)–C(1)–Si(2) 105.8(1), Si(1)–C(1)–Si(2) 108.5(1), N(3)–C(2)–C(61) 113.4(1), N(3)–C(2)–C(51) 108.6(1), C(61)–C(2)–C(51) 109.6(1), N(3)–C(2)–C(1) 98.2(1), C(61)–C(2)–C(1) 111.2(1), C(51)–C(2)–C(1) 115.6(1), C(2)–N(3)–Si(4) 95.3(1), C(2)–N(3)–Si(3) 131.7(1), Si(4)–N(3)–Si(3) 131.1(1), N(3)–Si(4)–C(42) 119.4(1).

C(85), C(86), respectively). Furthermore the angle Si(1)–O(1)–C(8) is widened to 127.2(1)°. The bicyclic ring system is characterized by alternating C–C single and double bonds [C(2)–C(3) 1.517(2) Å, C(3)–C(4) 1.333(3) Å, C(4)–C(5) 1.448(3) Å, C(5)–C(6) 1.349(2) Å, C(6)–C(7) 1.448(3) Å, C(7)–C(8) 1.365(2) Å]. The endocyclic single bond C(1)–C(2) [1.612(2) Å] is significantly elongated and is therefore comparable to that in the corresponding *t*Bu-substituted silaoxine [1.624(12) Å] [21].

Crystals of the silaazetidine **4** (see Fig. 4) were grown from pentane at room temperature, and belong to the monoclinic space group $P2_1/n$. The compound **4** consists of a four-membered ring with a Si–C and a Si–N bond of 1.909(1) Å and 1.734(1) Å, respectively. This C_2NSi heterocycle is nearly planar (r.m.s. deviation 0.045 Å). The H atoms bonded to the C atoms were geometrically positioned and refined using a riding model. The phenyl rings form dihedral angles with the heterocycle of 72.4(1)° and 53.7(4)°. All endocyclic bond angles in the heterocycle are significantly narrowed [C(2)–C(1)–Si(4) 84.4(1)°, N(3)–C(2)–C(1) 98.2(1)°, C(2)–N(3)–Si(4) 95.3(1)°, N(3)–Si(4)–C(1) 81.5(1)°].

Furthermore we could isolate single crystals of the olefin **6** from the reaction mixture. The compound crystallizes in the monoclinic space group *C*2/*c*. As shown in Fig. 5, its structure features a central C=C bond. Due to the bulky substituents, this double bond is elongated to 1.360(8) Å. The bond angle between the two ipso ring atoms at C(2) [C(11)–C(2)–C(21) 112.1(5)°] is significantly narrowed whereas the bond angles at C(1) are all close to 120° [Si(1)–C(1)–Si(2) 118.4(3)°, Si(1)–C(1)–C(2) 120.8(5)°, Si(2)–C(1)–C(2) 120.8(5)°].

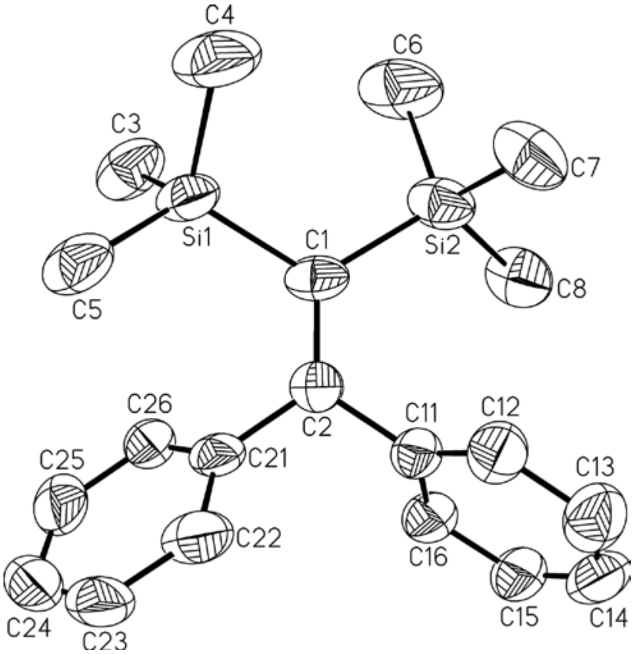


Fig. 5: Molecular structure of the olefin **6** in the solid state. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Si(1)–C(3) 1.862(7), Si(1)–C(5) 1.867(6), Si(1)–C(4) 1.883(8), Si(1)–C(1) 1.901(7), Si(2)–C(7) 1.860(8), Si(2)–C(8) 1.864(7), Si(2)–C(6) 1.883(8), Si(2)–C(1) 1.894(6), C(1)–C(2) 1.360(8), C(2)–C(21) 1.502(8), C(2)–C(11) 1.503(8); C(3)–Si(1)–C(5) 109.2(4), C(3)–Si(1)–C(4) 108.4(4), C(5)–Si(1)–C(4) 102.5(4), C(3)–Si(1)–C(1) 112.0(3), C(5)–Si(1)–C(1) 114.4(3), C(4)–Si(1)–C(1) 109.8(4), C(7)–Si(2)–C(8) 109.6(4), C(7)–Si(2)–C(6) 108.7(4), C(8)–Si(2)–C(6) 104.2(4), C(7)–Si(2)–C(1) 112.9(3), C(8)–Si(2)–C(1) 112.7(3), C(6)–Si(2)–C(1) 108.3(4), C(2)–C(1)–Si(2) 120.8(5), C(2)–C(1)–Si(1) 120.8(5), Si(2)–C(1)–Si(1) 118.4(3).

3 Experimental section

The solvents Et_2O, tetrahydrofuran, pentane, benzene, and C_6D_6 were stirred over sodium/benzophenone and distilled prior to use. $Me_2SiBr–CBr(SiMe_3)_2$ [22] and $Me_2SiF–CBr(SiMe_3)_2$ [15] were prepared according to the published procedures. All other starting materials were purchased from commercial sources and used without further purification. The NMR spectra were recorded on Bruker AM 250, DPX 250, Avance 400, and Avance 500 spectrometer. NMR chemical shifts are reported in ppm. A JASCO FT/IR 4200 spectrometer was used for recording the IR spectra.

3.1 Synthesis of the silaoxine 3

The silaoxine **3** was prepared according to the published procedure [14]. Single crystals were obtained by recrystallization from a 1:1 mixture of Et_2O and pentane. – ^1H NMR (300.032 MHz; C_6D_6; Me_4Si): $\delta = 0.18$ (s; $SiMe_3$), 0.24 (s; SiMe), 0.32 (s; $SiMe_3$), 0.42 (s; SiMe), 4.37 (m; CH), 5.84 (m; =CH), 7.25 ppm (m; *o*/*m*/*p*-H of Ph). – ^{13}C NMR (62.9 MHz; C_6D_6; Me_4Si): $\delta = 2.0$ (Si*Me*), 3.1 (Si*Me*$_3$), 3.6 (Si*Me*), 4.1 (Si*Me*$_3$), 14.4 (*C*Si_3), 39.1 (*C*H), 115.2/118.3/124.4/126.9/128.1 (*C*=C), 128.2/129.5/130.9/137.6 (*C*-Ph), 152.9 ppm (=*C*O). – ^{29}Si NMR (59.6 MHz; C_6D_6; Me_4Si): $\delta = -1.3$ ($SiMe_3$), 1.2 ($SiMe_3$), 14.4 ppm ($SiMe_2$).

3.2 Synthesis of the silaazetidine 4

The silaazetidine **4** was prepared according to the published procedure [15]. Single crystals were grown from a pentane solution at room temperature. – ^1H NMR (300.032 MHz; C_6D_6; Me_4Si): $\delta = 0.04$ (s; $SiMe_3$), 0.11 (s; $NSiMe_3$), 0.65 (s; $SiMe_2$), 7.14 ppm (m; *o*/*m*/*p*-H of Ph). – ^{13}C NMR (62.9 MHz; C_6D_6; Me_4Si): $\delta = 3.2$ (NSi*Me*$_3$), 5.7 (Si*Me*$_3$), 8.9 (Si*Me*$_2$), 36.1 (*C*Si_3), 79.4 (*C*N), 126.5/127.0/129.7/148.0 ppm (*C*-Ph). – ^{29}Si NMR (59.6 MHz; C_6D_6; Me_4Si): $\delta = -3.8$ ($SiMe_3$), 16.4 ppm ($SiMe_2$).

3.3 Reaction of 3 with CO_2

An NMR tube was charged with the silaoxine **3** [14] (40 mg, 0.1 mmol), benzene (0.6 mL) and CO_2 (0.1 mmol) and sealed, and the reaction mixture was heated for 24 h to 100°C. The ^1H, ^{13}C, and ^{29}Si NMR spectra of the reaction solution revealed signals which could be assigned to the silaoxetane **5** (NMR data of **5** see below). In addition a signal which is attributable to CO_2 [^{13}C NMR (62.9 MHz; C_6D_6; Me_4Si): $\delta = 124.9$ ppm] could be recognized. Heating of the reaction mixture for additional 24 h to 120°C yielded quantitatively the olefin **6** and $(Me_2SiO)_n$, as monitored by NMR spectroscopy. Crystals of **6** were grown from the reaction solution after 1 week at room temperature (yield: 10 mg, 31%).

5: ^1H NMR (300.032 MHz; C_6D_6; Me_4Si): $\delta = -0.01$ (s; $SiMe_3$), 0.48 (s; $SiMe_2$), 7.10 ppm (m; *o*/*m*/*p*-H of Ph). – ^{13}C NMR (62.9 MHz; C_6D_6; Me_4Si): $\delta = 5.3$ (Si*Me*$_3$), 7.5 (Si*Me*$_2$), 37.0 (*C*Si_3), 89.7 (*C*O), 126.9/128.0/130.1/149.5 ppm (*C*-Ph). – ^{29}Si NMR (59.6 MHz; C_6D_6; Me_4Si): $\delta = -3.2$ ($SiMe_3$), 34.8 ppm ($SiMe_2$).

6: M.p. 99°C. – ^1H NMR (300.032 MHz; C_6D_6; Me_4Si): $\delta = 0.06$ (s; $SiMe_3$), 7.20 ppm (m; *o*/*m*/*p*-H of Ph). – ^{13}C NMR (62.9 MHz; C_6D_6; Me_4Si): $\delta = 2.7$ (Si*Me*$_3$), 127.6/127.6/129.7/147.6 (*C*-Ph), 144.4 (Si_2*C*=C), 169.6 ppm (Si_2C=*C*). – ^{29}Si NMR (59.6 MHz; C_6D_6; Me_4Si): $\delta = -5.9$ ppm

Table 1: Crystal data and refinement of **3**, **4**, and **6**.

	3	**4**	**6**
Empirical formula	$C_{22}H_{34}OSi_3$	$C_{25}H_{43}NSi_4$	$C_{20}H_{28}Si_2$
M_r	398.76	469.96	324.60
Crystal size, mm^3	0.38 × 0.26 × 0.12	0.47 × 0.42 × 0.15	0.40 × 0.27 × 0.18
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	$Pna2_1$	$P2_1/n$	$C2/c$
a, Å	26.678(1)	9.5402(5)	24.290(5)
b, Å	9.0415(6)	17.6007(6)	9.0423(19)
c, Å	9.3342(5)	16.3546(8)	18.338(3)
β,°	90	91.806(4)	101.391(15)
V, Å^3	2251.5(2)	2744.8(2)	3948.4(13)
Z	4	4	8
$D_{calcd.}$, g cm^{-3}	1.176	1.137	1.092
μ(MoK$_\alpha$), mm^{-1}	0.220	0.229	0.176
F(000), e	864	1024	1408
hkl range	−33/30, ±11, ±11	±13, ±25, ±23	±28, ±10, ±21
$((\sin\theta)/\lambda)_{max}$, Å^{-1}	0.6315	0.7154	0.5953
Refl. measured	22 328	62 267	16 425
Refl. unique/R_{int}	4690/0.034	8369/0.041	3314/0.085
Param. refined	235	271	199
$R(F)^a$ (observed refls.)	0.0306	0.0470	0.1619
$wR(F^2)^b$ (all refls.)	0.0681	0.1191	0.2338
GoF $(F^2)^c$	0.987	1.057	1.087
a/b^b (weight. scheme)	0.0474/0.0	0.0814/0.1553	0.0821/4.8877
Flack parameter x	0.03(8)	–	–
$\Delta\rho_{fin}$ (max/min), e Å^{-3}	0.17/−0.21	0.43/−0.47	0.29/−0.46

$^aR(F)=\Sigma||F_o|-|F_c||/\Sigma|F_o|$; $^bwR(F^2)=[\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w=[\sigma^2(F_o^2)+(aP)^2+bP]^{-1}$, where $P=(\mathrm{Max}(F_o^2, 0)+2F_c^2)/3$; $^c\mathrm{GoF}=S=[\Sigma w(F_o^2-F_c^2)^2/(n_{obs}-n_{param})]^{1/2}$.

($SiMe_3$). – Anal. for $C_{20}H_{28}Si_2$ (324.61): calcd. C 74.00, H 8.69; found C 73.75, H 8.47.

3.4 Reaction of 4 with CO_2

An NMR tube was charged with the silaazetidine **4** [15] (23 mg, 0.05 mmol), benzene (0.6 mL) and CO_2 (0.1 mmol) and sealed. The reaction mixture was heated for 24 h to 100°C. The ^{1}H, ^{13}C, and ^{29}Si NMR spectra of the reaction solution revealed signals which could be assigned to the silaoxetanone **7** (NMR data see below) and the benzophenonimine $Ph_2C{=}N(SiMe_3)$ (NMR data see below). In addition a signal which is attributable to CO_2 [^{13}C NMR (62.9 MHz; C_6D_6; Me_4Si): $\delta = 124.9$ ppm] was detected. Heating of the reaction mixture for additional 24 h to 120°C yielded quantitatively the literature-known bis(trimethylsilyl) ketene **8** [IR: $\nu = 2084.4$ cm^{-1} (CCO); cf. ref. [18] ($\nu = 2085$ cm^{-1})] and polysiloxanes $(Me_2SiO)_n$, as monitored by NMR and IR spectroscopy.

7: ^{1}H NMR (300.032 MHz; C_6D_6; Me_4Si): $\delta = 0.16$ (s; $SiMe_3$), 0.27 (s; $SiMe_3$), 0.45 ppm (s; $SiMe_2$). – ^{13}C NMR (62.9 MHz; C_6D_6; Me_4Si): $\delta = 1.3$ ($Si\mathit{Me}_3$), 5.6 ($Si\mathit{Me}_3$), 7.5 ($Si\mathit{Me}_2$), 15.7 ($\mathit{C}Si_3$), 167.5 ppm ($\mathit{C}O$). – ^{29}Si NMR (59.6 MHz; C_6D_6; Me_4Si): $\delta = -3.8$ ($SiMe_3$), –1.6 ($SiMe_3$), 22.8 ppm ($SiMe_2$) (see footnote[3]).

$Ph_2C{=}N(SiMe_3)$: ^{1}H NMR (300.032 MHz; C_6D_6; Me_4Si): $\delta = 0.19$ (s; $SiMe_3$), 7.20 ppm (m; *o*/*m*/*p*-H of Ph). – ^{13}C NMR (62.9 MHz; C_6D_6; Me_4Si): $\delta = 0.7$ ($NSi\mathit{Me}_3$), 127.9/128.1/128.2/141.9 (*C*-Ph), 174.9 ppm (*C*=N). – ^{29}Si NMR (59.6 MHz; C_6D_6; Me_4Si): $\delta = -0.6$ ppm ($SiMe_3$).

3.5 Crystal structure determinations

Data were collected on a STOE IPDS II two-circle diffractometer with graphite-monochromatized MoK$_\alpha$ radiation ($\lambda = 0.71073$ Å) and corrected for absorption with an empirical absorption correction using the program PLATON [23]. The structures were solved by Direct Methods using the program SHELXS and refined against F^2 with full-matrix least-squares techniques using the program SHELXL-97

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[3] Due to butterfly-like structures of cyclobutanone derivatives substituents attached to the same atom are unequal.

[24]. The compound **3** is a racemate crystallizing in a noncentrosymmetric space group (*Pna*2_1). As a consequence of that, the absolute structure could be determined with the Flack *x* parameter being 0.03(8). Details of the crystal structure analyses are summarized in Table 1.

CCDC 948710 (**3**), 948709 (**4**), and 954167 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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