Inorganic Chemistry
ARTICLE
pubs.acs.org/IC

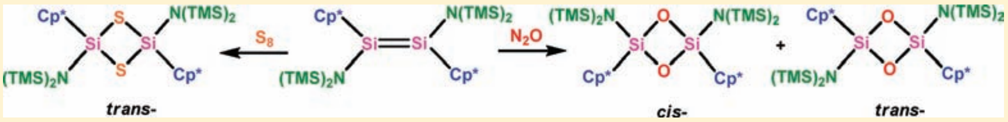
Reactivity Studies of a Disilene with N_2O and Elemental Sulfur

Shabana Khan,[†] Reent Michel,[†] Debasis Koley,[‡] Herbert W. Roesky,*[,†] and Dietmar Stalke*[,†]

[†]Institut für Anorganische Chemie der Universität Göttingen, Tammannstrasse 4, 37077 Göttingen, Germany
[‡]Department of Chemical Sciences, Indian Institute of Science Education and Research—Kolkata, Mohanpur-741252, India

Supporting Information

ABSTRACT:

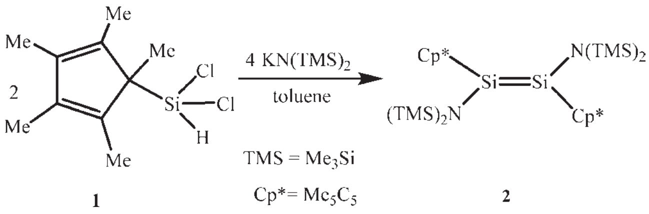


In a previous contribution, we have reported on a convenient and high yield synthesis of the disilene *trans*-[$(TMS)_2N(\eta^1\text{-}Me_5C_5)\text{-}Si{=}Si(\eta^1\text{-}Me_5C_5)N(TMS)_2$] (**2**). Herein, we show the reactions of **2** with N_2O and S_8. The former reaction affords two isomeric (*cis*- and *trans*-) dioxadisiletane ring compounds. To the best of our knowledge, this is the first report where both *cis*- and *trans*-isomers are isolated from the same disilene precursor and characterized structurally by single-crystal X-ray diffraction (XRD) studies. The reaction of **2** with elemental sulfur yields only the *trans*-isomer. To investigate this dissimilar reaction pattern exhibited by **2**, computational studies were performed. Density functional theory (DFT) calculations showed that the two dioxadisiletane ring isomers are isoenergetic, with the *trans* isomer being slightly more stable than the *cis* counterpart, by 3.3 kcal/mol, while that is not the case with sulfur. All the isolated compounds are characterized by single-crystal XRD studies, multinuclear NMR spectroscopy, and electron ionization—mass spectrometry (EI-MS).

INTRODUCTION

Since the remarkable isolation of the first stable disilene ($Mes_2Si{=}SiMes_2$, Mes = 2,4,6-$Me_3C_6H_2$) by West et al. in 1981,[1] considerable attention has been paid to developing the chemistry of disilenes.[2] One of the most commonly used synthetic protocols to access the disilenes is the generation of highly reactive silylenes as intermediates, followed by their dimerization. Therefore, the question arises whether an equilibrium exists between the silylene and the corresponding disilene. This has prompted substantial experimental and theoretical activity, although very few examples are known where an equilibrium is observed between silylene and the corresponding disilene. A first report by Okazaki and co-workers described the thermal dissociation of extremely hindered and kinetically stable disilene [Tbt(Mes)Si═Si(Mes)Tbt, Tbt = 2,4,6-tris{bis(trimethylsilyl)-methyl}phenyl] into very reactive silylene [Tb(Mes)Si] under mild conditions.[3] Later, the existence of thermal equilibrium between 2,3,4,6,7,8,2′,3′,4′,6′,7′,8′-dodeca-*tert*-butyl[5,5′]-bi{1,5-disilatricyclo[4.2.0.0]-octylidene}-2,7,2′,7′-tetraene and the corresponding silylene was proved by trapping experiments and DFT calculations by Tsutsui et al.[4a] Kira and co-workers further supported the existence of the equilibrium between disilene and the corresponding silylene by providing strong spectroscopic evidence for the existence of the silylene [$(R_2N)_2Si$, R = *i*Pr] in solution which is in equilibrium with the corresponding disilene at low temperature.[4b] West et al. then reported the existence of dynamic equilibrium between *cis*-diaminodisilyldisilene and saturated diaminosilylene by ^{29}Si NMR and UV—vis spectroscopy, although diaminosilylene was not the monomer of *cis*-diaminodisilyldisilene.[5] Recently, a noteworthy contribution in this field was made by Jutzi et al., describing the unique situation where both the silylene [$(TMS)_2N(\eta^1\text{-}Me_5C_5)Si$] as well as the corresponding disilene *trans*-[$(TMS)_2N(\eta^1\text{-}Me_5C_5)Si{=}Si(\eta^1\text{-}Me_5C_5)\text{-}N(TMS)_2$] (**2**) are stable and isolable under normal conditions, and this transformation can be easily recognized by the phase transfer from solution to solid state.[6] They explained this unusual behavior on the basis of steric strain in the solid disilene and flexibility in bonding modes (σ or π) of Cp* (Cp* = Me_5C_5) groups. Despite the successful isolation of **2**, chemistry of this unique compound is still in its infancy because of the synthetic constraints associated with the synthesis.[6] Recently we have successfully resynthesized **2** in 68% yield in a single step by treatment of $(Me_5C_5)SiHCl_2$ (**1**) with $KN(TMS)_2$ in a molar ratio of 1:2 in toluene (see Scheme 1).[7] The increase in the yield for **2** with the new method allows us to investigate its reactivity.

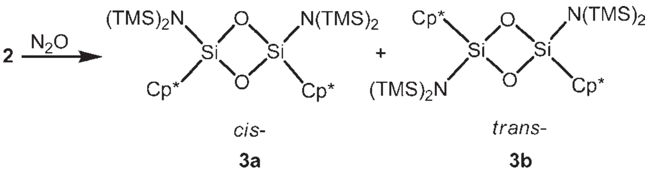
Scheme 1. Preparation of 2



In the course of our recent studies on the reactions of compounds having low valent silicon atoms with various unsaturated

Received: July 5, 2011
Published: September 28, 2011

Scheme 2. Preparation of 3a and 3b



organic compounds,[8−10] we became interested in investigating the unique reactions of **2** with N_2O and S_8.

RESULTS AND DISCUSSION

Reaction with Nitrous Oxide. N_2O is well-known to serve as a mono-oxygen donor. Reaction of **2** in toluene with N_2O at room temperature led to the formation of two dioxadisiletane isomers (*cis-* and *trans-*) (see Scheme 2). Analysis of ^{1}H, ^{13}C, and ^{29}Si NMR (δ 7. 32, 5.17, 3.88, −12.11, −22.31, and −28.53 ppm) spectral data indicated the presence of two compounds (*cis-* and *trans*-isomers) in an approximately 2:3 ratio. The removal of the solvent under vacuum, followed by recrystallization in *n*-pentane, furnished colorless crystals of **3** (**a** and **b**) suitable for single-crystal X-ray diffraction (XRD) studies. The crystals for the X-ray structural study of the *cis* and *trans* isomers were selected by hand from the crystal mixture under microscope. Note that this is the first example where both isomers were formed from the same disilene precursor. West et al. first reported the formation of *trans*-1,3-di-*tert*-butyl-1,3-dimesitylcyclodisiloxane from the corresponding *trans*-disilene and *cis*-1,3-bis[bis(trimethylsilyl)amino]-1,3-dimesitylcyclodisiloxane from the corresponding *cis*-disilene.[11a] The formation of *cis*-1,3-dioxa-2,4-disiletane ring from corresponding *cis*-disilene was further documented by Okazaki et al. upon treatment with molecular oxygen.[3c] Moreover, we reported the formation of two cyclodisiloxane derivatives from the reactions of LSiCl (L = PhC(N*t*Bu)$_2$) with trimethylamine oxide and *tert*-butyl isocyanate[8b] and L_2Si_2 with benzophenone.[8c] It is important to mention that, in both cases, we were able to isolate only the *trans*-isomer.

The presence of two isomers (*cis-* and *trans-*) was confirmed by single-crystal XRD studies. Compound **3a** crystallizes in the centrosymmetric monoclinic space group $P2_1/n$.[12] Selected bond lengths and bond angles are given in the legend of Figure 1. The molecular structure of **3a** reveals a *cis*-configured, almost-planar Si_2O_2 ring (mean deviation from plane: 0.0214 Å) with the dihedral angle of 4.1° between the O−Si−O three-membered planes. The independent endocyclic Si1−O1−Si2, Si1−O2−Si2, O1−Si1−O2, and O1−Si2−O2 angles are 91.42(4)°, 91.29(4)°, 88.34(4)°, and 88.81(4)°, respectively. All four Si−O distances fall in the range of 1.6750(8)−1.6840(8) Å and match well with the reported Si−O bond lengths for the several dioxadisiletane rings reported in the literature.[3c,8b,8c,11] The interatomic separation between two silicon atoms (Si···Si) in the ring is 2.4029(4) Å, which is slightly longer than the calculated value for $H_4Si_2O_2$ (calculated Si−O and Si···Si distances range between 1.661 and 1.671 Å and 2.383 and 2.394 Å, respectively)[13a] but significantly shorter than those of the previously reported $L_2Cl_2Si_2O_2$[8b] and $L_2(CHPh_2)_2Si_2O_2$[8c] (L = PhC(N*t*Bu)$_2$), where the Si···Si interatomic separations are 2.48 and 2.51 Å, respectively. Both of the Si atoms are tetra-coordinated and exhibit distorted tetrahedral geometry. An angle of 79.98° between the planes of the two Cp* rings (attached to two different Si atoms) discloses that these two Cp* are almost perpendicular to each other.

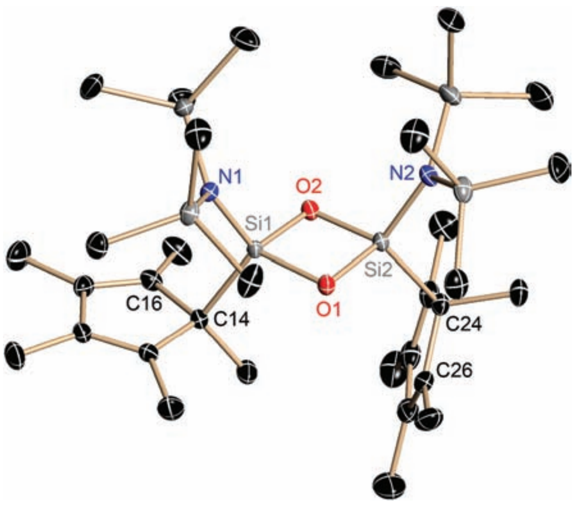


Figure 1. Molecular structure of **3a**. Hydrogen atoms are not shown, for the sake of clarity. Anisotropic displacement parameters are depicted at the 50% probability level. Selected bond distances are given as follows: Si1···Si2, 2.4030(7) Å; Si1−O1, 1.6820(8) Å; Si1−O2, 1.6840(8) Å; Si2−O1, 1.6750(8) Å; Si2−O2, 1.6768(8) Å; Si1−N1, 1.7182(9) Å; Si2−N2, 1.7260(10) Å; Si1−C14, 1.8996(11) Å; and Si2−C24, 1.9213(11) Å. Selected bond angles are given as follows: O1−Si1−O2, 88.34(4)°; O1−Si2−O2, 88.81(4)°; O1−Si1−N1, 112.90(4)°; O2−Si1−N1, 114.71(4)°; N1−Si1−C14, 115.34(4)°; N2−Si2−C24, 111.51(5)°; Si1−O1−Si2, 91.42(4)°; Si1−O2−Si2, 91.29(4)°; O1−Si1−C14, 112.34(4)°; O2−Si1−C14, 110.26(4)°; O1−Si2−N2, 113.64(4)°; O2−Si2−N2, 112.11(4)°; O1−Si2−C24, 113.42(4)°; O2−Si2−C24, 115.65(4)°; C26−C24−Si2, 114.26(7)°; and C16−C14−Si1, 106.91(7)°.

Compound **3b** crystallizes in the centrosymmetric monoclinic space group $P2_1/n$ and selected bond lengths and bond angles are given in the legend of Figure 2.[12] The molecular structure of **3b** displays the *trans*-configuration of Cp* and N(TMS)$_2$ groups attached to the four-membered Si_2O_2 ring. The Si_2O_2 ring is planar (mean deviation from plane is 0° due to a center of symmetry between Si1 and Si1A). The independent endocyclic Si−O−Si and O−Si−O bond angles are 90.55(8)° and 89.45(8)°, respectively. Another important feature is the bond distance between two Si atoms (2.3859(11) Å), which matches well with the calculated value (2.383−2.394 Å)[13a] and also with the *cis*-counterpart. The Si−O bond lengths fall between 1.6762(16) Å and 1.6819(15) Å, and are consistent with those found for **3a** and other Si_2O_2 rings.[3c,8b,8c,11] Both Si atoms are tetra-coordinated with distorted tetrahedral geometry and complete their coordination sphere with two O atoms of the four-membered Si_2O_2 ring, one Cp* ring and one nitrogen atom of the N(TMS)$_2$ group.

In order to understand the formation of two isomeric compounds in the same reaction, DFT calculations were performed. Reaction of **2c** (DFT optimized structure of **2**) with N_2O yielded for the first time the *cis*-(**3ac**) and *trans*-(**3bc**) isomers of Si_2O_2 rings (*vide supra*, Figure 3). The isomers are iso-energetic with the *trans*-isomer **3bc** slightly more stable than the *cis*-counterpart **3ac**, by 3.3 kcal/mol. There are mainly three mechanisms possible to explain the formation of the products.

According to the first mechanism, **2c** will react with one molecule of N_2O to yield the Si_2O ring product **3−1c** (Figure 3). The reaction

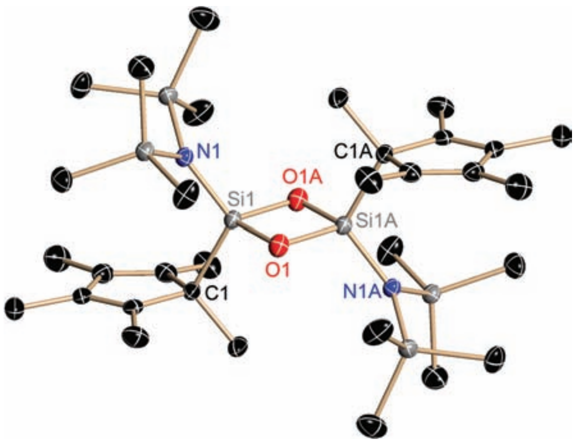


Figure 2. Molecular structure of **3b**. Hydrogen atoms and disordered moieties are not shown for clarity. Atoms labeled with an "A" are symmetry-generated by inversion between related atoms. Anisotropic displacement parameters are depicted at the 50% probability level. Selected bond distances are given as follows: Si1···Si1A, 2.3859(11) Å; Si1−O1, 1.6819(15) Å; Si1−O1A, 1.6762(16) Å; Si1−N1, 1.7205(18) Å; and Si1−C1, 1.910(3) Å. Selected bond angles are given as follows: O1−Si1−O1A, 89.45(8)°; N1−Si1−O1A, 114.59(8)°; N1−Si1−O1, 114.62(8)°; C1−Si1−O1A, 110.94(10)°; C1−Si1−O1, 108.67(10)°; N1−Si1−C1, 115.63(10)°; and Si1−O1−Si1A, 90.55(8)°.

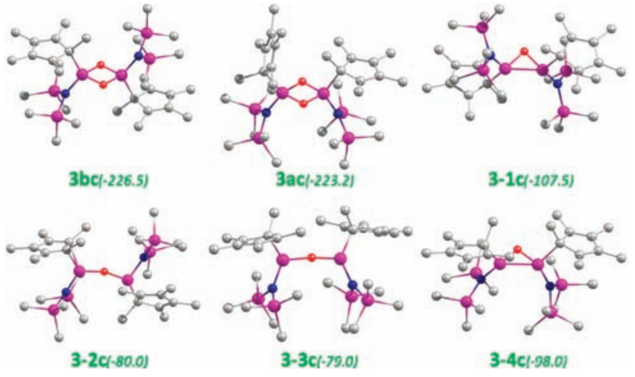


Figure 3. BP86/SVP optimized structures of the intermediates obtained during N_2O reaction. The values in parentheses are the electronic energy relative to the starting species **2c** calculated at BP86/TZVP//BP86/SVP level of theory. Color code: C gray, O red, N blue and Si pink. Hydrogens are removed for the sake of clarity.

energy ($\Delta E_e = \{\Sigma E_{\text{products}} - \Sigma E_{\text{reactants}}\}$) for the transformation (**2c** → **3**−**1c**) is −107.5 kcal mol^{-1}. This reaction is facilitated with the easy removal of N_2 when N_2O approaches disilene moiety **2c**. Further elongation of the Si−Si bond in **3**−**1c** yielded **3**−**2c**, which possesses a quasi-linear Si−O−Si unit (Si−O−Si = 144.8°). The energy barrier for this transformation (see Computational Details in the Supporting Information) is roughly 30.6 kcal/mol, and **3**−**2c** is energetically 27.5 kcal/mol less stable than **3**−**1c**. Rotation about the Si−O bond furnished the isoenergetic *cis*-isomer **3**−**3c** (Figure 3). This isomer undergoes rapid transformation to form **3**−**4c**, which is the *cis*-variant of the isomer **3**−**1c**. Intermediate **3**−**4c** can then further react with another N_2O molecule to form **3ac**. The energetics and the respective stabilities of all the important intermediates are depicted in Figure 3. The more stable *trans*-product **3bc** is obtained when **3**−**1c** species directly undergoes a second addition of oxygen atom from the N_2O moiety. However, this transformation entails an activation barrier of roughly 32 kcal/mol and, hence, will be energetically competitive with the **3**−**1c** → **3**−**2c** reaction step.

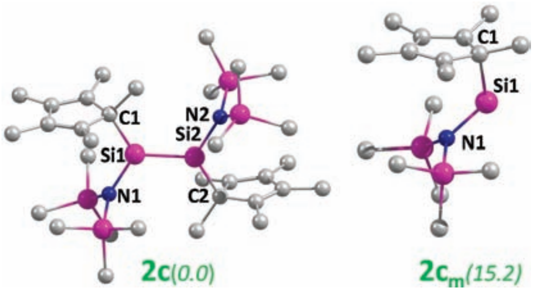


Figure 4. BP86/SVP optimized structures of the disilene **2** and in-situ-generated silylene (**2c**$_{\mathbf{m}}$). The values in parentheses are the electronic energy relative to the starting species **2c** calculated at BP86/TZVP//BP86/SVP level of theory. Color code: C, gray, P, green, N, blue and Si, pink. Hydrogens are removed for the sake of clarity.

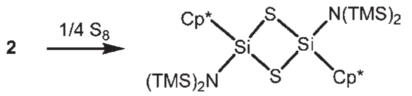
In the second mechanism, the disilene **2c** might undergo dissociation to form the respective silylenes (Figure 4) (**2c**$_{\mathbf{m}}$) that can further recombine to form the *cis*-variant of **2c**. The calculated disilene−silylene barrier (**2c** → 2×**2c**$_{\mathbf{m}}$) is 22 kcal/mol at the BP86/TZVP//BP86/SVP level of theory. It might be a viable pathway, since such types of dissociation−recombination steps are known for tetraaryldisilene.[3a] Subsequent addition of the two N_2O units can occur to both the *cis*- and *trans*-disilene isomers to yield the respective products **3bc** and **3ac**.

Finally, we have considered the *cis*−*trans* isomerization of disilenes via the rotation around the Si═Si bond. The calculated rotational barrier for such isomerization is roughly 18 kcal/mol. Indeed, this mechanistic route is feasible and the barrier calculated shows similar value (∼15 kcal/mol) observed by Kira et al. while performing dynamic NMR studies with tetrakis(trialkylsilyl)-disilene species.[14]

Reaction with Elemental Sulfur. Insertion of sulfur into the Si═Si double bond is not so common in the literature for atoms such as oxygen, but there are some examples where disilene was reacted with sulfur to afford dithiadisiletane derivatives.[15] In a recent article, Tokitoh et al. reported the formation of dithiasilarane and 1,3-dithia-2,4-disiletane derivatives by treatment of sulfur with 1,2-bis(ferrocenyl)disilene [Tip(Fc)Si═Si(Fc)Tip, Tip = 2,4,6-iPr$_3$C$_6$H$_2$].[16] Theoretical calculation on the relative reaction heat of sulfurization of the previously mentioned disilene predicted 1,3-dithia-2,4-disiletane derivative as the thermodynamic product, but experimentally that derivative remained elusive.[16] Reaction of disilene **2** with elemental sulfur in THF produced 1,3-dithia-2,4-disilacyclobutane (**4**) in 60% yield (see Scheme 3). Recrystallization in *n*-pentane afforded colorless crystals of **4** suitable for single-crystal XRD studies. Compound **4** is sparingly soluble in common organic solvents and stable under a dinitrogen atmosphere at room temperature. In the ^{29}Si NMR spectrum, a characteristic resonance was observed at δ = 6.15 ppm. The upfield shift in the ^{29}Si NMR spectrum compared to **3a** and **3b** is presumably due to the replacement of oxygen by sulfur. Moreover, it also indicates the presence of only one product in the reaction mixture. The molecular ion was observed in the EI-MS spectrum at m/z 710 with low intensity.

Compound **4** crystallizes in the triclinic space group $P\bar{1}$.[12] The molecular structure of **4** reveals the *trans*-configured planar Si_2S_2

Scheme 3. Preparation of 4



trans-
4

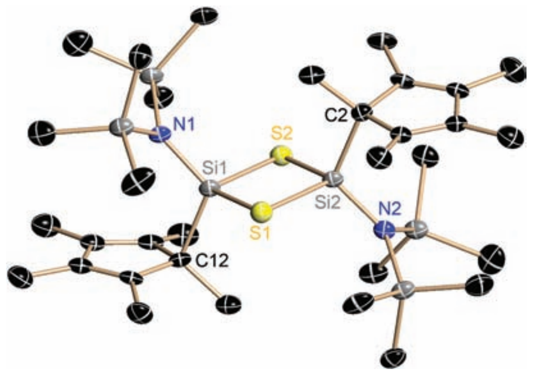


Figure 5. Crystal structure of **4**. Hydrogen atoms are not shown for the sake of clarity. Anisotropic displacement parameters are depicted at the 50% probability level. Selected bond distances are given as follows: Si1···Si2, 2.891(2) Å; S1–Si1, 2.1437(18) Å; S1–Si2, 2.1422(18) Å; S2–Si2, 2.1460(18) Å; S2–Si1, 2.1448(18) Å; Si1–N1, 1.720(4) Å; Si2–N2, 1.721(4) Å; Si1–C12, 1.940(4) Å; and Si2–C2, 1.932(4). Selected bond angles are given as follows: Si1–S1–Si2, 84.85(7)°; Si1–S2–Si2, 84.73(7)°; S1–Si1–S2, 95.20(7)°; S1–Si2–S2, 95.21(7)°; N1–Si1–S2, 110.57(13)°; N1–Si1–S1, 114.80(12)°; C12–Si1–S1, 106.72(14)°; C12–Si1–S2, 111.25(14)°; N2–Si2–S1, 115.36(13)°; N2–Si2–S2, 110.52(12)°; and N2–Si2–C2, 115.41(18)°.

ring (see Figure 5). The Si–S–Si bond angles are 84.73(7)° and 84.85(7)°, respectively, which are even more acute than the corresponding angle in **3b** (90.55°). The Si_2S_2 unit in **4** is planar, with a mean deviation of 0.0012 Å from the plane, which is different from the previously reported Si–S–Si–S rhombus of 1,3,2,4-dithiadisiletane derivative.[15d] Both Si atoms of **4** display distorted tetrahedral geometry and are attached to two S atoms, one N atom of the N(TMS)$_2$ group, and one Cp* group to complete the tetra-coordinated mode. All Si–S bonds are of equal lengths (mean = 2.14 Å) and comparable with the typical Si–S single bonds reported in the literature[17] and longer than that of the first reported silanethione, Tbt(Tip)Si=S (Tbt = 2,4,6-[(TMS)$_2$CH]$_2$C$_6$H$_2$), Tip = 2,4,6-*i*Pr$_3$C$_6$H$_2$] (1.948(4) Å).[15c]

Reaction of S_8 with **2** follows a similar mechanistic route as that discussed previously with N_2O. **2** reacts with S_8 to yield the three-membered complex **4–1c**, which is the sulfur analogue of **3–1c**. The reaction energy (ΔE_e) for this transformation (**2c** → **4–1c**) is −53.5 kcal/mol (see Figure 6). Similar Si–Si bond elongation produced **4–2c**, which is 30.3 kcal/mol less stable than **4–1c** and requires an activation barrier of ~35 kcal/mol. This particular reaction is comparatively more energy-demanding and witnesses a higher activation barrier than its oxygen variant (**3–1c** → **3–2c**). Further rotation about the Si–S bond furnished the *cis*-isomer, **4–3c**. The *cis*-isomer is unstable, compared to **4–2c**, by a value of 6.3 kcal/mol, making this rearrangement less facile than its oxygen analogue (vide supra). Further contraction of the Si–Si bond allows the formation of **4–4c**, which is −44.4 kcal/mol more stable than the starting material. However, the addition of a second S atom to **4–4c** to yield the *cis*-isomer of **4c** is not facilitated, because the highest occupied molecular orbital (HOMO) of **4–4c** does not possess the π molecular orbital (MO) over the Si–Si bond. To explain the unique bonding feature in disilaoxirane, the Dewar–Chatt–Duncanson (DCD) model is invoked.[18] In contrast, the HOMO of **3–4c** contains the bonding π-orbital over the Si atoms (see Figure 7), which allows electron donation (σ-bonding) to the electronegative O atom.[13b] This remains one of the important factors why the *cis*-isomer of **4c** (Figure 6) is not observed when **2** reacts with S_8, apart from the fact that the energetics for the S_8 activation process are comparatively high.

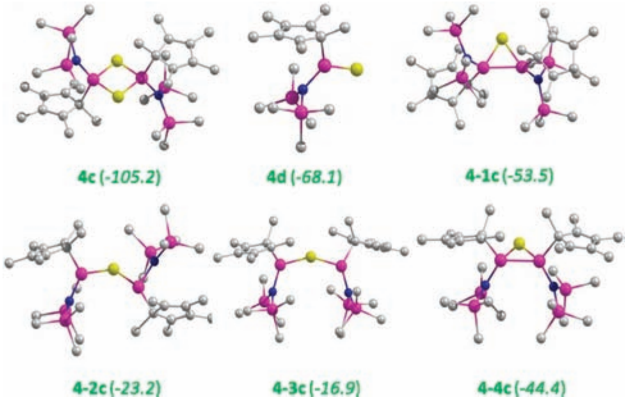


Figure 6. BP86/SVP-optimized structures of the intermediates obtained during S_8 reaction. The values in parentheses are the electronic energy relative to the starting species **2** calculated at BP86/TZVP//BP86/SVP level of theory. Color code: C, gray; S, yellow; N, blue; and Si, pink. Hydrogens are removed for the sake of clarity.

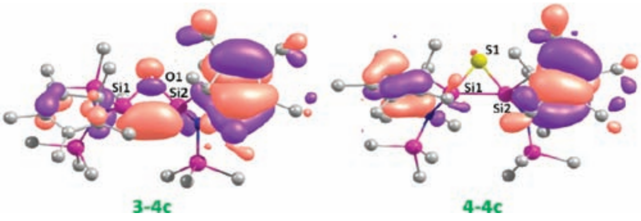


Figure 7. KS-HOMO of **3–4c** and **4–4c** (isodensity = 0.03 electron/bohr^3).

Moreover, the reaction of **2** with S_8 could yield **4d**, with a reaction energy of −68.1 kcal/mol; however, it has been previously reported by Suzuki et al.[15b] that species of the type **4d** are prone to dimerization.

■ CONCLUSION

We have successfully demonstrated the reaction of *trans*-[(TMS)$_2$N(η^1-Me$_5$C$_5$)Si=Si(η^1-Me$_5$C$_5$)N(TMS)$_2$] with N_2O and S_8 to give *cis*- and *trans*-disilaoxetane rings and the *trans*-dithiasiletane ring, respectively. To the best of our knowledge, this is the first example where two isomeric (*cis*- and *trans*-) Si_2O_2 ring compounds were isolated from the same disilene starting material. It is noteworthy to mention that the oxidative addition of **2** with S_8 afforded only the *trans*-dithiadisiletane ring. The formation of the above-mentioned different products was further explained by computational studies. All the compounds were well-characterized by multinuclear NMR spectroscopy, EI-MS spectrometry, elemental analysis, and single-crystal X-ray diffraction (XRD) studies.

EXPERIMENTAL SECTION

All manipulations were carried out in an inert atmosphere of dinitrogen (N_2), using standard Schlenk techniques and in a N_2-filled glovebox. Solvents were purified using a MBRAUN Model MB SPS-800 solvent purification system. All chemicals purchased from Aldrich were used without further purification. ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded in C_6D_6 with a Bruker Model Avance DPX 200 spectrometer or a Bruker Model Avance DRX 500 spectrometer. The chemical shifts δ are given relative to $SiMe_4$. EI-MS spectra were obtained using a Finnigan MAT 8230 instrument. Elemental analyses were performed by the Institut für Anorganische Chemie, Universität Göttingen. Melting points were measured in a sealed glass tube on a Büchi Model B-540 melting point apparatus.

Preparation of Compounds 3a and 3b. Dry N_2O was bubbled into a solution of **2** (0.646 g, 1 mmol) in toluene (40 mL) at room temperature. After 5 min the gas flow of N_2O was disconnected, and the solution was stirred for further 6 h. All the volatiles were removed in vacuo and *n*-pentane (40 mL) was added to the residue. The solution was concentrated to ca. 3 mL and stored at −30 °C in a freezer for few days to yield colorless crystals of **3a** and **3b** (0.30 g, 44%). Mp 135 °C (decomp). ^{1}H NMR (500 MHz, C_6D_6, 25 °C): δ 0.24−0.38 (m, 36 H, $SiMe_3$), 1.60−1.81(br, 30H, Me_5C_5) ppm; $^{13}C\{^{1}H\}$ NMR (125.75 MHz, C_6D_6, 25 °C): δ 1.36 (Me_3Si), 3.82 (Me_3Si), 5.82 (Me_3Si), 11.37 (Me_5C_5), 14.25 (Me_5C_5), 22.69 (Me_5C_5), 129.27 (Me_5C_5), 131.91 (Me_5C_5), 136.84 (Me_5C_5) ppm; $^{29}Si\{^{1}H\}$ NMR (99.36 MHz, C_6D_6, 25 °C): δ 7.32 ($SiMe_3$), 5.17 ($SiMe_3$), 3.88 ($SiMe_3$), −12.11, −22.31, −28.53 (Si_2O_2) ppm. EI-MS: *m*/*z*: 678 [M^+] (100%). Anal. Calcd for $C_{32}H_{66}N_2O_2Si_6$ (678.37): C, 56.57; H, 9.79; N, 4.12; Found: C, 56.11; H, 9.52; N, 4.18.

Note: Despite of repeated attempts, we could not separate these two isomers to record the pure spectra separately for each isomer.

Preparation of Compound 4. A solution of **2** (0.646 g, 1.0 mmol) in THF (20 mL) was added to a stirred suspension of elemental sulfur (0.064 g, 0.25 mmol) in THF (10 mL). The reaction mixture was stirred at room temperature for 14 h until the solution became colorless. Removal of the solvent, followed by extraction with *n*-pentane (25 mL), gave a colorless solution. The solution was concentrated to ca. 2 mL and stored at −32 °C in a freezer for 2−3 days to afford colorless crystals of **4** (0.43 g, 60%). Mp 140 °C (decomp). ^{1}H NMR (500 MHz, C_6D_6, 25 °C): δ 0.17 (s, 36 H, $SiMe_3$), 1.65 (s, 30H, Me_5C_5) ppm; $^{13}C\{^{1}H\}$ NMR (125.75 MHz, C_6D_6, 25 °C): δ 1.38 (Me_3Si), 11.57 (Me_5C_5), 129.27 (Me_5C_5) ppm; $^{29}Si\{^{1}H\}$ NMR (99.36 MHz, C_6D_6, 25 °C): δ 3.88 ($SiMe_3$), −6.11(Si_2S_2) ppm. EI-MS: *m*/*z*: 710 [M^+] (33%), 575 [M^+ − Cp*] (100%). Anal. Calcd for $C_{32}H_{66}N_2S_2Si_6$ (711.53): C, 54.02; H, 9.35; N, 3.94; Found: C, 53.94; H, 9.30; N, 3.91.

Crystal Structure Determination. Crystals of **3a** and **3b** were selected from the recrystallized crude product under microscopic examination, on the basis of their different shape (rhombohedral and needle-shaped crystals were present in the crude mixture). Shock cooled crystals were mounted under nitrogen atmosphere using the X-TEMP2 system.[12] The data for **3a**, **3b**, and **4** were collected at 100(2) K on a INCOATEC Mo Microsource[19] with Quazar mirror optics and APEX II detector on a D8 goniometer. The diffractometer was equipped with a low-temperature device and used Mo Kα radiation (λ = 0.71073 Å). The data of **3a**, **3b**, and **4** were integrated with SAINT[20a] and an empirical absorption with SADABS[20b] was applied. The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares methods against F^2 (SHELXL-97).[21] Crystal data of **3a**: $C_{32}H_{66}N_2O_2Si_6$, *M* = 679.41 g/mol, monoclinic, space group $P2_1/n$, *a* = 11.535(2) Å, *b* = 15.483(2) Å, *c* = 22.378(2) Å, α = 90°, β = 97.54(2), γ = 90°, *V* = 3962.1(9) Å^3, *Z* = 4, $\rho_{calc.}$ = 1.139 Mg/m^3, μ = 0.240 mm^{-1}, *F*(000): 1488, θ-range: 1.60°−31.06°, refl. coll.: 84 348, indep. refl.: 12 685, data/restraints/parameters: 12 685/0/401, goodness-of-fit (GOOF) on F^2: 1.058, *R*-indices [$I > 2\sigma(I)$]: R_1 = 0.0346/wR_2 = 0.0907, *R*-indices (all data): R_1 = 0.0427/ wR_2 = 0.0952, largest peak/deepest hole: 0.578/−0.283 eÅ^{-3}. **3b**: $C_{32}H_{66}N_2O_2Si_6$, *M* = 679.41 g/mol, monoclinic, space group $P2_1/n$, *a* = 9.169(2) Å, *b* = 13.640(2) Å, *c* = 15.669(2) Å, α = 90°, β = 90.73(2), γ = 90°, *V* = 1959.5(6) Å^3, *Z* = 2, $\rho_{calc.}$ = 1.152 Mg/m^3, μ = 0.242 mm^{-1}, *F*(000): 744, θ-range: 1.98°−26.36°, refl. coll.: 18 406, indep. refl.: 4007, data/restraints/parameters: 4007/753/353, GOOF on F^2: 1.030, *R*-indices [$I > 2\sigma(I)$]: R_1 = 0.0422/wR_2 = 0.1035, *R*-indices (all data): R_1 = 0.0572/wR_2 = 0.1121, largest peak/deepest hole: 0.361/−0.278 eÅ^{-3}. **4**: $C_{32}H_{66}N_2S_2Si_6$, *M* = 711.53 g/mol, triclinic, space group $P\bar{1}$, *a* = 10.384(6) Å, *b* = 12.874(7) Å, *c* = 16.360(9) Å, α = 72.12(2)°, β = 78.51(2)°, γ = 75.56(2)°, *V* = 1997.8(19) Å^3, *Z* = 2, $\rho_{calc.}$ = 1.183 Mg m^{-3}, μ = 0.338 mm^{-1}, *F*(000): 776, θ-range: 1.32°−20.87°, refl. coll.: 21 707, indep. refl.: 4202, data/restraints/parameters: 4202/0/401, GOOF on F^2: 1.045, *R*-indices [$I > 2\sigma(I)$]: R_1 = 0.0430/wR_2 = 0.1016, *R*-indices (all data): R_1 = 0.0636/wR_2 = 0.1116, largest peak/deepest hole: 0.347/-0.365 eÅ^{-3}. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as supplementary publications (Nos. 832194 (**3a**), 832195 (**3b**), and 832193 (**4**). Copies of the data can be obtained free of charge upon application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (internat.) +44(1223)336-033; E-mail, deposit@ccdc.cam.ac.uk).

ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Computational details and CIF files for **3a**, **3b**, and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail addresses: hroesky@gwdg.de, dstalke@chemie.uni-goettingen.de.

ACKNOWLEDGMENT

We are thankful to the Deutsche Forschungsgemeinschaft for supporting this work. S.K. is thankful to the Deutscher Akademischer Austausch Dienst for a research fellowship. D.K. acknowledges Prof. S. Ramakrishnan and Prof. S. Dattagupta for constant support and encouragement. D.K. is indebted to Dr. A. K. Roy and Dr. P. K. Ghorai for providing computational facilities and one of the reviewers for helpful suggestion. D.S. is grateful for funding from the DFG Priority Programme 1178, the DNRF-funded Center for Materials Crystallography (CMC) for support, and the Land Niedersachsen for providing a fellowship in the Catalysis for Sustainable Synthesis (CaSuS) Ph.D. program.

REFERENCES

(1) West, R.; Fink, M. J.; Michl, J. *Science* **1981**, *214*, 1343–1344.

(2) (a) Okazaki, R.; West, R. *Adv. Organometal. Chem.* **1996**, *39*, 231–273. (b) Kira, M.; Iwamoto, T. *Adv. Organomet. Chem.* **2006**, *54*, 73–148. (c) Weidenbruch, M. In *The Chemistry of Organosilicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, U.K., 2001; Vol. 3, pp 391−428. (d) Kira, M. *J. Organomet. Chem.* **2004**, *689*, 4475–4488. (e) Müller, T.; Ziche, W.; Auner, N. In *The Chemistry of*

Organic Silicon Compounds; Rappoport, Z., Apeloig, Y., Eds.; Wiley: New York, 1998; Vol. 2, p 857. (f) Brook, A. G.; Brook, M. A. *Adv. Organomet. Chem.* **1996**, *39*, 71–158. (g) Escudié, J.; Couret, C.; Ranaivonjatovo, H. *Coord. Chem. Rev.* **1998**, *178−180*, 565–592. (h) Weidenbruch, M. *Coord. Chem. Rev.* **1994**, *130*, 275–300. (i) Brook, A. G.; Baines, K. M. *Adv. Organomet. Chem.* **1986**, *25*, 1–44. (j) West, R. *Angew. Chem.* **1987**, *99*, 1231–1241; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1201–1211.

(3) (a) Tokitoh, N.; Suzuki, H.; Okazaki, R.; Ogawa, K. *J. Am. Chem. Soc.* **1993**, *115*, 10428–10429. (b) Takeda, N.; Tokitoh, N. *Synlett* **2007**, 2483–2491. (c) Suzuki, H.; Tokitoh, N.; Okazaki, R.; Harada, J.; Ogawa, K.; Tomoda, S.; Goto, M. *Organometallics* **1995**, *14*, 1016–1022.

(4) (a) Tsutsui, S.; Tanaka, H.; Kwon, E.; Matsumoto, S.; Sakamoto, K. *Organometallics* **2004**, *23*, 5659–5661. (b) Tsutsui, S.; Sakamoto, K.; Kira, M. *J. Am. Chem. Soc.* **1998**, *120*, 9955–9956.

(5) Schmedake, T. A.; Haaf, M.; Apeloig, Y.; Müller, T.; Bukalov, S.; West, R. *J. Am. Chem. Soc.* **1999**, *121*, 9479–9480.

(6) Jutzi, P.; Mix, A.; Neumann, B.; Rummel, B.; Schoeller, W. W.; Stammler, H.-G.; Rozhenko, A. B. *J. Am. Chem. Soc.* **2009**, *131*, 12137–12143.

(7) Khan, S.; Sen, S. S.; Roesky, H. W.; Kratzert, D.; Michel, R.; Stalke, D. *Inorg. Chem.* **2010**, *49*, 9689–9693.

(8) (a) Sen, S. S.; Khan, S.; Roesky, H. W.; Kratzert, D.; Meindl, K.; Henn, J.; Stalke, D.; Demers, J.-P.; Lange, A. *Angew. Chem.* **2011**, *123*, 2370–2373; *Angew. Chem., Int. Ed.* **2011**, *50*, 2322–2325. (b) Khan, S.; Sen, S. S.; Kratzert, D.; Tavčar, G.; Roesky, H. W.; Stalke, D. *Chem.—Eur. J.* **2011**, *17*, 4283–4290. (c) Sen, S. S.; Tavčar, G.; Roesky, H. W.; Kratzert, D.; Hey, J.; Stalke, D. *Organometallics* **2010**, *29*, 2343–2347. (d) Jana, A.; Leusser, D.; Objartel, I.; Roesky, H. W.; Stalke, D. *Dalton Trans.* **2011**, *40*, 5458–5463. (e) Sen, S. S.; Roesky, H. W.; Stern, J.; Henn, J.; Stalke, D. *J. Am. Chem. Soc.* **2010**, *132*, 1123–1126. (f) Sen, S. S.; Roesky, H. W.; Meindl, K.; Stern, J.; Henn, J.; Stückl, A. C.; Stalke, D. *Chem. Commun.* **2010**, *46*, 5873–5875. (g) Sen, S. S.; Khan, S.; Kratzert, D.; Roesky, H. W.; Stalke, D. *Eur. J. Inorg. Chem.* **2011**, 1370–1373. (h) Khan, S.; Sen, S. S.; Michel, R.; Kratzert, D.; Roesky, H. W.; Stalke, D. *Organometallics* **2011**, *30*, 2643–2645.

(9) (a) Ghadwal, R. S.; Roesky, H. W.; Granitzka, M.; Stalke, D. *J. Am. Chem. Soc.* **2010**, *132*, 10018–10020. (b) Ghadwal, R. S.; Roesky, H. W.; Schulzke, C.; Granitzka, M. *Organometallics* **2010**, *29*, 6329–6333.

(10) (a) Jana, A.; Schulzke, C.; Roesky, H. W. *J. Am. Chem. Soc.* **2009**, *131*, 4600–4601. (b) Jana, A.; Roesky, H. W.; Schulzke, C.; Samuel, P. P. *Organometallics* **2010**, *28*, 6574–6577.

(11) (a) Michalczyk, M. J.; Fink, M. J.; Haller, K. J.; West, R.; Michl, J. *Organometallics* **1986**, *5*, 531–536. (b) Fink, M. J.; Haller, K. J.; West, R.; Michl, J. *J. Am. Chem. Soc.* **1984**, *106*, 822–823. (c) Sohn, H.; Tan, R. P.; Powell, D. R.; West, R. *Organometallics* **1994**, *13*, 1390–1394. (d) Iwamoto, T.; Masuda, H.; Ishida, S.; Kabuto, C.; Kira, M. *J. Am. Chem. Soc.* **2003**, *125*, 9300–9301.

(12) (a) Kottke, T.; Stalke, D. *J. Appl. Crystallogr.* **1993**, *26*, 615–619. (b) Stalke, D. *Chem. Soc. Rev.* **1998**, *27*, 171–178.

(13) (a) Kudo, T.; Nagase, S. *J. Am. Chem. Soc.* **1985**, *107*, 2589–2595. (b) Grev, R. S.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1987**, *109*, 6577–6585. (c) Bachrach, S. M.; Streitwiesser, A., Jr. *J. Am. Chem. Soc.* **1985**, *107*, 1186–1190.

(14) Kira, M.; Ohya, S.; Iwamoto, T.; Ichinohe, M.; Kabuto, C. *Organometallics* **2000**, *19*, 1817–1819.

(15) (a) West, R.; Young, D. J. D.; Haller, K. J. *J. Am. Chem. Soc.* **1985**, *107*, 4942–4946. (b) Suzuki, H.; Tokitoh, N.; Okazaki, R.; Nagase, S.; Goto, M. *J. Am. Chem. Soc.* **1998**, *120*, 11096–11105. (c) Suzuki, H.; Tokitoh, N.; Okazaki, R.; Nagase, S. *J. Am. Chem. Soc.* **1994**, *116*, 11578–11579. (d) Wiberg, N.; Niedermayer, W.; Polborn, K.; Mayer, P. *Chem.—Eur. J.* **2002**, *8*, 2730–2739.

(16) Yuasa, A.; Sasamori, T.; Hosoi, Y.; Furukawa, Y.; Tokitoh, N. *Bull. Chem. Soc. Jpn.* **2009**, *82*, 793–805.

(17) Sheldrick, W. S. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Part 1, pp 227−304.

(18) Chatt, J.; Duncanson, L. A. *J. Chem. Soc.* **1953**, 2939.

(19) Schulz, T.; Meindl, K.; Leusser, D.; Stern, D.; Ruf, M.; Sheldrick, G. M.; Stalke, D. *J. Appl. Crystallogr.* **2009**, *42*, 885–891.

(20) (a) *SAINT v7.68A*; Bruker: Madison, WI, 2008. (b) Sheldrick, G. M. *SADABS 2008/1*; Göttingen, Germany, 2008.

(21) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122.