Reactivity Studies of a Disilene with N₂O and Elemental Sulfur

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Supporting Information

ABSTRACT:

In a previous contribution, we have reported on a convenient and high yield synthesis of the disilene trans-[(TMS)₂N(η¹-Me₂C₅)-Si=Si(η²-Me₂C₅)N(TMS)₂] (2). Herein, we show the reactions of 2 with N₂O and S₈. 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 isoelectronic, 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 (Mes₂Si=SiMes₂, Mes = 2,4,6-Me₃C₆H₂) 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] as well as the corresponding disilene [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-tet-butyl[5,5']-bi[1,5-disilatriacyclo[4.2.0.0]octadiene]-2,7,2',7'-tetraene and the corresponding silylene was proved by trapping experiments and DFT calculations by Tsutsui et al.⁴ 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 [(R₂N)₂Si, R = iPr] in solution which is in equilibrium with the corresponding disilene at low temperature.⁵ West et al. then reported the existence of dynamic equilibrium between cis-diaminodisilyldisilene and saturated dianiminosilene by ²⁹Si NMR and UV—vis spectroscopy, although dianiminosilene was not the monomer of cis-diaminodisilyldisilene.⁶ Recently, a noteworthy contribution in this field was made by Jutzi et al., describing the unique situation where both the silylene [(TMS)₂N(η¹-Me₂C₅)Si] as well as the corresponding disilene trans-[(TMS)₂N(η¹-Me₂C₅)Si=Si(η²-Me₂C₅)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* = Me₅C₅) 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 (Me₅C₅)₂SiHCl₂ (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.

In the course of our recent studies on the reactions of compounds having low valent silicon atoms with various unsaturated
organic compounds,8−10 we became interested in investigating the unique reactions of 2 with N2O and S8.

Results and Discussion

Reaction with Nitrous Oxide. N2O is well-known to serve as a mono-oxygen donor. Reaction of 2 in toluene with N2O at room temperature led to the formation of two dioxadisiletane isomers (cis- and trans-) (see Scheme 2). Analysis of 1H, 13C, and 29Si NMR (δ 7.3, 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 two dioxadisiletane isomers from the same disilene precursor.11a The formation of the products in the reaction mixture was further documented by Okazaki et al. upon treatment with molecular oxygen.11b Moreover, we reported the formation of the cis-1,3-dioxo-2,4-disiletane ring from corresponding cis-disilene was further documented by Okazaki et al. upon treatment with molecular oxygen.11c Moreover, we reported the formation of the cis-1,3-dioxo-2,4-disiletane ring from corresponding cis-disilene was further documented by Okazaki et al. upon treatment with molecular oxygen.11d The formation of cis-1,3-dioxo-2,4-disiletane ring from corresponding cis-disilene was further documented by Okazaki et al. upon treatment with molecular oxygen.11e 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 P21/n.12 Selected bond lengths and bond angles are given in the legend of Figure 1. The molecular structure of 3aa reveals a cis-configured, almost-planar Si2O2 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−O2−Si2, O1−Si1−O2, and O1−Si2−O2 angles are 91.29(4)°, 91.29(4)°, and 92.81(4)°, respectively. All four Si−O distances fall in the range of 1.6750(8)−1.6820(8) Å and match well with the reported Si−O bond lengths for the several dioxadisiletane rings reported in the literature.13a,13b,13c,13d 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 H2Si2O2 (calculated Si−Si distances range between 1.661 and 1.671 Å and 2.383 and 2.394 Å, respectively).13e It is important to mention that, in both cases, we were able to isolate only the trans-isomer.

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, 1.8966(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)°.

Cp* rings (attached to two different Si atoms) discloses that these two Cp* are almost perpendicular to each other.

Compound 3b crystallizes in the centrosymmetric monoclinic space group P21/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 Si2O2 ring. The Si2O2 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 Si2O2 rings.13a,13b,13c,13d Both Si atoms are tetra-coordinated with distorted tetrahedral geometry and complete their coordination sphere with two O atoms of the four-membered Si2O2 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 N2O yielded for the first time the cis-(3ac) and trans-(3bc) isomers of Si2O2 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 N2O to yield the Si2O2 ring product 3−1c (Figure 3). The reaction
energy \( \Delta E = \{ \Sigma E_{\text{products}} - \Sigma E_{\text{reactants}} \} \) for the transformation \( 2c \rightarrow S1 \rightarrow 1c \) is \(-107.5 \text{ kcal mol}^{-1} \). This reaction is facilitated with the easy removal of \( \text{N}_2 \) when \( \text{N}_2\text{O} \) approaches disilene moiety \( 2c \). Further elongation of the Si–Si bond in \( 3 \rightarrow 1c \) yielded \( 3 \rightarrow 2c \), 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 \( 3 \rightarrow 2c \) is energetically 27.5 kcal/mol less stable than \( 3 \rightarrow 1c \). Rotation about the Si–O bond furnished the isoequilergic \( \text{cis} \)-isomer \( 3 \rightarrow 3c \) (Figure 3). This isomer undergoes rapid transformation to form \( 3 \rightarrow 4c \), which is the \( \text{cis} \)-variant of the isomer \( 3 \rightarrow 1c \). Intermediate \( 3 \rightarrow 4c \) can then further react with another \( \text{N}_2\text{O} \) molecule to form \( 3ac \). The energetics and the respective stabilities of all the important intermediates are depicted in Figure 3. The more stable \( \text{trans} \)-product \( 3bc \) is obtained when \( 3 \rightarrow 1c \) species directly undergoes a second addition of oxygen atom from the \( \text{N}_2\text{O} \) moiety. However, this transformation entails an activation barrier of roughly 32 kcal/mol and, hence, will be energetically competitive with the \( 3 \rightarrow 1c \rightarrow S1 \rightarrow 2c \) reaction step.

In the second mechanism, the disilene \( 2c \) might undergo dissociation to form the respective silylenes (Figure 4) \( (2cm) \) that can further recombine to form the \( \text{cis} \)-variant of \( 2c \). The calculated disilene–silylene barrier \( 2c \rightarrow 2cm \) 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. Subsequent addition of the two \( \text{N}_2\text{O} \) units can occur to both the \( \text{cis} \)- and \( \text{trans} \)-disilene isomers to yield the respective products \( 3bc \) and \( 3ac \).

Finally, we have considered the \( \text{cis} \)-\( \text{trans} \) 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(trialkyldisilyl)-disilene species.

**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. In a recent article, Tokitoh et al. reported the formation of dithiasilane and 1,3-dithia-2,4-disiletane derivatives by treatment of sulfur with 1,2-bis(ferrocenyl)disilene \( \text{[Tip} \text{FcSi} = \text{Si} \text{FcTip}, \text{Tip} = 2,4,6-iPr}_3\text{C}_6\text{H}_{12} \). 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.

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 \( \eta \)-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 \( ^{29} \text{Si} \) NMR spectrum, a characteristic resonance was observed at \( \delta = 6.15 \) ppm. The upfield shift in the \( ^{29} \text{Si} \) 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 \( P\overline{1} \). The molecular structure of 4 reveals the \( \text{trans} \)-configured planar \( \text{Si}_2\text{S}_2 \)
N2
N1
Si1
106.72(14)

This particular reaction is comparatively more energy-demanding and witnesses a higher activation barrier than its oxygen analogical reaction (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 Si2-Si2 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 literature17 and longer than that of the first reported silanethione, Tbt(Tipp)Si=S(Tbt = 2,4,6-[(TMS)2CH]2C6H3) (1.948(4) Å).15c

Reaction of S8 with 2 follows a similar mechanistic route as that discussed previously with N2O. 2 reacts with S8 to yield the cis-isomer of 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–Clat拷 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.19 This remains one of the important factors why the cis-isomer of 4c (Figure 6) is not observed when 2 reacts with S8, apart from the fact that the energetics for the S8 activation process are comparatively high.

Moreover, the reaction of 2 with S8 could yield 4d, with a reaction energy of ~68.1 kcal/mol; however, it has been previously reported by Suzuki et al.16a that species of the type 4d are prone to dimerization.

**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; Si1–Si1 2.1437(18) Å; Si1–Si2 2.1422(18) Å; Si2–Si2 2.1460(18) Å; Si2–Si1 2.1448(18) Å; Si2–N1 1.721(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–Si1–Si2 84.85(7)°; Si1–Si1–S1 95.20(7)°; Si1–Si2–S2 92.21(7)°; N1–Si1–S1 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)°.

**Figure 6.** BP86/SVP-optimized structures of the intermediates obtained during S8 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/bohr3)

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–Clat拷 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.19 This remains one of the important factors why the cis-isomer of 4c (Figure 6) is not observed when 2 reacts with S8, apart from the fact that the energetics for the S8 activation process are comparatively high.

Moreover, the reaction of 2 with S8 could yield 4d, with a reaction energy of ~68.1 kcal/mol; however, it has been previously reported by Suzuki et al.16a that species of the type 4d are prone to dimerization.

**CONCLUSION**

We have successfully demonstrated the reaction of trans-
[(TMS)2N(η2- Me5C5)Si=Si(η2-Me5C5)] N(TMS)2] with N2O and S8 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-) Si2O2 ring compounds were isolated from the same disilene starting material. It is noteworthy to mention that the oxidative addition of 2 with S8 afforded only the trans-dithiasiletane 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 (N2), using standard Schlenk techniques and in a N2-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. 1H, 13C, and 29Si NMR spectra were recorded in CD3CN with a Bruker Avance DPX 200 spectrometer or a Bruker Model Avance DRX 500 spectrometer. The chemical shifts δ are given relative to SiMe4. 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 N2O was bubbled into a solution of 2 (0.64 g, 1 mmol) in toluene (40 mL) at room temperature. After 5 min the gas flow of N2O 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). 1H NMR (500 MHz, CD3CN, 25 °C): δ 0.24–0.38 (m, 36 H, SiMe3), 1.60–1.81 (br, 30H, Me3Si-Cppm); 13C{1H} NMR (125.75 MHz, CD3CN, 25 °C): δ 1.16 (MeSi), 3.82 (MeSi), 5.82 (MeSi), 11.37 (MeC), 14.25 (MeC), 22.69 (MeC), 129.27 (MeC), 131.91 (MeC), 136.84 (MeC) ppm; 29Si{1H} NMR (99.36 MHz, CD3CN, 25 °C): δ 7.32 (SiMe3), 5.17 (SiMe3), 3.88 (SiMe3), −12.11, −22.31, −28.55 (SiMe2) ppm. EI-MS: m/z: 678 [M]+ (100%). Anal.Calc. for C32H66N2Si6: C, 56.11; 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 (0.64 g, 1.0 mmol) in THF (20 mL) was added to a stirred suspension of elemental sulfur (0.43 g, 60%). Mp 140 °C (decomp). 1H NMR (500 MHz, CD3CN, 25 °C): δ 0.24–0.38 (m, 36 H, SiMe3), 1.60–1.81 (br, 30H, Me3Si-Cppm); 13C{1H} NMR (125.75 MHz, CD3CN, 25 °C): δ 1.16 (MeSi), 3.82 (MeSi), 5.82 (MeSi), 11.37 (MeC), 14.25 (MeC), 22.69 (MeC), 129.27 (MeC), 131.91 (MeC), 136.84 (MeC) ppm; 29Si{1H} NMR (99.36 MHz, CD3CN, 25 °C): δ 7.32 (SiMe3), 5.17 (SiMe3), 3.88 (SiMe3), −12.11, −22.31, −28.55 (SiMe2) ppm. EI-MS: m/z: 678 [M]+ (100%). Anal. Calc. for C32H66N2Si6Si2: 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 microscopical 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 Microsource19 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 = 0.7073 Å). The data of 3a, 3b, and 4 were integrated with SAINT20 and an empirical absorption with SADABS21 was applied. The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares methods against F2 (SHELXL-97).22 Crystal data of 3a: C32H66N2O2Si6. M = 679.41 g/mol, monoclinic, space group P21/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) Å³, Z = 4, ρcalc. = 1.139 Mg/m³, μ = 0.240 mm⁻¹, F(000) = 1488, θ-range: 1.6°–31.06°, refl. coll.: 84 348, indep. refl.: 12 685, data/restraints/parameters: 12 685/0/401, goodness-of-fit (GOOF) on F²: 1.058, R-indices [I > 2σ(I)]: R1 = 0.0346/wR2 = 0.0907, R-indices (all data): R1 = 0.0427/ wR2 = 0.0952, largest peak/hole: 0.578/−0.283 eÅ⁻³. 3b: C22H52N2O2Si4M = 679.41 g/mol, monoclinic, space group P21/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) Å³, Z = 2, ρcalc. = 1.512 Mg/m³, μ = 0.242 mm⁻¹, F(000) = 774, θ-range: 1.98°–26.36°, refl. coll.: 18 406, indep. refl.: 4007, data/restraints/parameters: 4007/753/ 350, GOOF on F²: 1.030, R-indices [I > 2σ(I)]: R1 = 0.0422/wR2 = 0.1035, R-indices (all data): R1 = 0.0572/wR2 = 0.1121, largest peak/hole: 0.361/−0.278 eÅ⁻³. 4: C32H66N2S2Si6 M = 711.53 g/mol, triclinic, space group P inadvertent. D.K. is indebted to Dr. A. K. Roy and encouragement. D.K. is indebted to Dr. A. K. Roy and encouragement. D.K. is indebted to Dr. A. K. Roy and encouragement.

**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.

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