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VIP

A Series of Isolable Silanoic Thio-, Seleno-, and Telluroesters (LSi(=X)OR) with Donor-Supported Si=X Double Bonds (L = β-Diketiminate; X = S, Se, Te)

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Dedicated to Professor Karl Wieghardt on the occasion of his 65th birthday

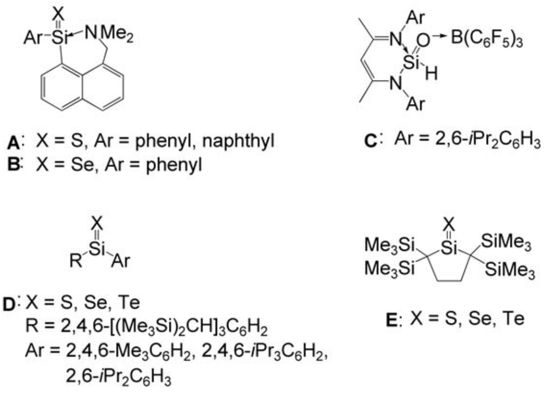
Abstract: The first silicon analogues of carbonic (carboxylic) esters, the silanoic thio-, seleno-, and tellurosilylesters **3** (Si=S), **4** (Si=Se), and **5** (Si=Te), were prepared and isolated in crystalline form in high yield. These thermally robust compounds are easily accessible by direct reaction of the stable siloxysilylene L(Si:)OSi(H)L′ **2** (L = HC-$(CMe)_2[N(aryl)_2]$, L′ = CH[(C=CH_2)-CMe][N(aryl)]$_2$; aryl = 2,6-$i\mathrm{Pr}_2C_6H_3$) with the respective elemental chalcogen. The novel compounds were fully characterized by methods including multinuclear NMR spectroscopy and single-crystal X-ray diffraction analysis. Owing to intramolecular N→Si donor–acceptor support of the Si=X moieties (X = S, Se, Te), these compounds have a classical valence-bond N^+–Si–X^- resonance betaine structure. At the same time, they also display a relatively strong nonclassical Si=X π-bonding interaction between the chalcogen lone-pair electrons (n_π donor orbitals) and two antibonding Si−N orbitals (σ^*_π acceptor orbitals mainly located at silicon), which was shown by IR and UV/Vis spectroscopy. Accordingly, the Si=X bonds in the chalcogenoesters are 7.4 (**3**), 6.7 (**4**), and 6.9 % (**5**) shorter than the corresponding Si−X single bonds and, thus, only a little longer than those in electronically less disturbed Si=X systems ("heavier" ketones).

Keywords: N ligands · selenium · silylenes · sulfur · tellurium

Introduction

Carbonyl (C=O) and thiocarbonyl compounds (C=S), including carbonic (C(=O)OR) and thiocarbonic systems (C(=S)OR), are ubiquitous building blocks in nature. The importance of the latter group of compounds has long inspired and prompted numerous chemists to synthesize stable heavier-element congeners with double bonds between heavier Group 14 and Group 16 elements ("heavier ketones"). After years of discouraging attempts to synthesize isolable heavier-element congeners of ketones, Corriu and co-workers reported in 1989 the first silanethione (Si=S) and silaneselone (Si=Se) derivatives **A** and **B** supported by an intramolecular N→Si donor–acceptor bond (Scheme 1).[1]

Although silanone derivatives ($R_2Si=O$) that are isolable at room temperature are still unknown, we recently succeeded in the preparation and structural characterization of the remarkable robust silaformamide–borane complex **C** with a donor–acceptor-supported silicon–oxygen double bond.[2] The first series of isolable diarylsilanechalcogenones $R_2Si=X$ (X = S, Se, Te) **D**[3] and **E**,[4] which bear, respectively, steri-



Scheme 1. Hitherto-known heavier silaketones.

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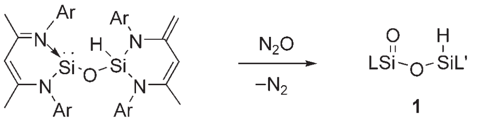
cally encumbered substituents at silicon and unsupported Si=X bonds, were reported by Tokitoh, Okazaki, and co-workers and more recently by Iwamoto, Kira, and co-workers. Besides the aforementioned silanechalcogenone systems hitherto known, a number of related heavier-ketone analogues with unsupported E=X double bonds (E = Ge, Sn, Pb; X = S, Se, Te) have also been reported.[5] In contrast, heavier Group 14 congeners of carbonic (carboxylic) acids isolable at room temperature are still elusive. Lately, the first germanoic thioacid with an N→Ge donor-supported Ge(=S)OH group, isolable at room temperature, was described by Roesky and co-workers.[6] We recently reported the synthesis and characterization of the first silicon analogue of a carbonic ester, silanoic silylester **1**, which bears an N→Si supported Si=O moiety.[7] The latter represents a unique donor-supported Si=O complex that results from gentle monoxygenation of the stable siloxysilylene **2** [Eq. (1)]. The remarkably simple access to silanoic silylester **1**, which is thermally stable up to 200 °C, encouraged us to apply silylene **2** to the synthesis and characterization of the first series of isolable silanoic ester analogues. Herein we report the synthesis and spectroscopic and structural characterization of the chalcogenoester analogues **3** (Si=S), **4** (Si=Se), and **5** (Si=Te).



(1)

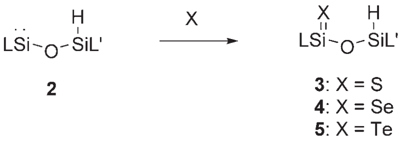
2: L(Si:)–O–SiH(L')

Abstract in German: Die ersten siliciumanalogen Carbonsäureester (Carboxylester) wurden hergestellt und in hoher Ausbeute in kristalliner Form isoliert: Der Thiosilonsäuresilylester **3** (Si=S) und seine Se- bzw. Te-Analoga **4** (Si=Se) bzw. **5** (Si=Te). Die Verbindungen **3**–**5** sind durch direkte Reaktion des stabilen Siloxysilylens L(Si:)OSi(H)L′ **2** (L = HC(CMe)$_2$[N(aryl)$_2$], L′ = CH[(C=CH$_2$)CMe][N(aryl)]$_2$; aryl = 2,6-*i*Pr$_2$C$_6$H$_3$) mit dem entsprechenden Chalkogen leicht zugänglich. Die neuen Verbindungen wurden vollständig charakterisiert, einschließlich Multikern-NMR Spektroskopie und Einkristallstrukturanalyse. Aufgrund intramolekularer N→Si Donor–Acceptorunterstützung der Si=X Gruppen (X = S, Se, Te) besitzen diese eine klassische Valence-Bond N$^+$–Si–X$^-$ Betain-Resonanzstruktur. Gleichzeitig zeigen diese auch das Vorliegen einer relativ starken nichtklassischen Si=X π-Bindungswechselwirkung zwischen den freien Elektronenpaaren am Chalkogen (n$_\pi$ Donororbitale) und den beiden antibindenden Si−N Bindungen (σ* Acceptororbitale mit überwiegender Lokalisierung an Silicium), was durch IR und UV/Vis Spektroskopie gesichert ist. In Einklang damit sind die Si=X Abstände in den Chalkogenoestern mit 7.4 (**3**), 6.7 (**4**), and 6.9 % (**5**) kürzer als die entsprechenden Abstände von Si−X Einfachbindungen und damit auch nur wenig länger als die Abstände in elektronisch weniger gestörten Si=X Systemen ("schwere" Ketone).

Results and Discussion

Synthesis and Spectroscopic Characterization of 3, 4, and 5

The desired silanoic chalcogenoesters **3**, **4**, and **5** are accessible in high yields by direct reaction of siloxysilylene **2** with the respective elemental chalcogen in toluene at room temperature [Eq (2)]. Thus, conversion of **2** with S$_8$ afforded the silanoic thioester **3**, which was isolated in the form of yellow crystals, in 69 % yield. The seleno- and telluroesters **4** and **5** were prepared in high yield (78 and 81 %) as orange and orange-brown crystals by the direct reaction of **2** with elemental selenium and tellurium, respectively [Eq. (2)]. The new compounds **3**–**5** are very soluble in aprotic organic solvents and remain unchanged in boiling benzene even after 2 days.



(2)

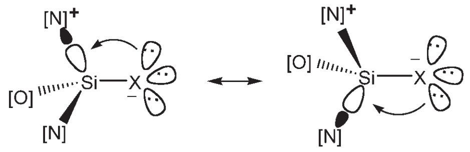
The ^{1}H, ^{13}C, and ^{29}Si NMR spectra of **3**–**5** each reveal, analogous to the situation of **1** and **2**,[2,7] the presence of mixtures of two rotational isomers in different ratios. The two isomers result from the presence of a tetracoordinate stereogenic silicon atom and hindered rotation around the Si−O bond. As expected, the ^{29}Si NMR signals for the Si=X moieties in **3**–**5** (Table 1) appeared at much lower frequencies than those of the unsupported Si=X compounds **D** and **E**.[3,4] Interestingly, the ^{29}Si nucleus of the Si=X group in **4** and **5** resonates at even higher field than that of **A** ($\delta(^{29}\mathrm{Si}) = 22.3$ ppm) and **B** ($\delta(^{29}\mathrm{Si}) = 29.4$ ppm), respectively,[1] owing to the strong additional π interaction (perturbation) of the silicon atom of the Si=X group with the C$_3$N$_2$ π system. The largest change in $\delta(^{29}\mathrm{Si})$ of the Si=X moieties in the series **1**, **3**, **4**, and **5** was observed on going from **1** (X=O) to **3** (X=S) ($\Delta\delta = 44.4$ ppm). In line with previous results, the latter suggests a weaker π-bonding interaction (π-bond strength) between the chalcogen lone-pair electrons (n$_\pi$ donor orbitals) and the two antibonding Si−N orbitals (σ^*_π acceptor orbitals mainly located at silicon) in **3** with respect to **1**

Table 1. Selected ^{29}Si NMR spectroscopic data of **1**, **3**, **4**, and **5**.

Compound	$\delta(^{29}\mathrm{Si{=}X})$ [ppm]	$\delta(^{29}\mathrm{Si{-}H})$ [ppm]	$^1J_{\mathrm{Si,H}}$ [Hz]
1[a]	−85.1, −85.8	−55.0, −55.5	281
3	−40.7, −41.3	−53.5	286
4	−38.4, −39.1	−53.5	288
5	−51.8, −52.2	−53.5	291

[a] See reference [7].

(Scheme 2).[2] As expected, the different strength of the donor–acceptor-supported Si=X bond in **1** (X = O) relative to **3** (X = S), **4** (X = Se), and **5** (X = Te) does not effectively affect the chemical shift of the SiH siloxy ^{29}Si atom and the corresponding $^{1}J_{\mathrm{Si,H}}$ coupling constants (Table 1).



Scheme 2. Formal description of Si=X π-bonding interaction (X = S, Se, Te) in **3**, **4**, and **5**, respectively, from lone-pair electrons of X (donor) to antibonding Si–N orbitals (acceptor).

The ^{77}Se NMR spectrum of the mixture of isomers of **4** shows two singlet signals at $\delta = -384.8$ and -401.3 ppm. In contrast, the ^{77}Se NMR signals of the unsupported Si=Se bonds in **D** appeared about 1000 ppm downfield.[8] The same is true for the ^{127}Te NMR signals of the two isomers of **5**, which appeared upfield at $\delta = -1076.7$ and -1105.5 ppm.[8] The relatively large shielding of the ^{29}Si and ^{77}Se (^{127}Te) nuclei of the Si=X moiety in **4** and **5**, respectively, indicates a strong participation of an N^{+}–Si–X^{-} resonance betaine structure. However, the $\tilde{\nu}$(Si=X) stretching frequencies in the IR spectra of **3**–**5** (Figure 1) suggest considerable π-bond character. The $\tilde{\nu}$(Si=X) values of **3**–**5** were unambiguously assigned by the expected bathochromic shifts of the stretching vibration modes on going from oxygen to tellurium (Figure 1 and Table 2).

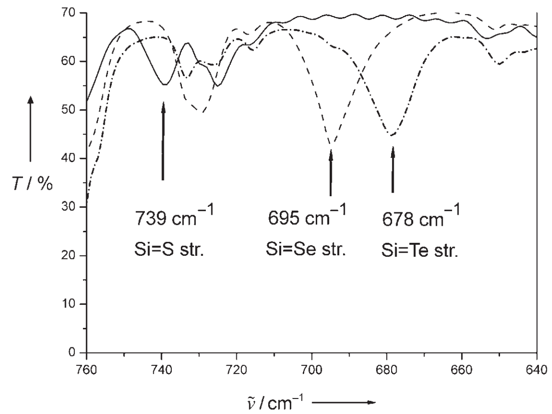


Figure 1. IR spectra of **3**, **4**, and **5** in the characteristic region of 760–640 cm^{-1}. —— = **3**, – – – = **4**, –•–• = **5**.

Table 2. Vibrational stretching frequencies of the Si=X moieties in **1**, **3**, **4**, and **5**.

	1 (X = O)[a]	**3** (X = S)	**4** (X = Se)	**5** (X = Te)
$\tilde{\nu}$(Si=X) [cm^{-1}]	≈1150	739	695	678

[a] See reference [7].

Remarkably, the $\tilde{\nu}$(Si=S) value of **3** at 739 cm^{-1} is even larger than that observed for the unsupported Si=S moiety in **D** (724 cm^{-1}).[3] Accordingly, the $\tilde{\nu}$(Si=Se) and $\tilde{\nu}$(Si=Te) values of 695 and 678 cm^{-1}, respectively, are also in the range of stretching frequencies of unsupported Si=X bonds (X = Se, Te). The relatively large stretching frequencies indicate that the covalent component of the Si=X bond is inseparable from the contribution of the electrostatic component of the betaine-like resonance form N^{+}–Si–X^{-} in the IR spectrum. Therefore, one should be cautious in using the stretching vibration mode as a reliable criterion for the assessment of bond order. Furthermore, considerable Si=X double-bond character is supported by the n→π* absorption in the UV/Vis spectra of **3** (355 nm), **4** (390 nm), and **5** (430 nm). The assignments are based on those reported for the respective unsupported Si=X systems.[4] The series exhibited a systematic red shift for $\lambda_{\max}$ on going from X = S to X = Te. As expected, the latter n→π* transitions underwent a significant blue shift from the corresponding values of the respective unsupported Si=X systems **D** and **E**.[3,4]

Molecular Structures of 3, 4, and 5

The molecular structures of **3**–**5** were elucidated by single-crystal X-ray diffraction analysis. The structures of the compounds are shown in Figures 2–4 together with their selected interatomic distances and angles. Whereas compound **3** crystallizes in the monoclinic space group $P2_1/c$, the heavier esters **4** and **5** are isotypic and crystallize in the triclinic space group $P\bar{1}$. The structures consist of two C$_3$N$_2$Si rings in a gauche conformation relative to each other linked by

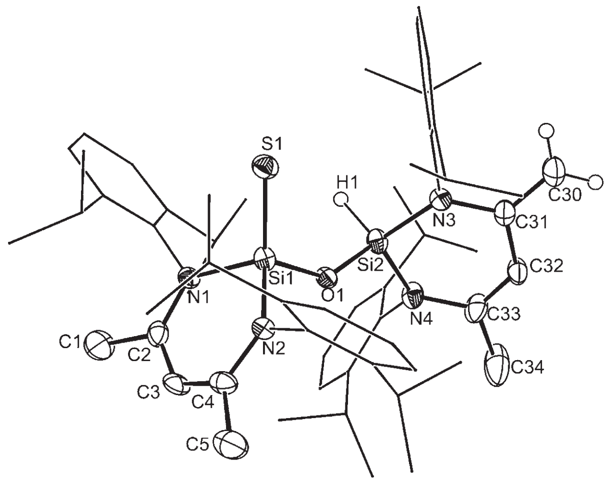


Figure 2. Molecular structure of **3**. Thermal ellipsoids are drawn at the 50 % probability level. Hydrogen atoms (except for H1 and those at C30) are omitted for clarity. Selected bond lengths (pm) and angles (°): Si1–S1 198.0(2), Si1–O1 165.2(3), O1–Si2 165.2(3), Si1–N1 183.3(4), Si1–N2 181.9(3), Si2–N3 173.7(4), Si2–N4 172.5(4), N1–C2 133.8(5), N2–C4 135.9(5), N3–C31 142.6(5), N4–C33 140.7(5), C1–C2 151.6(6), C2–C3 136.7(6), C3–C4 138.1(6), C4–C5 149.5(6), C30–C31 135.5(6), C31–C32 143.0(6), C32–C33 134.8(6), C33–C34 149.7(7); O1–Si1–S1 115.0(1), N1–Si1–S1 111.8(1), N2–Si1–S1 119.3(1), Si1–O1–Si2 138.1(2), N1–Si1–N2 97.4(2), N3–Si2–N4 103.9(2).

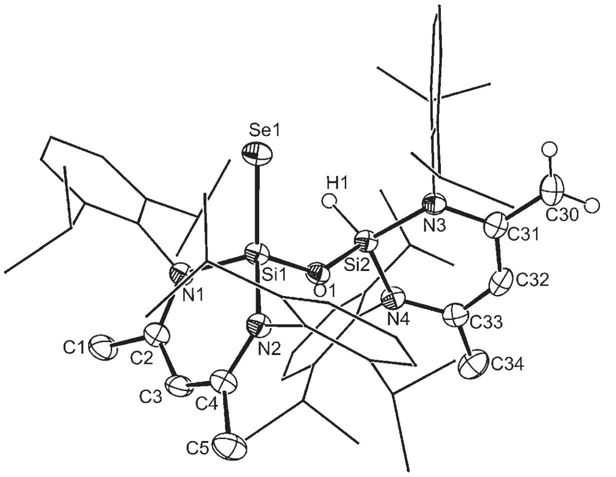


Figure 3. Molecular structure of **4**. Thermal ellipsoids are drawn at the 50 % probability level. Hydrogen atoms (except for H1 and those at C30) are omitted for clarity. Selected bond lengths (pm) and angles (°): Si1–Se1 211.7(1), Si1–O1 165.9(2), O1–Si2 164.4(2), Si1–N1 181.0(2), Si1–N2 184.3(2), Si2–N3 174.4(2), Si2–N4 174.6(2), N1–C2 135.8(3), N2–C4 134.2(3), N3–C31 141.8(3), N4–C33 141.4(4), C1–C2 150.3(4), C2–C3 137.8(4), C3–C4 139.3(4), C4–C5 151.6(4), C30–C31 140.6(4), C31–C32 142.0(4), C32–C33 138.0(4), C33–C34 146.0(4); O1–Si1–Se1 115.84(7), N1–Si1–Se1 111.92(8), N2–Si1–Se1 119.96(8), Si2–O1–Si1 141.1(1), N1–Si1–N2 97.6(1), N3–Si2–N4 105.2(1).

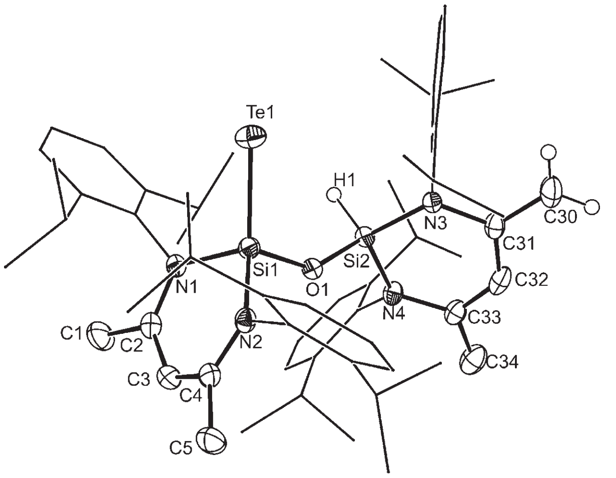


Figure 4. Molecular structure of **5**. Thermal ellipsoids are drawn at the 50 % probability level. Hydrogen atoms (except for H1 and those at C30) are omitted for clarity. Selected bond lengths (pm) and angles (°): Si1–Te1 234.6(1), Si1–O1 164.9(2), O1–Si2 164.4(2), Si1–N1 181.2(2), Si1–N2 184.0(2), Si2–N3 174.2(2), Si2–N4 173.4(2), N1–C2 135.3(3), N2–C4 134.6(3), N3–C31 143.6(3), N4–C33 142.1(3), C1–C2 150.2(4), C2–C3 137.7(4), C3–C4 138.6(4), C4–C5 151.6(4), C30–C31 141.2(4), C31–C32 139.7(4), C32–C33 139.0(4), C33–C34 142.6(4); O1–Si1–Te1 114.44(7), N1–Si1–Te1 111.69(8), N2–Si1–Te1 122.06(8), Si2–O1–Si1 140.3(1), N1–Si1–N2 97.5(1), N4–Si2–N3 105.6(1).

the O1 atom. As expected, the Si1−O1 and Si2−O1 bond lengths in **3**–**5** are practically identical and similar to those observed in common disiloxanes,[9] but a little longer than those observed in **1**.[7] The Si−O−Si angles in **3**–**5** are also similar to those in **1** and related disiloxanes. Although the Si1 and Si2 atoms in **3**–**5** are pyramidally coordinated, the Si1−S1, Si1−Se1, and Si1−Te1 bond lengths in **3**, **4**, and **5**, respectively, resemble the Si=X double-bond lengths (X = S, Se, Te), which are significantly shorter than the respective common Si−X single-bond lengths.[10] Remarkably, the Si1−S1 bond length in **3** of 198.0(2) pm is, as expected, somewhat longer than those observed in the unsupported silanethiones **D** (194.8(4)–195.2(4) pm)[3] and **E** (195.7(1) pm),[4] but significantly shorter than that in **A** (201.3(3) pm).[1] The same is true for the Si1−Se1 (211.7(1) pm) and Si1−Te1 bond lengths (234.6(1) pm) in **4** and **5** (Table 3), respectively, which are a little longer than those in the corresponding unsupported Si=X compounds of types **D** and **E**.

Table 3. Selected geometric parameters of **3**, **4**, and **5**.

Compound	d(Si=X) [pm]	%Δd[a] [%]	d(Si1−O1) [pm]	d(Si2−O1) [pm]	Si−O−Si [°]
3 (X = S)	198.0(2)	7.4	165.2(3)	165.2(3)	138.1(2)
4 (X = Se)	211.7(1)	6.7	165.9(2)	164.4(2)	141.1(1)
5 (X = Te)	234.6(1)	6.9	164.9(2)	164.4(2)	140.3(1)

[a] $\%\Delta d = [1 - d(\mathrm{Si{=}X})/d(\mathrm{Si{-}X})] \times 100\,\%$. Standard values for Si−S (214 pm), Si−Se (227 pm), and Si−Te single-bond lengths (252 pm) are taken from reference [10].

The percentage bond shortening, %Δd (Table 3), among **3**–**5** decreased on going from X = S (7.4 %) to X = Se (6.7 %), but increased slightly from X = Se to X = Te (6.9 %). This is in accordance with the fact that selenium is more electronegative than tellurium and, hence, the n_{π}(Te)→Si−N(σ^{*}_{π}) π bonding is somewhat more effective. The Si2−N3 and Si2−N4 bond lengths in **3**–**5** are about 7 pm longer than the corresponding values in **1** (Si=O), which indicates the presence of a relatively strong and competitive Si=X π-bonding interaction in accordance with the relatively large stretching frequencies observed in the IR spectra.

Conclusions

The first series of isolable silanoic esters with Si=X double bonds were successfully synthesized and characterized structurally. Although the compounds **3**–**5** contain donor–acceptor N→Si supported Si=X bonds that favor the classical N^{+}–Si–X^{-} resonance betaine structure, they contain considerable Si=X double-bond character due to π backdonation from the X atom lone-pair electrons into the antibonding Si−N σ* orbitals mainly located at silicon. The latter nonclassical Si=X bonds show characteristically large values for their stretching vibration modes and relatively short Si−X bond lengths. The highly nucleophilic chalcogen centers in the Si=X systems **3**–**5** represent a fascinating and novel type of sterically encumbered chalcogen donor ligand for the synthesis of unprecedented (low-coordinate) transition-metal complexes of the type [Si]=X→M; respective investigations are currently underway.

Experimental Section

General Considerations

All experiments and manipulations were carried out under dry oxygen-free nitrogen with standard Schlenk techniques or in an MBraun inert-atmosphere drybox containing an atmosphere of purified nitrogen. Solvents were dried by standard methods and freshly distilled prior to use. The starting material L(Si:)OSiH(L′) **2** was prepared according to the literature procedure.[2] ^{1}H, ^{13}C, ^{77}Se, ^{125}Te, and ^{29}Si NMR spectra were recorded on a Bruker AV 400 spectrometer. Chemical-shift references: ^{1}H NMR: [D$_6$]benzene, $\delta(C_6D_5H) = 7.15$ ppm; ^{13}C NMR: [D$_6$]benzene, $\delta = 128.02$ ppm; ^{29}Si NMR: SiMe$_4$ (external), $\delta = 0$ ppm; ^{77}Se NMR: SeMe$_2$ (external), $\delta = 0$ ppm; ^{125}Te NMR: diphenyl ditelluride, (PhTe)$_2$, in CDCl$_3$ (1 mol L^{-1}) (external), $\delta = 422$ ppm.

Syntheses

3: Elemental sulfur (0.0270 g, 0.844 mmol) was added to a suspension of **2** (0.766 g, 0.844 mmol) in toluene (15 mL) and triethylamine (0.02 mL) at room temperature with stirring. The solution turned from brown to yellow immediately. Volatiles were removed in vacuo, and the residue was extracted with toluene (15 mL). Concentration of the clear solution to about 8 mL and subsequent cooling to −20 °C for 24 h afforded yellow crystals of **3** (0.547 g, 0.582 mmol, 69 %). M.p.: 246 °C (decomp.); UV/Vis (hexane): λ (ε) = 315 nm (22 000), 355 nm (5100 M^{-1} cm^{-1}); IR (KBr): $\tilde{\nu}$ = 415 (w), 419 (w), 429 (w), 435 (w), 456 (w), 479 (w), 494 (w), 509 (w), 515 (w), 522 (w), 530 (w), 545 (w), 560 (w), 575 (w), 597 (w), 603 (w), 612 (w), 619 (w), 639 (w), 653 (w), 663 (w), 670 (w), 725 (m), 739 (m, Si=S stretch), 763 (m), 778 (m), 800 (s), 826 (w), 834 (w), 842 (w), 849 (w), 857 (w), 894 (m), 910 (s), 933 (s), 977 (m), 1027 (m), 1057 (m), 1099 (m), 1109 (m), 1177 (m), 1193 (m), 1230 (w), 1243 (m), 1254 (m), 1315 (m), 1352 (m), 1361 (m), 1382 (s), 1438 (m), 1465 (m), 1555 (s), 1590 (w), 1657 (m), 2258 (w), 2867 (m), 2930 (m), 2967 (s), 3061 (w), 3421 cm^{-1} (w); ^{1}H NMR (400.13 MHz, C$_6$D$_6$, 298 K): Two rotational isomers in different ratios were observed owing to the presence of a chiral Si center (L′(H)Si*) and hindered rotation of the Si−O bonds; δ = 0.58–1.98 (m, 114 H, CH*Me*$_2$, NCMe), 3.19, 3.37, 3.88, 4.01 (s, 4 H, NCCH$_2$), 2.78–3.94 (m, 16 H, C*H*Me$_2$), 5.28, 5.32 (s, 2 H, SiH, ^{29}Si satellites: $^{1}J_{H,Si}$ = 286 Hz), 4.87, 4.92, 5.23, 5.37 (s, 4 H, γ-CH), 6.90–7.34 ppm (br m, 24 H, arom. H); ^{13}C{^{1}H} NMR (100.61 MHz, C$_6$D$_6$, 298 K): δ = 14.3–31.9 (NC*Me*, *i*Pr), 88.4, 90.2 (NC*C*H$_2$), 102.4, 103.0, 103.5, 108.4 (γ-C), 124.0–171.1 ppm (2,6-*i*Pr$_2$*C*$_6$H$_3$, NC); ^{29}Si NMR (79.49 MHz, C$_6$D$_6$, 298 K): δ = −53.5 (d, $^{1}J_{H,Si}$ = 286 Hz, SiH), −40.7 (s, SiS), −41.3 ppm (s, SiS); MS (EI): *m/z* (%) = 939.5 [*M*]$^+$ (86), 924.5 [*M*−Me]$^+$ (81), 896.5 [*M*−*i*Pr]$^+$ (37), 202.3 [*i*Pr$_2$C$_6$H$_3$NCMe]$^+$ (100); elemental analysis: calcd (%) for C$_{58}$H$_{82}$N$_4$Si$_2$OS: C 74.2, H 8.8, N 6.0; found: C 74.4, H 8.8, N 5.6.

4: Elemental selenium (0.0485 g, 0.614 mmol) was added to a suspension of **2** (0.557 g, 0.614 mmol) in toluene (15 mL) and triethylamine (0.05 mL) at room temperature with stirring. The solution turned from brown to orange within 20 min. Volatiles were removed in vacuo, and the residue was extracted with toluene (15 mL). Concentration of the clear solution to about 6 mL and subsequent cooling to 4 °C for 24 h afforded orange crystals of **4** (0.472 g, 0.479 mmol, 78 %). M.p.: 254 °C (decomp.); UV/Vis (hexane): λ (ε) = 327 nm (39 000), 390 nm (3300 M^{-1} cm^{-1}); IR (KBr): $\tilde{\nu}$ = 405 (w), 410 (w), 420 (w), 457 (w), 496 (w), 511 (w), 544 (w), 559 (w), 574 (w), 594 (m), 613 (w), 636 (w), 651 (w), 695 (m, Si=Se stretch), 717 (w), 729 (w), 763 (m), 800 (s), 892 (s), 908 (s), 930 (s), 940 (s), 976 (m), 1028 (m), 1058 (m), 1099 (m), 1107 (m), 1177 (m), 1193 (m), 1227 (w), 1243 (m), 1254 (m), 1311 (s), 1317 (s), 1352 (s), 1382 (s), 1437 (s), 1464 (s), 1496 (w), 1535 (m), 1556 (s), 1589 (w), 1624 (w), 1645 (m), 1657 (m), 2260 (w), 2867 (m), 2929 (m), 2967 (s), 3061 (w), 3113 (w), 3430 cm^{-1} (w); ^{1}H NMR (400.13 MHz, C$_6$D$_6$, 298 K): Two rotational isomers in different ratios were observed due to the presence of a chiral Si center (L(H)Si*) and hindered rotation of the Si−O bonds; δ = 0.59–1.97 (m, 114 H, CH*Me*$_2$, NCMe), 3.22, 3.36, 3.90, 4.01 (s, 4 H, NCCH$_2$), 2.78–3.91 (m, 16 H, C*H*Me$_2$), 4.91, 4.96, 5.23, 5.37 (s, 4 H, γ-CH), 5.40, 5.44 (s, 2 H, SiH, ^{29}Si satellites: $^{1}J_{H,Si}$ = 288 Hz), 6.93–7.34 ppm (br m, 24 H, arom. H); ^{13}C{^{1}H} NMR (100.61 MHz, C$_6$D$_6$, 298 K): δ = 21.4–31.0 (NC*Me*, *i*Pr), 88.4, 90.4 (NC*C*H$_2$), 103.2, 103.6, 103.9, 108.5 (γ-C), 124.0–171.0 ppm (2,6-*i*Pr$_2$*C*$_6$H$_3$, NC); ^{29}Si NMR (79.49 MHz, C$_6$D$_6$, 298 K): δ = −53.5 (d, $^{1}J_{H,Si}$ = 288 Hz, SiH), −38.4 (s, SiSe), −39.1 ppm (s, SiSe); ^{77}Se NMR (76.31 MHz, C$_6$D$_6$, 298 K): δ = −384.8 (s), −401.3 ppm (s); MS (EI): *m/z* (%) = 986.4 [*M*]$^+$ (31), 971.4 [*M*−Me]$^+$ (100), 943.4 [*M*−*i*Pr]$^+$ (69); elemental analysis: calcd (%) for C$_{58}$H$_{82}$N$_4$Si$_2$OSe: C 70.6, H 8.4, N 5.7; found: C 70.6, H 8.3, N 5.9.

5: Elemental tellurium (0.0738 g, 0.578 mmol) was added to a suspension of **2** (0.524 g, 0.578 mmol) in toluene (15 mL) and triethylamine (0.05 mL) at room temperature with stirring. The solution turned from brown to orange within 48 h. Volatiles were removed in vacuo, and the residue was extracted with toluene (15 mL). Concentration to about 8 mL and subsequent cooling to −20 °C for 48 h afforded orange-brown crystals of **5** (0.484 g, 0.468 mmol, 81 %). M.p.: 279 °C (decomp.); UV/Vis (toluene): λ (ε) = 338 nm (24 000), 430 nm (570 M^{-1} cm^{-1}); IR (KBr): $\tilde{\nu}$ = 405 (w), 419 (w), 455 (m), 497 (w), 517 (m), 543 (w), 551 (w), 566 (m), 574 (m), 594 (w), 612 (w), 635 (w), 650 (w), 678 (m, Si=Te stretch), 716 (w), 726 (w), 733 (w), 762 (s), 773 (s), 798 (s), 802 (s), 896 (s), 909 (s), 928 (s), 940 (s), 976 (m), 1026 (m), 1044 (m), 1058 (s), 1098 (m), 1108 (m), 1179 (m), 1225 (m), 1242 (m), 1254 (m), 1307 (s), 1318 (s), 1352 (s), 1365 (s), 1384 (s), 1436 (s), 1465 (s), 1518 (s), 1562 (s), 1591 (m), 1617 (w), 1646 (m), 1657 (m), 2270 (w), 2868 (s), 2928 (s), 2969 (s), 3059 (w), 3423 cm^{-1} (w); ^{1}H NMR (400.13 MHz, C$_6$D$_6$, 298 K): Two rotational isomers in different ratios were observed due to the presence of a chiral Si center (L′(H)Si*) and hindered rotation of the Si−O bonds; δ = 0.58–1.96 (m, 114 H, CH*Me*$_2$, NCMe), 3.24, 3.30, 3.90, 4.00 (s, 4 H, NCC*H*$_2$), 2.76–3.96 (m, 16 H, C*H*Me$_2$), 4.99, 5.05, 5.23, 5.36 (s, 4 H, γ-CH), 5.61, 5.65 (s, 2 H, SiH, ^{29}Si satellites: $^{1}J_{H,Si}$ = 291 Hz), 6.93–7.35 ppm (br m, 24 H, arom. H); ^{13}C{^{1}H} NMR (100.61 MHz, C$_6$D$_6$, 298 K): δ = 21.4–31.0 (NC*Me*, *i*Pr), 88.6, 90.7 (NC*C*H$_2$), 103.8, 104.7, 105.4, 108.6 (γ-C), 123.6–171.2 ppm (2,6-*i*Pr$_2$C$_6$H$_3$, NC); ^{29}Si NMR (79.49 MHz, C$_6$D$_6$, 298 K): δ = −53.5 (d, $^{1}J_{H,Si}$ = 291 Hz, SiH), −51.8 (s, SiTe), −52.2 ppm (s, SiTe); ^{125}Te NMR (126.24 MHz, C$_6$D$_6$, 298 K): δ = −1076.7 (s), −1105.5 ppm (s); MS (EI): *m/z* (%) = 1035.1 [*M*]$^+$ (98), 1020.1 [*M*−Me]$^+$ (23), 992.0 [*M*−*i*Pr]$^+$ (52), 202.3 [*i*Pr$_2$C$_6$H$_3$NCMe]$^+$ (100); elemental analysis: calcd (%) for C$_{58}$H$_{82}$N$_4$Si$_2$OTe: C 67.3, H 8.0, N 5.4; found: C 67.0, H 7.9, N 5.5.

Single-Crystal X-ray Structure Determination

Crystals were mounted on a glass capillary in perfluorinated oil and measured in a cold flow of N$_2$. Data for **3**–**5** were collected on an Oxford Diffraction Xcalibur S Sapphire diffractometer at 150 K (Mo$_{K\alpha}$ radiation, λ = 0.71073 Å). Structures were solved by direct methods and were refined on F^2 with the SHELX-97[11] software package. The positions of the H atoms were calculated and considered isotropically according to a riding model (exceptions are the hydrogen atoms on silicon that have been found in the electron-density map). Crystals of **3** contain disordered diethyl ether molecules, which are squeezed. Crystals of **5** contain disordered toluene molecules. CCDC-656190, -656191, and -656192 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif.

3: Monoclinic, space group $P2_1/c$, $a = 13.840(3)$, $b = 17.714(2)$, $c = 24.733(3)$ Å, $\beta = 97.785(15)°$, $V = 6007.6(18)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.039$ mg m^{-3}, $\mu(Mo_{K\alpha}) = 0.132$ mm^{-1}, 29 603 collected reflections, 10 545 crystallographically independent reflections ($R_{int} = 0.0965$), 4932 reflections with $I > 2\sigma(I)$, $\theta_{max} = 25.00°$, $R(F_o) = 0.0762$ ($I > 2\sigma(I)$), $wR(F_o^2) = 0.1692$ (all data), 628 refined parameters.

4·2 Toluene: Triclinic, space group $P\bar{1}$, $a = 12.5973(7)$, $b = 13.9200(19)$, $c = 20.037(4)$ Å, $\alpha = 103.119(14)$, $\beta = 103.234(9)$, $\gamma = 97.484(8)°$, $V = 3268.9(8)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.189$ mg m^{-3}, $\mu(Mo_{K\alpha}) = 0.656$ mm^{-1}, 27 827 collected reflections, 11 379 crystallographically independent reflections ($R_{int} = 0.0465$), 7660 reflections with $I > 2\sigma(I)$, $\theta_{max} = 25°$, $R(F_o) = 0.0486$ ($I > 2\sigma(I)$), $wR(F_o^2) = 0.1089$ (all data), 745 refined parameters.

5·2 Toluene: Triclinic, space group $P\bar{1}$, $a = 12.603(2)$, $b = 13.8143(7)$, $c = 20.312(3)$ Å, $\alpha = 101.241(7)$, $\beta = 105.655(14)$, $\gamma = 97.397(8)°$, $V = 3277.7(7)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.235$ mg m^{-3}, $\mu(Mo_{K\alpha}) = 0.536$ mm^{-1}, 27 790 collected reflections, 11 355 crystallographically independent reflections ($R_{int} = 0.0348$), 8302 reflections with $I > 2\sigma(I)$, $\theta_{max} = 25°$, $R(F_o) = 0.0360$ ($I > 2\sigma(I)$), $wR(F_o^2) = 0.0798$ (all data), 810 refined parameters.

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