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## N-Heterocyclic Carbene (NHC)-Stabilized Silanechalcogenones: NHC $\rightarrow$ Si(R<sub>2</sub>)=E (E=O, S, Se, Te)

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Dedicated to Professor Hubert Schmidbaur

Abstract: A series of N-heterocyclic carbene-stabilized silanechalcogenones **2a,b** (Si=O), **3a,b** (Si=S), **4a,b** (Si=Se), and **5a,b** (Si=Te) are described. The silanone complexes **2a,b** were prepared by facile oxygenation of the carbene–silylene adducts **1a,b** with N<sub>2</sub>O, whereas their heavier congeners were synthesized by gentle chalcogenation of **1a,b** with equimolar amounts of elemental sulfur, selenium, and tellurium, respectively. These novel compounds have been isolated in a crystalline form in high yields and have been fully charac-

### Introduction

The chemistry of multiply bonded heavier main-group elements is currently one of the main areas of research in organometallic chemistry. Of especially great interest are compounds with a double bond that involves heavier Group 14 and Group 16 elements as heavier congeners of ubiquitous ketones.<sup>[11]</sup> Since Corriu et al. reported in 1989 the first stable silanethione (Si=S) and silaneselone (Si=Se) derivatives I and II (Scheme 1) supported by a intramolecular N $\rightarrow$ Si donor–acceptor bond,<sup>[2]</sup> several series of stable doubly bonded species have been developed by taking advantage of the kinetic protection from the bulky ligands and/or the thermodynamic stabilization from Lewis donors as well as acceptors. Striking examples, including a series of fascinating stable heavier diarylsilanechalcogenones III (Scheme 1)<sup>[3]</sup>

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terized by a variety of techniques including IR spectroscopy, ESIMS, and multinuclear NMR spectroscopy. The structures of **2b**, **3a**, **4a**, **4b**, and **5b** have been confirmed by single-crystal X-ray crystallography. Due to the NHC $\rightarrow$ Si donor-acceptor electronic interaction, the Si=E (E=O, S, Se, Te) moieties within these compounds are

**Keywords:** carbenes • chalcogens • heterocycles • multiple bonds • silanones

well stabilized and thus the compounds possess several ylide-like resonance structures. Nevertheless, these species also exhibit considerable Si=E doublebond character, presumably through a nonclassical Si=E  $\pi$ -bonding interaction between the chalcogen lone-pair electrons and two antibonding Si-N  $\sigma^*$ orbitals, as evidenced by their high stretching vibration modes and the shortening of the Si-E distances (between 5.4 and 6.3%) compared with the corresponding Si-E single-bond lengths.



Scheme 1. Isolable compounds with a double bond involving silicon and Group 16 elements.

tramolecular donor support, were described by Tokitoh, Okazaki et al. as well as by Iwamoto and Kira et al., respectively. Recently, a novel bis(silaneselone) with two donorsupported Si=Se double bonds was reported by Müller and West et al.<sup>[5]</sup>

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Although a "free" silanone derivative (R<sub>2</sub>Si=O) still remains elusive, we recently succeeded in synthesizing the remarkably stable silaformamide–borane complex<sup>[6]</sup> with a donor–acceptor-supported silicon–oxygen double bond starting from a zwitterionic silylene.<sup>[7]</sup>

Moreover, we reported the synthesis and characterization of an entire series of heavier congeners of silanoic silylesters **V** (Scheme 1)<sup>[8]</sup> that bore an N $\rightarrow$ Si-supported Si=E (E=O, S, Se, Te) moiety from gentle monochalcogenation of a stable siloxysilylene.<sup>[6]</sup> Inspired by the isolation of N-heterocyclic carbene (NHC)-stabilized main-group element species reported by Robinson et al.,<sup>[9]</sup> we preliminarily communicated the isolation of the NHC-supported silanone **2a** (Scheme 2) by facile oxygenation of a NHC–silylene adduct



Scheme 2. Synthesis of 2a,b-5a,b from NHC-silylene adducts 1a and 1b.

**1a** with N<sub>2</sub>O.<sup>[10]</sup> To extend this work, we probed the possibility for direct chalcogenation of the NHC-silylene adducts **1a** and **1b** with elemental heavier chalcogens for the preparation of the respective NHC-supported silanechalcogenones. Here we report on the synthesis as well as the spectroscopic and structural characterization of the first series of NHC-stabilized silanechalcogenones, which includes **2b** (Si= O), **3a,b** (Si=S), **4a,b** (Si=Se), and **5a,b** (Si=Te) (Scheme 2).

#### **Results and Discussion**

Synthesis and spectroscopic characterization: In a preliminary communication we reported that the NHC-silanone adduct **2a** is easily accessible by oxygenation of the NHC-silylene adduct **1a** with N<sub>2</sub>O (Scheme 2).<sup>[10]</sup> The same procedure is also suitable for the synthesis of the sterically more hindered NHC-silanone adduct **2b**. Accordingly, exposure of a yellow solution of the NHC-silylene adduct **1b**<sup>[11]</sup> in tol-

uene to N<sub>2</sub>O at -78 °C leads to a gradual loss of color. The desired product **2b** can be obtained as colorless crystals by crystallization of the resulting reaction solution at -20 °C in 88% yield.

The NHC-stabilized heavier silanechalcogenones 3a,b, 4a,b, and 5a,b are readily accessible by direct chalcogenation applying the respective elemental chalcogens. Thus, treatment of equimolar amounts of the NHC-silylene adducts 1a and 1b with elemental sulfur  $S_8$  in toluene at ambient temperature, respectively, leads to a color change from yellow to pale yellow and the formation of colorless precipitates (Scheme 2). Subsequent workup of the resulting mixtures affords 3a and 3b as a colorless crystalline solid in 79 and 71% yields, respectively. Similarly, the conversions of 1a and 1b with elemental selenium and tellurium enable the formation and isolation of **4a** (76%) and **4b** (69%) in the form of colorless crystals as well as 5a (74%) and 5b (68%) in the form of yellow crystals. Notably, the free silylene<sup>[7]</sup> without NHC is resistant towards elemental selenium and tellurium under the same conditions, whereas the treatment of the free silvlene with sulfur slowly results in complex unidentified products. This finding confirms the increase of nucleophilicity of the silicon(II) center in 1a and 1b by coordination of the NHC moiety.

The composition and constitution of the resulting new compounds were proven by elemental analysis, ESIMS, and multinuclear NMR spectroscopy. Although the <sup>1</sup>H and <sup>13</sup>C NMR signals of **2a,b–5a,b** for the N-heterocyclic supporting ligands are similar to those observed for their precursor **1a,b**, their <sup>29</sup>Si NMR spectra exhibit significant high-field shifts (Table 1) compared to those found for **1a** ( $\delta$ -

Table 1. NMR spectroscopic data of 2a,b-5a,b.

Complex	δ( <sup>29</sup> Si) [ppm]	δ( <sup>77</sup> Se) [ppm]	$\delta(^{125}\text{Te})$ [ppm]
2a	$-74.2^{[a]}$	_	_
2b	-72.9 <sup>[a]</sup>	-	-
3a	-34.9 <sup>[b]</sup>	_	-
3b	-33.5 <sup>[b]</sup>	_	-
4a	-33.3 <sup>[b]</sup>	-374.4	-
4b	$-32.9^{[b]}$	-470.2	-
5a	$-46.0^{[b]}$	-	-1010.4
5b	$-49.6^{[b]}$	-	-982.5

[a] Measured in [D<sub>6</sub>]benzene. [b] Measured in [D<sub>2</sub>]dichloromethane.

 $(^{29}\text{Si}) = -12.0 \text{ ppm})$  and **1b** ( $\delta(^{29}\text{Si}) = -7.6 \text{ ppm}$ ). In fact, the <sup>29</sup>Si NMR chemical shifts of **2a** ( $\delta = -74.2 \text{ ppm}$ ) and **2b** ( $\delta = -72.9 \text{ ppm}$ ) lie between the values observed for the two diastereomers of the N-donor-stabilized silanoic ester V ( $\delta = -85.1 \text{ and } -85.8 \text{ ppm})^{[8a]}$  and the silaformamide-borane complex ( $\delta = -61.5 \text{ ppm}$ ).<sup>[6]</sup> As expected, the <sup>29</sup>Si NMR spectra of the heavier NHC-silanechalcogenones **3a,b-5a,b** exhibit less-shielded silicon nuclei (ranging from  $\delta = -32.9$  to -49.6 ppm) relative to the NHC-supported silanones **2a** and **2b**. These chemical shifts of **3a,b-5a,b** are comparable to the corresponding chemical shifts of related silanoic thio-, seleno-, and telluroesters **V**, with  $\delta(^{29}\text{Si})$  values ranging from  $-38.4 \text{ to } -52.2 \text{ ppm}.^{[8b]}$  Expectedly, the <sup>29</sup>Si nuclei of the un-

supported Si=E (E=S, Se, Te) compounds III and IV resonate at much lower field; they range from  $\delta = 166.6$  to 229.5 ppm.<sup>[3,4]</sup> Even the intramolecular N-donor-supported silanechalcogenones I ( $\delta$ (<sup>29</sup>Si)=22.3 ppm) and II ( $\delta$ (<sup>29</sup>Si)=29.4 ppm)<sup>[2]</sup> are less shielded than **3a,b** and **4a,b**, respectively. Apparently, this observation is indicative of greater perturbation of the Si=E (E=O, S, Se, Te) double bonds caused by both the C<sub>3</sub>N<sub>2</sub>  $\pi$  system in the backbone and the NHC moiety, thereby leading to several resonance structures as depicted in Scheme 3.



Scheme 3. Resonance structures of 2a,b-5a,b (E=O, S, Se, Te; Ar=2,6- $iPr_2C_6H_3$ ; R=Me, iPr).

The <sup>77</sup>Se NMR spectra of **4a** and **4b** show a singlet signal at  $\delta = -374.4$  and -470.2 ppm, respectively, which are in sharp contrast to the downfield shifts of the unsupported Si=Se species III ( $\delta = 635$  ppm).<sup>[3]</sup> The latter chemical shifts are, however, comparable to those of **V** (E=Se;  $\delta = -384.8$ and -401.3 ppm).<sup>[8b]</sup> Likewise, the <sup>125</sup>Te NMR spectra of **5a** and **5b** display singlet signals ( $\delta = -1010.4$  for **5a** and -982.5 ppm for **5b**) very close to those of the two diastereomers of **V** (E=Te;  $\delta = -1076.7$  and -1105.5 ppm).<sup>[8b]</sup> The shielding of the <sup>77</sup>Se and <sup>125</sup>Te nuclei of the Si=E moiety in **4a,b-5a,b** is in accordance with their <sup>29</sup>Si NMR spectroscopy and implies again the resonance stabilization of the siliconchalcogen double bonds (Scheme 3).

Interestingly, a considerable Si=E  $\pi$ -bond character of complexes **2a**,**b**-**5a**,**b** can also be concluded from the vibrational stretching frequencies of the Si=E moieties (Table 2).

Table 2. Comparison of the vibrational stretching frequencies  $[cm^{-1}]$  of the Si=E moieties in **2a,b-5a,b** with the silanoic chalcogenesters **V**.<sup>[8]</sup>

	E = O	E = S	E=Se	E = Te
$V^{[8]}$	$\approx 1150$	739	695	678
2 a-5 a	1134	683	614	595
2b-5b	1133	679	606	588

As depicted in Figure 1, the assignment of the respective  $\tilde{v}$ -(Si=E) stretching vibration results from overlapping of the IR spectra; the characteristic frequencies are listed in Table 2.

The  $\tilde{\nu}(Si=O)$  stretching vibration modes of **2a** (1134 cm<sup>-1</sup>) and **2b** (1133 cm<sup>-1</sup>) are around 20–30 cm<sup>-1</sup> smaller than that observed for the silanoic ester ( $\approx 1150 \text{ cm}^{-1}$ )<sup>[8a]</sup> and the silaformamide–borane complex (1165 cm<sup>-1</sup>).<sup>[6]</sup> Similarly, the  $\tilde{\nu}$ -(Si=S),  $\tilde{\nu}(Si=Se)$ , and  $\tilde{\nu}(Si=Te)$  values are also significantly bathochromically shifted relative to the corresponding wave-



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Figure 1. IR spectra of **2b** (—), **3b** (–––), **4b** (•••••), and **5b** (–•–•) in the characteristic region of 550–1250 cm<sup>-1</sup>.

numbers of **V**<sup>[8b]</sup> Nevertheless, these  $\tilde{\nu}$ (Si=E) (E=O, S, Se, Te) stretching modes are drastically larger than the corresponding values observed for Si–E single-bond species (i.e., for (MeH<sub>2</sub>Si)<sub>2</sub>E, in which E=O, S, Se, Te),<sup>[12]</sup> which might suggest considerable double-bond character in **2a,b–5a,b**. The latter Si=E multiple-bond character can be rationalized as previously discussed by a nonclassical Si=E  $\pi$ -binding interaction between the chalcogen lone-pair electrons and two antibonding Si–N  $\sigma^*$  orbitals that are located mainly at the silicon site.<sup>[6,8b]</sup>

Molecular structures: The molecular structure of 2a has already been reported in a preliminary communication.<sup>[10]</sup> The molecular structures of 2b, 3a, 4a, 4b, and 5b were established by single-crystal X-ray diffraction analysis and their ORTEP drawings are shown in Figures 2, 3, 4, 5, and 6 together with their structural parameters. For comparison, the selected interatomic distances (d) and angles are compiled in Table 3. The structures of 3b and 5a have also been confirmed by X-ray diffraction but they cannot be discussed due to poor crystal quality. Whereas compounds 2b, 4b, and **5b** crystallize in the monoclinic space groups  $P2_1/c$  (**2b**, **5b**) and  $P2_1/n$  (4b), respectively, compounds 3a and 4a result in the triclinic space group  $P\overline{1}$ . Two independent molecules of **2b** are found in the asymmetric unit as shown in Figure 2. Similar to 2a, the new compounds are monomeric in the crystal, and the silicon centers adopt a strongly distorted tetrahedral coordination geometry with a terminal chalcogen atom. Whereas the six-membered C<sub>3</sub>N<sub>2</sub>Si rings in the compounds are slightly puckered, the five-membered NHC rings remain planar.

The Si=O bond lengths of 1.527(2) and 1.534(2) Å in **2b** are even shorter than that observed for **2a** (1.541(2) Å) and in the silanoic ester **V** (1.579(3) Å).<sup>[8a]</sup> To our knowledge, they are the shortest Si=O bond lengths hitherto reported among stable molecular silicon–oxygen compounds with terminal oxygen atoms.<sup>[6,8a,10]</sup> In contrast, although the Si=E (E=S, Se, Te) bond lengths in **3a** (Si=S: 2.006(1) Å), **4a** (Si=Se: 2.1457(9) Å), **4b** (Si=Se: 2.1399(9) Å), and **5b** (Si=Te: 2.383(2) Å) are significantly shorter than respective Si–

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Figure 2. The two independent molecules of **2b** in the asymmetric unit. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms, except those at C1 and C41, are omitted for clarity. Selected bond lengths [Å] and angles [°]: *Mol. 1:* Si1–O1 1.527(2), N1–C2 1.407(4), N1–Si1 1.751(3), Si1–N2 1.741(3), Si1–C30 1.978(3), N2–C4 1.418(4), C2–C3 1.450(5), N3–C30 1.356(4), N3–C31 1.377(4), C3–C4 1.334(5), N4–C30 1.361(4), N4–C32 1.383(4); N1-Si1-N2 101.8(1), N1-Si1-O1 118.8(1), N2-Si1-O1 114.0(1), C30-Si1-O1 107.8(1), N3-C30-N4 104.9(2); *Mol. 2:* Si2–O2 1.534(2), Si2–N6 1.744(3), Si2–N5 1.754(3), Si2–C70 1.963(3), N5–C42 1.408(4), N6–C44 1.418(4), N7–C70 1.355(4), N7–C71 1.385(4), N8–C70 1.359(3), N8–C72 1.388(4), C42–C43 1.458(5), C43–C44 1.324(5); O2-Si2-N6 115.0(1), O2-Si2-N5 1118.4(1), N6-Si2-N5 101.6(1), O2-Si2-C70 107.6(1), N7-C70-N8 105.1(2).

E single bonds, they are a little longer than the corresponding values observed in the series of silanoic esters V (Si=S 1.980(2), Si=Se 2.117(1), Si=Te 2.346(1) Å),<sup>[8b]</sup> respectively. The latter elongations correspond well with the bathochromic shifts of the Si=E stretching modes observed in the IR spectra (Table 2). However, as can be seen from the percentage of bond shortening with regard to the corresponding Si-E single bonds ( $\% \Delta d$ ) in Table 3, the Si=E moieties in **2a,b-5a,b** could have significant double-bond character, although zwitterionic Si<sup>+</sup>-E<sup>-</sup> bonding character could not be excluded.



Figure 3. Molecular structure of **3a**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: S1–Si1 2.006(1), Si1–N2 1.749(2), Si1–N1 1.752(2), Si1–C30 1.963(3), N1–C2 1.407(4), N2–C4 1.414(4), N3–C30 1.357(4), N3–C31 1.391(4), N4–C30 1.356(4), N4–C32 1.378(4), C2–C3 1.431(4), C3–C4 1.370(4); N2-Si1-N1 102.1(1), N2-Si1-S1 115.53(9), N1-Si1-S1 115.88(9), C30-Si1-S1 110.4(1), N4-C30-N3 103.7(3).



Figure 4. Molecular structure of **4a**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Se1–Si1 2.1457(9), Si1–N2 1.754(3), Si1–N1 1.759(2), Si1–C30 1.977(3), N1–C2 1.405(4), N2–C4 1.416(4), N3–C30 1.356(3), N3–C31 1.379(4), N4–C30 1.356(4), N4–C32 1.386(4), C2–C3 1.433(4), C3–C4 1.362(4); N2-Si1-N1 101.7(1), N2-Si1-Se1 114.98(9), N1-Si1-Se1 115.92(9), C30-Si1-Se1 111.6(1), N4-C30-N3 104.6(2).

Interestingly, the Si–N bond lengths in these new structures (ranging from 1.741(3) to 1.766(5) Å) are significantly shorter than those observed in precursors **1a** (1.802(3) and 1.805(3) Å) and **1b** (1.794(2) and 1.820(2) Å) in spite of the increased coordination number of the silicon atom in these NHC-supported silanechalcogenones. In addition, although the Si–C<sub>carbene</sub> bond lengths (ranging from 1.963(3) to 2.007(6) Å) in these species are much longer than a typical Si–C single-bond length in organosilanes (1.86 Å), they are shorter than those found for **1a** (2.016(3) Å) and **1b** (2.065(2) Å).<sup>[10,11]</sup> This shortening of the Si–N and Si–C



Figure 5. Molecular structure of **4b**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Se1–Si1 2.1399(9), N1–C2 1.414(4), N1–Si1 1.754(3), Si1–N2 1.762(3), Si1–C30 1.978(3), N2–C4 1.420(4), C2–C3 1.457(4), N3–C30 1.366(4), N3–C31 1.391(4), C3–C4 1.336(4), N4–C30 1.371(4), N4–C32 1.395(4); N1-Si1-N2 102.43(1), N1-Si1-Se1 120.41(9), N2-Si1-Se1 109.50(9), C30-Si1-Se1 111.2(1), N3-C30-N4 105.2(3).



Figure 6. Molecular structure of **5b**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Te1–Si1 2.383(2), Si1–N2 1.758(5), Si1–N1 1.766(5), Si1–C30 2.007(6), N1–C2 1.402(7), N2–C4 1.410(7), N3–C31 1.387(8), N3–C30 1.387(7), N4–C30 1.368(7), N4–C32 1.385(8), C2–C3 1.463(8), C3–C4 1.350(8); N2-Si1-N1 101.8(2), N2-Si1-Te1 112.4(2), N1-Si1-Te1 113.1(2), C30-Si1-Te1 114.1(2), N4-C30-N3 104.0(5).

bond lengths is ascribed to the presence of a ylide-like resonance stabilization of the Si=E double bonds.

#### Conclusion

The first entire series of NHC-stabilized silanechalcogenones 2a,b (Si=O), 3a,b (Si=S), 4a,b (Si=Se), and 5a,b (Si= Te) has been successfully prepared by gentle oxidation of the carbene–silylene adducts with N<sub>2</sub>O (in the case of 2a,b) and elemental chalcogens. They were isolated in a crystalline form in high yields and characterized by NMR and IR

Table 3.	Selected	structural	parameters	of 2 a,b-5 a,b
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	d(Si=E) [Å]	$\% \Delta d^{[a]}$	d(Si−C) [Å]	d(Si−N) [Å]	d(Si–N) [Å]
2a	1.541(2)	5.5	1.930(2)	1.745(2)	1.750(2)
(E = O)					
2b	1.527(2)	6.3	1.978(3)	1.751(3)	1.741(3)
(E = O)					
$\mathbf{Sa} (\mathbf{E} = \mathbf{S})$	1.534(2)	5.9	1.963(3)	1.754(3)	1.744(3)
4a	2.006(1)	6.3	1.963(3)	1.752(2)	1.749(2)
(E = Se)					
4b	2.1457(9)	5.5	1.977(3)	1.759(2)	1.754(3)
(E = Se)					
5b	2.1399(9)	5.7	1.978(3)	1.754(3)	1.762(3)
(E = Te)					
	2.383(2)	5.4	2.007(6)	1.766(5)	1.758(5)

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[a] %  $\Delta d = [1-d(Si=E)/d(Si-E)] \times 100$  %. Standard values for Si=O (1.63 Å), Si=S (2.14 Å), Si=Se (2.27 Å), and Si=Te single-bond lengths (2.52 Å) from ref. [13].

spectroscopy and X-ray diffraction. The Si=E (E=O, S, Se, Te) moieties within these compounds are electronically well supported by the  $C_3N_2$  backbone and the NHC ligands, thereby resulting in several ylide-like resonance structures. However, these species possess considerable Si=E double-bond character as indicated by their Si=E vibration modes and relatively short Si=E bond lengths. Due to the highly nucleophilic chalcogen centers in **2a,b–5a,b**, they represent a fascinating new type of strong  $\sigma$ -donor ligands capable of the synthesis of low-coordinate transition-metal complexes that could find applications in homogeneous catalysis. Respective investigations are currently underway.

#### **Experimental Section**

**General considerations**: All experiments and manipulations were carried out under dry oxygen-free nitrogen using 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 materials  $1a^{[10]}$  and  $1b^{[11]}$  were prepared according to literature procedures. Compound 2a was prepared according to the preliminary communication.<sup>[10]</sup> ESIMS were measured using a Thermo Scientific LTQ orbitrap XL. <sup>1</sup>H, <sup>13</sup>C, <sup>77</sup>Se, <sup>125</sup>Te, and <sup>29</sup>Si NMR spectra were recorded using Brucker spectrometers ARX 200 and AV 400 with residual solvent signals as internal reference (<sup>1</sup>H and <sup>13</sup>C[<sup>1</sup>H]) or with an external reference (SiMe<sub>4</sub> for <sup>29</sup>Si, SeMe<sub>2</sub> for <sup>77</sup>Se, (PhTe)<sub>2</sub> for <sup>125</sup>Te, respectively). Abbreviations: s=singlet; d=doublet; t=triplet; sept=septet; m=multiplet; br=broad.

**Single-crystal X-ray structure determination**: Crystals were each mounted on a glass capillary in perfluorinated oil and measured in a cold N<sub>2</sub> flow. The data of **2b**, **3a**, **4a**, **4b**, and **5b** were collected using an Oxford Diffraction Xcalibur S Sapphire at 150 K ( $Mo_{K\alpha}$  radiation,  $\lambda = 0.71073$  Å). The structures were solved by direct methods and refined on  $F^2$  with the SHELX-97<sup>[14]</sup> software package. The positions of the hydrogen atoms were calculated and considered isotropically according to a riding model. *Compound* **2b**: Monoclinic; space group  $P2_1/c$ ; a=21.202(1), b=16.8240(7), c=21.427(1) Å;  $\beta=94.281(3)^\circ$ ; V=7621.9(7) Å<sup>3</sup>; Z=8;  $\rho_{calcd}=1.117$  Mgm<sup>-3</sup>;  $\mu(Mo_{K\alpha})=0.096$  mm<sup>-1</sup>; 38707 collected reflections; 12890 crystallographically independent reflections ( $R_{int}=0.0949$ ); 7044 reflections ( $I > 2\sigma(I)$ );  $\theta_{max}=25.00^\circ$ ;  $R(F_o)=0.0707$  ( $I > 2\sigma(I)$ ),  $wR(F_o^2)=$ 0.1278 (all data); 859 refined parameters.

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*Compound* **3***a*: Triclinic, space group  $P\bar{1}$ ; a=9.8537(4), b=11.9875(4), c=19.6748(7) Å; a=76.60(3),  $\beta=79.852(3)$ ,  $\gamma=86.764(3)^{\circ}$ ; V=2225.63(14) Å<sup>3</sup>; Z=2;  $\rho_{calcd}=1.277$  Mg m<sup>-3</sup>;  $\mu(Mo_{K\alpha})=0.492$  mm<sup>-1</sup>; 16683 collected reflections; 7817 crystallographically independent reflections ( $R_{int}=0.0440$ ); 5115 reflections ( $I>2\sigma(I)$ );  $\theta_{max}=25^{\circ}$ ;  $R(F_{o})=0.0567$  ( $I>2\sigma(I)$ ),  $wR(F_{o}^{2})=0.1248$  (all data); 473 refined parameters.

Compound **4a**: Triclinic; space group  $P\bar{1}$ ; a=10.3516(3), b=11.8219(4), c=16.8403(6) Å; a=104.200(3),  $\beta=99.470(3)$ ,  $\gamma=92.487(2)^{\circ}$ ; V=1963.07(11) Å<sup>3</sup>; Z=2;  $\rho_{calcd}=1.240$  Mgm<sup>-3</sup>;  $\mu(Mo_{K\alpha})=1.153$  mm<sup>-1</sup>; 16482 collected reflections; 6887 crystallographically independent reflections ( $R_{int}=0.0509$ ); 4761 reflections ( $I>2\sigma(I)$ );  $\theta_{max}=25^{\circ}$ ;  $R(F_{o})=0.0483$  ( $I>2\sigma(I)$ ),  $wR(F_{o}^{2})=0.0793$  (all data); 419 refined parameters.

*Compound* **4b**: Monoclinic; space group  $P_{2_i}/n$ ; a=11.2340(4), b=17.2401(5), c=19.8093(7) Å;  $\beta=91.474(3)^\circ$ ; V=3835.3(2) Å<sup>3</sup>; Z=4;  $\rho_{calcd}=1.219$  Mg m<sup>-3</sup>;  $\mu(Mo_{Ka})=1.043$  mm<sup>-1</sup>; 18 505 collected reflections; 6756 crystallographically independent reflections ( $R_{int}=0.0599$ ); 4692 reflections ( $I>2\sigma(I)$ );  $\theta_{max}=25^\circ$ ;  $R(F_o)=0.0466$  ( $I>2\sigma(I)$ ),  $wR(F_o^2)=0.1003$  (all data); 430 refined parameters.

*Compound* **5***b*: Monoclinic; space group  $P2_1/c$ ; a=11.6985(5), b=20.0099(9), c=18.4557(7) Å;  $\beta=103.791(4)^\circ$ ; V=4195.7(3) Å<sup>3</sup>; Z=4;  $\rho_{calcd}=1.326$  Mg m<sup>-3</sup>;  $\mu(Mo_{K\alpha})=0.898$  mm<sup>-1</sup>; 20 485 collected reflections; 7334 crystallographically independent reflections ( $R_{int}=0.0664$ ); 5208 reflections ( $I>2\sigma(I)$ );  $\theta_{max}=25^\circ$ ;  $R(F_o)=0.0645$  ( $I>2\sigma(I)$ ),  $wR(F_o^2)=0.1532$  (all data); 457 refined parameters.

CCDC-746660 (2b), -746661 (3a), -746662 (4a), -746663 (4b), and -746664 (5b) 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.

Synthesis of 2b: A solution of 1b (0.62 g, 0.99 mmol) in toluene (15 mL) was cooled to  $-78\,{}^{\rm o}\!{\rm C}.$  The  $N_2$  atmosphere in the flask was exchanged by N<sub>2</sub>O and the reaction mixture was allowed to warm to room temperature. Subsequently, the concentrated reaction solution (5 mL) was chilled to -20°C for 48 h, thus affording colorless single crystals of 2b qualified for X-ray diffraction analysis (0.56 g, 0.87 mmol, 88%). M.p. 271-273°C (decomp); <sup>1</sup>H NMR (200.13 MHz, [D<sub>6</sub>]benzene, 25 °C):  $\delta = 0.37$  (d,  ${}^{3}J(H,H) = 7.0 \text{ Hz}, 3 \text{ H}; \text{ CH}Me_{2}), 0.53 \text{ (d, } {}^{3}J(H,H) = 7.0 \text{ Hz}, 3 \text{ H}; \text{ CH}Me_{2}),$ 0.93 (d,  ${}^{3}J(H,H) = 7.0$  Hz, 3H; CHM $e_2$ ), 0.95 (d,  ${}^{3}J(H,H) = 7.0$  Hz, 3H; CHMe<sub>2</sub>), 1.13 (d,  ${}^{3}J(H,H) = 7.0$  Hz, 3H; CHMe<sub>2</sub>), 1.29 (d,  ${}^{3}J(H,H) =$ 7.0 Hz, 6H; CHMe<sub>2</sub>), 1.39 (d,  ${}^{3}J(H,H) = 7.0$  Hz, 3H; CHMe<sub>2</sub>), 1.46 (d,  ${}^{3}J(H,H) = 7.0 \text{ Hz}, 3 \text{ H}; \text{ CH}Me_{2}), 1.49 \text{ (s, } 3 \text{ H}; Me), 1.52 \text{ (s, } 3 \text{ H}; Me), 1.63$ (s, 3H, Me), 1.53 (d,  ${}^{3}J(H,H) = 7.0$  Hz, 3H; CHMe<sub>2</sub>), 1.67 (d,  ${}^{3}J(H,H) =$ 7.0 Hz, 3H; CHMe<sub>2</sub>), 1.82 (d,  ${}^{3}J(H,H) = 7.0$  Hz, 3H; CHMe<sub>2</sub>), 2.84 (sept,  ${}^{3}J(H,H) = 7.0 \text{ Hz}, 1 \text{ H}; CHMe_{2}, 3.29 \text{ (sept, } {}^{3}J(H,H) = 7.0 \text{ Hz}, 1 \text{ H};$ CHMe<sub>2</sub>), 3.38 (s, 1H; NCCH<sub>2</sub>), 3.94 (s, 1H; NCCH<sub>2</sub>), 4.15 (sept,  ${}^{3}J(H,H) = 7.0 \text{ Hz}, 1 \text{ H}; CHMe_{2}, 4.44 \text{ (sept, } {}^{3}J(H,H) = 7.0 \text{ Hz}, 1 \text{ H};$ CHMe<sub>2</sub>), 5.51 (s, 1H;  $\gamma$ -CH), 5.63 (sept,  ${}^{3}J(H,H) = 7.0$  Hz, 1H; NCHMe<sub>2</sub>), 6.99–7.48 (brm, 6H; 2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), 8.48 ppm (sept,  ${}^{3}J(H,H) =$ 7.0 Hz, 1H; NCHMe<sub>2</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (100.61 MHz, [D<sub>6</sub>]benzene, 25°C):  $\delta = 10.2, 10.4 (C_2 M e_2); 20.8, 21.3, 21.4, 21.6, 22.5, 23.3, 23.4, 24.4, 24.6,$ 25.0, 25.2, 26.3, 26.9, 27.7, 27.8, 29.2, 29.5 (CHMe2, NCHMe2, NCMe); 49.8, 51.3 (NCHMe<sub>2</sub>); 85.8 (NCCH<sub>2</sub>), 107.7 (γ-C); 123.0, 123.8, 124.9, 125.6, 126.4, 126.7, 127.0, 129.3, 138.0, 140.0, 142.8, 146.2, 146.7, 149.9, 150.2, 152.0 (NCMe, NCCH<sub>2</sub>, 2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, C<sub>2</sub>Me<sub>2</sub>); 155.9 ppm (SiC); <sup>29</sup>Si NMR (79.49 MHz, [D<sub>6</sub>]benzene, 25 °C):  $\delta = -72.9$  ppm (s); IR (KBr):  $\tilde{\nu} = 460$  (m), 485 (m), 509 (w), 522 (w), 544 (w), 566 (w), 578 (w), 738(w), 761 (m), 771 (w), 804 (m), 920 (m), 938 (w), 979 (w), 1045 (w), 1053 (m), 1081 (w), 1110 (w), 1134 (s), 1177 (w), 1193 (m), 1207 (w), 1244 (w), 1254 (w), 1307 (m), 1323 (w), 1352 (s), 1378 (s), 1441 (m), 1466 (m), 1529 (w), 1583 (w), 1626 (w), 1645 (m), 2695 (w), 2865 (m), 2946 (m), 2973 (s),  $3057 \text{ cm}^{-1}$  (w); EIMS: m/z (%): 640.37 (4)  $[M]^+$ , 625.33 (8)  $[M-\text{Me}]^+$ , 597.31 (100)  $[M-iPr]^+$ ; elemental analysis calcd (%) for C<sub>40</sub>H<sub>60</sub>N<sub>4</sub>SiO: C 74.95, H 9.43, N 8.74; found: C 74.33, H 9.04, N 8.61.

Synthesis of 3a: Elemental sulfur (0.032 g, 0.98 mmol) was added to a solution of 1a (0.56 g, 0.98 mmol) in toluene (15 mL) at room temperature. After stirring overnight, the yellow color of the solution vanished and a colorless precipitate was formed. Volatiles were removed in vacuo, the residue washed with diethyl ether (20 mL) and extracted with dichloromethane (10 mL). Concentration of the clear solution to approximately

6 mL and subsequent cooling to -20 °C for 24 h afforded colorless crystals of 3a (0.47 g, 0.77 mmol, 79%). M.p. 245°C (decomp); <sup>1</sup>H NMR (400.13 MHz,  $[D_2]$  dichloromethane, 25 °C):  $\delta = 0.40$  (d,  ${}^{3}J(H,H) = 7$  Hz, 3H; CHMe<sub>2</sub>), 0.51 (d,  ${}^{3}J(H,H) = 7$  Hz, 3H; CHMe<sub>2</sub>), 1.08 (d,  ${}^{3}J(H,H) = 7$ 7 Hz, 3H; CH $Me_2$ ), 1.11 (d,  ${}^{3}J(H,H) = 7$  Hz, 3H; CH $Me_2$ ), 1.16 (d,  ${}^{3}J(H,H) = 7$  Hz, 3H; CHMe<sub>2</sub>), 1.21 (d,  ${}^{3}J(H,H) = 7$  Hz, 3H; CHMe<sub>2</sub>), 1.37  $(d, {}^{3}J(H,H) = 7 Hz, 3H; CHMe_{2}), 1.40 (d, {}^{3}J(H,H) = 7 Hz, 3H; CHMe_{2}),$ 1.50 (s, 3H; NCMe), 2.09 (s, 3H; C2Me2), 2.29 (s, 3H; C2Me2), 2.49 (sept,  $^{3}J(H,H) = 7$  Hz, 1H; CHMe<sub>2</sub>), 2.61 (sept,  $^{3}J(H,H) = 7$  Hz, 1H; CHMe<sub>2</sub>), 2.83 (s, 1 H; NCCH<sub>2</sub>), 3.66 (s, 1 H; NCCH<sub>2</sub>), 3.81 (sept,  ${}^{3}J(H,H) = 7$  Hz, 1H; CHMe<sub>2</sub>), 3.84 (sept,  ${}^{3}J(H,H) = 7$  Hz, 1H; CHMe<sub>2</sub>), 4.08 (s, 3H; NMe), 4.23 (s, 3H; NMe), 5.37 (s, 1H; γ-CH), 6.97-7.25 ppm (m, 6H; 2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (100.61 MHz, [D<sub>2</sub>]dichloromethane, 25°C):  $\delta = 9.1, 9.5 \text{ ppm} (C_2 M e_2); 23.1, 23.6, 23.7, 24.2, 24.5, 24.7, 25.6, 25.8, 26.3,$ 27.9, 28.3, 29.2, 29.3 (NCMe, CHMe<sub>2</sub>); 34.3, 36.2 (NMe); 86.6 (NCCH<sub>2</sub>); 105.1 (y- C); 123.1, 123.5, 124.7, 125.2, 126.7, 126.9, 128.8, 1389.0, 140.1, 143.1, 146.9, 147.6, 150.2, 150.3, 150.6 (NCMe, NCCH<sub>2</sub>, 2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>,  $C_2$ Me<sub>2</sub>); 153.6 ppm (SiC); <sup>29</sup>Si NMR (79.49 MHz, [D<sub>2</sub>]dichloromethane, 25°C):  $\delta = -34.9$  ppm; IR (KBr):  $\tilde{\nu} = 433$  (w), 452 (m), 467 (m), 523 (w), 547 (w), 562 (m), 599 (w), 649 (w), 682 (m), 734 (w), 748 (w), 759 (w), 802 (m), 852 (w), 917 (m), 936 (w), 975 (w), 1045 (m), 1056 (s), 1103 (m), 1175 (m), 1192 (m), 1243 (m), 1254 (m), 1307 (m), 1316 (m), 1352 (s), 1379 (s), 1441 (m), 1465 (m), 1528 (w), 1583 (w), 1637 (s), 2864 (m), 2926 (m), 2948 (m), 2966 (s), 3011 (m), 3054 (m), 3111 cm<sup>-1</sup> (w); ESIMS (ion spray voltage 5 kV, flow rate 5  $\mu$ Lmin<sup>-1</sup>, in dichloromethane): m/z: calcd for C<sub>36</sub>H<sub>53</sub>N<sub>4</sub>SiS [M+H]<sup>+</sup>: 601.38, found: 601.37; elemental analysis calcd (%) for C<sub>36</sub>H<sub>52</sub>N<sub>4</sub>SiS: C 71.95, H 8.72, N 9.32; found: C 71.42, H 8.74, N 9.28.

Synthesis of 3b: Elemental sulfur (0.037 g, 1.17 mmol) was added to a solution of 1b (0.73 g, 1.17 mmol) in toluene (20 mL) at room temperature. After stirring overnight, the yellow color of the solution vanished and a colorless precipitate was formed. Volatiles were removed in vacuo, the residue washed with diethyl ether (25 mL) and extracted with dichloromethane (15 mL). Concentration of the clear solution to approximately 8 mL and subsequent cooling to -20 °C for 24 h afforded colorless crystals of **3b** (0.52 g, 0.83 mmol, 71%). M.p. 177°C (decomp); <sup>1</sup>H NMR (400.13 MHz, [D<sub>2</sub>]dichloromethane, 25 °C):  $\delta = 0.52$  (d,  ${}^{3}J(H,H) = 7$  Hz, 3H; CHMe<sub>2</sub>), 0.85 (d,  ${}^{3}J(H,H) = 7$  Hz, 3H; CHMe<sub>2</sub>), 0.94 (d,  ${}^{3}J(H,H) = 7$ 7 Hz, 3H; CHM $e_2$ ), 1.04 (d,  ${}^{3}J(H,H) = 7$  Hz, 3H; CHM $e_2$ ), 1.09 (d,  ${}^{3}J(H,H) = 7 \text{ Hz}, 3 \text{ H}; \text{ CH}Me_{2}), 1.12 \text{ (d, } {}^{3}J(H,H) = 7 \text{ Hz}, 3 \text{ H}; \text{ CH}Me_{2}), 1.21$ (d,  ${}^{3}J(H,H) = 7$  Hz, 3H; CHMe<sub>2</sub>), 1.23 (d,  ${}^{3}J(H,H) = 7$  Hz, 3H; CHMe<sub>2</sub>), 1.36 (d,  ${}^{3}J(H,H) = 7$  Hz, 3H; CHMe<sub>2</sub>), 1.37 (d,  ${}^{3}J(H,H) = 7$  Hz, 3H;  $CHMe_2$ ), 1.53 (s, 3H; NCMe), 1.66 (d,  ${}^{3}J(H,H) = 7$  Hz, 3H;  $CHMe_2$ ), 1.68 (d,  ${}^{3}J(H,H) = 7 \text{ Hz}$ , 3H; CHMe<sub>2</sub>); 2.25 (s, 3H; C<sub>2</sub>Me<sub>2</sub>), 2.40 (s, 3H;  $C_2Me_2$ ), 2.57 (sept,  ${}^{3}J(H,H) = 7$  Hz, 1H; CHMe<sub>2</sub>), 2.92 (s, 1H; NCCH<sub>2</sub>), 3.02 (sept,  ${}^{3}J(H,H) = 7 \text{ Hz}$ , 1H; CHMe<sub>2</sub>), 3.72 (s, 1H; NCCH<sub>2</sub>), 3.74 (sept,  ${}^{3}J(H,H) = 7 \text{ Hz}$ , 1H; CHMe<sub>2</sub>), 3.90 (sept,  ${}^{3}J(H,H) = 7 \text{ Hz}$ , 1H; CHMe<sub>2</sub>), 5.45 (s, 1H;  $\gamma$ -CH), 5.81 (sept,  ${}^{3}J(H,H) = 7$  Hz, 1H; NCHMe<sub>2</sub>), 7.01–7.22 (m, 6H; 2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), 8.18 ppm (sept,  ${}^{3}J(H,H) = 7$  Hz, 1H; NCHMe<sub>2</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (100.61 MHz, [D<sub>2</sub>]dichloromethane, 25 °C):  $\delta =$ 11.3, 11.6 (C<sub>2</sub>Me<sub>2</sub>); 21.3, 21.7, 22.6, 23.3, 23.6, 23.8, 24.3, 24.6, 24.8, 24.9, 26.0, 26.3, 27.1, 27.7, 27.8, 29.2, 29.3 (NCHMe2, NCMe, CHMe2), 49.5, 52.2 (NCHMe<sub>2</sub>); 87.4 (NCCH<sub>2</sub>); 107.1 (γ-C); 123.2, 123.9, 124.6, 125.1, 126.5, 126.9, 127.4, 130.1, 138.6, 141.1, 142.8, 146.7, 147.2, 149.2, 150.2, 150.9 (NCMe, NCCH<sub>2</sub>, 2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, C<sub>2</sub>Me<sub>2</sub>); 153.7 ppm (SiC); <sup>29</sup>Si NMR (79.49 MHz, [D<sub>2</sub>]dichloromethane, 25 °C):  $\delta = -33.5$  ppm; IR (KBr):  $\tilde{\nu} =$ 430 (w), 452 (m), 470 (m), 523 (w), 547 (w), 565 (m), 599 (w), 650 (w), 679 (s), 735 (w), 761 (w), 772 (w), 801 (m), 916 (m), 936 (w), 978 (w), 1044 (m), 1057 (s), 1105 (m), 1172 (m), 1190 (m), 1203 w), 1243 (m), 1256 (m), 1306 (m), 1320 (m), 1353 (s), 1379 (s), 1441 (m), 1466 (m), 1538 (w), 1583 (w), 1625 (m), 1643 (m), 2864 (m), 2943 (m), 2968 (s), 3057 cm  $^{-1}$  (w); ESIMS (ion spray voltage 5 kV, flow rate 5  $\mu L\,min^{-1},$  in dichloromethane): m/z: calcd for C<sub>40</sub>H<sub>61</sub>N<sub>4</sub>SiS [M+H]<sup>+</sup>: 657.44, found: 657.43; elemental analysis calcd (%) for  $C_{40}H_{60}N_4SiS$ : C 73.12, H 9.20, N 8.53; found: C 72.88, H 9.17, N 8.29.

Synthesis of 4a: Elemental selenium (0.052 g, 0.67 mmol) was added to a solution of 1a (0.38 g, 0.67 mmol) in toluene (10 mL) at room temperature. After stirring for 3 h, the yellow color of the solution vanished and a colorless precipitate was formed. Volatiles were removed in vacuo, the

residue washed with diethyl ether (10 mL) and extracted with dichloromethane (10 mL). Concentration of the clear solution to approximately 4 mL and subsequent cooling to -20 °C for 24 h afforded colorless crystals of 4a (0.33 g, 0.51 mmol, 76%). M.p. 256°C (decomp); <sup>1</sup>H NMR (400.13 MHz, [D<sub>2</sub>]dichloromethane, 25 °C):  $\delta = 0.44$  (d,  ${}^{3}J(H,H) = 7$  Hz, 3H; CHMe<sub>2</sub>), 0.56 (d,  ${}^{3}J(H,H) = 7$  Hz, 3H; CHMe<sub>2</sub>), 1.08 (d,  ${}^{3}J(H,H) =$ 7 Hz, 3H; CHM $e_2$ ), 1.09 (d,  ${}^{3}J(H,H) = 7$  Hz, 3H; CHM $e_2$ ), 1.17 (d,  ${}^{3}J(H,H) = 7$  Hz, 3H; CHMe<sub>2</sub>), 1.22 (d,  ${}^{3}J(H,H) = 7$  Hz, 3H; CHMe<sub>2</sub>); 1.39  $(d, {}^{3}J(H,H) = 7 Hz, 3H; CHMe_{2}), 1.43 (d, {}^{3}J(H,H) = 7 Hz, 3H; CHMe_{2}),$ 1.51 (s, 3H; NCMe), 2.11 (s, 3H; C<sub>2</sub>Me<sub>2</sub>), 2.30 (s, 3H; C<sub>2</sub>Me<sub>2</sub>), 2.47 (sept,  ${}^{3}J(H,H) = 7$  Hz, 1H; CHMe<sub>2</sub>), 2.59 (sept,  ${}^{3}J(H,H) = 7$  Hz, 1H; CHMe<sub>2</sub>), 2.87 (s, 1H; NCCH<sub>2</sub>), 3.70 (s, 1H; NCCH<sub>2</sub>), 3.82 (sept,  ${}^{3}J(H,H) = 7$  Hz, 1H; CHMe<sub>2</sub>), 3.83 (sept,  ${}^{3}J(H,H) = 7$  Hz, 1H; CHMe<sub>2</sub>), 4.10 (s, 3H; NMe), 4.25 (s, 3H; NMe), 5.41 (s, 1H; γ-CH), 6.98-7.26 ppm (m, 6H; 2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>);  ${}^{13}C{}^{1}H$  NMR (100.61 MHz, [D<sub>2</sub>]dichloromethane, 25 °C):  $\delta = 9.1, 9.6 (C_2 M e_2); 23.1, 23.7, 24.0, 24.2, 24.5, 24.7, 25.6, 25.7, 26.4, 28.0,$ 28.4, 29.3, 29.4 (NCMe, CHMe2); 34.4, 37.4 (NMe); 87.5 (NCCH2); 105.8 (y- C); 123.0, 123.5, 124.7, 125.2, 126.6, 126.9, 127.0, 129.0, 139.3, 140.6, 143.0, 146.8, 147.7, 149.8, 150.1, 150.4 (NCMe, NCCH<sub>2</sub>, 2,6-iPr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>,  $C_2$ Me<sub>2</sub>); 153.1 ppm (SiC); <sup>29</sup>Si NMR (79.49 MHz, [D<sub>2</sub>]dichloromethane, 25°C):  $\delta = -33.3$  ppm (s); <sup>77</sup>Se NMR (76.31 MHz, [D<sub>2</sub>]dichloromethane, 25°C):  $\delta = -374.4$  ppm (s); IR (KBr):  $\tilde{\nu} = 419$  (w), 454 (m), 524 (w), 535 (m), 547 (w), 560 (w), 570 (w), 598 (w), 614 (s), 654 (w), 734 (w), 746 (w), 758 (m), 769 (w), 800 (s), 853 (m), 918 (m), 936 (m), 975 (m), 1052 (s), 1102 (m), 1174 (m), 1190 (m), 1242 (m), 1253 (m), 1307 (m), 1317 (m), 1330 (w), 1352 (s), 1378 (s), 1440 (m), 1465 (m), 1530 (w), 1583 (w), 1637 (s), 2867 (m), 2926 (m), 2946 (m), 2965 (s), 3011 (m), 3053 (m), 3111 cm<sup>-1</sup> (w); ESIMS (ion spray voltage 5 kV, flow rate 5  $\mu$ Lmin<sup>-1</sup>, in dichloromethane): m/z: calcd for C<sub>36</sub>H<sub>53</sub>N<sub>4</sub>SiSe [M+H]<sup>+</sup>: 649.32; found: 649.32; elemental analysis calcd (%) for  $C_{36}H_{52}N_4SiSe$ : C 66.74, H 8.09, N 8.65; found: C 66.51, H 8.00, N 8.57.

Synthesis of 4b: Elemental selenium (0.069 g, 0.90 mmol) was added to a solution of 1b (0.56 g, 0.90 mmol) in toluene (15 mL) at room temperature. After stirring for 3 h, the yellow color of the solution vanished and a colorless precipitate was formed. Volatiles were removed in vacuo, the residue washed with diethyl ether (15 mL) and extracted with dichloromethane (15 mL). Concentration of the clear solution to approximately 7 mL and subsequent cooling to -20 °C for 24 h afforded colorless crystals of **4b** (0.43 g, 0.62 mmol, 69%). M.p. 224°C (decomp); <sup>1</sup>H NMR (400.13 MHz, [D<sub>2</sub>]dichloromethane, 25 °C):  $\delta = 0.55$  (d,  ${}^{3}J(H,H) = 7$  Hz, 3H; CHMe<sub>2</sub>), 0.90 (d,  ${}^{3}J(H,H) = 7$  Hz, 3H; CHMe<sub>2</sub>), 0.98 (d,  ${}^{3}J(H,H) =$ 7 Hz, 3H; CHMe<sub>2</sub>), 1.04 (d,  ${}^{3}J(H,H) = 7$  Hz, 3H; CHMe<sub>2</sub>), 1.09 (d,  ${}^{3}J(H,H) = 7$  Hz, 3H; CHMe<sub>2</sub>), 1.14 (d,  ${}^{3}J(H,H) = 7$  Hz, 3H; CHMe<sub>2</sub>), 1.21 (d,  ${}^{3}J(H,H) = 7$  Hz, 3H; CHMe<sub>2</sub>), 1.23 (d,  ${}^{3}J(H,H) = 7$  Hz, 3H; CHMe<sub>2</sub>), 1.38 (d,  ${}^{3}J(H,H) = 7$  Hz, 3H; CHMe<sub>2</sub>), 1.40 (d,  ${}^{3}J(H,H) = 7$  Hz, 3H;  $CHMe_2$ ), 1.54 (s, 3H; NCMe), 1.66 (d,  ${}^{3}J(H,H) = 7$  Hz, 3H;  $CHMe_2$ ), 1.68 (d,  ${}^{3}J(H,H) = 7 Hz$ , 3H; CHMe<sub>2</sub>); 2.26 (s, 3H; C<sub>2</sub>Me<sub>2</sub>), 2.41 (s, 3H;  $C_2Me_2$ ), 2.53 (sept,  ${}^{3}J(H,H) = 7$  Hz, 1H; CHMe<sub>2</sub>), 2.93 (s, 1H; NCCH<sub>2</sub>), 2.99 (sept,  ${}^{3}J(H,H) = 7$  Hz, 1H; CHMe<sub>2</sub>), 3.74 (sept,  ${}^{3}J(H,H) = 7$  Hz, 1H;  $CHMe_2$ ), 3.76 (s, 1H; NCCH<sub>2</sub>), 3.90 (sept,  ${}^{3}J(H,H) = 7$  Hz, 1H; CHMe<sub>2</sub>), 5.47 (s, 1H;  $\gamma$ -CH), 5.84 (sept,  ${}^{3}J(H,H) = 7$  Hz, 1H; NCHMe<sub>2</sub>), 7.01–7.22 (m, 6H; 2,6-*i*Pr<sub>2</sub>C<sub>6</sub> $H_3$ ), 8.25 ppm (sept, <sup>3</sup>J(H,H)=7 Hz, 1H; NCHMe<sub>2</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (100.61 MHz, [D<sub>2</sub>]dichloromethane, 25 °C):  $\delta = 11.3$ , 11.7 (C2Me2); 21.4, 21.8, 22.6, 23.4, 23.6, 24.2, 24.3, 24.4, 24.8, 24.9, 26.0, 26.1, 27.2, 27.7, 29.3, 29.4 (NCHMe2, NCMe, CHMe2); 49.8, 52.3 (NCHMe2); 88.3 (NCCH<sub>2</sub>); 107.4 (γ-C); 123.2, 123.9, 124.6, 125.2, 126.6, 127.0, 127.3, 130.4, 139.1, 141.6, 142.6, 146.7, 147.3, 148.8, 150.2, 150.7 (NCMe, NCCH<sub>2</sub>, 2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, C<sub>2</sub>Me<sub>2</sub>); 152.6 ppm (SiC); <sup>29</sup>Si NMR (79.49 MHz, [D<sub>2</sub>]dichloromethane, 25 °C):  $\delta = -32.9$  ppm; <sup>77</sup>Se NMR (76.31 MHz, [D<sub>2</sub>]dichloromethane, 25 °C):  $\delta = -470.2$  ppm (s); IR (KBr):  $\tilde{\nu} = 418$  (w), 449 (m), 468 (m), 529 (w), 547 (w), 561 (w), 606 (m), 660 (w), 759 (m), 772 (w), 801 (m), 815 (w), 914 (m), 934 (w), 975 (m), 1044 (m), 1054 (s), 1076 (w), 1103 (m), 1109 (m), 1172 (m), 1188 (m), 1201 (w), 1242 (w), 1254 (w), 1306 (m), 1319 (m), 1351 (s), 1378 (s), 1439 (m), 1465 (m), 1541 (m), 1583 (w), 1623 (m), 1644 (m), 2864 (m), 2927 (m), 2944 (m), 2967 (s), 3054 cm<sup>-1</sup> (m); ESIMS (ion spray voltage 5 kV, flow rate 5  $\mu$ Lmin<sup>-1</sup>, in dichloromethane): m/z: calcd for  $C_{40}H_{60}N_4SiSe [M+H]^+$ : 705.38; found: 705.38; elemental analysis calcd (%) for C40H60N4SiSe: C 68.25, H 8.59, N 7.96; found: C 67.96, H 8.68, N 7.70.

# **FULL PAPER**

Synthesis of 5a: Elemental tellurium (0.18 g, 1.41 mmol) was added to a solution of 1a (0.80 g, 1.41 mmol) in toluene (30 mL) at room temperature. After stirring for 3 h, a yellow precipitate was formed. Volatiles were removed in vacuo, the residue washed with diethyl ether (30 mL) and extracted with dichloromethane (20 mL). Concentration of the clear solution to approximately 10 mL and subsequent cooling to -20 °C for 24 h afforded yellow crystals of 5a (0.59 g, 1.04 mmol, 74%). M.p. 193°C (decomp); <sup>1</sup>H NMR (400.13 MHz,  $[D_2]$  dichloromethane, 25 °C):  $\delta = 0.49$  $(d, {}^{3}J(H,H) = 7 Hz, 3H; CHMe_{2}), 0.66 (d, {}^{3}J(H,H) = 7 Hz, 3H; CHMe_{2}),$ 1.06 (d,  ${}^{3}J(H,H) = 7$  Hz, 3H; CHMe<sub>2</sub>), 1.08 (d,  ${}^{3}J(H,H) = 7$  Hz, 3H; CHMe<sub>2</sub>), 1.17 (d,  ${}^{3}J(H,H) = 7$  Hz, 3H; CHMe<sub>2</sub>), 1.22 (d,  ${}^{3}J(H,H) = 7$  Hz, 3H; CHMe<sub>2</sub>), 1.41 (d,  ${}^{3}J(H,H) = 7$  Hz, 3H; CHMe<sub>2</sub>), 1.46 (d,  ${}^{3}J(H,H) = 7$ 7 Hz, 3H; CHMe2), 1.54 (s, 3H; NCMe), 2.10 (s, 3H; C2Me2), 2.31 (s, 3H;  $C_2Me_2$ ), 2.44 (sept,  ${}^{3}J(H,H) = 7$  Hz, 1H; CHMe<sub>2</sub>), 2.58 (sept,  ${}^{3}J(H,H) = 7 \text{ Hz}, 1 \text{ H}; CHMe_{2}), 2.94 \text{ (s, 1H; NCC}H_{2}), 3.69 \text{ (s, 1H; }$ NCCH<sub>2</sub>), 3.76 (sept,  ${}^{3}J(H,H) = 7$  Hz, 1H; CHMe<sub>2</sub>), 3.80 (sept,  ${}^{3}J(H,H) =$ 7 Hz, 1H; CHMe<sub>2</sub>), 4.12 (s, 3H; NMe), 4.21 (s, 3H; NMe), 5.44 (s, 1H; γ-CH), 6.98–7.27 ppm (m, 6H; 2,6-iPr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (100.61 MHz,  $[D_2]$ dichloromethane, 25°C):  $\delta = 9.0, 9.7 (C_2 M e_2)$ ; 23.0, 23.7, 24.3, 24.4, 24.7, 24.9, 25.5, 25.6, 26.6, 28.0, 28.6, 29.3, 29.4 (NCMe, CHMe2); 34.4, 40.4 (NMe); 89.1 (NCCH<sub>2</sub>); 107.1 (γ-C); 123.0, 123.6, 124.7, 125.3, 126.3,  $127.0,\ 127.2,\ 129.2,\ 139.8,\ 141.9,\ 142.7,\ 147.0,\ 147.8,\ 149.0,\ 149.7,\ 150.1$ (NCMe, NCCH<sub>2</sub>, 2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>,  $C_2$ Me<sub>2</sub>); 152.6 ppm (SiC); <sup>29</sup>Si NMR (79.49 MHz, [D<sub>2</sub>]dichloromethane, 25 °C):  $\delta = -46.0$  ppm (s); <sup>125</sup>Te NMR (126.24 MHz,  $[D_2]$ dichloromethane, 25°C):  $\delta = -1010.4$  ppm; IR (KBr):  $\tilde{\nu} = 409$  (w), 446 (m), 513 (m), 559 (w), 569 (w), 595 (m), 651 (w), 733 (w), 744 (w), 757 (m), 772 (w), 800 (m), 851 (w), 916 (m), 935 (w), 974 (w), 1047 (m), 1101 (w), 1108 (w), 1173 (m), 1188 (m), 1240 (m), 1253 (m), 1306 (m), 1316 (m), 1350 (s), 1378 (s), 1394 (w), 1438 (m), 1464 (m), 1540 (w), 1583 (w), 1637 (m), 2864 (m), 2925 (m), 2945 (m), 2962 (s), 3012 (w), 3054 cm<sup>-1</sup> (w); ESIMS (ion spray voltage 5 kV, flow rate 5  $\mu$ Lmin<sup>-1</sup>, in dichloremethane): m/z: calcd for C<sub>36</sub>H<sub>53</sub>N<sub>4</sub>SiTe [M+H]<sup>+</sup>: 699.31; found: 699.31; elemental analysis calcd (%) for C<sub>36</sub>H<sub>52</sub>N<sub>4</sub>SiTe: C 62.08, H 7.52, N 8.04; found: C 62.40, H 7.67, N 7.79.

Synthesis of 5b: Elemental tellurium (0.098 g, 0.78 mmol) was added to a solution of 1b (0.49 g, 0.78 mmol) in toluene (30 mL) at room temperature. After stirring for 3 h, a yellow precipitate was formed. Volatiles were removed in vacuo, the residue washed with diethyl ether (30 mL) and extracted with dichloromethane (20 mL). Concentration of the clear solution to approximately 10 mL and subsequent cooling to -20 °C for 24 h afforded yellow crystals of 5b (0.33 g, 0.53 mmol, 68 %). M.p. 198°C (decomp); <sup>1</sup>H NMR (400.13 MHz, [D<sub>2</sub>]dichloromethane, 25 °C):  $\delta = 0.62$ (d,  ${}^{3}J(H,H) = 7$  Hz, 3H; CHMe<sub>2</sub>), 0.99 (d,  ${}^{3}J(H,H) = 7$  Hz, 3H; CHMe<sub>2</sub>), 1.02 (d,  ${}^{3}J(H,H) = 7 \text{ Hz}$ , 3H; CHMe<sub>2</sub>), 1.05 (d,  ${}^{3}J(H,H) = 7 \text{ Hz}$ , 3H;  $CHMe_2$ ), 1.10 (d,  ${}^{3}J(H,H) = 7$  Hz, 3H;  $CHMe_2$ ), 1.18 (d,  ${}^{3}J(H,H) = 7$  Hz, 3H; CHMe<sub>2</sub>), 1.22 (d,  ${}^{3}J(H,H) = 7$  Hz, 3H; CHMe<sub>2</sub>), 1.23 (d,  ${}^{3}J(H,H) = 7$ 7 Hz, 3H; CHM $e_2$ ), 1.45 (d,  ${}^{3}J(H,H) = 7$  Hz, 3H; CHM $e_2$ ), 1.48 (d,  ${}^{3}J(H,H) = 7$  Hz, 3H; CHMe<sub>2</sub>), 1.58 (s, 3H; NCMe), 1.65 (d,  ${}^{3}J(H,H) =$ 7 Hz, 3H; CHM $e_2$ ), 1.69 (d,  ${}^{3}J(H,H) = 7$  Hz, 3H; CHM $e_2$ ), 2.28 (s, 3H;  $C_2Me_2$ ), 2.43 (s, 3H;  $C_2Me_2$ ), 2.45 (sept,  ${}^{3}J(H,H) = 7$  Hz, 1H; CHMe<sub>2</sub>), 2.98 (sept,  ${}^{3}J(H,H) = 7 \text{ Hz}$ , 1H; CHMe<sub>2</sub>), 2.99 (s, 1H; NCCH<sub>2</sub>), 3.72 (sept,  ${}^{3}J(H,H) = 7$  Hz, 1H; CHMe<sub>2</sub>), 3.84 (s, 1H; NCCH<sub>2</sub>), 3.87 (sept,  ${}^{3}J(H,H) = 7 \text{ Hz}, 1 \text{ H}; CHMe_{2}), 5.50 \text{ (s, } 1 \text{ H}; \gamma \text{-}CH), 5.91 \text{ (sept, } {}^{3}J(H,H) =$ 7 Hz, 1 H; NCHMe<sub>2</sub>), 7.04–7.26 (m, 6 H; 2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), 8.26 ppm (sept,  $^{13}\mathrm{C}\{^{1}\mathrm{H}\}\ \mathrm{NMR}$  $^{3}J(H,H) = 7$  Hz, 1H; NCHMe<sub>2</sub>); (100.61 MHz, [D<sub>2</sub>]dichloromethane, 25°C): δ=11.2, 11.7 (C<sub>2</sub>Me<sub>2</sub>); 21.4-30.1 (NCHMe<sub>2</sub>, NCMe, CHMe<sub>2</sub>); 50.0, 52.3 (NCHMe<sub>2</sub>); 90.1 (NCCH<sub>2</sub>); 108.1 (γ-C); 122.9–150.0 (NCMe, NCCH<sub>2</sub>, 2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, C<sub>2</sub>Me<sub>2</sub>); 150.2 ppm (SiC); <sup>29</sup>Si NMR (79.49 MHz, [D<sub>2</sub>]dichloromethane, 25 °C):  $\delta = -49.6$  ppm; <sup>125</sup>Te NMR (126.24 MHz, [D<sub>2</sub>]dichloromethane, 25 °C):  $\delta = -982.5$  ppm; IR (KBr):  $\tilde{v} = 445$  (m), 466 (w), 510 (w), 545 (w), 559 (w), 588 (m), 657 (w), 732 (w), 758 (m), 799 (m), 912 (m), 934 (w), 973 (w), 1040 (m), 1073 (w), 1107 (m), 1170 (m), 1185 (m), 1221 (w), 1241 (w), 1254 (w), 1306 (m), 1318 (m), 1351 (s), 1377 (s), 1437 (m), 1464 (m), 1550 (w), 1584 (w), 1635 (m), 2864 (m), 2928 (m), 2940 (m), 2964 (s), 3055 (w), 3110  $\rm cm^{-1}$ (w); ESIMS (ion spray voltage 5 kV, flow rate 5  $\mu$ Lmin<sup>-1</sup>, in dichloromethane): m/z: calcd for C<sub>40</sub>H<sub>60</sub>N<sub>4</sub>SiTe [M+H]<sup>+</sup>: 755.37; found: 755.37; elemental analysis calcd (%) for C40H60N4SiTe: C 63.84, H 8.04, N 7.44; found: C 63.29, H 8.15, N 7.25.

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