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Formation of Unexpected Selenium-Rich Compounds by Selenation of the Very Bulky $(PhMe_2Si)_3CLi$: *s*-Tetraselenane, a Novel Polyseleno Heterocycle

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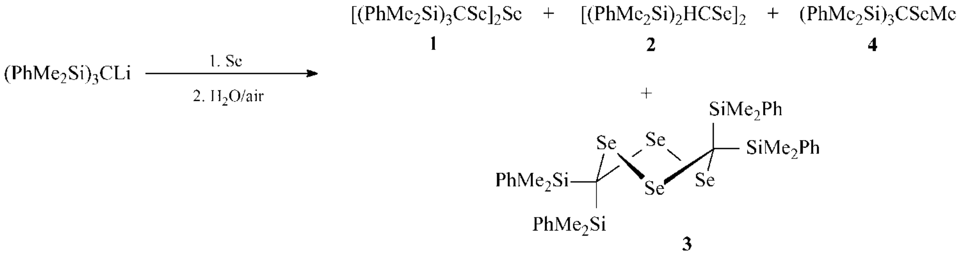
The reaction of the highly crowded trisilylmethyllithium compound $(PhMe_2Si)_3CLi$ with elemental selenium resulted in a variety of products, among them the triselane $[(PhMe_2Si)_3CSe]_2Se$, the unexpected diselane $[(PhMe_2Si)_2HCSe]_2$ and the novel heterocycle $[(PhMe_2Si)_2CSeSe]_2$. The constitution of the latter could be elucidated from the NMR spectroscopic data and was confirmed by the crystal structure which displays the C_2Se_4 cycle in the twist form. Calculations were performed for the chair and twist conformers of the heterocycles $[(H_3Si)_2CXX]_2$ (X = O, S, Se, Te, Po).

Introduction

The stabilization of low-coordinated main-group compounds is possible with extremely bulky substituents and has been reviewed recently in detail.[1] Chalcogen compounds containing the tris(trimethylsilyl)methyl group, $(Me_3Si)_3C$, have been prepared (sulfur,[2] selenium,[3–5] and tellurium[3,6]). The introduction of such sterically demanding substituents at the heavier chalcogen elements has been a part of our research for the recent time, because they have been useful to stabilize or detect rather reactive species or intermediates in tellurium(II),[7] and selenium(II) azide chemistry.[8] The tris[dimethyl(phenyl)silyl]methyl group, $(PhMe_2Si)_3C$, is expected to have some increased shielding properties compared to the permethylated substituent. The tellurolate $(PhMe_2Si)_3CTeLi$ and the corresponding ditellane, tellurenyl iodide and azide were isolated and characterized by us very recently. In this communication we would like to present our study of the reactivity of $(PhMe_2Si)_3CLi$ towards selenium.

Results and Discussion

The alkyllithium reagent $(PhMe_2Si)_3CLi$, generated as described,[7] was treated with elemental selenium to give the selenolate $(PhMe_2Si)_3CSeLi$ in a straightforward manner according to ^{77}Se NMR spectroscopy (in THF: δ = –63.3 ppm). The product mixture, which was obtained after hydrolysis and oxidation (exposure to air) of the selenolate, was surprisingly complex and, according to ^{77}Se NMR spectroscopy, consisted of several selenium-containing species. From this mixture the four main components could be separated, isolated and identified [Equation (1)].



(1)

No evidence was found for the formation of the diselane $(PhMe_2Si)_3CSeSeC(SiMe_2Ph)_3$, which is usually formed as the main product by oxidation of selenolates RSeLi or selenols RSeH; the corresponding ditellane is also the main product in the oxidation of $(PhMe_2Si)_3CTeLi$.[7] Here, the triselane $(PhMe_2Si)_3CSeSeSeC(SiMe_2Ph)_3$ (**1**) is the main

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product, which can be explained by the bulkiness of the substituent, to stabilize selanes with increased chain lengths in the case of smaller chalcogens. The triselane **1** was separated from the mixture because of its lower solubility in diethyl ether. The remaining mixture was subjected to column chromatography and resulted finally in the isolation and identification of two further selanes, the diselane $(PhMe_2Si)_2HCSeSeCH(SiMe_2Ph)_2$ (**2**) and the heterocycle $[(PhMe_2Si)_2CSeSe]_2$ (**3**). The formation and existence of **2** demonstrates that three dimethyl(phenyl)silyl groups attached to the carbon atom are too bulky for a corresponding diselane, but two dimethyl(phenyl)silyl groups, in the bis[dimethyl(phenyl)silyl]methyl group which is slightly less bulky, form a stable diselane **2**. The formation of the novel heterocycle **3**, a tetrasilyl-substituted *s*-tetraselenane, cannot be explained with certainty. Probably due to similar reasons as observed with **2**, one silyl group was eliminated and maybe a radical $(PhMe_2Si)_2CSeSe$, for which we have no evidence, dimerized to give the stable six-membered C_2Se_4 heterocycle **3**. The fourth main component of this reaction

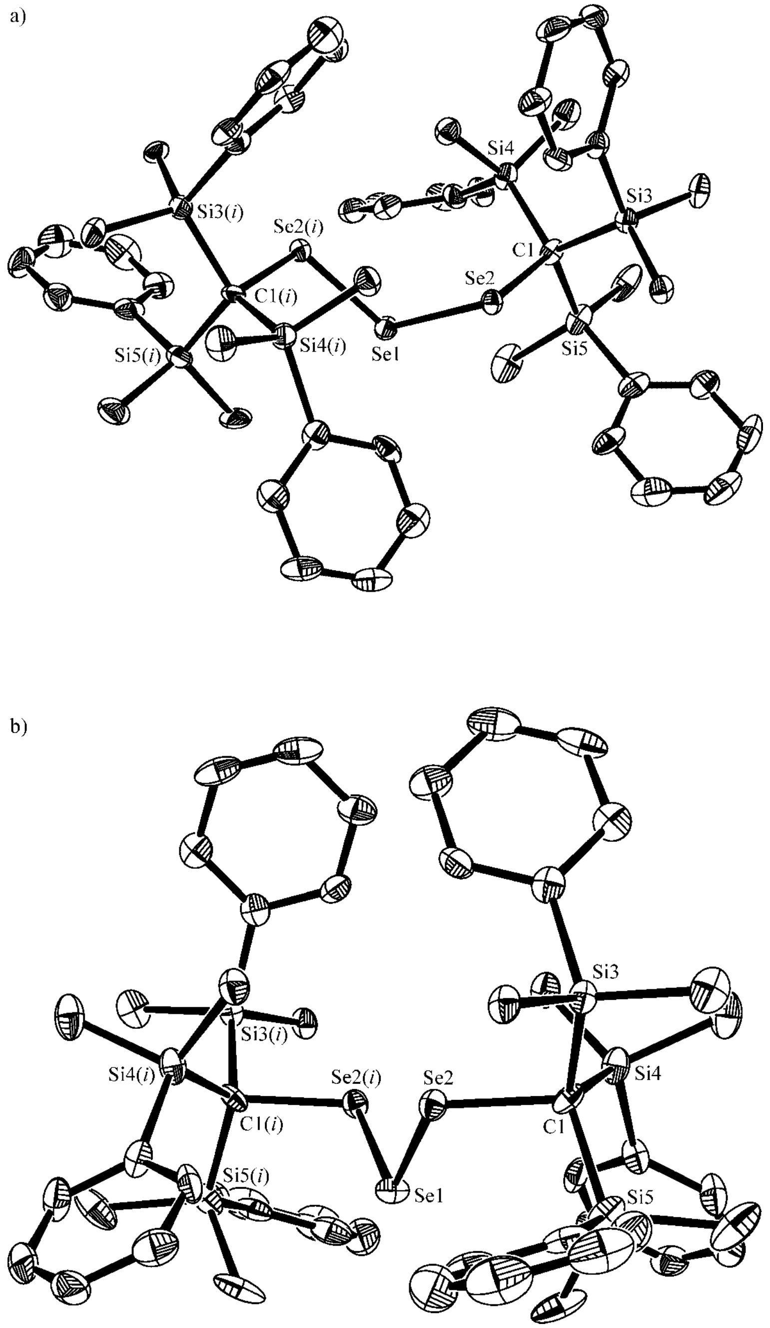

Figure 1. Different views (a) and (b) of the molecular structure of **1** with thermal ellipsoids of 50% probability. Selected bond lengths [Å] and angles [°]: Se1–Se2 2.340(1), Se2–C1 2.013(9); Se2–Se1–Se2(*i*) 109.90(7), C1–Se2–Se1 110.6(2), Si3–C1–Se2 98.7(4), Si4–C1–Se2 112.2(4), Si5–C1–Se2 104.5(4), Se2(*i*)–Se1–Se2–C1 –101.6(3); $i = 11/2-x,\ 11/2-y,\ z$.

was identified as the mixed monoselane $(PhMe_2Si)_3CSeMe$ (**4**). The formation of **4** can be explained by the always incomplete lithiation of $(PhMe_2Si)_2CH$ with methyllithium. Upon addition of selenium, immediate formation of MeSeLi occurs which can combine with tris[dimethyl(phenyl)silyl]methyl groups to give **4**. The monoselane **4** is already detected by ^{77}Se NMR in the THF solution of $(PhMe_2Si)_3CSeLi$ in amounts of ca 3–5% as the only other selenium-containing product.

The triselane **1** displays two resonances in the ^{77}Se NMR spectrum at $\delta = 666$ ppm for the central selenium atom, and 552 ppm for the two terminal selenium atoms. The coupling constant $^1J(^{77}\text{Se-}^{77}\text{Se}) = 20.7$ Hz is in the typical range found for other dialkyltriselanes.[9] The diselane **2**, as well as the symmetric *s*-tetraselenane **3**, exhibit single resonances at $\delta = 391$ ppm and $\delta = 456$ ppm, respectively. The resonance of the monoselane **4** is found at relatively high field at $\delta = 135$ ppm, displaying a quartet due to coupling with methyl hydrogen atoms.

The crystal structure of the triselane **1** is shown in Figure 1 and gives an impression of the rather extreme bulkiness of the tris[dimethyl(phenyl)silyl]methyl substituent which allows the stabilization of this triselane (Figure 1a). In general, triselanes show a high propensity to eliminate red selenium at higher temperatures or already in solution at lower temperatures to form the corresponding diselanes.[10,11] The characteristic features of the triselane chain consist of the typical V-shaped unit (Figure 1b) with an angle of 109.90(7)° and an Se–Se bond length of 2.340(1) Å, forming a torsion angle Se2(*i*)–Se1–Se2–C1 of –101.6(3)°, parameters which are comparable to the structures of other undisturbed dialkyl triselanes.[10,12]

The structure of the novel *s*-tetraselenane **3**, shown in Figure 2 also can be regarded a cyclic bis(diselane), adopting a twist-boat conformation. The analoguous sulfur heterocycle, an *s*-tetrathiane, is fairly well known and also crystal structures exist. Whereas the bis(pentamethylene) derivative displays a chair configuration of the heterocycle,[13] the tetramethyl derivative, "duplodithioacetone", adopts the twist-boat conformation.[14] The Se–Se [2.3120(6)/2.3085(6) Å] and C–Se bond lengths [1.993(4)–2.001(4) Å] of **3** are in the same range as found in the structures of

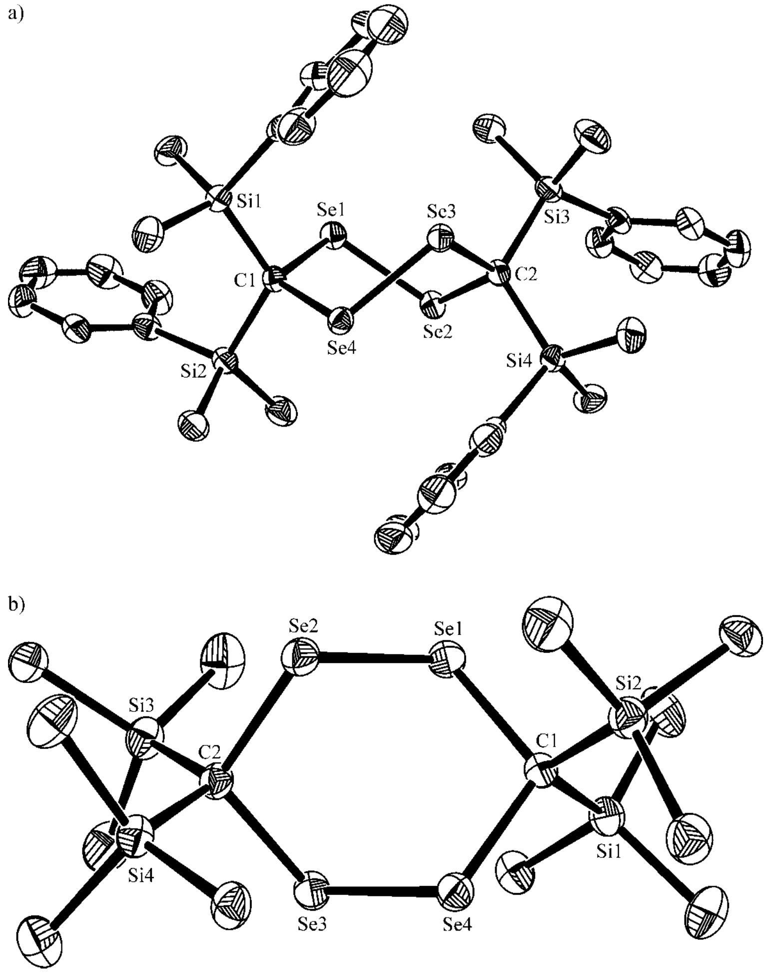

Figure 2. Different views (a) and (b) of the molecular structure of **3** with thermal ellipsoids of 30% probability. Selected bond lengths [Å] and angles [°]: Se1–Se2 2.3120(6), Se3–Se4 2.3085(6), Se1–C1 1.993(4), Se4–C1 2.001(4), Se2–C2 2.000(4), Se3–C2 1.999(3), Si1–C1 1.907(4), Si2–C1 1.905(4), Si3–C2 1.910(4), Si4–C2 1.903(4), C1–Se1–Se2 104.7(1), C1–Se4–Se3 104.0(1), C2–Se2–Se1 104.7(1), C2–Se3–Se4 103.2(1), Se1–C1–Se4 109.8(2), Se3–C2–Se2 110.3(2), Si2–C1–Si1 119.4(2), Si4–C2–Si3 119.2(2), C1–Se1–Se2–C2 –78.7(2), C2–Se3–Se4–C1 –81.9(2).

acyclic aliphatic and aromatic diselanes.[4,15] Figure 2a nicely shows the twisted six-membered heterocycle encumbered by two bis[dimethyl(phenyl)silyl]methylene moieties. In Figure 2b a view onto the heterocycle is given with all phenyl groups omitted for clarity.

The NMR spectra of **3** indicate a restricted rotation of the methyl groups, visible for the corresponding resonances in the ^1H and ^{13}C NMR spectra. At 25 °C two broadened resonances are observed for the methyl groups in the ^1H and ^{13}C NMR spectra, respectively. In the ^1H NMR spectrum coalescence is observed at 32 °C, whereas in the ^{13}C NMR spectrum at 47 °C both resonances coalesce. The resonance of the CSi_2Se_2 carbon atom remains unaffected. The variable-temperature ^{77}Se NMR spectrum of **3** shows only the temperature dependency of the resonance, i.e. spanning from δ = 462 ppm at 60 °C over δ = 456 ppm at 25 °C to δ = 443 ppm at –60 °C (all in $CDCl_3$). No additional resonances were detected within this temperature range, which then could indicate a change of the conformation of the heterocycle.

The experimentally observed twist conformation of **3** was subject of calculations for the sulfur analogue *s*-tetrathiane, where a molecular mechanics (MM) and an NMR study already predicted the twist conformer to be favored over the chair conformer by 0.7 kcal mol^{-1}.[16] In order to confirm the early MM study we now decided to compute the full series of O, S, Se, Te and Po heterocycles using hybrid density functional theory (DFT) at the B3LYP level. The model compounds, which were included in the computation were the chair and twist conformers of the heterocycles $[(H_3Si)_2CXX]_2$ (X = O, S, Se, Te, Po) (Table S1, Figure S1 in Supporting Information). The structures of all ten species were fully optimized and the vibrational frequencies calculated at the B3LYP/SDD level of theory. All ten entities represent stable minima on their potential energy surface. Whereas according to our calculations for the oxygen and sulfur compounds the chair conformers are favored by 5.8 and 0.4 kcal mol^{-1} (nicely in agreement with our X-ray structure for the selenium heterocycle), the twist conformers of the Se, Te and Po heterocycles represent the lower energy species, although the energy differences are again relatively small: ΔE(chair – twist) = +1.9 (Se), +3.1 (Te), +3.3 (Po) kcal mol^{-1}. It seems that the relative stability of the twist over the chair conformer increases with the heteroatoms (O → Po) descending within group 16 (Figure 3). For oxygen the chair is favored, for sulfur the chair and twist conformer are essentially identical in their energy, whereas for the heavier congeners Se, Te and Po the twist structure is favored over the chair conformer.

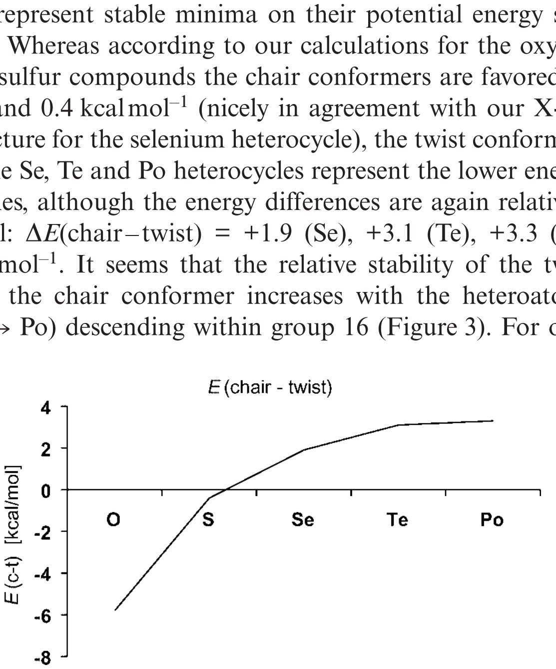

Figure 3. Relative stabilities of the chair and twist conformers of $[(H_3Si)_2CXX]_2$ (X = O, S, Se, Te, Po).

The existence of a claimed tetratellurium analogue, *s*-tetratellurane $(CH_2Te_2)_2$,[17] remains highly questionable in our opinion, due to the poor spectroscopic data. Substituted *s*-tetratellurane derivatives may possibly be prepared in the future, if one considers the relatively high stability of the corresponding sulfur and selenium heterocycles, and as well taking the calculations into account.

Experimental Section

General: All manipulations of air- and moisture-sensitive materials were performed under dry argon using flame-dried glass vessels and Schlenk techniques. The compounds $PhMe_2SiCl$,[18] and $(PhMe_2Si)_3CH$[19] were prepared according the literature, elemental selenium and methyllithium (1.6 M in Et_2O) (Aldrich) was used as received. Solvents were dried by standard methods and freshly distilled prior to use. NMR spectra were recorded with a JEOL Eclipse 400 instrument in $CDCl_3$ at 25 °C, and chemical shifts are with respect to Me_4Si (^1H: 400.2 MHz; ^{13}C: 100.6 MHz; ^{29}Si: 79.5 MHz) and Me_2Se (^{77}Se: 76.3 MHz). Raman spectra were recorded with a Perkin–Elmer 2000 NIR FT spectrometer fitted with an Nd-YAG laser (1064 nm, 100 mW, 25 °C), and only 100% peak and Se–Se stretching frequency listed. Mass spectrometric data were obtained with a JEOL MStation JMS spectrometer. Elemental analyses: Analytical service LMU. Melting points were determined in capillaries using a Büchi B540 instrument.

Lithiation and Selenation of $(PhMe_2Si)_3CH$: Into a solution of $(PhMe_2Si)_3CH$ (6.0 g, 14.3 mmol, sublimed at 90 °C/10^{-3} mbar) in 75 mL of THF was added methyllithium (10 mL, 16 mmol) in diethyl ether (1.6 M) at 25 °C within 1 h. This mixture was stirred at ambient temperature for an additional 1 h and then heated to 60 °C for 3 h. After cooling to ambient temperature, selenium (1.2 g, 15.2 mmol) was added in one portion and the mixture stirred for 1 h. The selenium reacted immediately and darkening of the solution occurred. This mixture was stirred at ambient temperature, now upon contact with air, for 3 d. All volatile materials were removed in vacuo, and the resulting dark orange residue was treated with 50 mL Et_2O, and 30 mL water was slowly added at 25 °C. Additionally, 20 mL of 10% HCl was added carefully at 0 °C and the mixture stirred for 2 h. The extracted dark red diethyl ether phases were separated and dried. The solvent was removed in vacuo, and the brown-red solid residue was treated again with small amounts of cold diethyl ether. The insoluble solid was washed repeatedly. This material was only poorly soluble in Et_2O and was shown to be pure triselane $(PhMe_2Si)_3CSeSeSeC(SiMe_2Ph)_3$ (**1**) (600 mg, ca. 8% yield). The remaining diethyl ether soluble fraction, a highly viscous red-brown oil, still containing considerable amounts of the triselane **1**, was subjected to column chromatography. The eluent was an *n*-hexane/chloroform mixture (10:1). The first fraction was the monoselane **4**, the second fraction contained a mixture of the diselane **2** and the *s*-tetraselenane **3**. The last fraction, containing a mixture of further other selenium-containing species that could not be separated, was discarded. The mixture consisting of **2** and **3**, could be separated by their different solubilities in diethyl ether. By repeated extraction of the mixture, the diselane **2** could be separated because of its slightly higher solubility in diethyl ether than that of the *s*-tetraselenane **3**.

(PhMe$_2$Si)$_3$CSeSeSeC(SiMe$_2$Ph)$_3$ (1): M.p. 176–178 °C. ^{1}H NMR: δ = 7.70 (2 H)/7.35 (1 H)/7.28 (2 H) (m, Ar-H), 0.37 [$^2J(^1$H-^{29}Si) = 6.0 Hz, 6 H, CH$_3$] ppm. ^{13}C NMR: δ = 139.5 [$^1J(^{13}$C-^{29}Si) = 66.5 Hz, C-1], 136.1 (C-3), 129.1 (C-4), 127.3 (C-2), 19.9 [$^1J(^{13}$C-^{29}Si) = 32.6 Hz, $^1J(^{13}$C-^{77}Se) = 84.2 Hz, CSi$_3$], 2.1 [$^1J(^{13}$C-^{29}Si) = 42.0 Hz, CH$_3$] ppm. ^{29}Si NMR: δ = –3.45 [$^2J(^{29}$Si-^{77}Se) = 8.7 Hz] ppm. ^{77}Se NMR: δ = 666 [$^1J(^{77}$Se-^{77}Se) = 20.7 Hz, 1 Se], 552 (2 Se) ppm. Raman: $\tilde{\nu}$ (%) = 1001 (100) [δ(Ph-H)], 272 (32) [ν(SeSe)] cm^{-1}. DEI-MS: *m*/*z* (%) = 1072 (0.1) [M$^+$], 994 (0.1) [M$^+$ – Se], 936 (0.1) [M$^+$ – PhMe$_2$Si], 860 (0.9) [M$^+$ – Se – PhMe$_2$Si], 726 (3) [M$^+$ – Se – 2 PhMe$_2$Si], 576 (8) [M$^+$ – Se – (PhMe$_2$Si)$_3$C], 495 (6) [M$^+$ – 2 Se – (PhMe$_2$Si)$_3$C], 135 (100) [PhMe$_2$Si$^+$]. C$_{50}$H$_{66}$Se$_3$Si$_6$ (1072.45): calcd. C 56.0, H 6.2; found C 54.6, H 6.1.

(PhMe$_2$Si)$_2$HCSeSeCH(SiMe$_2$Ph)$_2$ (2): M.p. 60–63 °C. ^{1}H NMR: δ = 7.44–7.32 (m, 10 H, Ar-H), 1.21 [$^2J(^1$H-^{29}Si) = 8.0 Hz, $^2J(^1$H-^{77}Se) = 10.5 Hz, 1 H, CH], 0.162/0.157 (12 H, CH$_3$) ppm. ^{13}C NMR: δ = 138.9 [$^1J(^{13}$C-^{29}Si) = 69.2 Hz, C-1], 134.1 (C-3), 129.0 (C-4), 127.5 [$^2J(^{13}$C-^{29}Si) = 23.4 Hz, C-2], 19.8 [$^1J(^{13}$C-^{29}Si) = 43.8 Hz, $^1J(^{13}$C-^{77}Se) = 75.3 Hz, CHSi$_2$], –1.6/–2.2 [$^1J(^{13}$C-^{29}Si) = 53.8/54.6 Hz, CH$_3$] ppm. ^{29}Si NMR: δ = –3.35 ppm [$^2J(^{29}$Si-^{77}Se) = 9.7 Hz]. ^{77}Se NMR: δ = 391 ppm. Raman: $\tilde{\nu}$ (%) = 1000 (100) [δ(Ph-H)], 293 (30) [ν(SeSe)] cm^{-1}. DEI-MS: *m*/*z* (%) = 726 (30) [M$^+$], 646 (0.5) [M$^+$ – Se], 442 (0.6) [M$^+$ – (PhMe$_2$Si)$_2$CH – H], 363 (10) [M$^+$ – SeCH(SiMe$_2$Ph)$_2$], 135 (100) [PhMe$_2$Si$^+$]. C$_{34}$H$_{46}$Se$_2$Si$_4$ (725.08): calcd. C 56.3, H 6.4; found C 54.6, H 6.3.

[(PhMe$_2$Si)$_2$CSeSe]$_2$ (3): M.p. 181–183 °C. ^{1}H NMR: δ = 7.56 (2 H)/7.40 (1 H)/7.31 (2 H) (m, Ar-H), 0.32/0.29 (6 H, CH$_3$) ppm. ^{13}C NMR: δ = 137.1 [$^1J(^{13}$C-^{29}Si) = 67.6 Hz, C-1], 135.4 (C-3), 129.3 (C-4), 127.4 (C-2), 9.7 [$^1J(^{13}$C-^{29}Si) = 12.3 Hz, $^1J(^{13}$C-^{77}Se) = 91.9 Hz, CSi$_2$Se$_2$], –1.7/–2.2 (br., CH$_3$) ppm. ^{29}Si NMR: δ = –0.56 [$^2J(^{29}$Si-^{77}Se) = 5.8 Hz] ppm. ^{77}Se NMR: δ = 456 ppm. Raman: $\tilde{\nu}$ (%) = 1000 (100) [δ(Ph-H)], 292 (48) [ν(SeSe)] cm^{-1}. DEI-MS: *m*/*z* (%) = 882 (3) [M$^+$], 667 (6) [M$^+$ – Se – PhMe$_2$Si], 520 (1) [M$^+$ – Se – (PhMe$_2$Si)$_2$C], 442 (16) [(PhMe$_2$Si)$_2$CSe$_2$$^+$], 362 (12) [(PhMe$_2$Si)$_2CSe^+$], 135 (100) [PhMe$_2Si^+$]. C$_{34}H_{44}Se_4Si_4$ (880.89): calcd. C 46.4, H 5.0; found C 45.2, H 5.0.

(PhMe$_2$Si)$_3$CSeMe (4): ^{1}H NMR: δ = 7.52–7.35 (m, 15 H, Ar-H), 0.59 [$^2J(^1$H-^{77}Se) = 9.8 Hz, 3 H, CH$_3$Se], 0.35 [$^2J(^1$H-^{29}Si) = 6.4 Hz, 18 H, CH$_3$Si] ppm. ^{13}C NMR: δ = 141.8 [$^1J(^{13}$C-^{29}Si) = 66.0 Hz, C-1], 133.2 (C-3), 128.3 (C-4), 127.5 (C-2), 2.0 [$^1J(^{13}$C-^{29}Si) = 5.8 Hz, $^1J(^{13}$C-^{77}Se) = 53.8 Hz, CSi$_3$], 1.6 [$^1J(^{13}$C-^{29}Si) = 52.7 Hz, CH$_3$Si], 0.1 [$^1J(^{13}$C-^{77}Se) = 38.1 Hz, CH$_3$Se] ppm. ^{29}Si NMR: δ = –3.65 [$^2J(^{29}$Si-^{77}Se) = 3.9 Hz] ppm. ^{77}Se NMR: δ = 135 (q) ppm.

Crystal Data for 1: C$_{50}$H$_{66}$Se$_3$Si$_6$ (1072.45), orange platelet, 0.58 × 0.11 × 0.52 mm, orthorhombic, space group *Pccn*, a = 13.8952(7), b = 17.1669(9), c = 21.759(1) Å, V = 5190.3(5) Å^3, Z = 4, $\rho_{\text{calcd.}}$ = 1.372 g/cm^{-3}, μ = 2.297 mm^{-1}, F(000) = 2208, Oxford XCalibur CCD, Mo-K_α, λ = 0.71073 Å, T = 200 K; θ range = 3.8–22.0°, $-9 \le h \le 14$, $-18 \le k \le 17$, $-22 \le l \le 22$, 17116 reflections collected, 3172 independent reflections (R_{int} = 0.1395), 2749 observed reflections [$I > 2\sigma(I)$], structure solution: SHELX-97,[20] direct methods, data/parameters ratio: 11.9:1 {10.3:1 [$I > 2\sigma(I)$]}, final R indices [$I > 2\sigma(I)$]: R_1 = 0.0824, wR_2 = 0.1293, R_1 = 0.0982, wR_2 = 0.1371 (all data), GOF on F^2 = 1.184.

Crystal Data for 3: C$_{34}$H$_{44}$Se$_4$Si$_4$ (880.89), orange platelet, 0.57 × 0.33 × 0.43 mm, monoclinic, space group *P*2$_1$/*c*, a = 11.846(1), b = 14.641(2), c = 22.313(2) Å, β = 97.56(1)°, V = 3836.3(7) Å^3, Z = 4, $\rho_{\text{calcd.}}$ = 1.525 g/cm^{-3}, μ = 3.972 mm^{-1}, F(000) = 1760, Nonius Kappa CCD, Mo-K_α, λ = 0.71073 Å, T = 295 K; θ range = 2.7–25.6°, $-14 \le h \le 0$, $-17 \le k \le 0$, $-26 \le l \le 27$, 7534 reflections collected, 7010 independent reflections (R_{int} = 0.0161), 4864 observed reflections [$I > 2\sigma(I)$], structure solution: SHELX-97,[20] direct methods, data/parameters ratio: 18.2:1 {12.6:1 [$I > 2\sigma(I)$]}, final R indices [$I > 2\sigma(I)$]: R_1 = 0.0312, wR_2 = 0.0683, R_1 = 0.0659, wR_2 = 0.0822 (all data), GOF on F^2 = 1.020.

CCDC-600115 (**1**) and -282655 (**3**) 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.

Supporting Information (see footnote on the first page of this article): Detailed description of the chair-twist calculations.

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