

Unsaturated five-membered selenium–silicon containing heterocycles based on the reactions of selenium di- and tetrahalides with diorganyl diethynyl silanes

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Abstract

Reactions of SeBr_2 and SeCl_2 with diorganyl diethynyl silanes $\text{RR}^1\text{Si}(\text{C}\equiv\text{CH})_2$ in CHCl_3 at room temperature result in regio- and stereoselective formation of a new class of unsaturated five-membered heterocycles, 4,4-*R*,*R*¹-3,6-dichloro(dibromo)-1,4-selenasilafulvenes (*Z*-isomers predominately), in preparative yields. Under similar conditions the reaction of SeBr_4 and SeCl_4 with diorganyl diethynyl silanes $\text{RR}^1\text{Si}(\text{C}\equiv\text{CH})_2$ proceeds regioselectively to afford another new class of unsaturated five-membered heterocycles, 2-dichloro(dibromo)-methyl-2,4-dichloro(dibromo)-3,3-diorganyl-1-selena-3-silacyclopentenes-4. The structures of the heterocycles were proved by multinuclear (^1H , ^{13}C , ^{29}Si , ^{77}Se) NMR spectroscopy, 2D NOESY NMR spectroscopy and mass-spectrometry. A long-range spin–spin interaction of protons through five bonds lacking in *E*-isomers was revealed in *Z*-isomers of fulvene-type heterocycles. In the MS spectra heterocycles of cyclopentene structure were shown to manifest themselves as fragmentary ions $[\text{M}-\text{HX}]^+$ or $[\text{M}-\text{X}]^+$. © 2006 Elsevier B.V. All rights reserved.

Keywords: Selenium dihalide; Selenium tetrahalides; Diorganyl diethynyl silanes; Selenium–silicon containing heterocycles; Unsaturated five-membered heterocycles

1. Introduction

Currently, unsaturated five-membered 1,3-dichalcogenole heterocycles are among the most vigorously investigating chalcogen-containing systems [1a–1j], since they represent the parent blocks leading to 2,2'-bis(1,3-dichalcogenolydienes). The latter, also referred to as “tetra-chalcogenofulvalenes”, have been intensively studied for the last three decades due to their unique electrochemical [2a–2i] and synthetic properties [3a,3b]. In the last few year considerable interest has been attracted to thiazole systems as analogs of 1,3-dithioles where one sulfur atom is substituted for nitrogen atom [4]. Sulfur-silicon containing heterocycles were known only as saturated derivatives [5]. In

particular, Voronkov et al. have reported on several derivatives of five-membered 1-thia-3-silacyclopentane [6a–6c]. But 1,3-chalcogenosiloles were unknown.

Earlier we shortly informed on the first representatives of unsaturated five-membered heterocycles incorporating selenium and silicon [7a,7b]. They were prepared by the reaction of selenium dichloride and dibromide or selenium tetrabromide with dimethyl diethynyl silane (**1d**). Up to date electrophilic additions of chalcogen di- and tetrahalides to the systems with two unsaturated moieties divided by the heterobridges were studied mainly on diallyl systems [8,9a–9e]. Electrophilic addition of selenium tetrahalides to triple bond was known only for monoacetylenic compounds. In particular, in a case of acetylene it leads to *Z,Z*- and *E,E*-bis(2-halovinyl)selenium dihalides at low temperatures (–45 to –78 °C) [10a–10e] or to *E,E*-bis(2-halovinyl)selenide at 20 °C [10f].

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Table 1
Reactions of diethynyl silanes (**1**) with SeX_2 and SeX_4

1	R	R ¹	SeX_n	Reaction time (h)	2, 3	Yield (%)	Z:E ^a	4, 5	Yield ^b (%)
1a	(CH ₂) ₄		SeBr ₂	5.5	3a	92.6 ^c	84:16		
1a	(CH ₂) ₄		SeCl ₂	7	2a	40.3 ^c	73:27		
1b	(CH ₂) ₅		SeBr ₂	6	3b	91.0 ^c	97.5:2.5		
1b	(CH ₂) ₅		SeCl ₂	6	2b	70.9 ^c	85:15		
1c	Me ₃ Si(CH ₂) ₂	Me	SeBr ₂	2	3c	86.5 ^c	89.5:10.5		
1d^d	Me	Me	SeBr ₂	3	3d	70.0	85.5:14.5		
1d^d	Me	Me	SeCl ₂	3	2d	72.0	83:17		
1a	(CH ₂) ₄		SeBr ₄	2	3a	27.0	74:26	5a	73.0
1a	(CH ₂) ₄		SeCl ₄	7	2a	73.0	68:32	4a	21.0
1b	(CH ₂) ₅		SeBr ₄	6	3b	35.5	70.5:29.5	5b	58.5
1b	(CH ₂) ₅		SeCl ₄	5	2b	18.0	60:40	4b	75.5
1c	Me ₃ Si(CH ₂) ₂	Me	SeBr ₄	1	3c			5c	62.0 ^e
1d^f	Me	Me	SeBr ₄	6				5d	60.0
1d	Me	Me	SeCl ₄	6	2d	40.0	75:25	4d	32

^a According to the ¹H NMR data.

^b According to GC–MS data.

^c After purification by silica gel column chromatography.

^d Data [7a].

^e Ratio of diastereomers 62:38, according to the ¹H NMR data.

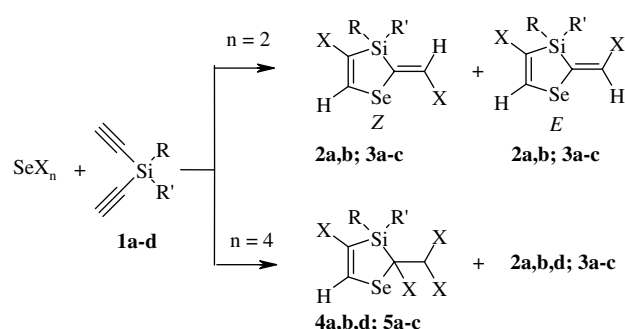
^f Data [7b].

This paper is aimed at the synthesis of new five-membered unsaturated selenium-silicon containing heterocycles of fulvene and cyclopentene structures on the basis of the electrophilic addition-cyclization reaction of selenium dichloride and tetrachloride and selenium dibromide and tetrabromide with diorganyl diethynyl silanes. The structures of the heterocycles prepared were proved by multinuclear NMR (¹H, ¹³C, ²⁹Si, ⁷⁷Se), 2D NOESY NMR techniques and mass-spectrometry.

2. Results and discussion

Five-membered heterocycles of fulvene structure **2a,b**, **3a–c** were obtained in preparative yields by the reaction of selenium dichloride and dibromide, generated in situ from elemental selenium and SO₂Cl₂ or Br₂ in chloroform at ambient temperature, with cyclic 1,1-diethynyl-1-silacyclopentane and -silacyclohexane (**1a,b**) and methyl 2-trimethylsilylethyl diethynyl silane (**1c**) (Scheme 1, Table 1). As evidenced from fine structures of the ¹H and ⁷⁷Se NMR spectra these heterocycles are formed exclusively or predominantly as Z-isomers. The usage of cyclic diethynyl silanes **1a,b** resulted in spirocyclic heterocycles **2a,b**, **3a,b**. Purification of the heterocycles **2, 3** by column chromatography on silica gel afforded the products as red or orange oils.

A similar reaction of selenium tetrahalides, generated in situ, with diethynyl silanes (**1a–d**) leads to the formation of a mixture of five-membered selenium-silicon containing cyclopentenes-4 **4a,b,d**, **5a–c** as well as heterofulvenes **2a,b,d**, **3a–c** (Scheme 1, Table 1). Heterocycles **2a,b**, **3a,b**, **4a,b**, **5a,b** prepared from 1,1-diethynyl-1-silacycloalkanes **1a,b** have spiro-structures. Since the attempts to separate these mixtures by column chromatography failed, these compounds were identified on a basis of multinuclear NMR and GC–MS.



1: RR¹ = (CH₂)₄(**a**), (CH₂)₅(**b**); R = Me, R¹ = (CH₂)₂SiMe₃(**c**); R = R¹ = Me(**d**)

2: X = Cl, RR¹ = (CH₂)₄(**a**); (CH₂)₅(**b**);

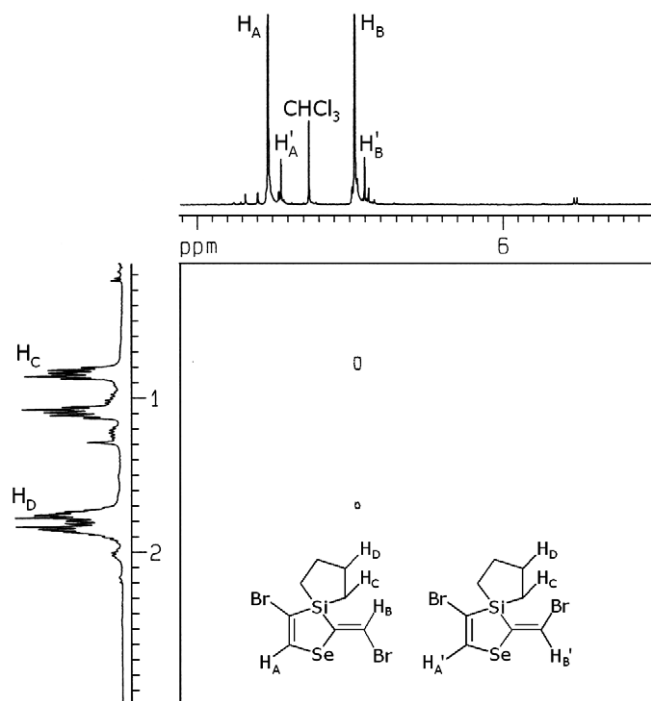
3: X = Br, RR¹ = (CH₂)₄(**a**); (CH₂)₅(**b**); R = Me, R¹ = (CH₂)₂SiMe₃(**c**);

4: X = Cl, RR¹ = (CH₂)₄(**a**); (CH₂)₅(**b**); R = R¹ = Me(**d**);

5: X = Br, RR¹ = (CH₂)₄(**a**); (CH₂)₅(**b**); R = Me, R¹ = (CH₂)₂SiMe₃(**c**)

Scheme 1.

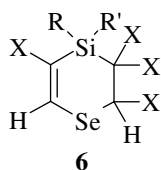
Fulvene structure of the heterocycles **2** and **3** is evidenced from a pattern of spin–spin coupling of the selenium atom signals in the ⁷⁷Se NMR spectra containing doublets of doublets with the geminal constants ²J_{Se–H} 54–57 Hz, which are typical for cyclic unsaturated selenides [11], and constants ⁷⁷Se–¹H through three bonds equal to 11–14 Hz for main isomers and 7–11 Hz for minor ones. Similar picture is observed in the ¹H NMR spectra of these heterocycles, where the spin–spin interactions of protons with selenium are manifested as satellites to the signals of the corresponding exocyclic and endocyclic olefinic protons. The value of 11–14 Hz for ³J_{Se–H} was regarded as an indicator of *cis*-arrangement of Se and H atoms in vinyl selenides [11,12]. But the long-range (through 5 bonds) spin-spin interaction between protons =CH–Se–C(Si)=CHHal (⁵J_{HH} 0.8–1.1 Hz) in the main isomer points to



Picture 1.

trans-arrangement of these atoms (transoid or W-shaped transfer of the long-range spin-spin interaction). This contradiction was solved by the 2D NOESY spectrum of both fulvene **3a** isomers (Picture 1) that enabled us to unambiguously assign the main isomer as *Z*. The presence in the spectrum of the cross peaks, induced by dipole–dipole interaction between exo-olefinic proton H_B and methylene protons H_C and H_D of the silacyclopentane moiety in this isomer, speaks in favor of *trans*-arrangement of Se and H atoms in its exocyclic double bond. In addition, the 1H NMR spectrum of the heterocycle **3a** degassed sample shows the satellite lines at the resonance line of the exocyclic olefinic proton, resulting from coupling with *cis*-atom of silicon-29 ($^3J_{Si-H}$ 3.9 Hz³¹) that also argues for the *Z*-configuration. On the contrary, the proton of the fulvene **3a** endocyclic double bond shows the coupling constant $^3J_{Si-H}$ (9.9 Hz), which is characteristic of *trans*-arrangement of the silicon atom [13].

In the case of heterocycles **4a,b,d**, **5a–c** the main task was to prove that they were five-membered 1-selena-3-silacyclopentenes-4, but not possible isomeric unsaturated six-membered 1-selena-4-silacyclohexanes-2 (**6**) (Picture 2). In the 1H NMR spectra endocyclic olefinic and exocyclic alkyl

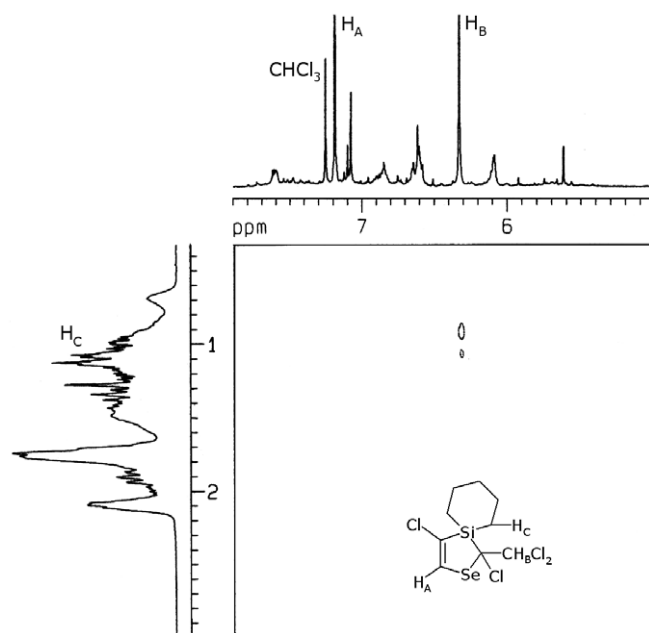


Picture 2.

protons of **4**, **5** appear as singlet signals, which could be true for the heterocycles **6** as well. In the ^{77}Se NMR spectra 1-selena-3-silacyclopentenes-4 **4a,b,d** and **5a–c** appear as doublets with the coupling constant $^2J_{Se-H}$ 54–57 Hz that is indicative of the geminal arrangement of Se and H atoms, which is realized in the structure of **6** as well. To settle this structural problem we have recorded 2D NOESY spectrum of the heterocycle **4b** (Picture 3). The presence of the cross-peaks due to dipole–dipole interaction between H_B and methylene protons H_C of silacyclohexane moiety unambiguously confirmed 1-selena-3-silacyclopentene-4 structure, since in 1-selena-4-silacyclohexanes-2 (**6**) such interactions were spatially impossible.

Of special interest was five-membered heterocycle **5c**, where silicon atom is bonded to two different substituents. This heterocycle is formed as two diastereomers that manifest themselves in GC–MS by two peaks with the same molecular ion. At the same time they are characterized by different NMR 1H , ^{13}C , ^{29}Si spectra. In this case alternative possible structure of six-membered 3,5,5,6-tetrabromo-4-methyl-4-trimethylsilylethyl-1-selena-4-silacyclohexene-2 (**6**) ($R = Me$, $R^1 = CH_2CH_2SiMe_3$) (Picture 2) was rejected because the calculated chemical shift of the proton of the $Se-CHBrCBr_2-Si$ group lies in the higher field (5.95 ± 0.96 ppm) as compared to the calculated (6.80 ± 0.65 ppm) and experimental (6.47 and 6.44 ppm) chemical shifts of the $CHBr_2$ proton of both diastereomers of the heterocycle **5c** and difference between these two calculated values is bigger than that found in the experiment.

The mass spectra of the fulvene-type heterocycles **2a,b**, **3a–c** are characterized by the pronounced polyisotopic molecular ions. In the mass spectra of the cyclopentene heterocycles **4a,b,d**, **5a–c** molecular ions are absent since under electron impact their dehydrohalogenation occurs and as a



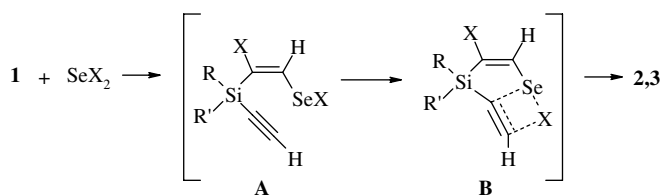
Picture 3.

result these heterocycles can be identified only by the fragment ions $[M-HX]^+$. Earlier we have found that 2-dihalomethyl-2,4-dihalogen-3,3-dimethyl-1-selena-3-silacyclopentenes-4 **4d** and **5d** ($R = R^1 = Me$), formed in the reaction of dimethyl diethynyl silane (**1d**) with selenium tetrahalides, were identified in the mass spectra with the fragment ions $[M-X_2]^+$ and $[M-HX]^+$ [14]. These findings correlate with the known fact that in the mass spectra of halogen containing diorganylselenium dihalides only $[M-X]^+$ ions are present [15].

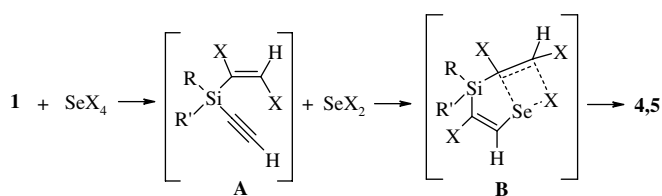
To explain formation of heterocycles **2**, **3** and **4**, **5** we suggest two routes.

It is quite obvious that in the case of selenium dihalides the cyclization occurs through two successive steps of electrophilic regio- and stereoselective addition to the triple bonds of the diethynyl silanes (**1**) (Scheme 2). In the first step of Markovnikov *anti*-addition, due to influence of the electron-donating diorganylsilyl group, 2-halovinyl selenenyl halide **A** is formed. In the second step *anti*-Markovnikov *syn*-addition of selenenyl halide moiety of the intermediate **A** to the second ethynyl group is realized, presumably via four-centered intermediate state **B**.

The reaction of selenium tetrahalides (Scheme 3) is more complicated because $SeCl_4$ and $SeBr_4$ participate in the reaction as halogenation agents thus leading to the formation of the intermediate ethynyl 1,2-dihalovinyl silane **A** in the first step. In the second step occurs regio- and stereospecific addition of selenium dihalide to the triple bond of this intermediate with formation of selenenyl halide at the β -position to the silicon atom. Intramolecular cyclization due to intramolecular electrophilic addition of this intermediate selenenyl halide to dihalovinyl moiety, presumably through four-centered intermediate state **B**, leads to the heterocycles **4**, **5**. Alternative reaction scheme through the formation of 1,1-dihalogen-1,4-selenasilafulvenes (**7**), followed by isomerization to cyclopentenes **4**, **5**, is not realized, since in the 1H and ^{77}Se NMR spectra no signals were found that could be attributed to the compound **7**.



Scheme 2.



Scheme 3.

In both cases the cyclization is seemed to be aided by the Thorpe-Ingold effect according to which the presence of two alkyl substituents at the carbon atom tethering two reacting centers favors to intramolecular cyclization due to contraction of the angle between these reacting groups [16]. Though in diethynyl silanes (**1**) the atom bridging two ethynyl groups is silicon but not carbon, the similarities in the chemistry of these two 14 group elements imply that this effect may manifest itself in the case of silanes **1** as well.

Formation of the fulvenes **2** and **3** in the reaction of diethynyl silanes (**1**) with selenium tetrahalides could be explained by the competitive reaction of these diethynyl silanes with SeX_2 generated in the reaction mixtures.

3. Experimental

3.1. General procedure

All reactions were carried out under atmosphere of dry argon. 1H (400.1 MHz), ^{13}C (100.6 MHz), ^{29}Si (79.5 MHz) and ^{77}Se (76.3 MHz) NMR spectra were recorded on a Bruker DPX-400 spectrometer in 5–10% solution in $CDCl_3$ or d_6 -acetone, internal reference – HMDS. GC–MS spectra were recorded on the spectrometer Shimadzu QP5050A at electron energy 70 eV, 60 m capillary column SPB-5 ms, injection temperature 260 °C, column temperature 70–260 °C.

3.2. Materials

1,1-Diethynyl-1-silacyclopentane (**1a**), -1-silacyclohexane (**1b**), methyl 2-trimethylsilyl ethyl diethynyl silane (**1c**) and dimethyl diethynyl silane (**1d**) were prepared according to the known procedure [17a–17c]. Methyl 2-trimethylsilyl ethyl diethynyl silane (**1c**) was kindly presented by Zhilitskaya L.V.

3.3. Reaction of selenium dihalides with diethynyl silanes (**1**)

3.3.1. Synthesis of 3,6-dichloro-4,4-tetramethylene-1,4-selenasilafulvene (**2a**)

To finely-ground elemental Se (0.40 g, 5.1 mg.a) in $CHCl_3$ (20 ml) under argon atmosphere was added SO_2Cl_2 (0.68 g, 5.1 mmol) over 20 min, the resulting solution was stirred at 20 °C for 2 h and then kept overnight. Into the brown solution of selenium dichloride was introduced diethynyl silane **1a** (0.68 g, 5.1 mmol) under argon for 10 min, this solution was stirred at room temperature for 7 h. After removal of the solvent under reduced pressure the residue was subjected to column chromatography on silica gel (eluent – hexane- CH_2Cl_2 , 95:5) to afford heterocycle **2a** (0.58 g, 40.3% yield) as an orange oil. Anal. Calc. for $C_8H_{10}Cl_2SeSi$: C, 33.82; H, 3.55; Cl, 24.96; Se, 27.79; Si, 9.89. Found: C, 33.50; H, 3.56; Cl, 24.90; Se, 28.15; Si, 9.54%. GC–MS (EI, m/z , %) (^{80}Se , ^{35}Cl , ^{28}Si): 2 compounds, 284(71) (M^+), 256(1), 242(3), 228(7), 203(5),

167(8), 153(35), 143(15), 123(38), 105(27), 78(45), 63(100), 53(97). ^1H NMR (CDCl_3 , δ) Z: 7.24(d, 1H, $^5J_{\text{HH}} = 1.1$ Hz, $\text{SiCCl}=\text{CHSe}$), 6.66(d, 1H, $^5J_{\text{HH}} = 1.1$ Hz, $\text{SeC}=\text{CHCl}$), 1.76, 1.72 (m, 4H, CH_2CH_2), 1.07, 0.83 (m, 2H, CH_2Si); E: 7.19 (s, 1H, $\text{SiCCl}=\text{CHSe}$), 6.68 (s, 1H, $\text{SeC}=\text{CHCl}$), 1.88, 1.83 (m, 4H, CH_2CH_2), 1.13, 0.98 (m, 1H, CH_2Si). ^{13}C NMR (CDCl_3 , δ) Z: 131.8, 130.7, 123.7, 123.3, 27.2, 12.7; E: 133.9, 129.2, 124.5, 124.3, 27.3, 10.4. ^{29}Si NMR (CDCl_3 , δ) Z: 19.2; E: 21.4. ^{77}Se NMR (CDCl_3 , δ) Z: 496.8 (dd, $^2J_{\text{SeH}} = 54.1$, $^3J_{\text{SeH}} = 11.5$ Hz); E: 509.1 (dd, $^2J_{\text{SeH}} = 54.9$, $^3J_{\text{SeH}} = 8.6$ Hz).

3.3.2. Synthesis of 3,6-dichloro-4,4-pentamethylene-1,4-selenasilafulvene (**2b**)

Similarly, the reaction of SeCl_2 (5.0 mmol), prepared from Se (0.40 g, 5.0 mg.a) and SO_2Cl_2 (0.60 g, 5.0 mmol), with diethynyl silane **1b** (5.0 mmol) in CHCl_3 (30 ml), argon atmosphere, 6 h, afforded heterocycle **2b** (1.06 g, 70.9%) purified by column chromatography (silica gel, eluent – hexane- CH_2Cl_2 , 95:5). Anal. Calc. for $\text{C}_9\text{H}_{12}\text{Cl}_2\text{SeSi}$: C, 36.26; H, 4.06; Cl, 23.78; Se, 26.48; Si, 9.42. Found: C, 36.46; H, 4.25; Cl, 23.77; Se, 26.50; Si, 9.58%. GC-MS (EI, m/z , %) (^{80}Se , ^{35}Cl , ^{28}Si): 2 compounds, 298(58) (M^+), 269(1), 255(1), 242(3), 229(15), 203(7), 165(6), 153(8), 145(13), 123(16), 105(43), 97(28), 79(32), 63(100), 53(70). ^1H NMR (CDCl_3 , δ) Z: 7.19 (d, 1H, $^5J_{\text{HH}} = 0.5$ Hz, $\text{SiCCl}=\text{CHSe}$), 6.75 (d, 1H, $^5J_{\text{HH}} = 0.5$ Hz, $\text{SeC}=\text{CHCl}$), 1.99, 1.73 (m, 4H, $\text{CH}_2\text{CH}_2\text{Si}$), 1.52 (m, 2H, CH_2), 1.04, 0.86 (m, 4H, CH_2Si); E: 7.14 (s, 1H, $\text{SiCCl}=\text{CHSe}$), 6.64 (s, 1H, $\text{SeC}=\text{CHCl}$), 1.99, 1.73 (m, 4H, $\text{CH}_2\text{CH}_2\text{Si}$), 1.52 (m, 2H, CH_2), 1.04, 0.86 (m, 4H, CH_2Si). ^{13}C NMR (CDCl_3 , δ) Z: 131.1, 130.01, 123.1, 122.6, 29.1, 23.9, 12.0; E: 134.5, 130.1, 125.2, 125.1, 29.0, 24.1, 10.4. ^{29}Si NMR (CDCl_3 , δ) Z: -1.9; E: -0.1. ^{77}Se NMR (CDCl_3 , δ) Z: 492.7 (dd, $^2J_{\text{SeH}} = 54.4$, $^3J_{\text{SeH}} = 11.5$ Hz); E: 504.6 (dd, $^2J_{\text{SeH}} = 50.2$, $^3J_{\text{SeH}} = 7.3$ Hz).

3.3.3. Synthesis of 3,6-dibromo-4,4-tetramethylene-1,4-selenasilafulvene (**3a**)

To finely-ground elemental Se (0.40 g, 5.1 mg.a) in CHCl_3 (15 ml), under argon atmosphere, was added Br_2 (0.81 g, 5.1 mmol) in CHCl_3 (15 ml) for 20 min, the resulting mixture was stirred for 3 h at 20°C and then kept overnight. The SeBr_2 solution, thus prepared, was introduced for 1 h at 20°C into the diethynyl silane **1a** (0.75 g, 5.6 mmol) in CHCl_3 (15 ml) and stirred under argon for 5.5 h. Solvent removal under reduced pressure, followed by column chromatography on silica gel, eluting with hexane- CHCl_3 (95:5) gave the heterocycle **3a** (1.76 g, 92.6%) as an orange oil. Anal. Calc. for $\text{C}_8\text{H}_{10}\text{Br}_2\text{SeSi}$: C, 25.76; H, 2.70; Br, 42.84; Se, 21.17; Si, 7.53. Found: C, 26.07; H, 2.30; Br, 42.64; Se, 21.12; Si, 6.99%. GC-MS (EI, m/z , %) (^{80}Se , ^{79}Br , ^{28}Si): 2 compounds, 372(37) (M^+), 293(2) ($\text{M}^+ - \text{Br}$), 265(5), 239(14), 211(11), 185(7), 133(14), 107(23), 79(25), 78(23), 53(100). ^1H NMR (CDCl_3 , δ) Z: 7.54 (d, 1H, $^5J_{\text{HH}} = 0.9$ Hz, $\text{SiCBr}=\text{CHSe}$), 6.97 (d, 1H, $^5J_{\text{HH}} = 0.9$ Hz, $\text{SeC}=\text{CHBr}$), 1.80, 1.77 (m,

4H, CH_2CH_2), 1.04, 0.83 (m, 4H, CH_2Si); E: 7.46 (s, 1H, $\text{SiCBr}=\text{CHSe}$), 6.92 (s, 1H, $\text{SeC}=\text{CHBr}$), 1.98, 1.89 (m, 4H, CH_2CH_2), 1.22, 1.00 (m, 4H, CH_2Si). ^{13}C NMR (CDCl_3 , δ) Z: 134.2, 132.8, 112.1, 111.1, 27.2, 12.7; E: 139.1, 131.8, 110.7, 110.5, 27.3, 10.4. ^{29}Si NMR (CDCl_3 , δ) Z: 20.7; E: 24.9. ^{77}Se NMR (CDCl_3 , δ) Z: 558.9 (dd, $^2J_{\text{SeH}} = 54.6$, $^3J_{\text{SeH}} = 13.6$ Hz); E: 573.9 (dd, $^2J_{\text{SeH}} = 55.4$, $^3J_{\text{SeH}} = 11.0$ Hz).

3.3.4. Synthesis of 3,6-dibromo-4,4-pentamethylene-1,4-selenasilafulvene (**3b**)

Similarly, reaction of SeBr_2 (5.0 mmol), prepared in situ for 3 h from Se (0.40 g, 5.1 mg.a) and Br_2 (0.80 g, 5.0 mmol) in CHCl_3 (10 ml), with diethynyl silane **1b** (0.74 g, 5.0 mmol) afforded after 6 h of stirring at room temperature under argon atmosphere the heterocycle **3b** (1.76 g, 91% yield) as a red oil. MS (EI, m/z , %) (^{80}Se , ^{79}Br , ^{28}Si): 386(32) (M^+), 330(1), 305(2), 251(2), 133(12), 107(24), 97(52), 79(18), 53(100). Anal. Calc. for $\text{C}_9\text{H}_{12}\text{Br}_2\text{SiSe}$: C, 27.93; H, 3.13; Br, 41.29; Se, 20.40; Si, 7.26. Found: C, 27.46; H, 2.95; Br, 41.60; Se, 20.08; Si, 7.12%. ^1H NMR (CDCl_3 , δ) Z: 7.49 (d, 1H, $^5J_{\text{HH}} = 0.8$ Hz, $\text{SiCBr}=\text{CHSe}$), 7.05 (d, 1H, $^5J_{\text{HH}} = 0.8$ Hz, $\text{SeC}=\text{CHBr}$), 2.01, 1.74 (m, 4H, $\text{CH}_2\text{CH}_2\text{Si}$), 1.52 (m, CH_2), 1.01, 0.85 (m, 4H, CH_2Si). ^{13}C NMR (CDCl_3 , δ) Z: 139.7, 133.5, 111.5, 111.3, 29.0, 23.8, 11.9. ^{29}Si NMR (CDCl_3 , δ) Z: -0.8. ^{77}Se NMR (CDCl_3 , δ) Z: 554.7 (dd, $^2J_{\text{SeH}} = 54.5$ Hz, $^3J_{\text{SeH}} = 14.4$ Hz).

3.3.5. Synthesis of 3,6-dibromo-4-methyl-4-(2-trimethylsilylethyl)-1,4-selenasilafulvene (**3c**)

Similarly, reaction of SeBr_2 (2.5 mmol), prepared in situ for 3 h from Se (0.20 g, 2.5 mg.a) and Br_2 (0.40 g, 2.5 mmol) in CHCl_3 (10 ml), with diethynyl silane **1c** (0.49 g, 2.5 mmol) afforded after 2 h of stirring at 20°C under argon, followed by silica gel column chromatography (hexane- CH_2Cl_2 , 95:5) the heterocycle **3c** (0.93 g, 86.5% yield) as an orange oil. Anal. Calc. for $\text{C}_{10}\text{H}_{18}\text{Si}_2\text{SeBr}_2$: C, 27.73; H, 4.19; Br, 36.89; Se, 18.23; Si, 12.98. Found: C, 28.02; H, 3.93; Br, 37.13; Se, 18.42; Si, 12.72%. GC-MS (EI, m/z , %) (^{80}Se , ^{79}Br , ^{28}Si): 2 compounds, 432(5) (M^+), 417(1), 389(1), 353(1) ($\text{M}^+ - \text{Br}$), 200(2), 187(1), 173(4), 161(1), 147(11), 135(1), 107(2), 85(1), 73(100) (Me_3Si^+), 53(7). ^1H NMR (CDCl_3 , δ) Z: 7.46 (d, 1H, $^5J_{\text{HH}} = 1.1$ Hz, $\text{SiCBr}=\text{CHSe}$), 6.90 (d, 1H, $^5J_{\text{HH}} = 1.1$ Hz, $\text{SeC}=\text{CHBr}$), 0.73-0.64 (m, 2H, CH_2Si), 0.49-0.44 (m, 2H, Me_3SiCH_2), 0.35 (s, 3H, Me), 0.01 (s, 9H, Me_3Si); E: 7.40 (s, 1H, $\text{SiCBr}=\text{CHSe}$), 6.81 (s, 1H, $\text{SeC}=\text{CHBr}$), 0.73-0.64 (m, 2H, CH_2Si), 0.49-0.44 (m, 2H, Me_3SiCH_2), 0.36 (s, 3H, Me), 0.01 (s, 9H, Me_3Si). ^{13}C NMR (CDCl_3 , δ) Z: 139.3, 133.1, 111.9, 111.1, 7.7, 6.9, -2.1, -4.2; E: 132.5, 131.2, 111.6, 109.6, 8.8, 5.4, -2.4, -5.2. ^{29}Si NMR (CDCl_3 , δ) Z: 8.8, 3.7; E: 6.6, 3.5. ^{77}Se NMR (CDCl_3 , δ) Z: 560.3 (dd, $^2J_{\text{SeH}} = 54.6$ Hz, $^3J_{\text{SeH}} = 14.1$ Hz); E: 523.2 (dd, $^2J_{\text{SeH}} = 53.8$ Hz, $^3J_{\text{SeH}} = 10.3$ Hz).

3.4. Reaction of selenium tetrahalides with diethynyl silanes (**1**)

3.4.1. Interaction of SeCl_4 with 1,1-diethynyl-1-silacyclopentane (**1a**)

To finely-ground elemental Se (0.40 g, 5.1 mg.a) in CHCl_3 (20 ml) under flow of argon and stirring was added for 20 min SO_2Cl_2 (1.36 g, 10.2 mmol) in CHCl_3 (15 ml), stirring was continued at 20 °C for 2 h, the resulting solution was kept overnight. To thus prepared solution of SeCl_4 was added a solution of diethynyl silane **1a** (0.68 g, 5.1 mmol) in CHCl_3 (15 ml) and stirring was continued at 20 °C for 7 h. Removal of the solvent under reduced pressure gave a mixture of 2-dichloromethyl-2,4-dichloro-3,3-tetramethylene-1-selena-3-silacyclopentene-4 (**4a**) and *Z*- and *E*-isomers of **2a** (1.73 g) (Table 1). The attempt to separate this mixture by column chromatography (silica gel, hexane- CH_2Cl_2 , 95:5) failed.

2-Dichloromethyl-2,4-dichloro-3,3-tetramethylene-1-selena-3-silacyclopentene-4 (**4a**). MS (EI, m/z , %) (^{80}Se , ^{35}Cl , ^{28}Si): 318(41) ($\text{M}^+ - \text{HCl}$), 219(6), 202(5), 167(7), 153(24), 143(11), 133(20), 103(12), 78(9), 63(100), 53(44). ^1H NMR (CDCl_3 , δ): 7.22 (s, 1H, $\text{SiCCl}=\text{CHSe}$), 6.44 (s, 1H, $\text{SeCCl}-\text{CHCl}_2$), 1.70 (m, 4H, CH_2CH_2), 1.16 (m, 4H, CH_2Si). ^{13}C NMR (CDCl_3 , δ): 141.5, 136.0, 66.0, 61.7, 27.5, 9.8, 9.4. ^{29}Si NMR (CDCl_3 , δ): 37.4. ^{77}Se NMR (CDCl_3 , δ): 649.4 (d, $^2J_{\text{SeH}} = 50.7$ Hz).

3.4.2. Interaction of SeCl_4 with 1,1-diethynyl-1-silacyclohexane (**1b**)

Similarly, reaction of SeCl_4 (5.1 mmol), prepared in situ from Se (0.40 g, 5.1 mmol) and SO_2Cl_2 (1.20 g, 10 mmol), with diethynyl silane **1b** (0.74 g, 5.0 mmol) in CHCl_3 (30 ml) afforded after 6 h of stirring a mixture of 2-dichloromethyl-2,4-dichloro-3,3-pentamethylene-1-selena-3-silacyclopentene-4 (**4b**) and *Z*- and *E*-isomers of **2b** (1.73 g) (Table 1). Attempts to separate this mixture by column chromatography (silica gel, hexane- CH_2Cl_2 , 95:5) failed.

2-Dichloromethyl-2,4-dichloro-3,3-pentamethylene-1-selena-3-silacyclopentene-4 (**4b**). MS (EI, m/z , %) (^{80}Se , ^{35}Cl , ^{28}Si): 332(58) ($\text{M}^+ - \text{HCl}$), 298(1) ($\text{M}^+ - \text{Cl}_2$), 263(4), 207(1), 179(6), 164(7), 141(10), 117(14), 105(32), 91(28), 79(19), 63(100), 53(33). ^1H NMR (CDCl_3 , δ): 7.20 (s, 1H, $\text{SiCCl}=\text{CHSe}$), 6.35 (s, 1H, $\text{SeCCl}-\text{CHCl}_2$), 2.06, 1.70 (m, 4H, $\text{CH}_2\text{CH}_2\text{Si}$), 1.50 (m, 2H, CH_2), 1.31–0.96 (m, 4H, CH_2Si). ^{13}C NMR (CDCl_3 , δ): 130.6, 118.4, 77.0, 67.3, 28.9, 24.0, 23.9, 10.2, 9.8. ^{29}Si NMR (CDCl_3 , δ): 11.8. ^{77}Se NMR (CDCl_3 , δ): 634.2 (d, $^2J_{\text{SeH}} = 51.2$ Hz).

3.4.3. Interaction of SeCl_4 with dimethyl diethynyl silane (**1d**)

Similarly, reaction of commercial grade SeCl_4 (0.45 g, 2 mmol, Aldrich) with diethynyl silane **1d** afforded for 6 h a mixture of 2-dichloromethyl-2,4-dichloro-3,3-dimethyl-1-selena-3-silacyclopentene-4 (**4d**) and *Z*- and *E*-isomers of **2d** (0.52 g) (Table 1). The attempt to separate this mixture

by column chromatography (silica gel, hexane/ CH_2Cl_2 , 95:5) failed.

2-Dichloromethyl-2,4-dichloro-3,3-dimethyl-1-selena-3-silacyclopentene-4 (**4d**). MS (EI, m/z , %) (^{80}Se , ^{79}Cl , ^{28}Si): 328(10) (M^+), 293(2) ($\text{M}^+ - \text{Cl}$), 258(4) ($\text{M}^+ - \text{Cl}_2$), 245(3), 210(23), 175(6), 165(9), 140(8), 123(5), 113(26), 103(13), 93(100), 83(6), 63(25), 53(13), 43(7). NMR ^1H (CDCl_3 , δ): 7.16 (s, 1H, $\text{SiCCl}=\text{CHSe}$), 6.40 (s, 1H, $\text{SeCCl}-\text{CHCl}_2$), 0.63 (s, 3H, *Me*), 0.36 (s, 3H, *Me*). ^{13}C NMR (CDCl_3 , δ): 131.0, 125.0, 80.4, 78.4, -2.7. ^{29}Si NMR (CDCl_3 , δ): 20.6. ^{77}Se NMR (CDCl_3 , δ): 638.0 (d, $^2J_{\text{SeH}} = 54.0$ Hz).

3.4.4. Interaction of SeBr_4 with 1,1-diethynyl-1-silacyclopentane (**1a**)

To finely-ground elemental Se (0.40 g, 5.1 mg.a) in CHCl_3 (15 ml) was added for 30 min, under argon, Br_2 (1.62 g, 10.1 mmol) in CHCl_3 (15 ml), the mixture was stirred at 20 °C for 5.5 h and then kept overnight. Thus prepared solution of SeBr_4 in CHCl_3 was introduced into a solution of diethynyl silane **1a** (0.68 g, 5.1 mmol) in CHCl_3 (15 ml), under argon, and the reaction mixture was stirred for 7 h at 20 °C. Removal of the solvent in vacuum afforded a mixture of 2-dibromomethyl-2,4-dibromo-3,3-tetramethylene-1-selena-3-silacyclopentene-4 (**5a**) and *Z*- and *E*-isomers of **3a** (2.51 g) (Table 1). Attempts to separate this mixture by column chromatography (silica gel, hexane- CH_2Cl_2 , 95:5) failed.

2-Dibromomethyl-2,4-dibromo-3,3-tetramethylene-1-selena-3-silacyclopentene-4 (**5a**). MS (EI, m/z , %) (^{80}Se , ^{79}Br , ^{28}Si): 450(57) ($\text{M}^+ - \text{HBr}$), 265(23), 239(18), 211(27), 185(15), 133(27), 107(52), 79(74), 53(100). ^1H NMR (CDCl_3 , δ): 7.51 (s, 1H, $\text{SiCBr}=\text{CHSe}$), 6.52 (s, 1H, $\text{SeCBr}-\text{CHBr}_2$), 1.90 (m, 4H, CH_2CH_2), 1.21 (m, 4H, CH_2Si). ^{13}C NMR (CDCl_3 , δ): 133.2, 113.2, 51.1, 48.5, 25.9, 12.1, 9.2. ^{29}Si NMR (CDCl_3 , δ): 30.9. ^{77}Se NMR (CDCl_3 , δ): 607.3 (d, $^2J_{\text{SeH}} = 56.4$ Hz).

3.4.5. Interaction of SeBr_4 with 1,1-diethynyl-1-silacyclohexane (**1b**)

Similarly, reaction of SeBr_4 , prepared in situ from Se (0.40 g, 5 mg.a) and Br_2 (1.60 g, 10 mmol) in CHCl_3 (20 ml), with diethynyl silane **1b** (0.74 g, 5 mmol) in CHCl_3 (20 ml), under argon atmosphere, afforded after 6 h of stirring a mixture of 2-dibromomethyl-2,4-dibromo-3,3-pentamethylene-1-selena-3-silacyclopentene-4 (**5b**) and *Z*- and *E*-isomers of **3b** (2.55 g) (Table 1). Attempted column chromatography on silica gel (hexane- CH_2Cl_2 , 95:5) failed to separate this mixture.

2-Dibromomethyl-2,4-dibromo-3,3-pentamethylene-1-selena-3-silacyclopentene-4 (**5b**). MS (EI, m/z , %) (^{80}Se , ^{79}Br , ^{28}Si): 464(54) ($\text{M}^+ - \text{HBr}$), 408(1), 357(13), 345(1), 133(23), 107(51), 97(100), 77(31), 53(91). ^1H NMR (CDCl_3 , δ): 7.48 (s, 1H, $\text{SiCBr}=\text{CHSe}$), 6.42 (s, 1H, $\text{SeCBr}-\text{CHBr}_2$), 2.11, 1.71 (m, 4H, $\text{CH}_2\text{CH}_2\text{Si}$), 1.40–1.37 (m, 2H, CH_2), 1.25–0.84 (m, 4H, CH_2Si). ^{13}C NMR (CDCl_3 , δ): 111.3, 51.0, 48.4, 28.7, 24.7, 24.1, 12.6, 11.9. ^{29}Si NMR (CDCl_3 , δ): 10.8. ^{77}Se NMR (CDCl_3 , δ): 604.0 (d, $^2J_{\text{SeH}} = 52.3$ Hz).

3.4.6. Interaction of SeBr_4 with methyl 2-trimethylsilylethyl diethynyl silane (**1c**)

Similarly, reaction of SeBr_4 , prepared in situ from Se (0.20 g, 2.53 mg.a) and Br_2 (0.80 g, 5.06 mmol) in CHCl_3 (20 ml), with diethynyl silane **1c** (0.49 g, 2.53 mmol) in CHCl_3 (10 ml), under argon atmosphere, afforded for 1 h a mixture of diastereomers of 2-dibromomethyl-2,4-dibromo-3-methyl-3-[2-(trimethylsilyl)-ethyl]-1-selena-3-silacyclopentene-4 (**5c**) (1.51 g) (Table 1). GC-MS (EI, m/z , %) (^{80}Se , ^{79}Br , ^{28}Si): 2 compounds, 510(3) ($\text{M}^+ - \text{HBr}$), 495(1), 287(3), 225(2), 201(5), 183(2), 161(1), 147(4), 137(3), 107(3), 85(11), 73(100) (Me_3Si^+), 53(4). ^1H NMR (CDCl_3 , δ) major diastereomer: 7.51 (s, 1H, $\text{SiCBr}=\text{CHSe}$), 6.47 (s, 1H, $\text{SeCBr}-\text{CHBr}_2$), 1.12–1.04 (m, 2H, CH_2Si), 0.92–0.80 (m, 2H, Me_3SiCH_2), 0.65 (s, 3H, *Me*), 0.01 (s, 9H, Me_3Si); minor diastereomer: 7.42 (s, 1H, $\text{SiCBr}=\text{CHSe}$), 6.44 (s, 1H, $\text{SeCBr}-\text{CHBr}_2$), 1.12–1.04 (m, 2H, CH_2Si), 0.92–0.80 (m, 2H, Me_3SiCH_2), 0.36 (s, 3H, *Me*), 0.01 (s, 9H, Me_3Si). ^{13}C NMR (CDCl_3 , δ) major diastereomer: 132.9, 113.3, 67.3, 48.3, 8.8, 3.4, –2.1, –3.9; minor diastereomer: 132.5, 112.2, 66.0, 48.9, 8.9, 7.1, –2.1, –8.5. ^{29}Si NMR (CDCl_3 , δ) major diastereomer: 20.7, 3.4; minor diastereomer: 19.3, 3.2. ^{77}Se NMR (CDCl_3 , δ) both diastereomers: 608.7 (d, $^2J_{\text{SeH}} = 55.7$ Hz).

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