

Chemistry of C_6F_5SeLi and C_6F_5SeCl : Precursors to New Pentafluorophenylselenium(II) Compounds

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Z. Naturforsch. **59b**, 547 – 553 (2004); received February 2, 2004

Dedicated to Professor Manfred Adelhelm on the occasion of his 65th birthday

Pentafluorobenzeselenenyl chloride, C_6F_5SeCl , was reacted with various nitrogen and chalcogen substituted trimethylsilyl nucleophiles. The products, C_6F_5SeSCN , C_6F_5SeNSO , $(C_6F_5Se)_2NMe$, $C_6F_5SeN(Me)SiMe_3$, $(C_6F_5Se)_2S$ and $(C_6F_5Se)_2Se$, were characterized by spectroscopic methods. The reaction of C_6F_5SeLi with Me_3XHal compounds gave the products $C_6F_5SeXMe_3$ ($X = Si, Ge, Sn, Pb$). The molecular structure of $(C_6F_5Se)_2S$ has been determined by X-ray diffraction.

Key words: Pentafluorobenzeselenenyl Pseudohalides, Pentafluorophenylselenolate,
Multinuclear NMR Spectroscopy

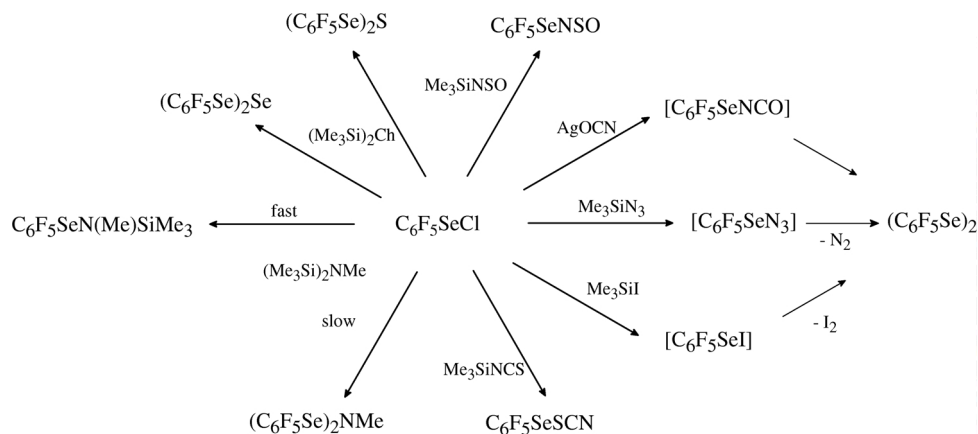
Introduction

The chemistry of pentafluorophenyl selenium species was initiated in the late 60's with the synthesis of the selane $(C_6F_5)_2Se$ and the diselane $(C_6F_5Se)_2$ [1–3]. Recently, we have discovered facile large scale syntheses for C_6F_5Se compounds which employ the starting material C_6F_5SeLi (**1**) and the product of chlorination, C_6F_5SeCl (**2**) [4, 5]. First reactions of **2** with trimethylsilyl nucleophiles furnished C_6F_5SeBr , C_6F_5SeCN and $C_6F_5SeNR_2$ ($R = Me, Et$). In this contribution we report on extended studies of reactions of **2** with various selected nucleophiles, as well as the preparation of trimethyl-Group14-element derivatives of the type $C_6F_5SeXMe_3$ ($X = Si, Ge, Sn, Pb$).

Results and Discussion

Pentafluorobenzeselenenyl chloride C_6F_5SeCl (**2**) is prepared by chlorination of diselane $(C_6F_5Se)_2$, which itself is formed by acidic hydrolysis and subsequent aerial oxidation of C_6F_5SeLi (**1**) [4]. Upon treatment of **2** with selected nucleophiles in dichloromethane as solvent, various new C_6F_5Se derivatives, such as C_6F_5SeSCN (**3**), C_6F_5SeNSO (**4**), $(C_6F_5Se)_2S$ (**5**), $(C_6F_5Se)_2Se$ (**6**), $C_6F_5SeN(Me)SiMe_3$ (**7**), and $(C_6F_5Se)_2NMe$ (**8**) are formed (Scheme 1).

In the reaction of **2** with Me_3SiNCS the question arises, whether a selenenyl isothiocyanate C_6F_5SeNCS , or a selenenyl thiocyanate C_6F_5SeSCN is formed. Based on spectroscopic arguments (^{77}Se NMR shift and vibrational data), we conclude that the selenenyl thiocyanate C_6F_5SeSCN (**3**) is formed. The ^{77}Se NMR resonance of the nitrogen-bound selenenyl isothiocyanate isomer would appear at lower field, in the region found for the other SeN species discussed in this report. Furthermore, the resonance at $\delta = 482$ ppm agrees nicely with that of the sulfur bonded derivative $(C_6F_5Se)_2S$ (**5**), found at $\delta = 510$ ppm. The non-fluorinated analogue, C_6H_5SeSCN , is believed to exist in the thiocyanate form as well, based on infrared data [6, 7]. The selenenyl thiocyanate **3** undergoes complete thermal decomposition into the diselane $(C_6F_5Se)_2$ and insoluble orange-red polymeric thiocyanogen, when heated in a vacuum or in solution. The precipitation of $(SCN)_x$ has also been reported for C_6H_5SeSCN [6] and CF_3SeSCN [8]. The triselane **6** is stable in the solid state, but in solution undergoes rapid elimination of red selenium to form the diselane $(C_6F_5Se)_2$ at ambient temperature. The corresponding sulfane **5** eliminates sulfur in solution after prolonged periods. A reaction between **2** and $(Me_3Si)_2Te$ occurred even at lower temperatures, but immediate tellurium elimina-



Scheme 1.

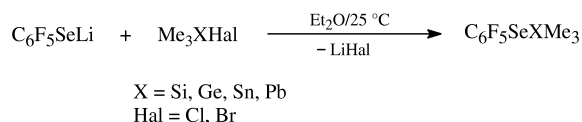
tion and formation of the diselane prevented the detection of (C₆F₅Se)₂Te.

The reactions of **2** with Me₃SiN₃ and AgOCN (Me₃SiNSO does not react) result in very unstable derivatives, C₆F₅SeN₃ and C₆F₅SeNCO, which decompose already at low temperatures into the diselane. A more detailed description of the reaction of Me₃SiN₃ with **2** and with RSeCl compounds in general, is given elsewhere [9]. Of comparable unstable nature as C₆F₅SeNCO is the trifluoromethyl derivative CF₃SeNCO, which is reported to oligomerize [8]. An exact description of the decomposition pathway of C₆F₅SeNCO cannot be given at this time, but at least another C₆F₅SeN species can be identified in the ⁷⁷Se NMR spectrum at δ = 806 ppm with increasing amounts of (C₆F₅Se)₂.

With Me₃SiI a slow reaction was observed, the product being the same as found in the reaction of (C₆F₅Se)₂ with iodine. Attempted separation of the product, “C₆F₅SeI”, resulted in the back reaction (elimination of iodine and formation of the diselane). The exact structure remains unknown. The existence of a labile charge-transfer adduct, (C₆F₅Se)₂·I₂, similar as found in the case of (C₆H₅Se)₂·I₂ [10], is proposed.

Following the reactions of **2** with trimethylsilyl amines Me₃SiNR₂ [4], it was of interest to check the reactivity towards bis(trimethylsilyl) amines (Me₃Si)₂NR and tris(trimethylsilyl) amine (Me₃Si)₃N. A reaction of **2** with (Me₃Si)₂NMe occurs, and depending on reaction time and stoichiometry, the mono-C₆F₅SeN(Me)SiMe₃ (**7**), and the di-substituted product, (C₆F₅Se)₂NMe (**8**), are isolable. No noticeable reaction of **2** was observed with (Me₃Si)₃N.

With trimethyl-group14-element chlorides or bromides, the selenolate C₆F₅SeLi (**1**) can be converted in a facile fashion into the corresponding selanes, C₆F₅SeSiMe₃ (**9**), C₆F₅SeGeMe₃ (**10**), C₆F₅SeSnMe₃ (**11**), and C₆F₅SePbMe₃ (**12**) (Scheme 2).



Scheme 2.

The compounds **9–12** are highly moisture sensitive liquids, which can be distilled and purified in a vacuum without decomposition, except for **12**, which decomposes above 50 °C in a vacuum into C₆F₅SeMe and Me₄Pb. Both products were identified by NMR spectroscopy. The derivatives **9–11**, in particular the silyl selane **9**, should be valuable transfer reagents of the nucleophilic pentafluorophenyl selenolate moiety.

The NMR data of **9–12** are displayed in Table 1. The increase in weight from silicon to lead causes an irregular trend for the ⁷⁷Se NMR shifts and also for the methyl ¹³C NMR resonances. A similar trend occurs for the series of the nonfluorinated analogues C₆H₅SeXMe₃ (X = Si, Ge, Sn, Pb) [11]. All selenium resonances of **9–12** are split into triplets due to coupling with *ortho*-fluorine atoms, and are accompanied by ²⁹Si, ¹¹⁷Sn/¹¹⁹Sn and ²⁰⁷Pb satellites. The ⁷⁷Se NMR spectrum of the plumbyl derivative **12** is shown in Fig. 1.

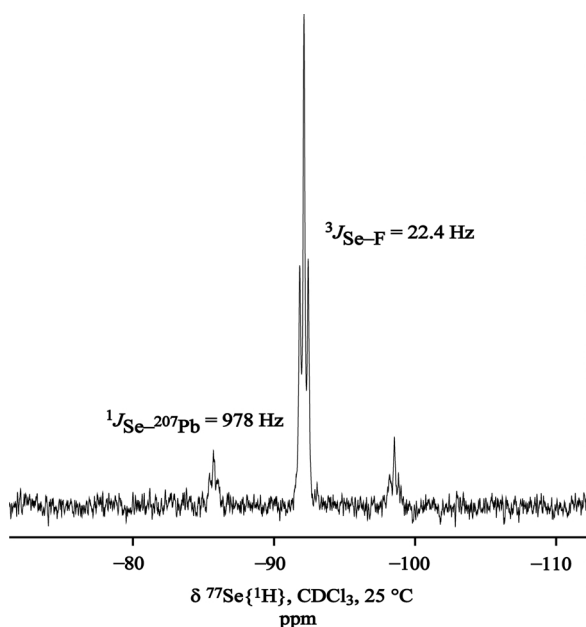
Crystal structure of (C₆F₅Se)₂S (**5**)

The molecular structure of bis(pentafluorobenzene-selenenyl) sulfane (**5**) is shown in Fig. 2. Other known

| | C ₆ F ₅ SeSiMe ₃ 9 | C ₆ F ₅ SeGeMe ₃ 10 | C ₆ F ₅ SeSnMe ₃ 11 | C ₆ F ₅ SePbMe ₃ 12 |
|--|---|--|--|--|
| $\delta^1\text{H}$ | 0.41 ^a | 0.61 | 0.51 | 1.35 |
| $^2J_{\text{H-Si/Sn/Pb}}$ | 4.5 | — | 56.1/53.8 | 61.6 |
| $\delta^{13}\text{C}$ CH ₃ | 1.7 | 3.0 | −3.7 | 9.6 |
| $^1J_{\text{C-Si/Sn/Pb}}$ | 53.0 | — | 343/328 | 235 |
| C-1 | 98.9 | 99.9 | 100.5 ^b | 102.6 |
| $^1J_{\text{C-Se}}$ | 126.8 | 132.2 | 136.1 | 142.6 |
| C-2 | 147.7 | 147.7 | 147.5 | 147.6 |
| $^2J_{\text{C-Se}}$ | 4.6 | 4.6 | 6.9 | 3.8 |
| C-3 | 137.5 ^c | 137.4 | 137.4 | 137.2 |
| C-4 | 140.7 | 140.4 | 139.8 | 139.5 |
| $\delta^{19}\text{F}$ <i>o</i> - | −125.2 | −125.1 | −125.1 | −125.0 |
| <i>p</i> - | −154.4 ^d | −154.9 ^d | −156.2 ^d | −157.1 ^d |
| <i>m</i> - | −161.4 | −161.5 | −161.8 | −162.3 |
| $\delta^{77}\text{Se}$ | −59 | −52 | −135 | −92 |
| $^1J_{\text{Se-Si/Sn/Pb}}$ | 99 | — | 901/860 | 978 |
| $^3J_{\text{Se-F}}$ | 18.4 | 18.9 | 21.3 | 22.4 |
| $\delta^{29}\text{Si}/^{119}\text{Sn}/^{207}\text{Pb}$ | 21.4 | (78) ^e | 92 | 247 |

Table 1. NMR data of **9**–**12** (δ in ppm, J in Hz, CDCl₃, 25 °C).

^a $^6J_{\text{H-F}} = 0.9$ Hz (triplet);
^b $^2J_{\text{C-Sn}} = 22.7$ Hz; ^c $^3J_{\text{C-Se}} = 3.1$ Hz; ^d $^3J_{\text{F-F}} = 20.6$ Hz; ^e ^{73}Ge , extremely broad (ca. 1500 Hz), uncertain.

Fig. 1. ^{77}Se NMR spectrum of **12**.

compounds of this type of which the crystal structure has been determined are [(Me₃Si)₃CSe]₂S [12] and (2-NO₂C₆H₄Se)₂S [13]. The molecule adopts a transoid conformation with respect to the C₂ symmetry at the sulfur atom. The Se–S bond length is with 2.177(1) Å slightly shorter than those in [(Me₃Si)₃CSe]₂S (2.213(1)/2.210(1) Å) and (2-NO₂C₆H₄Se)₂S (2.202(2) Å) and the Se–S–Se(*i*) angle (108.53(7)°) is slightly smaller than those found for the “trisyl” (112.1(1)°) and the *ortho*-nitrophenyl

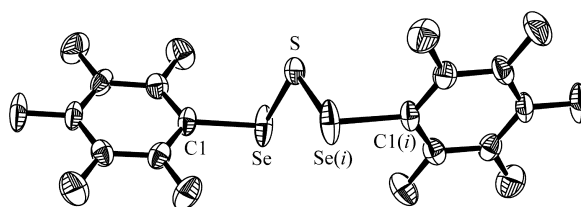


Fig. 2. Molecular structure of (C₆F₅Se)₂S (**5**) with thermal ellipsoids at the 50% probability level (only S, Se and C1 labeled for clarity). Selected bond lengths and angles (Å, °): Se–S 2.177(1), Se–C1 1.915(3), Se–S–Se(*i*) 108.53(7), S–Se–C1 99.7(1), C(1)–Se–S–Se(*i*) 101.9(1), with $i = 1 - x, y, 1/2 - z$.

derivative (111.82(1)°), probably due to the stronger electron-withdrawing effect of the pentafluorophenyl groups. The Se–C bond length (1.915(3) Å) is in the same range as found in other C₆F₅Se(II) compounds (1.90–1.92 Å) [4, 14], but shorter than those of C₆F₅Se(IV) compounds (1.95–1.96 Å) [4, 15].

Experimental Section

All reactions were carried out under dry nitrogen atmosphere with dried solvents. The trimethylsilyl reagents, silver cyanate, and the Me₃ × Hal derivatives were used as received (Aldrich), except for Me₃SiNSO, which was prepared according to the literature [16]. Infrared spectra were recorded as KBr pellets or neat between KBr or CsBr windows on a Nicolet 520 FT-IR spectrometer, Raman spectra on a Perkin-Elmer Spectrum 2000 NIR FT-Raman spectrometer (100 mW). The NMR spectra were obtained on a Jeol 400 Eclipse instrument using CDCl₃ as solvent at 25 °C. The chemical shifts are given with respect to (CH₃)₄Si (^1H , 400.18 MHz; ^{13}C , 100.63 MHz; ^{29}Si , 79.43 MHz), LiCl (^7Li ,

Table 2. Crystal data and structure refinement.

| | (C_6F_5Se) ₂ S |
|---|--|
| Empirical formula | $C_{12}F_{10}SSe_2$ |
| Formula weight | 524.10 |
| Temperature [K] | 200(3) |
| Crystal size [mm] | 0.17 × 0.12 × 0.07 |
| Crystal system | monoclinic |
| Space group | $C2/c$ |
| <i>a</i> [Å] | 29.250(2) |
| <i>b</i> [Å] | 4.8316(3) |
| <i>c</i> [Å] | 10.3548(7) |
| β [°] | 101.743(9) |
| <i>V</i> [Å ³] | 1432.8(2) |
| <i>Z</i> | 4 |
| ρ (calcd.) [g/cm ³] | 2.430 |
| μ_{Mo} [mm ^{−1}] | 5.417 |
| <i>F</i> (000) | 984 |
| θ range [°] | 2.85–25.85 |
| Index ranges | −33 ≤ <i>h</i> ≤ 35, −5 ≤ <i>k</i> ≤ 5, −12 ≤ <i>l</i> ≤ 12 |
| Reflections collected | 3158 |
| Independent reflections | 1290 (R_{int} = 0.0459) |
| Observed reflections | 1040 |
| Data/restraints/parameters | 1290/0/114 |
| Goodness-of-fit on <i>F</i> ² | 1.035 |
| <i>R</i> 1, <i>wR</i> 2 (<i>I</i> > 2 σ (<i>I</i>)) | 0.0352, 0.0959 |
| <i>R</i> 1, <i>wR</i> 2 (all data) | 0.0435, 0.0994 |
| Larg. diff. peak/hole [e/Å ³] | 0.642/−0.542 |

155.37 MHz), CH_3NO_2 ($^{14}/^{15}N$, 28.92/40.56 MHz), $CFCl_3$ (^{19}F , 376.55 MHz), $(CH_3)_4Ge$ (^{73}Ge , 13.96 MHz), $(CH_3)_2Se$ (^{77}Se , 76.36 MHz), $(CH_3)_4Sn$ (^{119}Sn , 149.08 MHz) and $(CH_3)_4Pb$ (^{207}Pb , 83.39 MHz). Mass spectroscopic data were obtained from a JEOL Mstation JMS 700 Spektrometer using the direct EI mode with fragments referring to the nuclei with the highest abundance (for example ^{80}Se). Elemental analyses were performed in-house.

A Stoe IPDS area detector was employed for data collection with Mo- $K\alpha$ radiation. The structure was solved by direct methods SIR97 [17] and refined by means of the full-matrix least squares procedures using SHELXL97 [18] (Table 2). All non-hydrogen atoms were refined anisotropically. Further details are available under the depository number CCDC-229732 from the Cambridge Crystallographic Data Centre.

Preparation of C_6F_5SeLi solution in ether. Into a solution of 30 mmol of pentafluorobenzene in 150 ml of diethylether was added 30 mmol of *n*-BuLi (2.5 M in hexanes) at −70 °C during a period of 1 h and the resulting clear solution of C_6F_5Li stirred for an additional hour at that temperature. A slight excess of selenium (33 mmol) was added in one portion and the mixture allowed to warm up to 0 °C in 2 h. The clear greenish solution of C_6F_5SeLi containing some excess selenium can be reacted with electrophiles as described below. **C_6F_5SeLi (1) in Et_2O .** – ^{19}F NMR: δ = −130.5 (m, 2F, 2-F), −167.7 (m, 2F, 3-F), −168.1 (t, 1F, 4-F, $^3J_{F-F}$ = 19.9 Hz). – $^{13}C\{^{19}F\}$ NMR: δ = 147.7 (C-2), 137.2 (C-

3), 135.8 (C-4), 111.9 (C-1). – ^{77}Se NMR: δ = −119 (t, J_{Se-F} = 27.7 Hz). 7Li NMR: δ = 0.8.

C_6F_5SeCl (2). This compound was prepared on a 50 mmol scale by chlorination of $(C_6F_5Se)_2$ with sulfonyl chloride as described in Ref. [4].

General procedure for the reaction of C_6F_5SeCl with Me_3Si -nucleophiles. Into solutions of 5 mmol of **2** in 10 ml of dichloromethane was added 6 mmol of Me_3SiNCS/Me_3SiNSO , or 3 mmol of $(Me_3Si)_2S/(Me_3Si)_2Se/(Me_3Si)_2NMe$ and the mixture stirred for 2 h at 25 °C. After removal of the volatile materials the liquid residues were distilled in a vacuum where appropriate (**4** and **7**), the solid residues were purified by vacuum sublimation (**5** and **6**), respectively. The compounds **3** and **8** decompose completely upon attempted distillation. Due to the slow reaction with $(Me_3Si)_2NMe$ to give $(C_6F_5Se)_2NMe$ (**8**), it was possible to isolate the monosubstituted product $C_6F_5SeN(Me)SiMe_3$ (**7**) by using an equimolar ratio of **2** and $(Me_3Si)_2NMe$.

C_6F_5SeSCN (3). Orange liquid (74%). – IR (neat): ν = 2150/2082 m (ν_{SCN}), 1634 m, 1591 w, 1514 s, 1492 s, 1422 w, 1397 m, 1376 m, 1346 w, 1286 m, 1257 w, 1148 w, 1105 m, 1089 s, 1034 w, 1011 m, 979 s, 847 w, 821 m, 721 w, 669 w, 625 w, 443 w, 404 w, 381 w, 311 w cm^{−1}. – Raman: ν = 2150 (76, ν_{SCN}), 1634 (22), 1397 (19), 1288 (5), 822 (14), 672 (6), 626 (3), 586 (26), 497 (36), 443 (35), 385 (20), 350 (100, ν_{SeS}), 243 (14), 224 (5), 163 (21), 133 (28) cm^{−1}. – ^{19}F NMR: δ = −123.5 (m, 2F, 2-F), −145.5 (tt, 1F, 4-F, $^3J_{F-F}$ = 20.6, $^4J_{F-F}$ = 5.0 Hz), −158.2 (m, 2F, 3-F). – $^{13}C\{^{19}F\}$ NMR: δ = 147.3 (C-2, $^2J_{C-Se}$ = 9.3 Hz), 144.2 (C-4), 137.5 (C-3, $^3J_{C-Se}$ = 5.0 Hz), 109.6 (SCN, br), 102.2 (C-1, $^1J_{C-Se}$ = 149.9 Hz). – ^{14}N NMR: δ = −98 (br, $\Delta\nu_{1/2}$ = 1000 Hz). – ^{77}Se NMR: δ = 482 (br). – MS *m/z* (%): 261 (12) [$C_6F_5SeN^+$], 247 (100) [$C_6F_5Se^+$], 228 (4) [$C_6F_4Se^+$], 197 (17) [$C_5F_3Se^+$], 155 (25) [$C_5F_3^+$], 117 (14) [$C_5F_3^+$]. – C_7F_5NSe (304.1): calcd. C 27.6, N 4.6; found C 27.6, N 4.7.

C_6F_5SeNSO (4). Yellow-orange liquid (89%), b.p. 31 °C/0.01 mbar. – IR (neat): ν = 1648 w, 1635 m, 1514 s, 1492 s, 1422 w, 1401 m, 1376 w, 1289 m, 1197 s, 1149 w, 1108 m, 1089 s, 1028 w, 1015 m, 978 s, 825 s, 722 w, 634 m, 613 w, 575 w, 498 w, 457 w, 383 w, 343 m, 311 w cm^{−1}. – Raman: ν = 1648 (7), 1636 (22), 1402 (18), 1290 (3), 1197 (8), 1150 (2), 1068 (6), 1013 (100, ν_{NSO}), 826 (11), 635 (9), 615 (5), 587 (39), 498 (38), 456 (32), 444 (20), 386 (20), 359 (8), 247 (14), 222 (6), 183 (6), 136 (31) cm^{−1}. – ^{19}F NMR: δ = −125.7 (m, 2F, 2-F), −147.2 (tt, 1F, 4-F, $^3J_{F-F}$ = 20.5, $^4J_{F-F}$ = 4.3 Hz), −159.2 (m, 2F, 3-F). – $^{13}C\{^{19}F\}$ NMR: δ = 146.0 (C-2, $^2J_{C-Se}$ = 9.2 Hz), 143.7 (C-4), 137.7 (C-3, $^3J_{C-Se}$ = 5.0 Hz), 103.9 (C-1, $^1J_{C-Se}$ = 131.5 Hz). – ^{15}N NMR: δ = −51.9 (J_{N-Se} = 77.6 Hz). – ^{77}Se NMR: δ = 830 (t, J_{Se-F} = 11.8 Hz). – MS *m/z* (%): 309 (42) [M^+], 261 (5) [$M^+ - SO$], 247 (100) [$C_6F_5Se^+$], 228 (5) [$C_6F_4Se^+$],

197 (24) [C₅F₃Se⁺], 155 (32) [C₅F₅⁺], 148 (6) [C₆F₄⁺], 126 (28) [SeNS⁺], 117 (23) [C₅F₃⁺], 93 (11) [C₃F₃⁺], 48 (5) [SO⁺], 46 (11) [SN⁺]. – C₆F₅NOSse (308.1): calcd. C 23.4, N 4.6; found C 23.8, N 4.7.

(C₆F₅Se)₂S (**5**). Yellow crystals (91%), m.p. 79–82 °C. – IR (KBr): ν = 1640 m, 1634 w, 1518 s, 1491 s, 1484 s, 1421 w, 1389 m, 1377 w, 1288 w, 1102 m, 1092 s, 1039 w, 1017 m, 978 s, 969 s, 819 m, 722 w, 626 w, 385 w, 311 w cm⁻¹. – Raman: ν = 1640 (32), 1632 (15), 1521 (2), 1389 (21), 1285 (6), 1141 (2), 1094 (2), 821 (31), 627 (8), 586 (50), 496 (51), 444 (28), 387 (68), 374 (27), 364 (100, ν_{SeSe}), 247 (30), 228 (14), 165 (20), 153 (12), 122 (21) cm⁻¹. – ¹⁹F NMR: δ = –125.3 (m, 2F, 2-F), –149.0 (tt, 1F, 4-F, ³J_{F–F} = 19.9, ⁴J_{F–F} = 3.5 Hz), –159.7 (m, 2F, 3-F). – ¹³C{¹⁹F} NMR: δ = 147.0 (C-2, ²J_{C–Se} = 8.4 Hz), 142.9 (C-4), 137.4 (C-3, ³J_{C–Se} = 5.0 Hz), 104.7 (C-1, ¹J_{C–Se} = 152.2 Hz). – ⁷⁷Se NMR: δ = 510 (tt, ³J_{Se–F} = 20.4, ⁵J_{Se–F} = 9.9 Hz). – MS *m/z* (%): 526 (6) [M⁺], 494 (17) [M⁺–S], 334 (3) [M⁺–S–2Se], 279 (10) [C₆F₅SeS⁺], 247 (76) [C₆F₅Se⁺], 228 (5) [C₆F₄Se⁺], 197 (16) [C₅F₃Se⁺], 167 (100) [C₆F₅⁺], 155 (28) [C₅F₅⁺], 148 (6) [C₆F₄⁺], 117 (22) [C₅F₃⁺], 93 (11) [C₃F₃⁺]. – C₁₂F₁₀SSe₂ (524.1): calcd. C 27.5; found C 27.4.

(C₆F₅Se)₂Se (**6**). Yellow-brown crystals (82%), m.p. 63–66 °C (dec.). – IR (KBr): ν = 1640 m, 1635 w, 1517 s, 1489 s, 1421 w, 1389 m, 1375 w, 1286 w, 1105 m, 1090 s, 1015 w, 978 s, 818 m, 723 w, 625 w, 377 w, 311 w cm⁻¹. – Raman: ν = 1639 (19), 1521 (1), 1389 (13), 1284 (4), 1142 (1), 1105 (1), 820 (22), 626 (5), 586 (30), 496 (30), 444 (17), 388 (21), 359 (9), 272 (100, ν_{SeSe}), 246 (22), 227 (20), 180 (4), 160 (14), 112 (10) cm⁻¹. – ¹⁹F NMR: δ = –125.0 (m, 2F, 2-F), –149.7 (tt, 1F, 4-F, ³J_{F–F} = 20.5, ⁴J_{F–F} = 3.9 Hz), –159.9 (m, 2F, 3-F). – ¹³C NMR: δ = 147.2 (C-2), 143.0 (C-4), 137.4 (C-3), 104.0 (C-1). – ⁷⁷Se NMR: δ = 815 (s, 1Se), 421 (tt, 2Se, ³J_{Se–F} = 21.2, ⁵J_{Se–F} = 8.7 Hz). – MS *m/z* (%): 574 (3) [M⁺], 494 (42) [M⁺–Se], 414 (3) [M⁺–2Se], 334 (7) [M⁺–3Se], 327 (5) [C₆F₅SeSe⁺], 247 (100) [C₆F₅Se⁺], 228 (4) [C₆F₄Se⁺], 197 (19) [C₅F₃Se⁺], 167 (3) [C₆F₅⁺], 155 (23) [C₅F₅⁺], 148 (4) [C₆F₄⁺], 117 (14) [C₅F₃⁺], 93 (5) [C₃F₃⁺]. – C₁₂F₁₀Se₃ (571.0): calcd. C 25.2; found C 25.8.

C₆F₅SeN(Me)SiMe₃ (**7**). Colorless liquid (74%), b.p. 35–40 °C/0.01 mbar. – Raman: ν = 2960 (50), 2903 (100), 2805 (13), 1636 (34), 1447 (8), 1411 (11), 1386 (8), 1249 (5), 1142 (4), 1058 (4), 848 (5), 804 (9), 749 (6), 686 (10), 632 (41), 584 (56), 493 (93), 477 (66), 443 (29), 387 (29), 357 (21), 316 (10), 245 (21), 217 (26), 176 (16), 145 (18) cm⁻¹. – ¹H NMR: δ = 3.10 (t, 3H, NCH₃, ⁶J_{H–F} = 1.3, ³J_{H–Se} = 11.0 Hz), 0.08 (s, 9H, SiCH₃, ²J_{H–Si} = 6.7 Hz). – ¹³C{¹⁹F} NMR: δ = 146.2 (C-2, ²J_{C–Se} = 10.9 Hz), 141.8 (C-4), 137.2 (C-3, ³J_{C–Se} = 5.8 Hz), 107.8 (C-1, ¹J_{C–Se} = 160 Hz), 44.0 (NCH₃), –0.3 (SiCH₃, ³J_{C–Si} = 56.9 Hz). – ¹⁴N NMR: δ = –360 (br). –

¹⁹F NMR: δ = –126.6 (m, 2F, 2-F), –152.2 (t, 1F, 4-F, ³J_{F–F} = 20.8 Hz), –160.8 (m, 2F, 3-F). – ²⁹Si NMR: δ = 18.9 (s, ²J_{Si–Se} = 3 Hz). – ⁷⁷Se NMR: δ = 679 (t, ³J_{Se–F} = 20.7 Hz). – MS *m/z* (%): 349 (54) [M⁺], 334 (19) [M⁺–CH₃], 277 (3) [C₆F₅SeNHCH₃⁺], 247 (11) [C₆F₅Se⁺], 229 (4) [C₆F₄SeH⁺], 197 (4) [C₅F₃Se⁺], 168 (7) [C₆F₅H⁺], 104 (45) [H₂NCH₃Si(CH₃)₃⁺], 73 (44) [Si(CH₃)₃⁺], 58 (39) [HNSiCH₃⁺], 43 (100) [SiCH₃⁺]. – C₁₀H₁₂F₅NSeSi (348.3): calcd. C 34.5, H 3.5, N 4.0; found C 33.8, H 3.1, N 4.1.

(C₆F₅Se)₂NMe (**8**). Pale yellow liquid (45%). – IR (neat): ν = 2938 m, 2894 m, 2786 w, 1635 m, 1512 s, 1486 s, 1441 w, 1387 m, 1284 m, 1145 w, 1086 s, 1044 w, 1013 m, 977 s, 813 m, 723 w, 699 w, 626 w, 395 w, 311 w cm⁻¹. – Raman: ν = 2936 (13), 2790 (6), 1635 (47), 1392 (15), 1285 (6), 1145 (6), 817 (12), 684 (8), 626 (10), 585 (75), 495 (100), 443 (68), 433 (70), 387 (46), 358 (28), 244 (20), 226 (23), 195 (18), 146 (15) cm⁻¹. – ¹H NMR: δ = 3.61 (quin, ⁶J_{H–F} = 0.9, ³J_{H–Se} = 8.6 Hz). – ¹³C{¹⁹F} NMR: δ = 146.0 (C-2, ²J_{C–Se} = 9.5 Hz), 142.9 (C-4), 137.4 (C-3, ³J_{C–Se} = 5.5 Hz), 106.1 (C-1, ¹J_{C–Se} = 163.0 Hz), 60.0 (NCH₃). – ¹⁵N NMR: δ = –365.3. – ¹⁹F NMR: δ = –124.8 (m, 2F, 2-F), –149.1 (tt, 1F, 4-F, ³J_{F–F} = 20.4, ⁴J_{F–F} = 3.9 Hz), –159.8 (m, 2F, 3-F). – ⁷⁷Se NMR: δ = 973 (m). – MS *m/z* (%): 523 (100) [M⁺], 504 (1) [M⁺–F], 494 (3) [M⁺–NCH₃], 276 (43) [C₆F₅SeNCH₃⁺], 247 (97) [C₆F₅Se⁺], 197 (21) [C₅F₃Se⁺], 168 (15) [C₆F₅H⁺], 155 (19) [C₅F₅⁺], 117 (11) [C₅F₃⁺], 93 (5) [C₃F₃⁺]. – C₁₃H₃F₁₀NSe₂ (521.1): calcd. C 30.0, H 0.6, N 2.7; found C 30.0, H 0.7, N 2.8.

Reaction of C₆F₅SeCl with Me₃SiN₃, AgOCN and Me₃SiI. The experiments were carried out as described above and were monitored by ¹⁹F and ⁷⁷Se NMR spectroscopy. The reactions with Me₃SiN₃ and AgOCN proceeded immediately under gas evolution, even at lower temperatures. The reaction with Me₃SiI was rather slow (several weeks), similar to the reaction of (C₆F₅Se)₂ with iodine, nevertheless resulting in the same NMR data.

Spectroscopic data for C₆F₅SeN₃. – ¹⁹F NMR: δ = –124.5 (m, 2F, 2-F), –147.1 (t, 1F, 4-F, ³J_{F–F} = 20.5 Hz), –159.2 (m, 2F, 3-F). – ⁷⁷Se NMR: δ = 911 (br).

Spectroscopic data for C₆F₅SeNCO. – ¹⁹F NMR: δ = –124.5 (m, 2F, 2-F), –146.6 (tt, 1F, 4-F, ³J_{F–F} = 20.8, ⁴J_{F–F} = 5.2 Hz), –159.1 (m, 2F, 3-F). – ⁷⁷Se NMR: δ = 819 (br).

Spectroscopic data for “C₆F₅SeI”. – ¹⁹F NMR: δ = –122.4 (m, 2F, 2-F), –147.8 (tt, 1F, 4-F, ³J_{F–F} = 20.0, ⁴J_{F–F} = 5.2 Hz), –159.6 (m, 2F, 3-F). – ¹³C NMR: δ = 148.3 (C-2), 143.8 (C-4), 137.3 (C-3), 98.3 (C-1). – ⁷⁷Se NMR: δ = 259 (t, ³J_{Se–F} = 22.9 Hz).

Reaction of 1 with trimethyl-group 14-element chlorides/bromides. An ethereal solution of **1** was treated with equimolar amounts of Me₃SiCl, Me₃GeBr, Me₃SnCl, or Me₃PbBr,

respectively, at 0–25 °C. Immediate precipitation of the lithium salts occurred with a color change into slight reddish, while warming to ambient temperature. The salts and still present excess selenium were filtered from the solution. After removal of the solvent the residue was distilled in a vacuum to give the silyl (**9**), germyl (**10**), stannyl (**11**) and plumbyl (**12**) selanes as extremely malodorous liquids, which should be stored at temperatures of ca. –18 °C at which they are crystalline solids. Note: distillation of **12** is not recommended because of nearly complete decomposition.

$C_6F_5SeSiMe_3$ (**9**). Colorless liquid (82%), b.p. 33–35 °C/0.01 mbar. – IR (neat): $\nu = 2963$ m, 2899 w, 1637 m, 1514 s, 1486 s, 1466 m, 1412 m, 1373 w, 1342 w, 1281 w, 1254 s, 1141 w, 1099 m, 1084 s, 1026 m, 1009 m, 976 s, 846 s, 816 s, 757 m, 719 w, 699 m, 626 m, 353 m, 311 w cm^{-1} . – Raman: $\nu = 2962$ (33), 2901 (98), 2789 (3), 1638 (30), 1510 (5), 1413 (12), 1397 (20), 1267 (9), 1251 (6), 1141 (4), 850 (4), 816 (18), 757 (11), 699 (8), 626 (73), 584 (52), 496 (76), 444 (26), 385 (29), 373 (30), 353 (100), 255 (23), 231 (41), 210 (42), 165 (32), 144 (20) cm^{-1} . – MS m/z (%): 320 (69) $[M^+]$, 290 (7) $[M^+ - 2CH_3]$, 247 (30) $[C_6F_5Se^+]$, 197 (12) $[C_5F_3Se^+]$, 168 (66) $[C_6F_5H^+]$, 117 (17) $[C_5F_3^+]$, 73 (100) $[Si(CH_3)_3^+]$, 43 (22) $[SiCH_3^+]$. – $C_9H_9F_5SeSi$ (319.2): calcd. C 33.9, H 2.9; found C 33.9, H 2.8.

$C_6F_5SeGeMe_3$ (**10**). Colorless liquid (73%), b.p. 39 °C/0.01 mbar. – IR (neat): $\nu = 2983$ m, 2909 m, 1636 m, 1510 s, 1484 s, 1411 m, 1372 w, 1342 w, 1281 w, 1241 m, 1140 w, 1082 s, 1008 m, 975 s, 833 m, 816 s, 760 w, 719 w, 612 m, 569 m, 314 w, 263 m, 244 w cm^{-1} . – Raman: $\nu = 2985$ (18), 2912 (50), 1637 (19), 1395 (11), 1251 (10), 815 (9), 613 (26), 584 (48), 569 (100, ν_{SeGe}), 495 (39), 444 (13), 386 (12), 361 (13), 263 (46), 245 (24), 190 (33), 144 (17) cm^{-1} . – MS m/z (%): 366 (9) $[M^+]$, 351 (6) $[M^+ - CH_3]$, 336 (3) $[M^+ - 2CH_3]$, 247 (20) $[C_6F_5Se^+]$, 197 (5) $[C_5F_3Se^+]$, 168 (9) $[C_6F_5H^+]$, 155 (5) $[C_5F_3^+]$, 119 (100) $[Ge(CH_3)_3^+]$, 89 (13) $[GeCH_3^+]$. – $C_9H_9F_5GeSe$ (363.7): calcd. C 29.7, H 2.5; found C 29.9, H 2.6.

$C_6F_5SeSnMe_3$ (**11**). Colorless liquid (90%), b.p. 35–38 °C/0.01 mbar. – IR (neat): $\nu = 2991$ m, 2916 m, 1638 m, 1607 w, 1510 s, 1483 s, 1394 m, 1369 w, 1338 w, 1279 w, 1203 w, 1193 m, 1138 m, 1100 m, 1083 s, 1076 s, 1007 m, 973 s, 908 w, 818 s, 778 s, 718 m, 620 w, 537 s, 510 m, 362 w, 311 w, 228 m cm^{-1} . – Raman: $\nu = 2994$ (8), 2922 (24), 1639 (10), 1509 (2), 1394 (8), 1279 (2), 1202 (16), 819 (6), 584 (22), 538 (28), 512 (100, ν_{SeSn}), 496 (24), 444 (6), 386 (6), 362 (6), 228 (24), 214 (22), 151 (22) cm^{-1} . – MS m/z (%): 412 (9) $[M^+]$, 397 (32) $[M^+ - CH_3]$, 382 (10) $[M^+ - 2CH_3]$, 367 (19) $[C_6F_5SeSn^+]$, 317 (4) $[C_5F_3SeSn^+]$, 247 (10) $[C_6F_5Se^+]$, 165 (100) $[Sn(CH_3)_3^+]$, 135 (34) $[SnCH_3^+]$, 120 (5) $[Sn^+]$. – $C_9H_9F_5SeSn$ (409.9): calcd. C 26.4, H 2.2; found C 26.4, H 2.3.

$C_6F_5SePbMe_3$ (**12**). Colorless liquid (75%), b.p. 42 °C/0.01 mbar (dec.). – IR (neat): $\nu = 3013$ w, 2931 m, 1636 m, 1608 w, 1509 s, 1480 s, 1393 m, 1365 w, 1171 m, 1156 m, 1136 m, 1083 s, 1074 m, 1005 m, 972 s, 817 s, 783 m, 716 w, 619 w, 483 m, 459 m, 312 w, 220 m cm^{-1} . – Raman: $\nu = 3029$ (13), 2932 (22), 1637 (18), 1510 (12), 1391 (16), 1271 (13), 1171 (24), 1156 (22), 817 (17), 584 (27), 484 (49), 460 (100, ν_{SePb}), 386 (17), 365 (16), 241 (17), 194 (27), 139 (20) cm^{-1} . – MS m/z (%): 500 (3) $[M^+]$, 485 (7) $[M^+ - CH_3]$, 455 (23) $[C_6F_5SePb^+]$, 262 (40) $[C_6F_5SeCH_3^+]$, 253 (100) $[Pb(CH_3)_3^+]$, 247 (44) $[C_6F_5Se^+]$, 223 (50) $[PbCH_3^+]$, 208 (52) $[Pb^+]$, 197 (9) $[C_5F_3Se^+]$, 168 (10) $[C_6F_5H^+]$, 155 (11) $[C_5F_3^+]$, 117 (9) $[C_5F_3^+]$, 93 (5) $[C_3F_3^+]$. – $C_9H_9F_5PbSe$ (498.3): calcd. C 21.7, H 1.8; found C 22.6, H 1.8.

Acknowledgements

The University of Munich and the Fonds der Chemischen Industrie are gratefully acknowledged for financial support. We would like to thank Priv.-Doz. Dr. Konstantin Karaghiosoff for a generous supply of $(Me_3Si)_2Ch$ ($Ch = S, Se, Te$) and Prof. Dr. Peter Klüfers for allocation of diffractometer time.

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