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

Thomas M. Klapötke, Burkhard Krumm, and Peter Mayer

Department Chemie, Ludwig-Maximilians-Universität München,
Butenandtstr. 5-13 (D), D-81377 München, Germany

Reprint requests to Prof. Dr. T. M. Klapötke. Fax: +49 (0)89 2180 77492.
E-mail: tmk@cup.uni-muenchen.de

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

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

Pentafluorobenzeneselenenyl 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:* Pentafluorobenzeneselenenyl 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 *C₆F₅Se* 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

Pentafluorobenzeneselenenyl 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 *C₆F₅Se* 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 $C_6F_5Se$ NCS, 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 nonfluorinated 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-

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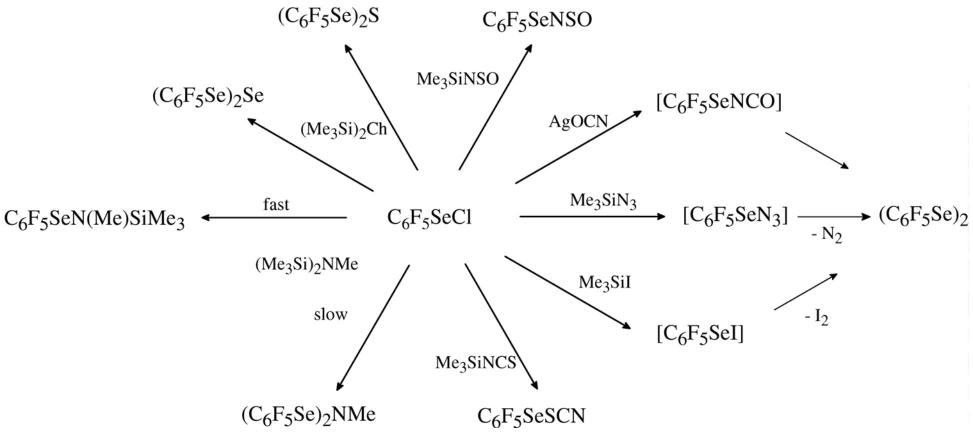

Scheme 1.

tion and formation of the diselane prevented the detection of $(C_6F_5Se)_2Te$.

The reactions of **2** with $Me_3SiN_3$ and AgOCN ($Me_3SiNCO$ does not react) result in very unstable derivatives, $C_6F_5SeN_3$ and $C_6F_5SeNCO$, which decompose already at low temperatures into the diselane. A more detailed description of the reaction of $Me_3SiN_3$ with **2** and with RSeCl compounds in general, is given elsewhere [9]. Of comparable unstable nature as $C_6F_5SeNCO$ is the trifluoromethyl derivative $CF_3SeNCO$, which is reported to oligomerize [8]. An exact description of the decomposition pathway of $C_6F_5SeNCO$ cannot be given at this time, but at least another $C_6F_5SeN$ species can be identified in the $^{77}$Se NMR spectrum at $\delta = 806$ ppm with increasing amounts of $(C_6F_5Se)_2$.

With $Me_3SiI$ a slow reaction was observed, the product being the same as found in the reaction of $(C_6F_5Se)_2$ with iodine. Attempted separation of the product, "$C_6F_5SeI$", 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, $(C_6F_5Se)_2{\cdot}I_2$, similar as found in the case of $(C_6H_5Se)_2{\cdot}I_2$ [10], is proposed.

Following the reactions of **2** with trimethylsilyl amines $Me_3SiNR_2$ [4], it was of interest to check the reactivity towards bis(trimethylsilyl) amines $(Me_3Si)_2NR$ and tris(trimethylsilyl) amine $(Me_3Si)_3N$. A reaction of **2** with $(Me_3Si)_2NMe$ occurs, and depending on reaction time and stoichiometry, the mono- $C_6F_5SeN(Me)SiMe_3$ (**7**), and the di-substituted product, $(C_6F_5Se)_2NMe$ (**8**), are isolable. No noticable reaction of **2** was observed with $(Me_3Si)_3N$.

With trimethyl-group14-element chlorides or bromides, the selenolate $C_6F_5SeLi$ (**1**) can be converted in a facile fashion into the corresponding selanes, $C_6F_5SeSiMe_3$ (**9**), $C_6F_5SeGeMe_3$ (**10**), $C_6F_5SeSnMe_3$ (**11**), and $C_6F_5SePbMe_3$ (**12**) (Scheme 2).

$$C_6F_5SeLi \quad + \quad Me_3XHal \xrightarrow[-\,LiHal]{Et_2O/25\ ^\circ C} C_6F_5SeXMe_3$$

X = Si, Ge, Sn, Pb
Hal = Cl, Br

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 $C_6F_5SeMe$ and $Me_4Pb$. 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 $^{77}$Se NMR shifts and also for the methyl $^{13}$C NMR resonances. A similar trend occurs for the series of the nonfluorinated analogues $C_6H_5SeXMe_3$ (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 $^{29}$Si, $^{117}$Sn/$^{119}$Sn and $^{207}$Pb satellites. The $^{77}$Se NMR spectrum of the plumbyl derivative **12** is shown in Fig. 1.

### *Crystal structure of $(C_6F_5Se)_2S$ (5)*

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

Table 1. NMR data of **9** – **12** ($\delta$ in ppm, $J$ in Hz, $CDCl_3$, 25 °C).

| | $C_6F_5SeSiMe_3$ **9** | $C_6F_5SeGeMe_3$ **10** | $C_6F_5SeSnMe_3$ **11** | $C_6F_5SePbMe_3$ **12** |
|---|---|---|---|---|
| $\delta^1$H | $0.41^a$ | 0.61 | 0.51 | 1.35 |
| $^2J_{\mathrm{H-Si/Sn/Pb}}$ | 4.5 | – | 56.1/53.8 | 61.6 |
| $\delta^{13}$C CH$_3$ | 1.7 | 3.0 | −3.7 | 9.6 |
| $^1J_{\mathrm{C-Si/Sn/Pb}}$ | 53.0 | – | 343/328 | 235 |
| C-1 | 98.9 | 99.9 | $100.5^b$ | 102.6 |
| $^1J_{\mathrm{C-Se}}$ | 126.8 | 132.2 | 136.1 | 142.6 |
| C-2 | 147.7 | 147.7 | 147.5 | 147.6 |
| $^2J_{\mathrm{C-Se}}$ | 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 |
| $\delta^{19}$F *o*- | −125.2 | −125.1 | −125.1 | −125.0 |
| *p*- | $-154.4^d$ | $-154.9^d$ | $-156.2^d$ | $-157.1^d$ |
| *m*- | −161.4 | −161.5 | −161.8 | −162.3 |
| $\delta^{77}$Se | −59 | −52 | −135 | −92 |
| $^1J_{\mathrm{Se-Si/Sn/Pb}}$ | 99 | – | 901/860 | 978 |
| $^3J_{\mathrm{Se-F}}$ | 18.4 | 18.9 | 21.3 | 22.4 |
| $\delta^{29}$Si/$^{119}$Sn/$^{207}$Pb | 21.4 | $(78)^e$ | 92 | 247 |

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

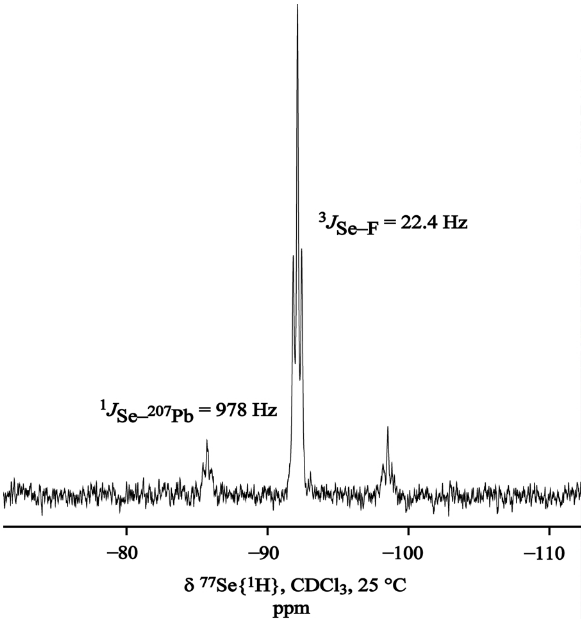

Fig. 1. $^{77}$Se NMR spectrum of **12**.

compounds of this type of which the crystal structure has been determined are $[(Me_3Si)_3CSe]_2S$ [12] and $(2\text{-}NO_2C_6H_4Se)_2S$ [13]. The molecule adopts a transoid conformation with respect to the $C_2$ symmetry at the sulfur atom. The Se–S bond length is with 2.177(1) Å slightly shorter than those in $[(Me_3Si)_3CSe]_2S$ (2.213(1)/2.210(1) Å) and $(2\text{-}NO_2C_6H_4Se)_2S$ (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 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 $C_6F_5$Se(II) compounds (1.90 – 1.92 Å) [4, 14], but shorter than those of $C_6F_5$Se(IV) compounds (1.95 – 1.96 Å) [4, 15].

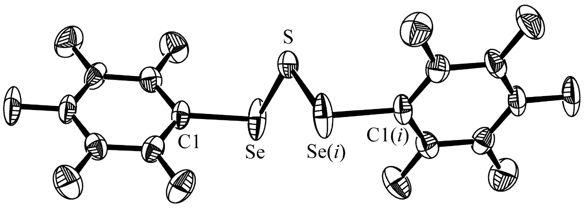

Fig. 2. Molecular structure of $(C_6F_5Se)_2S$ (**5**) with thermal ellipsoids at the 50% probability level (only S, Se and C1 labeled for clarity). Selected bond lengths and angles (Å, °): Se–S 2.177(1), Se–C1 1.915(3), Se–S–Se(*i*) 108.53(7), S–Se–C1 99.7(1), C(1)–Se–S–Se(*i*) 101.9(1), with $i = 1 - x, y, 1\frac{1}{2} - z$.

## Experimental Section

All reactions were carried out under dry nitrogen atmosphere with dried solvents. The trimethylsilyl reagents, silver cyanate, and the $Me_3 \times Hal$ derivates were used as received (Aldrich), except for $Me_3SiNSO$, 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 $CDCl_3$ as solvent at 25 °C. The chemical shifts are given with respect to $(CH_3)_4Si$ ($^1$H, 400.18 MHz; $^{13}$C, 100.63 MHz; $^{29}$Si, 79.43 MHz), LiCl ($^7$Li,

Table 2. Crystal data and structure refinement.

| | $(C_6F_5Se)_2S$ |
|---|---|
| Empirical formula | $C_{12}F_{10}SSe_2$ |
| Formula weight | 524.10 |
| Temperature [K] | 200(3) |
| Crystal size [mm] | $0.17 \times 0.12 \times 0.07$ |
| Crystal system | monoclinic |
| Space group | $C2/c$ |
| $a$ [Å] | 29.250(2) |
| $b$ [Å] | 4.8316(3) |
| $c$ [Å] | 10.3548(7) |
| $\beta$ [°] | 101.743(9) |
| $V$ [Å$^3$] | 1432.8(2) |
| $Z$ | 4 |
| $\rho$ (calcd.) [g/cm$^3$] | 2.430 |
| $\mu_{\text{Mo}}$ [mm$^{-1}$] | 5.417 |
| *F(000)* | 984 |
| $\theta$ range [°] | 2.85 – 25.85 |
| Index ranges | $-33 \le h \le 35$, $-5 \le k \le 5$,<br>$-12 \le l \le 12$ |
| Reflections collected | 3158 |
| Independent reflections | 1290 ($R_{\text{int}} = 0.0459$) |
| Observed reflections | 1040 |
| Data/restraints/parameters | 1290/0/114 |
| Goodness-of-fit on $F^2$ | 1.035 |
| $R1$, $wR2(I > 2\sigma(I))$ | 0.0352, 0.0959 |
| $R1$, $wR2$ (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: $\delta = -130.5$ (m, 2F, 2-F), −167.7 (m, 2F, 3-F), −168.1 (t, 1F, 4-F, $^3J_{\text{F−F}} =$ 19.9 Hz). – $^{13}$C{$^{19}$F} NMR: $\delta = 147.7$ (C-2), 137.2 (C-3), 135.8 (C-4), 111.9 (C-1). – $^{77}$Se NMR: $\delta = -119$ (t, $J_{\text{Se−F}} = 27.7$ Hz). $^7$Li NMR: $\delta = 0.8$.

*$C_6F_5SeCl$ (**2**).* This compound was prepared on a 50 mmol scale by chlorination of $(C_6F_5Se)_2$ with sulfuryl 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): $\nu =$ 2150/2082 m ($\nu_{\text{SCN}}$), 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: $\nu = 2150$ (76, $\nu_{\text{SCN}}$), 1634 (22), 1397 (19), 1288 (5), 822 (14), 672 (6), 626 (3), 586 (26), 497 (36), 443 (35), 385 (20), 350 (100, $\nu_{\text{SeS}}$), 243 (14), 224 (5), 163 (21), 133 (28) cm$^{-1}$. – $^{19}$F NMR: $\delta = -123.5$ (m, 2F, 2-F), −145.5 (tt, 1F, 4-F, $^3J_{\text{F−F}} = 20.6$, $^4J_{\text{F−F}} =$ 5.0 Hz), −158.2 (m, 2F, 3-F). – $^{13}$C{$^{19}$F} NMR: $\delta =$ 147.3 (C-2, $^2J_{\text{C−Se}} = 9.3$ Hz), 144.2 (C-4), 137.5 (C-3, $^3J_{\text{C−Se}} = 5.0$ Hz), 109.6 (SCN, br), 102.2 (C-1, $^1J_{\text{C−Se}} =$ 149.9 Hz). – $^{14}$N NMR: $\delta = -98$ (br, $\Delta\nu_{1/2} = 1000$ Hz). – $^{77}$Se NMR: $\delta = 482$ (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) [$C_5F_5^+$], 117 (14) [$C_5F_3^+$]. – $C_7F_5NSSe$ (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): $\nu = 1648$ 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: $\nu = 1648$ (7), 1636 (22), 1402 (18), 1290 (3), 1197 (8), 1150 (2), 1068 (6), 1013 (100, $\nu_{\text{NSO}}$), 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: $\delta = -125.7$ (m, 2F, 2-F), −147.2 (tt, 1F, 4-F, $^3J_{\text{F−F}} = 20.5$, $^4J_{\text{F−F}} = 4.3$ Hz), −159.2 (m, 2F, 3-F). – $^{13}$C{$^{19}$F} NMR: $\delta = 146.0$ (C-2, $^2J_{\text{C−Se}} = 9.2$ Hz), 143.7 (C-4), 137.7 (C-3, $^3J_{\text{C−Se}} =$ 5.0 Hz), 103.9 (C-1, $^1J_{\text{C−Se}} = 131.5$ Hz). – $^{15}$N NMR: $\delta = -51.9$ ($J_{\text{N−Se}} = 77.6$ Hz). – $^{77}$Se NMR: $\delta = 830$ (t, $J_{\text{Se−F}} = 11.8$ Hz). – MS *m/z* (%): 309 (42) [$M^+$], 261 (5) [$M^+$−SO], 247 (100) [$C_6F_5Se^+$], 228 (5) [$C_6F_4Se^+$],

197 (24) [$C_5F_3Se^+$], 155 (32) [$C_5F_5^+$], 148 (6) [$C_6F_4^+$], 126 (28) [$SeNS^+$], 117 (23) [$C_5F_3^+$], 93 (11) [$C_3F_3^+$], 48 (5) [$SO^+$], 46 (11) [$SN^+$]. – $C_6F_5NOSSe$ (308.1): calcd. C 23.4, N 4.6; found C 23.8, N 4.7.

*$(C_6F_5Se)_2S$* (**5**). Yellow crystals (91%), m.p. 79 – 82 °C. – IR (KBr): $\nu = 1640$ 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: $\nu = 1640$ (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, $\nu_{SSe}$), 247 (30), 228 (14), 165 (20), 153 (12), 122 (21) cm$^{-1}$. – $^{19}F$ NMR: $\delta = -125.3$ (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). – $^{13}C\{^{19}F\}$ NMR: $\delta = 147.0$ (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). – $^{77}Se$ NMR: $\delta = 510$ (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) [$C_6F_5SeS^+$], 247 (76) [$C_6F_5Se^+$], 228 (5) [$C_6F_4Se^+$], 197 (16) [$C_5F_3Se^+$], 167 (100) [$C_6F_5^+$], 155 (28) [$C_5F_5^+$], 148 (6) [$C_6F_4^+$], 117 (22) [$C_5F_3^+$], 93 (11) [$C_3F_3^+$]. – $C_{12}F_{10}SSe_2$ (524.1): calcd. C 27.5; found C 27.4.

*$(C_6F_5Se)_2Se$* (**6**). Yellow-brown crystals (82%), m. p. 63 – 66 °C (dec.). – IR (KBr): $\nu = 1640$ 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: $\nu = 1639$ (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, $\nu_{SeSe}$), 246 (22), 227 (20), 180 (4), 160 (14), 112 (10) cm$^{-1}$. – $^{19}F$ NMR: $\delta = -125.0$ (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). – $^{13}C$ NMR: $\delta = 147.2$ (C-2), 143.0 (C-4), 137.4 (C-3), 104.0 (C-1). – $^{77}Se$ NMR: $\delta = 815$ (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) [$C_6F_5SeSe^+$], 247 (100) [$C_6F_5Se^+$], 228 (4) [$C_6F_4Se^+$], 197 (19) [$C_5F_3Se^+$], 167 (3) [$C_6F_5^+$], 155 (23) [$C_5F_5^+$], 148 (4) [$C_6F_4^+$], 117 (14) [$C_5F_3^+$], 93 (5) [$C_3F_3^+$]. – $C_{12}F_{10}Se_3$ (571.0): calcd. C 25.2; found C 25.8.

*$C_6F_5SeN(Me)SiMe_3$* (**7**). Colorless liquid (74%), b.p. 35 – 40 °C/0.01 mbar. – Raman: $\nu = 2960$ (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: $\delta = 3.10$ (t, 3H, $NCH_3$, $^6J_{H-F} = 1.3$, $^3J_{H-Se} = 11.0$ Hz), 0.08 (s, 9H, $SiCH_3$, $^2J_{H-Si} = 6.7$ Hz). – $^{13}C\{^{19}F\}$ NMR: $\delta = 146.2$ (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 ($NCH_3$), $-0.3$ ($SiCH_3$, $^3J_{C-Si} = 56.9$ Hz). – $^{14}N$ NMR: $\delta = -360$ (br). – $^{19}F$ NMR: $\delta = -126.6$ (m, 2F, 2-F), $-152.2$ (t, 1F, 4-F, $^3J_{F-F} = 20.8$ Hz), $-160.8$ (m, 2F, 3-F). – $^{29}Si$ NMR: $\delta = 18.9$ (s, $^2J_{Si-Se} = 3$ Hz). – $^{77}Se$ NMR: $\delta = 679$ (t, $^3J_{Se-F} = 20.7$ Hz). – MS *m/z* (%): 349 (54) [$M^+$], 334 (19) [$M^+-CH_3$], 277 (3) [$C_6F_5SeNHCH_3^+$], 247 (11) [$C_6F_5Se^+$], 229 (4) [$C_6F_4SeH^+$], 197 (4) [$C_5F_3Se^+$], 168 (7) [$C_6F_5H^+$], 104 (45) [$H_2NCH_3Si(CH_3)_3^+$], 73 (44) [$Si(CH_3)_3^+$], 58 (39) [$HNSiCH_3^+$], 43 (100) [$SiCH_3^+$]. – $C_{10}H_{12}F_5NSeSi$ (348.3): calcd. C 34.5, H 3.5, N 4.0; found C 33.8, H 3.1, N 4.1.

*$(C_6F_5Se)_2NMe$* (**8**). Pale yellow liquid (45%). – IR (neat): $\nu = 2938$ 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: $\nu = 2936$ (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: $\delta = 3.61$ (quin, $^6J_{H-F} = 0.9$, $^3J_{H-Se} = 8.6$ Hz). – $^{13}C\{^{19}F\}$ NMR: $\delta = 146.0$ (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 ($NCH_3$). – $^{15}N$ NMR: $\delta = -365.3$. – $^{19}F$ NMR: $\delta = -124.8$ (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). – $^{77}Se$ NMR: $\delta = 973$ (m). – MS *m/z* (%): 523 (100) [$M^+$], 504 (1) [$M^+-F$], 494 (3) [$M^+-NCH_3$], 276 (43) [$C_6F_5SeNCH_3^+$], 247 (97) [$C_6F_5Se^+$], 197 (21) [$C_5F_3Se^+$], 168 (15) [$C_6F_5H^+$], 155 (19) [$C_5F_5^+$], 117 (11) [$C_5F_3^+$], 93 (5) [$C_3F_3^+$]. – $C_{13}H_3F_{10}NSe_2$ (521.1): calcd. C 30.0, H 0.6, N 2.7; found C 30.0, H 0.7, N 2.8.

*Reaction of $C_6F_5SeCl$ with $Me_3SiN_3$, AgOCN and $Me_3SiI$.* The experiments were carried out as described above and were monitored by $^{19}F$ and $^{77}Se$ NMR spectroscopy. The reactions with $Me_3SiN_3$ and AgOCN proceeded immediately under gas evolution, even at lower temperatures. The reaction with $Me_3SiI$ was rather slow (several weeks), similar to the reaction of $(C_6F_5Se)_2$ with iodine, nevertheless resulting in the same NMR data.

*Spectroscopic data for $C_6F_5SeN_3$.* – $^{19}F$ NMR: $\delta = -124.5$ (m, 2F, 2-F), $-147.1$ (t, 1F, 4-F, $^3J_{F-F} = 20.5$ Hz), $-159.2$ (m, 2F, 3-F). – $^{77}Se$ NMR: $\delta = 911$ (br).

*Spectroscopic data for $C_6F_5SeNCO$.* – $^{19}F$ NMR: $\delta = -124.5$ (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). – $^{77}Se$ NMR: $\delta = 819$ (br).

*Spectroscopic data for "$C_6F_5SeI$".* – $^{19}F$ NMR: $\delta = -122.4$ (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). – $^{13}C$ NMR: $\delta = 148.3$ (C-2), 143.8 (C-4), 137.3 (C-3), 98.3 (C-1). – $^{77}Se$ NMR: $\delta = 259$ (t, $J_{Se-F} = 22.9$ Hz).

*Reaction of* **1** *with trimethyl-group14-element chlorides/bromides.* An ethereal solution of **1** was treated with equimolar amounts of $Me_3SiCl$, $Me_3GeBr$, $Me_3SnCl$, or $Me_3PbBr$, 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, $\nu_{SeGe}$), 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) $[C_5F_5{}^+]$, 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, $\nu_{SeSn}$), 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, $\nu_{SePb}$), 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) $[C_5F_5{}^+]$, 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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