Synthesis, Chemistry, and Characterization of Perfluoroaromatic Selenium Derivatives

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Dedicated to Professor W.-P. Fehlhammer on the occasion of his 60th birthday

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The reaction of perfluoroaryllithium RC_6F_4Li, where R = F or 4-$CF_3C_6F_4O$, respectively, with selenium gives the known diselanes $(RC_6F_4Se)_2$ (**1a**, **1b)**. Redox reactions of **1** with hydrogen peroxide result in the formation of the seleninic acids RC_6F_4SeOOH which crystallize as hydrates (**2a**, **2b**); with mercury give the bis(arylseleno)mercuries $(RC_6F_4Se)_2Hg$ (**3a**, **3b**); with sulfuryl chloride or bromine give the selenenyl chlorides (**4a**, **4b**) or selenenyl bromides (**5a**, **5b**). Selenenyl chlorides (**4a**, **4b**) react with a variety of trimethylsilyl reagents Me_3SiX (X = Br, CN, NMe_2, NEt_2) to form **5a**, **5b**; selenocyanates RC_6F_4SeCN (**6a**, **6b**); selenenyl amides $RC_6F_4SeNMe_2$ (**7a**, **7b**) and $RC_6F_4SeNEt_2$ (**8a**, **8b**). A new synthetic route to diorgano selanes is developed by reaction of **4a**, **4b** with perfluoroaryllithium to give the symmetric $(RC_6F_4)_2Se$ (**9a**, **9b**). All derivatives are thoroughly characterized and in addition the molecular structures of **2a**, **6a**, and **9a** are established by X-ray crystallography.

Introduction

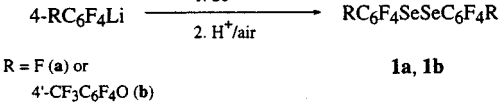
Selenium compounds with perfluorinated substituents have been known for three decades.[1][2] A considerable part consists of selenium species bound to perfluoroalkyl groups, which is reviewed by Haas.[3] However, the chemistry of perfluoroaromatic selenium species is rather limited to a few compounds. The diselanes $C_6F_5SeSeC_6F_5$ and (4-$CF_3C_6F_4)_2Se_2$, as well as the selane $C_6F_5SeC_6F_5$, have been reported to be synthesized by either rather low yield methods and/or requiring high temperatures,[4] or by reaction of the appropriate Grignard R_FMgBr (R_F = C_6F_5 or 4-$CF_3C_6F_4$) where in addition considerable amounts of the unwanted selane $(R_F)_2Se$ are formed.[5] Very recently, a high-yield synthesis of a new diselane [4-(4′-$CF_3C_6F_4O)C_6F_4]_2Se_2$ was reported by reaction of in situ generated 4-(4′-$CF_3C_6F_4O)C_6F_4Li$ with selenium.[6] This method is extended in this report to the synthesis of the known $C_6F_5SeSeC_6F_5$. Our findings show, that in the reaction of C_6F_5MgBr, which is easily formed by reacting C_6F_5Br and magnesium, with selenium no formation of the diselane is observed. This fact is likely to be attributed to the significantly increased reactivity of C_6F_5Li than C_6F_5MgBr towards selenium.

Pentafluorobenzeneselenenyl chloride, C_6F_5SeCl, is reported to be synthesized by chlorination of C_6F_5SeH as well as pentafluorobenzeneseleninic acid, C_6F_5SeOOH, by hydrolysis of $C_6F_5SeCl_3$.[5] The preparation of the bis(arylseleno)mercury $(C_6F_5Se)_2Hg$ is reported to proceed at elevated temperatures.[2] For those materials simplified routes were found and employed.

For some of the mentioned derivatives NMR data have been published.[7–10] The to date only crystal structure of a pentafluorophenylselenium derivative is established for the diselane $C_6F_5SeSeC_6F_5$.[11]

Results and Discussion

Suitable stable starting materials for the chemistry done in this work are the diselanes $C_6F_5SeSeC_6F_5$ (**1a**) and [4-(4′-$CF_3C_6F_4O)C_6F_4]_2Se_2$ (**1b**). As already indicated, they are accessible via the respective aryllithium reagents, generated in situ by lithiation of C_6F_5H, respectively 4-(4′-$CF_3C_6F_4O)C_6F_4H$,[12] with *n*-butyllithium (Scheme 1).



Scheme 1

The diselanes **1a**, **1b** undergo oxidation reactions with hydrogen peroxide, sulfuryl chloride, and bromine to give the seleninic acids **2a**, **2b**, the selenenyl chlorides **4a**, **4b**, and bromides **5a**, **5b**. Reduction with elemental mercury results in the formation of the bis(arylseleno)mercuries **3a**, **3b**. All reactions occur readily at ambient temperature. Sulfuryl chloride and bromine have to be employed in large excess, otherwise the back reaction occurs (Scheme 2).

The selenenyl chlorides **4a**, **4b** are useful precursors for further chemistry at the selenium center.

The trimethylsilyl nucleophiles Me_3SiX (X = Br, CN, NMe_2, NEt_2) react readily at 25°C under loss of trimethyl-

[+] X-ray structure analysis.

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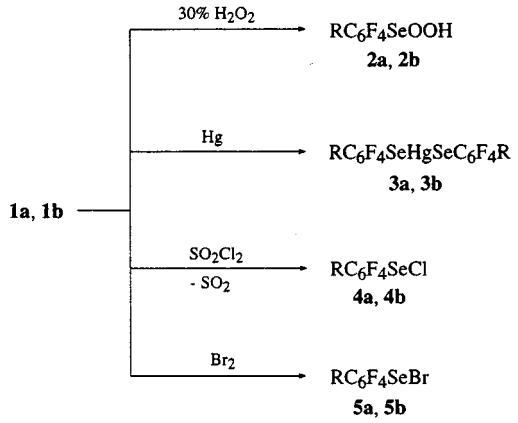
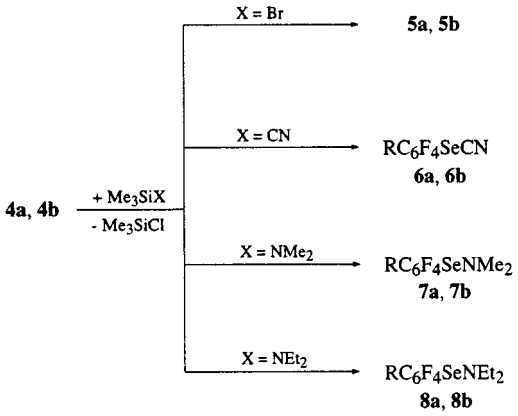


Scheme 2

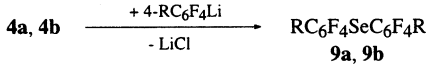
silylchloride to give **5a**, **5b**, the selenocyanates **6a**, **6b**, and the selenenylamides **7a**, **7b** and **8a**, **8b** (Scheme 3).



Scheme 3

Compounds **5**, **7**, and **8** are extremely moisture and light sensitive materials and tend to decompose at 25°C under re-formation of **1**, which can be suppressed by storage in the dark at 0°C. The reaction of **4** with Me_3SiBr displays an alternative route to synthesize **5**.

The reaction of **4a**, **4b** with 4-RC_6F_4Li is a new straightforward synthesis of diorganoselanes, here shown for the symmetric $(C_6F_5)_2Se$ (**9a**) and the new [4-(4′-$CF_3C_6F_4O)C_6F_4]_2Se$ (**9b**) (Scheme 4).



Scheme 4

Spectra

Table 1 illustrates the influence of the substituent attached to selenium for RC_6F_4Se derivatives on the ^{77}Se- and ^{19}F-NMR shift. For ^{19}F NMR are listed the resonances of the *ortho*-fluorine atoms (in 2- and 5-position to Se). In general, the resonances of the aromatic fluorine atoms appear in the ^{19}F-NMR spectrum as parts of AA′BB′, respectively AA′BB′X for C_6F_5Se, patterns. While the *ortho*- and *meta*-fluorine resonances were referred to multiplets, the resonances of the *para*-fluorine atoms in C_6F_5Se derivatives **1a**−**9a** can be solved first order (triplets of triplets, see Experimental Section). Changing from R = F to 4-$CF_3C_6F_4O$ results in a small but significant low field shift of 0.1−0.5 ppm for the *ortho*-fluorine resonances in the ^{19}F-NMR spectrum. This effect is much more pronounced for the ^{77}Se resonances (0−11 ppm). The ^{77}Se resonances are split into triplets due to coupling to the *ortho*-fluorine atoms (pentets for **9a/b**); the value for the $^3J_{SeF}$ coupling constant is in the range 13−28 Hz. A high field shift of the ^{77}Se resonance occurs for the here investigated derivatives in the following order: −SeCl (**4a/b**), $-SeNMe_2$ (**7a/b**), $-SeNEt_2$ (**8a/b**), −SeBr (**5a/b**), −SeSe− (**1a/b**), −SeCN (**6a/b**), −Se− (**9a/b**). A similar tendency is observed and discussed in detail for CF_3Se derivatives.[13] The derivatives −SeOOH (**2a/b**) and −SeHgSe− (**3a/b**) represent the most extreme ^{77}Se-NMR shifts in this work, but are measured in different solvents than the above.

Table 1. ^{77}Se and *ortho*-F ^{19}F-NMR data [ppm] of RC_6F_4Se derivatives, $^3J_{SeF}$ in parentheses [Hz][a]

R	$\delta^{77}Se$ F	$\delta^{77}Se$ 4-$CF_3C_6F_4O$	$\delta^{19}F$ F	$\delta^{19}F$ 4-$CF_3C_6F_4O$
$(RC_6F_4Se)_2$ (**1**)	373 (20.8)	377 (19.7)	−125.6	−125.4
RC_6F_4SeCl (**4**)	801 (20.5)	801 (20.8)	−122.5	−122.3
RC_6F_4SeBr (**5**)	619 (21.6)	617 (21.6)	−122.3	−122.1
RC_6F_4SeCN (**6**)	184 (14.9)	189 (14.6)	−124.4	−124.2
$RC_6F_4SeNMe_2$ (**7**)	768 (26.3)	774 (27.6)	−122.9	−122.8
$RC_6F_4SeNEt_2$ (**8**)	633 (br)	640 (br)	−123.1	−123.0
$(RC_6F_4)_2Se$ (**9**)	122 (14.0)	133 (13.4)	−126.6	−126.4
RC_6F_4SeOOH[b] (**2**)	1215 (br)	1220 (br)	−142.4	−142.1
$(RC_6F_4Se)_2Hg$[c] (**3**)	55 (22.7)	64 (br)	−126.2	−125.7

[a] $CDCl_3$. − [b] CD_3CN. − [c] C_6D_6.

Table 2 summarizes the ^{13}C-NMR data of C_6F_5Se derivatives **1a-9a** (from recording of ^{13}C-NMR data of the $CF_3C_6F_4OC_6F_4Se$ derivatives **1b**−**9b** was refrained due to the increased complexity of the resonances, requiring significantly higher number of accumulations). All resonances are split into multiplets due to couplings to the entire fluorine atoms present in the ring. Remarkable are the shift differences of the resonances of the C-1 carbon atoms, depending on the nature of the substituent bonded to selenium (range of δ = 95−123). The resonances of C-2/3/4 appear mainly at the same position (C-2 δ = ca. 137, C-3 δ = ca. 147 and C-4 δ = ca. 143). The values of the $^nJ_{CF}$ coupling constants are in the range of ca. 2−260 Hz (n = 1−4) (omitted in the Experimental Section). Further NMR characterization include $^{14}N/^{15}N$ NMR data of **6a**, **7a** and **8a**, as well as ^{199}Hg-NMR shifts for **3a/3b** (see Experimental Section).

Additionally to IR spectra the Raman spectra were recorded. In the Raman spectra are some important selenium containing vibrations visible which are difficult to observe in IR. Figure 1 depicts the Raman spectrum of the selenocyanate **6a** as a representative example. The CN stretching frequency is very intense at 2167 cm^{-1} (of medium to weak

Table 2. ^{13}C NMR data [ppm] of C_6F_5Se derivatives[a]

	C-1	C-2	C-3	C-4
$(C_6F_5Se)_2$ (**1a**)	102.9	137.3	147.3	143.1
C_6F_5SeCl (**4a**)	104.3	137.5	147.0	144.6
C_6F_5SeBr (**5a**)	101.8	137.4	147.5	144.3
C_6F_5SeCN[d] (**6a**)	94.9	137.9	146.8	143.9
$C_6F_5SeNMe_2$[e] (**7a**)	99.6	137.2	147.1	142.8
$C_6F_5SeNEt_2$[f] (**8a**)	101.1	137.1	147.4	142.5
$(C_6F_5)_2Se$ (**9a**)	100.5	137.6	147.0	142.7
C_6F_5SeOOH[b] (**2a**)	122.6	138.6	146.5	144.7
$(C_6F_5Se)_2Hg$[c] (**3a**)	100.1	137.8	146.6	140.1

[a] $CDCl_3$. – [b] CD_3CN. – [c] C_6D_6. – [d] $\delta = 97.2$ (SeCN, s, $^1J_{C-Se} = 241.3$ Hz). – [e] $\delta = 52.2$ (SeNC, s, $^2J_{C-Se} = 9.3$ Hz). – [f] $\delta = 54.7$ (SeNC, s, $^2J_{C-Se} = 8.5$ Hz), 14.9 (CH_3, s).

intensity in IR). The frequencies of νSeSe 282 (**1a**)/284 (**1b**) cm^{-1}, νSeCl 398 (**4a**)/375 (**4b**) cm^{-1}, νSeBr 289 (**5a**)/292 (**5b**) cm^{-1}, and νSeN 552 (**7a**) are assigned and appear as the strongest absorptions in Raman and very weak or not observable in IR. The SeN vibration for **8a** is tentatively assigned at 515 cm^{-1}. Definite assignment of the νSeC vibration is not possible.

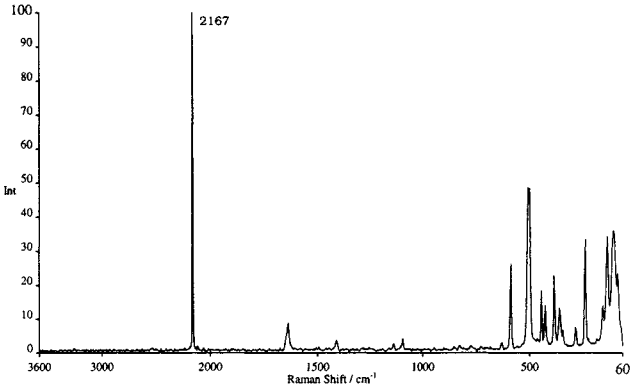


Figure 1. Raman spectrum of **6a**

Crystal Structures

As already indicated, the only crystal structure available of a selenium species having attached a C_6F_5 group, is established for the diselane $C_6F_5SeSeC_6F_5$.[11] The seleninic acid **2a** is recrystallized from water and forms crystals of a monohydrate. A view of the unit cell is shown in Figure 2. Strong hydrogen bonding is present on H(1)···O(3) = 1.76 Å and weak on O(2)···H(3Z) = 2.09 Å. The SeC distance Se(1)−C(1) = 1.962 Å is slightly lengthened compared to regular SeC bonds (see below), probably due to the strong electron-withdrawing effect of the SeOOH moiety. Interestingly, the molecular structure of the nonfluorinated analogue, C_6H_5SeOOH, is anhydrous, though crystallized from water.[14] Here, as well as in *p*-ClC_6H_4SeOOH,[15] strong intermolecular hydrogen bonds between two discrete SeOOH moieties are present.

The structure of the selenocyanate **6a**, shown in Figure 3, consists of two independent molecules. The phenyl rings

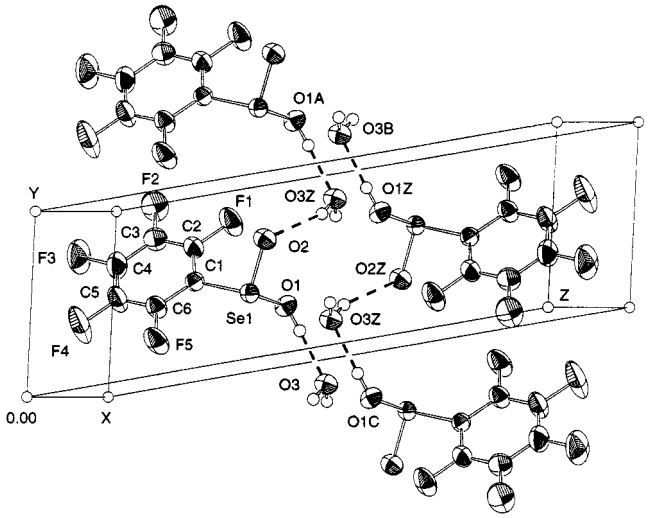


Figure 2. ORTEP plot of **2a** (unit cell); selected bond lengths [Å], angles [°]: Se(1)−O(1) 1.741(3), Se(1)−O(2) 1.638(3), Se(1)−C(1) 1.962(4), O(1)−H(1) 0.82, H(1)···O(3) 1.76, O(2)···H(3Z) 2.09; O(2)−Se(1)−O(1) 102.0(2), O(1)−Se(1)−C(1) 94.2(2), C(6)−C(1)−Se(1) 119.5(3), C(2)−C(1)−Se(1) 122.8(3), C(6)−C(1)−C(2) 117.6(4), F(1)−C(2)−C(1) 120.5(4), F(5)−C(6)−C(1) 119.7(4)

of both molecules are tilt by 35.0° to each other. The out of plane angle between the SeCN moiety and the phenyl ring is 71.5°, respectively 69.9°. There are two short intermolecular contacts involving the Se and N atom in each chain of identical molecules of N(1)···Se(1B) = 2.964 Å and N(1A)···Se(1C′) = 2.957 Å. Between the two independent molecules exist no direct Se···N contacts. The Se(1)−C(7) distance of 1.850 Å, respectively Se(1A)−C(7A) of 1.850 Å, is significantly shorter than a regular SeC bond, than expected, due to the greater contribution of *s* character by the cyano C atom, creating partial double-bond character. The Se(1)−C(1) bond length of 1.920 Å, respectively, Se(1A)−C(1A) of 1.906 Å, represents a typical SeC single bond. The CN bond length for N(1)−C(7) = 1.120 Å, respectively N(1A)−C(7A) = 1.111 Å, is consistent with cyano triple bonds. The only other existing crystal structures of aromatic selenocyanates are of 1,4-diselenocyanatobenzene, *p*-$C_6H_4(SeCN)_2$,[16] and of 3-selenocyanatopyridine, *m*-$C_5H_4N(SeCN)$.[17] Both structures show similar features and intermolecular SeN contacts of 3.06/3.32 Å[16] and 2.84/3.39 Å.[17]

The crystal structure of the selane **9a** is shown in Figure 4. Compound **9a** crystallizes in the noncentrosymmetric space group $P2_1$, allowing the determination of the absolute configuration of the structure. Flack′s parameter refined to −0.006(9) which suggests the correctness of the absolute configuration. The SeC distances Se(1)−C(1) = 1.920 Å, Se(1)−C(7) = 1.903 Å are similar to those found for $C_6F_5SeSeC_6F_5$ 1.899/1.921 Å.[11] The dihedral angle C(2)−C(1)−Se(1)−C(7) is 60.9°; the angle between the planes of both rings is 82.8°. The CSeC angle of 96.61(14)°, is as expected smaller than found for $(C_6F_5)_2S$ [CSC 100.6(5)°][18] and 4-$CF_3C_6F_4OC_6F_5$ [COC 116.2(2)°][12] but larger than found for $(C_6F_5)_2Te$ [CTeC 93.3(5)°].[19]

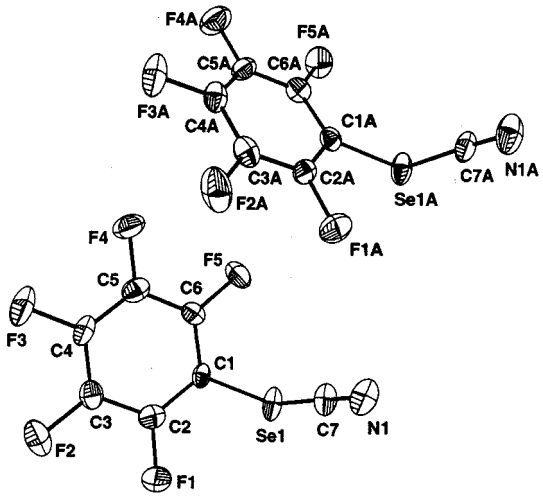


Figure 3. ORTEP plot of **6a**; selected bond lengths [Å], angles [°]: Se(1)−C(7) 1.850(10), Se(1)−C(1) 1.920(7), N(1)−C(7) 1.120(11), Se(1A)−C(7A) 1.856(11), Se(1A)−C(1A) 1.906(8), N(1A)−C(7A) 1.111(12); C(7)−Se(1)−C(1) 95.3(4), N(1)−C(7)−Se(1) 177.4(9), C(7A)−Se(1A)−C(1A) 94.7(4), N(1A)−C(7A)−Se(1A) 175.4(9)

Conclusion

Perfluoroaromatic diselanes, obtained in high yields from perfluoroaromatic lithium reagents, were used to prepare selenenyl chlorides and related derivatives. Further exploration of their synthetic potential is underway.

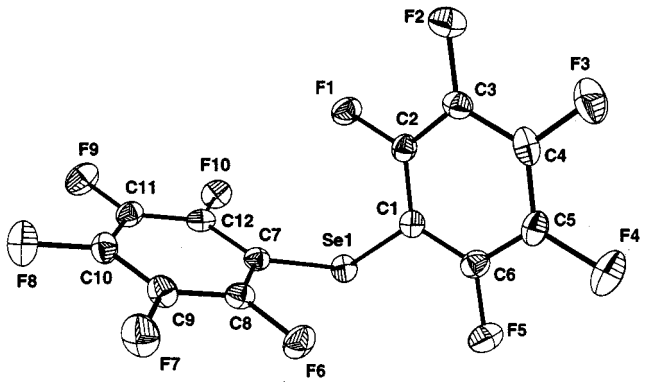


Figure 4. ORTEP plot of **9a**; selected bond lengths [Å], angles [°]: Se(1)−C(1) 1.920(4), Se(1)−C(7) 1.903(4); C(7)−Se(1)−C(1) 96.61(14), C(6)−C(1)−C(2) 117.4(4), C(6)−C(1)−Se(1) 121.0(3), C(2)−C(1)−Se(1) 121.6(3), C(2)−C(1)−Se(1)−C(7) 60.91

Experimental Section

General: The solvents were dried with common methods. Commercially available chemicals were used as received. − NMR: JEOL GSX270 and EX400; chemical shifts are reported with respect to $(CH_3)_4Si$ (^1H, ^{13}C), CH_3NO_2 (^{14}N, ^{15}N), $CFCl_3$ (^{19}F), $(CH_3)_2Se$ (^{77}Se) and $(CH_3)_2Hg$ (^{199}Hg). − IR: Nicolet 520 FT-IR (as KBr pellets or neat liquids). − Raman: Perkin−Elmer Spectrum 2000R NIR FT (Nd: YAG laser, 1064 nm). − MS: Finnigan MAT 90. Multi-isotope containing fragments refer to the isotope with the highest abundance (for example ^{80}Se). − Elemental analyses: C,H,N: in-house; F: Mikroanalytisches Labor Beller, Göttingen. − All reactions are carried out under dry nitrogen atmosphere.

Table 3. Crystal data and structure refinements for **2a**, **6a**, and **9a**

Compound	**2a**	**6a**	**9a**
Empirical Formula	$C_6H_3F_5O_3Se$	C_7F_5NSe	$C_{12}F_{10}Se$
Formula mass	297.04	272.04	413.08
Temperature [K]	293(2)	293(2)	293(2)
Crystal size [mm]	0.40 × 0.30 × 0.27	0.43 × 0.33 × 0.07	0.53 × 0.27 × 0.13
Crystal system	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1$
a [Å]	4.6849(6)	9.946(3)	9.2495(9)
b [Å]	5.3270(8)	5.9196(12)	7.4686(8)
c [Å]	17.427(4)	29.154(9)	9.3933(9)
a [°]	81.42(2)		
β [°]	88.49(2)	98.87(3)	106.508(8)
γ [°]	84.608(12)		
Volume [Å^3]	428.10(13)	1696.0(8)	622.15(11)
Z	2	8	2
ρ (calcd.) [mg/m^3]	2.304	2.131	2.205
μ_{Mo} [mm^{-1}]	4.455	4.466	3.138
F(000)	284	1024	392
θ range [°]	3.55−23.97	2.68−23.97	2.73−23.97
Index ranges	$-5 \le h \le 5$	$0 \le h \le 11$	$-10 \le h \le 10$
	$-6 \le k \le 0$	$0 \le k \le 6$	$-8 \le k \le 8$
	$-19 \le l \le 19$	$-33 \le l \le 32$	$0 \le l \le 10$
Reflections collected	1509	2827	2082
Independent reflections	1343 (R_{int} = 0.0107)	2656 (R_{int} = 0.0374)	1953 (R_{int} = 0.0114)
Observed reflections	1228	1720	1758
Max. and min. transmission	0.9994 and 0.8719	0.9985 and 0.3956	0.9990 and 0.7133
Data/restraints/parameters	1343/0/137	2656/0/253	1953/1/208
Goodness-of-fit on F^2	1.187	1.166	1.039
$R1$, $wR2$ [$I>2\sigma(I)$]	0.0302, 0.0753	0.0582, 0.1106	0.0235, 0.0534
$R1$, $wR2$ (all data)	0.0352, 0.0789	0.0927, 0.1239	0.0300, 0.0577
Larg. Diff. peak/hole [e/Å^3]	0.557/−0.483	0.550/−0.408	0.209/−0.301
Flack parameter			−0.006(9)

X-ray Crystallography: An Enraf Nonius CAD 4 diffractometer was employed for data collection using Mo-K_α radiation. The structures were solved by direct methods (SHELXS86) and were refined by means of the full-matrix least squares procedures using SHELXL93 (Table 3). All nonhydrogen atoms were refined anisotropically. For the hydrogen atoms in **2a** a riding model was employed. Further details of the crystal-structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository numbers CSD-410719, -410718 and -410720 for **2a**, **6a**, and **9a**, respectively.

CAUTION! *Experiments involving perfluoroaromatic lithium reagents should be handled with care, conducted at low temperatures and under strict exclusion of moisture!*

Bis(pentafluorophenyl)diselane (1a): Into a solution of 30 mmol of pentafluorobenzene in 150 mL of anhydrous ether, 30 mmol of *n*BuLi (2.5 M in hexane) is added dropwise at −70°C during a period of 30 min. After 1 h stirring at −70°C, 35.5 mmol of selenium is added in one portion. The resulting mixture is allowed to warm up to ambient temperature within 4 h. 20 mL of 10% HCl and 20 mL of H_2O are added for hydrolysis. After filtration from excess selenium and several extractions with ether/water the combined etheral extracts are dried with anhydrous $MgSO_4$. The etheral solution is stirred for 24 h in the presence of air. After removal of the solvent the residue is sublimed at 40°C/0.01 Torr and yielded orange needles of **1** (81%), m.p. 52−54°C (ref.[5] 49−50°C). − ^{19}F NMR ($CDCl_3$): δ = −125.6 (2-F, m, 2 F), −149.0 (4-F, tt, 1 F, $^3J_{F-F}$ = 20.8 Hz, $^4J_{F-F}$ = 3.5 Hz), −159.7 (3-F, m, 2 F). − IR (KBr): $\tilde{\nu}$ = 1641 m, 1633 m, 1587 w, 1513 s, 1489 s, 1393 m, 1376 m, 1349 w, 1282 m, 1249 w, 1146 m, 1105 m, 1086 s, 1081 s, 1029 w, 1014 m, 974 s, 819 s, 722 w, 626 w, 379 w, 310 w cm^{-1}. − Raman (100 mW): $\tilde{\nu}$ = 1634 (34), 1494 (8), 1395 (32), 1284 (10), 821 (30), 626 (9), 588 (43), 498 (54), 444 (31), 390 (34), 362 (18), 282 (100) [νSeSe], 242 (30), 225 (21), 164 (35), 100 (18) cm^{-1}. − EI MS (70 eV): *m/z* (%) = 494 (28) [M$^+$], 414 (1) [M$^+$ − Se], 334 (13) [M$^+$ − 2 Se], 327 (2) [$C_6F_5Se_2^+$], 247 (100) [$C_6F_5Se^+$], 197 (24) [$C_5F_3Se^+$], 167 (79) [$C_6F_5^+$], 155 (24) [$C_5F_5^+$], 117 (21) [$C_5F_3^+$], 93 (9) [$C_3F_3^+$]. − ^{19}F NMR data in CCl_4 given in ref.[2]; elemental analysis given in ref.[4]

Bis(4-(4′-trifluoromethyl-tetrafluorophenoxy)tetrafluorophenyl)-diselane (1b): 1b is prepared analogously and fully characterized according to ref.[6] − Raman (100 mW): $\tilde{\nu}$ = 1661 (47), 1632 (61), 1489 (6), 1432 (7), 1394 (64), 1344 (6), 1279 (7), 1226 (5), 1142 (5), 878 (5), 825 (22), 801 (9), 719 (18), 656 (6), 642 (8), 539 (16), 498 (82), 443 (30), 389 (42), 361 (13), 284 (100) [νSeSe], 246 (27), 162 (22), 151 (24), 116 (14) cm^{-1}.

Pentafluorobenzeneseleninic Acid Monohydrate (2a), 4-(4′-Trifluoromethyltetrafluorophenoxy)tetrafluorobenzeneseleninic Acid Monohydrate (2b): Into a solution of 1.0 mmol **1a** in 5 mL of CH_2Cl_2 is added 3 mL of H_2O_2 (30% in water). Immediate decolorization occurred and the mixture is stirred for 1 h. After removal of all volatiles in vacuum, the residue is recrystallized from water.

2a is obtained as colorless crystals (80%), m.p. 132−133°C (ref.[5] 123−123.5°C). − ^{1}H NMR (CD_3CN): δ = 3.65 (s). − ^{19}F NMR (CD_3CN): δ = −142.4 (2-F, m, 2 F), −150.6 (4-F, tt, 1 F, $^3J_{F-F}$ = 19.9 Hz, $^4J_{F-F}$ = 5.2 Hz), −161.9 (3-F, m, 2 F). − IR (KBr): $\tilde{\nu}$ = 3480/3258/2900/2408 vbr [νOH], 1672 m, 1640 m, 1588 w, 1521 s, 1486 s, 1470 m, 1385 m, 1379 m, 1349 w, 1294 m, 1276 w, 1110 m, 1099 s, 1040 w, 1016 m, 974 s, 931 m, 862 s, 841 m, 804 w, 756 w, 722 w, 684 m, 622 m, 586 w, 550 w, 495 w, 391 m, 353 m, 318 m, 300 m cm^{-1}. − Raman (100 mW): $\tilde{\nu}$ = 3250 (6), 1640 (22), 1140 (9), 1102 (14), 859 (99), 807 (17), 685 (62), 586 (69), 497 (83), 443 (46), 392 (100), 357 (39), 301 (22), 279 (21), 242 (30), 202 (71), 185 (48), 166 (27), 118 (32) cm^{-1}. − EI MS (70 eV): *m/z* (%) = 264 (19) [$C_6F_5SeOH^+$], 247 (44) [$C_6F_5Se^+$], 197 (9) [$C_5F_3Se^+$], 184 (36) [$C_6F_5OH^+$], 168 (100) [$C_6F_5H^+$], 155 (15) [$C_5F_5^+$], 117 (13) [$C_5F_3^+$], 93 (7) [$C_3F_3^+$]. Elemental analysis given in ref.[5]

2b (colorless powder, 72%, m.p. 152−155°C (dec.) is prepared from **1b** in a similar fashion and recrystallized from acetonitrile/water. − ^{1}H NMR (CD_3CN): δ = 3.52 (s). − ^{19}F NMR (CD_3CN): δ = −57.4 (4′-CF_3, t, 3 F, $^4J_{F-F}$ = 21.7 Hz), −142.1 (2-F, m, 2 F), −142.5 (3′-F, m, 2 F), −155.7 (2′-F, m, 2F), −156.6 (3-F, m, 2 F). − IR (KBr): $\tilde{\nu}$ = 3480 / 2870 / 2413 vbr [νOH], 1661 m, 1635 m, 1512 s, 1489 s, 1430 m, 1390 m, 1350 s, 1278 w, 1234 s, 1192 m, 1153 s, 1125 m, 1029 m, 1003 s, 979 s, 921 w, 878 m, 857 m, 837 m, 795 w, 718 m, 695 m, 643 w, 496 w, 420 w, 373 m, 320 m, 297 w cm^{-1}. − Raman (100 mW): $\tilde{\nu}$ = 1663 (20), 1637 (17), 1490 (7), 1429 (7), 1392 (9), 1352 (8), 1134 (7), 916 (7), 861 (9), 816 (27), 789 (12), 721 (20), 705 (18), 540 (17), 496 (62), 443 (28), 413 (20), 388 (37), 308 (14), 286 (17), 215 (16), 145 (26), 85 (100) cm^{-1}. − EI MS (70 eV): *m/z* (%) = 478 (2) [$CF_3C_6F_4OC_6F_4SeOH^+$], 461 (23) [$CF_3C_6F_4OC_6F_4Se^+$], 382 (100) [$CF_3C_6F_4OC_6F_4H^+$], 363 (39) [382 − F$^+$], 313 (19) [382 − CF_3^+], 244 (6) [$OC_6F_4Se^+$], 217 (7) [$CF_3C_6F_4^+$], 149 (16) [$C_6F_4H^+$], 117 (5) [$C_5F_3^+$]. − $C_{13}H_3F_{11}O_4Se$ (511.12): calcd. C 30.55, H 0.59, F 40.89; found C 30.49, H 0.38, F 40.6.

Bis(pentafluorophenylseleno)- and Bis[4-(4′-trifluoromethyltetrafluorophenoxy)tetrafluorophenylseleno]mercury (3a) and (3b): Into a solution of 1.0 mmol of **1a** in 10 mL of benzene is added 2.2 mmol of mercury. After stirring for 24 h the mixture is filtered from excess mercury. After removal of the solvent, the residue is recrystallized from chloroform to give pale yellow-green crystals **3a**, m.p. 173−175°C (ref.[2] 171−173°C) (86%). − ^{19}F NMR (C_6D_6): δ = −126.2 (2-F, m, 2 F), −156.1 (4-F, t, 1 F, $^3J_{F-F}$ = 21.7 Hz), −161.4 (3-F, m, 2 F). ^{19}F-NMR data in ether given in ref.[2] − ^{199}Hg NMR (C_6D_6): δ = −1562 (s). − IR (KBr): $\tilde{\nu}$ = 1638 m, 1633 m, 1586 w, 1518 s, 1483 s, 1394 m, 1369 m, 1343 w, 1293 w, 1141 m, 1101 m, 1094 m, 1086 m, 1014 m, 972 s, 821 s, 722 w, 622 w, 370 w, 312 w cm^{-1}. − Raman (100 mW): $\tilde{\nu}$ = 1636 (25), 1395 (31), 1289 (10), 824 (42), 625 (11), 588 (45), 499 (47), 445 (27), 396 (33), 373 (16), 364 (19), 284 (8), 243 (42), 228 (19), 202 (100), 177 (47), 151 (31), 100 (24) cm^{-1}. − EI MS (70 eV): *m/z* (%) = 696 (15) [M$^+$], 616 (1) [M$^+$ − Se], 494 (30) [M$^+$ − Hg], 414 (1) [M$^+$ − HgSe], 334 (2) [M$^+$ − Hg − 2 Se], 327 (2) [$C_6F_5Se_2^+$], 247 (100) [$C_6F_5Se^+$], 202 (12) [Hg$^+$], 197 (14) [$C_5F_3Se^+$], 167 (37) [$C_6F_5^+$], 155 (15) [$C_5F_5^+$], 117 (9) [$C_5F_3^+$], 93 (4) [$C_3F_3^+$]. − $C_{12}F_{10}HgSe_2$ (692.63): calcd. C 20.81, F 27.43; found C 20.92, F 27.6.

3b (pale yellow powder, m.p. 175−177 °C (dec.) (71%) is prepared from **1b** in a similar fashion and recrystallized from dichloromethane. − ^{19}F NMR (C_6D_6): δ = −56.4 (4′-CF_3, t, 3 F, $^4J_{F-F}$ = 21.7 Hz), −125.7 (2-F, m, 2 F), −140.8 (3′-F, m, 2 F), −155.9 (2′-F/3-F, m, 4 F). − ^{199}Hg NMR (C_6D_6): δ = −1573 (s). − IR (KBr): $\tilde{\nu}$ = 1658 m, 1630 w, 1513 s, 1483 s, 1430 m, 1394 w, 1352 s, 1273 w, 1232 s, 1193 m, 1160 m, 1127 m, 1026 m, 997 s, 972 m, 879 m, 824 w, 797 w, 719 m, 641 w, 378 w cm^{-1}. − Raman (100 mW): $\tilde{\nu}$ = 1660 (4), 1630 (5), 1394 (5), 826 (4), 725 (3), 540 (4), 503 (15), 440 (6), 394 (15), 280 (6), 245 (13), 226 (9), 198 (47), 148 (24), 83 (100) cm^{-1}. − EI MS (70 eV): *m/z* (%) = 1124 (6) [M$^+$], 1105 (1) [M$^+$ − F], 1044 (2) [M$^+$ − Se], 964 (4) [M$^+$ − 2 Se], 922 (24) [M$^+$ − Hg], 903 (2) [M$^+$ − Hg − F], 842 (4) [M$^+$ − HgSe], 762 (18) [M$^+$ − Hg − 2 Se], 461 (100) [$CF_3C_6F_4OC_6F_4Se^+$], 442 (5) [461 − F$^+$], 381 (74) [$CF_3C_6F_4OC_6F_4H^+$], 362 (29) [381 − F$^+$], 312 (17) [381 − CF_3^+], 244 (14) [$OC_6F_4Se^+$], 228 (6) [$C_6F_4Se^+$], 217 (11) [$CF_3C_6F_4^+$], 202 (42) [Hg$^+$], 148 (13) [$C_6F_4^+$], 117 (11) [$C_5F_3^+$], 69

(7) [CF_3^+]. − $C_{26}F_{22}HgO_2Se_2$ (1120.77): calcd. C 27.86, F 37.30; found C 27.75, F 37.3.

Pentafluorobenzeneselenenyl Chloride (4a), 4-(4′-Trifluoromethyltetrafluorophenoxy)tetrafluorobenzeneselenenyl Chloride (4b): Into a solution of 8.5 mmol of **1a** in 50 mL of CH_2Cl_2 is added 35 mL of sulfuryl chloride and heated 1 h to reflux. Then the solvent and excess sulfuryl chloride is slowly distilled off (under SO_2 evolution and darkening of the solution). The liquid residue is distilled in vacuum, the receiving flask is cooled with ice. Dark red **4a** is obtained in 70% yield, b.p. 25−26°C/0.01 Torr (ref.[5] 80°C/10 Torr). − ^{19}F NMR ($CDCl_3$): δ = −122.5 (2-F, m, 2 F), −145.5 (4-F, tt, 1 F, $^3J_{F-F}$ = 20.8 Hz, $^4J_{F-F}$ = 5.2 Hz), −159.1 (3-F, m, 2 F). − IR (liquid film/KBr): $\tilde{\nu}$ = 1633 m, 1514 s, 1492 s, 1396 m, 1377 w, 1350 w, 1288 m, 1259 w, 1152 w, 1108 m, 1091 s, 1013 w, 980 s, 824 m, 724 w, 627 w, 393 w cm^{-1}. − Raman (100 mW): $\tilde{\nu}$ = 1635 (31), 1494 (4), 1398 (26), 1290 (7), 1152 (4), 826 (20), 588 (37), 499 (51), 444 (22), 398 (100) [νSeCl], 381 (65), 283 (9), 245 (17), 225 (12), 156 (14), 133 (19) cm^{-1}. − EI MS (70 eV): *m/z* (%) = 282 (1) [M^+], 263 (1) [M^+ − F], 247 (100) [$C_6F_5Se^+$], 197 (11) [$C_5F_3Se^+$], 167 (18) [$C_6F_5^+$], 155 (6) [$C_5F_5^+$], 117 (5) [$C_5F_3^+$], 93 (3) [$C_3F_3^+$]. Elemental analysis given in ref.[5]

4b: (red-brown crystals, m.p. 50−52°C) is prepared from **1b** in a similar fashion and purified by sublimation at 40−50°C/0.01 Torr (91%). − ^{19}F NMR ($CDCl_3$): δ = −56.4 (4′-CF_3, t, 3 F, $^4J_{F-F}$ = 21.7 Hz), −122.3 (2-F, m, 2 F), −139.6 (3′-F, m, 2 F), −154.0 (2′-F, m, 2 F), −154.6 (3-F, m, 2 F). − IR (KBr): $\tilde{\nu}$ = 1659 m, 1630 m, 1605 w, 1513 s, 1490 s, 1431 m, 1394 m, 1344 s, 1262 w, 1229 s, 1193 m, 1156 m, 1122 m, 1029 m, 1002 s, 980 s, 877 m, 822 w, 798 w, 717 m, 643 w, 498 w cm^{-1}. − Raman (100 mW): $\tilde{\nu}$ = 1662 (8), 1630 (14), 1483 (2), 1429 (3), 1395 (17), 1348 (3), 1268 (2), 1232 (2), 1145 (3), 1117 (2), 827 (8), 719 (8), 658 (2), 647 (2), 633 (2), 568 (5), 538 (12), 500 (27), 452 (9), 441 (15), 412 (6), 390 (46), 375 (100) [νSeCl], 305 (5), 281 (8), 246 (10), 232 (5), 169 (12), 144 (14), 128 (19) cm^{-1}. − EI MS (70 eV): *m/z* (%) = 496 (9) [M^+], 477 (1) [M^+ − F], 461 (31) [M^+ − Cl], 381 (100) [M^+ − SeCl], 362 (41) [381 − F^+], 312 (23) [381 − CF_3^+], 244 (5) [$OC_6F_4Se^+$], 228 (2) [$C_6F_4Se^+$], 217 (6) [$CF_3C_6F_4^+$], 148 (16) [$C_6F_4^+$], 117 (7) [$C_5F_3^+$], 69 (13) [CF_3^+]. − $C_{13}ClF_{11}OSe$ (495.54): calcd. C 31.51, F 42.18; found C 31.39, F 41.9.

Pentafluorobenzeneselenenyl Bromide (5a), 4-(4′-Trifluoromethyltetrafluorophenoxy)tetrafluorobenzeneselenenyl Bromide (5b): A solution of 25 mmol of bromine in 3 mL of CH_2Cl_2 is added to a solution of 3 mmol of **1a** in 10 mL of CH_2Cl_2 at 25°C. The mixture is stirred for 2 h (^{19}F NMR shows reaction completed after 1 h) and all volatile materials are removed in vacuum at 25°C. The remaining residue is distilled under light exclusion (nevertheless under decomposition) to give **5a** as a black-red liquid, b.p. ca. 38°C/0.01 Torr (59%). The solid yellow residue consisted of the diselane **1a**, which can be recovered and rebrominated to form **5a**.

Alternative procedure: Into a solution of 1.0 mmol of **4a** in 10 mL of CH_2Cl_2 is added 2.0 mmol of Me_3SiBr at 25°C. The mixture is stirred for 10 h and after removal of all volatile materials in vacuum, the residue is distilled under light exclusion to give **5a** (60%). The yellow residue consisted of the diselane **1a**, which can be recovered and recycled to form **4a**.

5a: ^{19}F NMR ($CDCl_3$): δ = −122.3 (2-F, m, 2 F), −146.2 (4-F, tt, 1 F, $^3J_{F-F}$ = 19.9 Hz, $^4J_{F-F}$ = 5.2 Hz), −159.3 (3-F, m, 2 F). − IR (liquid film/KBr): $\tilde{\nu}$ = 1633 m, 1513 s, 1491 s, 1395 m, 1377 w, 1349 w, 1287 m, 1255 w, 1150 w, 1107 m, 1090 s, 1033 w, 1012 m, 980 s, 823 m, 723 w, 626 w cm^{-1}. − Raman (100 mW): $\tilde{\nu}$ = 1633 (25), 1397 (25), 1289 (13), 825 (19), 588 (26), 498 (32), 444 (17), 383 (16), 289 (100) [νSeBr], 243 (17), 223 (15), 153 (14), 119 (14) cm^{-1}. − EI MS (70 eV): *m/z* (%) = 326 (7) [M^+], 247 (100) [$C_6F_5Se^+$], 197 (15) [$C_5F_3Se^+$], 167 (8) [$C_6F_5^+$], 155 (18) [$C_5F_5^+$], 117 (11) [$C_5F_3^+$], 93 (5) [$C_3F_3^+$]. − C_6BrF_5Se (325.92): calcd. C 22.11, F 29.15; found C 22.03, F 29.1.

5b: (chocolate-brown solid, m.p. 64−66°C) is prepared from **1b** (and alternatively **4b**) in a similar fashion and purified by vacuum sublimation (51%). Compound **5b** as well partly decomposes under bromine evolution and formation of **1b** (residue). − ^{19}F NMR ($CDCl_3$): δ = −56.4 (4′-CF_3, t, 3 F, $^4J_{F-F}$ = 21.7 Hz), −122.1 (2-F, m, 2 F), −139.6 (3′-F, m, 2 F), −154.1 (2′-F, m, 2 F), −154.6 (3-F, m, 2 F). − IR (KBr): $\tilde{\nu}$ = 1659 m, 1629 m, 1608 w, 1513 s, 1490 s, 1431 m, 1394 m, 1344 s, 1278 w, 1263 w, 1229 s, 1193 m, 1156 m, 1122 m, 1029 m, 1001 s, 979 s, 877 m, 824 w, 797 w, 717 m, 644 w, 498 w cm^{-1}. − Raman (100 mW): $\tilde{\nu}$ = 1660 (16), 1630 (20), 1429 (5), 1393 (22), 1344 (6), 828 (11), 724 (11), 539 (9), 501 (39), 440 (12), 392 (31), 358 (6), 292 (100) [νSeBr], 279 (17), 245 (15), 160 (12), 141 (16), 127 (12) cm^{-1}. − EI MS (70 eV): *m/z* (%) = 540 (3) [M^+], 461 (14) [M^+ − Br], 381 (100) [M^+ − SeBr], 362 (44) [381 − F^+], 313 (21) [381 − CF_3^+], 217 (4) [$CF_3C_6F_4^+$], 148 (17) [$C_6F_4^+$], 117 (5) [$C_5F_3^+$]. − $C_{13}BrF_{11}OSe$ (539.99): calcd. C 28.91, F 38.70; found C 29.16, F 38.8.

Pentafluorophenylselenocyanate (6a), 4-(4′-Trifluoromethyltetrafluorophenoxy)tetrafluorophenylselenocyanate (6b): Into a solution of 1.5 mmol of **4a** in 5 mL of CH_2Cl_2 is added 2.0 mmol of Me_3SiCN at 25°C. Immediate decolorization occurred and the mixture is stirred for 30 min. After removal of all volatiles in vacuum, the residue is sublimed at 35°C/0.01 Torr. **6a** is obtained as colorless crystals, m.p. 41−42°C (83%). − ^{19}F NMR ($CDCl_3$): δ = −124.4 (2-F, m, 2 F), −146.2 (4-F, tt, 1 F, $^3J_{F-F}$ = 20.8 Hz, $^4J_{F-F}$ = 5.2 Hz), −157.8 (3-F, m, 2 F). − ^{14}N NMR ($CDCl_3$): δ = −91 (br, $\Delta\nu_{1/2}$ = 800 Hz). − ^{15}N NMR ($CDCl_3$): δ = −91.1 (s). − IR (KBr): $\tilde{\nu}$ = 2167 m [νCN], 1646 m, 1638 m, 1589 w, 1519 s, 1493 s, 1409 m, 1379 m, 1352 w, 1293 w, 1255 w, 1147 w, 1108 m, 1096 s, 1083 m, 1015 m, 1006 w, 975 s, 825 s, 722 m, 628 m, 507 m, 426 w, 353 w, 344 w, 312 w cm^{-1}. − Raman (100 mW): $\tilde{\nu}$ = 2167 (100) [νCN], 1639 (9), 1412 (4), 1099 (4), 629 (3), 588 (26), 507 (48), 500 (48), 445 (18), 428 (14), 386 (23), 362 (13), 346 (4), 285 (8), 241 (33), 157 (14), 136 (34), 107 (36) cm^{-1}. − EI MS (70 eV): *m/z* (%) = 273 (100) [M^+], 254 (1) [M^+ − F], 247 (53) [$C_6F_5Se^+$], 197 (26) [$C_5F_3Se^+$], 193 (73) [M^+ − Se], 167 (21) [$C_6F_5^+$], 155 (24) [$C_5F_5^+$], 117 (56) [$C_5F_3^+$], 93 (18) [$C_3F_3^+$], 80 (38) [Se^+]. − C_7F_5NSe (272.04): calcd. C 30.90, F 34.92, N 5.15; found C 30.70, F 35.0, N 5.14.

6b is prepared from **4b** in a similar fashion and obtained as colorless crystals, purified by vacuum sublimation at 70°C/0.01 Torr, m.p. 85−87°C (85%). − ^{19}F NMR ($CDCl_3$): δ = −56.4 (4′-CF_3, t, 3 F, $^4J_{F-F}$ = 21.7 Hz), −124.2 (2-F, m, 2 F), −139.4 (3′-F, m, 2 F), −152.7 (2′-F, m, 2 F), −154.5 (3-F, m, 2 F). − IR (KBr): $\tilde{\nu}$ = 2164 w [νCN], 1660 m, 1632 m, 1519 s, 1497 s, 1431 m, 1406 w, 1343 s, 1280 w, 1228 s, 1197 m, 1158 m, 1126 m, 1029 m, 1005 s, 981 s, 877 m, 828 w, 797 w, 716 m, 644 w, 509 w cm^{-1}. − Raman (100 mW): $\tilde{\nu}$ = 2165 (100) [νCN], 1662 (21), 1633 (16), 1491 (4), 1433 (7), 1406 (12), 1346 (7), 1274 (4), 1228 (4), 1149 (4), 720 (16), 570 (9), 542 (17), 501 (78), 441 (26), 390 (40), 281 (14), 243 (14), 160 (22), 125 (40) cm^{-1}. − EI MS (70 eV): *m/z* (%) = 487 (100) [M^+], 468 (13) [M^+ − F], 461 (89) [M^+ − CN], 407 (69) [M^+ − Se], 381 (20) [M^+ − SeCN], 362 (6) [381 − F^+], 338 (11) [M^+ − Se − CF_3], 254 (34) [$C_6F_4SeCN^+$], 244 (20) [$OC_6F_4Se^+$], 217 (21) [$CF_3C_6F_4^+$], 148 (17) [$C_6F_4^+$], 117 (14) [$C_5F_3^+$]. − $C_{14}F_{11}NOSe$ (486.11): calcd. C 34.59, F 42.99, N 2.88; found C 34.35, F 42.4, N 2.69.

***N,N*-Dimethyl(pentafluorobenzene)selenenylamide (7a), *N,N*-Dimethyl-4-(4′-trifluoromethyltetrafluorophenoxy)tetrafluorobenzene-**

selenenylamide (7b): Into a solution of 2.0 mmol of **4a** in 5 mL of CH_2Cl_2 is added 3.0 mmol of Me_3SiNMe_2 at 25°C. Immediate decolorization occurred and the mixture is stirred for 30 min. After removal of all volatiles in vacuum, the residue is distilled in vacuum. **7a** is obtained as a colorless liquid, b.p. 30−31°C/0.01 Torr (94%). − ^{1}H NMR ($CDCl_3$): δ = 2.79 (CH_3, t, $^6J_{H-F}$ = 1.3 Hz, $^3J_{H-Se}$ = 14.5 Hz). − ^{19}F NMR ($CDCl_3$): δ = −122.9 (2-F, m, 2 F), −149.0 (4-F, t, 1 F, $^3J_{F-F}$ = 20.8 Hz), −160.0 (3-F, m, 2 F). − ^{14}N NMR ($CDCl_3$): δ = −350 (vbr, $\Delta\nu_{1/2}$ = 1300 Hz). − ^{15}N NMR ($CDCl_3$): δ = −352.9 (s). − IR (liquid film/CsBr): $\tilde{\nu}$ = 2989/2936/2860/2824/2784 m [νCH], 1633 m, 1584 w, 1512 s, 1482 s, 1469 m, 1449 m, 1426 w, 1403 w, 1382 m, 1349 w, 1280 m, 1261 w, 1224 w, 1181 m, 1140 m, 1083 s, 1029 m, 1015 m, 975 s, 940 m, 806 m, 723 w, 626 m, 552 m, 493 w, 407 m, 348 w, 332 w, 312 w, 285 w cm^{-1}. − Raman (100 mW): $\tilde{\nu}$ = 2994 (15)/2937 (46)/2881 (13)/2859 (12)/2826 (19)/2783 (25) [νCH], 1634 (28), 1510 (3), 1466 (10), 1447 (11), 1403 (7), 1385 (6), 1272 (4), 1224 (12), 1180 (3), 1140 (6), 1088 (3), 1030 (3), 941 (11), 808 (6), 626 (8), 585 (48), 552 (100) [νSeN], 493 (68), 443 (30), 389 (28), 357 (35), 347 (51), 220 (21), 178 (8), 152 (18), 130 (17) cm^{-1}. − EI MS (70 eV): *m/z* (%) = 291 (3) [M^+], 262 (1) [$C_6F_5SeNH^+$], 247 (10) [$C_6F_5Se^+$], 197 (2) [$C_5F_3Se^+$], 167 (100) [$C_6F_5^+$], 155 (4) [$C_5F_5^+$], 117 (10) [$C_5F_3^+$], 93 (6) [$C_3F_3^+$], 45 (4) [$HN(CH_3)_2^+$]. − $C_8H_6F_5NSe$ (290.11): calcd. C 33.12, H 2.09, N 4.83; found C 32.94, H 2.12, N 4.83.

7b: (colorless solid, m.p. 66−68°C) is prepared from **4b** in a similar fashion and purified by vacuum sublimation at 60°C/0.01 Torr (74%). − ^{1}H NMR ($CDCl_3$): δ = 2.81 (CH_3, t, $^6J_{H-F}$ = 1.2 Hz, $^3J_{H-Se}$ = 14.5 Hz). − ^{19}F NMR ($CDCl_3$): δ = −56.4 (4′-CF_3, t, 3 F, $^4J_{F-F}$ = 21.7 Hz), −122.8 (2-F, m, 2 F), −139.9 (3′-F, m, 2 F), −154.6 (2′-F, m, 2 F), −154.9 (3-F, m, 2 F). − ^{13}C NMR ($CDCl_3$): δ = 52.3 (SeNC, s, $^2J_{C-Se}$ = 9.8 Hz). − IR (KBr): $\tilde{\nu}$ = 3003/2938/2865/2828/2784 w−m [νCH], 1659 m, 1629 m, 1510 s, 1488 s, 1450 w, 1431 m, 1404 w, 1385 w, 1346 s, 1266 w, 1228 s, 1193 m, 1162 s, 1116 m, 1083 s, 1027 m, 1000 s, 977 s, 943 m, 878 m, 812 w, 792 w, 718 m, 698 w, 640 w, 630 w, 553 w, 499 w, 419 m, 350 w cm^{-1}. − Raman (100 mW): $\tilde{\nu}$ = 3001 (27)/2954 (35)/2863 (12)/2831 (21)/2788 (26) [νCH], 1658 (38), 1628 (39), 1465 (12), 1422 (17), 1407 (11), 1382 (15), 1339 (11), 1266 (6), 1222 (19), 1161 (6), 1139 (8), 1029 (6), 940 (23), 879 (5), 810 (13), 789 (6), 761 (7), 719 (26), 699 (14), 645 (20), 629 (11), 558 (88), 538 (33) [νSeN], 496 (100), 451 (28), 439 (47), 420 (19), 393 (44), 384 (54), 349 (78), 322 (21), 270 (22), 199 (12), 158 (23), 140 (31), 117 (35) cm^{-1}. − EI MS (70 eV): *m/z* (%) = 505 (77) [M^+], 486 (6) [M^+ − F], 461 (61) [M^+ − $N(CH_3)_2$], 425 (26) [M^+ − Se], 381 (100) [M^+ − $SeN(CH_3)_2$], 362 (34) [381 − F^+], 312 (12) [381 − CF_3^+], 244 (12) [$OC_6F_4Se^+$], 218 (31) [$CF_3C_6F_4H^+$], 199 (31) [$CF_2C_6F_4H^+$], 149 (21) [$C_6F_4H^+$], 117 (18) [$C_5F_3^+$], 69 (9) [CF_3^+], 45 (17) [$HN(CH_3)_2^+$]. − $C_{15}H_6F_{11}NOSe$ (504.18): calcd. C 35.73, H 1.20, N 2.78; found C 35.60, H 1.29, N 2.82.

***N,N*-Diethyl(pentafluorobenzene)selenenylamide (8a), *N,N*-Diethyl-4-(4′-Trifluoromethyltetrafluorophenoxy)tetrafluorobenzeneselenenylamide (8b):** Compounds **8a** and **8b** are prepared analogously to **7a** and **7b** except using Me_3SiNEt_2. **8a** is obtained as a colorless liquid, b.p. 39−40°C/0.01 Torr (84%). − ^{1}H NMR ($CDCl_3$): δ = 2.78 (CH_2, q, 2 H, $^3J_{H-H}$ = 7.0 Hz), 1.19 (CH_3, t, 3 H). − ^{19}F NMR ($CDCl_3$): δ = −123.1 (2-F, m, 2 F), −149.8 (4-F, tt, 1 F, $^3J_{F-F}$ = 20.8 Hz, $^4J_{F-F}$ = 3.5 Hz), −160.2 (3-F, m, 2 F). − ^{14}N NMR ($CDCl_3$): δ = −310 (vbr, $\Delta\nu_{1/2}$ = 3000 Hz). − ^{15}N NMR ($CDCl_3$): δ = −316.8 (s). − IR (liquid film/CsBr): $\tilde{\nu}$ = 2975/2935/2873/2837 m [νCH], 1634 m, 1582 w, 1511 s, 1482 s, 1447 m, 1378 m, 1359 w, 1337 w, 1279 m, 1264 w, 1174 m, 1154 m, 1140 m, 1130 w, 1087 s, 1028 w, 1014 m, 975 s, 877 w, 817 m, 802 m, 743 m, 722 w, 625 m, 580 w, 513 w, 492 w, 453 w, 429 w, 410 w, 395 w, 314 w, 283 w cm^{-1}. − Raman (100 mW): $\tilde{\nu}$ = 2978 (41)/2938 (88)/2875 (42)/2852 (23) [νCH], 1635 (39), 1449 (31), 1386 (12), 1273 (10), 1056 (16), 1030 (13), 879 (16), 803 (13), 627 (19), 585 (93), 515 (54) [νSeN], 494 (90), 445 (41), 390 (39), 358 (41), 332 (20), 217 (25), 119 (28), 84 (100) cm^{-1}. − EI MS (70 eV): *m/z* (%) = 319 (53) [M^+], 304 (100) [M^+ − CH_3], 247 (49) [$C_6F_5Se^+$], 197 (8) [$C_5F_3Se^+$], 167 (22) [$C_6F_5^+$], 155 (10) [$C_5F_5^+$], 117 (6) [$C_5F_3^+$], 93 (3) [$C_3F_3^+$]. − $C_{10}H_{10}F_5NSe$ (318.17): calcd. C 37.75, H 3.17, N 4.40; found C 37.22, H 3.31, N 4.41.

8b is obtained as a colorless solid, m.p. 47−48°C, purified by vacuum sublimation at 40°C/0.01 Torr (90%). − ^{1}H NMR ($CDCl_3$): δ = 2.80 (CH_2, q, 2 H, $^3J_{H-H}$ = 6.9 Hz), 1.18 (CH_3, t, 3 H). − ^{19}F NMR ($CDCl_3$): δ = −56.4 (4′-CF_3, t, 3 F, $^4J_{F-F}$ = 21.7 Hz), −123.0 (2-F, m, 2 F), −140.0 (3′-F, m, 2 F), −154.8 (2′-F, m, 2 F), −155.0 (3-F, m, 2 F). − ^{13}C NMR ($CDCl_3$): δ = 54.8 (SeNC, s, $^2J_{C-Se}$ = 7.6 Hz), 14.9 (CH_3, s). − IR (KBr): $\tilde{\nu}$ = 2983 / 2937 / 2872 / 2849 w-m [νCH], 1660 m, 1629 m, 1512 s, 1486 s, 1446 w, 1425 m, 1400 w, 1382 m, 1348 s, 1262 w, 1229 s, 1191 m, 1155 m, 1117 m, 1080 w, 1061 w, 1025 m, 999 s, 978 s, 879 m, 810 m, 793 m, 718 m, 689 w, 647 w, 631 w, 513 w, 495 w, 447 w, 429 m, 374 w cm^{-1}. − EI MS (70 eV): *m/z* (%) = 533 (50) [M^+], 518 (100) [M^+ − CH_3], 461 (76) [M^+ − $N(CH_2CH_3)_2$], 381 (55) [M^+ − $SeN(CH_2CH_3)_2$], 362 (21) [381 − F^+], 312 (11) [381 − CF_3^+], 244 (10) [$OC_6F_4Se^+$], 217 (7) [$CF_3C_6F_4^+$], 198 (8) [$CF_2C_6F_4^+$], 148 (9) [$C_6F_4^+$], 117 (6) [$C_5F_3^+$], 73 (31) [$HN(CH_2CH_3)_2^+$]. − $C_{17}H_{10}F_{11}NOSe$ (532.24): calcd. C 38.36, H 1.90, N 2.63; found C 37.66, H 1.83, N 2.45.

Bis(pentafluorophenyl)selane (9a), Bis[4-(4′-trifluoromethyltetrafluorophenoxy)tetrafluorophenyl]selane (9b): Into a stirred solution of 2.0 mmol of C_6F_5Li in ether (see prep. of **1a**), 2.0 mmol of **4a** is added at −70°C. Immediate decolorization of the deep red **4a** occurs and resulted in an almost colorless solution. The mixture is stirred for 1 h and then slowly warmed to ambient temperature; then the lithium chloride precipitated. After evacuation of all volatile material the residue is sublimed at 40−50°C/0.01 Torr. Colorless crystals in X-ray diffraction quality are obtained in 61% yield, m.p. 76−77°C (ref.[4] 71−72°C). − ^{19}F NMR ($CDCl_3$): δ = −126.6 (2-F, m, 2 F), −150.0 (4-F, tt, 1 F, $^3J_{F-F}$ = 20.8 Hz, $^4J_{F-F}$ = 3.5 Hz), −159.7 (3-F, m, 2 F). − IR (KBr): $\tilde{\nu}$ = 1640 m, 1588 w, 1519 s, 1511 s, 1490 s, 1398 m, 1378 m, 1353 w, 1341 w, 1288 m, 1153 m, 1113 m, 1092 s, 1047 w, 1016 m, 1003 m, 972 s, 827 m, 817 s, 722 w, 631 m, 619 w, 394 m, 363 w, 313 m cm^{-1}. − Raman (100 mW): $\tilde{\nu}$ = 1639 (42), 1516 (5), 1445 (5), 1404 (19), 1305 (5), 1275 (11), 1255 (7), 1142 (8), 1090 (6), 975 (4), 827 (18), 770 (6), 721 (6), 632 (10), 586 (79), 498 (100), 445 (62), 386 (61), 362 (39), 284 (16), 252 (22), 225 (22), 184 (10), 161 (21), 137 (21), 120 (13), 100 (19) cm^{-1}. ^{19}F-NMR data in CCl_4 and mass spectrum given in ref.[2]; elemental analysis given in ref.[4]

9b: (colorless solid, m.p. 122−124°C) is prepared in a similar fashion by reaction of **4b** with $CF_3C_6F_4OC_6F_4Li$ and purified by vacuum sublimation at 100°C/0.01 Torr (47%). − ^{19}F NMR ($CDCl_3$): δ = −56.4 (4′-CF_3, t, 3 F, $^4J_{F-F}$ = 21.7 Hz), −126.4 (2-F, m, 2 F), −139.7 (3′-F, m, 2 F), −154.2 (2′-F, m, 2 F), −154.7 (3-F, m, 2 F). − IR (KBr): $\tilde{\nu}$ = 1659 m, 1630 m, 1508 s, 1495 s, 1485 s, 1431 m, 1397 w, 1350 s, 1342 s, 1278 w, 1227 s, 1189 m, 1154 m, 1111 m, 1028 m, 1001 m, 994 s, 973 s, 878 m, 822 w, 795 w, 718 m, 701 w, 640 w, 499 w, 420 w, 376 w cm^{-1}. − Raman (100 mW): $\tilde{\nu}$ = 1660 (43), 1631 (42), 1431 (22), 1404 (32), 1350 (19), 1226 (17), 1028 (15), 828 (18), 771 (16), 737 (16), 719 (36), 703 (16), 651 (16), 571 (22), 538 (38), 499 (100), 452 (34), 438 (51), 392 (75), 357 (22), 306 (24), 251 (26), 224 (17), 200 (17), 143 (34), 129 (24) cm^{-1}. − EI MS (70 eV): *m/z* (%) = 842 (100) [M^+], 823

(10) [$M^+ - F$], 762 (12) [$M^+ - Se$], 545 (7) [762 − $CF_3C_6F_4^+$], 461 (12) [$CF_3C_6F_4OC_6F_4Se^+$], 362 (3) [$CF_2C_6F_4OC_6F_4^+$], 244 (6) [$OC_6F_4Se^+$], 217 (4) [$CF_3C_6F_4^+$], 148 (3) [$C_6F_4^+$], 117 (2) [$C_5F_3^+$]. − $C_{26}F_{22}O_2Se$ (841.22): calcd. C 37.12, F 49.69; found C 37.56, F 49.7.

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