

First Detection of a Selenenyl Fluoride ArSe–F by NMR Spectroscopy: The Nature of Ar₂Se₂/XeF₂ and ArSe–SiMe₃/XeF₂ Reagents

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Abstract: Arylselenenyl fluorides ArSeF are obtained from diselenides Ar₂Se₂ or arylselenotrimethylsilanes ArSe–SiMe₃, and XeF₂. They are detected by low-temperature ¹⁹F and ⁷⁷Se NMR spectroscopy. Substitution in the *ortho* position of the aromatic ring to provide electronic or steric protection is a requirement for their formation. ArSe–F compounds decompose ac-

ording to 3 ArSe–F → [ArSe–SeF₂Ar] + ArSe–F → ArSeF₃ + Ar₂Se₂. Reaction energies for this disproportionation as well as that of the sulfur and

tellurium homologues have been calculated with MP2, CCSD(T), and B3LYP methods. They were found to be increasingly exothermic in the sequence S < Se < Te. For selected Se–C and Se–F compounds the ⁷⁷Se and ¹⁹F chemical shifts have been calculated by GIAO-MP2 and GIAO-B3LYP methods and are in good agreement with experimental values.

Keywords: ab initio calculations • density functional calculations • fluorine • NMR spectroscopy • selenium

Introduction

Selenenyl chlorides and bromides RSe–Cl and RSe–Br are stable compounds, PhSe–Cl and PhSe–Br are even commercial products. However, selenenyl iodides can only be obtained if an organic group, such as 2,4,6-tri-*tert*-butyl-phenyl^[1] or (Me₃Si)₃C[–],^[2] provides substantial steric protection. Without steric protection no organoselenenyl iodides are formed, for example, the Ph₂Se₂/I₂ reagent^[3] is a charge-transfer complex with intact Se–Se and I–I bonds.^[4] No selenenyl fluoride has been obtained so far. SeF₄,^[5] SeF₂, and Se₂F₂^[6] have only been detected in low-temperature matrices. But the Ph₂Se₂/XeF₂ reagent acts as a PhSe–F equivalent in addition reactions with alkenes and acetylenes.^[7–12] PhSe–F equivalents are also generated from PhSe–EMe₃ (E = Si, Ge, Sn, Pb) and XeF₂^[13] or from PhSeOTf/Et₃N·3 HF.^[14] Also the combinations PhSe–Br/AgF/ultrasound,^[15] PhSe–Cl/AgF/CH₃CN,^[16] *N*-phenylselenophthalimide (NPSp)/Py·9 HF,^[17] or NPSp/Et₃N·3 HF^[18] and electrooxidation of Ph₂Se₂ in Et₃N·3 HF^[19] act as PhSe–F equivalents. None of these procedures offer more detailed information about the nature of the reacting species.

The aim of this study was to achieve a detailed characterization of the intermediates generated from Ar₂Se₂ or ArSe–SiMe₃ and XeF₂ in the molar ratio 1:1.

Results and Discussion

The ¹⁹F and ⁷⁷Se NMR chemical shifts of the unknown ArSe–F compounds can be estimated with a certain accuracy. Sulfenyl fluorides exhibit extreme ¹⁹F chemical shifts of $\delta = -250$ to -360 ppm,^[20] and sulfur and selenium fluorides have surprisingly similar chemical shifts. A linear correlation between $\delta(^{77}\text{Se})$ and the electronegativity χ of X for CF₃Se–X compounds results in an extrapolated ⁷⁷Se chemical shift of $\delta = 1687$ ppm for unknown CF₃Se–F.^[21] A similar extrapolation for PhSe–X^[21,22] (X = Cl, Br, CN, H, $\delta(^{77}\text{Se}) = 981.7\chi - 2053.5$, χ values^[23]) results in $\delta(^{77}\text{Se}) = 1775$ ppm for PhSe–F.

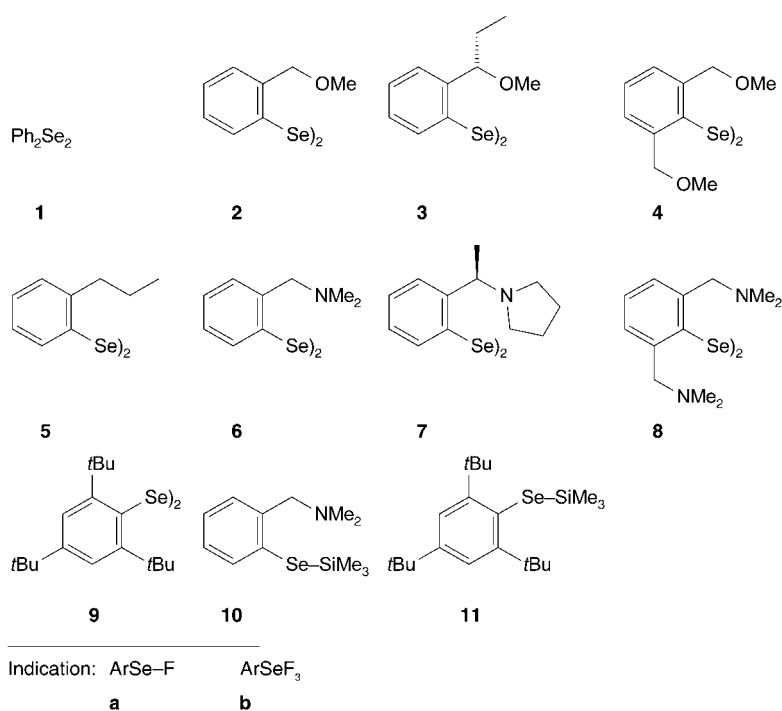
As is shown herein, ¹⁹F and ⁷⁷Se NMR chemical shifts of ArSeF can be predicted by ab initio and DFT calculations, and the values obtained confirm the expected extreme chemical shift values.

The diselenides **1–9** and the aryl selenotrimethylsilanes **10** and **11** were treated with XeF₂ in PFA (perfluoroethylene-perfluorovinylether copolymer) NMR tubes at low temperatures. The resulting NMR data are collected in Table 1.

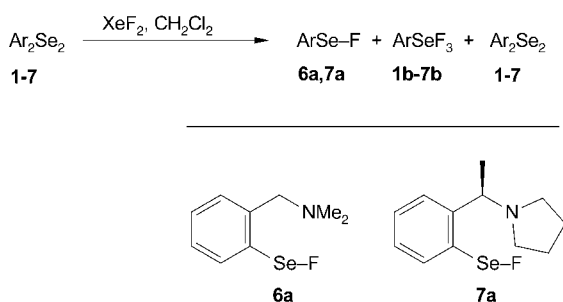
Reaction of 1 + XeF₂: Besides unreacted Ph₂Se₂ at $\delta = 465$ ppm in the ⁷⁷Se spectrum a new signal appears at $\delta = 1162$ ppm, but there is no signal in the expected range of $\delta = 1800$ ppm for ArSe–F. Use of excess XeF₂ leads to an in-

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crease in the signal at $\delta = 1162$ ppm (Scheme 1), which is clearly attributed to PhSeF₃.^[24] No ⁷⁷Se–¹⁹F coupling is observed, or even an ¹⁹F NMR signal, probably as a result of rapid intramolecular fluorine exchange.



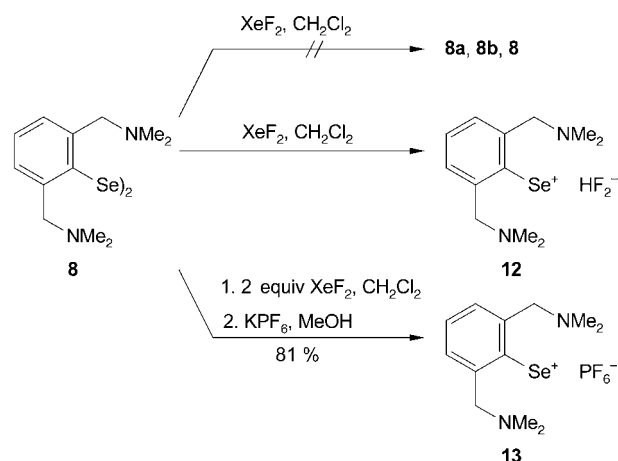
Scheme 1.

Reaction of 2–5 + XeF₂: In spite of the hope that *ortho*-methoxyalkyl groups^[25,26] might stabilize selenenyl fluorides, ArSeF₃ and Ar₂Se₂ compounds were again the only products. However, in this case the complete ⁷⁷Se and ¹⁹F couplings were observed, including the two chemical shifts for the nonequivalent fluorine atoms in the pseudo-trigonal-bipyramidal SeF₃ groups (Table 1, Scheme 1).

Reaction of 6–8 + XeF₂: The dialkylamino-substituted diselenides **6** and **7** were fluorinated by XeF₂ to give mixtures of products that for the first time contained aryl selenenyl fluorides, as was immediately obvious from the low-frequency ¹⁹F NMR resonances. ⁷⁷Se satellite lines indicate direct bonding of the fluorine atom to selenium, and the ⁷⁷Se NMR spectrum shows the corresponding doublet (Table 1,

Scheme 1). ArSeF₃ **6b** and **7b** are always also present. The ArSe–F/ArSeF₃ ratio was measured by integration of the NMR signals, and found to be **6a/6b** \approx 1.25:1 and **7a/7b** \approx 2.5:1.

The stabilization of the organoselenenyl fluoride by one *ortho*-dialkylaminoalkyl group led to the idea that two *ortho*-dialkylaminoalkyl groups might lead to even stronger stabilization. This is only indirectly the case. The fluorination product of **8** is the selenenium salt **12** with the anion HF₂[–]. This compound can be converted by KPF₆ in MeOH into the known PF₆[–] salt (Scheme 2), and the ⁷⁷Se, ¹³C, and ¹⁹F data are identical with literature data.^[27] It can be assumed that the sele-

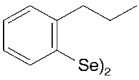
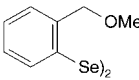
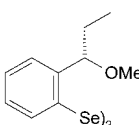
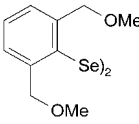
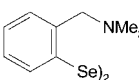
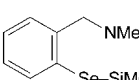
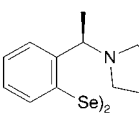
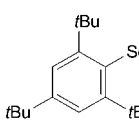
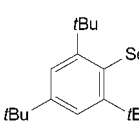


Scheme 2.

nyl fluoride **8a** is formed as an intermediate, but owing to the electron donation by two dialkylamino groups, the basicity of the fluorine atom has increased so that spontaneous F[–] elimination takes place under formation of the selenenium cation.

Reaction of 9 + XeF₂: The 2,4,6-tri-*t*-butylphenyl diselenide **9** was chosen to test the stabilization of a selenenyl fluoride merely by steric protection: indeed **9a** was obtained, and if handled in CHCl₃, the selenium trifluoride **9b** was also formed, similarly to **6a** and **7a**. In CFCl₃ solution almost no **9b** was present in the ⁷⁷Se spectrum, but some starting material **9** remained. This reaction is the one in which we came closest to the isolation of a pure organoselenenyl fluoride. The ⁷⁷Se NMR spectrum (doublet at $\delta = 1804.7$ ppm, ¹J(Se,F) = 816.3 Hz) and the ¹⁹F NMR spec-

Table 1. ⁷⁷Se and ¹⁹F NMR chemical shifts [δ] and coupling constants [Hz] of reaction products of diselenides **1–7** and **9** and silyl selenides **10** and **11** with XeF₂ in CH₂Cl₂; in brackets are the ⁷⁷Se, ¹⁹F coupling constants from the ⁷⁷Se satellites.

Starting material	<i>T</i> [°C]	Ar ₂ Se ₂ δ(⁷⁷ Se)	ArSe–F δ(⁷⁷ Se) (¹ <i>J</i> _{Se,F})	δ(¹⁹ F)[¹ <i>J</i> _{Se,F}]	ArSeF ₃ δ(⁷⁷ Se) (¹ <i>J</i> _{Se,F})	δ(¹⁹ F)(² <i>J</i> _{F,F})[¹ <i>J</i> _{Se,F}]
Ph ₂ Se ₂	1	–40 465.3(s)			1161.8(s)	not observed
Ph ₂ Se ₂	1 ^[a]	–40			1163.8(s)	not observed
	5	–80 410(broad)			1176.1(d, t)(812.2, F _c ; 89.9, F _a)	F _c : –73.52(t, 1F)(89.9)[812.5] F _a : 2.48 (d, 2F) (89.7)
	2	–80 394.4(s)			1144.7(d, t)(649.7, F _c ; 306.2, F _a)	F _c : –74.26(t, 1F)(116.5)[651.0] F _a : –14.83 (d, 2F) (116.5)[305.2]
	3	–80 390.1(s)(broad)			1141.5(d, d, d)(626.4, F _c ; 330.8, F _a ; 341.5, F _a)	F _c : –74.17(d, d)(107.4, 121.0)[626.4] F _a : –5.89(d, d)(121.8, 206.9)[343.7] F _a : –17.45 (d, d) (106.9, 207.2)[331.3]
	3 ^[b]	–80			1141.8(d, d, d)(625.5, F _c ; 331.6, F _a ; 343.5, F _a)	F _c : –74.15(d, d)(107.1, 121.1)[625.0] F _a : –6.05(d, d)(121.1, 207.2)[345.4] F _a : –17.59 (d, d) (106.7, 207.5)[329.7]
	4	–80 340.1(s)			1194.6(d, t)(600.0, F _c ; 328.8, F _a)	F _c : –72.06(t, 1F)(122.5)[597.8] F _a : –19.94 (d, 2F) (123.2)[327.6]
	6	–80 420.4(s)	1210.3(d)(935.8)	–162.77(s)[937.6]	1079.1(d, t)(201.5, F _c ; 519.2, F _a)	F _c : –43.91(t, 1F)(127.9)[200.9] F _a : –30.76(d, 2F)(127.6)[519.5]
	10 ^[c]	–80 420.2(s)	1210.8(d)(933.4)	–163.01(s)[935.1]	1079.1(d, t)(203.8, F _c ; 518.6, F _a)	F _c : –44.01(t, 1F)(128.1)[201.6] F _a : –30.72(d, 2F)(128.8)[519.0]
	7	–80 not observed	1145.5(d)(966.8)	–153.04(s)[957.3]	1062.9(d, d, d)(200.3, F _c ; 478.0, F _a ; 557.3, F _a)	F _c : –38.55(d, d)(103.7, 140.2)[196.3] F _a : –14.42(d, d)(140.9, 256.9)[560.8] F _a : –44.63(d, d)(102.4, 256.3)[473.4]
	9 ^[d]	–40 512.6(s)	1804.7(d)(816.3)	–312.5(s)[817.9]	not observed	F _c : –58.05(t, 1F)(39.7) F _a : 7.73 (d, 2F) (42.7)
	11 ^[d,f]	–40 512.4(s)	1805.1(d)(820.9)	–312.4(s)[819.4]	not observed	F _c : –59.82(t, 1F)(41.2)[813.3] F _a : 1.88(d, 2F)(41.2)[73.2]

[a] **1** + 3XeF₂. [b] **3** + 3XeF₂. [c] ¹⁹F NMR Me₃SiF: –159.4. [d] In CFCl₃. [e] In CHCl₃. [f] ¹⁹F NMR Me₃SiF: –158.9.

ArSeF₃: The complete ⁷⁷Se and ¹⁹F NMR spectra of arylselenium trifluorides are described here for the first time; for earlier syntheses of RSeF₃ see references [9,24,31–35]. The NMR data of **5b**, **2b**, **4b**, **6b**, and **9b** are in agreement with a pseudo-trigonal-bipyramidal structure for the selenium center, similar to that in SeF₄.^[36] It can be assumed that the organic ligand occupies an equatorial position since the ¹⁹F NMR spectra show one doublet and one triplet resonance, whereas the ⁷⁷Se NMR spectra show one resonance, split into a doublet of triplets (AB₂X spin system, numerical values see Table 1). For chiral ArSeF₃ **3b** (Figure 3) and **7b** the two axial fluorine atoms are no longer equivalent, resulting in an ABCX spin system, namely three doublets of doublets in the ¹⁹F NMR spectrum, and a doublet of doublets of doublets in the ⁷⁷Se NMR spectrum.

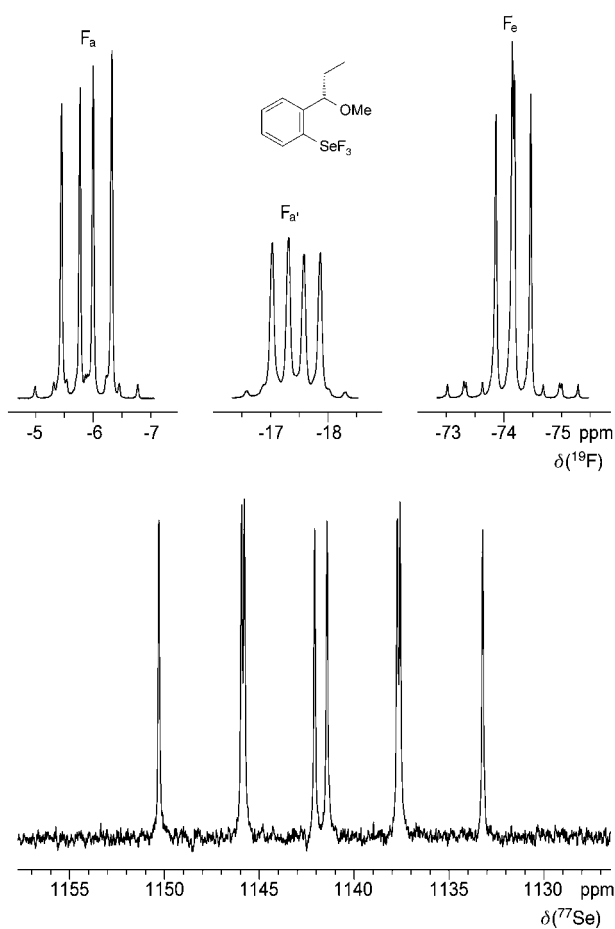


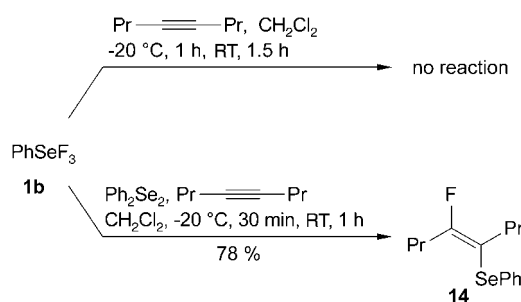
Figure 3. ¹⁹F and ⁷⁷Se NMR spectra of the reaction solution from **3** and 3XeF₂.

The observable coupling between both axial fluorine atoms ²J(F_a,F_a) = 207 (**3b**), 257 Hz (**7b**) is about twice as large as the ²J(F_a,F_e) coupling.

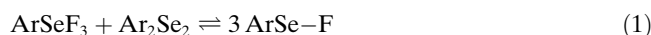
The increasing donor ability of substituents in the series **5b**, **9b**→**2b**–**4b**→**6b**, **7b** decreases the ¹J(Se,F) coupling of the equatorial F atoms F_e (812 Hz→600–650 Hz→200 Hz), whereas the ¹J(Se,F) coupling of the axial F atoms F_a increases (74–90 Hz→306–344 Hz→478–557 Hz). All ⁷⁷Se–¹⁹F

coupling can be assigned to individual fluorine atoms with the help of the ⁷⁷Se satellites in the ¹⁹F spectra. In contrast to the ⁷⁷Se chemical shift of ArSe–F, that of ArSeF₃ is only slightly dependent of the nature of the substituents.

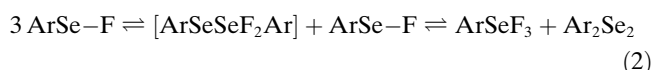
The nature of the Ar₂Se₂/XeF₂ and ArSe–SiMe₃/XeF₂ reagents: Although selenenyl fluorides ArSe–F are only observable in cases with steric protection or stabilization by one *ortho*-R₂N alkyl group, all Ar₂Se₂/XeF₂ reagents act as ArSe–F equivalents. No reaction takes place between an acetylene and PhSeF₃ at –20 °C. If Ph₂Se₂ is added to PhSeF₃ (**1b**), then [PhSe–F] addition occurs completely at this temperature (Scheme 5). This is indicative of the equilibrium in Equation (1).



Scheme 5.

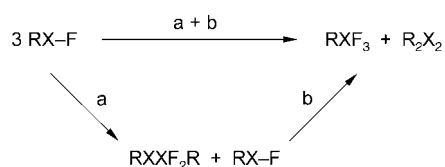


In the reaction of ArSe–SiMe₃ and XeF₂ the intermediate formation of the selenenyl fluoride is likely followed by reaction with ArSe–SiMe₃ to give Ar₂Se₂ (Scheme 4).^[37] There is an analogy with the sulfur series.^[38–40] Marginally stable CF₃S–F dimerizes to CF₃SSF₂CF₃. This reacts further to give CF₃SF₃ and CF₃SSCF₃ with an excess of CF₃S–F. The equilibrium mixture CF₃S–F/CF₃SSF₂CF₃ adds to alkenes such as pure monomeric CF₃S–F.^[41] For the overall disproportionation of ArSe–F we can therefore assume Equation (2).



Ab initio and DFT calculations: Since the organoselenenyl fluorides and organoselenium trifluorides have only been characterized by NMR methods so far, we calculated their structures and energies by ab initio and DFT methods to analyze the disproportionation reaction (Scheme 6).

The model compounds RSe–F, RSeF₃, RSeSeF₂R, and R₂Se₂ (R = Me, Ph) were calculated as were the sulfur (R = Me, CF₃, Ph) and tellurium homologues (R = Me, Ph). Calculations were performed at the MP2^[42] and CCSD(T)^[43] levels of theory, DFT calculations with the Becke3LYP method,^[44,45] both as implemented in the GAUSSIAN 98^[46] and GAUSSIAN 03 programs.^[47] 6–311+G(d,p) and 6–311+G(3df,3pd) basis sets were used for all elements except Te. For Te, the relativistic large core basis set was SDB-cc-pVTZ,^[48] the relativistic electron core potential was



X: S, Se, Te

Scheme 6.

taken from reference [49] (EMSL basis set library, internet: <http://www.emsl.pnl.gov/forms/basisform.html>). The geometries of all molecules were optimized and characterized by frequency calculations, giving energy values including zero-point energy. At the beginning of the calculations, the highest reasonable symmetry of each molecule was assumed (C_s for RXF and RXF_3 , C_2 for R_2X_2 compounds). In some cases the symmetry had to be lowered to C_1 . The resulting total and zero-point energies are shown in Table 2.

The zero-point corrected energies for the disproportionation as well as for steps a and b of Scheme 6 are collected in Table 3. The results show that fluorides RS-F, RSe-F, and RTe-F are all unstable with respect to disproportionation, regardless of the nature of R and the computation method applied. The disproportionation becomes more favorable in the series $\text{S} < \text{Se} < \text{Te}$, which agrees with the fact that RS-F compounds can be isolated, RSe-F compounds are at least proven to exist (this work), and RTe-F compounds remain unknown.

Particularly interesting are the energetics of steps a (dimerization) and b (trifluoride/dichalcogenide formation). The energetics of step b are fairly independent of the method, but the energetics of the dimerization (step a) vary substantially (see Scheme 6).

The importance of f-type polarization functions for correct ab initio and DFT calculations of sulfur compounds has been

established.^[50–52] Therefore calculations with the large basis set 6–311+G(3df,3pd) are included here. This results in a more strongly exothermic disproportionation energy, mainly for $\text{CF}_3\text{S-F}$, less so for MeSe-F ; in the case of MeTe-F the energies remain largely unchanged. Step a in the disproportionation reaction is affected up to 15 kcal mol^{-1} for $\text{CF}_3\text{S-F}$. We have then also added CCSD(T) calculations with this large basis set for MeS-F and MeSe-F , and consider the obtained reaction energies as those closest to reality.

Table 2. Total energies E_{tot} [a.u.] and zero-point energies ZPE of the S, Se, and Te compounds, as calculated with the MP2, CCSD(T), and B3LYP methods.

Compound	Symmetry	E_{tot}	ZPE	Symmetry	E_{tot}	ZPE
	MP2/6–311+G(d,p)			B3LYP/6–311+G(d,p)		
MeSF	C_s	–537.0834665	0.040489	C_s	–537.9844295	0.039607
MeSSF ₂ Me	C_1	–1074.1568464	0.084155	C_1	–1075.9578217	0.081955
MeSF ₃	C_s	–736.3976444	0.046713	C_s	–737.7018910	0.045613
Me ₂ S ₂	C_2	–874.8933968	0.078831	C_2	–876.2868836	0.076992
CF ₃ SF	C_s	–834.3251956	0.017465	C_s	–835.7881544	0.016785
CF ₃ SSF ₂ CF ₃	C_1	–1668.6256027	0.037284	C_1	–1671.5519165	0.035754
CF ₃ SF ₃	C_1	–1033.6195274	0.023612	C_1	–1035.4870442	0.022628
CF ₃ SSCF ₃	C_2	–1469.390299	0.032288	C_2	–1471.9068062	0.030923
PhSF	C_1	–728.2980012	0.091896	C_s	–729.7662713	0.092746
PhSF ₃	C_1	–927.6061165	0.098615	C_1	–929.4777597	0.098839
Ph ₂ S ₂	C_2	–1257.3358435	0.181983	C_2	–1259.8492423	0.182814
MeSeF	C_s	–2539.3479811	0.039324	C_s	–2541.3297112	0.038597
MeSeSeF ₂ Me	C_1	–5078.7078012	0.081031	C_1	–5082.6669581	0.079173
MeSeF ₃	C_s	–2738.6859084	0.044526	C_s	–2741.0689865	0.043655
Me ₂ Se ₂	C_2	–4879.4184521	0.076248	C_2	–4882.9714466	0.074862
PhSeF	C_s	–2730.5611825	0.090916	C_s	–2733.1103336	0.091968
PhSeF ₃	C_1	–2929.8948176	0.096676	C_s	–2932.8463515	0.097166
Ph ₂ Se ₂	C_2	–5261.8573523	0.180190	C_2	–5266.5306337	0.181145
MeTeF	C_s	–147.4617904	0.038588	C_s	–147.8872248	0.037928
MeTeTeF ₂ Me	C_1	–294.9583104	0.079238	C_1	–295.7991228	0.077753
MeTeF ₃	C_1	–346.8612238	0.043587	C_s	–347.6827634	0.042505
Me ₂ Te ₂	C_2	–95.6132477	0.074731	C_2	–96.0515549	0.073522
PhTeF	C_s	–338.674313	0.090412	C_s	–339.6661497	0.091553
PhTeF ₃	C_s	–538.0716029	0.096103	C_s	–539.4609596	0.096629
Ph ₂ Te ₂	C_2	–478.048684	0.179116	C_2	–479.6075891	0.180336
	MP2/6–311+G(3 df,3 pd)			B3LYP/6–311+G(3 df,3 pd)		
MeSF	C_s	–537.2193455	0.040495	C_s	–538.0060673	0.039693
MeSSF ₂ Me	C_1	–1074.4504208	0.084175	C_1	–1076.0095774	0.082246
MeSF ₃	C_1	–736.6712995	0.047231	C_s	–737.755684	0.045961
Me ₂ S ₂	C_2	–875.0550374	0.078471	C_2	–876.311377	0.076958
CF ₃ SF	C_s	–834.6155204	0.017597			
CF ₃ SSF ₂ CF ₃	C_1	–1669.2300923	0.037904			
CF ₃ SF ₃	C_1	–1034.0510852	0.024253			
CF ₃ SSCF ₃	C_2	–1469.8578394	0.032287			
MeSeF	C_s	–2539.4756706	0.039375	C_s	–2541.3460802	0.038698
MeSeSeF ₂ Me	C_1	–5078.9705312	0.081172	C_1	–5082.6993651	0.079402
MeSeF ₃	C_1	–2738.940191	0.045032	C_1	–2741.1056614	0.043817
Me ₂ Se ₂	C_2	–4879.5579394	0.076226	C_2	–4882.9866851	0.074931
MeTeF	C_s	–147.5473756	0.038523			
MeTeTeF ₂ Me	C_1	–295.1324012	0.079139			
MeTeF ₃	C_1	–347.058064	0.043363			
Me ₂ Te ₂	C_2	–95.6760387	0.074605			
	CCSD(T)/6–311+G(3 df,3 pd)//MP2/6–311+G(3 df,3 pd)					
MeSF	C_s	–537.2720623				
MeSSF ₂ Me	C_1	–1074.5467646				
MeSF ₃	C_1	–736.7306023				
Me ₂ S ₂	C_2	–875.1424247				
MeSeF	C_s	–2539.5240606				
MeSeSeF ₂ Me	C_1	–5079.0602566				
MeSeF ₃	C_1	–2738.9950544				
Me ₂ Se ₂	C_2	–4879.6391821				

Table 3. Reaction energies [kcal mol⁻¹], including ZPE of the total disproportionation reaction 3RX–F → RXF₃ + R₂X₂ (X = S, Se, Te) and the partial reactions, a: 2RX–F → RXXF₂R, b: RXXF₂R + RX–F → RXF₃ + R₂X₂. CCSD(T) energies are corrected with ZPEs of the MP2/6-311+G(3df,3pd) calculations.

	R\X	S	Se		Te		a	b
			a	b	a	b		
MP2/6-311+G(d,p)	CF ₃	-19.29	17.03	-36.32				
MP2/6-311+G(3df,3pd)	CF ₃	-36.78	2.30	-39.08				
MP2/6-311+G(d,p)	Me	-22.94	8.32	-31.27	-36.15	-5.93	-30.22	-54.31
MP2/6-311+G(3df,3pd)	Me	-40.21	-5.36	-34.85	-42.66	-10.52	-32.14	-56.21
CCSD(T)/6-311+G(3df,3pd)	Me	-33.02	0.34	-33.36	-36.97	-6.09	-30.88	-20.50
MP2/6-311+G(d,p)	Ph	-27.01						-22.31
B3LYP/6-311+G(d,p)	CF ₃	-16.43	16.68	-33.11				-33.90
B3LYP/6-311+G(d,p)	Me	-19.89	8.65	-28.54	-30.48	-3.49	-26.99	-44.17
B3LYP/6-311+G(3df,3pd)	Me	-28.25	3.40	-31.65	-32.28	-3.26	-29.02	-14.29
B3LYP/6-311+G(d,p)	Ph	-15.55			-27.35			-29.88
								-42.54

The calculated trend in terms of energy helps to explain why an addition of [PhTe–F] to unsaturated hydrocarbons is not observed.^[11] On the other hand it can be expected that R₂Se₂/XeF₂ acts as sulfenyl fluoride equivalents, but little is known about this. Fluorosulfonylations have so far been done with CF₃S–F/CF₃SSF₂CF₃,^[41] Me₂S⁺–SMe BF₄⁻/Et₃N·3 HF,^[53] and *N*-phenylthiophthalimide/Py·9 HF.^[18c]

GIAO-MP2 and GIAO-B3LYP calculations: GIAO calculations of the magnetic shielding constants are helpful for the prediction and interpretation of NMR chemical shifts, also for ¹⁹F and ⁷⁷Se NMR data.^[54–60] We have calculated the ⁷⁷Se and ¹⁹F chemical shifts of the species discussed to secure the chosen assignments of the experimental spectra. Included are calculations for SeF₂, SeF₄, and SeF₆, as well as CF₃S–F and CF₃SF₃. The optimized geometries have been used. Results are collected in Table 4.

⁷⁷Se chemical shifts: The chemical shift regions for RSe–F (δ = 2100–2500 ppm), RSeF₃ (δ = 1180–1320 ppm) and R₂Se₂ (δ = 270–700 ppm) are clearly distinguishable. The fairly broad ranges should be considered in relation to the known ⁷⁷Se chemical shift range of about 3000 ppm.^[22]

In many cases the MP2 calculations offer values closer to the experimental ones than the DFT calculations. GIAO-MP2 calculations with the basis set 6–311+G(3df,3pd) give better ⁷⁷Se values than with the 6–311+G(d,p) basis set. Unstable SeF₂ is predicted to have an extreme ⁷⁷Se chemical shift of δ = 3724 and 3458 (MP2), or 4368 ppm (DFT). If the ⁷⁷Se chemical shift/electronegativity dependence is assumed to be linear for SeX₂ (δ(⁷⁷Se) = 1881.1χ–4137.7 ppm, X = Cl, Br, I),^[22,23] then for SeF₂ a ⁷⁷Se shift of δ = 3199 ppm is predicted.

¹⁹F chemical shifts: MP2 and DFT methods predict extreme shielding values for selenenyl fluorides RSe–F that range from δ = –372 to –473 ppm. The calculated ¹⁹F chemical shifts for CF₃S–F, CF₃SF₃, PhSeF₃, SeF₄, and SeF₆ are in good agreement with the experimental values. Again the MP2 calculations offer slightly better values than the DFT calculations. SeF₂ should have a ¹⁹F chemical shift of about δ = –210 ppm. The larger basis set 6–311+G(3df,3pd) does not change the GIAO-MP2-calculated ¹⁹F chemical shifts considerably.

Experimental Section

Mass spectra were obtained with a Finnigan MAT 711 spectrometer with 80 eV electron excitation. NMR spectra were obtained on a JEOL JNM-LA 400 spectrometer: ¹³C 100.40 MHz (internal reference TMS), ⁷⁷Se 76.2 MHz (external reference Me₂Se 60 vol% in CDCl₃),^[62] ¹⁹F 376.00 MHz (external reference CFC₃). NMR spectra were recorded at room temperature, if not noted otherwise. Low-temperature spectra were referenced to an external standard at room temperature.

Calculations: Origine 3400 computer, Silicon Graphics Inc., internet: <http://www.zedat.fu-berlin.de/services/compute/>.

Chemicals: Compound **1** was obtained from Fluka, ⁷⁷Se NMR (CDCl₃): δ = 465.2 ppm. Compound **9** was prepared by a route analogous to that in reference [63] by lithiation of 2,4,6-tri-*tert*-butylbromobenzene (Aldrich) with *t*BuLi at –78 °C in THF according to reference [64]. ¹³C NMR (CDCl₃): δ = 155.84 (*o*-C), 150.03 (*p*-C) 127.76 (*i*-C), 123.37 (*m*-C), 38.94 (*o*-*t*Bu), 33.16 (CH₃, *o*-*t*Bu), 34.92 (*p*-*t*Bu), 31.28 ppm (CH₃, *p*-*t*Bu); ⁷⁷Se NMR (CDCl₃): δ = 517.6 ppm. Compound **11** was prepared according to reference [63]. ¹³C NMR (CDCl₃): δ = 154.64 (*o*-C), 148.12 (*p*-C), 122.52 (*i*-C), 121.60 (*m*-C), 38.73 (*o*-*t*Bu), 32.77 (CH₃, *o*-*t*Bu), 34.71 (*p*-*t*Bu), 31.35 (CH₃, *p*-*t*Bu), 1.61 ppm (SiCH₃); ⁷⁷Se NMR (CDCl₃): δ = 42.5 ppm (¹J_{Se,Si} = 111.5 Hz).

Precursors of diselenides

For compound 2: Methylation of *o*-bromobenzyl alcohol (ACROS) in THF with MeI/NaH^[65] yielded *o*-methoxymethyl bromobenzene. B.p. 102 °C/13 mbar; ¹³C NMR (CDCl₃): δ = 137.56, 132.37, 128.80, 128.76, 127.29, 122.53 (C_{arom}), 73.76 (OCH₂), 58.45 ppm (OCH₃).

For compound 3: Reaction of *o*-bromobenzaldehyde (Fluka) with Et₂Zn in toluene and **7** as chiral catalyst yielded (*S*)-*o*-(1-hydroxy-1-propyl)bromobenzene.^[66] ¹³C NMR (CDCl₃): δ = 143.59, 132.43, 128.50, 127.50, 127.39, 122.01 (C_{arom}), 73.89 (OCH), 30.52 (CH₂), 10.02 ppm (CH₃). Etherification of (*S*)-*o*-(1-hydroxy-1-propyl)bromobenzene with MeI/NaH^[65] in THF led to (*S*)-*o*-(1-methoxy-1-propyl)bromobenzene. B.p. 52 °C/0.1 mbar; ¹³C NMR (CDCl₃): δ = 141.48, 132.61, 128.60, 127.60, 127.52, 123.35 (C_{arom}), 83.35 (OCH), 56.94 (OCH₃), 29.92 (CH₂), 10.02 ppm (CH₃).

For compound 4: Reaction of 2,6-dimethylbromobenzene (Fluka) with *N*-bromosuccinimide (NBS) in CCl₄ yielded 2,6-bis(bromomethyl)bromobenzene.^[67] ¹³C NMR (CDCl₃): δ = 138.23 (*o*-C), 131.29 (*m*-C), 127.93 (*p*-C), 126.50 (*i*-C), 33.89 ppm (CH₂). Reaction with NaOMe yielded 2,6-bis(methoxymethyl)bromobenzene.^[68] B.p. 86 °C/0.016 mbar; ¹³C NMR (CDCl₃): δ = 137.89 (*o*-C), 127.72 (*m*-C), 127.12 (*p*-C), 122.63 (*i*-C), 74.07 (OCH₂), 58.53 ppm (OCH₃).

For compound 5: Reaction of *o*-bromobenzaldehyde with EtMgBr yielded *o*-(1-hydroxy-1-propyl)bromobenzene. B.p. 71 °C/0.02 mbar; ¹³C NMR (CDCl₃): δ = 143.59, 132.39, 128.48, 127.50, 127.39, 122.00 (C_{arom}), 73.83 (OCH), 30.51 (CH₂), 10.00 ppm (CH₃). Deoxygenation analogous to reference [69] with Me₂SiCl/NaI/CH₃CN/Zn/AcOH yielded *o*-propylbromobenzene. B.p. 97 °C/17 mbar; ¹³C NMR (CDCl₃): δ = 141.78, 132.69, 130.30, 127.32, 127.20, 124.51 (C_{arom}), 38.16 (1-CH₂), 23.07 (2-CH₂), 13.83 ppm (CH₃).

Table 4. GIAO-MP2 and GIAO-B3LYP-calculated ^{77}Se and ^{19}F shielding constants σ_{Se} , σ_{F} , ^{77}Se and ^{19}F chemical shifts δ_{Se} and δ_{F} (ppm) of selected selenium compounds, including experimental values.

Compound	Sym	σ_{Se}	δ_{Se}	σ_{F}	δ_{F}	Sym	σ_{Se}	δ_{Se}	σ_{F}	δ_{F}	δ_{Se}	δ_{F}
		GIAO-MP2/6-311+G(d,p)//MP2/6-311+G(d,p)					GIAO-B3LYP/6-311+G(d,p)//B3LYP/6-311+G(d,p)				experimental	
Me_2Se	C_s	1908.5	0			C_s	1621.8	0			0	
CFCl_3	C_{3v}			204.2	0	C_{3v}			153.7	0		0
CF_3SF	C_s			576.8	-372.6	C_s			539.8	-386.1		-351.5 ^[d]
CF_3SF_3	C_1			257.3	-53.1, F_e	C_1			186.5	-32.8, F_e		-48, ^[e] F_e
				157.2	47.0, F_a				80.1	73.6, F_a		52, F_a
				168.0	36.2, F_a				92.2	61.5, F_a		
MeSeF	C_s	-218.1	2126.6	640.6	-436.4	C_s	-882.9	2504.7	626.9	-473.2		
MeSeF_3	C_s	649.1	1259.4	281.1	-76.9, F_e	C_s	297.9	1323.9	211.1	-57.4, F_e		
				173.7	30.5, F_a				96.5	57.2, F_a		
Me_2Se_2	C_2	1634.6	273.9			C_2	1248.8	373.0			275 ^[a]	
PhSeF	C_s	-188.8	2097.3	578.7	-374.5	C_s	-776.3	2398.1	548.9	-395.2		
PhSeF_3	C_1	731.8	1176.7	243.1	-38.9, F_e	C_s	428.1	1193.7	163.8	-10.1, F_e	1161.8 ^[b]	
				207.4	-3.2, F_a				137.1	16.6, F_a		
				178.1	26.1, F_a							
Ph_2Se_2	C_2	1325.3	583.2			C_2	926.0	695.8			465.2 ^[b]	
SeF_2	C_{2v}	-1815.0	3723.5	413.1	-208.9	C_{2v}	-2746.2	4368.0	357.9	-204.2		
SeF_4	C_{2v}	683.9	1224.6	166.4	37.8, F_e	C_{2v}	380.8	1241.0	68.5	85.2, F_e	1083 ^[c]	12.1, ^[c] F_e
				125.9	78.3, F_a				37.8	115.9, F_a		37.7, F_a
SeF_6	O_h	1146.2	762.3	130.5	73.7	O_h	902.0	719.8	-12.3	166.0	600 ^[c]	49.6 ^[c]
		GIAO-MP2/6-311+G(3 df,3 pd)//MP2/6-311+G(3 df,3 pd)										
Me_2Se	C_s	1935.2	0									
CFCl_3	C_{3v}			206.8	0							
CF_3SF	C_s			578.8	-372.0							
CF_3SF_3	C_1			263.9	-57.1, F_e							
				148.6	58.2, F_a							
				162.6	44.2, F_a							
MeSeF	C_s	-68.9	2004.1	638.4	-431.6							
MeSeF_3	C_1	753.6	1181.6	284.4	-77.6, F_e							
				200.4	6.4, F_a							
				185.7	21.1, F_a							
Me_2Se_2	C_2	1693.9	241.3									
PhSeF	C_s	-66.7	2001.9	582.2	-375.4							
SeF_2	C_{2v}	-1523.0	3458.2	417.0	-210.2							
SeF_4	C_{2v}	835.5	1099.7	191.3	15.5, F_e							
				151.8	55.0, F_a							
SeF_6	O_h	1254.3	680.9	178.5	28.3							

[a] Ref. [22]. [b] This paper. [c] Ref. [36]. [d] Ref. [38,39]. [e] Ref [61].

For compound 7: Alkylation of (*R*)-1-phenyl-ethylamine (Aldrich) with 1,4-dibromobutane in EtOH/ K_2CO_3 yielded (*R*)-1-phenyl-ethylpyrrolidine.^[70] B.p. 107–109 °C/9 mbar; ^{13}C NMR (CDCl_3): δ = 145.79, 128.18, 127.08, 126.73 (C_{arom}), 65.95 (NCH), 52.91 (NCH₂), 23.41 (CH₂), 32.30 ppm (CH₃).

General procedure for the synthesis of diselenides 2–5: *t*BuLi (50 mmol, 29 mL 1.7 M in pentane, Aldrich) was added dropwise over 20 min to a stirred solution of *ortho*-substituted bromobenzene (25 mmol) in hexane (100 mL) –78 °C under argon. The mixture was stirred at this temperature for 1 h. After warming to room temperature, addition of THF (100 mL), and cooling to –78 °C, gray selenium powder (25 mmol, 1.79 g) was added. After slow warming to room temperature and stirring for 1 h, H₂O (200 mL) was added, and air blown through the solution. The product was extracted with diethyl ether (3 × 300 mL), the organic phase was washed with H₂O (2 × 100 mL), saturated aqueous NaCl solution (100 mL), and H₂O (100 mL), and was finally dried over MgSO_4 .

Diselenide 2: Column chromatography over silica gel, hexane/ether 10:1, yield 3.65 g (73%), orange oil. ^{13}C NMR (CDCl_3): δ = 138.23, 132.70, 131.62, 128.73, 128.29, 127.37 (C_{arom}), 74.60 (OCH₂), 57.87 ppm (OCH₃); ^{77}Se NMR (CDCl_3): δ = 417.3 ppm; MS: *m/z* (%): 402 (36) [M^+ , ^{80}Se], 200 (100).

Diselenide 3: Column chromatography over silica gel, hexane/ether 5:1, yield 4.91 g (86%), orange oil. ^{13}C NMR (CDCl_3): δ = 142.45, 133.05, 129.73, 128.10, 127.71, 126.78 (C_{arom}), 84.51 (OCH), 56.65 (OCH₃), 29.88 (CH₂), 10.32 ppm (CH₃); ^{77}Se NMR (CDCl_3): δ = 418.2 ppm; MS: *m/z* (%): 458 (54) [M^+ , ^{80}Se], 228 (42), 197 (100), 183 (27), 116 (62).

Diselenide 4: Recrystallized from EtOH, yield 3.10 g (51%), orange needles. M.p. 115–117.5 °C; ^{13}C NMR (CDCl_3): δ = 143.01 (*o*-C), 129.85 (*p*-C), 128.67 (*i*-C), 126.88 (*m*-C), 74.36 (OCH₂), 58.27 ppm (OCH₃); ^{77}Se NMR (CDCl_3): δ = 362.2 ppm; MS: *m/z* (%): 490 (57) [M^+ , ^{80}Se], 244 (33) [ArSe^+], 213 (100) [$\text{ArSe}^+ - \text{MeO}$].

Diselenide 5: Column chromatography over silica gel, hexane, yield 3.10 g (63%), orange oil. ^{13}C NMR (CDCl_3): δ = 143.12, 133.22, 130.94, 129.05, 127.89, 126.87 (C_{arom}), 37.98, 24.14, 13.93 ppm (Pr); ^{77}Se NMR (CDCl_3): δ = 415.0 ppm; MS: *m/z* (%): 398 (60) [M^+ , ^{80}Se], 318 (25) [$M^+ - \text{Se}$], 198 (85), 117 (46), 91 (100).

General procedure for the synthesis of diselenides 6–8:^[66,71] *t*BuLi (25 mmol, 17.7 mL 1.7 M, Aldrich) was added dropwise over 15 min to a stirred solution of amine (*N,N*-dimethylbenzylamine, (*R*)-1-phenylethylpyrrolidine, *m*-bis(*N,N*-dimethylaminomethyl)benzene,^[72] (25 mmol) in hexane (60 mL) at room temperature under argon. The mixture was stirred for 40 h at room temperature then THF (25 mL) was added. After the mixture was cooled to –78 °C, gray selenium powder (25 mmol, 1.97 g) was added and the mixture was allowed to slowly warm up to room temperature and stirred for 2 h. Addition of H₂O (200 mL) and pumping of air through the solution were followed by the work up described for diselenides 2–5.

Diselenide 6:^[26] Column chromatography over silica gel, acetone/pentane 1:3, yield 4.16 g (78%), red-orange oil. ^{13}C NMR (CDCl_3): δ = 139.0, 134.13, 131.24, 128.32, 128.00, 125.69 (C_{arom}), 64.49 (NCH₂), 44.23 ppm (NCH₃); ^{77}Se NMR (CDCl_3): δ = 430.9 ppm; MS: *m/z* (%): 428 (4) [M^+ , ^{80}Se], 214 (100) [ArSe^+].

Diselenide 7:^[66] Column chromatography on silica gel, acetone/pentane 1:3, yield 5.10 g (81%), red-orange oil. ¹³C NMR (CDCl₃): δ = 144.83, 132.91, 131.26, 127.38, 126.48, 126.04 (C_{arom}), 63.65 (NCH), 51.10 (NCH₂), 23.72 (CH₂), 18.99 (CH₃) ppm; ⁷⁷Se NMR (CDCl₃): δ = 429.8 ppm; MS: *m/z* (%): 508 (1) [M⁺, ⁸⁰Se], 359 (1), 254 (100) [ArSe⁺], 183 (24), 174 (19), 104 (18), 70 (41).

Diselenide 8: Column chromatography on silica gel, ethyl acetate with 2.5% Et₃N, yield 3.35 g (50%), red-orange oil. ¹³C NMR (CDCl₃): δ = 143.62 (*o*-C), 134.59 (*i*-C), 128.21 (*p*-C), 127.95 (*m*-C), 64.55 (NCH₂), 45.18 ppm (NCH₃); ⁷⁷Se NMR (CDCl₃): δ = 397.2 ppm; MS: *m/z* (%): 462 (1) [M⁺–Se, ⁸⁰Se], 271 (99) [ArSe⁺], 226 (100), 184 (47); FAB MS (*m*-nitrobenzyl alcohol/CH₂Cl₂, matrix): *m/z* (%): 542 (0.4) [M⁺–Se, ⁸⁰Se], 271 (100) [ArSe⁺], 226 (59).

Synthesis of silylselenide 10:^[13] Liquid NH₃ (70 mL) was condensed into a solution of diselenide **6** (3 mmol, 1.28 g) in THF (30 mL). Na (7 mmol, 161 mg) was added in small portions until the solution remained blue. All solvents were removed under vacuum. THF (30 mL) and Me₃SiCl (9 mmol, 1 g) were added over 5 min. After the mixture had been stirred for 20 h, the solvent was removed and the remaining solid was extracted with pentane (100 mL). The solution was filtered and the pentane removed under exclusion of moisture to yield a light yellow oil (1.27 g; 70%). ¹³C NMR (CDCl₃): δ = 142.63, 137.94, 129.73, 127.24, 126.87, 126.74 (C_{arom}), 64.33 (NCH₂), 45.43 (NCH₃), 1.65 ppm (SiCH₃); ⁷⁷Se NMR (CDCl₃): δ = 25.8 ppm (¹J_{Se,Si} = 106.9 Hz); MS: *m/z* (%): 227 (8) [M⁺–Me–Me₂NH, ⁸⁰Se], 212 (14) [227–Me⁺], 148 (95), 75 (56), 73 (100) [Me₃Si⁺].

Reaction of diselenides 1–9 and the silyl selenides 10, 11 with XeF₂, NMR experiments: The selenium starting materials (1 mmol) were placed into a previously dried 12-mm PFA^[73] tube. Under vacuum, dry CH₂Cl₂ (4 mL), in the case of **9** and **11** dry CHCl₃ or CFCI₃, were condensed in at –196°C. At –20°C (**1–5**), –30°C (**9–11**), or –40°C (**6–8**) XeF₂ (1 mmol, 169 mg) was added under argon and stirring for 30 min. For the preparation of ArSeF₃, XeF₂ (3 mmol, 507 mg) was added. Some of the solution was then transferred into a 4-mm PFA tube with help of a 1-mm Teflon tube and argon pressure. The 4-mm PFA tube was sealed and placed into a standard 5-mm NMR glass tube that also contained some [D₆]acetone for internal locking. After cooling to –78°C these samples were inserted into the precooled spectrometer and measured as summarized in Table 1.

Reaction of diselenide 8 with XeF₂ to yielding selenium salt 12: ¹⁹F NMR (CH₂Cl₂, –80°C): δ = –151.39 (¹J_{F,H} = 121.0 Hz; HF₂[–]); ⁷⁷Se NMR (CH₂Cl₂, –80°C): δ = 1168.5 (**12**).

Reaction of diselenide 8 with 2XeF₂ and KPF₆ to yield selenium salt 13: Diselenide **8** (1 mmol, 540 mg) and XeF₂ (2 mmol, 339 mg) in CH₂Cl₂ (8 mL) reacted over 30 min at –40°C in a PFA tube. After removal of the solvent under vacuum, MeOH (20 mL) and then KPF₆ (2 mmol, 370 mg) were added and the mixture was stirred for 1 h. Crystallization was completed by cooling to –20°C. After filtration, washing with Et₂O (2 × 20 mL), and drying in vacuum, traces of red selenium were removed by washing with CH₂Cl₂ (10 mL), followed by filtration, and removal of the solvent. This yielded **13** (0.67 g; 81% yield). M.p. 174–176°C (decomp), (176–180°C (decomp));^[27] ¹³C NMR (CD₃CN): δ = 134.02 (*o*-C), 133.98 (*i*-C), 129.16 (*p*-C), 126.16 (*m*-C), 64.57 (NCH₂), 49.10 ppm (NCH₃); ⁷⁷Se NMR (CD₃CN): δ = 1213.1 ppm (1208.3).^[27]

(E)-4-Fluoro-5-phenylseleno-oct-4-ene (14): PhSeF₃ (2 mmol) in CH₂Cl₂ (10 mL) was combined with Ph₂Se₂ (2 mmol, 624 mg) at –20°C and stirred for 10 min. Oct-4-yne (6 mmol, 660 mg) was added followed by stirring for 1 h at –20°C and 2 h at room temperature. Purification by column chromatography on silica gel in hexane afforded **14** as a colorless oil (1.33 g; 78%). Mass and NMR spectra agree with our previous data.^[11,74]

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