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Selenenyl Fluorides

$Trip_2C_6H_3SeF$: The First Isolated Selenenyl Fluoride[**]

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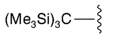
In memory of Reiner Radeglia

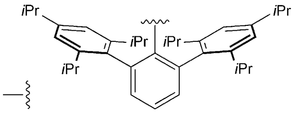
In spite of intensive research in modern fluorine and selenium chemistry there are still unknown compounds among these seemingly simple compounds. The long-sought class of selenenyl fluorides, RSeF, are clearly very unstable and SeF_2 and FSeSeF have only been identified under matrix conditions.[1] The existence of CF_3SeF has only been shown indirectly.[2] But reagents of the type *N*-phenylselenophthalimide/$Et_3N{\cdot}3\,HF$,[3] Ph_2Se_2/XeF_2,[4,5] $PhSeEMe_3/XeF_2$ (E = Si, Ge, Sn, Pb),[5a,6] and $PhSeOTf/Et_3N{\cdot}3HF$[7] function as PhSeF equivalents and can be used for the addition of PhSeF across C−C double and triple bonds. The addition to alkynes occurs with intermediate formation of selenirenium ions.[8] We identified arylselenium monofluorides, ArSeF, for the first time by their characteristic NMR spectroscopic signals, when the compounds are stabilized by steric protection (Ar = 2,4,6-tri-*tert*-butylphenyl = supermesityl, Mes*) or by intramolecular coordination with amino groups[9] (Ar = 2-$Me_2NCH_2C_6H_4$).[10] These experiments showed, supported by quantum chemical calculations, that non-stabilized RSeF disproportionate in a reversible equilibrium reaction into diselenides R_2Se_2 and organo selenium trifluorides $RSeF_3$, most likely with the intermediate formation of $RSeF_2$−SeR.[10,11]

Monomeric tellurenyl fluorides, ArTeF, such as 2-$Me_2NCH_2C_6H_4TeF$, have been identified by NMR spectroscopy in solution.[12] Recently a report appeared about the dimer $BbtTeF_2$−TeBbt with the sterically demanding 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]-phenyl group (Bbt).[13]

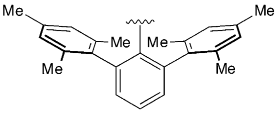
The aim of our investigations, starting in 2005, has been to obtain RSeF and possibly RTeF in pure, crystalline states with even larger steric protection groups than Mes*. We have worked with the following ligands: tris(trimethylsilyl)methyl (Trisyl, Tsi), 2,6-bis(2,4,6-tri-*iso*-propylphenyl)phenyl ($Trip_2C_6H_3$), and 2,6-bis(mesityl)phenyl ($Mes_2C_6H_3$).



Tsi–



$Trip_2C_6H_3$–



$Mes_2C_6H_3$–

m-Terphenyl groups in particular have found much use as steric protection groups[14] and have also been used in selenium and tellurium chemistry.[15,11]

To obtain the REF (E = Se, Te) compounds, the dichalcogenides, R_2E_2, and the trimethylsilyl and trimethylstannyl chalcogenides, $RESiMe_3$ and $RESnMe_3$, were to be fluorinated with XeF_2.[4–6,10] The optimization of the reaction conditions was usually carried out by low-temperature NMR spectroscopy.

Tsi_2Se_2[16] reacts with XeF_2 at −40 °C in $CFCl_3$ or CH_2Cl_2 forming TsiSeF, but its crystallization has been unsuccessful (Scheme 2, NMR data see Table 1). TsiSeF has the expected ^{19}F resonance of $\delta = -371.0$ ppm for the highly shielded F atom in combination with the ^{77}Se resonance of $\delta = 2028.1$ ppm, $^1J_{Se,F} = 791.9$ Hz; cf. Ref. [10] for the extremely deshielded Se center.

Attempts to obtain the diselenide $(Trip_2C_6H_3)_2Se_2$ in pure form starting with $Trip_2C_6H_3I$[14a,17] resulted only in mixtures of diselenide and triselenide (cf. Ref. [18]). Pure $(Trip_2C_6H_3)_2Se_2$, however, can be obtained by nitrosation of the selenole $Trip_2C_6H_3SeH$ with isoamyl nitrite[15b,d,e,19] (Scheme 1, structure[20]). It reacts with XeF_2 in CH_2Cl_2 or $CFCl_3$ within 4 h at −30 °C to $Trip_2C_6H_3SeF$ ($\delta_F = -343.6$ ppm) in trace amounts. Besides residual diselenide mainly the trifluoride $Trip_2C_6H_3SeF_3$ is formed (Scheme 2).

Similarly the synthesis of $Trip_2C_6H_3SeSiMe_3$ is unsuccessful: Reaction of $Trip_2C_6H_3SeLi$ with Me_3SiCl or Me_3SiOTf produces largely $Trip_2C_6H_3SeH$ ($\delta_{Se} = 107.8$ ppm, $^1J_{Se,H} = 63.1$ Hz, cf. Ref. [15a]). But the analogue reaction with $tBuMe_2SiOTf$ affords $Trip_2C_6H_3SeSiMe_2tBu$ (cf. Ref. [21], Scheme 1, structure[20]). This compound does not react with XeF_2 in $CFCl_3$ in 3 h at −30 °C, although $PhSeSiMe_2tBu$ is easily cleaved by XeF_2 to [PhSeF] and $tBuMe_2SiF$.[5a] Carrying

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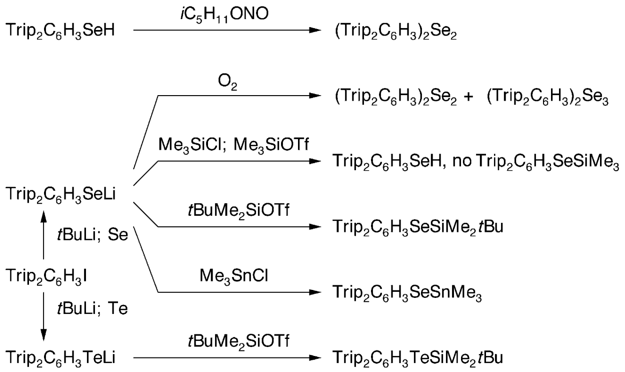
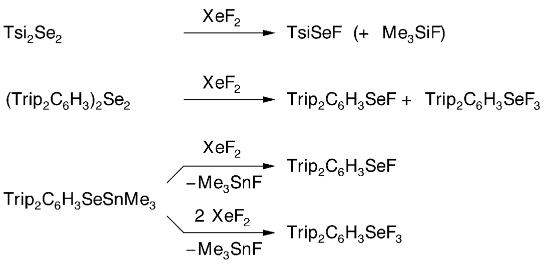
Table 1: ^{77}Se, ^{125}Te, and ^{19}F NMR data [ppm, Hz] of the Se-F and Te-F compounds, at measurement temperature *T* [°C].

Compound	Solvent	*T*	$\delta(^{77}\mathrm{Se})$ ($^{1}J_{\mathrm{Se,F}}$) | $\delta(^{125}\mathrm{Te})$ ($^{1}J_{\mathrm{Te,F}}$)	$\delta(^{19}\mathrm{F})$ ($^{2}J_{\mathrm{F,F}}$) [$^{1}J_{\mathrm{Se,F}}$] | [$^{1}J_{\mathrm{Te,F}}$]
TsiSeF	$CFCl_3$	−80	2028.1 (d, 791.9)	−371.0 [785.8]
$Trip_2C_6H_3SeF$	$CFCl_3$	−40	1784.0 (d, 755.0)	−343.6 [754.0]
$Trip_2C_6H_3SeF_3$	CD_2Cl_2	RT	1182.6 (d, t) (794.7, F_e; 110.4, F_a)	F_e: −73.69 (t, 1F) (83.8) [794.2] F_a: −0.37 (d, 2F) (83.8) [110.9]
$Mes_2C_6H_3TeF_2{-}TeC_6H_3Mes_2$	CH_2Cl_2	−80	1516.6 (t, 1162.0) 1164.9 (s)	−95.9
$Mes_2C_6H_3TeF_3$	CH_2Cl_2	−40	1640.2 (d, t) (2286.5, F_e; 261.8, F_a)	F_e: −127.0 [2276.6] F_a: −62.8
$Trip_2C_6H_3TeF_2{-}TeC_6H_3Trip_2$	CD_2Cl_2	RT	1502.4 (t, 909.2, *Te*F_2-Te) 1285.5 (s, TeF_2-*Te*)	-91.38 (s) [909.6]
$Trip_2C_6H_3TeF_3$	CD_2Cl_2	−20	1636.8 (d, t) (2273.6, F_e; 352.2, F_a)	F_e: −125.8 (t, 1F) (27.5) [2273.9] F_a: −62.9 (d, 2F) (27.2) [373.2]



Scheme 1. Synthesis of the Se and Te starting compounds.



Scheme 2. Fluorination of the Se compounds.

out the fluorination by XeF_2 in a solution of CH_2Cl_2 or $CHCl_3$ for 3 h at −30 °C yields mainly $Trip_2C_6H_3SeF_3$ and tBuMe$_2$SiF ($\delta_F = -171.1$ ppm, cf. Ref. [22]). However the target, $Trip_2C_6H_3SeF$ is not even present in traces amounts.

We were finally able to synthesize the tin selenide $Trip_2C_6H_3SeSnMe_3$ by reaction of $Trip_2C_6H_3SeLi$ and Me_3SnCl, and by the same method, $Mes_2C_6H_3SeSnMe_3$ (Scheme 1, structures[20]). The reaction of $Mes_2C_6H_3SeSnMe_3$ with XeF_2 was unsuccessful. Only $Trip_2C_6H_3SeSnMe_3$ reacts with XeF_2 at −30 °C within 3 h selectively to the selenenyl fluoride $Trip_2C_6H_3SeF$ and insoluble Me_3SnF without formation of the selenium trifluoride. The ^{19}F signal appears at $\delta = -343.6$ ppm and the ^{77}Se resonance at $\delta = 1784.0$ ppm with a coupling constant of $^{1}J_{\mathrm{Se,F}} = 755.0$ Hz. Single crystals of $Trip_2C_6H_3SeF$ were obtained from its diethyl ether solution. Figure 1 shows the main result of this work, the first molecular structure of a selenenyl fluoride.[23] For comparison we have

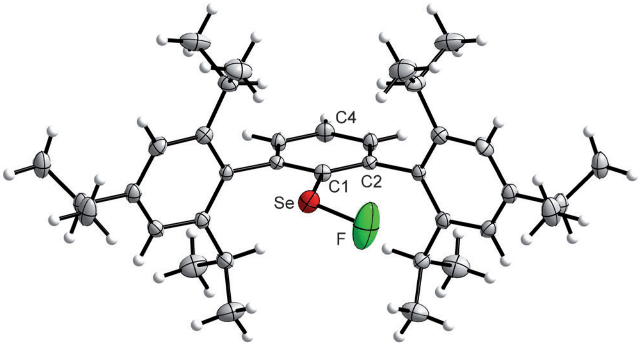
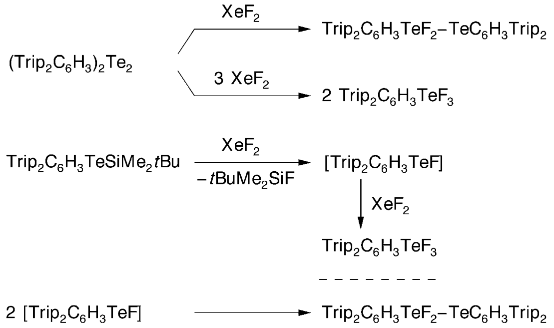


Figure 1. Molecular structure of $Trip_2C_6H_3SeF$ with thermal ellipsoids set at 50% probability (DIAMOND[28]). The SeF group is twofold disordered, only one position is shown. Selected bond lengths [pm] and angles [°]: Se–F 168.23(5), Se–C1 191.65(4); C1-Se-F 102.84(1), Se-C1-C2 128.78(1), C2-C1-Se-F −14.61(2). The dihedral angle between the Se–F bond and the plane of the central benzene ring is 14.6°.

synthesized $Trip_2C_6H_3SeF_3$ by fluorination of the tin-selenium compound with two equivalents XeF_2. However in attempts to crystallize this compound $Trip_2C_6H_3SeOF$ was obtained, clearly by partial hydrolysis (structure[20]).

The Se–F bond length in $Trip_2C_6H_3SeF$ is fairly short, 168.23(5) pm and resembles the bond length to the equatorial F atom in SeF_4,[24] 168.2 pm (gas phase) and in the $SeOF_3^-$ ion,[25] 176.68 pm. Mes_2SeF_2[26] with 188.87 and 187.76 pm and bis(2,2-biphenylen)selenium difluoride[27] with 185.3 pm have longer Se–F bonds. Also the bond angle at the selenium atom, 102.84(1)° resembles the bond angle between equatorial fluorine atoms in SeF_4,[24] 100.6°.

In the tellurium system we began with the fluorination of $(Mes_2C_6H_3)_2Te_2$.[11] Reaction with XeF_2 in CH_2Cl_2 at −30 °C gave first indications for a mixed-valent difluoride $Mes_2C_6H_3TeF_2{-}TeC_6H_3Mes_2$: The ^{125}Te NMR spectrum shows a triplet at $\delta = 1516.6$ ppm and a singlet at $\delta = 1164.9$ ppm, but no indication for a monomer $Mes_2C_6H_3TeF$ compound. The fluorination of $(Trip_2C_6H_3)_2Te_2$[29] (structure[20]) with XeF_2 in 3 h at −30 °C in $CFCl_3$ or CH_2Cl_2 produces wine-red solutions. From these a similar colored room-temperature- and air-stable compound can be isolated after removal of the solvents (Scheme 3). Again no indication for a monomeric $Trip_2C_6H_3TeF$ exists. The ^{125}Te NMR spectrum again shows, besides traces of $Trip_2C_6H_3TeF_3$, two



Scheme 3. Fluorination of the Te compounds.

signals, a triplet at $\delta = 1502.4$ ppm and a singlet at $\delta = 1285.5$ ppm. The ^{19}F NMR signal appears at $\delta = -91.38$ ppm. The red compound can be recrystallized from pentane and the crystal-structure determination[23] shows the mixed-valent $\mathrm{Trip_2C_6H_3TeF_2{-}TeC_6H_3Trip_2}$ (Figure 2). This result corresponds to the structure of $\mathrm{BbtTeF_2{-}TeBbt}$:[13] Sterically protected tellurenyl fluorides are stable in the dimerized molecular form $\mathrm{RTeF_2{-}TeR}$. This structure type was first described for tellurenyl chlorides and bromides,[11,30a] but in the meantime has also been found for iodides.[30b]

The trifluoride $\mathrm{Trip_2C_6H_3TeF_3}$ is obtained from the ditelluride and 3 equivalents $\mathrm{XeF_2}$ and is structurally characterized as well.[20]

To find out if starting compounds with a single tellurium atom might give monomeric ArTeF we tried to prepare $\mathrm{Mes_2C_6H_3TeSnMe_3}$ and $\mathrm{Trip_2C_6H_3TeSnMe_3}$. But inevitably product mixtures containing large amounts ditelluride have been obtained (structure of $\mathrm{Mes_2C_6H_3TeSnMe_3}$[20]). The synthesis of pure $\mathrm{TripC_6H_3TeSiMe_2}t\mathrm{Bu}$ was successful, however. This reacts, in contrast to the analogous selenium compound, with $\mathrm{XeF_2}$ in 3 h at −30 °C. But in the wine-red solution no monomeric $\mathrm{Trip_2C_6H_3TeF}$ is found. The main product is the dimeric difluoride $\mathrm{Trip_2C_6H_3TeF_2{-}TeC_6H_3Trip_2}$ and $t\mathrm{BuMe_2SiF}$ with traces of $\mathrm{Trip_2C_6H_3TeF_3}$ (^{125}Te NMR spectrum[20]). This interesting result shows directly the tendency of RTeF dimerize to $\mathrm{RTeF_2{-}TeR}$, if no donor group is present to stabilize the monomeric form.[12]

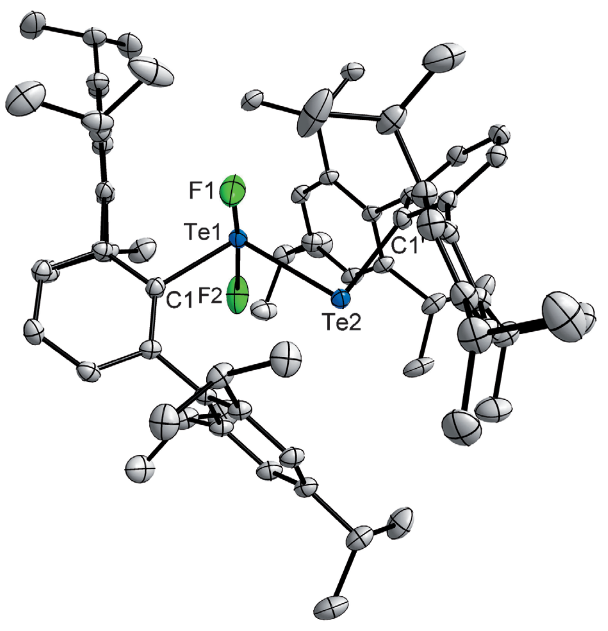


Figure 2. Molecular structure of $\mathrm{Trip_2C_6H_3TeF_2{-}TeC_6H_3Trip_2}$, hydrogen atoms and solvent molecules omitted, thermal ellipsoids set at 50% probability (DIAMOND[28]). The $\mathrm{TeF_2}$-Te group is twofold disordered, only one orientation is shown. Selected bond lengths [pm] and angles [°]: Te1–C1 214.10(23), Te2–C11 216.27(21), Te1–Te2 272.81(33), Te1–F1 200.82(22), Te1–F2 196.18(23); Te2-Te1-C1 107.878(62), Te1-Te2-C11 95.072(60), F1-Te1-F2 167.861(74), C1-Te1-Te2-C11 −159.109(75).

The crystal structure of the ditellurium difluoride has a disorder of the $\mathrm{TeF_2{-}Te}$ part of the molecule. The Te–F bonds have lengths similar to those of the axial tellurium fluorine bonds in $\mathrm{TeF_4{\cdot}2\,THF}$,[31] 196.6(2) and 194.1(2) pm, or in $\mathrm{TripC_6H_3TeF_3}$,[20] 198.57(11) and 192.82(11) pm. The Te–Te distance in the difluoride is almost the same as in the ditelluride,[20] 273.05(5) pm. But the already large C-Te-Te-C dihedral angle in the ditelluride[20] of 146.97(1)° increases further to 159.11(8)° in the difluoride. The structure is quite similar to the $\mathrm{TeF_2{-}Te}$ core of $\mathrm{BbtTeF_2{-}TeBbt}$.[13]

We have calculated the reaction energies of the dimerization $\mathrm{2\,REF \rightarrow REF_2{-}ER}$ and the disproportionation $\mathrm{3\,REF \rightarrow REF_3 + R_2E_2}$ for E = Se and Te. Geometry optimization reproduced the structures of all the compounds without imaginary frequencies, particularly the bi-axial $\mathrm{EF_2}$ geometry of $\mathrm{REF_2{-}ER}$, cf. Ref. [10,11]. The results are shown in Table 2. The Se and Te compounds with Me and Ph groups are thermodynamically unstable against dimerization and disproportionation: the tellurium compounds about 5 kcal mol^{-1} more exothermic than the selenium compounds (see also Ref. [11]). With the bulky Tsi ligand both processes are reduced by 8–12 kcal mol^{-1}, so that the reaction energies for the selenium compound (TsiSeF) are close to zero, while those of the tellurium compound (TsiTeF) remain exothermic. This result is in accord with TsiSeF being observable experimentally. Even the reaction $\mathrm{2\,BbtTeF \rightarrow BbtTeF_2\text{-}TeBbt}$ remains exothermic by 8.5 kcal mol^{-1}.[13] On the other hand for the bulky Bbt ligand the dimerizations of the chlorides, bromides, and iodides BbtTeX (X = Cl, Br, I) are endothermic, they exist as monomers.[32] The $\mathrm{2\text{-}Me_2NCH_2C_6H_4}$ ligand reduces the tendency to dimerize: Dimerization of the selenium compound becomes endothermic and of the tellurium compound with −2 kcal mol^{-1} close to zero. In line with this situation, monomeric RSeF and RTeF compounds with this donor ligand have been shown to exist.[10,12]

Table 2: Zero point energy corrected reaction energies per chalcogen atom calculated with B3PW91/6-311+G(d,p) (Se and Te basis set: SDB-aug-cc-pVTZ) for the dimerization, ΔE_1, $\mathrm{2\,REF \rightarrow REF_2\text{-}ER} + 2\,\Delta E_1$ and the disproportionation, ΔE_2, $\mathrm{3\,REF \rightarrow REF_3 + R_2E_2} + 3\,\Delta E_2$, values in kcal mol^{-1}.

R	E	ΔE_1	ΔE_2	E	ΔE_1	ΔE_2
Me	Se	−12.30	−11.74	Te	−17.03	−16.36
Ph	Se	−10.91	−10.89	Te	−15.97	−15.79
Tsi	Se	−0.28	−2.65	Te	−5.64	−7.33
$\mathrm{2\text{-}Me_2NCH_2C_6H_4}$	Se	2.03	−1.23	Te	−1.95	−5.19

Experimental Section

The Se or Te starting compound (0.5 mmol) is given into 12 mm PFA tube[33] and in vacuum dry $\mathrm{CFCl_3}$ or $\mathrm{CH_2Cl_2}$ (5 mL) are condensed in at −196 °C. At −40 °C ($\mathrm{Tsi_2Se_2}$), in all other cases at −30 °C, $\mathrm{XeF_2}$ (0.5 mmol, 85 mg) is added and the mixture is stirred for 3 h at this temperature. Clear solutions are reduced in volume to ca. 1 mL under further cooling at −40 °C. Cloudy solutions, particularly when $\mathrm{Me_3SnF}$ has formed, are filtered through a precooled syringe filter and given under argon into another precooled 12 mm PFA tube. The solution is likewise reduced in volume to ca. 1 mL. A trace of $\mathrm{CD_2Cl_2}$ for the NMR lock is added. This solution is transferred with argon pressure at −40 °C through a 1 mm teflon tube or by a cooled syringe into a 4 mm PFA tube. This tube is sealed and fitted into a 5 mm NMR tube.

The isolation of $\mathrm{Trip_2C_6H_3SeF}$, $\mathrm{Trip_2C_6H_3SeF_3}$, $\mathrm{Trip_2C_6H_3TeF_2{-}TeC_6H_3Trip_2}$, and $\mathrm{Trip_2C_6H_3TeF_3}$ is performed similarly with the same amounts, except that the clear solutions are evaporated to dryness at the end.

The trifluorides $\mathrm{Trip_2C_6H_3SeF_3}$ (from $\mathrm{Trip_2C_6H_3SeSnMe_3}$) 1 mmol $\mathrm{XeF_2}$ is required, and $\mathrm{Trip_2C_6H_3TeF_3}$ (from $\mathrm{(Trip_2C_6H_3)_2Te_2}$) requires 1.5 mmol $\mathrm{XeF_2}$ for the reaction. NMR data are shown in Table 1. M.p. $\mathrm{Trip_2C_6H_3TeF_2{-}TeC_6H_3Trip_2}$: 235–236 °C (decomp. under blue coloration). IR spectrum: Bands at 471 $\mathrm{cm^{-1}}$ (Te−F) and 205 $\mathrm{cm^{-1}}$ (Te−Te).

Single crystals of $\mathrm{Trip_2C_6H_3SeF}$ are obtained by slow cooling of a $\mathrm{CFCl_3}$ solution from −40 to −80 °C. These crystals contain disordered $\mathrm{CFCl_3}$ solvent molecules. Solvent-free crystals are obtained after completely removing all $\mathrm{CFCl_3}$ in vacuum and recrystallization from diethyl ether by slow cooling from −40 to −80 °C.

Single crystals of $\mathrm{Trip_2C_6H_3TeF_2{-}TeC_6H_3Trip_2}$ are obtained by slow cooling of a solution in pentane from room temperature to −80 °C.

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