Reactive E=C [p−p] π Systems, 46[◇]

Syntheses and X-ray Crystal-Structure Analyses of Trifluoromethyl-Substituted Ketiminodiselanes, Selenoamides and Selenoacrylamides☆

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Bis(trifluoromethylketiminoalkyl)diselanes $[SeC(=NR)CF_3]_2$ (**6**) [R = Me (**a**), *i*Pr (**b**), *t*Bu (**c**)] have been prepared in high yields (55−70%) by reaction of the diselane $(SeC_2F_5)_2$ (**2**) with RNH_2. However, the analogous reaction of **2** with secondary amines, R_2NH, results in the cleavage of the Se−Se bond and leads to the *N,N*-dialkyl-2,2,2-trifluoroselenoacetamides $Se=C(NR_2)CF_3$ (**7**) [R = Me (**a**), *i*Pr (**b**)]. Cleavage of **6a**−**6c** with Me_3SnH affords the selenoamides $Se=C(NHR)CF_3$ (**9**) and the corresponding stannylselanes $Me_3SnSeC(=NR)CF_3$ (**10**) [R = Me (**a**), *i*Pr (**b**), *t*Bu (**c**)]. Selenoamides **7** and **9** can also be prepared from pentafluoroethylselenol $HSeC_2F_5$ (**3**), $Se=C(F)CF_3$ (**1**) or its polymer $[SeC(F)CF_3]_n$ (**4**) and primary or secondary amines. *N,N*-dialkyl-2-methyl-3-fluoro-4,4,4-trifluoroselenoacrylamides $Se=C(NR_2)C(Me)=C(F)CF_3$ [R = Et (**13a**), *i*Pr (**13b**)] are prepared in moderate yields under mild conditions by treating either trifluoromethylselenocarbonyl fluoride (**1**) or its polymer $[SeC(F)CF_3]_n$ with 1-dialkylamino-1-propynes. The reaction proceeds by [2 + 2] cycloaddition and stereospecific electrocyclic ring-opening, yielding, with respect to the resulting C=C double bond, the *E* isomer as the only product. The molecular structures of **7b**, **9a** and **13b** show the typical features of selenoamides with C(Se)−N bond shortening and C−Se bond elongation due to π interaction of the N lone pair with the C=Se double bond. The observed perpendicular orientation of the selenoamide and the alkene units of **13b** prevents π delocalization.

The chemistry of selenoamides has been of considerable interest in the last ten years[2], and a number of efficient preparative routes for alkyl[3−6] and aryl derivatives[6−9] has been described. However, perhalogenoselenoamides are still rare inspite of the fact that fluorinated selenocarbonyl compounds have recently been investigated[10−14]. The first representatives of the type $Se=C(NR_2)CF_3$ were prepared in 1990 by reaction of the trifluoromethylselenocarbonyl fluoride $Se=C(F)CF_3$ (**1**) with secondary amines[12b]. This procedure depends on a multistep preparation of the labile species **1**. There was therefore a demand for more inert and easily available precursors. This led us to investigate the application of the diselane $(SeC_2F_5)_2$ (**2**), the selenol $HSeC_2F_5$ (**3**)[15] and the selenocarbonyl polymer $[SeC(F)CF_3]_n$ (**4**)[12b] as alternative starting compounds. They were selected on the basis of various earlier results:

(i) **2** may be used as a starting compound for the preparation of **1**, **3** or **4** and can be cleaved at the Se−Se bond with organometallic hydrides such as Me_3SnH[12b,15−16] or L_nMH[17] (M = transition metal) affording the selenol **3** and the corresponding Me_3Sn or L_nM derivatives $Me_3SnSeC_2F_5$ and $L_nMSeC_2F_5$. So far, similar reactions of diselanes with amines RNH_2 or R_2NH have not been studied.

(ii) The course of the reaction expected for the selenol **3** will be similar to that of perfluoroalkyl alcohols[18], sulfanes[19], phosphanes[20] and arsanes[21] with dialkylamines, for which HF elimination and formation of the *C*-amino-substituted fluoroheteroalkenes $E=C(NR_2)R_F$ (E = O, S, R_FP, R_FAs) have been observed.

(iii) Polymeric trifluoromethylselenocarbonyl fluoride (**4**) is known to give a mixture of **1** and its dimer $[SeC(F)CF_3]_2$ (**5**) on thermolysis[11,12b] and, therefore, will probably react with alkylamines by stepwise degradation.

Functionalized fluorinated selenoamide derivatives, especially selenoacrylamides, can possibly also be synthesized by [2 + 2] cycloaddition of fluorinated selenocarbonyl compounds to ynamines followed by spontaneous opening of the resulting four-membered heterocycles. This assumption is based on the fact that thio- and selenocarbonyl compounds, due to their particular electronic structure, are both better nucleophiles (high-energy HOMO) and better electrophiles (low-energy LUMO) than the analogous aldehydes or ketones[23] and therefore are suitable as versatile reagents for cycloaddition reactions[2,23]. The selenocarbonyl derivatives are expected to exhibit higher reactivity[24] and fluoro- or perfluoroalkyl substituents at the C(Se) atom will enhance both their reactivity[25] and their stability[26]. This is one of the reasons why perfluorinated selenoketones have become of increasing interest as synthons during the

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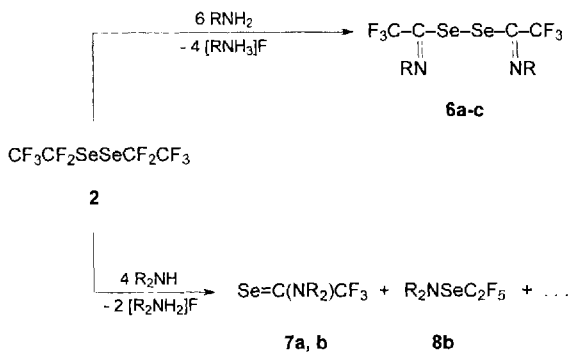
last decade[10–15]. While there exist extensive studies on reactions of selenocarbonyl compounds with 1,3-dipoles[24,27,28] and 1,3-dienes[11–13,28,29], so far only few examples of [2 + 2] cycloaddition reactions have been described for Se=C species coordinated to $M(CO)_5$ complex fragments using π-donor-substituted alkynes as partners[4]. This is not surprising since sterically unshielded derivatives are known to react by self-addition to give the more stable 1,3-diselenetanes[11–14]. Our present study was prompted by an early report of Middleton[25] on the easy [2 + 2] reaction of hexafluorothioacetone with electron-rich olefines.

Here, we report on a systematic study of the reactions of **1** to **4** with primary or secondary amines and on the first investigation of [2 + 2] cycloadditions of a noncoordinated selenocarbonyl derivative to ynamines.

Bis(trifluoromethylketiminoalkyl)diselanes 6 and *N,N*-Dialkylamino-2,2,2-trifluoroselenoacetamides 7 from 2 and RNH_2 or R_2NH

Bis(perfluoroethyl)diselane **2** reacted with primary amines RNH_2 (molar ratio **2**/amine = 1:6) on warming up the reaction mixture from −196°C to room temperature and yielded the bis(trifluoromethylketiminoalkyl)diselanes $[SeC(=NR)CF_3]_2$ [R = Me (**6a**), *i*Pr (**6b**), *t*Bu (**6c**)].

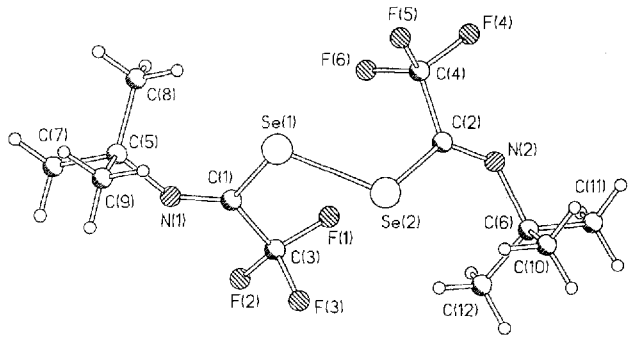
Scheme 1



[R = Me (**a**), *i*Pr (**b**), *t*Bu (**c**); **8a** not identified]

The molecular and electronic structure of **6a**–**6c** was deduced from spectroscopic investigations, and conclusively ascertained by an X-ray diffraction study of **6c**. The $^{77}Se\{^1H\}$ resonances of **6a**–**6c** between δ = 379 and 483 are typical for dialkyldiselanes[30]. In contrast to **6a** and **6b**, derivative **6c** showed a quadruplet signal in the ^{77}Se spectrum which is due to coupling with the fluorine nuclei [^3J(SeF) = 18.3 Hz]. In the Raman spectra of **6b** and **6c**, the C–H stretching modes were observed between 2988 and 2872 cm^{-1}, the C=N valence frequencies $\tilde{\nu}$ (C=N) at 1651 (**6b**) and 1669 cm^{-1} (**6c**). The $\tilde{\nu}$ (Se–Se) absorption for both compounds was found at 273 cm^{-1} in accord with data of other CF_3-containing diselanes[31]. Suitable crystals of **6c** were obtained at −5°C from a pentane solution. The compound crystallizes in the monoclinic crystal system with the space group $P2_1/n$. The molecular structure and a selection of typical bond lengths and angles are presented in Figure 1.

Figure 1. Molecular structure of **6c**[a]



[a] Selected bond lengths [Å] and angles [°]: Se1–Se2 2.319(1), Se1–C1 1.971(5), Se2–C2 1.989(6), C1–C3 1.522(8), C2–C4 1.511(8), N1–C1 1.241(8), N1–C5 1.479(7), N2–C2 1.236(8), N2–C6 1.488(7); Se1–Se2–C1 107.6(2), Se1–Se2–C2 105.2(2), C1–N1–C5 128.4(5), C2–N2–C6 128.8(5), Se1–C1–N1 126.7(4), Se1–C1–C3 116.7(5), N1–C1–C3 116.6(5), Se2–C2–N2 127.4(4), Se2–C2–C4 115.0(4), N2–C2–C4 117.6(5).

The Se(1)–Se(2) distance of 2.319(1) Å and the Se–C distances [Se(1)–C(1) 1.971(5); Se(2)–C(2) 1.989(6) Å] are characteristic for single bonds and agree with data found for other diselanes[32,33]. As expected, the C=N distances [N(1)–C(1) 1.241; N(2)–C(2) 1.236 Å] correspond to true double bonds. The dihedral angles C(3)–C(1)–N(1)–C(5) and C(4)–C(2)–N(2)–C(6) of 179.9° display the *trans* conformation of the CF_3 and the respective *t*Bu group.

The torsion angle ω[C(1)–Se(1)–Se(2)–C(2)] of 86.4° for **6c** is typical for organosubstituted diselanes, as demonstrated by the following examples: $(MeSe)_2$ 87.5(4)° (electron diffraction)[34], 85.64° (ab initio, 3-21G basis set)[35]; $(SeCF_3)_2$ 84.5(3)° (electron diffraction)[36]; $(p\text{-}NO_2C_6H_4Se)_2$ 87.8° (X-ray)[37]. Derivatives with bulky substituents, however, show larger torsional angles[38,39]; an unusual value of 180° is observed for $[(Me_3Si)_3CSe]_2$[40].

Diselane **2** reacted with secondary amines such as Me_2NH or iPr_2NH more slowly than with primary amines. Starting with a molar ratio **2**/amine >1:4 at 20°C, the selenoamides **7a** and **7b** were formed as main products (ca. 40%; Scheme 1). The ^{19}F-NMR spectrum of the reaction mixture contained signals and coupling patterns which indicate the formation of further dialkylamino-substituted selanes and diselanes besides **7**. A complete characterization of these high-boiling components was not possible, because they could not be isolated from the mixture. During the reaction of **2** with iPr_2NH, the intermediate $iPr_2NSeC_2F_5$ (**8b**) was identified by NMR measurements; however, the related dimethylamino compound $Me_2NSeC_2F_5$ (**8a**)[41] obviously undergoes a fast subsequent reaction and could not be detected in the ^{19}F-NMR spectrum.

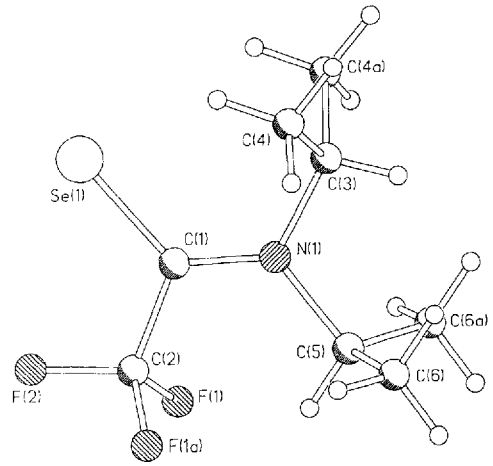
To explain the experimental results, we assumed that the secondary amines, by analogy to the RNH_2 derivatives, first attacked one of the CF_2 groups of **2**. The resulting products $[CF_3C(F)(NR_2)SeSeC_2F_5]$ were then cleaved at the Se–Se bond by R_2NH yielding **7** and **8**. In a competitive reaction, the primary products, as well as **2** and **8**, may undergo an energetically favoured substitution of a CF_2 fluorine atom

by NR_2. The alternative formation of **7**, from the selenol **3**, is less probable since the aminolysis of **3** was found to be a very fast reaction even at low temperatures (see below).

7a and **7b** were characterized by spectroscopic methods. The results obtained are identical with those for the same products prepared from **1** and the corresponding amines[12b]. The $^{77}Se\{^1H\}$-NMR data in ref.[12b] were completed by the result for **7b**.

Definite and important additional information about the molecular and electronic structure of compounds **7** was obtained from a single crystal X-ray diffraction analysis of **7b**. Figure 2 shows the molecular structure together with selected bond lengths and bond angles.

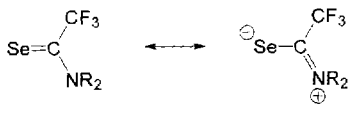
Figure 2. Molecular structure of **7b**[a]



[a] Selected bond lengths [Å] and angles [°]: Se1–C1 1.811(4), N1–C1 1.338(5), C2–C1 1.533(6), N1–C3 1.498(5), N1–C5 1.508(5), F1–C2 1.335(3), F2–C2 1.333(5), Se1–C1–C2 116.3(3), Se1–C1–N1 127.3(3), N1–C1–C2 116.3(3), C3–N1–C5 113.6(3), C1–N1–C5 123.9(3), C1–N1–C3 122.5(3).

These data indicate that the framework of the molecule lies in one plane, which also contains the substituents F(2), H(3a) and H(5a). The π delocalization showing up in the planarity of the skeleton of **7b** gains further support from the Se(1)–C(1) distance of 1.811(4) Å being considerably shorter than Se–C single bonds (1.970 Å)[32] and longer than the double bond in $Se{=}CF_2$ (1.743 Å)[42]. The data are in good agreement with those of seleno urea $Se{=}C(NH_2)_2$ (1.86 Å)[43] and its derivatives[4,5,9]. In accord with the NMR results[12b], the short C(1)–N(1) distance of 1.338(5) Å also confirms the expected electronic π interaction between the lone pair of the nitrogen atom and the (Se=C) π system as shown in Scheme 2.

Scheme 2

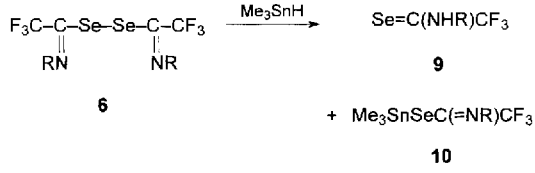


A B

Cleavage of the Ketimino diselanes 6a–6c with Trimethylstannane

6a–6c contain two reactive centers, the Se–Se bond and the unsaturated C=NR group. The structural data for **6c** indicate that the Se–Se bond is typical for diselanes and, therefore, **6a–6c** are expected to react with Me_3SnH in a similar way to perfluoroalkyldiselanes $(R_FSe)_2$. The results obtained in the cleavage reaction of **6a–6c** with Me_3SnH are presented in Scheme 3.

Scheme 3

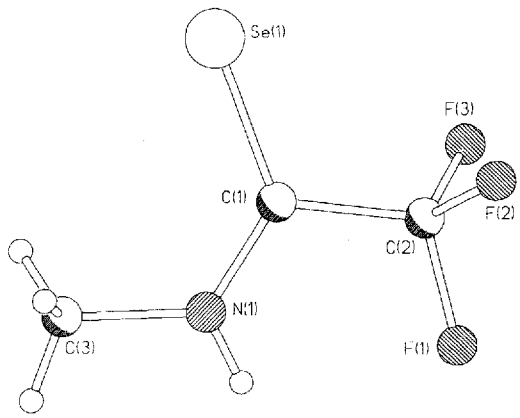


6, 9, 10 : R = Me (**a**), *i*Pr (**b**), *t*Bu (**c**)

Fission of the Se–Se bond occurred under very mild conditions at temperatures between −196 and 20°C affording the volatile *N*-alkylamino-2,2,2-trifluoroselenoacetamides **9a–9c** and the corresponding stannylselanes **10a–10c** in high yields (see Experimental Section). Composition and molecular structures of **9a–9c** were deduced from their elemental analyses and spectroscopic data together with an X-ray diffraction study of **9a**. Typical results that prove the formation of N–H instead of Se–H bonds, include the N–H valence bands between 3355 cm^{-1} (**9b**) and 3418 cm^{-1} (**9a**), the ^1H-NMR signals of the NH groups at δ = 8.26 to 8.96 and the $^{77}Se\{^1H\}$ resonances near δ = 700 which are characteristic for selenoamides[3c,44].

Figure 3 shows the molecular structure of **9a** which confirms the spectroscopic results and corresponds well to the structure of **7b** with an enlarged C=Se double bond and a C(1)–N(1) distance close to a double bond typical for this type of compounds. The observed *trans* conformation (Se=C/N–H and CH_3/CF_3) is the energetically most favourable arrangement and is in accord with literature results for oxo-, thio- and selenoamides[45].

Figure 3. Molecular structure of **9a**[a]



[a] Selected bond lengths [Å] and angles [°]: Se1–C1 1.804(3), N1–C1 1.306(4), C1–C2 1.524(5), N1–C3 1.458(5), F1–C2 1.342(4), F2–C2 1.333(4), F3–C2 1.327(4); Se1–C1–N1 126.3(3), Se1–C1–C2 118.8(2), N1–C1–C2 114.9(3).

The first-step products expected from the cleavage of **6a–6c** with Me_3SnH are the ketiminoalkylselenols $HSeC(=NR)CF_3$ and the stannylselanes **10a–10c**. Obvi-

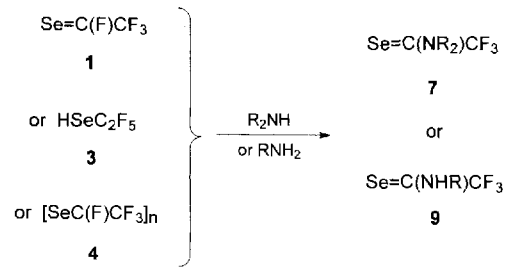
ously, the iminoselenols undergo a fast 1,3-hydrogen migration from Se to N yielding the tautomeric selenoamides **9a–9c**. Similar tautomeric equilibria are known for the related sulfur compounds[46]. The hydrogen migration after cleavage of the Se–Se bond is so fast that the selenol intermediates cannot be detected by NMR measurements[47].

The stannylselanes **10a–10c** were obtained as high-boiling yellow oils. Their $^{77}Se\{^1H\}$ resonances are shifted to high field [δ_{Se} = −26.0 (**10b**); 64.6 (**10c**)] as compared to those of trialkyl- or triphenylstannylselenocarbamates[48]. The mass spectra of **10a–10c** do not show the molecular ions M^+ but the fragments [$M^+ - CH_3$] as peaks with the highest *m/z* values; base peaks of the spectra are generally due to the fragment [Me_3Sn^+].

Reactions of the Selenol 3 and the Poly(trifluoromethylselenocarbonyl fluoride) 4 with Primary or Secondary Amines

The formation of the selenoamides **7a** and **7b** according to Scheme 1 was tested by the direct reaction of **3** with R_2NH or RNH_2. The reactions were carried out at −20°C in ether solution and led to high yields of the corresponding selenoacetamides **7a** and **7b** or **9a–9c** (Scheme 4). Most likely, the initial step of this process is the base-induced HF elimination giving the trifluoromethylselenocarbonyl fluoride $Se{=}C(F)CF_3$ (**1**) as a very reactive intermediate. As shown in separate experiments with authentic **1**, its reactions with primary amines in a molar ratio 1:2 proceed like those of secondary amines[12b] yielding the monoalkylselenoacetamides **9a–9c**.

Scheme 4

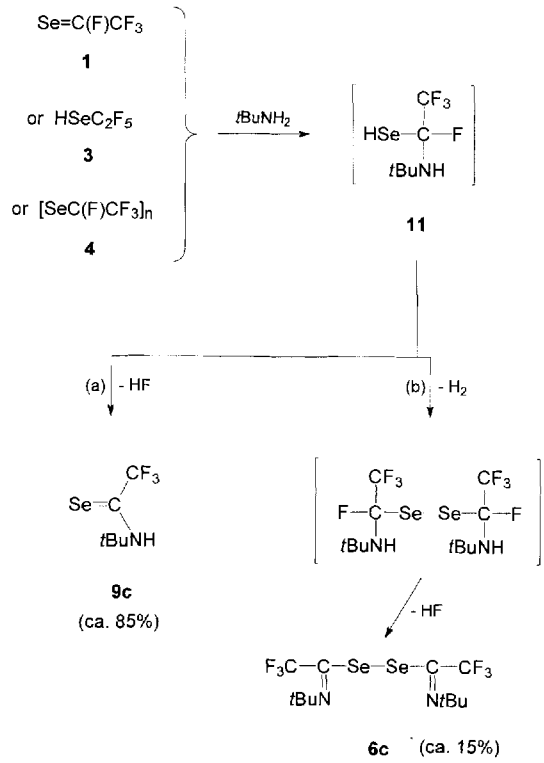


7, 9 : R = Me (**a**), *i*Pr (**b**), *t*Bu (**c**)

A surprising and interesting result is the observation that the polymer of **1** is attacked by amines already under mild conditions. Thus, a suspension of the polymer **4** reacted with R_2NH or RNH_2 at 20°C completely within 30 minutes affording the corresponding selenoacetamides **7a** and **7b** or **9a–9c** in almost quantitative yields (exception: **9c**). Since **4** undergoes thermal degradation to monomeric **1** and the dimer $[SeC(F)CF_3]_2$ (**5**) only at elevated temperatures (ca. 200°C)[11,12b], the activation energy necessary for the reaction with amines is obviously supplied by the exothermic formation of the stable selenoamides.

In the reaction of **1**, **3**, or **4** with *tert*-butylamine, the ketiminodiselane **6c** was formed as a side-product in about 15% yield together with **9c**. Since hydrogen gas was evolved during this process, the formation of **6c** can be attributed to a competitive subsequent reaction of the primary addition product **11** (Scheme 5). The main route (a) leading to **9c** is governed by the intramolecular HF elimination, while side route (b) starts from an intermolecular metathesis giving H_2 and the diselane $[SeC(tBuNH)(F)CF_3]_2$. A similar reaction has already been reported for pentafluoroethaneselenol **3**[15,49].

Scheme 5

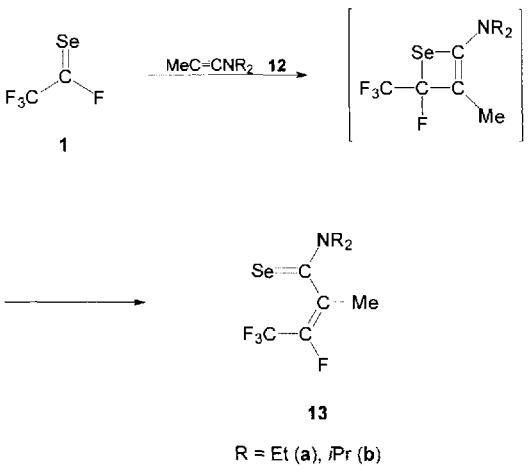


[2 + 2] Cycloaddition of Trifluoromethylselenocarbonyl Fluoride (1) with Ynamines

Trifluoromethylselenocarbonyl fluoride (**1**) reacted with equimolar amounts of 1-diethylamino-1-propyne (**12a**) or 1-diisopropylamino-1-propyne (**12b**) in dichloromethane after quick thawing of the mixture from −196 to 20°C affording the novel selenoacrylamides **13a** or **13b** (Scheme 6) within minutes. The reaction could be followed by a fast colour change from violet to orange.

The known dimer $[SeC(F)CF_3]_2$ (**5**) was formed as a by-product in about 10 to 15% yield (^{19}F NMR)[11,12b]. Compounds **13a** and **13b** could be isolated in pure form by pumping off the volatile components of the reaction mixture (dichloromethane, dimer **5** and unreacted **12a** or **12b**) and washing the residue with pentane (yield ca. 60%). Composition and constitution of the novel selenocarbonylamides **13a**, **13b** have been determined by elemental analysis, spectroscopic methods (IR, MS; ^1H-, ^{13}C, ^{19}F-, ^{77}Se NMR) and an X-ray diffraction study of **13b**. The data indicate that **13a** and **13b** are formed exclusively in one of the possible isomeric structures thereby proving that the cycload-

Scheme 6



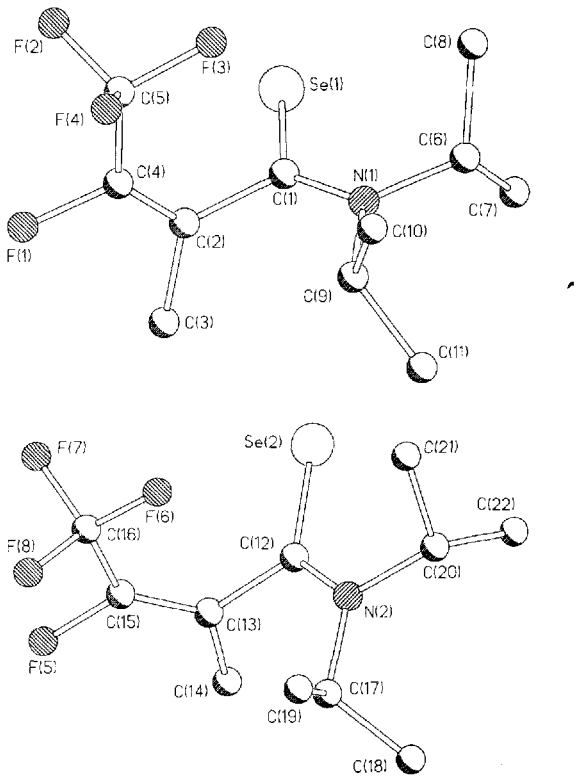
dition reaction is regiospecific and the electrocyclic ring opening stereoselective.

In accord with reactions of coordinated selenoaldehydes or -ketones with ynamines[4], the 2*H*-selenetenes expected as the first-step intermediates could not be detected by NMR measurements. Obviously, the ring opening reaction due to the influence of the π-donor substituents R_2N is very fast. Fischer et al.[50] have recently shown that the analogous reactions of pentacarbonyl(selenoaldehyde)tungsten complexes with other π-donor-substituted alkynes or alkenes, e.g. bis(*tert*-butylthio)ethyne or ethyl vinyl ether, result in the preparation of the corresponding coordinated four-membered ring systems (2*H*-selenetene[50a] or selenetane derivatives[50b]).

As expected, the alkyl substituents of the amide groups in **13a** and **13b** are chemically not equivalent because of the π interaction within the Se−C−N unit and, therefore, give rise to separate signals in the ^{1}H- and ^{13}C-NMR spectra. The detected resonances have been assigned to the *syn*- or *anti*-alkyl group at the nitrogen atom with respect to the Se=C fragment on the basis of literature data[4,51]. The ^{13}C and ^{77}Se signals of the C=Se group are observed at chemical shifts typical for trifluoromethyl-, alkyl- or arylselenocarbonylamides[4,52] indicating that in **13a** and **13b** the olefinic group at the C(Se) atom has only little effect on the electronic structure. In conclusion, π interaction between the C=C and the C=Se group can be excluded. According to a spectroscopic study of Abraham et al.[53] about H,F couplings in fluoro olefines, the ^4J(F,H) coupling constants of 4.2 (**13a**) and 3.9 Hz (**13b**) suggest *cis* configuration of CH_3 and F at the C=C double bond. However, this assignment is somewhat uncertain because the constants ^4J(F,H) for the *cis* and *trans* compounds differ only by ca. 1 Hz[53], e.g. for $Me_2C{=}C(F)CO_2Et$: $^4J(F,H)_{cis}$ = 4.2 Hz, $^4J(F,H)_{trans}$ = 3.3 Hz.

Definite information about the molecular structure of the selenoacrylamides **13** was obtained by a single-crystal X-ray diffraction analysis of **13b** (Figure 4) which crystallizes as a racemic twin in the orthorhombic crystal system (space group $P2_12_12_1$) with two molecules in the asymmetric unit. The structural data of both molecules differ only a little; they confirm the acyclic constitution already deduced from the NMR parameters and the *cis* position of CH_3 and F in the alkene unit. Thus, compounds **13** are formed only as *E* isomers (CF_3 *trans* to CH_3).

Figure 4. Molecular structure of **13b**[a]



[a] Selected bond lengths [Å] and angles [°]: Se1−C1 1.823(9), N1−C1 1.34(1), C1−C2 1.49(1), C2−C4 1.30(2); Se2−C12 1.828(9), N2−C12 1.32(1), C12−C13 1.51(1), C3−C15 1.35(2); Se1−C1−N1 128.1(8), Se1−C1−C2 113.7(6), N1−C1−C2 118.1(9), C1−N1−C6 122.6(9), C1−N1−C9 121.1(8), C6−N1−C9 116.2(8); Se2−C12−N2 128.6(7), Se2−C12−C13 112.2(7), C13−C12−N2 119.2(8), C12−N2−C20 123.4(8), C12−N2−C17 121.6(8), C17−N2−C20 114.9(7).

The data for the Se=C(N*i*Pr$_2$) fragment correspond to those of **7b** and **9a** and to literature values of selenocarbonylamides[5,9]. Thus both selenoketone C atoms C(1) and C(12) (sum of angles: 360.0 and 359.9°), as well as the amide nitrogen atoms N(1) and N(2) (sum of angles: 360.0 and 359.8°) have planar configurations with Se=C bond lengths of 1.823(9) and 1.828(9) Å, values between Se−C single bonds (1.970 Å)[32] and Se=C double bonds (Se=CF_2: 1.743 Å[42]; 1,5-dimethyl-3,7-dithiacyclo[3.3.1]-nonane-9-selone: 1.774 Å[54]; 4,4'-dimethoxyselenobenzophenone: 1.790 Å[55]). The coplanarity of the planes through Se(1)−N(1)−C(1)−C(2) and N(1)−C(6)−C(9) or Se(2)−N(2)−C(12)−C(13) and N(2)−C(17)−C(20) together with the short N(1)−C(1) or N(2)−C(12) distances of 1.34(1) and 1.32(1) Å prove that the lone pair at the nitrogen atom takes part in a delocalized π system. On the other hand, the alkene plane is almost perpendicular (angles of 90.8 and 98.0°, respectively) to the selenocarbon-

ylamide plane. Comparison with the structures of two ether selenoacrylamides[4], the tungsten complex $(CO)_5W[Se=C(NEt_2)C(Me)=C(H)Ph]$ and the noncoordinated compound $Se=C(NEt_2)C(Me)=CPh_2$, reveals a close correspondence of the dihedral angles of **13b** and the ligand in the complex (89°), but a considerable discrepancy to the angle of 66.5° for the latter derivative. The observed perpendicular orientation of the selenocarbonylamide and the alkene plane in **13b** excludes conjugation between the corresponding π systems and hetero Diels–Alder reactions[23] of **13a** or **13b** with highly reactive dienophiles such as **1**[11–13].

In the reaction of poly(trifluoromethylselenocarbonyl fluoride) $[SeC(F)CF_3]_n$ (**4**) with primary or secondary amines described above, **4** acts as a synthetic equivalent for **1**. Similarly, the step-by-step degradation of **4** can be used for the formal [2 + 2] cycloaddition with the ynamines **12a** or **12b** which already occur at room temperature yielding the selenoacrylamide derivatives **13a** or **13b**. The reactions of **1** and **4** differ in the formed amounts of the dimer $[SeC(F)CF_3]_2$ (**5**) (**1**: 15%; **4**: 30%). It is surprising that **12a** and **12b** attack the polymer **4**, but not the dimer **5**. In an effort to understand this result, we have studied in separate experiments the reaction of **5** with primary and secondary amines and observed that in contrast to **1** or **4** the dimer does not react, demonstrating its inertness against nitrogen bases.

Conclusion

Various synthetic routes to fluorine-containing selenoacetamides have been developed starting from trifluoromethylselenocarbonyl fluoride (**1**), its polymer $[SeC(F)CF_3]_n$ (**4**) or the diselane $(SeC_2F_5)_2$ (**2**). The *N,N*-dialkyl derivatives **7** generally can be obtained by reaction of the precursors **1**, **2**, $HSeC_2F_5$ (**3**) or the polymer **4** with secondary amines R_2NH in moderate to high yields. The most appropriate starting compound is the diselane **2** because it also serves as a precursor for the other starting compounds. The novel *N*-alkylselenoacetamides **9** can be prepared by similar procedures from **1**, **3**, or **4** and primary amines RNH_2. For these derivatives, however, the starting compound **2** is not suited because its reaction with primary amines does not produce compounds of type **9** but yields the ketiminodiselanes $[SeC(=NR)CF_3]_2$ (**6**), which are interesting starting compounds for further investigations, such as cleavage reactions of the Se–Se bond with a variety of reagents. The reaction of **6a–6c** with trimethylstannane leading to **9a–9c** and ketimino-functionalized stannylselanes of the type $Me_3SnSeC(=NR)CF_3$ (**10**) may suffice for illustration.

The present investigation has established that the selenocarbonyl compound $Se=C(F)CF_3$ (**1**) and its polymer **4** react with ynamines under very mild conditions affording the novel selenoacrylamides **13a** and **13b** by [2 + 2] cycloaddition and a stereospecific ring opening. Similar results, but with detection of the four-membered ring as the first-step intermediate, were recently obtained in reactivity studies of the related fluorophosphaalkenes. Thus, perfluoro-2-phosphapropene undergoes a smooth [2 + 2] cycloaddition with ethoxyacetylene or dimethylaminopropyne at temperatures below 0°C[56]. Alkyl or aryl derivatives of the type $RP=CR'_2$, however, only react with electron-rich alkenes or alkynes if coordinated to a $W(CO)_5$ fragment[57]. Therefore, further successful [2 + 2] reactions are to be expected for the other fluoroheteroalkenes $R_FE=C(F)R'_F$ or $E'=C(F)R_F$ (E = P, As; E' = S, Se).

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Experimental Section

General: The sensitivity, disagreeable smell, and the possible high toxicity of the organoselenium compounds required handling in closed vessels or under argon using a standard high-vacuum line. All solvents were purified, dried, and degassed. – Starting compounds: trifluoromethylselenocarbonyl fluoride (**1**)[12b], bis(perfluoroethyl)diselane (**2**)[58], pentafluoroethanselenol (**3**)[15], trimethylstannane[59], 1-(diethylamino)-1-propyne (**12a**)[60a], and 1-(diisopropylamino)-1-propyne (**12b**)[60b] have been prepared according to the literature. – NMR: Bruker WH 90, AC 200, ARX 300 (^1H, standard: TMS; ^{13}C, standard: TMS; ^{19}F, standard: CCl_3F); Bruker AM 360 (68.68 MHz, ^{77}Se, standard: Me_2Se, 60% in $CDCl_3$). – MS(EI): Model CH5, Varian MAT (70 eV, gas inlet at 20°C, direct inlet at 20 or 40°C). – IR: Bruker 48 IFS. – Raman: Bruker 66-FRA 106; Neodymium YAG Laser 1064 nm. – Elemental analyses: Perkin-Elmer Analyser 240.

1,2-[1-(Methylimino)-2-(trifluoromethyl)ethyl]diselane (**6a**): 2.9 g (7.3 mmol) of $(SeC_2F_5)_2$ (**2**), 8 ml of CH_2Cl_2 and 1.13 g (36.5 mmol) of $MeNH_2$ were condensed in a small ampoule and sealed under vacuum. After slowly increasing the temperature, the yellow colour of the stirred mixture intensified at −30°C, indicating the start of the reaction. The conversion was complete when room temperature was reached by warming slowly. All volatiles were removed and the residue was dissolved in 25 ml pentane and then transferred under argon to a glass frit. The remaining residue was washed with 20 ml of additional pentane. Removal of the solvent by vacuum condensation gave the pure product in the form of an orange oil, yield 1.5 g (55%). The use of a more than 5:1 ratio of the starting materials $[MeNH_2/(C_2F_5Se)_2]$ caused a strong exothermic reaction accompanied by decomposition, precipitation of elemental selenium and a reduced yield. – IR (film): $\tilde{\nu}$ = 2981 cm^{-1} (m), 2920 (m), 1661 (vs), 1457 (m), 1437 (m), 1430 (m), 1395 (s), 1370 (m), 1302 (s), 1273 (vs), 1198 (vs), 1147 (vs), 1100 (m), 1085 (s), 999 (s), 906 (s), 717 (s), 580 (m). – ^1H NMR (300.13 MHz, $CDCl_3$, 25°C): δ = 3.53 (s). – $^{13}C\{^1H\}$ NMR (75.43 MHz, $CDCl_3$, 25°C): δ = 44.1 (s, CH_3), 117.8 (q, $^1J(F,C)$ = 279.0 Hz, CF_3], 144.9 [q, $^2J(F,C)$ = 38.3 Hz, CSe]. – ^{19}F NMR (84.66 MHz, $CDCl_3$, 25°C): δ = −66.0 (s). – $^{77}Sc\{^1H\}$ NMR (68.68 MHz, $CDCl_3$, 25°C): δ = 379.1 (s).

1,2-[1-(Isopropylimino)-2-(trifluoromethyl)ethyl]diselane (**6b**): The preparation corresponds to that of **6a** by reaction of **2** (3.22 g, 8.13 mmol) with $iPrNH_2$ (2.89 g, 48.8 mmol) in dichloromethane (8 ml). Yield 2.50 g (71%), orange oil. – IR (film): $\tilde{\nu}$ = 2977 cm^{-1} (s), 2935 (m), 2874 (m), 1649 (s), 1466 (m), 1445 (m), 1385 (m), 1366 (m), 1337 (m), 1271 (vs), 1246 (m), 1229 (m), 1194 (vs), 1150 (vs), 914 (s), 709 (s), 539 (m), 416 (m). – Raman (liquid): $\tilde{\nu}$ = 2971 cm^{-1} (s), 2930 (s), 2919 (s), 2872 (s), 1651 (m), 1453 (m), 698 (m),

291 (m), 273 (s), 81 (m). – ^{1}H NMR (300.13 MHz, CD_2Cl_2, 25°C): δ = 1.29 (d, J = 6.2 Hz, 12H, CH_3), 4.08 [sept, J = 6.2 Hz, 2H, $CH(CH_3)_2$]. – ^{13}C{^{1}H} NMR (73.43 MHz, CD_2Cl_2, 25°C): δ = 23.3 (s, CH_3), 59.6 (s, CH), 119.0 [q, ^1J(F,C) = 279.4 Hz, CF_3], 142.0 [q, ^2J(F,C) = 36.9 Hz, CSe). – ^{19}F NMR (84.66 MHz, CD_2Cl_2, 25°C): δ = –63.3 (s). – ^{77}Se{^{1}H} NMR (68.68 MHz, $CDCl_3$, 25°C): δ = 396.4 (s). – $C_{10}H_{14}F_6N_2Se_2$ (434.13): calcd. C 27.66, H 3.23, N 6.46; found C 27.37, H 3.18, N 6.67.

1,2-[1-(tert-Butylimino)-2-(trifluoromethyl)ethyl]diselane (**6c**): 3.0 g (7.6 mmol) of $(SeC_2F_5)_2$ (**2**), 10 ml of CH_2Cl_2 and 3.33 g (45.5 mmol) of tBuNH$_2$ were condensed into an ampoule. After sealing, the reaction mixture was brought to –30°C and then slowly warmed up to room temperature whilst stirring. The reaction started at –10°C, discernible by the gradual increase of the yellow colour of the solution. To complete the reaction, the mixture was stirred at room temperature for an additional 30 minutes. All volatiles were removed by vacuum condensation, 30 ml of pentane were condensed onto the yellow residue and the mixture was filtered through a glass frit under argon. After washing with 50 ml of pentane, the solvent was removed from the combined solutions. Precipitation of elemental selenium indicated partial decomposition of the product. Repeated dissolving in 40 ml pentane followed by filtration under argon gave, after removal of the solvent under high vacuum, a stable product at room temperature if light was avoided. Crystallization from 30 ml of pentane at –5°C gave flaky, yellow crystals of **6c** suitable for a crystal structure analysis, yield 2.5 g (70%). – IR (KBr): $\tilde{\nu}$ = 2976 cm^{-1} (m), 2933 (m), 1656 (s), 1641 (m), 1368 (m), 1274 (m), 1258 (s), 1230 (m), 1187 (vs), 1150 (s), 1139 (vs), 924 (m), 911 (m), 900 (s), 765 (m), 695 (s). – Raman (solid): $\tilde{\nu}$ = 2988 cm^{-1} (s), 2930 (s), 2919 (s), 1669 (m), 1465 (m), 1227 (m), 709 (m), 488 (m), 291 (m), 273 (s), 163 (s), 116 (s), 93 (s), 81 (s). – ^{1}H NMR (300.13 MHz, CD_2Cl_3, 25°C): δ = 1.44 (s). – ^{13}C{^{1}H} NMR (75.43 MHz, $CDCl_3$, 25C): δ = 29.4 [s, $C(CH_3)_3$], 59.8 [s, $C(CH_3)_3$], 117.8 [q, ^1J(F,C) = 281.8 Hz, CF_3], 137.0 [q, ^2J(F,C) = 37.0 Hz, CSe]. – ^{19}F NMR (84.66 (MHz, $CDCl_3$, 25°C): δ = –63.1 (s). – ^{77}Se{^{1}H} NMR (68.68 MHz, $CDCl_3$, 25°C): δ = 483.2 [q, ^3J(Se,F) = 18.3 Hz]. – MS (70 eV, 40°C, direct inlet), based on ^{80}Se; *m/z* (%): 464 (1) [M$^+$], 369 (4) [M$^+$ – tBu – 2F], 312 (31) [M$^+$ – CF_3 – CNtBu + H], 242 (50) [M$^+$ – 2 CF_3 – CNtBu], 57 (100) [$C_4H_9^+$] and further fragments. – $C_{12}H_{18}F_6N_2Se_2$ (462.18): calcd. C 31.18, H 3.93, N 6.06; found C 31.44, H 4.00, N 6.02.

General Procedure for the Preparation of Selenoamides **7a** and **7b**: 1.09 g (2.75 mmol) of $(SeC_2F_5)_2$ (**2**), 6 ml of CH_2Cl_2, and 11.0 mmol of Me_2NH or iPr_2NH were condensed in a 50-ml Schlenk vessel and carefully warmed up. A colour change of the solution from yellow to orange indicated the start of the reaction at –10°C. After reaching room temperature, all volatiles were removed under high vacuum. In the remaining residue decomposition was observed with formation of elemental selenium. Pure **7a**, or **7b** was isolated by sublimation onto a cold finger under high vacuum at room temperature. Yield **7a**: 0.14 g (24.8%), **7b**: 0.23 g (32.2%). The spectroscopic data of 2,2,2-trifluoro-*N,N*-dimethylselenoacetamide (**7a**) and 2,2,2-trifluoro-*N,N*-diisopropylselenoacetamide (**7b**) are identical with previous results[12b]. **7b** was further characterized by the ^{77}Se-NMR spectrum and an X-ray diffraction study. – ^{77}Se{^{1}H} NMR ($CDCl_3$, 25°C): δ = 828.8 (s).

General Procedure for the Preparation of the Selenoacetamides **9a–9c**. – *Method A:* Cleavage reaction of the diselanes **6a–6c** with Me_3SnH giving **9a–9c** together with the stannylselanes **10a–10c** (see below). – *Method B:* 0.45 g (2.5 mmol) of Se=C(F)CF_3 (**1**), 3 ml of CH_2Cl_2 and 7.5 mmol of the relevant primary amine (R = Me: 0.23 g; iPr: 0.44 g; tBu: 0.55 g) were condensed in a small ampoule. After sealing under high vacuum, the mixtures were rapidly brought to room temperature with shaking. The start of the reaction was accompanied by instantaneous colour changes. After a few seconds, the completion of the reaction was indicated by the disappearance of the purple colour of **1**. All volatiles, including the corresponding *N*-alkylselenoacetamides **9a–9c**, were quickly condensed off. The purification of the volatile products by trap-to-trap condensation [–50°C (R = Me: –65°C); –196°C] delivered the pure compounds in the first traps. To isolate the side product [SeC(NtBu)CF_3]$_2$ (**6c**), formed in the reaction with tBuNH$_2$, the residue was treated with 10 ml of pentane and all the insoluble compounds were filtered off with a glass frit under argon. Removal of the solvent by vacuum condensation gave the pure yellow side product **6c**. Yields: **9a**: 0.27 g (56%); **9b**: 0.35 g (64%); **9c**: 0.23 g (39%); **6c**: 0.10 g (17%). – *Method C:* 0.50 g (2.8 mmol) of Se=C(F)CF_3 (**1**) was condensed in a 50 ml Schlenk flask in the smallest area possible and thawed very slowly. Usually, the polymerization of **1** started immediately. For completion, the flask was repeatedly warmed up and cooled before pumping off all remaining volatile compounds. Then 8 ml of CH_2Cl_2 and 5.6 mmol of the corresponding primary amine (R = Me: 0.17 g; iPr: 0.33 g; tBu: 0.41 g) were added by condensation and the mixture was stirred at room temperature. Reactions of the components were signalled by a colour change to yellow and the gradual disappearance of the polymer $[SeC(F)CF_3]_n$, which is insoluble in CH_2Cl_2. Within 30 min the reactions were complete, and the mixtures were worked up as described under *Method B*. Yields: **9a**: 0.51 g (96%); **9b**: 0.59 g (97%); **9c**: 0.42 (g (64%); **6c**: 0.17 g (27%). – *Method D:* At –25°C, 9.3 mmol of the corresponding amine (R = Me: 0.29 g; iPr: 0.55 g; tBu: 0.68 g) was slowly condensed onto a solution of 0.62 g (3.1 mmol) $HSeC_2F_5$ (**3**) in 3 ml of diethyl ether. During addition, a colour change of the reaction mixture to orange and precipitation of elemental selenium was observed. After complete addition of the respective amine, the mixtures were worked up as described. Yields: **9a**: 0.44 g (75%); **9b**: 0.54 g (79%); **9c**: 0.44 g (61%); **6c**: 0.39 g (27%).

2,2,2-Trifluoro-N-methylselenoacetamide (**9a**): IR (pentane): $\tilde{\nu}$ = 3418 cm^{-1} (m), 2933 (m), 1525 (s), 1358 (s), 1289 (s), 1276 (s), 1191 (m), 1136 (m), 1036 (m), 946 (w), 719 (w), 536 (w). – ^{1}H NMR (200.13 MHz, CD_2Cl_2, 25°C): δ = 3.06 (s, 3H, CH_3), 8.96 (br., 1H, NH). – ^{13}C{^{1}H} NMR (50.32 MHz, CD_2Cl_2, 25°C): δ = 35.9 [q, ^4J(F,C) = 1.7 Hz, CH_3), 120.3 [q, ^1J(F,C) = 277.6 Hz, CF_3], 185.0 [q, ^2J(F,C) = 36.4 Hz, CSe]. – ^{19}F NMR (188.31 MHz, CD_2Cl_2, 25°C): δ = –66.3 (s). – ^{77}Se{^{1}H} NMR (68.68 MHz, $CDCl_3$, 25°C): δ = 717.4 (s). – MS (70 eV, gas inlet), based on ^{80}Se, *m/z* (%): 191 (100) [M$^+$], 161 (9) [M$^+$ – MeNH], 142 (5) [M$^+$ – F], 122 (49) [M$^+$ – CF_3], 69 (42) [CF_3^+]. – $C_3H_4F_3NSe$ (190.03): calcd. C 18.96, H 2.12, N 7.36; found C 18.90, H 2.12, N 7.31.

2,2,2-Trifluoro-N-isopropylselenoacetamide (**9b**): IR ($CDCl_3$): $\tilde{\nu}$ = 3355 cm^{-1} (m), 2975 (m), 2933 (w), 1664 (w), 1518 (vs), 1465 (m), 1400 (vs), 1369 (m), 1341 (w), 1274 (vs), 1205 (s, br.), 1148 (s, br.), 974 (m), 930 (m), 731 (w), 723 (m), 586 (w, br.). – ^{1}H NMR (200.13 MHz, $CDCl_3$, 25°C): δ = 1.35 (d, J = 6.5 Hz, 6H, CH_3), 4.58 [sept, J = 6.5 Hz, 1H, $CH(CH_3)_2$], 8.59 (br., 1H, NH). – ^{13}C{^{1}H} NMR (50.32 MHz, $CDCl_3$, 25°C): δ = 20.3 (s, CH_3), 51.0 (s, CH), 120.2 [q, ^1J(F,C) = 278.5 Hz, CF_3], 186.0 [q, ^2J(F,C) = 35.2 Hz, CSe]. – ^{19}F NMR (188.31 MHz, $CDCl_3$, 25°C): δ = –66.3 (s). – ^{77}Se{^{1}H} NMR (68.68 MHz, $CDCl_3$, 25°C): δ = 679.1 (s). – MS (70 eV, gas inlet), based on ^{80}Se, *m/z* (%): 219 (36) [M$^+$], 177 (11) [M$^+$ – *i*-Pr + H], 69 (18) [CF_3^+], 43 (100) [$C_3H_7^+$].

N-tert-Butyl-2,2,2-trifluoroselenoacetamide (**9c**): IR (film): $\tilde{\nu}$ = 3392 cm^{-1} (m), 3000 (vs), 2913 (s), 1518 (m), 1462 (s), 1441 (m),

1409 (vs), 1375 (s), 1368 (s), 1275 (s), 1238 (m), 1207 (s), 1139 (m), 981 (m). – ^{1}H NMR (300.13 MHz, $CDCl_3$, 25°C): δ = 1.63 (s, 9H, CH_3), 8.26 (br., 1H, NH). – $^{13}C\{^1H\}$ NMR (75.43 MHz, $CDCl_3$, 25°C): δ = 26.9 (s, CH_3), 58.4 [s, $C(CH_3)_3$], 120.1 [q, $^1J(F,C)$ = 279.0 Hz, CF_3], 184.9 [q, $^2J(F,C)$ = 34.7 Hz, CSe]. – ^{19}F NMR (282.47 MHz, $CDCl_3$, 25°C): δ = −69.4 (s). – $^{77}Se\{^1H\}$ NMR (68.68 MHz, $CDCl_3$, 25°C): δ = 752.1 (s). – MS (70 eV, gas inlet), based on ^{80}Se, *m/z* (%): 233 (39) [M^+], 177 (14) [M^+ − *t*-Bu + H], 69 (9) [CF_3^+], 57 (100) [$C_4H_9^+$].

Standard Procedure for the Cleavage Reaction of the Diselanes **6a–6c** *to the Selenoamides* **9a–9c** *and the Stannylselanes* **10a–10c**: The corresponding diselane (**6a**: 1.08 g, 2.85 mmol; **6b**: 1.15 g, 2.65 mmol; **6c**: 0.92 g, 2.0 mmol), equimolar amounts of Me_3SnH and dichloromethane (9 ml for **6a** and **6b**, 5 ml for **6c**) were condensed into a 50-ml Schlenk vessel. On warming up the mixtures slowly to −30°C, the reactions started, indicated by a slight clouding. They were complete when room temperature was reached. Purification and isolation of the products were successfully carried out by trap-to-trap condensation (**6a**: −30, −65, −196°C; **6b**: −10, −50, −196°C; **6c**: −50, −196°C). The products were collected at −65/−30°C (**9a/10a**) or at −50/−10°C (**9b/10b**; **9c/10c**) and the solvent at −196°C. Separation of the product mixtures was accomplished by high condensation vacuum within 2 d (traps at −30 and −196°C for **10a/9a**; −10 and −196°C for **10b/9b**; 20 and −50°C for **10c/9c**).

Products/Trap Temperatures/Yields: **9a** (yellow crystals)/−196°C/0.50 g (92%); **9b** (orange glass)/−196°C/0.52 g (90%); **9c** (orange oil)/−50°C/0.45 g (98%); **10a** (yellow oil)/−30°C/0.91 g (91%); **10b** (yellow oil)/−10°C/0.86 g (85%); **10c** (light yellow oil)/20°C/0.78 g (98%).

Alternative Isolation Process for **10b** *and* **10c**: A quicker and better purification of **10b** or **10c** was possible after removal of **9b** or **9c** under high vacuum by taking up the residue in pentane, filtration through a glass frit under argon and pumping of the solvent.

[1-(Methylimino)-2-(trifluoromethyl)ethyl](trimethylstannyl)-selane (**10a**): IR (in $CHCl_3$): $\tilde{\nu}$ = 2995 cm^{-1} (m), 2926 (m), 1648 (s), 1630 (m), 1536 (m), 1367 (m), 1277 (vs), 1186 (s), 1145 (vs), 1009 (s), 945 (m), 916 (s), 538 (m), 511 (m). – ^{1}H NMR (200.13 MHz, $CDCl_3$, 25°C): δ = 0.56 [s, Sn satellites, $^2J(Sn,H)$ = 53.8, 56.3 Hz, 9H, $Sn(CH_3)_3$], 3.28 (s, 3H, NCH_3). – $^{13}C\{^1H\}$ NMR (50.32 MHz, $CDCl_3$, 25°C): δ = 3.2 [s, Sn satellites, $^1J(Sn,C)$ = 332.3, 347.9 Hz, $Sn(CH_3)_3$], 44.8 (s, NCH_3), 119.1 [q, $^1J(F,C)$ = 277.5 Hz, CF_3], 142.5 [q, $^2J(F,C)$ = 39.5 Hz, CSe]. – ^{19}F NMR (188.31 MHz, $CDCl_3$, 25°C): δ = −69.5 (s). – $^{77}Se\{^1H\}$ NMR (68.68 MHz, $CDCl_3$, 25°C): δ = −13.2 [s, Sn satellites, $^1J(Sn,Se)$ = 903.2 Hz]. – MS (70 eV, 20°C, direct inlet), based on ^{80}Se and ^{120}Sn, *m/z* (%): 340 (1) [M^+ − Me], 191 (100) [M^+ − Me_3Sn + H], 165 (60) [Me_3Sn^+], 150 (22) [Me_2Sn^+], 135 (44) [$MeSn^+$], 120 (54) [Sn^+], 69 (50) [CF_3^+].

[1-(Isopropylimino)-2-(trifluoromethyl)ethyl](trimethylstannyl)-selane (**10b**): IR (in $CHCl_3$): $\tilde{\nu}$ = 2976 cm^{-1} (s), 2934 (m), 1639 (m), 1621 (m), 1520 (m), 1403 (m), 1275 (vs), 1203 (m), 1186 (vs), 1143 (s), 944 (m), 921 (m), 798 (vs), 708 (m). – ^{1}H NMR (200.13 MHz, $CDCl_3$, 25°C): δ = 0.50 [s, Sn satellites, $^2J(Sn,H)$ = 55.1, 57.4 Hz, 9H, $Sn(CH_3)_3$], 1.16 [d, *J* = 6.3 Hz, 6H, $CH(CH_3)_2$], 4.14 [sept, *J* = 6.3 Hz, 1H, $CH(CH_3)_2$]. – $^{13}C\{^1H\}$ NMR (50.32 MHz, $CDCl_3$, 25°C): δ = 3.2 [s, Sn satellites, $^1J(Sn,C)$ = 332.9, 348.2 Hz, $Sn(CH_3)_3$], 21.4 [s, $CH(CH_3)_2$], 55.6 [br., $CH(CH_3)_2$], 119.4 [q, $^1J(F,C)$ = 277.3 Hz, CF_3], 159.0 (br., CSe). – ^{19}F NMR (188.31 MHz, $CDCl_3$, 25°C): δ = −66.7 (s). – $^{77}Se\{^1H\}$ NMR (68.68 MHz, $CDCl_3$, 25°C): δ = −26.0 [s, Sn satellites, $^1J(Sn,Se)$ = 930.0, 965.6 Hz]. – MS (70 eV; 20°C, direct inlet), based on ^{80}Sc and ^{120}Sn, *m/z* (%): 368 (44) [M^+ − Me], 306 (5) [M^+ − *i*-Pr − Me − F], 219 (81) [M^+ − Me_3Sn + H], 165 (100) [Me_3Sn^+], 150 (24) [Me_2Sn^+], 135 (65) [$MeSn^+$], 120 (24) [Sn^+], 69 (19) [CF_3^+], 43 (72) [$C_3H_7^+$].

[1-(tert-Butylimino)-2-(trifluoromethyl)ethyl](trimethylstannyl)selane (**10c**): IR (in $CHCl_3$): $\tilde{\nu}$ = 2976 cm^{-1} (s), 2931 (m), 1638 (s), 1521 (m), 1417 (s), 1391 (m), 1364 (m), 1267 (s), 1216 (vs), 1184 (s), 1136 (s), 926 (s), 913 (s), 694 (s), 536 (m), 510 (m). – ^{1}H NMR (200.13 MHz, $CDCl_3$, 25°C): δ = 0.61 [s, Sn satellites, $^2J(Sn,H)$ = 54.4, 56.6 Hz, 9H, $Sn(CH_3)_3$], 1.47 [s, 9H, $C(CH_3)_3$]. – $^{13}C\{^1H\}$ NMR (75.43 MHz, $CDCl_3$, 25°C): δ = 3.3 [s, Sn satellites, $^1J(Sn,C)$ = 331.0, 345.9 Hz, $Sn(CH_3)_3$], 28.3 [s, $C(CH_3)_3$], 58.6 [s, $C(CH_3)_3$], 118.2 [q, $^1J(F,C)$ = 278.1 Hz, CF_3], 138.4 [q, $^2J(F,C)$ = 38.1 Hz, CSe]. – ^{19}F NMR (188.31 MHz, $CDCl_3$, 25°C): δ = −69.9 (s). – $^{77}Se\{^1H\}$ NMR (68.68 MHz, $CDCl_3$, 25°C): δ = 64.6 [s, Sn satellites, $^1J(Sn,Se)$ = 946.8, 991.0 Hz]. – MS (70 eV, 20°C, direct inlet), based on ^{80}Se and ^{120}Sn, *m/z* (%): 382 (13) [M^+ − Me], 326 (5) [M^+ − *t*BuN], 233 (47) [M^+ − Me_3Sn + H], 165 (100) [Me_3Sn^+], 150 (20) [Me_2Sn^+], 135 (54) [$MeSn^+$], 120 (18) [Sn^+], 69 (25) [CF_3^+], 57 (28) [$C_4H_9^+$].

N,N-Diethyl-3,4,4,4-tetrafluoro-2-methylselenoacrylamide (**13a**). – *Method A (from Selenocarbonyl* **1**): 0.44 g (2.46 mmol) of **1**, 0.27 g (2.46 mmol) of 1-(diethylamino)-1-propyne (**12a**) and 3 ml of dichloromethane were condensed in layers in a Schlenk vessel (volume: 50 ml). The mixture was thawed quickly (−196°C to 20°C) and stirred. After a few seconds the reaction was complete, indicated by the orange colour of the mixture. Then, all of the volatile compounds (solvent, unreacted **12a** and the by-product **5**) were pumped off under vacuum, and the remaining oily residue was treated with 5 ml pentane. For separation of the alkyne polymer from the product, the pentane solution was transferred to another Schlenk vessel under argon. Removal of the solvent by vacuum condensation gave the pure orange oily product **13a**, yield 59%. – *Method B* (**from Polymer 4**): A Schlenk vessel was charged with 0.50 g (2.80 mmol of **1**) of $[SeC(F)CF_3]_n$ (**4**), 0.31 g (2.80 mmol) of 1-(diethylamino)-1-propyne (**12a**) and 6 ml of dichloromethane. The reaction mixture was slowly warmed to room temperature with stirring. The gradual appearance of an orange tint of the mixture indicated the start of the reaction. For completion, the reaction mixture was stirred at 20°C for an additional 15 min until the insoluble polymer **4** had disappeared and a clear solution was obtained. This was worked up as described under *Method A*. Yield 50% (relative to **1**). – IR (film): $\tilde{\nu}$ = 2981 cm^{-1} (m), 2939 (m), 2879 (m), 1464 (m), 1444 (s), 1432 (s), 1377 (vs), 1363 (m), 1339 (s), 1287 (s), 1232 (vs, br.), 1198 (vs, br.), 1142 (vs), 1099 (m), 1076 (m), 1025 (m), 981 (m), 710 (s). – ^{1}H NMR (200.13 MHz, CD_2Cl_2, 25°C): δ = 1.23 (t, *J* = 7.2 Hz, 3H, *anti* CH_2CH_3), 1.28 (t, *J* = 7.1 Hz, 3H, *syn* CH_2CH_3), 2.06 [dq, $^4J(F,H)$ = 4.2, $^5J(F,H)$ = 1.8 Hz, 3H, CH_3], 3.43 [dq, J_{AB} = 14.0, *J* = 7.2 Hz, 1H, *anti* CHH_B], 3.58 [dq, J_{AB} = 14.0, *J* = 7.2 Hz, 1H, *anti* CHH_A], 3.84 [dq, J_{AB} = 13.0, *J* = 7.1 Hz, 1H, *syn* CHH_B], 4.24 [dq, J_{AB} = 13.0, *J* = 7.1 Hz, 1H, *syn* CHH_A]. – $^{13}C\{^1H\}$ NMR (50.32 MHz, CD_2Cl_2, 25°C): δ = 10.5 (s, *anti* CH_2CH_3), 12.7 (s, *syn* CH_2CH_3), 16.1 [d, $^3J(F,C)$ = 5.0 Hz, CH_3], 48.5 (s, *syn* CH_2CH_3), 48.7 (s, *anti* CH_2CH_3), 118.8 [qd, $^1J(F,C)$ = 272.2, $^2J(F,C)$ = 42.1 Hz, CF_3], 128.6 [dq, $^2J(F,C)$ = 15.4 $^3J(F,C)$ = 2.7 Hz, *C*=CF], 136.8 [dq, $^1J(F,C)$ = 253.8, $^2J(F,C)$ = 38.7 Hz, CF], 195.3 [d, $^3J(F,C)$ = 5.2 Hz, C=Se]. – ^{19}F NMR (188.31 MHz, CD_2Cl_2, 25°C) δ = −65.7 [dq, $^3J(F,F)$ = 11.3, $^5J(F,H)$ = 1.8 Hz, CF_3], −135.2 [qq, $^3J(F,F)$ = 11.3, $^4J(F,H)$ = 4.2 Hz, CF]. – $^{77}Se\{^1H\}$ NMR (68.68 MHz, CD_2Cl_2, 25°C): δ = 683.1 (s). – MS (70 eV), based on ^{80}Se, *m/z* (%): 291 (100) [M^+], 276 (19) [M^+ − Me], 272 (16) [M^+ − F], 222 (52) [M^+ − CF_3], 219 (66) [M^+ − NEt_2], 183 (48) [M^+ − Se − Et + H], 182 (40) [M^+

Table 1. Crystallographic data and parameters of the crystal structure determinations

compound	**6c**	**7b**	**9a**	**13b**
chem. formula	$C_{12}H_{18}F_6N_2Se_2$	$C_8H_{14}F_3NSe$	$C_3H_4F_3NSe$	$C_{11}H_{17}F_4NSe$
form wght.	462.18	260.17	190.03	318.2
cryst size [mm]	0.5 x 0.5 x 0.05	0.15 x 0.25 x 0.4	0.18 x 0.13 x 0.32	0.22 x 0.14 x 0.35
cryst system	monoclinic	orthorhombic	monoclinic	orthorhombic
space group	$P2_1/n$	*Pbcm*	$P2_1/n$	$P2_12_12_1$
a [Å]	10.710(4)	7.301(1)	4.539(1)	7.512(1)
b [Å]	8.644(3)	14.461(2)	13.008(3)	14.117(3)
c [Å]	18.570(6)	10.158(2)	9.925(3)	26.030(5)
β [°]	100.02(3)		99.26(2)	
V [Å^3]	1692.9	1072.5	578.4	2760.4(9)
Z	4	4	4	8
ρ_{calcd} [g·cm^{-3}]	1.81	1.611	2.185	1.531
μ [mm^{-1}]	4.42	3.50	6.45	2.75
$F(000)$	904	520	360	1280
temperature [K]	150	150	170	150
$2\Theta_{max}$ [°]	54.11	54.13	54.11	54.16
index ranges	$0 \le h \le 13$	$0 \le h \le 9$	$0 \le h \le 5$	$0 \le h \le 9$
	$0 \le k \le 11$	$0 \le k \le 18$	$0 \le k \le 16$	$0 \le k \le 18$
	$-23 \le l \le 23$	$0 \le l \le 13$	$-12 \le l \le 12$	$-33 \le l \le 33$
transmission (min/max)	0.139/ 0.350	0.288/ 0.221	0.508/ 0.991	0.492/ 0.934
no. of reflections measured	4172	1394	1477	6237
no. of independent rflns with $I>2\sigma(I)$	2823	945	1025	3450
no. of parameters	217	70	89	308
$R1$	0.0634	0.0348	0.0322	0.0794
$wR2$	0.1794	0.0733	0.0820	0.1810
GooF on F^2	1.027	1.089	1.057	0.962
resid. electron density [eÅ^{-3}]	+1.46/ −1.76	+0.34/ −0.42	+0.52/−0.58	+4.02/−0.50

− Se − Et], 154 (72) [M$^+$ − Se − 2 Et + H], 141 (66) [M$^+$ − Se − CF_3 − H] and further fragments. − $C_9H_{13}F_4NSe$ (290.15): calcd. C 37.26, H 4.52, N 4.83; found C 37.17, H 4.56, N 4.83.

3,4,4,4-Tetrafluoro-N,N-diisopropyl-2-methylselenoacrylamide (**13b**): The preparation corresponded to that of **13a** by reaction of **1** (0.40 g, 2.23 mmol) with 1-(diisopropylamino)-1-propyne (**12b**) (0.31 g, 2.23 mmol) in dichloromethane (3 ml). Repeated crystallization from pentane at −20°C gave crystals of **13b** suitable for an X-ray crystal structure analysis, yield 67%. − *Alternative Preparation of* **13b**: The polymer [SeC(F)CF_3]$_n$ (**4**) (0.50 g, 2.80 mmol of **1**) in dichloromethane (8 ml) was treated with **12b** (0.38 g, 2.80 mmol). After 15 min the reaction was complete. The mixture was worked up as described, yield 36% (relative to **1**). − IR (KBr): $\tilde{\nu}$ = 2985 cm^{-1} (w), 2970 (m), 2930 (m), 1502 (s), 1463 (m), 1447 (m), 1378 (m), 1364 (m), 1353 (m), 1335 (s), 1222 (s), 1209 (s), 1190 (vs), 1144 (vs, br.), 1010 (m), 809 (w), 698 (m). − ^{1}H NMR (200.13 MHz, CD_2Cl_2, −30°C): δ = 1.20 [d, J = 6.5 Hz, 6H, *anti* CH(CH_3)], 1.23 [d, J = 6.5 Hz, 3H, *anti* CH(CH_3)], 1.76 [d, J = 7.0 Hz, *syn* CH(CH_3)], 2.0 [dq, ^4J(F,H) = 3.9, ^5J(F,H) = 1.8 Hz, 3H, CH_3], 3.99 [sept, J = 6.5 Hz, 1H, *anti* CH(CH$_3$)$_2$], 4.17 [sept, J = 7.0 Hz, 1H, *syn* CH(CH$_3$)$_2$]. − ^{13}C{^{1}H} NMR (50.32 MHz, CD_2Cl_2, −30°C): δ = 15.5 [d, ^3J(F,C) = 4.8 Hz, CH_3], 17.6 [s, *anti* CH(CH_3)$_2$], 17.7 [s, *anti* CH(CH_3)$_2$], 17.9 [s, *anti* CH(CH_3)$_2$], 19.4 [s, *syn* CH(CH_3)$_2$], 52.4 [s, *syn* CH(CH$_3$)$_2$], 59.5 [s, *anti* CH(CH$_3$)$_2$], 119.0 [qd, ^1J(F,C) = 271.9, ^2J(F,C) = 43.3 Hz, CF_3], 129.9 [dq, ^2J(F,C) = 15.1, ^3J(F,C) = 3.0 Hz, *C*=CF], 136.2 [dq, ^1J(F,C) = 251.2, ^2J(F,C) = 38.7 Hz, CF], 192.6 (br., C=Se). − ^{19}F NMR (188.31 MHz, CD_2Cl_2, −30°C): δ = −66.1 [dq, ^3J(F,F) = 12.1, ^5J(F,H) = 1.8 Hz, CF_3], −140.3 [qq, ^3J(F,F) = 12.1, ^4J(F,H) = 3.9 Hz, CF]. − ^{77}Se{^{1}H} NMR (68.68 MHz, CD_2Cl_2, 25°C): δ = 743.2 (s). − MS (70 eV), based on ^{80}Se, *m/z* (%): 319 (32) [M$^+$], 276 (8) [m$^+$ − *i*Pr], 257 (28) [M$^+$ − C_2F_4], 196 (63) [M$^+$ − Se − *i*Pr], 69 (18) [CF_3^+], 43 (100) [*i*Pr$^+$] and further fragments. − $C_{11}H_{17}F_4NSe$ (318.21): calcd. C 41.51, H 5.38, N 4.40; found C 41.68, H 5.31, N 4.48.

Crystal Structure Determination[61] *of* **6c**, **7b**, **9a**, *and* **13b**: X-ray data of **7b** and **13b** were collected with a Syntex $P2/_1$ diffractometer, those of **6c** and **9a** with a Siemens-P3 diffractometer by using Mo-K_α radiation and Θ/2Θ-scan technique (for **6c**, **7b**) or ω-scan technique (for **9a**, **13b**). The structures were solved by direct methods (SHELXL-93[62]; for **6c**, **7b**) or Patterson (SHELXL-93[62]; for **9a**, **13b**) and refined by full-matrix least-squares techniques. Non-hydrogen atoms were refined anisotropically. For **9a** all hydrogen atoms were located in a difference Fourier map and refined isotropically. For **6c** and **7b** hydrogen atoms were included in calculated positions; for **6c** isotropic temperature factors were refined. Crystallographic data are given in Table 1.

☆ Dedicated to Professor *Peter Sartori* on the occasion of his 65th birthday.

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