

# Reactions of RSe–EMe<sub>3</sub> (E = Si, Ge, Sn, Pb) with XeF<sub>2</sub> – RSe–F Equivalents in the Fluoroselenenylation of Acetylenes<sup>[1]</sup>

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*Dedicated to Professor Egon Fanghänel on the occasion of his 65th birthday*

**Keywords:** Xenon / Fluorine / Selenides / Acetylenes / Silicon / Germanium / Tin / Lead

Selenides of the type R<sup>1</sup>Se–EMe<sub>3</sub> (E = Si, Ge, Sn, Pb) react with xenon difluoride by cleavage of the Se–E bond to yield the R<sup>1</sup>Se–F intermediate and the fluorides Me<sub>3</sub>E–F, whereas the Se–C bond in PhSe–*t*Bu (E = C) is stable against XeF<sub>2</sub>. The presence of R<sup>1</sup>Se–F intermediates is confirmed by addition to acetylenes (4-octyne, 3-hexyne). Thus, the fluoroselenenylation of acetylenes gives fluoro(organylseleno)olefins in preparative yields. In the cases of E = Si, Ge, Sn, and Pb,

aryl and *n*-alkyl groups are suitable as the substituent R<sup>1</sup>. The X-ray crystal structural analysis of (*E*)-3-(*p*-carboxyphenylseleno)-4-fluorohex-3-ene – the first example of an uncharged fluoroselenoolefin synthesized from *p*-EtO<sub>2</sub>C–C<sub>6</sub>H<sub>4</sub>–Se–SnMe<sub>3</sub>, XeF<sub>2</sub>, and 3-hexyne followed by an ester hydrolysis – shows that the addition of the selenenylfluoride intermediate to the acetylene proceeds via a *trans*-addition, as is known for the R<sub>2</sub>Se<sub>2</sub>–XeF<sub>2</sub> reagents.

## Introduction

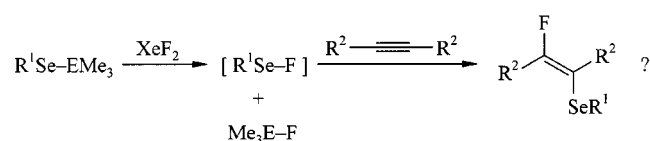
Selenium reagents are good tools for the introduction of fluorine into organic substrates. Known methods for the addition of PhSe–F equivalents to olefins and acetylenes are PhSeBr–AgF–ultra sound,<sup>[2,3]</sup> PhSeCl–AgF–MeCN,<sup>[4]</sup> *N*-phenylselenophthalimide (NPSP)–Py·9HF,<sup>[5,6]</sup> and NPSPEt<sub>3</sub>N·3HF.<sup>[7]</sup> The PhSe–F intermediate was obtained exceptionally elegantly by reaction of Ph<sub>2</sub>Se<sub>2</sub> with XeF<sub>2</sub> in a molar ratio of 1:1<sup>[8]</sup> and used in the fluoroselenenylation of olefins<sup>[8–10]</sup> and bis-selenenylation of phosphaacetylenes.<sup>[11]</sup> PhSeF<sub>3</sub> (Ph<sub>2</sub>Se<sub>2</sub> + 3 XeF<sub>2</sub>) reacts either by addition of PhSeF<sub>2</sub>/F<sup>[9,12,13]</sup> or as the F<sub>2</sub> equivalent, depending on the olefin concerned,<sup>[13,14]</sup> and PhSeF<sub>5</sub> (Ph<sub>2</sub>Se<sub>2</sub> + 5XeF<sub>2</sub>) (and PhTeF<sub>5</sub>) react with olefins as the F<sub>2</sub> equivalent.<sup>[15]</sup>

In earlier papers we reported a highly efficient synthesis of vicinal fluoro(organylseleno)olefins by fluoroselenenylation of acetylenes with R<sub>2</sub>Se<sub>2</sub>–XeF<sub>2</sub> reagents.<sup>[16,17]</sup> This method was shown to be useful in a very broad range concerning the acetylenes (symmetrical and unsymmetrical dialkylacetylenes, arylalkylacetylenes, terminal acetylenes, and cycloalkynes) and the applied diselenides (diaryl-,

primary and secondary dialkyldiselenides, functionalized diselenides). The fluoroselenoolefins were characterized by X-ray crystal structural analysis in the form of a fluoro-vinylidimethylselenonium picrate as (*E*)-isomers,<sup>[17,18]</sup> and investigated in detail by <sup>13</sup>C, <sup>19</sup>F, and <sup>77</sup>Se NMR spectroscopy.<sup>[19]</sup>

Preliminary experiments showed that silyl selenides of the type PhSe–SiR<sub>3</sub> (PhSe–SiMe<sub>3</sub> and PhSe–Si*t*BuMe<sub>2</sub>) react with XeF<sub>2</sub> by cleavage of the Se–Si bond to yield the PhSe–F intermediate which is added to acetylenes.<sup>[16]</sup> The high affinity of the fluorine for the silicon is the driving force responsible for the Se–Si bond breaking. However, nothing is known about the reactivity of the selenides RSe–EMe<sub>3</sub> of the higher group 14 elements, i.e., the corresponding germanium, tin, and lead selenides, with XeF<sub>2</sub>. Therefore, the question was which of the trimethylelementorganyl selenides R<sup>1</sup>Se–EMe<sub>3</sub> (E = C, Si, Ge, Sn, Pb) would react with XeF<sub>2</sub> to give the R<sup>1</sup>Se–F intermediate and Me<sub>3</sub>E–F by cleavage of the Se–E bond. Thus, the aim of the present paper is to report on our investigations of the reactions of the selenides R<sup>1</sup>Se–EMe<sub>3</sub> (E = C, Si, Ge, Sn, Pb) with XeF<sub>2</sub>. Aryl and *n*-alkyl groups were used as the substituents R<sup>1</sup>. In order to prove their formation, the R<sup>1</sup>Se–F moieties were trapped with simple reactive dialkylacetylenes (3-hexyne, 4-octyne) as model compounds to give fluoro(organylseleno)olefins (Scheme 1).

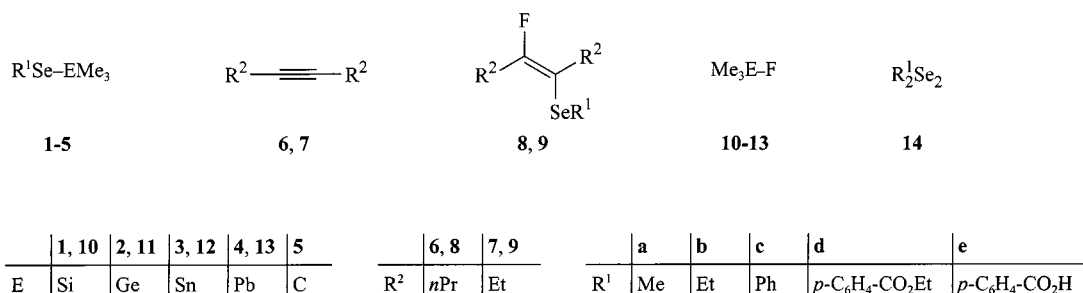
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Scheme 1. Topic of the investigation

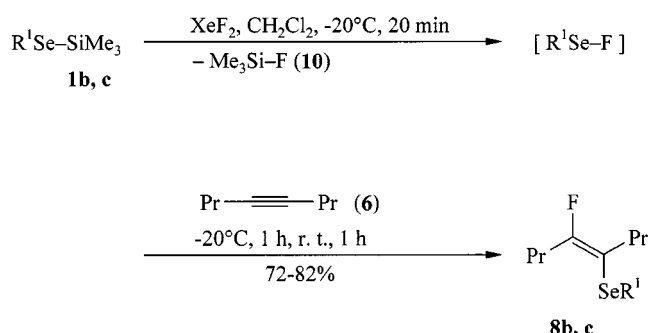
## Results and Discussion

The compounds investigated are shown below:



## Si Selenides

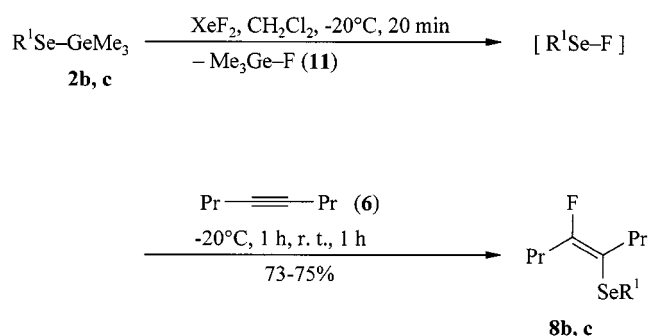
Ethylselenotrimethylsilane (**1b**) and phenylselenotrimethylsilane (**1c**) react in CH<sub>2</sub>Cl<sub>2</sub> at -20 °C with one equivalent of XeF<sub>2</sub> to give the trimethylfluorosilane (**10**) and the R<sup>1</sup>Se-F intermediate by cleavage of the Se-Si bond. 4-Octyne (**6**) was added to the selenenyl fluoride intermediates to give the fluoroselenoolefins **8b,c** in good yields (72–82%) (Scheme 2). Me<sub>3</sub>Si-F (**10**) was identified after reaction of **1b** with XeF<sub>2</sub> and **6** in CDCl<sub>3</sub> by <sup>19</sup>F NMR spectroscopy. Thus, the reaction of the R<sup>1</sup>Se-SiMe<sub>3</sub> **1** with XeF<sub>2</sub> takes place analogous to the synthesis of the trialkylsilyl halides R<sub>3</sub>Si-X (X = Cl, Br, I) from PhSe-SiR<sub>3</sub> and the halogens.<sup>[20]</sup>



Scheme 2. Reactions of the Si selenides

## Ge Selenides

Ethylselenotrimethylgermane (**2b**) and phenylselenotrimethylgermane (**2c**) react in CH<sub>2</sub>Cl<sub>2</sub> at -20 °C with XeF<sub>2</sub> in a molar ratio of 1:1; the intermediates are trapped with **6**.



Scheme 3. Reactions of the Ge selenides

The resulting fluoroselenoolefins **8b** and **8c** (73–75% yield) showed the cleavage of the Se-Ge bond caused by the fluorinating agent. After the reaction of **8c** with XeF<sub>2</sub> and **6** in CDCl<sub>3</sub>, Me<sub>3</sub>Ge-F (**11**) was observed by <sup>19</sup>F NMR spectroscopy (Scheme 3).

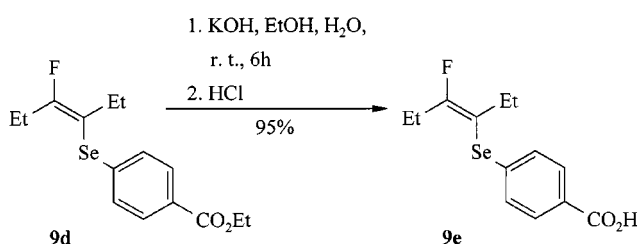
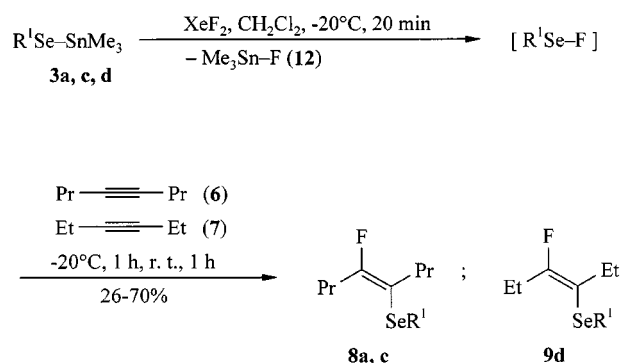
## Sn Selenides

Methylselenotrimethylstannane (**3b**) and phenylselenotrimethylstannane (**3c**) react in CH<sub>2</sub>Cl<sub>2</sub> at -20 °C with one equivalent XeF<sub>2</sub> to give trimethyltin fluoride (**12**), which precipitates immediately. The corresponding fluoroselenoolefins **8a** and **8c** (66–70% yield) were obtained after addition of **6** to this suspension (Scheme 4). The reaction of *p*-(ethoxycarbonyl)-phenylselenotrimethylstannane (**3d**) with XeF<sub>2</sub> and 3-hexyne (**7**) led to the formation of trimethyltin fluoride (**12**) and the adduct **9d**. Its yield was with 26%, as in the case of the corresponding *p*-CO<sub>2</sub>Et-substituted diphenyldiselenide,<sup>[17]</sup> much smaller than with non-functionalized PhSe precursors.<sup>[16,17]</sup> Me<sub>3</sub>Sn-F, which was isolated in almost quantitative yields, was confirmed by mass spectrometry and by <sup>119</sup>Sn Mößbauer spectroscopy. The resulting spectra were in good agreement with the literature.<sup>[21]</sup> The elementary composition of the ions [M<sup>+</sup>], [M<sup>+</sup> - Me] and [M<sup>+</sup> - F] was confirmed by high-resolution mass spectrometry. The cleavage of the Se-Sn bond by fluorination of the tin selenides **3** with XeF<sub>2</sub> corresponds to the reaction of R<sup>1</sup>Se-SnR<sub>3</sub> with iodine to give R<sub>3</sub>Sn-I and R<sub>2</sub>Se<sub>2</sub>.<sup>[22]</sup>

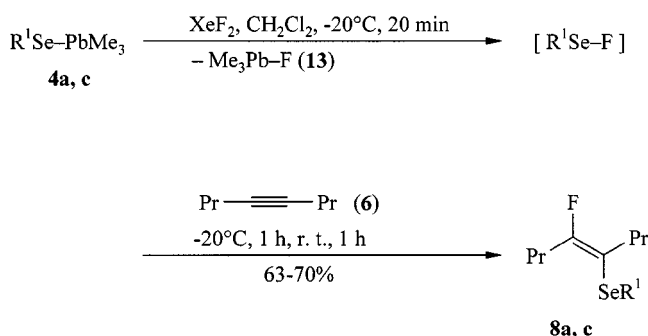
The carboxylic acid **9e** was synthesized by saponification of the carboxylic acid ester **9d**. Suitable crystals for the X-ray structural analysis could be obtained from *n*-hexane (Scheme 4).

## Pb Selenides

Analogous to the tin compounds **3**, precipitation of trimethyllead fluoride (**13**) occurred during the reaction of methylselenotrimethylplumbane (**4a**) or phenylselenotrimethylplumbane (**4c**) with one equivalent XeF<sub>2</sub> at -20 °C in CH<sub>2</sub>Cl<sub>2</sub>. Subsequent reaction of the selenenyl fluoride intermediates with **6** resulted in the fluoroselenoolefins **8a** and **8c** (63–70%) (Scheme 5). Me<sub>3</sub>Pb-F (71–83%) was characterized by mass spectrometry after isolation. The elementary composition of the ions [M<sup>+</sup> - Me] and [M<sup>+</sup> - F] was confirmed by high-resolution mass spectrometry.



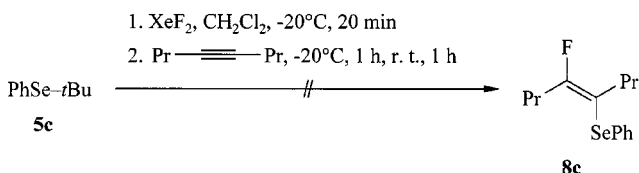
Scheme 4. Reactions of the Sn selenides



Scheme 5. Reactions of the Pb selenides

### C Selenides

The reaction of *tert*-butylphenylselenide (**5c**) with XeF<sub>2</sub>, under the conditions described above, differs from that of compounds **1–4**. The PhSe–F intermediate was not obtained and the adduct **8c** could not be obtained after treatment with **6** (Scheme 6). Cleavage of the Se–C bond by XeF<sub>2</sub> was not observed. This is also reported for the compound PhSe–CN.<sup>[16]</sup> However, a possible fluorination of the selenide **5c** to *t*BuPhSeF<sub>2</sub>, in analogy to Me<sub>2</sub>SeF<sub>2</sub>,<sup>[23]</sup> was not investigated.



Scheme 6. Experiment with a C selenide

The mass spectra of the synthesized fluoroselenoolefins **8a–c** and **9d,e** showed the correct molecular peak with the expected isotope pattern for one Se atom. The high resolu-

tion of these peaks proved the elemental composition of these compounds. The <sup>13</sup>C NMR spectra of **8a–c** and **9d,e** agreed well with the spectra of the products obtained from the R'<sub>2</sub>Se<sub>2</sub>–XeF<sub>2</sub> reagents.<sup>[16,17]</sup> A detailed assignment and discussion of the spectra of these compounds is given in ref.<sup>[19]</sup>

### X-ray Crystal Structure Analysis of 9e

Although the structure of the selenonium ion Pr(F)C=CPr(Se<sup>+</sup>Me<sub>2</sub>) has previously been reported,<sup>[17,18]</sup> this is the first structure of a noncharged vicinal fluoroselenoolefin. Details of the structure solution and refinement are given in the experimental section (Table 4). As can be seen from Figure 1, this compound possesses an (*E*)-configuration [torsional angles: Se–C3–C4–F –170.1(4)°; C2–C3–C4–F 3.0(9)°]. This is the most important structural information regarding the reaction course: *trans*-addition of the R<sup>1</sup>Se–F intermediate (R<sup>1</sup>Se–SnMe<sub>3</sub> + XeF<sub>2</sub>) to an acetylene.

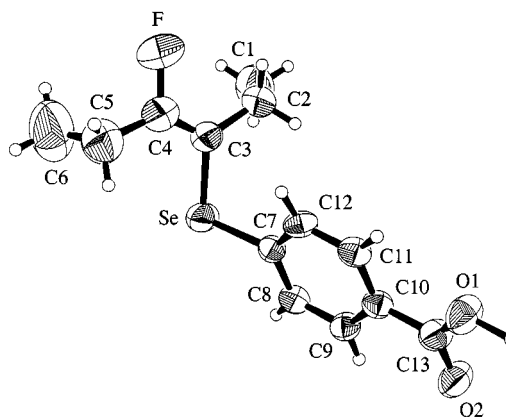
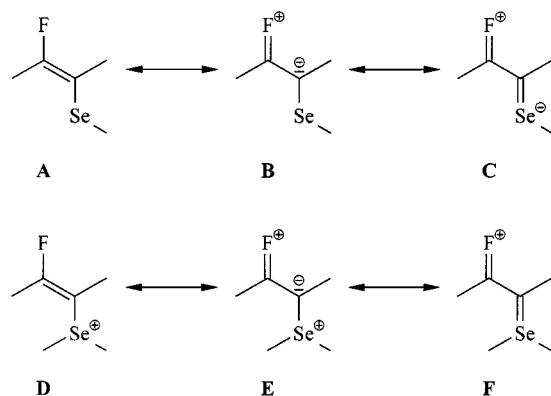


Figure 1. ORTEP plot (thermal ellipsoids 40%) of the molecular structure of the carboxylic acid **9e**; selected bond lengths [Å] and angles [°]: C1–C2 1.472(10), C2–C3 1.507(8), C3–C4 1.285(8), C4–C5 1.498(10), C5–C6 1.353(11), F–C4 1.385(7), Se–C3 1.914(5), Se–C7 1.906(4), C7–C12 1.384(6), C7–C8 1.391(6), C8–C9 1.374(7), C9–C10 1.380(6), C10–C11 1.389(6), C11–C12 1.384(6), C10–C13 1.466(6), C13–O2 1.247(6), C13–O1 1.280(5), O1–H1 1.18(5); C3–C4–F 115.6(6), C3–C4–C5 132.9(6), C4–C3–Se 117.4(5), C4–C3–C2 123.9(5), C7–Se–C3 100.3(2), Se–C3–C4–F –170.1(4), C2–C3–C4–F 3.0(9), C7–Se–C3–C2 64.4(4), C12–C7–Se–C3 23.5(4), C1–C2–C3–C4 –98.1(8), C3–C4–C5–C6 –107.8(12).

Compared with the above-mentioned selenonium ion [C–F 1.368(3) Å, C–Se 1.927(2) Å, C=C 1.328(3) Å] **9e** has a longer C–F and a shorter C–Se bond (Se–C3). The considerably shortened C=C distance in **9e** is especially noticeable. This corresponds well with the longer C–F bond and, thus, with a stronger participation of the mesomeric structure **A** against **B** and **C** in the electronic structure of the fluoroselenoolefins than of the mesomeric structure **D** against **E** and **F** in the selenonium ion. The C3–C4–C5 bond angle in **9e** is made considerably larger by the fluoro-substitution as it was found also in other fluoroolefins and the selenonium ion [133.8(2)°].<sup>[18]</sup> Both of the ethyl substituents on the C=C moiety are situated behind the π-bond plane with torsional angles of –98.1(8)° (C1–C2–C3–C4) and –107.8(12)° (C3–C4–C5–C6), respectively. The Ar–Se substituent is situated in front of the C=C plane with a torsional angle of 64.4(4)° (C7–Se–C3–C2); the Ar group is

twisted towards the C=C double bond with a torsional angle of  $23.5(4)^\circ$  (C12–C7–Se–C3). Obviously, in this conformation, the steric interaction between the H atoms on C2 and in the *o*-position of the aryl group is small. Two molecules are linked by two hydrogen bonds between O1 and O2 via H1 forming pairs [O1...O2 2.640(4) Å, H1...O2 1.489(11) Å, O1–H1...O2 164.55(4)°; symmetry operator  $1 - x, 1 - y, -z$ ].



## Conclusions

$\text{XeF}_2$  is able to cleave the Se–Si, Se–Ge, Se–Sn or Se–Pb bond of the selenides  $\text{R}^1\text{Se–EME}_3$  with  $\text{E} = \text{Si, Ge, Sn or Pb}$ , respectively, to give  $\text{R}^1\text{Se–F}$  intermediates and  $\text{Me}_3\text{E–F}$  fluorides. By contrast, the Se–C bond in  $\text{PhSe–}t\text{Bu}$  is not broken by  $\text{XeF}_2$ . The formation of  $\text{R}^1\text{Se–F}$  intermediates is confirmed by their addition to acetylenes. The yields of the obtained fluoro(organylseleno)olefins are in the same range as in the case of  $\text{XeF}_2\text{–R}_2\text{Se}_2$  reagents.<sup>[16,17]</sup> In this reaction the substituents  $\text{R}^1$  can be *n*-alkyl or aryl. The reaction proceeds as a *trans*-addition of the  $\text{R}^1\text{Se–F}$  intermediates to acetylenes, as is the case for  $\text{R}_2\text{Se}_2\text{–XeF}_2$  reagents.<sup>[17,18]</sup> Comparable yields of fluoro(organylseleno)olefins from  $\text{R}^1\text{Se–EME}_3\text{–XeF}_2$  and  $\text{R}_2\text{Se}_2\text{–XeF}_2$ , and the corresponding stereochemistry of additions for the two reactions, indicate that the same reaction course is taking place in both cases.

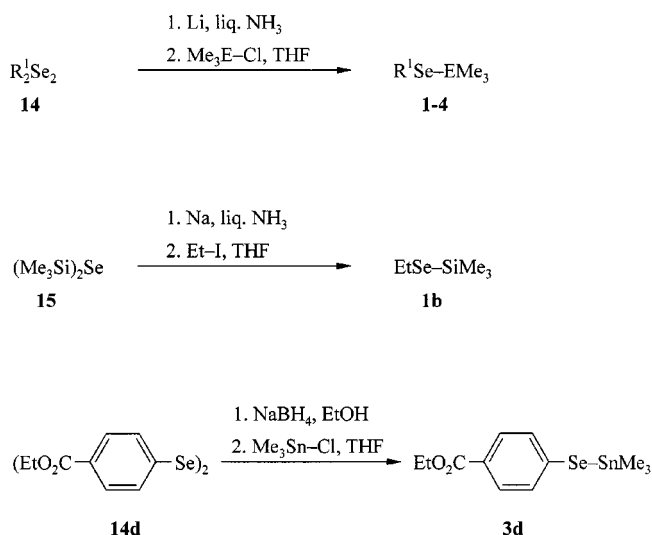
Of further interest is whether there are other groups besides the  $\text{Me}_3\text{Si}$  and  $t\text{BuMe}_2\text{Si}$  moieties, for example, OH-protecting groups<sup>[24–27]</sup> such as  $\text{Me}_2\text{PhSi}$ ,  $i\text{Pr}_3\text{Si}$  and  $t\text{BuPh}_2\text{Si}$ , that permit cleavage of  $\text{R}^1\text{Se–SiR}_3$  by  $\text{XeF}_2$ . A further question is a possible bond cleavage by  $\text{XeF}_2$  of other selenides of elements with a strong affinity to fluorine, e.g. compounds with Se–B, Se–Al, and Se–P bonds.

## Syntheses of the Selenides $\text{R}^1\text{Se–EME}_3$ 1–4

Different methods are known to synthesize selenides of the type  $\text{R}^1\text{Se–EME}_3$  ( $\text{E} = \text{Si}$ :  $\text{PhLi/Se/Me}_3\text{SiCl}$ ,<sup>[28]</sup>  $\text{Ph}_2\text{Se}_2/\text{Na(THF)/Me}_3\text{SiCl}$ ,<sup>[29,20c]</sup>  $\text{Ph}_2\text{Se}_2/\text{Na(THF)/R}_3\text{SiCl(18-crown-6)}$ ,<sup>[24]</sup>  $\text{PhSeH/BuLi/Me}_3\text{SiCl}$ ,<sup>[20c]</sup>  $\text{PhSeH/Me}_3\text{SiH/Rh-cat}$ ,<sup>[20c]</sup> and  $\text{PhMgBr(Et}_2\text{O)/Se/Me}_3\text{SiCl}$  resp. ( $\text{Me}_3\text{Si}$ )<sub>2</sub> $\text{Se/Na(liq. NH}_3\text{)/RX}$ ,<sup>[30]</sup>  $\text{E} = \text{Ge}$ :  $\text{PhSeSiMe}_3/\text{Me}_3\text{GeF}$ ,<sup>[28]</sup> and  $\text{Ph}_2\text{Se}_2/\text{Na(THF)/Me}_3\text{GeCl}$ ,<sup>[31]</sup>  $\text{E} = \text{Sn}$ :  $\text{PhSeH/}$

$\text{Me}_3\text{SnCl/NaOH(H}_2\text{O)}$ ,<sup>[32]</sup>  $\text{RSeH/Me}_3\text{SnCl/Et}_3\text{N}$ ,<sup>[33,22]</sup>  $\text{Li[Al(SeMe)}_4\text{]/Me}_3\text{SnCl}$ ,<sup>[34]</sup>  $\text{Me}_6\text{Sn}_2/\text{BuLi/Se/RX}$  ( $\text{R} = \text{alkyl}$ );<sup>[35]</sup>  $\text{E} = \text{Pb}$ . Only two patents are known:  $\text{RMgBr(Et}_2\text{O)/Se/Me}_3\text{PbCl}$  ( $\text{R} = \text{Me, Ph}$ ).<sup>[36]</sup>

In this work, we report a uniform synthesis of the compounds **1–4** using the same selenium starting materials. The diselenides  $\text{R}_2\text{Se}_2$  (**14**) were found to be most suitable, because of the possibility of their quantitative reduction to their corresponding lithium selenolates  $\text{R}^1\text{SeLi}$  in liquid ammonia with lithium. This way is superior to the reduction in the heterogeneous system  $\text{Na/THF}$ . Further reaction with the chlorides  $\text{Me}_3\text{E–Cl}$  to the compounds **1–4** was carried out in THF after complete removal of the ammonia. The reaction course using the bis(trimethylsilyl)selenide (**15**) was chosen for the synthesis of ethylselenotrimethylsilane **1b** only. The reduction of the functionalized diselenide **14d** was carried out with  $\text{NaBH}_4$  and subsequent stannylation in EtOH (Scheme 7).



Scheme 7. Syntheses of the selenides **1–4**

For  $\text{R}^1\text{Se–EME}_3$  derivatives, NMR spectroscopic data are known for only a few  $\text{Ge}$ <sup>[31a,37]</sup> and  $\text{Sn}$  compounds.<sup>[33,38]</sup> For this reason,  $^{13}\text{C}$  and  $^{77}\text{Se}$  NMR data of the compounds **1b,c**, **2b,c**, **3a,c,d**, **4a,c** and **15** are given in Table 1.

## Experimental Section

The diselenides **14a,b**,<sup>[39]</sup> **14d**,<sup>[17]</sup> the selenides **5c**<sup>[40]</sup> and **15**<sup>[30,41]</sup> and  $\text{XeF}_2$ <sup>[42]</sup> were prepared by literature methods. **14c**, the acetylenes **6** and **7** and the chlorides  $\text{Me}_3\text{E–Cl}$  ( $\text{E} = \text{Si, Ge, Sn, Pb}$ ) are commercially available. – Mass spectra were recorded with Finnigan–MAT 95 and Finnigan–MAT 711 at 70 eV and 80 eV, respectively. The measurements of high-resolution spectra were carried out by the peak-match method using PFK as a reference substance. – NMR spectra were measured with a Bruker ARX 300 spectrometer in  $\text{CDCl}_3$  in 5 mm sample tubes at room temperature:  $^{13}\text{C}$  at 75.47 MHz ( $^{13}\text{C}$  reference  $\text{CDCl}_3$ :  $\delta = 77$ ),  $^{19}\text{F}$  at 282.40 MHz ( $^{19}\text{F}$  reference  $\text{CFCl}_3$ :  $\delta = 0$ ), and  $^{77}\text{Se}$  at 57.25 MHz ( $^{77}\text{Se}$  reference  $\text{Me}_2\text{Se}$ :  $\delta = 0$ ).

**Reactions of  $\text{R}^1\text{Se–EME}_3$  (**1–4**) with  $\text{XeF}_2$ /Acetylene. – General Procedure:**  $\text{XeF}_2$  (4.1 mmol, 694 mg) was added in small portions un-



Table 1.  $^{13}\text{C}$  and  $^{77}\text{Se}$  NMR chemical shifts ( $\delta$ ) and related coupling constants (Hz) of compounds **1–4** and **15**

Compound	$^{13}\text{C}$ Pos. 1	2	3	4	$\text{EMe}_3$ ( $^1J_{\text{E,C}}$ )	$^{77}\text{Se}$ ( $^1J_{\text{Se,E}}$ )
<b>15</b> ( $\text{Me}_3\text{Si}$ ) $_2\text{Se}$					4.5 (52.7)	–332.4 (107.0)
<b>1b</b> EtSe–SiMe $_3$	12.2 ( $^1J_{\text{Se,C}} = 51.0$ )	18.6			1.7 (52.3)	–64.9 (107.3)
<b>1c</b> PhSe–SiMe $_3$	125.1	136.5	128.7	126.8	1.4	85.8 (103.3)
<b>2b</b> EtSe–GeMe $_3$	12.1 ( $^1J_{\text{Se,C}} = 54.3$ )	18.9			2.1	–44.6
<b>2c</b> PhSe–GeMe $_3$	126.1	136.4	128.7	126.7	2.2	97.3
<b>3a</b> MeSe–SnMe $_3$	–4.0				–6.1 [316.6 ( $^{119}\text{Sn}$ ), 288.7 ( $^{117}\text{Sn}$ )]	–287.6 [1002.2 ( $^{119}\text{Sn}$ ), 957.8 ( $^{117}\text{Sn}$ )]
<b>3c</b> PhSe–SnMe $_3$	126.0	136.2	128.6	126.2	–5.0 [339.2 ( $^{119}\text{Sn}$ ), 324.2 ( $^{117}\text{Sn}$ )]	8.1 [969.8 ( $^{119}\text{Sn}$ ), 926.5 ( $^{117}\text{Sn}$ )]
<b>3d</b> <i>p</i> -EtO $_2\text{C}$ –C $_6\text{H}_4\text{Se}$ –SnMe $_3$ [a]	133.8	136.0	129.4	128.3	–4.8 [341.2 ( $^{119}\text{Sn}$ ), 326.0 ( $^{117}\text{Sn}$ )]	
<b>4a</b> MeSe–PbMe $_3$	–3.1 ( $^2J_{\text{Pb,C}} = 19.4$ )				4.7 (239.4)	–210.2 (1169.8)
<b>4c</b> PhSe–PbMe $_3$	131.4	136.5	128.4	126.0	7.1 (232.3)	73.5 (1114.1)

[a] 166.2, 60.7, 14.2 (CO $_2\text{Et}$ ).

der argon to a solution of 4 mmol selenide **1–4** in 20 mL of dry CH $_2\text{Cl}_2$  at  $-20^\circ\text{C}$  and stirred for 30 min. The acetylene **6** or **7** (4 mmol) was then added and stirred for 1 h at  $-20^\circ\text{C}$  and for 1 h at room temperature. In the cases of **3** and **4** the precipitate Me $_3\text{Sn}$ –F (**10**) and Me $_3\text{Pb}$ –F (**11**), respectively, was separated and washed with *n*-pentane (2  $\times$  10 mL) and the solvent was then removed under vacuum. The crude product was purified by column chromatography (10 cm silica gel, diameter 2 cm, *n*-hexane). For yields see Table 2.

Table 2. Reactions of the selenides **1–4** with XeF $_2$  and acetylenes **6**, **7** to the products **8**, **9**, **12** and **13**

Starting material	Products	Yields
<b>1b</b> , XeF $_2$ , <b>6</b>	<b>8b</b>	0.68 g (72%)
<b>1c</b> , XeF $_2$ , <b>6</b>	<b>8c</b>	0.94 g (82%) <sup>[16]</sup>
<b>2b</b> , XeF $_2$ , <b>6</b>	<b>8b</b>	0.69 g (73%)
<b>2c</b> , XeF $_2$ , <b>6</b>	<b>8c</b>	0.86 g (75%)
<b>3a</b> , XeF $_2$ , <b>6</b>	<b>8a</b> , <b>12</b>	0.63 g (71%), 0.66 g (90%)
<b>3c</b> , XeF $_2$ , <b>6</b>	<b>8c</b> , <b>12</b>	0.75 g (66%), 0.70 g (96%)
<b>3d</b> , XeF $_2$ , <b>7</b>	<b>9d</b> , <b>12</b>	0.34 g (26%), 0.72 g (98%)
<b>4a</b> , XeF $_2$ , <b>6</b>	<b>8a</b> , <b>13</b>	0.56 g (63%), 0.90 g (83%)
<b>4c</b> , XeF $_2$ , <b>6</b>	<b>8c</b> , <b>13</b>	0.79 g (69%), 0.77 g (71%)

(**E**)-4-Fluoro-5-methylselenooct-4-ene (**8a**): HR-MS (C $_9\text{H}_{17}\text{F}^{80}\text{Se}$ ): calcd. 224.04794; found 222.04771. –  $^{13}\text{C}$  NMR (CDCl $_3$ ):  $\delta$  = 6.2 (SeCH $_3$ ), 13.3 (C-8), 13.4 (C-1), 20.2 (C-2), 21.6 (C-7), 31.6 ( $^3J_{\text{F-C}} = 6.6$  Hz, C-6), 33.0 ( $^2J_{\text{F-C}} = 28.7$  Hz, C-3), 109.2 ( $^2J_{\text{F-C}} = 19.1$  Hz, C-5), 160.5 ( $^1J_{\text{F-C}} = 263.7$  Hz, C-4).

(**E**)-4-Ethylseleno-5-fluorooct-4-ene (**8b**): HR-MS (C $_{10}\text{H}_{19}\text{F}^{80}\text{Se}$ ): calcd. 238.06359; found 238.06333. –  $^{13}\text{C}$  NMR (CDCl $_3$ ):  $\delta$  = 13.3 (C-1), 13.4 (C-8), 15.5 (SeCH $_2\text{CH}_3$ ), 19.1 (SeCH $_2\text{CH}_3$ ), 20.3 (C-7), 21.6 (C-2), 32.0 ( $^3J_{\text{F-C}} = 6.7$  Hz, C-3), 33.0 ( $^2J_{\text{F-C}} = 28.8$  Hz, C-6), 108.0 ( $^2J_{\text{F-C}} = 18.8$  Hz, C-4), 161.4 ( $^1J_{\text{F-C}} = 264.3$  Hz, C-5).

(**E**)-4-Fluoro-5-phenylselenooct-4-ene (**8c**): HR-MS (C $_{14}\text{H}_{19}\text{F}^{80}\text{Se}$ ): calcd. 286.06359; found 286.06381. –  $^{13}\text{C}$  NMR (CDCl $_3$ ):  $\delta$  = 13.4 (C-8), 13.5 (C-1), 20.3 (C-2), 21.7 (C-7), 32.4 ( $^3J_{\text{F-C}} = 5.9$  Hz, C-6), 33.2 ( $^2J_{\text{F-C}} = 28.2$  Hz, C-3), 109.7 ( $^2J_{\text{F-C}} = 20.9$  Hz, C-5), 126.3 (*p*-C), 129.1 (*m*-C), 130.3 (*o*-C), 130.8 (*i*-C), 163.3 ( $^1J_{\text{F-C}} = 267.3$  Hz, C-4).

(**E**)-3-[(*p*-Ethoxycarbonyl)phenylseleno]-4-fluorohex-3-ene (**9d**): HR-MS (C $_{15}\text{H}_{19}\text{FO}_2^{80}\text{Se}$ ): calcd. 330.05342; found 330.05235. –  $^{13}\text{C}$  NMR (CDCl $_3$ ):  $\delta$  = 11.4 (C-6), 13.4 (C-1), 14.2 (OCH $_2\text{CH}_3$ ), 24.5 ( $^3J_{\text{F-C}} = 6.9$  Hz, C-2), 25.0 ( $^2J_{\text{F-C}} = 28.8$  Hz, C-5), 60.8 (OCH $_2\text{CH}_3$ ), 109.4 ( $^2J_{\text{F-C}} = 21.6$  Hz, C-3), 128.1 (*p*-C), 128.6 (*o*-C), 130.0 (*m*-C), 138.5 (*i*-C, C–Se), 165.4 ( $^1J_{\text{F-C}} = 269.2$  Hz, C-4), 166.2 (CO $_2\text{Et}$ ).

**Characterization of Me $_3\text{E}$ –F (**10–13**):** EtSe–SiMe $_3$  (**1b**; 1 mmol, 181 mg) and PhSe–GeMe $_3$  (**2c**; 1 mmol, 274 mg) and XeF $_2$  (1 mmol, 169 mg) reacted with 4-octyne (**6**; 1 mmol, 110 mg) in 2 mL CDCl $_3$  as already described.

**Me $_3\text{Si}$ –F (**10**):**  $^{19}\text{F}$  NMR (CDCl $_3$ ):  $\delta$  = –158.2 (–159.3 ppm<sup>[43]</sup>).

**Me $_3\text{Ge}$ –F (**11**):**  $^{19}\text{F}$  NMR (CDCl $_3$ ):  $\delta$  = –192.1 (–190.5 ppm<sup>[44]</sup>).

**Me $_3\text{Sn}$ –F (**12**):** MS: *m/z* = 184 [ $\text{M}^+$ ], 169 [ $\text{M}^+ - \text{Me}$ ], 165 [ $\text{M}^+ - \text{F}$ ]. – HR-MS (C $_3\text{H}_9\text{F}^{120}\text{Sn}$ ): calcd. 183.97103; found 183.97531. (C $_2\text{H}_6\text{F}^{120}\text{Sn}$ ) [ $\text{M}^+ - \text{Me}$ ]: calcd. 168.94755; found 168.94523. (C $_3\text{H}_9\text{F}^{120}\text{Sn}$ ) [ $\text{M}^+ - \text{F}$ ]: calcd. 164.97262; found 164.97543. –  $^{119}\text{Sn}$ -Möbbauser (source  $^{119}\text{mSn}$  in CaSnO $_3$ , reference: SnO $_2$ , sample temperature 77 K):  $\delta$  = 1.357 mm/s,  $\Delta$  3.840 mm/s,  $\Gamma$  0.834 mm/s ( $\delta$  1.36 mm/s,  $\Delta$  3.80 mm/s<sup>[21]</sup>).

**Me $_3\text{Pb}$ –F (**13**):** MS: *m/z* = 257 [ $\text{M}^+ - \text{Me}$ ], 253 [ $\text{M}^+ - \text{F}$ ]. – HR-MS (C $_2\text{H}_6\text{F}^{208}\text{Pb}$ ) [ $\text{M}^+ - \text{Me}$ ]: calcd. 275.02199; found 275.02688. (C $_3\text{H}_9\text{F}^{208}\text{Pb}$ ) [ $\text{M}^+ - \text{F}$ ]: calcd. 253.04707; found 253.04321.

(**E**)-3-(*p*-Carboxyphenylseleno)-4-fluorohex-3-ene (**9e**): The saponification of the ester **9d** was carried out with KOH/EtOH/H $_2\text{O}$ , as described in ref.<sup>[17]</sup> Yield of **9e** (from 2 mmol) 0.57 g (95%), m.p. 115–117  $^\circ\text{C}$  (*n*-hexane). – HR-MS (C $_{13}\text{H}_{15}\text{FO}_2^{80}\text{Se}$ ): calcd. 302.02212; found 302.02003. –  $^{13}\text{C}$  NMR (CDCl $_3$ ):  $\delta$  = 11.4 (C-6), 13.5 (C-1), 24.6 ( $^3J_{\text{F-C}} = 6.8$  Hz, C-2), 25.1 ( $^2J_{\text{F-C}} = 28.8$  Hz, C-5), 109.3 ( $^2J_{\text{F-C}} = 21.8$  Hz, C-3), 126.8 (*p*-C), 128.6 (*o*-C), 130.7 (*m*-C), 140.4 ( $^4J_{\text{F-C}} = 2.1$  Hz, *i*-C, C–Se), 165.7 ( $^1J_{\text{F-C}} = 269.7$  Hz, C-4), 172.1 (CO $_2\text{H}$ ).

**Syntheses of R $^1\text{Se}$ –EMe $_3$  (**1–4**). – General Procedure:** Approximately 100 mL liquid ammonia was added to 15 mmol diselenide **14**. To this stirred solution, 30 mmol (210 mg) lithium was added, until the solution was slightly blue. After evaporation of the solvent under argon the remaining NH $_3$  was completely removed under vacuum. To the colorless solid 50 mL dry THF was added. To this

mixture was added a solution of 30 mmol  $\text{Me}_3\text{Si}-\text{Cl}$  (3.26 g),  $\text{Me}_3\text{Ge}-\text{Cl}$  (4.60 g) or  $\text{Me}_3\text{Sn}-\text{Cl}$  (5.98 g) in 10 mL THF, or solid  $\text{Me}_3\text{Pb}-\text{Cl}$  (8.63 g), over 20 min under Ar at room temperature, and subsequently stirred for 3 h. For the Si, Ge, and Sn derivatives the THF was removed at normal pressure and the product was distilled directly from the reaction flask. It was then redistilled for further purification. For the Pb derivatives, after adding 500 mL ice water, the organic layer was separated. The aqueous phase was treated with ether ( $3 \times 100$  mL), the ether-containing phases were washed with ice water ( $1 \times 100$  mL) and dried ( $\text{Na}_2\text{SO}_4$ ). After removal of the solvent the product was purified by column chromatography (5 cm silica gel, *n*-hexane). For yields see Table 3.

Table 3. Syntheses of the selenides 1–4

$\text{R}^1\text{Se}-\text{EMe}_3$	Yield	
$\text{PhSe}-\text{SiMe}_3$ ( <b>1c</b> )	4.13 g (60%)	b.p. 66–68 °C/1.3 mbar
$\text{EtSe}-\text{GeMe}_3$ ( <b>2b</b> )	5.42 g (80%)	b.p. 52–55 °C/23 mbar
$\text{PhSe}-\text{GeMe}_3$ ( <b>2c</b> )	6.82 g (83%)	b.p. 65 °C/0.07 mbar
$\text{MeSe}-\text{SnMe}_3$ ( <b>3a</b> )	6.11 g (79%)	b.p. 65–67 °C/23 mbar
$\text{PhSe}-\text{SnMe}_3$ ( <b>3c</b> )	8.16 g (85%)	b.p. 72 °C/0.09 mbar
$\text{MeSe}-\text{PbMe}_3$ ( <b>4a</b> )	8.31 g (80%)	after chromatography
$\text{PhSe}-\text{PbMe}_3$ ( <b>4c</b> )	10.54 g (86%)	after chromatography

Table 4. Crystal data and structure refinement for compound 9e

Formula	$\text{C}_{13}\text{H}_{15}\text{FO}_2\text{Se}$
Molecular weight	301.21
Crystal system	Monoclinic
Space group	$P2_1/n$
Crystal size [mm]	$0.798 \times 0.152 \times 0.152$
$a$ [Å]	14.719(2)
$b$ [Å]	5.6667(16)
$c$ [Å]	16.348(3)
$\alpha$ [°]	90.00
$\beta$ [°]	92.699(13)
$\gamma$ [°]	90.00
$V$ [Å <sup>3</sup> ]	1362.1(5)
$\rho_{\text{calcd.}}$ [gcm <sup>−3</sup> ]	1.469
$Z$	4
$F(000)$ [e]	608
$\mu$ (Mo- $K_\alpha$ ) [mm <sup>−1</sup> ]	2.756
Data collection	
Diffractometer	STOE Stadi4
Radiation	Mo- $K_\alpha$ , 0.71071 Å graphite monochromator
$T$ [K]	298 (2)
Scan mode	$2\theta/\omega = 1.0$
$hkl$ range	−13/13, 0/7, 0/11
Measured reflections	2040
Unique refl. ( $>2\sigma_I$ )	1953
$R_{\text{int}}$	0.0277
Used refl.	1953
$T_{\text{min}}/T_{\text{max}}$	0.4872/0.5841
Refinement	
Refined parameters	175
$R_1^{[a]}$	0.0393 (1098 refl.)
$[F_o > 4\sigma(F_o)]$	
$wR_2^{[b]}$	0.1129
(all)	
GoF (all)	0.976
Weighting par. $a, b^{[c]}$	0.0724/0.0169
$\rho_{\text{final}}$ (max/min) [eÅ <sup>−3</sup> ]	0.408/−0.270

<sup>[a]</sup>  $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$ ; <sup>[b]</sup>  $R_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$ ; <sup>[c]</sup>  $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ ;  $P = (F_o^2 + 2F_c^2)/3$

**Ethylselenotrimethylsilane (1b):** Analogously to ref.<sup>[30]</sup> bis(trimethylsilyl)selenide (**15**; 50 mmol, 11.3 g) was added to a solution of Na (50 mmol, 1.15 g) in ca. 100 mL of liquid  $\text{NH}_3$  and stirred until it decolorized. After evaporation of the ammonia under Ar, the resulting  $(\text{Me}_3\text{Si})_2\text{NH}$  was removed under vacuum at 50 °C. 50 mL of pure THF was added to the remaining  $\text{Me}_3\text{Si}-\text{SeNa}$ . To this mixture ethyl iodide (50 mmol, 7.80 g) was added over 30 min under argon and stirring. It was then stirred for a further 4 h. After filtration and washing of the NaI precipitate with 30 mL of pentane the filtrate was fractionated using a short Vigreux column. Yield of **1b** 5.93 g (65%), b.p. 32–34 °C/20 mbar.

***p*-(Ethoxycarbonyl)phenylselenotrimethylstannane (3d):** Bis[*p*-(ethoxycarbonyl)phenyl]diselenide (**14d**; 5 mmol, 2.28 g) was suspended in 40 mL EtOH under stirring at room temperature and Ar and reduced by addition of small portions of  $\text{NaBH}_4$  (10 mmol, 380 mg). After stirring (30 min), a solution  $\text{Me}_3\text{Sn}-\text{Cl}$  (10 mmol, 2.00 g) in 5 mL of THF was added to this suspension and further stirred for 30 min. This mixture was taken up with 250 mL of  $\text{H}_2\text{O}$  and extracted with  $\text{CHCl}_3$  ( $3 \times 50$  mL). The extract was washed with water and dried ( $\text{Na}_2\text{SO}_4$ ). The product was purified by column chromatography (silica gel, *n*-hexane/ether 10:1). Yield of **3d** 2.77 g (71%).

**X-ray Crystal Structure Analysis of Compound 9e:** A single crystal of compound **9e** was examined with a four-circle diffractometer at room temperature in air. Intensity data were corrected for Lorentz and polarization effects. An absorption correction had to be applied with the  $\psi$ -scan technique. The structure was solved by direct methods and refined by full-matrix least-squares techniques against  $F^2$  (see Table 4).<sup>[45]</sup> The thermal motion of all non-hydrogen atoms was treated anisotropically. The hydrogen atom at O1 was located from the difference Fourier map. All the other hydrogen atoms were calculated in idealized positions and allowed to ride on their corresponding carbon atoms. Their isotropic thermal parameters were set to 1.2 times that of the adjacent C atom.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-138770. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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