# **CHEMISTRY** A European Journal



# **Accepted Article** Title: Silyl Chalconium Ions - Their Synthesis, Structure and Application in Hydrodefluorination Reactions Authors: Thomas Müller, Kordts Natalie, Künzler Sandra, Saskia Rathjen, Thorben Sieling, Henning Großekappenberg, and Marc Schmidtmann This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article. To be cited as: Chem. Eur. J. 10.1002/chem.201700995 Link to VoR: http://dx.doi.org/10.1002/chem.201700995 **Supported by**

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# Silyl Chalconium Ions – Their Synthesis, Structure and Application in Hydrodefluorination Reactions

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Abstract: The synthesis of two series of silvlated chalconium borates, 9 and 10, that are based on the peri-naphthyl and peri-acenaphthyl framework is reported (chalcogen (Ch): O, S, Se, Te). NMR investigations of the selenium and tellurium containing precursor silanes 3d - f and 8d, f revealed a significant through - space J coupling between the chalcogen nuclei and the Me<sub>2</sub>SiH group. Experimental and computational results typifies the synthesized cations 9 and 10 as chalconium ions. The imposed ring strain weakens the Si - Ch linkage compared to acyclic chalconium ions. This attenuation of the Si - Ch bond strength is more pronounced in the acenaphthene series. Surprisingly, the Si - O bonds in oxonium ions 9a and 10a are the weakest Si - Ch linkage in both series. The synthesized silyl chalconium borates are active in hydrodefluorination reactions of alkyl fluorides with silanes. A cooperative activation of the silane by the Lewis acidic (silicon) and by the Lewis basic side (chalcogen) is suggested.

#### Introduction

Silyl cations and in particular tricoordinated silylium ions I are strong Lewis acids (LA) and as such they are relevant species for organic synthesis and in catalytic reactions.<sup>[1-3]</sup> The prerequisite for the beneficial use of silylium ions in these fields is however a clear control over this Lewis acidity. Previous studies by the Siegel group have shown that in cases in which an intramolecular Lewis basic group (LB), as in tetra-coordinated cation II, pacifies the Lewis acidity of the cationic silicon atom their structures, spectroscopic properties, and reactivities are greatly determined by the electron donating ability of the LB group.<sup>[4]</sup> As the control over the Lewis acidity is accomplished by LA/LB interaction in a spatially confined reaction compartment, the analogy to intramolecular frustrated Lewis Pairs (FLP) is obvious.<sup>[5]</sup> A possible amphiphilic reactivity of the stabilized silvl cation as suggested by the equilibrium II / III shown in Figure 1 is a matter of the strength of silvl cation LB interaction.

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Figure 1. Silyl cationic compounds (LB Lewis basic group, Ch = O, S, Se, Te).



Figure 2. Selected LA/LB pairs based on the naphthene and acenaphthene framework.

Based on our previous experience with stabilized silvl cations.<sup>[7]</sup> we utilized the 1,8-naphthalenediyl-, IV, and the 5,6-acenaphthenediyl, V, scaffold to study the intramolecular interaction between the dimethylsilyl cation unit and a series of chalcogena ether groups (Chalcogen (Ch) = O, S, Se, Te) (Figure 1). Beginning with the landmark investigations by Alder and by Katz, <sup>[8, 9]</sup> many groups have shown that these naphthalene-derived frameworks are ideal for the study of cooperative phenomena between spatially confined groups. Recent systematic studies by the groups of Gabbai, Woollins and Beckmann are here particularly noteworthy.<sup>[10, 11]</sup> Several intramolecular naphthalenelinked LA/LB systems including B/P, B/N, Si/N and P/P systems have been studied, and some were tested in bond activation chemistry (Figure 2).<sup>[12-14]</sup> Tamao and coworkers have used peri-Ch / Si (Ch = O, S, Se) interactions to form silaylides.<sup>[15]</sup> The use of chalcogena ether units as electron donating LB substituents in cations IV and V seems to us very attractive, as we expected to

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vary its electron donor capability with the chalcogen atom over a wide range. The Oestreich and Landais groups have recently disclosed that silyl cations, which are stabilized by intramolecular interactions with remote ether or thioether substituents are stable and are in some cases active Lewis acidic catalyst.<sup>[16, 17]</sup> In addition, Jutzi and coworkers achieved the synthesis of pentacoordinated siliconium ions using pincer type substituents with flanking ether and thioether groups.<sup>[18]</sup> Based on these previous results, we report here on the synthesis and the NMR spectroscopic and structural characterization of a series of silylated chalconium ions (chalcogen = O, S, Se, Te) based on the 1,8-naphthalene and 5,6-acenaphthene scaffolds. The influence of the diverse donor atoms and the different carbon-backbones on the bonding situation in these cations is discussed. First experimental studies disclose their catalytic activity in HDF reactions and indicate the amphiphilic reactivity of these silylated chalconium ions.

#### **Results and Discussion**

The naphthyl phenyl ether 3a was prepared in 66% isolated yield from dibromide 1 via naphthyl bromide 2 by an Ullmann-type reaction and a subsequent metalation / salt metathesis sequence using dimethylsilyl chloride as electrophile (Scheme 1).[19] Direct peri-lithiation of 1-methoxynaphthalene 4 and reaction with dimethylsilyl chloride gave 8-methoxysilylnaphthalene 3b in moderate yields (57%, Scheme 1).<sup>[15a]</sup> The synthesis of 1,8-disubstituted naphthyl compounds 3c-f was accomplished by two subsequent lithiation / salt metathesis reaction sequences starting from dibromide 1. After installation of the dimethylsilyl group to give 8-dimethylsilylnaphthylbromide 5, the aryl chalcogenyl group was introduced by halogen metal exchange and reaction of the lithiated intermediate with the dichalcogenyl compound in moderate to good yields (66 - 99%) (Scheme 1).<sup>[20]</sup> In close analogy, the acenaphthene derivatives 8 were prepared from dibromide 6 either via the 6-phenoxy-acenaphtene-5-bromide or via the 6-silyl-acenapthene-5-bromide 7 (Scheme 1). The composition and identity of silanes 3 and 8 was established by NMR spectroscopy. In addition, X-ray diffraction analysis were performed for selenylethers 3e and 8d. The most important NMR parameter for these compounds are summarized in Table 1. The investigated silanes 3, 8, are characterized by <sup>1</sup>H NMR chemical shifts for the silane hydrogen atom between  $\delta^{1}$ H = 4.62 – 5.50 and corresponding <sup>29</sup>Si NMR chemical shifts between  $\delta^{29}Si = -12.4$ - -22.0. The collected <sup>29</sup>Si NMR data show a noticeable trend for the silicon resonance towards higher field with increasing atomic weight of the remote chalcogen atom (see Table 1). The <sup>77</sup>Se NMR chemical shifts of compounds **3d.e** and **8d** ( $\delta^{77}$ Se = 304 – 397) are in the expected range for diarylselenides and also the position of the <sup>125</sup>Te NMR resonance of compounds 3f, 8f are unremarkable. <sup>[21, 22]</sup>

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Figure 3. Left: Part of the 499.9 MHz <sup>1</sup>H NMR spectra of silyInaphthyltellane 3f (Si - H region,  $\delta^{1}H = 5.70 - 5.15$  ppm, # unidentified by-product). Right: Part of the 157.8 MHz <sup>125</sup>Te NMR spectra of silyInaphthyltellane 3f ( $\delta^{125}Te = 693 - 690$  ppm).

A quite unexpected feature in the NMR spectra of the selenium and tellurium containing compounds **3d-f**, **8d**,**f** is the detection of *J* couplings between the chalcogenyl atom and the hydrogen atom of the silyl group. As an example, relevant parts of the <sup>1</sup>H NMR and of the <sup>125</sup>Te NMR spectrum of compound **3f** are shown

in Figure 3. The J(TeH) coupling constant of 74 Hz is clearly visible in both spectra. The detected chalcogen/hydrogen coupling is largest for the tellurium compounds 3f and 8f (Table 1). In the series of selenium compounds it decreases from the mesityl-substituted compound 3e (J(SeH) = 35 Hz) to the phenyl selane 3d (J(SeH) = 18 Hz). The change from the naphthyl skeleton (3d) to the acenaphthene backbone (8d) is associated with a further reduction of the J(SeH) coupling constant (J(SeH)(8d) = 10 Hz). The relative large size of the coupling constants excludes a through-bond coupling mechanism. Instead, it suggests that the spin-spin interaction is transferred through space rather than along the carbon skeleton.<sup>[23, 24]</sup> For the selenium compound 3e and for tellurium compounds 3f, 8f also through space spin-spin couplings between the <sup>77</sup>Se / <sup>125</sup>Te and the <sup>29</sup>Si nuclei are detectable (J(SeSi) = 31 Hz (3e), J(TeSi) = 93 Hz (3f), 103 Hz (8f)). These data suggests through space interaction between the Si-H group and the chalcogen atom. Further investigations concerning its nature are currently under investigation in our laboratories. Previously, the group of Woollins has reported similar through space J-coupling between heavy group 15 and 16 elements in peri-substituted naphthalene and acenaphthene derivatives and guite recently Beckmann and coworkers disclosed a related Si-H---P interaction in acenaphthene based compounds.[25, 26]

Single crystals suitable for X-ray diffraction (XRD) analysis have been obtained for selanes 3e and 8d. Their overall molecular structures are unremarkable (Figure 4). Not unexpected, the perisubstitution in both compounds is accompanied with steric strain which is manifested in their molecular structures by relative large bond angles in the bay region and displacements of the heteroatoms from the plane of the naphthalene/acenaphthene rings.<sup>[27]</sup> In particular, for compound **3e** the sum of the bay angles (Se - C<sup>1</sup> - C<sup>10</sup>; C<sup>1</sup> - C<sup>10</sup> - C<sup>8</sup>, C<sup>10</sup> - C<sup>8</sup> - Si)  $\Sigma\beta$  is 379.6°, significant more than in unstrained naphthalenes ( $\Sigma\beta \sim 360^\circ$ ). The silicon atom is placed 13 pm above the plane spanned by the ten carbon atoms of the naphthalene ring, while the selenium atom is pushed by 7 pm below this plane. These distortions lead to a distance between the peri-atoms, selenium and silicon, of d(Se - Si) = 322.9 pm which is markedly larger than in unstrained naphthalenes (244 pm). Similar distortions have been noticed for compound **8d**:  $(\Sigma\beta \sim 380.6^\circ; \text{ displacement } d(Si) = 20.4 \text{ pm, } d(Se)$ = 25.6 pm, d (Se - Si) = 331.6 pm, compared to 270 pm for unstrained acenaphthenes). The increased Se / Si separation going from the naphthalene compound to the acenaphtene system parallels the decreased through-space coupling between the Si-H hydrogen atom and the selenium atom.



**Figure 4.** Left: Molecular structure of silyInaphthylselane **3e** in the crystal (thermal ellipsoids at 50% probability; only the Si-H hydrogen atom is shown) pertinent bond lengths [pm], bond angles and dihedral angles [°]: Se – Si 322.86(4), Se – C<sup>1</sup> 193.22(9), Si – C<sup>8</sup> 189.71(9), Si – H 140(1), Se / H 276(1), Se – C<sup>1</sup> - C<sup>10</sup> 122.45(6), Si – C<sup>8</sup> - C<sup>10</sup> 131.06(6), C<sup>1</sup> - C<sup>10</sup> – C<sup>8</sup> 126.05(6), C<sup>ipso</sup> – Se – C<sup>1</sup> 99.51(3). Right: Molecular structure of silyIacenaphthylselane **8d** in the crystal. (thermal ellipsoids at 50% probability; only the Si-H hydrogen atom is shown) pertinent bond lengths [pm], bond angles and dihedral angles [°]: Se – Si 331.61(5), Se – C<sup>5</sup> 192.87(12), Si – C<sup>6</sup> 189.30(12), Si – H 137(2), Se / H 289(2), Se – C<sup>5</sup> - C<sup>10</sup> 122.44(2), Si – C<sup>6</sup> - C<sup>10</sup> 128.55(9), C<sup>6</sup> - C<sup>10</sup> – C<sup>5</sup> 129.56(1), C<sup>ipso</sup> – Se – C<sup>1</sup> 99.80(6).



Scheme 2. Synthesis of silyl borates 9 and 10 (Ch = O, S, Se, Te; Ar = Ph, Mes). a) 1 equiv.  $[Ph_3C][B(C_6F_5)_4]$ , benzene, r.t.

Reaction of silanes 3a,c-f and 8 with trityl tetrakispentafluorophenyl borate yielded the corresponding silvl borates 9a,c-f  $[B(C_6F_5)_4]$  and 10a,c,d,f  $[B(C_6F_5)_4]$  in nearly quantitative yields (Scheme 2).<sup>[28]</sup> At ambient conditions, solutions of the silvl borates in aromatic hydrocarbons or halogenated aromatic hydrocarbons are stable and once formed most of the borates are stable also in methylene chloride solution. One exception is oxonium borate 10a[B( $C_6F_5$ )<sub>4</sub>] which decomposes in methylene chloride at r.t. within one day. All prepared silvl borates were fully characterized by multinuclear NMR spectroscopy and pertinent NMR data are summarized in Table 1. In all cases, the <sup>29</sup>Si NMR chemical shift was found to be invariable with the tested solvent, with nearly identical <sup>29</sup>Si NMR chemical shifts in benzene and in toluene. The effected ionization is apparent by the significant low field chemical shift of the <sup>29</sup>Si NMR resonance of the product. The low field shift is largest for the oxygen substituted compounds  $9a[B(C_6F_5)_4]$  $(\delta^{29}Si = 71.4)$  and **10a**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] ( $\delta^{29}Si = 77.5$ ). For the naphthalene and for the acenaphthene systems, the  $\delta^{29}Si$  NMR chemical shift decreases along the series of sulfur (9c, 10c), selenium (9d,e, 10d) and tellurium (9f, 10f) substituted silyl cations (Table 1). The smallest <sup>29</sup>Si NMR chemical shift was detected for the tellurium containing compound  $9f[B(C_6F_5)_4](\delta^{29}Si$ = 45.4). The change from the naphthalene to the acenaphthene

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system is associated with a low field shift of the <sup>29</sup>Si NMR resonance of  $\Delta \delta^{29}$ Si = 6.1 – 8.4. The analysis of the <sup>29</sup>Si NMR chemical shift data reveals the expected trend that the <sup>29</sup>Si NMR chemical shift decreases with the size and polarizability of the chalcogen atom. It is largest for the oxygen donor and smallest for the tellurium substituent. The observed deshielding for the acenaphthene based cations **10** indicates a slightly smaller interaction between the chalcogen atom.

The significant high field shift of the <sup>77</sup>Se NMR resonance in silyl cations 9d,e and 10d compared to the respective precursor silanes ( $\Delta \delta^{77}$ Se (**9d/3d**) = -149;  $\Delta \delta^{77}$ Se (**9e/3e**) = -86;  $\Delta \delta^{77}$ Se (10d/8d) = -123) gives a clear indication for the increase of the coordination number at the selenium atom due to interaction with the positively charged silicon atom. As expected this effect is even more pronounced for the tellurium substituted silvl cations 9f and **10f** ( $\Delta \delta^{125}$ Te = -411 (**9f/3f**), -210 (**10f/8f**)). The detection of J coupling constants of considerable size between the silicon atom and the chalcogen atoms selenium and tellurium in cations 9d.e.f and **10d**. f provides additional strong evidence for a direct bonding interaction. The observed  ${}^{1}J(SiSe)$  coupling constants in cations 9d,e and 10d fall in a close range of  ${}^{1}J(SiSe) = 58 - 66$  Hz, with the smallest coupling constant detected for the acenaphthene cation **10d**. These values are however significantly smaller than reported for silvlselenoethers with dicoordinated selenium atoms such as trimethylsilylphenylselane ( ${}^{1}J(SeSi) = 107 \text{ Hz}$ ).<sup>[29]</sup> Similarly, the detected <sup>1</sup>J(SiTe) constants in cations 9f and 10f are substantial ( ${}^{1}J(SiTe) = 161 \text{ Hz} (9f)$ , 169 Hz (10f)) but are small compared to that of model compounds with dicoordinated tellurium atoms such as bis-trimethylsilyltelluride ( ${}^{1}J(SiTe) = 278$ Hz).<sup>[30]</sup> Finally, also the non-equivalence of the <sup>1</sup>H NMR and <sup>13</sup>C NMR signals for the methyl groups at the silicon atom of the sulfur, selenium and tellurium containing cations 9c-f, 10c,d,f indicated the formation of a direct linkage between the chalcogen and the silicon atom. In these cases, the pyramidalization of the chalcogen atom implicates a syn/anti relation of the arylsubstituent at the chalcogen atom relative to the methyl groups at the silicon atom (Scheme 3). NOE spectroscopy indicated that the <sup>1</sup>H and <sup>13</sup>C NMR signals for the methyl group syn to the aryl substituent appear in cations 9c-f, 10c,d,f at higher field. Interestingly, we noticed only for the <sup>13</sup>C NMR signal of the antimethyl group in the selenium, 9d,e, 10d, and tellurium substituted compounds 9f satellite signals corresponding to a <sup>2</sup>J(CCh) spin spin coupling (Ch = Se, Te, see Table 1)). While the presence of these satellite signals provide further support for the direct bonding relation between the silicon and the chalcogen atom, its exclusive detection for the anti-methyl group suggests that it is a valuable tool for conformational analysis of selenium and tellurium ring compounds. In the case of the mesityl substituted cation 9e broad signals for the ortho-methyl groups and meta-hydrogen atoms are detected even at room temperature indicating hindered rotation around the C(Mesityl) - Se bond. The <sup>1</sup>H NMR signals of the diastereotopic methyl groups at the silicon atom in cations 9c**f**, **10d**, **f** show no significant kinetic line broadening ( $\Delta v < 3Hz$ ) up to temperatures of T = 70°C. In contrast, for the sulfur containing cation 10c coalescence between both signals is detected at T = 105°C in toluene-d<sub>8</sub>, which corresponds to an approximate free energy barrier of  $\Delta G^{\ddagger}(378K) = 74 \text{ kJ mol}^{-1}$  (see Figure S74). For

the tellurium-substituted cations, **9f**, two-dimensional exchange spectroscopy (EXSY) at T = 90°C indicated magnetization transfer between the two diastereomeric methyl groups due to a slow exchange process. Similar results were obtained for borates **10d**,f[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (see Figures S68, S73). As underlying process for the magnetization transfer between the methyl groups, we suggest the inversion of the configuration at the chalcogen atom, which is slow on the NMR time scale at room temperature. (Scheme 3).



Scheme 3. Planar coordination of the oxygen atom in cations 9a, 10a and inversion of the configuration of the chalcogen atom in chalcogenyl substituted silyl cations 9 and 10 (Ch = S, Se, Te; Ar = Ph, Mes).

At this point, we note that the aryloxy-substituted cations **9a** and **10a** showed only one signal for both methyl groups in the temperature range from  $T = -90^{\circ}C - 30^{\circ}C$  (see Figure S74). This suggests that either the above described inversion process is fast on the NMR time scale even at  $T = -90^{\circ}C$  or that cations **9a**, **10a** adopt a ground state conformation of higher symmetry than its heavier congeners **9c-f**, **10c,d,f**.

Single crystals suitable for X-ray diffraction analysis were obtained from a dichloromethane solution of 9a[HCB11H5Br6] and from a benzene solution of  $9d[B(C_6F_5)_4]$ . The selenium substituted silvl borate 9d[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] crystallizes in the triclinic space group P-1 as benzene solvate. Cation and anion are well separated with the shortest silicon fluorine distance well above the sum of the van der Waals radii, ∑vdW (Si / F = 377 pm vs. ∑vdW(Si / F) = 357 pm).<sup>[31]</sup> The closest contact between selenium and fluorine is 333 pm, close to the  $\Sigma vdW(Se/F) = 337 \text{ pm}.^{[31]}$  The molecular structure of cation 9d (Figure 5) reveals the expected short Si Se separation (Se - Si = 240.6 pm), which is only slightly longer than a regular Si - Se single bond (232 pm).[32] Consequently, the silicon atom is tetra-coordinated. The sum of the bond angles between the silicon atom and its carbon substituents,  $\Sigma\alpha$ (Si), is 345.6° and indicates a significant trigonal flattening of the tetrahedral coordination of the silicon atom. The coordination environment of the selenium atom is trigonal pyramidal with a mean bond angle around the selenium atom of 96.5° ( $\Sigma\alpha$ (Se) = 289.5) and mean Se - C bond lengths of 192.8 pm. The attractive Lewis acid / base interaction between the two atoms in periposition of the naphthalene moiety does not lead to significant

strain in cation **9d**.<sup>[27]</sup> The sum of the bay angles  $\Sigma\beta$  is 357.3°, close to the ideal value of 360°. The silicon atom is placed 15 pm above the plane of the naphthalene ring, while the selenium atom is pushed by merely 2 pm below this plane. In summary, the molecular structure of cation 9d shows all features of a selenonium ion, similar to the classical Ph<sub>3</sub>Se<sup>+</sup>.<sup>[33]</sup> There are no structural indications for increased strain imposed by the formation of the new Si - Se bond. The crystal structure of the carborate **9a**[HCB<sub>11</sub>H<sub>5</sub>Br<sub>6</sub>] (monoclinic space group P1 21/c) reveals separated cations and anions as well. The closest contacts between the bromine substituents of the carborane cage and silicon or oxygen atoms of the cation are larger than van der Waals contacts (Si / Br = 404 pm; O / Br = 395 pm,  $\Sigma vdW(Si/Br)$ = 393 pm,  $\Sigma vdW(O/Br)$  = 335 pm).<sup>[31]</sup> Despite the close chemical relation between the cations 9a and 9d, the molecular structure of the aryloxy substituted cation 9a is in several aspects distinctively different from that of the selenium cation 9d (Figure 5). The Si / O distance in cation 9a (183.8 pm) is by 20 pm longer than the mean Si - O bond length for tetra-coordinated silicon atoms and dicoordinated oxygen atoms (163 pm). It is also longer than the Si-O bonds in silvlated oxonium ions (Si – O 177.7 – 178.5 pm).[34 – <sup>36]</sup> Remarkable is the pronounced trigonal flattening of the tetracoordinated silicon atom. The measured  $\Sigma \alpha$ (Si) is 351.3°, which is well removed from tetrahedrality (ideal value  $\Sigma \alpha(Si) = 328.2^{\circ}$ ). The oxygen atom in cation 9a adopts a nearly perfect trigonal planar coordination environment ( $\Sigma \alpha(O) = 360^{\circ}$ ). This is in agreement with the previously reported structural data for silylated oxonium ions 11 - 13 (Figure 6).[34 - 36] Furthermore, it suggests that the appearance of only one signal for the methyl groups in the <sup>1</sup>H and <sup>13</sup>C NMR spectra of **9a**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] is not a result of a fast equilibrium between syn/anti isomers, but is due to the symmetric ground state structure with a trigonal planar coordinated oxygen atom. Our finding contrasts the results of Ducos et al. who proposed for the silylated oxonium ion 14 a pyramidal structure based on NMR measurements.<sup>[17]</sup> In contrast to the relaxed structure of the selenonium ion 9d, the molecular structure of oxonium ion 9a indicates the consequences of the attractive Lewis acid base interaction. To accomplish the short Si - O peri-distance of 184 pm both atoms are forced nearly into one plane with the naphthalene system, the silicon atom is placed 3.7 pm above and the oxygen atom 9.8 pm below the plane of the naphthalene ring. More noticeable are however the acute bond angles in the bay region of cation **9a** ( $\Sigma\beta$  = 337.9°, see Figure 5).

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**Figure 5.** Left: Molecular structure of cation **9a** in the crystal of **9a**[HCB<sub>11</sub>H<sub>5</sub>Br<sub>6</sub>] (thermal ellipsoids at 50% probability, hydrogen atoms are not shown) pertinent bond lengths [pm], bond angles and dihedral angles [°]: O – Si 183.79(17), O – C<sup>8</sup> 143.99(29), Si – C<sup>1</sup> 185.05(25), O – C<sup>8</sup> - C<sup>10</sup> 109.920(191), Si – C<sup>1</sup> - C<sup>10</sup> 109.294(168), C<sup>1</sup> - C<sup>10</sup> – C<sup>6</sup> 118.709(206), C<sup>1/pso</sup> - O – C<sup>8</sup> 121.322(176), C<sup>1</sup> - C<sup>8</sup> – O - Si 1.660(122), C<sup>1/pso</sup> - O – C<sup>8</sup> – C<sup>10</sup> - 177.911(191). Right: Molecular structure of cation **9d** in the crystal of **9d**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]. (thermal ellipsoids at 50% probability; hydrogen atoms are not shown) pertinent bond lengths [pm], bond angles and dihedral angles [°]: Se – Si 240.56(5), Se – C<sup>1</sup> 192.02(15), Si – C<sup>8</sup> 186.02(14), Se – C<sup>1</sup> - C<sup>10</sup> 117.64(11), Si – C<sup>8</sup> - C<sup>10</sup> 117.52(11), C<sup>8</sup> - C<sup>10</sup> – C<sup>1</sup> 122.13(13), C<sup>1/pso</sup> - Se – C<sup>1</sup> 101.72(7), C<sup>8</sup> – C<sup>1</sup> – Se - Si 2.490(53), C<sup>1/pso</sup> - Se – C<sup>1</sup> – C<sup>10</sup> – 96.00(13).







The reaction of methoxy-substituted naphthylsilane **3b** with trityl cation took a quite unexpected course. Reaction of trityl borate with silane **3b** at r.t. resulted in noticeable heat evolvement and in gas evolution. NMR analysis revealed that only small amounts of triphenylmethane were formed and most of the trityl borate was still present in the reaction mixture. Although naphthylsilane **3b** was completely consumed, there was no indication for the formation of the expected cyclic methoxonium ion **9b**. Instead, the cyclic siloxane **15** was formed in nearly quantitative yield as indicated by NMR spectroscopy ( $\delta^{29}$ Si = 27.9) and GC/MS analysis (m/z = 200) (see Supporting Information for further analytic details). Siloxane **15** is formed in an autocatalytic reaction with methoxonium ion **9b** as the key intermediate (Scheme 4), a process which can be regarded as an intramolecular variant of the



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Piers-Rubinsztajn reaction.<sup>[37, 38]</sup> Cation **9b** is formed as expected by the reaction of silane **3b** with trityl cation. It reacts however with the starting silane **3b** with loss of methane and recovery of cation **9b**. Trityl cation serves in this reaction sequence only as initiator. Additional runs with only 0.01 and 0.03 equivalents of trityl borate confirmed this. In both cases, siloxane **15** was isolated in quantitative yields. Methane formation was confirmed by its <sup>1</sup>H NMR resonance at  $\delta^{1}H = 0.20$  in benzene-d<sub>6</sub>. Attempts to synthesize methoxonium ion **9b** at low temperatures under careful controlled conditions avoiding excess of silane **3b** gave strong indications for the formation of cation **9b** (in CD<sub>2</sub>Cl<sub>2</sub> at -70°C:  $\delta^{29}Si = 70$ ,  $\delta^{4}H(OMe) = 4.64$ ). The isolation and definite characterization of the borate **9b**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] was not possible due to its beginning decomposition.



Scheme 4. Reaction of silane 3b with catalytic amounts of trityl cation, a) 0.01 - 0.03 equiv. [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>], benzene, r.t..

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compd <sup>[a]</sup>	δ <sup>29</sup> Si <sup>n</sup> J(SiX) [Hz]	δ <sup>1</sup> H(SiH) <sup>[b]</sup> <sup>□</sup> J(HX) [Hz]	δ <sup>77</sup> Se <sup>n</sup> J(SeX) [Hz]	$\delta^{125}$ Te <sup>n</sup> J(TeX) [Hz]	$\delta^{1}$ H(Si(C <i>H</i> <sub>3</sub> ) <sub>2</sub> )	δ <sup>13</sup> C(Si(C <i>H</i> <sub>3</sub> ) <sub>2</sub> ) <sup>n</sup> J(CX) [Hz]
3a	-12.4 <sup>1</sup> J(SiH) = 192	5.11 <sup>1</sup> J(HSi) = 192			0.55	-1.0
3b	-12.7 <sup>1</sup> J(SiH) = 188	5.09 <sup>1</sup> J(HSi) = 188			0.52	-0.9
3c	-17.1 <sup>1</sup> J(SiH) = 199	5.36 <sup>1</sup> J(HSi) = 199			0.60	0.8
<b>3d</b> Ar = Ph	-18.6 <sup>1</sup> J(SiH) = 199	5.50 <sup>1</sup> J(HSi) = 199	397.1 <i>J</i> (SeH) = 18		0.60	1.0
<b>3e</b> Ar = Mes	-17.9 <sup>1</sup> J(SiH) = 196 J(SiSe) = 31	5.75 <sup>1</sup> J(HSi) = 196 J(HSe) = 35	304.0 J(SeH) = 35 J(SeSi) = 31		0.68	0.8
<b>3f</b> Ar = Ph	-22.0 ¹J(SiH) = 191 J(SiTe) = 93	5.43 <sup>1</sup> J(HSi) = 191 J(HTe) = 74		690.5 J(TeH) = 74	0.57	0.7
8a <sup>[b]</sup>	-14.0	4.62 <sup>1</sup> J(HSi) = 191			0.40	-1.5
8c	-17.7	5.39 <sup>1</sup> J(HSi) = 198			0.63	0.2
<b>8d</b> Ar = Ph	-18.7 ¹J(SiH) = 198	5.53 ¹J(HSi) = 198	376.0 <i>J</i> (SeH) = 10		0.64	0.6
<b>8f</b> Ar = Mes	-21.6 <sup>1</sup> J(SiH) = 188 J(SiTe) = 103	5.68 <sup>1</sup> J(HSi) = 188 J(HTe) = 82		425.9 J(TeH) = 82 J(TeSi) = 103	0.69	0.8
9a	71.4				0.32	-1.3
9c	57.4				-0.02 (syn); 0.41 (anti)	-3.7 ( <i>syn</i> ); -1.0 (anti)
<b>9d</b> Ar = Ph	55.7 <sup>1</sup> J(SiSe) = 60 55.7 <sup>[a]</sup>		248.0 <sup>1</sup> J(SiSe) = 60 247.9 <sup>[a]</sup>		0.03 (syn); 0.45 (anti)	-2.9 ( <i>syn</i> ) -0.6 (anti) <sup>2</sup> J(CSe) = 18
<b>9e</b> Ar = Mes	48.7 ¹J(SiSe) = 66		218.1 <sup>1</sup> J(SiSe) = 66		0.26 ( <i>syn</i> ); <sup>3</sup> J(HSe) = 7 0.49 ( <i>anti</i> ) <sup>3</sup> J(HSe) = 8	-2.3 ( <i>syn</i> ) -0.3 (anti) ² <i>J</i> (CSe) = 22
9f	45.4 ¹J(SiTe) = 161			280.0 <sup>1</sup> J(SeTe) = 161	0.11 ( <i>syn</i> ); 0.50 ( <i>anti</i> ) <sup>3</sup> J(HTe) = 17	-1.9 ( <i>syn</i> ) -0.2 (anti) <sup>2</sup> J(CTe) = 38
10a <sup>[a]</sup>	77.4 77.5 <sup>[a]</sup>				0.41	-0.6
10c	65.8				-0.01 (syn); 0.47 (anti)	-3.0 ( <i>syn</i> ); -0.3 ( <i>anti</i> )
<b>10d</b> Ar = Ph	64.0 <sup>1</sup> J(SiSe) = 58 64.2 <sup>[a]</sup> 64.6 <sup>[b]</sup>		253.4 <sup>1</sup> J(SeSi) = 58 253.4 <sup>[a]</sup> 259.2 <sup>[b]</sup>		0.05 ( <i>syn</i> ); 0.51 ( <i>anti</i> ) <sup>]</sup>	-2.3 ( <i>syn</i> ) -0.1 (anti) <sup>2</sup> <i>J</i> (CSe) = 19

Table 1. Selected NMR parameter of naphthylsilanes 3, 8 and silyl borates 9, 10

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10f         49.1         215.9         0.28 (syn);         -0.1 (syn);           Ar = Mes         'J(SiTe) = 169         'J(SeTe) = 169         0.57 (anti)         0.9 (anti)						-
Ar = Mes ${}^{1}J(SiTe) = 169$ ${}^{1}J(SeTe) = 169$ 0.57 ( <i>anti</i> ) 0.9 (anti)	10f	49.1	215.9	0.28 (syn);	-0.1 ( <i>syn</i> );	
	Ar = Mes	<sup>1</sup> <i>J</i> (SiTe) = 169	<sup>1</sup> <i>J</i> (SeTe) = 169	0.57 ( <i>anti</i> )	0.9 (anti)	

[a] In  $C_7D_8$  at r.t.. [b] In  $CD_2Cl_2$  at r.t..

compd.	Ch	Si - Ch [pm]	Σα(Si) [°]	Σα(Ch) [°]	Σβ [°]	δ <sup>29</sup> Si
9a	0	183.2ª (183.8)	351.6 (351.3)	359.5 (360.0)	337.7 (337.9)	65.0 (71.4)
9c	S	229.6ª	343.4	299.3	353.6	63 (57.4)
9d	Se	242.3 <sup>a</sup> (240.6)	347.1 (345.6)	289.2 (289.5)	357.3 (357.3)	58 (55.7)
9f	Те	260.0 <sup>ª</sup>	345.3	276.9	360.9	51 (45.4)
10a	0	185.4	352.1	360.0	337.3	70 (77.5)
10c	S	232.1	349.3	299.5	353.4	71 (65.8)
10d	Se	244.7ª	347.9	289.0	359.1	67 (64)
10f	Те	261.4	345.4	293.0	361.9	48 (49.1)

[a] Single bond lengths [pm] calculated from self-consistent covalent radii: Si – O 179; Si – S 219, Si – Se 232; Si – Te 252.<sup>[32]</sup> [b]  $\Sigma$ vdW [pm]: Si / O 362; Si / S 390; Si / Se 400; Si / Te 416.<sup>[31]</sup>

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**Table 3.** Calculated characteristic parameter for the Si – Ch linkage in cations **9**, **10** and related compounds (at M06-2X/def2tzvp, BDE: bond dissociation energy; WBI: Wiberg bond index, Charge: Charge according to the NBO analysis,  $\rho$  electron density at the bond critical point (bcp),  $\nabla^2 \rho$ : Laplacian of the electron density at the bcp; H: total energy at the bcp).

compd.	Ch	Si - Ch [pm]	BDE (Si - Ch)ª [kJ mol <sup>-1</sup> ]	WBI	Charge(Si)	Charge(Ch)	ρ [a.u.]	∇²ρ [a.u.]	H [a.u.]
9a 10a 18a 19a	0	183.2 185.4 166.9 182.4	136 104 214	0.36 0.36 0.58 0.36	1.93 1.92 1.94 1.95	-0.56 -0.56 -0.83 -0.59	0.085 0.081 0.128 0.086	+0.405 +0.369 +0.759 +0.409	-0.025 -0.024 -0.044 -0.026
9c 10c 18c 19c	S	229.6 232.1 216.0 229.7	188 144 215	0.64 0.63 0.87 0.63	1.64 1.64 1.56 1.64	0.47 0.47 -0.18 0.46	0.074 0.071 0.093 0.072	+0.057 +0.047 +0.102 +0.061	-0.039 -0.037 -0.054 -0.037
9d 10d 18d 19d	Se	242.3 244.7 230.7 244.3	190 151 211	0.69 0.68 0.90 0.67	1.60 1.60 1.51 1.60	0.61 0.61 -0.09 0.60	0.072 0.068 0.085 0.067	-0.003 -0.006 +0.005 -0.002	-0.041 -0.037 -0.054 -0.037
9f 10f 18f 19f	Te	260.0 261.4 251.8 263.3	191 149 212	0.74 0.75 0.93 0.73	1.52 1.52 1.44 1.52	0.87 0.86 0.07 0.88	0.069 0.068 0.080 0.065	-0.063 -0.069 -0.108 -0.064	-0.040 -0.040 -0.051 -0.037

[a] Approximate bond energy of the Si - Ch according to isodesmic equations (Scheme 5).

The interaction between the chalcogen and the silicon atom in cations 9a,c-f and 10a,c,d,f was studied in detail using quantum mechanical calculations at the DFT M06-2X/def-2tzvp level of theory.<sup>[39, 40]</sup> This model chemistry provided calculated molecular structures for cations 9a and 9d that are close to those determined in the solid state, i.e. the deviation of the computed Si - Ch bond lengths from the experimentally determined is less than 1% in both cases (see Table 2 for a comparison of pertinent structural parameter). The Si - Ch distances in the naphthalene-based cations 9 are all significantly smaller than the corresponding sum of the van der Waals radii but they are larger by 11% (Ch = O) -4% (Ch = Te) than calculated for the corresponding silvlaryl chalcogenides 18. They are almost identical to the predicted Si -Ch bond lengths in acyclic diarylsilylchalconium ions 19 (see Tables 2 and 3). The change from the naphthalene based cations 9 to the acenaphthene systems 10 is connected with a slight increase of the Si - Ch bond lengths by approximatively 2 pm. The molecular structures of sulfur, selenium and tellurium stabilized cations 9c, d, f and 10c, d, f show only minor indications of steric stress.<sup>[27]</sup> For example, the sum of the bay angles,  $\Sigma\beta$ , are close to 360° (Table 2). In contrast, the computed molecular structures of the oxygen stabilized cations 9a and 10a show very short Si - O distances and consequently small bond angles in the bay region ( $\Sigma\beta$  = 337.7° (**9a**), 337.3° (**10a**), Table 2). Cations 9a and 10a differ also from their heavier homologues by the planar coordination environment of the tricoordinated oxygen atom ( $\Sigma\alpha(O)$  = 360°) in agreement with the XRD results for 9a[HCB<sub>11</sub>H<sub>5</sub>Br<sub>6</sub>]. All heavier homologues adopt the trigonal pyramidal coordination expected for a chalconium ion ( $\Sigma \alpha$ (Ch) = 277 - 300°).



The bond dissociation energy for the newly formed Si – Ch bond is estimated using the isodesmic equations shown in Scheme 5 and the results are given in Table 3.<sup>[41]</sup> These isodesmic equations are not ideal for two reasons: silanes **3**, **8** are destabilized compared to their isomers **16**, **20** by the *peri*disubstitution. This leads to the prediction of too strong Si – Ch bonds in cations **9** and **10** by the isodesmic equations. In addition, the conformation of the SiMe<sub>2</sub> units in cations **17**, **21** relative to the naphthalene / acenaphthene backbone allow significant conjugation between the 3p(Si) orbital and the  $\pi$ -system of the arene unit, which is not possible in the chalcogenyl stabilized cations **9**, **10**. This latter imbalance of the isodesmic equations leads to the prediction of too weak Ch – Si bonds. These opposing and in consequence cancelling effects in mind, we suggest that the calculated reaction enthalpies of the isodesmic equations that are shown in Scheme 5 are a good first approximation for the strength of the Si-Ch linkage in cations  ${\bf 9}$  and  ${\bf 10}$ .



Scheme 5. Isodesmic reactions for the assessment of the strength of the Si – Ch bond in naphthalene and acenaphthene based silyl cations  ${\bf 9}$  and  ${\bf 10}$ .

The calculated bond dissociation energies of the Ch - Si bond for the acyclic chalconium ions 19 are nearly independent of the chalcogen atom and fall in a narrow range between 211 (Ch = Se) and 215 kJ mol<sup>-1</sup> (Ch = S, Table 3). The BDEs predicted for the naphthalene-based cations 9 are significantly smaller. The Si -Ch bonds in cations 9c, d, f are weaker by 21 – 27 kJ mol<sup>-1</sup>. This weakening of the Si - Ch is due to the formation of the fivemembered rings. Remarkably, the Si - O bond in 9a is weaker than the Si – O linkage in oxoniumion 19a by even 78 kJ mol<sup>-1</sup>. This is in agreement with the computed and observed structural indications of strain in cation 9a. For the acenaphthene series 10, an additional decrease of the BDE by 32 – 44 kJ mol<sup>-1</sup> relative to the corresponding naphthalene compound is computed, which agrees with the longer calculated Si - Ch bonds for cations 10. At this point, we notice that in the series of cations 9 and 10 the oxonium ions 9a and 10a show the weakest Si - Ch interactions (136 kJ mol<sup>-1</sup> (9a), 104 kJ mol<sup>-1</sup> (10a)) and that the Si – Te bond in cation 9f is the strongest Si - Ch linkage in this series (191 kJ mol<sup>-1</sup> (9f)). In general, the differences between the calculated bond energies for the three series of cations 9, 10 and 19 confirm the trend inferred from the structural parameter.

The comparison of the NBO results for the cations 9, 10 and 19 with that of the corresponding aryl-silyl chalcogenides 18 indicate that for each chalcogen atom the Wiberg Bond Index (WBI) of the Si - Ch bond decreases significantly upon formation of an onium ion (by app 0.19 - 0.24, see Table 3).<sup>[42, 43]</sup> Notably, for a given chalcogen atom the WBI of the Si - Ch bond is constant for all three types of onium ions. A particularly low WBI is computed for the oxonium ions 9a, 10a and 19a. In these three cations, the charge at silicon and the charge difference to the oxygen atom is the largest calculated in the whole series of chalcogenyl-stabilized cations. Remarkably, the charge at the silicon atom in cations 9a, 10a and 19a is the same as calculated for the silyl ether 18a, only the negative charge at the oxygen atom decreases upon formation of the oxonium ions (Table 3). As expected the polarity of the Si - Ch bond decreases markedly from the oxygencontaining cations to the sulfur-substituted species and

decreases further along the series of selenium and tellurium containing compounds (Table 3). For each series of S-, Se- and Te-substituted compounds the calculated charge at the silicon atoms remains nearly constant upon onium ion formation and only the positive charge at the chalcogen atom increases, as shown by comparison between disubstituted chalcogenides 18 and cations 9, 10, 19 (Table 3). This comparison of calculated charge distributions in silvlchalcogenides 18 and cations 9, 10, 19 suggest that the cations are best termed onium ions. The analysis of the computed electron density of the cations 9, 10 and 19 in the framework of Bader's quantum theory of atoms in molecules (QTAIM) reveals for all cations topological molecular graphs that enclose bond paths between the chalcogen and the silicon atoms.<sup>[44]</sup> 2D-Laplacian contour plots of the S-, Se- and Tesubstituted cations are very similar and Figure 6 provides the relevant part of the Laplacian contour plot of selenonium cation 9d as a representative example. The direct comparison with that of oxonium cation 9a reveals obvious differences in the Laplace distribution. The bonding interaction between the oxygen and the silicon atom in cation 9a is typified as being strongly polar covalent by the properties at the bond critical point (bcp).<sup>[46]</sup> The bcp is shifted to the electropositive silicon atom and it shows a relative large electron density  $\rho(bcp)$ , a positive Laplacian  $\nabla^2 \rho(bcp)$  and a negative total energy density H(bcp) (see Table 3). The 1D-Laplacian profile along the Si - O bond path reveals the expected pronounced valence shell charge concentration (VSCC) close to the oxygen atom and a second weak VSCC in the direction of the silicon atom (Figure 7). Both VSCCs belong to the atomic basin of the oxygen atom. Similarly, the bcp of the Si - Se linkage is shifted to the more electropositive silicon atom as expected from the different electronegativities of silicon and selenium (Figure 7). The bcp is located close to a nodal surface of the Laplace distribution and both weak VSCCs along the bond path have slightly negative Laplacian values. These properties characterize the Si - Se bond as a covalent bond with only small polarity.[46]



**Figure 6.** 2D contour plots of the calculated Laplacian of the electron density,  $\nabla^2 \rho$  (r), in the Si - C<sup>10</sup> – Ch plane of cations **9a** (left) and **9d** (right). Relevant parts of the molecular graphs of the cations are projected onto the respective contour plot. Solid black lines show the bond paths, which follow the line of maximum electron density between bonded atoms. The corresponding bond critical points (bcp's) are shown as green circles. Ring critical points are shown as red circles. Red contours indicate regions of local charge accumulation  $(\nabla^2 \rho (r) < 0)$ ; blue contours indicate regions of local charge depletion  $(\nabla^2 \rho (r) > 0)$ .



**Figure 7.** 1D profiles of the calculated Laplacian of the electron density,  $\nabla^2 \rho$  (r), along Si – Ch bond path of cations **9a** (top) and **9d** (bottom). Bond critical points (bcp's) are shown as circles.

The synthesized stabilized silyl cations are typical silyl Lewis acids and can be used as catalyst in organic synthesis. To provide an example, we concentrate here on one particular and prominent feature of strong silyl Lewis acids, on the catalytic hydrodefluorination (HDF) reaction.[47-49] In a standardized reaction, we used 5 mol% of the tetraaryl borates of cations 9a, c - f as catalyst for the HDF reaction of decyl fluoride as shown in Scheme 6. Moderate turn over numbers (TONs) between 13 and 124 indicate for all investigated cations a catalytic reaction (Table 4). In our hand, the sulfonium borate  $9c[B(C_6F_5)_4]$  is the most efficient catalyst for our test reaction while the selonium (9d) and oxonium (9a) borates show comparable TONs. A significant smaller TON was measured for the tellonium borate  $9a[B(C_6F_5)_4]$ (Table 4). Increase of the steric congestion at the chalcogen atom decreases the TON, as shown by comparison of the catalytic activity of the borates of selonium ions 9d and 9e. Exchange of the anion to the more robust brominated closo-carboranate [CB<sub>11</sub>H<sub>6</sub>Br<sub>6</sub>]<sup>-</sup> leads for the sulfonium ion **9c** to a significant lower activity. This is an unexpected result, in particular in view of literature reports on the exquisite performance of silyl-closoborates in HDF reactions.<sup>[47b]</sup> We note however that the closo

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carborate 9c[CB<sub>11</sub>H<sub>6</sub>Br<sub>6</sub>] is hardly soluble in the solvent mixture odichlorobenzene / Et<sub>3</sub>SiH.

	<b>9</b> [B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ]	
	5 mol%	
n-C40H04-E+ EtoSi-H	Et <sub>3</sub> SiH, o-C <sub>6</sub> H <sub>4</sub> Cl <sub>2,</sub> r.t.	n-CuoHoo + EtoSi-E
<i>n</i> -0 <sub>10</sub> -21-1 · Ll30-11	-	11-010122 · El301-1

Scheme 6. Hydrodefluorination reaction of decyl fluoride using borates  $9[B(C_6F_5)_4]$  as catalyst.

Table 4. TON of the HDF reaction of decyl fluoride using with different

tetraaryi dorates as catalysts.							
cation	Chalcogen	Ar	Anion <sup>[c]</sup>	TON			
9a	0	Ph	$[B(C_6F_5)_4]$	82			
9c	S	Ph	$[B(C_6F_5)_4]$	124			
9c	S	Ph	[CB11H6Br6]	28			
9d	Se	Ph	$[B(C_6F_5)_4]$	109			
9e	Se	Mes	$[B(C_6F_5)_4]$	52			
9f	Те	Ph	$[B(C_6F_5)_4]$	13			

Based on mechanistic investigations by the Oestreich group on related HDF reactions using the cationic ruthenium complex **22** as catalyst,<sup>[50]</sup> we suggest the catalytic cycle shown in Scheme 7 for the HDF reaction of decyl fluoride. This mechanistic proposal is in agreement with the observed different reactivity of the chalconium ions **9a** < **9c** > **9d** > **9f**. It reflects the expected Lewis basicity of the different chalcogen centers (O < S > Se > Te), which is a prerequisite for the activation of the silane (step A, Scheme 7). In addition, the absence of rearranged hydrocarbons in the product formation (step B, Scheme 7). This mechanistic proposal and other reactions that are mediated by cations **9** and **10** are currently subject of intensive experimental and computational investigations in our laboratories.





Scheme 7. Suggested cycle for the HDF reaction of primary alkyl fluorides catalyzed by silylchalconium ions 9.

#### Conclusions

We report the synthesis and characterization of two series of silylated chalconium borates, **9** and **10**, that are based on the *peri*-naphthyl and *peri*-acenaphthyl framework. Their synthesis was accomplished using the standard Corey - hydride transfer reaction with the corresponding silanes, **3** and **8** as starting materials. NMR investigations of the selenium and tellurium containing silanes **3d** – **f** and **8d**, **f** revealed a significant through-space *J* – coupling between the chalcogen nuclei and the Me<sub>2</sub>SiH group. Experimental (NMR spectroscopic and structural) and computational (DFT-based bonding analysis) results typifies the synthesized cations **9** and **10** as chalconium ions, best represented by the canonical structure **B** (Scheme 8). The imposed ring strain weakens the Si – Ch linkage compared to acyclic chalconium ions. This attenuation of the Si – Ch bond strength is more pronounced in the acenaphthene series.



Scheme 8. Resonance structures of silylated chalconium ions 9 and 10.

The oxonium ions **9a** and **10a** differ from their heavier homologues in having a trigonal planar coordination for the oxygen atom instead the expected trigonal pyramidal configuration (Scheme 3, Figure 5). In addition, the small size of the oxygen atoms results in significant distorted molecular structures of the silylated oxonium ions **9a** and **10a**. This imposed strain weakens the Si – O bond and as a surprising result the Si – O bonds in oxonium ions **9a** and **10a** are the weakest Si – Ch linkage in both series. The heavier chalconium ions **9c** - **f** and **10c**,

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**d**, **f** (Ch = S, Se, Te) show the expected trigonal pyramidal coordination environment for the chalcogen atom (Scheme 3). In these cases, variable temperature NMR investigations and two dimensional exchange spectroscopy (EXSY) indicate an inversion process of the trigonal pyramidal coordinated chalcogen atom, similar to related processes in isoelectronic phosphanes and arsanes.

Although borates of the synthesized cations are stable compounds in the absence of moisture and air, they are highly reactive. They catalyze HDF reactions of alkyl fluorides with silanes with TON between 13 and 124. For the activation process, we suggest a cooperative activation of the silane by the Lewisbasic chalcogen center and the Lewis acidic silyl group (Scheme 7).

#### Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft (DFG-Mu1440/12-1) and by the Carl von Ossietzky University Oldenburg. The simulations were performed at the HPC Cluster HERO (High End Computing Resource Oldenburg), located at the University of Oldenburg (Germany) and funded by the DFG through its Major Research Instrumentation Program (INST 184/108-1 FUGG) and the Ministry of Science and Culture (MWK) of the Lower Saxony State.

# **Keywords:** silicon • chalcogens • cations • NMR • X-ray diffraction • bond activation

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#### Entry for the Table of Contents (Please choose one layout)

Layout 1:

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**Oxygen Breaks Ranks.** The structural, spectroscopic and computerchemical characterization of two series of silylated chalconium ions (Ch = O, S, Se, Te) revealed significant differences between the second row element oxygen and its higher congeners.



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