▌ **Sulfur and Selenium Chemistry** |*Hot Paper*|

# Attempts to Synthesize a Thiirane, Selenirane, and Thiirene by Dealkylation of Chalcogeniranium and Thiirenium Salts

Helmut Poleschner* and Konrad Seppelt[a]

**Abstract:** Thiiranium salts $[Ad_2SR]^+X^-$ (**5**, **8**, **9**, **11**, **12**; $X^- =$ $Tf_2N^-$ ($Tf = CF_3SO_2$), $SbCl_6^-$) and seleniranium salts $[Ad_2SeR]^+$ $X^-$ (**14**, **16**, **17**, **23–25**; $X^- = Tf_2N^-$, $BF_4^-$, $CHB_{11}Cl_{11}^-$, $SbCl_6^-$) are synthesized from strained alkene bis(adamantylidene) (**1**). The disulfides and the diselenides $(Me_3SiCH_2CH_2E)_2$ (**4**, **13**), $(tBuMe_2SiCH_2CH_2E)_2$ (**7**, **22**), and $(NCCH_2CH_2E)_2$ (**10**, **15**; $E = S$, Se) have been used. The thiirenium salts $[tBu_2C_2SR]^+X^-$ (**34**) and $[Ad_2C_2SR]^+X^-$ (**35**, **36**) are prepared from the bis-*tert*-butylacetylene (**2**) and bis-adamantyl-acetylene (**3**) with $R = Me_3SiCH_2CH_2$ and $tBuMe_2SiCH_2CH_2$. Attempts to cleave off the groups $Me_3SiCH_2CH_2$, $tBuMe_2SiCH_2CH_2$, and $NCCH_2CH_2$ resulted in thiiranes **27**, **30**. No selenirane $Ad_2Se$ (**33**) is formed from seleniranium salts, instead cleavage to the alkene (**1**) and diselenide (**13**, **15**) occurs. The thiirenium salt $[Ad_2C_2SCH_2CH_2SiMe_3]^+Tf_2N^-$ (**35**) does not yield the thiirene $Ad_2C_2S$ (**37**), the three-membered ring is cleaved, forming the alkyne (**3**) and disulfide (**4**). All compounds are characterized by ESI mass spectra, NMR spectra, and by quantum chemical calculations. Crystal structures of the salts **8**, **12**, **25**, **17**, **26**, **36** and the thiiranes **27**, **30** are presented.

## Introduction

Thiiranium[1] and thiirenium salts[2] are long known. In recent years, we have prepared selenirenium und tellurirenium salts[3,4] and also the saturated seleniranium and telluriranium salts,[5] see also ref. [6]. These are key intermediates in electrophilic addition reactions of organochalcogen cation equivalents $[RE^+X^-]$ to alkynes and alkenes.[7–14]
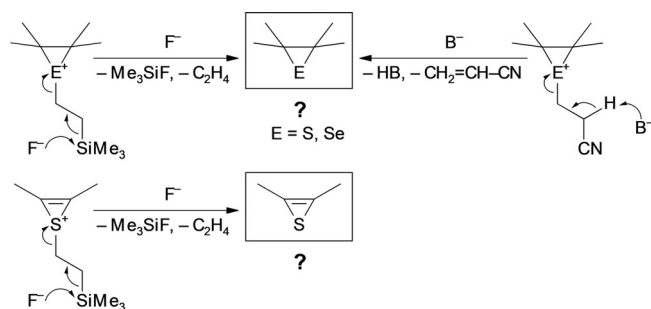
However, the knowledge about uncharged $C_2$-chalcogen three-membered rings is limited almost to thiiranes.[15] Seleniranes[16] have been described as unstable intermediates[17] and also in substance,[18] but no structural proof for this class of compounds exists. The postulated instability, meaning the easy decomposition into alkene and elemental selenium, calls into question their existence, see here the discussion about seleniranes and telluriranes by Braunschweig.[19] Unexpectedly, results by Sardar et al. are surprising,[18d] who claim to have made seleniranes at high temperatures, which have very unusual ^{77}Se NMR shifts in the region of 600–700 ppm. So far, telluriranes have not been mentioned in the literature. The search for thiirenes has been going on for a long time. These would be of great theoretical interest as antiaromatic cyclic $4\pi$-electron compounds.[20,15b] This would explain their extreme instability. The calculated nucleus-independent chemical shift (NICS (1)) value of $-2.2$ ppm does not allow a clear statement on the question of antiaromaticity. With natural bond orbital (NBO), a hybridization of $3s^{1.8} 3p^{4.16}$ is calculated for the S atom in thiirene (see Table S1 in the Supporting Information). Early synthetic attempts employed photolysis of 1,2,3-thiadiazoles. At best, thiirenes have been characterized by the matrix isolation technique at very low temperatures in combination with IR spectroscopy, but structural proof is lacking.[21] Thiirensulfoxides and thiirensulfones are known, however,[20] but attempts of deoxygenation to thiirenes failed.[22] Our long-running work with such unstable three-membered ring chalcogen compounds has motivated us to erase this white spot with some new attempts. Our plan for generating thiiranes, seleniranes, and thiirenes was first to generate the $C_2$-chalcogen three-membered ring motive by electrophilic addition of an $[RE^+X^-]$ equivalent to an alkene or alkyne under formation of chalcogeniranium and thiirenium salts.[3–5] The positively charged S or Se atoms should bear a cleavable group, so that after cleavage the uncharged thiiranes, seleniranes, and thiirenes should be obtained. The cleavage of a $Me_3SiCH_2CH_2$ group should be done by $F^-$, whereas the $NCCH_2CH_2$ group can be cleaved of by bases such as $OH^-$. Both are well known protecting groups for the SH and the SeH functions[23,24] (see Scheme 1). We wanted to test these methods by the dealkylation reactions of thiiranium salts under formation of stable thiiranes. Then, this procedure should be transferred to the preparation of seleniranes und thiirenes. The expected highly unstable seleniranes should be stabilized by the use of the extreme sterically demanding alkene bis(adamantylidene) Ad=Ad (**1**). The latter has

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**Chemistry–A European Journal**

**Full Paper**
doi.org/10.1002/chem.202003461

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Scheme 1. Synthetic concept for thiiranes, seleniranes, and thiirenes.

enabled us already to achieve the isolation of the extremely unstable telluriranium salts.[5]

Thiirenes should be stabilized by the sterically demanding alkynes $t$BuC≡C$t$Bu (**2**) and diadamantyl acetylene AdC≡CAd (**3**).[3,4] The interesting question is whether F⁻ or OH⁻ would indeed attack at the protecting group, or if the reaction would occur at the C or chalcogen ring atoms.

## Results and Discussion

We used RE⁺ electrophiles for the preparation of the three-membered ring salts that we developed previously: either by two-electron oxidation of the disulfides and diselenides with $XeF_2$ in combination with fluoride ion acceptors like $Tf_2NSiMe_3$, $BF_3 \cdot OEt_2$, or $Me_3Si^+CHB_{11}Cl_{11}^-$,[4,5] or by chlorination with $SO_2Cl_2$. The reagent [RE⁺SbCl₆⁻] is generated subsequently by reaction with $SbCl_5$.[3,5]

### Thiiranium salts

The disulfide $(Me_3SiCH_2CH_2S)_2$ (**4**) is oxidized with $XeF_2/Tf_2NSiMe_3$ and reacted in the presence of the alkene **1**, yielding the thiiranium salt [Ad₂SCH₂CH₂SiMe₃]⁺Tf₂N⁻ (**5**). The Me₃Si group in **4** is not attacked by $XeF_2$. By chlorination of **4** with $SO_2Cl_2$ and subsequent reaction with $SbCl_5$ and **1**, the chloroethyl thiiranium salt [Ad₂SCH₂CH₂Cl]⁺SbCl₆⁻ (**6**) is formed, which is identified by ESI-MS. Here, the Me₃Si group is cleaved off and substituted by Cl. When using the more stable $t$BuMe₂Si group in the disulfide $(t$BuMe₂SiCH₂CH₂S)_2$ (**7**), the method with $SO_2Cl_2/SbCl_5$ and **1** produces the salt [Ad₂SCH₂CH₂SiMe₂$t$Bu]⁺SbCl₆⁻ (**8**). With **7**, $XeF_2/Tf_2NSiMe_3$, and **1**, the salt **9** is formed.

The cyanoethyl thiiranium salts **11** and **12** are reacted with $(NCCH_2CH_2S)_2$ (**10**) and **1**, either with $XeF_2/Tf_2NSiMe_3$, or with $SO_2Cl_2/SbCl_5$ (see Scheme 2).

In the ESI mass spectra, the new thiiranium salts show the expected molecular peaks for the cations and anions. The ¹³C NMR spectra show the characteristic signal of the three-membered ring C atoms at 96–99 ppm, compared with 67–105 ppm in ref. [1e] and [25]. The less soluble SbCl₆⁻ salts crystallize well, and the crystal structures of [Ad₂SCH₂CH₂SiMe₂$t$Bu]⁺SbCl₆⁻ (**8**) and [Ad₂SCH₂CH₂CN]⁺SbCl₆⁻ (**12**) have been obtained (see Figures 1 and 2). These new thiiranium ions have C–C bond lengths of 150.0–150.6 pm
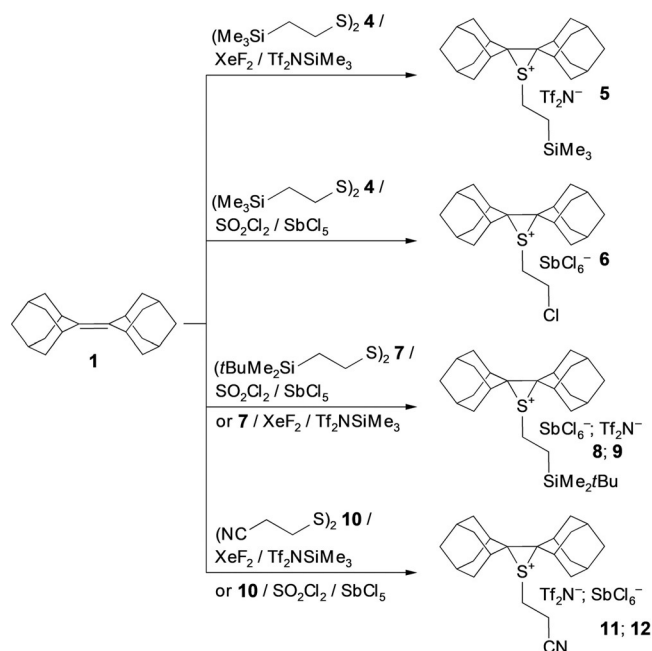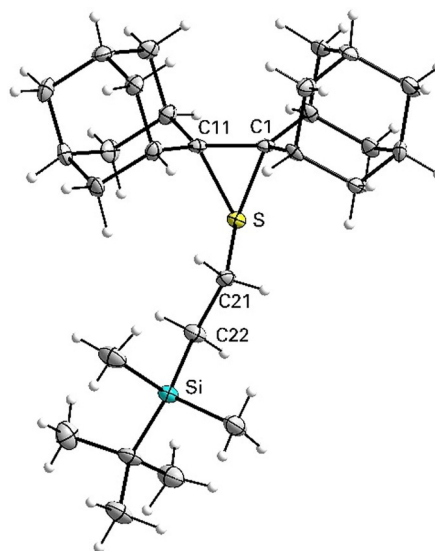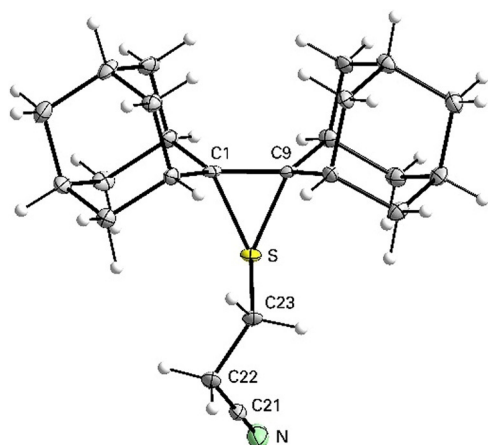
Scheme 2. Synthesis of the thiiranium salts with the $Me_3SiCH_2CH_2$, $t$Bu-$Me_2SiCH_2CH_2$, and $NCCH_2CH_2$ groups.

Figure 1. Molecular structure of [Ad₂SCH₂CH₂SiMe₂$t$Bu]⁺SbCl₆⁻·EtCN (**8**),[40] with the probability ellipsoids drawn at 50%. The anion and solvent have been omitted for clarity. Selected bond parameters [pm/°]: C1–C11 150.6(6), S–C1 190.1(5), S–C11 191.6(5), S–C21 183.8(5), C21–C22 153.2(7), Si–C22 189.8(5); C1-S-C11 46.47(19).
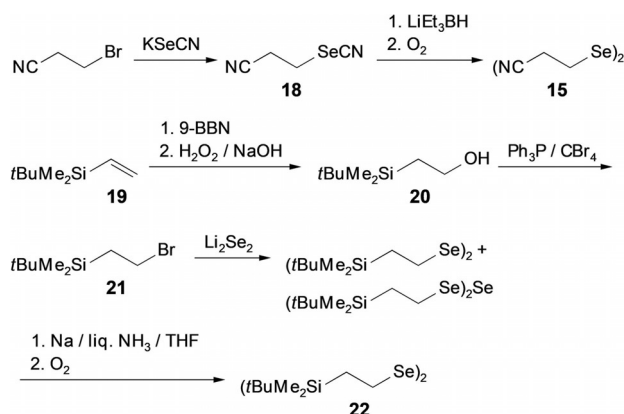
within the three-membered ring, C–S bond lengths of 189.4–191.8 pm, and C-S-C angles of 46.4°. The C–S bond to the substituent at the S atom are a little shorter (182.3–183.8 pm) than the C–S bonds within the ring. Known thiiranium salts have quite similar bond parameters.[1e,25,26]

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**Figure 2.** Molecular structure of [Ad$_2$SCH$_2$CH$_2$CN]$^+$SbCl$_6^-$·CH$_2$Cl$_2$ (**12**),[40] with the probability ellipsoids drawn at 50%. The anion and solvent have been omitted for clarity. Selected bond parameters [pm/°]: C1–C9 150.0(4), S–C1 191.8(3), S–C9 189.4(3), S–C23 182.3(3), C22–C23 153.1(5), C21–C22 146.5(1), N–C21 113.9(5); C1-S-C9 46.35(12).
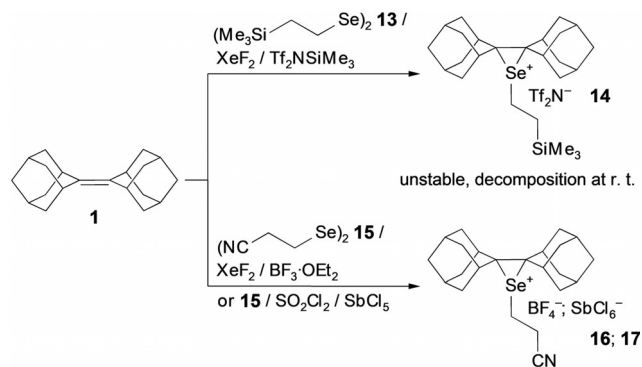
### Seleniranium salts

These methods of synthesis can only be applied in part to the Se compounds. The diselenide (Me$_3$SiCH$_2$CH$_2$Se)$_2$ (**13**) reacts with XeF$_2$/Tf$_2$NSiMe$_3$ and **1**, forming the seleniranium salt **14**, which decomposes already at room temperature with formation of elemental selenium (see Scheme 3). However, $^{13}$C and $^{77}$Se NMR spectra can be obtained directly from the reacting solution at −40 °C, which are in accordance with the structure of **14**. In particular, the $^{13}$C signal of the ring C atom at 110 ppm and the $^{77}$Se signal of the highly shielded Se atom at 35 ppm are typical values.[5] With the diselenide (NCCH$_2$CH$_2$Se)$_2$ (**15**) both synthetic routes are successful, namely with the oxidation by XeF$_2$/BF$_3$·OEt$_2$, and the chlorination with SO$_2$Cl$_2$, reaction with SbCl$_5$ and addition of **1**. For this sake, the synthesis of the cyanoethyldiselenide (**15**) had to be improved, as according to ref. [24a] only mixtures of di- and triselenide are obtained. The initially prepared cyanoethyl selenocyanate[27] (**18**) reacts with LiEt$_3$BH, and oxidation with O$_2$ selectively gives the diselenide **15** (see Scheme 4).[28] The instability of the seleniranium salts with the Me$_3$SiCH$_2$CH$_2$ group contrasts with the
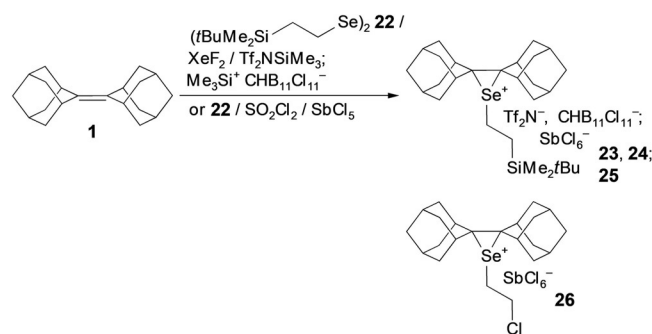
much higher stability of the non-functionalized seleniranium salts.[5] Therefore, we tried to prepare the salts carrying the tBuMe$_2$SiCH$_2$CH$_2$ group, as we assumed that these would be more stable. The corresponding diselenide (tBu-Me$_2$SiCH$_2$CH$_2$Se)$_2$ (**22**) is synthesized from the vinylsilane (**19**). Hydroboration with 9-borabicyclononane (9-BBN) and oxidation of the borane with H$_2$O$_2$ gives the silylethanol (**20**), see also ref.[29], followed by bromination with PPh$_3$/CBr$_4$ affording tBuMe$_2$SiCH$_2$CH$_2$Br (**21**).[23c] This, however, reacts with Li$_2$Se$_2$ to diselenide, which is contaminated with considerable amounts of triselenide. The product mixture is reduced in liquid NH$_3$/THF with Na and afterwards reoxidized with O$_2$ to the diselenide **22** (see Scheme 4). The disulfide (tBuMe$_2$SiCH$_2$CH$_2$S)$_2$ (**7**) is prepared similarly with Li$_2$S$_2$.

(tBuMe$_2$SiCH$_2$CH$_2$Se)$_2$ (**22**) reacts with **1** and XeF$_2$/Tf$_2$NSiMe$_3$ or XeF$_2$/Me$_3$Si$^+$CHB$_{11}$Cl$_{11}^-$, and here also with SO$_2$Cl$_2$/SbCl$_5$ to the seleniranium salts **23–25** (see Scheme 5). The salts carrying the tBuMe$_2$SiCH$_2$CH$_2$ group decompose slowly in solution at room temperature, for example, during NMR measurements. They can be isolated as solid compounds and are stable for prolonged time at −20 °C. The $^{13}$C NMR spectrum shows signals that are typical for the three-membered ring at 110 ppm, and $^{77}$Se signals at high field 24–39 ppm. These values are very close to those of the [Ad$_2$SeEt]$^+$ ion.[5] ESI mass spectra have the correct molecular peaks for cations and anions.



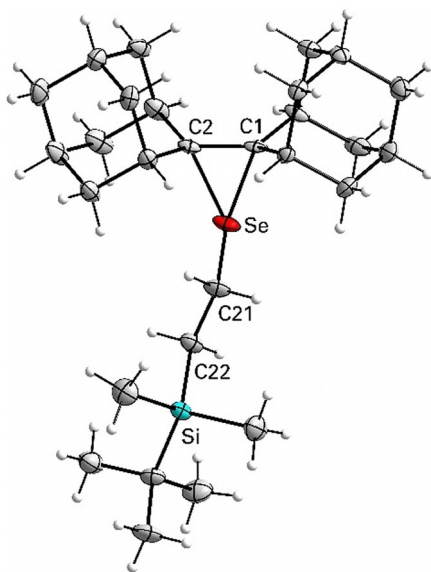**Scheme 4.** Synthesis of the diselenides **15** and **22**.



**Scheme 3.** Synthesis of the seleniranium salts carrying the Me$_3$SiCH$_2$CH$_2$ and NCCH$_2$CH$_2$ groups.



**Scheme 5.** Synthesis of the seleniranium salts carrying the tBuMe$_2$SiCH$_2$CH$_2$ group.

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Crystal structure determinations of the new seleniranium salts [Ad$_2$SeCH$_2$CH$_2$SiMe$_2$tBu]$^+$SbCl$_6^-$ (**25**) and [Ad$_2$SeCH$_2$CH$_2$CN]$^+$SbCl$_6^-$ (**17**) prove the structures (see Figures 3 and 4). By reacting of **22** with SO$_2$Cl$_2$/SbCl$_5$ and **1**, the side product [Ad$_2$SeCH$_2$CH$_2$Cl]$^+$SbCl$_6^-$ (**26**) is isolated and characterized by ESI-MS and crystal structure determination (see Figure S1 in the Supporting Information). Here also, a partial cleavage takes place even of the tBuMe$_2$Si group. The structural parameters within the three-membered rings in these seleniranium salts (C–C bond lengths of 147.9–148.9 pm, C–Se bond lengths of 205.5–209.7 pm, C–Se bond lengths to the groups at the Se atoms of 196.5–200.2 pm, and C-Se-C bond angle of 41.8–42.4°) are almost identical to those of our [Ad$_2$SeEt]$^+$ salt,[5] see also ref. [6a].



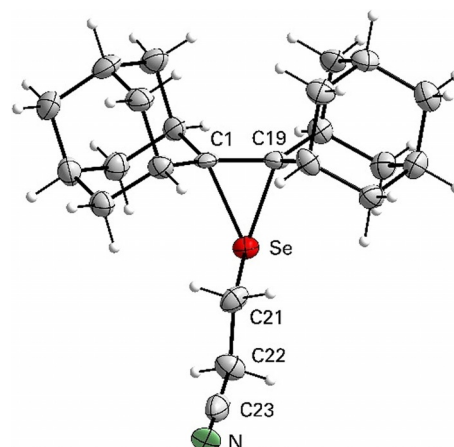**Figure 4.** Molecular structure of [Ad$_2$SeCH$_2$CH$_2$CN]$^+$SbCl$_6^-$·CH$_2$Cl$_2$ (**17**),[40] with the probability ellipsoids drawn at 50%. The anion and solvent have been omitted for clarity. Selected bond parameters [pm/°]: C1–C19 148.9(9), Se–C1 209.7(5), Se–C19 207.7(5), Se–C21 200.2(6), C21–C22 149.1(9), C22–C23 146.7(10), N–C23 111.1(9); C1-Se-C19 41.8(2).



**Figure 3.** Molecular structure of [Ad$_2$SeCH$_2$CH$_2$SiMe$_2$tBu]$^+$SbCl$_6^-$·CH$_2$Cl$_2$ (**25**),[40] with the probability ellipsoids drawn at 50%. The anion and solvent have been omitted for clarity. Selected bond parameters [pm/°]: C1–C2 147.9(4), Se–C1 206.0(3), Se–C2 207.3(3), Se–C21 197.3(3), C21–C22 152.8(4), Si–C22 189.6(3); C1-Se-C2 41.94(11).



**Figure 5.** Molecular structure of thiirane **27**,[40] with the probability ellipsoids drawn at 50%. Selected bond parameters [pm/°]: C1–C11 150.73(16), S–C1 184.92(12), S–C11 185.11(12); C1-S-C11 48.08(5).
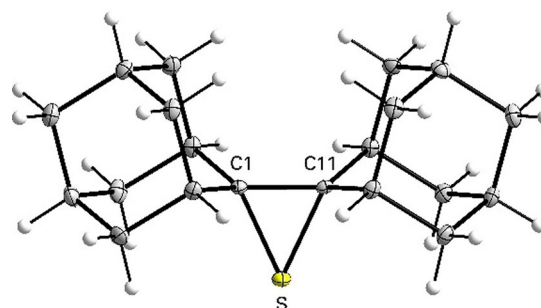
## Dealkylation of the thiiranium salts—thiiranes

We began the attempts to cleave off the protecting groups with the thiiranium salts. Salt **5** reacts surprisingly selectively with Bu$_4$NF in THF and under cleavage of the Me$_3$SiCH$_2$CH$_2$ group at −40°. The thiirane Ad$_2$S **27** was isolated. Then, we tried to combine the preparation of the thiiranium salt and its dealkylation in a one-pot procedure. Alkene **1** reacts with disulfide **4** and XeF$_2$/BF$_3$·OEt$_2$ and the formed thiiranium salt is reacted with the Bu$_4$NF solution without isolating it. The expected thiirane **27** is obtained in quantitative yield. Its molecular structure has been determined by crystal structure determination (see Figure 5).

*Cis*-cyclooctene (**28**) as a simple sterically unstrained alkene is reacted in a one-pot procedure with **4** and XeF$_2$/BF$_3$·OEt$_2$, and subsequently with Bu$_4$NF. The preparation of the thiirane **30** was also successful, as proven by the *cis*-structure in the

crystal. Thiirane **30** exists in the solid state in two different forms in a 1:1 ratio, and these are mirror images of each other. Figure 6 shows both molecules, the S atoms pointing to the viewer. In the crystalline state they are oriented in a different manner.

If *trans*-cyclooctene **29** is subjected to the same protocol, the same *cis*-thiirane **30** is formed as with the *cis*-alkene; the products have identical $^{13}$C NMR spectra. Addition of the
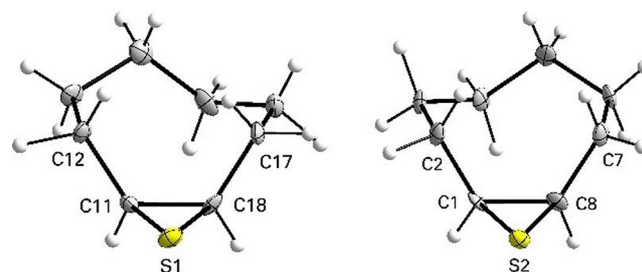


**Figure 6.** Molecular structure of thiirane **30**,[40] with the probability ellipsoids drawn at 50%. Selected bond parameters [pm/°]: C11–C18 147.2(6), S1–C11 183.4(5), S1–C18 183.1(5); C11-S1-C18 47.38(18), C12-C11-C18-C17 −1.902(720); C1–C8 148.9(6), S2–C1 184.0(5), S2–C8 184.2(5); C1-S2-C8 47.71(19), C2-C1-C8-C7 0.039(743).

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Me$_3$SiCH$_2$CH$_2$S$^+$ electrophile to the *trans*-alkene results in a configuration inversion of the strained eight-membered ring system. *Cis–trans* isomerization of thiiranium ions occur via ring-opened carbocations.[1h,i] There are incorrect data in ref.[30]: a postulated *trans*-9-thiabicyclo[6.1.0]nonane has exactly the same $^{13}$C NMR data as our *cis*-compound **30**. For other $^{13}$C NMR data of the *trans*-isomer, see ref.[31].

The reaction of Bu$_4$NF with the thiiranium salt **9** carrying the *t*BuMe$_2$SiCH$_2$CH$_2$ group does not give the thiirane **27**, but the cleavage of the *t*BuMe$_2$SiCH$_2$CH$_2$S group is observed. The three-membered ring is attacked instead: the $^{13}$C NMR spectrum shows only the alkene **1** and the disulfide (*t*Bu-Me$_2$SiCH$_2$CH$_2$S)$_2$ (**7**), and only traces of the thiirane **27**. The *t*Bu-Me$_2$SiCH$_2$CH$_2$ group is clearly too stable as a protecting group for our purposes (see Scheme 6).

The NCCH$_2$CH$_2$ group in the thiiranium salts **11** and **12** is also not a useful protecting group for the liberation of the thiirane **27**. Instead, **11** and **12** react after 3 h at 0 °C with CsOH in H$_2$O/THF or MeOH/THF to mixtures of **1** and the thiirane **27** in the ratios of 1:3 to 1:1, according to the $^{13}$C NMR spectra. Besides the dealkylation, a lot of cleavage takes place of the three-membered ring.

The structures of the thiirane **27** and thiiranium salts **8** and **12** have C—C bonds of similar lengths (150.0–150.7 pm). In the thiirane, the C—S bonds are a little shorter (185 pm) than in the salts (189.4–191.8 pm). In **27**, the C-S-C angle is consequently a little larger (48.1°) compared with **8** and **12** (46.4–46.5°).
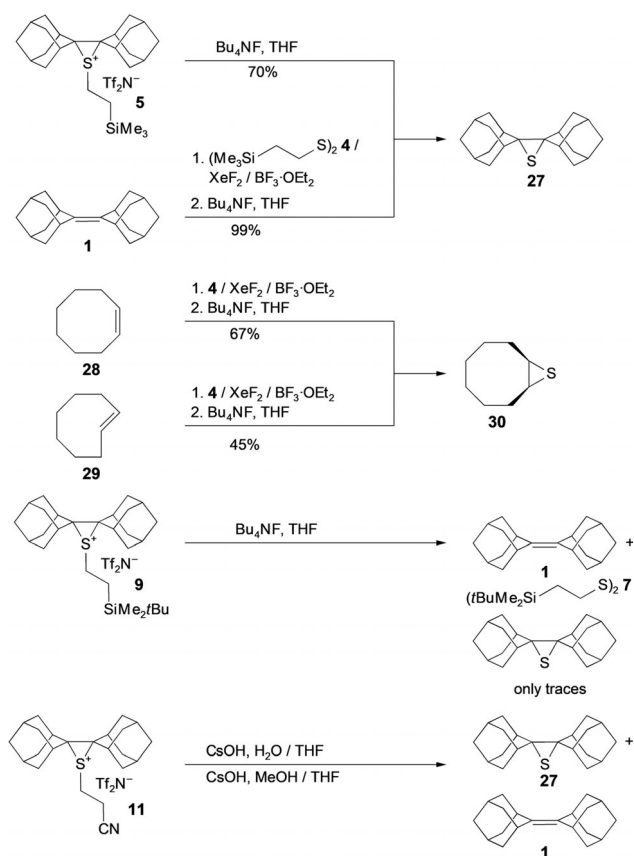


**Scheme 6.** Cleavage of the protecting groups from the thiiranium salts.

## Attempts to dealkylate seleniranium salts—selenirane?

For the sake of detection and preparation of a selenirane, reactions were undertaken to cleave off the Me$_3$SiCH$_2$CH$_2$ group from seleniranium salts. Learning from the results with the thiiranium salts, we have used for these reactions solely compounds with this protecting group. The [Ad$_2$SeCH$_2$CH$_2$SiMe$_3$]$^+$ salts turned out to be unstable, so these reactions were done in a one-pot procedure, meaning the preparation of the seleniranium salts is followed by immediate reaction with Bu$_4$NF. Because of the expected instability of the target compound, the preparation of the seleniranium salt and the dealkylation were done at −40 °C.

We calculated by DFT the $^{13}$C and $^{77}$Se NMR shifts of the selenirane ring, together with those of the thiiranium and seleniranium ions and the thiirane **27**. Considering the small differences between the calculated and experimental data, the selenirane should have a $^{13}$C signal at about 85 ppm and a $^{77}$Se resonance at about 70 ppm (see Scheme 7).
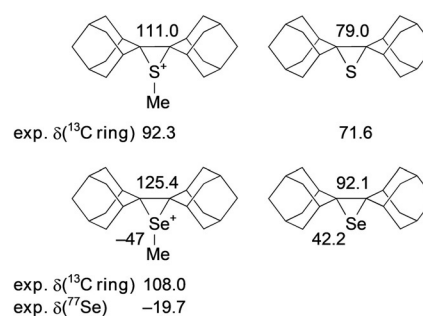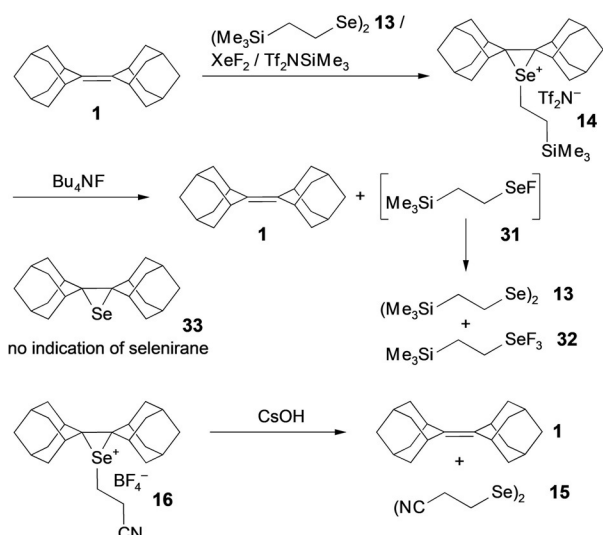


**Scheme 7.** Calculated $^{13}$C and $^{77}$Se NMR chemical shifts [ppm] ($\delta = \sigma_{ref} - \sigma_{comp}$; by using GIAO-B3PW91/cc-pVTZ//B3PW91/6-311+G(d,p) theory), relative to TMS and Me$_2$Se, including experimental data.

First, we prepared the seleniranium salt **14** by reacting **1**, the diselenide **13**, and XeF$_2$/Tf$_2$NSiMe$_3$ at −40 °C. A solution of Bu$_4$NF in THF is added at −78 °C, followed by stirring at −40 °C. The $^{13}$C NMR measurement of the reaction solution at −78 °C shows only the compounds **1** and **13**, whereas the $^{77}$Se spectra show the presence of **13** and an organoselenium trifluoride, most likely Me$_3$SiCH$_2$CH$_2$SeF$_3$ by a new signal at 1187 ppm (for the NMR spectra of RSeF$_3$, see refs. [32], [33]). There is no indication of the selenirane **33**. The F$^-$ ion possibly attacks the selenium atom of the seleniranium ring, which is cleaved to the alkene **1** and the selenium monofluoride Me$_3$SiCH$_2$CH$_2$SeF (**31**). The latter is unstable and disproportionates according to 3RSeF→R$_2$Se$_2$+RSeF$_3$ in a known manner[32–34] to the diselenide (Me$_3$SiCH$_2$CH$_2$Se)$_2$ (**13**) and the trifluoride Me$_3$SiCH$_2$CH$_2$SeF$_3$ (**32**; see Scheme 8).

We also attempted a reaction of **1**, **13**, XeF$_2$/BF$_3$·OEt$_2$, and Bu$_4$NF, with the same results.

The reaction of the seleniranium salt **16** with CsOH in THF/H$_2$O at −40 °C cleaves the three-membered ring selectively to the olefin **1** and the diselenide **15**, a selenirane is not observed (see Scheme 8).
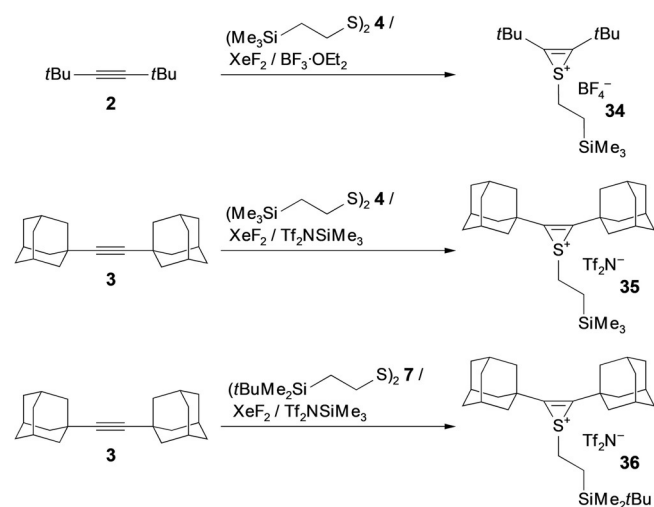
**Scheme 8.** Attempts for preparation of a selenirane.



**Figure 7.** Molecular structure of [Ad$_2$C$_2$SCH$_2$CH$_2$SiMe$_2$tBu]$^+$Tf$_2$N$^-$ (**36**),[40] with the probability ellipsoids drawn at 30%. The anion has been omitted for clarity. Selected bond parameters [pm/°]: C21–C22 128.9(11), S–C21 185.4(11), S–C22 181.0(9), S–C23 182.6(6), C23–C24 152.6(7), Si–C24 188.7(6); C21-S-C22 41.2(3).

### Thiirenium salts

The thiirenium salt **34** is prepared by oxidation of the disulfide **4** with XeF$_2$/BF$_3$·OEt$_2$ in the presence of di-*tert*-butylacetylene (**2**). The synthesis succeeds also for the thiirenium salts **35** and **36** by reaction of the diadamantylacetylene (**3**) with **4** and XeF$_2$/Tf$_2$NSiMe$_3$ or the disulfide **7** and XeF$_2$/Tf$_2$NSiMe$_3$ (see Scheme 9). These compounds crystallize badly and often are obtained as oils. However, single crystals have been obtained of the compound **36**. Figure 7 shows the crystal structure.

The $^{13}$C NMR signals of the ring C atoms of these thiirenium ions are in the same region (113–115 ppm) as in the unsubstituted thiirenium salts.[1f, 2a,b, 4]

The structure of **36** has a C=C bond length of 128.9 pm within the three-membered ring, the S–C bonds are 185.4 and 181.0 pm long, to the *t*BuMe$_2$SiCH$_2$CH$_2$ group 182.6 pm. The C-S-C angle is 41.2°. This three-membered ring is quite similar to those in the non-substituted alkylthiirenium salts.[26, 35, 4]

### Attempts towards dealkylation of thiirenium salts—thiirene?

We tried to cleave off the Me$_3$SiCH$_2$CH$_2$ group from the thiirenium salt **35** by reaction with Bu$_4$F at −60 °C. $^{13}$C NMR shows that, analogously to the seleniranium salts, a selective attack by the F$^-$ ions occurs at the sulfur atom. Alkyne **3** is liberated, and there is no indication of the formation of thiirene **37**. No cleavage of the Me$_3$SiCH$_2$CH$_2$ group is observed (see Scheme 10).

Summing up: The method of cleaving off the protecting groups works only with thiiranium salts, where the Me$_3$SiCH$_2$CH$_2$ group leaves and a thiirane is liberated. In thiiranium salts with the *t*BuMe$_2$SiCH$_2$CH$_2$ or NCCH$_2$CH$_2$ groups, in seleniranium salts with the Me$_3$SiCH$_2$CH$_2$ and NCCH$_2$CH$_2$ groups, and in thiirenium salts with the Me$_3$SiCH$_2$CH$_2$ group, the attack by F$^-$ or OH$^-$ takes place at the heteroatom of the three-membered ring. In these cases, the RS$^+$ or RSe$^+$ part is cleaved off, and an alkene or alkyne is formed. In sterically unprotected thiiranium and seleniranium ions, the attack by nucleophiles happens mostly at the C atom of the three-membered rings,[6b,8–14] very similar to the thiirenium ions.[2d] This is also the case during the fluorothiolation and fluoroselenation of alkenes and the fluoroselenation of alkynes.[36,37,7] But there are examples known where the RS$^+$ group is transferred from thiirenium ions to transition metal complexes or C nucleophiles.[38,2d] Finally, we want to point to the transition of RS$^+$ and



**Scheme 9.** Synthesis of thiirenium salts.
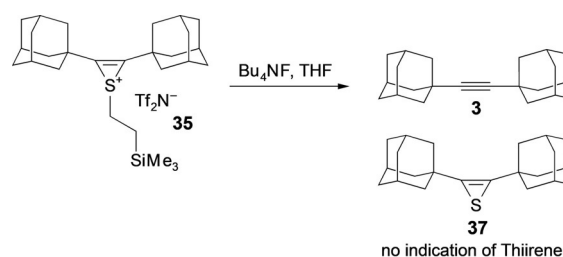


**Scheme 10.** Attempts for syntheses a thiirene.

RSe⁺ groups in thiiranium, seleniranium, or thiirenium ions to alkenes and alkynes, where the C–C-multiple bond preferably interacts with the heteroatom of the three-membered ring.[1g,6,2d,39]

We tried to understand the different reactivity of the compounds carrying the Me₃SiCH₂CH₂ groups by calculating the HOMOs and LUMOs of the thiiranium (**A**), seleniranium (**B**), and thiirenium ions (**C**), as shown in Figure 8. In all three ions, the HOMO is spread over the entire molecule including the Me₃SiCH₂CH₂ group. The LUMO, however, is localized at the three-membered ring, especially at the heteroatom. This is also the case in the unsubstituted ions [Ad₂EEt]⁺ (**D**, **E**) and those with the cyanoethyl group [Ad₂ECH₂CH₂CN]⁺ (**F**, **G**; E = S, Se, see Figure S2 in the Supporting Information). In an orbital controlled attack by the F⁻ ions there should be an interaction with the LUMO of the three-membered ring. Therefore, the cleavage of the RSe⁺ group from **B** or the cleavage of the RS⁺ group from **C** by the F⁻ ion is more likely than the attack at the Me₃Si group. The lower lying LUMO energy in the ions **B** and **C** relative to **A** should favor the attack at the three-membered ring. As the NBO-calculated positive charge on the S atom in thiiranium ion **A** is lower than at the heteroatoms in **B** and **C**, an attack by the F⁻ ions at the Si atom in **A** in competition to the S atom is comprehensible.
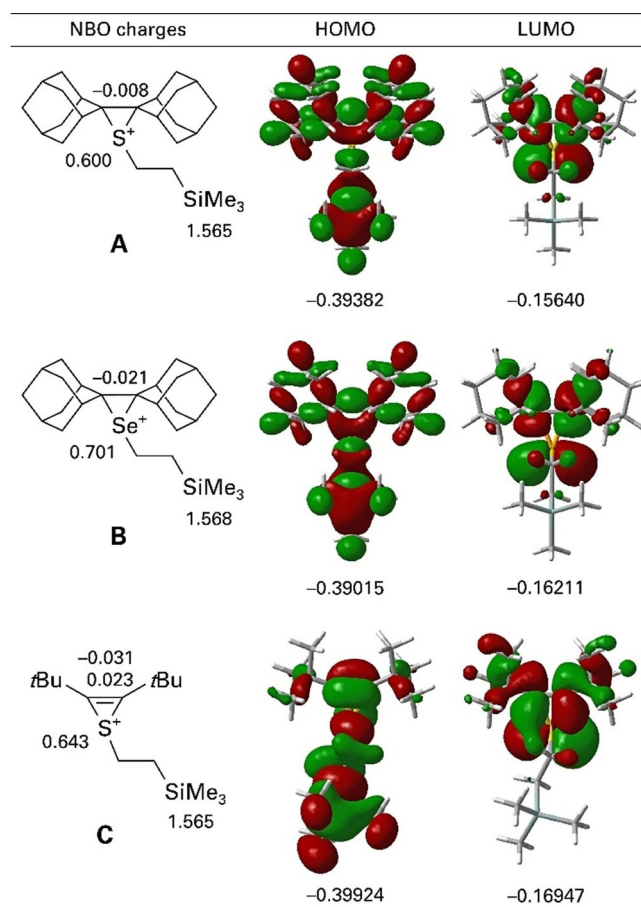


**Figure 8.** HOMO and LUMO of the ions **A**–**C**, orbital energies [Hartrees], and NBO charges, calculated at the B3PW91/6-311+G(d,p) level of theory.

## Conclusion

Thiiranium salts [Ad₂SCH₂CH₂SiMe₃]⁺X⁻ are dealkylated by the F⁻ ion, giving the thiirane Ad₂S. Thiiranium salts with the tBu-Me₂SiCH₂CH₂ or NCCH₂CH₂ group, seleniranium salts [Ad₂SeCH₂CH₂SiMe₃]⁺X⁻, and [Ad₂SeCH₂CH₂CN]⁺X⁻ as well as thiirenium salts [Ad₂C₂SCH₂CH₂SiMe₃]⁺X⁻ are attacked by F⁻ or OH⁻ at the chalcogen atom of the three-membered ring, under cleavage of the RS⁺ or RSe⁺ groups and liberation of the alkene and alkynes. The synthesis of a selenirane and a thiirene remains an open challenge.

## Experimental Section

### General

Dried solvents and argon as protection gas were used. ¹¹B, ¹³C, ¹⁹F, ²⁹Si, and ⁷⁷Se NMR spectra were recorded with a JEOL ECZ 400R or with a JEOL ECS 400 spectrometer (128.25, 100.51, 376.13, 79, and 76.24 MHz, respectively). Chemical shifts δ are reported in ppm relative to BF₃·OEt₂ (¹¹B), Me₄Si (¹³C, ²⁹Si), CFCl₃ (¹⁹F), and Me₂Se (⁷⁷Se). For ESI-TOF mass spectra, the samples were measured from CH₃CN, CH₃CN/CH₂Cl₂, CH₃OH, or CH₃CN/CH₃OH solutions with an Agilent 6210 ESI-TOF, Agilent Technologies, Santa Clara, CA, USA. The solvent flow rate was adjusted to 4 μL min⁻¹, spray voltage set to 4 kV, drying gas flow rate was set to 15 psi (1 bar; ESI-TOF = electrospray ionization–time of flight). Non-ionic compounds were analyzed with a HR-EI-MS (Autospec Premier, Waters Co., Milford, MA, USA) using 80 eV electron energy.

### Quantum chemical calculations

Calculations were performed with Gaussian 16[41] on a high-performance computer system SOROBAN at Zedat, Freie Universität Berlin, https://www.zedat.fu-berlin.de/HPC/Soroban.

The olefin Ad=Ad (**1**),[42] trans-cyclooctene (**29**),[43] the alkynes tBuC≡CtBu (**2**) and AdC≡CAd (**3**),[44] the Si compounds Tf₂NSiMe₃[45] and Me₃Si⁺ CHB₁₁Cl₁₁[4] were prepared according to known procedures.

**1**: ¹³C NMR (CDCl₃): δ = 133.17 (C=C), 39.64 (8×CH₂), 37.37 (2×CH₂), 31.93 (4×CH), 28.60 (4×CH) ppm.

**2**: ¹³C NMR (CDCl₃): δ = 87.08 (C≡C), 31.58 (CMe₃), 27.14 (CMe₃) ppm.

**3**: ¹³C NMR (CDCl₃): δ = 87.59 (C≡C), 43.55 (6×CH₂), 36.47 (6×CH₂), 29.19 (C_q), 28.19 (6×CH) ppm.

### Syntheses of (Me₃SiCH₂CH₂S)₂ (4) and (Me₃SiCH₂CH₂Se)₂ (13)[23c]

Li₂S₂ and Li₂Se₂ are prepared by reacting Li (420 mg, 60 mmol) with S (1.92 g, 60 mmol) or Se (4.47 g, 60 mmol) in liq. NH₃ (150 mL). After evaporation of the NH₃, THF (50 mL) was added. Under stirring, Me₃SiCH₂CH₂Br (10.87 g, 60 mmol) was added dropwise followed by stirring at room temperature for 12 h. Addition of water and extraction with CH₂Cl₂ was followed by vacuum distillation.

**4**: Yield: 6.2 g (78%); b.p.: 86°C/0.19 mbar; EI-MS: [266, M⁺] (C₁₀H₂₆S₂Si₂); ¹³C NMR (CDCl₃): δ = 34.77 (CH₂S), 17.23 (¹J_Si,C = 47.9 Hz, CH₂Si), −1.60 (¹J_Si,C = 51.0 Hz, CH₃Si) ppm.

**13**: Yield: 7.61 g (70%); b.p.: 100°C/0.08 mbar; EI-MS: [362, M⁺] (C₁₀H₂₆Se₂Si₂); ⁷⁷Se NMR (CDCl₃): δ = 355.8 ppm; ¹³C NMR (CDCl₃):

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doi.org/10.1002/chem.202003461

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$\delta = 24.92$ ($^1J_{Se,C} = 69.8$ Hz, CH$_2$Se), 19.55 ($^1J_{Si,C} = 47.2$ Hz, CH$_2$Si), $-1.63$ ($^1J_{Si,C} = 50.9$ Hz, CH$_3$Si) ppm.

### Synthesis of (NCCH$_2$CH$_2$Se)$_2$ (15)

NCCH$_2$CH$_2$SeCN (**18**) was prepared from NCCH$_2$CH$_2$Br (13.4 g, 0.1 mol) and KSeCN (14.4 g, 0.1 mol) in DMF (50 mL) according to ref. [27].

To **18** (9.54 g, 60 mmol) in THF (100 mL) was added dropwise at $-78\,°$C LiEt$_3$BH (65 mL, 65 mmol, 1 M in THF),[27,28] followed by 1 h stirring at this temperature. After warming to room temperature and further stirring for 1 h, O$_2$ was bubbled through the reaction solution for 30 min. THF was removed under vacuum. The remainder was dissolved in H$_2$O (300 mL) and extracted with CH$_2$Cl$_2$. The product was purified by column chromatography on silica gel with mixtures of CH$_2$Cl$_2$/hexane: 300 mL 30:70, 450 mL 40:60, 150 mL 50:50, 150 mL 60:40, 150 mL 70:30, 150 mL 80:20.

**18**: Yield: 13.1 g (82 %); b.p.: 133 °C/0.09 mbar; EI-MS: [160, $M^+$] (C$_4$H$_4$N$_2$Se); $^{77}$Se NMR (CDCl$_3$): $\delta = 244.2$ ppm; $^{13}$C NMR (CDCl$_3$): $\delta =$ 117.97 (CN), 101.46 ($^1J_{Se,C} = 237.5$ Hz, SeCN), 23.24 ($^1J_{Se,C} = 59.4$ Hz, CH$_2$Se), 20.21 (<u>C</u>H$_2$CN) ppm.

**15**: Yield: 5.2 g (49 %); EI-MS: [268, $M^+$] (C$_6$H$_8$N$_2$Se$_2$); $^{77}$Se NMR (CDCl$_3$): $\delta = 326.5$ ppm; $^{13}$C NMR (CDCl$_3$): $\delta =$ 119.14 (CN), 23.00 ($^1J_{Se,C} = 81.0$ Hz, CH$_2$Se), 19.79 (<u>C</u>H$_2$CN) ppm.

### Syntheses of (tBuMe$_2$SiCH$_2$CH$_2$S)$_2$ (7) and (tBuMe$_2$SiCH$_2$CH$_2$Se)$_2$ (22)

Under argon, vinylsilane **19** (14.2 g, 0.1 mol) was added dropwise to a stirred solution of 9-BBN (230 mL, 0.114 mol, 0.5 M in THF), followed by heating at reflux for 2 h, see ref. [29]. After cooling to room temperature, H$_2$O (100 mL) was carefully added, then NaOH (14 g in 120 mL H$_2$O) and H$_2$O$_2$ (120 mL, 30 %) were added, followed by heating at reflux for 1.5 h. After extraction with Et$_2$O, very pure silylethanol **20** was obtained.

Into a stirred solution of **20** (12 g, 75 mmol) and CBr$_4$ (27.4 g, 82.5 mmol) in CH$_2$Cl$_2$ (80 mL), Ph$_3$P (21.6 g, 82.5 mmol) were added within 5 min at 0 °C, followed by 2 h stirring at 0 °C. After evaporation of the THF, the product was dissolved in pentane, filtered through silica gel, and the bromide **21** was vacuum distilled.

Compounds **7** and **22** were synthesized by producing Li$_2$S$_2$ or Li$_2$Se$_2$ from Li (208 mg, 30 mmol) and S (962 mg, 30 mmol) or Se (2.37 g, 30 mmol) in liq. NH$_3$ (150 mL). Li$_2$S$_2$ or Li$_2$Se$_2$ were reacted with **4** and **13** similar to the described method above with tBuMe$_2$SiCH$_2$CH$_2$Br **21** (6.7 g, 30 mmol). After aqueous workup and extraction with Et$_2$O, the disulfide **7** was purified by column chromatography on silica gel with hexane.

The raw product of the selenium compound was freed from triselenide by dissolving in liq. NH$_3$ (100 mL) and dry THF (50 mL). Na (1.4 g, 60 mmol) was added and the blue solution was stirred for 1 h. After evaporation of the NH$_3$ and addition of H$_2$O (100 mL), O$_2$ was bubbled through the solution for 1 h. Purification was done by extraction with Et$_2$O and column chromatography in hexane.

**20**: Yield: 16 g (100 %); $^{13}$C NMR (CDCl$_3$): $\delta = 59.42$ (CH$_2$OH), 26.35 (C<u>Me</u>$_3$), 17.80 ($^1J_{Si,C} = 46.0$ Hz, CH$_2$Si), 16.27 (<u>C</u>Me$_3$), $-6.09$ ($^1J_{Si,C} = 49.8$ Hz, CH$_3$Si) ppm; $^{29}$Si NMR (CDCl$_3$): $\delta = 6.31$ ppm.

**21**: Yield: 11.6 g (69 %); b.p.: 49–51 °C/0.2 mbar; $^{13}$C NMR (CDCl$_3$): $\delta = 32.33$ (CH$_2$Br), 26.42 (C<u>Me</u>$_3$), 20.41 ($^1J_{Si,C} = 43.0$ Hz, CH$_2$Si), 16.60 (<u>C</u>Me$_3$), $-6.26$ ($^1J_{Si,C} = 50.2$ Hz, CH$_3$Si) ppm; $^{29}$Si NMR (CDCl$_3$): $\delta = 8.34$ ppm.

**7**: Yield: 4.54 g (86 %); EI-MS: [350.1959, $M^+$] (C$_{16}$H$_{38}$S$_2$Si$_2$); $^{13}$C NMR (CDCl$_3$): $\delta = 35.28$ (CH$_2$S), 26.61 (C<u>Me</u>$_3$), 16.69 (<u>C</u>Me$_3$), 13.37 ($^1J_{Si,C} =$

46.4 Hz, CH$_2$Si), $-6.16$ ($^1J_{Si,C} = 50.0$ Hz, CH$_3$Si) ppm; $^{29}$Si NMR (CDCl$_3$): $\delta = 8.61$ ppm.

**22**: Yield: 4.2 g (63 %); EI-MS: [446, $M^+$] (C$_{16}$H$_{38}$Se$_2$Si$_2$); $^{77}$Se NMR (CDCl$_3$): $\delta = 361.5$ ppm; $^{13}$C NMR (CDCl$_3$): $\delta = 26.69$ (C<u>Me</u>$_3$), 25.37 ($^1J_{Se,C} = 69.9$ Hz, CH$_2$Se), 16.77 (<u>C</u>Me$_3$), 15.74 ($^1J_{Si,C} = 45.7$ Hz, CH$_2$Si), $-6.16$ ($^1J_{Si,C} = 49.9$ Hz, CH$_3$Si) ppm; $^{29}$Si NMR: (CDCl$_3$): $\delta = 8.70$ ppm.

### Syntheses of the thiiranium und seleniranium salts

#### Method A: 1/R$_2$S$_2$ or R$_2$Se$_2$/XeF$_2$/fluoride ion acceptor

Dry CH$_2$Cl$_2$ (15 mL) was condensed on Ad=Ad **1** (2 mmol, 537 mg) and the disulfide **4** (1 mmol, 267 mg), **7** (1 mmol, 351 mg), **10** (1 mmol, 172 mg), or diselenide **13** (1 mmol, 360 mg), **15** (1 mmol, 266 mg), **22** (1 mmol, 445 mg) at $-196\,°$C. XeF$_2$ (1 mmol, 169 mg), and Tf$_2$NSiMe$_3$ (2 mmol, 707 mg), BF$_3$·OEt$_2$ (2 mmol, 284 mg), or Me$_3$Si$^+$CHB$_{11}$Cl$_{11}$ (2 mmol, 1.34 g) were added at $-78\,°$C, followed by stirring for 30 min at this temperature and 2 h at $-40\,°$C. Half of the solvent was pumped off, and by slow addition of hexane (30 mL), the salt was crystallized. The product was filtered off, washed with hexane (3×20 mL), and dried in vacuum. Compound **14** was measured by NMR spectroscopy after addition of a little CD$_2$Cl$_2$.

#### Method B: R$_2$S$_2$ or R$_2$Se$_2$/SO$_2$Cl$_2$/SbCl$_5$/1

Dry CH$_2$Cl$_2$ (15 mL) was condensed on disulfide **7** (1 mmol, 351 mg), **10** (1 mmol, 172 mg), or diselenide **15** (1 mmol, 266 mg), **22** (1 mmol, 445 mg) at $-196\,°$C. SO$_2$Cl$_2$ (1.1 mmol, 135 mg) was added at $-20\,°$C, followed by stirring for 30 min at this temperature. SbCl$_5$ (2 mmol, 598 mg) was slowly added at $-78\,°$C, followed by stirring for 10 min at this temperature. Then, Ad=Ad **1** (2 mmol, 537 mg) was added and stirred for 2 h at $-40\,°$C. Half of the solvent was pumped off, and by slow addition of hexane (30 mL), crystallization initiated. The salt was filtrated off, washed with hexane (3×20 mL), and dried in vacuum.

#### Thiiranium salts 5, 9, 11, according to method A

[Ad$_2$SCH$_2$CH$_2$SiMe$_3$]$^+$Tf$_2$N$^-$ (**5**): Yield: 0.99 g (73 %); ESI-MS (CH$_3$CN/CH$_2$Cl$_2$): [401.2692]$^+$ (C$_{25}$H$_{41}$SSi$^+$), [279.9180]$^-$ (C$_2$F$_6$NO$_4$S$_2^-$); $^{13}$C NMR (CD$_2$Cl$_2$): $\delta = 119.88$ (q, $^1J_{F,C} = 321.9$ Hz, CF$_3$), 95.87 (ring C), 38.55 (2×CH$_2$), 38.19 (2×CH$_2$), 38.08 (2×CH$_2$), 37.02 (2×CH$_2$), 36.07 (2×CH$_2$), 33.57 (2×CH), 30.31 (2×CH), 27.53 (CH$_2$S), 26.50 (4×CH), 16.17 ($^1J_{Si,C} = 42.5$ Hz, CH$_2$Si), $-2.66$ ($^1J_{Si,C} = 52.0$ Hz, CH$_3$Si) ppm; $^{29}$Si NMR (CD$_2$Cl$_2$): $\delta = 3.52$ ppm.

[Ad$_2$SCH$_2$CH$_2$SiMe$_2$tBu]$^+$Tf$_2$N$^-$ (**9**): Yield: 1.16 g (80 %); ESI-MS (CH$_3$CN): [443.3198]$^+$ (C$_{28}$H$_{47}$SSi$^+$), [279.9248]$^-$ (C$_2$F$_6$NO$_4$S$_2^-$); $^{13}$C NMR (CD$_2$Cl$_2$): $\delta = 119.83$ (q, $^1J_{F,C} = 321.6$ Hz, CF$_3$), 96.15 (ring C), 38.57 (2×CH$_2$), 38.21 (2×CH$_2$), 38.09 (2×CH$_2$), 37.03 (2×CH$_2$), 36.05 (2×CH$_2$), 33.56 (2×CH), 30.31 (2×CH), 27.91 (CH$_2$S), 26.50 (2×CH), 26.48 (C<u>Me</u>$_3$), 25.91 (2×CH), 16.43 (<u>C</u>Me$_3$), 12.37 (CH$_2$Si), $-7.15$ (MeSi); $^{29}$Si NMR (CD$_2$Cl$_2$): $\delta = 10.05$ ppm.

[Ad$_2$SCH$_2$CH$_2$CN]$^+$Tf$_2$N$^-$ (**11**): Yield: 580 mg (46 %); ESI-MS (CH$_3$CN): [354.2268]$^+$ (C$_{23}$H$_{32}$NS$^+$), [279.9181]$^-$ (C$_2$F$_6$NO$_4$S$_2^-$); $^{13}$C NMR (CD$_2$Cl$_2$): $\delta = 119.71$ (q, $^1J_{F,C} = 321.3$ Hz, CF$_3$), 115.99 (CN), 99.00 (ring C), 38.94 (2×CH$_2$), 38.54 (2×CH$_2$), 37.85 (2×CH$_2$), 36.49 (2×CH$_2$), 35.95 (2×CH$_2$), 33.93 (2×CH), 30.19 (2×CH), 26.40 (2×CH), 26.30 (2×CH), 25.18 (CH$_2$S), 16.23 (<u>C</u>H$_2$CN) ppm.

#### Thiiranium salts 8, 12, according to method B

[Ad$_2$SCH$_2$CH$_2$SiMe$_2$tBu]$^+$SbCl$_6^-$ (**8**): Yield: 1.46 g (94 %); ESI-MS (CH$_3$OH): [443.3177]$^+$ (C$_{28}$H$_{47}$SSi$^+$), [334.7208]$^-$ (SbCl$_6^-$); $^{13}$C NMR

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($CD_2Cl_2$): $\delta = 96.75$ (ring C), 38.91 ($2\times CH_2$), 38.42 ($2\times CH_2$), 38.38 ($2\times CH_2$), 37.27 ($2\times CH_2$), 36.15 ($2\times CH_2$), 33.78 ($2\times CH$), 30.63 ($2\times CH$), 28.12 ($CH_2S$), 26.62 ($2\times CH$), 26.59 ($2\times CH$), 26.15 ($CMe_3$), 16.62 ($CMe_3$), 12.70 ($CH_2Si$), $-6.63$ ($MeSi$) ppm.

Single crystals of **8** are prepared by slow cooling of a solution in EtCN from room temperature to $-80\,°C$.

$[Ad_2SCH_2CH_2CN]^+SbCl_6^-$ (**12**): Yield: 1.13 g (82%); ESI-MS ($CH_3CN$): $[354.2286]^+$ ($C_{23}H_{32}NS^+$), $[334.7125]^-$ ($SbCl_6^-$).

Single crystals of **12** were obtained by slow addition of pentane into a solution $CH_2Cl_2$ at $-20\,°C$ until cloudiness begins to set in, and slow cooling from room temperature to $-80\,°C$.

### Seleniranium salts 14, 16, 23, 24 according to method A

$[Ad_2SeCH_2CH_2SiMe_3]^+Tf_2N^-$ (**14**): Low-temperature NMR measurement at $-40\,°C$: $^{77}Se$ NMR ($CD_2Cl_2$): $\delta = 35.3$ ppm; $^{13}C$ NMR ($CD_2Cl_2$): $\delta = 119.08$ (q, $^1J_{F,C} = 321.0$ Hz, $CF_3$), 109.66 (ring C), 39.38 ($2\times CH_2$), 39.33 ($2\times CH_2$), 39.20 ($2\times CH_2$), 38.19 ($2\times CH_2$), 37.05 ($2\times CH_2$), 33.56 ($2\times CH$), 31.14 ($2\times CH$), 27.55 ($CH_2Se$), 26.63 ($4\times CH$), 15.47 ($CH_2Si$), $-2.72$ ($MeSi$) ppm.

$[Ad_2SeCH_2CH_2CN]^+BF_4^-$ (**16**): Yield: 0.8 g (82%); ESI-MS ($CH_3CN/CH_2Cl_2$): $[402.1845]^+$ ($C_{23}H_{32}NSe^+$), $[87.0002]^-$ ($BF_4^-$); $^{77}Se$ NMR ($CD_2Cl_2$): $\delta = 24.1$ ppm; $^{13}C$ NMR ($CD_2Cl_2$): $\delta = 117.22$ (CN), 111.87 (ring C), 39.97 ($2\times CH_2$), 39.71 ($2\times CH_2$), 39.48 ($2\times CH_2$), 38.09 ($2\times CH_2$), 36.66 ($2\times CH_2$), 34.28 ($2\times CH$), 31.29 ($2\times CH$), 26.96 ($2\times CH$), 26.87 ($2\times CH$), 24.15 ($CH_2Se$), 15.78 ($CH_2CN$) ppm; $^{19}F$ NMR ($CD_2Cl_2$): $\delta = -151.04$ ppm.

$[Ad_2SeCH_2CH_2SiMe_2tBu]^+Tf_2N^-$ (**23**): Yield: 0.78 g (51%); ESI-MS ($CH_3CN$): $[491.2611]^+$ ($C_{28}H_{47}SeSi^+$), $[279.9217]^-$ ($C_2F_6NO_4S_2^-$); $^{77}Se$ NMR ($CD_2Cl_2$): $\delta = 44.8$ ppm.

$[Ad_2SeCH_2CH_2SiMe_2tBu]^+CHB_{11}Cl_{11}^-$ (**24**): Yield: 1.32 g (65%); ESI-MS ($CH_3CN$): $[491.2597]^+$ ($C_{28}H_{47}SeSi^+$), $[521.7698]^-$ ($CHB_{11}Cl_{11}^-$); $^{77}Se$ NMR ($CD_2Cl_2$): $\delta = 39.1$ ppm; $^{13}C$ NMR ($CD_2Cl_2$): $\delta = 111.12$ (ring C), 46.73 ($CHB_{11}Cl_{11}^-$), 39.81 ($2\times CH_2$), 39.73 ($2\times CH_2$), 39.52 ($2\times CH_2$), 38.51 ($2\times CH_2$), 36.52 ($2\times CH_2$), 33.96 ($2\times CH$), 31.55 ($2\times CH$), 28.22 ($CH_2Se$), 26.79 ($4\times CH$), 26.11 ($CMe_3$), 16.64 ($CMe_3$), 12.03 ($CH_2Si$), $-6.78$ ($MeSi$) ppm; $^{11}B$ NMR ($CD_2Cl_2$): $\delta = -2.52$, $-10.14$, $-13.18$ ppm.

### Seleniranium salts 17, 25, according to method B

$[Ad_2SeCH_2CH_2CN]^+SbCl_6^-$ (**17**): Yield: 0.67 g (66%); ESI-MS ($CH_3CN$): $[402.1730]^+$ ($C_{23}H_{32}NSe^+$), $[334.7094]^-$ ($SbCl_6^-$); $^{77}Se$ NMR ($CD_2Cl_2$): $\delta = 27.4$ ppm; $^{13}C$ NMR ($CD_2Cl_2$): $\delta = 115.01$ (CN), 100.00 (ring C), 40.28 ($CH_2$), 39.99 ($CH_2$), 39.87 ($CH_2$), 38.58 ($CH_2$), 36.53 ($CH_2$), 34.58 (CH), 31.82 (CH), 26.90 (CH), 26.81 (CH), 23.82 ($CH_2Se$), 16.86 ($CH_2CN$) ppm.

Single crystals were obtained by slow addition of $Et_2O$ into a solution $CH_2Cl_2$ at $-20\,°C$ until cloudiness begins to set in, and slow cooling from $-20\,°C$ to $-80\,°C$.

$[Ad_2SeCH_2CH_2SiMe_2tBu]^+SbCl_6^-$ (**25**): Yield: 1.37 g (93%); ESI-MS ($CH_3CN$): $[491.2635]^+$ ($C_{28}H_{47}SeSi^+$), $[334.7133]^-$ ($SbCl_6^-$).

Single crystals were obtained by slow addition of $Et_2O$ into a solution $CH_2Cl_2$ at $-20\,°C$ until cloudiness begins to set in, and slow cooling from $-20\,°C$ to $-80\,°C$.

Single crystals of the chloroethyl compound **26** were obtained in the same manner.

## Attempts to dealkylate the thiiranium salts, the thiiranes 27 and 30

### Cleavage of the Me₃SiCH₂CH₂ group?

A solution of $Bu_4NF$ in THF (2 mL, 1 M, 2 mmol) was added to the thiiranium salt **5** (1 mmol, 682 mg), dissolved in dry THF (5 mL) at $-196\,°C$, followed by 2 h of stirring at $-78\,°C$. The solvent was removed completely and the remainder was purified by chromatography in a mixture of $CH_2Cl_2$ (10 mL) and hexane (20 mL) with silica gel.

**27**: Yield: 210 mg (70%).

### One-pot method

The thiiranium salt $[Ad_2SCH_2CH_2SiMe_3]^+BF_4^-$ was made by reacting **1** (2 mmol, 537 mg), $(Me_3SiCH_2CH_2S)_2$ (**4**) (1 mmol, 267 mg), $XeF_2$ (1 mmol, 169 mg), and $BF_3\cdot OEt_2$ (2 mmol, 284 mg) in $CH_2Cl_2$ (15 mL) according to method A. Into the solution, $Bu_4NF$ in THF (4 mL, 1 M, 4 mmol) was added dropwise at $-78\,°C$, followed by stirring for 2 h at $-40\,°C$. The solvents were pumped off and the remainder was purified by chromatography in a mixture of $CH_2Cl_2$ (10 mL) and hexane (20 mL) with silica gel.

**27**: Yield: 600 mg (100%); EI-MS: 300 (33, $M^+$, $C_{20}H_{28}S$), 268 (100, $M^+-S$); $^{13}C$ NMR ($CDCl_3$): $\delta = 71.61$ (ring C), 38.72 ($4\times CH_2$), 38.53 ($4\times CH_2$), 37.91 ($4\times CH_2$), 35.06 ($4\times CH$), 27.87 ($2\times CH$), 27.27 ($2\times CH$) ppm.

The thiiranium salt $[C_8H_{14}SCH_2CH_2SiMe_3]^+BF_4^-$ was prepared from *cis*-cyclooctene (**28**; 2 mmol, 220 mg), $(Me_3SiCH_2CH_2S)_2$ (**4**) (1 mmol, 267 mg), $XeF_2$ (1 mmol, 169 mg), and $BF_3\cdot OEt_2$ (2 mmol, 284 mg) in $CH_2Cl_2$ (15 mL) according to method A, and reacted and worked up in the same manner as described for **27** with $Bu_4NF$ (2 mmol, 2 mL, 1 M in THF).

Thiirane **30**: Yield: 190 mg (67%); EI-MS: 142 (74, $M^+$, $C_8H_{14}S$), 109 (64, $M^+-SH$), 67 (100); $^{13}C$ NMR ($CD_2Cl_2$): $\delta = 41.09$ (ring C), 29.67 ($CH_2$), 29.45 ($CH_2$), 26.43 ($CH_2$) ppm.

Thiirane **30** was also obtained from *trans*-cyclooctene (**29**) in the same manner. Yield: **30** 250 mg (44%); $^{13}C$ NMR ($CD_2Cl_2$): $\delta = 41.11$ (ring C), 29.66 ($CH_2$), 29.45 ($CH_2$), 26.42 ($CH_2$) ppm.

### Cleavage of the tBuMe₂SiCH₂CH₂ group?

Thiiranium salt **9** (1 mmol, 724 mg) was reacted in dry THF (5 mL) at $-78\,°C$ with a solution of $Bu_4NF$ in THF (2 mL, 1 M, 2 mmol), followed by stirring for 2 h at this temperature. The solvent was pumped off completely in vacuum. The remainder is dissolved in $CH_2Cl_2$ (10 mL) and hexane (20 mL) and purified by chromatography over silica gel.

The $^{13}C$ NMR spectrum shows the presence of alkene **1** and disulfide **4** as the main products, and thiirane **27** in less than 10% in the product mixture.

### Cleavage of the NCCH₂CH₂ group?

Thiiranium salt **11** (1 mmol, 635 mg), dissolved in THF (5 mL), was reacted with CsOH (2.5 mmol, 375 mg) in $H_2O$ or MeOH (3 mL) for 30 min at $-40\,°C$, and stirred for 30 min at this temperature and 3 h at $0\,°C$. After removal of the solvent, the mixture was purified by chromatography.

$^{13}C$ NMR spectra indicate a mixture of thiirane **27** and alkene **1** in the ratio 1:1 (reaction in MeOH) and 3:1 (reaction in $H_2O$).

Single crystals of the thiiranes **27** and **30** were obtained by slow cooling of solutions in pentane from room temperature to $-80\,°C$.

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doi.org/10.1002/chem.202003461

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## Attempts to dealkylate seleniranium salts

The seleniranium salt [Ad$_2$SeCH$_2$CH$_2$SiMe$_3$]$^+$Tf$_2$N$^-$ (**14**) was prepared by reacting (Me$_3$SiCH$_2$CH$_2$Se)$_2$ (**13**; 2 mmol, 537 mg), XeF$_2$ (1 mmol, 169 mg), and Tf$_2$NSiMe$_3$ (2 mmol, 707 mg) in CH$_2$Cl$_2$ (15 mL) according to method A. A solution of Bu$_4$NF in THF (4 mL, 1 M, 4 mmol) was added dropwise to the reaction mixture at −78 °C, followed by stirring for 30 min at −78 °C and 2 h at −40 °C. Half of the solvent was pumped off under vacuum, some CD$_2$Cl$_2$ was added, and the NMR spectrum of this solution was measured at −40 °C. [Ad$_2$SeCH$_2$CH$_2$SiMe$_3$]$^+$BF$_4$$^-$, made from **1**, **13**, XeF$_2$, and BF$_3$·OEt$_2$, were reacted with Bu$_4$NF in the same manner.

$^{13}$C NMR (CD$_2$Cl$_2$, at −40 °C): $\delta = 132.86$, 39.26, 36.99, 31.59, 28.36 (Ad = Ad **1**); 24.64, 18.95, −2.40 (diselenide **13**); 119.59 (q, $^1J_{F,C} = 321.1$ Hz, Tf$_2$N$^-$); 57.86, 23.40, 19.46, 13.40 (Bu$_4$N$^+$); 67.59, 25.44 (THF); 54.16 (CH$_2$Cl$_2$) ppm; $^{77}$Se NMR (CD$_2$Cl$_2$, at −40 °C): $\delta = 339.9$ (diselenide **13**) and 1187.5 (Me$_3$SiCH$_2$CH$_2$SeF$_3$ **32**) ppm, signal intensity **13**/**32** 2:1.

## Syntheses of the thiirenium salts 34–36

To disulfide **7** (1 mmol, 351 mg) or **4** (1 mmol, 267 mg) and alkyne **2** (2 mmol, 277 mg) or **3** (2 mmol, 589 mg) dry CH$_2$Cl$_2$ (15 mL) were condensed at −196 °C. At −78 °C, XeF$_2$ (1 mmol, 169 mg) and BF$_3$·OEt$_2$ (2 mmol, 284 mg) or Tf$_2$NSiMe$_3$ (2 mmol, 707 mg) were added, and stirred at this temperature for 30 min and for 2 h at −40 °C. Half of the solvent was pumped off and after slow addition of hexane (30 mL), the salt was crystallized. The product was filtered off, washed with hexane (3 × 20 mL), and dried in vacuum.

[$t$Bu$_2$C$_2$SCH$_2$CH$_2$SiMe$_3$]$^+$BF$_4$$^-$ (**34**): Yield: 545 mg (76 %); ESI-MS (CH$_3$CN/CH$_3$OH): [271.1930]$^+$ (C$_{15}$H$_{31}$SSi$^+$), [87.0097]$^-$ (BF$_4$$^-$); $^{13}$C NMR (CD$_2$Cl$_2$): $\delta = 114.84$ (ring C), 42.20 (CH$_2$S), 32.96 (CMe$_3$), 27.69 (CMe$_3$), 13.79 (CH$_2$Si), −2.48 (MeSi) ppm.

[Ad$_2$C$_2$SCH$_2$CH$_2$SiMe$_3$]$^+$Tf$_2$N$^-$ (**35**): Yield **35**: 934 mg (66 %); ESI-MS (CH$_3$CN): [427.2832]$^+$ (C$_{27}$H$_{43}$SSi$^+$), [279.9196]$^-$ (C$_2$F$_6$NO$_4$S$_2$$^-$).

[Ad$_2$C$_2$SCH$_2$CH$_2$SiMe$_2$$t$Bu]$^+$Tf$_2$N$^-$ (**36**): Yield **36**: 1.94 g (65 %); ESI-MS (CH$_3$CN): [469.3356]$^+$ (C$_{30}$H$_{49}$SSi$^+$), [279.9232]$^-$ (C$_2$F$_6$NO$_4$S$_2$$^-$); $^{13}$C NMR (CD$_2$Cl$_2$): $\delta = 119.84$ (q, $^1J_{F,C} = 321.5$ Hz, CF$_3$), 113.28 (ring C), 43,47 (SCH$_2$), 40,04 (Ad, CH$_2$), 35.42 (Ad, CH$_2$), 34.56 (CMe$_3$), 27.59 (CMe$_3$), 26.00 (Ad, CH), 16.48 (Ad, C$_q$), 10.43 (CH$_2$Si), −6.96 (MeSi) ppm; $^{29}$Si NMR (CD$_2$Cl$_2$): $\delta = 10.27$ ppm.

Single crystals of **36** were obtained by careful addition of Et$_2$O and pentane to a solution in CH$_2$Cl$_2$ until clouding, filtration, and slow cooling from room temperature to −80 °C (CH$_2$Cl$_2$/Et$_2$O/pentane 1:1:1).

## Attempts to dealkylate thiirenium salts

Thiirenium salt **35** (1 mmol, 708 mg) was dissolved in dry CH$_2$Cl$_2$ (5 mL) and at −78 °C a solution of Bu$_4$NF in THF (2 mL, 1 M, 2 mmol) was added dropwise. After stirring for 2 h at this temperature and 3 h at −60 °C, half of the solvent was pumped off, and some CD$_2$Cl$_2$ was added.

$^{13}$C NMR (CD$_2$Cl$_2$, at −60 °C): $\delta = 86.66$, 42.76, 35.78, 28.56, 27.64 (AdC≡CAd **3**); 119.38 (q, $^1J_{F,C} = 321.1$ Hz, Tf$_2$N$^-$); 57.20, 23.12, 19.19, 13.28 (Bu$_4$N$^+$); 67.28, 25.23 (THF); 54.17 (CH$_2$Cl$_2$); −2.67 (**4**) ppm.

## Crystal structure determinations

Single crystals were grown by slow cooling to −80 °C in appropriate solvents and transferred onto the diffractometer under cooling and exclusion of moisture: Bruker Smart CCD 1000 TU diffractometer, Mo$_{K\alpha}$ irradiation, scan width 0.3 deg in ω, full sphere by 2400 frames, usually 20 s per frame. After multi-scan absorption corrections (SADABS) by equalizing symmetry-equivalent reflections. The structures were solved and refined with the SHELX programs.[46] All atoms except hydrogen were refined anisotropically. Hydrogen atoms were refined isotropically in positions located by difference Fourier maps or placed in pre-calculated positions, depending on the quality of the data contain the supplementary crystallographic data for these compounds. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif. The experimental details of all determined structures of this paper are collected in Table S2 in the Supporting Information. The structure figures have been generated with the program DIAMOND.[47]

## Conflict of interest

The authors declare no conflict of interest.

**Keywords:** ab-initio calculations · NMR spectroscopy · selenium · sulfur · X-ray diffraction

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