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FULL PAPER

Attempts to synthesize a Thiirane, Selenirane, and Thiirene by Dealkylation of Chalcogeniranium and Thiirenium Salts.

Helmut Poleschner*, Konrad Seppelt[a]

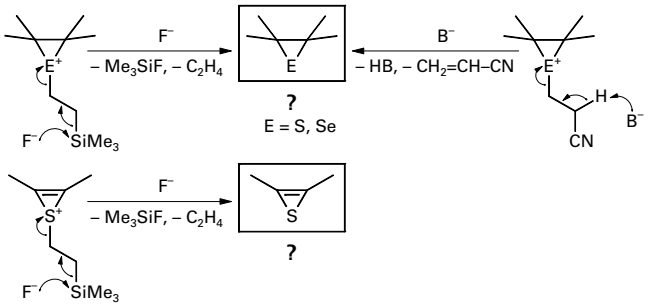
Abstract: Thiiranium salts $[Ad_2SR]^+ X^-$ (**5**, **8**, **9**, **11**, **12**) ($X^- = Tf_2N^-$ ($Tf=CF_3SO_2$), $SbCl_6^-$) and seleniranium salts $[Ad_2SeR]^+ X^-$ (**14**, **16**, **17**, **23**–**25**) ($X^- = Tf_2N^-$, BF_4^-, $CHB_{11}Cl_{11}^-$, $SbCl_6^-$) are synthesized from strained alkene 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-adamantylacetylene (**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 thiiren 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, however. 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 lasts already long. These would be of great theoretical interest as antiaromatic cyclic 4π-electron compounds.[20,15b] This would explain their extreme instability. The calculated NICS (1) value of –2.2 ppm does not allow a clear statement on the question of antiaromaticity. With 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 used 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 a structural proof is lacking.[21] Thiirensulfoxides and Thiirensulfones are known, however,[20] but attempts of deoxygenation to thiirenes failed.[22] Our long lasting work with such unstable three-membered ring chalcogen compounds have motivated us to erase this white spot by new attempts. Our plan for generating thiiranes, seleniranes, and thiirenes has been such, at 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^-, while 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 sterical demanding alkene bis(adamantylidene) Ad=Ad (**1**). The latter has enabled us already in the isolation of the extreme 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 has been whether F^- or OH^- would indeed attack at the protecting group, or if the reaction would occur at the C or chalcogen ring atoms.



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

Results and Discussion

We used RE^+ electrophiles for the preparation of the three-membered ring salts that we have developed earlier: 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 $[RE^+ SbCl_6^-]$ is generated subsequently by reaction with $SbCl_5$.[3,5]

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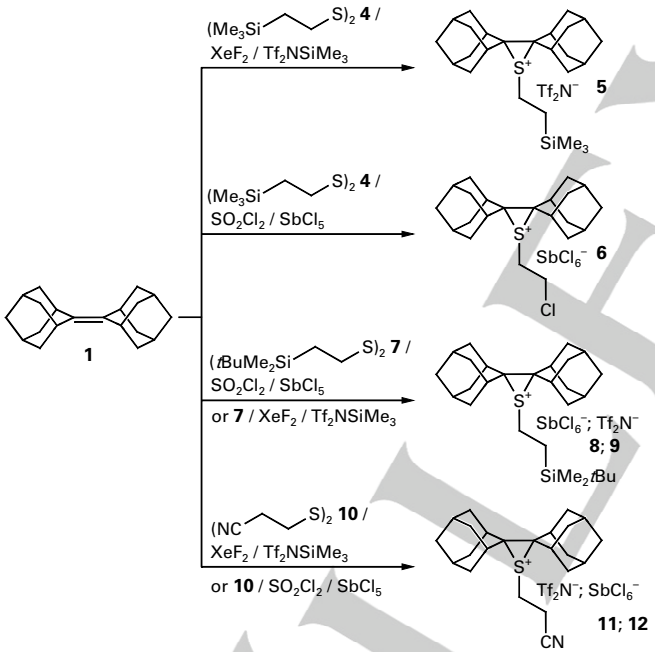
FULL PAPER

Thiiranium Salts

The disulfide $(Me_3SiCH_2CH_2S)_2$ (**4**) is oxidized with XeF_2/Tf_2NSiMe_3 and reacted in presence of the alkene **1,** yielding the thiiranium salt $[Ad_2SCH_2CH_2SiMe_3]^+ Tf_2N^-$ (**5**). The Me_3Si 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 $[Ad_2SCH_2CH_2Cl]^+ SbCl_6^-$ (**6**) is formed, which is identified by ESI-MS. Here the Me_3Si group is cleaved off and substituted by Cl. Use of the more stable *t*$BuMe_2Si$ group in the disulfide $(tBuMe_2SiCH_2CH_2S)_2$ (**7**) the method with $SO_2Cl_2/SbCl_5$ and **1** produces the salt $[Ad_2SCH_2CH_2SiMe_2tBu]^+ SbCl_6^-$ (**8**). With **7**, XeF_2/Tf_2NSiMe_3, and **1** the salt **9** is formed.
The cyanoethyl thiiranium salts **11**, **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).
The new thiiranium salts show in the ESI mass spectra the expected mol peaks for the cations and anions. The ^{13}C NMR spectra show the characteristic signal of the three-membered ring C-atoms at 96-99 ppm, as compared to 67 – 105 ppm in ref. [25]. The less soluble $SbCl_6^-$ salts crystallize well, and crystal structures of $[Ad_2SCH_2CH_2SiMe_2tBu]^+ SbCl_6^-$ (**8**) and $[Ad_2SCH_2CH_2CN]^+ SbCl_6^-$ (**12**) had been obtained (see Figures 1 and 2). These new thiiranium ions have C–C bond lengths of 150.0 – 150.6 pm 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.[25,26]



Scheme 2. Synthesis of the thiiranium salts with the $Me_3SiCH_2CH_2$, *t*$BuMe_2SiCH_2CH_2$, and $NCCH_2CH_2$ groups.

Seleniranium Salts

These methods of synthesis can only applied in part to the Se compounds. The diselenide $(Me_3SiCH_2CH_2Se)_2$ (**13**) reacts with XeF_2/Tf_2NSiMe_3 and **1** forming the seleniranium salt **14**, which decomposes already at room temperature under 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**. Specially 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 $(NCCH_2CH_2Se)_2$ (**15**) both synthetic routes are successful, namely with the oxidation by $XeF_2/BF_3{\cdot}OEt_2$, and the chlorination with SO_2Cl_2, reaction with $SbCl_5$ and addition of **1**. For this sake the synthesis of the cyanoethyldiselenide (**15**) had to be improved, since according to ref. [24a] only mixtures of di and triselenide are obtained. The at first prepared cyanoethyl selenocyanate[27] (**18**) reacts with $LiEt_3BH$, and oxidation with O_2 selectively gives the diselenide **15** (see Scheme 4).[28] The instability of the seleniranium salts with the $Me_3SiCH_2CH_2$ group contrasts with the much higher stability of the non-functionalized seleniranium salts.[5] Therefore we tried to prepare the salts carrying the *t*$BuMe_2SiCH_2CH_2$ group, since we assumed that

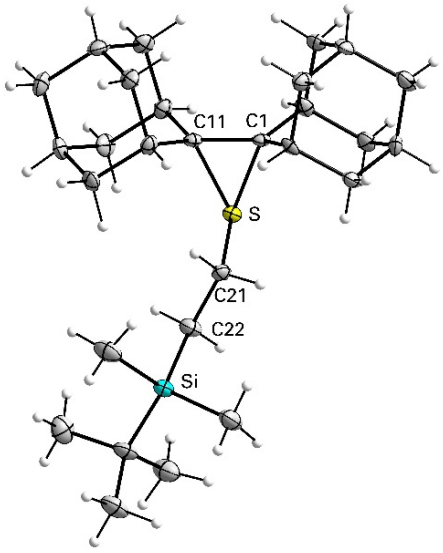


Figure 1. Molecular structure of $[Ad_2SCH_2CH_2SiMe_2tBu]^+ SbCl_6^-{\cdot}EtCN$ (**8**),[41] 50 % probability ellipsoids. The anion and solvent have been omitted for clarity. Selected bond parameters [pm,°]: C1–C11 150.6(6), S–C1 190.1(5), S–C11 191.6(5), S–C21 183.8(5), C21–C22 153.2(7), Si–C22 189.8(5), C1-S-C11 46.47(19).

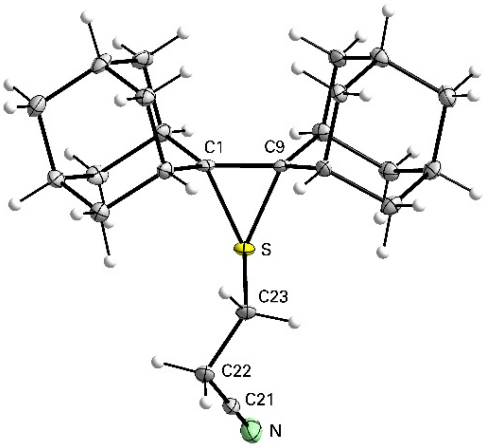


Figure 2. Molecular structure of $[Ad_2SCH_2CH_2CN]^+ SbCl_6^-{\cdot}CH_2Cl_2$ (**12**),[41] 50 % probability ellipsoids. The anion and solvent have been omitted for clarity. Selected bond parameters [pm,°]: C1–C9 150.0(4), S–C1 191.8(3), S–C9 189.4(3), S–C23 182.3(3), C22–C23 153.1(5), C21–C22 146.5(1), N–C21 113.9(5), C1-S-C9 46.35(12).

these would be more stable. The corresponding diselenide $(tBuMe_2SiCH_2CH_2Se)_2$ (**22**) is synthesized from the vinylsilane (**19**). Hydroboration with 9-borabicyclononane (9-BBN) and oxidation of the borane with H_2O_2 gives the silylethanol (**20**), see also ref. [29], followed by bromination with PPh_3/CBr_4 affording *t*$BuMe_2SiCH_2CH_2Br$ (**21**).[23c] This, however, reacts with Li_2Se_2 to diselenide that 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 $(tBuMe_2SiCH_2CH_2S)_2$ (**7**) is prepared similarly with Li_2S_2.

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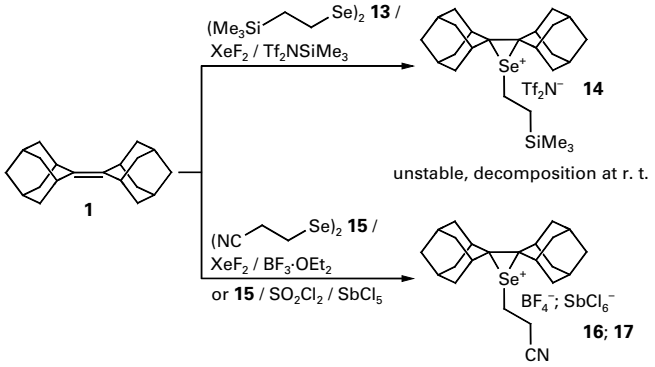
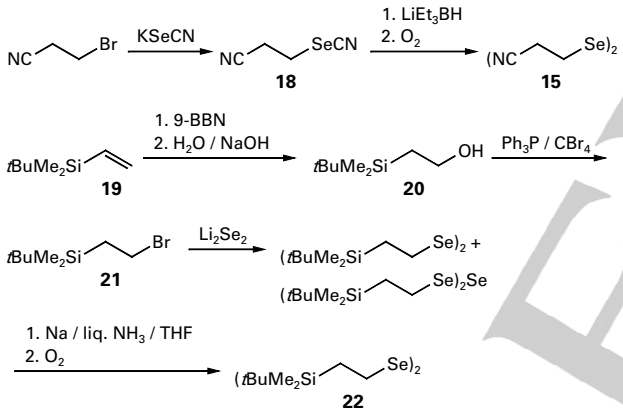
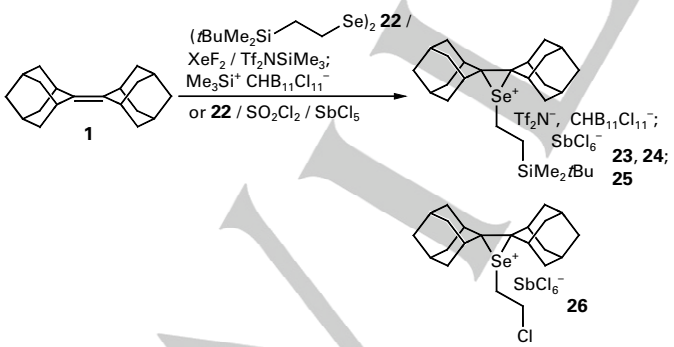
(*t*BuMe$_2$SiCH$_2$CH$_2$Se)$_2$ (**22**) reacts with **1** and XeF$_2$/Tf$_2$NSiMe$_3$ or XeF$_2$/Me$_3$Si$^+$ CHB$_{11}$Cl$_{11}^-$, and here also with SO$_2$Cl$_2$/SbCl$_5$ to the seleniranium salts **23**–**25** (see Schema 5). The salts carrying the *t*BuMe$_2$SiCH$_2$CH$_2$ group decompose slowly in solution at room temperature, e.g. during NMR measurements. They can be isolated as solid compounds and are stable for prolonged time at –20°C. The ^{13}C NMR 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 correct molecular peaks for cations and anions.



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



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



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

Crystal structure determinations of the new seleniranium salts [Ad$_2$SeCH$_2$CH$_2$SiMe$_2$*t*Bu]$^+$ SbCl$_6^-$ (**25**) and [Ad$_2$SeCH$_2$CH$_2$CN]$^+$ SbCl$_6^-$ (**17**) prove the structures (see Figures 3 und 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 und a crystal structure determination (see Figure S1 in the supporting information). Here also a partial cleavage takes place even of the *t*BuMe$_2$Si group. The structurale 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 the 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].

Dealkylation of the Thiiranium Salts – Thiiranes.

We began the attempts to cleave off the protecting groups with the thiiranium salts. Salt **5** reacts surprisingly selective 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 its crystal structure determination (see Figure 5).

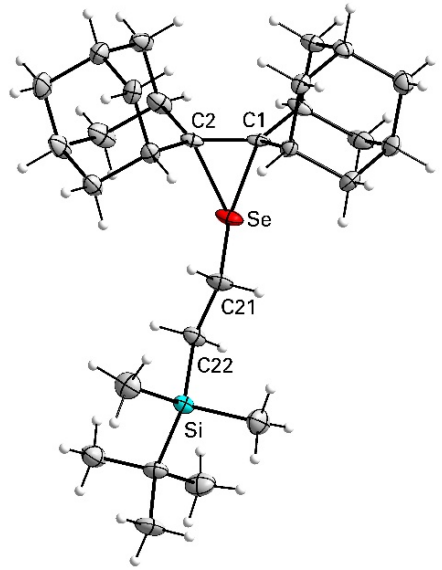


Figure 3. Molecular structure of [Ad$_2$SeCH$_2$CH$_2$SiMe$_2$*t*Bu]$^+$ SbCl$_6^-$·CH$_2$Cl$_2$ (**25**),[41] 50 % probability ellipsoids. The anion and solvent have been omitted for clarity. Selected bond parameters [pm,°]: C1–C2 147.9(4), Se–C1 206.0(3), Se–C2 207.3(3), Se–C21 197.3(3), C21–C22 152.8(4), Si–C22 189.6(3), C1-Se-C2 41.94(11).

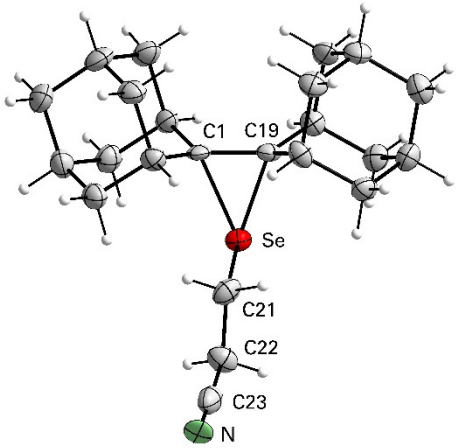


Figure 4. Molecular structure of [Ad$_2$SeCH$_2$CH$_2$CN]$^+$ SbCl$_6^-$·CH$_2$Cl$_2$ (**17**),[41] 50 % probability ellipsoids. The anion and solvent have been omitted for clarity. Selected bond parameters [pm,°]: C1–C19 148.9(9), Se–C1 209.7(5), Se–C19 207.7(5), Se–C21 200.2(6), C21–C22 149.1(9), C22–C23 146.7(10), N–C23 111.1(9), C1-Se-C19 41.8(2).

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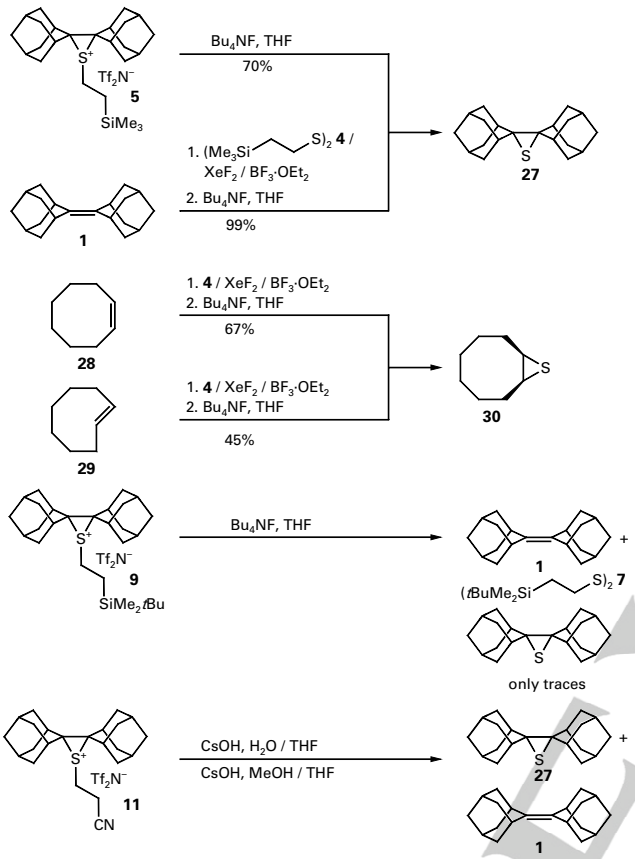
Cis-cyclooctene (**28**) as a simple sterically unstrained alkene is reacted in a one-pot procedure with **4** and $XeF_2/BF_3{\cdot}OEt_2$, and subsequently with Bu_4NF. The preparation of the thiirane **30** was also successful, as proven by the *cis*-structure in the crystal. **30** exists in the 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.



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

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 $Me_3SiCH_2CH_2S^+$-electrophile to the *trans*-alkene results in a configuration inversion of the strained 8-membered ring system. On *cis*-*trans* isomerizations of thiiranium ions via ring-opened carbocations see refs. [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_4NF with the thiiranium salt **9** carrying the tBuMe$_2$SiCH$_2$CH$_2$ group does not give the thiirane **27**, but the cleavage of the tBuMe$_2$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 (tBuMe$_2$SiCH$_2$CH$_2$S)$_2$ (**7**), and only traces of the thiirane **27**. The tBuMe$_2$SiCH$_2$CH$_2$ group is obviously too stable as protecting group for our purposes (see Scheme 6).

The NCCH$_2$CH$_2$ group in the thiiranium salts **11** and **12** is also no useful protecting group for the liberation of the thiirane **27**. **11** and **12** react after 3 h at 0°C with CsOH in H_2O/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 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°) as compared to **8** and **12** (46.4 – 46.5°).

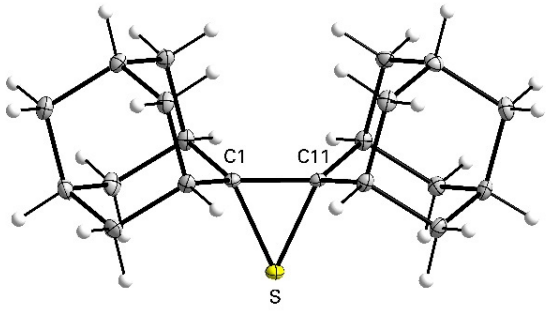


Figure 5. Molecular structure of Thiirane **27**,[41] 50 % probability ellipsoids. Selected bond parameters [pm,°]: C1–C11 150.73(16), S–C1 184.92(12), S–C11 185.11(12), C1-S-C11 48.08(5).

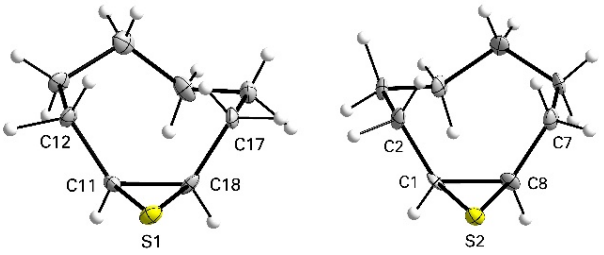
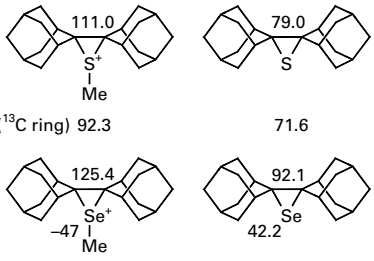


Figure 6. Molecular structure of Thiirane **30**,[41] 50 % probability ellipsoids. Selected bond parameters [pm,°]: C11–C18 147.2(6), S1–C11 183.4(5), S1–C18 183.1(5), C11-S1-C18 47.38(18), C12-C11-C18-C17 –1.902(720); C1–C8 148.9(6), S2–C1 184.0(5), S2–C8 184.2(5), C1-S2-C8 47.71(19), C2-C1-C8-C7 0.039(743).

Attepts to Dealkylation of Seleniranium Salts – Selenirane?

For the sake of detection and preparation of a selenirane reactions were undertaken to cleave off the $Me_3SiCH_2CH_2$ 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 $[Ad_2SeCH_2CH_2SiMe_3]^+$ 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_4NF. 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 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. By GIAO-B3PW91/cc-pVTZ//B3PW91/6-311+G(d,p) theory calculated ^{13}C and ^{77}Se NMR chemical shifts [ppm] ($\delta = \sigma_{ref} - \sigma_{comp}$), relative to TMS and Me_2Se, including experimental data.

At first we prepared the seleniranium salt **14** by reacting **1**, the diselenide **13**, and XeF_2/Tf_2NSiMe_3 at –40°C. A solution of Bu_4NF in THF is added at –78°C, followed by stirring at –40°. The ^{13}C

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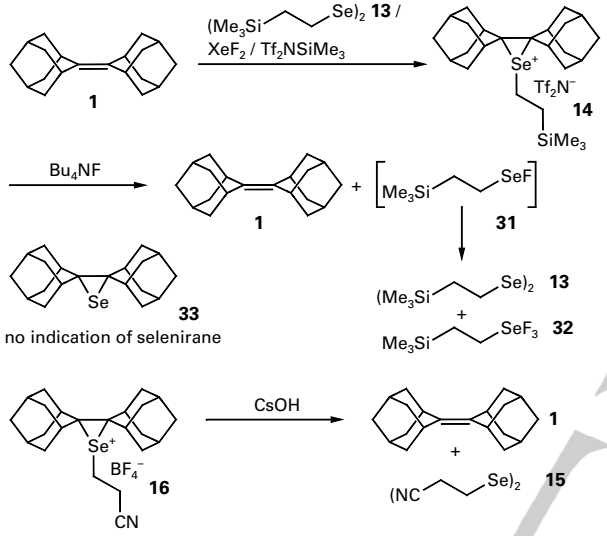
NMR measurement of the reaction solution at –78°C shows only the compounds **1** and **13**, while ^{77}Se spectra show the presence of **13** and an organoselenium trifluoride, most likely $Me_3SiCH_2CH_2SeF_3$ by a new signal at 1187 ppm (NMR spectra of $RSeF_3$ see refs. [32,33]). There is no indication for 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 $Me_3SiCH_2CH_2SeF$ (**31**). The latter is unstable and disproportionates according to $3RSeF \rightarrow R_2Se_2 + RSeF_3$ in a known manner[32-34] to the diselenide $(Me_3SiCH_2CH_2Se)_2$ (**13**) and the trifluoride $Me_3SiCH_2CH_2SeF_3$ (**32**) (see Scheme 8).
We also attempted a reaction of **1**, **13**, $XeF_2/BF_3{\cdot}OEt_2$ and Bu_4NF, with the same results.
The reaction of the seleniranium salt **16** with CsOH in THF/H_2O 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 prepration of a selenirane.

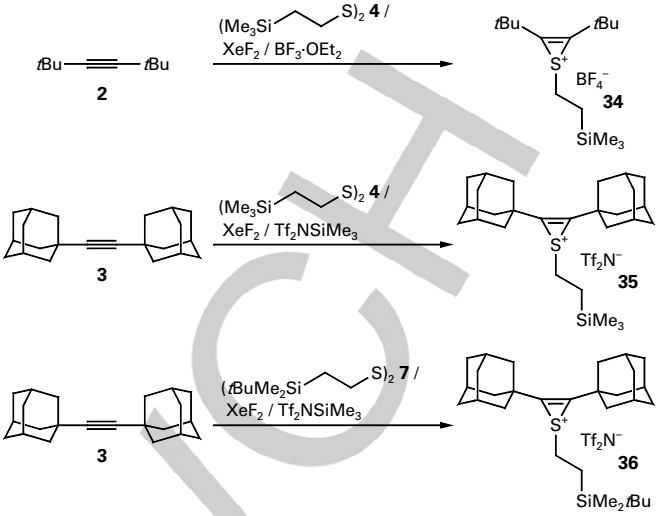
Thiirenium Salts

The thiirenium salt **34** is prepared by oxidation of the disulfide **4** with $XeF_2/BF_3{\cdot}OEt_2$ in 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_2NSiMe_3 or the disulfide **7** and XeF_2/Tf_2NSiMe_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,4,35]
The structure of **36** has a C=C bond length of 128.9 pm within the three-membered ring, die S–C bonds are 185.4 und 181.0 pm long, to the tBuMe$_2$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.[26,36,5]

Attempts towards Dealkylation of Thiirenium Salts – Thiirene?

We tried to cleave off the $Me_3SiCH_2CH_2$ group from the thiirenium salt **35** by reaction with Bu_4F 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 for the formation of a thiirene **37**. No cleavage of the $Me_3SiCH_2CH_2$ group is observed (see Scheme 10).

Summing up: The method of cleaving off the protecting groups works only with thiiranium salts, where the $Me_3SiCH_2CH_2$ group is



Scheme 9. Synthesis of thiirenium salts.

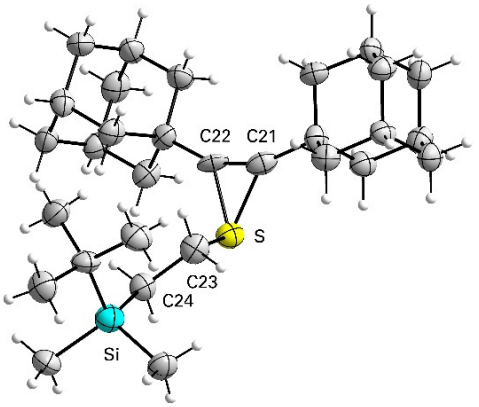
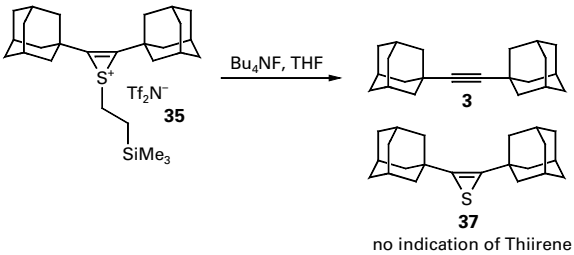


Figure 7. Molecular structure of $[Ad_2C_2SCH_2CH_2SiMe_2tBu]^+ Tf_2N^-$ (**36**),[41] 30 % probability ellipsoids. The anion has been omitted for clarity. Selected bond parameters [pm,°]: C21–C22 128.9(11), S–C21 185.4(11), S–C22 181.0(9), S–C23 182.6(6), C23–C24 152.6(7), Si–C24 188.7(6), C21-S-C22 41.2(3).



Schema 10. Attempts for syntheses a thiirene.

leaving and a thiirane is liberated. In thiiranium salts with the tBuMe$_2$SiCH$_2$CH$_2$ or NCCH$_2$CH$_2$ groups, in seleniranium salts with the $Me_3SiCH_2CH_2$ and $NCCH_2CH_2$ groups, and in thiirenium salts with the $Me_3SiCH_2CH_2$ 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 much alike to thiirenium ions.[2d] This is also the case during the fluorothiolation and fluoroselenation of alkenes and the fluoroselenation of alkynes.[37,38,7] But there are examples known where the RS^+ group is transferred from thiirenium ions to transition metal complexes or C nucleophiles.[39,2d] Finally we want to point to the

10.1002/chem.202003461

transition of RS^+ and 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,40]

We tried to understand the different reactivity of the compounds carrying the $Me_3SiCH_2CH_2$ groups by calculating HOMO and LUMO 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 $Me_3SiCH_2CH_2$ group. The LUMO, however, is localized at the three-membered ring, especially at the heteroatom. This is also the case in the unsubstituted ions $[Ad_2EEt]^+$ (**D**, **E**) and those with the cyanoethyl group $[Ad_2ECH_2CH_2CN]^+$ (**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 rings. Therefor 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 Me_3Si group. The lower lying LUMO energy in the ions **B** and **C** relative to **A** should favor the attack at the three-membered rings. Since 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.

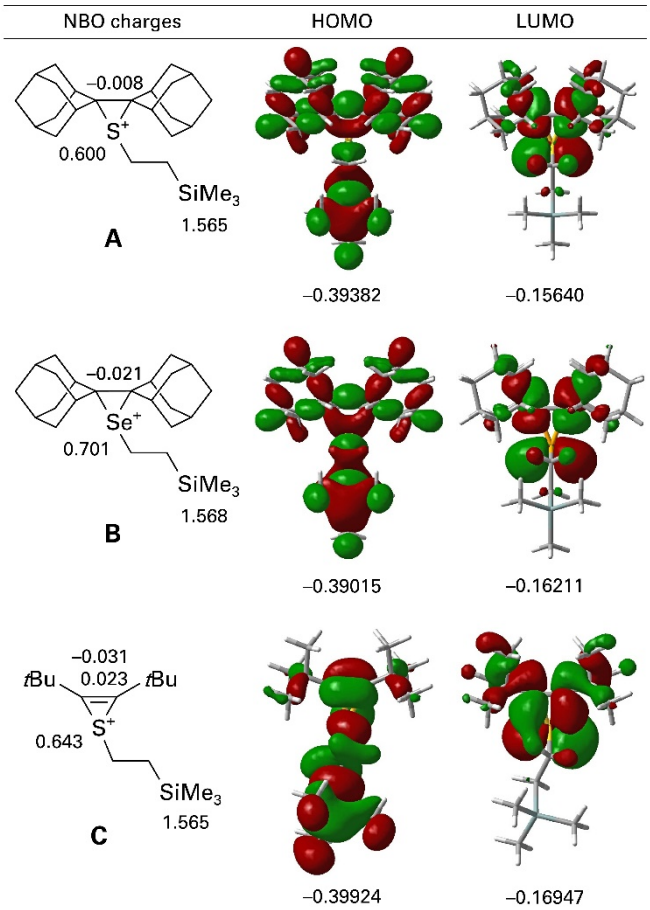


Figure 8. HOMO and LUMO of the ions **A** – **C**, orbital energies [Hartrees] and NBO charges, calculated on B3PW91/6-311+G(d,p) level of theory.

Conclusions

Thiiranium salts $[Ad_2SCH_2CH_2SiMe_3]^+ X^-$ are dealkylated by the F^- ion giving the thiiran Ad_2S. Thiiranium salts with the $tBuMe_2SiCH_2CH_2$ or $NCCH_2CH_2$ group, seleniranium salts $[Ad_2SeCH_2CH_2SiMe_3]^+ X^-$ and $[Ad_2SeCH_2CH_2CN]^+ X^-$ as well as thiirenium salts $[Ad_2C_2SCH_2CH_2SiMe_3]^+ X^-$ 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. ^{11}B ^{13}C, ^{19}F, ^{29}Si and ^{77}Se NMR spectra were recorded on a JEOL ECZ 400R or on 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 $BF_3{\cdot}OEt_2$ (^{11}B), Me_4Si (^{13}C, ^{29}Si), $CFCl_3$ (^{19}F) and Me_2Se (^{77}Se).

For ESI-TOF mass spectra the samples were measured from CH_3CN, CH_3CN/CH_2Cl_2, CH_3OH or CH_3CN/CH_3OH solutions on an Agilent 6210 ESI-TOF, Agilent Technologies, Santa Clara, CA, USA. Solvent flow rate was adjusted to 4 µL/min, 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[42] on high-performance computer system SOROBAN at Zedat, Freie Universität Berlin, https://www.zedat.fu-berlin.de/HPC/Soroban.

The Olefin Ad=Ad (**1**),[43] *trans*-cyclooctene (**29**),[44] the alkynes *t*BuC≡C*t*Bu (**2**) and AdC≡CAd (**3**),[45] the Si compounds Tf_2NSiMe_3[46] and Me_3Si^+ $CHB_{11}Cl_{11}$[4] were prepared according to known procedures.

1: ^{13}C NMR ($CDCl_3$) δ = 133.17 (C=C), 39.64 (8xCH_2), 37.37 (2xCH_2), 31.93 (4xCH), 28.60 (4xCH).

2: ^{13}C NMR ($CDCl_3$) δ = 87.08 (C≡C), 31.58 (C$\underline{Me}_3$), 27.14 ($\underline{C}Me_3$).

3: ^{13}C NMR ($CDCl_3$) δ = 87.59 (C≡C), 43.55 (6xCH_2), 36.47 (6xCH_2), 29.19 (C_q), 28.19 (6xCH).

Syntheses of $(Me_3SiCH_2CH_2S)_2$ (4) and $(Me_3SiCH_2CH_2Se)_2$ (13)[23c]

Li_2S_2 and Li_2Se_2 are prepared by reacting 60 mmol Li (420 mg) with 60 mmol S (1.92 g) or 60 mmol Se (4.47 g) in 150 mL liq. NH_3. After evaporation of the NH_3 50 mL THF is added. Under stirring 60 mmol $Me_3SiCH_2CH_2Br$ is added dropwise followed by stirring at room temperature for 12 h. Addition of water and extraction with CH_2Cl_2 is followed by vacuum distillation.

4: Yield 6.2 g (78%), b.p. 86°C/0.19 mbar. EI-MS: [266, M^+] ($C_{10}H_{26}S_2Si_2$). ^{13}C NMR ($CDCl_3$) δ = 34.77 (CH_2S), 17.23 ($^1J_{Si,C}$ = 47.9 Hz, CH_2Si), –1.60 ($^1J_{Si,C}$ = 51.0 Hz, CH_3Si).

13: Yield 7.61 g (70%), b.p. 100°C/0.08 mbar. EI-MS: [362, M^+] ($C_{10}H_{26}Se_2Si_2$). ^{77}Se NMR ($CDCl_3$) δ = 355.8. ^{13}C NMR ($CDCl_3$) δ = 24.92 ($^1J_{Se,C}$ = 69.8 Hz, CH_2Se), 19.55 ($^1J_{Si,C}$ = 47.2 Hz, CH_2Si), –1.63 ($^1J_{Si,C}$ = 50.9 Hz, CH_3Si).

Synthesis of $(NCCH_2CH_2Se)_2$ (15)

$NCCH_2CH_2SeCN$ (**18**) is prepared from 0.1 mol $NCCH_2CH_2Br$ (13.4 g) and 0.1 mol KSeCN (14.4 g) in 50 mL DMF according to ref. [27].

To 60 mmol **18** (9.54 g) in 100 mL THF are added dropwise at–78°C 65 mmol $LiEt_3BH$ (65 mL 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 is bubbled through the reaction solution for 30 min. THF is pumped off in vacuum. The remainder is dissolved in H_2O (300 mL) and extracted with CH_2Cl_2. The product is purified by column chromatography on silica gel with mixtures of CH_2Cl_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^+] ($C_4H_4N_2Se$). ^{77}Se NMR ($CDCl_3$) δ = 244.2. ^{13}C NMR ($CDCl_3$) δ = 117.97 (CN), 101.46 ($^1J_{Se,C}$ = 237.5 Hz, SeCN), 23.24 ($^1J_{Se,C}$ = 59.4 Hz, CH_2Se), 20.21 ($\underline{CH}_2CN$).

15: Yield 5.2 g (49%). EI-MS: [268, M^+] ($C_6H_8N_2Se_2$). ^{77}Se NMR ($CDCl_3$) δ = 326.5. ^{13}C NMR ($CDCl_3$) δ = 119.14 (CN), 23.00 ($^1J_{Se,C}$ = 81.0 Hz, CH_2Se), 19.79 ($\underline{CH}_2CN$).

Syntheses of $(tBuMe_2SiCH_2CH_2S)_2$ (7) and $(tBuMe_2SiCH_2CH_2Se)_2$ (22)

Under argon 0.1 mol vinylsilane **19** (14.2 g) are added dropwise to a stirred solution of 0.114 mol 9-BBN (230 mL 0.5 M in THF), followed by refluxing for 2 h, see ref. [29]. After cooling to room temperature H_2O (100 mL) is carefully added, then NaOH (14 g in 120 mL H_2O) and 120 mL 30% H_2O_2 are added, followed by refluxing for 1.5 h. After extraction with Et_2O very pure silylethanol **20** is obtained.
Into a stirred solution of 75 mmol **20** (12 g) and 82.5 mmol CBr_4 (27.4 g) in 80 mL CH_2Cl_2 82.5 mmol Ph_3P (21.6 g) are added within 5 min at 0°C, followed by 2 h stirring at 0°C. After evaporation of the THF the product is dissolved in pentane, filtered through silica gel, and the bromide **21** is vacuum distilled.

7 und **22** are synthesized by producing Li_2S_2 or Li_2Se_2 from 30 mmol Li (208 mg) and 30 mmol S (962 mg) or Se (2.37 g) in 150 mL liq. NH_3 (2.37 g). Li_2S_2 or Li_2Se_2 are reacted to **4** and **13** similar to the described way above with 30 mmol *t*$BuMe_2SiCH_2CH_2Br$ **21** (6.7 g). After aqueous workup and extraction with Et_2O the disulfide **7** is purified by column chromatography on silica gel with hexane.
The raw product of the selenium compound is freed from triselenide by dissolving in 100 mL liq. NH_3 and 50 mL dry THF. 60 mmol Na (1.4 g) is added and the blue solution is stirred for 1 h. After evaporation of the NH_3 and addition of 100 mL H_2O O_2 is bubbled through the solution for 1 h. Purification is done by extraction with Et_2O and column chromatography in hexane.

20: Yield 16 g (100 %). ^{13}C NMR ($CDCl_3$) δ = 59.42 (CH_2OH), 26.35 (C<u>Me</u>$_3$), 17.80 ($^1J_{Si,C}$ = 46.0 Hz, CH_2Si) , 16.27 (<u>C</u>Me_3), –6.09 ($^1J_{Si,C}$ = 49.8 Hz, CH_3Si). ^{29}Si NMR ($CDCl_3$) δ = 6.31.

21: Yield 11.6 g (69%), b.p. 49-51°C/0.2 mbar. ^{13}C NMR ($CDCl_3$) δ = 32.33 (CH_2Br), 26.42 (C<u>Me</u>$_3$), 20.41 ($^1J_{Si,C}$ = 43.0 Hz, CH_2Si), 16.60 (<u>C</u>Me_3), –6.26 ($^1J_{Si,C}$ = 50.2 Hz, CH_3Si). ^{29}Si NMR ($CDCl_3$) δ = 8.34.

7: Yield 4,54 g (86%). EI-MS: [350.1959, M^+] ($C_{16}H_{38}S_2Si_2$). ^{13}C NMR ($CDCl_3$) δ = 35.28 (CH_2S), 26.61 (C<u>Me</u>$_3$), 16.69 (<u>C</u>Me_3), 13.37 ($^1J_{Si,C}$ = 46.4 Hz, CH_2Si), –6.16 ($^1J_{Si,C}$ = 50.0 Hz, CH_3Si). ^{29}Si NMR ($CDCl_3$) δ = 8.61.

22: Yield 4,2 g (63%). EI-MS: [446, M^+] ($C_{16}H_{38}Se_2Si_2$). ^{77}Se NMR ($CDCl_3$) δ = 361.5. ^{13}C NMR ($CDCl_3$) δ = 26.69 (C<u>Me</u>$_3$), 25.37 ($^1J_{Se,C}$ = 69.9 Hz, CH_2Se), 16.77 (<u>C</u>Me_3), 15.74 ($^1J_{Si,C}$ = 45.7 Hz, CH_2Si), –6.16 ($^1J_{Si,C}$ = 49.9 Hz, CH_3Si). ^{29}Si NMR ($CDCl_3$) δ = 8.70.

Syntheses of the Thiiranium und Seleniranium Salts

Method A: 1/R_2S_2 or R_2Se_2/XeF_2/fluoride ion acceptor
15 mL dry CH_2Cl_2 are 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_2NSiMe_3 (2 mmol, 707 mg), $BF_3{\cdot}OEt_2$ (2 mmol, 284 mg), or Me_3Si^+ $CHB_{11}Cl_{11}$ (2 mmol, 1.34 g) are added at –78°C, followed by stirring 30 min at this temperature and 2 h at –40° C. Half of the solvent is pumped off, and by slow addition of 30 mL hexane the salt is crystallized. The product is filtered off, washed 3x with 20 mL hexane and dried in vacuum. Compound **14** is measured after addition of little CD_2Cl_2 by NMR.

Method B: R_2S_2 or R_2Se_2/SO_2Cl_2/$SbCl_5$/1.
15 mL dry CH_2Cl_2 are 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_2Cl_2 (1.1 mmol, 135 mg) is added at –20°C, followed by stirring for 30 min at this temperature. $SbCl_5$ (2 mmol, 598 mg) is slowly added at –78°C, followed by stirring for 10 min at this temperature. Then Ad=Ad **1** (2 mmol, 537 mg) is added and stirred for 2 h at –40°C. Half of the solvent is pumped off, and by slow addition 30 mL hexane crystallization initiated. The salt is filtrated off, washed 3x with 20 mL hexane and dried in vacuum.

Thiiranium Salts 5, 9, 11, according to method A
$[Ad_2SCH_2CH_2SiMe_3]^+$ Tf_2N^- (**5**)
Yield 0.99 g (73%). ESI-MS (CH_3CN/CH_2Cl_2): [401.2692]$^+$ ($C_{25}H_{41}SSi^+$), [279.9180]$^-$ ($C_2F_6NO_4S_2^-$). ^{13}C NMR (CD_2Cl_2) δ = 119.88 (q, $^1J_{F,C}$ = 321.9 Hz, CF_3), 95.87 (ring C), 38.55 (2xCH_2), 38.19 (2xCH_2), 38.08 (2xCH_2), 37.02 (2xCH_2), 36.07 (2xCH_2), 33.57 (2xCH), 30.31 (2xCH), 27.53 (CH_2S), 26.50 (4xCH), 16.17 ($^1J_{Si,C}$ = 42.5 Hz, CH_2Si), –2.66 ($^1J_{Si,C}$ = 52.0 Hz, CH_3Si). ^{29}Si NMR (CD_2Cl_2)) δ = 3.52.
$[Ad_2SCH_2CH_2SiMe_2tBu]^+$ Tf_2N^- (**9**)
Yield 1.16 g (80%). ESI-MS (CH_3CN): [443.3198]$^+$ ($C_{28}H_{47}SSi^+$), [279.9248]$^-$ ($C_2F_6NO_4S_2^-$). ^{13}C NMR (CD_2Cl_2)) δ = 119.83 (q, $^1J_{F,C}$ = 321.6 Hz, CF_3), 96.15 (ring C), 38.57 (2xCH_2), 38.21 (2xCH_2), 38.09 (2xCH_2), 37.03 (2xCH_2), 36.05 (2xCH_2), 33.56 (2xCH), 30.31 (2xCH), 27.91 (CH_2S), 26.50 (2xCH), 26.48 (C<u>Me</u>$_3$), 25.91 (2xCH), 16.43 (<u>C</u>Me_3), 12.37 (CH_2Si), –7.15 (MeSi). ^{29}Si NMR (CD_2Cl_2) δ = 10.05.
$[Ad_2SCH_2CH_2CN]^+$ Tf_2N^- (**11**)
Yield 580 mg (46%). ESI-MS (CH_3CN): [354.2268]$^+$ ($C_{23}H_{32}NS^+$), [279.9181]$^-$ ($C_2F_6NO_4S_2^-$). ^{13}C NMR (CD_2Cl_2)) δ = 119.71 (q, $^1J_{F,C}$ = 321.3 Hz, CF_3), 115.99 (CN), 99.00 (ring C), 38.94 (2xCH_2), 38.54 (2xCH_2), 37.85 (2xCH_2), 36.49 (2xCH_2), 35.95 (2xCH_2), 33.93 (2xCH), 30.19 (2xCH), 26.40 (2xCH), 26.30 (2xCH), 25.18 (CH_2S), 16.23 (<u>C</u>H_2CN)
.
Thiiranium Salts 8, 12, according to method B
$[Ad_2SCH_2CH_2SiMe_2tBu]^+$ $SbCl_6^-$ (**8**)
Yield 1.46 g (94%). ESI-MS (CH_3OH): [443.3177]$^+$ ($C_{28}H_{47}SSi^+$), [334.7208]$^-$ ($SbCl_6^-$). ^{13}C NMR (CD_2Cl_2)) δ = 96.75 (ring C), 38.91 (2xCH_2), 38.42 (2xCH_2), 38.38 (2xCH_2), 37.27 (2xCH_2), 36.15 (2xCH_2), 33.78 (2xCH), 30.63 (2xCH), 28.12 (CH_2S), 26.62 (2xCH), 26.59 (2xCH), 26.15 (C<u>Me</u>$_3$), 16.62 (<u>C</u>Me_3), 12.70 (CH_2Si), –6.63 (MeSi).
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** are obtained by slow addition of pentane into a solution CH_2Cl_2 at –20°C until beginning clouding sets 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) δ = 35.3. ^{13}C NMR (CD_2Cl_2) δ = 119.08 (q, $^1J_{F,C}$ = 321.0 Hz, CF_3), 109.66 (ring C), 39.38 (2xCH_2), 39.33 (2xCH_2), 39.20 (2xCH_2), 38.19 (2xCH_2), 37.05 (2xCH_2), 33.56 (2xCH), 31.14 (2xCH), 27.55 (CH_2Se), 26.63 (4xCH), 15.47 (CH_2Si), –2.72 (MeSi).

$[Ad_2SeCH_2CH_2CN]^+$ BF_4^- (**16**)
Yield 0.8g (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) δ = 24.1. ^{13}C NMR (CD_2Cl_2) δ = 117.22 (CN), 111.87 (ring C), 39.97 (2xCH_2), 39.71 (2xCH_2), 39.48 (2xCH_2), 38.09 (2xCH_2), 36.66 (2xCH_2), 34.28 (2xCH), 31.29 (2xCH), 26.96 (2xCH), 26.87 (2xCH), 24.15 (CH_2Se), 15.78 (<u>C</u>H_2CN). ^{19}F NMR (CD_2Cl_2)) δ = –151.04.

$[Ad_2SeCH_2CH_2SiMe_2tBu]^+$ 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) δ = 44.8.

$[Ad_2SeCH_2CH_2SiMe_2tBu]^+$ $CHB_{11}Cl_{11}^-$ (**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) δ = 39.1. ^{13}C NMR (CD_2Cl_2) δ = 111.12 (ring C), 46.73 ($CHB_{11}Cl_{11}^-$), 39.81 (2xCH_2), 39.73 (2xCH_2), 39.52 (2xCH_2), 38.51 (2xCH_2), 36.52 (2xCH_2), 33.96 (2xCH), 31.55 (2xCH), 28.22 (CH_2Se), 26.79 (4xCH), 26.11 (C<u>Me</u>$_3$), 16.64 (<u>C</u>Me_3), 12.03 (CH_2Si), –6.78 (MeSi). ^{11}B NMR (CD_2Cl_2) δ = –2.52, –10.14, –13.18.

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) δ = 27.4. ^{13}C NMR (CD_2Cl_2) δ = 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 (<u>C</u>H_2CN).
Single crystals are obtained by slow addition of Et_2O into a solution CH_2Cl_2 at –20°C until beginning clouding sets 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 are obtained by slow addition of Et_2O into a solution CH_2Cl_2 at –20°C until beginning clouding sets in, and slow cooling from –20°C to –80°C.
Single crystals of the chloroethyl compound **26** are obtained in the same manner.

Attempts to dealkylate the Thiiranium Salts, the Thiiranes 27 und 30

Cleavage of the $Me_3SiCH_2CH_2$ group?
A solution of Bu_4NF in THF (2 mL 1M, 2 mmol) is added to the thiiranium salt **5** (1 mmol, 682 mg), dissolved in 5 ml dry THF at –196°C, followed by 2 h stirring at –78°C. The solvent is removed completely and the remainder

is chromatographed 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 $[Ad_2SCH_2CH_2SiMe_3]^+ BF_4^-$ is made by reacting **1** (2 mmol, 537 mg), $(Me_3SiCH_2CH_2S)_2$ (**4**), XeF_2 (1 mmol, 169 mg), and $BF_3{\cdot}OEt_2$ (2 mmol, 284 mg) in 15 mL CH_2Cl_2 according to method A. Into the solution Bu_4NF in THF (4 mL 1M, 4 mmol) is added dropwise at –78°C, followed by stirring for 2 h at –40°C. The solvents are pumped off and the remainder is chromatographed 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 ($CDCl_3$) δ = 71.61 (ring C), 38.72 (4xCH_2), 38.53 (4xCH_2), 37.91 (2xCH_2), 35.06 (4xCH), 27.87 (2xCH), 27.27 (2xCH).

The thiiranium salt $[C_8H_{14}SCH_2CH_2SiMe_3]^+ BF_4^-$ is prepared from *cis*-cyclooctene (**28**) (2 mmol, 220 mg), $(Me_3SiCH_2CH_2S)_2$ (**4**), XeF_2 (1 mmol, 169 mg) and $BF_3{\cdot}OEt_2$ (2 mmol, 284 mg) in 15 mL CH_2Cl_2 according to method A, and reacted and worked up in the same manner as described for **27** with 2 mmol Bu_4NF (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) δ = 41.09 (ring C), 29.67 (CH_2), 29.45 (CH_2), 26.43 (CH_2).

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

Cleavage of the *t*BuMe$_2$SiCH$_2$CH$_2$ group?
Thiiranium salt **9** (1 mmol, 724 mg) is reacted in 5 mL dry THF at –78°C with a solution of Bu_4NF in THF (2 mL 1M, 2 mmol), followed by stirring for 2 h at this temperature. The solvent is pumped off completely in vacuum. The remainder is dissolved in CH_2Cl_2 (10 mL) and hexane (20 mL) and chromatographed over silica gel.
The ^{13}C NMR spectrum shows the presence of alkene **1** and disulfide **4** as main products, and thiirane **27** less than 10% in the product mixture.

Cleavage of the NCCH$_2$CH$_2$ group?
Thiiranium salt **11** (1 mmol, 635 mg), dissolved in 5 mL THF, is reacted with CsOH (2.5 mmol, 375 mg) in 3 mL H_2O or MeOH 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 is chromatographed.
^{13}C NMR spectra indicate a mixture of thiiran **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** are obtained by slow cooling of solutions in pentane from room temperature to –80°C.

Attempts to dealkylate Seleniranium Salts
The seleniranium salt $[Ad_2SeCH_2CH_2SiMe_3]^+ Tf_2N^-$ (**14**) is prepared by reacting $(Me_3SiCH_2CH_2Se)_2$ (**13**) (2 mmol, 537 mg), XeF_2 (1 mmol, 169 mg), and Tf_2NSiMe_3 (2 mmol, 707 mg) in 15 mL CH_2Cl_2 according to method A. A solution of Bu_4NF in THF (4 mL 1M, 4 mmol) is added dropwise to the reaction mixture at –78°C, followed by stirring for 30 min at –78°C and 2 h and at –40°C. Half of the solvent is pumped off in vacuum, some CD_2Cl_2 is added, and the NMR of this solution is measured at –40°C. $[Ad_2SeCH_2CH_2SiMe_3]^+ BF_4^-$ made from **1**, **13**, XeF_2, and $BF_3{\cdot}OEt_2$ are reacted with Bu_4NF in the same manner.

^{13}C NMR (CD_2Cl_2, at –40°C) δ = 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_2N^-); 57.86, 23.40, 19.46, 13.40 (Bu_4N^+); 67.59, 25.44 (THF); 54.16 (CH_2Cl_2). ^{77}Se NMR (CD_2Cl_2, at –40° C) δ = 339.9 (diselenide **13**) and 1187.5 ($Me_3SiCH_2CH_2SeF_3$ **32**), signal intensity **13**/**32** 2:1.

Syntheses of the Thiirenium Salts 34–36
Onto alkyne **2** (2 mmol, 277 mg), **3** (2 mmol, 589 mg) and disulfide **4** (1 mmol, 267 mg); **7** (1 mmol, 351 mg) 15 mL dry CH_2Cl_2 are condensed at –196°C. At –78°C XeF_2 (1 mmol, 169 mg) and $BF_3{\cdot}OEt_2$ (2 mmol, 284 mg) or Tf_2NSiMe_3 (2 mmol, 707 mg) are added, and stirred at this temperature 30 min und 2 h at –40°C . Half of the solvent is pumped off and after slow addition of 30 mL hexane the salt is crystallized. The product is filtered off, washed 3x with 20 mL hexane and dried in vacuum.

$[tBu_2C_2SCH_2CH_2SiMe_3]^+ BF_4^-$ (**34**). Yield 545 mg (76%). ESI-MS (CH_3CN/CH_3OH): $[271.1930]^+$ ($C_{15}H_{31}SSi^+$), $[87.0097]^-$ (BF_4^-). ^{13}C NMR (CD_2Cl_2) δ = 114.84 (ring C), 42.20 (CH_2S), 32.96 ($\underline{C}Me_3$), 27.69 ($C\underline{Me}_3$), 13.79 (CH_2Si), –2.48 (MeSi).

$[Ad_2C_2SCH_2CH_2SiMe_3]^+ Tf_2N^-$ (**35**)
Yield **35** 934 mg (66%). ESI-MS (CH_3CN): $[427.2832]^+$ ($C_{27}H_{43}SSi^+$), $[279.9196]^-$ ($C_2F_6NO_4S_2^-$).
$[Ad_2C_2SCH_2CH_2SiMe_2tBu]^+ Tf_2N^-$ (**36**)
Yield **36** 1.94 g (65%). ESI-MS (CH_3CN): $[469.3356]^+$ ($C_{30}H_{49}SSi^+$), $[279.9232]^-$ ($C_2F_6NO_4S_2^-$). ^{13}C NMR (CD_2Cl_2) δ = 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 ($\underline{C}Me_3$), 27.59 ($C\underline{Me}_3$), 26.00 (Ad, CH), 16.48 (Ad, C_q), 10.43 (CH_2Si), –6.96 (MeSi). ^{29}Si NMR (CD_2Cl_2) δ = 10.27.
Single crystals of **36** are obtained by careful addition of Et_2O and pentane to a solution in CH_2Cl_2 until clouding, filtration and slow cooling from room temperature to –80°C (CH_2Cl_2/Et_2O/pentane 1:1:1).

Attempts to dealkylate Thiirenium Salts
Thiirenium salt **35** (1 mmol, 708 mg) are dissolved in 5 mL dry CH_2Cl_2 and at –78°C a solution of Bu_4NF in THF (2 mL 1M, 2 mmol) is added dropwise. After stirring for 2 h at this remperature and 3 h at –60°C half of the solvent is pumped off, some CD_2Cl_2 is added.
^{13}C NMR (CD_2Cl_2, at –60°C) δ = 86.66, 42.76, 35.78, 28.56, 27.64 (AdC≡CAd **3**); 119.38 (q, $^1J_{F,C}$ = 321.1 Hz, Tf_2N^-); 57.20, 23.12, 19.19, 13.28 (Bu_4N^+); 67.28, 25.23 (THF); 54.17 (CH_2Cl_2); –2.67 (**4**).

Crystal structure determinations: Single crystals are 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-Kα irradiation, scan width 0.3deg in ω, full sphere by 2400 frames, usually 20 sec per frame. After multi-scan absorption corrections (SADABS) by equalizing symmetry-equivalent reflections. The structures are solved and refined with the SHELX programs.[47] All atoms except hydrogen are refined anisotropically. Hydrogen atoms are 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.[48]

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Conflict of interest

The authors declare no conflict of interest.

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[41] CCDC-1993913 $[Ad_2SCH_2CH_2SiMe_2tBu]^+ SbCl_6^-\cdot EtCN$ (**8**), CCDC-1993912 $[Ad_2SCH_2CH_2CN]^+ SbCl_6^-\cdot CH_2Cl_2$ (**12**), CCDC-1993938 $[Ad_2SeCH_2CH_2CN]^+ SbCl_6^-\cdot CH_2Cl_2$ (**17**), CCDC-1993916 $[Ad_2SeCH_2CH_2SiMe_2tBu]^+ SbCl_6^-\cdot CH_2Cl_2$ (**25**), CCDC-1993914 $[Ad_2SeCH_2CH_2Cl]^+ SbCl_6^-\cdot$ (**26**), CCDC-1993911 thiirane Ad_2S (**27**), CCDC-1993917 $C_8H_{14}S$ (**30**) and CCDC-1993910 $[Ad_2C_2SCH_2CH_2SiMe_2tBu]^+ Tf_2N^-\cdot$ (**36**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Further experimental details and data of the X-ray single-crystal structure determinations are given in the supporting information, Table S2.

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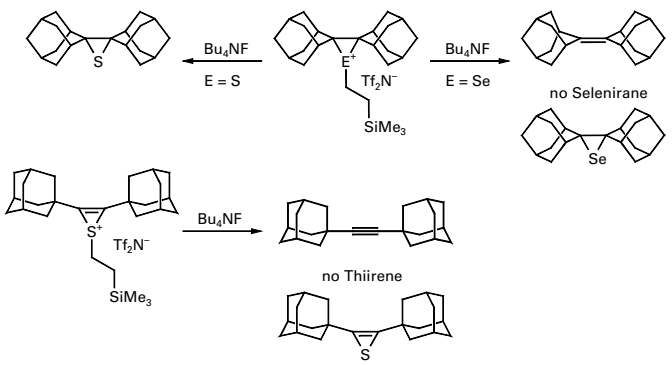
Entry for the Table of Contents



Helmut Poleschner,* Konrad Seppelt

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Attempts to synthesize a Thiirane, Selenirane, and Thiirene by Dealkylation of Chalcogeniranium and Thiirenium Salts.

Thiiranium salts $[Ad_2SCH_2CH_2SiMe_3]^+ X^-$ are dealkylated to the thiirane Ad_2S by F^-. Thiiranium salts $[Ad_2SCH_2CH_2SiMe_2tBu]^+ X^-$, seleniranium salts $[Ad_2SeCH_2CH_2SiMe_3]^+ X^-$, and thiirenium salts $[Ad_2C_2SCH_2CH_2SiMe_3]^+ X^-$ are not dealkylated by F^-. Instead they are cleaved at the chalcogene atom to the alkene Ad=Ad and alkyne AdC≡CAd under liberation of RS^+ and RSe^+.