

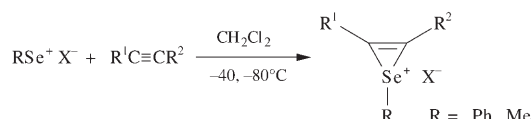
Selenirenium and Tellurirenium Ions**

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Reactive compounds with three-membered rings, such as borirenes,^[1] phosphirenes,^[2] or the silicon and germanium analogues of the cyclopropenyl cation,^[3] are particularly challenging to synthesize. Apart from thiirenium salts,^[4] seleniranium ions which play a key role in the asymmetric synthesis with chiral diselenides have also been investigated.^[5] Selenirenium ions have been postulated as principal intermediates in addition reactions of selenium-containing electrophiles to acetylenes, although they have never been identified.^[6] The early ¹³C NMR spectroscopic identification by Schmid and Garratt^[7] is incorrect, and possible decomposition products may have been detected instead. Tellurirenium ions have not been mentioned in the literature at all.

We found a strong indication for the existence of selenirenium ions in the distinct steric influence of the group R on the addition of PhSeF^[8] to BuC≡CR.^[9] We expected that these three-membered ring ions should have low stability, and therefore initial detection experiments used low-temperature NMR spectroscopy.

The following PhSe⁺X[−] equivalents are used for the addition to alkynes: Ph₂Se₂/XeF₂/2 SbF₅, Ph₂Se₂/Br₂/2 AgSbF₆,^[5,10] Ph₂Se₂/2 NOSbF₆,^[11] (PhSeO)₂O/2 Ph₂Se₂/3 Tf₂O (Tf₂O = trifluoromethanesulfonic acid anhydride),^[12] and PhSeCl/SbCl₅.^[4] (MeSe)₃⁺SbCl₆[−]^[13] is used as a MeSe⁺ source. The reaction of the RSe⁺X[−] reagents with acetylenes in CH₂Cl₂ between −40 and −80 °C produces the selenirenium ions, which are detected by ⁷⁷Se NMR spectroscopy (Scheme 1, Table 1). Signals are substantially upfield (between −79 and −105 ppm (R = Ph) and −169 and



Scheme 1. Preparation of the selenirenium ions.

−185 ppm (R = Me); cf. Me₃Se⁺ 254 ppm^[14]). The ¹³C signal also showed upfield shifts for the ring carbon atoms that are similar to those found for thiirenium ions.^[4] GIAO-MP2

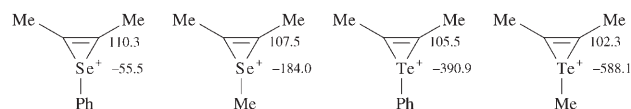
Table 1: Reactions of RSe⁺X[−] reagents with acetylenes, and detection of the selenirenium ions by ⁷⁷Se and ¹³C NMR spectroscopy.^[a]

RSe ⁺ X [−] Reagent	Acetylene	T [°C] ^[b]	δ (⁷⁷ Se)	δ (¹³ C _{ring})
Ph ₂ Se ₂ /XeF ₂ / 2 SbF ₅	tBuC≡CtBu	−40	−88.0	112.5
Ph ₂ Se ₂ /Br ₂ / 2 AgSbF ₆	tBuC≡CtBu	−40	−86.5	112.9
Ph ₂ Se ₂ / 2 NOSbF ₆	tBuC≡CtBu	−40	−86.8	112.8
(PhSeO) ₂ O/ 2 Ph ₂ Se ₂ /3 Tf ₂ O	tBuC≡CtBu	−40	−82.9	112.8
PhSeCl/SbCl ₅	tBuC≡CtBu	−40	−83.7	113.3
PhSeCl/SbCl ₅	AdC≡CAd ^[d]	−40	−105.3	111.0
PhSeCl/SbCl ₅	PhC≡CtBu	−40	−78.7	101.9, 114.4
PhSeCl/SbCl ₅	BuC≡CtBu	−40	−81.4	107.0, 117.3
PhSeCl/SbCl ₅	iPrC≡CiPr	−40	−87.5	112.9
PhSeCl/SbCl ₅	BuC≡CBu	−40	− ^[e]	—
		−80	−95.3	109.8
PhSeCl/SbCl ₅		−80	−82.8 ^[e]	110.3 ^[e]
PhSeCl/SbCl ₅		−80	−95.6 ^[e]	110.4
(MeSe) ₃ ⁺ SbCl ₆ [−]	tBuC≡CtBu	−40	−169.0	112.7
(MeSe) ₃ ⁺ SbCl ₆ [−]	AdC≡CAd	−40	−185.0	109.3

[a] δ values in ppm. [b] Temperature of reaction and NMR measurement. [c] No selenirenium ion detectable. [d] Ad = 1-adamantyl. [e] Broad.

calculations^[15] of ⁷⁷Se and ¹³C NMR shifts of model compounds agree well with the experimental data and confirm the structure (Scheme 2). Strong magnetic shielding in three-membered rings as compared to larger rings is a common phenomenon, for example, in cycloalkanes and cycloalkenes (¹³C), in cyclic ethers (¹⁷O), thioethers (³³S), amines (¹⁵N) and phosphines (³¹P).^[16]

With di-*tert*-butylacetylene, all the PhSe⁺X[−] equivalents produce the expected three-membered rings. Acetylenes



Scheme 2. GIAO-MP2/6-311 + G(d,p) calculations on the ⁷⁷Se, ¹²⁵Te, and ¹³C NMR chemical shifts of selenirenium and tellurirenium ions (C_s symmetry) relative to Me₂Se, Me₂Te, and TMS; δ value in ppm (optimization with MP2/6-311 + G(d,p), Te basis: SDB-cc-pVTZ, Te basis for GIAO: IGLO II-type^[15]).

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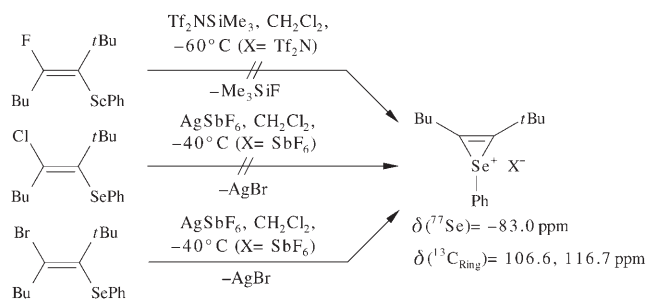
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having the substituents Ad/Ad, Ph/*t*Bu, *n*Bu/*t*Bu and *i*Pr/*i*Pr also react with PhSeCl/SbCl₅ to give selenirenium ions at –40 °C. Products formed with 5-decyne, cycloundecyne, and cyclododecyne decompose at –40 °C, and selenirenium ions are observed only at below –80 °C. Cyclododecyne and 2-butyne do not form selenirenium ions with PhSeCl/SbCl₅, even at –80 °C, and 2-butyne also fails to react with Ph₂Se₂/Br₂/2 AgSbF₆ at –80 °C.

Schmid and Garratt worked with 2-butyne and *p*-tolyl-SeCl/AgPF₆ at room temperature. The ¹³C NMR signal at 136 ppm, which they assigned to the three-membered ring, can only come from decomposition products.^[7] The MeSe⁺ source (MeSe)₃⁺SbCl₆[–] reacts with di-*tert*-butylacetylene or diadamantylacetylene to form methylselenirenium ions.

Selenirenium ions can also be formed by elimination of a halide ion from vicinal (*E*)-halogen(phenylseleno)olefins. Fluoro^[9] and chloro^[15] olefins are however too stable, and fluoride ion abstraction by Tf₂NSiMe₃ or chloride ion abstraction by AgSbF₆ does not take place. Only the bromoolefins^[15] react with AgSbF₆ with a configuration change from (*E*) to (*Z*) with formation of the three-membered ring (Scheme 3).



Scheme 3. Attempts to obtain selenirenium ions by halide abstraction from (*E*)-halogen(phenylseleno)olefins.

The structure of 1-phenyl-2,3-di-*tert*-butyl-, 1-phenyl-2,3-diadamantyl-, and 1-methyl-2,3-di-*tert* butylselenirenium salts have been determined by single-crystal X-ray diffraction (Figures 1 and 2).^[15,17] Se–C bonds within the three-membered rings are markedly longer (197.1–198.6 pm) than those between selenium and the phenyl or methyl groups (191.4 and 195.2 pm). The latter are similar to those in normal selenonium ions, such as PhMeEtSe⁺ (Se–Ph 193.0 pm, Se–Me 192.6 pm).^[18] The bond angles at the selenium atom are small (38°) and are thus even smaller than in the thiirenium ion (40.85°).^[4] The C=C bond lengths (127.9 and 128.5 pm, sulfur analogues 127.8 pm^[4]) are remarkable short, and are intermediate between a double bond ((*Z*)-*t*BuCH=CH*t*Bu 134.3 pm) and a triple bond (*t*BuC≡C*t*Bu 120.2 pm).^[19] There is a linear correlation between the Raman C–C vibrational frequency and C–C bond lengths.^[15] The C=C distance and the C=C–C angle of about 156° are indicative of a sp^{1.5} hybridization of the carbon ring atoms. The natural bond orbital (NBO) analysis^[15] of the trimethylselenirenium ion results in sp^{1.35} hybridization for the C=C bond.

The compounds that were determined crystallographically are stable to the extent that isolation of

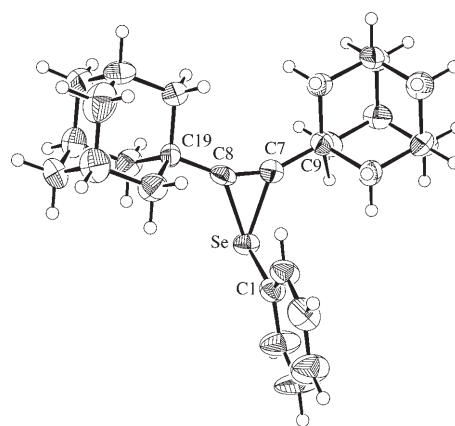


Figure 1. Molecular structure of the cation of (Ad₂C₂SePh)⁺SbCl₆[–]·CH₂Cl₂. Ellipsoids are set at 50% probability. Selected bond lengths [pm] and angles [°]: Se–C1 191.4(8), Se–C7 197.1(8), Se–C8 198.6(9), C7–C8 128.5(12), C7–C9 147.9(12), C8–C19 147.9(12); C7–Se–C8 37.9(3), C1–Se–C7 105.6(4), C1–Se–C8 106.5(4), C7–C8–C19 155.7(9), C8–C7–C9 156.0(9).

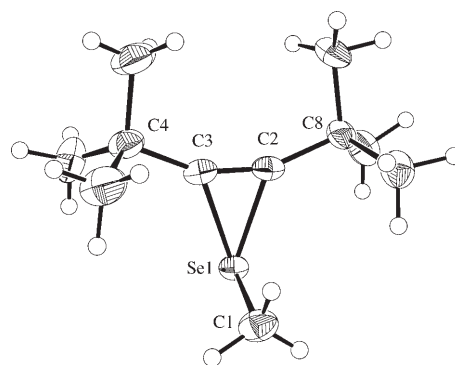
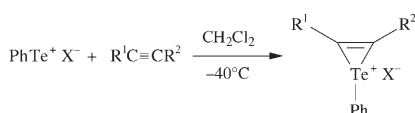


Figure 2. Molecular structure of the cation of (tBu₂C₂SeMe)⁺SbCl₆[–]·0.5 CH₂Cl₂. Ellipsoids are set at 50% probability. Selected bond lengths [pm] and angles [°]: Se1–C1 195.2(4), Se1–C2 198.4(3), Se1–C3 198.5(3), C2–C3 127.9(5), C3–C4 150.1(5), C2–C8 150.5(5); C2–Se1–C3 37.60(14), C1–Se1–C2 102.51(16), C1–Se1–C3 102.02(16), C2–C3–C4 156.2(3), C3–C2–C8 157.3(3).

the salts (tBu₂C₂SePh)⁺SbCl₆[–], (Ad₂C₂SePh)⁺SbCl₆[–], (tBu₂C₂SeMe)⁺SbCl₆[–], and (Ad₂C₂SeMe)⁺SbCl₆[–] was possible. The colorless or slightly yellow compounds can be kept under argon for a few hours at room temperature, but decompose within one week to a significant extent. These salts have an intense peak in the FAB mass spectrum for the molecular cation.

To obtain tellurirenium ions, the PhTe⁺X[–] reagents Ph₂Te₂/XeF₂/2 SbF₅, Ph₂Te₂/Br₂/2 AgSbF₆,^[20] and Ph₂Te₂/2 NOSbF₆^[11] were reacted exclusively with di-*tert*-alkylacetylenes at –40 °C in CH₂Cl₂ (Scheme 4, Table 2). Tellurirenium ions could be clearly identified under the chosen conditions, with ¹²⁵Te NMR signals at –380 to –426 ppm. Relative to Me₃Te⁺ (408 ppm),^[14] the ¹²⁵Te signals are extremely upfield. The ¹³C δ values are often detectable only at very low temperatures, and are similar to those of the selenium compounds. GIAO-MP2 calculations confirm the high magnetic shielding of the tellurium and carbon ring atoms that is observed (Scheme 2). No reagent exists for methyltellurire-



Scheme 4. Preparation of tellurirenium ions.

Table 2: Reactions of $\text{PhTe}^+\text{SbF}_6^-$ reagents with acetylenes, and detection of the tellurirenium ions by ^{125}Te and ^{13}C NMR spectroscopy at -40°C .^[a]

$\text{PhTe}^+\text{SbF}_6^-$ Reagent	Acetylene	$\delta(^{125}\text{Te})$	$\delta(^{13}\text{C}_{\text{ring}})$
$\text{Ph}_2\text{Te}_2/\text{XeF}_2/2\text{SbF}_5$	$t\text{BuC}\equiv\text{CtBu}$	−381.0	— ^[b]
$\text{Ph}_2\text{Te}_2/\text{Br}_2/2\text{AgSbF}_6$	$t\text{BuC}\equiv\text{CtBu}$	−383.5	112.2
$\text{Ph}_2\text{Te}_2/2\text{NOSbF}_6$	$t\text{BuC}\equiv\text{CtBu}$	−380.5	110.7 ^[b,c]
$\text{Ph}_2\text{Te}_2/2\text{NOSbF}_6$	$\text{AdC}\equiv\text{CAd}$	−426.3	108.8 ^[b,c]
$\text{Ph}_2\text{Te}_2/\text{Br}_2/2\text{AgSbF}_6$	$\text{AdC}\equiv\text{CtBu}$	−407.1	— ^[b]
$\text{Ph}_2\text{Te}_2/2\text{NOSbF}_6$	$\text{AdC}\equiv\text{CtBu}$	−402.1	109.9, 109.5 ^[b,c]

[a] δ values in ppm. [b] No signal at -40°C . [c] Broad signal at -90°C .

nium ions: $\text{Me}_2\text{Te}_2/2\text{NOSbF}_6/t\text{BuC}\equiv\text{CtBu}$ forms only decomposition products, and $(\text{Me}_2\text{TeTeMe})^+\text{BF}_4^-$ ^[15,21] and the novel $(\text{Me}_2\text{SeSeMe})^+\text{BF}_4^-$ ^[15] do not react with acetylenes. Attempts to prepare $(\text{MeTe})_3^+$ salts as in reference [13] resulted in the formation of the new four-membered ring $(\text{R}_4\text{Te}_4)^{2+}$.^[22]

Crystallization of the tellurirenium ions has been very difficult, even with the asymmetric acetylene $\text{AdC}\equiv\text{CtBu}$. Only decomposition and a black coloration is usually observed. However, the reaction of $t\text{BuC}\equiv\text{CtBu}$ with $\text{Ph}_2\text{Te}_2/\text{Br}_2/2\text{AgSbF}_6$ yields 1-phenyl-2,3-di-*tert*-butyltellurireniumhexafluoroantimonate (Figure 3).^[17]

In a similar fashion to the selenium compounds, the Te–C bonds within the heterocycle (219.0 and 220.1 pm) are longer

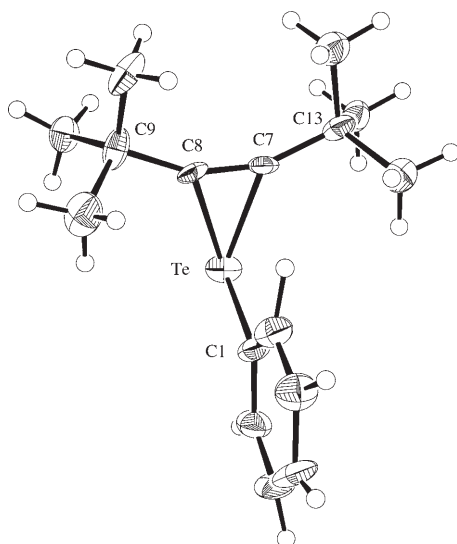


Figure 3. Molecular structure of the cation of $(t\text{Bu}_2\text{C}_2\text{SePh})^+\text{SbF}_6^- \cdot 1.5\text{CCl}_4$. Ellipsoids are set at 50% probability. Selected bond lengths [pm] and angles [°]: Te–C1 213.7(10), Te–C7 220.1(9), Te–C8 219.0(9), C7–C8 128.8(14), C7–C13 149.7(15); C8–C9 149.9(14); C7–Te–C8 34.1(4), C1–Te–C7 99.3(4), C1–Te–C8 99.3(4), C7–C8–C9 155.5(10), C8–C7–C13 157.6(9).

than the Te–Ph bond (213.7 pm). The latter value is similar to those in telluronium ions such as PhMeEtTe^+ (211.7 pm).^[18] The C=C bond length (128.8 pm) is as was found in the selenium compounds, but the C–Te–C angle (34.1°) is even smaller. Ring strain, and the Te–C bond, which is weaker than a Se–C bond, and in this case even more elongated, explain the low stability of these compounds.

Calculations of the nucleus-independent chemical shifts (NICS)^[23,24] for the chalcogenirenium ions give negative values: $(\text{H}_2\text{C}_2\text{SH})^+$ NICS(1) −7.82 ppm, $(\text{H}_2\text{C}_2\text{SeH})^+$ NICS(1) −10.34 ppm, $(\text{H}_2\text{C}_2\text{TeH})^+$ NICS(1) −12.32 ppm.^[15] These three-membered rings should therefore have a diamagnetic ring current as a result of aromatic electron delocalisation (cf. NICS of silicon- and germanium-containing aromatic three-membered rings^[3]). However, according to CCSD(T)/aug-cc-pVTZ calculations, the ions $(\text{Me}_2\text{C}_2\text{EMe})^+$ have only small aromatic stabilization energies:^[23,25] $\text{E}=\text{S}$ −2.72 kcal mol^{−1}, $\text{E}=\text{Se}$ −2.79 kcal mol^{−1}, and $\text{E}=\text{Te}$ −4.72 kcal mol^{−1} (E = chalcogen).^[15] Thus the question of aromaticity remains unclear. Further experimental investigations into the reactivity of these compounds with nucleophiles, and theoretical calculations to clarify the bonding situation are planned.

Experimental Section

For the preparation of the PhSe^+ , PhTe^+ , and MeSe^+ reagents, NMR spectroscopic detection of the selenirenium and tellurirenium ions, and ab initio calculations, see the Supporting Information.

Preparation of the selenirenium salts: Di-*tert*-butylacetylene (420 mg, 3 mmol) or diadamantylacetylene (884 mg, 3 mmol, dissolved in 5 mL CH_2Cl_2) is added dropwise to a 3 mmol solution of the reagent $\text{PhSe}^+\text{SbCl}_6^-$ or $(\text{MeSe})_3^+\text{SbCl}_6^-$ in CH_2Cl_2 (20 mL) at -40°C , followed by stirring at this temperature for 30 min, cooling to -78°C , and addition of pentane (50 mL). After filtration, the crystals are washed three times with pentane (30 mL) and then dried in vacuum. Recrystallization is carried out with CH_2Cl_2 /pentane at -78°C .

$(t\text{Bu}_2\text{C}_2\text{SePh})^+\text{SbCl}_6^-$: Yield 1.19 g (63 %), mp. 111–111.5°C (decomp). FAB-MS: m/z 295 (100, M^+ for ^{80}Se). ^{77}Se NMR (CD_2Cl_2): δ = −70.6 ppm. ^{13}C NMR (CD_2Cl_2): δ = 115.64 (C=C), 33.77 (CMe_3), 29.40 (CMe_3); Ph: 126.04 (*i*), 131.60 (*o*), 129.10 (*m*), 132.90 ppm (*p*).

$(\text{Ad}_2\text{C}_2\text{SePh})^+\text{SbCl}_6^-$: Yield 1.96 g (83 %), mp. 105–106°C (decomp). FAB-MS: m/z 451 (55, M^+ for ^{80}Se), 293 (19, $M^+ - \text{PhSeH}$), 135 (100, $\text{C}_{10}\text{H}_{15}^+$). Raman: ν = 1856 cm^{−1} (C=C). ^{77}Se NMR (CD_2Cl_2): δ = −93.5 ppm. ^{13}C NMR (CD_2Cl_2): δ = 113.55 (C=C); Ad: 35.27 (C1), 41.36 (C2), 28.10 (C3), 35.67 (C4); Ph: 126.60 (*i*), 131.46 (*o*), 128.88 (*m*), 132.64 ppm (*p*).

$(t\text{Bu}_2\text{C}_2\text{SeMe})^+\text{SbCl}_6^-$: Yield 1.37 g (81 %), mp. 130°C (decomp). FAB-MS: m/z 233 (100, M^+ for ^{80}Se). ^{77}Se NMR (CD_2Cl_2): δ = −161.4 ppm. ^{13}C NMR (CD_2Cl_2): δ = 114.09 (C=C), 33.36 (CMe_3), 28.78 (CMe_3), 22.10 ppm (MeSe).

$(\text{Ad}_2\text{C}_2\text{SeMe})^+\text{SbCl}_6^-$: Yield 1.96 g (90 %), mp. 140–141°C (decomp). FAB-MS: m/z 389 (55, M^+ for ^{80}Se), 293 (47, $M^+ - \text{MeSeH}$), 135 (100, $\text{C}_{10}\text{H}_{15}^+$). ^{77}Se NMR (CD_2Cl_2): δ = −184.0 ppm. ^{13}C NMR (CD_2Cl_2): δ = 112.54 (C=C); Ad: 34.75 (C1), 40.95 (C2), 28.01 (C3), 35.77 (C4); 23.27 ppm (MeSe).

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