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**Selenium and Tellurium**

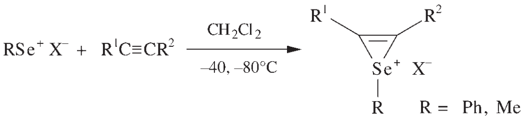
# Selenirenium and Tellurirenium Ions**

*Helmut Poleschner* and Konrad Seppelt*

Reactive compounds with three-membered rings, such as borirenes,[1] phosphirenes,[2] or the silicon and germanium analogues of the cyclopropenylium ion,[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 $^{13}$C 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.

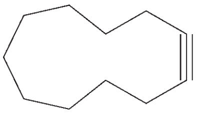
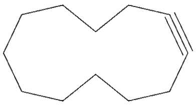
We found a strong indication for the existence of selenirenium ions in the distinct steric influence of the group R on the addition of PhSeF[8] to BuC≡CR.[9] We expected that these three-membered ring ions should have low stability, and therefore initial detection experiments used low-temperature NMR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

The following $PhSe^+X^-$ equivalents are used for the addition to alkynes: $Ph_2Se_2/XeF_2/2\,SbF_5$, $Ph_2Se_2/Br_2/2\,AgSbF_6$,[5,10] $Ph_2Se_2/2\,NOSbF_6$,[11] $(PhSeO)_2O/2\,Ph_2Se_2/3Tf_2O$ ($Tf_2O$ = trifluoromethanesulfonic acid anhydride),[12] and $PhSeCl/SbCl_5$.[4] $(MeSe)_3^+SbCl_6^-$[13] is used as a $MeSe^+$ source. The reaction of the $RSe^+X^-$ reagents with acetylenes in $CH_2Cl_2$ between −40 and −80 °C produces the selenirenium ions, which are detected by $^{77}$Se NMR spectroscopy (Scheme 1, Table 1). Signals are substantially upfield (between −79 and −105 ppm (R = Ph) and −169 and −185 ppm (R = Me); cf. $Me_3Se^+$ 254 ppm[14]). The $^{13}$C signal also showed upfield shifts for the ring carbon atoms that are similar to those found for thiirenium ions.[4] GIAO-MP2 calculations[15] of $^{77}$Se and $^{13}$C 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 ($^{13}$C), in cyclic ethers ($^{17}$O), thioethers ($^{33}$S), amines ($^{15}$N) and phosphines ($^{31}$P).[16]



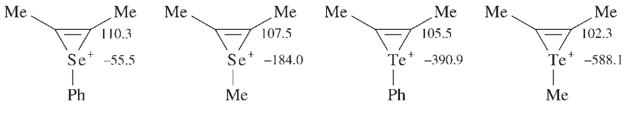
**Scheme 1.** Preparation of the selenirenium ions.

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

| $RSe^+X^-$ Reagent | Acetylene | $T$ [°C][b] | $\delta(^{77}Se)$ | $\delta(^{13}C_{Ring})$ |
|---|---|---|---|---|
| $Ph_2Se_2/XeF_2/2\,SbF_5$ | $t$BuC≡C$t$Bu | −40 | −88.0 | 112.5 |
| $Ph_2Se_2/Br_2/2\,AgSbF_6$ | $t$BuC≡C$t$Bu | −40 | −86.5 | 112.9 |
| $Ph_2Se_2/2\,NOSbF_6$ | $t$BuC≡C$t$Bu | −40 | −86.8 | 112.8 |
| $(PhSeO)_2O/2\,Ph_2Se_2/3Tf_2O$ | $t$BuC≡C$t$Bu | −40 | −82.9 | 112.8 |
| $PhSeCl/SbCl_5$ | $t$BuC≡C$t$Bu | −40 | −83.7 | 113.3 |
| $PhSeCl/SbCl_5$ | AdC≡CAd[d] | −40 | −105.3 | 111.0 |
| $PhSeCl/SbCl_5$ | PhC≡C$t$Bu | −40 | −78.7 | 101.9, 114.4 |
| $PhSeCl/SbCl_5$ | BuC≡C$t$Bu | −40 | −81.4 | 107.0, 117.3 |
| $PhSeCl/SbCl_5$ | $i$PrC≡C$i$Pr | −40 | −87.5 | 112.9 |
| $PhSeCl/SbCl_5$ | BuC≡CBu | −40 | –[c] | – |
|  |  | −80 | −95.3 | 109.8 |
| $PhSeCl/SbCl_5$ |  | −80 | −82.8[e] | 110.3[e] |
| $PhSeCl/SbCl_5$ |  | −80 | −95.6[e] | 110.4 |
| $(MeSe)_3^+\,SbCl_6^-$ | $t$BuC≡C$t$Bu | −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.

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 $^{77}$Se, $^{125}$Te, and $^{13}$C NMR chemical shifts of selenirenium and tellurirenium ions ($C_s$ symmetry) relative to $Me_2Se$, $Me_2Te$, 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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[*] Dr. H. Poleschner, Prof. Dr. K. Seppelt
Institut für Chemie und Biochemie
Anorganische und Analytische Chemie
Freie Universität Berlin
Fabeckstrasse 34-36, 14195 Berlin (Germany)
Fax: (+49) 30-8385-3310
E-mail: hpol@chemie.fu-berlin.de

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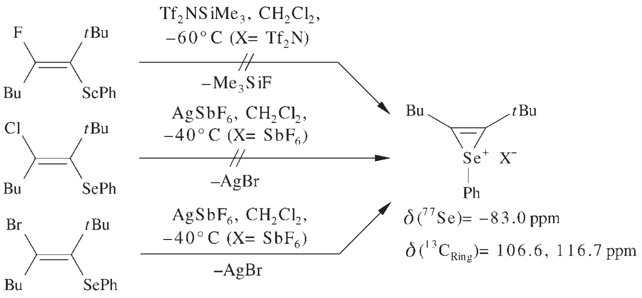
having the substituents Ad/Ad, Ph/*t*Bu, *n*Bu/*t*Bu and *i*Pr/*i*Pr also react with $PhSeCl/SbCl_5$ to give selenirenium ions at −40 °C. Products formed with 5-decyne, cycloundecyne, and cyclododecyne decompose at −40 °C, and selenirenium ions are observed only at below −80 °C. Cyclododecyne and 2-butyne do not form selenirenium ions with $PhSeCl/SbCl_5$, even at −80 °C, and 2-butyne also fails to react with $Ph_2Se_2/Br_2/2\,AgSbF_6$ at −80 °C.

Schmid and Garratt worked with 2-butyne and *p*-tolyl-$SeCl/AgPF_6$ at room temperature. The $^{13}C$ NMR signal at 136 ppm, which they assigned to the three-membered ring, can only come from decomposition products.[7] The $MeSe^+$ source $(MeSe)_3{}^+SbCl_6{}^-$ 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 $Tf_2NSiMe_3$ or chloride ion abstraction by $AgSbF_6$ does not take place. Only the bromoolefins[15] react with $AgSbF_6$ 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 the salts $(tBu_2C_2SePh)^+SbCl_6{}^-$, $(Ad_2C_2SePh)^+SbCl_6{}^-$, $(tBu_2C_2SeMe)^+SbCl_6{}^-$, and $(Ad_2C_2SeMe)^+\,SbCl_6{}^-$ 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.

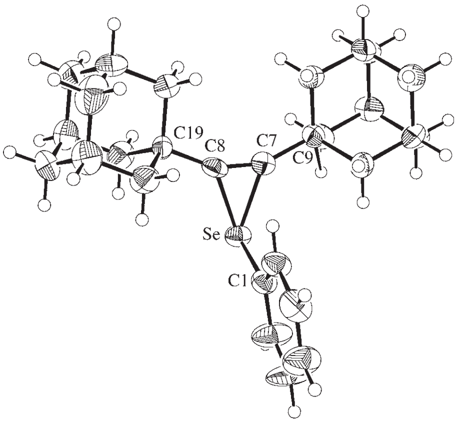


***Figure 1.*** Molecular structure of the cation of $(Ad_2C_2SePh)^+SbCl_6{}^-\cdot CH_2Cl_2$. Ellipsoids are set at 50% probability. Selected bond lengths [pm] and angles [°]: Se–C1 191.4(8), Se–C7 197.1(8), Se–C8 198.6(9), C7–C8 128.5(12) C7–C9 147.9(12), C8–C19 147.9(12); C7-Se-C8 37.9(3), C1-Se-C7 105.6(4), C1-Se-C8 106.5(4), C7-C8-C19 155.7(9), C8-C7-C9 156.0(9).

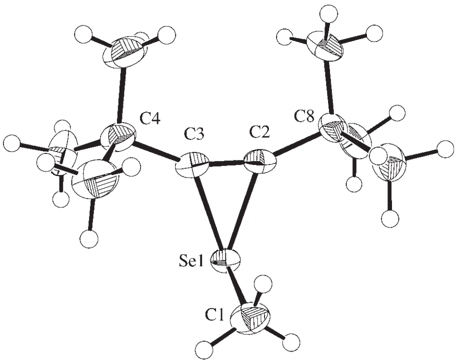
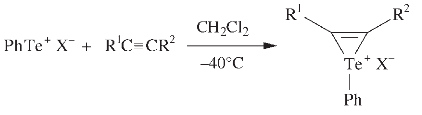


***Figure 2.*** Molecular structure of the cation of $(tBu_2C_2SeMe)^+SbCl_6{}^-\cdot 0.5\,CH_2Cl_2$. Ellipsoids are set at 50% probability. Selected bond lengths [pm] and angles [°]: Se1–C1 195.2(4), Se1–C2 198.4(3), Se1–C3 198.5(3), C2–C3 127.9(5), C3–C4 150.1(5), C2–C8 150.5(5); C2-Se1-C3 37.60(14), C1-Se1-C2 102.51(16), C1-Se1-C3 102.02(16), C2-C3-C4 156.2(3), C3-C2-C8 157.3(3).

To obtain tellurirenium ions, the $PhTe^+X^-$ reagents $Ph_2Te_2/XeF_2/2\,SbF_5$, $Ph_2Te_2/Br_2/2\,AgSbF_6$,[20] and $Ph_2Te_2/2\,NOSbF_6$[11] were reacted exclusively with di-*tert*-alkylacetylenes at −40 °C in $CH_2Cl_2$ (Scheme 4, Table 2). Tellurirenium ions could be clearly identified under the chosen conditions, with $^{125}Te$ NMR signals at −380 to −426 ppm. Relative to $Me_3Te^+$ (408 ppm),[14] the $^{125}Te$ signals are extremely upfield. The $^{13}C$ $\delta$ 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 $PhTe^+SbF_6^-$ reagents with acetylenes, and detection of the tellurirenium ions by $^{125}$Te and $^{13}$C NMR spectroscopy at −40 °C.[a]

| $PhTe^+SbF_6^-$ Reagent | Acetylene | $\delta$($^{125}$Te) | $\delta$($^{13}C_{ring}$) |
|---|---|---|---|
| $Ph_2Te_2/XeF_2/2\,SbF_5$ | $t$BuC≡C$t$Bu | −381.0 | –[b] |
| $Ph_2Te_2/Br_2/2\,AgSbF_6$ | $t$BuC≡C$t$Bu | −383.5 | 112.2 |
| $Ph_2Te_2/2\,NOSbF_6$ | $t$BuC≡C$t$Bu | −380.5 | 110.7[b,c] |
| $Ph_2Te_2/2\,NOSbF_6$ | AdC≡CAd | −426.3 | 108.8[b,c] |
| $Ph_2Te_2/Br_2/2\,AgSbF_6$ | AdC≡C$t$Bu | −407.1 | –[b] |
| $Ph_2Te_2/2\,NOSbF_6$ | AdC≡C$t$Bu | −402.1 | 109.9, 109.5[b,c] |

[a] $\delta$ values in ppm. [b] No signal at −40 °C. [c] Broad signal at −90 °C.

nium ions: $Me_2Te_2/2\,NOSbF_6/t$BuC≡C$t$Bu forms only decomposition products, and $(Me_2TeTeMe)^+BF_4^-$[15,21] and the novel $(Me_2SeSeMe)^+BF_4^-$[15] do not react with acetylenes. Attempts to prepare $(MeTe)_3^+$ salts as in reference [13] resulted in the formation of the new four-membered ring $(R_4Te_4)^{2+}$.[22]

Crystallization of the tellurirenium ions has been very difficult, even with the asymmetric acetylene AdC≡C$t$Bu. Only decomposition and a black coloration is usually observed. However, the reaction of $t$BuC≡C$t$Bu with $Ph_2Te_2/Br_2/2AgSbF_6$ 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 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.

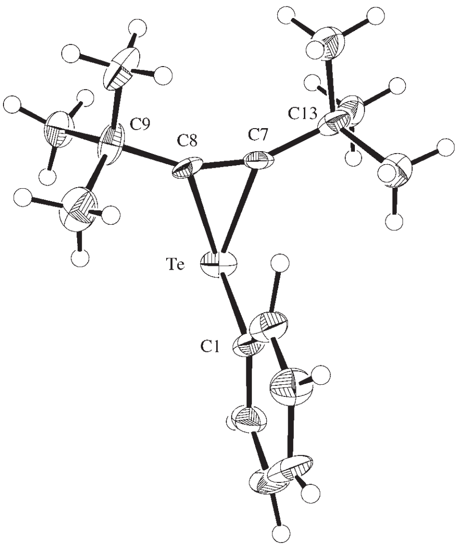


**Figure 3.** Molecular structure of the cation of $(tBu_2C_2TePh)^+SbF_6^-\cdot1.5\,CCl_4$. Ellipsoids are set at 50% probability. Selected bond lengths [pm] and angles [°]: Te–C1 213.7(10), Te–C7 220.1(9), Te–C8 219.0(9), C7–C8 128.8(14), C7–C13 149.7(15); C8–C9 149.9(14); C7-Te-C8 34.1(4), C1-Te-C7 99.3(4), C1-Te-C8 99.3(4), C7-C8-C9 155.5(10), C8-C7-C13 157.6(9).

Calculations of the nucleus-independent chemical shifts (NICS)[23,24] for the chalcogenirenium ions give negative values: $(H_2C_2SH)^+$ NICS(1) −7.82 ppm, $(H_2C_2SeH)^+$ NICS(1) −10.34 ppm, $(H_2C_2TeH)^+$ 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 $(Me_2C_2EMe)^+$ have only small aromatic stabilization energies:[23,25] E=S −2.72 kcal mol$^{-1}$, E=Se −2.79 kcal mol$^{-1}$, and E=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 $PhSe^+SbCl_6^-$ or $(MeSe)_3^+SbCl_6^-$ 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.

$(tBu_2C_2SePh)^+SbCl_6^-$: Yield 1,19 g (63 %), mp. 111–111.5 °C (decomp). FAB-MS: $m/z$ 295 (100, $M^+$ for $^{80}$Se). $^{77}$Se NMR ($CD_2Cl_2$): $\delta = -70.6$ ppm. $^{13}$C NMR ($CD_2Cl_2$) $\delta = 115.64$ (C=C), 33.77 ($CMe_3$), 29.40 ($CMe_3$); Ph: 126.04 ($i$), 131.60 ($o$), 129.10 ($m$), 132.90 ppm ($p$).

$(Ad_2C_2SePh)^+SbCl_6^-$: Yield 1.96 g (83 %), mp. 105–106 °C (decomp). FAB-MS: $m/z$ 451 (55, $M^+$ for $^{80}$Se), 293 (19, $M^+$−PhSeH), 135 (100, $C_{10}H_{15}^+$). Raman: $\nu = 1856$ cm$^{-1}$ (C=C). $^{77}$Se NMR ($CD_2Cl_2$): $\delta = -93.5$ ppm. $^{13}$C NMR ($CD_2Cl_2$): $\delta = 113.55$ (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 ($p$).

$(tBu_2C_2SeMe)^+SbCl_6^-$: Yield 1.37 g (81 %), mp. 130 °C (decomp). FAB-MS: $m/z$ 233 (100, $M^+$ for $^{80}$Se). $^{77}$Se NMR ($CD_2Cl_2$): $\delta = -161.4$ ppm. $^{13}$C NMR ($CD_2Cl_2$): $\delta = 114.09$ (C=C), 33.36 ($CMe_3$), 28.78 ($CMe_3$), 22.10 ppm ($Me$Se).

$(Ad_2C_2SeMe)^+SbCl_6^-$: Yield 1.96 g (90 %), mp. 140–141 °C (decomp). FAB-MS: $m/z$ 389 (55, $M^+$ for $^{80}$Se), 293 (47, $M^+$−MeSeH), 135 (100, $C_{10}H_{15}^+$). $^{77}$Se NMR ($CD_2Cl_2$): $\delta = -184.0$ ppm. $^{13}$C NMR ($CD_2Cl_2$): $\delta = 112.54$ (C=C); Ad: 34.75 (C1), 40.95 (C2), 28.01 (C3), 35.77 (C4); 23.27 ppm ($Me$Se).

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**Keywords:** Ab initio calculations · NMR spectroscopy · selenium · tellurium · X-ray diffraction

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[17] a) Crystal data for $(\mathrm{Ad_2C_2SePh})^+\mathrm{SbCl_6}^-\cdot\mathrm{CH_2Cl_2}$ ($\mathrm{C_{28}H_{35}Cl_6SbSe\cdot CH_2Cl_2}$): $M_r = 869.95$, monoclinic, $P2/c$, $a = 1877.0(5)$, $b = 1021.6(2)$, $c = 1980.1(5)$ pm, $\beta = 115.2(0)^\circ$, $V = 3434.5(14) \times 10^6$ pm$^3$, $Z = 4$, 23895 measured and 4807 independent reflections, 364 parameters, $GooF = 1.009$, $R_1 = 0.0441$, $wR_2 = 0.1222$. b) Crystal data for $(t\mathrm{Bu_2C_2SeMe})^+\mathrm{SbCl_6}^-\cdot 0.5\,\mathrm{CH_2Cl_2}$ ($\mathrm{C_{11}H_{21}Cl_6SbSe\cdot 0.5\,CH_2Cl_2}$): $M_r = 609.15$, orthorhombic, $Cmc2_1$, $a = 1491.73(16)$, $b = 3618.4(4)$, $c = 1670.6(3)$ pm, $V = 9017(2) \times 10^6$ pm$^3$, $Z = 16$, 55909 measured and 14210 independent reflections, 538 parameters, $GooF = 1.003$, $R_1 = 0.0278$, $wR_2 = 0.0679$. c) Crystal data for $(t\mathrm{Bu_2C_2TePh})^+\mathrm{SbF_6}^-\cdot 1.5\,\mathrm{CCl_4}$ ($\mathrm{C_{16}H_{23}F_6SbTe\cdot 1.5\,CCl_4}$): $M_r = 809.41$, monoclinic, $P2/c$, $a = 1649.0(7)$, $b = 935.3(4)$, $c = 1954.1(8)$ pm, $\beta = 110.01(1)^\circ$, $V = 2832(2) \times 10^6$ pm$^3$, $Z = 4$, 34549 measured and 6845 independent reflections, 336 parameters, $GooF = 1.092$, $R_1 = 0.0737$, $wR_2 = 0.1941$. CCDC-638635 ($(\mathrm{Ad_2C_2SePh})^+\mathrm{SbCl_6}^-\cdot\mathrm{CH_2Cl_2}$), CCDC-683631 ($(t\mathrm{Bu_2C_2SeMe})^+\mathrm{SbCl_6}^-\cdot 0.5\,\mathrm{CH_2Cl_2}$), and CCDC-683634 ($(t\mathrm{Bu_2C_2TePh})^+\mathrm{SbF_6}^-\cdot 1.5\,\mathrm{CCl_4}$) 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.

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