One-Electron Oxidants

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XeF_2/Fluoride Acceptors as Versatile One-Electron Oxidants**

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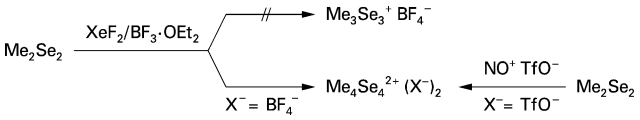
The special bonding situation in three-membered cyclic selenirenium ions[1] was planned to be investigated by an experimental electron density distribution. For this purpose the anions of these salts should contain only light elements. The idea was to synthesize $Me_3Se_3^+$ BF_4^- as the $MeSe^+$ transfer reagent by oxidation of Me_2Se_2 with XeF_2 and $BF_3{\cdot}OEt_2$ as fluoride acceptor, similar to the preparation of $Me_3Se_3^+$ $SbCl_6^-$.[2] Surprisingly however, this oxidation led to the four-membered cyclic $Me_4Se_4^{2+}$ $(BF_4^-)_2$ rather than to $Me_3Se_3^+$ BF_4^- (Scheme 1).



Scheme 1. Oxidations of Me_2Se_2.

This result indicates that $XeF_2/BF_3{\cdot}OEt_2$ acts as one-electron oxidant, as $R_4E_4^{2+}$ $(TfO^-)_2$ (E = Se, Te) have been prepared by oxidation of the dialkyl dichalcogenides R_2E_2 with the one-electron oxidant NO^+ TfO^- ($Tf = CF_3SO_2$)[3a] (see also Ref. [3b]). The structure of the dication in $Me_4Se_4^{2+}$ $(BF_4^-)_2$ is identical to the cation in $Me_4Se_4^{2+}$ $(TfO^-)_2$[3a] (Figure 1).

The 50 year-old species XeF_2[4] has become a convenient fluorination agent,[5,6] and in particular in the chemistry of chalcogens.[7] It can act as ligand in metal complexes,[6] and it is an important starting material for organoxenon compounds.[8] There have only been two reports on oxidation reactions with XeF_2/BF_3: the oxidation of Ar_4S to Ar_4S^{2+} $(BF_4^-)_2$[9] and the oxidative carbonylation of metal carbonyls, for example, $[Fe(CO)_5]$ to $[Fe(CO)_6]^{2+}$ $(BF_4^-)_2$.[10] Both reactions are two-electron oxidations. The authors did not recognize the potential of XeF_2/BF_3 as one-electron oxidant, and the use of other fluoride ion acceptors was also not attempted.

Since Lavoisier, oxidation has been a fundamental chemical reaction,[11] and potent one-electron oxidants are very important reagents. Therefore we investigated the combination XeF_2 with fluoride ion acceptors as a general principle for new one-electron oxidants. Fluoride ion acceptors tested by us include 1) non-oxidative Lewis acids (LA), such as BF_3, $B(C_6F_5)_3$, and $Al\{OC(CF_3)_3\}_3$; and 2) silylated derivatives of strong Brønsted acids (A–SiR_3), such as $TfOSiMe_3$, Tf_2NSiMe_3, $F_5TeOSiMe_3$, Me_3Si^+ $B(C_6F_5)_4^-$, $(Et_3Si^+)_2$ $B_{12}Cl_{12}^{2-}$, and Me_3Si^+ $CHB_{11}Cl_{11}^-$.

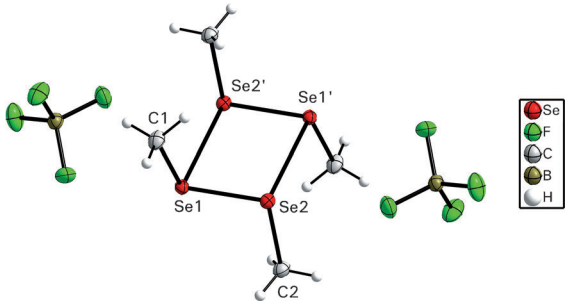


Figure 1. Molecular structure of $Me_4Se_4^{2+}$ $(BF_4^-)_2$. Ellipsoids are set at 50% probability; selected parameters [pm,°]: Se1–Se2 225.92(4), Se1–Se2′ 298.94(4), Se1–C1 194.57(3), Se2–C2 194.76(3); Se1-Se2-Se1′ 90.472(3).

Anions for cationic oxidation products could be generated in two ways: Lewis acids form fluoroanions LA–F^- under fluoride ion abstraction, while with A–SiR_3 the fluoride is fixed as R_3SiF and the anion A^- is set free [Equations (1) and (2)]:

$$2\,LA + XeF_2 + 2\,e^- \rightarrow 2\,LA{-}F^- + Xe \quad (1)$$

$$2\,R_3Si{-}A + XeF_2 + 2\,e^- \rightarrow 2\,A^- + 2\,R_3SiF + Xe \quad (2)$$

The introduction of weakly coordinating anions[12] in oxidation products has been a particularly important aspect. Model compounds to be oxidized have been dichalcogenides and compounds that form reversible redox systems[13,14] with a known oxidation potential: ferrocene, thianthrene, tris(2,4-dibromphenyl) amine, tetrathiafulvalene (TTF),[15] and the iron–sulfur cluster $[(FeCpS)_4]$[16] (Table 1). The broadness of application and the oxidation strength is to be established.

Oxidation of Me_2Se_2 or Me_2Te_2 in CH_2Cl_2 with Me_2E_2/XeF_2/fluoride ion acceptor in a molar ratio of 2:1:2 produce the cyclic $Me_4Se_4^{2+}$ and $Me_4Te_4^{2+}$ salts (often in very good yields): The orange–yellow colored $Me_4Se_4^{2+}$ $(BF_4^-)_2$, $Me_4Se_4^{2+}$ $(TfO^-)_2$, $Me_4Se_4^{2+}$ $(Tf_2N^-)_2$, $Me_4Se_4^{2+}$ $\{FB(C_6F_5)_3^-\}_2$, $Me_4Se_4^{2+}$ $\{B(C_6F_5)_4^-\}_2$, and the wine-red $Me_4Te_4^{2+}$ $(Tf_2N^-)_2$ (for the structure, see the Supporting Information, Figure S1), $Me_4Te_4^{2+}$ $\{FB(C_6F_5)_3^-\}_2$, and $Me_4Te_4^{2+}$ $\{B(C_6F_5)_4^-\}_2$ as first $Me_4Te_4^{2+}$ salts[3] (Scheme 2). Ph_2Se_2 and Ph_2Te_2 do not give cyclic dications. However, the oxidation of the diselenide $\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}_2Se_2$ with XeF_2 and two equivalents of

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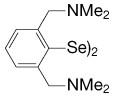
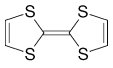
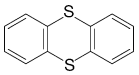
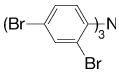
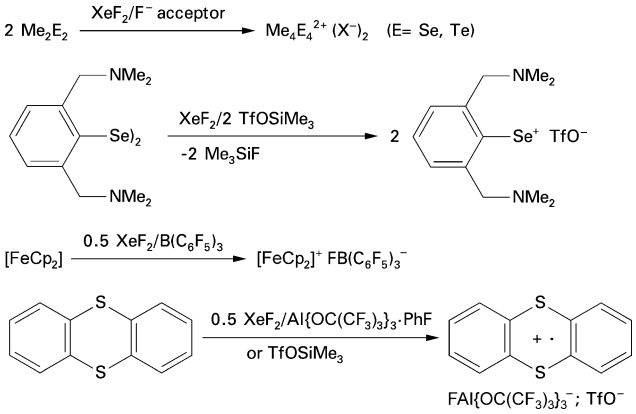
Table 1: Model compounds to be oxidized, oxidation potentials in V vs. NHE.[a]

Me_2S_2, 1.65[17] Me_2Se_2 Me_2Te_2	Ph_2S_2 1.75[18] Ph_2Se_2 1.59[19] Ph_2Te_2 0.99[20]	$[FeCp_2]$ 0.7[14]	$[(FeCpS)_4]$ $^0/^+$ −0.05, $^+/^{2+}$ 0.57[16a]
	 TTF $^0/^+$ 0.58, $^+/^{2+}$ 0.95[21]	 Thianthrene 1.56[14]	 1.84[14]

[a] Conversion from SCE to NHE: 0.2415 V, Ag/0.1 M $AgNO_3$/SCE 0.36 V, $[FeCp_2]^+/[FeCp_2]$/SCE 0.46 V; Ref. [14].



Scheme 2. Oxidations of Me_2Se_2, Me_2Te_2, $\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}_2Se_2$, ferrocene, and thianthrene.

$TfOSiMe_3$ gives the only known stable selenenium salt[22,7b] as the triflate in high yield (Scheme 2; structure: Supporting Information, Figure S2).

Oxidation of ferrocene with XeF_2 in presence of $B(C_6F_5)_3$ produces the dark blue ferrocenium fluoroborate salt $[FeCp_2]^+$ $FB(C_6F_5)_3^-$ in quantitative yield (Scheme 2; structure: Supporting Information, Figure S3).

Thianthrene, with a 0.86 V higher oxidation potential, is quantitatively oxidized to the deep-violet thianthrenium triflate and is oxidized with XeF_2 and the Lewis superacid $Al\{OC(CF_3)_3\}_3\cdot PhF$[23] into the wine-red $C_{12}H_8S_2^{+\bullet}$ $FAl\{OC(CF_3)_3\}_3^-$ (Scheme 2).

The crystal structure of the fluoroaluminate salt in Figure 2 was difficult to obtain. The thianthrenium ion is strongly flattened (14.37°) in contrast to the neutral molecule[24] (128°). The anion is partially disordered. The Al–F bond (165.74(6) pm) agrees with recent values.[25a] In the fluorine-bridged anion $F[Al\{OC(CF_3)_3\}_3]_2^-$, the Al–F distances are markedly larger (176.1 pm); at the same time the Al–O bonds are slightly shorter (169 pm).[25]

The model compound that was most difficult to oxidize is tris(2,4-dibromphenyl)amine. Oxidation was achieved with XeF_2 and $BF_3\cdot OEt_2$ or Tf_2NSiMe_3, resulting in dark-green aminium radical salts. $(2,4\text{-}Br_2C_6H_3)_3N$ has been oxidized with the strong oxidizers $SbCl_5$, SbF_5, or Br_2/Ag^+ $CH_6B_{11}Br_6^-$ to the aminium salts,[26] which are strong oxidants by themselves.

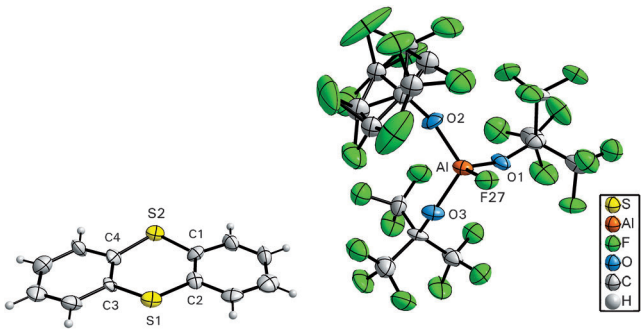
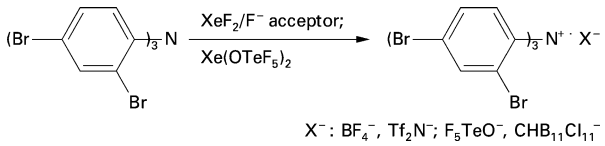


Figure 2. Molecular structure of $C_{12}H_8S_2^{+\bullet}$ $FAl\{OC(CF_3)_3\}_3^-\cdot 0.5\,Et_2O$, without solvent molecule, ellipsoids set at 50% probability; selected parameters [pm,°]: Al–F27 165.74(6), Al–O1 172.95(7), Al–O2 170.73(6), Al–O3 171.50(7), S1–C2 171.40(7), S1–C3 172.81(7), S2–C1 173.15(7), S2–C4 170.39(6); C2-S1-C3 106.517(36), C4-S2-C1 106.965(36); intermolecular S···S 298.34(13); folding angle between the two benzene ring planes 14.37 (2).

In contrast, $XeF_2/F_5TeOSiMe_3$ is not suitable for the oxidation of this amine. Because of the nearly similar electronegativity of fluorine and the $OTeF_5$ group,[27] the formation of Me_3SiF is energetically not favored, so XeF_2 is not activated. If $Xe(OTeF_5)_2$ is used, however, the reaction occurs at a temperature as low as −78°, but the resulting radical salts are oils and crystallize very slowly.

The use of $(Et_3Si^+)_2$ $B_{12}Cl_{12}^{2-}$[28a] for oxidations of $(2,4\text{-}Br_2C_6H_3)_3N$, thianthrene, Me_2Te_2, and TTF with XeF_2 results in very rapid reactions, even at −78 °C, which was indicated by a color change, but often only very insoluble and poorly characterizable solids are formed. Therefore, the anion $B_{12}Cl_{12}^{2-}$[28] seems to be less well-suited for such oxidations. However, the oxidation of $(2,4\text{-}Br_2C_6H_3)_3N$ with XeF_2 and Me_3Si^+ $CHB_{11}Cl_{11}^-$ produces the dark green, crystalline radical salt $(2,4\text{-}Br_2C_6H_3)_3N^{+\bullet}$ $CHB_{11}Cl_{11}^-$. For this compound, which is soluble in CH_2Cl_2, no single crystals could be obtained (Scheme 3).

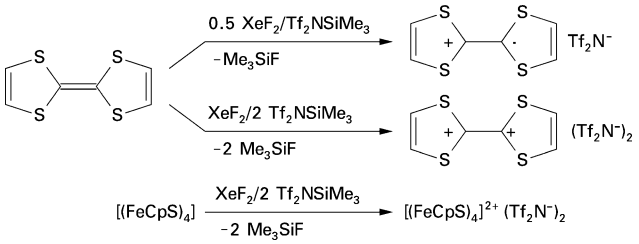


Scheme 3. Oxidations of $(2,4\text{-}Br_2C_6H_3)_3N$.

One- and two-step oxidations have been investigated with TTF[13,15,21] and $[(FeCpS)_4]$.[16] TTF is oxidized by XeF_2 and Tf_2NSiMe_3 to the brown-colored $TTF^{+\bullet}$ Tf_2N^- (structure: Supporting Information, Figure S4), as well as to the yellow TTF^{2+} $(Tf_2N^-)_2$.

$[(FeCpS)_4]$ is oxidized by XeF_2 and two equivalents of Tf_2NSiMe_3 directly to the black dication salt $[(FeCpS)_4]^{2+}$ $(Tf_2N^-)_2$ (Scheme 4; structure: Figure 3). $[(FeCpS)_4]^{2+}$ $(Tf_2N^-)_2$ has a distorted Fe_4S_4 cube.[16] The multistep reactions were carried out in propionitrile to avoid crystallizations of intermediates, whereas the previously presented reactions were carried out in CH_2Cl_2.

In search for new $MeSe^+$ transfer agents $Me_4Se_4^{2+}$ $(Tf_2N^-)_2$ is reacted with *t*BuC≡C*t*Bu at −40 °C. NMR analysis



Scheme 4. Oxidations of TTF and $[(FeCpS)_4]$.

at this temperature confirms that $Me_4Se_4^{2+}$ reacts completely to the methylselenirenium ion and Me_2Se_2; thus two $MeSe^+$ equivalents are transferred. $Me_4Te_4^{2+}$ $(Tf_2N^-)_2$ does not react with the same acetylene at −40 °C within 2 h.

An alternative is the direct generation of RSe^+ and RTe^+ ions. $PhSe^+$, $MeSe^+$, $PhTe^+$, or $MeTe^+$ ions have been formed in situ by double oxidation of the corresponding dichalcogenides with $XeF_2/2\,Tf_2NSiMe_3$ at −40 °C and add quantitatively to *t*BuC≡C*t*Bu. By this way selenirenium and tellurirenium ions,[1] for the first time even MeTe compounds can be prepared easily in a one-pot reaction. Ph_2Se_2 and $XeF_2/2\,BF_3{\cdot}OEt_2$ react with 2,3-dimethylbutadiene quantitatively to 1-phenyl-3,4-dimetyl-2,5-dihydroselenophenium tetrafluoroborate (Scheme 5; for $ArTe^+$ ions, see also Ref. [29,30]).

These results can be extended to the more difficult-to-oxidize disulfides. Me_2S_2 reacts with XeF_2 and two equivalents of Me_3Si^+ $CHB_{11}Cl_{11}^-$ in the presence of *t*BuC≡C*t*Bu to the methylthiirenium carborate salt $[tBu_2C_2SMe]^+$ $CHB_{11}Cl_{11}^-$ (structure: Figure 4). The structural parameters of the $[tBu_2C_2SMe]^+$ ion are similar to these in $[tBu_2C_2SMe]^+$ BF_4^-.[31] Similarly the reaction of Ph_2S_2 with XeF_2, two equivalents Me_3Si^+ $B(C_6F_5)_4^-$, and *t*BuC≡C*t*Bu gives the phenylthiireniumsalt $[tBu_2C_2SPh]^+$ $B(C_6F_5)_4^-$ (structure: Supporting Information, Figure S5); with XeF_2/Tf_2NSiMe_3, $[tBu_2C_2SPh]^+$ Tf_2N^- is formed (Scheme 6).

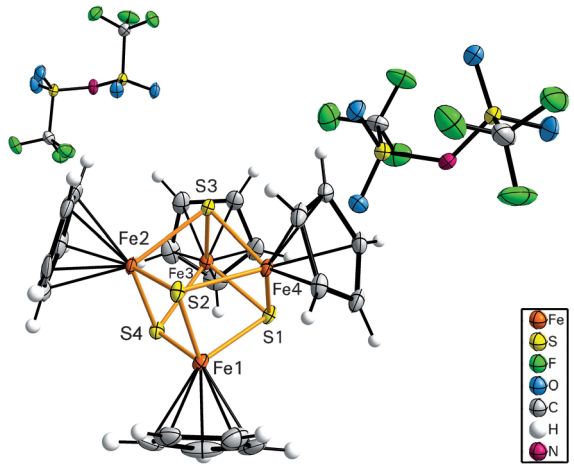
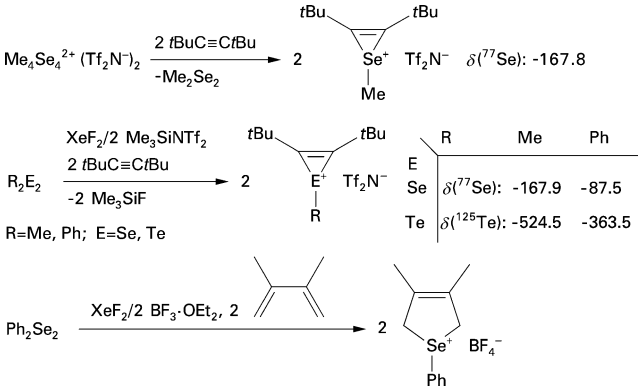


Figure 3. Molecular structure of $[(FeCpS)_4]^{2+}$ $(Tf_2N^-)_2{\cdot}2\,CH_2Cl_2$, solvent molecules omitted, ellipsoids set at 50% probability; selected parameters [pm,°]: Fe1–S1 220.91(11), Fe3–S1 228.77(11), Fe4–S1 218.73(11), Fe1–S2 218.15(11), Fe2–S2 222.74(11), Fe4–S2 208.52(10), Fe2–S3 220.39(11), Fe3–S3 219.58(11), Fe4–S3 227.46(12), Fe1–S4 223.43(12), Fe2–S4 218.30(11), Fe3–S4 211.17(12); anion: C23–S5···S6–C22 −167.486(202), C24–S7···S8–C25 170.722(256).



Scheme 5. Generation of RE^+ transfer agents by oxidation and their addition reactions.

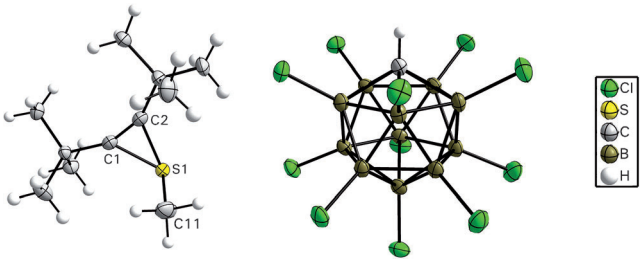
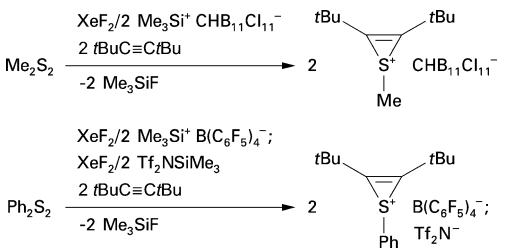


Figure 4. Molecular structure of $[tBu_2C_2SMe]^+$ $CHB_{11}Cl_{11}^-{\cdot}CH_2Cl_2$, solvent molecule omitted, ellipsoids set at 50% probability; selected parameters [pm,°]: C1–C2 129.29(43), S1–C1 183.08(30), S1–C2 183.25(31), S1–C11 181.53(36); C1-S1-C2 41.32(13).

This direct generation of sulfenium ions from disulfides is without alternatives except electro-oxidation.[17,18,32] Whereas diselenides and ditellurides can be oxidized with NO^+ salts,[29,1,3] dialkyl disulfides and NO^+ salts form charge-transfer complexes without electron transfer[33] (standard potential of NO^+ in CH_2Cl_2: 1.7 V vs. NHE).[14] It is not known whether the stronger NO_2^+ salts can oxidize R_2S_2. In summary, a general method of direct generation of the RE^+ (E = S, Se, Te) from dialkyl und diaryldichalkogenides R_2E_2 is now available, and the often-used lengthy path via R_2E_2/Br_2 and an Ag^+ salt can be avoided.[34]

To estimate the maximal oxidation potential of the XeF_2/F^- acceptor reagents, we tried to oxidize C_{60}, which has an oxidation potential of 1.96 V vs. NHE.[35] After addition of the silylcarborate salt Me_3Si^+ $CHB_{11}Cl_{11}^-$ to a cold (−20 °C) C_{60} solution in *o*-dichlorobenzene, which already contains the



Scheme 6. Oxidative generation of RS^+ ions and the syntheses of thiirenium salts.

XeF_2, the violet color disappears immediately and turns to dark red/red brown after a few minutes. The same color change is also observed with XeF_2/Me_3Si^+ $B(C_6F_5)_4^-$ under otherwise the same conditions. This indicates the presence of the $C_{60}^{+\cdot}$ radical cation.[35] The oxidation of hexabromobenzene is not achieved: the green color of $C_6Br_6^{+\cdot}$ ions[36a] cannot be observed with XeF_2/Me_3Si^+ $CHB_{11}Cl_{11}^-$ in CH_2Cl_2 or SO_2ClF or with XeF_2/Me_3Si^+ $B(C_6F_5)_4^-$ in SO_2. The oxidation potential for such halogenobenzenes is not large enough.[36]

The new reagents presented herein with an oxidation potential of at least 2 V vs. NHE close the gap between the classical NO^+ salts and extreme oxidizers such as O_2^+, see the discussion of the oxidation with P_4.[37] The oxidizing power of the carboranyl radikal $CB_{11}Me_{12}^{\cdot}$ with 1.9 V is slightly smaller.[38]

With these new oxidation reagents very different anions can be introduced into cationic oxidation products, like the small BF_4^- and TfO^-, the medium-sized Tf_2N^-, and the large, weakly coordinating anions $FB(C_6F_5)_3^-$, $B(C_6F_5)_4^-$, $FAl\{OC(CF_3)_3\}_3^-$, $CHB_{11}Cl_{11}^-$ (and $B_{12}Cl_{12}^{2-}$). The oxidative force of the reagents is not stronger than the oxidation potential of the anions used.[39]

Increasing anion size enhances the solubility in non-polar solvents such as CH_2Cl_2. This hampers occasionally the growth of single crystals. The reaction can be carried out in glass equipment. Apart from Xe and R_3SiF, no side products are formed, so that the salts usually precipitate in high purity. If R_3SiF would interfere, or if the fluoride ion affinity needs to be very high, $Al\{OC(CF_3)_3\}_3$ is the reactant of choice. Other possible fluoride ion acceptors for oxidations with XeF_2 are Me_3Si^+ $CHB_{11}F_{11}^-$,[40] $C_6F_5C(Tf)_2SiMe_3$[41] and the to date unknown Me_3Si^+ $Al\{OC(CF_3)_3\}_4^-$. The activation of XeF_2 goes possibly via $XeF_2 \rightarrow XeF^+$ and finally $XeF \rightarrow Xe^+$. The intermediate ions XeF^+ and Xe^+ are the real oxidizers, which are able even to generate the green $(2,4\text{-}Br_2C_6H_3)_3N^{+\cdot}$ ion. The investigated model reactions only indicate the broadness of the method. Insofar the method can be used in the field of homopolyatomic cations,[42] and especially in oxidations of chalcogens or of P_4,[37] it needs to be tested by experiments in the future.

Experimental Section

Oxidations of Me_2Se_2: By a vacuum line, anhydrous CH_2Cl_2 (20 mL) was condensed to Me_2Se_2 (1.13 g, 6 mmol) at −196 °C. Under argon at −78 °C, XeF_2 (508 mg, 3 mmol) and by injection $BF_3{\cdot}OEt_2$ (852 mg, 6 mmol), $TfOSiMe_3$ (1.33 g, 6 mmol), or Tf_2NSiMe_3 (2,12 g, 6 mmol) were added, followed by 10 min stirring at −78 °C and 2 h at −40 °C. Diethyl ether (30 mL) was added, and the precipitated products are filtered off, washed with diethyl ether (3 × 15 mL), and dried in vacuum. Yields: $Me_4Se_4^{2+}$ $(BF_4^-)_2$ 1.6 g (97 %), $Me_4Se_4^{2+}$ $(TfO^-)_2$ 1 g (49 %), $Me_4Se_4^{2+}$ $(Tf_2N^-)_2$ 2.17 g (77 %).

Oxidations of thianthrene: Similar to above, thianthrene (433 mg, 2 mmol) was oxidized with XeF_2 (169 mg, 1 mmol) and $TfOSiMe_3$ (446 mg, 2 mmol) in CH_2Cl_2 (10 mL). Alternatively, a solution of $Al\{OC(CF_3)_3\}_3$ (2 mL, 1M in PhF) in PhF (10 mL) as solvent is used. The triflate is crystallized by addition of diethyl ether (30 mL), the aluminate with hexane (30 mL). $C_{12}H_8S_2^{+\cdot}$ TfO^-: yield 0.71 g (97 %), mp. 117–120 °C, ESI-MS: $[216.0073]^+$, $[148.9563]^-$, $C_{12}H_8S_2^{+\cdot}$ $FAl\{OC(CF_3)_3\}_3^-$: yield 0.8 g (41 %), ESI-MS: $[216.0057]^+$, $[750.9341]^-$.

Double oxidation of TTF und $[(FeCpS)_4]$: TTF (204 mg, 1 mmol) or $[(FeCpS)_4]$ (612 mg, 1 mmol) were oxidized with XeF_2 (169 mg, 1 mmol) and Tf_2NSiMe_3 (705 mg, 2 mmol) in EtCN (10 mL) in the same manner as described above. The salts are crystallized by addition of diethyl ether (80 mL). TTF^{2+} $(Tf_2N^-)_2$: yield 0.63 g (82 %), ESI-MS: $[203.9196]^+$, $[279.9181]^-$; $[(FeCpS)_4]^{2+}$ $(Tf_2N^-)_2$: yield 1.02 g (87 %), mp. 139–140 °C, ESI-MS: $[611.7877]^+$, $[279.9176]^-$.

Thiirenium salt $[t\text{Bu}_2C_2SMe]^+$ $CHB_{11}Cl_{11}^-$: At −196 °C, CH_2Cl_2 (5 mL) was condensed on Me_2S_2 (24 mg, 0.25 mmol) and tBuC≡CtBu (69 mg, 0.5 mmol). At −78 °C, XeF_2 (51 mg, 0.3 mmol) and Me_3Si^+ $CHB_{11}Cl_{11}^-$ (298 mg, 0.5 mmol) were added. Stirring 15 min at −78 °C and 2 h at −40 °C was followed by filtration and crystallization by addition of hexane (30 mL). $[t\text{Bu}_2C_2SMe]^+$ $CHB_{11}Cl_{11}^-$: yield 0.34 g (96 %), ESI-MS: $[185.1363]^+$, $[521.7685]^-$.

Further experimental details and data of the X-ray single-crystal structure determinations are given in the supporting information.

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