Electronic Supplementary Information

TeX_4 (X = F, Cl, Br) as Lewis acids – complexes with soft thio- and seleno-ether ligands

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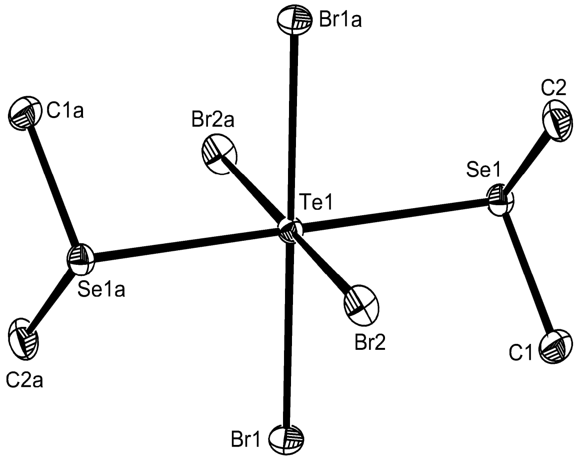

Fig. S1 Crystal structure of the centrosymmetric [$TeBr_4(SeMe_2)_2$] showing the atom numbering scheme. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Symmetry operation: a = – x, – y, – z. Selected bond lengths (Å) and angles (°): Te1–Br1 = 2.6726(7), Te1–Br2 = 2.6745(8), Te1–Se1 = 2.8789(7), Br1–Te1–Br2 = 89.55(2), Br1–Te1–Se1 = 91.23(2), Br2–Te1–Se1 = 90.54(2), C2–Se1–C1 = 96.47(16), C2–Se1–Te1 = 99.19(11), C1–Se1–Te1 = 98.99(11).

[$SeMe_3$]$_2$[$TeCl_6$]: On standing at ambient temperatures the initially intensely coloured dichloromethane solutions of [$TeX_4(SeMe_2)_2$] pale to yellow brown, and the chloride deposited a few crystals which were shown by a structure determination to be the selenonium salt [$SeMe_3$]$_2$[$TeCl_6$] (Table S1). Whilst the structure is unexceptional (and it is obviously not the only, maybe not even, the major product) it demonstrates ligand fragmentation is facile in these systems.

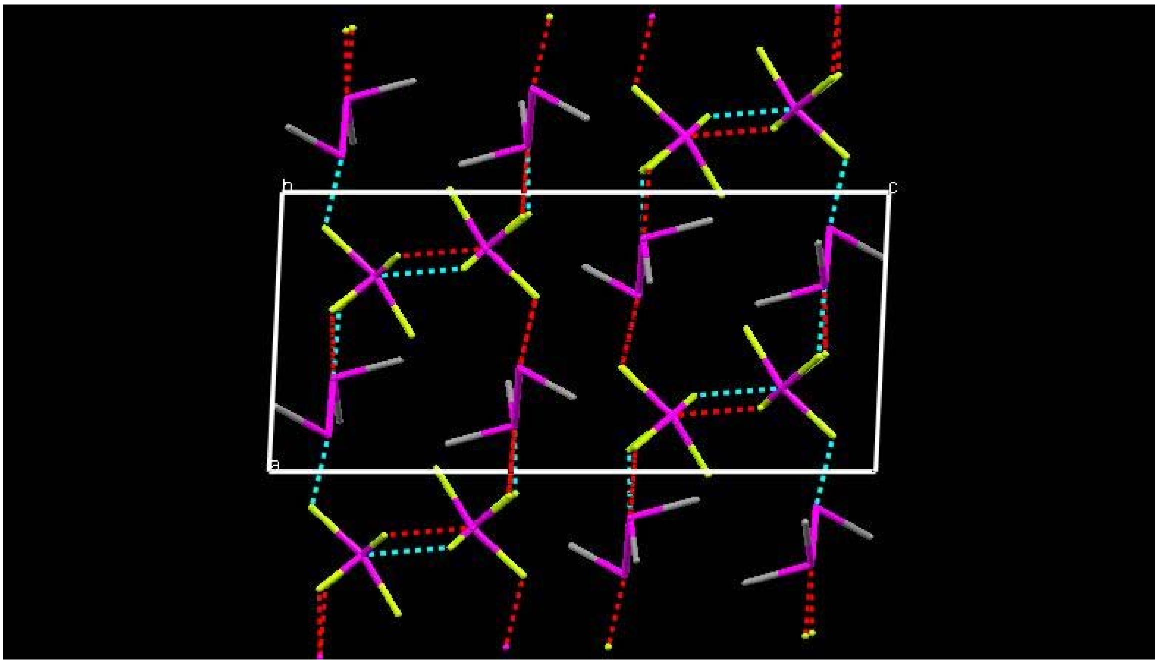

Fig. S2 View of the extended structure of [$Me_2SeSeMe$][TeF_5] (Table S1). The [TeF_5]$^-$ anions link into chains (Te1···F3) and these link to the cation *via* F···Se1 and F···Se2 contacts to form sheets.

Reaction of *o*-$C_6H_4(CH_2SeCH_3)_2$ with $TeCl_4$: $TeCl_4$ (0.268 g, 9.95×10^{-4} mol) was suspended in CH_2Cl_2 (40 mL) and the mixture was cooled to 0 °C with the aid of an external ice bath. With stirring, there was added *o*-$C_6H_4(CH_2SeCH_3)_2$ (0.17 mL, 1.05×10^{-3} mol), which caused a rapid colour change to orange-yellow, concomitant with the formation of a yellow precipitate. The mixture was stirred at 0 °C for a further 30 mins, after which time more solid appeared to have formed. This was collected by filtration, washed with CH_2Cl_2 and dried *in vacuo*. Storage of the filtrate at *ca*. −18 °C yielded more of the yellow powder product. Combined yield: 0.213 g. This product was identified as the cyclic selenonium salt [$C_9H_{11}Se$]$_2$[$TeCl_6$]. $^{77}Se\{^1H\}$ NMR (DMF/$(CD_3)_2CO$, 298 K): 407 (s). MS (ES$^+$, MeCN): m/z = 199. IR (Nujol/cm^{-1}): 248 ([$TeCl_6$]$^{2-}$).

Reaction of *o*-$C_6H_4(CH_2SeCH_3)_2$ with $TeBr_4$: Analogous procedure, using $TeBr_4$ (0.231 g, 5.17×10^{-4} mol), *o*-$C_6H_4(CH_2SeCH_3)_2$ (0.08 mL, 4.93×10^{-4} mol) and THF (20 mL). Orange solid. Yield: 0.273 g. The product was identified as the cyclic selenonium salt [$C_9H_{11}Se$]$_2$[$TeBr_6$]. Elemental analysis, calculated for $C_{18}H_{22}Se_2Br_6Te$ (%): C, 21.5; H, 2.2. Found: C, 21.2; H, 2.2. $^{77}Se\{^1H\}$ NMR (DMF/$(CD_3)_2CO$, 298 K): 406 (s).

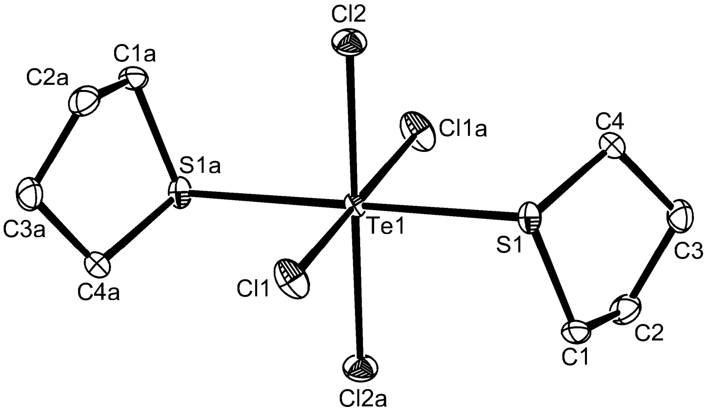

Fig. S3 Crystal structure of *trans*-[$TeCl_4(tht)_2$] showing the atom numbering scheme. Te1 is positioned on a centre of symmetry. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Symmetry operation: a = –x, –y, –z. Selected bond lengths (Å) and angles (°): Te1–Cl1 = 2.5038(10), Te1–Cl2 = 2.5079(7), Te1–S1 = 2.7502(8), Cl1–Te1–Cl2 = 90.39(2), Cl1–Te1–S1 = 83.70(3), Cl2–Te1–S1 = 83.59(3).

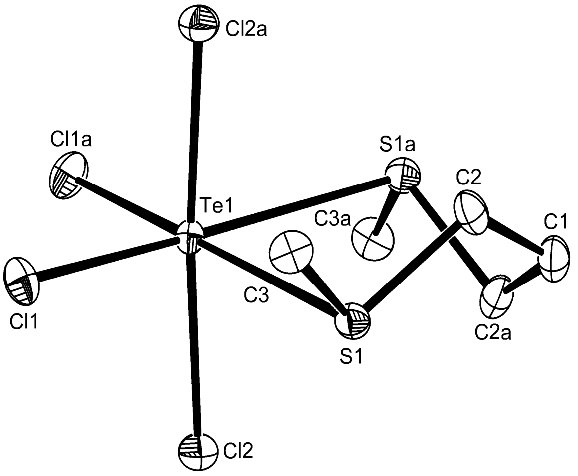

Fig. S4 Crystal structure of the [$TeCl_4\{MeS(CH_2)_3SMe\}$] showing the atom numbering scheme. The molecule has two-fold symmetry. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Symmetry operation: a = 1 – x, 1/2 – y, z. Selected bond lengths (Å) and angles (°): Te1–Cl1 = 2.431(1), Te1–Cl2 = 2.502(2), Te1–S1 = 2.866(1), Cl1–Te1–Cl1a = 93.53(7), Cl1–Te1–Cl2a = 89.96(5), Cl1–Te1–Cl2 = 93.15(5), Cl2–Te1–Cl2a = 175.46(6), Cl1–Te1–S1a = 173.12(5), Cl1–Te1–S1 = 92.19(5), Cl2–Te1–S1 = 85.90(4), Cl2–Te1–S1a = 90.68(4), S1–Te1–S1a 82.37(6).

Table S1 Crystal data and structure refinement details[a]

Compound	$[SeMe_3]_2[TeCl_6]$	$[Me_2SeSeMe][TeF_5]$
Formula	$C_6H_{18}Cl_6Se_2Te$	$C_3H_9F_5Se_2Te$
M	588.42	425.62
Crystal system	Cubic	Monoclinic
Space group (no.)	Pa–3 (205)	$P2_1/n$ (14)
a /Å	12.513(3)	7.864(3)
b /Å	12.513(3)	7.253(2)
c /Å	12.513(3)	17.044(6)
α /°	90	90
β /°	90	92.737(7)
γ /°	90	90
U /Å^3	1959.2(8)	971.1(5)
Z	4	4
μ(Mo-K$_\alpha$) /mm^{-1}	6.029	10.577
F(000)	1104	768
Total number reflns	6437	5338
R_{int}	0.136	0.041
Unique reflns	662	2205
No. of parameters, restraints	25, 0	103, 0
R_1, wR_2 [$I > 2\sigma(I)$][b]	0.059, 0.097	0.027, 0.056
R_1, wR_2 (all data)	0.108, 0.112	0.037, 0.058

temperature = 100 K; wavelength (Mo-K$_\alpha$) = 0.71073 Å; θ(max) = 27.5°. b $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$