

Perfluoroalkyltellurocarbonyl fluorides, their cyclic dimers and perfluoroalkanetellurenyl iodides: preparation and reactivity†

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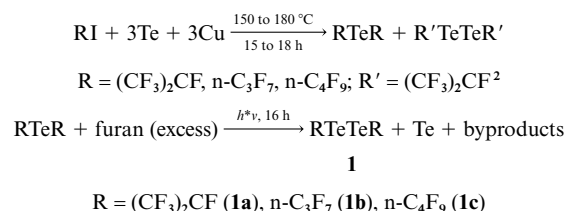
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With the synthesis of new perfluoroalkyltellurocarbonyls, their precursors and cyclic dimers additional valuable information about these classes of compounds has become available. They were prepared *via* pyrolysis of $\text{Me}_3\text{SnTeCF}(\text{CF}_3)_2$ and the novel compounds Me_3SnTeR ($\text{R} = \text{n-C}_3\text{F}_7$, $\text{n-C}_4\text{F}_9$). The monomer $(\text{CF}_3)_2\text{C}=\text{Te}$ could not be detected as it dimerises quantitatively to the corresponding 1,3-ditellurethane. It was possible to isolate $\text{R}(\text{F})\text{C}=\text{Te}$ ($\text{R} = \text{C}_2\text{F}_5$, $\text{n-C}_3\text{F}_7$) at -196°C , but slightly above this temperature, these compounds cyclise to mixtures of *cis/trans* 1,3-ditellurethanes. The tellurocarbonyls undergo $[4 + 2]$ -cycloaddition reactions with 2,3-dimethylbutadiene providing the corresponding tellurins. The reaction between RTeTeR and mercury yielded $\text{Hg}(\text{TeR})_2$ which have been converted with iodine in CH_2Cl_2 solution to RTeI . With AgCN the *in situ* prepared iodides form RTeCN ($\text{R} = \text{CF}(\text{CF}_3)_2$, $\text{n-C}_3\text{F}_7$, $\text{n-C}_4\text{F}_9$) in good yields. A new type of compound has been synthesized by chlorination of tetrafluoro-1,3-ditellurethane: 1,3-dichloro-2,2,4,4-tetrafluoro-1 λ^4 ,3 λ^4 -ditellurabicyclo[1.1.0]butane. It is only stable below -20°C and rearranges almost quantitatively at room temperature to $\text{ClF}_2\text{CTeTeCF}_2\text{Cl}$.

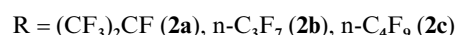
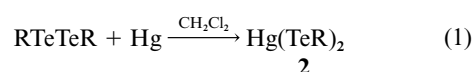
In 1991 the preparation and characterisation of the first compound with a $\text{C}=\text{Te}$ double bond was published. Meanwhile other examples were synthesized. Their stability is based either on the perfluoro effect or on bulky ligands. In Chart 1 the pub-

irradiating monotellurides dissolved in furan with UV-light as demonstrated in Scheme 1. The ditellurides **1a**, **1b** and **1c** reacted

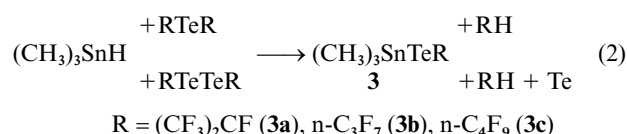


Scheme 1

with Hg in CH_2Cl_2 yielding $\text{Hg}(\text{TeR})_2$ as shown in eqn. (1).



Metathesis of RTe_xR ($x = 1, 2$) with $(\text{CH}_3)_3\text{SnH}$ provided $(\text{CH}_3)_3\text{SnTeR}$ according to eqn. (2).



The aim of this paper is: to prove that pyrolysis of $(\text{CH}_3)_3\text{SnTeR}$ provides new highly reactive tellurocarbonyls, to study their chemistry and to synthesize perfluoroalkyltellurenyl reactants as versatile synthons.

Results and discussion

The pyrolysis of $(\text{CH}_3)_3\text{SnTeCF}(\text{CF}_3)_2$ at 500°C and 10^{-3} Torr provided for the first time, compared with analogous reactions, not the monomer $(\text{CF}_3)_2\text{C}=\text{Te}$, but its cyclic dimer. The very


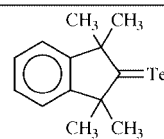
		
	$\text{R} = \text{F}, \text{CF}_3$	
Type of stabilisation	electronegative substituents (perfluoro effect)	kinetically (steric shielding)
characterisation	MS-, IR-, PE-spectra	UV, ^{13}C , ^{125}Te NMR
reactivity	highly	modest
stability	only at -196°C	stable up to 70°C
chemical reactivity	a) dimerisation b) codimerisation of $\text{F}_2\text{C}=\text{Te}$ with $\text{F}_2\text{C}=\text{Se}$ c) $[4 + 2]$ -cycloaddition with 2,3-dimethylbutadiene	a) reversible dimerisation ¹ b) $[4 + 2]$ -cycloaddition with 2,3-dimethylbutadiene and mesonitrile (MesCNO)

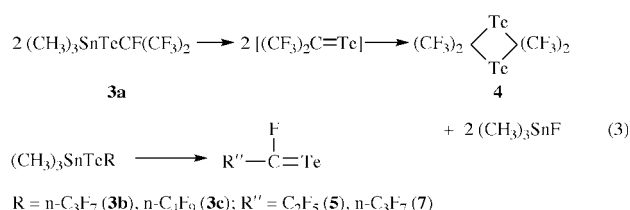
Chart 1

lished tellurocarbonyls are listed with their known properties. The best synthesis for perfluorinated tellurocarbonyls is the pyrolysis of $(\text{CH}_3)_3\text{SnTeR}$ ($\text{R} = \text{CF}_3$,¹ C_2F_5 ,² made by reacting $(\text{CH}_3)_3\text{SnH}$ with $\text{R}_f\text{Te}_x\text{R}_f$ ($x = 1, 2$); methods which proved to be generally applicable. The required starting materials, such as RTe_xR ($x = 1$, $\text{R} = (\text{CF}_3)_2\text{CF}$, $\text{n-C}_3\text{F}_7$, $\text{n-C}_4\text{F}_9$, $x = 2$, $\text{R} = (\text{CF}_3)_2\text{CF}$,² $\text{n-C}_3\text{F}_7$, $\text{n-C}_4\text{F}_9$) were made from RI and Te in the presence of copper as a catalyst.² The ditellurides were also made by

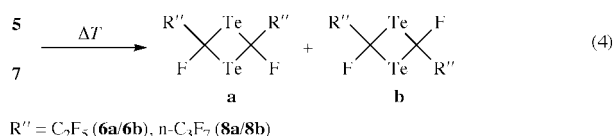
† Supplementary data available: rotatable 3-D crystal structure diagram in CHIME format. See <http://www.rsc.org/suppdata/dt/a9/a907549f/>

Also available: NMR, IR and mass spectroscopic data for compounds **1b–15c**. See <http://www.rsc.org/suppdata/dt/a9/a907549f/>. See Instructions for Authors, 2000, Issue 1 (<http://www.rsc.org/dalton>).

unstable intermediate (and there can be no doubt that it is formed primarily) condensed at -196°C already in its dimeric form. With other perfluoroalkyl groups the corresponding monomers **5** and **7**, formed according to eqn. (3), could be



isolated and characterised by IR **5** and mass spectra **5**, **7**. On warming compounds **5** and **7** a few degrees above -196°C a spontaneous change of colour from green to red was observed, yielding quantitative formation of the *cis/trans*-isomers of **6** and **8** [eqn. (4)].



With the aid of a special apparatus^{1,2} compound **5**, generated by pyrolysis of **3a**, was allowed to pass through an IR cell before being trapped at -196°C . In this manner the IR spectrum of pure gaseous **5** was obtained. If the pyrolysis apparatus was coupled to the gas inlet of a mass spectrometer, the mass spectra of **5** and **7** could be registered. Although ν_1 [$\nu_{\text{asm}}(\text{C}=\text{Te})$] = 1240.0 cm^{-1} and ν_4 [$\nu_{\text{asm}}(\text{CF}_2)$] = 1206.7 , 1095.4 cm^{-1} were assigned to $\text{Te}=\text{CF}_2$,¹ it was not possible to assign vibrations of strong to medium intensities in the area of 1257 to 1140 cm^{-1} for **5**, because any assignment would have remained speculative and was therefore avoided. The mass spectra of compounds **5** and **7** showed M^+ and the expected fragmentation pattern being different from those of the corresponding dimers **6a/6b** and **8a/8b**.

Chemical evidence for the formation of $(\text{CF}_3)_2\text{C}=\text{Te}$, **5** and **7** comes from their dimerisation either immediately or by warming the product trap. The mixtures of *cis/trans*-isomers cannot be separated by physical methods, including preparative gas chromatography [eqn. (4)].

Crystal structure of compounds **4** and **4a**

The compounds **4** and **4a** are isostructural and both are isotopic to *trans*- $[(\text{F}_3\text{C})(\text{F})\text{C}=\text{Se}]_2$ ⁵ and $[(\text{F}_3\text{C})(\text{F})\text{C}=\text{Te}]_2$.²

Views of the molecules are given in Fig. 1, selected bond lengths and angles in Table 1. Both molecules are centrosymmetric with molecular symmetry C_i and contain a planar C_2Te_2 ring. The transannular Te–Te distance is 3.246 \AA for **4**, and 3.1263 \AA for **4a** which is longer than a Te–Te single bond, e.g. 2.669 \AA in $(\text{F}_3\text{C})\text{TeTe}(\text{CF}_3)$,⁶ but much less than the sum of the van der Waals radii (4.40 \AA).⁷ Transannular Te–Te distances of these lengths are typical for molecules with C_2Te_2 rings: $[(\text{F}_3\text{C})(\text{F})\text{C}=\text{Te}]_2$ 3.271 \AA , $[\text{F}_2\text{C}=\text{Te}]_2$ 3.385 \AA .^{1a} In the structure of **4a** the molecules are present in the *trans* form. The C(1)–Cl bond of 1.77 \AA is in the expected range. The structure determination did not reach very high levels of accuracy. Especially the C(2)–F(2) bond with a length of 1.10 \AA is unreasonably short. The peaks in the residual electron density map can be interpreted by positioning a second Cl atom near F(2) and a second CF_3 group near Cl. The attempts to refine a disordered model with a superposed second molecule of $[(\text{F}_3\text{C})\text{C}=\text{Te}]_2$ in the ratio 80:20 generated by a twofold rotation around the C(1)–C(1') axis resulted not in lowering the reliability factors but in some instability of the refinement. The marked effects of *cis/trans* disorder or dynamic exchange as

Table 1 Selected bond lengths (\AA) and angles ($^{\circ}$) for compounds **4** and **4a**

$[(\text{F}_3\text{C})_2\text{C}=\text{Te}]_2$ 4		$[(\text{F}_3\text{C})(\text{Cl})\text{C}=\text{Te}]_2$ 4a	
Te–C(1)	2.172(3)	Te–C(1)	2.16(1)
Te–C(1)	2.171(3)	Te–C(1')	2.22(1)
C(1)–C(11)	1.526(5)	C(1)–Cl	1.77(1)
C(1)–C(21)	1.517(5)	C(1)–C(2)	1.58(3)
C(11)–F(11)	1.325(5)	C(2)–F(1)	1.27(2)
C(11)–F(12)	1.388(4)	C(2)–F(2)	1.10(2)
C(11)–F(13)	1.314(5)	C(2)–F(3)	1.33(2)
C(21)–F(21)	1.322(5)		
C(21)–F(22)	1.329(4)		
C(21)–F(23)	1.320(5)		
Te–C(1)–Te	96.8(1)	Te–C(1)–Te'	97.0
C(1)–Te–C(1)	83.2(1)	C(1)–Te–C(1')	83.0(5)
C(11)–C(1)–C(21)	111.6(3)	C(2)–C(1)–Cl	109(1)
C(11)–C(1)–Te	111.3(2)	Te–C(1)–Cl	112.5(7)
C(11)–C(1)–Te'	111.9(2)	Te'–C(1)–Cl	114.1(8)
C(21)–C(1)–Te	113.1(2)	C(2)–C(1)–Te	112(1)
C(21)–C(1)–Te'	111.4(2)	C(2)–C(1)–Te'	112(1)
C(1)–C(11)–F	111.6(3)–112.8(3)	C(1)–C(2)–F	106(2)–111(2)
C(1)–C(21)–F	111.9(3)–112.5(3)	F–C(2)–F	109(2)–110(2)
F–C(11)–F	106.5(3)–107.0(4)		
F–C(21)–F	106.2(3)–106.9(3)		

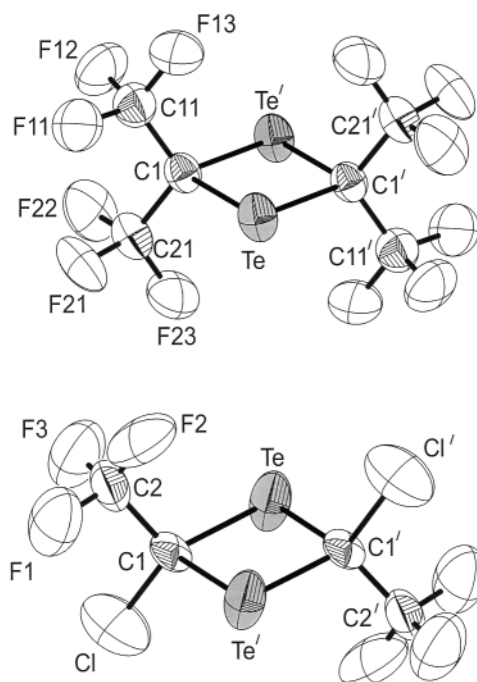
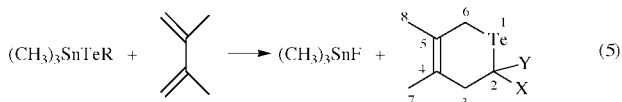


Fig. 1 Molecular structures and atomic labelling scheme of $[(\text{F}_3\text{C})_2\text{C}=\text{Te}]_2$ (**4**) (top) and $[(\text{F}_3\text{C})(\text{Cl})\text{C}=\text{Te}]_2$ **4a** (bottom) with thermal ellipsoids shown at the 50% probability level.

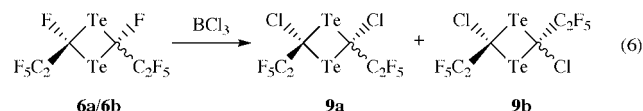
observed in the crystals of $[(\text{F}_3\text{C})(\text{F})\text{C}=\text{Te}]_2$ ² were not evident in the structure of **4a**.

For further characterization of $(\text{CF}_3)_2\text{C}=\text{Te}$ as well as of compounds **5** and **7**, [4 + 2]-cycloaddition reactions with 1,3-dimethylbutadiene have been carried out. The reaction took place *in situ* without isolation of the telluroketones following a procedure already employed for $\text{F}_2\text{C}=\text{Te}$ ¹ and $\text{CF}_3(\text{F})\text{C}=\text{Te}$.² Heating compound **3a** or **3b** to 160°C for 8 or 15 h dissolved in CHCl_3 in the presence of a large excess of 2,3-dimethylbutadiene produces 3,6-dihydro-4,5-dimethyl-2,2-bis(trifluoromethyl)tellurin **10** or 2-fluoro-3,6-dihydro-4,5-dimethyl-2-(pentafluoroethyl)tellurin **11** according to eqn. (5). Compounds **10** and **11** are pale yellow oils of low volatility which are extremely sensitive to air. In solution they decompose at room temperature with separation of tellurium. Another general applicable reaction is the successful F/Cl exchange in **6a/6b** with



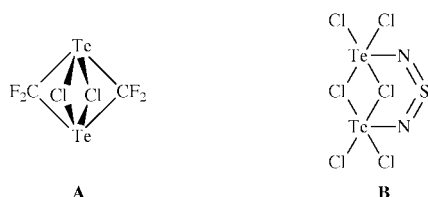
R = (CF₃)₂CF (3a), n-C₃F₇ (3b) X = Y = CF₃ (10); X = F, Y = C₂F₅ (11)

BCl₃ occurring at the same rate to give a mixture of *cis* and *trans* forms of 9a, 9b [eqn. (6)]. So the mixture of 6a/6b could not be separated by use of the chemical reaction with BCl₃.

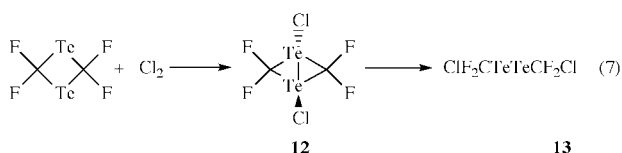


1,3-Dichloro-2,2,4,4-tetrafluoro-1λ⁴,3λ⁴-ditellurabicyclo[1.1.0]-butane (12) and bis(chlorodifluoromethyl) ditelluride (13)

Chlorination of tetrafluoro-1,3-ditellurethane, dissolved in CH₂Cl₂ with excess Cl₂ at –80 °C provides insoluble red-orange crystals of composition C₂Cl₂F₄Te₂. Spectroscopic investigations were applied for elucidating its structure. The NMR spectra, measured at –40 °C in acetonitrile solution, showed singlets at δ_F –63.25, proving four equivalent fluorine atoms, δ_C 84.09 (m) and a quintet at δ_{Te} 2009.00 showing equivalent carbon and tellurium atoms. The mass spectrum evidenced M⁺ and the expected fragmentation pattern containing TeCl⁺, but no TeCl₂⁺ fragments. These results are in good agreement with a planar C₂Te₂-ring frame having the two Cl-atoms at each Te-atom in a *trans*-position. The oxidative chlorination leads also to a Te–Te bond yielding bicyclic 12. Conclusive evidence is also obtained by its instability. On the basis of NMR-arguments, structure A cannot be ruled out, as such Te...Cl...Te bond-



ing had been observed for compound B.^{8,9} At room temperature orange-red 12, dissolved in CH₃CN, changed colour to dark brown. Fractional condensation at 20 °C *in vacuo* gave an orange liquid condensate at –50 °C. Spectroscopic investigations and a quantitative chlorine analysis evidenced the formation of ClF₂CTeTeCF₂Cl 13 as shown in eqn. (7).

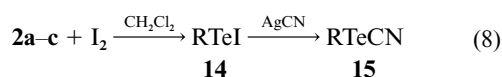


Oxidation of the two tellurium atoms in [F₂C=Te]₂ by chlorine are accompanied by a shift of δ_{Te} 313.0 to lower field compared with δ_{Te}, of the starting material. This effect was also observed in other similar chlorination processes. When (CF₃)₂Te was chlorinated to (CF₃)₂TeCl₂, δ_{Te} was shifted 254 ppm to lower field from δ_{Te} 1368 to δ_{Te} 1114.¹⁰

An interesting class of compounds are the perfluoroalkyl-tellurenyl iodides 14. Although only stable in solution, they are versatile reactants, *e.g.* metathetical reactions, and were made from compounds 2a, 2b or 2c and I₂, dissolved in CH₂Cl₂, reacting with for example AgCN to give the corresponding cyano derivatives 15 according to eqn. (8).

Table 2 Experimental details of the crystallographic studies

	[(CF ₃) ₂ C=Te] ₂ (4)	[(CF ₃) ₂ (Cl)C=Te] ₂ (4a)
Chemical formula	C ₂ F ₁₂ Te ₂	C ₄ Cl ₂ F ₆ Te ₂
Formula weight	555.24	488.14
Crystal system	Monoclinic	Monoclinic
Space group	P2 ₁ /c	P2 ₁ /c
μ(Mo-Kα)/cm ^{–1}	48.8	59.9
a/Å	7.6033(6)	7.771(7)
b/Å	7.2595(6)	6.749(2)
c/Å	11.5378(8)	10.685(2)
β/°	105.715(7)	105.30(4)
V/Å ³	613.0	540.5
Z	2	2
T/K	295	295
No. data collected	7372	6493
No. unique data	1789	1566
R _{int}	0.027	0.061
Final R(F ²) for all data	0.056	0.250
Final R(F) for F _o > 4σ(F _o)	0.025	0.125



R = (CF₃)₂CF, a; n-C₃F₇, b; n-C₄F₉, c

Experimental

All reactions were carried out in a standard vacuum system with Teflon-stemmed Young valves; solvents were dried according to published procedures. Deuteriated solvents were dried and transferred from activated 400 pm sieves. Microanalyses were performed on a 1106 Carlo-Erba Elemental analyser. The NMR spectra were recorded for CDCl₃ solutions unless noted otherwise, using a Bruker WM 250 PFT spectrometer [standards: CDCl₃ (¹³C), SiMe₄ (¹H), CFCl₃ (¹⁹F), TeMe₂ (¹²⁵Te) and SnMe₄ (¹¹⁹Sn)], infrared spectra on a Bruker FT-IR IFS 66, Raman spectra using a Raman attachment (FRA 106) to the Bruker FT-IR IFS 66 and mass spectra were recorded on a MAT CH7 spectrometer, using the direct-inlet method with 70 eV ionisation radiation. Compound 4a was synthesized according to the literature² method.

Crystal structure determination of compounds 4 and 4a

Crystals of 4 and 4a were selected under paraffin and placed in 0.3 mm glass capillaries which were flame sealed. Data collections were performed with a STOE AED 2 four-circle diffractometer using Mo-Kα radiation. Numerical absorption corrections were applied to both data sets. The crystal shapes were optimised by minimisation of R_{int} (HABITUS,¹¹ 4: transmission factors 0.6106–0.6878, 4a: 0.4133–0.6030). The structures were solved by direct methods (SHELXS-86)¹² and refined by full matrix least squares on F² (SHELXL-93)¹³ with anisotropic displacement parameters for all atoms. Crystallographic data are given in Table 2.

CCDC reference number 186/1729.

See <http://www.rsc.org/suppdata/dt/2000/a907549f/> for crystallographic files in .cif format.

Bis(perfluoroisopropyl)- (1a), bis(perfluoro-*n*-propyl)- (1b) and bis(perfluoro-*n*-butyl)-ditelluride (1c)

In a quartz Carius tube (200 cm³) equipped with a Teflon-stemmed Young valve and a magnetic stirring bar 15 ml of furan and (n-C₃F₇)₂Te (5.21 g, 11.20 mmol) or (n-C₄F₉)₂Te (4.30 g, 7.60 mmol) respectively were condensed *in vacuo* at –196 °C and degassed. The mixtures were irradiated at 20 °C (16 h) with a UV-lamp (type Heraeus TQ 150, 250 nm). Separation of the products was accomplished by fractional condensation using U-shaped traps kept at 20, –40 or –5 and –196 °C. Pure 1b

(2.42 g, 73%) condensed at -40°C or **1c** (1.19 g, 45%) at -5°C respectively as yellow-red liquids. **1b**: (found: C, 12.3. $\text{C}_4\text{F}_{14}\text{Te}_2$ requires C, 12.1%). **1c**: (found: C, 14.2. $\text{C}_8\text{F}_{18}\text{Te}_2$ requires C, 13.9%). **1a**: physical data are identical with published ones.² See SUP data for IR, ^{13}C , ^{19}F , ^{125}Te NMR and MS data for **1b** and **1c**.

Bis(perfluoroalkanetellurenyl)mercury (2)

These compounds were synthesized in a glass apparatus fitted with two 50 ml Carius tubes closed with Teflon valves and a medium sintered glass frit. One tube contained a magnetic stirring bar and a solution of the ditelluride in 10 ml CH_2Cl_2 . A threefold excess of mercury was added under argon and stirred at 20°C for 1 h. The yellow solution was filtered into the other Carius tube and evaporated *in vacuo* to dryness yielding yellow $\text{Hg}(\text{TeR}_f)_2$. The compounds $\text{Hg}(\text{TeR}_f)_2$, $\text{R}_f = (\text{CF}_3)_2\text{CF}$ (**2a**), $n\text{-C}_3\text{F}_7$ (**2b**) and $n\text{-C}_4\text{F}_9$ (**2c**) are made from (2.10 g, 3.54 mmol) $(\text{CF}_3)_2\text{CFTeTeCF}(\text{CF}_3)_2$, (2.42 g, 4.08 mmol) **1a** and (1.26 g, 1.82 mmol) **1b** yielding **2a** (2.54 g, 90%), **2b** (2.87 g, 89%) and **2c** (1.47 g, 90%) respectively. **2a**: (found: C, 8.6. $\text{C}_6\text{F}_{14}\text{HgTe}_2$ requires 9.1%). **2b**: (found: C, 8.7. $\text{C}_6\text{F}_{14}\text{HgTe}_2$ requires 9.1%). **2c**: (found: C, 10.3. $\text{C}_8\text{F}_{18}\text{HgTe}_2$ requires 10.8%). See SUP data for IR, ^{13}C , ^{19}F , ^{125}Te NMR and MS data for **2a-c**.

Perfluoroalkyltrimethylstannyltelluride (3)

In a Carius tube (50 ml) equipped with Teflon-stemmed Young valves and magnetic stirring bar ($n\text{-C}_3\text{F}_7$)₂Te (1.80 g, 3.87 mmol) or ($n\text{-C}_4\text{F}_9$)₂Te (3.50 g, 6.19 mmol) respectively was dissolved in diethyl ether (10 cm³). The yellow solution was cooled to -196°C and Me_3SnH (0.64 g, 3.87 mmol or 1.02 g, 6.19 mmol respectively) was condensed in. The mixture was warmed under the exclusion of light to -15 or 0°C with stirring for 1 or 2 h respectively, changing from bright yellow to pale yellow. After trap to trap condensation *in vacuo* (-40 to -196 or -15 to -196°C respectively) $\text{Me}_3\text{SnTe}(n\text{-C}_3\text{F}_7)$ (**3b**, 1.16 g, 65%) or $\text{Me}_3\text{SnTe}(n\text{-C}_4\text{F}_9)$ (**3c**, 1.64 g, 52%) were obtained as pale yellow, light sensitive liquids. **3b**: (found: C, 15.4; H, 2.1. $\text{C}_6\text{H}_9\text{F}_7\text{SnTe}$ requires C, 15.7; H, 2.0%). **3c**: (found: C, 16.6; H, 1.8. $\text{C}_7\text{H}_9\text{F}_9\text{SnTe}$ requires C, 16.5; H, 1.8%).

From $\text{Te}_2(\text{R}_f)_2$. Compound **1b** (0.83 g, 1.40 mmol) or compound **1c** (1.30 g, 1.88 mmol) was treated with Me_3SnH (0.23 g, 1.40 mmol or 0.31 g, 1.88 mmol). After purification **3b** (0.48 g, 75%) or **3c** (0.39 g, 41%) was obtained. See SUP data for IR, ^1H , ^{13}C , ^{19}F , ^{119}Sn , ^{125}Te NMR and MS data for **3b** and **3c**.

2,2,4,4-Tetrakis(trifluoromethyl)-1,3-ditellurethane (4)

A sample of $\text{Me}_3\text{SnTeCF}(\text{CF}_3)_2$ (2.15 g, 4.67 mmol) was passed at 10^{-3} Torr and 550°C through a quartz-glass pyrolysis tube (20 cm, diameter 1 cm). This was connected to two U-tubes, the first cooled to -30°C and the second to -196°C . The pyrolysis reaction took 1.5 h. In the U-tube at -30°C some Me_3SnF and unchanged $\text{Me}_3\text{SnTeCF}(\text{CF}_3)_2$ were retained. The main amount of Me_3SnF sublimed to the cooler zone of the quartz tube. In the following trap **4** was condensed as a dark red solid which was purified by sublimation (0.73 g, 56%). It is stable at 20°C , not air sensitive and soluble in common organic solvents. The formation of the monomeric intermediate $(\text{CF}_3)_2\text{C}=\text{Te}$ could not be detected. Mp 113°C (Found: C, 13.1. $\text{C}_6\text{F}_{12}\text{Te}_2$ requires C, 13.0%). See SUP data for IR, Raman, ^{13}C , ^{19}F , ^{125}Te NMR and MS data for **4**.

Pentafluoroethyltellurocarbonyl fluoride (5)

This compound was prepared as described for **4** by pyrolysing **3a** (1.87 g, 4.06 mmol) at 10^{-3} Torr and 500°C . In the U-tube, cooled to -40°C , unchanged **3a** was retained. In the following trap **5** was condensed as a green solid material. (In order to avoid dimerisation the liquid nitrogen surface should be kept

higher than the condensation zone.) Experimental details for the characterisation of perfluorinated telluroketones are provided elsewhere.^{1,2} See SUP data for IR and MS data for compound **5**.

cis/trans-2,4-Difluoro-2,4-bis(pentafluoroethyl)-1,3-ditellurethane (6a/6b)

A sample of compound **5**, obtained in a trap cooled to -196°C was warmed by removing the liquid nitrogen Dewar. A spontaneous change in the deposit from green to red was observed, yielding quantitative formation of **6**. Compound **6** separated from trace impurities *via* fractional condensation *in vacuo* with the sample at ambient temperature. Fractions were collected at -40 and -196°C . The product **6a/6b** (0.72 g, 64% based on **3a**) was found to condense at -40°C as an air sensitive violet liquid, which is stable at 20°C under argon for a few days. The *cis* and *trans* isomers could not be separated either by physical or by chemical methods. **6a/6b**: (found: C, 13.0. $\text{C}_6\text{F}_{12}\text{Te}_2$ requires C, 13.0%). See SUP data for IR, Raman, ^{13}C , ^{19}F , ^{125}Te NMR and MS data for **6a/6b**.

Heptafluoropropyltellurocarbonyl fluoride (7)

Compound **7** was prepared as described for **5** from **3b** (1.30 g, 2.55 mmol). After 1.5 to 2 h the monomer **7** condensed at -196°C as a green glassy compound which was characterised by its mass spectrum (see SUP data). Unchanged **3b** was retained at -10°C .

cis/trans-2,4-Difluoro-2,4-bis(heptafluoropropyl)-1,3-ditellurethane (8a/8b)

Isomers **8a/8b** were made as described for **6a/6b** and purified by fractional condensation *in vacuo* at 20°C . Compound **8a/8b** (0.41 g, 49% based on **3b**) condensed at -40°C as a violet solid. At 22°C the deep violet liquid was stable for a few days under exclusion of air (Found: C, 14.5. $\text{C}_8\text{F}_{16}\text{Te}_2$ requires C, 14.7%). See SUP data for IR, Raman, ^{13}C , ^{19}F , ^{125}Te NMR and MS data for **8a/8b**.

cis/trans-2,4-Dichloro-2,4-bis(pentafluoroethyl)-1,3-ditellurethane (9a/9b)

A sample of compound **6a/6b** (0.15 g, 0.27 mmol) was deposited under an atmosphere of argon in a Carius tube (100 ml) and cooled to -196°C . All argon was removed *in vacuo* and BCl_3 (3 cm³) was added to the reactor. The mixture was initially warmed to -40°C and thereafter the temperature was raised slowly to 22°C over a period of 12 h. At -40°C **6a/6b** began to dissolve in BCl_3 to give a deep violet solution. At room temperature the mixture turned blue. Compound **9a/9b** was isolated by fractionation *in vacuo*. The product was collected in the trap cooled to -20°C as violet crystals (0.13 g, 82%). It was not possible to separate the *cis* and *trans* isomers of **9**, so all analyses were obtained on an isomeric mixture of **9a** and **9b**. See SUP data for ^{19}F and MS data for **9a/9b**.

3,6-Dihydro-4,5-dimethyl-2,2-bis(trifluoromethyl)tellurin (10)

Compound **10** was obtained by the direct reaction of $(\text{CH}_3)_3\text{SnTeCF}(\text{CF}_3)_2$ (2.00 g, 4.34 mmol) with 2,3-dimethylbutadiene (1.09 g, 13.3 mmol) dissolved in CHCl_3 (5 ml) in a sealed glass ampoule (30 cm³). The mixture was heated to 160°C for 8 h. Compound **10** was isolated by fractional condensation *in vacuo* and collected at -30°C as a bright yellow, light and moisture sensitive liquid (1.05 g, 67%) (Found: C, 30.2; H, 2.7. $\text{C}_9\text{H}_{10}\text{F}_6\text{Te}$ requires C, 30.0; H, 2.8%). See SUP data for IR, ^1H , ^{13}C , ^{19}F , ^{125}Te NMR and MS data for **10**.

2-Fluoro-3,6-dihydro-4,5-dimethyl-2-pentafluoroethyltellurin (11)

This compound was prepared as described for **10** by reacting

excess 2,3-dimethylbutadiene (0.36 g, 4.42 mmol) with **3a** (1.06 g, 2.30 mmol) in CHCl_3 (5 ml) at 160 °C for 15 h. Compound **11** (0.62 g, 75%) was isolated by fractional condensation *in vacuo* at –30 °C as a bright yellow, moisture sensitive liquid, which slowly decomposed at 20 °C in solution depositing tellurium (Found: C, 29.8; H, 3.1. $\text{C}_9\text{H}_{10}\text{F}_6\text{Te}$ requires C, 30.1; H, 2.8%). See SUP data for IR, ^1H , ^{13}C , ^{19}F , ^{125}Te NMR and MS data for **11**.

1,3-Dichloro-2,2,4,4-tetrafluoro-1 λ^4 ,3 λ^4 -ditellurabicyclo[1.1.0]-butane (**12**)

In a Carius tube (50 ml) equipped with a Teflon-stemmed Young valve and a magnetic stirring bar 2,2,4,4-tetrafluoro-1,3-ditellurethane (43.4 mg, 0.122 mmol) was deposited and dissolved in CH_2Cl_2 (1 cm^3). The dark blue solution was cooled to –196 °C and evacuated. Thereafter Cl_2 (26 mg, 0.733 mmol) was condensed in. The mixture was warmed to –80 °C and stirred for 1 h. Solvent and excess Cl_2 were removed at –50 °C *in vacuo* providing temperature sensitive red-orange **12** (51.0 mg, 98%) soluble in CH_3CN . Decomposition temperature –15 °C. See SUP data for IR, ^{13}C , ^{19}F , ^{125}Te NMR and MS data for **12**.

Bis(chlorodifluoromethyl)ditelluride (**13**)

A sample of compound **12**, obtained in a Carius tube cooled to –50 °C, was warmed to room temperature and kept for 1 h. A colour change from red-orange to dark brown was observed. Compound **13** was purified by fractional condensation at ambient temperature. Fractions were collected at –50 and –196 °C. The product (47.0 mg, 90%) was found to condense at –50 °C as a bright yellow liquid changing to orange on warming to 20 °C. It is soluble in common solvents and decomposed slowly depositing tellurium. Mp –56 °C (Found: Cl, 16.0. $\text{C}_2\text{Cl}_2\text{F}_4\text{Te}_2$ requires Cl, 16.6%). See SUP data for IR, ^{13}C , ^{19}F , ^{125}Te NMR and MS data for **13**.

Perfluoroalkantellurenyl iodides R_fTeI [$\text{R}_f = (\text{CF}_3)_2\text{CF}$, **14a**; $\text{n-C}_3\text{F}_7$, **14b**; $\text{n-C}_4\text{F}_9$, **14c**]

General procedure: in a carefully dried Carius tube (100 cm^3) equipped with a Teflon-stemmed valve and magnetic stirring bar solutions of $[(\text{CF}_3)_2\text{CF}]_2\text{Te}_2$, **1a**, **1b** or **1c** dissolved in CHCl_3 (10 cm^3) were deposited together with equivalent amounts of I_2 under an argon atmosphere. The solution was cooled to –196 °C and the argon removed *in vacuo*. With continuous stirring, the reaction mixture was annealed to room temperature; in the process it was observed to turn blue. The ^{19}F NMR spectrum of the solution indicated that **14a**, **b** or **c** had been formed quantitatively. The solutions were found to be stable at –25 °C over long periods. **14a**: $[(\text{CF}_3)_2\text{CF}]_2\text{Te}_2$ (1.19 g, 2.01 mmol) and I_2 (0.51 g, 2.01 mmol). **14b**: $(\text{n-C}_3\text{F}_7)_2\text{Te}_2$ (1.28 g, 2.16 mmol) and I_2 (0.55 g, 2.16 mmol). **14c**: $(\text{n-C}_4\text{F}_9)_2\text{Te}_2$ (1.95 g, 2.81 mmol) and I_2 (0.71 g, 2.81 mmol). See SUP data for ^{13}C , ^{19}F , ^{125}Te NMR and MS data for **14a–c**.

Cyano(perfluoroalkyl)tellurium $[(\text{CF}_3)_2\text{CFTeCN}$, **15a**; $\text{n-C}_3\text{F}_7\text{-TeCN}$, **15b**; $\text{n-C}_4\text{F}_9\text{TeCN}$, **15c**]

General procedure: to samples of compounds **14a**, **b** or **c** obtained at –196 °C under argon equivalent amounts of AgCN were added. Thereafter argon was removed *in vacuo* and the mixtures were warmed to 22 °C with stirring. Yellow AgI desposited and the solution became green. The compounds were isolated by fractional condensation *in vacuo* with the samples at ambient temperature. Fractions were collected at –40 and –196 °C. The products were found to condense at –40 °C as air stable, slightly yellow coloured compounds soluble in common solvents. **15a**: $(\text{CF}_3)_2\text{CFTeI}$ (0.63 g, 1.96 mmol) and AgCN (0.26 g, 1.96 mmol) provided **15a** (0.51 g, 81%) (Found: C, 15.3; N, 4.5. $\text{C}_4\text{F}_7\text{NTe}$ requires C, 14.9; N, 4.3%). **15b**: $\text{n-C}_3\text{F}_7\text{TeI}$ (1.83 g, 4.32 mmol) and AgCN (0.58 g, 4.32 mmol) gave $\text{n-C}_3\text{F}_7\text{TeCN}$ (1.28 g, 92%), mp 89 °C (Found: C, 14.4; N, 3.9. $\text{C}_4\text{F}_7\text{NTe}$ requires C, 14.9; N, 4.3%). **15c**: $\text{n-C}_4\text{F}_9\text{TeI}$ (2.67 g, 5.62 mmol) and AgCN (0.75 g, 5.63 mmol) provided $\text{n-C}_4\text{F}_9\text{TeCN}$ (1.86 g, 89%); mp 98 °C (Found: C, 16.0; N, 3.7. $\text{C}_5\text{F}_9\text{NTe}$ requires C, 16.1; N, 3.8%). See SUP data for IR, ^{13}C , ^{19}F , ^{125}Te NMR and MS data for **15a–c**.

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