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Trifluorotelluroacetyl fluoride, its cyclic dimer and precursors: preparation, characterisation and reactivity†

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With the synthesis of $CF_3(F)C{=}Te$, the second, non-resonance stabilised perfluorinated telluracarbonyl has been isolated and characterised by gas-phase IR and mass spectrometry. It was prepared *via* pyrolysis of the novel compound $Me_3SnTeC_2F_5$ at 500 °C, 10^{-3} Torr in 40–50% yield. The compound $CF_3(F)C{=}Te$ is only stable at −196 °C and dimerises quantitatively a few degrees above this temperature to the corresponding mixture of *cis/trans*-2,4-bis(trifluoromethyl)-2,4-difluoro-1,3-ditelluranes which cannot be separated by physical nor chemical procedures. Their reaction with BX_3 (X = Cl or Br) yielded chlorinated and brominated *cis/trans*-1,3-ditelluretanes. Additionally the telluracarbonyl undergoes a cycloaddition reaction with 2,3-dimethylbutadiene forming 2-fluoro-3,6-dihydro-4,5-dimethyl-2-trifluoromethyltellurin. The required precusors for the synthesis of the perfluorinated telluracarbonyls TeR_2 and Te_2R_2 were prepared by three different methods. The compounds Me_3SnTeR [R = C_2F_5 or $(CF_3)_2CF$] were obtained from $Te_x(C_2F_5)_2$ (*x* = 1 or 2) or $Te[(CF_3)_2CF]_2$ and Me_3SnH in good yield.

With the preparation and characterisation of $F_2C{=}Te$[1] and 1,1,3,3-tetramethylindan-2-tellurone[2] **1** the first telluroketones could be detected by spectroscopic methods. For $F_2C{=}Te$ gas-phase IR and mass spectra of a pure substance, only stable at −196 °C, could be obtained. In solution at ambient temperatures ^1H, ^{13}C, ^{125}Te NMR and UV spectra of **1** could be measured. Both compounds are sensitive to oxygen and light. They are differently coloured, solid $F_2C{=}Te$ is violet while **1** in $CHCl_3$ solution is green, but both show markedly different reactivities: $F_2C{=}Te$ dimerises slightly above −196 °C to the corresponding 1,3-ditelluretane; **1** when heated in a dilute solution at 80 °C for 6 h does not dimerise at all. A similar difference is observed for Diels–Alder reactions with 2,3-dimethylbuta-1,3-diene.

There are different reasons for the relative stabilities of the two tellurocarbonyls. While $F_2C{=}Te$ is stabilised by electronic effects caused by highly electronegative substituents, the so-called 'perfluoro effect',[3] strengthening of the skeletal σ bonding by 2.5–4 eV, **1** is kinetically stabilised by bulky substituents in the neighbourhood of the C=Te moiety. Here we describe the synthesis, characterisation and selected reactions of the second, non-resonance-stabilised perfluorinated tellurocarbonyl, $CF_3(F)C{=}Te$, which has a genuine carbon–tellurium double bond, its cyclic dimers and a number of precursors such as R_2Te_x (*x* = 1 or 2) or $Me_3SnTeC_2F_5$, respectively.

Results and Discussion

Preparation of bis(perfluoroalkyl)-tellurides and -ditellurides

Besides $(CF_3)_2Te$[4,5] and $(CF_3)_2Te_2$[6–8] only $(C_2F_5)_2Te_x$ (*x* = 1[9] or 2[10]) and $[(CF_3)_2CF]_2Te_x$[9] (*x* = 1 or 2) have been reported previously. The known synthetic routes to R_2Te_x [R = C_2F_5 or $(CF_3)_2CF$, *x* = 1 or 2] are not suitable for a large-scale synthesis and are not generally applicable. Better and more efficient procedures are the reaction between the mercurials HgR_2 (method a) or HgR(I) (method b) with a three-fold molar excess of tellurium in the presence of catalytic amounts of copper. Even better is the treatment of RI with an equimolar mixture of tellurium with copper in excess (method c). Equations for synthetic reactions of the compounds obtained, yields, the nature of products and the optional reaction parameters are given in Scheme 1. The ratio bis(perfluoroalkyl) mono- to di-tellurides depends mainly on the nature of the perfluoromethyl group and the synthetic method applied. Since perfluoroiodoalkanes are commercially available, synthesis c, where copper is not only used as a catalyst but also as an iodine scavenger, is found to be the best procedure to obtain the corresponding bis(perfluoroalkyl) monotellurides **2** in high yields and sufficient quantities. This reaction has some similarities to the Müller–Rochow synthesis.[11] Iodoalkanes are replaced by their fluorinated analogues and instead of an Si/Cu catalyst, Te/Cu is employed under comparable reaction conditions. The main products in all three routes are monotellurides of the type R_2Te. Their conversion into the corresponding bis(perfluoroalkyl) ditellurides **3** is accomplished by heating RTeR, R = C_2F_5, with an excess of tellurium in the presence of copper to 200 °C (for 60 h) with a conversion rate of 20%. This observation and the formation of $C_2F_5TeTeC_2F_5$ from C_2F_5I and Te/Cu at 180 °C (60 h) is seen as evidence that the amount of **3b** obtained depends on the reaction time. It can be assumed that in all three procedures intermediates of the type 'RCu' are responsible for the tellurane formation.

Method			
a	$HgR_2 + 3\,Te \xrightarrow{(i)}$	RTeR + **2**	RTeTeR **3**
	R = CF_3, 180 °C (48 h)	**2a**, 40%	**3a**, —
	R = C_2F_5, 200 °C (15 h)	**2b**, 85%	**3b**, 10%
b	$Hg(C_2F_5)I + 3\,Te \xrightarrow{(i)}$ 200 °C (15 h)	$C_2F_5TeC_2F_5$ + **2b**, 93%	$C_2F_5TeTeC_2F_5$ **3b**, —
c	$R'I + 3\,Te + 3\,Cu \longrightarrow$	R'TeR' +	R'TeTeR'
	R' = C_2F_5, 180 °C (36 h)	**2b**, 68%	**3b**, —
	180 °C (60 h)	**2b**, 58%	**3b**, 16%
	R' = $(CF_3)_2CF$, 150 °C (15 h)	**2c**, 30%	**3c**, 10%
	R' = $CF_3CF_2CF_2$, 180 °C (18 h)	**2d**, 43%	**3d**, —
	R' = *n*-C_4F_9, 180 °C (18 h)	**2e**, 33%	**3e**, —

Scheme 1 (*i*) Catalytic amount of Cu

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† *Non-SI units employed:* eV ≈ 1.60 × 10^{-19} J, Torr ≈ 133 Pa.

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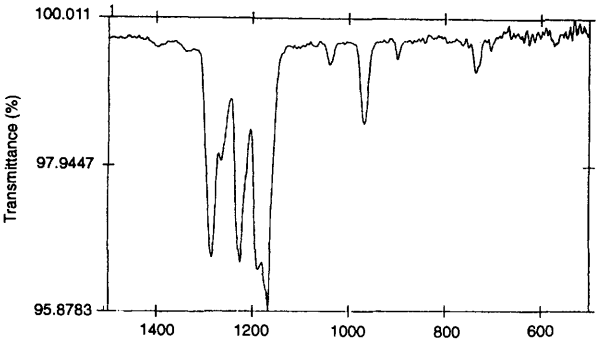


Fig. 1 Infrared spectrum of the vapour of compound **5**

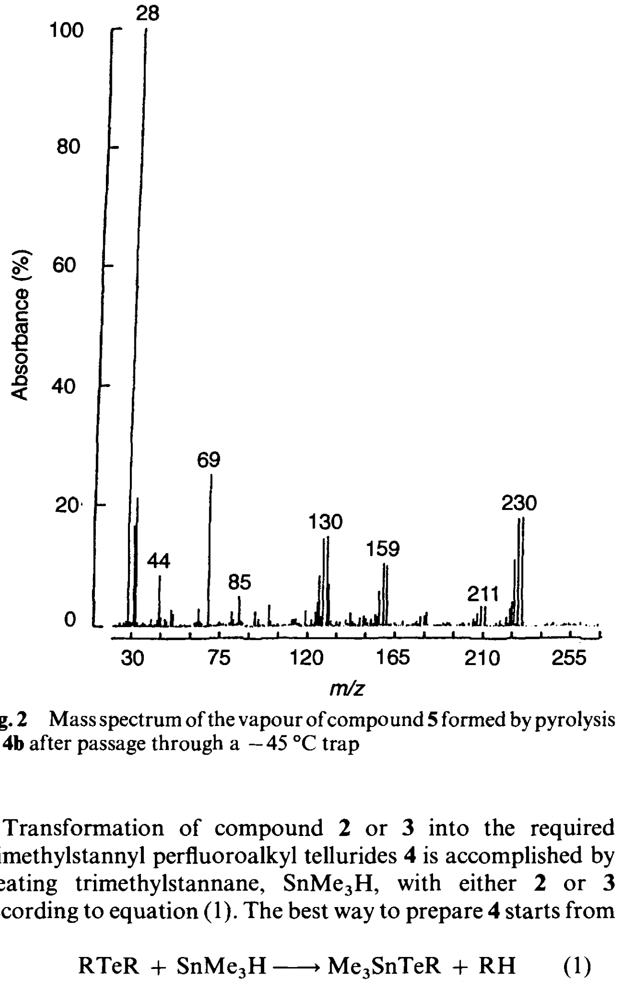


Fig. 2 Mass spectrum of the vapour of compound **5** formed by pyrolysis of **4b** after passage through a −45 °C trap

Transformation of compound **2** or **3** into the required trimethylstannyl perfluoroalkyl tellurides **4** is accomplished by treating trimethylstannane, $\mathrm{SnMe_3H}$, with either **2** or **3** according to equation (1). The best way to prepare **4** starts from

$$\begin{aligned} &\mathrm{RTeR + SnMe_3H \longrightarrow Me_3SnTeR + RH} \quad (1)\\ &\mathbf{4a}\ \mathrm{R = CF_3}^{1}\\ &\mathbf{4b}\ \mathrm{R = C_2F_5}\\ &\mathbf{4c}\ \mathrm{R = (CF_3)_2CF}\end{aligned}$$

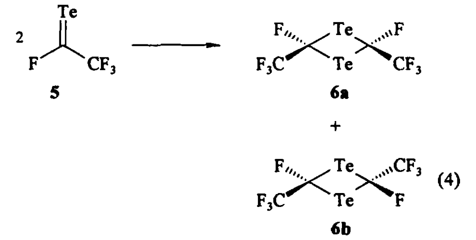
2, by reaction of the components dissolved in diethyl ether in a 1 : 1 molar ratio according to equation (1). Slightly lower yields of **4b** are obtained when $\mathrm{SnMe_3H}$ is treated with $\mathrm{C_2F_5TeTeC_2F_5}$, molar ratio 1 : 1, under comparable conditions. If the molar ratio of **3b** to $\mathrm{SnMe_3H}$ is increased to 2 : 1 the yield decreases substantially, on account of side reactions, as shown in equation (2).

$$\begin{aligned} &\mathbf{3b} + \mathrm{SnMe_3H \longrightarrow} \mathbf{4b} + \mathrm{Te + C_2F_5H}\\ &\mathbf{4b} + \mathrm{SnMe_3H \longrightarrow Me_3SnTeSnMe_3 + C_2F_5H} \quad (2)\\ \hline &\mathbf{3b} + \mathrm{2\,SnMe_3H \longrightarrow Me_3SnTeSnMe_3 + 2\,C_2F_5H + Te}\end{aligned}$$

With compound **4b** available in sufficient quantities, a suitable synthon for the preparation of trifluorotelluroacetyl fluoride **5** is now accessible. If **4b** is allowed to flow through a heated Pyrex tube (500 °C) packed with glass-wool, **5** is generated in yields of 50–60% [equation (3)]. The monomeric

$$\mathrm{Me_3SnTeCF_2CF_3 \longrightarrow \underset{\mathbf{5}}{CF_3(F)C{=}Te} + SnMe_3F} \quad (3)$$

species is trapped at −196 °C and dimerises almost quantitatively a few degrees above this temperature. This process takes place within seconds and is evidenced by a change from green through orange to red [equation (4)]. Although



5 **6a** **6b** (4)

attempts to characterise **5**, in the condensed phase, are prevented by dimerisation, the monomer seems to be reasonably stable at low concentrations in the gas phase. This suggests the possibility to identify monomeric **5** by spectroscopic means.

With the aid of a special apparatus, compound **5**, generated by pyrolysis of **4b**, was caused to pass through an IR cell before being trapped at −196 °C. In this manner the IR spectrum of pure gaseous **5** was obtained (Fig. 1). When the pyrolysis apparatus was coupled to the gas inlet of a mass spectrometer the mass spectrum of **5** was obtained (Fig. 2). Although ν(C=Te), which is coupled with the normal vibration ν_{sym}(C–F), can be assigned for $\mathrm{Te{=}CF_2}$[1] to a band at 1240 cm^{-1}, it is not possible to assign the remaining vibrations, observed in the IR spectrum of gaseous **5**. In the region 1150–1300 cm^{-1} where ν(C=Te), ν_{sym}(C–F) and ν_{asym}(C–F) are expected, three strong bands are observed at 1284s, 1224s and 1166vs cm^{-1}, but any assignment remains speculative and is therefore avoided.

Chemical evidence for the formation of compound **5** comes from a study of the dimerisation reaction which occurs on warming the product trap and is initiated by tapping the reactor. A spontaneous change from green through orange to red of the condensed material can be observed, which suggest dimerisation to the corresponding mixture of *cis*/*trans*-2,4-difluoro-2,4-bis(trifluoromethyl)-1,3-ditelluretanes **6a**/**6b** [equation (4)]. This mixture cannot be separated by physical methods, including preparative gas chromatography.

Crystal and molecular structure of compounds of 6a/6b

The structure of compounds **6a**/**6b** is isotypic to the selenium analogue *trans*-$\mathrm{[(F_3C)FC{=}Se]_2}$.[12] Both have the same crystal system and space group, the atomic coordinates show only small differences and a slightly enlarged unit-cell volume for the tellurium-containing compound was found.

Views of the molecule are given in Fig. 3, selected bond lengths and angles in Table 1. The molecule consists of a planar $\mathrm{C_2Te_4}$ ring with a centre of inversion and the point group C_i. The first data set was recorded at ambient temperature and led to a structure model with some unusual features [Fig. 3(*a*)]. The displacement ellipsoids of the four carbon atoms showed a strong elongation perpendicular to the plane of the $\mathrm{C_2Te_2}$ ring, C(2) was placed almost in the plane of the central ring, and the bond lengths were curious [*e.g.* C(1)–F(1) 1.81(3), C(1)–F(21) 1.89(4), C(1)–C(2) 1.21(2) Å]. Since no superstructure reflections were observed and no indications of crystal twinning were present, the structure determination was repeated with another crystal and under low temperature. Two data sets at 211 and

Table 1 Selected bond lengths (Å) and angles (°) for compounds **6a**/**6b**. The values refer to the *trans* form of the molecule according to a split model for the carbon atoms as represented in Fig. 1(*d*)

Te–C(1A)	2.21(2)	C(2A)–F(21)	1.40(2)
C(1A)–C(2A)	1.47(3)	C(2A)–F(22)	1.38(2)
C(1A)–Te′	2.19(2)	C(2A)–F(23)	1.40(2)
C(1A)–F(1)	1.44(2)		
C(1A)–Te–C(1A′)	83.9(6)	C(1A)–C(2A)–F(21)	105(1)
Te–C(1A)–Te′	96.1(6)	C(1A)–C(2A)–F(22)	108(2)
Te–C(1A)–F(1)	118(1)	C(1A)–C(2A)–F(23)	104(1)
Te–C(1A)–C(2A)	113(1)	F(21)–C(2A)–F(23)	121(2)
Te′–C(1A)–C(2A)	113(1)	F(22)–C(2A)–F(23)	100(1)
F(1)–C(1A)–C(2A)	99(1)		

169 K were recorded, the results of the refinements being presented in Fig. 3(*b*) and 3(*c*). The elongated ellipsoids of the carbon atoms are still present at 211 K and even increased in length at 169 K. A satisfactory structure model could be obtained by introducing a split model for the two carbon atoms [Fig. 3(*d*)]. If C(1) occupies the upper and C(2) the lower position with respect to the central C_2Te_2 ring the centre of symmetry inverts this occupation at the other two carbon atoms. The *trans* configuration of the molecule results which exactly fits with the molecular shape of the *trans* form of the selenium analogue. Bond lengths also lie now much better in the expected range. The two Te–C bonds in the four-membered ring [2.18(2) Å] are equal within errors. The transannular Te • • • Te′ distance of only 3.271(4) Å is closer to that expected for a Te–Te bond (2.75 Å) than the sum of the van der Waals radii (4.40 Å).[13] The structure model with split positions for the C atoms also allows the presence of the *cis* form [Fig. 3(*e*)]. Both C(1) atoms occupy the lower and both C(2) atoms the upper positions, annulating the centre of symmetry. According to this model the *cis* form contains a butterfly-shaped C_2Te_2 ring with an interplanar angle between the two CTe_2 planes of 144.3°. A stereoscopic view of the unit cell is given in Fig. 4.

This disorder model implies that the crystals contain simultaneously the *trans* and *cis* forms of **6** in two different orientations. On the other hand the impossibility of the separation of the two forms compared with the ease of separation of the two forms of the selenium analogue[11] together with the spectroscopically demonstrated presence of both forms in the crystals of **6** gives rise to the interpretation of a dynamic behaviour of the molecules. Different models for a dynamic interconversion of *cis* and *trans* form of **6** can be developed. A simple positional exchange of the two carbon atoms C(1) and C(2) is accompanied by breakage of strong C–F bonds and is therefore improbable. Another possibility is the simultaneous breakage of both relatively weak C(1)–Te bonds and a rotation of the $F_3C(F)C$ carbene fragment. The crystal-structure analysis cannot make a definite distinction between the possibilities of molecular disorder or molecular dynamics. The increasing length of the displacement ellipsoids of the C atoms with decreasing temperature supports a dynamic process. A lower frequency of the interconversion should lead to an increase in electron density in the reversing positions.

For further characterisation a [4 + 2]-cycloaddition reaction with a diene was carried out. In this case, 2,3-dimethylbutadiene, one of the most reactive dienes which is not prone to dimerise, was used. The reaction took place *in situ* without isolation of compound **5** following a procedure already employed in the syntheses of some phosphaalkenes,[14] selenocarbonyls[15] and $Te{=}CF_2$.[1] Heating **4b** dissolved in $CHCl_3$ in the presence of a large excess of 2,3-dimethylbutadiene to 150 °C (4 h) produces 2-fluoro-3,6-dihydro-4,5-dimethyl-2-trifluoromethyltellurin **7** [equation (5)]. Compound **7** is a yellowish oil of low volatility, which is extremely sensitive to air. Hence it is also possible to

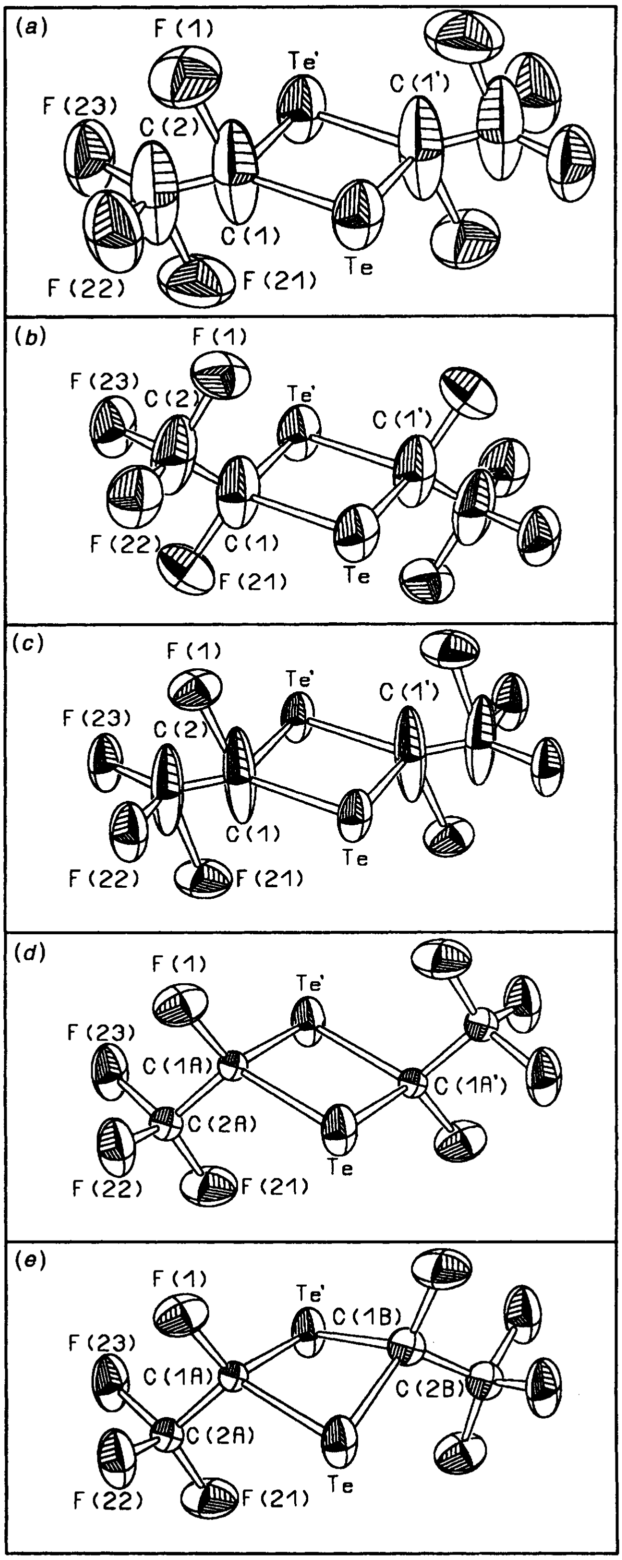
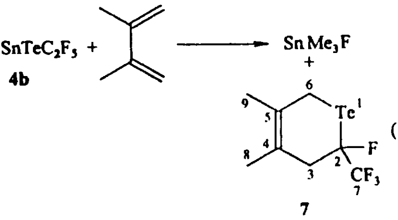


Fig. 3 Molecular structures and atomic labelling scheme of $[(F_3C)FC{=}Te]_2$ **6a**/**6b** with thermal ellipsoids shown at the 40% probability level: (*a*) from data obtained at room temperature; (*b*) at 211 K; (*c*) at 169 K; (*d*) *trans*-**6** according to a split model with 50% occupancy for C(1) and C(2) at 169 K; (*e*) *cis*-**6** at 169 K



(5)

7

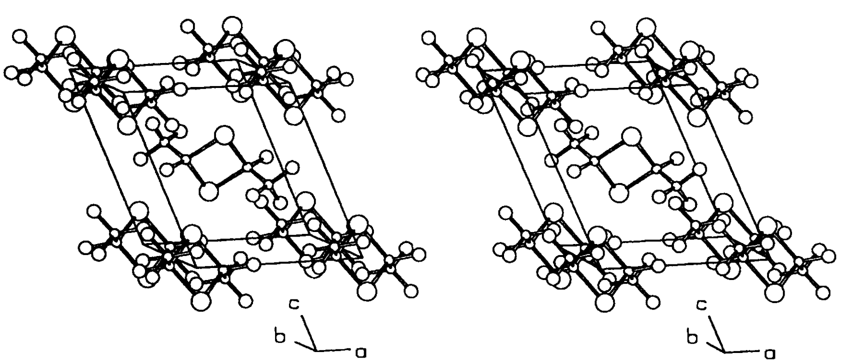
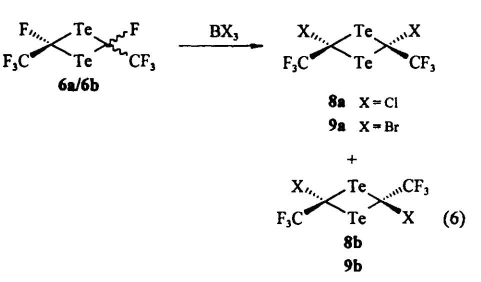


Fig. 4 Stereoscopic view of the unit cell of compounds **6a**/**6b**. For the graphical representation the *trans* form was used; large circles, Te; medium circles, F; small circles, C

obtain evidence for **5** as an intermediate *via* its chemical reactions.

Compounds **6a**/**6b** appear to be useful starting materials for further reactions. The successful F/X exchange in $(TeCF_2)_2$ with BX_3 (X = Cl, Br or I)[1] suggests the possibility of similar reactions with **6a**/**6b**. Since the F/Cl exchange of *cis*-$[SeCF(CF_3)]_2$ is found to be faster than for the *trans* isomer, it is now possible to isolate and characterise the pure *trans* isomer. In contrast to $[SeCF(CF_3)]_2$, **6a** and **6b** reacted with BX_3 (X = Cl or Br) at the same rate to give a mixture of *cis* and *trans* forms of **8a**, **8b** and **9a**, **9b** [equation (6)]. So the mixture of **6a**/**6b**



6a/6b

8a X = Cl

9a X = Br

8b

9b

could not be separated by use of the chemical reaction with BX_3 (X = Cl or Br).

NMR spectra of 1,3-ditelluretanes

Analysis of perfluorinated 1,3-dithia- and 1,3-diselena-etanes showed two characteristic distinctive trends for the assignment of *cis*- and *trans*-fluorine atoms attached to ring carbons: (1) the ^{19}F NMR resonances δ(CF) of the *trans* isomers (Table 2) are shifted 10–20 ppm to higher fields than those of the *cis* isomers; (2) the coupling constants for these fluorine atoms ^4J(F–F) for the *trans* isomer are in the region 30–40 Hz and are larger compared with those for the *cis* isomers which are only 0–4 Hz. A similar but ten times smaller effect can be observed for the CF_3 groups directly bonded to the ring. So far the difference in the chemical shift is the only criterion to differentiate between *cis* and *trans* isomers of **8** and **9**.

The coupling constant ^4J(F–F) cannot be obtained directly from the higher-order spectrum of compound **6**. According to Harris' rules[16] this value could be calculated for a $AA'X_3X_3'$ spin system as $^4J(F\text{–}F) = 32.4$ Hz. This was the value expected for a *trans* form. Isomer **8a** exhibits an example of the so-called 'deceptively simple spectra' as it only consists of a doublet and a quartet with two independent AX_3 systems with $J(AA')$ and $J(AX') \longrightarrow 0$ (special case B). The condition $(N \approx L)/|J(AA')| \gg 0$ can only give an upper limit of about 1 Hz for the desired constant, a value typical of the *cis* form.[16]

The ^{19}F NMR spectrum for compound **6** was also recorded on a Bruker AMX2 600 instrument, but no resolution of the higher-order region could be achieved.

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 model 1106 Carlo-Erba Elemental analyser. The NMR spectra were recorded for $CDCl_3$ solutions unless noted otherwise, using a Bruker WM 250 PFT spectrometer [standards: $CDCl_3$ (^{13}C), $SiMe_4$ (^1H), $CFCl_3$ (^{19}F), $TeMe_2$ (^{125}Te) and $SnMe_4$ (^{119}Sn)], 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 ionising radiation.

Bis(perfluoroalkyl) mono- (2) and di-tellurides (3)

In all three procedures tellurium was used in a three-fold molar excess with respect to the perfluorinated adduct. In the first and second methods Cu was used as a catalyst, in the third in a three-fold excess. All reactions were carried out in glass ampoules (50 cm^3) sealed either *in vacuo* (10^{-3} Torr) or at atmospheric pressure under argon and heated in a tube oven. Reaction parameters, products and yields are given in Scheme 1. For the method, reagents, amounts in g (mmol), pressure in Torr, condensation temperatures and analyses see Table 3. Spectroscopic data are listed in Table 4. Ampoules were sealed at normal pressure under an atmosphere of argon or *in vacuo* (see Table 3). Reaction mixtures were transferred in a normal vacuum system and separated by fractional condensation.

Pentafluoroethyl trimethylstannyl telluride 4b

From $Te(C_2F_5)_2$. In a Carius tube (250 cm^3) equipped with Teflon-stemmed Young valves, compound **2b** (3.41 g, 9.33 mmol) was dissolved in diethyl ether (5 cm^3). The yellow solution was cooled to −196 °C and $SnMe_3H$ (1.53 g, 9.33 mmol) was condensed in. The mixture was warmed to 0 °C with stirring for 1 h at this temperature, changing from yellow to bright yellow. After trap-to-trap condensation *in vacuo* (−40 to −196 °C), **4b** (2.52 g, 66%) was obtained as a yellow, very air-sensitive liquid (Found: C, 14.6; H, 2.2. $C_5H_9F_5SnTe$ requires C, 14.6; H, 2.2%); $\tilde{\nu}/cm^{-1}$ (gas) 2989m, 2869m, 1394w, 1315s, 1231vs, 1143vs, 913s and 741m; δ_H 0.74 [9 H, s, $^2J(H\text{–}^{117}Sn)$ 53.89, $^2J(H\text{–}^{119}Sn)$ 56.53 as determined from the satellites]; δ_C −3.77 [3 C, q, ^1J(CH) 131], 96.65 [1 C, qnt, ^1J(CF) 284.2, ^2J(CF) 32.4, CF_2] and 118.4 (1 C, tq, CF_3); δ_F −74.99 [2 F, q, ^3J(FF) 3.9, CF_2] and −84.6 (3 F, t, CF_3); δ_{Sn} 14.4 [1 Sn, qntdec, ^2J(SnH) 56.96, ^3J(SnF) 22.5, ^4J(SnF) 3.3 Hz]; δ_{Te} 173.97 (1 Te, m); *m*/*z* 412 (20, M^+), 397 (5, $M - CH_3$), 261 (20, $CHTeSn^+$), 248 (20, $SnTe^+$), 211 (25, $TeC_2F_5^+$), 169 (100, Me_2SnF^+), 150 (15, Me_2Sn^+), 135 (40, $MeSn^+$), 130 (20, Te^+), 120 (19, Sn^+), 81 (10, $C_2F_3^+$) and 69 (15%, CF_3^+).

Table 2 Values elucidated from the ^{19}F NMR spectra of compounds **6**, **8** and **9**

Compound	$\delta(CF)_{cis}$	$\delta(CF)_{trans}$	Δ(CF)	$\delta(CF_3)_{cis}$	$\delta(CF_3)_{trans}$	$\Delta(CF_3)$
6	−147.01	−154.38	7.37	−78.19	−79.41	1.22
8				−74.15	−75.05	0.81
9				−72.69	−73.36	0.68

Table 3 Method, reagents, amounts, pressures, condensation temperatures and analyses

Method	Reagents (amount/g, mmol)	p^a/Torr	Condensation temperature/°C	Carbon analysis (%)
a	$Hg(CF_3)_2$ (1.9, 2.95) Te (1.13, 8.85) Cu, catalytic amounts	10^{-3}	−50, −130,[b] −196	
a	$Hg(C_2F_5)_2$ (1.0, 2.28) Te (2.3, 18) Cu, catalytic amounts	760	−40,[c] −78,[b] −196	**2b**: found 13.1, requires 13.1 **3b**: found 9.7, requires 10.3
b	$Hg(C_2F_5)I$ (1.3, 2.91) Te (1.1, 8.6) Cu, catalytic amounts	760	−40, −78,[b] −196	
c	C_2F_5I (3, 12.3) Te (4.7, 36.9) Cu (2.3, 36.9)	10^{-3}	−40,[c] −78,[b] −196	
c	*iso*-C_3F_7I (3, 10.5) Te (4, 31.4) Cu (2, 31.4)	10^{-3}	−25,[c] −45,[b] −196	**2c**: found 15.5, requires 15.5 **3c**: found 12.1, requires 12.1
c	*n*-C_3F_7I (3.37, 11.39) Te (2.9, 22.7) Cu (1.45, 22.7)	10^{-3}	−40, −63,[b] −196	**2d**: found 15.8, requires 15.5
c	C_4F_9I (4.2, 12.1) Te (4.63, 36.3) Cu (2.3, 36.3)	760	−30,[b] −196	**2e**: found 16.9, requires 17.0

[a] Pressure in samples while sealing. [b] Condensation of monotellurides. [c] Condensation of ditellurides.

Table 4 Spectroscopic data

Compound	IR (gas)/cm^{-1}	^{13}C NMR (δ, J/Hz)	^{19}F NMR (δ) {$^{125}Te^-$}	Mass spectrum, *m/z* (%)
2b	1316vs, 1232vs, 1148m, 1099s, 912vs, 751s, 614w, 542vw	105.2 [2 C, qnt, ^1J(CF) 317, ^2J(CF) 45, CF_2], 118.1 [2 C, tq, ^1J(CF) 285, ^2J(CF) 32, CF_3]	−83.48 (6 F, s, CF_3), −86.6 (4 F, s, CF_2) {1203.7 (m)}	368 (15, M^+), 249 (58), 230 (22), 180 (10), 161 (16), 149 (66), 130 (92), 119 (72), 100 (11), 69 (100), 50 (11)
2c	1275vs, 1228vs, 1185m, 1140m, 1118m, 952s, 910vs, 890vs, 732vs, 709s, 667m, 655m, 539w	82.5 [2C, sptd, ^1J(CF) 265.1, ^2J(CF) 22.9, CF], 121.2 [4 C, dq, ^1J(CF) 285.1, CF_3]	−73.8 [12 F, d, ^3J(FF) 7.3, CF_3], −169.1 (2 F, spt, CF) {1139.9 [mt, ^2J(Te) 56.8]}	468 (5, M^+), 299 (18), 181 (8), 149 (20), 130 (10), 119 (7), 100 (5), 69 (100), 50 (20)
2d	1332s, 1274m, 1246vs, 1222vs, 1201m, 1153m, 1122s, 1070w, 1037w, 878w, 811m, 730s, 667m, 531w	108.6 (2 C, m), 109.9 (2 C, m), 116.9 [2 C, td, ^1J(CF) 289.4, ^2J(CF) 34.3]	−79.6 (6 F, s), −80.1 (4 F, s) {1255.1 (m)}	468 (14, M^+), 299 (22), 181 (8), 149 (20), 130 (16), 119 (7), 100 (5), 69 (100), 50 (30)
2e	1348m, 1253vs, 1221s, 1144m, 1089w, 1006w, 776w, 744w, 715m, 681m, 530w	108.5 (2 C, m), 109.9 (2 C, m), 117.4 [2 C, tq, ^1J(CF) 287.5, ^2J(CF) 33.1]	−79.2 (4 F, s), −81.62 (6 F, s), −116.3 (4 F, s), −126 (4 F, s) {1278.6 (m)}	568 (M^+), 549 (8), 399 (8), 349 (50), 330 (21), 219 (21), 211 (4), 149 (30), 130 (33), 119 (12), 100 (13), 69 (100)
3b	1317s, 1222vs, 1140w, 1101m, 914s, 740m	91.2 [2 C, qt, ^1J(CF) 317.6, ^2J(CF) 43.9, CF_2], 117.9 [2 C, tq, ^1J(CF) 284.2, ^2J(CF) 32.4, CF_3]	−82.6 (6 F, s, CF_3), −86.5 (4 F, s, CF_2) {633.5 (m)}	396 (25, M^+), 375 (65), 256 (100), 249 (22), 149 (17), 130 (42), 119 (15), 100 (5), 81 (12), 69 (40), 50 (7)
3c	1292vs, 1276vs, 1228vs, 1184w, 1140w, 1119w, 953m, 889m, 747m, 708m, 538w	70.4 [2 C, sptd, ^1J(CF) 259.4, ^2J(CF) 24.8, CF], 21.4 [4 C, dq, ^1J(CF) 284.2 CF_3]	−71.93 [12 F, d, ^3J(FF) 12.2, CF_3], −163 (2 F, spt, CF) {7672.7 (m)}	594 (7, M^+), 425 (18), 297 (11), 256 (100), 168 (11), 149 (43), 130 (71), 100 (25), 69 (100), 50 (9)

From $Te_2(C_2F_5)_2$. Compound **3b** (1.5 g, 3.04 mmol) was treated with $SnMe_3H$ (0.5 g, 3.04 mmol). After purification **4b** (0.74 g, 60%) was obtained.

Perfluoroisopropyl trimethylstannyl telluride 4c

This compound was prepared as described for **4b** by treating **3c** (2.0 g, 4.29 mmol) with $SnMe_3H$ (0.71 g, 4.29 mmol). The mixture was stirred at −45 °C (0.5 h) and **4c** was isolated by fractional condensation *in vacuo*. The trap cooled to −40 °C contained **4c** (1.25 g, 64%) as a bright yellow liquid. Elemental analyses could not be carried out as the substance was rather unstable at 20 °C. $\tilde{\nu}$/cm^{-1} (gas) 1391m, 1306s, 1275s, 1244s, 1222vs, 1127s, 908w, 860w and 689w; δ_H 0.72 (9 H, s); δ_C −3.65 [3 C, q, ^1J(CH) 131.6, CH_3], 74.23 [1 C, sptd, ^1J(CF) 211.72, ^2J(CF) 26.7, CF] and 122.02 [2 C, dd, ^1J(CF) 284.19, CF_3]; δ_F −73.11 [6 F, d, ^3J(FF) 15.7, CF_3] and −159.02 (1 F, m, CF); δ_{Sn} 18.93 [1 Sn, dec, ^2J(SnH) 55.66 Hz]; δ_{Te} 184.31 (1 Te, m); *m/z* 462 (7, M^+), 447 (5, $M - CH_3$), 293 (7, Me_3SnTe^+), 261 (33, $CHSnTe^+$), 248 (10, $SnTe^+$), 185 (23,

Me_3SnHF^+), 169 (40, $C_3F_7^+$), 165 (100, Me_3Sn^+), 150 (16, Me_2Sn^+), 135 (35, $MeSn^+$), 130 (21, Te^+), 120 (16, Sn^+), 100 (13, $C_2F_4^+$) and 69 (75%, CF_3^+).

Trifluorotelluroacetyl fluoride (5)

Compound **4b** (1.26 g, 3.1 mmol) was passed at 10^{-3} Torr and 500 °C through a Pyrex-glass pyrolysis tube (length 30 cm, diameter 2 cm) packed with glass-wool. This was connected to two U-tubes, the first cooled to −45 and the second to −196 °C. The pyrolysis reaction took 1–1.5 h. In the U-tube at −45 °C both $SnMe_3F$ and unchanged **4b** were retained. In the following trap **5** was condensed as a bright green glassy material. By continuously raising the liquid-nitrogen level the whole wall of the trap could be covered with a film of **5** (0.33 g, 47%). The yield varied depending on the packing density of the glass-wool in the pyrolysis tube. If the density was too high some of the **5** formed decomposed to tellurium and other unidentified products; if it was too low the pyrolysis reaction was not very efficient.

Characterisation. To obtain an IR spectrum of compound **5** in the gas phase the pyrolysis apparatus described above was modified by connecting an IR flow cell (10 cm pathlength, KBr windows) between the two traps and placing the cell in the sample chamber of a spectrometer. As described previously,[1] the pyrolysis was performed under continuous pumping, while the IR spectrometer (Bruker FT-IR IFS 85) was scanning continuously. The success of this pyrolysis could be judged by the observation of green **5** condensing in the second trap. By performing the pyrolysis in an apparatus with a mass-spectrometer inlet situated between the two traps described before a mass spectrum was also obtained. To record this during pyrolysis, a part of the gas flowing between the traps was admitted to the mass spectrometer by opening the valve to the gas inlet. Additionally, peaks associated with O_2^+ and N_2^+ appeared, caused by a working pressure during pyrolysis (10^{-4} Torr) higher than that in the ionisation chamber of the mass spectrometer (10^{-7} Torr). $\tilde{\nu}$/cm^{-1} (gas) 1284s, 1224s, 1166vs, 1039w, 968m, 896w and 736w; *m/z* 230 (18, M^+), 211 (2, M − F), 161 (10, $TeCF^+$), 130 (16, Te^+) and 69 (26%, CF_3^+).

cis/trans-2,4-Difluoro-2,4-bis(trifluoromethyl)-1,3-ditelluretane 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 through orange to red was observed, yielding quantitative formation of **6**. Compound **6** was 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** was found to condense at −40 °C, either as a finely divided light red solid or as deep red-violet crystals. Large crystals were grown by allowing **6** to sublime at ambient temperatures onto a finger cooled to 16 °C. The mixture consisting of *cis* and *trans* forms could not be separated either by physical or by chemical methods. Consequently all analyses were obtained on a mixture of **6a** and **6b**. In solvents with different donor properties, differently coloured solutions were observed. Compound **6** is very volatile and stable to air over a long period. The ratio of the isomers **6a**:**6b** = 3:4 (based on ^{19}F NMR data); m.p. 71 °C (Found: C, 10.3. Calc. for $C_4F_8Te_2$: C, 10.5%); $\tilde{\nu}$/cm^{-1} (gas) 1309m, 1285m, 1257vs, 1233vs, 1151s, 1070w, 1029s, 949m, 901m, 730m, 690w, 668vw and 480vw; Raman $\Delta\tilde{\nu}$/cm^{-1} 1266vw, 1194vw, 1149vw, 1027vw, 760m, 711m, 534vw, 436vw, 298m, 283w, 261vs, 226s, 184vs, 152w, 141vw and 113vw; *m/z* 456 (100, M^+), 356 (7, $CF_3CFTe_2^+$), 256 (44, Te_2^+), 230 (84, CF_3CTeF^+), 211 (43, CF_3CTe^+), 192 (11, CF_2CTe^+), 161 (32, $CFTe^+$), 130 (86, Te^+) and 69 (6%, CF_3^+). Compound **6a**: δ_C 24.56 [C, md, ^1J(CF) 301.4, CF] and 121 [2 C, mq, ^1J(CF) 303.3, CF_3]; δ_F −78.19 [6 F, d, ^3J(FF) 16.36, CF_3] and −147 (2 F, q, CF); δ_{Te} 1775.95 [2 Te, sptt, ^2J(TeF) 318, ^3J(TeF) 22.12 Hz]. Compound **6b**: δ_C 23.95 [2 C, md, ^1J(CF) 299.5, CF] and 121.4 [2 C, mq, ^1J(CF) 278.5, CF_3]; δ_F −79.41 (6 F, m, CF_3) and −154.38 (2 F, m, CF); δ_{Te} 1781.2 [2 Te, sptt, ^2J(TeF) 297.2, ^3J(TeF) 21.7 Hz].

Crystallography

The red transparent crystals of compounds **6a**/**6b** are extremely volatile and change their shape in the light of a microscope lamp within a few seconds. So suitable crystals were selected under paraffin and placed in sealed 0.5 mm glass capillaries. Data collection at room temperature was performed on a STOE image-plate diffraction system. The unit-cell dimensions were determined by refinement of the angular positions of 205 reflections distributed over four images. Low-temperature data collections were performed with a second crystal on a STOE AED 2 four-circle diffractometer. The temperatures were measured by a microthermocouple at the position of the crystal. Both diffractometers were equipped with graphite-monochromated Mo-Kα radiation. Unit-cell determinations were performed by refinement of the setting angles of 24 reflections. Lorentz-polarisation and a numerical absorption correction was applied to all three data sets. The crystal shape was optimised by minimisation of R_{merge} (HABITUS)[17] (maximum, minimum transmission factors, crystal 1, 0.3801–0.1240; crystal 2, 0.2186, 0.0400). The structure was solved by direct methods (SHELXS 86)[18] and refined by full-matrix least squares on F^2 (SHELXL 93)[19] with anisotropic thermal motion for all atoms. Scattering factors for neutral atoms, as embedded in the program SHELXL 93, and the weighting scheme $w = [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$ with $P = (F_o^2 + 2F_c^2)/3$ were used; $\sigma(F_o^2)$ was estimated from counting statistics. Details of the data collection and structure refinement are given in Table 5.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/253.

2-Fluoro-3,6-dihydro-4,5-dimethyl-2-trifluoromethyltellurin 7

Compound **7** was obtained by the direct reaction of **4b** (0.78 g, 1.9 mmol) with 2,3-dimethylbutadiene (1.45 g, 17.7 mmol) dissolved in $CHCl_3$ (2 cm^3) in a sealed glass ampoule (30 cm^3). The mixture was heated to 150 °C for 4 h. During this time the formation of white crystals of $SnMe_3F$ could be observed. Compound **7** was isolated by fractional condensation *in vacuo* and collected at −10 °C as a yellow oil (0.51 g, 86%) extremely sensitive to air (Found: C, 32.1; H, 3.2. $C_8H_{10}F_4Te$ requires C, 31.1; H, 3.2%); $\tilde{\nu}$/cm^{-1} (gas) 2994w, 2921m, 2861w, 1442m, 1384w, 1315m, 1289vs, 1260vs, 1229m, 1188vs, 1077s, 975s, 952m, 897m, 849s, 737w, 699m, 656w, 587w, 548w and 513w; δ_H 1.88 (6 H, s, H^8/H^9), 2.65 (2 H, m, H^3), 3.42 [1 H, dd, ^2J(HH) 129.95, ^4J(HF) 3.97, H^6] and 3.46 (1 H, dd, $H^{6'}$); δ_C 7.38 [1 C, t, ^1J(CH) 144, C^6], 18.02 [1 C, tq, ^1J(CH) 126.53, ^3J(CH) 3.82, C^9], 21.21 [1 C, tq, ^1J(CH) 126.52, ^3J(CH) 3.82, C^8], 40.2 [1 C, dq, ^1J(CH) 130.66, ^2J(CF) 20.98, C^3], 104.8 [1 C, mqd, ^1J(CF) 202.18, ^2J(CF) 32.4, C^2], 125.14 [1 C, dq, ^1J(CF) 280.38, ^2J(CF) 30.52, C^7], 128.55 (1 C, m, C^4) and 132.13 (1 C, m, C^5); δ_F −76.1 [3 F, d, ^3J(FF) 13.78, CF_3] and −148.57 (1 F, m, CF); δ_{Te} 708.97 [1 Te, dm, ^2J(TeF) 250 Hz]; *m/z* 312 (100, M^+), 297 (5, M − CH_3), 251 (10, $C_5F_3H_4Te^+$), 197 (10, $C_5H_7Te^+$), 181 (40, M − TeH), 141 (40, M − TeH − 2 HF) and 67 (100%, $C_5H_7^+$).

Table 5 Experimental details of the crystallographic study of compounds **6a**/**6b**

Formula	$C_4F_8Te_2$
M_r	455.2
Space group	$P2_1/n$
Crystal system	Monoclinic
Z	2
$F(000)$	400
μ(Mo-Kα)/cm^{-1}	62.9

	T/K		
	298	211	169
a/Å	8.40(1)	8.42(1)	8.26(1)
b/Å	6.578(8)	6.500(8)	6.544(8)
c/Å	9.51(1)	9.34(1)	9.30(1)
β/°	112.52(9)	113.27(9)	113.46(9)
U/Å^3	485.22	469.6	461.1
2θ range/°	9.5–56.3	3.0–60.0	3.0–60
No. data collected	3509	1741	1116
No. unique data	1122	819	815
hkl Ranges	±10, ±8, ±12	−10 to −7, 0–9, 7–10	−9 to −7, 0–9, 2–11
R_{merge}	0.054	0.094	0.048
No. data in refinement	1122	819	815
No. refined parameters	64	64	64
Final $R(F^2)$ for all data	0.172	0.255	0.167
Final $R(\|F\|)$ for $F_o > 4\sigma(F_o)$	0.069	0.089	0.062
Goodness of fit	1.060	1.090	1.120
Maximum shift/e.s.d. in last cycle	0.000	0.000	0.000
Weighting parameters a, b	0.0590, 3.0237	0.1748, 1.3967	0.1082, 3.3833
Largest remaining features in electron-density map/e Å^{-3}	1.70, −1.03	2.43, −2.25	2.43, −1.59

cis/*trans*-2,4-Dichloro-2,4-bis(trifluoromethyl)-1,3-ditelluretane 8a/8b

A sample of compounds **6a**/**6b** (0.165 g, 0.36 mmol) was deposited under an atmosphere of argon in a Carius tube (100 cm^3) and cooled to −196 °C. All argon was removed *in vacuo*, and BCl_3 (2 cm^3) was added to the reactor. The mixture was initially warmed to −50 °C and thereafter the temperature was raised slowly to ambient over a period of 12 h. At −40 °C **6a**/**6b** began to dissolve in BCl_3 to give a violet solution. At room temperature the mixture turned blue. Compound **8a**/**8b** was isolated by fractionation *in vacuo*. The product was collected in the trap cooled to −10 °C as violet crystals (0.165 g, 93%). It was not possible to separate the *cis* and *trans* forms of **8**, so all the analyses were obtained on an isomer mixture of **8a** and **8b**. Ratio of isomers **8a**:**8b** = 3:4 (based on ^{19}F NMR spectra), m.p. 108 °C (Found: C, 9.8; Cl, 12.7. $C_4Cl_2F_6Te_2$ requires C, 9.8; Cl, 14.5%); $\tilde{\nu}$/cm^{-1} (KBr) 1220vs, 1162vs, 876s, 785vs, 745m, 719s, 684vs, 677vs and 546m; Raman $\Delta\tilde{\nu}$/cm^{-1} 1226vw, 1149vw, 813vw, 723m, 685w, 550w, 532m, 370m, 298m, 263s, 237w, 200s, 183s, 163s, 140m and 114w; *m*/*z* 490 (28, M^+), 455 (3, $M^+ - Cl$), 256 (24, Te_2^+), 246 (100, CF_3CTeCl^+), 211 (31, CF_3CTe^+), 192 (12, CF_2CTe^+), 177 (25, $TeCCl^+$), 161 (14, $TeCF^+$), 130 (35, Te^+), 69 (6, CF_3^+) and 47 (5%, CCl^+). Compound **8a**: δ_C 12.17 [2 C, q, ^2J(CF) 38.15] and 124.02 [2 C, q, ^1J(CF) 276.6 Hz, CF_3]; δ_F −74.15 (6 F, s); δ_{Te} 2058.86 [2 Te, spt, ^3J(TeF) 16.2 Hz]. Compound **8b**: δ_C 12.75 [2 C, q, ^2J(CF) 36.24] and 123.56 [2 C, ^1J(CF) 276.5 Hz, CF_3]; δ_F −75.05 (6 F, s); δ_{Te} 2083.44 [2 Te, spt, ^3J(TeF) 18.4 Hz].

cis/*trans*-2,4-Dibromo-2,4-bis(trifluoromethyl)-1,3-ditelluretane 9a/9b

The method used was analogous to that in the preparation of compounds **8a**/**8b**. An excess of BBr_3 was treated with **6a**/**6b** (0.14 g, 0.31 mmol). After the mixture had reached room temperature, the excess of boron halides was removed *in vacuo* and the brown solid (0.165 g, 92%) dried *in vacuo*. Ratio of isomers **9a**:**9b** = 1:1 (based on ^{19}F NMR spectra); decomposition temperature 111 °C (Found: C, 7.7. requires C, 8.3%); $\tilde{\nu}$/cm^{-1} (KBr) 1213vs, 1150vs, 871m, 733vs, 669vs and 533m; *m*/*z* 578 (29, M^+), 500 (2, $M^+ - Br$), 419 [100, $Te_2C_2(CF_3)_2^+$], 291 (14, CF_3CTeBr^+), 256 (74, Te_2^+), 209 (26, $TeBr^+$), 149 (26, TeF^+), 130 (71, Te^+), 79 (11, Br^+) and 69 (15, CF_3^+). **9a**: δ_C(fluorine decoupled) 33.45 (2 C, s), 124.12 (2 C, s, CF_3); δ_F −72.69 (6 F, s); δ_{Te} 2105.96 [2 Te, spt, ^3J(TeF) 10.99 Hz]. Compound **9b**: δ_C(fluorine decoupled) 34.09 (2 C, s) and 124.69 (2 C, s, CF_3); δ_F −73.36 (6F, s); δ_{Te} 2128.33 [2 Te, spt, ^3J(TeF) 13.4 Hz].

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References

1 R. Boese, A. Haas and C. Limberg, *J. Chem. Soc., Dalton Trans.*, 1993, 2547.
2 M. Minoura, T. Kawashima and R. Okazaki, *J. Am. Chem. Soc.*, 1993, **115**, 7019.
3 C. R. Brundle, M. B. Robin, N. A. Kuebler and H. Basek, *J. Am. Chem. Soc.*, 1972, **94**, 1451.
4 M. L. Denniston and D. R. Martin, *J. Inorg. Nucl. Chem.*, 1975, **37**, 1871.
5 S. Herberg and D. Naumann, *Z. Anorg. Allg. Chem.*, 1982, **402**, 95.
6 T. N. Bell, B. J. Pullmann and B. D. West, *Aust. J. Chem.*, 1963, **16**, 722.
7 R. J. Lagow, L. L. Gerchman, R. A. Jacob and J. A. Morrison, *J. Am. Chem. Soc.*, 1975, **97**, 518.
8 J. Kischkewitz and D. Naumann, *Z. Anorg. Allg. Chem.*, 1987, **547**, 167.
9 D. Naumann and G. Klein, *Z. Anorg. Allg. Chem.*, 1987, **550**, 4535.
10 C. D. Desjardins, H. J. Paige, J. Passmore and P. Teylor, *J. Chem. Soc., Dalton Trans.*, 1974, 488.
11 J. J. Zuckermann, *Adv. Inorg. Chem. Radiochem.*, 1964, **6**, 383.
12 R. Boese, A. Haas and M. Spehr, *Chem. Ber.*, 1991, **124**, 51.
13 L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, *Itaca*, 1960.
14 J. Grobe, D. Le Van and J. Welzel, *J. Organomet. Chem.*, 1990, **386**, 321.

15 J. Grobe and D. Le Van, *Tetrahedron Lett.*, 1985, **26**, 3681; *J. Organomet. Chem.*, 1986, **26b**, 3681; J. Grobe and J. Szamirtat, *Z. Naturforsch., Teil B*, 1988, **43**, 427.

16 R. K. Harris, *Can. J. Chem.*, 1964, **42**, 2275; D. J. Mowthorpe and A. C. Chapman, *Spectrochim. Acta, Part A*, 1962, **23**, 451.

17 W. Herrendorf and H. Bärnighausen, HABITUS, Program for the optimisation of the crystal shape for numerical absorption correction, University of Karlsruhe, 1993.

18 G. M. Sheldrick, SHELXS 86, Program for crystal structure solution, University of Göttingen, 1986.

19 G. M. Sheldrick, SHELXL 93, Program for crystal structure refinement, University of Göttingen, 1993.

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