Preparation, Characterisation and Reactions of Tellurocarbonyl Difluoride and Trifluoromethanetellurenyl Iodide†

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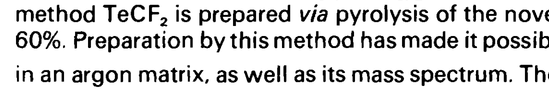
With the synthesis of Te=CF_2 the first telluroketone has been isolated. Two different types of preparation are described. In the first $Hg(TeCF_3)_2$ is treated with Et_2AlI to give low yields of $TeCF_2$. In the second method $TeCF_2$ is prepared *via* pyrolysis of the novel compound $Me_3SnTeCF_3$ at 280 °C with yields of 50–60%. Preparation by this method has made it possible to obtain the IR spectra of $TeCF_2$ in the gas phase and in an argon matrix, as well as its mass spectrum. The compound reacts with $SeCF_2$ to give $\overline{SeCF_2TeCF_2}$ and undergoes a cycloaddition reaction with 2,3-dimethylbutadiene. It is thermally very unstable: on warming its cyclic dimer is formed quantitatively. This reacts with BX_3 (X = Cl or Br) to give the corresponding chlorinated and brominated 1,3-ditelluretanes. Dissolution of these in dimethylformamide yields complexes with the solvent. In the initially described method for the generation of $TeCF_2$, $CF_3TeI{\cdot}I_2$ is also formed as a by-product. An alternative route to this compound involves the formation of CF_3TeI in solution by reactions of $CF_3TeTeCF_3$ with I_2. On cooling to −70 °C, the corresponding I_2 adduct is precipitated. The existence of CF_3TeI has been proven by its reaction with $Hg(SeCF_3)_2$ and $Hg(NSO)_2$, yielding the novel compounds $CF_3SeTeCF_3$ and CF_3TeNSO, respectively.

In general it is to be expected that replacement of selenium by tellurium in selenocarbonyl compounds will lead to a considerable increase in the reactivity of such compounds. This reactivity, which is very high even for the selenocarbonyls, can be decreased by the choice of suitable ligands. For instance, the lability of this class of substances can be reduced considerably by substituting the sp^2-hybridised carbon with groups, like RO and R_2N, which are able to stabilise the Se=C bond through resonance contributions to the bonding.[1–3] The greater the ability of a ligand to function as a π donor, the more it stabilises the Se=C bond *via* the following mesomeric structures.



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Only in the absence of such stabilising substituents, the main contribution comes from I, as can be verified by determining the bond lengths of representative molecules.[4,5] Of course, only those substances which possess actual Se=C double bonds exhibit the expected high reactivity. It is no surprise, therefore, that the first examples of 'tellurocarbonyls' to be reported were telluro-amides and -esters.[6]

An alternative approach is to stabilise selenocarbonyls by co-ordination to transition-metal fragments. This method can also be extended to tellurocarbonyls.[7] Stable compounds can also be obtained by kinetic stabilisation with the aid of bulky ligands. A few tellurocarbonyls can be prepared by this method, but additional resonance stabilisation is necessary.[8] The Se=C double bond can also be stabilised by using electronegative substituents, in particular F, CF_3 and C_2F_5[9,10] since the so-called 'perfluoro effect' leads to a strengthening of the skeletal σ bonding.[11] The advantage of such a method is that the Se=C double-bond character remains undiminished, so that compounds of this kind contain 'real' Se=C double bonds, as evidenced by their spectroscopic properties.[12,13] Thus, the resulting substances are metastable systems which can be isolated, characterised and employed in chemical reactions.[14] In this context, the isolation of Te=CF_2 appeared to be of greatest interest because in this molecule the existence of a genuine Te=C double bond is to be expected. Although no tellurocarbonyls of this sort have been isolated previously, there exist theoretical studies regarding such species.[15] The elusiveness of tellurocarbonyls showing the typical character of a Te=C double bond can be explained by the following argument. In the systems E=C (E = O, S, Se or Te) the bond lengths increase with increasing atomic number of E. This leads to a decreasing π overlap, which results from both the increasing atomic radii of the chalcogens, and the increasingly diffuse character of the p orbitals.[1] The only characteristic Te=C bond length which has been previously determined is that in S=C=Te (r = 1.904 Å), in which tellurium is bonded to a sp-hybridised C atom.[16]

Recently a few simple telluro-ketones and -aldehydes have been generated *in situ*, but their existence has been proved only by [4 + 2]-cycloadditions.[17,18] The cyclic dimers—more properly 1,3-ditelluretanes—of the discussed compounds have also remained unknown. Only one 1,3-ditelluretane has as yet been identified. This resulted from the dimerisation of a telluroketene and contains therefore sp^2-hybridised carbon.[19] In this paper we describe the synthesis, characterisation and reactions of the first non-resonance-stabilised tellurocarbonyl, Te=CF_2, and its cyclic dimer.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Non-SI units employed: Torr ≈ 133 Pa.

Results and Discussion

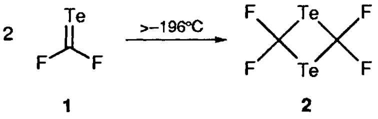
Syntheses, Characterisation and Reactions of Tellurocarbonyl Difluoride and its Cyclic Dimer.—None of the synthetic routes which lead to resonance-stabilised tellurocarbonyls or to tellurocarbonyls generated *in situ* was suitable for the preparation and isolation of $TeCF_2$. Hence we followed a synthetic strategy similar to that employed for the preparation of perfluorinated selenocarbonyls. These are produced by three different methods: (*i*) reaction of $Hg(SeCF_2R_f)_2$ with Et_2AlI (R_f = F, CF_3 or C_2F_5),[10] (*ii*) pyrolysis of $B(SeCF_3)_3$ in the presence of KF or CsF,[20] and (*iii*) pyrolysis of $Me_3SnSeCF_2R_f$ (R_f = F or CF_3).[13,21]

At the outset of the work, the most suitable starting material appeared to be $Hg(TeCF_3)_2$,[22] because compounds of the types $B(TeCF_3)_3$ and $Me_3SnTeCF_3$ were not known. The initial attempts focused on experiments to generate $TeCF_2$ by reaction of the mercury salt with Et_2AlI; the successful outcome has been briefly reported.[6]

The analogous reaction leading to selenocarbonyl difluoride has been carried out in octamethylcyclotetrasiloxane (omcts) as a solvent which fulfils all the necessary conditions (low volatility, low Lewis basicity, good solubility for mercury salts);[10] the reaction of $Hg(TeCF_3)_2$ with Et_2AlI had to be carried out in the absence of a solvent because of the insolubility of the mercury salt in omcts. This limited the amount of $Hg(TeCF_3)_2$ which could be used. Reaction takes place according to equation (1).

$$Hg(TeCF_3)_2 + 2Et_2AlI \longrightarrow 2\underset{\mathbf{1}}{Te{=}CF_2} + HgI_2 + 2Et_2AlF \quad (1)$$

If the Et_2AlI is dropped too quickly on to the mercury salt, the exothermic reaction proceeds uncontrollably. This results in decreased yields of **1** and leads to the formation of a black-brown solid (see below). The reactivity of **1** greatly exceeds those of the selenocarbonyls. It is not transferable *in vacuo* and warming to temperatures slightly above 77 K results in its rapid dimerisation [equation (2)] to the intensely coloured $Te_2C_2F_4$, which was characterised structurally by X-ray crystallography.



1 **2** (2)

This dimerisation proceeds in the solid phase without the evolution of any gas. Hence it was impossible to characterise **1** by conventional methods involving IR, NMR and mass spectroscopy. Evidence for the existence of this compound was limited to the products of its reactions.

At this stage the synthesis of **1** could be performed only on a milligram scale. In the search for a larger-scale preparation we tried to synthesise $Me_3SnTeCF_3$ with the intention of pyrolysing it following the precedent set by the corresponding selenium compound.[12,21] The stannyl telluride can be produced in yields of 90–95% by the reaction of $CF_3TeTeCF_3$ with Me_3SnH according to equation (3). Using this synthetic route, **3**

$$CF_3TeTeCF_3 + 2Me_3SnH \longrightarrow 2\underset{\mathbf{3}}{Me_3SnTeCF_3} + H_2 \quad (3)$$

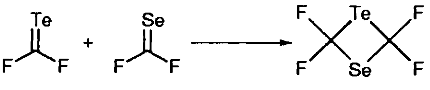
can be prepared on a 10 g scale and therefore appeared to be a promising starting material for the synthesis of **1** on a useful scale [equation (4)].

$$\underset{\mathbf{3}}{Me_3SnTeCF_3} \longrightarrow Me_3SnF + \underset{\mathbf{1}}{Te{=}CF_2} \quad (4)$$

We have recently communicated the success of this method.[23] If **3** is caused to flow through a heated tube (280 °C) packed with glass wool, **1** is generated in yields of 50–60%. Although all attempts to characterise **1**, starting from the condensed phase, were thwarted by dimerisation, this molecule seemed to be reasonably stable at low concentrations in the gas phase. This suggested a possible method to identify monomeric **1** spectroscopically.

With the aid of a special apparatus, **1**, generated by pyrolysis of **3**, was caused to pass through an IR cell before being trapped at 77 K. In this manner the IR spectrum of pure gaseous $Te{=}CF_2$ was obtained and a similar procedure also lead to an IR spectrum of **1** isolated in an argon matrix at 13 K; on the evidence of the spectrum the matrix included only trace amounts of $CF_3TeTeCF_3$ as impurity. Performance of the pyrolysis in an apparatus coupled to the gas-inlet of a mass spectrometer likewise yielded the mass spectrum of **1** (Fig. 1).

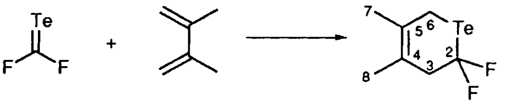
Turning attention to chemical evidence of **1**, the first reaction studied was the dimerisation of **1**, which occurs simply on warming the product trap (as described previously[6,23]). The reaction of **1** with $Se{=}CF_2$ by co-condensation has also been mentioned previously.[6] At that time, however, we were able only to obtain **1** in milligram amounts and so the yields of $\overline{SeCF_2TeCF_2}$ were even lower [equation (5)]. With the new



1 **4** (5)

method for the synthesis of **1** *via* **3** it is now possible to obtain much greater amounts of **4**, enough even to measure its ^{13}C NMR spectrum.

For further characterisation a [4 + 2]-cycloaddition reaction with a diene was suitable. In this case 2,3-dimethylbutadiene was used, because it is one of the most reactive dienes in this type of reaction[21] and it is much less prone to dimerise than is cyclopentadiene. Because **1** is not condensable, 2,3-dimethylbutadiene was co-condensed at 77 K with **1** and reacted by warming the mixture rapidly to engineer optimal mixing. Despite this, most of **1** dimerised before reacting with the diene so that the yield of the cycloadduct was less than 1%, of that implied by equation (6).



1 **5** (6)

This is due to the relatively high m.p. of 2,3-dimethylbutadiene and to its poor solvent behaviour properties towards **1** as compared with $SeCF_2$. Use of solutions of the diene in $CFCl_3$ increased the yield to only 1–2%. Because of this it was not possible to isolate **5** in the earlier experiments involving **1**, obtained by the $Hg(TeCF_3)_2$ method. Using the new $Me_3SnTeCF_3$ method, pure **5** could be isolated in small amounts from the reaction mixture but the yields were still too low to permit it to be characterised fully. In this context we tried to prepare **5** directly from **3**, without having to isolate **1**, following a procedure analogous to that already exploited for some phosphaalkenes[24] and selenocarbonyls.[12] Heating **3** in $CHCl_3$ in the presence of a large excess of 2,3-dimethylbutadiene yields **5** slowly but in high yields, so that it was possible to carry out complete characterisation. Compound **5** is a yellowish oil with a low volatility and which is stable in air.

Hence we also succeeded in characterising **1** *via* its chemical reactions. Compound **2** appeared to be a useful starting material for further reactions. The successful F/Cl and F/Br exchange in

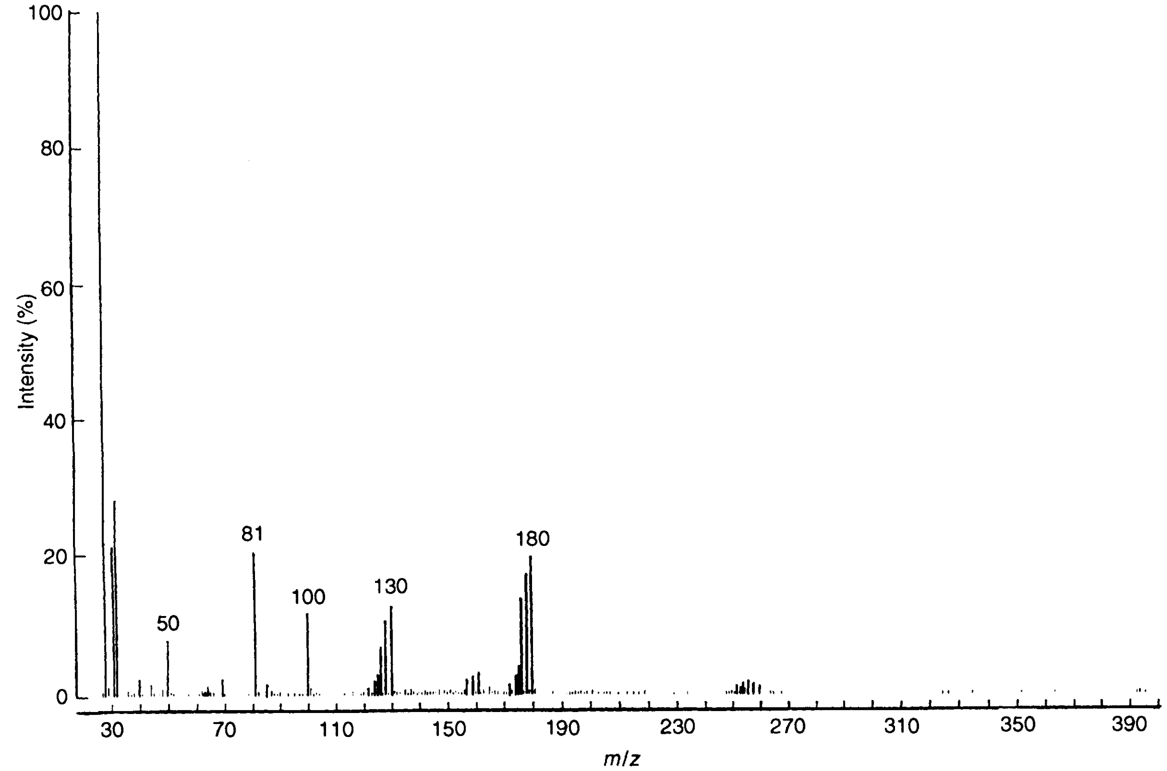
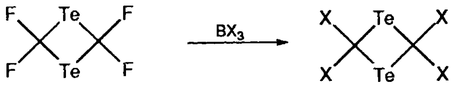


Fig. 1 Mass spectrum of the vapour of **1** after passing through a −45 °C trap and formed by the pyrolysis of **3**

$\overline{\text{SeCF}_2\text{SeCF}_2}$ with BX_3 (X = Cl or Br)[25,26] provided the impetus to attempt similar reactions with the tellurium analogue. In contrast to $\overline{\text{SeCF}_2\text{SeCF}_2}$, **2** reacts with BCl_3 and BBr_3 even at −20 °C to give the chlorinated and brominated compounds **6** and **7** in high yield [equation (7)]. These

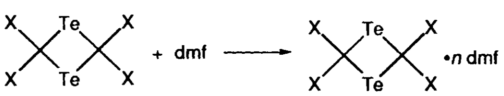


(7)

2

X = Cl **6**
X = Br **7**

compounds have no measurable vapour pressure and are completely insoluble in any solvents with donor numbers[27] lower than that of dimethylformamide (dmf). However, they are quantitatively dissolved by dmf to yield complexes of **6** and **7** with the solvent molecules, reflecting the Lewis acidity of the bridging Te atoms.[28] By removing the solvent, the compounds **8** and **9** are obtained [equation (8)] as deeply coloured, air-stable solids.



(8)

8 X = Cl, n = 0.5
9 X = Br, n = 1

In conclusion, with tellurocarbonyl difluoride, the first telluroketone has been isolated and characterised. Using this as a starting material, it has proved possible also to open up the chemistry of the 1,3-ditelluretanes.

The IR Spectra of $Te{=}CF_2$.—Molecules of the type $E{=}CF_2$ (E = O, S or Se) exhibit C_{2v} symmetry,[10,11,29–31] as presumably does **1**. As such, it is an asymmetric top with three different moments of inertia $I_a \neq I_b \neq I_c$. This leads to very characteristic band contours in the IR spectrum of the vapour. The six normal vibrations of such a molecule are characterised as follows: ν(mode, band contour, irreducible representation), $\nu_1[\nu_{sym}(C{=}E), A, a_1]$, $\nu_2[\nu_{sym}(CF_2), A, a_1]$, $\nu_3[\delta_{sym}(CF_2), A, a_1]$, $\nu_4[\nu_{asym}(CF_2), B, b_1]$, $\nu_5[\nu_{asym}(ECF), B, b_1]$, $\nu_6[\delta(ECF_2)$ out-of-plane, C, $b_2]$.[11,31]

Because of the small mass of the F atoms, these cannot be considered as rigid during the $\nu(C{=}E)$ vibration, precluding isolation of this mode.[32] The effect increases with the mass of the chalcogen. Hence for OCF_2[33] and, still more, for SCF_2[30] and $SeCF_2$,[31] there is coupling of the vibrations belonging to the same class.

Analysis of the IR spectrum of gaseous **1** is aided by consideration of that of $SeCF_2$. The IR spectrum of matrix-isolated $SeCF_2$ exhibits only five of the six fundamental vibrations[11] in the region 400–4000 cm^{-1}. Of these only ν_1 and ν_4 appear as intense absorptions, ν_3 as an absorption of medium intensity and ν_2 and ν_6 as very weak bands.

Even in the IR spectrum of gaseous SCF_2, the relatively weak bands ν_2, ν_3 and ν_6 are observable with a 10 cm pathlength only at vapour pressures of 300 Torr.[31] As the spectrum of $SeCF_2$ could be measured only at pressures up to 10 Torr before the onset of oligomerisation, only the three bands ν_1, ν_3 and ν_4 could be identified.[31] In comparison with $SeCF_2$ (432 cm^{-1}), the ν_3 vibration of **1** is expected at lower wavenumbers so that this should be absent from the region 400–4000 cm^{-1} (see Fig. 3). Hence only two bands (ν_1 and ν_4) are expected in the IR spectrum of gaseous $Te{=}CF_2$. These should have band contours similar to those of the corresponding bands of $SeCF_2$. Such a situation is in fact observed (Fig. 2).

To detect the missing ν_2 and ν_6 vibrations, which are expected to lie in the region 400–4000 cm^{-1}, we recorded the IR spectrum of **1** in an argon matrix at 13 K (Fig. 4). Because of the much smaller dimensions of the pyrolysis apparatus necessary for the matrix measurements, however, the experiments could not be performed in an optimal way, leading to higher pyrolysis temperatures. Furthermore, some of the parameters applying to all the matrix experiments, such as the pressure (10^{-7} Torr) and

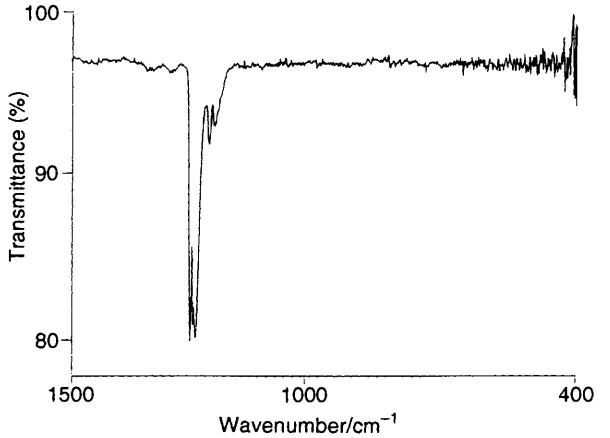


Fig. 2 Infrared spectrum of the vapour of **1**; pressure *ca.* 10^{-2} Torr, pathlength 10 cm, T = 298 K

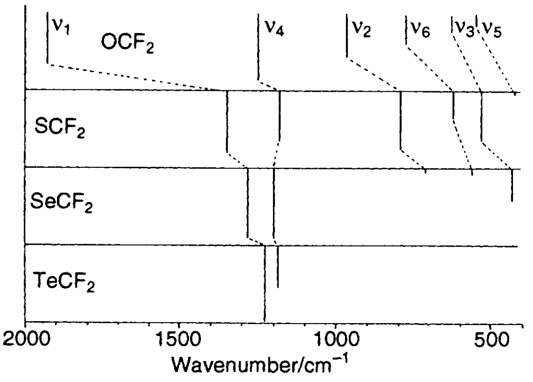


Fig. 3 Line diagram depicting the principal features in the region 400–2000 cm^{-1} of the infrared spectra, displayed by matrix-isolated molecules of the type E=CF$_2$ (E = O, S, Se, Te)

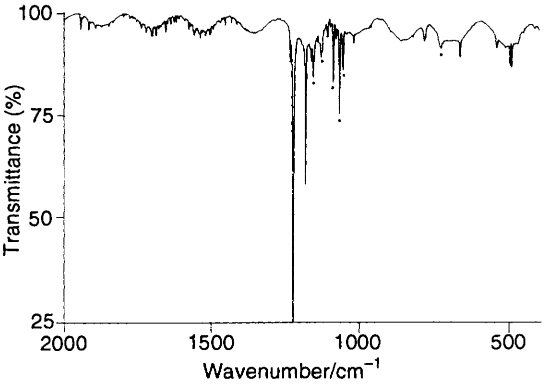


Fig. 4 The IR spectrum of **1** trapped in a solid argon matrix at *ca.* 13 K; bands marked with a dot are due to the contamination, $CF_3TeTeCF_3$

the dilution of the starting material with argon, seemed not to be advantageous for repeating the synthesis of **1** on a laboratory scale at the matrix assembly. So it was not possible to isolate a totally pure sample of **1**. The best spectrum was obtained under the conditions given in the Experimental section (Fig. 4). This exhibited relatively few absorptions ascribable to impurities; the majority of these bands are identified with $CF_3TeTeCF_3$. Hence most of the impurity features are accounted for.

Apart from ν_1 and ν_4, there exist a few remaining bands in the region expected for the missing vibrations of **1**. However, any attempt at assignment must be speculative. The vibrations ν_1 and ν_4 are unambiguously identified in the infrared spectra of both the gas and the matrix samples; the IR bands (given in cm^{-1}) exhibited by gaseous **1** in the region of 400–4000 cm^{-1} are ν_1 (R 1244.4, Q 1240.0, P 1232.2) and ν_4 (R 1206.7, P 1195.4). Matrix-isolated **1** shows ν_1 at 1226.0 and ν_4 at 1185.5 cm^{-1}.

Table 1 Atomic coordinates (× 10^4) for compound **2**

Atom	*x*	*y*	*z*
Te(1)	3534(1)	−1585(1)	−5512(1)
Te(2)	−73(1)	376(1)	−5760(1)
Te(3)	−3971(1)	0	1237(1)
Te(4)	−2413(1)	−1315(1)	−2512(1)
C(1)	755(20)	−1313(17)	−6852(20)
C(2)	2767(21)	97(16)	−4458(21)
C(3)	−2346(21)	378(16)	−1167(21)
C(4)	−4034(20)	−1735(15)	−129(19)
F(1)	−495(12)	−2224(9)	−6424(12)
F(2)	807(12)	−1369(11)	−8635(12)
F(3)	3952(13)	983(11)	−4944(13)
F(4)	2677(13)	131(11)	−2654(12)
F(5)	−3158(12)	1244(10)	−2207(13)
F(6)	−592(12)	760(10)	−794(12)
F(7)	−3248(14)	−2611(11)	865(14)
F(8)	−5836(13)	−2080(10)	−540(13)

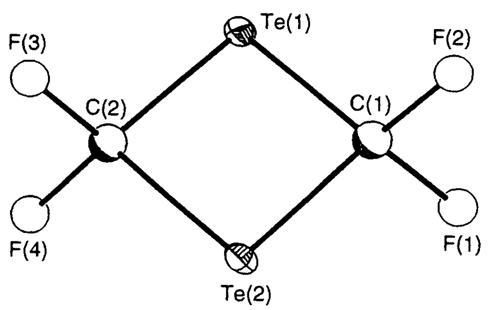


Fig. 5 Structure of one of the two independent molecules found in the asymmetric unit in crystals of **2**. Anisotropically refined atoms are displayed at 50% probability level, the radii for isotropically refined atoms are arbitrary

Assignment of the spectrum of the vapour was aided by reference to the correlation of the $\Delta\nu_{PR}$ separation with the moments of inertia, *via* a method reported by Seth-Paul.[34] The CF$_2$ group was assumed to have the same geometry as in SeCF$_2$, a reasonable assumption given that the series E=CF$_2$ (E = O, S or Se) shows relatively small geometrical differences in the CF$_2$ moiety.[10] The Te=C bond length was that calculated by Pauling.[35] Hence the parameters used for the calculation were: r(Te=C) = 1.94, r(C–F) = 1.314 Å, F–C–F = 107.5°, giving the following $\Delta\nu_{PR}$ values, which could be compared with the observed data (band-contour, $\Delta\nu_{PR}$ calc./cm^{-1}, $\Delta\nu_{PR}$ obs./cm^{-1}): A, 12.5, 12.2; B, 10.4, 11.3; C, 18.8, 0. The observed P–R separations, which are in good agreement with those calculated, show the behaviour expected on the basis of the properties compared with the values of the lighter homologues.[30,31]

In conclusion, it may be added that the slight shift in wavenumber for the ν_1 vibration on going from sulfur to selenium and from selenium to tellurium implies a decreased contribution to this mode from the E=C stretching vibration with increasing mass of E. In contrast, the participation of the ν_{sym}(C–F) vibration (only 16% in OCF$_2$[36]) increases significantly, so that the ν_1 band probably has more ν_{sym}(C–F) than ν(Te=C) character in **1**. An isolated ν(Te=C) vibration should appear at much lower wavenumber and with reduced intensity.

The Crystal Structure of Compound **2**.—In order to establish the dimeric character and to evaluate the geometry of the four-membered ring we investigated the X-ray crystal structure of **2**. Atomic parameters are given in Table 1. Two independent molecules were found in the asymmetric unit (Fig. 5). Both possess the expected D_{2h} symmetry within the limits of significance, with Te–C distances [2.191(10) Å, mean value] which are equal, based on the 3σ criterion. The C_2Te_2 unit forms a rhombus with smaller angles at the Te atoms [78.9(3)°, mean value] than at the C atoms [101.1(5)°, mean value]. This is in accord with the same framework found for *trans*-2,4-dibenzylidine-1,3-ditelluretane (79.8 and 100.2°) with sp^2-hybridised C atoms[19a] and a Te–Te distance of 3.236 Å. However, here the Te–C distances were found shorter (2.112 Å) than in **2**, indicating some p_π–d_π C–Te back bonding.

A shortening of the Se–C distance was also confirmed for $Se_2C_2(CF_3)_4$[37] which was explained in terms of Se–Se interactions at a distance of 2.931 Å, which is in between that of a covalent bond and the sum of van der Waals radii (2.34 and 4.00 Å, respectively). The same was confirmed by complete neglect of differential overlap (CNDO/2) calculations for $Se_2C_2F_4$[38] and must also be assumed for **2** with a Te–Te distance of 3.385 Å which is also closer to 2.74 than to 4.40 Å for covalent and van der Waals distances, respectively.

The mean F–C–F angles in **2** are 105(1)°, smaller than the exocyclic C–C–C angles for $Se_2C_2(CF_3)_4$[37] and F–C–F angles for $(SOCF_2)_2$[39] (109.8°), but in the same range as for $Se_2C_2F_4$ (106.3°),[39] and for 1,1,3,3-tetrachloro-1,3-disilacyclobutane (104°)[40] and 1,1-dichloro-1-silacyclobutane (105°).[40]

Synthesis and Reactions of CF_3TeI.—Interest focused also on the nature of the black-brown solid described above, and formed by the vigorous reaction of Et_2AlI with $Hg(TeCF_3)_2$. This material can be isolated and characterised. It dissolves in $CHCl_3$ giving an intense violet solution, and its mass spectrum can be interpreted in terms of that expected for CF_3TeI, with an additional peak due to I_2^+. The ^{19}F NMR spectrum of the compound shows a singlet which is shifted only 0.4 ppm from the signal associated with $CF_3TeTeCF_3$.[22] So it seemed that a Te–I bond had been formed. The analytical data suggested a weak adduct between I_2 and CF_3TeI. This behaviour can be understood in the general context of chalcogen iodides, as outlined below.

Binary compounds of selenium and iodine are as yet unknown, but bulky ligands activate the Se–Se bond in diselenides to the extent that I_2 reacts to give selenyl iodides.[41] Most of these reactions are equilibria from which the selenyl iodides can sometimes be isolated; in other cases only an iodine–diselenide adduct is obtainable. In the last few years this kind of chemistry could be extended to the tellurium analogues, using bulky ligands such as $C(SiMe_3)_3$ or just bulky organic groups.[42]

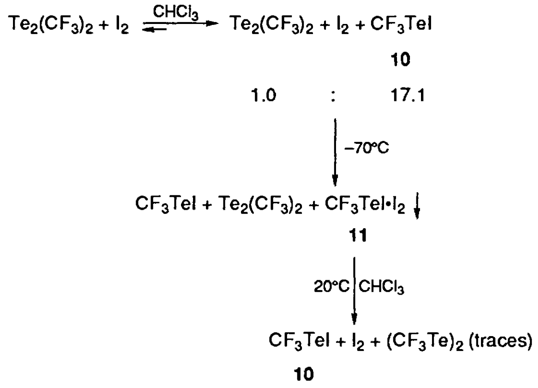
Most of the reactions of iodine with ditellurides reported previously lead only to organotellurium triiodides.[43] To gain stable compounds of the type RTeI, R must contain donor groups in a position *ortho* to tellurium in order to protect it from further attack of iodine.[44] A second method of generating RTeI compounds involves the use of solvents in which the products are insoluble, and from which they are precipitated, thereby protecting them from further reaction with iodine.[45]

Substances of the type REI (E = Se or Te), containing small, σ-bonding, fluorinated groups like CF_3 are as yet unknown; CF_3SI was generated in 1985 which is a very fragile molecule, stable only at low temperatures and high dilution.[46] The compound CF_3TeI was reportedly obtainable from the reaction of $CF_3TeTeCF_3$ with I_2 but it was not characterised unambiguously, nor was the alternative reaction pathway (the formation of a ditelluride–iodine adduct, which would have similar properties) excluded or even discussed, so that no clear evidence for this molecule is available hitherto.[47]

To elucidate the formation of a Te–I bond in the reaction of $Hg(TeCF_3)_2$ with Et_2AlI, certain reactions with these starting materials and other by-products formed during the reaction were investigated. To this end $CF_3TeTeCF_3$, which is formed during the reaction *via* decomposition of the mercury salt,[6] and I_2 were allowed to react in $CHCl_3$. Trifluoromethanetellurenyl iodide **10** was obtained in almost quantitative yield from the equilibrium (9).

$$CF_3TeTeCF_3 + I_2 \rightleftarrows \underset{\mathbf{10}}{2CF_3TeI} \qquad (9)$$

Compound **10** cannot be isolated from the solution but its existence was demonstrated unambiguously by NMR spectroscopic investigations. Removal of the solvent led to decomposition with the regeneration of the starting materials, but cooling of the solution to −70 °C caused the precipitation of a black-brown solid, whose chemical and physical properties were identical with those of the solid isolated after the synthesis of **1**. Its further characterisation again endorsed the previously assumed composition $CF_3TeI{\cdot}I_2$ **11**. The decanted solution showed, in addition to a signal for **10**, a signal for $CF_3TeTeCF_3$. In solution **11** decomposes to **10** and I_2, so that the NMR properties of **10** can be deduced. These results are encompassed in Scheme 1.



Scheme 1

That **11** contains Te^{IV} and not Te^{II} was excluded because of the following reasons: (*i*) $CF_3Te^{IV}I_3$ would probably not decompose in solution to yield **10** and I_2; (*ii*) Mehdi and Miller[48] showed in a kinetic study that the reaction of $RTe^{II}I_3 \longrightarrow RTe^{IV}I_3$ proceeds very slowly at room temperature; (*iii*) the compound $CF_3Te^{IV}I_3$ would be expected to be less volatile than **11**, if compounds such as $(CF_3)_2TeX_2$ (X = Cl or Br) are taken into consideration;[49] (*iv*) the synthesis of $CF_3Te^{IV}I_3$ has been attempted, but it appeared to be too unstable to be obtainable;[49] (*v*) concerning the charge-transfer complex formation of halogens with donor compounds, only oxidative addition is observed, if the electronegativity of the halogen is higher than that of the donor, which cannot be expected from I_2 in comparison with a Te atom substituted with a CF_3 group.[50]

To prove the existence of **10** in solution, two reactions with different mercury salts were carried out. Initially $Hg(SeCF_3)_2$ suggested itself for this reaction for two reasons: (*i*) all possible products should be easily identifiable by their ^{19}F NMR spectra, and (*ii*) the expected main product would be an interesting and, hitherto missing, link in the series of perfluoroorganochalcogen compounds.

Addition of $Hg(SeCF_3)_2$ to a solution of **10** in $CHCl_3$ [equation (11)] caused HgI_2 to precipitate immediately. The ^{19}F NMR spectrum of the resulting mixture shows that **12** was formed in 89% yield. Compound **12** can be isolated only by preparative gas chromatography, followed by low-temperature distillation, in 48% yield as an orange oil, which decomposes slowly at room temperature to $CF_3SeSeCF_3$ and $CF_3TeTeCF_3$.

$$\underset{\mathbf{10}}{2CF_3TeI} + Hg(SeCF_3)_2 \longrightarrow \underset{\mathbf{12}}{2CF_3SeTeCF_3} + HgI_2 \qquad (11)$$

To test further the ability of **10** to act as a potential agent for the synthesis of CF_3Te-substituted substances, it was treated

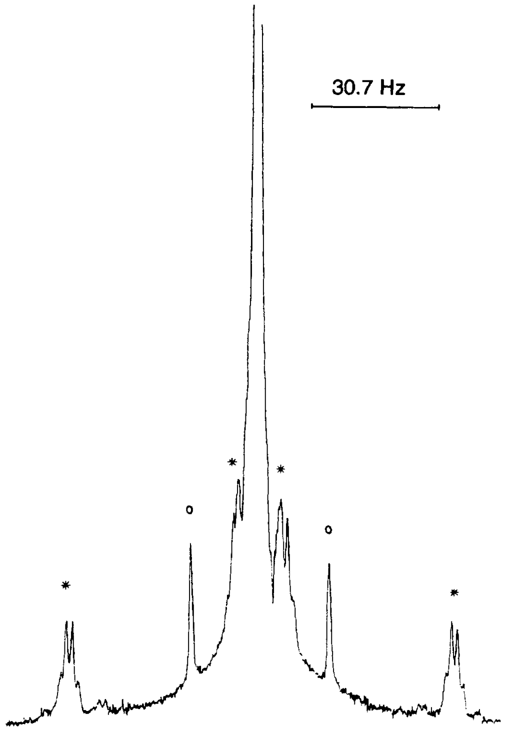


Fig. 6 Fluorine-19 NMR spectrum of $CF_3TeTeCF_3$ in $CDCl_3$ solution at 298 K measured at 250 MHz and showing the quartet structure of the ^{125}Te satellites (marked with an asterisk). The signals marked with an o are spinning side bands

with another mercury salt. Because interest in compounds with Te–N bonds has been considerably heightened in the last few years, and because at the time of this work no substance containing a C–Te–N group was known, it was decided to attempt to prepare such a compound with the aid of **10**.*

Since NSO ligands have been shown to be useful in many types of reaction in this area,[52] we treated **10** in $CHCl_3$ with $Hg(NSO)_2$ suspended in tetrahydrofuran (thf) [equation (12)].

$$\underset{\mathbf{10}}{2CF_3TeI} + Hg(NSO)_2 \longrightarrow \underset{\mathbf{13}}{2CF_3TeNSO} + HgI_2 \quad (12)$$

After fractionation of the mixture, **13** is obtained in 38% yield as an orange oil, which is extremely sensitive to air.

Compounds **12** and **13** strengthen the evidence for the existence of **10** in solution. Additionally **13** may be an interesting starting material for further reactions and **10** is a useful reagent for the preparation of CF_3Te-substituted compounds, of which only a few are known as yet.[53]

NMR Spectra of Compound **10**.—The product of the reaction between $CF_3TeTeCF_3$ and I_2 was investigated by NMR spectroscopy in order to ascertain whether the Te–Te bond had indeed undergone cleavage to give the product **10** or whether an adduct of I_2 and the ditelluride had simply been formed. Because of the expected similarity in ^{19}F chemical shift and $^2J(FTe)$ coupling constant of both possible products it was impossible on the basis of this simple information to distinguish between them, and so it was necessary to use high-resolution ^{19}F NMR spectroscopy to obtain additional information.

The compound $CF_3TeTeCF_3$ possesses two magnetically equivalent CF_3 groups, resulting in a singlet in the ^{19}F NMR spectrum. However, if one of the Te nuclei is ^{125}Te ($I = \frac{1}{2}$, natural abundance = 6.99%) the ^{19}F resonance is split into a doublet by coupling to the ^{125}Te nucleus and these satellites are then further split into quartets by coupling to the three F nuclei of the other CF_3 group, the groups now being no longer magnetically equivalent. This resulting quartet structure, as can be seen in Fig. 6 [$^5J(FF) = 1.5$, $^2J(TeF) = 95.9$ Hz (lit.,[22] 95 Hz)], may be observed only at high resolution.

It is clear that the observation of such a quartet structure indicates the presence of the Te–Te bond and so would be observed only if the reaction product were a simple adduct. That no such fine structure was observed for the product formed in [equation (9)] indicates cleavage of the Te–Te bond and argues for the formation of the product **10**.

Further support may be obtained by considering the ^{125}Te NMR spectrum of the product. The ^{125}Te NMR spectrum of $CF_3TeTeCF_3$ is observed to consist of a quartet of quartets formed by the coupling to the 3 F nuclei of each of the two magnetically inequivalent CF_3 groups [$^2J(TeF) = 95.9$, $^3J(TeF) = 12.2$ Hz]. An adduct of the ditelluride would again be expected to give a spectrum similar in form, but the spectrum of the reaction product showed only a quartet structure. Hence it appears again that the Te–Te bond has been broken and the product **10** formed.

The proposed identification of **10** is further strengthened by the observation that **11** may be obtained by cooling a solution containing **10**. The identification of **11** as the iodine adduct of **10** implies that formation of the Te–I bond has occurred.

Experimental

All reactions were carried out on a vacuum line or in a glove-box under an argon atmosphere; solvents were dried according to published procedures.[54] Deuteriated solvents were dried and transferred from activated 4 Å sieves. Microanalyses were performed by Carbo-Erba Elementanalyser model 1106. NMR spectra were recorded for $CDCl_3$ solutions unless noted otherwise, using a Bruker WM 250 PFT spectrometer [standards used: $CDCl_3$ (^{13}C), $SiMe_4$ (^1H), $CFCl_3$ (^{19}F), $TeMe_2$ (^{125}Te), $SeMe_2$ (^{77}Se) and $SnMe_4$ (^{119}Sn)]. Infrared spectra were recorded on a Bruker FT-IR IFS 85 spectrometer. Matrices were prepared by diluting the starting material in the gas phase with argon in proportions 1:250–1:500. Such mixtures at pressures of *ca.* 20 Torr were either passed through the pyrolysis tube or condensed directly on the CsI window which was held at *ca.* 13 K. Compound **2**, which has no measurable vapour pressure at room temperature, was transported in a stream of argon to the window. IR spectra of the matrices were recorded using a Bruker IFS 66 spectrometer. Mass spectra were recorded on a MAT CH7 spectrometer, using the direct inlet method with 70 eV ($\approx 1.12 \times 10^{-17}$ J) ionising radiation. The UV/VIS measurements were performed using a Perkin Elmer Lamda 9 UV/VIS/NIR spectrometer.

Synthesis of Tellurocarbonyl Difluoride **1**, *from* $Hg(TeCF_3)_2$.—The compound $Hg(TeCF_3)_2$ (1.2 g, 2.1 mmol) was placed in a 25 cm^3 two-necked flask which had been baked out previously under continuous pumping and was connected to a reflux condenser and a dropping funnel. Diethylaluminium iodide (1 cm^3, 7.5 mmol) was introduced under argon into the dropping funnel and the apparatus was connected *via* the reflux condenser and two U-tube traps with greaseless valves to a vacuum line. After the whole apparatus had been evacuated to a pressure of 10^{-4} Torr, the reflux condenser was cooled to − 20 °C, the first trap to −40 °C and the second trap to − 196 °C. With the valve to the vacuum pump open, the powdered mercury salt was stirred and the valve on the dropping funnel carefully opened until the optimum dropping rate (1–2 drops per second) was reached. Immediately a highly exothermic reaction commenced and the yellow colour of $Hg(TeCF_3)_2$ turned to brown. At the same time **1** condensed in the liquid nitrogen-cooled trap as a deep violet glass. After approximately 5 s no further **1** was evolved and the valves of the trap were closed to avoid contamination. In the meantime the temperature of the flask had increased to 60 °C

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* Recently the first C–Te–N compound has been reported.[51]

and its contents turned black. The lower part of the reflux condenser was covered with a tellurium mirror and the trap held at −40 °C contained $CF_3TeTeCF_3$ as a red oil. Compound **1** was then available to undergo reactions or dimerisation. The yield of **1**, which was determined by weighing the dimer, formed quantitatively after annealing, amounted to 50 mg (7%). The reaction is extremely sensitive to small deviations from optimum conditions, such as increased pressure, too large amounts of the starting materials, higher dropping rates, and contamination of the mercury salt.

Synthesis of Trifluoromethyl Trimethylstannyl Telluride **3**.—In a Carius tube equipped with greaseless valves $CF_3TeTeCF_3$ (4.20 g, 10.7 mmol) was dissolved in diethyl ether. The orange solution was cooled to −196 °C and $SnHMe_3$ (3.52 g, 21.4 mmol) was added by condensation. The solution was then annealed to room temperature with continuous agitation with a resulting change in colour to bright yellow. After trap-to-trap condensation *in vacuo* ($0 \longrightarrow -50 \longrightarrow -196$ °C), pure **3** (7.32 g, 95%) was obtained as a yellow liquid. This reaction can also be performed on a scale bigger than that described here. M.p. −47 °C (Found: C, 14.0, 13.9; H, 2.5, 2.5%; M^+ 362. $C_4H_9F_3SnTe$ requires C, 13.35; H, 2.50%; $M = 362$); $\tilde{\nu}/cm^{-1}$(film) 2990w, 2981w, 1374w, 1285m, 1072vs, 780s, 722s, 535s and 509m; (Ar matrix) 3002vw, 2981vw, 1205vw, 1160w, 1134w, 1122vs, 1103vs, 1092m, 1078vs, 1071s, 777s, 726m, 574vw, 537w and 513w; δ_H 0.76 [9 H, s, CH_3, $^2J(H-^{117}Sn)$ 54.2, $^2J(H-^{119}Sn)$ 56.7 Hz as determined by the satellites]; δ_C −4.0 [3C, q, $^1J(CH)$ 132.9, CH_3] and 93.5 [1C, q, $^1J(CF)$ 351.3 Hz, CF_3]; δ_F −10.0 (3F, s, CF_3), $\delta_{^{125}Te}$ 248.8 [1Te, q, $^2J(TeF)$ 134.3; $^1J(Te-^{117}Sn)$ 2118, $^1J(Te-^{119}Sn)$ 2216 Hz as determined by the satellites]; $\delta_{^{119}Sn}$ 13.4 [1Sn, dec, $^2J(SnH)$ 56.7 Hz]; *m/z* 362 (25, M^+), 347 (35, $M - CH_3$), 317 (17, CF_3TeSn^+), 261 (22, $CHSnTe^+$), 248 (28, $SnTe^+$), 185 (8, $C_3H_9SnHF^+$), 169 (80, $C_2H_6SnF^+$), 150 (24, $C_2H_6Sn^+$), 135 (52, CH_3Sn^+), 120 (40, Sn^+) and 69 (43%, CF_3^+).

Synthesis of Compound **1** *from* **3**.—Compound **3** (0.81 g, 2.2 mmol) was passed at 10^{-3} Torr and 280 °C through a pyrolysis tube (length 30 cm, diameter 2.5 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 0.5–1 h. In the U-tube at −45 °C both $SnFMe_3$ and unchanged **3** were retained; the latter can be pyrolysed again. In the following trap **1** was obtained as a violet glass. By continuously raising the liquid nitrogen level, the whole wall of the trap could be covered with a film of **1**. This had a purity of *ca.* 95% and was suitable for further reactions in the −196 °C trap. Yield: 0.23 g, 59%. The yields varied depending on the packing density of the glass wool in the pyrolysis tube. If the density was too high, some of the **1** formed decomposed to tellurium and C_2F_4; if it was too low **3** was not pyrolysed very effectively.

Characterisation of **1**.—To obtain an IR spectrum of **1** in the gas phase, the pyrolysis apparatus described above was modified by connecting an IR flow cell (10 cm pathlength) between the two traps and placing the cell in the sample chamber of a spectrometer. As described previously, the pyrolysis was performed under continuous pumping, while the IR spectrometer was scanning continuously. The success of this pyrolysis could be judged by observation of the violet **1** condensing in the second trap. The IR spectra obtained showed that the pyrolysis is most effective at 280 °C, but weak bands of C_2F_4 could also be observed. At 265 °C a spectrum of pure **1** was observed. To obtain an IR spectrum of **1** in an argon matrix, **3** was diluted with argon at 10^{-7} Torr and passed through a pyrolysis tube (length 8 cm, diameter 0.6 cm), packed with passivated glass wool. The resulting gases were initially passed through a trap for purification (−80 °C) and were then quenched on a CsI window at 13 K. A dilution ratio of **3**:argon = 1:250 was found to be optimal and a flow rate of 20 μmol h^{-1} was used. Because of the smaller pyrolysis tube which had to be used, a temperature of 350 °C was required to yield the cleanest spectrum. The degree of contamination is lower than 30%, and by comparison with the IR spectrum of matrix-isolated $CF_3TeTeCF_3$, most of the impurity bands were identified as belonging to this molecule. The ditelluride impurity could not be eliminated by lowering the temperature of the purification trap because at temperatures lower than −80 °C **1** also condensed. By performing the pyrolysis in an apparatus with a mass-spectrometer inlet situated between the two traps described above, a mass spectrum of **1** was also obtained. To measure 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. The only minor impurities observed were elemental tellurium (indicated by a Te_2^+ peak) and C_2F_4 both formed through the decomposition of **1** *en route* to the spectrometer. 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); *m/z* 256 (2, Te_2^+), 180 (M^+, 20), 161 (3, $M - F$), 130 (16, Te^+), 100 (15, $C_2F_4^+$), 81 (21, $C_2F_3^+$), 50 (9, CF_2^+), 32 (27, O_2^+), 31 (31, CF^+) and 28 (100%, N_2^+).

Synthesis of 2,2,4,4-*Tetrafluoro*-1,3-*ditelluretane* **2**.—In line with methods described earlier, a sample of **1** was obtained in a glass ampoule cooled to −196 °C. If the liquid-nitrogen Dewar was removed, after *ca.* 5 s a spontaneous change in the colour of the deposit from violet to red could be observed, corresponding to the quantitative formation of **2**. The separation of **2** from trace impurities was performed *via* fractional condensation *in vacuo*, the sample held at ambient temperatures being permitted to expand successively through traps held at −20 and −196 °C. The product **2** was observed to condense in the trap cooled to −20 °C as either a finely divided light red solid or deep red-violet crystals. Large crystals may be grown by allowing **2** to sublime at ambient temperatures on to a finger cooled to 16 °C. Compound **2** is sensitive to both air and light but stable under argon for several days. In solvents having different donor numbers it dissolves giving different colours. M.p. 106 °C (decomp.) (Found: C, 7.1; 7.1; F, 20.5%; M^+ 356. $C_2F_4Te_2$ requires C, 6.75; F, 21.4%; M 356); λ_{max}/nm (*n*-hexane) 646 ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$ 193), (CH_3NO_2) 572 (126), (CH_3CN) 536 (108), (dmf) 500 (124); $\tilde{\nu}/cm^{-1}$ (KBr) 1020vs (br) and 739s (sh), (Ar matrix) 1059s, 1042vs and 749m; δ_C 45.3 (2C, m, CF_2); δ_F −38.8 (4F, s, CF_2); $\delta_{^{125}Te}$ 2322 [2Te, qnt, $^2J(TeF)$ 122.1 Hz]; *m/z* 356 (84, M^+), 300 (86, $M - CF_2$), 287 (21, Te_2CF^+), 256 (70, Te_2^+), 180 (58, $TeCF_2^+$), 161 (15, $TeCF^+$), 142 (5, TeC^+), 130 (100, Te^+), 50 (18, CF^+) and 31 (14%, CF^+).

X-Ray Crystal Structure Determination of Compound **2**.—$C_2F_4Te_2$, $M_r = 355.2$, approximate crystal dimensions 0.08 × 0.05 × 0.01 mm, $T = 115$ K, monoclinic, space group $P2_1$, $a = 7.053(1)$, $b = 11.361(2)$, $c = 7.482(1)$ Å, $\beta = 91.43(1)°$, $U = 599.3(2)$ Å^3, $F(000) = 608$, $Z = 4$, $D_c = 3.94$ g cm^{-3}, μ(Mo-Kα) = 9.74 mm^{-1}, data collection of 1849 independent intensities ($2\theta_{max} = 50°$), 1031 observed [$F_o \geqslant 4\sigma(F)$], empirical absorption correction (maximum/minimum transmission 0.904/0.421), R_{merge} before/after correction 0.076/0.030, structure solution with direct methods using the SHELXTL PLUS program,[55] 85 parameters refined for anisotropic thermal parameters for Te atoms, $R = 0.0345$, $R' = 0.0349$, $w^{-1} = \sigma^2(F_o) + 0.001F_o^2$, absolute structure confirmed by refinement of $\eta = 0.8(4)$.[56]

Synthesis of 2,2,4,4-*Tetrafluoro*-1-*selena*-3-*telluretane* **4**.—Compound **1** was generated as before by pyrolysis of **3** (0.60 g, 1.7 mmol). The pyrolysis was continued until a condensate to a depth of 2 cm was formed in the trap cooled to −196 °C. At this stage the pyrolysis was interrupted and $SeCF_2$ was co-condensed with the deposit. The procedure was continued until the entire surface of the trap had been coated in this way. In total 3.0 g (23.3 mmol) of $SeCF_2$ were needed. The trap was then allowed to warm slowly but the temperature was never permitted to exceed −80 °C (to avoid polymerisation of the excess of $SeCF_2$). When the entire trap had reached −80 °C, the mixture was fractionated *in vacuo* through traps held at −70 °C and −196 °C as the sample warmed to room temperature. While the original trap retained polymers of $SeCF_2$, **4** was observed to condense in the −70 °C trap. Following the first fractionation, a ^{19}F NMR spectrum showed the presence of a mixture with the composition **2**:**4**:$Se_2C_2F_4$ = 7.8:1:1.2 indicating a yield for **4**, based on quantity of starting material **1** employed, of 6%. Further purification was carried out by trap-to-trap condensation, the impure material being expanded from 0 °C with **4** observed to condense in a trap held at −55 °C as light red crystals (0.011 g, yield 2.4% based on **1**). It may be stored for indefinite periods at −80 °C but is extremely sensitive to light. M.p. 69 °C. Elemental analyses could not be obtained because of the volatility of **4** (Found: M^+ 308. C_2F_4SeTe requires M 308); $\tilde{\nu}$/cm^{-1} (gas) 1088s, 1067vs and 808m; δ_C 67.5 (2C, m, CF_2); δ_F −42.0 (4 F, s, CF_2); $\delta_{^{77}Se}$ 1220 [1Se, qnt, ^2J(SeF) 73.4 Hz]; $\delta_{^{125}Te}$ 2273 [1Te, qnt, ^2J(TeF) 103.7 Hz]; m/z 308 (30, M^+), 258 (18, $M - CF_2$), 239 (7, $SeTeCF^+$), 208 (15, $SeTe^+$), 180 (100, $TeCF_2^+$), 161 (10, $TeCF^+$), 149 (3, TeF^+), 130 (70, $SeCF_2^+$), 111 (15, $SeCF^+$), 80 (17, Se^+), 50 (11, CF^+), 43 (22, C_2F^+) and 31 (20%, CF^+).

Synthesis of 6,6-*difluoro*-3,4-*dimethyl*-1-*telluracyclohex*-3-*ene* **5**.—The method for the preparation of **5** was analogous to that used for the synthesis of **4**, again commencing with the pyrolysis of **3** (0.5 g, 1.4 mmol). In this case the $SeCF_2$ was replaced by a mixture of 2,3-dimethylbutadiene (2 g, 24.4 mmol) and $CFCl_3$ (20 cm^3). The co-condensed reagents were permitted to warm from −196 °C as described previously, but in this case it was observed that the bulk of **1** dimerised before the reaction partner (2,3-dimethylbutadiene) had reached its melting point. After the sample had warmed to room temperature, a green-blue solution was obtained, this colour being due to the main reaction product **2**. The mixture was fractionated *in vacuo*, the vapour being passed through traps held at −30 and −196 °C. In the trap cooled to −30 °C **2**, **5** and small amounts of the dimer of the diene were isolated. After a further fractionation through traps held at 0 and −20 °C pure **5** collected in the −20 °C trap as yellow crystals (2–5 mg, < 1%).

Compound **5** could also be obtained by the direct reaction of **3** (0.29 g, 0.8 mmol) with 2,3-dimethylbutadiene (0.5 g, 6.1 mmol) dissolved in $CHCl_3$ (2 cm^3) in a sealed tube. The mixture was heated to 70 °C with exclusion of light. This temperature is high enough to generate the reactive intermediate at a useful rate, but low enough to avoid decomposition of the cycloadduct. During six months $SnFMe_3$ separated from the solution as white crystals. A ^{19}F NMR spectrum showed that 50% of **1** had reacted to give **5** which was the sole product detectable in solution. Compound **5** was isolated by fractionation *in vacuo*, the vapour being passed through traps held at 0, −20 and −196 °C. In the trap cooled to −20 °C **5** was obtained as yellow crystals (0.10 g, 48%). At room temperature it was found to be a yellow oil which is stable to air but decomposes rapidly in the light. M.p. 17 °C (Found: C, 30.0, 32.2; H, 3.6, 3.3%; M^+ 262. $C_7H_{10}F_2Te$ requires C, 32.35; H, 3.85%; M 262); $\tilde{\nu}$/cm^{-1} (film) 2993w, 2918m, 1441m, 1382w, 1321w, 1265w, 1220s, 1151vs, 1136vs, 1112m, 1066m, 1051vs, 1022s, 995s, 972vs, 925m, 868vs, 644m, 603m, 567m and 520w; δ_H 1.87 (6 H, s, H^7/H^8), 2.78 [2 H, t, ^3J(HF) 15.8, H^3] and 3.60 [2 H, t, ^4J(HF) 2.6 Hz, H^6]; δ_C (proton decoupled) 10.5 (1C, s, C^6), 20.0/22.8 (1C, s, C^7/C^8), 49.0 [1C, t, ^2J(CF) 18.8, C^3], 130.3 [1C, t, ^3J(CF) 4.4, C^4], 134.2 [1C, t, ^1J(CF) 294.1, C^2] and 134.9 (1C, s, C^5); δ_F −58.1 [2F, tt, ^3J(FH) 15.8, ^4J(CF) 2.6 Hz]; $\delta_{^{125}Te}$ 720 [1Te, tt, ^2J(TeF) 113.0, ^2J(TeH) 33.7 Hz]; m/z 262 (57, M^+), 213 (3, $C_5H_4TeF^+$), 197 (3, $C_5H_7Te^+$), 131 (69, M − TeH), 111 (52, M − TeH − HF), 91 (35, M − TeH − 2HF), 67 (87, $C_5H_7^+$) and 43 (100%, $C_3H_7^+$).

Synthesis of 2,2,4,4-*Tetrachloro*-1,3-*ditelluretane* **6**.—A sample of **2** (0.070 g, 0.20 mmol) was deposited under an atmosphere of argon in a Carius tube, which had been previously passivated by exposure to SF_4. The reaction tube was cooled to −196 °C, the argon removed by pumping, and BCl_3 (2 cm^3) condensed in the vessel. The mixture was warmed initially to −40 °C and thereafter permitted to warm slowly to ambient temperatures over a period of 12 h, with continuous stirring. At −20 °C **2** began to dissolve in the BCl_3 giving a blue coloration, this being accompanied by the separation of a violet solid. After the mixture had reached room temperature, the excess of boron halides were removed by pumping and the violet solid (84 mg) was dried *in vacuo*. The solid was then washed using CH_2Cl_2 in a Soxhlet apparatus over a period of 12 h. The dried product thus obtained consisted of almost pure **6**, showing only slight contamination by traces of $B(OH)_3$ and tellurium (0.046 g, 55%). Compound **6** decomposes at 70 °C and is not observed to be volatile at this temperature under high vacuum. It was found to be insoluble in all solvents possessing donor numbers lower than dmf, and with the latter it forms isolatable complexes. It was thus impossible to obtain NMR spectra of free **6** (Found: C, 5.6, 5.8; Cl, 32.6, 33.0. $C_2Cl_4Te_2$ requires C, 5.70; Cl, 33.70%); $\tilde{\nu}$/cm^{-1} (KBr) 817m; m/z 328 (7, $Te_2Cl_4^+$), 293 (5, $Te_2Cl_3^+$), 269 (48, Te_2C^+), 200 (61, $TeCl_2^+$), 177 (60, $TeCCl^+$), 165 (53, $TeCl^+$), 130 (20, Te^+) and 35 (100%, Cl^+).

Synthesis of **8**, *the Complex of* **6** *with dmf*.—Compound **6** (0.046 g, 0.11 mmol) was dissolved in dmf and the solvent was then removed *in vacuo*. The remaining violet solid was washed three times with diethyl ether (20 cm^3) and dried *in vacuo*. The complex **8** (0.046 g, 91%) thus obtained is stable to air, but decomposes when dissolved in dmf over a period of a few hours. Decomposition temperature 80 °C (Found: C, 9.0, 9,0; H, 0.7, 0.7; Cl, 30.1, 31.0; N, 1.6, 1.6. $C_{3.5}H_{3.5}Cl_4N_{0.5}O_{0.5}Te_2$ requires C, 9.20; H, 0.75; Cl, 31.00; N, 1.55%); $\tilde{\nu}$/cm^{-1}(KBr) 1653vs, 1385s, 1107m, 820s, 603m; $\delta_{^{125}Te}$ ($^2H_6$benzene–dmf) 1276 (2Te, s, br); m/z 256 (6, Te_2^+), 200 (46, $TeCl_2^+$), 165 (100, $TeCl^+$), 130 (31, Te^+), 107 (62, $C_3H_6NOCl^+$), 73 (35, dmf$^+$), 44 (80, NMe_2^+), 36 (83, HCl^+) and 35 (50%, Cl^+).

Synthesis of 2,2,4,4-*Tetrabromo*-1,3-*ditelluretane* **7**.—The method used for the preparation of **7** was analogous to that employed for the preparation of **6**, in this case using an excess of BBr_3 brought into reaction with **2** (0.120 g, 0.3 mmol). At −20 °C **2** was also observed to dissolve in BBr_3, but the separating solid was brown. The procedure for the isolation and purification of **7** was the same as that used for **6** and yielded **7** as a brown powder (0.174 g, 65%), possessing properties similar to those found for **6**. Decomposition temperature 80 °C (Found: C, 4.0, 3.9. $C_2Br_4Te_2$ requires C, 4.00%); $\tilde{\nu}$/cm^{-1} (KBr) 734m; m/z (60 °C) 253 (100, CBr_3^+), 172 (25, CBr_2^+), 93 (31, CBr^+) and 79 (43%, Br^+), (100 °C) 288 (57, $TeBr_2^+$), 209 (100, $TeBr^+$), 130 (22, Te^+) and 79 (20%, Br^+).

Synthesis of **9**, *the Complex of* **7** *with dmf*.—The preparation of the complex **9** was achieved in the same way as the synthesis of **8**, namely by dissolving the substrate, here **7** (0.174 g, 0.29 mmol), in dmf. The resulting dark red solution was filtered, the solvent removed *in vacuo* and, after washing with diethyl ether, **9** was obtained as an orange-brown powder (0.183 mg, 94%). Decomposition temperature 110 °C (Found: C, 9.0, 9.0; H, 1.4, 1.4; N, 2.3, 2.3. $C_5H_7Br_4NOTe_2$ requires C, 8.95; H, 1.05; N, 2.10%); $\tilde{\nu}$/cm^{-1} (KBr) 1652vs, 1495m, 1385s, 1250m, 1106m, 732m and 667m; $\delta_{^{125}Te}$ ([$^2H_6$]benzene–dmf) 1221 (2Te, s br); m/z 288 (7, $TeBr_2^+$), 256 (2, Te_2^+), 209 (32, $TeBr^+$), 174 [3, $TeN(CH_3)_2^+$], 130 (18, Te^+), 93 (5, CH_2Br^+), 79 (19, Br^+), 73 (80, dmf$^+$), 55 (12, dmf–CH_3) and 44 (100%, NMe_2^+).

Synthesis of Trifluoromethanetellurenyl Iodide **10**.—In a Carius tube fitted with a Teflon valve I_2 (0.73 g, 2.8 mmol) was dissolved $CHCl_3$ (80 cm^3) under an argon atmosphere.

The solution was cooled to −196 °C, the argon removed by pumping, and $CF_3TeTeCF_3$ (1.13 g, 2.88 mmol) condensed in the tube. 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 **10** had been formed in 90% yield. The solution was found to be stable at room temperature over long periods, but care had to be taken against exposure to moisture or light; δ_C 85.9 [1C, q, ^1J(CF) 356.6 Hz]; δ_F −25.7 (3F, s); $\delta_{^{125}Te}$ 1246 [1Te, q, ^2J(TeF) 93.5 Hz].

Synthesis of $CF_3TeI{\cdot}I_2$ **11**.—The synthesis of compound **11** employed a glass apparatus consisting of two 150 cm^3 Carius tubes connected by a Teflon valve. One tube contained a sample of the blue solution of **10**, obtained by the method described above. This solution was cooled to −70 °C for 12 h, causing the separation of **11** as black-brown crystals. The liquid maintained at −70 °C was decanted into the other Carius tube, which was then cooled to −80 °C while allowing the first to warm to ambient temperatures until all the solvent had been removed by condensation in the second tube. The connecting valve was then closed. Compound **11** was found to have a volatility similar to that of I_2 and to be stable at room temperature for several days. When dissolved in $CHCl_3$, it decomposed to yield **10** and I_2 so that the NMR properties of **11** were identical to those found for **10**. Yield: 0.20 g, 36%; decomposition temperature 100 °C (Found: C, 2.3, 2.3, 2.2. CF_3I_3Te requires C, 2.10%); $\tilde{v}/cm^{-1}$ (gas) 1100m, 1051s and 722w; *m/z* 326 (23, CF_3TeI^+), 257 (33, TeI^+), 254 (100, I_2^+), 199 (18, CF_3Te^+), 130 (19, Te^+), 127 (83, I^+), 69 (17, CF_3^+) and 50 (4%, CF_2^+).

Synthesis of Trifluoromethyl(*trifluoromethyltelluro*)*selenium* **12**.—Compound **10** was prepared, as described previously, from $Te_2(CF_3)_2$ (0.120 g, 0.305 mmol) and I_2 (0.077, 0.305 mmol) in $CHCl_3$ (80 cm^3). The blue solution was cooled to 0 °C and $Hg(SeCF_3)_2$ (0.150 g, 0.303 mmol) was added slowly under an atmosphere of argon to the stirred solution. Immediately HgI_2 was observed to precipitate and the solution turned yellow. Following the complete addition of the mercury salt, the resulting suspension was stirred for 15 min; it was then filtered. The ^{19}F NMR spectrum of the solution indicated the reaction products to be $Te_2(CF_3)_2$, **12** and $Se_2(CF_3)_2$ in the proportions 1 : 16.3 : 3.6. Using gas chromatography (column length 4.5 m, internal diameter 6 mm, OV 101, 10% on Chromosorb PAW 45–60 mesh, 80 °C) it was possible to isolate **12** in 90% purity. The contaminants were found to be $Se_2(CF_3)_2$ and $Te_2(CF_3)_2$ formed by the decomposition of **12** on the column and were thus unavoidable. The diselenide could be removed by condensing the mixture in a finger cooled to −196 °C and then warming the sample to −80 °C, while allowing the material volatile at this temperature to expand into a 110 cm^3 bulb. The sample was then isolated and the 110 cm^3 bulb evacuated. This procedure was then repeated one more time. A low-temperature distillation of the remaining liquid through traps held at −60 and −196 °C was then carried out, the $Te_2(CF_3)_2$ condensing in the −60 °C trap and allowing a pure sample of **12** to collect in the −196 °C trap. Compound **12** thus obtained is observed to be an orange oil (0.05 g, 48%). It decomposes slowly at room temperature to give $Se_2(CF_3)_2$ and $Te_2(CF_3)_2$, and was therefore stored at −80 °C. M.p. < 80 °C (Found: C, 6.9%; M^+ 346. C_2F_6SeTe requires C, 6.95%; *M* 346); $\tilde{v}/cm^{-1}$ (film) 1149vs (br), 1055vs (br), 761m and 725m; δ_C 117.2 [1C, q, ^1J(CF) 335.7, $SeCF_3$] and 96.1 [1C, q, ^1J(CF) 358.6 Hz, $TeCF_3$]; δ_F − 33.9 [3F, q, ^5J(FF) 2.2 Hz, $SeCF_3$] and −27.8 [3F, q, ^5J(FF) 2.2 Hz, $TeCF_3$]; $\delta_{^{77}Se}$ 384.8 [1Se, q, ^2J(SeF) 38.1 Hz]; $\delta_{^{125}Te}$ 1031.9 [1Te, qq, ^2J(TeF) 81.5, ^3J(TeF) 8.1 Hz]; *m/z* 346 (81, M^+), 327 (3, *M* − F), 277 (78, *M* − CF_3), 208 (43, $SeTe^+$), 199 (23, $TeCF_3^+$), 149 (8, $SeCF_3^+$), 130 (26, Te^+), 80 (12, Se^+), 69 (100, CF_3^+) and 50 (4%, CF_2^+).

Synthesis of Sulfinylamino(*trifluoromethyl*)*tellurium* **13**.—Compound **10** was prepared according to the method described previously employing $Te_2(CF_3)_2$ (0.40 g, 1.02 mmol) and I_2 (0.26 g, 1.02 mmol) in $CHCl_3$ (80 cm^3). The resulting blue solution was transferred to a 250 cm^3 flask under an argon atmosphere. The flask was fitted with a dropping funnel containing a suspension of $Hg(NSO)_2$ (0.33 g, 1.02 mmol) in thf under argon. This suspension was added dropwise over a 2 h period to the stirred solution of **10**, cooled to 0 °C. During the addition the solution turned yellow. After the addition was complete, the material volatile at 0 °C was removed by pumping through traps held at −60 and −196 °C to yield a crude product in the −60 °C trap. This product was then fractionated several times *in vacuo*, the volatiles at −40 °C being passed through traps held at −55 and −196 °C, before pure **13** was obtained as yellowish crystals in the trap cooled to −55 °C. These crystals were found to be extremely sensitive to air and could be stored for long periods only at low temperatures. At room temperature **13** is an orange oil. Yield: 0.10 g (38%), m.p. 15 °C (Found: C, 4.8, 5.2; N, 5.6, 5.8; S, 11.1%; M^+ 261. CF_3NOSTe requires C, 4.65; N, 5.40; S, 12.35%; *M* 261); $\tilde{v}/cm^{-1}$ (gas) 1217m, 1155s, 1099vs, 731w and 596vw; δ_C 111.1 [1C, q, ^1J(CF) 354.8 Hz]; δ_F ($CDCl_3$–thf) −29.1 [3F, s, ^2J(FTe) 52.0 Hz]; $\delta_{^{125}Te}$ 1908 (1Te, s, br); *m/z* 261 (24, M^+), 199 (15, CF_3Te^+), 192 (43, $TeNSO^+$), 176 (7, $TeSn^+$), 162 (3, TeS^+), 144 (20, TeN^+), 130 (66, Te^+), 69 (98, CF_3^+), 50 (22, CF_2^+), 48 (44, SO^+), 46 (100, SN^+) and 32 (42%, S^+).

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