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The reactivity of perfluoroaryltellurium(IV) dihalides towards cyanide, crystal structures of $(C_6F_5)_3TeCl$ and $C_6F_5TeTeC_6F_5$

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Dedicated to Prof. Dr. Karl O. Christe on the occasion of his 65th birthday

Abstract

The reactivity of R_2TeHal_2 ($R = C_6F_5$, 4-$CF_3C_6F_4$; Hal = F, Cl, Br) towards AgCN and Me_3SiCN was examined. The perfluoroaryl substituted tellurium(IV) difluorides reacted with AgCN and Me_3SiCN to give the tellurium(IV) dicyanides $(C_6F_5)_2Te(CN)_2$ (**1**) and $(CF_3C_6F_4)_2Te(CN)_2$ (**2**). Treatment of the corresponding tellurium dichlorides and tellurium dibromides with AgCN and Me_3SiCN did not result in the formation of **1** and **2**. Performing the reaction in a haloform as solvent gave the tris(perfluoroaryl)telluronium halides $(C_6F_5)_3TeCl$ (**3**), $(C_6F_5)_3TeBr$ (**4**), $(CF_3C_6F_4)_3TeCl$ (**5**) and $(CF_3C_6F_4)_3TeBr$ (**6**), whereas the counter ion of the telluronium ion depended on the used solvent, $CHCl_3$ or $CHBr_3$. All new compounds were investigated by analytical and spectroscopic methods. The constitution of **3–6** was confirmed by the determination of the crystal structure of **3**. The reaction of C_6F_5Li with I_2 led mainly to the monotelluride $(C_6F_5)_2Te$ and gave the hoped-for ditelluride $C_6F_5TeTeC_6F_5$ (**7**) only as a by-product. The crystal structure of **7** was determined.

Keywords: Cyanide; Perfluoroaryl; Tellurium; X-ray crystallography

1. Introduction

The family of tellurium(IV) dipseudohalides is limited to few examples, such as $(C_6H_5)_2Te(NCS)_2$ [1,2], $Cl_2Te(NSO)_2$ [3], $(C_6F_5)_2Te(NSO)_2$ [4] and $(CF_3)_2Te(NSO)_2$ [5]. Furthermore the ionic triphenyltelluronium(IV) pseudohalides Ph_3TeX (X = OCN, SCN, N_3, CN) are known [6]. The preparation of a fluorinated derivative, $(C_6F_5)_3TeCl$, by reaction of C_6F_5Li with $TeCl_4$ [7], was shown to be not reproducible in our studies. Recently, we reported about the synthesis of some fluorinated and non-fluorinated diorganotellurium(IV) diazides and organotellurium(IV) triazides [8,9], potentially explosive compounds. So far, diorganotellurium(IV) dicyanides are still elusive compounds and no data available. In this contribution, we wish to report our studies on the reactivity of perfluoroaryltellurium(IV) dihalides R_2TeHal_2 ($R = C_6F_5$, $CF_3C_6F_4$; Hal = F, Cl, Br) towards AgCN and Me_3SiCN.

Although, the synthesis of aliphatic and aromatic diorganoditellurides is well known [10–14], routes to perfluorinated diorgano ditellurides seem to be problematic. Photochemical syntheses are reported for $C_6F_5TeTeC_6F_5$ [15] and $CF_3TeTeCF_3$ [16,17], compounds that are not accessible by the usual methods to prepare ditellurides. Because of the poor reproducibility of the photolytic reaction to give $C_6F_5TeTeC_6F_5$ [18], we decided to re-examine this compound and search for alternative routes of preparation.

2. Results and discussion

The reaction of R_2TeF_2 ($R = C_6F_5$, $CF_3C_6F_4$) with AgCN or Me_3SiCN gave the bis(perfluoroaryl)tellurium(IV) dicyanides $(C_6F_5)_2Te(CN)_2$ (**1**) and $(CF_3C_6F_4)_2Te(CN)_2$ (**2**) in good yields (Eq. (1)). No difference in the reactivity employing AgCN or Me_3SiCN in this reaction was observed.

$$R_2TeF_2 + 2\,Me_3SiCN \xrightarrow[-2Me_3SiF]{CH_2CL_2} R_2Te(CN)_2$$
$$R = C_6F_5(\mathbf{1}), CF_3C_6F_4(\mathbf{2}) \quad (1)$$

With **1** and **2** the first members of diorganotellurium(IV) dicyanides were prepared. They are stable in the solid state, but very sensitive against moisture and decompose rapidly on air and in solution mainly under formation of the

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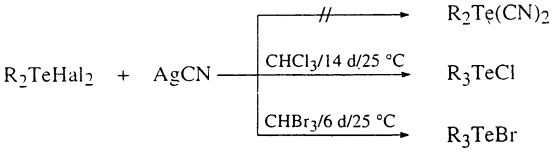
monotellurides R_2Te (confirmed by ^{19}F and ^{125}Te NMR) and probably dicyanogen. Somewhat surprisingly they are less stable than the corresponding diorganotellurium(IV) diazides, which is probably due to the presence of four tellurium carbon bonds. A general tendency of C_4Te compounds to decompose into C_2Te and C_2 is reported and a similar behavior was also observed in our case with $C_2Te(CN)_2$. The tetra-aryl derivatives Ph_4Te and $(C_6F_5)_4Te$ [19,20] tend to decompose into diaryltellurium and the corresponding biphenyls. The dicyanides **1** and **2** can be identified by the presence of ν_{CN} vibrations which are of diagnostic value. In the Raman spectrum **1** reveals two peaks of medium intensity for ν_{CN} at 2155 and 2148 cm^{-1}, whereas ν_{CN} for **2** three peaks with strong intensity at 2165/2157/2140 cm^{-1} are observed. For ν_{TeC} peaks are found at 492/444/387 cm^{-1} for **1** and 503/440/391 cm^{-1} for **2**.

However, treatment of R_2TeCl_2 and R_2TeBr_2 ($R = C_6F_5$, $CF_3C_6F_4$) with AgCN or Me_3SiCN resulted in a more complex reaction under formation of tris(perfluoroaryl) telluronium(IV) halides $(C_6F_5)_3TeCl$ (**3**), $(C_6F_5)_3TeBr$ (**4**), $(CF_3C_6F_4)_3TeCl$ (**5**) and $(CF_3C_6F_4)_3TeBr$ (**6**). For a complete conversion a large excess of AgCN is required. The reactions with Me_3SiCN were significantly slower. It was found that the type of the halogen in the product depends on the used solvent (Eq. (2)) and not on the tellurium(IV) dihalide.



(2)

where R = C_6F_5 (**3**,**4**), $CF_3C_6F_4$ (**5**,**6**), Hal = Cl, Br.

With chloroform as solvent always chlorides **3** and **5** were formed, even when the corresponding dibromides were reacted with AgCN. In case of bromoform as solvent always the bromides **4** and **6** were isolated. This indicates that the halide of the products is originated from the solvent. During the long reaction time, up to 14 days in case of the formation of the telluronium chlorides, C_6F_5H was observed in the ^{19}F NMR spectrum. Unfortunately no other products, that might

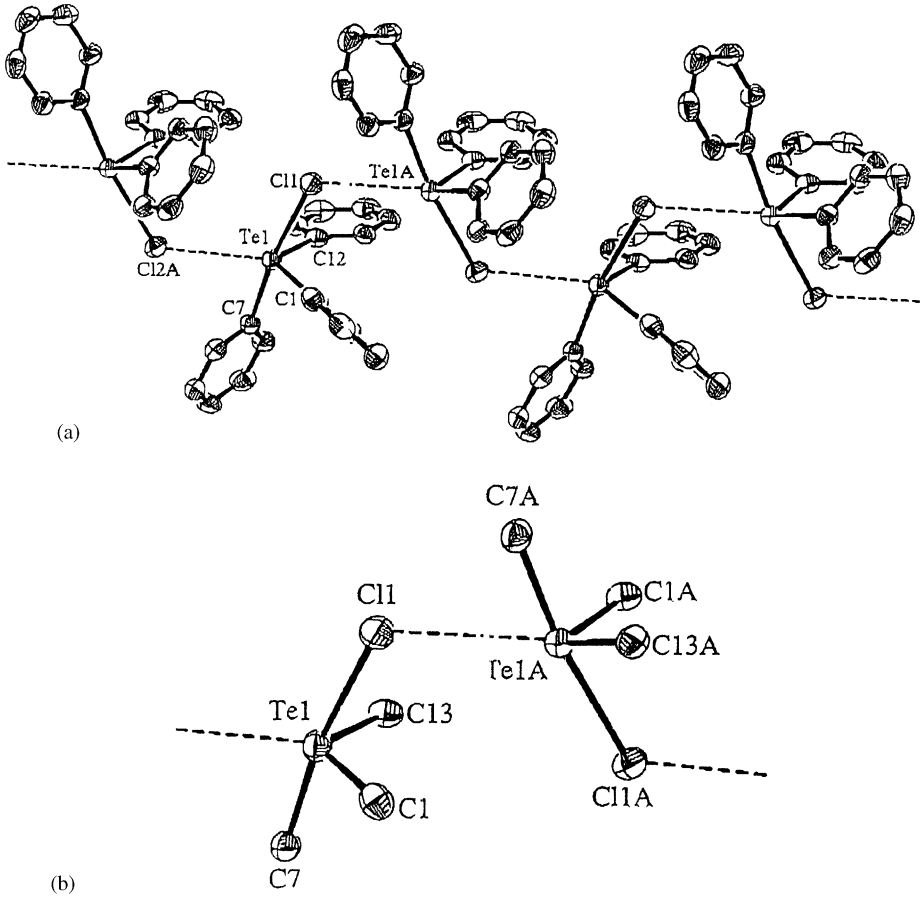


Fig. 1. (a) ORTEP plot of the molecular structure of **3** with thermal ellipsoids at 50% probability level. Fluorine atoms and benzene are omitted for clarity. Selected bond lengths (Å) and angles (°): Te(1)–C(1) 2.108(4); Te(1)–C(7) 2.207(4); Te(1)–C(13) 2.119(4); Te(1)–Cl(1) 2.670(2); Te(1)···Cl(2A) 3.47; C(1)–Te(1)–C(7) 87.8(2); C(1)–Te(1)–C(13) 102.3(2); C(1)–Te(1)–Cl(1) 85.1(2); C(7)–Te(1)–C(13) 93.5(2); C(7)–Te(1)–Cl(1) 171.1(2); C(1)–Te(1)···Cl(2A) 143.5; C(7)–Te(1)···Cl(2A) 72.2; C(13)–Te(1)···Cl(2A) 108.07; Cl(1)–Te(1)···Cl(2A) 116.5. (b) View of the TeC_3Cl skeletons of **3**.

give more insight in this reaction, could be detected. In other solvents such as CH_2Cl_2, CH_3CN or THF no reaction at all occurred. The telluronium halides **3**–**6** show in the vibrational spectra very similar values for the ν_{TeHal} and ν_{TeC} vibrations likely to a partial ionic character of these compounds. This makes an exact assignment for ν_{TeCl}, ν_{TeBr} and ν_{TeC} difficult. As one would expect, the ^{125}Te NMR resonances of **3**–**6** are also very similar and found within a narrow range ($\delta = 400$–380). They are clearly identified by their elemental analysis in addition to the crystal structure of **3**.

For a possible alternative synthesis of the ditelluride $C_6F_5TeTeC_6F_5$ (**7**) the generation of C_6F_5TeLi by the reaction of C_6F_5Li and Te was attempted, as is described for C_6H_5Li and Te [21]. Lithium pentafluorophenyltellurolate was reacted with iodine to give the intermediate C_6F_5TeI. The tellurenyl iodide should then decompose into the ditelluride and iodine, due to the low stability of organotellurenyl halides [22,23]. However, the formed C_6F_5TeI reacted immediately with still remaining C_6F_5Li to the monotelluride $(C_6F_5)_2Te$, which was obtained as the main product (Eq. (3)). Bis(pentafluorophenyl) ditelluride (**7**) was identified and isolated only as a minor product with yields lower than 4%.

$$C_6F_5Li \xrightarrow[-LiI]{1.Te/2.I_2/Et_2O/25\,^\circ C} \underset{60-70\%}{(C_6F_5)_2Te} + \underset{(\mathbf{7})<4\%}{C_6F_5TeTeC_6F_5} \qquad (3)$$

2.1. Crystal structures

The telluronium chloride **3** crystallizes in the monoclinic space group $P2_1$ with $Z = 4$ with benzene (1/2) as solvate. The tellurium carbon distances Te(1)–C(1) 2.108(4) Å, Te(1)–C(7) 2.207(4) Å and Te(1)–C(13) 2.119(4) Å are in the usual range [24], with one significant longer axial TeC bond. The tellurium chlorine distance Te(1)–Cl(1) 2.670(2) Å is slightly elongated compared to the Te Cl bond in $R_2Te\,Cl_2$ derivatives (2.4–2.5 Å [24,25]). In fact this does not indicate a total ionic character, such as found in Ph_3 TeX derivatives, qualifying the term ''telluronium halide'' only in part with our perfluoroaryl substituents. The distances from a tellurium atom to a chlorine atom of a second molecule is $Te(1A)\cdots Cl(1)$ 3.47 Å ($r_{vdW} = 3.81$ Å) and in the range expected for tellurium chlorine interactions (Fig. 1a). This interaction, including the free electron pair at Te, leads to a distorted octahedral coordination of the tellurium atom (Fig. 1b).

The ditelluride **7** crystallizes in the trigonal space group $R\bar{3}$ with $Z = 18$ (Fig. 2). The Te–Te distance is with 2.7028(5) Å slightly longer as found in $CF_3TeTeCF_3$ (2.669(3) Å) [26] and similar as in $C_6H_5TeTeC_6H_5$ (2.712(2) Å) [27]. The Te–C distances in **7** (2.124(3) Å) are again shorter compared to those of $CF_3TeTeCF_3$ (2.186(6)/2.175(6) Å), similar as in $C_6H_5TeTeC_6H_5$ (2.09(1)/2.16(1) Å). The C–Te–Te angles in **7** (98.94(8)/98.35(8)°) are found to be similar as in C_6H_5-$TeTeC_6H_5$ (100.3(5)/97.4(4)°), but larger than in CF_3Te-$TeCF_3$ (96.3(1)/95.3(1)°). The dihedral angle C–Te–Te–C in **7** is larger (91.8(1)°) than in $CF_3TeTeCF_3$ (88.3(2)°) or $C_6H_5TeTeC_6H_5$ (88.55°). This is probably due to the larger sterical demand of the fluorine atoms of the C_6F_5 groups compared to the CF_3 groups in $CF_3TeTeCF_3$ and the phenyl groups in $C_6H_5TeTeC_6H_5$. Crystal data and structure refinements for **3** and **7** are given in Table 1.

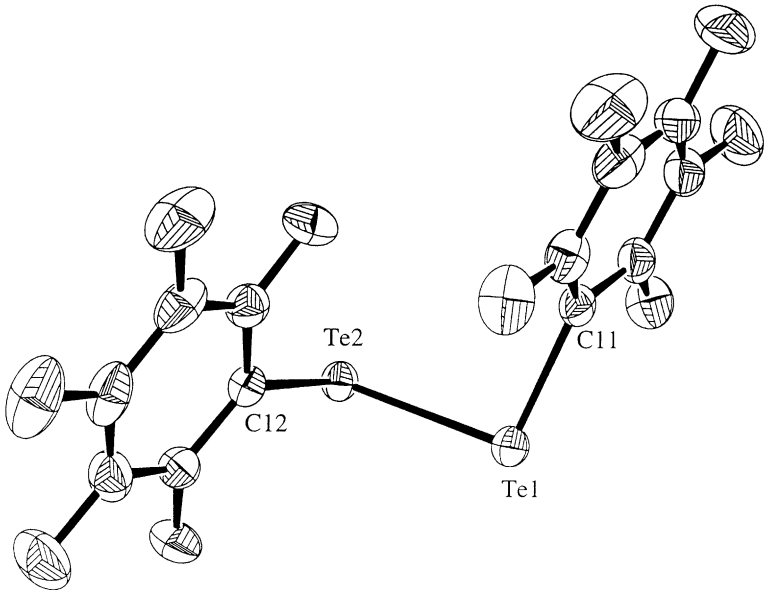


Fig. 2. ORTEP plot of the molecular structure of **7** with thermal ellipsoids at 50% probability level. Selected bond lengths (Å) and angles (°): Te(1)–C(11) 2.124(3); Te(1)–Te(2) 2.7028(5); Te(2)–C(12) 2.124(3); C–F 1.329(5)–1.341(4); C(11)–Te(1)–Te(2) 98.94(8); Te(1)–Te(2)–C(12) 98.35(8); C(11)–Te(1)–Te(2)–C(12) 91.8(1).

Table 1
Crystal data and structure refinements for **3** and **7**

	3	**7**
Empirical formula	$C_{21}H_3ClF_{15}Te$	$C_{12}F_{10}Te_2$
Formula weight	703.28	589.31
Temperature (K)	295(2)	200(3)
Crystal size (mm)	0.20 × 0.33 × 0.43	0.35 × 0.30 × 0.25
Crystal color and habit	Colorless platelet	Red prismatic
Crystal system	Monoclinic	Trigonal
Space group	$P2_1/c$	$R\bar{3}$
a (Å)	10.946(3)	14.4006(7)
b (Å)	21.883(7)	14.4006(7)
c (Å)	9.415(6)	36.281(2)
β (°)	102.00(4)	
γ (°)		120.00
Volume (Å^3)	2206(2)	6516(3)
Z	4	18
ρ (calcd.) (g cm^{-3})	2.118	2.703
μ (mm^{-1})	1.605	4.136
F(0 0 0)	1332	4788
Reflections collected	3688	7807
Independent reflections	3452 (R_{int} = 0.0112)	2763 (R_{int} = 0.0265)
Observed reflections	3002	2763
Data/restraints/parameters	3452/0/344	2763/0/217
Goodness-of-fit on F^2	1.272	1.140
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0318, 0.0791	0.0226, 0.0532
$R1$, $wR2$ (all data)	0.0390, 0.0815	0.0246, 0.0542
Larger diffraction peak/hole (e/Å^3)	0.626/−0.739	0.656/−0.420

3. Experimental section

3.1. General experimental procedures

All reactions were carried out under nitrogen as inert gas atmosphere using standard Schlenk techniques. Solvents were dried by standard methods. Commercially available chemicals were used as received. The diaryltellurium(IV) dihalides were synthesized according to [24]. IR spectra were recorded as nujol mulls or as neat liquids between KBr plates on a Nicolet 520 FT–IR spectrometer and on a Perkin-Elmer Spectrum One FT–IR spectrometer, Raman spectra on a Perkin-Elmer 2000 NIR FT-Raman spectrometer. The NMR spectra were recorded on Jeol 400Eclipse and EX400 instruments; chemical shifts are with respect to $(CH_3)_4Si$ (^{13}C), $CFCl_3$ (^{19}F), CH_3NO_2 (^{14}N) and $(CH_3)_2Te$ (^{125}Te). The ^{13}C NMR spectra were recorded fluorine decoupled except for **7**. Mass spectral data were obtained from a Finnigan MAT 90 instrument. Elemental analysis were performed in-house.

3.2. General procedure for the preparation of $(C_6F_5)_2Te(CN)_2$ (**1**) and $(CF_3C_6F_4)_2Te(CN)_2$ (**2**)

Into a solution of 1.6 mmol R_2Te in 8 ml CH_2Cl_2 are added at 0 °C within 5 min 1.7 mmol XeF_2. After stirring for 15 min the mixture is allowed to warm up to 25 °C. After further 20 min 3.4 mmol Me_3SiCN is added and a colorless solid precipitated. The solid is separated after stirring for 1 h at 25 °C, and is washed with 2 ml cold (−18 °C) CH_2Cl_2. The cyanides were obtained as colorless solids.

3.2.1. $(C_6F_5)_2Te(CN)_2$ (**1**)

Yield 85%, mp 98–101 °C. Raman: v = 2155/2148 (52/50, v_{CN}), 1640 (21), 1521 (10), 1401 (11), 1154 (12), 1093 (14), 804 (15), 771 (12), 640 (17), 619 (16), 586 (60), 492 (100), 444 (53), 385 (87), 353 (48), 317 (40), 281 (53), 229 (29), 200 (75), 130 (57) cm^{-1}. IR: v = 2143 m, 1638 s, 1593 m, 1502 vs, 1519 vs, 1397 s, 1291 m, 1260 m, 1090 s, 1038 w, 1005 m, 978 s, 802 m, 619 m, 580 m cm^{-1}. ^{19}F NMR [C_6D_6]: δ = −125.0/−127.4 (2F, m, 2/6-F), −140.1 (1F, tt, $^3J_{FF}$ = 21.8 Hz, $^4J_{FF}$ = 6.7 Hz, 4-F), −155.6 (2F, m, 3-F). ^{13}C NMR [C_6D_6]: δ = 146.3 (C-2), 144.0 (C-4), 137.2 (C-3), 122.7 (CN), 99.7 (C-1). ^{14}N NMR ($\Delta\nu_{1/2}$ (Hz)) [C_6D_6]: δ = −121 (110, CN). $^{125}Te\{^{19}F\}$ NMR [C_6D_6]: δ = 177. EIMS 70 eV, m/z (rel. int.): 594 $[C_6F_5TeTeC_6F_5]^+$ (3), 464 $[M-2CN]^+$ (97), 297 $[C_6F_5Te]^+$ (100), 167 $[C_6F_5]^+$ (6), 149 $[TeF]^+$ (15), 130 $[Te]^+$ (15), 117 $[C_3F_5]^+$ (34). Anal. Calcd. for $C_{14}F_{10}N_2Te$: C, 32.7; N, 5.4. Found: C, 32.0; N, 4.1.

3.2.2. $(CF_3C_6F_4)_2Te(CN)_2$ (**2**)

Yield 81%, mp 111–114 °C (dec.). Raman: v = 2165/2157/2140 (39/85/51 v_{CN}), 1647 (16), 1607 (7), 1493 (7), 1461 (10), 1424 (8), 1332 (13), 1154 (8), 992 (7), 926 (17), 789 (15), 717 (39), 538 (16), 503 (100), 440 (50), 391 (71), 374 (90), 342 (27), 299 (71), 280 (73), 189 (66), 145 (42), 120 (120) cm^{-1}. IR: v = 2161 w, 2153 m, 2141 w, 2135 w, 1646 m, 1603 m, 1322 vs, 1298 m, 1257 m, 1194 m, 1174 m,

1044 w, 981 s, 925 s, 854 w, 788 m, 715 s, 666 w, 647 m, 547 w, 425 m cm^{-1}. ^{19}F NMR [C_6D_6]: $\delta = -56.8$ (3F, m, 4-CF_3), −122.1/−125.1 (2F, m, 2/6-F), −133.9 (2F, m, 3-F). Other NMR spectra were not possible due to the extremely low solubility of **2**. EIMS 70 eV, *m/z* (rel. int.): 564 $[M-2CN]^+$ (100), 545 $[M-2CN-F]^+$ (22), 434 $[(CF_3C_6F_4)_2]^+$ (5), 415 $[(CF_3C_6F_4)_2-F]^+$ (4), 347 $[CF_3C_6F_4Te]^+$ (81), 217 $[CF_3C_6F_4]^+$ (12), 198 $[CF_3C_6F_3]^+$ (26), 179 $[CF_3C_6F_2]^+$ (48), 149 $[TeF]^+$ (11), 130 $[Te]^+$ (10), 117 $[C_5F_3]^+$ (8), 93 $[C_3F_3]^+$ (8), 69 $[CF_3]^+$ (7), 52 $[(CN)_2]^+$ (5). Anal. Calcd. for $C_{16}F_{14}N_2Te$: C, 31.3; N, 4.6. Found: C, 30.7; N, 4.1.

3.3. General procedure for $(C_6F_5)_3TeCl$ (3) and $(CF_3C_6F_4)_3TeCl$ (4)

Into a solution of 8.5 mmol R_2TeX_2 (X = Cl, Br) in 120 ml $CHCl_3$ are added 101.7 mmol AgCN and the mixture is stirred at 25 °C for 14 days (monitored by ^{19}F NMR spectroscopy). The solid is separated and washed three times with 10 ml $CHCl_3$. The solvent is removed under vacuum from the combined extracts, and the remaining residue is recrystallized from benzene to yield colorless solids.

3.3.1. $(C_6F_5)_3TeCl$ (3)

Yield 38%, mp 175–176 °C. Raman: ν = 1638 (38), 1602 (22), 1580 (21), 1519 (23), 1480 (21), 1402 (24), 1372 (22), 1279 (26), 1145 (25), 1090 (27), 1074 (30), 1043 (24), 802 (26), 775 (36), 619 (36), 587 (71), 490 (100), 444 (70), 385 (65), 349 (56), 282 (43), 240 (41), 229 (41), 205 (82), 189 (62), 172 (82), 126 (60) cm^{-1}. IR: ν = 1738 w, 1718 w, 1637 s, 1553 m, 1516 vs, 1500 vs, 1493 vs, 1475 vs, 1423 w, 1397 m, 1367 s, 1336 w, 1292 w, 1279 m, 1261 w, 1180 m, 1154 m, 1134 w, 1090 vs, 1077 vs, 1047 m, 1030 m, 1003 m, 978 vs, 799 m, 760 w, 748 w, 715 w, 616 m, 584 m, 484 m, 378 m, 360 m, 348 w, 312 w cm^{-1}. ^{19}F NMR [$CDCl_3$]: $\delta = -126.5$ (2F, m, 2-F), −144.5 (1F, t, $^3J_{FF}$ = 19.1 Hz, 4-F), −156.0 (2F, m, 3-F). $^{13}C\{^{19}F\}$ NMR [$CDCl_3$]: δ = 146.7 ($^2J_{TeC}$ = 28.1 Hz, C-2), 144.4 (C-4), 137.8 ($^3J_{TeC}$ = 8.1 Hz, C-3), 106.0 ($^1J_{TeC}$ = 275.6 Hz, C-1). ^{125}Te NMR [$CDCl_3$]: δ = 384 (m). EIMS 70 eV, *m/z* (rel. int.): 631 $[M-Cl]^+$ (10), 499 $[M-C_6F_5]^+$ (5), 464 $[(C_6F_5)_2Te]^+$ (100), 334 $[(C_6F_5)_2]^+$ (5), 297 $[C_6F_5Te]^+$ (70), 202 $[C_6F_5Cl]^+$ (5), 167 $[C_6F_5]^+$ (30), 148 $[C_6F_4]^+$ (15), 130 $[Te]^+$ (20). Anal. Calcd. for $C_{18}ClF_{15}Te$: C, 32.5; Cl, 5.3. Found: C, 32.7; Cl, 5.4.

3.3.2. $(CF_3C_6F_4)_3TeCl$ (4)

Yield 38%, mp 262–263 °C. Raman: ν = 1646 (25), 1602 (20), 1595 (20), 1396 (15), 1325 (16), 1180 (12), 1049 (7), 994 (15), 783 (30), 716 (36), 690 (29), 502 (100), 443 (72), 403 (64), 308 (53), 282 (40), 163 (47), 119 (41) cm^{-1}. IR: ν = 1646 m, 1602 m, 1595 w, 1493 w, 1396 m, 1325 m, 1292 m, 1180 w, 1049 w, 994 vs, 924 s, 783 m, 716 s, 646 w, 690 w, 502 w cm^{-1}. ^{19}F NMR [$CDCl_3$]: $\delta = -57.7$ (3F, t, $^4J_{FF}$ = 22.7 Hz, 4-CF_3), −137.1 (2F, m, 2-F), −141.3 (2F, m, 3-F). $^{13}C\{^{19}F\}$ NMR [$CDCl_3$]: δ = 146.4 ($^2J_{TeC}$ = 27.9 Hz, C-2), 144.3 (C-4), 138.1 ($^3J_{TeC}$ = 7.9 Hz, C-3), 105.2 ($^1J_{TeC}$ = 275.3 Hz, C-1). ^{125}Te NMR [$CDCl_3$]: δ = 390 (m). EIMS 70 eV, *m/z* (rel. int.): 781 $[M-Cl]^+$ (10), 762 $[M-Cl-F]^+$ (5), 599 $[M-CF_3C_6F_4]^+$ (5), 564 $[(CF_3C_6F_4)_2Te]^+$ (100), 545 $[M-Cl-F]^+$ (10), 347 $[CF_3C_6F_4Te]^+$ (55), 252 $[CF_3C_6F_4Cl]^+$ (3), 217 $[CF_3C_6F_4]^+$ (15), 198 $[CF_3C_6F_3]^+$ (10), 179 $[CF_3C_6F_2]^+$ (5), 130 $[Te]^+$ (20). Anal. Calcd. for $C_{21}ClF_{21}Te$: C, 31.0; Cl, 4.4. Found: C, 31.2; Cl, 4.4.

3.4. General procedure for $(C_6F_5)_3TeBr$ (5) and $(CF_3C_6F_4)_3TeBr$ (6)

Into a solution of 8.5 mmol R_2TeX_2 (X = Cl, Br) in 120 ml $CHBr_3$ are added 101.7 mmol AgCN and the mixture is stirred at 25 °C for 6 days (monitored by ^{19}F NMR spectroscopy). The solid is separated and washed three times with 10 ml $CHBr_3$. The solvent is removed under vacuum from the combined extracts, and the remaining residue is recrystallized from benzene to yield colorless solids.

3.4.1. $(C_6F_5)_3TeBr$ (5)

Yield 35%, mp 205−206 °C (dec.). Raman: ν = 1637 (35), 1599 (22), 1440 (13), 1408 (17), 1373 (10), 1273 (21), 1172 (14), 1081 (30), 990 (28), 946 (19), 681 (23), 657 (25), 613 (17), 585 (55), 490 (100), 443 (31), 385 (34), 349 (36), 283 (22), 233 (9), 198 (44), 168 (62), 120 (13) cm^{-1}. IR: ν = 1638 m, 1518 vs, 1500 vs, 1474 vs, 1452 m, 1396 m, 1385 m, 1369 s, 1337 m, 1288 m, 1275 m, 1148 m, 1137 m, 1091 s, 1079 s, 1040 w, 1032 w, 1006 m, 977 s, 969 s, 797 m, 684 m, 608 w, 584 w, 483 w, 379 w, 312 w cm^{-1}. ^{19}F NMR [$CDCl_3$]: $\delta = -126.1$ (2F, m, 2-F), −144.1 (1F, t, $^3J_{FF}$ = 20.3 Hz, 4-F), −155.7 (2F, m, 3-F). $^{13}C\{^{19}F\}$ NMR [$CDCl_3$]: δ = 146.7 ($^2J_{TeC}$ = 28.1 Hz, C-2), 144.5 (C-4), 137.8 ($^3J_{TeC}$ = 7.7 Hz, C-3), 104.6 ($^1J_{TeC}$ = 272.5 Hz, C-1). ^{125}Te NMR [$CDCl_3$]: δ = 398 (m). EIMS 70 eV, *m/z* (rel. int.): 631 $[M-Br]^+$ (11), 612 $[M-Br-F]^+$ (3), 464 $[(C_6F_5)_2Te]^+$ (79), 445 $[C_6F_5Te]^+$ (4), 334 $[(C_6F_5)_2]^+$ (13), 297 $[C_6F_5Te]^+$ (100), 204 $[C_3F_2Te]^+$ (11), 167 $[C_6F_5]^+$ (99), 148 $[C_6F_4]^+$ (24), 130 $[Te]^+$ (25), 117 $[C_5F_3]^+$ (30). Anal. Calcd. for $C_{18}BrF_{15}Te$: C, 35.2; Br, 13.0. Found: C, 35.0; Br, 12.2.

3.4.2. $(CF_3C_6F_4)_3TeBr$ (6)

Yield 31%, mp 285–288 °C. Raman: ν = 1646 (23), 1600 (22), 1595 (20), 1396 (14), 1326 (11), 1181 (12), 1048 (5), 994 (16), 786 (29), 716 (42), 691 (33), 501 (100), 443 (69), 410 (63), 312 (67), 282 (31), 164 (47), 121 (44) cm^{-1}. IR: ν = 1644 m, 1600 m, 1597 w, 1493 w, 1474 m, 1398 m, 1326 m, 1293 m, 1212 m, 1180 w, 1049 w, 995 vs, 926 s, 787 m, 715 s, 646 w, 688 w, 499 w (cm^{-1}). ^{19}F NMR [$CDCl_3$]: $\delta = -57.5$ (3F, t, $^4J_{FF}$ = 23.0 Hz, 4-CF_3), −136.9 (2F, m, 2-F), −140.9 (2F, m, 3-F). $^{13}C\{^{19}F\}$ NMR [$CDCl_3$]: δ = 146.4 ($^2J_{TeC}$ = 28.0 Hz, C-2), 144.6 (C-4), 137.7 (C-3), 104.3

($^1J_{TeC} = 273.0$ Hz, C-1). ^{125}Te NMR [$CDCl_3$]: $\delta = 396$ (m). EIMS 70 eV, *m/z* (rel. int.): 781 $[M-Br]^+$ (12), 762 $[M-BrF]$ (5), 643 $[M-CF_3C_6F_4]^+$ (3), 564 $[(CF_3C_6F_4)_2Te]^+$ (66), 434 $[(CF_3C_6F_4)_2]^+$ (24), 347 $[CF_3C_6F_4Te]^+$ (100), 217 $[CF_3C_6F_4]^+$ (26), 198 $[CF_3C_6F_3]^+$ (13), 179 $[CF_3C_6F_2]^+$ (4), 130 $[Te]^+$ (34), 79 $[Br]^+$ (3). Anal. Calcd. for $C_{21}BrF_{21}Te$: C, 29.4; Br, 9.3. Found: C, 28.7; Br, 8.7.

3.5. Attempted preparation of $C_6F_5TeTeC_6F_5$ (7)

Into a solution of 5 mmol C_6F_5H in 20 ml Et_2O is added at −70 °C within 15 min 5 mmol *n*-BuLi. The mixture is stirred for 1 h at −70 °C and then 5 mmol tellurium added. After 30 min the mixture is allowed to warm up to 25 °C and stirred for 1 h. A suspension of 5 mmol iodine in 3 ml Et_2O is added slowly to the mixture. The solvent and the volatile materials are removed after further 15 min stirring. The remaining residue is separated by slow vacuum sublimation to give the monotelluride $(C_6F_5)_2Te$ (50 °C/0.05 mbar) as pale yellow crystals, and the ditelluride $C_6F_5TeTeC_6F_5$ (**7**) (55 °C/0.05 mbar) as red crystals.

3.5.1. $C_6F_5TeTeC_6F_5$ (7)

Yield max. 4%, mp 99–100 °C.^{19}F NMR [$CDCl_3$]: $\delta = -114.0$ (2F, m, 2-F), −149.4 (1F, t, $^3J_{FF} = 20.8$ Hz, 4-F), −159.4 (2F, m, 3-F). ^{13}C NMR [$CDCl_3$]: $\delta = 148.8$ (dm, $^1J_{CF} = 244.5$ Hz, C-2), 143.2 (dm, $^1J_{CF} = 256.8$ Hz, C-4), 136.1 (dm, $^1J_{CF} = 254.4$ Hz, C-3), 79.4 (tm, $^2J_{CF} = 32.3$ Hz, C-1). ^{125}Te NMR [$CDCl_3$]: $\delta = 316$ (tm, $^3J_{TeF} = 69.5$ Hz). NMR, IR, MS and elemental analysis see also [15].

3.6. X-ray crystallography

For the determination of the single crystal structures of **3** an Enraf Nonius CAD 4 diffractometer and for **7** a Stoe IPDS area detector was employed for data collection using Mo-K_α radiation. The structures were solved by direct methods (SHELXS86) [28] and were refined by means of the full-matrix least squares procedures using SHELXL97 [29]. All atoms were refined anisotropically.

Crystallographic data (excluding structure factors) for the structures have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 161951 and 161952. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033 or E-mail: deposit@ccdc.cam.ac.uk).

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References

[1] F.H. Musa, W.R. McWhinnie, A.W. Downs, J. Organomet. Chem. 134 (1977) 43–44.
[2] F.H. Musa, W.R. McWhinnie, J. Organomet. Chem. 159 (1978) 37–45.
[3] R. Boese, J. Dworak, A. Haas, M. Pryka, Chem. Ber. 128 (1995) 477–481.
[4] J. Aust, A. Haas, M. Kauch, A. Pritsch, B. Stange, J. Fluorine Chem. 96 (1999) 147–157.
[5] S. Gockel, A. Haas, V. Probst, R. Boese, I. Müller, J. Fluorine Chem. 102 (2000) 301–311.
[6] R.F. Ziolo, K. Pritchett, J. Organomet. Chem. 116 (1976) 211–217.
[7] S.C. Cohen, A.G. Massey, in: J.C. Tatlow, R.D. Peacock, H.H. Hyman (Eds.), Advances in Fluorine Chemistry, Vol. 6, Butterworths, London, 1970, pp. 234–235.
[8] T.M. Klapötke, B. Krumm, P. Mayer, O.P. Ruscitti, Inorg. Chem. 39 (2000) 5426–5427.
[9] T.M. Klapötke, B. Krumm, P. Mayer, H. Piotrowski, O.P. Ruscitti, A. Schiller, submitted.
[10] M.T. Chen, J.W. George, J. Organomet. Chem. 12 (1968) 401–403.
[11] G.M. Bogolyubov, Y.N. Shlyk, A.A. Petrov, Zh. Obshch. Khim. 39 (1969) 1768–1771.
[12] J.-L. Piette, M. Renson, Bull. Soc. Chim. Belg. 79 (1970) 353–365.
[13] L. Engman, M.P. Cava, Organometallics 1 (1982) 470–473.
[14] M. Akiba, M.V. Lakshmikantham, K.-Y. Jen, M.P. Cava, J. Org. Chem. 49 (1984) 4819–4821.
[15] R. Kasemann, D. Naumann, J. Fluorine Chem. 48 (1990) 207–217.
[16] T.N. Bell, B.J. Pullman, B.O. West, Aust. J. Chem. 16 (1963) 722–724.
[17] J. Kischkewitz, D. Naumann, Z. Anorg. Allg. Chem. 547 (1987) 167–172.
[18] D. Naumann, private communication.
[19] C.S. Smith, J.-S. Lee, D.D. Titus, R.F. Ziolo, Organometallics 1 (1982) 350–354.
[20] S.C. Cohen, M.L.N. Massey, G. Alan, J. Organomet. Chem. 11 (1968) 563–566.
[21] D. Seebach, A.K. Beck, Chem. Ber. 108 (1975) 314–321.
[22] I.D. Sadekov, V.I. Minkin, Russ. Chem. Rev. 64 (1995) 491–522.
[23] E. Schulz-Lang, R.M. Fernandes Junior, E.T. Silveira, U. Abram, E.M. Vazquez-Lopez, Z. Anorg. Allg. Chem. 625 (1999) 1401–1404.
[24] T.M. Klapötke, B. Krumm, P. Mayer, K. Polborn, O.P. Ruscitti, Inorg. Chem. 40 (2001) 5169–5176 and references therein.
[25] D. Naumann, L. Ehmanns, K.-F. Tebbe, W. Crump, Z. Anorg. Allg. Chem. 619 (1993) 1269–1276.
[26] W. Dukat, F. Gall, C. Meyer, D. Mootz, D. Naumann, G. Nowicki, K. Schulz, Z. Anorg. Allg. Chem. 622 (1996) 617–621.
[27] P.G. Llabres, O. Didberg, L. Dupont, Acta Crystallogr. B28 (1972) 2438–2444.
[28] G.M. Sheldrick, SHELXS 86, University of Göttingen, 1986.
[29] G.M. Sheldrick, SHELXL 97, University of Göttingen, 1997.