Synthesis and Structures of Cycloalkanetellurium(IV) Fluorides and Azides

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Dedicated to Professor Karl O. Christe on the occasion of his 70th birthday

Telluracycloalkanes were fluorinated with XeF_2 and the resulting tellurium(IV) fluorides were reacted with $(CH_3)_3SiN_3$ to obtain the corresponding tellurium(IV) azides. The products, $(CH_2)_5TeF_2$, $(CH_2)_4TeF_2$, $(CH_2)_5Te(N_3)_2$ and $(CH_2)_4Te(N_3)_2$, were characterized by spectroscopic methods. The molecular structure of $(CH_2)_4TeF_2$ as well as the structure of an oxygen bridged species, $[(CH_2)_5TeN_3]_2O$, have been determined by X-ray diffraction.

Key words: Tellurium Fluorides, Tellurium Azides, Multinuclear NMR Spectroscopy,
X-Ray Crystallography

Introduction

Not at least because of our research in the past years, tellurium(IV) halides and azides are well known in literature [1 – 10]. Compounds of the formula $R_2Te(N_3)_2$, respectively $RTe(N_3)_3$, with various organic alkyl, aryl or fluorinated substituents were synthesized a few years ago. Binary tellurium(IV) azides, $Te(N_3)_4$, $Te(N_3)_5^-$ and $Te(N_3)_6^{2-}$, have been prepared and could be isolated as well [11, 12]. In this contribution we decided to investigate the chemistry of cyclic tellurium(IV) fluorides and azides.

Results and Discussion

Telluracyclohexane (**1**) and -pentane (**2**) were prepared by the reaction of sodium telluride with the appropriate α, ω-dibromoalkanes in methanol as solvent (see Scheme 1) [13 – 15].

The telluracycles were isolated by repeated phase separation, which worked best if methanol as solvent is used. The compounds **1** and **2** are yellow, malodorous liquids, which slowly decompose upon contact with air. Isolation by distillation is not possible because with methanol or *i*-propanol as solvents the estimated boiling points of **1** or **2** (*ca.* 120 – 140 ℃) are slightly higher, and since with high-boiling alcohols such as *n*-hexanol or *n*-decanol always azeotropic mixtures are formed. The only chance of purification is phase separation of concentrated methanolic mixtures of **1** and **2**. The lower, heavier tellurium containing phase is separated and the methanolic mixture repeatedly frozen and warmed up to room temperature with subsequent product separation. Overall, moderate yields of pure telluracycloalkanes result, since still significant amounts remain as methanolic solutions.

The isolation of a four-membered ring containing one tellurium atom, telluracyclobutane $(CH_2)_3Te$, which was briefly mentioned early in literature [14], was despite our many attempts not successful. The reaction between 1,3-dibromopropane and Na_2Te in analogy to the synthesis of the six- and five-membered heterocycles likely leads probably initially to telluracyclobutane, which seems to be too unstable and rapidly decomposes to unidentifiable products. Supposable is the formation of polymeric products. Tar-like residues were always obtained, and based on ^{125}Te NMR shifts

Scheme 1.

$$1, 2 \xrightarrow[-Xe]{XeF_2 / CH_2Cl_2}$$

n = 1 (**3**)
n = 0 (**4**)
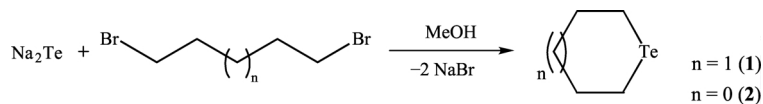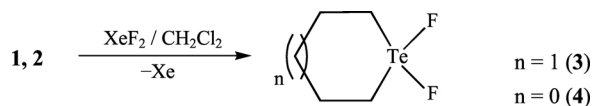
Scheme 2.

we conclude that a four-membered ring is formed, but readily decomposes to give several further ^{125}Te resonances. The resonance of a telluracyclobutane ($\delta = 310 - 360$ ppm solvent dependent) is, compared to those of **1** ($\delta = 224$ ppm) and **2** ($\delta = 255$ ppm), significantly shifted to lower field, which is in accord to the observed trend of the heterocycles regarding decreasing ring size.

The preparation of ditelluracycloalkanes by using in analogy Na_2Te_2 instead of Na_2Te according the existing literature [16 – 19] has not been reproducible, and did not lead to any of the desired products. In a specific report the preparation and isolation of ditelluracyclohexane in aqueous solutions was claimed [19], which is rather absurd taking the instability of those materials in moist environment into account, which we observed. In own attempts the reaction of 1,4-dibromobutane with Na_2Te_2 with the exclusion of moisture has led according to ^{125}Te NMR spectra exclusively to telluracyclopentane (**2**) in poor yields. No direct evidence for the formation of $(CH_2)_4Te_2$ could be obtained.

The telluracycloalkanes **1** and **2** were fluorinated with XeF_2 in CH_2Cl_2 as solvent (see Scheme 2), as in previous reports demonstrated for the synthesis of cyclic R_2TeF_2 [2].

The corresponding cycloalkanetellurium(IV) difluorides $(CH_2)_5TeF_2$ (**3**) and $(CH_2)_4TeF_2$ (**4**) were obtained as colorless solids, which are storable at 0 °C under inert atmosphere. They have been fully characterized by multinuclear NMR, IR, Raman, mass spectroscopy and elemental analyses. In the vibrational spectra **3** and **4** show intense peaks corresponding to the TeF stretching vibration ν_{TeF} 485 – 466 cm^{-1} (IR and Raman assignments see Experimental Section). The TeC stretching vibration is assigned in the Raman spectra to intense peaks in the range of 599 – 543 cm^{-1}. In the ^{125}Te NMR spectrum the resonance for **3** appears at $\delta = 1175$ ppm, whereas the resonance of **4** ($\delta = 1391$ ppm), according to the decreasing ring size, is shifted to lower field. The resonances of the TeF$_2$ group in the ^{19}F NMR spectra appear both at about -139 ppm (for an overview see also Table 1). The coupling constants, $^1J_{Te-F} = 1060$ Hz (**4**) and 1011 Hz (**3**), are larger than found for $(CH_3)_2TeF_2$

Table 1. ^{125}Te, ^{19}F and ^{14}N NMR shifts of the cyclohexane(pentane)tellurium(IV) fluorides and azides (δ in ppm, CDCl$_3$, 25 °C).

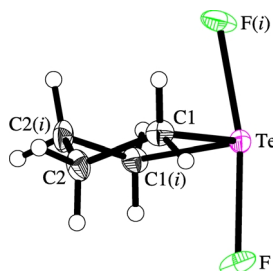|	δ^{125}Te	δ^{19}F	δ^{14}N
$(CH_2)_5TeF_2$ (**3**)	1175	-138.2	
$(CH_2)_4TeF_2$ (**4**)	1391	-139.7	
$(CH_2)_5Te(N_3)_2$ (**5**)	830		$-137, -207, -300$
$[(CH_2)_5TeN_3]_2O$ (**5a**)	1005		
$(CH_2)_4Te(N_3)_2$ (**6**)	1047		$-138, -206, -301$

Fig. 1. Molecular structure of $(CH_2)_4TeF_2$ (**4**). Selected bond lengths (Å) and angles (°): Te–F 2.019(3), Te–C1 2.103(4), C1–C2 1.522(5), C2–C2(*i*) 1.515(5), F–Te–F(*i*) 168.8(1), C1–Te–C1(*i*) 85.9(1), with $i = 2 - x, 2 - y, z$.

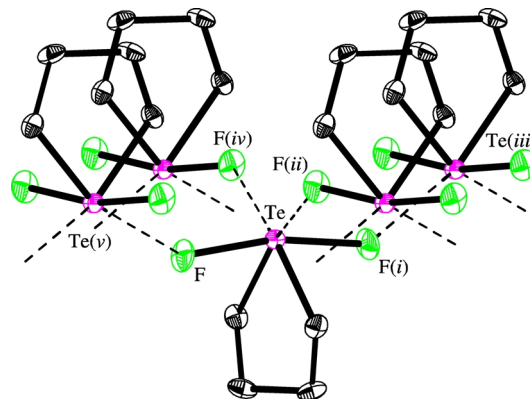Fig. 2. Crystal structure of **4** showing Te$\cdots$F interactions (Å) (hydrogen atoms omitted for clarity). Te$\cdots$F 3.023(3), with $i = 2 - x, 2 - y, z$; $ii = 1/2 + x, 21/2 - y, 1 - z$; $iii = 1/2 + x, 11/2 - y, 1 - z$, $iv = 11/2 - x, -1/2 + y, 1 - z$ and $v = -1/2 + x, 21/2 - y, 1 - z$.

(871 Hz [2]) and significantly larger than for diaryltellurium(IV) difluorides (300 – 600 Hz [5]).

Single crystals of **4** were obtained by slow evaporation of a solution in dichloromethane. The difluoride crystallizes in colorless blocks in the orthorhombic system, space group $P2_12_12$, with $Z = 2$. The five-membered ring adopts a half-chair conformation, which is also present in the structures of the lighter dihalides $(CH_2)_4TeX_2$ (X = Cl, Br [20]). The molecules are located on twofold rotation axes passing through the tellurium atom and exist as infinite chains with secondary Te$\cdots$F contacts. The Te–F bond is 2.02 Å, which is very similar for example to that found in Mes_2TeF_2 (2.01 Å), Mes = 2,4,6-trimethylphenyl [21],

3, 4 $\xrightarrow[-\ 2\ Me_3SiF]{2\ Me_3SiN_3\ /\ CH_2Cl_2}$

n = 1 (**5**)
n = 0 (**6**)
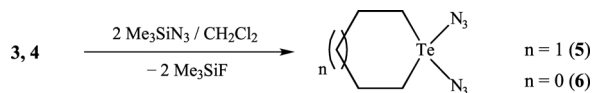
Scheme 3.

and slightly longer than in the perfluoroaryl derivative $(4\text{-}CF_3C_6F_4)_2TeF_2$ (1.96 Å) [5].

The F–Te–F(i) angle is 168.8° and marginally widened compared to the angles in Mes_2TeF_2 (167.2°) and $(4\text{-}CF_3C_6F_4)_2TeF_2$ (164.7°). The molecular structure of **4** is shown in Fig. 1. The Te···F interactions (see Fig. 2) are about 1 Å longer than the regular TeF bond lengths (1.96 – 2.00 Å), but significantly shorter than the tellurium–fluorine van der Waals radii (vdWr TeF 3.53 Å [22]). These secondary contacts lead to heptacoordination of the tellurium atom.

The previous reports dealing with the preparation of **3** and **4** are again questionable, as already pointed out in previous articles on some of our earlier work regarding R_2TeF_2 and $R_2Te(N_3)_2$, because of the large differences in the melting points of **3** (m. p. 94 – 99 °C, *vs.* 210 °C [23]) and **4** (m. p. 116 – 123 °C, *vs.* 72 °C [24]). In those reports the only characterization was the determination of the melting points and elemental analysis; the apparent preparation was carried out in water as solvent (R_2TeF_2 in general is moisture sensitive!).

Since telluracyclobutane is not feasible, another approach to the corresponding difluoride was the fluorination of a mixture of Na_2Te and 1,3-dibromopropane. The idea was the possibility of a reaction of *in situ* generated telluracyclobutane with XeF_2. The choice of the solvent is important, because Na_2Te is only soluble in alcohols, but the desired fluorination has to be carried out in solvents such as dichloromethane, otherwise byproducts of solvent fluorination cannot be avoided. The only chance to perform this reaction is in a first step to react dibromopropane with Na_2Te in methanol, and in a second step the treatment of the reaction mixture with XeF_2 under addition of some dichloromethane. Unfortunately, again no products were isolable, and the signals observed in the ^{19}F and ^{125}Te NMR spectra could not be assigned unequivocally.

The azidation of **3** and **4** with two equivalents of Me_3SiN_3 leads to the corresponding tellurium(IV) diazides, $(CH_2)_5Te(N_3)_2$ (**5**) respectively $(CH_2)_4Te(N_3)_2$ (**6**) (see Scheme 3).

The azides **5** and **6** are sensitive towards hydrolysis as common for azides of the type $R_2Te(N_3)_2$. The colorless solids are not explosive upon contact with a

flame, in contrast with $(C_2H_5)_2Te(N_3)_2$ having an almost identical nitrogen content ($\sim 31\%$) [2]. The cyclization apparently leads to a stabilization of dialkyltellurium(IV) diazides. The melting points of **5** and **6** agree better than those of the difluorides [23, 24], but again no further details were given except elemental analyses. The ^{125}Te NMR resonances of the diazides **5** ($\delta = 830$ ppm) and **6** ($\delta = 1047$ ppm) are, compared to those of the corresponding difluorides **3** and **4**, shifted approximately 350 ppm to higher field, along with a similar shift with increasing ring size. In the ^{14}N NMR spectra all resonances for the nitrogen atoms of the azide groups can be detected and are given in Table 1. As usual for covalent azides the resonances, especially for N_α, are more or less broadened. Due to the poor solubility of compounds with the formula $R_2Te(N_3)_2$ no ^{15}N NMR data were available until now. The compounds **5** and **6** show an increased solubility and in case of **5** in the ^{15}N NMR spectrum the resonances for N_β (-137.3 ppm) and, with low resolution, for N_γ (-206.9 ppm) were observed. Nevertheless the resonance for N_α still could not be detected within the noise of the spectrum. The TeN stretching vibrations (ν_{TeN}) in the vibrational spectra of **5** and **6** are detected around 350 cm^{-1} as very intense peaks. The antisymmetric azide stretching vibrations ν_{asN3} are found as intense peaks in the IR spectra and medium intense peaks in the Raman spectra at 2072 – 2006 cm^{-1}.

After extended storage periods (4 months) of **5** in CH_2Cl_2 at -20 °C, colorless single crystals were obtained. The determination of the crystal structure yielded an oxygen bridged tellurium(IV) azide, $[(CH_2)_5TeN_3]_2O$ (**5a**), shown in Fig. 3.

Likely partial hydrolysis by traces of moisture led to the formation of a ditelluroxane moiety. The tellurium(IV) monoazide **5a** crystallized in colorless prisms in the monoclinic system, space group $P2_1/c$, with $Z = 4$. The Te–O bond distances are 2.01 Å (Te1–O) respectively 1.99 Å (Te2–O), which are in the range of the Te–O bond distance found in the similar $(Ph_2TeN_3)_2O$ (1.97 Å) [25], the only other known tellurium(IV) azide of that type, and as well comparable to the Te–O bond distance in the tellurium(IV) cyanide $(Mes_2TeCN)_2O$ (2.00 Å) [21]. In contrast to these molecules there is no intramolecular center of symmetry in **5a**. Both telluracyclohexane moieties appear in the chair conformation of the six-membered ring. Interestingly, there are two different azide parameters found (Te1–N1 2.42 Å, N1–N2 1.19 Å, N2–N3 1.14 Å, Te2–N4 2.58 Å, N4–N5 1.03 Å, N5–N6 1.22 Å).
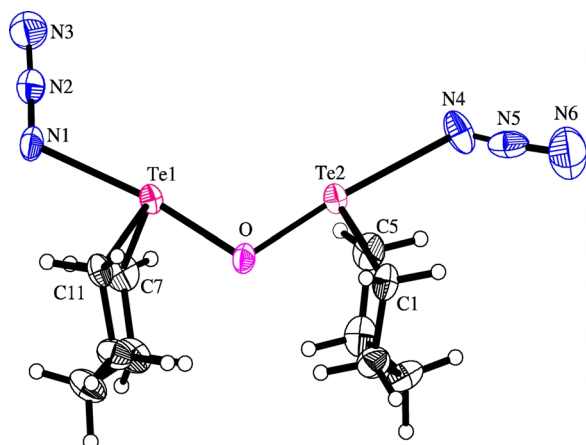
Fig. 3. Molecular structure of $[(CH_2)_5TeN_3]_2O$ (**5a**). Selected bond lengths (Å) and angles (°): Te1−O 2.011(4), Te2−O 1.986(4), Te1−N1 2.423(6), Te2−N4 2.575(7), N1−N2 1.186(8), N2−N3 1.143(9), N4−N5 1.03(1), N5−N6 1.21(1), Te1−O−Te2 116.9(2), N1−N2−N3 177.7(8), N4−N5−N6 175.1(9), O−Te1−N1 172.7(2), O−Te1−C11 91.1(2), O−Te1−C7 88.2(2), N1−Te1−C7 86.4(2), N1−Te1−C11 84.1(2), O−Te2−N4 174.8(2), O−Te2−C1 90.4(2), O−Te2−C5 91.1(2), N4−Te2−C1 87.1(3), N4−Te2−C5 84.5(3), Te1−N1−N2 113.8(5), Te2−N4−N5 132.0(7).

Whereas the azide parameters at Te1 are normal, the azide moiety at Te2 has a longer Te2–N4 bond and inverted N–N distances, *i. e.* N5–N6 bond is longer than N4–N5 bond. The corresponding N4–N5–N6 angle has been refined to 175.1° (*vs.* N1–N2–N3 177.7°) and is significantly more bent. A similar phenomenon has been reported earlier for some platinum and gold azides [26 – 28], but no explanation was given. In addition, one example of a tellurium azide compound exists, where chloride/azide exchange from the solvent was claimed to be likely [12]. However, after careful examination of the data set of **5a** such a slow exchange and therefore a partial presence of chlorine at tellurium can be excluded.

As observed with other tellurium(IV) azides, there are also intermolecular Te$\cdots$N contacts found, which are shorter than the sum of the van der Waals radii tellurium and nitrogen (vdW distance TeN 3.61 Å [22]). The three different Te$\cdots$N interactions are shown in Fig. 4 and are in each case between tellurium and N_α of the azide group. Apart from those interactions there are several weaker contacts detected between tellurium and N_β, only marginally shorter than the tellurium–nitrogen van der Waals distance, but not considered further.
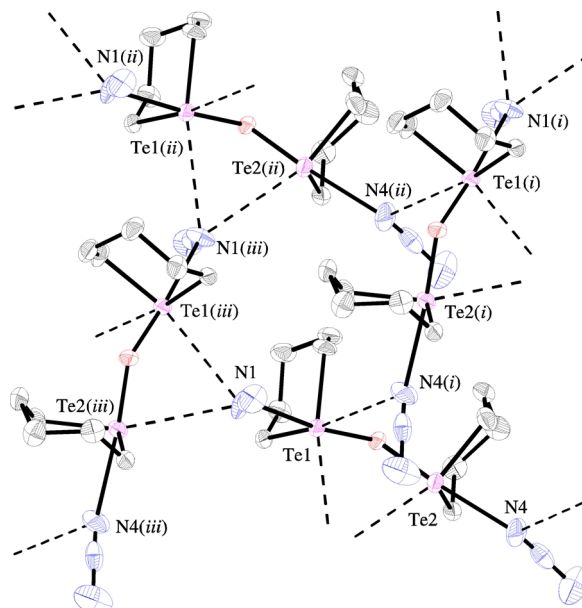

Fig. 4. Crystal structure of **5a** showing Te$\cdots$N$_\alpha$ interactions (Å) (hydrogen atoms omitted and only Te and N$_\alpha$ labeled for clarity). Te1$\cdots$N4(*i*) 3.17(1), Te2(*iii*)$\cdots$N1 3.243(7), Te1(*iii*)$\cdots$N1 3.315(6), with $i = 1-x, 1/2+y, 1/2-z$; $ii = x, 1+y, z$ and $iii = -x, 1/2+y, 1/2-z$.

The interactions in the range of 3.17 – 3.32 Å build up a three dimensional network, leading to hexa- (Te2) and heptacoordination (Te1) around tellurium. Besides the previously mentioned oxygen bridged azide $(Ph_2TeN_3)_2O$, which was obtained as a by-product [25], **5a** is the second oxygen bridged tellurium azide, but the first one for which Te$\cdots$N secondary interactions were reported. After obtaining the structure of **5a**, the remaining crystals were dissolved in $CDCl_3$ and besides the resonance of **5** that of **5a** was detected at $\delta = 1005$ ppm in the ^{125}Te NMR spectrum. The resonance is found at slightly lower field compared to that of **5** ($\delta = 830$ ppm), which we explain with the stronger electron withdrawing effect of oxygen.

Experimental Section

All manipulation of air- and moisture-sensitive materials were performed under an inert atmosphere of dry argon using flame-dried glass vessels and Schlenk techniques [29]; the solvents methanol and dichloromethane were distilled and stored under dry nitrogen prior to use. The sodium tellurides Na_2Te/Na_2Te_2 were prepared according to literature procedures [30]. The dibromoalkanes (Fluka), Me_3SiN_3 (Aldrich) and elemental tellurium (Aldrich, 200 mesh) were used as received. Infrared spectra were recorded on Perkin-

Table 2. Crystal data and structure refinements.

	$(CH_2)_4TeF_2$ (**4**)	$[(CH_2)_5TeN_3]_2O$ (**5a**)
Empirical formula	$C_4H_8F_2Te$	$C_{10}H_{20}N_6OTe_2$
Formula weight	221.70	495.52
Temperature [K]	200	200
Crystal size [mm]	$0.22 \times 0.30 \times 0.40$	$0.17 \times 0.21 \times 0.17$
Crystal system	orthorhombic	monoclinic
Space group	$P2_12_12$	$P2_1/c$
a [Å]	5.509(1)	8.8064(7)
b [Å]	7.617(2)	8.8238(7)
c [Å]	7.131(2)	20.005(2)
β [°]		94.913(7)
V [Å^3]	299.2(1)	1548.8(2)
Z	2	4
ρ_{calc} [g/cm^3]	2.461	2.125
μ [mm^{-1}]	4.889	3.770
$F(000)$	204	936
θ Range [°]	2.9 – 28.0	3.8 – 26.0
Index ranges	$-7 \le h \le 7$	$-9 \le h \le 10$
	$-10 \le k \le 9$	$-10 \le k \le 10$
	$-9 \le l \le 9$	$-24 \le l \le 16$
Reflections collected	2539	7747
Reflections observed	724 ($R_{int} = 0.054$)	7747 ($R_{int} = 0.072$)
Reflections unique	704	2477
$R1/wR2$ (2σ)	0.0158 / 0.0378	0.0413 / 0.0904
$R1/wR2$ (all)	0.0169 / 0.0382	0.0548 / 0.0978
Data/restraints/parameters	704/0/50	3030/0/172
GOOF on F^2	1.18	1.02
Larg. diff. peak/	−0.51/	−1.30/
hole [e/Å^3]	0.59	1.45

Elmer Spektrum One FT-IR (as KBr pellets or between KBr plates in Nujol), and Raman spectra on a Perkin-Elmer 2000 NIR FT spectrometer (as neat solids) fitted with a Nd:YAG laser (1064 nm). NMR spectra were recorded on a JEOL Eclipse 400 instrument at 25 °C using CDCl$_3$ as solvent, and chemical shifts were determined with respect to external Me$_4$Si (^{1}H, 399.8 MHz; ^{13}C, 100.5 MHz), MeNO$_2$ (^{14}N/^{15}N, 28.9/40.6 MHz), CFCl$_3$ (^{19}F, 376.1 MHz) and Me$_2$Te (^{125}Te, 126.1 MHz). Mass spectrometric data were obtained from a JEOL MStation JMS 700 spectrometer using the direct EI mode with fragments referring to the nuclei with the highest abundance (for example ^{130}Te). Elemental analyses: Analytical Service LMU. Melting points were determined on a Büchi B450 instrument.

For compound **4** a Stoe IPDS area detector and for **5a** an Oxford Xcalibur diffractometer with an CCD area detector were employed for data collection using Mo-K$_\alpha$ radiation. The structures were solved using direct methods (SHELXS [31] and SIR97 [32]) and refined by full-matrix least-squares on F^2 (SHELXL [31]). All non-hydrogen atoms were refined anisotropically. All ORTEP plots are shown with thermal ellipsoids at the 50% probability level. Further details are available under the depository numbers CCDC 295487 and 295610 from the Cambridge Crystallographic Data Centre.

General procedure for the preparation of $(CH_2)_nTe$

Into a suspension of 20.0 mmol sodium telluride in 30 ml of methanol was slowly added 18.0 mmol of dibromo-butane or -propane at 0 °C and the resulting deep violet solution was stirred for 30 min at this temperature. After slowly warming up to room temperature the solution was stirred over night at 25 °C. All volatile materials were condensed into a trap in vacuum. The contents of the trap were warmed up to r. t. and two phases resulted. The lower phase consisted entirely of pure telluracyclohexane (**1**) and telluracyclopentane (**2**), respectively. The upper phase contained besides methanol still substantial amounts of **1** or **2**. After separation, this upper phase is frozen again and warmed up, and with the occurring phase separations, further **1** or **2** could be isolated. This procedure is repeated up to six times until only few milligrams of **1** or **2** were separated. Compounds **1** and **2** were isolated as yellow liquids.

$(CH_2)_5Te$ (**1**)

Yield 28%. – ^{1}H NMR: $\delta = 2.71$ (m, CH$_2$Te, 4H), 2.00 (m, CH$_2$CH$_2$Te, 4H), 1.55 (m, CH$_2$(CH$_2$)$_2$Te, 2H). – ^{13}C{^{1}H} NMR: $\delta = 29.5$ (CH$_2$(CH$_2$)$_2$Te), 28.5 (CH$_2$CH$_2$Te), −3.7 (CH$_2$Te, $^1J_{C-125Te} = 129.1$ Hz). – ^{125}Te{^{1}H} NMR: $\delta = 224$.

$(CH_2)_4Te$ (**2**)

Yield 35 %. – ^{1}H NMR: $\delta = 3.12$ (m, CH$_2$Te, 4H), 2.00 (m, CH$_2$CH$_2$Te, 4H). – ^{13}C{^{1}H} NMR: $\delta = 36.0$ (CH$_2$CH$_2$Te), 6.1 (CH$_2$Te, $^1J_{C-125Te} = 124.5$ Hz). – ^{125}Te{^{1}H} NMR (CDCl$_3$): $\delta = 255$.

General procedure for the preparation of $(CH_2)_nTeF_2$

Into a solution of 1.20 mmol telluracyclo-hexane or -pentane in 13 ml of CH$_2$Cl$_2$ was added 1.26 mmol XeF$_2$ at 0 °C. After stirring for 1 h at 0 °C, the colorless solution was allowed to warm up to r. t. and all volatile materials were removed *in vacuo*, and pure products **3** and **4** obtained.

$(CH_2)_5TeF_2$ (**3**)

Colorless solid, yield 96%, m. p. 94 – 99 °C. – Raman: $\nu = 2995$ (19), 2935 (56), 2865 (29), 1447 (13), 1201 (21), 924 (14), 793 (11), 543 (100, νTeC), 478 (53, νTeF), 462 (37), 377 (33), 275 (28), 226 (13), 191 (18) cm^{-1}. – IR (KBr): $\nu = 2994$ w, 2953 m, 2930 vs, 2861 m, 1640 br, 1525 br, 1457 m, 1446 m, 1422 w, 1408 m, 1351 w, 1340 m, 1297 w, 1249 s, 1194 m, 1131 w, 1094 br, 1024 w, 1011 w, 935 s, 885 m, 800 s, 790 w, 655 br, 538 m, 485 (νTeF) vs cm^{-1}. – ^{1}H NMR: $\delta = 2.92$ (m, CH$_2$Te, 4H), 1.90 (m, CH$_2$CH$_2$Te, 4H), 1.78 (m, CH$_2$(CH$_2$)$_2$Te, 2H). – ^{13}C{^{1}H} NMR: $\delta = 34.5$ (CH$_2$Te, $^1J_{C-125Te} = 195.6$ Hz),

26.9 (CH_2CH_2Te), 19.0 ($CH_2(CH_2)_2Te$). – ^{19}F NMR: $\delta =$ −138.2 ($^1J_{F-125Te} = 1011$ Hz, $^1J_{F-123Te} = 841$ Hz). – $^{125}Te\{^1H\}$ NMR: $\delta = 1175$ (t). – MS *m/z* (%): 238 (4) [M^+], 219 (16) [$M^+ - F$], 200 (7) [$M^+ - 2F$], 69 (100) [$C_5H_{10}^+$], 41 (76) [$C_3H_6^+$]. – $C_5H_{10}F_2Te$ (235.7): calcd. C 25.5, H 4.3; found C 25.8, H 4.4.

$(CH_2)_4TeF_2$ (**4**)

Colorless solid, yield 91%, m. p. 116 – 123 °C. – Raman: $v = 3012$ (35), 2955 (52), 2931 (59), 2863 (11), 1419 (15), 1253 (22), 1112 (15), 953 (16), 858 (12), 763 (12), 599 (100, vTeC), 573 (20), 565 (22), 466 (55, vTeF), 448 (48), 340 (57), 266 (13), 216 (16), 200 (13) cm^{-1}. – IR (KBr): $v = 3012$ m, 2955 vs, 2925 m, 2855 m, 2104 w, 1525 s, 1448 m, 1411 s, 1310 m, 1251 s, 1108 m, 1045 w, 831 m, 631 w, 564 m, 472 (vTeF) vs cm^{-1}. – ^1H NMR: $\delta = 3.10$ (br, CH_2Te, 4H), 2.59 (m, CH_2CH_2Te, 4H). – $^{13}C\{^1H\}$ NMR: $\delta = 49.3$ (CH_2Te, $^1J_{C-125Te} = 185.3$ Hz), 31.9 (CH_2CH_2Te, $^2J_{C-125Te} = 11.5$ Hz). – ^{19}F NMR: $\delta =$ −139.7 (s, $^1J_{F-125Te} = 1060$ Hz, $^1J_{F-123Te} = 879$ Hz). – $^{125}Te\{^1H\}$ NMR: $\delta = 1391$ (t). – MS *m/z* (%): 224 (6) [M^+], 205 (9) [$M^+ - F$], 186 (2) [$M^+ - 2F$], 55 (100) [$C_4H_8^+$]. – $C_4H_8F_2Te$ (221.7): calcd. C 21.7, H 3.6; found C 21.7, H 3.7.

General procedure for the preparation of $(CH_2)_nTe(N_3)_2$

Into a solution of 0.41 mmol cyclohexane(pentane) tellurium(IV) difluoride in 20 ml CH_2Cl_2 was added 1.13 mmol of Me_3SiN_3 at 0 °C and the colorless solution was stirred for 1 h at 0 °C. After additional stirring for 2 h at room temperature all volatile materials were removed *in vacuo*, and pure products **5** and **6** obtained.

$(CH_2)_5Te(N_3)_2$ (**5**)

Colorless solid, yield 93%, m. p. 146 – 149 °C (dec.). – Raman: $v = 2945$ (21), 2914 (16), 2052 (11)/2021 (12)

($v_{as}N_3$), 1445 (9), 1409 (9), 1320 (11), 1242 (10), 1195 (11), 921 (8), 650 (10), 531 (48)/471 (34) (vTeC), 349 (100, vTeN), 266 (20), 178 (31) cm^{-1}. – IR (Nujol): $v = 2020$ vs/2006 vs ($v_{as}N_3$), 1683 w, 1261 w, 1234 w, 1168 m, 927 m, 868 w, 625 s, 518 cm^{-1}. – ^1H NMR: $\delta = 3.15$ (t, CH_2Te, 4H), 1.92 (m, CH_2CH_2Te, 4H), 1.78 (m, $CH_2(CH_2)_2Te$, 2H). – $^{13}C\{^1H\}$ NMR: $\delta = 30.9$ (br, CH_2Te), 26.0 ($CH_2(CH_2)_2Te$), 19.4 (CH_2CH_2Te). – ^{14}N NMR: $\delta = -137$ (N_β), −207 (N_γ), −300 (N_α). – $^{125}Te\{^1H\}$ NMR: $\delta = 830$. – MS *m/z* (%): 279 (2) [M^+], 242 (3) [$M^+ - N_3$], 200 (39) [$M^+ - 2N_3$], 69 (89) [$C_5H_{10}^+$]. – $C_5H_{10}N_6Te$ (281.8): calcd. C 21.3, H 3.6 N 29.8; found C 22.5, H 3.4, N 23.6.

$(CH_2)_4Te(N_3)_2$ (**6**)

Colorless solid, yield 86%, m. p. 162 – 164 °C (dec.). – Raman: $v = 3013$ (6), 2985 (23), 2924 (10), 2049 (13)/2015 (13) ($v_{as}N_3$), 1437 (5), 1321 (6), 1237 (7), 1187 (5), 1039 (5), 945 (9), 856 (7), 652 (6), 579 (41)/549 (16) (vTeC), 459 (18), 351 (100, vTeN), 235 (28), 180 (30) cm^{-1}. – IR (Nujol): $v = 2072$ vs/2033 vs/2008 vs ($v_{as}N_3$), 1316 m, 1266 s, 1234 m, 1184 w, 1087 w, 1036 w, 958 w, 942 w, 854 w, 820 m, 755 w, 650 m, 594 m, 576 w, 548 m, 457 cm^{-1}. – ^1H NMR: $\delta = 3.35$ (br, CH_2Te, 4H), 2.61 (br, CH_2CH_2Te, 4H). – $^{13}C\{^1H\}$ NMR: $\delta = 45.9$ (CH_2Te), 33.1 (CH_2CH_2Te). – ^{14}N NMR: $\delta = -138$ (N_β), −206 (N_γ), −301 (N_α). – $^{125}Te\{^1H\}$ NMR: $\delta = 1047$. – MS *m/z* (%): 228 (1) [$M^+ - N_3$], 186 (28) [$M^+ - 2N_3$], 55 (100) [$C_4H_8^+$]. – $C_4H_8N_6Te$ (267.7): calcd. C 17.9, H 3.0, N 31.4; found C 18.0, H 2.9, N 30.8.

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