First Synthesis and Structures of Aryltellurium(IV) Diazides

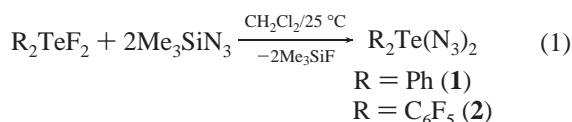## Thomas M. Klapötke,* Burkhard Krumm, Peter Mayer, and Oliver P. Ruscitti

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The number of tellurium azides in the literature is limited to only a few examples. Research in this area did not start before 1972;[1] and the number of well-characterized compounds is still small.[2−5] Tellurium(IV) azides were obtained previously and isolated by treatment of $TeCl_4$ or Ph_2TeO with trimethylsilyl azide. While $TeCl_3N_3$ and $TeCl_2(N_3)_2$ were reported to be explosive solids, the ionic and more stable $[Te(N_3)_3][SbF_6]$ [2] and $(Ph_2-TeN_3)_2O$[5] were structurally investigated. A general and easy route to tellurium azides is still unknown. All these facts encouraged us to find systematic synthetic routes to various Te azides.

Here we present the preparation of the first diorganotellurium-(IV) diazides, $Ph_2Te(N_3)_2$ (**1**) and $(C_6F_5)_2Te(N_3)_2$ (**2**), and their full characterization by spectroscopic and structural methods. The different influence of phenyl and the stronger electron withdrawing pentafluorophenyl group on the sterical arrangement of the $Te(N_3)_2$ moiety is discussed. With these derivatives a gap in tellurium azide chemistry has been closed and easy access to this class of substances achieved.[6]

The reaction of diaromatic tellurium difluorides with an excess of trimethylsilyl azide[7] at ambient temperature (eq 1) leads to a straightforward formation of the corresponding tellurium(IV) azides. The formation of trimethylsilyl fluoride was detected by its ^{19}F NMR resonance. Interestingly, the corresponding dichlo-

$$R_2TeF_2 + 2Me_3SiN_3 \xrightarrow[-2Me_3SiF]{CH_2Cl_2/25 \text{ °C}} R_2Te(N_3)_2 \qquad (1)$$
$$R = Ph \text{ (1)}$$
$$R = C_6F_5 \text{ (2)}$$

rides or dibromides gave no reaction with trimethylsilyl azide. The azides **1**[8] and **2**[9] are colorless solids and, in contrast to the apparently shock-sensitive $TeCl_2(N_3)_2$, nonexplosive. They hydrolyze slowly in air, and traces of moisture promote decomposition with formation of HN_3. Hydrolysis products, probably $(C_6F_5)_2TeO$ and HN_3, of the fluorinated azide **2** in solution were detected by NMR spectroscopy after short periods. The nonfluorinated azide **1** is less sensitive. The synthesis of the precursors, the diaromatic tellurium(IV) difluorides, was achieved using slightly modified literature methods.[10]

The ^{125}Te NMR spectra show resonances at δ 983 for **1** and δ 807 for **2**, a typical range for tetrasubstituted tellurium compounds.[11] In comparison, the resonances of the corresponding

difluorides are shifted to lower field, Ph_2TeF_2 δ 1128 and $(C_6F_5)_2$-TeF_2 δ 1080, whereas the dichlorides are shifted to higher field, Ph_2TeCl_2 δ 921[11] and $(C_6F_5)_2TeCl_2$ δ 665. A change from phenyl to pentafluorophenyl leads to a general high-field shift of the ^{125}Te resonance. In addition the signal of **2** is split into a quintet due to coupling with the *ortho* fluorine atoms. The ^{13}C and ^{19}F NMR resonances of the carbon and fluorine atoms in the *ortho* and the *meta* position in **2** are broadened, which is likely due to a restricted rotation about the TeC bonds. A detailed investigation of this phenomenom in tellurium(IV) dihalides is currently in progress. To the best of our knowledge, there have been no earlier reports on ^{125}Te or ^{14}N NMR data of tellurium(IV) azides. The ^{14}N NMR spectra of **1** and **2** show three resonances at δ −137 (N_β), −200 (N_γ), −289 (N_α) and at −141 (N_β), −186 (N_γ), −284 (N_α), respectively, as proof for two covalently bound azide groups (connectivity $Te-N_\alpha-N_\beta-N_\gamma$). In the Raman spectrum of **1** there are two peaks of medium intensity visible in the region of the antisymmetric azide stretching vibration ($v_{as}N_3$) at 2060/2030 cm^{-1} and for **2** at 2059/2021 cm^{-1}. The TeN stretching vibrations are assigned for **1** at 330 cm^{-1} and for **2** at 356/347 cm^{-1} as very intense peaks in the Raman spectra. In the IR spectrum of **1** the absorptions of the azide group $v_{as}N_3$ are at 2061/2052/2031 cm^{-1} and vTeN is found at 329 cm^{-1}. For **2** these vibrations are shifted to higher wavenumbers: $v_{as}N_3$ is found at 2131/2066/2027 cm^{-1} and vTeN at 355/347 cm^{-1}. The TeN stretching vibrations of **1** and **2** are shifted considerably to lower energies compared to those

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(7) *CAUTION:* **Covalent azides are potentially hazardous; small-scale synthesis recommended!** Typical procedure: Into a solution of 0.7 mmol of R_2TeF_2 in 5 mL of CH_2Cl_2 was added 2.0 mmol of trimethylsilyl azide. After 2 h of stirring, volatile materials were removed in vacuo, and the yellowish residue was washed with 2 mL of CH_2Cl_2. The resulting powder was recrystallized from CH_2Cl_2 to give colorless crystals.

(8) $(C_6H_5)_2Te(N_3)_2$ (**1**): yield 66%, mp 115 °C dec. Raman (100 mW): 3075 (12), 3057 (22), 2060 (10)/2030 (12) ($v_{as}N_3$), 1575 (11), 1318 (4), 1265 (5), 1184 (5), 1172 (4), 1022 (11), 997 (22), 659 (10), 330 (100) (vTeN), 290 (14), 271 (13), 223 (10) cm^{-1}. IR (Nujol): 3059 (m), 2967 (vs), 2934 (vs), 2882 (m), 2061/2052/2031 (vs) ($v_{as}N_3$), 1615 (m), 1575 (m), 1477 (m), 1444 (m), 1434 (m), 1397 (w), 1316 (m), 1264 (vs), 1255 (vs), 1185 (m), 1123 (m), 1071 (m), 994 (m), 798 (w), 737 (vs), 691 (m), 650 (m), 585 (m), 461 (m), 329 (m) (vTeN), 294 (s) cm^{-1}. ^{125}Te NMR (CDCl₃): δ 983 (s, $^1J_{Te-C}$ = 241.9 Hz). ^{14}N NMR (CDCl₃, $\Delta v_{1/2}$ [Hz]): δ −137 (80, N_β), −200 (310, N_γ), −289 (1350, N_α). $^{13}C\{^1H\}$ NMR (CDCl₃): δ 132.4 (C2, $^2J_{C-Te}$ = 34.6 Hz), 131.8 (C4), 130.3 (C1, $^1J_{C-Te}$ = 242.9 Hz), 130.1 (C3, $^3J_{C-Te}$ = 9.2 Hz). ^1H NMR (CDCl₃): δ 7.87−7.53 (C_6H_5). MS (EI), *m/e* (%): 284 (36) [M^+ − $2N_3$], 207 (15) [$C_6H_5Te^+$], 154 (100) [$C_{12}H_{10}^+$], 130 (3) [Te^+], 77 (62) [$C_6H_5^+$]. Anal. Calcd for $C_{12}H_{10}N_6Te$: C, 39.4; H, 2.8; N, 23.0. Found: C, 39.4; H, 2.9; N, 21.8.

(9) $(C_6F_5)_2Te(N_3)_2$ (**2**): yield 71%, mp 144 °C dec. Raman (150 mW): 2059 (21)/2021 (8) ($v_{as}N_3$), 1639 (6), 1402 (2), 1316 (2), 649 (4), 585 (8), 495 (11), 445 (8), 385 (12), 356 (100)/347 (79) (vTeN), 316 (7), 302 (7), 283 (4), 242 (3), 216 (14) cm^{-1}. IR (Nujol): 2131/2066/2027 (m−vs) ($v_{as}N_3$), 1641 (m), 1520 (vs), 1489 (vs), 1398 (m), 1372 (m), 1316 (m), 1287 (m), 1250 (s), 1154 (m), 1146 (m), 1091 (s), 1007 (m), 975 (s), 800 (m), 758 (w), 719 (m), 646 (m), 616 (m), 585 (m), 382 (m), 355/347 (m) (vTeN), 305 (s) cm^{-1}. ^{125}Te NMR (CDCl₃): δ 807 (quin, $^3J_{Te-F}$ = 72.2 Hz). ^{14}N NMR (CDCl₃, $\Delta v_{1/2}$ [Hz]): δ −141 (110, N_β), −186 (460, N_γ), −284 (1700, N_α). $^{13}C\{^{19}F\}$ NMR (CDCl₃): δ 146.5 (br, C2), 144.9 (C4), 138.0 (br, C3), 102.9 (C1). ^{19}F NMR (CDCl₃): δ −124.5 (br, 4F, *o*-F), −143.1 (tt, $^3J_{F-F}$ = 20.4 Hz, $^4J_{F-F}$ = 5.9 Hz, 2F, *p*-F), −155.8 (br, 4F, *m*-F). MS (EI), *m/e* (%): 464 (67) [M^+ − $2N_3$], 445 (3) [M^+ − $2N_3$ − F], 334 (26) [$C_{12}F_{10}^+$], 297 (67) [$C_6F_5Te^+$], 167 (28) [$C_6F_5^+$], 130 (46) [Te^+], 117 (100) [$C_5F_3^+$]. Anal. Calcd for $C_{12}F_{10}N_6$-Te: C, 26.4; N, 15.4. Found: C, 26.0; N, 16.9.

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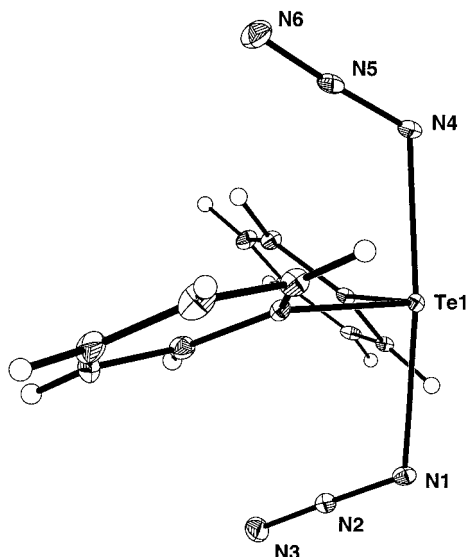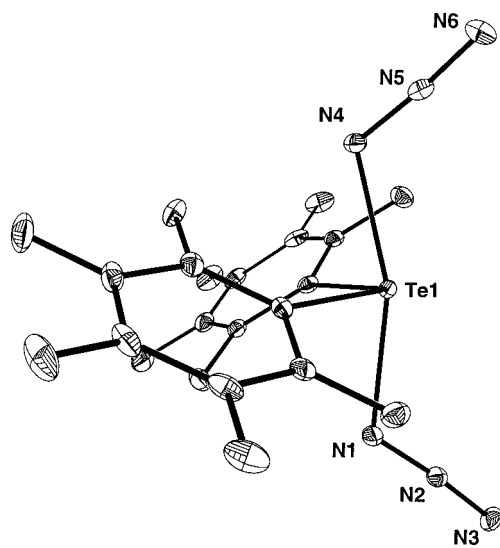
Figure 1. Molecular structure of **1** with thermal ellipsoids at the 50% probability level. Hydrogen and carbon atoms are not labeled for clarity. Selected distances (Å) and angles (deg): Te−N(1) 2.253(3), Te−N(4) 2.204(3), Te−C(11) 2.104(3), Te−C(12) 2.113(2), N(1)−N(2) 1.220(4), N(2)−N(3) 1.143(4), N(4)−N(5) 1.217(3), N(5)−N(6) 1.138(3); N(1)−Te−N(4) 173.64(9), C(11)−Te−C(12) 102.6(1), Te−N(1)−N(2) 116.5-(2), N(1)−N(2)−N(3) 178.0(3), Te−N(4)−N(5) 118.3(2), N(4)−N(5)−N(6) 176.4(3).

Figure 2. Molecular structure of **2** with thermal ellipsoids at the 50% probability level. Fluorine and carbon atoms are not labeled for clarity. Selected distances (Å) and angles (deg): Te−N(1) 2.208(2), Te−N(4) 2.185(2), Te−C(11) 2.106(3), Te−C(12) 2.106(3), N(1)−N(2) 1.208(4), N(2)−N(3) 1.143(4), N(4)−N(5) 1.216(4), N(5)−N(6) 1.144(4); N(1)−Te−N(4) 161.65(9), C(11)−Te−C(12) 100.3(1), Te−N(1)−N(2) 118.5-(2), N(1)−N(2)−N(3) 174.2(3), Te−N(4)−N(5) 115.5(2), N(4)−N(5)−N(6) 175.2(3).

(IR) of TeCl₃N₃ (νTeN = 412 cm⁻¹), TeCl₂(N₃)₂ (νTeN = 413/400 cm⁻¹), and [Te(N₃)₃][SbF₆] (νTeN = 460/440/426 cm⁻¹).[1,2]

Diphenyltellurium diazide (**1**) crystallizes in the orthorhombic space group *Pbca* (*Z* = 8),[12] and bis(pentafluorophenyl)tellurium diazide (**2**) crystallizes in the monoclinic space group *P*2₁/*c* (*Z* = 4).[13] Both compounds show the expected ψ-trigonal bipyramidal structure for a four-coordinated central atom with an additional Te(IV) electron pair in the equatorial position. The tellurium nitrogen distances are Te−N1 2.253(3) Å, Te−N4 2.204(3) Å for **1** and Te−N1 2.208(2) Å, Te−N4 2.185(2) Å for **2**. They are considerably shorter than the TeN distance in (Ph₂TeN₃)₂O (Te−N1 2.397(8) Å).[5] As expected for covalent azides, longer

NN bonds of N1−N2 1.220(4) Å and N4−N5 1.217(3) Å in **1** and N1−N2 1.208(4) Å and N4−N5 1.216(4) Å in **2** are found. Shorter NN distances indicating weak triple bond character of N2−N3 1.143(4) Å and N5−N6 1.138(3) Å in **1** and N2−N3 1.143(4) Å and N5−N6 1.144(4) Å in **2** are found. These distances are typical for covalently bound azides.[6] In **1** and **2** the azide groups are slightly bent, with NNN angles between 174° and 178°. The NTeN angles in **1** and **2** are N1−Te−N4 173.64-(9)° and 161.65(9)°, respectively, in the range also found for the corresponding Hal−Te−Hal angles in diorganotellurium diha-lides.[14] But although both compounds have nearly the same bonding parameters, a striking difference in the sterical arrange-ments of **1** (Figure 1) and **2** (Figure 2) is obvious. In **1** both the axial azides are bent toward the phenyl substituents and away from the Te(IV) electron pair. This differs from **2**, where the two azide groups are bent away from the fluorinated phenyl rings and toward the Te(IV) electron pair. This effect is likely due to steric reasons and electrostatic repulsions between free electron pairs of fluorine and nitrogen. In **1** the azides find a favorable energy conformation in relatively close packing with hydrogens of the phenyl rings. In addition both compounds exhibit unique inter-molecular tellurium nitrogen interactions in the range 3.1−3.5 Å which are shorter than the sum of their van der Waals radii (3.70 Å), resulting in heptacoordination of each tellurium atom. The number of reported Te···Hal interactions in Te(IV) halides is large, but only rarely are cases of Te···N interactions found. [15] Interestingly, whereas for **1** coordination of one N$_\alpha$ nitrogen to one tellurium atom (Te···N 3.141/3.497 Å) occurs, for **2** coordination of one N$_\gamma$ nitrogen to two tellurium atoms (Te···N 3.349/3.388 Å) has been found.

A study of the reactivity of dialkyltellurium difluorides toward azide is currently underway.

Supporting Information Available: Crystallographic files in CIF format for compounds **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) Crystal data for **1** were recorded on a Stoe IPDS area detector, Mo Kα radiation, wavelength λ = 0.71073, graphite monochromator: C₁₂H₁₀N₆-Te (365.85), colorless needles, 0.08 × 0.10 × 0.47, orthorhombic, space group *Pbca*, *a* = 7.5801(4) Å, *b* = 14.9046(9) Å, *c* = 23.084(1) Å, *V* = 2608.0(3) Å³, *Z* = 8, ρ_{calc} = 1.864 g/cm⁻³, μ = 2.277 mm⁻¹, *F*(000) = 1408, *T* = 200 K; θ range = 3.14−25.83, −9 ≤ *h* ≤ 8, −8 ≤ *k* ≤ 17, −28 ≤ *l* ≤ 28; reflections collected, 8285; independent reflections, 2295 (*R*ᵢₙₜ = 0.0387); observed reflections, 1798 [*I* ≥ 2σ(*I*)]; structure solution, SIR97 (Cascarano et al. *Acta Crystallogr. Sect. A* **1996**, *C79*); structure refinement, SHELXL-97 (Sheldrick, G. M. University of Göttingen, Germany, 1997); molecular graphics, ORTEP (Burnett, M. N.; Johnson, C. K. Ortep-III: Oak Ridge Thermal Ellipsoid Plot Program for Crystal Structure Illustrations. Report ORNL-6895; Oak Ridge National Laboratory: Oak Ridge, TN, 1996), Windows version (Farrugia, L. J. University of Glasgow, U.K.), direct methods; final *R* indices [*I* ≥ 2σ(*I*)]: R1 = 0.0209, wR2 = 0.0429; all data, R1 = 0.0319, wR2 = 0.0447, GOF on *F*² = 0.917.

(13) Crystal data for **2** were recorded on a Stoe IPDS area detector, Mo Kα radiation, wavelength λ = 0.71073, graphite monochromator: C₁₂F₁₀N₆-Te (545.75), colorless needles, 0.06 × 0.15 × 0.25, monoclinic, space group *P*2₁/*c*, *a* = 15.310(1) Å, *b* = 6.1035(3) Å, *c* = 18.015(1) Å, β = 113.348(9)°, *V* = 1545.6(2) Å³, *Z* = 4, ρ_{calc} = 2.345 g/cm⁻³, μ = 2.052 mm⁻¹, *F*(000) = 1024, *T* = 200 K; θ range = 2.31−25.86, −11 ≤ *h* ≤ 18, −7 ≤ *k* ≤ 7, −22 ≤ *l* ≤ 22; reflections collected, 6923; independent reflections, 2868 (*R*ᵢₙₜ = 0.0309); observed reflections, 2060 [*I* ≥ 2σ-(*I*)]; for structural solution and refinement see ref 12; final *R* indices [*I* ≥ 2σ(*I*)], R1 = 0.0204, wR2 = 0.0417; all data, R1 = 0.0361, wR2 = 0.0444, GOF on *F*² = 0.892.

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