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Organotellurium(VI) Azides and Halides†

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Abstract: The reaction of azide with organotellurium(VI) halides Ph_5TeBr and *cis*-$(biphen)_2TeF_2$ (biphen = 2,2′-biphenyldiyl) resulted in the formation and isolation of Ph_5TeN_3 (**1**) and *cis*-$(biphen)_2Te(N_3)_2$ (**2**), which are the first tellurium(VI)-azide species. In addition to spectroscopic data, both crystal structures have been determined. Furthermore, the stability of possible Te(VI) species with higher azide contents $Ph_xTe(N_3)_{6-x}$ and $Me_xTe(N_3)_{6-x}$ as well as the syntheses and properties of their Ph/Me_xTeF_y precursors was investigated, including the crystal structure determination of *trans*-Ph_2TeF_4 (**3**). Ab initio and density functional studies of all molecules regarding the structures and electronic populations were performed.

Introduction

Since the discovery of Me_6Te and Ar_6Te,[1,2] the still uncommon hypercoordinated Te(VI) compounds are of continuing interest concerning their synthesis and theoretical aspects.[3−6] Apart from the homoleptic compounds TeF_6 and $Te(OR)_6$, some Ph_xTeF_y[7−11] species, *trans*-$(C_2F_5)_2TeF_4$,[12] *cis*-$(C_6F_5)_2TeF_4$,[13] and $ClCF_2CH_2TeF_5$[14] as well as *cis*-Me_4TeF_2 and *mer*-Me_3TeF_3[1] are hitherto, in part fragmentarily, characterized, and rather little is known about Te(VI) pseudohalides. The exploration of tellurium-azide chemistry proceeded from the initial $TeCl_3(N_3)$ and $TeCl_2(N_3)_2$[15] via Te(II), i.e., $RTeN_3$ and structurally characterized compounds of that type,[16] toward the recent syntheses of various organotellurium(IV) azides $R_2Te(N_3)_2$ and $RTe(N_3)_3$.[17−19] After the development of the binary species $[Te(N_3)_3]^+$,[20] $Te(N_3)_4$, $[Te(N_3)_5]^-$, and $[Te(N_3)_6]^{2-}$,[21,22] one field of research remained almost untouched: Te(VI) azides. Until now, to the best of our knowledge, the only evidence of Te(VI) azides is found in a ^{19}F NMR spectroscopic study of TeF_6/Me_3SiN_3 mixtures,[23] during which no compound had been isolated. Hence, we focused upon the possible preparation of organotellurium(VI) azides, which we herewith present.

Results and Discussion

Recently, the group of Akiba reported a one-pot synthesis of Ph_5TeHal (Hal = F, Cl, Br),[24] thereby avoiding the isolation of the intermediate Ph_4Te.[25] One approach to obtain a corresponding azide, Ph_5TeN_3, would obviously be fluorine exchange with Me_3SiN_3, which has been used to synthesize most of the tellurium azides so far.[17−19] A major drawback is the fact that in solution the Ph_5TeHal compounds are not as stable as one

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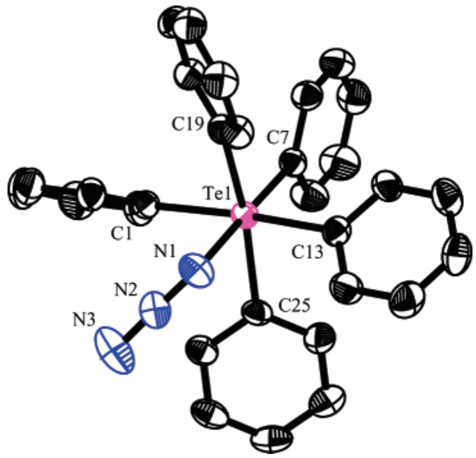

Figure 1. Molecular structure of Ph_5TeN_3 (**1**) with hydrogen atoms omitted. Selected bond lengths (Å) and angles (deg): Te1−C1 2.200(4), Te1−C7 2.159(4), Te1−C13 2.196(4), Te1−C19 2.196(4), Te1−C25 2.195(4), Te1−N1 2.292(4), N1−N2 1.161(5), N2−N3 1.158(6), N1−N2−N3 175.6(5), C1−Te1−N1 88.1(2), C13−Te1−N1 84.2(2), C19−Te1−N1 82.3(1), C25−Te1−N1 85.4(1), C7−Te1−N 178.4(1), C1−Te1−C13 172.3(2).

may expect. If the ^{125}Te NMR spectroscopy is performed in $CDCl_3$, impurities of Ph_5TeCl and $[Ph_3Te]^+$ [26] are always detected, due to halogen exchange or decomposition (in contrast, Ar_6Te species are very stable[2]). The preparation of the bromo derivative Ph_5TeBr was found to be sufficient to undergo a reaction with AgN_3, resulting in the formation of Ph_5TeN_3 (**1**) in nearly colorless solutions (see eq 1).

$$Ph_5TeBr \xrightarrow[-\ AgBr]{AgN_3/CH_2Cl_2/Hexane/25\ °C} Ph_5TeN_3\ (\mathbf{1})$$

Azidopentaphenyl-λ^6-tellane (**1**) is stable but decomposes slowly in vacuo; crystallization is the only choice of purification. Slow evaporation of a CH_2Cl_2 solution gave pale yellow plates of **1** which were suitable for X-ray structure analysis (see Figure 1).

The molecular structure shows an octahedrally coordinated tellurium atom, and a Te−N distance of 2.292(4) Å, which compared to organotellurium(IV) azides[17−19] is significantly elongated by 0.25 Å, similar to the Te−Hal distances in Ph_5TeHal (Hal = F, Cl, Br)[24] compared to those of the Te(IV) halides, and in good agreement with the calculated values 2.271 Å (B3LYP/TZVP) and 2.279 Å (B3LYP/cc-pVDZ) for Te(VI)−N. Also, the almost identical N1−N2 and N2−N3 distances are remarkable, in that they indicate increased ionic character of the N_3 moiety. The bond angles in the slightly distorted octahedral coordination of **1** reveal that the positions of the phenyl substituents resemble those found in the structures of Ph_5TeHal derivatives.[24]

The Raman spectrum of Ph_5TeN_3 exhibits the $\nu_{as}N_3$ stretching vibration at 2035 cm^{-1}, which is absent in the IR spectrum, though predicted with high intensity in the calculated IR spectrum (see Supporting Information). The Te−N stretching vibration, usually appearing between 420 ($TeCl_3N_3$)[15] and 330 cm^{-1} ($(C_6H_5)_2Te(N_3)_2$)[17] with high intensity, cannot be unambiguously assigned in either the IR or the Raman spectra. This is contradictory to the detection of three more or less broadened ^{14}N NMR resonances typical for covalent azides and indicates

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Scheme 1. Identified Products of the Reactivity of Further Organotellurium(VI) Fluorides with Me_3SiN_3

$$cis\text{-}Me_4TeF_2 \xrightarrow[-\ Me_3SiF]{2\ Me_3SiN_3\ /\ 25°C} Me_2Te(N_3)_2 + [Me_3Te]N_3 + N_2$$

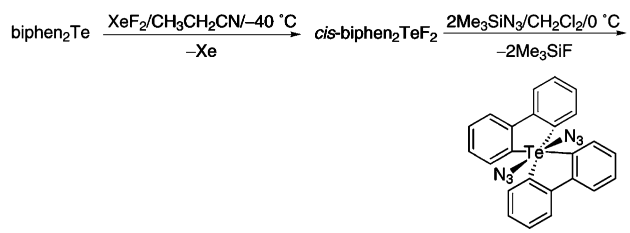
$$mer\text{-}R_3TeF_3 \xrightarrow[-\ Me_3SiF]{3\ Me_3SiN_3\ /\ 25°C} R_2Te(N_3)_2 + [R_3Te]N_3 + N_2 \quad (R = Ph, Me)$$

$$trans\text{-}R_2TeF_4 \xrightarrow[-\ Me_3SiF]{4\ Me_3SiN_3\ /\ 25–50°C} R_2Te(N_3)_2 + TeF_4 + N_2 \quad (R = Ph, Me)$$

$$PhTeF_5 \xrightarrow[-Me_3SiF]{5\ Me_3SiN_3\ /\ 25°C} Ph_2Te(N_3)_2 + TeF_4 + N_2$$

that **1** is a borderline case between a covalent and an ionic Te(VI) azide (Figure 2; compare to clearly ionic $[Ph_3Te]N_3$). Additional support toward a more covalent nature of **1** in solution is provided by Ph_5TeF, which shows a doublet in ^{125}Te NMR ($CDCl_3$) due to coupling to ^{19}F, thereby excluding chlorine exchange for azide in chlorinated solvents.[24] The ^{125}Te NMR resonance of the ionic $[Ph_5Te][B(C_6F_5)_4]$ [4] in $CDCl_3$ appears at lower frequency (δ 659 ppm), significantly distinguishable from those of Ph_5TeHal and **1** (δ 564−580 ppm).

In a fashion similar to the standard reaction pathway for the preparation of organotellurium(IV) azides, the synthesis of an organotellurium(VI) diazide was attempted employing a sterically stabilized Te(IV) compound. Bis(2,2′-biphenyldiyl)-λ^4-tellane[27] was fluorinated to give *cis*-difluoro-bis(2,2′-biphenyldiyl)-λ^6-tellane.[28,29] The fluorine atoms in $biphen_2TeF_2$ can be successfully substituted by azide groups with trimethylsilyl azide, as performed with Te(IV) difluorides and trifluorides, to form *cis*-diazido-bis(2,2′-biphenyldiyl)-λ^6-tellane (**2**) (see eq 2).



(**2**)

Whereas various tellurium(IV) diazides and triazides are stable in solution and in the solid state, compound **2** is, to our knowledge, the first organotellurium(VI) di-pseudohalide which can be isolated in pure form. The azides **1** and **2** are stable in the solid state at 4 °C at least for several weeks, but the diazide **2** decomposes within days in solution and, as opposed to **1**, does not melt without decomposition. Although its nitrogen content is low compared to organotellurium(IV) di- and triazides bearing small substituents, upon contact with a flame, a noticeable fizzling occurred. In contrast, the reaction of $biphen_2TeF_2$ with Me_3SiCN does not lead to a Te(VI) dicyanide, and a tetramethyl Te(VI) diazide, in sharp distinction to **2**, is not stable with respect to reductive decomposition (see Scheme 1). Furthermore, our efforts to prepare pure *cis*-Ph_4TeF_2 by fluorination of Ph_4Te according to the literature procedure[2]

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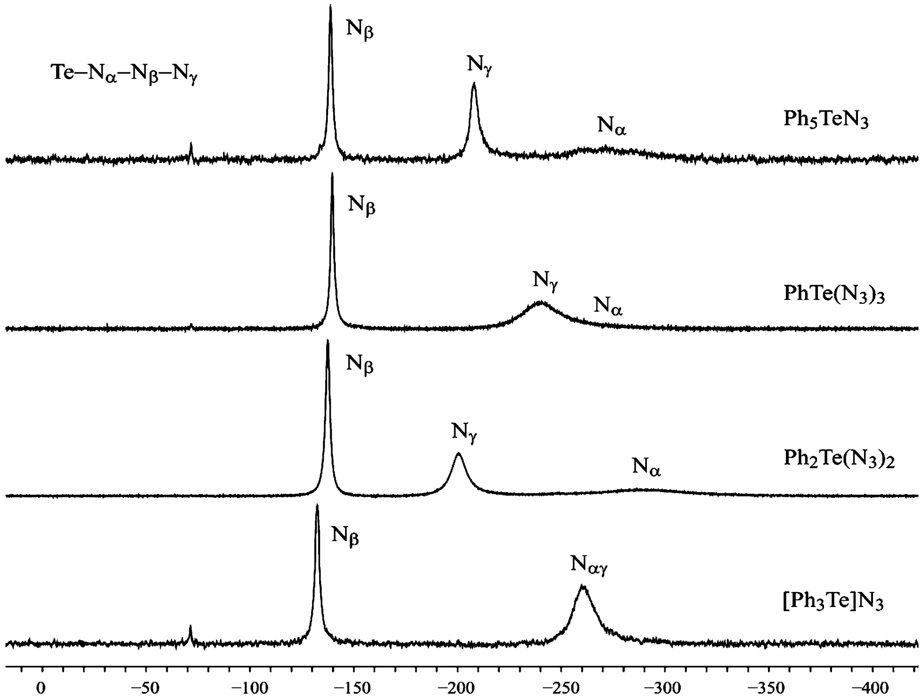

Figure 2. ^{14}N NMR spectra of $Ph_xTe(N_3)_y$ in $CDCl_3$ at 25 °C (the resonance visible at −71 ppm belongs to N_2).

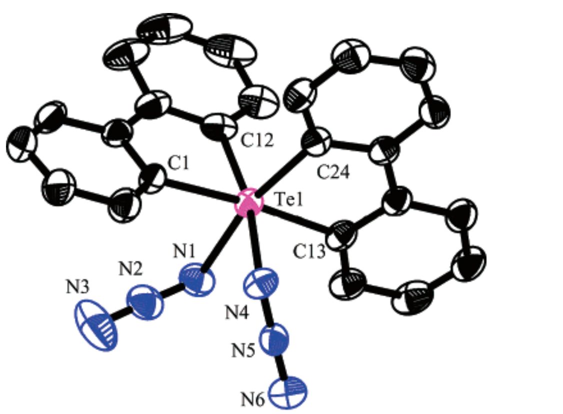

Figure 3. Molecular structure of *cis*-biphen$_2$Te$(N_3)_2$ (**2**) with hydrogen atoms omitted. Selected bond lengths (Å) and angles (deg): Te1−C1 2.134(3), Te1−C12 2.109(3), Te1−C13 2.129(3), Te1−C24 2.109(3), Te1−N1 2.209(3), Te1−N4 2.220(3), N1−N2 1.197(5), N2−N3 1.129(5), N4−N5 1.206(4), N5−N6 1.141(4); N1−Te1−N4 87.2(1), N1−N2−N3 177.6(5), N4−N5−N6 177.7(4), C1−Te1−N1 88.4(1), C1−Te1−N4 88.2(1), C1−Te1−C13 174.7(1), C12−Te1−C24 96.8(1).

failed, since it was not possible to separate the latter from Ph_2Te byproduct. Because of its cumbersome synthesis, *cis*-biphen$_2$Te$(N_3)_2$ (**2**) was obtained in small amounts but nonetheless could be unambiguously characterized, including by X-ray crystallography (see Figure 3). Whereas the spectroscopic and structural features of **1** do point to some extent to a λ^5-telluronium-like character, i.e., elongated Te−N bond and missing or very weak Te−N stretching vibration, the organotellurium(VI) diazide **2** possesses more covalent character, since both the Te−N distances are significantly shorter compared to those in **1** and the vibrational spectra reveal the antisymmetric stretching vibrations ($\nu_{as}N_3$) in both the IR (very strong) and Raman (medium) spectra at 2054−2037 cm^{-1} (see Supporting Information). The calculated values for the Te−N bond lengths of 2.225 Å (B3LYP/cc-pVDZ) agree well with those determined by X-ray diffraction (Te1−N1 2.209(3), Te1−N4 2.220(3)), the difference of the Nα−Nβ and the Nα−Nγ bond lengths is greater than for **1**, thus confirming the higher degree of covalence for the azide substituents in **2**. Neither **1** nor **2** exhibit intermolecular interactions, such as secondary bonding with short Te···N contacts; hence, the total coordination of these Te(VI) species is lower than those of structurally characterized Te(IV) azides, which feature hepta- or octacoordination spheres around tellurium.[17−19]

With the successful characterization of the monoazide **1** and the diazide **2**, we turned our attention to the possible existence of some higher substituted organotellurium(VI) azides. As suitable precursors, a complete synthesis of Me_xTeF_{6-x} (x = 1−5) and Ph_xTeF_{6-x} (x = 1, 2, 3) species was of interest, some of which have been briefly described.[1,2,7−11] The available procedures for Ph_xTeF_{6-x} (x = 1, 2, 3) were found to be appropriate for the synthesis of larger amounts of organotellurium(VI) fluorides on a preparative scale, even when only NMR experiments had been reported.[7,8] An elegant improvement for the preparation of the R_3TeF_3 species was achieved by fluorination of the corresponding triorganotelluronium azides $[R_3Te]N_3$,[26] thereby avoiding the problematic preparation of pure $[R_3Te]F$.[30] Apart from *cis*-Me_4TeF_2 being used as the precursor for the first synthesis of Me_6Te,[1] no other Me_xTeF_{6-x} (x = 1−5) derivative was reported until this study. In that earlier work, an indication for a slow conversion of *cis*-Me_4TeF_2 to *mer*-Me_3TeF_3 in solution was identified by ^{19}F NMR spectroscopy.[1]

The experimental procedures for phenyltellurium(VI) compounds are also suitable for the synthesis of the corresponding methyl derivatives, with an increased volatility of the methyl species. In general, the one-pot procedures for Me_xTeF_{6-x} and Ph_xTeF_{6-x} (x = 1, 2) involve oxidation of mono- or ditellanes to Te(IV) with XeF_2 in a rapid first step. This is followed by a second, relatively slow further oxidation to Te(VI), which can be catalyzed successfully with $[Et_4N]Cl$ without chlorine

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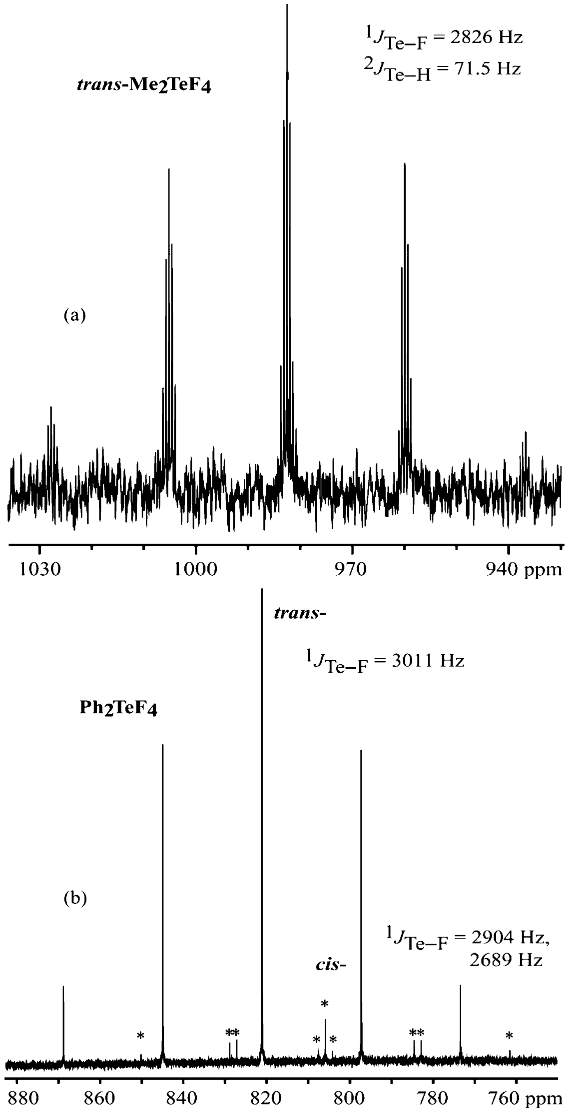

Figure 4. ^{125}Te NMR spectrum of *trans*-Me_2TeF_4 in ((a) CD_2Cl_2), featuring the $^1J_{Te-F}$ (quin, 2826 Hz) and $^2J_{Te-H}$ (sept, 71.5 Hz) couplings. In the ^{125}Te{^{1}H} spectrum, no trace of the *cis*-isomer was detected, in contrast to Ph_2TeF_4 ((b) recorded in C_6D_6) representing an 84 (*trans*, quintet):16 (*cis*, triplet of triplets *) mixture.

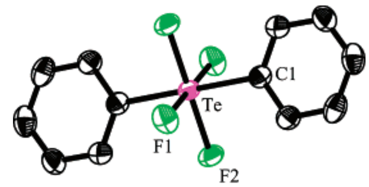

Figure 5. Molecular structure of *trans*-Ph_2TeF_4 (**3**) with hydrogen atoms omitted. Selected bond lengths (Å) and angles (deg): Te−F1 1.900(2), Te−F2 1.896(2), Te−C1 2.088(3); F1−Te−F2 89.6(1), F2−Te1−C1 89.8(1), F1−Te1−C1 89.9(1), C1−Te−C1 180.00.

contamination of the products. For both the phenyl and methyl tellurium(VI) fluorides, the same stereochemical preference is observed; i.e., for both the R_3TeF_3 (R = Ph or Me) compounds, the *mer* isomer is always formed. The R_2TeF_4 compounds show a propensity to isomerize in solution to the *trans*-isomer (R = Me, rapidly; R = Ph, slowly), whereas the Me_xTeF_{6-x} and Ph_xTeF_{6-x} (x = 3, 4) tend to form initially only the *mer*- and the *cis*-isomer, respectively. The extended reaction times for the preparation of Me_2TeF_4 combined with a quick isomerization process prevent the detection of *cis*-Me_2TeF_4 (see Figure 4). This is also predicted by MP2(FC)/cc-pVDZ calculations of the corresponding isomers, which favor *mer*-Me_3TeF_3 by 15.9 kJ/mol. In the case of the *cis*- and *trans*-isomers of Me_4TeF_2 and Me_2TeF_4, the energy differences are 14.5 and 33.6 kJ/mol, respectively, supporting the observed *cis*-Me_4TeF_2 and *trans*-Me_2TeF_4 compounds (see Table 2). Neat *mer*-Me_3TeF_3 and *mer*-Ph_3TeF_3 are rather difficult to prepare, since they easily decompose to the stable telluronium salts [Me_3Te]F and [Ph_3Te]F.[30] Attempts to synthesize Me_5TeF in an analogous manner to Ph_5TeCl/Br, i.e., by one-pot reaction via a "Me_5-TeLi" route at very low temperatures, failed. Instead, mixtures of Me_6Te, Me_4Te, and Me_2Te were always identified by ^{125}Te NMR spectroscopy. We found no evidence of a reaction of Me_4-Te with MeLi in diethyl ether or THF, proven by ^{125}Te NMR spectroscopy between −90 and 25 °C.

In contrast to the preparation of $PhTeF_5$, which has been described before, the corresponding methyl compound, $MeTeF_5$, was not successfully isolated, but indications for a highly reactive species were found: after a vigorous reaction of XeF_2 with $(MeTe)_2$, only the hydrolysis product *trans*-$MeTeF_4OH$ could be obtained, identified by a singlet at δ −32.1 ppm in the ^{19}F NMR spectrum and a quintet of quartets at δ 832 ppm in the ^{125}Te NMR spectrum. For $PhTeF_5$, the corresponding product of controlled hydrolysis, $PhTeF_4OH$, was described before as a mixture of *cis*- and *trans*-isomers.[9] However, during the course of the reaction of [Me_3Te]N_3 with XeF_2, ^{19}F NMR spectra revealed the existence of small amounts of $MeTeF_5$, which could be identified as a quintet and a doublet at δ −21.4 and −36.2 ppm, respectively, in $CDCl_3$. Besides $MeTeF_5$, the only other report of an alkyl TeF_5 compound is that of the moderately stable $ClCF_2CH_2TeF_5$.[14]

A high-field shift tendency for the ^{125}Te NMR resonances is caused by azido substitution of Ph_5TeHal (Hal = F, δ 580 ppm; Br, δ 571 ppm) and $biphen_2TeF_2$ (δ 719 ppm), similar to those of the corresponding Te(IV) azides and fluorides.[17−19] The shift difference is smaller for **1** (δ 568 ppm) than for **2** (δ 633 ppm). The ^{125}Te NMR resonances of the series Ph_xTeF_{6-x} (x = 1−5) were found in the region between δ 580−725 ppm with Te−F coupling constants in the range of 1500−3600 Hz. For the methyl derivatives Me_xTeF_{6-x} (x = 1−4), similar shift ranges and coupling constants were found.

In contrast to *cis*-Me_4TeF_2 and *trans*-Me_2TeF_4, for which all crystals obtained were inappropriate, *trans*-Ph_2TeF_4 (**3**) can be readily crystallized to yield colorless plates suitable for X-ray analysis (see Figure 5), revealing a center of inversion for **3** at the site of the Te atom. Therefore, the coordination around tellurium is D_{4h}, exactly what one would expect for such a highly symmetrically substituted Te(VI) molecule. On the other hand, DFT and RI-MP2 calculations show (see Supporting Information), that in the gas-phase one should expect D_2 symmetry, since here the two phenyl rings are not coplanar. The two Te−F distances (1.896(2), 1.900(2) Å) in crystalline **3** differ only marginally and are significantly smaller than typical lengths of Te−F bonds in Te(IV) compounds (≈2.0 Å).[31] Slightly larger differences are found in the calculated D_2 structures (Te−F 1.951/1.962 Å), which distinctly overestimate the absolute lengths. This is most likely due to the lack of electron correlation

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Table 1. Energies (hartrees), ZPE Corrections (kJ/mol), and Relative Energies Δ*E* (kJ/mol) of Ph_5TeN_3 (**1**), *cis*/*trans*-biphen$_2$Te$(N_3)_2$ (**2**), and Ph_2TeF_4 (**3**) at Different Levels of Theory

	RI-BP86/SVP		RI-BP86/TZVP			RI-MP2/SVP		RI-MP2/TZVP	
	E	Δ*E*	*E*	Δ*E*	ZPE	*E*	Δ*E*	*E*	Δ*E*
Ph_5TeN_3 (**1**)	−1329.4598		−1330.8804		1181.7[a]	−1320.4361		−1321.8694	
trans-biphen$_2$Te$(N_3)_2$	−1259.7316	0	−1261.0598	0		−1251.3464		−1252.6928	
cis-biphen$_2$Te$(N_3)_2$ (**2**)	−1259.7536	−57.7	−1261.0819	−58.2	875.0[a]	−1251.3787	−84.7	−1252.7253	−85.4
cis-Ph_2TeF_4 (C_1)	−870.1055	0	−871.0929	0		−865.0934	0	−866.0601	0
trans-Ph_2TeF_4 (D_2)[c] (**3**)	−870.1149	−24.8	−871.1053	−32.6	480.4[b]	−865.0739	−51.4	−866.0758	−41.2

[a] Numerical frequency calculations with SNF.[41] [b] Analytical frequency calculations with AOFORCE.[42] [c] ZPE for *trans*-Ph_2TeF_4 (D_2) at RI-BP86/SVP level, 484.77 kJ/mol;[b] at RI-MP2/SVP level, 529.44 kJ/mol;[b] at RI-MP2/TZVP level, 527.49 kJ/mol.[b]

at the B3LYP/cc-pVDZ level as these distances are considerably lowered (Te−F Å) in an RI-MP2/TZVP (D_2) calculation (see Table 1).

Whereas the aryltellurium(VI) azides **1** and **2** are fairly stable, all attempts to detect methyltellurium(VI) azides by reaction of the corresponding fluorides with Me_3SiN_3 at various conditions were unsuccessful. In all cases only decomposition products resulting from elimination of dinitrogen, the corresponding dimethyltellurium(IV) azide $Me_2Te(N_3)_2$, [18] and trimethyltelluronium azide $[Me_3Te]N_3$ [26] were detected by NMR in the reaction solutions. In the case of $PhTeF_5$ and R_2TeF_4 with Me_3SiN_3, also significant amounts of TeF_4 were identified by their ^{125}Te NMR resonance. It remains unclear at this point why the subsequent azidation product, $Te(N_3)_4$, could not be detected. Possibly, all the azide transfer reagent was already consumed as reducing agent. Higher azide-substituted phenyltellurium(VI) derivatives than the diazide **2** were not detected, and again, only reductive decomposition products were identified. Scheme 1 illustrates qualitatively the reactivity of organotellurium(VI) fluorides toward azide. This tendency of the organo Te(VI) fluorides to undergo reductive decomposition with azide is also observed for TeF_6.[22,23]

Furthermore, when SO_2Cl_2 was reacted with Me_4Te, no evidence for the existence of Me_4TeCl_2 could be found. Instead, reductive decomposition to $[Me_3Te]Cl$ occurred, in analogy to the decomposition observed during *cis*-Me_4TeF_2/azide reactions.

Quite recently, we and others reported on the isolation and properties of neutral and anionic binary tellurium(IV) azides,[21,22] which included a discussion of ab initio calculations on $Te(N_3)_4$, $[Te(N_3)_5]^-$, and $[Te(N_3)_6]^{2-}$. Since our own results regarding the structure of $Te(N_3)_4$ differ somewhat from those in ref 22 and are essential for the study of the neutral $Te(N_3)_6$ molecule, we will briefly discuss our findings. As expected, the molecule $Te(N_3)_6$ is found to have S_6 symmetry (see Figure 6, left), and its experimentally confirmed reductive decomposition to $Te(N_3)_4$ and three nitrogen molecules is highly exothermic, leading to a Δ*E* of −686.43 kJ mol^{-1} at the MP2(FC)/cc-pVDZ level (B3LYP/cc-pVTZ: −679.50 kJ mol^{-1}). The molecule is found to have a different conformation than previously reported,[22] which as well deviates from our own calculations sometime ago.[32] With regard to the different structures, it should be noted that the floppy azido groups of $Te(N_3)_4$ cause very small energy differences and shallow minima during optimization. This makes the optimized geometry strongly dependent on the computational method and basis set used.

The calculation of the Me_xTeF_{6-x} and $Me_xTe(N_3)_{6-x}$ (x = 0−6) molecules was carried out in order to clarify their stability

(32) Ruscitti, O. P. Ph.D. Thesis, Ludwig-Maximilian University, Munich, 2001, p 162.

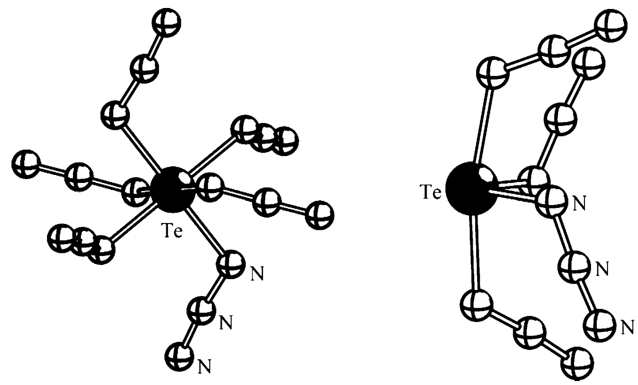

Figure 6. Calculated molecular structures of the neutral $Te(N_3)_6$ (left) and $Te(N_3)_4$ (right) molecules at the MP2(FC)/cc-pVDZ level of theory. The axial azido groups in $Te(N_3)_4$ are oriented away from the site of the free electron pair at tellurium.

toward reductive decomposition and the bonding situation of the substituted species compared to TeF_6 and Me_6Te, which were already examined using theoretical methods in the past.[33] All molecular structures were fully optimized and converged to global minima without imaginary frequencies; Table 2 gives an overview of the calculations. Geometries and frequency analyses are reported as Supporting Information.

As the Me_xTeF_{6-x} series of molecules shows an ever increasing number of ionic bonds with increasing number of fluorine atoms, the main purposes of our theoretical calculations were the elucidation of the bonding situation around tellurium and the determination of the energetic difference between possible isomers of these apparently hypervalent molecules. Whereas chalcogen(VI) species such as EF_6 were believed in the past to violate Lewis' rule of eight and thereby employing an spd hybridization scheme, further theoretical studies excluded significant participation of d orbitals in the E−F bonding, instead they act as polarization functions.[34] Nevertheless, definition of the term "hypervalency" itself and the characterization of molecules to be hypervalent or hypercoordinated is still a subject of ongoing debates; even the widely accepted concepts of NBO (*natural bond orbital*) analysis are disputable.[5,35]

Without 5d atomic orbital (AO) participation as hybridization functions, TeF_6, Me_6Te and $Te(N_3)_6$ involve two four-electron

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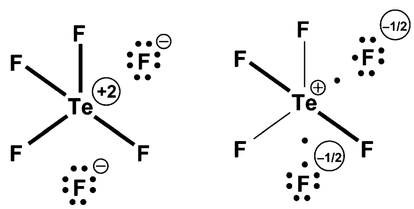
Table 2. Energies (hartrees), ZPE Corrections (kJ/mol), and Relative Energies ΔE (kJ/mol) of the *cis*/*trans*- and *fac*/*mer*-Isomers, Respectively, for the Me_xTeF_{6-x} and $Me_xTe(N_3)_{6-x}$ ($x = 0-6$) Molecules at Different Levels of Theory

	B3LYP [a]			MP2(FC) [a]			CCSD(T) [a,c]		MP2(FC) [b]	
	E	ZPE	ΔE	*E*	ZPE	ΔE	*E*	ΔE	*E*	ΔE
TeF_6	−867.1244	38.14		−864.8704	39.92		−864.8610		−7210.1569	
$MeTeF_5$	−807.2087	131.12		−805.0177	131.11		−805.0293		−7148.7684	
$MeTe(N_3)_5$	−1128.9384	262.98		−1125.7324	264.85		−1125.7627		−7470.9543	
cis-Me_2TeF_4	−747.2697	216.00	0	−745.1461	221.80	0	−745.1778	0	−7090.3253	0
trans-Me_2TeF_4	−747.2858	216.33	−42.4	−745.1589	222.44	−33.6	−745.1916	−36.2	−7090.3353	−26.1
cis-$Me_2Te(N_3)_4$	−1004.6451	327.20	0	−1001.7145	330.34	0	*d*	0	−7346.883	0
trans -$Me_2Te(N_3)_4$	−1004.6465	325.69	−3.6	−1001.7168	329.38	−5.8	−1001.7594	*d*	−7346.89	−19.6
fac-Me_3TeF_3	−687.3180	304.97	0	−685.2647	312.29	0	−685.3156	0	−7030.3960	0
mer-Me_3TeF_3	−687.3272	305.15	−24.1	−685.2707	312.65	−15.9	−685.3226	−18.5	−7030.4001	−10.7
fac-$Me_3Te(N_3)_3$	−880.3462	387.87	0	−877.6902	393.64	0	−877.7474	0	−7222.8188	0
mer-$Me_3Te(N_3)_3$	−880.3482	388.51	−5.3	−877.6930	393.36	−7.5	−877.7489	−4.0	−7222.8197	−2.3
trans-Me_4TeF_2	−627.3586	391.94	0	−625.3741	401.50	0	−625.4451	0	−6970.4562	0
cis-Me_4TeF_2	−627.3631	394.13	−11.9	−625.3796	402.04	−14.5	−625.4499	−12.6	−6970.4637	−19.6
trans-$Me_4Te(N_3)_2$	−756.0370	448.30	0	−753.6566	456.38	0	−753.7295	0	−7098.7373	0
cis-$Me_4Te(N_3)_2$	−756.0439	450.14	−18.2	−753.6629	456.50	−16.7	−753.7333	−10.1	−7098.7445	−18.9
Me_5TeF	−567.3883	479.74		−565.4783	489.73		−565.5671		−6910.5169	
Me_5TeN_3	−631.7292	509.03		−629.6221	518.26		−629.7101		−6974.6590	
Me_6Te	−507.4062	566.39		−505.5712	577.71		−505.6780		−6850.5649	
$Te(N_3)_6$	−1253.2227	199.41		−1249.7369	199.53		−1249.5810		−7595.0113	

[a] Basis set = cc-pVDZ ((8s6p6d)/[4s3p2d]) with MDF28 small-core pseudopotential.[43] [b] Basis set = TZVPall.[44,45] [c] Optimized geometries from preceding MP2(FC) calculations. [d] Neither CCSD(T) calculations with GAUSSIAN03 nor those with MOLPRO gave reasonable results (the calculated energy obviously is too high with $E = 1001.6585$ hartrees).

Scheme 2. Kekulé (**I**) and Increased-Valence (**II**) Structures for TeF_6



I **II**

three-center bonding units. As discussed previously for TeF_6, from the Kekulé-type Lewis structure **I**, we can generate the increased-valence structures **II** (see Scheme 2) via one-electron delocalizations from two F^- ions into $F^-{-}Te^{2+}$ bonding MOs.[36,37] With O_h symmetry for TeF_6, there are 12 equivalent increased-valence structures, which participate in resonance. The tellurium atom of TeF_6 utilizes two sp hybrid AOs to form two “normal” Te−F bonds in each of the VB structures. The remaining 5p AOs participate in the two four-electron three-center bonding units. In ref 36, increased-valence structures for SF_6 (TeF_6 can be treated accordingly) are provided in which expansion of the sulfur valence shell has occurred.

The development of topological methods regarding electron density[38] and the electron localization function[5,6,39] offer alternatives to NBO analysis and supersede the discussion of Mulliken populations.[40] For Me_6Te and other permethylated elements, recent ELF (*electron localization function*) investigations reported effective valence shell populations greater than eight and classified the rule of eight as of “no fundamental significance”.[5,6]

Yet, the dispute between supporters of different models on this topic cannot be settled without a careful redefinition of commonly used terms and confinement to physically meaningful concepts and observables, which is beyond the scope of this paper.

When a topological analysis of the ELF function for the Me_xTeF_{6-x} and $Me_xTe(N_3)_{6-x}$ ($x = 0-6$) molecules is performed, on one hand, one finds that all the Me−Te bonds possess strong covalent character, with a disynaptic basin near the middle of the nuclei connecting line and a population of nearly 2.0. The predominantly ionic nature of the Te−F and Te−N bonds, on the other hand, prohibits the assignment of the corresponding disynaptic basins *V*(Te, F), in contrast to, e.g., the S−F bonds in SF_6. Instead, for Te−F bonds, the disynaptic basins are merged with the monosynaptic basins *V*(F) of the ligands. Most likely because the difference in Pauling electronegativity (Te, 2.1; N, 3.04; F, 3.98) is smaller between Te and N, the disynaptic basin *V*(Te, N) for the Te(VI) azides can be identified (see Figure 7). The results of ELF, AIM (*atoms in molecules*), and NPA (*natural population*) analyses of the Me_xTeF_{6-x} and $Me_xTe(N_3)_{6-x}$ ($x = 0-6$) molecules are summarized in Table 3. Regarding the difference in electronegativity and the ionicity of a bond, simply dividing the Me_xTeF_{6-x} and $Me_xTe(N_3)_{6-x}$ ($x = 0-6$) molecules in two categories by the sum of their valence shell populations being above or below eight is not reasonable, since all these molecules are quite similar as regards their chemical properties, e.g., their NMR chemical shifts.

Experimental Section

All manipulations of air and moisture sensitive materials were performed under an inert atmosphere of dry argon using flame-dried glass vessels or oven-dried custom-made plastic equipment and Schlenk techniques,[46] ethers and hydrocarbons were freshly distilled from

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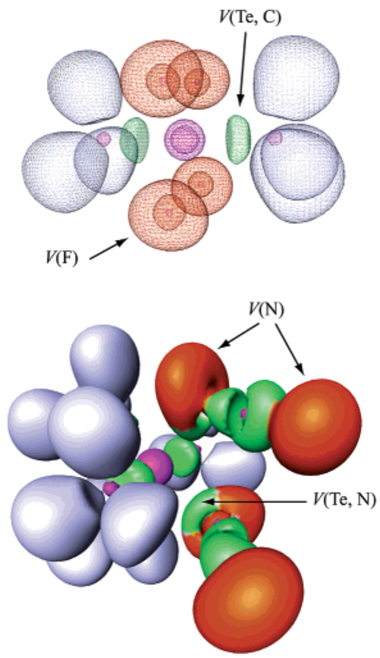

Figure 7. Wireframe of the ELF isosurfaces for *trans*-Me_2TeF_4 (top), showing the *V*(Te, C) disynaptic basins corresponding to the covalent Te−C bond (green) and the highly ionic Te−F bonds, for which only merged *V*(F) monosynaptic basins ($N(\Omega_{F1})$ = 7.8, red) exist. Rendered ELF isosurface and basin assignment for *cis*-$Me_4Te(N_3)_2$ (bottom) with disynaptic basins for Te−C and Te−N_α bonds (green) and monosynaptic basins *V*(N) at N_α and N_γ (red). Attractor positions: Te−*V*(Te, C1) 1.351 Å, *V*(Te, C1)−C1 0.814 Å, $N(\Omega_{Te,C1})$ 2.00; Te−*V*(Te, N1) 1.553 Å, *V*(Te, N1)−N1 0.665 Å, $N(\Omega_{Te,N1})$ 1.47, N_v(Te) 10.78. Representations at $\eta = 0.75$, grid increment 0.1 Å, core basins in purple, protonated basins in blue.

sodium/benzophenone, CH_2Cl_2 and CH_3CN from P_4O_{10}. The compounds Ph_5TeBr,[24] $(biphen)_2TeF_2$,[28] AgN_3,[47] $Ph_2Te/(PhTe)_2/(MeTe)_2/Me_2Te$,[48] $[Me_3Te]N_3/[Ph_3Te]N_3$,[26] and Me_4Te[49] were prepared according to the literature, xenon difluoride (ABCR) and trimethylsilyl azide (Aldrich) were used as received. Infrared spectra were recorded on Perkin-Elmer Spektrum One FT-IR or Nicolet 520 FT-IR spectrometers (as KBr pellets or between KBr plates), Raman spectra on a Perkin-Elmer 2000 NIR FT spectrometer fitted with a Nd:YAG laser (1064 nm). NMR spectra were recorded on a JEOL Eclipse 400 instrument at 25 °C, and chemical shifts were determined with respect to $(CH_3)_4Si$ (^1H, 399.8 MHz; ^{13}C, 100.5 MHz), CH_3NO_2 (^{14}N, 28.9 MHz), $CFCl_3$ (^{19}F, 376.1 MHz), and Me_2Te (^{125}Te, 126.1 MHz). Mass spectra were recorded on a JEOL MStation JMS 700 spectrometer; tellurium containing fragments refer to ^{130}Te. Elemental analyses: in-house. **CAUTION!** Silver azide is potentially explosive. This necessitates meticulous safety precautions during its preparation and handling; please see ref 21.

For compounds **1**, **2**, and **3**, a Nonius CAD4 device was employed for data collection using Mo K_α radiation. The structures were solved using direct methods and refined by full-matrix least-squares on F^2 and displayed with thermal ellipsoids at 40% probability (Table 4).

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Azidopentaphenyl-λ^6-tellane Ph_5TeN_3 (1): Into a solution of Ph_5TeBr (1 mmol) in 20 mL of CH_2Cl_2/hexane 1:1 was added AgN_3 (1.5 mmol) and stirred for 1 day. After filtration, into the yellow solution 10 mL of hexane were added, upon which crystallization at 4 °C afforded **1** as pale yellow plates (48% yield; mp 160 °C); Raman (200 mW) 3057 (60), 2035 (10, $\nu_{as}N_3$), 1573 (40), 1474 (10), 1433 (5), 1324 (10), 1182 (15), 1014 (50), 1001 (100), 643 (50), 614 (10), 270 (35), 215 (65), 120 (60) cm^{-1}; IR (KBr) 3047 m, 3011 w, 2982 w, 1576 w, 1566 m, 1479 m, 1432 s, 1327 w, 1302 w, 1270 w, 1180 m, 1157 w, 1057 w, 1045 m, 1017 w, 996 m, 969 w, 914 w, 843 w, 732 vs, 689 s, 665 w, 640 w, 612 w, 474 m, 457 s, 279 s, 261 vs cm^{-1}; ^1H NMR (CD_2Cl_2) δ 7.65−7.23 (m, ar-H); ^{13}C NMR (CD_2Cl_2) δ 150.4, 133.2, 129.5, 128.2 ppm; ^{14}N NMR (CD_2Cl_2) δ −139 (N_β), −207 (N_γ), −275 (N_α) ppm; $^{125}Te\{^1H\}$ NMR (CD_2Cl_2) δ 568 ppm; MS (D-EI) [*m*/*e* (intensity, species)] 515 (2) [$M^+ - N_3$], 436 (10) [$M^+ - Ph - N_3$], 361 (25) [$M^+ - 2Ph - N_3$], 282 (30) [Ph_2Te^+], 154 (100) [$C_{12}H_{10}^+$]. Anal. Calcd for $C_{30}H_{25}N_3Te$: C, 64.9; H, 4.5; N, 7.6. Found: C, 64.1; H, 4.7; N, 6.6.

***cis*-Diazido-bis(2,2′-biphenyldiyl)-λ^6-tellane (2):** Into a solution of 1 mmol of *cis*-$(biphen)_2TeF_2$ in 10 mL of CH_2Cl_2 were added 1.5 mmol of Me_3SiN_3 at 0 °C. After the mixture was warmed to ambient temperature and stirred for 5 h, all volatiles were removed in vacuo, which afforded **2** as a yellow powder (70% yield, mp 153 °C (dec); ^1H NMR (CD_2Cl_2) δ 8.30 (dd), 8.24 (dd), 8.05 (d), 7.75 (m), 7.53 (td), 7.20 (td), 6.77 (dd) ppm; ^{13}C NMR (CD_2Cl_2) δ 135.8, 135.2, 135.1, 134.0, 133.2, 132.6, 131.8, 130.1, 129.9, 127.0, 134.4, 123.4 ppm; ^{14}N NMR (CD_2Cl_2): δ −140 (N_β), −182 (N_γ), −268 (N_α) ppm; $^{125}Te\{^1H\}$ NMR (CD_2Cl_2) δ 633 ppm; Raman (200 mW) 3056 (25), 2044 (20)/2037 (10, $\nu_{as}N_3$), 1579 (100), 1468 (15), 1291 (65), 1268 (10), 1234 (10), 1157 (15), 1038 (20), 1028 (25), 666 (10), 381 (25), 316 (55, νTeN), 283 (40), 188 (25), 135 (30) cm^{-1}; IR (KBr) 3055 m, 2916 w, 2850 w, 2054 vs/ 2045 vs/ 2038 vs ($\nu_{as}N_3$), 1626 br, 1582 m, 1468 m, 1439 s, 1314 s, 1289 s, 1258 vs, 1166 m, 1157 m, 1109 w, 1060 w, 873 w, 749 vs, 706 m, 665 w, 612 w, 483 m, 415 m, 328 vs cm^{-1}; MS (D-EI) [*m*/*e* (intensity, species)] 476 (0.2) [$M^+ - N_3$], 434 (1) [$M^+ - 2N_3$], 280 (100) [$biphenTe^+$], 152 (80) [$biphen^+$]. Anal. Calcd for $C_{24}H_{16}N_6Te$: C, 55.9; H, 3.1; N, 16.3. Found: C, 54.5; H, 2.8; N, 15.4.

***trans*-Tetrafluoro-diphenyl-λ^6-tellane (3):** Analogous to the procedure described in ref 7, diphenyl tellane (1 mmol) was reacted at room temperature with XeF_2 (2 mmol) to form **3** after 2 days. The fraction of *cis*-isomer in the reaction solution (16%, according to ^{19}F NMR spectroscopy) slowly diminishes within days. After removal of all volatile materials, a colorless solid was obtained (86% yield). Data for the *trans*-isomer **3**: mp 167−169 °C; Raman (200 mW) 3081 (35), 3076 (35), 1582 (10), 1176 (5), 1161 (5), 1060 (10), 1021 (30), 1001 (50), 668 (15), 613 (15), 546 (100), 281 (10), 221 (70), 127 (3) cm^{-1}; IR (KBr) 3098 w, 3079 w, 1629 br, 1567 m, 1475 s, 1442 s, 1331 m, 1281 m, 1177 m, 1018 m, 991 s, 738 s, 679 s, 609 s, 601 vs, 466 s cm^{-1}; ^1H NMR (C_6D_6) δ 8.03, 7.55, 6.90 ppm; $^{13}C\{^1H\}$ NMR (C_6D_6) δ 147.2, (C1, quin, $^2J_{C-F}$ = 16.2 Hz), 131.2 (C3), 128.7 (C2, quin, $^3J_{C-F}$ = 2.7 Hz), 128.2 (C4) ppm; ^{19}F NMR (C_6D_6) δ −57.2 (s, $^1J_{F-123Te}$ = 2497 Hz, $^1J_{F-125Te}$ = 3011 Hz) ppm; $^{125}Te\{^1H\}$ NMR (C_6D_6) δ 821 (quin, $^1J_{Te-F}$ = 3011 Hz) ppm; MS (D-EI) [*m*/*e* (intensity, species)] 360 (20) [M^+], 341 (5) [$M^+ - F$], 245 (10) [$PhTeF_2^+$], 96 (100) [PhF^+]. Anal. Calcd for $C_{12}H_{10}F_4Te$: C, 40.0; H, 2.8. Found: C, 40.1; H, 2.8.

***cis*-Tetrafluoro-diphenyl-λ^6-tellane:** ^{19}F NMR (C_6D_6) δ −33.6 (t, $^1J_{F-F}$ = 87.2 Hz, 2F), −75.8 (t, 2F) ppm; $^{125}Te\{^1H\}$ NMR (C_6D_6) δ 806 (tt, $^1J_{Te-F}$ = 2904, 2689 Hz) ppm.

***mer*-Trifluoro-triphenyl-λ^6-tellane:** Into a solution of $[Ph_3Te]N_3$ (0.25 mmol) in 5 mL of CH_2Cl_2 was added XeF_2 (0.4 mmol) under vigorous stirring. After 3 h at ambient temperature, the slow evolution of xenon and nitrogen ceased. All volatile materials were removed in vacuo, and the remaining colorless solid dissolved in C_6D_6. ^{19}F NMR (C_6D_6) δ −3.5 (t, 1F, $^2J_{F-F}$ = 37.0 Hz), −95.5 (d, 2F) ppm; $^{125}Te\{^1H\}$ NMR (C_6D_6) δ 786 ppm.

Table 3. Te−F Bond Distances (Å), Te−N$_\alpha$ Bond Distances (Å), Te−C Bond Distances (Å), ELF Valence Shell Populations N_v(Te), and ELF/AIM/NPA Atomic Charges, and NPA Electron Configuration for the Me_xTeF_{6-x} and $Me_xTe(N_3)_{6-x}$ ($x = 0-6$) Molecules at Different Levels of Theory

	Te–F	Te–N$_\alpha$	Te–C	*ELF* N_v(Te)	AIM *q*(Te)	NPA *q*(Te)	NPA valence electron configuration (Te)
TeF_6	1.880				+3.89	+3.24	5s(1.05) 5p(1.41) 6s(0.01) 5d(0.13) 6p(0.05)
$MeTeF_5$	1.886 1.904		2.080		+3.56	+3.18	5s(1.12) 5p(1.52) 6s(0.01) 5d(0.12) 6p(0.06)
$MeTe(N_3)_5$		2.078 2.090 2.095 2.118 2.146	2.105	9.22	+3.32	+2.50	5s(1.31) 5p(2.08) 6s(0.01) 5d(0.08) 6p(0.04)
trans-Me_2TeF_4	1.935		2.079		+3.23	+2.98	5s(1.19) 5p(1.67) 6s(0.01) 5d(0.11) 6p(0.06)
cis-Me_2TeF_4 (C_i)	1.915 1.925		2.098		+3.39	+3.00	5s(1.16) 5p(1.68) 6s(0.01) 5d(0.11) 6p(0.06)
trans-$Me_2Te(N_3)_4$		2.094 2.118 2.151 2.161	2.117 2.122	9.53	+3.20	+2.41	5s(1.31) 5p(2.18) 6s(0.01) 5d(0.08) 6p(0.04)
cis-$Me_2Te(N_3)_4$ (C_i)		2.119 2.121	2.133	9.86	+2.89	+2.43	5s(1.31) 5p(2.16) 6s(0.01) 5d(0.08) 6p(0.03)
mer-Me_3TeF_3	1.951 1.961		2.102 2.123		+3.02	+2.79	5s(1.20) 5p(1.86) 6s(0.01) 5d(0.10) 6p(0.05)
fac-Me_3TeF_3	1.940		2.114		+3.19	+2.80	5s(1.18) 5p(1.89) 6s(0.01) 5d(0.09) 6p(0.05)
mer-$Me_3Te(N_3)_3$		2.129 2.132 2.193	2.127 2.137 2.156	10.10	+2.93	+2.33	5s(1.30) 5p(2.27) 6s(0.01) 5d(0.07) 6p(0.03)
fac-$Me_3Te(N_3)_3$		2.138 2.150 2.198	2.122 2.134 2.145	10.06	+3.10	+2.32	5s(1.30) 5p(2.29) 6s(0.01) 5d(0.07) 6p(0.03)
cis-Me_4TeF_2	1.983		2.124 2.138		+2.91	+2.57	5s(1.21) 5p(2.10) 6s(0.01) 5d(0.09) 6p(0.04)
trans-Me_4TeF_2	1.969		2.144		+2.87	+2.62	5s(1.23) 5p(2.03) 6s(0.01) 5d(0.09) 6p(0.04)
cis-$Me_4Te(N_3)_2$		2.197 2.215	2.138 2.145 2.147 2.162	10.78	+3.06	+2.24	5s(1.29) 5p(2.39) 6s(0.01) 5d(0.07) 6p(0.03)
trans-$Me_4Te(N_3)_2$		2.155 2.155	2.162 2.162 2.168 2.168	10.60	+3.10	+2.29	5s(1.29) 5p(2.33) 6s(0.01) 5d(0.07) 6p(0.03)
Me_5TeF	2.004		2.157 2.163 2.165 2.166		+2.68	+2.38	5s(1.24) 5p(2.29) 6s(0.01) 5d(0.08) 6p(0.03)
Me_5TeN_3		2.244	2.155 2.169 2.170 2.177 2.181	10.79	+3.03	+2.19	5s(1.28) 5p(2.45) 5d(0.07) 6p(0.02)
Me_6Te			2.192	11.04	+2.63	+2.17	5s(1.25) 5p(2.50) 5d(0.07) 6p(0.02)
$Te(N_3)_6$		2.080		8.89	+3.52	+2.62	5s(1.29) 5p(1.96) 6s(0.01) 5d(0.09) 6p(0.04)

Pentafluoro-phenyl-λ^6-tellane: Based on the procedure outlined,[7,10] $(PhTe)_2$ (0.5 mmol) in 15 mL of CH_2Cl_2 was reacted with XeF_2 (2.5 mmol) and $[Et_4N]Cl$ (0.1 mmol) for 1 d at ambient temperature. After all volatile materials were evaporated in vacuo, a colorless oil was obtained in 89% yield. ^{19}F NMR (C_6D_6) δ −36.8 (quin, $^2J_{F-F} = 150.3$ Hz), −53.5 (d) ppm; $^{125}Te\{^1H\}$ NMR (C_6D_6) δ 725 (dquin, $^1J_{Te-Fax} = 3610$ Hz, $^1J_{Te-Feq} = 3016$ Hz) ppm.

***cis*-Difluoro-tetramethyl-λ^6-tellane:** Based on the procedure outlined,[1] into a stirred solution of Me_4Te (1.7 mmol) in 5 mL of CH_3CN at −40 °C was added XeF_2 (1.7 mmol). After slow warming to 0 °C in 3 h, the colorless solution was evaporated at −10 °C/10^{-3} mbar until no detectable vapor pressure remained. Extraction with 10 mL of Et_2O/pentane yielded an almost pure solution of *cis*-Me_4TeF_2. A colorless solid was obtained after carefully removing all volatile materials at −10 °C/10^{-3} mbar, which could be recrystallized from toluene/pentane solution. ^{19}F NMR (C_6D_6) δ 7.0 ppm; $^{125}Te\{^1H\}$ NMR (C_6D_6) δ 592 (t, $^1J_{Te-F} = 1790$ Hz) ppm. See also ref 1.

***mer*-Trifluoro-trimethyl-λ^6-tellane:** Into a solution of $[Me_3Te]N_3$ (0.46 mmol) in 5 mL of CH_2Cl_2 were added XeF_2 (0.8 mmol) and $[Et_4N]Cl$ (0.1 mmol) at 0 °C, and then the mixture stirred at room temperature for 3 h until no further effervescence was observed. Subsequently, all volatile material was pumped off at −45 °C to yield a colorless residue. ^{19}F NMR (C_6D_6) δ −22.8 (t, F_a, 1F, $^2J_{F-F} = 32.0$ Hz), −65.1 (d, F_b, 2F) ppm; $^{125}Te\{^1H\}$ NMR (C_6D_6) δ 937 (dt, $^1J_{Te-F} = 2728$ (F_a), 1780 Hz (F_b)) ppm. Additionally, significant amounts of $MeTeF_5$ and Me_2TeF_2 were identified.

***trans*-Tetrafluoro-dimethyl-λ^6-tellane:** Into a solution of Me_2Te (1.1 mmol) in 10 mL of CH_2Cl_2 were added XeF_2 (2.2 mmol) and $[Et_4N]Cl$ (0.1 mmol) at 0 °C, and afterward the mixture stirred at room temperature for 48 h. Subsequently, all volatile material was pumped off at −40 °C to yield a colorless residue. ^1H NMR (CD_2Cl_2) δ 3.0 (quin) ppm; ^{19}F NMR (CD_2Cl_2) δ −34.6 (sept, $^1J_{F-H} = 4.7$ Hz) ppm; ^{125}Te NMR (CD_2Cl_2) δ 983 ($^1J_{Te-F} = 2826$ Hz, $^2J_{Te-H} = 71.5$ Hz) ppm.

Attempted Preparation of Pentafluoro-methyl-λ^6-tellane: Into a solution of $(MeTe)_2$ (1.5 mmol) in 5 mL of CH_2Cl_2, XeF_2 (7.5 mmol) and $[Et_4N]Cl$ (0.1 mmol) were added at −40 °C. The mixture was stirred and slowly warmed to room temperature within 2 h and decanted from

Table 4. Crystal Data and Structure Refinements

	Ph_5TeN_3 (**1**)	*cis*-$biphen_2Te(N_3)_2$ (**2**)	*trans*-Ph_2TeF_4 (**3**)
empirical formula	$C_{30}H_{25}N_3Te$	$C_{24}H_{16}N_6Te$	$C_{12}H_{10}F_4Te$
formula mass	555.13	516.03	357.80
temperature [K]	295(2)	295(2)	295(2)
crystal size [mm]	0.53 × 0.30 × 0.13	0.53 × 0.30 × 0.10	0.57 × 0.43 × 0.13
crystal description	yellow plate	yellow parallelepiped	colorless blocks
crystal system	monoclinic	monoclinic	triclinic
space group	$P2_1/n$	$P2_1/c$	$P\bar{1}$
a [Å]	10.411(2)	8.350(2)	6.6539(9)
b [Å]	17.363(4)	27.805(6)	7.299(1)
c [Å]	13.854(2)	9.803(2)	7.820(1)
β [°]	92.13(2)	114.60(1)	66.84(1)[a]
V [Å^3]	2502.5(9)	2069.5(7)	297.77(7)
Z	4	4	1
ρ_{calcd} [g cm^{-3}]	1.473	1.656	1.995
μ [mm^{-1}]	1.211	1.462	2.522
F(000)	1112	1016	170
θ range [deg]	2.35−23.98	2.68−23.97	3.11−23.97
index ranges	$-11 \le h \le 11$	$-9 \le h \le 8$	$-7 \le h \le 7$
	$0 \le k \le 19$	$0 \le k \le 31$	$-8 \le k \le 0$
	$-15 \le l \le 0$	$0 \le l \le 11$	$-8 \le l \le 7$
reflections collected	4091	3446	1016
reflections observed	3360	2640	932
reflections unique	3915 (R_{int} = 0.0164)	3242 (R_{int} = 0.0158)	933 (R_{int} = 0.0109)
$R1$, $wR2$ (2σ data)	0.0309, 0.0796	0.0267, 0.0575	0.0220, 0.0540
$R1$, $wR2$ (all data)	0.0403, 0.0848	0.0398, 0.0627	0.0220, 0.0540
max/min transm.	0.8938, 0.5806	0.9996, 0.8880	0.9980, 0.7088
data/restr/param	3915/0/307	3242/0/280	933/0/79
GOOF on F^2	1.165	1.111	1.168
larg diff peak/hole [e/Å^3]	0.736/−0.556	0.579/−0.338	0.934/−0.754

[a] $\alpha = 60.50(1)°$, $\gamma = 69.29(1)°$.

a colorless precipitate, which was extracted 3 times with CH_2Cl_2. The combined extracts were evaporated at −40 °C, yielding a colorless oil containing approximately 90% *trans*-$MeTeF_4OH$: ^1H NMR (C_6D_6) δ 2.16 (m, CH_3), 6.17 (br, OH) ppm; $^{13}C\{^1H\}$ NMR (C_6D_6) δ 37.1 (quin, $^2J_{C-F}$ = 8.1 Hz) ppm; ^{19}F NMR (C_6D_6) δ −32.1 (s) ppm; ^{125}Te NMR (C_6D_6) δ 832 (quintet of quartets, $^1J_{Te-F}$ = 3384 Hz, $^2J_{Te-H}$ = 71.4 Hz) ppm. The desired product, $MeTeF_5$, was detected only as a byproduct in the synthesis of *mer*-Me_3TeF_3. ^{19}F NMR ($CDCl_3$) δ −21.4 (quin, 1F, $^2J_{F-F}$ = 175.8 Hz), −36.2 (d, 2F, $^2J_{F-125Te}$ = 3653 Hz) ppm; ^{125}Te NMR resonance not unambiguously identified.

Attempted Preparation of Halogeno-pentamethyl-λ^6-tellanes: Similarly to the one-pot synthesis of Ph_5TeHal,[24] into freshly prepared solutions of Me_4Te in diethyl ether or THF, a fifth equivalent of MeLi was added at −110 °C. After 10 min at −110 °C, 1 equiv of XeF_2, SO_2Cl_2, or Br_2 was added, and the resulting mixture was slowly warmed to ambient temperature. For the reactions with SO_2Cl_2 and Br_2, only decomposition to the telluronium salts $[Me_3Te]Cl$ and $[Me_3Te]Br$ was observed, with XeF_2 a mixture of Me_2Te (δ 19 ppm, sept, $^2J_{Te-H}$ = 20.5 Hz), Me_4Te (δ −45 ppm, tridecet, 11 lines observed, $^2J_{Te-H}$ = 34.1 Hz), and Me_6Te (δ 35 ppm, $^2J_{Te-H}$ < 3 Hz) was identified by ^{125}Te NMR spectroscopy (unlocked) in Et_2O.

Attempted Preparation of *cis*-Dichloro-tetramethyl-λ^6-tellane: Into a freshly prepared solution of Me_4Te (1.6 mmol) in diethyl ether SO_2Cl_2 (1.6 mmol) was added at −70 °C under vigorous stirring. The resulting yellow mixture was stirred for 3 h and thereby slowly warmed to ambient temperature. All volatile material was removed in vacuo at −50 °C and 10^{-3} mbar. The ^{125}Te NMR spectrum of the solid residue showed only evidence for the formation of $[Me_3Te]Cl$.[26]

Computational Details. The electronic structures of the Me_xTeF_{6-x} and $Me_xTe(N_3)_{6-x}$ (x = 0−6) molecules have been calculated using density functional (B3LYP[50,51]) and second-order Møller−Plesset theory (frozen core) employing the cc-pVDZ basis sets of Dunning[52] for H, C, N, and F atoms. For Te, the systematically convergent cc-pVDZ basis ((8s6p6d)/[4s3p2d]) adapted to the SDB-MDF28 small-core relativistic pseudopotential of the energy-consistent variety was selected,[43,53] treating the outercore 4spd shells explicitly together with the 5sp valence shell. All structures were optimized in internal redundant coordinates (C_1 symmetry unless noted otherwise) such that no imaginary frequency (NIMAG) remained. In addition, also MP2(FC) structure optimizations without ECPs and analytical frequencies employing the TZVP/TZVPall basis[44,45,54] sets were performed. The use of smaller all-electron basis sets does not lead to acceptable structures in comparison with those from B3LYP or MP2(FC)/cc-pVDZ calculations employing pseudopotentials. The minimum structures obtained with the MP2(FC)/cc-pVDZ combination were subject to CCSD(T) calculations, as well as NBO and AIM/ELF analyses. Structure optimization and NBO analysis were performed using the program package GAUSSIAN 03 (rev. B 01),[55] the subsequent coupled cluster calculations with the MOLPRO program system.[56] The AIM, respectively ELF analyses were performed with the ToPMoD package using the MP2(FC)/cc-pVDZ wave function output.[57] The AIM module of the ToPMoD package should lead to quantitatively accurate results in combination with the small-core pseudopotentials used in this study. For Ph_5TeN_3 (**1**), $biphen_2Te(N_3)_2$ (**2**), and *trans*-Ph_2TeF_4 (**3**), RI-DFT and RI-MP2 structure optimizations with TURBOMOLE V5.3[58] using SVP and afterward TZVP basis sets were perfomed,[44,54] using

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the Becke-Perdew86 exchange-correlation functional[50,59] and the large-core MWB46 ECP for tellurium,[60] since TURBOMOLE currently does not support ECPs with $l > 3$, i.e., SDB-MDF28. With the RI-BP86/TZVP optimized structures, MPI-parallelized numerical frequency calculations for **1**, **2**, and **3** were carried out with the SNF program.[41]

Conclusion

The present study provides access to novel organotellurium(VI) azides, which represent the first Te(VI) pseudohalides. Whereas the synthesis of stable aryl substituted Te(VI)−N_3 and Te(VI)−$(N_3)_2$ species was accomplished, molecules of higher azide content were proven to be unstable toward reductive decomposition of the Te−N_3 moieties, resulting in Te(IV) derivatives and dinitrogen. Alkyl substituted Te(VI) molecules, namely methyl compounds in our study, did not give feasible methyltellurium(VI) azides, in all cases Te(IV) species and dinitrogen were observed. Experimental routes to the precursors Ph/Me_xTeF_{6-x}, inaccessible for Me_5TeF and $MeTeF_5$, were provided, respectively confirmed.

X-ray crystallographic studies of Ph_5TeN_3, *cis*-$biphen_2Te(N_3)_2$, and *trans*-Ph_2TeF_4 show the expected octahedral environment around the tellurium center, without secondary interactions. The crystal structure and some spectroscopic data of Ph_5TeN_3 indicate, in contrast to *cis*-$biphen_2Te(N_3)_2$ and organotellurium(IV) azides, a rather λ^5-telluronium-like character.

Computational studies including geometry optimization, frequency, and population analysis of Ph_5TeN_3 and all possible isomers for *cis*-$biphen_2Te(N_3)_2$ and Ph_2TeF_4, as well as all the Me_xTeF_{6-x} and $Me_xTe(N_3)_{6-x}$ ($x = 0-6$) molecules, confirmed the experimental data, where possible. Additional topological analyses of the electron localization function (ELF) for *trans*-Me_2TeF_4 and *cis*-$Me_4Te(N_3)_2$, as model compounds for *trans*-Ph_2TeF_4 and *cis*-$biphen_2Te(N_3)_2$, gave insight into the bonding situation of the tellurium atom in these molecules.

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Supporting Information Available: X-ray crystallographic files for compounds **1**, **2**, and **3** (CIF); Cartesian coordinates for the optimized structures, calculated and experimental vibrational spectra of **1**−**3**; Cartesian coordinates for the optimized structures, figures and calculated frequencies of the Me_xTeF_{6-x} and $Me_xTe(N_3)_{6-x}$ ($x = 0-6$) molecules (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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