# Synthesis and Characterization of Fluorinated Hypervalent Tellurium Derivatives

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#### **S** Supporting Information

**ABSTRACT:** The synthesis of tellurium derivatives bearing fluorinated groups, similar in structure to their hypervalent iodine congeners, is reported. Thus, a series of CF<sub>3</sub>, CF<sub>2</sub>H, and C<sub>6</sub>F<sub>5</sub> aryltellurium(II) species bearing various functional groups interacting with the Te atom was obtained. The installation of the various fluorinated groups relies on the use of the corresponding trimethylsilyl precursors. The hypervalent nature of the products is discussed on the basis of their NMR spectroscopic and X-ray crystallographic characterization.



### INTRODUCTION

Since their introduction in 2006, hypervalent iodine reagents 1 and 2 (Figure 1) have found numerous applications in



**Figure 1.** Hypervalent iodine reagents for electrophilic trifluoromethylation and a structurally related tellurium-centered analogue. Y = heteroatom,  $R_F = C_u F_m$ .

electrophilic trifluoromethylation reactions.<sup>1</sup> In the process of designing more broadly applicable reagents, we reported modifications of the parent structures, including functionalizations of the aromatic ring,<sup>2</sup> modifications of the five-membered ring incorporating the iodine atom,<sup>3</sup> exchange of the heteroatom bound to the iodine center,<sup>4</sup> and introduction of perfluoroalkyl substituents replacing the CF<sub>3</sub> group.<sup>5</sup> However, a formal replacement of the element iodine by its neighbor chalcogen tellurium has not yet been attempted. Therefore, we decided to embark on a detailed study of tellurium compounds structurally analogous to 1 and 2 with the aim of possibly broadening our fundamental knowledge of the reactivity of compounds of these heavy main-group elements as viewed in comparison to each other.

As defined by Musher in 1969,<sup>6</sup> hypervalent compounds are molecular species containing an atom of group 13–18 of the periodic system displaying more than eight electrons in its valence shell. This condition is clearly fulfilled in the case of

compounds 1 and 2, in which six electrons account for bonding and two free electron pairs are assigned to the iodine(III) center, giving a total of 10 valence electrons. The situation is somehow more complex in case of organotellurium compounds, since the oxidation state III is not stable for tellurium.

However, a hypervalent tellurium structure can be obtained if a tellurium(II) center with two substituents connected by single bonds interacts with a lone pair of a proximal heteroatom (structure A in Figure 1).<sup>7</sup> The total number of valence electrons for tellurium is 10 in this case, and the resulting molecule is isolectronic with that of the known hypervalent iodine reagents.

Interactions of this type are common for chalcogens and have received considerable attention in the literature. Depending on the publication, they are denoted as hypervalent bonds, threecenter-four-electron (3c-4e), charge-transfer, or secondary bonding interactions (SBIs). However, in each case the fundamental description of the bonding is the same. The distinction is based either on the strength of the interaction or simply on the publication context.

Reported models being considered as relevant for the work presented in this paper are shown in Figure 2. In the work by Woollins and co-workers<sup>8–16</sup> and in the early work by Nakanishi and co-workers<sup>17–21</sup> systems derived from 1,8-disubstituted naphthalenes (type **B**) were analyzed using X-ray diffraction and solid-state and solution NMR spectroscopy, as well as quantum mechanical calculations (e.g., determination of interaction energies, natural bond orbital analysis, and topological analysis of electron densities). It was demonstrated that structures with Y, X, and Z atoms aligned are preferred. These structures are

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**Figure 2.** (left) Selection of chalcogen compounds studied in the literature as models for hypervalent interactions. X = chalcogen, Y = chalcogen, halogen, Z = alkyl, aryl, or halogen. Atoms participating in this interaction are marked blue. (right) Orbital interaction relevant for hypervalent bonding.

stabilized by a 3c-4e interaction originating from donation of electron density from a lone pair on Y into the  $\sigma^*$  orbital on X ( $\sigma$ -type n(Y)… $\sigma^*$ (X-Z) 3c-4e interaction and n(Y) $\rightarrow \sigma^*$ (X-Z) charge transfer; Figure 2, right). The stabilization increases from the lighter to the heavier chalcogens and reaches its maximum for X = Te, due to its larger size and higher polarizability in comparison to the lighter chalcogens.

By applying atoms in molecules dual functional analysis to type C compounds, Nakanishi and co-workers classified the 3c-4e interaction in these molecules as a regular closed-shell interaction, meaning a covalent interaction between atoms fulfilling the octet rule.<sup>22</sup> That fact that the interaction falls in the covalent regime means that contributions from orbital mixing dominate over the electrostatic counterpart and supports the 3c-4e bond model.

In the work by Vargas-Baca and co-workers,<sup>23–28</sup> intermolecular interactions of this kind (denoted SBIs) were studied, originally in the context of polymer formation from structures of type **D**. Evidence for dimer formation in the gas phase was provided using UVLDI-MS in concert with DFT calculations.<sup>24</sup> Furthermore, numerous examples of solid-state Y…Te–Z SBIs available from the Cambridge Crystallographic Database were analyzed.<sup>26</sup> The shortest Y…Te–Z distances were found when the electronegativity of both Y and Z substituents was high. The influence of electronegativity of the Z substituent can be rationalized by MO considerations: the  $\sigma^*(Te–Z)$  orbital becomes more localized on Te and its energy decreases as the electronegativity of Z increases; this in turn lowers the energy gap between  $\sigma^*(Te–Z)$  and n(Y) and allows for more efficient mixing of these orbitals.

However, a different model is necessary to explain the effect of electronegativity of the X substituent. Gleiter and co-workers<sup>29-31</sup> applied symmetry-adapted perturbation theory (SAPT) as one of the tools to analyze the bonding in type E compounds. The study showed that, for chalcogens heavier than O, the dispersive contribution to the interaction energy is dominant.<sup>29</sup> Since dispersion can only be taken into account in models considering electron correlation, MO diagrams, including those applied for 3c-4e bonds, are not suitable to describe these types of interactions since they are derived from single-electron models. Indeed, the effect of the electronegativity of Y on the interaction strength is correctly predicted by the SAPT model. On the other hand, it is also shown that the simple MO model often provides correct predictions of trends and molecular structures.

In this work, NMR correlation experiments and X-ray diffraction measurements were used to characterize the interaction between Te and Y. Since the compounds presented

were developed as analogues of reagents 1 and 2, this interaction is denoted as a hypervalent bond.

Transformations involving tellurium compounds are well established in organic synthesis and material science.<sup>32</sup> Over the past few decades, tellurium(II) compounds referred to as hypervalent kept appearing in the literature. The first examples were reported during the 1970s, including the seminal work of Piette (Figure 3).<sup>33–36</sup> More recently, the scope has been expanded by Singh<sup>37,38</sup> and Engman.<sup>39</sup>



**Figure 3.** Selection of hypervalent tellurium compounds reported in the literature. Z = halogen, pseudohalogen, R = alkyl, aryl.

Although tellurium compounds directly involving a  $CF_3$  group attached to tellurium atom are known, with the simplest example being  $Te(CF_3)_{2}$ ,<sup>40</sup> reports on hypervalent  $CF_3$  tellurium compounds are rare. The only structurally related molecule originates from the work of Umemoto and co-workers<sup>41</sup> and is a synthetic intermediate in Umemoto's reagent synthesis (Figure 4). Umemoto's reagents are known as electrophilic trifluor-



Figure 4. Synthesis of Umemoto's reagents.

omethylation agents in organic syntheses. The vast majority of literature examples report the use of a sulfur-centered compound, due to its shelf stability and large substrate scope. Its less reactive tellurium analogue did not receive significant attention though.

#### SYNTHESIS

The targeted structures of type A were accessed starting from the ditellurides that were prepared following conditions reported by Engman and co-workers.<sup>39</sup> Thus, a lithium halogen exchange of an aryl bromide, followed by quenching of the resulting lithiated species with tellurium metal and subsequent air oxidation, afforded the corresponding ditellurides (Scheme 1). However, in our hands direct quenching of the intermediate tellurium-centered anion with an electrophile failed, presumably due to the low nucleophilicity of the corresponding lithium aryl telluride.

Originally, acetals were chosen as substrates for ditelluride synthesis. The acetal group is compatible with the necessary Scheme 1. Synthesis of Ditellurides Following Literature Conditions



reaction conditions (use of highly reactive *t*BuLi followed by air oxidation in water), and the oxygen atom in the acetal group is capable of coordination to the tellurium center, as illustrated by the general structure **A**. Moreover, an acetal can be converted to a carbonyl group that can also participate in hypervalent bond formation or be subjected to further transformations.

The method reported by Engman is suitable for acetals 3a-c. The corresponding products were obtained in up to quantitative yields as yellow solids or oils. No decomposition was observed over months upon storing at low temperature.

Next we focused our attention on esters. The ester functional group is also capable of coordination to the tellurium center. In addition, an ester can be hydrolyzed to the corresponding carboxylic acid. In the presence of a suitable base, such acids may form salts with a formally negatively charged tellurium atom and hence the concept illustrated in structure **A** could be extended to ionic compounds.

Unfortunately, inferior results were obtained for ester functional groups, presumably due to their base-sensitive nature. When 2-(trimethylsilyl)ethyl 2-bromobenzoate (a protected form of 2-bromobenzoic acid that can be deprotected in the presence of a fluoride source) was subjected to standard reaction conditions, only decomposition of the starting material was observed. On the other hand, the hindered *tert*-butoxycarbonyl substrate can be converted to the corresponding ditelluride **3d**, albeit in low yield.

To efficiently introduce the trifluoromethyl group on the tellurium atom, we were successful when applying conditions originally reported by Umemoto and co-workers.<sup>41</sup> Thus, a ditelluride was reduced with NaBH<sub>4</sub> in ethanolic solution and the resulting anionic intermediate reacted with liquified CF<sub>3</sub>I (Scheme 2). This pathway allowed access to compound 4a, but a competing side reaction leading to compound 5 was additionally operating. Compounds 4a and 5 were formed in a 88:12 ratio, as indicated by <sup>19</sup>F NMR analysis of the crude material, and could not be separated.

Hence, it was reasoned that the presence of an electronwithdrawing  $CF_3$  group on the tellurium atom renders this center Lewis acidic. This in turn strengthens the O–Te bond and Scheme 2. Installation of  $CF_3$  Group on Tellurium by Use of  $CF_3I^a$ 



<sup>a</sup>The proposed mechanism of side product formation is shown.

weakens the C–O bond, effectively promoting the C–O bond cleavage. Consequently, nucleophilic attack of a hydride leads to a formal reduction at carbon, yielding an ether.

It is worth mentioning that the C–O bond cleavage in an acetal is not a straightforward transformation and usually requires harsh conditions in order to proceed. In an early example provided by Akhmatdinov and co-workers,<sup>42</sup> a strong acid, HSO<sub>3</sub>F, was used to promote this reactivity pattern and yield the corresponding carbocation. More recent examples, summarized by Larson et al.,<sup>43</sup> utilize organosilanes in combination with Lewis acids or transition-metal complexes. A reaction of TiF<sub>4</sub> with an acetal also yields the corresponding ether as one of the products.<sup>44</sup>

In order to avoid this competing side reaction, ditelluride **3b** containing a cyclic acetal protecting group was employed. Surprisingly, the starting material or the corresponding product (**4b** in Scheme 4) undergoes transacetalization under reaction conditions, yielding compound **4a** (Scheme 3).

# Scheme 3. Unexpected Transacetalization Encountered during Reduction of 3b



In a control experiment, 2-(2-bromophenyl)-1,3-dioxolane was stirred in ethanol in the presence of NaBH<sub>4</sub> overnight. However, only traces of the corresponding transacetalization product were observed after this time. Moreover, no acyclic acetal formation was observed when ditelluride **3b** was recrystallized from ethanol. These observations suggest that the transacetalization leading to **4a** takes place after the installation of the CF<sub>3</sub> group and is most likely promoted by the electron-withdrawing properties of this substituent.

Ostensibly, the mechanism of ditelluride reductions includes nucleophilic attack of a hydride on one of the tellurium atoms followed by the displacement of an anionic tellurium species as a leaving group. This interpretation, together with a literature report by Irgolic in which a ditelluride reaction with a Grignard reagent was proposed,<sup>45</sup> prompted us to study another strategy for the installation of a  $CF_3$  group. Thus, the alternative pathway included Te–Te bond scission with a nucleophilic  $CF_3$  source (Scheme 4). Although this method cannot be considered to be

Scheme 4. Installation of CF<sub>3</sub> Group on Tellurium by Use of the Ruppert–Prakash Reagent



atom economical by virtue of utilizing half of the ditelluride molecule as a nucleofuge, it does allow access to a variety of structures that cannot be obtained with the  $CF_3I$  method. For example, compound **4b** could be isolated in acceptable yield. Moreover, the synthesis is operationally simpler, since it does not require the use of expensive and difficult to handle  $CF_3I$  gas.

Interestingly, when KF was replaced by CsF in the aforementioned procedure, an unexpected compound was isolated (Scheme 5). Analysis of the isolated material revealed

Scheme 5. Unexpected Product Formation in the Presence of CsF



a compound having structure **6**. The mechanism of its formation includes deprotonation of acetonitrile by anhydrous and highly basic fluoride.<sup>46</sup> Nucleophilic attack of the resulting anion on the ditelluride yields compound **6**.

Another advantage of this method is the opportunity to replace TMSCF<sub>3</sub> by another silane-protected nucleophile, as it provides a general, convenient route to tellurium derivatives carrying fluorinated substituents on the tellurium atom, as shown in the general structure **A**. Hence, under conditions developed for difluoromethylation of disulfides,<sup>47</sup> the CF<sub>2</sub>H tellurium compound 7 could be prepared in moderate yield (Scheme 6). The synthesis of CF<sub>2</sub>H tellurium compounds was reported more than 30 years ago,<sup>48</sup> but the procedure required Freon 22 gas under

#### Article

# Scheme 6. Synthesis of Hypervalent CF<sub>2</sub>H Tellurium Compound



high pressure. Difluoro(chalcogen)methylation reported more recently by Hu and co-workers<sup>49</sup> uses the same approach for the synthesis of CF<sub>2</sub>H aryltellurides. Since the synthesis of CF<sub>2</sub>H analogues of reagents **1** or **2** using TMSCF<sub>2</sub>H under conditions developed for their original preparation of has been unsuccessful so far, compound 7 is of particular interest, especially as a potential electrophilic or radical CF<sub>2</sub>H source.

In order to further demonstrate the generality of this method, we chose the installation of the perfluorophenyl group on tellurium as our next goal. The synthesis of a related compound,  $Te(C_6F_5)_2$ , was reported in 1968 starting from  $Hg(C_6F_5)_2$  and elemental tellurium.<sup>50</sup> Thus, when (pentafluorophenyl)-trimethylsilane was reacted with **3b** under reaction conditions developed for the CF<sub>2</sub>H transfer, two new compounds could be isolated from the reaction mixture (Scheme 7). Apart from the target product **8a**, the side product **8b** was formed. This compound results from nucleophilic aromatic substitution on **8a**. The aryltelluride anion formed from **3b** upon nucleophilic attack of fluoride-activated TMSC<sub>6</sub>F<sub>5</sub> acts as a nucleophile in this reaction.

Electrophilic aromatic substitution on the perfluorophenyl ring has been reported previously, e.g. as a side pathway in the reaction between dimethyl disulfide and  $\text{Li}(\text{C}_6\text{F}_5)$ .<sup>51</sup> Additionally, a study covering reactions of different pentafluorobenzenes with NaSMe and NaOH revealed that the para-substituted product is formed preferentially.<sup>52</sup>

The nature of the counterion and/or the solvent used for the reaction in Scheme 7 seems critical for the formation of **8b**. When

# Scheme 7. Reaction of Ditelluride 3b with (Pentafluorophenyl)trimethylsilane



the reaction is conducted in diethyl ether using  $\text{LiC}_6\text{F}_5$  as a nucleophile, this side product is not detected. Unfortunately, under these conditions target product **8a** is formed only in trace amounts, probably due to the poor solubility of the starting material in ethereal solvents. In addition, literature studies<sup>53</sup> of tellurium compounds bearing the pentafluorophenyl group installed using  $\text{LiC}_6\text{F}_5$  do not mention  $S_N\text{Ar}$  reaction pathways.

The functional group coordinated to the tellurium atom in tellurium  $CF_3$  derivatives described so far can be modified, as illustrated by acetal cleavage<sup>54–56</sup> and imine formation (Scheme 8).<sup>57</sup> In the case of **4a**, deprotection proceeds readily upon

# Scheme 8. Modifications of Functional Group Interacting with the Tellurium Atom



standing in chloroform solution. For cyclic acetals **4c** and **8a** longer reaction times and higher temperatures are necessary. In each case the target carbonyl compound could be isolated after column chromatography in high yields as a yellow or orange solid. Furthermore, aldehyde **9** could be converted to imine **10**. The reaction is carried out in refluxing toluene; therefore, the high yield reflects the thermal stability of both compounds.

### SOLID-STATE STRUCTURES

Upon standing in a refrigerator, compounds 4b, 9, and 10 crystallized in the form of needles suitable for X-ray diffraction measurements. Representations of the molecular structures are shown in Figure 5, and selected parameters (bond lengths and angles) are compared in Table 1. In each case, the heteroatom (oxygen in 4b and 9, nitrogen in 10) is pointing toward the tellurium center. For molecules 9 and 10 the angle defined by the



**Figure 5.** (top) ORTEP views of the single-crystal structures of tellurium compounds **4b**, **9**, and **10**. Thermal ellipsoids are set to 30% probability, and hydrogen atoms are omitted for clarity. (bottom left) Known molecules chosen for comparison of selected bond lengths and angles. (bottom right) General description of compounds compared in Table 1.

 $CF_3$  group, Te atom, and heteroatom differs from the theoretical value of 180° by about  $-12^\circ$ . This difference is larger but still similar to that observed in iodine reagent 2 ( $-9.5(1)^\circ$ ). A larger deviation is measured for **4b**, in which the acetal ring is tilted with respect to the aromatic ring. This tilt is quantified by selected torsion angles and most likely occurs due to steric interactions.

In the previously reported compound 13,<sup>58</sup> the Te–Br bond is longer than the Te–O distance. This trend is reversed in the case of Te–CF<sub>3</sub> compounds in that the Te–CF<sub>3</sub> bond is shorter than the Te–heteroatom bond (by 0.699(2), 0.382(6), and 0.275(11) Å for 4b, 9, and 10, respectively). This is also in contrast to iodine compound 2, for which the lengths of the corresponding bonds are similar (difference of 0.064(4) Å). This observation indicates that the Te–CF<sub>3</sub> interaction is stronger than the Te–heteroatom

Table 1. Selected Bond Lengths and Angles Measured for Hypervalent Tellurium Compounds in the Solid State<sup>a</sup>

param	2	13	4b	9	10
X–Y distance (Å)	2.283(2)	2.309	2.868(2)	2.570(3)	2.481(6)
X–Z distance (Å)	2.219(4)	2.618	2.169(2)	2.188(5)	2.206(9)
X–C1 distance (Å)	2.113(4)	2.097	2.123(2)	2.104(5)	2.119(7)
Z–X–Y angle (deg)	170.5(1)	168.5	159.9(7)	168.3(2)	167.4(3)
C1–X–Z angle (deg)	93.8(1)	94.6	93.9(9)	94.7(2)	93.8(3)
C1-X-Y angle (deg)	76.8(1)	74.0	70.1(7)	73.6(2)	73.7(2)
C2-C1-X-Y torsion (deg)	0.3(2)	0.1	19.8(2)	0.5(4)	2.1(5)
C6-C1-X-Y torsion (deg)	0.7(3)	3.8	34.9(2)	0.7(5)	5.7(7)

<sup>*a*</sup>Atom numbering as in Figure 4.

interaction and most likely reflects a weak three-center-fourelectron interaction.

Among the three tellurium compounds, 9 displays geometrical features very similar to those of iodine compound 2. The resemblance is illustrated by overlaying the two crystal structures (Figure 6). Although the tellurium–oxygen distance is longer



Figure 6. Overlay of crystal structures obtained for  $2^{59}$  (blue) and for 9 (red).

than the iodine-oxygen bond, the tellurium-carbon and iodine-carbon bond lengths are almost the same (0.031(6) Å shorter in 9 than in 2).

### NMR ANALYSIS

The element tellurium has two spin 1/2 nuclei, <sup>125</sup>Te and <sup>123</sup>Te; therefore, tellurium compounds can be characterized using NMR spectroscopy. Due to its higher natural abundance (7%), <sup>125</sup>Te is the isotope of choice. The chemical shift range for this isotope spans from about -1400 to 3400 ppm, assuming that Me<sub>2</sub>Te resonates at 0 ppm.<sup>60</sup>

Although it is possible to measure <sup>125</sup>Te NMR directly, we decided to use  ${}^{1}\text{H}-{}^{125}\text{Te}$  and  ${}^{19}\text{F}-{}^{125}\text{Te}$  correlation techniques because measurement times are shorter and additional structural information on a chosen compound is gained from a 2D spectrum.

The results are summarized in Figure 7. Some known hypervalent tellurium compounds (3e, 4e, 14, 15) were also prepared, and the corresponding shifts are provided for comparison.

It is evident that the chemical shift range for hypervalent  $CF_3$  tellurium compound lies within 844 and 1014 ppm. The lowest chemical shift in this group is observed for compound 10, in which a nitrogen atom is coordinated to the tellurium center. Higher shifts are observed for compounds with oxygen coordinated, with aldehyde 9 having the highest value. Umemoto's intermediate 4e also falls in this range.

In contrast, alkyl aryl tellurides resonate at significantly lower frequency. In both analyzed examples (6 and 14) negative chemical shifts were obtained. It can therefore be concluded that the CF<sub>3</sub> group has a pronounced deshielding effect on the <sup>125</sup>Te chemical shift. In addition, compound 15, in which a chlorine atom is directly bound to tellurium, has the highest chemical shift of all synthesized compounds. Therefore, it can be concluded that the <sup>125</sup>Te chemical shift increases with the electronegativity of the substituent attached to tellurium. On the other hand, it has to be kept in mind that the chemical shifts of nuclei different from <sup>1</sup>H are determined by additional factors, including energies of excited states, and not only electronegativity of the substituent. Further analysis beyond the scope of this work would be necessary to identify the various contributions.



**Figure 7.** Chemical shifts of tellurium compounds obtained in this work.  $CDCl_3$  was used as a solvent, and the measurements were done at room temperature. All shifts are reported with respect to Me<sub>2</sub>Te.

Compounds carrying the perfluorophenyl fragment on the tellurium atom (8a,b, 12) follow this trend—they appear in the range 428–580 ppm, which is intermediate between alkyl and CF<sub>3</sub> tellurium compounds. The perfluoroalkyl substituent is expected to be less electrophilic than the CF<sub>3</sub> group, because tellurium and fluorine are separated by three bonds (in comparison to the to two-bond separation in the case of the CF<sub>3</sub> group). As in the case of CF<sub>3</sub> compounds, a molecule with an aldehyde group (12) has the highest shift.

 $CF_2H$  compound 7 resonates at 741 ppm, suggesting that in addition to the number of bonds separating fluorine and tellurium the total number of fluorine atoms has an effect on increasing the chemical shift. Finally, ditellurides resonate around 300–400 ppm, in accordance with literature data.<sup>61</sup> Both findings are in agreement with the trend.

In addition to being a tool for characterization, NMR spectroscopy provides evidence indicative of the hypervalent nature of the compounds obtained. For example, in case of 9 a cross peak between the aldehyde proton and one of the aromatic protons is observed in the NOESY spectrum. This observation strongly suggests that the aldehyde oxygen is pointing toward the tellurium center, since only in this conformation both protons are close in space. Furthermore, in the <sup>1</sup>H-<sup>125</sup>Te correlation spectrum couplings between the tellurium center and both aromatic and aldehyde protons are observed when sufficiently long delay times are applied. The latter correlation may result from a coupling through the scaffold in that the nuclei (tellurium and aldehyde proton) are separated by four bonds. On the other hand, it may also indicate the presence of a hypervalent bond, since the nuclei are separated by three bonds in this model. A coupling through three bonds is more likely to be observed than that through four. In addition, cross peaks between the tellurium



Figure 8. <sup>1</sup>H-<sup>125</sup>Te correlation spectrum of molecule 10. The <sup>1</sup>H NMR spectrum of 10 is shown as an external projection.

center and aromatic protons other than those in ortho positions were not detected.

In the case of molecule **10**, the presence of methyl groups on the mesidine fragment allows us to observe an additional effect. In the  ${}^{1}\text{H}-{}^{125}\text{Te}$  correlation spectrum, a coupling between the mesidine ortho methyl protons and the tellurium center is observed (Figure 8). This is an indication of the A-type structure in which these protons and tellurium are close enough in space to allow for orbital overlap between tellurium lone pairs and the hydrogen s orbital. If the coupling between these protons and the tellurium nucleus were through the scaffold, it would have to be mediated by eight bonds. Such a long-range coupling is unlikely to be observed.

#### DFT CALCULATIONS

The interaction between the oxygen atom and the tellurium center in 9 was further characterized by density functional theory at the B3LYP/cc-pVDZ-PP level. A similar analysis of structurally related organotellurium compounds has been reported previously.<sup>62</sup> According to the calculations in the gas phase, conformer 9 is 8.3 kcal/mol lower in energy in comparison to conformer 9a, in which the oxygen is pointing away from tellurium (Figure 9). The strength of the interaction



Figure 9. Possible conformers of aldehyde 9.

between the oxygen lone pair and  $Te-CF_3$  antibonding orbital is 13.42 kcal/mol, as determined by natural bond orbital secondorder perturbation analysis. Therefore, structure **9** is the preferred conformation, in accordance with observations made in the solid state.

### CONCLUSION

In summary, a series of new hypervalent  $CF_3$  tellurium compounds were successfully prepared. X-ray analysis revealed a close structural resemblance between these molecules and hypervalent iodine derivatives known as reagents for perfluoroalkylation. In addition,  $CF_2H$  and  $C_6F_5$  groups could be installed on tellurium, providing structures so far unknown for iodine analogues. Further studies concerning the use of these molecules as perfuoroalkyl transfer agents are currently being carried out in our laboratory and will be reported in due course.

## ASSOCIATED CONTENT

### **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.7b00535.

Experimental procedures, characterization of compounds, NMR and IR spectra, crystallographic data for compounds **4b**, **9**, and **10**, and computational details (PDF)

#### Accession Codes

CCDC 1548965–1548967 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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#### Notes

The authors declare no competing financial interest.

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