A Journal of the Gesellschaft Deutscher Chemiker

Angewandte Chemie

International Edition

www.angewandte.org

Title: Pentafluoro(aryl)-λ6-tellanes and Tetrafluoro(aryl)(trifluoromethyl)-λ6-tellanes: From SF5 to the TeF5 and TeF4CF3 Groups

Authors: Dustin Bornemann, Cody Ross Pitts, Carmen J. Ziegler, Ewa Pietrasiak, Nils Trapp, Sebastian Küng, Nico Santschi, and Antonio Togni

To be cited as: *Angew. Chem. Int. Ed.* 10.1002/anie.201907359
Angew. Chem. 10.1002/ange.201907359

Link to VoR: http://dx.doi.org/10.1002/anie.201907359
http://dx.doi.org/10.1002/ange.201907359

WILEY-VCH

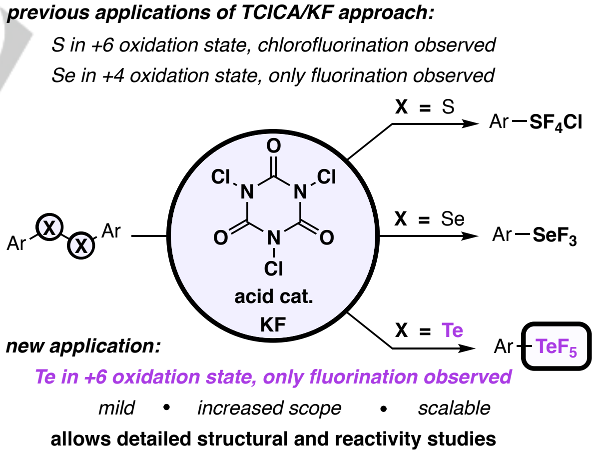
Pentafluoro(aryl)-λ^6-tellanes and Tetrafluoro(aryl)(trifluoromethyl)-λ^6-tellanes: From SF_5 to the TeF_5 and TeF_4CF_3 Groups

Dustin Bornemann,† Cody Ross Pitts,†* Carmen J. Ziegler, Ewa Pietrasiak, Nils Trapp, Sebastian Kueng, Nico Santschi,* and Antonio Togni*

Abstract: The TeF_5 group is significantly underexplored as a highly fluorinated substituent on an organic framework, despite it being a larger congener of the acclaimed SF_5 group. In fact, only one aryl-TeF_5 compound (phenyl-TeF_5) has been reported in the literature to date, synthesized using XeF_2 – a testament to a clear lack of synthetic accessibility. Herein, our recently developed mild TCICA/KF approach to oxidative fluorination addresses this problem by providing an affordable and scalable alternative to XeF_2. Using this method, we report a scope of extensively characterized aryl-TeF_5 compounds, along with the first SC-XRD data on this compound class. The methodology was also extended to the synthesis and structural study of heretofore unknown aryl-TeF_4CF_3 compounds. Additionally, preliminary reactivity studies unveiled some inconsistencies with previous literature regarding phenyl-TeF_5. Ultimately, although our studies conclude that the arene-based TeF_5 (and TeF_4CF_3) group is not quite as robust as the SF_5 group, we find that the TeF_5 group is arguably more stable than previous literature suggests, thus opening a door to explore new applications of this motif.

In the last year, our laboratory developed a mild, gas-reagent-free approach to the synthesis of aryl-SF_4Cl compounds using trichloroisocyanuric acid (TCICA), potassium fluoride (KF), and catalytic acid.[1] Under identical conditions, we also observed that diaryl diselenides display divergent behavior, providing aryl-SeF_3 compounds as opposed to the corresponding Se^{VI} species.[1,2] Initially out of sheer academic curiosity, our focus more recently drifted further down the chalcogen series, and we asked: how would *diaryl ditellurides* react? Surprisingly, we found that similar TCICA/KF oxidative fluorination conditions allow direct access to pentafluoro(aryl)-λ^6-tellanes (aryl-TeF_5 compounds), i.e. with the Te atom in a different oxidation state and/or with a different degree of fluorination than S or Se in the aforementioned products of diaryl disulfide and diaryl diselenide oxidative fluorination (Scheme 1). This curiosity evolved into an unexpected foray into organotellurium chemistry.[3,4]

Considering the TeF_5 group is ostensibly a larger, greasier, underexplored congener of the SF_5 group (which has shown promising applications in medicinal chemistry, agrochemistry, and materials, such as liquid crystals),[5] we decided to examine it more closely. To the best of our knowledge, the only compound containing an arene-based TeF_5 group that has been reported to date is phenyl-TeF_5, which was synthesized on a small scale using XeF_2 and was never isolated.[6-10] Herein, we discuss the development of a remarkably mild and inexpensive TCICA/KF approach that, for the first time, generates a substrate scope and demonstrates scalability of aryl-TeF_5 compound synthesis. Moreover, upon isolation of these compounds, we discovered that the TeF_5 group is less prone to degradation and slightly more robust than formerly described. This finding has allowed us to conduct the first extensive analysis of the molecular structure of the TeF_5 group on an arene (and subsequently, a novel TeF_4CF_3 group) in the solid state using X-ray diffraction data, as well as study the stability and reactivity of this group. It was during these studies that we also unveiled inconsistencies with the previous literature on the "known" reactivity of phenyl-TeF_5 and, accordingly, we begin to address misconceptions about aryl-TeF_5 compounds.



Scheme 1. *Discovery of a new application of the TCICA/KF approach vis-à-vis mild aryl-TeF_5 synthesis, whereby diaryl ditellurides display divergent behavior from their disulfide and diselenide congeners under similar reaction conditions.*

Regarding reaction optimization, it was determined that consistent, high yields of aryl-TeF_5 compounds can be obtained by stirring the corresponding diaryl ditelluride substrates with 6.0 equiv. TCICA, 24 equiv. KF, and 10 mol % TFA in MeCN at ambient temperature overnight (ca. 16 h). See Table S1 in the Supporting Information for more details.

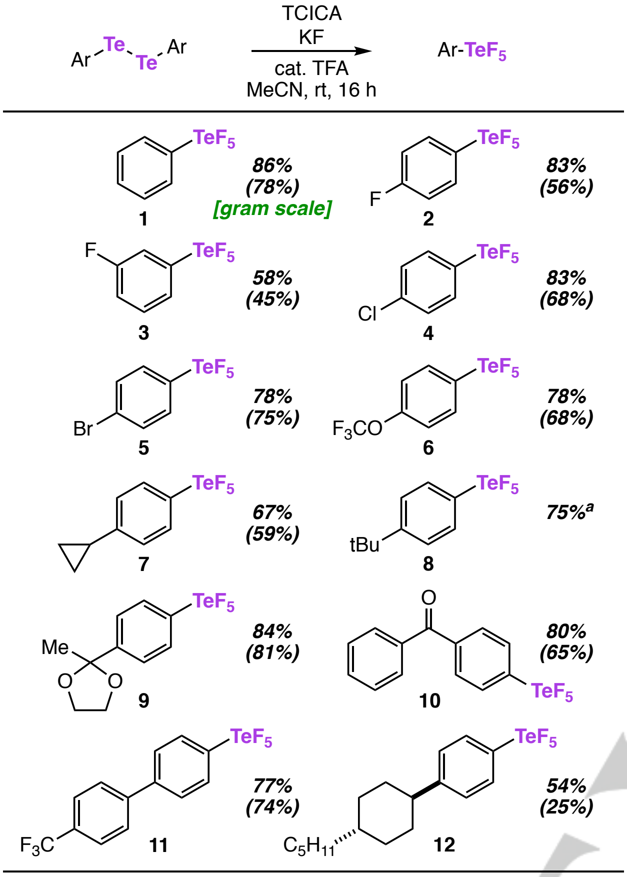
---

[*] D. Bornemann,† Dr. C. R. Pitts,†* C. J. Ziegler, E. Pietrasiak, Dr. N. Trapp, S. Küng, Dr. N. Santschi,* Prof. Dr. A. Togni*
Department of Chemistry and Applied Biosciences
ETH Zürich
Vladimir-Prelog-Weg 2, 8093 Zürich (Switzerland)
E-mail: cpitts@ethz.ch
nicosantschi@gmail.com
atogni@ethz.ch

†These authors contributed equally.

Supporting information for this article is given via a link at the end of the document.

Table 1. *Substrate scope of aryl-TeF$_5$ formation.*

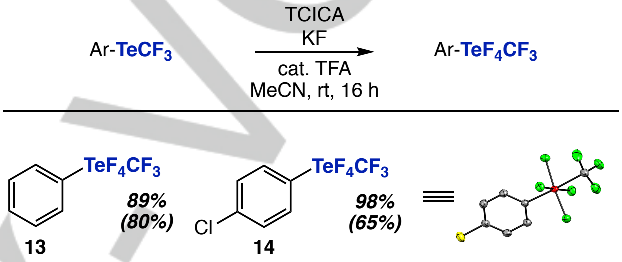


^{19}F NMR yields reported. Isolated yields in parentheses for compounds isolable via extraction. ^{a}Unable to obtain pure isolated product.

Under these conditions, the unsubstituted phenyl-TeF$_5$ (**1**) was formed in 86% yield by ^{19}F NMR. Immediately thereafter, we also found that **1** can be synthesized on a 2-gram scale and isolated by extraction (i.e. without chromatography) in 78% yield. Interestingly, however, the material could also be subjected to flash chromatographic separation on silica without undergoing complete decomposition. Subsequently, we explored the reaction scope (Table 1). Notably, diphenyl ditelluride is the only commercially available starting material, to our knowledge. All other ditelluride starting materials were synthesized with varying degrees of success using the methods of Engman,[11] Stefani,[12] and Zhou.[13]

This reaction tolerates standard electron-withdrawing groups well in the *meta*- and *para*-positions, such as halogens (**2**-**5**) and a trifluoromethoxy substituent (**6**). An initial oxidative fluorination attempt using a substrate with an *ortho*-fluoro-substitution pattern resulted in an unclear and complicated ^{19}F NMR spectrum; it is possible that the TeF$_5$ group is too large to form selectively in the presence of *ortho*-substituents, though this may not be purely a steric effect. Additionally, mild electron-donating groups are tolerated in the form of cyclopropyl (**7**), *tert*-butyl (**8**), and acetal (**9**) substituents. (In the last case, note that ketones do not necessarily require protection as acetals, e.g. benzophenone derivative **10** was formed in good yield under TCICA/KF conditions.) When employing stronger electron-donating groups or alkyl groups with benzylic sites, known background reactions with TCICA (e.g. ring or benzylic chlorination) may become competitive.[14] For instance, we found that an unsubstituted biphenyl ditelluride is electron-rich enough for unselective ring chlorination to be problematic (however, note that a crystal structure was obtained for one of the chlorinated isomers). Conversely, biphenyl ditellurides substituted with electron-withdrawing groups, e.g. a CF$_3$ group, convert to their corresponding aryl-TeF$_5$ compounds selectively (**11**). In addition, we were able to access the slightly more complex compound **12**, albeit in a lower yield, whose overall structure is reminiscent of a liquid crystal.

Table 2. *Proof-of-concept for novel aryl-TeF$_4$CF$_3$ formation.*



^{19}F NMR yields reported. Isolated yields in parentheses. Crystal structure of compound **14** determined from single-crystal X-ray diffraction (displacement ellipsoids given at 50% probability level).

Beyond diaryl ditelluride substrates, we became interested in the oxidative fluorination of aryl-TeCF$_3$ compounds. Syntheses of aryl-TeCF$_3$ compounds have been developed by Umemoto,[15] and more recently in our laboratory[16] and by Schönebeck.[17] To our satisfaction, under TCICA/KF conditions, we were able to convert phenyl-TeCF$_3$ to *trans*-phenyl-TeF$_4$CF$_3$ (**13**), obtaining the product in 80% isolated yield as an oil (Table 2). As this is, to our knowledge, the first time this TeF$_4$CF$_3$ group has been observed, we also synthesized *para*-chloro-derivative **14** in order to obtain X-ray diffraction data (discussed in more detail below).

The TeF$_5$ and TeF$_4$CF$_3$ groups display interesting spectroscopic differences. For one, the ^{19}F NMR spectrum of **1** displays a doublet ($^2J_{F\text{-}F} \approx 151$ Hz) at -53.39 ppm that corresponds to the four equatorial fluorine atoms on the TeF$_5$ group, whereas the equatorial fluorine atoms of the TeF$_4$CF$_3$ group (quartet, $^3J_{F\text{-}F} \approx 22$ Hz) are markedly shifted upfield to -68.75 ppm.[18] Slight shift differences also manifest in the ^{125}Te NMR spectra, i.e. the ^{125}Te signal of **1** appears at ca. 709 ppm vs. **13** at ca. 757 ppm. We also found that both compounds exhibit broad, intense asymmetric Te-F stretch signals in the IR spectra, though the Te-F stretch signal for **13** ($\nu = 625$ cm^{-1}) is red-shifted from that of **1** ($\nu = 655$ cm^{-1}), indicating a weaker Te-F bond. Lastly, we should note that although there is a possibility for stereoisomers for aryl-TeF$_4$CF$_3$ compounds, we observe formation of the *trans*-isomers exclusively. In part, this may be due to the fact that the *trans*-isomer is calculated to be -5.6 kcal/mol more stable at wB97XD/aug-cc-pVTZ, with an aug-cc-pVTZ-PP basis set used for the Te atom.[19-22]

Another comparison lies in the TeF$_5$ group versus the SF$_5$ group. By ^{19}F NMR, there are drastic chemical shift differences

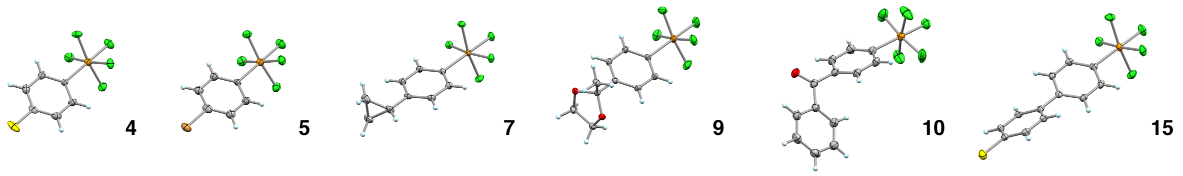


Figure 1. *Crystal structures, from left to right, of **4**, **5**, **7**, **9**, **10**, and **15** determined from single-crystal X-ray diffraction (displacement ellipsoids depicted at 50% probability level).*

in both the equatorial and axial fluorine atoms on phenyl-TeF_5 (ca. -53 and -37 ppm, respectively) from phenyl-SF_5 (ca. +63 and +85 ppm), though $^2J_{F\text{-}F}$-values are nearly identical at ca. 150 Hz. Additionally, in the IR spectra, the Te-F asymmetric stretch frequencies of **1** are 176 cm^{-1} red-shifted from the corresponding S-F stretches of phenyl-SF_5 (ν = 831 cm^{-1}).

As 1) the aryl-TeF_5 compounds in Table 1 were unexpectedly stable in air and easy to isolate and 2) the solid-state structure of aryl-TeF_5 is heretofore unknown, we grew several single crystals that proved suitable for X-ray diffraction measurements (Figure 1). The TeF_5 group exhibits a slightly distorted octahedral geometry, consistent with the ^{19}F NMR data. Analysis of the bond lengths about the Te atom in these six structures indicates average d(C_{ipso}–Te) = 2.068 Å, average d(Te–F_{ax}) = 1.838 Å, and average d(Te–F_{eq}) = 1.856 Å. Here, note that the average lengths of the Te–F_{eq} bonds are greater than the Te–F_{ax} bonds. Additionally, the average $\theta_{C\text{-}Te\text{-}Fax}$ = 179.4° does not deviate significantly from linearity; however, an average $\theta_{C\text{-}Te\text{-}Feq}$ = 94.4° indicates that the four equatorial fluorine atoms are puckered away from the arene.

To put these aspects into perspective, we examined molecular structures of **10** and **15** in juxtaposition with their SF_5 congeners **16** and **17** (Figure 2). It is evident in both cases that $\theta_{C\text{-}Te\text{-}Fax} \approx \theta_{C\text{-}S\text{-}Fax}$, but $\theta_{C\text{-}Te\text{-}Feq} > \theta_{C\text{-}S\text{-}Feq}$, indicating that equatorial fluorine atoms in the TeF_5 group deviate from 90° to a greater extent than in the SF_5 group. Unsurprisingly, the Te–C and Te–F bonds are longer than the S–C and S–F bonds, but an interesting comparison may lie the ratio of the equatorial:axial chalcogen–fluorine bonds. As mentioned above, the Te–F_{eq} bonds are longer than the Te–F_{ax} bonds on average in every aryl-TeF_5 compound discussed thus far, but this is not necessarily consistent in aryl-SF_5 compounds (i.e. there appears to be more variation in this ratio). For instance, in **16**, average d(S–F_{eq}) = 1.562 Å is approximately equal to d(S–F_{ax}) = 1.569 Å whereas in **17**, average d(S–F_{eq}) = 1.590 Å is greater than d(S–F_{ax}) = 1.549 Å.

Subsequently, we compared molecular structures of **4** and **14** for a closer look at TeF_5 vs. TeF_4CF_3 (Figure 2). Compound **14** exhibits a similar distorted octahedral geometry, although with $\theta_{C\text{-}Te\text{-}CF3}$ = 176.8° (deviating from linearity more significantly) and an average $\theta_{C\text{-}Te\text{-}Feq}$ value of 92.8° (closer to 90° than observed for the TeF_5 group). Moreover, the C_{ipso}–Te bond distances of **4** and **14** are similar, but the Te–F_{eq} bonds in **14** are notably longer (i.e. average d(1.889) = Å), which is consistent with the observed red shift of **14** in our IR data. It is also interesting to note that the F_3C–Te bond in **14** is ca. 6% longer than the C_{ipso}–Te bond. Further detailed comparisons can be made from the X-ray data tabulated in the Supporting Information.

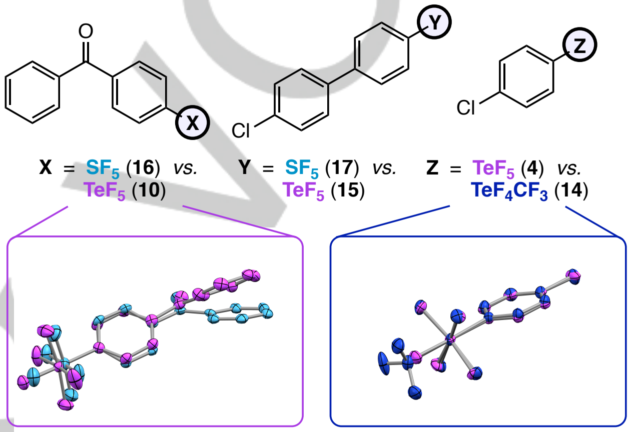


Figure 2. *(Top) Scaffolds used to compare SF_5, TeF_5, and TeF_4CF_3 in the solid state. (Bottom) Superpositions of **10** and **16** (left) and **4** and **14** (right), with hydrogen atoms omitted for clarity (displacement ellipsoids depicted at 50% probability level).*

As a final point in our structural analysis, we assessed the relative volume (V_M) of the TeF_5 group in **10** to the SF_5 group in **16** using our X-ray data (inspired by reports that have compared the volume of the SF_5 group to the CF_3 group[23,24]). Considering there are many ways to interpret and to derive V_M, we provide results from three different analyses in Table 3.[25] Just as SF_5 is ca. 1.5-1.6 times larger in volume than CF_3, TeF_5 is ca. 1.3-1.5 larger than SF_5. To take it one step further, a comparative analysis between the molecular structures of **4** and **14** revealed that the TeF_4CF_3 group, in its "highly fluorinated glory," is 1.4-1.5 times larger in volume than the TeF_5 group.

Beyond synthesis and structure, we further studied the reactivity of the TeF_5 group. According to literature precedent, phenyl-TeF_5 was used as a putative reagent in the vicinal difluorination of olefins.[8,9] First, it was synthesized from combining diphenyl ditelluride and stoichiometric XeF_2 in CH_2Cl_2 in an NMR tube, and later, an olefin was introduced directly to this mixture (i.e. phenyl-TeF_5 did not appear to be isolated or purified prior to the reaction). However, when we exposed several olefins to phenyl-TeF_5 **1** that was synthesized and isolated using our TCICA/KF protocol, *no reactivity was observed in any case.* Reactions were attempted in both CH_2Cl_2 and MeCN, at temperatures ranging from rt to 81 °C, and were monitored from hours to days (see SI for details).

Table 3. *Relative volumes (V_M) of CF_3, SF_5, TeF_5, and TeF_4CF_3 groups determined using X-ray diffraction data.*[26-28]

Substituent	*V_1/Z_1-V_2/Z_2 (Å^3)^a*	*Hirshfeld (Å^3)^b*	*Promolecule (Å^3)^b*
CF_3	39.2^c	47.9	44.0
SF_5	62.6^c	75.7	66.5
TeF_5	**95.1^c**	**92.6^e**	**82.5^e**
TeF_4CF_3	**138.1^d**	**125.0**	**112.2**

[a]Referenced to unsubstituted benzophenone molecular structure to obtain initial value for CF_3, assuming a spherical hydrogen atom with V_{vdW} = 7.2 Å^3. [b]Calculated using Crystal Explorer. [c]Determined by comparing molecular structures with same benzophenone core. [d]Determined by comparing molecular structures with same *para*-chloro-phenyl core. [e]Determined for benzophenone derivative.

We found this quite peculiar; therefore, we conducted a short series of control experiments. First, using styrene as a substrate, we were able to reproduce the literature procedure (albeit synthesizing (1,2-difluoroethyl)benzene in a significantly lower yield than previously reported).[8,9] Notably, (1,2-difluoroethyl)benzene (and all other reported products of putative difluorination with phenyl-TeF_5) would also be the expected products of a reaction with XeF_2.[29] Indeed, we confirmed that this product is also formed in 70% yield using only stoichiometric XeF_2. We then wondered if unreacted XeF_2 could initiate a chain reaction with phenyl-TeF_5, but doping a reaction mixture of **1** and styrene with 30 mol % XeF_2 only resulted in 14% yield of the difluoride product, with no degradation of **1** by ^{19}F NMR. In light of the fact that product formation was only observed in reaction mixtures where XeF_2 could have been present, XeF_2 may be the real actor in difluorination under previously reported conditions. Accordingly, the behavior of phenyl-TeF_5 as a "difluorination reagent" may be a misconception, as pure phenyl-TeF_5 in our hands was *completely unreactive* toward styrene and several other olefins (as well as alkynes) under conditions outlined in the SI. Or, at the very least, phenyl-TeF_5 requires some form of activation for such a reaction to occur; this remains unclear.

On the other hand, we were able to reproduce a number of the reactions of phenyl-TeF_5 with nucleophiles (such as alcohols,[7] secondary amines,[7] and azides[30] – see SI for details) that have been reported in the last few decades. Primarily *cis*-isomers were formed in each case (by substitution of an equatorial fluorine atom with a nucleophile), which is consistent with our observation in the X-ray data that Te-F_{eq} bonds are, on average, longer than Te-F_{ax} bonds. In an attempt to expand upon these reports, we examined reactions of **1** with a variety of additional nucleophiles (e.g. KCN, tBuNC, $AgSCF_3$, KSCN, PhLi, and MeLi), only to find that **1** stays completely intact. Additionally, we explored the reactivity of **1** with a number of substrates under 300 nm irradiation, in both the presence and absence of sensitizers. Again, in all cases, **1** is ostensibly unreactive. From another perspective, we also examined the behavior of **1** in the presence of TMS-X reagents (e.g. X = CF_3, CF_2H, CF_2CF_3, CN, and acetylide) – with and without CsF – and observed no reactivity.

Lastly, we investigated the hydrolytic stability of **1** and **13**. A sample of each was stored in a borosilicate vial and kept in a refrigerator for ca. 1 year with virtually no degradation by ^{19}F NMR analysis. Moreover, most of the single crystals were grown in vessels that were open to air from days to months, with virtually no observable degradation. However, when dissolved in MeCN and exposed to excess H_2O, **1** and **13** underwent rapid and virtually complete conversion to *cis*-phenyl-TeF_4OH (**18**) and putative *eq*-phenyl-$TeF_3(CF_3)OH$ (**19**), respectively, in 5 min (Figure 3). The ^{19}F NMR spectrum of **18** is consistent with what was reported by Janzen and co-workers,[31] and we can now characterize **19** by ^{19}F NMR: -49.99 ppm (1F, tq, *J* = 59.2, 28.5 Hz), -59.74 (3F, dt, *J* = 28.5, 19.6 Hz), -73.24 (2F, dq, *J* = 59.2, 19.6 Hz). In addition, we note that the ^{125}Te NMR chemical shift difference between **1** (709 ppm) and its corresponding monohydrolysis product **18** (735 ppm) is more pronounced than the shift difference between **13** (757 ppm) and its corresponding monohydrolysis product **19** (762 ppm). It was also observed that exchange of additional fluorine atoms with OH groups will continue to happen more slowly over time.[32]

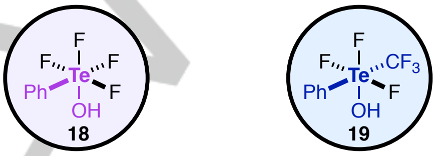


Figure 3. *Monohydrolysis products derived from* ***1*** *(left) and* ***13*** *(right) characterized by ^{19}F NMR.*

Yet, overall, the TeF_5 and TeF_4CF_3 groups on arenes are surprisingly more robust than previous literature implies. Leading up to this finding, the divergent behavior of Te-based substrates from previously reported S- and Se-based substrates using our newly-developed TCICA/KF oxidative fluorination approach has enabled us 1) to synthesize several new aryl-TeF_5 and aryl-TeF_4CF_3 compounds, 2) to analyze their solid-state structures in detail, and 3) to investigate (and begin to address some misconceptions regarding) reactivity. Given the observed decomposition of aryl-TeF_5 and aryl-TeF_4CF_3 compounds on *direct* contact with water in solution, these compounds may less likely be of interest to the medicinal chemistry and agrochemistry communities; rather, their otherwise relative stability, size, and properties may have a more realistic appeal to applications in certain materials, such as liquid crystals.[33] Investigations are currently ongoing in our group.

Acknowledgements

We thank the ETH transfer office for support in filing a patent application on this work, in which C.R.P., N.S., and A.T. are listed as inventors, as well as Dr. René Verel (ETH Zürich) for his help. MoBiAS (ETH) is acknowledged for assistance with HRMS analyses. Financial support was provided by ETH Zürich and the ETH Postdoctoral Fellowship Program (C.R.P.).

Conflict of Interest

The authors declare no conflict of interest.

Keywords: fluorine chemistry • structural chemistry • oxidative fluorination • trichloroisocyanuric acid • tellurium

[1] C. R. Pitts, D. Bornemann, P. Liebing, N. Santschi, A. Togni, *Angew. Chem. Int. Ed.* **2019**, *58*, 1950-1954.

[2] More recently, we also reported an application of this TCICA/KF oxidative fluorination approach to aryl iodides in the synthesis of aryl-IF_2 and aryl-IF_4 compounds. See: J. Häfliger, C. R. Pitts, D. Bornemann, R. Käser, N. Santschi, J. Charpentier, E. Otth, N. Trapp, R. Verel, H. P. Lüthi, A. Togni, *Chem. Sci.* **2019**, DOI: 10.1039/c9sc02162k.

[3] L. Engman, *Acc. Chem. Res.* **1985**, *18*, 274-279.

[4] T. Chivers, R. S. Laitinen, *Chem. Soc. Rev.* **2015**, *44*, 1725-1739.

[5] P. R. Savoie, J. T. Welch, *Chem. Rev.* **2015**, *115*, 1130–1190.

[6] K. Alam, A. F. Janzen, *J. Fluorine Chem.* **1985**, *27*, 467-470.

[7] A. F. Janzen, K. Alam, B. J. Blackburn, *J. Fluorine Chem.* **1989**, *42*, 173-178.

[8] S. A. Lermontov, S. I. Zavorin, I. V. Bakhtin, N. S. Zefirov, P. J. Stang, *Phosphorus, Sulfur Silicon Relat. Elem.* **1995**, *102*, 283-286.

[9] S. A. Lermontov, S. I. Zavorin, I. V. Bakhtin, A. N. Pushin, N. S. Zefirov, P. J. Stang, *J. Fluorine Chem.* **1998**, *87*, 75-83.

[10] X. Ou, A. F. Janzen, *J. Fluorine Chem.* **2000**, *101*, 279-283.

[11] L. Engman, J. Persson, *J. Organomet. Chem.* **1990**, *388*, 71-74.

[12] F. V. Singh, H. A. Stefani, *Tetrahedron Lett.* **2010**, *51*, 863-867.

[13] J. Liu, M. Qiu, X. Zhou, *Synth. Commun.* **1990**, *20*, 2759-2767.

[14] U. Tilstam, H. Weinmann, *Org. Process Res. Dev.* **2002**, *6*, 384–393.

[15] T. Umemoto, S. Ishihara, *J. Am. Chem. Soc.* 1993, **115**, 2156–2164.

[16] E. Pietrasiak, A. Togni, *Organometallics*2017, **36**, 3750–3757.

[17] T. Sperger, S. Guven, F. Schoenebeck, *Angew. Chem. Int. Ed.* **2018**, *57*, 16903-16906.

[18] Another interesting comparison to the arene-based TeF_4CF_3 group is the corresponding SF_4CF_3 group, for instance, see: P. Kirsch, A. Hahn, *Eur. J. Org. Chem.* **2006**, *2006*, 1125-1131.

[19] Gaussian 09, Revision D.01; Gaussian, Inc.: Wallingford, CT, 2013.

[20] J.-D. Chai, M. Head-Gordon, *Phys. Chem. Chem. Phys.* **2008,** *10,* 6615-6620.

[21] T. H. Dunning, *J. Chem. Phys.* **1989**, *90*, 1007-1023.

[22] K. A. Peterson, D. Figgen, E. Goll, H. Stoll, M. Dolg, *J. Chem. Phys.* **2003**, *119*, 11113-11123.

[23] C. Hansch, A. Leo, S. H. Unger, K. H. Kim, D. Nikaitan, E. J. Lien, *J. Med. Chem.* **1973**, *16*, 1207–1216.

[24] M. F. Sowaileh, R. A. Hazlitt, D. A. Colby, *ChemMedChem* **2017**, *12*, 1481-1490, and references cited therein.

[25] The molecular structures for benzophenone, 4-(trifluoromethyl)-benzophenone, and 4-(pentafluorosulfanyl)benzophenone used in this comparative analysis were previously reported, and have CCDC deposition numbers of 1114983, 1005255, and 1865801, respectively.

[26] M. J. Turner, J. J. McKinnon, S. K. Wolff, D. J. Grimwood, P. R. Spackman, D. Jayatilaka, M. A. Spackman, CrystalExplorer17 (2017). University of Western Australia. http://hirshfeldsurface.net.

[27] M. A. Spackman, D. Jayatilaka, *CrystEngComm* **2009**, *11*, 19-32.

[28] M. A. Spackman, *Phys. Scr.* **2013**, *87*, 048103.

[29] For instance, see: M. Zupan, A. Pollak, *J. Org. Chem.* **1976**, *41*, 4002-4004.

[30] T. M. Klapötke, B. Krumm, K. Polborn, I. Schwab, *J. Am. Chem. Soc.* **2004**, *126*, 14166-14175.

[31] A. F. Janzen, K. Alam, M. Jang, B. J. Blackburn, A. S. Secco, *Can. J. Chem.* **1988**, *66*, 1308-1312.

[32] For instance, after 36 h, Ph-$TeF_2(OH)_2(CF_3)$ – the putative dihydrolysis product – was observed as the major species: ^{19}F NMR (282 MHz, CD_3CN): -59.97 (3F, t, *J* = 16.6 Hz), -72.16 (2F, q, *J* = 16.6 Hz).

[33] M. Bremer, P. Kirsch, M. Klasen-Memmer, K. Tarumi, *Angew. Chem. Int. Ed.* **2013**, *52*, 8880-8896.