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Synthetic Approaches to Fluoroalkyltelluryl-Substituted Compounds

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Abstract: Fluorinated substituents confer specific properties to molecules. Merging of chalcogenes with trifluoromethyl or fluoroalkyl moieties has known, these last years, a growing interest. However, the last non-radioactive family member, namely tellurium, has relatively been forgotten. This review will present and discuss a state of the art of R_FTe chemistry to describe the already available methods and to bring to light the future developments to consider.

1. Introduction

Because of the specific properties of fluorine atom, fluorinated compounds have known a growing interest these last decades.^[1] Because of this huge interest, these last years have seen a high development in the seeking of new emerging fluorinated groups to brought new, modulative, properties to substrates for various applications.^[2] In this new quest, merging of fluoroalkyl moieties with heteroatoms has blossomed, with a particular attention to chalcogen family because of the peculiar obtained properties. For instance, CF₃E (E = O, S, Se) substituents are known, among other things, to increase lipophilicity of molecules, as illustrated by their Hansch-Leo parameters (CF₃O: $\pi_R = 1.04$, CF₃S: $\pi_R = 1.44$, CF₃Se: $\pi_R = 1.29$),^[3] which can contribute to favor bioavailability of bioactive compounds.

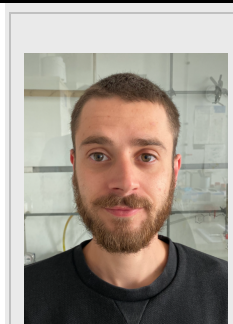
If the association of R_F groups with O, S, Se begins to be well documented, with recent elegant and efficient strategies and reagents,^[4] the last, non-radioactive, chalcogen, namely tellurium, appears as the “forgotten element”.

Contrary to its congeners, tellurium has no apparent role in biology.^[5] However, tellurium derivatives have found these last years some applications in materials and electronics.^[6] Furthermore, tellurolated compounds have been also developed in medicinal chemistry.^[7]

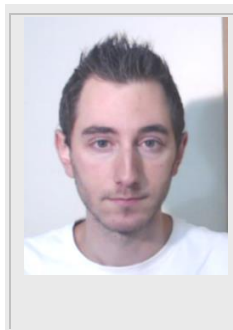
Consequently, molecules bearing a CF₃Te, and more generally R_FTe, group could be pertinent to develop, not only to determine properties of these substituents in comparison of their other chalcogen analogues, but also to study the relevance and potentialities of the obtained compounds.

In this objective, this review will propose a state-of-art concerning R_FTe chemistry to expose the synthetic possibilities already available and, maybe, to underline the “missing reactions” to develop to enlarge the available toolbox.

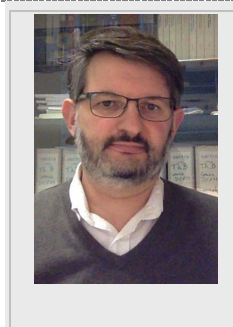
Kevin Grollier is born in 1995 in Nîmes (France). He graduated his Technical University Degree in Montpellier then obtained his Bachelor and Master's degree in organic chemistry at the University of Lyon in 2018. Currently in Ph.D under the supervision of Dr. Thierry Billard at the university of Lyon. His main Ph.D research topic is about developing new accesses to trifluoromethylselenolated molecules.



Alexis Taponard graduated his Technical University Degree in chemistry in 2016 at the University of Lyon and then his Chemical Engineering Degree in 2019 at the ECPM engineering school, a component of the University of Strasbourg. He is currently finishing his Master's Degree in organic chemistry by doing his end-of-studies internship under the supervision of Dr. Thierry Billard at the University of Lyon.



Dr. Thierry Billard is CNRS Research Director. He carried out his Ph.D. on fluorine chemistry (University of Lyon, France), a postdoctoral research in medicinal chemistry (University of Louvain, Belgium) and has completed an industrial postdoctoral stay (Rhône-Poulenc). His research activities are interdisciplinary involving chemistry and medicine with a focus on fluorine chemistry, medicinal chemistry, radiochemistry and their applications in medical imaging and neurosciences.



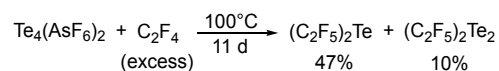
2. De novo construction

Few fluoroalkyltellurolated compounds have been obtained by fluoro tellurolation of tetrafluoroethylene. Thus, reactions between C₂F₄ and solid Te₄(AsF₆)₂ or Te₆(AsF₆)₂ led to mixture of (C₂F₅)₂Te, (C₂F₅)₂Te₂ and C₄F₉TeC₂F₅. Similar results were observed with SO₂F₂ as solvent. In presence of SO₂ as solvent, C₂F₅TeC₃F₆C(O)F was obtained in addition of previous

products.^[8] In these reactions, tellurium (hexafluoroarsenate) derivatives act as tellurolating and fluorinating reagents.

However, the lone preparative method, with products isolation, described is the neat reaction between C₂F₄ and solid Te₄(AsF₆)₂ (Scheme 1).^[8b] Nevertheless, this method appears to be very specific and cannot, reasonably, be considered as a "standard" synthetic procedure.

Noteworthy, ditelluride ((C₂F₅)₂Te₂) readily decomposes in light into monotelluride ((C₂F₅)₂Te) through extrusion of tellurium metal.^[8b]



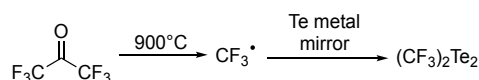
Scheme 1. Fluoro tellurolation of tetrafluoroethylene.

3. Indirect Approach

Another strategy to achieve fluoroalkyltellurolated molecules is based on the R_F-TeR bond disconnection via the fluoroalkylation of tellurolated substrates.

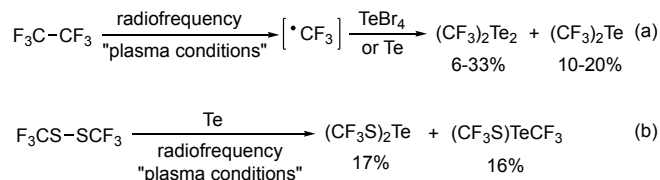
3.1. Radical fluoroalkylation

The first synthesis of a trifluoromethyltellurolated derivative was described in early sixties by trapping trifluoromethyl radical, generated by pyrolysis of hexafluoroacetone, with a tellurium metal mirror. Thus bis(trifluoromethyl)ditelluride was formed, but no yields were provided (Scheme 2).^[9]



Scheme 2. Radical trifluoromethylation of tellurium metal mirror.

Reactive trifluoromethyl radicals can be generated by using a plasma source. In these conditions, homolytic C-C bond scission of hexafluoroethane produced CF₃[•] radical which reacted with tellurium metal or TeBr₄ to yield ditelluride (CF₃)₂Te₂ and monotelluride (CF₃)₂Te (Scheme 3a).^[10]



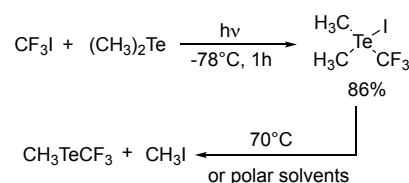
Scheme 3. Trifluoromethylation of tellurium derivatives under plasma conditions.

Similar reaction has been also described starting with CF₃SSCF₃. In this example, the expected (CF₃S)₂Te was obtained along with (CF₃S)TeCF₃ coming from generation of trifluoromethyl radical from CF₃SSCF₃ (Scheme 3b).^[11]

Even if this method is conceptually original, it requires very specific technical equipment to provide expected compounds in

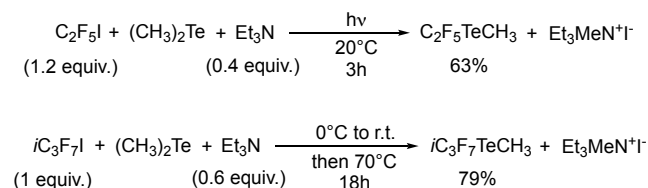
low yields and with a very limited scope. That reasonably precludes such an approach as preparative and synthetic tool.

Photochemical reactions between R_FI and dimethyl telluride have been also described.^[12] CF₃I and (CH₃)₂Te react at -78°C under irradiation to form [(CH₃)₂TeCF₃]I salt. This species decomposes from 70°C, or slowly in highly polar solvents, to CH₃TeCF₃ and MeI (Scheme 4).^[12b, 12c]



Scheme 4. Photochemical reaction of CF₃I with (CH₃)₂Te.

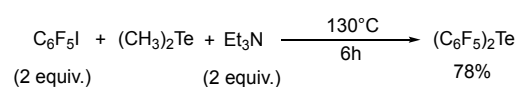
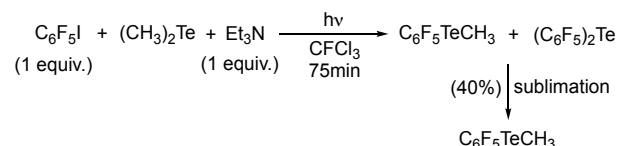
In the cases of pentafluoroethyl iodide (C₂F₅I) and heptafluoroisopropyl iodide (iC₃F₇I), equilibrated reaction was rather observed to directly provide MeTeR_F and MeI. The addition of triethyl amine, which traps the formed MeI, favored the formation of MeTeR_F, by equilibrium displacement. If irradiation is required with C₂F₅I, the more reactive iC₃F₇I, thermal reaction was preferred to avoid complex reaction (Scheme 5).^[12b]



Scheme 5. Reaction between R_FI and (CH₃)₂Te.

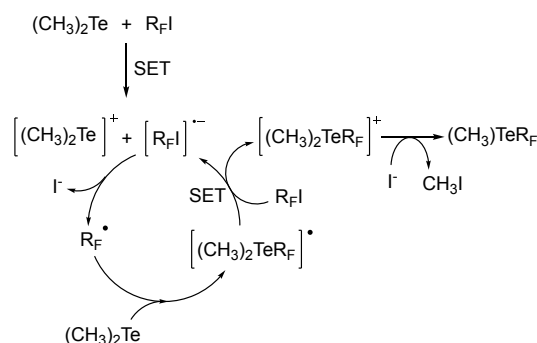
Nevertheless, the preparation of di(perfluoroalkyl)-telluride or ditelluride with this method by using an excess of R_FI is not recommended because mixtures, difficult to separate, were generally obtained.

Similar reaction was also performed in aromatic series with C₆F₅I. In photochemical conditions, mixture of C₆F₅TeCH₃ and (C₆F₅)₂Te was obtained. However, both compounds are easy to separate by sublimation (Scheme 6). Thus, C₆F₅TeCH₃ had been successfully prepared with medium yield. Under thermal conditions, monotelluride is the major obtained product (Scheme 6).^[12b]



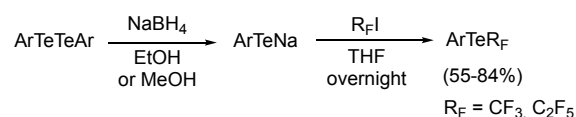
Scheme 6. Reaction of (C₆F₅)I with (CH₃)₂Te.

The proposed mechanism for these reactions is a SET process between R_FI and telluride species (Scheme 7).^[12b]

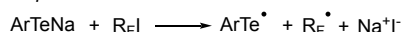


Scheme 7. Mechanism of the reaction of R_FI with (CH₃)₂Te.

Aryltelluride anions, easily generated by reduction of corresponding ditellurides, can also react with R_FI, through a SET process, to give expected fluoroalkyltellurolated compounds (Scheme 8).^[13]

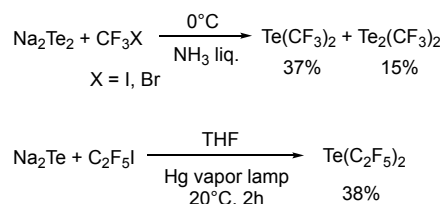


SET process :



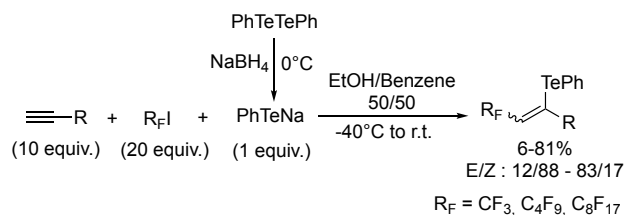
Scheme 8. Reaction of R_FI with aryltelluride anions.

Noteworthy, a similar reaction was also performed with CF₃Br instead of CF₃I, but with a longer reaction time (2 days). Similar reaction was performed with disodium ditelluride and trifluoromethyl or pentafluoroethyl halogenides.^[14] Thus, CF₃I or CF₃Br react with Na₂Te₂ in liquid ammoniac to give a mixture of mono- and ditelluride (Scheme 9). In the case of C₂F₅I, better results were obtained in THF under irradiation (Scheme 9). Even if, no mechanism is suggested, we can also reasonably suppose a SET process.^[14]



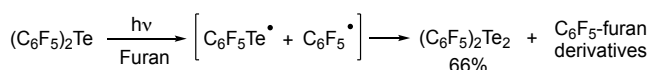
Scheme 9. Preparation of fluoroalkyltellurides from R_FI and Na₂Te₂.

This concept of SET process was also applied to the addition of fluoroalkyl and phenyltelluryl moieties onto terminal alkynes (Scheme 10).^[15]



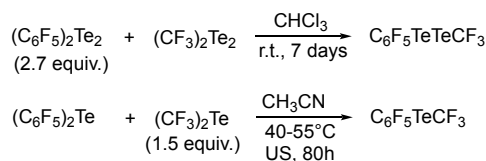
Scheme 10. Addition onto triple bond of R_F and PhTe.

Bis(pentafluorophenyl)ditelluride was prepared and isolated in pure form by irradiation of bis(pentafluorophenyl)monotelluride through a radical process (Scheme 11).^[16]



Scheme 11. Synthesis of bis(pentafluorophenyl)ditelluride.

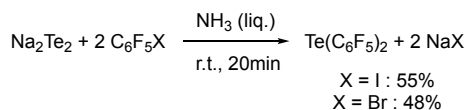
Unsymmetrical tellurides were obtained by mixing two different fluoroalkyl tellurides (Scheme 12). However, no yields were reported. Mechanistically, this cross fluorinated groups exchange can be envisaged through radical or nucleophilic pathway, but no precisions were provided.^[16]



Scheme 12. Unsymmetrical tellurides synthesis.

3.2. Electrophilic fluoroalkylation

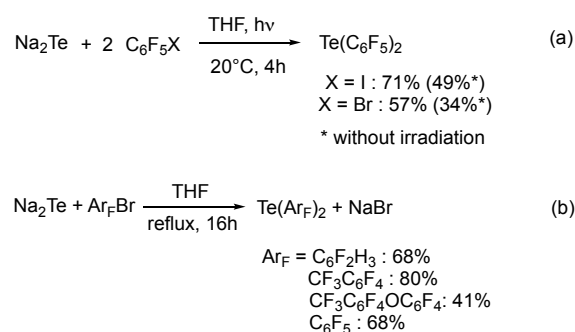
Pentafluorophenyl iodide and bromide were reacted with disodium ditelluride to form the corresponding telluride in moderate yields (Scheme 13). Noteworthy, the same reaction was done with disodium telluride but only traces of the expected product were formed, mainly due to the poor solubility of Na₂Te in liquid ammoniac.^[14]



Scheme 13. Preparation of Te(C₆F₅)₂ from C₆F₅X and Na₂Te₂.

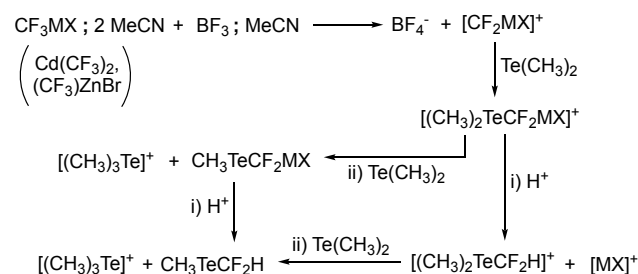
To circumvent this solubility issue, the same reaction was optimized in THF. Better yields were obtained under white lamp irradiation (Scheme 14a). A modified version of this procedure, without any irradiation, was applied to provide other fluoroaryl tellurides. The mandatory presence of both fluorine atoms in ortho-positions of bromine was demonstrated, which would lead to envisage an aromatic nucleophilic substitution mechanism. However, other evidences (blue color in liquid NH₃, influence of

irradiation) could also advocate for a SET pathway, as previously suggest in aliphatic series (Scheme 14b).^[17]



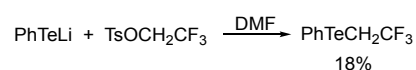
Scheme 14. Reaction between Ar_FX and Na_2Te .

An interesting approach to obtain mono-difluoromethyl telluride was based on the electrophilic reactivity of difluorinated carbenoid species with di(methyl)telluride. Metallic carbenoid species is generated by fluorine abstraction with BF_3 from trifluoromethylated metallic complexes ($\text{Cd}(\text{CF}_3)_2$; 2 MeCN or $\text{Zn}(\text{CF}_3)_2$; 2 MeCN). This electrophilic species can then react with di(methyl)telluride, which acts as a Lewis base, to afford a (difluoromethyl)tellurium cation intermediate. This last one leads to the expected difluoromethyl methyl telluride by a sequence: (i) protonation, (ii) abstraction of methyl group by $\text{Te}(\text{CH}_3)_2$ to generate a trimethylchalcogenium ion. Noteworthy this reaction sequence can also be inverted (Scheme 15). Nevertheless, no yields were given for this original reaction.^[18]



Scheme 15. Preparation of $\text{CH}_3\text{TeCF}_2\text{H}$ from carbenoid species.

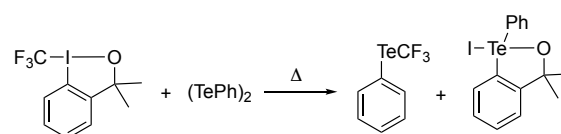
If substitution reactions onto CF_3 carbon are generally extremely difficult to perform, the insertion of a CH_2 spacer can facilitate such reactions. Thus, trifluoromethyl phenyl telluride was prepared through nucleophilic substitution of tosylate group by lithium telluride species. Unfortunately, only 18% of the expected product was obtained, certainly due to the low electrophilicity of $\text{TsOCH}_2\text{CF}_3$ (Scheme 16).^[19]



Scheme 16. Preparation of $\text{PhTeCH}_2\text{CF}_3$ from $\text{TsOCH}_2\text{CF}_3$ and PhTeLi .

One of the most common electrophilic trifluoromethylating reagent was developed by the Togni group and is based on a hypervalent iodide structure. Recently, they shown the possible

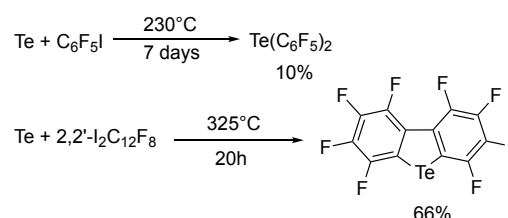
attack of this reagent onto diphenyl telluride to form PhTeCF_3 . Nevertheless, no yield was specified because a hypervalent tellurium compound was concomitantly formed and has focused more attention from the authors (Scheme 17).^[20]



Scheme 17. Preparation of PhTeCF_3 from a Togni's reagent.

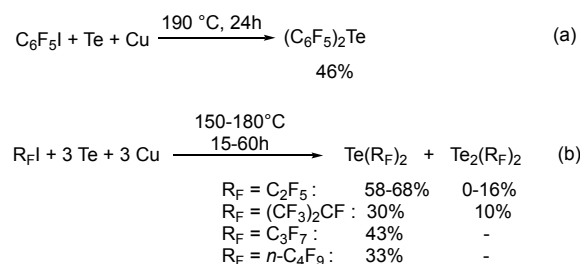
3.3. Nucleophilic fluoroalkylation

Perfluoroaryl tellurides were obtained by reaction of perfluoroaryl iodide and tellurium metal at high temperature. If bis(pentafluorophenyl)telluride was only obtained in very low yield, cyclic perfluorodibenzotellurophene was prepared in 66% yield. No mechanism details were provided and both radical pathway and transient organometallic species formation could be considered (Scheme 18).^[21]



Scheme 18. Reaction of perfluoroaryl iodides with Te.

Such reactions were favored in presence of Cu, as catalyst and iodine scavenger, and $\text{Te}(\text{C}_6\text{F}_5)_2$ was then obtained in 46% yield (Scheme 19a).^[22] The method was also extended to perfluoroalkyl iodides to afford various $\text{Te}(\text{R}_F)_2$ in moderate to good yields. In some cases, the formation of $\text{Te}_2(\text{R}_F)_2$ as byproduct was observed (Scheme 19b).^[23] The authors suggest the formation of " $\text{R}_F\text{-Cu}$ " intermediates.

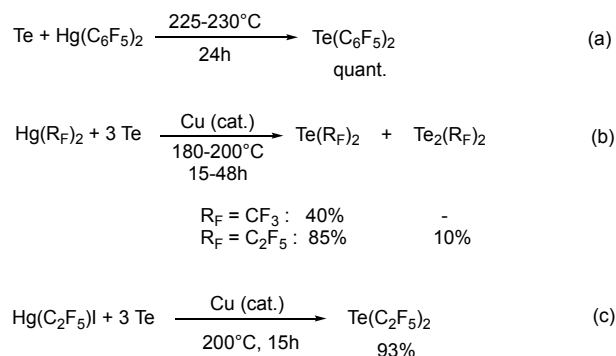


Scheme 19. Copper catalyzed reactions between R_FI and Te.

The use of mercurial derivatives as effective nucleophilic organometallic reagents was more efficient to form $\text{Te}(\text{C}_6\text{F}_5)_2$, in quantitative yield (Scheme 20).^[21, 24]

This reaction was also applied to prepare aliphatic fluoroalkyltellurated compounds, but in presence of elemental copper as catalyst. Depending on the starting fluoroalkyl mercurial reagent and the reaction conditions, ditelluride can be

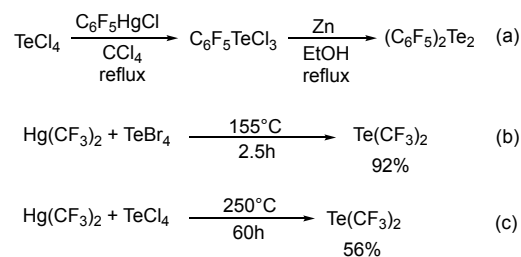
observed as by product (up to 20% after 60h at 200-220°C). However, with the appropriate procedure only the expected monotelluride can be obtained in moderate to excellent yields (Scheme 20). According to the authors, a R_F-Cu intermediate would seem to be the transient reactive species.^[23]



Scheme 20. Reaction of fluorinated mercurial reagents and Te.

To avoid tellurium metal, tellurium tetrahalides were also used. Thus, Te₂(C₆F₅)₂ was obtained by reaction between C₆F₅HgCl and TeCl₄ followed by a zinc mediated dechlorination. However, a low yield is revendicated by the authors without any other precisions (Scheme 21a).^[25]

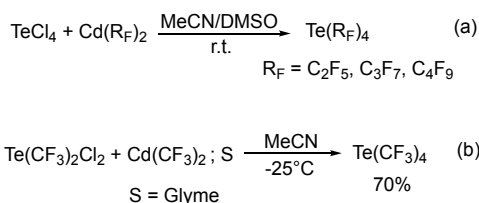
Nevertheless, similar procedures afforded the preparation of di(methyl)telluride with excellent yields. In this case, tellurium tetrabromide is more reactive than chloride derivative and provides better results in milder conditions (Scheme 21b-c).^[26]



Scheme 21. Reaction of fluorinated mercury reagents with TeX₄.

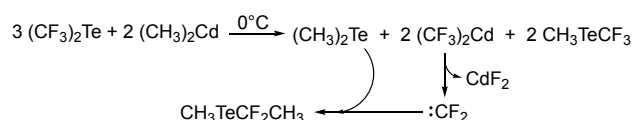
Cadmium derivatives are also known as fluoroalkylating reagents. Therefore, they can also react with TeCl₄ to give the corresponding tetra(fluoroalkyl)tellurides (Scheme 22a). Unfortunately, no yields were mentioned.^[27]

Tetra(trifluoromethyl)telluride was formed by reaction of bis(trifluoromethyl) cadmium ; glyme complex with (CF₃)₂TeCl₂ (obtained by chlorination of (CF₃)₂Te^[28]) with good yields.^[26b, 27, 29] Noteworthy, (CF₃)₄Te appeared to be sensitive to light and temperature. Similar procedure was extended to higher fluorinated homologs but no yields were reported (Scheme 22b).^[27]



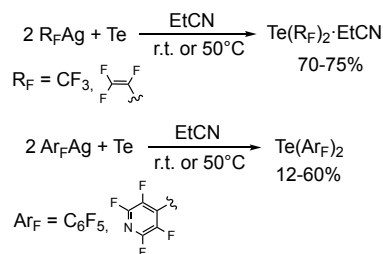
Scheme 22. Synthesis of Te(R_F)₄ from Cd(R_F)₂.

Cd(CF₃)₂ was also used as difluorocarbene generator to perform carbene insertion within (CH₃)₂Te. These two reagents were in situ generated from Te(CF₃)₂ and Cd(CH₃)₂ (Zn(CH₃)₂ is also mentioned) by ligand exchanges between tellurium and cadmium. This process requires low temperature (0°C) because the reaction is violent in absence of a complexing agent of cadmium reagent (Scheme 23).^[30] Same reactions can be performed at higher temperature in presence of a complexing agent (diglyme, glyme, pyridine or acetonitrile). Formation of difluorocarbene occurred between -20°C and 50°C with an optimal temperature around 30-40°C with Cd(CF₃)₂ ; diglyme complex (or Zn equivalent).^[30] Nevertheless, no yields were provided for this reaction.



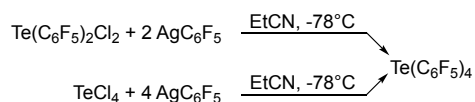
Scheme 23. Difluorocarbene insertion within (CH₃)₂Te.

Silver salts are well-known to stabilize fluoroalkyl anions, and in particular CF₃⁻ anion. Trifluoromethyl silver can react with tellurium metal to provide the corresponding bis(trifluoromethyl)telluride (Scheme 24). The authors described the formation of a complex with solvent. No precisions about isolation of this compound were specified.^[31] Similar reaction was performed with C₂F₅Ag (Scheme 24). However, as with CF₃, the obtained (C₂F₅)₂Te appears to be difficult to isolate in pure form, because of Lewis acid-base interactions with the solvent.^[32] With perfluoroaryl silver reagents, it would seem that pure compounds were obtained (Scheme 24).^[31, 33]



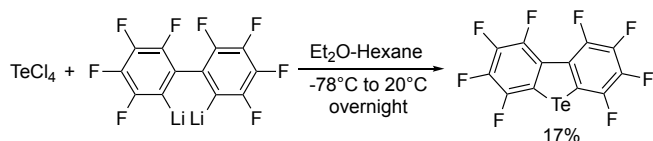
Scheme 24. Preparation of (R_F)₂Te from R_FAg.

Tetra(perfluorophenyl)telluride was also obtained starting from tellurium chloride derivatives. However, even if good yields are claimed, no values are clearly mentioned (Scheme 25).^[34]



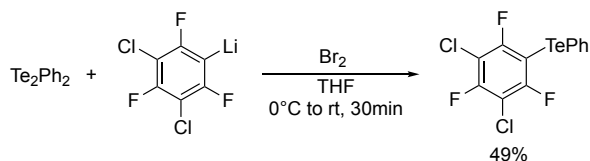
Scheme 25. Preparation of $\text{Te}(\text{C}_6\text{F}_5)_4$.

Perfluoroaryl lithium reagents are easy to access and can be used as nucleophilic reagents. Thus, they can react with tellurium tetrachloride to provide corresponding bis(perfluoroaryl)telluride.^[21, 25, 35] Nevertheless, low yields or no yields were described. Same conditions were applied to 2,2'-(perfluorobiphenyl)dilithium to synthesize perfluorodibenzotellurophene but again with low yield (Scheme 26).^[21]



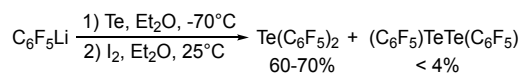
Scheme 26. Synthesis of perfluorodibenzotellurophene.

Unsymmetrical telluride was obtained by reaction between 3,5-dichloro-2,4,6-trifluorophenyllithium and diphenylditelluride, in presence of bromide, with a good yield (Scheme 27).^[36]



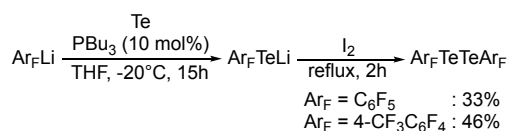
Scheme 27. Preparation of 3,5-dichloro-2,4,6-trifluorophenyl phenyl telluride.

Formation of bis(perfluorophenyl)ditelluride was envisaged by forming, in situ, $\text{C}_6\text{F}_5\text{TeI}$ as intermediate which was expected to decompose into the ditelluride. However, it reacted mainly with remaining $\text{C}_6\text{F}_5\text{Li}$ to provide, finally, the corresponding $\text{Te}(\text{C}_6\text{F}_5)_2$ with a good yield (Scheme 28).^[37]



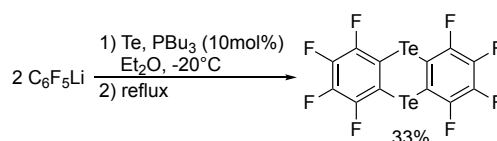
Scheme 28. Preparation of $\text{Te}(\text{C}_6\text{F}_5)_2$ from $\text{C}_6\text{F}_5\text{Li}$ and elemental tellurium.

A few years later, the same authors developed a new strategy to prepare $\text{Te}_2(\text{Ar}_F)_2$ compounds with improved yields. The first step was always the reaction of Ar_FLi with tellurium metal. This insertion was described as rather difficult which could explain the disappointing yield of ditelluride formation in their previous work. Consequently, they used phosphines to catalyze this tellurium insertion. The intermediate formation of phosphane tellurides as soluble tellurium sources is revindicated. In a second step, oxidation of Ar_FTeI with iodine led to the desired ditellurides in moderate yields (Scheme 29).^[38]



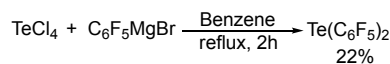
Scheme 29. Preparation of $\text{Te}_2(\text{Ar}_F)_2$ from Ar_FLi .

Stability of lithium perfluoroaryltellurolates differs depending on the solvent. In THF, the solution is stable under reflux but quite sensitive to hydrolysis. In Et_2O , in the case of $\text{C}_6\text{F}_5\text{Li}$, a significant amount of another fluorinated compound is detected, even at -20°C . This latter was identified as octafluorotelluranthrene and is formed by dimerization of two molecules of $\text{C}_6\text{F}_5\text{TeLi}$ with elimination of LiF , through a suspected $\text{S}_{\text{N}}\text{Ar}$ reactions (Scheme 30).^[38] Under the same conditions, $p\text{-CF}_3\text{C}_6\text{F}_4\text{TeLi}$ provided only a complex mixture.



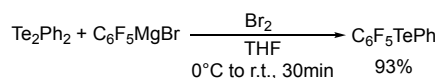
Scheme 30. Synthesis of octafluorotelluranthrene.

Like lithium compounds, perfluoroaryl Grignard reagents were also used as nucleophilic sources. Thus, $\text{Te}(\text{C}_6\text{F}_5)_2$ was prepared from $\text{C}_6\text{F}_5\text{MgBr}$ and TeCl_4 (Scheme 31). Only crude yield was mentioned.^[39]



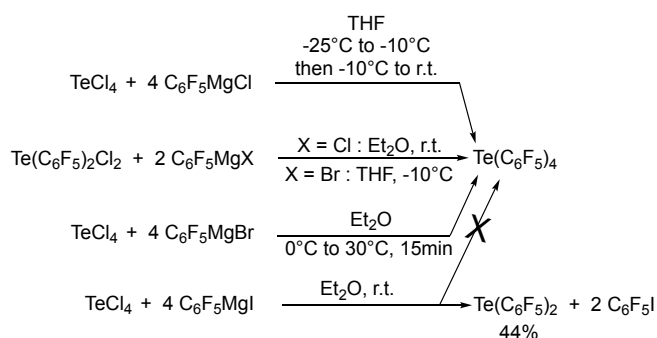
Scheme 31. Preparation of $\text{Te}(\text{C}_6\text{F}_5)_2$ from $\text{C}_6\text{F}_5\text{MgBr}$ and TeCl_4 .

Unsymmetrical $\text{C}_6\text{F}_5\text{TePh}$ was obtained with excellent yield from $\text{C}_6\text{F}_5\text{MgBr}$ and Te_2Ph_2 in presence of bromine, through the intermediate formation of PhTeBr (Scheme 32).^[36]



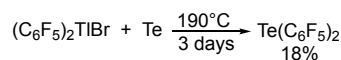
Scheme 32. Synthesis of $\text{C}_6\text{F}_5\text{TePh}$ from $\text{C}_6\text{F}_5\text{MgBr}$ and Te_2Ph_2 .

Finally, the synthesis of $\text{Te}(\text{C}_6\text{F}_5)_4$ was investigated with various Grignard reagents as well as different tellurium sources. Apart with iodide derivatives which led to $\text{Te}(\text{C}_6\text{F}_5)_2$, the different methods are claimed to give good results. However, the exact yields are often not clearly mentioned (Scheme 33). According to the authors, reaction between $\text{C}_6\text{F}_5\text{MgBr}$ and TeCl_4 would be the cheapest and most interesting strategy.^[34]



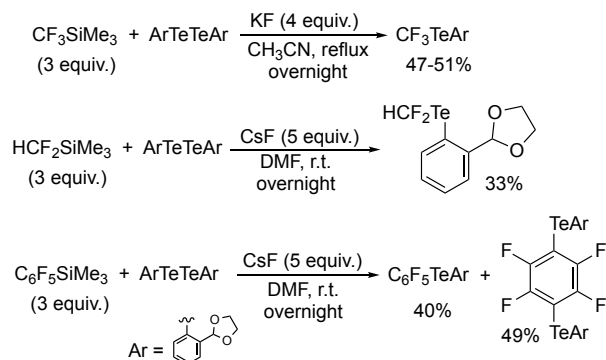
Scheme 33. Synthesis of $\text{Te}(\text{C}_6\text{F}_5)_4$ with Grignard reagents.

Interestingly, $\text{Te}(\text{C}_6\text{F}_5)_4$ was then used as nucleophilic C_6F_5 donor. In some reactions, $\text{Te}(\text{C}_6\text{F}_5)_2$ was formed as co-product. More anecdotally, thalium derivative was also used as nucleophilic source of C_6F_5 to react with tellurium metal under thermic conditions. $\text{Te}(\text{C}_6\text{F}_5)_2$ was then formed by with a low yield (Scheme 34).^[40]



Scheme 34. Synthesis of $\text{Te}(\text{C}_6\text{F}_5)_2$ from $(\text{C}_6\text{F}_5)_2\text{TlBr}$.

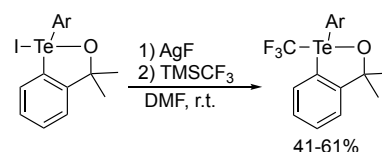
The most known and maybe used today as nucleophilic source of CF_3 is the Ruppert-Prakash reagent (CF_3SiMe_3) and by extension its higher homologs. Their reactivity with disulfide and diselenide was already described.^[4f, 4h] Recently, Togni et al. prepared ArTeCF_3 in good yields from the corresponding ditellurides (Scheme 35).^[13b] Noteworthy, using cesium fluoride instead of potassium fluoride led to unexpected formation of a non-fluorinated telluride via the nucleophilic attack of CNCH_2^- (arising from deprotonation of CH_3CN by fluoride anion) on the ditelluride. This method was extended to few other fluoroalkyl groups by using the corresponding fluoroalkylsilylated reagents. In these cases, CsF was successfully used by using DMF as solvent (Scheme 35).^[13b] With perfluorophenyl reagent, ditellurated by-product was also observed through an $\text{S}_{\text{N}}\text{Ar}$ reaction of in situ generated aryltelluride anion onto perfluorophenyl telluride (Scheme 35).^[13b]



Scheme 35 Synthesis of $\text{R}_\text{F}\text{TeAr}$ with $\text{R}_\text{F}\text{SiMe}_3$ reagents.

Togni et al. succeeded also to obtain the tellurated analogs of their electrophilic trifluoromethylating hypervalent iodine

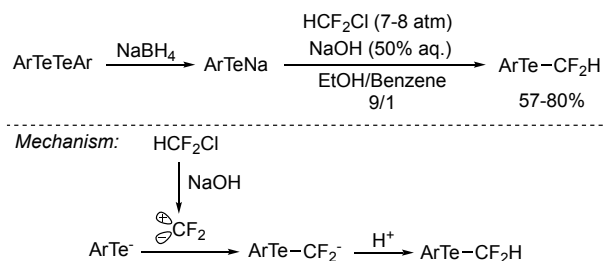
reagent.^[41] These new compounds were synthesized by nucleophilic trifluoromethylation with Ruppert-Prakash reagent of fluoro tellurium (III) substrates, in situ formed by fluorination of the corresponding iodinated molecules (Scheme 36).^[20]



Scheme 36. Synthesis of trifluoromethyl hypervalent tellurium compounds.

3.4. Reaction with difluorocarbene

As for other chalcogenes, difluoromethyl aryl tellurides were obtained by reaction of aryltelluride anions with in situ generated difluorocarbene.^[42] This last one was classically formed by deprotonation of chlorodifluoromethane with sodium hydroxide (Scheme 37).



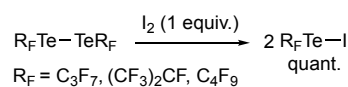
Scheme 37. Reaction of ArTe^- anion with difluorocarbene.

4. Direct Approach

From a retrosynthetic point of view, $\text{R}_\text{F}\text{Te}-\text{C}$ bond disconnection is, maybe, the more elegant approach. In particular such strategy opens the possibility of late stage fluoroalkyltellurolation of molecules.

4.1. Electrophilic fluoroalkyltellurolation

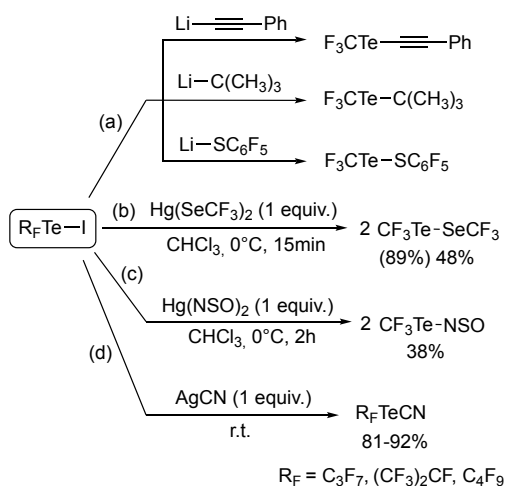
Direct electrophilic perfluoroalkyltellurolation is one of the least developed direct pathways. Indeed, only three publications describe the synthesis and the utilization of the electrophilic reagents $\text{R}_\text{F}\text{Tel}$ obtained from the reaction between $(\text{R}_\text{F})_2\text{Te}_2$ and I_2 (Scheme 38). However, even if the resulting solution can be stored at room temperature (preventing exposure to moisture and light) over a long period, pure $\text{R}_\text{F}\text{Tel}$ reagent cannot be isolated.^[43]



Scheme 38. Preparation of $\text{R}_\text{F}\text{Tel}$.

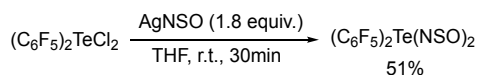
The in situ prepared $\text{R}_\text{F}\text{Tel}$ can react with nucleophilic reagents such as organomercury, organosilver or organolithium derivatives (Scheme 39). Reaction of CF_3Tel with $\text{Hg}(\text{SeCF}_3)_2$

affords $\text{CF}_3\text{TeSeCF}_3$ with a good NMR yield but with an isolated yield, by preparative gas chromatography, of only 48% (Scheme 39b).^[44] However, the resulting orange oil decomposes slowly at room temperature into $\text{F}_3\text{CSeSeCF}_3$ and $\text{F}_3\text{CTeTeCF}_3$. Syntheses of CF_3TeNSO and R_fTeCN were also described with modest to excellent yields starting from $\text{Hg}(\text{NSO})_2$ and AgCN salts respectively (Scheme 39c-d).^[43a, 44] Concerning the reactivity of CF_3TeI with organolithiums (Scheme 39a), the products characterizations were given, but no information concerning the reactions conditions and yields were described.^[43b]



Scheme 39. Reaction of R_fTeI with various organometallic reagents.

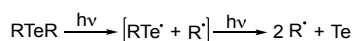
A single example of direct electrophilic pentafluorophenyltellurolation was also described in 1999.^[22] Thus, $(\text{C}_6\text{F}_5)_2\text{TeCl}_2$ reacts with AgNSO in mild conditions leading to $(\text{C}_6\text{F}_5)_2\text{Te}(\text{NSO})_2$ in moderate yield (Scheme 40).



Scheme 40. Pentafluorophenyltellurolation using $(\text{C}_6\text{F}_5)_2\text{TeCl}_2$ reagent.

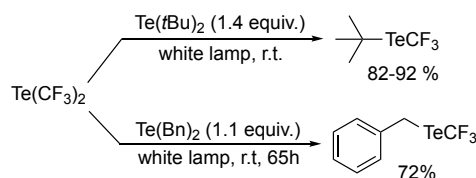
4.2. Radical fluoroalkyltellurolation

The homolytic scission of TeR_2 derivatives under light irradiation or thermic activation was described to finally lead to the Te atom extrusion (Scheme 41).^[12b, 45]



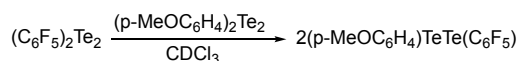
Scheme 41. Homolytic scission of RTeR .

However, the intermediate RTe^\cdot radical was used to prepare some trifluoromethyltellurolated molecules via a radical pathway. Irradiation of two different symmetric tellurides led to the formation of unsymmetric tellurides through a radical recombination (Scheme 42). In this process both direct radical trifluoromethyltellurolation and radical trifluoromethylation of tellurolated compounds have to be considered.^[46]



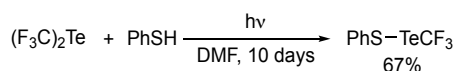
Scheme 42. Synthesis of CF_3TeR from $\text{Te}(\text{CF}_3)_2$.

A similar approach was described with the bis(pentafluorophenyl)telluride but, in this case, the formation of unsymmetric ditelluride was supposed (Scheme 43).^[47] Unfortunately, no characterization and yield were given.



Scheme 43. Preparation of PhSTeCF_3 .

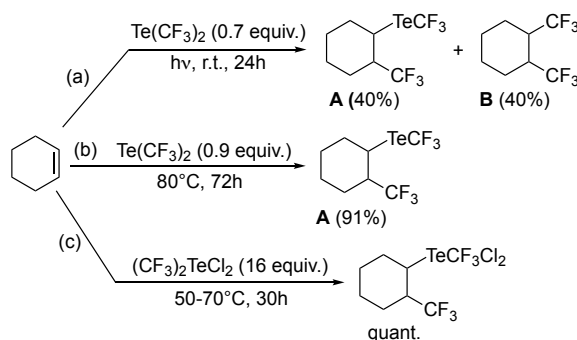
Radical trifluoromethyltellurolation of thiophenol was also described (Scheme 44).^[48] The reaction proceeds in DMF for 10 days under ultraviolet irradiation and gives the desired compound with 67% yield.



Scheme 44. Preparation of PhSTeCF_3 .

Radical addition of $\text{Te}(\text{CF}_3)_2$ onto cyclohexene through light or thermic activation afforded a mixture of cis/trans 1-trifluoromethyltelluryl-2-trifluoromethylcyclohexane (**A**).^[45] Due to photochemical instability, the product degrades into 1,2-di(trifluoromethyl)cyclohexane (**B**) leading to a mixture of the two products under light activation (Scheme 45a). Under thermic activation, only expected 1-trifluoromethyltelluryl-2-trifluoromethylcyclohexane (**A**) was obtained at 80°C with excellent yields (Scheme 45b). Nevertheless, at higher temperature (155°C) only the di(trifluoromethyl) product **B** was obtained.

With $(\text{CF}_3)_2\text{TeCl}_2$, under thermic activation, 1-trifluoromethyldichlorotelluryl-2-trifluoromethyl-cyclohexane was obtained quantitatively (Scheme 45c).^[49] This compound can also be prepared by direct chlorination of the previous 1-trifluoromethyltelluryl-2-trifluoromethylcyclohexane (**A**). Noteworthy, when $(\text{CF}_3)_2\text{TeBr}_2$ was used, only 1,2-dibromocyclohexane was observed.

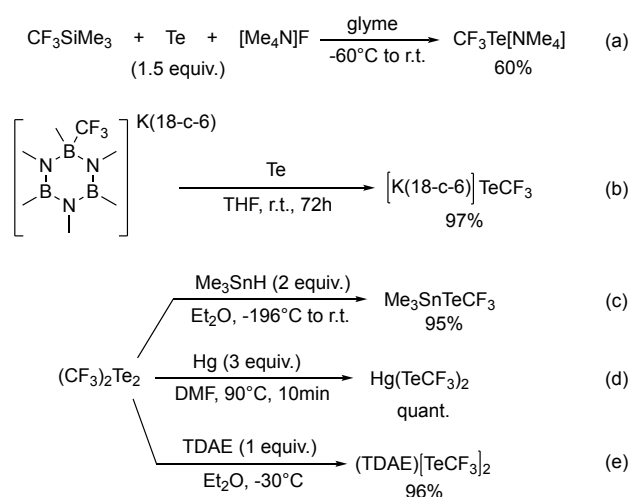


Scheme 45. Radical additions onto cyclohexene.

Finally, this radical process was also applied to prepare different CF_3Te complexes with some metals (Hg, Cd, Cu or Ag).^[12b]

4.3. Nucleophilic fluoroalkyltellurolation

The nucleophilic perfluoroalkyltellurolation is the most studied direct pathway. Different sources of R_fTe^- anions were described (Scheme 46). They were prepared from different tellurium sources such as tellurium metal or $(\text{CF}_3)_2\text{Te}_2$. Tellurium metal reacts with Ruppert-Prakash reagent in presence of $[\text{NMe}_4]\text{F}$ to form $[\text{NMe}_4]\text{TeCF}_3$ with 60% yield (Scheme 46a).^[50] A recent publication described the synthesis of $[\text{K}(18\text{-c-}6)]\text{TeCF}_3$ from Te and a [borazine- CF_3] derivative (Scheme 46b) with an excellent yield.^[51] Di(trifluoromethyl)ditelluride can react with metallic reagents, such as Me_3SnH or Hg, to provide corresponding $\text{Me}_3\text{SnTeCF}_3$ or $\text{Hg}(\text{TeCF}_3)_2$ (Scheme 46c-d).^[44, 52] Finally, di(trifluoromethyl)ditelluride was also reduced by TDAE in mild conditions to form $(\text{TDAE})(\text{TeCF}_3)_2$ with 96% yield (Scheme 46e), but no reactions using this compound were described.^[53]



Scheme 46. Preparation of R_fTe^- anions.

First described in 2004 by Tyrra et al, $[\text{NMe}_4]\text{TeCF}_3$ salt is certainly the most used reagent to perform direct nucleophilic trifluoromethyltellurolation.^[54] This reagent was easily prepared from Ruppert-Prakash reagent (Scheme 47a), and this method was also extended to $\text{C}_2\text{F}_5\text{SiMe}_3$.

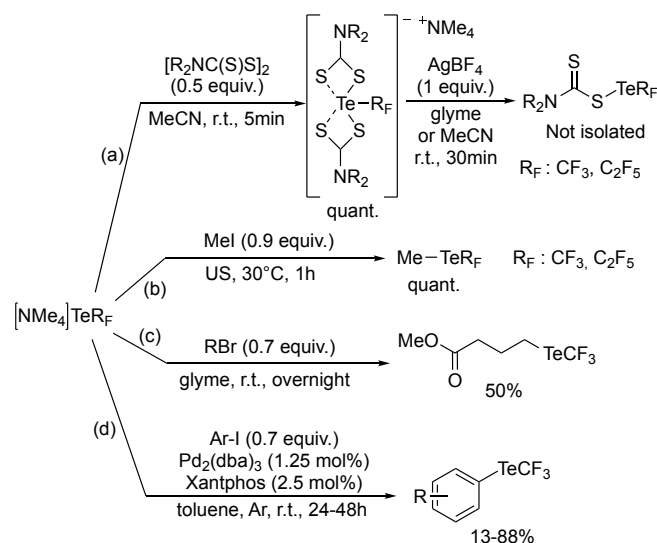
While reacting with bis(dialkylthiocarbamyl) disulfides, symmetric complexes between two thiocarbamate moieties and TeR_f , with $[\text{NMe}_4]^+$ as counter cation, were formed in nearly quantitative yields. Noteworthy, these complexes were also prepared via an indirect pathway using $[\text{TeSC}(\text{S})\text{NR}_2]_2$, $[\text{NMe}_4]\text{F}$ and Ruppert-Prakash derivatives. The addition of $\text{Ag}[\text{BF}_4]$ onto these complexes led to the formation of corresponding $\{[(\text{trifluoromethyl})\text{tellanyl}]sulfanyl\}$ carbothioamide (Scheme 47a).^[55] However these compounds couldn't be isolated due to their decomposition in solution.

Reaction between MeI and $[\text{NMe}_4]\text{TeR}_f$ in solvent free conditions (under ultrasonic irradiation) or in solution yielded MeTeR_f quantitatively (Scheme 47b).^[56] While the trifluoromethyl derivative decomposes quickly, the C_2F_5 one is

stable for several months at 28°C. Noteworthy, MeTeR_f can be oxidized leading to $\text{MeTe}(\text{R}_f)_2$ ($\text{Y} = \text{F}, \text{Cl}, \text{Br}$ or OCOCF_3) with excellent yields.^[56]

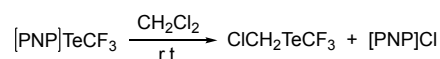
One example of substitution reaction with alkylbromide was reported, leading to corresponding RTeCF_3 with 50% yield (Scheme 47c).^[57] The resulting RTeCF_3 molecule could then be post-functionalized.

A recent publication of Schoenebeck et al. described a palladium coupling between aryl iodides and $[\text{NMe}_4]\text{TeCF}_3$ (Scheme 47d).^[58] After oxidative addition of palladium, CF_3Te^- is inserted onto palladium via a nucleophile exchange with the iodine anion. The reductive elimination, then, affords the expected ArTeCF_3 . The reaction conditions are compatible with a wide range of functional groups (halogens, aldehyde, ketone, ester and triflate). Sixteen examples were described with a yields range of 13-88%.



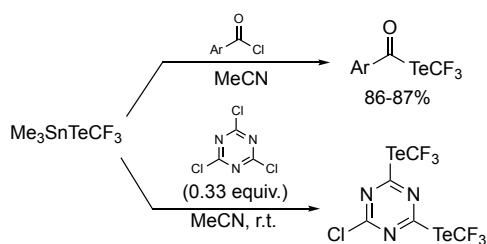
Scheme 47. Reactivity of $\text{R}_f\text{Te}[\text{NMe}_4]$.

$[\text{NMe}_4]\text{TeCF}_3$ reagent was also used to prepare different complexes with transition metals such as Cu, Ag, Au or Pt.^[59] It also underwent cation exchange with bis(triphenylphosphine)iminium bromide ($[\text{PNP}]\text{Br}$) or $[\text{K}(\text{dibenzo-}18\text{-c-}6)]\text{Br}$.^[54] These salts in solution remain stable in MeCN or DMF but they react with dichloromethane. Indeed, $[\text{NMe}_4]\text{TeCF}_3$ shows a two hours half-life time in CH_2Cl_2 and $[\text{PNP}]\text{TeCF}_3$ degrades quickly while reacting with the solvent at room temperature (Scheme 48).



Scheme 48. Reaction of $[\text{PNP}]\text{TeCF}_3$ with CH_2Cl_2 .

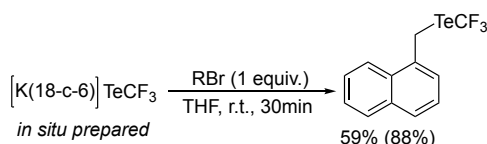
$\text{Me}_3\text{SnTeCF}_3$ was used as source of CF_3Te^- anion which was trapped with acyl chlorides (Scheme 49).^[60]



Scheme 49. Reaction of $\text{Me}_3\text{SnTeCF}_3$ with acyl chlorides.

With cyanuric chloride, only the disubstituted compound was formed, despite the use of 3 equivalents of $\text{Me}_3\text{SnTeCF}_3$ (Scheme 49). Unfortunately, this product was not isolated and only mass spectrometry proved its formation.

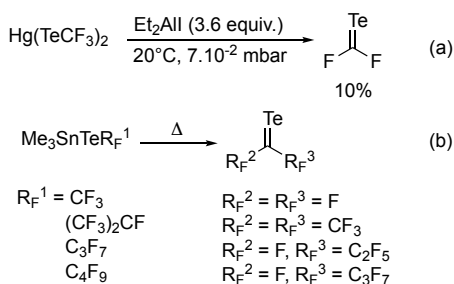
Only one example of nucleophilic substitution with $[\text{K}(18\text{-c-}6)]\text{TeCF}_3$ was described with 2-bromomethylnaphthalene (Scheme 50).^[51] It should be noticed that the anion was preliminary formed in situ with 96% yield in 3 days (Scheme 46).



Scheme 50. Reactivity of $[\text{K}(18\text{-c-}6)]\text{TeCF}_3$ (in parentheses crude yield determined by ^{19}F NMR).

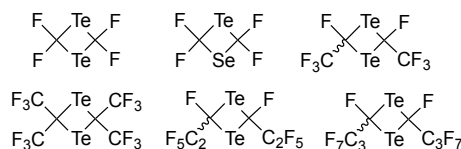
4.4. Reactions with di(perfluoroalkyl)tellurocarbonyls

Fluorotellurophosgene was first synthesized in 1991, by reaction of $\text{Hg}(\text{TeCF}_3)_2$ with Et_2AlI in solvent free conditions at 20°C under vacuum.^[61] The thermally unstable TeCF_2 was isolated with 10% yield at low temperature (Scheme 51a). Other di(perfluoroalkyl)tellurocarbonyls were prepared by thermal decomposition of perfluoroalkyltellurostannane derivatives (Scheme 51b).^[23, 43a, 44, 52, 62]



Scheme 51. Synthesis of fluorotellurophosgene and di(perfluoro)tellurocarbonyls.

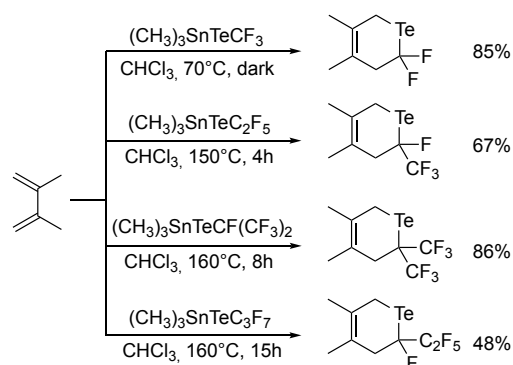
These compounds were involved in [2+2] cycloadditions with other telluro- or selenocarbonyl derivatives, leading to the symmetric and non-symmetric corresponding cycloadducts (Scheme 52).^[23, 43a, 44, 52, 61-62]



Scheme 52. Different dimers resulting from [2+2] cycloadditions.

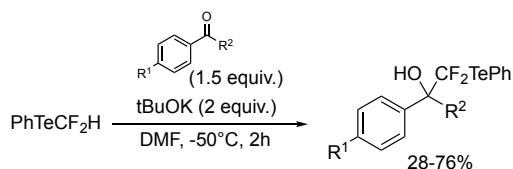
These cyclic dimers can be post-functionalized by halogen exchange using BX_3 ($\text{X} = \text{Cl}$ or Br) or by direct halogenation of tellurium using Cl_2 .^[23, 43a, 44]

Some examples of [4+2] cycloadditions of di(perfluoro)tellurocarbonyls with 2,3-dimethyl-1,3-butadiene were also reported (Scheme 53).^[23, 43a, 44] The tellurocarbonyls derivatives were in situ prepared by thermal degradation of $(\text{Me}_3\text{SnTeR}_F)$ and various cyclic perfluoroalkyl compounds were obtained with moderate to good yields.



Scheme 53. [4+2] cycloaddition with di(perfluoro)tellurocarbonyls.

Finally, another approach was described. In this case a fluoroalkyltelluryl motif was also directly added onto organic substrates, corresponding formally well to a direct approach. However, a $\text{C-CF}_2\text{Te}$ bond is formed instead of a C-TReR_F one. Thus, the addition of in situ generated PhTeCF_2^- anion to aldehydes and ketones derivatives was also described (Scheme 54).^[63] This anion was obtained by deprotonation with $t\text{BuOK}$ of PhTeCF_2H (prepared as described in Scheme 37). Eleven examples, with yields ranging from 28 to 76% using aliphatic or aromatic aldehydes and ketones were described.



Scheme 54. Reaction of aldehydes and ketones with PhTeCF_2H and a base.

5. Conclusion

From sixties to nowadays, some methods to obtain fluoroalkyltellurolated molecules have already been described.

Nevertheless, only a few ones turn out to be effective in a practical point of view and can be considered as efficient approaches to synthesized elaborated R_FTe-compounds. Consequently, development of new strategies to introduce R_FTe moieties, and more especially CF₃Te, onto organic substrates remains challenging. In particular, direct trifluoromethyltellurolation (and fluoroalkyltellurolation) is clearly underdeveloped and progresses in this field would open the way to late-stage functionalizations of various molecules, as recently illustrated by the seminal work of Schoenebeck.^[58] Development of new strategies to perform direct trifluoromethyltellurolation, easy to realize even for non-specialized chemists, would broaden the toolbox of trifluoromethylchalcogenation reactions to propose all the non-radioactive group 16 elements in the conception of new emerging fluorinated groups with dedicated properties.

Acknowledgements

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Keywords: Fluorine • Tellurium • Trifluoromethyl • Trifluoromethyltellurolation • Fluoroalkyl

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Key Topic

Trifluoromethyltellurolation

Entry for the Table of Contents

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The missing element: CF₃O, CF₃S and CF₃Se chemistries have been widely described these last years. Tellurium is the following chalcogen but the CF₃Te chemistry remains poorly described. This review presents the different strategies and methods already existing and described in literature.