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$TMSCF_3$ as a Convenient Source of CF_2=CF_2 for Pentafluoroethylation, (Aryloxy)tetrafluoroethylation and Tetrafluoroethylation**

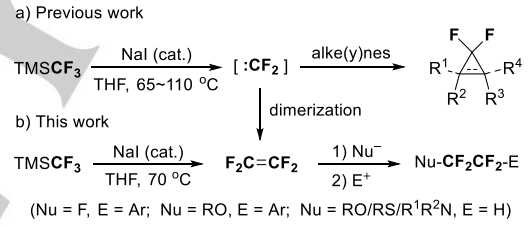
Lingchun Li, Chuanfa Ni, Qiqiang Xie, Mingyou Hu, Fei Wang, and Jinbo Hu*

Abstract: *A new protocol for on-site preparation of tetrafluoroethylene (TFE) and its efficient use in pentafluoroethylation by fluoride addition were developed using a simple two-chamber system. The on-site preparation of TFE was accomplished by dimerization of difluorocarbene derived from (trifluoromethyl)trimethylsilane ($TMSCF_3$) under mild conditions. Other fluoroalkylations such as (aryloxy)tetrafluoroethylation and tetrafluoroethylation were also achieved using a similar protocol. This work not only demonstrates a convenient and safe approach to generate and use TFE for academic labs, but also provides a new strategy for pentafluoroethylation.*

Organofluorine compounds are widely used as functional materials, agrochemicals, as well as pharmaceuticals owing to the unique physical, chemical and biological features brought by fluorine substitutions.[1] Therefore, developing novel methods for straightforward incorporation of per- or polyfluorinated groups into organic molecules has intrigued numerous attention in both academia and industry.[2] Tetrafluoroethylene (TFE, CF_2=CF_2), as a bulk fluorochemical for the industrial manufacture of poly(tetrafluoroethylene) and copolymers with other alkenes,[3] is an ideal C2 building block for incorporating fluorinated moieties such as -CF_2CF_2-, HCF_2CF_2-, and CF_2=CF- into small molecules.[4] However, TFE is suspected to be carcinogenic, unstable towards radicals, and prone to explode when contacting with air, all of which in turn require that TFE gas is handled with extreme caution, including storage and transport.[3d, 5]

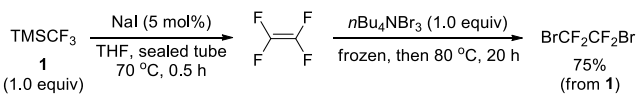
To overcome the inherent limitations involved using TFE gas in academic labs, several TFE precursors have been developed to release TFE gas on site in small amounts. Available methods include reduction of 1,2-dihalotetrafluoroethane (XCF_2CF_2Y; X, Y = Br, Cl) with zinc powder[6] and pyrolysis of sodium perfluoropropionate[3d] or poly(tetrafluoroethylene)[7] at high temperatures. However, the restricted availability of XCF_2CF_2Y and the harsh conditions for the pyrolysis reactions have limited the utilizations of these methods, thus preventing the development of fluoroalkylation reactions with TFE in common research laboratories. Therefore, the development of practical and operationally simple methods for the laboratory preparation of TFE is highly desirable.

Ruppert-Prakash reagent ($TMSCF_3$) is readily available and is the most extensively used trifluoromethylation reagent for a variety of applications.[8] In 2011, our group and Prakash's group cooperatively developed an efficient method for the preparation of *gem*-difluorocyclopropa(e)nes by using $TMSCF_3$ as a novel difluorocarbene source under the initiation of NaI (Scheme 1a).[9] During the investigation, we noticed that TFE was normally formed as a side product (supporting information).[9a] In 2014, Baker and co-workers observed that a mixture of $TMSCF_3$ and NaI in THF could produce TFE and thus proposed that the so-formed TFE could directly added to cobalt complexes.[10] Although this TFE generation method is very intriguing due to its mildness, it is still unclear whether it is synthetically useful,[10,11] since the gaseous TMSF is also present as a byproduct. Herein, we report the synthetic application of readily available $TMSCF_3$ as a convenient TFE source for per- and polyfluoroalkylations. The usefulness of this protocol is demonstrated by the efficient pentafluoroethylation and (aryloxy)tetrafluoroethylation of aryl iodides and 1,1,2,2-tetrafluoroethylation of heteroatom nucleophiles (Scheme 1b).



Scheme 1. Fluoroalkylation with $TMSCF_3$ via difluorocarbene and TFE

We first optimized the conditions for the generation of TFE from $TMSCF_3$/NaI in THF. The efficiency of this protocol was evaluated by converting TFE into $BrCF_2CF_2Br$ (Scheme 2). A survey of catalyst loading, reaction temperature and time revealed that the evolution of TFE could complete in 30 minutes when performed at 70 °C using 5 mol% of NaI (for details, see Supporting Information). Larger amounts of NaI had little influence on the formation of TFE, but a smaller amount decreased the yield significantly. Moreover, it was found that the generation of TFE from $TMSCF_3$/NaI was not sensitive to the temperature. When 20 mol% of NaI was used, the reactions proceeding at the temperatures ranging from 65 to 80 °C basically gave similar results.



Scheme 2. Generation of TFE and its quantitative characterization. The Yield was determined by ^{19}F NMR spectroscopy using $PhCF_3$ as an internal standard.

Having the optimal parameters for NaI-catalyzed release of TFE from $TMSCF_3$ in hand, we attempted to combine this protocol with the further fluoroalkylation reactions. Considering that $TMSCF_3$ is a volatile liquid, the evolution of TFE and the

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[**] TMS = trimethylsilyl.

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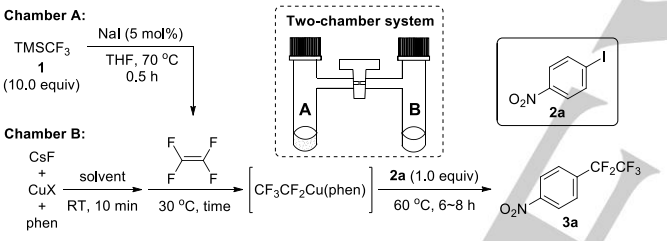
further reaction should be conducted separately. Therefore, we designed a simple reaction system consisting of two pressure tubes (TFE generation chamber A and reaction chamber B), which were connected through a three-way valve (Table 1; see Supporting Information).[12] TFE was first prepared and stored in chamber A, and was then introduced into chamber B for further reaction.

The addition of fluoride sources to fluoroalkenes is a concise and convenient method to obtain poly- or perfluorocarbanions.[13] Since Miller's first report on the nucleophilic addition of AgF to perfluoroalkenes to give perfluoroalkylsilver compounds,[14] many poly- and perfluoroalkylmetal complexes have been prepared in such a way and used for fluoroalkylations.[4f,13-15] *However, pentafluoroethylmetal (CF_3CF_2M) complex has never been prepared via the combination of TFE and fluoride ion.* Considering that copper-mediated fluoroalkylations are an important strategy to obtain organofluorine compounds,[2g,16] we sought to use the fluorocupration of TFE to prepare the CF_3CF_2Cu complex as a key intermediate for pentafluoroethylation. Previously, several well-defined CF_3CF_2Cu complexes such as CF_3CF_2Cu(phen) (phen = 1,10-phenanthroline) have been prepared via cupration of $TMSCF_2CF_3$ or CF_3CF_2H and used for pentafluoroethylation.[16a-d]

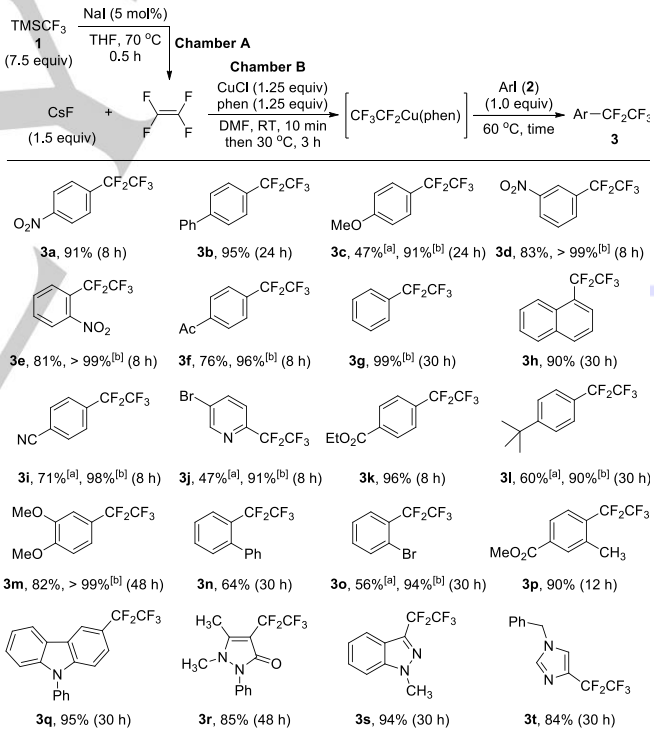
Table 1. Survey of reaction conditions.[a]



Entry	CuX	Solvent	**2a**/CsF/CuX/phen[b]	Time [h]	Yield [%][c]
1	CuI	THF	1.0:1.25:1.25:1.25	10	0
2	CuI	DMF	1.0:1.25:1.25:1.25	10	94
3	CuI	DMF	1.0:1.25:1.25:0	10	28
4	CuCl	DMF	1.0:1.25:1.25:1.25	10	93
5	CuCl	NMP	1.0:1.25:1.25:1.25	10	89
6	CuCl	DMF	1.0:1.1:1.1:1.1	10	82
7	CuCl	DMF	1.0:1.25:1.25:1.25	5	92
8	CuCl	DMF	1.0:1.25:1.25:1.25	3	96
9	CuCl	DMF	1.0:1.21:1.1:1.1	3	92
10	CuCl	DMF	1.0:1.32:1.1:1.1	3	97
11	CuCl	DMF	1.0:1.32:1.2:1.2	3	95
12[d]	CuCl	DMF	1.0:1.5:1.25:1.25	3	>99 (91)
13[d,e]	CuCl	DMF	1.0:1.5:1.25:1.25	3	9

[a] Reactions were performed on 0.2 mmol scale. [b] Molar ratio. [c] Yields were determined by ^{19}F NMR spectroscopy using $PhCF_3$ as an internal standard. The isolated yield is given in the parentheses. [d] 7.5 equiv of **1** was used. [e] KF was used instead of CsF. THF = tetrahydrofuran; DMF = *N*,*N*-dimethyformamide; NMP = *N*-methyl pyrrolidone.

As shown in Table 1, we investigated the fluorocupration of TFE by using CsF as the fluoride source and further pentafluoroethylation by using 1-iodo-4-nitrobenzene (**2a**) as a model substrate. The process was carried out by introducing the pre-generated TFE to a mixture of CsF, CuI and 1,10-phenanthroline (phen) followed by the addition of **2a**. The ligand phen was used to stabilize CF_3CF_2Cu and to promote the further cross-coupling reaction. Initial attempt using THF as the solvent did not give the desired product **3a**, probably arising from the inefficient fluorocupration due to the low solubility of CsF in THF (entry 1). When DMF was used instead of THF, the reaction proceeded smoothly to give **3a** in 94% yield, indicating that an efficient fluorocupration reaction took place (entry 2). The use of phen was crucial to this reaction; otherwise the $CF_3CF_2^-$ could further react with TFE to give various side products (entry 3). Notably, an identical yield of **3a** was obtained by using CuCl instead of CuI (entry 4). NMP was also a suitable solvent, albeit giving **3a** in a slightly lower yield (entry 5). When KF was used instead of CsF, a significantly lower yield of **3a** was obtained (entries 12 and 13). After a careful screening (entries 6-12), we obtained the optimal reaction conditions by using CsF as fluoride source, CuCl as promotor, phen as ligand and DMF as solvent, with **2**/**1**/CsF/CuCl/phen being in a molar ratio of 1.0:7.5:1.5:1.5:1.25:1.25, and by conducting the fluorocupration at 30 °C for 3 hours (entry 12).



Scheme 3. Pentafluoroethylation of iodoarenes. Reactions were performed on 0.4 mmol scale. Yields given refer to the isolated yields. [a] The relatively low isoalted yields arise from the volatility of the products. [b] Yields were determined by ^{19}F NMR spectroscopy using $PhCF_3$ as an internal standard.

To test the usefulness of the CF_3CF_2Cu(phen) reagent prepared from $TMSCF_3$ via TFE, we explored the pentafluoroethylation of various iodoarenes using the optimized conditions as shown in Table 1, entry 12. The results are sumarized in Scheme 3. Generally, both electron-rich and deficient iodoarenes reacted smoothly to give

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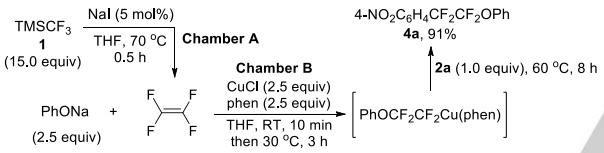
pentafluoroethylarenes in excellent yields. The reactions with electron-rich and sterically hindered substrates were sluggish, but after prolonged reaction time, the corresponding coupling products (**3b**-**c**, **3h**, **3l**-**t**) were obtained in high yields. This method tolerates various functional groups such as nitro (**3a**, **3d**, **3e**), methoxy (**3c**, **3m**), acetyl (**3f**), nitrile (**3i**), bromide (**3j**, **3o**) and esters (**3k**, **3p**). It is noteworthy that heterocyclic iodoarenes could also be transformed to the corresponding pentafluoroethylation products in excellent yields (**3j**, **3q**-**t**).

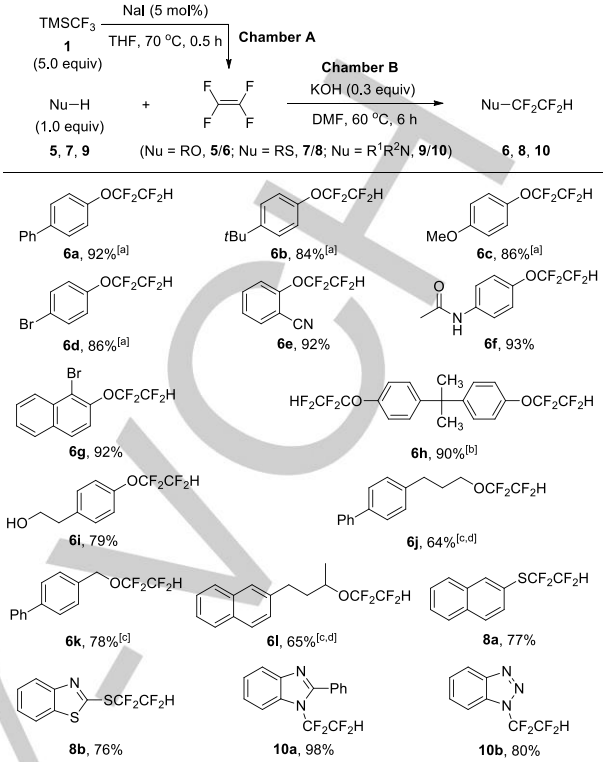
Encouraged by the above results, we then tried the use of other nucleophiles for similar coupling reactions instead of fluoride ion. Since Ogoshi *et al*. have prepared a variety of 1,2-difunctionalized-1,1,2,2-tetrafluoroethylene derivatives via the carbocupration of TFE,[4f] we turned our attention to the still unknown oxycupration by using PhONa as a nucleophile (Scheme 4). To our delight, the corresponding (aryloxy)tetrafluoroethylation product **4a** could be obtained in high yield when the oxycupration intermediate $PhOCF_2CF_2Cu(phen)$ was subjected to the reaction of **2a**.[17] Notably, the good solubility of PhONa allowed this reaction to proceed smoothly in THF.



Scheme 4. Oxycupration of TFE with PhONa/CuCl and subsequent cross-coupling with **2a**.

To further demonstrate the synthetic potential of TFE prepared from $TMSCF_3$, we also investigated its capability for direct 1,1,2,2-tetrafluoroethylation of heteroatom nucleophiles.[18] An examination of the substrate scope showed that this heteroatom-tetrafluoroethylation is general for *O*-, *S*- and *N*-nucleophiles, and no trifluorovinylated compounds arising from the *β*-fluoride elimination were detected (Scheme 5). Initailly, THF was used as the solvent for the reaction of phenols and the desired aryl ethers (**6a**-**d**) were obtained in good yields. However, in the cases of phenols bearing ortho- or highly polar groups, DMF was superior to THF, affording the desired ethers(**6e**-**i**) in higher yields. Note that when KOH was used as the initiator, phenol substrates bearing an amide or alcoholic hydroxyl group were fluoroalkylated selectively at the phenol position (**6f** and **6i**). By using DMF as the optimal solvent, both primary and secondary alcohols underwent the *O*-fluoroalkylation smoothly in 24 hours to deliver the corresponding ether products (**6j**-**l**) in moderate to good yields; however, the reactions of alkyl substituted alcohols required using NaH instead of KOH. Furthermore, the 1,1,2,2-tetrafluoroethylations of aryl thiols (**8a**, **8b**) and heterocyclic amines (**10a**, **10b**) were also achieved in good to excellent yields under the optimal reaction conditions.

In conclusion, we have developed highly efficient methods for the pentafluoroethylation and (aryloxy)tetrafluoroethylation of iodoarenes as well as 1,1,2,2-tetrafluoroethylation of heteroatom nucleophiles with tetrafluoroethylene (TFE) on-site prepared



Scheme 5. 1,1,2,2-Tetrafluoroethylation of *O*-, *S*-, and *N*-Nucleophiles. All reactions were performed on 0.5 mmol scale. Yields given refer to the isolated yields. [a] The solvent was THF. [b] **5h**/KOH/$TMSCF_3$ = 1.0 : 0.6 : 10.0. [c] Reaction time is 24 h instead of 6 h. [d] NaH was used instaed of KOH.

from $TMSCF_3$. The current reactions were carried out in a two-chamber system, involving the generation of TFE using $TMSCF_3$/NaI as a readily available precursor in one sealed chamber and the subsequent introduction of TFE to another sealed chamber for further fluoroalkylations. Currently, TFE is generally not accessible in most academic research laboratories which severely limits the further development of TFE-related chemistry. Therefore, since our current work demonstrates a convenient and safe method to generate and use TFE in standard laboratories, it promises to stimulate the investigation of TFE-involved chemistry in the near future. In addition, compared with the reported pentafluoroethylation with C_2F_5-containing reagents, the current strategy represents a novel method for pentafluoroethylation, and may find applications in the synthesis of ^{18}F-labelled CF_3CF_2 compounds. Further explorations of new fluoroalkylation reactions using $TMSCF_3$ as a starting material are underway in our laboratory.

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Keywords: tetrafluoroethylene • pentafluoroethylation • tetrafluoroethylation • difluorocarbene • copper

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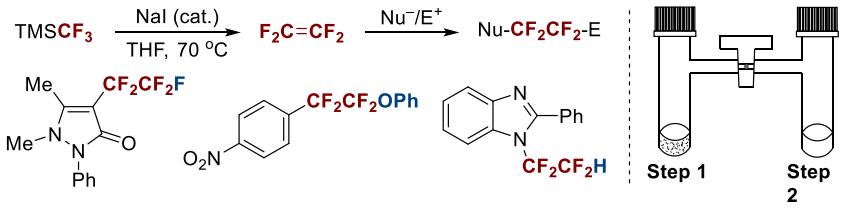

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TMSCF$_3$ as a Convenient Source of CF$_2$=CF$_2$ for Pentafluoroethylation, (Aryloxy)tetrafluoroethylation and Tetrafluoroethylation

Do it in your lab: The on-site generation of CF_2=CF_2 from $TMSCF_3$ under mild conditions for per(poly)fluoroalkylation is reported using a two-chamber system. Not only does this investigation demonstrate a convenient and safe approach to use CF_2=CF_2 in standard labs, but also provides a novel protocol for pentafluoroethylation.