Fluorination Hot Paper

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

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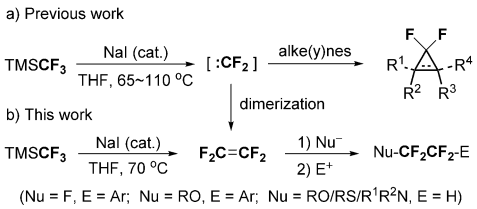
Abstract: *A new method for the on-site preparation of tetrafluoroethylene (TFE) and a procedure for its efficient use in pentafluoroethylation by fluoride addition were developed by using a simple two-chamber system. The on-site preparation of TFE was accomplished by dimerization of difluorocarbene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

Organofluorine compounds are widely used as functional materials, agrochemicals, and pharmaceuticals owing to the unique physical, chemical, and biological features that result from fluorine substitution.[1] Therefore, developing novel methods for the straightforward incorporation of per- or polyfluorinated groups into organic molecules has received significant 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 in contact with air, all of which in turn require that TFE gas is handled with extreme caution, including during storage and transport.[3d,5]

To overcome the inherent limitations associated with using TFE gas in academic laboratories, several TFE precursors have been developed that release TFE gas on site in small amounts. Available methods include the reduction of 1,2-dihalotetrafluoroethanes (XCF_2CF_2Y; X, Y = Br, Cl) with zinc powder[6] and the pyrolysis of sodium perfluoropropionate[3d] or poly(tetrafluoroethylene)[7] at high temperatures. However, the restricted availability of XCF_2CF_2Y and the harsh conditions required 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.

The 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 the Prakash group cooperatively developed an efficient method for the preparation of *gem*-difluorocyclopropa(e)nes by using $TMSCF_3$ as a novel difluorocarbene source in the presence of NaI (Scheme 1 a).[9] During the investigation, we



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

noticed that TFE was normally formed as a side product (see the Supporting Information).[9a] In 2014, Baker and coworkers observed that a mixture of $TMSCF_3$ and NaI in THF could produce TFE and thus proposed that the thus-formed TFE could directly add to cobalt complexes.[10] Although this TFE generation method is very intriguing owing to its mildness, it is still unclear whether it is synthetically useful[10,11] as 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 polyfluoroalkylation reactions. The usefulness of this method is demonstrated by the efficient pentafluoroethylation and (aryloxy)tetrafluoroethylation of aryl iodides and the 1,1,2,2-tetrafluoroethylation of heteroatom nucleophiles (Scheme 1 b).

We first optimized the conditions for the generation of TFE from $TMSCF_3$/NaI in THF. The efficiency of this method 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 reached completion in 30 min when performed at 70 °C using 5 mol % of NaI (for details, see the Supporting Information). Larger amounts of NaI had little influence on the formation of TFE, but a smaller amount decreased the yield significantly.

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[**] TMS = trimethylsilyl.

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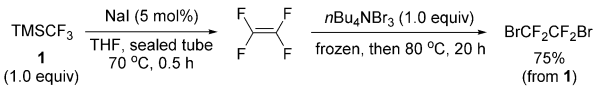


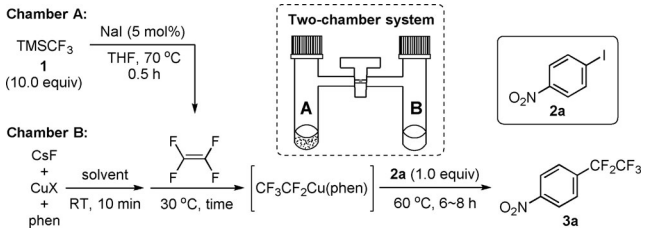
Scheme 2. Generation of TFE and its quantitative characterization. The yield was determined by ^{19}F NMR spectroscopy using $PhCF_3$ as an internal standard.

Moreover, it was found that the generation of TFE from $TMSCF_3$/NaI was not sensitive to the temperature. When 20 mol% of NaI were used, reactions at temperatures ranging from 65 to 80 °C gave similar results.

With optimized reaction conditions for the NaI-catalyzed release of TFE from $TMSCF_3$ in hand, we attempted to combine this procedure with fluoroalkylation reactions. Considering that $TMSCF_3$ is a volatile liquid, the evolution of TFE and the subsequent 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 the 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 and Burnard'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 fluoroalkylation reactions.[4f,13–15] However, pentafluoroethylmetal (CF_3CF_2M) complexes have never been prepared by 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 a 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 by cupration of $TMSCF_2CF_3$ or CF_3CF_2H and used for pentafluoroethylation.[16a–d]

Table 1: Optimization of the reaction conditions.[a]



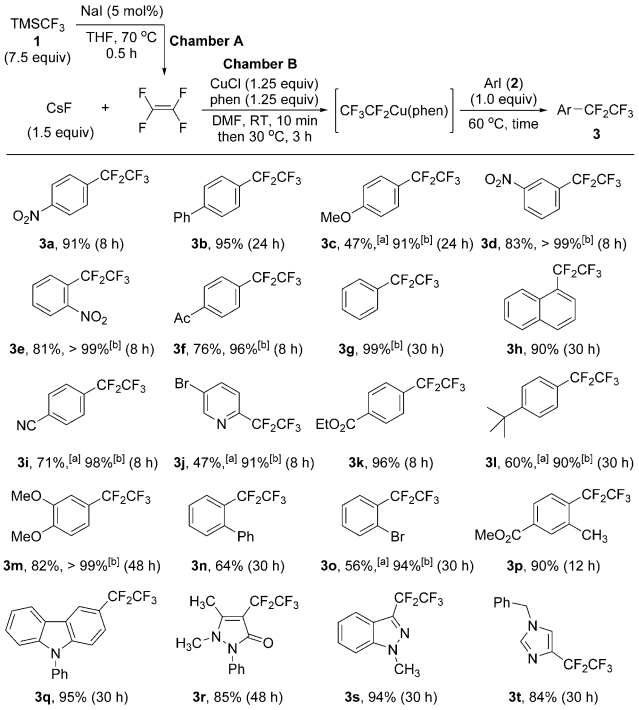
Entry	CuX	Solvent	**2a**/CsF/CuX/phen[b]	*t* [h]	Yield [%][c]
1	CuI	THF	1.0:1.25:1.25:1.25	10	0
2	CuI	DMF	1.0:1.25:1.25:1.25	10	94
3	CuI	DMF	1.0:1.25:1.25:0	10	28
4	CuCl	DMF	1.0:1.25:1.25:1.25	10	93
5	CuCl	NMP	1.0:1.25:1.25:1.25	10	89
6	CuCl	DMF	1.0:1.1:1.1:1.1	10	82
7	CuCl	DMF	1.0:1.25:1.25:1.25	5	92
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] Determined by ^{19}F NMR spectroscopy using $PhCF_3$ as an internal standard. Yields of isolated products given in parentheses. [d] **1** (7.5 equiv). [e] KF was used instead of CsF. DMF = *N*,*N*-dimethylformamide, NMP = *N*-methylpyrrolidone.

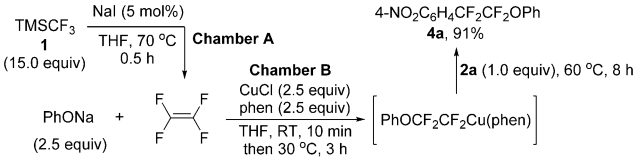
As shown in Table 1, we investigated the fluorocupration of TFE by using CsF as the fluoride source and further pentafluoroethylation by using 1-iodo-4-nitrobenzene (**2a**) as a model substrate. The process was carried out by introducing the pregenerated TFE into a mixture of CsF, CuI, and 1,10-phenanthroline (phen) followed by the addition of **2a**. The ligand phen was used to stabilize CF_3CF_2Cu and to promote the cross-coupling reaction. Initial attempts using THF as the solvent did not give the desired product **3a**, probably because of inefficient fluorocupration owing 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 had taken place (entry 2). The use of phen was crucial; otherwise, $CF_3CF_2^-$ further reacted with TFE to give various side products (entry 3). Notably, **3a** was obtained in identical yield when CuCl was used instead of CuI (entry 4). NMP was also a suitable solvent, but gave **3a** in a slightly lower yield (entry 5). When KF was used instead of CsF, **3a** was obtained in significantly lower yield (entries 12 and 13). After a careful screening (entries 6–12), we found that the optimal reaction conditions involve the use of CsF as the fluoride source, CuCl as the promotor, phen as the ligand, and DMF as the solvent, with a **2**/**1**/CsF/CuCl/phen molar ratio of 1.0:7.5:1.5:1.25:1.25 and conducting the fluorocupration at 30 °C for 3 hours (entry 12).

To test the usefulness of the CF_3CF_2Cu(phen) reagent prepared from $TMSCF_3$ via TFE, we explored the pentafluoroethylation of various iodoarenes under the optimized conditions (Table 1, entry 12). The results are summarized in Scheme 3. Generally, both electron-rich and electron-deficient iodoarenes reacted smoothly to give pentafluoroethyl-substituted arenes in excellent yields. The reactions with electron-rich and sterically hindered substrates were sluggish, but after prolonged reaction times, the corresponding coupling products (**3b**, **3c**, **3h**, **3l**–**3t**) 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 ester (**3k**, **3p**) moieties. It is noteworthy that heterocyclic iodoarenes could also be transformed into the corresponding pentafluoroethylation products in excellent yields (**3j**, **3q**–**3t**).

Encouraged by the above results, we then tried the use of other nucleophiles for similar coupling reactions instead of fluoride ion. As Ogoshi and co-workers have prepared a variety of 1,2-difunctionalized 1,1,2,2-tetrafluoroethylene derivatives by the carbocupration of TFE,[4f] we turned our attention to the still unknown oxycupration by using PhONa as the nucleophile (Scheme 4). To our delight, the corresponding (aryloxy)tetrafluoroethylation product **4a** was



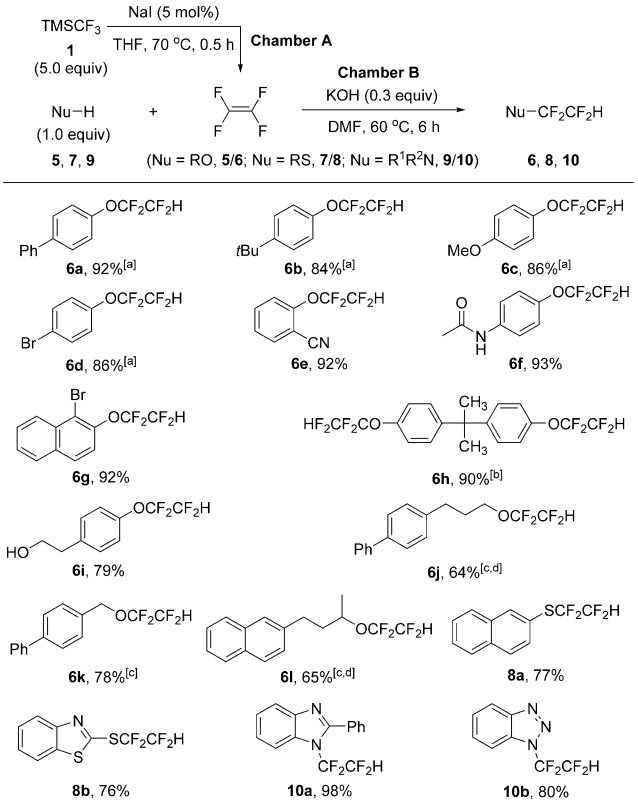
Scheme 3. Pentafluoroethylation of iodoarenes. Reactions were performed on 0.4 mmol scale. Yields of isolated products are given. [a] The relatively low yields of isolated products are due to the volatility of the products. [b] Yield determined by ^{19}F NMR spectroscopy using $PhCF_3$ as an internal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



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

obtained in high yield when the oxycupration intermediate $PhOCF_2CF_2Cu(phen)$ was subjected to the reaction with **2a**.[17] Notably, owing to the good solubility of PhONa, this reaction proceeded smoothly in THF.

To further demonstrate the synthetic potential of TFE prepared from $TMSCF_3$, we also investigated its use for the direct 1,1,2,2-tetrafluoroethylation of heteroatom nucleophiles.[18,19] An examination of the substrate scope showed that this heteroatom tetrafluoroethylation is general for oxygen, sulfur, and nitrogen nucleophiles, and trifluorovinylated compounds arising from β-fluoride elimination were not detected (Scheme 5). Initially, THF was used as the solvent for the reaction of phenols, and the desired aryl ethers (**6a**–**6d**) were obtained in good yields. However, for phenols bearing *ortho* substituents or highly polar groups, DMF was superior to THF, affording the desired ethers(**6e**–**6i**) in higher yields. Note that when KOH was used as the initiator, phenol substrates bearing an amide or alkyl hydroxy group were fluoroalkylated selectively at the phenol (**6f** and **6i**). With DMF as the optimal solvent, both primary and secondary



Scheme 5. 1,1,2,2-Tetrafluoroethylation of O, S, and N nucleophiles. All reactions were performed on 0.5 mmol scale. Yields of isolated products are given. [a] In THF. [b] **5h**/KOH/$TMSCF_3$ = 1.0:0.6:10.0. [c] 24 h instead of 6 h. [d] NaH was used instead of KOH.

alcohols underwent the oxygen fluoroalkylation smoothly in 24 h to deliver the corresponding ether products (**6j**–**6l**) in moderate to good yields; however, the reactions of alkyl-substituted alcohols required the use of NaH instead of KOH (**6j**, **6l**). Furthermore, the 1,1,2,2-tetrafluoroethylation of aryl thiols (**8a**, **8b**) and heterocyclic amines (**10a**, **10b**) also proceeded in good to excellent yields under the optimized reaction conditions.

In conclusion, we have developed highly efficient methods for the pentafluoroethylation and (aryloxy)tetrafluoroethylation of iodoarenes as well as the 1,1,2,2-tetrafluoroethylation of heteroatom nucleophiles with tetrafluoroethylene (TFE) that was prepared on site from $TMSCF_3$. These reactions were carried out in a two-chamber system, and involved the generation of TFE from $TMSCF_3$/NaI as a readily available precursor in one sealed chamber and the subsequent introduction of TFE into 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, as our current work describes a convenient and safe method for the generation and use of TFE in standard laboratories, it promises to stimulate the investigation of TFE-based processes in the near future. In addition, compared with the reported pentafluoroethylation with C_2F_5-containing reagents, the current strategy constitutes a new method for pentafluoroethylation, and may find applications

in the synthesis of ^{18}F-labeled 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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Conflict of interest

The authors declare no conflict of interest.

Keywords: copper · difluorocarbene · pentafluoroethylation · tetrafluoroethylation · tetrafluoroethylene

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[19] For details on the development of the reaction conditions with **5a**, see the Supporting Information.

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Communications

Fluorination

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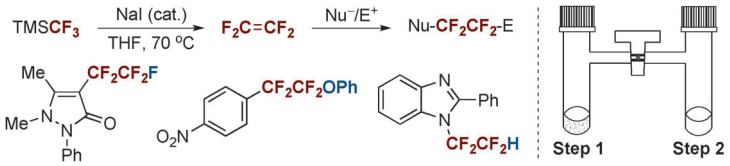
TMSCF$_3$ as a Convenient Source of CF$_2$=CF$_2$ for Pentafluoroethylation, (Aryloxy)tetrafluoroethylation, and Tetrafluoroethylation



In your own lab: The on-site generation of CF$_2$=CF$_2$ from TMSCF$_3$ under mild conditions is possible with a two-chamber system and can be used for per- or polyfluoroalkylation. This study describes a convenient and safe approach for the use of CF$_2$=CF$_2$ in standard laboratories, and provides a new method for pentafluoroethylation.

