



Trifluoromethylation Hot Paper

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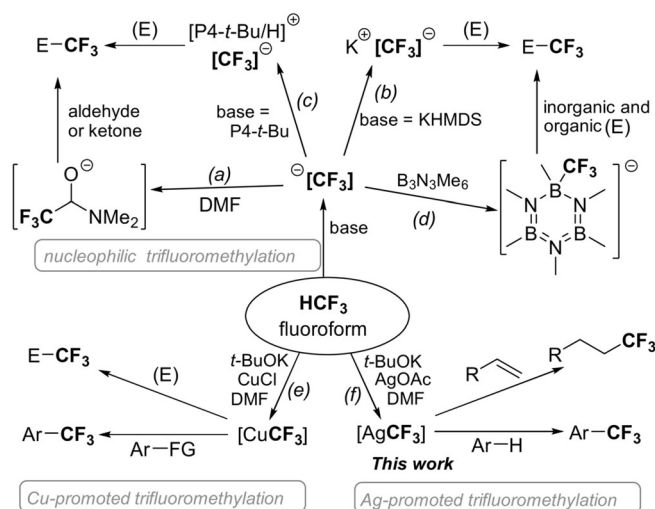
Argentation of Fluoroform: Preparation of a Stable AgCF_3 Solution with Diverse Reactivities

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Abstract: The transformation of a large-volume industrial by-product and stable greenhouse gas fluoroform (HCF_3) to useful products has recently received significant attention. Now, a simple and scalable preparation of AgCF_3 by treatment of HCF_3 with *t*-BuOK and AgOAc is disclosed. The reactivity of the HCF_3 -derived AgCF_3 has been demonstrated by hydrotrifluoromethylation of alkenes and C–H trifluoromethylation of (hetero)arenes. This work not only provides a new avenue for the utilization of HCF_3 , but also presents a reliable and easy-to-execute synthesis of the relatively stable AgCF_3 solution.

Fluoroform (HCF_3) is a large-volume by-product from fluoropolymer manufacturing and has a large greenhouse effect.^[1] The utilization of fluoroform as a feedstock for the preparation of valuable fluorinated compounds is a clearly preferred alternative to the destruction of fluoroform. Obviously, the application of fluoroform for the trifluoromethylation reaction is a highly attractive and much-sought-after goal,^[2] as it is the cheapest and most atom-economical but lowest-reactivity CF_3 source.

The common strategy to use HCF_3 in trifluoromethylation reactions is based on deprotonation with strong bases. Several groups have reported the nucleophilic trifluoromethylation of carbonyl compounds with HCF_3 in the presence of electrogenerated bases or alkali metal bases in DMF (Scheme 1 a).^[3] The solvent DMF traps the CF_3^- anion generated in situ, which easily decomposes to the fluoride anion and difluorocarbene,^[4] producing a reservoir of trifluoromethylating hemiaminolate species. Prakash (Scheme 1 b)^[5] and Shibata (Scheme 1 c)^[6] described the nucleophilic trifluoromethylation with HCF_3 in common organic solvents such as THF, ether, and toluene using KHMDS or *P4-t*-Bu, respectively as the base. Very recently, Szymczak disclosed that hexamethylborazine ($\text{B}_3\text{N}_3\text{Me}_6$) could act as a suitable Lewis acid to stabilize the CF_3^- anion.^[7] This HCF_3 -derived borazine CF_3^- adduct is



Scheme 1. Use of HCF_3 in trifluoromethylation reactions.

highly nucleophilic and reacts with a broad variety of inorganic and organic electrophiles (Scheme 1 d).

In 2011, Grushin discovered a methodologically different approach to activation of HCF_3 through direct cupration of HCF_3 with *t*-BuOK and CuCl in DMF (Scheme 1 e).^[8a] This HCF_3 -derived CuCF_3 not only reacts with electrophiles, but also trifluoromethylates aryl halides, boronic acids, and diazonium salts.^[8] Following Grushin's pioneering work, several groups further extended the application of HCF_3 -derived CuCF_3 for Cu-promoted trifluoromethylation of a wider range of substrates.^[9] Beside cupration of HCF_3 , the direct metalation of HCF_3 with other metals (Zn ,^[10] Ir ,^[11] and Pd ^[12]) has also been reported. However, the synthetic applications of these metal- CF_3 complexes are limited.^[10–12]

Recently, our group^[13] and others^[14,15] developed a series of Ag-promoted trifluoromethylation reactions in which AgCF_3 was formed as the reactant^[14] or reaction intermediate.^[13,15] Owing to thermal and light sensitivity, AgCF_3 normally needs to be freshly prepared^[14] or generated in situ^[13,15] from TMSCF_3 and AgF . On the other hand, although the stable ligand-supported AgCF_3 complexes^[14d,15b,16] are available, they are only used as transmetalating agents. Therefore, the synthesis of stable AgCF_3 with diverse reactivities is highly desirable. As part of our research interest in the development of trifluoromethylation reaction using cheap CF_3 sources,^[17] herein we disclose a practical preparation of the stable AgCF_3 solution from simple and inexpensive materials HCF_3 , *t*-BuOK, and AgOAc (Scheme 1 f). The synthetic utility of the HCF_3 -derived AgCF_3 is exemplified by hydrotrifluoromethylation of alkenes and C–H trifluorome-

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thylation of (hetero)arenes. Notably, it is difficult to achieve these transformations directly from the HCF₃-derived CuCF₃.

Our investigation started with the preparation of AgCF₃ by treatment of an excess of HCF₃ with *t*-BuOK in the presence of Ag^I salts using DMF as the solvent (Table 1). The

Table 1: Preparation of AgCF₃ from HCF₃.^[a]

HCF ₃	+ Ag salt	$\xrightarrow[\text{DMF, rt}]{t\text{-BuOK}}$	[AgCF ₃]	+ [Ag(CF ₃) ₂] ⁻
Entry	Ag salt	Yield [AgCF ₃] [%] ^[b]	Yield [Ag(CF ₃) ₂] ⁻ [%] ^[b]	
1	AgCl	41	4	
2	AgBr	20	28	
3	AgNO ₃	0	22	
4	AgBF ₄	0	23	
5	AgOAc	59	12	
6	AgOCOCF ₃	48	8	
7 ^[c]	AgOAc	80	4	
8 ^[c,d]	AgOAc	80	4	
9 ^[e]	AgOAc	87	3	

[a] Reaction conditions: HCF₃ (excess), Ag salt (0.2 mmol), *t*-BuOK (1.0 mmol), DMF (2.0 mL), N₂, rt, 8 h. [b] Yields determined by ¹⁹F NMR spectroscopy using trifluorotoluene as an internal standard. [c] The reaction was performed for 1 h. [d] HCF₃ (0.2 mmol), *t*-BuOK (0.4 mmol). [e] HCF₃ (40.0 mmol), AgOAc (40.0 mmol), *t*-BuOK (80.0 mmol), DMF (40.0 mL), N₂, rt, 1 h.

use of AgCl afforded the [AgCF₃] (resonates at $\delta = -20.7$ ppm, d, $J(^{107/109}\text{Ag}-\text{F}) = 109.0/124.1$ Hz)^[14a,18] in 41% yield along with [Ag(CF₃)₂]⁻ (resonates at $\delta = -25.4$ ppm, d, $J(^{107/109}\text{Ag}-\text{F}) = 86.5/101.5$ Hz)^[14a,18] in 4% yield (entry 1). Then, other Ag^I salts were screened to improve the yield of AgCF₃. Among all the Ag^I salts (entries 2–6), AgOAc was optimal to afford AgCF₃ in highest yield (entry 5). Reducing the reaction time from 8 to 1 h further improved the yield (entry 7). The use of stoichiometric amount of CF₃H also led to satisfactory yield (entry 8). Notably, this reaction can be easily scaled up to 40.0 mmol in 87% yield (entry 9).

Like the HCF₃-derived CuCF₃,^[8a] HCF₃-derived AgCF₃ also exhibited high stability. The solution of HCF₃-derived AgCF₃ in DMF was stored under N₂ atmosphere in the refrigerator for months without noticeable decomposition. Even a solution of AgCF₃ in DMF (0.55 M) was placed under air at room temperature, only slow decomposition of AgCF₃ was detected (Table 2). Furthermore, the thermal stability of the HCF₃-derived AgCF₃ solution was probed. This solution was found to have reasonable stability at 60°C for hours (Table 2).

Table 2: Stability of HCF₃-derived AgCF₃ solution.

Entry	<i>t</i> [h]	in air at rt		under N ₂ at 60°C	
		M ([AgCF ₃] + [Ag(CF ₃) ₂] ⁻) ^[a]	M ([AgCF ₃] + [Ag(CF ₃) ₂] ⁻) ^[a]	M ([AgCF ₃] + [Ag(CF ₃) ₂] ⁻) ^[a]	M ([AgCF ₃] + [Ag(CF ₃) ₂] ⁻) ^[a]
1	0	0.53 ± 0.02	0.53 ± 0.02	0.53 ± 0.02	0.53 ± 0.02
2	4	0.52 ± 0.02	0.52 ± 0.02	0.32 ± 0.03	0.32 ± 0.03
3	12	0.50 ± 0.02	0.50 ± 0.02	0.25 ± 0.02	0.25 ± 0.02
4	24	0.44 ± 0.02	0.44 ± 0.02	0.15 ± 0.01	0.15 ± 0.01
5	48	0.41 ± 0.02	0.41 ± 0.02	0.08 ± 0.01	0.08 ± 0.01

[a] Concentrations determined by ¹⁹F NMR spectroscopy using trifluorotoluene as an internal standard.

This HCF₃-derived AgCF₃ solution is a rare example of stable AgCF₃ reagents. It is much more stable than the common AgCF₃ reagent prepared from TMSCF₃ and AgF in MeCN (Table 3, entries 1 and 2). When DMF was used as

Table 3: Comparison of HCF₃-derived AgCF₃ with those prepared from TMSCF₃.

Entry	Preparation of AgCF ₃	% remained in air at rt ^[a]			
		0 h	4 h	12 h	24 h
1	HCF ₃ <i>t</i> -BuOK/AgOAc/DMF	100	98	95	84
2	TMSCF ₃ AgF/MeCN	100	68	39	trace
3	TMSCF ₃ AgF/DMF	100	70	46	trace
4	TMSCF ₃ AgF/DMF/KOAc	100	76	66	18
5	TMSCF ₃ AgF/DMF/ <i>t</i> -BuOK	100	83	73	53
6	TMSCF ₃ AgF/DMF/ <i>t</i> -BuOH	100	74	11	trace

[a] Percentages determined by ¹⁹F NMR spectroscopy using trifluorotoluene as an internal standard.

solvent instead of CH₃CN for the formation of AgCF₃ from TMSCF₃ and AgF, the stability of AgCF₃ reagent was slightly improved, but was still significantly lower than that of HCF₃-derived AgCF₃ solution (entry 3). Furthermore, the effect of additive on the stability of AgCF₃ generated from TMSCF₃ and AgF was investigated. Among these additives, including KOAc, *t*-BuOK, and *t*-BuOH, it was found that *t*-BuOK was crucial to the stability of AgCF₃ (entries 4–6).

With the HCF₃-derived AgCF₃ in hand, the hydrotrifluoromethylation of alkenes was then examined using methyl undec-10-enoate (**1a**) as the model substrate.^[19] The reaction of **1a** with a solution of AgCF₃ in DMF in the presence of 1,4-cyclohexadiene (1,4-CHD) failed to afford the desired product **2a** (Table 4, entry 1). As HCF₃-derived AgCF₃ is too stable to spontaneously collapse to form the CF₃ radical,

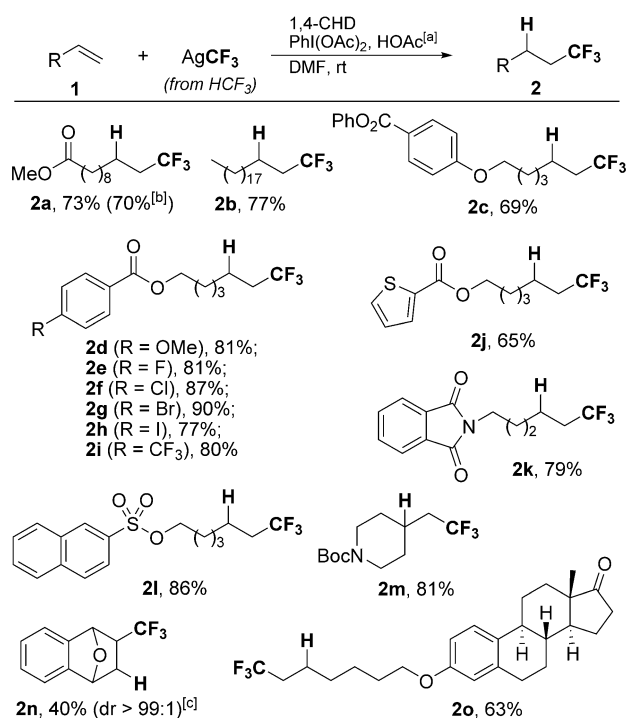
Table 4: Optimization of reaction conditions for hydrotrifluoromethylation of alkene **1a**.^[a]

Entry	Oxidant	Additive	Yield [%] ^[b]
1	–	–	0
2	PhI(OAc) ₂	–	50
3	PhI(OCOCF ₃) ₂	–	43
4	PhI(OAc) ₂	pyridine	42
5	PhI(OAc) ₂	NEt ₃	48
6	PhI(OAc) ₂	<i>t</i> -BuOH	60
7	PhI(OAc) ₂	HOAc	85
8	PhI(OAc) ₂	CF ₃ CO ₂ H	70
9	PhI(OAc) ₂	CF ₃ SO ₃ H	75

[a] Reaction conditions: **1a** (0.2 mmol), AgCF₃ (0.4 M, 2.0 mL, 0.8 mmol), 1,4-CHD (0.4 mmol), oxidant (0.8 mmol), additive (0.2 mmol), DMF (2.0 mL), N₂, rt, 12 h. [b] Yields determined by ¹⁹F NMR spectroscopy using trifluorotoluene as an internal standard.

the extra oxidant was used to oxidize AgCF_3 to generate CF_3 radical. Accordingly, when $\text{PhI}(\text{OAc})_2$ was added to the reaction mixture, the desired product **2a** was formed in 50% yield (entry 2). Switching the oxidant to $\text{PhI}(\text{OCOCF}_3)_2$ led to lower yield (entry 3). Subsequently, different additives including *N*- or *O*-containing donors were added to further improve the yield of **2a** (entries 4–9). Among them, HOAc was optimal to furnish **2a** in 85% yield (entry 7). The role of HOAc might be to activate *t*-BuOH- and/or DMF-coordinated AgCF_3 complex through ligand exchange.^[9m,20]

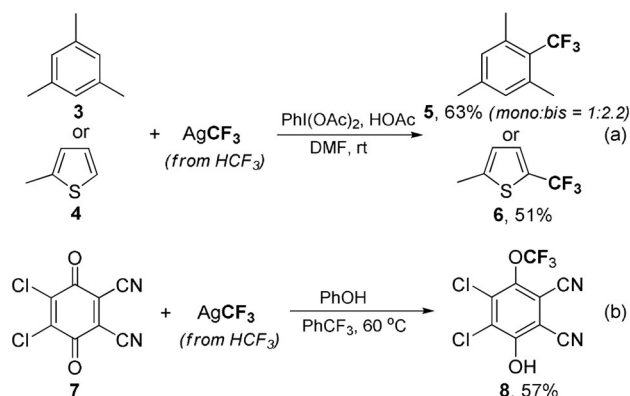
The scope of this oxidative hydrotrifluoromethylation was then investigated using HCF_3 -derived AgCF_3 under optimized reaction conditions. As shown in Scheme 2, various



Scheme 2. Hydrotrifluoromethylation of alkenes with AgCF_3 . [a] Reaction conditions: **1** (0.6 mmol), AgCF_3 (0.4 M, 6.0 mL, 2.4 mmol), 1,4-CHD (1.2 mmol), $\text{PhI}(\text{OAc})_2$ (2.4 mmol), HOAc (0.6 mmol), DMF (6.0 mL), N_2 , rt, 12 h, yields of isolated products. [b] The reaction was performed on 6.0 mmol. [c] Diastereomeric ratio was determined by ^{19}F NMR analysis of the reaction mixture.

alkenes were converted to the hydrotrifluoromethylated products in moderate to excellent yields. Interestingly, the reaction of **1a** was scaled up to 6.0 mmol with good efficiency. A wide range of functional groups, such as ether, ester, sulfonate, amide, and halogen atoms were well-tolerated under the reaction conditions. It should be noted that alkene **1j** bearing thienyl moiety was compatible with the reaction protocol. Furthermore, 1,1-disubstituted alkene **1m** delivered **2m** in 81% yield, whereas 1,2-disubstituted alkene **1n** furnished **2n** in 40% yield. The synthetic utility of this reaction was also demonstrated by late-stage hydrotrifluoromethylation of estrone derivative (**1o**).

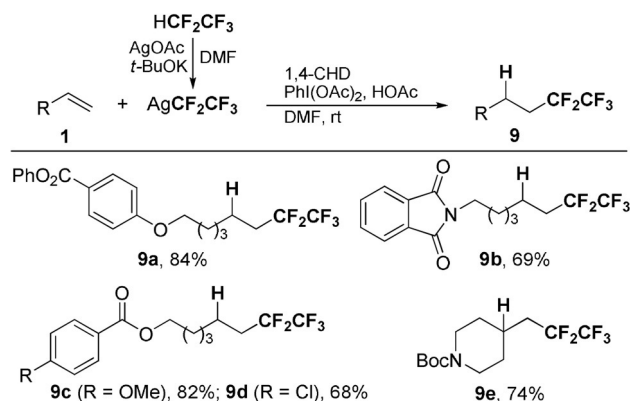
This HCF_3 -derived AgCF_3 was applied to other types of trifluoromethylation reactions. For instance, the C–H trifluoromethylation of arene **3** and heteroarene **4** with AgCF_3 afforded trifluoromethylated products **5** and **6** in moderate yields (Scheme 3a). Furthermore, treatment of 2,3-dicyano-



Scheme 3. Trifluoromethylation of (hetero)arenes and quinone with AgCF_3 .

5,6-dichlorobenzoquinone (DDQ, **7**) with AgCF_3 using PhOH as a proton donor furnished 1,6-hydrotrifluoromethylated^[21] product **8** in 57% yield (Scheme 3b). The 1,6-hydrotrifluoromethylation of quinones is previously unknown and might find applications for the preparation of novel 4-trifluoromethoxyphenols.

To extend the application of this protocol, AgCF_2CF_3 was prepared from HCF_2CF_3 (HFC-125, fire extinguishing agent) and applied to the hypopentafluoroethylation of alkenes (Scheme 4). Being different from the preparation of AgCF_3 along with formation of minor $[\text{Ag}(\text{CF}_3)_2]^-$ (Table 1), $[\text{AgCF}_2\text{CF}_3]$ was solely formed when HCF_2CF_3 was treated with *t*-BuOK and AgOAc .^[22] The oxidative hypopentafluoroethylation of alkenes in the presence of $\text{PhI}(\text{OAc})_2$, 1,4-CHD, and HOAc also proceeded efficiently to give the



Scheme 4. Hypopentafluoroethylation of alkenes with AgCF_2CF_3 . Reaction conditions: **1** (0.6 mmol), AgCF_2CF_3 (0.4 M, 6.0 mL, 2.4 mmol), 1,4-CHD (1.2 mmol), $\text{PhI}(\text{OAc})_2$ (2.4 mmol), HOAc (0.6 mmol), DMF (6.0 mL), N_2 , rt, 12 h, yields of isolated products.

pentafluoroethylated products in moderate to excellent yields.^[23]

In conclusion, we have described a new protocol for the utilization of fluoroform through the transformation to the synthetically useful AgCF₃. The HCF₃-derived AgCF₃ solution exhibited unique stability and diverse reactivities. Furthermore, HCF₂CF₃ was also converted to AgCF₂CF₃ solution for the preparation of pentafluoroethylated products. Further developments of new applications of R_pH-derived R_pAg are under investigation in our laboratory.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: alkenes · fluoroform · pentafluoroethylation · silver · trifluoromethylation

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