Cooperative Effect of Silver in Copper-Catalyzed Trifluoromethylation of Aryl Iodides Using Me$_3$SiCF$_3$

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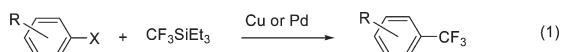
Ⓢ *Supporting Information*

ABSTRACT: An effective model of cooperative effect of silver for the copper-catalyzed trifluoromethylation of activated and unactivated aryl iodides to trifluoromethylated arenes using Me$_3$SiCF$_3$ was achieved with a broad substrate scope.
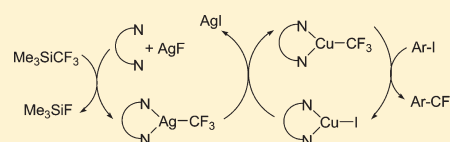
1. INTRODUCTION

Trifluoromethylated aromatics are one of most important classes of fluorinated organic compounds, which play a key role in pharmaceutical and fine chemical industries.[1,2] For instance, the highly commercially successful antidepressant fluoxetine (under the names of Prozac and Sarafem) and a number of herbicides, e.g., fluazifop-butyl (Fusilade), fluometuron (Cotoran), and acifluorfen (Blazer), all contain the CF$_3$ group on the aromatic ring. Only a few methods have been reported for the catalytic trifluoromethylation of haloarenes (eq 1), even though there is a great commercial driving force for developing such transformations.[3−8]

$$R\text{-}\langle\!\!\bigcirc\!\!\rangle\text{-}X \ + \ CF_3SiEt_3 \ \xrightarrow{\text{Cu or Pd}} \ R\text{-}\langle\!\!\bigcirc\!\!\rangle\text{-}CF_3 \qquad (1)$$

Conceivably, nucleophilic trifluoromethylation using metal-CF$_3$ reagents, e.g., Grignard reagents (CF$_3$MgX) and organolithium (CF$_3$Li),[9−11] is one of the more successful strategies for trifluoromethylation reactions. Unfortunately, inherent in these approaches are a number of limitations, especially in the formation of polymeric materials, difluorocarbene, and fluoride species, due to the strong repulsive interactions of the filled orbital on the carbanion with the lone pairs of the fluorine substituents.

"Cu−CF$_3$" species generated stoichiometrically *in situ* from early examples of (1) di- or trifluorinated methanes,[12−17] (2) group 12 trifluoromethyl derivatives, M(CF$_3$)$_2$ (where M = Zn, Cd, or Hg),[18−20] (3) trifluoroacetic and fluorosulfonyldifluoroacetic acid derivatives,[21−33] and (4) Ruppert's or Ruppert−Prakash reagent[34−36] and its ethyl derivative, CF$_3$SiEt$_3$,[37] have shown very promising reactivities toward trifluoromethylation of aryl halides. Prolific reports on the utility and expansion of these methods are well comprehensively compiled in numerous excellent reviews.[38−41] Important progress in the utilization of

well-defined Cu(I)−CF$_3$ complexes has also been demonstrated.[34,42] However, these methods are not favorable for large-scale practical applications because of the use of harsh reaction conditions, toxic or expensive sources of the CF$_3$ group, and low yields of the trifluoromethylated products. Metal-catalyzed trifluoromethylation of aryl halides is not unprecedented, but reports are scarce. In 1989, Chen and Wu reported the use of fluorosulfonyldifluoroacetic acid for the transformation using catalytic amounts of copper.[26] More recently, Amii and co-workers demonstrated a catalytic system by employing CuI, 1,10-phenanthroline, and CF$_3$SiEt$_3$ as the trifluoromethylation source.[6] Contravening the conventional wisdom of a highly difficult reductive elimination of aryl and −CF$_3$ groups from Pd, Buchwald and co-workers successfully demonstrated a Pd-catalyzed model for chloroarenes using BrettPhos as the ligand and CF$_3$SiEt$_3$ as the trifluoromethylating agent.[7] While the work by the Amii and Buchwald groups using Cu and Pd catalysts and Et$_3$SiCF$_3$ are remarkable breakthroughs, low yields were observed when the more economical Me$_3$SiCF$_3$ (Ruppert's reagent)[43] was employed, presumably due to its self-decomposition in the presence of fluoride under those reaction conditions.[44] Herein, we report a cooperative catalytic model of silver-assisted copper-catalyzed trifluoromethylation of aryl iodides using Me$_3$SiCF$_3$.

2. RESULTS AND DISCUSSION

As part of our interest in the development of metal-catalyzed cross-coupling reactions and heterobimetallic catalysis,[45,46] we continue to pursue new methodologies by combining the different reactivities of two metals for trifluoromethylation of

Table 1. Impact of Reaction Parameters on the Trifluoro-methylation of Aryl Iodides
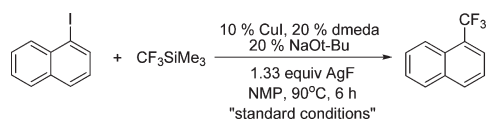
entry	variation from the "standard conditions"	yield^a (%)
1	standard	71
2	no CuI	<2
3	10% NiCl$_2$(DME) [instead of CuI]	<5
4	1.33 equiv of KF [instead of AgF]	18
5	1.33 equiv of t-Bu$_4$NF·3H$_2$O [instead of AgF]	0
6	AgOTf [instead of AgF]	<2
7	no NaOt-Bu [instead of 20% NaOt-Bu]	41
8	DMSO [instead of NMP]	58
9	DMF [instead of NMP]	54
10	rt, 20 h [instead of 90 °C, 6 h]	<5

^{a} Determined by ^{19}F NMR relative to 4-fluorobenzonitrile as an internal standard. Yields are based on aryl iodides as the limiting reagent.

aryl iodides. We began our studies by examining the reactions of aryl iodide and Me$_3$SiCF$_3$ in the presence of CuI, AgF, NaOt-Bu, and N,N'-dimethylethylenediamine (dmeda) (Table 1). It was intuitive to predict that AgF may promote the reaction due to the high affinity between the silver cation and the iodide as well as that between the fluoride ion and silicon. Indeed, it was found that 1-iodonaphthalene coupled with Me$_3$SiCF$_3$ at 90 °C in N-methylpyrrolidone (NMP) to produce 1-(trifluoromethyl)-naphthalene in 71% yield in the presences of AgF (entry 1). In the absence of CuI, essentially none of the desired Ar—CF$_3$ bond formation was observed (entry 2). NiCl$_2$(DME) was proved to be inefficient for the trifluoromethylation of aryl halides (entry 3). It was noted that the use of KF furnished the target compound only in a significantly lower yield (18%, entry 4), while Amii et al. have shown that it performs well in similar reactions with Et$_3$SiCF$_3$.[6] Other fluoride sources, such as t-Bu$_4$NF·3H$_2$O, are totally inactive (entry 5). Using AgOTf instead of AgF does not promote the reaction with copper (entry 6). These results suggest that both CuI and AgF are essential for efficient catalysis. NaOt-Bu was identified to be necessary for higher yields (entry 7). The coupling reactions proceed with less efficiency in DMF and DMSO (entries 8 and 9).

This new methodology was further found to be successfully applied to catalyze the trifluoromethylation of a range of iodoarenes with Me$_3$SiCF$_3$, affording the desired trifluoromethy-lated aromatics in moderate to excellent yields (Table 2). It was found noteworthy that activated electron-poor aryl iodides as well as deactivated electron-rich ones (e.g., entries 9, 10) are both suitable reaction substrates. Functional groups, such as cyano, nitro, acetals, and the trifluoromethyl group, are tolerated.

In an effort to elucidate the role that AgF plays to significantly enhance the yields for the Cu-catalyzed trifluoromethylation using Me$_3$SiCF$_3$, we designed and prepared dinitrogen-ligated trifluoromethyl silver(I) and copper(I) complexes and tested their reactivities toward aryl iodides. We focused our attention on bathophenanthroline ligands. Adopting the literature method for the synthesis of perfluoroorganosilver(I) compounds,[47] the colorless sliver(I) complex (bathophenanthroline)AgCF$_3$ (**1**)

Table 2. Catalytic Trifluoromethylation of Aryl Halides

entry	aryl halides	ligand^a	products	Yield (%)^b
1		L1	CF$_3$	75^c
2	NC—I	L1	NC—CF$_3$	89
3	NC—I	L2	NC—CF$_3$	74
4	O$_2$N—I	L1	O$_2$N—CF$_3$	98^c
5	O$_2$N—I	L2	O$_2$N—CF$_3$	60
6	F$_3$C—I	L1	F$_3$C—CF$_3$	64
7	H$_3$C—I	L1	H$_3$C—CF$_3$	73
8	CH$_3$	L1	CH$_3$	59
9	OCH$_3$	L1	OCH$_3$	47
10	OCH$_3$	L1	OCH$_3$	66
11	CF$_3$	L1	CF$_3$	61
12		L1	CF$_3$	76^c

^{a} **L1**: N,N'-dimethylethylenediamine; **L2**: 1,10-phenanthroline. ^{b} Determined by ^{19}F NMR. ^{c} Isolated yield.
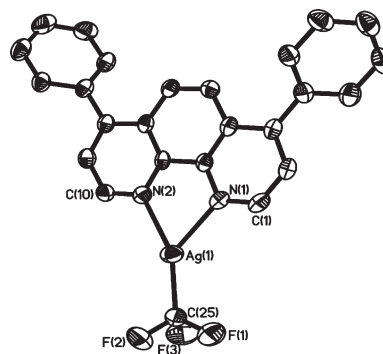
Figure 1. ORTEP diagram of (bathophenanthroline)AgCF$_3$ (**1**) with thermal ellipsoids at the 30% probability level. Selected bond lengths (Å) and angles (deg): Ag(1)—C(25) 2.092(6), Ag(1)—N(1) 2.389(5), Ag(1)—N(2) 2.263(5), N(1)—Ag(1)—N(2) 70.57(17).

was successfully synthesized in 74% yield from a reaction mixture of AgF, Me$_3$SiCF$_3$, and bathophenanthroline in THF. The analogous copper complex (bathophenanthroline)CuCF$_3$ (**2**) was prepared in 64% yield from a reaction of Cu(Ot-Bu), Me$_3$SiCF$_3$, and bathophenanthroline as orange solids.

Suitable crystals of **1** and **2** for X-ray crystallography were obtained by recrystallization in THF/n-hexane at −25 °C. Their molecular structures are shown in Figures 1 and 2. Both structures show a three-coordinated trigonal-planar geometry in which the Ag(I) or Cu(I) center is bound by one neutral
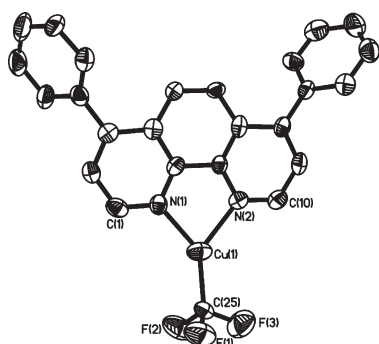
Figure 2. ORTEP diagram of (bathophenanthroline)CuCF$_3$ (**2**) with thermal ellipsoids at the 30% probability level. Selected bond lengths (Å) and angles (deg): Cu(1)−C(25) 1.907(9), Cu(1)−N(1) 2.024(8), Cu(1)−N(2) 2.096(8), N(1)−Cu(1)−N(2) 79.3(3).

bidentate bathophenanthroline ligand and one anionic CF$_3$ group. To the best of our knowledge, complex **1** is the first example of an isolable neutral Ag(I)−CF$_3$ complex, although certain ionic forms have been reported in the literature.[47] The metal−CF$_3$ distance in **1** (2.092(6) Å) is found to be significantly longer than that of **2** (1.907(9) Å) and that of a NHC−Cu complex (IPr)CuCF$_3$ (2.022(4) Å).[34] The N−M−N angle in **1** (70.57°) is significantly smaller than that in **2** (79.3°).

Since **1** was readily formed by mixing AgF, Me$_3$SiCF$_3$, and bathophenanthroline, we propose that the Ag−CF$_3$ bond was first generated under our Cu-catalyzed trifluoromethylation conditions. It is noted that in contrast to copper and palladium the investigations on the utilization of silver in trifluoromethylation reactions are limited, although "Ag(I)CF$_3$" species are known for their use in nucleophilic substitutions.[47,48] We sought to evaluate the reactivity of silver complex **1** for the trifluoromethylation of aryl halides. The reaction of **1** with 5 equiv of 4-iodobenzonitrile, however, formed no coupling products in NMP after 3 h at 90 °C (eq 2). In sharp contrast, the reactions of copper complex **2** with 5 equiv of 4-iodobenzonitrile in NMP proceeded smoothly and formed the coupling product in 81% yield after 30 min (eq 3). The results suggest the possibility of transferring the CF$_3$ group from **1** to a Cu center to allow the coupling reactions to proceed. Indeed, we confirmed that the reaction of the well-documented copper iodide complex **3**[49] with **1** yielded complex **2** in 80% yield at room temperature (eq 4).
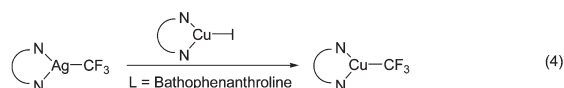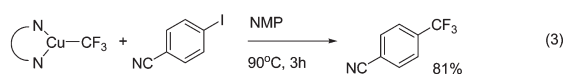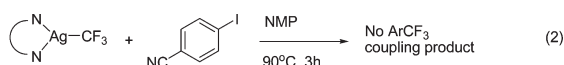
These observations strongly support the collaborative effect by the combination of Ag and Cu for the trifluoromethylation of iodoarenes: the transmetalation of the *in situ* generated trifluoromethylsilver species with copper iodide forms the trifluoromethylcopper species, which is followed by the reaction with iodoarenes to release the Ar−CF$_3$ coupling products and to regenerate copper iodide (Scheme 1).

Scheme 1. Proposed Reaction Pathway for the Cu/Ag-Catalyzed Trifluoromethylation of Aryl Iodides
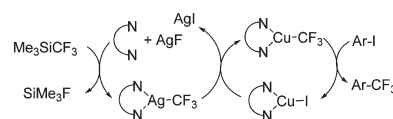
3. CONCLUSION

In summary, we have demonstrated a cooperative effect of silver for the copper-catalyzed trifluoromethylation of activated and unactivated aryl iodides to trifluoromethylated arenes using the more desirable Me$_3$SiCF$_3$ reagent. The present methodology can tolerate a variety of functional groups. We have also prepared the well-defined dinitrogen-ligated trifluoromethyl Ag(I) and Cu(I) complexes **1** and **2** to elucidate their cooperative interactions. Work on kinetic analysis and the extension to more practical applications is ongoing in our laboratories and will be reported in due course.

4. EXPERIMENTAL SECTION

General Procedures. All reactions were carried out using conventional Schlenk techniques under an inert atmosphere of nitrogen or argon with an MBraun Labmaster 130 inert gas system. NMR spectra were measured on Bruker ACF300 300 MHz FT NMR spectrometers (^{1}H at 300.14 MHz, ^{13}C at 75.43 MHz). ^{19}F NMR spectra (282.38 MHz) were recorded using hexafluorobenzene (C$_6$F$_6$) as an internal standard (δ 0 ppm). Elemental analyses were performed by the microanalytical laboratory in-house. All chemicals were obtained from Sigma-Aldrich or Strem Chemicals unless stated otherwise. [(Bathophenanthroline)CuI]$_2$ was synthesized according to the literature.[49]

*(Bathophenanthroline)AgCF$_3$ (**1**).* A mixture of AgF (13.0 mg, 0.102 mmol) and bathophenanthroline (33.2 mg, 0.100 mmol) in THF (6 mL) was stirred at rt for 10 min. To the resulting suspension was added a THF (1 mL) solution of Me$_3$SiCF$_3$ (28.0 mg, 0.197 mmol). The mixture was further stirred at rt for 6 h and then filtered through a layer of Celite. The filtrate was diluted with 4 mL of *n*-hexanes. The resulting solution was then cooled at −25 °C for 36 h. Colorless needles were formed, separated, washed with 2 × 2 mL of *n*-hexanes, and dried to give 38 mg of **1** (73%): ^{1}H NMR (300 MHz, THF-d_8) δ 9.13 (br, 2H), 7.86 (br, 2H), 7.65−7.54 (m, 12H); ^{13}C{^{1}H} NMR (75.5 MHz, THF-d_8) δ 147.9, 146.7, 144.1, 135.9, 127.6, 126.5, 126.4, 124.3, 121.9, 121.7; ^{19}F NMR (282 MHz, THF-d_8) δ 144.3 (d, J = 29.2 Hz). Anal. Calcd for C$_{25}$H$_{16}$AgF$_3$N$_2$: C, 58.96; H, 3.17; N, 5.50. Found: C, 58.54; H, 3.48; N, 5.04.

*(Bathophenanthroline)CuCF$_3$ (**2**).* A solution of NaO*t*-Bu (18.0 mg, 0.188 mmol) in 2 mL of THF was added to a suspension of CuCl (15.0 mg, 0.152 mmol) in 3 mL of THF, and the resulting light yellow mixture was stirred at rt for 1 h. The solution was filtered through a layer of Celite. To this filtrate was added a suspension of bathophenanthroline (50.0 mg, 0.150 mmol) in 3 mL of THF, followed by addition of a THF (0.5 mL) solution of Me$_3$SiCF$_3$ (28.0 mg, 0.197 mmol). The mixture turned red immediately and was further stirred at rt for an additional 5 min. The solution was filtered, and to the filtrate was added 8 mL of *n*-hexanes. The resulting solution was then cooled at −25 °C for 36 h. The resulting red crystals were washed with 2 × 2 mL of *n*-hexanes and dried to give 45 mg of **2** (64%): ^{1}H NMR (300 MHz, THF-d_8) δ 9.18 (d, J = 3.8 Hz, 2H), 7.91 (s, 2H), 7.72 (d, J = 4.1 Hz, 2H), 7.57−7.55 (m, 10H); ^{13}C{^{1}H} NMR (75.5 MHz, THF-d_8) δ 147.3, 146.6, 143.9, 135.7, 127.6, 126.6, 124.4, 122.2, 122.0; ^{19}F NMR (282 MHz, THF-d_8)

δ 132.2. Anal. Calcd for $C_{25}H_{16}CuF_3N_2$: C, 64.58; H, 3.47; N, 6.03. Found: C, 64.12; H, 3.58; N, 5.59.

General Procedures for Trifluoromethylation Reactions. A light yellow mixture of CuI (2.9 mg, 0.015 mmol, 10 mol %) and NaO-t-Bu (3.0 mg, 0.030 mmol) in 0.5 mL of NMP is a reaction vial was stirred at rt for 10 min. To this mixture was added N,N'-dimethylethylenediamine (2.7 mg, 0.030 mmol, 20 mol %), and the resulting mixture was stirred at rt for an additional 2 min, followed by the addition of iodoarene (0.15 mmol), AgF (25.4 mg, 0.20 mmol), and Me_3SiCF_3 (43.0 mg, 0.30 mmol). The vial was sealed with a Teflon screw cap, and the reaction mixture was stirred at 90 °C for 30 min. The mixture was cooled to rt, and a second portion of Me_3SiCF_3 (16 mg, 0.11 mmol) was added. After stirring at 90 °C for an additional 5 h, the mixture was cooled to rt and filtered through a layer of Celite. The filtrate was analyzed by GC-MS. The yield of the product was calculated by ^{19}F NMR.

Crystal Structure Analyses. Suitable crystal of **1** and **2** were mounted on quartz fibers, and X-ray data collected on a Bruker AXS APEX diffractometer, equipped with a CCD detector at −50 °C, using Mo Kα radiation (λ 0.71073 Å). The data were corrected for Lorentz and polarization effects with the SMART suite of programs[50] and for absorption effects with SADABS.[51] Structure solution and refinement were carried out with the SHELXTL suite of programs.[52] The structure was solved by direct methods to locate the heavy atoms, followed by difference maps for the light non-hydrogen atoms. In crystal **1**, the asymmetric unit contains two molecules of $C_{25}H_{16}F_3N_2Cu$ and on average 2.5 THF; in **2**, the asymmetric unit contains two molecules of $C_{25}H_{16}F_3N_2Ag$ and on average 2.5 THF.

■ ASSOCIATED CONTENT

ⓢ Supporting Information. Product analysis and crystal data for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

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