

# A Broadly Applicable Copper Reagent for Trifluoromethylations and Perfluoroalkylations of Aryl Iodides and Bromides\*\*

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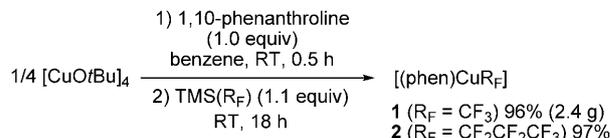
A large number of recently launched pharmaceuticals and pharmaceutical candidates contain perfluoroalkyl groups because these moieties affect the physical properties and biological processing of organic molecules, while being stable to degradation.<sup>[1]</sup> For this reason, the introduction of trifluoromethyl groups into aryl halides by simple laboratory procedures is a major synthetic goal. Despite much effort to develop reactions that introduce trifluoromethyl groups into arene substrates, current methods are limited by some combination of high temperatures, high catalyst loadings, expensive reagents, catalysts, and ligands, low reactivity with electron-rich aromatic groups, and intolerance toward protic and electrophilic functional groups.<sup>[2–6]</sup> Methods to introduce longer perfluoroalkyl groups into aryl halides are even more limited.<sup>[7,8]</sup>

Recently, Amii and co-workers published a seminal report on copper-catalyzed trifluoromethylation of electron-deficient aryl iodides with triethyl(trifluoromethyl)silane (TESCF<sub>3</sub>) as reagent.<sup>[3]</sup> They suggested that the reaction proceeds through the phenanthroline-ligated copper(I) complex [(phen)CuCF<sub>3</sub>], but this complex had not been generated previously and was not isolated or detected spectroscopically in the catalytic system. The reaction was shown to occur with electron-poor aryl iodides, but no product was observed from reactions with electron-rich aryl iodides and the reaction of electron-neutral 4-butyl iodobenzene occurred in less than 50% yield. Furthermore, we found (see below) that the same reaction conducted with superstoichiometric amounts of copper and ligand gave the same modest yield of product from trifluoromethylation of 4-butyl iodobenzene.

As part of our studies on the structures and reactions of isolated copper complexes that are potential intermediates in cross-coupling reactions,<sup>[9]</sup> we sought to determine the structure and stability of the proposed [(phen)CuCF<sub>3</sub>] (**1**) and to determine the relative reactivity of this complex as a

discrete species toward electron-poor and electron-rich iodoarenes. We report two routes to form [(phen)CuCF<sub>3</sub>] (**1**) and its higher perfluoroalkyl homologue [(phen)CuCF<sub>2</sub>CF<sub>2</sub>CF<sub>3</sub>] (**2**) in high yield, one route that forms these two complexes as pure, isolated species and one that forms them in high yield in DMF. Most striking, isolated **1** and **2** react in high yield at room temperature with not only electron-poor iodoarenes, but also electron-neutral and electron-rich iodoarenes that possess a wide range of functional groups. Because these complexes are prepared from inexpensive reagents, complexes **1** and **2** represent practical reagents for the perfluoroalkylation of iodoarenes and selected bromoarenes. Mechanistic studies show that these complexes react without the intermediacy of aryl radicals.

Phen-ligated trifluoromethylcopper complex **1** was prepared by the reaction of [CuOtBu]<sub>4</sub><sup>[10]</sup> with 1,10-phenanthroline, followed by the addition of TMSCF<sub>3</sub>. From this process, complex **1** was isolated as an orange-red solid in 96% yield. Perfluoropropylcopper complex **2** was synthesized in 97% yield by an analogous reaction starting with commercially available (perfluoropropyl)trimethylsilane (Scheme 1). Both



**Scheme 1.** Synthesis of 1,10-phenanthroline-ligated (perfluoroalkyl)copper(I) complexes **1** and **2**.

complexes were characterized by <sup>1</sup>H, <sup>13</sup>C, and <sup>19</sup>F NMR spectroscopy and elemental analysis. The only previously isolated trifluoromethyl complex was the NHC-ligated complex reported by Vicić et al.<sup>[11,12]</sup> No isolated higher perfluoroalkyl complexes have been reported.

Complexes **1** and **2** are soluble in polar, aprotic solvents, such as DMF and DMSO, partially soluble in THF and CH<sub>2</sub>Cl<sub>2</sub>, and insoluble in less polar solvents, such as benzene and Et<sub>2</sub>O. Conductivity experiments on **1** indicate that this species adopts the ionic form [(phen)<sub>2</sub>Cu][Cu(CF<sub>3</sub>)<sub>2</sub>] in DMF (See Supporting Information for details of these measurements). The <sup>19</sup>F NMR spectrum of **1** in DMF clearly shows two species; one component [(phen)<sub>2</sub>Cu][Cu(CF<sub>3</sub>)<sub>2</sub>] resonates at δ = −30.8 ppm, and the second component [(phen)CuCF<sub>3</sub>] resonates at δ = −22.6 ppm.<sup>[2e]</sup> Isolated **1** and **2** were stable at room temperature under nitrogen atmosphere for over one month without decomposition.

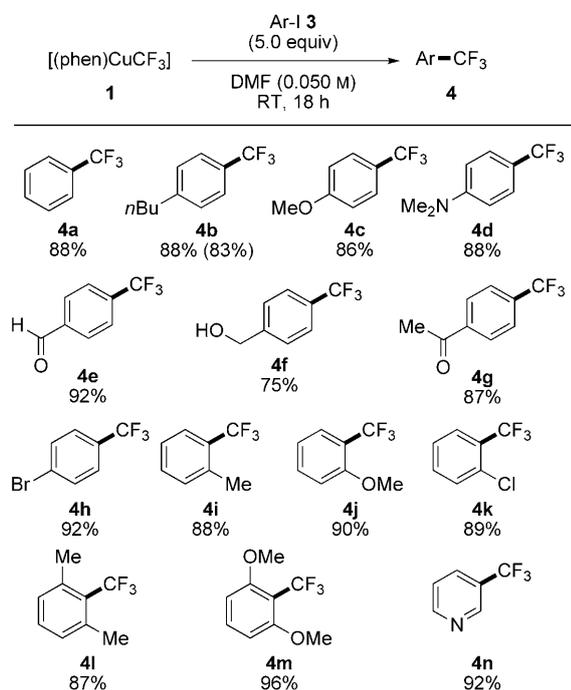
In contrast to the catalytic reactions proposed to occur through complex **1**, isolated **1** reacts in high yields with

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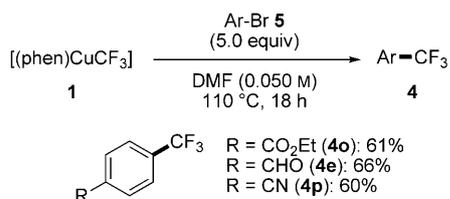
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electron-neutral and electron-rich aryl iodides. Complex **1** also reacts in high yield with aryl iodides containing a wide range of potentially reactive functional groups. The reactions of isolated **1** with excess aryl iodides and bromides are shown in Schemes 2 and 3. The reaction of **1** with **3a–3n** gave



**Scheme 2.** Reactivity of complex **1** with 5 equivalents aryl iodide **3** at room temperature. Yield was determined by  $^{19}\text{F}$  NMR analysis with  $4\text{-CF}_3\text{OC}_6\text{H}_4\text{OMe}$  as internal standard. The yield was reported as an average of two runs. Yield of **4b** in parentheses was obtained from the reaction with complex **1** stored over 1 month under nitrogen atmosphere.



**Scheme 3.** Reactivity of complex **1** with 5 equivalents aryl bromide **5** at  $110^\circ\text{C}$ .

trifluoromethylarenes **4a–4n** in good yield. The reaction of **3a** and **3b** shows that compound **1** converts electron-neutral iodoarenes to trifluoromethylarenes in nearly quantitative yields, and the reactions of **3c** and **3d** show that this compound also converts electron-rich iodoarenes to trifluoromethylarenes in equally high yields. The reactions of **1** also tolerate a significant degree of steric hindrance. The combination of **1** and even 2,6-disubstituted aryl iodides **3l** and **3m** formed **4l** and **4m** in good yield. These results imply that iodoarenes react with an intermediate other than complex **1** in

the previously reported catalytic reactions or that this complex is formed in only very small quantities under those reaction conditions.<sup>[3]</sup>

Results of reactions of iodoarenes containing typically reactive functional groups, such as amino, alkoxy, hydroxyalkyl, halo, keto, and formyl groups, are also displayed in Scheme 2. Bromo- and chloro-substituted iodoarenes **3h** and **3k** reacted selectively at the iodide. In addition to the reactions of electron-rich iodoarenes noted above, the reactions with haloarenes containing aldehyde, alcohol, and ketone functionalities (**3e**, **3f**, and **3g**) are particularly striking. Substrates containing these functional groups were not reported to undergo palladium- or copper-catalyzed trifluoromethylation reactions,<sup>[2a,c,3,4,6]</sup> but they do react with **1** to form the trifluoromethylarenes in high yield.

The reactivity of **1** with substrates **3e** and **3g** containing formyl and acetyl groups also contrasts with the reaction of these substrates groups with  $\text{CF}_3$  anions generated from Ruppert's reagent in the presence of fluoride activators.<sup>[13]</sup> For example, conditions reported by Fuchikami and co-workers for the copper-mediated trifluoromethylation without added ligand ( $\text{CuI} + \text{TESCF}_3 + \text{KF}$ ) led to reaction of aryl iodide **3g** to give a mixture of the desired cross-coupled product **4g** and trifluoromethyl carbinols from nucleophilic addition to the ketone function.<sup>[8]</sup> In contrast, isolated **1** reacted with **3e** and **3g** to form the corresponding trifluoromethylarenes in high yield.

As shown in Scheme 3, reactions of electron-deficient bromides **5** also gave trifluoromethylarene products in good yield. Like reactions of aryl iodides, the reactions of aryl bromides tolerated electrophilic functional groups, such as ester, aldehyde, and nitrile moieties.

To gain insight into the differences between the reactivity of isolated **1** and the catalytic reactions proposed to occur through **1**, we submitted several of the substrates in Scheme 2 to the recently reported catalytic reaction conditions.<sup>[3]</sup> In each case, we found that less than half the yield of the reaction of isolated **1** was observed from the reactions with catalytic amounts of **1**.<sup>[14]</sup> In addition, the reaction of benzaldehyde **3e** under published conditions involving catalytic amounts of phen and CuI formed the trifluoromethyl carbinol without any of the desired trifluoromethylarene, and reaction of acetophenone **3g** under these conditions gave low conversion to a 1:1:2 mixture of 1-(4-(trifluoromethyl)phenyl)ethanone (**4g**), 1,1,1-trifluoro-2-(4-(trifluoromethyl)phenyl)propan-2-ol, and 1,1,1-trifluoro-2-(4-iodophenyl)propan-2-ol. This mixture of products is the same as that observed by Fuchikami and co-workers by copper-mediated trifluoromethylation without added ligand.<sup>[8]</sup> Moreover, reactions conducted with a copper and ligand loading of 100% under conditions otherwise identical to the catalytic conditions did not give product yields comparable to those observed with complex **1**. Thus, the milder conditions and broader scope we observe for the reactions of complex **1** likely stems from the generation of **1** as a discrete species in high yield.

The unprecedented substrate scope displayed by **1** and the facile synthesis of this complex led us to appreciate that complex **1** itself represents a practical reagent for trifluoromethylation. For this complex to be useful, it must react with

iodoarenes when the ratio of iodoarenes and copper complex **1** is nearly 1:1 and the iodoarene is the limiting reagent. Indeed, simply reducing the concentration of iodoarenes led to reactions of aryl iodides **3c**, **3e**, and **3g** with 1.5 equiv compound **1** in yields similar to those obtained when using the copper complex as limiting reagent (Scheme 4). Simple aryl iodides, like **3t** and **3q**, and functionalized aryl iodides containing amide (**3r**), ester (**3o** and **3u**), aldehyde (**3u**), bromide (**3v**), and heterocyclic (**3w**, **3x**, **3y**) functionality reacted with **1** to give trifluoromethylarenes **4** in good yields. Quinoline **3x** containing an exposed basic nitrogen was converted to the corresponding trifluoromethyl heteroarene in greater than 90% yield at room temperature, and similar results were obtained for the purine and indole derivatives **3w** and **3y**. The functionalized aryl iodide **3z**, which is available by metalation with Knochel's LiCl-(TMP)MgX reagent and

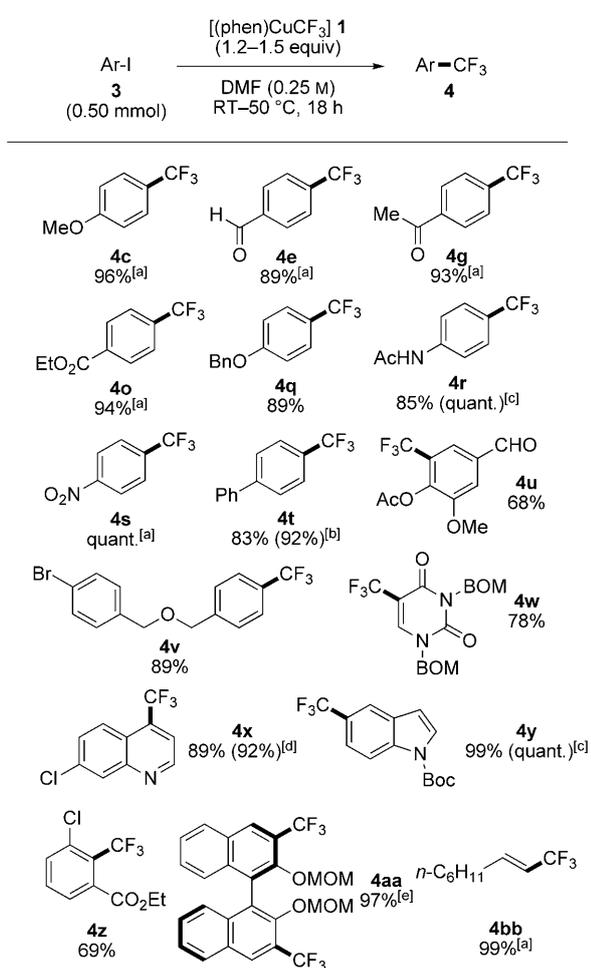
iodination of the arylmagnesium intermediate,<sup>[15]</sup> also gave product **4z** in good yield. Finally, trifluoromethylation of the 3,3'-diiodo-binol derivative **3aa** gave the MOM-protected 3,3'-(CF<sub>3</sub>)<sub>2</sub>-binol **4aa** under mild conditions. Previous syntheses of 3,3'-(CF<sub>3</sub>)<sub>2</sub>-binol have required superstoichiometric amounts of Burton's CuCF<sub>3</sub> reagent or generate stoichiometric amounts of SO<sub>2</sub> and MeI.<sup>[16,17]</sup>

Complex **1** that was stored for long periods under nitrogen displayed reactivity that is similar to that of freshly prepared complex. The reaction of **3b** with **1** stored in glove box over one month gave **4b** in 83% yield, which is comparable to the result with freshly prepared **1**. Moreover, a glove box is unnecessary for conducting these reactions. The reaction of *p*-phenyl iodoarenes **3t** with **1** that was weighed quickly in air formed the trifluoromethylarene product in 92% yield. Vinyl iodide **3bb** reacted with **1** to afford the trifluoromethylalkene **4bb** in 99% yield.

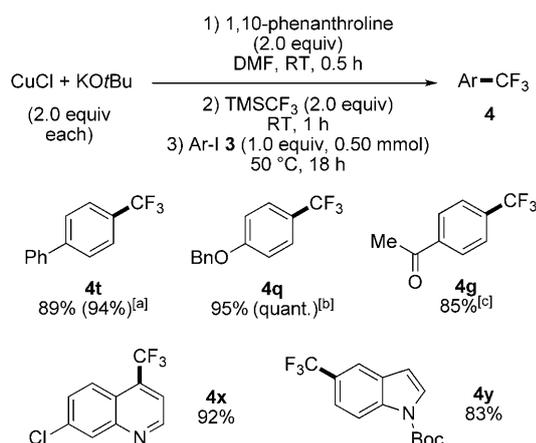
Having established a method to prepare **1** in isolated form, we sought a method to generate **1** as a discrete species in situ prior to addition of the iodoarenes to enable the use of **1** on larger scales. We prepared [(phen)CuOtBu] in situ in DMF from commercially available copper chloride, potassium *tert*-butoxide, and 1,10-phenanthroline, which were all weighed outside of the glove box. The solution of [(phen)-CuOtBu] was then treated with Ruppert's reagent to afford phen-ligated trifluoromethylcopper **1**. Subsequent addition of aryl iodides **3** to the mixture provided trifluoromethylarenes **4** in 83 to 99% yield. The use of copper chloride and potassium *tert*-butoxide, as well as formation of complex **1** prior to the addition of the aryl halide was important to achieve these high yields.

The results of reactions conducted under these conditions that generate **1** in situ are shown in Scheme 5. These reactions include those of aryl halides containing electron-donating groups, electron-withdrawing groups, potentially reactive functional groups, and both electron-rich and electron-poor heterocyclic compounds. Each of these reactions occurred in yields that were comparable to those of reactions of these iodoarenes with isolated **1**. In addition, the reaction of benzyloxy-substituted **3q** on a 10 mmol scale formed the trifluoromethylarene in quantitative yield after 24 h to give 2.5 g of the product **4q**. Thus, the reactions of complex **1** generated in situ represent a procedure for trifluoromethylation of aryl iodides that occurs under mild conditions from inexpensive, commercially available reagents. The total cost of the reagents to generate **1** in situ is less than \$1/mmol.

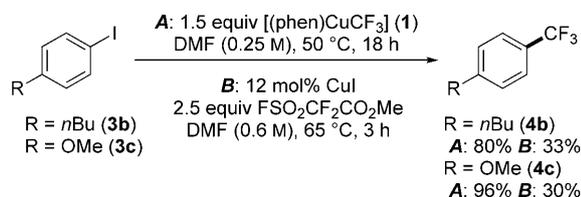
Prior to this work, one of the most general copper-mediated methods for arene trifluoromethylation involved the combination of catalytic CuI with methyl fluorosulfonyldifluoroacetate FSO<sub>2</sub>CF<sub>2</sub>CO<sub>2</sub>Me. We compared the scope of this trifluoromethylation reaction under the reported conditions, but with the aryl halide as limiting reagent, to our method with complex **1** (Scheme 6).<sup>[18]</sup> An electron-rich and an electron-neutral aryl iodide were chosen to compare the reaction conditions. The yields of trifluoromethylarene products, as determined by <sup>19</sup>F NMR analysis using 4-CF<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>OMe as internal standard, were much higher under the reaction conditions with 1.5 equiv phen-ligated **1** than with catalytic CuI and 2.5 equiv FSO<sub>2</sub>CF<sub>2</sub>CO<sub>2</sub>Me.



**Scheme 4.** Copper-mediated trifluoromethylation with isolated (trifluoromethyl)copper(I) complex **1**. The reactions were conducted with 0.50 mmol aryl iodide **3** and 0.75 mmol **1** in DMF (0.25 M) at 50 °C; yields of isolated products are reported unless otherwise noted. The reactions of **3c**, **3e** and **3bb** were run on a 0.10 mmol scale. [a] The yield was determined by <sup>19</sup>F NMR spectroscopy with 4-CF<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>OMe as internal standard. [b] The reaction was performed with **1** that was weighed in air. [c] The reaction was performed at room temperature. [d] The reaction was performed with 1.2 equivalents **1** at room temperature. [e] 3.0 equivalents **1** was used.



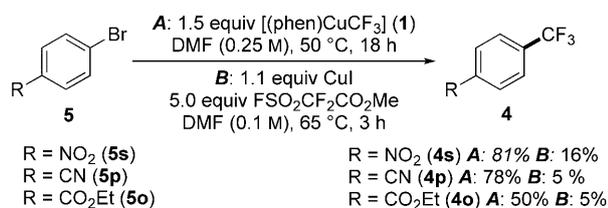
**Scheme 5.** Copper-mediated trifluoromethylation with (trifluoromethyl)copper complex **1** generated in situ. All reactions were performed with 0.50 mmol haloarene as limiting agent without the use of a glove box unless otherwise noted. [a] The reaction was conducted with 1.5 equivalents **1** prepared in situ. [b] The reaction was conducted with 10 mmol iodoarene for 24 h. [c] The yield was determined by <sup>19</sup>F NMR spectroscopy with 4-CF<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>OMe as internal standard.



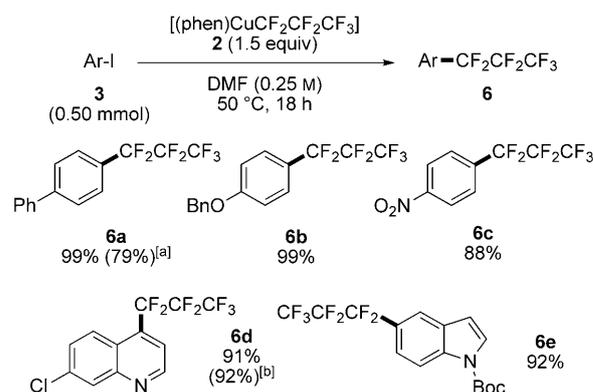
**Scheme 6.** Comparison of the reactions of aryl iodides **3**. The yields were determined by <sup>19</sup>F NMR spectroscopy with 4-CF<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>OMe as internal standard.

The reactivity of **1** with aryl bromides as the limiting reagent was also examined and compared to the reaction of CuI and 5 equiv FSO<sub>2</sub>CF<sub>2</sub>CO<sub>2</sub>Me. (Scheme 7). Electron-poor aryl bromides, including those with nitro, cyano, and ethoxycarbonyl groups, reacted with **1** to give high yields of trifluoromethylarene products. In contrast, the reactions of these haloarenes with the combination of FSO<sub>2</sub>CF<sub>2</sub>CO<sub>2</sub>Me and CuI occurred in low yield.

Finally, these protocols were extended to the perfluoroalkylation<sup>[19,20]</sup> of iodoarenes to install fluoroalkyl groups that are longer than a per fluoromethyl group (Scheme 8). Similar to the trifluoromethylation described above, the perfluoroal-



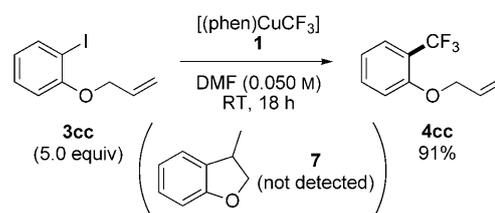
**Scheme 7.** Comparison of the reactions of aryl bromides **5**. The yields were determined by <sup>19</sup>F NMR spectroscopy with 4-CF<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>OMe as internal standard.



**Scheme 8.** Perfluoroalkylation of aryl iodides **3**. The reaction was performed with 1.5 equivalents **2** at 50 °C unless otherwise noted. [a] The reaction was conducted at 80 °C with perfluoropropylcopper complex **2** prepared in situ under the same conditions as for reactions in Scheme 5. [b] The reaction was performed at room temperature.

kylation of iodoarenes with perfluoropropylcopper complex **2** formed perfluoropropylarenes **6** in good yields under mild conditions. These reactions occurred with electron-rich and electron-poor iodoarenes, as well as iodoarenes containing potentially reactive quinoline and nitroarene units. The yield of nitro-substituted **6c** (88%) from the reaction of complex **2** was higher than that reported previously with the combination of CuI, KF, and TMS-CF<sub>2</sub>CF<sub>2</sub>CF<sub>3</sub> (41%).<sup>[8]</sup> The reaction of complex **2** prepared in situ outside of the glove box gave the product **6a** in 79% yield after 18 h at 80 °C. This transformation is milder and occurs in higher yields than previous perfluoroalkylations conducted by reductively coupling aryl iodides with perfluoroalkyl iodides.<sup>[7]</sup>

Preliminary data on the mechanism of the trifluoromethylation have been gained. To assess whether the reaction proceeds by free aryl radical intermediates,<sup>[21]</sup> we conducted the trifluoromethylation of 2-(allyloxy)iodobenzene **3cc**. The aryl radical derived from this haloarene cyclizes with a rate constant of 10<sup>10</sup> s<sup>-1</sup>.<sup>[22,23]</sup> Thus, if the trifluoromethylation occurs through an aryl radical, then cyclized product **7** should be observed (Scheme 9).<sup>[9b,c]</sup> Instead, the trifluoro-



**Scheme 9.** Trifluoromethylation of 2-(allyloxy)iodobenzene. Trifluoromethylarene **4cc** was obtained in 91% yield; cyclized product **7** was not detected by GC-MS analysis.

methylarene **4cc** was obtained in 91% yield, and cyclized product **7** was not detected by GC/MS analysis. This result implies that the copper-mediated trifluoromethylation reaction proceeds without the intermediacy of an aryl radical from electron transfer and expulsion of iodide.<sup>[24–26]</sup>

In summary, we have isolated a trifluoromethylcopper(I) reagent ligated by 1,10-phenanthroline that reacts with unprecedented range of aryl halides at room temperature to 50°C. In comparison to current alternative methods for trifluoromethylation of aryl halides, this system reacts under much milder conditions, tolerates a wider range of functional groups, tolerates basic heterocycles, reacts with more hindered substrates, can be extended to perfluoroalkylation, and occurs with a low total cost of goods. On a more fundamental level, the high reactivity of complexes **1** and **2** with a broad range of iodoarenes demonstrates that a general catalytic perfluoroalkylation of aryl iodides is not limited by the reactivity of the trifluoromethylcopper intermediate.

### Experimental Section

Preparation of [(phen)CuCF<sub>3</sub>] (**1**): To an oven-dried 250 mL round-bottomed flask equipped with a stir bar were added [CuOrBu]<sub>4</sub> (1.094 g, 2.00 mmol, 8.00 mmol for monomeric CuOrBu), 1,10-phenanthroline (1.442 g, 8.00 mmol, 1.00 equiv), and benzene (80 mL). The flask was sealed with a septum and the dark purple mixture was stirred at room temperature for 30 min, then TMSCF<sub>3</sub> (1.31 mL, 8.80 mmol, 1.1 equiv) was added dropwise. The mixture was stirred at room temperature for 18 h to give a red-orange suspension. The suspension was filtered through a medium fritted funnel, and the solid was washed with Et<sub>2</sub>O (50 mL) and dried under vacuum to give **1** as an orange solid (2.397 g, 96% yield). <sup>1</sup>H NMR (400 MHz, [D<sub>7</sub>]DMF): δ = 9.18 (d, *J* = 4.2 Hz, 2H), 8.89 (d, *J* = 8.0 Hz, 2H), 8.31 (s, 2H), 8.10 ppm (dd, *J* = 4.2, 8.0 Hz, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, [D<sub>7</sub>]DMF): δ = 150.4, 144.2, 138.3, 130.0, 127.8, 126.5 ppm (note that a carbon peak for CF<sub>3</sub> was not observed due to 1) dynamic behavior of the complex, 2) broadening the peak through Cu–C coupling, and 3) splitting of the peak through C–F coupling). <sup>19</sup>F NMR (376 MHz, [D<sub>7</sub>]DMF): δ = –22.6 (br), –30.9 ppm (s). Anal. calcd for C<sub>13</sub>H<sub>8</sub>CuN<sub>2</sub>F<sub>3</sub>: C 49.92, H 2.58, N 8.96, F 18.22; found: C 49.74, H 2.52, N 8.99, F 18.17.

General procedure for the reaction of isolated **1** with aryl iodides **3** as limiting agent: To a 20 mL vial equipped with a stir bar was added ArI **3** (if solid, 0.50 mmol), **1** (235 mg, 0.75 mmol, 1.5 equiv), and DMF (2.0 mL). Then ArI **3** (if liquid, 0.50 mmol) was added, and the mixture was stirred at the indicated temperature in Scheme 4 (room temperature or 50°C). After 18 h, the stirring was stopped, and the reaction mixture was diluted with Et<sub>2</sub>O and filtered through a pad of Celite. The Celite pad was washed with Et<sub>2</sub>O. The combined filtrate was washed with 1M aqueous HCl, saturated aqueous NaHCO<sub>3</sub> solution and brine, and dried over Na<sub>2</sub>SO<sub>4</sub>. After filtration and evaporation of the solvent, the crude mixture was purified by flash silica gel column chromatography using pentane/Et<sub>2</sub>O or pentane as eluent to give ArCF<sub>3</sub> **4**.

General procedure for the reaction of **1** generated in situ. General procedure outside glove box: To a 20 mL vial equipped with a stir bar and a Teflon-lined screw cap was added CuCl (99 mg, 1.0 mmol, 2.0 equiv). Then air in the vial was evacuated and dry nitrogen was refilled (once). KOtBu (112 mg, 1.0 mmol, 2.0 equiv) and 1,10-phenanthroline (180 mg, 1.0 mmol, 2.0 equiv) were added, then air in the vial was evacuated and dry nitrogen was refilled (twice). To the mixture was added DMF (2.0 mL), and the dark red mixture was stirred at room temperature for 30 min under nitrogen, then TMSCF<sub>3</sub> (0.148 mL, 1.0 mmol, 2.0 equiv) was slowly added. The resulting mixture was further stirred at room temperature for 1 h and the stirring was stopped. Then the screw cap was removed and ArI **3** (0.50 mmol) was expeditiously added. While opening the cap, surface of the vial turned green, implying partial decomposition of the copper reagent. The cap of the vial was closed tightly and the vial was evacuated and refilled with dry nitrogen. The resulting mixture was

stirred at 50°C for 18 h, then cooled, diluted with Et<sub>2</sub>O and filtered through a pad of Celite. The Celite pad was washed with Et<sub>2</sub>O and the combined organic layer was washed with 1M aqueous HCl, saturated aqueous NaHCO<sub>3</sub> solution and brine, and dried over Na<sub>2</sub>SO<sub>4</sub>. After filtration and evaporation of the solvent, the crude mixture was purified by flash silica gel column chromatography using pentane/Et<sub>2</sub>O as eluent to give ArCF<sub>3</sub> **4**.

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were determined by  $^{19}\text{F}$  NMR spectroscopy with 4- $\text{CF}_3\text{OC}_6\text{H}_4\text{OMe}$  as internal standard. Substrate **3b** gave **4b** in 36% yield. Substrate **3c** gave **4c** in 43% yield. Substrate **3g** gave **4g** in approximately 10% yield with the trifluoromethyl carbinols as the major products. Substrate **3e** gave none of **4e** and formed exclusively the trifluoromethyl carbinol product. **3p** gave **4p** in 41% yield; **3o** gave **4o** in 43% yield. Substrates **3i** and **3m** gave **4i** and **4m** in 17 and 39% yield.

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