Trifluoromethylthiolation

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An Air-Stable Copper Reagent for Nucleophilic Trifluoromethylthiolation of Aryl Halides**

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Compounds that contain a trifluoromethylthio group (–SCF_3) are found in many pharmaceutical and agrochemical products, such as Tiflorex and Vaniliprole.[1] Owing to their high lipophilicity and hydrophobicity, aryl trifluoromethylthioethers ($ArSCF_3$) have attracted increasing attention from synthetic chemists. There have been considerable efforts in both academic and industrial laboratories towards achieving straightforward, efficient, high-yielded, and economical preparation of these molecules. A number of methods are now available for synthesizing $ArSCF_3$ compounds; examples include the nucleophilic and radical trifluoromethylation of aryl sulfides, disulfides, sulfenyl chlorides and thiocyanates[2] and the reaction of trifluoromethylthiolate with aryl halides.[3] Togni and co-workers have made major progress in the field of electrophilic trifluoromethylations of thiolate nucleophiles.[4] However, these transformations are encumbered by significant limitations, for example, the requirement of high reaction temperatures, the use of expensive and/or toxic reagents, and the requirement of electron-poor aromatic groups.

One approach to address these drawbacks would be the development of metal-mediated or metal-catalyzed trifluoromethylthiolation to produce aryl trifluoromethylthioethers. Although there has been substantial progress in the metal-mediated or metal-catalyzed trifluoromethylation of aromatic substituents in recent years,[5–7] fewer studies on trifluoromethylthiolation has been reported. Chen et al described a direct trifluoromethylthiolation of aryl halides by using methyldifluoro(fluorosulfonyl)acetate and elemental sulfur, and mediated by cuprous iodide.[8] Buchwald and co-workers recently developed Pd-catalyzed reactions of aryl bromides to form trifluoromethylthioethers with $AgSCF_3$ as the nucleophile.[9] Notably, Vicic and Zhang published the trifluoromethylthiolation of aryl iodides and aryl bromides with the thermal sensitive reagent $[NMe_4][SCF_3]$, catalyzed by a nickel bipyridine complex at room temperature.[10] Most recently, the Qing and the Vicic groups independently reported Cu-catalyzed oxidative trifluoromethylthiolation of aryl boronic acids with Me_3SiCF_3 and S_8[11] or with $[NMe_4][SCF_3]$.[10b]

However, the use of an efficient and easily available organometallic reagent for the direct conversion of bromo- or iodoarenes and heteroarenes into the corresponding trifluoromethylthioethers would be a simple alternative to these methods. Such a reagent should be inexpensive to prepare, and should be stable enough to be stored for an extended period. Based on the extensive studies into Cu-mediated C–S bond formation reactions,[12] copper trifluoromethylthiolate ($CuSCF_3$) is considered to be a promising reagent for the trifluoromethylthiolation of arenes.[3b,13] Unfortunately, the practical application of this compound has not been extensively explored presumably because of its ill-defined nature. Herein, we report a convenient procedure for the preparation of a series of air-stable copper reagents and demonstrate their application for the efficient nucleophilic trifluoromethylthiolation of aryl halides.

In our recent investigations into trifluoromethylation[14] we have demonstrated the cooperative effect of silver in the copper-catalyzed trifluoromethylation of aryl iodides with Me_3SiCF_3. Isolated trifluoromethyl copper complexes containing chelating nitrogen ligands were also found to react smoothly with aryl halides to produce trifluoromethylated arenes.[6f] These results, together with our interest in the C–S bond formation[15] led us to explore the trifluoromethylthiolation of aryl halides by a ligated copper trifluoromethylthiolate species generated in situ from a mixture of simple copper salts, elemental sulfur, a trifluoromethyl source, and an electron-donating ligand.

We initially focused on the synthesis of copper(I) trifluoromethylthiolate complexes. Gratifyingly, the reactions of $Cu^{II}F_2$ with the Ruppert's reagent (Me_3SiCF_3) and S_8 in the presence of diimine ligands in CH_3CN afforded monomeric, copper(I) trifluoromethylthiolate complexes ligated by chelating nitrogen ligands $[(bpy)Cu^I(SCF_3)]$ (**1a**), $[(dmbpy)Cu^I(SCF_3)]$ (**1b**), and $[(dtbpy)Cu^I(SCF_3)]$ (**1c**), and dimeric complexes $[\{(phen)Cu^I(SCF_3)\}_2]$ (**1d**) and $[\{(Me_2phen)Cu^I(SCF_3)\}_2]$ (**1e**), in 42–49% yields based on Cu (Scheme 1). CF_3H, Me_3SiF, and $(CF_3)_2S$ were observed as major side products. In the solid state, all of these complexes are stable in air for several days; in solution, all of the compounds are unchanged after several hours in air.

The molecular structures of **1a**, and **1c–e** have been determined by the single crystal X-ray crystallography.[16] The

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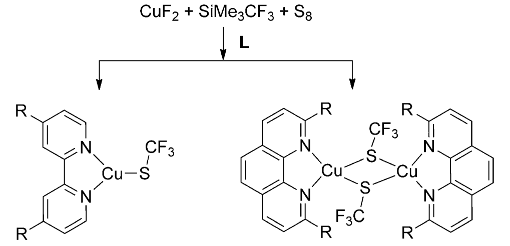


1a, 44%, R = H, L = bpy
1b, 48%, R = Me, L = dmbpy
1c, 47%, R = *t*-Bu, L = dtbpy
1d, 49%, R = H, L = phen
1e, 42%, R = Me, L = Me$_2$phen

Scheme 1. Synthesis of CuSCF$_3$ complexes **1a–1e**. bpy = bipyridine, dmbpy = 4,4′-di-methylbipyridine, dtbpy = 4,4′-di-*tert*-butylbipyridine, phen = 1,10-phenanthroline, Me$_2$phen = neocuproine.

ORTEP diagrams of **1a** and **1d** are shown in Figure 1. Complexes **1a** and **1c** possess a three-coordinated trigonal planar geometry around the copper atom. The metal center is bound by one neutral bidentate bipyridine ligand and one anionic SCF$_3$ group. The Cu–S bond distance of 2.2729(6) Å in **1a** is comparable with those found in the structures of acetonitrile-solvated copper(I) trifluoromethylthiolate complexes (CF$_3$SCu)$_{10}$(CH$_3$CN)$_8$ (the average of the Cu–S bond distances in the three-coordinate environment is 2.23 Å) and the monomeric alkyne-stabilized Cu(SCF$_3$) complex (2.272(2) Å).[17] The average Cu–N bond distance of 2.0855(2) Å is also close to the values seen in the previously reported analogous complex [(bathophenanthroline)CuCF$_3$] (2.062 Å).[14a] Compounds **1d** and **1e** form dimeric complexes. The two Cu atoms are bridged by the S atoms of the trifluoromethylthiolate anions forming a planar Cu$_2$S$_2$ ring. In **1d**, the Cu–Cu separation inside the dimer is 2.5781(9) Å. This distance suggests the presence of a metal–metal interaction (for comparison, the Cu–Cu distance in the copper metal lattice is equal to 2.56 Å).[18] This Cu–Cu distance is marginally shorter than the values found in closely related Cu^{I} thiolato complex [{Cu(SC$_6$H$_4$CH$_3$-*o*)(1,10-phenanthroline)}$_2$]·CH$_3$CN (2.613(3) Å).[19] The Cu–S bond distances of 2.3303(10) Å in **1d** are significantly longer than that in the monomeric complex **1a**. The Cu–N distances of 2.0617(19) Å in **1d** are comparable with those found in **1a**. The N-Cu-N angle (81.84(10)°) in **1d** is larger than those in **1a** (78.69(8)°) and in (bathophenanthroline)CuCF$_3$ (79.3°).[14a]

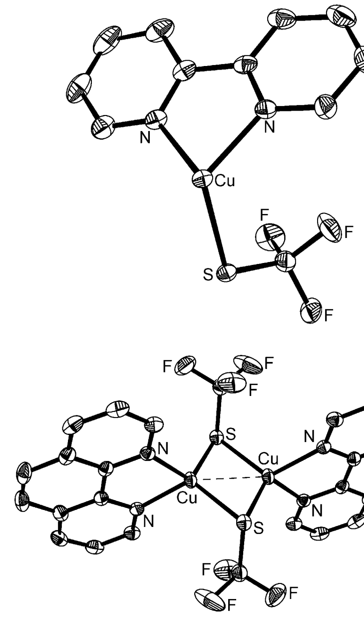
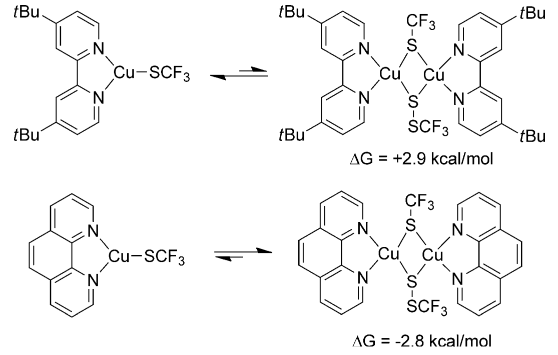


Figure 1. ORTEP diagram of **1a** (top) and **1d** (bottom). The thermal ellipsoids are set at 40% probability and hydrogen atoms are omitted for clarity.

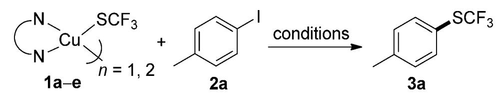
Density functional theory (DFT) calculations based on the B3LYP functional were performed to analyze the dimerization behavior of complexes **1c** and **1d** (see the Supporting Information for details). The energies of the gas-phase optimized structures of the copper trimethylthiolate dimers bearing dtbpy and phen ligands were compared, and it was observed that the dimerization process for the [{(phen)Cu(SCF$_3$)}$_2$] complex was exergonic and thermodynamically favorable ($\Delta G = -2.8$ kcal mol^{-1}), whereas that for the [{(dtbpy)Cu(SCF$_3$)}$_2$] complex was endergonic and not favored ($\Delta G = 2.9$ kcal mol^{-1}). These data are consistent with the experimental observations.



After isolation and characterization of copper(I) trifluoromethylthiolate complexes **1a–e**, we evaluated the reactivity of these complexes for the trifluoromethylthiolation of aryl halides. Initially, 4-iodotoluene was chosen as model substrate, and various solvents, temperatures, and reaction times were evaluated to optimize the trifluoromethylthiolation conditions (Table 1).

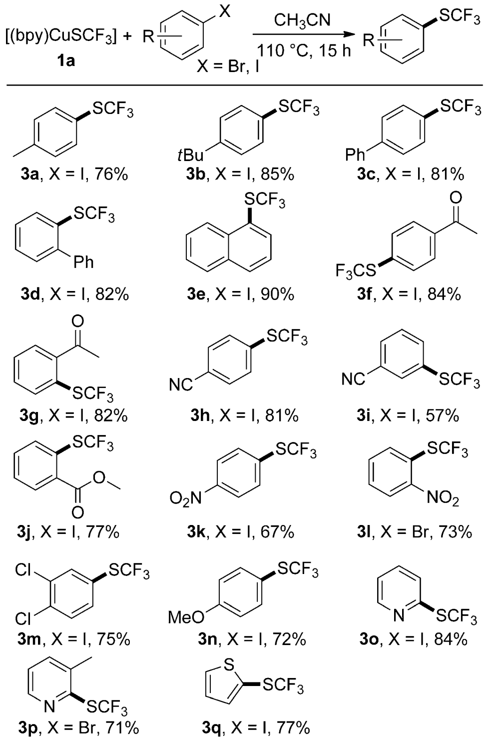
Our results showed that nature of the nitrogen ligands strongly affected the formation of trifluoromethylthiolation products. For example, we found that treatment of **1a**, ligated by bipyridine, with 1.2 equivalents of 4-iodotoluene in CH$_3$CN at 110 °C for 15 h afforded 4-(trifluoromethylthio)-toluene in 84% yield (Table 1, entry 1). Under similar reaction conditions, complex **1b** ligated by 4,4′-dimethylbipyridine gave the desired product in a comparable yield (Table 1, entry 2). **1c** containing 4,4′-di-*tert*-butylbipyridine showed excellent activities and afforded **3a** in 97% yield (Table 1, entry 3). However, the reactions of **1d** and **1e**, which are ligated by 1,10-phenanthroline and neocuproine, respectively, resulted in much lower yields (Table 1, entries 4 and 5). These results suggested that bipyridine was the most effective ligand for the trifluoromethylthiolation, presumably owing to its preference to maintain the monomeric form, which is

Table 1: Optimization of trifluoromethylthiolation of 4-iodotoluene with **1a–e**.[a]



Entry	[Cu]	Solvent	*t* [h]	*T* [°C]	Yield [%][b]
1	**1a**	CH_3CN	15	110	84
2	**1b**	CH_3CN	15	110	88
3	**1c**	CH_3CN	15	110	97
4	**1d**	CH_3CN	15	110	53
5	**1e**	CH_3CN	15	110	18
6	**1a**	toluene	15	150	69
7	**1a**	THF	15	90	21
8	**1a**	DMSO	15	150	3
9	**1a**	CH_2Cl_2	15	60	8
10	**1a**	DMF	15	150	4
11	**1a**	NMP	15	150	8
12	**1a**	CH_3CN	7	110	51
13	**1a**	CH_3CN	15	90	55

[a] Reaction conditions: [Cu] (0.15 mmol), **2a** (0.15 mmol), solvent (1.0 mL), under N_2 atmosphere. [b] Yields were determined by the ^{19}F NMR analysis of the crude reaction mixture with (trifluoromethoxy)benzene as an internal standard.



Scheme 2. Scope of trifluoromethylthiolation of aryl and heteroaryl halides by **1a**. Reaction conditions: **1a** (0.25 mmol), aryl halides (0.25 mmol), 15 h, N_2, 110°C. Yields of isolated products are shown.

active towards the cross coupling reactions, as observed in the X-ray crystallographic and DFT analyses.

We next examined the effect of different solvents on the reaction. Reactions performed in toluene or THF proceeded less efficiently (Table 1, entries 6 and 7) than those in CH_3CN. Reactions in other solvents, such as DMSO, CH_2Cl_2, DMF, or NMP, occurred very slowly (Table 1, entries 8–11). Thus, CH_3CN was identified as the best solvent for the reaction. To further elucidate the factors that affect the reaction rate, the reaction temperature and time were also evaluated. The yield of product decreased from 84% to 51% when the reaction time was shortened from 15 to 7 h (Table 1, entry 12). Furthermore, a reaction temperature of 110°C was essential for efficient trifluoromethylthiolation. The reaction conducted at the lower temperature of 90°C resulted in substantially lower product yields (55%; Table 1, entry 13).

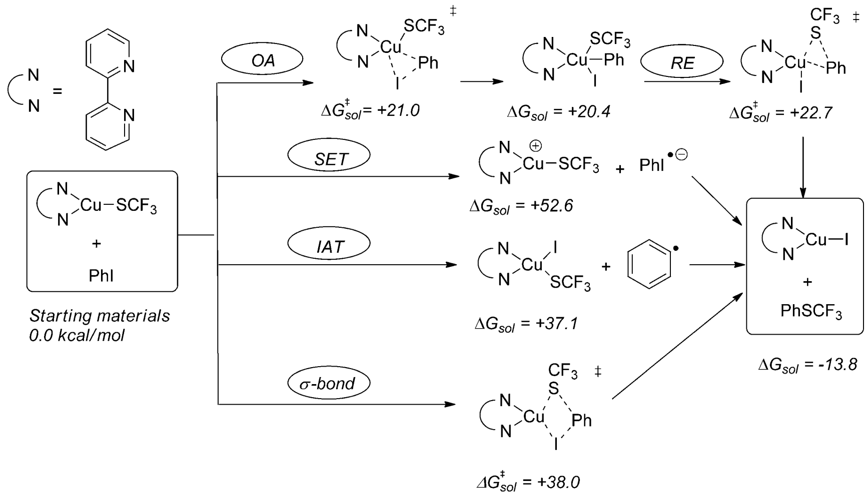
Having established this trifluoromethylthiolation method, we explored the scope of the reactions with various aryl and heteroaryl halides (Scheme 2). Complex **1a** was selected as the trifluoromethylthiolation reagent and the reactions of various electronically and structurally diverse aryl and heteroaromatic halides were evaluated. The reaction proceeded smoothly with neutral alkyl- and aryl-substituted aromatic iodides to give the corresponding products **3a–e** in good to excellent yields (76–90%). The reactions *para*- and *ortho*-acetyl substituted iodoarenes also gave good results, affording the desired products **3f** and **3g** in 84% and 82%, respectively. Reactions of iodoarenes bearing electron-deficient groups, as well as those containing electron-donating moieties, give products **3h–l** and **3n** in moderate to good yields (57–81%). It is noteworthy that the chlorine functionality on the aryl iodide was tolerated and produced **3m** in 75% yield. Heteroaryl iodides and bromides also reacted to afford the products **3o–q**, again in good yields (71–84%).

As these reactions started with a well-defined $CuSCF_3$ complex, they provided a model for the plausible reaction pathways to be evaluated by DFT to increase our mechanistic understanding of the C–SCF_3 bond formation process (see the Supporting Information for details). Four reaction mechanisms were considered: oxidative addition/reductive elimination (OA/RE), single electron transfer (SET), iodine atom transfer (IAT), and σ-bond metathesis (σ-bond).[20] Although the mechanism for the Cu-mediated C–S bond cross-coupling reaction is still controversial, the computed energies for the proposed transition states and intermediates with solvent effect favored the OA/RE process, supporting the cycle containing Cu^I/Cu^{III} species (Scheme 3).[21]

In conclusion, we have prepared a series of copper(I) trifluoromethylthiolate complexes ligated by bipyridine ligands. These complexes react with a wide range of aryl and heteroaryl halides to produce aryl trifluoromethyl thioethers in modest to excellent yields. The bipyridine ligated complexes were showed to be the most effective for the trifluoromethylthiolation. These reactions provide a novel and convenient approach for trifluoromethylthiolation of aryl halides starting from a well-defined, readily available copper reagent prepared from inexpensive materials. Computational studies suggest that the reaction may proceed through a Cu^{III} intermediate in an OA/RE pathway.

Experimental Section

Synthesis of [(bpy)$CuSCF_3$] (**1a**): In a glovebox, CuF_2 (714 mg, 7.0 mmol), S_8 (224 mg, 7.0 mmol), and 30 mL CH_3CN were added to an oven-dried resealable Schlenk tube possessing a Teflon screw valve. CF_3SiMe_3 (2.98 g, 21.0 mmol) was added into this tube and the



Scheme 3. Four plausible pathways leading to the trifluoromethylthiolated product are shown. Reported values (ΔG_{sol} or $\Delta G^{\pm}{}_{sol}$) are the free energies relative to starting materials with solvent effect (in kcal mol^{-1}).

tube was sealed. The reaction mixture was stirred in a preheated oil bath at 80 °C for 10 h. The reaction mixture was then allowed to cool to room temperature and filtered through Celite. The volatiles were removed under reduced pressure and the resulting dark-brown solid was washed with Et_2O (3 × 15 mL). The solid was redissolved in 6 mL of CH_3CN and 2,2′-bipyridine (1.09 g, 7.0 mmol) in 15 mL of Et_2O was carefully added to this solution. The resulting solution was then kept at −25 °C for 24 h. The resulting red crystals were washed with diethyl ether (2 × 5 mL), and dried to give 984 mg of the desired product **1a** (44 % yield). ^1H NMR (400 MHz, CD_2Cl_2): $\delta = 8.80$ (s, 2 H), 8.30 (d, $J = 7.6$ Hz, 2 H), 7.99 (td, $J = 7.9$, 1.6 Hz, 2 H), 7.60–7.46 ppm (m, 2 H); ^{19}F NMR (376 MHz, CD_2Cl_2): $\delta = -20.96$ ppm (s, 3 F); ^{13}C NMR (101 MHz, CD_2Cl_2): $\delta = 153.3$ (s), 149.8 (s), 137.9 (s), 125.2 (s), 121.0 ppm (s), SCF_3 was not observed. Elemental analysis calcd (%) for $C_{11}H_8CuF_3N_2S$: C, 41.18; H, 2.51; N, 8.73; found: C, 40.98; H, 2.64; N, 8.87.

General Procedure for Trifluoromethylthiolation of Aryl Halides by complex [(bpy)$CuSCF_3$] (**1a**): **1a** (80 mg, 0.25 mmol), the starting aryl halides (0.25 mmol), and CH_3CN (1.2 mL) were added to a flame-dried 5 mL test tube with Teflon screw cap equipped with a magnetic stir bar. The tube was sealed and then placed into a preheated 110 °C oil bath for 15 h. The tube was removed from the oil bath and allowed to cool. The reaction mixture was then filtered through SiO_2, eluted with diethyl ether, washed with brine, and concentrated in vacuo. The residue was purified by silica gel column chromatography with pentane.

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[16] CCDC 900611 (**1a**), 900612 (**1c**), 900613 (**1d**), 900614 (**1e**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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