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Copper Complexes

Synthesis of Cu^{I} Trifluoromethylselenates for Trifluoromethylselenolation of Aryl and Alkyl Halides

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Abstract: The development of new strategies for synthesis of trifluoromethylthiolate compounds is of considerable importance in pharmaceuticals, agrochemicals, and advanced materials. Accordingly, currently much attention is being devoted to the development of effective methods and reagents for their synthesis. In contrast, considerably less effort has been afforded to the development of preparing C–$SeCF_3$ bonds. Herein we report a concise route to synthesize a family of copper(I) trifluoromethylselenolate reagents by the reaction of CuI with the Ruppert's reagent (Me_3SiCF_3), KF, and elemental selenium in the presence of dinitrogen ligands in CH_3CN at room temperature. The reagent $[Cu(bpy)(SeCF_3)]_2$ was proven to be air-stable and highly efficient for nucleophilic trifluoromethylthselenolation of a broad range of (hetero)aryl halides and alkyl halides. This method represents a powerful protocol for the construction trifluoromethylselenolate compounds.

Trifluoromethylthio (–SCF_3)-substituted motifs usually possess interesting biological and physical properties and have been extensively applied in the preparation of pharmaceuticals, agrochemicals, and advanced materials.[1] Consequently, the development of more efficient and practical protocols for trifluoromethylthiolation has been the subject of intense research effort.[2] The traditional approaches for the preparation of aryl trifluoromethyl thioethers involve the reaction of trifluoromethylthiolate with aryl halides, or trifluoromethylation of aryl sulfides and disulfides with a trifluoromethylating reagent.[3–5] Useful alternatives for the preparation of aryl trifluoromethyl thioethers were developed by employing transition-metal-catalyzed trifluoromethylthiolation of aryl-X compounds (X = Br, I, and H)[6] and aryl boronic acids[7] in recent years.

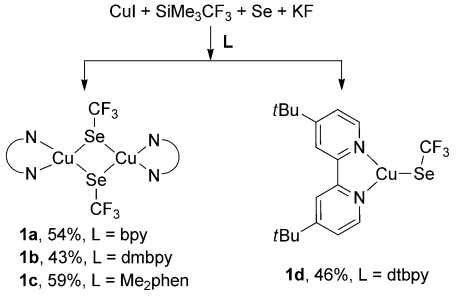
While the general applicability of these procedures for preparing C–SCF_3 bonds has been established, there were considerably less efforts devoted to the development of the construction C–$SeCF_3$ bonds.[8] Most of these existing methods for synthesizing trifluoromethylselenolated compounds require the use of functionalized substrates, such as selenocyanates or diselenides.[3a,b,d–f,9]

Despite their toxic nature in general, organoselenium compounds represent an important class of molecules[10,11] which have shown useful biological and enzyme inhibitory activities.[12] Given the considerable interest in trifluoromethyl selenide compounds, the development of new, more efficient procedures is a subject of great importance.

During the course of our studies on copper-catalyzed and -mediated trifluoromethylation[13] and trifluoromethylthiolation[14] chemistry, we have successfully developed a novel and concise route to synthesize a copper(I) trifluoromethylthiolate reagent $[Cu(bpy)(SCF_3)]$ for nucleophilic trifluoromethylthiolation of haloarenes,[15] benzyl bromides,[14a] and allylic bromides.[14b]

This led us to search for a new route for the preparation of their selenium analogues.[16] Herein we report the synthesis and molecular structures of a series of copper(I) trifluoromethylselenolate complexes and their reactivities as trifluoromethylselenolation reagents towards aryl and alkyl halides.

The reaction of CuI, Me_3SiCF_3, elemental selenium, and KF with dinitrogen ligands in CH_3CN at ambient temperature successfully gave dimeric copper(I) trifluoromethylselenolate complexes, $[Cu(bpy)(SeCF_3)]_2$ (**1a**), $[Cu(dmbpy)(SeCF_3)]_2$ (**1b**), and $[Cu(Me_2phen)(SeCF_3)]_2$ (**1c**), in 43–59% yields based on Cu (Scheme 1). When a more electron-rich ligand, 4,4′-di-*tert*-butyl-2,2′-bipyridine (dtbpy) was employed, the isolation of the monomeric complex, $[Cu(dtbpy)(SeCF_3)]$ (**1d**), was achieved in 46% yield. These copper(I) trifluoromethylselenolate complexes were fully characterized by elemental analysis and NMR



Scheme 1. Synthesis of $Cu(SeCF_3)$ complexes **1a**–**d**. bpy = bipyridine, dmbpy = 4,4′-di-methylbipyridine, dtbpy = 4,4′-di-tert-butylbipyridine, Me_2phen = neocuproine.

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spectroscopy. All of these complexes are air-stable for months and can be conveniently weighted and handled in air as solids without taking special precautions.

Thus far there have never been any crystal structures of copper complexes containing trifluoromethylseleno groups reported in the literature and we were prompted to conduct single-crystal X-ray crystallographic studies on our complexes (Figure 1).[17] In sharp contrast to its monomeric trifluoromethylthiolate analogue,[15] the bipyridine ligated complex **1a** adopts a dimeric structure in the solid state. Two Cu^{I} centers in **1a** are bridged by two Se atoms from the trifluoromethylselenolate anions. Each Cu atom is coordinated by one bipyridine ligand to form a distorted tetrahedral geometry, a similar figuration shared by complexes **1b** and **1c** as well. The Cu–Cu distance of 2.6146(9) Å in **1a** is slightly longer than those found in copper(I) dimeric trifluoromethylthiolate complex $[Cu(phen)(SCF_3)]_2$ (2.5781(9) Å),[15] and closely related Cu^{I} selenolato complex $[Cu(bpy)\{Se(2,4,6\text{-}iPr_3C_6H_2)\}]_2$ (2.524(4) Å).[18] The Cu–Se bond lengths in **1a** are not equal (2.3967(6) and 2.4463(6) Å), and are comparable to those in $[Cu(bpy)\{Se(2,4,6\text{-}iPr_3C_6H_2)\}]_2$ (2.449(3) Å).[18]

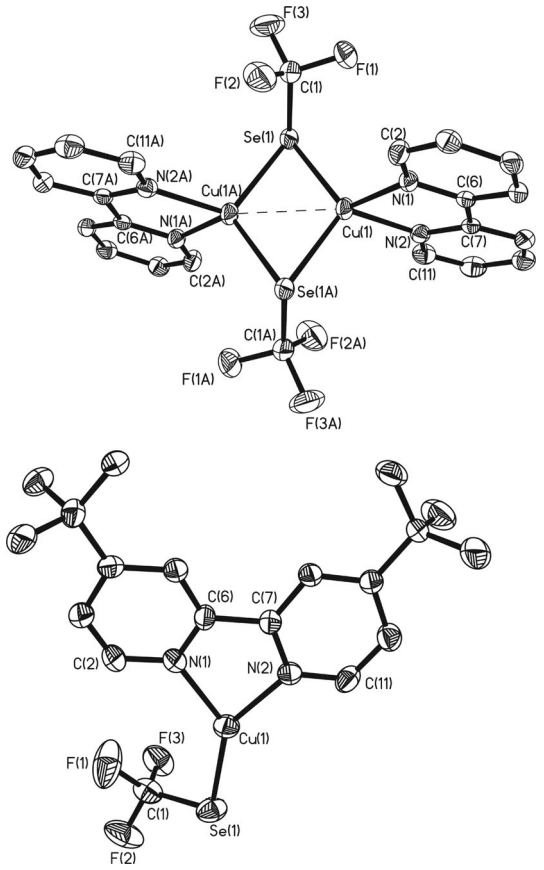
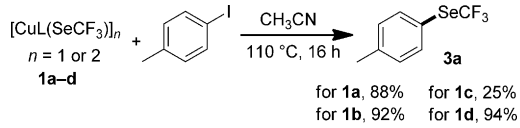


Figure 1. ORTEP diagram of **1a** (top) and **1d** (bottom) with thermal ellipsoids at the 40% probability level.

Complex **1d** consists of discrete monomeric units. The copper(I) atom is coordinated by one anionic $SeCF_3$ group and the two nitrogen atoms of the neutral bipyridine ligand to give a distorted trigonal planar structure. The Cu–Se bond distance of 2.2622(14) Å in **1e** is shorter than those found in the dimeric complex **1a** (2.3967(6) and 2.4463(6) Å). The Cu–N bond distances (2.016(7) and 2.050(7) Å) are approximately equal and are close to the values found in **1a** (2.049(2) and 2.063(2) Å).

The reactivity of the resulting copper(I) complexes for trifluoromethylselenolation of aryl halides was then evaluated (Scheme 2). We started our investigation on 4-iodotoluene as the substrate, by using our previously reported optimized conditions for copper reagent mediated trifluoromethylthiolation.[15] Thus, the four complexes were treated with one equivalent of 4-iodotoluene at 110 °C in CH_3CN and analyzed by ^{19}F NMR spectroscopy.



Scheme 2. Trifluoromethylselenolation of 4-iodotoluene with **1a–d** (^{19}F NMR spectroscopic yields).

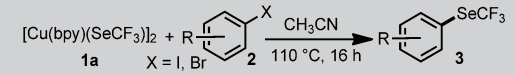
Nitrogen ligands were identified to have a pronounced effect on the trifluoromethylselenolation. In the case of the bpy, dmbpy, and dtbpy complexes, reactions had occurred to give the *p*-tolyl(trifluoromethyl)selane products **3a** in 88–94% yields, while the Me_2phen complex gave only low yield (25%). These observations suggest that the more economical and easily available bipyridine ligand could be used advantageously.

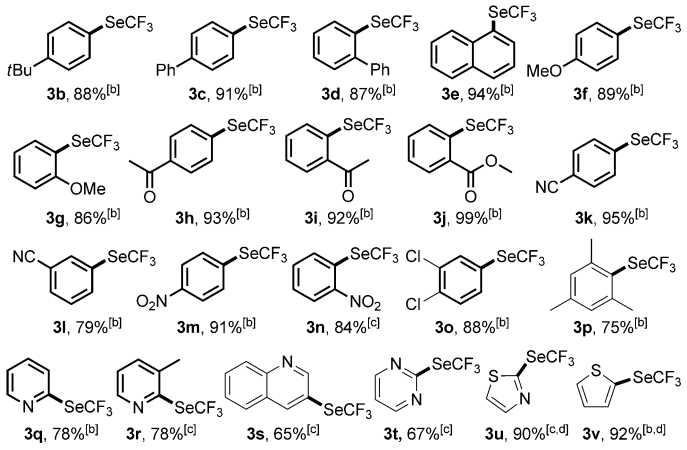
Under these reaction conditions, the scope and generality of the present strategy were explored by reacting complex **1a** with various aryl and heteroaromatic halides **2** (Table 1).

In general, the trifluoromethylselenolation proceeded smoothly with all electron-poor, -neutral, and -rich aryl iodides to afford the desired products in good yields. Moreover, a great degree of functional groups, such as ketone, ester, nitrile, nitro, methoxy, and chloro groups were well tolerated under these reaction conditions. Trifluoromethylselenolation of alkyl- and aryl-substituted aryl iodides and 1-iodonaphthalene furnished the corresponding products in satisfactory yield (**3a–e**, 81–94%). Electron-rich aryl iodides smoothly underwent reaction to give product **3f** and **3g** in 89 and 86% yields, respectively. Reaction of aryl iodides with electron-withdrawing groups proceeded efficiently to afford products **3h–o** in good to excellent yields of 79–99%. The trifluoromethylselenolation of sterically congested aryl iodides also furnished the desired product **3p** in 75% yield. This newly developed trifluoromethylselenolation protocol was also applied to heterocyclic aryl halide substrates. A wide array of heteroaryl bromides, including 2-pyridyl, 3-quinolinyl, 2-pyrimidinyl, 2-thiazolyl, and 2-thiophenyl halides, could be efficiently transformed to the corresponding products **3q–v** in 65–92% yields.

In an effort to extend the scope of this reaction, primary and secondary alkyl halides were subjected to the standard reaction conditions (Table 2). More electrophilic halides such as benzyl bromides containing either electron-withdrawing or

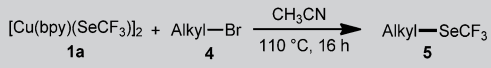
Table 1. Scope of trifluoromethylselenolation of aryl and heteroaryl halides by **1a**.[a]

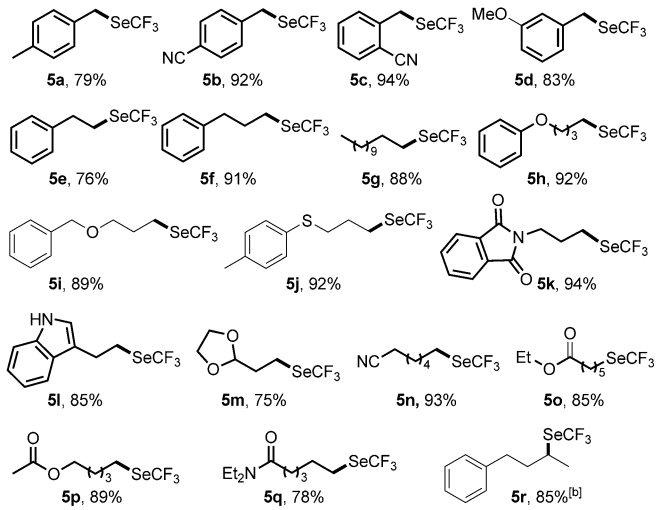




[a] Reaction conditions: **1a** (0.15 mmol), aryl halides **2** (0.25 mmol), 16 h, N_2, 110 °C. Yields of isolated products are shown. [b] X = I. [c] X = Br. [d] The yield was determined by ^{19}F NMR spectroscopy with $PhOCF_3$ as internal standard.

Table 2. Scope of trifluoromethylselenolation of alkyl bromides.[a]





[a] Reaction conditions: **1a** (0.15 mmol), alkyl bromides **4** (0.25 mmol), 16 h, N_2, 110 °C. Yields of isolated products are shown. [b] Alkyl iodide.

-donating groups gave the corresponding trifluoromethylselenolate products **5a**–**d** in 79–94% yields. The unfunctionalized alkyl halides were allowed to react with **1a** to afford products **5e**–**g** in 76–91% yields.

Trifluoromethylselenolation with functionalized alkyl halides was also examined. Gratifyingly, a wide range of functional groups, including ether (**5h**, **5i**), thioether (**5j**), amide (**5k**, **5q**), ketal (**5m**), nitrile (**5n**), and ester (**5o**, **5p**) are tolerated. The desired trifluoromethylselenolated products could be easily separated from the reaction mixture in high isolated yields (75–94%). This reaction is also applicable to pharmaceutically interesting heterocycle-containing alkyl bromide, which afforded the corresponding product (**5l**) in good yield (85%). A secondary alkyl iodide also proved to be a suitable substrate and furnished the desired product **5r** in 85% yield.

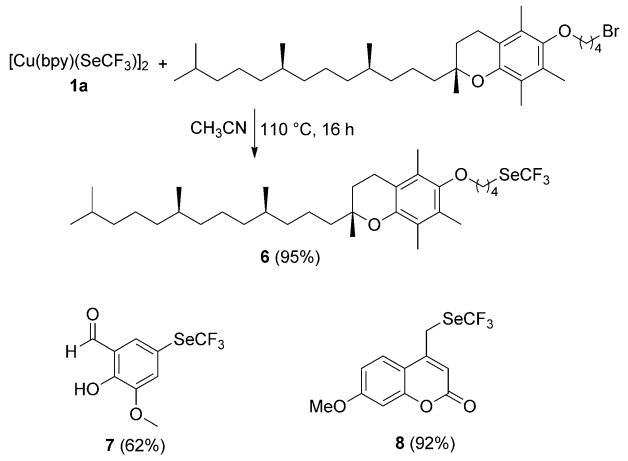
After having established an excellent scope with aryl halides, heteroaryl halides, and alkyl halides, the usefulness of the protocol with complex small molecules as substrates was addressed. To our delight, biologically and pharmaceutically important substrates were observed to be compatible with our trifluoromethylselenolation conditions (Scheme 3). Hence, trifluoromethylselenolated vitamin E, vanillin, and coumarin derivatives **6**–**8** were isolated in 95, 62, and 92% yields, respectively. The present method provides convenient access to highly functionalized molecules by a late-stage trifluoromethylselenolation reaction.

To gain some insights into the mechanism of the reaction process, a series of experiments were rationally designed and performed. To probe whether any radical intermediates are involved in this transformation (Scheme 4), the reaction of **1a** with **4h** was carried out in the presence of a radical scavenger, cyclohexa-1,4-diene (CHD). The yield of **5h** was not affected (92%).

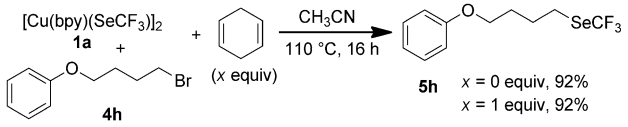
Furthermore, the reaction of **1a** with (bromomethyl)cyclopropane **9** or 6-bromo-1-hexene **12** in CD_3CN at 80 °C for 16 h gave the trifluoromethylselenolate product **10** and **13** as a sole products in 82 and 57% yields, respectively (Scheme 5). The absence of ring-opening product **11** and cyclization product **14** and the observation of no influence on the product formation with the addition of CHD allowed us to rule out the radical pathway in the trifluoromethylselenolation.

When **1a** reacted with 1-(allyloxy)-2-iodobenzene **15**[19] in CH_3CN at 110 °C for 16 h, [2-(allyloxy)phenyl]-(trifluoromethyl)selane **16** was observed as the only product in 86% yield (Scheme 5). No cyclization product, 3-methyl-2,3-dihydrobenzofuran **17**, was detected. This result also suggests that the trifluoromethylselenolation does not proceed by an aryl radical pathway.[20]

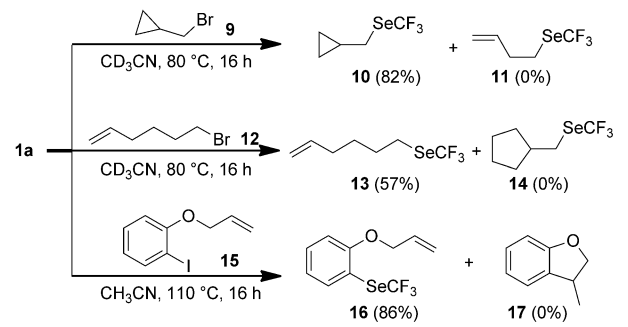
In summary, a family of copper(I) trifluoromethylselenolate complexes ligated by dinitrogen ligands have been synthesized from inexpensive, readily available starting materials. The complex ligated by the bipyridine ligand proved to be a useful reagent for the nucleophilic trifluoromethylselenolation. A wide range of aryl and heteoaryl halides and alkyl halides with a number of synthetically relevant functional groups, including ether, thioether, amide, ketal, nitrile, and ester, may be used in this process to afford the corresponding trifluoro-



Scheme 3. Trifluoromethylselenolation of complex small molecules.



Scheme 4. Radical scavenger experiments.



Scheme 5. Radical clock experiments.

methylselenolated products in modest to excellent yields. This work represents a major step forward in the development of the copper-mediated trifluoromethylselenolation.

Experimental Section

Synthesis of $[Cu(bpy)(SeCF_3)]_2$ (1 a)

In a glovebox, CuI (1.33 g, 7.0 mmol), Se (1.12 g, 14.0 mmol), KF (1.22 g, 21.0 mmol), and CH_3CN (10 mL) were added to an oven-dried resealable Schlenk tube possessing a Teflon screw valve. CF_3SiMe_3 (3.2 mL, 21.0 mmol) was added into this tube and the tube was sealed. The mixture was vigorously stirred at RT for 14 h. The reaction mixture was then filtered through a layer of Celite. The volatiles were removed under reduced pressure and the resulting dark-brown solid was washed with hexane (3×3 mL). The solid was re-dissolved in CH_3CN (5 mL) and 2,2′-bipyridine (1.09 g, 7.0 mmol) in Et_2O (20 mL) was carefully added to this solution. The resulting solution was then kept at −25 °C for 48 h. The resulting red crystals were washed with Et_2O (3×3 mL) and dried to give 1.06 g of **1 a** (41% yield). ^1H NMR (400 MHz, CD_3CN): $\delta = 8.70$ (s, 4H), 8.40 (d, $J = 7.8$ Hz, 4H), 8.06 (t, $J = 7.8$ Hz, 4H), 7.66–7.51 ppm (m, 4H); ^{19}F NMR (376 MHz, CD_3CN): $\delta = -22.2$ ppm (s, 6F); IR (KBr): $\tilde{\nu} = 1594$, 1471, 1440, 1312, 1079, 764, 736, 619 cm^{-1}; elemental analysis calcd (%) for $C_{22}H_{16}Cu_2F_6N_4Se_2$: C, 35.93; H, 2.19; N, 7.62; found: C, 35.86; H, 2.30; N, 7.69.

Acknowledgements

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Keywords: complexes · copper · cross coupling · C–Se bonds · trifluoromethylselenolation

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