Electrophilic Trifluoromethylselenolation of Boronic Acids

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Abstract: Trifluoromethylselenylated compounds are emergent compounds with interesting physicochemical properties that still suffer from a lack of efficient synthetic methods. We recently developed an efficient one-pot strategy to generate in situ CF₃SeCl and use it in various reactions. Herein, we continue our study of the reactivity scope of this preformed reagent. Cross-coupling reactions with aromatic and heteroaromatic boronic acids have been investigated. The expected products have been obtained, using a stoichiometric amount of copper, with moderate yields.

Keywords: trifluoromethylselenolation; boronic acids; trifluoromethylselenyl chloride; fluorine; selenium

1. Introduction

Fluorinated compounds play a more and more important role in various fields of application. Among all the fluorinated substitutes, the CF₃ group occupies a particular place due to its specific properties [1–13]. Furthermore, the association of this CF₃ moiety with chalcogens leads to new fluorinated substituents with very interesting electronic and physicochemical properties. This has been well illustrated by CF₃O- and CF₃S-molecules [14–18], especially due to their high lipophilicities (Hansch–Leo parameters: πR(OCF₃) = 1.04, πR(SCF₃) = 1.44) [19] which contribute to their favoring of membrane permeation and, consequently, increase their bioavailability. In the series of chalcogens, the CF₃Se group has been less investigated. However, selenylated compounds also play an important role in various fields of application, from materials to life sciences [20–31]. This is illustrated, for example, by the drug Ebselen [32–35]. Furthermore, the Hansch–Leo lipophilicity parameter of the CF₃Se group has been recently measured to πR(SeCF₃) = 1.29 [36].

Despite the strong interest in this group, synthetic methods to obtain trifluoromethylselenylated molecules are still limited. Trifluoromethylation of selenylated compounds has recently been investigated for the first time [37–49]. Although this strategy gave good results, the preliminary preparation of selenylated adducts can be a drawback. Late stage direct trifluoromethylselenolation appears to be the most versatile approach. Nucleophilic reactions have been the most investigated, with a large panel of organic compounds from nucleophilic substitutions onto halogen compounds or diazonium salts, to cross-coupling reactions with halogen substrates or boronic acids [50–64]. Nevertheless, this approach required the preparation of CF₃Se⁻ anions using a stoichiometric amount of selenium metal. Electrophilic trifluoromethylselenolations have been less described. The only available reagent for such reactions is CF₃SeCl, which is volatile, potentially toxic and, until recently, difficult to synthesize [65,66].

To favor a safe and easy handling of this reagent, we have recently described an efficient procedure to generate in situ this species from benzyl trifluoromethyl selenide (I). This strategy has already been
applied to electrophilic aromatic substitutions [67] and reactions with Grignard reagents and lithium alkynides [36].

2. Results and Discussion

In our objective to extend the scope of the reactivity of CF$_3$SeCl, following our one-pot strategy, we decided to study the trifluoromethylselenolation of boronic acids.

The reaction was first optimized with biphenyl boronic acid (2a). All the attempts are summarized in Table 1.

**Table 1.** Coupling reaction between CF$_3$SeCl, generated in situ, and boronic acid 3a.

| Entry | [Cu] | Ligand | Base | Solvent | 3a (%) |
|-------|------|--------|------|---------|--------|
| 1     | CuI  (1 eq.) | L1 (2 eq.) | K$_2$CO$_3$ (1 eq.) | CH$_3$CN | 5     |
| 2     | Cu(OAc)$_2$ (1 eq.) | L1 (2 eq.) | K$_2$CO$_3$ (1 eq.) | CH$_3$CN | 23    |
| 3     | Cu(OAc)$_2$ (1 eq.) | L1 (2 eq.) | - | CH$_3$CN | 0     |
| 4     | Cu(OAc)$_2$ (1 eq.) | L1 (2 eq.) | K$_2$CO$_3$ (1 eq.) | CH$_3$CN | 4     |
| 5     | Cu(OAc)$_2$ (1 eq.) | L2 (1 eq.) | K$_2$CO$_3$ (1 eq.) | CH$_3$CN | 14    |
| 6     | Cu(OAc)$_2$ (1 eq.) | L3 (1 eq.) | K$_2$CO$_3$ (1 eq.) | CH$_3$CN | 3     |
| 7     | Cu(OAc)$_2$ (1 eq.) | L4 (1 eq.) | Cs$_2$CO$_3$ (1 eq.) | CH$_3$CN | 0     |
| 8     | Cu(OAc)$_2$ (1 eq.) | L5 (1 eq.) | K$_2$CO$_3$ (1 eq.) | CH$_3$CN | 6     |
| 9     | Cu(OAc)$_2$ (1 eq.) | L6 (1 eq.) | K$_2$CO$_3$ (1 eq.) | CH$_3$CN | 3     |
| 10    | Cu(OAc)$_2$ (1 eq.) | L7 (1 eq.) | K$_2$CO$_3$ (1 eq.) | CH$_3$CN | 0     |
| 11    | Cu(OAc)$_2$ (1 eq.) | L8 (1 eq.) | CsF (1 eq.) | CH$_3$CN | 70    |
| 12    | Cu(OAc)$_2$ (1 eq.) | L9 (1 eq.) | K$_3$PO$_4$ (1 eq.) | CH$_3$CN | 48    |
| 13    | Cu(OAc)$_2$ (1 eq.) | L10 (1 eq.) | Cs$_2$CO$_3$ (1 eq.) | CH$_3$CN | 0     |
| 14    | Cu(OAc)$_2$ (1 eq.) | L11 (1 eq.) | Et$_3$N (1 eq.) | CH$_3$CN | 0     |
| 15    | Cu(OAc)$_2$ (1 eq.) | L12 (1 eq.) | Pyridine (1 eq.) | CH$_3$CN | 0     |
| 16    | Cu(OAc)$_2$ (1 eq.) | L13 (1 eq.) | Cs$_2$CO$_3$ (1 eq.) | CH$_3$CN | 37    |
| 17    | Cu(OAc)$_2$ (0.2 eq.) | L14 (0.2 eq.) | Cs$_2$CO$_3$ (1 eq.) | CH$_3$CN | 56    |
| 18    | Cu(OAc)$_2$ (0.2 eq.) | L15 (0.2 eq.) | Cs$_2$CO$_3$ (1 eq.) | CH$_3$CN | 50    |
| 19    | Cu(OAc)$_2$ (0.2 eq.) | L16 (0.6 eq.) | Cs$_2$CO$_3$ (1 eq.) | CH$_3$CN | -     |
| 20    | Cu(OAc)$_2$ (0.2 eq.) | L17 (0.2 eq.) | Cs$_2$CO$_3$ (1 eq.) | CH$_3$CN | 60    |

$^a$ See Figure 1 for ligand structures. $^b$ Yield was determined by $^{19}$F-NMR spectroscopy by using PhOCF$_3$ as an internal standard. $^c$ 50 °C instead of r.t. $^d$ Addition of 7 eq. of H$_2$O.

The use of CuI as a catalyst with bipyridine L1 led to the expected compounds with a very low yield (Entry 1). With Cu(OAc)$_2$, a better yield was observed, but was still low (Entry 2). In order to improve this encouraging result, the base or ligand first had to be removed. Without the base, the reaction failed, although a small amount of 3a was observed without L1 (Entries 3–4). This led us to reduce the quantity of the ligand, and 40% of 3a was then formed (Entry 5). Next, various other ligands (Figure 1) were screened without success (Entries 6–12); bipyridine L1 remained the more efficient.
The influence of the nature of the base was then explored. A good yield was obtained with Cs₂CO₃, whereas K₃PO₄ led to a similar result to that of K₃CO₃ (Entries 13–14). Surprisingly, CsF, often used in cross-coupling reactions with boronic acid, provided a low yield (Entry 15). Organic nitrogen bases appeared to be deleterious for the reaction (Entries 16–17). This could be explained by a competitive copper coordination between these bases and L₁. At higher temperatures, no improvement was observed but, on contrary, this resulted in a decrease of yield (Entry 18). This may be due to the outgassing of the highly volatile CF₃SeCl reagent.

Catalytic amounts of copper (II) and ligand were then tested, but lower yields were observed (Entries 19–20). Again, heating proved to be deleterious (Entry 21). Inspired by our previous work with a sulfur series [68], some water (7 eq.) was added resulting, in this case, in a non-significant effect (Entry 22). Consequently, stoichiometric conditions (Entry 13) remained the better ones.

These conditions were applied to other aromatic boronic acids (Scheme 1).

![Ligands used in Table 1.](image)

**Scheme 1.** Trifluoromethylselenolation of aromatic boronic acids. Yields shown are those of the isolated products.

Only moderate yields were obtained with substituted aromatic compounds, whatever the donor or acceptor electronic character of the substituents. In heteroaromatic series, the same moderate results were observed.

When these lukewarm results were obtained, some amounts of CF₃SeSeCF₃ were detected as well as homocoupling products from the boronic reagents. This could be rationalized by the high reactivity...
of CF$_3$SeCl, which leads to a competition between the kinetically low coupling reaction and the more rapid dimerization. The homocoupling reaction could then come from the lack of CF$_3$SeCl for the expected reaction. Despite the use of an excess of preformed CF$_3$SeCl, no better results were observed. Furthermore, during the preliminary formation of CF$_3$SeCl, one equivalent of benzyl chloride was also formed, which could possibly disturb the cross-coupling reaction.

3. Materials and Methods

Commercial reagents were used as supplied. Reagent 1 was synthesized following procedures described in the literature [36,67]. Anhydrous solvents were used as supplied. NMR spectra were recorded on a Bruker AV 400 (Billerica, MA, USA) spectrometer at 400 MHz ($^1$H-NMR), 101 MHz ($^{13}$C-NMR), and 376 MHz ($^{19}$F-NMR), or on a Bruker AV 300 spectrometer at 300 MHz ($^1$H-NMR) and 282 MHz ($^{19}$F-NMR). Multiplicities are indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), p (quintet), sext (sextet), m (multiplet), b (broad). All coupling constants are reported in Hz.

3.1. Synthesis of Benzyl Trifluoromethyl Selenide (1)

To a dry round-bottom flask equipped with a magnetic stirrer, benzylselenocyanate (13.7 g, 70.0 mmol, 1.0 equiv.) and dry THF (140 mL) were added. The flask was evacuated and refilled with nitrogen three times, and then trifluoromethyl trimethylsilane (TMSCF$_3$) (20.7 mL, 140 mmol, 2.0 equiv.) was added. The reaction mixture was cooled to 0 °C, and then tetrabutylammonium fluoride (TBAF) in THF 1 M (14.0 mL, 14.0 mmol, 0.2 equiv.) was added dropwise. After 10 min at 0 °C under nitrogen, the reaction was allowed to warm to 23 °C and was stirred for 7 h. The conversion was checked by $^{19}$F-NMR with PhOCF$_3$ as an internal standard. The reaction mixture was then partitioned with pentane: 100 parts, and the aqueous layer was extracted with pentane. The combined organic layers were washed with brine, dried over MgSO$_4$, filtered and concentrated to dryness (under moderate vacuum). The crude residue was purified by chromatography (pentane: 100) and then trifluoromethyl trimethylsilane (TMSCF$_3$) (0.36 mmol, 1.1 equiv.), SO$_2$Cl$_2$ (0.40 mmol, 1.1 equiv.) and anhydrous acetonitrile (1 mL) were added under nitrogen. The flask was evacuated and refilled with nitrogen. The reaction mixture was stirred for 6 h at 20 °C.

3.2. Typical Procedure

Solution A: To a flame-dried flask equipped with a magnetic stirrer, BnSeCF$_3$ (1) (0.40 mmol, 1.1 equiv.), SO$_2$Cl$_2$ (0.40 mmol, 1.1 equiv.) and anhydrous acetonitrile (1 mL) were added under nitrogen. The reaction mixture was stirred for 6 h at 20 °C.

Solution B: To a flame-dried flask equipped with a magnetic stirrer, biphenylboronic acid 2 (0.36 mmol, 1 equiv.), copper (II) acetate (0.36 mmol, 1 equiv.), bipyridine (L1) (0.36 mmol, 1 equiv.) and cesium carbonate (0.36 mmol, 1 equiv.) were added under nitrogen. Solution A was then poured into solution B by syringe and the mixture was stirred at 20 °C for 16 h. The reaction mixture was partitioned between CH$_2$Cl$_2$ and water. The aqueous layer was extracted with CH$_2$Cl$_2$ and the combined organic layers were washed with brine, dried over MgSO$_4$, and concentrated to dryness. The crude residue was purified by flash chromatography to afford the desired product 3.

Synthesis of 4-[[trifluoromethyl]selenyl]-1,1′-biphenyl (3a). Eluent for flash chromatography: cyclohexane/AcOEt 98:2. $^1$H-NMR (300 MHz, CDCl$_3$) δ = 7.83 (m, 2H), 7.65–7.60 (massif, 4H), 7.50 (m, 2H), 7.42 (m, 1H). $^{19}$F-NMR (282 MHz, CDCl$_3$) δ = −36.05 (s, 3F). The results are in accordance with the literature [57].
Synthesis of 1-bromo-4-[(trifluoromethyl)selenyl]benzene (3b). Eluent for flash chromatography: pentane 100%. $^1$H-NMR (300 MHz, CDCl$_3$) $\delta = 7.60$ (m, 2H), 7.53 (m, 2H). $^{19}$F-NMR (282 MHz, CDCl$_3$) $\delta = -36.03$ (s, 3F). The results are in accordance with the literature [61].

Synthesis of 1-methoxy-4-[(trifluoromethyl)selenyl]benzene (3c). Eluent for flash chromatography: cyclohexane/toluene 9:1. $^1$H-NMR (300 MHz, CDCl$_3$) $\delta = 7.66$ (m, 2H), 6.91 (m, 2H), 3.83 (s, 3H). $^{19}$F-NMR (282 MHz, CDCl$_3$) $\delta = -37.18$ (s, 3F). The results are in accordance with the literature [61].

Synthesis of methyl 4-[(trifluoromethyl)selenyl]benzoate (3d). Eluent for flash chromatography: cyclohexane/EtOAc 97:3 to 95:5. $^1$H-NMR (300 MHz, CDCl$_3$) $\delta = 8.04$ (m, 2H), 7.81 (m, 2H), 3.94 (s, 3H). $^{19}$F-NMR (282 MHz, CDCl$_3$) $\delta = -35.21$ (s, 3F). The results are in accordance with the literature [57].

Synthesis of 3-[(trifluoromethyl)selenyl]quinoline (3e). Eluent for flash chromatography: cyclohexane/Et$_2$O 8:2. $^1$H-NMR (300 MHz, CDCl$_3$) $\delta = 9.14$ (s, 1H), 8.65 (d, $J = 1.8$ Hz, 1H), 8.21 (d, $J = 8.7$ Hz, 1H), 7.86 (m, 2H), 7.67 (m, 1H). $^{19}$F-NMR (282 MHz, CDCl$_3$) $\delta = -35.50$ (s, 3F). The results are in accordance with the literature [53].

Synthesis of 3-[(trifluoromethyl)selenyl]-1-benzothiophene (3f). Eluent for flash chromatography: cyclohexane/toluene 98:2. $^1$H-NMR (300 MHz, CDCl$_3$) $\delta = 8.02$ (d, $J = 7.7$ Hz, 1H), 7.96 (s, 1H), 7.92 (m, 1H), 7.51 (m, 1H), 7.44 (m, 1H). $^{19}$F-NMR (282 MHz, CDCl$_3$) $\delta = -35.66$ (s, 3F). The results are in accordance with the literature [57].

4. Conclusions

In our study of its reactivity scope, we have demonstrated that CF$_3$SeCl, in situ preformed, could react with boronic acids to perform trifluoromethylselenolation of aromatic or heteroaromatic compounds. However, moderate yields were generally observed due to the overly high reactivity of CF$_3$SeCl and the presence of generated benzyl chloride. This points out the major issue of this one-pot strategy; the subsequently formed benzyl chloride may limit this approach by inducing side-reactions. Furthermore, the high reactivity of CF$_3$SeCl, which can easily dimerize, could also constitute a drawback with reactions which are kinetically too low. This underlines the necessity of developing new reagents, that are isolable, easy to handle and have a modular reactivity that is easier to control.

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