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Nickel-Catalyzed Electrochemical Synthesis of (Hetero)Aryl Trifluoromethyl Selenides

Serhii Krykun^[a] and Muriel Durandetti^{*[a]}

A convenient and efficient approach for the construction of aryl trifluoromethyl selenoethers from aryl iodides under mild conditions is reported. Electrochemical activation of stable and inexpensive NiBr₂bipy (bipy – bipyridine) complex instead of labile Ni(COD)₂ (COD – cyclooctadiene) catalyst. [NMe₄][SeCF₃] is

employed as shelf-stable source of SeCF₃ fragment. The reaction tolerates a wide range of substrates, including modification of drug-like molecules. Cyclic voltammetry studies allow insight into the reaction mechanism.

Introduction

Fluorine and fluorine-containing groups have long been known to be of great interest in the world of agrochemicals, pharmaceuticals, and functional materials.^[1] Among those, trifluoromethyl (CF₃) group is the most widely used structural unit due to its high lipophilicity and strong electron-withdrawing character. Further development of this idea led to significant interest in trifluoromethyl ether (OCF₃) and its chalcogen analogs (SCF₃, SeCF₃).

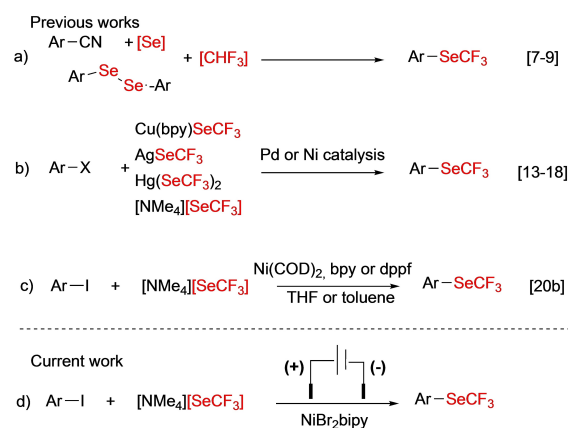
Among these, we decided to focus on trifluoromethylseleno (SeCF₃) group in the present work. It possesses useful electronic characteristics (Hammett constants $\sigma_p = 0.45$, $\sigma_m = 0.44$). Recently corrected Hansh-Leo parameter ($\pi_R = 1.61$) is higher compared with its CF₃ ($\pi_R = 0.88$), OCF₃ ($\pi_R = 1.04$) and SCF₃ ($\pi_R = 1.44$) analogs.^[2] Therefore, it can be of great interest as a tool to fine-tune molecular properties, including late-stage modifications of lead candidates.^[3] For example, in 2019 Billard and coworkers showed increased lipophilicity without impacting microsomal stability for SCF₃ and SeCF₃ isosteric replacements of OCF₃-containing drugs, allowing to increase in vivo half-life and adjust ADME parameters.^[4]

Selenium in general is an essential microelement for humans^[5] and is widely used in supplements and demonstrates promising results for its introduction into pharmaceuticals.^[6] SeCF₃ group does not occur naturally, however a number of approaches for its introduction were developed over the years (Scheme 1).^[7] Traditionally, the first procedures involved conversion of diselenides and selenocyanites using TMSCF₃/fluoride mixture to generate in situ CF₃ anions^[8] and later expanded to a

wide range of conditions^[7b,9] (Scheme 1a). However, these approaches suffered from harsh reaction conditions and toxic reagents. This led to the development of direct trifluoromethylselenolation using electrophilic, radical, or nucleophilic reagents. Electrophilic reagents containing selenium cover several approaches, such as benzothiazoliumSeCF₃,^[10] TsSeCF₃,^[11] or trifluoromethyl selenoxides.^[12]

Nucleophilic reagents are used in combination with aryl halides and using various sources like CuSeCF₃, Hg(SeCF₃)₂, [NMe₄][SeCF₃], ClSeCF₃ and [(bpy)Cu(SeCF₃)₂]^[13] (Scheme 1b). From these, [NMe₄][SeCF₃] is the most promising due to its good stability and ease of synthesis.^[14] Most of these procedures rely on the transition metal catalysis, using Cu,^[15] Pd,^[16] Au^[17] or Ni.^[18]

Nickel catalysis is one of the most readily available and powerful alternatives to other more expensive metals such as Pd or Au, while offering good C-X bond activation potential.^[19] In 2012, Zhang and Vici first demonstrated efficient conversion of aryl halides to SCF₃,^[20a] and later in 2017 to SeCF₃ derivatives^[20b] (Scheme 1c). While their method allowed to obtain target compounds in good yields, it required the use of tedious Ni(COD)₂ as a catalyst, and must be used in a glove-box. To avoid this, we decided to develop an easy-to-handle alternative process and turned to our experience in nickel-



Scheme 1. Previous works (a-c) and current work (d).

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catalyzed electrosynthesis.^[21] The use of electrochemistry offers considerable advantages, both in terms of efficiency and sustainability, and can be applied to the synthesis of complex molecules.^[22] Stable Ni(II) complexes can be electrochemically reduced to form catalytically active Ni(0) species, generated in situ in solution.^[21,23] This simplifies the reaction procedure considerably, as all the initial components are stable and easy to handle (Scheme 1d).

Results and Discussion

Based on our initial results, which we have already developed using electro-reductive nickel catalysis,^[21] we first used NiBr₂bipy complex as catalyst, in our model reaction, combined with the sacrificial anode process.^[24] As source of SeCF₃ fragment, shelf-stable salt [NMe₄][SeCF₃] **2** was synthesized using established procedure.^[14a] Initial tests using an aluminum rod as anode and a nickel foam as cathode gave promising results, showing almost, by gas chromatography, a complete consumption of the starting aryl iodide **1**, in favor of the trifluoromethylselenolation product **3** in 59% GC yield, but also the formation of Ar-Ar homocoupling by-product (24%) and reduction product Ar-H in 17% GC yield (Table 1, entry 1). Increasing the amount of bipyridine ligand minimized the formation of biaryl by-products, but also led to a decrease in conversion (27% conversion, Table 1, entry 2).

Therefore, we performed optimization of anode material, using both consumable and inert electrodes (Table 1, entries 3–7). With graphite anode freshly distilled NEt₃ was used as a

consumable oxidant, (Table 1, entry 3). Nickel and zinc plate as anodes gave the best results, and in order to not release nickel salt during the process, the Zn/Ni foam pair was chosen for its better performance (Table 1, entry 7). All reactions were performed under constant current electrolysis. Intensity of 15 mA was found to be optimal and a total charge of 2F/mol regarding to the catalyst (total charge of 50 C) was found to be sufficient for full conversion of the starting material **1**. NBu₄BF₄ was employed as supporting electrolyte, and was necessary. In fact, experiments without NBu₄BF₄, with only [NMe₄][SeCF₃] **2** as both electrolyte and reagent showed some decrease in conversion of starting ArI **1** (38% conversion, Table 1, entry 8). DMF proved to be the optimal solvent, as little conversion took place in DMAc, NMP or THF (Table 1, entries 9–11). It should be mentioned that in the latter case the conductivity was so low that electrosynthesis was difficult to achieve. The addition of acetonitrile didn't result in a significant improvement, as sometimes shown in some cases (Table 1, entry 12).^[25] Room temperature gave the best results, while increasing the temperature to 50 °C led to some degradation, and finally **1** was mainly recovered with a small amount of coupling product **3** (Table 1, entry 13). Changing the ligand for tbbpy resulted in lower conversion, while PPh₃ ligand didn't catalyze the reaction at all (Table 1, entries 14–15). The optimization reactions were carried out on a scale of 0.5 mmol of **1**, with a relatively high catalyst loading of 50 mol%. In an effort to optimize the scale and reaction loading, the reaction was scaled up to 1 mmol of **1** and 25% of NiBr₂bpy as catalyst, providing the coupling product **3** in 85% GC yield, again with 2F/mol over the nickel salt (total charge of 50 C, Table 1, entry 16).

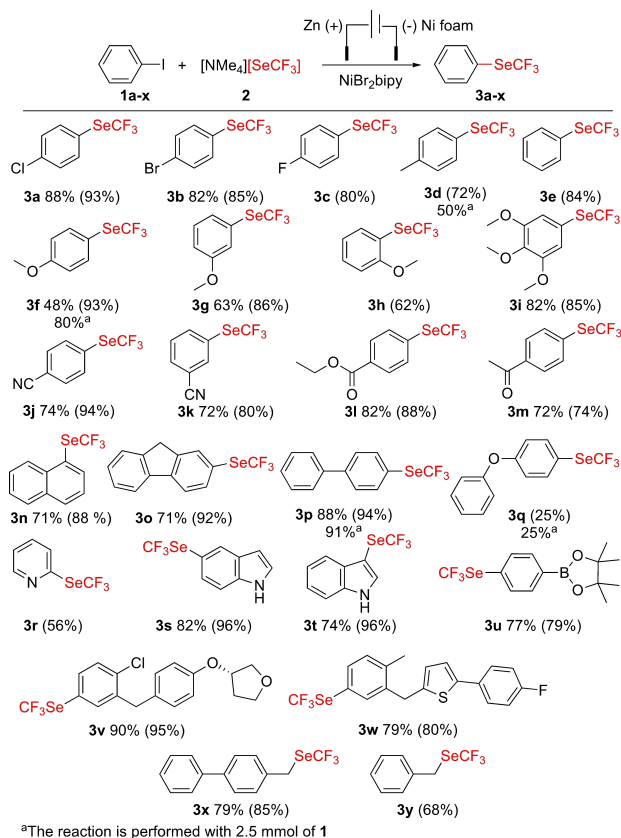
Prompted by these results, the experimental study led us to apply the following typical procedure: electrolysis was run in a one-compartment cell fitted with a nickel sponge (area ca. 2 cm²) as a cathode and a zinc plate as the anode. NBu₄BF₄ (0.15 equiv., 0.15 mmol, supporting electrolyte) was dissolved in 8 mL of dry DMF under argon atmosphere, then NiBr₂bipy (0.25 equiv., 0.25 mmol), aryl iodide **1** (1.0 equiv., 1.0 mmol) and [NMe₄][SeCF₃] **2** (1.1 equiv., 1.1 mmol) were added. The electrolysis was carried out at room temperature under argon at a constant current intensity of 15 mA until a total charge of 50 C (~50 min., 2 F/mol of NiBr₂bipy) was passed, and the reaction was stirred an additional 1 h after the end of the electrolysis to achieve complete conversion of the aryl iodide.

Once the conditions were optimized, we applied this procedure to a wide range of substrates (Scheme 2). We were able to convert aromatic iodides in good yields for both electron-poor and electron-rich aromatic compounds. In the case of smaller molecules, the high volatility and similar polarity to the corresponding reduction product ArH prevented proper isolation and ¹⁹F NMR yields are shown in brackets. As expected, substituents in the ortho position gave slightly lower yields due to steric hindrance (Scheme 2, compared product **3h** vs. **3f** and **3g**). Procedure shows a good tolerance for functional groups. Significant difference in reactivity between halogens allows to efficiently convert aryl iodides containing bromine (**3b**), chloride (**3a**), or fluorine (**3c**) groups. In case of 4-bromoiodobenzene substrate **1b**, small amount of disubstituted by-

Table 1. Reaction optimization using iodoanisole as substrate.

entry	Catalyst	Anode	Solvent	Conversion ^[a]
1	NiBr ₂ bipy 0.5 equiv.	Al	DMF	0/59/17/24
2	NiBr ₂ bipy 0.5 equiv. + 1 equiv. bipy	Al	DMF	73/24/3/0
3	NiBr ₂ bipy 0.5 equiv.	C ^[b]	DMF	78/20/1/1
4	NiBr ₂ bipy 0.5 equiv.	Ni	DMF	8/80/6/6
5	NiBr ₂ bipy 0.5 equiv.	stainless	DMF	91/3/6/0
6	NiBr ₂ bipy 0.5 equiv.	Mg	DMF	63/3/34/0
7	NiBr ₂ bipy 0.5 equiv.	Zn	DMF	5/78/17/0
8	NiBr ₂ bipy 0.5 equiv.	Zn	DMF ^[c]	62/28/10/0
9	NiBr ₂ bipy 0.5 equiv.	Ni	DMAc	79/3/18/0
10	NiBr ₂ bipy 0.5 equiv.	Ni	NMP	71/29/0/0
11	NiBr ₂ bipy 0.5 equiv.	Ni	THF ^[d]	100/0/0/0
12	NiBr ₂ bipy 0.5 equiv.	Zn	DMF/ CH ₃ CN 1/9	0/88/12/0
13	NiBr ₂ bipy 0.5 equiv.	Zn	DMF ^[e]	74/26/0/0
14	NiBr ₂ 0.5 equiv. + 0.5 equiv. tbbpy	Zn	DMF	22/64/14/0
15	NiBr ₂ 0.5 equiv. + 1 equiv. PPh ₃	Zn	DMF	75/0.5/29.5/0
16	NiBr ₂ bipy 0.25 equiv.	Zn	DMF	0/85/15/0

[a] ArI/ArSeCF₃/ArH/ArAr ratio determined by GC. [b] Reaction is run using NEt₃ as consumable oxidant. [c] Reaction is run without NBu₄BF₄. [d] Not conductive enough for electrochemistry, even with 0.1 M of NBu₄BF₄. [e] Reaction is run at 50 °C.



Scheme 2. Ni-catalyzed trifluoromethylselenolation of aryl iodides with [NMe₄][SeCF₃] under electrochemical conditions. ¹⁹F NMR yields in brackets, using trifluoromethylbenzene as internal standard.

product was observed. We also applied this process to the cross-coupling reaction of heteroaromatics iodides. While 2-iodopyridine gave a modest ¹⁹F NMR yield of 56% to compound **3r**, the process could be applied to iodo-indoles, and 5- and 3-trifluoromethylselenanyl-1H-indole were isolated in 82 and 74% yields respectively (compounds **3s** and **3t**). Finally, high chemoselectivity was demonstrated by applying the process to *p*-iodo boronic ester **1u**, which allows the product **3u** in 77% isolated yield.

In order to increase the scale of the process and decrease the catalyst loading, the reaction was scaled up to 2.5 mmol of substrate **2** and 10% of NiBr₂·bipy as catalyst, resulting in excellent results such as **3f** in 80% isolated yield (86% NMR), or **3p** in 91% isolated yield.

Finally, this method offers an efficient methodology for the late-stage modification of compounds. To demonstrate this, we introduced SeCF₃ fragment to Empagliflozin and Canagliflozin intermediates, two antidiabetic medication.^[26] Compounds **3v** and **3w** were thus isolated in good yields of 90% and 79% respectively (Scheme 2). Benzyl chlorides^[27] as starting material were also found to be competent and afford good yields as shown with compound **3x** and **3y**.

In order to better understand the mechanism of the reaction, electrochemical studies were conducted, using cyclic voltammetry. In particular, it seems essential to understand the

electron catalytic aspect, as processes using NiBr₂·bipy catalysis generally required 2F/mol of substrate (200 C for 1 mmol of starting material).^[21] We have already reported the electrochemical behavior of NiBr₂·bipy in DMF.^[28] The cyclic voltammograms have been obtained in DMF, on a gold microelectrode, at 200 mV/s. The Ni(II) complex presents a quasi-reversible system at -1.15 V/SCE, with the consumption of 2 electrons, giving Ni⁰·bipy, which is further reduced at -1.9 V/SCE into Ni⁰·bipy⁻ (Figure 1, blue curve and Supporting Information). The addition of 1 equivalent of [NMe₄][SeCF₃] shows a significant change in the electrochemical behavior of NiBr₂·bipy (Figure 1, black curve). In particular, the reduction wave is split, and during the reverse scan, the reoxidation wave of Ni⁰·bipy at -1.0 V/SCE disappears and, at the same time, a new system appears at +0.1 V/SCE. This system is not due to [NMe₄][SeCF₃], as it does not appear for the salt alone (Figure 1, red curve). Considering the significant change in solubility, color and reduction wave upon addition of [NMe₄][SeCF₃] to the NiBr₂·bipy solution in DMF, we propose the formation of another nickel(II) complex, in the form of Ni^(II)Br[SeCF₃]·bipy. Ni⁰[SeCF₃]·bipy⁻ will reoxidize at +0.1 V/SCE.

After addition of one equiv. of iodobenzene, these changes remain, and a further oxidation wave is observed at +0.4 V/SCE (Figure 2, orange curve). Interestingly, a new reduction wave appears just after the Ni(II) reduction, which can be attributed to an σ -arylnickel intermediate resulting from the oxidative addition of Ni⁰[SeCF₃]·bipy⁻ in the C-I bond.

Our experimental conditions and CV experiments suggest that this reaction relies on a Ni(0) catalytic cycle, as proposed in Scheme 3.

The initial NiBr₂·bipy complex first undergoes anion exchange to form the Ni^(II)Br[SeCF₃]·bipy complex upon addition of [NMe₄][SeCF₃], as confirmed by color change and CV curve. By application of electrical current, Ni(II) is reduced at -1.15 V/SCE allowing the catalytic form [Ni⁰][SeCF₃]·bipy⁻. Then an oxidative addition occurs with the aryl iodide **1** leading to the σ -arylnickel(II) intermediate ArNiSeCF₃·bipy.^[19,28–29] Subsequently, a reductive elimination step occurs, leading to the product

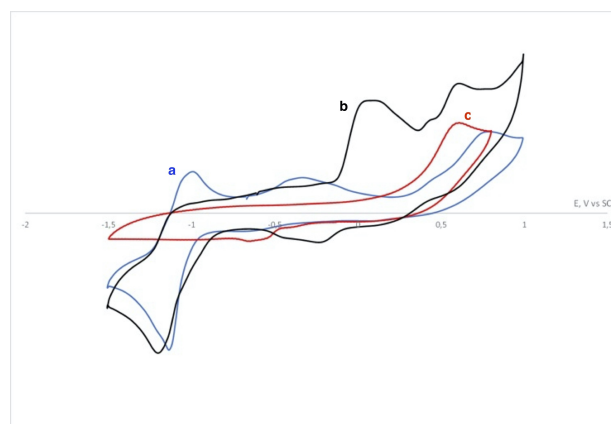


Figure 1. Cyclic voltammetry of a) NiBr₂·bipy (blue); b) NiBr₂·bipy + 1 equiv. of [NMe₄][SeCF₃] (black); and c) [NMe₄][SeCF₃] (red) at a gold-disk μ -electrode (0.25 mm diameter) in DMF, 0.1 M NBu₄BF₄, at 200 mV/s.

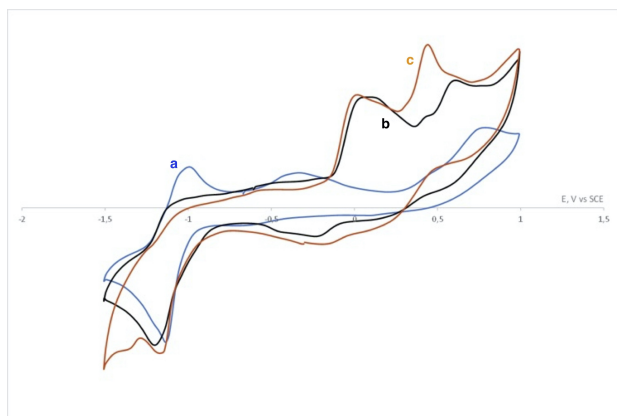
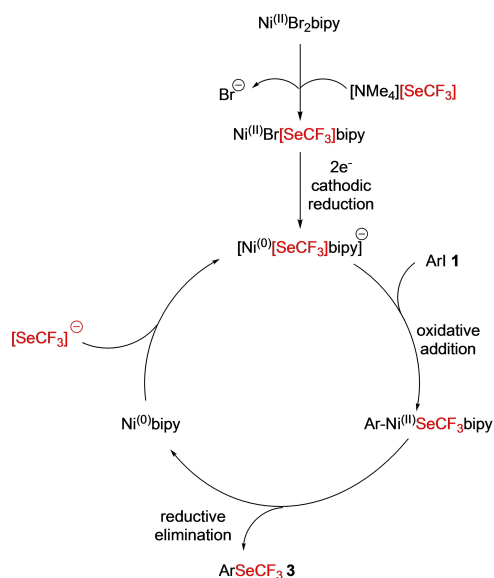


Figure 2. Cyclic voltammetry of a) NiBr_2bipy (blue); b) NiBr_2bipy + 1 equiv. of $[\text{NMe}_4][\text{SeCF}_3]$ (black); and c) NiBr_2bipy + 1 equiv. of $[\text{NMe}_4][\text{SeCF}_3]$ + 1 equiv. of PhI (orange) at a gold-disk μ -electrode (0.25 mm diameter) in DMF, 0.1 M NBu_4BF_4 , at 200 mV/s.



Scheme 3. Proposed catalytic cycle.

ArSeCF_3 **3** and releasing free $[\text{Ni}^0\text{bipy}]$, which can then react with $[\text{SeCF}_3]^-$ present in solution to regenerate the active catalyst $[\text{Ni}^0[\text{SeCF}_3]\text{bipy}]^-$. This mechanism is in good agreement with the catalytic amount of electron. In fact, the catalytic cycle doesn't release Ni(II) salt as usual after reductive elimination, but Ni(0) , which does not need to be reduced again. This may also explain the absence of homocoupling reaction, resulting in an Ar–Ar by-product, which is not observed at all or only in trace in our case. Furthermore, we were able to adapt this electrochemical reduction by employing a catalytic amount of alternative reductant and **3f** was obtained in about 50–60% yields with 20% of manganese metal or Et_2Zn . Similarly, NiBr_2bipy can be replaced by Ni(COD)_2 + 1 equiv. of bipy, without any reductant, in DMF, leading to **3f** in the same good yield, in good agreement with a Ni(0) -based catalytic cycle.

Further DFT studies are planned to verify our proposed mechanism.

Conclusion

In conclusion, we have developed an efficient procedure for the preparation of aryl trifluoromethyl selenoethers from aryl iodides using stable compounds and mild reaction conditions. The use of an electrochemistry process avoids the handling of tedious catalysts such as Ni(COD)_2 . Our methodology allows wide tolerance for other functional groups, as well as possibility to scale up the reaction. Cyclic voltammetry permitted to get insight into the reaction mechanism. Finally, reaction conditions are shown to be useful for synthesis of potentially biologically active compounds by late-stage modification of lead molecules for drug discovery. Attempts to further extend this procedure to aryl bromides and chlorides are on the way.

Experimental Section

General procedure for the trifluoromethylselenation of aryl iodides: Starting aryl iodide **1** (1 mmol), NiBr_2bipy (0.25 equiv., 0.25 mmol) and supporting electrolyte (NBu_4BF_4 , 50 mg) were mixed directly in an undivided electrochemical cell, which was degassed with argon, and 8 ml of dry DMF was added. Resulting system was stirred for 5 min until formation of clear green solution. Then $[\text{NMe}_4][\text{SeCF}_3]$ **2** was added (1.1 equiv., 1.1 mmol) and system was stirred for 5 min, resulting in a pale-yellow-green suspension. At this point electrodes were introduced (Zn plate as anode and Nickel foam as cathode). The electrolysis was run at constant current of 15 mA for 2F/mol regarding the NiBr_2bipy pre-catalyst (48 C), upon which system gradually turned black and dark precipitate was formed. After electrolysis, the cell was allowed to stir for additional 1 h under Ar. Reaction was monitored by GC and ^{19}F NMR (in this case 0.5 equiv. of PhCF_3 was added, as internal standard, into the reaction mixture before the start of the reaction). After reaction, the crude was filtered through celite pad, which was rinsed few times with Et_2O . Resulting filtrate was diluted with Et_2O , washed three times with water, organic phase was dried over MgSO_4 , and evaporated. Resulting crude compound was purified via flash chromatography using appropriate solvent.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: C-Se bond formation · electrosynthesis · nickel catalysis · selenium · trifluoromethylselenolation

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