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Communication

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# Bismuth-Catalyzed Oxidative Coupling of Arylboronic Acids with Triflate and Nonaflate Salts

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*Supporting Information Placeholder*

**ABSTRACT:** Herein we present a Bi-catalyzed cross-coupling of arylboronic acids with perfluoroalkyl sulfonate salts based on a Bi(III)/Bi(V) redox cycle. An electron-deficient sulfone ligand proved to be key for the successful implementation of this protocol, which allows the unusual construction of C(sp$^2$)–O bonds using commercially available NaOTf and KONf as coupling partners. Preliminary mechanistic studies as well as theoretical investigations reveal the intermediacy of a highly electrophilic Bi(V) species, which rapidly eliminates phenyl triflate.

Functional groups such as the trifluoromethanesulfonate (triflate, OTf) or the nonafluorobutanesulfonate (nonaflate, ONf) are highly useful moieties when present in organic compounds, especially when attached to a carbon atom (C–OTf or C–ONf).[1] Indeed, C(sp$^2$)–OTf and C(sp$^2$)–ONf have been utilized as surrogates of aryl halides (*aka* pseudohalides) due to their ability to heavily polarize the C–O bond, facilitating oxidative addition by d-block metals. This strategy has been largely exploited with a myriad of combinations of both transition metals and coupling partners,[2] thus placing aryl triflates and nonaflates as routine electrophiles in this large arena.[3] From the organometallic standpoint, OTf anions have also many attractive features. The coordinating properties of triflate anions have been a matter of intense debate in the recent literature.[4] However, it is evident that differently than Ar–Cl, oxidative addition complexes of Ar–OTf would result in a remarkably weaker interaction of the OTf anion and the metal center in solution. Furthermore, in polar and coordinating solvents the OTf anion is generally relegated to the outer sphere, leaving a vacant coordination site (Figure 1A), which has been exploited for a variety of organometallic and coordination purposes.[5] Yet, the great attributes of OTf anions – highly electronegative, poor nucleophiles and labile ligands – inherently situates them as one of the foulest anions to undergo C–O reductive elimination.[6]

Many examples with high-valent transition metals have been reported to accommodate OTf anions in the primary coordination sphere.[7] However, reductive elimination primarily occurred at other anionic ligand sites and the M–OTf bond remained unaltered.[8] During the synthesis of tri-substituted olefins, Gaunt and co-workers suggested that C(sp$^2$)–OTf bonds could be formed through an unusual reductive elimination from a Cu(III) center,[9] although further evidence was not provided. Indeed, examples of well-defined transition metal complexes that forge C(sp$^2$)–OTf bonds still remain elusive. Notwithstanding, the development of a catalytic protocol which enables the formation of Ar–OTf from the corresponding organometallic reagent (Ar–M) and a commercially available triflate salt (MOTf) would be highly desirable both from the synthetic and fundamental point of view.

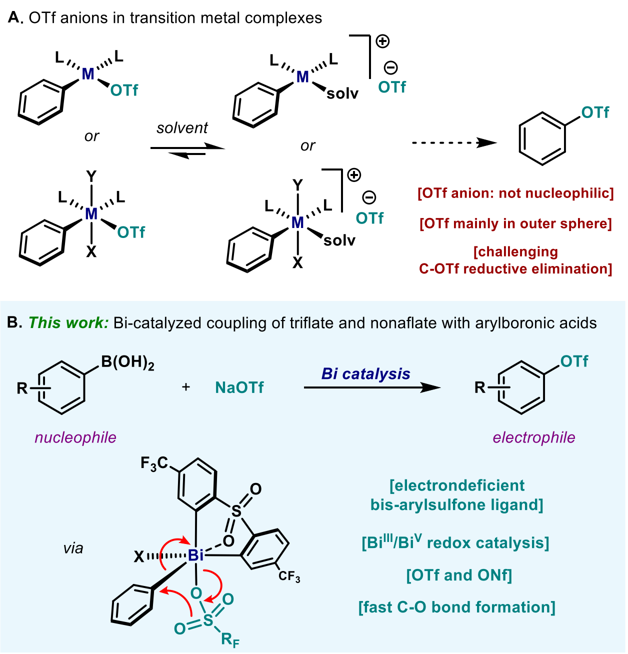
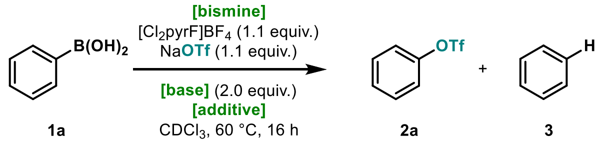


**Figure 1. (A)** OTf anions as ligands in transition metal chemistry; **(B)** catalytic Ar–OTf formation through a Bi(III)/Bi(V) redox system.

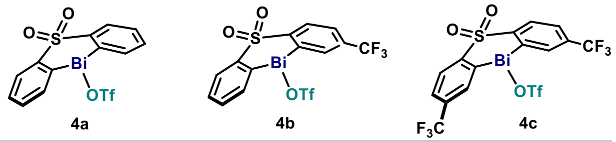
Our group has recently started a program to study the catalytic redox properties of bismuth (Bi) complexes,[10] to facilitate transformations beyond the reactivity of transition metals.[11] Hence, based on the known oxophilicity of Bi complexes[12] and their ability to bind triflate,[13] we envisaged that an oxidative protocol based on the redox couple Bi(III)/Bi(V) could fulfill this synthetic challenge. Indeed, a decade ago Mukaiyama and co-workers demonstrated that C–OTf bonds could be forged from Bi(V) compounds and HOTf, albeit in low yields.[14] Inspired by this early precedent, herein we report on a catalytic oxidative coupling between arylboronic acids and triflate salts to furnish Ar–OTf species (Figure 1B). A rationally designed Bi complex bearing an electron-deficient diarylsulfone ligand unlocks a catalytic redox process and enables the use of triflate (OTf) and nonaflate (ONf) salts as coupling partners. Preliminary mechanistic investigations and theoretical analysis revealed that the C(sp$^2$)–O bond formation is extremely fast from Bi(V), and is suggested to proceed through a 5-membered transition state.

We started our investigations by optimizing the coupling of phenylboronic acid (**1a**) with NaOTf to generate phenyltriflate (**2a**) (Table 1). Based on our previous studies on Bi-catalyzed fluorination, bismines featuring a diarylsulfone backbone (**4a**-**c**) were selected as catalysts,[15] together with *N*-fluoro-2,6-dichloropyiridinium tetrafluoroborate ($[Cl_2pyrF]BF_4$) as oxidant. To promote transmetalation, we selected $K_2CO_3$ as it has been recently demonstrated to be an excellent base for this purpose.[16] In our initial attempts, the unsubstituted bismine catalyst (**4a**) provided no reactivity towards **2a** (entry 1). However, when a $CF_3$ group was introduced in *meta*-position to the Bi (**4b**), an encouraging 11% of **2a** was obtained; interestingly, the formation of protodeboronation byproduct **3** was largely suppressed (entry 2). In line with these results, when two $CF_3$ are introduced in the backbone of the sulfone (**4c**) the reactivity towards **2a** increased to 32%, while the formation of **3** was still largely reduced (entry 3). When $K_2CO_3$ is replaced by NaF, a reversed trend in the product distribution is observed, substantially favoring undesired **3** (entry 4). Surprisingly, addition of 4Å molecular sieves (MS) boosted the formation of **2a** to 54% yield, while formation of **3** was still minimized (entry 5). Remarkably, when $K_2CO_3$ was replaced by the weaker $Na_3PO_4$, nearly quantitative formation of **2a** was achieved (entry 6). The use of 5Å MS proved crucial to completely suppress the formation of **3**, thus obtaining the desired **2a** in >95% yield (90% isolated) (entry 7). Unfortunately, lower catalyst loadings resulted in poor yields (entry 8).

**Table 1.** Optimization of the reaction conditions.[a]



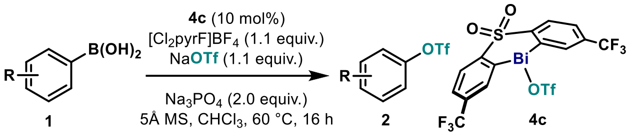
| Entry | [base] | [additive] (mg) | [bismine] (mol%) | **2a**, yield (%) | **3**, yield (%) |
|---|---|---|---|---|---|
| 1 | $K_2CO_3$ | - | **4a** (10) | 6 | <5 |
| 2 | $K_2CO_3$ | - | **4b** (10) | 11 | <5 |
| 3 | $K_2CO_3$ | - | **4c** (10) | 32 | 5 |
| 4 | NaF | - | **4c** (10) | 31 | 60 |
| 5 | $K_2CO_3$ | 4Å MS (20) | **4c** (10) | 54 | 5 |
| 6 | $Na_3PO_4$ | 4Å MS (20) | **4c** (10) | 93 | 6 |
| 7 | $Na_3PO_4$ | 5Å MS (10) | **4c** (10) | >95 (90)[b] | trace |
| 8 | $Na_3PO_4$ | 5Å MS (10) | **4c** (5) | 21 | <5 |

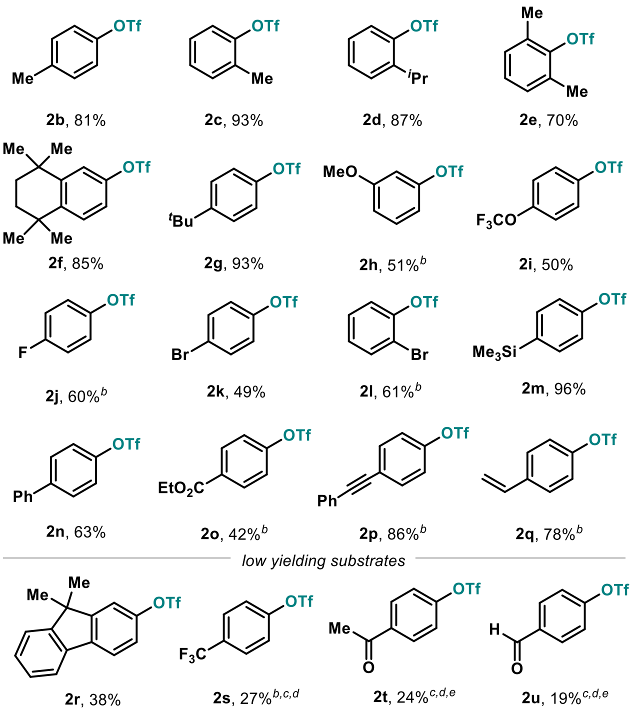


[a]Reactions performed at 0.025 mmol of **1a**. Yields determined by $^{19}F$ NMR using 1-fluoro-4-nitrobenzene as internal standard. [b] Isolated yield of pure material of a reaction performed at 0.3 mmols of **1a**.

With the optimal conditions in hand, the scope of the Bi-catalyzed C(sp$^2$)–OTf bond reaction was investigated using a variety of arylboronic acid derivatives (Table 2). The methodology boded well with Me groups in both *para*- (**2b**) and *ortho*-positions (**2c**). Remarkably, when the steric encumbrance at the *ortho*-position was further increased, excellent yields of the corresponding triflate were obtained (**2d** and **2e**). Furthermore, the presence of alkyl moieties in other positions of the aryl ring did not affect the reactivity (**2f** and **2g**). The protocol accommodates various functional groups, including ethers (**2h** and **2i**) and halogens (**2j**, **2k**, and **2l**), albeit in moderate yields. Arylboronic acids substituted with a trimethylsilyl group (TMS), Ph or an ester at the *para*-position afforded good to excellent yields of the corresponding aryl triflates (**2m** - **2o**). Arylboronic acids bearing unsaturated moieties boded well in this methodology, as exemplified by the presence of alkynyl (**2p**) and vinyl (**2q**) groups. In spite of the large variety of arylboronic acids amenable for this transformation, modest yields were obtained in the presence of certain functionalities. Due to the high reactivity towards oxidation with $[Cl_2pyrF]BF_4$, fluorene derivative **2r** was obtained in 38% yield.[15] Substrates bearing strong electron-withdrawing groups such as $CF_3$ (**2s**) and reactive carbonyl functionalities at the *para*-position (**2t** and **2u**) also struggled to undergo C–O bond formation, demonstrating some limitations to the scope of this reaction.

**Table 2.** Scope of the Bi-catalyzed oxidative coupling of arylboronic acids and sodium triflate.[a]

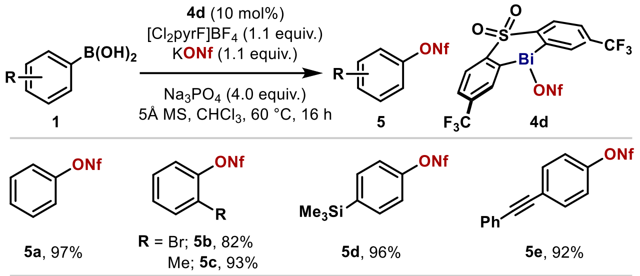




[a]Reaction conditions: **1** (0.3 mmol), NaOTf (0.33 mmol), **4c** (0.03 mmol), $[Cl_2pyrF]BF_4$ (0.33 mmol), $Na_3PO_4$ (0.6 mmol) and 5Å MS (120 mg) in $CHCl_3$ at 60 °C for 16 h. Yields of isolated pure material. [b]Reaction performed at 90 °C with 2.0 equiv. of NaF as base. [c]Yields determined by $^{19}F$ NMR using 1-fluoro-4-nitrobenzene as internal standard. [d]Reactions performed at 0.025 mmol of the corresponding arylboronic acids. [e]Reaction performed at 90 °C with 4.0 equiv. of $Na_3PO_4$ as base.

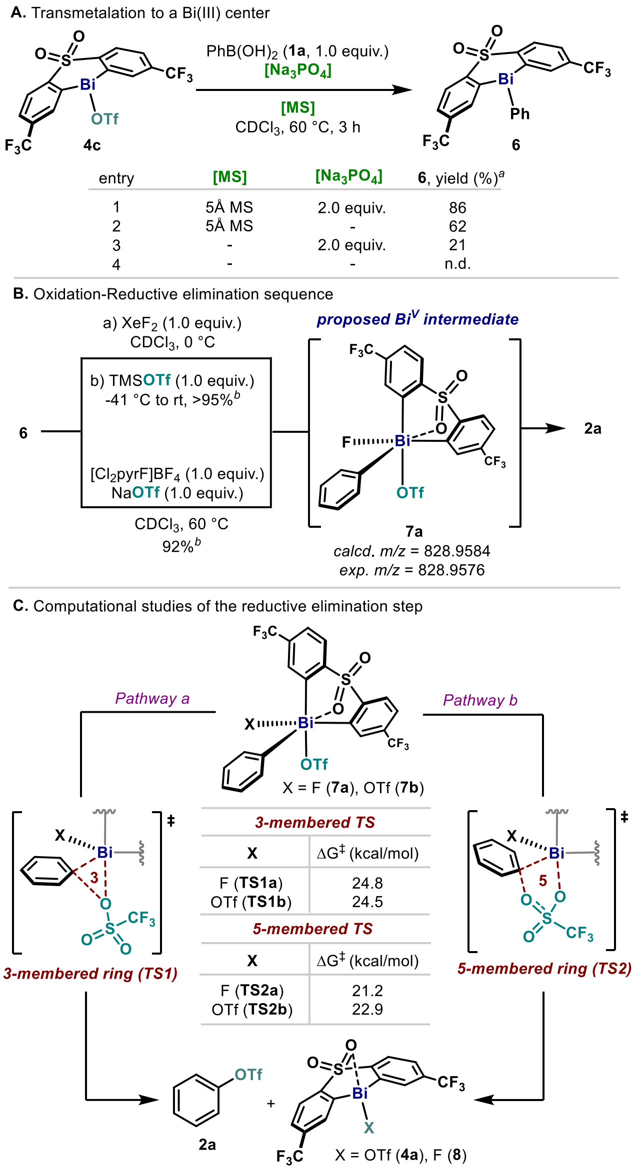
Having established a protocol for the successful coupling of NaOTf, we turned our attention to the use of less nucleophilic nonaflate salts as coupling partners. A brief re-examination of the reaction parameters revealed bismine nonaflate **4d** as the catalyst of choice to couple arylboronic acids with commercially available KONf.[15] With the optimized conditions shown in Table 3, Ph–ONf (**5a**) was isolated in a satisfactory 97% yield. The various arylboronic acids scrutinized in the nonaflate synthesis revealed comparable reactivity to NaOTf. Aryl nonaflates containing *ortho*-substituents such as Br (**5b**) and Me (**5c**) were obtained in excellent yields. Furthermore, a TMS moiety can also be accommodated to the protocol (**5d**) as well as unsaturated alkynyl functionalities (**5e**).

**Table 3.** Scope of the Bi-catalyzed oxidative coupling of arylboronic acids and potassium nonaflate.[a]



[a] Reaction conditions: **1** (0.3 mmol), KONf (0.33 mmol), **4d** (0.03 mmol), [Cl$_2$pyrF]BF$_4$ (0.33 mmol), Na$_3$PO$_4$ (1.2 mmol) and 5Å MS (120 mg) in CHCl$_3$ at 60 °C for 16 h. Yields of isolated pure material.

The unprecedented catalytic C–OTf and C–ONf bond forming reaction using **4c** and **4d** led us to explore the operative mechanism governing this transformation. First, we interrogated the transmetalation step between **1a** and **4c** (Figure 2A). When the reaction was performed in the presence of Na$_3$PO$_4$ and 5Å MS, transmetalation occurred efficiently and **6** was obtained in 86% yield (entry 1). In the absence of base, **6** was also obtained in slightly lower yields (62%, entry 2). In sharp contrast, when the reaction was performed without MS (entry 3), formation of **6** was dramatically reduced (21%). In absence of both MS and Na$_3$PO$_4$ **6** was not detected. These results demonstrate the importance of molecular sieves in this transformation, not only as dehydrating agent,[17] but also as potential heterogeneous Brønsted base,[18] promoting transmetalation to the Bi(III) center. At this point, the oxidation-reductive elimination sequence from phenylbismine **6** was studied utilizing different oxidants and triflate sources (Figure 2B, top). After oxidizing **6** with XeF$_2$ to the high-valent Bi(V) difluoride species,[10b, 15] TMSOTf was added, resulting in a rapid color change from pale to dark yellow. Analysis of the reaction crude revealed quantitative formation of **2a**. This result points to the formation of a highly electrophilic Bi(V) intermediate (**7a**) bearing a OTf moiety, as a consequence of fluoride abstraction by TMSOTf. Indeed, when TMSOTf was added at –41 °C, intermediate **7a** could be detected by HRMS (Figure 2B). Furthermore, using [Cl$_2$pyrF]BF$_4$ as oxidant together with NaOTf similar yields for **2a** were obtained (92%, Figure 2B, bottom). It is important to mention that only trace amounts of fluorobenzene were detected, which shows the preferential formation of C–OTf over C–F bonds (*vide infra*).[19] Related intermediates have been previously postulated by Mukaiyama, in the C(sp$^2$)–OTs coupling from Bi(V) intermediates.[14] Based on these experimental results, preliminary theoretical studies were performed to investigate a putative reductive elimination from **7,** bearing both a F (**7a**) or a OTf (**7b**) as counterions.[15] As shown in Figure 2C, two possible scenarios were postulated. On one hand, reductive elimination can occur through a 3-membered transition state (Figure 2C, *pathway a*), reminiscent of concerted reductive eliminations performed by d-block elements. Alternatively, reductive elimination could also occur via a 5-membered transition state (Figure 2C, *pathway b*), where two oxygens of the OTf are involved. This latter hypothesis has been previously invoked to explain the selectivity of Bi-mediated couplings such as α-arylation of phenols[20] and *N*-arylation of pyridones,[21] among other transformations.[22] In accordance with these previous reports, our theoretical analysis predicts that the 5-membered **TS2** is slightly favored over **TS1**, pointing towards **TS2** as the preferable pathway for the C–O bond forming event. NBO analysis on the Bi center also provided additional information about this process.[23] In the case of **7a**, the NBO charge on the Bi decreases from 2.17 to 1.84 in **TS1** and 1.88 in **TS2**; and is further reduced to 1.50 in **8**. The same trend is observed from **7b**.[15] This progressive change in charge at the metal center has been previously observed in high-valent Cu cross-couplings,[24] suggesting a concerted reductive elimination through the metal.



| entry | [MS] | [Na$_3$PO$_4$] | **6**, yield (%)[a] |
|---|---|---|---|
| 1 | 5Å MS | 2.0 equiv. | 86 |
| 2 | 5Å MS | - | 62 |
| 3 | - | 2.0 equiv. | 21 |
| 4 | - | - | n.d. |

| *3-membered TS* | |
|---|---|
| X | ΔG‡ (kcal/mol) |
| F (**TS1a**) | 24.8 |
| OTf (**TS1b**) | 24.5 |
| *5-membered TS* | |
| X | ΔG‡ (kcal/mol) |
| F (**TS2a**) | 21.2 |
| OTf (**TS2b**) | 22.9 |

**Figure 2. (A)** Study of the transmetalation step: influence of the molecular sieves and the base; **(B)** Stoichiometric sequence of oxidative addition – reductive elimination; **(C)** Theoretical analysis of the C–O bond forming step. [a] Yields determined by $^1$H NMR using 1,3,5-trimethoxybenzene as internal standard. [b] Yields determined by $^{19}$F NMR using 1-fluoro-4-nitrobenzen as internal standard.

Taken these results together, the reaction is proposed to follow the catalytic cycle depicted in Figure 3. Initially, bismine **A** undergoes transmetalation (TM) with the corresponding arylboronic acid, thus forming aryl bismine **B**. Subsequently, **B** undergoes formal oxidative addition (OA) with [Cl$_2$pyrF]BF$_4$, furnishing the proposed high-valent Bi(V) intermediate **C**. Reductive elimination (RE) from **C** delivers the desired aryl triflate with concomitant regeneration of **A**. Due to the structural similarities between OTf and ONf, we believe that a similar mechanism is operating for the coupling of the latter.

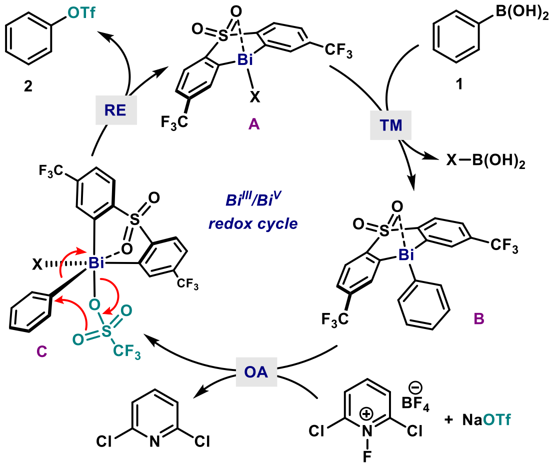


**Figure 3.** Postulated mechanism for the Bi-catalyzed oxidative coupling of arylboronic acids and triflate salts.

In summary, an unprecedented oxidative coupling of arylboronic acids with triflate and nonaflate salts has been developed exploiting the reactivity of the Bi(III)/Bi(V) redox couple. A highly electron withdrawing diarylsulfone ligand unlocked a catalytic process which proceeds under mild conditions and accommodates various functional groups. The results presented in this study unveil bismuth redox catalysis as a promising tool to perform transformations beyond the scope of transition metals, while mimicking their fundamental organometallic steps.

## ASSOCIATED CONTENT

### Supporting Information

Experimental procedures, analytical data ($^{1}$H, $^{19}$F, $^{11}$B and $^{13}$C NMR, HRMS) for all new compounds, computational results, including Tables (S1-S10) and Figures (S1-S20). This material is available free of charge via the internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interests.

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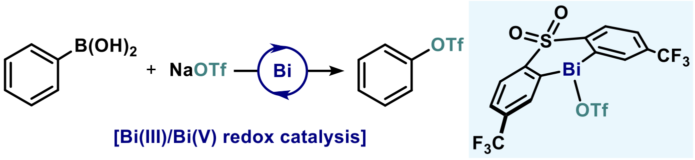
B(OH)2
+ NaOTf
Bi
OTf
[Bi(III)/Bi(V) redox catalysis]
O
O
S
Bi
OTf
CF3
F3C