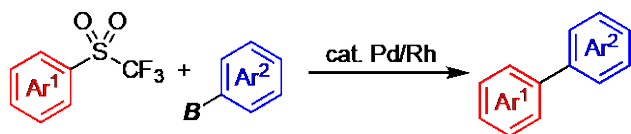


Cross-Coupling of Aryl Trifluoromethyl Sulfones with Arylboronates by Cooperative Palladium/Rhodium Catalysis

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ABSTRACT: Suzuki-Miyaura arylation of aryl trifluoromethyl sulfones via C–SO₂ bond cleavage has been developed by means of cooperative palladium/rhodium catalysis. A series of aryl trifluoromethyl sulfones and arylboronic acid neopentylglycol esters are converted to the corresponding biaryls. Mechanistic investigations suggest (1) the rhodium catalyst mediates transfer of the aryl ring from arylboronate to palladium resulting in acceleration of the transmetalation step; (2) C–C-bond-forming reductive elimination step would be the turnover-limiting step.

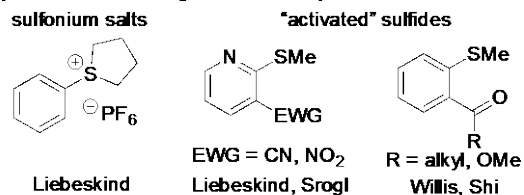
Biaryl skeletons represent a pivotal substructure in organic chemistry and related fields including pharmaceutical and agrochemical industry as well as advanced material science. Suzuki-Miyaura cross-coupling of aryl electrophiles with arylboronic acid derivatives is among the most important methodologies for construction of biaryl skeletons.¹ Besides conventional aryl halides and triflates, Suzuki-Miyaura arylation of less reactive aryl electrophiles containing C–F,² C–O,³ and C–N^{4,5} bonds has been emerging.

On the other hand, Suzuki-Miyaura arylation of aromatic organosulfur compounds has been relatively unexplored while catalytic C–S transformation has attracted much attention in the cross-coupling arena.⁶ As a seminal work, Liebeskind developed palladium-catalyzed arylation of arylsulfonium salts (Figure 1a, left).^{7,8} Although the reaction proceeded under mild conditions due to their enhanced reactivity, the starting sulfonium salts intrinsically suffer from dealkylative decomposition. In 2002, Liebeskind and Srogl accomplished Suzuki-Miyaura cross-coupling of aryl sulfides by means of a palladium catalyst and copper thiophenecarboxylate (CuTC) (Figure 1a, center).^{9,10} However, the applicable substrates were limited to azaaryl sulfides such as electron-deficient pyridyl and thiazolyl sulfides. Although Willis and Shi independently reported the arylation of aryl sulfides with rhodium catalysts, the reactions require carbonyl directing groups at the *ortho* positions (Figure 1a, right).¹¹

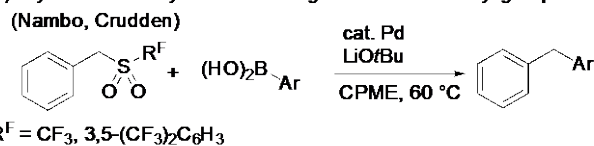
To develop a new class of Suzuki-Miyaura arylation of aromatic organosulfur compounds, we focused on the use of fluorinated sulfonyl leaving group. Recently, Nambo and Crudden accomplished Suzuki-Miyaura arylation of benzyl sulfones by means of the rationally designed fluorinated sulfonyl leaving groups (Figure 1b),¹² where the departing sulfinate anions would be stabilized to facilitate the C–SO₂ bond cleavage. Along this line, we envisioned that trifluoromethylsulfonyl (CF₃SO₂–) group can be a suitable leaving group for Suzuki-Miyaura arylation of aryl sulfones. Here, we report Suzuki-Miyaura arylation of aryl trifluoromethyl sulfones with arylboronates (Figure 1c). Cooperative palladium/rhodium catalysis was particularly effective for efficient conversion. Mechanistic investigations suggest that

the rhodium catalyst mediates the transfer of the aryl ring from arylboronates to the palladium catalyst resulting in acceleration of the transmetalation on the palladium center. During preparation of the manuscript, Moran also reported Suzuki-Miyaura arylation of aryl trifluoromethyl sulfones under palladium–RuPhos catalysis (Figure 1d).¹³

(a) Applicable aromatic organosulfur compounds

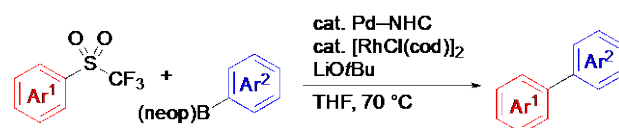


(b) Arylation of benzyl sulfones using fluorinated sulfonyl groups



(c) This Work

Arylation of aryl trifluoromethyl sulfones by means of Pd/Rh catalysis



(d) Moran's recent work

Pd-catalyzed arylation with arylboronic acids

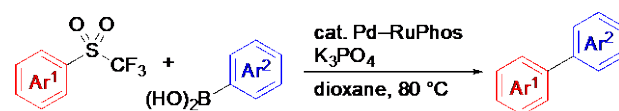


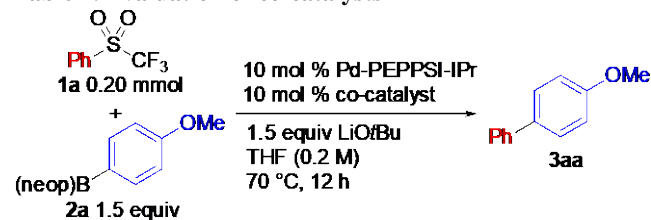
Figure 1. Suzuki-Miyaura arylation of organosulfur compounds.

We chose the reaction of phenyl trifluoromethyl sulfone (**1a**) with 4-methoxyphenylboronic acid neopentylglycol ester (**2a**) as a model reaction. Because Pd–NHC (*N*-heterocyclic carbene) complexes showed good catalytic activity in our previous C–S

transformations,^{6d} we performed the reaction with 10 mol % of Pd-PEPPSI-IPr (See Figure 2 for the structures of ligands and metal complexes) in the presence of LiOtBu as a base. While desired biaryl **3aa** was formed, the yield was only 27%, and 56% of sulfone **1a** was recovered (Table 1, entry 1).

To facilitate the reaction, we next attempted the addition of a metal co-catalyst to the reaction system because previous Suzuki-Miyaura arylations of azaaryl sulfides require the addition of CuTC⁹ (See Table S1 for details of the evaluation of co-catalysts). The thiophilic copper salt would interact with the thiolate anion on the palladium catalyst resulting in acceleration of the transmetalation process. Although the use of CuTC and copper-phosphine complexes lowered the yield of **3aa**, 10 mol % of CuCl(IPr) increased the yield to 40% (Table 1, entries 2–4). Gratifyingly, in place of copper, rhodium complexes showed good catalytic activities; employment of [RhCl(cod)]₂ and [Rh(OH)(cod)]₂ gave **3aa** in 75% and 74% yields, respectively (entries 5 and 6). On the other hand, [RhCl(nbd)]₂ (nbd = norbornadiene) was less effective for the reaction, and no **3aa** was obtained with RhH(PPh₃)₄ (entries 7 and 8).

Table 1. Evaluation of co-catalysts



entry	co-catalyst	GC yield (%)
1	none	27
2	CuTC	13
3	CuCl(IPr)	40
4	CuCl(dppe)	4
5 ^a	[RhCl(cod)] ₂	75
6 ^a	[Rh(OH)(cod)] ₂	74
7 ^a	[RhCl(nbd)] ₂	32
8	RhH(PPh ₃) ₄	0

^a5 mol % of co-catalyst was used.

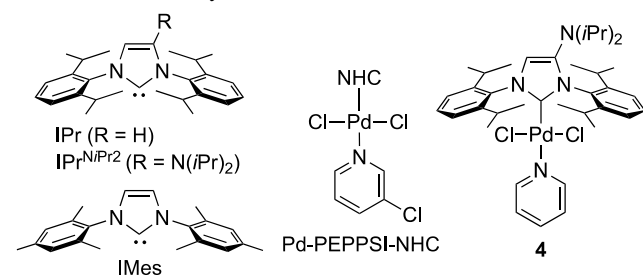
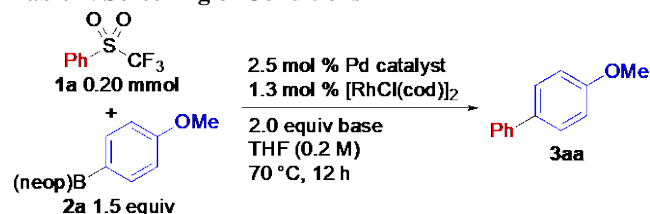


Figure 2. Structures of ligands and catalysts.

With [RhCl(cod)]₂ as the optimal co-catalyst, we continued the optimization study with lower catalyst loadings: 2.5 mol % of a palladium catalyst and 1.3 mol % of [RhCl(cod)]₂ (Table 2, See Table S2 for details of the screening of palladium catalysts). When Pd-PEPPSI-IPr was employed, **3aa** was obtained in 40% yield, although Pd-PEPPSI-IMes entirely shut down the reaction (entries 1 and 2). To our delight, diisopropylamino-substituted IPr (IPr^{N(iPr)₂})¹⁴ was found to be highly effective; the yield of **3aa** was considerably improved to 85% by means of IPr^{N(iPr)₂}-ligated palladium complex **4** (entry 3). The choice of the counter cation of bases has great impact on the yield of the product,

and the yields of **3aa** significantly dropped with NaOtBu and KOtBu (entries 4 and 5). Unfortunately, milder bases such as LiOAc, and Li₂CO₃ were not suitable for this reaction whereas CsF afforded **3aa** in a moderate yield (entries 6–8). Eventually, **3aa** was obtained in 91% isolated yield under more concentrated conditions (0.5 M) (entry 9). Naturally, the absence of palladium catalyst **4** did not give the product at all (entry 10). The use of the rhodium co-catalyst again proved to be important for high yield of the product; **3aa** was obtained in 52% yield in the absence of [RhCl(cod)]₂ (entry 11). We also tested other arylboron reagents instead of **2a**. Although 4-MeOC₆H₄B(OH)₂ could also be used for the reaction, the use of the corresponding pinacol ester, 4-MeOC₆H₄B(pin), resulted in a much lower yield of **3aa** (entries 12 and 13).¹⁵

Table 2. Screening of Conditions

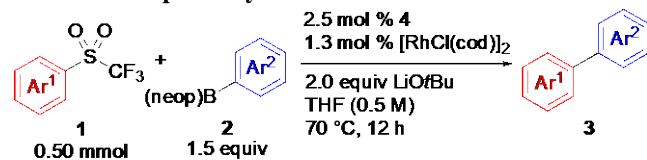


entry	Pd catalyst	base	GC yield (%)
1	Pd-PEPPSI-IPr	LiOtBu	40
2	Pd-PEPPSI-IMes	LiOtBu	0
3	4	LiOtBu	85
4	4	NaOtBu	28
5	4	KOtBu	8
6	4	LiOAc	0
7	4	Li ₂ CO ₃	0
8	4	CsF	65
9 ^a	4	LiOtBu	91 ^b , 92 ^{b,c}
10 ^a	none	LiOtBu	0
11 ^{a,d}	4	LiOtBu	52
12 ^{a,e}	4	LiOtBu	78
13 ^{a,f}	4	LiOtBu	25

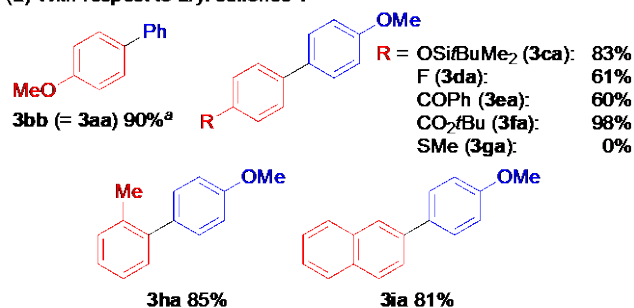
^aConcentration: 0.5 M. ^bIsolated yield. ^c2.0 mmol scale. ^dWithout [RhCl(cod)]₂. ^e4-MeOC₆H₄B(OH)₂ instead of **2a**. ^f4-MeOC₆H₄B(pin) instead of **2a**.

Having the optimized conditions in hand (Table 2, entry 9), the reaction scope with respect to aryl trifluoromethyl sulfones **1** was investigated (Scheme 1a). Electron-rich 4-methoxyphenyl sulfone **1b** underwent the arylation while higher catalyst loadings (5.0 mol % of **4** and 2.5 mol % of [RhCl(cod)]₂) were necessary for a high yield of the product. Several functional groups including siloxy, fluoro, benzoyl, and *tert*-butyl ester were compatible with the present arylation to yield biaryls **3ca–fa**. Unfortunately, methylsulfanyl-substituted phenyl sulfone **1g** did not undergo the reaction resulting in quantitative recovery of **1g**. Deactivated palladium thiolate species might be formed via the C–SMe cleavage resulting in no turnover of the palladium catalyst. The methyl group at the *ortho*-position of **1h** did not hamper the reaction to afford **3ha** in 85% yield. 2-Naphthyl sulfone **1i** uneventfully took part in the arylation to provide **3ia**.

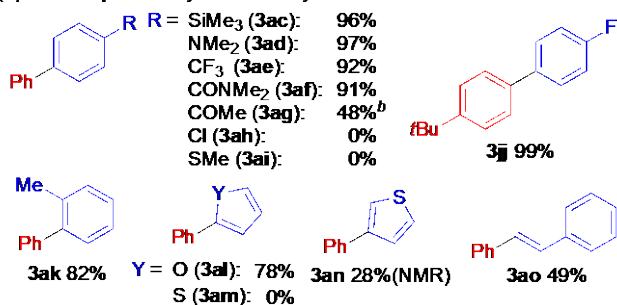
Scheme 1. Scope of arylation



(a) With respect to aryl sulfones **1**



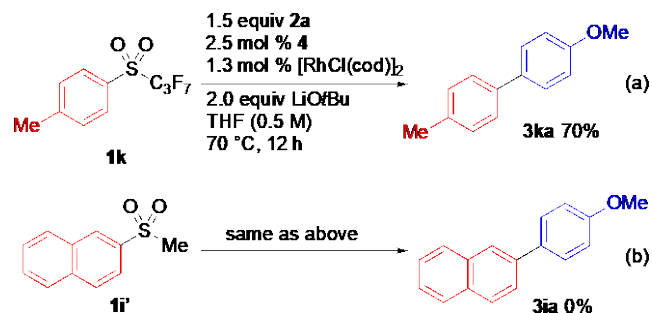
(b) With respect to aryl- and alkenylboronates **2**



^a5.0 mol % of **4**, 2.5 mol % of $[\text{RhCl}(\text{cod})]_2$, 24 h. ^b $\text{LiOH} \cdot \text{H}_2\text{O}$ instead of LiOtBu .

The reaction scope with respect to arylboronates **2** was then explored (Scheme 1b). Both electron-rich and -poor arylboronates underwent the present arylation to afford the desired biaryls in high yields. The trimethylsilyl group on **2c** was also tolerated; desired product **3ac** was obtained in 96% yield. Employment of arylboronate **2g** having an acetyl moiety resulted in the formation of a 31% yield of **3ag** under the standard conditions. Degradation of the acetyl group by strongly basic LiOtBu was thought to be problematic. The use of $\text{LiOH} \cdot \text{H}_2\text{O}$ as a milder base improved the yield of **3ag** to 48%. 4-Chlorophenylboronate **2h** did not participate in the reaction; **2h** would be consumed by polymerization via the C–Cl bond cleavage. The methylsulfanyl group on arylboronate **2i** was detrimental to the reaction, and both of aryl sulfone **1a** and arylboronate **2i** were recovered after the reaction. Deactivation of the palladium catalyst via the C–SMe cleavage would be problematic (*vide supra*). The reaction with *ortho*-substituted arylboronate **2k** proceeded efficiently to give 2-methyl-1,1'-biphenyl (**3ak**) in 82% yield. The use of 2-furylboronate **2l** did not retard the reaction and 2-phenylfuran (**3al**) was obtained in 78% yield, whereas 2- or 3-thienylboronate **2m** or **2n** failed to be applied to the arylation. Not only arylboronates, *trans*-2-phenylvinylboronate **2o** also undergo the reaction to furnish *trans*-stilbene (**3ao**) in a moderate yield.

Scheme 2. Reactions of aryl sulfones bearing sulfonyl groups other than trifluoromethylsulfonyl group.



Instead of trifluoromethyl sulfones, heptafluoropropyl sulfone **1k** could be employed for the arylation, and desired product **3ka** was obtained in 70% yield (Scheme 2a). Perfluorinated sulfonyl groups proved to be essential for the reaction; no biaryl **3ia** was obtained from methyl 2-naphthyl sulfone (**1i'**) resulting in quantitative recovery of **1i'** (Scheme 2b).

As shown in Table 1, the addition of $[\text{RhCl}(\text{cod})]_2$ as the co-catalyst dramatically promotes the present arylation. To learn about the effect of the rhodium catalyst, we assessed the kinetic profile of the arylation in the presence (**4**: 2.5 mol %, $[\text{RhCl}(\text{cod})]_2$: 1.3 mol %) or the absence (**4**: 5.0 mol %) of the rhodium catalyst. As shown in Figure 3, initial reaction rate (r_0) of the co-catalyzed system (red) was much higher than that of the reaction without $[\text{RhCl}(\text{cod})]_2$ (blue). These results demonstrate the acceleration effect of the rhodium catalyst. Moreover, significantly longer induction period (until 50 min) was observed in the absence of $[\text{RhCl}(\text{cod})]_2$, which implies that the rhodium catalyst would facilitate generation of active Pd(0) species from precatalyst **4**.

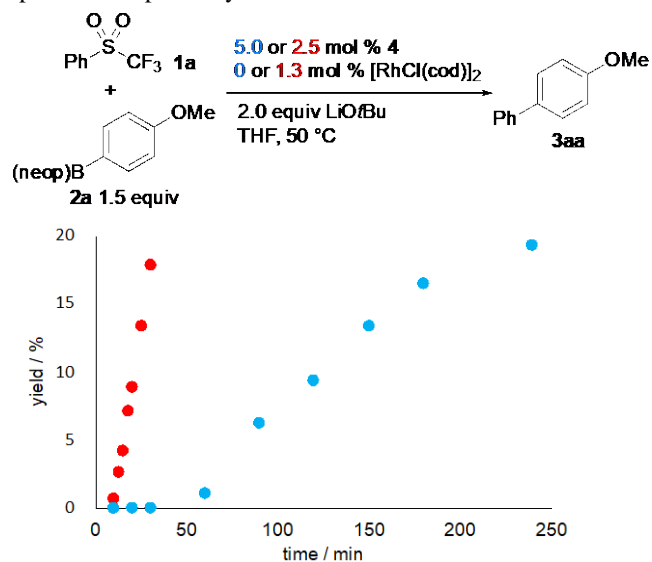
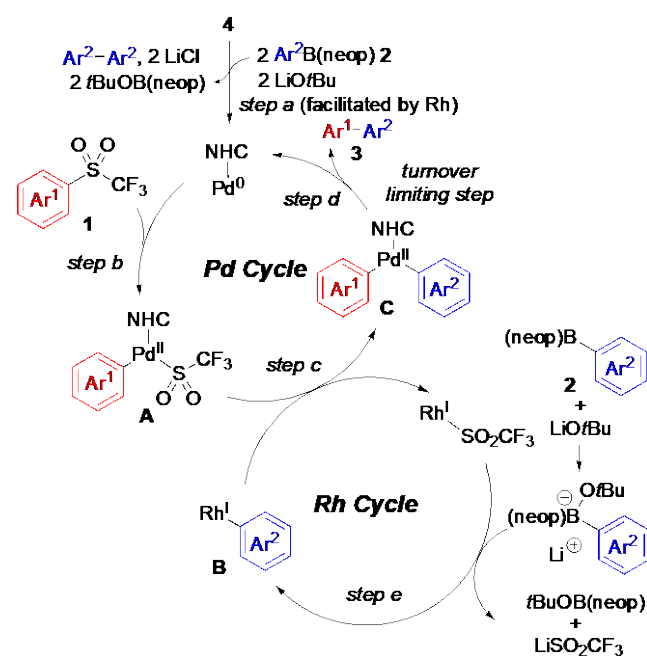


Figure 3. Time profiles of the yields of **3aa** with (red) or without (blue) $[\text{RhCl}(\text{cod})]_2$ (with Rh: 2.5 mol % of **4** and 1.3 mol % of $[\text{RhCl}(\text{cod})]_2$; without Rh: 5.0 mol % of **4**).

Rhodium complexes readily react with arylboronates to generate arylrhodium species.¹⁶ We thus hypothesized that $[\text{RhCl}(\text{cod})]_2$ would mediate transfer of the aryl ring from arylboronate to the palladium catalyst to accelerate the transmetalation step on the palladium center.

Scheme 3. Possible catalytic cycle of Pd/Rh-co-catalyzed cross-coupling.



A possible mechanism based on this hypothesis is depicted in Scheme 3. First, palladium precatalyst **4** would be reduced to Pd(0) via two-fold transmetalation with **2** and subsequent reductive elimination (*step a*) because a much shorter induction period was observed in the presence of [RhCl(cod)]₂ (Figure 3, red). We assume that the rhodium catalyst would accelerate the transmetalation step resulting in rapid generation of the Pd(0) species. Aryl trifluoromethyl sulfone **1** undergoes oxidative addition with the Pd(0) species to afford arylpalladium(II) **A** (*step b*). Intermediate **A** would go through transmetalation with arylrhodium **B** generated from Rh(I) species and arylboronate **2** with the aid of LiOtBu to provide diarylpalladium **C** (*step c*). Finally, reductive elimination from **C** furnishes coupling product **3** with regeneration of NHC–Pd(0) (*step d*).

To gain further insight into the transmetalation step, we then measured r_0 while changing the initial concentrations of **2a** and LiOtBu (See Figures S3–S5 for details).¹⁷ In the presence of [RhCl(cod)]₂, under the concentrations studied, r_0 of the reaction was estimated to almost zero-order in the initial concentration of **2a** ([**2a**]₀) (Figure 4, red).^{18,19} The transmetalation step between arylpalladium **A** and arylrhodium **B** (Scheme 3, *step c*) would not be a turnover-limiting step. Conversely, in the absence of the rhodium catalyst, the plotting of r_0 against [**2a**]₀ showed a positive dependence under the concentrations studied (Figure 4, blue). The reaction would be approximately 1.6th-order in [**2a**]₀, which intimates that the transmetalation between palladium and arylboronate would be the turnover-limiting step in the absence of [RhCl(cod)]₂. These indicate the intermediacy of the rhodium catalyst for rapid transfer of the aryl ring from arylboronate to the palladium catalyst.

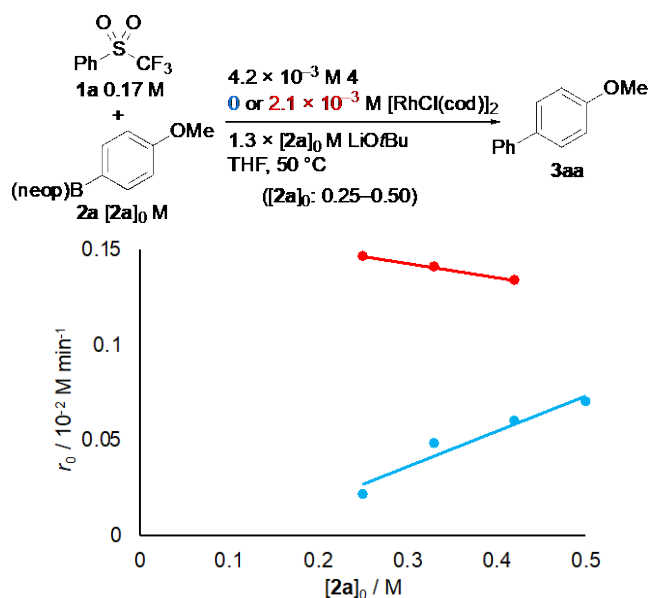


Figure 4. Plots of initial reaction rate (r_0) against [**2a**]₀ with (red) or without (blue) [RhCl(cod)]₂.

We also measured r_0 against the initial concentrations of **1a** ([**1a**]₀) and [RhCl(cod)]₂ ([**Rh**]₀), respectively (See Figures S1, S2, S8, and S9 for details). Under the concentrations studied, it turned out that r_0 was almost zero-order in [**1a**]₀ and [**Rh**]₀, respectively. These results imply that neither of the steps, oxidative addition of **1** (Scheme 3, *step b*) nor generation of arylrhodium **B** (Scheme 3, *step e*) would be a turnover-limiting step.

On the other hand, the plotting of r_0 against the initial concentration of palladium precatalyst **4** ([**4**]₀) showed positive dependence and the reaction was estimated to nearly 1st-order in [**4**]₀ (See Figures S6 and S7 for details). These observations are consistent with the turnover-limiting step would be the reductive elimination step to afford biaryls **3** (Scheme 3, *step d*). César found that bulky IPr^{NiPr2} ligand facilitates the C–N bond-forming reductive elimination resulting in acceleration of the Buchwald–Hartwig amination with bulky tertiary amines.¹⁴ In a similar fashion, IPr^{NiPr2} ligand would accelerate the turnover limiting reductive elimination step, the Pd–IPr^{NiPr2} complex thus showed the highest catalytic activity in our arylation.

Based on their mechanistic and computational studies, Moran *et al.* suggested that oxidative addition of the C–S bond of an aryl trifluoromethyl sulfone to a Pd(0)–RuPhos complex would be the turnover-limiting step in their system.¹³ On the other hand, in our system, electron-rich IPr^{NiPr2} ligand would accelerate the C–S cleavage, thus the oxidative addition would not be a turnover-limiting step.

In conclusion, we have developed Suzuki–Miyaura arylation of aryl trifluoromethyl sulfones under cooperative palladium/rhodium catalysis. The arylation herein presented accommodates a series of aryl trifluoromethyl sulfones as well as arylboronates to give the corresponding biaryls in moderate to excellent yields. Kinetic measurements indicate (1) the rhodium catalyst mediates transfer of the aryl ring from arylboronate to palladium resulting in acceleration of the transmetalation on the palladium center; (2) C–C bond-forming reductive elimination step would be the turnover-limiting step that would be accelerated by IPr^{NiPr2} ligand.

ASSOCIATED CONTENT

Supporting Information

Experimental procedures, kinetic measurements, and spectral data. 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 interest.

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- (18) In the presence of the Rh catalyst, the aryl transfer from arylboronate to the Rh would be sufficiently fast. Therefore, under the concentration studied, it can be consistent that a considerable y intercept is observed.
- (19) In the present cross-coupling, homo-coupling of arylboronates **2** to the corresponding biaryls was observed as a side reaction. The homo-coupling was accelerated by increasing [2a]₀ because this process can be 2nd order in [2a]₀. The palladium and rhodium catalysts would be involved not only in the cross-coupling but also in the competing homo-coupling, which resulted in apparent deceleration of the cross-coupling by increasing [2a]₀. The slightly negative slope of the plot would be consistent with these considerations.