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C–H Activation

Rhodium or Ruthenium-Catalyzed Oxidative C–H/C–H Cross-Coupling: Direct Access to Extended π-Conjugated Systems**

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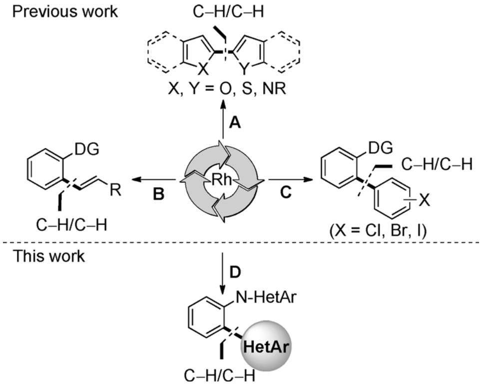
Extended π-conjugated structures containing bi-, ter-, tetra-, and poly(hetero)aryl motifs are found in many biologically active molecules, ligands, agrochemicals, pharmaceuticals, natural products, and especially, in optical and photochromic materials.[1] Conventional wisdom states that the construction of bi(hetero)arenes mostly relies on the transition-metal-catalyzed C–X/C–M cross-coupling of a (hetero)aryl halide or pseudohalide with a (hetero)aryl organometallic reagent. The further extension of π-conjugated systems from bi(hetero)aryls to ter-, tetra- and poly(hetero)aryls usually requires the installation of activating groups (such as, Cl, Br, I, OTs, SiR_3, BR_2, SnR_3, ZnR) onto the coupling partners. However, these preactivation methods can suffer from long multistep reaction sequences, poor regio- and/or chemoselectivity, and even poor availability. In particular, the resulting prefunctionalized coupling partners may also possess inadequately stability for participation in the subsequent coupling reactions. Moreover, heteroaryl halides generally undergo coupling reactions reluctantly.[2] Therefore, direct oxidative C–H/C–H cross-coupling between two (hetero)aryl scaffolds through a twofold C–H activation would be one of the most ideal approaches to expand π-conjugated systems.[3] Herein, we wish to explore a concise and general method to elongate π-conjugated systems through the formation of heteroaryl-aryl linkages.

Most of the successful twofold C–H oxidative cross-couplings between an arene and a heteroarene have been achieved through palladium-catalyzed methods. Nevertheless, the arene coupling parters usually suffer from regioselectivity problems and are used in considerable excess as a solvent or co-solvent. This is due to the generally low reactivity of their C–H bonds,[4] which limits their application scope to some extent, especially for high-melting-point substrates and those which are not readily available. In 2011, Miura and co-workers disclosed that the copper-mediated oxidative cross-coupling could proceed between a directing-group-containing arene and just 2 equiv of heteroarene in the presence of 5.0 equiv of $Cu(OAc)_2$ at 170 °C.[5] However, the heteroaryl coupling partners were limited to those with acidic C–H bonds (such as, benzoxazoles, 5-aryloxazoles, and caffeine). In recent years, rhodium complexes have been shown to be powerful catalysts for C–H bond functionalization, with the advantages of high catalytic efficiency, good functional group tolerance, and mild reaction conditions, all of which are complementary to palladium catalysis.[6] However, the rhodium-catalyzed oxidative C–H/C–H cross-coupling reaction is still in its infancy, and the selectivity and reactivity issues remain to be addressed. To date, only the cross-coupling reactions of furan, thiophene, and indole derivatives (Scheme 1, route A),[7] and directing-group-containing arenes with alkenes (route B)[8] or arenes (route C)[9] have been disclosed.



Scheme 1. Rh-catalyzed oxidative C–H/C–H cross-coupling. DG = directing group, HetAr = heteraryl.

As part of our continued efforts to extend π-conjugated systems,[10] we envisioned that a Rh-catalyzed oxidative C–H/C–H cross-coupling between an arene and a heteroarene would provide new access to poly(hetero)aryls (route D). In our attempts to acheive this type of transformation without using a large excess of either of the two partners, we expected to encounter some obstacles: 1) the low reactivity of arene C–H bonds, 2) the notorious tendency for homo-coupling of reaction partners (heteroarenes in particular),[11] and 3) troubles with regioselectivity. Herein, we disclose the discovery and development of the solution to these substantial challenges. Furthermore, the potential of the use of more economical ruthenium catalysts in the dehydrogenative cross-coupling between an arene and a heteroarene is displayed for the first time.

We initiated our investigation by examining the feasibility of the rhodium-catalyzed cross-coupling of 2-phenylpyridine

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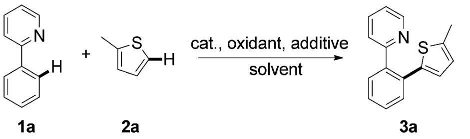
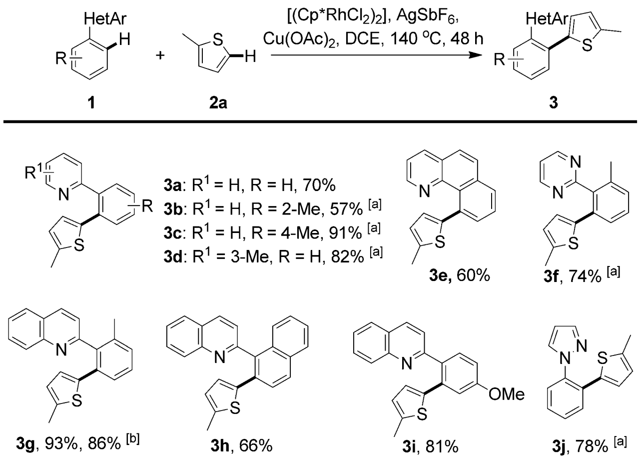
(**1a**) and 2-methylthiophene (**2a**) [Eq. (1); see also the Supporting Information, Table S1].[12,13] Gratifyingly, ter(hetero)arene **3a** was obtained in 61% yield when [(Cp*RhCl$_2$)$_2$] was used in combination with AgSbF$_6$ (20 mol%) and Cu(OAc)$_2$ (3.0 equiv) in dioxane at 140°C for 48 h. Further optimization of solvent improved the yield of **3a** to 70%. However, the addition of both acid and base to the reaction system diminished the reaction effectiveness. Other oxidants, such as Cu(OPiv)$_2$, Cu(TFA)$_2$, and CuCl$_2$ were significantly less effective, whereas Ag$_2$CO$_3$ gave a comparable result. In view of the high cost of silver salts, Cu(OAc)$_2$ was preferentially chosen as the oxidant. In the absence of AgSbF$_6$, the yield decreased to 54%. The reaction did not proceed without rhodium catalyst or Cu(OAc)$_2$ oxidant. Finally, the cross-coupling proceeded well with a catalytic system composed of [(Cp*RhCl$_2$)$_2$] (5 mol%), AgSbF$_6$ (20 mol%), and Cu(OAc)$_2$ (3.0 equiv) in 1,2-dichloroethane (DCE) at 140°C for 48 h.



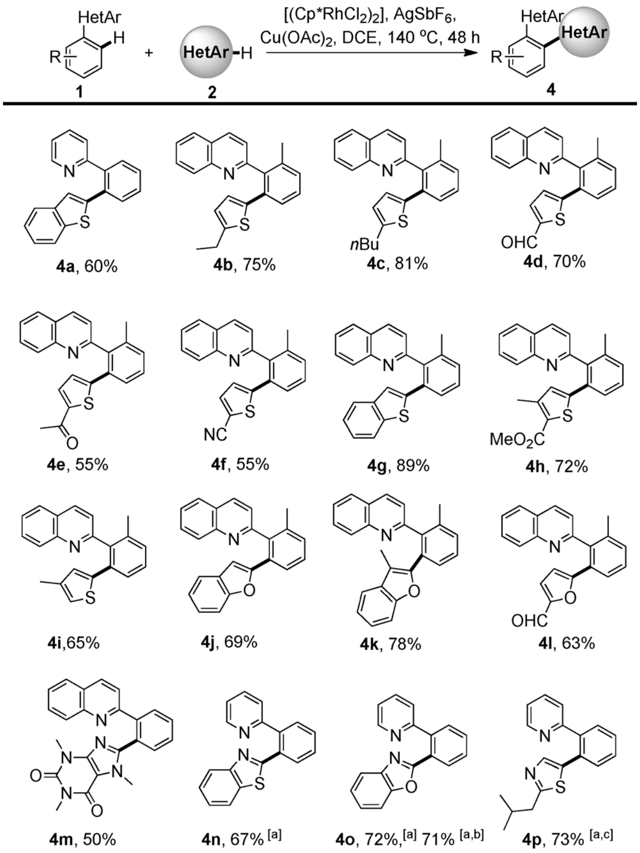
(1)

With the optimized conditions in hand, we next set out to explore the scope of the method with respect to the arene coupling partners. As summarized in Scheme 2, a range of biaryls containing N-heteroarenes such as pyridine, quinoline, pyrimidine, and pyrazole smoothly underwent oxidative cross-coupling with 2-methylthiophene (**2a**), delivering a series of π-conjugated poly(hetero)arenes in moderate to excellent yields. The positions of the substituents on the arenes had a negligible effect on the transformation. Whether the substituents were installed in the *para*- or *ortho*-position on the arenes, biaryls could be converted into the desired products. The reaction also performed well when the pyridine ring had a substituent at the 3 position (**3d**). Moreover, when the phenyl ring was replaced by a naphthyl group, the reaction also afforded the target molecule **3h** in 66% yield.

Subsequently, we applied our method to other heteroarenes to prepare an array of 1,2-diheteroaryl-substituted arenes (**4**; Scheme 3). Thiophenes with either electron-withdrawing groups or electron-donating groups successfully engaged in this reaction (**4b–f** and **4h–l**; Scheme 3). Functional groups, such as esters, aldehydes, acyls, and nitriles, which are useful in further synthetic transformations, were tolerated under the current conditions (**4d–f** and **4h**; Scheme 3). When 3-methylthiophene was employed as the substrate, the coupling reaction occurred at the less sterically hindered C5-position (**4l**; Scheme 3). Other electron-rich heterocycles such as benzofurans and furans could also be applied in the coupling reaction to produce products in satisfactory yields (**4j–l**; Scheme 3). Moreover, electron-rich five-membered heteroarenes, thiazoles, and oxazoles could undergo arylation at the acidic C–H bond in the C2 position (**4n–o**; Scheme 3). When the C2 position of the thiazole ring was blocked with an isobutyl group, heteroarylation selec-



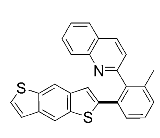
Scheme 2. Rh-catalyzed cross-coupling of N-heteroarene-containing arenes (**1**) with 2-methylthiophene (**2a**) by double C–H activation. Reaction conditions: biaryl (0.25 mmol), 2-methylthiophene (0.75 mmol), [(Cp*RhCl$_2$)$_2$] (5 mol%), AgSbF$_6$ (20 mol%), Cu(OAc)$_2$ (3.0 equiv) and DCE (2 mL) at 140°C for 48 h. [a] Ag$_2$CO$_3$ (3.0 equiv) instead of Cu(OAc)$_2$, pivalic acid (PivOH; 0.5 mmol), and DMF (2 mL) instead of DCE. [b] 1.0 mmol scale.



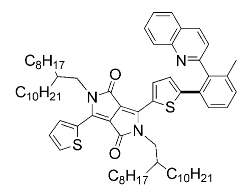
Scheme 3. Rh-catalyzed C–H/C–H cross-coupling of aryl-substituted quinolines or pyridines with various heteroarenes. Reaction conditions: biaryl (0.25 mmol), heteroarene (0.75 mmol), [(Cp*RhCl$_2$)$_2$] (5 mol%), AgSbF$_6$ (20 mol%), Cu(OAc)$_2$ (3.0 equiv) and DCE (2 mL) at 140°C for 48 h. [a] Ag$_2$CO$_3$ (3.0 equiv) instead of Cu(OAc)$_2$, PivOH (0.5 mmol), and DMF (2 mL) instead of DCE. [b] 1.0 mmol scale. [c] The diheteroarylated product **4q** was obtained in 23% yield.

tively occurred at the thiazole C5 position in 73 % yield (**4p**; Scheme 3,). Caffeine, a biologically important active alkaloid with an imidazole skeleton, reacted with 2-phenylquinoline to provide **4m** in a synthetically useful yield (Scheme 3).

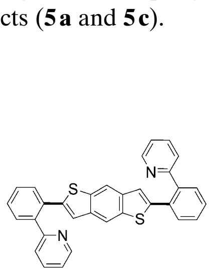
Benzodithiophene (**2q**, BDT) and 3,6-di(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (**2r**) are important structural units that frequently appear in organic functional materials such as OLEDs and solar cells.[14] These versatile dithiophenes smoothly coupled with bi(hetero)arene to elongate π-conjugated systems through the formation of heteroaryl–aryl linkages. As shown in Figure S1 in the Supporting Information, the coupled poly(hetero)aryl product **5b** exhibited bathochromic shifts in absorption and emission maxima with a strong red emission (λ_{ex}: 566–601 nm). It was found that **2q** could undergo cross-coupling to give both mono- and di-arylated products (**5a** and **5c**).



5a, 50%



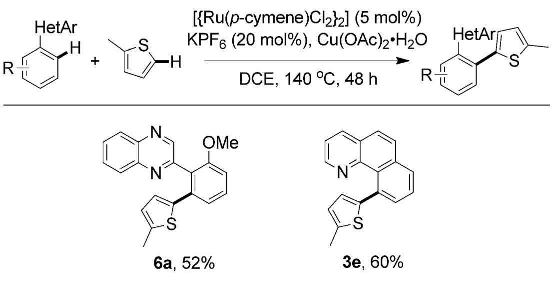
5b, 58%



5c, 75%

We finally turned our attention to exploring a more economical alternative to rhodium complexes. Ruthenium catalysts are usually inexpensive and have demonstrated some catalytic properties similar to those of rhodium catalysts.[15] We were pleased to find that a catalyst system composed of [Ru(*p*-cymene)Cl_2}$_2$] and KPF_6 was able to promote the oxidative cross-coupling of 2-methylthiophene with benzo[*h*]quinoline and 2-aryl quinoxaline in acceptable yields (Scheme 4). These preliminary results indicated the intrinsic potential of ruthenium to catalyze the oxidative cross-coupling between two (hetero)arenes, and the detailed results of these couplings will be reported in due course.

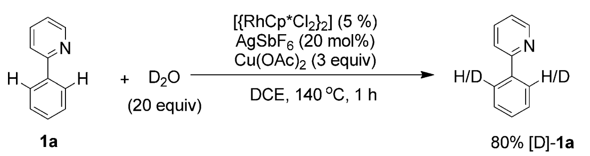
Compared to the previous examples, the Rh- or Ru-catalyzed C–H/C–H cross-coupling reactions developed herein exhibited the following advantages: 1) The homocoupling products of each coupling partner, which are frequently encountered in palladium catalysis, were not observed.[16] 2) The transformation was completely regioselective. 3) Only the mono-heteroarylated product of arenes was obtained, except in the case of **4q**. In particular, the ratio of the two partners could be decreased to 3:1, unlike with other dehydrogenative coupling reactions, which often require the use of arenes as solvent or co-solvent.[4,9a]



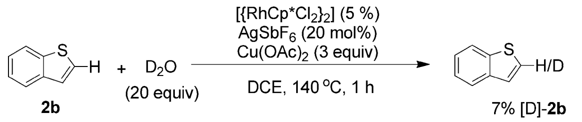
Scheme 4. Ru-catalyzed direct heteroarylation of N-heteroarene-substituted arenes by double C–H activation. Reaction conditions: biaryl (0.25 mmol), 2-methylthiophene (0.75 mmol), [{Ru(*p*-cymene)Cl_2}$_2$] (5 mol %), KPF_6 (20 mol %), $Cu(OAc)_2{\cdot}H_2O$ (2.0 equiv), and DCE (2 mL) at 140 °C for 48 h.

To get some mechanistic insight, H/D exchange experiments were carried out [Eqs. (2)–(4)]. When 2-phenylpyridine (**1a**) alone was treated with D_2O under the standard reaction conditions for 1 hour, 80 % of deuterated [D]-**1a** was obtained [Eq. (2)]. On the other hand, only 7 % H/D scrambling was observed with benzothiophene (**2b**) [Eq. (3)]. The exposure of **1a** and **2b** to D_2O gave a similar ratio of deuterated products under the same conditions [Eq. (4)], which suggested that a reaction starting from 2-phenylpyridine was reasonable. Importantly, the cyclometalated Rh^{III} complex **7** could catalyze the reaction of **1a** and benzoxazole (**2o**) to give **4o** in 73 % yield [Eq. (5); Cp* = 1,2,3,4,5-pentamethylcyclopentadienyl], which implied that complex **7** could be a plausible intermediate in the catalytic cycle.

To demonstrate the importance of acetate anion in the reaction system, a stoichiometric amount of the Rh^{III} complex Cp*ArRhCl **7** and 2-methylthiophene (**2a**) were heated at 140 °C in DCE in the presence of 1.0 equiv of $AgSbF_6$ for 48 h, but only a trace amount of the cross-coupled product **3a** was observed. Subsequently, NaOAc (3.0 equiv) was added to the reaction system, and **3a** was successfully obtained, albeit in a 38 % yield (Scheme 5). When $Cu(OAc)_2$ was replaced by $CuCl_2$ in the catalytic system, only a trace amount of **3a** was obtained (Supporting Information, Table S1). Upon adding an additional 3.0 equiv of NaOAc to the reaction system, **3a** was obtained in 35 % yield. These observations indicated that

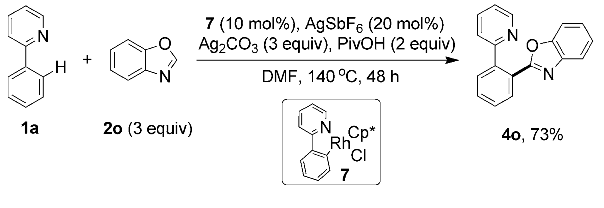


(2)

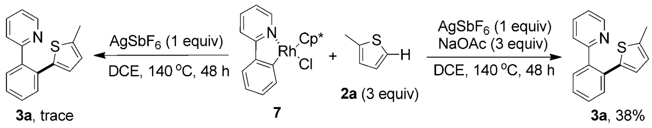


(3)

$$\underset{}{\mathbf{1a}} + \underset{(3\ \text{equiv})}{\mathbf{2b}} + \underset{(20\ \text{equiv})}{D_2O} \xrightarrow[\text{DCE, 140 °C, 1 h}]{[\{RhCp^*Cl_2\}_2]\ (5\ \%),\ AgSbF_6\ (20\ \text{mol\%}),\ Cu(OAc)_2\ (3\ \text{equiv})} \underset{73\%}{[D]\text{-}\mathbf{1a}} + \underset{7\%}{[D]\text{-}\mathbf{2b}} \qquad (4)$$



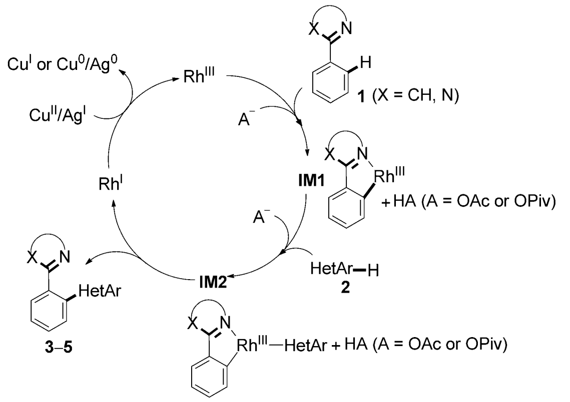
(5)



Scheme 5. Reactions of the Rh^{III} complex Cp*ArRhCl **7** and 2-methylthiophene **2a**.

the acetate anion played an important role in the catalytic cycle; it may serve as a hydrogen acceptor and/or a ligand for the Rh-catalyst.[17]

Although the detailed mechanism is not clear at this stage, a free-radical pathway can be ruled out, because of the negligible impact on the reaction when the radical scavenger 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO; 20 mol%) was added to the reaction system composed of **1a** and **2a** (Table S1). Thus, a tentative mechanism was proposed (Scheme 6). First, N-heteroarene-containing arene **1** reacts with Cp*Rh^{III} to generate intermediate **IM1** through chelation with the N-heteroaryl substituent of the biaryl and subsequent C–H bond activation of the arene. Next, **IM1** reacts with heteroarene **2** to form rhodacycle **IM2** through a regioselective electrophilic C–H substitution (SEAr; preferred for electron-rich substrates)[10b,11a] or a concerted metalation deprotonation (CMD; preferred for acidic C–H bond-containing substrates).[5,9a] Reductive elimination of **IM2** would then afford the desired product. Finally, the Rh^{III} is regenerated by the oxidation of Cu^{II} or Ag^{I} salts to fulfill the catalytic cycle.



Scheme 6. Tentative mechanism for the oxidative cross-coupling of N-heteroarene-containing arenes with heteroarenes.

In summary, we have presented a Rh or Ru-catalyzed oxidative cross-coupling between various N-heteroarene-containing arenes and heteroarenes by twofold C–H activation, which provides a direct means of expanding π-conjugated systems. The coupling reactions are highly chemo- and regioselective and are applicable to various heteroarenes (thiophenes, furans, oxazoles, thiazoles, and xanthines). Further studies to elucidate the mechanism and to find new applications for these reactions are currently underway.

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[11] For the inevitability of homo-coupling in the Pd or Rh-catalyzed oxidative C–H/C–H cross-coupling of two heteroarenes, see Refs. [7] and [10b,c,e].

[12] The palladium catalytic systems reported in our previous work could not give desired product **3a**; see Refs. [10b,c,e].

[13] Applying the reaction conditions reported by Miura et al. failed to afford the coupled product **3a**. See Ref. [5].

[14] a) K. Müllen, U. Scherf, *Organic light emitting devices: Synthesis properties and applications*; Wiley-VCH, Weinheim, **2006**; b) Y.-J. Cheng, S.-H. Yang, C.-S. Hsu, *Chem. Rev.* **2009**, *109*, 5868 – 5923; c) P. M. Beaujuge, J. M. J. Fréchet, *J. Am. Chem. Soc.* **2011**, *133*, 20009 – 20029.

[15] For a recent review, see: P. B. Arockiam, C. Bruneau, P. H. Dixneuf, *Chem. Rev.* **2012**, 10.1021/cr300153j, and references therein.

[16] 2-*o*-Tolylquinoline and benzothiophene gave homocoupled products in trace and less than 5% yield, respectively (determined by ^{1}H NMR spectroscopy), in the absence of another partner under the reaction conditions. For details, see the Supporting Information.

[17] L. Ackermann, *Chem. Rev.* **2011**, *111*, 1315 – 1345.