Double C–H Activation

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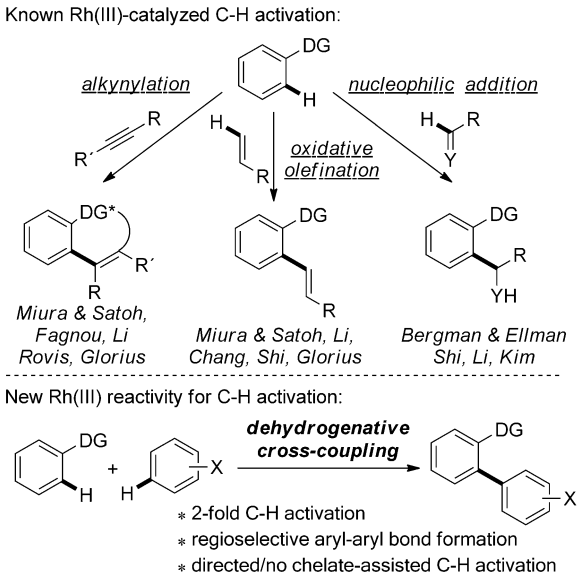
[$Rh^{III}Cp^*$]-Catalyzed Dehydrogenative Aryl–Aryl Bond Formation**

*Joanna Wencel-Delord, Corinna Nimphius, Frederic W. Patureau, and Frank Glorius**

The omnipresence of biaryl scaffolds in natural products, medicinal agents, and organic materials places their construction amongst the key transformations of organic chemistry. Indeed, cross-coupling reactions leading to this C–C bond formation have seen tremendous development over the past decades. However, in the context of green and sustainable chemistry, construction of these biaryl moieties by using C–H bonds as latent functional groups through twofold direct C–H bond functionalization has emerged as an attractive alternative.[1] Indeed, catalyzed cross-dehydrogenative couplings (CDC) obviate the need for prefunctionalized coupling partners (minimizing reaction steps and waste) and are only accompanied by the formal formation of hydrogen as the sole byproduct. However, multiple obstacles such as unfavorable thermodynamics, the generally low reactivity of C–H bonds, and selectivity issues (functionalization of one C–H bond in the presence of others, competition between heterocoupling and homocoupling) make this synthetic pathway particularly challenging. Over the last few years important efforts have been made to overcome these difficulties, and several Pd-catalyzed dehydrogenative biaryl formations have been reported.[2] Very recently, a seminal contribution in this field was made by Yu et al.[2k] By using $Pd(OAc)_2$ as a catalyst in combination with a "F^+" oxidant, they succeeded in a *para*-selective CDC, consisting of C–H bond activation of benzamides followed by an electrophilic aromatic palladation of simple arenes.

However, alternative methods and mechanisms are required, since an electrophilic aromatic metalation step limits the substrate scope (electron-rich substrates preferred) and selectivity pattern (*ortho*/*para*-directing groups). Besides the development of Pd-catalyzed C–H bond-functionalization reactions, cationic Rh^{III} catalysts have recently been shown to be particularly suitable for the activation of this latent bond,[3] mostly resulting in oxidative Heck reactions,[4] alkynylations,[5] and nucleophilic addition type transformations.[6] Many new synthetic disconnections for the synthesis of many highly valuable compounds (such as derivatives of indenoles[5j] and indoles,[5g] fulvenes,[5j] pyrroles,[5i,g] isoquinolines,[5e] acenes,[5d] and anthrylazoles[5a]) could be established. However, to the best of our knowledge, no Rh^{III}-catalyzed dehydrogenative Ar–Ar bond formation proceeding through C–H bond activation has been developed.[7] Inspired by our very recent observation that $[RhCp^*(SbF_6)_2]$ (Cp^* = pentamethylcyclopentadienyl) is capable of performing undirected C–H activation of bromoarenes,[8] we focused our effort on the use of this reactivity for biaryl formation. Herein, we report the first example of Rh-catalyzed Ar–Ar cross-coupling by means of double C–H activation (Scheme 1).

We commenced our study using tertiary benzamide **1a** and bromobenzene as coupling partners, $[(RhCp^*Cl_2)_2]$ combined with $AgSbF_6$ as the catalyst, $Cu(OAc)_2$, and PivOH. We noticed with delight that the desired product **3a** was formed and could be isolated in 23% yield as a 2.6:1 mixture of *meta*/*para* regioisomers (Scheme 2). Interestingly, no coupling at the *ortho* position of bromobenzene was observed. The efficiency of this reaction was, however, compromised by a significant amount of homocoupling of **1a**.[9] Intriguingly, the employment of a catalytic amount of CsOPiv (20 mol%) together with 1.1 equiv of PivOH pre-



Scheme 1.

[*] Dr. J. Wencel-Delord, C. Nimphius, Prof. Dr. F. Glorius
Universität Münster, Organisch-Chemisches Institut
Corrensstrasse 40, 48149 Münster (Germany)
E-mail: glorius@uni-muenster.de
Homepage: http://www.uni-muenster.de/Chemie.oc/glorius/index.html
Prof. Dr. F. W. Patureau
Fachbereich Chemie – Organische Chemie, Technische Universität Kaiserslautern, Erwin-Schrödinger-Strasse, Geb. 52, 67663 Kaiserslautern (Germany)

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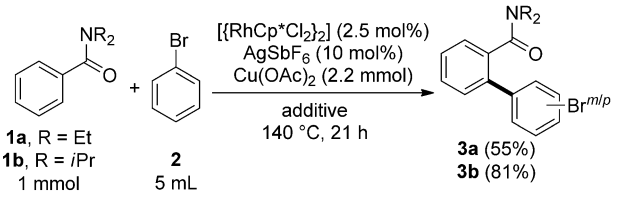
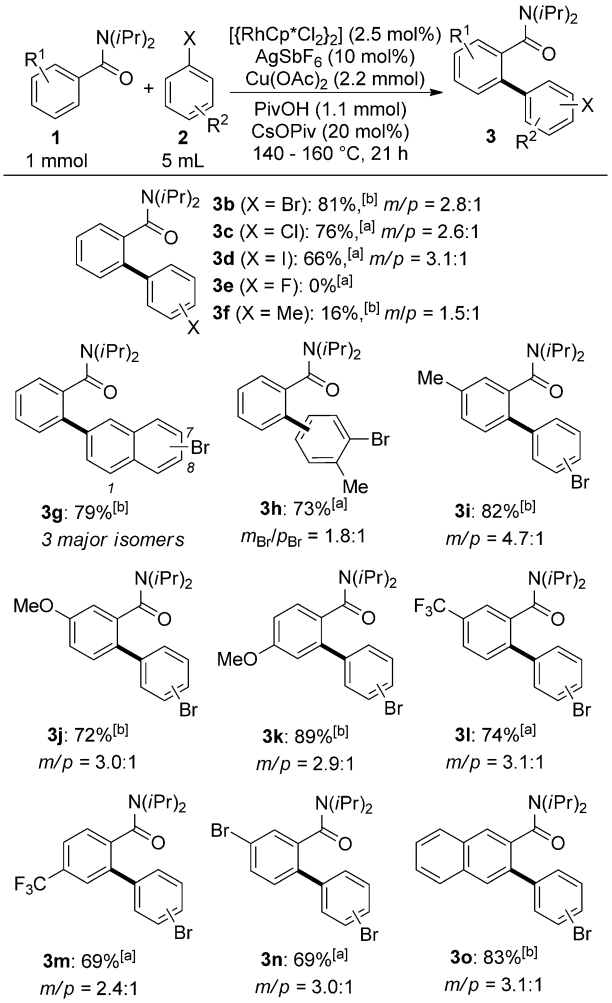


Scheme 2. Initial study of the CDC of benzamides and PhBr.

vented the undesired homocoupling and thus improved the yield of **3a** to 55%. Replacement of PivOH by a stoichiometric amount of either CsOPiv or CsOAc shut down the reactivity. Further improvement was achieved by a slight modification of the directing group. When benzamide **1b** bearing a N*i*Pr$_2$ group was used, the cross-coupling product **3b** could be isolated as a *meta*/*para* mixture (2.8:1) in 81% yield. Control reactions showed that omission of either the Rh precatalyst or Cu(OAc)$_2$ led to total inactivity of this catalytic system. Similarly, the use of a catalytic amount of Cu(OAc)$_2$ (25 mol%) or increased concentration (0.4 M and 1.0 M) resulted in a severe decrease of the efficiency of the coupling (**3b** isolated in 22, 69 and 49% yield, respectively).

Under these optimized conditions, the scope of arenes bearing no chelating group site was examined (Scheme 3, **3b**–**h**). Both chloro- and iodobenzene provided the cross-coupled products **3c** and **3d** in good yields (76 and 66%, respectively), albeit an increased reaction temperature (160 °C) was required to reach full conversion. Intriguingly, utilization of fluorobenzene as the coupling partner shut down the reactivity and coupling of toluene with **1b** afforded **3f** in drastically decreased yield (16%).[10] When 1-bromonaphthalene and 1,2-bromotoluene were engaged in the reaction, the expected products **3g** and **3h** were formed efficiently as mixtures of three and two regioisomers, respectively. Furthermore, an array of synthetically useful benzamides were reacted with bromobenzene (Scheme 3, **3i**–**o**). A number of functional groups at either the *meta* or *para* position of the aryl ring were compatible with our catalytic system.[11] Benzamides bearing electron-donating groups such as Me or OMe in *meta* position were arylated smoothly to give the desired products **3i** and **3j**, isolated in 82 and 72% yield, respectively. Introduction of the OMe group in *para* position of the benzamide had a beneficial effect on the efficiency of the reaction giving corresponding **3k** with an improved yield (89%). In contrast, benzamides containing electron-withdrawing substituents reacted more sluggishly and an increase of the reaction temperature to 160 °C was required for completion of these CDCs. Importantly, brominated benzamide could also be efficiently used as coupling partner to give the dibrominated biphenyl product **3n** in 69% of yield. When naphthalene 2-carboxamide was used, C–H activation occurred at only one position leading to **3o** in good yield.

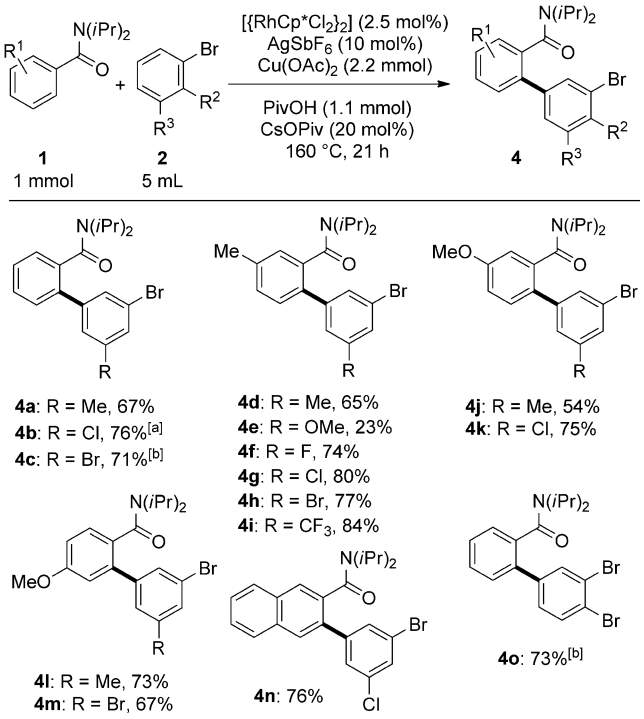
Encouraged by these results showing that steric hindrance disfavors cross-coupling in the *ortho* position of bromobenzene, we turned our attention to 3-substituted bromobenzenes (Scheme 4). Gratifyingly, coupling of the standard benzamide **1b** with 1-bromo-3-methylbenzene gave the cross-coupling product **4a** as a single regioisomer (67% yield at



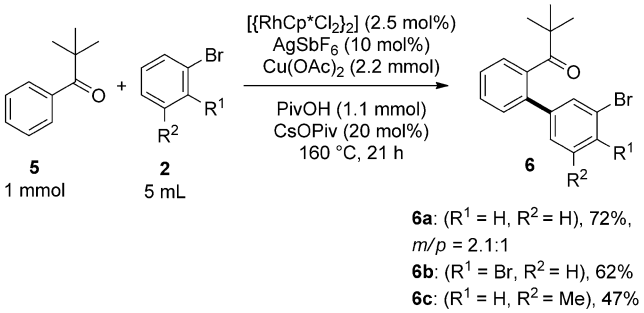
Scheme 3. CDC of benzamides with monosubstituted arenes. General reaction conditions: **1** (1.0 mmol, 1.0 equiv), PhBr (5 mL), [(RhCp*Cl$_2$)$_2$] (2.5 mol%), AgSbF$_6$ (10 mol%), Cu(OAc)$_2$ (2.2 mmol, 2.2 equiv), PivOH (1.1 mmol, 1.1 equiv), CsOPiv (0.2 mmol, 20 mol%), 140–160 °C, 21 h. [a] At 160 °C. [b] At 140 °C.

160 °C). Subsequently, numerous different 1,3-disubstituted arenes turned out to be efficient coupling partners. Intriguingly, while 1-bromo-3-methylbenzene gave good to moderate yields, slight improvement of the efficiency of these CDCs was observed when electron-deficient bromoarenes were used. Thus coupling of a *meta*-substituted electron-rich benzamide with electron-poor 1-bromo-3-trifluoromethylbenzene led to the formation of biphenyl **4i** in 84% yield. 1-Bromo-3-methoxybenzene showed drastically lower reactivity (**4e** isolated in 23% yield). In addition, regioselective cross-coupling was also successful using 1,2-dibromobenzene.

To additionally establish the power of this methodology, a ketone directing group was also evaluated (Scheme 5). The initial attempt to couple 2,2-dimethyl-1-phenylpropan-1-one (**5**) and bromobenzene under standard reaction conditions gave the desired product **6a**, but the reaction was significantly more sluggish. Higher reaction temperatures led to full conversion and **6a** could be isolated in 72% yield as a 2.1:1 mixture of *meta*/*para* regioisomers. As expected, when 1,2-



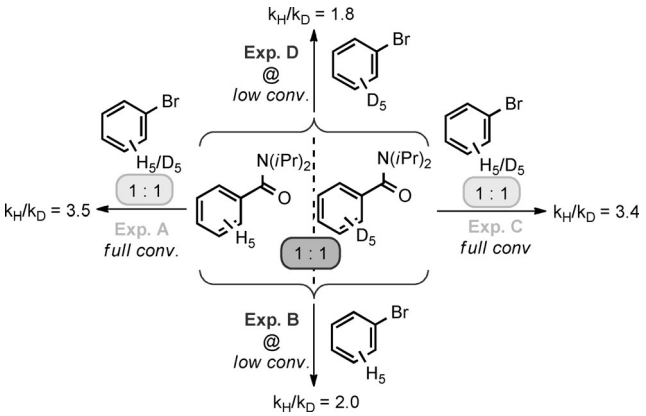
Scheme 4. Highly regioselective CDC of benzamides using 1,3-haloarenes. For general reaction conditions, see Scheme 2. [a] On a 3 mmol scale. [b] At 140 °C.



Scheme 5. CDC of ketone **5**.

dibromobenzene was employed as a coupling partner, the corresponding biphenyl ketone **6b** was isolated in moderate yield as a single regioisomer. A slight decrease of the yield (47 %) was observed in the case of 1-bromo-3-methylbenzene.

For obtaining mechanistic insight, and determining the values of the kinetic isotope effects (KIEs) for both benzamide and bromobenzene, a series of cross-coupling reactions involving deuterated coupling partners were performed (Scheme 6). An intermolecular competition experiment between bromobenzene and [D_5]bromobenzene, with substrate **1b** as the reaction partner, showed a significant KIE of 3.5 (experiment A). Likewise, when the deuterated benzamide [D_5]-**1b** was submitted to the same reaction conditions, a similar KIE of 3.4 was measured (experiment C).[12] Furthermore, KIEs of 1.8–2.0 on the benzamide were determined by comparison of the initial reaction rate of the

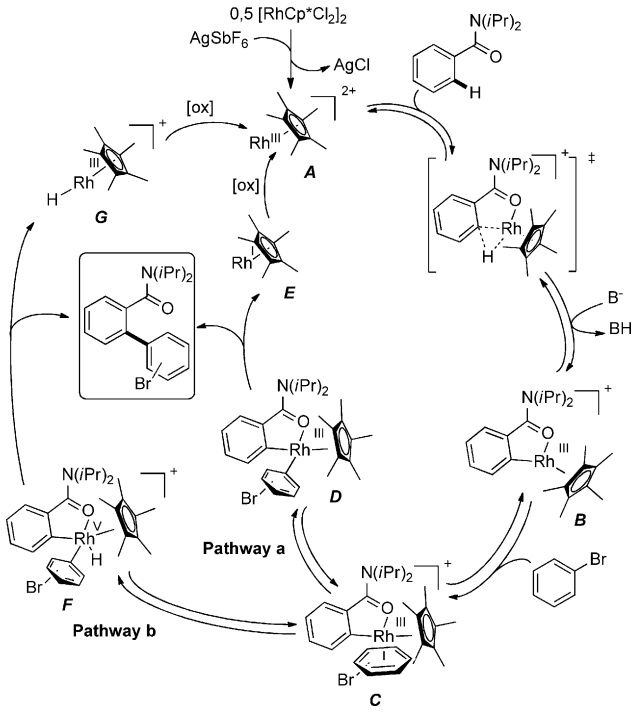


Scheme 6. Study of the kinetic isotope effect.

coupling between a 1:1 mixture of **1b** and [D_5]-**1b** and either bromobenzene (experiment B) or [D_5]bromobenzene (experiment D).[13]

These results clearly suggest that true C–H bond activation occurs on both coupling partners.[14] The important KIEs observed for experiments A and C, combined with data from previous reports on CDCs indicate that the C–H bond cleavage of the simple arene is of substantial importance for the total rate of this cross-coupling. Additionally to these KIEs studies, a noticeable H/D scrambling on both reaction partners was observed. Likewise, H/D exchange was observed when **3b** was submitted to the reaction conditions in the presence of pentadeuterated bromobenzene (solvent). These observations clearly indicate the reversible nature of both C–H activation events.

On the basis of the data above and precedent literature, a plausible catalytic cycle is proposed in Scheme 7. It is postulated that, in the presence of $AgSbF_6$, a Rh precatalyst generates a highly electrophilic Rh species **A**, which coordinates to the carbonyl group of the benzamide. A chelate-assisted reversible C–H activation occurs at the *ortho* position and could proceed by means of a base-assisted concerted metalation/deprotonation (CMD) pathway.[15] The five-membered rhodacycle **B** has a free coordination site and could therefore coordinate bromobenzene in a η^2 manner. At this stage of the catalytic cycle, two distinct pathways are plausible. In the first case, pathway a, the η^2-coordinated bromobenzene would undergo C–H activation (probably by σ-bond metathesis or CMD mechanism) affording the neutral rhodium complex **D**. After sequential reductive elimination of the cross-coupling product and reoxidation of the Rh^I intermediate **E**, the regenerated Rh^{III} catalyst **A** could reenter the catalytic cycle. In contrast, pathway b starts with a C–H activation of bromobenzene affording the rhodium(V) hydride complex **F**. This high oxidation state of rhodium would enhance the reductive elimination of the biphenyl adduct,[16] and a subsequent hydride abstraction/oxidation would provide the regenerated catalyst **A**. The experimental observations of important H/D scrambling on both coupling partners and the biaryl product could be explained either by the existence of Rh–H intermediates (which support pathway b) or by the protonolysis of intermediate **D**. The

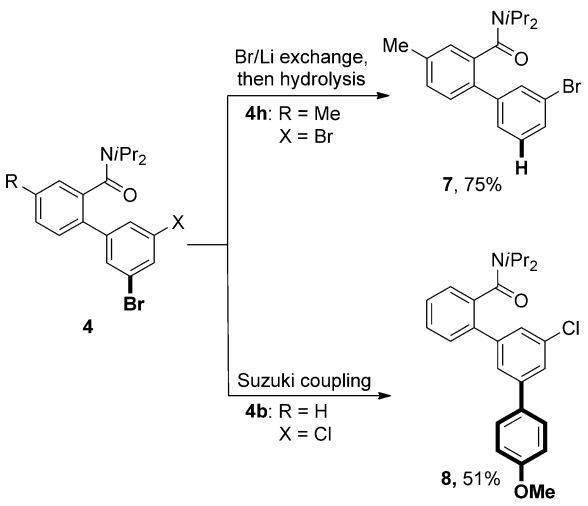


Scheme 7. Postulated catalytic cycle. (Not all ligands on Rh are depicted.)

existence of a rhodium(V) hydride species bearing a Cp* ligand has already been evoked;[17,18] however, no direct proof of its existence in this case could be obtained so far. Consequently, it is difficult to draw a conclusion concerning the mechanism of this transformation. Moreover, the role of $Cu(OAc)_2$ and the particular effectiveness of bromoarenes as coupling partners (which could potentially act as an oxidant[7,8] and/or a catalyst modifier[8]) remain unclear.

Finally, in order to highlight the synthetic value of this new strategy, we investigated possible transformations of the generated biaryl products (Scheme 8). Gratifyingly, product **4h** underwent smooth bromine/lithium exchange, and subsequent quenching of the reaction with water led to the formation of the one *meta*-Br substituted biaryl product **7**. An additional advantage of this transformation is the fact that many different electrophiles can be introduced. We were pleased to see that under unoptimized conditions the Suzuki coupling of **4b** with 4-methoxyphenylboronic acid gave the desired product **8** in 51% yield. This new triphenyl moiety still bears a chloro substituent, allowing for further functionalization.

In conclusion, a novel RhCp*-catalyzed aryl–aryl bond formation has been disclosed, a selective dehydrogenative cross-coupling between arenes bearing a directing group and halogen-substituted (I, Br, Cl) benzene derivatives. The scope of this transformation is broad with regard to both coupling partners and the employment of 1,3-disubstituted bromoarenes leads to the regioselective formation of valuable *meta*-substituted biphenyl products with moderate to good yields. Finally, mechanistic studies indicate that this catalytic system, in contrast to other Pd-catalyzed CDCs, proceeds by "real" C–H activations on each coupling partner. This discovery



Scheme 8. Potential synthetic applications of halogen-substituted biaryls. For reaction conditions, see the Supporting Information.

opens opportunities for the development of new Rh^{III}-catalyzed C–H bond activations, leading to more efficient and milder transformations .[19]

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[9] High-resolution ESI mass spectrometric analysis of the crude reaction mixture shows also the presence of dehalogenated biaryl product. During the whole project, the formation of trace amounts of these dehalogenated products was observed.

[10] Application of benzene as a coupling partner led to the formation of only trace amounts of the desired coupling product (reaction run at 140 °C).

[11] Introduction of a methyl substituent at the *ortho* position of the benzamide led to inhibition of the reaction and the desired product was not obtained.

[12] A comparable KIE for the undirected Pd-catalyzed C–H activation of simple arenes was previously observed by Dong et al.[2i]

[13] a) Recently, Bergman and Ellman have reported a KIE of 2 for the Rh^{III}-catalyzed C–H bond activation of acetanilides.[6b] b) Likewise, for the alkynylation of an acetanilide a KIE of 4.2 was measured for the C–H activation step; see: D. R. Stuart, P. Alsabeh, M. Kuhn, K. Fagnou, *J. Am. Chem. Soc.* **2010**, *132*, 18326 – 18339. Chang et al. measured a KIE of 2.3 for the C–H bond activation of arenes bearing an ester as a directing group.[4e]

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