



Rhodium-catalyzed cross-coupling of aryl carbamates with arylboron reagents



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ABSTRACT

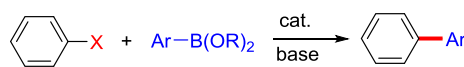
A new method has been developed for the rhodium-catalyzed cross-coupling of aryl carbamates with organoboron reagents. The use of an NHC ligand bearing a 2-adamantyl group, i.e., I(2-Ad), is essential to the success of the reaction. The reaction involves the rhodium-mediated activation of the relatively inert C(aryl)–O bond of aryl carbamates.

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1. Introduction

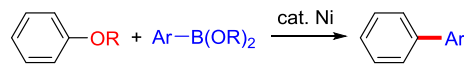
Cross-coupling reactions between organic halides and organometallic reagents are recognized as one of the most powerful methods for the formation of carbon–carbon bonds, especially C(aryl)–C(aryl) bonds.¹ Among them, the Suzuki–Miyaura reaction represents one of the most useful processes, largely because of the functional group compatibility and stability of organoboron nucleophiles.² Although this reaction has seen significant advancement since it was first discovered in 1979,^{2a,b} the scope of the electrophilic coupling partner still remains rather limited to organic halides and sulfonates (Scheme 1a). In 2004, the use of anisoles containing an ortho directing group in the cross-coupling reaction with organoboron nucleophiles was reported to proceed with a ruthenium catalyst.³ In this reaction, an inert C(aryl)–OMe bond is activated through a chelation-assisted oxidative addition. The scope of the electrophile used in Suzuki–Miyaura type reactions was significantly expanded by the use of nickel catalysts,⁴ which allowed for the cross-coupling of simple unactivated phenol derivatives such as aryl ethers,⁵ esters,⁶ carbamates,⁷ carbonates,⁸ and naphtholate⁹ (Scheme 1b). The success of these reactions indicated that low valent nickel species possess exceptionally high levels of

(a) The Suzuki–Miyaura reaction



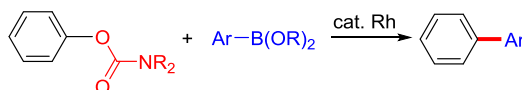
X = I, Br, Cl, OTf, OTs, etc

(b) Nickel-catalyzed variants using inert phenol derivatives



OR = OMe, OCOR, OCONR₂, OH etc

(c) This work



Scheme 1. Aryl electrophiles for use in the Suzuki–Miyaura reaction.

reactivity towards C(aryl)–O bonds that could not otherwise be activated under conventional palladium-catalyzed conditions.¹⁰ From a fundamental perspective, it would be intriguing to know whether transition metals other than nickel could be used to promote the Suzuki–Miyaura reaction of such unactivated phenol derivatives. It has also been reported that the C(aryl)–O bonds of aryl esters and pivalates can be activated by iron¹¹ and cobalt¹² catalysts, although these reactions require the addition of more than

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a stoichiometric amount of Grignard reagents.^{13,14} Furthermore, these catalysts cannot be used to affect cross-coupling reactions with organoboron reagents. Our group recently found that the rhodium-catalyzed reaction of aryl pivalates with a diboron reagent resulted in the formation of borylated products.¹⁵ The use of a diboron reagent in this reaction was found to be essential to promote the cleavage of the C(aryl)-O bond of aryl pivalates under these rhodium-catalyzed conditions (i.e., [RhCl(cod)]₂/P(4-MeOC₆H₄)₃), and the catalyst system was therefore only applicable to carbon–boron bond-forming reactions. Based on these results, it was envisaged that the Suzuki–Miyaura reaction of inert phenol derivatives could be realized by identifying an appropriate rhodium catalyst system. Ozerov et al.¹⁶ reported that a rhodium complex bearing a PNP-pincer ligand could be used to mediate the oxidative addition of phenyl pivalate and carbamate, and this observation also encouraged us to investigate the development of a new rhodium-catalyzed reaction. Pleasingly, our investigative efforts in this area culminated in the development of a rhodium-catalyzed cross-coupling of aryl carbamates with arylboronic esters, which we report herein (Scheme 1c).

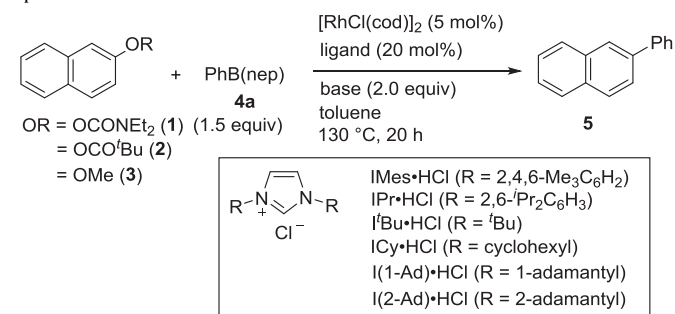
2. Results and discussion

At the outset of our studies, we decided to investigate the reaction of 2-naphthyl carbamates **1** with boronic ester **4a** (nep=neopentylglycolate) in the presence of [RhCl(cod)]₂ as a catalyst and NaOEt as a base (Table 1). However, virtually none of the desired cross-coupling product **5** was formed in the absence of a ligand (Entry 1) and in the presence of phosphine ligands, such as PPh₃ (Entry 2) and PCy₃ (Entry 3). Based on our experience of nickel-catalyzed C(aryl)-O bond activation processes^{5b,17} as well as related reports from others¹⁸ it was assumed that a stronger σ -

donor would provide a better ligand candidate, and we therefore preceded to examine a series of NHC ligands. As expected, the use of IMes as a ligand led to the formation of **5** in 25% yield (Entry 4). Although the use of an NHC ligand bearing bulkier aryl groups (i.e., IPr) inhibited the arylation (Entry 5), the use of a ^tBu-substituted NHC ligand (I^tBu) led to a significant increase in the yield of **5**—77% (Entry 6). Furthermore, the use of an NHC ligand bearing adamantyl groups led to even higher catalytic activity, with the 2-adamantyl derivative I(2-Ad) (Entry 9) performing much more effectively than the 1-adamantyl isomer I(1-Ad) (Entry 8). In terms of the base, NaOEt could be replaced with CsF, although this led to a slight decrease in the yield of **5** from 98 to 74% (Entry 10). The boronic acid PhB(OH)₂ could also be used as an arylating reagent under these conditions, without any discernible decrease in the efficiency of the reaction (Entry 11), whereas the use of the bulkier PhB(pin) resulted in a much lower yield of **5** (Entry 12). The cross-coupling of aryl pivalate **2** with **4a** did not occur under these conditions, but resulted instead in the exclusive formation of a hydrolyzed naphthol product (Entry 13). The use of the corresponding *tert*-butyl carbonate also led to the formation of 2-naphthol (see ESI for details). Aryl methyl ether **3** was found to be completely unreactive under the current conditions (Entry 14).

Having identified I(2-Ad) as the optimal ligand for the reaction (Table 1, Entry 9), we preceded to examine the scope of aryl carbamates. Although 2-naphthyl carbamate **1** underwent the cross-coupling with **4a** to form **5** in excellent yield, use of less reactive substrates led to a significant reduction in the yield. For example, phenyl carbamate **6** underwent the cross-coupling with **4a** to afford **8** in only 38% yield, with the hydrolyzed compound **9** being formed as the major product in 56% yield (Scheme 2). This undesired hydrolysis could be suppressed completely by increasing the steric bulk of the carbamate moiety, as exemplified by the use of an OCONⁱPr₂ group, which delivered **8** in 86% yield. Based on these results, the bulky diisopropyl carbamate group (-OCONⁱPr₂) was selected as the best group for further exploration. It is noteworthy that this carbamate moiety can be readily introduced at a phenolic hydroxyl group by the reaction of the appropriate phenol with ClCONⁱPr₂, which is commercially available (See Experimental Section for details).

Table 1
Optimization studies^a



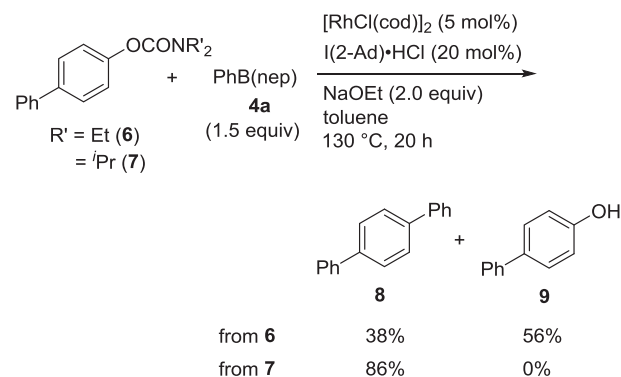
Entry	Substrate	Ligand	Base	Yield/% ^b
1	1	None	NaOEt	8
2	1	PPh ₃	NaOEt	0
3	1	PCy ₃	NaOEt	0
4	1	IMes·HCl	NaOEt	25
5	1	IPr·HCl	NaOEt	3
6	1	I ^t Bu·HCl	NaOEt	77
7	1	ICy·HCl	NaOEt	5
8	1	I(1-Ad)·HCl	NaOEt	54
9	1	I(2-Ad)·HCl	NaOEt	94
10	1	I(2-Ad)·HCl	CsF	74
11 ^c	1	I(2-Ad)·HCl	NaOEt	73
12 ^d	1	I(2-Ad)·HCl	NaOEt	16
13	2	I(2-Ad)·HCl	NaOEt	3
14	3	I(2-Ad)·HCl	NaOEt	0

^a Reaction conditions: substrate (0.30 mmol), **4a** (0.45 mmol), [RhCl(cod)]₂ (0.015 mmol), ligand (0.060 mmol), and base (0.60 mmol) in toluene (1.0 mL) at 130 °C for 20 h in a sealed tube.

^b GC yield of **5** based on the substrate.

^c *p*-TolylB(OH)₂ was used instead of **4a**.

^d *p*-TolylB(pin) was used instead of **4a**.



Scheme 2. Effect of the substituent of the carbamoyl group.

The scope of the rhodium/I(2-Ad)-catalyzed cross-coupling of aryl carbamates with boronic ester **4a** is shown in Table 2. Phenyl carbamate **12** (Entry 2) proved to be significantly less reactive than the naphthyl substrate **10** (Entry 1), as is often observed in nickel-catalyzed C(aryl)-O bond activation reactions.¹⁹ Interestingly, the introduction of a phenyl group to the substrate led to a significant improvement in the yield of the product, as evidenced by biphenyl carbamates **14** (Entry 3) and **16** (Entry 4), which reacted successfully under the optimized conditions to give **15** and **17** in 86 and 82% yields, respectively. Several biaryl derivatives bearing CF₃ and

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