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## Cp\*Rh(III)-catalyzed electrophilic amination of arylboronic acids with azo compounds for synthesis of arylhydrazides†

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A [Cp\*Rh(III)]-catalyzed electrophilic amination of arylboronic acids with diethyl azodicarboxylate (DEAD) was developed, and arylhydrazides were produced in excellent yields and selectivity. The analogous amination with the arylazocarboxylates afforded the corresponding *N,N*-diarylhazides. The electrophilic amination of arylboronic acids with azocarboxylates proceeds readily under mild conditions with excellent functional group tolerance. Up to 99% yields were obtained. Preliminary mechanistic studies revealed that prior formation of an arylrhodium(III) intermediate for the azo coupling reaction can be ruled out.

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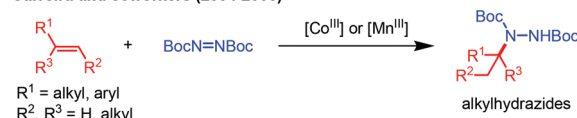
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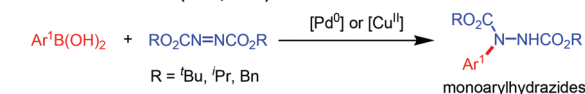
Transition metal-catalyzed electrophilic (umpolung) aminations are attractive approaches for arylamine synthesis under mild conditions.<sup>1</sup> Characterized by weak N–X (X = leaving group)  $\sigma$ -bonds, haloamines and hydroxyamine derivatives have been extensively investigated for electrophilic amination with organolithium and -magnesium reagents.<sup>2</sup> Dialkyl azodicarboxylates are conceptually different classes of electrophilic amination reagents. Unlike the halo/hydroxyamine-type reagents, the azodicarboxylates react with carbanionic nucleophiles *via* N–N  $\pi$ -bond cleavage. While dialkyl azodicarboxylates are known to react with stoichiometric organometallic reagents for C–N bond coupling reactions,<sup>3</sup> examples involving transition metal catalysis are sparse in the literature (Scheme 1). About a decade ago, Carreira and coworkers reported a Co- and Mn-catalyzed alkene hydrohydrazination using di-*tert*-butyl azodicarboxylate and triphenylsilane as reagents.<sup>3e–g</sup> Recently, Chatani and coworkers reported a Cu-catalyzed hydroarylation of azodicarboxylates.<sup>3h</sup> Muniz and coworkers reported a Pd-catalyzed coupling of arylboronic acids with diethyl azodicarboxylate (DEAD). A palladiaziridine complex was structurally characterized and was shown to mediate the C–N bond coupling reaction.<sup>3i,j</sup>

Owing to an interest in developing transition metal catalyzed C–H bond aminations under mild conditions,<sup>4</sup> we previously accomplished regioselective Pd-/Rh-catalyzed *ortho*-selective arene C–H amination with tosyloxycarbamates and *N*-chloroamines.<sup>4k–o</sup> The catalytic arene C–H amination should

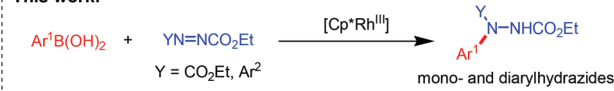
Carreira and coworkers (2004–2006)



Chatani and coworkers (2005)  
Muniz and coworkers (2006, 2007)



This work:



Scheme 1 Recent examples of transition metal-catalyzed electrophilic amination with azo reagents.

proceed by coupling of reactive arylpalladium(II) and -rhodium(III) complexes with the amination reagents. By virtue of the weak N–N  $\pi$ -bond, we envisioned that dialkyl azodicarboxylates would be effective coupling partners with aryl-metal complexes for C–N bond formation. Here we describe [Cp\*Rh(III)]-catalyzed (Cp\* = 1,2,3,4,5-pentamethyl-cyclopentadienyl) cross coupling of arylboronic acids with azo compounds for the synthesis of arylhydrazides.

When phenylboronic acid (**1a**; 0.3 mmol) was treated with DEAD (0.2 mmol) and [Cp\*Rh(OAc)<sub>2</sub>] (5 mol%) in THF at 80 °C under an N<sub>2</sub> atmosphere for 4 h, phenylhydrazide (**2a**) was obtained in 85% yield (Table 1, entry 1). In this work, we found that employing phenylboronic acid pinacol ester and potassium phenyltrifluoroborate alone did not bring about effective C–N coupling reactions (entries 2 and 3). The boron reagents were fully recovered with substantial decomposition

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Table 1 Reaction optimization<sup>a</sup>

Entry	Aryl boron reagent	Catalyst	Solvent	T (°C)	Yield <sup>b</sup> (%)
1	PhB(OH) <sub>2</sub> ( <b>1a</b> )	[Cp*Rh(OAc) <sub>2</sub> ]	THF	80	85
2	PhB(pin)	[Cp*Rh(OAc) <sub>2</sub> ]	THF	80	n.d. <sup>c</sup>
3	KPhBF <sub>3</sub>	[Cp*Rh(OAc) <sub>2</sub> ]	THF	80	n.d. <sup>c</sup>
4 <sup>d</sup>	KPhBF <sub>3</sub>	[Cp*Rh(OAc) <sub>2</sub> ]	THF	80	70
5	<b>1a</b>	[Cp*RhCl <sub>2</sub> ] <sub>2</sub>	THF	80	10
6	<b>1a</b>	[Rh(COD)Cl] <sub>2</sub>	THF	80	11
7	<b>1a</b>	[Rh(COD)(OH)] <sub>2</sub>	THF	80	n.d. <sup>c</sup>
8	<b>1a</b>	[Cp*IrCl <sub>2</sub> ] <sub>2</sub>	THF	80	n.d. <sup>c</sup>
9	<b>1a</b>	[Cp*Rh(OAc) <sub>2</sub> ]	<sup>t</sup> BuOH	80	64
10	<b>1a</b>	[Cp*Rh(OAc) <sub>2</sub> ]	MeCN	80	3
11	<b>1a</b>	[Cp*Rh(OAc) <sub>2</sub> ]	Dioxane	80	50
12	<b>1a</b>	[Cp*Rh(OAc) <sub>2</sub> ]	DCE	80	31
13 <sup>e</sup>	<b>1a</b>	[Cp*Rh(OAc) <sub>2</sub> ]	DMF	40	99
14 <sup>f</sup>	<b>1a</b>	[Cp*Rh(OAc) <sub>2</sub> ]	THF	80	42

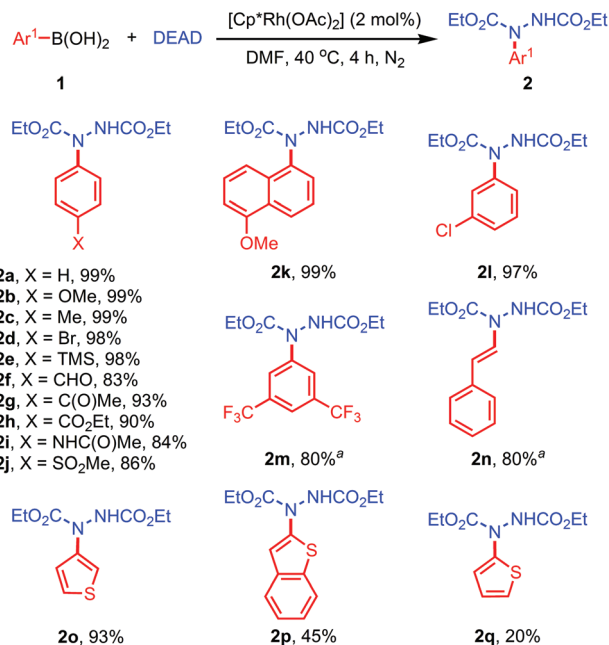
<sup>a</sup> Conditions: aryl boron reagent (0.3 mmol), DEAD (0.2 mmol), catalyst (5 mol%), solvent (1 mL), 4 h in an N<sub>2</sub> atmosphere. <sup>b</sup> Isolated yield. <sup>c</sup> n.d. = not detected. <sup>d</sup> B(OH)<sub>3</sub> (0.3 mmol) was added. <sup>e</sup> [Cp\*Rh(OAc)<sub>2</sub>] (2 mol%) was used. <sup>f</sup> Di-*tert*-butyl azodicarboxylate (0.2 mmol) was used instead.

of the DEAD. Interestingly, when potassium phenyltrifluoroborate was employed together with B(OH)<sub>3</sub> as additives and DMF as the solvent, **2a** was formed in 70% yield (entry 4).

Other rhodium catalysts such as [Cp\*RhCl<sub>2</sub>]<sub>2</sub> are less effective catalysts (entry 5). According to the literature, rhodium(i) diene complexes such as [Rh(COD)X]<sub>2</sub> (X = Cl, OH) are known to catalyze arylation of enones with arylboron reagents.<sup>5</sup> However, these Rh(i)-diene complexes were found to be ineffective catalysts for the reaction of **1a** with DEAD (entries 6 and 7). In this work, the related [Cp\*IrCl<sub>2</sub>]<sub>2</sub> complex exhibited negligible catalytic activities under our reaction conditions (entry 8).

Other solvents such as <sup>t</sup>BuOH, MeCN, dioxane and DCE gave inferior results compared to THF (entries 9–12). After several trials, we found that DMF gave the best result with **2a** being formed in a nearly quantitative yield.<sup>6</sup> Upon further refinement of several experimental parameters, an optimized reaction protocol was established: [Cp\*Rh(OAc)<sub>2</sub>] (2 mol%), **1a** (0.3 mmol), DEAD (0.2 mmol) in DMF at 40 °C (entry 13). It is noteworthy that the azo coupling reaction is sensitive to the ester substituents on the azocarboxylates. For instance, the amination of **1a** with di-*tert*-butyl azodicarboxylate produced the corresponding arylhydrazides in only 42% yield (entry 14). The coupling with azobenzene was unsuccessful, and no C–N coupled products were obtained.<sup>6</sup>

With DEAD as the model substrate, the scope of the arylboronic acids was examined (Scheme 2). The reactions of arylboronic acids containing electron-donating and -withdrawing groups (e.g. OMe, Me and Br) afforded the corresponding hydrazides (**2a–2d**) in excellent yields. Other functionalized arylboro-



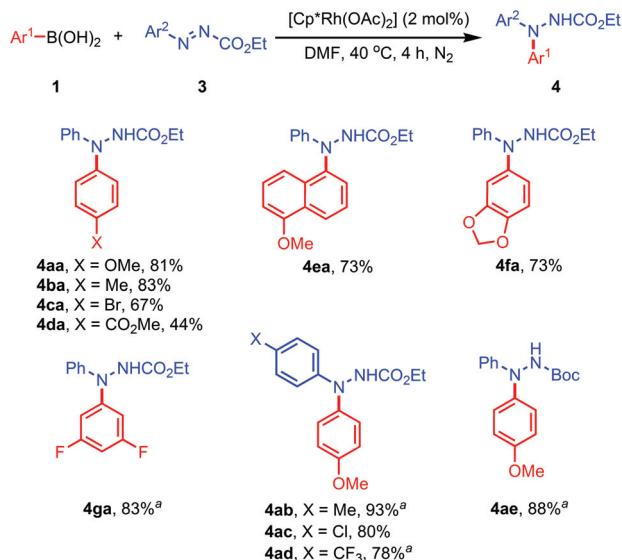
Scheme 2 Scope of the arylation of DEAD. Yields of isolated products are given. General reaction conditions: **1** (0.3 mmol), DEAD (0.2 mmol), [Cp\*Rh(OAc)<sub>2</sub>] (2 mol%), DMF (1 mL), 40 °C for 4 h in an N<sub>2</sub> atmosphere. <sup>a</sup>The reaction was performed at 80 °C.

nic acids bearing TMS, CHO, C(OMe), CO<sub>2</sub>Et, NHC(O)Me and SO<sub>2</sub>Me were converted to **2e–2j** in 83–98% yields. Fruitful results were achieved for the analogous amidation of 6-methoxy-1-naphthyl, 3-chloro and 3,5-bis(trifluoromethyl) phenylboronic acids with **2k–2m** being formed in excellent yields. Likewise, effective transformations of styrylboronic acid and heteroaromatic boronic acids were also achieved to give the corresponding products (**2n–2q**) in good to moderate yields.

Diarylamines are prevalent scaffolds found in many natural products, pharmaceuticals and functional materials.<sup>7</sup> The Pd- and Cu-catalyzed arylation of anilines with haloarenes are widely employed for diarylamine synthesis.<sup>8</sup> Yet, examples of diarylamine synthesis *via* electrophilic amination are sparse.<sup>9</sup> Lei and coworkers reported the synthesis of diarylamines by Cu-catalyzed arylation of *N*-chloroanilides with arylboronic acids.<sup>9e</sup> Recently, Chang and coworkers reported a reaction of aryl azides with aryliridium(III) complexes for diarylamine synthesis.<sup>9f–h</sup> In this work, we developed the catalytic arylation of arylazocarboxylates for the synthesis of *N,N*-diaryldihydrazides.

The arylazocarboxylate was prepared by reacting arylhydrazine with ethyl chloroformate, followed by NBS oxidation. When phenylazocarboxylate (**3a**) was treated with 4-methoxyphenylboronic acid (**1b**) and [Cp\*Rh(OAc)<sub>2</sub>] (2 mol%) in DMF at 40 °C under an N<sub>2</sub> atmosphere, *N,N*-diaryldihydrazides (**4aa**) was isolated as a single regioisomer in 81% yield (Scheme 3). The molecular structure of **4aa** has been established by single-crystal X-ray crystallography. Arylboronic acids containing elec-



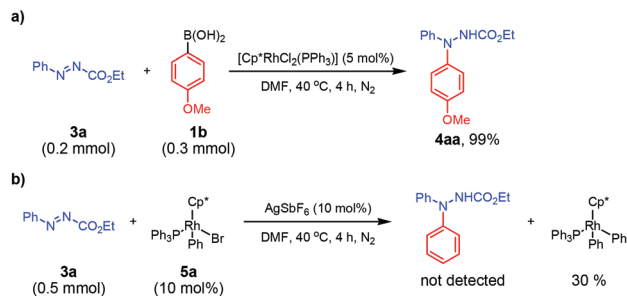
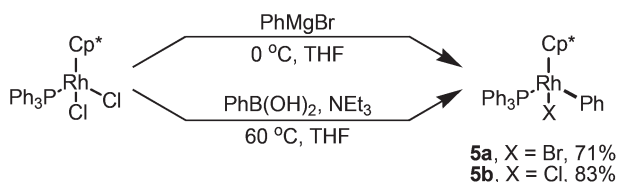


tron-donating and -withdrawing substituents were well tolerated (see results for **4ba–4da**). Similarly, amidation of 6-methoxy-1-naphthyl, 3,4-(methylenedioxy) and 3,5-difluorophenylboronic acids furnished **4ea–4ga** in excellent yields.

With 4-methoxyphenylboronic acid as the arylating reagent, the reactions of some substituted arylazocarboxylates were examined. Effective C–N coupling was observed in all cases, and the diarylhydrazides (**4ab–4ae**) were formed in 78–93% yields.

Arylrhodium(III) complexes are known to mediate catalytic C–N bond coupling reactions.<sup>4m,10</sup> To examine the involvement of the arylrhodium(III) complexes, we prepared the well-defined  $[\text{Cp}^*\text{Rh}(\text{Ph})(\text{Br})(\text{PPh}_3)]$  complex **5a** (71% yield) by reacting  $[\text{Cp}^*\text{RhCl}_2(\text{PPh}_3)]$  with  $\text{PhMgBr}$ .<sup>11</sup> The analogous  $[\text{Cp}^*\text{Rh}(\text{Ph})(\text{Cl})(\text{PPh}_3)]$  complex **5b** (83% yield) was also prepared by employing phenylboronic acid as the aryl source (Scheme 4).<sup>12</sup> The molecular structures of **5a** and **5b** have been confirmed by single-crystal X-ray crystallography.<sup>6</sup>

In this work, when  $[\text{Cp}^*\text{Rh}(\text{Ph})(\text{Br})(\text{PPh}_3)]$  (**5a**) (10 mol%) was treated with  $\text{AgSbF}_6$  (10 mol%) and phenylazocarboxylate (0.5 mmol) in DMF at 40 °C for 4 h, no *N,N*-diphenylhydrazide was formed. Notably,  $[\text{Cp}^*\text{Rh}(\text{Ph})_2(\text{PPh}_3)]$  was isolated in 30% yield, and 18% of the starting  $[\text{Cp}^*\text{Rh}(\text{Ph})(\text{Br})(\text{PPh}_3)]$  was recov-



**Scheme 5** Investigation of the stoichiometric reaction of arylrhodium(III) complexes with phenylazocarboxylate.

ered (Scheme 5). Notwithstanding,  $[\text{Cp}^*\text{RhCl}_2(\text{PPh}_3)]$  was found to be an effective catalyst for the arylation reaction. For example, reacting  $[\text{Cp}^*\text{RhCl}_2(\text{PPh}_3)]$  (5 mol%) with 4-methoxyphenylboronic acid (**1b**) and phenylazocarboxylate (**3a**) in DMF at 40 °C afforded **4aa** in 99% yield. Based on the above findings, direct coupling of arylrhodium(III) with the azo reagent may not be a productive step for the arylation reaction.

Previously, Muniz and coworkers reported the Pd-catalyzed arylation of DEAD by arylboronic acids, and palladadiaziridine complexes have been characterized as the key intermediate. However, the attempt to characterize well-defined rhodalladiaziridine complexes was unsuccessful. The preparation and characterization of some reactive metalladiaziridine complexes are currently in progress, and the results will be reported separately.

## Conclusions

In conclusion, we developed a  $[\text{Cp}^*\text{Rh}(\text{III})]$ -catalyzed electrophilic amination of arylboronic acids by employing azo reagents. Effective coupling of DEAD and the aryl azocarboxylates with arylboronic acids afforded mono- and diarylhydrazides in good yields under mild conditions.

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