## PAPER

# 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*-diarylhydrazides. 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.
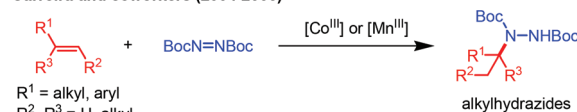
Transition metal-catalyzed electrophilic (umpolung) aminations are attractive approaches for arylamine synthesis under mild conditions.[1] Characterized by weak N–X (X = leaving group) σ-bonds, haloamines and hydroxyamine derivatives have been extensively investigated for electrophilic amination with organolithium and -magnesium reagents.[2] 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 π-bond cleavage. While dialkyl azodicarboxylates are known to react with stoichiometric organometallic reagents for C–N bond coupling reactions,[3] 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.[3e–g] Recently, Chatani and coworkers reported a Cu-catalyzed hydroarylation of azodicarboxylates.[3h] Muniz and coworkers reported a Pd-catalyzed coupling of arylboronic acids with diethyl azodicarboxylate (DEAD). A palladadiaziridine complex was structurally characterized and was shown to mediate the C–N bond coupling reaction.[3i,j]
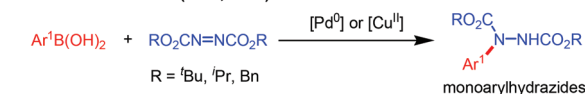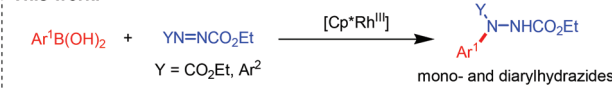
Owing to an interest in developing transition metal catalyzed C–H bond aminations under mild conditions,[4] we previously accomplished regioselective Pd-/Rh-catalyzed *ortho*-selective arene C–H amination with tosyloxycarbamates and *N*-chloroamines.[4k–o] The catalytic arene C–H amination should

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**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 π-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)$_2$] (5 mol%) in THF at 80 °C under an N$_2$ 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[a]



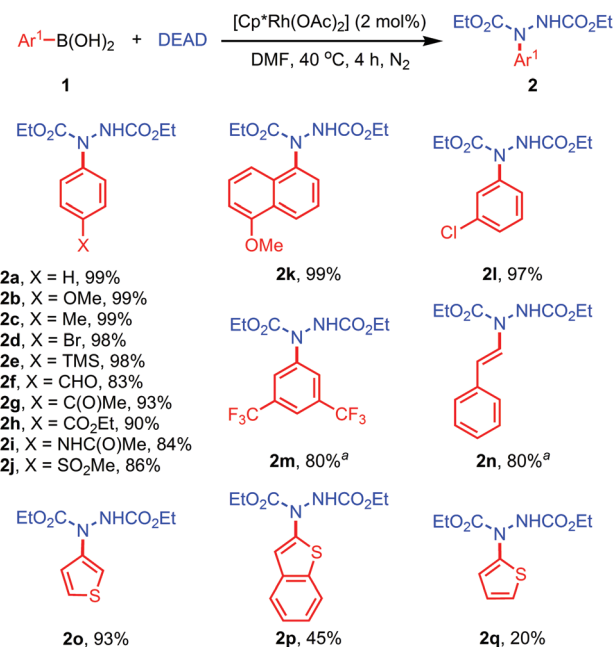| Entry | Aryl boron reagent | Catalyst | Solvent | $T$ (°C) | Yield[b] (%) |
|---|---|---|---|---|---|
| 1 | PhB(OH)$_2$ (**1a**) | [Cp*Rh(OAc)$_2$] | THF | 80 | 85 |
| 2 | PhB(pin) | [Cp*Rh(OAc)$_2$] | THF | 80 | n.d.[c] |
| 3 | KPhBF$_3$ | [Cp*Rh(OAc)$_2$] | THF | 80 | n.d.[c] |
| 4[d] | KPhBF$_3$ | [Cp*Rh(OAc)$_2$] | THF | 80 | 70 |
| 5 | **1a** | [Cp*RhCl$_2$]$_2$ | THF | 80 | 10 |
| 6 | **1a** | [Rh(COD)Cl]$_2$ | THF | 80 | 11 |
| 7 | **1a** | [Rh(COD)(OH)]$_2$ | THF | 80 | n.d.[c] |
| 8 | **1a** | [Cp*IrCl$_2$]$_2$ | THF | 80 | n.d.[c] |
| 9 | **1a** | [Cp*Rh(OAc)$_2$] | $^t$BuOH | 80 | 64 |
| 10 | **1a** | [Cp*Rh(OAc)$_2$] | MeCN | 80 | 3 |
| 11 | **1a** | [Cp*Rh(OAc)$_2$] | Dioxane | 80 | 50 |
| 12 | **1a** | [Cp*Rh(OAc)$_2$] | DCE | 80 | 31 |
| 13[e] | **1a** | [Cp*Rh(OAc)$_2$] | DMF | 40 | 99 |
| 14[f] | **1a** | [Cp*Rh(OAc)$_2$] | THF | 80 | 42 |

[a] Conditions: aryl boron reagent (0.3 mmol), DEAD (0.2 mmol), catalyst (5 mol%), solvent (1 mL), 4 h in an N$_2$ atmosphere. [b] Isolated yield. [c] n.d. = not detected. [d] B(OH)$_3$ (0.3 mmol) was added. [e] [Cp*Rh(OAc)$_2$] (2 mol%) was used. [f] Di-*tert*-butyl azodicarboxylate (0.2 mmol) was used instead.
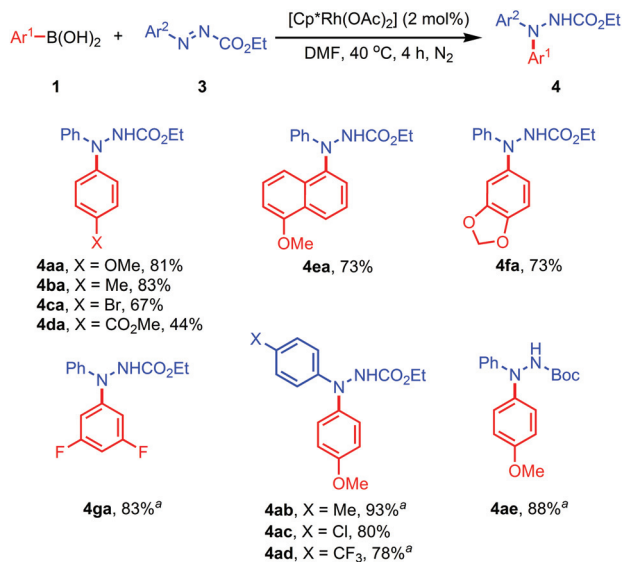


**Scheme 2** Scope of the arylation of DEAD. Yields of isolated products are given. General reaction conditions: **1** (0.3 mmol), DEAD (0.2 mmol), [Cp*Rh(OAc)$_2$] (2 mol%), DMF (1 mL), 40 °C for 4 h in an N$_2$ atmosphere. [a]The reaction was performed at 80 °C.

of the DEAD. Interestingly, when potassium phenyltrifluoroborate was employed together with B(OH)$_3$ as additives and DMF as the solvent, **2a** was formed in 70% yield (entry 4).

Other rhodium catalysts such as [Cp*RhCl$_2$]$_2$ are less effective catalysts (entry 5). According to the literature, rhodium(I) diene complexes such as [Rh(COD)X]$_2$ (X = Cl, OH) are known to catalyze arylation of enones with arylboron reagents.[5] 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$_2$]$_2$ complex exhibited negligible catalytic activities under our reaction conditions (entry 8).

Other solvents such as $^t$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.[6] Upon further refinement of several experimental parameters, an optimized reaction protocol was established: [Cp*Rh(OAc)$_2$] (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.[6]

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-

nic acids bearing TMS, CHO, C(O)Me, CO$_2$Et, NHC(O)Me and SO$_2$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.[7] The Pd- and Cu-catalyzed arylation of anilines with haloarenes are widely employed for diarylamine synthesis.[8] Yet, examples of diarylamine synthesis *via* electrophilic amination are sparse.[9] Lei and coworkers reported the synthesis of diarylamines by Cu-catalyzed arylation of N-chloroanilides with arylboronic acids.[9e] Recently, Chang and coworkers reported a reaction of aryl azides with aryliridium(III) complexes for diarylamine synthesis.[9f–h] In this work, we developed the catalytic arylation of arylazocarboxylates for the synthesis of N,N-diarylhydrazides.

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)$_2$] (2 mol%) in DMF at 40 °C under an N$_2$ atmosphere, N,N-diarylhydrazides (**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-

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**Scheme 3** Scope of the arylation of arylazocarboxylate. Yields of isolated products are given. General reaction conditions: **1** (0.3 mmol), **3** (0.2 mmol), [Cp*Rh(OAc)$_2$] (2 mol%), DMF (1 mL), 40 °C for 4 h in an N$_2$ atmosphere. $^a$The reaction was performed at 80 °C.

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-ditrifluorophenylboronic 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.[4m,10] To examine the involvement of the arylrhodium(III) complexes, we prepared the well-defined [Cp*Rh(Ph)(Br)(PPh$_3$)] complex **5a** (71% yield) by reacting [Cp*RhCl$_2$(PPh$_3$)] with PhMgBr.[11] The analogous [Cp*Rh(Ph)(Cl)(PPh$_3$)] complex **5b** (83% yield) was also prepared by employing phenylboronic acid as the aryl source (Scheme 4).[12] The molecular structures of **5a** and **5b** have been confirmed by single-crystal X-ray crystallography.[6]

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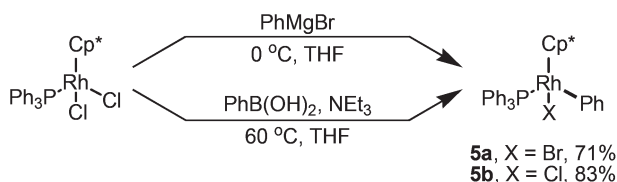


**Scheme 4** Synthesis of [Cp*Rh(Ph)(X)(PPh$_3$)].
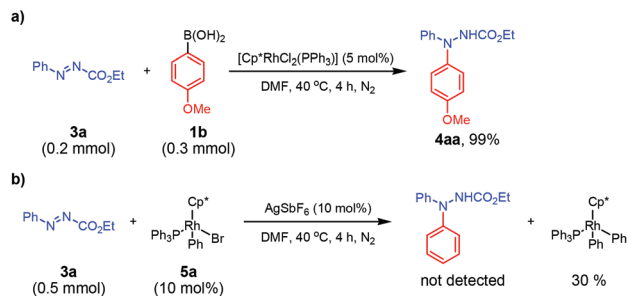


**Scheme 5** Investigation of the stoichiometric reaction of arylrhodium(III) complexes with phenylazocarboxylate.

ered (Scheme 5). Notwithstanding, [Cp*RhCl$_2$(PPh$_3$)] was found to be an effective catalyst for the arylation reaction. For example, reacting [Cp*RhCl$_2$(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 [Cp*Rh(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.

## Acknowledgements

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