



Cite this: *Org. Biomol. Chem.*, 2016, **14**, 6821

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

Yan-Fung Lau, Chun-Ming Chan, Zhongyuan Zhou and Wing-Yiu Yu*

Received 6th April 2016,
Accepted 14th June 2016

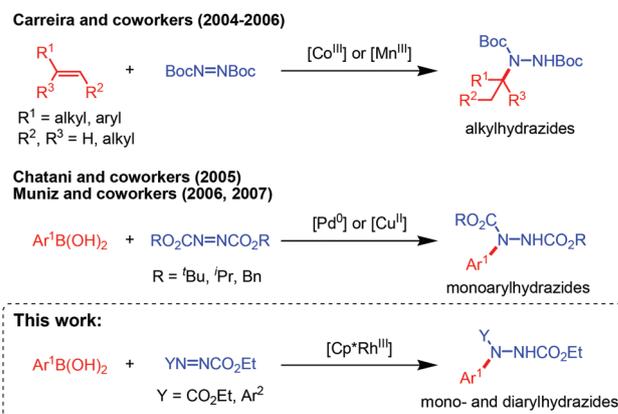
DOI: 10.1039/c6ob00719h

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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.

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 palladiaziridine 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



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 N₂ 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

The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, China.
E-mail: wing-yiu.yu@polyu.edu.hk

† Electronic supplementary information (ESI) available. CCDC 1455768–1455771. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6ob00719h



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 |

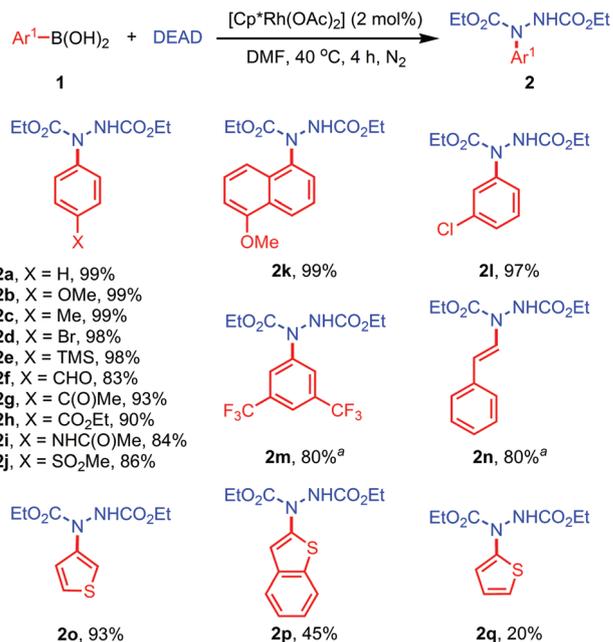
^a Conditions: aryl boron reagent (0.3 mmol), DEAD (0.2 mmol), catalyst (5 mol%), solvent (1 mL), 4 h in an N₂ atmosphere. ^b Isolated yield. ^c n.d. = not detected. ^d B(OH)₃ (0.3 mmol) was added. ^e [Cp*Rh(OAc)₂] (2 mol%) was used. ^f Di-*tert*-butyl azodicarboxylate (0.2 mmol) was used instead.

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*RhCl₂]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*IrCl₂]₂ complex exhibited negligible catalytic activities under our reaction conditions (entry 8).

Other solvents such as ^tBuOH, 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-



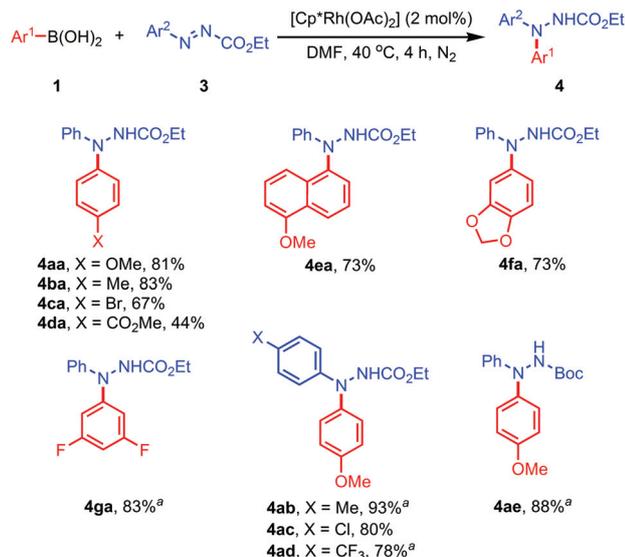
Scheme 2 Scope of the arylation of DEAD. Yields of isolated products are given. General reaction conditions: **1** (0.3 mmol), DEAD (0.2 mmol), [Cp*Rh(OAc)₂] (2 mol%), DMF (1 mL), 40 °C for 4 h in an N₂ atmosphere. ^aThe reaction was performed at 80 °C.

nic acids bearing TMS, CHO, C(O)Me, CO₂Et, NHC(O)Me and SO₂Me 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 N₂ 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-





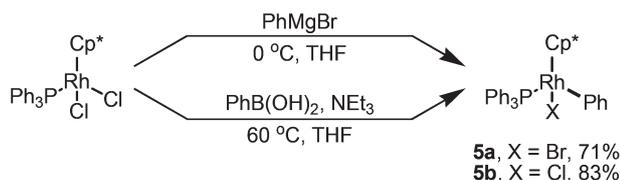
Scheme 3 Scope of the arylation of arylazocarboxylate. Yields of isolated products are given. General reaction conditions: **1** (0.3 mmol), **3** (0.2 mmol), [Cp^{*}Rh(OAc)₂] (2 mol%), DMF (1 mL), 40 °C for 4 h in an N₂ atmosphere. ^aThe reaction was performed at 80 °C.

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-difluorophenylboronic acids furnished **4ea–4ga** in excellent yields.

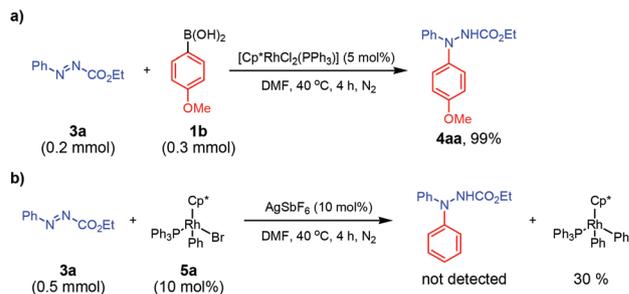
With 4-methoxyphenylboronic acid as the arylating reagent, the reactions of some substituted arylazocarboxylates were examined. Effective C–N coupling was observed in all cases, and the diarylhydrazides (**4ab–4ae**) were formed in 78–93% yields.

Arylrhodium(III) complexes are known to mediate catalytic C–N bond coupling reactions.^{4m,10} To examine the involvement of the arylrhodium(III) complexes, we prepared the well-defined [Cp^{*}Rh(Ph)(Br)(PPh₃)] complex **5a** (71% yield) by reacting [Cp^{*}RhCl₂(PPh₃)] with PhMgBr.¹¹ The analogous [Cp^{*}Rh(Ph)(Cl)(PPh₃)] 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)(PPh₃)] (**5a**) (10 mol%) was treated with AgSbF₆ (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(PPh₃)] was isolated in 30% yield, and 18% of the starting [Cp^{*}Rh(Ph)(Br)(PPh₃)] was recov-



Scheme 4 Synthesis of [Cp^{*}Rh(Ph)(X)(PPh₃)].



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

ered (Scheme 5). Notwithstanding, [Cp^{*}RhCl₂(PPh₃)] was found to be an effective catalyst for the arylation reaction. For example, reacting [Cp^{*}RhCl₂(PPh₃)] (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 rhodadiaziridine 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

We thank the Hong Kong Research Grants Council (PolyU5032/13P, C5023/14G) for financial support.

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