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

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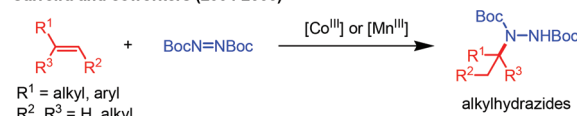
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Transition metal-catalyzed electrophilic (umpolung) aminations are attractive approaches for arylamine synthesis under mild conditions.¹ Characterized by weak N–X (X = leaving group) σ -bonds, haloamines and hydroxylamine derivatives have been extensively investigated for electrophilic amination with organolithium and -magnesium reagents.² Dialkyl azodicarboxylates are conceptually different classes of electrophilic amination reagents. Unlike the halo/hydroxylamine-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}

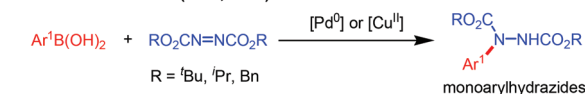
Owing to an interest in developing transition metal catalyzed C–H bond aminations under mild conditions,⁴ we previously accomplished regioselective Pd-/Rh-catalyzed *ortho*-selective arene C–H amination with tosyloxycarbamates and *N*-chloroamines.^{4k–o} The catalytic arene C–H amination should

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.

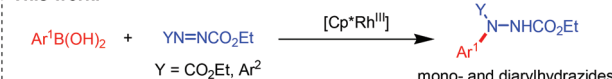
Carreira and coworkers (2004–2006)



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 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

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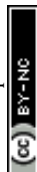


Table 1 Reaction optimization^a

$\text{aryl boron reagent} + \text{EtO}_2\text{CN=NCO}_2\text{Et (DEAD)} \xrightarrow[\text{solvent, T, N}_2]{\text{catalyst}} \text{EtO}_2\text{C-N(Ph)-NHCO}_2\text{Et}$					
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]	<i>t</i> 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

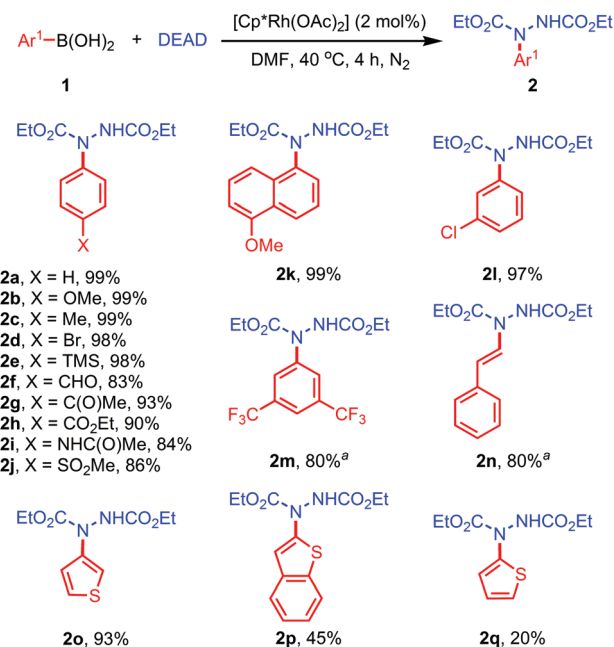
^a Conditions: aryl boron reagent (0.3 mmol), DEAD (0.2 mmol), catalyst (5 mol%), solvent (1 mL), 4 h in an N₂ atmosphere. ^b Isolated yield. ^c n.d. = not detected. ^d B(OH)₃ (0.3 mmol) was added. ^e [Cp*Rh(OAc)₂] (2 mol%) was used. ^f Di-*tert*-butyl azodicarboxylate (0.2 mmol) was used instead.

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 *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-



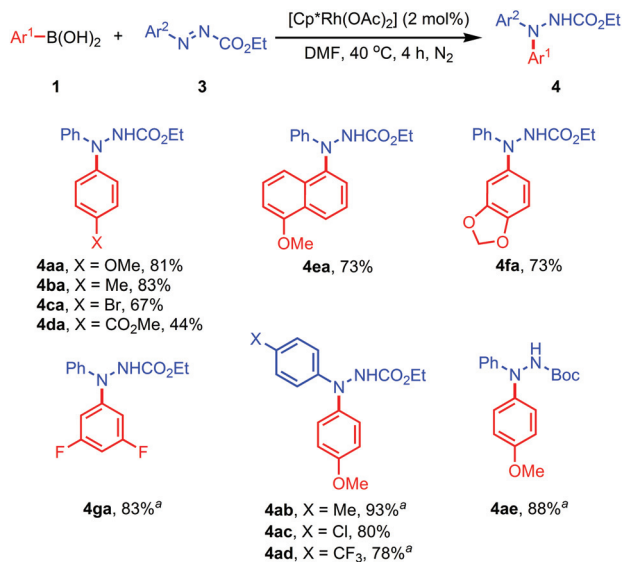
Scheme 2 Scope of the arylation of DEAD. Yields of isolated products are given. General reaction conditions: **1** (0.3 mmol), DEAD (0.2 mmol), [Cp*Rh(OAc)₂] (2 mol%), DMF (1 mL), 40 °C for 4 h in an N₂ atmosphere. ^a The reaction was performed at 80 °C.

nic acids bearing TMS, CHO, C(OMe), CO₂Et, NHC(OMe) 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-





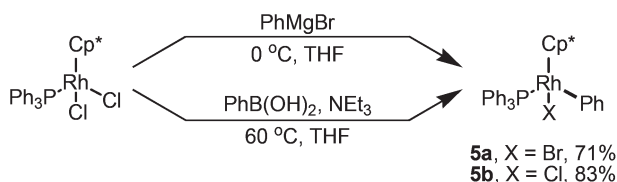
Scheme 3 Scope of the arylation of arylazocarboxylate. Yields of isolated products are given. General reaction conditions: **1** (0.3 mmol), **3** (0.2 mmol), [Cp*Rh(OAc)₂] (2 mol%), DMF (1 mL), 40 °C for 4 h in an N₂ atmosphere. ^aThe reaction was performed at 80 °C.

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

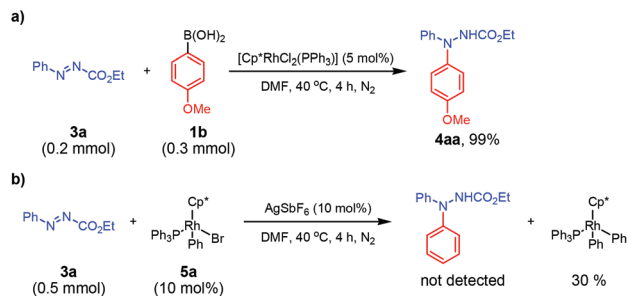
With 4-methoxyphenylboronic acid as the arylating reagent, the reactions of some substituted arylazocarboxylates were examined. Effective C–N coupling was observed in all cases, and the diarylhydrazides (**4ab–4ae**) were formed in 78–93% yields.

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)(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

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