

Synthesis of imidazo and benzimidazo[2,1-a]-isoquinolines by rhodium-catalyzed intramolecular double C–H bond activation†

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The rhodium-catalyzed intramolecular direct arylation of imidazole and benzimidazole derivatives *via* double C–H bond activation is described. This approach provides new access to a wide range of imidazo and benzimidazo[2,1-a]isoquinoline derivatives in moderate to high yields. This reaction provides an alternative method to the known Pd-catalyzed intramolecular oxidative cross-coupling reactions.

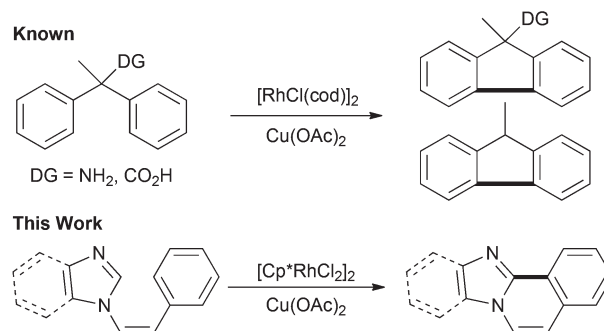
Introduction

Nitrogen-containing heterocycles and their derivatives are often found in natural products and in pharmaceuticals and agrochemicals.^{1,2} Since imidazo and benzimidazo[2,1-a]isoquinoline derivatives show interesting biological activities such as anticancer, anti-HIV-1, antimicrobial and antiviral properties,^{3,4} a variety of synthetic protocols have been developed for the preparation of imidazo and benzimidazo[2,1-a]isoquinoline derivatives based on condensation reactions⁵ and the photocyclization of 1-styrylimidazoles.⁶ In addition, coupling reactions catalyzed by transition metals, such as palladium and copper, have recently been reported and successfully applied to the preparation of such heterocyclic compounds through C–N and C–C cross-coupling.⁷ However, these protocols require the use of organohalides^{7a–d} or boranes^{7e} or both^{7f} as starting materials. These prefunctionalized starting materials are not readily available from commercial sources and are often difficult to synthesize. Therefore, the development of more general and convenient processes using readily accessible and inexpensive substrates is an important theme. As a promising strategy for the synthesis of the imidazo and

benzimidazo[2,1-a]isoquinoline derivatives, the intramolecular oxidative cross-coupling *via* cleavage of two C–H bonds would be a more straightforward and efficient route to these compounds.

It has long been known that Pd catalyzes the oxidative homo-coupling of arenes^{8a,b} and cross-coupling between arenes and olefins.^{8c,d} This transformation has been successfully applied to cyclization by intramolecular oxidative cross-coupling reactions.^{8e–m} This successful Pd-catalyzed functionalization of C–H bonds^{8n,o} prompted the study of Rh catalyzed systems leading to the recent remarkable development of useful transformations *via* C–H bond cleavage⁹ such as oxidative Heck-type reactions,¹⁰ oxidative aryl–aryl coupling,¹¹ as well as addition to carbon–carbon^{10c,d,k,q,12} or carbon–heteroatom¹³ unsaturated bonds.

During the course of our study on transition metal-catalyzed cross-coupling reactions,¹⁴ we developed a straightforward procedure for the synthesis of imidazo and benzimidazo[2,1-a]isoquinoline derivatives. The method involves a rhodium-catalyzed cross-coupling reaction *via* double C–H bond cleavage as the first example of the rhodium-catalyzed intramolecular oxidative cross-coupling of heteroarenes with arenes, although the corresponding aryl–aryl intramolecular coupling reactions are known (Scheme 1).¹⁵

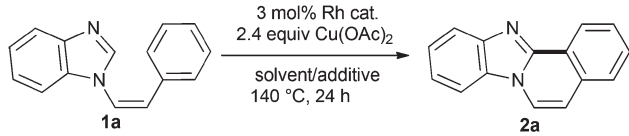


Scheme 1 Rhodium-catalyzed intramolecular oxidative cross-coupling reaction.

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Table 1 Optimization of the rhodium-catalyzed intramolecular C–H arylation^a


Entry	Catalyst	Solvent	Additive	Yield ^b (%)
1	[Cp*RhCl ₂] ₂	DMA	None	49
2	[Cp*RhCl ₂] ₂	Mesitylene	None	56
3	[Cp*RhCl ₂] ₂	DMF	None	18
4	[Cp*RhCl ₂] ₂	Toluene	None	25
5	[Cp*RhCl ₂] ₂	Mesitylene	PivOH	77
6	[Cp*RhCl ₂] ₂	Mesitylene	AcOH	65
7	[Cp*RhCl ₂] ₂	Mesitylene	1-AdCO ₂ H	72
8	[Cp*RhCl ₂] ₂	DMA	PivOH	63
9	[Cp*RhCl ₂] ₂	DMF	PivOH	30
10	[Cp*RhCl ₂] ₂	Toluene	PivOH	42
11	[Cp*RhCl ₂] ₂	None	PivOH	26
12	[Rh(cod)Cl] ₂	Mesitylene	PivOH	71
13 ^c	[Rh(nbd)Cl] ₂	Mesitylene	PivOH	46
14 ^c	Rh ₂ (OAc) ₄	Mesitylene	PivOH	49
15 ^c	Rh(PPh ₃) ₃ Cl	Mesitylene	PivOH	42
16 ^c	RhCl ₃	Mesitylene	PivOH	36
17 ^d	[Cp*RhCl ₂] ₂	Mesitylene	PivOH	48
18	None	Mesitylene	PivOH	0
19 ^e	[Cp*RhCl ₂] ₂	Mesitylene	PivOH	31

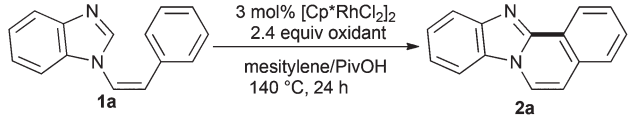
^a Reaction conditions: **1a** (0.25 mmol), [Cp*RhCl₂]₂ (3.0 mol%), Cu(OAc)₂ (0.6 mmol), additive (0.5 mmol), solvent (1.0 mL), 24 h, 140 °C.

^b Isolated yields. ^c Rh (10 mol%). ^d [Cp*RhCl₂]₂ (1.5 mol%). ^e At 70 °C. Cp*: pentamethylcyclopentadienyl; cod: 1,5-cyclooctadiene; nbd: bicyclo[2.2.1]hepta-2,5-diene.

Results and discussion

We carried out the reaction under different conditions using (Z)-1-styryl-1H-benzimidazole (**1a**) as a model substrate and the results are summarized in Table 1. Among the various solvents tested, DMA and mesitylene afforded the best results (Table 1, entries 1, 2, 5, 8), whereas DMF and toluene gave lower yields (entries 3, 4, 9, 10). PivOH was found to be an effective additive (entry 5). Among the Rh complexes examined, [Cp*RhCl₂]₂ proved to be preeminent for this reaction (entries 5, 12–16). When the amount of [Cp*RhCl₂]₂ was reduced to half from 3.0 mol%, the yield decreased (entries 5 and 17). No reaction took place in the absence of the metal catalyst (entry 18). The reaction was slow at 70 °C and the coupling product was produced in low yield (entry 19).

Table 2 shows the effect of various oxidants on this reaction and Cu(OAc)₂ was found to be an excellent oxidant (entry 6). The use of AgOAc gave products in low yield (entry 1) and other oxidants such as Ag₂CO₃, AgF, CuCl₂, CuCO₃, (NH₄)₂S₂O₈, TBHP (*tert*-butyl hydroperoxide) and K₂S₂O₈ were ineffective (entries 2–5 and 10–12). In the absence of an oxidant, no reaction occurred (entry 13). The best yield was obtained when 3.0 mol% amount of [Cp*RhCl₂]₂ was employed in combination with Cu(OAc)₂ (2.4 equiv.) as the oxidant and PivOH (0.5 mmol) as the additive in mesitylene (1.0 mL) at 140 °C for 24 h (entry 6). This reaction proceeded

Table 2 Screening of oxidants^a


Entry	Oxidant	Yield ^b (%)	Entry	Oxidant	Yield ^b (%)
1	AgOAc	21	8 ^d	Cu(OAc) ₂	47
2	Ag ₂ CO ₃	Trace	9 ^e	Cu(OAc) ₂	65
3	AgF	0	10	(NH ₄) ₂ S ₂ O ₈	0
4	CuCl ₂	Trace	11 ^f	TBHP	0
5	CuCO ₃	Trace	12	K ₂ S ₂ O ₈	0
6	Cu(OAc) ₂	77	13	—	0
7 ^c	Cu(OAc) ₂ ·H ₂ O	81			

^a Reaction conditions: **1a** (0.25 mmol), [Cp*RhCl₂]₂ (3.0 mol%), oxidants (0.6 mmol), PivOH (0.5 mmol), mesitylene (1.0 mL), 24 h, 140 °C. ^b Isolated yields. ^c [Cp*RhCl₂]₂ (5.0 mol%), Cu(OAc)₂·H₂O (0.3 mmol) and AgSbF₆ (20 mol%) in mesitylene (1.0 mL) without using PivOH. ^d Cu(OAc)₂ (0.3 mmol). ^e Cu(OAc)₂ (0.45 mmol). ^f 2.0 equiv.

similarly in the absence of PivOH to give a comparative yield of product **2a** (entry 7).

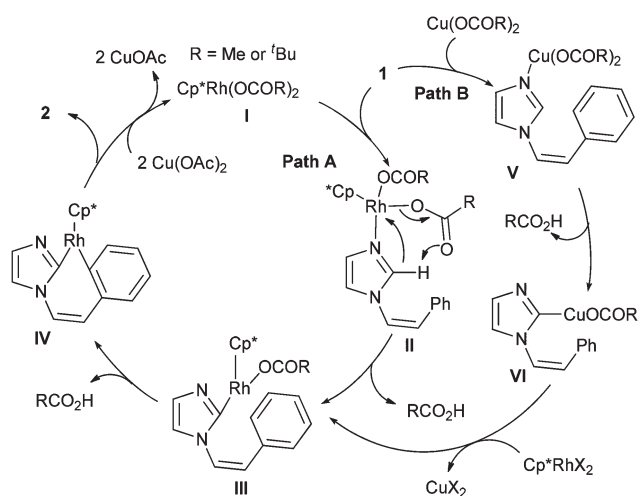
To explore the scope of this rhodium-catalyzed intramolecular oxidative cross-coupling, the reactions of **1a–n** were examined under optimized conditions. As shown in Table 3, the corresponding imidazo and benzimidazo[2,1-*a*]isoquinoline derivatives **2a–l** were obtained in moderate to high yields. Alkyl and methoxy substituents exerted little effect on the yield, but substituents at the *ortho* position of the benzene ring slightly reduced the yields due to the steric effect (**2c** and **2j**). When **1h** carrying a 1,2-diphenylvinyl moiety was employed, the reaction proceeded efficiently to give the corresponding cyclized product **2h** in 62% yield, indicating that the phenyl group on the vinylic tether carbon did not affect the reaction.¹⁶ However, **1m**, having a thiophene ring, and **1n**, having an (*E*)-styryl group, did not afford coupling products. The procedure using AgSbF₆ and Cu(OAc)₂·H₂O in mesitylene gave slightly better results than the procedure using PivOH as the additive as shown in Table 3.

A plausible catalytic cycle for the reaction is illustrated in Scheme 2. The reaction starts from Cp*Rh(OPiv)₂ or Cp*Rh(OAc)₂ which is derived from the ligand exchange between rhodium dimer and the pivalic acid or Cu(OAc)₂. Thus formed Cp*Rh(OCOR)₂ is coordinated with a nitrogen lone pair of imidazole to give intermediate **II** in Path A. Rh then undergoes insertion into the C–H bond at the C2 position assisted by the carboxylate ligand leading to the formation of intermediate **III** with the loss of carboxylic acid.¹⁷ The subsequent C–H bond cleavage by Rh(III) generates a seven-membered rhodacyclic intermediate **IV** which undergoes reductive elimination to give product **2** and a Rh(I) species, and the latter is oxidized by Cu(II) to complete the catalytic cycle. A possible alternative pathway is shown by Path B, where the catalytic cycle is triggered by the coordination of the nitrogen lone pair of imidazole to Cu(OCOR)₂ affording intermediate **V**. The insertion of

Table 3 Rhodium-catalyzed intramolecular oxidative cross-coupling of various imidazoles^a

1	2
2a: 77% (81%)	2d: 63% (69%)
2b: 79% (84%)	2e: 74%
2f: 69% (71%)	2g: 61%
2k: 83%	2h: 62% (68%)
2l: 77%	2i: 79%
1m: no reaction	2j: 51% (56%)
	1n: no reaction

^a The same reaction conditions as in Table 2, entry 6. Results obtained under the conditions indicated in Table 2, entry 7 are in parentheses.

**Scheme 2** Plausible reaction pathways of rhodium-catalyzed oxidative cross-coupling.

Cu into a C–H bond followed by transmetalation with rhodium then gives intermediate **III** via **VI**.¹⁸

Conclusions

We report herein on the rhodium-catalyzed synthesis of imidazo and benzimidazo[2,1-*a*]isoquinolines via the intramolecular oxidative cross-coupling reaction through double C–H bond cleavage. This protocol can be applied to the synthesis of various heterocyclic compounds. The scope of the reaction and further applications as well as mechanistic studies of the rhodium-catalyzed C–H activation reactions are currently under investigation.

Acknowledgements

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