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Rh(III)-catalyzed sequential C–H activation and annulation: access to N-fused heterocycles from arylazoles and α -diazocarbonyl compounds†

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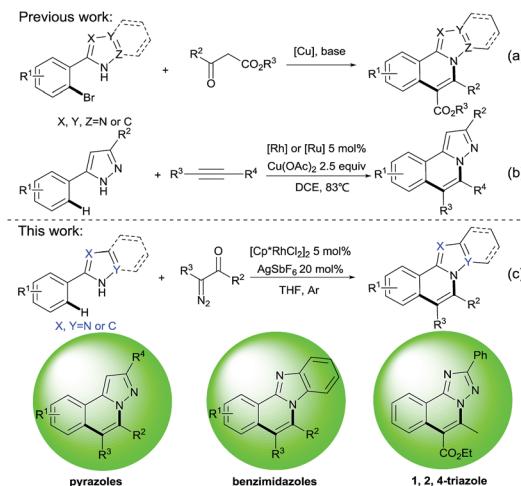
A mild and simple protocol has been developed for the synthesis of N-fused heterocycles from arylazoles and α -diazocarbonyl compounds via Rh(III)-catalyzed sequential C–H activation and annulation. Three kinds of N-fused heterocycles derived from arylpyrazoles, arylbenzimidazoles and aryl 1,2,4-triazole were successfully obtained. The reactivity of the other four arylazole analogues was also investigated.

Introduction

N-fused heterocycles are important due to their widespread applications in the pharmaceutical industry and advanced materials.^{1,2} Synthesis of various N-fused heterocycles has thus attracted much attention, particularly for drug development.³ Most syntheses have been completed *via* traditional approaches under harsh reaction conditions like high temperature and microwave irradiation.⁴ The past decades have seen the development of numerous protocols *via* transition-metal-catalyzed coupling for this purpose,⁵ among which Cu- or Pd-catalyzed coupling reactions⁶ and transition-metal-catalyzed C–H activation⁷ represent two attractive strategies in forming carbon–carbon and carbon–heteroatom bonds. For instance, Fu *et al.* reported several elegant examples of copper-catalyzed cascade reactions to access N-fused heterocycles from aryl halides and active methylene compounds in 2011 and 2012 (Scheme 1a).^{6a,b,d} Later, Macgregor and co-workers reported a more direct Rh- or Ru-catalyzed synthesis of pyrazoloisoquinolines using C–H activation of 3-phenylpyrazoles with aryl- and alkylalkynes,^{7f} avoiding the use of aryl halides; however, an excess amount of oxidant was needed (Scheme 1b). Therefore, the development of a more efficient and greener synthetic approach to access N-fused heterocycles *via* C–H activation remains highly desirable.

Carbene migratory insertion is a well established method to directly functionalize C–H bonds,⁸ with α -diazocarbonyl compounds predominantly used in the directing group (DG)-

assisted Rh(III)-, Co(III)- and Ru(II)-catalyzed C–H activation.⁹ In 2012, Yu and co-workers first developed chelation-assisted Rh(III)-catalyzed intermolecular cross-coupling of diazo-malonates with arene C–H bonds.¹⁰ Recently, Li *et al.* developed a new Ru(II)-catalyzed intermolecular coupling of diazo substrates with arenes to access indoles,¹¹ and the Glorius group reported the first example of Co(III)-catalyzed C–H bond activation of imines with diazo compounds for the synthesis of isoquinolin-3-ones.¹² Directing groups previously used in this type of transformation included, among others, imines,¹³ oximes,¹⁴ amines,¹⁵ hydrazines,¹⁶ azides,¹⁷ azobenzenes¹⁸ and amides,¹⁹ delivering the corresponding isoquinolines, benzothiazine, lactams, isoquinolones, indoles and indolines. In view of the importance of N-fused heterocycles and our continued interest in Rh(III)-catalyzed C–H activation reactions and the construction of N-fused heterocycles,²⁰ we envision using arylazoles and diazo compounds as the substrates in a Rh(III)-



Scheme 1 Synthesis of N-fused heterocycles from arylazoles.

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catalyzed sequential C–H activation and annulation that would provide valuable N-fused heterocycles (Scheme 1c).

Results and discussion

To verify the assumption mentioned above, 3,5-diphenyl-1*H*-pyrazole (**1a**) and ethyl 2-diazo-3-oxobutanoate (**2a**) were selected as coupling partners (Table 1). We studied the reaction between **1a** and **2a** in the presence of $[\text{Cp}^*\text{RhCl}_2]_2$ (5 mol%) and AgSbF_6 (20 mol%) at room temperature under Ar atmosphere in THF (2 mL) for 12 h. Fortunately, the desired product **3aa** was obtained in 37% yield (Table 1, entry 1). Encouraged by this result, three other solvents were tested, and the results revealed that THF was the best (Table 1, compare entries 2–4). Then, considering the conversion of the substrate, the reaction time was prolonged to 24 h, and we were pleased to see that the yield of **3aa** directly increased to 92% (Table 1, entry 5). Furthermore, to investigate the catalytic activity of other transition-metal catalysts, the performances of four other metal catalyst systems were compared. No desired product **3aa** was obtained using $[\text{Cp}^*(\text{IrCl}_2)]_2/\text{AgNTf}_2$ or $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2/\text{AgSbF}_6$ as the catalyst system (Table 1, entries 7 and 8). $\text{Cp}^*\text{Co}(\text{CO})\text{I}_2/\text{AgSbF}_6$ was less effective; the desired product **3aa** was obtained in 24% yield (Table 1, entry 6). By changing the silver salt to AgNTf_2 , the yield of **3aa** declined to 75%. In addition, no conversion of the substrate was observed without Ag salt or Rh salt (Table 1, entries 10, 11 and 12).

Having established the feasibility of Rh(III)-catalyzed sequential C–H activation and annulation to deliver N-fused

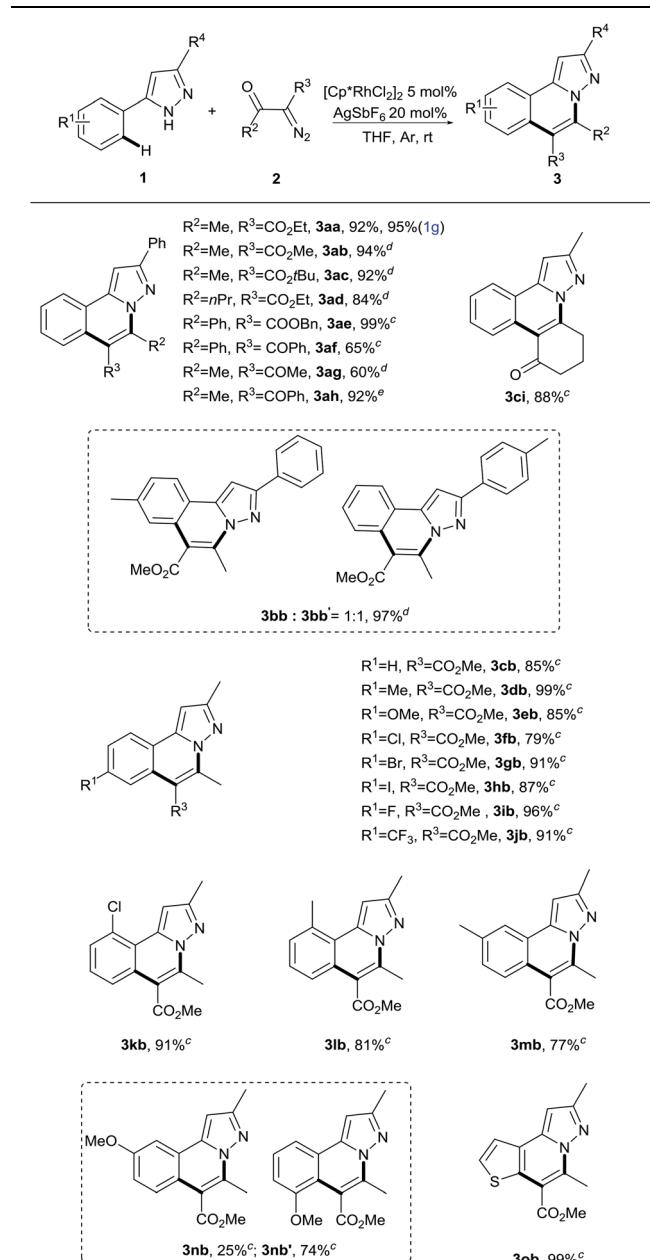
Table 1 Rh(III)-catalyzed sequential C–H activation and annulation of 3,5-diphenyl-1*H*-pyrazole (**1a**) with ethyl 2-diazo-3-oxobutanoate (**2a**): optimization of conditions^a

Entry	Cat. (mol%)	Reaction time	Solvent	Yield ^b (%)
1	$[\text{Cp}^*\text{RhCl}_2]_2$ (5)/ AgSbF_6 (20)	12 h	THF	37
2	$[\text{Cp}^*\text{RhCl}_2]_2$ (5)/ AgSbF_6 (20)	12 h	DCE	Trace
3	$[\text{Cp}^*\text{RhCl}_2]_2$ (5)/ AgSbF_6 (20)	12 h	MeOH	Trace
4	$[\text{Cp}^*\text{RhCl}_2]_2$ (5)/ AgSbF_6 (20)	12 h	EtOH	9
5	$[\text{Cp}^*\text{RhCl}_2]_2$ (5)/ AgSbF_6 (20)	24 h	THF	92
6	$\text{Cp}^*\text{Co}(\text{CO})\text{I}_2$ (5)/ AgSbF_6 (20)	24 h	THF	24
7	$[\text{Cp}^*(\text{IrCl}_2)]_2$ (5)/ AgNTf_2 (20)	24 h	THF	Trace
8	$\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$ (5)/ AgSbF_6 (20)	24 h	THF	0
9	$[\text{Cp}^*\text{RhCl}_2]_2$ (5)/ AgNTf_2 (20)	24 h	THF	75
10	None	24 h	THF	0
11	$[\text{Cp}^*\text{RhCl}_2]_2$ (5)	24 h	THF	0
12	AgSbF_6 (20)	24 h	THF	0

^a Reaction conditions: **1a** (0.2 mmol), **2a** (0.25 mmol), catalyst, and solvent (2 mL) were stirred at room temperature under Ar. ^b Isolated yield.

heterocycles, the reactions of various 5-phenyl-1*H*-pyrazoles with α -diazocarbonyl compounds were explored to examine the scope and generality of the present process. As depicted in Table 2, at first, 3,5-diphenyl-1*H*-pyrazole (**1a**) was kept as the representative reaction partner. A variety of diazoketoesters participated well in this transformation, affording the corresponding products in 84–99% yields (**3aa**–**3ae**). α -Diazoo- β -diketo

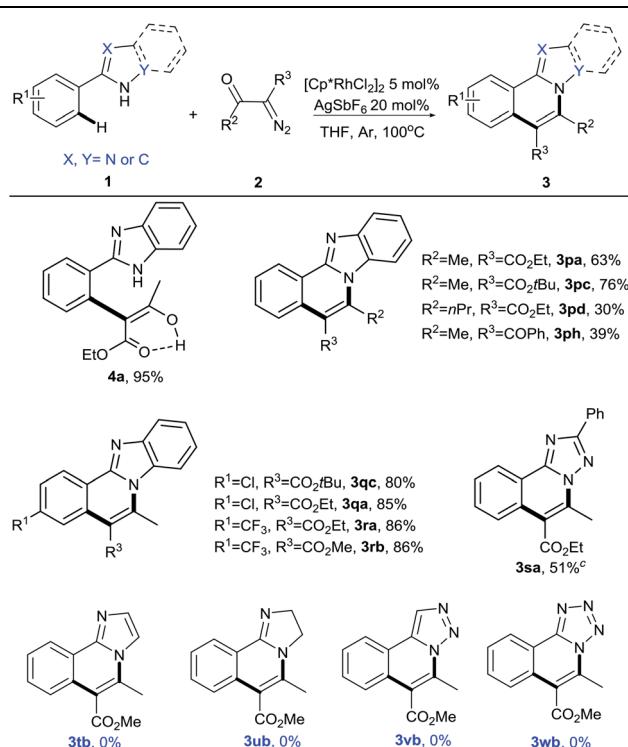
Table 2 Rh(III)-catalyzed sequential C–H activation and annulation of substituted 3,5-diphenyl-1*H*-pyrazole with α -diazocarbonyl compounds^{a,b}



^a Reaction conditions: **1** (0.2 mmol), **2** (0.25 mmol), $[\text{Cp}^*\text{RhCl}_2]_2$ (5 mol%), AgSbF_6 (20 mol%), and THF (2 mL) were stirred at room temperature (ca. 25 °C) under Ar for 24 h. ^b Isolated yield. ^c The reaction temperature is 60 °C. ^d The reaction time is 48 h. ^e The reaction temperature is 40 °C.

substrates **2f–h** also showed good efficiency in the cyclization to give the desired products in good yields. Among them, unsymmetrical diketone **2h** performed well; only one regioisomer of **3ah** was obtained in 72% yield. Then we found that the reaction of 3-phenyl-5-(*p*-tolyl)-1*H*-pyrazole (**1b**) with methyl 2-diazo-3-oxobutanoate (**2b**) afforded a mixture of regioisomeric products **3bb** and **3bb'** in 97% total yield with a ratio of 1 : 1 based on NMR analysis of the crude mixture. For 5-methyl-3-phenyl-1*H*-pyrazole, substituents at the *ortho* or *para* position including methyl, methoxy, trifluoromethyl, iodo, fluoro, chloro or bromo showed less reactivity; by raising the reaction temperature to 60 °C, all reacted well with diazo-ketoester (**2b**) and symmetrical diketone **2i**, which was prepared from cyclohexane-1,3-dione, providing **3cb–3lb** and **3ci** in good yields. Interestingly, a methyl substituent at the *meta* position (**1m**) underwent the transformation with good regioselectivity to give a single regioisomer in 77% yield (**3mb**). However, the reaction of the methoxy substituent at the *meta* position (**1n**) gave separable regioisomeric products **3nb** and **3nb'** in 25% and 74% yield, respectively. Additionally, 3-methyl-5-(thiophen-3-yl)-1*H*-pyrazole (**1o**) also presented good reactivity in this reaction, giving the desired product **3ob** in 99% yield. Pleasingly, a gram-scale reaction was also conducted under standard conditions, and **3aa** was obtained in 95% yield.

Table 3 Rh(III)-catalyzed sequential C–H activation and annulation of other arylazoles with α -diazocarbonyl compounds^{a,b}



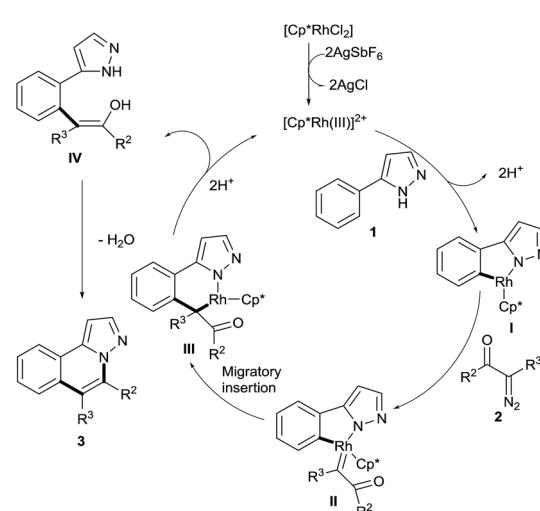
^a Reaction conditions: **1** (0.2 mmol), $[\text{Cp}^*\text{RhCl}_2]_2$ (5 mol%), AgSbF_6 (20 mol%), and THF (2 mL) were stirred at 100 °C under Ar for 24 h.

^b Isolated yield. ^c The reaction temperature is 60 °C.

Next, other arylazoles were examined to broaden the scope of this protocol (Table 3). Unfortunately, only the coupling of 2-phenylbenzimidazole (**1p**) with 2-diazo-3-oxobutanoate (**2a**) was successful under the optimal reaction conditions above, affording the coupling product **4a** in 95% yield. The structure of **4a** was confirmed by NMR and HRMS (see ESI†). To our delight, by raising the reaction temperature to 100 °C, the cyclization product **3pa** was isolated in 63% yield. This indicates the difference in N-nucleophilicity among indole, pyrazole and imidazole, which is consistent with previous reports.^{6e,7m,n} At the same reaction temperature, other α -diazocarbonyl compounds also reacted with **1p**, giving **3pa–3ph** in moderate yields. Chloro and trifluoromethyl substituents of 2-phenylbenzimidazole at the *para* position were readily converted into the desired products in good yields (**3qc**, **3ra**, **3rb**). Notably, this tandem reaction was also compatible with 5-phenyl-1*H*-1,2,4-triazole to form **3sa** in 51% yield. However, for other arylazoles, including aryl imidazole, aryl dihydroimidazole, aryl 1,2,3-triazole and aryl tetrazole, no desired product was observed under our conditions (**3tb–3wb**).

To better understand this chemistry, we used Density Functional Theory (DFT) calculations to study the activation energy, specifically with regard to the C–H activation step.²¹ The C–H bond activation is facilitated by the basic pyrazole group in the substrate **S1** via **TS1** with an activation energy of 26.2 kcal mol⁻¹. However, the activation energy increases to 33.2 kcal mol⁻¹ when we use imidazole **S2** as the substrate (ESI Fig. 1†). These results are consistent with the experimental observations.

Considering the previous reports^{9–21} on chelation-assisted Rh(III)-catalyzed intermolecular cross-coupling of diazo compounds and the formation of coupling product **4a** described above, we believe that this protocol likely involves sequential C–H activation and intramolecular cyclization; thus a plausible mechanism is proposed (Scheme 2). To begin with, anion exchange occurs between $[\text{Cp}^*\text{RhCl}_2]_2$ and AgSbF_6 , followed by the formation of a cationic Rh(III) species. Then the arylazole **1** undergoes directed C–H cleavage with $\text{Cp}^*\text{Rh}(\text{III})$ to



Scheme 2 Proposed reaction pathway.

give a five-membered rhodacyclic intermediate **I**. Next, the diazo compound **2** coordinates with it to form the intermediate **II**. Subsequently, migratory insertion of the carbene into the Rh–C bond gives the intermediate **III**, which undergoes protodemetalation to afford the alkylated product **IV**, releasing the Rh(III) catalyst for a new catalytic cycle. Finally, an enol intermediate is generated *in situ* by the tautomerization of intermediate **IV**, and gives the final product **3** via nucleophilic cyclization.

Conclusions

To sum up, we have developed a facile and practical method for the synthesis of valuable N-fused heterocycles *via* Rh(III)-catalyzed sequential C–H activation and annulation, using arylazoles and α -diazocarbonyl compounds as substrates. In this protocol, pyrazoles, benzimidazoles and one 1,2,4-triazole were obtained, and most of the pyrazoles were synthesized smoothly and efficiently under mild conditions. Additionally, a comparison of the reactivity for other arylazoles was conducted. This provides a new and alternative method for the construction of diverse and potentially bioactive N-fused heterocycles for drug candidate screening.

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