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Rhodium-Catalyzed Addition−Cyclization of Hydrazines with Alkynes: Pyrazole Synthesis via Unexpected C−N Bond Cleavage

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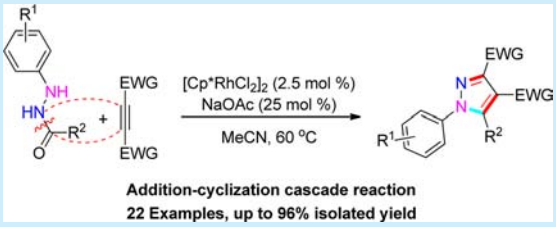
Supporting Information

ABSTRACT: Rhodium-catalyzed addition−cyclization of hydrazines with alkynes has been achieved to afford highly substituted pyrazoles under mild conditions. The cascade reaction involves two transformations: addition of the C−N bond of hydrazines to alkynes via unexpected C−N bond cleavage and intramolecular dehydration cyclization.



Direct addition of carbon−heteroatom bonds to unsaturated carbon−carbon bonds provides a powerful tool to construct carbon−carbon and carbon−heteroatom bonds simultaneously with 100% atom efficiency, fulfilling the requirements of green chemistry.[1] These transformations usually require transition-metal catalysts such as nickel,[2] palladium,[3] platinum,[4] rhodium,[5] and gold.[6] Despite extensive research in this area, to the best of our knowledge, rhodium-catalyzed addition of a carbon−nitrogen bond to alkynes has not been reported.

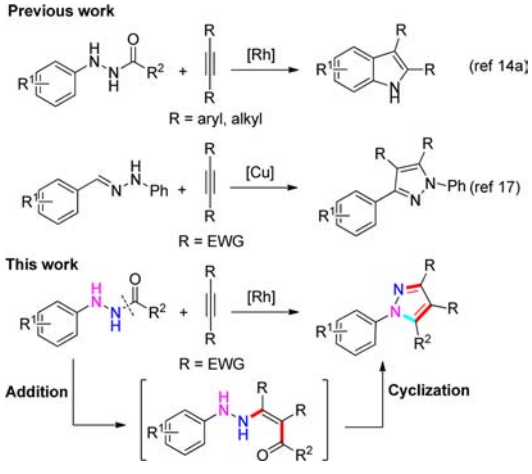
Substituted pyrazoles are important heterocyclic compounds used extensively in agrochemical and especially pharmaceutical applications.[7] For example, substituted pyrazoles form the core of several commercial drugs, including Celebrex,[8a,b] Acomplia,[8c] and Viagra,[8d] as well as the insecticide Fipronil.[8e] These pyrazoles display a broad spectrum of biological activities, including anti-inflammatory, analgesic, sedative, and hypnotic properties. They can also act as ligands in coordination compounds[9a] and serve as optical brighteners,[9b] UV stabilizers,[9c] and building blocks in supramolecular assemblies.[9d]

The functional versatility of pyrazoles has led organic chemists to explore different ways to construct them efficiently with diverse substitutions.[10,11] In these approaches, hydrazine has proven to be one of the most convenient and versatile starting materials.[12] In fact, hydrazines are important synthons for numerous structurally fascinating heterocyclics, which in turn can be transformed directly and efficiently into complex compounds.[13] Recently, Glorius,[14a] Hua,[14b] and Cheng[14c] independently synthesized indole by reacting hydrazine with alkynes in the presence of a rhodium catalyst. Subsequently, Kim[15] reported a rhodium-catalyzed oxidative olefination of 1,2-disubstituted arylhydrazines with alkenes to synthesize 2,3-dihydro-1*H*-indazoles. More recently, Wang[16] achieved the rhodium-catalyzed synthesis of 1-aminoindole from 2-acetyl-1-arylhydrazines and diazo compounds.

In 2011, Huang[17] reported the synthesis of pyrazoles by the copper-catalyzed [3 + 2] cycloaddition of phenylhydrazones and dialkyl ethylenedicarboxylates. As part of our ongoing interest in constructing heterocyclic compounds, we recently developed some efficient methods to synthesize useful molecules such as isochromen-1(1*H*)-one, isoquinolin-1(2*H*)-one, and dihydroisobenzofuran.[18] Here we continue these efforts by using hydrazine in a rhodium-catalyzed addition−cyclization cascade reaction with alkynes under mild reaction conditions, producing highly substituted pyrazoles via formal [3 + 2] cycloaddition involving unexpected C−N cleavage (Scheme 1).

Initially, *N*′-phenylacetohydrazide (**1a**) was treated with dimethyl but-2-ynedioate (**2a**) in the presence of $[Cp^*RhCl_2]_2$ (2.5 mol %) and AgOAc (25 mol %) in MeCN at 60 °C for 5 h. Interestingly, an unexpected product dimethyl 5-methyl-1-phenyl-1*H*-pyrazole-3,4-dicarboxylate (**3a**) was obtained in

Scheme 1. Rhodium-Catalyzed Reaction of Hydrazines with Alkynes



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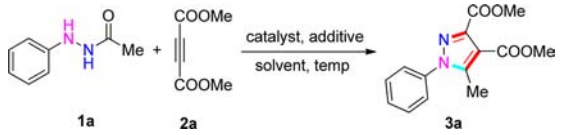
35% isolated yield (Table 1, entry 1). The structure was fully consistent with the reported data for ^{1}H and ^{13}C{^{1}H} NMR and

Table 1. Optimization of Reaction Conditions for Rhodium-Catalyzed Addition−Cyclization of Hydrazine (1a) with Alkyne (2a)[a]



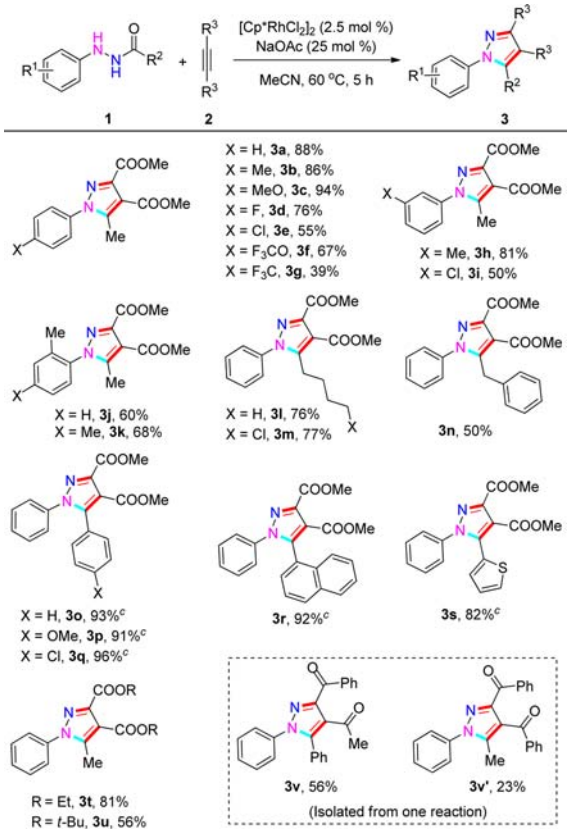
entry	additive	solvent	temp (°C)	yield (3a, %)[b]
1	AgOAc	MeCN	60	35
2	$AgSbF_6$	MeCN	60	ND
3	$Cu(OAc)_2·H_2O$	MeCN	60	71
4	CsOAc	MeCN	60	trace
5	KOAc	MeCN	60	22
6	NaOAc	MeCN	60	78
7	NaOAc	MeOH	60	52
8	NaOAc	CH_2Cl_2	60	62
9	NaOAc	1,2-DCE	60	46
10	NaOAc	THF	60	61
11	NaOAc	toluene	60	36
12[c]	NaOAc	MeCN	60	73
13[d]	**NaOAc**	**MeCN**	**60**	**88**
14	NaOAc	MeCN	25	46
15	NaOAc	MeCN	80	68
16[e]	NaOAc	MeCN	60	10
17[f]	NaOAc	MeCN	60	55
18[g]	NaOAc	MeCN	60	42
19[h]	NaOAc	MeCN	60	0
20[i]	NaOAc	MeCN	60	80

[a]Reaction conditions: **1a** (0.3 mmol), **2a** (0.33 mmol), $[Cp^*RhCl_2]_2$ (0.0075 mmol), NaOAc (0.075 mmol), MeCN (1.5 mL), 60 °C, 5 h, under N_2, unless otherwise noted. [b]Isolated yield. [c]**1a** (0.3 mmol) and **2a** (0.45 mmol) were used. [d]**1a** (0.45 mmol) and **2a** (0.3 mmol) were used. [e]$[Cp^*RhCl_2]_2$ (0.003 mmol) was used. [f]NaOAc (0.03 mmol) was used. [g]HOAc (0.3 mmol) was added. [h]Without $[Cp^*RhCl_2]_2$ catalyst. [i]**1a** (7.5 mmol), **2a** (5 mmol), $[Cp^*RhCl_2]_2$ (0.125 mmol), NaOAc (1.25 mmol), and MeCN (25 mL) were used.

mass spectrometry.[11h] Inspired by this result, we explored a variety of reaction conditions in order to optimize the catalytic process. When $AgSbF_6$ was used as the additive, the product **3a** was not detected, demonstrating the essential role of the acetate anion (entry 2). The additive $Cu(OAc)_2·H_2O$ led to the product **3a** in 71% yield (entry 3). Finally, NaOAc was found to be the best choice, giving **3a** in 78% yield (entries 4−6). Testing solvents showed that MeCN led to a higher yield of **3a** than did MeOH, CH_2Cl_2, 1,2-DCE, THF, and toluene (entries 7−11). Changing the **1a**:**2a** ratio from 1.0:1.1 to 1.0:1.5 led to a slightly decreased 73% yield, while inverting the ratio to 1.5:1.0 improved the yield to a satisfactory 88% (entries 12 and 13). Decreasing the reaction temperature of 60 to 25 °C or increasing it to 80 °C led to lower yields of **3a** (entries 14 and 15). Similarly, lowering the loading of catalyst or additive substantially reduced the product yield (entries 16 and 17). Adding 1.0 equiv of HOAc also reduced the yield to 42% (entry 18). A controlled experiment confirmed that the $[Cp^*RhCl_2]_2$ catalyst was essential for the formation of pyrazoles (entry 19). Notably, the reaction proceeded smoothly even on the gram scale, producing **3a** (1.1 g) in 80% yield (entry 20).

Using these optimized reaction conditions, we probed the scope and limitation of this cascade transformation (Scheme 2).

Scheme 2. Scope of Rhodium-Catalyzed Addition−Cyclization To Form Pyrazoles (3)[a,b]



[a]Reaction conditions: **1** (0.45 mmol), **2** (0.3 mmol), $[Cp^*RhCl_2]_2$ (0.0075 mmol), NaOAc (0.075 mmol), MeCN (1.5 mL), 60 °C, 5 h, under N_2, unless otherwise noted. [b]Isolated yield. [c]**1** (0.33 mmol) was used.

First we examined various substituted hydrazines for their ability to react with dimethyl but-2-ynedioate (**2a**) to form pyrazoles. *N*′-Phenylacetohydrazides with electron-donating Me or MeO at the *para* position of the benzene ring gave the corresponding products **3b** and **3c** in 86% and 94% yields, respectively. *N*′-Phenylacetohydrazides substituted with the electron-withdrawing groups F, Cl, CF_3O, or CF_3 gave substantially lower yields of products **3d**−**3g**. These results suggest that the catalytic reaction prefers electron-donating substituents over electron-withdrawing ones on the benzene ring of *N*′-phenylacetohydrazide. Consistent with this idea, substituting the R^1 position of *N*′-phenylacetohydrazide with *meta*-Me or *meta*-Cl and reacting with **2a** furnished the corresponding products **3h** and **3i** in 81% and 50% yield, respectively.

The *ortho*-Me substituted *N*′-phenylacetohydrazide also gave the desired product **3j** in a slightly lower 60% yield. This may reflect a steric hindrance that works against cyclization in the reaction mechanism. Nevertheless, the cascade reaction tolerated simultaneous Me substitution at both the *ortho* and *para* positions, affording product **3k** in 68% yield.

Next we investigated hydrazines with various substitutions at the R^2 position. Placing a long alkyl chain there led to pyrazoles **3l** and **3m** in 76% and 77% yields, whereas a benzyl substituent at that position gave product **3n** in only 50% yield. Adding a

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substituted aryl to the R^2 position gave the desired products **3o**–**3q** in 91–96% yields. Similarly, naphthyl- or thiophenyl-substituted hydrazines reacted well, giving products **3r** and **3s** in 92% and 82% yields, respectively. Single-crystal X-ray diffraction analysis of **3q** (Figure 1) was consistent with the

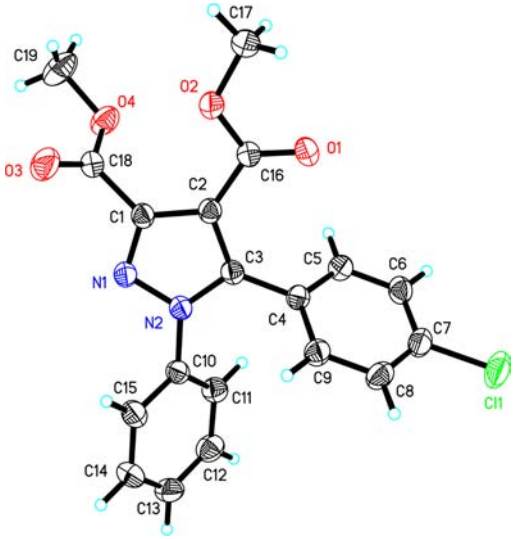


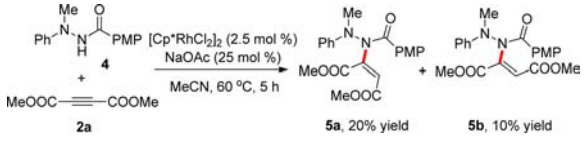
Figure 1. ORTEP diagram of cascade product **3q**.

desired product structure, confirming the predicted structures of the cascade reaction products. Note that the alkylhydrazines such as *N*′-octylacetohydrazide and 1-octyl-2-phenylhydrazine did not react with **2a** to afford the pyrazoles.

To further explore the flexibility of this cascade reaction, we tried to react *N*′-phenylacetohydrazide with various substituted alkynes. Reaction of **1a** with diethyl but-2-ynedioate gave pyrazole **3t** in 81% yield. Di-*tert*-butyl but-2-ynedioate also reacted with **1a** to afford the desired product **3u**, albeit in a slightly lower yield. Interestingly, the reaction of 1,4-diphenylbut-2-yne-1,4-dione with **1a** gave the mixture of pyrazoles **3v** and **3v**′ in 56% yield and 23% yield, respectively. This result revealed that the reaction proceeded via the intermediate with two ketone groups in the same carbon which then underwent intramolecular dehydration cyclization to genearate the products. However, the diaryl or alkyl acetylene tested did not afford pyrazoles under the optimized reaction conditions, and the substituted indoles can be detected in the reactions.[14a] Note that the unsymmetrical alkynes such as ethyl but-2-ynoate, ethyl 3-phenyl-propiolate, 4-phenylbut-3-yn-2-one, (((trifluoromethyl)sulfonyl)ethynyl)benzene, and 1-((trifluoromethyl)sulfonyl)oct-1-yne could not react with **1a** to give the corresponding pyrazoles.

To clarify the cascade reaction mechanism, a controlled experiment was carried out (Scheme 3). When 4-methoxy-*N*′-methyl-*N*′-phenylbenzohydrazide (**4**) was reacted with dimethyl but-2-ynedioate (**2a**) under optimized reaction conditions, the

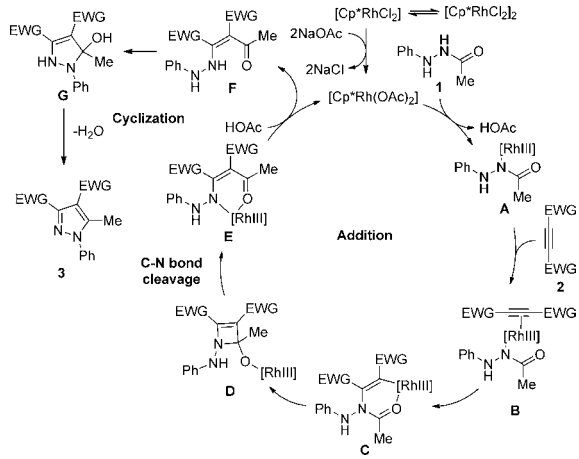
Scheme 3. Experimental Investigation of the Reaction Mechanism



addition products **5a** and **5b** were obtained in 30% yield as isomers (**5a**:**5b** = 2.0:1.0). The structures of both isomers were verified by single-crystal X-ray diffraction analysis (see Supporting Information). This result indicates that the amide N–H bond in substrate **4** undergoes addition with alkyne **2a** to form a C–N bond and suggests that the formal [3 + 2] cycloaddition proceeds via C–N bond cleavage to afford the pyrazole.

On the basis of the experimental results and previous studies of hydrazines that undergo reactions catalyzed by [Cp*Rh-Cl_2]$_2$,[14–16] we tentatively propose a mechanism for the cascade reaction (Scheme 4), although no active intermediate was

Scheme 4. Proposed Mechanism of Rhodium-Catalyzed Addition–Cyclization of Hydrazines with Alkynes



isolated directly. First, [Cp*$RhCl_2$] reacts with NaOAc to form the active catalyst [Cp*Rh$(OAc)_2$]. This promotes the deprotonation of NH in the hydrazine to form the intermediate **A**, which subsequently undergoes alkyne coordination to generate intermediate **B**. Then intramolecular insertion generates the six-membered [C–Rh–O] complex **C**, which undergoes intramolecular nucleophilic addition to form intermediate **D** with a four-membered ring. The following ring opening cleaves the C–N bond to form the six-membered [N–Rh–O] complex **E**. After the protonation, the intermediate **F** can be formed and the active catalyst [Cp*Rh$(OAc)_2$] is regenerated. Finally, the cyclization of **F** proceeds via intramolecular nucleophilic addition and dehydration to afford the desired pyrazole product.

In summary, we have developed a mild and efficient rhodium-catalyzed addition–cyclization cascade reaction of hydrazines with alkynes to afford highly substituted pyrazoles. The formal [3 + 2] cycloaddition was found to involve the addition of a C–N bond to alkyne, subsequent cleavage of the C–N bond, and finally cyclization. This transformation provides a highly concise and effective protocol to construct the substituted pyrazoles, and it may expand the usefulness of transition-metal-catalyzed heterocycle synthesis.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures, characterization data, ^{1}H and ^{13}C NMR spectra for all compounds, and the X-ray crystallographic data of **3q**, **5a**, and **5b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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