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Rh(III)-Catalyzed Synthesis of *N*-Unprotected Indoles from Imidamides and Diazo Ketoesters via C−H Activation and C−C/C−N Bond Cleavage

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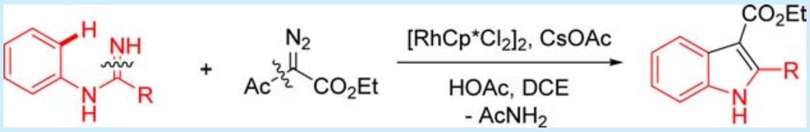
Supporting Information



ABSTRACT: The synthesis of *N*-unprotected indoles has been realized via Rh(III)-catalyzed C−H activation/annulation of imidamides with α-diazo β-ketoesters. The reaction occurs with the release of an amide coproduct, which originates from both the imidamide and the diazo as a result of C═N cleavage of the imidamide and C−C(acyl) cleavage of the diazo. A rhodacyclic intermediate has been isolated and a plausible mechanism has been proposed.

Arguably, indoles are one of the most important heterocycles widely present in natural products, pharmaceuticals, and agrochemicals.[1] Therefore, numerous efficient methodologies to access this motif have been developed,[2] the majority of which involve Fischer-type indole synthesis.[3] In addition, metal-catalyzed cyclization of *o*-alkynylanilines,[4] annulation of *ortho*-halogenated anilines with alkynes,[5] reductive cyclization of 2-substituted nitroarenes,[6] and other coupling/condensation cascades are also well-known.[7] However, most of these approaches still suffer from limited availability or high cost of starting materials.

Recently, transition-metal-catalyzed C−H bond activation has emerged as an important strategy in organic syntheses,[8] and several indole syntheses via C−H activation have been reported. Takemoto reported synthesis of indoles via activation of benzylic C−H bonds and insertion into isocyanides.[9] Cross-dehydrogenative coupling reactions have also been employed as useful synthetic tools for indoles.[10] In 2008, Fagnou and co-workers reported an elegant Rh(III)-catalyzed intermolecular oxidative annulation between internal alkynes and acetanilides to access *N*-protected indoles.[11] Afterward, Pd-, Rh-, and Ru-catalyzed indole syntheses via C−H activation were widely explored under oxidative or redox-neutral conditions.[12] For example, the Glorius group reported a Rh(III)-catalyzed C−H activation/cyclization approach to access NH indoles by taking advantage of an oxidizing directing group.[12f] Very recently, Wan and co-workers developed a regioselective synthesis of unsymmetrically 2,3-disubstituted NH indoles via Rh(III)-catalyzed annulation of nitrones with symmetrical alkynes.[12i] Despite these significant advances, direct access to unsymmetrically 2,3-disubstituted protic indoles using a C−H activation strategy still needs further exploration.

It has been recently demonstrated that rhodium- and iridium-catalyzed C−H activation of arenes bearing a protic directing group in the coupling with diazo compounds occurred under redox-neutral conditions to furnish various heterocycles.[13] On the other hand, in the rhodium(III)-catalyzed oxidative annulation between imidamides and alkynes, the steric bulk of the *C*-phenyl of imidamides has a significant influence on the reaction selectivity.[14] As a continuation of our interest in Rh(III)-catalyzed C−H activation of arenes and construction of heterocycles,[15] we reasoned that changing the *C*-aryl of imidamides to a *C*-alkyl group may favor the selectivity of the C−H activation at the *N*-aryl ring, leading to efficient indole synthesis. We now report a convenient, redox-neutral approach to synthesize unprotected indoles via Rh(III)-catalyzed C−H activation of imidamides in the coupling with diazo compounds, and this reaction occurred with cleavage of C−C and C═N bonds.

We initiated our investigations with the coupling of *N*-phenylacetimidamide (**1a**) with ethyl 2-diazo-3-oxobutanoate (**2a**) using $[RhCp^*Cl_2]_2$ as a catalyst in the presence of CsOAc. To our delight, indole **3aa** was isolated in 56% yield (Table 1, entry 1). Employment of other bases such as NaOAc and CsOPiv gave lower yields (entries 2 and 3). Further screening of solvents revealed that acetone, MeCN, and MeOH were inferior to DCE (entries 4−6). Gratifyingly, addition of HOAc (0.2 equiv) resulted in formation of desired product **3aa** in 74% yield (entry 7). This encouraged us to further increase the amount of HOAc. Product **3aa** was isolated in 79% yield when the amount of HOAc was increased to 0.5 equiv (entry 8), and the optimal yield (89%) was obtained when 1.5 equiv of HOAc was introduced (entries 9). Control experiments revealed that no reaction occurred when the rhodium catalyst was omitted (entry 11). Thus, the following conditions were eventually established for subsequent studies: $[RhCp^*Cl_2]_2$ (4 mol %), CsOAc (30 mol %), and HOAc (1.5 equiv) in DCE at 80 °C for 12 h.

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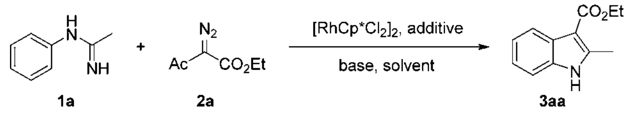
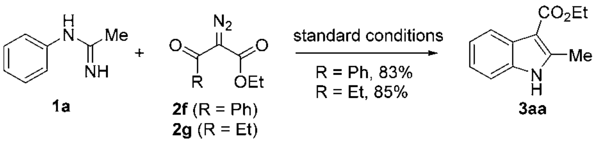
Table 1. Screening of Reaction Parameters[a]



entry	additive (equiv)	base	solvent	yield[b] (%)
1		CsOAc	DCE	56
2		NaOAc	DCE	42
3		CsOPiv	DCE	27
4		CsOAc	acetone	31
5		CsOAc	MeCN	38
6		CsOAc	MeOH	<5
7	HOAc (0.2)	CsOAc	DCE	74
8	HOAc (0.5)	CsOAc	DCE	79
9	HOAc (1.5)	CsOAc	DCE	89
10	HOAc (2.0)	CsOAc	DCE	88
11[c]	HOAc (1.5)	CsOAc	DCE	nd

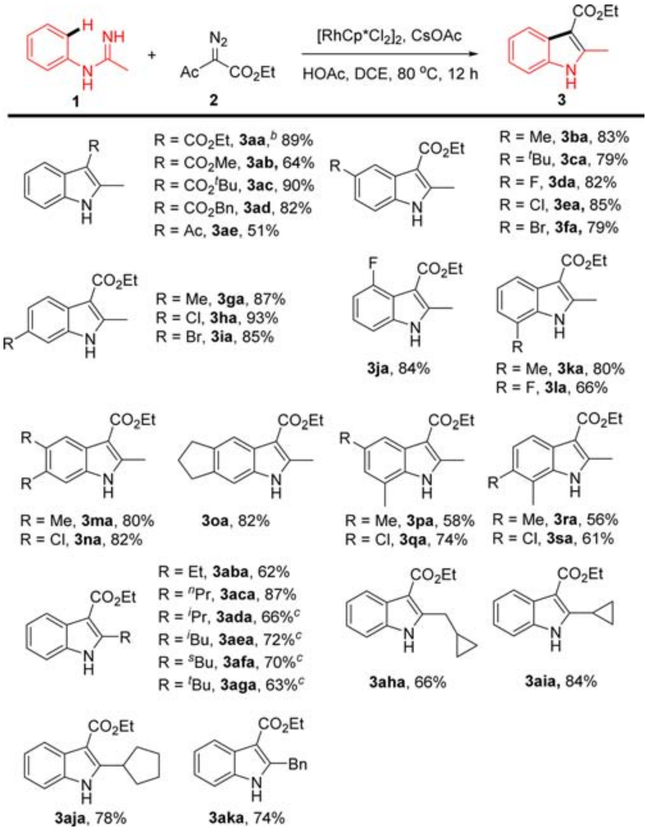
[a] Reaction conditions: **1a** (0.2 mmol), **2a** (1.5 equiv), $[RhCp^*Cl_2]_2$ (4 mol %), additive, base (30 mol %), solvent (2 mL), at 80 °C for 12 h. [b] Isolated yield. [c] No $[RhCp^*Cl_2]_2$ was used.

With the optimized reaction conditions in hand, we first examined the scope and limitations of the diazo substrate in the coupling with **1a** (eq 1 and Scheme 1, **3aa**−**ae**). Surprisingly, the couplings of ethyl 2-diazo-3-oxo-3-phenylpropanoate (**2f**) and ethyl 2-diazo-3-oxopentanoate (**2g**) with **2a** all afforded the same product (**3aa**) in good yields (eq 1). Furthermore, benzamide was detected as a coproduct by GC−MS in the coupling of **1a** with **2f**, suggesting the relevancy of C−N bond cleavage of imidamides and C−C(acyl) bond cleavage of diazo compounds.[16] Thus, the coupling for symmetrical α-diazo acetylacetone (**2e**) and other unsymmetrical diazo compounds delivered protic indoles in 51−90% yields (**3ab**−**ae**). We next investigated the scope of the imidamide substrate (Scheme 1). Acetimidamides bearing methyl, *tert*-butyl, and halo group at the *para* position of the *N*-phenyl ring all underwent smooth coupling and afforded indoles **3ba**−**fa** in 79−89% yields. Acetimidamides bearing methyl and halo group at the *meta* position also reacted smoothly in good yields (**3ga**−**ja**), and the coupling occurred at the less hindered *ortho* site. However, C−H activation occurred exclusively at the more hindered *ortho* site for a *m*-fluoro-substituted imidamide (**1j**), as elucidated from ^{1}H and ^{13}C NMR spectroscopic analyses of **3ja**. Moreover, *ortho*-substituted imidamides are also applicable as in the isolation of products **3ka** and **3la** in 80% and 66% yields, respectively. Notably, several imidamides bearing two substituents (**1m**−**s**) in the phenyl ring have also been examined, affording the corresponding indoles (**3ma**−**sa**) in moderate to good yields and in high regioselectivity. In addition, the cyclization system could be extended to other *N*-phenylalkylimidamides (**1ab**−**ak**), furnishing the desired products in moderate to good yields (**3aba**−**aka**). In some cases, the imidamide was used in excess to facilitate the isolation of the products **3ada**−**aga**. In contrast to these efficient couplings, *N*-phenylbenzimidamide only reacted with poor efficiency under the standard conditions.



(1)

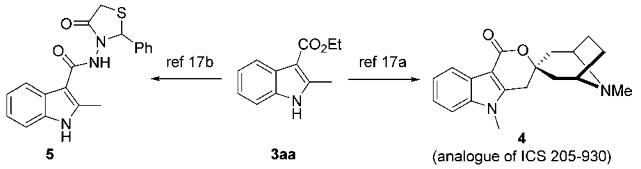
Scheme 1. Rh(III)-Catalyzed Synthesis of *N*-Unprotected Indoles[a]



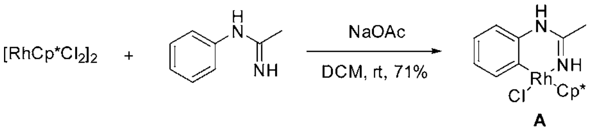
[a] Reaction conditions: **1** (0.3 mmol), **2** (0.45 mmol), $[RhCp^*Cl_2]_2$ (4 mol %), CsOAc (30 mol %), HOAc (0.3 mmol), DCE (3 mL), at 80 °C for 12 h, isolated yields. [b] The reaction of **1a** with ethyl 2-diazo-3-oxo-3-phenylpropanoate (**2f**) or ethyl 2-diazo-3-oxopentanoate (**2g**) afforded **3aa** in 83% and 85% isolated yields, respectively. [c] **1** (0.36 mmol) and **2** (0.3 mmol) were used.

The synthetic applications of indoles have been well-documented. For example, **3aa** could be converted to **4**, an analogue of the seroonin antagonist ICS 205-903 and to **5** that is known to exhibit anti-inflammatory and analgesic activities (Scheme 2).[17]

Scheme 2. Synthetic Utilities of an Indole Product



To probe the reaction mechanism, several experiments have been performed. An intermolecular competitive reaction has been performed using an equimolar mixture of **1a** and **1a**-d_5 in the coupling with **2a**. ^{1}H NMR analysis of the product mixture revealed a kinetic isotope effect (KIE) of 3.3 at a low conversion, indicating that the C−H bond cleavage may be involved in the turnover-limiting step (see the SI). In another experiment, a stoichiometric reaction between **1a** and $[RhCp^*Cl_2]_2$ was performed in the presence of NaOAc from which a rhodacyclic complex (**A**) was isolated in 71% yield (eq 2 and Figure 1).



(2)

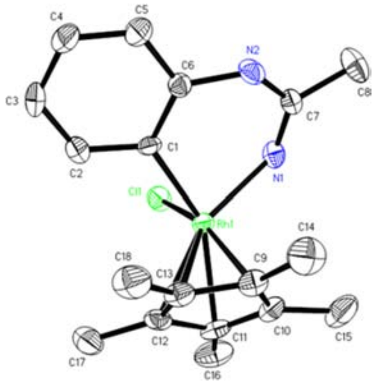
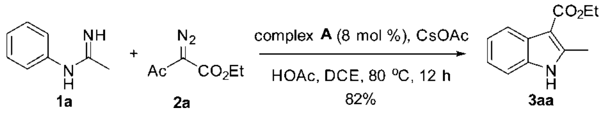


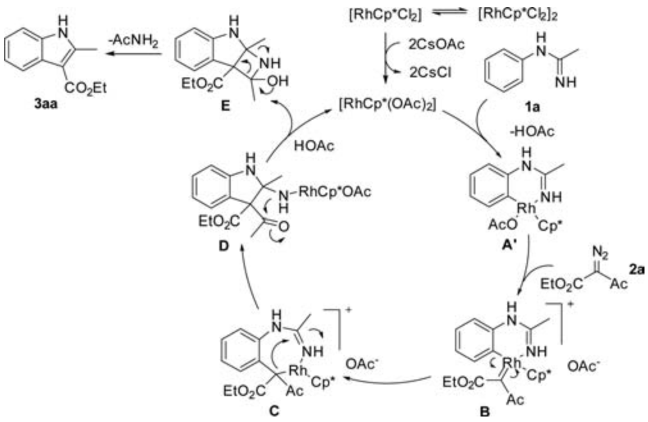
Figure 1. ORTEP drawing of the molecular structure of complex **A** (hydrogen atoms were omitted for clarity).

Complex **A**, which has been fully characterized by NMR, mass spectrometry, and X-ray crystallography, proved to be an active catalyst because when it was designated as a catalyst (8 mol %) for the coupling of **1a** with **2a**, the product **3aa** was isolated in a comparable yield (82%, eq 3).



(3)

Scheme 3. Proposed Mechanism



On the basis of these observations and literature precedents,[12i,13i] a plausible mechanism is given in Scheme 3. First, an active catalyst $[\mathrm{RhCp^*(OAc)_2}]$ is generated through anion exchange. Coordination of **1a** to the catalyst and subsequent cyclometalation generate a rhodacyclic intermediate **A′**. Coordination of the diazo substrate followed by elimination of nitrogen gives a rhodium carbene species **B**, the Rh−Ar bond of which is proposed to undergo migratory insertion into the carbene unit to generate an intermediate **C**. The Rh−C(alkyl) bond then undergoes migratory insertion into the C═N bond to afford an amide species **D**. The active Rh(III) catalyst and an intermediate **E** are released from **D** upon protonolysis and intramolecular nucleophilic addition. The product **3aa** is eventually formed from **E** by elimination of one molecule of $AcNH_2$.

In summary, we have developed a redox-neutral and efficient synthetic route to access *N*-unprotected indoles by Rh(III)-catalyzed C−H activation of readily available imidamides in the coupling with *α*-diazo *β*-ketoesters. This reaction proceeded under relatively mild conditions with broad substrate scope. Interestingly, this coupling occurred with the release of a molecule of amide, which originated from the nitrogen of the imidamide and the acyl group of the *α*-diazo *β*-ketoester as a result of the C═N cleavage of the imidamide and C−C(acyl) cleavage of the diazo. The coupling occurred via a C−H activation mechanism with the isolation of a rhodacyclic intermediate. This method to access unprotected indoles and the cleavage of C−C bond of diazos may find applications in the synthesis of complex structures.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b03669.

Crystallographic data of complex **A** (CIF)

Experimental procedure, characterization of the products, and copies of the ^{1}H and ^{13}C NMR spectra of selected products (PDF)

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Notes

The authors declare no competing financial interest.

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