Heterocycles

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Rhodium(III)-Catalyzed Cyclative Capture Approach to Diverse 1-Aminoindoline Derivatives at Room Temperature**

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In memory of Ekkehard Winterfeldt

Abstract: *A Rh^{III}-catalyzed C–H activation/cyclative capture approach, involving a nucleophilic addition of $C(sp^3)$–Rh species to polarized double bonds is reported. This constitutes the first intermolecular catalytic method to directly access 1-aminoindolines with a broad substituent scope under mild conditions.*

The 1-aminoindoline unit is prevalent in numerous commercial drugs and biologically active compounds (Figure 1),[1] and has also been widely utilized as a chemical feedstock to access a large number of important skeletal motifs.[2] 1-Aminoindolines are typically formed by the nitrosylation/reduction of free indolines or by intramolecular amination.[3] These methods suffer from disadvantages such as multistep syntheses, moderate to poor yields, harsh reaction conditions, and limited substrate scope. Moreover, indoline as the parent heterocycle must be prepared in advance.[4] To date, no intermolecular catalytic method is available to directly access the 1-aminoindoline core.[5]

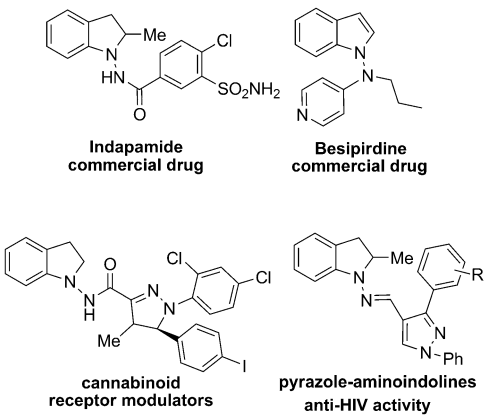

Figure 1. Some biologically active 1-aminoindolines and -indoles.

Rh^{III}-catalyzed directed C–H functionalization has emerged as a versatile synthetic approach to access complex molecules.[6] Recently, several groups have demonstrated that $C(sp^2)$–Rh intermediates formed by insertion of alkynes into the C–Rh bond could undergo Grignard-type addition to ketone-, imine-, amide-, and ester-based directing groups (Figure 2 A).[7] However, the nucleophilic attack of $C(sp^3)$–Rh species, generated upon alkene insertion, to polarized double bonds has never been reported, presumably due to problematic preferential β-hydride elimination (Figure 2 B).[8] We wondered whether nucleophilic additions of $C(sp^3)$–Rh species to polarized unsaturated directing groups might be possible if β-hydride elimination is inhibited. Herein, we introduce diazenecarboxylate as a directing group to trigger a new cyclative capture approach where alkenes undergo insertion followed by intramolecular addition of the $C(sp^3)$–Rh species to the N=N bond to afford diverse 1-aminoindolines without any external oxidants (Figure 2 C). This reaction proceeds at room temperature with a wide range of functionalized substrates, and, moreover, has been extended to the synthesis of pharmaceutically important 1-aminoindoles.

Besides disfavoring β-hydride elimination of the $C(sp^3)$–Rh species, two other potential difficulties must be overcome:

1) Even though 1,2-diaryl- and 1-alkyl-2-aryl-substituted diazenes have been used as directing groups, diazenecarboxylate has never been used as a directing group;[9]
2) Although the addition of organometallic reagents to N=N bonds has been reported,[10] it has not been observed in Rh^{III}-catalyzed C–H activation. Furthermore, the issue of regioselectivity in additions to N=N bonds must also be addressed.

We initially focused on the reaction of *tert*-butyl 2-phenyldiazenecarboxylate **1a** and *n*-butyl acrylate (**2a**) with $[(Cp^*RhCl_2)_2]$ (2.5 mol%) in 1,2-dichloroethane (DCE, 1 mL). After extensive screening, we found that the tandem C–H bond activation/N=N bond addition occurred smoothly in the presence of $[\{RhCp^*Cl_2\}_2]$ (2.5 mol%; $Cp^* = C_5Me_5$) and AgOAc (10 mol%) in a mixture of HOAc and DCE (1:3) at room temperature for 24 h to afford 1-aminoindoline **3a** in 88% yield. To confirm the structure, we further converted the oily **3a** to the corresponding 1-aminoindole which formed single crystals suitable for X-ray analysis (see the Supporting

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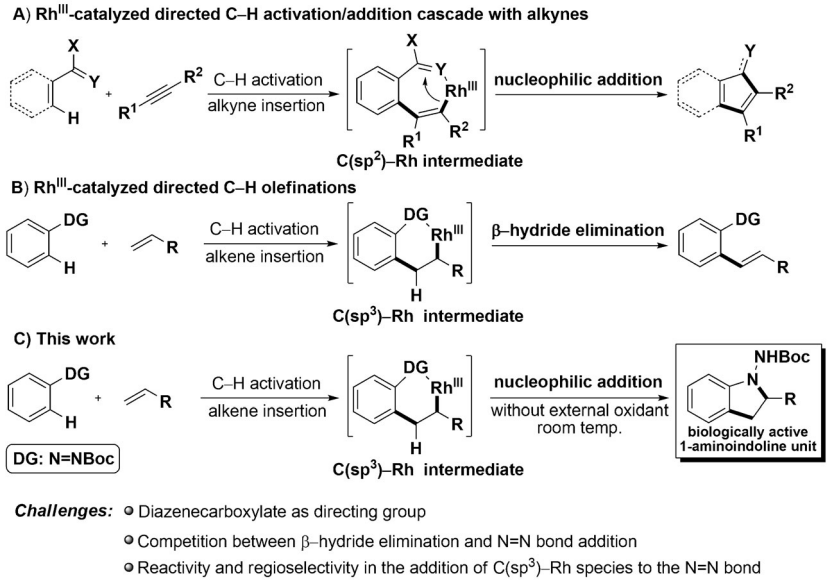
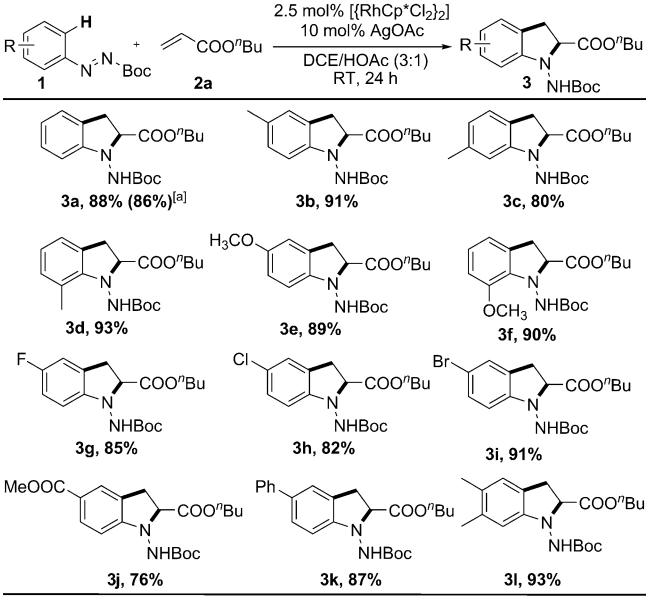


Figure 2. Examples of β-hydride elimination and Grignard-type additions in Rh^{III}-catalyzed C–H functionalization reactions.

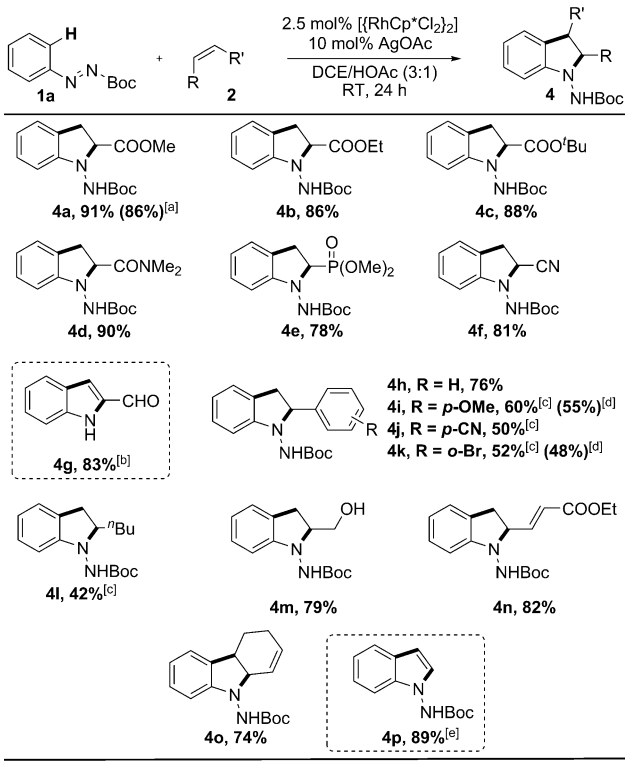
Information).[11] Subsequently, the scope of the aryl-substituted diazenecarboxylate substrates was investigated. A series of 1-aminoindolines bearing substituents at the 5-, 6-, and/or 7-positions were synthesized in good yields (Scheme 1; **3a**–**l**). A variety of important functional groups such as halogens (F, Cl, and Br), ester, and methoxy groups were well tolerated (Scheme 1; **3e**–**j**). In addition, we proved that the reaction can be conducted on a gram scale without a significant decrease in yield (ca. 0.9 g of **3a**, 86% yield). It is also worth noting that a remarkable yield was also obtained with a lower catalyst loading (85% yield, 1 mol% [{RhCp*Cl_2}$_2$]).



Scheme 1. Scope of aryl-substituted diazenecarboxylates. Reaction conditions: **1** (0.2 mmol), **2a** (1.5 equiv); see SI. [a] 3.0 mmol scale.

We next examined the scope of the alkenes (Scheme 2). A variety of electron-deficient alkenes could be efficiently converted into the corresponding products (Scheme 2; **4a**–**f**). Unexpectedly, the reaction with acrolein directly afforded the indole-2-carbaldehyde **4g**.[12] Moreover, various substituted styrenes also reacted with **1a** to furnish the products in moderate yields (Scheme 2; **4h**–**k**). In addition to styrenes, alkyl alkenes could also give the desired products (Scheme 2; **4l**,**m**). It is important to note that 1,3-dienes are well-tolerated in this reaction (Scheme 2; **4n**,**o**). Interestingly, when we switched the substrate to vinyl acetate, we could directly access the aminoindole product **4p** in excellent yield; this reaction might involve an elimination of acetic acid after cyclization.[13]

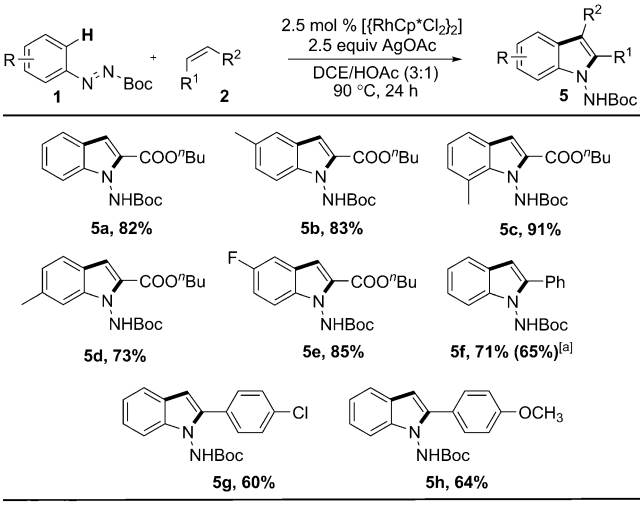
To date, synthetic approaches to 1-aminoindoles, which also display very important pharmacological properties,[14] have been quite limited.[15] We wondered if we could utilize the present transformation for the straightforward synthesis of 1-aminoindoles by introducing an additional oxidant. We found that 1-aminoindole **5a** could be formed when AgOAc was used as the external oxidant under the standard conditions. Further optimization lead to



Scheme 2. Scope of alkenes. Reaction conditions: **1** (0.2 mmol), **2** (1.5 equiv); see SI. [a] 3.0 mmol scale. [b] Acrolein was used. [c] 0.4 mmol scale. [d] 2.5 mmol scale. [e] Vinyl acetate was used.

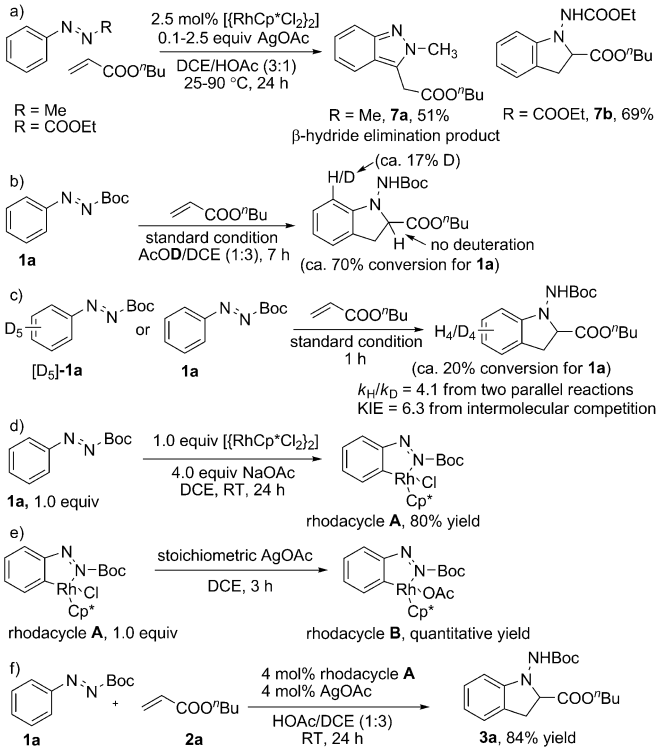
82% yield when the reaction temperature was increased to 90°C. Using this procedure, a variety of aryl-substituted diazenecarboxylates and alkenes were tested to access various 1-aminoindoles. As shown in Scheme 3, the desired products were generally obtained in good yields.

Furthermore, we demonstrated the synthetic usefulness of the 1-aminoindolines by conducting five additional transformations with our products (Scheme 4). First, the N–N bond of the 1-aminoindoline was easily cleaved to yield the free indolines **6a**,**b** using $TiCl_3$.[16] We could also submit compound **4h** to an initial deprotection, followed by a photocatalytic oxidation with $[Ir\{dF(CF_3)ppy\}_2(dtbbpy)]PF_6$ (dF-(CF_3)ppy = 2-(2,4-difluorophenyl)-5-trifluoromethylpyridine, dtbbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine), visible light, and air to afford the free indole **6c**.[17] Cinnoline **6d** could also be prepared from 2-phenyl-1-aminoindole in good yield.[18] The tetracyclic fused indole skeleton **6e**, which exists in numerous privileged pharmaceuticals and natural alkaloids,[2g–i] could also be constructed from 1-aminoindoline by a Fischer indole synthesis (Scheme 4; **6e**). In addition, we also made the backbone of indolo[1,2-*b*]indazoles, which have been shown to be potent inhibitors to DNA topoisomerases I and II (Scheme 4; **6f**).[19]

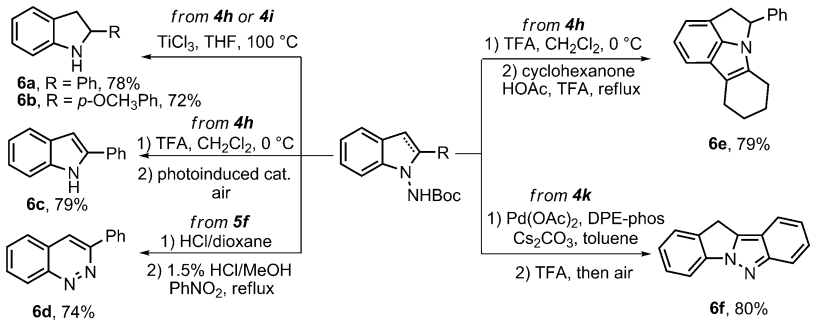


Scheme 3. Synthesis of 1-aminoindoles. Reaction conditions: **1** (0.2 mmol), **2** (1.5 equiv); see SI. [a] 3.0 mmol scale.

A series of mechanistically insightful experiments were carried out. First, we submitted 1-methyl-2-phenyldiazene as the substrate to the standard conditions with *n*-butyl acrylate (Scheme 5a). The β-hydride elimination takes place preferentially to afford the product **7a** in moderate yield.[20] However, if we change the Boc group to -COOEt, the cyclative capture step occurs smoothly to afford 1-aminoindoline **7b** in 69% yield (Scheme 5a). These observations imply that the carboxyl substituent in our directing group might be crucial in precluding β-hydride elimination. When the reaction was performed with AcOD to roughly 70% conversion, deuterium incorporation was observed at the C7-position of **3a** (Scheme 5b). This deuteration might be induced by reversible C–H activation or acid-catalyzed tautomerism. Also, deuterium incorporation was not observed at the C2-position of the product (Scheme 5b),



Scheme 5. Mechanistic experiments.



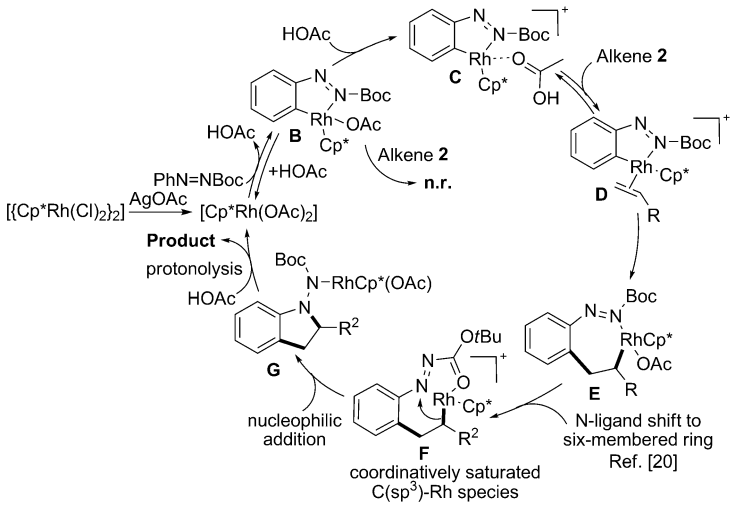
Scheme 4. Applications of 1-aminoindolines/1-aminoindoles. DPE-phos = Bis[(2-diphenylphosphino)phenyl] ether, TFA = trifluoroacetic acid.

which indicates that migratory insertion of alkene might be irreversible. Furthermore, deuterium incorporation was also observed using substrate **1a** in AcOD/DCE in the absence of Rh catalyst implying that the acid-catalyzed tautomerism might occur during the reaction (see SI). The kinetic isotope effect (KIE) experiment was also carried out to independently assess the rate of reaction for *ortho*-C–H versus *ortho*-C–D activation. The value of $k_H/k_D = 4.1$ from two parallel reactions as well as the value of KIE = 6.3 from intermolecular competition indicated

that the C–H bond-cleavage process is likely involved in the rate-determining step (Scheme 5c).[21] Additionally, it was observed that the reactivities of aryl-substituted diazenecarboxylates with an electron-donating substituent (e.g., OCH_3) are obviously higher than those with an electron-withdrawing substituent (e.g., *p*-COOMe), which is consistent with an electrophilic
C–H activation mechanism.[22]

Furthermore, we prepared the rhodacycle **A** (Scheme 5d),[23] which can be easily transformed to rhodacycle **B** in the presence of stoichiometric silver acetate (Scheme 5e). Importantly, when 4 mol% rhodacycle **A** served as the catalyst in the presence of 4 mol% AgOAc in HOAc/DCE (1:3) at RT, the reaction of **1a** and **2a** works efficiently (Scheme 5f), suggesting the plausible intermediacy of a cyclometalated complex **B** in the catalytic cycle. Furthermore, we monitored the reaction of rhodacycle **B** with methyl acrylate in CD_2Cl_2 by ^1H NMR spectroscopy (see SI). No reaction was observed in the absence of HOAc. When HOAc was added to the reaction system, the signal of product **4a** was detected immediately. Presumably HOAc promotes the dissociation of the coordinated acetate of rhodacycle **B** to form the key intermediate cation **C** to initiate this reaction.[22]

On the basis of our preliminarily mechanistic experiments and literature precedence,[6,7] we propose that a directed C–H bond cleavage forms intermediate **B** as the first step after generation of $[RhCp^*(OAc)_2]$. An acetate ligand of rhodacycle **B** dissociates to give the cationic complex **C** with assistance from HOAc;[22] this is followed by alkene coordination and insertion, thus affording the rhodacycle **E** (Scheme 6). The resulting seven-membered metallacycle presumably rearranges to the more stable six-membered coordinately saturated Rh species **F** by chelation with the Boc substituent,[24] which efficiently prevents competitive β-hydride elimination.[25] Complex **F** might undergo a nucleophilic addition to the N=N bond to form intermediate **G**, which is finally protonated by HOAc to yield the desired 1-aminoindoline.



Scheme 6. Proposed reaction mechanism.

In summary, we have developed the first Rh^{III}-catalyzed synthesis of 1-aminoindolines and 1-aminoindoles from aryl-substituted diazenecarboxylates and alkenes. Mechanistic studies support a pathway that proceeds via reversible C–H activation, alkene insertion, and Grignard-type addition. This intermolecular annulation proceeds under mild conditions, does not require external oxidants, and displays a broad scope with respect to the substituents.

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Keywords: C–H functionalization · directing groups · heterocycles · indolines · rhodium

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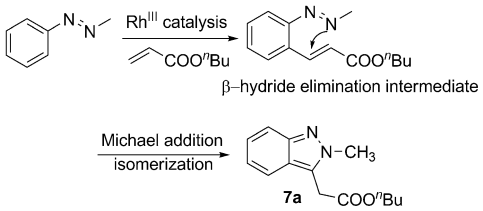

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Communications

Heterocycles

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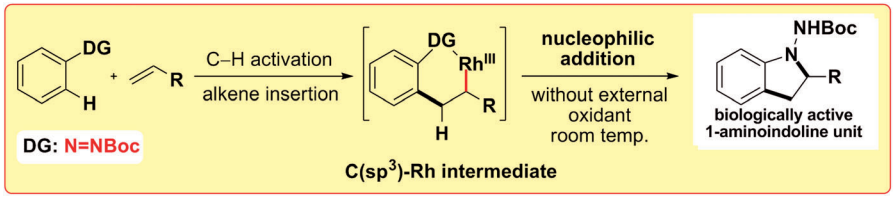
Rhodium(III)-Catalyzed Cyclative Capture Approach to Diverse 1-Aminoindoline Derivatives at Room Temperature



Buckle up! The nucleophilic addition of C(sp^3)–Rh species to polarized double bonds is the key step in a Rh^{III}-catalyzed C–H activation/cyclative capture reaction. This constitutes the first intermolecular catalytic method to directly access the 1-aminoindoline core with a broad substituent scope under mild conditions (Boc = *tert*-butoxycarbonyl, DG = directing group).

