

C–H Activation

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Catalyst-Controlled Regiodivergent Alkyne Insertion in the Context of C–H Activation and Diels–Alder Reactions: Synthesis of Fused and Bridged Cycles

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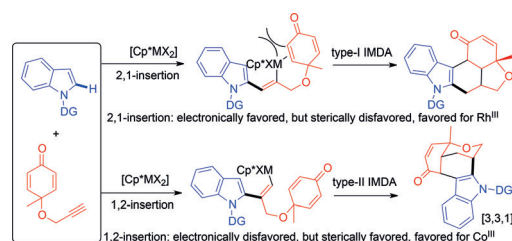
Abstract: Rhodium(III)- and cobalt(III)-catalyzed C–H activation of indoles and coupling with 1,6-enynes is discussed. Under rhodium(III) catalysis, the alkyne insertion follows 2,1-regioselectivity with a subsequent type-I intramolecular Diels–Alder reaction (IMDA) to afford [6,5]-fused cycles. When catalyzed by the cobalt(III) congener, 1,2-insertion of the alkyne is preferred, and followed by a rare type-II IMDA, thus leading to bridged [3,3,1]-cycles. This selectivity of the alkyne insertion was mainly tuned by the steric sensitivity of the catalyst.

C–H activation of arenes, especially using [Cp**Rh*^{III}] and [Cp**Co*^{III}] catalysts, has been established as an important strategy in the construction of important complex molecules such as polycycles^[1] owing to sufficient metal–substrate interactions. In general, they are accessed by C–H activation/intramolecular couplings,^[2] sequential twofold C–H activation and couplings,^[3] and C–H activation/coupling with π -bonds and further interactions with a proximal group in the arene.^[4] Given the power of cycloaddition reactions in synthesis of cyclic products, it is desirable to integrate C–H activation with cycloaddition reactions. However, examples are rather limited.^[5]

We recently reported a C–H activation/intramolecular 1,3-dipolar addition assisted by a nitron directing group (DG).^[5c] Despite the progress, only dipolar addition was accommodated because of the specificity of the DG. Thus, we resorted to the combination of C–H activation with Diels–Alder (DA) reactions to solve the limitation. In this strategy, a diene moiety is constructed by C–H activation and alkyne insertion.^[6] As an important C–C forming process for alkynes,^[7] the regioselectivity of alkyne insertion constitutes a fundamental issue. For a 1-alkyne, the insertion can follow the regioselectivity of either 2,1-insertion [C(aryl)–C1 coupling] or 1,2-insertion [C(aryl)–C2 coupling]. Previously, regioselectivity of alkyne insertion mostly relied on substrate control, and the 2,1-insertion is commonly encountered,^[7]

although the 1,2-insertion seems more sterically accessible. In fact, controlling the regioselectivity^[8] of alkyne insertion is important not only in determining the regioisomer of the product but also in the outcome of subsequent DA reactions.

The groups of Glorius and Chang independently reported differences of [Cp**Rh*^{III}] and [Cp**Co*^{III}] catalysts in terms of Lewis acidity and steric effects.^[9] We reasoned that besides being a more Lewis-acidic catalyst,^[6b,10] the smaller radius of a cobalt(III) center renders it more sensitive to steric perturbation,^[9a] and it may favor the less common 1,2-insertion (Scheme 1). Although alkyne insertion has been



Scheme 1. Design of divergent couplings of indoles with 1,6-enynes. Cp* = C₅Me₅.

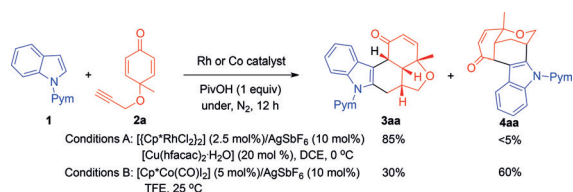
reported under cobalt(III) catalysis, the regioselectivity was not tunable, and catalytic annulation reactions were limited to either SN-type coupling^[10,11] or oxidative coupling with an nucleophilic DG.^[12] To address the limitation, we focused on 1,6-enynes^[4d,13] as has been reported by Lin and Tian in C–H activation.^[4d] Our initial objective was to introduce both an olefin and a dienophile moiety using this reagent. Thus, starting from an indole as a C–H substrate, regio- and stereoselective olefination to create an electron-rich diene is ideally realized under catalyst control, and sets up two types of intramolecular DA (IMDA) reactions (Scheme 1). In particular, the type-II IMDA following the 1,2-insertion is highly challenging because of Bredt's rule in the formation of [3,3,1]-bridged cycles (Scheme 1), which have been mostly limited to gas-phase reactions.^[14] We now report divergent couplings of indoles with 1,6-enynes, thus leading to construction of both fused and bridged cycles.

We commenced our exploration with optimization studies on the coupling of *N*-pyrimidylindole (**1a**) with the 1,6-enyne **2a** (Scheme 2 and see the Supporting Information). A reaction did occur, even at room temperature, when catalyzed by a [Cp**Rh*^{III}] complex, thus affording the isomeric products **3aa** and **4aa** in high total yield. The product **3aa** was identified as an all-*cis* 6,5-fused polycycle bearing four continuous stereogenic centers, while **4aa** was established as

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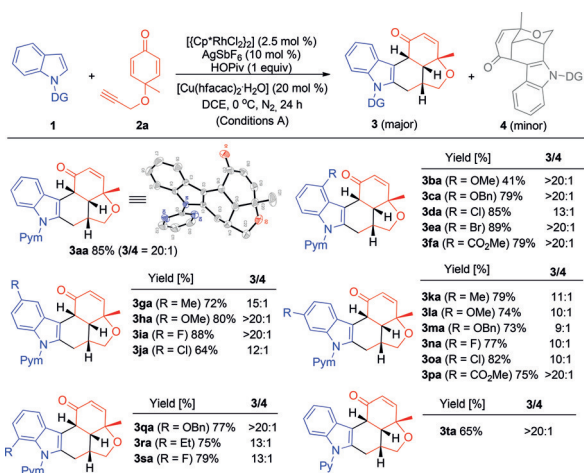


Scheme 2. Catalyst-controlled synthesis of bridged and fused cycles. DCE = 1,2-dichloroethane, hfacac = hexafluoroacetylacetonate, Piv = pivaloyl.

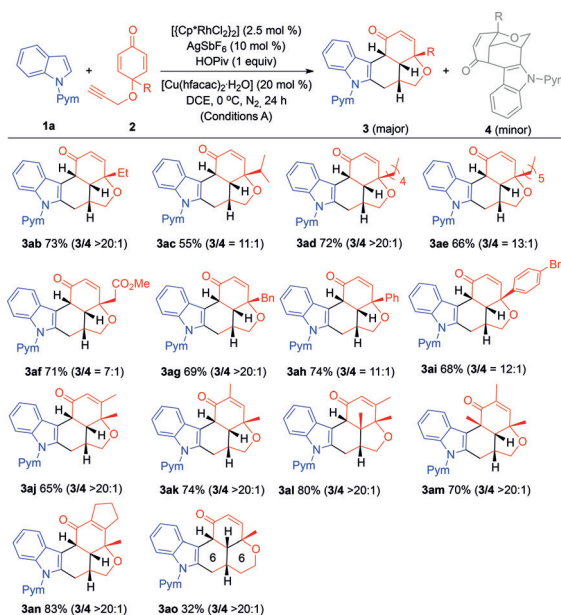
a bridged [3,3,1]-bicycle which is commonly found in bioactive molecules such as Tasmanine, Lucidulin, Neoline, and Hetidine. Further optimization using various solvents generally offered high total yield, but the selectivity toward **3aa** formation was only moderate. To our delight, both high yield and high selectivity (20:1) were achieved when a catalytic amount of $[Cu(hfacac)_2]$ was introduced (Conditions A). In contrast, extensive attempts have been made to switch the selectivity, and the product **4aa** was slightly preferred under various cobalt(III)-catalyzed conditions. Nevertheless, the highest yield of isolated **4aa** was obtained using CF_3CH_2OH (TFE) as a solvent (Conditions B).

With the establishment of optimal reaction conditions, we next examined the scope with respect to the indole substrate (Scheme 3). Introduction of various electron-donating, electron-withdrawing, and halogen groups to the 4-, 5-, 6-, and 7-position of the indole ring is fully tolerated, and the fused cyclic products were isolated in consistently good to high yields as a single diastereomer. The selectivity of the fused to the bridged ring is greater than 10:1 in almost all cases. Furthermore, the directing group was also smoothly extended to an *N*-pyridyl ring (**3ta**).

We next focused on the scope with respect to the enyne substrate (Scheme 4). 1,6-Enynes bearing a diverse array of alkyl and aryl groups at the 5-position all coupled smoothly



Scheme 3. Scope with respect to indoles in the synthesis of fused cycles. Reaction conditions: Reaction was carried out using **1** (0.2 mmol), **2a** (0.24 mmol), $[(Cp^*RhCl_2)_2]$ (2.5 mol%), $AgSbF_6$ (10 mol%), $HOPIv$ (1 equiv), $[Cu(hfacac)_2 \cdot H_2O]$ (20 mol%), DCE (2.0 mL), 0 °C, for 24 h, under N_2 . Yield is that of isolated products. For X-ray structure thermal ellipsoids shown at 30% probability.^[17]

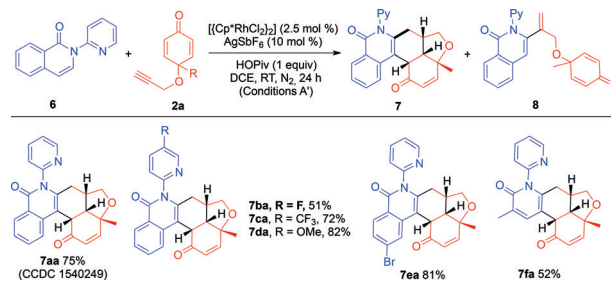


Scheme 4. Scope with respect to enynes in fused cycle synthesis.

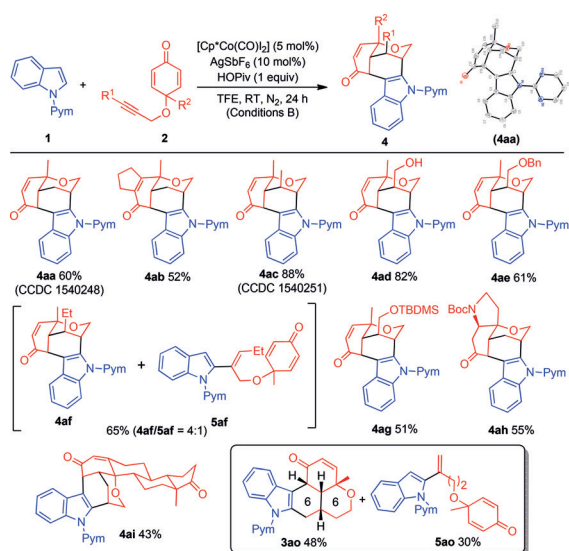
with **1a** to afford the fused cycle **3** as a single diastereomer in moderate to good yield (**3ab–ai**). The ratio of **3/4** remains high but it seems to correlate inversely with steric bulk of the 5-substituent. Introduction of alkyl groups to the olefin unit is well tolerated and the annulation occurred at the more sterically accessible olefin (**3aj–an**). The enyne has been extended to a 1,7-enyne and bears an ethylene group, thus affording a [6,6]-fused ring **3ao**. In contrast, attempts to couple **1a** with internal alkynes under the standard reaction conditions met with failure.

It follows that the arene substrate could be extended to *N*-pyridylisoquinolones and 3-substituted *N*-pyridyl-2-pyridones (Scheme 5). Thus, under modified reaction conditions (Conditions A') the analogous fused cycles were isolated in moderate to good yield (**7aa–fa**), and the product **7aa** was characterized by X-ray crystallography.^[17] In this coupling system, a small amount of terminal olefin (**8**) was generally isolated as a side product.

Having defined the scope of the fused cycle synthesis, we then investigated the scope of cobalt-catalyzed C–H activation of indoles for [3,3,1]-bicycle synthesis (Scheme 6). Of note, only very limited (medium-sized) bridged cycles have been previously synthesized on the basis of IMDA.^[14] Both



Scheme 5. Scope with respect to isoquinolones in annulation reactions.

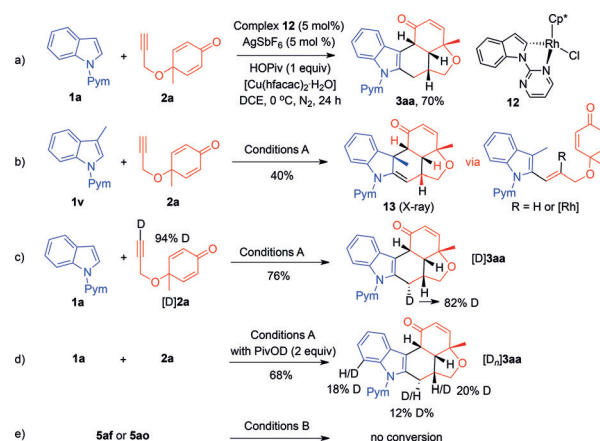
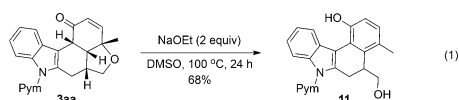


Scheme 6. Cobalt-catalyzed bridged cycle synthesis. Reactions were carried out using **1** (0.2 mmol), **2** (0.24 mmol), [Cp*Co(CO)₂] (5 mol %), AgSbF₆ (10 mol %), and HOPIv (1 equiv) in TFE (2.0 mL) at 25 °C for 24 h under N₂. Yield is that of isolated product. For X-ray structure thermal ellipsoids shown at 30% probability.^[17]

terminal alkynes (**4aa**, **4ab**, **4ah**) and internal enynes bearing an alkyl, CH₂OH, and CH₂OBn terminus all coupled smoothly to afford **4** as a single diastereomer in 51–88% yield. In contrast to the failure of internal enyne under rhodium(III) conditions, the more Lewis-acidic cobalt(III) catalyst activated and polarized the electronically less biased internal alkynes. The presence of a free alcohol in the enyne (**4ad**) should allow further functionalizations. Moreover, enyne fused with a five-membered ring at the olefin unit is also a viable coupling acceptor (**4ab**). Interestingly, the enyne bearing a pendant NHBoc group at the 5-position coupled to offer a bridged cycle with an extra five-membered ring (**4ah**), as a result of in situ aza-Michael addition of the NHBoc to the enone.^[4d] The synthetic utility of this coupling system was further showcased with an estrone-derived 1,6-enyne, and the bicycle **4ai** was isolated as the major product in 43% yields. Extension to a 1,7-enyne, however, only afforded a mixture of fused cycle **3ao** and olefin **5ao** (see Scheme 4).

Derivatization of representative products has been performed to demonstrate the synthetic applications of this method. Hydrogenation of **3aa** and **4aa** afforded the saturated product **9** and **10**, respectively, in excellent yield (see the Supporting Information). Treatment of **3aa** with NaOEt led to elimination of an alkoxide group, thus delivering the phenol **11** in 68% yield by aromatization [Eq (1); DMSO = dimethylsulfoxide].

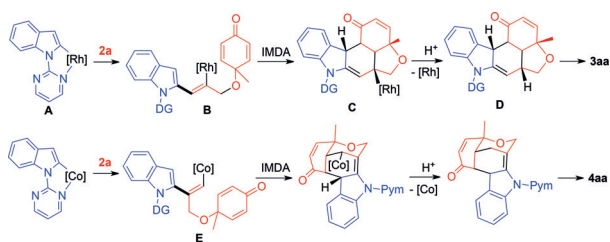
A series of experiments have been performed to explore the mechanism (Scheme 7). To probe the C–H cleavage process, the rhodacycle **12** was prepared and was designated as a catalyst for the coupling of **1a** with **2a**, from which **3aa**



Scheme 7. Mechanistic studies.

was isolated in good yield (Scheme 7a). This result suggests relevancy of C–H activation. To probe the IMDA process, 3-methylindole (**1v**) was subjected to the reaction conditions A. An all-*cis* fused cycle **13**^[17] with partially interrupted aromaticity was isolated (40%) and was crystallographically characterized (Scheme 7b). Here **13** likely originated from an *endo*-specific IMDA reaction. This reaction terminated at the stage of **13** for **1v**, while for 3-unsubstituted indoles, a subsequent 1,3-hydrogen shift regains the aromaticity. To probe whether the alkynyl C–H bond undergoes any cleavage, [D]**2a** was employed for the coupling with **1a** (Scheme 7c). ¹H NMR analysis of the product indicated that the deuterium is mostly localized at a diastereotopically specific α -methylene position, indicative of the selective suprafacial 1,3-hydrogen shift. The deuterium-labeling result also indicated direct insertion of an alkyne, with no vinylidene being involved.^[15] Another deuterium-labeling experiment was performed using [D₄]**2a** (91% D at the olefinic positions), and essentially no erosion of the level of deuteration was observed (see the Supporting Information). A third deuterium experiment was performed between **1a** and **2a** in the presence of PivOD (Scheme 7d). ¹H NMR analysis revealed that a methine CH was partially deuterated, and is consistent with protonolysis of the corresponding Rh–C bond in the catalytic cycle. To further probe the sequence of protonolysis of the M–C bond versus the IMDA in [3,3,1]-bicycle synthesis, the terminal olefin **5af** was subjected to reaction conditions B (Scheme 7e). Essentially no conversion was observed in both cases. The same scenario was observed for olefin **5ao**, thus suggesting that the protonolysis takes place after the IMDA of the metal alkenyl intermediate.^[16]

On the basis of our experimental results, a plausible pathway is given in Scheme 8. C–H activation of indole gives the metallacycle **A**. In the case of rhodium(III) catalysis, 2,1-insertion of the Rh–C bond into the enyne **2a** gives **B** with possible coordination of the pendant olefin to saturate the coordination sphere. **B** undergoes type-I IMDA to give the intermediate **C** followed by protonolysis (shown) or vice versa. The intermediate **D** then undergoes suprafacial 1,3-hydrogen shift to furnish the product **3aa**. In the case of cobalt(III) catalysis, the 1,2-insertion of **2a** leading to C-(aryl)–C₂ coupling (**E**) is governed by the steric sensitivity of



Scheme 8. Proposed divergent pathways.

the cobalt catalyst. Subsequently, type-II IMDA takes place prior to the protonolysis to eventually yield the bridged bicycle **4aa**. This regioselectivity is also delicately tuned by the steric effect of the enyne in the following aspects. Firstly, under rhodium catalysis increase of the steric bulkiness of the 5-substituent also enhanced the steric effect of the enyne, thus giving rise to a lower ratio of **3/4** (Scheme 4). Secondly, the ethylene linker in a 1,7-enyne substrate reduces the steric hindrance and enhances the molecular flexibility of the enyne, so that both 1,2- and 2,1-insertions were observed (**3ao** and **5ao**; Scheme 6).

In summary, we have realized divergent couplings of indoles with enynes. Under rhodium(III) catalysis, the formation of fused cycles corresponds to alkyne 2,1-insertion followed by a type-I IMDA reaction. In contrast, both internal and terminal alkynes are applicable under cobalt catalysis, in which 1,2-insertion occurred preferentially. Subsequent rare type-II IMDA reaction provided a [3,3,1]-bicyclic scaffold. In all cases, the products were obtained as a single diastereomer. Given the divergent and controllable syntheses of cyclic products, these coupling systems may find applications in synthesis of complex structures.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: C–H activation · cobalt · cycloadditions · polycycles · rhodium

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