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Switching of Reaction Pathway from C–C Rollover to C–N Ring-Extension Annulation

Ranjeesh Thenarukandiyil,[a] Champak Dutta,[a] and Joyanta Choudhury*[a]

Abstract: This work discloses that a simple change in *anion* of a copper(II) reagent along with the reaction solvent can dramatically alter the course of a Cp*Rh(III)-catalyzed C–H activation-annulation reaction leading to completely switchable chemoselective products. The nature of the anion in terms of its coordinating ability and basicity, and also the polarity of the solvent have been found to be the crucial factor in the observed divergence.

Introduction

Advancement of fundamental knowledge and basic concepts in chemistry has had a tremendous impact on modern-day catalysis. It has benefited to widen the spectrum of catalyst development from simple and highly efficient to all sorts of complex and smart catalysts, thereby addressing the issues of sustainability and diversity. It is an (unrealistic) dream of any catalysis researcher to develop one single catalyst performing a large number of different synthetic reactions with an equal great degree of efficiency. Similarly, to achieve different chemo-/regio-/enantio-divergent products from a common substrate with high selectivity control by using same catalyst is an ambitious and formidable task. To tackle the intricacies present in transition-metal-based this type of diversity-oriented catalysis, a) a good understanding of bond-breaking/bond-making mechanistic scenarios, and b) ability to control the property and reactivity of organometallic intermediate(s) are required. In chemodivergent processes, as expected, strategies involving tuning the nature of ligand and/or metal, design of substrate, or use of different solvents and reagents have been applied to perturb the chemoselectivity-controlling step(s), and thus alter the reaction outcome (Figure 1a).[1] At this juncture, we paid attention to Cp*Rh(III)-catalyzed C–H activation-functionalization reactions which are prevalent and versatile in modern synthetic chemistry, and considered as step-economic, straightforward, and highly desirable transformations.[2] Most of these methodologies often use stoichiometric amount of a copper(II) compound (CuX_2) as oxidant. Interestingly, CuX_2 is known to participate in anion-exchange processes with the catalyst $[Cp^*RhCl_2]_2$, generating 'Cp^*RhX_2' type species under the reaction conditions. We hypothesized that the coordinating ability and basicity of X can affect the nature (electrophilicity and Lewis acidity of the metal center) as well as reactivity of the subsequent organo-Rh intermediate(s), and C–H activation step of the reaction. Therefore, a judicious change in X can cause a mechanistic dichotomy and provide the opportunity to explore a novel way to accomplish *switchable* chemoselective C–H functionalization protocol under tuned reaction conditions.

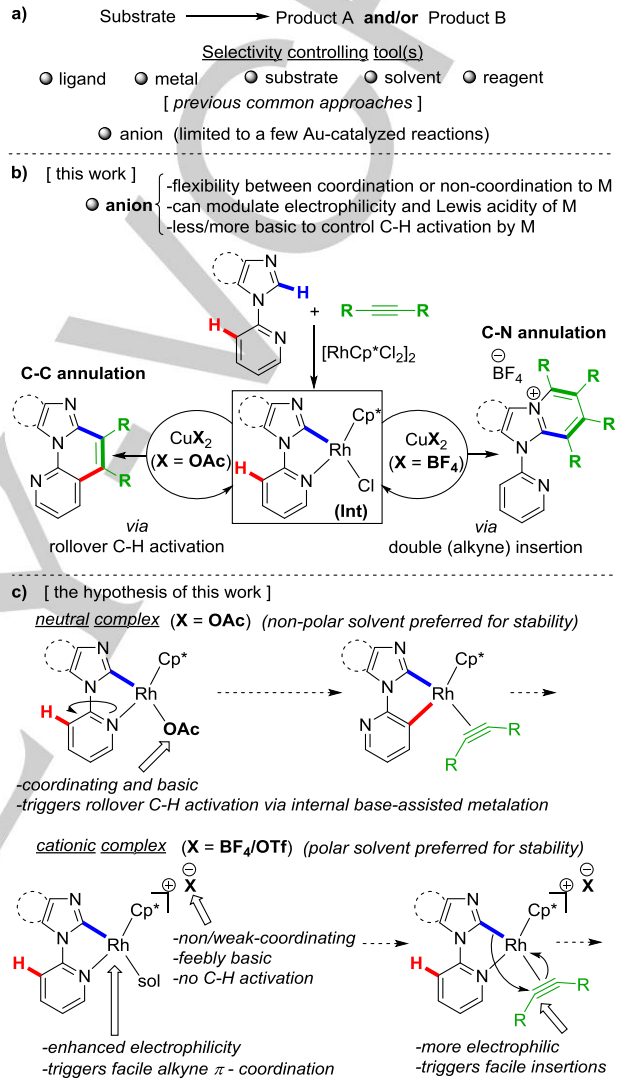

Figure 1. Controlling chemodivergent processes: a) different tools; b) anion as a tool; c) hypothesis of this work based on the nature of the anion.

The proof-of-concept of this hypothesis has been described herein by choosing C–H activation-functionalization of pyridine-appended imidazole substrates to the fused imidazopyridine derivatives. Imidazolium motif containing molecules are known to be of significant interest in diverse research areas, but there is a lack of functionalization protocols of these molecules. On the other hand, the fused imidazopyridines represent an important class of compounds known as pharmaceutically active and potential drugs (Figure 1b, and Supporting Information).[3] Additionally, such types of N-doped extended π-conjugated

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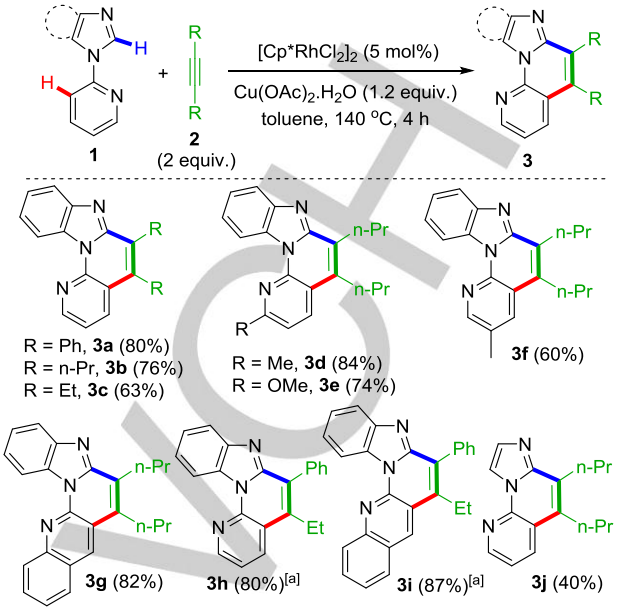
polycyclic aromatic hydrocarbons are considered as potential electronic materials as well.[4] After the initial pyridine-directed imidazole C(2) –H activation by $[Cp^*RhCl_2]_2$, the resulting five-membered cyclometalated intermediate (**Int**, Figure 1b) might be prone to chloride dissociation-exchange with available anion (X). When X = OAc, its coordinating and fairly basic character[5] may trigger the intermediate to undergo a 'rollover' C–H activation[6] of the coordinated pyridine backbone via internal base-assisted metalation (BAM)/ concerted metalation-deprotonation (CMD) pathway. Subsequent insertion of an alkyne into Rh–$C_{pyridine}$ or Rh–$C_{imidazole}$ followed by reductive elimination may produce C–C annulated product (Figure 1b,c). On the contrary, if X = BF_4 or CF_3SO_3, due to their feebly basic character,[5] a base-assisted similar rollover C–H activation at the Rh center may not be facilitated any more. Rather, their non-/less-coordinating nature[7] may enhance the electrophilicity of Rh through the formation of cationic complex. This, in turn, would increase the electrophilic character of coordinated alkyne to trigger insertion processes prior to a C–N reductive elimination step providing the C–N annulated product (Figure 1b,c). Because of the cationic nature of the intermediate, the C–N reductive elimination would also be favored. Notably, this type of anion-dependent divergent outcomes in transition-metal catalysis are severely limited to only a few gold-catalyzed reactions.[8] Comparatively, in a broader sense, anion-guided chemistry was previously explored in the field of crystals and materials, host-guest chemistry, self-assembled systems such as cages, macrocycles, metal-organic frameworks etc.[9]

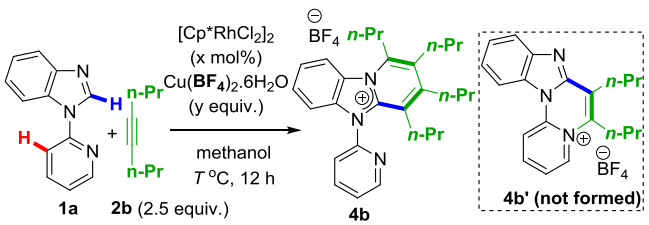
Results and Discussion

Keeping the above-mentioned hypothesis in mind, the prospective divergent catalytic reactions were explored under two distinct reaction conditions (e.g., polarity of the solvents used) to deal with the plausible neutral or cationic rhodacyclic intermediates. Thus, the rollover C–C annulation catalysis was achieved via the reaction of various N-pyridylbenzimidazoles (**1**) with different internal alkynes (**2**) using 1.2 equiv. of $Cu(OAc)_2$ and catalytic $[Cp^*RhCl_2]_2$ in non-polar solvent toluene (ε 2.38), as shown in Scheme 1. N-pyridylbenzimidazole **1a** was successfully transformed to the C–C coupled products not only with diarylalkynes but also with dialkylalkynes in good yields (**3a-3c**, 63-80%). It is to note that only one specific example of the reaction of **1a** with diphenylacetylene producing **3a** was reported earlier[6a-b]. However, in this work, this protocol has not only been generalized for the N-pyridylimidazole class of substrates, but a mechanistic rationale and viewpoint has also been provided. Introduction of substituents at the ortho or para position of the pyridyl moiety did not alter the efficiency of the reaction (**3d-3f**, 84-60%). Similar to the pyridine, quinoline substitution also effectively furnished the rollover C–C annulated product in good yield (**3g**, 82%). Importantly the reactions with unsymmetrical alkyne provided single regioisomers as major products with better yields (**3h-3i**, 80-87%). The imidazole version of **1a** also gave the product but in lesser yield (**3j**, 40%).



Scheme 1. Examples of C–C annulation. **1** (0.1 mmol), **2** (0.2 mmol), $Cu(OAc)_2.H_2O$ (0.12 mmol), $[Cp^*RhCl_2]_2$ (5 mol%), toluene (1 mL). [a]<10% of the other regioisomer was observed.

Next, when the same substrates **1a** and **2b** were treated by employing 2.0 equiv. of $Cu(BF_4)_2$ instead of $Cu(OAc)_2$ in a more polar solvent MeOH (ε 32.7) at 100 °C in the presence of 5 mol% catalyst, it did not result any pyridyl C–H activation product, but it furnished a new product in <10% yield (Scheme 2). ^{1}H NMR analysis of this new product indicated that it consisted of two sets of protons from the alkyne moiety and all the aromatic protons from the pyridyl benzimidazole backbone except the imidazole-NC*H*N proton. The same product was formed in 92% yield when an elevated temperature of 140 °C was used under the above conditions (Scheme 2). The product was later confirmed as double alkyne-inserted imidazole C–N annulated compound **4b** by $^{13}C\{^1H\}$ NMR and ESI-HRMS analysis (Supporting Information for details). Later the loading of the catalyst (3 mol%) and $Cu(BF_4)_2$ (1.5 equiv.) was optimized (Scheme 2). During the screening of the reaction conditions, it was confirmed that an expected mono alkyne-inserted



(a) Cat: 5 mol%, $Cu(BF_4)_2$: 2.0 equiv., 100 °C, yield of **4b** = <10%.
(b) Cat: 5 mol%, $Cu(BF_4)_2$: 2.0 equiv., 140 °C, yield of **4b** = 92%.
(c) Cat: 3 mol%, $Cu(BF_4)_2$: 1.5 equiv., 140 °C, yield of **4b** = 82%; **4b'** = not formed.
(d) Same as in (c) but **2b**: 1.0 equiv. to **1a**, yield of **4b** = 45%; **4b'** = not formed.

Scheme 2. Reaction conditions for C-N annulation.

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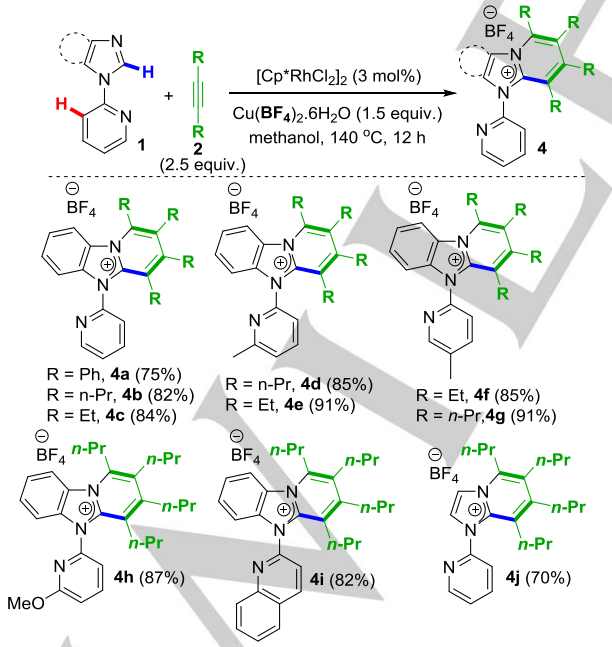
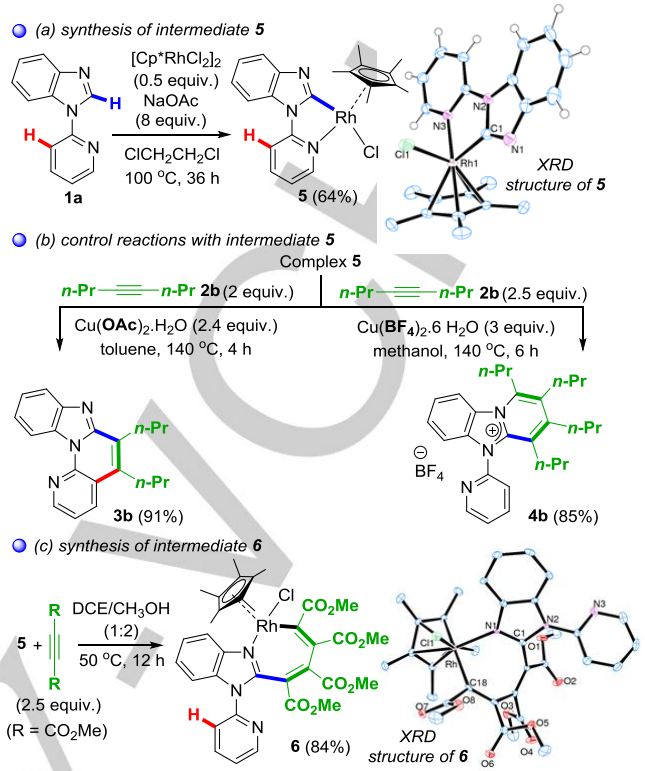
pyridine-N annulated compound **4b'** was not formed even when 1 equiv. of alkyne was used, and only **4b** was obtained as the sole product (Scheme 2). It is important to mention that all non-coordinating anion containing oxidizing agents such as $Cu(BF_4)_2$, $Cu(OTf)_2$, and $AgBF_4$ successfully produced C–$N_{imidazole}$ annulated product (see Supporting Information).

Next, we examined the reactions with different N-pyridyl benzimidazoles and various internal alkynes (Scheme 3). Diarylalkynes as well as dialkylalkynes furnished the doubly inserted C–N coupled cationic products in high yields (**4a-4c**, 75-84%). Ortho and para substitution on the pyridine ring did not affect the reaction much and provided excellent yields (**4d-4h**, 85-91%). The quinoline substituted benzimidazole also led to the similar product formation in higher yield (**4i**, 82%). The transformation of 2-(1H-imidazol-1-yl)pyridine to the C–N coupled product in good yield (**4j**, 70%) under this condition widened the substrate scope. The fact that the formation of exclusively C–C product in ~43% yield with $Cu(OAc)_2$ and C–N product in ~77% yield with $Cu(BF_4)_2$ under identical reaction conditions in a common and moderately polar solvent 1,2-dichloroethane (ε 10.36) emphasized the major role of anion and a less-pronounced role of solvent in guiding the selectivity in the present chemistry (see Supporting Information). Notably, no C–$N_{imidazole}$ coupled product formed with N-phenylimidazole as substrate, which emphasized that probably the initial ortho pyridine coordination was essential for the catalysis to proceed. Similarly, N-pyridylindole did not provide any C–$N_{pyridine}$ coupled product under $Cu(BF_4)_2$ conditions, suggesting that the monoannulation reaction from a putative pyridine-coordinated intermediate was not facile under the employed reaction conditions (see Supporting Information).

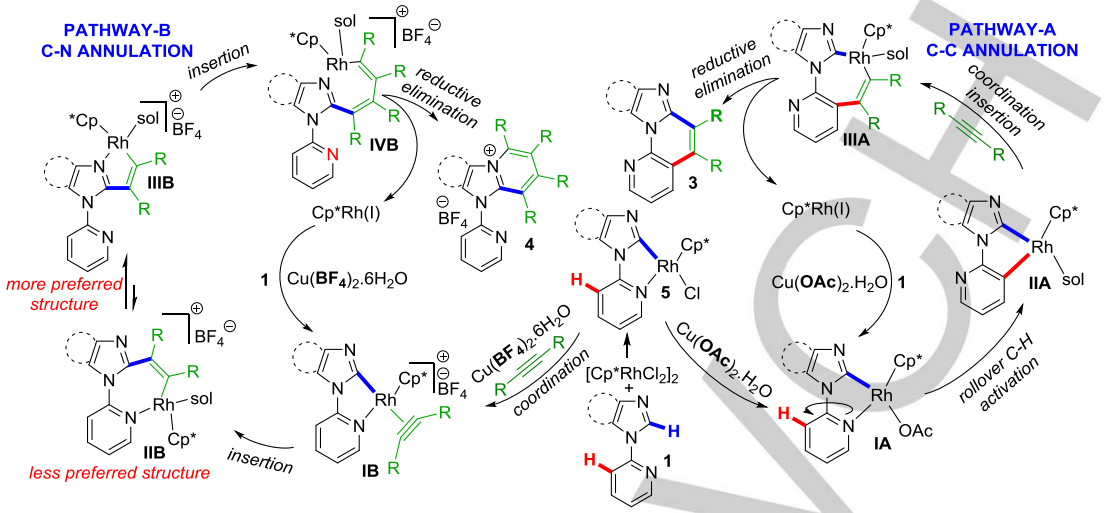


Scheme 3. Examples of C–N annulation. **1** (0.1 mmol), **2** (0.25 mmol), $Cu(BF_4)_2.6H_2O$ (0.15 mmol), $[Cp^*RhCl_2]_2$ (3 mol%), MeOH (1 mL).



Scheme 4. Mechanistic investigation.

Mechanistic investigation was performed for this novel divergent chemistry. A five-membered cyclometalated rho-dium(III) intermediate **5** was isolated in good yield (64%) from the reaction of the substrate **1a** (0.3 mmol) and $[Cp^*RhCl_2]_2$ (0.15 mmol) in the presence of NaOAc (2.4 mmol) as base in $ClCH_2CH_2Cl$ (Scheme 4a). Full characterization of the complex **5** was accomplished by ^1H and $^{13}C\{^1H\}$ NMR spectroscopic, and mass spectrometric (ESI-MS) methods. The structure of **5** was confirmed by single crystal X-ray diffraction studies.[10] It is important to mention that there was no indication of the presence of N–H proton in the ^1H NMR spectrum, which eliminated the possibility of the formation of a protic NHC complex[11] under this condition. This was further confirmed by comparing the <N-C-N bond angle value of 110.8(3)° in **5** with a known Cp*Rh-complex (109.4(2)° for imidazolyl-Rh versus 104.4(2)° for NHC-Rh).[12]. The intermediacy of **5** for the two different modes of reactivity was confirmed via performing two separate control experiments by treating **5** with alkyne **2b** in presence of $Cu(OAc)_2$ and $Cu(BF_4)_2$ which provided high yields of **3b** (91%) and **4b** (85%) respectively (Scheme 4b). Significantly, the seven-membered double alkyne-inserted metallacyclic intermediate **6** for this new C–N annulation reaction could also be isolated from a reaction with complex **5** and dimethylacetylene dicarboxylate (DMAD) as alkyne in the absence of $Cu(BF_4)_2$ (Scheme 4c). The presence of the Cl ligand was probably found to be essential to stabilize the complex **6**. Full characterization of **6** was accomplished by spectroscopic and single-crystal X-ray diffraction analysis[10].



Scheme 5. Proposed catalytic cycles.

However, complex **6** was proved extremely reluctant to further reductive elimination reaction, indicating that DMAD is dramatically different from normal alkynes in electronic nature.

Plausible catalytic cycles for both the transformations were proposed based on our hypothesis, the mechanistic information gained through the control experiments, and previous literature reports[2] (Scheme 5). After the generation of a cyclometalated intermediate **5** from **1** with the rhodium center, the next step is the chloride dissociation-exchange with the X of CuX_2 and the intermediate formation is highly dependent on the nature of X. In the presence of $Cu(OAc)_2$ (X = OAc), the reaction follows pathway-A. Being a reasonably basic and coordinating ligand, OAc can first coordinate to form **IA**, and then direct the intermediate to undergo a 'rollover' C–H activation[6] leading to the formation of a new cyclometalated intermediate **IIA**. Then alkyne insertion to **IIA** generates **IIIA** which upon reductive elimination produces the C–C annulated product **3**. Re-oxidationof the [Cp*Rh^{I}] species triggers the catalytic cycle to continue. On the other hand, in presence of $Cu(BF_4)_2$, (X= BF_4), the reaction proceeds through pathway-B. The less basic and weakly/non-coordinating nature of BF_4 does not favor the rollover C–H activation at the Rh center. Rather it prefers to form a cationic complex from which a facile formation of alkyne coordinated intermediate **IB** is expected. From here, the insertion of alkyne into Rh–C can provide the seven-membered rhodacycle intermediate **IIB**. However, we never observed a possible $C–N_{pyridine}$ reductive eliminated product from **IIB**, even with one equivalent of alkyne. So it is logical to think that either this intermediate does not form or it is transformed immediately into more stable five-membered metallacycle intermediate **IIIB**. Indeed, the latter is the case as DFT calculation suggested that **IIIB** is more stable than **IIB** by ~ 18.6 kcal (see Supporting Information for details). The second alkyne insertion to **IIIB** can lead to the formation of a seven-membered rhodacycle intermediate **IVB**. The reductive elimination from **IVB** provides the $C–N_{imidazole}$ coupled product **4** and Cp*Rh^{I} species for further regeneration and continuation of the catalytic cycle. It is to note that, even if the BF_4 anion is not directly coordinated to the catalytic metal center, it tunes the electrophilicity and Lewis acidity of the metal center to control reactivity throughout the catalytic cycle.

Conclusions

In summary, a controlled mechanistic dichotomy led to switch the pathway of a Cp*Rh(III)-catalyzed C–H functionalization reaction. With the basic and coordinating OAc anion, a rollover C–H activation pathway was favored resulting C-C annulation products in non-polar solvent. In contrast, feebly basic and less/non-coordinating BF_4 anion triggered double alkyne insertion instead of C–H activation leading to C–N annulated cationic products in polar solvent. The key to the success of this switchable chemodivergent protocol is the control over the nature and reactivity of the organometallic rhodacyclic intermediates based on anion and solvent polarity. Not only the above novel aspect of reaction control, but the presented chemistry of easily switchable selectivity in Rh(III)-catalyzed C–H activation reaction allows also to access neutral and ionic π-conjugated organic materials.

Experimental Section

General procedure for catalytic C–C rollover annulation

In an oven-dried sealed tube, **1** (0.1 mmol), $[RhCp^*Cl_2]_2$ (5 mol%), **2** (0.2 mmol) and $Cu(OAc)_2.H_2O$ (0.12 mmol) were taken. To this mixture, 1 mL of toluene was added and the reaction mixture was stirred at 140 °C for 4

h. After that, the mixture was cooled to room temperature and the solvent was removed by evaporation in vacuo. Then CH_2Cl_2 (10 mL) was added to this residue followed by washing with aqueous K_2CO_3. The organic layer was collected. The extraction was repeated with CH_2Cl_2 (10 mL x 2) and the organic layers were combined and evaporated to dryness. This crude mixture was adsorbed on to silica and purified by silica gel column chromatography by using 2% EtOAc in Et_2O solvent system.

General procedure for catalytic C–N ring-extension annulation

In an oven-dried sealed tube **1** (0.1 mmol), $[RhCp^*Cl_2]_2$ (3 mol%), **2** (0.25 mmol) and $Cu(BF_4)_2.6H_2O$ (0.15 mmol) were taken. To this, 1 mL of MeOH was added and the reaction mixture was stirred at 140 °C for 12 h. After that, the mixture was cooled to room temperature and the solvent was removed by evaporation in vacuo. Then CH_2Cl_2 (7 mL) was added to this mixture followed by washing with ethylenediamine in water (300 µL ethylenediamine in 5 mL water). The organic layer was collected and the extraction was repeated with CH_2Cl_2 (7 mL x 2) and the organic layers were combined and evaporated to dryness. This crude mixture was adsorbed on to silica and purified by silica gel column chromatography by using 5% MeOH in $CHCl_3$ solvent system.

Acknowledgements

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Keywords: chemoselectivity • rhodium • C–H activation • annulation • anion.

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[10] CCDC 1554665 (**5**) and 1554664 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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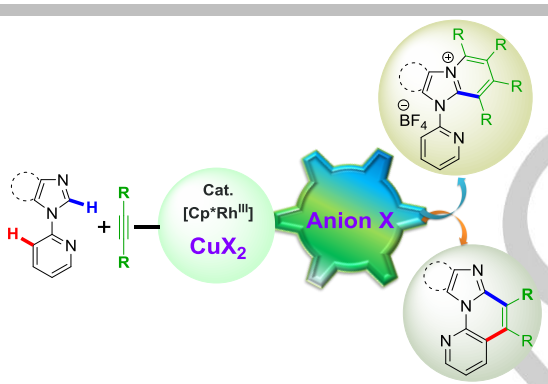
FULL PAPER

A simple change in anion of a copper(II) reagent dramatically altered the course of a Cp*Rh(III)-catalyzed C–H activation-annulation reaction leading to completely switchable chemoselective products in suitably chosen solvents. Different coordinating ability and basicity of the anions and the polarity of the solvents played crucial role in the observed divergence.



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Switching of Reaction Pathway from C–C Rollover to C–N Ring- Extension Annulation