

A Comparative Investigation: Group 9 Cp*M(III)-Catalyzed Formal [4 + 2] Cycloaddition as an Atom-Economic Approach to Quinazolines

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Supporting Information

ABSTRACT: A comparative study on the catalytic activity of different group 9 [Cp*M(III)] complexes in the formal [4 + 2] cycloaddition of arenes with rarely explored free imines and dioxazolones for the construction of multisubstituted quinazolines is reported herein. This investigation revealed that the cobalt catalyst is uniquely suited to this transformation due to its strong Lewis acidity and high sensitivity to steric hindrance.



T he quinazoline motif is a key core structure commonly found in many natural products, pharmaceutical compounds, pesticides, and functional organic materials (Figure 1a).^{1,2} For example, 4-oxy-substituted quinazolines have recently



Figure 1. Examples of biologically active molecules and comparison between traditional methods and this work.

attracted interest due to their anticancer and anti-HIV biological properties.³ Although there are various methods to construct these privileged structures, most of them employ comparatively less available starting materials such as *ortho*-functionalized anilines, suffer from a limited scope of substituents at the 2- or 4-positions, or involve multistep procedures or harsh reaction conditions.^{4,5} Thus, it is highly desirable to develop new convenient and efficient approaches to synthesize multisubstituted quinazolines from simple starting materials. From the viewpoint of synthesis analysis, formal [4 + 2] cycloaddition of arenes with a free imine and a formal "cyano-unit" would be a highly effective and atom-economic approach to directly construct multisubstituted quinazolines (Figure 1b).

Over the past few decades, the development of the first-row transition-metal-catalyzed reactions has attracted great attention because of the use of cheap, earth-abundant, and less toxic base metals.⁶ Among them, high-valent Cp*Co(III) catalysts have been developed as robust, powerful, and cheap metal catalysts for the C-H activation of arenes, as demonstrated in several reports by the groups of Kanai and Matsunaga,⁷ Ellman,⁸ Chang,⁹ Ackermann,¹⁰ Glorius,¹¹ and others.^{12,13} Notably, most applications of [Cp*Co(III)] complexes, however, are limited to reactions similar to those developed with [Cp*Rh(III)] complexes.¹⁴ Since metals of the same group have different physicochemical properties (e.g., ionic radius and electronegativity), it is highly rewarding to investigate factors controlling their catalytic activities between Cp*Co(III) and Cp*Rh(III)/Ir(III) to further expand the utility of the Cp*Co(III) catalysts.^{7f-h,9a,d,11b,12g} We report herein a Cp*M-(III)-catalyzed formal [4 + 2] cycloaddition of arenes with a rarely explored free imine unit and readily available dioxazolones. This reaction represents a new complementary process to synthesize multisubstituted quinazolines, which features a broad scope and functional group tolerance (Figure 1c). This comparative study on the catalytic activity of different Group 9 [Cp*M(III)] complexes revealed that the Cp*Co(III) complex is uniquely capable of catalyzing this C-H amidation and cyclization process affording diversely substituted quinazolines directly from simple starting materials due to its strong Lewis acidity and high sensitivity to steric hindrance.

Recently, the groups of Chang, Li, Jiao and Ackermann developed several attractive Cp*Rh(III) and/or Cp*Co(III)-catalyzed C–H amidation strategies of arenes containing stable and strongly coordinating directing groups and employing dioxazolones as user-friendly amidating reagents.¹⁵ Inspired by these results, we designed a novel tandem approach to synthesize quinazolines where a Cp*M(III) catalyst mediates both an initial

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C-H amidation and a subsequent cyclization. For this purpose, we selected the rarely explored free imine unit as atom-economic directing group and chose readily available dioxazolones as amidating reagents (Figure 1c). As is known, tandem C-H amidation (or amination)/cyclization approach is a challenging and less developed approach for the construction of heterocycles.¹⁶ Indeed, the successful realization of this desirable transformation would require overcoming several intricate challenges, including the risk of decomposition of the C=NH unit in the substrates and amidated intermediates because of the Lewis acidity of [Cp*M(III)] complexes, as well as the compatibility of the reaction conditions for the C-H amidation and intramolecular cyclization process. Furthermore, both the C=NH unit in the substrate and the pyrimidine core in the product could act as directing group that can lead to competing C-H amidation, and overamidation could feasibly occur.

In order to examine and compare the catalytic performance of different group 9 triad [Cp*M(III)] catalysts, we selected ethyl benzimidate 1a as a model substrate and reacted it with 2a (see the Supporting Information for details of the reaction conditions). To our delight, all of the Cp*M(III) complexes led to the formation of the desired product 4aa in the presence of NaOAc (Figure 2a). The reaction employing Cp*Co(III) as the



Figure 2. Comparison of the reaction performance of Cp*M(III) in the synthesis of **4aa**. (a) **1a** (0.1 mmol), **2a** (0.15 mmol), NaOAc (50 mol %), DCE (1.0 mL), 60 °C, 5 h. GC yields are shown and isolated yield is given in parentheses. (b) Reaction profiles until 3.0 h. Cp*Rh = $[Cp*RhCl_2]_2$ (5 mol %), Cp*Ir = $[Cp*IrCl_2]_2$ (5 mol %) and Cp*Co = $[Cp*Co(CO)I_2]$ (10 mol %).

catalyst led to the highest yield of 4aa (98%), while much lower yields were observed with Cp*Rh(III) and Cp*Ir(III) (55% and 39%, respectively). No reaction was observed in the absence of the Cp*M(III) complexes, indicating that the reaction is indeed a Cp*M(III)-catalyzed process. In addition to assessing the reaction outcome, the rate of formation of 4aa in each case was also compared. As shown in Figure 2b, the reaction with Cp*Ir(III) as catalyst was very slow, whereas 4aa was produced fastest with Cp*Co(III). However, the reaction catalyzed by Cp*Rh(III) exhibited a more complicated kinetic profile where the yield of 4aa appeared to decrease over time. This observation implies that the desired product 4aa is further transformed into byproducts under the reaction conditions. Indeed, analysis of each of the reaction mixtures at 1 and 5 h revealed that the overamidation product 5aa was formed when Cp*Rh(III) was used as catalyst. Moreover, this compound (5aa) could be

isolated in 29% yield in the end of the reaction. In the ESI-MS spectra of the reaction mixture with Cp*Ir(III) as catalyst, the intermediate **3aa** could be obviously detected, indicating that the cyclization process may be more difficult using this catalyst. Only the reaction with the Cp*Co(III) catalyst afforded the clean formation of **4aa**. These results clearly demonstrate that, among the group 9 triad metals, Cp*Co(III) is the optimum catalyst for this tandem process, mediating the cyclization step more efficiently than Cp*Ir(III) and avoiding the overamidation encountered with Cp*Rh(III).

Under the optimized conditions using the Cp*Co(III) catalyst, the scope with respect to the amidating reagent 2 was first examined (Scheme 1). Thus, aryl-substituted dioxazolones





bearing various electron-donating and electron-withdrawing groups at different positions of the aryl ring reacted smoothly with 1a, affording the corresponding products 4aa—ai in good to excellent yields. Furthermore, substituents on the amidating reagents were not limited to aryl groups. The heterocycle-bearing dioxazolone also reacted with 1a to afford the desired product 4aj in 97% yield. Moreover, alkyl substituents could be readily installed at the 2-position of the corresponding quinazoline products 4ak and 4al in synthetically useful yields using methyland cyclohexyl-substituted amidating reagents.

Subsequently, we tested the versatility of the Cp*Co(III)catalyzed C-H amidation/cyclization with arylimidates. As shown in Scheme 2, various *para*-substituted arylimidates smoothly afforded the desired products **4ba**-**ha** in high yields irrespective of the substrate electronics. For unsymmetrical substrates, such as *meta*-substituted and *meta*,*para*-disubstituted arylimidates, the reactions showed excellent selectivity (>20:1) for the C-H bond with less steric hindrance, selectively





^aFor reaction conditions, see the Supporting Information.

delivering products 4ia-ka in good yields. Moreover, an orthosubstituted imidate also afforded the desired product 4la in 77% yield. It should be noted that the catalytic system tolerated various kinds of functional groups on the arene such as EtO, PhO, NMe₂, CO₂Et, F, and Cl, which can be transformed to other functionalities. Additionally, 2-naphthyl imidate and ethyl thiophene-3-carbimidate also showed good reactivity in these reactions, giving the corresponding products 4ma and 4na. Finally, the effect of modifying the ethylimidate directing group was examined. Switching to 2-methoxyethylimidate did not decrease the reactivity, and the corresponding product 40a was isolated in 94% yield. Moreover, N-tert-butylbenzimidamide, diphenylmethanimine, and 1-phenylpentan-1-imine, which all feature different imine-based directing groups, also led smoothly to the cyclized products 4pa-ra in moderate to good yields. Overall, this methodology is a highly efficient and convenient strategy to synthesize multisubstituted quinazolines, with a broad scope of substituents at the benzene position as well as in the 2and 4-positions from simple starting materials.

It should be noted that the standard product 4aa, further entitled as HMJ-53A, can inhibit arachidonic acid-induced platelet aggregation (Scheme 3).^{3c,d} Additionally, the hydrolysis

Scheme 3. Synthesis of Biologically Active Molecules



of 4 opens an alternative access to quinazolinone derivatives¹⁷ that are also known for their biological and medicinal activities, such as **6ak**, which is a natural product from *Bacillus cereus*^{17b} and 6ik, which could be utilized in the synthesis of antimetabolite drug raltitrexed and ICI 198583.^{17c,d} Compared to the traditional syntheses starting from multifunctionalized substrates, the approach presented herein offers the desired quinazoline products in an efficient, one-step procedure under mild conditions from easy and readily available starting materials. Moreover, using this procedure, a convenient and simple synthesis for such derivatives could be helpful for drug discovery, especially for the compiling of libraries. Additionally, several compounds synthesized herein bearing electron-donating substituents such as 4ma, 4ea, and 4ad showed potential applications as colorimetric and luminescent pH sensors (for details, see the Supporting Information).^{2a}

For analysis of a possible reaction mechanism, the kinetic isotope effect (KIE) of 2.36 was measured for parallel experiments, indicating that C–H activation is plausibly involved in the rate-determining step. Moreover, a competition experiment between electronically different arylimidates showed that the electron-rich substrate is more favored. Based on these experiments and previously reported studies,¹⁵ a plausible catalytic cycle is proposed in Scheme S1 (see the Supporting Information). The reaction likely involves the directed Cp*Co-(III)-catalyzed C–H amidation to afford intermediate **3aa**. This amide intermediate is proposed to undergo Lewis acid-promoted nucleophilic addition and dehydration, affording the desired

product 4aa. By careful analysis of the reaction outcomes with different metals, the factors controlling their catalytic activities between Cp*Co(III) and Cp*Rh(III)/Ir(III) were investigated (Scheme 4). Compared with its Cp*Rh(III) and Cp*Ir(III)





congeners, Cp*Co(III) is the most Lewis acidic catalyst and is expected to promote the cyclization of intermediate 3aa more efficiently.^{11b} Indeed, the amidated intermediate 3aa was not detected during the reaction using Cp*Co(III) as catalyst whereas this compound was observed in the ESI-MS of the reaction mixture when Cp*Ir(III) was employed. The addition of Lewis acid $[Sc(OTf)_3 (20 \text{ mol } \%)]$ in the reaction with Cp*Ir(III) as catalyst could improve the yield of 4aa (78%), showing that the cyclization may be promoted by a Lewis acid. Moreover, using 4aa as the starting material under the standard conditions, the reaction with the Cp*Co(III) catalyst did not lead to further amidation to 5aa and 4aa was recovered (86%), while Cp*Rh(III) showed high reactivity, affording 5aa in 81% yield and Cp*Ir(III) also showed reactivity (15% yield of 5aa). This is proposed to be due to the smallest ionic radius of cobalt among the group 9 metals, meaning that Cp*Co(III) is more sensitive to steric hindrance than Cp*Rh(III).^{7h} Thus, steric repulsion between the Cp*-ligand and the substituent groups in the pyrimidine-core of 4 (e.g., the ethoxy, and benzo-part in 4aa) is more significant with Cp*Co(III) than with Cp*Rh(III) (Scheme 4, G). Therefore, the coordination of the cobalt catalyst to 4aa is less favorable and the overamidation process observed with Cp*Rh(III) is prevented. These combined effects of high Lewis acidity and small ionic radius are crucial in making Cp*Co(III) such an efficient and selective catalyst for this transformation.

In summary, we have demonstrated the excellent efficiency and selectivity of the Cp*Co(III) catalyst in a novel synthesis of quinazolines involving a tandem direct C–H amidation and cyclization.¹⁸ The cobalt complex exhibited significantly higher reactivity than Cp*Ir(III), while the overamidation observed with Cp*Rh(III) was suppressed using Cp*Co(III). This unique reactivity can be attributed to the strong Lewis acidity and the high sensitivity to steric hindrance of Cp*Co(III) catalyst. The highly efficient methodology developed herein represents a convenient strategy to synthesize multisubstituted quinazolines of interest for drug discovery and photophysical applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b00716.

Experimental procedures, spectroscopic data, and mechanistic experiments (PDF)

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Notes

The authors declare no competing financial interest.

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