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Mild Synthesis of Chalcones via Rhodium(III)-Catalyzed C–C Coupling of Arenes and Cyclopropenones

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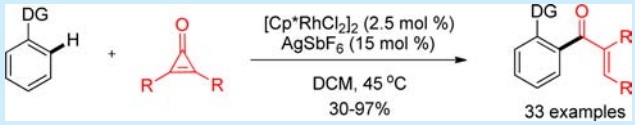
Supporting Information

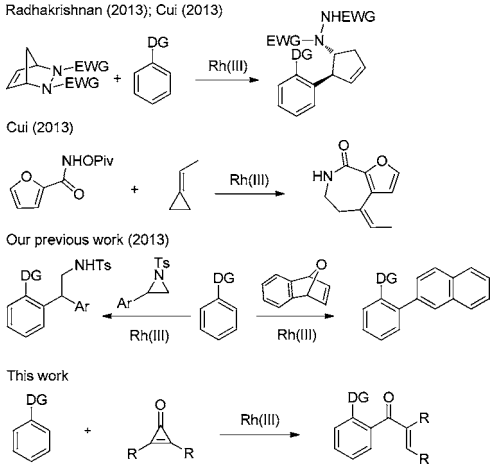
ABSTRACT: A Rh(III)-catalyzed aryl C–H bond insertion into cyclopropenones via a C–H activation pathway has been reported. A series of arenes bearing directing groups such as 2-pyridyl, 2-pyrimidyl, *N*-pyrazyl, and oxime can be applicable, providing chalcones in excellent yields under mild conditions. Several possible Rh(III) intermediates in this reaction were investigated.



In the past decades, transition-metal-catalyzed C–H activation has emerged as a powerful strategy to construct organic building blocks of complex structures in a step- and atom-economic fashion.[1] Among the transition metals, rhodium(III) complexes provide some of the most attractive catalysts for the formation of C–C bonds with high activity, high selectivity, broad scope, and high functional-group tolerance.[2] Rh(III) complexes have been shown to catalyze sp^2 C–H bond insertion into various (polarized) π bonds including alkenes,[3] alkynes,[4] aldehydes,[5] imines,[6] isocyanates,[7] and others[8] via a C–H activation pathway. In addition to using unsaturated bonds as coupling partners, applications of strained rings represent an important strategy to construct a new framework, with the release of the ring strain being the driving force.[9]

Recently, we and others have successfully applied strained rings such as aziridines,[9f] 7-oxa/azabenzonorbornadienes,[9c] and diazabicycles[9a,d] to the coupling with arenes by Rh(III) catalysis (Scheme 1). Despite the success, these rings are limited in scope, and it is necessary to develop new categories of coupling patterns thus broadening the scope and applications of rhodium(III)-catalyzed C–C couplings. In this sense, cyclopropenones have received significant attention as an important building block in coupling reactions.[10] We reasoned that rhodium(III) may activate C–H bond toward the insertion into cyclopentenones to lead to a chalcone moiety after ring-opening. Significantly, chalcone has been recognized as a privileged structure in pharmaceutical industry and synthetic chemistry and this unique template is associated with several biological activities.[11] A general synthetic strategy employed to prepare chalcone analogues was based on Claisen–Schmidt condensation, which suffered from strong bases and a limited substrate scope. We now report formation of chalcone derivatives by a C–H activation strategy using cyclopropenones under mild conditions.

Scheme 1. Representative Rh(III)-Catalyzed Ring-Opening Reactions



An initial coupling of 2-phenylpyridine **1a** with cyclopropenone **2a** using 2.5 mol % of $[Cp^*RhCl_2]_2$ and 10 mol % of $AgSbF_6$ as catalysts gave the desired product **3aa** in 39% yield (Table 1, entry 1). Product **3aa** was fully characterized, including by X-ray crystallography. The preformed cationic rhodium catalyst $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ could also effect this C–C coupling, but **3aa** was only isolated in 35% yield (Table 1, entry 2). To our delight, the yield of isolated **3aa** was dramatically improved to 91% when the molar ratio of $AgSbF_6$ to $[Cp^*RhCl_2]_2$ was increased to 6:1 (Table 1, entry 3), where $AgSbF_6$ may play an important role in the activation of the cyclopropenone by coordination to the carbonyl group, thus changing the polarity of C–C bond.[12] Further screening of different solvents gave DCM as the best choice (Table 1, entries 3–6). Similar yield was obtained when AgOTf was used as an additive. Lowering the reaction temperature to rt gave rise to a much lower yield (Table 1, entry 8). No desired product was observed when either $[Cp^*RhCl_2]_2$ or $AgSbF_6$ alone was used as a catalyst, which suggested that a cationic Rh(III)

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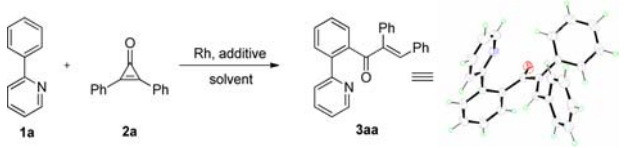
Table 1. Optimization of the Reaction Conditions[a]



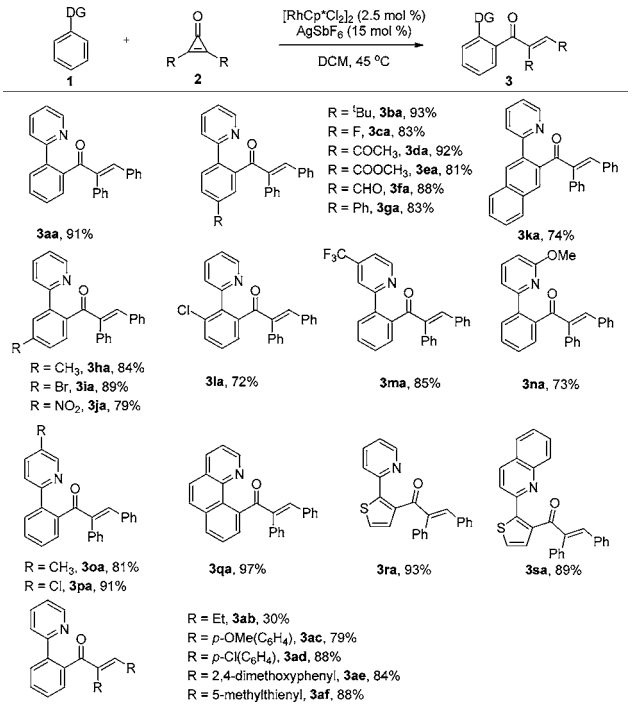
entry	catalyst (mol %)	solvent	yield[b] (%)
1	$[Cp^*RhCl_2]_2$ (2.5)/$AgSbF_6$ (10)	DCM	39
2	$[Cp^*Rh(MeCN)_3](SbF_6)_2$ (5)	DCM	35
3	$[Cp^*RhCl_2]_2$ (2.5)/$AgSbF_6$ (15)	DCM	91
4	$[Cp^*RhCl_2]_2$ (2.5)/$AgSbF_6$ (15)	acetone	<5
5	$[Cp^*RhCl_2]_2$ (2.5)/$AgSbF_6$ (15)	DCE	90
6	$[Cp^*RhCl_2]_2$ (2.5)/$AgSbF_6$ (15)	THF	75
7	$[Cp^*RhCl_2]_2$ (2.5)/AgOTf (15)	DCM	89
8[c]	$[Cp^*RhCl_2]_2$ (2.5)/$AgSbF_6$ (15)	DCM	40
9	$[Cp^*RhCl_2]_2$ (2.5)/$AgSbF_6$ (0)	DCM	0
10	$[Cp^*RhCl_2]_2$ (0)/$AgSbF_6$ (15)	DCM	0

[a]Reactions conditions: 2-phenylpyridine (0.24 mmol), cyclopropenone (0.2 mmol), 20 h, rhodium catalyst, solvent (3 mL), 45 °C, sealed tube under argon. [b]Isolated yield. [c]Room temperature.

species was required for this C−C coupling process (Table 1, entries 9 and 10).

Having identified the optimal conditions, we sought to explore the scope of this coupling system (Scheme 2). 2-Phenylpyridines were examined first. With either electron-donating or -withdrawing groups such as alkyl (**3ba**, **3ha**), phenyl (**3ga**, **3ka**), carbonyl (**3da**, **3ea**, **3fa**), and halide groups (**3ca**, **3ia**) at the *para* and *meta* position of the phenyl ring, the reaction proceeded smoothly, affording the corresponding products in 83−93% yields. Notably, a *meta* nitro substituent is

Scheme 2. Scope of 2-Arylpyridines and Cyclopropenones[a,b]

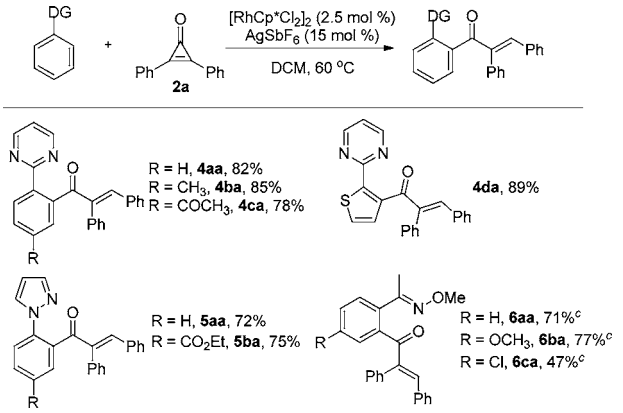


[a]Reactions conditions: 2-phenylpyridine (0.24 mmol), cyclopropenone (0.2 mmol), $[RhCp^*Cl_2]_2$ (2.5 mol %), $AgSbF_6$ (15 mol %), DCM (3 mL), 45 °C, 20 h, sealed tube under argon. [b]Isolated yield.

tolerated, and the coupled product was isolated in 79% yield (**3ja**). Investigation of the effect of the substituent on the pyridinyl ring also showed broad functional group compatibility, where both donating and withdrawing groups allowed the coupling with **2a** in good to excellent yields (**3ma**−**pa**). Efficient C−H functionalization was achieved for benzo[*h*]-quinoline to afford product **3qa** in 97% yield. Furthermore, heteroarenes were also applicable (**3ra, 3sa**). The scope of the cyclopropenone substrate was next explored in the coupling with 2-phenylpyridine. Coupling of symmetrical diphenylcyclopropenones bearing electron-donating and electron-withdrawing groups in the benzene ring is tolerated (**3ac**, **3ad**, **3ae**). Delightfully, 5-methylthienyl-substituted cyclopropenone also reacted with **1a** in high efficiency. In contrast, dialkyl-substituted cyclopropenone only gave poor result (**3ab**), and poor conversion (<10%) was observed for 2-ethyl-3-phenyl-cyclopropenone.

To further define the substrate scope, this C−H functionalization reaction was applied to other arene substrates (Scheme 3). Arenes bearing *N*-pyrazyl as well as 2-pyrimidyl

Scheme 3. Scope of Other Arene Substrates[a,bc]

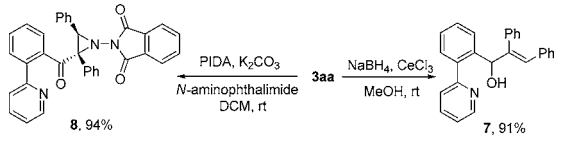


[a]Reactions conditions: arene (0.24 mmol), cyclopropenone (0.2 mmol), $[RhCp^*Cl_2]_2$ (2.5 mol %), $AgSbF_6$ (15 mol %), DCM (3 mL), 60 °C, 20 h, sealed tube under argon. [b]Isolated yield. [c]$[RhCp^*Cl_2]_2$ (5 mol %), $AgSbF_6$ (30 mol %).

directing groups also showed excellent reactivity. 2-Phenylpyrimidine and 1-phenylpyrazole bearing both electron-donating and electron-withdrawing groups at the *para* position all coupled smoothly with **2a**, and the corresponding products were isolated in 72−85% yields (**4aa**−**ca** and **5aa**−**ba**). When directed by a pyrimidyl group, a thiophene underwent the same coupling efficiently and the product **4da** was isolated in 89% yield. In addition, coupling with *O*-methyl ketoximes were also accessible, albeit with somewhat lower efficiency. Lower yield was obtained for a *p*-Cl substituted oxime, indicating that electron-withdrawing substituents retarded the reaction.

The synthetic utility of this reaction has been demonstrated with derivatization of product **3aa** (Scheme 4). The chemo-

Scheme 4. Functionalization of Product 3aa



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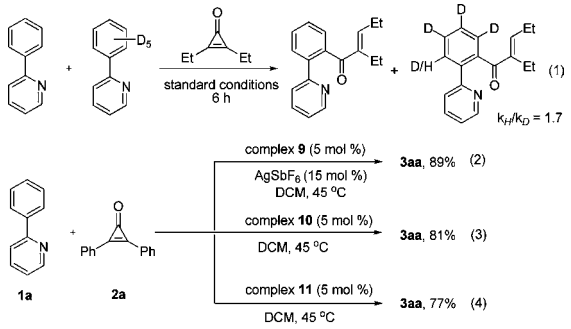
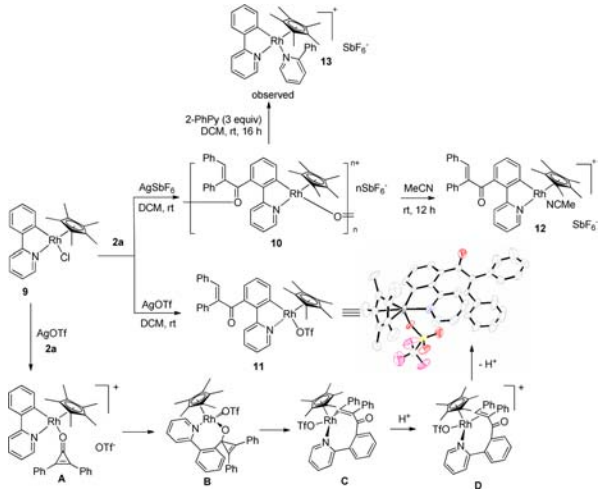
selective 1,2-reduction of enone **3aa** with $NaBH_4$ in combination with $CeCl_3$ afforded a functionalized allylic alcohol (**7**). Treatment of **3aa** with $PhI(OAc)_2/K_2CO_3$ at rt provided the aziridination product **8** in 94% yield as a single diasteriomer.

To cast light on the mechanism, kinetic isotopic study was performed under the standard conditions. The intermolecular competitive coupling of **1a** and **1a**-d_5 with **2a** at a low conversion gave k_H/k_D = 1.7 (eq 1), which further indicates that C−H activation is involved.



Several possible rhodium(III) intermediates in this reaction were next investigated. Cyclometalated rhodium(III) chloride complex **9** was prepared and was applied as a catalyst precursor (5 mol %) for the coupling of **1a** and **2a** in the presence of $AgSbF_6$ (15 mol %), where product **3aa** was isolated in 89% yield (eq 2). This suggests the intermediacy of a cationic cyclometalated Rh(III) complex via C−H activation. To probe the interaction between the Rh−C bond and cyclopropenone, an equimolar mixture of complex **9**, cyclopropenone **2a**, and AgX (X= SbF_6 and OTf) was allowed to react (DCM, rt), from which complexes **10** and **11**, respectively, were isolated (Scheme 5). Complex **11** was fully characterized by NMR

Scheme 5. Synthesis of Rh(III) Complexes

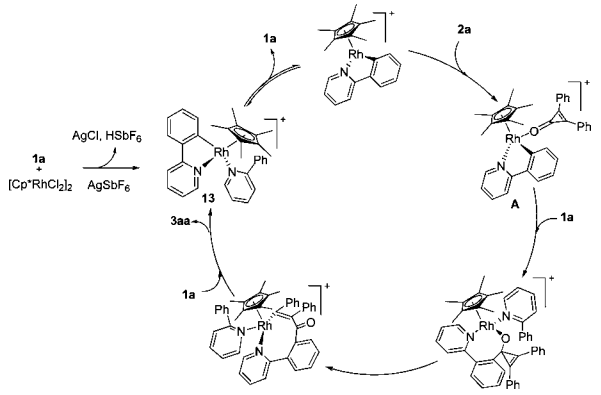


spectroscopy and X-ray crystallography. The coordination sphere of complex **11** includes a cyclometalating N∧C ligand bearing a diphenylacryloyl moiety at the *ortho'* position, a triflate anion, and a Cp* ligand. Complex **10**, however, is insoluble in non- or weakly coordinating solvents (DCM, acetone, $CHCl_3$) and is probably a polymeric ionic species. Dissolution in MeCN afforded the adduct **12**, which was fully characterized by NMR spectroscopy and ESI-MS. Both complexes **10** and **11** proved to be active catalyst precursors for the coupling of **1a** and **2a** (eq 3 and 4). Furthermore, when complex **10** was treated with **1a** (3 equiv), cyclometalated complex **13** bearing two units of 2-PhPy was also detected as the major organometallic product by ^1H and ^{13}C NMR spectroscopy with the concomitant formation of product **3aa**, which was obtained in 79% yield by GC analysis. These results indicate that these cyclometalated rhodium complexes are possible active intermediates. The release of coupled product **3aa** and the concomitant formation of complex **13** from the interaction of 2-PhPy and complex **10** might occur via a σ-complex-assisted metathesis (σ-CAM) mechanism.[13]

The formation of complex **11** from the reaction of **9** and **2a** is proposed in Scheme 5. Chloride abstraction by AgOTf followed by coordination of **2a** gives intermediate **A**. Migratory insertion of the Rh−aryl bond into the carbonyl group generates alkoxide intermediate **B**. Subsequent β-carbon elimination is proposed to give a rhodium(III) alkenyl **C**, which is expected to undergo protonolysis to **D** by a catalytic amount of acid. The final product **11** was obtained by roll-over cyclometalation.[14,15]

Based on our preliminary studies of these stoichiometric reactions, the mechanism of this coupling was proposed in Scheme 6. Complex **13** generated from $[Cp^*RhCl_2]_2/AgSbF_6$

Scheme 6. Proposed Mechanism



and **1a** undergoes ligand decoordination to yield a 16-VE intermediate, which is subsequently saturated by cyclopropenone coordination. Migratory insertion of the aryl group into the carbonyl group of cyclopropenone and subsequent β-carbon elimination leads to a ring-opening intermediate, a proposed eight-membered metallacycle. The final product was released, and the catalytic cycle was completed when an incoming **1a** undergoes coordination and cyclometalation, again likely via a σ-CAM mechanism. In the absence of any 2-PhPy substrate, the reaction of intermediate **A** eventually furnishes the roll-over cyclometation product **11** when a weak coordinating anion such as triflate is present.

In summary, we have developed a redox-neutral Rh(III)-catalyzed C−C coupling of arenes with cyclopropenones for the synthesis of chalcones. This process features mild conditions, high yield, broad substrate scope, and excellent functional group tolerance. Moreover, several Rh(III) complexes related to the mechanism have been synthesized and characterized, and a plausible mechanism was proposed.

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■ ASSOCIATED CONTENT

Supporting Information

Experimental details, characterization data, and copies of NMR spectra of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(15) CCDC 974185 (**3aa**) and CCDC 974189 (**11**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.