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Transition metal-catalysed couplings between arenes and strained or reactive rings: combination of C–H activation and ring scission

Fen Wang, Songjie Yu and Xingwei Li*

Organic transformations that involve direct functionalization of C–H bonds represent an attractive synthetic strategy that maximizes atom- and step-economy. With the generally high stability of C–H bonds, these processes have mostly required harsh reaction conditions, in combination with the necessity of activation of the C–H substrates and/or the coupling partners. As a class of activated coupling partners, strained or reactive rings exhibited high activity in the coupling with aryl and alkyl C–H bonds. Such a high reactivity of the rings allowed the facile construction of various new structural platforms *via* coupling with scission of the ring structures. The combination of C–H activation and scission of the rings allowed for applications of a broader scope of C–H bonds, including those less reactive alkyl ones. This synthetic diversity of these rings has been realized owing to the intrinsically different mechanisms of the interactions of transition metal catalysts and the strained/reactive rings.

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Key learning points

1. Although strained rings are generally reactive, compatibility between strained rings and arenes in C–H functionalization may represent a challenge.
2. When properly designed, the high reactivity of strained/reactive rings can compensate the low reactivity of the C–H substrate, allowing the applicability of some less reactive C–H substrates.
3. Coupling of arenes with strained rings may result in ring opening. Thus, the skeleton of the product can be readily reconstructed.
4. The scission of a ring may follow five intrinsically different mechanisms as a result of the interactions between the ring and the organometallic species or the metal catalyst.

1. Introduction

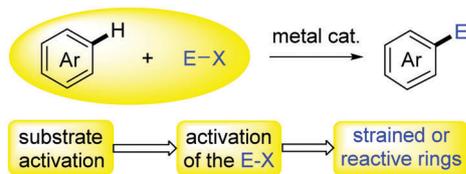
Hydrocarbons are widely abundant and serve as ideal substrates in catalytic synthesis of value-added organics. Classical organic synthesis relied heavily on functional group transformation chemistry, which requires prefunctionalized starting materials and generated stoichiometric amounts of waste. In the past few decades, C–H bond activation has received increasing attention owing to the high step- and atom-economy and availability of starting materials. Catalytic functionalization of C–H bonds involves two processes, namely the C–H activation process and the functionalization process. The former involves the cleavage of a C–H bond to form a reactive M–C intermediate. To ensure the reactivity and the selectivity of C–H bonds in an arene substrate bearing multiple C–H bonds, several strategies have been employed, which include chelation-assistance (employment of directing

groups, DGs) and employment of acidic or electronically or sterically differentiable C–H bonds.¹

The most challenging stage of C–H functionalization is arguably the functionalization process, where the M–C bond interacts with a coupling partner. Moreover, this functionalization process is the product-forming process that can deliver molecular diversity and versatility of the coupled products. Most, if not all, late transition metals are known to affect C–H cleavage. However, with the structural and functional diversity of metal catalysts and substrates, the compatibility between the arene and the coupling partner needs to be carefully addressed. For example, a late transition metal–carbon bond resulting from C–H activation is typically covalent and less polarized. Thus, its reactivity is mostly limited to organometallic chemistry of late metals. To overcome some of the limitations and to achieve diversity in C–H activation chemistry, strategies of substrate activation and catalyst activation can be employed.

In the regime of substrate activation, activation of the coupling partner is particularly useful (Scheme 1). Thus, three- and

Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China. E-mail: xwli@dicp.ac.cn



Scheme 1 Substrate activation by the employment of strained/reactive rings.

four-membered rings are intrinsically reactive due to ring strain (Scheme 2).²⁻⁵ Significantly, with the opening of a ring structure, the skeleton of the product can be readily reconstructed, leading to rapid access to structural complexity. However, the high reactivity of these rings may often cause issues such as decomposition and self-coupling. In addition, other functional groups embedded in the strained ring might also react preferentially with no ring scission. Therefore, the compatibility between strained

				
ring strain (kcal/mol)	27.5	26.7	18.2	7.4

Scheme 2 Strains of three- to five-membered cycloalkanes.²

rings and arenes in C–H functionalization needs to be fully addressed.

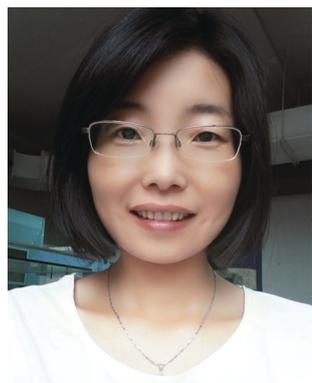
We have briefly discussed substrate activation strategies in C–H activation.⁶ However, they were limited to Rh(III)-catalysed systems. Despite the significance of both C–H activation and chemistry of strained rings, no related review has been reported. We now summarize recent findings in coupling systems that combine the C–H activation of arenes and the opening of strained or reactive rings. In many cases, the reaction was initiated by the C–H activation of arenes to generate an active M–C bond, but occasionally ring scission may induce subsequent (intramolecular) C–H activation. This review focuses on the coupling of intrinsically unactivated arenes *via* a C–H activation mechanism, so Lewis-acid mediated opening of a ring that gives an unsaturated intermediate that interacts with an arene will not be discussed (Scheme 3a).

2. Interactions between a metal–C(aryl) bond and a strained/reactive ring

Ring scission in this review is metal-mediated. The mechanisms of the interactions of an M–C bond and a strained ring leading to ring-opening coupling vary with the nature of the ring. The following mechanisms are generally followed (Scheme 3).

Scission of rings *via* β -elimination

Tertiary alcohols are known to undergo β -carbon elimination upon O-binding. Obviously, this reactivity also applies to the



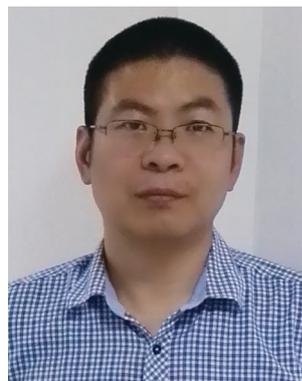
Fen Wang

Fen Wang was born in Shaanxi, China. She received her BS degree from Yulin College in 2008 and MS degree from the Northwest Normal University in 2011, during which time she was co-supervised by Prof. Xingwei Li at the Dalian Institute of Chemical Physics, CAS. She has worked in the Li group as a Research Assistant since 2011. She will obtain her PhD degree in 2016. Her current research interests include transition metal-catalysed C–H bond functionalization.



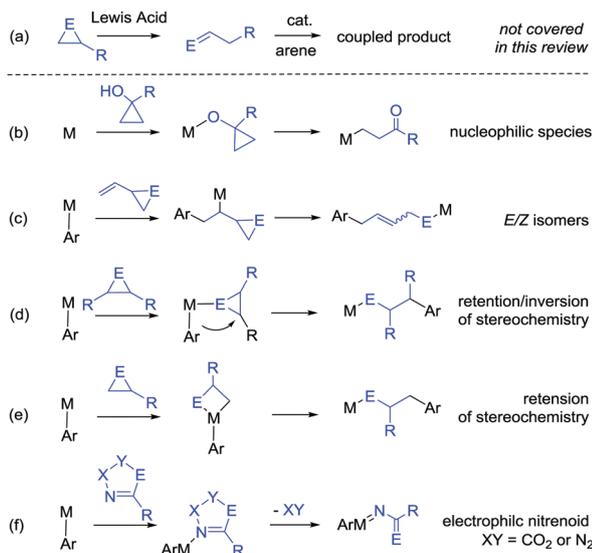
Songjie Yu

Songjie Yu received his BS in chemistry in 2008 from Shandong University, and then obtained his MS from Lanzhou Institute of Chemical Physics, CAS in 2011 with Prof. Wei Sun in the area of biomimetic catalysis. He received his PhD from Dalian Institute of Chemical Physics, CAS in 2015 with Prof. Xingwei Li and Prof. Boshun Wan, after which he became a research assistant in the Li group. In June 2016, he joined the Ge research group at NUS as a research fellow working on catalysis by first-row transition metals.



Xingwei Li

Xingwei Li obtained his BS degree from Fudan University in 1996. He then studied at the Yale University and obtained his PhD degree in 2005 under the supervision of Prof. Robert H. Crabtree. After postdoctoral research at the Caltech in Prof. John E. Bercaw's laboratory (2005–2006), he started his independent career at the Nanyang Technological University (Singapore) in 2006. He has been a Professor of Chemistry at the Dalian Institute of Chemical Physics, Chinese Academy of Sciences since 2010. His research interests include the development of novel synthetic methods via bond activation, isolation of reactive intermediates, and organo-metallic chemistry.



Scheme 3 Mechanisms of the opening of a strained/reactive ring.

more reactive, strained cyclic tertiary alcohols. Cyclopropanols fall into this category, and the β -carbon elimination affords a nucleophilic metal-carbon bond (Scheme 3b).

Although strained rings are intrinsically activated, they might need further avenues of activation, particularly when the ring is not sufficiently coordinating. Attaching a π -bond (C=C, C=N, and C=O) provided an extra handle for the enhancement of reactivity owing to the facile migratory insertion chemistry, and the resulting M-E (E = C, N, and O) species may further induce beta-elimination of the strained ring, leading to ring scission (Scheme 3c). Previously both *endo*- and *exo*-cyclic π bonds have been incorporated into ring systems, which will be discussed in detail.

Nucleophilic substitution (SN) type scission of the ring

Polarized rings with a good leaving group may participate as electrophiles in formal SN type reactions (Scheme 3d). Their interactions with a nucleophilic M-C bond may parallel the two extreme mechanisms given in textbook reactions between oxiranes and nucleophiles. Under basic conditions (as in the interaction between Grignard reagents and styrene oxide), the SN₂ mechanism is followed, while under acidic conditions the SN₁ mechanism is operative. These two pathways can be distinguished between using a stereochemistry probe in combination with examination of the site-selectivity of the ring. Of course, the continuous mechanism in between these two extremes may exist.

Oxidative addition of a strained ring

When a strained ring is activated by an electron-withdrawing group (EWG) or contains an oxidizing single bond, oxidative addition may occur, especially for low valent transition metal catalysts (Scheme 3e). Following oxidative addition, the high valent metal species may readily undergo C-C or C-E reductive elimination to furnish the same product. Since the stereochemistry

of the ligand is usually retained during oxidative addition *via* a concerted pathway, a stereochemical probe can be employed to elucidate this pathway.

Metal-assisted elimination of a ring leading to carbene and nitrenoid formation

Five-membered rings are poorly strained, so other driving forces need to be employed to sustain an otherwise thermodynamically unfavourable ring scission. Occasionally, unsaturated five-membered rings such as nitrene transfer reagents may undergo elimination of a small molecule (Scheme 3f). For example, the interactions between a Rh(III) centre and dioxazolones afforded an Rh(V) nitrenoid species, which occurred *via* concerted elimination-rhodium nitrenoid formation as suggested by Chang's DFT and experimental studies.⁷ Since these rings are largely unstrained, additional driving forces including aromatization and evolution of gases need to be provided.

3. Coupling of arenes with strained/reactive rings

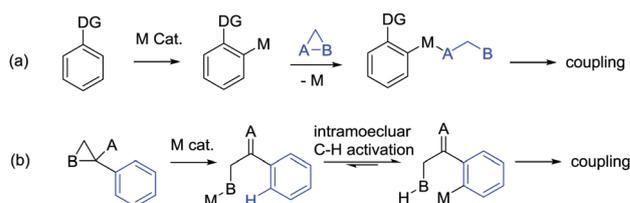
Two classes of couplings that combine C-H activation and ring opening will be discussed in this review (Scheme 4), depending on the sequence of C-H activation and ring scission.

3.1 C-H activation leading to the formation of a M-C bond that induces ring opening

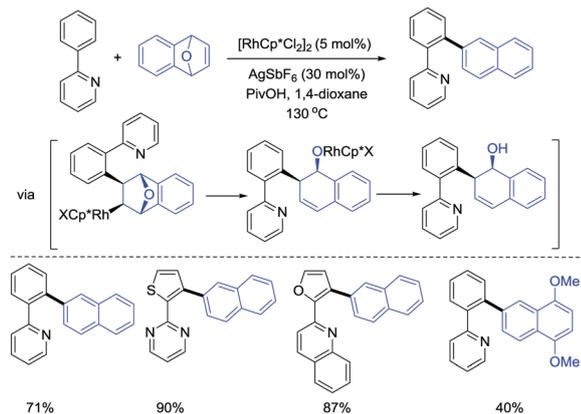
In this category (Scheme 4a), C-H activation occurs first, and the resulting M-C bond interacts with a (strained) ring, leading to ring scission and subsequent coupling. The reaction mechanisms and types vary with the nature of the M-C bond and the ring structure. Three types of systems can be classified on the basis of the interactions between the M-C bond and the ring structure.

3.1.1 Coupling *via* typical organometallic properties of the M-C bond: ring scission induced by migratory insertion of the M-C bond. For late transition metals, the resulting M-C bonds are typically covalent in nature and exhibit traditional organometallic properties, especially in the interactions with soft or less polar unsaturated coupling partners. Insertion of a M-C bond into an *endo*- or *exo*-double bond embedded in a strained ring can induce ring opening *via* β -elimination.

We reported the first rhodium(III)-catalysed C-H activation of arenes with subsequent coupling with a strained cyclic olefin (Scheme 5).⁸ 7-oxa/azabenzonorbornadienes have the characteristics



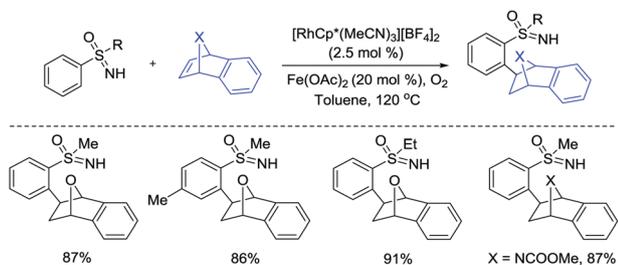
Scheme 4 Two classes of couplings that combine C-H activation and ring opening.



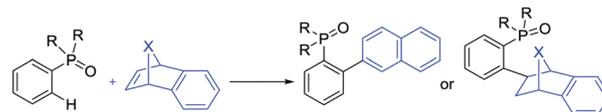
Scheme 5 Naphthylation using 7-oxabenzonorbornyldienes.

of both an internal olefin and a strained ring. The migratory insertion of an M–C bond into such an endocyclic olefin generates a metal alkyl that can undergo β -oxygen or -nitrogen elimination, instead of β -hydrogen elimination. Although ring opening interactions between Pd–C bonds and 7-oxa/azabenzonorbornadienes had been reported, the Pd–C bond was generated from C-halo oxidative addition.⁸ The Rh(III)-catalysed coupling between an arene bearing a directing group and 7-oxabenzonorbornadiene occurred at 130 °C in the presence of PivOH, leading to 2-naphthylation with water as the only byproduct. The C–C coupling is proposed to occur *via* the migratory insertion of the Rh–C bond into the C=C bond. β -Oxygen elimination and subsequent dehydration delivered the final product. The PivOH additive likely facilitated C–H activation as has been typically proposed in C–H activation *via* a concerted metalation–deprotonation mechanism. In addition, the dehydration process is jointly promoted by the Lewis acidic Rh(III) catalyst and the excess AgSbF₆.

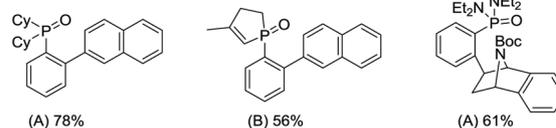
By employing a sulfoximine as a directing group, Bolm achieved Rh(III)-catalysed hydroarylation of 7-oxabenzonorbornadiene in the presence of a Fe(OAc)₂ additive (Scheme 6).⁹ Although it was conducted at a comparably high temperature, the reaction only afforded the hydroarylation product with no direct ring scission. The difference in selectivity might be ascribable to the absence of a Lewis acidic AgSbF₆ or PivOH in this coupling system. The authors demonstrated that ring scission–dehydration was achievable when it was subsequently treated with MeSO₃H. By employing [Ru(*p*-cymene)Cl₂]₂ as a catalyst, Bolm also realized the bicyclic



Scheme 6 Bicyclic-retentive hydroarylation of 7-oxa/azabenzonorbornadienes.



Conditions A: [RhCp*(MeCN)₃][SbF₆]₂ (4 mol %), AgOAc (20 mol %), DCE, 130 °C, 12 h.
Conditions B: Conditions A, followed by NaCl (2 equiv) and TMSCl (2 equiv) in MeCN.

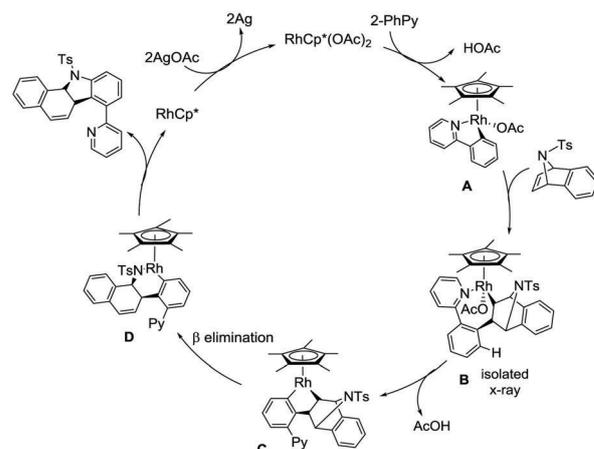
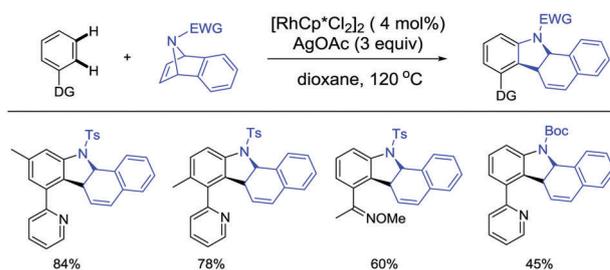


Scheme 7 Naphthylation or ring scission assisted by P=O directing groups.

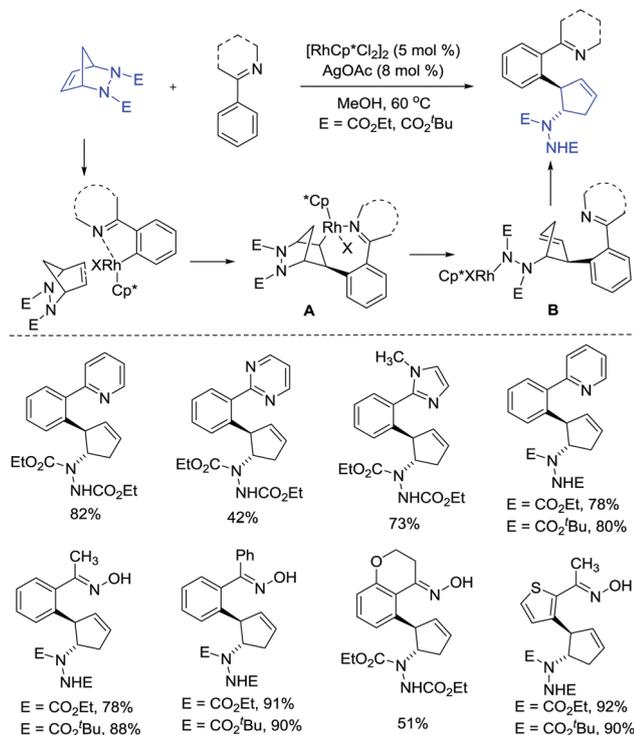
scaffold-retentive coupling between 2-arylpyridines and 7-oxa/azabenzonorbornadiene.¹⁰ Starting from the same substrates, the bicyclic product remains complementary to our 2-naphthylated products.

Recently, Miura extended the arene substrate to a tertiary phosphine oxide/sulfide under Rh(III) catalysis, where the same type of 2-naphthylation reaction was observed for 7-oxabenzonorbornadienes (Scheme 7).¹¹ In contrast, *N*-Boc-substituted azabenzonorbornadienes reacted to afford the bicyclic-retentive scaffold under the same conditions.

Despite their structural similarity, 7-oxabenzonorbornadienes and 7-azabenzonorbornadienes behave differently. The Rh(III)-catalysed coupling between 2-arylpyridines and 7-azabenzonorbornadienes failed to occur under the redox-neutral conditions (Scheme 8).⁸ Instead, with AgOAc being an oxidant, the



Scheme 8 Oxidative difunctionalization of arenes.

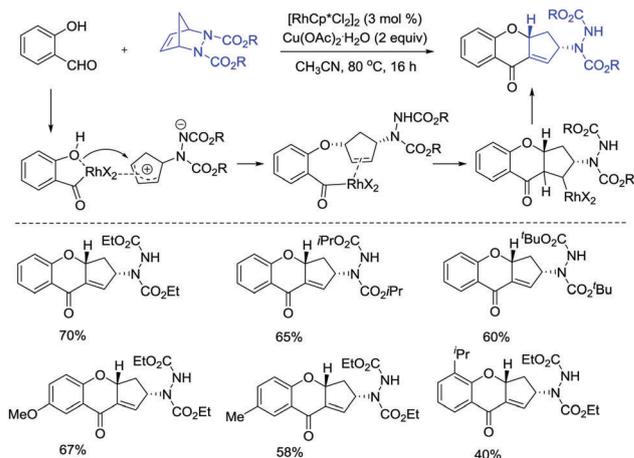


Scheme 9 Redox-neutral couplings with diazabicyclic olefins.

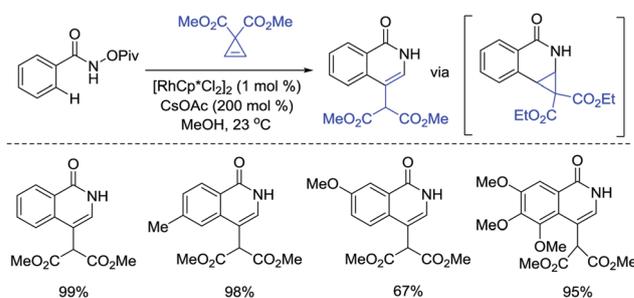
coupling afforded a *cis*-dihydrocarbazole as a result of oxidative C–C/C–N difunctionalization of the arene. The reaction proceeded with twofold sequential C–H activation, first at the *ortho* position and then at the *meta* position. Studies on kinetic isotope effects revealed that the first C–H activation is turnover-limiting. To investigate the interactions between the Rh–C(aryl) bond and the strained olefin, a stoichiometric reaction was performed using a rhodacyclic chloride complex (chloride analogue of **A**), a 7-azabenzonornadiene, and AgOAc. This reaction afforded a seven-membered rhodacycle (**B**) *via* migratory insertion, and this insertion is *cis* to the nitrogen. Further mechanistic studies have been performed regarding the sequence of the β-nitrogen elimination *versus* the second C–H activation. It follows that the second (*meta*) C–H activation took place after dechelation of the pyridine directing group (**C**). Subsequent β-nitrogen elimination occurred to give a Rh(III)sulfonamido species (**D**) that released the product upon C–N reduction elimination.

In 2013, Cui *et al.* took advantage of the strain in a diazabicyclic olefin, the coupling of which with 2-arylpiperidines or oximes (Scheme 9) afforded a *trans* cyclopentene with broad functional group tolerance.¹² The reaction is proposed to proceed *via* initial C–H activation followed by migratory insertion of the Rh–C(aryl) bond into the strained olefin (**A**). Subsequent β-nitrogen elimination leads to ring scission (**B**). The final product is delivered upon protonolysis. Of note, the *trans* stereochemistry originates from the *syn* insertion of the Rh–Ar bond, and this insertion is *cis* to the methylene bridge.

The Radhakrishnan group developed an oxidative coupling of salicylaldehyde with this strained ring (Scheme 10),¹³ where a cyclopentene-fused chromanone was obtained as the coupled



Scheme 10 Oxidative couplings with diazabicyclic olefins.

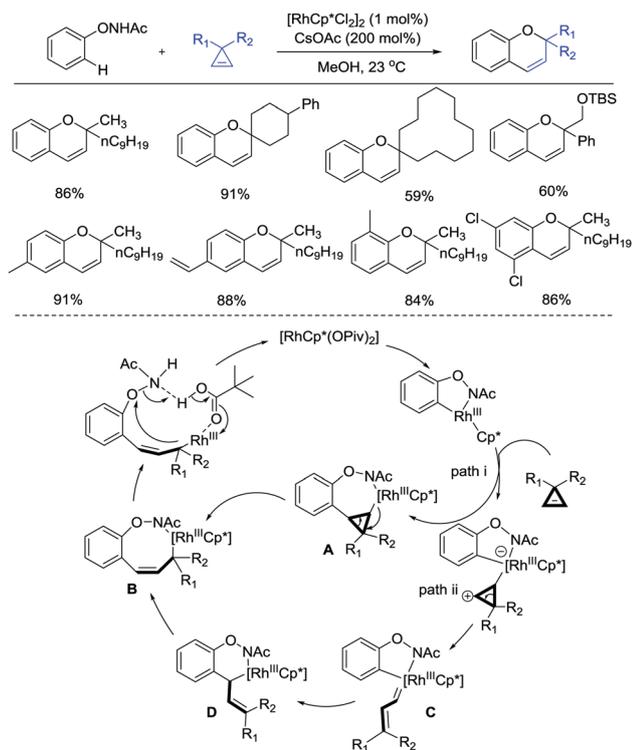


Scheme 11 Transannulation using activated cyclopropenes.

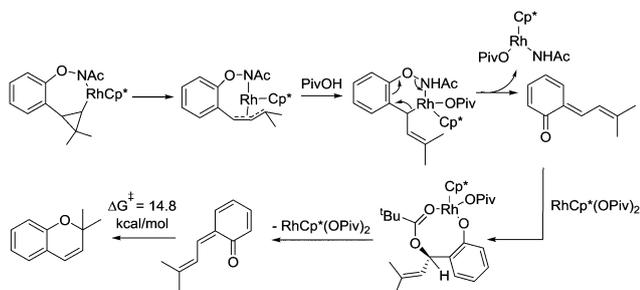
product. Despite the proposed attack on an allylic cation, a mechanism featuring migratory insertion of the Rh–acyl group and subsequent β-nitrogen elimination remains possible.

In 2013, Rovis and Hyster reported the coupling of *N*-(pivaloyloxy)benzamide with *gem*-diester-functionalized cyclopropenes, leading to redox-neutral synthesis of NH quinolones under mild conditions (Scheme 11).¹⁴ The coupling was believed to proceed *via* initial [4+2] annulation to yield a dihydroquinolone.¹⁵ The subsequent ring-opening is likely catalysed by the Rh(III) catalyst and/or the PivOH. The quinolinone product is complementary in terms of regioselectivity to those obtained using alkynes as a coupling partner under Rh(III) catalysis; the latter afforded quinolinone with a substituent adjacent to the nitrogen atom.¹⁵

Wang elegantly applied a *gem*-disubstituted cyclopropene,¹⁶ which is also known as a possible carbene precursor, to Rh(III)-catalysed C–H activation, while previously such carbene precursors had been mostly limited to those activated by at least one electron-withdrawing group. The redox-neutral coupling between *N*-phenoxyacetamides and such cyclopropenes afforded 2*H*-chromenes as a result of transannulation (Scheme 12). Two possible mechanisms have been suggested by the authors. In path (1), the migratory insertion of the Rh–C bond generates a seven-membered rhodacycle (**A**), which undergoes beta-carbon elimination to lead to an eight-membered Rh(III) alkyl species (**B**). Alternatively (path 2), the cyclopropene undergoes ring scission to deliver a reactive carbene species (**C**). Migratory insertion



Scheme 12 Transannulation using cyclopropenes.

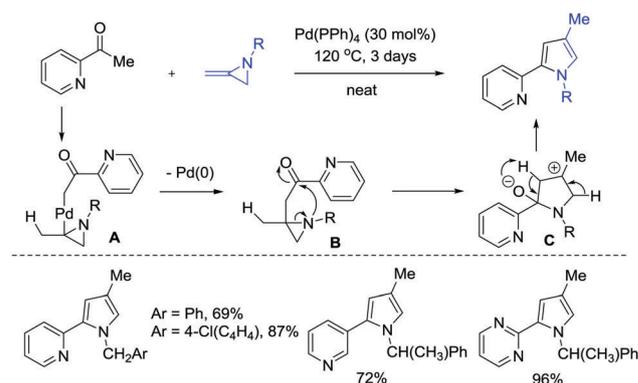


Scheme 13 DFT studies on the coupling with cyclopropenes.

of the Rh–Ar bond followed by *eta*-1 to *eta*-1 allyl slippage (*via* D) afforded the same eight-membered ring intermediate (B).

DFT studies by Xia and co-workers provided mechanistic details (Scheme 13).¹⁷ It was found that the β-carbon elimination occurs more easily from the corresponding seven-membered rhodacyclic species and subsequent O–N bond cleavage led to an unexpected dearomatized (*E*)-6-alkenylcyclohexa-2,4-dienone. *E/Z* Isomerization of this intermediate is required for the final cyclization to 2*H*-chromene, and this isomerization of the C=C bond was catalysed by a Cp*Rh(OPiv)₂ species with the proposed reversible migratory insertion of the OPiv group.

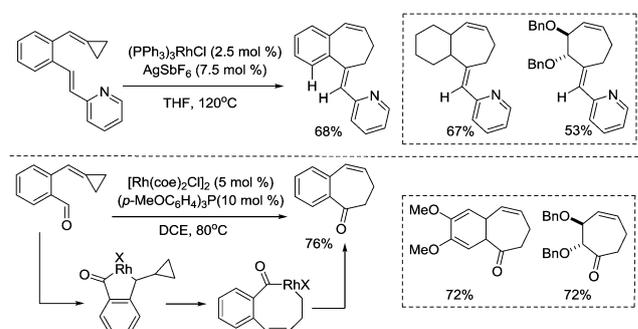
Migratory insertion into an exocyclic olefin can also induce ring opening. In 2004, Yamamoto and co-workers disclosed a Pd(0)-catalysed C–H activation of methyl ketones such as acetylpyridines in the coupling with methyleneaziridines (Scheme 14).¹⁸ The coupling afforded substituted pyridylpyrroles *via* transannulation. Besides acetylpyridines, simple acetophenone

Scheme 14 Pyrrole synthesis *via* coupling with methyleneaziridines.

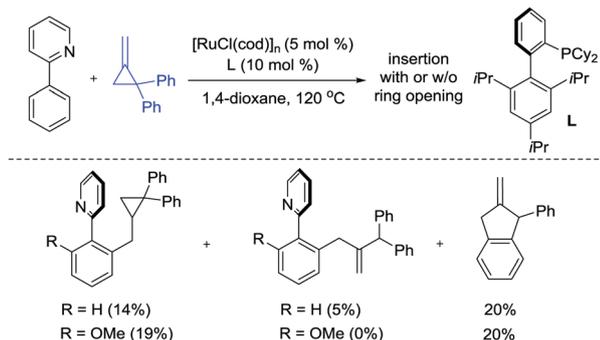
is also a viable substrate. The reaction was proposed to be initiated by methyl C–H oxidative addition to give a C-bound Pd(II) enolate hydride followed by hydropalladation of the olefin unit (A). The resulting Pd(II) tertiary alkyl species undergoes C–C reductive elimination (B) and nucleophilic addition of the nitrogen to the carbonyl group (C), and the pyrrole was delivered after dehydration. Alternatively, β-nitrogen elimination of the Pd(II) tertiary alkyl species (A) should also be possible.

In 2007, Fürstner reported the first Rh(I)-catalysed C–H activation system that incorporated methylenecyclopropanes (MCPs, Scheme 15).¹⁹ The intramolecular coupling of MCP bearing a vinylpyridine directing group was catalysed by the Wilkinson catalyst, and a seven-membered ring was obtained in moderate to high yields. The reaction was initiated by chelation-assisted C–H activation of the olefinic C–H bond, followed by β-hydrogen insertion into the proximal MCP C=C bond. β-Carbon elimination afforded an eight-membered rhodacycle, which reductively eliminated the final product. Besides this substrate, the reaction was also applicable to a MCP functionalized by an *ortho* formyl group, where the reaction was triggered by formyl C–H activation under chelation-assistance by the olefin unit. Notably, the formation of seven-membered rings *via* a C–H activation strategy remains largely underexplored.

In 2012, Ackermann and co-workers applied MCPs as a special olefin to the intermolecular coupling with a variety of arenes under ruthenium catalysis (Scheme 16).²⁰ In most cases, the coupling afforded hydroarylation products with the retention of



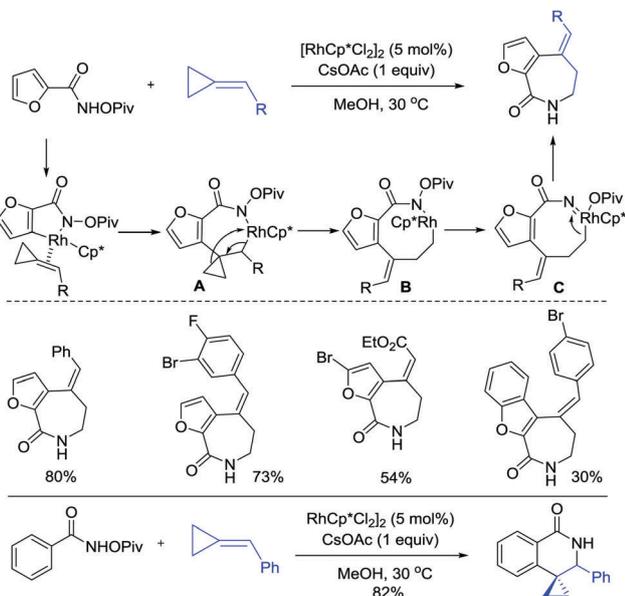
Scheme 15 Intramolecular coupling of methylenecyclopropane.



Scheme 16 Ru-catalysed coupling of methylenecyclopropane.

the cyclopropane ring. Occasionally, the ring-scission product was obtainable as the major one. Despite the limited reaction selectivity, this represented the first combination of Ru-catalysed C–H activation of arenes and ring-opening of MCPs.

In 2013, Cui and co-workers took advantage of the ring strain in MCPs and extended it to Rh(III) catalysis (Scheme 17).²¹ The coupling between *N*-(pivaloyloxy)furan-2-carboxamide and MCPs occurred under mild conditions to give furan-fused azepinone products, where the MCP acts as a C3 coupling partner. The catalytic cycle likely involved the migratory insertion of Rh–C into the MCP C=C bond followed by β -carbon elimination to deliver an eight-membered rhodacyclic intermediate. Subsequent C–N formation and N–O cleavage furnished the final product and regenerated the active Rh(III) species. However, the authors gave no detailed explanation on mechanistic possibilities of this process (*vide infra*). Xia and co-workers performed DFT studies on this system (Scheme 17).²² It was found that the direct reductive elimination of the eight-membered rhodacyclic intermediate (**B**) was kinetically unfavourable. Instead, the OPiv

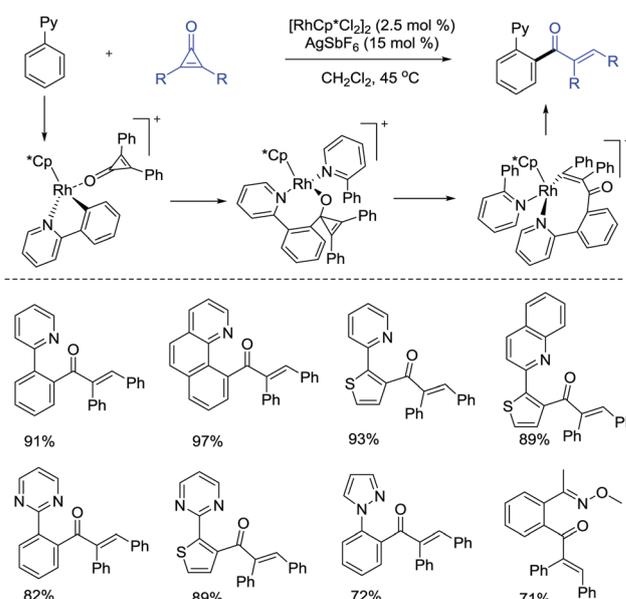


Scheme 17 Synthesis of seven-membered rings using methylenecyclopropanes.

group undergoes migration to afford a Rh(V)nitrenoid species (**C**), which undergoes facile alkyl migratory insertion into the Rh=N, and C–N reductive elimination yielded the final product with regeneration of the active Rh(III) species. In contrast to *N*-(pivaloyloxy)furan-2-carboxamides, *N*-(pivaloyloxy)benzamide coupled with MCP to yield *spiro* dihydroisoquinolinones with no opening of the MCP ring, where it functioned as a π -partner in 4+2 coupling.

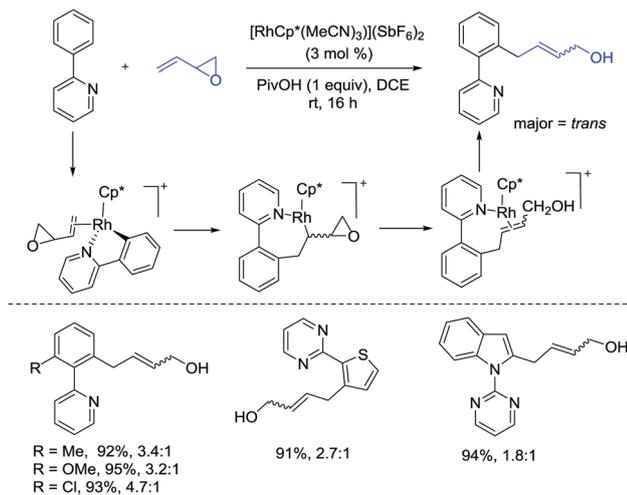
Cyclopropenone is a highly polarized and strained aromatic ring. By taking advantage of the electrophilicity of the carbonyl group, we successfully applied it to Rh(III)-catalysed C–H activation-acylation (Scheme 18).²³ The mild, redox-neutral coupling between arenes and disubstituted cyclopropenone afforded chalcones, where arenes bearing pyridine, pyrimidine, pyrazole, and oxime ether DGs are all viable. Unfortunately, only symmetrical cyclopropenones have been demonstrated such that no conclusion on the site selectivity of cyclopropenone could be drawn. The reaction is proposed to proceed *via* migratory insertion of the Rh–C bond into the highly polarized C=O bond, which triggers a β -carbon elimination to generate a Rh(III) alkenyl species. Protonolysis of the Rh–C bond furnished the final product. Our studies showed that acylation using the corresponding acid chloride failed to occur under various Rh(III)-catalysed conditions, likely because of the low coordination ability and/or poor oxidizing ability of the C–Cl bond.

As strained electrophiles, oxiranes have found a wide range of applications in metal-catalysed coupling reactions. Unfortunately, simple oxiranes such as styrene oxides failed to undergo Rh(III)-catalysed coupling with a variety of arenes. This is likely caused by the rather weak ligating properties of the epoxide. Furthermore its oxidative addition to a high valent metal such as Rh(III) is also unlikely. To solve this limitation, we introduced a vinyl group to an oxirane unit, which indeed provided a handle for the manipulation of the incipient Rh–C(aryl) bond.²⁴



Scheme 18 Acylation using coupling of cyclopropenones.

Tutorial Review

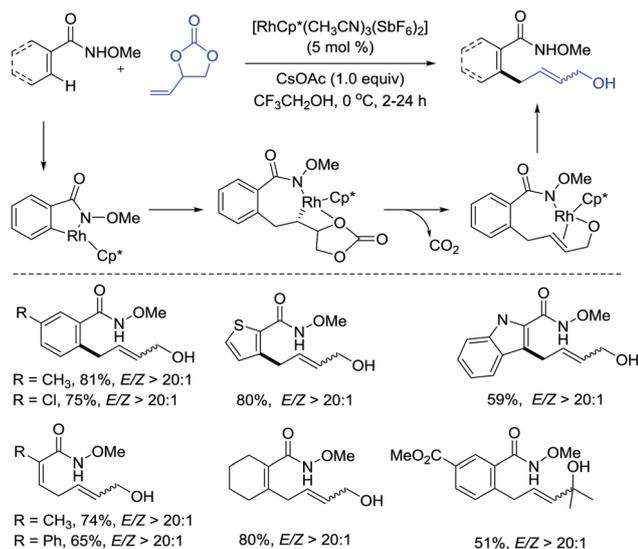


Scheme 19 Coupling using vinyloxiranes.

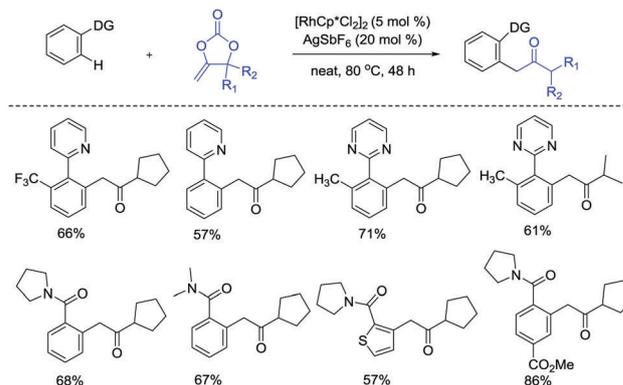
Under Rh(III) catalysis, the mild coupling of arenes such as 2-arylpyridines or *N*-pyrimidylindoles with 2-vinyloxirane afforded the corresponding allylic alcohols as a mixture of *Z/E* isomers (Scheme 19). Unfortunately, the stereoselectivity was low to moderate in all cases.

To solve the above-mentioned limited *E/Z* stereoselectivity, Wang and co-workers extended the 2-vinyloxirane to 4-vinyl-1,3-dioxolan-2-one (Scheme 20).²⁵ The Rh(III)-catalysed coupling of *N*-methoxybenzamide with 4-vinyl-1,3-dioxolan-2-one occurred at 0 °C. Although it is not a strained ring, 4-vinyl-1,3-dioxolan-2-one exhibited high activity with the evolution of CO₂ as a driving force. The reaction is highly stereoselective with *E/Z* ratio up to >20:1 in many cases.

The analogous strategy has been elegantly employed by Kakiuchi and co-workers (Scheme 21).²⁶ The coupling of arenes with an unstrained cyclic alkenyl carbonate under Rh(III) catalysis afforded an α -aryl ketone. Besides using typically reactive arene



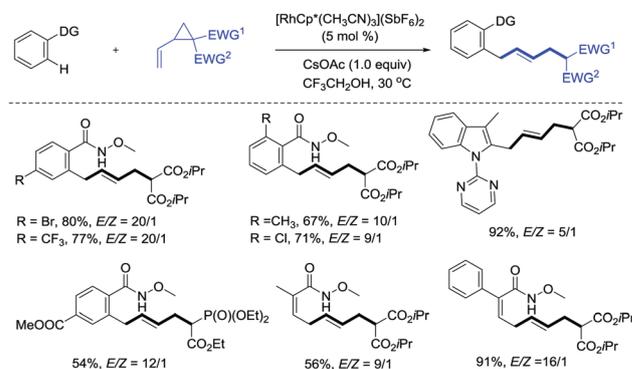
Scheme 20 Coupling using 4-vinyl-1,3-dioxolan-2-ones.



Scheme 21 Coupling using cyclic alkenyl carbonate.

substrates such as 2-arylpyridines, the arenes have been extended to weakly coordinating tertiary amides. Although the olefin is disubstituted and consequently leads to the formation of a less reactive tertiary alkyl species after migratory insertion, the cyclic alkenyl carbonate is still quite reactive. The coupled products are highly useful as synthetic building blocks. In comparison, although Glorius attempted related Rh(III)-catalysed phenacylation of arenes using phenacyl halides and analogues, the reaction did not stop at the stage of phenacylation and only further cyclization products were isolated in high yields.²⁷

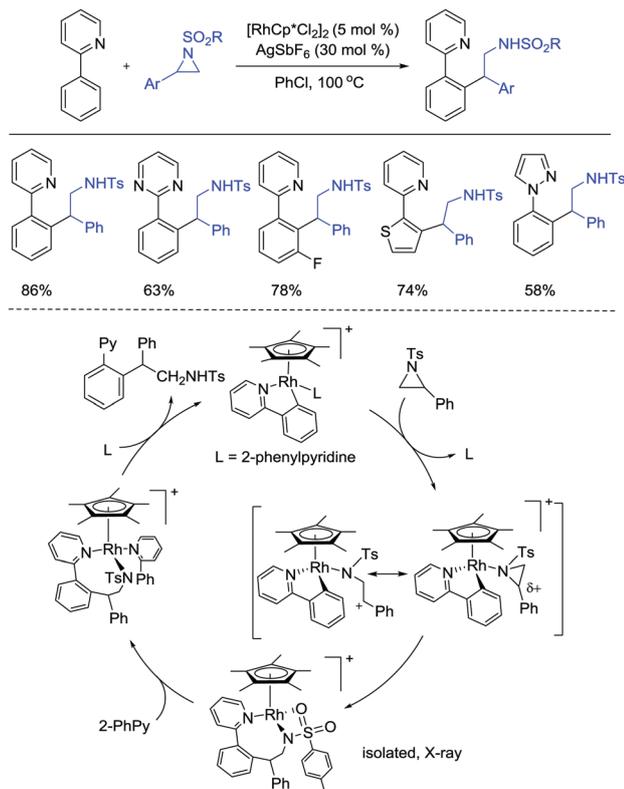
Wang and co-workers extended the strained ring to a vinylcyclopropane (VCP, Scheme 22).²⁸ The coupling of vinylcyclopropanes (VCPs) bearing *gem*-diesters with arenes such as *N*-methoxybenzamides and oximes occurred under mild conditions to deliver the allylated product with high efficiency and good *E* stereoselectivity (mostly >10:1). The arene substrate was also extendable to a corresponding acrylamide. The choice of geminal di-isopropyl ester is crucial; the reaction failed when these ester groups were omitted or replaced by alkyls, and the *E/Z* selectivity was only moderate for the *gem*-dimethyl ester. Following this seminal Rh(III)-catalysis, Ackermann examined this type of C–C coupling for various arenes using a Cp*Co(III) catalyst,²⁹ where the C–H activation of (hetero)arenes was assisted by pyridyl, pyrimidyl, and pyrazolyl DGs. Significantly moderate to high *Z*-selectivity was consistently maintained, which remains in sharp contrast to the major *E* selectivity in the rhodium system.



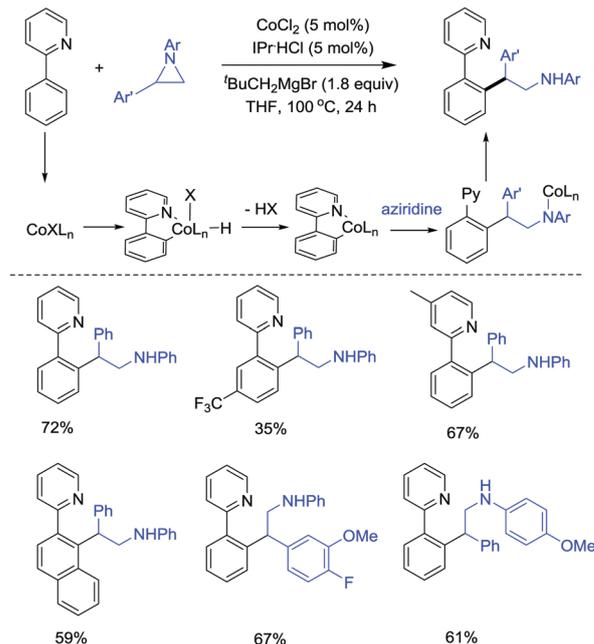
Scheme 22 Coupling using vinylcyclopropanes.

3.1.2 Formal SN-type coupling of arenes with a polar bond in electrophilic rings. For early metals or high valent metals, their M–C(aryl) bonds are more ionic in nature and have more pronounced single bond character, and the high polarity of the M–C bond allows efficient interactions with a polar coupling partner in both addition and substitution reactions.⁶ Thus, besides reactivity in typical migratory insertion into soft π bonds as in olefins or alkynes, these M–C bonds can react with polar, electrophilic rings such as aziridines and oxiranes.

Aziridines are readily available electrophiles even in *enanti*-enriched form, and coupling of aziridines with electron-rich arenes has been reported using Lewis acid catalysis, typically *via* the Friedel–Crafts mechanism. However, until 2013 their ring-opening with electron-poor arenes had not been reported. We and collaborators reported the efficient substitution-type coupling of 2-arylpiperidines with styrene-derived *N*-Ts aziridine, affording β -branched *N*-sulfonyl ethylamines (Scheme 23).³⁰ A [RhCp*Cl₂]₂/AgSbF₆ catalyst system affected this transformation in synthetically useful yields. Importantly, a ratio of AgSbF₆/[RhCp*Cl₂]₂ = 6:1 ensured high efficiency, where the AgSbF₆ activated both the aziridine substrate (as a Lewis acid) and the catalyst (as a chloride scavenger). The fact that the coupling occurred at the more sterically hindered site suggested the possible buildup of a carbocation in the aziridine ring. Furthermore, a stereochemistry probe revealed that when starting from a highly enantioenriched aziridine, a partially racemized product was obtained. These results likely suggested intermediacy of a tight ion pair. Moreover, stoichiometric interactions between



Scheme 23 Rhodium-catalysed coupling with aziridines.

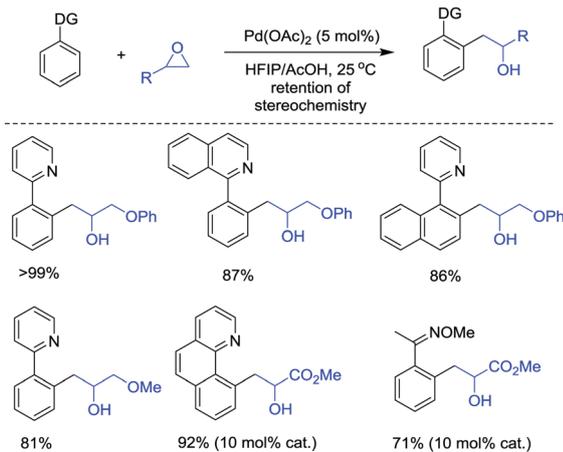


Scheme 24 Cobalt-catalysed coupling with aziridines.

the Rh(III)–C bond in a rhodacyclic complex and an aziridine ring have been examined, from which a stable tripodal N,N,O complex was isolated as a key intermediate, where a 8-membered rhodacycle is fused to a 4-membered ring (Scheme 23).

In 2014, Yoshikai and co-workers reported related cobalt-catalysed coupling between the same types of arene and *N*-aryl aziridines (Scheme 24).³¹ The reaction was catalysed by CoCl₂–IPr–^tBuCH₂MgBr, and the same site-selectivity was followed. A low valent cobalt species was proposed to be an active catalyst, likely generated from the reduction of Co(II) by the Grignard reagent. This coupling was proposed to occur *via* an oxidative addition mechanism (Scheme 3e), subsequent interaction between the Co–aryl bond and the aziridine ring delivered the β -branched *N*-arylethylamine. However, SN-type direct interaction between the Co–aryl bond and the aziridine remains possible. Despite the mechanistic ambiguity, this method provided a complementary scope with respect to the aziridine since *N*-aryl aziridines failed in the Rh(III) catalysed system (Scheme 23).

Simple oxiranes have been proved to be inactive in Rh(III)-catalysed coupling. Significantly, Kanai and Kuninobu successfully applied palladium catalysis to the coupling of arenes with 2-(phenoxy)methyl)oxirane or 2-(alkoxymethyl)oxirane, leading to ring opening of oxiranes at the less hindered site (Scheme 25).³² The reaction proceeded under very mild conditions, where pyridyl, aminoquinolinyl, oxime ether, and amide are efficient directing groups. The presence of a phenoxy or alkoxy group is vital in ensuring high reactivity. Stereochemical probes using an enantiopure oxirane revealed the retention of the stereochemistry, which ruled out a SN₁ pathway and this observation remains in stark contrast to that in the rhodium(III)-catalysed coupling of aziridines. The authors suggested that palladium(IV) species generated *via* oxidative addition of substrate oxiranes might be an active catalyst for this reaction (Scheme 3e). Alternatively, an all-Pd(II) pathway



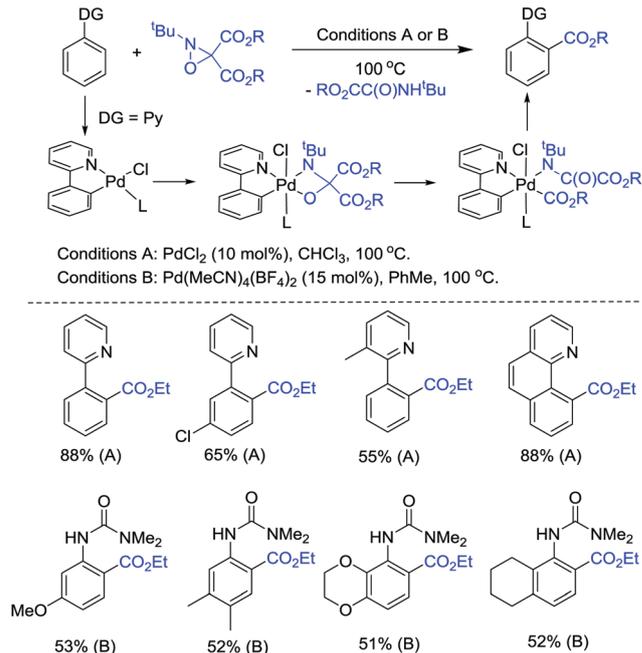
Scheme 25 Coupling using functionalized oxiranes.

involving S_N -type coupling with opening at the less hindered CH_2 position remains possible (Scheme 3c). However, the exact sequence of C–H activation and ring scission remains ambiguous.

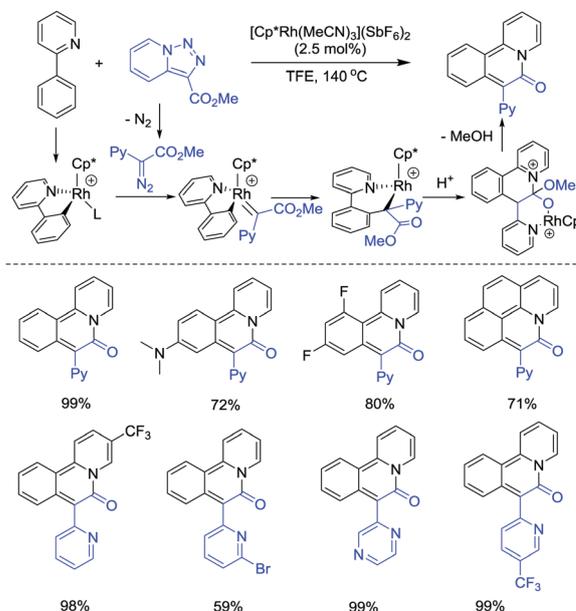
In 2011, Shi reported that a palladium-catalysed coupling of arenes with oxaziridine bearing *gem*-diesters led to ethoxy-carbonylation as a result of N–O and C–C bond cleavage (Scheme 26),³³ with *N*-*tert*-butyl carbamate being a coproduct. Two classes of arenes namely 2-arylpyridines and aryl ureas were proved to be viable substrates, and the products were obtained in moderate to good yields. The reaction likely proceeded *via* cyclometalation of the arene followed by oxidative addition of the N–O bond of the oxaziridine to generate a putative Pd(IV) species. Subsequent β -carbon elimination and C–C reductive elimination produced the coupled product and a Pd(II) species with the formation of the *N*-*tert*-butyl amide co-product. This reaction is unique because C–H alkoxy-carbonylation reactions of arenes are very rare, indicating the power of catalysis using strained rings.

3.1.3 Coupling *via* interaction of a polar M–C bond with essentially unstrained rings: ring scission leading to a carbene or nitrenoid species. The coupling partner to arenes is not limited to strained rings. The scission of unstrained but reactive rings might also occur, which requires driving forces such as transannulation and/or liberation of a gas molecule (Scheme 3f). With the scission of these unstrained rings, the formation of a highly electrophilic carbene/nitrene species plays an important role in ensuring high reactivity towards a nucleophilic M–C bond.

Glorius and co-workers designed pyridotriazoles as a bifunctional carbene precursor for the coupling with 2-arylpyridines (Scheme 27).³⁴ The pyridotriazole substrates are accessed from picoline and alkyl chloroformate in two steps *via* diazotization. This rhodium(III)-catalysed transannulative coupling afforded π -extended fluorophores in high efficiency. The reaction likely involves cyclometalation of the 2-arylpyridine. Meanwhile, the pyridotriazoles underwent ring scission to afford a stabilized diazo intermediate although the mechanism of this ring scission was not further discussed. Denitrogenation leads to a carbene, and subsequent carbene insertion gave a corresponding alkylated intermediate that contains nucleophilic and electrophilic



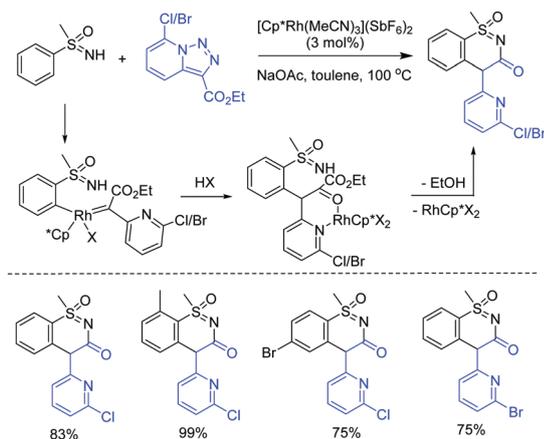
Scheme 26 Coupling with oxaziridines.



Scheme 27 Coupling of pyridotriazoles.

moieties. A subsequent metal-assisted nucleophilic addition–elimination process delivered the final products. In this reaction the role of the pyridyl moiety in the pyridotriazoles is multifold. It is the ester group that stabilizes the diazo intermediate, and it also serves as a chelating group that stabilizes the nucleophilic addition intermediate.

Inspired by this work, Lee and coworkers applied halogen-substituted pyridotriazoles to the coupling with *S*-aryl sulfoximines (Scheme 28).³⁵ This rhodium(III)-catalysed reaction afforded 1,2-benzothiazines. The reaction is proposed to occur

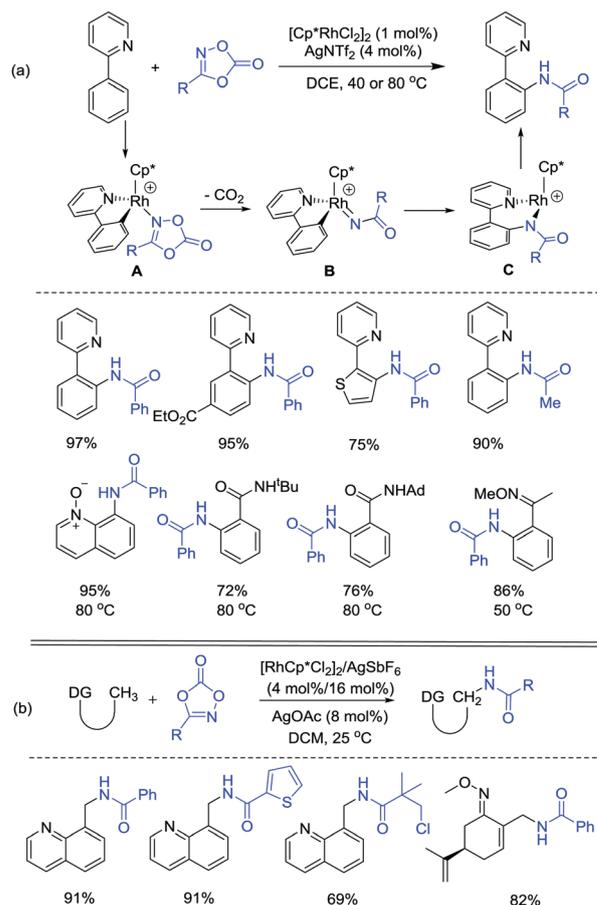


Scheme 28 Coupling of halo-substituted pyridotriazoles.

via cyclometalation and denitrogenation of the pyridotriazole to produce a rhodium carbene species. Subsequent migratory insertion into the carbene with further protonolysis of the resulting Rh–C(alkyl) bond is followed by intramolecular condensation, where the NH imine directing group also acts as a nucleophile. The presence of halogen substituent is necessary to ensure high efficiency because the ring opening and denitrogenation are facilitated by an EWG. In addition, the installed halogen group adjacent to the nitrogen renders it less coordinating so that no binding inhibition is caused. Comparisons have been made between the reactivities of a pyridotriazole and a diazo substrate, where the pyridotriazole showed higher reactivity.

Ring-opening coupling in C–H activation is not limited to initial C–C formation. Dioxazolones are stable rings that have been employed as amido transfer reagents *via* ring scission, and they are easily accessed from condensation reactions between hydroxamic acids and carbonyl diimidazole in one step. In 2015, Chang designed dioxazolones as highly efficient amidating reagents in C–H activation (Scheme 29a).⁷ The rhodium-catalysed C–H amidation of arenes occurred under mild conditions with a rather low catalyst loading. Although the same amidated product might also be obtained using acyl azides, dioxazolones exhibited significantly higher activity than other amide sources such as PhC(O)N₃, and the high activity is related to its robustness and high coordinating ability. DFT studies by Chang suggested that coordination and elimination of CO₂ generated a highly reactive formal Rh(v) nitrenoid species that is susceptible to migratory insertion of the Rh–C bond.

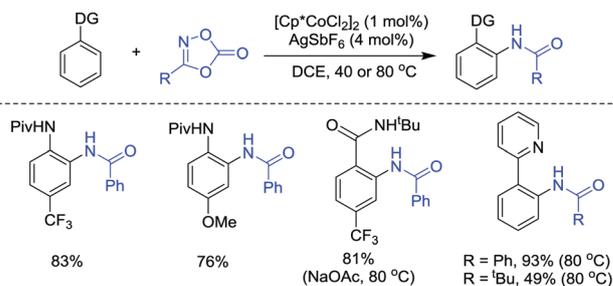
In 2016, Li and coworkers extended the arenes to sp³ C–H substrates using the same amidating reagent under mild rhodium catalysis (Scheme 29b).³⁶ A broad scope of sp³ C–H substrates assisted by a pyridine ring or an oxime ether has been proved to be viable and even methylene CH bonds are also amidated in high efficiency. Later the Sundararaju group examined the Co(III)-catalysed amidation of 8-methylquinolines using the same reagent.³⁷ The amidation occurred at the methyl group under mild conditions. However, only 8-methylquinoline substrates have been demonstrated.



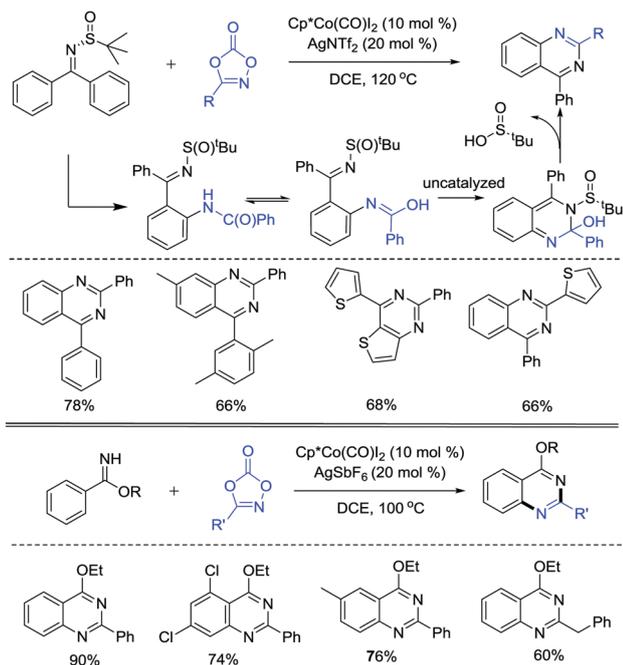
Scheme 29 Rhodium-catalysed amidation using dioxazolones.

In 2015, Chang beautifully extended the C–H amidation of arenes to Cp*Co(III) catalysis under mild conditions (Scheme 30).³⁸ In contrast to the generally high loading of Co(III) catalysts in most cases, this amidation system is exceptionally efficient, and an order of activity of Co(III) > Ir(III) > Rh(III) has been established based on a survey of a large array of arene substrates. Soon after the publication of this work, the groups of Jiao³⁹ and Ackermann⁴⁰ independently reported related Co(III)-catalysed systems.

Ideally, dioxazolones are applied as a bifunctional coupling partner for heterocycle synthesis. Under Co(III) catalysis, we achieved the C–H activation of *N*-sulfinyl imine or imidate ester with subsequent coupling with a dioxazolone, affording a



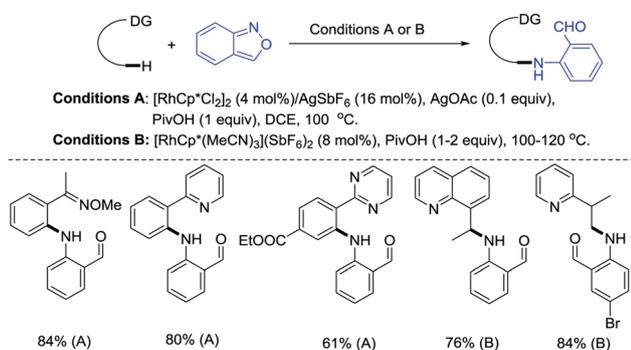
Scheme 30 Cobalt-catalysed amidation using dioxazolones.



Scheme 31 Dioxazolones in amidation-cyclization.

quinazolone under redox-neutral conditions (Scheme 31).⁴¹ The dioxazolone can be regarded as a bifunctional amidating reagent in this transannulation process. With cleavage of the N-S bond, *N*-sulfinyl imine acted as a synthon of NH imine that allowed further annulation as a nucleophile. In contrast, a simple benzophenone imine substrate only exhibited poor efficiency with hydrolysis being a major side reaction. Mechanistic studies suggested that the reaction proceeded *via* initial C-H amidation, followed by uncatalysed cyclization with N-S cleavage. Of note, Rh(III) or Ir(III) complexes also catalysed this coupling but the efficiency and the mono/di-selectivity were low.

Anthranils are structurally related to dioxazolones, and they are prepared from *ortho*-acyl nitrobenzenes *via* reduction. Inspired by the report of using anthranil as an aminating reagent in the coupling with an organometallic reagent,⁴² we applied anthranil as a bifunctional aminating reagent for a broad scope of aryl C-H as well as methyl and methylene C-H bonds (Scheme 32).⁴³ Thus, arenes bearing pyridyl, pyrimidyl, and

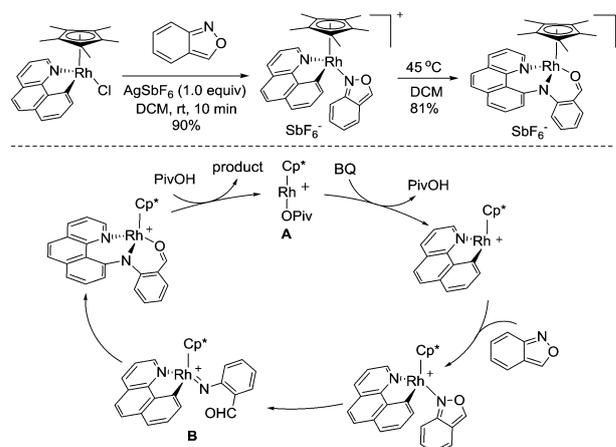


Scheme 32 Amination using anthranils.

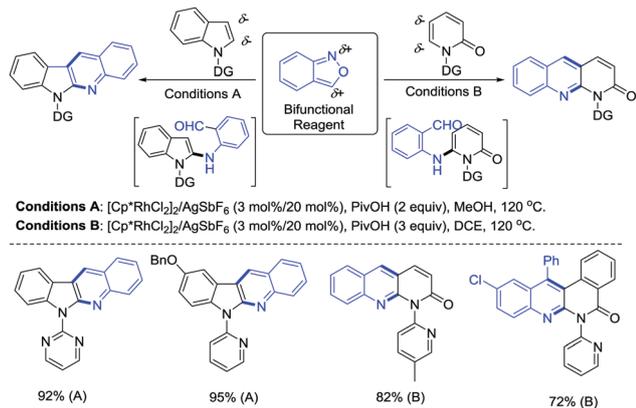
oxime ether DGs were efficiently aminated under redox-neutral conditions in 100% atom-economy. This amination delivered a nucleophilic amino group tethered to an electrophilic formyl group that would be otherwise hard to introduce since the formyl group may experience compatibility issues in many coupling systems. The resulting skeleton containing an amino and a carbonyl group represents an important synthetic building block. Control experiments also confirmed that *ortho*-azido-benzaldehyde only reacted with poor efficiency, indicating that the combination of reactivity and stability plays an important role in ensuring high efficiency.

Stoichiometric interactions between a Rh-C(aryl) bond and the *N*-bound anthranil resulted in the formation of a stable tripodal N,N,O complex (Scheme 33),⁴³ which was proved to be an active catalyst as well as the resting state. Further collaborative DFT studies provided detailed insights. The anthranil complex undergoes elimination of a formyl group with the current formation of a rhodium nitrido species. Subsequent migratory insertion of the aryl group into the Rh=N bond led to C-N formation. This mechanism closely parallels that of the rhodium-catalysed coupling of arenes with dioxazolone.⁷ In addition to the formation of an reactive nitrido species that is trappable, the scission of anthranil rings is assisted by the high reactivity of a polarized N-O bond, formation of a C=O bond, and rearomatization of the benzene ring.

The above amination reaction generated an aniline bearing a proximal carbonyl group that was not further directly utilized. To make full use of the electrophilicity of the carbonyl group, we applied electron-rich arenes as bifunctional, dinucleophilic substrates, which electronically matched the bifunctional aminating reagent. Thus indoles, 2-pyridones, and 2-quinolones bearing an *N*-directing group coupled with anthranils to afford the corresponding quinoline-fused heterocycles (Scheme 34).⁴⁴ This transannulation reaction occurred *via* initial amination of an arene. The C-H site in the vicinity of the initially cleaved C-H bond then underwent Friedel-Crafts-type addition-dehydration. This coupling represents a straightforward access to condensed heterocycles with biological interest from readily available bifunctional substrates.



Scheme 33 Mechanistic aspects of amination using anthranils.

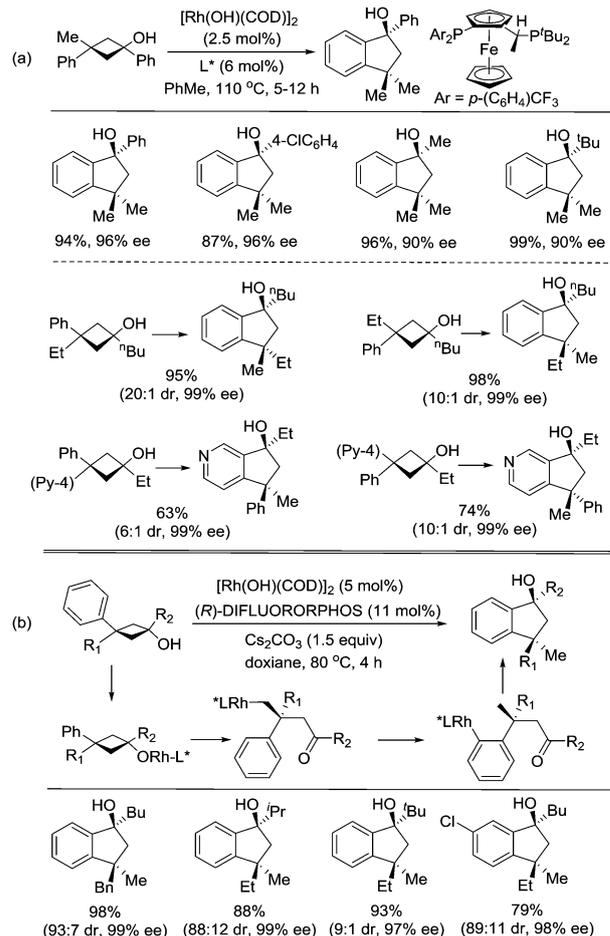


Scheme 34 Anthranils in amination–cyclization.

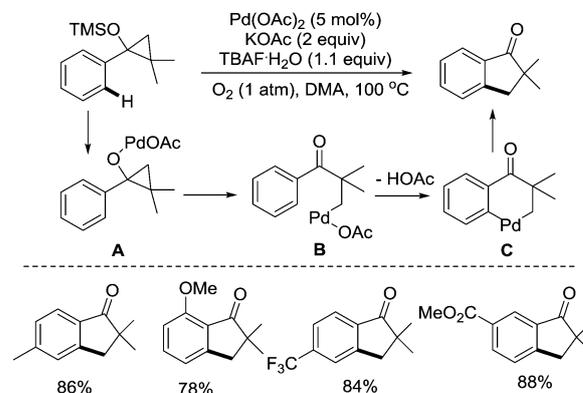
3.2 Coupling *via* initial generation of a M–C bond that induces intramolecular C(aryl)–H activation

While in many cases, the ring opening was initiated by C–H activation, in some cases C–H activation took place after the ring scission (Scheme 4b). Cyclopropanols and cyclobutanols are known to participate in a variety of C–C coupling reactions. When mediated by a transition metal, the ring-opening gives a homoenolate as a result of β -carbon elimination. In 2009 Cramer⁴⁵ (Scheme 35a) and Murakami⁴⁶ (Scheme 35b) independently reported Rh(i)-catalysed enantioselective synthesis of indanols from intramolecular transannulation of *tert*-cyclobutanols bearing a 3-aryl group. The reaction was diastereo- and enantioselective and proceeded in the presence of a ferrocene-based chiral diphosphine ligand or a DIFLUOROPHOS ligand. The excellent yield and enantioselectivity (mostly > 95% ee) were obtained with a broad scope. The reaction was likely initiated by coordination and β -carbon elimination leading to a Rh(i) γ -alkyl intermediate (Scheme 35b). This alkyl group then directed the intramolecular C–H activation at the *ortho* position of the aryl ring *via* a stereoselective 1,4-rhodium shift, giving a Rh(i) aryl species. The 1,4-rhodium shift was also chemoselective at the pyridine ring when both pyridine and benzene rings were accessible (Scheme 35a). The aryl group then undergoes stereoselective migratory insertion into the electrophilic carbonyl group to furnish the indanol core.

Given the nucleophilic nature of a homoenolate species, the C–C coupling of cyclopropanols with a C–H bonds requires oxidative conditions. In 2012, Orellana and Rosa reported palladium-catalysed intramolecular oxidative coupling of the silyl ether of cyclopropanols to afford indanones (Scheme 36).⁴⁷ TBAF was used to cleave the O–Si bond to generate the corresponding palladium cyclopropoxide (A). The cyclopropanol ring was limited to tetrasubstitution, and attempts to generate a homoenolate bearing at least one β -hydrogen all resulted in the formation of an enone, indicating that at β -hydrogen elimination occurred more readily. The resulting palladium(II) homoenolate species (B) served as a directing group to assist the intramolecular C–H activation at the *ortho* position of the benzene ring to give a Pd(II) aryl species (C). Subsequent C–C reductive elimination delivered the indanone product. Although the same product could be obtained from palladium-catalysed intramolecular



Scheme 35 Asymmetric synthesis using cyclobutanols.

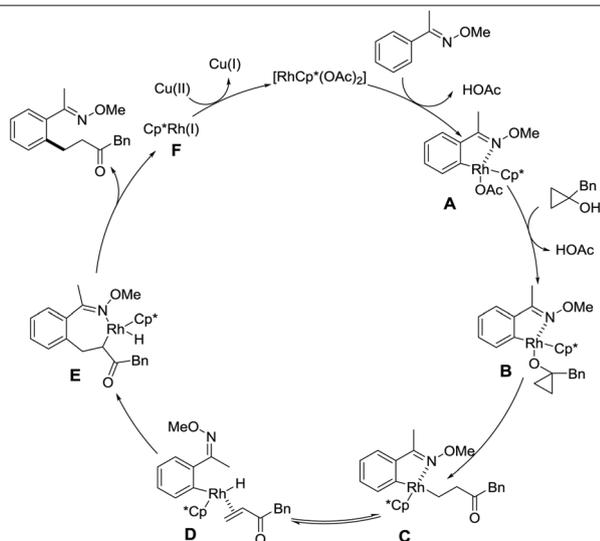
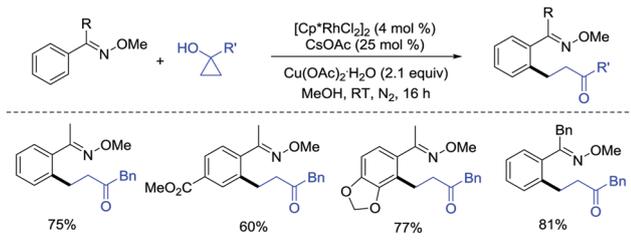


Scheme 36 Intramolecular coupling of cyclopropanols.

C–C coupling of *ortho* bromo-substituted 2,2-dimethyl-1-phenylpropan-1-one, the reaction required harsh conditions and a stoichiometric amount of base.⁴⁷

We reported the first intermolecular oxidative coupling of arenes with *tert*-cyclopropanols, leading to the synthesis of β -aryl ketones (Scheme 37).⁴⁸ Although it is initiated by C–H activation rather than ring scission, this coupling is discussed here for the purpose of comparison with the intramolecular

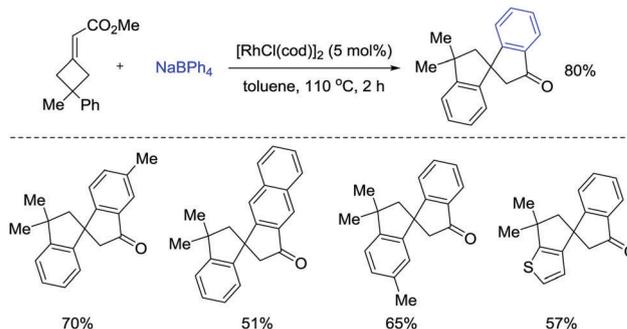
Tutorial Review



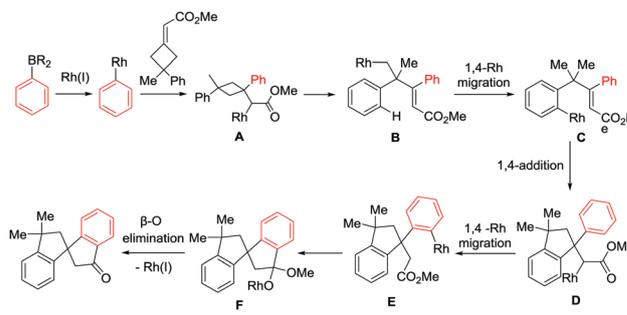
Scheme 37 Intermolecular coupling using cyclopropanols.

version. Under Rh(III) catalysis, a stoichiometric amount of Cu(OAc)₂ was used as an oxidant, and both oxime ethers and *N*-pyrimidylindoles were viable arenes. The reaction conditions are exceptionally mild for oxime ether substrates, and essentially no enone side product was detected. Mechanistic studies (Scheme 38) were performed by introducing an enone, and the observed incorporation of the enone suggested that the Rh(III) homoenolate (C) did undergo β-hydrogen elimination (D), and the olefin was trapped by the Rh–aryl bond *via* migratory insertion to give a seven-membered rhodacycle (E). The coupled product was released by C–H reductive elimination or protolysis of this rhodacycle. Mechanistic evidence also revealed that the Rh(III) aryl homoenolate species did not undergo direct C–C reductive elimination. Although the alkylated products could be conceivably obtained from the redox-neutral insertion of arenes into enones, the application of various enones as a coupling partner only afforded traces of the products in the presence or the absence of Cu(OAc)₂, indicating that ring scission can strongly enhance the efficiency of the coupling.

Matsuda and coworkers relied on transmetalation of arylboronic acid to a Rh(I) catalyst (Scheme 38) for initial Rh–C bond formation.⁴⁹ The coupling of EWG-functionalized methylenecyclobutanes and arylboron reagents afforded a structurally unique spirobiindane that is hardly accessible by other methods. Initiated by transmetalation (Scheme 39), the Rh–Ar bond undergoes 1,4-addition to the olefin unit (A). β-Carbon elimination led to ring scission and formation of a Rh(I) alkyl species (B). The subsequent 1,4-rhodium shift (C) and migratory insertion of the



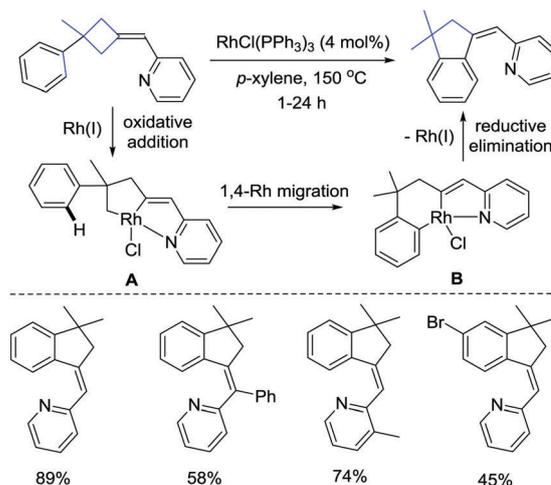
Scheme 38 Coupling of methylenecyclobutane with arylboron reagents.



Scheme 39 Proposed mechanism of coupling of methylenecyclobutane.

aryl group into the activated C=C bond provided a second Rh(II) alkyl (D). Following a second 1,4-rhodium shift (E), the aryl group further inserts into the ester carbonyl group, leading to spirocyclization (F). The product was generated with the elimination of the methoxy group.

The initial M–C bond can also be generated *via* an oxidative addition mechanism. Matsuda (Scheme 40) recently reported Rh(I)-catalysed ring expansion-coupling of MCBs such as 1-aryl-3-(2-pyridylmethylene)cyclobutanes.⁵⁰ This method provided direct access to methyleneindanes in one step from an operationally simple reaction. The reaction was initiated by pyridine ring-assisted C–C bond oxidative addition to give a five-membered



Scheme 40 Coupling using methylenecyclobutanes.

rhodacyclic intermediate (A). Intramolecular C–H activation (1,4-rhodium shift) generated a Rh(III) aryl alkenyl species (B) that underwent reductive elimination to release the product.

4. Conclusions

Employment of strained or reactive rings served as a means of activation of the coupling partner in the catalytic C–H activation of arenes. Three- and four-membered strained rings as well as unstrained but reactive five membered rings coupled efficiently with a variety of C–H bonds in both an intra- and intermolecular fashion, leading to C–C and C–N formation with facile reconstructions of new core structures. The opening of these rings followed different mechanisms, which allowed the direct manipulation of diverse ring substrates. Despite the impressive progress, these ring substrates are mostly limited to reactive three- and four-membered rings. In addition, the catalysts are mostly limited to noble metals such as Pd, Rh, and Ru. Thus, design of both reactive and robust rings that allows the extension of arene substrates to more general ones and that extends the functionalization beyond C–C and C–N coupling remains an important task. This strategy is particularly appealing for the construction of complex structure frameworks starting from readily available substrates. We anticipate that rich synthetic methods will be developed on the basis of the intrinsic reactivity of such rings and rich chemistry of organometallic species. These new methods should serve to take up the challenges posed by the molecular complexity during the construction of natural products and functional molecules.

Acknowledgements

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