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Rhodium-Catalyzed Redox-Neutral Olefination of Aryldiazenes with Acrylate Esters via C−H Activation and Transfer Hydrogenation

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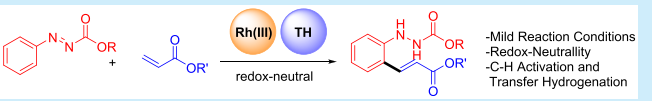
ABSTRACT: Rh(III)-catalyzed redox-neutral C−H olefination of aryldiazenecarboxylates has been realized using arylate esters as the olefinating reagents. This reaction proceeds under mild and redox-neutral conditions, resulting in integration of C−H activation and transfer hydrogenation. The chemoselectivity complements that of previously reported rhodium-catalyzed coupling of the same substrates.



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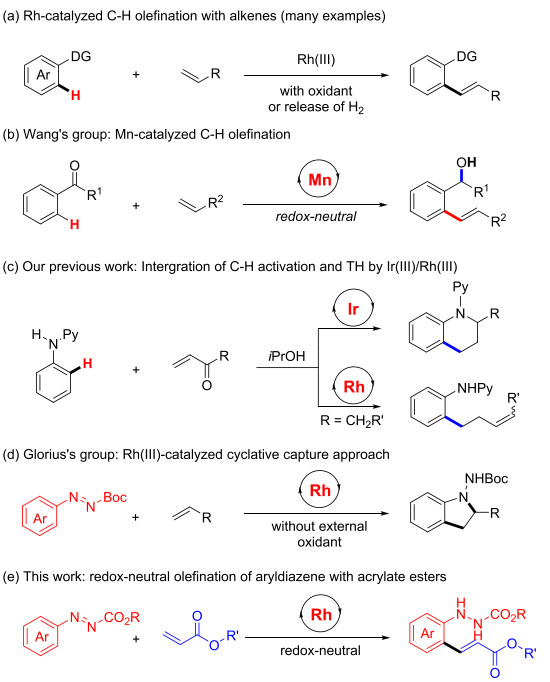
Transition-metal-catalyzed C−H activation has attracted increasing attention over the past decades.[1] Among the various transition metal complexes, rhodium complexes have been widely employed as catalysts owing to their high catalytic reactivity and selectivity, especially in direct C−H functionalization of arenes.[2] In particular, rhodium catalysis has allowed olefination of diversified classes of arenes,[3] which was performed (mostly) under oxidative conditions,[3a,e,4] redox-neutral conditions,[5] and, occasionally, hydrogen-releasing conditions,[6] depending on the nature of the arene substrates and the reaction conditions (Scheme 1). While the redox-neutral or H_2-releasing conditions may circumvent the employment of stoichiometric metal or organic oxidants with reduced production of metal or organic wastes, there is still room for improvement regarding the reaction atom economy.

Scheme 1. Catalytic Systems via C−H Activation and TH



The outstanding performance of Cp*Rh(III) catalysts in catalytic C−H activation is due to their versatility in promoting distinct transformations in the catalytic cycle.[7] For example, Rh(III) species have been known for decades to catalyze transfer hydrogenation[8] besides C−H bond activation. Such functional versatility should streamline the synthesis of complex structures and be conducive to atom-economic transformations of arenes. However, these two areas mostly evolved independently, and the rarity in this regard is probably ascribed to the poor compatibility of C−H activation and transfer hydrogenation. A breakthrough was made in 2018 by the Wang group,[9] who reported the first redox-neutral C−H olefination of ketones using styrenes as olefinating reagents by Mn−Zn bimetallic synergy (Scheme 1b). Of note, the hydrogen transfer is intramolecular via the ligand-to-ligand hydrogen transfer (LLHT) mechanism.[10] In the same year, our group reported the reductive C−C coupling of aniline with enones,[11] which utilized isopropanol as the hydrogen source, and varying chemoselectivity was realized using rhodium and iridium catalysts (Scheme 1c).

The rarity of C−H activation en route to intramolecular transfer hydrogenation inspired us to further explore this chemistry using Rh(III) catalysis. To this end, we designed arenes bearing a built-in hydrogen acceptor, and the coupling with olefin may serve this purpose. We now report the redox-

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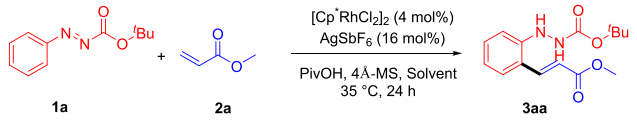
neutral coupling of aryldiazenecarboxylates and acrylates via Rh(III) catalysis.

With this rationale, we designated aryldiazenecarboxylates as such arenes. Although the C−H activation of these substrates has been reported by Glorius in annulative coupling with activated and unactivated olefins (Scheme 1d),[12] we rationalized that the chemoselectivity may be switched to transfer hydrogenation under proper reaction conditions (Scheme 1e). We started our investigation by examining the reaction parameters of the coupling of *tert*-butyl 2-aryldiazenecarboxylate **1a** with methyl acrylate **2a**. The desired product **3aa** was indeed isolated in 38% yield when treated with $[Cp^*RhCl_2]_2/AgSbF_6$, PivOH, and 4 Å-MS in tetrahydrofuran (Table 1, entry 1). The yield was improved to 46% when the solvent was switched to 1,2-dimethoxyethane (DME, Table 1, entry 2). Other acids such as $MesCO_2H$ and AcOH were also examined, which failed to increase the yield of product **3aa** (Table 1, entries 3 and 4). Different amounts of PivOH were then examined, and a better yield of 58% was realized in the presence of 8 equiv of PivOH (Table 1, entries 3−6). Meanwhile, 100 mg of 4 Å-MS were optimal, affording product **3aa** in 79% yield. In all cases, no annulative coupling product was observed. Thus, the conditions in entry 8 were used for further studies.

Table 1. Optimizations of the Reaction Conditions[a]



entry	acid/equiv	solvent	yield (%)[b]
1	PivOH (2)	THF	38
2	PivOH (2)	DME	46
3	$MesCO_2H$ (2)	DME	36
4	AcOH (2)	DME	<5
3	PivOH (4)	DME	41
4	PivOH (6)	DME	46
5	PivOH (8)	DME	58
6	PivOH (10)	DME	57
7	PivOH (8)	DME	21[c]
8	PivOH (8)	DME	79[d]
9	PivOH (8)	DME	55[e]
10	PivOH (8)	DME	46[f]

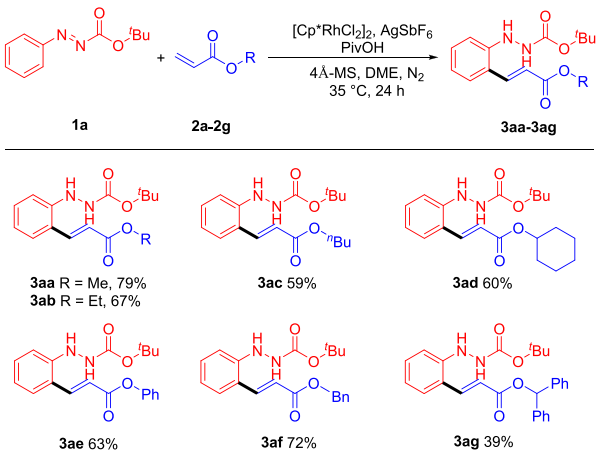
[a]Reaction conditions: **1a** (0.1 mmol), **2a** (2.0 equiv), $[Cp^*RhCl_2]_2$ (4 mol %), $AgSbF_6$ (16 mol %), PivOH (2.0 equiv), 4 Å-MS (0.050g), solvent (1 mL) under a N_2 atmosphere, 35 °C for 24 h. [b]Isolated yield. [c]No 4 Å-MS. [d]4 Å-MS (0.100 g). [e]4 Å-MS (0.150 g). [f]4 Å-MS (0.200 g).

To evaluate the generality of this reaction, the scope with respect to the acrylate ester was first explored under the optimal conditions (Scheme 2). To our delight, alky, benzyl, and aryl acrylates all worked well with **1a**, affording the desire hydrazines (**3aa**−**3af**) in 59−79% yields. However, a benzhydryl acrylate **2g** reacted only in low yield, indicating the steric effect of the ester group.

Encouraged by the above results, we next investigated the scope of aryldiazenecarboxylates with methyl acrylate **2a** being a coupling reagent (Scheme 3). A series of *para* substituted phenyldiazene substrates containing electron-donating (Me, OMe, ^{i}Pr) groups generally worked well, affording the desired products in 35−82% yields. However, introduction of electron-withdrawing groups (F, Br, CF_3) led to moderate yields (**3da**−**3ha**).

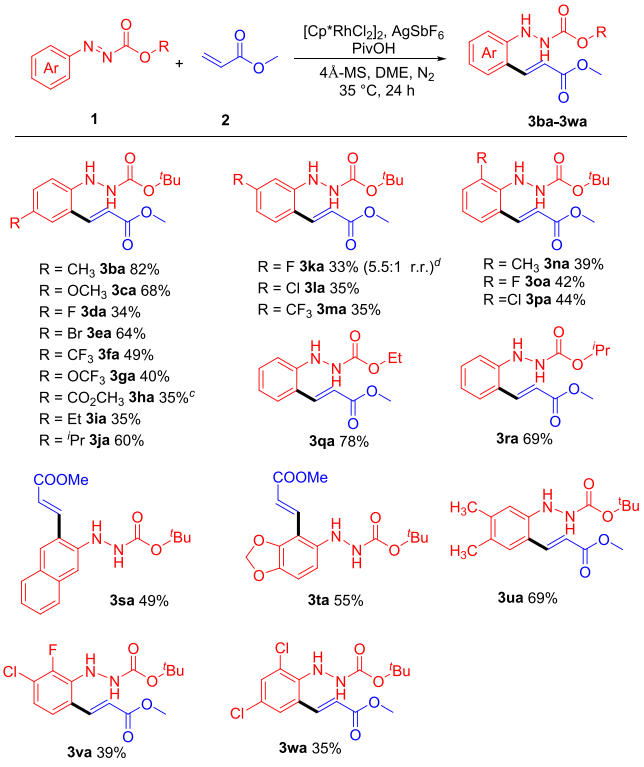
When F, Cl, and CF_3 groups were introduced into the *meta* position, the C−H bond cleavage occurred mostly (F) or exclusively (Br and CF_3) at the less hindered site, generating the corresponding products **3ka**−**3ma** in 33−35% yields. The

Scheme 2. Scope of Acrylic Esters[a,b]



[a]Reaction conditions: **1a** (0.2 mmol), **2** (2.0 equiv), $[Cp^*RhCl_2]_2$ (4 mol %), $AgSbF_6$ (16 mol %), PivOH (8.0 equiv), 4 Å-MS (200 mg), DME (2 mL) under N_2 atmosphere, 35 °C for 24 h. [b]Isolated yield after column chromatography.

Scheme 3. Scope of the Phenyldiazene Carboxylates[a,b]



[a]Reaction conditions: **1a** (0.2 mmol), **2** (2.0 equiv), $[Cp^*RhCl_2]_2$ (4 mol %), $AgSbF_6$ (16 mol %), PivOH (8.0 equiv), 4 Å-MS (200 mg), DME (2 mL) under a N_2 atmosphere, 35 °C for 24 h. [b]Isolated yield after column chromatography. [c]~92% purity (determined by ^{1}H NMR spectroscopy). [d]The r.r. was determined by ^{1}H NMR spectroscopy.

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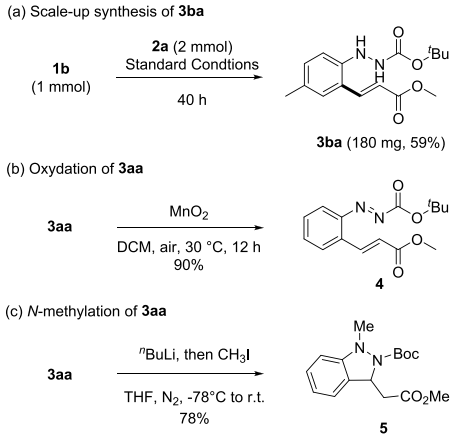
coupling of a *meta*-F substituted substrate led to C−H functionalization at both *ortho* sites, and the regioisomeric products (**3ka** and **3ka′**) were isolated as a mixture.

A variety of *ortho*-substituents (CH_3, F, and Cl) also proved amenable to the reaction conditions, producing the desired products **3na**−**3pa** in lower but acceptable yields (39−44%). These results indicate that the reaction system is sensitive to the electronic nature and the position of the substituents. The Et and ^{i}Pr esters of the phenyldiazenes also proved to be suitable for this transformation, affording the corresponding products in 78% and 69% yields, respectively. In addition, diazenes bearing a disubstituted benzene ring also turned out to be applicable (**3sa**−**3wa**, 35−69%).

To demonstrate the synthetic applications of this reaction, a scale-up coupling of **1b** and **2a** was conducted under standard conditions, from which product **3ba** was isolated in 59% yield (see Scheme 4a). Derivatization reactions have been carried

Scheme 4. Scale-up Synthesis and Derivatization of a Coupled Product

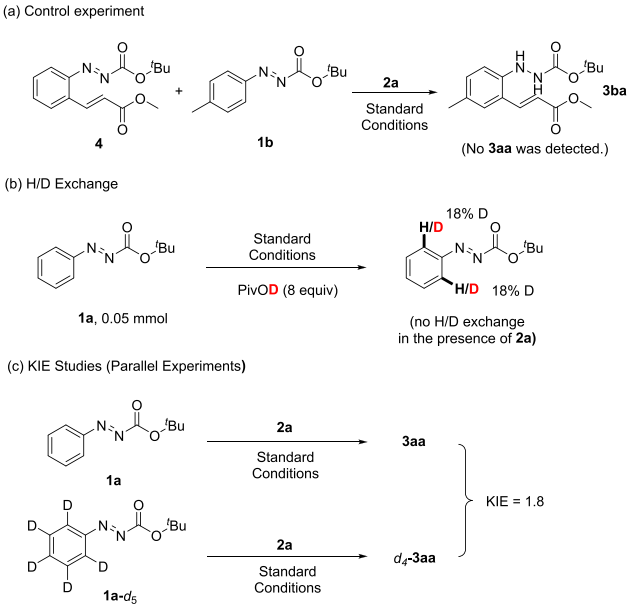


out to showcase the synthetic applicability. Oxidation of **3aa** under aerobic conditions afforded the corresponding diazene **4** in 90% yield (Scheme 4b). Meanwhile, base treatment of **3aa** followed by methylation and Michael addition afforded the compound **5** in 78% yield (Scheme 4c).

Several experiments have been carried out to explore the mechanism of this coupling system. To probe the hydrogenation of the putative olefinated diazene intermediate, the coupling of 4-methyl phenyldiazene (**1b**) and methyl acrylate (**2a**) was conducted in the presence of a preolefinated phenyldiazene **4** (0.3 equiv) under the standard reaction conditions. NMR and GC analysis indicated that only product **3ba** was produced and no **3aa** was detected, together with recovery of the introduced diazene **4** (Scheme 5a). This control experiment suggests a pathway defined by olefin insertion, *β*-H elimination, and subsequent hydrogenation of the N═N bond to be less likely, on the premise that the putative diazine-olefin species can undergo facile ligand exchange.

Next, the H/D exchange reaction between **1a** and PivOD in the absence of alkene **2a** revealed significant H/D exchange at the phenyldiazene C(2) and C(6) position (Scheme 5b), indicating the relevance of C−H bond activation. However, no H/D exchange was observed in product **3aa** when alkene **2a** was present, suggesting that the C−H activation was largely irreversible in the catalytic system. To further understand the

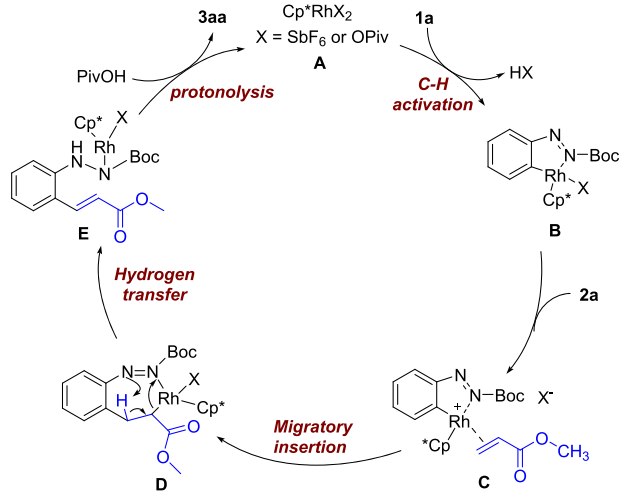
Scheme 5. Mechanistic Studies



C−H activation process, the kinetic isotope effect has been measured based on parallel reactions, and a borderline KIE value (k_H/k_D = 1.8) was obtained (Scheme 3c), indicating that the C−H bond cleavage occurs prior to the RDS, and this cleavage process only contributes partially to the overall barrier.

A plausible mechanism is proposed on the basis of our experimental data and literature precedents (Scheme 6).[12]

Scheme 6. Proposed Reaction Pathway



Cyclometalation of **1a** with the active catalyst **A** affords a rhodacyclic intermediate **B**, along with generation of an acid (HX). Subsequent coordination of acrylic ester **2a** gives the intermediate **C**, which undergoes migratory insertion of the aryl group into alkene to deliver a seven-membered ring **D**. An intramolecular hydrogen transfer together with Rh−N formation is proposed to give intermediate **E**. The fact that poor reactivity and decomposition were observed in the absence of 4 Å MS may suggest that the adventitious water weakens the basicity of the azo group (via hydrogen-bonding) toward subsequent hydrogen abstraction or transfer. Proto-

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nolysis of the Rh−N bond in intermediate **E** byPivOH generates the desired product **3aa** with regeneration of the active catalyst **A**. We had planned to use deuterated olefins to probe the mechanism. However, it seems that the lability of the two NH protons in the products may defy any solid conclusion toward mechanistic understanding. At this stage we cannot rule out the possibility of the β-H elimination pathway because our proposal is based on the assumption of rapid exchange (coordination/dissociation) of an olefinated diazene intermediate during our mechanistic studies (see Supporting Information).

In summary, we have realized Cp*Rh(III) catalyzed coupling of aryldiazenecarboxylates and acrylic esters under redox-neutral conditions, which provides a new system that integrates C−H activation and transfer hydrogenation. The coupling reaction proceeded with a moderate scope, and the chemoselectivity remained complementary to that previously reported in the Rh(III) catalyzed coupling of the same substrates. Further studies of other transfer hydrogenation systems are underway in our laboratories.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c00107.

Experimental procedures and spectral data (PDF)

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Notes

The authors declare no competing financial interest.

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