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Dirhodium(II)-Catalyzed (3 + 2) Cycloaddition of the *N*-Arylaminocyclopropane with Alkene Derivatives

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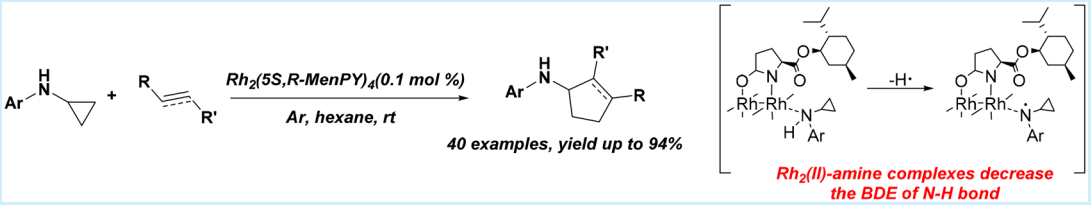
Supporting Information



ABSTRACT: Several (3 + 2) cycloaddition reactions catalyzed by dirhodium(II) complexes between *N*-arylaminocyclopropane and alkenes derivative have been developed. Preliminary mechanism studies suggest that dirhodium(II) complexes may decrease the bond-dissociation energy (BDE) of the N−H bond of *N*-arylaminocyclopropanes for N−H bond activation, thus facilitating the formation of N-centered radicals by loss of a hydrogen radical.

The formation of compounds possessing a five- or six-membered ring by the ring-opening reaction of a smaller ring, particularly a cyclopropane or cyclobutane, is widely used in synthetic chemistry.[1] The *N*-arylaminocyclopropane **1** is prone to single-electron oxidation of the nitrogen, and subsequent ring opening, to generate a distonic radical cation, which can be trapped by an alkene or alkyne to form a cycloamine[2] or triplet oxygen to yield a dioxolane (Scheme 1).[3] These characteristics make the *N*-arylaminocyclopropane motif a useful building block for entry into a variety of biologically active compounds.[4] To advance synthetic methodology, several research studies have focused on this ring-opening reaction and have developed ways of accelerating the process of radical cation generation. These methods include using the stoichiometric oxidant ceric ammonium nitrate (CAN),[5] the catalytic single-electron oxidizing $Fe^{III}(phen)_3(PF_6)_3$,[3a] the hydrogen-abstracting agents benzoyl peroxide or *tert*-butyl peroxide/UV light,[3a] and visible-light photocatalysis with ruthenium catalysts (Scheme 1).[2] Fortunately, recent studies have reported an efficient synthesis of compounds of structure **1**, which has provided a great opportunity to develop a good synthetic methodology for the above reaction.[6] In continuation of our study of reactions of dirhodium(II) complexes (Rh_2(II,II)) with *tert*-butyl hydroperoxide (TBHP),[7] we envisaged $Rh_2(esp)_2$/70% TBHP in water (T-HYDRO) generating *tert*-butylperoxy radicals that could induce the ring-opening reaction of aminocyclopropane **1**. During the investigation, it was discovered that the Rh_2(II,II) complex could catalyze the ring-opening reaction of **1** efficiently by itself under an argon atmosphere (Scheme 1). Therefore, the efforts of this investigation have focused on this ring-opening reaction catalyzed by Rh_2(II,II) complexes.

Initially, the α,β-unsaturated ester **2a** was selected to trap the generated distonic radical cation from *N*-phenylaminocyclopropane **1a** (Table 1). The desired cycloaddition product **3aa** was obtained in moderate yield when 1 mol % of $Rh_2(esp)_2$ and T-HYDRO was used in the reaction with dichloromethane (DCM) as the solvent under an argon atmosphere (Table 1, entry 1). Of particular interest was the yield of **3aa** increasing to 68% when the T-HYDRO was left out (Table 1, entry 2). No conversion to the desired product occurred without a metal catalyst, but **1a** spontaneously decomposed in DCM (Table 1, entry 3). Further solvent screening disclosed nonpolar *n*-hexane as the best solvent (Table 1, entries 4−7). In *n*-hexane, the yield of product **3aa** increased to 84% catalyzed by $Rh_2(esp)_2$ (Table 1, entry 5). It was reasoned that the decomposition rate of **1a** slowed in *n*-hexane. Coordinating solvents, such as dimethoxymethane (DME), inhibited the reaction (Table 1, entry 6). No products were formed when the strong coordinating solvent dimethylformamide (DMF) was used (Table 1, entry 7). This indicated that the axial sites of the Rh_2(II,II) catalyst play an important role in the reaction. Decreasing the $Rh_2(esp)_2$ catalyst loading to 0.1 mol % gave the lowest yield of **3aa** (Table 1, entry 8). Other Rh_2(II,II) compounds were found to still be feasible in the reactions. Doyle's $Rh_2(cap)_4$ catalyst generated a high yield of 88%, though the catalyst was insoluble in *n*-hexane (Table 1, entry 9). Another Doyle's catalyst, $Rh_2(5S,R\text{-MenPY})_4$,[8] was found to exhibit excellent solubility in *n*-hexane and even generate a 94% product yield (Table 1, entry 10). When the reaction was

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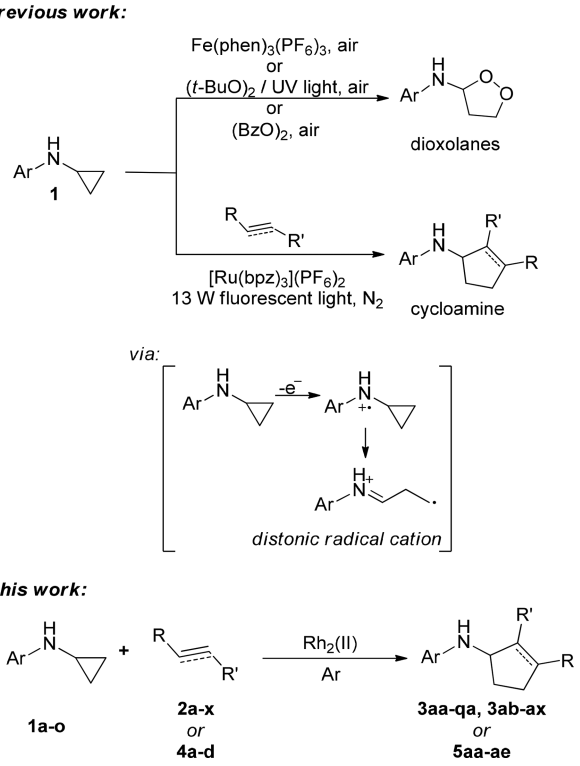
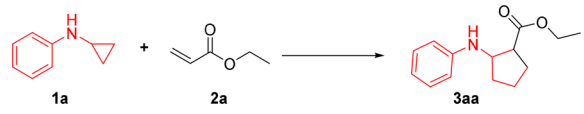
Scheme 1. Distonic Radical Cation Generation and Cycloaddition Reactions



conducted in the dark with Rh_2(5*S*,*R*-MenPY)$_4$, the yield of **3aa** reached 92%, which indicated the reaction was not photosensitive (Table 1, entry 11). Even 0.01 mol % of Rh_2(5*S*,*R*-MenPY)$_4$ gave the desired product in 60% yield after 48 h (Table 1, entry 12). Regrettably, the obtained products were optically inactive, though the Rh_2(5*S*,*R*-MenPY)$_4$ was a chiral catalyst. The Rh_2(II,II) compounds bearing carboxylate ligands (i.e., $Rh_2(OAc)_4$, $Rh_2(oct)_4$) were not as efficient as the amide Rh_2(II,II) catalysts (Table 1, entries 13 and 14). For comparison, rhodium metal complexes in other oxidation states and additional metal complexes were also evaluated in the reactions (Table 1, entries 15−18). The Rh(I) species generated a product in not so high yield, while the Rh(III) species provided decent product yield but was still inferior to the Rh_2(5*S*,*R*-MenPY)$_4$ catalyst (Table 1, entries 15 and 16). Except for the cobalt species, other metal complexes each generated product **3aa** in poor yield (see Supporting Information (SI)). $Fe(phen)_3(PF_6)_3$, which has been reported as an efficient catalyst to oxidize **1a** and generate the radical, catalyzed the reaction in DCM with 53% yield (Table 1, entry 18). Nevertheless, due to solubility issues, no reaction in *n*-hexane was observed with $Fe(phen)_3(PF_6)_3$ (Table 1, entry 17). Despite this, the measured diastereomeric ratios of the selected reactions in Table 1 gave moderate values, which suggested that a free radical mechanism was operative.

Next, with the optimized reaction conditions, Rh_2(5*S*,*R*-MenPY)$_4$ was selected to investigate the scope of the reaction with respect to different *N*-arylaminocyclopropanes **1**. As shown in Scheme 2, various substituted versions of **1** were synthesized according to the reported procedure[6] and reacted with ester **2a** to yield the desired products **3** with moderate diastereomeric ratios. Compounds of structure **1** bearing electron-donating groups, such as methoxy, methyl, and ethyl,

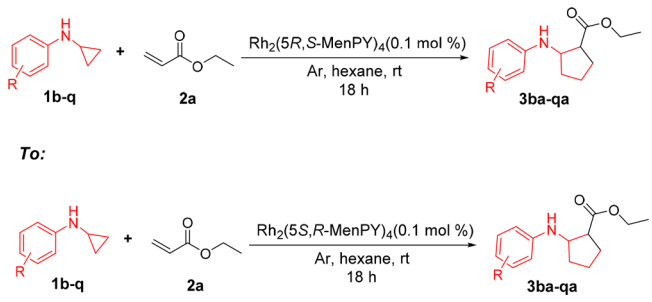
Table 1. Optimization of Reaction Conditions[a]



entry	conditions	solvent	yield (%)[b] (*cis*/*trans*)[c]
1[d]	$Rh_2(esp)_2$, TBHP	DCM	45
2	$Rh_2(esp)_2$	DCM	68
3	No catalyst	DCM	NR
4	$Rh_2(esp)_2$	toluene	69
5	$Rh_2(esp)_2$	hexane	84
6	$Rh_2(esp)_2$	DME	50
7	$Rh_2(esp)_2$	DMF	NR
8[e]	$Rh_2(esp)_2$	hexane	60
9	$Rh_2(cap)_4$	hexane	88 (40/60)
10[e]	Rh_2(5*S*,*R*-MenPY)$_4$	hexane	94 (41/59)
11[e,f]	Rh_2(5*S*,*R*-MenPY)$_4$	hexane	92
12[g]	Rh_2(5*S*,*R*-MenPY)$_4$	hexane	60
13	$Rh_2(OAc)_4$	hexane	44 (40/60)
14	$Rh_2(oct)_4$	hexane	70 (39/61)
15	$[Rh(CH_2CH_2)_2Cl]_2$	hexane	41 (41/59)
16	$[Rh(Cp^*)Cl_2]_2$	hexane	80 (44/56)
17	$Fe(phen)_3(PF_6)_3$	hexane	trace
18	$Fe(phen)_3(PF_6)_3$	DCM	53 (64/36)

[a]Reaction conditions: **1a** (0.5 mmol, 0.2 M in degassed solvent), **2a** (2.5 mmol), catalyst (1 mol %) under argon at rt for 18 h, unless otherwise noted. [b]Isolated yield. [c]Determined by ^{1}H NMR spectroscopy of crude product. [d]2 equiv of TBHP in water. [e]0.1 mol % of catalyst. [f]Reaction was conducted in the dark. [g]0.01 mol % catalyst, 48 h. esp = α,α,α′,α′-tetramethyl-1,3-benzenedipropionate, cap = caprolactamate, 5*S*,*R*-MenPY = (*S*)-(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 2-oxopyrrolidine-5-carboxylate, oct = *n*-octyl, NR = no reaction, phen = 1,10-phenanthroline monohydrate. For more information, see the SI.

Scheme 2. Substrate Scope of *N*-Arylaminocyclopropanes[a]



[a]Reaction conditions: **1b−q** (1 mmol, 0.2 M in degassed solvent), **2a** (5 mmol), catalyst (0.1 mol %) at rt for 18 h, unless otherwise noted. Isolated yields of two isomers. *cis*/*trans* ratio was determined by ^{1}H NMR spectroscopy of crude products. NR = no reaction. [b]36 h.

or electron-withdrawing groups, such as CF_3, Cl, and *p*-phenyl, all gave high yields of products **3ba−ja**. Multiple substituted cyclopropylanilines with the 3,5-dimethyl group **1l** and 3,5-disubstituted trifluoromethyl **1m** generated products **3la** and **3ma** in 76% and 80% yields, respectively. However, steric interactions played a major role in the reaction. *o*-Methyl-substituted cyclopylamines **1j** gave the least yields of product **3ja**. A poor yield of product **3ka** was obtained when the bulky *o*-phenyl **1k** was applied. Nonetheless, the 1- or 2-naphthalene-substituted cyclopylamines **1n** and **1o** both gave good yields of the products **3na** and **3oa**. Substrate **1p** bearing the pyridine

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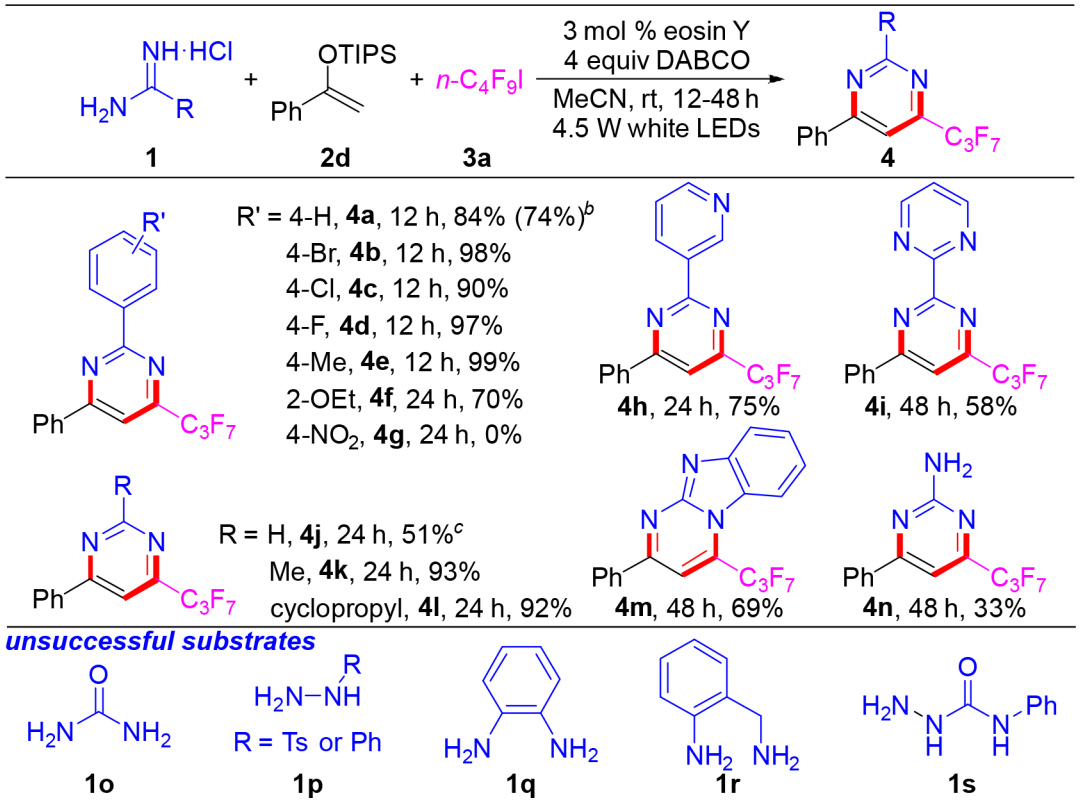
Scheme 3. Substrate Scope of Alkene and Alkyne Derivatives[a]



[a]Reaction conditions: **1a** (1 mmol, 0.2 M in degassed solvent), **2b–x** (5 mmol) or **4a–d** (5 mmol), Rh_2(5*S*,*R*-MenPY)$_4$ (0.1 mol %) at rt for 18 h, unless otherwise noted. Isolated yields of two isomers. The *cis*/*trans* ratio was determined by ^{1}H NMR spectroscopy of crude products. [b]36 h. [c]DCM as solvent.

group gave only a trace product due to the pyridine group to which Rh_2(II,II) was coordinated, which inhibited coordination of amine to Rh_2(II,II) complex. It is worth mentioning that no reaction occurred when the intrinsically reactive molecule 1-methyl-2-phenyl-2-azabicyclo[3.1.0]hexane (**1q**) was used (see the SI), suggesting that the hydrogen was important in the reaction. Subsequently, a variety of *α*,*β*-unsaturated esters **2b–q** were catalyzed by Rh_2(5*S*,*R*-MenPY)$_4$ and reacted with **1a** for 18 h at room temperature under an argon atmosphere (Scheme 3). The various substituted unsaturated esters **2b–n** produced cycloaddition products **3ab–an** with good yields, but with moderate diastereomeric ratios. A diastereomeric ratio of 83/17 for **3ah** with the *trans* configuration prevailing was obtained when trisubstituted esters **2h** were used. Additionally, the *cis* configuration of **3ai** predominated (71/29) when the esters **2i** contained a hydroxyl group. The *β*-substituted methyl ester **2j** gave the *β*-amino ester **3aj**, while the *β*-substituted phenyl ester **2k** gave the *γ*-amino ester **3ak**. The crystal structure of (1*RS*,2*RS*,3*SR*)-**3ak** was obtained by crystallizing the inseparable product mixture, and the *γ*-amino ester motif of **3ak** was confirmed by X-ray crystallography. It was reasoned that this different regioselectivity derived from the radical stability of the intermediate.[2e] In contrast to the pyridine substituent, when the amide group was present in the substrate **2l**, the reactions proceeded smoothly, providing **3al** in 71% yield. In particular, the reaction of the *cis*- or *trans*-dimethyl fumarate **2m** and **2n** with **1a** produced the products **3am** and **3an** in yields of 84% and 76% respectively, with a similar diastereomeric ratio. In addition, after treatment with the *cis* product **3ba** with CAN, the desired *β*-amino ester **6a** was obtained in 79% yield (see the SI). It was reported the **6a** can undergo facile transformation to the chiral *β*-amino acid by chiral resolution.[9]

Furthermore, except for the *α*,*β*-unsaturated esters, the reaction of **1a** was probed using different alkenes. Reactions with the aromatic alkenes **2q–x**, bearing either electron-rich or electron-poor substituents on the aromatic ring, proceeded smoothly with **1a** to yield the desired products **3aq–ax** with moderate diastereomeric ratios. Modest yields were obtained when alkyne derivatives **4a–d** were used in the reactions after an extended period of time. Though no reaction occurred with cyclohexenone **2o** (Scheme 3), **1a** reacted with 2*H*-chromen-2-one **4d** to generate a product mixture in 53% yield containing the cycloaddition compound **5ad** and amide compound **5ae**. It was supposed that **5ae** formed spontaneously through the intramolecular amide reaction with **5ad**.

Next, we investigated the plausible mechanism for the reactions. The key issue is how the Rh_2(II,II) catalyst initiates the radical process. Unsubstituted aminocyclopropanes are reported to undergo facile oxidation to a radical cation species, in which the oxidation process is essentially barrier free.[10] However, compound **1** generated radicals slowly due to stereoelectronic and resonance effects, which is in accordance with the report by Zheng et al.[2a] In Zheng's report, no (3 + 2) cycloaddition product was obtained without light or Ru catalyst. Despite this, the conversion of **1a** reached 14% after 12 h without light and a Ru catalyst, indicating that **1a** decomposed and generated a radical or active species, thus leading to a reaction pathway different from the (3 + 2) cycloaddition. UV/vis spectra demonstrate that the Rh_2(II,II) catalyst coordinated with **1a** to form a metal complex. The characteristic band of

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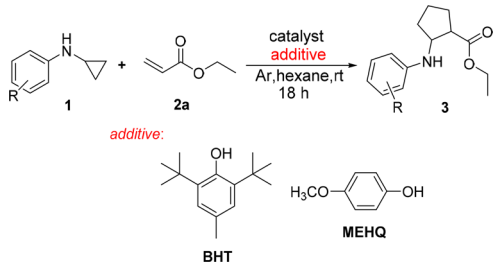
Rh_2 π^* to Rh_2 σ^* moved from 665 to 592 nm when the $Rh_2(esp)_2$ coordinated to **1a** in DCM. In regard to the UV/vis spectra analysis, no change in the oxidative state of $Rh_2(esp)_2$ was observed (Figure S1). Chirik et al. recently reported a study addressing the weakness of the N−H, and they found that the bond-dissociation energy (BDE) of an N−H decreased when the metal was coordinated to an amine.[11] On the basis of this work, it is inferred that the N−H bond of **1** may be activated by the Rh_2(II,II) by axially coordinating to **1**, which facilitates proton transfer (PT) and electron transfer (ET) to lose the hydrogen radical as a result of the decreased BDE_{N-H}. Experiments were designed to demonstrate how the Rh_2(II,II) complex tunes the BDE of the N−H bond by comparing various efficiencies catalyzed by $Rh_2(esp)_2$ and Rh_2(5*S*,*R*-MenPY)$_4$ in the reaction. Table 2 displays the radical

Table 2. Rh_2(II,II) Complex Tunes the BDE of the N−H Bond of 1a[a]

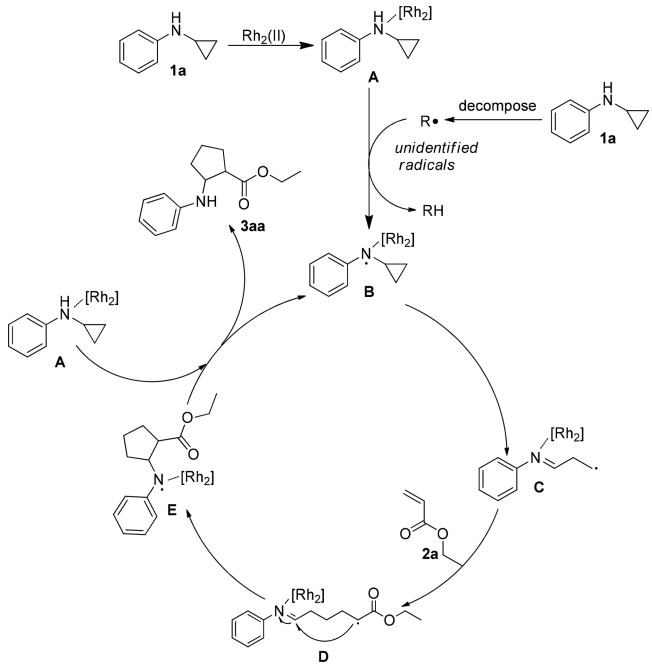


entry	substrate	catalyst	additive	yield[b] (%)
1	**1a**	none	MEHQ	trace
2	**1a**	none	BHT	trace
3[c]	**1a**	$Rh_2(esp)_2$	MEHQ	65
4	**1a**	Rh_2(5*S*,*R*-MenPY)$_4$	MEHQ	76
5[c]	**1a**	$Rh_2(esp)_2$	BHT	<5
6	**1a**	Rh_2(5*S*,*R*-MenPY)$_4$	BHT	64
7	**1m**	Rh_2(5*S*,*R*-MenPY)$_4$	none	80
8	**1m**	Rh_2(5*S*,*R*-MenPY)$_4$	MEHQ	trace

[a]Reaction conditions: **1a** (0.5 mmol, 0.2 M in degassed solvent), **2a** (2.5 mmol), catalyst (0.1 mol %), and additive (20 mol %) at rt for 18 h, unless otherwise noted. [b]Isolated yields of two isomers. [c]1 mol % of catalyst was used.

terminating reagents 4-methoxyphenol (MEHQ) or butylated hydroxytoluene (BHT) with different BDE_{O-H} that were added to the reactions. The experimental results showed that MEHQ (BDE_{O-H} = 81.7 kcal/mol)[12] was unable to inhibit the reaction catalyzed by $Rh_2(esp)_2$ or Rh_2(5*S*,*R*-MenPY)$_4$, indicating that these two Rh_2(II,II) compounds lowered the BDE_{N-H} of **1a** to be less than the BDE_{O-H} of MEHQ. However, when BHT (BDE_{O-H} = 79.9 kcal/mol)[12] was added, the reaction catalyzed by $Rh_2(esp)_2$ was efficiently inhibited, but not for the reaction catalyzed by Rh_2(5*S*,*R*-MenPY)$_4$ These results suggest that the BDE_{N-H} of **1a**, tuned by Rh_2(5*S*,*R*-MenPY)$_4$, was lower than the BDE_{O-H} of BHT. This can help clarify why Rh_2(5*S*,*R*-MenPY)$_4$ was sought out. Further experimentation demon strated that the BDE_{N-H} plays an important role in the reaction. As literatures reported, the electron-withdrawing groups on the arenes increase the BDE_{N-H} of the aromatic amines.[12] The **1m** bearing two CF_3 groups substituted phenyl group of **1a** catalyzed by Rh_2(5*S*,*R*-MenPY)$_4$ to yield **3ma** in 80% yield. However, the addition of MEHQ inhibited this reaction effectively (Table 2, entry 8). It is reasoned that **1m** has such a high BDE_{N-H} value that Rh_2(5*S*,*R*-MenPY)$_4$ cannot reduce the BDE_{N-H} beyond the BDE_{O-H} of MEHQ. On the basis of the investigation, the proposed mechanism is described in Scheme 4. Since **1a** decomposes spontaneously to generate

Scheme 4. Proposed Mechanism



unidentified radicals, these trace radicals abstract H atom from the Rh_2(II,II)-**1a** complex **A** and form the *N*-centered radical **B.** This is followed by cyclopropane ring-opening to generate radical **C**, which is trapped by **2a** to form intermediate **D**. The formation of **D** occurs by intramolecular radical addition to yield **E**. After hydrogen atom transfer (HAT) from complex **A**, the desired product **3aa** is obtained and regenerates the *N*-centered radical **B**. During the catalytic cycle, it was proposed that the Rh_2(II,II) complex "tames" the radicals to complete the cycloaddition reaction efficiently.

This study detailed the development of a (3 + 2) cycloaddition reaction catalyzed by Rh_2(II,II) complexes between *N*-arylaminocyclopropane and alkenes derivatives. The reaction exhibited a wide tolerance for various functional groups and could be used to produce β-amino acids. It appears that the Rh_2(II,II) complex coordinates axially to the *N*-arylaminocyclopropane to activate the N−H bond and decreases the BDE of N−H bond in the aminocyclopropane. This mechanism facilitates formation of an *N*-centered radical by loss of a hydrogen radical. Future experiments will focus on elucidating the structure of Rh_2(II,II) complexes related to the N−H bond activation and broadening the scope of this method.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b00904.

Additional experimental procedures and spectroscopic data for all new compounds (PDF)

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Accession Codes

CCDC 1581725, 1581760, and 1581762 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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