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Direct Oxidative Coupling of Arenes with Olefins by Rh-Catalyzed C–H Activation in Air: Observation of a Strong Cooperation of the Acid

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Abstract: A [{RhCl(cod)}₂]/CCl₃COOH system was developed for the oxidative coupling of non-chelate-assisted arenes with olefins in the presence of catalytic amounts of Cu(OAc)₂·H₂O as a co-oxidant and oxygen as the terminal oxidant. The acid was an indispensable component in this system and played a very important role in the coupling reaction. This catalytic system was applied to the direct oxidative coupling

Keywords: C-H activation • olefination • rhodium • oxidative coupling • vinylarenes of a series of arenes and olefins and the corresponding products were afforded in high yields with special chemo- and regioselectivity. This reaction provides an atom-efficient route to vinylarenes, which are widely used in various fine chemicals.

Introduction

Vinylarene derivatives are important intermediates for the construction of more-complex organic molecules.^[1] One of the most popular and most distinct methods for the construction of vinylarene structures is the Heck reaction.^[2] Although a great deal of progress has been made since this reaction was first discovered, it still suffers from many drawbacks.^[3] For example, a large amount of salt waste is produced during these reactions and the atom economy is not satisfactory. An attractive alternative to the Heck reaction is the direct oxidative coupling of aryl C-H bonds with olefins,^[4] which obviates the need for prior functionalization steps and is thus more atom economical and versatile. Several transition-metal complexes, such as rhodium,^[5] palladium,^[6] and ruthenium complexes,^[7] have been demonstrated to be highly active catalysts for such reactions. One of the most popular strategies is the use of a chelate assistant, which uses a neighboring directing group that precomplexes the metal and directs it to the desired position.^[5-7] For example, aromatic compounds that contain carbonyl groups, such as benzoic acids^[5f,j,7f] or phenones,^[5n,7b,c] or nitrogen-containing groups, such as aromatic amides^[5d,6h] or benzylamines,^[6i] have been found to react with alkenes through catalytic direct-coupling reactions in which the activation of a C-H bond is the key step. However, the topography of the substrate in these reactions is crucial because the proximal directing group must possess the proper bonding strength and alignment toward the targeted C-H bond. Only a few non-

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chelate-assisted cases have been reported.^[8-11] A direct oxidative coupling reaction between benzene and ethylene in the presence of a cyclometalated Rh^{III} catalyst was achieved by Matsumoto and Yoshida.^[8] The direct oxidative coupling of aromatic compounds with alkenes catalyzed by Pd compounds has also been reported,^[9,10] but this catalytic system was limited to a few electron-rich arenes. In the presence of a special pyridine ligand, a Pd-catalyzed system was found to be suitable for the oxidative coupling of electron-deficient arenes with olefins.^[11]

Although rhodium complexes stand out in the area of catalytic C-C coupling reactions through the chelate-assisted cleavage of C-H bonds,^[12] the direct oxidative olefination of aromatic compounds that do not contain a directing group has been less well studied. Quite recently, a Rh^{III}-catalyzed oxidative olefination reaction of bromoarenes was reported.^[13a] However, this reaction requires an unusually long incubation time and is limited to only a few substrates with particular electronic effects; even chlorobenzene afforded only traces of the desired product and toluene did not react at all. Therefore, a more efficient system for the direct oxidative olefination of non-chelate-assisted arenes through C-H bond activation that is suitable for a broad scope of substrates under mild conditions is desired. Herein, we describe an effective catalytic system for the direct oxidative coupling of a diverse range arenes that contain no directing groups with different classes of olefins (Scheme 1). In this system, $[{RhCl(cod)}_2]$ (cod = 1,5-cyclooctadiene) and Cu- $(OAc)_2 \cdot H_2O$ were used as the catalysts, oxygen was used as



Scheme 1. $[{RhCl(cod)}_2]$ -catalyzed olefination of an arene through oxidative coupling.

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a terminal oxidant, and trichloroacetic acid was used as an additive, which was demonstrated to be an essential component in this reaction.

Results and Discussion

Initially, the reaction of toluene (1a) with butyl acrylate (2a) was conducted in the presence of $[{RhCl(cod)}_2]$ (2.0 mol%), Cu(OAc)₂·H₂O (0.5 equiv), and benzoic acid (1.0 equiv to 2a) at 120 °C for 22 h in air. Trace amounts of the olefination products were observed. Importantly, this reaction did not occur in the absence of benzoic acid, thus indicating that the acid is a crucial element in the catalysis.

Next, a set of experiments were performed to determine the optimal acid in this system. Different acids, including commercially available organic and inorganic acids, were tested as the additive in the [{RhCl(cod)}₂]-catalyzed oxidative coupling of compound 2a with neat compound 1a (Table 1). In general, the effect of the acid largely depended on its structure, substitution pattern, and solubility. Neither benzoic acid nor substituted benzoic acids (Table 1, entries 14-17) gave yields above 15%. The yields were also influenced by the substituents: When 2-methylbenzoic acid, benzoic acid, 4-chlorobenzoic acid, and 3-nitrobenzoic acid was used as the additive, the yields of the product of the olefination reaction of toluene were 13%, 5%, 4% and 2%, respectively, thus indicating that benzoic acid that was substituted with electron-donating groups was superior to that with electron-withdrawing groups. With aliphatic acids, such as formic or acetic acid (Table 1, entries 6, 7), the oxidative olefination reaction of toluene completely shut-down. When trifluoroacetic acid, dichloroacetic acid, chloroacetic acid, propionic acid, hexanoic acid, and octanoic acid were used as the additive (Table 1, entries 1, 4, 5, 8-10), the olefination reaction did not reach completion. With the often-used PivOH (Piv=pivaloyl; Table 1, entry 11), the yield of the olefination reaction was only 22% after 22 h. Some sulfonic acids, such as CH₃SO₃H and TsOH (Table 1, entries 12 and 13), were also tested as the additive and the yields of the olefination reactions were 3% and 22%, respectively. The olefination reaction did not take place when inorganic acids (Table 1, entries 19-22) were used as the additive, except when phosphoric acid was used. Then, the olefination reaction had a yield of about 5%, which was not suitable for organic synthesis. In the case of organic acid salt 1-carboxymethyl-pyridinium chloride (Table 1, entry 18), no product was detected, mostly because of its solubility. Of all of the acids tested, trichloroacetic acid was the most efficient additive and a high yield (94% based on butyl acrylate) was obtained in the olefination reaction of toluene under the optimized reaction conditions. Moreover, no side-products from the polymerization or dimerization of butyl acrylate were observed in this reaction.

The yield of the coupling products was markedly influenced by the amount of trichloroacetic acid in the reaction (Table 1, entries 2, 3, 19–24). The yield of the products of Table 1. Influence of the acid on the olefination of toluene (1a) with butyl acrylate (2a).

[{RhCl(cod)} ₂] (2.0 mol %)											
	+ OBu _Cu(OAc) ₂ H	₂ O (0.5 equiv)		OBu							
	O Additive	Additive, 120 °C, air		Ϋ́							
1a	2a		3aa,4aa	0							
Entry	Additive	<i>t</i> [h]	Equiv of alkene	Yield [%] ^[a,b]							
1	CF ₃ COOH	22	1.0	77							
2	CCl ₃ COOH	8	1.0	82							
3	CCl ₃ COOH	22	1.0	94							
4	CHCl ₂ COOH	22	1.0	42							
5	CICH ₂ COOH	22	1.0	38							
6	НСООН	22	1.0	0							
7	CH ₃ COOH	22	1.0	0							
8	CH ₃ CH ₂ COOH	22	1.0	22							
9	hexanoic acid	22	1.0	27							
10	<i>n</i> -caprylic acid	22	1.0	42							
11	PivOH	22	1.0	22							
12	CH ₃ SO ₃ H	22	1.0	3							
13	TsOH	22	1.0	19							
14	PhCOOH	22	1.0	5							
15	2-Me-C ₆ H ₄ COOH	22	1.0	13							
16	4-Cl-C ₆ H ₄ COOH	22	1.0	4							
17	3-NO ₂ -C ₆ H ₄ COOH	22	1.0	2							
18	1-(carboxymethyl)-	22	1.0	0							
	pyridin-1-ium chloride										
19	HBF_4	22	1.0	<2							
20	HCl	22	1.0	<2							
21	H_2SO_4	22	1.0	0							
22	H ₃ PO ₃	22	1.0	5							
23	CCl₃COOH	22	0.10	21							
24	CCl ₃ COOH	22	0.25	30							
25	CCl ₃ COOH	22	0.50	62							
26	CCl ₃ COOH	22	0.75	89							
27	CCl₃COOH	8	2.0	87							
28	CCl ₃ COOH	22	2.0	92							

[a] Reaction conditions, unless otherwise indicated: toluene (**1a**, 0.60 mL, 5.7 mmol), butyl acrylate (**2a**, 0.20 mmol, 1.0 equiv), Cu(OAc)₂·H₂O (20.0 mg, 0.5 equiv), and [{RhCl(cod)}₂] (2.0 mol% with respect to butyl acrylate), acid (1.0 equiv), 120 °C, in the presence of air. [b] Yields (based on butyl acrylate) were obtained by GCMS. Ts=*para*-methylphenylsulfonyl.

the olefination of butyl acrylate (3aa and 4aa) reached 82% after 8 h (Table 1, entry 2) and 94% after 22 h (Table 1, entry 3) when one equivalent of trichloroacetic acid (to butyl acrylate) was used. Increasing the amount of trichloroacetic acid did not improve the yield any further (Table 1, entry 27, 28). However, if the amount of trichloroacetic acid was lowered to 0.75 equivalents, the yield of the olefination product decreased to 89%. When the amount of trichloroacetic acid was further lowered to 0.50, 0.25, and 0.10 equivalents, the yield dropped to 62%, 30%, and 21%, respectively. To further understand the important role of the acid, kinetic studies of the oxidative olefination of toluene by different acids were conducted under similar conditions. Figure 1 shows the time-dependent curves for the oxidative olefination of toluene in air. With 1.0 equivalent of trichloroacetic acid additive, the conversion of butyl acrylate (into compounds 3aa and 4aa) was 32% after 1 h and increased to 82% after 8 h, which was 2-3-times faster than

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Figure 1. Yield of the olefination product as a function of time in the presence of: • CCl₃COOH (1.20 mmol); • CF₃COOH (1.20 mmol); • ctanoic acid (1.20 mmol); • CICH₂COOH (1.20 mmol); • 2-MeC₆H₄COOH (1.20 mmol); + CCl₃COOH (1.20 mmol) under an O₂ atmosphere without Cu(OAc)₂·H₂O. Other reaction conditions: compound **1a** (3.60 mL), compound **2a** (1.20 mmol), [{RhCl(cod)}₂] (2.0 mol% with respect to **2a**), Cu(OAc)₂·H₂O (1.20 mmol, 120 mg), air, 120 °C.

the reaction with trifluoroacetic acid and many times faster than the reactions with other acids, such as chloroacetic acid, octanoic acid, or substituted benzoic acid. product mixture when iodobenzene was used. Moreover, the yield did not decrease significantly when the reaction was conducted on a larger scale (Table 2, entry 4).

Interestingly, the regioisomeric ratios that were obtained do not correspond to a classical electrophilic aromatic substitution. Instead, the olefination products correspond to a "quasi-statistical" distribution of the *meta-* and *para-*olefination products, in which the monosubstituted arenes tend to afford a 2:1 mixture of the *meta-* and *para* isomers, the 1,2-disubstituted arenes tend to afford a 1:1 mixture of the 1,2,4- and 1,2,5-trisubstituted products, and the 1,3-disubstituted arenes only yield the *meta* regioisomer. These results are similar to those reported previously.^[13] Steric hindrance may play an important role in obtaining this quasi-statistical distribution of the products in the current system. A 1,4-disubstitution of the arenes prevents olefination of the *ortho* positions.

Next, the scope of the system for alkenes was explored. Table 3 summarizes the C-C coupling of various alkenes with toluene or xylene under similar conditions. Toluene (1a) showed good reactivity with several acrylates to give the desired products (Table 3, entries 1-3); styrene (2d) and 1-allylbenzene (2f) also reacted to generate their corresponding products (3ad and 4ad and 3ef, respectively) in low yields (26% and 50%, respectively; Table 3, entries 4 and 7). Trichloroacetic acid quickly reacted directly with styrene (2d) and 1-allylbenzene (2f) to give many side-prod-

Under the optimal conditions, high yields of the olefination products were achieved for the reactions of a variety of arenes with compound 2a (Table 2). Both substituted (mono-substituted, 1,2-, and 1,3-disubstituted) and non-substitute arenes, including chloroarenes (Table 2, entries 1, 5, 7, 10, 11), bromoarenes (Table 2, entries 2, 6, 8, 12), iodoarenes entry 3), (Table 2, xylene (Table 2, entries 4 and 9), and benzene (Table 2, entry 15), reacted smoothly with compound 2a to give their corresponding coupling products. In sharp contrast to the 1,2- and 1,3-substituated arenes, the 1,4-disubstituted arenes did not give any olefination product under similar conditions (Table 2, entry 14). Gratifyingly, no products from the Heck reaction were detected when chloroarene or bromoarene were used as the substrate and only a little deiodinated product (about 10%) was observed in the

Table 2. Oxidative coupling of various arenes with butyl acrylate (2a) by using the $[{RhCl(cod)}_2]/CCl_3COOH$ catalytic system in air.

	R^{2} R^{4} R^{4} OBu			[{RhCl(i Cu(OAc CCl ₃ 0 120	cod)} ₂] (2.0 mol %) s) ₂ ·H ₂ O (0.5 equiv) COOH (1.0 equiv) °C, under air	R^{2}	R ⁴ R ⁴ + R ¹	R ³ R ⁴ OBu	
	1		2a			(O OBu 3	4	
Entry	\mathbb{R}^1	\mathbb{R}^2	R ³	\mathbb{R}^4	Substrate 1	<i>t</i> [h]	Product	Conv.(Yield) [%] ^[a,b,c]	3/4
1	Н	Cl	Н	Н	1b	22	3ba, 4ba	97 (85)	67/33
2	Н	Br	Н	Н	1c	22	3ca, 4ca	95 (80)	66/34
3	Н	Ι	Н	Н	1d	22	3da, 4da	88 (75)	69/31
4	Н	Me	Н	Me	1e	22	3ea	$(88, 82^{[d]})$	100/0
5	Н	Cl	Н	Me	1f	22	3fa	90 (82)	100/0
6	Н	Br	Н	Me	1g	22	3ga	97 (83)	100/0
7	Н	Cl	Н	Cl	1ĥ	22	3ha	96 (82)	100/0
8	Н	Br	Н	Br	1i	22	3ia	96 (79)	100/0
9	Н	Me	Me	Н	1j	22	3ja	(87)	100/0
10	Н	Cl	Cl	Н	1k	22	3ka	97 (82)	100/0
11	Н	Cl	Me	Н	11	22	3la, 4la	97 (84)	1/1
12	Н	Br	Me	Н	1m	22	3ma, 4ma	98 (81)	1/1
13	Н	-(CH	₂) ₄ -	Н	1n	22	3na	70 (63)	100/0
14	Me	Ĥ	H	Me	10	22	_	0	_
15 ^[e]	Н	Н	Н	Н	1p	22	3pa	63 (58)	100/0

[a] Reaction conditions, unless otherwise indicated: arene (0.6 mL, 24–30 equiv with respect to compound 2a), butyl acrylate (2a, 0.20 mmol, 1.0 equiv), $Cu(OAc)_2 H_2O$ (20.0 mg, 0.5 equiv), $[{RhCl(cod)}_2]$ (2.0 mol% with respect to compound 2a), CCl_3COOH (32.7 mg, 1.0 equiv), 120°C, air. [b] Regioselectivities were obtained by ¹H NMR spectroscopy and GCMS. [c] Conversions were obtained by GCMS and the yields of the isolated products are given in parentheses. [d] A larger-scale reaction (2 mmol 2a) was performed under similar conditions, the yield is given in parentheses. [e] The reaction was performed at 90°C.

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Table 3. Oxidative coupling of toluene or xylene with various alkenes by using the $[{RhCl(cod)}_2]/CCl_3COOH$ catalytic system in air.



[a] Reaction conditions, unless otherwise indicated: arene (0.60 mL), alkene (0.20 mmol, 1.0 equiv), Cu-(OAc)₂·H₂O (20.0 mg, 0.5 equiv) and [{RhCl(cod)}₂] (2.0 mol% relative to the alkene), CCl₃COOH (32.7 mg, 1.0 equiv), 120 °C, air. [b] Regioselectivities were obtained by ¹H NMR spectroscopy and GCMS. [c] Conversions were obtained by GCMS and the yields of the isolated products are also given in parentheses. [d] Butyl 2-(3,5-dimethylbenzyl)acrylate (**3ee**^r) was produced and the ratio of **3ee/3ee**^r is 31/69. [e] Butyl 2-(3,4-dimethylbenzyl)acrylate (**3je**^r) was produced and the ratio of **3je/3je**^r is 33/67. [f] 1-(3,3-Dimethylbut-1-en-2-yl)-3,5-dimethylbenzene (**3ge**) was produced and the ratio of **3eg/3ge** is 23/77. [g] When the reaction time is 22 h, the *E*/ *Z* (**3eg**) is 17/6. [h] I₂ was used as substrate and 1-iodo-3,5-dimethylbenzene was produced.

ucts. Thus, the yield of the desired product fell when these compounds were used as olefination reagents. Butyl methacrylate (2e) underwent the coupling reaction with *m*-xylene (1e) and o-xylene (1j) in 55% and 66% yield, respectively, to give product mixtures in which rearrangement of the double bond was also observed. For the inactivated olefin of 3,3-dimethylbut-1-ene (2g), a mixture of the α -olefination product (*E* isomer, **3eg**) and the β -olefination product (**3ge**) was obtained when it reacted with compound 1e after 13 h. After a prolonged reaction time, a small amount of the Z isomer α -olefination product (3eg) was also observed. Appealingly, iodoarene, which is a useful intermediate in the synthesis of many complex products, was obtained in a high yield (Table 3, entry 9) under these conditions. Notably, no polymerization olefin products were found in the current catalytic system.

Next, control experiments were performed to explore the mechanism of the Rh-catalyzed oxidative olefination reaction. Under the optimized reaction conditions, no reaction occurred between compound **2a** and neat compound **1a** in the presence of $[{RhCl(cod)}_2]/CCl_3COOH$ without an oxidant. Adducts **3aa** and **4aa** were observed in low yields (Figure 1) when Cu(OAc)_2·H₂O was replaced with an oxygen balloon in the model reaction, thus suggesting that the formation of the Rh^{III} species is one of the most important steps in the reaction. Under the optimized reaction conditions, the consumption of trichloroacetic acid and the yield of the olefination product were monitored by GCMS after different reaction times (Figure 2). The yields of the product and the consumption of trichloroacetic acid showed

near-linear relationship, а thereby indicating that trichloroacetic acid was a consumable reagent in these reactions. However, the slope of the line was 1.2, slightly higher than 1.0, thus suggesting that some trichloroacetic acid may act as a catalyst in this system. On the basis of these results, a plausible mechanism for this catalytic process proposed is in Scheme 2. First, dissociation of the pre-catalyst [{RhCl(cod)}₂] gives monomer Rh^I complex 5, which is further oxidized by the Cu^{II} additive in the presence of trichloroacetic acid and oxygen to form Rh^{III} complex 6, which is the active species. Next, there are two possible ways to initiate the olefination reaction: In path A, a trichloromethyl-rhodium intermediate (7) is generated by the decarboxylation of the Rh complex of compound 6, which is complexed by an

arene. Then, a stochastical attack of compound **7** on an accessible C–H position of the arene leads to a σ -aryl–Rh^{III} complex (8). After coordination with the alkene and *trans*-insertion of a C=C double bond to the σ -aryl–Rh^{III} bond, complex **9** was produced. Next, the vinylarene coupling product was formed by β -hydride elimination from complex **9** and Rh–H complex **10** was generated at the same time. The Rh–H complex (**10**) is readily reduced into Rh^I com-



Figure 2. Product yield versus amount of consumed CCl₃COOH; reaction conditions: toluene (0.60 mL), butyl acrylate (0.20 mmol, 1.0 equiv), Cu-(OAc)₂-H₂O (20.0 mg, 0.5 equiv), [{RhCl(cod)}₂] (2.0 mol % with respect to butyl acrylate), acid (1.0 equiv), 120 °C, air. Yield (based on butyl acrylate) and the amount of CCl₃COOH consumed were obtained by GCMS.

 $HA = CCI_3COOH$

Scheme 2. Plausible mechanism for the oxidative coupling of an arene with an alkene.

plex 5 by the liberation of trichloroacetic acid and compound 5 then enters into another cycle. In this catalytic model, one molecule of olefin product is generated at the expense of one molecule of trichloroacetic acid, which can explain the linear plot of the yield of olefin product versus the consumption of trichloroacetic acid. In path B, the reaction is directly initiated by a stochastical attack of compound 6 on an accessible C-H position of the arene, thus leading to a σ -aryl-Rh^{III} complex (8) after releasing one molecule of trichloroacetic acid. In this catalytic model, trichloroacetic acid acts as a catalyst. Under these reaction conditions, the research data suggest that path A is the major catalytic pathway and that path B is the minor pathway. The coordination of trichloroacetic acid to the Rh^{III} metal center significantly changes the redox potential of the Rh^{III} metal center and the strong electron-withdrawing effect of the trichloromethyl group makes the rhodium(III)trichloroacetate complex (6) prone to decarboxylation to generate rhodium(III)-trichloromethyl intermediate 7, which explains why trichloroacetic acid is a better additive in this system compared with other normal fatty acids.

Conclusion

An efficient [{RhCl(cod)}₂]/CCl₃COOH catalytic system for the oxidative olefination of arenes has been developed with oxygen as the terminal oxidant. A strong cooperation effect of the acid with the Rh complex was observed. Trichloroacetic acid was the most-efficient additive and high yields were obtained for the reactions of a series of mono-, 1,2-, and 1,3substitued arenes with olefins. In comparison with other reported catalyst systems, this system is more attractive because the substrates do not require a chelate-assisted directing group and the scope of the substrates is broad; even halogen-substituted arenes react smoothly to give their corresponding products in high yields. The selectivity of the reaction is appealing when 1,3-disubstituted arenes or 1,2disubstituted arenes with the same two substituents are used as the substrates; a single product is produced in each case. The compatibility and simplicity of this catalyst system and the high chemo- and regioselectivity of the reaction make this method useful for the synthesis of vinylarene structures.

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Experimental Section

General information: All reactions were carried out in air and monitored by analytical thin layer chromatography on 0.20 mm silica gel plates (Anhui Liangchen Chem. Company, Ltd.); spots were detected by UV absorption. Silica gel (200–300 mesh; Anhui Liangchen Chem. Company, Ltd.) was used for column chromatography. All arenes and alkenes were purchased from commercial sources and used as received. ¹H and ¹³C NMR spectra were recorded on Bruker AV 400 or 500 spectrometers by using CDCl₃ as the solvent. ¹H and ¹³C NMR chemical shifts were referenced to the residual solvent peak. Coupling constants (*J*) are quoted in Hz. The NMR data of known compounds were in agreement with literature values.

General procedure for the Rh-catalyzed reactions: A flask that was charged with an alkene (0.20 mmol), $[{RhCl(cod)}_2]$ (1.0 mg, 0.004 mmol), CCl₃COOH (32.7 mg, 0.20 mmol), Cu(OAc)₂·H₂O (20.0 mg, 0.10 mmol), and an arene (0.60 mL) was heated at 120 °C with a balloon of air for the required time. The reaction was then cooled to RT and the crude mixture (typically, a brown slurry) was filtered through a short plug of silica gel (EtOAc). After monitoring the yield by GCMS, the products were purified by column chromatography on silica gel. The products were analyzed by NMR spectroscopy; the spectroscopic data were in agreement with the literature values of the known compounds.

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