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Rhodium-Catalyzed Direct Alkenylation and Arylation of Arene C−H Bonds via Decarbonylation of Cinnamoyl Chlorides, Cinnamic Anhydrides, and Poly(aroyl) Chlorides

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Summary: Efficient regioselective direct alkenylation of benzo[h]quinoline was realized with cinnamoyl chlorides as the coupling partners via decarbonylation of the chlorides and C−H bond activation by means of $[Rh(CO)_2Cl]_2$ *as the catalyst in refluxing o-xylene under phosphine-free conditions. For 2-phenylpyridine,* $[Rh(CO)_2Cl]_2$ *or* $[Rh(COD)Cl]_2$ *efficiently promoted its direct alkenylation with cinnamic anhydrides. Polyarenes were synthesized from* $[Rh(COD)Cl]_2$*-catalyzed decarbonylative poly(arylation) of isophthaloyl dichloride, terephthaloyl dichloride, or benzene-1,3,5-tricarbonyl chloride with benzo[h]quinoline.*

Introduction

Alkenylation is a useful synthetic protocol to prepare functional materials, natural products, and bioactive molecules.[1,2] Recently, transition-metal-catalyzed functionalization of arene C−H bonds has become more and more attractive for construction of carbon−carbon bonds.[3] Chelation-assisted functionalization of arenes via C−H bond activation by using a directing group such as carbonyl,[4] imino,[5] amino,[6] and pyridyl[7] has been paid much attention due to the high regioselectivity of the desired products. Although a lot of examples of direct arylation of arenes have been documented, direct alkenylation of arenes has not received considerable attention. So far, chelation-assisted C−H functionalization of arenes with alkenylboron reagents,[8] alkenes,[9] alkynes,[10] alkyl acrylates,[11] and alkenyl acetates[12] has been reported for this purpose. A variety of coupling partners were successfully explored, but they have been applied in C−H functionalization with limitations.[1,13] As potential coupling compounds, acid chlorides were used for carbon−carbon couplings under controlled conditions.[7c,e,f,14] Although carboxylic acids can be decarbonylatively transformed by transition metals,[15] only a few examples have been scattered.[16] Recently, we found that aroyl chlorides and benzoic and cinnamic anhydrides can be used as decarbonylative coupling partners

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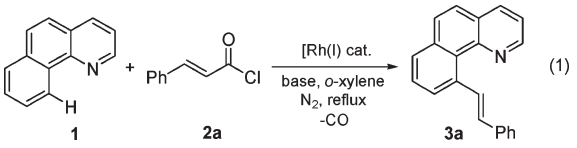
Table 1. Screening of Reaction Conditions[a]



entry	**1**:**2a**[b]	catalyst	base (equiv)	solvent	conversion[c] (%)
1	1:1.5	$[RhCl(COD)]_2$	Na_2CO_3 (2.0)	*o*-xylene	91
2	1:1.5	$[RhCl(CO)_2]_2$	Na_2CO_3 (2.0)	*o*-xylene	95
3	1:1.5	$[RhCl(CO)_2]_2$[d]	Na_2CO_3 (2.0)	*o*-xylene	86
4	1:1.5	$Rh(COD)_2BF_4$	Na_2CO_3 (2.0)	*o*-xylene	61
5	1:1.5	$RhCl(PPh)_3$	Na_2CO_3 (2.0)	*o*-xylene	56
6	1:1.5	$[RhCl(CO)_2]_2$	K_3PO_4 (2.0)	*o*-xylene	53
7	1:1.5	$[RhCl(CO)_2]_2$	K_2CO_3 (2.0.)	*o*-xylene	68
8	1:1.5	$[RhCl(CO)_2]_2$	KF (2.0)	*o*-xylene	72
9	1:1.5	$[RhCl(CO)_2]_2$	Cs_2CO_3 (2.0)	*o*-xylene	<1
10	1:2.0	$[RhCl(CO)_2]_2$	DBU (2.5)	*o*-xylene	14
11	1:1.5	$[RhCl(CO)_2]_2$	Na_2CO_3 (2.0)	toluene[e]	90
12	1:1.5	$[RhCl(CO)_2]_2$	Na_2CO_3 (2.0)	DMF	24
13	1:1.5	$[RhCl(CO)_2]_2$	Na_2CO_3 (2.0)	NMP	0
14	1:2.0	$[RhCl(CO)_2]_2$	Na_2CO_3 (2.0)	*o*-xylene	97 (74)[f]
15	1:3.0	$[RhCl(CO)_2]_2$	Na_2CO_3 (3.5)	*o*-xylene	99 (77)[f,g]

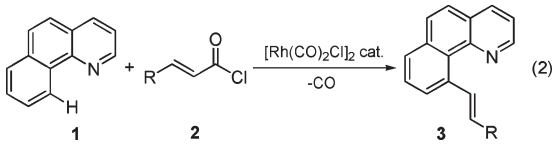
[a] Conditions: **1**, 0.5 mmol; catalyst, 5 mol %; base, 2.0−3.5 equiv; 4 Å molecular sieves; solvent, 5 mL; 145 °C, 16 h. [b] Molar ratio of **1** to **2a**. [c] Determined by GC analysis. [d] 2.5 mol % catalyst. [e] 110 °C. [f] Isolated yields in parentheses. [g] 24 h.

in $[Rh(COD)Cl]_2$-catalyzed direct functionalization of arenes under phosphine-free conditions.[7c,17] Herein, we report $[Rh(CO)_2Cl]_2$- and $[Rh(COD)Cl]_2$-catalyzed direct alkenylation of arene C−H bonds via decarbonylation of cinnamoyl chlorides and substituted cinnamic anhydrides as well as synthesis of polyarenes from poly(aroyl) chlorides.

Results and Discussion

In our initial studies, the Rh(I)-catalyzed reaction of benzo[*h*]quinoline (**1**) with cinnamoyl chloride (**2a**) was carried out in *o*-xylene at 145 °C under nitrogen atmosphere to screen the reaction conditions (eq 1 and Table 1). Under the conditions employed for C−H functionalization of arenes with $[RhCl(COD)]_2$ as the catalyst and aroyl chlorides as the coupling partners,[7c] catalyst $[RhCl(CO)_2]_2$ exhibited a higher catalytic activity than $[RhCl(COD)]_2$ for the reaction shown in eq 1 (Table 1, enties 1 and 2). As we investigated before,[7c] 4 Å molecular sieves accelerated the reaction. Decreasing the loading of $[RhCl(CO)_2]_2$ from 5 mol % to 2.5 mol % led to a lower reaction efficiency (entry 3). $Rh(COD)_2BF_4$ and Wilkinson's catalyst $RhCl(PPh)_3$ showed much lower catalytic activity than $[RhCl(CO)_2]_2$ under the same conditions (entries 4 and 5). Inorganic bases K_3PO_4, K_2CO_3, KF, and Cs_2CO_3 and the organic base DBU acted less effectively than Na_2CO_3 (entries 6−10). In refluxing toluene at 110 °C, the reaction proceeded slowly (entry 11). In strong polar solvents such as DMF and NMP the reaction proceeded very slowly or no reaction occurred (entries 12 and 13). As expected, increasing the amount of the coupling partner **2a** from 1.5 to 2 or 3 equiv, the conversion of **1** approached 97−99% and the desired product **3a** could be isolated in 74−77% yields (entries 14 and 15). Thus, the reaction conditions were optimized to the following: molar ratio of **1**:**2a** = 1:3, 5 mol % $[RhCl(CO)_2]_2$ as the catalyst, Na_2CO_3 as the base, 4 Å MS as the promoter, in refluxing *o*-xylene, and reaction time 24 h. It should be noted that alkenylation of **1** with **2a** is less efficient than the arylation of **1** with benzoyl chlorides[7c] under the same conditions.

Table 2. Direct Alkenylation of 1 via Decarbonylation of the Substituted Cinnamoyl Chlorides (2) and C−H Bond Activation[a]



entry	R	product	yield[b] (%)
1	Ph (**2a**)	**3a**	77
2	2-MeC_6H_4 (**2b**)	**3b**	77
3	3-MeC_6H_4 (**2c**)	**3c**	65
4	4-MeC_6H_4 (**2d**)	**3d**	69
5	2-$MeOC_6H_4$ (**2e**)	**3e**	30
6	3-$MeOC_6H_4$ (**2f**)	**3f**	55
7	4-$MeOC_6H_4$ (**2g**)[c]	**3g**	53
8	4-FC_6H_4 (**2h**)	**3h**	76
9	4-ClC_6H_4 (**2i**)	**3i**	77
10	4-BrC_6H_4 (**2j**)	**3j**	43
11	3-$CF_3C_6H_4$ (**2k**)	**3k**	60
12	2-naphthyl (**2l**)	**3l**	47
13	2-furyl (**2m**)	**3m**	55
14	2-thiophenyl (**2n**)	**3n**	52

[a] Conditions: **1**, 0.5 mmol; **2**, 1.5 mmol; $[Rh(CO)_2Cl]_2$, 5 mol %; Na_2CO_3, 3.5 equiv; 4 Å molecular sieves; *o*-xylene, 5 mL; 145 °C, 24 h. [b] Isolated yields. [c] **2**, 2.0 equiv; Na_2CO_3, 3.0 equiv.

Next, the direct alkenylation of **1** with substituted cinnamoyl chlorides was carried out under the optimized conditions to probe the protocol generality (eq 2, Table 2). With 2-, 3-, or 4-methyl as the substituent in the aryl moiety of a cinnamoyl chloride substrate, the target products **3b**−**d** were obtained in 65−77% yields (entries 2−4). A 2-methoxy substituent in **2e** led to a low yield (30%) for **3e**. With 3- or 4-methoxy as the substituent in **2f** or **2g**, compounds **3f** and **3g** were isolated in moderate yields (53−55%). The yields of the products **3h**−**k** from the reactions of **1** with electron-withdrawing substituent-bearing cinnamoyl chlorides, i.e., **2h**−**k**, varied from 43% to 77% (entries 8−11). The naphthyl substituent presumably increased the steric hindrance, and thus the reaction of **2l** produced **3l** in only moderate yield (47%) (entry 12). From the reactions of **1** with furyl- and thiophenyl-substituted acryloyl chlorides **2m** and **2n** the target products **3m** and **3n** could be formed in good yields (52−55%), respectively (entries 13 and 14). The same protocol was also applied in the alkenylation of 2-arylpyridines (**4a**−**c**) with cinnamoyl chloride (**2a**) (eq 3).

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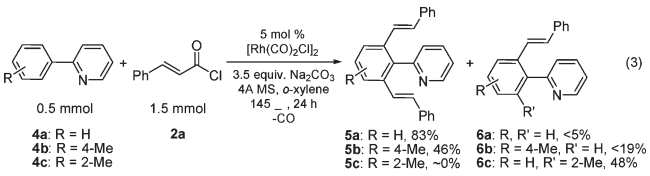
The target double-alkenylation products **5a** and **5b** were obtained in 46−83% yields with minor formation of the monoalkenylation products **6a** (< 5%) and **6b** (< 19%). From the reaction of

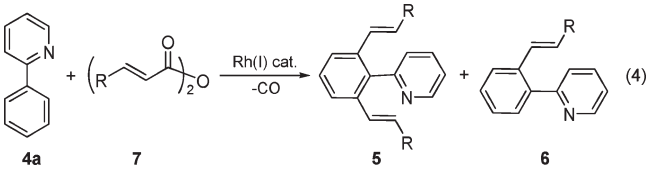


(3)

arene **4c**, only the monoalkenylation product **6c** was isolated (48%). However, under similar conditions the reaction of **4a** with cinnamic anhydride (**7a**) afforded **5a** in 91% isolated yield.[17] Thus, double-alkenylation of **4a** with substituted cinnamic anhydrides was investigated in order to synthesize the desired products of type **5** (eq 4, Table 3).

With 5 mol % $[RhCl(CO)_2]_2$ as the catalyst, the reaction of **4a** and **7a** produced **5a** in 88% yield (entry 1, Table 3), exhibiting a lower efficiency than the catalytic system using $[RhCl(COD)]_2$ as the catalyst.[17] Similar results were obtained with **7b** as the substrate (entry 2). In the case using anhydride **7c** and catalyst $[RhCl(COD)]_2$, a 7:3 mixture of **5e** and **6e** was collected (total yield 74%), whereas **5e** was isolated in 67% yield with $[RhCl(CO)_2]_2$ as the catalyst (entry 3). From the reactions of **4a** with anhydrides **7d**−**h**, $[RhCl(COD)]_2$ exhibited a better catalytic efficiency than $[RhCl(CO)_2]_2$, affording the desired double-alkenylation products **5f**−**j** in 63−95% yields (entries 4−8). However, $[RhCl(COD)]_2$-catalyzed reaction of **4a** with **7i** formed a 6:5 mixture of **5k** and **6k** in 63% total yield, while the same reaction promoted by $[RhCl(CO)_2]_2$ afforded **5k** in 63% yield (entry 9).

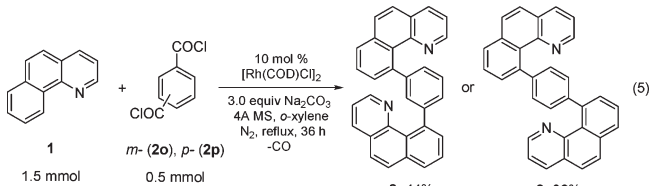
Table 3. Direct Alkenylation of 2-Phenylpyridine (4a) via Decarbonylation of Substituted Cinnamic Anhydrides (7) and C−H Bond Activation[a]



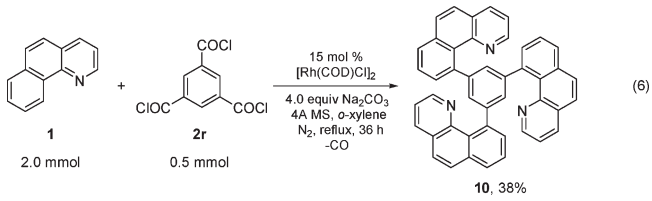
(4)

entry	R	catalyst	product	yield[b] (%)
1	Ph (**7a**)	$[Rh(COD)Cl]_2$	**5a**	91[c]
		$[Rh(CO)_2Cl]_2$	**5a**	88
2	2-MeC_6H_4 (**7b**)	$[Rh(COD)Cl]_2$	**5d**	96
		$[Rh(CO)_2Cl]_2$	**5d**	79
3[d]	4-MeC_6H_4 (**7c**)	$[Rh(COD)Cl]_2$	**5e**+**6e**	74 (7:3)[e]
		$[Rh(CO)_2Cl]_2$	**5e**	67
4	3-$OMeC_6H_4$ (**7d**)	$[Rh(COD)Cl]_2$	**5f**	95
5	4-$OMeC_6H_4$ (**7e**)	$[Rh(COD)Cl]_2$	**5g**	63
		$[Rh(CO)_2Cl]_2$	**5g**+**6g**	72 (5:1)[e]
6	4-ClC_6H_4 (**7f**)	$[Rh(COD)Cl]_2$	**5h**	83
7	3-$CF_3C_6H_4$ (**7g**)	$[Rh(COD)Cl]_2$	**5i**	92
8[f]	2-naphthyl (**7h**)	$[Rh(COD)Cl]_2$	**5j**	67
9	2-furyl (**7i**)	$[Rh(COD)Cl]_2$	**5k**+**6k**	63 (6:5)[e]
		$[Rh(CO)_2Cl]_2$	**5k**	63

[a] Conditions: **4a**, 0.5 mmol; **7**, 1.5 mmol; catalyst, 5 mol %; Na_2CO_3, 4.0 equiv; 4 Å molecular sieves; *o*-xylene, 3 mL; 145 °C, 12 h. [b] Isolated yields. [c] Ref 17. [d] 24 h. [e] Molar ratio of **5** to **6** determined by ^1H NMR analysis. [f] 18 h.



(5)



(6)

Intrigued by an interest in poly(C−H functionalization) of arenes by means of our recently developed methodologies,[7c,17] the one-pot reactions of benzo[*h*]quinoline (**1**) with isophthaloyl dichloride (**2o**), terephthaloyl dichloride (**2p**), and benzene-1,3,5-tricarbonyl chloride (**2r**) were carried out to produce the polyarene products, respectively (eqs 5 and 6). Using 10 mol % $[RhCl(COD)]_2$ as the catalyst, treatment of **1** with 3.0 equiv of **2o** or **2p** in refluxing *o*-xylene afforded the target diarylation products **8** (44%) and **9** (32%), respectively (eq 5). However, the *ortho*-diacid dichloride, i.e., phthaloyl dichloride (**2q**), did not undergo the same type of decarbonylative arylation with **1**, presumably due to the higher steric hindrance from the *ortho*-substituents. Interestingly, the acid trichloride (**2r**) underwent poly(decarbonylation) to form the triarylation product, i.e., **10**, in 38% yield (eq 6). As π-conjugated systems, aromatic compounds **8**−**10** may be potentially applied in the manufacture of electronic devices.[2a]

A plausible mechanism is proposed in Scheme 1 by demonstrating the reaction of **1** with acid chloride or anhydride (**2**). Initially, the acid chloride or anhydride is oxidatively added to the Rh(I) center, forming an aroyl- or acryloyl-chlorometal complex RCORh(III)Cl(X) (**11**), which undergoes decarbonylation to generate aryl- or alkenyl-chlororhodium(III) species (**12**) at elevated temperatures. Species **12** reacts with arene **1** to produce intermediate complex **13** by C−H bond activation via intramolecular *ortho*-chelating assistance in the presence of a base. The target product **3** is then formed via the reductive elimination of **13**. Such a proton abstraction mechanism is reasonable to explain the C−H functionalization of arenes by acid chlorides and anhydrides.[18] It is also possible for the reaction to occur via a decarbonylative concerted metalation deprotonation (CMD) mechanism.[19]

In conclusion, efficient regioselective direct alkenylation of arene C−H bonds has been achieved by means of Rh(I)-catalysis using substituted cinnamoyl chlorides and cinnamic anhydrides as the coupling partners via decarbonylative C−H bond activation with arene or N-heteroaromatic

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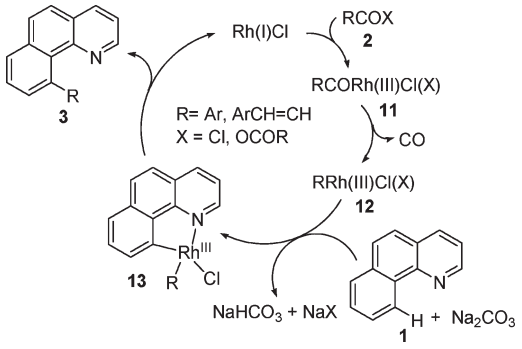
(19) García-Cuadrado, D.; de Mendoza, P.; Braga, A. A. C.; Maseras, F.; Echavarren, A. M. *J. Am. Chem. Soc.* **2007**, *129*, 6880.

Scheme 1. Proposed Mechanism



substrates under phosphine-free conditions. Polyarenes were successfully synthesized from the one-pot poly(arylation) of poly(aroyl) di- or trichlorides with benzo[*h*]quinoline.

Experimental Section

Typical Procedure for Alkenylation of Benzo[*h*]quinoline (1): Alkenylation of 1 with Cinnamoyl Chloride (2a). Under a nitrogen atmosphere, to a 25 mL Schlenk tube were successively added $[Rh(CO)_2Cl]_2$ (10 mg, 0.025 mmol), Na_2CO_3 (186 mg, 1.75 mmol), 4 Å molecular sieves (600 mg), benzo[*h*]quinoline **1** (89 mg, 0.5 mmol), cinnamoyl chloride **2a** (250 mg, 1.5 mmol), and *o*-xylene (5 mL). The reactor was equipped with an air condenser, and the mixture was stirred at 145 °C for 24 h. After cooling to ambient temperature, the resulting mixture was filtered through a short pad of Celite and rinsed with 20 mL of toluene. All the volatiles were evaporated from combined filtrate under reduced pressure, and the resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether (60−90 °C)/CH_2Cl_2, 20:1, v/v), affording the target product **3a** as a colorless oil (108 mg, 77%).

Typical Procedure for Dialkenylation of 2-Arylpyridines (4): Dialkenylation of 2-Phenylpyridine (4a) with Cinnamic Anhydride (7a). Under a nitrogen atmosphere, to a 25 mL Schlenk tube were successively added $[Rh(CO)_2Cl]_2$ (10 mg, 0.025 mmol), Na_2CO_3 (212 mg, 2.0 mmol), 4 Å molecular sieves (600 mg), 2-phenylpyridine **4a** (78 mg, 0.5 mmol), cinnamic anhydride **7a** (439 mg, 1.5 mmol), and *o*-xylene (3 mL). The Schlenk tube was equipped with an air condenser, and the mixture was stirred at 145 °C for 12 h. After cooling to ambient temperature, the resulting mixture was filtered through a short pad of Celite and rinsed with 20 mL of toluene. All the volatiles were evaporated from the combined filtrate under reduced pressure, and the resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether (60−90 °C)/CH_2Cl_2, 20:1, v/v), affording the target product **5a** as a white solid (159 mg, 88%).

Typical Procedure for Poly(arylation) with Benzo[*h*]quinoline (1): Reaction of 1 with Isophthaloyl Dichloride (2o). Under a nitrogen atmosphere, to a 25 mL Schlenk tube were successively added $[Rh(COD)Cl]_2$ (25 mg, 0.05 mmol), Na_2CO_3 (213 mg, 2.0 mmol), 4 Å molecular sieves (1000 mg), benzo[*h*]quinoline **1** (224 mg, 1.25 mmol), isophthaloyl dichloride **2o** (100 mg, 0.5 mmol), and *o*-xylene (5 mL). The Schlenk tube was equipped with an air condenser, and the mixture was stirred at 145 °C for 36 h. After cooling to ambient temperature, the resultant mixture was filtered through a short pad of Celite and rinsed with 20 mL of toluene. All the volatiles were evaporated from the combined filtrate under reduced pressure, and the resulting residue was purified by flash silica gel column chromatography (eluent: petroleum ether (60−90 °C)/EtOAc, 30:1, v/v), affording the target product **8** as a white solid (96 mg, 44%).

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Supporting Information Available: Experimental procedures and spectroscopic data for the new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.