ORGANIC
LETTERS

2009
Vol. 11, No. 6
1317−1320

Efficient Rh(I)-Catalyzed Direct Arylation and Alkenylation of Arene C−H Bonds via Decarbonylation of Benzoic and Cinnamic Anhydrides

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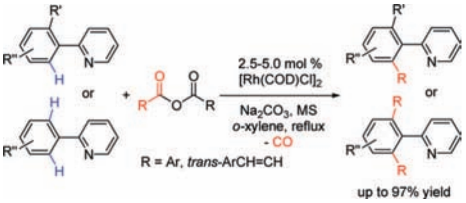
Received January 17, 2009

ABSTRACT



Efficient rhodium(I)-catalyzed regioselective direct arylation and alkenylation of aromatic C−H bonds has been realized with aromatic carboxylic and cinnamic anhydrides as the coupling partners via decarbonylation and C−H activation under phosphine-free conditions.

Transition-metal-catalyzed functionalization of arene C−H bonds has recently been paid much attention.[1] *ortho*-Arylation, alkenylation, and alkylation of sp^{2}C−H bonds involving subsequent regioselective formation of new C−C or C−X bonds assisted by various directing groups under palladium,[2] rhodium,[3] ruthenium,[4] copper,[5] nickel,[6] and iron[7] catalysis have attracted rapidly growing interest. Arenes and heterocycles usually undergo chelation-assisted C−H functionalization with organic or organometallic coupling partners such as aromatic halides,[2c,3−5,8] sulfonate esters,[4c,9] boronic acids,[7a,10] alkynes,[3c,5c,6] olefins,[11] alkyl acrylates,[12] arenes,[13] cycloalkanes,[14] arylsilanes,[15] organotrifluoroborates,[16] organotin,[17] and arylzinc[7b] reagents, producing the cross-coupling products. Peroxides,[18a] diethyl azodicarboxylate,[18b,c] arenediazonium salts,[18d] PhI═NNs,[18e] aldehydes,[18f] di-*tert*-butyldiaziridinone,[18g] epoxides,[18h] and unactivated aromatic

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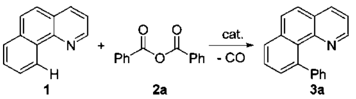
10.1021/ol9000729 CCC: $40.75

Table 1. Screening of Reaction Conditions[a]



(1)

entry	cat./mol %	additive	base	T (°C)	time (h)	conversion[b] (%)
1	$[Rh(COD)Cl]_2$/5	MS	Na_2CO_3	145	16	100 (92)[c]
2	$[Rh(COD)Cl]_2$/5	MS	Na_2CO_3	145	6	>99 (93)[c]
3	$[Rh(COD)Cl]_2$/2.5	MS	Na_2CO_3	145	9	>99 (92)[c]
4	$[Rh(COD)Cl]_2$/1	MS	Na_2CO_3	145	9	85
5	$[Rh(COD)Cl]_2$/2.5	MS	Na_2CO_3	130	9	90
6	$[Rh(COD)Cl]_2$/2.5		Na_2CO_3	145	9	70
7	$[Rh(COD)Cl]_2$/5		Na_2CO_3	145	13	97
8	$[Rh(COD)Cl]_2$/2.5	MS	K_3PO_4	145	9	>99
9	$[Rh(COD)Cl]_2$/2.5	MS	KF	145	9	97
10	$[Rh(COD)Cl]_2$/2.5	MS	K_2CO_3	145	9	64
11	$[Rh(CO)_2Cl]_2$/2.5	MS	Na_2CO_3	145	9	88
12	$[Rh(CO)_2Cl]_2$/5	MS	Na_2CO_3	145	16	100
13	$Rh(COD)_2BF_4$/2.5	MS	Na_2CO_3	145	9	87
14	$Rh(COD)_2BF_4$/5	MS	Na_2CO_3	145	16	98
15	$RhCl(PPh_3)_3$/5	MS	Na_2CO_3	145	16	8
16[d]	$[Rh(COD)Cl]_2$/2.5	MS	Na_2CO_3	145	9	10
17[e]	$Pd(OAc)_2$/2.5	MS	Na_2CO_3	145	9	0

[a] Conditions: **1**, 0.5 mmol; **2a**, 1.5 equiv; base, 2 equiv; MS = 4A molecular sieves, 0.600 g; *o*-xylene, 3 mL. [b] Conversion of **1** determined by GC analysis. [c] Isolated yield of **3a** in parentheses. [d] 20 mol % of PPh_3 was added. [e] 1,4-Benzoquinone (1.0 equiv) was added.

rings[2c,19] were also reported for this purpose. Although a variety of coupling partners were successfully explored, they have been applied in C−H functionalization with limited generality.[1,20] Very recently, we reported Rh(I)-catalyzed decarbonylative C−H functionalization by using acid chlorides as the coupling partners.[21] More recently, we found that benzoic anhydrides, as the coupling partners for Rh(I)-catalyzed aromatic C−H activation, are much more efficient than their benzoyl chloride analogues. Anhydrides are usually cheap and can be readily derived from their mother acids. Carboxylic acids can be decarbonylatively transformed by transition metals,[22] but only scattered examples have been documented.[23] Herein, we report $[Rh(COD)Cl]_2$-catalyzed direct arylation and alkenylation of arene C−H bonds via decarbonylation of benzoic and cinnamic anhydrides.

First, we carried out the reactions of benzo[*h*]quinoline (**1**) with benzoic anhydride (**2a**) under the typical Rh(I) catalysis conditions for decarbonylative arylation of **1** with benzoyl chlorides.[21] The $[Rh(COD)Cl]_2$-catalyzed reaction of **1** with **2a** efficiently afforded the desired arylation product **3a** in 92% isolated yield via decarbonylation of **2a** (Table 1, entry 1). Within 6 h, the reaction was also complete to give **3a** in a decent yield (93%, entry 2), suggesting that the present catalytic system is more efficient than that using benzoyl chloride for the same purpose. Lowering the catalyst amount to 2.5 mol %, the reaction also proceeded efficiently (entry 3). Further lowering the catalyst to 1 mol % or decreasing the reaction temperature to 130 °C (entries 4 and

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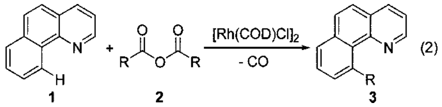
5) led to incomplete conversion of **1**. Surprisingly, in contrast to the Rh(I)/benzoyl chloride system,[21] the present catalytic system worked well without molecular sieves, achieving 97% conversion for **1** with 5 mol % catalyst over a period of 13 h (entries 6 and 7), but it is obvious that 4A molecular sieves improved the transformation (entries 1−7). K_3PO_4 and KF also worked efficiently as the bases, while K_2CO_3 was less effective (entries 8−10). Both $[Rh(CO)_2Cl]_2$ and $Rh(COD)_2BF_4$ can be used as the catalysts with a 5 mol % loading (entries 11−14). However, Wilkinson's catalyst $RhCl(PPh_3)_3$ only showed poor catalytic activity, which is similar to the result obtained in the presence of PPh_3 (entries 15 and 16). $Pd(OAc)_2$ did not effect the arylation reaction (entry 17), although palladium can catalyze the decarbonylative reactions of aroyl chlorides.[24] The reaction conditions were thus optimized as shown for entry 3: 2.5 mol % of $[Rh(COD)Cl]_2$ as the catalyst, Na_2CO_3 as the base, and 4A MS as the promoter in refluxing *o*-xylene for 9 h.

The reactions of **1** with other carboxylic anhydrides were then carried out to define the protocol scope (Table 2). When methyl-substituted benzoic anhydrides (**2b**−**e**) were used as the coupling partners, the products **3b**−**e** were obtained in decent yields (75−97%, entries 2−5). The reactions of **1** with 4- and 3-chloro- or -bromobenzoic anhydrides **2f**−**i** produced products **3f**−**i** in 40−66% yields, but increasing the catalyst loading to 5 mol % and/or extending the reaction time to 12−24 h gave the same products in 74−97% yields, respectively (entries 6−9). The reaction of **1** with 4-nitrobenzoic anhydride (**2j**) was complicated, affording product **3j** in 23% yield (entry 10), and no desired product was isolated from the reaction of **1** and 3-nitrobenzoic anhydride. However, the reaction of **1** with 3-nitro-4-methylbenzoic anhydride (**2k**) produced product **3k** in 72% yield (entry 11), revealing that an electron-donating substituent in anhydride **2** facilitates the arylation reaction.

Table 2. Direct Arylation of **1** via Decarbonylation of **2** and C−H Bond Activation[a]



entry	R	**2**	product	yield[b] (%)
1	Ph	**2a**	**3a**	92
2	4-MeC_6H_4	**2b**	**3b**	97
3	3-MeC_6H_4	**2c**	**3c**	75
4	3,4-$Me_2C_6H_3$	**2d**	**3d**	95
5	3,5-$Me_2C_6H_3$	**2e**	**3e**	81
6	4-ClC_6H_4	**2f**	**3f**	62 (97)[c]
7	3-ClC_6H_4	**2g**	**3g**	62 (76)[c]
8	4-BrC_6H_4	**2h**	**3h**	66 (76)[d]
9	3-BrC_6H_4	**2i**	**3i**	40 (74)[e]
10	4-$NO_2C_6H_4$	**2j**	**3j**	23[e]
11	3-NO_2-4-MeC_6H_3	**2k**	**3k**	72
12	2-thiophenyl	**2l**	**3l**	64[e]
13	2-furanyl	**2m**	**3m**	57[e]
14	$C_6H_5CH{=}CH$	**2n**	**3n**	60 (82)[d]

[a] Conditions: **1**, 0.5 mmol; **2**, 1.5 equiv; $[Rh(COD)Cl]_2$, 2.5 mol %; Na_2CO_3, 2 eq; MS, 0.600 g; *o*-xylene, 3 mL; 145 °C, 9 h. [b] Isolated yields. [c] 24 h. [d] 5.0 mol % of catalyst, 12 h. [e] 5.0 mol % catalyst, 24 h.

Unexpectedly, thiophene-2-carboxylic anhydride (**2l**) and furoic anhydride (**2m**) also underwent the direct decarbonylative arylation with **1**, forming **3l** and **3m** in 64% and 57% yields, respectively (entries 12 and 13). Surprisingly, cinnamic anhydride (**2n**) underwent the same type of reaction to form the direct alkenylation product **3n** in 82% yield (entry 14). It should be noted that the reactions of **1** with 2-chloro-, 2-bromo-, and 2-methylbenzoic anhydrides did not take place due to the *ortho*-steric hindrance from the substituents.

N-Heteroaromatic substrates were also applied to explore the generality of the direct arylation and alkenylation method. The reaction of 2-phenylpyridine (**4a**) with **2a** was chosen as the model reaction to optimize the reaction conditions. Using 5.0−7.5 mol % of $[Rh(COD)Cl]_2$ as the catalyst, >1.0 equiv of **2a** as the coupling partner, Na_2CO_3 as the base, and 4A MS as the promoter in refluxing *o*-xylene, >99% conversion was obtained for **4a**, forming a mixture of mono- and double arylation products. Both increasing the molar ratio of **2a** to **4a** and extending the reaction time favored formation of the double arylation product **5a**. Eventually, the reaction of **4a** (0.5 mmol) with **2a** (3 equiv) was carried out using 5 mol % catalyst, 4 equiv of Na_2CO_3, and 4A MS in refluxing *o*-xylene at 145 °C for 12 h, affording a mixture of the mono- and double-arylation products (1:99) with >99% conversion for **4a**. The desired double-arylation product **5a** was then isolated in 79% yield (Table 3, entry 1). For 2-pyridine-substituted arenes **4b**−**f**, their direct arylation with **2a** gave the desired products **5b**−**f** in 57−78% yields (entries 2−6). For 2-benzoylpyridine **4g** and *N*-heterocycle **4h** (entries 7 and 8), they were also efficiently arylated by **2a** to form **5g** (86%) and **5h** (64%), respectively, as compared to the reported results (33−34% yields) by using Rh(I)/benzoyl chloride.[21] A reactivity order of oxidative addition to Pd(0) has been established: $PhI \gg (PhCO)_2O > PhOTf > PhBr$,[25] which suggests that $(PhCO)_2O$ is a more reactive coupling reagent than PhOTf and PhBr. Thus, anhydrides $(ArCO)_2O$ may be used as the more capable coupling partners than ArBr in C−H functionalization. With cinnamic anhydride (**2n**) as the coupling partner, the reactions of **4a**−**h** efficiently produced the alkenylation products **6a**−**h** in 64−97% yields (entries 9−16), suggesting a promising alternative to compounds of type **6** instead from Heck reactions of aryl halides and styrene.[26] Alkenylation of arenes and *N*-heterocycles via C−H bond activation usually utilize alkynes,[6] olefins,[11] and alkyl acrylates[12] as the coupling reagents.

To investigate the reactivity of the substrates and coupling partners further, three competition reactions were explored

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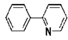
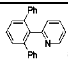
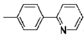
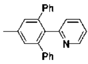
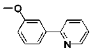
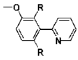
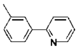
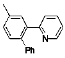
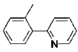
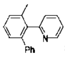
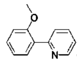
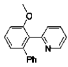
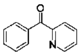
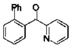
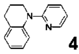
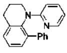
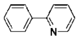
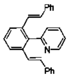
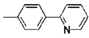
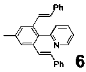
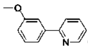
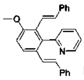
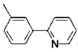
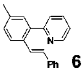
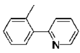
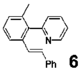
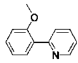
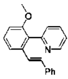
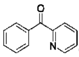
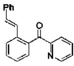
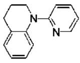
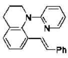
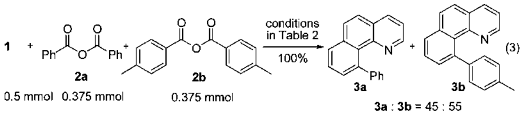
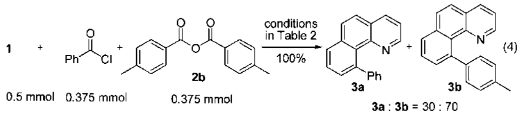
Table 3. Direct Arylation of 2-Arylpyridines (**4**) via Decarbonylation of **2a** or **2n** and C−H Bond Activation[a]

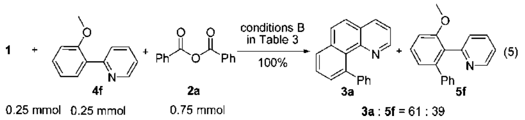
entry	substrate	cond.	product	yield (%)[b]
1	 **4a**	A	 **5a**	79
2	 **4b**	A	 **5b**	78
3	 **4c**	A	 **5c**	71
4	 **4d**	B	 **5d**	67[c]
5	 **4e**	B	 **5e**	63
6	 **4f**	B	 **5f**	57
7	 **4g**	B	 **5g**	86[d]
8	 **4h**	B	 **5h**	64[d]
9	 **4a**	A	 **6a**	91
10	 **4b**	A	 **6b**	93
11	 **4c**	A	 **6c**	84
12	 **4d**	B	 **6d**	77
13	 **4e**	B	 **6e**	64
14	 **4f**	B	 **6f**	97
15	 **4g**	B	 **6g**	79 (E/Z=96:4)
16	 **4h**	B	 **6h**	70 (E/Z=63:37)

[a] Conditions: **4**, 0.5 mmol; [Rh(COD)Cl]$_2$, 5 mol %; MS, 0.600 g; *o*-xylene, 3 mL; 145 °C, 12 h. (A) **2a** or **2n**, 3.0 equiv; Na$_2$CO$_3$, 4 eq. (B) **2a** or **2n**, 1.5 equiv; Na$_2$CO$_3$, 2 equiv. [b] Isolated yields. [c] GC yield (100% conversion for **4d**, a mixture of 33:67 di- and monoarylation products was obtained). [d] 16 h.

under the typical conditions as shown in Tables 2 and 3 (eqs 3−5). A 1:1 molar ratio mixture of **2a** and **2b** was reacted with **1**, affording the arylation products **3a** and **3b** in a 45:55 molar ratio (eq 3), which further demonstrates that an electron-donating substituent in the anhydride favors the arylation. Under the same conditions, using benzoyl chloride instead of benzoic anhydride **2a** led to less of **3a** (eq 4), revealing that benzoyl chloride is less reactive than benzoic anhydride in the Rh(I)-catalyzed decarbonylative arylation of **1**. Arene **1** exhibited a higher reactivity than 2-arylpyridine **4f**, producing **3a** as the major product in the reaction of **1**/**4f** (1:1) with **2a** (eq 5).

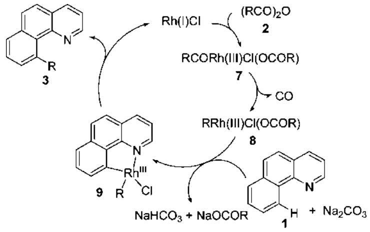






A possible mechanism is proposed in Scheme 1. Anhydride **2** is oxidatively added to the Rh(I) species to form an aroylcarboxylate metal complex [RCORh(III)Cl (OCOR)] (**7**) which undergoes decarbonylation to form aryl carboxylate−Rh(III) (**8**). Intermediate **8** reacts with arene **1** to generate complex **9** by C−H bond activation via intramolecular *ortho*-chelating assistance in the presence of Na$_2$CO$_3$ base. The desired product **3** is then produced via the reductive elimination of **9**. This proton abstraction mechanism is plausible to explain functionalization of the aromatic C−H bonds by carboxylic anhydrides.[4a,27]

Scheme 1. Proposed Mechanism



In summary, efficient regioselective direct arylation and alkenylation of aromatic C−H bonds has been realized by Rh(I) catalysis using aromatic carboxylic and cinnamic anhydrides as the coupling partners via decarbonylative C−H bond activation with arene or *N*-heteroaromatic substrates under phosphine-free conditions. The present catalytic system is much more efficient than the Rh(I)/aroyl chloride system[21] for the same purpose.

Acknowledgment. We are grateful to the National Natural Science Foundation of China (20772124) and the National Basic Research Program of China (2009CB825300) for support of this research.

Supporting Information Available: Experimental procedures, analytical data, and copies of NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

OL9000729

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