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Rhodium(I)-Catalyzed Carbonylative Annulation of Iodobenzenes with Strained Olefins and 4-Octyne in the Presence of Furfural Involving *ortho*-C–H Bond Cleavage

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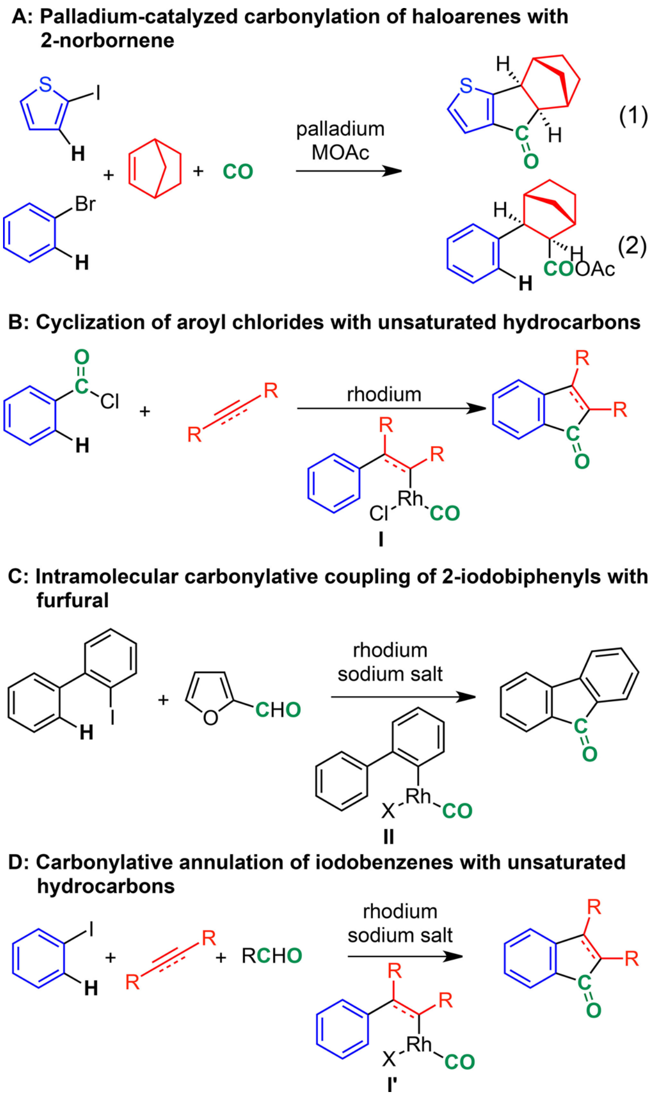
Abstract: The rhodium(I)-catalyzed carbonylative annulation of iodobenzenes with strained olefins in the presence of furfural as a carbonyl source, accompanied by *ortho*-C–H bond cleavage, is reported. The use of 4-octyne in place of strained olefins also leads to the formation of the corresponding inden-9-one. The timely release of the carbonyl moiety *via* the rhodium-catalyzed decarbonylation of furfural plays a decisive role in this reaction.

Keywords: carbonylative annulation; C–H functionalization; furfural; rhodium catalyst; three-component reactions

The transition metal-catalyzed three-component carbonylative annulation of *ortho*-functionalized aryl halides, π-unsaturated compounds, such as alkynes and olefins, and carbon monoxide is an attractive method for preparing cyclic carbonyl-containing compounds[1] which are found in a wide variety of natural products and pharmaceutically important compounds.[2] While significant efforts have been devoted to developing the concise synthesis of heterocyclic carbonyl compounds, only a few examples of three-component carbonylative annulation for the synthesis of carbocyclic carbonyl compounds such as indenones and indanones have been reported in the literature.[3] In 2007, the first report, the rhodium-catalyzed carbonylative cyclization of 2-halophenylboronic acids with alkynes or 2-norbornene under atmospheric carbon monoxide, was published by Chatani's group.[4] Later, our group demonstrated that paraformaldehyde can be used as a carbonyl source in this transformation.[5] Although high yields of the desired products could be achieved, these procedures have a problem from the viewpoint of atom- and step-economy, and waste generation; the preparation of 2-halophenylboronic acids is generally a multistep process.[6] Therefore, the straightforward functionalization at a C–H bond of simple haloarenes is an ideal method.[7] In this context, Grigg in fact reported that 2-iodothiophene reacts with 2-norbornene and carbon monoxide in the presence of a palladium catalyst to furnish the cyclic carbonyl compound through C–H metallation at the C-3 position of the thiophene [Scheme 1A, Eq. (1)].[8] Even though the palladacycle formation and the subsequent transformation have been extensively studied,[9] the reaction of halobenzene and 2-norbornene with carbon monoxide failed to produce an annulated carbonyl compound [Eq. (2)].[10] To the best of our knowledge, the carbonylative annulation of halobenzenes *via* C–H bond cleavage remains an undeveloped area.

During the course of our studies on the direct catalytic carbonylation reactions of C–H bonds,[11] we focused on the fact that the following rhodium species, **I** and **II**, can cyclize, along with the cleavage of a C–H bond, followed by the insertion of a carbonyl moiety, to form benzene ring-fused cyclopenta(e)none frameworks. An elegant work by Miura and co-workers showed that the rhodium complex catalyzes the direct C–H cyclization of benzoyl chlorides with internal alkynes and 2-norbornene (Scheme 1B).[12] In that report, the complex **I** was proposed as the key intermediate. We recently developed the intramolecular carbonylative coupling of 2-iodobiphenyl with furfural produced from biomass resources[13] as a carbonyl source *via* the formation of 2-rhodabiphenyl **II**, which is analogous to complex **I**, to give fluoren-9-one (Scheme 1C).[11b] These findings encouraged us to investigate the three-component carbonylative annula-


A: Palladium-catalyzed carbonylation of haloarenes with 2-norbornene

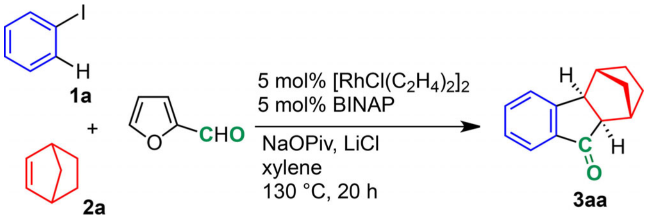
B: Cyclization of aroyl chlorides with unsaturated hydrocarbons

C: Intramolecular carbonylative coupling of 2-iodobiphenyls with furfural

D: Carbonylative annulation of iodobenzenes with unsaturated hydrocarbons

Scheme 1. Carbonylative annulation involving C–H bond cleavage.

Table 1. Optimization of the reaction conditions.[a]



Entry	Deviation from standard conditions	Yield[b]
1	none	80%
2	no $[RhCl(C_2H_4)]_2$	0%
3	$[RhCl(cod)]_2$ as catalyst precursor	31%
4	no BINAP[c]	15%
5	10 mol% of BINAP[c]	6%
6	(*R*)-BINAP[c]	78%[d]
7	DPPP[e] as ligand	62%
8	BIPHEP[f] as ligand	72%
9	no base	20%
10	Na_2CO_3 as base	60%
11	$MesCO_2Na$ as base	70%
12	no LiCl	65%
13	dioxane as solvent	40%
14	100 °C in toluene	77%
15	$(CH_2O)_n$ as carbonyl source	31%

[a] *Standard reaction conditions:* **1a** (0.5 mmol), **2a** (2.5 mmol), furfural (2.5 mmol), $[RhCl(C_2H_4)_2]_2$ (0.025 mmol), BINAP (0.025 mmol), NaOPiv (1.0 mmol), LiCl (0.1 mmol), and xylene (1 mL) at 130 °C for 20 h.

[b] Isolated yield.

[c] 2,2′-Bis(diphenylphosphino)-1,1′-binaphthyl.

[d] 2% *ee.*

[e] 1,3-Bis(diphenylphosphino)propane.

[f] 2,2′-Bis(diphenylphosphino)-1,1′-biphenyl.

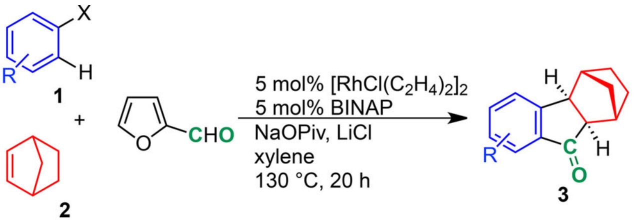
tion of iodobenzenes, unsaturated hydrocarbons, and a carbonyl moiety using a rhodium catalyst (Scheme 1D). The present paper describes the successful realization of this transformation.

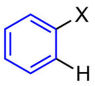
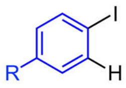
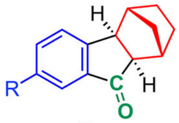
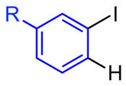
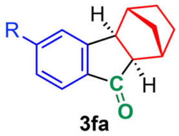
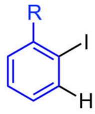
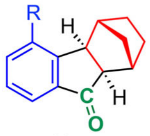
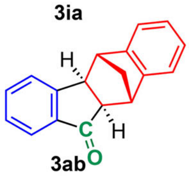
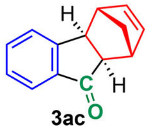
Our initial studies focused on the carbonylative annulation of iodobenzene (**1a**) with 2-norbornene (**2a**). In this examination, we used, not gaseous carbon monoxide, but rather furfural as the carbonyl source, because of the difficulty arising from the chemical and physical properties of carbon monoxide.[14] In addition, it was anticipated that large amounts of carbon monoxide in the reaction system would interfere with the coordination and the oxidative addition of substrates to a rhodium center.[11b] After extensive investigations of reaction parameters,[15] we determined the following optimal reaction conditions: **1a** (0.5 mmol), **2a** (2.5 mmol), furfural (2.5 mmol), $[RhCl(C_2H_4)]_2$ (0.025 mmol), BINAP (0.025 mmol), NaOPiv (1.0 mmol), and LiCl (0.1 mmol) in xylene (1 mL) at 130 °C for 20 h to afford **3aa** in 80% yield (Table 1, entry 1). Removing the rhodium catalyst from the catalytic system resulted in no formation of the desired product (entry 2). When using $[RhCl(cod)]_2$ instead of $[RhCl(C_2H_4)_2]_2$, the product yield remarkably diminished (entry 3).[12a] The addition of 0.5 equivalent of BINAP to the rhodium center gave the highest yield of **3aa**, suggesting that both BINAP-ligated and BINAP-free rhodium species play a crucial role in the decarbonylation of furfural and the subsequent carbonylative annulation of **1a** with **2a**, respectively (entries 1, 4, and 5).[5,12] The use of (*R*)-BINAP gave quite low enantiomeric excess (2% *ee*).[15] Other bidentate phosphanes also showed activity as a ligand, albeit the yield of **3aa** was slightly lower (entries 7 and 8). In sharp contrast to Miura's report, it was necessary to add a base in order to achieve an efficient reaction (entry 9).[12a] Among the various bases examined, NaOPiv was found to be the best choice (entries 10 and 11). The absence of LiCl retarded the progress of the reaction (entry 12). It can be assumed that the rhodate species generated by the coordination of a chloride to the rhodium center permits a more facile oxidative addition of the C–I bond.[16] Changing the solvent away from xylene led to a significant loss in the efficiency of the reaction (entry 13). The reaction also proceeded smoothly in toluene at 100 °C to afford the corresponding compound in 77% yield (entry 14). Paraformaldehyde, which has great advantages in terms of cost and atom economy in comparison with other reported carbonyl surrogates,[17,18] was tested as a carbonyl source (entry 15). However, the formation of substantial amounts of side products, such as biphenyl, benzophenone, and benzoic acid, caused a low yield of the desired product **3aa**.

Having optimized the reaction conditions, we investigated the scope and limitations of halobenzenes and strained olefins (Table 2). Bromobenzene (**1b**) showed a much lower reactivity for this carbonylation (entry 2). 4-Substituted iodobenzenes (**1c**–**e**) were able to react with **2a** to produce the corresponding indanones in moderate to good yields (entries 3–5). The carbonylative annulation of 3-substituted iodobenzenes (**1f** and **g**) also proceeded efficiently with exclusive site selectivity (entries 6 and 7). On the other hand, 2-substituted iodobenzenes such as 2-iodotoluene (**1h**) and 2-iodoanisole (**1i**) were barely converted into the desired products under the standard reaction conditions, probably due to steric hindrance. The use of Na_2CO_3, which is an effective base for the intramolecular carbonylation of 2-iodobiphenyls,[11] in place of NaOPiv gave **3ha** in 16% yield. Furthermore, when 2-substituted iodobenzenes were reacted with **2a** and furfural at 150 °C, **3ha** and **3ia** were obtained in moderate yields (entries 8 and 9). Benzonorbornadiene (**2b**) was applicable to the transformation to afford **3ab** in 74% yield (entry 10). Unfortunately, the reaction of **1a** with 2,5-norbornadiene (**2c**) provided an unidentified and inseparable complex mixture (entry 11). With cyclohexene and styrene, Mizoroki–Heck-type reactions occurred leading to no formation of indanone products.[12a,16b]

The synthesis of 2,3-dipropylinden-1-ones (**5aa** and **ca**) was also achieved when 4-octyne (**4a**) was employed in place of **2a** (Scheme 2). However, the formation of naphthalene derivatives[12b,19] as side reaction products led to moderate yields of the desired indenones. The use of diphenylacetylene (**4b**) dramatically lowered the efficiency of the reaction, and 63% of **4b** was recovered from the reaction mixture, although 2-iodo-1,1,2-triphenylethylene reacted with furfural to produce **5ab** in 72% yield.[20] This can be attributed to the stronger back donation from rhodium to **4b** than with **2a** and **4a** resulting in the stabilization of the rhodium(I) complex and the inhibition of the oxidative addition of iodobenzene.[21]

Table 2. Scope of the rhodium-catalyzed carbonylative annulation.[a]



Entry	1	2	3	Yield[b]
1	 X = I: **1a**	 **2a**	 **3aa**	80%
2	X = Br: **1b**	**2a**	**3aa**	10%
3	 R = Me: **1c**	**2a**	 **3ca**	75%
4	R = Br: **1d**	**2a**	**3da**	66%
5	R = NO_2: **1e**	**2a**	**3ea**	52%
6	 R = OMe: **1f**	**2a**	 **3fa**	74%
7	R = Me: **1g**	**2a**	**3ga**	76%
8	 R = Me: **1h**	**2a**	 **3ha**	44%[c]
9	R = OMe: **1i**	**2a**	**3ia**	40%[c]
10[d]	**1a**	 **2b**	 **3ab**	74%
11	**1a**	 **2c**	 **3ac**	0%

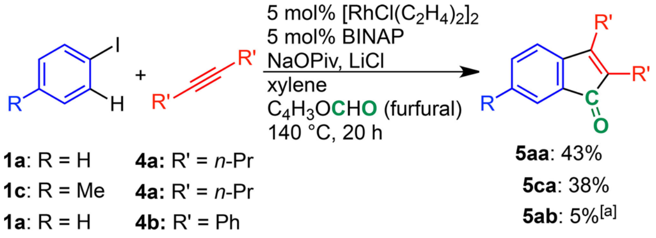
[a] *Reaction conditions:* **1** (0.5 mmol), **2** (2.5 mmol), furfural (2.5 mmol), $[RhCl(C_2H_4)_2]_2$ (0.025 mmol), BINAP (0.025 mmol), NaOPiv (1.0 mmol), LiCl (0.1 mmol), and xylene (1 mL) at 130 °C for 20 h.

[b] Isolated yield.

[c] The reaction was carried out at 150 °C using Na_2CO_3 instead of NaOPiv.

[d] **2b** (1.5 mmol) was employed.

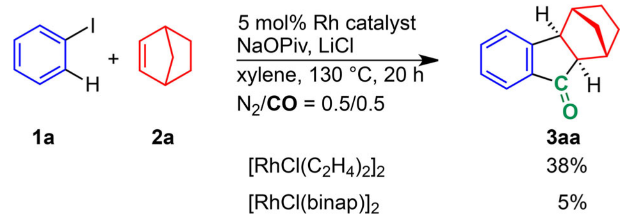
We then conducted some experiments to determine the active catalyst for the carbonylative annulation.



[a] **1a** (2.5 mmol), **4b** (0.5 mmol), furfural (2.5 mmol), $[RhCl(C_2H_4)_2]_2$ (0.025 mmol), BINAP (0.025 mmol), NaOPiv (1.0 mmol), LiCl (0.1 mmol), and xylene (1 mL) at 140 °C.

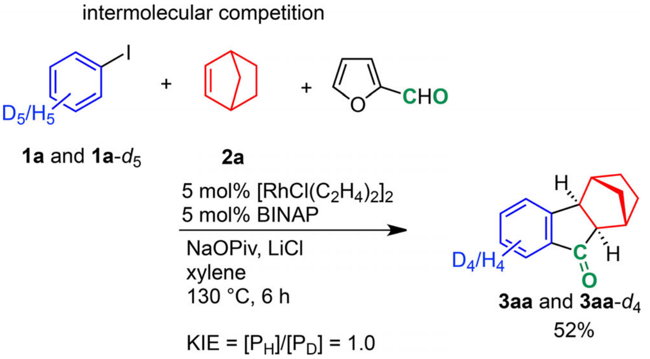
Scheme 2. Synthesis of inden-1-ones. *Reaction conditions:* **1** (0.5 mmol), **4a** (1.0 mmol), furfural (2.5 mmol), $[RhCl(C_2H_4)_2]_2$ (0.025 mmol), BINAP (0.025 mmol), NaOPiv (1.0 mmol), LiCl (0.1 mmol), and xylene (1 mL) at 140 °C. Isolated yields are given.

The ^{31}P NMR spectrum of the mixture containing $[RhCl(C_2H_4)_2]_2$ and BINAP (0.5 equivalent to rhodium center) in toluene-d_8 showed a sole signal at $\delta = 50.7$ which correspond to $[RhCl(binap)]_2$. Thus, the carbonylative annulation of **1a** and **2a** under a partial pressure of 0.5 atm of CO and 0.5 atm of N_2 was examined using $[RhCl(C_2H_4)_2]_2$ and $[RhCl(binap)]_2$ (Scheme 3). While $[RhCl(C_2H_4)_2]_2$ gave the desired product **3aa** in 38% yield, $[RhCl(binap)]_2$, which has higher activity for the decarbonylation of aldehydes than the phosphine-free rhodium complex,[22] was found to be catalytically ineffective for this reaction. According to our initial expectations, the reaction under atmospheric carbon monoxide catalyzed by $[RhCl(C_2H_4)_2]_2$ was considerably slower. This phenomenon suggests that the timely release of the carbonyl moiety from furfural plays a decisive role in the efficient reaction, consistent with findings in a previous report.[11b]



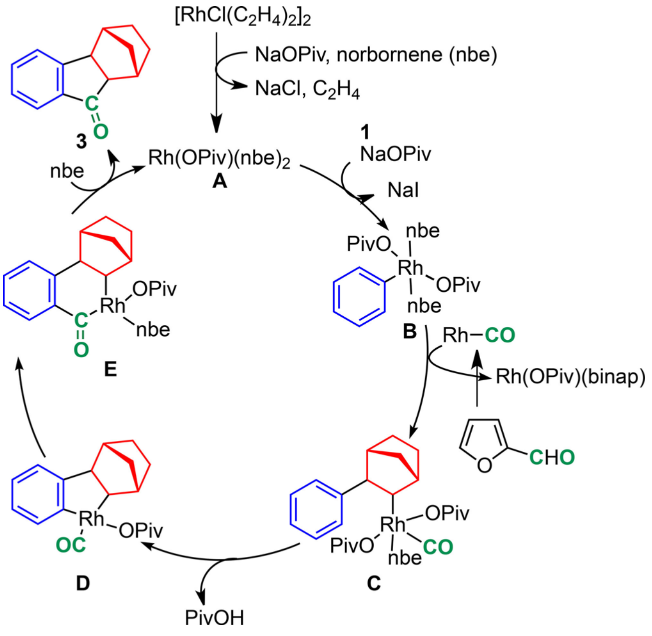
Scheme 3. Reaction with carbon monoxide.

The kinetic isotope effect (KIE) was investigated by means of an intermolecular competition experiment between **1a** and **1a**-d_5 (Scheme 4). A KIE value ($[P_H]/[P_D]$) of 1.0 was obtained, indicating that cleavage of the C–H bond is not the rate-determining step.[23,24] Considering our experimental observations and a previous report,[11b] we propose that oxidative addition of the C–I bond is involved in the rate-determining step.



Scheme 4. Deuterium labelling experiment.

A plausible catalytic cycle for the present reaction with 2-norbornene is illustrated in Scheme 5.[11,12] The Rh(III) species **B** is generated *via* the oxidative addition of an iodobenzene to Rh(I) **A**, which is generated *in situ* from $[RhCl(C_2H_4)_2]_2$ and NaOPiv in the presence of 2-norbornene. The migratory insertion of the norbornene, followed by the transfer of a carbonyl moiety *via* the decarbonylation of furfural catalyzed by the $[Rh(OPiv)(binap)]_2$ complex,[25] generates the key intermediate **C**. This undergoes cleavage of a C–H bond at the *ortho*-position, furnishing the five-membered rhodacycle **D**. Although details of the C–H bond dissociation are unclear at present,[26] it is likely that the pivalate as a ligand assists in the cleavage of the C–H bond.[27] The incorporation of the carbonyl moiety into **D** gives the acyl species **E**. Finally, the annulated carbonyl product is liberated from **E** to complete the catalytic cycle.



Scheme 5. Plausible catalytic cycle.

In summary, we reported on the carbonylative annulation of iodobenzenes, strained olefins or 4-octyne, and using furfural as the carbonyl source, *via ortho*-C–H bond cleavage leading to the formation of indanone and indenone derivatives. This carbonylative annulation represents the first example of the three-component carbonylative annulation of iodobenzenes with unsaturated hydrocarbons involving C–H cleavage. Importantly, furfural rather than gaseous carbon monoxide served as the carbonyl source. We expect that the carbonylation method depending on the aldehydes will serve as a unique protocol for the development of novel carbonylation reactions which are difficult to achieve by the traditional method using gaseous carbon monoxide.[28]

Experimental Section

Typical Procedure for the Rh-Catalyzed Carbonylative Annulation of Iodobenzene, 2-Norbornene, and Furfural

A 10-mL dry sealed tube equipped with a stir bar was charged with $[RhCl(C_2H_4)_2]_2$ (0.025 mmol, 9.72 mg), BINAP (0.025 mmol, 15.57 mg), NaOPiv (1.0 mmol, 124.11 mg), LiCl (0.1 mmol, 4.24 mg), and 2-norbornene (2.5 mmol, 235.40 mg) under an N_2 flow. Xylene (1 mL), iodobenzene (0.5 mmol, 102.01 mg), and furfural (2.5 mmol, 240.23 mg) were then added. After degassing the reaction mixture by the freeze-pump-thaw method three times, the tube was filled with N_2. The mixture was then placed in an oil bath that had been preheated to 130 °C for 20 h. After cooling to room temperature, the resulting solution was filtered through a celite pad, and the filtrate was concentrated under vacuum. The resulting crude product was purified by flash column chromatography on silica gel (hexane/EtOAc = 20/1) to afford **3aa**.

Acknowledgements

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[21] The fact that the reaction of **1a** (0.5 mmol) and **2a** (2.5 mmol) with furfural (2.5 mmol) in the presence of **5b** (2.5 mmol) gave 18% yield of **3aa** and trace amount of **5ab** supports our conclusions.

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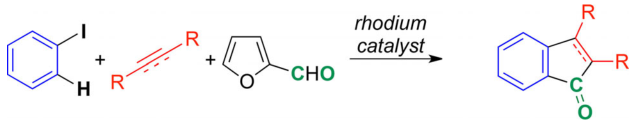
Rhodium(I)-Catalyzed Carbonylative Annulation of Iodobenzenes with Strained Olefins and 4-Octyne in the Presence of Furfural Involving *ortho*-C–H Bond Cleavage

7



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