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CO Gas-free Intramolecular Cyclocarbonylation Reactions of Haloarenes Having a *C*-Nucleophile through CO-Relay between Rhodium and Palladium

Tsumoru Morimoto,* Mana Yamashita, Ai Tomiie, Hiroki Tanimoto, and Kiyomi Kakiuchi[a]

Abstract: We describe transfer carbonylation reactions of 2-bromoarenes that contain a carbon-nucleophile using aldehydes as a substitute for CO, leading to the formation of indanone derivatives. The transformation proceeds efficiently under Rh(I)/Pd(0)-hybrid catalytic conditions consisting of two discrete transition metals, rhodium and palladium, which catalyze the decarbonylation of aldehydes and the subsequent carbonylation of bromoarenes using the resulting carbonyl moiety, respectively. The majority of the abstracted CO is transferred directly to the product via a CO-relay process from rhodium to palladium.

Transition-metal-catalyzed carbonylation is a powerful method for the straightforward construction of a wide variety of carbonyl functionalities.[1] Recent notable progress in the field is the elimination of the need for the direct use of carbon monoxide, and, novel substitutes for CO continue to grow.[2],[3] Thus, the use of various organic and inorganic carbonyl-containing compounds as a substitute for carbon monoxide (CO) allows CO gas-free carbonylation reactions to be carried out. These reactions involve the *in* and *ex situ*-generation of a carbonyl unit from the substituent (decarbonylation) followed by the incorporation of the resulting carbonyl unit into a carbonylated substrate (carbonylation). Aldehydes, including formaldehyde, represent one of the more interesting substitutes for CO in such transfer carbonylation reactions, from the aspect of the availability and the ease of handling of the donor molecule.[4],[5] The methodology is based on two cooperative catalytic processes, the decarbonylation of aldehydes by a transition metal catalyst, such as Rh(I), Ir(I), Ru(II), or a Pd(0) complex, and the subsequent introduction of the resulting carbonyl moiety into a substrate by the catalyst. Single catalysts have been used for both the decarbonylation and the carbonylation processes. The simultaneous use of two discrete catalysts suitable for each process, however, permits the the transfer carbonylation method using aldehydes to be extended to wider type of carbonylation reactions. We have also reported on other catalyst systems that can be used in this type of reaction. These include a combination of a phosphine-ligated rhodium(I) for decarbonylation and a phosphine-free rhodium(I) for carbonylation,[6] two types of rhodium(I) catalysts that contain two discrete phosphines,[7] and catalysts that contain both a neutral and a cationic rhodium(I) species.[8] In this report, we describe a new strategy for a transfer carbonylation reaction using aldehydes as a substitute for CO. The reaction proceeds effectively in the presence of a hybrid catalyst consisting of two discrete transition metals, namely, rhodium and palladium.[9] Chang et al. reported on the use of a hybrid catalyst system consisting of Ru(0) and Pd(0) that catalyzes some CO gas-free carbonylation reactions using formate[10a] and formamide[10b] derivatives, which includes a pyridine core, as a carbonyl source. In these cases, Ru(0) and Pd(0) catalyze the decarbonylation of formate and formamide derivatives which are specifically designed for decarbonylation and carbonylation using the resulting carbonyl moiety through the CO-relay from a ruthenium to a palladium species, respectively. The present catalysis represents the first example of a transfer carbonylation in which simple (non-designed) aldehydes are used as CO donors through a CO-relay between two discrete transition metal complexes.

Our previous reports on the CO gas-free cyclocarbonylation of haloarenes having a carbon-nucleophile moiety with aldehydes clarified that the use of a single rhodium(I) complex, $[RhCl(cod)]_2$, catalyzes the transfer a carbonyl group from 2-naphthaldehyde to the iodobenzene derivative **1a** to give the cyclocarbonylated product **2** and more available bromo-derivative **1b** is not carbonylated (Scheme 1a and b).[11],[12] We began our study with the reaction of bromobenzene **1b** containing a malonate-nucleophile with an aldehyde with the goal of achieving CO gas-free cyclocarbonylation. The use of $Pd(dppp)_2$ as a singly catalyst resulted in no formation of **2**, similar to that for of $[RhCl(cod)]_2$/dppp (b and c). Taking into account that Rh(I) and Pd(0) complxes are effective for the decarbonylation of aldehydes and the carbonylation of haloarenes, such as Heck-type amidation and esterification reactions, respectively, we adopted a strategy in which Rh(I) and Pd(0) complexes are used simultaneously as cooperative catalysts. Catalytic conditions consisting of $[RhCl(cod)]_2$, $Pd(dppp)_2$, and dppp (1,3-bis(diphenylphosphino)propane) catalysed the reaction of **1b** with 2-naphthaldehyde to give the indanone derivative **2** in 85% yield (d). The carbonylation was found to be catalyzed only by the mixed complexes of $[RhCl(cod)]_2$/dppp and $Pd(dppp)_2$. In addition, under the above catalytic conditions, chlorobenzene **1c**, which is the most available but most unreactive substrate among the analogues, could be catalytically transformed into **2** although in low yield (23%) (e). The use of large excess of the aldehyde (5 eq) is not essential for the catalysis. Thus, although the reaction of **1b** (0.50 mmol) with 2 eq of 2-naphthaldehyde (1.0 mmol) under the above catalytic conditions for 6 h did not complete, the desired product **2** in 60% yield was obtained.

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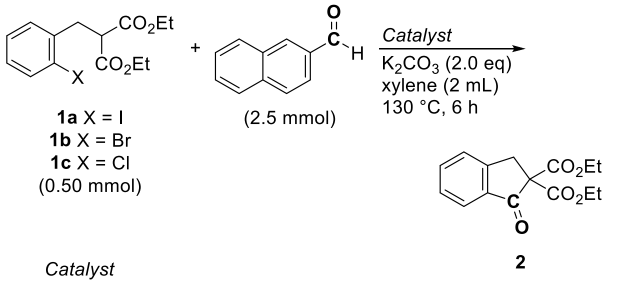


Catalyst	**2**
(a) $[RhCl(cod)]_2$ (2.5 mol%) / dppp (5.5 mol%)	75% (**1a**)
(b) $[RhCl(cod)]_2$ (2.5 mol%) / dppp (5.5 mol%)	0% (**1b**)
(c) $Pd(dppp)_2$ (5.0 mol%)	0% (**1b**)
(d) $[RhCl(cod)]_2$ (2.5 mol%) / dppp (5.5 mol%) $Pd(dppp)_2$ (5.0 mol%)	85% (**1b**)
(e) $[RhCl(cod)]_2$ (2.5 mol%) / dppp (5.5 mol%) $Pd(dppp)_2$ (5.0 mol%)	23% (**1c**) (24 h)

Scheme 1. Rh(I)/Pd(0)-Hybrid Catalyst Leads to Transfer Carbonylation of **1** with 2-naphthaldehyde.

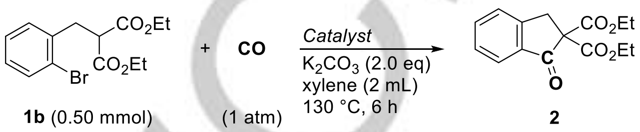
The ability of various aldehydes to donate their carbonyl group was also investigated: pentafluorobenzaldehyde (entry 2), *p*-trifluoromethylbenzaldehyde (entry 3), benzaldehyde (entry 4), *p*-anisaldehyde (entry 5), *trans*-cinnamaldehyde (entry 6), hydrociinamaldehyde (entry 7), and paraformaldehyde (entry 8) and the results are summarized in Table 1. Regardless of the electronic nature of the substituent in the aromatic ring of the aromatic aldehyde, all of the examined aldehydes functioned as a carbonyl donor.[13] The CO-donation ability from each aldehyde should depend on both how easy it is decarbonylated and it suffers from the nucleophilic attack by the malonate moiety to give an alcohol, which cannot be decarbonylated. As a result, the electronic and/or steric property of aldehydes does not directly contribute to their CO-donation ability. It is particularly noteworthy that the use of 2-naphthaldehyde and paraformaldehyde as carbonyl sources led to the formation of **2** in high yields (Table 1, entries 1 and 8).

Table 1. Investigation on Ability of Aldehydes as a CO Source[a]

Entry	Aldehyde	Conversion	Yield of **2**[b]
1	2-Naphthaldehyde	100%	85%
2	C_6F_5CHO	33%	22%
3	*p*-CF_3-C_6H_4CHO	100%	15%
4	PhCHO	57%	41%
5	*p*-MeO-C_6H_4CHO	65%	47%
6	(*E*)-PhCH=CHCHO	61%	19%
7	$PhCH_2CH_2CHO$	84%	38%
8	$(CH_2O)_n$	96%	58%

[a] Reaction conditions: **1b** (0.5 mmol), aldehyde (2.5 mmol), $[RhCl(cod)]_2$ (2.5 mol%), dppp (5.5 mol%), $Pd(dppp)_2$ (5.0 mol%), and K_2CO_3 (1.0 mmol) in xylene (2 mL) at 130 °C for 6 h. [b] Isolated yield.

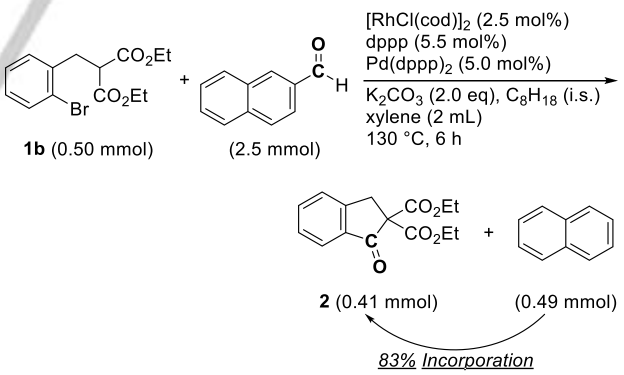
In order to elucidate role of rhodium and palladium in the catalytic process, carbonylation reactions of **1b** using CO gas as a carbonyl source was investigated. When atmospheric CO was used, the rhodium catalyst system, $[RhCl(cod)]_2$/dppp, gave no cyclocarbonylated product **2** (Scheme 2a), while the palladium complex, $Pd(dppp)_2$, catalyzed the same transformation efficiently to give the product **2** in a similar yield as was obtained when both of them were simultaneously used in the reaction with 2-naphthaldehyde as a carbonyl source (b).[11] These results indicate that the presence of a carbonyl moiety, carbon monoxide itself, or a carbonyl ligand enables the palladium complex to catalyze the cyclocarbonylation process.



Catalyst	
(a) $[RhCl(cod)]_2$ (2.5 mol%) dppp (5.5 mol%)	0%
(b) $Pd(dppp)_2$ (5.0 mol%)	86%

Scheme 2. Reactions of **1b** with CO (1 atm).

It was found that the abstracted CO is incorporated effectively into the product. The reaction of the bromobenzene derivative **1b** (0.50 mmol) with 2-naphthaldehyde (2.5 mmol) afforded the carbonylated product **2** (0.41 mmol) in 80% yield (83% GC yield), along with the decarbonylated product, naphthalene (0.49 mmol) (Scheme 3). The majority (84%) of the CO groups that were abstracted from the aldehyde were utilized in the carbonylation step. The profile of this reaction also showed that the transfer of the carbonyl moiety from the aldehyde to the substrate takes place efficiently (Figure 1).[14]



Scheme 3. Transfer Cyclocarbonylation of **1b** with 2-naphthalene.

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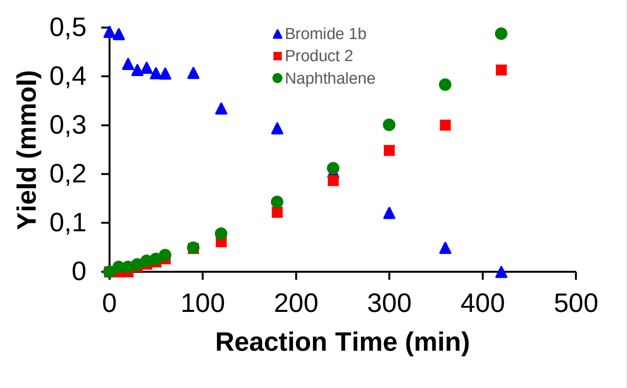
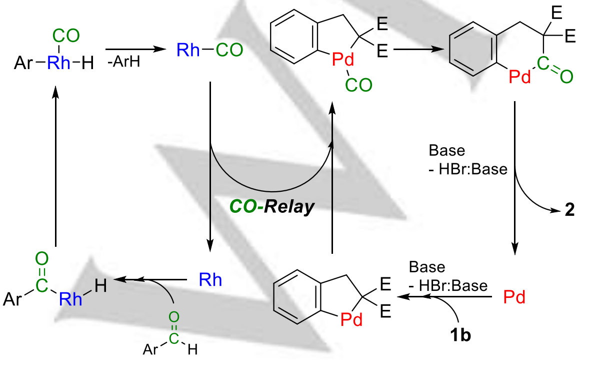


Figure 1. Reaction Profile for the cyclocarbonylation of **1b** with 2-naphthalene to yield **2**. Plots are the GC yields of **1b**, **2**, and naphthalene that are determined using octadecane as an internal standard.

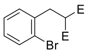
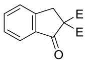
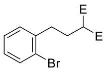
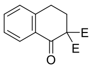
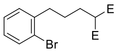
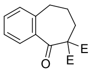
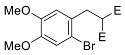
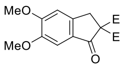
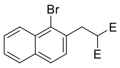
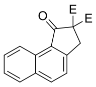
A possible reaction pathway for the present reaction, which rationalizes the above results, is outlined in Scheme 4. The reaction proceeds via the abstraction of a carbonyl moiety from aldehydes by the Rh(I) catalyst, followed by the incorporation of the resulting carbonyl group into bromobenzene **1b** catalyzed by Pd(0). The rhodium-catalyzed decarbonylation process begins with the oxidative addition of the aldehyde C-H to a CO ligand-free rhodium(I) complex, followed by the migratory extrusion of the carbonyl in the acyl ligand and the reductive elimination of the organic ligand to give the rhodium(I) carbonyl species, Rh-CO, and the decarbonylated product, ArH.[15] According to the above results (Scheme 3 and Figure 1), Rh-CO would relay its CO ligand directly to a palladium complex in most cases (83%) and would release it in the form of free carbon monoxide in other cases (17%) to regenerate a CO ligand-free rhodium(I) complex, which has the ability to decarbonylate aldehydes. On the other hand, the palladium(0)-loaded complex is transformed to a five-membered palladacyle via the oxidative addition of a C-Br bond of **1b** and the subsequent intramolecular transmetalation of the deprotonated malonate part. It receives the CO ligand from the rhodium-catalyzed decarbonylation process, followed by its insertion into a C(sp$_3$)-Pd bond,[16] to afford an acyl-palladium intermediate. Finally, product **2** is reductively eliminated, accompanied by the regeneration of a palladium(0) complex. During the overall catalysis, these two processes that involve two discrete types of transition metals function cooperatively without interfering with each other, resulting in a CO gas-free cyclocarbonylation reaction.

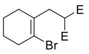
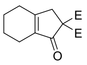
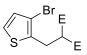
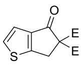


Scheme 4. Outline of a Plausible Reaction Pathway.

We next examined the Rh(I)-catalyzed reactions of various substrates with 2-naphthaldehyde or paraformaldehyde as a carbonyl source under the standard conditions: bromide (0.5 mmol), aldehyde (2.5 mmol), $[RhCl(cod)]_2$ (0.0125 mmol), dppp (0.0275 mmol), $Pd(dppp)_2$ (0.0250 mmol), and K_2CO_3 (1.0 mmol) in xylene (2 mL) at 130 °C and the results are summarized in Table 2. Only a malonate derivative could be used as a carbon-nucleophile in the present catalysis, and the exchange of the nucleophilic moiety to acetoacetate, benzenesulfonyl acetate, or cyanoacetate afforded no corresponding cyclocarbonylated product. The elongation of the carbon-chain linking a malonate-nucleophilic part and a bromobenzene framework by one- or two carbons (**3** and **5**) resulted in the formation of the corresponding cyclic ketones **4** and **6**, respectively (entries 3 and 5). The cyclocarbonylation of bromobenzene **7** having a MeO-functionality on the aromatic ring proceeded smoothly to give the indanone derivative **8** in 79% yield (entry 7). The present transformation is not limited to bromobenzene derivatives as a substrate. Bromoacene (naphthalene) **9**, an alkene (cyclohexene) **11**, and a heterocycle (thiophene) **13** having a malonate-nucleophile were tolerated to the reaction conditions and were transformed to the corresponding cyclocarbonylated products **10**, **12**, and **14**, respectively (entries 9, 11, and 13). Although paraformaldehyde was applicable as a carbonyl source instead of 2-bromonaphthalene to give the desired cyclocarbonylated products, the reactions showed lower chemical yields than when 2-bromonaphthalene was used because reduced compounds of the bromide were produced as byproducts (even number of entries).

Table 2. Rh(I)/Pd(0)-Catalyzed CO gas-free Cyclocarbonylation of Various Bromides[a]

Entry	Bromide	RCHO[b]	Time	Product	Yield[c]
1	 **1** (E = CO$_2$Et)	A	6 h	 **2**	85%
2	**1**	B	8 h	**2**	65%
3	 **3**	A	6 h	 **4**	83%
4	**3**	B	12 h	**4**	44%
5	 **5**	A	4 h	 **6**	57%
6	**5**	B	10 h	**6**	22%
7	 **7**	A	5 h	 **8**	79%
8	**7**	B	11 h	**8**	47%
9	 **9**	A	15 h	 **10**	74%

10	**9**	B	12 h	**10**	57%
11	 **11**	A	6 h	 **12**	80%
12	**11**	B	8 h	**12**	67%
13	 **13**	A	5 h	 **14**	74%
14	**13**	B	10 h	**14**	8%

[a] Reaction conditions: bromide (0.5 mmol), aldehyde (2.5 mmol), $[RhCl(cod)]_2$ (2.5 mol%), dppp (5.5 mol%), $Pd(dppp)_2$ (5.0 mol%), and K_2CO_3 (1.0 mmol) in xylene (2 mL) at 130 °C for 6 h. [b] A: 2-naphthaldehyde; B paraformaldehyde. [c] Isolated yield.

In conclusion, we report on the CO gas-free cyclocarbonylation reaction of haloarenes having a carbon-nucleophile using aldehydes as a carbonyl source. The reaction is catalysed by two discrete complexes, Rh(I) and Pd(0), which are responsible for the decarbonylative degradation of aldehydes and the introduction of the resulting carbonyl moiety via the CO-relay from Rh(I) to Pd(0), respectively. These two catalysts function cooperatively without interfering with each other, resulting in an overall CO gas-free carbonylation. This represents the first successful demonstration of a CO gas-free carbonylation reaction including a CO-relay between discrete transition-metal complexes in carbonylation reactions using aldehydes as a carbonyl source. The present findings, showing that a number of readily available carbonyl sources can be used, indicate that this is a straightforward process for producing a variety of carbonylative transformations.

Experimental Section

General Procedure for the Cyclocarbonylation of Bromoarenes with Aldehydes: To a 10 mL two-necked flask equipped with a reflux condenser and a 2 L gas-bag were placed $[RhCl(cod)]_2$ (0.0125 mmol, 6.21 mg), dppp (0.0275 mmol, 11.70 mg), $Pd(dppp)_2$ (0.025 mmol, 23.29 mg), K_2CO_3 (1.0 mmol, 138.21 mg), an aldehyde (2.5 mmol), the substrate (0.5 mmol), and xylene (2 mL) under a flow of nitrogen. The mixture was degassed by three freeze-pump-thaw cycles, and purged with nitrogen. The mixture was stirred at 130 °C in an oil-bath until the substrate was consumed. The progress of the reaction was monitored by GC or TLC. After the substrate was consumed, water was added to the reaction mixture and the organic solution was separated. The aqueous solution was extracted with Et_2O, and the combined organic solution was dried over $MgSO_4$. After removing the $MgSO_4$ by filtration, the filtrate was concentrated *in vacuo*, and the residue was purified by column chromatography on silica-gel.

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Keywords: transfer carbonylation • dual catalysis • intramolecular cyclocarbonylation • aldehydes • indanones

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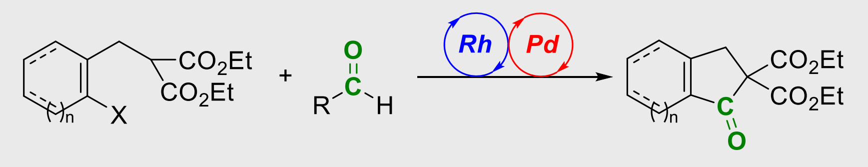

Rh(I)/Pd(0)-hybrid catalytic system catalyzes the transfer carbonylation reaction of haloarenes having a carbon-nucleophile using aldehydes as a substitute for CO, leading to the formation of indanone derivatives. Rh(I) and Pd(0) are responsible for the decarbonylation of aldehydes and the subsequent carbonylation of haloarenes using the resulting carbonyl moiety, respectively. The majority of the abstracted CO is ransferred directly to the product via CO-relay from the rhodium to the palladium.

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CO Gas-free Intramolecular Cyclocarbonylation Reaction of Haloarenes Having a *C*-Nucleophile through CO-Relay between Rhodium and Palladium