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# Recyclable heterogeneous palladium-catalyzed carbonylative Sonogashira coupling under CO gas-free conditions

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#### ABSTRACT

A convenient, efficient and practical heterogeneous palladium-catalyzed carbonylative Sonogashira coupling of aryl iodides with terminal alkynes under CO gas-free conditions has been developed by using an MCM-41-supported bidentate phosphine palladium acetate complex as catalyst. Here, formic acid was used as the CO source with dicyclohexylcarbodiimide (DCC) as the activator and a wide variety of alkynyl ketones were generated in moderate to high yields. This heterogeneous palladium catalyst can be easily recovered via a simple filtration process and recycled up to 8 times without apparent loss of activity.

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#### **KEYWORDS**

Palladium; carbonylative Sonogashira coupling; alkynyl ketone; formic acid; heterogeneous catalysis

#### **GRAPHICAL ABSTRACT**



#### Introduction

Alkynyl ketones are important structural motifs present in various biologically active molecules,<sup>[1]</sup> and play a crucial role as key intermediates in the synthesis of natural products<sup>[2]</sup> and numerous heterocyclic compounds<sup>[3]</sup> due to their multifunctional properties. The traditional method for the preparation of alkynyl ketones involves the acylation reaction of acid chlorides with terminal alkynes<sup>[4]</sup> or alkynyl metals.<sup>[5]</sup> However, acid chlorides are corrosive and moisture-sensitive, and they are usually only accessible

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with a limited scope of functional groups. The palladium-catalyzed carbonylative Sonogashira cross-coupling reaction is a viable alternative for the construction of alkynyl ketones since this methodology employs readily available aryl halides (or pseudohalides) and terminal alkynes as starting materials and displays good functional group tolerance.<sup>[6]</sup> Since the first palladium-catalyzed carbonylative Sonogashira cross-coupling reaction was reported by Kobayashi and Tanaka in 1981,<sup>[6a]</sup> significant efforts have been made to improve this particular transformation. However, most of these methods suffer from difficult recovery and non-recyclability of expensive homogeneous palladium catalysts and employ gaseous carbon monoxide as the CO source. Although gaseous CO has some advantages, it is a toxic, flammable, colorless and odorless gas whose inhalation even in ppm amounts can be lethal, which prevents extended applications of these methods in organic synthesis.

Over the past decades, various CO surrogates, including metal carbonyls, formic acid, aldehydes, formamides, and oxalyl chloride have been developed and utilized in carbonylation reactions.<sup>[7]</sup> Wu and coworkers reported the first palladium-catalyzed carbonylative Sonogashira coupling reaction with formic acid as the CO source and acetic anhydride as the activator.<sup>[8]</sup> However, pre-preparation of acetic formic anhydride and the use of a large excess amount of  $Et_3N$  to neutralize the *in situ* formed acetic acid were required. Dicyclohexylcarbodiimide (DCC) is a readily available, inexpensive and good dehydrating reagent in organic synthesis. Recently, Wu and coworkers developed a convenient and efficient carbonylative Sonogashira coupling reaction using Pd(OAc)<sub>2</sub>/2PPh<sub>3</sub> as the catalyst with formic acid as the CO source and DCC as the activator,<sup>[9]</sup> but the difficult separation and recovery from the reaction mixture and non-recyclability of the homogeneous Pd(OAc)<sub>2</sub>/2PPh<sub>3</sub> system are still the main drawbacks. Therefore, developing a convenient, efficient, and practical route to alkynyl ketones is highly desirable.

In recent years, microporous and mesoporous materials have found wide applications in catalysis science and immobilization of homogeneous catalysts on heterogeneous supports.<sup>[10]</sup> Mesoporous silica MCM-41 has been widely utilized as a powerful support for anchoring homogeneous catalysts due to its outstanding advantages, including extremely high surface area, large and defined pore size, and big pore volume in comparison with other solid supports.<sup>[11]</sup> So far, some palladium complexes anchored onto MCM-41 have been successfully used as highly efficient and recyclable catalysts in organic reactions.<sup>[12]</sup> However, to our knowledge, no example of carbonylative Sonogashira coupling catalyzed by an MCM-41-supported palladium complex with formic acid as the CO source has been reported until now. We herein report our newly developed heterogeneous palladium-catalyzed carbonylative Sonogashira coupling with HCOOH as the CO source and DCC as the activator by using an MCM-41-supported bidentate phosphine palladium acetate complex [MCM-41-2P-Pd(OAc)<sub>2</sub>] as catalyst (Scheme 1). The reaction



Scheme 1. Heterogeneous palladium-catalyzed carbonylative synthesis of alkynyl ketones with formic acid as the CO source.



Scheme 2. Preparation of the MCM-41-2P-Pd(OAc)<sub>2</sub> complex.

was conducted in a one-step, one-pot manner; a wide variety of alkynyl ketones were produced under mild conditions in moderate to high yields with good functional group tolerance. Compared with the methodology reported by Wu et al. using  $Pd(OAc)_2/2PPh_3$  as the catalyst with formic acid as the CO source and DCC as the activator,<sup>[9]</sup> the present protocol has the advantages of easy separation of the expensive palladium catalyst from the product and the catalyst recycling for eight times without apparent loss of activity.

#### **Results and discussion**

The MCM-41-2P-Pd(OAc)<sub>2</sub> catalyst was easily prepared according to our previously reported procedure,<sup>[13]</sup> as shown in Scheme 2. Firstly, the reaction of mesoporous silica MCM-41 with *N*,*N*-bis((diphenylphosphino)methyl)-3-(triethoxysilyl)propan-1-amine in toluene at reflux for 24 h, followed by treatment with Me<sub>3</sub>SiCl at room temperature for 24 h afforded a bidentate phosphino-modified MCM-41 material (MCM-41-2P). The latter was then coordinated with Pd(OAc)<sub>2</sub> in acetone at reflux for 48 h to give the MCM-41-supported bidentate phosphine palladium acetate complex [MCM-41-2P-Pd(OAc)<sub>2</sub>] as a light yellow powder with palladium content of 0.36 mmol/g. The structure of the catalyst was characterized by FT-IR, XRD, EDS, TGA, SEM, TEM, BET and XPS analysis (see the Supporting Information).

The MCM-41-2P-Pd(OAc)<sub>2</sub> complex was then used as a catalyst for carbonylative Sonogashira coupling of aryl iodides with terminal alkynes with formic acid as the CO source and DCC as the activator. Initial experiments with iodobenzene **1a** and phenylacetylene **2a** were carried out to optimize the reaction conditions, and the results are summarized in Table 1. Firstly, the effect of various bases on the model reaction was evaluated with toluene as solvent at 30 °C (entries 1–6). Among tertiary amine bases tested, Et<sub>3</sub>N gave an excellent yield of 95% (entry 3), while other organic bases such as *i*-Pr<sub>2</sub>NEt, DBU, *n*-Bu<sub>3</sub>N and pyridine were substantially less effective and inorganic bases such as K<sub>2</sub>CO<sub>3</sub> was ineffective. Reducing the amount of Et<sub>3</sub>N to 1.0 equiv. gave a lower yield of 73% (entry 7). Replacement of toluene with other solvents such as DMF, THF, dioxane and MeCN led to a decreased yield (entries 8–11). We next examined the

	MCM-41-2P-Pd(OAc) <sub>2</sub> (3 mol%)	0
+ <u></u> Ph 1a 2a	base, HCO <sub>2</sub> H (2 equiv.) DCC (2 equiv.), solvent 30 °C 24 h	Ph 3a
	50 0, 24 11	

Table 1	1.	Optimization	of	the	reaction	conditions. <sup>a</sup>
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Entry	Base	Solvent	Temp. (°C)	Yield (%) <sup>b</sup>
1	<i>i</i> -Pr <sub>2</sub> NEt	toluene	30	11
2	DBU	toluene	30	20
3	Et <sub>3</sub> N	toluene	30	95
4	<i>n</i> -Bu <sub>3</sub> N	toluene	30	56
5	pyridine	toluene	30	27
6	K <sub>2</sub> CO <sub>3</sub>	toluene	30	0
7 <sup>c</sup>	Et <sub>3</sub> N	toluene	30	73
8	Et <sub>3</sub> N	DMF	30	39
9	Et <sub>3</sub> N	THF	30	61
10	Et <sub>3</sub> N	dioxane	30	81
11	Et <sub>3</sub> N	MeCN	30	78
12	Et <sub>3</sub> N	toluene	60	79
13	Et <sub>3</sub> N	toluene	80	32
14	Et <sub>3</sub> N	toluene	100	11
15 <sup>d</sup>	Et <sub>3</sub> N	toluene	30	76
16 <sup>e</sup>	Et <sub>3</sub> N	toluene	30	54
17 <sup>f</sup>	Et <sub>3</sub> N	toluene	30	96
18 <sup>g</sup>	Et <sub>3</sub> N	toluene	30	97

<sup>a</sup>Reaction conditions: **1a** (1.0 mmol), **2a** (2.0 mmol), MCM-41-2P-Pd(OAc)<sub>2</sub> (3 mol%), base (2.0 mmol), HCOOH (2.0 mmol), DCC (2.0 mmol), solvent (4 mL), 30  $^{\circ}$ C, 24 h.

<sup>b</sup>lsolated yield.

<sup>c</sup>Et<sub>3</sub>N (1.0 mmol) was used.

<sup>d</sup>HCOOH (1.5 mmol) and DCC (1.5 mmol) were used.

<sup>e</sup>1 mol% catalyst was used.

<sup>f</sup>5 mol% catalyst was used.

<sup>g</sup>Pd(OAc)<sub>2</sub> (3 mol%) and PPh<sub>3</sub> (6 mol%) were used as the catalyst.

effect of reaction temperatures on the reaction (entries 12–14). When the reaction was conducted at a higher temperature, the yield of **3a** reduced significantly, which may be due to the decreased solubility of CO in toluene at high temperatures. The use of 1.5 equiv. of HCOOH and DCC also resulted in a decreased yield (entry 15). Finally, the amount of the catalyst was screened. Reducing the amount of the catalyst to 1 mol% led to a significant decrease in the yield of **3a** (entry 16), whilst increasing the amount of the catalyst to 5 mol% did not improve the yield obviously (entry 17). When homogeneous  $Pd(OAc)_2$  (3 mol%)/PPh<sub>3</sub> (6 mol%) system was used as the catalyst, the desired **3a** was also isolated in 97% yield (entry 18), indicating that the catalytic efficiency of MCM-41-2P-Pd(OAc)<sub>2</sub> was comparable to that of  $Pd(OAc)_2$  (3 mol%) in toluene with Et<sub>3</sub>N as base at 30 °C for 24 h (entry 3).

With the optimal conditions in hand, we began to study the substrate scope of this heterogeneous palladium-catalyzed carbonylative Sonogashira coupling reaction. First, a variety of aryl iodides were successfully applied to this reaction, and the results are summarized in Table 2. *para-* or *meta-*Substituted iodobenzenes **1b-h** bearing electron-donating or electron-withdrawing groups could undergo the carbonylative Sonogashira coupling smoothly with phenylacetylene to give the corresponding alkynyl ketones **3b-h** 



Table 2. Heterogeneous Pd-catalyzed carbonylative Sonogashira coupling of various aryl iodides with phenylacetylene 2a.<sup>a,b</sup>

<sup>a</sup>Reaction conditions: 1 (1.0 mmol), 2a (2.0 mmol), MCM-41-2P-Pd(OAc)<sub>2</sub> (3 mol%), Et<sub>3</sub>N (2.0 mmol), HCOOH (2.0 mmol), DCC (2.0 mmol), toluene (4 mL), 30 °C, 24 h. <sup>b</sup>Isolated yield.

in moderate to high yields. Generally, electron-rich aryl iodides displayed a slightly higher reactivity than electron-poor ones. Moreover, aryl iodides 1f-h bearing strong electron-withdrawing groups delivered the desired products 3f-h in relatively lower yields because of the formation of byproducts derived from the direct coupling reaction. In addition, rigid 4-iododiphenyl 1i and bulky 1-iodonaphthalene 1j were also good substrates and afforded the expected products 3i and 3j in 78-89% yields. The sterically hindered methyl 2-iodobenzoate 1k gave the target product 3k in only a 60% yield. Notably, heteroaryl iodides such as 2-iodothiophene 11 and 6-iodoquinoline 1m were compatible with the standard conditions and provided the corresponding products 31 and **3m** in high yields. A wide range of functional groups such as methyl, methoxy, chloro, cyano, trifluoromethyl and ester were well tolerated in this heterogeneous palladium-catalyzed carbonylative coupling reaction. We also performed the carbonylative Sonogashira coupling reaction of aryl bromides with phenylacetylene under the optimized conditions, unfortunately, aryl bromides were not reactive in this transformation, even if some active aryl bromides such as 4-bromonitrobenzene and 4-bromobenzaldehyde were used as substrates at 30 or 60 °C, no desired products were produced.

Subsequently, we turned our attention to examining the generality of the alkyne coupling partner with various terminal alkynes. As shown in Table 3, the electron-rich



Table 3. Heterogeneous Pd-catalyzed carbonylative Sonogashira coupling of various terminal alkynes with iodobenzene 1a.<sup>a,b</sup>

<sup>a</sup>Reaction conditions: **1a** (1.0 mmol), **2** (2.0 mmol), MCM-41-2P-Pd(OAc)<sub>2</sub> (3 mol%), Et<sub>3</sub>N (2.0 mmol), HCOOH (2.0 mmol), DCC (2.0 mmol), toluene (4 mL), 30 °C, 24 h.

<sup>c</sup>The reaction was conducted at 60 °C.

arylacetylenes **2b-e** showed a similar reactivity with phenylacetylene **2a** and delivered the corresponding coupling products **3n-q** in excellent yields. By contrast, electron-deficient arylacetylenes **2f-h** showed a slightly lower reactivity and gave the desired products **3r-t** in 80–89% yields. 4-Fluorophenylacetylene **2f** provided a better yield of product than 4-chlorophenylacetylene **2g** and 4-bromophenylacetylene **2h**. This may be due to the stronger electron-withdrawing effect of fluorine, which aids in the reaction of the alkyne with the acylpalladium intermediate. In addition, heteroarylacetylenes such as 3-ethynylpyridine **2i** and 3-ethynylthiophene **2j** underwent this reaction at a relatively higher temperature and furnished the expected products **3u** and **3v** in moderate yields. Notably, a conjugated enyne, 1-ethynylcyclohexene **2k** reacted well in this transformation at 60 °C, delivering the target product **3w** in 82% yield. Moreover, cycloalkyl alkynes such as cyclohexylacetylene **2l** and cyclopropylacetylene **2m** were successfully transformed into the corresponding products **3x** and **3y** at 60 °C in good yields. But, 1-octyne **2n** was a poor substrate and afforded the desired product **3z** in only 20% yield.

To confirm whether the observed catalysis was due to the heterogeneous catalyst  $MCM-41-2P-Pd(OAc)_2$  or a soluble Pd species leached from  $MCM-41-2P-Pd(OAc)_2$ ,

<sup>&</sup>lt;sup>b</sup>Isolated yield.



Scheme 3. Proposed catalytic cycle.

the heterogeneity of the catalyst was further confirmed by hot filtration experiment.<sup>[14]</sup> For this, we carried out the carbonylative Sonogashira coupling of iodobenzene **1a** with cyclohexylacetylene **2l**, and removed the palladium catalyst from the reaction mixture by filtration at  $60 \,^{\circ}$ C at approximately 40% conversion of **1a**. The catalyst-free filtrate was then allowed to react further at  $60 \,^{\circ}$ C for 12 h with the addition of HCOOH (1.0 equiv.) and DCC (1.0 equiv.). It was found that no increase in conversion of **1a** was observed in the filtrate, which rules out the contribution to the observed reaction from a leached Pd species in the solution, indicating the heterogeneous nature of this transformation.

A possible mechanism for this heterogeneous palladium-catalyzed carbonylative Sonogashira coupling reaction is outlined in Scheme 3. Firstly, the MCM-41-2P-Pd(OAc)<sub>2</sub> complex is reduced by CO, generated *in situ* from formic acid and DCC to the MCM-41-2P-Pd(0) complex.<sup>[15]</sup> Oxidative addition of Ar-I (1) to the MCM-41- 2 P-Pd(0) complex generates an MCM-41-anchored arylpalladium(II) complex (**A**), which is followed by migratory insertion of carbon monoxide yielding an MCM-41-anchored acylpalladium(II) complex (**B**). Subsequent reaction between intermediate **B** and terminal alkyne (2) with the aid of Et<sub>3</sub>N gives intermediate **C**. Finally, reductive elimination of intermediate **C** affords the desired alkynyl ketone (**3**) and regenerates the MCM-41-2P-Pd(0) complex to complete the catalytic cycle.

	I	-MCM-41 (3 ا	2P-Pd(OAc) <sub>2</sub> nol%)	0	
	+ — P 1a 2a	h Et <sub>3</sub> N, HCC DCC (2 ec 30 °	D <sub>2</sub> H (2 equiv.) quiv.), toluene C, 24 h	Ph 3a	
Entry	MCM-41-2P-Pd(OAc) <sub>2</sub>	Yield <sup>b</sup> (%)	Entry	MCM-41-2P-Pd(OAc) <sub>2</sub>	Yield <sup>b</sup> (%)
1	Fresh	95	5	Recycle 4	92
2	Recycle 1	94	6	Recycle 5	93
3	Recycle 2	94	7	Recycle 6	92
4	Recycle 3	93	8	Recycle 7	91

Table 4.	Recycle of the	e MCM-41-2P-Pd(OAc) <sub>2</sub>	catalyst. <sup>a</sup>
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<sup>a</sup>Reaction conditions: **1a** (1.0 mmol), **2a** (2.0 mmol), MCM-41-2P-Pd(OAc)<sub>2</sub> (3 mol%), Et<sub>3</sub>N (2.0 mmol), HCOOH (2.0 mmol), DCC (2.0 mmol), toluene (4 mL), 30 °C, 24 h.

<sup>b</sup>lsolated yield.

For a heterogeneous precious metal catalyst, it is important to investigate its ease of separation from the product and reusability. We next examined the recyclability of the MCM-41-2P-Pd(OAc)<sub>2</sub> catalyst in the carbonylative Sonogashira coupling reaction of iodobenzene **1a** with phenylacetylene **2a**. After the reaction was completed, the reaction mixture was diluted with ethyl acetate and filtered. The catalyst was washed with DMF, distilled water and ethanol, and dried at 80 °C in vacuo for 1 h. The recovered catalyst can be used directly in the next cycle with the same substrates under the identical conditions. As shown in Table 4, this heterogeneous palladium catalyst could be recycled up to eight times with almost consistent catalytic activity. The excellent reusability of the MCM-41-2P-Pd(OAc)<sub>2</sub> catalyst may arise from the stronger chelation action between the bidentate phosphine ligand and palladium, which prevents palladium leaching effectively.

#### Conclusions

In summary, we have developed a convenient, economic and practical method for the construction of alkynyl ketones under carbon monoxide gas-free conditions. Through the heterogeneous palladium-catalyzed carbonylative Sonogashira coupling reactions of aryl iodides with terminal alkynes, with formic acid as the CO source, a wide range of alkynyl ketones could be produced in moderate to high yields. Importantly, this hetero-geneous palladium catalyst can be easily recovered via a simple filtration process and recycled at least eight times without apparent loss of activity. Our system not only avoids the usage of gaseous CO, but also solves the basic problems of palladium catalyst recovery and reuse. Thus, the present method represents the first example of both using formic acid as a liquid CO source and an MCM-41-supported palladium complex as a recyclable catalyst for the carbonylative Sonogashira coupling reaction.

#### **Experimental**

All reagents were purchased from different commercial sources and used as received without further purification. All solvents were dried and purified by distillation prior

to use. All reactions were performed under an atmosphere of argon. The products were purified by flash column chromatography on silica gel. A mixture of light petroleum ether and ethyl acetate (v/v = 19:1) was generally employed as eluent. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker Avance 400 NMR spectrometer (400 MHz or 100 MHz, respectively) in CDCl<sub>3</sub> as solvent with TMS as internal reference. Melting points were determined on a Beijing Tech Instrument Co., LTD X-6 melting point apparatus and are uncorrected. HRMS spectra were recorded on a Q-Tof spectrometer with micromass MS software using electrospray ionization (ESI). The MCM-41-2P-Pd(OAc)<sub>2</sub> complex was prepared according to our previously reported procedure,<sup>[13]</sup> the content of palladium was measured to be 0.36 mmol/g based on ICP-AES analysis.

## General procedure for the heterogeneous palladium-catalyzed carbonylative synthesis of alkynyl ketones

MCM-41-2P-Pd(OAc)<sub>2</sub> (3 mol%) was transferred into an oven-dried reaction tube under Ar. Then aryl iodide (1.0 mmol), alkyne (2.0 mmol), formic acid (2.0 mmol), and toluene (4 mL) were added to the reaction tube. After DCC (2.0 mmol) and Et<sub>3</sub>N (2.0 mmol) were added, the tube was sealed, and the reaction mixture was stirred at 30 °C for 24 h. After completion of the reaction, the reaction mixture was diluted with ethyl acetate (10 mL) and filtered. The catalyst was washed with DMF ( $2 \times 5$  mL), distilled water ( $2 \times 5$  mL), ethanol ( $2 \times 5$  mL), and dried at 80 °C in vacuo for 1 h and reused in the next run. The filtrate was concentrated under vacuum and the residue was purified by chromatography on silica gel (eluent: light petroleum ether/ethyl acetate = 19:1) to afford the alkynyl ketone product **3**.

Full experimental detail, characterization data of all compounds. This material can be found via the "Supplementary Content" section of this article's webpage.

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