

Carbonylative Suzuki Coupling of Aryl Iodides using Pd@KAPs(Ph-PPh₃) as a Recyclable Catalyst

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Abstract

An efficient route for the catalytic synthesis of diphenylketone via carbonylative Suzuki coupling of aryl iodides is described using palladium supported on triphenylphosphine functionalized porous organic polymer (Pd@KAPs(Ph-PPh₃)) as the catalyst. Under 5 bar of carbon monoxide pressure, the catalyst exhibited remarkable activity, and only 1 mol% palladium loading was required to achieve moderate yield of diphenylketone. The catalyst can be easily separated by a simple filtration process and recycled up to three times with only minor loss of activity. The salient features of this protocol are the simplicity in handling of the catalyst, low CO pressure, high catalytic activity, negligible palladium leaching and effective catalyst recyclability.

Keywords

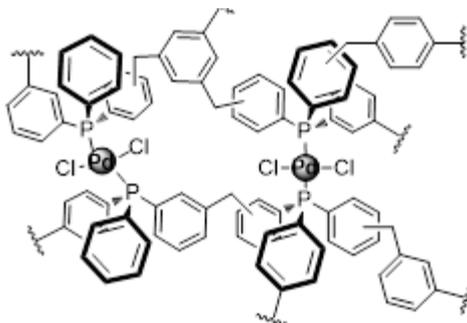
Carbonylation, heterogeneous, palladium, Suzuki.

1. Introduction

Biaryl ketones are important building blocks in numerous natural products, pharmaceuticals, photosensitizers, and advanced organic materials [1–6]. Among many well-documented synthetic strategies [7,8], the palladium-catalyzed carbonylative Suzuki coupling of aryl-X compounds, carbon monoxide, and arylboronic acids is a powerful and convenient tool for the synthesis of biaryl ketones [9,10], due to that boronic acids are generally nontoxic and air- and moisture-stable [11]. Therefore, many efforts have been devoted to the advancement of this transformation over the past few decades [12–16]. Much of the recent research has focused on the development of highly active homogeneous Pd catalysts [17,18]. These homogeneous catalytic systems generally exhibit excellent activity and selectivity, but they suffer from the practical problems such as catalyst separation and recycling.

The combination of the advantageous properties of molecular and solid catalysts was considered as the “Holy Grail” in catalysis research. Great potential was provided by porous polymers [19]. Porous organic polymers (POPs), emerged as a new class of functional materials just in a few years ago. Due to their extraordinarily high surface area, well-defined pore structure, low skeletal density, and the ability to introduce chemical functionalities within their porous framework, porous organic polymers have recently used as versatile materials for the development of catalysts [19–22]. Triphenylphosphine (PPh₃) is one of the most valuable phosphine ligands in homogeneous catalysis. Therefore, the introduction of triphenylphosphine ligand into the porous organic frameworks would be an efficient way to construct highly active catalytic supports and has thus attracted considerable attention [23–25]. Recently, Lei et al. reported palladium supported on triphenylphosphine functionalized porous organic polymer (Pd@KAPs(Ph-PPh₃)) having low levels of palladium loading as a highly active and recyclable catalyst for the alkoxy carbonylation of aryl iodides. Under atmospheric pressure of carbon

monoxide, the catalyst showed high catalytic activity and quantitative yields of the corresponding esters were achieved [26].



Scheme 1 The structure of Pd@KAPs(Ph-PPh₃) catalyst

To continue our interest on heterogeneous transformation of organic halides [27] and extend the application of the active Pd@KAPs(Ph-PPh₃) catalyst, in this paper, we investigate the synthesis of biaryl ketone via carbonylative Suzuki coupling of aryl iodides using Pd@KAPs(Ph-PPh₃) as a heterogeneous catalyst (Scheme 1).

2. Experimental

2.1 Reagents

Benzene, triphenylphosphine, PdCl₂, FeCl₃ (anhydrous) and 1,2-dichloroethane, acetonitrile were obtained from National Medicines Corporation Ltd. of China, all of which were of analytical grade and were used as received. Aryl iodides, aromatic boric acids and bases were of analytical reagent grade and commercially available. Formaldehyde dimethyl acetal (Alfa Aesar, 98 %) was also used as received. All solvents were analytical grade and distilled prior to use. Pd/Al₂O₃ (5 wt.%), Pd/SiO₂ (5 wt.%) and Pd/C (5 wt.%) were purchased from Shaanxi Rock New Materials Co. Ltd (China). All solvents were analytical grade and distilled prior to use.

2.2 Preparation of the catalysts

Pd@KAPs(Ph-PPh₃) [26] were prepared as we have reported recently, and the Pd content were 0.8 wt.%.

2.3 Preparation of the catalysts

The catalytic reactions were carried out in a Teflon-lined stainless steel autoclave (50 mL) that was lined with a magnetic stirrer bar and an automatic temperature controller. In a typical experiment, a catalyst containing 1 mol% Pd, aryl iodide (1.0 mmol), phenylboronic acid (2.0 mmol), K₂CO₃ (3.0 mmol) were added to anisole (3 mL) and allowed to react under CO atmosphere (5 bar) at 80 °C for 10 h. After the reaction, the reactor was cooled to room temperature. The reaction mixture was centrifuged at 5000 rpm for 10 min and the clear supernatant which was added ethyl phenylacetate as an internal standard was analyzed with GC.

3. Results and discussion

3.1 Catalytic activity

To evaluate the catalytic activity of the Pd@KAPs(Ph-PPh₃) catalyst for carbonylative Suzuki coupling reaction, the carbonylative Suzuki coupling of iodobenzene with phenylboronic acid was selected as a model reaction. Initially, the activities of several catalysts were examined on the model reaction, and the obtained results are summarized in Table 1. Under CO atmosphere (5 bar), 1.0 mol% Pd@KAPs(Ph-PPh₃) gave 75% yield of the desired diphenylketone in the presence of K₂CO₃ as the base (Table 1, entry 1). Ligand free Pd catalysts, such as PdCl₂, Pd/C, Pd/Al₂O₃, and Pd/SiO₂ were

also tested under the same reaction conditions, but the yields of the desired diphenylketone reached only to 13%, 18%, 5%, and 9%, respectively (Table 1, entries 2-5). Further to prolong the reaction time to 10 h, an 89% yield of diphenylketone was obtained with Pd@KAPs(Ph-PPh₃) as a catalyst (Table 1, entry 6).

Table 1 Effect of catalyst

Numble	Catalyst	Conversion (%)	Yield a(%)
1	Pd@KAPs(Ph-PPh ₃)	82	75
2	PdCl ₂	17	13
3	Pd/C	24	18
4	Pd/Al ₂ O ₃	9	5
5	Pd/SiO ₂	13	9
6 ^b	Pd@KAPs(Ph-PPh ₃)	99	89

Reaction conditions: Pd (1.0 mol%), PhI (1 mmol), phenylboronic acid (2.0 mmol), CO (5 bar), K₂CO₃ (3.0 mmol), anisole (3 mL).

^a GC Yield. ^b 10 h.

3.2 Hot filtration test

When a supported metal catalyst was used in a liquid phase reaction, two points need to be clarified. The first one is the metal leaching that sometimes is partially responsible for the observed good catalytic activity in a reaction in liquid phase. In order to determine whether the catalysis recycle was derived from the Pd@KAPs(Ph-PPh₃) or from leaching palladium released from the solid catalyst during the reaction, we performed a hot filtration test. A Pd@KAPs(Ph-PPh₃)-catalyzed carbonylative Suzuki coupling reaction of iodobenzene with phenylboronic acid was stopped after 4 hour, when the yield reached to 63%. Rapid separation of the Pd@KAPs(Ph-PPh₃) catalyst by centrifugation and allowed the hot liquid mixture to react further 4 h under the same conditions. However, the yield (63%) was mostly invariable. We also tested Pd content in the filtrate by means of AAS, the result showed that palladium leaching is very low, to be ca. 1.2 ppm. These results suggested that all the palladium species were strongly absorbed on to the support and no significant quantity of metal was lost to the reaction liquid during the process.

3.3 Catalyst recycling

The second one is the recyclability of the catalyst. To this end, at the end of the model reaction, Pd@KAPs(Ph-PPh₃) was separated by simple centrifugation and extracted with copious anisole and then subjected to the next run. As shown in Figure 1, the catalyst exhibited good reusability and could be reused for three times. Only a slight decrease of its activity was observed, which can be attributed partially to a physical loss of the catalyst during the operation.

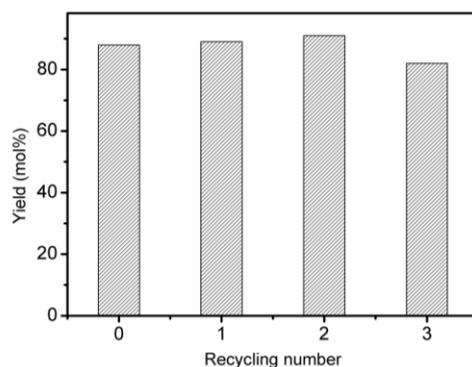


Figure 1 Recycling test of Pd@KAPs(Ph-PPh₃)

Reaction conditions: Pd@KAPs(Ph-PPh₃) (1.0 mol%), PhI (1 mmol), phenylboronic acid (2.0 mmol), CO (5 bar), K₂CO₃ (3.0 mmol), anisole (3 mL), 10 h.

4. Conclusion

In conclusion, an efficient protocol for the carbonylative Suzuki coupling reaction of aryl iodides for synthesis of diphenylketone using Pd@KAPs(Ph-PPh₃) as a highly active and reusable catalyst has been developed. Under low CO pressure, a palladium catalyst loading as low as 1.0 mol% was sufficient for moderate yield of diphenylketone. The catalyst can be recycled three times with a slight decrease in activity. The easy availability and simple separation make such supported palladium catalyst an interesting alternative to the homogeneous catalysts in carbonylation reactions.

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