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A simple, efficient and recyclable phosphine-free catalytic system for Suzuki–Miyaura reaction of aryl bromides

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ABSTRACT

The Suzuki–Miyaura reaction of aryl bromides using 3-(2-aminoethylamino)propyl-functionalized MCM-41-immobilized palladium(II) complex [MCM-41-2N-Pd(II)] as an efficient heterogeneous catalyst is described. Developed catalytic system is found to be effective for the Suzuki–Miyaura reaction of aryl bromides with arylboronic acids providing good to excellent yield of the desired products. This heterogeneous palladium catalyst can be reused at least 10 times without any decrease in activity. Our system not only avoids the use of phosphine ligands, but also solves the basic problem of palladium catalyst recovery and reuse.

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1. Introduction

The importance of biaryl units as molecular components in pharmaceuticals, herbicides and natural products, as well as in engineering materials such as conducting polymers, molecular wires and liquid crystals, has attracted enormous interest [1,2]. The Suzuki reaction is proving to be increasingly popular method for the construction of unsymmetrical biaryl compounds as it represents an attractive alternative over other methods using organometallics because organoboranes are air- and moisture-stable with relatively low toxicity [3,4]. However, catalysts used in the Suzuki reaction have been traditionally based on homogeneous palladium complexes such as $Pd(PPh_3)_4$, $Pd(PPh_3)_2Cl_2$, which are rarely recoverable without elaborate and wasteful procedures that are commercially unacceptable [5]. In contrast, heterogeneous catalysts can be easily separated from the reaction mixture by simple filtration and reused in successive reactions provided that the active sites have not become deactivated. Heterogeneous catalysis also helps to minimize wastes derived from reaction workup, contributing to the development of green chemical processes [6–9]. From the standpoint of environmentally benign organic synthesis, development of immobilized palladium catalysts is challenging and important [10-12]. In an ideal system, they can be recovered from the reaction mixture by simple filtration and re-used infinitely, and

contamination of products by palladium is prevented. Despite the general use of the Suzuki reaction in organic synthesis, polymersupported palladium catalysts have not been widely used for this reaction yet [13–19]. Study of new types of polymer-supported palladium catalysts which might be suitable for the Suzuki reaction has theoretical and practical significance. In the past, some of these studies have been related to polymer-supported phosphine palladium catalysts [13–16]. It is known that the catalysts containing phosphine ligands at higher temperatures are unstable [20–22]. Furthermore, the procedure for preparing the polymer-supported phosphine palladium complexes is rather complicated since the synthesis of the phosphine ligands requires multi-step sequences. Therefore, the development of phosphine-free heterogeneous palladium catalysts having a high activity and good stability is a topic of enormous importance.

Our approach was guided by three imperatives: the polymeric ligand should be easily accessible (1), starting from readily available and cheap reagents (2). The polymeric palladium catalyst should be air stable at room temperature, which should allow its storage in normal bottles with unlimited shelf life (3). Developments on the mesoporous material MCM-41 provided a new possible candidate for a solid support for immobilization of homogeneous catalysts [23]. MCM-41 has a regular pore diameter of ca. 5 nm and a specific surface area >700 m² g⁻¹ [24]. Its large pore size allows passage of large molecules such as organic reactants and metal complexes through the pores to reach to the surface of the channel [25–27]. It is generally believed that high surface area of heterogeneous catalyst results in high catalytic activity. Very recently, Yang

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Scheme 1. Preparation of the MCM-41-2N-Pd(II).

et al. have reported that palladium-guanidine complex immobilized on mesoporous materials [28,29] and N-heterocyclic carbene palladium complex supported on ionic liquid-modified SBA-16 [30] are highly active and recyclable catalysts for the Suzuki coupling. Considering the fact that the MCM-41 support has an extremely high surface area and the catalytic palladium species is anchored on the inner surface of the mesopore of MCM-41 support, we expect that MCM-41-supported palladium catalyst will exhibit high activity and good reusability. To date, a few palladium complexes on functionalized MCM-41 support have been prepared and used in organic reactions [31-34]. In continuing our efforts to develop greener synthetic pathways for organic transformations, our new approach, described in this paper, was to design and synthesize a new 3-(2-aminoethylamino)propyl-functionalized MCM-41-immobilized palladium(II) complex, which was used as an effective palladium catalyst for the Suzuki-Miyaura reaction of aryl bromides with arylboronic acids.

2. Experimental

All chemicals were reagent grade and used as purchased. The mesoporous material MCM-41 was prepared according to a literature procedure [35]. All reactions were performed under an inert atmosphere of dry argon using distilled dried solvents. All coupling products were characterized by comparison of their spectra and physical data with authentic samples. IR spectra were determined on a Perkin-Elmer 683 instrument. ¹H NMR spectra were recorded on a Bruker AC-P400 (400 MHz) spectrometer with TMS as an internal standard in CDCl₃ as solvent. ¹³C NMR spectra were recorded on a Bruker AC-P400 (100 MHz) spectrometer in CDCl₃ as solvent. Palladium content was determined with inductively coupled plasma atom emission Atomscan16 (ICP-AES, TJA Corporation). X-ray powder diffraction patterns were obtained on Damx-rA (Rigaka). X-ray photoelectron spectra were recorded on XSAM 800 (Kratos).

2.1. Preparation of MCM-41-2N

A solution of 1.54 g of 3-(2-aminoethylamino)propyltrimethoxysilane in 18 ml of dry chloroform was added to a suspension of 2.2 g of the MCM-41 in 180 ml of dry toluene. The mixture was stirred for 24 h at 100 °C. Then the solid was filtered and washed by CHCl₃ (2× 20 ml), and dried in vacuum at 160 °C for 5 h. The dried white solid was then soaked in a solution of 3.1 g of Me₃SiCl in 100 ml of dry toluene at room temperature under stirring for 24 h. Then the solid was filtered, washed with acetone (3× 20 ml) and diethyl ether (3× 20 ml), and dried in vacuum at 120 °C for 5 h to obtain 3.49 g of hybrid material MCM-41-2N. The nitrogen content was found to be 1.84 mmol/g by elemental analysis.

2.2. Preparation of MCM-41-2N-Pd(II)

In a small Schlenk tube, 2.03 g of the above-functionalized MCM-41 (MCM-41-2N) was mixed with 0.137 g (0.61 mmol) of Pd(OAc)₂ in 50 ml of dry acetone. The mixture was refluxed for 72 h under an argon atmosphere. The solid product was filtered by suction, washed with acetone, distilled water and acetone successively and dried at 70 °C/26.7 Pa under Ar for 5 h to give 2.12 g of a yellow palladium complex [MCM-41-2N-Pd(II)]. The nitrogen and palladium content was found to be 1.68 mmol/g and 0.27 mmol/g, respectively.

2.3. General procedure for Suzuki reaction of aryl bromides with arylboronic acids

A mixture of aryl bromide (1.0 mmol), arylboronic acid (1.5 mmol), potassium carbonate (2.0 mmol), xylene (3 ml) and the MCM-41-2N-Pd(II) complex (7 mg, 0.002 mmol of Pd) was stirred under Ar in an oil bath at 90 °C for 2–10 h. The mixture was cooled and filtered. The MCM-41-2N-Pd(II) complex was washed with distilled water (2×10 ml), dioxane (2×10 ml) and Et₂O (2×10 ml) and reused in the next run. The filtrate was poured into a saturated aqueous NaCl solution (50 ml) and extracted with methylene chloride (2×50 ml). The extracts were washed with water (3×30 ml) and dried over MgSO₄. After removal of the solvent, the residue was purified by column chromatography on silica gel.

3. Results and discussion

Although the phosphine ligands stabilize palladium and influence its reactivity, the simplest and cheapest palladium catalysts are of course the phosphine-free systems, specifically when used in low loading. A novel 3-(2-aminoethylamino)propyl-functionalized MCM-41-immobilized palladium(II) complex [MCM-41-2N-Pd(II)] was very conveniently synthesized from commercially available and cheap 3-(2-aminoethylamino)propyltrimethoxysilane via immobilization on MCM-41, followed by reacting with palladium acetate (Scheme 1). X-ray powder diffraction (XRD) patterns of the parent MCM-41 and the modified material MCM-41-2N-Pd(II) are displayed in Fig. 1. Small angle X-ray powder diffraction of the parent MCM-41 gave the peaks corresponding to hexagonally ordered mesoporous phases. For MCM-41-2N-Pd(II), the (100) reflection of the parent MCM-41 with decreased intensity was remained after functionalization, while the (110) and (200) reflections became weak and diffuse, which could be due to contrast matching between the silicate framework and organic moieties which are located inside the channels of MCM-41. These results indicated that the basic structure of the parent MCM-41 was not damaged in the whole process of catalyst preparation.



Fig. 1. XRD patterns of the parent MCM-41 (1) and MCM-41-2N-Pd(II) (2).

Elemental analyses and X-ray photoelectron spectroscopy (XPS) were used to characterize the 3-(2-aminoethylamino)propyl-functionalized MCM-41-immobilized palladium(II) complex. The N:Pd mole ratio of the MCM-41-2N-Pd(II) was determined to be 6.22. The XPS data for MCM-41-2N-Pd(II), MCM-41-2N, Pd(OAc)₂ and metal Pd are listed in Table 1. It can be seen that the binding energies of Si_{2p} and O_{1s} of MCM-41-2N-Pd(II) are similar to those of MCM-41-2N. However the difference of N_{1s} binding energies between MCM-41-2N-Pd(II) and MCM-41-2N is 1.2 eV. The binding energy of Pd_{3d5/2} in MCM-41-2N-Pd(II) is 0.7 eV less than that in Pd(OAc)₂, but 2.1 eV larger than that in metal Pd. These results show that a coordination bond between N and Pd is formed in MCM-41-2N-Pd(II).

The Suzuki-Miyaura cross-coupling reaction of phenylboronic acid (1.5 equiv.) with 4-bromoanisole was chosen as a model reaction, and the influences of various reaction parameters such as base, solvent, and palladium catalyst quantity on the reaction were tested. The results are summarized in Table 2. For the bases evaluated [K₃PO₄, Na₂CO₃, and K₂CO₃], K₂CO₃ was found to be the most effective. Other bases such as Na₂CO₃ and K₃PO₄ were substantially less effective. We then turned our attention to investigate the effect of solvents on the Suzuki-Miyaura cross-coupling reaction. Among the solvents used [DMF, dioxane, and xylene], xylene was the best choice. Increasing the amount of palladium catalyst could shorten the reaction time, but did not increase the yield of 4-methoxybiphenyl (entry 12). The low palladium concentration usually led to a long period of reaction, which was consistent with our experimental results (entries 10 and 11). Taken together, excellent result was obtained when the coupling reaction was carried out with 0.2 mol% of the catalyst using K₂CO₃ as base in xylene at 90 °C (entry 7).

To examine the scope for this heterogeneous Suzuki–Miyaura cross-coupling reaction, we have investigated the reactions using a variety of arylboronic acids and a wide range of aryl bromides as the substrates under the optimized reaction conditions

Table 1

XPS data for MCM-41	-2N-Pd(II), MCM-41-2N,	Pd(OAc) ₂ and metal Pd. ^a

Sample	Pd _{3d5/2}	N _{1s}	Si _{2p}	0 _{1s}
MCM-41-2N-Pd(II) MCM-41-2N	337.5	400.8 399.6	103.3 103.2	533.1 533.2
Pd(OAc) ₂ Metal Pd	338.2 335.4			

 a The binding energies are referenced to C1s (284.6 eV) and the energy differences were determined with an accuracy of ± 0.2 eV.

Table 2

Coupling reaction of 4-bromoanisole with phenylboronic acid in the presence of several bases and solvents.^a

Entry	Base	Solvent	MCM-41-2N- Pd(II) (mol%)	Time (h)	Yield ^b (%)
1	K ₃ PO ₄	Xylene	0.2	10	79
2	K ₃ PO ₄	DMF	0.2	10	75
3	K_3PO_4	Dioxane	0.2	10	76
4	Na ₂ CO ₃	Xylene	0.2	8	92
5	Na ₂ CO ₃	DMF	0.2	9	84
6	Na ₂ CO ₃	Dioxane	0.2	8	88
7	K_2CO_3	Xylene	0.2	6	95
8	K ₂ CO ₃	DMF	0.2	8	86
9	K ₂ CO ₃	Dioxane	0.2	7	91
10	K ₂ CO ₃	Xylene	0.1	14	94
11	K ₂ CO ₃	Xylene	0.05	24	91
12	K ₂ CO ₃	Xylene	0.5	3	95

^a All reactions were performed using 1.0 mmol of 4-bromoanisole, 1.5 mmol of phenylboronic acid, 2.0 mmol of base in 3.0 ml of solvent at 90 °C under Ar. ^b Isolated yield based on the 4-bromoanisole used.

$$Ar-Br + Ar^{1}-B(OH)_{2} \xrightarrow{0.2 \text{ mol}\%MCM-41-2N-Pd(II)}{K_{2}CO_{3}, \text{ xylene, 90-110 °C}} Ar-Ar^{1}$$

Scheme 2. Suzuki reaction of aryl bromides with arylboronic acids catalyzed by MCM-41-2N-Pd(II).

(Scheme 2) and the results are outlined in Table 3. As shown in Table 3, the Suzuki–Miyaura coupling reactions of a variety of substituted bromobenzene with phenylboronic acid proceeded very smoothly at 90 °C to afford the corresponding coupled products in excellent isolated yields (entries 1–4). The reactions of sterically hindered 2-methylbromobenzene and bulky 1-bromonaphthalene with phenylboronic acid also provided good yields of the desired biaryls **3e** and **3f** under the optimized reaction conditions, respec-

Table 3

Heterogeneous Suzuki-Miyaura reaction of aryl bromides with arylboronic acids catalyzed by MCM-41-2N-Pd(II).^a

Entry	Ar	Ar ¹	Temp. (°C)	Time (h)	Product	Yield (%) ^b
1	Ph	Ph	90	4	3a	93
2	4-CH ₃ OC ₆ H ₄	Ph	90	6	3b	95
3	4-02NC6H4	Ph	90	2	3c	92
4	4-PhC ₆ H ₄	Ph	90	4	3d	93
5	$2-CH_3C_6H_4$	Ph	100	8	3e	85
6	1-Naphthyl	Ph	90	5	3f	83
7	2-Thienyl	Ph	90	3	3g	86
8	2-Pyridyl	Ph	90	3	3h	89
9	$4-CH_3OC_6H_4$	4-ClC ₆ H ₄	90	6	3i	94
10	$4-CH_3COC_6H_4$	4-ClC ₆ H ₄	90	3	3j	97
11	$2-CH_3C_6H_4$	4-ClC ₆ H ₄	100	8	3k	83
12	$3 - O_2 NC_6 H_4$	$4-ClC_6H_4$	90	3	31	93
13	4-PhC ₆ H ₄	4-ClC ₆ H ₄	90	3	3m	96
14	1-Naphthyl	4-ClC ₆ H ₄	90	5	3n	86
15	2-Thienyl	4-ClC ₆ H ₄	90	3	30	84
16	4-ClC ₆ H ₄	$4-CH_3C_6H_4$	90	3	3р	93
17	$4-CH_3OC_6H_4$	$4-CH_3C_6H_4$	90	6	3q	91
18	4-CHOC ₆ H ₄	$4-CH_3C_6H_4$	90	3	3r	95
19	$4-CH_3OCOC_6H_4$	$4-CH_3C_6H_4$	90	3	3s	92
20	2-Pyridyl	$4-CH_3C_6H_4$	90	4	3t	85
21	3-CNC ₆ H ₄	$4-CH_3C_6H_4$	90	3	3u	94
22	$2-CH_3C_6H_4$	$4-CH_3C_6H_4$	100	7	3v	84
23	1-Naphthyl	$4-CH_3C_6H_4$	90	5	3w	85
24	$3-CH_3C_6H_4$	$2-CH_3C_6H_4$	110	10	3x	68
25	$4-CH_3C_6H_4$	$2-CF_3C_6H_4$	110	10	Зу	71
26	3-CNC ₆ H ₄	$2-CH_3C_6H_4$	110	10	3z	75

^a Reactions were carried out with 1 mmol of aryl bromide, 1.5 mmol of arylboronic acid, 0.002 mmol of palladium catalyst, 2 mmol of K₂CO₃ in 3.0 ml of xylene. ^b Yield of isolated product **3** based on the aryl bromide.

Table 4

Suzuki cross-coupling reaction of 4-bromoanisole with phenylboronic acid catalyzed by recycled catalyst.

MeO-	+ PhB(OH) ₂	(1st-10th use)	MeO-Ph		
		K_2CO_3 , xylene, 90 °C, 6 h			
10 mmol	15 mmol		3b .		
Entry	Cata	lyst cycle	Time (h)	Isolated yield (%)	TON
1	1st		6	95	475
2	2nd		6	94	470
3	3rd		6	95	475
4	4th		6	94	470
5	5th		6	94	470
6	6th		6	93	465
7	7th		6	94	470
8	8th		6	94	470
9	9th		6	93	465
10	10th		6	93	465
11	1st t	o 10th consecutive		Av. 94	Total of 4700

tively (entries 5 and 6). The Suzuki–Miyaura cross-coupling reactions of heteroaryl bromides such as 2-bromothiophene and 2-bromopyridine with phenylboronic acid gave the corresponding coupled products **3g** and **3h** in 86% and 89% yields, respectively (entries 7 and 8).

The optimized reaction conditions were also applied to the Suzuki-Miyaura cross-coupling of substituted phenylboronic acids such as 4-methylphenylboronic acid and 4-chlorophenylboronic acid with a variety of aryl bromides, the results are also summarized in Table 3. Various electron-donating and electron-withdrawing groups such as -CH₃, -OCH₃, -Ph, -Cl, -CN, -NO₂, -CF₃, -COCH₃, -CHO, and -CO₂CH₃ on both aryl bromides and arylboronic acids were well tolerated to give the desired unsymmetrical biaryls in good to excellent yields (entries 9-23). A favorable effect of electron-withdrawing substituents is normally observed in palladium-catalyzed reactions [36]. With our catalyst however, electron-withdrawing groups in aryl bromides have relatively little effect on the Suzuki coupling reaction. Substituted chlorobenzenes are inert under the same conditions giving traces of cross-coupling products. To further illustrate that chloroarenes are inert in the reaction system, 4-chloro-4'-methylbiphenyl was selectively produced in the coupling reaction of (4-methylphenyl)boronic acid with 1-bromo-4-chlorobenzene (Table 3, entry 16). The Suzuki-Miyaura cross-coupling reactions of sterically hindered arylboronic acids with aryl bromides could also proceed smoothly at 110°C, affording the desired coupled products 3x-3z in good yields after 10 h (entries 24-26). The present method provides a quite general route for the synthesis of unsymmetrical biaryls having various functionalities.

In order to determine whether the catalysis was due to the MCM-41-2N-Pd(II) complex or to a homogeneous palladium complex that comes off the support during the reaction and then returns to the support at the end, we performed the hot filtration test [37]. We focused on the coupling reaction of bromobenzene with phenylboronic acid (1.5 equiv.). We filtered off the MCM-41-2N-Pd(II) complex after 30 min of reaction time and allowed the filtrate to react further. The catalyst filtration was performed at the reaction temperature (90 °C) in order to avoid possible re-coordination or precipitation of soluble palladium upon cooling. We found that, after this hot filtration, no further reaction was observed and no palladium could be detected in the hot filtered solution by atomic absorption spectroscopy (AAS). This result suggests that the palladium catalyst remains on the support at elevated temperatures during the reaction.

This heterogeneous palladium catalyst can be easily recovered by simple filtration. We also investigated the possibility to reuse the catalyst by using the Suzuki cross-coupling reaction of 4-

bromoanisole with phenylboronic acid. In general, the continuous recycle of resin-supported palladium catalysts is difficult owing to leaching of the palladium species from the polymer supports, which often reduces their activity within a five-recycle run. However, when the reaction of 4-bromoanisole with phenylboronic acid was performed even with 0.2 mol% of MCM-41-2N-Pd(II), the catalyst could be recycled 10 times without any loss of activity. The reaction promoted by the 10th recycled catalyst gave 3b in 93% vield (Table 4, entry 10). The average vield of 3b in consecutive reactions promoted by the 1st through the 10th recycled catalyst was 94% (entry 11). The palladium content of the reused catalyst was determined by ICP to be 0.26 mmol/g after ten consecutive runs, only 3.7% of palladium had been lost from the MCM-41 support. The high stability and excellent reusability of the catalyst should result from the chelating action of bidentate 2-aminoethylamino ligand on palladium and the mesoporous structure of the MCM-41 support. The result is important from a practical point of view. The high catalytic activity, excellent reusability and the easy accessibility of the MCM-41-2N-Pd(II) make them a highly attractive heterogeneous palladium catalyst for the parallel solution phase synthesis of diverse libraries of compounds.

4. Conclusion

We have developed a novel, phosphine-free, practical and economic catalyst system for the Suzuki–Miyaura cross-coupling reaction of aryl bromides with arylboronic acids by using 3-(2aminoethylamino)propyl-functionalized MCM-41-immobilized palladium(II) complex [MCM-41-2N-Pd(II)] as catalyst. This novel heterogeneous palladium catalyst can be conveniently prepared by a simple two-step procedure from commercially available and cheap reagents and can be reused at least 10 times without any decreases in activity. The Suzuki–Miyaura cross-coupling reaction of aryl bromides with arylboronic acids catalyzed by MCM-41-2N-Pd(II) provides a better and practical procedure for the synthesis of unsymmetrical biaryls.

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