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PAPER

A phosphine-free carbonylative cross-coupling reaction of aryl iodides with arylboronic acids catalyzed by immobilization of palladium in MCM-41†

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The phosphine-free heterogeneous carbonylative cross-coupling of aryl iodides with arylboronic acids under an atmospheric pressure of carbon monoxide was achieved in anisole at 80 °C in the presence of a 3-(2-aminoethylamino)propyl-functionalized MCM-41-immobilized palladium(II) complex [MCM-41–2N–Pd(II)], yielding a variety of unsymmetrical biaryl ketones in good to high yield. This heterogeneous palladium catalyst exhibited higher activity and selectivity than $PdCl_2(PPh_3)_2$, can be recovered and recycled by a simple filtration of the reaction solution, and used for at least 10 consecutive trials 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.

Introduction

Biaryl ketones are important moieties in many biologically active molecules, natural products and pharmaceuticals, and many methods for the preparation of them have been reported.[1] One general approach for the synthesis of biaryl ketones is the Friedel–Crafts acylation of substituted aromatic rings.[2] The crucial disadvantage of traditional Friedel–Crafts acylation is the use of more than a stoichiometric amount of aluminium trichloride, which is incompatible with many functional groups and generates a large amount of waste. Furthermore, the formation of *ortho* and *para* isomers with the untunable regioselectivity results in separation problems and makes biaryl ketones with a *meta* substituent difficult to access. The transition metal-catalyzed three-component cross-coupling reaction between arylmetal reagents, carbon monoxide and aryl electrophiles has provided a straightforward and convenient route for the synthesis of unsymmetrical biaryl ketones.[3] Various arylmetal reagents including magnesium,[4] aluminium,[5] silicon,[6] tin,[7] zinc[8] and indium[9] compounds have been reported to undergo carbonylative cross-coupling reactions. However, the known protocol is limited due to the formation of side products ensuing from direct coupling of the aryl groups without carbon monoxide insertion. Among carbonylative cross-coupling reactions, the Suzuki carbonylative coupling reaction is one of the most promising methods for the direct synthesis of biaryl ketones from carbon monoxide, aryl halides and arylboronic acids since a wide variety of functionalities can be tolerated on either partner and the arylboronic acids are generally nontoxic and thermally-, air- and moisture-stable.[10] Several groups have reported a variety of palladium-based homogeneous catalytic systems such as $PdCl_2(PPh_3)_2$,[11] $Pd(PPh_3)_4$,[12] $Pd(OAc)_2$-imidazolium salts,[13] $Pd(OAc)_2$/*N*,*N*-bis(2,6-diisopropylphenyl)dihydroimidazolium chloride,[14] $Pd(tmhd)_2/Pd(OAc)_2$ (tmhd = 2,2,6,6-tetramethyl-3,5-heptanedionate)[15] and *N*-heterocyclic carbene palladium complexes[16] for this reaction. However, the problem with homogeneous catalysis is the difficulty of separating the catalyst from the reaction mixture and the impossibility of reusing it in consecutive reactions. 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. The high costs of the transition metal catalysts coupled with the toxic effects associated with many transition metals has led to an increased interest in immobilizing catalysts onto a support. Heterogeneous catalysis also helps to minimize wastes derived from reaction workup, contributing to the development of green chemical processes.[17] So far, supported palladium catalysts have successfully been used for the Heck reaction,[18] the Suzuki–Miyaura reaction,[19] the Sonogashira reaction[20] and the Stille reaction,[21] *etc.* In spite of the significant advances in this area, there are very few reports that employ heterogeneous palladium complexes as catalysts for carbonylative cross-coupling reactions.

Developments on the mesoporous material MCM-41 provided a new possible candidate for a solid support for the immobilization of homogeneous catalysts.[22] MCM-41 has a regular pore diameter of *ca.* 5 nm and a specific surface

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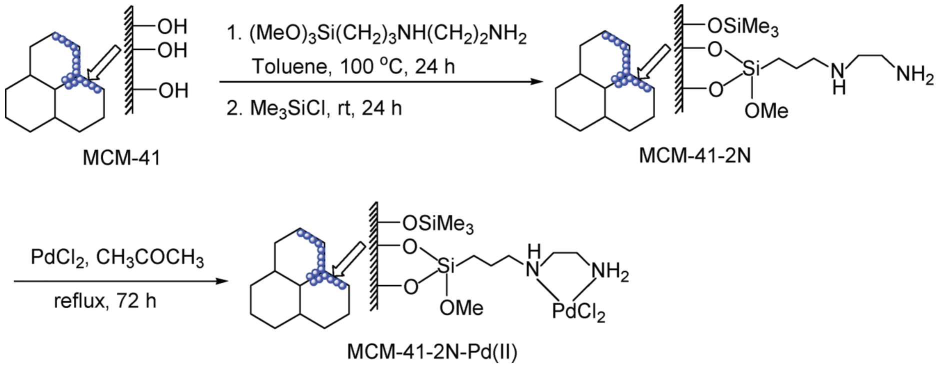


Scheme 1

area > 700 m^2 g^{-1}.[23] Its large pore size allows the passage of large molecules such as organic reactants and metal complexes through the pores to reach to the surface of the channels.[24] It is generally believed that the high surface area of heterogeneous catalysts results in their high catalytic activity. 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 the MCM-41 support, we expect that an MCM-41-supported palladium catalyst will exhibit a high activity and good reusability. To date, a few palladium complexes on functionalized MCM-41 supports have been prepared and successfully used in organic reactions.[25] In our previous work, we reported the synthesis of an MCM-41-supported bidentate phosphine palladium complex and found that this palladium complex is an efficient and recyclable catalyst for the carbonylative cross-coupling reaction of aryl halides with sodium tetraphenylborate[26] and the carbonylative Stille cross-coupling reaction.[27] However, the procedure for preparing the MCM-41-supported bidentate phosphine palladium complex was rather complicated, since the synthesis of the bidentate phosphine ligand required a multi-step sequence. Therefore, the development of phosphine-free heterogeneous palladium catalysts having a high activity and a good stability is a topic of enormous importance. 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 complex, which was used as an effective, phosphine-free palladium catalyst for the carbonylative cross-coupling reaction of aryl halides with arylboronic acids under an atmospheric pressure of carbon monoxide.

Table 1 XPS data for MCM-41–2N–Pd(II), MCM-41–2N, $PdCl_2$ and metal Pd[a]

Sample	$Pd_{3d5/2}$	N_{1s}	Si_{2p}	O_{1s}	Cl_{2p}
MCM-41–2N–Pd(II)	337.4	400.5	103.4	533.1	199.1
MCM-41–2N		399.6	103.2	533.1	
$PdCl_2$	338.1				199.2
Metal Pd	335.2				

[a] The binding energies are referenced to C_{1s} (284.6 eV) and the energy differences were determined with an accuracy of ± 0.2 eV.

Results and discussion

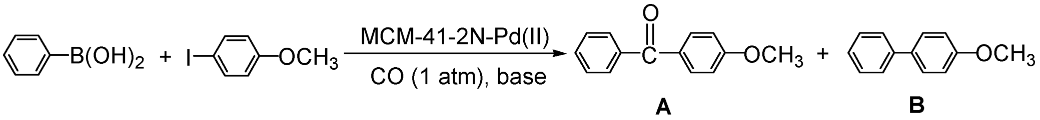
Although phosphine ligands stabilize palladium and influence its reactivity, the simplest and cheapest palladium catalysts are of course phosphine-free systems, specifically when used in low loadings. A novel 3-(2-aminoethylamino)propyl-functionalized MCM-41-immobilized palladium complex [MCM-41–2N–Pd(II)] was very conveniently synthesized from commercially available and cheap 3-(2-aminoethylamino)propyltrimethoxysilane *via* immobilization on MCM-41, followed by reacting it with palladium chloride (Scheme 1).

The X-ray powder diffraction (XRD) analysis of the MCM-41–2N–Pd(II) indicated that, in addition to an intense diffraction peak (100), two higher order peaks, (110) and (200), with lower intensities were also detected, and therefore the chemical bonding procedure did not diminish the structural ordering of the MCM-41.

Elemental analyses and X-ray photoelectron spectroscopy (XPS) were used to characterize the 3-(2-aminoethylamino)propyl-functionalized MCM-41-immobilized palladium complex. The N : Pd mole ratio of the MCM-41–2N–Pd(II) was determined to be 4.94. The XPS data for MCM-41–2N–Pd(II), MCM-41–2N, $PdCl_2$ 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, and the binding energy of Cl_{2p} of MCM-41–2N–Pd(II) is similar to that of $PdCl_2$. However, the difference of the N_{1s} binding energies between MCM-41–2N–Pd(II) and MCM-41–2N is 0.9 eV. The binding energy of $Pd_{3d5/2}$ in MCM-41–2N–Pd(II) is 0.7 eV less than that in $PdCl_2$, but 2.2 eV larger than that in metallic Pd. These results show that a coordination bond between N and Pd is formed.

The carbonylative cross-coupling reaction of phenylboronic acid (1.1 equiv.) with 4-iodoanisole under an atmospheric pressure of carbon monoxide was chosen as a model reaction, and the influences of various reaction parameters, such as reaction temperature, solvent, palladium catalyst quantity, Pd loading and base, on the reaction were tested. The results are summarized in Table 2. For the temperatures evaluated [40, 60, 80 and 100 °C], 80 °C was found to be the most effective. Other temperatures, such as 60 and 100 °C, were substantially less effective, and no carbonylative cross-coupling reaction occurred at 40 °C (Table 2, entry 1). We then turned our attention to

Table 2 The carbonylative cross-coupling of phenylboronic acid with 4-iodoanisole under different conditions[a]



Entry	Solvent	Base	Catalyst amount (mol%)	Temp./°C	Time/h	Yield (%)[b] A	Yield (%)[b] B
1	Anisole	K_2CO_3	2	40	24	0	0
2	Anisole	K_2CO_3	2	60	24	36	21
3	Anisole	K_2CO_3	2	80	8	91	4
4	Anisole	K_2CO_3	2	100	6	88	6
5	Dioxane	K_2CO_3	2	80	10	85	6
6	*o*-Xylene	K_2CO_3	2	80	13	82	8
7	Toluene	K_2CO_3	2	80	16	78	7
8	DMF	K_2CO_3	2	80	24	25	17
9	Anisole	Na_2CO_3	2	80	10	86	6
10	Anisole	Cs_2CO_3	2	80	12	62	23
11	Anisole	K_3PO_4	2	80	18	54	18
12	Anisole	K_2CO_3	4	80	5	89	4
13	Anisole	K_2CO_3	1	80	20	87	5
14	Anisole	K_2CO_3	0.5	80	40	86	6
15[c]	Anisole	K_2CO_3	2	80	8	89	5
16[d]	Anisole	K_2CO_3	2	80	7	90	4

[a] Reaction conditions: phenylboronic acid (1.1 mmol), 4-iodoanisole (1.0 mmol), CO (1 atm), base (3 mmol) and solvent (5 mL). [b] Isolated yield. [c] Catalyst with Pd loading of 0.54 mmol Pd g^{-1}. [d] Catalyst with Pd loading of 0.24 mmol Pd g^{-1}.

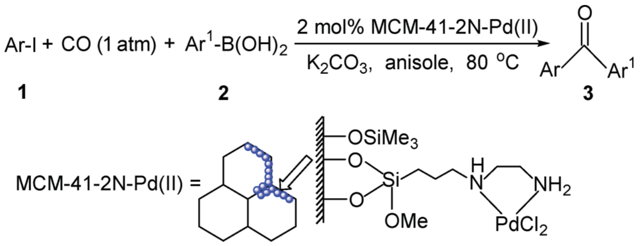
investigate the effect of solvents on the carbonylative cross-coupling reaction. When the reaction was conducted in less polar solvents, such as anisole, dioxane, *o*-xylene or toluene, good to high yields of carbonylative cross-coupling product **A** were isolated, and anisole was found to be the best choice. However, the carbonylative cross-coupling product was obtained in low yield in polar solvents such as DMF (Table 2, entry 8). Bases affected the selectivity of the reaction. Cs_2CO_3 and K_3PO_4, which have been utilized in Suzuki–Miyaura coupling reactions of organoboron compounds,[10] had a strong tendency to produce a direct coupling product, 4-methoxybiphenyl (18–23%) (Table 2, entries 10 and 11). K_2CO_3 (3 equiv.) suspended in anisole is the most efficient to yield 4-methoxybenzophenone in 91% yield, which, however, was still accompanied by 4-methoxybiphenyl (4%) (Table 2, entry 3). Increasing the amount of palladium catalyst could shorten the reaction time, but did not increase the yield of 4-methoxybenzophenone (Table 2, entry 12). The low palladium concentration usually led to a long period of reaction, which was consistent with our experimental results (Table 2, entries 13 and 14). MCM-41–2N–Pd(II) complexes with different Pd loadings were also tried as the catalyst in order to assess the Pd loading effect on activity. However, similar results were obtained (Table 2, entries 3, 15 and 16). Thus, the optimized reaction conditions for this carbonylative cross-coupling reaction are MCM-41–2N–Pd(II) (2 mol%) in anisole using K_2CO_3 as the base at 80 °C under an atmospheric pressure of carbon monoxide for 8 h (Table 2, entry 3).

Table 3 The synthesis of unsymmetrical biaryl ketones[a]

Entry	Ar	Ar[1]	Time/h	Product	Yield (%)[b]
1	$4\text{-}CH_3OC_6H_4$	Ph	8	**3a**	91
2	$4\text{-}CH_3COC_6H_4$	Ph	6	**3b**	86
3	$4\text{-}O_2NC_6H_4$	Ph	5	**3c**	82
4	$3\text{-}O_2NC_6H_4$	Ph	6	**3d**	85
5	$2\text{-}CH_3OC_6H_4$	Ph	15	**3e**	74
6	$4\text{-}H_2NC_6H_4$	Ph	9	**3f**	90
7	$2\text{-}H_2NC_6H_4$	Ph	12	**3g**	89
8	1-Naphthyl	Ph	24	**3h**	75
9	2-Thienyl	Ph	8	**3i**	80
10	3-Pyridinyl	Ph	9	**3j**	82
11	$4\text{-}ClC_6H_4$	$4\text{-}CH_3C_6H_4$	6	**3k**	84
12	2-Thienyl	$4\text{-}CH_3C_6H_4$	8	**3l**	83
13	$3\text{-}CH_3OCOC_6H_4$	$4\text{-}CH_3C_6H_4$	7	**3m**	84
14	$4\text{-}O_2NC_6H_4$	$4\text{-}CH_3C_6H_4$	5	**3n**	83
15	$4\text{-}CH_3OC_6H_4$	$4\text{-}CH_3C_6H_4$	9	**3o**	89
16	$4\text{-}CH_3COC_6H_4$	$4\text{-}CH_3C_6H_4$	6	**3p**	86
17	$4\text{-}BrC_6H_4$	$4\text{-}CH_3C_6H_4$	7	**3q**	83
18	$4\text{-}CH_3OCOC_6H_4$	$4\text{-}CH_3C_6H_4$	6	**3r**	85
19	$4\text{-}O_2NC_6H_4$	$4\text{-}ClC_6H_4$	5	**3s**	79
20	$4\text{-}CH_3OC_6H_4$	$4\text{-}ClC_6H_4$	8	**3t**	90
21	$4\text{-}ClC_6H_4$	$4\text{-}ClC_6H_4$	6	**3u**	87
22	$4\text{-}BrC_6H_4$	$4\text{-}ClC_6H_4$	7	**3v**	85
23	$2\text{-}CF_3C_6H_4$	$4\text{-}ClC_6H_4$	24	**3w**	64
24	2-Thienyl	$4\text{-}ClC_6H_4$	8	**3x**	81
25	$3\text{-}NCC_6H_4$	$4\text{-}ClC_6H_4$	7	**3y**	86

[a] Reactions were carried out with arylboronic acid (1.1 mmol), aryl iodide (1.0 mmol), CO (1 atm), K_2CO_3 (3 mmol) and 2 mol% palladium catalyst in anisole (5 mL) at 80 °C. [b] Isolated yield.

To examine the scope of this heterogeneous carbonylative cross-coupling reaction, we have investigated the reactions using a variety of arylboronic acids and a wide range of aryl iodides as substrates under the optimized reaction conditions (Scheme 2). The results are outlined in Table 3. As shown in Table 3, the carbonylative cross-coupling reaction of phenylboronic acid with a variety of aryl iodides proceeded smoothly under mild conditions, affording the corresponding carbonylative coupling products **3a–j** in good to high yields. Various electron-donating



Scheme 2

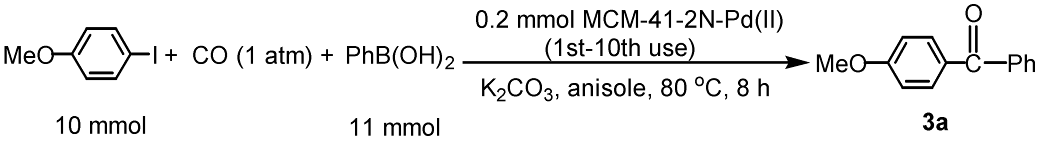
and electron-withdrawing groups, such as –OCH_3, –NH_2, –NO_2 and –$COCH_3$, on the aryl iodide were well tolerated. Electron-donating groups, such as –OCH_3 and –NH_2, on the iodoaryl partner gave excellent results. The presence of a strong electron-withdrawing group, such as –NO_2, is known to promote the direct coupling, producing the biaryl. For example, the carbonylative cross-coupling reaction of triphenylalane with 4-iodonitrobenzene was reported to provide a 41% yield of 4-nitrobenzophenone and a 55% yield of 4-nitrobiphenyl,[5] and an analogous reaction with tributyltin hydride resulted in only a 9% yield of 4-nitrobenzaldehyde with an accompanying 84% yield of nitrobenzene.[28] This heterogeneous palladium catalyst exhibits a higher activity and selectivity than $PdCl_2(PPh_3)_2$. For example, the carbonylative cross-coupling reaction of 4-iodonitrobenzene with phenylboronic acid in the presence of 2 mol% of MCM-41–2N–Pd(II) in anisole using K_2CO_3 as the base at 80 °C for 5 h gave an 82% yield of carbonylative coupling product **3c**, along with only 12% yield of 4-nitrobiphenyl (Table 3, entry 3). The same reaction in the presence of 3 mol% of $PdCl_2(PPh_3)_2$ in anisole using K_2CO_3 as the base at 80 °C for 5 h gave **3c** in 50% yield and 4-nitrobiphenyl in 35% yield.[11a] The same reaction in the presence of 2 mol% of a phosphine-free palladium complex [Pd(tmhd)$_2$] in anisole using K_2CO_3 as the base at 80 °C for 6 h afforded **3c** in 72% yield, but the use of carbon monoxide under pressure (100 psi) was required.[15] The reactions of sterically-hindered 2-iodoanisole and bulky 1-iodonaphthalene with phenylboronic acid also provided good yields of desired biaryl ketones **3e** and **3h** under the optimized reaction conditions, respectively (Table 3, entries 5 and 8). The carbonylative cross-coupling reactions of heteroaryl iodides such as 2-iodothiophene and 3-iodopyridine with phenylboronic acid gave corresponding heteroaryl ketones **3i** and **3j** in 80 and 82% yields, respectively (Table 3, entries 9 and 10). We also performed the carbonylative cross-coupling reaction of phenylboronic acid with 4-iodoanisole under a CO pressure of 100 psi in the presence of 2 mol% of MCM-41–2N–Pd(II) in anisole using K_2CO_3 as the base at 80 °C; desired product **3a** was obtained in 93% yield after 7 h, which is slightly higher than that obtained from the reaction under an atmospheric pressure of CO.

The optimized reaction conditions were also applied to the carbonylative cross-coupling of substituted phenylboronic acids such as 4-methylphenylboronic acid and 4-chlorophenylboronic acid with a variety of aryl iodides. The results are summarized in Table 3. Various electron-donating and electron-withdrawing groups, such as –CH_3, –OCH_3, –Br, –Cl, –CN, –NO_2, –CF_3, –$COCH_3$ and –CO_2CH_3, on both aryl iodides and arylboronic acids were well tolerated to give the desired unsymmetrical biaryl ketones in good to high yields (Table 3, entries 11–25). The method provides a quite general route for the synthesis of unsymmetrical biaryl ketones having various functionalities. The results above prompted us to investigate the reaction of aryl bromides, but aryl bromides were not reactive under the conditions optimized for the iodides, and thus 4-bromoiodobenzene could be converted into a bromophenyl ketone selectively (Table 3, entries 17 and 22). Even though NaI or KI (3 equiv.) were used as the additive as reported by Miyaura,[11a] the carbonylative cross-coupling reaction of aryl bromides with arylboronic acids in anisole at 80 or 100 °C afforded traces of carbonylative coupling products after 24 h. A comparison with homogeneous analogous catalysts, such as $PdCl_2/H_2N(CH_2)_2NH_2$, was also made in order to assess the immobilization effect on activity. When 2 mol% of $PdCl_2/H_2N(CH_2)_2NH_2$ (1 : 1) or $PdCl_2/H_2N(CH_2)_2NH_2$ (1 : 2) was used as the catalyst, the carbonylative cross-coupling of phenylboronic acid with 4-iodoanisole in anisole using K_2CO_3 as the base at 80 °C afforded **3a** in 64 and 57% yields, respectively, and the direct coupling product 4-methoxybiphenyl was formed in 13 and 17% yields. We then prepared a 3-(2-aminoethylamino)propyl-functionalized amorphous silica-supported palladium complex [SiO_2–2N–Pd(II)] according to a literature procedure[20d] for comparison with MCM-41–2N–Pd(II); the palladium content was 0.36 mmol g^{-1}. It was found that the carbonylative cross-coupling of phenylboronic acid with 4-iodoanisole using 2 mol% of SiO_2–2N–Pd(II) as the catalyst and K_2CO_3 as the base also proceeded smoothly in anisole at 80 °C, giving **3a** in 83% yield after 10 h. The catalytic activity of SiO_2–2N–Pd(II) was lower than that of MCM-41–2N–Pd(II) due to the faster diffusion of reactants and products in MCM-41 than in amorphous silica, since the pores are more regular in the former and MCM-41 has a higher surface area than amorphous silica.

In order to determine whether the catalysis was due to the MCM-41–2N–Pd(II) complex or to a homogeneous palladium complex that is released from the support during the reaction and then re-attached to the support at the end, we performed a hot filtration test.[29] We focused on the carbonylative coupling reaction of 3-iodonitrobenzene with phenylboronic acid. We filtered off the MCM-41–2N–Pd(II) complex after a 1 h reaction time and allowed the filtrate to react further. Catalyst filtration was performed at the reaction temperature (80 °C) in order to avoid the possible recoordination 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 in the carbonylative cross-coupling reaction of 4-iodoanisole with phenylboronic acid. In general, the continuous recycling of resin-supported palladium catalysts is difficult owing to leaching of the palladium species from the polymer supports, which often reduces their activity within five recycles.[30] However, when the reaction of 4-iodoanisole with phenylboronic acid was performed, even with 2 mol% of MCM-41–2N–Pd(II),

Table 4 The carbonylative cross-coupling reaction of 4-iodoanisole with phenylboronic acid catalyzed by recycled catalyst



Entry	Catalyst cycle	Isolated yield (%)	TON
1	1st	91	45.5
2	10th	89	44.5
3	1st to 10th consecutive	av. 90	Total of 450

the catalyst could be recycled 10 times without any loss of activity. The reaction promoted by the 10th recycled catalyst gave **3a** in 89% yield (Table 4, entry 2). The average yield of **3a** in consecutive reactions promoted by the 1st through to the 10th recycled catalyst was 90% (Table 4, entry 3). The palladium content of the catalyst was determined by ICP to be 0.32 mmol g^{-1} after ten consecutive runs; only 3% of the 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 the bidentate 2-aminoethylamino ligand on the palladium and the mesoporous structure of the MCM-41 support. The result is important from a practical point of view. The recovered catalyst was analyzed by XPS. It was found that the binding energies of Si_{2p}, O_{1s} and N_{1s} of the recovered catalyst were similar to those of fresh catalyst. However, the binding energy of $Pd_{3d5/2}$ in the used catalyst was 335.7 eV and the binding energy of Cl_{2p} could not be detected. These results indicate that the reduction of the starting palladium(II) complex to the lower valent state [Pd(0)] had taken place during the carbonylative cross-coupling reaction. The high catalytic activity, excellent reusability and easy accessibility of MCM-41–2N–Pd(II) make it a highly attractive heterogeneous palladium catalyst for the parallel solution phase synthesis of diverse libraries of compounds.

Experimental

All chemicals were of reagent grade and used as purchased. All solvents were dried and distilled before use. The products were purified by flash chromatography on silica gel. A mixture of EtOAc and hexane was generally used as the eluent. All carbonylative 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 $CDCl_3$ as the solvent. ^{13}C NMR spectra were recorded on a Bruker AC-P400 (100 MHz) spectrometer in $CDCl_3$ as the solvent. Melting points are uncorrected. The palladium content was determined by inductively coupled plasma atom emission Atomscan16 (ICP-AES, TJA Corporation). X-Ray powder diffraction was undertaken on a Damx-rA (Rigaka) instrument. X-Ray photoelectron spectra were recorded on an XSAM 800 (Kratos) instrument. Microanalyses were measured by using a Yanaco MT-3 CHN microelemental analyzer. The mesoporous material MCM-41 was easily prepared according to a literature procedure.[31]

Synthesis of 3-(2-aminoethylamino)propyl-functionalized MCM-41-immobilized palladium complex [MCM-41–2N–Pd(II)]

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 with $CHCl_3$ (2 × 20 mL) and dried in a vacuum at 160 °C for 5 h. The dried white solid was then soaked in a solution of 3.1 g of Me_3SiCl 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 a 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^{-1} by elemental analysis.

In a small Schlenk tube, 3.3 g of the above-functionalized MCM-41 (MCM-41–2N) was mixed with 0.226 g (1.27 mmol) of $PdCl_2$ 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 3.47 g of the yellow palladium complex [MCM-41-2N-Pd(II)]. The nitrogen and palladium contents were found to be 1.63 and 0.33 mmol g^{-1}, respectively. Catalysts with different Pd loadings could be prepared by varying the feed ratios of $PdCl_2$ to MCM-41–2N.

Typical procedure for the carbonylative Suzuki coupling reaction

A 50 mL round-bottomed flask equipped with a gas inlet tube, a reflux condenser and a magnetic stirring bar was charged with MCM-41–2N–Pd(II) (60 mg, 0.02 mmol Pd), aryl iodide (1.0 mmol), arylboronic acid (1.1 mmol) and K_2CO_3 (3 mmol). The flask was flushed with carbon monoxide, and anisole (5 mL) was then added. After being stirred at 80 °C for 5–24 h under CO (1 atm), the reaction mixture was cooled to room temperature and diluted with diethyl ether (50 mL). The mixture was vacuum filtered using a sintered glass funnel and washed with diethyl ether (2 × 5 mL). The ethereal solution was washed with water (3 × 20 mL), dried over anhydrous magnesium sulfate and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexane–ethyl acetate = 10 : 1).

The recyclability of the MCM-41–2N–Pd(II)

After carrying out the reaction, the mixture was vacuum filtered using a sintered glass funnel, and the residue washed with distilled water (3 × 5 mL), ethanol (2 × 5 mL) and diethyl ether (2 × 5 mL), respectively. After being dried in an oven, the catalyst could be reused directly without further purification.

Conclusions

In summary, we have developed a novel, phosphine-free, practical and economic catalyst system for the carbonylative Suzuki–Miyaura cross-coupling reaction by using 3-(2-aminoethylamino)propyl-functionalized MCM-41-supported palladium as the catalyst in anisole under an atmospheric pressure of carbon monoxide. This novel heterogeneous palladium catalyst can be conveniently prepared by a simple two-step procedure from commercially available and cheap reagents, it exhibits a higher activity and selectivity than $PdCl_2(PPh_3)_2$, and can be reused at least 10 times without any decrease in its activity. The carbonylative cross-coupling reaction of aryl iodides with arylboronic acids catalyzed by the MCM-41–2N–Pd(II) complex under an atmospheric pressure of carbon monoxide provides a better and practical procedure for the synthesis of a variety of unsymmetrical biaryl ketone compounds.

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