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Note

A practical synthesis of unsymmetrical triarylphosphines by heterogeneous palladium(0)-catalyzed cross-coupling of aryl iodides with diphenylphosphine

Zhaotao Xu [a], Pingping Wang [b], Qiurong Chen [a], Mingzhong Cai [a, *]

[a] Key Laboratory of Functional Small Organic Molecule, Ministry of Education and College of Chemistry & Chemical Engineering, Jiangxi Normal University, Nanchang, 330022, PR China
[b] Department of Chemistry, Jiujiang University, Jiujiang, 332000, PR China

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ABSTRACT

The heterogeneous cross-coupling reaction of aryl iodides with diphenylphosphine was achieved in DMAc at 130 °C in the presence of 1.0 mol% of MCM-41-supported tridentate nitrogen palladium(0) complex [MCM-41-3N-Pd(0)] with KOAc as base, yielding a variety of unsymmetrical triarylphosphines in good to excellent yields. The turnover frequency (TOF) of the catalyst can reach 30.67 h^{-1}. This new heterogeneous palladium(0) catalyst could easily be prepared by a simple procedure from commercially readily available reagents, and exhibited the same catalytic activity as homogeneous $Pd(OAc)_2$ or $Pd(PPh_3)_4$, and could be recovered by filtration of the reaction solution and recycled at least seven times without significant loss of catalytic activity.

1. Introduction

Tertiary arylphosphines have widely been applied in many organic transformations catalyzed by transition metals as one of the most useful ligands and are ubiquitous in organometallic chemistry [1–7]. Besides, triarylphosphines can also be used as catalysts [8–10] and fundamental building blocks [11,12] in organic synthesis. The traditional routes to arylphosphines involve reactions of phosphine halides with arylmagnesium or aryllithium reagents, and are therefore intolerant to a wide range of functional groups [1–3]. Among various methods for the preparation of arylphosphine ligands, direct carbon-phosphorous (C–P) bond formation via transition metal-catalyzed cross-coupling between unprotected secondary phosphines and aryl halides/triflates is one of the most valuable and highly efficient routes due to the tolerance of a wide variety of functional groups. Since Stelzer and coworkers first reported the palladium-catalyzed cross-couplings between aryl iodides/bromides and diarylphosphines [13,14], considerable effort has been devoted to the development of palladium- [15–24], copper- [25–28], and nickel [29–34]-catalyzed phosphinations of aryl iodides/bromides or aryl triflates for the synthesis of tertiary phosphines. Recently, catalytic reduction of tertiary phosphine oxides has also proven to be an alternative method for the synthesis of tertiary phosphines [35–38].

Despite significant progress made in homogeneous Pd-, Cu- and Ni-catalyzed synthesis of triarylphosphines, the use of expensive palladium catalysts as well as difficult recovery and non-recyclability of the metal catalysts make these methods of limited synthetic utility from environmental and economic points of view [39]. What's more, homogeneous catalysis might result in heavy metal contamination of the desired isolated product due to the easy formation of complexes of palladium, nickel and copper with triarylphosphines. Recycling of homogeneous metal catalysts is a task of great economic and environmental importance in the chemical and pharmaceutical industries, especially when expensive and/or toxic heavy metal complexes are utilized [40]. The heterogenization of the existing homogeneous metal catalysts appears to be a logical solution to these problems [41,42]. In recent years, heterogeneous palladium catalysts have been successfully applied in carbon-carbon and carbon-heteroatom bond formation reactions [43,44]. However, to the best of our knowledge, no examples of heterogeneous palladium-catalyzed C–P bond construction via direct

* Corresponding author.
E-mail addresses: caimzhong@163.com, mzcai@jxnu.edu.cn (M. Cai).

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coupling of secondary phosphines with aryl halides/triflates have been described until now.

Mesoporous MCM-41 materials have recently been shown to be powerful supports for immobilization of homogeneous catalysts [45–47]. So far, some functionalized MCM-41-immobilized palladium [48–52], rhodium [53], molybdenum [54], gold [55,56], and copper [57,58] complexes have been successfully used as highly efficient and recyclable catalysts in organic reactions. In continuing our efforts to develop greener synthetic pathways for organic transformations [50–52,57,58], herein we report the first synthesis of an MCM-41-supported tridentate nitrogen palladium(0) complex [MCM-41-3N-Pd(0)] and its successful application to cross-coupling of aryl iodides with diphenylphosphine leading to a variety of unsymmetrical triaylphosphines in good to excellent yields (Scheme 1).

2. Experimental

2.1. General remarks

All chemicals were reagent grade and used as purchased. The mesoporous material MCM-41 was prepared according to a literature procedure [45]. The products were purified by flash chromatography on silica gel. Mixture of CH_2Cl_2 and hexane was generally used as eluent. All coupling products were characterized by comparison of their spectra and physical data with authentic samples. ^1H NMR spectra were recoded on a Bruker Avance 400 MHz spectrometer with TMS as an internal standard in $CDCl_3$ as solvent. ^{13}C NMR spectra (100 MHz) were recorded on a Bruker Avance 400 MHz spectrometer in $CDCl_3$ as solvent. ^{31}P NMR spectra (121 MHz) were recorded on a Bruker Avance 400 MHz spectrometer in $CDCl_3$ 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 (Rigaku). Nitrogen adsorption/desorption isotherms were obtained using a Bel Japan Inc. Belsorp-HP at 77 K. Prior to gas adsorption measurements materials were degassed for 6 h at 423 K. TEM images were recorded in a transmission electron microscope operated at an accelerated voltage of 200 kV. X-ray photoelectron spectra were recorded on XSAM 800 (Kratos).

2.2. Preparation of MCM-41-3N-Pd(0) complex

A solution of 1.54 g of 3-(2-aminoethylamino)propyltrimethoxysilane in 18 mL of dry $CHCl_3$ was added to a suspension of 2.2 g of the MCM-41 in 180 mL of dry toluene under Ar. The mixture was stirred at 100 °C for 24 h. Then the solid was filtered and washed by $CHCl_3$ (2 × 20 mL), and dried in vacuum at 160 °C for 5 h. The dried white solid (1.725 g) was then reacted with pyridine-2-carboxaldehyde (0.251 g, 2.34 mmol) in 10 mL of dry ethanol at 80 °C for 24 h. The solid product was filtered, washed with ethanol (3 × 20 mL) and diethyl ether (20 mL), and dried in vacuum at 120 °C for 5 h to obtain 1.813 g of hybrid material MCM-41-3 N. The nitrogen content was found to be 2.62 mmol/g by elemental analysis.

In a small Schlenk tube, 1.70 g of the above-functionalized MCM-41 (MCM-41-3 N) was mixed with 0.177 g (1.0 mmol) of $PdCl_2$ in 40 mL of dry acetone. The mixture was refluxed for 72 h under an argon atmosphere. The solid product was filtered, washed with distilled water (2 × 10 mL) and ethanol (2 × 10 mL), and dried under vacuum. The yellow solid was then mixed with hydrazine hydrate (1.5 mL) in ethanol (20 mL) at 30 °C for 5 h. The resulting product was filtered, washed with distilled water (3 × 10 mL) and acetone (2 × 10 mL) and dried under vacuum at 60 °C for 5 h to afford 1.82 g of a gray palladium(0) complex [MCM-41-3N-Pd(0)]. The nitrogen and palladium contents were found to be 2.36 mmol/g and 0.49 mmol/g, respectively.

2.3. General procedure for C–P coupling reaction of various aryl iodides with diphenylphosphine

MCM-41-3N-Pd(0) (21 mg, 0.01 mmol), KOAc (1.5 mmol) and aryl iodide **1** (1.0 mmol) (if solid) were placed in an oven-dried 20 mL Schlenk tube, the reaction vessel was evacuated and filled with argon for three times. Then aryl iodide **1** (1.0 mmol) (if liquid), diphenylphosphine (1.2 mmol) and DMAc (1 mL) were added with a syringe under a counter flow of argon. The reaction mixture was stirred at 130 °C for 3 h. After completion of the reaction, the mixture was cooled to room temperature and diluted with CH_2Cl_2 (20 mL) and filtered. The MCM-41-3N-Pd(0) catalyst was washed with distilled water (2 × 5 mL) and ethanol (2 × 5 mL), and reused in the next run. The filtrate was concentrated in vacuo and the residue was purified by flash column chromatography on silica gel to provide the product **2**.

2.3.1. Triphenylphosphine, **2a** [26]

White solid, m.p.: 79–80 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.44–7.23 (m, 15H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.3, 137.2, 133.9, 133.7, 128.8, 128.6, 128.5; ^{31}P NMR (121 MHz, $CDCl_3$): δ = −5.45 (s).

2.3.2. Diphenyl(4-methylphenyl)phosphine, **2b** [26]

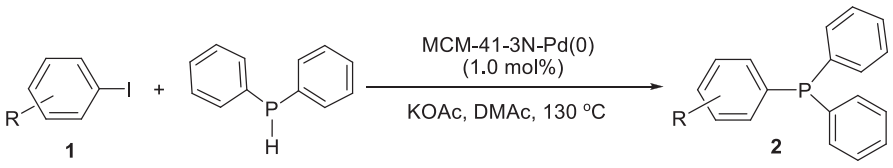
White solid, m.p.: 68–69 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.14 (m, 14H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.9, 137.5, 137.4, 134.1, 133.9, 133.7, 133.6, 129.5, 129.4, 128.7, 128.5, 128.4, 21.4; ^{31}P NMR (121 MHz, $CDCl_3$): δ = −6.30 (s).

2.3.3. Diphenyl(4-methoxyphenyl)phosphine, **2c** [59]

White solid, m.p.: 67–68 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.25–7.16 (m, 12H), 6.82 (d, J = 8.0 Hz, 2H), 3.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.4, 137.8, 137.7, 137.6, 135.8, 135.6, 133.6, 133.4, 128.6, 128.5, 128.4, 114.3, 114.2, 55.2; ^{31}P NMR (121 MHz, $CDCl_3$): δ = −7.10 (s).

2.3.4. Diphenyl(3-methylphenyl)phosphine, **2d** [60]

White solid, m.p.: 50–51 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.42–7.06 (m, 14H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.1, 137.1, 134.6, 134.4, 133.9, 133.7, 132.1, 130.9, 130.7, 129.6, 128.7, 128.5, 128.4, 21.5; ^{31}P NMR (121 MHz, $CDCl_3$): δ = −5.23 (s).



Scheme 1. Heterogeneous Pd(0)-catalyzed C–P coupling of aryl iodides with Ph_2PH.

2.3.5. Diphenyl(3,5-dimethylphenyl)phosphine, ***2e*** *[13]*

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25–7.12 (m, 10H), 6.89–6.83 (m, 3H), 2.16 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.1, 138.0, 137.3, 137.2, 135.1, 133.9, 133.7, 131.7, 131.5, 130.8, 128.7, 128.5, 128.4, 21.4; ^{31}P NMR (121 MHz, $CDCl_3$): δ = −5.28 (s).

2.3.6. Diphenyl(4-aminophenyl)phosphine, ***2f*** *[13]*

White solid, m.p.: 37–38 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.23–7.12 (m, 10H), 7.06 (t, J = 7.6 Hz, 2H), 6.54 (d, J = 7.6 Hz, 2H), 3.43 (br, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.2, 138.3, 135.8, 135.6, 133.5, 133.3, 128.4, 128.3, 124.8, 115.3, 115.2; ^{31}P NMR (121 MHz, $CDCl_3$): δ = −6.61 (s).

2.3.7. 4-(Diphenylphosphino)biphenyl, ***2g*** *[61]*

White solid, m.p.: 83–84 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58 (t, J = 8.0 Hz, 4H), 7.45–7.32 (m, 15H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.5, 140.6, 137.3, 137.2, 136.2, 136.1, 134.3, 134.1, 133.9, 133.7, 128.8, 128.6, 128.5, 127.5, 127.2, 127.1; ^{31}P NMR (121 MHz, $CDCl_3$): δ = −5.99 (s).

2.3.8. Diphenyl(4-fluorophenyl)phosphine, ***2h*** *[62]*

White solid, m.p.: 53–54 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35–7.24 (m, 12H), 7.03 (t, J = 8.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.6, 162.2, 136.0, 135.9, 133.7, 133.5, 128.8, 128.6, 128.5, 115.9, 115.8, 115.7, 115.6; ^{31}P NMR (121 MHz, $CDCl_3$): δ = −6.57 (d).

2.3.9. Diphenyl(4-chlorophenyl)phosphine, ***2i*** *[59]*

White solid, m.p.: 44–45 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31–7.20 (m, 12H), 7.14 (t, J = 7.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.7, 136.6, 136.0, 135.9, 135.1, 134.9, 133.8, 133.6, 129.0, 128.8, 128.7, 128.6; ^{31}P NMR (121 MHz, $CDCl_3$): δ = −6.50 (s).

2.3.10. Diphenyl(4-bomophenyl)phosphine, ***2j*** *[59]*

White solid, m.p.: 78–79 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45 (d, J = 7.6 Hz, 2H), 7.35–7.24 (m, 10H), 7.15 (t, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.7, 136.6, 135.4, 135.2, 133.9, 133.7, 131.8, 131.7, 129.1, 128.7, 128.6, 123.5; ^{31}P NMR (121 MHz, $CDCl_3$): δ = −6.44 (s).

2.3.11. Diphenyl(4-cyanophenyl)phosphine, ***2k*** *[63]*

White solid, M.p. 86–87 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.55 (dd, J = 8.4, 1.6 Hz, 2H), 7.38–7.29 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 145.2, 145.1, 135.5, 135.4, 134.2, 134.0, 133.6, 133.5, 131.8, 129.6, 129.0, 128.9, 118.8, 111.9.^{31}P NMR (121 MHz, $CDCl_3$) δ = −4.46 (s).

2.3.12. Diphenyl(4-acetylphenyl)phosphine, ***2l*** *[26]*

White solid, m.p.: 121–122 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 (d, J = 7.2 Hz, 2H), 7.35–7.15 (m, 12H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.8, 144.5, 144.4, 136.9, 136.2, 136.1, 134.1, 133.9, 133.5, 133.3, 129.2, 128.8, 128.7, 128.1, 128.0, 26.6; ^{31}P NMR (121 MHz, $CDCl_3$): δ = −5.07 (s).

2.3.13. Diphenyl(3-trifluoromethylphenyl)phosphine, ***2m*** *[64]*

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60–7.56 (m, 2H), 7.44–7.41 (m, 2H), 7.37–7.28 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.3, 139.2, 136.8, 136.7, 136.1, 136.0, 133.9, 133.8, 131.0, 130.9, 130.7, 130.6, 130.3, 130.1, 129.3, 128.9, 128.8, 125.5, 125.4, 122.7; ^{31}P NMR (121 MHz, $CDCl_3$): δ = −5.30 (s).

2.3.14. Diphenyl(4-nitrophenyl)phosphine, ***2n*** *[65]*

Yellow solid, M.p. 134–135 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.14 (d, J = 7.6 Hz, 2H), 7.42–7.27 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 147.8, 135.3, 135.2, 134.2, 134.0, 133.8, 133.6, 129.6, 129.0, 128.9, 123.2, 123.1.^{31}P NMR (121 MHz, $CDCl_3$) δ = −4.48 (s).

2.3.15. Methyl 4-(diphenylphosphino)benzoate, ***2o*** *[26]*

White solid, m.p.: 103–104 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97 (d, J = 7.2 Hz, 2H), 7.41–7.28 (m, 12H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.9, 144.1, 144.0, 136.2, 136.1, 134.1, 133.9, 133.3, 133.1, 130.0, 129.4, 129.3, 129.2, 128.8, 128.7, 52.2; ^{31}P NMR (121 MHz, $CDCl_3$): δ = −5.05 (s).

2.3.16. Ethyl 4-(diphenylphosphino)benzoate, ***2p*** *[64]*

White solid, m.p.: 83–84 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 (d, J = 8.4 Hz, 2H), 7.42–7.24 (m, 12H), 4.36 (q, J = 7.2 Hz, 2H), 1.37 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.4, 143.9, 143.8, 136.3, 136.2, 134.1, 133.9, 133.3, 133.1, 130.4, 129.3, 129.2, 129.1, 128.7, 128.6, 61.0, 14.3; ^{31}P NMR (121 MHz, $CDCl_3$): δ = −5.07 (s).

2.3.17. Diphenyl(2-chlorophenyl)phosphine, ***2q*** *[66]*

White solid, m.p.: 103–104 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34–7.15 (m, 12H), 7.06 (t, J = 7.4 Hz, 1H), 6.69–6.65 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.3, 139.1, 137.0, 136.9, 135.7, 135.6, 134.1, 133.9, 130.0, 129.6, 129.1, 128.7, 128.6, 126.8; ^{31}P NMR (121 MHz, $CDCl_3$): δ = −10.87 (s).

2.3.18. Diphenyl(2-methylphenyl)phosphine, ***2r*** *[26]*

White solid, m.p.: 65–66 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35–7.21 (m, 12H), 7.15–7.04 (m, 1H), 6.79–6.73 (m, 1H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.4, 142.1, 139.0, 136.4, 136.3, 130.2, 130.1, 128.8, 128.7, 128.6, 126.1, 21.3; ^{31}P NMR (121 MHz, $CDCl_3$): δ = −13.27 (s).

2.3.19. Diphenyl(2-methoxyphenyl)phosphine, ***2s*** *[26]*

White solid, m.p.: 122–123 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45–7.27 (m, 11H), 6.91–6.85 (m, 2H), 6.73–6.68 (m, 1H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.3, 161.1, 136.7, 136.6, 134.0, 133.8, 133.7, 130.4, 128.6, 128.4, 128.3, 125.6, 125.5, 121.1, 110.3, 55.6; ^{31}P NMR (121 MHz, $CDCl_3$): δ = −16.61 (s).

2.3.20. 2-(Diphenylphosphino)biphenyl, ***2t*** *[67]*

White solid, m.p.: 60–61 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33–7.09 (m, 18H), 7.00–6.96 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.5, 148.2, 141.8, 141.7, 137.8, 137.7, 136.0, 135.9, 134.1, 134.0, 133.8, 130.2, 130.1, 129.8, 129.7, 128.7, 128.5, 128.4, 128.3, 127.6, 127.4, 127.2; ^{31}P NMR (121 MHz, $CDCl_3$): δ = −13.33 (s).

2.3.21. Methyl 2-(diphenylphosphino)benzoate, ***2u*** *[59]*

White solid, m.p.: 97–98 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05 (d, J = 2.8 Hz, 1H), 7.38–7.23 (m, 12H), 6.94 (m, 1H), 3.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.3, 140.6, 140.4, 137.9, 137.8, 134.3, 134.0, 133.8, 132.0, 130.7, 128.7, 128.6, 128.5, 128.3, 52.1; ^{31}P NMR (121 MHz, $CDCl_3$): δ = −4.26 (s).

2.3.22. 1-(Diphenylphosphino)naphthalene, ***2v*** *[26]*

White solid, m.p.: 122–123 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 (t, J = 8.8 Hz, 2H), 7.49–7.23 (m, 15H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.4, 136.3, 135.4, 135.2, 134.3, 134.1, 133.5, 133.4, 132.1, 129.5, 128.9, 128.8, 128.7, 128.6, 126.3, 126.0, 125.6; ^{31}P NMR (121 MHz, $CDCl_3$): δ = −14.13 (s).

2.3.23. 2-(Diphenylphosphino)pyridine, ***2w*** *[68]*

White solid, m.p.: 82–83 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.72 (d, J = 3.6 Hz, 1H), 7.57 (t, J = 7.6 Hz, 1H), 7.40–7.25 (m, 10H), 7.18 (t, J = 5.8 Hz, 1H), 7.08 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.0, 150.4, 150.3, 136.2, 136.1, 135.8, 134.3, 134.1, 129.1, 128.7, 128.6, 127.9, 127.8, 122.2; ^{31}P NMR (121 MHz, $CDCl_3$): δ = −4.06 (s).

2.3.24. 2-(Diphenylphosphino)thiophene, ***2x*** *[26]*

White solid, m.p.: 44–45 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58

(d, $J = 3.2$ Hz, 1H), 7.48–7.06 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 138.0, 137.9, 136.5, 136.3, 133.2, 133.0, 132.1, 128.9, 128.6, 128.5, 128.4, 128.1, 128.0$; ^{31}P NMR (121 MHz, $CDCl_3$): $\delta = -19.99$ (s).

3. Results and discussion

3.1. Synthesis and characterization of MCM-41-3N-Pd(0) complex

Although the phosphine ligands can stabilize palladium and affect its catalytic activity, undoubtedly, the simplest and cheapest palladium catalysts are of course phosphine-free systems. A novel MCM-41-supported tridentate nitrogen palladium(0) complex [MCM-41-3N-Pd(0)] was easily prepared according to the procedure as shown in Scheme 2. First, the mesoporous MCM-41 [45] was condensed with 3-(2- aminoethylamino)propyltrimethoxysilane in toluene under reflux for 24 h to afford the bidentate nitrogen-functionalized MCM-41 [MCM-41-2 N]. The latter was reacted with pyridine-2-carboxaldehyde in dry ethanol at reflux for 24 h to give the tridentate nitrogen-functionalized MCM-41 [MCM-41-3 N]. The MCM-41-3 N was then treated with $PdCl_2$ in acetone at reflux for 72 h, followed by reduction with hydrazine hydrate in ethanol at 30 °C for 5 h to generate the MCM-41-supported tridentate nitrogen palladium(0) complex [MCM-41-3N-Pd(0)] as a gray powder.

X-ray powder diffraction (XRD) patterns of the parent MCM-41 and the modified material MCM-41-3N-Pd(0) are displayed in Fig. 1. Small angle X-ray diffraction of MCM-41 gave the peaks corresponding to hexagonally ordered mesoporous phases. For the MCM-41-3N-Pd(0) complex, the (100) reflection of the parent MCM-41 with decreased intensity was remained after grafting palladium complex, while the (110) and (200) reflections became weak and diffuse, which may be mainly due to contrast matching between the silicate framework and organic moieties which are located inside the channels of MCM-41. These results indicate that the mesoporous structure of the parent MCM-41 remains intact through the grafting procedure and the forma-tion of the palladium complex has taken place preferentially inside the pore system of MCM-41.

The N_2 adsorption-desorption isotherms and pore size distributions for the parent MCM-41 and the MCM-41-3N-Pd(0) complex are illustrated in Fig. 2 and Fig. 3, respectively. The isotherms in Fig. 2 have remarkable changes before and after grafting the palladium complex as expected because the organic moieties entered the channels, but both samples showed type IV isotherms,

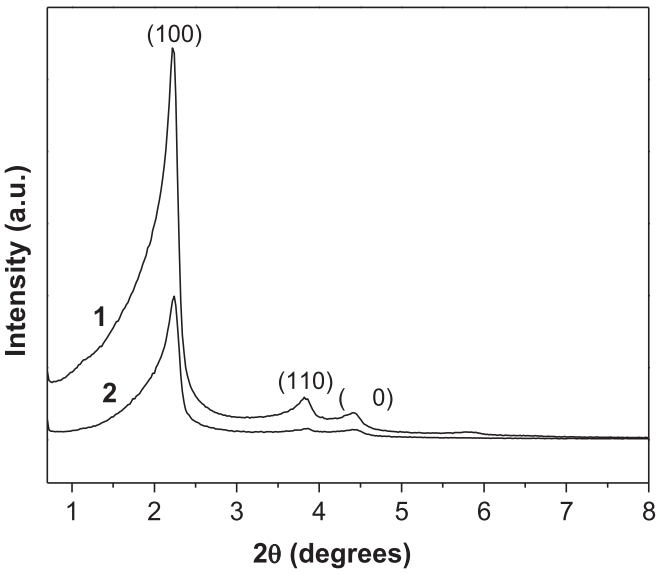


Fig. 1. Small angle XRD patterns of MCM-41 (1) and MCM-41-3N-Pd(0) (2).

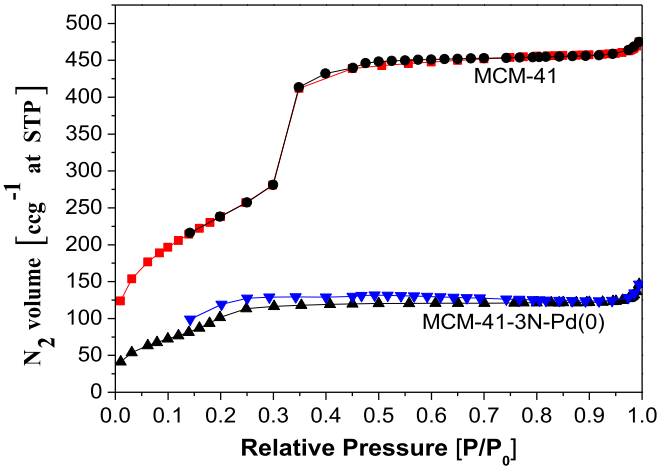
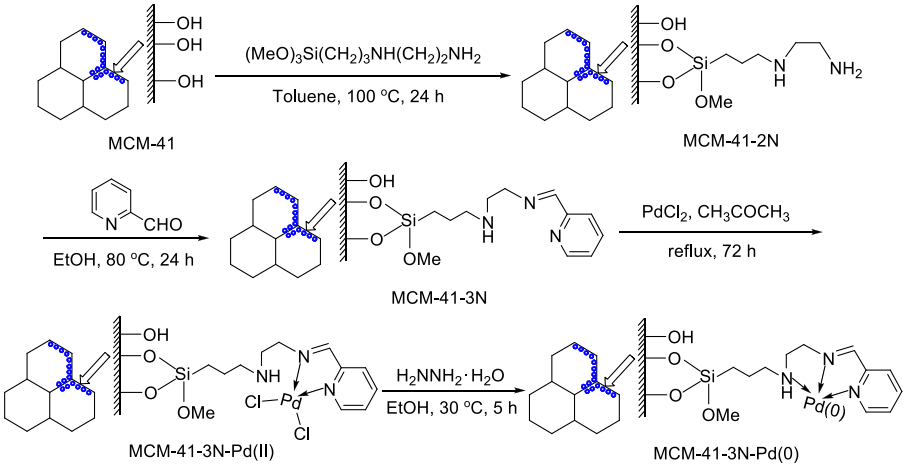


Fig. 2. N_2 adsorption/desorption isotherms of MCM-41 and MCM-41-3N-Pd(0).



Scheme 2. Preparation of MCM-41-3N-Pd(0) complex.

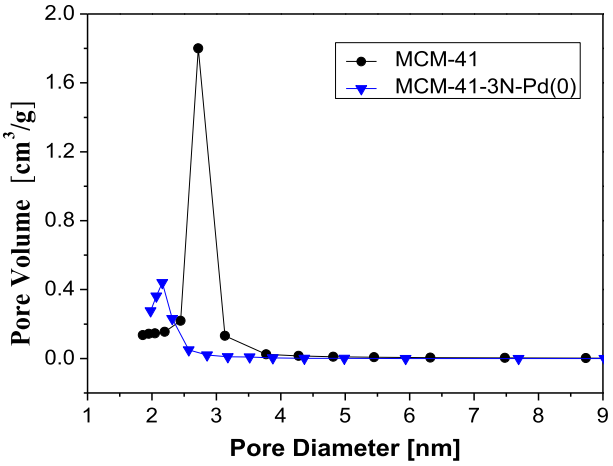


Fig. 3. Pore size distributions of MCM-41 and MCM-41-3N-Pd(0).

characteristic of mesoporous materials according to the IUPAC classification. As shown in Fig. 3, the pore volume and size of the MCM-41-3N-Pd(0) complex reduced apparently compared with the parent MCM-41, also indicating the organic moieties were introduced into the inner channels, but the pore still remained a narrow distribution. After the grafting the tridentate nitrogen palladium(0) complex onto MCM-41, the surface area and pore diameter decreased from 906 m^2/g and 2.7 nm to 652 m^2/g and 2.2 nm, respectively, indicating that the ordered mesostructure of the parent MCM-41 remained almost unchanged.

Fig. 4 shows the transmission electron micrograph (TEM) image of MCM-41-3N-Pd(0) complex. The highly ordered structure with a hexagonal ordered porous parallel channels can be clearly observed in this figure, which indicating that the Pd complex grafting did not cause a drastic change on the mesoporous structure of parent MCM-41. In addition, we can easily observe the palladium(0) nanoparticles as black dots either inside the pore of the mesoporous MCM-41 or impregnated on the external surface of MCM-41. The wide angle XRD pattern of MCM-41-3N-Pd(0) complex is presented in Fig. 5. The MCM-41-3N-Pd(0) exhibited characteristic peaks of palladium(0) nanoparticles with diffraction peaks at 2θ of ca. 39.0°, 45.3°, and 66.1° where these peaks correspond to (111), (200), and (220) reflections, respectively [69].

Elemental analyses and X-ray photoelectron spectroscopy (XPS) were also used to characterize the MCM-41-supported tridentate nitrogen palladium(0) complex. The N: Pd mole ratio of the MCM-41-3N-Pd(0) was determined to be 4.81. The XPS data for MCM-41-3N-Pd(0) (fresh), MCM-41-3N-Pd(II), MCM-41-3 N, $PdCl_2$, metal Pd, and MCM-41-3N-Pd(0) (used) are listed in Table 1. It can be seen that the binding energies of Si_{2p} and O_{1s} of MCM-41-3N-Pd(II) are similar to those of MCM-41-3 N. However the difference of N_{1s} binding energies between MCM-41-3N-Pd(II) and MCM-41-3 N is 0.8 eV. The binding energy of $Pd_{3d5/2}$ in MCM-41-3N-Pd(II) is 0.7 eV less than that in $PdCl_2$, but 2.2 eV larger than that in metal Pd. These results show that a coordination bond between N and Pd is formed in MCM-41-3N-Pd(II). The binding energy of $Pd_{3d5/2}$ in MCM-41-3N-Pd(0) (fresh) is 1.8 eV less than that in MCM-41-3N-Pd(II) and similar to that in metal Pd, which indicating that the oxidation state of palladium in freshly prepared MCM-41-3N-Pd(0) was Pd(0) [70]. The difference of N_{1s} binding energies between MCM-41-3N-Pd(0) (fresh) and MCM-41-3 N is 0.6 eV, which can be attributed to the formation of coordination bonds between N and Pd in MCM-41-3N-Pd(0) (fresh). In addition, the binding energy of Cl_{2p} in the MCM-41-3N-Pd(0) (fresh) cannot be detected, together with the change in color (from light yellow to gray) also suggests that the reduction of the starting MCM-41-3N-Pd(II) to the MCM-41-3N-Pd(0) has taken place.

3.2. Heterogeneous palladium(0)-catalyzed cross-coupling reaction of aryl iodides with diphenylphosphine

The MCM-41-supported tridentate nitrogen palladium(0) complex was then used as catalyst for the C—P coupling reaction of aryl iodides with diphenylphosphine. Initial experiments with iodobenzene (**1a**) and diphenylphosphine were performed to optimize the reaction conditions, and the results are summarized in Table 2. At first, the effect of base on the model reaction was examined with DMAc as solvent at 120 °C (Table 2, entries 1–5). For the bases evaluated [Cs_2CO_3, K_2CO_3, KOAc, K_3PO_4 and *n*-Bu_3N], KOAc gave the best result, while other bases were substantially less effective. When DMAc was replaced by other solvents, DMF and NMP also

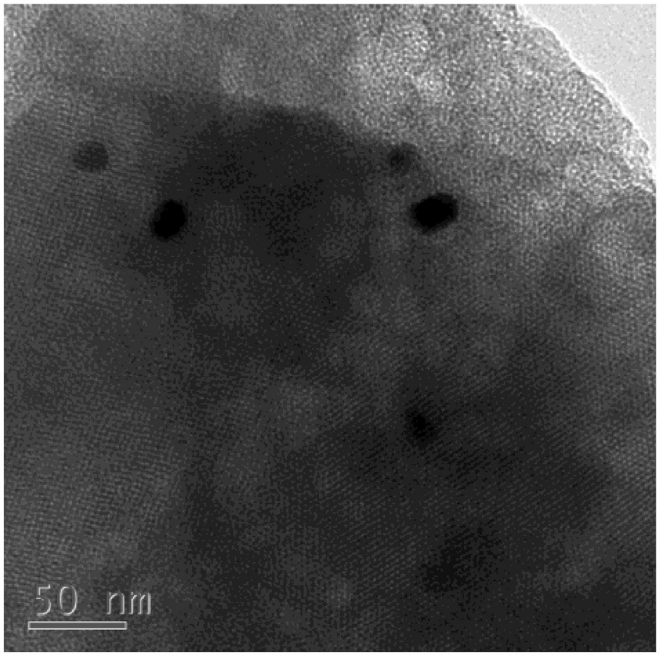


Fig. 4. TEM image of MCM-41-3N-Pd(0).

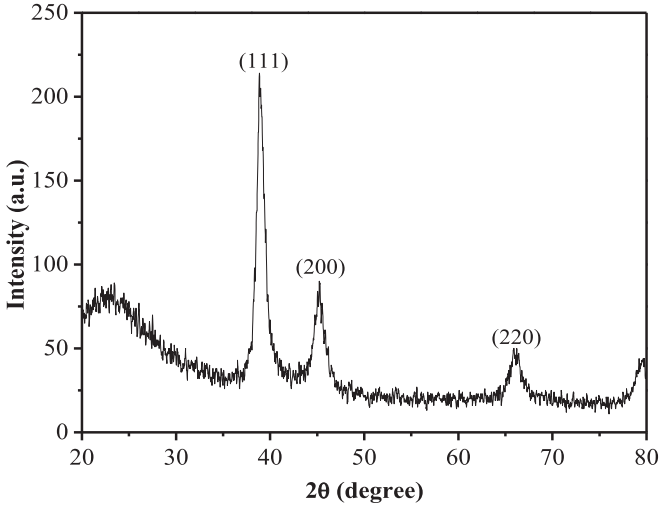


Fig. 5. Wide angle XRD patterns of MCM-41-3N-Pd(0).

Table 1
XPS data for MCM-41-3N-Pd(0) (fresh), MCM-41-3N-Pd(II), MCM-41-3 N, $PdCl_2$, metal Pd and MCM-41-3N-Pd(0) (used).[a]

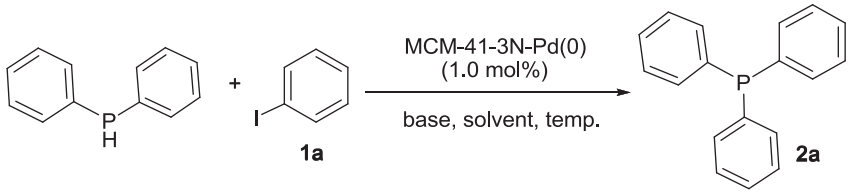
Sample	$Pd_{3d5/2}$	N_{1s}	Si_{2p}	O_{1s}	Cl_{2p}
MCM-41-3N-Pd(0) (fresh)	335.6	400.4	103.2	533.3	
MCM-41-3N-Pd(II)	337.4	400.6	103.3	533.3	199.2
MCM-41-3 N		399.8	103.2	533.4	
$PdCl_2$	338.1				199.3
Metal Pd	335.2				
MCM-41-3N-Pd(0) (used)	335.5	400.5	103.3	533.4	

[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.

provided good results, whilst DMSO and toluene gave lower yields (Table 2, entries 6–9), so DMAc was the best choice, which may be due to the good solubility of KOAc in DMAc (Table 2, entry 3). Our next studies focused on the effect of reaction temperature on the model reaction. When reaction temperature was raised to 130 °C, the yield of **2a** was improved to 86% within 3 h (Table 2, entry 10), but further raising temperature to 140 °C resulted in a slightly decreased yield due to the easy oxidation of diphenylphosphine at high temperature (Table 2, entry 11). When a homogeneous $Pd(OAc)_2$ or $Pd(PPh_3)_4$ was used as the catalyst, the desired product **2a** was also isolated in 87 and 86% yield, respectively (Table 2, entries 12 and 13), which indicating that catalytic activity of MCM-41-3N-Pd(0) was comparable to that of homogeneous $Pd(OAc)_2$ or $Pd(PPh_3)_4$. Finally, the amount of the supported palladium catalyst was screened, and 1 mol% loading of palladium was found to be optimal, a lower yield was observed and a longer reaction time was required when the amount of the catalyst was decreased to 0.5 mol % (Table 2, entry 14). Increasing the amount of the palladium catalyst could shorten the reaction time, but did not improve the yield of **2a** significantly (Table 2, entry 15). Therefore, the optimal catalytic system involved the use of MCM-41-3N-Pd(0) (1 mol%), KOAc as base in DMAc at 130 °C under Ar for 3 h (Table 2, entry 10).

With the optimized conditions established, we tried to investigate the scope and limitations of this heterogeneous palladium(0)-catalyzed C–P coupling reaction and the results are summarized in Table 3. As shown in Table 3, both electron-rich and electron-deficient aryl iodides **1b-1u** proved to be suitable coupling partners and gave the corresponding unsymmetrical triarylphosphines **2b-2u** in good to excellent yields. For instance, aryl iodides bearing various electron-donating groups **1b-1g** underwent the cross-coupling reaction smoothly to give the desired products **2b-2g** in 79–92% yields. For electron-deficient aryl iodides having either weak electron-withdrawing groups such as fluoro, chloro and bromo **1h-1j** or strong electron-withdrawing groups such as cyano, acetyl, trifluoromethyl, nitro, and ester **1k-1p**, the cross-coupling reactions also proceeded effectively to afford the corresponding triarylphosphines **2h-2p** in 77–87% yields. These results indicate that the electronic nature of the substituent on the benzene ring has limited influence on the heterogeneous palladium-catalyzed C–P bond formation reaction. Base-sensitive functional groups such as methyl ketone (**1l**) and esters (**1o**, **1p**) are tolerated by this method. In addition, the sterically congested *o*-substituted aryl iodides such as 2-chloroiodobenzene **1q**, 2-iodotoluene **1r**, 2-iodoanisole **1s**, 2-iodobiphenyl **1t** and methyl 2-iodobenzoate **1u** were also coupled with diphenylphosphine effectively to furnish the desired coupled products **2q-u** in 61–83% yields. It is noteworthy that the bulky 1-iodonaphthalene **1v** showed high reactivity and produced the desired product **2v** in 90% yield. Heteroatoms turned out to be compatible with the employed reaction conditions, the reactions of 2-iodopyridine **1w** and 2-iodothiophene **1x** with diphenylphosphine afforded the corresponding products **2w** and **2x** in 80 and 84% yields, respectively. Encouraged by the above results, we attempted to perform the

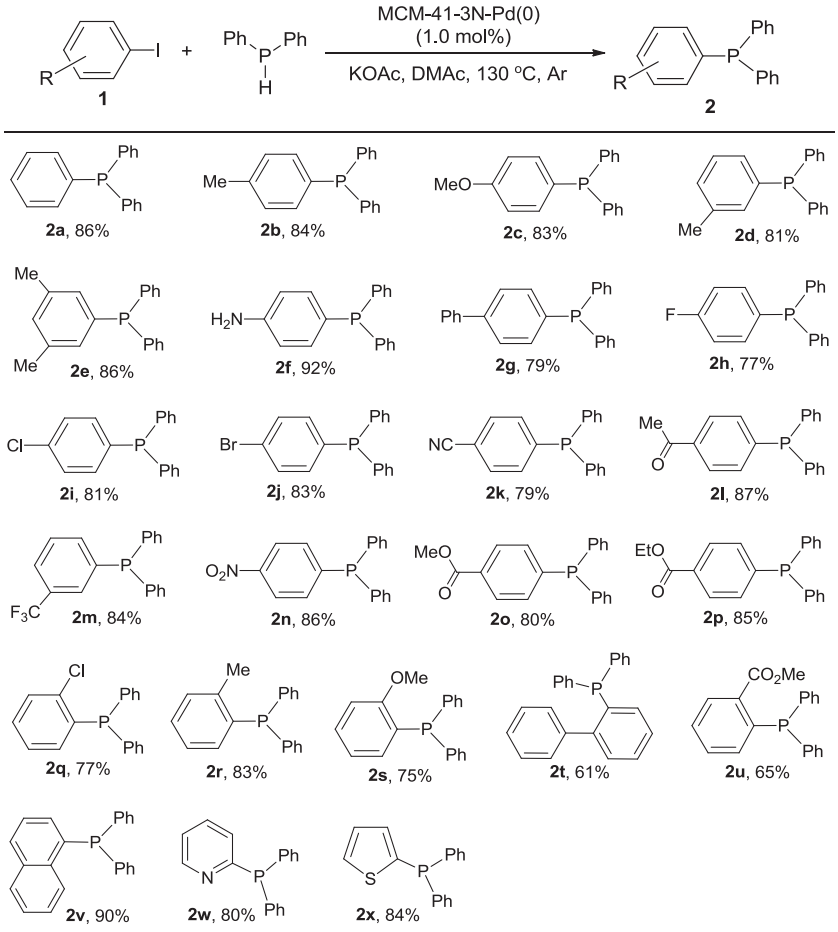
Table 2
Optimization of reaction conditions for the cross-coupling of iodobenzene with diphenylphosphine.[a]



Entry	Base	Solvent	Temp. (°C)	Time (h)	Yield (%)[b]
1	Cs_2CO_3	DMAc	120	12	45
2	K_2CO_3	DMAc	120	12	33
3	KOAc	DMAc	120	6	74
4	K_3PO_4	DMAc	120	12	22
5	n-Bu_3N	DMAc	120	12	51
6	KOAc	DMF	120	6	67
7	KOAc	NMP	120	6	70
8	KOAc	DMSO	120	12	49
9	KOAc	toluene	120	12	43
10	KOAc	DMAc	130	3	86
11	KOAc	DMAc	140	2	83
12[c]	KOAc	DMAc	130	3	87
13[d]	KOAc	DMAc	130	3	86
14[e]	KOAc	DMAc	130	7	73
15[f]	KOAc	DMAc	130	2	87

[a] Reaction was performed with **1a** (1.0 mmol), Ph_2PH (1.2 mmol), base (1.5 mmol) and MCM-41-3N-Pd(0) (0.01 mmol, 1 mol%) in solvent (1 mL) under Ar.
[b] Isolated yield based on **1a**.
[c] $Pd(OAc)_2$ (1 mol%) was used.
[d] $Pd(PPh_3)_4$ (1 mol%) was used.
[e] 0.5 mol% MCM-41-3N-Pd(0) was used.
[f] 2 mol% MCM-41-3N-Pd(0) was used.

Table 3
Heterogeneous palladium-catalyzed synthesis of unsymmetrical triarylphosphines via cross-coupling of aryl iodides with Ph_2PH.[a,b]



[a] Reaction was performed with **1** (1.0 mmol), Ph_2PH (1.2 mmol), KOAc (1.5 mmol) and MCM-41-3N-Pd(0) (0.01 mmol, 1 mol%) in DMAc (1 mL) at 130 °C under Ar for 3 h. [b] Isolated yield based on **1**.

reaction of bromobenzene with diphenylphosphine under the same conditions, unfortunately, only a trace of the desired product **2a** was detected, so 4-bromoiodobenzene **1j** was selectively subjected to the C—P coupling reaction to give the desired product **2j** in 83% yield. Even if 4-nitrobromobenzene bearing a strong electron-withdrawing group was used as substrate, the desired product **2n** was obtained in only 12% isolated yield after 24 h. The present protocol provides a quite general and practical route for the synthesis of a wide variety of unsymmetrical triarylphosphines having various functionalities.

In order to determine whether the observed catalysis was due to the heterogeneous catalyst MCM-41-3N-Pd(0) or to a leached palladium species in solution, the reaction of iodobenzene **1a** with diphenylphosphine was carried out until an approximately 30% conversion of iodobenzene **1a** was reached. Then MCM-41-3N-Pd(0) catalyst was removed from the reaction mixture by hot filtration [71] and the filtrate was allowed to react further at 130 °C under Ar atmosphere for 3 h. In this case, no significant increase in conversion of iodobenzene **1a** was observed, indicating that leached palladium species from the supported catalyst (if any) are not responsible for the observed activity. It was also confirmed by ICP-AES analysis that no palladium species could be detected in the filtrate (below the detection limit). These results rule out any contribution to the observed catalysis from a homogeneous palladium species demonstrating that the MCM-41-3N-Pd(0) catalyst

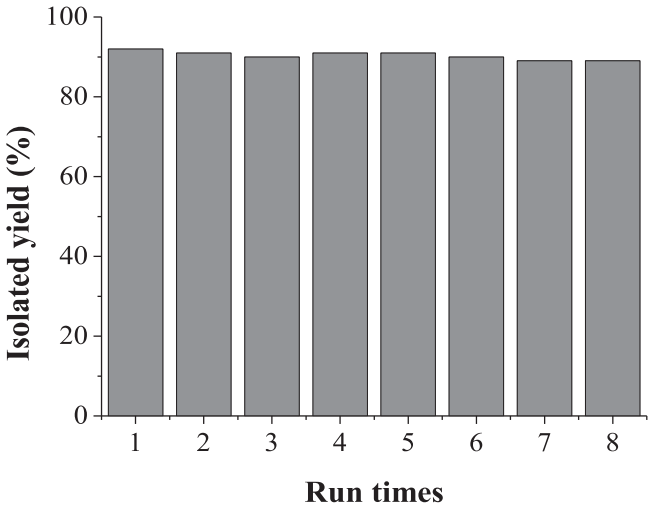


Fig. 6. Recycle of MCM-41-3N-Pd(0) catalyst.

was stable during the reaction and the observed catalysis was intrinsically heterogeneous. In order to further examine the stability of MCM-41-3N-Pd(0) complex at the catalytic temperature of 130 °C, the XPS analysis of the used MCM-41-3N-Pd(0) was performed and the results are also listed in Table 1. As shown in Table 1, the binding energies of $Pd_{3d5/2}$ and N_{1s} of the used MCM-41-3N-Pd(0) are similar to those of the fresh one, which indicating that the MCM-41-3N-Pd(0) complex is stable at the reaction temperature and is in this form but not metal Pd(0) alone. The mechanism for this heterogeneous palladium-catalyzed C–P coupling reaction could follow the proposal made by Buchwald and Beller for the palladium-catalyzed amination of aryl bromides [72,73].

3.3. Recycling of the catalyst

For the practical application of a supported precious metal catalyst, its stability and recyclability are important factors. We next examined the recycle of the MCM-41-3N-Pd(0) complex by using cross-coupling reaction of 4-iodobenzenamine (1 mmol) and diphenylphosphine (1.2 mmol) in DMAc (1 mL) with KOAc (1.5 mmol) as base in the presence of 1.0 mol% of MCM-41-3N-Pd(0) at 130 °C under argon atmosphere for 3 h. After completion of the reaction, the catalyst was separated by a simple filtration of the reaction solution and washed with distilled water and ethanol. After being air-dried, it can be reused directly without further purification. The recovered catalyst was used in the next run, and almost the same yield of **2f** was observed for 8 consecutive cycles (Fig. 6). In order to show that the catalyst remains the same after each run of catalytic cycle, palladium leaching in the heterogeneous catalyst was also determined by ICP-AES analysis on the recovered catalyst after each run, the palladium content was found to be 0.48, 0.49, 0.47, 0.48, 0.48, 0.47, and 0.48 mmol/g respectively, which revealing almost the same palladium content as the fresh one. In our opinion, the high catalytic activity and excellent recyclability of the palladium catalyst may be due to the efficient site isolation, to the optimal dispersion of the active sites on the inner channel walls and to the relatively strong interaction between the tridentate nitrogen ligand and the palladium centre supported on the MCM-41. The result is important from the standpoint of green and sustainable chemistry.

4. Conclusion

In conclusion, an efficient and phosphine-free MCM-41-3N-Pd(0) catalyst has been synthesized by a simple procedure from commercially readily available materials. The new heterogeneous palladium catalyst was characterized by various characterization techniques like elemental analysis, XRD, N_2 sorption analyses, TEM and XPS. We have shown that MCM-41-3N-Pd(0) can catalyze the cross-coupling of various aryl iodides with diphenylphosphine to yield a variety of unsymmetrical triarylphosphines in good to excellent yields and exhibit the same catalytic activity as homogeneous $Pd(OAc)_2$ or $Pd(PPh_3)_4$ complex. The reactions tolerated a wide range of functional groups, including base-sensitive groups. The catalyst can be easily recovered by a simple filtration and reused at least seven times without significant loss of activity, thus making this procedure economically and environmentally more acceptable. Further work is in progress to develop new carbon-heteroatom bond formations catalyzed by this catalytic system.

Acknowledgements

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