Palladium–quaternary phosphonium phase transfer catalyst brush assembly as reusable and environmentally benign catalyst for coupling of aryl halides and sodium tetraphenylborate in neat water

Abdol R. Hajipour[a,b]* and Ghobad Azizi[a]

A first example of simultaneous covalent anchoring of a palladate anion–phosphonium cation matrix on the surface of silica nanoparticles and application in the Suzuki coupling reaction of a variety of different haloarenes and sodium tetraphenylborate in neat aqueous media without the addition of any organic co-solvent are described. Copyright © 2015 John Wiley & Sons, Ltd.

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Introduction

A palladium-catalyzed reaction between an aryl halide and an arylboronic acid yields a biphenyl derivative and is called a Suzuki coupling reaction. This transformation is a very efficient tool for building up biphenyl derivatives, which are required for many pharmaceutical intermediates[1,2] and fine chemicals.[3,4] Palladium is one of the most important transition metals used as catalyst in Suzuki coupling reactions and many ligands such as phosphine ligands,[5,6] N-heterocyclic carbene ligands[7–9] and palladacycles[10–13] have been reported for this coupling reaction. Under increasing environmental awareness and with the increasing interest in green chemistry processing, the replacement of toxic ligands and organic solvents is highly desirable. So, the Suzuki coupling reaction in aqueous media such as neat water or water–organic co-solvent has also received much attention. However, due to the limited water solubility, the use of organic substrates and catalysts in pure water without the use of any organic co-solvent remains still a challenging task. To solve this problem, most works involving aqueous media have used water-soluble ligands,[14–21] polymers[3] or phase-transfer catalysts (PTCs).[22,23] One of the major concerns in using a PTC in soluble form is its separation from the reaction mixture. By using an immobilized PTC to catalyze reactions in a liquid–liquid–solid system, those drawbacks can be easily overcome. Similarly, although homogeneous palladium catalysts have many advantages, immobilization of palladium on a solid support is a well-known methodology to allow efficient catalyst separation and to obtain metal-free products. In this regard, several methodologies have been utilized to develop the Suzuki reaction by immobilization of palladium catalysts with the aid of ionic liquids on various solid supports. Hagiwara *et al.* have demonstrated the physical coating of an ionic liquid containing homogeneous palladium acetate as a thin film on the surface of a silica support. The prepared catalyst showed efficient catalytic activity in Suzuki reactions of aryl iodides and bromides with 0.05 mol% Pd at 70°C in water–ethanol solution.[24]

Jin *et al.* have immobilized palladium acetate with a thin ionic liquid layer by covalently grafting ionic liquid molecules on the surface of the mesopore walls of MFI zeolite for Suzuki coupling in water in the presence of tetrabutylammonium bromide.[25] Rashinkar and co-workers have reported the synthesis of a heterogeneous ferrocene-tethered N-heterocyclic carbene–Pd complex using a supported ionic liquid-phase catalyst as a precursor for Suzuki coupling reaction in refluxing ethanol.[26] Yang *et al.* have reported grafting of N-heterocyclic carbene palladium complex and ionic liquid on SBA-16 as a recyclable heterogeneous catalyst for the Suzuki reaction in a 1:1 mixture of ethanol and water.[27] Wei *et al.* have developed a series of ionic liquid brush immobilized palladium catalysts for Suzuki coupling of arylboronic acids with aryl iodides and bromides in neat water without PTC and organic co-solvent.[28] The use of phosphonium salts for cross-coupling reactions was previously reported by Gerritsma *et al.* using trihexyl(tetradecyl)phosphonium chloride ionic liquid.[29] McNulty *et al.* reported the use of tetradecyltrihexylphosphonium chloride in CHCl₃.[30] Lou and Fu

* Correspondence to: Abdol R. Hajipour, Pharmaceutical Research Laboratory, Department of Chemistry, Isfahan University of Technology, Isfahan 84156, IR Iran. E-mail: haji@cc.iut.ac.ir

a Pharmaceutical Research Laboratory, Department of Chemistry, Isfahan University of Technology, Isfahan 84156, IR Iran

b Department of Neuroscience, Medical School, University of Wisconsin, 1300 University Avenue, Madison, WI 53706-1532, USA

used a palladium–tris(*tert*-butyl)phosphine system for the Suzuki reaction in tetrahydrofuran in the presence of water.[31] Recently, we have reported on the synthesis of new palladium catalysts bearing phosphonium counter cations in their structures,[32] and covalently immobilized a matrix consisting of palladate anions and phosphonium cations simultaneously on a solid support for the Heck coupling reaction.[33] The use of this catalyst was investigated in the Suzuki reaction in neat water, being an environmentally friendly procedure.

Results and discussion

The synthesis of the catalyst is divided into three stages, as described in Scheme 1: (i) the preparation of quaternary phosphonium silane coupling agent triphenyl(3-trimethoxysilylpropyl)phosphonium iodide (**1**); (ii) complexation of an excess of **1** with palladium chloride; and (iii) simultaneous immobilization of PTC and palladium catalyst on a support of silica nanoparticles. The silane coupling agent **1** was first synthesized by the reaction of triphenylphosphine and 3-(iodopropyl)trimethoxysilane in refluxing toluene.[34] Then, 16 eq. of the resulting pale yellow phosphonium salt was reacted with 1 eq. of PdCl$_2$ under an inert atmosphere at reflux temperature for 2 h in dry CHCl$_3$ to afford a dark purple solution. This solution was further treated with silica nanoparticles for 5 h at reflux temperature to form the corresponding silica-supported Pd/PTC matrix system (Fig. 1). Due to mass transfer limitations of the supported catalyst, we chose silica nanoparticles for better dispersion in reaction media.

A transmission electron microscopy image of the catalyst (Fig. 2S) shows that the average diameter of the catalyst nanoparticles is about 12 nm with a very narrow size distribution. Figure 2 shows the Fourier transform infrared (FT-IR) spectrum of the quaternary phosphonium-modified silane coupling agent **1**. Figure 3 also shows the FT-IR spectrum of quaternary phosphonium-modified
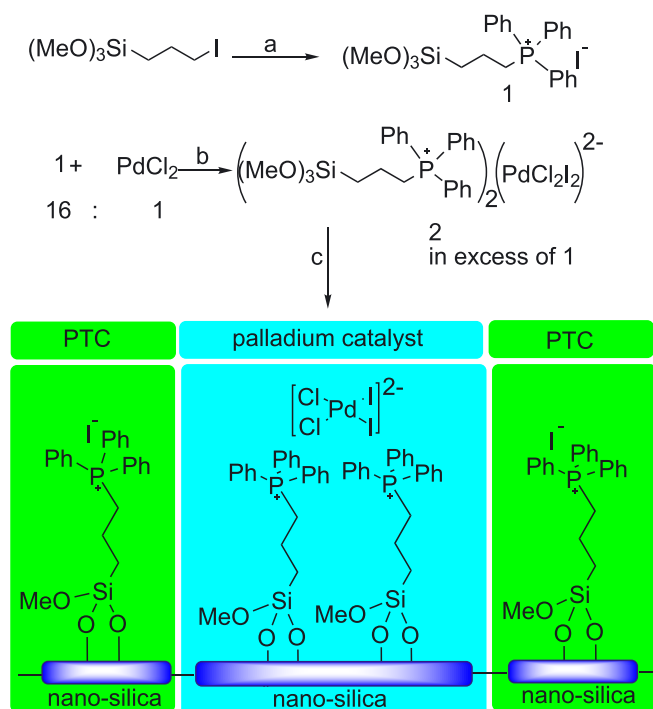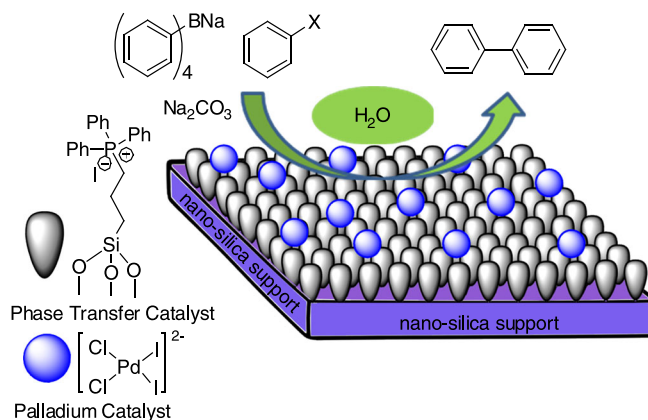

Figure 1. Pd/PTC matrix immobilized on silica nanoparticles, applied for Suzuki reaction in neat water.
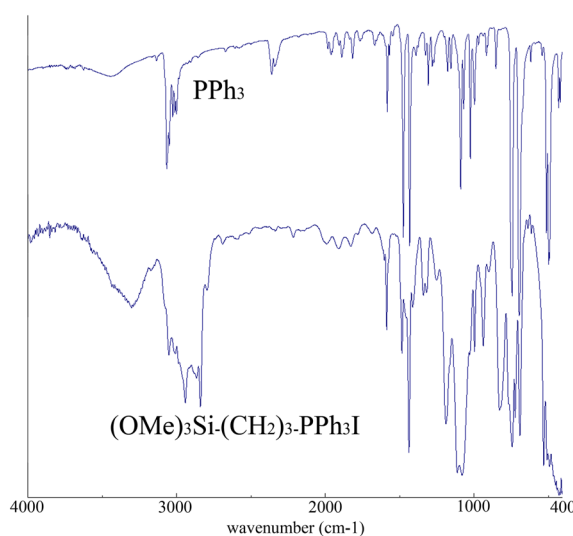

Figure 2. FT-IR spectrum of compound **2** compared with that of PPh$_3$.

nanosilica. The bands at 3065 (C–H phenyl), 1587 and 1486 (C–C phenyl), 746 and 690 cm^{-1} (C–H phenyl OOP) confirm the presence of triphenylphosphine moiety on the silica nanoparticles. No change in the FT-IR spectrum is observed upon complexation of compound **1** with palladium chloride. The ^{1}H NMR spectrum of compound **1** in CDCl$_3$ solution confirms the true structure of **1** (Fig. 3S). The diffuse reflectance UV–visible spectrum of Pd/PTC-modified nanosilica compared with that of CH$_2$Cl$_2$ solution of palladium complex **2** shows that both spectra exhibit absorption bands in the 240–280 nm region (Figs. 5S and 6S). Scanning electron microscopy combined with energy-dispersive X-ray analysis of the supported Pd/PTC shows the presence of palladium, iodide and chloride in the catalyst matrix (Fig. 7S). These results clearly indicate the successful covalent attachment of the catalyst matrix onto the silica surface.

As a type of borate source, sodium tetraphenylborate is a stable, commercially available and water-soluble reagent for the Suzuki coupling reaction. Therefore, in the work reported in this communication, we used tetraphenylborate instead of phenylboronic acid due to the solubility of the former in water.

Initially, we evaluated the effect of catalyst and base on the reaction of iodobenzene and sodium tetraphenylborate in neat water as a solvent and in the presence of palladium catalysts. The results are presented in Table 1. The reaction proceeds rapidly at room
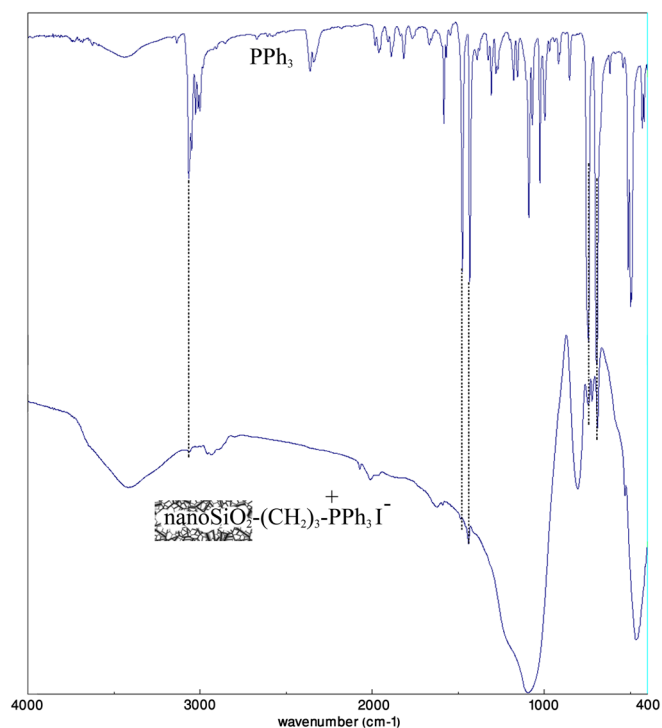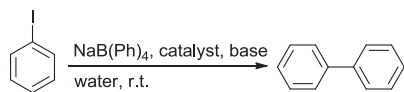

Scheme 1. Synthesis of Pd/PTC: (a) PPh$_3$, toluene, reflux; (b) CHCl$_3$, reflux; (c) silica nanoparticles, CHCl$_3$, reflux.

Figure 3. FT-IR spectrum of compound **1** immobilized on silica nanoparticles compared with that of PPh3.

Table 1. Suzuki reaction of sodium tetraphenylborate and iodobenzene under various reaction conditions[a]

Entry	Catalyst	Base	Time (h)	Conversion (%)[b]
1	Pd(OAc)2	NaOH	7	92
2	PdCl2	NaOH	7	90
3	Pd/PTC	NaOH	5	95
4	Pd/PTC	KOH	7	52
5	Pd(OAc)	Na2CO3	5	87
6	PdCl2	Na2CO3	5	85
7	Pd/PTC	Na2CO3	5	95
8	Pd/PTC	K2CO3	7	71
9	Pd/PTC	K3PO4	8	88
10	Pd/PTC	NaOAc	12	86
11	Pd/PTC[c]	Na2CO3 (2 eq.)	1	>99
12	Pd/PTC[d]	Na2CO3 (2 eq.)	1	>99

[a]Reactions carried out in water (1.5 ml) using 1 mmol of ArX, 1.2 mmol of Ph4BNa, 1.5 eq. of base, Pd(OAc)2 (0.1 mg, 0.0004 mmol) or PdCl2 (0.1 mg, 0.0006 mmol) under aerobic conditions at room temperature.
[b]GC yield based on ArI.
[c]10 mg, 0.00024 mmol of catalyst.
[d]5 mg, 0.00012 mmol of catalyst was used.

temperature in the presence of 5 mg of supported Pd/PTC (0.00012 mmol Pd) and 2 eq. of Na2CO3 as base. Among the inorganic bases utilized in this reaction, sodium bases are more reactive than potassium ones. The reaction occurs more slowly in the presence of palladium acetate and chloride, but the conversion remains high at longer reaction time.

The scope of the coupling reaction was evaluated by investigating a variety of functionalized aryl halides with sodium tetraphenylborate (Table 2). It is noteworthy that water-insoluble aryl halides react readily at room temperature using our supported Pd/PTC catalyst. The use of reflux temperature or organic co-solvents is needed under previously reported conditions.[35,36] The reactions of *ortho*-substituted aryl iodides occur slowly under such conditions, and the yield of reactions does not exceed 75%. Reactions of bromobenzenes proceed with longer reaction time at room temperature, while at reflux temperature and a greater amount of catalyst the reaction takes place in an acceptable time. Sodium tetraphenylborate also reacts with aryl chlorides in the presence of Pd/PTC and NaOH at reflux temperature in water. In the case of more reactive aryl chlorides bearing electron-withdrawing groups, the cross-coupling proceeds smoothly in the presence of NaOH as base at reflux temperature. Aryl chlorides bearing electron-donating groups react at high temperature to give the cross-coupling product in moderate yields.

As shown in Scheme 2, the supported PTC functions to bring sodium tetraphenylborate into contact with organic substrates on the solid phase as a $P^+BPh_4^-$ ion pair, liberating Na^+I^- into aqueous phase. $P^+BPh_4^-$ then reacts with Ar–X to form a Suzuki coupling product.
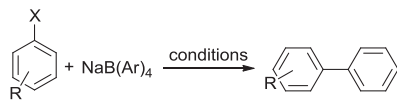
It is noteworthy that the recovered catalyst possesses high catalytic activity. Although the catalytic activity is gradually diminished, the yield is still 80% even for the seventh reuse without any activating procedure, but in longer times. After each cycle, the catalyst was recovered by centrifugation, followed by washing with water and acetone. After drying, the recovered catalyst was used for the next run. The results are presented in Table 2 (entry 1). After the first run, the purple color of the catalyst becomes black. This change indicates the formation of metallic palladium on the surface of the silica nanoparticles (Fig. 4). The formation of metallic palladium is confirmed using powder X-ray diffraction (XRD) analysis. In the XRD spectrum of the original catalyst (Fig. 5, top), a broad maximum is seen at $2\theta = 22.18°$, assigned to the amorphous silica support. This confirms the presence of highly dispersed palladium(II) deposited on the silica matrix. Moreover, apart from the original peaks, new peaks at $2\theta = 40.11°$, 46.65°, 67.86° and 82.16° which correspond to crystalline planes of palladium are observed in the spectrum (Fig. 5, bottom), indicating that metallic palladium phase exists in the form of palladium(0).

The extent of palladium leaching for the reaction of NaB(Ph)4 and iodobenzene was measured by removing the solid catalyst from reaction solution by centrifugation after completion of the reaction, and analyzing the resulting solutions using inductively coupled plasma (ICP) optical emission spectroscopy. The catalyst was examined after the first and the last reuse. No palladium leaching is observed for iodobenzene at room temperature. The extent of palladium leaching under reflux condition for bromobenzene was measured by removing the solid catalyst by centrifugation from hot reaction solution and analyzing the resulting solutions using ICP analysis. The catalyst was examined after the first and the last reuse. Palladium levels in hot filtered reaction solution are 0.1 ppm (ICP, $\lambda = 340.458$ nm, DL = 0.0440 ppm) after the first run, which eventually increase to 0.3 ppm after eight runs. The total palladium leaching after eight runs is 14% from the fresh catalyst in recycling experiments.

Experimental

General

(3-Iodopropyl)trimethoxysilane was synthesized from (3-chloropropyl)trimethoxysilane (Merck) and NaI in refluxing dry acetone for 24 h.

Table 2. Suzuki coupling reaction of various aryl halides with sodium tetraphenylborate catalyzed by Pd/PTC system

$$X\text{-}C_6H_4R + NaB(Ar)_4 \xrightarrow{\text{conditions}} R\text{-}C_6H_4\text{-}C_6H_5$$

Entry	X	R	Ar	Temp. (°C)	Time (h)	Yield (%)[a]
1	I	H	Ph	Ambient		
	TON	TOF (h^{-1})	Ph			
Run 1	7916	7916	Ph		1	95
Run 2	8000	8000	Ph		1	96
Run 3	7750	7750	Ph		1	93
Run 4	7500	7500	Ph		1	90
Run 5	7500	5000	Ph		1.5	90
Run 6	7333	4889	Ph		1.5	88
Run 7	7333	3666	Ph		2	88
Run 8	6666	3333	Ph		2	80
Total TON	59 998		Ph			
2	I	4-NO$_2$	Ph	Ambient	0.83	93
3	I	3-NO$_2$	Ph	Ambient	1	88
4	I	2-NO$_2$	Ph	Ambient	3	75
5	I	4-OMe	Ph	Ambient	7	60
6	I	2-Me	Ph	Ambient	10	70
7	Br	H	Ph	Reflux	4	96
8	Br	4-NO$_2$	Ph	Reflux	2	93[b]
9	Br	COMe	Ph	Reflux	2	95[b]
10	Br	2-COMe	Ph	Reflux	4	75[b]
11	Br	4-OMe	Ph	Reflux	12	82[b]
12	Br	4-NO$_2$	Ph	Reflux	2	90[b]
13	Br	4-CN	Ph	Reflux	1.5	89[b]
14	Br	4-CHO	Ph	Reflux	2	78[b]
15	1-Bromonaphthalene		Ph	Reflux	12	65[b]
16	9-Bromophenanthrene		Ph	Reflux	12	55[b]
17	Cl	4-COMe	Ph	Reflux	12	70[b]
18	Cl	4-CHO	Ph	Reflux	12	72[b]
19	Cl	4-NO$_2$	Ph	Reflux	12	75[b]
20	Cl	H	Ph	130	12	52[b]
21	Cl	4-OMe	Ph	130	12	48[b]
22	I	H	4-MePh	Ambient	0.75	95
23	I	H	3,5-(CF$_3$)Ph	Reflux	5	84
24	Br	H	4-MePh	Reflux	3	95
25	Br	H	3,5-(CF$_3$)Ph	Reflux	7	50
26	Cl	H	4-MePh	130	12	67

[a]Conditions: water (1.5 ml), 1 mmol of ArX, 1.12 mmol of Ph$_4$BNa, 2 eq. of base (Na$_2$CO$_3$ for aryl bromides and iodides, NaOH for aryl chlorides) and 5 mg (0.00012 mmol Pd) of Pd/PTC under aerobic conditions at room temperature.
[b]10 mg of catalyst.
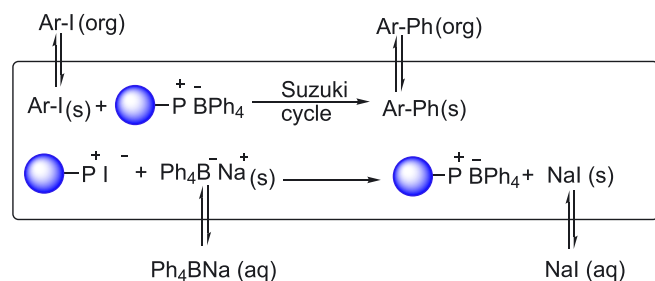
Scheme 2. Phase transfer catalysis of Suzuki reaction catalyzed by supported Pd/PTC matrix immobilized on silica nanoparticles.
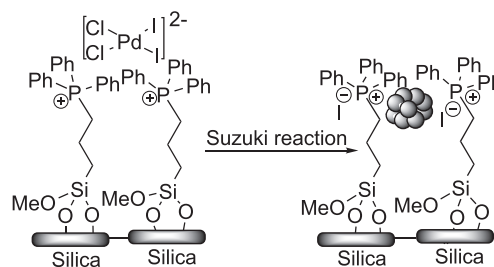

Figure 4. Formation of palladium nanoparticles after Suzuki reaction.
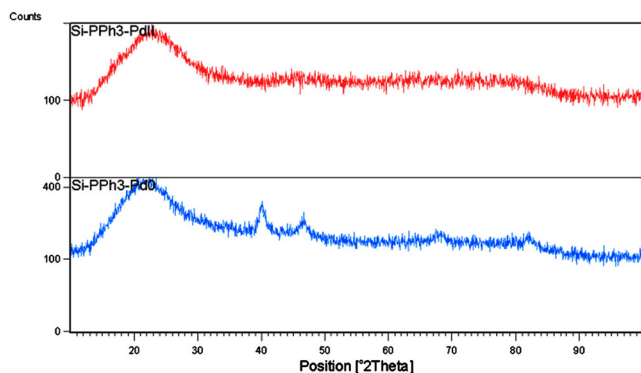
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Figure 5. Powder XRD diffraction patterns of original catalyst (top) and reused catalyst (bottom).

Palladium chloride (99%, reagent plus) was purchased from Sigma-Aldrich. Triphenylphosphine, $NaHCO_3$ and aryl halides were purchased from Merck.

NMR spectra were recorded with a Bruker Avance DPX spectrometer (^{1}H NMR 400 or 300 MHz) in $CDCl_3$ with tetramethylsilane as the internal standard. UV–visible spectra were recorded with a Jasco V-570 UV-vis-NIR spectrometer and a Jasco ARN-475 accessory for diffuse reflectance. Transmission electron microscopy images were obtained with a Philips CM10. Palladium content of the catalyst was measured using a PerkinElmer 2380 atomic absorption spectrophotometer.

Preparation of catalyst

The catalyst was prepared according to our previous work,[33] as described in the following.

Preparation of compound 1

In a well-dried 100 ml round-bottom flask, a solution of triphenylphosphine (1.311 g, 5 mmol) in dry toluene (30 ml) and (3-iodopropyl)trimethoxysilane (1.450 g, 5 mmol) were added. The system was then filled with argon three times and refluxed for 24 h under an argon atmosphere. The progress of the reaction was monitored using TLC (80:20, hexane–EtOAc). After completion of the reaction, the resulting two-phase reaction mixture was then allowed to cool to room temperature and the organic layer was separated from the phosphonium salt layer. The resulting glassy pale yellow material was then thoroughly washed with dry toluene under gentle heating (1 × 10 ml) and Et_2O (3 × 5 ml) and finally dried under vacuum (640 mmHg) for 1 h at 40°C (80%, 2.2 g, 4 mmol).

Preparation of phosphonium salt–Pd complex 2

In a well-dried 100 ml round-bottom flask equipped with magnetic stirrer bar and containing a $CHCl_3$ (40 ml) solution of **1** (2.2 g, 4 mmol) was added $PdCl_2$ (44.5 mg, 0.25 mmol). The system was then evacuated and refilled with argon. The mixture was then allowed to react with stirring at reflux temperature for 1 h under an argon atmosphere. The system was then allowed to cool to room temperature to afford a dark red–purple complex solution (Fig. 1S).

Preparation of phosphonium–Pd complex/PTC matrix immobilized on silica nanoparticles

Silica nanoparticles with a size of about 12 nm were synthesized according to a previously reported procedure.[37] Silica nanoparticles were activated by heating with aqueous 5 M HCl with vigorous stirring overnight. The activated silica was separated by centrifugation (6000 rpm, 10 min), washed thoroughly with distilled water and dried at 150°C overnight before undergoing chemical surface modification. The above solution containing 4 mmol of **1** was added to a suspension of nanosilica (10 g) in dry $CHCl_3$ (60 ml) under argon atmosphere. The resulting mixture was refluxed for 5 h. After cooling, the solid materials were filtered off and the residue was subjected to Soxhlet extraction with $CHCl_3$ overnight and then dried in an oven at 80°C to afford palladium complex/PTC matrix immobilized on silica nanoparticles as a purple solid (Fig. 1S). The final material had a palladium loading of 0.024 mmol g^{-1} as determined using atomic absorption spectroscopy.

General procedure for coupling reactions

In a 5 ml round-bottom flask equipped with magnetic stirrer bar, the aryl halide (1 mmol) was mixed with sodium tetraphenylborate (1.12 mmol), base (2 mmol), water (1.5 ml) and catalyst (5 mg). The mixture was then stirred at room temperature for the specified time. After completion of the reaction, the catalyst was removed by centrifugation and the reaction mixture was extracted with EtOAc (3 × 5 ml). The filtrates were combined together and dried over anhydrous $CaCl_2$. The solvent was evaporated under reduced pressure to give the corresponding products. In most cases, the purity of the products was found, using GC, to be more than 95% without any chromatographic purification. Other products were purified using column chromatography (80:20, hexane–EtOAc). In the case of aryl bromides and activated aryl chlorides, reactions were performed at reflux temperature. A 3 ml stainless steel reactor was used at 130°C for less reactive aryl chlorides.

Conclusions

A new supported matrix containing palladium and PTC and its application in the cross-coupling reactions of aryl halides and water-soluble sodium tetraphenylborate have been developed based on simple simultaneous anchoring of palladium and PTC on silica nanoparticles. These reactions take place in water as solvent without the need for addition of any organic co-solvent, thus rendering this process economically and ecologically acceptable.

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717