

Palladium nanoparticles supported on silica diphenylphosphinite as efficient catalyst for C-O and C-S arylation of aryl halides

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Silica diphenylphosphinite (SDPP) can be easily obtained through direct phosphorylation of silica gel. Further reaction of SDPP with Pd(II) produces nano Pd(0)/SDPP. This nano Pd(0) catalyst exhibits excellent reactivity for the C-O and C-S arylation of different aryl iodides, bromides and chloride with phenols and thiophenols. This heterogeneous catalyst shows excellent recyclability and can be easily recovered and reused for several runs. Copyright © 2013 John Wiley & Sons, Ltd.

Supporting information may be found in the online version of this article.

Keywords: silica support; palladium nanoparticle; C-O bond formation; C-S bond formation

Introduction

Diaryl ethers are an important class of organic compounds with high applicability in the polymer and life science industries as well as in medicinal chemistry.^[1,2] Due to their importance, development of efficient methods for their synthesis is still a challenging and active area of research. Apart from the conventional methods of their synthesis,^[3] methods based on using transition metals have been considered as the most popular routes and are represented by the following transformations: Ullmann-type reactions, which are based on the copper-catalyzed coupling of phenols and aryl halides,^[4] Buchwald–Hartwig palladium-catalyzed cross-couplings involving phenols and aryl halides,^{3d,5} and Chan–Evans–Lam-type reactions, which can be represented by the coupling of organoboron reagents and phenols in the presence of copper.^[6]

Because of the potential advantages of using heterogeneous catalysts for fine chemical synthesis, recently iron-catalyzed coupling has been reported.^[7] The C-O bond formation by cross-coupling of phenols with aryl iodides and bromides using natural clay as a reusable and economic solid catalyst has also been reported.^[7–9]

N-Heterocyclic carbene (NHC) rhodium catalysts have also been successfully applied for the N- and O-arylation reactions of aryl iodides and bromides.^[10,11]

Diaryl sulfides have also been found to show a broad spectrum of medicinal applications.^[12] However, the tendency of organic compounds to bind with transition metals could be partially responsible for the less studied C-S bond formation reactions compared with the C-N and C-O processes.^[13–15] To overcome the problems of traditional methods for the formation of C-S bonds which take place usually in hexamethylphosphoramide, and at elevated temperatures around 200°C,^[14] Migita and co-workers reported the cross-coupling reactions of aryl halides with thiols in the presence of Pd(PPh₃)₄.^[16] Recently, nickel,^[17] palladium,^[18] iron^[19] and cobalt^[15–20] catalysts have also been employed for this reaction. Copper salts have also been used as useful catalysts for C-S bond forming reaction.^[20]

Although thiols or metal sulfides are used as common sources of sulfur in the C-S bond formation reactions, less common sources such as thiourea and disulfides are also reported.^[21–23] The use of samarium thiolates and potassium thiocyanate has also been reported for the conversion of aryl halides to their aryl sulfides.^[24] In this regard, recently we also reported the *in situ* generated thiols for S-arylation of aryl halides.^[25] In continuation of our studies on the coupling reactions,^[26,27] we now report on the use of recently reported Pd(0)/silica diphenylphosphinite (SDPP)^[28] as a heterogeneous silica-based nano-palladium catalyst for the efficient formation of C-O and C-S bonds through the cross-coupling of phenols and thiols with aryl halides (X = I, Br, Cl) in aqueous tetra-*n*-butyl ammonium hydroxide at 70°C.

Experimental

FT-IR spectra were run on a Shimadzu FTIR-8300 spectrophotometer. ¹H and ¹³C NMR spectra were recorded on a Bruker Avance DPX-250 spectrometer using tetramethylsilane (TMS) as internal standard in pure deuterated solvents. X-ray diffraction (XRD) data were obtained with Bruker D8 Advance AXS. Analysis by transmission electron microscopy (TEM) was performed on a Philips model CM 10 instrument. Scanning electron micrography (SEM) was performed using a Philips XL-30 FEG instrument, at 20 kV. Reaction monitoring was carried out on silica gel analytical sheets or by gas chromatography (GC) using a 3 m length column packed with DC-200 stationary phase.

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Preparation of Phosphorylated Silica-Based Reagents (I–IV)

Silphos (I), silica diethylphosphite (SDEP) (II), silica diisopropylphosphite (SDIPP) (III) and silica diphenylphosphinite (SDPP) (IV) were prepared according to our previous reports.^[29,30]

Preparation of SDPP-Supported Palladium(0) Catalyst

SDPP (0.1 g) and PdCl₂ (0.25 mmol, 44 mg) or Pd(OAc)₂ (0.25 mmol, 56 mg) were added either to an aqueous solution of ⁿBu₄NOH 20% (8 ml) at 70–80°C or to DMF (10 ml) at 90–100°C for 2 h. A black precipitate was formed immediately. After 2 h, the reaction mixtures were cooled to room temperature and the precipitates were filtered and washed with distilled water (4 × 10 ml). After drying under vacuum 0.12 and 0.13 g of the Pd(0)/SDPP catalyst were obtained, respectively. The content of palladium was determined by inductively coupled plasma (ICP) analysis to be 2.5–2.6 mmol g⁻¹.

General Procedure for C–O and C–S Bond Formation Reactions of Aryl Halides with Phenols and Thiophenols with *in situ* Generated Pd(0)/SDPP

PdCl₂ (3.0 mol%, 6 mg) and SDPP (9.0 mg), NaOH (1.5 mmol, 60.0 mg), phenol (1.5 mmol) and aryl halide (1.0 mmol) were placed in a 25 ml flask equipped with a magnetic stirring bar containing 2 ml of 20% aqueous ⁿBu₄NOH. The reaction mixture was then heated at 70°C for 0.15–15 h. Completion of the reaction was monitored by GC or thin-layer chromatography. After completion of the reaction, the mixture was cooled down to room temperature and filtered to remove the catalyst. The filtrate was purified by column chromatography over silica gel using *n*-hexane/ethyl acetate (15:1) as eluent to afford the pure product in 60–99% yield (Tables 5–7). The filtered catalyst was washed with diethyl ether and reused in a similar reaction.

Results and Discussion

Metal complexes of phosphines and phosphinites are considered as the most studied catalysts in many catalytic reactions. For economic and chemical reasons, as well as the ease of synthesis,

phosphinites are considered an important class of P(III) ligands. In continuation of our studies on using Pd(0)/SDPP,^[29] we report on the use of this nano-Pd catalyst with excellent activity, stability and recyclability in C–O and C–S arylation of different aryl iodides, bromides and also chlorides.

Phosphorylated silica ligands were obtained easily through the reaction of silphos (I) with ethanol and isopropanol. SDEP (II) and SDIPP (III) were obtained by replacement of the chlorine atom of silphos by ethanol and isopropanol, respectively (Scheme 1).^[29,30]

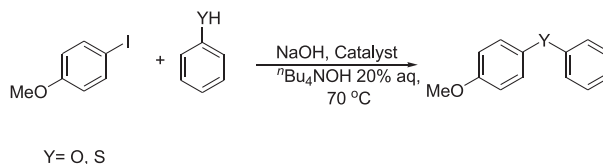
SDPP was also prepared through direct reaction of activated plate silica gel with chlorodiphenylphosphine using solvent-free conditions under argon atmosphere (Scheme 2).^[29]

In this work, the Pd(0) complexes of the two silica phosphites (II, III) and also the silica phosphinite (IV) were studied as heterogeneous catalysts for C–O and C–S arylation of aryl halides with phenols and thiophenols. First, we studied the effect of silica-based ligand (II, III and IV) on the reactivity of Pd(0) catalyst on the Ullmann and Migita reactions as versatile and sharpening methods for C–O and C–S bond formation in organic synthesis.

We initially studied the coupling of 4-iodoanisole with phenol and thiophenol as model reactions. These reactions were carried out by the *in situ* generated Pd(0) catalyst using PdCl₂ in conjunction with SDPP (IV), SDEP (II) and/or SDIPP (III) (Table 1, entries 1–3). Comparison of the results of entries 1–3 (Table 1) shows that the reaction occurs slightly faster in the presence of SDPP (IV). Since SDPP contains a higher loading of the active P (III) content compared to the SDEP and SDIPP,^[29] and showed slightly more reactivity in the reactions of 4-iodoanisole with phenol and thiophenol, it was selected as the most suitable silica-based P(III) ligand for this study. We next prepared the complex of Pd(0)/SDPP according to our previous report^[29] and performed the reaction in the presence of this catalyst. This comparative study showed that no considerable change in the reaction time and the isolated yield was observed (Table 1, entry 4). Therefore it was concluded that the reaction can be performed either in the presence of the pre-prepared Pd(0)/SDPP or using the *in situ* generated catalyst.

We optimized the reaction conditions for the use of SDPP (IV) as a heterogeneous ligand for the carbon–oxygen and carbon–sulfur coupling reactions between 4-iodoanisole and phenol or thiophenol.

Table 1. Reaction of 4-iodoanisole with phenol and thiophenol in the presence of different phosphorylated silica based ligands^a



Entry	Time (h) phenol/thiophenol	Catalyst	Isolated yield (%) phenol/thiophenol
1	4 (2)	PdCl ₂ /SDPP	97 (95)
2	5 (3)	PdCl ₂ /SDEP	95 (93)
3	5 (3)	PdCl ₂ /SDIPP	93 (90)
4	4 (2)	Pd(0)/SDPP ^b	96 (94)
5	24 (24)	PdCl ₂	60 (67)

^aReaction conditions: 0.006 g PdCl₂, 0.009 g SDPP, 1.0 mmol 4-iodoanisole, 1.5 mmol phenol or thiophenol, 1.5 mmol NaOH, 2.0 ml 20% aqueous solution ⁿBu₄NOH.

^bPd(0)/SDPP (0.004 g).

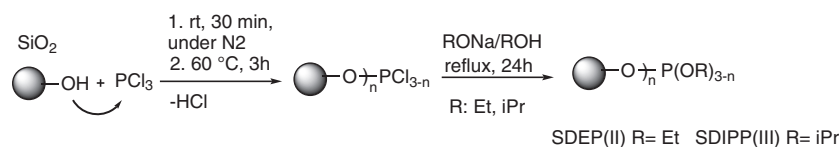
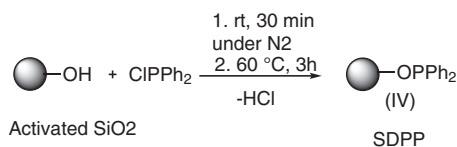
**Scheme 1.** Preparation of silphos (I), SDEP (II) and SDIPP (III).**Scheme 2.** Preparation of SDPP (IV) from activated silica.

Table 2. Effect of different solvents on the reaction of 4-iodoanisole with phenol/thiophenol in the presence of PdCl₂/SDPP^a

Entry	Time (h) phenol/thiophenol	Isolated Yield (%) phenol/thiophenol	Solvent	Time (°C)
1	7/5	75/80	DMF	120
2	5/3	80/85	DMSO	120
3	3/1	70/80	PEG	120
4	7/1	60/63	H ₂ O	100
5	7/1	60/63	Toluene	100
6	3/1	75/70	ⁿ Bu ₄ NOH	100
7	4/2	97/95	ⁿ Bu ₄ NOH	70
8	4/2	65/62	ⁿ Bu ₄ NOH	50
9	24/24	30/35	ⁿ Bu ₄ NOH	rt

^aReaction conditions: 0.006 g PdCl₂, 0.009 g SDPP, 1.0 mmol 4-iodoanisole, 1.5 mmol phenol/thiophenol, 1.5 mmol NaOH, 2.0 ml 20% aqueous solution ⁿ Bu₄NOH.

Table 3. Effect of different bases on the reaction of 4-iodoanisole with phenol/thiophenol^a

Entry	Base	Time (h) phenol/thiophenol	Conversion yield (%) phenol/thiophenol
1	NaOH	4/2.5	97/95
2	K ₂ CO ₃	5/3.5	90/80
3	Cs ₂ CO ₃	4/2.5	97/95
4	Et ₃ N	8/7	40/46
5	None	10/8	32/30

^aReaction conditions: 0.006 g PdCl₂, 0.009 g ligand, 1.0 mmol 4-iodoanisole, 1.5 mmol phenol/thiophenol, 1.5 mmol NaOH, 2.0 mL aqueous ⁿBu₄NOH.

Table 4. Effect of different amounts of Pd and SDPP on the reaction of 4-iodoanisole with phenol/thiophenol^a

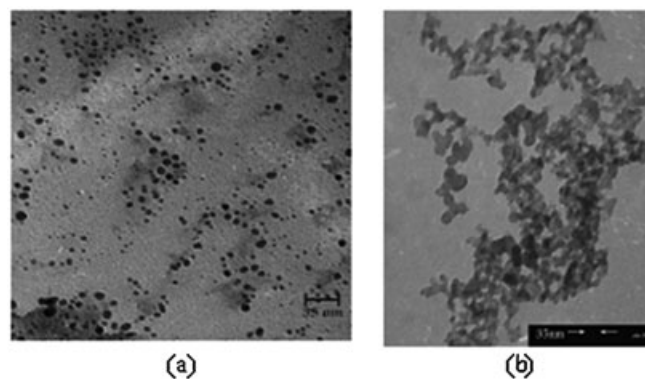
Entry	SDPP (g)	PdCl ₂ (g)	Time (h) phenol/thiophenol	Isolated yield (%) phenol/thiophenol
1	0.005	0.003	7/6	50/50
2	0.008	0.004	5/4	85/80
3	0.009	0.006	4/2.5	97/95
4	0.009	0.003	6/5	60/60

^aReaction conditions: 1.0 mmol 4-iodoanisole, 1.5 mmol phenol, 1.5 mmol NaOH, 2.0 ml 20% aqueous ⁿBu₄NOH.

The effect of different solvents was also studied on the reaction of 4-iodoanisole with phenol and or with thiophenol at different temperatures and it was found that these reactions do not complete in different organic solvents such as DMF, DMSO, polyethylene glycol (PEG) and toluene, or in neat H₂O (Table 2, entries 1–7). Although the reaction did not complete in water, because of the problems and disadvantages in using organic solvents we decided to use aqueous ⁿBu₄NOH as solvent. We therefore tried our model coupling reaction in this solvent at different temperatures (Table 2, entries 6–9). It was observed that the use of ⁿBu₄NOH as solvent at 70°C was very suitable and the reaction went to completion after 4 h (Table 2, entry 7).

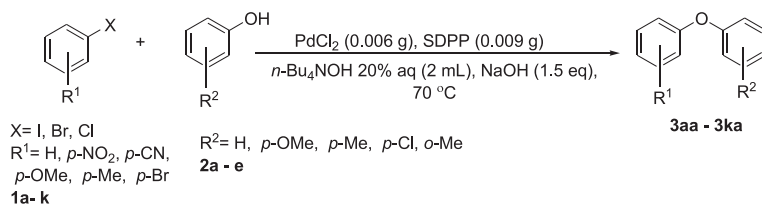
Our study on the use of organic and inorganic bases showed that, among these bases, Cs₂CO₃ and NaOH are the most suitable ones for the reaction of 4-iodoanisole with phenol or thiophenol under the catalytic system of PdCl₂/SDPP using ⁿBu₄NOH as solvent at 70°C (Table 3, entries 1 and 3). In the absence of base, the reactions with both phenol and thiophenol were found to be very slow, and after 10 and 8 h only 32% and 30% conversion was observed, respectively (Table 3, entry 5).

In continuation, we investigated the optimum amount of the required PdCl₂ and SDPP for the reaction of 4-iodoanisole with phenol. On the basis of this study, the amount of PdCl₂ (0.006

**Figure 1.** TEM of Pd-supported SDPP prepared (a) in DMF^[19] and (b) in aqueous ⁿBu₄NOH.

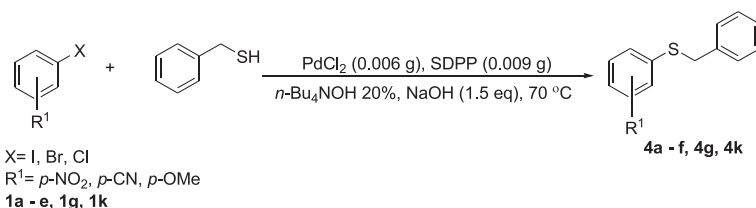
g) and SDPP (0.009 g) were found to give the most efficient and suitable catalytic system (Table 4, entry 3).

Since the reaction in ⁿBu₄NOH was found to be much better than in other solvents, we decided to prepare the Pd(0)/SDPP catalyst in this solvent and compare its nano size with the one which we have already prepared in DMF^[29] and use it in this

Table 5. Ullmann reaction of aryl halides with phenols catalyzed by Pd/SDPP^a

Entry	Aryl halide	Phenol	Time (h)	Product ^[Ref.]	Isolated yield (%)
1	Ph-I (1a)	Ph-OH (2a)	1.5	PhOPh (3aa) ^[20]b,c]	98
2	4-MeOPh-I (1b)	Ph-OH (2a)	4	4-MeOPhOPh (3ba) ^[20]b,c]	97
3	4-NO ₂ Ph-I (1c)	Ph-OH (2a)	0.5	4-NO ₂ PhOPh (3ca) ^[20]c]	92
4	Ph-I (1a)	4-MeO-PhOH (2b)	6	PhOPhOMe-4 (3ab) ^[20]b,c]	80
5	Ph-I (1a)	4-Me-Ph-OH (2c)	5	PhOPhMe-4 (3ac) ^[20]b,c]	85
6	Ph-I (1a)	2-Me-Ph-OH (2d)	5	PhOPhMe-2 (3ad) ^[20]c]	80
7	Ph-I (1a)	4-Cl-Ph-OH (2e)	10	PhOPhCl-4 (3ae) ^[20]c,d]	70
8	4-NO ₂ Ph-Br (1d)	2-Me-Ph-OH (2d)	6	4-NO ₂ PhOPhMe-2 (3dd) ^[20]c]	90
9	4-NO ₂ Ph-Br (1d)	4-Me-Ph-OH (2c)	6	4-NO ₂ PhOPhMe-4 (3dc) ^[20]c]	99
10	4-NO ₂ Ph-Br (1d)	Ph-OH (2a)	2.5	4-NO ₂ PhOPh (3da) ^[20]b]	90
11	4-CNPh-Br (1e)	Ph-OH (2a)	3	4-CNPhOPh (3ea) ^[20]b]	90
12	4-BrPh-Cl (1f)	Ph-OH (2a)	4	4-BrPhOPh (3fa) ^[20]d]	90
13	4-CNPh-Cl (1g)	Ph-OH (2a)	6	4-CNPhOPh (3ga) ^[20]b]	85
14	4-NO ₂ Ph-Cl (1k)	Ph-OH (2a)	5	4-NO ₂ PhOPh (3ka) ^[20]b]	85

^aReaction conditions: 0.006 g PdCl₂, 0.009 g SDPP, 1.0 mmol 4-iodoanisole, 1.5 mmol phenol, 1.5 mmol NaOH, 2.0 mL 20% aqueous ⁿBu₄NOH.

Table 6. Migita reaction of aryl halides with benzyl mercaptane^a

Entry	Aryl halide R ¹ (X = halogen)	Time (h)	Product ^b	Isolated yield (%)
1	Ph-I (1a)	0.8	4a	94
2	4-MeOPh-I (1b)	2	4b	93
3	4-NO ₂ Ph-I (1c)	0.1	4c	96
4	4-NO ₂ Ph-Br (1d)	1	4c	87
5	4-CNPh-Br (1e)	2	4e	92
6	4-CNPh-Cl (1g)	5	4e	80
7	4-NO ₂ -Ph-Cl (1k)	4.5	4c	87

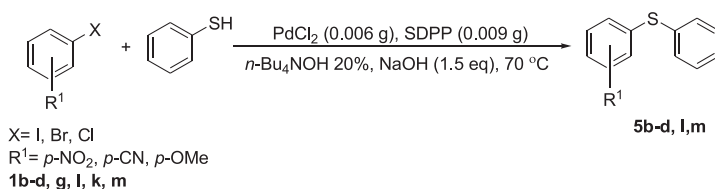
^aReaction conditions: 0.006 g PdCl₂, 0.009 g SDPP, 1.0 mmol 4-iodoanisole, 1.5 mmol of benzylmercaptane, 1.5 mmol NaOH, 2.0 ml 20% aqueous ⁿBu₄NOH.

^bAll the products are known compounds and identified by comparison with known samples.^[25]

study (Table 1, entry 4). We therefore reacted SDPP with PdCl₂ in aqueous solution of ⁿBu₄NOH at the optimized temperature of 70–80 °C, as we reported before at 90–100 °C in DMF.^[29] In ⁿBu₄NOH, Pd(0)/SDPP was obtained as a black precipitate. Determination of the Pd content was carried out by ICP analysis on digested catalyst in refluxing aqueous HCl (37%). The obtained results revealed that the immobilization of Pd in Pd(0)/SDPP prepared in both solvents was very similar and was in the range 2.5–2.6 mmol g⁻¹. SEM and

TEM images of the catalyst obtained in aqueous solution of ⁿBu₄NOH were very similar to those we have already reported for DMF. The TEM image of Pd(0)/SDPP in aqueous solution of ⁿBu₄NOH and DMF showed that Pd nanoparticles were formed in the silica matrix with an average size of ~7 nm (Fig. 1a, b).

This study showed that the nano sizes of the obtained catalysts in both solvents were nearly the same but the reaction was much more efficient in ⁿBu₄NOH than in DMF. Therefore, the obtained

Table 7. Migita reaction of aryl halides with thiophenols^a

Entry	Aryl halide R ¹ (X = Halogen)	Time (h)	Product ^[Ref.]	Isolated yield (%)
1	4-MeOPh-I (1b)	2.5	5b ^{13d}	95
2	4-NO ₂ Ph-I (1c)	0.1	5c ^{13c}	95
3	4-NO ₂ -2-MePh-I (1l)	1.5 ^b	4l	94
4	4-NO ₂ Ph-Br (1d)	2	5d ^{13c}	90
5	4-CNPh-I (1m)	3	5m ^{13e}	87
6	4-CNPh-Cl (1g)	6	5m ^{13e}	85
7	4-NO ₂ Ph-Cl (1k)	5	5k ^{13c}	87

^aReaction conditions: 0.006 g PdCl₂, 0.009 g SDPP, 1.0 mmol 4-iodoanisole, 1.5 mmol thiophenol, 1.5 mmol NaOH, 2.0 ml 20% aqueous ⁿBu₄NOH.

^b¹H-NMR (250 MHz, CDCl₃) δ (ppm): 2.53 (s, 3H), 7.2–7.39 (m, 5H), 7.7–7.9 (m, 3H); ¹³C-NMR (62.9 MHz, CDCl₃) δ (ppm): 20.2, 121.4, 125.0, 127.4, 129.0, 129.5, 130.0, 134.3, 136.0, 145.1, 147.5; C₁₃H₁₁NO₂S requires: C, 63.65; H, 4.52; N, 5.71; found: C, 63.38; H, 4.69; N, 5.80.

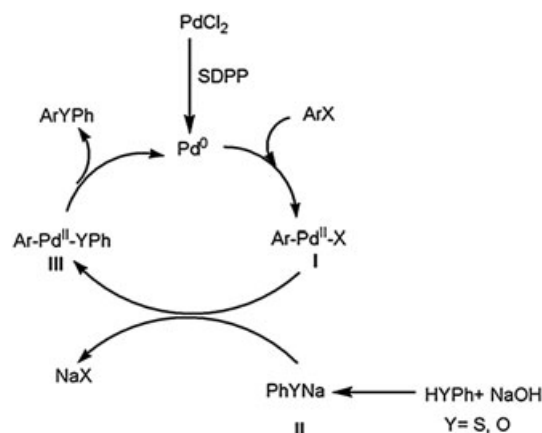
Table 8. Recycling of Pd catalyst for the reaction of iodobenzene with phenol

Run	Time (min)	Pd leaching (%) ^b	Isolated yield (%)	TON ^c
1	90	3.2	99	33
2	90	3.6	92	30
3	110	4.2	88	29
4	150	5.4	75	25
5	180	7.4	60	20

^aReaction conditions: iodobenzene (1.0 mmol), phenol (1.5 mmol), NaOH (1.5 mmol), Pd(0)/SDPP (4 mg, 1.0 mol%) at 70 °C.

^bThe analysis was performed by ICP technique.

^cTON, mmoles of product/mmoles of catalyst.

**Figure 2.** General mechanism for Pd-catalyzed aryl ether and aryl thioether synthesis.

optimum conditions were applied in ⁿBu₄NOH for *O*- and *S*-arylation of aryl halides. In general, we were successful in performing the reaction between aryl iodides and bromides as well as aryl chlorides with phenols (Tables 5 and 7) and thiols (Tables 6 and 7). A substituent such as methyl at the *ortho* position of the phenol, which has some steric effect, produced the desired product in high yield (Table 5, entries 6 and 8). The catalytic system was equally efficient for electron-deficient aryl halides such as 1-bromo-4-nitrobenzene and 4-bromobenzonitrile, (Table 5, entries 8–11). Among the aryl halides studied, it was observed that 2-iodotoluene did not produce the *O*-arylated product and gave the homo-coupling product as the major one. Also we observed that the derivatives of pyridines were inactive in this reaction. In addition, the reaction could be affected by steric effects and highly sterically hindered phenols such as 2,5 di-*tert*-butylphenol and for aryl halides such as 1-iodo-2-methylbenzene did not perform the *O*-arylation reaction; instead, a homocoupling reaction occurred. However, the coupling reaction of 1-iodonaphthalene with phenol completed within 4 h and the corresponding 1-phenoxy-naphthalene was isolated in 80% yield.

Due to the importance of using heterogeneous catalysts in industry, the recovery and reusability of Pd(0)/SDPP catalyst was

investigated in the coupling reaction of iodobenzene with phenol as the model substrate. To probe the palladium leaching in our system, the filtrate of the reaction between iodobenzene and phenol was analyzed by ICP in six repeating cycles. Low palladium leaching was observed during the experiments, illustrating that the catalyst was highly reusable. The Pd catalyst exhibited only a slight loss in its activity and required a slightly longer reaction time to achieve full conversion during three cycles. Analysis of the crude reaction mixture for the first reaction indicates a leaching of 3.2% of the palladium. Residual palladium levels present in the solution in different catalytic runs were analyzed. This catalytic system shows only 7.4% (0.042 mg) palladium leaching after five runs. The results are tabulated in Table 8.

In order to know whether the reaction took place heterogeneously at the surface of solid Pd or the leaching Pd acts as catalyst, the hot filtration test was performed. The reaction of iodobenzene and phenol in the presence of Pd(0)/SDPP in ⁿBu₄NOH at 70 °C was monitored after 20 min by GC analysis, which showed

45% conversion. The reaction mixture was filtered off to remove the catalyst and the filtrate was left to react further. ICP analysis of the filtrate showed 2.5% of Pd leaching. GC analysis showed that after 1.5 h only 55% conversion had occurred. This observation demonstrates that the solid catalyst had the main function as a heterogeneous catalyst in this catalytic system.

A mechanistic pathway was proposed (Fig. 2). Pd(II) was reduced by SDPP to the nanoparticles of Pd(0), followed by the oxidative addition of aryl halide to give the aryl palladium species (**1a**). This species could then react with species **2a** to produce **3a**, which underwent reductive elimination to give the product together with the regenerated Pd(0) catalyst (Fig. 2).

Conclusion

We have developed a useful and efficient procedure for preparation of aryl ethers and aryl thioethers in good to excellent yields by a catalytic coupling reaction between phenols or thiophenols and aryl halides using nanoparticles of Pd(0)/SDPP as catalyst. The method is applicable to aryl iodides, bromides as well as chlorides and was also found to be useful for coupling of benzyl thiol. The ease of synthesis and recyclability of the catalyst together with the mild reaction conditions make this method very useful for this transformation.

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