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Nano tetraimine Pd(0) complex as an efficient catalyst for phosphine-free Suzuki reaction in water and copper-free Sonogashira reaction under aerobic conditions

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A nano tetraimine Pd(0) complex catalyst was successfully used as an efficient heterogeneous catalyst for the phosphine-free palladium-catalysed Suzuki coupling reaction in water at 80 °C. This nano tetraimine Pd(0) complex was also used for copper-free Sonogashira reaction in dimethylformamide at 100 °C. The catalyst was easily recovered from the reaction mixture by centrifugation and reused for at least six cycles without any significant loss in its catalytic activity. Analysis of the reaction mixture using inductively coupled plasma analysis showed that leaching of palladium from the catalyst was negligible. The reactions can be performed efficiently for aryl iodides, bromides and also chlorides. Copyright © 2016 John Wiley & Sons, Ltd.

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Keywords: nano tetraimine Pd(0) complex; Suzuki reactions; Sonogashira reactions; phosphine-free and copper-free; heterogeneous catalyst

Introduction

Palladium is one of the most critical metals in catalysis and it is generally used to catalyse a wide variety of carbon–carbon bond forming reactions.[1] Palladium complexes of a large number of phosphorus,[2] carbene,[3] oxime,[4] imine[5] and other ligands[6] have been reported as catalysts for such coupling.

Nitrogen-donor ligands were pioneered at the end of the nineteenth century. These ligands perform a highly significant role in the field of coordination chemistry.[7] Nitrogen coordination compounds such as imidazole, benzimidazole, imines, pyridine or pyrazole as well as thioether or mercapto groups[8,9] have been designed to produce different kinds of transition metal complexes. Some of these complexes have been shown to possess some characteristics of proteins[10] or to exhibit biocidal activities such as antibacterial, antifungal, pesticidal[11] and catalytic activities.[12,13]

Carbon–carbon bond formation is among the most important reactions in organic chemistry.[14] Transition metals or their complexes have been applied as catalysts and promoters in many of these reactions.[15] To catalyse a large variety of carbon–carbon bond forming reactions, palladium is one of the most essential transition metals which is commonly used.[1] Various kinds of cross-coupling reactions have been investigated; among them coupling reactions such as the Heck–Mizoroki reaction,[16–18] the Suzuki reaction,[19,20] the Sonogashira reaction,[21–24] the Kumada reaction,[25] the Negishi reaction[22,26] and the Stille reaction are interesting examples of C–;C bond formation.[27]

Various types of palladium catalytic systems have been reported for these valuable cross-coupling reactions.[28–35] Phosphine ligands have been used for the promotion of these reactions; however, they are sensitive to air and moisture. Thus air-free and dry conditions pose significant inconvenience for synthetic applications of phosphine ligands.[36–38] A key feature for phosphine-free catalysts is the stabilization of an active catalyst, which is highly related to ligand stability, chelation or steric shielding of the metal centre and the strength of the metal–ligand bond. Therefore, transition metal complexes containing nitrogen-donor ligands have received much attention and can stabilize various oxidation states of metals by strong electron-donating ligands to the metal centre.[39,40] In addition, in the Sonogashira coupling reaction, the formed copper acetylides very much tend to undergo homocoupling reaction (Glaser coupling).[41,42] Thus, several synthetic methodologies have been designed to eliminate copper and phosphine from reaction mixtures.[43–45] Most of the palladium catalysts that have been used in the Suzuki and Sonogashira reactions are homogeneous.[46–49] Although homogeneous palladium catalysts often offer higher activities for these reactions, they suffer from disadvantages such as difficulties in product separation, handling sensitive ligands and catalyst recovery, and recycling of expensive ligands and palladium complexes. These problems can be solved by the use of heterogeneous catalysts consisting of supported palladium complexes. These heterogeneous catalysts can be simply recovered from the reaction mixture by simple filtration or centrifugation and then they can be reused in further reactions.[50–58] Some heterogeneous catalysts have been supported on carbon nanofibers,[59] montmorillonite,[60] magnetic mesoporous silica,[61] metal oxides[62] and zeolites.[63]

Recently various heterogeneous catalysts have been reported, such as polymer-supported *N*-heterocyclic carbene–palladium catalyst for Sonogashira reactions,[64] poly(vinyl chloride)-

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supported Pd(II) complex for Sonogashira reactions,[65] Pd(II) Schiff base complex supported on multiwalled carbon nanotubes for Suzuki and Sonogashira reactions,[66] palladium supported on feather keratin for Suzuki reactions,[67] palladium particles from oxime-derived palladacycle supported on Fe_3O_4/oleic acid for Sonogashira reactions,[68] PCP-pincer palladium nanoparticles supported on modified Merrifield resin for carbon–carbon cross-coupling reactions[69] and HypoGel-supported palladium nanocatalysts for Suzuki reactions.[70] The features of these catalysts have made them important from environmental and economic points of view due to their facile recycling and ease of separation.

Very recently, we have introduced a novel nano tetraimine Pd(0) complex as a heterogeneous catalyst for the Heck–Mizoroki coupling reaction of aryl halides with *n*-butyl acrylate in water.[71] Herein, we describe another application of this heterogeneous nano tetraimine Pd(0) complex for the phosphine-free Suzuki and copper-free Sonogashira coupling reactions.

Experimental

General

All chemicals were purchased from Merck, Fluka or Acros and were used without any further purification. The progress of the reactions was followed by TLC using silica gel polygrams SIL G/UV 254 plates or by GC using a Shimadzu GC-14A gas chromatograph, equipped with a flame ionization detector and a 3 m length glass column packed with DC-200 stationary phase and nitrogen as the carrier gas. Fourier transform infrared (FT-IR) spectroscopic analysis of samples was conducted using a Shimadzu FT-IR 8300 spectrophotometer, with samples and KBr pressed to form tablets. ^1H NMR and ^{13}C NMR spectra were recorded with a Bruker Avance DPX 250 MHz spectrometer in $CDCl_3$ or DMSO-d_6 solvents using tetramethylsilane as an internal standard. Mass spectra were obtained at 70 eV. The amount of palladium nanoparticles supported on *N*,*N*-bisimine ligand was measured using an inductively coupled plasma (ICP) analyser (Varian, Vista-pro) and atomic absorption spectroscopy. All yields refer to the isolated products. Elemental analysis was done with a 2400 series PerkinElmer analyser. Melting points were determined with a Buchi 510 instrument in open capillary tubes and are uncorrected. All products were identified by comparison of their spectral data and physical properties with those of authentic samples.

Procedure for preparation of *N*,*N*-bisimine ligand (3)

Ethylenediamine (2.0 mmol, 0.13 ml) was dissolved in 10 ml of ethanol and added dropwise to a stoichiometric amount of 4-chlorobenzaldehyde (4.0 mmol, 0.56 g) dissolved in 5 ml of ethanol. The crude mixture was stirred at room temperature for 10 h to give ligand **3** as a white precipitate. The resulting product was separated by filtration and washed with ethanol (2 × 5 ml) and then dried in vacuum. The crude product was recrystallized from ethanol to obtain the pure product.

General procedure for preparation of nano tetraimine Pd(0) complex (4)

The synthesis of the nano tetraimine Pd(0) complex catalyst was conducted according to a procedure previously reported.[71] The nano tetraimine Pd(0) complex was prepared by reacting a mixture of $Pd(OAc)_2$ (1.0 mmol, 0.22 g) and a solution of **3** (2.0 mmol, 0.61 g) in ethanol (10 ml) under nitrogen atmosphere. The mixture was refluxed for 3 h to complete the reaction. After that, the resulting solid product was centrifugation and washed with hot ethanol (3 × 2 ml) and water (3 × 2 ml) and dried at 80 °C overnight. Yield: 0.64 g (92.7%).

The catalyst was characterized using FT-IR spectroscopy, X-ray diffraction, X-ray photoelectron spectroscopy, UV–visible spectroscopy and elemental analysis. FT-IR spectra of pure *N*,*N*-bisimine ligand and its nano tetraimine Pd(0) complex were obtained. The spectrum of the *N*,*N*-bisimine ligand exhibits a band at 1643 cm^{-1} due to azomethine ν(C=;N) stretch. From the ICP and atomic absorption spectroscopy results, the amount of palladium is 0.78 mmol per gram of the complex.

General procedure for Suzuki reaction using nano tetraimine Pd(0) complex as catalyst

To a 10 ml flask equipped with a magnetic stirring bar was added a mixture of nano tetraimine Pd(0) complex (0.2 mol%, 0.003 g, contains 0.0025 mmol of palladium), NaOH (2 mmol), phenylboronic acid (1.2 mmol), aryl halide (1.0 mmol) and water (3.0 ml) which was heated at 80 °C. The completion of the reaction was monitored by TLC or GC. After that, the resulting hot reaction mixture was filtered quickly through a thick cellulose filter paper under reduced pressure and washed with diethyl ether (2 × 5 ml). The combined organic phase was separated and dried over anhydrous Na_2SO_4 and evaporated under vacuum. The resulting crude product was purified by flash chromatography to give the desired pure product in high to excellent (78–96%) isolated yields.

General procedure for copper-free Sonogashira reaction using tetraimine Pd(0) complex as catalyst

Phenylacetylene (1.2 mmol) was added to a suspension of aryl halide (1.0 mmol), K_2CO_3 (2.0 mmol) and palladium complex (0.4 mol%, 0.005 g, contains 0.004 mmol of palladium) in dimethylformamide (DMF; 3 ml) in a10 ml reaction flask. The reaction mixture was stirred at 100 °C for an appropriate time. The progress of the reaction was monitored by TLC or GC. After completion of the reaction and separation of catalyst by simple filtration, 15 ml of water was added and the mixture was extracted with diethyl ether (2 × 5 ml). The organic phase was washed with water (2 × 10 ml) and dried over anhydrous Na_2SO_4. Then, the solvent was removed under reduced pressure. The resulting crude product was purified by flash chromatography to give the desired cross-coupling products in excellent (70–96%) isolated yields.

General procedure for recycling of catalyst in Suzuki and Sonogashira reactions

In a 5 ml flask, iodobenzene (2 mmol, 0.2 ml) was reacted with phenylboronic acid (2.4 mmol, 240 mg) in neat water (6 ml) in the presence of nano tetraimine Pd(0) complex (6 mg, contains 0.0050 mmol of palladium) and NaOH (4 mmol, 160 mg) at 80 °C. After completion of the reaction as determined using GC and TLC analysis and cooling the mixture to room temperature, the black solid catalyst was separated by centrifugation and washed with diethyl ether to remove any remaining organic compound. The catalyst was dried in a vacuum oven and was used again for the next run in another batch of the reaction. This recycling was repeated for six runs without appreciable loss of activity of the catalyst.

For the Sonogashira reaction, after completion of the reaction of iodobenzene (2.0 mmol, 0.02 ml) with phenylacetylene (2.4 mmol, 0.26 ml) and K_2CO_3 (4.0 mmol, 0.55 g) in DMF (6 ml) in the presence of nano tetraimine Pd(0) complex (10 mg, contains 0.0080 mmol of palladium), the reaction mixture was centrifuged to separate solid material and washed with diethyl ether. The catalyst was dried and reused for a similar reaction. The recycling of the catalyst was repeated for six runs without appreciable loss of its catalytic activity.

Large-scale Suzuki and Sonogashira reactions

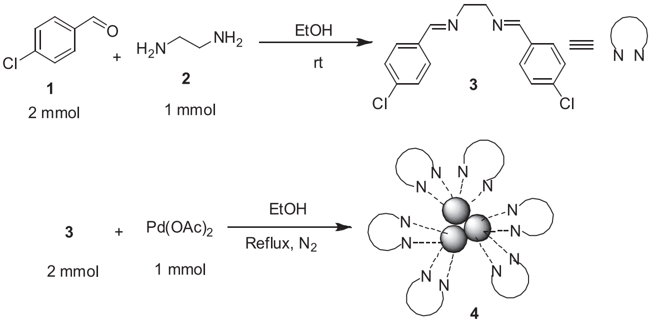
We also studied large-scale Suzuki and Sonogashira reactions. For this goal, according to the general procedure, iodobenzene (10 mmol, 1.0 ml) and 2.0 mol% (0.05 g) of the Pd(0) complex were reacted with phenylboronic acid (12 mmol, 1.2 g) and NaOH (20 mmol, 0.8 g) in water (30 mL) and with phenylacetylene (12 mmol, 1.3 ml) and K_2CO_3 (20 mmol, 2.76 g) in DMF (30 ml), respectively, for Suzuki and Sonogashira reactions. After workup, the desired coupled products were obtained in 90% yield (1.36 g, 154.2 g mol^{-1}) for Suzuki reaction and 86% yield (1.53 g, 178.23 g mol^{-1}) for Sonogashira reaction. The catalyst was also separated as described above and reused for the next run.

Results and discussion

In this study, ligand **3** was synthesized from 4-chlorobenzaldehyde (**1**) and 1,2-ethandiamine (**2**) in ethanol at room temperature. Ligand **3** was used for the synthesis of nano tetraimine Pd(0) complex **4** in the presence of $Pd(OAc)_2$ under nitrogen atmosphere in ethanol reflux (Scheme 1).[71]

Catalytic application of nano tetramine in Suzuki cross-coupling reactions

To explore the catalytic activity, the Suzuki cross-coupling reaction of aryl halides with phenylboronic acid was conducted. The rate of the coupling reaction is dependent on a variety of parameters such as solvent, base, temperature and catalyst loading. For optimization of the reaction conditions, we chose the cross-coupling of 4-iodobenzene (1.0 mmol) with phenylboronic acid (1.2 mmol), under aerobic conditions, as a model reaction using the nano tetraimine Pd(0) complex (0.2 mol%, 0.003 g) as catalyst in water at 80 °C for 4 h in the presence of 2 mmol of base. The catalyst and the effect of solvent, base, temperature and also the amount of catalyst on the reaction were examined (Table 1). As evident from Table 1, of the screened bases, NaOH shows the best result, and the corresponding coupling product is obtained in 95% yield (Table 1, entry 1). When the amount of catalyst is decreased from 0.004 to 0.001 g, the yield of product is decreased to 28% (Table 1, entry 12). The effect of temperature on the activity of the catalyst was also studied by carrying out the model reaction at various temperatures; the best result is obtained at 80 °C (Table 1, entry 1). Furthermore, we also investigated the use of various protic and aprotic solvents such as DMF, *N*-methyl-2-pyrrolidone (NMP), dimethylsulfoxide (DMSO), CH_3CN, EtOH, EtOH–H_2O, tetrahydrofuran and toluene at 90 °C (Table 1, entries 1–11), with excellent yields of the product being obtained in water (Table 1, entry 1).



Scheme 1. Route for synthesis of nano tetraimine Pd(0) complex.

Furthermore, under these optimized conditions, we investigated the usefulness of the catalyst in the Suzuki reaction involving cross-coupling of an aryl halide with phenylboronic acid. Table 2 illustrates that the reaction is effective in the presence of a wide variety of functional groups on aryl iodides, aryl bromides and aryl chlorides, giving good to excellent conversions to the corresponding products.

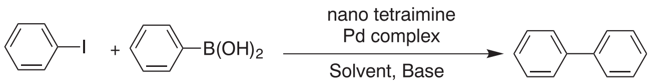
Aryl halides with electron-donating groups (Table 2, entries 2, 7–9, 13) are less active than those with electron-withdrawing groups (Table 2, entries 3, 5, 6, 11, 12). As expected, the coupling of phenylboronic acid with iodides or bromides leads to the desired products in moderate to high yields (Table 2, entries 1–9). In particular, the reaction of aryl iodide substituted with electron-withdrawing groups affords high yield after 0.5 h at 100 °C (Table 2, entry 3). In the case of deactivated bromides, longer reaction time is required for the reaction to produce good yields (Table 2, entries 7–9). The catalyst effect is also evident for chlorides, where only those substituted with electron-withdrawing groups give reasonable yields for the coupling product (Table 2, entries 11 and 12). Non-activated aryl chlorides gave a low yield in coupling reactions under similar conditions (Table 2, entry 13).

Catalytic application of nano tetramine in Sonogashira coupling reaction

Upon screening the reaction conditions for the copper-free Sonogashira coupling with the nano tetraimine Pd(0) complex catalyst, we find that the reaction efficiency is enhanced when K_2CO_3 is employed as base. Thus, the coupling of iodobenzene (1 mmol) and phenylacetylene (1.2 mmol) was carried out in DMF with the nano tetraimine Pd(0) complex (0.4 mol%, 0.005 g) at 100 °C for 3 h in the presence of 2 mmol of various bases. Bases including K_2CO_3, Na_2CO_3, Cs_2CO_3, Et_3N, CsOH and NaOH were tested (Table 3, entries 6, 9–13) and, among them, K_2CO_3 proves to be the most efficient and gives a GC yield of 94% (Table 3, entry 6). We further evaluated the effects of temperature and amount of catalyst on the reaction. As evident from Table 3 (entries 20, 21 and 1–4), both reducing the amount of catalyst and lowering the temperature lead to a decrease in the yield. So, based on these results, we selected K_2CO_3 as the base and DMF as solvent in the presence of 0.005 g of the catalyst at 100 °C as the best conditions for the Sonogashira reaction.

Under our optimized reaction conditions, we accomplished the Sonogashira-type cross-coupling of a wide range of structurally diverse aryl halides (Table 4). As expected, the coupling of phenylacetylene with iodides or bromides leads to the desired products in moderate to high yields (Table 4, entries 1–8). In particular, the reaction of aryl iodides substituted with electron-withdrawing groups affords high yield after 0.5 h at 100 °C (Table 4, entry 2). In the case of deactivated bromides, longer reaction time is required

Table 1. Optimization of conditions for Suzuki reaction using nano tetraimine Pd(0) complex as catalyst[a]

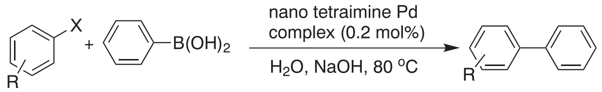


Entry	Solvent	Catalyst amount (g)	Base	Temperature (°C)	Yield (%)[b]
1	H_2O	0.003	NaOH	80	95
2	EtOH	0.003	NaOH	Reflux	76
3	EtOH–H_2O (3:1 v/v)	0.003	NaOH	80	80
4	EtOH–H_2O (2:1 v/v)	0.003	NaOH	80	81
5	EtOH–H_2O (1:1 v/v)	0.003	NaOH	80	87
6	CH_3CN	0.003	NaOH	80	51
7	Toluene	0.003	NaOH	80	23
8	NMP	0.003	NaOH	80	83
9	DMSO	0.003	NaOH	80	66
10	DMF	0.003	NaOH	80	85
11	H_2O	None	NaOH	140	0
12	H_2O	0.001	NaOH	80	28
13	H_2O	0.002	NaOH	80	72
14	H_2O	0.004	NaOH	80	95
15	H_2O	0.003	None	140	Trace
16	H_2O	0.003	K_3PO_4	80	55
18	H_2O	0.003	K_2CO_3	80	79
19	H_2O	0.003	Na_2CO_3	80	74
20	H_2O	0.003	KOH	80	82
21	H_2O	0.003	NaOAc	80	36
22	H_2O	0.003	NaOH	r.t.	17
23	H_2O	0.003	NaOH	70	81
24	H_2O	0.003	NaOH	90	94

[a] Reaction conditions: iodobenzene (1.0 mmol), phenylboronic acid (1.2 mmol), base (2.0 mmol), solvent (3.0 ml), 4 h.

[b] Isolated yield.

Table 2. Suzuki coupling of aryl halides with phenylboronic acid in the presence of nano tetraimine Pd(0) complex[a]



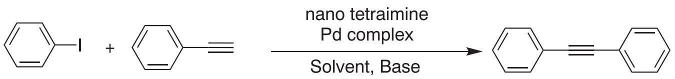
Entry	Ar	X	Time (h)	Isolated yield (%)[b]	Ref.
1	C_6H_5	I	1	95	72
2	4-OMeC_6H_4	I	2	90	72
3	4-$NO_2C_6H_4$	I	0.5	96	72
4	C_6H_5	Br	3	88	73
5	4-$NO_2C_6H_4$	Br	2	90	73
6	4-ClC_6H_4	Br	2.5	87	50
7	4-MeC_6H_4	Br	4	84	50
8	2-MeC_6H_4	Br	4	86	17
9	4-OMeC_6H_4	Br	4	82	72
10	C_6H_5	Cl	8	80	72
11	4-$NO_2C_6H_4$	Cl	3	83	72
12	4-CNC_6H_4	Cl	3.5	81	73
13	4-MeC_6H_4	Cl	12	78	72

[a] Reaction conditions: ArX (1.0 mmol), phenylboronic acid (1.2 mmol), NaOH (2.0 mmol) in the presence of Pd complex 0.2 mol% (0.003 g) in H_2O (3.0 ml) at 80 °C.

[b] Isolated yield.

for the reaction to produce good yields (Table 4, entries 4–8). The catalyst effect is also evident for chlorides, where only those substituted with electron-withdrawing groups give reasonable yield of coupling product (Table 4, entries 12 and 13). Non-activated aryl chlorides give a low yield in coupling reactions under similar conditions (Table 4, entries 10 and 11).

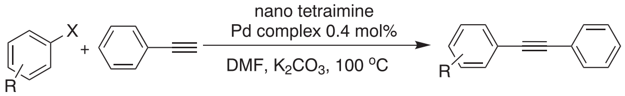
Table 3. Optimization of reaction conditions for Sonogashira reaction catalysed by nano tetraimine Pd(0) complex[a]



Entry	Solvent	Catalyst amount (g)	Base	Temperature (°C)	Yield (%)[b]
1	DMF	None	K_2CO_3	130	Trace
2	DMF	0.001	K_2CO_3	100	17
3	DMF	0.002	K_2CO_3	100	38
4	DMF	0.003	K_2CO_3	100	75
5	DMF	0.004	K_2CO_3	100	90
6	DMF	0.005	K_2CO_3	100	94
7	DMF	0.006	K_2CO_3	100	94
8	DMF	0.005	None	130	Trace
9	DMF	0.005	Na_2CO_3	100	82
10	DMF	0.005	Cs_2CO_3	100	86
11	DMF	0.005	Et_3N	100	44
12	DMF	0.005	CsOH	100	62
13	DMF	0.005	NaOH	100	38
14	DMSO	0.005	K_2CO_3	100	59
15	NMP	0.005	K_2CO_3	100	87
16	CH_3CN	0.005	K_2CO_3	Reflux	31
17	Toluene	0.005	K_2CO_3	Reflux	28
18	H_2O	0.005	K_2CO_3	Reflux	32
19	EtOH	0.005	K_2CO_3	Reflux	37
20	DMF	0.005	K_2CO_3	r.t.	11
21	DMF	0.005	K_2CO_3	9	79
22	DMF	0.005	K_2CO_3	110	94

[a] Reactions were run in 5 ml of solvent with 1.0 mmol of iodobenzene, 1.2 mmol of phenylacetylene and 2 mmol of base for 3 h.
[b] Isolated yield.

Table 4. Sonogashira coupling of aryl halides with phenylacetylene in the presence nano tetraimine Pd(0) complex[a]



Entry	Ar	X	Time (h)	Yield (%)[b]	Ref.
1	C_6H_5	I	0.75	94	72
2	4-$NO_2C_6H_4$	I	0.5	96	72
3	4-$OMeC_6H_4$	I	2	91	72
4	C_6H_5	Br	2.5	89	17
5	4-ClC_6H_4	Br	2.5	90	72
6	4-$NO_2C_6H_4$	Br	1.5	93	17
7	4-MeC_6H_4	Br	3.5	87	17
8	3-NC_5H_4	Br	3	89	72
9	C_6H_4	Cl	6	78	73
10	4-MeC_6H_4	Cl	10	73	74
11	4-$OMeC_6H_4$	Cl	12	71	17
12	4-CNC_6H_4	Cl	5	84	74
13	4-$NO_2C_6H_4$	Cl	3	87	17

[a] Reaction conditions: ArX (1.0 mmol), phenylacetylene (1.2 mmol) and K_2CO_3 (2.0 mmol) in the presence of nano tetraimine Pd(0) complex (0.4 mol%, 0.005 g) in DMF (3.0 ml) at 100 °C.
[b] Isolated yield.

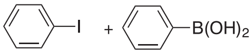
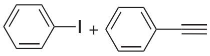
Several methods for Suzuki and Sonogashira reactions have been reported with various heterogeneous catalysts. For comparison, several results are summarized in Table 5. In our investigation it would be useful to introduce the nano tetraimine Pd(0) complex as an active catalyst for mild conditions in high yield, short time and low temperature of these reactions in comparison to other heterogeneous catalyst systems.

The possibility of the recycling of the catalyst is very important and makes it useful for commercial applications. Thus, we investigated the recovery and reusability of the catalyst using iodobenzene with phenylboronic acid (Suzuki reaction; Fig. 1) and iodobenzene with phenylacetylene (Sonogashira reaction; Fig. 2) as model substrates under optimized conditions. After completion of the reactions, the solid catalyst was separated by centrifugation and was reused for subsequent reactions under similar reaction conditions. Six consecutive cycles of the reaction show that the catalyst does not lose its activity and can be completely recycled.

The amounts of the nano tetraimine Pd(0) leaching during the reactions under the optimized conditions were determined. The palladium content in the Suzuki and Sonogashira reactions media after each reaction cycle was measured using ICP analysis and the results are provided in Figs. 3 and 4. The ICP analyses show that leaching is negligible for both reactions.

To determine the nature of the palladium species responsible for the observed reactions and to measure the extent of palladium leaching after the reactions, we used the hot filtration test. For this aim, we have studied the coupling reaction of iodobenzene with phenylboronic acid under optimized conditions. The hot reaction mixture was filtered after 36% conversion of iodobenzene (GC) to remove the catalyst. Continuation of the reaction of the resulting filtrate under the same conditions showed 41% conversion (GC) of iodoobenzene after 5 h. This result shows that the

Table 5. Comparison of efficiency of nano tetraimine Pd(0) complex with that of some reported heterogeneous catalysts for phosphine-free Suzuki and copper-free Sonogashira reactions

Entry	Catalyst	Suzuki			Sonogashira			Ref.
								
		Time (h)	Condition	Yield (%)	Time (h)	Condition	Yield (%)	
1	Nano tetraimine Pd(0) complex	1	H_2O/NaOH/80 °C/0.2 mol%	95[a]	0.75	DMF/K_2CO_3/100 °C/0.4 mol%	94[a]	This work
2	FDU-NHC/Pd(II)	—	—	—	3	DMA/K_2CO_3/100 °C/1.0 mol%, CuI 10 mol%	94[a]	64
3	PVC-dtz-Pd(II)	—	—	—	3	Solvent free/Et_3N/r.t./1.0 mol%	99[b]	65
4	Pd Schiff base@MWCNTs	2	DMF/H_2O (1:1 v/v) /K_2CO_3/60 °C/0.1 mol%	99[a]	1	H_2O/Et_3N/90 °C/1.2 mol%	95[a]	66
5	Feather keratin-Pd	5	H_2O/NaOH/75 °C/0.55 mol%	99[a]	—	—	—	67
6	Fe_3O_4/oleic acid/Pd	—	—	—	6	EtOH/K_2CO_3/100 °C/0.05 mol%	100[b]	68
7	PCP-pincer Pd	1	DMF/K_2CO_3/80 °C/3.0 mol%	96[a]	3	DMF/K_2CO_3/120 °C/3.0 mol%	90[a]	69
8	HypoGel-supported Pd	6	H_2O/K_2CO_3/90 °C/12 mol%	88[a]	—	—	—	70

[a] Isolated yield.

[b] Conversion determined by GC.

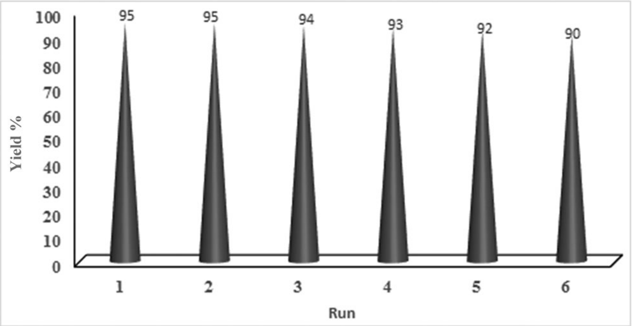


Figure 1. Recycling of catalyst for Suzuki reaction. Reaction conditions: iodobenzene (1.0 mmol), phenylboronic acid (1.2 mmol), NaOH (2.0 mmol.), catalyst (0.2 mol%), H_2O (3.0 ml), 1 h.

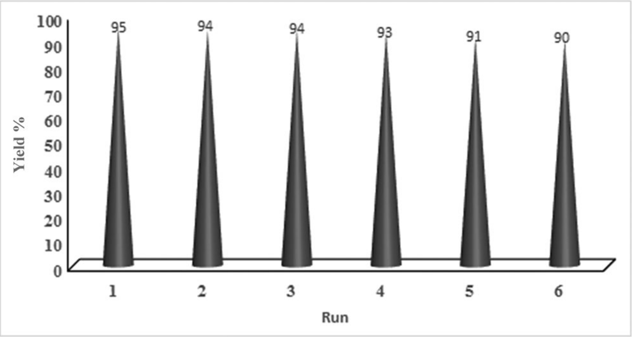


Figure 2. Recycling of catalyst for Sonogashira reaction. Reaction conditions: iodobenzene (1 mmol), phenylacetylene (1.2 mmol), catalyst (0.2 mol%), K_2CO_3 (2.0 mmol) in DMF (3.0 ml) at 100 °C, 0.75 h.

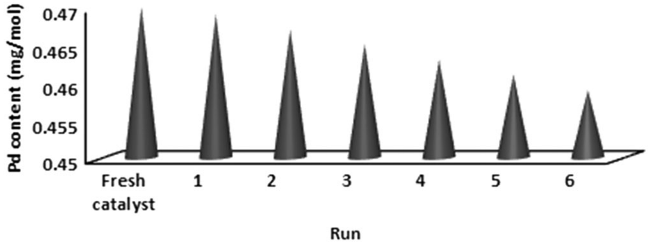


Figure 3. Palladium content (mg mol^{-1}) of fresh catalyst and catalyst used for up to six cycles in Suzuki reaction.

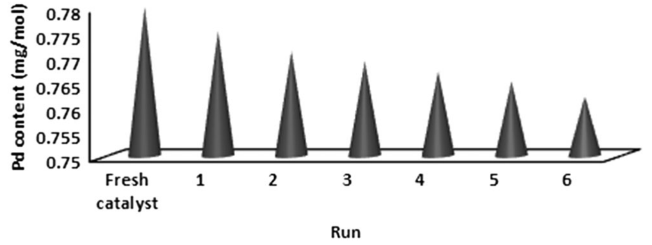


Figure 4. Palladium content (mg mol^{-1}) of fresh catalyst and catalyst used for up to six cycles in Sonogashira reaction.

amount of leaching of the catalyst into the reaction mixture is low and confirms that the catalyst acts heterogeneously in the reaction.

In order to get more information about the leaching of palladium, the reaction of iodobenzene with phenylboronic acid as model reaction was studied. After completion of the reactions and workup, the amount of leaching was determined using ICP analysis. The amount of palladium leaching after the first run is only 0.23%, and after six repeat recycles is 4.14%.

Conclusions

We have developed a novel, practical and economic nano tetraimine Pd(0) complex catalyst system for cross-coupling reactions. This catalyst demonstrated high catalytic activities in Suzuki and Sonogashira reactions in comparison to similar systems for synthesizing various biphenyl and alkyne derivatives with high yield under mild reaction conditions in a heterogeneous system. Moreover, the catalyst offers notable advantages such as facile recovery from reaction mixtures, good to excellent product yields, easy preparation, short reaction times and simplicity of handling. All these advantages make the protocol a convenient one for other important metal-catalysed reactions. After the reaction, the leaching of palladium into the solution is very low as determined using ICP analysis. In addition, the catalyst can be readily recovered and reused several times without significant loss of catalytic activity.

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