

Palladium(II)-Schiff base complex supported on multi-walled carbon nanotubes: A heterogeneous and reusable catalyst in the Suzuki-Miyaura and copper-free Sonogashira-Hagihara reactions

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Abstract:

The air-moisture stable and recyclable palladium(II) Schiff base complex anchored to multi-walled carbon nanotubes (Pd-Schiff base@MWCNTs) behaves as a very efficient heterogeneous catalyst in the Suzuki-Miyaura coupling of arylboronic acids and aryl halides, and the Sonogashira-Hagihara reaction of aryl iodides and terminal alkynes in aqueous media to afford the corresponding C-C couplings in high yields.

Keywords:

Cross-coupling reactions; Palladium complex; Suzuki reaction; Sonogashira reaction; Multi-walled carbon nanotubes

1. Introduction

Palladium catalyzed carbon-carbon bond-forming reactions have played a crucial role in synthetic organic chemistry. The palladium-catalyzed coupling of aryl halides with aryl boronic acids (Suzuki-Miyaura coupling) or terminal alkynes (Sonogashira-Hagihara coupling) represent as the most successful methods for the preparation of biaryls and internal acetylenes, respectively. These reactions have shown to have widespread applications in the synthesis of natural products, biologically active molecules, and materials science [1-7].

Many catalytic systems have been developed for the Suzuki-Miyaura and Sonogashira-Hagihara cross-coupling reactions using different palladium catalysts such as Pd(PPh₃)₄, Pd(OAc)₂, PdCl₂(PPh₃)₂, and PdCl₂(CH₃CN)₂ [8-14]. However, phosphine ligands used in these reactions are sensitive to air oxidation and thus require air-free conditions which pose significant

inconvenience on synthetic applications [15-17]. In addition, the copper acetylides formed in the Sonogashira-Hagihara coupling are very much prone to homocoupling reaction (Glaser coupling) [18,19]. Thus, many efforts have been made to eliminate copper and phosphorous from the synthetic methodologies [20-23]. Moreover, many palladium catalysts used in the Suzuki-Miyaura and Sonogashira-Hagihara reactions are homogeneous [24-27]; these catalysts, in spite of many advantages, are impossible to be recovered. Also, the residual palladium left in the product confines their use in bioactive molecules and large-scale synthesis. In order to overcome these drawbacks, in recent years, great efforts in catalysis research have been devoted to the introduction and application of effective heterogeneous catalysts [28-36]. In this context, ligand-free palladium nanoparticles [28, 37-40], as well as different ligands like palladacycles [41,42], *N*-heterocyclic carbenes [43,44], Schiff bases [45,46], and dendrimers [47] have been explored to be grafted on various inorganic and organic supports such as mesoporous silica [48-51], ionic liquids [52,53] and polymers [54-56] for the preparation of precious heterogeneous catalysts. Facile recycling and ease of separation of these catalysts make them important from environmental and economical points of view.

Studies on the isolation, characterization and catalytic activities of functionalized carbon nanotubes (CNTs) have received particular attention during the last decade owing to their specific catalytic applications compared to homogeneous complexes. Metal nanoparticles as well as various transition metal complexes such as polymers and porphyrins were used for carbon nanotubes' functionalization [57-59]. Schiff bases, which are an important class of ligands with extensive applications in different fields [60], also showed excellent catalytic activity when grafted on CNTs [61,62].

We have already reported the results obtained for the solvent-free synthesis of ynones using the air/moisture stable and reusable multi-walled carbon nanotubes functionalized with a Pd(II)-Schiff base complex (Pd-Schiff base@MWCNTs, Fig. 1) [63]. In order to further establish other heterogeneous palladium-catalyzed C-C cross-coupling reactions with our catalyst, we herein report the application of this catalyst in Suzuki-Miyaura and Sonogashira-Hagihara coupling reactions under aerial condition.

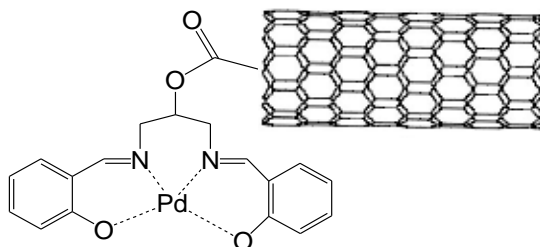


Fig. 1. Heterogeneous Pd-Schiff base@MWCNTs Catalyst

2. Experimental

2.1 General

NMR Spectra were recorded with either a Bruker DRX-400 or AQS-300 spectrometer with nominal frequencies of 400 and 300 MHz for proton or 100 and 75 MHz for carbon, respectively in CDCl_3 solutions. IR spectra were obtained using an ABB FTLA 2000 instrument. All reagents and solvents were commercially available and used without any further purification.

2.2 Preparation of Pd-Schiff base@MWCNTs

The synthesis of the Pd-Schiff base@MWCNTs catalyst was conducted according to the procedure previously reported [63]. The purchased CO_2H -MWCNTs (100 mg) were suspended in a solution of thionyl chloride (25 mL) and DMF (1 mL). The suspension was stirred at 65 °C for 24 h. The solid was then separated by filtration and washed with anhydrous THF (30 mL), and dried in vacuum to obtain COCl -MWCNTs. COCl -MWCNTs (50 mg) were added to a solution of the previously prepared Pd(II)-Schiff base (100 mg) in degassed CHCl_3 (8 mL), and the suspension was refluxed for 20 h under N_2 atmosphere. The solid was then filtered and washed with THF (3×10 mL) and CH_2Cl_2 (2×10 mL) and dried in vacuum to afford the desired catalyst.

The catalyst was also characterized by attenuated total reflection infrared spectroscopy (ATR), Raman spectroscopy, ICP, XRD, XPS, TEM, and TG-DTA data. The ATR spectrum of the catalyst showed a band at 1708 cm^{-1} associated with $\text{C}=\text{O}$ stretch of the ester linkage between the carbon nanotube and the Schiff base complex. Moreover, the metal content of the complex was found to be 16.20 ppm using ICP, and the ratio of Pd/N in the catalyst was obtained to be 1.82%.

2.3 General procedure for the Suzuki-Miyaura reactions

A RB flask was charged with aryl halide (1.0 mmol), arylboronic acid (1.5 mmol), K_2CO_3 (2 mmol), DMF/ H_2O (v/v= 1:1, 4 mL) and catalyst (0.1 mol% Pd); the mixture was magnetically stirred at 60 °C under air atmosphere. After 2-7 h, the reactions were completed (TLC). The mixture was cooled to room temperature, Et_2O (10 mL) and H_2O (5 mL) were added, and filtered. The organic phase was separated and dried over $MgSO_4$. The solvent was evaporated and the residual was purified by preparative TLC on silica gel plates eluting with *n*-hexane/ $EtOAc$ = 9:1. All the products were known compounds and were identified by comparison of their physical and spectroscopic data with those of authentic samples.

2.4 Recycling of the catalyst in Suzuki-Miyaura reaction

Recycling of the catalyst was performed upon the reaction of 4-bromoanisole with phenylboronic acid under the condition discussed in the preceding section. After completion of the reaction in the first run, the catalyst was separated from the reaction mixture by filtration, washed with H_2O (5 mL) and Et_2O (10 mL) and dried in vacuum at 70 °C for 24 h. The resulting solid mass was reused for another batch of the similar reaction. This process was repeated for four runs.

2.5 General procedure for the Sonogashira-Hagihara reactions

A mixture of aryl iodide (1.0 mmol), terminal alkyne (1.5 mmol), Et_3N (2.0 mmol), H_2O (2 mL), and the catalyst (0.012 mmol, 1.2 mol% Pd) was stirred at 90 °C under aerial conditions. The progress of the reaction was monitored by TLC. After completion, H_2O was evaporated, and $CHCl_3$ (10 mL) was added to the reaction mixture, and the catalyst was recovered with centrifugation. The organic layer was washed with H_2O (2×5 mL), dried over anhydrous $MgSO_4$, filtered and concentrated in vacuum. The crude product was further purified by preparative TLC (silica gel) using *n*-hexane as eluent to afford the desired product. All the products were characterized by IR, 1H , and ^{13}C NMR spectroscopy.

2.6. Selected spectral data of the compounds

Compound **2b**: 1H NMR ($CDCl_3$, 300 MHz): δ (ppm): 7.28-7.48 (m, 9H), 2.32 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm): 141.99, 141.96, 135.4, 130.3, 129.8, 129.2, 128.1, 127.3, 126.8, 125.8, 20.5; **3b**: 1H NMR ($CDCl_3$, 300 MHz): δ (ppm): 7.54-7.59 (m, 4H), 7.44 (t, $J = 7.3$ Hz, 2H), 7.32 (t, $J = 7.3$ Hz, 1H), 7.00 (d, $J = 8.6$ Hz, 2H), 3.87 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm): 159.2, 140.8, 133.8, 128.7, 128.2, 126.8, 126.7, 114.2, 55.3; **7b**: 1H NMR

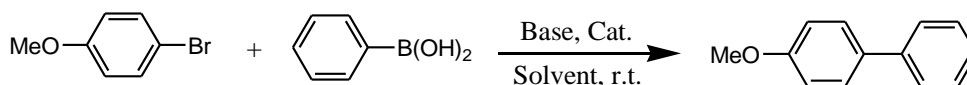
(CDCl₃, 300 MHz): δ (ppm): 10.07 (s, 1H), 7.96 (d, J = 8.0 Hz, 2H), 7.76 (d, J = 8.2 Hz, 2H), 7.65 (d, J = 8.0 Hz, 2H), 7.41-7.52 (m, 3H); ¹³C NMR (CDCl₃, 75 MHz): δ (ppm): 192.1, 147.2, 139.7, 135.2, 130.3, 129.1, 128.5, 127.7, 127.4; **15b**: ¹H NMR (CDCl₃, 300 MHz): δ (ppm): 8.01 (d, J = 8.1 Hz, 2H), 7.64 (d, J = 8.1 Hz, 2H), 7.58 (d, J = 8.5 Hz, 2H), 7.00 (d, J = 8.5 Hz, 2H), 3.86 (s, 3H), 2.63 (s, 3H); ¹³C NMR (CDCl₃, 75 MHz): δ (ppm): 197.7, 159.9, 145.3, 135.3, 132.2, 129.0, 128.4, 126.6, 114.4, 55.4, 26.6; **2c**: ¹H NMR (CDCl₃, 300 MHz): δ (ppm): 7.57 (d, J = 3.9 Hz, 1H), 7.55 (d, J = 2.1 Hz, 1H), 7.36-7.39 (m, 3H), 7.31-7.32 (m, 2H), 7.04 (dd, J = 5.0, 3.8 Hz, 1H); ¹³C NMR (CDCl₃, 75 MHz): δ (ppm): 132.0, 131.5, 128.5, 128.4, 127.3, 127.2, 123.3, 123.0, 93.1, 82.7; **6c**: ¹H NMR (CDCl₃, 300 MHz): δ (ppm): 7.53 (dd, J = 7.4, 2.4 Hz, 2H), 7.49 (d, J = 8.7 Hz, 2H), 7.30-7.38 (m, 3H), 6.89 (d, J = 8.7 Hz, 2H), 3.84 (s, 3H); ¹³C NMR (CDCl₃, 75 MHz): δ (ppm): 159.6, 133.1, 131.5, 128.3, 128.0, 123.6, 115.4, 114.0, 89.4, 88.1, 55.3; **8c**: ¹H NMR (CDCl₃, 300 MHz): δ (ppm): 7.94 (d, J = 8.3 Hz, 2H), 7.61 (d, J = 8.3 Hz, 2H), 7.55-7.58 (m, 2H), 7.36-7.39 (m, 3H), 2.61 (s, 3H); ¹³C NMR (CDCl₃, 75 MHz): δ (ppm): 197.3, 136.2, 131.8, 131.7, 128.8, 128.5, 128.3, 128.2, 122.7, 92.7, 88.6, 26.6.

3. Results and discussion

3.1 Catalytic Suzuki-Miyaura cross-coupling reactions

To explore the catalytic activity, the Suzuki-Miyaura cross-coupling reaction of aryl halides with arylboronic acids was conducted with the present catalyst. The rate of the coupling is dependent on a variety of parameters such as solvent, base, temperature and the catalyst loading. For optimization of the reaction conditions, we chose the cross-coupling of 4-bromoanisole with benzenboronic acid under aerobic condition as the model reaction, and the effect of solvent on the reaction was examined (Table 1). Single solvents such as DMF and H₂O, and even solventless condition gave low yields ranging from 14 to 36% (Table 1, entries 1-3). However, when the organic/aqueous co-solvent was adopted, satisfactory results were obtained (Table 1, entries 4-6). The merit of the co-solvent is attributed to the good solubility of the organic reactants and the inorganic base. Clearly, the best reaction solvent was found to be DMF/H₂O (v/v = 1:1) (Table 1, entry 4).

Next, various bases, catalyst loadings, and temperatures were screened (Table 2). Different organic and inorganic bases were studied; the yield of the cross-coupling products was reduced when organic bases such as Et₃N or DIPEA were employed (Table 2, entries 4 and 5). A

Table 1. Effect of solvents for the Suzuki-Miyaura reaction.^a

Entry	Solvent	Base	Time (h)	Yield (%) ^b
1	DMF	K ₂ CO ₃	16	36
2	H ₂ O	K ₂ CO ₃	16	14
3	–	K ₂ CO ₃	16	28
4	DMF/H ₂ O (v/v= 1:1)	K ₂ CO ₃	16	98
5	MeOH/H ₂ O (v/v= 1:1)	K ₂ CO ₃	16	53
6	DMSO/H ₂ O (v/v= 1:1)	K ₂ CO ₃	16	67

^a Reaction conditions: 4-bromoanisole (1.0 mmol), benzeneboronic acid (1.5 mmol), base (2 mmol), Pd-Schiff base@MWCNTs (0.5 mol% of Pd), in 4 mL solvent at room temperature (25 °C).

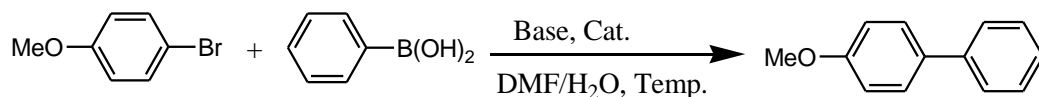
^b Isolated yield.

considerable increase in the product formation was observed in the presence of Cs₂CO₃ and K₂CO₃ at room temperature (Table 2, entries 1 and 2); hence, the economically cheaper K₂CO₃ was chosen as a base for these coupling reactions. Increasing the temperature from 25 °C to higher temperatures (50, 60, 80, and 100 °C) had a substantial rate acceleration of the reaction (Table 2, entries 6-9). Due to its mildness and low risk of Pd leaching 60 °C was selected as the best temperature. Then, different catalyst loadings between 0.5 and 0.05 mol% were investigated for the reaction (Table 2, entries 7, 10-12). Among the various catalyst loadings, 0.1 mol% of the catalyst was found to be the best (Table 2, entry 11). Therefore, it was decided to use K₂CO₃ as the base, DMF/H₂O in volume ratio of 1:1 as solvent, and 0.1 mol% catalyst as the optimal conditions in further studies.

To survey the generality of the catalytic protocol, we investigated the reaction using various aryl halides coupled with arylboronic acids under the optimized conditions. The results are summarized in Table 3. When benzeneboronic acid was coupled with aryl iodides and bromides containing both electron-donating and electron-withdrawing groups in the *para* position, the corresponding products were obtained in excellent yields. The *ortho*-substituted aryl iodide, 2-iodotoluene (Table 3, entry 2), and aryl bromide, 2-bromotoluene (Table 3, entry 6), gave the corresponding products in slightly lower yields due to the steric effects. The coupling reaction of aryl chlorides with benzeneboronic acid required extended reaction time than aryl iodides and bromides, giving the desired product in moderate yields (Table 3, entries 16-18). Also, coupling

reaction of two electron-rich arylboronic acids with various arylbromides were examined (Table 3, entries 19-24); they afforded the corresponding products in lower yields than those of the benzenboronic acid. The activity of the catalyst was also superior with other reported heterogeneous catalysts for the reaction of aryl halides under aerobic condition [31, 64-68].

Table 2. Effect of bases, catalyst loadings, and temperature for the Suzuki-Miyaura reaction.^a

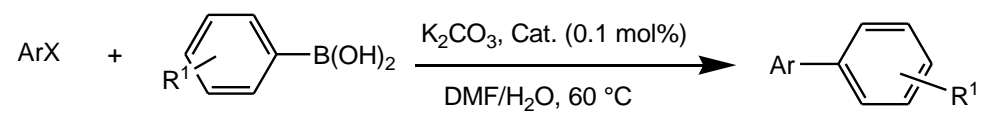


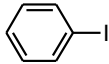
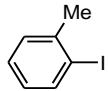
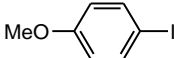
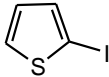
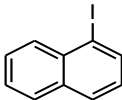
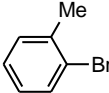
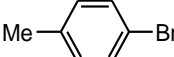
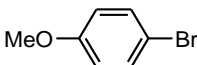
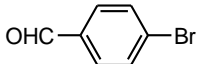
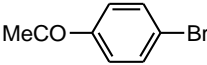
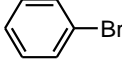
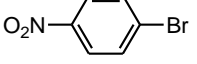
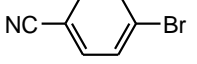
Entry	Base	Temp. (°C)	Catalyst loading (mol% of Pd)	Time (h)	Yield (%) ^b
1	Cs ₂ CO ₃	25	0.5	16	96
2	K ₂ CO ₃	25	0.5	16	98
3	KO ^t Bu	25	0.5	16	37
4	Et ₃ N	25	0.5	16	47
5	DIPEA	25	0.5	16	56
6	K ₂ CO ₃	50	0.5	6	99
7	K ₂ CO ₃	60	0.5	3	99
8	K ₂ CO ₃	80	0.5	1	99
9	K ₂ CO ₃	100	0.5	0.5	99
10	K ₂ CO ₃	60	0.25	3	98
11	K ₂ CO ₃	60	0.1	3	98
12	K ₂ CO ₃	60	0.05	3	82

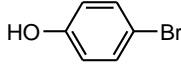
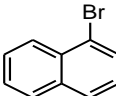
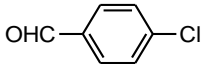
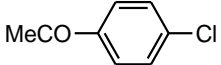
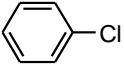
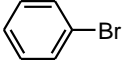
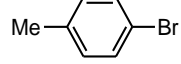
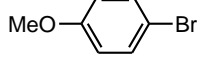
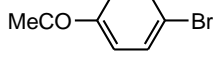
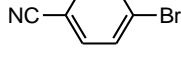
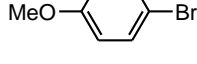
^a Reaction conditions: 4-bromoanisole (1.0 mmol), benzenboronic acid (1.5 mmol), base (2 mmol), Pd-Schiff base@MWCNTs in 4 mL DMF/H₂O (v/v= 1:1) at various temperatures.

^b Isolated yield.

The reusability of this heterogeneous palladium catalyst was also examined for the Suzuki coupling reaction of 4-bromoanisole with phenylboronic acid using K₂CO₃ as the base in DMF/H₂O (1:1) medium. After the first run, the catalyst was separated by simple filtration, washed thoroughly with water, and ether, and dried at 70 °C for 24 h. The dried catalyst was then

Table 3. Suzuki-Miyaura cross-coupling reactions of aryl halides with arylboronic acids.^a

Entry	Aryl halide	R ¹	Time (h)	Product	Yield (%) ^b
1		H	2	1b	99
2		H	3	2b	93
3		H	2	3b	99
4		H	3	4b	92
5		H	3	5b	95
6		H	4	2b	90
7		H	2	6b	98
8		H	3	3b	99
9		H	4	7b	98
10		H	2	8b	99
11		H	3	1b	98
12		H	6	9b	98
13		H	3	10b	97

14		H	6	11b	94
15		H	5	5b	91
16		H	7	7b	53 (64) ^c
17		H	7	8b	57 (68) ^c
18		H	7	1b	38 (53) ^c
19		4-CH ₃	5	12b	81
20		4-CH ₃	5	13b	85
21		4-CH ₃	5	14b	86
22		4-OCH ₃	7	15b	71
23		4-OCH ₃	7	16b	70
24		4-OCH ₃	7	17b	74

^a Reaction conditions: aryl halide (1.0 mmol), arylboronic acid (1.5 mmol), K₂CO₃ (2 mmol), Pd-Schiff base@MWCNTs (0.1 mol% of Pd) in 4 mL DMF/H₂O (v/v= 1:1) at 60 °C.

^b Isolated yield.

^c At 60 °C, 7 h, using 0.2 mol% of Pd of the catalyst.

reused with a fresh reaction mixture without any further activation. As shown in Fig. 2, the catalyst can be recovered and reused in further reactions without a significant loss of activity. Although the catalytic activity gradually diminished, a yield of 82% was still achieved in the fourth cycle.

3.2 Catalytic Sonogashira-Hagihara coupling reaction

For this study, we initiated our investigation of Sonogashira-Hagihara reaction between iodobenzene and phenylacetylene as a model reaction and the role of various bases, solvents, and temperatures was screened using Pd-Schiff base@MWCNTs as heterogeneous catalyst (Table 4).

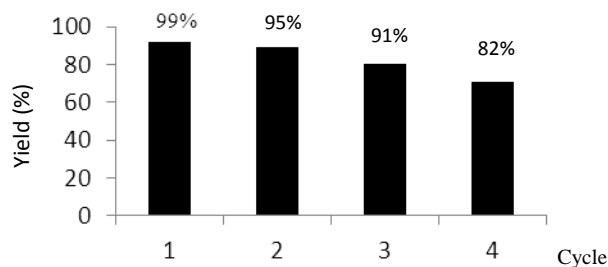


Fig. 2. Reusability of Pd-Schiff base@MWCNTs catalyst for the Suzuki-Miyaura reaction.

Table 4. Optimization of the conditions for the Sonogashira-Hagihara reaction of iodobenzene with Phenylacetylene^a

Entry	Catalyst (mol% of Pd)	Base	Solvent	Time (h)	Temp. (°C)	Yield (%) ^b
1	0.6	Et ₃ N	-	24	27	45
2	0.9	Et ₃ N	-	24	27	70
3	1.2	Et ₃ N	-	24	27	87
4	1.5	Et ₃ N	-	24	27	56
5	1.2	DIPEA	-	24	27	50
6	1.2	K ₂ CO ₃	-	24	27	62
7	1.2	Cs ₂ CO ₃	-	24	27	40
8	1.2	Piperidine	-	24	27	70
9	1.2	Et ₃ N	CH ₃ CN	24	27	74
10	1.2	Et ₃ N	NMP	24	27	48
11	1.2	Et ₃ N	THF	24	27	50
12	1.2	Et ₃ N	DMF	24	27	45
13	1.2	Et ₃ N	Dioxane	24	27	36
14	1.2	Et₃N	-	1	90	93
15	1.2	Et ₃ N	H ₂ O	24	27	64
16	1.2	Et ₃ N	H ₂ O	6	55	81
17	1.2	Et ₃ N	H ₂ O	6	80	91
18	1.2	Et₃N	H₂O	1	90	95
19	1.2	Et ₃ N	H ₂ O	6	100	94

^aReaction conditions: iodobenzene (1.0 mmol), phenylacetylene (1.5 mmol), base (2 mmol), solvent (2 mL) in the presence of Pd-Schiff base@MWCNTs.

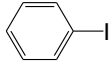
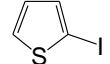
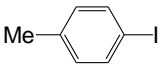
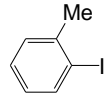
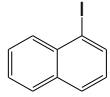
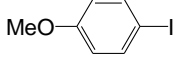
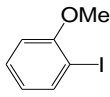
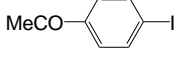
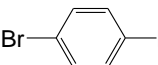
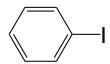
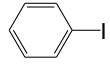
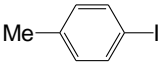
^bIsolated yields.

The yield of the cross-coupled product was not satisfactory when inorganic bases such as K_2CO_3 or Cs_2CO_3 were employed (Table 4, entries 6 and 7). Other organic solvents including CH_3CN , *N*-methylpyrrolidone (NMP), tetrahydrofuran (THF), *N,N*-dimethylformamide (DMF), and dioxane were also surveyed under reaction conditions, but all gave inferior results compared to H_2O and neat conditions. Also, low palladium concentrations gave decreased yields (Table 4, entries 1 and 2). An increase in the catalyst loading (10 mg, 1.5 mol %) gave poorer result (Table 4, entry 4). It was concluded that the reaction was more favorable using Et_3N as base and environmentally benign water as solvent or neat conditions at 90 °C in the presence of 8 mg (1.2 mol %) of the catalyst (Table 4, entries 14 and 18). The efficiency of the system was further extended for coupling of various aryl iodides having different steric and electronic properties with terminal alkynes. The results are summarized in Table 5. As shown in Table 5, with exception of entries 1 and 2, there are appreciable differences in isolated yields of the products between the results obtained in water and those in neat conditions. Reactions in water proceeded smoothly giving the corresponding coupling products in high to excellent yields in short reaction times. It was clear that the coupling of electron-rich 4- and 2-iodoanisole with phenylacetylene provided the products in relatively lower yields (83 and 80% yields, respectively, Table 5, entries 6 and 7) than others. The coupling reactions of iodobenzene and 4-iodotoluene with 1-octyne (Table 5, entries 11 and 12) were very slow under the same reaction conditions giving moderate yields of cross-coupling products after 8 h.

The coupling reaction of bromobenzene with phenylacetylene were very slow under the same reaction conditions giving traces of cross-coupling product after 24 h of reaction time and the coupling reaction of chlorobenzene with phenylacetylene did not occur at all. To further illustrate that arylbromides were inert in the reaction system, the above coupling reaction, bromobenzene with phenylacetylene, was performed using CuI as co-catalyst; it was found that only trace amount of the corresponding product was obtained and considerable amount of homo-coupling product of phenylacetylene was formed. Even, when TBAB was used as an additive, only poor result (20% yield) was obtained.

Table 5. Pd-Schiff base@MWCNTs Catalyzed Sonogashira-Hagihara reaction^a

$$\text{Arl} + \text{R}-\text{C}\equiv\text{C}-\text{H} \xrightarrow[\text{Et}_3\text{N, H}_2\text{O or Neat, 90 }^\circ\text{C}]{\text{Pd-Schiff-base@MWCNTs}} \text{Ar}-\text{C}\equiv\text{C}-\text{R}$$

Entry	Aryl iodides	R	Product	H ₂ O		Neat	
				Time (h)	Yield (%) ^b	Time (h)	Yield (%) ^b
1		C ₆ H ₅	1c	1	95	1	93
2		C ₆ H ₅	2c	0.33	97	0.5	95
3		C ₆ H ₅	3c	0.5	92	0.92	64
4		C ₆ H ₅	4c	0.75	88	1	57
5		C ₆ H ₅	5c	0.38	84	2.5	65
6		C ₆ H ₅	6c	0.92	83	1	50
7		C ₆ H ₅	7c	1	80	1.25	68
8		C ₆ H ₅	8c	0.42	94	0.83	83
9		C ₆ H ₅	9c^c	1.75	92	2	75
10		4-MeC ₆ H ₄	10c	1	88	1.83	62
11		CH ₃ (CH ₂) ₄ CH ₂	11c	8	54	8	37
12		CH ₃ (CH ₂) ₄ CH ₂	12c	8	50	8	32

^a Reaction conditions: aryl iodide (1.0 mmol), alkyne (1.5 mmol), Pd-Schiff base@MWCNTs (1.2 mol% of Pd), Et₃N (2.0 mmol), water (2 mL), 90 °C, under air.

^b Isolated yields.

^c 4-Bromodiphenylacetylene

4. Conclusions

In summary, we have presented a multi walled carbon nanotubes anchored Pd(II)-Schiff base complex which was efficiently used as a heterogeneous catalyst for Suzuki-Miyaura cross-coupling reactions and copper- and phosphorous-free Sonogashira-Hagihara cross-coupling reactions in aqueous media under aerobic condition. The catalyst shows not only high catalytic

activity, but also offers many practical advantages such as thermal stability, oxygen insensitivity, and recyclability. The catalyst was reused for four consecutive runs in Suzuki-Miyaura reaction with consistent activity. The excellent catalytic performance in aqueous media and the easy preparation and separation of the catalyst make it a good heterogeneous system and a useful alternative to other heterogeneous palladium catalysts.

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