Palladium nanoparticles supported on the modified single-walled carbon nanotubes: A heterogeneous and reusable catalyst in the Ullmann-type N-arylation of imidazole and indoles

Journal:	*New Journal of Chemistry*
Manuscript ID:	NJ-ART-11-2014-002108.R2
Article Type:	Paper
Date Submitted by the Author:	29-Jan-2015
Complete List of Authors:	Veisi, Hojat; Payame Noor University, Morakabati, Nekoo; Department of Chemistry, Tonekabon branch, Islamic Azad University, Tonekabon, Iran,

Palladium nanoparticles supported on the modified single-walled carbon nanotubes: A heterogeneous and reusable catalyst in the Ullmann-type *N*-arylation of imidazole and indoles

Hojat Veisi,[a],* Nekoo Morakabati[b]

[a]*Department of Chemistry, Payame Noor University (PNU), Tehran, Iran*
[b]*Department of Chemistry, Tonekabon branch, Islamic Azad University, Tonekabon, Iran*
Fax +98(833)8380709; E-mail: hojatveisi@yahoo.com

The air- and moisture-stable and recyclable palladium nanoparticles supported on the modified single-walled carbon nanotubes (SWCNT-Met/Pd) behaves as a very efficient heterogeneous catalyst in the Ullmann coupling of imidazole and indoles with aryl iodides to afford the corresponding C-N couplings under aerobic conditions. These cross coupled products were produced in excellent yields at low palladium loading (∼0.2 mol%) and the heterogeneous catalyst can be readily recovered by simple filtration and reused five times without a noticeable loss in its catalytic activity.

Introduction

The formation of aryl-nitrogen bonds via cross-coupling reactions represents powerful techniques for the preparation of various compounds (e.g., arylpyrroles, arylpyrazoles, arylimidazoles, aryltriazoles, arylindoles, arylcarbazoles, etc.) that are of biological, biochemical, pharmaceutical and materials interest.[1-3] Traditionally, these compounds have been synthesized via nucleophilic aromatic substitution of N-H containing π-electron-rich nitrogen heterocycles with electron-deficient aryl halides, which limits its scope,[4] or by coupling with organometallic reagents. They have also been prepared by the classical Ullmann-type coupling with aryl halides, which some of them suffers from limitations such as high reaction temperatures (often 150 °C or as high as 200 °C), the use of stoichiometric amounts of copper reagents, insolubility of copper(I) salts in organic solvents, moderate yields, sensitivity of the substituted aryl halide to the harsh reaction conditions, and poor substrate generality. Therefore a mild, economic, and efficient catalytic system is still desirable for this process.

Catalyst plays a significant role in the production of chemicals today and nanomaterials have the potential for improving efficiency, selectivity, and yield of catalytic process. The higher surface to volume ratio means that much more catalyst is actively participating in the reaction. The potential for cost saving is tremendous from a material, equipment, labour, and time standpoint. Higher selectivity means less waste and fewer impurities, which could lead to safer and reduced environmental impact. The study of application of metal nanoparticles in catalysis, particularly, on organic transformations, has become a frontier area of research in nanocatalysis.[5] Among the different metal nanocatalysts, immobilized Pd(II) complex have gained much reputation, because palladium is a versatile catalyst in modern organic synthesis and is widely used for a significant number of synthetic transformations[6] such as, Heck, Suzuki, Stille, Sonogashira cross coupling reactions and *N*-arylation of heterocycles.[7-17]

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.[18-20] Schiff bases, which are an important class of ligands with extensive applications in different fields,[21] also showed excellent catalytic activity when grafted on CNTs.[22-24]

We have already reported the preparation of a Pd supported on biguanide(metformine)-functionalized single-walled carbon nanotubes (SWCNT-Met/Pd) and its catalytic application in the Suzuki-Miyaura coupling reactions.[25] In order to further establish other heterogeneous palladium-catalyzed C-N cross-coupling reactions with our catalyst, we herein report the application of this catalyst in Ullmann coupling of imidazole and indoles with aryl iodides under aerobic condition (Scheme 1).

Results and discussion

First of all, after successful fabrication of the catalyst,[25] we have investigated again the morphology surface by FESEM, EDS and TEM images (Figure 1, 2). FESEM and EDS image of the SWCNTs-Met/Pd (Figure 1) shows that the attachment of organic components to the SWCNTs materials has no distinct influence on the morphology of composition and also indicated that the metformine and Pd presented in the catalyst. The concentration of palladium in SWCNT-Met/Pd was 19 wt%, which were determined by ICP-AES.

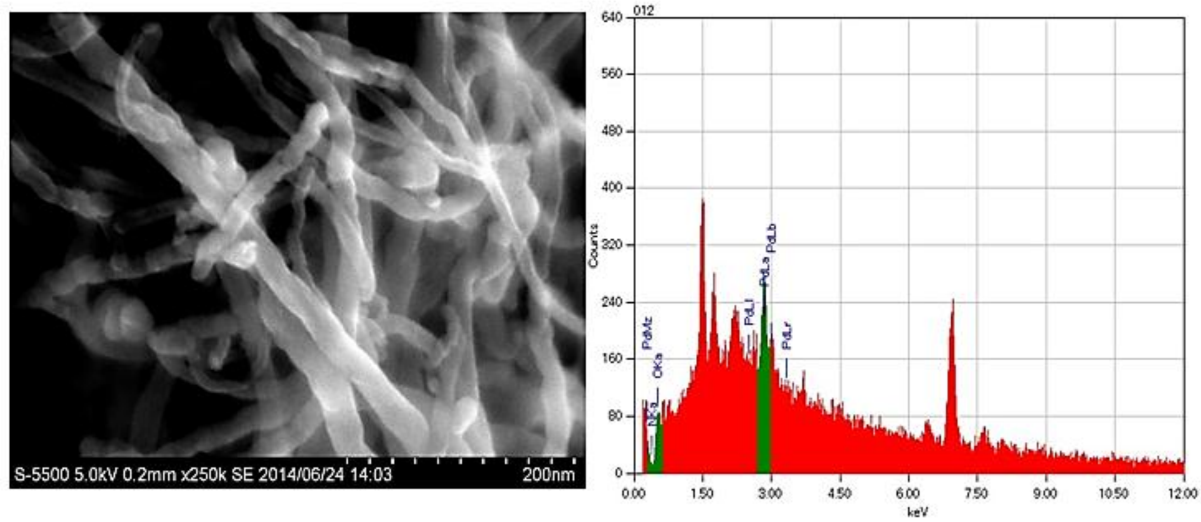


Fig. 1. FESEM and EDS images of SWCNTs-Met/Pd**.**

Transmission electron microscopy (TEM) investigations are carried out to observe the morphology and distribution of palladium nanoparticles supported on SWCNT after its reduction with hydrazine (Figure 2). It can be seen that although Pd-NPs are distributed on SWCNTs, they do not aggregate with each other because the imine groups of metformin effectively isolate adjacent Pd-NPs. The average Pd-NPs size is ~10 nm.

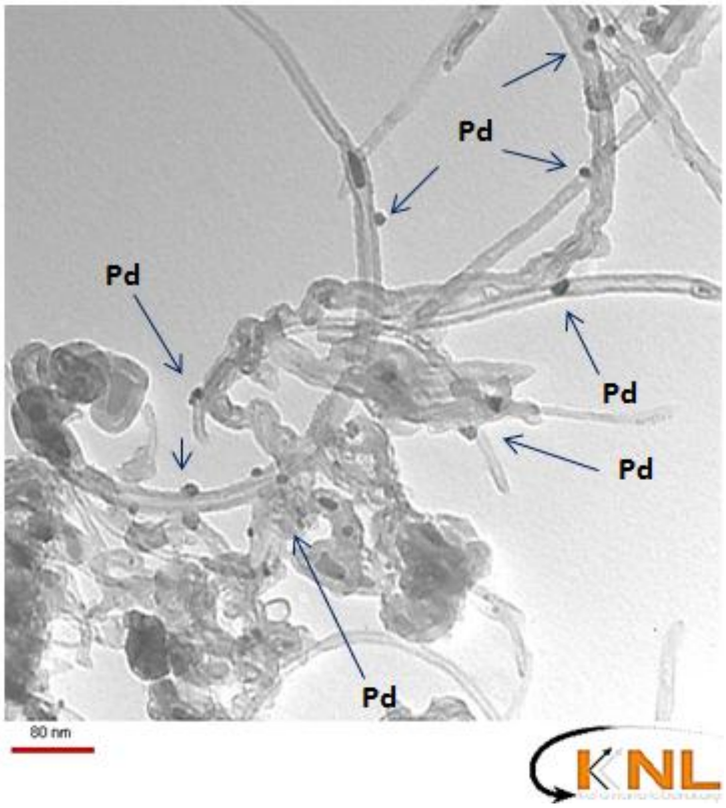
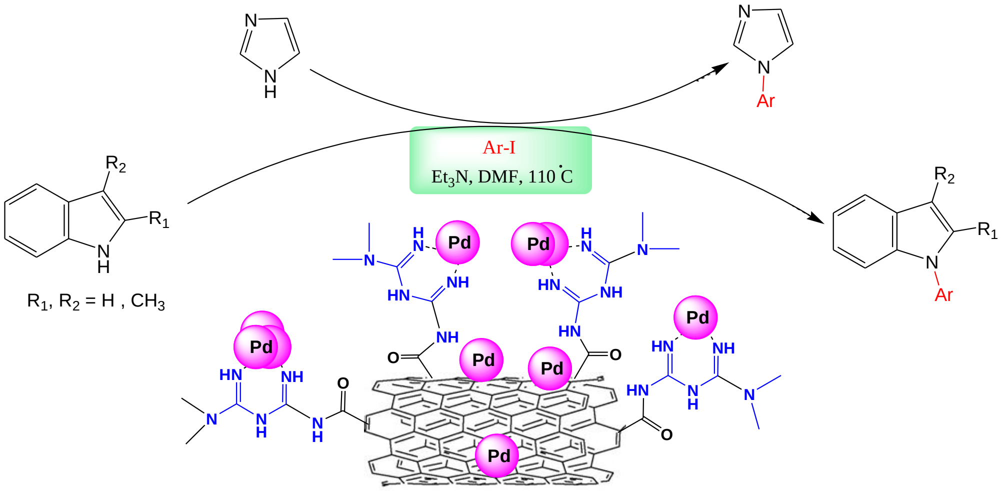


Fig. 2. TEM image of SWCNTs-Met/Pd.



Scheme 1. SWCNTs-Met/Pd catalyzed *N*-arylation of indoles and imidazole.

In our initial screening experiments, the *N*-arylation reaction of indole with iodobenzene was investigated to optimize the reaction conditions including Pd concentration, solvent, bases and temperature without the protection by an inert gas, and the results are summarized in Table 1.

Table 1

Optimization of reaction condition for the *N*-arylation of indole with iodobenzene.[a]

Entry	Pd (mol%)	Base	Solvent	T (ºC)	t (h)	Yield (%)[b]
1	0.3	Et_3N	CH_3CN	82	10	50
2	0.3	Et_3N	EtOH	78	10	45
3	0.3	Et_3N	Toluene	110	10	75
4	0.3	Et_3N	H_2O	100	10	30
5	0.3	Et_3N	CH_2Cl_2	40	10	35
6	0.3	Et_3N	DMSO	110	10	90
7	0.3	Et_3N	DMF	110	6	95
8	0.1	Et_3N	DMF	110	10	60
9	0.2	Et_3N	DMF	110	6	98
10	0.2	-	DMF	110	24	Trace
11	0.0	Et_3N	DMF	110	24	0
12	0.2	K_2CO_3	DMF	110	10	75
13	0.2	Na_2CO_3	DMF	110	10	50
14	0.2	K_3PO_4	DMF	110	10	55
15	0.2	KOH	DMF	110	10	75
16	0.2	$NaHCO_3$	DMF	110	10	55
17	0.2	Et_3N	DMF	25	10	Trace
18	0.2	Et_3N	DMF	70	10	45

[a] Reaction conditions: indole (1.0 mmol), iodobenzene (1.1 mmol), Pd catalyst, base (2.0 mmol), solvent (5.0 mL).

[b] Isolated yield.

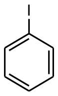
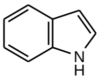
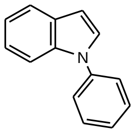
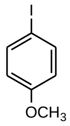
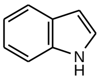
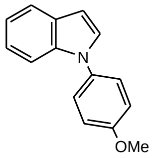
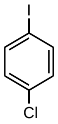
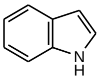
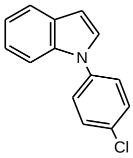
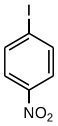
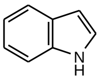
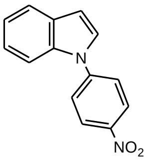
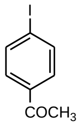
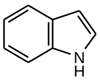
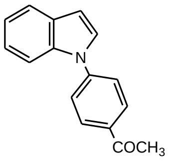
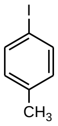
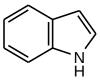
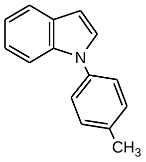
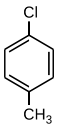
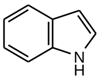
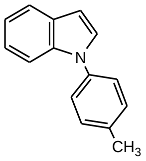
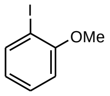
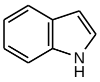
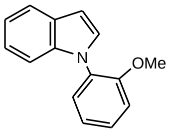
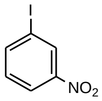
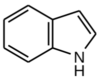
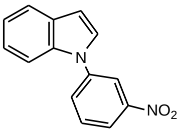
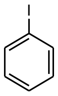
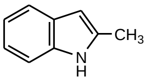
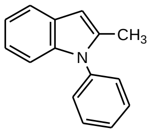
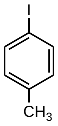
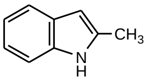
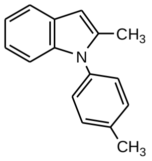
Initially, various solvents such as DMF, EtOH, CH_3CN, Toluene, CH_2Cl_2, DMSO and H_2O were studied in the presence of 0.3 mol% Pd catalyst and 2 equiv, of Et_3N at 110 ºC (Table 1, entries 1-7). As could be seen in the Table 1, the best result was obtained in DMF (Table 1, Entry 7). Next, the bases, including Et_3N, KOH, K_3PO_4, Na_2CO_3, $NaHCO_3$ and K_2CO_3 were explored, and Et_3N gave the best yields (Table 1, entries 1, 12-16). However, a low yield was obtained without any base (Table 1, entry 10). It was also found that the reaction temperature has a great influence on this transformation (Table 1, entries 9, 17, 18). The obvious improvement in the conversion (98%) was achieved for the reaction at 110 ºC (Table 1, entry 9).

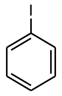
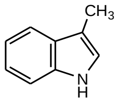
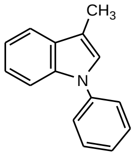
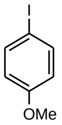
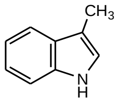
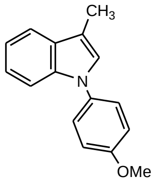
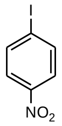
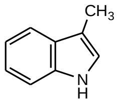
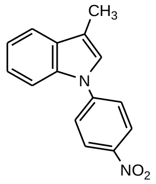
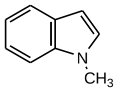
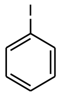
In addition, when the loading of Pd was reduced from 0.3 mol% to 0.2 mol%, the excellent yield was also afforded. However, when 0.1 mol% of Pd was employed, the reaction yield decreased to 60% (Table 1, entries 7- 9). It is important to mention that *N*-arylation of indole did not take place in absence of Pd catalyst (Table 1, entry 11). In summary, the optimal condition for the *N*-arylation of indole with iodobenzene involves the use of 0.2 mol% of Pd catalyst, 2 equiv. of Et_3N in DMF at 110 ºC for 6 h (Table 1, Entry 9).

With these optimum reaction conditions in hand, the scope and generality of the *N*-arylation method was investigated by the variations of aryl iodides and indoles with different substituent’s and the results are summarized in Table 2.

Table 2

Synthesis of *N*-aryl-indoles catalyzed by SWCNTs-Met/Pd[a]

Entry	Aryl halide	Indole	Product	Yield (%)[b]	Ref.
1				98	26i
2				98	26i
3				96	26i
4				95	26j
5				90	26i
6				95	26i
7				60	26i
8				90	26i
9				85	26k
10				90	26j
11				92	27

12				98	26i
13				95	26i
14				90	26i
15			No Reaction	0	-

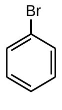
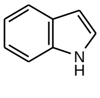
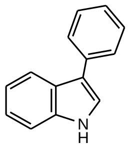
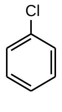
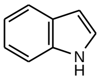
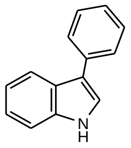
[a] Reactions were carried out under aerobic conditions in 5 mL of DMF, 1.1 mmol aryliodides, 1.0 mmol indoles and 2 mmol Et_3N in the presence of Pd catalyst (0.020 g, 0.2 mol% Pd) and 110 ˚C for 6 h.
[b] Isolated yield.

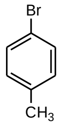
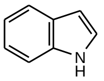
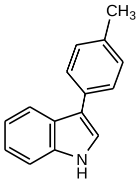
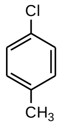
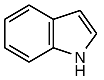
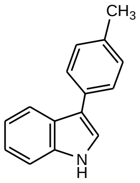
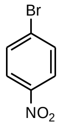
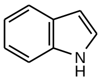
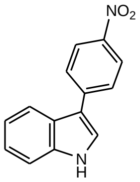
We examined the reaction of indoles with substituted aryl iodides (Table 3, entries 1-14). All the substituted aryl iodides reacted with indoles to afford the coupling products in good to high yield. We did not observe any limitation as for aryl iodide derivatives. The reactivity of 2-methylindole was slightly lower than that of indole and 3-methyl-indole due to the steric effect (Table 2, entries 1, 10, 12).

To ensure that there was no C-arylation taken place in the reaction, the reaction was carried out with 1-methyl indole and found that there was no product formed (Table 2, Entry 17). This shows the high selectivity of SWCNTs-Met/Pd as catalyst in the *N*-arylation of indole using aryl iodides.

Interestingly, less reactive aryl halide such as bromobenzenes and chlorobenzenes also couples with indole furnishing *C*3-aryl indole in good to appreciable yields on longer reaction times (Table 3).

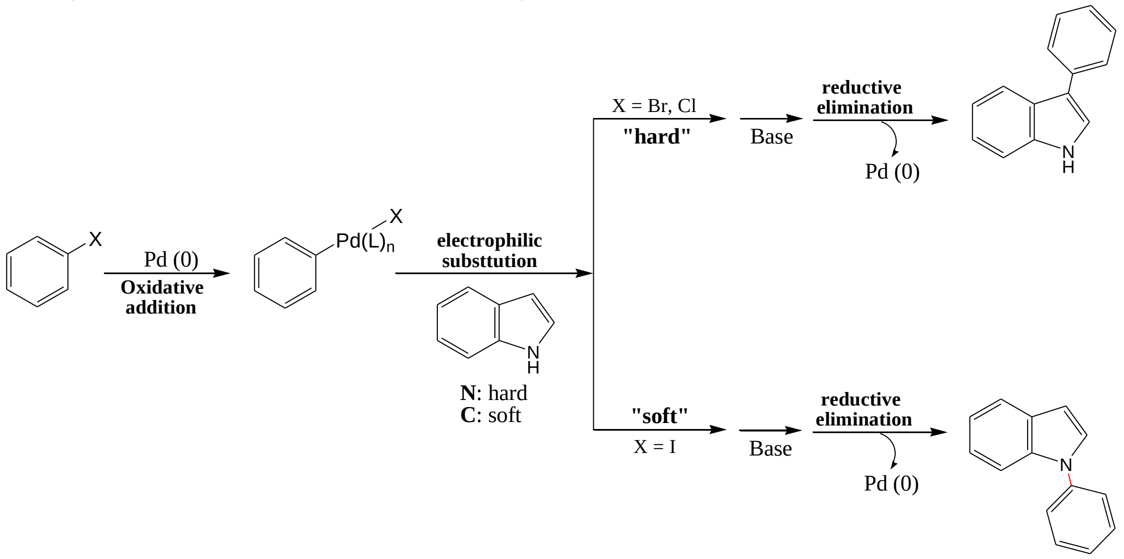
Table 3
palladium-catalyzed C-3 arylation of indole[a]

Entry	Aryl halide	Indole	Product	Yield (%)[b]	Ref.
1				90	28
2				70	28

3				82	28
4				65	28
5				75	28

[a] Reactions were carried out under aerobic conditions in 5 mL of DMF, 1.1 mmol arylhalyde, 1.0 mmol indoles and 3 mmol K$_2$CO$_3$ in the presence of Pd catalyst (0.020 g, 0.2 mol% Pd) and 110 °C for 10 h.
[b] Isolated yield.

The results indicate that the selectivity of the reaction is mainly controlled by the ‘‘*electronic character*’’ of the Pd(II)-intermediate.[29] Using an aryl bromide or aryl chloride in same conditions would generate an electron deficient Pd(II)-species (‘‘*hard electrophile*’’) more able to perform a C3-arylation, while using aryl iodide would generate electron rich Pd(II)-species (‘‘*soft electrophile*’’) due to orbital overlapping between the Pd(II)-centre and the iodide ligand, species involved in the N1-arylation (Scheme 2).

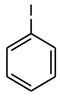
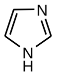
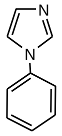
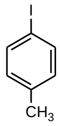
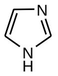
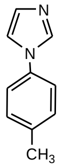
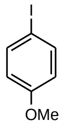
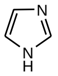
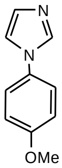
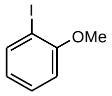
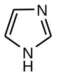
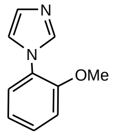
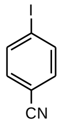
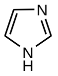
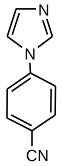
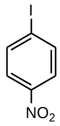
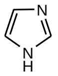
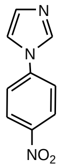
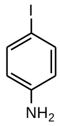
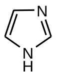
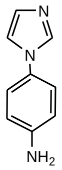
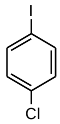
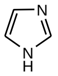
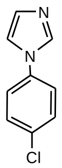
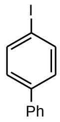
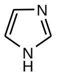
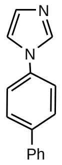


Scheme 2. Selectivity study for N1-/C3-arylation of indole in the presence of various aryl halides.

We were pleased to find that the arylation reactions also proceed with imidazole in good yields under same conditions (Table 4, entries 1-9). We found that aryl iodides containing electron-donating groups as well as those with electron-withdrawing groups reacted with imidazole to give the corresponding *N*-arylated imidazoles.

Table 4

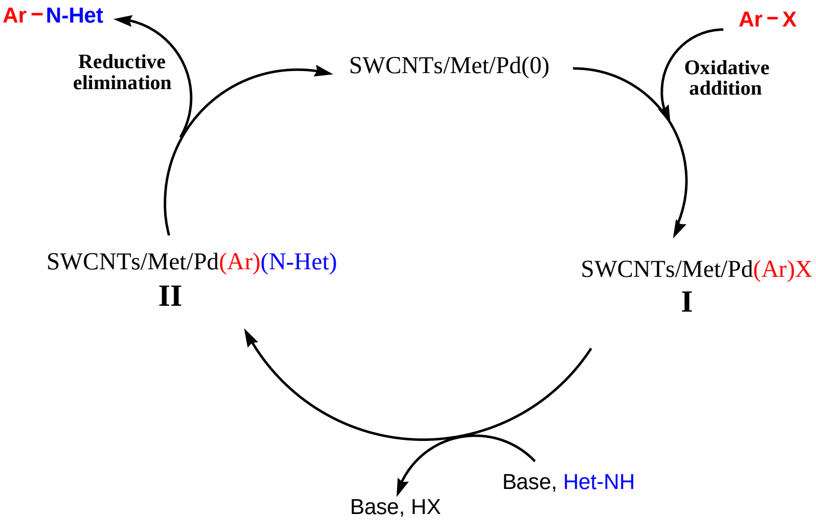
SWCNTs-Met/Pd-catalyzed *N*-arylation of imidazole with aryl iodides

Entry	Aryl iodides	Imidazole	Product	Yield (%)[b]	Ref.
1				96	30
2				98	31
3				96	30
4				85	31
5				92	30
6				96	31
7				90	30
8				96	31
9				85	31

[a] Reactions were carried out under aerobic conditions in 3 mL of DMF, 1.1 mmol aryliodide, 1.0 mmol imidazole and 2 mmol Et_3N in the presence of Pd catalyst (0.020 g, 0.2 mol% Pd) and 110 °C for 10 h.

[b] Isolated yield.

To probe the leaching of the catalyst, hot filteration test was performed. The reaction between indole and iodobenzene was stopped after 2 hours (40% yields) and the resin filtered off while the solution was still hot. The filtrate was heated further and the reaction mixture analyzed by GC after 4 hours. The results indicated that reaction stops after the catalyst is filtered off. Additionally the reaction mixture was extracted with ether and aqueous layer analyzed for palladium by ICP-AAS. Total palladium concentration was found to be 150 ± 10 ppb. The negative results of hot filtration test indicate that the leaching of palladium is negligible and most probably the reaction is heterogeneous in nature. Based on these results, it appears that the reaction studied has the same mechanism as that reported in other Pd-catalyzed *N*-arylations (Scheme 3).[32] According to the general mechanism depicted in Scheme 3, the reaction of Het-NH with the oxidative addition product **I** in the presence of base lead to a novel **II** complex. When the latter complex undergoes a reductive elimination, the coupled product *N*-aryl-Het is produced, and the catalyst is released to complete the catalytic cycle.



Scheme 3. Plausible mechanism for the *N*-arylation.

Another important point concerning heterogeneous catalysis is the deactivation and re-cyclability of the catalyst. In order to investigate this, a series of 5 consecutive runs of the coupling between indole and iodobenzene (*N*-arylation) in the presence of SWCNTs-Met/Pd was carried out (Figure 3). These results demonstrate that nanocatalyst could be reused 5th times without a noticeable loss of its catalytic activity. The stability and good reusability of the catalyst should result from the chelating action of bidentate metformine groups on palladium and the mesoporous structure of the SWCNTs support.

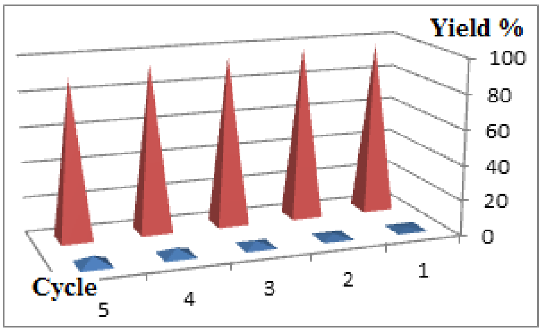


Fig. 3. Reusability of SWCNTs-Met/Pd catalyst for the *N*-arylation of indole under similar conditions.

The XPS spectroscopic analysis of the heterogeneous catalyst is a quantitative technique to indicate the electron properties of the species immobilized on the surface, such as oxidation state, the electron environment and the binding of the core electron (E binding) of the metal. Fig. 4 displays the Pd binding energy of SWCNTs-Met/Pd. The study of the SWCNTs-Met/Pd at the Pd 3p level shows peaks at 531.4 and 553.7 eV for Pd $3p_{3/2}$, which clearly indicates that the Pd nanoparticles are stable as metallic state in the nanocomposite structure. In comparison to the standard binding energy of Pd^0, with Pd $3p_{3/2}$ of about 532.4 eV and Pd $3p_{1/2}$ of about 560.2 eV, it can be concluded that the Pd peaks in the SWCNTs-Met/Pd shifted to lower binding energy than Pd^0 standard binding energy. The previous studies[33,34] indicated that the position of Pd 3p peak is usually influenced by the local chemical/physical environment around Pd species besides the formal oxidation state, and shifts to lower binding energy when the charge density around it increases. Therefore, the peaks at 553.7 and 531.4 could be due to Pd^0 species bound directly to metformine groups in the SWCNTs-Met/Pd.

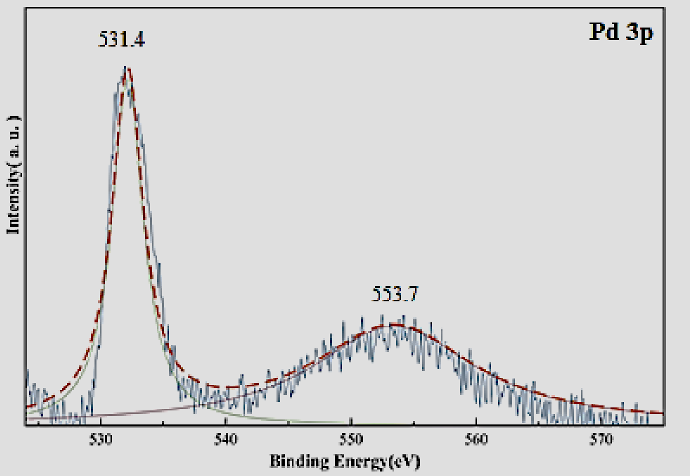


Fig. 4. XPS spectra of SWCNTs-Met/Pd.

Conclusion

In conclusion, we have applied palladium nanoparticles supported on the modified single-walled carbon nanotubes (SWCNT-Met/Pd) as a very efficient heterogeneous catalyst in the Ullmann coupling of imidazole and indoles with aryl iodides to afford the corresponding C-N couplings under aerobic conditions. The corresponding *N*-arylindoles and *N*-arylimidazoles were obtained in good yields and were applicable to various indoles, imidazole and a variety of aryl iodides. Less reactive aryl halide such as bromobenzenes and chlorobenzenes also couples with indole furnishing *C*3-aryl indoles in good yields in the presence of the catalyst. Moreover, the catalyst could be reused for four consecutive cycles without a noticeable loss of its catalytic activity. The stability of the palladium nanoparticles on the support was studied by XPS and ICP-AAS analysis and also with hot filtration test. These advantages make the process highly valuable from the synthetic and environmental points of view. Further efforts to extend the application of this system in other reactions are currently in progress in our laboratory.

Experimental

N-Arylation of indoles and imidazole in the presence of SWCNT-Met/Pd under mild conditions. In a typical reaction, 20 mg of the catalyst (20 mg catalyst = 0.002 mmol Pd, 0.2 mol%) was placed in a 25 mL round-bottom flask, 1.1 mmol of the aryl iodides in 3 mL of DMF was added 1 mmol of indoles or imidazole and 2 mmol of Et_3N. The mixture was then refluxed for the appropriate amount of time at 110 ˚C (see Table 2, 4). After completion of reaction monitored by TLC (hexane/acetone, 4:1), the reaction mixture was cooled to room temperature (the catalyst was recovered by centrifuge) and was extracted with diethyl ether three times (3 x 10 mL). The combined organic layers were washed with brine solution and dried over anhydrous Na_2SO_4 and concentrated *in vacuum*. The crude product was purified by column chromatography on silica gel (60-120 mesh) to provide the *N*-aryl indoles and *N*-aryl imidazoles.

C3-Arylation of indole in the presence of SWCNT-Met/Pd under mild conditions. In a typical reaction, 20 mg of the catalyst (20 mg catalyst = 0.002 mmol Pd, 0.2 mol%) was placed in a 25 mL round-bottom flask, 1.1 mmol of the arylbromides or arylchlorides in 3 mL of DMF was added 1 mmol of indole and 3 mmol of K_2CO_3. The mixture was then refluxed for 10 hours at 110 ˚C (see Table 3). After completion of reaction monitored by TLC (hexane/acetone, 5:1), the reaction mixture was cooled to room temperature (the catalyst was recovered by centrifuge) and was extracted with ethyl acetate three times (3 x 10 mL). The combined organic layers were washed with brine solution and dried over anhydrous Na_2SO_4 and concentrated *in vacuum*. The crude product was purified by column chromatography on silica gel (60-120 mesh) to provide the *C3*-aryl indoles.

Analytical data for selected products

N-Phenylindole (Table 2, entry 1): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.71 (d, *J* = 3.0 Hz, 1H), 7.20 (t, *J* = 8.0 Hz, 1H), 7.23 (t, *J* = 8.0 Hz, 1H), 7.32-7.40 (m, 2H), 7.50-7.56 (m, 4H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H).

N-Phenylimidazole (Table 3, entry 1): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (s, 1H), 7.76 (t, 1H), 7.67 (q, *J* = 5.8 Hz, 2H), 7.53 (t, 2H), 7.37 (t, 1H), 7.14 (s, 1H).

Acknowledgement

We are thankful to Payame Noor University (PNU) for financial support.

References

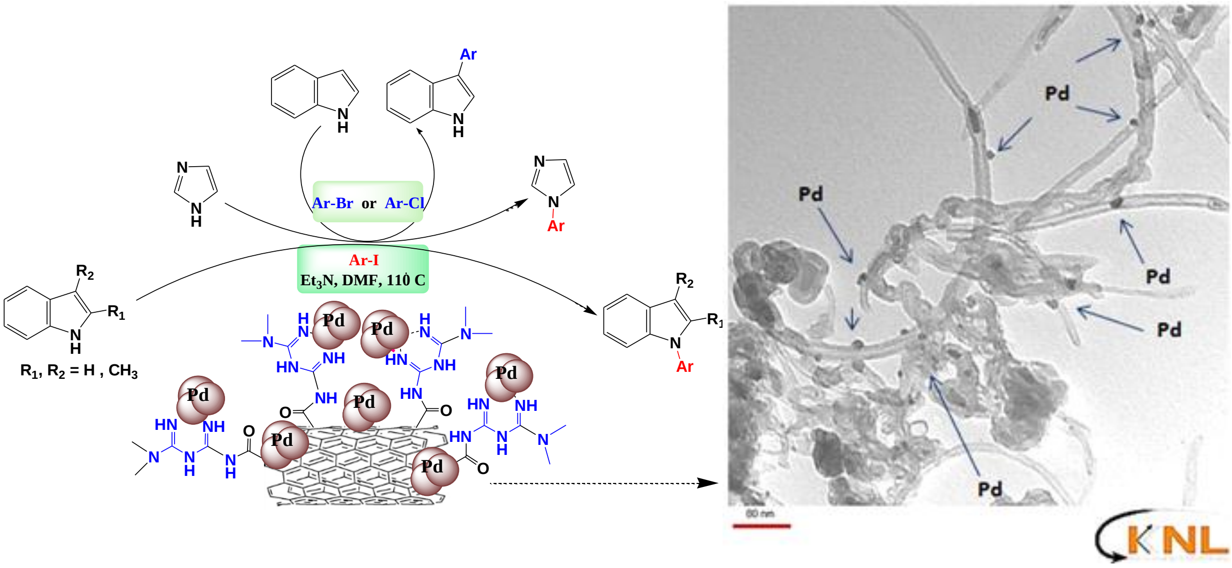
1. M. L. Quan, P. Y. S. Lam, Q. Han, D.J.P. Pinto, M.Y. He, R. Li, C.D. Ellis, C.G. Clark, C. A. Teleha, J.H. Sun, R.S. Alexander, S. Bai, J.M. Luettgen, R.M. Knabb, P.C. Wong, P. R. R. Wexler, *J. Med. Chem*. 2005, **48**, 1729.
2. (a) B.K. Singh, V.S. Christian, R.J.A. Davy, S.P. Virinder, V.V.E. Erik, *Tetrahedron Lett.* 2009, **50**, 15; (b) G. Pai, A. P. Chattopadhyay, *Tetrahedron Lett*. 2014, **55**, 941; (c) Y. Zhang, X. Yang, Q. Yao, D. Ma, *Org. Lett*. 2012, **14**, 3056; (d) Kunz, Klaus; Scholz, Ulrich; Ganzer, Dirk, *Synlett*, 2003, **15**, 2428.
3. N. Yamazaki, I. Washio, Y. Shibasaki, M. Mitsuru Ueda, *Org. Lett*. 2006, **8**, 2321.
4. (a) R. Bambal, R.P. Haznlik, *J. Org. Chem.* 1994, **59**, 729; (b) M. C. Venuti, R.A. Stephenson, R. Alvarez, J.J. Bruno, A.M. Strosberg, *J. Med. Chem.* 1988, **31**, 2136; (c) J.X. Qiao, X. Cheng, D.P. Modi, K.A. Rossi, J.M. Luettgen, R.M. Knabb, P.K. Jadhav, R.R. Wexler, *Bioorg. Med. Chem. Lett.* 2005, **15**, 29.
5. A. Molnar, *Chem. Rev*. 2011, **111**, 2251.
6. J. -H. Kim, J. -S. Park, H. -W. Chung, B. W. Boote, T. R. Lee, *RSC Adv*. 2012, **2**, 3968.
7. B. Tamami, H. Allahyari, S. Ghasemi, F. Farjadian, *J. Organomet. Chem*. 2011, **696**, 594.
8. A. F. Lee, P. J. Ellis, I. J. S. Fairlamb, K. Wilson, *Dalton Trans*. 2010, **39**, 10473.
9. V. Calo, A. Nacci, A. Monopoli, F. Montingelli, *J. Org. Chem*. 2005, **70**, 6040.
10. X. Gao, N. Zhao, M. Shu, S. Che, *Appl. Catal. A: Gen*. 2010, **388**, 196.
11. (a) G. Mann, J. F. Hartwig, M. S. Driver, C. Fernandez-Rivas, *J. Am. Chem. Soc.* 1998, **120**, 827; (b) J. F. Hartwig, M. Kawatsura, S. I. Hauck, K. H. Shaughnessy, L. M. Alcazar-Roman, *J. Org. Chem*. 1999, **64**, 5575; (c) D. W. Old, M. C. Harris, S. L. Buchwald, *Org. Lett*. 2000, **2**, 1403; (d) M. Watanabe, M. Nishiyama, T. Yamamoto, Y. Koie, *Tetrahedron Lett*. 2000, **41**, 481; (e) G. A. Grasa, M. S. Viciu, J. Huang, S. P. Nolan, *J. Org. Chem*. 2001, **66**, 7729.
12. H. Veisi, D. Kordestani, A. R. Faraji, *J. Porous Mater*. 2014, **21**, 141.
13. H. Veisi, R. Masti, D. Kordestani, M. Safaei, O. Sahin, *J. Mol. Catal. A: Chem*. 2014, **384**, 61.
14 H. Veisi, M. Hamelian, S. Hemmati, *J. Mol. Catal. A: Chem*. 2014, **395,** 25.
15. H. Veisi, *Tetrahedron Lett*. 2010, **51**, 2109.
16. H. Veisi, J. Gholami, H. Ueda, P. Mohammadi, M. Noroozi, *J. Mol. Catal. A: Chem*. 2015, **396**, 216.
17. H. Veisi, P. Mohammadi, J. Gholami, *Apply. Organomet. Chem*. 2014, **28**, 868.
18. H.X. Wu, R. Tong, X.Q. Qiu, H. F. Yang, Y.H. Lin, R.F. Cai, S.X. Qian, *Carbon*, 2007, **45**, 152-159.
19. J. Jin, Z. Dong, J. He, R. Li, J. Ma, *Nanoscale Res. Lett*. 2009, **4**, 578-583.
20. J. Guerra, M.A. Herrero, *Nanoscale*, 2010, **2**, 1390-1400.
21. S. Kumar, D. N. Dhar, P.N. Saxena, *J. Sci. Ind. Res*. 2009, **68**, 181-187.
22. M. Salavati-Niasari, M. Bazarganipour, *Transit. Met. Chem*. 2009, **34**, 605-612.
23. M. Salavati-Niasari, M. Bazarganipour, *Appl. Surf. Sci*. 2009, **255**, 7610-7617.
24. M. Navidi, B. Movassagh, S. Rayati, *Appl. Catal. A: Gen*. 2013, **452**, 24-28.
25. H. Veisi, A. Khazaei, M. Safaei, D. Kordestani, *J. Mol. Catal. A: Chem*. 2014, **382**, 106-113.

26. (a) F. Ullmann, Ber. Dtsch. *Chem. Ges*. 1903, **36**, 2382; (b) F. Ullmann, *Ber. Dtsch. Chem. Ges.* 1904, **37**, 853; (c) B. Sreedhar, K. B. S. Kumar, P. Srinivas, V. Balasubrahmanyam, G. T. Venkanna, *J. Mol. Catal. A: Chem*. 2007, **265**, 183; (d) Y. X. Xie, S. F. Pi, J. Wang, D. L. Yin, J. H. Li, *J. Org. Chem*. 2006, **71**, 8324; (e) H. H. Rao, Y. Jin, H. Fu, Y. Y. Jiang, Y. F. Zhao, *Chem. Eur. J*. 2006, **12**, 3636; (f) L. B. Liu, M. Frohn, N. Xi, C. Dominguez, R. Hungate, P. J. Reider, *J. Org. Chem*. 2005, **70**, 10135; (g) H. C. Ma, X. Z. Jiang, *J. Org. Chem*. 2007, **72**, 8943; (h) A. F. Pozharskii, B. K. Martsokha, A. M. Simonov, *J. Gen. Chem. USSR* 1963, **33**, 994; (i) R. Xiao, H. Zhao, M. Cai, *Tetrahedron*, 2013, **69**, 5444; (j) H. Chen, M. Lei, L. Hu, *Tetrahedron*, 2014, **70**, 5626; (k) S. Haneda, Y. Adachi, M. Hayashi, *Tetrahedron*, 2009, **65**, 10459; (l) R. K. Rao, A. B. Naidu, E. A. Jaseer, G. Sekar, *Tetrahedron*, 2009, **65**, 4619; (m) D. K. T. Yadav, S. S. Rajak, B. M. Bhanage, *Tetrahedron Lett*. 2014, **55**, 931; (n) N. V. Suramwara, S. R. Thakareb, N. N. Karadec, N. T. J. Khaty, *J. Mol. Catal. A: Chem*. 2012, **359**, 28; (o) A. K. Verma, J. Singh, R. C. Larock, *Tetrahedron*, 2009, **65**, 8434; p) K. Balaswamy, P. C. Pullaiah, M. M. Rao, *Appl. Catal. A: Gen*. 2014, **483**, 110.
27. D. W. Old, M. C. Harris, S. L. Buchwald, *Org. Lett*. 2000, **2**, 1403.
28. Zhang, Z.; Hu, Z.; Yu, Z.; Lei, P.; Chi, H.; Wang, Y.; He, R. *Tetrahedron Lett*. 2007, **48**, 2415.
29. L. Djakovitch, P. Rouge, R. Zaidi, *Catal. Commun*. 2007, **8**, 1561.
30. J. -B. Zhu, L. Cheng, Y. Zhang, R. G. Xie, J.-S. You, *J. Org. Chem.* 2007, **72**, 2737.
31. S. M. Islam, S. Mondal, P. Mondal, S. Singh Roy, K. Tuhin, N. Salam, M. Mobarak, *J. Organometal. Chem*. 2012, **696**, 4264.
32. D. Prim, J. –M. Campagne, D. Joseph, B. Andrioletti, *Tetrahedron*, 2002, **58**, 2041.
33. D. Zhang, Z. Liu, S. Han, C. Li, B. Lei, M. P. Stewart, J. M. Tour and C. Zhou, *Nano Lett*. 2004, **4**, 2151.
34. M. C. Militello and S. J. Simko, *Surf. Sci. Spectra*, 1994, **3**, 387.

Graphical Abstract

Palladium nanoparticles supported on the modified single-walled carbon nanotubes: A heterogeneous and reusable catalyst in the Ullmann-type *N*-arylation of imidazole and indoles

Hojat Veisi, Nekoo Morakabati



Apply SWCNT-Met/Pd as an efficient and heterogeneous catalyst in the Ullmann coupling of imidazole and indoles with aryl iodides.