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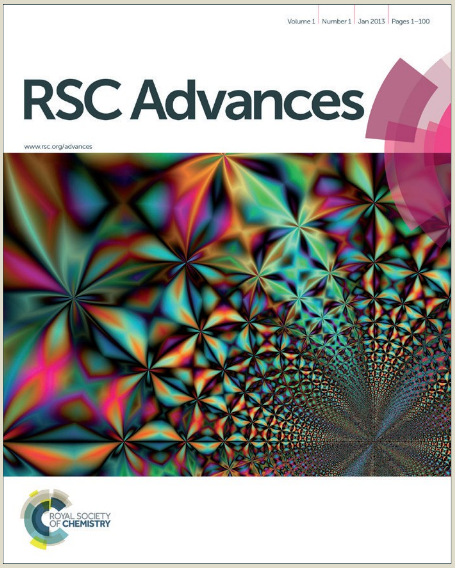

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3, 6-di(pyridin-2-yl)-1,2,4,5-tetrazine capped Pd(0) nanoparticles: catalyst for copper-free Sonogashira coupling of aryl halide in aqueous medium†

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3, 6-di(pyridin-2-yl)-1,2,4,5-tetrazine (pytz) capped Pd(0) nanoparticles (TzPdNPs) as a catalyst in Sonogashira coupling of aryl halides in aqueous medium with diminished homocoupling is reported. The methodology provides a facile route to obtain polyfunctional alkynes under ligand and copper free conditions. The procedure is also efficient for aryl chlorides.

Introduction

Synthesis of new donor-acceptor terminal alkynes or π-conjugated aromatic alkynes had always a demanding starting material in organic synthesis including natural products.[1] Moreover, its recent application in OLEDs as nonlinear optical material[2] and in molecular electronics[3] had enhanced the importance of its synthetic route. Sonogashira cross-coupling[4] proves to be a most reliable practical tool for this challenging objective in construction of these alkynes.

Traditionally this cross-coupling of aryl halides and alkynes proceeded in presence of palladium and copper but it suffered from several limitations like homogeneous catalytic condition, higher activity of palladium-based catalyst[5] and formation of undesired Glaser-Hay homo coupling products.[6] Although lot of modification are under process with other metal co-catalyst[1a,b,h,7] or copper free[8] and co-catalyst free[7] conditions to diminish self-coupling. Another current challenge associated with Sonogashira coupling reaction is its inefficiency when "unreactive" aryl chlorides are used. Application of aryl chlorides are advantageous due to their low cost relative to aryl bromides or iodides and increased availability. Till date only few methods have been reported involving aryl chlorides in the Sonogashira cross-coupling.[9] It is also important to remove expensive ligand choices which are generally used to activate alkyl halides especially for chlorides as a coupling partner. Consequently, search for a new protocol using green solvent, diminishing other side product and activating aryl chlorides without using ligands is quint-essential. Recently, a ligand- and copper salt-free Sonogashira reaction in aqueous medium using heterogeneous 10% Pd/C as the catalyst has also been developed but catalyst is only active with aryl iodides.[10] Here in we report synthesis of the 3, 6-di(pyridin-2-yl)-1,2,4,5-tetrazine (pytz) capped Pd(0) nanoparticles (TzPdNPs) as a potential catalyst in cross-coupling of aryl halides including aryl chloride and aryl acetylenes with diminished homo coupling in aqueous medium using tetrabutyl ammonium bromide (TBAB) as phase transfer catalyst (PTC).

Results and discussion

The syntheses of TzPdNPs was carried out according to the method reported earlier by us.[11] Aqueous solution of Na_2PdCl_4 was reacted with 3,6-di(pyridin-2-yl)-1,4-dihydro-1,2,4,5-tetrazine (H_2pytz) in ethanol under sonication (details in Electronic Supplementary Information). In this synthesis 3,6-di(pyridin-2-yl)-1,4-dihydro-1,2,4,5-tetrazine (H_2pytz) acts as reducing agent for Na_2PdCl_4. On the other hand, H_2pytz oxidizes to 3,6-Di(pyridin-2-yl)-1,2,4,5-s-tetrazine (pytz) which finally capped Pd(0) nanoparticles to produce TzPdNPs. TzPdNPs was characterized by using FT-IR, powder X-ray diffraction (PXRD) and transmission electron microscopy (TEM). The crystallinity and purity of TzPdNPs were examined (Fig. 1a) by the powder X-ray diffraction (XRD) technique. The XRD pattern of TzPdNPs shows the inter planar d-spacing of XRD peaks correspond to (111), (200), (220) and (311) planes of Pd(0) with fcc structure (JCPDS No. 01-1310), without any impurity

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phase. The XRD pattern TzPdNPs is similar to that of pure PdNPs, indicating that nanoparticles have not been affected by the capping with pytz. Fairly intense peaks observed is indicative of their crystallinity, whereas, the peak broadening indicating the presence of smaller materials (particle size). The morphology and size distribution of the prepared nanoparticles were elucidated from the transmission electron micrographs. Figure 1b exhibits morphological images of the prepared palladium nanoparticles. Size of the particles varies from 1.5 to 3 nm and the average size observed was 2.2 ± 0.4 nm (Fig. S1). The shape of the particles is almost spherical and shows no faceted surfaces. It can also be noted that, despite the small size, the particles are separated from one another and no significant aggregation is observed. The SAED pattern of TzPdNPs (Fig. 1c) shows spots and the rings indexed to (111) and (200) planes of palladium with an fcc structure. This is in agreement with the X-ray diffraction studies. The HRTEM image, depicted in (Fig. 1d) shows lattice fringes corresponding to the (111) plane of the Pd metal. The FT–IR spectrum of the TzPdNPs exhibits all characteristic bands observed for pytz (Fig. S2).

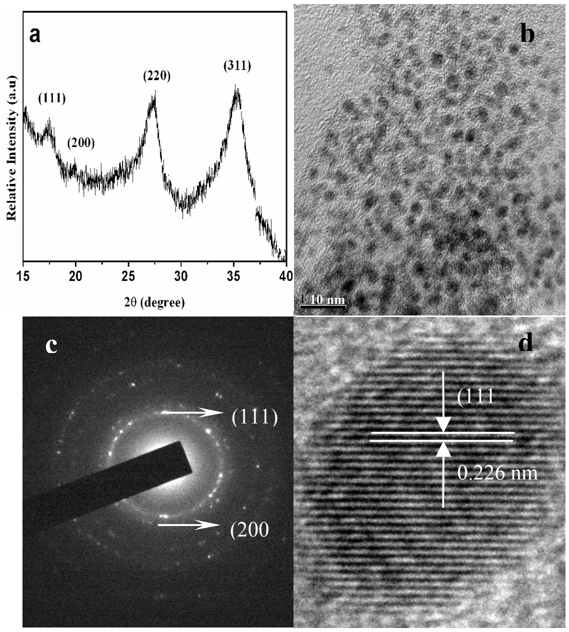
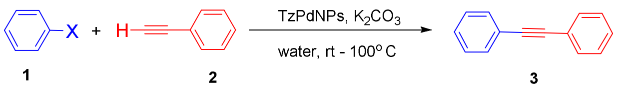


Fig. 1. (a) Powder XRD (b) TEM (c) SAED pattern and (d) HRTEM of TzPdNPs.

We began our investigation with the coupling of phenylacetylene and iodobenzene at room temperature in the presence of 2 mg catalyst. Initial results revealed that in presence of 2 equiv of K_2CO_3 in water afforded desired coupled product at room temperature with 94% yield in 2 h (Table 1, entry 1). This preliminary catalytic system was also capable of coupling both bromobenzene and chlorobenzene (Table 1, entries 4, 5) in high yield. The formation of desired product was observed with 86% yield within 3 h for chlorobenzene, although reaction proceeded at 100º C. Coupling of bromobenzene was also furnished excellent yield of 90% after 3 h at 60ºC.

With a preliminary idea of the limitations of the protocol, we chose the coupling of chlorobenzene and phenylacetylene to further optimize our catalytic system. Various common organic solvents like DMF, DMSO, THF, 1, 4–dioxane and toluene were also screened, but they are not as effective as water and also produce (Table 2, entries **2–6**) substantial amount of undesired homo-coupled product. Utilizing water as solvent, we next examined the effect of base in the model coupling of phenylacetylene and chlorobenzene.

Table 1 Initial Studies[a]

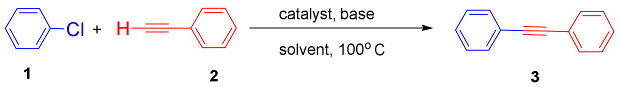


Entry	X	Catalyst (mg)	Time (h)	Yield[b] (%)
1	I	2	2	94
2	I	1	2	72
3	I	3	2	95
4	Br[c]	2	3	90
5	Cl[d]	2	3	86

[a]Reaction conditions (unless otherwise specified): **1** (2 mmol), **2** (2 mmol), catalyst (2 mg), TBAB (20 mg), water (10 mL), K_2CO_3 (2 mmol), room temperature. [b]Yields of the isolated product. [c]Temperature: 60ºC, time: 3 h. [d]Temperature: 100ºC, time: 3 h.

Several organic bases ranging from primary to tertiary amines afforded poor yields (Table 2, entries 7–9) with considerable quantity of homo-coupled products. On the other hand, inorganic bases like K_2CO_3 or Cs_2CO_3 resulted in good yields (Table 2, entries **1** and **10**).We chose K_2CO_3 as it is low cost material and also yield is relatively higher. Then we screened different Pd-catalysts like $PdCl_2$, $Pd(PPh_3)_2Cl_2$ and PVP stabilized Pd(0) nanoparticles.[12] However, the reaction did not proceed at all in the presence of $PdCl_2$ and $Pd(PPh_3)_2Cl_2$ (Table 2, entries **11** and **12**). PVP stabilized Pd(0) (for PXRD, see Fig. S3) nanoparticles furnished very poor yields (Table 2, entry **13**).

Table 2 Optimization of the Reaction Parameters[a]

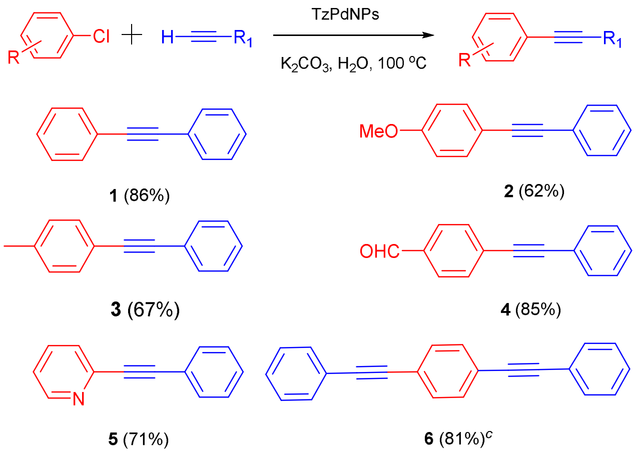


Entry	Catalyst	Solvent	Base	Yield[b] (%)
1	TzPdNPs	H_2O	K_2CO_3	92
2	TzPdNPs	DMF	K_2CO_3	10
3	TzPdNPs	DMSO	K_2CO_3	15
4	TzPdNPs	THF[c]	K_2CO_3	5
5	TzPdNPs	dioxane	K_2CO_3	7
6	TzPdNPs	toluene	K_2CO_3	12
7	TzPdNPs	H_2O	$EtNH_2$	5
8	TzPdNPs	H_2O	Et_2NH	12
9	TzPdNPs	H_2O	Et_3N	20
10	TzPdNPs	H_2O	Cs_2CO_3	82
11	$PdCl_2$	H_2O	K_2CO_3	traces
12	$Pd(PPh_3)_2Cl_2$	H_2O	K_2CO_3	traces
13	Pd(0) NPs[c]	H_2O	K_2CO_3	11

[a]Reaction conditions (unless otherwise specified): **1** (2 mmol), **2** (2 mmol), catalyst (2 mg), TBAB (20 mg), solvent (10 mL), base (2 mmol), temperature: 100ºC, time: 3 h. [b]Yields of the isolated product. [c]PVP stabilized Pd(0) nanoparticles.

With the optimized conditions in hand, at first a variety of aryl chlorides were coupled with aryl alkynes (Scheme 1).

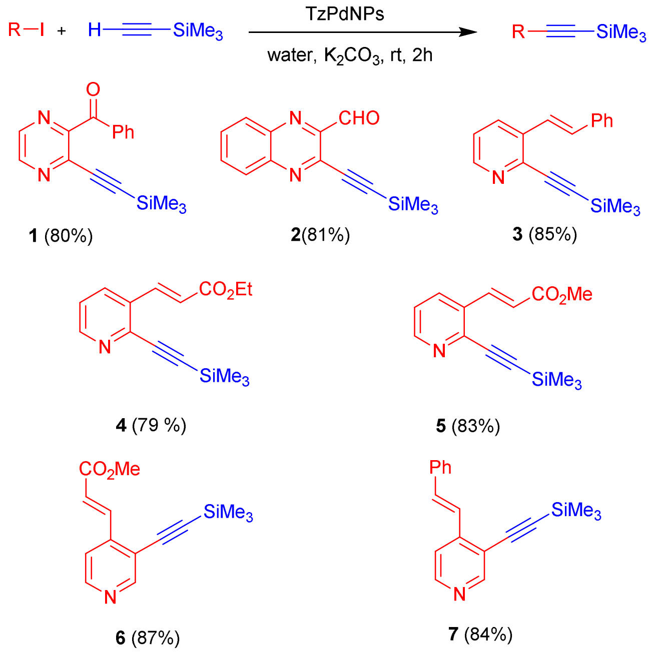
Scheme 1. Sonogashira reactions of aryl chlorides[a,b] and aryl acetylenes catalyzed by TzPdNPs.



[a]Reaction conditions: aryl chloride (2 mmol), aryl acetylenes (2 mmol), catalyst (2 mg), TBAB (20 mg), water (10 mL), temperature: 100ºC, time: 3 h. [b]Isolated yield. [c]Aryl chloride (2 mmol), aryl acetylenes (4 mmol).

Phenyl acetylene was coupled with a series of neutral (Scheme 1, **1, 7**), electron-rich (Scheme 1, **2, 3**), electron-poor (Scheme 1, **4**) and heterocyclic chlorides (Scheme 1, **5**), in yields ranging from 62% to 95%. With respect to the aryl chlorides, both electron-neutral and electron poor aryl chlorides react with phenyl acetylene to afford the products in excellent yields. More remarkable was that even extremely electron-rich aryl chloride 4-chloroanisole (Scheme 1, **2**) coupled efficiently with alkynes in the presence of this catalyst. When 1,4-dicholorobenzene was reacted with phenyl acetylene, 1,4-bis(phenylethynyl)benzene (Scheme 1, **6**) was obtained almost exclusively irrespective of ratio of the reactants. Application of trimethylsilyl acetylene under the same conditions predominantly affords the corresponding diaryl acetylenes. These indicates that the present catalyst system also exhibited the high catalytic activity to catalyze the cross-coupling reaction of aryl chlorides with 1-aryl-2-(trimethylsilyl) acetylene via activation of the C-Si bond at high temperature.[13]

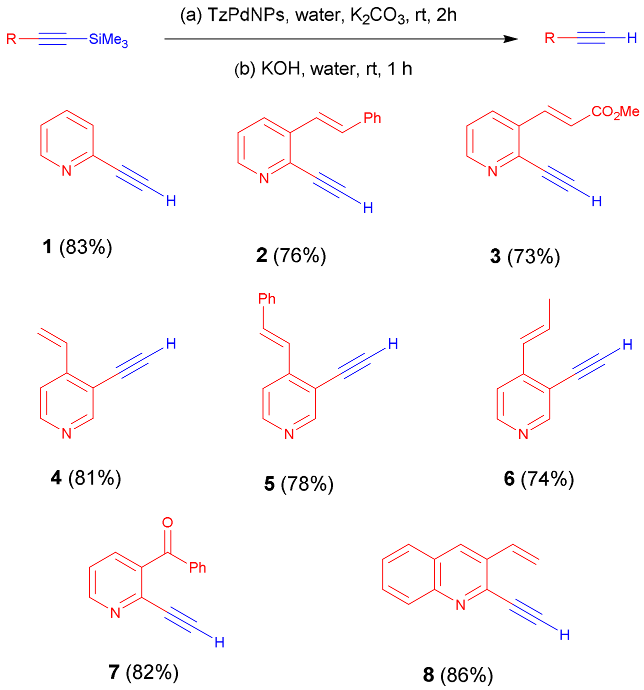
Scheme 2. Sonogashira reactions of heterocyclic iodides[a,b] and trimethylsilyl acetylene catalyzed by TzPdNPs.



[a]Reaction conditions for Sonogashira coupling: heterocyclic iodide (2 mmol), trimethylsilyl acetylene (2 mmol), catalyst (2 mg), TBAB (20 mg), water (10 mL), room temperature, time: 2 h. [b]Isolated yield.

In further experiments to expand the scope of this method, several heterocyclic iodo compounds were coupled with trimethylsilyl acetylene to afford corresponding 1-aryl-2-(trimethylsilyl)acetylenes (Scheme 2, **1-7**) at ambient temperature in aqueous medium. The C-Si bonds in the 1-aryl-2-(trimethylsilyl) acetylenes can easily be hydrolyzed in presence of KOH in aqueous medium at ambient temperature to produce pyridine, pyrazine, quinoline and quinoxaline based terminal alkynes (Scheme 3, **1-8**) in one pot. Pyridine, pyrazine, quinoline, quinoxaline and their derivatives have been widely used as a functional building block in the fabrication of the π-conjugated host materials for organic light-emitting diodes (OLEDs),[14] saccharide recognition,[15] nonlinear optical materials,[16] solar cells[17] and columnar mesophase[18] due to their specific optical and electrochemical properties.

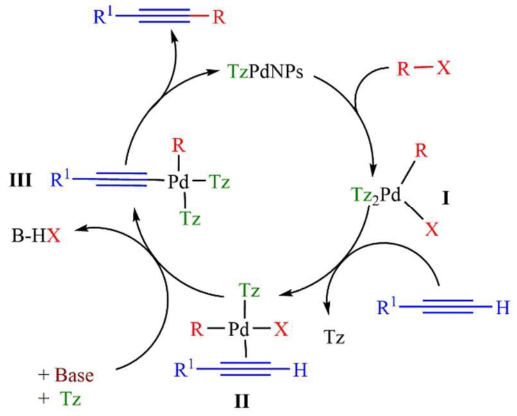
Scheme 3. One pot synthesis of pyridine, pyrazine, quinoline and quinoxaline based terminal alkynes[a,b,c] in presence of KF.



[a]Reaction conditions for Sonogashira coupling: heterocyclic iodide (2 mmol), trimethylsilyl acetylene (2 mmol), catalyst (2 mg), TBAB (20 mg), water (10 mL), room temperature, time: 2 h. [b]Reaction conditions for hydrolysis: 1-aryl-2-(trimethylsilyl) acetylenes (2 mmol), KOH (1.0 mmol), water (10 mL), room temperature, time: 1 h. [c]Isolated yield.

A plausible mechanism for the reaction is illustrated in the Scheme 4, based on the classical description of the Sonogashira reaction.[19] The catalytic cycle goes through $Pd^0/Pd^{II}/Pd^0$ oxidative addition/transmetalation/reductive elimination processes. Initially oxidative addition of the organohalide R–X to the TzPdNPs gives rise to the intermediate I. During the formation of the intermediate I, capping tetrazine (Tz) molecules act as ligands for Pd(II). The subsequent step is the attachment of the alkyne to the complex I, followed by the deprotonation results in the cis-configured complex (III). Then the acetylenic derivative is formed through the reductive elimination and the active, low oxidation state palladium catalyst is regenerated.

Scheme 4. Proposed mechanism for TzPdNPs catalysed Sonogashira reaction.



Conclusion

In summary we have developed a 3, 6-di(pyridin-2-yl)-1,2,4,5-tetrazine (pytz) capped Pd(0) nanoparticles catalysed efficient procedure for the Sonogashira cross coupling reaction of aryl chloride with aryl acetylenes in aqueous medium under copper free condition. Another advantage of the protocol is that the reaction operates at mild condition for aryl iodides. This protocol is also suitable for synthesis of the terminal alkynes from aryl iodides with trimethylsilyl acetylene. In addition, inert atmosphere is not required to carry out the reaction, offering a simple methodology for the Sonogashira reaction.

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