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# Short Communication

# Palladium nanoparticles catalyzed Sonogashira reactions for the one-pot synthesis of symmetrical and unsymmetrical diarylacetylenes



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### ARTICLE INFO

## ABSTRACT

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#### 1. Introduction

The uses of palladium reagents to mediate a range of organic transformations have been well explored during the past decades [1]. The roles of palladium nanoparticles (PdNPs) in related transformation reactions have been recognized as one of the current trends in catalysis research [2–4]. In this line, ligand stabilized palladium nanoparticles (LS-PdNPs) are exploited as catalysts in a few cross-coupling reactions e.g. Suzuki, Heck and Sonogashira [5–11]. The more frequently used stabilizers of these NPs are polymers, dendrimers, ionic liquids and some other organic ligands. Recently, the less expensive ligand free palladium nanoparticles (LF-PdNPs) are also being explored for a variety of coupling reactions [12–16]. The scope of the present work embraces the role of LF-PdNPs in the one-pot synthesis of symmetrical and unsymmetrical diarylacetylenes.

Generally, diarylacetylenes are synthesized via Sonogashira coupling reactions of monoarylacetylenes with aryl halides under established reaction conditions [17]. In the alternative and more convenient approaches, the arylacetylenes are generated in situ from aryl halides where the aryl halides are partly/completely converted to the corresponding arylacetylenes using suitable source of acetylene moiety. The in situ generated terminal acetylenes were eventually coupled with, the other part/sequentially added, aryl halides to afford the targeted diarylacetylenes. The sources of acetylene used in these one-pot protocols include trimethylsilylacetylene (TMSA) [18–21], bis(trimethylsilyl) acetylene [22], bis(tri-*n*-butylstannyl)acetylene [23], calcium carbide [24,25], acetylene(g) [26,27], propiolic acid [28], but-2-ynedioic acid

A variety of symmetrical and unsymmetrical diarylacetylenes are synthesized by ligand-free palladium nanoparticles catalyzed copper-free and amine-free Sonogashira cross-coupling reactions between aryl iodides and trimethylsilylacetylene (TMSA) under mild reaction conditions.

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[29] and 2-methyl-3-butyn-2-ol [30]. Phosphine compounds are employed either as ligand or co-ligand for the palladium-based catalyst systems in all these protocols. In most of the cases copper based co-catalysts are also employed and in some of the methods high boiling solvents are used for achieving success. Thus a reconsideration of the reaction conditions already available is necessary to offer a more attractive protocol.

To the best of our knowledge there is no report on PdNPs catalyzed one-pot synthesis of diarylacetylenes using any source of acetylenes. Herein, we report LF-PdNPs catalyzed one-pot synthesis of both symmetrical and unsymmetrical diarylacetylenes under mild reaction conditions in the absence of any copper and amine additives.

## 2. Experimental

### 2.1. Synthesis of palladium nanoparticles (PdNPs)

The PdNPs were prepared by using a protocol established from our group [16]. Palladium (II) acetate (0.0022 g) was dissolved in a 1:1 MeOH/MeCN mixture (5 mL) to get a yellow color solution. The yellow solution was stirred at room temperature for about 3 h whereupon brownish-black color was developed due to reduction of Pd(II) to Pd(0).

### 2.2. General procedure for synthesis of diarylacetylenes

4-Iodoanisole (1 mmol), TMSA (1.1 mmol) and  $K_2CO_3$  (2 mmol) were added to a freshly prepared solution of PdNPs (5 mL) in a 25 mL round bottomed flask fitted with stopper. Then, the reaction mixture was stirred at 40 °C. The reaction progress was monitored by TLC, until complete consumption of aryl iodide. To the reaction mixture containing in situ formed 4-ethynylanisole the next batch of aryliodide



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(1 mmol) was added and the reaction mixture was further allowed to stir until complete consumption of the arylacetylene. In this manner the targeted unsymmetrical diarylacetylene was formed. The detailed procedure is provided in the Supp. Info. Detailed procedure for synthesis of symmetrical diarylacetylenes is also mentioned in SI.

### 3. Results and discussion

Palladium nanoparticles (PdNPs) were prepared according to a protocol established by us [13,16]. Sonogashira coupling reactions of 4iodoanisole and TMSA was carried out as a model reaction to achieve the corresponding diarylacetylene. Initially the reactions were optimized by screening some usual bases as summarized in Table (see SI). Among the bases chosen for optimization, K<sub>2</sub>CO<sub>3</sub> was found to be most efficient. The carbonates used for catalytic reactions are hydrated salts. The carbonates are directly used from the reagent bottle without further drying/dehydration. It is proposed that, in the first step a portion of the aryl iodide reacted with TMSA followed by the deprotection of TMS group from the product to give the corresponding terminal acetylene. Deprotection of TMS group is well known and very facile in polar solvents (e.g. MeOH) when exposed to an alkali base (e.g.  $K_2CO_3$ ) [31]. The terminal acetylene so generated further coupled with the remaining portion of the aryl iodide to afford the targeted symmetrical diarvlacetvlene.

With the optimized reaction conditions in hand, we have tested the selectivity of the catalyst towards various aryl iodides to form diarylacetylenes and the result is summarized in Table 1. Aryl halides bearing both electron withdrawing substrates (Table 1, entries 3-5) and electron donating substrates (Table 1, entries 6 and 8) gave the corresponding diarylacetylenes in good yields. The catalyst compatibility towards steric hindrance was successfully tested by coupling 2-iodo-1,3,5-trimethyliodobenzene with TMSA (Table 1, entry 9). Among these substrates, 4-chloro-1-iodobenzene coupled with TMSA to give bis(p-chlorophenyl)acetylene thus providing chance for further derivatization with other protocols if required (Table 1, entry 11). One-pot synthesis of diarylacetylenes using aryl halides and TMSA as coupling partners is less explored [18-21]. The efficiency of our PdNPs based catalytic system is compared with the reported data and summarized in Table 2. The ICP-AES analysis revealed that there was no palladium content in the isolated diarylacetylenes derivatives. Since all diarylacetylenes derivatives are isolated by column chromatography contamination of Pd if any is already avoided.

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#### Table 1

One-pot synthesis of symmetrical diarylacetylenes.<sup>a</sup>

$ \begin{array}{c} \begin{array}{c} \begin{array}{c} \\ \\ \end{array} \\ \end{array} \\ \end{array} \\ = - \operatorname{Si}(\operatorname{CH}_3)_3 \xrightarrow{\begin{array}{c} 2 \mod \% \operatorname{PdNPs} \\ \end{array} \\ \xrightarrow{\begin{array}{c} \\ \end{array} \\ \xrightarrow{\begin{array}{c} \\ \end{array} \\ \xrightarrow{\begin{array}{c} \\ \end{array} \\ \end{array} \\ \xrightarrow{\begin{array}{c} \\ \end{array} \\ \xrightarrow{\begin{array}{c} \\ \end{array} \\ \end{array} \\ \xrightarrow{\begin{array}{c} \\ \end{array} \\ \end{array} \\ \xrightarrow{\begin{array}{c} \\ \end{array} \\ \xrightarrow{\begin{array}{c} \\ \end{array} \\ \end{array} \\ \xrightarrow{\begin{array}{c} \\ \end{array} \\ \xrightarrow{\begin{array}{c} \\ \end{array} \\ \xrightarrow{\begin{array}{c} \\ \end{array} \\ \end{array} \\ \xrightarrow{\begin{array}{c} \\ \end{array} \end{array} \\ \xrightarrow{\begin{array}{c} \\ \end{array} \\ \xrightarrow{\begin{array}{c} \\ \end{array} \end{array} \\ \xrightarrow{\begin{array}{c} \end{array} \end{array} \\ \xrightarrow{\begin{array}{c} \end{array} \end{array} \\ \xrightarrow{\begin{array}{c} \end{array} \end{array} \end{array} \\ \xrightarrow{\begin{array}{c} \end{array} \end{array} \end{array} \\ \xrightarrow{\begin{array}{c} \end{array} \end{array} \end{array} $ \\ \begin{array}{c} \end{array} \end{array}  \\ \begin{array}{c} \end{array} \end{array} \\ \begin{array}{c} \end{array} \end{array} \\ \begin{array}{c} \end{array} \end{array} \\ \begin{array}{c} \end{array} \\ \xrightarrow{\begin{array}{c} \end{array} \end{array} \\ \begin{array}{c} \end{array} \end{array} \\ \begin{array}{c} \end{array} \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \end{array} \\ \begin{array}{c} \end{array} \end{array} \\ \begin{array}{c} \end{array} \end{array} \\ \begin{array}{c} \end{array} \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \end{array} \\ \\ \end{array} \\ \begin{array}{c} \end{array} \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} \\ \\ \end{array} \\ \end{array} \\ \end{array}  \\ \\ \end{array} \\ \end{array}  \\ \begin{array}{c} \end{array} \end{array} \\ \end{array} \\ \\ \end{array} \\ \end{array} \\ \end{array}  \\ \\ \end{array} \\ \end{array}  \\ \end{array}  \\ \end{array}  \\ \end{array} \\ \end{array}				
Entry	R	Time (h)	Yield (%) <sup>b</sup>	
1	4-H	2	92	
2	4-CH <sub>3</sub>	2	90	
3	4-NO <sub>2</sub>	1.5	93	
4	4-COCH <sub>3</sub>	2	91	
5	4-CF <sub>3</sub>	2	90	
6	4-OCH <sub>3</sub>	3.5	84	
7	2-CH <sub>3</sub>	2	91	
8	2-OCH <sub>3</sub>	4.5	82 <sup>d</sup>	
9	1,3,5-CH <sub>3</sub>	16	74 <sup>e</sup>	
10	l-napthyl <sup>c</sup>	3	86	
11	4-C1	3	89	

<sup>a</sup> Reaction conditions: Arl (1 mmol), TMSA (0.6 mmol), K<sub>2</sub>CO<sub>3</sub> (approx. 2 mmol), CH<sub>3</sub>CN: CH<sub>3</sub>OH = 2.5: 2.5 mL.

<sup>b</sup> Isolated yields.

<sup>c</sup> The substrate is 1-iodonapthalene.

<sup>d</sup> 5% of 2-iodoanisole is isolated.

<sup>e</sup> Temperature is 45 °C and 11% of 2-ethynyl-l,3,5-trimethylbenzene is isolated.

To examine the reusability of the catalyst, after the first run, the reaction mixture was centrifuged and the residue was separated from the supernatant. Both the residue and supernatant parts were studied separately for recycle experiments (see SI). The supernatant was observed to be active for two further catalytic cycles with yields 98 and 75%, respectively. The ICP-OES analysis of the supernatant after first cycle revealed that it contains 6.38 ppm of Pd (i.e. 16 wt.% of Pd) which is responsible for the catalytic activity. The products were not separated from the supernatant during the recycling experiments and that could be a probable factor to hamper the yields in subsequent cycles. However, the residue was found to be active for four cycles with slight decrease in the catalytic activity (Fig. 1). The slight decrease in the yields during subsequent runs can be attributed to the agglomeration of PdNPs which was supported by TEM (see SI) recorded after second run. Thus, from the series of experiments performed, it can be inferred that the catalytic processes are operated in both homogeneous and heterogeneous path ways with associated leaching of Pd(0) species.



Fig. 1. Data showing the recyclability of PdNPs.

The mechanistic pathway of PdNPs was comparable with palladium complexes or ions towards Sonogashira coupling reactions [32,33]. In case of copper-free Pd complexes or ions, initially Pd(0) species were generated from the palladium precursors like Pd(PPh<sub>3</sub>)<sub>4</sub>, PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, Pd(OAc)<sub>2</sub> etc., by reacting with solvents, additives or ligands. These species undergo oxidative addition with aryl halide (ArX) to form ArPd(II)X species. The base participates in the deprotonation of the terminal alkyne forming an alkynyl which is also coordinated to the Pd center. Further, reductive elimination of the intermediate results in the

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## Table 2

Comparison of the efficiency of PdNPs reported in this work with related Pd catalytic systems reported in the literature for preparation of diarylacetylenes.

		$\stackrel{1}{\smile}$ + =-Si(CH <sub>3</sub> )	Catalyst <sup>3</sup> Co-ligand/Co-catalyst				
S. no.	Catalyst (mol%)	Co-ligand/co-catalyst	Solvent	Base	Temp (°C)	Time (h)	Ref.
1. 2. 3. 4. 5.	PdNPs (2) Pd(PPh <sub>3</sub> ) <sub>4</sub> (10) Pd(PPh <sub>3</sub> ) <sub>4</sub> (5) PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> (6) Pd(OAc) <sub>2</sub> (2)	PPh <sub>3</sub> /Cul(15 mol%) PPh <sub>3</sub> PPh <sub>3</sub> /Cul (10 mol%) <i>t</i> -Bu <sub>3</sub> P (8 mol%)	CH <sub>3</sub> CN:CH <sub>3</sub> OH(l:1) C <sub>6</sub> H <sub>6</sub> CH <sub>3</sub> OH H <sub>2</sub> O DMA	K <sub>2</sub> CO <sub>3</sub> TEBAC, NaOH NaOCH <sub>3</sub> DBU TBAF	40 °C 40 °C Reflux RT to 80 °C 100 °C	2 48 6 18 1	Present work 18 <sup>a</sup> 19 20 21

<sup>a</sup> 2-iodothiophene was used as substrate.

diarylacetylene product and Pd(0) is regenerated at the end of a catalytic cycle [6]. In case of PdNPs as a catalyst, the oxidative addition of aryl halide (ArX) takes place on the surface of catalyst giving rise to ArPd(II) X species and that undergoes similar mechanistic steps as described for Pd complexes regenerating the PdNPs after a catalytic cycle [4]. However, exact reaction mechanisms of PdNPs catalyzed coupling reactions are not known. de Vries suggested and proved the participation of anionic intermediates like ArPdX<sub>2</sub><sup>-</sup> and PdX<sub>3</sub><sup>-</sup> during the catalytic cycle in the event of ligand-free PdNPs as catalyst for C–C coupling reactions [34].

Powder XRD pattern of PdNPs before and after catalytic coupling reactions confirmed the fcc lattice of the catalyst. Size of the PdNPs before and after the catalysis was analyzed by TEM measurements and found to be 4.5–7 nm. Although, the size of the particles was unaltered, agglomeration was noticed after the second recycle (see SI). The XPS data was utilized to check the valence state of metal in the catalyst. The XPS spectrum of catalyst before the catalysis shows the two peaks at 335.7 eV and 340.9 eV corresponding to Pd3d<sub>5/2</sub> and Pd3d<sub>3/2</sub> respectively, indicating the zerovalent Pd. The peaks at 337.5 eV and 342.8 eV represent the PdO. The percentage of Pd(0) and PdO was confirmed as 70.2% and 29.8% by considering relative peak areas. XPS spectrum of PdNPs after the catalysis revealed major amount of Pd present in zero oxidation state. However, oxidation of Pd surface during the sample preparation could not be avoided [35].

To evaluate the activity of catalyst towards the chemoselectivity and to prepare bis(bromoaryl)acetylenes, we have chosen bromo derivatives of aryl iodides as potential substrates. Further detail of the product profiles is collected in Table 3. The resultant products contain derivatizable bromo substituents that can be starting materials for higher analog of acetylenes under proper conditions. The PdNPs used in this work is a known catalyst for Suzuki coupling reactions [16]. Thus, Suzuki coupling reaction of bis(3-bromophenyl)acetylene and 4methoxyphenylboronic acid was carried out to extend the scope of the reaction (Scheme 1). Interestingly, coupling of the boronic acid with the internal acetylene group also happened along with the desired Suzuki coupling giving a mixture of products (see SI). The crude reaction mixture was characterized by ESI-MS and the products identified on the basis of a preliminary analysis are shown in Scheme 1. The coupling reaction between 1,4-diiodobenzene and TMSA resulted in a mixture of products (Table 3, entry 1). The heterocycle bearing both iodide and bromide was also successfully coupled with TMSA resulting in the bromo-substituted compound in good yield (Table 3, entry 5).

The catalytic activity of PdNPs was further exploited by one-pot synthesis of unsymmetrical diarylacetylenes as shown in Table 4. Initially, 4-iodoanisole was coupled with required amount of TMSA to afford trimethylsilyl protected 4-ethynylanisole. The in situ formed compound undergoes deprotection to give the terminal acetylene. The next step was carried out by adding a fresh batch of aryl iodide, however, without any further addition of catalyst or base. Thus the desired unsymmetrical diarylacetylene was formed within 2 h (Table 4, entry 1). When we have chosen aryl iodide containing electron withdrawing substrates such as 4-iodoacetophenone and 4-iodonitrobenzene for the synthesis of unsymmetrical moieties, instead of TMS deprotected product we isolated the symmetrical diarylacetylenes. The substrate scope was examined by employing various aryl halides to couple with 4-ethynylanisole (Table 4, entries 2–9). All the coupling reactions conceded unsymmetrical diarylacetylenes in good yields. The sterically hindered substrates like 2-iodotoluene, 2-iodoanisole and 2-iodo-1,3,5-trimethyliodobenzene were coupled with 4-ethynylanisole to afford corresponding unsymmetrical diarylacetylenes in good yields (Table 4, entries 6-8).

In an alternative manner, 4-iodoanisole, 4-iodotoluene and TMSA were combined at same time to synthesize 4-methoxy-4'-methyldiphenylacetylene. The desired product was isolated and the yield was found to be 80% in contrast with the 90% yield when performed in a step wise manner. Also 5% of bis(*p*-tolylphenyl)acetylene and 10% of bis(*p*-methoxyphenyl)acetylene were formed along with the desired product.

#### Table 3

One-pot synthesis of bis(bromo)arylacetylenes.<sup>a</sup>



Entry	Х	Y	Time(h)	Yield (%) <sup>b</sup>
1	4-I	СН	3	_c
2	4-Br	СН	4	81
3	3-Br	СН	2.5	76 <sup>d</sup>
4	2-Br	СН	3	74 <sup>e</sup>
5	5-Br	N	2	72 <sup>f</sup>

<sup>a</sup> Reaction conditions: ArI (1 mmol), TMSA (0.6 mmol), K<sub>2</sub>CO<sub>3</sub> (approx. 2 mmol), CH<sub>3</sub>CN: CH<sub>3</sub>OH = 2.5:2.5 mL.

<sup>b</sup> Isolated yields.

<sup>c</sup> Formation of a mixture of products.

<sup>d</sup> 5% of 1-bromo-3-iodobenzene is isolated.

<sup>e</sup> 9% of 1-bromo-2-iodobenzene is isolated.

<sup>f</sup> 11% of 5-bromo-2-iodopyridine is isolated.



+mixture of compounds

Scheme 1. Coupling reaction of bis(3-bromophenyl)acetylene with 4-methoxyphenylboronic acid.

To investigate the effect of the amount of Pd towards the catalysis. three different loadings of Pd were screened like 2, 1.5 and 1 mol% towards Sonogashira coupling reaction between 4-iodotoluene and TMSA at 40 °C. It was noticed that under optimized catalytic loading i.e. 2 mol% the conversion to product is 99% (see SI). However, at 1.5 and 1 mol% of catalyst loading the yields were 90 and 80%, respectively. We found that the nature of the PdNPs prepared at three different concentrations of Pd those are used in the catalysis are comparable as can be seen from their UV-vis spectra and powder XRD pattern (see SI).

#### 4. Conclusion

In conclusion, we have demonstrated ligand-free palladium nanoparticles catalyzed one-pot synthesis of diarylacetylenes under mild reaction conditions. A variety of symmetrical and unsymmetrical diarylacetylenes were synthesized in good yields. The catalyst could be recycled with slight decrease in activity up to four catalytic cycles.

#### Acknowledgments

D.K.C. thanks CSIR, India for the financial support. P. K. M. thanks IIT Madras for a fellowship.

#### Table 4

One-pot synthesis of unsymmetrical diarylacetylenes.<sup>a</sup>

#### Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx. doi.org/10.1016/j.catcom.2013.12.029.

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ÓCH<sub>3</sub>

Entry	R	Time (h)	Yield (%) <sup>b</sup>
1	4-H	2	87
2	4-CH <sub>3</sub>	2	90
3	4-COCH <sub>3</sub>	2	87
4	4-NO <sub>2</sub>	2	87
5	4-Cl	2.5	84
6	2-CH <sub>3</sub>	4	81
7	2-0CH <sub>3</sub>	4	85
8	1,3,5-CH <sub>3</sub>	8	82
9	l-napthyl <sup>c</sup>	3	81

Reaction conditions: step 1: 2 mol% PdNPs, 4-iodoanisole (1 mmol), TMSA (1.1 mmol), K2CO3 (approx. 2 mmol), CH3CN: CH3OH = 2.5: 2.5 mL; step 2: ArI (1 mmol). b

Isolated yields.

<sup>c</sup> The substrate is 1-iodonapthalene.

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