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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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ABSTRACT

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.

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 [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 4-iodoanisole 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_2CO_3 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 diarylacetylene.

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.

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.

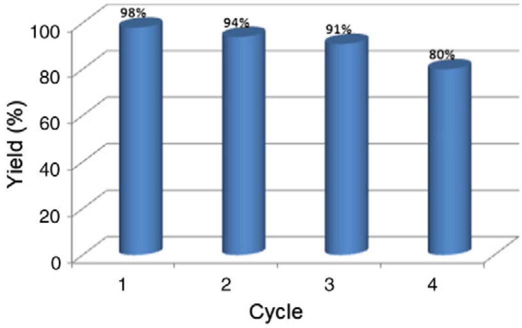
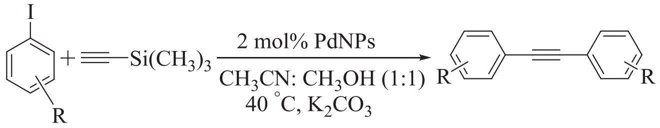


Fig. 1. Data showing the recyclability of PdNPs.

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 $Pd(PPh_3)_4$, $PdCl_2(PPh_3)_2$, $Pd(OAc)_2$ 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

Table 1

One-pot synthesis of symmetrical diarylacetylenes.[a]



Entry	R	Time (h)	Yield (%)[b]
1	4-H	2	92
2	4-CH_3	2	90
3	4-NO_2	1.5	93
4	4-$COCH_3$	2	91
5	4-CF_3	2	90
6	4-OCH_3	3.5	84
7	2-CH_3	2	91
8	2-OCH_3	4.5	82[d]
9	1,3,5-CH_3	16	74[e]
10	l-napthyl[c]	3	86
11	4-C1	3	89

[a] Reaction conditions: ArI (1 mmol), TMSA (0.6 mmol), K_2CO_3 (approx. 2 mmol), CH_3CN: CH_3OH = 2.5: 2.5 mL.

[b] Isolated yields.

[c] The substrate is 1-iodonapthalene.

[d] 5% of 2-iodoanisole is isolated.

[e] Temperature is 45 °C and 11% of 2-ethynyl-l,3,5-trimethylbenzene is isolated.