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Green synthesis of Pd nanoparticles mediated by *Euphorbia thymifolia* L. leaf extract: Catalytic activity for cyanation of aryl iodides under ligand-free conditions

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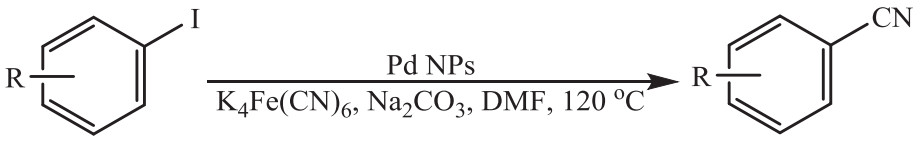
HIGHLIGHTS

- Green synthesis of Pd NPs by extract of leaves of *Euphorbia thymifolia* L.
- Catalytic cyanation of aryl iodides under ligand-free conditions.
- The catalyst could be easily recovered and reused several times.

GRAPHICAL ABSTRACT



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ABSTRACT

Pd nanoparticles (NPs) were synthesized by using aqueous extract of leaves of *Euphorbia thymifolia* L., a non-toxic ecofriendly material. The catalytic activity of the Pd NPs was investigated in the cyanation of aryl iodides using $K_4Fe(CN)_6$ as the cyanating agent under ligand-free conditions. The nitriles were obtained in good to excellent yield and the catalyst can be recovered and reused for five times without significant loss of catalytic activity.

1. Introduction

Nitriles are key structures in biologically active substances and in industry for the manufacture of pharmaceuticals, herbicides, agrochemicals and dyes [1]. Additionally, these compounds are very important units for synthesizing nitrogen-containing heterocycles, carboxylic acids, amides, amines and aldehydes [2].

A number of synthetic methods have been reported in the literature for the synthesis of aryl nitriles. However, many employ toxic inorganic or organic cyanide sources for this purpose, such as alkali-metal cyanides, trimethylsilyl cyanide [3,4] or acetone cyanohydrins [5].

Earlier reported methods for the synthesis of aryl nitriles suffered from drawbacks such as the use of expensive, toxic and moisture sensitive reagents and catalysts, environmental pollution caused by formation of heavy metal waste, low yields, long reaction times, harsh reaction conditions, the poor availability or difficulty in preparing the starting materials or catalysts, tedious work-ups, and formation of side products [6–11]. Therefore, the need for improved methods that reduce or eliminate the use and generation of hazardous compounds is essential.

$K_4Fe(CN)_6$ is not explosive or flammable, is inexpensive, non-toxic and no very volatile. Also, it is a very useful and efficient reagent, can be easily prepared on ton scale, and is cheaper than

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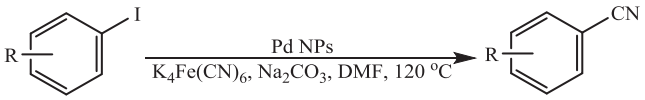

Scheme 1. Cyanation of aryl iodides using $K_4Fe(CN)_6$ in the presence of Pd NPs.

KCN and NaCN. For these reasons, it has received much attention as a cyanide source in the synthesis of aryl nitriles [12–17].

Several syntheses of aryl nitriles have been reported using $K_4Fe(CN)_6$ in the presence of homogeneous catalysts and various ligands such as *N*,*N*′-dimethylethylenediamine (DMEDA) and ethylenediamine [6,18–27] while less expensive heterogeneous catalysts have less received attention. However, the high cost of preparation of heterogeneous catalysts restricts their applications, especially in large-scale process. Thus, the development of a new system for the synthesis of aryl nitriles under ligand-free conditions still remains an active research area. Considering the fact that metal nanoparticles are less expensive than complex heterogeneous catalysts, our attention was drawn to developing a Pd NPs-catalyzed procedure.

Quite recently, we reported the green synthesis of Pd NPs aqueous extract of leaves of *Euphorbia thymifolia* L. and investigated their good catalytic efficiency in the ligand-free Stille and Hiyama cross-coupling reactions [28].

In continuation of our efforts to develop environmentally friendly synthetic methodologies [29–34], we report the procedure for the direct cyanation of aryl iodides using $K_4Fe(CN)_6$ in the presence of catalytic amounts of Pd NPs under ligand-free conditions (Scheme 1). Pd NPs were characterized using the powder XRD, TEM, UV–vis and FT-IR in our previous work [28].

2. Experimental

High-purity chemical reagents were purchased from the Merck and Aldrich chemical companies. All materials were of commercial reagent grade. Melting points were deter-mined in open capillaries using a BUCHI 510 melting point apparatus and are uncorrected. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance DRX spectrometer at 400 and 100 MHz, respectively. FT-IR spectra were recorded on a Nicolet 370 FT/IR spectrometer (Thermo Nicolet, USA) using pressed KBr pellets. The element analyses (C, H, N) were obtained from a Carlo ERBA Model EA 1108 analyzer carried out on Perkin–Elmer 240c analyzer. UV–visible spectral analysis was recorded on a double-beam spectrophotometer (Hitachi,

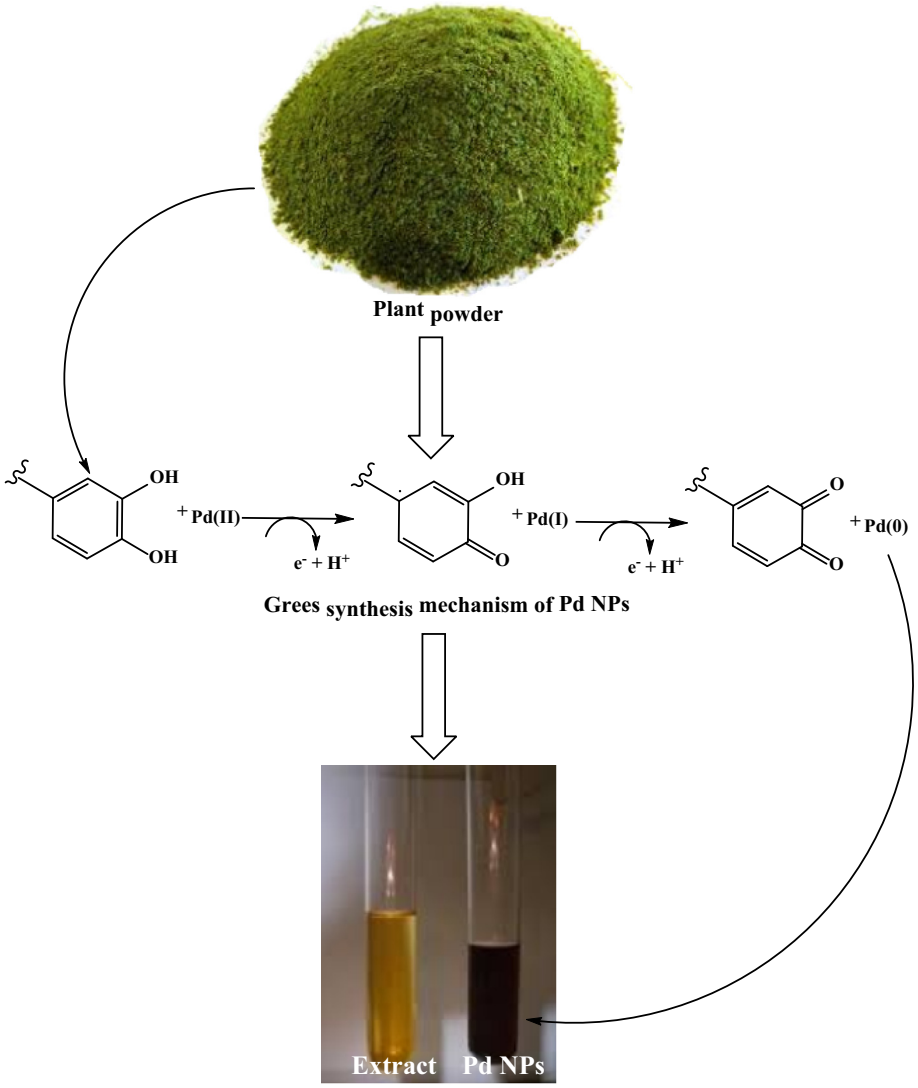

Fig. 1. Mechanism of the Pd NPs green synthesis; oxidation of polyol by metal ions to α, β-unsaturated carbonyl groups. Reproduced with permission from Ref. [29]