



# A dithizone-functionalized polystyrene resin-supported Pd(II) complex as an effective catalyst for Suzuki, Heck, and copper-free Sonogashira reactions under aerobic conditions in water

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## ABSTRACT

A novel polystyrene-supported palladium(II) dithizone complex is found to be a highly active catalyst for the Suzuki, Heck, and Sonogashira reactions of aryl halides in water. By this protocol, aryl halides, coupled with phenyl boronic acid (Suzuki reaction), alkenes (Heck reaction) or terminal alkyne (Sonogashira reaction), smoothly affords the corresponding cross-coupling products in good to excellent yields. Furthermore, the catalyst shows good thermal stability and recyclability. The catalyst was recycled for the Suzuki, Heck, and Sonogashira reactions for five runs without appreciable loss of its catalytic activity and negligible metal leaching.

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## 1. Introduction

Regarding the C–C bond formation reactions, particular attention has been paid to the coupling of aryl halides with organoboronic acids (Suzuki coupling reaction) [1–7], alkenes (Heck reaction) [8–14], and alkynes (Sonogashira coupling reaction) [15–19], respectively. These Pd-catalyzed coupling reactions are ranked today among the most general transformations in organic synthesis, which have great industrial potential for the synthesis of chemicals, therapeutic drugs, and their intermediates.

The original Heck, Suzuki, and Sonogashira reactions generally proceed in the presence of a homogeneous palladium catalyst, which makes its separation and recovery tedious, if not impossible, and might result in unacceptable palladium contamination of the products. A way to overcome this difficulty would be the use of a heterogeneous palladium catalyst.

From the standpoint of green chemistry, development of more environmentally benign conditions for the reaction such as the use of a heterogeneous palladium catalyst would be desirable [20–23]. Palladacycles have recently emerged as one of the most promising

classes of catalysts or catalyst precursors in the Pd catalyzed C–C bond forming reactions such as Heck–Mizoroki [24–34], Suzuki–Miyaura [1,35–41], and Sonogashira reactions [42–49].

The immobilization methods used to deposit palladium into heterogeneous solid beds have been studied extensively, and diverse supports such as clay [50], carbon nanofiber [51], montmorillonite [52], magnetic mesoporous silica [53], zeolite [54], and metal oxides [55] have been investigated.

A current challenge in this area is the development of efficient immobilized systems that could simultaneously fulfill the usual targets of achieving high TON values and facilitate recovering and reuse as well as the need for obtaining Pd-free final products [56,57], meeting the strict purity specifications for the pharmaceutical industry [58,59].

In this regard, different types of heterogeneous catalysts have been prepared with the goal of achieving catalyst recovery and recycling [60,61].

To date, development of green chemistry through organic reactions conducted in water has become one of the most exciting research endeavors in organic synthesis [62–65]. Several examples of Pd-catalyzed Suzuki–Miyaura, Mizoroki–Heck, and Sonogashira reactions in aqueous media have been reported [66–69].

Recently, Xia et al. described cross-linked polymer supported Palladium catalyzed carbonylative Sonogashira coupling reaction in water [70]. Singh et al. reported synthesis and characterization

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of recyclable and recoverable MMT-clay exchanged ammonium tagged carbapalladacycle catalyst for Mizoroki-Heck and Sonogashira reactions in ionic liquid media [71]. Furthermore, Iranpoor et al. illustrated Palladium nano-particles supported on agarose as efficient catalyst and bioorganic ligand for C–C bond formation *via* solvent less Mizoroki-Heck reaction and Sonogashira reaction in polyethylene glycol (PEG 400) [72]. Wu et al. exemplified ionic liquid functionalized phosphine-ligated Palladium complex for the Sonogashira reactions under aerobic and copper-free conditions [73]. Above all the methods provide good yield, but some of these reactions are sluggish requiring at least 24 h for completion, lengthy work-up procedure, harsh reaction conditions and require absolutely dry and inert media.

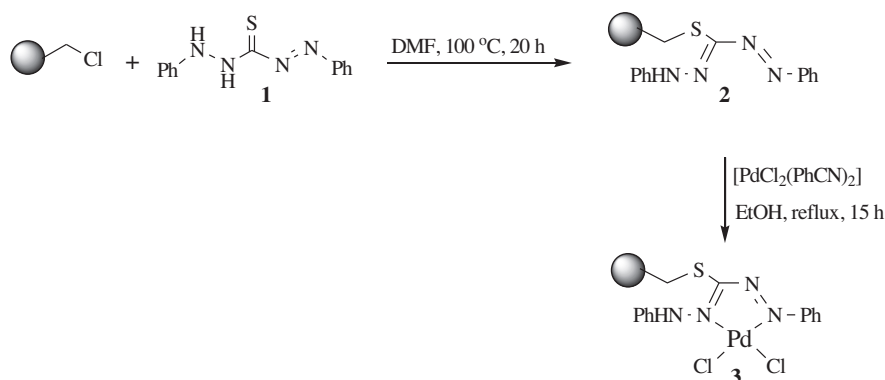
So far, polystyrene-supported palladium catalysts have successfully been used for the Heck [74] and Suzuki [75–78] reactions, and have shown lower levels of palladium leaching during cross-coupling. To date, a few palladium complexes on functionalized polystyrene support have been prepared and successfully used in Sonogashira reaction [79–85]. Very recently, our research team have reported the synthesis of the polystyrene-supported bidentate phosphine palladium(0) complex [abbreviated as PS-dpp-Pd(0)], and the polystyrene-supported palladium(II) 1-phenyl-1,2-propanedione-2-oxime thiosemi-carbazone complex [abbreviated as PS-ppdot-Pd(II)], and found that these complexes are a highly active and recyclable catalyst for Sonogashira reaction of aryl iodides [86,87] or benzoyl chlorides [88,89] with terminal alkynes.

Our approach was guided by three imperatives: (i) the support should be easily accessible; (ii) develop an efficient synthetic process for the facile conversion of Heck, Suzuki, and Sonogashira coupling reactions; and (iii) the ligand anchored on the support should be thermal stability, air-stable at room temperature, which should allow its storage in normal bottles with unlimited shelf-life.

Herein, we report the synthesis of polystyrene-supported palladium(II) dithizone complex [abbreviated as PS-dtz-Pd(II)] catalyst and its application to cross-couplings such as Suzuki-Miyaura, Mizoroki-Heck, and copper-free Sonogashira reactions in water under aerobic conditions. The ease of preparation of the complex, its long shelf-life, stability toward air, and compatibility with a wide variety of aryl halides and alkynes make it ideal for the above mentioned reactions.

## 2. Experimental

All materials were commercial reagent grade. Chloromethylated polystyrene (4–5% Cl and 2% cross-linked with divinylbenzene) was a product of Merck. Alkyne and aryl halide compounds were obtained from Merck or Fluka.



**Scheme 1.** Preparation of the heterogeneous catalyst PS-dtz-Pd(II) **3**.

### 2.1. Preparation of polymer-anchored PS-dtz-Pd(II) **3**

To a 250-ml of round bottom flask equipped with a magnetic stirrer bar and containing DMF (50 ml), were added chloromethylated polystyrene (2 g, 1.25 mmol/g of Cl) and dithizone (7.5 mmol). The reaction mixture was stirred for 24 h at 100 °C, and was subsequently filtered and washed thoroughly with DMF, and dried in vacuo for 12 h. The dithizone functionalized polymer **2** (3.0 g) was treated with ethanol (50 ml) for 30 min. An ethanolic solution of PdCl<sub>2</sub>(PhCN)<sub>2</sub> (1.2 g) was added, and the resulting mixture was heated to 80 °C for 15 h. The resulting bright yellow colored polymer, impregnated with the metal complex, was filtered and washed with ethanol to obtain PS-dtz-Pd(II) **3** (Scheme 1).

### 2.2. General procedure for the Suzuki coupling reaction

A mixture of aryl halide (1.0 mmol), phenyl boronic acid (1.2 mmol), PS-dtz-Pd(II) (0.001 mmol), K<sub>2</sub>CO<sub>3</sub> (2 mmol), and water (3 ml) was stirred at 70 °C for 5 h. After completion of the reaction, the mixture was filtered to recover the catalyst. The polymer was washed with water and acetonitrile, vacuum dried, and stored for a new run. After GC analysis, the solvent was removed under vacuum, and the crude product was subjected to silica gel column chromatography using CHCl<sub>3</sub>–CH<sub>3</sub>OH (97:3) as eluent to afford the pure product.

### 2.3. General procedure for the Heck reaction

A mixture of aryl halide (1.0 mmol), methyl acrylate (1.5 mmol), PS-dtz-Pd(II) (0.001 mmol), K<sub>2</sub>CO<sub>3</sub> (2.0 mmol), and water (3 ml) was stirred at 70 °C for 5 h. After completion of the reaction, the mixture was filtered to recover the catalyst. The polymer was washed with water and acetonitrile, vacuum dried, and stored for a new run. After GC analysis, the solvent was removed under vacuum, and the crude product was subjected to silica gel column chromatography using CHCl<sub>3</sub>–CH<sub>3</sub>OH (97:3) as eluent to afford the pure product.

### 2.4. General procedure for the Sonogashira coupling reaction

An aryl halide (1.0 mmol) and a terminal alkyne (1.2 mmol) were added to a mixture of PS-dtz-Pd(II) (0.001 mmol), piperidine (2.0 mmol), and water (3 ml) in a glass flask under vigorous stirring. The mixture was stirred at room temperature for 3 h under aerobic conditions. After completion of the reaction, the mixture was filtered to recover the catalyst. The polymer was washed with water and acetonitrile, vacuum dried, and stored for a new run. After GC analysis, the solvent was removed under vacuum, and the crude

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