Applied Catalysis A: General 496 (2015) 58–63

Contents lists available at ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

Polystyrene supported salen type bis-thiopseudourea Pd(II)-complex catalyzed Suzuki coupling reaction in aqueous media

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ARTICLE INFO

Article history:
Received 21 November 2014
Received in revised form 16 February 2015
Accepted 18 February 2015
Available online 26 February 2015

Keywords:
Thiopseudourea
Suzuki
C–C coupling
Palladium

ABSTRACT

A new salen type *N′*,*N*-1,2-phenylenebis(3-(4-fluorobenzoyl-2-benzyl-2-thiopseudourea) functionalized polystyrene resin supported palladium(II) complex (**3**) was found to be highly efficient catalyst for the Suzuki cross-coupling reaction of aryl halides with arylboronic acids. The coupled products of various activated and deactivated aryl halides were produced in good to excellent yields under low catalyst loadings and in water/methanol system. Further, the catalyst showed excellent recyclability without any significant loss in its activity.

1. Introduction

The development of environmentally benign and efficient reaction procedures in industrial research has been growing importance in the recent times. Among these systems, water conducted organic transformations have much attention [1–5], because water is harmless, non-combustible and readily available. The main advantage of water as a solvent offers simplification of workup procedures and acceleration of reaction rates [6]. Palladium catalyzed organic reactions conducted in water have become one of the most interesting research endeavors in organic synthesis [7–10]. Polymer supported palladium catalysts are important in many organic transformations including C—C bond formation reactions [11–20]. These heterogeneous catalysts have proved to be potential with broad applicability, high efficiency and recyclability. Suzuki reaction is an important method for C—C bond formation that has several applications in the synthesis of natural products [21], and bioactive compounds [22]. Peter Styring has reported polymer-supported salen-type palladium complex as a catalyst for the Suzuki–Miyaura cross-coupling reaction [23,24]. Lei has described Pd(salen)/polyoxo-metalate compound for Suzuki cross-coupling in EtOH/H_2O under mild reaction conditions [25]. Palladium(II) salen complexes have been reported as catalysts for different C—C cross-coupling reactions and hydrogenation of imines [26,27]. Most of the reported metal salen complexes belong to the first transition series [28], and the second series of these complexes are still rare [29]. In this context, we considered polystyrene supported bis-thiopseudourea Pd(II) complex (**3**) [abbreviated as PS-btsu-Pd(II)] as catalyst for the Suzuki reaction of aryl halides under aqueous conditions at room temperature. To the best of our knowledge, this is the first report on the use of polymer supported bis-thiopseudourea ligand that shows excellent catalytic activity with various aryl halides and arylboronic acids in the palladium catalyzed Suzuki reaction.

Recently, we have reported homogeneous and heterogeneous thiopseudourea palladium(II) complexes (**4** & **5**) as catalysts for Sonogashira, Suzuki–Miyaura, Heck, Hiyama and Larock heteroannulation cross-coupling reactions (Fig. 1) [30–32]. Although it showed significant catalytic activity for the Suzuki cross-coupling reactions of aryl halides, the disadvantages associated with it are overwhelmed by our PS-btsu-Pd(II) complex (**3**).

2. Experimental

All materials were commercial reagent grade. Chloromethylated polystyrene (1% cross-linked, 200–400 mesh with 1.0–1.3 mmol/g)

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http://dx.doi.org/10.1016/j.apcata.2015.02.029
0926-860X/

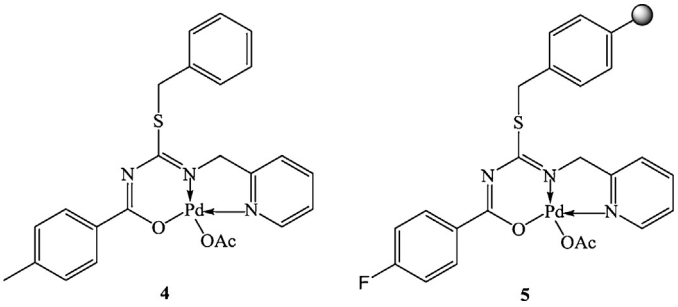
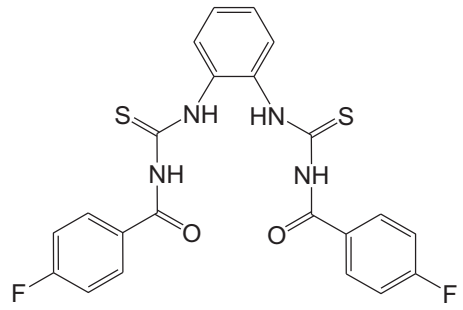


Fig. 1. Thiopseudourea-Pd(II) complex **4** & **5**.

was a product of Alfa-acer. Arylboronic acid and aryl halide compounds were obtained from Aldrich.

2.1. General procedure for the preparation of N′,N-1,2-phenylenebis(3-4-fluorobenzoyl-2-thiourea (*1*)

To a solution of NH_4SCN (0.912 g, 12 mmol) in 50 mL of acetone 4-fluorobenzoyl chloride (10 mmol) was added dropwise at 0 °C and stirred for 30 min. To this, benzene-1,2-diamine (0.540 g, 5 mmol) was added at the same temperature and allowed to stir for an additional 3 h at room temperature. The mixture was concentrated to a solid; water (50 mL) was added, and extracted with ethyl acetate (2 × 50 mL). The organic layer was washed with brine (20 mL), dried over $MgSO_4$, and filtered, after which the solvent was removed under vacuum. The crude product was purified by column chromatography on silica gel using ethyl acetate/hexane as the eluent to give the desired products (**1a** & **1b**) in 75–80% yield.

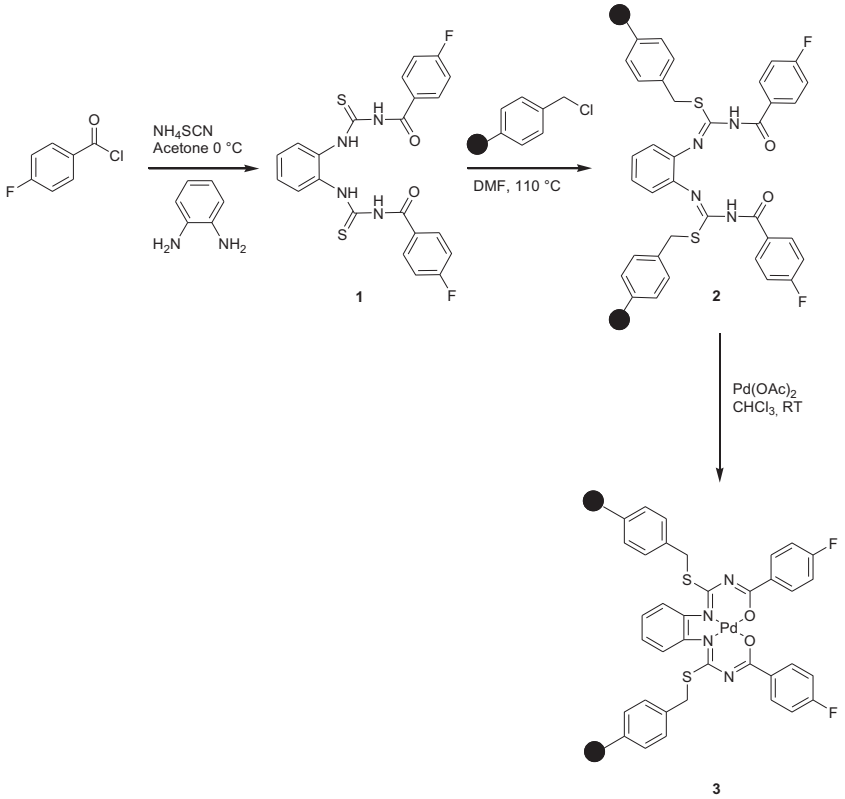


2.1.1. N′,N-1,2-Phenylenebis(3-4-fluorobenzoyl-2-thiourea)

^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 12.27 (s, 2*H*), 9.18 (s, 2*H*), 7.92–7.85 (m, 6*H*), 7.47–7.42 (m, 2*H*), 7.19–7.15 (m, 4*H*); ^{13}C NMR (75 MHz, $CDCl_3$) δ 179.9, 167.2, 165.6, 164.6, 133.0, 130.3, 130.2, 128.1, 127.7, 126.9, 116.5, 116.2; LCMS (*m*/*z*) $(M)^+$ = 470. Anal. Calc. for $C_{22}H_{16}F_2N_4O_2S_2$: C, 56.16; H, 3.43; N, 11.91; S, 13.63. Found: C, 56.04; H, 3.35; N, 11.87; S, 13.51%.

2.2. Preparation of polymer supported bis-thiopseudourea-Pd(II) complex (*3*)

To a 250-mL round bottom flask containing DMF (50 mL), equipped with magnetic stirrer bar is added with chloromethylated polystyrene (4.6 g, 1.25 mmol/g of Cl) and *N*′,*N*-1,2-phenylenebis(3-(4-fluorobenzoyl-2-thiourea) (2.5 mmol). The reaction mixture was stirred for 24 h at 110 °C and was subsequently filtered and washed thoroughly with DMF, dried in oven at 80 °C for 24 h. To the chloroform (50 mL) solution polystyrene supported thiopseudourea **2** (2.5 mmol) and $Pd(OAc)_2$ (2.5 mmol) were added and the resulting mixture was allowed to stir at room temperature for 24 h.



Scheme 1. Preparation of polystyrene-supported Pd(II) complex **3**.