

Short communication

High-turnover aminopyridine-based Pd-catalysts for Suzuki–Miyaura reaction in aqueous media



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ARTICLE INFO

Article history:

Received 26 December 2015

Received in revised form 17 February 2016

Accepted 18 February 2016

Available online 21 February 2016

Keywords:

Aminopyridines

Palladium

High-turnover catalyst

Suzuki–Miyaura reaction

Aqueous media

ABSTRACT

A high-turnover catalytic system based on commercially available aminopyridines (L) and PdCl₂ has been developed for Suzuki–Miyaura reaction in aqueous media. Reactions of arylboronic acids with a wide range of aryl iodides, bromides and chlorides proceeded in the presence of these catalysts for a short time in aqueous media to afford the cross-coupling products in high yields. Furthermore, this protocol allows tolerating a wide range of functional groups.

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1. Introduction

The palladium-catalyzed Suzuki–Miyaura reaction has become one of the most powerful and convenient synthetic tools for preparation of biaryl compounds [1]. The reaction is typically performed in organic solvents in the presence of a suitable base, 1–5 mol% of a palladium catalyst precursor and a ligand that coordinate to palladium center to stabilize the catalyst. In addition to traditional triphenylphosphine ligand [2], electron-rich bulky phosphines [3], phosphine oxides [4] and P- and N-based palladacycles [5] have been suggested as efficient ligands or catalyst precursor. Recently a number of catalytic systems with phosphine-free ligands, such as C-based heterocyclic carbenes [6], C,N-based 2-aryl-2-oxazolines [7], aryloximes [8], arylimines [9], N,N-based diazabutadienes [10], DABCO [11], tetrahydropyrimidinium salts [12], EDTA [13], pyrimidines [14], N-phenylurea [15], N,N-dimethyl-β-alanine [16], L-proline [17], β-oxo amides [18], guanidines [19], 1,2-azoles [20] and quinoline-2-carboxamide [21] have been reported [22]. However, some of these new ligands and complexes are not readily available and expensive. So, simple, inexpensive, easily prepared, and stable catalysts are still desired for this reaction. Earlier we have synthesized for the first time the palladium complex Pd(DMAP)₄Cl₂ and evaluated its catalytic activity for the Heck reaction in water and aqueous ethylene glycol [23a].

Analogous palladium complex, Pd(DMAP)₄(OH)₂, has been obtained by oxidation of DMAP-stabilized Pd nanoparticles by air and demonstrated a high catalytic activity in the Suzuki–Miyaura reaction of 4-

halobenzoic acids with phenylboronic acid in water [23b,c]. However, to the best of our knowledge, the potential of simple aminopyridine ligands has not been used in Suzuki–Miyaura reaction.

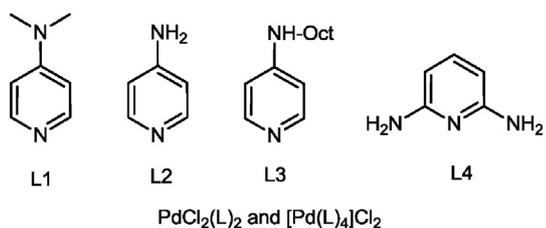
Herein, we report an efficient, green and high-turnover catalytic system based on complexes of simple aminopyridines and PdCl₂ [24] (Scheme 1) for Suzuki–Miyaura reaction in aqueous media and the successful application of this protocol to a wide variety of reagents, such as aryl(heteroaryl) bromides, aryl iodides, aryl(heteroaryl) chlorides and aryl(heteroaryl)boronic acids in high yields (Scheme 2).

2. Experimental

2.1. General procedure

A 20 mL Schlenk tube with a magnetic stir bar was charged with aryl halide (2 mmol), arylboronic acid (2.4 mmol), K₂CO₃ (5 mmol), 10 mL of solvent [H₂O, H₂O–MeOH (1:1), H₂O–EtOH (1:1), H₂O–EG (1:1)] and an aliquot of 0.01 M solution of palladium complexes PdCl₂(L)₂ or Pd[(L)₄]Cl₂ in MeOH (0.001–0.2 mol%) under air atmosphere. The reaction mixture was placed in a preheated oil bath: at 100 °C for MeOH–H₂O, at 110 °C for EtOH–H₂O, at 140 °C for H₂O and at 160 °C for EG–H₂O; and stirred under reflux for the given time. After this time, the mixture was cooled, acidified by 5 M HCl (in the case of acids) and diluted with 10 mL of H₂O and 10 mL of Et₂O (or EtOAc). The organic phase was separated, and the aqueous layer was extracted with Et₂O EtOAc (2 × 10 mL). The combined organic layers were washed with H₂O (10 mL), brine (10 mL), and dried over Na₂SO₄. The pure products were obtained by a simple filtration of ether solution through silica gel pad and evaporation of a solvent.

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Scheme 1. Structure of aminopyridine ligands and palladium complexes.

3. Result and discussion

Initially, to test the activity of PdCl₂–aminopyridines, the model reactions of 3-iodobenzoic acid, 4-bromoaniline, 2-bromoaniline and 4-bromoanisole with 3(4)-methoxy-, 4-chloro- and 4-methylphenylboronic acids were studied under air atmosphere. Water, aqueous ethanol and ethylene glycol (EG) were used as solvents and K₂CO₃ as a base (Table 1) for these reactions, based on our previous results [25]. These results indicate that aminopyridine complexes, PdCl₂(L)₂ and [Pd(L)₄]Cl₂, are very effective and high-turnover catalysts for Suzuki–Miyaura reaction in aqueous media. In the reaction of water-soluble aryl iodides catalyst amount can be reduced up to 0.001 mol% level without noticeable activity decrease. For instance, 3-iodobenzoic acid reacted with 4-methoxyphenylboronic acids (entry 3) for 5 min with turnover numbers (TON) up to 100,000 and turnover frequencies (TOF) up to 1,200,000 h⁻¹. The yield of cross-coupling product did not exceed 65% in the absence of ligands and the reaction could not go to completion (entry 8). It was surprising that in the presence of 0.1 mol% of complex PdCl₂(L3)₂ even such electron-rich aryl bromide as 4-bromoanisole interacted in water without organic co-solvent at 100 °C for less than 10 min, also indicating on high activity of new catalysts. The product was obtained with quantitative yield (entry 11). Then, we examined the effect of bases on the reaction of 4-bromoaniline and 4-methoxyphenylboronic acid in the presence of 0.1 mol% of PdCl₂(L1)₂ in ethanol–water mixture (1:1) at 85 °C. The use of Na₂CO₃, K₂CO₃, and K₃PO₄ as bases resulted in quantitative yield of the coupling product (Table 2, entries 4–6). KF and KOH provided the cross-coupling product in good yields (entries 2, 3). It was not surprising that the cross-coupling reaction proceeded in low yield with NaOAc, a fairly weak base relative to Na₂CO₃, K₂CO₃ or K₃PO₄. The effect of solvent in the model reaction of 2-bromoaniline and 4-methylphenylboronic acid in the presence of 0.1 mol% of complexes PdCl₂(L3)₂ and [Pd(L3)₄]Cl₂ using K₂CO₃ as a base under reflux was examined. As expected, the high or good yields of product were obtained in protic solvents: in water, aqueous ethanol, ethylene glycol and isopropanol (Table 3, entries 1–5). In nonpolar aprotic solvents such as toluene, which is commonly used in Suzuki–Miyaura coupling, the reaction proceeded in low yield (entry 7).

We next estimated the scope and limitations of substrates for the Suzuki–Miyaura reaction using PdCl₂–aminopyridines as catalysts and K₂CO₃ as a base in water and aqueous alcoholic solvents at reflux temperatures (Table 4). Reactions of water-soluble and water-insoluble aryl iodides and bromides in water without organic co-solvent in the presence of 0.02–0.1 mol% of palladium giving cross-coupling products with high yields for 5–10 min (entries 1, 8 and 14). Reactions of arylboronic acids which are unstable to protodeboration

Table 1
Screening of the aminopyridine ligands on Suzuki–Miyaura reactions.

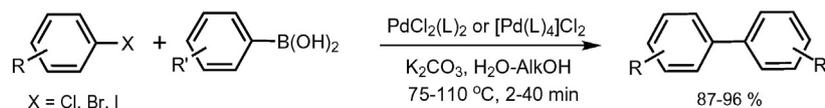
Entry	Pd–L	Pd, mol%	Time, min	Yield, % ^a
3-IC ₆ H ₄ COOH (1 mmol), 4-MeOC ₆ H ₄ B(OH) ₂ (1.2 mmol), K ₂ CO ₃ (2.5 mmol), H ₂ O, 100 °C				
1	PdCl ₂ (L1) ₂	0.02	10	99
2	PdCl ₂ (L2) ₂	0.02	10	99
3	PdCl ₂ (L4) ₂	0.001	5	100
4-BrC ₆ H ₄ NH ₂ (1 mmol), 4-MeOC ₆ H ₄ B(OH) ₂ (1.2 mmol), K ₂ CO ₃ (1.5 mmol), H ₂ O–EtOH, 85 °C				
4	PdCl ₂ (L1) ₂	0.1	10	99
5	Pd[(L1) ₄]Cl ₂	0.2	10	94
6	Pd[(L2) ₄]Cl ₂	0.02	10	91
7	PdCl ₂ (L4) ₂	0.05	2	99
2-BrC ₆ H ₄ NH ₂ (1 mmol), 4-ClC ₆ H ₄ B(OH) ₂ (1.2 mmol), K ₂ CO ₃ (1.5 mmol), H ₂ O–EG, 110 °C				
8	PdCl ₂	0.1	15	65
9	PdCl ₂ (L3) ₂	0.1	15	96
10	Pd[(L3) ₄]Cl ₂	0.1	15	94
4-BrC ₆ H ₄ OMe (1 mmol), 4-MeC ₆ H ₄ B(OH) ₂ (1.2 mmol), K ₂ CO ₃ (1.5 mmol), H ₂ O, 100 °C				
11	PdCl ₂ (L3) ₂	0.1	10	100

^a NMR yield.

were carried out in aqueous methanol (1:1). In this solvent 4-iodobenzoic acid, 2- and 4-iodoanilines reacted easily with 2-furyl- and 2-thienylboronic acids in 89–92% yields for 10 min at 0.01 mol% loading of palladium, corresponding to 8900–9200 TON and 53,400–55,200 h⁻¹ TOF (entries 2, 6, and 7). Aryl(heteroaryl) bromides with electron-withdrawing groups gave also the coupling products in high yields at low catalyst loading for 10–20 min (entries 9–14). The amount of Pd-catalyst should be increased up to 0.05–0.1 mol% in the case of electron-rich bromoanilines and 4-bromoanisole (entries 3–5, and 8). This catalytic system is highly tolerant to a broad range of functional groups. The cross-couplings proceeded smoothly to give the products in high yields in the presence of sensitive groups, such as CHO, MeCO, COOH, and NH₂ without any protection. In addition to substituted aryl halides and arylboronic acids, the coupling reactions of heteroaryl halides and heteroarylboronic acids also led to the formation of the desired products in high yields (entries 2, 6, 7, 12–14). Even aryl(heteroaryl) chlorides reacted with aryl(heteroaryl)boronic acids in the presence of new catalysts (entries 15–18). The reactions of chloro analogs gave also high yields, but required more catalyst (0.1–0.2 mol%) and longer times (15–40 min). For comparison, under catalysis of 3 mol% of Pd[P(*t*-Bu)₃]₂ the reaction of 3-amino-2-chloropyridine with 2-furylboronic acid proceeds in boiling dioxane for 18 h in 88% yield and requires two-fold excess of boronic reagent [26]. It is also noteworthy that PdCl₂–aminopyridines catalyzed reactions can be performed for a short time with low catalyst loadings (<0.2 mol%). The pure products were obtained by a simple procedure without chromatography. As a result, the developed catalytic system provides a really green, easy, quick, and convenient protocol for Suzuki–Miyaura reaction.

4. Conclusions

In summary, PdCl₂–aminopyridine complexes were found to be effective catalysts for the Suzuki–Miyaura cross-coupling under green



Scheme 2. Cross-coupling of aryl halides with arylboronic acids catalyzed by PdCl₂–aminopyridine complexes.

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