



Activation of C–X (=Cl, Br) bond in aryl halides toward the palladium-catalyzed Heck reaction using 2,6-bis(diphenylphosphino)pyridine

Ali Ataei^a, Shirin Nadri^a, Ezzat Rafiee^a, Sirous Jamali^b, Mohammad Joshaghani^{a,*}

^a Faculty of Chemistry, Razi University, Kermanshah 67149, Iran

^b Chemistry Department, Sharif University of Technology, P.O. Box 11155-3615, Tehran, Iran

ARTICLE INFO

Article history:

Received 28 May 2012

Received in revised form 26 August 2012

Accepted 27 August 2012

Available online 3 September 2012

Keywords:

C–C coupling

Heck reaction

2,6-Bis(diphenylphosphino)pyridine

Palladium catalyst

ABSTRACT

The 2,6-bis(diphenylphosphino)pyridine/palladium catalytic system successfully catalyzes the Heck coupling reaction of less reactive aryl chlorides as well as aryl bromides with styrene to give the corresponding olefins in reasonable yields. TBAB (tetrabutylammoniumbromide) as an additive was found to be essential for these reactions. The results of Heck reaction exhibited a high selectivity (>99/1) favoring the *trans* product.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Palladium-catalyzed Heck coupling has been recognized as one of the most important tools for building up of carbon–carbon bond and represents the best technology for the synthesis of the arylated olefins [1–5]. In recent years, numerous papers have been reported concerning improvements to the Heck reaction, but it still is an attractive synthetic goal in academia as well as in industry [6–9].

In Heck reaction, depending on the reaction conditions including the properties of the aryl substrate, olefin, solvent and catalytic system a mixture of arylated products, *trans/cis* isomers (β -arylation), and *gem* isomer (α -arylation) can be formed (Scheme 1).

On the other hand, the readily accessible and cheaper aryl chlorides have not been employed much in cross-coupling reactions, due to their reluctance to oxidatively add to Pd(0) center. Therefore, coupling aryl chlorides as industrially important compounds by Heck reaction has become another equally important topic of research [10–12].

On the basis of these considerations, it is important to develop rewarding catalytic system that meets the goals of high selectivity and high activity to aryl chlorides. It is clear that the nature of the ligand plays an important role in determining the catalytic activity. The use of multifunctional ligands gives advantage as high capacity chelating molecules for the stabilization of catalytic

active species during the catalytic process, which manipulate the activity of the catalyst. Also, increasing the rigidity of the supporting ligand decreases the number of the possible conformations of the metal–ligand assembly, thus leading to improved selectivity [13,14].

The presence of both soft and hard donor sites (e.g. P and N) in phosphorus–nitrogen containing ligands forms an ideal acceptor–donor pair for catalytic uses [15–17]. Indeed, the π -acceptor ability of the phosphorous atom, together with σ -donor nature of nitrogen, synergistically induce an alteration of the catalyst reactivity, though the stabilization of the low-valent transition metals (by phosphine), and promote the oxidative addition of the aryl halide on metal center (by nitrogen).

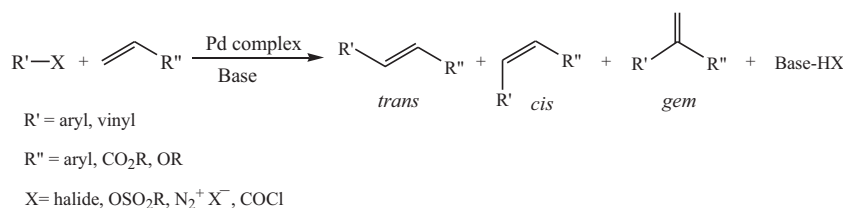
The juxtaposition of a pyridine and two phosphine moieties, presenting a P–N–P framework, in a 2,6-relationship of type shown in Fig. 1, has found considerable attention in the field of organometallic chemistry [18–22].

Of special interest in this context is 2,6-bis(diphenylphosphino)pyridine, (Ph₂P)₂py (**1**), first synthesized by Newkome and Hager [23], owing to its rigid backbone. Absence of the methylene groups connecting the phosphorus atoms and the pyridine ring make (Ph₂P)₂py (**1**), more rigid than other phosphine–pyridine ligands presented in Fig. 1. The coordination chemistry of (Ph₂P)₂py has been well studied [24–28], but relatively scarce attention has been given to its application as a supporting ligand in catalysis.

Because of rigidity and multi-donor nature of (Ph₂P)₂py, and also based on our experience in C–C coupling reaction [29–35], herein, we thought to use this ligand in Heck reaction of aryl

* Corresponding author. Tel.: +98 831 4274559; fax: +98 831 4274559.

E-mail addresses: mjoshaghani@razi.ac.ir,
joshaghanim@yahoo.com (M. Joshaghani).



Scheme 1. The Heck coupling reaction, principle and possible isomers.

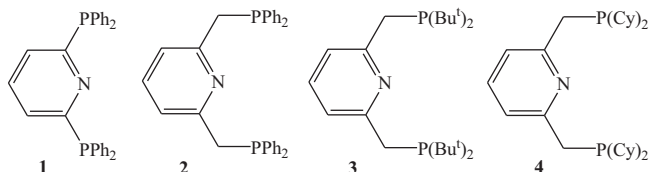


Fig. 1. Selected examples of 2,6-disubstituted phosphine-pyridine ligands.

chlorides as well as aryl bromides. To the best of our knowledge, this is the first report for the use of $(\text{Ph}_2\text{P})_2\text{py}$ for palladium-catalyzed C–C coupling reactions with high efficiency.

2. Experimental

2.1. General remarks

All reactions were performed under an atmosphere of dry nitrogen. All chemicals purchased from Fluka and/or Merck companies were used without further purification. 2,6-bis(diphenylphosphino)pyridine was commercially available.

^1H (200 MHz), ^{13}C (100 MHz) NMR spectra were recorded on a Bruker Avance Spectrometer. Elemental analysis was performed using CHN Herause rapid model. Thin layer chromatography on pre-coated silica gel Fluorescent 254 nm (0.2 mm) on aluminum plates were used for monitoring the reactions. The cross coupling products were characterized by their ^1H NMR spectra.

2.2. General procedure for Heck coupling of styrene with aryl halides

A reaction tube was charged with chlorobenzene (4 mmol), styrene (4 mmol), TBAB (3 mmol), and K_2CO_3 (4 mmol) under

a dry nitrogen atmosphere. A solution of $(\text{Ph}_2\text{P})_2\text{py}$ (0.05 mol% in 2 mL of DMAc) and prepared solution of palladium acetate (0.025 mol% in 2 mL) was added through a rubber septum, and the resulting mixture was refluxed at 135°C for appropriate time. Upon completion of the reaction, the reaction mixture was then cooled to room temperature. After extraction with CH_2Cl_2 ($3 \times 20\text{ mL}$), the combined organic layer was dried over MgSO_4 . The solvent was evaporated and the crude product was characterized by ^1H NMR spectroscopy. Isolated yield of coupling products of chlorobenzene, and 4-bromotoluene were 82% and 86%, respectively.

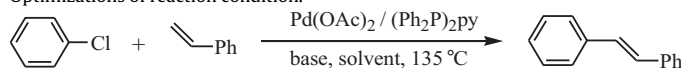
3. Results and discussion

3.1. Initial optimization

By employing a reaction of chlorobenzene and styrene as a probe, the reaction conditions were optimized. We were pleased to find that the reaction proceeded smoothly with only 0.05 mol% $\text{Pd}(\text{OAc})_2/0.1\text{ mol}\%$ $(\text{Ph}_2\text{P})_2\text{py}$ when K_2CO_3 and DMAc were used as the base and solvent respectively. Thus, after 24 h at 135°C , the product *trans*-stilbene was obtained in 75% yield, corresponding to a turnover number (TON) of 1500 (Table 1, entry 1). It should be noted that in the absence of $(\text{Ph}_2\text{P})_2\text{py}$ (ligand free condition) no amount of the desired product was formed (not shown in the table). When the palladium loading was reduced to 0.025 mol% the process was less efficient (Table 1, entry 2). Significantly lower yield (20%, 24 h) was obtained in the presence of triethylamine as a representative organic base (Table 1, entry 3). One possible interpretation of this result is blocking of free coordination sites on the palladium center by amine [36,37].

The effect of tetraalkylammonium salts, the so-called Jeffery condition [38], was also considered. Addition of 0.5 mmol

Table 1
Optimizations of reaction condition.^a



Entry	$\text{Pd}(\text{OAc})_2$ (mol%)	Base	Solvent	TBAB (mmol)	Yield (%) ^b	TON
1	0.05	K_2CO_3	DMAc	–	25 (75)	500 (1500)
2	0.025	K_2CO_3	DMAc	–	12 (55)	480 (2200)
3	0.025	NEt_3	DMAc	–	0 (20)	0 (800)
4	0.025	K_2CO_3	DMAc	0.5	30 (55)	1200 (2200)
5	0.025	K_2CO_3	DMAc	1.5	53 (90)	2120 (3600)
6 ^c	0.025	K_2CO_3	DMAc	3	57 (90) [82]	2280 (3600)
7	0.025	K_2CO_3	DMAc	5	58 (92)	2280 (3600)
8	0.025	–	DMAc	5	25 (75)	100 (3000)
9	0.025	K_2CO_3	DMSO	3	0 (0)	0 (0)
10	0.025	K_2CO_3	Toluene	3	0 (15)	0 (600)
11	0.025	K_2CO_3	DMF	3	48 (67)	1920 (2680)

^a Reaction conditions: chlorobenzene (4 mmol), styrene (4 mmol), K_2CO_3 (4 mmol), $\text{Pd}/(\text{Ph}_2\text{P})_2\text{py}$ and DMAc (4 mL), 135°C , 5 h. Only *trans* isomer was observed in the ^1H NMR spectrum.

^b NMR yield. The numbers in parentheses are from the reaction time 24 h.

^c The number in the bracket is isolated yield after 24 h.

Download English Version:

<https://daneshyari.com/en/article/65935>

Download Persian Version:

<https://daneshyari.com/article/65935>

[Daneshyari.com](https://daneshyari.com)