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Highly efficient amine-based catalytic system for room temperature Suzuki–Miyaura reactions of aryl halides with arylboronic acids

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An *in situ*-generated catalytic system based on PdCl₂ and primary amine-based ligand exhibited excellent activity (up to 98% isolated yield) in the Suzuki–Miyaura cross-coupling reactions of aryl bromides with arylboronic acids in water, at room temperature, without any additive. The efficiencies of the ligands follow the order: $(C_6H_5)_3CNH_2 > C_6H_5CH_2NH_2 > C_6H_5NH_2 > C_6H_{11}NH_2$, which is in accordance with the palladacycle forming capacity of the respective ligands. Moderate-to-good yields (up to 78% isolated yield) of the coupling products were also obtained with less reactive aryl chlorides as substrates at room temperature in isopropanol using an alternative protocol based on Pd(OAc)₂ and $(C_6H_5)_3CNH_2$. Copyright © 2011 John Wiley & Sons, Ltd.

Supporting information may be found in the online version of this article.

Keywords: Suzuki-Miyaura reaction; amine-based ligand; room temperature; aqueous medium

Introduction

Ligand-promoted palladium catalyzed Suzuki-Miyaura crosscoupling reactions have proven to be one of the most powerful strategies for synthesizing diversified biaryls, which constitute an important class of compounds for the pharmaceutical as well as agrochemical industries.^[1-6] Among different ligands, noticeable advances have been achieved with phosphinebased ligands (such as simple tertiaryphosphines,^[1,2,7,8] hemilabile-type phosphines,^[2,9-13] sterically crowded biphenyltype phosphines^[14,15] and other electron-rich phosphines^[16-18]) and with other ligands that are capable of forming palladacycles (e.g. phosphapalladacycles,^[19-23] N-heterocyclic carbenes,^[24-27] amine-based,^[21,28,29] oxime-based^[30,31] and imine-based^[32,33]). Although complexes containing such ligands often show excellent activities, in the majority of cases the ligands are either commercially unavailable or very expensive or difficult to synthesize. Moreover, the insolubility in water of most of the ligands restricts their use in water as a solvent. From environmental and economic points of view, the use of water as a solvent in the Suzuki-Miyaura reactions has received tremendous interests because water is very cheap, readily available and non-toxic.^[22,34] Although there are some reports available^[22,26,35-42] where water was successfully used as a solvent for the Suzuki-Miyaura reactions, in most of the cases either elevated reaction temperatures^[21,33,34,41] or the use of phase-transfer catalysts^[45,39] or organic co-solvents^[35,36] were necessary to maximize catalytic performances. Indeed, only very few reports are available where neat water was succesfully used as a solvent in Suzuki – Mivaura reactions at room temperature without the use of any additive. Shaughnessy et al.^[36] developed a highly effecient catalytic system, based on water-soluble alkylphopshines as ligands, for carrying out Suzuki-Miyaura reactions of aryl bromides at room temperature and excellent turnover numbers (up to 734000) were achieved. Recently, Eppinger et al.^[22] reported a palladacycle-based catalytic system that effectively underwent

coupling reactions in water at room temperature. Thus, we believe that the development of a new catalytic system that can promote Suzuki–Miyaura reactions in aqueous medium under mild reaction conditions using a highly accessible and cheap ligand system would be extremely advantageous.

Amines are generally used as bases in palladium-mediated cross-coupling reactions and display some interesting properties as ligands. Until now, only very few amines have been employed as ligands in the Suzuki-Miyaura reactions and, importantly, all the reactions with amines were performed in organic solvents.^[43-49]. Among different amines, secondary or tertiary amines were found to be highly efficient and high efficiencies of such amines were attributed to their established role to form five- or six-membered palladacycles.^[3,49] A notable exception was observed by Suss-Fink et al.[48] where they demonstrated that a diacetatopalladium-based catalytic system derived from secondary amine-based ligands, that was unlikely to form palladacycles, showed good catalytic activity. Compared with secondary or tertiary amines, primary amines as ligands remain largely unexplored in Suzuki-Miyaura reactions, even though a large number of such amines are commercially available and very cheap. Few years back, Boykin et al. screened a series of commercially available amines, including some primary amines, as ligands with palladium acetate in the Suzuki-Miyaura reactions of aryl bromides with arylboronic acids and found that sterically bulky primary amines appeared to be better ligands than comparable bulky tertiary amines.^[45,46] Herein, as a part of our ongoing research on Suzuki-Miyaura reactions,^[50] we have extended the scope of different commercially available primary amine-based ligands

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Scheme 1. Primary amine-based ligands tested for the Suzuki–Miyaura reactions.

(Scheme 1) in the Suzuki-Miyaura reactions of aryl halides with arylboronic acids.

Experimental

General Information

All the reactions were carried out in air. The reactions were monitored by thin-layer chromatography using aluminum coated TLC plates (Merck) under UV-light. Column chromatographic purifications were performed using silica gel (60-120 mesh). PdCl₂, Pd(OAc)₂, aniline (L3) and benzylamine (L2) were purchased from Merck chemicals and triphenylmethylamine (L1) and cyclohexylamine (L4) were purchased from Fluka. All other solvents and reagents were purchased from different Indian firms. The solvents were distilled prior to use. All the products were characterized by melting point determination, mass spectra and ¹H NMR spectroscopy and were compared with the authentic samples. NMR spectra were recorded in CDCl₃ on a Bruker A VII 500 MHz NMR spectrometer using TMS as internal standard. Mass spectra of the compounds were recorded in GEOL GCmate instrument in El+ mode. The melting points were determined by BUCHI B450 melting point apparatus.

General Procedure for the Suzuki-Miyaura Reactions of Aryl Bromides using $\mathsf{PdCl}_2-\mathsf{RNH}_2$

A 50 ml round-bottom flask was charged with a mixture of aryl bromide (0.5 mmol), arylboronic acid (0.55 mmol), K_2CO_3 (1.5 mmol), $PdCl_2$ (1 mol%) and ligand (1 mol%) and the mixture was stirred in H_2O (6 ml) at room temperature for the required time. After completion, the reaction mixture was diluted with water (20 ml) and extracted with ether (3 × 20 ml). The combined extract was washed with brine (3 × 20 ml) and dried over Na_2SO_4 . After evaporation of the solvent under reduced pressure, the residue was chromatographed (silica gel, ethyl acetate – hexane) to obtain the desired products.

General Procedure for the Suzuki-Miyaura Reactions of Aryl Chlorides using $PdCl_2-L1$

A 50 ml round bottom flask was charged with aryl chloride (0.5 mmol), phenylboronic acid (0.55 mmol), K₂CO₃ (1.5 mmol), TBAB (0.5 mmol), solvent (6 ml), PdCl₂ (1-4 mol%) and the ligand **L1** (1-4 mol%), and the reaction mixture was stirred at room temperature for the required time. After completion, the reaction mixture was worked up by following the same procedure as mentioned in the reaction of aryl bromides.

General procedure for the Suzuki-Miyaura reactions of aryl chlorides using $Pd(OAc)_2-L1$

A 50 ml round-bottom flask was charged with appropriate aryl chloride (0.5 mmol), phenylboronic acid (0.55 mmol), K_2CO_3

(1.5 mmol), solvent (6 ml), $Pd(OAc)_2$ (1 mol%) and the ligand **L1** (1 mol%), and the reaction mixture was stirred at room temperature for the required time. After completion, the reaction mixture was worked up by following the same procedure mentioned in the reaction of aryl bromides.

Results and Discussion

Screening of Amine-based Ligands for Suzuki-Miyaura Reactions

To investigate the efficiencies of primary amine-based ligands, L1–L4, in Suzuki–Miyaura reaction, initially, we chose the reaction between 4-bromonitrobenzene with phenylboronic acid as a model reaction using K₂CO₃ as base and water as a solvent. The reactions were performed at room temperature, without any additive, in the presence of catalysts generated in situ from PdCl₂ (1 mol%) and respective ligands in 1:1 molar ratio (Table 1). The ligand L1 was found to be extremely efficient, affording the desired biaryl in nearly quantitative yield along with small amount of biphenyl as side product formed from the homocoupling reactions of phenylboronic acid (Table 1, entry 2). On the other hand, the corresponding ligand L4 was found almost inefficient and exhibited only negligible conversion (entry 6) under similar condition. It is important to mention that, generally, aryl bromides with electron-withdrawing groups at para position are much more reactive than aryl bromides bearing electrondonating groups. Thus, to investigate the effects of ligands



^d Determined with respect to initial amount of Ar-B(OH)₂ used.

L1-L4 with an electron-donating substrate, we performed the reaction between 4-bromotoluene and phenylboronic acid under similar conditions. It is surprising to see that 4-bromotoluene gave superior product formation compared to 4-bromonitrobenzene when L3 and L4 was used as ligand (Table 1, entry 5 vs 10; 6 vs 11). However, the observed efficiencies of the ligands for both the aryl bromides follow the order: L1 > L2 > L3 > L4, which is in consistent with the palladacycle forming capacity of the respective ligands.^[3,51,52] An indirect support for intermediatery involvement of a palladacycle may be derived from Table 1 (entry 3) that the use of two equivalent of the ligand L1 substantially reduces the catalytic performance, since 2 equivalents of the ligand normaly produce non-palladacyclic complex [PdCl₂(amine)₂].^[49] A similar type of decrease in activities on increasing L: Pd ratio from 1:1 to 1:2 was also observed by other in situ-generated palladacyclebased catalytic systems.^[35,36] Generally, primary amines are important substrates that undergo amination reactions with aryl halides to form secondary amines in the presence of Pd-catalysts (Buchwald-Hartwig reaction^[53]); however, in our case no such side-product formation was observed from TLC spot analysis.

Effects of Bases and Solvents

To study the effects of different solvents and bases in our catalytic system we have examined the reaction between 4-bromotoluene with phenylboronic acid in presence of various solvents and bases by using triphenylmethylamine (**L1**) as ligand and the results are summarized in Table 2. Screening of solvents using K₂CO₃ as base showed that solvent has a profound effect in our catalytic system. As shown in Table 2, the polar protic solvents such as water and isopropanol were found to be the most effective



^b Isolated yield.

^c Yields are of average of two runs.

solvents and gave almost comparable results (entries 2–5 and 7). On the other hand aprotic solvents, both polar (entries 6, 10 and 11) and non-polar (entry 9), gave comparatively less yields. The lowest yield (61%) was obtained with DCM. Our results clearly show that base is essential for the coupling reactions since no coupling product was obtained in the absence of base (entry 1). Besides K_2CO_3 , the reaction can tolerate other inorganic bases such as Na₂CO₃, NaOH, KOH and gave almost comparable yields of the cross-coupling product (Table 2, entries 2–5).

Effects of Substrates and Boronic Acids

To evaluate the scope and limitations of the current procedure, reactions of a wide array of electronically diverse aryl bromides with aryllboronic acids were examined using the catalyst derived from PdCl₂-L1 (Table 3). It might be important to indicate here that, although water and alcohol gave almost comparable yields of the product, considering the advantage of water as green solvent, it has been used for subsequent reactions using arvl bromides. It can been seen from Table 3 that the aryl bromides with electron withdrawing substituents (Table 3, entries 1-4) underwent the coupling reactions with phenylboronic acid effectively to afford the desired biaryls in nearly quantitative yields (94-98%). The nonactivated aryl bromides (such as bromobenzene, 4-bromotolune and 4-bromoanisole) also gave the coupling products in goodto-excellent yields (entries 8-12). Furthermore, under slightly extended reaction time, the sterically demanding substrates such as 2-bromotolune and 2-bromoanisole (entries 13 and

Table 3. Suzuki-Miyaura cross-coupling reactions of various aryl bromides with arylboronic acids using PdCl2-L1 as catalyst ^a								
$R \xrightarrow{PdCl_2 (1 \text{ mol}\%)}_{H_2O, K_2CO_3, \text{ rt,}} R \xrightarrow{PdCl_2 (1 \text{ mol}\%)}_{R} \xrightarrow{PdCl_2 (1 \text{ mol}\%)}_{R} \xrightarrow{PdCl_2 (1 \text{ mol}\%)}_{R} \xrightarrow{PdCl_2 (1 \text{ mol}\%)}_{R}$								
Entry	R	R′	Time (h)	Yield (%) ^{b,c}				
1	4-NO ₂	Н	20	98				
2	4-COMe	Н	16	98				
3	4-COOH	Н	16	96				
4	4-CHO	Н	16	94				
5	4-NO ₂	4-Cl	16	98				
6	4-NO ₂	4-Me	24	62				
7	4-NO ₂	4-NO ₂	24	trace				
8	Н	Н	24	89				
9	Н	4-Cl	24	89				
10	4-Me	Н	24	94				
11	4-Me	4-Me	24	79				
12	4-OMe	Н	24	88				
13	2-Me	Н	32	81				
14	2-OMe	Н	32	83				
^a Reaction conditions: 0.5 mmol aryl bromide, 0.55 mmol boronic acid, 1.5 mmol K-CO ₂ , H-O (6 ml).								

^b Isolated yield.

^c Yields are the average of two runs.

Table 4.	4. Effects of reaction conditions in the Suzuki–Miyaura reaction of 4-chloronitrobenzene with phenylboronic acid ^a										
$O_2 N - CI + CI + B(OH)_2 \xrightarrow{PdCl_2 : L1 = 1:1}_{Solvent, K_2 CO_3, t, stirring}} Z = NO_2 (A)$											
					Yield	Yield (%) ^{c,d}					
Entry	Pd source	Catalyst (mol%)	Solvent	Additive ^b	Time (h)	A	Be				
1	PdCl ₂	1.0	H ₂ O	-	24	trace	99				
2	PdCl ₂	4.0	H ₂ O	-	24	trace	97				
3	PdCl ₂	4.0	H ₂ O	TBAB	24	10	46				
4	PdCl ₂	2.0	ⁱ PrOH	TBAB	48	30	29				
5	PdCl ₂	2.0	ⁱ PrOH:H ₂ O(1:1)	TBAB	48	52	27				
6	Pd(OAc) ₂	1.0	H ₂ O	-	36	30	22				
7	Pd(OAc) ₂	1.0	ⁱ PrOH	-	36	78 (76) ^f	17 (15) ^f				
8	Pd(OAc) ₂	1.0	ⁱ PrOH:H ₂ O(1:1)	-	36	68	21				
^a Reaction ^b TBAB: 0. ^c Isolated ^d Yields a	n conditions: 0.5 mm .5 mmol. yield. re of average of two	ol 4-chloronitrobenzene runs.	, 0.55 mmol phenylboronic	acid, 1.5 mmol K _{2'}	CO ₃ , solvent 6 ml.						

^e Determined with respect to initial amount of phenylboronic acid used.

^f Values in parentheses are the yield for the reaction performed under N₂ atmosphere.

14) could also be coupled with phenylboronic acid to give the desired product in good yield. It is important to mention here that, although the electronic properties of aryl bromides have little influence on the coupling reactions, the nature of arylboronic acids has a substantial influence on the overall performance of the catalyst. For example, phenylboronic and 4chlorophenylboronic acid were found to be extremely efficient with 4-bromonitrobenzene to afford the desired product in almost quantitative yield (Table 3, entries 1 and 5), while 4-tolylboronic acid gave only 62% yield (entry 6) and the performance of 4-nitrophenylboronic acid was disappointing, showing almost no conversion (entry 7). It may be interesting to highlight from the literature^[43-49] that the use of other amine-based ligands in the Suzuki-Miyaura reactions of aryl bromides with arylboronic acids to produce good yields generally requires high reaction temperatures, and/or higher catalyst loading (upto 3 mol%) and/or the use of organic solvents with tetrabutylammonium bromide (TBAB) as additive. Thus, our present result is quite significant as the desired biaryls could be achieved at room temperature using water as a solvent and with relatively low catalyst loading (1 mol%) without using any additive.

Suzuki-Miyaura Reactions of Aryl Chlorides

Although coupling reactions of aryl bromides proceeded smoothly in water at room temperature without any additive, under the same experimental condition the reactions between aryl chlorides with phenylboronic acid failed to produce the desired cross-coupling products and only biphenyl was isolated as the sole product (Table 4, entry 1). However, we were intrigued to see if there was any role of the aryl chlorides in this biphenyl formation or biphenyl was simply formed from the homocoupling reactions of aryl boronic acids. Thus to investigate the fact, we performed a reaction using phenylboronic acid as the sole reactant (without adding aryl chloride), PdCl₂–**L1** as catalyst, K₂CO₃ as base, water as solvent. After 24 h of reaction time, almost the same quantity of biphenyl was isolated as the product of the reaction indicating biphenyl was formed from homocoupling reactions of aryl boronic acids. It may be important to mention that traditionally aryl chlorides are less reactive than aryl bromides in Suzuki-Miyaura reactions and generally require more drastic conditions and/or higher catalyst loading. Since, using 1 mol% of the catalyst (PdCl₂-L1), no crosscoupling product was isolated (Table 4, entry 1), we have increased the catalyst quantity up to 4 times (entry 2) but no improvement in the cross-coupling product formation was observed. Thus, we have decided to use TBAB as additive because TBAB was previously used on a number of occasions to improve the cross-coupling results of aryl chlorides in water.^[37,38,55,56] Unfortunately, using TBAB in our system, no significant improvement in the cross-coupling product formation was observed, although significant reduction in the biphenyl formation was noticed (Table 4, entry 3). Thus, to find out an alternative protocol for effective using aryl chlorides as substrates, we have explored different experimental possibilities (Table 4) using 4-chloronitrobenzene and phenylboronic acid as coupling partner. Comparison between entries 3 and 4 suggests isopropanol is a better solvent than neat water in $(PdCl_2-L1)$ system. However, entry 5 showed that use of aqueous isopropanol (1:1) instead of neat isopropanol further improved the reaction progress and 52% cross-coupling product was isolated. It may be important to mention here that, in several in situ-generated catalytic systems, Pd(OAc)₂ was found to be a highly efficient source for Suzuki-Miyaura reactions in water-alcohol.^[35,43] In the present case, changing the Pd source from $PdCl_2$ to $Pd(OAc)_2$ a dramatic improvement of the overall product formation was noticed. For instance, 1 mol% of Pd(OAc)₂-L1 in isopropanol gave 78% yield (Table 4, entry 7) of the cross-coupling product whereas using double the amount of PdCl₂-L1 in the same solvent gave only 30% yield (Table 4, entry 5). Unfortunately, in the $Pd(OAc)_2 - L1$ system, water was found to be a less effective solvent than isopropanol and gave only 30% cross-coupling product but, use of isopropanol-water mixture (1:1) gave 68% yield (Table 4,



^c Yields are of average of two runs.

entries 6 and 8). Moderate-to-good yields of the coupling products were also achieved with other electron-deficient aryl chlorides in isopropanol (Table 5, entries 2–4). Our results showed that under slightly extended reaction time, the non-activated aryl chlorides such as 4-chlorobenzene and 4-chlorotoluene also gave modest yield (Table 5, entries 5–7). However, with a sterically demanding substrate such as 2-chlorotoluene (Table 5, entry 8) only poor yield (32%) was obtained. Although reduced yields of the coupling products were obtained for aryl chlorides compared with aryl bromides, these results are very significant, as we are able to use aryl chlorides as substrates in the Suzuki–Miyaura reaction at room temperature using water–alcohol as solvent.

Conclusions

In conclusion, we have developed a simple catalytic system based on PdCl₂ and some commercially available primary aminebased ligands for Suzuki–Miyaura cross-coupling reactions of aryl bromides with arylboronic acids. Good-to-excellent yields of the coupling products were obtained at room temperature using neat water as solvent. The efficiencies of the ligands follow the order (C₆H₅)₃CNH₂ > C₆H₅CH₂ NH₂ > C₆H₅ NH₂ > C₆H₁₁ NH₂, which is consistent with the palladacycle-forming capacity of the respective ligands. Furthermore, changing the palladium source from PdCl₂ to Pd(OAc)₂ with the ligand (C₆H₅)₃CNH₂, the less reactive aryl chlorides could also be used as subtrates in ^{*i*}PrOH or ^{*i*}PrOH–H₂O (1:1) at room temperature to gave the desired products in reasonably good yields.

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Supporting Information

Supplimentary information containing characterization information on all the known compounds are available in the online version of the article.

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