



Palladium(II)-catalyzed Suzuki–Miyaura reactions of arylboronic acid with aryl halide in water in the presence of 4-(benzylthio)-*N,N,N*-trimethylbenzenammonium chloride



De-Xian Liu^a, Wei-Jie Gong^a, Hong-Xi Li^{a,*}, Jun Gao^a, Fei-Long Li^a, Jian-Ping Lang^{a,b,*}

^a College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, PR China

^b State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 210032, PR China

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ABSTRACT

This work reported that Suzuki–Miyaura coupling reactions of arylboronic acid with aryl bromide or iodides were mediated by Pd(OAc)₂ and 4-(benzylthio)-*N,N,N*-trimethylbenzenammonium chloride in the presence of Na₂CO₃ in water under the mild conditions. The corresponding Suzuki–Miyaura coupling products were obtained in good to excellent yields.

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1. Introduction

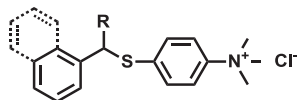
Suzuki–Miyaura coupling reaction of aryl halides with arylboronic acids is one of the most established methodologies in preparing both symmetric and unsymmetrical biaryls in organic synthesis.¹ Palladium catalysts carrying organic ligands such as phosphines,² nitrogen-donor,³ NHCs (*N*-heterocyclic carbenes) ligands,⁴ and others,⁵ have provided a highly efficient route for the formation of biaryl compounds. However, these methods have some potential limitations because these crossing reactions are often carried out in organic solvents. The solvent-recovery process is needed for such biaryl products, which may cause the environment pollution and increase the production cost. Water as a solvent has attracted numerous attention as a potential replacement for organic solvents due to its low cost, nonflammability, low toxicity, and the fact that it is a renewable resource. Thus, it would be a greener and more economic approach if the Suzuki–Miyaura coupling reactions could be conducted in water.⁶ It is noted that water-soluble catalysts could be obtained by incorporating hydrophilic moieties into the hydrophobic P-, N-containing and NHCs organic ligands. A wide variety of polar functional substituent

groups such as sulfonate,⁷ carboxylate,⁸ imidazolium salts,⁹ ammonium groups,^{7d,10} polyethers¹¹ have been incorporated on the above organic ligands in order to render the corresponding ligands to be water-soluble.

On the other hand, the sulfur-containing organic compounds have been recognized as efficient ligands for catalytic applications.¹² But their potential utility in pure water is largely limited in comparison with other organic ligands.^{4c,13} Up to now, some water-soluble crown ether¹⁴ and polyethers¹⁵ have been combined into the S-donor ligands. However, there is no report that the water-soluble ammonium group is functionalized on the S-donor ligands. Recently, we have been interested in the syntheses and catalytic properties of water-soluble transition metal coordination complexes. For example, the water-soluble Cu(II) complex of a zwitterionic calix[4]arene [Cu(II)L(H₂O)]₂ (H₄L⁴⁻=[5,11,17,23-tetrakis(trimethylammonium)-25,26,27,28-tetrahydroxycalix[4]arene]) with four ammonium groups attached on the phenyl rings, exhibited high catalytic activity in the oxidative polymerization of 2,6-dimethylphenol in water.¹⁶ In addition, we have synthesized a family of metal coordination complexes of a zwitterionic trimethylammoniumbenzenethiolate (Tab) ligand with a water-soluble NMe₃⁺ substituent group.¹⁷ Could Tab/Pd system initiate the Suzuki–Miyaura coupling reaction in aqueous media? Herein we report the synthesis of three novel water-soluble sulfur-donor ligands with an NMe₃⁺ group (Scheme 1), which could work as auxiliary

* Corresponding authors. Tel.: +86 512 6588 2865; fax: +86 512 6588 0328; e-mail address: jplang@suda.edu.cn (J.-P. Lang).

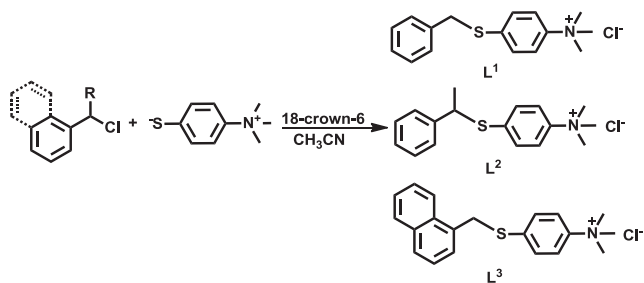
ligands to accelerate Pd-catalyzed the Suzuki–Miyaura coupling reactions of arylboronic acids with aryl bromides or iodides in water under milder conditions.



Scheme 1. The sulfur-containing ligands with an ammonium group.

2. Results and discussion

As shown in **Scheme 2**, treatment of 4-(trimethylammonio) benzenethiolate (Tab) with benzyl chloride and 18-crown-6 in MeCN followed by a standard workup afforded 4-(benzylthio)-*N,N,N*-trimethylbenzenammonium chloride (**L**¹) in 88% yield. The other two ligands *N,N,N*-trimethyl-4-((1-phenylethyl)thio)benzenammonium chloride (**L**²) and *N,N,N*-trimethyl-4-((naphthalen-1-ylmethyl)thio)benzenammonium chloride (**L**³) were prepared by analogous reactions of Tab with (1-chloroethyl)benzene or (1-chloromethyl)naphthalene in high yields. These ligands are stable toward air and moisture, and freely soluble in polar solvents such as water, methanol, DMSO, but insoluble in non-polar solvents such as CH₂Cl₂, toluene, CCl₄. The ¹H NMR spectra of these ligands showed the singlets at $\delta=4.37$, 4.83, and 4.85 ppm, which were assigned as the protons of the methine or methylene group in ligands **L**¹, **L**², and **L**³, respectively. The singlet at $\delta=3.61$ (**L**¹), 3.54 (**L**²), or 3.62 (**L**³) ppm was ascribed to the protons of the trimethylammonium group.



Scheme 2. Synthesis of the S-donor ligands **L**¹, **L**², and **L**³.

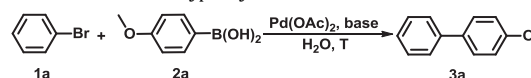
The ligands **L**¹, **L**², and **L**³ could readily dissolve in water and work as auxiliary ligands to accelerate the Suzuki–Miyaura coupling reactions of aryl halides with arylboronic acids in aqueous solution. Bromobenzene (**1a**) with 4-methoxyphenylboronic acid (**2a**) were initially chosen as the model substrates to optimize the reaction conditions including bases and temperatures (**Table 1**). Interestingly, reactions of **1a** with 1.5 equiv of **2a** in water at 95 °C afforded 4-methoxy-1,1'-biphenyl (**3a**) in 66% yield with 2 mol % of Pd(OAc)₂ as a catalyst, 2 mol % of **L**¹ as the ligand, and 2 equiv of K₂CO₃ as the base (entry 1). The ligands **L**² and **L**³ were also tested (entries 2 and 3), and **L**¹ was proven to be more effective. Reactions of **1a** with **2a** provided 36% yield in the absence of **L**¹ ligand (entry 4). The loading of the **L**¹ ligand for this reaction could be increased from 2 to 4 mol % without affecting the product yield (entry 5). We also attempted various bases such as NaOH, Cs₂CO₃, K₃PO₄·3H₂O, NaHCO₃, Na₂CO₃, KF, and NaOAc for this reaction. It seems that Na₂CO₃ works the best in water (entries 6–10). As we all know, the reaction temperature usually exerts great impact on this type of reaction. When the reaction temperature was increased from 95 °C to 120 °C, the yield of **3a** was decreased from 68% to 66% (entry 13). However, when the reaction temperature was decreased to 80 °C, the reaction gave the product in a higher yield 74% (entry 14). At lower temperature (60 °C), the reaction gave the product in a lower

yield (entry 15). The product yield was decreased from 74% to 51% when the catalyst loading was changed from 2 mol % to 1 mol % at 80 °C. When the –CH₂S– group in the **L**¹ ligand was replaced by –CH₂– group, the resulting ligand 4-benzyl-*N,N,N*-trimethylbenzenammonium iodide (**L**⁴) was obtained. The analogous reactions of **1a** with **2a** catalyzed by Pd(OAc)₂/**L**⁴ produced **3a** in 38% yield (entry 18). This result suggested that the S atom in the **L**¹ ligand played an important role in the catalytic performance of the catalyst. Thus the optimized reaction conditions were found to be 2 mol % of Pd(OAc)₂, **L**¹ (2 mol %) as the ligand and Na₂CO₃ (as the base) for 12 h at 80 °C in H₂O.

With the optimized reaction conditions in hand, we carried out various Suzuki–Miyaura coupling reactions of aryl bromides with arylboronic acids and found that a variety of functional groups could be tolerated for aryl bromides including methyl, carbonyl, methoxyl, nitril, and cyano groups and for arylboronic acids bearing methyl, fluoride, methoxyl substituent groups. As shown in **Table 2**, the coupling reactions were performed well for all the substrates examined, and the expected products were isolated in good to moderate yields. Relative to those with electron-deficient substituent groups, the electron-donating *p*-substituted aryl bromides were found to proceed in higher yields. For example, reactions with aryl bromides bearing electron-donating substituent groups (methyl and methoxyl) gave the coupling products in higher yields (entries 2 and 3) compared with those with electron-withdrawing ones (carbonyl, nitril, and cyano) (entries 4, 5, and 6). However, the substituted arylboronic acids containing electron-withdrawing group (80%, entry 11) showed the lower yields than those containing electron-donating groups (88%, entry 2; 84%, entry 10; and 83%, entry 13). The result was consistent with those reported in the literature.¹⁸ The steric hindrance of aryl bromides and arylboronic acids may affect the yields of the coupling products.¹⁸ The moderate to low yields were obtained for 2-bromotoluene (33%, entry 7), 1-naphthylboronic acid (42%, entry 12), and 2-tolylboronic acid (34%, entry 14). It is noted that the reactions having heteroaromatic bromides such as 2-bromopyridine performed well to give moderate yields (40%, entry 8).

Table 1

Optimizing the reaction conditions for the Suzuki–Miyaura coupling reactions of bromobenzene with 4-methoxyphenylboronic acid^a



Entry	Ligand	Base	T (°C)	Yield ^b (%)
1	L ¹	K ₂ CO ₃	95	66
2	L ²	K ₂ CO ₃	95	62
3	L ³	K ₂ CO ₃	95	60
4		K ₂ CO ₃	95	36
5 ^c	L ¹	K ₂ CO ₃	95	65
6	L ¹	NaOH	95	53
7	L ¹	Cs ₂ CO ₃	95	55
8	L ¹	K ₃ PO ₄ ·3H ₂ O	95	61
9	L ¹	NaHCO ₃	95	64
10	L ¹	Na ₂ CO ₃	95	68
11	L ¹	KF	95	62
12	L ¹	NaOAc	95	33
13	L ¹	Na ₂ CO ₃	120	66
14	L ¹	Na ₂ CO ₃	80	74
15	L ¹	Na ₂ CO ₃	60	55
16 ^d	L ¹	Na ₂ CO ₃	80	73
17 ^e	L ¹	Na ₂ CO ₃	80	51
18 ^f	L ⁴	Na ₂ CO ₃	80	38

^a The coupling reactions were carried out at N₂ in the presence of 0.5 mmol of PhBr; 0.75 mmol of PhB(OH)₂; 2 mol % cat **L**¹; and 1 mmol base in 3 mL of H₂O for 12 h.

^b Isolated yield.

^c **L**¹ (4 mol %).

^d Reaction time=24 h.

^e Catalyst loading: 1 mol %.

^f Catalyst=**L**⁴.

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