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ARTICLE TYPE

‘On-water’ organic synthesis: A green, highly efficient, low cost and reusable catalyst system for biaryl synthesis under aerobic conditions at room temperature

Bishwajit Saikia*, Preeti Rekha Boruah, Abdul Aziz Ali and Diganta Sarma

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

A simple, greener, efficient, low cost and mild protocol has been developed for sucrose assisted palladium-catalyzed Suzuki reactions in water at room temperature under aerobic condition. The results demonstrate that the sucrose played a crucial role making this protocol a highly efficient. The $PdCl_2$/Sucrose/K_2CO_3/H_2O system showed the superb catalytic activity towards the Suzuki reaction of a wide range of aryl/heteroaryl halides with different substituted phenylboronic acids. This method offers an attractive alternative to the existing protocols since the reaction proceeds in aqueous media at room temperature under operational simplicity, shorter reaction time, cost-effective and also provides the products in high yields. The catalytic system is highly recyclable, allowing the reuse of the palladium catalyst in subsequent catalytic runs without significant loss of activity.

New advances in cross-coupling techniques have made very significant contribution to organic synthesis as well as pharmaceutical, agricultural and advanced functional materials.[1] The recent literature findings reveal that Suzuki–Miyaura cross-coupling reaction is one of the highly attractive and useful protocol for carbon-carbon bond formation due to its extensive range of functional groups tolerance, commercial availability of organoboron reagents and low toxicity of boron by-products.[2] At the present time, synthetic researchers have a growing awareness in developing greener processes, as the sustainability has become a very crucial matter in all kind of human activity.[3] Among the principles of green chemistry, the choice of solvents is a key factor, since it might gives rise to hazards, toxicity, pollution and waste are generated and mixed with the effluent water.[4] With consideration of safety, economy and environment problems, most industries and pharmaceutical companies are currently approaching green chemistry and considering water as a potentially useful and safe alternative[5] because it is an extremely abundant, non-toxic, non-corrosive and non-flammable green solvent. As a result, the use of water as a sole reaction medium is one of the growing challenges for modern researchers, particularly in chemistry.[6] To date, a lot of efforts have been made by researchers to carry out organic reactions in neat water.[7] Among those developed transformations, the palladium-catalyzed Suzuki–Miyaura cross-coupling reaction is an unique example, which is one of the most versatile and powerful tools for the construction of biaryls.[8] In this regard, the progress of catalytic system in pure water look like particularly appropriate for the Suzuki–Miyaura reaction due to the excellent stability of boronic acids in aqueous medium.

The problems related with the use of water as a sole reaction media are the solubility of substrate as well as stability of metal catalyst. However, to some extent, these problems have been overcome by using different alternatives such as additives,[9] organic co-solvent,[10] phase-transfer catalyst,[11] surfactant,[12] microwave heating,[13] ultrasound,[14] heterogeneous catalysts,[15] ligand-free approach and water soluble catalysts or ligands *etc*.[16] Although, majority of these strategies were found to be effective in carrying out this transformation, most of these systems are associated with several drawbacks such as low reactivity, long reaction time, requirement of large amount of catalysts, cost, harsh reaction conditions, toxic and moisture sensitive nature, tedious procedure for the synthesis of ligand (few of them also involve two or more steps), use of expensive reagents *etc*. In addition, there are just few reported catalytic systems for the Suzuki–Miyaura cross-coupling of highly challenging hateroaryl halides with arylboronic acids in aqueous media.[17] Therefore, the development of Pd-catalyzed Suzuki–Miyaura cross-coupling reaction of aryl/heteroaryl halides with arylboronic acids in water using very cheap and abundant water soluble ligand is very much attractive. Similarly, the design of efficient catalysts producing high yields under aerobic conditions continues to be an important challenge.

At the moment, we are interested in developing a simple and general protocol for the palladium-catalyzed and aerobic Suzuki reaction in pure water. Herein, we describe a very mild, efficient, simple and highly cost-effective one-pot protocol for the Suzuki–Miyaura cross-coupling reactions of aryl/heteroaryl halides with various arylboronic acids at room temperature in water using truly nontoxic, very cheap and economically important disaccharide ‘Sucrose’ as a water soluble ligand. Most importantly sucrose is enormously available at price comparable to those of synthetic organic base chemicals. Sucrose is the ordinary table sugar which we eat every day, it is the most abundant non-polymeric biogenic raw material consequently its use as a ligand in Suzuki reaction is considered as highly

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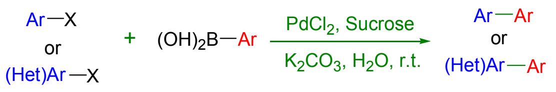
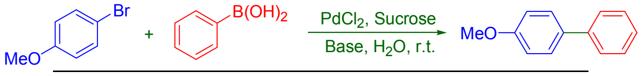
environmental friendly in terms of abundance and availability as a feedstock. This interesting finding gives us an opportunity to make known the catalytic performance of $PdCl_2$–Sucrose for the Suzuki–Miyaura cross-coupling reaction in water at room temperature (**Scheme 1**). To the best of our knowledge this is the first 'On-water' one-pot Pd-catalyzed aerobic Suzuki–Miyaura cross-coupling reaction assisted by 'Sucrose' that requires neither heating nor the addition of any additives. The procedural simplicity using most abundant and renewable resource sucrose is an advantage and we believed that, the present work surpass the criteria in terms of novelty. Therefore, the present synthetic method would be extremely beneficial and more efficient to synthetic chemistry community.



Scheme 1. Synthesis of biaryls/heterobiaryls

Considering the key role of base in the Suzuki–Miyaura cross-coupling reactions, different bases were screened in the presence of $PdCl_2$ and sucrose in water at room temperature (**Table 1**, entries 1–14) and it was found that base had a significant influence on the cross-coupling efficiency (*i.e.* the nature of the bases plays an important role in Suzuki reaction). Generally, a strong base stimulates side reactions lowering the yield of the desired product, and a weak base remains unable to activate boronic acids. A model reaction of 4-bromoanisole and phenylboronic acid was chosen to screen the reaction conditions and the results are summarized in Table 1. It was found that, in comparison to the other bases, metal carbonates provide higher yields with excellent reaction rate. Among the various bases screened in water, K_2CO_3 provided the highest cross-coupling yield of 96% in 1 h (**Table 1**, entry 3) and we believed that the ability to dissolve bases in water for activating arylboronic acid has enhanced the rate of the reaction in an aqueous medium. It is also important to mention that during the presented experiments, homo coupling of phenylboronic acid to unsubstituted biphenyl was negligible. Triethylamine, a typical organic base, was tested in this system, providing a negative result of <5% isolated yield of the cross-coupled product in 12 h (**Table 1**, entry 11). Moreover, this reaction was unsuccessful in the absence of base (**Table 1**, entry 12), which confirmed the essentiality of base for the smooth Suzuki–Miyaura cross-coupling reaction.

Table 1. Optimization of the Suzuki–Miyaura reaction of 4-bromoanisole with phenylboronic acid in the presence of $PdCl_2$ and sucrose catalytic system at room temperature[a]



Entry	Base	Time (h)	Yield[b] (%)
1	Na_2CO_3	2	90
2	$NaHCO_3$	6	60
3	K_2CO_3	1	96
4	Cs_2CO_3	2	86
5	$Na_3PO_4.12H_2O$	6	28
6	Na_2HPO_4	6	32
7	NaO^tBu	6	25
8	K_3PO_4	6	<10
9	NaOH	8	28
10	KOH	8	25
11	Et_3N	12	<5
12	–	24	No reaction[c]
13	K_2CO_3	12	25[d]
14	K_2CO_3	12	No reaction[e]

[a] Reaction conditions: 4-bromoanisole (1 mmol), phenylboronic acid (1.2 mmol), $PdCl_2$ (0.01 mmol), sucrose (0.005 mmol), base (1.2 mmol) in H_2O (3 mL) at room temperature.
[b] Isolated yield after chromatography.
[c] Without base.
[d] Without sucrose.
[e] Without $PdCl_2$.

Additionally we had performed two controlled experiments to demonstrate the need of $PdCl_2$ as a catalyst and sucrose as a ligand in this reaction. The coupling reaction of phenylboronic acid and 4-bromoanisole without using sucrose was very sluggish and took 12 h to achieve only 25% yields of 4-methoxybiphenyl in neat water (**Table 1**, entry 13). From this experiment, now it is clear that sucrose played a crucial role in the high efficiency of this system. But there was no product formation between phenyl boronic acid and 4-bromoanisole in the absence of $PdCl_2$ under this reaction condition (**Table 1**, entry 14).

With the optimized conditions in hand, we further studied the generality of the cross-coupling reactions between aryl halides and arylboronic acids in our 'On-Water' one-pot protocol ($PdCl_2$/Sucrose/K_2CO_3/r.t.) and the results are presented in Table 2. As shown in Table 2, the Suzuki reactions of aryl bromides with phenylboronic acid proceeded very smoothly under aerobic conditions in H_2O at room temperature to afford the corresponding coupled products in high yields. A wide range of electronically and structurally diverse aryl halides (including the deactivated aryl halides), were readily converted to the corresponding coupled products with different substituted aryl boronic acids under this green reaction condition. Various electron-donating and electron-withdrawing groups such as $-CH_3$, $-OCH_3$, –CN, $-COCH_3$, –CHO and $-NO_2$, $-CF_3$ were well tolerated to give the desired unsymmetrical biaryls in excellent yields (**Table 2**, entries 1-18). However, various substituted arylboronic acids, bearing either electron-donating or electron-withdrawing groups, such as $-CH_3$, –OMe, $-COCH_3$, $-CF_3$ and $-NO_2$, provided the corresponding products in 98% to 48% isolated yields (**Table 2**, entries 3, 9, 10, 12-17). These results show that the stronger the electron-donating group in arylboronic acid, the higher the catalytic activity. This is because an electron-rich arylboronic acid could accelerate the rate of the transmetalation step in the Suzuki–Miyaura cross-coupling reaction.

Encouraged by such promising results, we next turned our attention to the Suzuki reaction of phenylboronic acid with challenging heteroaryl halides, and the results are summarized in Table 2. The reactions carried out using 3-bromothiophene and 2-bromopyridine with arylboronic acids under this protocol, afforded good to excellent isolated yields of the desired products in a very short reaction time (**Table 2**, entries 17 and 18). For our

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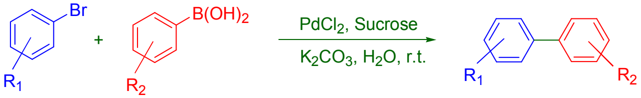
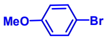
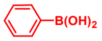
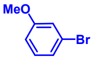
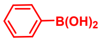
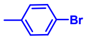
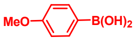
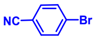
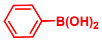
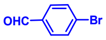
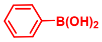
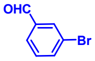
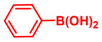
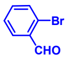
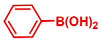
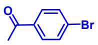
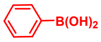
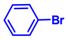
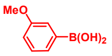
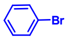
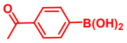
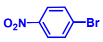
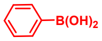
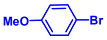
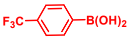
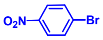
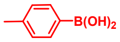
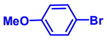
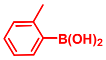
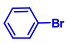
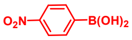
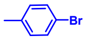
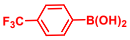
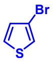
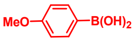
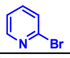
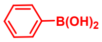
satisfaction we performed all the reactions three times to verify the reproducibility of results and also yield of the desired cross-coupled products (**Table 2**, entries 1-18).

Table 2. $PdCl_2$ and sucrose catalysed Suzuki–Miyaura cross-coupling reaction of aryl/heteroaryl halides with aryl boronic acids[a]

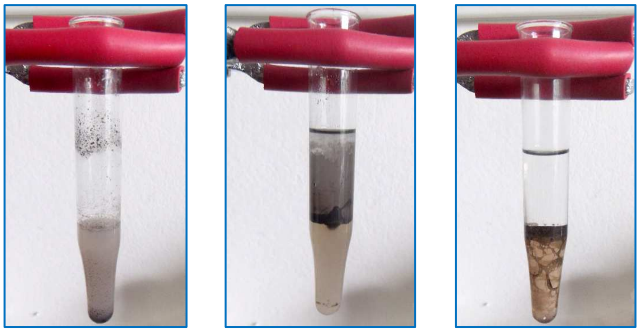


Entry	ArX	ArB(OH)$_2$	Time (h)	Yield^b (%)
1			1^c, 1^d, 1^e	96^c, 96^d, 95^e
2			1^c, 1^d, 1^e	96^c, 96^d, 96^e
3			1^c, 1^d, 1^e	98^c, 98^d, 98^e
4			1^c, 1.5^d, 1.5^e	91^c, 91^d, 89^e
5			2^c, 2^d, 2^e	90^c, 90^d, 90^e
6			2^c, 2^d, 2^e	92^c, 89^d, 90^e
7			2.5^c, 2.5^d, 2.5^e	90^c, 88^d, 90^e
8			1.5^c, 1.5^d, 1.5^e	88^c, 88^d, 87^e
9			2^c, 2^d, 2^e	91^c, 91^d, 90^e
10			2.5^c, 2.5^d, 2.5^e	90^c, 90^d, 88^e
11			1^c, 1^d, 1.5^e	92^c, 90^d, 90^e
12			1.5^c, 2^d, 1.5^e	90^c, 92^d, 90^e
13			1^c, 1^d, 1^e	94^c, 94^d, 91^e
14			2^c, 2^d, 2^e	91^c, 90^d, 90^e
15			3^c, 3^d, 3^e	48^c, 48^d, 47^e
16			2^c, 2^d, 2^e	91^c, 90^d, 90^e
17			2.5^c, 2.5^d, 2.5^e	90^c, 90^d, 88^e
18			3^c, 3^d, 3^e	79^c, 79^d, 75^e

[a] Reaction conditions: aryl/heteroaryl halide (1 mmol), arylboronic acid (1.2 mmol), $PdCl_2$ (0.01 mmol), sucrose (0.005 mmol), K_2CO_3 (1.2 mmol) in H_2O (3 mL) at room temperature.
[b] Isolated yield after chromatography.
[c] 1st run.
[d] 2nd run.
[e] 3rd run.

Literature report revealed that in carbohydrate chemistry, the general route of reaction control with transition metal catalysis is mostly unclear.[18] The key reason seems to be the low crystallization tendency of carbohydrate-transition metal complexes which may be partly due to the lack of a predominant metal-binding site of carbohydrates. The lack of proper understanding of the mode of bonding between carbohydrate and transition metal ions results in the limited use of metal catalysis. The exact mechanism for the $PdCl_2$ catalyzed sucrose assisted Suzuki cross-coupling reaction is not clear. In view of the fact that the molecule of sucrose has several pathetic coordination sites[19] as well as palladium(II) is particularly suitable for the complexation of various types of diols and therefore, it is believed that $PdCl_2$ units are attached to 1,2-(D-glucopyranosid-$O^{3'}$,$O^{4'}$) and 1,3-(D-fructofuranosyl-O^{1},O^{3}) diolate groups of sucrose to form five- and six- membered chelate rings[20] during the course of a metal-mediated reaction leading to the significant improvement of the catalytic efficiency of the system.

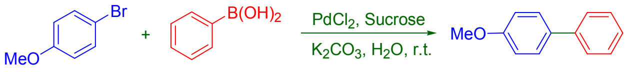
The reusability of transition metal catalysts are the trends of the catalysis industry along with the development of green chemistry, not only for lowering costs, but also for avoiding environmental pollution. Recycling experiments were performed using the standard 4-bromoanisole/phenylboronic cross-coupling test reaction. After the first reaction cycle diethyl ether was added to the system followed by centrifugation, the clearly separated diethyl ether layer has been removed from the system and dried to get the desired crude product. After each run, the catalyst system was washed with diethyl ether to completely remove the adsorbed organic substrates and then used for the next run without any further treatment (**Figure 1**). Fresh substrates were added again to the reused catalyst system, which was stirred for another 1 h (**Table 3**). After the first recycling step full catalytic activity is preserved and a slight loss in activity is observed for only after the 5th run. The average yield over 5 runs was 93% (**Table 3**, entries 1-5). Therefore, in that order several cycles of catalyst use and reuse are possible and the results are summarized in Table 3.



(a) (b) (c)

Figure 1. Recycling of the catalyst system: (a) Reaction mixture; (b) Addition of diethyl ether to the reaction mixture; (c) After centrifugation, clearly separated diethyl ether (containing organic compounds) and aqueous layer (containing catalyst system)

Table 3. A summary of catalyst reuse for Suzuki–Miyaura cross-coupling reaction of 4-bromoanisole with phenylboronic acid[a]



Entry	Run	Time (h)	Yield^b (%)
1	1st	1	96
2	2nd	1	96
3	3rd	1	94
4	4th	1.5	92

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5	5th	1.5	88

[a] Reaction conditions: 4-bromoanisole (1 mmol), phenylboronic acid (1.2 mmol), $PdCl_2$ (0.01 mmol), sucrose (0.005 mmol), K_2CO_3 (1.2 mmol) in H_2O (3 mL) at room temperature.
[b] Isolated yield after chromatography.

In conclusion we report a highly environmentally friendly reaction protocol for aqueous Suzuki–Miyaura cross-coupling catalysis under air at room temperature, which is applicable to a broad range of substrates. The ability to use water as the reaction medium and sucrose as ligand greatly increases the green credentials of the method. Correspondingly, recycling of the active catalytic species can be performed several times without significant loss in catalytic activity. We anticipate that this approach will offer an alternative synthetic strategy for the practical construction of biaryl/heterobiaryl compounds in near future. Studies aimed at extending the scope of this catalyst system to other types of cross-coupling and related reactions are currently ongoing in our laboratory.

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Notes and references

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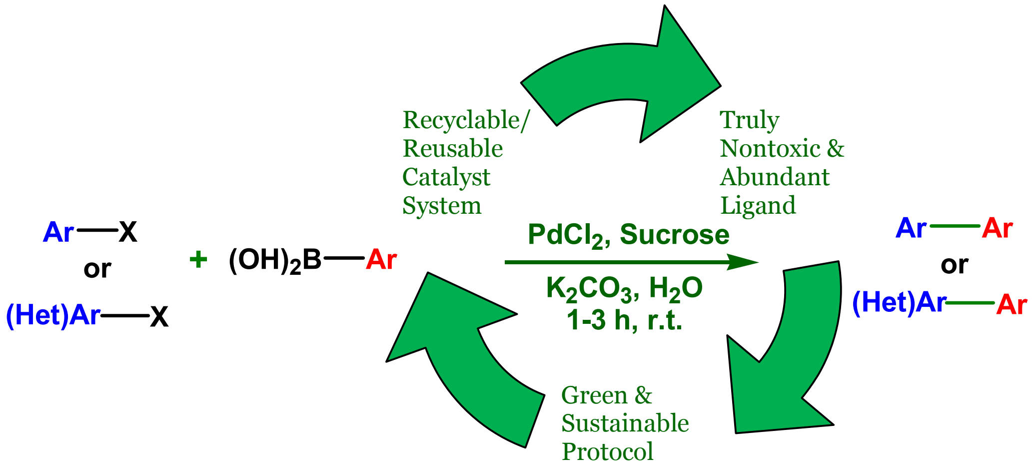
Graphical Abstract:

'On-water' organic synthesis: A green, highly efficient, low cost and reusable catalyst system for biaryl synthesis under aerobic conditions at room temperature

Bishwajit Saikia*, Preeti Rekha Boruah, Abdul Aziz Ali and Diganta Sarma

The $PdCl_2$/Sucrose/K_2CO_3/H_2O system showed the superb catalytic activity towards the Suzuki reaction of a wide range of aryl/heteroaryl halides with diverse phenylboronic acids at room temperature under operational simplicity and shorter reaction time. The ability to use water and sucrose greatly increases the green credentials of the method.



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