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Aerobic Ligand-Free Suzuki Coupling Reaction of Aryl Chlorides Catalyzed by *In Situ* Generated Palladium Nanoparticles at Room Temperature

Wei Han,[a] Chun Liu,[a,*] and Zilin Jin[a]

[a] State Key Lab of Fine Chemicals, Dalian University of Technology, Zhongshan Road 158, Dalian 116012, People's Republic of China
Fax: (+86)-411-8899-3854; e-mail: chunliu70@yahoo.com

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Abstract: An aerobic, ligand-free Suzuki coupling reaction catalyzed by *in situ* generated palladium nanoparticles in polyethylene glycol with an average molecular weight of 400 Da (PEG-400) at room temperature has been developed. This catalytic system is a very simple and highly active protocol for the Suzuki coupling of aryl chlorides with arylboronic acids, which proceed smoothly in excellent yields in short times using low catalyst loadings. Control experiments demonstrated that the Suzuki reaction catalyzed by the *in situ* generated palladium nanoparticles can be carried out much quicker than that using the preprepared particles under the same conditions. The formation of palladium nanoparticles in PEG-400 was promoted by arylboronic acids.

Keywords: biaryls; C–C coupling; nanotechnology; palladium; Suzuki reaction

Introduction

The palladium-catalyzed Suzuki coupling reaction of aryl halides with arylboronic acids for the construction of the aryl-aryl bond is one of the most general and powerful tools for the synthesis of pharmaceuticals, herbicides, polymers, liquid crystals, natural products, ligands for catalysis and advanced materials.[1] Since the first report of the Suzuki reaction in 1979,[2] a great number of monographs and review articles on this topic have been published. In the last decade, there has been an increasing research interest in the Suzuki reaction of aryl chlorides since these substrates are cheaper and more widely available than aryl bromides and iodides.[3] However, they are much more difficult to activate than aryl bromides and iodides. Among the approaches described in the literature, numerous efforts have been devoted to the development of ligand-promoted catalytic systems. The groups of Fu,[4] Buchwald,[5] Beller,[6] Herrmann,[7] Bedford,[8] Nolan,[9] and others[10] have achieved significant success.

However, most of ligands are not only sensitive to air and/or moisture but also comparatively difficult to prepare or rather expensive; attempts have also been made to develop "ligand-free" catalytic systems for activating aryl chlorides, which is one of the most challenging fields in organic chemistry, although only a few examples have been successful up to now.[11] In 2001, Sowa et al. reported a ligand-less Pd/C catalyst for the Suzuki coupling of aryl chlorides and found that the solvent system had a great effect on the catalytic activity.[11a] Later, Choudary et al. described a ligand-free heterogeneous layered double hydroxide-supported nanopalladium catalyst for the Suzuki reaction of chloroarenes.[11b] Recently, Wang et al. demonstrated a ligand-free system of $PdCl_2$/PEG-300 for the Suzuki coupling of aryl chlorides at room temperature.[11c] In 2007, Diaconescu et al. reported that palladium nanoparticles supported on polyaniline nanofibers were active catalysts for the Suzuki coupling of aryl chlorides using low palladium loadings in water and air.[11d] Although the above-mentioned examples were carried out either using high palladium loadings[11a,c] of 5 mol% or using higher reaction temperatures of 80–100 °C,[11a,b,d] they pointed out a promising direction for the efficient activation of aryl chlorides for the Suzuki reaction in a ligand-free system by using a suitable combination of palladium species with solvents.

The metal nanoparticles offer high catalytic efficiency due to their large surface area-to-volume ratio[12] and have been widely applied in the Suzuki reaction.[11b,d,13] Although some important advances

have been achieved in the palladium nanoparticles-catalyzed Suzuki reaction in recent years, it still needed harsh conditions to activate aryl chlorides.[11b,d,13i] Generally, metal nanoparticles are prepared by a complicated process in the presence of reducing agents and stabilizers in advance and are used to catalyze a reaction thereafter. However, the small nanoparticles could be aggregated to reduce their surface energy to the state of stabilization in this manner.[14]

For economic and environmental concerns and good solubility to organic compounds as well, polyethylene glycol (PEG) as a green and easily available solvent has been used in the Suzuki reaction in the last two years.[11c,15] PEG enables the reduction of Pd(II) to Pd(0) while its hydroxy groups are oxidized into aldehyde groups,[16] which makes it possible to prepare palladium nanoparticles easily in PEG in the absence of the normally adopted reducing agents. Furthermore, PEG has been widely used to stabilize nanoparticles in many types of transformations due to its special molecular structure. Therefore, it is possible to make use of the unique advantages of PEG to prepare palladium nanoparticles easily *in situ* for the ligand-free Suzuki coupling reaction of aryl chlorides under mild conditions.

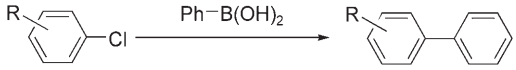
In a recent preliminary communication,[17] we presented an oxygen-promoted ligand-free Suzuki coupling reaction of aryl chlorides with phenylboronic acid catalyzed by the *in situ* generated palladium nanoparticles in PEG-400 at 45 °C. Herein, we report a detailed study of an aerobic ligand-free Suzuki coupling reaction catalyzed by the *in situ* generated palladium nanoparticles in PEG-400 at room temperature. To our knowledge, this is the first example of a palladium nanoparticles-catalyzed, aerobic, ligand-free Suzuki coupling reaction of aryl chlorides at room temperature. Moreover, control experiments have been designed for the first time to investigate the catalytic property differences between the *in situ* generated palladium nanoparticles and the preprepared ones in the aerobic, ligand-free Suzuki reaction of aryl chlorides.

Results and Discussion

Optimization of Reaction Conditions

Generally, the palladium-catalyzed Suzuki coupling reaction is performed under an inert atmosphere because the catalytic species are sensitive to oxygen or moisture. In this study, we first investigated the effect of the atmosphere on the Suzuki reaction catalyzed by the PEG-400/$Pd(OAc)_2$ system. The results are shown in Table 1. To our surprise, the reactions performed in open air were much quicker than those in nitrogen. These results were consistent with what Corma et al. reported.[15b] Therefore, we carried out all reactions in air for the study.

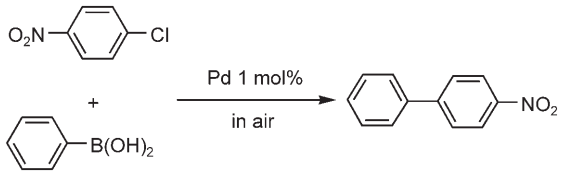
Table 1. Suzuki coupling reactions of aryl chlorides with phenylboronic acid in PEG-400 under different conditions.[a]



Entry[a]	R	Conditions	Time	Yield [%][b]
1a	4-CF_3	Air	2 h	96
1b	4-CF_3	N_2	2 h	40[c]
2a	4-MeCO	Air	2 h	97
2b	4-MeCO	N_2	2 h	54[c]
3a	2-CN	Air	5 h	90
3b	2-CN	N_2	5 h	60[c]
4a	2-NO_2	Air	1.5 h	96
4b	2-NO_2	N_2	4 h	88[c]

[a] *Reaction conditions (not optimized):* aryl halides (0.5 mmol), phenylboronic acid (0.75 mmol), $Pd(OAc)_2$ (2 mol%), K_2CO_3 (1 mmol), PEG-400 (4 g), 45 °C. The reactions were monitored by GC.
[b] Isolated yields.
[c] PEG-400 was degassed.

Table 2. Effect of palladium species on the Suzuki coupling reaction of 4-chloronitrobenzene with phenylboronic acid in PEG-400.[a]



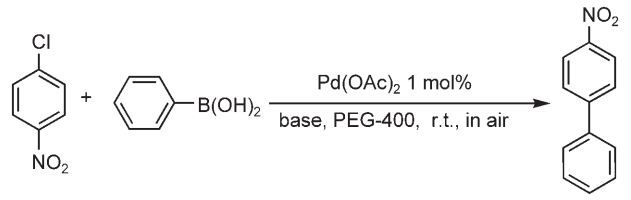
Entry	Pd Species	Time	Isolated Yield [%]
1	$Pd(OAc)_2$	1 h	94
2	$Pd_2(dba)_3$	1 h	no reaction
3	Pd/C	1 h	no reaction

[a] *Reaction conditions:* 4-chloronitrobenzene (0.5 mmol), phenylboronic acid (0.75 mmol), Pd (1 mol%), K_2CO_3 (1 mmol), PEG-400 (4 g), room temperature. The reaction was monitored by TLC.

The next investigation of this study was to optimize the conditions of the Suzuki coupling reaction in terms of palladium species and bases. A model coupling reaction between 4-chloronitrobenzene and phenylboronic acid in PEG-400 at room temperature was chosen to study the catalytic activity of palladium species (Table 2).

The reaction catalyzed by $Pd(OAc)_2$ resulted in an excellent yield in 1 h (Table 2, entry 1). It was surprising that the cross-coupling reaction did not occur when using $Pd_2(dba)_3$ (Table 2, entry 2) or Pd/C (Table 2, entry 3) under the same reaction conditions. The reason for this was that both $Pd_2(dba)_3$ and Pd/C

Table 3. The effect of base on Suzuki coupling reaction of 4-chloronitrobenzene with phenylboronic acid in PEG-400.[a]



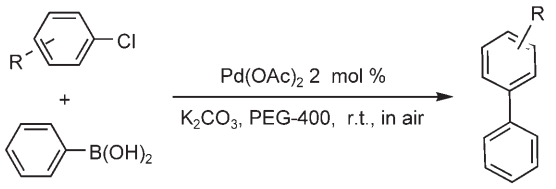
Entry	Base	Time	Isolated Yield [%]
1	K_2CO_3	1 h	94
2	$KF{\cdot}2H_2O$	1.5 h	92
3	$K_3PO_4{\cdot}3H_2O$	5 h	90
4	NaOH	1 h	73
5	$LiOH{\cdot}H_2O$	1 h	6
6	$Ba(OH)_2{\cdot}8H_2O$	1 h	trace
7	Na_2CO_3	1 h	27
8	$NaHCO_3$	1 h	11
9	Li_2CO_3	1 h	trace
10	$HCOONa{\cdot}2H_2O$	1 h	10
11	$CH_3COONa{\cdot}3H_2O$	1 h	52
12	*t*-BuONa	1 h	trace
13	CH_3ONa	1 h	88
14	NEt_3	1 h	trace
15	HMTA	1 h	no reaction
16	$NH_3{\cdot}H_2O$	1 h	no reaction
17	Na_2SO_3	1 h	trace

[a] *Reaction conditions:* 4-chloronitrobenzene (0.5 mmol), phenylboronic acid (0.75 mmol), $Pd(OAc)_2$ (1 mol%), base (1 mmol), PEG-400 (4 g), room temperature. The reaction was monitored by TLC.

were not activated at room temperature, because the reaction only occurred at 80 °C. Thus, we selected $Pd(OAc)_2$ as the catalyst for our research.

Further investigation was carried out to study the influence of the bases on the same model reaction. The results are summarized in Table 3. The use of inorganic bases such as K_2CO_3, $KF{\cdot}2H_2O$, $K_3PO_4{\cdot}3H_2O$, NaOH or CH_3ONa, gave the cross-coupling products in good to excellent yields (Table 3, entries 1, 2, 3, 4, and 13). However, some inorganic bases of $LiOH{\cdot}H_2O$, Na_2CO_3, $NaHCO_3$, $HCOONa{\cdot}2H_2O$ or $CH_3COONa{\cdot}3H_2O$ resulted in lower yields (Table 3, entries 5, 7, 8, 10, and 11). Other inorganic bases like Li_2CO_3, *t*-BuONa, $NH_3{\cdot}H_2O$, Na_2SO_3, and organic bases such as NEt_3, hexamethylenetetraamine (HMTA) were completely ineffective in the catalytic system (Table 3, entries 9, 12, 16, 17, 14, and 15). The best result was obtained with K_2CO_3, which provided the highest cross-coupling yield of 94% in 1 h (Table 3, entry 1).

Table 4. PEG-400/$Pd(OAc)_2$ catalyzed Suzuki cross-coupling of aryl chlorides with phenylboronic acid at room temperature in air.[a]



Entry	R	Time	Isolated Yield [%]
1	4-NO_2	1 h	94
2	4-CHO	2 h	98
3	4-CF_3	2 h	93
4	4-CN	4 h	85
5	4-COMe	6 h	87
6[b]	2-NO_2	1.5 h	96
7[b]	H	3 h	91
8[b]	3-OMe	3 h	82

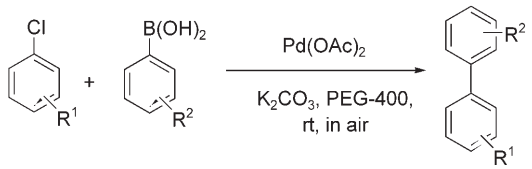
[a] *Reaction conditions:* aryl chloride (0.5 mmol), phenylboronic acid (0.75 mmol), $Pd(OAc)_2$ 2 mol% [for 4-chloronitrobenzene, $Pd(OAc)_2$ 1 mol%], K_2CO_3 (1 mmol), PEG-400 (4 g), room temperature.
[b] 45 °C.

Scope and Limitations of Substrates

We explored the scope and limitations of substrates for the Suzuki coupling reaction under the optimized conditions using 1–2 mol% $Pd(OAc)_2$ in PEG-400, K_2CO_3 as a base at room temperature. The results are illustrated in Table 4.

A wide range of aryl chlorides gave the cross-coupling products with excellent isolated yields in the system of PEG-400/$Pd(OAc)_2$. Moreover, various functional groups such as nitro, aldehyde, cyano, acetyl, trifluoromethyl, and methoxy groups were tolerated in the reaction and not affected. The substrates with electron-withdrawing groups or electron-donating groups were all achieved in good yields (Table 4). For example, 4-chloronitrobenzene was more reactive than other substrates and 94% isolated yield was obtained using a $Pd(OAc)_2$ loading of 1 mol% (Table 4, entry 1). Steric hindrance due to the *ortho* substituents on the aryl chlorides affected the reaction progress. Thus, 2-chloronitrobenzene needed a higher temperature (45 °C) and a two-fold higher catalyst loading (2 mol%) than 4-chloronitrobenzene (Table 4, entry 6). Excitingly, the non-activated aryl chlorides such as chlorobenzene and 3-chloroanisole were consumed in 3 h (Table 4, entries 7 and 8).

Table 5. PEG-400/$Pd(OAc)_2$-catalyzed Suzuki cross-coupling of aryl chlorides with arylboronic acids at room temperature.[a]



Entry	R^1	R_2	Time	Isolated Yield [%]
1	4-NO_2	2-OMe	50 min	93
2	4-NO_2	4-OMe	50 min	95
3	4-NO_2	3-OMe	6 h	84
4	4-COMe	3-OMe	6 h	85
5	4-CF_3	3-OMe	3 h	87
6	4-NO_2	2-Me	1 h	95
7	4-NO_2	3-Me	1.5 h	91
8	4-NO_2	4-Me	50 min	96
9	4-NO_2	3-F, 5-F	50 min	96
10	4-NO_2	4-CF_3	8 h	85

[a] *Reaction conditions:* aryl chloride (0.5 mmol), arylboronic acid (0.75 mmol), $Pd(OAc)_2$ 1 mol% [for entries 4 and 5, $Pd(OAc)_2$ 2 mol%], K_2CO_3 (1 mmol), PEG-400 (4 g), room temperature. The reaction was monitored by TLC.

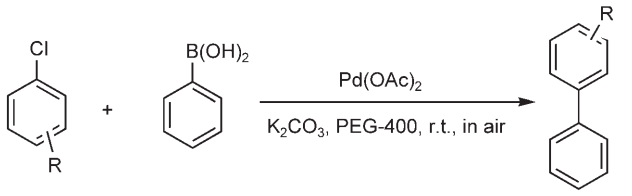
Effect of Various Arylboronic Acids

The effect of the substituents in different positions of an arylboronic acid on the Suzuki coupling reaction was studied (Table 5). It was clear from the Table 5 that the cross-couplings of aryl chlorides with the arylboronic acids bearing either electron-rich or electron-deficient functional groups were carried out smoothly in the catalytic system. In agreement with the results reported by Sajiki et al.,[18] the coupling reactions of arylboronic acids containing electron-rich groups such as 2-MeO, 4-MeO, and 4-Me (Table 5, entries 1, 2, and 8; 50 min) proceeded more efficiently than those of phenylboronic acid (Table 4, entry 1; 1 h), while the arylboronic acid with an electron-withdrawing substituent needed a longer reaction time for completion (Table 5, entry 10; 8 h). Interestingly, an electron-donating group in the *meta* position of an arylboronic acid such as 3-MeO or 3-Me (Table 5, entries 3 and 7) showed lower reactivity,[19] however, the 3,5-difluoro substituents promoted the reaction (Table 5, entry 9). This is because of the effect of the substituents on the nucleophilicity of arylboronic acids. The stronger the nucleophilicity, the more active is the arylboronic acid. An electron-donating group in the *ortho* or *para* position of an arylboronic acid increases the nucleophilicity of the carbon atom bounded to the boron atom, while an electron-withdrawing group in the same position decreases the nucleophilicity. Comparably, an electron-donating group in the *meta* position of an arylboronic acid decreases the nucleophilicity. As for the 3,5-difluoro substituents, they increase the nucleophilicity by presenting δ-transfer due to the participation of the lone-pair electron.[20]

Control Experiments of *In Situ* and Preprepared Palladium Nanocatalysis

Generally, transition metal nanoparticles are preprepared for nanocatalysis. There are only a few examples of *in situ* nanocatalysis.[21] To our knowledge, the present work was the first example of the *in situ* generated palladium nanoparticles-catalyzed Suzuki reaction at room temperature. To disclose the catalytic properties of the *in situ* generated palladium nanoparticles and the preprepared ones[22] in the aerobic ligand-free Suzuki coupling reaction of aryl chlorides, control experiments were carried out under the same reaction conditions, respectively. The catalytic results are shown in Table 6 and the average sizes of the palladium nanoparticles were characterized by the transmission electron microscopy (TEM). As expected, the catalytic properties were quite different. The *in situ* generated palladium nanoparticles showed much higher activity than the preprepared ones (Table 6). The results were consistent with the TEM micrographs: the average diameters of the *in situ* generated palladium nanoparticles in the whole reaction process were *ca.* 1.5 nm (Figure 1, *top row*), while the prepre-

Table 6. Control experiments of the *in situ* generated and the preprepared[22] palladium nanoparticles-catalyzed Suzuki cross-coupling reaction in PEG-400 in air.[a]



Entry	R	Catalyst Type	Time [h]	Yield [%][b]
1a	4-NO_2	*in situ*	1	94
1b	4-NO_2	preprepared	12	82
2a	4-CF_3	*in situ*	2	93
2b	4-CF_3	preprepared	12	49
3a	2-NO_2	*in situ*	1.5	96
3b	2-NO_2	preprepared	12	76
4	4-NO_2	10% Pd/C	1	no reaction

[a] *Reaction conditions:* aryl chlorides (0.5 mmol), phenyl boronic acid (0.75 mmol), $Pd(OAc)_2$ 2 mol% (1 mol% for entries 1a and 1b, 1 mol% 10% Pd/C for entry 4), K_2CO_3 (1 mmol), PEG-400 (4 g), room temperature (45 °C for entries 3a and 3b). The reactions were monitored by GC and TLC.

[b] Isolated yields.

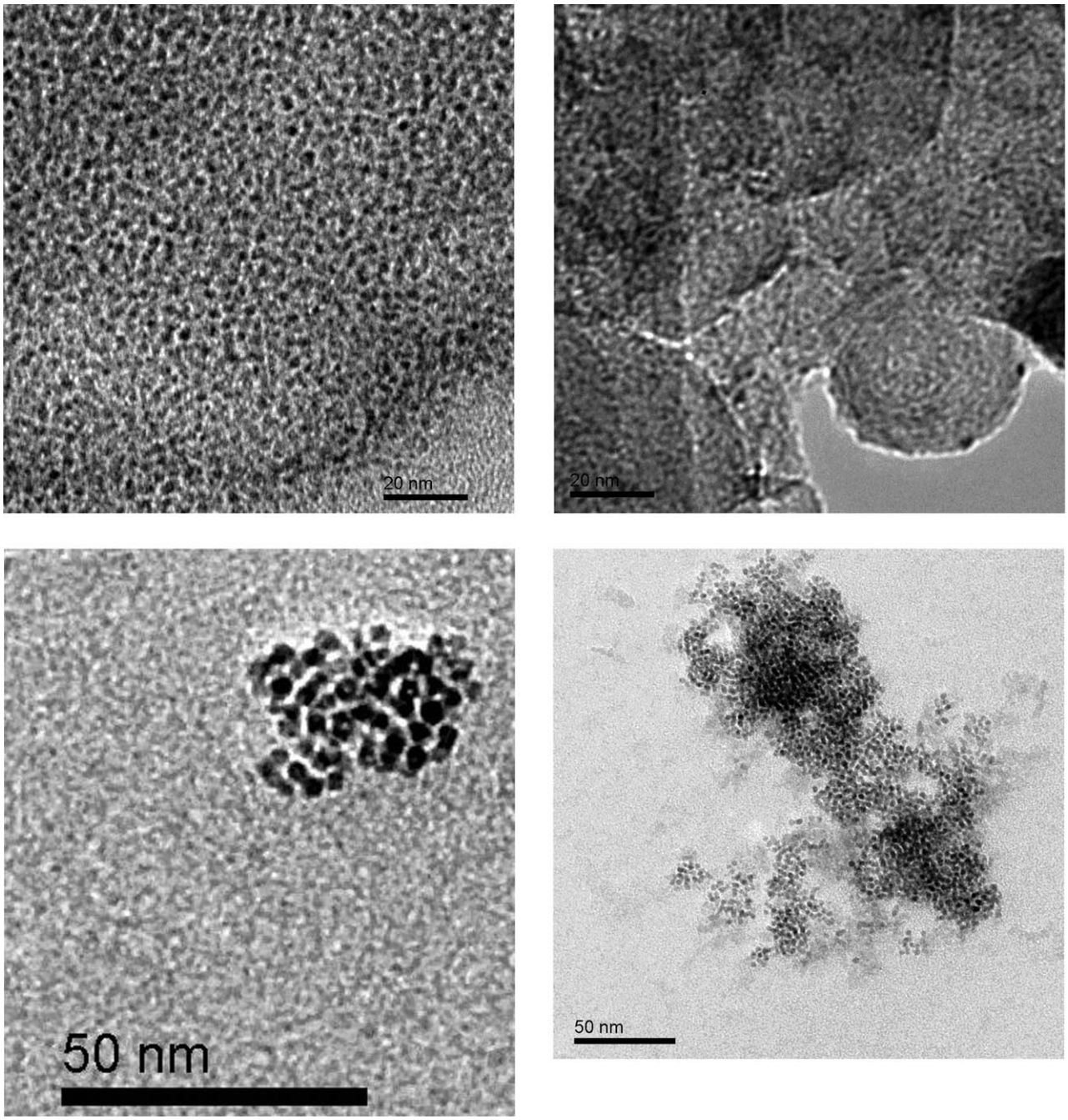


Figure 1. TEM micrographs of Pd nanoparticles; *reaction conditions:* 4-chlorobenzotrifluoride (0.5 mmol), phenylboronic acid (0.75 mmol), $Pd(OAc)_2$ (1 mol%), K_2CO_3 (1 mmol), PEG-400 (4 g) at room temperature for (a), (b), and (c): (a, *top left*) 5 min after reaction in air, (b, *top right*) 75 min after reaction in air, (c, *bottom left*) preprepared Pd nanoparticles[22] [$Pd(OAc)_2$ 2 mol%] in PEG-400 at room temperature in nitrogen, (d, *bottom right*) 75 min after preprepared Pd nanoparticles catalyzed the reaction in air.

pared palladium nanoparticles were *ca.* 3.6 nm (Figure 1, *bottom left*). It is known that nanoparticles have a large surface to volume ratio leading to high energy surfaces and easy aggregation. In our manner, the formation of palladium nanoparticles *in situ* accompanied with the Suzuki coupling reaction occurred immediately. And in view of the molecular collision theory, the reaction might be catalyzed by palladium at an atom level. However, the preprepared nanoparticles were easy to congregate to be in the state of stability to catalyze the reaction in a big diameter and exhibited low activity. Surprisingly, there

no reaction occurred on using 1 mol% 10% Pd/C (Table 6, entry 4).

It was interesting that the average diameters of palladium nanoparticles became smaller (2.5 nm, Figure 1, *bottom right*) than the original ones (3.6 nm, Figure 1, *bottom left*), when the Suzuki reaction of 4-chlorobenzotrifluoride with phenylboronic acid was performed after 75 min catalyzed by the preprepared palladium nanoparticles. This phenomena could be explained by the Ostwald ripening process.[14] During the reaction, the palladium nanoparticles were in a growth phase and formed large palladium clusters. Consequently, the larger palladium particles were aggregated and precipitated out of the reaction solution, while the smaller ones stayed in the solution. In fact, we observed palladium black in the final reaction. However, the system of the *in situ* generated palladium nanoparticles in PEG-400 in air was stable for months, and no palladium black was observed.

Roles of Arylboronic Acids

In the preliminary communication,[17] we presented a proposed mechanism of an oxygen-promoted, ligand-free Suzuki coupling reaction catalyzed by the *in situ* generated palladium nanoparticles in PEG-400. The PEG-400 played important roles as a reducing agent and stabilizer for the formation of palladium nanoparticles. However, the reason why the palladium nanoparticles formed much quicker than those described in literature[16] was unclear. In this work, we further investigated the role of the phenylboronic acid in the formation of the palladium nanoparticles. Control experiments have been carried out to prepare the palladium nanoparticles in the presence or in the absence of the phenylboronic acid, respectively. We found that the *in situ* generated palladium nanoparticles were formed much faster than the preprepared palladium nanoparticles under the same conditions. In fact, this was confirmed by UV-vis spectroscopy (Figure 2).

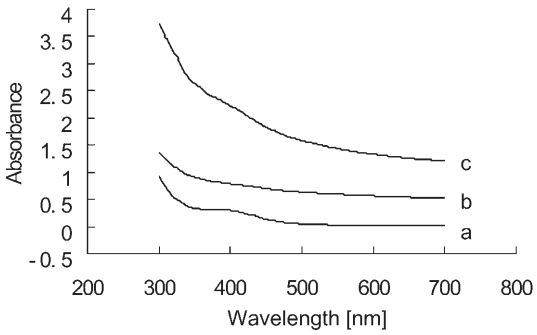


Figure 2. UV-vis absorption spectra of (a) $Pd(OAc)_2$ (0.2 mmol) in DMF, (b) $Pd(OAc)_2$ (0.2 mmol) and phenylboronic acid (1.5 mmol) in PEG-400 (4 g) was stirred 2 h at room temperature in air, and (c) $Pd(OAc)_2$ (0.2 mmol) in PEG-400 (4 g) was stirred 12 h at room temperature.

Table 7. Effect of the amount of phenylboronic acid on the Suzuki reaction of 4-chloronitrobenzene in PEG-400 in air.[a]

Entry	Molar Ratio of Phenylboronic Acid to 4-Chloronitrobenzene	Time [h]	Isolated Yield [%]
1	1.1	15	58
2	1.5	1	94
3	2.0	1	95

[a] *Reaction conditions:* 4-chloronitrobenzene (0.5 mmol), $Pd(OAc)_2$ 1 mol%, K_2CO_3 (1 mmol), PEG-400 (4 g), room temperature. The reactions were monitored by GC and TLC.

It was clear that there was a peak at 400 nm assigned to Pd(II) (Figure 2, a). In the presence of phenylboronic acid, this peak completely disappeared, revealing the full conversation of Pd(II) to Pd(0) within 2 h (Figure 2, b). In the case of the absence of phenylboronic acid, a weak peak of the absorbance at 400 nm was observed, showing that the Pd(II) could not be reduced to Pd(0) totally even after 12 h (Figure 2, c). This was because the phenylboronic acid played a role as an associate reducing agent[11a] and quickened the formation of palladium nanoparticles in PEG-400. Moreover, arylboronic acids could act as stabilizers and keep the palladium nanoparticles constant in size.[14]

To further reveal the effect of phenylboronic acid on the Suzuki reaction, different molar ratios of phenylboronic acid to 4-chloronitrobenzene have been studied. The results shown in Table 7 demonstrate that a suitable excess amount of the phenylboronic acid was necessary to complete the reaction (Table 7, entries 2 and 3). Lower amounts of the phenylboronic acid resulted in incomplete reaction (Table 7, entry 1), from which it was concluded that a portion of phenylboronic acids was consumed for the formation of palladium nanoparticles.

Conclusions

We have developed an aerobic, ligand-free Suzuki coupling reaction catalyzed by the *in situ* generated palladium nanoparticles in PEG-400 at room temperature, which was a very simple and highly active protocol for the Suzuki coupling of aryl chlorides with arylboronic acids in excellent isolated yields in short times. Control experiments illustrated that the reactivity of the *in situ* palladium nanoparticles was much higher than that of the preprepared ones. The arylboronic acids played roles as both a substrate and an as-

sistant reductant. It is noteworthy that the reaction can be performed efficiently at room temperature in air, which is of great interest for industrial application.

Experimental Section

General Information

All aryl halides and arylboronic acids were used as received (Alfa Aesar, Avocado). The PEG-400 was purchased from Acros. All other chemicals were purchased from commercial sources and used without further purification. ^{1}H NMR spectra were recorded on a Varian Inova 400 spectrometer. Chemical shifts are reported in ppm relative to TMS. Mass spectra were obtained using a GCT (EI, 70 eV). Gas chromatography analyses were performed on a Tianmei 7890 Gas Chromatograph with a FID and 50-meter OV-101 column. Transmission electron microscopy (TEM) was performed on a Tecnai 20 microscope operating at 200 kV. All products were isolated by short chromatography on a silica gel (200–300 mesh) column using petroleum ether (60–90 °C), unless otherwise noted. UV-vis spectroscopy measurements (300–700 nm) were performed on a Bejing Rui Li UV-2100 using quartz cells.

General Procedure for the Suzuki Cross-Coupling of Aryl Chlorides with Arylboronic Acids

A mixture of aryl chloride (0.5 mmol), arylboronic acid (0.75 mmol), $Pd(OAc)_2$ (2 mol%, 2.2 mg, 1 mol% for 4-chloronitrobenzene), K_2CO_3 (1 mmol, 138 mg) and PEG-400 (4 g) was stirred at room temperature for the indicated time until complete consumption of starting material as monitored by GC. The mixture was added to brine (15 mL) and extracted four times with diethyl ether (4 × 15 mL). The solvent was concentrated under vacuum and the product was isolated by short chromatography on a silica gel (200–300 mesh) column.

Supporting Information

Experimental details and characterization of the products are given in the Supporting Information.

Acknowledgements

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[22] Method for preprepared palladium nanoparticles: $Pd(OAc)_2$ 2 mol% (1 mol% for entries 1a and 1b in Table 6) was added into deoxygened PEG-400 (4 g) at room temperature (45 °C for entries 3a and 3b in Table 6) by magnetic stirring for 12 h (2 h at 45 °C) under N_2. During the process the colour of the solution turned from light yellow to dark, indicating the generation of palladium nanoparticles. Then, the as prepared palladium nanoparticles were used to catalyze Suzuki cross-coupling reactions in air.

