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Palladium Nanoparticles in Ionic Liquid by Sputter Deposition as Catalysts for Suzuki–Miyaura Coupling in Water

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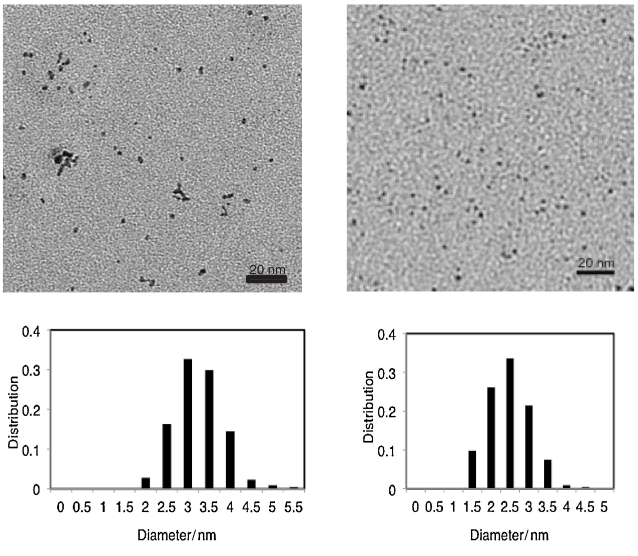
Palladium nanoparticles in an ionic liquid prepared readily by sputter deposition efficiently catalyze the Suzuki–Miyaura coupling of hydrophobic as well as hydrophilic aryl halides in water.

Palladium nanoparticles have received much attention in modern synthetic chemistry since they have intrinsic potential to show high performance as catalysts for carbon–carbon bond forming reactions.[1] In particular, the Suzuki–Miyaura cross-coupling, which is of genuine synthetic utility, has been extensively studied with a variety of nanoparticles stabilized or immobilized by ionic liquids,[2] polymers,[3] carbon,[4] silica,[5] and alumina.[6] However, in most cases, their preparation or generation protocols rely on the in situ reduction of palladium(II) precursors with additional chemical species. Recently, one of our groups has developed a highly clean method to fabricate metal nanoparticles including Au, Ag, Au/Ag, and Pt in ionic liquids at room temperature: the nonvolatility of ionic liquids enables the deposition of metals onto them under high vacuum, which leads to the high dispersion of nanoparticles with diameters of several nanometers and allows the investigation of inherent activity of nanoparticles in an ionic liquid without the contamination of reducing reagents.[7] Herein, we report an application of the sputter methodology to the rapid and facile preparation of waste-free palladium nanoparticles in ionic liquids. The nanoparticles show good catalytic activity for the Suzuki–Miyaura coupling in water and enable use of both water-soluble and -insoluble aryl halides in the reaction without employing excess ionic liquid,[2,8] organic/aqueous mixed solvent system,[9] special hydrophilic polymer support,[10] or additional phase transfer catalyst.[11]

We chose 1-butyl-3-methylimidazolium hexafluorophosphate (BMI-PF_6) and 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (BMI-TFSI) as typical room-temperature ionic liquids. A 0.20-cm^3 aliquot of the degassed ionic liquid was spread on a soda glass plate (2.5 cm × 2.5 cm), and the plate was horizontally set in a Cressigngton 108 auto SE sputter coater, which was located at a distance of 4.5 cm from a Pd foil target (57 mm diameter). Sputter deposition was then carried out at room temperature for 300 s with a 40 mA current under argon, whose pressure did not exceed 8 Pa. The concentration of Pd obtained in the ionic liquids was determined by ICP analysis: the BMI-PF_6 and BMI-TFSI contained ca. 0.011 and 0.030 $\mu mol\,mg^{-1}$ as Pd atoms, respectively. Their TEM images and size distributions are illustrated in Figure 1: Pd nanoparticles in BMI-PF_6 were generated with an average diameter of ca. 3.0 nm, whereas the use of BMI-TFSI resulted in a ca. 2.2 nm average diameter. Thus, the size of nanoparticles depends on the counter anion of ionic liquids employed as is anticipated.[7] The nanoparticles were stable at least for 1 month when stored even under ambient conditions.



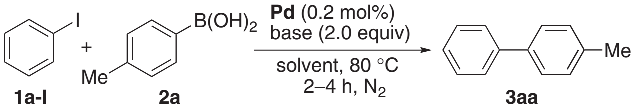
Pd/BMI-PF_6 Pd/BMI-TFSI

Figure 1. TEM images and size distributions of Pd nanoparticles prepared by sputter deposition in BMI-PF_6 (left) and BMI-TFSI (right).

With the palladium nanoparticles in BMI-PF_6 (Pd/BMI-PF_6) and BMI-TFSI (Pd/BMI-TFSI) in hand, we began the investigation of their catalytic activities for the Suzuki–Miyaura coupling using iodobenzene (**1a-I**) and *p*-tolylboronic acid (**2a**) as starting substrates (Table 1). The extensive screening of reaction parameters with 0.2 mol % catalyst loading revealed that a combination of *i*-Pr_2NEt and water as base and solvent, respectively, proved to be optimal for the Pd/BMI-PF_6 catalyst (Entries 1–9). On the other hand, in the case of Pd/BMI-TFSI, an inorganic base, Cs_2CO_3, gave a better result (Entries 10 and 11).[12,13] It is worth noting that due to the insolubility of **1a-I** in water, the reaction should proceed in a biphasic system, i.e., organic particles in water. The beneficial behavior of water would arise from the hydrophobic effect of the substrate.[14]

We then conducted the Suzuki–Miyaura coupling of various aryl iodides and bromides with arylboronic acids with the Pd/BMI-TFSI catalyst (Table 2). In general, 0.3 mol % catalyst loading and 4.0 equiv of Cs_2CO_3 gave good reproducibility. Not only electron-rich but also electron-deficient aryl iodides **1b-I**–

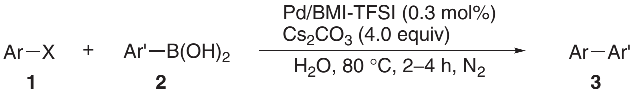
Table 1. Optimization studies^a



Entry	Pd	Base	Solvent	**3aa**, Yield^b/%
1	Pd/BMI-PF$_6$	K_3PO_4	toluene	trace
2	Pd/BMI-PF$_6$	KOAc	toluene	trace
3	Pd/BMI-PF$_6$	Et_3N	toluene	trace
4	Pd/BMI-PF$_6$	*i*-Pr$_2$NEt	toluene	8
5	Pd/BMI-PF$_6$	*i*-Pr$_2$NEt	EtOH	trace
6	Pd/BMI-PF$_6$	*i*-Pr$_2$NEt	H_2O/toluene	24
7	Pd/BMI-PF$_6$	*i*-Pr$_2$NEt	H_2O/EtOH	59
8	Pd/BMI-PF$_6$	*i*-Pr$_2$NEt	H_2O	70
9	Pd/BMI-PF$_6$	Cs_2CO_3	H_2O	20
10	Pd/BMI-TFSI	*i*-Pr$_2$NEt	H_2O	65
11	Pd/BMI-TFSI	Cs_2CO_3	H_2O	72

^{a}A mixture of **1a-I** (0.20 mmol), **2a** (0.40 mmol), **Pd** (0.2 mol %, 36 mg for Pd/BMI-PF$_6$, 13 mg for Pd/BMI-TFSI), and base (0.40 mmol) in the indicated solvent (1.0 or 1.0/1.0 mL) was stirred for 2–4 h at 80 °C under N_2. ^{b}GC yield.

Table 2. Pd/BMI-TFSI-catalyzed Suzuki–Miyaura coupling of various aryl iodides and bromides **1**^{a}



Entry	**1**	Ar′ **2**	**3**, Yield^b/%
1	Ph–I (**1a-I**)	4-MeC$_6$H$_4$ (**2a**)	**3aa**, 75^c
2	4-MeOC$_6$H$_4$–I (**1b-I**)	**2a**	**3ba**, 65^d
3	4-ClC$_6$H$_4$–I (**1c-I**)	**2a**	**3ca**, 65
4	4-AcC$_6$H$_4$–I (**1d-I**)	**2a**	**3da**, 95
5	4-MeO$_2$CC$_6$H$_4$–I (**1e-I**)	**2a**	**3ea**, 83
6	4-HOC$_6$H$_4$–I (**1f-I**)	**2a**	**3fa**, 78
7	2-HOC$_6$H$_4$–I (**1g-I**)	**2a**	**3ga**, 72
8	1-naphthyl–I (**1h-I**)	**2a**	**3ha**, 80
9	**1a-I**	4-MeOC$_6$H$_4$ (**2b**)	**3ab**, 66
10	**1d-I**	3-thienyl (**2c**)	**3dc**, 97
11	**1d-I**	2-thienyl (**2d**)	**3dd**, 81
12^e	4-AcC$_6$H$_4$–Br (**1d-Br**)	**2a**	**3da**, 43
13^{e,f}	**1d-Br**	**2a**	**3da**, 66
14^{e,f}	4-MeO$_2$CC$_6$H$_4$–Br (**1e-Br**)	**2a**	**3ea**, 71
15^{e,f}	4-HOC$_6$H$_4$–Br (**1f-Br**)	**2a**	**3fa**, 84
16^{e,f}	4-HO$_2$C$_6$H$_4$–Br (**1i-Br**)	**2a**	**3ia**, 99^g
17^{e,f}	4-MeOC$_6$H$_4$–Br (**1b-Br**)	**2a**	**3ba**, 8^c

^{a}A mixture of **1** (0.20 mmol), **2** (0.40 mmol), Pd/BMI-TFSI (0.3 mol %, 20 mg), and Cs_2CO_3 (0.80 mmol) in H_2O (1.0 mL) was stirred for 2–4 h at 80 °C under N_2. ^{b}Isolated yield. ^{c}GC yield. ^{d}NMR yield. ^{e}At 100 °C. ^{f}Under air. ^{g}Isolation as **3ea** after methylation with MeI and K_2CO_3.

1e-I participated in the reaction with **2a** (Entries 2–5). Notably, the phenolic substrates **1f-I** and **1g-I**, which would be hydrophilic under basic conditions, reacted with **2a** without any difficulties (Entries 6 and 7). The steric hindrance of 1-iodonaphthalene (**1h-I**) did not interfere with the coupling (Entry 8). Moreover, an electron-donating (4-methoxyphenyl)boronic acid (**2b**) and thienylboronic acids **2c** and **2d** also participated in the reaction (Entries 9–11). On the other hand, aryl bromide **1d-Br** showed lower reactivity (Entry 12). After additional optimization studies, an air atmosphere instead of nitrogen was found to improve the yield (Entry 13). This is probably because the Pd nanoparticles could absorb molecular oxygen and be more stable against aggregation and maintain catalytic activity.[15] Under the O_2-promoted conditions, the hydrophobic **1e-Br** as well as hydrophilic **1f-Br** and **1i-Br** underwent the cross-coupling efficiently as observed in the case of aryl iodides (Entries 14–16). However, even with the modified system, an electron-donating substituent was detrimental (Entry 17).

In summary, we have prepared clean Pd nanoparticles in ionic liquids by sputter deposition and succeeded in their application as catalysts for the aqueous Suzuki–Miyaura coupling of both water-soluble and -insoluble aryl halides.[16] Ongoing work seeks to prepare other transition metal nanoparticles of high catalytic activity using the sputter methodology.

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