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A SELF–SUPPORTED PALLADIUM–BIPYRIDYL CATALYST FOR THE SUZUKI–MIYAURA COUPLING IN WATER

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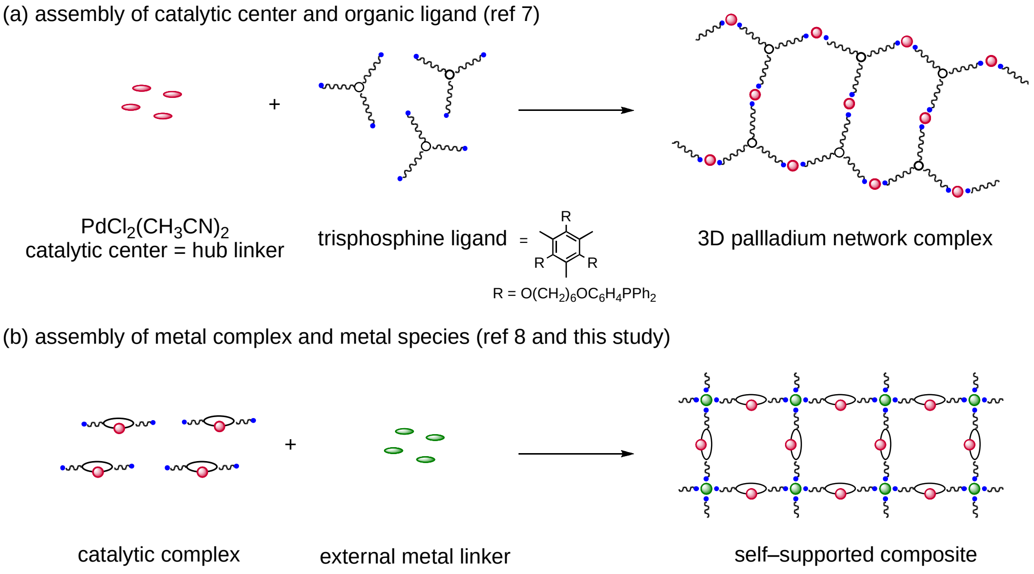
Abstract – A self-supported palladium catalyst ($PdCl_2BPy$–Cu) was prepared via construction of a metal-organic framework (MOF) of a bipyridyl-palladium complex bearing carboxylic groups and a copper(II) linker. $PdCl_2BPy$–Cu efficiently catalyzed the Suzuki-Miyaura coupling of phenyl halides with arylboronic acids in water under atmospheric conditions to afford the corresponding biaryl products in high yield. The catalyst was reused four times without loss of catalytic activity.

INTRODUCTION

The Suzuki-Miyaura coupling is one of the most important and useful reactions for the formation of sp^2-sp^2 carbon-carbon bonds.[1] To date, various excellent catalyst systems for the Suzuki-Miyaura coupling have been developed and widely utilized to synthesize biaryl compounds. From a viewpoint of green sustainable chemistry, many researchers have recently paid much attention to recycle the catalyst and reduce the consumption of organic solvents. In particular, heterogeneous-switching of homogeneous catalysts, e.g. polymeric immobilization, and aqueous-switching of organic solvents are recognized as the major keys for the achievement of environmentally benign Suzuki-Miyaura coupling.[2,3] Self-supported polymeric transition metal complexes have recently emerged as a new type of immobilized catalysts[4] where catalytic metal species are incorporated in the polymeric composites via construction of metal-organic frameworks (MOFs)[5] with organic ligands. Only a few self-supported catalysts have been reported for the Suzuki-Miyaura coupling reaction so far.[6,7] We have previously developed a 3D palladium-network complex via assembly of $PdCl_2(CH_3CN)_2$ and a trisphosphine ligand (Scheme 1a) to exhibit high catalytic activity and recyclability in the Suzuki-Miyaura coupling in water to achieve a high level of chemical greenness, where the palladium species concurrently serves as a catalytically active center as well as a *hub* linker of the network complex.[7] If a catalytically active transition metal complex is assembled with an external linker unit to form an insoluble polymeric composite (Scheme 1b), the resulting composite should reflect the catalytic properties of the mother monomeric complex to make development of a self-supported catalyst more flexible and practical. We have previously reported that the palladium(II) trifluoroacetate complex of a bipyridyl ligand bearing carboxylic groups assembled with copper nitrate to afford an insoluble self-supported palladium-bipyridyl complex, which efficiently catalyzed the aerobic oxidation of benzylic alcohols in water with high recyclability.[8] In this report, we describe the extended application of the self-supported palladium-bipyridyl complex to the aqueous Suzuki-Miyaura coupling of phenyl halides with arylboronic acids.

Scheme 1. Strategy for the Construction of Self-Supported Catalysts

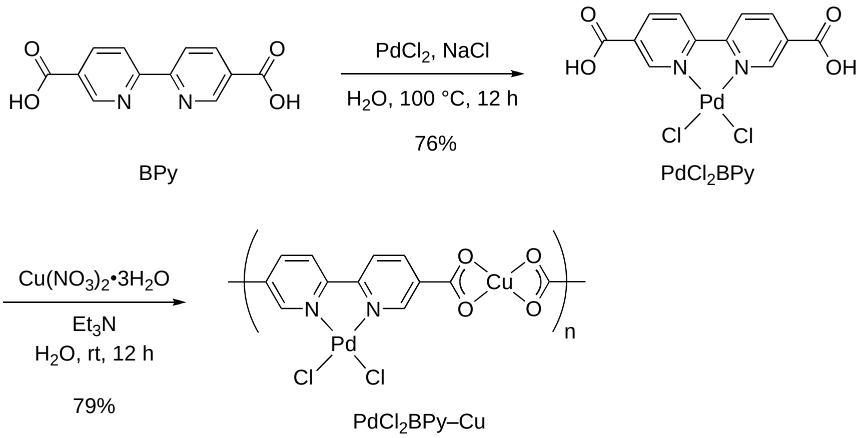


RESULTS AND DISCUSSION

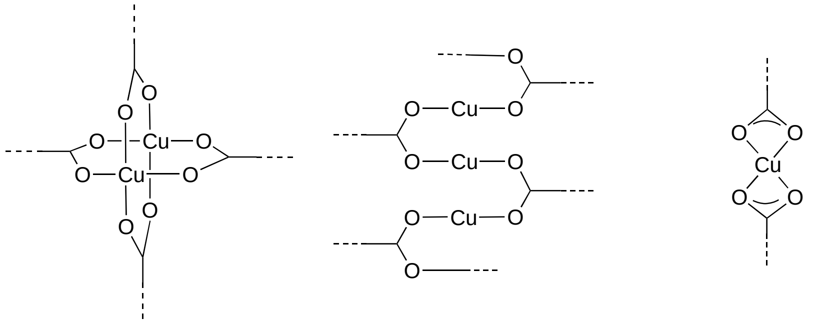
The palladium(II) chloride complex coordinated with a 2,2'-bipyridyl ligand having carboxylic groups at 5- and 5'-positions ($PdCl_2BPy$) was prepared by mixing $PdCl_2$ and 2,2'-bipyridine-5,5'-dicarboxylic acid (BPy)[9] in the presence of an excess amount of NaCl in H_2O at 100 °C (76% yield) (Scheme 2). The self-supported palladium(II) bipyridyl complex ($PdCl_2BPy$–Cu) was obtained by treatment of $PdCl_2BPy$ and $Cu(NO_3)_2•3H_2O$ in water in the presence of Et_3N at room temperature for 12 h to give the desired insoluble polymeric composite in 79% yield.

Scanning electron microscopy (SEM) analysis of $PdCl_2BPy$–Cu revealed that block-like nanoclusters were assembled to form big cluster units (Figure 1a). Transmission electron microscopy (TEM) analysis supported that the size of the block-like nanoclusters was about 10–100 nm (Figure 1b). ICP analysis

Scheme 2. Preparation of $PdCl_2BPy$–Cu



Scheme 3. Representive Linkage Modes of the Copper-Carboxylate Unit in MOF Structures



1) linkage mode A (porous MOF)
2) linkage mode B (sheet MOF)
3) linkage mode C (linear MOF)

showed that the ratio of Pd:Cu was 1.0:0.98 in the self-supported composite. Combustion elemental analysis revealed that the self-supported composite $PdCl_2BPy$–Cu was comprised of $PdCl_2(OC(O)\text{-}C_5H_3N\text{-}C_5H_3N\text{-}COO)Cu\bullet 4H_2O$. Typically, the assembly of a dicarboxylate derivative and a copper(II) ion would afford three different linkage modes of the copper-carboxylate unit in MOFs (Scheme 3).[10] The nitrogen adsorption experiment indicated that the nitrogen BET surface area of $PdCl_2BPy$–Cu was very small (1.99 $m^2\ g^{-1}$). The porous MOF structure could provide a large BET area. X-ray powder diffraction (XRPD) analysis of $PdCl_2BPy$–Cu showed the diffraction pattern derived from a crystalline structure having monoclinic P2/2m (#10) space group (Figure 2), though the detailed structure of $PdCl_2BPy$–Cu was not exactly determined.

With the self-supported Pd(II)-bipyridyl polymeric composite in hand, we initiated to investigate the Suzuki–Miyaura coupling reaction of phenyl halides with arylboronic acids in water. The reaction of iodobenzene (1.0 mmol) with *p*-tolylboronic acid (1.5 mmol) was carried out with 0.5 mol% of $PdCl_2BPy$–Cu in the presence of Na_2CO_3 (3.0 mmol) in refluxing water (2 mL) for 6 h under atmospheric conditions to afford 4-methylbiphenyl in 90% yield (Scheme 4).

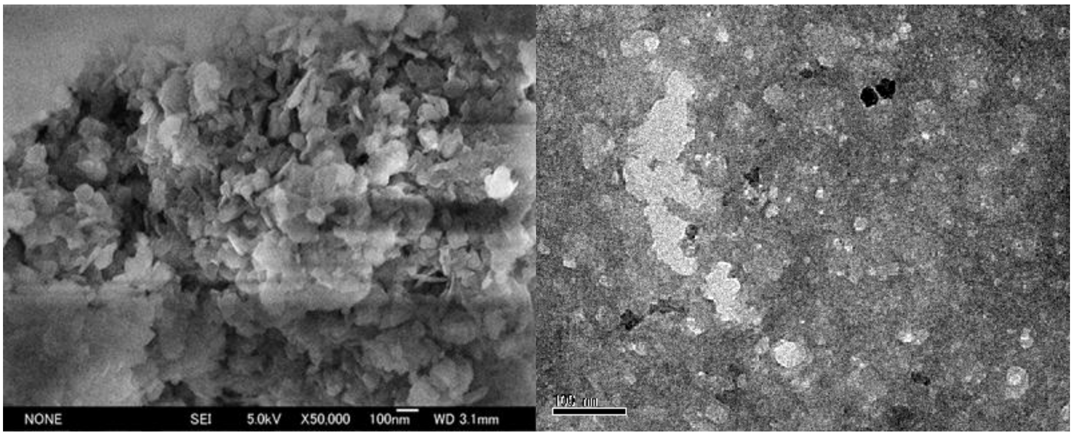


Figure 1. SEM (left) and TEM (right) images of $PdCl_2BPy$–Cu

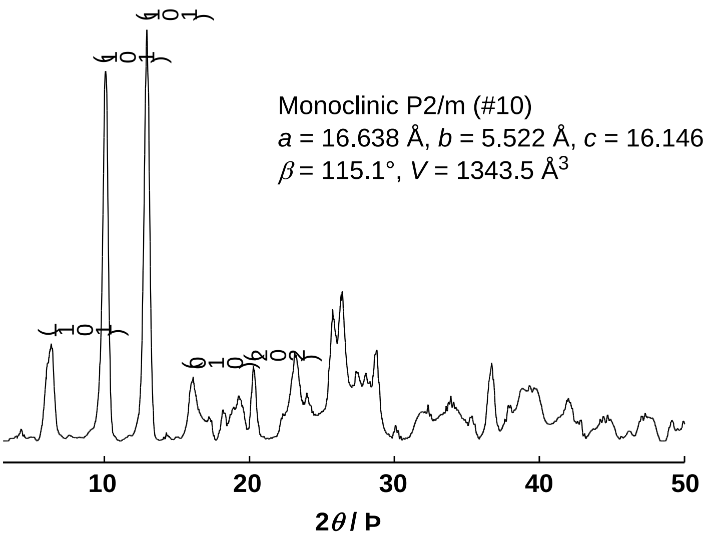
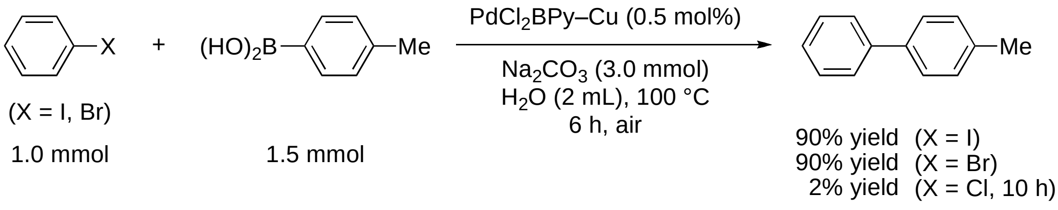


Figure 2. XRPD pattern of $PdCl_2BPy$–Cu

The self-supported composite also catalyzed the reaction of bromobenzene with *p*-tolylboronic acid to give 4-methylbiphenyl in 90% yield. However, the reaction of chlorobenzene gave only a 2% yield of the product even for longer reaction time (10 h).

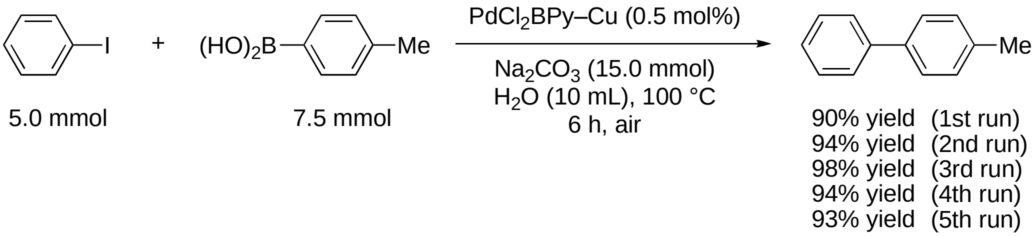
Scheme 4. Suzuki-Miyaura Coupling of Phenyl Halides with *p*-Tolylboronic Acid with $PdCl_2BPy$–Cu



The scope of arylboronic acids was examined for the Suzuki–Miyaura coupling with phenyl halides in water using the self-supported catalyst $PdCl_2BPy$–Cu. Representative results are summarized in Table 1. $PdCl_2BPy$–Cu efficiently catalyzed the coupling of iodobenzene and bromobenzene with phenylboronic acid to afford biphenyl in 99% and 91% yield, respectively (entries 3 and 4). The coupling reaction of various arylboronic acids bearing both electron-donating and electron-withdrawing *p*-substituents also proceeded to give the corresponding *p*-substituted biphenyls in 76–97% yield (entries 5–14). Ortho- and meta-substituted arylboronic acids were tolerated for the reaction (77–93% yield in entries 15–18). 1-Naphthylboronic acid also underwent the Suzuki-Miyaura coupling with phenyl halides to give 1-phenylnaphthalene in 75% yield (entries 19 and 20).

The recyclability of the insoluble self-supported catalyst $PdCl_2BPy$–Cu was examined for the Suzuki–Miyaura coupling reaction of iodobenzene with *p*-tolylboronic acid (Scheme 5). Thus, after the first reaction, which gave 90% of 4-methylbiphenyl, the catalyst was recovered by centrifugation, washed with H_2O, dried under vacuum, and successively subjected to a second, third, fourth, and fifth reaction under the same conditions to afford 4-methylbiphenyl in 94%, 98%, 94%, and 93% yield, respectively (Scheme 5). TEM analysis of the recovered catalyst after the reaction showed the block nanoclusters (ca. 100 nm) were assembled to form the big clusters and the palladium nanoparticles (ca. 5 nm) were generated in the clusters (Figure 3).

Scheme 5. Catalyst Recycling Experiment



In conclusion, we have developed a novel self-supported catalyst $PdCl_2BPy$–Cu via mixing a palladium-bipyridyl complex bearing carboxylic groups at the 5- and 5’ positions and a copper(II) ion, which efficiently catalyzed the Suzuki-Miyaura coupling of phenyl halides with arylboronic acids in water under atmospheric conditions to give the corresponding biaryls with high recyclability. Further extensive scope for the Suzuki-Miyaura reaction and the application of this catalyst to the other organic transformations are in progress in our lab.

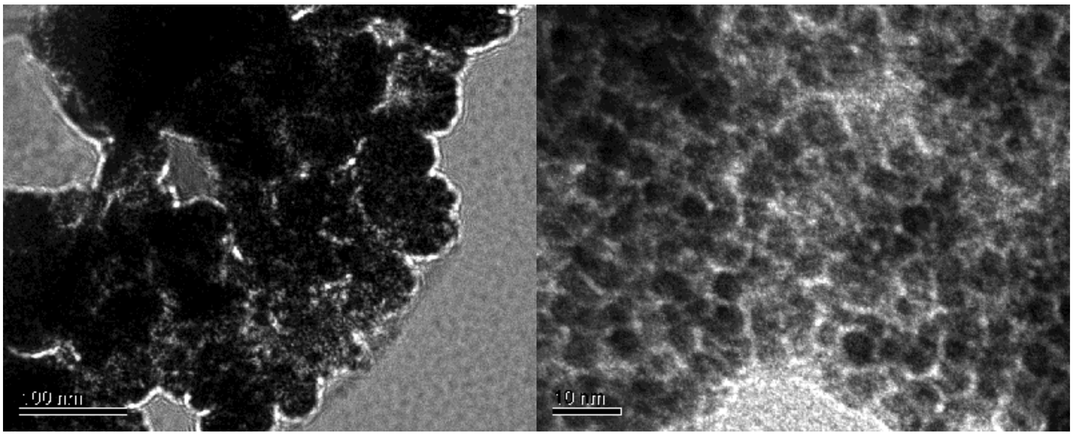
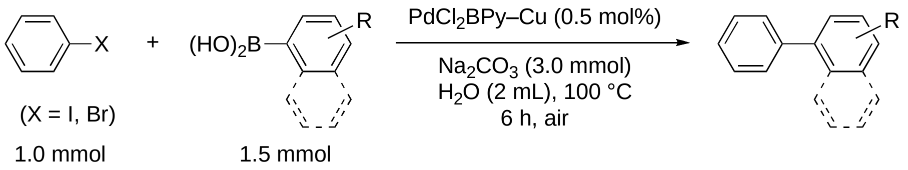
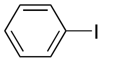
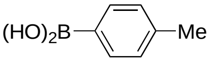
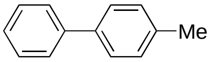
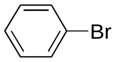
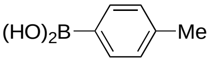
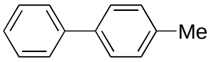
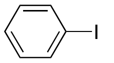
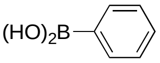
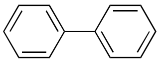
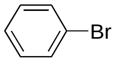
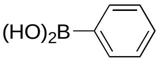
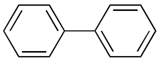
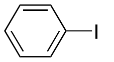
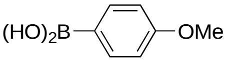
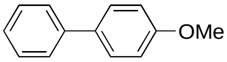
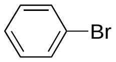
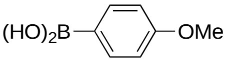
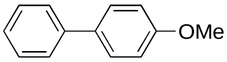
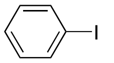
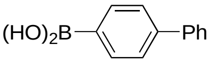
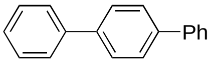
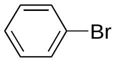
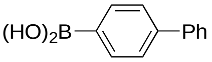
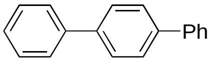
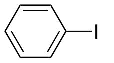
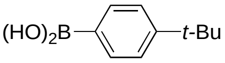
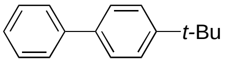
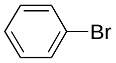
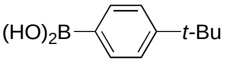
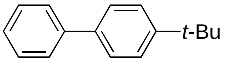
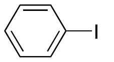
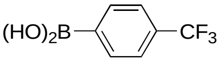
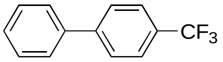
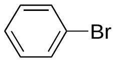
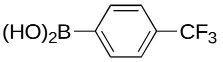
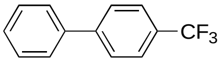
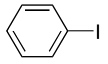
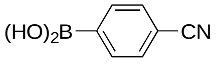
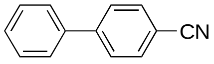
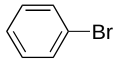
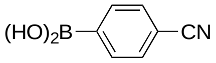
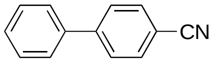
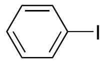
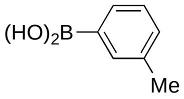
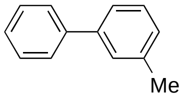
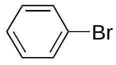
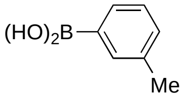
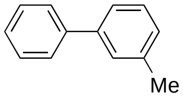
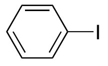
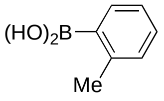
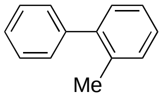
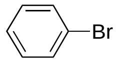
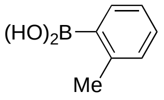
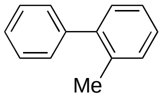
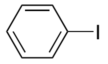
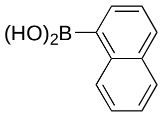
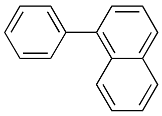
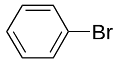
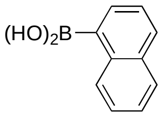
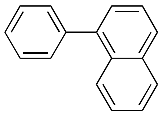


Figure 3. TEM images of the recovered catalyst after the reaction.

Table 1. Suzuki–Miyaura Coupling of Phenyl Halides with Arylboronic Acids Catalyzed by $PdCl_2BPy$–Cu in Water [a]



entry	phenyl halide	arylboronic acid	product	yield / %[b]
1				90
2				90
3				99
4				91
5				79
6				89
7				91
8				76
9				94
10				95
11				95
12				94

13				95
14				97
15				93
16				87
17				77
18				93
19				75
20				75

[a] All the reactions were carried out with 0.5 mol% of the catalyst and Na_2CO_3 (3 equiv) in water (2 mL) at 100 °C for 6 h under atmospheric conditions. [b] GC yield.

EXPERIMENTAL

General. All chemicals were commercially available and used without further purification. 2,2'-Bipyridine-5,5'-dicarboxylic acid (BPy) was prepared according to the reported procedure.[9] Water was deionized with a Millipore system as a Milli-Q grade. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a JEOL JNM-AL500 spectrometer. GC analysis was carried out on a Hewlett Packard 4890 system. GC-MS was measured with an Agilent 6890 GC/5973 N MS detector. IR spectra were recorded on a JASCO FT/IR 460 Plus spectrometer. SEM images were obtained by a JEOL JSM-6700F scanning electron microscope. TEM images were obtained by a JEOL JEM-2100F transmission electron microscope. ICP analysis was performed on a LEEMAN LABS Profile plus plasma spectrometer. Elemental analysis was conducted on a Yanaco CHN Corder MT-6 elemental analyzer. XRPD analysis was carried out on a Rigaku RINT-Ultima III powder X-ray diffractometer. Nitrogen adsorption was analyzed on a BEL BELSORP-mini II.

Synthesis:

$PdCl_2BPy$. A suspension of $PdCl_2$ (0.35 g, 2.0 mmol), NaCl (1.16 g, 200 mmol), and BPy (0.49 mg, 2.0 mmol) in H_2O (40 mL) was heated at 100 ˚C for 12 h. After being cooled, the resulting solid was collected by filtration, washed with H_2O (10 mL x 3), and dried under vacuum to give a pale yellow powder (0.64 g, 75.6%). ^1H NMR (500 MHz, D_2O, NaOD): δ 8.63 (d, J = 2.0 Hz, 2H, $H_{Py\text{-}6}$), 8.43 (d, J = 8.5 Hz, 2H, $H_{Py\text{-}3}$), 8.21 (d, J = 8.5 Hz, 2H, $H_{Py\text{-}4}$). FT-IR/cm^{-1} (ATR): 3029, 3015, 2996, 2975, 2958, 2363, 2340, 2005, 1701, 1611, 1542, 1424, 1413, 1400, 1256, 1139, 1051, 944, 868, 856, 823, 760, 683, 660, 570 cm^{-1}. Anal. Calcd for $PdCl_2BPy\bullet 2H_2O$ ($C_{12}H_{12}Cl_2N_2O_6Pd$): C, 31.50%; H, 2.64%; N, 6.12%. Found: C, 31.48%; H, 2.17%; N, 6.16%.

$PdCl_2BPy$–Cu. A mixture of $PdCl_2BPy$ (211 mg, 0.5 mmol), Et_3N (101 mg, 1.0 mmol), $Cu(NO_3)_2\bullet 3H_2O$ (362 mg, 1.5 mmol), and H_2O (20 mL) was stirred for 12 h at room temperature. The resulting solid was collected by filtration, washed by H_2O (5 mL x 3) and acetone (5 mL x 3) and dried under vacuum to give a green solid (191 mg, 79%). FT-IR (ATR): 3511, 3427, 2360, 2342, 1616, 1563, 1415, 1318, 1138, 1047, 857, 768, 739, 710, 600, 592, 584, 572, 562 cm^{-1}. ICP analysis showed the ratio of Pd:Cu was 1.0:0.98. Anal. Calcd for $PdCl_2BPy$–$Cu\bullet 4H_2O$ ($C_{12}H_{14}N_2O_8Cl_2PdCu$): C, 25.96%; H, 2.54%; N, 5.05%. Found: C, 26.22%; H, 2.81%; N, 5.16%.

General Procedure for the Suzuki–Miyaura Coupling of Boronic Acids with Pheny Halides in Water with $PdCl_2BPy$–Cu. A mixture of phenyl halide (1.0 mmol), arylboronic acid (1.5 mmol), $PdCl_2BPy$–Cu (2.41 mg, 5.0 μmol), Na_2CO_3 (249.0 mg, 3.0 mmol), and water (2 mL) was stirred at 100 °C for 6 h under air. After being cooled, the resulting mixture was extracted with EtOAc (1 mL x 5). The extract was analyzed with GC and GC–MS. The yields of the products were determined by GC with an internal standard (mesitylene). The chemical identification of the product was performed using the NIST Mass Spectral Search Program Ver. 1.6d for Windows unless otherwise noted.

All products are known compounds whose CAS registry numbers are provided as below:

4-Methylbiphenyl: 644-08-6 (Table 1, entries 1 and 2); biphenyl: 92-52-4 (entries 3 and 4); 4-methoxybiphenyl: 613-37-6 (entries 5 and 6); *p*-terphenyl: 92-94-4 (entries 7 and 8); 4-*tert*-butylbiphenyl: 1625-92-9 (entries 9 and 10); 4-(trifluoromethyl)biphenyl: 398-36-7 (entries 11 and 12); 4-phenylbenzonitrile: 2920-38-9 (entries 13 and 14); 3-methylbiphenyl: 643-93-6 (entries 15 and 16); 2-methylbiphenyl: 643-58-3 (entries 17 and 18); 1-phenylnaphthalene: 605-02-7 (entries 19 and 20).

Catalyst Recycling Experiment. A mixture of phenyl iodide (1.02 g, 5.0 mmol), *p*-tolylboronic acid (1.02 g, 7.5 mmol), $PdCl_2BPy$–Cu (12.1 mg, 25.0 μmol), and Na_2CO_3 (1.25 g, 15.0 mmol) in water (10 mL) was stirred at 100 °C for 6 h under air. After being cooled, ethyl acetate (5 mL) was added to the reaction mixture, which then stirred vigorously. The ethyl acetate layer was decanted and analyzed by GC to determine the yield. The aqueous layer was centrifugated at 4000 rpm for 5 min. After concentration in vacuo, the resulting black powder was subjected to the next reaction.

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