# Support-Free Palladium−NHC Catalyst for Highly Recyclable Heterogeneous Suzuki−Miyaura Coupling in Neat Water

Mathieu Charbonneau, George Addoumieh, Paul Oguadinma, and Andreea R. Schmitzer*

Department of Chemistry, Université de Montréal, 2900 Édouard Montpetit CP 6128 succ. Centre-Ville, Montréal, Québec, Canada, H3C 3J7

S *Supporting Information*

ABSTRACT: Among the various new challenges of chemical processes in water, research on stable, highly active, and recyclable catalysts is a prosperous field. We present here a palladium−NHC catalyst that was synthesized with good yields through a series of simple synthetic steps. This organometallic species was used as a heterogeneous catalyst in low loadings for Suzuki−Miyaura coupling in neat water, under mild conditions. Reaction conditions were optimized for a simple, green, and support-free procedure, without using any phase transfer agent. The catalyst shows excellent reactivity in short times toward different substrates and a very good recyclability.
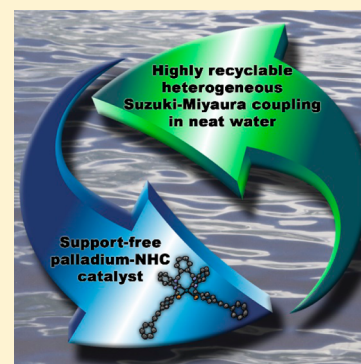
INTRODUCTION

Reaction solvents play a key role in determining the outcome of chemical processes, having an impact on the reaction rate, its feasibility, or reactivity with substrates to form byproducts. Lately, the environmental impact associated with the use of organic solvents has become a rising concern in our society. Water, being nontoxic and abundant, is a promising medium to eventually replace organic solvents. To this end, there is still room for progress toward water-compatible catalysts that can be as active as their organic predecessors under mild conditions, while being stable, recyclable, and easy to work with. In the particular case of Suzuki−Miyaura coupling reaction, the choice of water as the medium is particularly suitable due to the excellent stability of boronic acids in aqueous media.[1,2]

Suzuki−Miyaura coupling is one of the most used coupling reactions for carbon−carbon bond formation, mostly due to the wide variety and accessibility of the starting materials, as well as the mild reaction conditions used.[3] This reaction is usually carried out in organic solvents because they offer a wide range of properties (polarity, protic/aprotic, boiling point, viscosity), and they can solubilize almost every organic reagent. On the other hand, water is a good alternative, but it presents some disadvantages such as its reactivity toward many useful reagents, either the catalyst species or the reactants.[4] Therefore, many studies have highlighted the importance of stabilizing the catalyst in neat water and presented various ways to prevent the formation of inactive palladium black.[5,6] Research has been mainly oriented toward homogeneous catalysts,[7−9] while heterogeneous compounds have scarcely been used. Research in this field could lead to different effective methods of carrying out the reaction and may contribute to developing highly recyclable processes.

First, the use of triphenylphospine derivatives as an additive to stabilize the Pd(0) species is the most common method when using organic solvents.[10] However, the transposition of this process to water synthesis leads to the use of amphiphilic phosphine derivatives. These ligands are often toxic and may require handling under nitrogen, and their use involves extensive and often expensive synthesis. These drawbacks make them less suitable from a green chemistry perspective.[11]

As an alternative, heterogeneous Pd-catalyzed coupling reactions using a solid support have been reported as being good candidates for stabilization.[12,13] The advantages of solid-supported catalysts are numerous; for instance, they are easily removed from the reaction mixture for recycling, and they have high stability compared to free Pd species.[14,15] On the other hand, they often show less reactivity, which ultimately leads to the use of harsher reaction conditions.[14] Nonetheless, Karimi et al. have developed an interesting self-supported heterogeneous catalyst that is very active at low loadings, but its molecular weight is very high (136 kDa).[16] This last aspect makes the process less attractive from a green chemistry perspective. Indeed, the use of high molecular weight polymers often implies additional synthetic steps and raises the total elemental cost of the system, therefore increasing its "mass impact", which is clearly incompatible with the 12 principles of green chemistry listed by Warner and Anastas.[10]

Another interesting avenue is the use of magnetically recyclable nanocatalysts (MRNCs), but the latest developments in this new trend do not include recyclability.[17] Finally, other groups have focused on using N-heterocyclic carbenes to

Scheme 1. Synthesis of Palladium Complex 1
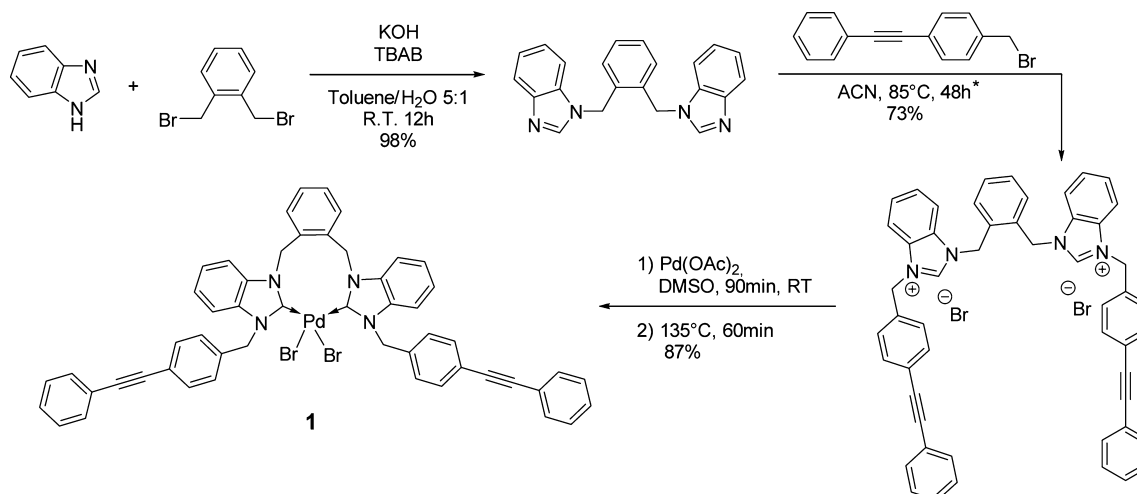
*The synthesis of 1-(bromomethyl)-4-(phenylethynyl)benzene was previously reported.[24]

stabilize Pd(0) species. In the case of homogeneous catalysis, many research groups reported very active catalysts in water.[7−9] However, only few have used the NHC approach for heterogeneous Suzuki−Miyaura coupling in water.[18−20] Of the few studies found in the literature for this type of compound, only a handful showed recyclability with moderate to good yields after a few catalytic runs (under phosphine-free and support-free conditions, as heterogeneous processes in water).[18] Nevertheless, it is common knowledge that N-heterocyclic carbenes are an effective choice of ligands to carry out such reactions since they can stabilize highly active organometallic species.[21,22]

Our group recently demonstrated the use of imidazolium-functionalized α-cyclodextrins as ligands for the Suzuki−Miyaura coupling in water.[23] We demonstrated that this method protects the active palladium species from the aqueous medium, thereby reducing its deactivation and making the whole process recyclable. Concurrent with this research, we also ventured into a different field, that is, heterogeneous catalysis.

Herein, we report the synthesis and characterization of a new heterogeneous air- and water-stable bidentate-NHC palladium complex for Suzuki−Miyaura coupling in water and assess its efficacy, efficiency, and recyclability. The process uses readily available substrates at a low cost, does not involve the use a solid support, and can be recycled up to 10 catalytic runs without any decrease in its activity.

RESULTS AND DISCUSSION

Synthesis and Characterization of the Bis-NHC Palladium Complex. The presence of N-heterocyclic carbene (NHC) precursors in the structure of the catalyst usually provides high stability to the compound.[25] Likewise, conjugated systems incorporated in the structure of the catalyst may also increase its overall stability.[26] It is known that the electron-rich nature of numerous π-systems promotes the oxidative addition of the carbon−halogen bond on the metal, which generally leads to better yields or reaction rates.[27−29] This last phenomenon has been enhanced with the use of electron-rich benzimidazole moieties rather than the most common imidazole units.[30] We hypothesized that the *ortho*-substituted aromatic unit would be the most effective spacer to obtain a

bidentate coordination complex with palladium. The choice of the phenylethynyl unit was made based on several considerations: first, it is less bulky around the catalytic site compared to the highly used mesityl group. Second, its rigidity ensures a steady approach of the substrates and prevents steric hindrance of the transition state. Third, its higher hydrophobicity ensures very low water solubility and thus the heterogeneity of the catalytic process.

The use of the benzimidazole moiety led to a simple and easy six-step synthesis of the bidentate palladium complex. The benzimidazolium salt was obtained without difficulty by the reaction of benzimidazole with the halogenated phenyl-ethynylbenzyl unit as shown in Scheme 1. The synthesized salt was then combined with Pd(OAc)$_2$ to give palladacycle **1** with an overall yield of 60%. This complex is air- and moisture-stable, both in the solid state and in solution. Palladacycle **1** is completely insoluble in water at any pH ranging from 1 to 12, a property that contributes to making it stable in this medium. It is also completely insoluble in diethyl ether, but can be easily solubilized in other common solvents such as dichloromethane, chloroform, and dimethylformamide.

The ligand has been fully characterized by elemental analysis, ^{1}H NMR, ^{13}C NMR, HRMS, and X-ray crystallography. The formation of the NHC complex was confirmed by the single resonance at 177.2 for NCN in the ^{13}C NMR spectrum and the absence of the singlet corresponding to the proton of the NC*H*N group of the imidazole ring in the ^{1}H NMR spectrum. Single crystals suitable for X-ray analysis were grown by crystallization from chloroform. The molecular structure of the palladium catalyst is shown in Figure 1, and the crystallographic data can be found in the Supporting Information.

Catalysis of the Suzuki−Miyaura Reaction. The reaction of *p*-bromoacetophenone with phenylboronic acid was carried out under different conditions using potassium carbonate as a base to confirm our cost effectiveness and green chemistry objectives. The study began with the catalyst loading optimization shown in Table 1 and showed very promising results. The high turnover number and frequency achieved with 10^{-3} mol % catalyst are excellent for the Suzuki−Miyaura coupling in neat water, and they are similar to other studies presenting Suzuki−Miyaura palladium species in water.[31]
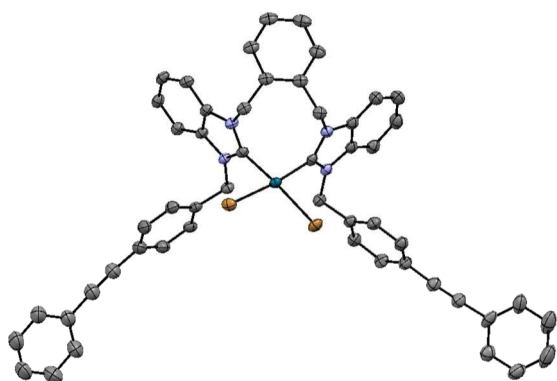
Figure 1. X-ray single-crystal structural analysis of the catalyst **1**. All hydrogen atoms and solvent molecules were omitted for clarity.

Table 1. Catalyst 1 Loading Optimization

entry	catalyst 1 loading (mol %)	reaction time (h)	isolated yield (%)	TON	TOF (s^{-1})
1	0.5	0.5	100	200	0.11
2	10^{-1}	0.5	100	1000	0.52
3	10^{-2}	0.5	100	7800	4.3
4	10^{-3}	0.5	28	22 000	12.2
5	10^{-3}	2	100	100 000	13.9
6	5×10^{-4}	2	42	84 000	11.7
7	5×10^{-4}	16	66	132 000	2.3
8	10^{-4}	2	<2		

All the reactions were carried under normal atmosphere, without degassing the water or using a cosolvent, therefore leading to the formation of small quantities of palladium black precipitate. The presence of this compound in the reaction mixture is the result of a common catalyst deactivation pathway that is known to occur to some extent in almost every reaction involving palladium species in water.[32] However, the presence of small amounts of palladium black in our reactions did not compromise the activity of the catalyst down to 10^{-3} mol %, even for the recycling experiments at 10^{-1} mol % (results presented further on). Nonetheless, degassing the aqueous medium with nitrogen prior to adding the reagents and reactants completely inhibited the formation of palladium black. Therefore, in cases where recycling could be harder, there is still the option to degas in order to enhance the lifetime of the catalyst. As the reaction using 10^{-3} mol % requires either the use of very low quantities of the catalyst or high quantities of reactants, all further tests were carried at 10^{-1} mol % catalyst, and we decided not to degas, for simplicity. We then performed a temperature dependence study on the same model reaction, which led to the conclusion that the Suzuki–Miyaura reaction can be carried out at lower temperatures with some substrates without any loss of activity (Table 2).

Next, the extent of the method was assessed by performing a substrate scope using commonly used aryl halides. Under optimized conditions (K_2CO_3, H_2O, 100 °C, 0.1 mol %), a

Table 2. Influence of the Temperature on the Activity of Catalyst 1

entry	temperature (°C)	yield (%)
1	23 (rt)	33
2	50	99
3	100	>99

number of aryl iodides and bromides have been successfully coupled with arylboronic acids. Table 3 shows the high versatility of the method, giving a moderate to high yield for many substrates with the exception of the less reactive chloride substrates, for which low yields were obtained, especially in the case of the substrates not containing activating functional groups. We believe that the reaction mechanism implies the use of the boronic acid as an activator, leading the PdX_2L_2 catalyst to a PdL_2 state and releasing negligible quantities of biphenyl. Neither this compound nor the homocoupling product was detected in any case.
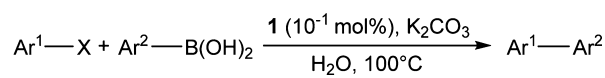
Catalyst **1** showed less reactivity toward bulkier aromatic substrates. It is common in these cases to raise the catalyst loadings,[33] and the results obtained when the catalyst loading was increased to 2 mol % were better in terms of yields (entry 17b). This confirms that the catalyst can be used even with such bulky substrates to some extent. This last result could lead to some specific applications where the catalyst's "immediate concentration" corresponds to a very high loading, such as in a flow chemistry system using a packed bed reactor.
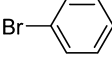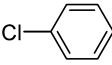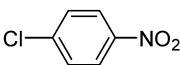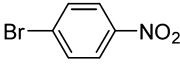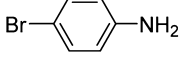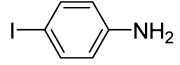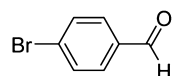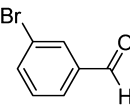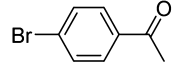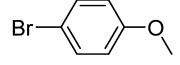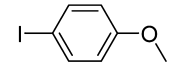
Recyclability. Recyclability has been assessed with the identified model reaction on a reaction time of 30 min. The latter experiment was performed up to 10 times in a row, with no detectable deactivation or leaching of the catalyst other than the appearance of a black precipitate that did not seem to affect subsequent runs at this loading. As shown in Table 4, the yield was still quantitative after 10 runs, which is currently higher than all the processes previously described. In addition, the simplicity of the method is another asset of catalyst **1**. Once the reaction was over, the mixture was cooled to room temperature, then extracted with diethyl ether in situ with a syringe, in order to prevent the loss of the catalytic species. Then 1 equiv of base, aryl halide, and boronic acid were added to the same aqueous phase for a subsequent catalytic run.

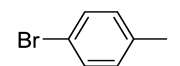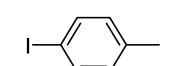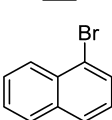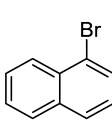Using the method previously described, the recycling experiments were also performed using 10^{-2} mol % of catalyst **1**. Unfortunately, the yield almost dropped by half after the first run. As a comparison, we investigated the impact of nitrogen degassing on the reuse of the catalyst. The results shown in Table 5 confirm that, even with a stable NHC ligand, dissolved gases may contribute to reduce the catalyst's lifetime. Moreover, a visual comparison test at 10^{-1} mol % catalyst showed the appearance of palladium black after one reaction in nondegassed water, while there was absolutely no visible trace of it in the degassed experiment.

Nature of the Active Species. As catalyst **1** seems to be totally water insoluble, we decided to investigate the nature of

**Table 3. Substrate Scope of Suzuki Cross-Coupling by Palladium Catalyst 1**

$$Ar^1\!-\!X + Ar^2\!-\!B(OH)_2 \xrightarrow[\text{H}_2\text{O, 100°C}]{\textbf{1 }(10^{-1}\text{ mol\%), K}_2\text{CO}_3} Ar^1\!-\!Ar^2$$

Entry	Ar-X	Time (h)	Isolated Yield (%)
1	I—⬡	0.5	>99
2	Br—⬡	0.5	>99
3	Cl—⬡	a - 0.5 b - 2	trace trace
4	Cl—⬡—NO₂	a - 0.5 b - 2	22% 31%
5	Br—⬡—NO₂	0.5	68
6	Br—⬡—NH₂	a - 0.5 b - 2	75 >99
7	I—⬡—NH₂	a - 0.5 b - 2	20 11
8	Br—⬡—CHO	0.5	>99
9	(3-Br benzaldehyde)	a - 0.5 b - 2	92 >99
10	Br—⬡—C(O)CH₃	0.5	>99
11	Br—⬡—O	a - 0.5 b - 2	75 94
12	I—⬡—O	a - 0.5 b - 2	85 87
13	Br—⬡—	a - 0.5 b - 2	71 92
14	I—⬡—	a - 0.5 b - 2	98 >99
15	(1-Br naphthalene)	a - 0.5 b - 2	35 46
16[a]	(1-Br naphthalene) and Naphthalene boronic acid	2 2[b]	33 55

[a]Using naphthaleneboronic acid instead of phenylboronic acid. [b]Using 2 mol % of catalyst **1**.

the active catalytic species in this coupling reaction and to assess the heterogeneity of the process. Several tests were performed and suggest a heterogeneous catalytic reaction.[34] First, the mercury drop test leads to the amalgamation of mercury on the surface of the nonsoluble catalyst, inhibiting
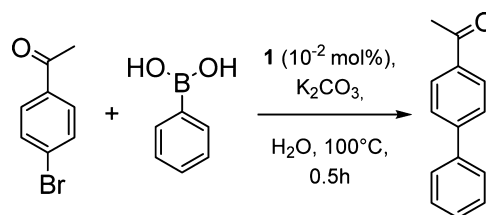
Table 4. Recyclability of Catalyst 1 for Suzuki−Miyaura Coupling in Water
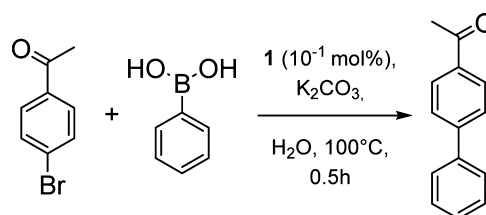
run	yield (%)[a]	TON	TOF (s⁻¹)
1	>99	1000	0.56
2	>99	1000	0.56
3	>99	1000	0.56
4	>99	1000	0.56
5	>99	1000	0.56
6	>99	1000	0.56
7	>99	1000	0.56
8	>99	1000	0.56
9	>99	1000	0.56
10	98	1000	0.56
cumulative TON:		10 000	

[a]Followed by ¹H NMR. A final isolated yield of 99% was obtained when combining the product from all 10 runs.

Table 5. Recyclability of Catalyst 1 at Lower Loadings for Suzuki−Miyaura Coupling in Water

| run	yield (%) no N₂ degassing	yield (%) with N₂ degassing[a]
1	100	100
2	57	100
3	42	99
4	32	50
5	29	43

[a]Degassing was made for 10 min prior to each catalytic run.

completely its activity. On the other hand, if the catalyst is soluble, the mercury drop test has no effect at all on the activity of the catalyst.[35,36] In our case, when a drop of mercury was added to the reaction mixture before starting the model reaction, no catalytic activity was observed.

On the basis of the fact that the surface of a heterogeneous catalyst contains a limited number of active metal atoms, strong poisons used in substoichiometric amounts may be sufficient to prevent entirely its catalytic activity. Commonly used ligands for such reactions are CS₂ and PPh₃. When poisoning catalyst **1** with these additives at less than 1.0 equiv per metal atom, no significant activity was noted, which leads to the early conclusion that **1** is acting as a heterogeneous catalyst. It should be noted that the experiment using carbon disulfide was performed at 45 °C because this ligand dissociates from the palladium species at temperatures greater than 50 °C. This change in temperature should not have altered the results, as it was proven earlier that our model reaction normally leads to a quantitative yield at 50 °C.

However, there was still the possibility that the active species was not the desired palladacycle, but could have been soluble-metal-particle heterogeneous catalysis. Indeed, using similar catalysts under similar conditions, SanMartin, Domínguez, et al. have stated that palladium−NHC complexes may sometimes serve as mere Pd(0) reservoirs, leaking palladium atoms that self-assemble into nanoparticles.[31] However, the poisoning results or our experiments state otherwise in the case of this heterogeneous catalyst. In order to shed light on the nature of the active species, a comparison test using pyridine and poly(4-vinylpyridine) polymer has been carried in order to detect the formation of palladium nanoparticles while using water-soluble pyridine and water-insoluble poly(4-vinylpyridine).[36] As a matter of fact, both nitrogen ligands should bind easily to palladium, but the insoluble polymer would additionally remove metallic particles from the reaction medium, further deactivating the catalyst, if it were homogeneous, by preventing its contact with the reagents. Therefore, if one identifies a large difference between these two experiments, the active species are Pd(0) nanoparticles. If the catalyst is the starting palladacycle, then no major difference should be observed between both experiments, as the binding mechanism is the same (e.g., replacement of the bromide ligand). As shown in Table 6, the results obtained for catalyst **1** with pyridine (25%) and poly(4-vinylpyridine) (13%) are very similar, indicating a palladacycle-driven mechanism.

Table 6. Poisoning Experiments of Catalyst 1
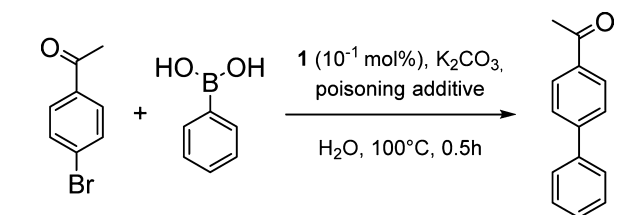
entry	poisoning additive	yield (%)
1[a]	Hg	0
2[b]	CS_2	0
3[c]	PPh_3	5
4[d]	pyridine	25
5[e]	poly(4-vinylpyridine)	13

[a]One drop of Hg. [b]0.5 equiv of CS_2 (per metal atom), reaction ran at 45 °C. [c]0.3 equiv of PPh_3 (per metal atom). [d]150 equiv of pyridine (per metal atom). [e]150 equiv of poly(4-vinylpyridine) (per metal atom), quantity calculated using the monomer's molecular weight.

CONCLUSION

We have successfully demonstrated that a heterogeneous NHC-based palladium species is a good alternative catalyst to what is currently used for Suzuki−Miyaura couplings in water. Its high stability and activity led to convincing results, with quantitative activity toward a wide variety of substrates using catalyst loadings as low as 10^{-3} mol %. To the best of our knowledge, the recyclability of this process is yet unmatched by any other phosphine-free, heterogeneous, and support-free NHC-Pd complex performing Suzuki−Miyaura coupling in water. The high recyclability and the low catalyst loadings used contribute to the overall atom economy that makes this process greener than many other previously reported processes. Additionally, the mild conditions, low-cost reagents, and simple manipu-

lations that do not require either cosolvent or dry environment increase the interest in this research. When compared to the literature, our poisoning experiment results raise a question on the intrinsic parameters in the catalyst's structure that affect the leading mechanistic pathway of this reaction in water.[31] As an early hypothesis, we suggest that while water-soluble NHC-palladacycles could act as reservoirs of palladium nanoparticles, their insoluble counterparts seem to be the active species themselves. Work is currently in progress to use the same catalyst for different carbon−carbon coupling reactions such as Heck coupling, in water.

EXPERIMENTAL SECTION

NMR spectra were recorded on 400 and 300 MHz spectrometers. [1]H and ^{13}C chemical shifts (δ) are given in ppm (residual peak of deuterated solvents was used as reference). The single crystals suitable for X-ray analysis were sealed into a glass capillary, and the intensity data of the single crystal were collected. High-resolution mass spectra (HRMS) were recorded on an LC-MSD-Tof spectrometer in positive electrospray mode.

Synthesis of the Palladium Complex. *α,α′-Bis(benzimidazole)-o-xylene.* To 2 mL of an aqueous solution of KOH (17.8 M, 2 g of dry KOH) were added benzimidazole (1.1000 g, 9.3100 mmol, 2 equiv) and tetrabutylammonium bromide (TBAB) (120 mg, 0.3249 mmol, 0.07 equiv). Then 10 mL of toluene was added to the mixture, which was then vigorously stirred for 5 min. *α,α′-Dibromo-o-xylene* (1.2289 g, 4.6555 mmol, 1 equiv) was added to the solution, which was kept under vigorous stirring overnight. The toluene was evaporated under reduced pressure, and the product was recovered and rinsed with 100 mL of distilled water. The white powder was recuperated and dried under vacuum to give 1.5440 g of *α,α′-bis(benzimidazole)-o-xylene* (yield = 98%). ^{1}H NMR (CDCl₃, 300 MHz): δ 7.87 (m, 1H), 7.85 (m, 1H), 7.79 (s, 2H), 7.36 (m, 2H), 7.33 (d, 1H, J < 3Hz), 7.30 (d, 1H, J < 3 Hz), 7.26 (td, 2H, J_1 = 9 Hz, J_2 < 3 Hz), 7.16 (m, 1H), 7.13 (m, 1H), 7.09 (m, 2H), 5.32 (s, 4H). ^{13}C NMR (75 MHz, CDCl₃): δ 143.9, 142.8, 133.8, 133.0, 129.1, 123.5, 122.7, 120.8, 109.7, 46.3. HRMS (ESI): calcd for $C_{22}H_{19}N_4^+$ [M + H]⁺ 339.160 97, found 339.161 70.

Precursor Salt. *α,α′-Bis(benzimidazole)-o-xylene* (1.5440 g, 4.5625 mmol, 1 equiv) and 4-(phenylethynyl)benzyl) bromide (2.5980 g, 9.5813 mmol, 2.1 equiv) were placed in 100 mL of acetonitrile. The mixture was heated to 85 °C and kept at this temperature under agitation for 48 h. The precipitate was filtered and rinsed with 2 × 30 mL of acetonitrile. The yellow-white powder was dried under vacuum to give 2.9333 g of the precursor salt (yield = 73%). ^{1}H NMR (DMSO-d₆, 300 MHz): δ 9.96 (s, 2H), 7.97 (m, 4H), 7.69 (m, 4H), 7.61 (s, 8H), 7.53 (m, 4H), 7.44 (m, 8H), 7.26 (m, 2H), 6.07 (s, 4H), 5.85 (s, 4H). ^{13}C NMR (CDCl₃, 100 MHz): δ 143.6, 134.9, 132.4, 131.9, 131.6, 129.9, 129.5, 129.3, 129.2, 127.5, 127.4, 123.1, 122.4, 114.5, 90.6, 89.1, 65.4. HRMS (ESI): calcd for $C_{52}H_{40}N_4^{2+}$ [M + H]²⁺ 360.162 10, found 360.163 41.

NHC-Pd Complex 1. Palladium acetate (0.2114 g, 0.2400 mmol, 1 equiv) was dissolved in 50 mL of dimethyl sulfoxide. The precursor salt (0.0539 g, 0.2400 mmol, 1 equiv) was dissolved in an additional 50 mL of dimethyl sulfoxide. Both solutions were mixed and then stirred at room temperature for 90 min. The mixture was then heated to 135 °C for an additional 60 min. The solvent was evaporated under reduced pressure at high temperature. The resulting powder was then triturated with 20 mL of methanol, rinsed with 2 × 20 mL of methanol, and rinsed again with 2 × 20 mL of acetonitrile. After drying under vacuum, 0.2057 g of a whitish-yellow powder was obtained (yield = 87%). Anal. Calcd for $C_{52}H_{38}Br_2N_4Pd$: C, 63.40; H, 3.89; Br, 16.22; N, 5.69; Pd, 10.8. Found: C, 59.54; H, 3.92; N, 5.33; S, 1.36. ^{1}H NMR (CDCl₃, 400 MHz): δ 8.05 (br s, 2H), 7.88 (d, 2H, J = 8 Hz), 7.60 (br s, 2H), 7.53 (s, 4H), 7.36 (m, 15H), 7.08 (t, 5H, J = 6 Hz), 6.83 (d, 2H, J = 8 Hz), 6.19 (d, 2H, J = 16 Hz), 5.53 (d, 2H, J = 12 Hz), 5.38 (d, 2H, J = 16 Hz). ^{13}C NMR (CDCl₃, 100 MHz): δ 177.11, 134.82, 134.49, 134.31, 134.24, 134.01, 132.04, 131.61, 129.91, 128.48,

128.37, 127.16, 123.83, 123.29, 122.86, 112.11, 111.66, 90.24, 88.55, 52.70, 52.09. HRMS (ESI): m/z calcd for $C_{52}H_{38}Br_2N_4Pd^+$ $[M + Na]^+$ 1005.039 03, found 1005.040 71.

Typical Procedure for Coupling Reactions of Aryl Halides with Boronic Acids. All manipulations were performed in water, under normal atmosphere, using vials in a Chemglass Pie-Block system. No degassing was made prior to any reaction unless stated otherwise.

1-Bromo-4-acetophenone (0.1874 g, 1.0130 mmol, 1 equiv), phenylboronic acid (0.1359 g, 1.1143 mmol, 1.1 equiv), K_2CO_3 (0.2800 g, 2.0260 mmol, 2 equiv), and **1** (1.0 mg, 0.0010 mmol, 0.001 equiv) were mixed in 10 mL of distilled water. The vial was placed in the heated pie-block at 100 °C for 30 min under vigorous agitation. The reaction mixture was then cooled in an ice bath and extracted three times with 10 mL of diethyl ether. The combined organic layers were then dried with anhydrous $MgSO_4$ and evaporated under reduced pressure, leading to 0.199 g of a white powder (yield = 100%).

Recycling Procedure. Typical procedure for Suzuki coupling reaction was performed as mentioned above. The extractions were made in situ in the vial using a 12 mL syringe with a flat end needle to collect the organic layers. K_2CO_3 (0.1400 g, 1.0130 mmol, 1 equiv), 1-bromo-4-acetophenone (0.1874 g, 1.0130 mmol, 1 equiv), and phenylboronic acid (0.1235 g, 1.0130 mmol, 1 equiv) were then added to the aqueous phase, and the same manipulations were repeated 10 times. Degassing with nitrogen was done for 10 min between each catalytic run for results in Table 6.

Poisoning Experiments. Typical procedure for Suzuki coupling reaction was performed as mentioned above. The poisoning additive was added to the mixture prior to the reactants.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed synthesis of **1**, detailed experimental section, NMR spectra, and crystallographic data (tables, figure, and raw data). This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: ar.schmitzer@umontreal.ca.

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) Franzén, R.; Xu, Y. *Can. J. Chem.* **2005**, *83*, 266.
(2) Shaughnessy, K. H.; DeVasher, R. B. *Curr. Org. Chem.* **2005**, *9*, 595.
(3) Selander, N.; Szabó, K. J. *Chem. Rev.* **2011**, *111*, 2048−2076.
(4) Shaughnessy, K. H., Chapter 1: Metal-Catalyzed Cross-Couplings of Aryl Halides to Form C-C Bonds in Aqueous Media. In *Metal-Catalyzed Reactions in Water*; Dixneuf, P. H., Cadierno, V., Ed.; Wiley-VCH, 2013; p 426.
(5) Iwasawa, T.; Tokunaga, M.; Obora, Y.; Tsuji, Y. *J. Am. Chem. Soc.* **2004**, *126*, 6554−6555.
(6) Steinhoff, B. A.; Stahl, S. S. *Org. Lett.* **2002**, *4*, 4179−4181.
(7) Fleckenstein, C.; Roy, S.; Leuthäuβer, S.; Plenio, H. *Chem. Commun.* **2007**, 2870−2872.
(8) Roy, S.; Plenio, H. *Adv. Synth. Catal.* **2010**, 1014.
(9) Rajabi, F.; Thiel, W. R. *Adv. Synth. Catal.* **2014**, 1873.
(10) Anastas, P. T., Warner, J. C. *Green Chemistry: Theory and Practice*; Oxford University Press: New York, 1998; p 30.
(11) Yakusawa, T.; Miyamura, H.; Kobayashi, S. *Chem. Soc. Rev.* **2014**, *43*, 1450.
(12) Wall, V. M.; Eisenstadt, A.; Ager, D. J.; Laneman, S. A. *Platinum Met. Rev.* **1999**, *43*, 138.
(13) Ennis, D. S.; Mcmanus, J.; Woor-Kaczmar, W.; Richardson, J.; Smith, G. E.; Carstais, A. *Org. Process Res. Dev.* **1999**, *3*, 248.
(14) Djakovitch, L.; Wagner, M.; Hartung, C. G.; Beller, M.; Koehler, K. *J. Mol. Catal. A: Chem.* **2004**, *219*, 121.
(15) Heidenreich, R. G.; Krauter, J. G. E.; Pietsch, J.; Köhler, K. *J. Mol. Catal. A: Chem.* **2002**, *182*, 499.
(16) Karimi, B.; Akhavan, P. F. *Inorg. Chem.* **2011**, *50*, 6063−6072.
(17) Cano, R.; Ramón, D. J.; Yus, M. *Tetrahedron* **2011**, *67*, 5432.
(18) Turkmen, H.; Can, R.; Cetinkaya, B. *Dalton Trans.* **2009**, 7039.
(19) Han, Y.; Lee, L. J.; Huynh, H. V. *Organometallics* **2009**, *28*, 2278.
(20) Ines, B.; SanMartin, R.; Churraca, F.; Dominguez, E.; Urtiaga, M. K.; Arriortua, M. I. *Organometallics* **2008**, *27*, 2833.
(21) Regitz, M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 725.
(22) Weskamp, T.; Böcher, V. P. W.; Herrmann, W. A. *J. Organomet. Chem.* **2000**, *600*, 12.
(23) Kairouz, V.; Schmitzer, A. R. *Green Chem.* **2014**, *16*, 3117.
(24) Elie, C.-R.; Noujeim, N.; Pardin, C.; Schmitzer, A. R. *Chem. Commun.* **2011**, *47*, 1788.
(25) Godoy, F.; Segarra, C.; Poyatos, M.; Peris, E. *Organometallics* **2011**, *30*, 684−688.
(26) Howell, T. O.; Huckaba, A. J.; Hollis, T. K. *Org. Lett.* **2014**, *16*, 2570−2572.
(27) Carrow, B. P. *Mechanistic Studies on Palladium-Catalyzed Coupling Reactions*; University of Illinois, 2011.
(28) Portnoy, M.; Milstein, D. *Organometallics* **1993**, *12*, 1665−1673.
(29) Barder, T. E.; Walker, S. D.; Martinelli, J. R.; Buchwald, S. L. *J. Am. Chem. Soc.* **2005**, *127*, 4685−4696.
(30) Yuan, D.; Teng, Q.; Huynh, H. V. *Organometallics* **2014**, *33*, 1794−1800.
(31) Inés, B.; SanMartin, R.; Moure, M. J.; Dominguez, E. *Adv. Synth. Catal.* **2009**, *351*, 2124−2132.
(32) Phan, T. S.; Van Der Sluys, M.; Jones, C. W. *Adv. Synth. Catal.* **2006**, *348*, 609.
(33) Debono, N.; Labande, A.; Manoury, E.; Daran, J.-C.; Poli, R. *Organometallics* **2010**, *29*, 1879.
(34) Widegren, R. G.; Finke, R. G. *J. Mol. Catal. A: Chem.* **2003**, *198*, 317.
(35) Eberhard, M. R. *Org. Lett.* **2004**, *6*, 2125.
(36) Yu, K.; Sommer, W.; Richardson, J. M.; Week, M.; Jones, C. W. *Adv. Synth. Catal.* **2001**, 161.