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Polymer-Supported *N*-Heterocyclic Carbene−Palladium Complex for Heterogeneous Suzuki Cross-Coupling Reaction

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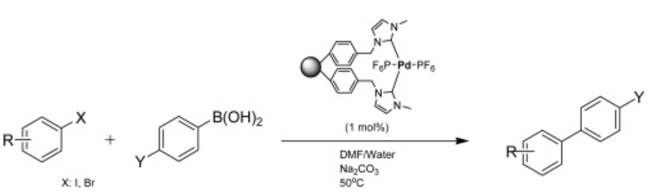

Poly(1-methylimidazoliummethyl styrene)-*surface grafted*-poly(styrene) resin was prepared for the first time as a polymer-supported *N*-heterocyclic carbene (NHC) precursor for palladium complex by suspension polymerization. To prepare this polymer-supported NHC precursor, 1-methyl-3-(4-vinylbenzyl)imidazolium hexafluorophosphate, [MVBIM][PF_6^-], was synthesized as a monomer and copolymerized with styrene and DVB in water. This polymer-supported NHC precursor with imidazolium as a ligand, which exists solely on the surface of the resin, was well characterized by FE-SEM, CLSM, and IR spectroscopy. The precursor containing imidazolium readily formed a stable complex with Pd(OAc)$_2$, and this polymer-supported *N*-heterocyclic carbene−palladium complex exhibited excellent catalytic activity for Suzuki cross-coupling reaction in an aqueous medium. The catalyst was recovered quantitatively from the reaction mixture by simple filtration and was able to be reused for a number of recycles with consistent activity in all of the coupling reactions.

Introduction

N-Heterocyclic carbenes (NHCs) have garnered a great deal of interest as transition metal ligands in the area of organic and inorganic chemistry since they were first discovered by Öfele and Wanzlick[1] in the late 1960s. These NHCs have the same σ-donor and exhibit a low π-acceptor ability as phosphine in terms of their metal coordination chemistry.[2] Recently, the NHC ligands have turned out to have an excellent air and moisture stability and dissociation energies quantified by theoretical calculations for different metals[3] higher than those of other ligands. Therefore, they have been applied to many organic reactions, utilizing the transition metal catalysts as efficient ligands.

There have been many successful demonstrations of homogeneous catalysis using NHCs as ligands for transition metals such as palladium,[4] ruthenium,[5] rhodium,[6] and nickel.[7] However, these homogeneous catalyst systems have some basic problems in terms of the separation and recycling of the catalysts. Additionally, they induce contamination of the ligand residue in the products.

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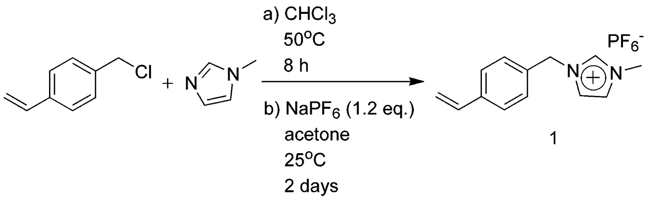
Therefore, the development of polymer-supported and insoluble transition metal catalysts has attracted a great deal of attention in organic chemistry. This heterogeneous catalysis system has several advantages, such as fast recovery and the simple recycling of the catalysts by filtration, which in turn prevents the contamination of the ligand and decreases the environmental pollution caused by residual metals in the waste. Several kinds of supported NHC−transition metal complexes have been designed, so as to combine the advantages of both homogeneous and heterogeneous catalysts. For example, Herrmann's group synthesized an NHC−palladium complex in solution and then immobilized it on Wang resin, which was used in Heck coupling reaction.[8] Blechert's group reported a polymer-supported olefin metathesis catalyst.[9] In this case, they built up the polymer-anchored ligand precursor and then treated it with a metal compound. The monolithic system, which was functionalized by living NHC−ruthenium termini, was prepared by Buchmeister's group for ring-closing and ring-opening metathesis reactions.[10] Very recently, we also reported that the NHC−Pd catalyst, which was immobilized onto Merrifield resin, exhibited excellent catalytic activity in Suzuki reaction.[11] However, all of the previously reported polymer-supported catalysts have their catalytic active sites in the entire regions of the supports, which makes it difficult for the reagents to diffuse into the interior of the supports and eventually decreases the reaction rate and catalytic activity. If the catalytic active sites were located at the surface of the resin, all of the chemical reactions would be more effective.[12]

In this article, we describe the development of a polymer-supported NHC precursor prepared by suspension polymerization, the development of its palladium complex, which has the catalytic active sites located only on the surface of the polymer, and the application of the palladium complex to heterogeneous Suzuki cross-coupling reaction in an aqueous phase. When the heterogeneous catalytic system is applied to Suzuki reaction, the reaction proceeds very rapidly and affords excellent yields owing to the existence of the catalyst on the surface of the resin beads. This polymer-supported NHC−palladium catalyst shows outstanding reusability without the loss of its catalytic activity.

SCHEME 1. Synthesis of the Polymerizable Ionic Liquid Monomer (1), [MVBIM][PF$_6$−]



Results and Discussion

Preparation of Poly(1-methylimidazoliummethyl styrene)-*sg*-PS Resin. (a) Synthesis of the Polymerizable Ionic Liquid Monomer (1). As shown in Scheme 1, to prepare poly(1-methylimidazoliummethyl styrene)-*sg*-PS resin by suspension polymerization, where *sg* denotes surface grafted, 1-methyl-3-(4-vinylbenzyl)imidazolium hexafluorophosphate (**1**), [MVBIM][PF$_6^-$], was first synthesized as a monomer, which plays the role of a carbene ligand. To accomplish this, 1-methylimidazole was dissolved in CHCl$_3$ and reacted with 4-chloromethyl styrene. After the reaction was completed, the resulting 1-methyl-3-(4-vinylbenzyl)imidazolium chloride, [MVBIM][Cl$^-$], was obtained in 98% yield. [MVBIM][Cl$^-$] was dissolved in acetone, and NaPF$_6$ was added to replace Cl$^-$ with PF$_6^-$. The final [MVBIM][PF$_6^-$] monomer (**1**) was synthesized in 97% yield. This ionic liquid monomer was not only insoluble in the aqueous phase, but also in the styrene phase, and consequently, it was located at the interface between the aqueous phase and the organic phase in the suspension polymerization system.

(b) Suspension Polymerization. Poly(1-methylimidazoliummethyl styrene)-*sg*-PS resin was prepared by utilizing a conventional suspension polymerization system with a reactor and an overhead stirrer, as shown in Scheme 2. The synthetic ionic liquid monomer was suspended in an aqueous phase. The organic phase consisted of styrene, DVB, and benzoyl peroxide as an initiator, and this was added to the aqueous phase with a constant stirring (250 rpm) under a nitrogen atmosphere. After the completion of the polymerization, spherical particles with a white color were obtained.

The polymer-supported NHC precursor, poly(1-methylimidazoliummethyl styrene)-*sg*-PS resin, was analyzed by an elemental analyzer to quantify the amount of imidazolium groups on the beads by measuring the nitrogen content. The loading level of the imidazolium groups was 0.23 mmol/g when 3 g of the ionic liquid monomer and 7 mL of styrene were used. This loading level could be adjusted by changing the amount of ionic liquid monomer.

Characterization of Poly(1-methylimidazoliummethyl Styrene)-*sg*-PS Resin with Scanning Electron Microscopy (SEM) and Confocal Laser Scanning Microscopy (CLSM). As shown in Figure 1, all of the resins were the bead types with a special shape and a diameter of ~38−150 μm. The fluorescent dye, 5(6)-carboxytetramethyl rhodamine, was adsorbed by the beads. These fluorescent dye-adsorbed beads were visualized by CLSM to confirm the location of imidazolium, which plays the role of the carbene precursor on the beads. As shown in the CLSM image, all of the red

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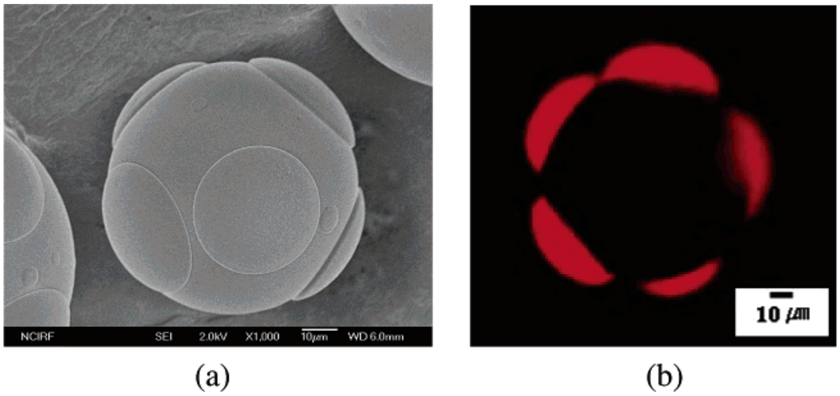
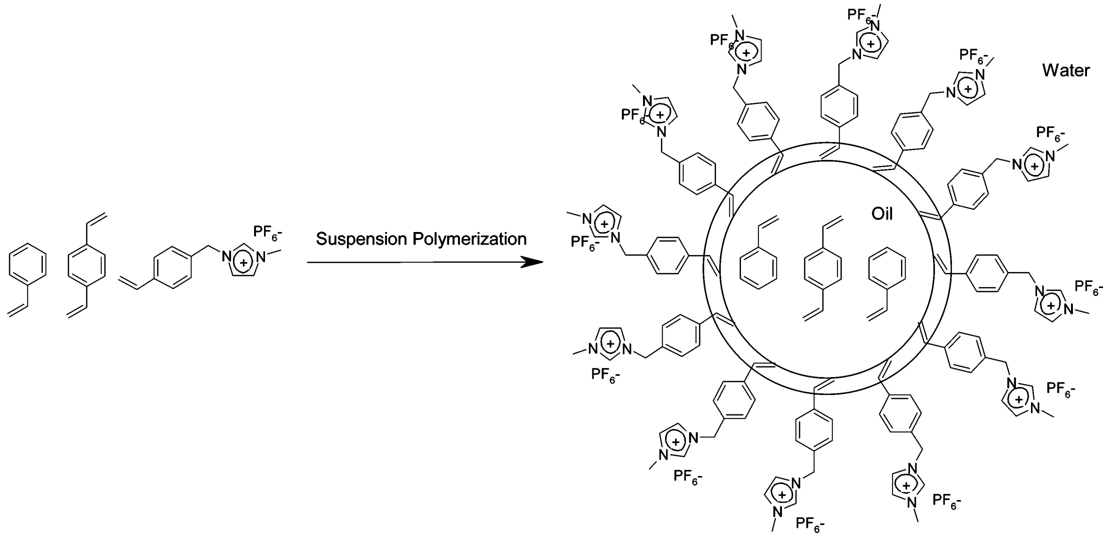


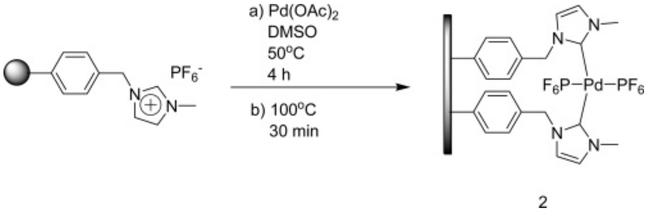
(a) (b)

FIGURE 1. (a) SEM image of the poly(1-methylimidazoliummethyl styrene)-*sg*-PS resin. (b) CLSM image of the 5(6)-carboxytetramethyl rhodamine-adsorbed poly(1-methylimidazoliummethyl styrene)-*sg*-PS resin.

SCHEME 2. Suspension Polymerization for the Preparation of the Poly(1-methylimidazoliummethyl styrene)-*sg*-PS Resin



SCHEME 3. Preparation of the Polymer-Supported NHC−Palladium Complex (2)



colored imidazolium groups, which resemble islands, were located on the surface of the beads (Figure 1b).

Preparation of Polymer-Supported NHC−Palladium Complex (2). As shown in Scheme 3, a mixture of the polymer-supported NHC precursor and $Pd(OAc)_2$ was shaken in DMSO at 50 °C for 4 h, and then the temperature was increased to 100 °C.[13] The reaction was then allowed to proceed for a further 30 min at 100 °C, leading to the production of beads with a dark green color. Various amounts of $Pd(OAc)_2$ were used to determine the optimal loading of immobilized palladium, as shown in Table 1.

TABLE 1. Loading Levels of the Immobilized Pd on the Resin[a]

amount of $Pd(OAc)_2$ (μmol)	23 (1 equiv)	46 (2 equiv)	92 (4 equiv)
loading level of Pd (mmol/g)[b]	0.017	0.03	0.11

[a] The initial loading capacity of imidazolium on the beads was 0.23 mmol/g. [b] The loading levels of palladium on the beads were calculated by ICP-AES.

Characterization of Polymer-Supported NHC−Palladium Complex (2). (a) Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES). The polymer-supported NHC−palladium complex (**2**) with a dark green color was analyzed by ICP-AES to quantify the amount of palladium immobilized on the beads. The loading level of the palladium on the beads was 0.11 mmol/g when a 4-fold excess amount of $Pd(OAc)_2$ was used, as shown in Table 1. We concluded that almost all of the imidazolium groups (0.23 mmol/g) on the surface of the beads participated in the formation of the Pd−NHC complex.

(b) Energy Dispersive X-ray (EDX) and Infrared Spectroscopy. After immobilizing the palladium, the polymer-supported NHC−palladium complex (**2**) was

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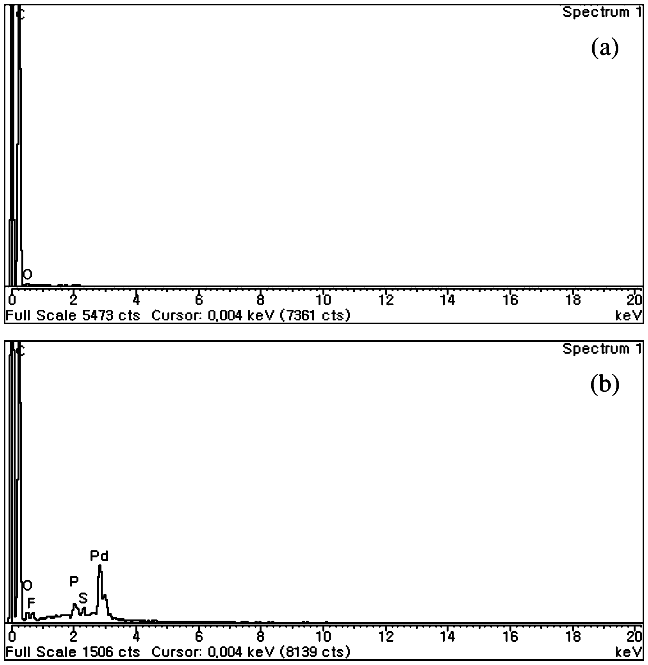


FIGURE 2. (a) EDX spectrum for the PS region in the polymer-supported NHC−palladium complex (**2**). (b) EDX spectrum for the imidazolium region in the polymer-supported NHC−palladium complex (**2**).

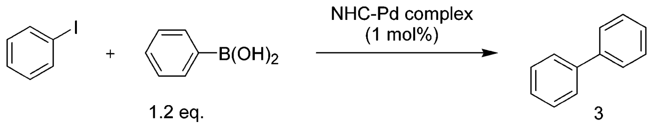
TABLE 2. Heterogeneous Suzuki Cross-Coupling Reaction of Ph−I and Ph−B(OH)$_2$[a]

entry	solvent	base	T (°C)	t (h)	yield[b] (%)
1	DMF/water (1:1)	Na_2CO_3	50	1	95
2	dioxane/water (1:1)	Na_2CO_3	50	1	94
3	THF/water (1:1)	Na_2CO_3	50	1	72
4	DMF/water (1:3)	Na_2CO_3	50	2	94
5	DMF/water (1:7)	Na_2CO_3	50	3	94
6	water	Na_2CO_3	50	3	20
7	water	Na_2CO_3	50	12	36
8	water	Cs_2CO_3	50	12	45
9	water	KO^tBu	50	12	−

[a] Iodobenzene (0.5 mmol), phenylboronic acid (0.6 mmol), NHC−Pd (1 mol %), and bases (2.5 mmol). [b] Isolated by column chromatography.

analyzed by EDX to ascertain whether palladium binds specifically to the ligand or not. According to the results of the EDX spectra shown in Figure 2, palladium was only present in the imidazolium region (Figure 2b), and no palladium was detected in the PS region (Figure 2a). We concluded that the palladium was immobilized specifically to the carbene ligand on the surface of the beads. Considering the results of the ICP-AES and EDX observations, we were able to indirectly determine the structure of the polymer-supported NHC−palladium complex (**2**). Additionally, we also confirmed that palladium was immobilized specifically at the C2 position of the imidazolium on the bead with IR spectroscopy. Before immobilization of palladium, the strong band of quaternary imidazolium on the bead appeared at 1157 cm^{-1} in the IR spectrum.[14] However, it disappeared, and the band of alkene at 1665 cm^{-1} became stronger after immobilization of palladium.

SCHEME 4. Heterogeneous Suzuki Cross-Coupling Reaction of Ph−I and Ph−B(OH)$_2$



SCHEME 5. Reusability of the Polymer-Supported NHC−Pd Complex in Suzuki Cross-Coupling Reaction

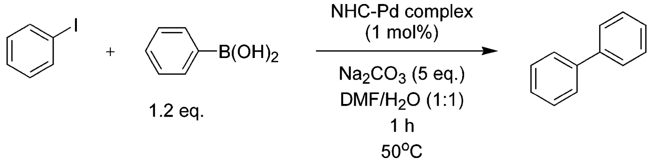


TABLE 3. Reusability of the Polymer-Supported NHC−Pd Complex in Suzuki Cross-Coupling Reaction[a]

recycle	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th
yield (%)[b]	95	95	94	93	95	94	95	94	94	92

[a] Iodobenzene (0.5 mmol), phenylboronic acid (0.6 mmol), NHC−Pd (1 mol %), Na_2CO_3 (2.5 mmol), and DMF/H_2O (1:1), 50 °C and 1 h. [b] Isolated by column chromatography.

Heterogeneous Suzuki Cross-Coupling Reaction. (a) Catalytic Activity of Polymer-Supported NHC−Palladium Complex (2). The catalytic activity of the polymer-supported NHC−palladium catalyst (**2**) with a palladium loading of 0.11 mmol/g was investigated in the palladium-catalyzed Suzuki reaction, as shown in Table 2. First, several solvents were examined by using the polymer-supported NHC−Pd catalyst (1 mol %) in the reaction of iodobenzene and phenylboronic acid as a model reaction. Biphenyl was obtained with an excellent yield in both DMF/water (1:1) and dioxane/water (1:1) (95 and 94%, respectively; Table 2, entries 1 and 2). In addition, the reaction rate was so fast that most of the iodobenzene was converted into biphenyl within l h at 50 °C, which was quite different from the previous results.[15] Comparing to the results of other polystyrene-based polymer bead derived from Merrifield resin,[15c] which has imidazolium group in the whole region of the bead, this high reaction rate might be due to the distinctive feature of the catalyst, in that all of the catalytically active sites were located on the surface of the beads, which means that the reagents do not need to diffuse into the interior of the beads. Moreover, the local concentration of the reagents was higher in the catalytically active species on the surface of the beads, and this may have promoted the rapid reaction.

Recently, water has received much attention as a solvent in organic reactions,[16] because it is readily available and environmentally safe. Hence, we decreased the amount of organic solvents in heterogeneous Suzuki reaction. Even the reaction in mixtures of DMF and water with ratios of 1:3 and 1:7 gave biphenyl in excellent

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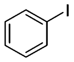
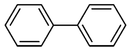
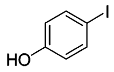
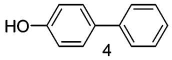
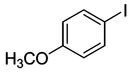
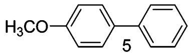
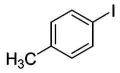
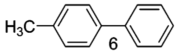
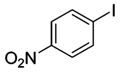
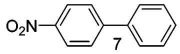
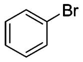
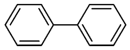
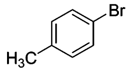
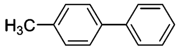
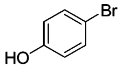
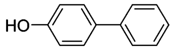
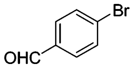
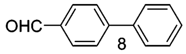
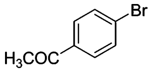
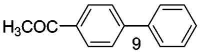
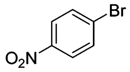
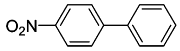
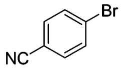
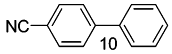
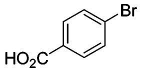
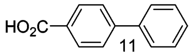
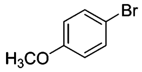
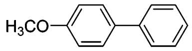
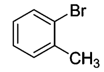
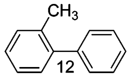
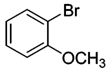
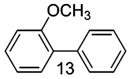
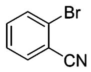
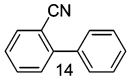
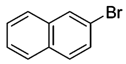
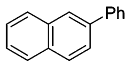
TABLE 4. Heterogeneous Suzuki Cross-Coupling Reaction of Aryl Iodides and Bromides with Phenyl Boronic Acid[a]

Entry	Aryl halides	Product	Time (h)	Yield (%)[b]
1			1	95
2		 4	1	95
3		 5	1	94
4		 6	1	94
5		 7	1	97
6			6	95
7			6	93
8			6	92
9		 8	6	94
10		 9	6	96
11			6	94
12		 10	6	96
13		 11	6	94
14			6	95
15		 12	6	92
16		 13	6	91
17		 14	6	93
18		 15	6	96

[a] Aryl halides (0.5 mmol), phenylboronic acid (0.6 mmol), NHC−Pd (1 mol %), Na_2CO_3 (2.5 mmol), and DMF/H_2O (1:1), 50 °C. [b] Isolated by column chromatography.

SCHEME 6. Heterogeneous Suzuki Cross-Coupling Reaction of Aryl Iodides and Bromides with Phenyl Boronic Acid

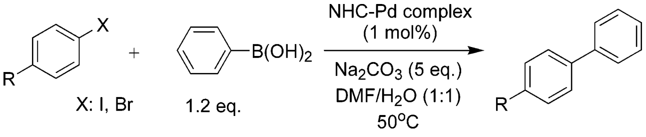
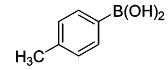
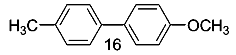
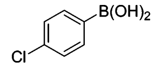
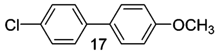
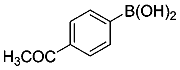
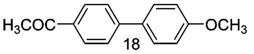
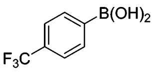
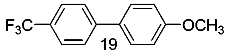
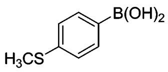
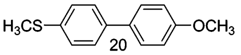
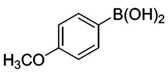
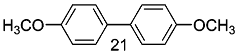


TABLE 5. Heterogeneous Suzuki Cross-Coupling Reaction of Arylboronic Acids with 4-Iodoanisole[a]

Entry	Arylboronic acid	Product	Time (h)	Yield (%)[b]
1		 16	1	94
2		 17	1	95
3		 18	1	93
4		 19	1	93
5		 20	1.5	94
6		 21	1	95

[a] 4-Iodoanisole (0.5 mmol), arylboronic acid (0.6 mmol), NHC−Pd (1 mol %), Na_2CO_3 (2.5 mmol), and DMF/H_2O (1:1), 50 °C. [b] Isolated by column chromatography.

yields (Table 2, entries 4 and 5), which is appropriate for an industrial application. However, biphenyl was obtained in low yield in water only, because of the poor solubility of iodobenzene in water. Using Na_2CO_3 as a base gave a good yield in Suzuki reaction. Scheme 4 shows the heterogeneous Suzuki cross-coupling reaction of Ph−I and Ph−$B(OH)_2$.

(b) Reusability of Polymer-Supported NHC−Palladium Complex. For the industrial application of heterogeneous Suzuki cross-coupling reaction, the lifetime of the polymer-supported NHC−Pd catalyst and its level of reusability are very important factors. In this experiment, the catalyst was reused 10 times in the reaction of iodobenzene and phenylboronic acid under DMF/water (1:1) for 1 h at 50 °C (Scheme 5). It was notable that the polymer-supported NHC−Pd catalyst still showed consistent catalytic activity after being reused so many times. The reaction at the 9th and 10th recycled runs gave biphenyl in 94 and 92% yields, respectively, as shown in Table 3. In addition, the filtrate resulting from the reaction mixture had no catalytic activity under identical conditions. We concluded that there was no leaching of the catalytically active species from the beads during the reaction.

(c) Suzuki Cross-Coupling Reaction of Aryl Iodides and Bromides with Phenylboronic Acid. To extend the scope of the heterogeneous reaction, Suzuki cross-coupling reaction of various aryl iodides and bromides with phenylboronic acid was examined in very mild conditions, as shown in Table 4.[17] All of the aryl iodides were converted to the corresponding biaryls with excellent yields within 1 h at 50 °C, regardless of the substituent, as shown in Table 4 and Scheme 6. The reaction of the electron-deficient aryl bromides with phenylboronic acid proceeded smoothly to afford the biaryls with excellent yields within 6 h at 50 °C (Table 4, entries 9−12 and 17). The electron-rich aryl bromides including 4-bromotoluene and 4-bromoanisole were also

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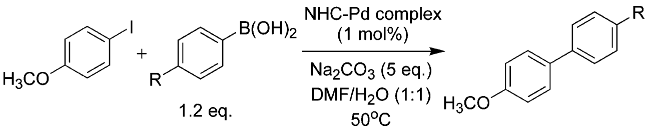
(17) The coupling of these substrates was reviewed in Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457.

SCHEME 7. Heterogeneous Suzuki Cross-Coupling Reaction of Arylboronic Acids with 4-Iodoanisole



easily converted to the corresponding biaryls with yields of 93 and 95%, respectively, for 6 h at 50 °C (Table 4, entries 7, and 14−16). As mentioned above, this polymer-supported NHC−Pd catalyst was so effective that all of the aryl iodides and bromides with the electron-deficient and -rich substituents were converted very rapidly to the corresponding products under mild conditions.

(d) Suzuki Cross-Coupling Reaction of Arylboronic Acids with 4-Iodoanisole. We further examined the reactions of various arylboronic acids with 4-iodoanisole in DMF/water (1:1), as shown in Table 5.[17] The reaction with the electron-rich arylboronic acids proceeded readily to afford the respective biaryls with a high yield within 1 h at 50 °C (Scheme 7). Generally, in a Suzuki reaction, the hydrolysis of arylboronic acids with the electron-withdrawing groups occurs and causes the yield to be decreased.[18] However, the reaction of the electron-deficient arylboronic acids with 4-iodoanisole using the polymer-supported NHC−Pd catalyst (1 mol %) was performed successfully in DMF/water (1:1).

Conclusion

In summary, a poly(1-methylimidazoliummethyl styrene)-*sg*-poly(styrene) resin was developed as a polymer-supported NHC precursor, with the ligand present only on the surface of the beads, by simple suspension polymerization. This precursor readily formed a stable complex with palladium, and this polymer-supported NHC−Pd catalyst showed excellent catalytic activity in Suzuki cross-coupling reactions of various aryl iodides and bromides with arylboronic acids in a DMF/aqueous phase. Of particular note is that this polymer-supported catalyst showed outstanding reusability without any loss of catalytic activity in Suzuki cross-coupling reaction.

Experimental Section

Preparation of Poly(1-methylimidazoliummehyl styrene)-*sg*-PS Resin. (a) Synthesis of the Polymerizable Ionic Liquid Monomer (1). 1-Methylimidazole (5 g, 61 mmol) was dissolved in $CHCl_3$ (50 mL), and 4-chloromethyl styrene (12 g, 79.3 mmol) was added. After stirring the mixture for 8 h at 50 °C, we washed the resulting 1-methyl-3-(4-vinylbenzyl)imidazolium chloride, [MVBIM][Cl^-], with ethyl acetate several times. After evaporating the solvent, we dissolved [MVBIM][Cl^-] (14 g, 59.8 mmol) in acetone (300 mL) and added $NaPF_6$ (12 g, 71.8 mmol) with constant stirring. The reaction was then allowed to proceed for 2 days at room temperature. After evaporating the solvent, the final ionic liquid monomer (**1**), [MVBIM][PF_6^-], was extracted from water with MC and then dried in vacuo overnight.

(b) Suspension Polymerization. The synthetic ionic liquid monomer (3.0 g), [MVBIM][PF_6^-], was suspended in an aqueous phase, which consisted of water (150 mL) and PVA (0.75 g). An organic phase, which consisted of styrene (7.0 mL), DVB (0.7 mL, 50% in ethylvinylbenzene), and benzoyl peroxide (0.22 g) as an initiator, was added to the aqueous phase with constant stirring (250 rpm) under a nitrogen atmosphere. The mixture was then polymerized for 24 h at 80 °C. The resulting polymer resins were sieved and washed with distilled water, MeOH, and MC. They were dried in vacuo overnight.

(c) CLSM Analysis. The fluorescent dye, 5(6)-carboxy tetramethyl rhodamine (34.5 μmol, 3 equiv), was dissolved in DMF (3 mL) and added to the resin (0.23 mmol/g, 50 mg). After shaking the mixture for 4 h at room temperature, we washed the resin extensively with DMF, MC, and MeOH. The resin beads were examined by means of a CLSM.

Preparation of Polymer-Supported NHC−Palladium Complex (2). (a) Immobilization of Palladium on the Resin. The poly(1-methylimidazoliummethyl styrene)-*sg*-PS resin (100 mg, 0.23 mmol/g) and $Pd(OAc)_2$ (1, 2, and 4 equiv) were mixed and stirred in DMSO (10 mL) at 50 °C for 4 h. After increasing the temperature to 100 °C, the stirring was continued for a further 30 min. After the completion of the reaction, the resin was filtered and washed vigorously with DMSO (10 mL × 5), distilled water (10 mL × 5), and MeOH (10 mL × 5). The resin was then dried under reduced pressure to give the complex (**2**).

(b) ICP-AES Analysis. The resin beads (50 mg) were treated with a mixture (5 mL) of hydrochloric acid and nitric acid (3:1, v/v) at 100 °C for 4 h. Following this, the resulting orange colored solution was filtered, and the recovered resin beads were washed with distilled water (2.5 mL × 6). The filtrate was diluted to 50 mL with distilled water and analyzed by ICP-AES.

General Procedure for Heterogeneous Suzuki Cross-Coupling Reaction. The polymer-supported NHC−Pd complex (**2**) (50 mg, 1 mol % Pd, 0.11 mmol-Pd/g) was suspended in DMF (2 mL). After adding a mixture of arylhalide (0.5 mmol), arylboronic acid (0.6 mmol, 1.2 equiv), and Na_2CO_3 (2.5 mmol, 5.0 equiv) in distilled water (2 mL), we agitated the reaction mixture in a shaking incubator at 50 °C for a specific period of time. The coupling reactions were performed under an air atmosphere. The resulting reaction mixture was filtered and washed with distilled water (4 mL × 5) and diethyl ether (4 mL × 5). The organic phase was separated and dried over $MgSO_4$, and diethyl ether was evaporated under reduced pressure. The final biaryl product was isolated by column chromatography and identified by gas chromatography/mass spectroscopy (GC−MS) and nuclear magnetic resonance spectroscopy (NMR). The isolation yield was calculated from the mass value of the product.

Biphenyl (3). ^1H NMR (DMSO-d_6): δ (ppm) 7.33 (q, 2H), 7.44 (q, 4H), 7.64 (d, 4H). GC−MS: *m/z* 154.

4-Hydroxybiphenyl (4). ^1H NMR ($CDCl_3$): δ (ppm) 4.82 (s, 1H), 6.89 (d, 2H), 7.29 (q, 1H), 7.42 (m, 4H), 7.55 (d, 2H). GC−MS: *m/z* 170.

4-Acetyl-4′-methoxybiphenyl (18). ^1H NMR ($CDCl_3$): δ (ppm) 2.63 (s, 3H), 3.87 (s, 3H), 6.99 (d, 2H), 7.52 (d, 2H), 7.66 (d, 2H), 8.02 (d, 2H). GC−MS: *m/z* 266.

Experimental Procedure for Reusability Test of Polymer-Supported NHC−Pd Complex. The polymer-supported NHC−Pd complex (**2**) (50 mg, 1 mol % Pd, 0.11 mmol-Pd/g) was suspended in DMF (2 mL). After adding a mixture of iodobenzene (102 mg, 0.5 mmol), phenylboronic acid (75 mg, 0.6 mmol), and Na_2CO_3 (265 mg, 2.5 mmol) in distilled water (2 mL), we agitated the reaction mixture in a shaking incubator at 50 °C for 1 h. The resulting reaction mixture was filtered and washed with distilled water and diethyl ether. The filtered catalyst was reused 10 times for the same reaction. The yield was calculated from the mass value of the product after isolation with column chromatography.

Acknowledgment. This work was supported by the Nano-Systems Institute-National Core Research Center (NSI-NCRC) program of KOSEF, Korea, and the Brain

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[18] Watanabe, T.; Miyaura, N.; Suzuki, A. *Synlett* **1992**, *2*, 207.

Korea 21 Program supported by the Ministry of Education & Human Resources Development.

Supporting Information Available: Solid-state ^{13}C NMR data and IR spectra for polymer support and palladium complex, ESI-MS, ^{1}H NMR, and ^{31}P NMR data for the polymerizable ionic liquid monomer, and GC−MS and ^{1}H NMR data for all of the products obtained from Suzuki cross-coupling reactions. This material is available free of charge via the Internet at http://pubs.acs.org.

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