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Novel Polymer Incarcerated Palladium with Phosphinated Polymers: Active Catalyst for Suzuki–Miyaura Coupling without External Phosphines

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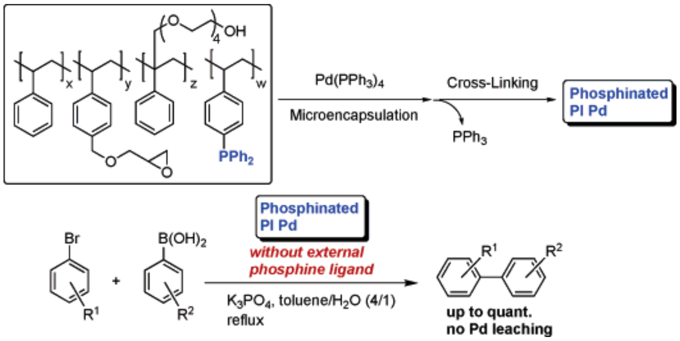
ABSTRACT



Immobilization of a palladium catalyst with use of new phosphinated polymers was carried out utilizing the polymer incarcerated (PI) method. This phosphinated PI Pd catalyst showed excellent activity in Suzuki–Miyaura couplings without addition of external phosphine ligands. No leaching of Pd was observed in this reaction, and the catalyst was recovered quantitatively by simple filtration and reused several times without loss of activity.

Palladium-catalyzed Suzuki−Miyaura coupling of organoborons with aryl or vinyl halides is known as one of the most useful carbon−carbon bond-forming reactions.[1] Since the first report in 1981 (Pd(PPh$_3$)$_4$ as a catalyst),[2] the reaction has been widely used not only in academic laboratories but also in industry. Recently heterogeneous catalysts for Suzuki−Miyaura coupling have been the focus of much attention.[3,4] In general, heterogeneous catalysts have advantages in recovery and reuse, but exhibit lower catalytic activity compared to homogeneous catalysts. Although

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(4) Recently, a highly active hydroxyapatite-supported Pd(II) catalyst has been reported. Mori, K.; Yamaguchi, K.; Hara, T.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *J. Am. Chem. Soc.* **2002**, *124*, 11572.

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additives such as phosphines and amines enhance the catalytic activity or selectivity in heterogeneous systems,[5,6] leaching of Pd during or after reaction is often observed due to those additives.

Recently, we have reported the polymer incarcerated (PI) method for immobilization of palladium catalysts into polystyrene-based polymers.[1,8] The heterogeneous PI palladium catalysts are highly active for hydrogenation and carbon−carbon bond-forming reactions. These catalysts are recovered quantitatively by simple filtration and can be reused several times without loss of activity. For example, PI Pd-catalyzed Suzuki−Miyaura couplings proceed in high yields in the presence of an externally added phosphine ligand such as tris(*o*-methoxyphenyl)phosphine without leaching of palladium.[7d] In this case, however, the phosphine ligand is lost during filtration of the catalyst, and addition of the phosphine ligand is necessary in every recycling use. In this paper, we describe new PI Pd catalysts using polymer supports which contain the diphenylphosphino group instead of adding external phosphine ligands, and their applications to Suzuki−Miyaura couplings.

PI Pd **2a**−**g** were prepared from $Pd(PPh_3)_4$ and copolymer **1a**−**g** by the PI method (microencapsulation and cross-linking of polymer chains) as reported previously (Figure 1). Since some phosphines were oxidized to the corresponding phosphine oxides during the preparation of the catalyst, $HSiCl_3$ reduction gave phosphinated PI Pd. It was revealed from ^{31}P SR-MAS NMR analysis[9] that the phosphine oxides on the copolymer were completely reduced to the corresponding phosphines. Furthermore, 4 equiv of triphenylphosphine from $Pd(PPh_3)_4$ were eliminated during the immobilization and recovered from the filtrate after washing (THF and hexane). PI Pd **2a**−**g** thus prepared were then analyzed by transmission electron microscopic (TEM). Judging from the magnified TEM image of PI Pd **2b** (Figure 2), small Pd clusters were dispersed on the polymer support without formation of large Pd clusters (TEM detection limit = ca. 1 nm). Formation of extremely small Pd clusters might be due to a stabilization effect of the polymer.

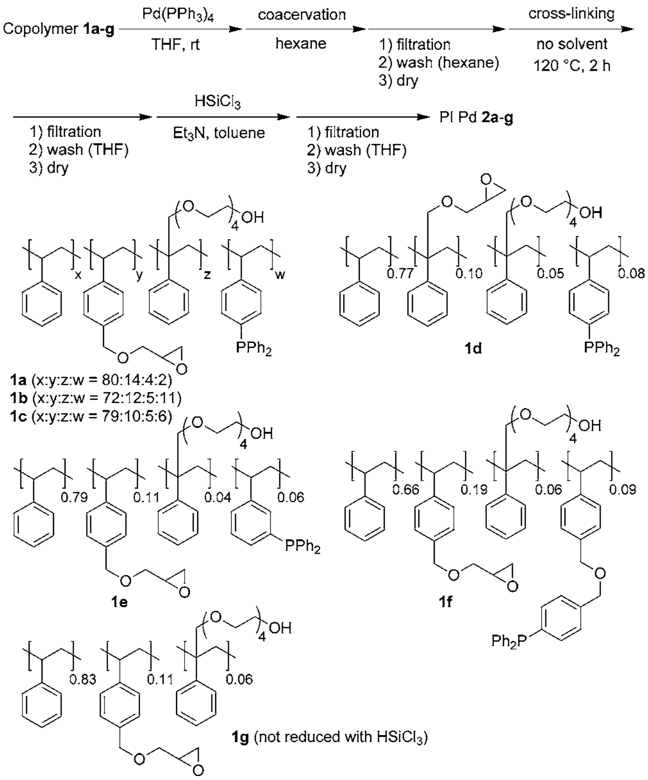

Figure 1. Preparation of phosphinated PI Pd **2a**−**f** and nonphosphinated PI Pd **2g** incarcerated Pd with copolymers.

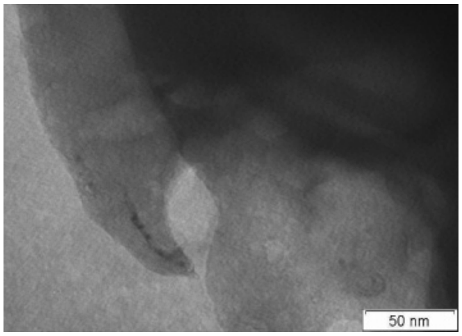

Figure 2. TEM image of PI Pd **2b**.

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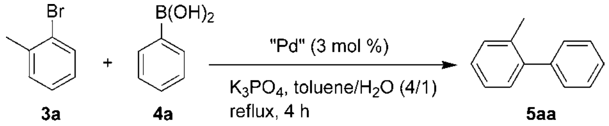
PI Pd **2a**−**g** were initially examined in the coupling reaction of 2-bromotoluene (**3a**) with phenylboronic acid (**4a**) without addition of any phosphine ligand (Table 1).

Table 1. Catalytic Activity of Phosphinated PI Pd



3a **4a** **5aa**

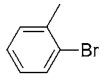
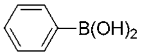
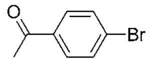
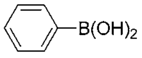
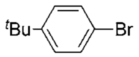
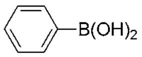
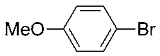
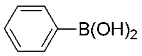
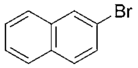
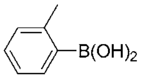
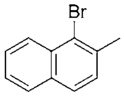
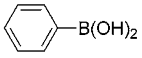
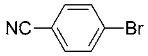
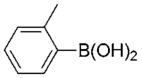
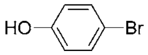
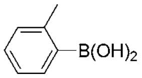
entry	catalyst (P/Pd)[a]	yield[b] (%)	leaching of Pd[c] (%)
1	Pl Pd **2a** (0.58)	81	nd
2	Pl Pd **2b** (2.1)	96	nd
3	Pl Pd **2c** (6.2)	93	nd
4	Pl Pd **2d** (1.8)	64	nd
5	Pl Pd **2e** (1.2)	73	nd
6	Pl Pd **2f** (2.1)	70	nd
7	Pl Pd **2g** (0)	9	nd
8[d]	Pl Pd **2g** (0)	19	nd

[a] The ratio of the diphenylphosphino groups in the polymer to Pd atoms. [b] Isolated yield. [c] Determined by XRF analysis. nd = not detected (<0.94%). [d] Adding 3 mol % of PPh_3 as a ligand.

The structure of the polymer supports was found to influence the catalytic activity. PI Pd **2a**−**c** which were prepared from the same type of polymer support as **1a**−**c** were more effective than other catalysts derived from polymer **1d**−**f**. As for the amount of phosphine in the catalyst, the best result was obtained when the ratio of the diphenylphosphino groups in the polymer to Pd atoms was ca. 2:1, and the coupling compound **5aa** was obtained in 96% yield. In contrast to phosphinated PI Pd **2a**−**f**, non-phosphinated PI Pd **2g** did not allow high catalytic activity even when triphenylphosphine was added as an external ligand. Leaching of the palladium was measured by fluorescence X-ray (XRF) analysis after removal of the catalyst; no leaching was detected in all cases. Furthermore, we also confirmed that no leaching of Pd occurred during the reaction by using the hot filtration method[7d,10] (see the Supporting Information). This result indicates that small palladium clusters could be strongly coordinated by both the π-electrons of benzene rings and phosphines on the polymer support. The role of the phosphines in the polymer support seems to be very important in this reaction: suppressing the leaching of palladium as well as increasing the catalytic activity by acting as ligands.

Several examples of PI Pd-catalyzed Suzuki−Miyaura couplings of aryl halides with arylboronic acids are summarized in Table 2. In the reactions using both electron-rich and electron-deficient aryl halides, the corresponding biaryl coupling products were obtained in high yields without any leaching of the palladium.

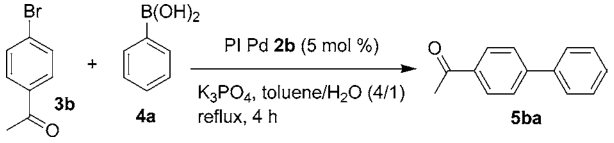
Table 2. Phosphinated PI Pd-Catalyzed Suzuki−Miyaura Coupling of Various Substrates without External Phosphine Ligand[a]

entry	arylhalide	boronic acid	yield[b] (%)	leaching of Pd[c] (%)
1			96	nd
2			quant.	nd
3			quant.	nd
4			84	nd
5			94	nd
6			85	nd
7			85	nd
8			92	nd

[a] Reaction conditions: 1.0 equiv of aryl halide, 1.5 equiv of boronic acid, 1.5 equiv of K_3PO_4, 3 mol % of Pl Pd **2b** (0.36 mmol/g, P/Pd 2.1), toluene/H_2O (4/1), reflux, 4 h. Workup conditions: the reaction mixture was diluted with hexane, and the catalyst was filtered off and then extracted with EtOAc and brine. [b] Isolated yield. [c] Determined by XRF analysis. nd = not detected (<0.94%).

Furthermore, PI Pd was recovered by simple filtration and could be reused several times (Table 3). Even after the fifth use, the same levels of yields were obtained. It was confirmed by XRF analysis that no leaching of Pd from the catalysts occurred in all cases.

Table 3. Recovery and Reuse of Phosphinated PI Pd



3b **4a** **5ba**

	run				
	first	second	third	fourth	fifth
yield[a]	quant	quant	98%	99%	quant
leaching of Pd[b]	nd	nd	nd	nd	nd

[a] Isolated yield. [b] Determined by XRF analysis. nd = not detected (<0.94%).

In summary, we have developed new PI Pd using phosphinated polymers, which showed high catalytic activity

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(10) (a) Choudary, B. M.; Madhi, S.; Chowdari, N. S.; Kantam, M. L.; Sreedhar, B. *J. Am. Chem. Soc.* **2002**, *124*, 14127. (b) Djakovitch, L.; Rollet, P. *Adv. Synth. Catal.* **2004**, *346*, 1782.

in Suzuki–Miyaura couplings without addition of any external phosphine ligands. Phosphines within polymer supports have two main roles: suppressing the leaching of palladium and increasing the catalytic activity as ligands. The PI Pd catalysts could be applied to several types of substrates, and no leaching of the palladium was observed. Moreover, the catalysts were recovered quantitatively by simple filtration, and reused several times without loss of activity.

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Supporting Information Available: Experimental details and spectral data of products. This material is available free of charge via the Internet at http://pubs.acs.org.

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