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In Situ Trapped and Immobilized Palladium Nanoparticles as Active and Clean Catalysts for Suzuki–Miyaura Reaction

Yan Li,[a] Fei Mao,[a] Ting Chen,[a] Zhicheng Zhou,[a] Yong Wang,[a] and Jun Huang[a,]*

[a] State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemical Engineering, Nanjing Tech University, Nanjing 210009, People's Republic of China
Fax: (+86) 25-83172261; e-mail: junhuang@njtech.edu.cn

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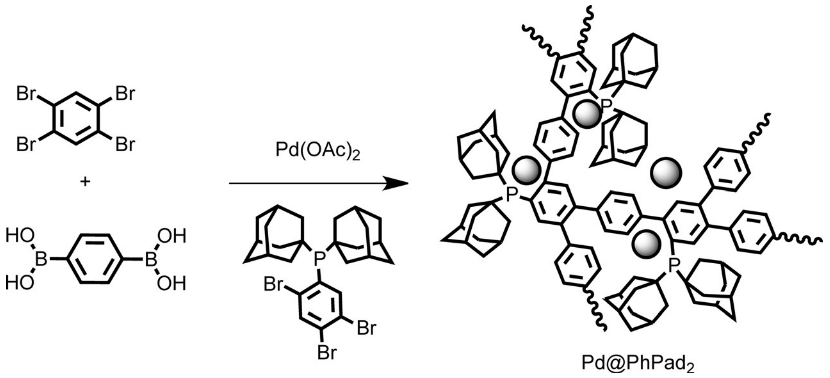
Abstract: Active palladium nanoparticles were trapped and immobilized *in situ* by Pd-catalyzed Suzuki–Miyaura reaction to form heterogeneous Pd catalysts. This Pd@PhPad$_2$ catalyst was found to be highly active, recyclable and clean for the Suzuki–Miyaura reaction. Both the anchored diadamantylphosphine ligand and the formation of polyphenylene polymer improved the activity and stability of the Pd@PhPad$_2$ catalyst for Suzuki–Miyaura reaction. The Pd@PhPad$_2$ catalyst was reusable, and no contamination (P ligand or Pd) was detected from the catalyst system for the coupling reaction.

Keywords: immobilization; nanoparticles; palladium; Suzuki–Miyaura reaction

Palladium-catalyzed C–C cross-coupling reactions have proved to be powerful tools for the synthesis of natural products, pharmaceuticals, agrochemicals, and optoelectronic materials.[1] To enhance the catalytic efficiency, some highly active ligand/palladium systems were designed and used for the Pd-catalyzed Suzuki–Miyaura reaction,[2] Heck reaction,[3] Sonogashira reaction[4] and Negishi reaction.[5] However, most of these active reaction systems involve homogeneous catalysts, and they are usually expensive and with complicated organic synthesis. Thus the recovery of the active Pd/Ligands catalyst systems is highly desirable not only for the economic reasons but also for avoiding product contamination. Therefore, some promising heterogeneous Pd catalysts were developed for the coupling reactions, including Pd supported on carbon, mesoporous zeolites, metal oxides and polymers.[6] However, heterogeneous Pd catalysts usually exhibit lower activity than the Pd/ligand systems. To achieve highly active heterogeneous Pd catalysts, some catalysts were studied and high activity can be achieved for the cross-coupling reactions with aryl bromides.[7] However, it is still desirable to develop highly active heterogeneous Pd catalysts for the cross-coupling reactions using aryl chlorides. Aryl chlorides are inexpensive and extensively available, but they are difficult to be activated, which requires more active Pd catalysts. Until now, there were few heterogeneous Pd catalysts active enough for the activation of aryl chlorides (for example, TON > 1000 with chloroanisole).[8] Recently, we have reported Pd nanoparticles formed *in situ* in ionic solid polymers as highly active heterogeneous catalysts for the Suzuki–Miyaura reaction, and only 10 ppm Pd catalysts were required for the reaction of aryl bromides.[9] Moreover, we also reported the C–O coupling and C–CN coupling of aryl chlorides and bromides with heterogeneous or homogeneous catalyst systems.[10] And here, highly active Pd nanoparticles were trapped and immobilized *in situ* as heterogeneous catalysts for the Suzuki–Miyaura reaction. An electron-rich and bulky P ligand was anchored onto the Pd-catalyzed polyphenylene polymer. Along with the formation of the polyphenylene polymer, the active Pd nanoparticles were trapped and immobilized into the polymer, forming the Pd heterogeneous catalysts. The activity is kept in the Pd catalysts, and the activity can be released in a further Suzuki–Miyaura reaction. The Pd nanocatalysts exhibited high efficiency for Suzuki–Miyaura coupling of aryl bromides and chlorides with arylboronic acids, and no contaminant, either Pd or P ligand, was leaked into the solution from the catalyst system in the coupling reaction. Thus, the Pd nanocatalysts are active and clean for Suzuki–Miyaura reactions.

The Pd nanocatalysts were prepared by a one-pot method with the Pd-catalyzed C–P coupling reaction initially, followed by the Pd-catalyzed Suzuki–Miyaura reaction of aryl multibromides with 1,4-phenylenebisboronic acid. The P ligands containing aryl bromides can participate (as catalyst and reactant) in



Scheme 1. The preparation of the Pd nanocatalysts.

the Suzuki–Miyaura reaction of 1,2,4,5-tetrabromobenzene with 1,4-phenylenebisboronic acid, forming the polyphenylene polymer. At the same time, Pd nanoparticles were trapped and immobilized into the polyphenylene polymer as the heterogeneous Pd catalysts (see Scheme 1, and the detailed procedure for preparing Pd@PhPad$_2$ and Pd@PhPad$_2$-2 in the Supporting Information).

The chemical structure of Pd@PhPad$_2$ (Pd contained 0.96 wt%) was characterized by solid state ^{31}P NMR, ^{1}H NMR and IR spectroscopy. In the solid state ^{31}P NMR spectrum (Supporting Information, Figure S1) of Pd@PhPad$_2$, the peak at 24 ppm corresponds to diadamantylphosphine, which shows that diadamantylphosphine is connected on the polymers. The solid state ^{1}H NMR spectrum of Pd@PhPad$_2$ shows three signals at 2.7 ppm, 2.8 ppm and 7.8 ppm, respectively, which can be assigned to hydrogen of adamantly and hydrogen of phenyl rings, respectively (Supporting Information, Figure S2). The IR bands (Supporting Information, Figure S3) between 3000 cm^{-1} and 2750 cm^{-1} and the band at 1500 cm^{-1} originate from adamantyl groups. The IR bands between 1500 cm^{-1} and 500 cm^{-1} are from the phenyl rings. In the thermogravimetric curve (TG) (Supporting Information, Figure S4) of the Pd@PhPad$_2$ catalyst, there is a sharp weight loss at a temperature of less than 250 °C, which is due to the desorption of solvent (DMF) and moisture. No evident mass loss is observed between 250 °C and 450 °C, which indicates that the Pd@PhPad$_2$ catalyst is stable up to 450 °C. Scanning electron microscopy (SEM) images (Supporting Information, Figure S5) indicate that the catalyst is an aggregate of irregularly shaped particles, and the particles are intertwined with each other, forming a sponge-cake structure. The EDX elemental analysis reveals the presence of Pd and P in the catalyst (Supporting Information, Figure S6). The surface area was measured by the nitrogen sorption method (Supporting Information, Figure S7). As shown in Figure S7 (Supporting Information), the catalyst shows a type II nitrogen sorption isotherm, which corresponds to a surface area of 22.3 m^2 g^{-1} and an average pore diameter of 8.89 nm. To better understand the surface composition of the catalyst, in particular the valence state of palladium, the catalyst was characterized by X-ray photoelectron spectroscopy (XPS). As shown in Figure S8 (Supporting Information), the Pd 3*d* region is deconvoluted into two spin-orbital pairs, indicating the presence of two types of palladium species [Pd^{2+} and Pd(0)]. The binding energy peaks at 340.2 (Pd 3$d_{3/2}$) and 335.5 eV (Pd 3$d_{5/2}$) are assigned to Pd(0) species. The binding energy peaks at 341.8 (Pd 3$d_{3/2}$) and 337.1 eV (Pd 3$d_{5/2}$) correspond to Pd(II) species. The molar ratio of Pd(0)/Pd(II) in the Pd@PhPad$_2$ changed from about 2:1 before the reaction to about 1:1 after the reaction as evaluated by XPS (Supporting Information, Figure S9), which should be due to the oxidation by air. The catalyst was examined by transmission electron microscope (TEM) to reveal the distribution of the palladium nanoparticles in the catalyst. As can be seen from Figure 1, the palladium nanoparticles are dispersed homogeneously, and the average diameter is about 3 nm.

The catalytic performance of Pd@PhPad$_2$ was evaluated in Suzuki–Miyaura reaction. The coupling of 4-chloroanisole with phenylboronic acid was used as the model reaction. As shown in Table 1, the added base

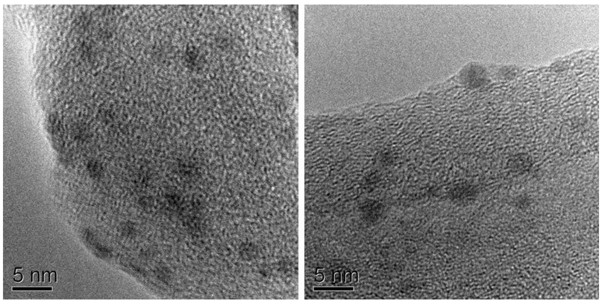


Figure 1. Transmission electron micrograph of the fresh Pd@PhPad$_2$ catalyst (*left*) and the catalyst after eight reaction runs (*right*).

Table 1. Pd-catalyzed Suzuki–Miyaura coupling of 4-chloroanisole with phenylboronic acid [a]

Entry	Base	Solvent	Pd [mol%]	Yield [%]
1	K_2CO_3	DMF	0.5	55
2	Cs_2CO_3	DMF	0.5	65
3	K_3PO_4	DMF	0.5	98
4	K_3PO_4	PX	0.5	70
5	K_3PO_4	BE	0.5	65
6[b]	K_3PO_4	DMF	0.5	97
7[c]	K_3PO_4	DMF	0.05	95
8[d]	K_3PO_4	DMF	0.5	51
9[e]	K_3PO_4	DMF	0.5	75
10[f]	K_3PO_4	DMF	0.5	7

[a] *Reaction conditions:* 4-methoxybiphenyl (1.0 mmol), phenylboronic acid (1.2 mmol), catalyst Pd@PhPad$_2$ (Pd content 0.96 wt%), K_2CO_3 and Cs_2CO_3 (2.0 mmol), K_3PO_4 (1.3 mmol) at 120 °C for 15 h under argon.

[b] Catalyst Pd@PhPad$_2$-2 (Pd content 1.8 wt%) was used.

[c] Phenylboronic acid (1.5 mmol) at 160 °C.

[d] The catalyst Pd@PhPh$_2$ was used.

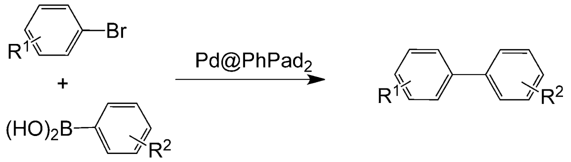
[e] The catalyst Pd@PhPad$_2$ was exposed to air for a week.

[f] The catalyst Pd/PPhen was used.

and solvent are important in the coupling reaction. The reaction produced *p*-methoxybiphenyl in the yield of 55% and 65% in *N,N*-dimethylformamide (DMF) at 120 °C in the presence of K_2CO_3 and Cs_2CO_3, respectively (Table 1, entries 1 and 2). However, K_3PO_4 is a more suitable base for the reaction, and *p*-methoxybiphenyl was obtained in a yield as high as 98% (Table 1, entry 3). When the reaction was conducted in *p*-xylene (PX) and dibutyl ether (BE) in the presence of K_3PO_4, we obtained low yields of *p*-methoxybiphenyl (Table 1, entries 4 and 5). As the Pd@PhPad$_2$ catalyst is insoluble in the reaction system, DMF, as a better solvent, can bring the reactants into and out of the Pd catalytic centers. The Pd content in the catalysts is not essential, and the Pd@PhPad$_2$-2 (Pd content: 1.8 wt%) was similarly active for the coupling reaction of 4-chloroanisole with phenylboronic acid (Table 1, entry 6). Interestingly, the coupling reaction of 4-chloroanisole with phenylboronic acid gave 4-methoxybiphenyl in 95% yield even using 500 ppm (0.05 mol%) loading of Pd at 160 °C (Table 1, entry 7), which showed the extremely high activity of the catalyst system. In contrast, when Pd@PhPPh$_2$ (PPh$_2$ instead of Pad$_2$) was used for the coupling of 4-chloroanisole with phenylboronic acid, *p*-methoxybiphenyl was obtained in low yield (51% yield, Table 1, entry 8), which indicated that the Pd@PhPad$_2$ was the better catalyst for the coupling reaction. In order to study the resistance to O_2, the Pd@PhPad$_2$ was exposed in air for 1 week. The Pd@PhPad$_2$ was used for the coupling of 4-chloroanisole with phenylboronic acid, and *p*-methoxybiphenyl was obtained in good yield (75%, Table 1, entry 9). We also prepared the catalyst Pd/PPhen without the P ligand. The Pd/PPhen was nearly inactive for the coupling of 4-chloroanisole with phenylboronic acid under similar reaction conditions (7% yield, Table 1, entry 10). The optimization of the Pd loading for the coupling reaction of aryl bromides, activated aryl chlorides and heteroaryl bromides is given in Table S1 (Supporting Information). It is noteworthy that the coupling reaction was conducted in the absence of a phase-transfer agent, such as TBAB (tetra-*n*-butylammonium bromide), as some catalyst systems were active with the presence of stoichiometric TBAB.[11]

With the optimized reaction conditions in hand, we tested the applicable scope of the Pd@PhPad$_2$ catalyst for cross-coupling reactions. Initially, various aryl bromides were coupled with phenylboronic acid with 0.01 mol% Pd loading (100 ppm) under the optimized reaction conditions. As shown in Table 2, the catalyst showed high efficiency for the cross- coupling reaction, and a large number of functional groups survived the reaction conditions. The cross-coupling of 4-methoxyphenyl bromide with phenylboronic acid afforded 4-methoxybiphenyl in excellent yields. The *p*- and *o*-substituents, including methoxy, nitrile, nitro,

Table 2. Suzuki–Miyaura coupling of aryl bromides and phenylboronic acids.[a]



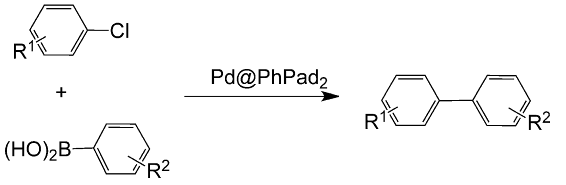
Entry	R^1	R^2	Yield [%][b]
1	4-MeO	H	98
2	2-MeO	H	97
3	4-*tert*-butyl	H	98
4	4-CHO	H	97
5	4-MeCO	H	99
6	4-CN	H	99
7	2-Me	H	97
8	2-NO_2	H	98
9	2-CN	H	98
10	2,6-di-Me	H	90
11	2,6-di-Me	2-Me	65
12	1,3,5-tri-*i*-Pr	H	15
13[c]	H	4-CN	94
14[c]	H	4-MeO	91

[a] *Reaction conditions:* aryl bromide (5.0 mmol), phenylboronic acid (6.0 mmol), Pd@PhPad$_2$ catalyst (Pd, 0.01 mol%), K_3PO_4 (7.0 mmol) DMF (5.0 mL) at 120 °C for 6 h under argon.

[b] Isolated yield.

[c] Bromobenzene (1.0 mmol), arylboronic acid (1.5 mmol), Pd (0.05 mol%), K_3PO_4 (1.3 mmol), DMF (1 mL) at 120 °C for 6 h.

Table 3. Suzuki–Miyaura coupling of aryl chlorides and phenylboronic acids.[a]



Entry	R^1	R^2	Yield [%][b]
1	4-MeCO	H	97
2	4-CN	H	98
3	4-CHO	H	98
4	$2\text{-}NO_2$	H	96
5	2-CN	H	96
6[c]	4-*t*-butyl	H	95
7[c]	2-Me	H	94
8[c]	2-MeO	H	93
9	H	4-CN	90
10	H	4-MeO	90

[a] *Reaction conditions:* aryl chloride (1.0 mmol), phenylboronic acid (1.2 mmol), Pd@PhPad$_2$ catalyst (Pd, 0.07 mol%), K_3PO_4 (1.3 mmol), DMF (1.0 mL) at 120 °C for 12 h under argon.

[b] Isolated yield.

[c] Pd (0.5 mol%).

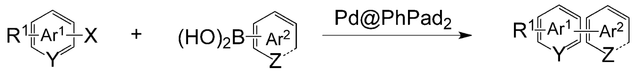
aldehyde and ketone groups, were well tolerated under the reaction conditions, and the corresponding products were obtained in high yields (Table 2, entries 1–9). The coupling of 2,6-dimethylbromobenzene with phenylboronic acid gave the corresponding product in high yield also, which implied that a hindered aryl bromide can be used in the cross-coupling reaction (Table 2, entry 10). To further study the steric hindrance effect in the coupling reaction with the Pd@PhPad$_2$ catalyst, the coupling reaction of 2,6-dimethylbromobenzene with 2-tolueneboronic acid was tested, and 2,6,2′-trimethyl-1,1′-biphenyl was obtained in 65% yield (Table 2, entry 11). However, when 2,4,6-triisopropylbromobenzene was used as substrate for the cross-coupling with phenylboronic acid, the corresponding product was obtained in only 15% yield (Table 2, entry 12). Moreover, the coupling of bromobenzene with functional phenylboronic acids (4-CN, 4-MeO) also gave high yields (Table 2, entries 13 and 14).

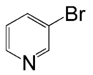
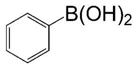
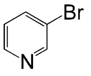
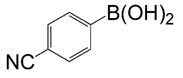
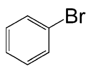
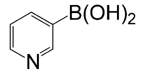
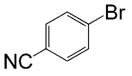
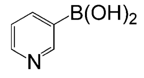
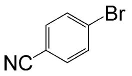
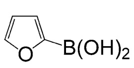
Next, several aryl chlorides were used for the cross-coupling reaction with Pd@PhPad$_2$ as the catalyst, and the results are listed in Table 3. The cross-coupling reaction of electron-poor aryl chlorides afforded the corresponding biphenyl compounds in excellent yields with 0.07 mol% Pd loading (Table 3, entries 1–5). Furthermore, the electron-rich aryl chlorides can also be coupled with phenylboronic acid in good yield (Table 3, entries 6–8). Phenylboronic acids with functional groups, including methoxy and nitrile groups, were examined for the cross-coupling reaction with chlorobenzene, and the corresponding biphenyl compounds were obtained in good yields. (Table 3, entries 10 and 11).

As heterobiaryl compounds are useful in medicine and as agrochemicals, the cross-coupling reactions of some heteroaryl bromides or heteroarylboronic acids were also performed (Table 4). The cross-coupling reaction of heteroaryl halides or heteroarylboronic acids is challenging and highly desirable, and normally a high Pd loading is required even with molecular catalysts. The Pd@PhPad$_2$ catalyst showed high efficiency for the coupling reaction of 3-bromopyridine with phenylboronic acid or 4-cyanophenylbornic acid (Table 4, entries 1 and 2), and the corresponding products were obtained in high yields. The Pd@PhPad$_2$-catalyzed cross-coupling of 3-pyridinylboronic acid with bromobenzene and 4-bromobenzonitrile gave the corresponding products both in 91% yields (Table 4, entries 3 and 4). Additionally, the coupling of 4-bromobenzonitrile with 2-furanylboronic acid gave the corresponding product in 92% yield (Table 4, entry 5).

To explore the Pd@PhPad$_2$ catalyst in industrial applications, sartanbiphenyl (2-cyano-4′-menthylbiphenyl) was produced (10 times scaled up) as sartanbiphenyl is a key intermediate for the production of sartans (hypertension drugs). The Pd@PhPad$_2$ catalyst showed high activity for the coupling of 2-chloroben-

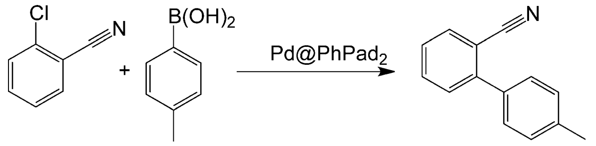
Table 4. Suzuki–Miyaura coupling of heteroaryl compounds catalyzed by Pd@PhPad$_2$.[a]



Entry	Ar^1	Ar^2	Yield [%][b]
1			93
2			95
3			91
4			91
5			92

[a] *Reaction conditions*: Ar^1 (2.0 mmol), Ar^2 (2.5 mmol), Pd@PhPad$_2$ catalyst (Pd, 0.01 mol%), K_3PO_4 (2.5 mmol), DMF (2 mL) at 100 °C for 6 h under argon.

[b] Isolated yield.



Scheme 2. Production of sartanbiphenyl by Pd@PhPad$_2$-catalyzed coupling of 2-chlorobenzonitrile with 4-methylphenylboronic acid.

zonitrile with 4-methylphenylboronic acid, and sartanbiphenyl was obtained in high yield (97%) (Scheme 2). Moreover, the Pd@PhPad$_2$ catalyst can be recovered easily by centrifugation, and the recovered Pd@PhPad$_2$ catalyst can be reused several times. As shown in Figure 2, after eight reaction runs, sartanbiphenyl was obtained in 78% yield. The slightly deactivation of the Pd@PhPad$_2$ catalyst may be due to the loss of the catalyst in the recycle processes (the detailed recycle procedure is given in the Supporting Information). To test for the leaching of Pd@PhPad$_2$ catalyst, we measured the content of Pd in the reaction solution by ICP-AES, and no Pd was detected in the solution (below detection limit, <7 ppb). Moreover, no P (from the P ligand) was leached into the solution. The Pd@PhPad$_2$ catalyst is a heterogeneous catalyst for Suzuki–Miyaura reaction, and no P ligand or Pd contaminants was found from the catalyst system, which is essential for the pharmaceutical industry. Moreover, the Pd@PhPad$_2$ catalyst is recyclable and durable for Suzuki–Miyaura reaction, which is also desirable for the reduction of cost in the industrial applications. In addition, the eighth recovered Pd@PhPad$_2$ catalyst was also observed by TEM, and the Pd particles still remained their pristine morphology with the diameter of about 3 nm (Figure 1, *right*).

Obviously, more active Pd nanoparticles were trapped and immobilized preferentially onto the polyphenylene polymer in the one-pot process, as the polymerization was catalyzed by the active Pd nanoparticles. Thus, we can obtain the highly active Pd@PhPad$_2$ catalysts. In the Pd@PhPad$_2$ catalyzed Suzuki–Miyaura reaction, the activity of the trapped and immobilized Pd nanoparticles can be released. Although the surface area of the Pd@PhPad$_2$ is low, the Pd@PhPad$_2$ is found to be highly active for coupling reactions.

Good ligands for cross-coupling reactions combine both electronic and steric properties. The electron-rich ligands can help the oxidative addition into the Pd center to activate aryl halides. The sterically demanding ligands can improve the reductive elimination from the Pd center to form products. The diadamantylphosphine in the Pd@PhPad$_2$ catalysts is electron-rich and sterically bulky, which is highly beneficial for coupling reactions. The formation of the polyphenylene polymer enhances the electron density of the P ligands on one hand, and enhances the steric hindrance of the P ligands in the Pd@PhPad$_2$ catalyst on the other hand. Moreover, the formation of the polyphenylene polymer can trap and immobilize the active Pd nanoparticles, thus Pd@PhPad$_2$ catalysts are active, clean and reusable for cross-coupling reactions. Furthermore, the bulky ligand and the polyphenylene polymer in the Pd@PhPad$_2$ are also useful for the stabilization of the Pd nanoparticles as the P ligand is well protected from O$_2$ gas.

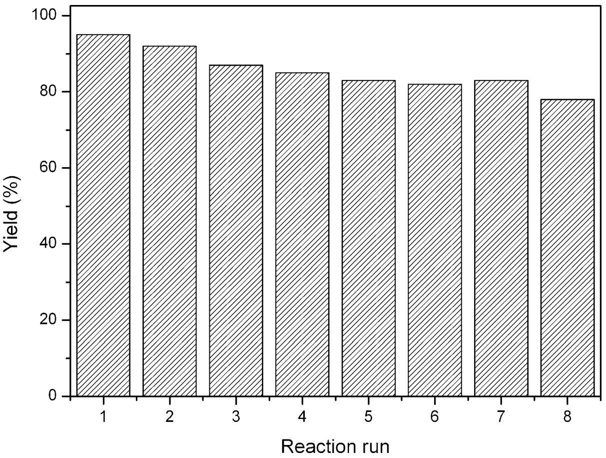


Figure 2. Recycling of the Pd@PhPad$_2$ catalyst in the preparation of sartanbiphenyl.

In conclusion, novel active and heterogeneous Pd catalysts were developed for the Suzuki–Miyaura reaction. Active Pd nanoparticles were trapped and immobilized *in situ* by Pd-catalyzed Suzuki–Miyaura reaction, forming the heterogeneous Pd catalysts. The Pd@PhPad$_2$ catalyst was found to be highly active, recyclable and clean for Suzuki–Miyaura reactions. The Pd@PhPad$_2$ catalyst can be reused several times, and no Pd or P leached into the reaction mixture. Thus no contamination (ligand or Pd) occurred from the catalyst system (clean catalyst system), which is important in pharmaceuticals. Both the anchored diadamantylphosphine ligand and the formation of polyphenylene polymer are beneficial for the high efficiency of the Pd@PhPad$_2$ catalyst. The combination of electronic and steric properties in the Pd@PhPad$_2$ catalyst is important to the activity and stability of the Pd@PhPad$_2$ catalyst. We believe this method can be used to design catalysts in more cross-coupling reactions, and possibly upscaled in industrial applications.

Experimental Section

The Pd@PhPad$_2$-Catalyzed Suzuki–Miyaura Coupling of Aryl Chlorides with Phenylboronic Acid

Typically, 4-chloroanisole (1.0 mmol), phenylboronic acid (1.2 mmol), Pd@PhPad$_2$ catalyst (55 mg, 0.5 mol% Pd),

K_3PO_4 (280 mg, 1.3 mmol) and DMF (1.0 mL) were added to a pressure tube under argon. The pressure tube was placed in an oil bath for 12 h at 120 °C. The reaction mixture was cooled to room temperature and 100 μL $C_{16}H_{34}$ were added as internal standard for GC. The mixture was extracted with ethyl acetate (3×10 mL). The organic extract was dried with anhydrous $MgSO_4$ and analyzed by GC to determine the yield. The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexane).

Acknowledgements

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