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Synthesis of dendrimers terminated by DABCO ligands and applications of its palladium nanoparticles for catalyzing Suzuki–Miyaura and Mizoroki–Heck couplings

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A new kind of silica-supported third-generation dendrimers capped by 1,4-diaza-bicyclo[2.2.2]octane (DABCO) group-stabilized palladium(0) nanoparticles, and their enhanced catalytic activity in Suzuki–Miyaura and Mizoroki–Heck reactions in excellent yield under mild conditions, was reported. The resulting silica-supported dendrimer-stabilized palladium(0) nanoparticles with a particle size of 10–20 nm were prepared *in situ* by treatment with PdCl₂ and hydrazine in ethanol at 60 °C for 24 h. The catalyst as prepared was characterized by FT-IR, X-ray diffraction, thermal analysis, elementary analysis (EA), scanning electron microscopy and transmission electron microscopy. Recycling experiments showed that the catalyst could be easily recovered by simple filtration and reused for up to five cycles without losing its activity. Copyright © 2012 John Wiley & Sons, Ltd.

Supporting information may be found in the online version of this article.

Keywords: dendrimer; nanopalladium; Suzuki-Miyaura reaction; Mizoroki-Heck reaction; supported catalyst

Introduction

Palladium nanoparticles (PdNPs) are of considerable current interest in fundamental academic fields, as well as in industrial catalytic applications,^[1,2] due to the advantages offered by these 'semi-heterogeneous catalysts' combining the characteristics of heterogeneous catalysis (recovery and recyclability) with those of homogeneous catalysis (relatively low catalyst loadings and good selectivity).^[3] In particular, the nanopalladium-catalyzed Suzuki-Miyaura and Mizoroki-Heck reactions are widely useful methods in forming carbon-carbon bonds in synthetic chemistry, as well as in industrial applications.^[4-8] Because of their large surface-to-volume ratio,^[3,9] nanosized transition metal particles offer higher catalytic efficiency than larger materials. Unfortunately, metal nanoparticles are unstable and easily aggregate and precipitate to bulk metal. Recently, a number of methods^[3,9] have been developed to stabilize metal nanoparticles by using surfactants, organic ligands, polymers and dendrimers as stabilizers. Among these methods, the homogeneous Suzuki-Miyaura and Mizoroki-Heck reaction generally employs a homogeneous catalyst with various ligands such as phosphines,^[10] imidazole,^[11] *N*-heterocyclic carbens,^[12] 1,4-diaza-bicyclo[2.2.2]octane (DABCO)^[13] and Schiff bases.^[14-16] Homogeneous catalytic systems have the merits of high reactivity, good reusability and mild reaction conditions. However, most of them suffer from problems such as separation, availability, tedious workup and metal contamination in the products. To overcome these drawbacks, PdNPs immobilized on various soluble and insoluble matrices have been a challenge for a long time because such carriers can efficiently control the formation of metal nanoparticles and further prevent nanoparticle agglomeration, as well as combining all the merits of both homogeneous and heterogeneous catalytic systems.^[17-21] Moreover, these catalysts can be easily recovered and recycled with high activity

and selectivity. A number of effective catalysts have been developed for Suzuki–Miyaura and Mizoroki–Heck reactions as well as various other reactions. In some cases, however, dramatic changes in the properties of neat palladium nanoparticles and some undesirable effects (e.g. decrease of reaction rate or selectivity changes) were observed. Such drawbacks can be partly overcome by the use of such classes of carriers as dendrimers. Dendrimers are hyperbranched regular macromolecules with a highly symmetrical structure.^[22–25] Their structure and chemical properties can be controlled by modifying the core, type and number of branches and the terminal functional groups. The features of the structure allow immobilization of PdNPs in different regions (core, branches or periphery) of a dendrimer molecule.

DABCO is a type of spindle-shaped molecule with two nitrogen atoms located at both tips. It was found to minimize hindrance for reactants approaching the palladium active sites^[26] and to be an efficient ligand for Pd-mediated coupling.^[13] In addition, we found that polymer-supported ethylenediamine was a highly efficient nitrogen ligand for palladium-catalyzed Suzuki–Miyaura cross-coupling and achieved excellent yields.^[27] In the discussion mentioned above on the intriguing structural features of dendrimers and nature of the ligands, the approach for immobilizing PdNPs in dendrimer matrices is fascinating, and we envisaged that dendrimers incorporated with multi-nitrogen ligands would be more powerful tools for the immobilization of PdNPs as matrices, which work as high-performance and durable heterogeneous catalysts. Considering the importance of these compounds, we describe here the synthesis of a new type of nitrogen-containing dendrimer

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(N donating units) capped with DABCO groups (N donating units), up to the third generation (Scheme 1), and the use of corresponding palladium particles immobilized on it as catalysts for Suzuki–Miyaura and Mizoroki–Heck coupling reactions.

Experimental

Melting points were measured on an Electrothermal X₆ microscopic digital melting point apparatus. FT-IR spectra were recorded on a Bruker Equinox-55 spectrometer as KBr pellets in the range 4000–400 cm⁻¹. ¹HNMR spectra were obtained with a 300 MHz and 500 MHz Bruker Avance instrument with CDCl₃ and DMSO- d₆ as solvent and TMS as internal standard. Elemental analyses were performed on a PerkinElmer EA2400II elemental analyzer. The elemental palladium content of the polymeric catalysts was determined by PerkinElmer Optima 2000DV inductively coupled plasma (ICP) spectroscopy. Scanning electron microscopy (SEM) was performed with a Philips XL 30ESEM instrument. Transmission electron microscopy (TEM) was performed with a Philips Tecnai instrument operating at 40–100 kV. X-ray diffraction (XRD) patterns were obtained with an MSAL-XRD2 diffractometer using Cu-K radiation.

SiO₂ (200–300 mesh) was a commercial chromatographic silica gel and activated at 120 °C in an oven for 2 h prior to use. All other chemicals were reagent grade and used as purchased.

Preparation of Silica-Supported Dendrimer Terminated by DABCO (SiO₂-DEA-DABCO)

The activated silica (5.0 g) and (3-chloropropyl)trimethoxysilane (5.0 ml) was refluxed in dry toluene (125.0 ml) for 24 h. The solids were isolated and washed successively with toluene and ethanol and dried at 80 °C for 10 h under vacuum. The chlorinated silica gel (1) as prepared was then further reacted with diethanolamine (DEA) (5.25 g, 50.0 mmol) in toluene (125.0 ml) at 110 °C for 12 h. The reaction mixture was washed subsequently with a large amount of toluene and ethanol and dried under vacuum at 80 °C for 10 h to

afford aminated silica gel (2). Subsequently, in a 100 ml flask with a magnetic stirring bar, the obtained aminated silica gel (2) (G1) (7.0 g) and DMF (50.0 mL) were heated to 90 °C. Thionyl chloride (35.0 ml, 68.95 mmol) was then added to the mixture dropwise over 2.5 h. After filtering, the solids were washed completely with deionized water and dried under vacuum at 80 °C for 10 h. The products (3) were then treated with diethanolamine (7.5 g, 71.33 mmol) in toluene at 110°C for 12 h. The above procedure was repeated using the G2 product. Repetition of the above steps afforded the third-generation dendrimer (G3) product. The obtained yellow solid was reacted with 1,4- diazabicyclo[2.2.2]octane (DABCO) (5.85 g, 52.15 mmol) in toluene (125 ml) at 110 °C for 12 h to afford the DABCO capped dendrimers grafted on to the surface of silica (SiO₂-DEA-DABCO) (Scheme 1). The amount of N content was determined by elemental microanalysis to confirm the formation of dendrimers. The elemental analysis data in Table 1 show the amount of N in G1, G2, G3 and G3-DABCO.

Preparation of Nano-Pd Immobilized on Silica-Supported Dendrimer Capped by DABCO (SiO₂-DEA-DABCO-Pd⁰)

 SiO_2 -DEA-DABCO (1.0 g), palladium chloride (0.36 g, 2.0 mmol) and ethanol (50.0 ml) were added to a 100 ml flask preheated to 60 °C in an oil bath. The reduction was carried out by the addition of 0.5 ml of 30% hydrazine. The color of the solution changed from yellow to black. The resulting solution was heated at 60 °C for 24 h. The solid

Table 1. N content of modified silica					
Sample identifier	Analysis N (%)				
G1	1.13				
G2	1.33				
G3	1.43				
G3-DABCO	2.05				



Scheme 1. Preparation route and schematic model of SiO_2 -DEA-DABCO-Pd⁰ dendrimer.

was then filtered and washed completely with ethanol (40 ml \times 2) and water (20 ml \times 2), then dried under vacuum at 80 $^\circ C$ for 12 h (Scheme 1).

General Procedure for the Catalytic Suzuki-Miyaura Reactions

Under air atmosphere, a round-bottomed flask was charged with SiO₂–DEA–DABCO–Pd⁰ catalyst (3.0 mg, 0.04 mol% palladium content), K₂CO₃ (2.0 mmol), aryl halide (1.0 mmol), arylboronic compound (1.2 mmol) and C₂H₅OH/H₂O (1:1, v/v, 2.0 ml). The reaction mixture was stirred at 78 °C for a specific time (Table 8). The progress was monitored by thin-layer chromatography. Upon completion of the reaction, the catalyst was removed by filtration, washed completely with ethanol (20.0 ml) and dried under vacuum for the next run. The organic fractions were then concentrated in a rotary evaporator to obtain the desired biaryl in excellent yield. The crude products were further purified by recrystallization. All of the products (**1a–k**) are known compounds and they were characterized by comparing their melting point, ¹H NMR (see the supplementary material) and IR spectra with those found in the literature.

General Procedure for the Catalytic Mizoroki-Heck Reactions

To a mixture of aryl halide (1.0 mmol), K₃PO₄·3H₂O (2.0 mmol) and olefin (1.2 mmol) in DMF (2.0 mL), SiO₂-DEA-DABCO-Pd⁰ catalyst (3.0 mg, 0.04 mol% of palladium content) was added and the mixture stirred at 130 °C for a specific time (Table 9). Upon completion of the reaction, the reaction mixture was filtered, and the residue catalyst was washed with 95% ethanol successively and dried under vacuum for the next run. When a styrene was used as substrate, the filtrate was extracted with diethyl ether, the organic layer was washed with deionized water, separated and dried over anhydrous Na₂SO₄, and the solvent was removed under vacuum. The resultant residue was purified to obtain the desired product; when an acrylic acid was used as substrate, the filtrate was poured into water and neutralized with dilute HCl to precipitate the product, which was further purified by recrystallization. All the products were known and characterized by melting point, IR and ¹H NMR spectroscopy (see the supplementary material); the data were found to be identical to those reported in the literature.

Recovery of the Catalyst

Reusability of silica–dendrimers–DABCO–Pd⁰ was investigated by using the reactions of *p*-bromoanisole with phenylboronic acid. After completion of the reaction, the mixture was centrifuged and filtered. The catalyst was then washed with water (5 × 5 ml), followed by ethanol (3 × 5 ml). After drying at 80 °C for 6 h, the catalyst could be reused directly without further purification, and it could be recycled for five runs without obvious loss of activity (Table 10).

Results and Discussion

Preparation and Characterization of SiO₂-DEA-DABCO-Pd⁰

Since 'naked' nanoparticles are kinetically unstable in solution, all preparation methods must use stabilizing agents which adsorb at the particle surface. Nanopalladium immobilized on the surface of a traditional dendrimer via steric stabilization effects (aggregation is prevented through the adsorption of large molecules) can prevent its agglomeration. To obtain more stable palladium nanoparticles, we designed a new DABCO functionalized dendrimer and used it as both steric and ligated stabilizing agents. The palladium nanocluster-stabilized model is illustrated in Scheme 1.

 SiO_2 -DEA-DABCO-Pd⁰ was obtained using the following strategy, which involves the coordination of an excess amount of PdCl₂ with the amine groups of a DABCO-terminated SiO₂-supported dendrimer and subsequent reduction of Pd²⁺ to Pd⁰ with hydrazine in ethanol.

Characterization of Catalyst

Figure 1 shows the FT-IR spectra of each generation of the SiO₂–DEA and DABCO-terminated SiO₂–DEA–DABCO. As can be seen from Fig. 1, the absorption band at 3480 cm⁻¹ was attributed to the — OH group. The relative increasing intensity of the above peaks indicates that diethanolamine was successfully grafted on to the surface of silica. The peak at 1083 cm⁻¹ was attributed to Si—O stretching.

The thermal stability of catalyst has a great effect on its catalytic activity and recyclability because the Suzuki–Miyaura and Mizoroki–Heck reactions are usually performed under heating conditions. The TGA of SiO₂–DEA–DABCO–Pd⁰ was recorded by heating the sample at the rate of $10 \,^\circ$ C min⁻¹ under a nitrogen atmosphere (Fig. 2). The TGA curve shows that the first weight loss occurs before $100 \,^\circ$ C, which was assigned to the release of adsorbed



Figure 1. FT-IR spectra for silica-supported dendrimers.



Figure 2. Weight loss as measured by TGA for SiO_2 -DEA-DABCO-Pd⁰.

water; another at 200 °C was related to the decomposition of organic ligands grafted on to the silica support. The evaluated temperature for graft removal indicates the high thermal stability for the SiO₂–DEA–DABCO–Pd⁰ catalyst. TGA of the catalyst systems demonstrated high thermal stability, with decomposition starting at around 250 °C under a nitrogen atmosphere.

Figure 3 shows powder XRD diffraction patterns of the SiO₂–DEA–DABCO–Pd⁰ catalyst. Three peaks are observed in the XRD pattern at 2 θ of 40, 47 and 69, attributed to 111, 200 and 220 facets of elemental palladium. Nanoparticle size was determined by using the Scherrer equation [$L = K\lambda/(\beta \cos \theta)$], where λ is the wavelength of the Cu-*K* radiation (0.154178 nm), θ is the Bragg angle, β is the FWHM (full width at half maximum) value of the respective peaks, and *K* is a constant of value 0.89. The size of nano-palladium particles was calculated to be 18–20 nm, which is consistent with the TEM test results. The less intense peak at 23–24 was most probably attributed to silica. To confirm the Pd content, the silica-supported catalyst was treated with concentrated HCl and HNO₃ to digest the Pd and then measured by inductively coupled plasma atomic emission spectrometry (ICP) analysis. The Pd content was determined to be 0.146 mmol g⁻¹.

The morphology of SiO_2 –DEA–DABCO–Pd⁰ and SiO_2 –DEA– DABCO were studied by SEM and TEM. A clear change in morphology was observed after anchoring palladium on to the polymer support. The TEM image of the SiO_2 –DEA–DABCO–Pd⁰ catalyst shows that the average size of the nanopalladium particles is in the range of



Figure 3. Powder XRD pattern of silica-supported palladium (0) dendrimers.



Figure 4. TEM image of (a) fresh catalyst and (b) recovered catalyst.

10–20 nm (Fig. 4a). The TEM image of the used catalyst indicates that the size and morphology of the nanopalladium have suffered slightly from agglomeration in the recovered catalyst after being reused five times (Fig. 4b).

With the goal of examining the catalytic performance of the catalyst, we report their use in Suzuki–Miyaura and Mizoroki–Heck reactions. The effects of base, solvent and temperature were investigated to optimize the reaction conditions. It was found that the Suzuki–Miyaura coupling reaction catalyzed by the silica–dendrimers–DABCO–Pd⁰ gave the highest yield when using 50% EtOH



Reaction conditions: aryl halide (1.0 mmol), phenylboronic acid (1.2 mmol), K_2CO_3 (2 mmol), silica–dendrimers–DABCO–Pd⁰ (3.0 mg, 0.04 mol%), solvent (2.0 ml) at 78 °C.



Reaction conditions: aryl halide (1.0 mmol), phenylboronic acid (1.2 mmol), base (2.0 mmol), silica–dendrimers–DABCO–Pd⁰ (3.0 mg, 0.04 mol%), 50% EtOH (2.0 ml) at 78 $^{\circ}$ C.



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Table 4. Effect of temperatures on the Suzuki reactions							
H ₃ CO-							
Entry	Temperature (°C)	Time (min)	Yield (%)				
1	20	50	67				
2	40	40	82				
3	60	30	95				
4	78	20	99				

Reaction conditions: aryl halide (1.0 mmol), phenylboronic acid (1.2 mmol), K_2CO_3 (2.0 mmol), silica–dendrimers–DABCO–Pd⁰ (3.0 mg, 0.04 mol%), 50% EtOH (2.0 ml).

as solvent (Table 2) and K₂CO₃ as base (Table 3) at 78 °C (Table 4). The optimal conditions for the Mizoroki–Heck reaction were also screened. As can be seen in Tables 5 and 6, DMF and K₃PO₄·3H₂O were found to be a suitable solvent and base. The optimal reaction temperature was 130 °C (Table 7).

To explore the scope of this reaction, we extended various aryl halides carrying either electron-withdrawing or electron-releasing constituents in aromatic rings with various phenylboronic acids for Suzuki–Miyaura reaction and with alkenes for Mizoroki–Heck reaction. In most cases, moderate to excellent yields were obtained. The results are listed in Tables 8 and 9. With regard to Suzuki couplings, the aryl halide-bearing substituent at the 2- position gave

Table 5. Effect of solvents on the Heck reactions							
H ₃ CO-{_}-I + {_}-/ <u>Cat.0.04mol</u> % H ₃ CO-{_}-/							
Entry	Solvent	Time (h)	Yield (%)				
1	DMF	3	98				
2	DMF:H ₂ O = 2:1	2	95				
3	DMF: $H_2O = 3:1$	2.5	85				
4	DMF: $H_2O = 4:1$	3	90				
5	DMF: $H_2O = 5:1$	3	83				

Reaction conditions: aryl halide (1.0 mmol), olefin (1.2 mmol), $K_3PO_4.3H_2O$ (2.0 mmol), silica-dendrimers-DABCO-Pd⁰ (3.0 mg, 0.04 mol%), solvent (2.0 ml) at 130 °C.

Table 6. Effect of bases on the Heck reactions					
H ₃ CO-					
Entry	Base	Time (h)	Yield (%)		
1	NaOH	3	83		
2	Bu₃N	3	95		
3	Et ₃ N	3	96		
4	K₃PO₄·3H₂O	3	98		
5	K ₂ CO ₃	3	83		
Reaction conditions: aryl halide (1.0 mmol), olefin (1.2 mmol), base (2 mmol), silica-dendrimers-DABCO-Pd ⁰ (3.0 mg, 0.04 mol%), DMF (2.0 ml) at 130 $^{\circ}$ C.					

Table 7.	Effect of temperatures on the Heck reactions					
			// Cat 0.041.0/			

Entry	Temperature (°C)	Time (h)	Yield (%)
1	100	10	75
ו ר	100	7	7.5 95
2	170	6	96
4	130	3	98
Reaction c (2.0 mmol) (2.0 ml)	onditions: aryl halide (1.0 mn , silica-dendrimers-DABCO	nol), olefin (1.2 mma –Pd ⁰ (3.0 mg, 0.04	ol), K ₃ PO ₄ .3H ₂ O 4 mol%), DMF

trace product (Table 8, entry 6). It is worth noting that the aryl chloride worked less efficiently than aryl iodide and aryl bromide and the best yields could be obtained using 0.08 mol% catalyst (Table 8, entries 12–15). In particular, as the electron-donating group at the *para* position (Table 8, entry 16), and the electronwithdrawing group at the *meta* position (Table 8, entry 17) on the aromatic ring of the aryl chloride, yields of Suzuki–Miyaura product were obtained in trace amounts. With regard to the Mizoroki–Heck reaction, similar results were also shown using aryl bromide as substrate (Table 9, entries 6 and 9).

For practical applications of a heterogeneous catalyst, reusability of the catalyst is a very important factor. To clarify this issue, catalytic

Table 8. Suzuki coupling reactions of benzene halide with phenylboronic $\operatorname{acid}^{\operatorname{a}}$

$$X + R^2 - B(OH)_2 \xrightarrow{Cat.0.04mol\%}_{K_2CO_3} R^1 - - R^2 - R^2$$

Enti	γ R ¹	R ²	Х	Time (h)	Yield (%)	m.p. (°C)	Product [ref.]
1	4-OCH ₃	Н	Br	0.5	99 ^a	86-88	1a 28
2	4-OH	Н	Br	0.5	67	164–166	1b 29
3	4-CHO	Н	Br	0.5	92	57–59	1c 30
4	$4-CO_2CH_3$	Н	Br	0.5	96	122-123	1d 31
5	3-NO ₂	Н	Br	0.5	97	59–60	1e 30
6	2-NO ₂	Н	Br	0.5	Trace	_	
7	4-NO ₂	Н	Br	0.5	99	112-113	1f 30
8	4-NO ₂	F	Br	0.5	85	126–127	1g 30
9	4-NO ₂	Cl	Br	0.5	93	138–139	1h 30
10	4-NO ₂	CH_3	Br	0.5	93	144–145	1i 30
11	4-NO ₂	OCH ₃	Br	0.5	94	104–106	1j 30
12	4-NO ₂	Н	Cl	24	89 ^b	112-113	1f 30
13	4-NO ₂	F	Cl	24	78 ^b	126–127	1g 30
14	4-NO ₂	OCH ₃	Cl	24	77 ^b	104–106	1j 30
15	4-CN	Н	Cl	24	86 ^b	153–154	1k 28
16	4-OCH ₃	Н	Cl	24	Trace ^b	86-88	1a 28
17	3-NO ₂	Н	Cl	36	Trace ^b	59–60	1e 30

^aReaction conditions: aryl halide (1.0 mmol), phenylboronic acid (1.2 mmol), K_2CO_3 (2.0 mmol), silica–dendrimers–DABCO–Pd⁰ (3.0 mg, 0.04 mol%), 50% EtOH (2.0 ml) at 78 °C.

^bReaction conditions: aryl halide(1.0 mmol), phenylboronic acid (1.2 mmol), K_3PO_4 ; $3H_2O$ (2.0 mmol), silica–dendrimers–DABCO–Pd⁰ (6 mg, 0.08 mol%), DMF (2.0 ml) at 130 °C.

Table 9. Heck coupling reactions of benzene halide with olefin							
$R^{1} - \begin{array}{@} & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & $							
Entry	R ¹	R ²	Х	Time (h)	Yield (%)	m.p. (°C)	Product [ref.]
1	4-OCH ₃	Ph	Ι	1	97	129–131	2a 32
2	4-Cl	Ph	L	1	84	127–128	2b 33
3	Н	Ph	L	1	98	120-121	2c 34
4	4-NO ₂	Ph	Br	2	89	155–157	2d 35
5	Н	Ph	Br	2	25	120-121	2c 34
6	4-OCH ₃	Ph	Br	2	Trace	129–131	2a 32
7	$4-CH_3$	Ph	Br	2	19	117–119	2e 35
8	$4-CO_2CH_3$	Ph	Br	2	78	157–159	2f 32
9	3-NO ₂	Ph	Br	2	Trace	109–110	—
10	4-NO ₂	Ph	Cl	5	61	155–157	2d 35
11	4-OCH ₃	$\rm CO_2 H$	L	10	84	171–172	2g 35
12	4-NO ₂	CO ₂ H	Br	10	83	283–285	2h 35

Reaction conditions: aryl halide (1.0 mmol), olefin (1.2 mmol), K_3PO_4 ·3H₂O (2.0 mmol), silica–dendrimers–DABCO–Pd⁰ (3.0 mg, 0.04 mol%), DMF (2.0 ml) at 130 °C.



Reaction conditions: aryl halide (1.0 mmol), phenylboronic acid (1.2 mmol), K₂CO₃ (2 mmol), silica–dendrimers–DABCO–Pd⁰ (3.0 mg, 0.04 mol%), 50% EtOH (2.0 ml) at 78 °C.

^alsolated yield based on *p*-bromoanisole.

^bTON (turnover number) = product (mol)/catalyst (mol).

^cTOF (turnover frequency) = TON/reaction time (min).

recycling experiments were carried out using a Suzuki–Miyaura reaction of 4-bromoanisole and phenylboronic acid as model reactions. After completion of the reaction, the catalyst could be conveniently and efficiently recovered from the reaction mixture by filtering, and can be used in the next run after washing with water and ethanol and drying. The results revealed that this catalyst can be reused without any modification for up to five cycles, and no significant loss of activity was observed. The recovery of catalyst shows high turnover number and turnover frequency in Suzuki–Miyaura reactions (Table 10).

Conclusion

In summary, new silica-supported third-generation dendrimers capped by DABCO group-stabilized palladium(0) nanoparticles

have been developed and used in the Suzuki–Miyaura and Mizoroki–Heck reactions, in which the dendrimer acted as a stabilizer for preventing the nanoparticles from agglomeration, as a recycling vehicle, as well as a ligand in catalysis. This novel catalyst exhibited high activity and stability for the coupling reactions. The advantages of this procedure are simple operation, short reaction time, trace amount of catalyst needed, good to excellent yield and environmental friendliness. Furthermore, it can be easily recovered and reused up to five times without any apparent loss of activity.

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