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Phosphine Dendrimer-Stabilized Palladium Nanoparticles, a Highly Active and Recyclable Catalyst for the Suzuki–Miyaura Reaction and Hydrogenation

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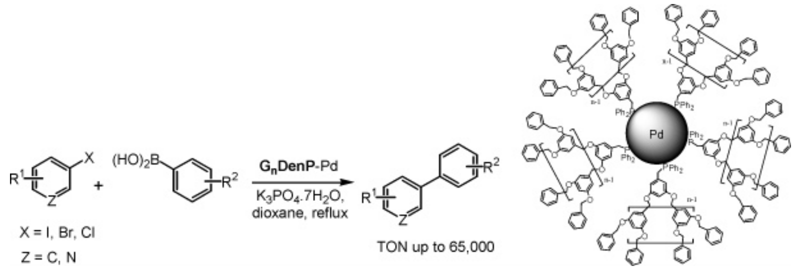
ABSTRACT



Phosphine dendrimer-stabilized palladium nanoparticles were synthesized and found to be highly effective for Suzuki coupling reactions, affording good to excellent product yields, high turnover number (up to 65 000), and excellent reusability (up to 9 catalytic runs). Furthermore, these Pd nanoparticles are efficient and selective catalysts for hydrogenations.

The application of metal nanoparticles in catalysis is an important frontier of research in recent years.[1] Due to their large surface-to-volume ratio, nanosized transition metal particles offer higher catalytic efficiency than larger materials. Since metal nanoparticles are unstable with respect to aggregation and precipitation to the bulk metal, stabilizers such as surfactants,[2] organic ligands,[3] polymers,[4] and dendrimers[1b] are used in their preparation to prevent agglomeration and to control the particle size. For the preparation of metal nanoparticles with small size, narrow size distribution, high stability, and tunable catalytic property,

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(1) (a) El-Sayed, M. A. *Acc. Chem. Res.* **2001**, *34*, 257. (b) Crooks, R. M.; Zhao, M. Q.; Sun, L.; Chechik, V.; Yeung, L. K. *Acc. Chem. Res.* **2001**, *34*, 181. (c) Roucoux, A.; Schulz, J.; Patin, H. *Chem. Rev.* **2002**, *102*, 3757. (d) Bell, A. T. *Science* **2003**, *299*, 1688. (e) Moreno-Mañas, M.; Pleixats, R. *Acc. Chem. Res.* **2003**, *36*, 638. (f) Studer, M.; Blaser, H.-U.; Exner, C. *Adv. Synth. Catal.* **2003**, *345*, 45. (g) Astruc, D.; Lu, F.; Aranzaes, J. R. *Angew. Chem., Int. Ed.* **2005**, *44*, 7852.

(2) (a) Yoon, B.-H.; Kim, H.; Wai, C. M. *Chem. Commun.* **2003**, 1040. (b) Isaacs, S. R.; Cutler, E. C.; Park, J.-S.; Lee, T. R.; Shon, Y.-S. *Langmuir* **2005**, *21*, 5689.

(3) (a) Strimbu, L.; Liu, J.; Kaifer, A. E. *Langmuir* **2003**, *19*, 483. (b) Lu, F.; Ruiz, J.; Astruc, D. *Tetrahedron Lett.* **2004**, *45*, 9443. (c) Nasar, K.; Fache, F.; Lemaire, M.; Draye, M.; Béziat, J. C.; Besson, M.; Galez, P. *J. Mol. Catal.* **1994**, *87*, 107. (d) Bönnemann, H.; Braun, G. A. *Chem. Eur. J.* **1997**, *3*, 1200. (e) Exner, C.; Pfaltz, A.; Studer, M.; Blaser, H.-U. *Adv. Synth. Catal.* **2003**, *345*, 1253. (f) Weare, W. W.; Reed, S. M.; Warner, M. G.; Hutchison, J. E. *J. Am. Chem. Soc.* **2000**, *122*, 12890. (g) Son, S. U.; Jang, Y.; Yoon, K. Y.; Kang, E.; Hyeon, T. *Nano Lett.* **2004**, *4*, 1147. (h) Moores, A.; Goettmanm, F.; Sanchez, C.; Floch, P. L. *Chem. Commun.* **2004**, 2842. (i) Tamura, M.; Fujihara, H. *J. Am. Chem. Soc.* **2003**, *125*, 15742. (j) Jansat, S.; Gómez, M.; Philippot, K.; Muller, G.; Guiu, E.; Claver, C.; Castillón, S.; Chaudret, B. *J. Am. Chem. Soc.* **2004**, *126*, 1592.

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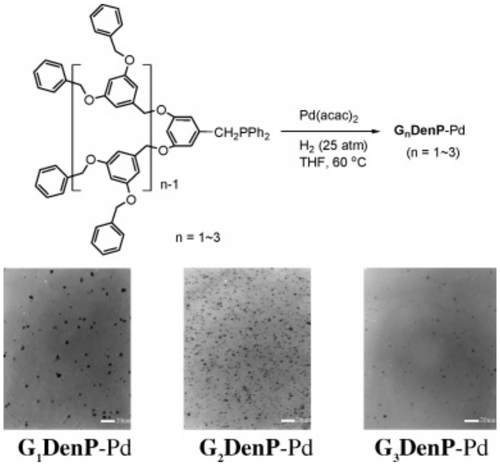
the use of protective ligands such as thiol,[3a,b] amine,[1f,3c−e] and phosphine[3f−j] has been extensively studied.

Encapsulation of metal nanoparticles inside dendrimers was originally demonstrated by the groups of Tomalia[5] and Crooks,[6] and has been attracting considerable attention.[1b,7] Polyamidoamines (PAMAMs)-encapsulated metal particles have been demonstrated to be effective catalysts for olefin hydrogenations[7a−d] and C−C coupling reactions,[7e−i] and the dendrimers acted as both templates and porous nanoreactors. Alternatively, a dendron with a coordinating group at the focal point can be used as a capping ligand for the preparation and stabilization of metal nanoparticles.[8] In sharp contrast to the small molecule ligand-stabilized nanoparticles, limited dendritic ligands could be bound to the metallic core due to the sterically demanding dendritic structure. Thus, a substantial fraction of the surface area of the core metal particle is activated and available for participation in catalytic reactions. These properties could promote the activity of the nanoparticle catalysts. However, the successful examples of such metal nanoparticles reported in catalysis are rather limited.[8e] Recently, Fox et al. reported the first example of thiol dendrimer-stabilized Pd nanoparticles using a third-generation Fréchet-type dendrimer with a disulfide group at the core. Although it could efficiently catalyze Heck and Suzuki coupling reactions, no activity was observed for the hydrogenation reaction. As part of our continuing interest in the synthesis of dendritic phosphines and their applications in catalysis,[9] we report here the first example of phosphine dendrimer-stabilized Pd nanoparticles and their applications in the Suzuki coupling reaction and hydrogenation, in which the dendrimer acted as a stabilizer, a recycling vehicle, as well as a ligand in catalysis.

Fréchet-type polyaryl ether dendrons were chosen for this study owing to their chemical inertness and inability to coordinate palladium.[10] The three different generation phosphine ligands $\mathbf{G}_n\mathbf{DenP}$ ($n = 1-3$) were synthesized by reaction of the corresponding dendritic bromides with $KPPh_2$ according to the reported procedure with some modifications.[11] The synthetic route to the phosphine dendrimer-stabilized Pd nanoparticles (referenced as $\mathbf{G}_n\mathbf{DenP}$-Pd, $n = 1-3$) was outlined in Figure 1. Reduction of $Pd(acac)_2$ with hydrogen was successfully carried out in THF in the presence of the dendritic ligands, giving $\mathbf{G}_n\mathbf{DenP}$-Pd as black powders.[12] The formation of Pd nanoparticles was confirmed by transmission electron microscopy (TEM) and ^{31}P NMR spectra.[13] The diameter and size distribution of the nanosized catalysts were examined by TEM, which ranged from 5.0 ± 0.4 to 4.6 ± 0.5 to 3.2 ± 0.5 nm, decreasing with increase of the generation of the dendritic ligands. These dendrimer catalysts are soluble in common nonprotic organic solvents such as toluene, THF, and dichloromethane, but insoluble in methanol.



$\mathbf{G}_1\mathbf{DenP}$-Pd $\mathbf{G}_2\mathbf{DenP}$-Pd $\mathbf{G}_3\mathbf{DenP}$-Pd

Figure 1. Synthesis and TEM images of $\mathbf{G}_n\mathbf{DenP}$-Pd catalysts.

The catalytic activity of $\mathbf{G}_n\mathbf{DenP}$-Pd was examined in the Suzuki coupling reactions. This choice was based on the fact that such reaction provides a powerful tool for the synthesis of biaryls, which are found in many natural and synthetic

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(4) (a) Li, Y.; Hong, X. M.; Collard, D. M.; El-Sayed, M. A. *Org. Lett.* **2000**, *2*, 2385. (b) Ramarao, C.; Ley, S. V.; Smith, S. C.; Shirley, I. M.; DeAlmeida, N. *Chem. Commun.* **2002**, 1132. (c) Narayanan, R.; El-Sayed, M. A. *J. Am. Chem. Soc.* **2003**, *125*, 8340. (d) Chauhan, B. P. S.; Rathore, J. S.; Bandoo, T. *J. Am. Chem. Soc.* **2004**, *126*, 8493. (e) Liu, Y. B.; Khemtong, C.; Hu, J. *Chem. Commun.* **2004**, 398. (f) Kim, S. W.; Kim, S.; Tracy, J. B.; Jasanoff, A.; Bawendi, M. G. *J. Am. Chem. Soc.* **2005**, *127*, 4556. (g) Nishio, R.; Sugiura, M.; Kobayashi, S. *Org. Lett.* **2005**, *7*, 4831.

(5) Balogh, L.; Tomalia, D. A. *J. Am. Chem. Soc.* **1998**, *120*, 7355.

(6) Zhao, M. Q.; Sun, L.; Crooks, R. M. *J. Am. Chem. Soc.* **1998**, *120*, 4877.

(7) For selected recent examples, see: (a) Niu, Y.; Yeung, L. K.; Crooks, R. M. *J. Am. Chem. Soc*. **2001**, *123*, 6840. (b) Ooe, M.; Murata, M.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *Nano Lett.* **2002**, *2*, 999. (c) Scott, R. W. J.; Datye, A. K.; Crooks, R. M. *J. Am. Chem. Soc*. **2003**, *125*, 3708. (d) Jiang, Y.; Gao, Q. *J. Am. Chem. Soc*. **2006**, *128*, 716. (e) Rahim, E. H.; Kamounah, F. S.; Frederiksen, J.; Christensen, J. B. *Nano Lett.* **2001**. *1*, 499. (f) Li, Y.; El-Sayed, M. A. *J. Phys. Chem. B* **2001**, *105*, 8938. (g) Pittelkow, M.; Moth-Poulsen, K.; Boas, U.; Christensen, J. B. *Langmuir* **2003**, *19*, 7682. (h) Narayanan, R.; El-Sayed, M. A. *J. Phys. Chem. B* **2004**, *108*, 8572. (i) Garcia-Martinez, J. C.; Lezutekong, R.; Crooks, R. M. *J. Am. Chem. Soc*. **2005**, *127*, 5097.

(8) For selected examples, see: (a) Chechik, V.; Crooks, R. M. *Langmuir* **1999**, *15*, 6364. (b) Wang, R.; Yang, J.; Zheng, Z.; Carducci, M. D.; Jiao, J.; Seraphin, S. *Angew. Chem., Int. Ed.* **2001**, *40*, 549. (c) Kim, M. K.; Jeon, Y. M.; Jeon, W. S.; Kim, H. J.; Hong, S. G.; Park, C. G.; Kim. K. *Chem. Commun.* **2001**, 667. (d) Gopidas, K. R.; Whitesell, J. K.; Fox, M. A. *J. Am. Chem. Soc*. **2003**, *125*, 6491. (e) Gopidas, K. R.; Whitesell, J. K.; Fox, M. A. *Nano Lett.* **2003**, *3*, 1757. (f) Guo, W.; Li, J. J.; Wang, Y. A.; Peng, X. *J. Am. Chem. Soc*. **2003**, *125*, 3901. (g) Love, C. S.; Chechik, V.; Smith, D. K.; Brennan, C. *J. Mater. Chem.* **2004**, *14*, 919.

(9) (a) Fan, Q. H.; Li, Y. M.; Chan, A. S. C. *Chem. Rev.* **2002**, *102*, 3385. (b) Fan, Q. H.; Chen, Y. M.; Chen, X. M. *Chem. Commun*. **2000**, 789. (c) Deng, G. J.; Fan, Q. H.; Chen, X. M. *Chem. Commun*. **2002**, 1570. (d) Yi, B.; Fan, Q. H.; Deng, G. J. *Org. Lett.* **2004**, *6*, 1361. (e) Deng, G. J.; Li, G. R.; Zhu, L. Y.; Zhou, H. F.; He, Y. M.; Fan, Q. H.; Shuai, Z. G. *J. Mol. Catal. A*: *Chem.* **2006**, *244*, 118.

(10) Hawker, C. J.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1990**, *112*, 7638.

(11) Catalano, V. J.; Parodi, N. *Inorg. Chem.* **1997**, *36*, 537.

(12) $\mathbf{G}_n\mathbf{DenP}$-Pd dendrimers were synthesized as follows: A 25-mL glass-lined stainless autoclave with a magnetic stirring bar was charged with 20 mg of $Pd(acac)_2$ (0.066 mmol), 2 equiv of $\mathbf{G}_n\mathbf{DenP}$, and 10 mL of dried, degassed THF. The autoclave was pressurized with hydrogen to 25 atm, and the mixture was stirred at 60 °C for 18 h. After the H_2 was carefully released, the solvent was removed under reduced pressure. The resulting black powders were further purified by sonication in ethanol more than 20 times. The Pd content of $\mathbf{G}_n\mathbf{DenP}$-Pd was determined by ICP-XRF as follows: $\mathbf{G}_1\mathbf{DenP}$-Pd, 6.46%; $\mathbf{G}_2\mathbf{DenP}$-Pd, 5.96%; $\mathbf{G}_3\mathbf{DenP}$-Pd, 5.15%.

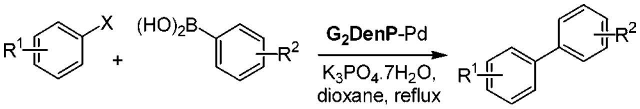
(13) For details, see the Supporting Information.

products.[14] Furthermore, the coupling reactions are generally carried out at high temperature and in the presence of a base, which requires a catalyst with high stability.

First, the coupling reaction of bromobenzene with phenylboronic acid in the presence of **G_2DenP**-Pd was studied to optimize the reaction conditions. A variety of solvents and bases were screened (see the Supporting Information), and the solvent/base combination of 1,4-dioxane/K_3PO_4•$7H_2O$ was finally found to be the best.

On the basis of the optimized reaction conditions, the coupling reactions between a range of aryl halides (I and Br) and several aryl boronic acids were carried out to explore the general effectiveness of the **G_2DenP**-Pd catalyst. In all cases (Table 1), the corresponding biphenyl products were obtained in good to excellent yields with low catalyst loading (0.06 mol %). No obvious difference in the catalytic activity was observed when aryl iodides or aryl bromides were used in the reactions. In contrast, when PAMAM-encapsulated Pd nanoparticles were used as catalyst, aryl bromides reacted only at elevated temperature (153 °C in DMF).[7g] For electron-deficient arylboronic acids, the yields decreased slightly (entries 16−19). Notably, the sterically hindered ortho-substituted aryl bromides also gave good to excellent yields (entries 9, 11, 13, 15, 17, and 19).

Table 1. The **G_2DenP**-Pd-Catalyzed Coupling Reactions of Various Aryl Halides with Arylboronic Acid[a]



entry	R^1	X	R^2	yield (%) [b]
1	H	I	H	99
2	p-$COOCH_3$	I	H	quant
3	p-OH	I	H	98
4	H	Br	H	97
5	p-$COCH_3$	Br	H	99
6	p-$COOCH_3$	Br	H	quant
7	m-$COOCH_3$	Br	H	99
8	p-CHO	Br	H	99
9	o-CHO	Br	H	97
10	m-NO_2	Br	H	99
11	o-NO_2	Br	H	99
12	p-CH_3	Br	H	98
13	o-CH_3	Br	H	96
14	p-$COOCH_3$	Br	p-CH_3	quant
15	o-CH_3	Br	p-CH_3	98
16	p-$COOCH_3$	Br	p-$COCH_3$	92
17	o-CH_3	Br	p-$COCH_3$	90
18	p-$COOCH_3$	Br	p-F	88
19	o-CH_3	Br	p-F	86[c]

[a] 1.25 mmol of aryl halide, 1.875 mmol of arylboronic acid, 2.5 mmol of K_3PO_4•$7H_2O$, 0.06 mol % of **G_2DenP**-Pd, dioxane, reflux, 20 h. [b] Isolated yield. Purity was confirmed by ^{1}H NMR. [c] Trace amount of homocoupling product was found.

Next, the coupling reaction of bromobenzene with phenylboronic acid was used to assess the minimum amount of catalysts (Table 2). In the presence of 0.003 mol % of **G_2DenP**-Pd, the reaction proceeded smoothly upon prolonged reaction time, giving 89% yield. Notably, the third generation catalyst **G_3DenP**-Pd was reserved under air atmosphere for three months, and found to be very active under rather low catalyst loading (0.001 mol %). The maximum TON thus reached is 65 000 (entry 5), to our knowledge, which is the highest TON obtained so far for the preformed Pd nanoparticles.[4e,7g] In contrast, when using the most commonly employed catalyst $Pd(PPh_3)_4$, the reaction provided much lower yields (15%) even under 0.5 mol % catalyst loadings, and palladium black was observed from the beginning of the reaction.[15]

Table 2. The Minimum Amount of Catalyst[a]

entry	**G_2DenP**-Pd (mol %)	time (h)	yield (%)[b]	TON
1	0.03	20	97 (15)[c]	3 250
2	0.012	20	52	4 330
3	0.012	72	95	7 900
4	0.003	72	89	29 750
5[d]	0.001	96	65	65 000

[a] 1.0 equiv of aryl bromide, 1.5 equiv of phenylboronic acid, 2.0 equiv of K_3PO_4•$7H_2O$, dioxane, reflux, 20 h. [b] Isolated yield. Purity was confirmed by ^{1}H NMR. [c] Data in parentheses was obtained by using 0.5 mol % $Pd(PPh_3)_4$ as catalyst. [d] **G_3DenP**-Pd was stored in air for 3 months before use.

Encouraged by these excellent results, we decided to further investigate the coupling between aryl or heteroaryl chlorides and several aryl boronic acids, which are considerably more challenging reactions.[16] The possible dendrimer generation effect on the catalytic activity was first studied with 2 mol % **G_nDenP**-Pd (n = 1−3) catalyst (Table 3, entries 1−3). It was found that the catalytic activity increased with increasing generation of the dendrons. The generation effect was most pronounced between the second and the third generations. Then, several deactivated or sterically hindered ortho-substituted aryl chlorides were employed in the **G_3DenP**-Pd catalyzed coupling reaction with boronic acids. Good yields were achieved with 2 mol % catalyst (entries 4−9). To our delight, the coupling reactions of pyridyl bromides, even pyridyl chlorides with phenylboronic acid, proceeded smoothly with good yields (entries 10−14). To our knowledge, these were the best results so far obtained for the polymer- and dendrimer-stabilized Pd nanoparticles.[17]

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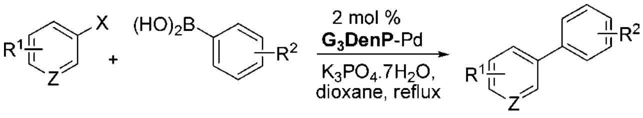
(14) (a) Miyaura, N. In *Metal-Catalyzed Cross-Coupling Reactions*; de Meijere, A., Diederich, F., Eds.; Wiley-VCH: New York, 2004, Chapter 2. (b) Suzuki, A. In *Handbook of Organopalladium Chemistry for Organic Synthesis*; Negishi, E., Ed.; Wiley-Interscience: New York, 2002; Chapter III.2.2.

(15) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457.

(16) Guram, A. S.; King, A. O.; Allen, J. G.; Wang, X.; Schenkel, L. B.; Chan, J.; Bunel, E. E.; Faul, M. M.; Larsen, R. D.; Martinelli, M. J.; Reider P. J. *Org. Lett.* **2006**, *8*, 1787.

(17) For the activation of aryl chlorides by Pd nanoparticles in ionic liquid, see: Calo, V.; Nacci, A.; Monopoli, A.; Montingelli, F. *J. Org. Chem.* **2005**, *70*, 6040.

Table 3. The **G$_3$DenP**-Pd-Catalyzed Coupling Reactions of Arylboronic Acid with Various Aryl Chlorides and Heteroaryl Halides[a]



entry	X	Z	R^1	R^2	yield (%)[b]
1	Cl	C	*p*-COOCH$_3$	H	51[c]
					66[d]
					94
2	Cl	C	*p*-CHO	H	48[c]
					62[d]
					90
3	Cl	C	*o*-CHO	H	44[c]
					59[d]
					88
4	Cl	C	*p*-CH$_3$	H	83
5	Cl	C	*o*-COCH$_3$	H	81
6	Cl	C	*o*-CH$_3$	H	80
7	Cl	C	*o*-CH$_3$	*p*-CH$_3$	88
8	Cl	C	*o*-CH$_3$	*p*-COCH$_3$	86
9	Cl	C	*o*-CH$_3$	*p*-F	84
10	2-Br	N	H	H	89
11	3-Br	N	H	H	92
12	2-Cl	N	H	H	82
13	4-Cl	N	H	H	84
14	6-chloroquinoline			H	90

[a] 0.75 mmol of aryl chlorides (or heteroaryl halides), 1.125 mmol of arylboronic acid, 1.5 mmol of K$_3$PO$_4$•7H$_2$O, dioxane, reflux, 48 h. [b] Isolated yield. Purity was confirmed by ^{1}H NMR. [c] **G$_1$DenP**-Pd was used as catalyst. [d] **G$_2$DenP**-Pd was used as catalyst.

The high efficiency of the **G$_3$DenP**-Pd catalyst was probably due to the following factors: (1) a substantial fraction of the surface of the Pd nanoparticles was activated and (2) the phosphine dendrimers acted as ligands to enhance the catalytic activity.[4g]

Having established the efficacy of the **G$_n$DenP**-Pd phosphine dendrimer-stabilized Pd nanoparticles, we then investigated their recyclability. Although, as homogeneous catalysts, the soluble polymer- and dendrimer-stabilized noble metal nanoparticles showed unique catalytic characteristics, they still suffered from difficulties in separation and reuse.[1b,4a,c,7g] For the recycling experiment, the coupling reaction of 4-hydroxyphenyl iodide with phenylboronic acid in the presence of **G$_3$DenP**-Pd was chosen as the standard reaction. Upon completion of the reaction, the catalyst was quantitatively precipitated by the addition of methanol, and reused at least eight times without any loss in activity in the first four runs and with reducing yields from the fifth run. High yield also could be achieved at prolonged time. The leaching of palladium was measured by ICP-XRF at the second and third cycles, and found to be no more than 0.84% (8.1 ppm) and 0.37% (3.6 ppm), respectively. To further expand the catalytic scope of the phosphine dendrimer-stabilized Pd nanoparticles, we investigated the catalytic hydrogenation of a variety of olefins. The preliminary results are summarized in Table 5. In all cases, the hydrogenation reactions were carried out in a homogeneous manner, giving almost quantitative yields and high selectivity. Unlike the reported thiol dendrimer-stabilized Pd nanoparticles, no palladium aggregation was observed.[8e]

Table 4. Recovery and Recycling of **G$_3$DenP**-Pd (0.2 mol %)[a]

	run 1	run 2	run 3	run 4	run 5	run 6	run 7	run 8	run 9
Y (%)[b]	98	95	96	97	79	94	95	94	75

[a] For catalyst recycling, see the Supporting Information. Reaction time: runs 1−5, 20 h; runs 6−9, 48 h. [b] Isolated yield. Purity was confirmed by ^{1}H NMR.

Table 5. Hydrogenation of Several Olefin Substrates[a]

substrates	H$_2$ (atm)	temp (°C)	time (h)	yield (%)[b]
styrene	5	40	4	100
phenylacetylene	5	60	5	99[c]
cyclohexene	15	60	6	100
1-dodecene	5	60	3	100
p-nitrotoluene	30	80	12	100
2-cyclohexen-1-one	15	60	8	99[d]

[a] Hydrogenations were carried out in CHCl$_3$ with 0.5 mol % of **G$_2$DenP**-Pd. [b] Based on GC analysis. [c] 1% product was styrene. [d] The main product was cyclohexanone.

In conclusion, we have successfully prepared for the first time a series of phosphine dendrimer-stabilized Pd nanoparitcles as recyclable highly effective catalysts for Suzuki coupling reactions and hydrogenations. It was demonstrated that the dendritic wedges served multiple functions: as a stabilizer for keeping the nanoparticles from aggregating; as a ligand for adjusting the catalytic activity; and as a vehicle for facilitating the catalysts recycling. We are currently studying the synthesis of chiral phosphine dendrimer-stablized metal nanoparticles and their applications in enantioselective organic reactions.

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Supporting Information Available: General experimental methods, preparation and characterization data for dendritic ligands, ^{31}P NMR spectral data for the **G$_3$DenP** ligand, the **G$_3$DenP**-Pd nanoparticle, and the **G$_3$DenP**-Pd(0) complex, and ^{1}H NMR spectral data for the coupling products. This material is available free of charge via the Internet at http://pubs.acs.org.

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