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A Highly Active and Recyclable Catalyst: Phosphine Dendrimer-Stabilized Nickel Nanoparticles for the Suzuki Coupling Reaction

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Abstract: We report here the first dendritic phosphine-stabilized nickel nanoparticles, which can be prepared from nickel(II) chloride, a third generation phosphine dendrimer and the surfactant tetraoctylammonium bromide (TOABr) by two-phase reduction using sodium borohydride. The resulting nickel nanoparticles are found to be a highly active and recyclable catalyst for Suzuki coupling reactions, especially those extended to aryl chloride substrates, affording the biaryls in moderate to good yields.

Keywords: nickel nanoparticles; phosphine dendrimers; recyclable catalyst; Suzuki coupling; twophase reduction

As an important frontier of chemical research for several decades, nanosized transition metal particles have attracted much attention in catalysis, which profits from the higher catalytic efficiency offered by their large surface-to-volume ratio as compared to bulky materials.^[1] Recently, a number of stabilization methods has been reported to prevent the aggregation and precipitation of metal nanoparticles, such as using surfactants,^[2] organic ligands,^[3] polymers,^[4] and dendrimers.^[1b,5] Dendrimers as highly branched, three-dimensional macromolecules, can encapsulate metal nanoparticles, or serve as a wedge, and thus control the size, shape, solubility, and catalytic activity of the corresponding particles. Although some achievements have been made in the dendrimer-encapsulated nanoparticles (as so-called DENs), such as Cu,^[6] Pd,^[7] Au,^[8] Rh,^[7b,9] Pt,^[7a,9a] or Ag,^[10] etc., reports on nickel nanoparticles are very limited.^[11] It has been demonstrated that dendrons with coordinating groups at the focal point can be used as capping ligands for the preparation and stabilization of metal nanoparticles. In contrast to the small molecule ligand-stabilized nanoparticles, only a limited number of dendritic ligands can be bound to metallic cores due to the sterically demanding dendritic structure. Therefore, more unpassivated surfaces are susceptible to catalytic transformations, which eventually promote the catalytic activity of the metal nanoparticles.^[12] However, phosphine dendrimers-stabilized nickel nanoparticles have as yet not been investigated. Since nickel-based molecular catalysts exhibited superior activities compared to palladium or ruthenium analogues in some catalytic reactions.^[13] we hypothesized that the dendrimer-stabilized nickel nanoparticles could be a better option for coupling reactions over other investigated metal nanoparticles. As part of our continuing interest in the synthesis of stabilized metal nanoparticles and easily recyclable catalysts,^[12,14] herein we report the first preparation of phosphine dendrimer-stabilized nickel nanoparticles, and an investigation of their highly active catalytic performance in the Suzuki coupling reaction.

Our previous related work demonstrated that the third-generation Fréchet-type dendrimer was the best stabilizer for palladium nanoparticles in carboncarbon coupling reactions, we thus employed the same ligand for preparing nickel nanoparticles. Firstly, the third-generation phosphine dendrimer (G₃DenP) was synthesized by reaction of dendritic bromide with commercial KPPh₂ according to the procedures reported.^[14] Then, the G₃DenP ligand and nickel precursor in the presence of TOABr were *in situ* reduced by NaBH₄ in toluene-water biphasic mixture,^[15] giving phosphine dendrimer-stabilized nickel nanoparticles (**G₃DenP**-Ni) as black powders (Figure 1). The solubility of the nickel nanoparticles is determined by the Fréchet-type dendritic shell, they are well soluble in



Figure 1. The preparation of G_3 DenP-Ni by two-phase reduction (*bottom*), and TEM image of the nickel nanoparticles with distributions (*top*) (scale bar = 8 nm).

common non-protic organic solvents such as toluene, THF, acetone and dichloromethane, but insoluble in hexanes, ethyl ether, or alcohol solvents. Further purifications were repeated several times in a Soxhlet extractor according to Schiffrin's method to remove residual surfactants.^[16] The resulting **G₃DenP**-Ni was characterized by TEM and ICP-XRF: the diameter of this nano-sized catalyst was found to be 3.5 ± 0.5 nm, and the nickel content was determined as 3.10 wt%. We also investigated the content of nickel and dendrons by using an elemental analysis method. A similar result (3.22 wt%) was obtained for nickel content as compared to that obtained from ICP-XRF (see Supporting Information for details). The molar ratio of nickel to dendrons was calculated as 1:1 based on the elemental analysis. Furthermore, the concentration of the element N was below the lowest detection limit, which indicated the complete removal of surfactant TOABr from the nickel nanoparticles.

With the synthesized catalyst in hand, we studied the coupling reaction of bromobenzene with phenylboronic acid to optimize the reaction conditions. Under the same optimized conditions with G_3DenP -Pd catalyst, 1 mol% nickel nanoparticles afforded 99% yield of biphenyl product within 20 h (Table 1, entry 1). The coupling catalysis proceeded smoothly

	$ \begin{array}{c} & & \\ & & $							
Entry	Catalyst loading	Solvent/base	Time [h]	Temperature [°C]	Yield [%] ^[b]			
1	1 mol%	dioxane/K ₃ PO ₄ ·7H ₂ O	20	100	99			
2	1 mol%	dioxane/K ₃ PO ₄ ·7H ₂ O	20	80	98			
3	1 mol%	THF/K ₃ PO ₄ ·7H ₂ O	20	60	98			
4	1 mol%	THF/Et ₃ N	20	60	77			
5	1 mol%	THF/DBU	20	60	95			
6	1 mol%	THF/NaOAc	20	60	49			
7	1 mol%	toluene/K ₃ PO ₄ ·7H ₂ O	20	60	< 10			
8	0.1 mol%	THF/K ₃ PO ₄ ·7H ₂ O	20	60	98			
9	0.01 mol%	THF/K ₃ PO ₄ ·7H ₂ O	20	60	97			
10	0.001 mol%	THF/K ₃ PO ₄ ·7H ₂ O	36	60	99			
11 ^[c]	0.1 mol%	THF/K ₃ PO ₄ ·7H ₂ O	20	60	N.R.			
12 ^[d]	0.1 mol%	THF/K ₃ PO ₄ ·7H ₂ O	20	60	35			

Table 1. Reaction condition optimization for the coupling of bromobenzene and phenylboronic acid catalyzed by G_3 DenP-Ni.^[a]

^[a] 1 mmol bromobenzene, 1.5 mmol phenylboronic acid, 2 mmol base, 10 mL solvent.

^[b] Isolated yield based on aryl halide.

^[c] 0.1 mol% NiCl₂ (or Ni(acac)₂) was used instead of G_3 DenP-Ni.

^[d] 0.1 mol% Ni(acac)₂, 0.1 mol% G₃DenP ligand were used instead of G₃DenP-Ni.

under milder conditions with lower temperature, and THF also proved to be viable solvent as alternative to toluene (entries 2, 3, and 7). Tripotassium phosphate heptahydrate was found to be the best base compared with Et₃N, DBU or NaOAc (entries 3-6). Notably, even when the catalyst loading was decreased to 0.001 mol%, the reaction still performed smoothly upon a prolonged reaction time of up to 36 h, giving a 99% yield, thus the maximum TON reached 99,000 (entry 10). To the best of our knowledge, this should be the highest TON for the performed nickel nanoparticles or nickel complexes in Suzuki coupling reactions.^[17,18] Although the comparision with mononuclear nickel complexes could not exclude the possibility of homogeneous catalysis (entry 12), a major catalytic cycle on nickel nanoparticle surface could be deduced from the differentiated yield. To our delight, the G₃DenP-Ni did exhibit much higher catalytic activities than the G₃DenP-Pd catalyst with lower reaction temperature and higher TON (60°C, 99,000 vs. 110°C, 65,000, respectively).^[12,14]

In an effort to explore the scope and versatility of the nano-sized nickel catalyst, the coupling reactions between a range of aryl bromides and various arylboronic acids were carried out under the optimized conditions. For all the cases in Table 2, the corresponding biaryl products were obtained in excellent yields with 0.01 mol% **G₃DenP**-Ni within 24 h. The coupling reactions between aryl bromides bearing electron-withdrawing substituents with phenylboronic acid were found to give near quantitative yields (entries 1–6). For aryl bromide substrates with electron-rich groups like *meta*-methoxy, *ortho*-methoxy, *meta*-methyl, *meta*-methyl, and *para*-amino, the coupling products were isolated with excellent yield after longer reaction time (entries 7–10, 12). Interestingly, when the

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Table 2. The coupling reactions of aryl bromides with various arylboronic acids catalyzed by G_3DenP -Ni.^[a]

	$\int_{-\infty}^{-Br} R^2 \frac{\pi}{\mu} \int_{-\infty}^{-Br} R^2 \frac{\pi}{\mu}$	0.01 (OH) ₂ G ₃ De THF, K ₃ P	mol% enP-Ni ⊡0 ₄ •7 H ₂ O, R ¹	
		60	°C	~
Entry	\mathbb{R}^1	R ²	Time [h]	Yield [%] ^[b]
1	<i>p</i> -COOMe	Н	8	quant.
2	<i>m</i> -COOMe	Н	8	<u>9</u> 9
3	o-CHO	Н	10	99
4	$o-NO_2$	Н	8	99
5	$p-NO_2$	Н	8	quant.
6	<i>p</i> -COCH ₃	Н	12	<u>9</u> 9
7	<i>m</i> -OCH ₃	Н	20	98
8	p-OCH ₃	Н	24	99
9	o-CH ₃	Н	18	98
10	p-CH ₃	Н	18	97
11	o,o'-dimethyl	Н	20	95
12	p-NH ₂	Н	18	96
13	<i>p</i> -COOMe	$p-CH_3$	6	99
14	<i>p</i> -COOMe	p-COCH ₃	10	98
15	<i>p</i> -COOMe	<i>p</i> -F	15	95
[a] 1 m	mol and bro	mida 15 m	mol arulh	oronia agid

^{a)} 1 mmol aryl bromide, 1.5 mmol arylboronic acid, 0.01 mol% **G₃DenP**-Ni, 2 mmol K_3PO_4 ·7 H₂O, 10 mL THF, 60 °C.

^[b] Isolated yield based on aryl halide.

Table 3. The coupling reactions of aryl chlorides with various arylboronic acids catalyzed by G₃DenP-Ni.^[a]



r.1					<u> </u>
14	o,o'-dimethyl	o,o'-dimethyl	30	86	
13	o-CH ₃	p-F	30	89	
12	o-CH ₃	p-COCH ₃	24	91	
11	o-CH ₃	p-CH ₃	20	96	
10	o,o'-dimethyl	Η	30	95	
9	p-CH ₃	Н	24	93	

[a] 1 mmol aryl chloride, 1.5 mmol arylboronic acid, 0.1 mol% G₃DenP-Ni, 2 mmolK₃PO₄·7H₂O, 10 mL THF, 60°C.

^[b] Isolated yield based on aryl halide.

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sterically hindered ortho-substituted aryl bromides were used, the yield only decreased slightly, also giving good to excellent yields (entries 3, 4, 9, and 11). The high activities of the catalyst were further proved by the reaction of methyl 4-bromobenzoate with electron-donating and electron-deficient arylboronic acids (entries 13-15).

To further investigate the general effectiveness of this nano-sized catalyst, we extended the substrates to aryl chlorides, which are considerably more challenging and readily accessible than aryl iodides and bromides. Notably, there is no report on aryl chloride substrates catalyzed by nickel nanoparticles up to now. With only 0.01 mol% G₃DenP-Ni as catalyst, the coupling reaction of chlorobenzene with phenylboronic acid was found to be sluggish. However, when we enhanced the catalyst loading to 0.1 mol%, the catalytic activity was substantially improved. As illustrated in Table 3, reactions between phenylboronic acid and a variety of electron-deficient substrates like para-ester, ortho-aldehyde, para-nitro and para-acetyl aryl chlorides, proceeded smoothly, giving the biaryl products in excellent yields (entries 1-5). Even for the substrates with electron-donating groups or sterically hindred ortho-substitutients, the coupling reaction went to completion within 30 h, providing the desired products in more than 90% yields (entries 6-10). The effectiveness of arylboronic acids were also examined by reacting them with ortho-methylchlorobenzene to afford excellent yields, among which the yield dropped slightly to 89% for the para-fluoro substrate (entry 13). To our delight, the coupling reaction performed well when a more sterically hindred aromatic chloride and boronic acid were employed (entry 14).

As described above, the dendrtic shell endowed special solubility to the stabilized nanosized catalyst. This would be an ideal solution to overcome the difficulties in catalyst separation and reusage. For the recycling experiment, we selected the coupling of methyl 4-chlorobenzoate with phenylboronic acid in the presence of 0.1 mol% G₃DenP-Ni as standard reaction. Upon the completion of coupling reaction, the catalyst was quantitatively precipitated by adding dropwise a large amount of methanol, and then collected by centrifugation. The recovered catalyst was used directly in the next run, which could be reused for six runs without any loss in activity within the same reaction time, and the yields were 96%, 95%, 95%, 96%, 97% and 95%, respectively. The leaching rate of nickel was monitored by ICP-XRF for 1st, 2nd, and 3rd cycles, and was found to be lower than 0.73% (~7 ppm).

In summary, the novel phosphine dendrimer-stabilized nickel nanoparticles were prepared from nickel(-II) chloride, a third-generation phosphine dendrimer and the surfactant TOABr by a two-phase reduction method using NaBH₄. The resulting G₃DenP-Ni exhibited highly catalytic efficiency in the Suzuki coupling of aryl bromides and aryl chlorides with arylboronic acids, in all the cases, good to excellent yields were obtained. Furthermore, the Fréchet-type dendritic shell facilitated recovery and recycle of the nanosized nickel catalyst, which was reused for six runs without any loss in activity. We are presently investigating the application of this efficient catalyst to a novel intermolecular cyclization.

Experimental Section

Typical Procedure for the Suzuki Coupling Reactions and Catalyst Recycling

To a 25-mL flask under argon was added aryl halide (1 mmol), arylboronic acid (1.5 mmol), $K_3PO_4 \cdot 7H_2O$ (2 mmol), 0.1 mol% G₃DenP-Ni and 10 mL degassed THF. The reaction mixture was then heated to 60°C and stirred for the time listed in Table 2 and Table 3. After all of the volatiles were removed under reduced pressure, the residue was poured into 50 mL methanol to extract the products and precipitate the catalyst. The recovered catalyst was washed with 5 mL water for three times, dried under vacuum, and can then be used directly in the next run. The coupling products in the combined methanol solution were collected and purified by flash chromatography.

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