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Modular metal–carbon stabilized palladium nanoparticles for the catalytic hydrogenation of *N*-heterocycles

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ABSTRACT

We report here the first modular metal–carbon stabilized palladium nanoparticles based on binaphthyl scaffolds, which can be prepared from palladium salts and substituted binaphthyl diazonium salts in homogeneous system through direct reduction using sodium borohydride. The resulting palladium nanoparticles subjected to the electron density of modular moieties are found to be novel and efficient catalysts for the catalytic hydrogenation of *N*-heterocycles, affording the corresponding adducts in good to excellent yields under mild conditions.

Introduction

Nanocatalysis has become a frontier domain in recent decades owing to the high catalytic efficiency offered by their large surface-to-volume ratio.[1–3] It is well-known that the surface energy increases with the decreasing size of the metal nanoparticles. Metal nanoparticles of smaller size, however, are known to aggregate more easily and seriously, which would further lead to the decrease/loss of catalytic activity and selectivity. The growth dynamics of the particles has been supposed to be controlled by two competing processes, nucleation of zero valence metal atoms to form the cores and passivation of the surfactant ligands to limit the growth of the cores.[4] Besides, the charge also affected the reactivity of supported transition metal catalysts.[5] Thus, the choice of the organic capping ligands plays a vital role in the regulation of nanoparticle structure and hence their chemical/physical properties and functional applications. So far, various stabilizers have been employed, including micelles,[6] microemulsions,[7,8] surfactants[9] and coordinated ligands where polymers[10] and dendrimers[11] with binding heteroatoms are extensively explored in catalysis. Until recently, covalent stabilization of nanoparticles via carbon–metal bonds is emerging as novel type of surface functionalities. In 2006, Mirkhalaf and co-workers firstly synthesized the metal–carbon stabilized gold nanoparticles and platinum nanoparticles.[12] Subsequently, Ghosh and co-workers determined the bonding energy of Pd–C bond to be about 436 kJ/mol, much larger than that of metal–S and metal–N bonds.[13] This remarkable bond strength differentiates the catalytic performance from metal–carbon nanoparticles to traditional coordinative stabilized nanoparticles.

However, only limited investigations on the catalytic properties of the carbon–metal stabilized nanoparticles have been reported. In Gopidas's work, for an instance, the palladium nanoparticles-cored G1-dendrimer stabilized by Pd–carbon bonds was firstly synthesized and applied to reduction of carbon–carbon multiple bonds (Fig. 1a).[14] Recently, Sekar et al. reported the efficiency and reusability of palladium nanoparticles stabilized by Pd–C (binaphthyl) covalent bonds in the Heck, Suzuki–Miyaura and Sonogashira cross-coupling reactions,[15] lately in polysubstituted olefin synthesis (Fig. 1b).[16] To be noted, the above-mentioned reports focused on modification of palladium nanoparticles surface utilizing ordinary aryl scaffolds, where no modular position was considered in the precursor of nanocatalyst. We envisioned that binaphthyl scaffolds with modular moiety could regulate the electron density on metal surface via conjugation effect, towards tunable catalytic efficiency, which might expand the potential applications of metal–carbon stabilized nanoparticles in organic transformations. In addition, although palladium has been well-known to hydrogenate the *N*-heterocycles, they presented clear drawbacks of harsh conditions (high hydrogen pressure or elevated temperature).[17] Thus, the development of novel nanocatalyst for hydrogenation is still in a great demand. As part of our continuing interests in the synthesis and application of nanocatalysts,[18]

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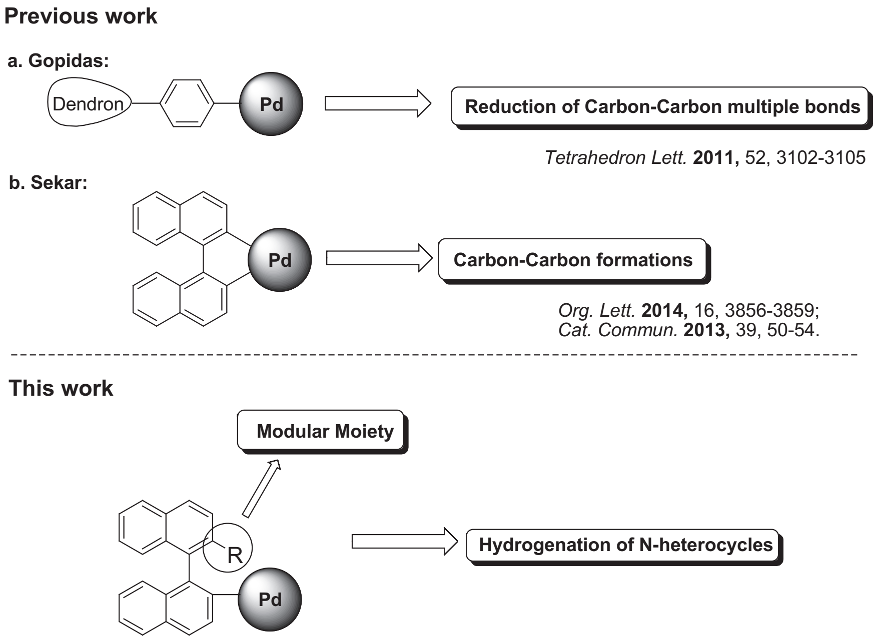


Figure 1. Current metal–carbon stabilized PdNPs in catalysis.

herein, we report the first preparation of a series of modular palladium-carbon stabilized nanoparticles based on binaphthyl scaffolds and their unprecedented applications in the catalytic hydrogenation of *N*-heterocycles (Fig. 1).[14–16]

Results and discussion

The diazonium precursors (**B**) were readily synthesized from various mono-protected 1,1′-binaphthyl-2,2′-diamine (BINAM) and the substitution groups are listed in Figure 2. Initial attempt to synthesize palladium nanoparticles via two-phase reduction[15] led to 'palladium black' unfortunately. The preparation process was finally succeeded when 'one-phase reduction' method was tried with palladium salts and diazonium precursors in the mixture solvent of THF and MeOH, affording a homogeneous black solution. The resulting serial palladium nanoparticles (**C**), obtained as black powders, were freely soluble in aprotic solvents, such as THF, toluene and dichloromethane; but insoluble in hexanes, MeOH and water. The palladium nanoparticle was further characterized by transition electron microscopy (TEM) and Inductively Coupled Plasma (ICP). As illustrated in Figure 2, the TEM analysis indicated that palladium nanoparticles were highly dispersed well with an average particle size of 2 ± 0.5 nm (e.g., catalyst **C-2**), and the palladium contents were determined as 8.14 wt % (**C1**), 4.61 wt % (**C2**), 11.7 wt % (**C3**), 1.14 wt % (**C4**), and 0.43 wt % (**C5**), respectively. IR and ^{1}H NMR spectra of the catalyst **C2** witnessed the existence of organic shell on the nanoparticles (S2 and S24 in Supporting Information).

With the synthesized catalysts in hand, we studied their catalytic performance in the hydrogenation of quinoline. This choice was based on the fact that such a reaction provides a powerful approach for the synthesis of tetraquinoline skeleton, which was found in many natural and synthetic products.[19] Furthermore, reports on catalytic hydrogenation of quinolines using nanocatalysts were rare,[20] let alone metal–carbon stabilized nanoparticles. Our preliminary study started with hydrogenation of quinoline under 2.5 MPa H_2, in the presence of 3 mol % of palladium nanoparticles (**C1**) at room temperature. The reaction afforded 58% of 1,2,3,4-tetrahydroquinoline after 24 h. Encouraged by this initial result, we were curious to investigate the impact of electron density on catalytic efficiency as mentioned above. Thus, nanocatalysts bearing electron-deficient and electron-rich groups (**C2–C5**) were introduced in this reaction. The hydrogenation took place smoothly depending on the structure of modular moiety, and the results are summarized in Table 1. Strong electron-deficient groups on binaphthyl led to lowered conversion; moreover, high steric groups seriously impaired the catalytic efficiency (entry 5). The catalyst **C-2** with acetyl group was found to enable the hydrogenation with highest conversion up to 80% in THF. To improve the yield and efficiency of this reaction, the effects of solvents and pressure were further studied (entries 8–22), albeit the catalyst was also active for heterogeneous system in water and alcoholic solvents. Eventually, the optimized hydrogenation reaction was achieved with quantitative conversion in dichloromethane under 1.0 MPa H_2 pressure for 12 h (entry 21).

Finally, the substrate scopes of the catalytic hydrogenation of *N*-heterocycles including quinoline, quinoxane and derivatives were investigated under the conditions of ambient temperature and pressure of 1.0 MPa H_2 using 3 mol % of the nano-sized palladium catalyst **C-2** for 12 h. The results are listed in Table 2. In general, all of the quinoline derivates were hydrogenated smoothly with good selectivity and excellent conversion (70–99%) with 3 mol % catalyst, except for entry 6, 9 and 12 with 10 mol %, 10 mol % and 5 mol %, respectively. The catalytic activity was relatively insensitive to the position of substituents on aryl or heteroaryl moiety of quinolines (entries 1–12); moreover, the catalyst was quite stable for substrates with multi-coordination groups (entries 5, 6, 10). Notably, hydrogenation of quinoline-2-carbaldehyde led to thereduction of both heteroaryl and aldehyde group (entries 11). Excellent results were also achieved with quinoxaline, phenazine and their derivatives (entries 13–16).

Conclusion

In summary, we have synthesized and characterized a novel class of modular metal–carbon stabilized palladium nanoparticles based on binaphthyl scaffolds. The nanocatalysts performed efficiently when applied to the hydrogenation of *N*-heterocycles,

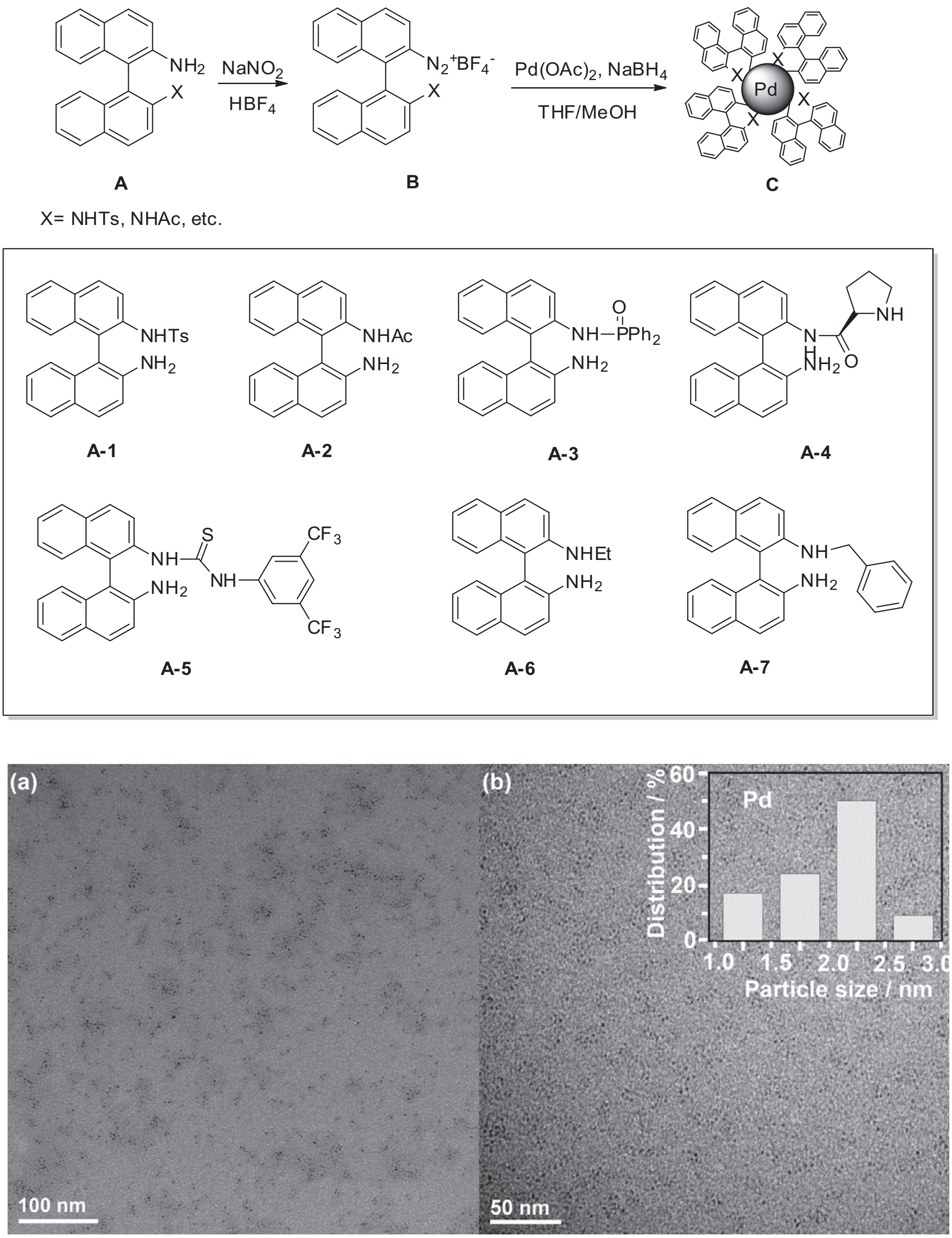
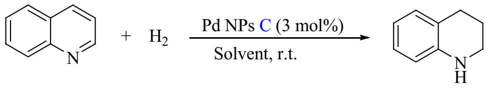


Figure 2. The preparation of modular metal–carbon stabilized PdNPs (top), and TEM images of the palladium nanoparticles with distributions (inset (b) is the corresponding morphology distribution of the PdNPs derived from 50 of PdNPs in image (a)).

Table 1
Optimization of reaction conditions



Entry	Catalyst	Solvent	Time (h)	H_2 Pressure (MPa)	Conv. (%)[a]
1	**C-1**	THF	24	2.5	58
2	**C-2**	THF	24	2.5	80

(*continued on next page*)

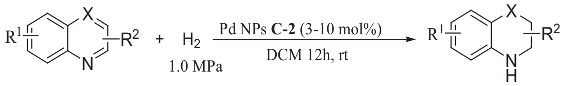
Table 1 (*continued*)

Entry	Catalyst	Solvent	Time (h)	H_2 Pressure (MPa)	Conv. (%)[a]
3	**C-3**	THF	24	2.5	39
4	**C-4**	THF	24	2.5	40
5	**C-5**	THF	24	2.5	Trace
6	**C-6**	THF	24	2.5	12
7	**C-7**	THF	24	2.5	46
8	**C-2**	DMF	24	2.5	10
9	**C-2**	CH_2Cl_2	24	2.5	>99
10	**C-2**	Toluene	24	2.5	16
11	**C-2**	1,4-Dioxane	24	2.5	17
12	**C-2**	MeOH	24	2.5	60
13	**C-2**	*i*-propanol	24	2.5	19
14	**C-2**	H_2O	24	2.5	37
15	**C-2**	CH_2Cl_2	6	2.5	57
16	**C-2**	CH_2Cl_2	9	2.5	73
17	**C-2**	CH_2Cl_2	12	2.5	>99
18	**C-2**	CH_2Cl_2	15	2.5	>99
19	**C-2**	CH_2Cl_2	12	0.1	65
20	**C-2**	CH_2Cl_2	12	0.5	74
21	**C-2**	$\mathbf{CH_2Cl_2}$	**12**	**1.0**	**>99**
22	**C-2**	CH_2Cl_2	12	1.5	>99

[a] The conversions were determined by ^1H NMR.

Table 2

Nanocatalyst **C-1** catalyzed hydrogenation of quinoline derivatives



Entry	X	R^1	R^2	Catalyst (mol %)	Conv. (%)[a]
1	C	H	H	3	>99
2	C	6-MeO	H	3	>99(92)
3	C	6-OH	H	3	70
4	C	8-Me	H	3	>99
5	C	8-OH	H	3	>99
6	C	8-NH_2	H	10	94
7	C	H	2-Me	3	>99(90)
8	C	H	3-Me	3	>99
9	C	H	4-Me	10	>99(88)
10	C	H	2-NH_2	3	>99
11	C	H	3-CHO	3	98[b]
12	C	6-Me	2-Me	5	>99
13	N	H	Quinoxane	3	>99
14	N	H	2-Methyl-quinoxane	3	>99
15	N	5-Me	Quinoxane	3	>99
16	N	H	Phenazine	3	>99

[a] The conversions were determined by ^1H NMR. Isolated yields are shown in parentheses.

[b] The aldehyde group was reduced.

affording the corresponding adducts in good to excellent yields under mild conditions. Notably, the rationally designed modular moiety bearing electron-rich and electron-deficient groups regulated the catalytic performance for hydrogenation efficiently. In this context, we are designing and exploring the potential application of chiral metal–carbon stabilized palladium nanoparticles for asymmetric catalysis. These studies are underway in our laboratory.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2015.12.008.

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