Tetrahedron Letters 52 (2011) 3102–3105

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Palladium nanoparticle-cored G_1-dendrimer stabilized by carbon–Pd bonds: synthesis, characterization and use as chemoselective, room temperature hydrogenation catalyst

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ARTICLE INFO

Article history:
Received 15 February 2011
Revised 29 March 2011
Accepted 1 April 2011
Available online 9 April 2011

Keywords:
Nanoparticle-cored dendrimer
Diazodendron
Palladium
Catalysis
Hydrogenation

ABSTRACT

Palladium nanoparticle-cored Fréchet type G_1-dendrimer (**Pd-G_1**) stabilized by Pd–carbon bonds is synthesized and characterized by IR, NMR, UV–Vis and TEM. **Pd-G_1** was found to be a highly efficient, chemoselective and reusable catalyst for the room temperature hydrogenation of carbon–carbon multiple bonds. Reducible functionalities like CHO, CO, COOR, CN, NO_2 and halogens were unaffected. **Pd-G_1** is projected as an efficient catalyst for the selective hydrogenation of carbon-carbon multiple bonds in multifunctional organic molecules.

Nanoparticle-cored dendrimers (NCD) are core-shell materials possessing nanometer-sized metal cluster at the core and a shell made of dendrons of different generations, which are attached radially to the core.[1–4] Because of the conical shape and steric requirements of the dendrons, their assembly on the metal surface is decided by a sterically induced stoichiometry, leaving large number of voids at the metal surface as shown in Figure 1. The unpassivated metal surface at the voids can function as catalytic sites. NCDs with different metals and dendrons were synthesized and characterized in the past and several of them have been studied for their catalytic activities.[3,5,6]

One of us in collaboration with Fox and Whitesell designed and synthesized the first catalytically active NCD.[3] Our idea was to design a Pd catalyst that is capable of catalyzing several reactions. We observed that the Heck and Suzuki reactions catalyzed by Pd–NCD were successful but it failed as a hydrogenation catalyst due to the hydrogenolysis of the NCD, leading to its decomposition and precipitation of Pd. We felt that if the Pd–S bonds in the NCD are replaced by Pd–C bonds, then hydrogenolysis could be prevented and the NCD might function as good hydrogenation catalyst also. In this Letter, we report the synthesis and characterization of a Pd-cored G_1-dendrimer (**Pd-G_1**), where the Fréchet–type G_1-dendrons are linked to the Pd core through Pd–carbon bonds. We also show that **Pd-G_1** is a very effective catalyst for the chemoselective hydrogenation of olefinic and acetylenic bonds at room temperature and atmospheric pressure in the presence of other reducible groups like CHO, NO_2 and halogens.

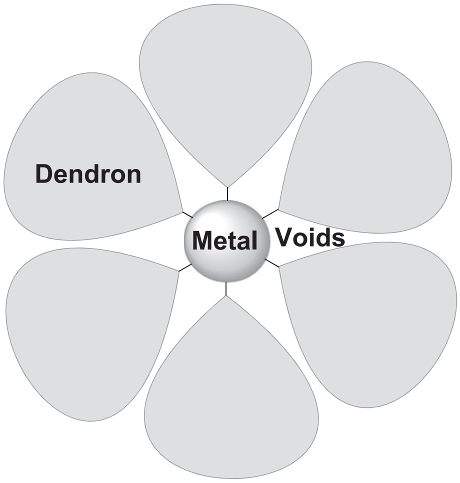

Figure 1. Schematic of a NCD.

We have recently reported the synthesis and characterization of Au–NCDs, where the Fréchet dendrons are linked to the gold cluster through Au–C covalent bonds.[7] We employed a similar strategy

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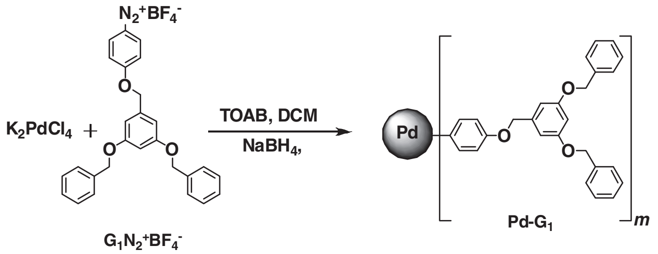
0040-4039/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2011.04.011

for the synthesis[8] of **Pd-G$_1$** which involved the simultaneous reduction of G$_1$-diazadendron and Pd(II) phase-transferred into dichloromethane using TOAB by NaBH$_4$.[7,9–11] During reduction Pd(II) is reduced to palladium atoms, which through nucleation and growth process grows into small Pd clusters. The diazodendron upon reduction forms a phenyl radical terminated dendron. At some stage of reduction, the dendron radicals get attached to the growing Pd nanoparticles to give **Pd-G$_1$** as shown in Scheme 1 (see SI for synthesis). **Pd-G$_1$**, obtained as a black powder, was freely soluble in chloroform, dichloromethane, tetrahydrofuran and insoluble in alcohols, diethyl ether and water. It was very stable for several months both in the solid state and in solution.

TEM image of the **Pd-G$_1$** thus prepared is shown in Figure 2. Figure 2 shows that the Pd core in **Pd-G$_1$** has average diameter of 2.7 nm. Thermogravimetric analysis showed that nearly 60% of the weight of **Pd-G$_1$** is due to Pd metal ($\approx$700 Pd atoms, see SI). A simple calculation[1–3] would show that approximately 131 dendrons are linked to the Pd core in **Pd-G$_1$**.

Pd-G$_1$ was characterized by UV–Vis, FTIR, and NMR spectroscopies (see SI for UV, IR and NMR spectra). The UV–Visible spectrum of **Pd-G$_1$** gave a progressively decreasing absorption profile with no plasmon band, consistent with earlier reports.[3] The G$_1$-diazodendron exhibited vibrational stretching of the diazo group at 2237 cm^{-1}, which was absent in the IR spectrum of **Pd-G$_1$** and except for this difference, IR spectra of **Pd-G$_1$** and G$_1$-diazodendron were identical. ^{1}H NMR of G$_1$-diazodendron showed signals at δ 8.2 and 7.0 due to the diazophenyl ring protons[7,9] and upon reduction, these peaks disappeared along with considerable signal broadening. Broadening of the NMR signals due to fast spin-spin relaxation of atoms close to metal core or size-dependent spin-spin relaxation clearly support the metal core-organic shell type structure of **Pd-G$_1$**.[1–4,7,12–14] The signals at δ <3 ppm in the ^{1}H NMR of **Pd-G$_1$** can be due to trapped TOAB.[7] In the ^{13}C NMR spectrum of G$_1$-diazodendron signals at δ 168, 135 and 118 ppm are identified as belonging to the diazo bearing phenyl group, which disappeared upon reduction to **Pd-G$_1$**. Similar observations were made earlier for monolayer protected gold cluster where Au is attached directly to the phenyl group and it was suggested that the signals due to phenyl ring carbons linked directly to the metal have broadened so much that they are indistinguishable from the background.[7,9–14] XRD studies indicated the presence of diffraction peak at 40° (2θ) corresponding to the {111} plane of metallic palladium fcc lattice. However, calculation of particle size from diffraction line broadening was difficult due to their low intensity.



Scheme 1. Synthesis of **Pd-G$_1$**.

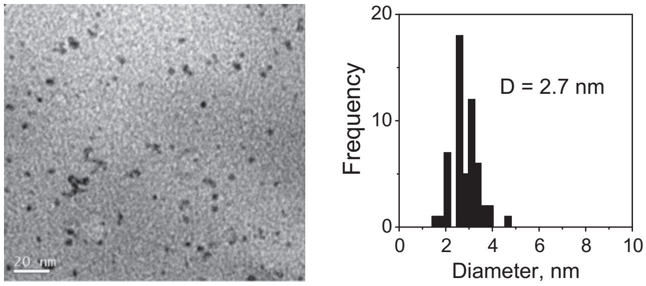


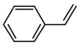
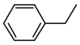
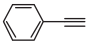
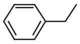
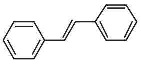
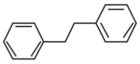
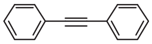
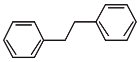
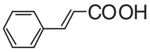
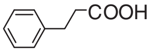
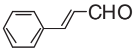
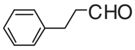
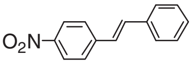
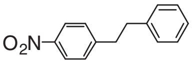
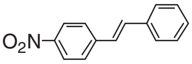
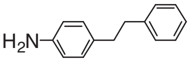
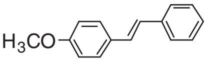
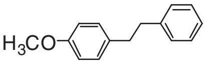
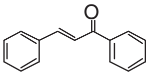
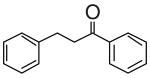
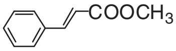
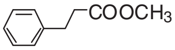
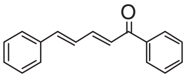
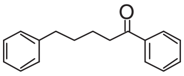
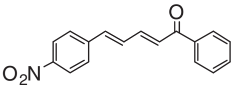
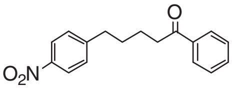
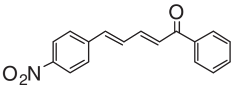
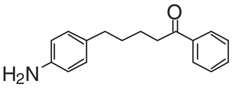
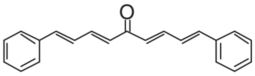
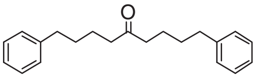
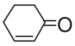
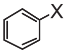
Figure 2. (a) TEM image (b) core-size histogram of **Pd-G$_1$**.

Having characterized **Pd-G$_1$**, we evaluated its catalytic activity in hydrogenation reactions. We have attempted hydrogenation[15] of different substrates listed in Table 1 using catalytic amounts of **Pd-G$_1$**. The yields reported in Table 1 are isolated product yields and purity has been confirmed by NMR and GC–MS analysis (see SI). It may be noted that for entries 1–13 in Table 1, product yields are nearly quantitative and reaction times were low. The reaction conditions employed[15] were very mild compared to hydrogenation reactions of similar substrates using other palladium catalysts where complete reduction of substrates including aromatic rings were reported.[16] Inspection of Table 1 also reveals that **Pd-G$_1$** is a very selective catalyst for the reduction of C=C and C≡C at room temperature and mild hydrogen pressure, even in the presence of sensitive groups like nitro (entries 5–13 in Table 1). Selective reduction of C–C multiple bonds in multifunctional organic molecules is always challenging especially in the presence of groups like NO$_2$ and CHO which can also undergo reduction under the hydrogenation conditions.[16–20] In **Pd-G$_1$** catalyzed hydrogenations, these groups remain unaffected. Entries 14–15 show that halogens (Cl, Br and I) and endocyclic double bonds are also unaffected under the reaction conditions. We have calculated turnover number (TON = moles of product formed/moles of palladium atoms) and turnover frequency (TOF = moles of product formed/moles of palladium atom/hours) for **Pd-G$_1$** and the values are given in Table 1.

Designing an efficient hydrogenation catalyst that can perform under mild reaction conditions with high chemoselectivity is still an active challenge in organic synthesis. The commonly employed hydrogenation catalyst Pd/C do not normally exhibit selectivity in the reduction of multifunctional organic compounds.[17,19,20] Table 1 shows that **Pd-G$_1$** can catalyze chemoselective reduction of C=C in the presence of NO$_2$ group (substrates **7** and 12). Reduction of NO$_2$ did not occur even after reaction time was extended to 8 h (see SI). Our control experiments with these substrates showed that hydrogenation with Pd/C (under same reaction conditions with respect to time and Pd content in the catalyst) led to reduction of both nitro and C=C moieties (entries 7[e] and 12[e] in Table 1). With only 5 mg Pd/C (reaction time 6 h), mixture of products arising from the reduction of C=C (80%) and C=C plus nitro (20%) were obtained. It is reported that chemoselectivity can be observed with Pd/C if suitable catalyst poisons were employed.[17,19,20] But, the presence of these additives may demand their separation from the final products after reaction. Thus, if chemoselective hydrogenation is desired **Pd-G$_1$** is a better choice. Our studies show that endocyclic double bonds are insensitive to hydrogenation conditions with **Pd-G$_1$** and at present we are not certain about the reason for this selectivity which requires further understanding of the reaction mechanism. In addition to the substrates reported in Table 1, we have carried out reduction of compounds containing isolated carbon-carbon multiple bonds such as 1-dodecyne, 1-octyne and hex-5-ene-2-one. In these cases GC–MS analysis of reaction mixtures indicated complete reduction of carbon-carbon multiple bonds and formation of corresponding products. However, these products being volatile liquids could not be isolated completely using the standard procedure employed here. Hence these reactions are not reported in Table 1.

We observed that most of the **Pd-G$_1$** could be recovered and reused a few times without loss of catalytic activity. Catalyst

Table 1
Hydrogenation using **Pd-G$_1$**[a]

Entry	Substrate	Product	Yield[b] (%)	TON[c]	Time (h)	TOF[d] (h^{-1})
1			90	77.6	4	19.4
2			92	83.0	4	20.8
3			99	19.6	6	3.3
4			98	19.8	6	3.3
5			95	23.3	6	3.9
6			81	29.0	7	4.2
7			98	15.7	6	2.6
7[e]			75	11.7	6	1.9
8			98	16.9	6	2.8
9			99	17.2	6	2.9
10			98	21.7	5	4.3
11			97	14.8	6	2.5
12			95	12.2	6	2.1
12[e]			95	11.9	6	1.9
13			94	11.8	7	1.7
14		No reaction			24	
15	 X = Cl, Br, I, -COCH$_3$, -CH$_2$CN, -OCH$_3$, -OH, -COOH	No reaction			24	

[a] Substrate and **Pd-G$_1$** (2.8×10^{-5} mol Pd) were taken in ethyl acetate (15 mL) and stirred under hydrogen atmosphere (hydrogen balloon) for the indicated time.
[b] Isolated product yield.
[c] TON = moles of product/moles of Pd atom.
[d] TOF = moles of product / moles of Pd atom/hour.
[e] Control experiment using 10% Pd/C (2.8×10^{-5} mol Pd).

recovery studies with phenylacetylene (2 mmol) and **Pd-G$_1$** (5 mg) showed nearly 92% conversion efficiency for three cycles after which product yields decreased, most probably due to incomplete recovery of catalyst in the previous cycles (see SI for experimental details).

The importance of transition metals in hydrogenation catalysis is well documented in the literature.[20–29] Although there are several reports dealing with hydrogenations catalyzed by dendrimer-encapsulated Pd nanoparticles,[21,22] and Pd/Pt nanoparticle-cored dendrimers,[5,6] there are few reports dealing with chemoselective hydrogenations using these catalysts. Previously reported Pd–NCDs required elevated temperature and pressure conditions to carry out hydrogenation reactions.[6] Catalyst recovery and recycling were also not possible with these systems. In these cases, the Pd nanoparticles were stabilized by either noncovalent interactions or weak coordinate bonds. In **Pd-G$_1$**, the dendrons are linked to Pd cluster by very strong Pd-C bonds (bond energy ≈436 kJM^{-1}).[11] These materials are expected to be very stable and active compared to other NCDs.

In conclusion, present work describes the synthesis and characterization of a palladium nanoparticle-cored Fréchet type G$_1$-dendrimer, **Pd-G$_1$**, where the dendrons are linked to Pd core through Pd–C bonds. **Pd-G$_1$** was characterized using IR, NMR and UV–visible spectroscopies. TEM analysis indicated the presence of nearly spherical, polydisperse particles with average diameter of 2.7 nm. Preliminary studies show that **Pd-G$_1$** meets all the requirements to act as a highly efficient, chemoselective, room temperature hydrogenation catalyst with good recyclability and short reaction times giving excellent product yields. We are interested in developing nanoparticle catalysts that are capable of catalyzing several reactions. In this context we are exploring the catalytic efficiency of **Pd-G$_1$** in other C–C bond forming reactions and the results are very encouraging. These studies are in progress in our laboratory.

Acknowledgments

The authors thank the Council of Scientific and Industrial Research (CSIR) and the Department of Science and Technology (DST grant No. SR/S5/OC-15/2003), Government of India, for financial support. V.K.R.K. thanks University Grants Commission (UGC), Government of India, for research fellowship. This is contribution number NIIST-PPG-309.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2011.04.011.

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8. *Procedure for the synthesis of* **Pd-G$_1$**: To a stirred solution of $G_1N_2^+BF_4^-$ (1.4 mmol) in dichloromethane, aqueous K_2PdCl_4 (1.4 mmol) was added followed by tetra-*n*-octylammonium bromide (TOAB) (2.1 mmol). Organic phase was separated, washed with water and cooled to −30 °C followed by the addition of 20 mL methanolic $NaBH_4$ (14 mmol). The mixture was stirred at −30 °C for 4 h and at room temperature for 20 h. The organic phase was separated and washed with 0.5 M H_2SO_4, 0.5 M Na_2CO_3 and finally with water. The crude product was purified by column chromatography (silica gel 100–200 mesh). The column was first eluted with dichloromethane to remove organic impurities and then with methanol to obtain **Pd-G$_1$**. (see Supplementary data for characterization).
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