

Synthesis of Water-Dispersible Pd Nanoparticles Using a Novel Oxacalixarene Derivative and their Catalytic Application in C–C Coupling Reactions

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Received: 15 May 2016/Accepted: 6 June 2016 © Springer Science+Business Media New York 2016

Abstract A novel 5,17-di(hydrazinecarbonyl) tetranitrooxacalix[4]arene (DHOC) derivative has been synthesized and characterized using various spectroscopic techniques. This DHOC derivative has been used to produce water-dispersible catalytically active Pd nanoparticles (PdNps). In the nanoparticle synthesis, DHOC serves as both a reducing and a stabilizing agent, thus simplifying the preparation of the PdNps because no separate reagents are required to reduce and stabilize the nanoparticles. These PdNps were characterized by a number of techniques such as Transmission Electron Microscopy and UV–Visible spectroscopy. The water-dispersible PdNps were 5 ± 2 nm in size and showed high catalytic activity in numerous C–C coupling reactions such as the Sonogashira, Suzuki-Miyuara and Heck reactions.

$H_{1} = \frac{1}{10^{10} \text{ M}^{10} \text{ M}^{10}$

Keywords Oxacalix[4]arene · PdNps · Catalysis · C–C coupling reactions

Electronic supplementary material The online version of this article (doi:10.1007/s10562-016-1781-y) contains supplementary material, which is available to authorized users.

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1 Introduction

Nanoscience is considered an innovative and interdisciplinary science with applications in catalysis, electro analysis, biology and medicine, among other fields [1-3]. The synthesis of metal nanoparticles of diverse sizes, controlled mono-dispersity and varied chemical compositions has become an important area of research in



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nanotechnology [4]. The small size of the nanoparticles is favorable for several catalytic reactions [5]. As catalysis takes place on the metal surface, the reactivity of metal nanoparticles is higher than their particulate metal counterparts due to the nanoparticles' high surface to volume ratio. These nanoparticles have found practical application in many fields [6, 7]. Metal nanoparticles are predominantly synthesized from metals such as silver (Ag), platinum(Pt), gold(Au) and palladium (Pd) [8]. Due to their applications in catalysis, palladium nanoparticles (PdNps) have gained great significance in synthesis [9].

Because of their unique properties, the study of catalytically active palladium nanoparticles has gained substantial prominence as they have come to play an important role in organic synthetic chemistry [10]. Many organic reactions with industrial applications, such as the Sonogashira [11], Suzuki-Miyuara [12], Stille [13], Heck [14, 15], Hiyama [16], and hydrogenation reactions [17, 18] can be progressed, and numerous complex organic compounds are usually synthesized in non-aqueous/aqueous media by using catalytically active palladium complexes [19]. A number of carbon–carbon and carbonheteroatom coupling reactions can be catalyzed by palladium complexes such as (PPh₃)₄Pd [20]. However, these complexes are sensitive to air, are toxic and are difficult to separate from the reaction products.

The preparation of metal nanoparticles often requires the use of chemical reduction methods in which a reducing agent and a number of stabilizers are used to prevent the accumulation of metal nanoparticles [21, 22] and the leaching of the activity of the Catalyst [21]. Intriguingly, supramolecules such as Cyclodextrins [23], Porphyrin [24], and Calixarenes [25, 26] have been used as both reducing and stabilizing agents in the preparation of many types of nanoparticles. In contrast, the use of oxacalixarenes in the field of nanoscience has not been explored much because they are still in the synthetic stage [27, 28]. Hence, the use of oxacalixarenes to synthesize nanoparticles is anticipated to show their significance in the field of nanoscience and nanotechnology.

Therefore, 5,17-di(hydrazinecarbonyl) tetranitrooxacalix [4] arene (DHOC) has been synthesized, characterized and used as both a reducing and a stabilizing agent for the formation of DHOC-PdNps. We report the use of DHOC to synthesize Pd nanoparticles in water because the preparation and stabilization of nanoparticles in an aqueous medium have a number of significant benefits such as avoidance of organic solvent, lower cost and potential for the use of these nanoparticles in biological applications. Metal nanoparticles with a size of 1–5 nm [10] display great catalytic activity and also regulate the catalyst selectivity [29]; as a result, DHOC-PdNps with a size of 5 ± 2 nm can very effectively catalyze various C–C coupling reactions. Therefore, these nanoparticles were further used as catalysts for the Sonogashira, Suzuki-Miyuara and Heck coupling reactions.

2 Experimental Section

2.1 Chemicals and Reagents

All the chemicals used were of the highest purity, were procured from Sigma-Aldrich and used without further purification. Water used in the experiments was obtained from a Millipore system (resistivity, 18 M Ω cm at 25 °C, Millipore Systems). All of the solvents employed for synthesis were commercially available and were used as received without further purification. The purity of the compounds and the progress of the reactions were monitored by TLC on pre-coated silica gel-aluminum plates (Type 60 F₂₅₄, Merck, Darmstadt, Germany) and were visualized by exposure to UV-light (254 nm) or I₂ vapor.

2.2 Instrumentation

A VEEGO (Model No: VMP-DS) melting point apparatus (Mumbai, India) was used to measure the melting points (uncorrected) in a single capillary tube. Centrifugation of the colloidal solutions was done using a Remi, Model No. C-24BL laboratory centrifuge. ¹H NMR and ¹³C NMR spectra were obtained on a Bruker AV-(III)-400 MHz spectrometer using a BBFO probe. ESI-Mass spectra were taken on a micromassQuarter2 mass spectrometer (Utah, USA) with a capillary voltage of 3000 V and source temperature of 120 °C. The absorption spectra were recorded using a Jasco V-570 UV-Vis recording spectrophotometer (Tokyo, Japan) in the range of 200-800 nm. Transmission Electron Microscopy(TEM) images and Selective Area Electron Diffraction (SAED) pattern were recorded on a JEOL model, JEM 2100 microscope using an accelerated voltage of 200 kV. The zeta potential and particle size were obtained by the Malvern Zeta sizer (Model; ZEN3600) as such without dilution. Inductively Coupled Plasma-Atomic Emission Spectrophotometer (ICP-AES) JY 2000-2 model was used to check the absence of Pd in supernatant liquid collected after centrifugation.

3 Synthesis

3.1 Synthesis of 5,17-Di(ethoxycarbonyl) Tetranitrooxacalix[4]arene (DEOC) (4)

3,5-dihydroxy ethyl benzoate (2) was prepared from 3,5dihydroxybenzoic acid (1), as per the reported procedure [30]. Compound (2) (4 gm, 21.9 mmol), compound (3), 1,5-difluoro-2,4-dinitrobenzene (21.9 mmol) and finely ground anhydrous K_2CO_3 (54.9 mmol) were stirred in DMSO (80 mL) in a 250 mL round bottom flask at room temperature for 30 min. The reaction was monitored by TLC. The reaction mixture was added drop wise to 1 M HCl (400 mL). The aqueous layer was extracted with EtOAc (500 mL × 2). The combined organic layers were washed with brine (500 mL), dried over anhydrous Na₂. SO₄, filtered, and concentrated in vacuo. The DEOC (4, Scheme 1) was purified using 30 % ethyl acetate in hexane as the eluent, with a yield of 80 %.

Mass *ESI* (+); m/z = 692.7 (M + 1); ¹H NMR (400 MHz, CDCl₃) δ 1.36 (t, J = 7.0 Hz, 3H), 4.35 (q, J = 7.1 Hz, 2H), 7.17 (s, 1H), 7.49 (t, J = 2.2 Hz, 1H), 7.63 (d, J = 2.3 Hz, 2H), 8.86 (s, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 67.5, 100.1, 101.6, 116.2, 118.8, 122.0, 123.0, 125.6, 131.7, 134.6, 151.4, 151.8, 153.5, 158.4, 160.2, 169.5.; M.P.:190 °C.

3.2 Synthesis of 5,17-Di(hydrazinecarbonyl) Tetranitrooxacalix[4]arene (DHOC) (5)

A mixture of DEOC(3 gm, 4.3 mmol) and hydrazine hydrate (10.8 mmol) in 30 mL of THF was refluxed for 24 h and the reaction mixture was concentrated in vacuo. The DHOC (5, Scheme 1) was purified using 80 % ethyl acetate in hexane as the eluent, with a yield of 65 %.

Mass *ESI* (+); m/z = 665.62 (M + 1); ¹H NMR (400 MHz, CDCl₃) δ 4.77 (S, 2H), 6.44 (t, J = 2.2 Hz, 2H), 6.82 (d, J = 2.2 Hz, 2H), 7.19 (s, 1H),9.33 (s, 1H),9.65 (s, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 90.7, 104.8, 106.9, 122.3, 128.4, 131.5, 149.4, 158.4, 166.2; M.P.: 250 °C.

3.3 Synthesis of DHOC Stabilized Palladium Nanoparticles

First, 100 mL of a solution of palladium acetate (0.022 g) in double distilled water was heated to 60 °C. To this heated solution, DHOC (0.066 g) in 100 mL water was added, and the mixture was kept under vigorous stirring with heating for 6 h. The complete reduction of the palladium salt was confirmed by the color change from brownish yellow to blackish brown. The formation of DHOC-PdNps was confirmed by TEM, and UV-Vis spectroscopy. Because DHOC is water soluble, the content of DHOC in the DHOC-PdNps was 66.0 mg and the Pd loading in the DHOC-PdNps was 10.4 mg. The final yield of DHOC-PdNps collected by centrifugation was 76.4 mg. After centrifugation at 3000 rpm for 15 min, the supernatant liquid was confirmed for the absence of DHOC and any unreacted Pd by UV-Visible spectrophotometry and ICP-AES, respectively. Thus, this procedure for the preparation of PdNps is a simple one-pot process in the presence of an ecologically friendly solvent, i.e., water (Table 1).

4 DHOC-PdNps Catalyzed Various C-C Coupling Reactions

4.1 Suzuki Reaction of Aryl Halides

To a mixture of phenyl boronic acid (0.5 gm, 4.1 mmol), aryl halide (4.5 mmol) and Na_2CO_3 (4.5 mmol) in DMF:Water (1:1), the DHOC-PdNps (0.0077 mmol) were added. The reaction mixture was then stirred at 50 °C (Table 2). The reaction was monitored by TLC, and after completion of the reaction, the reaction mixture was cooled



Scheme 1 Synthetic route for 5,17-di(hydrazinecarbonyl) tetranitrooxacalix[4]arene (DHOC)





Entry	Solvent	Catalyst amount (mmol)	Base	Temperature (°C)	Time (min)	Yield ^d (%)
1	Acetone/water	0.0077^{a}	Sodium carbonate	50	60	88
2	THF/water	0.0077^{a}	Sodium carbonate	50	80	85
3	DCM/water	0.0077^{a}	Sodium carbonate	50	120	65
4	1,4-dioxane/water	0.0077^{a}	Sodium carbonate	50	50	89
5	Toluene/water	0.0077^{a}	Sodium carbonate	50	70	79
6	DMF/water	0.0077^{a}	Sodium carbonate	50	20	92
7	Ethanol/water	0.0077^{a}	Sodium carbonate	50	45	88
8	DMF/water	0.0077^{a}	Potassium carbonate	50	40	85
9	DMF/water	0.0077^{a}	Triethylamine	50	45	80
10	DMF/water	0.0077^{a}	Sodium acetate	50	60	65
11	DMF/water	0.0077^{a}	Potassium hydroxide	50	50	63
12	DMF/water	0.0077^{a}	Sodium bicarbonate	50	60	72
13	DMF/water	0.006^{a}	Sodium carbonate	50	35	88
14	DMF/water	0.110^{a}	Sodium carbonate	50	30	92
15	DMF/water	0.0077^{a}	Sodium carbonate	25	40	88
16	DMF/water	0.0077^{a}	Sodium carbonate	40	45	89
17	DMF/water	0.0077^{a}	Sodium carbonate	50	20	92
18	DMF/water	0.0077^{a}	Sodium carbonate	60	22	90
19	DMF/water	0.0077^{a}	Sodium carbonate	70	21	91
20	DMF/water	0.0077^{a}	Sodium carbonate	80	20	91
21	DMF/water	0.0077 ^b	Sodium carbonate	50	60	80
22	DMF/water	0.0077 ^c	Sodium carbonate	50	120	83

Reaction conditions: phenyl boronic acid (0.5 gm, 4.1 mmol), aryl halide (4.5 mmol), base (4.5 mmol), catalyst (0.0077 mmol), water:solvent (1:1) (10 mL), temperature (°C) in air

For catalyst, ^a PdNps, ^b Palladium acetate, ^c Tetrakis(triphenylphosphine)-palladium(0), ^d Isolated yield after drying the product

 Table 2 DHOC-PdNps-catalyzed Suzuki coupling reaction of different aryl halides

	HO.B.OH	Ar-X Nanopart	icles, ter,	Ar
Entry	Aryl halide	Product	Time (min)	Yield ^a (%)
1			20	90
2	I		22	92
3			20	89

Reaction conditions: phenyl boronic acid (0.5 gm, 4.1 mmol), aryl halide (4.5 mmol), base (4.5 mmol), PdNps (0.0077 mmol), Water:DMF (1:1) (10 mL), temperature (50 °C)

^a Isolated yield after drying the product

to room temperature. Then, the reaction mixture was extracted with ethyl acetate (50 mL \times 2) and washed with water (50 mL). The organic phase was washed with brine (25 mL), dried over Na₂SO₄, filtered and concentrated in vacuo. The products were purified using 10 % ethyl acetate in hexane as the eluent.

4.2 Sonogashira Reaction of Aryl Halides

To a mixture of phenyl acetylene (0.5 gm, 4.9 mmol), aryl halide (5.4 mmol) and Na₂CO₃ (5.4 mmol) in N-methyl 2-pyrrolidone (NMP):Water, the DHOC-PdNps (0.0077 mmol) were added. The reaction mixture was then stirred at 60 °C (Table 3). The reaction was monitored by TLC, and after completion of the reaction, the reaction mixture was cooled to room temperature. Then, the reaction mixture was extracted with ethyl acetate (60 mL \times 2) and washed with water (60 mL). The organic phase was washed with brine (50 mL), dried over Na₂SO₄, filtered

 Table 3 DHOC-PdNps catalyzed Sonogashira coupling reaction of different aryl halides



Reaction conditions: phenyl acetylene (0.5 gm, 4.9 mmol), aryl halide (5.4 mmol), base (5.4 mmol), PdNPs (0.0077 mmol), NMP:Water (1:1) (10 mL), temperature (60 $^{\circ}$ C)

^a Isolated yield after drying the product

and concentrated in vacuo. The products were purified using 5 % ethyl acetate in hexane as the eluent.

4.3 Heck Reaction of Aryl Halides

To a mixture of alkene (0.5, 4.8 mmol), aryl halides (5.3 mmol) and Na₂CO₃ (5.3 mmol) in NMP:Water, the DHOC-PdNps (0.0077 mmol) were added. The reaction mixture was then stirred at 40 °C (Table 4). The reaction was monitored by TLC, and after completion of the reaction, the reaction mixture was cooled to room temperature. Then, the reaction mixture was extracted with ether (30 mL \times 2) and washed with water (30 mL). The organic phase was washed with brine (30 mL), dried over Na₂SO₄, filtered and concentrated in vacuo. The products were purified using 2 % ethyl acetate in hexane as the eluent.

5 Results and Discussion

Reetz demonstrated palladium nanoparticle-catalyzed coupling reactions and used surfactants as stabilizers [31, 32]. For aryl iodides, EI-Sayed et al. described the significance of Pd nanoparticles stabilized by PVP [33]. Pd nanoparticles are primarily synthesized by numerous stabilizers such as dendrimer [34] and polymers [35]. Nevertheless, the preparation of nanoparticles with use of the calix system is more efficient due to its combined reducing and stabilizing properties [36–38]. Hence, we introduce a dihydrazide derivative of oxacalixarene which works as a suitable reductant and stabilizer for preparing PdNps. This procedure is very advantageous for the synthesis of PdNps as the use of separate reducing and stabilizing agents can

 Table 4
 DHOC-PdNps catalyzed Heck coupling reaction of different aryl halides



Reaction conditions: alkene (Styrene) (0.5 gm, 4.8 mmol), aryl halide (5.3 mmol), base (5.3 mmol), PdNps (0.0077 mmol), NMP: Water (1:1) (10 mL), temperature (50 °C)

^a Isolated yield after drying the product

be avoided. It is believed that the hydrazide part of oxacalixarene provide electrons for reduction to the metal ions and its inherent echoing cavity and web-type structure [26, 36–40] offer stability to the nanoparticles. Hence, the facile formation of PdNps was achieved using aqueous solutions of Pd(OAc)₂ and DHOC, without any external reductant/stabilizer. The formation of DHOC-PdNps has also been confirmed through TEM, and UV–Visible spectroscopy.

The UV–Visible spectroscopy study was carried out to confirm the formation of DHOC-PdNps. Unlike Gold and Silver nanoparticles, PdNps has no explicit Surface Plasmon Resonance (SPR) band; hence, the disappearance of the band at 400 nm attributed to Pd(OAc)₂ (Fig. 1), along with a distinctive color change from brownish yellow to blackish brown (Fig. 2), confirms the formation of DHOC-PdNps [41].

The PdNps have zeta potential values of -30.8 mV (Fig. 3), which are consistent with reported values for nanoparticles with good stability [42]. The poly-dispersity of the particles was ascertained by TEM analysis (Figure). The lattice spacing value was found to be 0.224 nm in the high-resolution transmission electron microscopy image (Fig. 4). The PdNps were approximately spherical, as well as the narrow size distribution had an average diameter of



Fig. 1 UV-Visible spectra of DHOC-PdNps shows the absence of the broad peak at 400 nm



Fig. 2 Photograph showing a palladium acetate and b DHOC-PdNps

 5 ± 2 nm (Fig. 5). Also, Crystalline nature of palladium nanoparticles is confirmed by the SAED pattern, which exhibits four diffused rings which are assigned to (111), (200), (220) and (311) reflections of *fcc* Pd (Fig. 6) [43]. The DHOC-PdNps was isolated in the solid state for Powder X-ray Diffraction (PXRD) analysis (Fig. 7). The as prepared nanoparticles were confirmed to be metallic giving the expected *fcc* Pd pattern. The peaks were assigned to diffraction from the (111), (200) and (220) planes of *fcc* palladium (0) lattice respectively [44]. After obtaining proper characteristics for PdNps, we show its utility for different catalytic reactions such as Suzuki, Heck and Sonogashira in the present study.

5.1 Suzuki Reaction

The effects of temperature, solvents and bases on the yield of the model reaction were studied using a 1:1 mixture of water and various organic solvents. Dimethylformamide (DMF) proved to be a better co-solvent than acetone, THF, DCM, 1,4-dioxane, toluene and ethanol (Table 1: Entries 1-7), and Na₂CO₃was a better base than were Triethylamine, K₂CO₃, NaHCO₃ and CH₃COONa (Table 1: Entries 8-12, 17). It was also observed that increasing the temperature does not increase the yield (Table 1: Entries 17-20). Therefore, a temperature of 50 °C was selected as the optimum temperature for the model reaction. The effect of the amount of catalyst (Table 1: Entries 13, 14) on the percent vield was also studied. An amount of 0.0077 mmol of PdNps was found to be optimum. Moreover, the optimized reaction conditions for DHOC-PdNps were compared to those of conventional low-yield Pd catalysts such as palladium acetate and Tetrakis (triphenylphosphine)palladium(0) (Table 1: Entries 21, 22). Therefore, the optimized reaction conditions of the model reaction [solvent, Water:DMF (1:1); base, Na₂CO₃;temperature, 50 °C;amount of PdNps,0.0077 mmol] were used in all Suzuki cross-coupling reactions. As shown in Table 2, all of the aryl halides gave the desired cross-coupled products with a good to excellent yield.

5.2 Sonogashira Reaction

Sonogashira reactions are very useful in the synthesis of natural products such as enediyne antibiotics. Although copper (I) has been most commonly used as the co-catalyst, a few Cu-free preparations have been successively developed. These preparations, however, require the use of ultrasound or microwave irradiation techniques. Our catalyst alone is sufficient for the Sonogashira reaction. The same optimization procedure as described for the Suzuki reaction was adopted for the Sonogashira reaction. Likewise, the use of a mixture of NMP:Water (1:1) and Na₂CO₃ proved to be superior to the other solvents and bases. Consequently, the optimized reaction conditions of the model reaction [solvent, NMP:Water (1:1); base, Na₂CO₃; temperature, 60 °C and amount of PdNps (0.0077 mmol)] were used in the Sonogashira reactions. As shown in Table 3, all of the aryl halides gave the preferred products with a good to excellent yield.

5.3 Heck Reaction

The vinylation of aryl halides is known as the Heck reaction. As described for the Suzuki and Sonogashira reactions, the conditions for the Heck reaction were also optimized, and as observed for the Suzuki and Sonogashira





Fig. 5 Histogram showing particle size distribution

Fig. 6 SAED pattern of crystalline PdNps

(200)



Fig. 7 PXRD pattern of DHOC-PdNps



reactions, the mixture of NMP:Water (1:1) and Na_2CO_3 yielded better results than did other solvents and bases. Therefore, the optimized reaction conditions of the model reaction [solvent, NMP:Water (1:1);base, Na_2CO_3 ;temperature, 60 °C and amount of PdNps (0.0077 mmol)] were used in the Heck reactions. As shown in Table 4, all of the aryl halides gave the preferred products with a good to excellent yield.

6 Recyclability

The recyclability of the prepared PdNps was assessed for all C–C coupling reactions under optimized reaction conditions. The reaction mixture was centrifuged for 15 min at 3000 rpm. The separated DHOC-PdNps were washed with the appropriate mixture of organic solvents and water and the recovered catalyst was dried overnight at 60 °C. The





Fig. 8 Recyclability of PdNps in all C-C reactions

catalyst was used without any further activation for five cycles, with only a minor loss of effectiveness (Fig. 8). Thus, the DHOC-PdNps can be reused efficiently in all C–C coupling reactions for at least five cycles. The reaction mixture was subjected to ICP-AES to check the leaching of PdNps from the catalyst with the successful result indicating the absence of leaching from the catalyst.

7 Conclusion

We have synthesized a novel dihydrazide derivative of oxacalixarene and have successfully shown that the DHOC derivative can be employed to prepare DHOC-PdNps in water. DHOC worked as both a reducing and a stabilizing agent, thus making it more efficient than other methods. TEM analysis showed the nanoparticles to be 5 ± 2 nm. Furthermore, the particles showed good stability and demonstrated astonishing catalytic activities for various C–C coupling reactions of aryl halides such as the Suzuki, Heck and Sonogashira reactions.

We are presently looking forward to exploiting the utility of these nanoparticles in biological applications.

Acknowledgments The authors thank the financial assistance provided by DRDO (New Delhi) and University Grant Commission-Basic Scientific Research (UGC-BSR) New Delhi. The authors also acknowledge Gujarat Forensic Science University, Gandhinagar (GFSU), Central Salt and Marine Chemicals Research Institute, Bhavnagar (CSMCRI), Central University of Gujarat-Gandhinagar (CUG), National Facility for Drug Centre Discovery-Rajkot (NFDD), Oxygen Healthcare-Ahmedabad (O2 h) for providing instrumental facilities, and UGC-Info net & INFLIBNET for e-journals.

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