Electronic Supplementary Information (ESI) for Chemical Communications

Investigation of Size-dependent Properties of Sub-nanometer Palladium Clusters Encapsulated within a Polyamine Dendrimer

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1) General

^{1}H and ^{13}C{^{1}H}-NMR spectra were obtained using a JEOL JNM-AL400 spectrometer with tetramethylsilane as an internal standard. Infrared absorption spectra were obtained with a JASCO FTIR-410 instrument. The Pd K-edge X-ray absorption spectra were recorded at BL01B1 and BL14B2 stations attached to Si(311) monochromator at SPring-8 (JASRI), Harima, Japan (Proposal No. 2010A1788, 2010B1795, 2011A1295, 2012A1757). The Pd L_3-edge X-ray absorption spectra were recorded at the BL-10 station attached to the Ge(111) monochromator at SR Center, Ritsumeikan University, Kusatsu, Japan. Data analyses were performed using REX2000 program ver. 2.5.7 (RIGAKU) and Athena program[1S] ver. 0.8.056. Coordination number (CN) and interatomic distance (*R*) were estimated by curve-fitting analysis using Pd-Pd, Pd-Cl, and Pd-N shell parameters extracted from Pd foil, $PdCl_2$, and $Pd(NH_3)_4Cl_2$ as reference samples. The particle sizes of the Pd clusters were calculated from the CN values based on the relation between CN and diameter.[2S] HR-TEM experiments were conducted using a Hitachi HF-2000 (200kV) instrument in the Research Center for Ultrahigh Voltage Electron Microscopy, Osaka University.

2) Chemicals

The third generation (G_3, subscript denotes the generation) poly(propylene imine) (PPI) dendrimer (Astramol™ Am-16) was purchased from SyMO-Chem (The Netherlands). $PdCl_2$ was obtained from N.E. Chemcat and used as received. Other chemicals were available from Wako Pure Chemicals, Tokyo Kasei Co., and Aldrich Inc. and were used after appropriate purification. The fifth generation (G_5) PPI dendrimer was synthesized using a repetitive reaction sequence of a double Michael addition of a periphery amine to acrylonitrile, followed by reduction of the nitriles to primary amines using high-pressure hydrogen and pretreated Raney cobalt from the G_3 PPI dendrimer.[3S] Peripheral amino groups on the G_5 PPI dendrimer was modified with 3,4,5-triethoxybenzoyl chloride to give the capsular dendrimer (G_5-TEBA).[4S]

3) Preparation of catalysts

The dendrimers encapsulating subnano Pd clusters were prepared using previously described methods.[5S] A chloroform solution of G_5-TEBA was prepared. To this solution under vigorous stirring, 4, 8, or 16 equiv of an aqueous Na_2PdCl_4 solution was added to yield G_5-Pd^{II}_n (n = 4, 8, or 16) Pd^{2+}/dendrimer complexes, respectively. These precursor complexes were extracted and reduced in methanol solution using a freshly prepared aqueous KBH_4 solution under Ar atmosphere. The dark brown solution of the dendrimer obtained was dialyzed against MeOH/H_2O (4/1 v/v) using CE membrane tube (MWCO 100-500, available from Spectrum Laboratories, Inc.) for 16 h. The solutions obtained were evaporated to dryness at 30°C to give a dark brown waxy solid, which were kept under Ar atmosphere.

4) XAFS experiments

The size of the Pd clusters was estimated using Pd K-edge X-ray absorption fine structure (XAFS) and high resolution transmission electron micrograph (HR-TEM).[5S] Results from curve-fitting of Fourier transformed EXAFS spectra (Figure S1), after the reduction of G_5-Pd^0_n (n = 4, 8, and 16), gave the coordination number (CN) of the Pd-Pd shells as 3.1, 4.6, and 5.9, respectively. The number of Pd atoms in a cluster and size for G_5-Pd^0_n were estimated using a typical cluster model to be 4, 8, and 16, corresponding to 0.50, 0.76, and 0.97 nm, respectively (Table S1). Figure S2 shows the most stable cluster model and average coordination numbers of Pd-Pd shell.[6S] To confirm stability of the subnano Pd clusters during the allylic substitution, the catalyst was removed from the reaction solution by filtration. To precipitate the dendrimer catalyst from the reaction solution, *n*-hexane was added and the slurry was collected by filtration by a disk membrane filter (0.20 μm PTFE membrane, 25 mm diameter). The used catalysts were analyzed by XAFS as shown in Figure S1 (d, f, h) and Table S1. In the FT-EXAFS spectrum of G_5-Pd^0_{16} after the allylic substitution reactions, intensity of a weak peak around 1.6 Å corresponding to Pd-N shell was similar to that of fresh G_5-Pd^0_{16}. In addition, a new weak shoulder peak attributed to Pd-O shell appeared around 1.8 Å (Figure S1, d). This may be due to the coordination of the excess benzoic acid to the Pd cluster. The above phenomena in the difference between the relative peak intensities before and after the catalysis were also observed for G_5-Pd^0_4 and G_5-Pd^0_8, respectively (Figure S1, f and h).

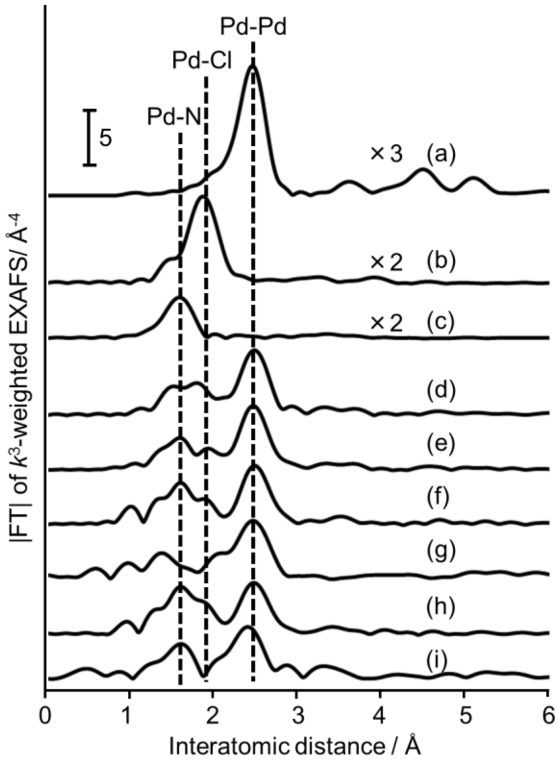

Figure S1. Pd K-edge EXAFS spectra of (a) Pd foil, (b) $PdCl_2$, (c) $Pd(NH_3)_4Cl_2$, (d) G_5-Pd^0_{16} (after reaction in toluene), (e) G_5-Pd^0_{16}, (f) G_5-Pd^0_8 (after reaction in toluene), (g) G_5-Pd^0_8, (h) G_5-Pd^0_4 (after reaction in toluene), (i) G_5-Pd^0_4.

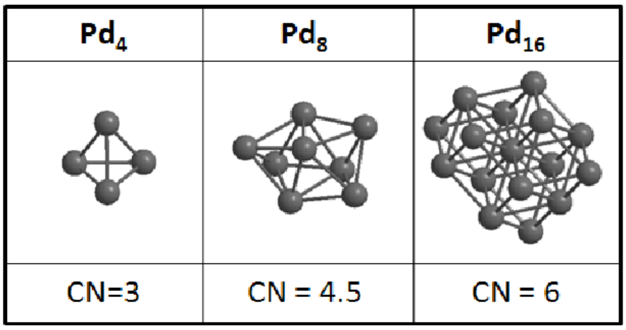

Figure S2. Optimal structures of subnano Pd clusters and their average coordination numbers [6S]

Table S1. Curve-fitting results for Pd K-edge EXAFS[a]

Sample	Shell	CN[b]	R[c] / Å	$\Delta\sigma^{2}$[d] / Å	No. of Pd atoms[e]	Diameter[f] /nm
G_5-Pd^0_4	Pd-Pd	3.1	2.73	0.0069	4	0.50
G_5-Pd^0_4[g]	Pd-Pd	3.2	2.77	0.0072	4	0.50
G_5-Pd^0_8	Pd-Pd	4.6	2.76	0.0074	8	0.76
G_5-Pd^0_8[g]	Pd-Pd	4.4	2.78	0.0094	8	0.76
G_5-Pd^0_{16}	Pd-Pd	5.9	2.77	0.0071	16	0.97
G_5-Pd^0_{16}[g]	Pd-Pd	5.9	2.78	0.0100	16	0.97

[a] The region of 1.8-2.9 Å in FT of the reduced samples was inversely transformed. [b] Coordination number. [c] Interatomic distance. [d] Difference between Debye-Waller factor of G_5-Pd^0_n and that of the reference sample. [e] Number of Pd atoms in a cluster. [f] Diameter of Pd clusters calculated from the CN. [g] After reaction in toluene.

5) TEM experiments

Average diameter of the G_5-$Pd^{\mathbf{0}}_{16}$ was calculated from the magnified TEM images by measuring the size of *ca*. 200 clusters. The Pd clusters observed were all within the sizes of 0.8 to 1.2 nm range. Resolution of the HRTEM was 0.2 nm. The Pd clusters could not be observed by HRTEM for G_5-Pd^0_4 and G_5-Pd^0_8. The cluster sizes estimated by TEM images agree well with the results obtained by EXAFS. Therefore, aggregation/agglomeration of the Pd clusters during the TEM analysis was negligible.

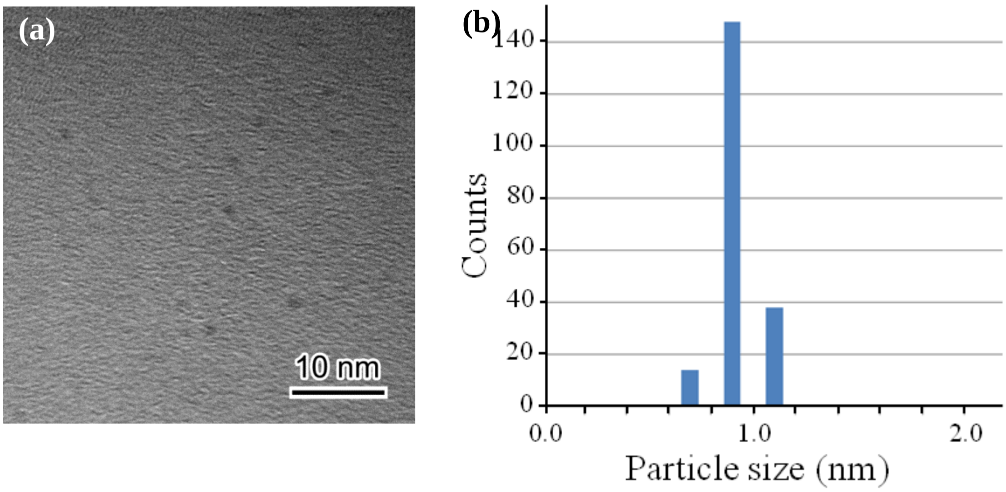

Figure S3. (a) TEM image and (b) size distribution of G_5-Pd^0_{16} (d_{Av} = 0.95 nm, σ = 0.09 nm).

6) CO adsorption IR study of Pd clusters

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) experiments were conducted under vacuum with a base pressure of 0.3 Pa (Figure S4). The light passed through a viton-O-ring sealed KBr-window before and after reflection from the sample surface. A liquid nitrogen-cooled MCT detector was used. Infrared spectra were recorded with a spectral resolution of 1 cm^{-1} accumulating 128 scans for each spectrum. A flow of 10 % carbon monoxide mixture gas balanced with He was introduced to the sample cell at 1 atm for 2 h. The sample then was purged under vacuum for 6 h. The background spectrum was subtracted from each spectrum corresponding to a specified purging time.

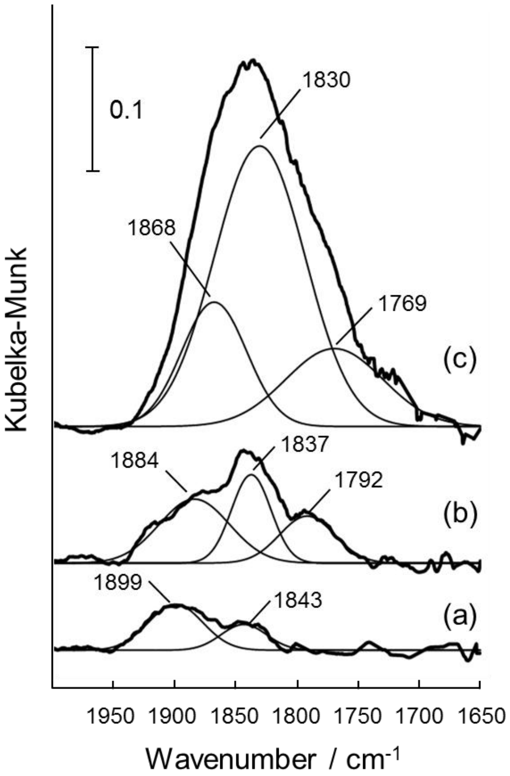

Figure S4. Diffuse reflectance infrared Fourier transform spectra measured after CO adsorption on (a) G_5-Pd^0_4, (b) G_5-Pd^0_8, (c) G_5-Pd^0_{16}.

7) General procedure for allylic substitution reactions

The catalytic reaction using G_5-Pd^0_n was conducted in a Schlenk tube equipped with a reflux condenser. G_5-Pd^0_n (Pd: 2.5 μmol) was placed in a Schlenk tube, followed by the addition of solvents (2 mL), allyl methyl carbonate **1** (0.1 mmol), and benzoic acid **2** (0.5 mmol). The mixture was vigorously stirred at 80°C under Ar atmosphere for 24 h. The product was identified by GC-MS and quantitative analysis was performed by GC-FID using an internal standard method. The initial turnover frequency (initial TOF) was defined as the initial rate at 10% yield of **3**, normalized by the number of surface Pd atoms in the subnano clusters. The TOF was calculated using the following equation.

$$\mathrm{TOF}\ (\mathrm{h}^{-1}) = \frac{\text{Production of } \mathbf{3}\ (\text{mol})}{\text{Surface Pd atoms (mol)} \cdot \text{Time (h)}}$$

8) Reuse experiment of the G_5-Pd^0_{16} catalyst

After the allylic substitution reaction using the fresh G_5-Pd^0_{16} catalyst, *n*-hexane (5 mL) was added to the reaction mixtures to precipitate the catalyst. Then, the reaction mixture was centrifuged and the supernatant was decanted. Remaining catalyst was washed several times with a small portion of *n*-hexane. The catalyst was re-dissolved in toluene (2 mL), followed by addition of allyl methyl carbonate (0.1 mmol) and benzoic acid (0.5 mmol) under Ar atmosphere. The reaction mixture was vigorously stirred at 80°C under Ar atmosphere for 24 h. The G_5-Pd^0_{16} catalyst could be reused without any loss of its activity; 92 % yield of **3** was obtained after 24 h (Table 2, entry 1).

9) Kinetics of the reaction

A series of catalytic reactions was conducted for kinetic studies of the allylic substitution reaction of **1** with **2** in toluene in the presence of G_5-Pd^0_n (n = 4, 8, and 16) as catalysts at 80°C. As shown Figure S5, the reaction rate of the production of allyl benzoate **3** shows a dependency on the initial concentration of **1**. In contrast, the initial concentration of **2** as nucleophile has no influence on initial rate. These results show that formation of π-allyl Pd clusters is the turnover-limiting step.

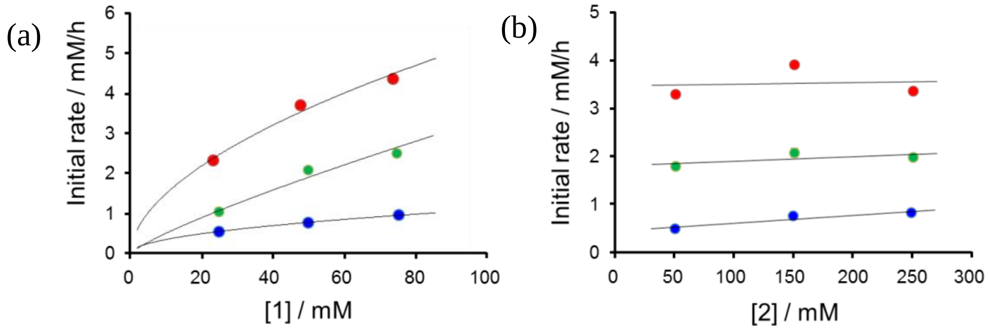

Figure S5. Plot of the initial rate (mM/h) vs. concentration of (a) allyl methyl carbonate **1** and (b) benzoic acid **2** ((a) [**1**] = 25—75 mM, [**2**] = 150 mM (b) [**1**] = 50 mM, [**2**] = 50—250 mM). Reaction conditions: catalyst (Pd 2.5 μmol), toluene 2 mL, 80°C, Ar. ● G_5-Pd^0_4, ● G_5-Pd^0_8, ● G_5-Pd^0_{16}.

10) References

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