Supporting Information for

Nanocage Catalyst —Rhodium Nanoclusters Encapsulated with Dendrimers as Accessible and Stable Catalysts for Olefin and Nitroarene Hydrogenations

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Experimental Section

1.1. Materials and chemicals

Porphyrin-core phenylazomethine dendrimer generation 4 (**TPP-DPA G4**) was synthesized with the method reported before.[1] Methanol and toluene were purchased from Godo Solvents Co. and used without further purification except for UV-vis measurement. For UV-vis measurement, HPLC grade methanol and toluene purchased from Kanto Chemical Co., Inc. were used. For ^{1}H NMR measurement, dichloromethane–d_2 99.8 atom % D as the solvent was purchased from Kanto Chemical Co., Inc. and tetramethylsilane as internal standard was purchased from Tokyo Chemical Industry Co., Inc. Diethyl ether was purchased from Showa Ether Co., Ltd and distilled from sodium and benzophenone before use. Distilled water was purified with Millipore water system. Polyamidoamine dendrimer and chlorotris(triphenylphosphine)rhodium(I) (Wilkinson catalyst) were purchased from Aldrich. Rhodium (III) chloride was purchased from Tanaka Kikinzoku Kogyo K. K. 1-Bromo-3-phenylpropane and 1,5-cyclooctadiene were purchased from Tokyo Chemical Industry Co., Ltd. Allyl bromide, butyl acrylate and sodium borohydride were purchased from Kanto Chemical Co., Inc. and magnesium turnings for the preparation of Grignard reagent were purchased from Nacalai Tesque. Styrene and 1-decene were purchased from Wako Pure Chemical Industries, Ltd. Pure styrene and 1,5-cyclooctadiene were obtained by distillation.

1.2. Measuring equipments

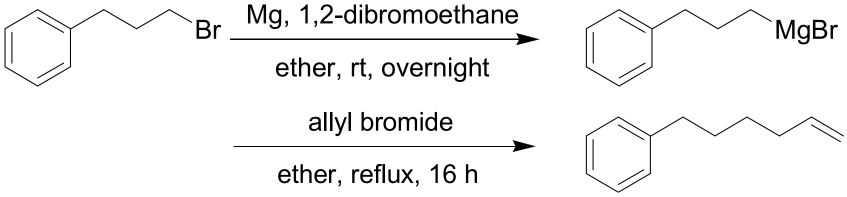
The ^{1}H NMR spectra were measured by JEOL AL-400 operating at 400 MHz. The ^{1}H NMR chemical shifts were referenced to tetramethylsilane (TMS: 0.00 ppm) as an internal standard. The MALDI-TOF-mass spectra were recorded with a mass spectrometer (Shimadzu/Kratos, AXIMA CFR plus: Positive mode). α-Cyano-4-hydroxy cinnamic acid (CHCA) was used as the matrix for the MALDI-TOF-mass measurements. The field-emission transmission electron microscope (FE-TEM) images were obtained at an accelerating voltage of 200 kV with a Hitachi HF-2000. The XPS spectra were recorded with a XPS-7000 (Rigaku) using Mg Kα (10 kV, 30 mA) radiation. The GC-MS spectra were obtained with a QP-5000 (Shimadzu).

1.3. Preparation of substrates

1.3.1. Styrene

Commercially available styrene was successively washed with 10 % NaOH aq., 10 % $NaHSO_3$ aq., then distilled water twice, respectively. After dried over Na_2SO_4 overnight, styrene was purified by distillation under reduced pressure (bp. 38 °C/25 mmHg, lit: 146 °C/760 mmHg).

1.3.2. 6-Phenyl-1-hexene



This reaction was performed with modification method based on the literature.[2] 3-Phenyl-1-propyl magnesium bromide was prepared by the reaction of 1-bromo-3-phenylpropane (18.9 mL, 126 mmol) and magnesium (4.58 g, 188 mmol) in dry diethyl ether (100 mL) in the presence of 1,2-dibromoehane (a few drops). After the removal of excess amount of magnesium, allyl bromide (10.9 mL, 126 mmol) in ether (6 mL) was added dropwise to the Grignard reagent for 20 min. After the addition of allyl bromide, the reaction mixture was refluxed for 16 h. The mixture was cooled to room temperature and poured into slurry of concentrated HCl and ice. The aqueous layer was extracted with ether four times, and then combined organic layer was washed with distilled water. The organic layer was dried over sodium sulfate (Na_2SO_4) and the solvent was removed under reduced pressure. The residue was chromatographed on silica gel (elute: hexane) to give 6-phenyl-1-hexene in 80 % yield (16 g). This compound was distilled under a dry nitrogen condition before use for hydrogenation (bp. 99 °C/10 mmHg, lit: 97-98 °C/10 mmHg). 6-Phenyl-1-hexene: ^{1}H NMR (CD_2Cl_2) δ 7.20 (m, 5H), 5.81 (ddt, 1H, *J* = 6.8 Hz), 4.99 (d, 1H, *J* = 17 Hz), 4.92 (ddt, 1H, *J* = 10 Hz), 2.60 (t, 2H, *J* = 7.6 Hz), 2.08 (q, 2H, *J* = 7.1 Hz), 1.62 (quin, 2H, *J* = 7.8 Hz), 1.42 (quin, 2H, *J* = 7.3 Hz); MS *m/z* cal. 160.26, found 160.15.

1.4. Preparation of dendrimer-stabilized Rh nanoparticles

1.4.1. Rh_{60}@**PAMAM G4-OH**

All processes were carried out under a dry nitrogen atmosphere and in the dark. The solvent of **PAMAM G4-OH** (0.500 g, 3.50 μmol in 10 % methanol solution) was evaporated under reduced pressure. Then the residue was dissolved in distilled water (4 mL). Rhodium (III) chloride (55 mg, 210 μmol, 60 equiv for dendrimer) in distilled water (2 mL) was added to the **PAMAM G4-OH** aqueous solution. The solution was degassed by a vacuum pump. After stirred for 30 min, $NaBH_4$ (40 mg, 1050 μmol, 5 equiv for rhodium) in methanol (2 mL) was added dropwise into the solution. This solution was stirred overnight and dendrimer-stabilized Rh nanoparticles in solution were obtained.

1.4.2. Rh_{60}@**TPP-DPA G4**

All processes were carried out under a dry nitrogen atmosphere and in the dark. Rhodium (III) chloride (1.4 mg, 5.3 μmol, 60 equiv for dendrimer) in methanol (1 mL) was added to the **TPP-DPA G4** (1.0 mg, 0.088 μmol) solution in toluene (3 mL). After stirred for 30 min, $NaBH_4$ (1.0 mg, 26 μmol, 5 equiv for rhodium) in methanol (1 mL) was added dropwise into the solution. This solution was stirred overnight and dendrimer-stabilized Rh nanoparticles in solution were obtained. The MALDI-TOF-MS of Rh_{60}@**TPP-DPA G4** was shown in Figure S1.

1.5. Hydrogenation

The general procedure for the hydrogenation of olefins with Rh nanoparticles was as follows. All processes were carried out at room temperature in the dark. A carefully dried schlenk flask equipped with a magnetic stirring bar was charged with a dry nitrogen and then olefin (1.75 mmol) in methanol (5 mL). Dendrimer-stabilized Rh nanoparticles (0.3 mol % as rhodium for olefin) in solution were added to this olefin solution. Hydrogen gas was supplied from a balloon. The reaction was followed by measuring the GC-MS of a drop of the reaction mixture in methanol at different periods.

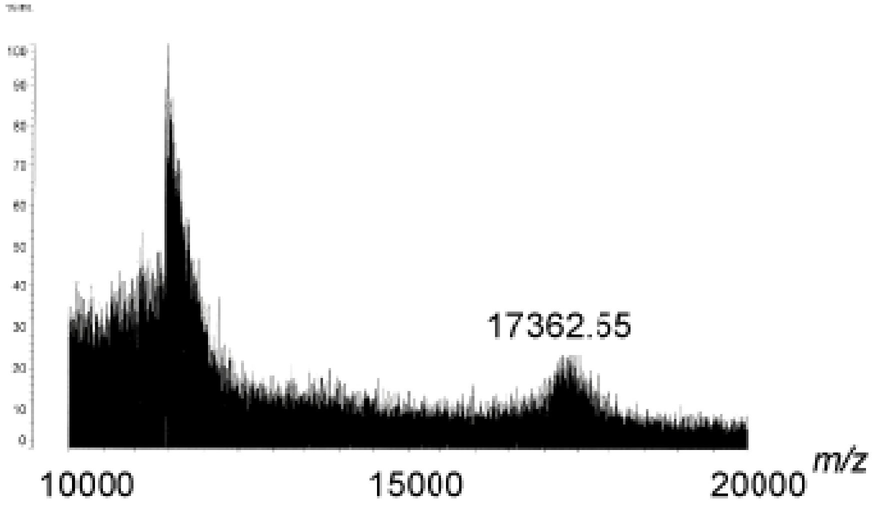


Fig. S1 MALDI-TOF-MS spectrum of Rh_{60}@**TPP-DPA G4**

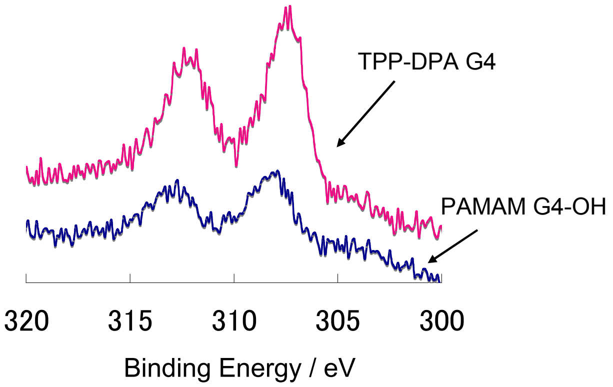


Fig. S2 XPS spectra of Rh_{60}@**TPP-DPA G4** and Rh@**PAMAM G4-OH** in the Rh 3d region.

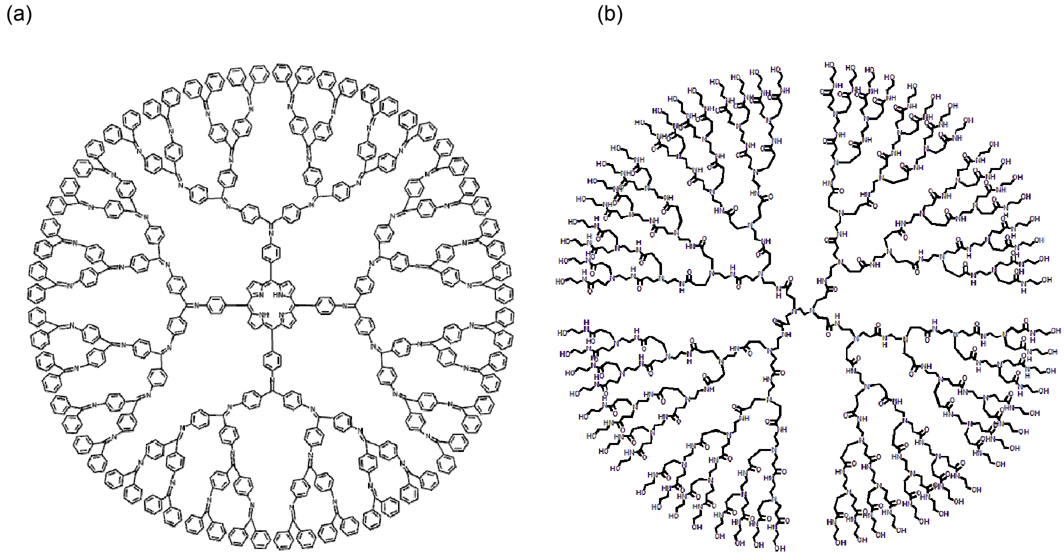


Fig. S3 Structures of **TPP-DPA G4** (a) and **PAMAM G4-OH** (b).

References

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