Nanocage catalysts—rhodium nanoclusters encapsulated with dendrimers as accessible and stable catalysts for olefin and nitroarene hydrogenations†

Ikuse Nakamula,[a] Yoshinori Yamanoi,[a] Tetsu Yonezawa,[a] Takane Imaoka,[b]
Kimihisa Yamamoto*[b] and Hiroshi Nishihara*[a]

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The phenylazomethine dendrimer generation 4 (TPP-DPA G4) and polyamidoamine dendrimer (PAMAM G4-OH) encapsulating rhodium nanocluster were found to be highly effective for olefin and nitroarene hydrogenations, affording high TOF (up to 17520 h^{-1}); the important feature of the nanocage catalyst is that substrates can pass through the branches of the protecting groups of nanoclusters without releasing nanoclusters from the dendrimer.

Recently, colloidal nanoclusters of transition metals have been used as quasi-homogeneous catalysts in organic transformation.[1] Although the bulk metals have little catalytic activity, metal nanoclusters show high catalytic efficiency due to the large surface-to-volume ratio. In order to prepare the metal nanoclusters, stabilizers such as surfactants, polymers and dendrimers are utilized for the suppression of aggregation and for the control of cluster size. The most serious problem in using metal clusters as a catalyst is the negative relationship between stability and catalytic activity, *i.e.* stabilization of clusters brings about a decrease in substrate accessibility. During the course of our study of dendrimers,[2] we have been interested in the development of accessible and stable metal nanocluster catalysts encapsulated inside dendrimers.[3] We report here phenylazomethine dendrimer- and polyamidoamine dendrimer-stabilized rhodium nanoclusters and their applications to olefin and nitroarene hydrogenations. In these clusters, the dendrimer acts as a stabilizer as well as a substrate-capturing nanoreactor.

Rhodium complexes have been used as a catalyst for hydrogenation reactions.[4] Wilkinson's complex ($RhCl(PPh_3)_3$) is the representative complex catalyst enabling catalytic hydrogenation of alkenes and other unsaturated compounds in homogeneous solution. Although Wilkinson's complex can be used for hydrogenation of various kinds of substrates under relatively mild conditions, it is unstable against oxygen in solution. To improve this defect, we designed rhodium nanoclusters protected by rigid and hydrophobic phenylazomethine dendrimer generation 4 (**TPP-DPA G4**) as well as flexible and hydrophilic ployamidoamine dendrimer generation 4 with a terminal hydroxy group (**PAMAM G4-OH**)[5] as an effective catalyst for hydrogenation.[6] These dendrimers have coordination sites at the branching points working as good electron-donating groups for Lewis acids. Consequently, it is expected that nanoclusters prepared using these dendrimers are well-controlled in size with a narrow size distribution.

Scheme 1 shows the preparation procedure of phenylazomethine dendrimer-encapsulated rhodium nanoclusters as an example. Initially, the complex **1** was obtained by coordination of $RhCl_3$ to **TPP-DPA G4**. Reduction of the rhodium complex with sodium tetrahydroborate then gave rhodium cluster stabilized with **TPP-DPA G4** (Rh_{60}@**TPP-DPA G4**). The formation of rhodium nanoclusters was confirmed by transmission electron microscopy (TEM), matrix assisted laser desorption ionization-time of flight (MALDI-TOF)-MS, and X-ray photoelectron spectroscopy (XPS). The TEM study indicated that the average diameter was 1.2 ± 0.3 nm (Fig. 1(a)). This diameter corresponds to 64 rhodium atoms in a cluster, on the assumption of a face-centered cubic (fcc) close-packed structure. The distribution of the cluster diameter is very narrow, and these nanoclusters are almost uniform. Furthermore, the peak around 17 000 in the MALDI-TOF-MS spectrum shows that approximately 58 rhodium atoms are encapsulated in a single dendrimer molecule.[7] Both values obtained from TEM and MALDI-TOF-MS measurements are in accord with the quantity of rhodium added initially, and the error is primarily due to the ambiguity of the TEM images and the MALDI-TOF-MS peaks. The XPS spectra showed the surface rhodium atoms of these nanoclusters to be zero-valent (lit.[8] Rh(0): $3d_{5/2}$ 307.0 eV, $3d_{3/2}$ 311.8 eV, found: $3d_{5/2}$ 307.0 eV, $3d_{3/2}$ 311.5 eV). One of the significant features of encapsulation with **TPP-DPA G4** is the exact match in the number of rhodium atoms before and after cluster formation. While **TPP-DPA G4** could exactly produce the Rh_{60} cluster in the dendrimer template (Rh_{60}@**TPP-DPA G4**), a well-known dendrimer template based on polyamidoamine architecture (**PAMAM G4-OH**) did not afford such a finely regulated rhodium nanocluster by the same in-solution-phase synthesis. The average diameter was 1.8 ± 0.4 nm by the TEM study (Fig. 1(b)). The averaged number of rhodium atoms calculated from the cluster size with a broader distribution was approximately 200 on the assumption of an fcc structure. However, the electronic status observed by the XPS spectra ($3d_{5/2}$ 306.9 eV, $3d_{3/2}$ 311.6 eV)

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[a] *Department of Chemistry, School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo, 113-003, Japan. E-mail: nisihara@chem.s.u-tokyo.ac.jp; Fax: (+81) 3-5841-8063*
[b] *Department of Chemistry, Faculty of Science and Technology, Keio University, Hiyoshi, 3-14-1, Kouhoku-ku, Yokohama, Kanagawa, 223-0061, Japan. E-mail: yamamoto@chem.keio.ac.jp; Fax: (+81) 45-566-1718*

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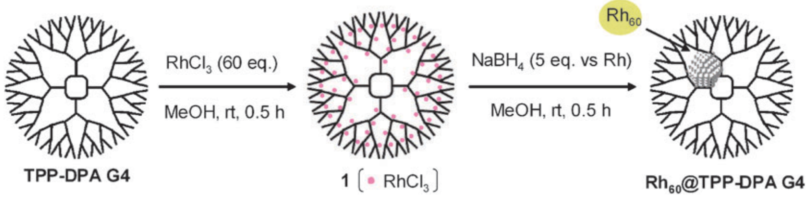


Scheme 1 Synthetic procedure of Rh$_{60}$@**TPP-DPA G4**.

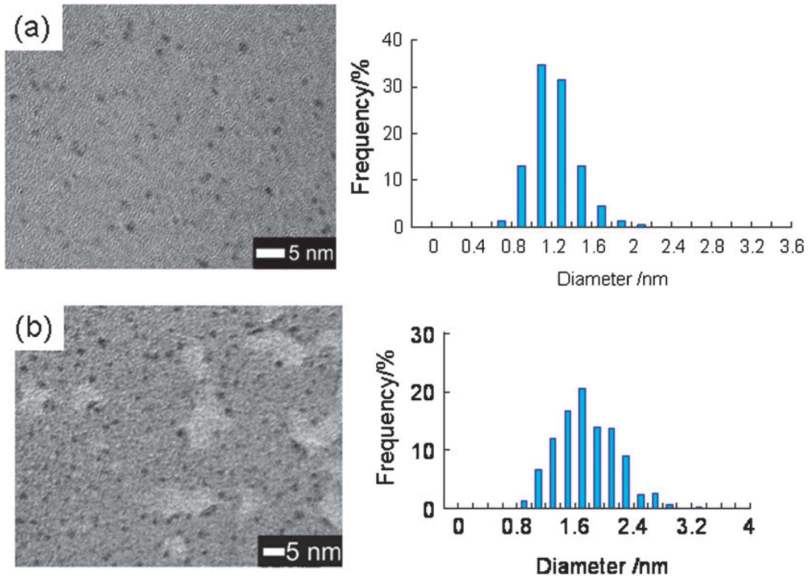


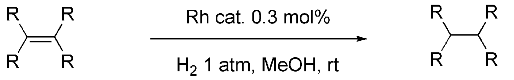
Fig. 1 TEM images and the particle size distributions of (a) Rh$_{60}$@**TPP-DPA G4** and (b) Rh@**PAMAM G4-OH**.

was the same as that obtained with **TPP-DPA G4**. These results strongly suggest that the character of dendritic encapsulation between the rigid **TPP-DPA G4** and flexible **PAMAM G4-OH** differ from each other. Observations of the catalytic activity, as shown below, also reflect the structural and dynamic aspects of these chemical encapsulations.

The catalytic activities of these rhodium nanoclusters were examined by olefin hydrogenation. Table 1 represents the results of hydrogenation of some substrates under mild conditions catalyzed by the rhodium cluster in **TPP-DPA G4**, **PAMAM G4-OH**, and Wilkinson's complex. The turnover frequencies (TOFs) were calculated using the reaction rate at the final stage. Rh$_{60}$@**TPP-DPA G4** shows up to 1460 times higher catalytic activity per rhodium atom than other rhodium catalysts. The smaller size of the cluster in **TPP-DPA G4** is one of the reasons for the relatively higher activity because the effective surface area for one rhodium atom calculated for the observed cluster size (7.54 [Å^2 atom^{-1}] for 1.2 nm) is greater than that of **PAMAM G4-OH** (4.63 [Å^2 atom^{-1}] for 1.8 nm). However, this result is not sufficient to explain the difference in the TOFs. The primary reason would be based on the difference in dendritic encapsulations for each catalytic system that act as stabilizers for these unprotected rhodium clusters.

Functionalized aniline derivatives are important intermediates in the production of pharmaceuticals.[9,10] We next carried out a reduction of nitroarenes using these rhodium catalysts under hydrogen atmosphere (1 atm) to expand the scope of this method, because catalytic hydrogenation of nitroarenes is a simple method for the production of aminoaromatics. The results are shown in Table 2. Although there was no reactivity

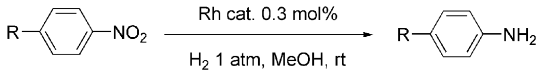
Table 1 TOFs (h^{-1})/atom (TOFs (h^{-1})/cluster) of olefin hydrogenation



Entry	Substrate	**TPP-DPA G4**	**PAMAM G4-OH**	RhCl(PPh$_3$)$_3$
1	Butyl acrylate	**292 (17 520)**[a]	4 (800)[b]	12
2	6-Phenyl-1-hexene	**210 (12 600)**[a]	3 (600)[b]	12
3	1-Decene	**199 (11940)**[a]	1 (200)[b]	24
4	Styrene	**173 (10 380)**[a]	3 (600)[b]	8
5	1,5-Cyclooctadiene	**17 (1020)**[a]	3 (600)[b]	11
6	1,1-Diphenylethylene	**11 (660)**[a]	1 (200)[b]	9

[a] Calculated as Rh$_{60}$@**TPP-DPA G4**. [b] Calculated as Rh$_{200}$@**PAMAM G4-OH**.

Table 2 TOFs (h^{-1})/atom (TOFs (h^{-1})/cluster) of nitroarene hydrogenation



Entry	R	**TPP-DPA G4**	**PAMAM G4-OH**	RhCl(PPh$_3$)$_3$
1	H	1 (60)[a]	**22 (4400)**[b]	0
2	MeOCO	18 (1080)[a]	**48 (9600)**[b]	0
3	MeCO	13 (780)[a]	**33 (6600)**[b]	0
4	H$_2$N	2 (120)[a]	**17 (3400)**[b]	0
5	MeO	5 (300)[a]	**19 (3800)**[b]	0

[a] Calculated as Rh$_{60}$@**TPP-DPA G4**. [b] Calculated as Rh$_{200}$@**PAMAM G4-OH**.

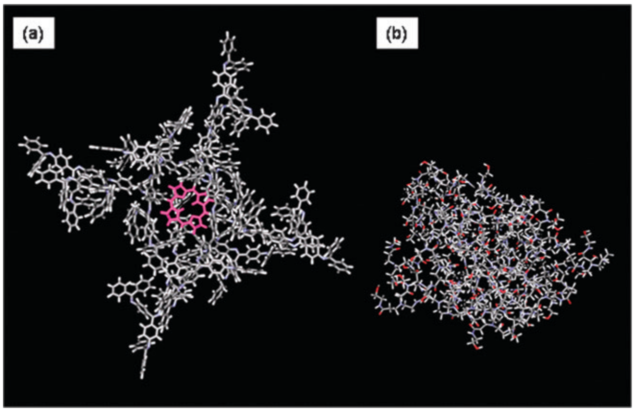


Fig. 2 Back folding images of **TPP-DPA G4**[2b] (a) and **PAMAM G4-OH**[12] (b).

upon nitroarene hydrogenation in the presence of Wilkinson's complex, the nitro group was reduced to the amino moiety in the presence of rhodium nanoclusters. In particular, **PAMAM G4-OH**-stabilized rhodium nanoclusters were more effective in this transformation. In addition, no reduction of ester or ketone groups was observed during the hydrogenation (entries 2 and 3).

It should be noted that no significant difference was observed by the comparison of the average diameters of rhodium nanoclusters using TEM analysis during both the olefin and nitroarene hydrogenations for both dendrimer-stabilized nanoparticles. From the perspective of catalytic activity, the solid shell of **TPP-DPA G4** with a sufficient inner-cavity (Fig. 2(a)) allows a wide variety of hydrophobic substrates to access the rhodium cluster surface. In contrast, the liquid shell of **PAMAM G4-OH** swelled with polar solvents (Fig. 2(b)) refuses hydrophobic substrates approaching the interior, whereas it assists in the transmission of polar substrates such as nitroarenes.[11]

In conclusion, rhodium nanoclusters stabilized with phenylazomethine and polyamidoamine dendrimers were prepared with a narrow size distribution. These nanoclusters proved to be an effective catalyst for hydrogenation of olefins and nitroarenes, demonstrating that the catalytic activity of Rh nanoclusters can be altered by the type of encapsulating dendrimers. Additional developments in this area will be reported in due course in our laboratories.

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