



## A recyclable dendritic osmium catalyst for homogeneous dihydroxylation of olefins

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### ABSTRACT

A series of osmate ( $\text{OsO}_4^{2-}$ ) core dendrimers was prepared by an ion-exchange technique through the mixing of  $\text{K}_2\text{OsO}_4$  and a bis(quaternary ammonium bromide) core dendrimer, which consisted of poly(benzyl ether) dendron. By employing an osmate core dendrimer as a homogeneous catalyst, dihydroxylation reactions of olefins proceeded rapidly, and the dendritic osmium catalyst was recovered by reprecipitation and then reused. Furthermore, a dendritic effect on the recyclability of a catalyst was observed. In the case of asymmetric dihydroxylation reactions, the corresponding diol was obtained in a high chemical yield with a fair enantiomeric excess (ee). In this case, not only the dendritic osmium catalyst but also the chiral ligand could be recovered by reprecipitation and reused efficiently up to five times.

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### 1. Introduction

Osmium-catalyzed dihydroxylation and asymmetric dihydroxylation with chiral ligands are some of the most useful transformations for the preparation of vicinal diols from olefins.<sup>1</sup> Although these reactions have had widespread application in the synthesis of chiral drugs, natural products, fine chemicals, and so on, few fruitful industrial applications have been identified due to their high cost, toxicity, and possible contamination with toxic osmium in the final product.<sup>2</sup> One of the most promising solutions to these problems is the immobilization of the catalytic osmium to an insoluble matrix. Kobayashi et al. have used the microencapsulation of  $\text{OsO}_4$  in polymer to achieve the recyclability of the catalyst.<sup>3</sup> Choudary et al. have heterogenized the osmium catalyst by an ion-exchange technique.<sup>4</sup> In another fascinating design,  $\text{OsO}_4$  was immobilized onto a silica-anchored tetrasubstituted olefin by Jacobs et al.<sup>5</sup> Efforts have thus been directed at heterogenizing the catalytic osmium on a polymer or silica gel, or even via encapsulation, to avoid contamination of the final product and also to recycle the osmium species.<sup>6</sup> But the lower activity of the heterogeneous catalysts remains severe problems. There are few examples of recyclable homogeneous osmium catalysts that have higher levels of activity than those of heterogeneous catalysts.<sup>7</sup>

Dendrimers are fascinating macromolecules due to their unique physical and chemical properties, which are caused by their well-defined hyperbranched framework.<sup>8</sup> Metallodendrimers, with

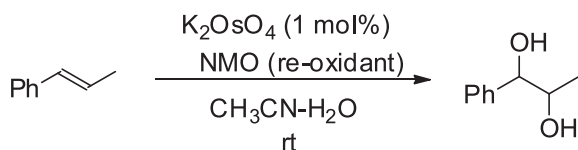
catalytic sites immobilized within the dendrimer, are particularly useful as synthetic catalysts not only because of their unique reactivity and fair solubility but also because of their recyclability by reprecipitation.<sup>9</sup> Presently, metallodendrimers with a catalytic site at the core have received considerable attention due to their unique selectivity and reactivity caused by specific reaction fields constructed by the dendron.<sup>10</sup> Some of them show a positive dendritic effect on regio- or stereoselectivity, meaning that their selectivity is enhanced by an increase in the generation number of the dendrimer.<sup>11,12</sup> Recently, several examples of positive dendritic effects on chemical yields have been reported by us<sup>13</sup> and by other groups.<sup>14</sup> A few examples of these unique phenomena are thought to be caused by the suppression of the decomposition of catalytic metal within the dendrimer.<sup>13b,14d,15</sup> Thus, by the introduction of catalytic osmium at the core site of the dendrimer, the decomposition of osmium catalyst was expected to be suppressed. We have expected that recyclable homogeneous osmium catalysts, with higher levels of activity than heterogeneous catalysts, would be produced by the use of the core site of high-generation dendrimers. We report herein the simple synthesis of a series of novel dendritic supports with a bis(quaternary ammonium bromide) core, the preparation of the corresponding osmate ( $\text{OsO}_4^{2-}$ ) core dendrimer by an ion-exchange technique and its application to homogeneous dihydroxylation of olefins and their asymmetric version. We found that the third-generation dendritic osmium catalyst could be recovered most efficiently by reprecipitation after the dihydroxylation reaction and reused. We also observed the dendritic effect on the recyclability of a catalyst.<sup>16</sup>

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## 2. Results and discussion

### 2.1. Preparation of dendritic osmium catalyst **2(Gn)**

For the catalytic dihydroxylation reaction of olefins,  $\text{OsO}_4$ , and  $\text{K}_2\text{OsO}_4$  were each used as a catalyst. Recently,  $\text{K}_2\text{OsO}_4$  was widely used due to its low volatility. By carrying out the dihydroxylation reaction in aqueous acetonitrile by the use of 1 mol % of  $\text{K}_2\text{OsO}_4$  according to Scheme 1, a brown solid appeared on the glassware surface, as shown in Fig. 1. It is thought to be osmium oxide, which is probably produced by the aggregation of catalytic osmium species before the reaction is complete. From this result, in the case of the preparation of a recyclable homogeneous osmium catalyst, it is thought that not only we immobilize the catalytic osmium on soluble polymer-supports, but also we must suppress the aggregation of the introduced catalytic osmium. Then, it is expected that the introduction of catalytic osmium at the core site of a high-generation dendrimer would suppress the decomposition of the catalyst, which is caused by the aggregation of osmium.



Scheme 1. Dihydroxylation catalyzed by  $\text{K}_2\text{OsO}_4$ .

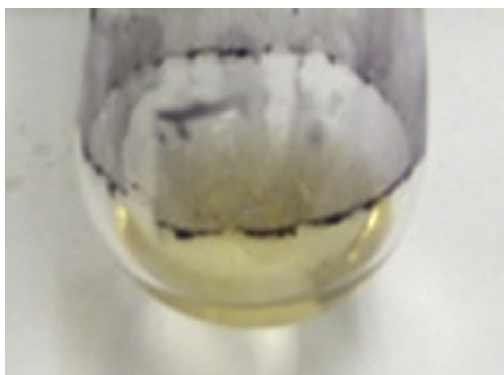
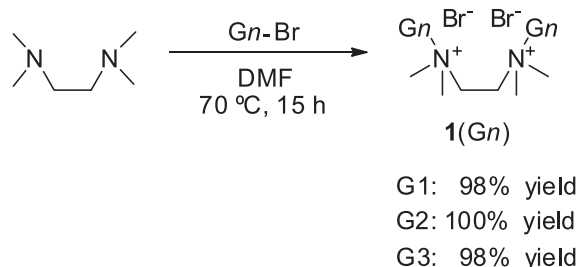


Fig. 1. Dihydroxylation catalyzed by  $\text{K}_2\text{OsO}_4$ .

In this study, we have introduced  $\text{OsO}_4^{2-}$  at the core site of the (quaternary ammonium bromide) core dendrimer by an ion-exchange technique. To suppress the leaching of osmium off the soluble polymer-backbone during the catalytic dihydroxylation reaction, we synthesized bis(quaternary ammonium bromide) core dendrimers **1(Gn)**, which immobilized catalytic osmium with the bidentate ligation, according to Scheme 2.<sup>17</sup> After the addition of  $N,N,N',N'$ -tetramethylethylenediamine to an  $N,N$ -dimethylformamide (DMF) solution of poly(benzyl ether) dendritic bromide  $\text{Gn-Br}$ <sup>18</sup> (structural formulas of  $\text{Gn}$  are shown in Fig. 2), the reaction mixture was stirred at 70 °C for 15 h under an argon atmosphere. In all generations, the corresponding bis(quaternary ammonium bromide) core dendrimers **1(Gn)** were obtained in excellent chemical yields.



Scheme 2. Synthesis of dendrimer **1(Gn)**.

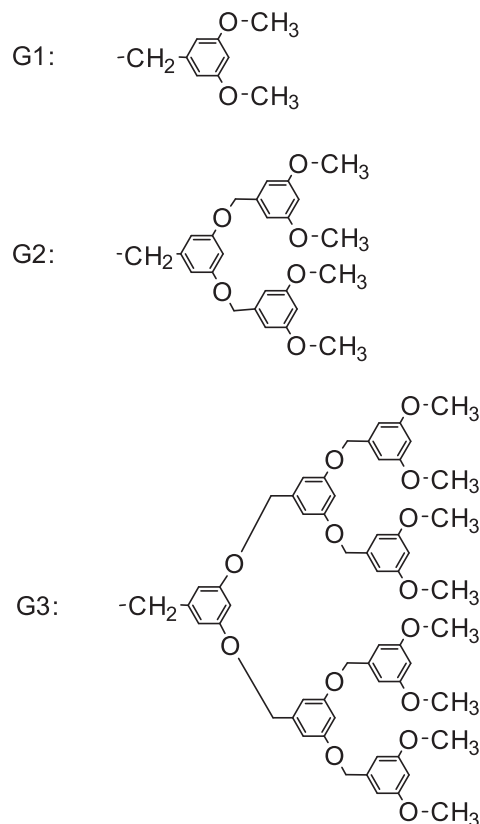


Fig. 2. Structural formulas of  $\text{Gn}$  dendrons ( $n=1-3$ ).

Next, novel  $\text{OsO}_4^{2-}$  core dendrimers were prepared by an ion-exchange procedure, as follows (Table 1). In the case of  $\text{G1}$ , **1(G1)**, which has low solubility in water and in most organic solvents, and  $\text{K}_2\text{OsO}_4$  were vigorously stirred in water to afford **2(G1)**, which was

Table 1  
Preparation of  $\text{OsO}_4^{2-}$  core dendrimer **2(Gn)**<sup>a</sup>

$\text{Gn}$	Solvent	Os content <sup>b</sup> of <b>2(Gn)</b> (mmol/g)	
		Found	Calcd
G1	$\text{H}_2\text{O}$	0.36	1.49
G2	$\text{H}_2\text{O}/\text{CH}_2\text{Cl}_2$	0.76	0.82
G3	$\text{H}_2\text{O}/\text{Toluene}$	0.22	0.43

<sup>a</sup> Reaction conditions: **1(Gn)**, an equimolar amount of  $\text{K}_2\text{OsO}_4$ , carried out at room temperature for 5 h.

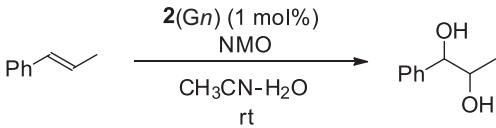
<sup>b</sup> Determined by ICP-AES.

collected by filtration of the reaction mixture. In the cases of G2 and G3, **1**(Gn) and K<sub>2</sub>OsO<sub>4</sub> were vigorously stirred in water and dendrimer-soluble organic solvent as a two-phase condition, followed by extraction. The Os content of **2**(Gn) was determined by ICP-AES after microwave digestion. The Os content of **2**(G1) was much lower than the calculated value, likely due to the low solubility of **1**(G1) in water in the preparation of **2**(G1). In all generations, it was found that the ion-exchange for OsO<sub>4</sub><sup>2-</sup> was incomplete.

## 2.2. Homogeneous dihydroxylation of olefins with dendritic osmium catalyst

We then examined the utility of the dendrimer **2**(Gn) as an osmium catalyst by performing *cis*-dihydroxylation of olefins (Table 2). By employing 1 mol % of various generations of dendritic osmium catalysts **2**(Gn), *cis*-dihydroxylation reactions of *trans*- $\beta$ -methylstyrene were carried out by the use of *N*-methylmorpholine *N*-oxide (NMO) as a re-oxidant in aqueous acetonitrile (CH<sub>3</sub>CN/H<sub>2</sub>O=4:1 (v/v)) at room temperature. After the disappearance of *trans*- $\beta$ -methylstyrene, which was monitored by thin-layer chromatography (TLC), the reaction mixture was evaporated and dissolved in a small amount of acetone. The acetone solution was poured into water and the precipitated dendritic osmium catalysts were recovered and subsequently reused.

**Table 2**  
Dihydroxylation of *trans*- $\beta$ -methylstyrene catalyzed by **2**(Gn)<sup>a</sup>



Gn	Yield <sup>b</sup> (%) (Time (h))		
	First	Second	Third
G1	90 (0.5)	97 (2)	43 (14)
G2	97 (0.5)	97 (1)	93 (2)
G3	93 (0.5)	97 (0.5)	96 (0.7)

<sup>a</sup> Reaction conditions: **2**(Gn) (1 mol %), olefin (1 equiv), NMO (1.2 equiv), CH<sub>3</sub>CN/H<sub>2</sub>O (4:1, v/v, 0.25 M based on olefin), carried out at room temperature for indicated time.

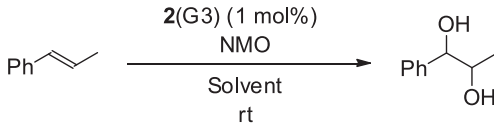
<sup>b</sup> Determined by integration of <sup>1</sup>H NMR absorptions referring to an internal standard.

In these catalytic conversions, **2**(Gn) was completely dissolved in the reaction mixture, allowing the dihydroxylation reactions to proceed homogeneously to complete in 0.5 h in all generations ('First' column in Table 2). Next, by carrying out reprecipitation for the catalyst recycling, the recovery of **2**(Gn) was low in the cases of G1 and G2 (ca. 50% and 80% for G1 and G2, respectively). This is likely due to the dendritic catalyst **2**(Gn) having a lower molecular weight, as it was somewhat dissolved in the water solvent. In contrast, in the case of G3, catalyst **2**(G3) was recovered nearly quantitatively.

Furthermore, in the case of G3, even the third round of dihydroxylation was completed within 0.7 h with an excellent chemical yield. In contrast, in the case of G1, the third round of dihydroxylation proceeded very slowly to afford the corresponding diol in only a 43% yield, even when allowed to proceed for 14 h. A comparison of increases in the reaction time by increasing the recycling number shows that the increase in the reaction time for G3 (0.5 h  $\rightarrow$  0.7 h) is the smallest among all generations. The relationship between the generation number of **2**(Gn) and increases in the reaction time by increasing the recycling number is one of the positive dendritic effects.<sup>11–14</sup> To our knowledge, these results are the first to be reported of the dendritic effect on the recyclability of a catalyst.

Next, we carried out the dihydroxylation reaction of *trans*- $\beta$ -methylstyrene by the use of 1 mol % of the third-generation **2**(G3) under various aqueous conditions (Table 3). In aqueous *tert*-butyl alcohol, the dihydroxylation proceeded slowly to afford the corresponding diol in a low chemical yield, probably because of the low solubility of **2**(G3) (Table 3, 29% for entry 1). In aqueous acetone, on the other hand, the corresponding diol was obtained in a good chemical yield (Table 3, 87% for entry 2) although the reaction time in this case exceeded that in aqueous acetonitrile. As a result, it was found that aqueous acetonitrile was the most suitable solvent for the dihydroxylation reaction catalyzed by the dendritic osmium catalyst **2**(G3).

**Table 3**  
Dihydroxylation of *trans*- $\beta$ -methylstyrene in various solvents<sup>a</sup>



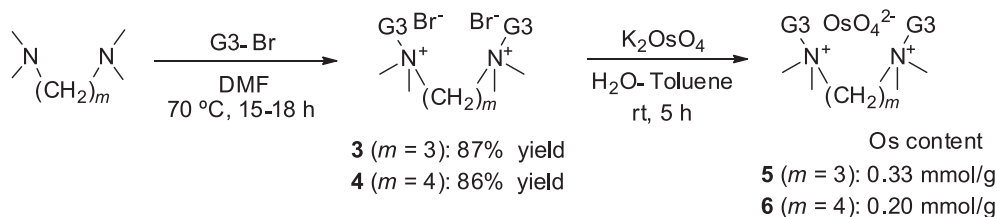
Entry	Solvent	Time (h)	Yield <sup>b</sup> (%)
1	<sup>t</sup> BuOH/H <sub>2</sub> O	5	29
2	Acetone/H <sub>2</sub> O	1	87
3	CH <sub>3</sub> CN/H <sub>2</sub> O	0.5	93

<sup>a</sup> Reaction conditions: **2**(G3) (1 mol %), olefin (1 equiv), NMO (1.2 equiv), organic solvent/H<sub>2</sub>O (4:1, v/v, 0.25 M based on olefin), carried out at room temperature for indicated time.

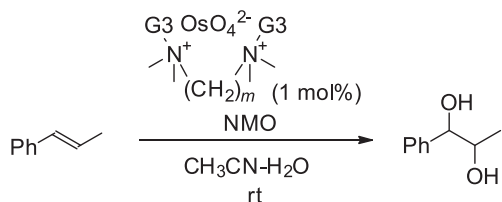
<sup>b</sup> Determined by integration of <sup>1</sup>H NMR absorptions referring to an internal standard.

We then prepared various third-generation dendritic catalysts **5** and **6**, which differed in the length between two nitrogens. Bis (quaternary ammonium bromide) core dendrimers **3**, **4**, and the corresponding osmate core dendrimers **5**, **6** were prepared according to the procedures similar to those used for **1**(G3) and **2**(G3), respectively (Scheme 3).

We carried out the dihydroxylation reaction of *trans*- $\beta$ -methylstyrene by the use of 1 mol % of the third-generation dendritic catalysts **2**, **5**, **6**. The reaction conditions and the catalyst recycling procedure were the same as in Table 2. The chemical yield,



**Scheme 3.** Synthesis of dendrimer **3**, **4** and preparation of **5**, **6**.

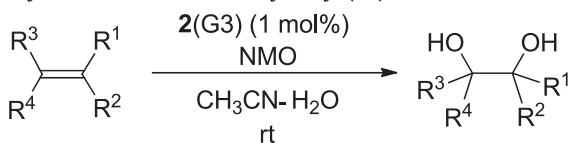
**Table 4**Dihydroxylation of *trans*- $\beta$ -methylstyrene catalyzed by the third-generation dendritic catalysts<sup>a</sup>

Entry	Catalyst	<i>m</i>	Yield (%) <sup>b</sup> (Reaction time, Os leaching)		
			First	Second	Third
1	2	2	93 (0.5 h, 2.2%)	97 (0.5h, 1.5%)	96 (0.7 h, 0.9%)
2	5	3	88 (0.7 h, 2.2%)	91 (0.7 h, 2.7%)	89 (1 h, 3.5%)
3	6	4	86 (0.5 h, 3.6%)	95 (0.7 h, 2.4%)	93 (1.3 h, 2.8%)

<sup>a</sup> Reaction conditions: Catalyst (1 mol %), olefin (1 equiv), NMO (1.2 equiv), CH<sub>3</sub>CN/H<sub>2</sub>O (4:1, v/v, 0.25 M based on olefin), carried out at room temperature for indicated time.

<sup>b</sup> Determined by integration of <sup>1</sup>H NMR absorptions referring to an internal standard.

the reaction time, and the leaching of osmium off each dendrimer backbone are shown in Table 4. The dihydroxylation reaction proceeded smoothly to afford the corresponding diol in a good chemical yield in all cases. On the other hand, the leaching of osmium was larger in the cases of **5** and **6** than in the case of **2**. Therefore, the increase in the reaction time by increasing the recycling number in the case of **2** (0.5 h → 0.7 h) was smallest among all catalysts. As a result, it was found that **2** could be recycled most efficiently in the catalytic dihydroxylation reaction.

**Table 5**Dihydroxylation of various olefins catalyzed by **2**(G3)<sup>a</sup>

Entry	Olefin	Product	Time (h)	Yield <sup>b</sup> (%)
1			0.5	86
2			0.5	90
3			0.5	92
4			0.5	86
5			1	91

(continued on next page)

**Table 5** (continued)

Entry	Olefin	Product	Time (h)	Yield <sup>b</sup> (%)
6			0.5	81
7			0.5	87
8			2	90
9			3	89
10			1.5	94

<sup>a</sup> The reaction conditions were the same as in Table 2.

<sup>b</sup> Isolated yield.

We subsequently performed *cis*-dihydroxylation of various olefins by employing 1 mol % of the third-generation dendritic osmium catalyst **2**(G3) according to Table 5. In all cases, the dihydroxylation reactions proceeded smoothly. Especially, in the case in which substituted styrene derivatives were used, the dihydroxylation were completed within 0.5 h (Table 5, entries 1–4). The dihydroxylation catalyzed by the dendritic osmium catalyst **2**(G3) were more rapid than those reported for the immobilized osmium catalysts,<sup>3–6</sup> due to the homogeneity of **2**(G3).

The reusability of catalyst **2**(G3) was examined again using various olefins (Table 6). In these experiments, it was found that catalyst **2**(G3) could be efficiently recycled up to five times by reprecipitation, and the corresponding diols were consistently obtained in good chemical yields in 0.5–2 h in all cases. The reaction mixture was homogeneous and the decomposition of catalyst **2**(G3) was not observed in the reaction vessel, unlike the case when K<sub>2</sub>OsO<sub>4</sub> was used as a catalyst (Fig. 1), as shown in Fig. 3. Also considering the dendritic effect on the recyclability of a catalyst (Table 2), the efficient recycling of **2**(G3) was probably due to the aggregative decomposition of the catalytic osmium being suppressed by the steric hindrance of the dendron owing to the introduction of OsO<sub>4</sub><sup>2-</sup> at the core site of the dendrimer (Fig. 4).

**Table 6**Catalyst recycling in dihydroxylation by use of **2**(G3)<sup>a</sup>

Entry	Olefin	Yield (%) <sup>b</sup>				
		First	Second	Third	Fourth	Fifth
1		86	90	87	88	91
2		90	91	92	88	83
3		92	93	86	88	93
4		86	92	89	87	95
5		81	90	86	80	89

<sup>a</sup> The reaction conditions were the same as in Table 2. Carried out for 0.5–2 h.

<sup>b</sup> Isolated yield.



Fig. 3. Dihydroxylation catalyzed by 2(G3).

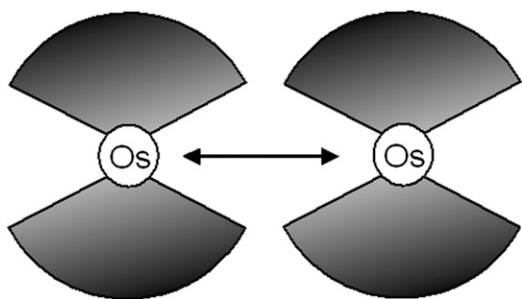


Fig. 4. The aggregation of catalytic osmium is suppressed by the steric hindrance of the dendron.

### 2.3. Asymmetric dihydroxylation of olefins with dendritic osmium catalyst and chiral ligand

The catalytic asymmetric dihydroxylation of olefins, using a catalytic amount of osmium tetroxide in the presence of a chiral ligand, allows access to a wide variety of enantiomerically pure vicinal diols.<sup>19</sup> In 1992, Sharpless et al. reported a catalytic system based on bisinchona alkaloids such as 1,4-bis(9-*O*-dihydroquininyl)phthalazine ((DHQ)<sub>2</sub>-PHAL), which has received a great deal of interest due to the broad scope of substances available and the high enantioselectivities attained.<sup>20</sup> Encouraged by our previous results, we

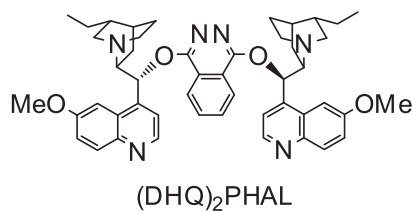
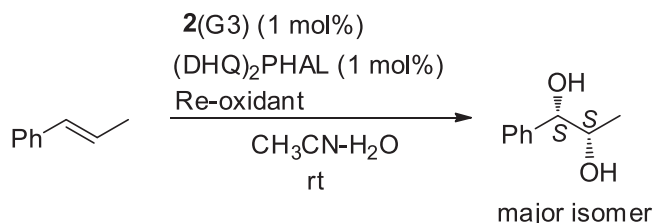
then attempted the asymmetric dihydroxylation of olefins according to the Sharpless procedure.

First, we examined a re-oxidant of the asymmetric dihydroxylation (Table 7). After the stirring of the mixture of the dendritic osmate 2(G3) (1 mol %) and the chiral ligand (DHQ)<sub>2</sub>-PHAL (1 mol %) in aqueous acetonitrile (CH<sub>3</sub>CN/H<sub>2</sub>O=4:1 (v/v)), a re-oxidant, such as NMO and K<sub>3</sub>[Fe(CN)<sub>6</sub>], and *trans*-β-methylstyrene were added. The stereochemistry of the major isomer, which was determined by HPLC in the use of a chiral phase column, is shown in Table 7. When NMO was used as a re-oxidant, the asymmetric dihydroxylation proceeded smoothly to afford the corresponding diol with an 87% enantiomeric excess (ee) (Table 7, entry 1). On the other hand, when K<sub>3</sub>[Fe(CN)<sub>6</sub>] was used, the asymmetric dihydroxylation was rather slow and the chemical yield was low, although the ee was slightly higher than that when NMO was used (Table 7, entry 2). In this case, as the reaction mixture was muddy because of the low solubility of K<sub>3</sub>[Fe(CN)<sub>6</sub>] in aqueous acetonitrile, the dendritic catalyst could not be recovered by reprecipitation after the dihydroxylation reaction. Next, by employing NMO as a re-oxidant, we carried out asymmetric dihydroxylation by the slow addition of *trans*-β-methylstyrene for the indicated times (Table 7, 0.5 h and 4 h in entries 3 and 4, respectively). The dihydroxylation reaction proceeded completely as soon as we added an olefin. Although the ratio of catalysts to olefins in entries 3 and 4 was much larger than that in entry 1 due to the slow addition of an olefin, ee's in entries 3 and 4 did not exceed that in entry 1, contrary to our expectation.

We subsequently performed the asymmetric dihydroxylation of various olefins by employing 1 mol % of the chiral dendritic osmium catalyst and NMO as a re-oxidant in aqueous acetonitrile, as shown in Table 8. In all cases, the asymmetric dihydroxylation reactions proceeded smoothly to afford the corresponding diol in good chemical yields. In the case of aromatic olefins, the asymmetric dihydroxylation reactions were completed in 0.5 h and the ee's were moderate to excellent. In contrast, in the case of aliphatic olefins such as 1-decene and *trans*-5-decene, the asymmetric reactions were slightly slow with completion in 1–1.5 h, and the ee's were somewhat low (Table 8, entries 9 and 10).

Finally, the reusability of the chiral osmium catalyst was examined (Table 9). The reaction conditions were the same as in Table 8, and the chiral osmium catalyst was recycled according to the same procedure as shown in Table 2. The asymmetric dihydroxylation reactions proceeded smoothly to complete within 0.5–2 h in each round, and the ee's were hardly decreased even in the fifth

Table 7  
Asymmetric dihydroxylation in various conditions



Entry	Re-oxidant	Time (h)	Yield <sup>a</sup> (%)	ee (%)
1	NMO	0.5	85	87
2	K <sub>3</sub> [Fe(CN) <sub>6</sub> ]	2	66	90
3	NMO	0.5 <sup>b</sup>	87	86
4	NMO	4 <sup>b</sup>	99	86

<sup>a</sup> Isolated yield.

<sup>b</sup> An olefin was added slowly for the indicated time.



**Table 8**  
Asymmetric dihydroxylation of various olefins

Entry	Olefin	Time (h)	Yield <sup>a</sup> (%)	ee (%)
1		0.5	85	87
2		0.5	95	70
3		0.5	94	63
4		0.5	88	68
5		0.5	91	69
6		0.5	81	90
7		0.5	87	94
8		0.5	92	96
9		1	96	45
10		1.5	96	65

<sup>a</sup> Isolated yield.**Table 9**  
Chiral catalyst recycling in asymmetric dihydroxylations by use of **2(G3)**<sup>a</sup>

Olefin		First	Second	Third	Fourth	Fifth
	Yield <sup>b</sup> (%)	85	92	95	94	92
	ee (%)	87	86	86	85	85
	Yield <sup>b</sup> (%)	95	98	99	97	97
	ee (%)	70	67	67	68	67

<sup>a</sup> The reaction conditions were the same as in Table 8. Carried out for 0.5–2 h.<sup>b</sup> Isolated yield.

dihydroxylation reaction of either olefin.<sup>21</sup> As a result, it was supposed that not only the dendritic osmium catalyst **2(G3)** but also the chiral ligand (DHQ)<sub>2</sub>-PHAL could be recovered completely by reprecipitation so that the subsequent asymmetric dihydroxylation reaction proceeded efficiently. In the case of the commercially available microencapsulated OsO<sub>4</sub> catalyst, the chiral ligand was recovered by acid–base extraction after the filtration of the immobilized OsO<sub>4</sub> catalyst.<sup>3c</sup> In our catalyst recycling system, both the immobilized osmium catalyst and the chiral ligand were recovered simultaneously to promote the subsequent asymmetric dihydroxylation efficiently.

### 3. Conclusion

We prepared novel osmate core dendrimers to be used as homogeneous catalysts for the dihydroxylation of olefins. These dendritic osmium catalysts were recovered by reprecipitation after the dihydroxylation reaction and then reused. Furthermore, a positive dendritic effect on the recyclability of a catalyst was observed. The third-generation dendritic osmium catalyst was recycled up to five times. It is supposed that the efficient catalyst recycling was probably due to the aggregative decomposition of the catalytic osmium being suppressed by the steric hindrance of the dendron owing to the introduction of OsO<sub>4</sub><sup>2-</sup> at the core site of the dendrimer.

Furthermore, by applying these dendritic osmium catalysts to the asymmetric version, the corresponding diol was obtained in a high chemical yield with a fair ee. In this case, by reprecipitation after the asymmetric dihydroxylation, both the dendritic osmium catalyst and the chiral ligand were recovered simultaneously and reused.

It was found that the immobilization of catalytic metals on dendrimers at the core position is suitable for the design of homogeneous recyclable catalysts.

### 4. Experimental section

#### 4.1. Materials

G3-Br was prepared by the method in the literature.<sup>12c</sup> Degassed solvent, which was bubbled by argon for more than 1 h was used in the preparation of **2**, **5**, and **6**. Other reagents and dry solvents were commercially available and were used as received. Kieselgel 60 F<sub>254</sub> (Merck) was used for TLC, and Wakogel C-300 (Wako) was used for silica gel column chromatography.

#### 4.2. Measurement

Microanalyses were performed with a CE Instruments EA1110 elemental analyzer. IR spectra were recorded on a Shimadzu IR Prestige-21 FT-IR spectrophotometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured with a Bruker Avance III 400 spectrometer (<sup>1</sup>H: 400 MHz, <sup>13</sup>C: 100 MHz). Chemical shifts were reported as parts per million downfield from TMS as an internal standard in  $\delta$  units. Coupling constants (*J*) are given in hertz (Hz). Melting points were determined on a Mettler FP90 microscopic plate, and were uncorrected. High performance liquid chromatography (HPLC) was performed with a Shimadzu 10ADVP LCsolution system using a Daicel chiral column. ICP-AES was recorded on a Shimadzu ICPS-8100 analyzer.

#### 4.3. Synthesis of dendritic quaternary ammonium bromide **1(Gn)**, **3** and **4**: typical procedure

A dry DMF solution (8 mL) of *N,N,N',N'*-tetramethylethylenediamine (74.6 mg, 0.642 mmol) and 3,5-bis[3,5-bis(3,5-dimethoxybenzyloxy)benzyloxy]benzyl bromide (1.408 g, 1.343 mmol) was stirred at 70 °C for 15 h under an argon atmosphere. The reaction mixture was evaporated to dryness, and the residue was purified with silica gel column chromatography (ethyl acetate/methanol=3/1 as an eluent) to obtain **1(G3)** (1.398 g, 0.632 mmol) in a 98% yield.

Compounds **1(G2)**, **3** and **4** were synthesized according to the above procedure. In the case of the synthesis of **1(G1)**, a white powder was formed during the reaction. The reaction mixture was evaporated to dryness and was filtered to obtain **1(G1)**, followed by washing with acetone.

4.3.1. *N,N'*-Ethane-1,2-diyl *N,N'*-bis(3,5-dimethoxybenzyloxy) *N,N,N',N'*-tetramethylammonium dibromide (**1(G1)**). White powder; mp 201.5–202 °C; IR (KBr) 3483, 2976, 2952, 1598, 1350, 1208, 1175, 1154, 1066, 1044, 934, 843 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>/CD<sub>3</sub>OD) δ=6.81 (d, *J*=2.0 Hz, 4H), 6.60 (t, *J*=2.0 Hz, 2H), 4.78 (s, 4H), 4.55 (s, 4H), 3.84 (s, 12H), 3.28 (s, 12H); <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>/CD<sub>3</sub>OD) δ=162.0, 128.9, 111.9, 103.1, 69.1, 57.9, 56.0, 50.7. Anal. Calcd for C<sub>24</sub>H<sub>38</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>4</sub>·0.2H<sub>2</sub>O: C, 49.53; H, 6.65; N, 4.81; Br, 27.46%. Found: C, 49.64; H, 6.68; N, 4.83; Br, 27.16%.

4.3.2. *N,N'*-Ethane-1,2-diyl *N,N'*-[3,5-bis(3,5-dimethoxybenzyloxy)-benzyloxy]*N,N,N',N'*-tetramethylammonium dibromide (**1(G2)**). White powder; mp 183–184.5 °C; IR (KBr) 3386, 3002, 2962, 2838, 1597, 1465, 1430, 1298, 1205, 1159, 1052, 834 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>) δ=6.77 (d, *J*=1.8 Hz, 4H), 6.62–6.59 (m, 2H), 6.55 (d, *J*=2.2 Hz, 8H), 6.37 (t, *J*=2.2 Hz, 4H), 4.97 (s, 4H), 4.94 (s, 8H), 4.82 (s, 4H), 3.75 (s, 24H), 3.20 (s, 12H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ=161.0, 160.0, 138.6, 127.9, 112.1, 105.5, 104.7, 99.9, 70.1, 67.6, 57.9, 55.5, 50.0. Anal. Calcd for C<sub>56</sub>H<sub>70</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>12</sub>: C, 59.89; H, 6.28; N, 2.49; Br, 14.23%. Found: C, 59.88; H, 6.12; N, 2.41; Br, 13.96%.

4.3.3. *N,N'*-Ethane-1,2-diyl *N,N'*-[3,5-bis[3,5-bis(3,5-dimethoxybenzyloxy)benzyloxy]benzyloxy] *N,N,N',N'*-tetramethylammonium dibromide (**1(G3)**). White powder; mp 72.5–74.5 °C; IR (KBr) 3356, 3000, 2937, 2838, 1590, 1429, 1300, 1270, 1205, 1150, 1052, 1009, 834 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>) δ=6.71 (d, *J*=1.6 Hz, 4H), 6.67 (d, *J*=2.0 Hz, 8H), 6.61–6.56 (m, 2H), 6.52 (d, *J*=2.0 Hz, 16H), 6.51 (t, *J*=2.0 Hz, 4H), 6.35 (t, *J*=2.2 Hz, 8H), 4.90 (s, 24H), 4.86 (s, 4H), 4.67 (s, 4H), 3.72 (s, 48H), 3.10 (s, 12H); <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>) δ=160.9, 160.0, 159.9, 139.1, 138.8, 127.8, 111.9, 106.6, 105.3, 104.7, 101.7, 99.8, 70.0, 67.7, 57.9, 55.4, 49.9. Anal. Calcd for C<sub>120</sub>H<sub>134</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>28</sub>: C, 65.15; H, 6.11; N, 1.27; Br, 7.22%. Found: C, 64.99; H, 5.93; N, 1.22; Br, 7.08%.

4.3.4. *N,N'*-Propane-1,2-diyl *N,N'*-[3,5-bis[3,5-bis(3,5-dimethoxybenzyloxy)benzyloxy]benzyloxy] *N,N,N',N'*-tetramethylammonium dibromide (**3**). White powder; mp 71–73 °C; IR (KBr) 3399, 2999, 2936, 2837, 1595, 1458, 1373, 1298, 1206, 1153, 1049, 831, 681 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>) δ=6.78 (d, *J*=1.7 Hz, 4H), 6.67 (d, *J*=2.1 Hz, 8H), 6.64–6.62 (m, 2H), 6.54 (d, *J*=2.2 Hz, 16H), 6.52 (t, *J*=2.0 Hz, 4H), 6.37 (t, *J*=2.2 Hz, 8H), 4.95 (s, 8H), 4.92 (s, 16H), 4.64 (s, 4H), 3.74 (s, 52H), 3.05 (s, 12H), 2.46 (s, 2H); <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>) δ=160.9, 160.0, 159.9, 139.1, 138.8, 128.6, 112.0, 106.6, 105.3, 104.5, 101.7, 99.8, 70.1, 70.0, 67.8, 62.4, 55.4, 50.2, 19.1. Anal. Calcd for C<sub>121</sub>H<sub>136</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>28</sub>: C, 65.28; H, 6.16; N, 1.26; Br, 7.18%. Found: C, 65.00; H, 6.18; N, 1.22; Br, 7.08%.

4.3.5. *N,N'*-Butane-1,2-diyl *N,N'*-[3,5-bis[3,5-bis(3,5-dimethoxybenzyloxy)benzyloxy]benzyloxy] *N,N,N',N'*-tetramethylammonium dibromide (**4**). White powder; mp 68.5–70.5 °C; IR (KBr) 2995, 2936, 2837, 1595, 1458, 1319, 1206, 1153, 1049, 831, 681 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>) δ=6.78 (d, *J*=1.7 Hz, 4H), 6.66 (d, *J*=2.1 Hz, 8H), 6.63–6.60 (m, 2H), 6.53 (d, *J*=2.2 Hz, 16H), 6.50 (t, *J*=2.0 Hz, 4H), 6.35 (t, *J*=2.2 Hz, 8H), 4.95 (s, 8H), 4.92 (s, 16H), 4.59 (s, 4H), 3.87 (br s, 4H), 3.72 (s, 48H), 3.00 (s, 12H), 2.07 (s, 4H); <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>) δ=161.0, 160.03, 159.95, 139.2, 138.8, 128.8, 112.1, 106.6, 105.3, 104.4, 101.7, 99.9, 70.1, 70.0, 67.6, 64.5, 55.4, 49.8, 20.2. Anal. Calcd for C<sub>122</sub>H<sub>138</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>28</sub>·2H<sub>2</sub>O: C, 64.37; H, 6.29; N, 1.23; Br, 7.02%. Found: C, 64.33; H, 6.13; N, 1.16; Br, 7.04%.

#### 4.4. Preparation of dendritic osmate **2(Gn)**, **5**, and **6**: typical procedure

To a toluene solution (degassed; 80 mL) of **1(G3)** (1.547 g, 0.698 mmol), an aqueous solution (degassed; 50 mL) of K<sub>2</sub>OsO<sub>4</sub>·2H<sub>2</sub>O (256 mg, 0.695 mmol) was added at room

temperature under an argon atmosphere. The resulting two-phase mixture was vigorously stirred for 5 h. The reaction mixture was extracted with toluene (80 mL×3). After removal of the solvent under reduced pressure, **2(G3)** was obtained as a black solid (1.667 g). The Os content of **2(G3)** was determined by ICP-AES after microwave digestion by the addition of HNO<sub>3</sub>.

4.4.1. *Compound 2(G1)*. Black powder; mp 203–205 °C; Os content: 0.36 mmol/g; IR (KBr) 3418, 3000, 2966, 2943, 2841, 1595, 1328, 1207, 1157, 1065, 853, 833 cm<sup>-1</sup>. Anal. Found: C, 41.46; H, 5.71; N, 3.96%.

4.4.2. *Compound 2(G2)*. Black powder; mp 79–81 °C; Os content: 0.76 mmol/g; IR (KBr) 3446, 2955, 2938, 2837, 1598, 1205, 1155, 1052, 833 cm<sup>-1</sup>. Anal. Found: C, 54.39; H, 5.85; N, 2.41%.

4.4.3. *Compound 2(G3)*. Black powder; mp 49–51 °C; Os content: 0.22 mmol/g; IR (KBr) 3447, 2961, 2936, 2838, 1457, 1205, 1155, 1052, 832 cm<sup>-1</sup>. Anal. Found: C, 63.29; H, 5.95; N, 1.21%.

4.4.4. *Compound 5*. Black powder; mp 76–78 °C; Os content: 0.33 mmol/g; IR (KBr) 3383, 3001, 2936, 2837, 1597, 1456, 1373, 1323, 1206, 1155, 1051, 835 cm<sup>-1</sup>. Anal. Found: C, 60.78; H, 5.66; N, 1.09%.

4.4.5. *Compound 6*. Black powder; mp 70.5–72.5 °C; Os content: 0.20 mmol/g; IR (KBr) 3399, 2999, 2938, 2839, 1597, 1458, 1342, 1323, 1206, 1155, 1051, 837 cm<sup>-1</sup>. Anal. Found: C, 62.56; H, 5.99; N, 1.08%.

#### 4.5. Dihydroxylation reaction: typical procedure

To a CH<sub>3</sub>CN/H<sub>2</sub>O (4:1, v/v) solution (3.75 mL) of **2(G3)** (48.5 mg, 0.01 mmol) were added *trans*-β-methylstyrene (120.2 mg, 1.017 mmol) and *N*-methylmorpholine *N*-oxide (NMO; 141.6 mg, 1.209 mmol) successively at room temperature under an argon atmosphere. After stirring the resulting mixture for 0.5 h, the dihydroxylation reaction was completed (monitored by TLC). The reaction mixture was evaporated and dissolved in a small amount of acetone. The acetone solution was poured into 6 mL of water to precipitate **2(G3)** as a grayish powder. After centrifugal separation, the aqueous solution was decanted, and the recovered **2(G3)** was reused for subsequent dihydroxylation reactions.

The decanted aqueous solution was concentrated under reduced pressure, and was purified with silica gel column chromatography (hexane/ethyl acetate=1/1 as an eluent) to obtain 1-phenyl-1,2-propanediol (133.3 mg, 0.876 mmol) in an 86% yield.

In Tables 2–4, the chemical yields were determined by integrating <sup>1</sup>H NMR absorptions by referring to an internal standard, which was added to the decanted aqueous solution. The leaching of osmium in Table 4 was determined by ICP-AES measurement of the decanted aqueous solution.

#### 4.6. Asymmetric dihydroxylation reaction: typical procedure

To a CH<sub>3</sub>CN/H<sub>2</sub>O (4:1, v/v) solution (2.5 mL) of **2(G3)** (46.6 mg, 0.01 mmol) was added 1,4-bis(9-*O*-dihydroquininyl)phthalazine ((DHQ)<sub>2</sub>-PHAL) (8.2 mg, 0.011 mmol). After the reaction mixture was stirred for 10 min, *trans*-β-methylstyrene (118.3 mg, 1.00 mmol) and *N*-methylmorpholine *N*-oxide (NMO; 140.5 mg, 1.20 mmol) were added successively at room temperature under an argon atmosphere. After the resulting mixture was stirred for 0.5 h, the dihydroxylation reaction was completed (monitored by TLC). The reaction mixture was evaporated and dissolved in a small amount of acetone. The acetone solution was poured into 6 mL of water to precipitate **2(G3)** and (DHQ)<sub>2</sub>-PHAL as a grayish powder. After centrifugal separation, the aqueous solution was decanted, and the

recovered **2**(G3) and (DHQ)<sub>2</sub>-PHAL were reused for subsequent asymmetric dihydroxylation reactions.

The decanted aqueous solution was concentrated under reduced pressure and was purified with silica gel column chromatography (hexane/ethyl acetate=1/1 as eluent) to obtain 1-phenyl-1,2-propanediol (128.7 mg, 0.846 mmol) in an 85% chemical yield. Enantiomeric excess (ee) was determined by HPLC analysis using Daicel Chiralcel OD (87% ee).

### Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.tet.2010.08.062.

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