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Magnetically recoverable osmium catalysts for dihydroxylation of olefins

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ABSTRACT

We prepared magnetically recoverable osmium catalysts by use of magnetite, quaternary ammonium salts, and potassium osmate(VI), and applied them to the dihydroxylation of olefins. By employing 2 mol% of the magnetic osmium catalyst, the dihydroxylation reaction proceeded smoothly to provide the corresponding vicinal diol in a good chemical yield. The osmium catalyst was readily recovered by use of an external magnet, and was reused repeatedly.

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Osmium-catalyzed dihydroxylation of olefins is one of the most useful transformations for the preparation of vicinal diols.¹ Although these reactions have had widespread application in organic synthesis, several obstacles stand in the way of their large-scale application to the drugs and fine chemicals industries-namely, their high cost, toxicity, volatility and possible contamination with toxic osmium in the final product.² One of the most promising solutions to these problems is the immobilization of the catalytic osmium to an insoluble matrix. Previously, heterogenization of catalytic osmium by immobilization on various organic and inorganic supports has been successful, so that the immobilized osmium catalyst could be recovered by filtration of the reaction mixture.³⁻⁵ But the lower activity of the immobilized catalyst remains a major problem. Recently, the immobilized homogeneous osmium catalysts, which have soluble backbones such as dendrimer and poly(ethylene glycol), were reported by us⁶ and by other groups.⁷ In these cases, the activity of the immobilized homogeneous catalysts were as high as those of the non-supported ones, and the former could be recovered by reprecipitation of the reaction mixture.

Magnetic nanoparticles have emerged as effective new supports for immobilization, because magnetic nanoparticle-supported catalysts can be separated from the reaction medium by an external permanent magnet.⁸ The magnetic separation circumvents timeconsuming and laborious separation steps, and allows for practical continuous catalysis. Very recently, magnetic nanoparticlesupported and magnetically recoverable transition metal catalysts such as palladium,⁹ ruthenium,¹⁰ nickel,¹¹ and copper¹² have been increasingly reported.¹³ Most magnetic catalysts have excellent activity, because the catalytic active sites are immobilized on nanoparticles having high surface areas. We report herein the synthesis of magnetically recoverable osmium catalysts by use of

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quaternary ammonium salts immobilized on magnetite and potassium osmate(VI) and their application to the dihydroxylation reaction of olefins. We found that the introduction of a dendritic skeleton to the quaternary nitrogen immobilized on a magnetite backbone caused an efficient recovery of the magnetic osmium catalyst and a decrease in the leaching of osmium during the dihydroxylation reaction. At the outset of this study, no example of a magnetically recoverable osmium catalyst had been reported.¹⁴

A magnetic nanoparticle-supported osmium catalyst 4 was synthesized as follows (Scheme 1). Magnetite (Fe₃O₄) nanoparticles were chosen for use as magnetic supports since they could be readily prepared by the conventional coprecipitation method.¹⁵ The silane coupling agent 2 was synthesized by stirring of the acetonitrile solution of [(chloromethyl)phenylethyl] trimethoxysilane 1 and triethyl amine at 70 °C for 5 h under an argon atmosphere. The reaction mixture was evaporated to dryness and the thus obtained 2 was used for the next step without further purification. Next, magnetite and 2 were refluxed in ethanol for 20 h under an argon atmosphere to afford magnetite-supported ammonium chloride 3, which was separated by magnetic decantation using an external magnet. The loading of **3** was 0.18 mmol/g, which was determined by elemental analysis of chlorine. The magnetite-supported osmium catalyst 4 was prepared by an ionexchange procedure. Namely, **3** and K₂OsO₄ were vigorously stirred in water at room temperature, followed by magnetic decantation. It was found that the ion-exchange for OsO_4^{2-} was complete, because the osmium species were not detected by ICP-AES in the decanted solution (Os content of 4: 0.083 mmol/g).

We then examined the utility of **4** as an osmium catalyst by performing *cis*-dihydroxylation of olefins (Table 1). By employing 2 mol% of the catalyst **4**, *cis*-dihydroxylation reaction of *trans*- β -methylstyrene was carried out by the use of *N*-methylmorpholine *N*-oxide (NMO) as a re-oxidant in aqueous acetone (acetone:H₂O = 2:1 (v/v)) at room temperature. The dihydroxylation reaction smoothly proceeded to completion in 5 h. The magnetic





Scheme 1. Preparation of 4.

Table 1

Dihydroxylation of *trans*-β-methylstyrene catalysed by **4**^a



^a Reaction conditions: **4** (2 mol%), olefin (1 equiv), NMO (1.3 equiv), acetone– H_2O (2:1, v/v, 0.33 M based on olefin), carried out at room temperature for 5 h. ^b Determined by integration of ¹H NMR absorptions referring to an internal standard.

osmium catalyst **4** was collected using an external magnet, and the reaction mixture was then transferred out of the reaction vessel.¹⁶ As a result, the corresponding diol was obtained in a good chemical yield (85%), but the leaching of osmium off the catalyst, which was determined by ICP-AES, was large (17.7%), contrary to our expectation (see the column labeled 'First' in Table 1). In addition, the reuse of the catalyst **4** did not afford sufficient activity (see the column labeled 'Second' in Table 1).

Recently, we have found that an OsO_4^{2-} core dendrimer that consists of poly(benzyl ether) dendron is very effective for the dihydroxylation reaction.⁶ The higher generation-derived dendritic osmium catalyst was more efficiently recycled by reprecipitation,



Figure 1. Structural formulas of Gn dendrons (n = 0-2).

and thus we observed a positive dendritic effect on the recyclability of the catalyst. In consideration of these results, we next designed $\mathbf{9}[Gn]$, which has a dendritic skeleton attached to the quaternary nitrogen immobilized on a magnetite backbone.

The silane coupling agent **7**[*Gn*], the magnetite-supported dendritic quaternary ammonium bromide **8**[*Gn*] (the structural formulas of *Gn* are shown in Figure 1), and the corresponding osmate(VI) **9**[*Gn*] were prepared according to Scheme 2, which was similar to Scheme 1.¹⁷ Also, in the preparation of **9**[*Gn*], the ion-exchange for OsO_4^{2-} was complete. The Os contents of **9**[*Gn*] are also shown in Scheme 2.

We then examined the catalytic activity and recyclability of the various generations of 9[Gn] by performing the *cis*-dihydroxylation reactions of *trans*- β -methylstyrene (Table 2). As a result, the



Scheme 2. Preparation of 9[Gn].

Table 2

Dihydroxylation of *trans*- β -methylstyrene catalysed by $\mathbf{9}[Gn]^a$



Gn	Yield ^b (%) (Reaction time, Os leaching)			
	First	Second		
G0	91 (3 h, 14.3%)	94 (7 h, 9.4%)		
G1	87 (3 h, 5.4%)	88 (4 h, 3.7%)		
G2	91 (2 h, 3.3%)	95 (2 h, 3.1%)		

^a Reaction conditions: 9[Gn] (2 mol%), olefin (1 equiv), NMO (1.3 equiv), acetone–H₂O (2:1, v/v, 0.33 M based on olefin), carried out at room temperature for indicated time.

^b Determined by integration of ¹H NMR absorptions referring to an internal standard.



Figure 2. Dihydroxylation catalyzed by 9[G2].



Figure 3. Recovery of 9[G2].

dihydroxylation proceeded smoothly in all generations. Figure 2 shows the reaction mixture of the dihydroxylation catalyzed by **9**[G2]. In the magnetic separation after the dihydroxylation, the second-generation magnetic catalyst **9**[G2] was most clearly collected from the reaction mixture, as shown in Figure 3. Furthermore, the leaching of osmium in the use of **9**[G2] was the least among all generations (see the column labeled 'First' in Table 2). Also in the case of recycling of the catalyst **9**[Gn], G2 afforded the least osmium leaching (see the column labeled 'Second' in Table 2). Although we have no definitive explanation at the moment for the finding that the osmium leaching was lowest in G2, the surrounding of catalytic osmium by the dendron having a

Table 3

Dihydroxylation of various olefins catalysed by 9[G2]^a

R ³ R	9 [G2] (2 mol% Os) NMO	но	он
R ⁴ R ²	Acetone–H ₂ O rt	R ³ R ⁴	R^2

		-		
Entry	Olefin	Product	Time (h)	Yield ^b (%)
1	Ph	OH Ph OH	2	96
2	Ph	он Ph OH	3	87
3	Ph	он Ph OH	3	95
4	Ph	Ph OH	3	90
5	Ph		4	93
6	\bigcirc	HOHOHO	2	86
7	Ph	OH Ph OH	3	97
8	Ph ^O	OH Ph ^{_O} OH	8	91
9	C ₈ H ₁₇	OH C ₈ H ₁₇ OH	6	89
10	C ₄ H ₉ C ₄ H ₉	$C_4H_9 \xrightarrow{OH} C_4H_9$	9	88

^a The reaction conditions were the same as in Table 2.

^b Isolated yield.

Table 4	
Catalyst recycling in dihydr	oxylations by use of 9 [G2] ^a

Entry	Olefin	Yield ^b , Reaction time				
		First	Second	Third	Fourth	Fifth
1	Ph	96%, 2 h	98%, 2 h	95%, 3 h	97%, 3 h	96%, 3 h
2	Ph	95%, 3 h	96%, 3 h	95%, 3 h	94%, 4 h	97%, 5 h
3	Ph	90%, 2 h	99%, 2 h	88%, 2 h	93%, 3 h	92%, 4 h
4	Ph	97%, 3 h	99%, 3 h	99%, 3 h	96%, 4 h	95%, 7 h

^a The reaction conditions were the same as in Table 2.

^b Isolated yield.

hydrophobic periphery could be responsible. The relationship between the generation number of **9**[*Gn*] and the osmium leaching is one of the positive dendritic effects.^{6,18,19} Our present results also indicate the dendritic effect on the recyclability of a catalyst, similar to those in the case of our recently reported OsO_4^{2-} core dendrimer.⁶

Encouraged by these results, we subsequently performed cis-dihydroxylation of various olefins by employing 2 mol% of the second-generation dendritic osmium catalyst **9**[G2], which was

recycled most efficiently in the catalytic system, as shown in Table 3. In all cases, the dihydroxylation reactions proceeded to completion. In particular, in the case in which substituted styrene derivatives were used, the dihydroxylations were completed in 2-3 h (Table 3, entries 1-4).

Finally, the reusability of the catalyst **9**[G2] was examined again using various olefins (Table 4). In these experiments, it was found that the catalyst **9**[G2] could be efficiently recycled up to five times by magnetic separation, and the corresponding diols were consistently obtained in good chemical yields in 2–7 h in all cases.

In summary, by employing a novel magnetic osmium catalyst having a dendritic skeleton, the dihydroxylation reaction proceeded smoothly and the osmium catalyst was efficiently recycled up to five times. Furthermore, a positive dendritic effect on the osmium leaching was observed. It would be expected that the design of the magnetically recoverable catalyst, in which a dendron is introduced to the active site, could be applied to various transition metal catalysts.

Supplementary data

X-ray diffraction patterns of magnetite, **8**[G2], and **9**[G2] and typical procedures for the preparations of **7**[Gn], **8**[Gn], and **9**[Gn] are available. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2011.04.030.

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- 16. General procedure: To an acetone-H₂O (2:1, v/v) solution (3 mL) of olefin (1 mmol) was added a magnetic osmium catalyst (0.02 mmol) and *N*-methylmorpholine *N*-oxide (NMO; 1.3 mmol) successively at room temperature under an argon atmosphere. After stirring the resulting mixture, the dihydroxylation reaction was completed (monitored by TLC). After the reaction mixture was slightly evaporated to remove acetone, a magnetic osmium catalyst was separated by magnetic decantation using an external magnet followed by washing with H₂O, and the recovered magnetic cosmium catalyst was reused for subsequent dihydroxylation reactions.
- 17. Selected data: Compound **7**[C2] Colorless oil; ¹H NMR (400 MHz; CDCl₃) δ = 7.44–7.26 (m, 20H), 6.89 (d, *J* = 2.2 Hz, 2H), 6.70 (d, *J* = 2.2 Hz, 4H), 6.64 (t, *J* = 2.0 Hz, 1H), 6.54 (t, *J* = 2.2 Hz, 2H), 5.03 (s, 8H), 5.00 (s, 4H), 4.94 (s, 2H), 3.52 (s, 9H), 3.47–3.38 (m, 2H), 3.14 (s, 6H), 1.85–1.73 (m, 2H), 0.58 (t, *J* = 7.9 Hz, 2H); ¹³C NMR (100 MHz; CDCl₃) δ = 160.1, 159.9, 138.8, 136.7, 128.9, 128.5, 127.9, 127.5, 112.1, 106.5, 104.4, 101.7, 70.1, 67.6, 65.6, 50.7, 49.6, 16.5, 5.6. Compound **8**[G2] Black powder; IR (KBr) 3061, 3026, 2882, 1595, 1159, 1045, 584 cm⁻¹; Anal. Found: C, 8.14; H, 0.76; N, 0.17; Br, 0.96. Compound **9**[G2] Black powder; IR (KBr) 3441, 1595, 1161, 1045, 584 cm⁻¹; Anal. Found: C, 7.94; H, 0.80; N, 0.18; Os, 1.06.
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