Remarkable enhancement of catalytic activity of a 2 : 1 complex between a non-planar Mo(V) porphyrin and a ruthenium-substituted Keggin-type heteropolyoxometalate in catalytic oxidation of benzyl alcohols

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Dalton transactions

41

33

10006-10013

2012-04

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doi: 10.1039/C2DT30424D
Remarkable enhancement of catalytic activity of a 2:1 complex between a non-planar Mo(V)-porphyrin and a ruthenium-substituted Keggin-type heteropolyoxometalate in catalytic oxidation of benzyl alcohols

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Received (in XXX, XXX) Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXX 20XX
DOI: 10.1039/b000000x

A 2:1 complex composed between a non-planar Mo(V)-porphyrin complex ([Mo(DPP)(O)] +, DPP²⁻ = dodecaphenylporphyrin) and a ruthenium-substituted Keggin-type heteropolyoxometalate (Ru-POM), [SiW₁₁O₃9Ru⁶⁺(DMSO)]₂⁻, acts as an efficient catalyst for oxidation of benzyl alcohols with iodosobenzene as an oxidant in CDCl₃ at room temperature. The catalytic oxidation afforded the corresponding benzaldehydes, whereas neither the ammonium salt of Ru-POM nor [Mo(DPP)(O)] + alone exhibited catalytic reactivity under the same experimental conditions. This enhancement can be attributed to a large anodic shift of the redox potential of the ruthenium centre due to the complexation of the Ru-POM with two cationic (Mo(DPP)(O))⁺ units. The kinetic analysis demonstrated that the catalytic oxidation proceeded via formation of a catalyst-substrate complex, and electron-withdrawing substituents at the para position of benzyl alcohol accelerated the reaction. The rate constants of the oxidation reactions correlate to the bond dissociation energies of the C-H bonds of the substrate. A linear correlation was observed for logarithm of the rate constants of oxidation reactions of benzyl alcohols with that of hydrogen abstraction by cumyl peroxyl radical, indicating the reaction proceeds via hydrogen abstraction. The observed kinetic isotope effect (KIE) indicates that the hydrogen abstraction occurs from the benzyl group rather than the hydroxy group.

Introduction

Polyoxometalates and heteropolyoxometalates (POMs) are widely known as functional materials in catalytic oxidation reactions, 1-14 photocatalytic reactions, 15,16 medicines, 17 and solid-state chemistry 18 due to their robust structures and rich redox chemistry. 19 Especially, a number of POMs and their derivatives were prepared as oxidation catalysts for the organic substrates, such as lacunary-type POM, 2 “sandwich” type POM, 3 and metalorganic-POm hybrid catalysts. 5 In particular, the facile incorporation of transition-metals into lacunary-type POMs has attracted significant interest for preparation of oxidation catalysts with high activity. 10 For example, a ruthenium-substituted Keggin-type POM (Ru-POM), [XW₁₁O₃9Ru⁶⁺(H₂O)]²⁻ (X= P or Si, Fig. 1), catalyzes oxygenation reactions of hydrocarbons with various oxidants to afford the corresponding aldehydes, aldehydes and carboxylic acids at relatively high temperature (> 60 °C). 11 Moreover, the Ru-POM can act as a heterogeneous catalyst for oxidations of alkanes and alcohols by using molecular oxygen as an oxidant. 12 In most cases, POMs are synthesized as inorganic salts (Na⁺, K⁺, and Cs⁺), because they are only soluble in water and used with phase transfer catalysts under two-phase reaction conditions for organic substrates. In order to improve the solubility in organic solvents, many POMs have been prepared as ammonium-salts ([C₆H₅)₃N]⁺ (TBA), [(C₆H₅)₄N]⁺ (THA)). However, the counter cation has yet to be utilized to improve the catalytic reactivity of POMs.

In this context, we have previously reported construction of 2:1 complexes composed of a non-planar Mo(V)-porphyrin, [Mo(DPP)(O)(H₂O)]⁺ (1) (DPP²⁻: dodecaphenylporphyrin, Figure 1), and Keggin-type POMs, which are soluble in toluene, chloroform (CHCl₃) and dichloromethane (CH₂Cl₂). 20 Each

![Fig. 1 Non-planar Mo(V)-porphyrin complex, [Mo(DPP)(O)(H₂O)]⁺ (1), and ruthenium-substituted Keggin-type POM, [SiW₁₁O₃9Ru⁶⁺(DMSO)]₂⁻ (2), used in this study. Component is connected via direct coordination bonds due to the high Lewis acidity of the Mo(V) center bound to the distorted porphyrin ligand and the strong coordination bonds make it...](image-url)
possible to maintain their structures in solution.\textsuperscript{20} The merit of such complexes is not only the improvement of the solubility of POMs into less polar solvents, but also the elevation of the oxidation potentials of POMs by coordination of the cationic metalloporphyrin unit. Thus, when metal-substituted POMs are employed in the metalloporphyrin-POM assembly, the oxidation potential of the inserted metal center is expected to be positively shifted to provide the higher reactivity in oxidation reactions. However, the catalytic reactivity of such a metalloporphyrin-POM assembly has yet to be examined.

We report herein formation of a 2:1 complex between a non-planar Mo(V)-porphyrin, ([Mo(DPP)(O)(H$_2$O)]$^+$ (1)) and a Ru-POM ([SiW$_{11}$O$_{39}$Ru$^{III}$(DMSO)]$^+$ (2)) which acts as an efficient catalyst for oxidation of benzyl alcohols\textsuperscript{33,34} by iodosobenzene (PhIO) in CDCl$_3$ at room temperature to afford the corresponding benzaldehydes. The [Mo(DPP)(O)(H$_2$O)]$^+$ unit is shown to play an essential role to enhance the catalytic reactivity of Ru-POM. The catalytic mechanism is clarified by the detailed kinetic study in comparison with the reactivity of cumyl peroxy radical in hydrogen abstraction from benzyl alcohols.

**Experimental**

**Materials and methods**

All chemicals were available from commercial sources and used as received without further purification unless otherwise noted. Dichloromethane (CH$_2$Cl$_2$) and acetonitrile (CH$_3$CN) were obtained from Waco Pure Chemicals. Dichloromethane (CH$_2$Cl$_2$) was distilled from CaH$_2$ just prior to use. All other solvents were special grade and were used as received from commercial sources without further purification. Column chromatography was performed on a silica gel Waco-gel C-200 (60–200 mesh) or activated alumina (ca. 200 mesh), both from Waco Pure Chemicals. UV-vis spectroscopy was carried out on a JASCO V-570 UV/VIS/NIR spectrometer at room temperature. MALDI-TOF-MS spectra were recorded on a Bruker Daltonics ultrafleXtreme spectrometer using α-cyano-4-hydroxycinnamic acid (CHCA) as a matrix. EPR spectra were recorded on a Bruker EMXPlus 9.5/2.7 spectrometer in distilled and deaerated CH$_2$Cl$_2$ at 5 K.

**Safety Note. Caution!**

Perchlorate salts of metal complexes with organic ligands are potentially explosive. They should be handled with great care in small quantities.

**Synthesis**

[Mo(DPP)(O)(H$_2$O)]ClO$_4$ (1),\textsuperscript{30} α-C$_{3}$Si$_{3}$K$_{6}$[SiW$_{11}$O$_{39}$Ru$^{III}$](DMSO)]$^{11+}$, deuterated benzyl alcohols (PhCH$_2$OD)\textsuperscript{33} and PhCD$_2$OH$^{3\delta}$ were prepared in accordance with the literature methods.

(TBA)$_2$[SiW$_{11}$O$_{39}$Ru$^{III}$](DMSO)]$^+$·3H$_2$O (2)

α-C$_{3}$Si$_{3}$K$_{6}$[SiW$_{11}$O$_{39}$Ru$^{III}$](DMSO)]$^{11+}$ (200 mg, 57 μmol) and (n-butyl)N]Br (TBABr) (193 mg, 600 μmol) were dissolved in 20 mL of water and stirred vigorously at 50 °C for 3 hours. Dark orange precipitate was collected and washed by a large amount of water. Recrystallization from CH$_2$CN/H$_2$O gave dark orange powder, and was filtered and dried up under vacuum (115 mg, 49%). Anal. Caled for C$_{6}$H$_{18}$N$_{6}$O$_{24}$SiW$_{11}$SRu·3H$_2$O: C 23.90, H 4.69, N 1.70. Found: C 23.63, H 4.20, N 1.63. IR spectrum (in KBr): ν$\equiv$O 1100 cm$^{-1}$.

(TBA)$_2$[Mo(DPP)(O)]$_{2}$[SiW$_{11}$O$_{39}$Ru$^{III}$](DMSO)]) (3)

1 (100 mg, 69 μmol) in 10 mL of CH$_2$Cl$_2$ was mixed with 2 (122 mg, 30 μmol) dissolved in 10 mL of CH$_2$CN. The solution was heated at 50 °C for 3 hours and evaporated to dryness. Recrystallization from CH$_2$Cl$_2$/hexane gave dark greenish brown powder. The powder was dried up under vacuum (153 mg). MALDI-TOF-MS (negative mode): 5444.71 (observed, [M–DMSO + 2H]$^-$); 5444.30 (calcd for [C$_{184}$H$_{122}$N$_{6}$O$_{24}$SiMo$_{11}$W$_{11}$]).

**IR spectrum (in KBr): ν$\equiv$O 1100 cm$^{-1}$. Anal. Caled for 3×1.5C$_{3}$H$_{14}$t-$\text{O}$H$_2$O (C$_{234}$H$_{272}$N$_{1}$O$_{3}$SSiRuMo$_{11}$H$_{11}$): C, 44.51; H, 4.23; N, 2.35%. Found: C, 44.33; H, 4.50; N, 2.57%.

**Electrochemical Measurements**

Cyclic voltammograms (CV), differential pulse voltammograms (DPV) and second-harmonic AC voltammograms (SHACV) were obtained on an ALS 630B electrochemical analyzer in deaerated PhCN in the presence of 0.1 M (n-butyl)N]PF$_6$ (TBAPF$_6$) as a supporting electrolyte under Ar at room temperature, with use of a glassy carbon electrode as a working electrode, Ag/AgNO$_3$ as a reference electrode, a Pt wire as a auxiliary electrode. All potentials were calibrated with respect to the ferrocene/ferrocenium redox couple as 0 V.

**General Procedure for Oxidation of Alcohols and Aldehydes**

Reactions were carried out in a light-shielded glass vial (5 mL).

100 μmol of the each substrate (p-nitro-, p-chloro-, o-chloro-, p-methyl- and o-methylbenzyl alcohols, benzyl alcohol, p-nitro- and p-methoxybenzaldehyde), iodosobenzene (44 mg, 200 μmol) and 1 μmol of each the catalyst (1, 2, and 3) were dissolved in 600 μL of CDC$_1$$_3$ at room temperature. Monitoring reactions were performed by $^1$H NMR measurements; 50 μL of each reaction mixture was filtered and diluted by 500 μL of CDC$_1$$_3$.

**Results and discussion**

**Preparation of a Mo(V)-porphyrin-[Ru-POM] assembly**

A non-planar Mo(V)-porphyrin ([Mo(DPP)(O)(H$_2$O)]ClO$_4$ (1))\textsuperscript{30} and a Ru-POM, (TBA)$_2$[SiW$_{11}$O$_{39}$Ru$^{III}$](DMSO)]) (2),\textsuperscript{30} were used in this study (Fig. 1). The reaction of 1 and 2 was carried out in a mixed solvent (CH$_2$Cl$_2$/CH$_3$CN) at 50 °C to obtain the mixed complex, {[Mo(DPP)(O)]$_2$[H$_2$SiW$_{11}$O$_{39}$Ru$^{III}$](DMSO)]} (3). The coordination of DMSO was confirmed by IR spectroscopy to observe ν$\equiv$O at 1100 cm$^{-1}$, which was consistent with that observed for 2. After removing the solvents, crystallization from CH$_2$Cl$_2$/hexane gave dark greenish brown powder. In the MALDI-TOF-MS spectrum of 3, a molecular ion peak cluster was observed at 5444.71 (m/z) with use of CHCA (α-cyano-4-hydroxycinnamic acid) as a matrix (Fig. 2), assignable to that of a diprotonated 2:1 assembly of [Mo(DPP)(O)]$^{11+}$ unit and [SiW$_{11}$O$_{39}$Ru$^{III}$]$^{11+}$ ([{[Mo(DPP)(O)]$_2$[H$_2$SiW$_{11}$O$_{39}$Ru$^{III}$]} + 3 – DMSO}) : m/z = 5444.30. This result indicates that the POM coordinates to the Mo(V) center directly in place of the H$_2$O ligand. On the basis of crystal structures of hybrid complexes composed of two {Mo$^{6+}$(DPP)(O)} fragments and one Keggin-type POM,\textsuperscript{19} the Mo$^{6+}$(DPP)(O) moiety in 3 should form a coordination bond with one of the terminal oxo ligands of the
Ru\textsuperscript{III}-substituted Keggin-type polyoxometalate.

**Oxidation states of molybdenum and ruthenium in 3**

In the EPR spectrum of 2, a signal assigned to Ru\textsuperscript{III} (S = 1/2) was observed at g\textsubscript{R} = 2.289, g\textsubscript{L} = 2.020, and g\textsubscript{z} = 1.873 in CH\textsubscript{2}Cl\textsubscript{2} at 5 K (Fig. 3a).\textsuperscript{11b,23} As for 3, two kinds of signals were observed:

- for Ru\textsuperscript{II} (S = 1/2, I = 0) and Ru\textsuperscript{III} (S = 1/2) at 5 K in CH\textsubscript{2}Cl\textsubscript{2}:
  - Frequency, 9.39 GHz; Power, 10 mW; Modulation, 100 GHz, 10 G.

**Fig. 3** EPR spectra of (a) 2 (0.2 mM) and PhIO (40 mM), (b) 3 (0.2 mM) and PhIO (40 mM) for the Mo\textsuperscript{V} (S = 1/2, I = 0) and Ru\textsuperscript{III} (S = 1/2) at 5 K in CH\textsubscript{2}Cl\textsubscript{2}:
  - Frequency, 9.39 GHz; Power, 10 mW; Modulation, 100 GHz, 10 G.

The redox wave at −0.46 V was assigned to reduction of Mo(V) ion (Mo\textsuperscript{V}/Mo\textsuperscript{III}). Based on the EPR measurement, the first and second oxidation redox waves of 2 are assigned to Ru\textsuperscript{III}/Ru\textsuperscript{IV} (0.07 V) and Ru\textsuperscript{IV}/Ru\textsuperscript{V} (0.86 V), respectively. In the case of 3, and irreversible redox wave was observed below −1.0 V. According to the DPV measurement of 3, the one- and two-electron oxidation processes of the ruthenium center (Ru\textsuperscript{III}/Ru\textsuperscript{IV} and Ru\textsuperscript{IV}/Ru\textsuperscript{V}) were observed at 0.90 V and 1.28 V, whereas the one- and two-electron oxidation processes of the porphyrin unit (Por\textsuperscript{III}/Por\textsuperscript{IV} and Por\textsuperscript{IV}/Por\textsuperscript{V}) at 0.73 V and 1.15 V, respectively. Thus, the large anodic shifts of the redox potentials of the ruthenium center in 3 were observed, resulting from the strong coordination of the cationic [Mo(DPP)(O)]\textsuperscript{+} unit to the POM unit.

**Catalytic oxidation reactions of benzyl alcohols**

With use of 3, catalytic oxidation reactions of benzyl alcohol (p-H) and its para-substituted and ortho-substituted derivatives with PhIO were carried out in CDCl\textsubscript{3} at room temperature (Scheme 1). The reactions ([substrate] = 160 mM, [oxidant] = 330 mM, [catalyst] = 1.6 mM) were performed in the light shielded vials and the conversions were monitored by \textsuperscript{1}H NMR measurements. As comparison, the reactivity of precursors (1 and 2) was also examined as homogeneous catalysts for each reaction.

The \textsuperscript{1}H NMR spectra after the reactions for 6 hours were shown in Fig. 6. The oxidation reaction can be stopped by

**Fig. 5** Cyclic voltammograms (CV) and differential pulse voltammograms (DPV) of (a) 1, (b) 2 and (c) 3 in CH\textsubscript{2}Cl\textsubscript{2} at room temperature under Ar in the presence of 0.1 M TBAPF\textsubscript{6}.

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filtering the reaction mixture to eliminate the insoluble oxidant. This manipulation allows us to follow the reaction by \(^{1}\)H NMR measurements. In the case of benzyl alcohol (\(p\)-H) as a substrate in the absence of catalyst, only the substrate and iodobenzene (PhI) derived from the decomposition of PhIO were detected by NMR measurements (Fig. 6a). When the complex \(1\) and \(2\) were used as catalysts, the catalytic oxidation hardly occurred at room temperature as compared to the blank reaction (Figs. 6b, c). In sharp contrast, the addition of \(3\) efficiently afforded benzaldehyde as an oxidation product from \(p\)-H (Fig. 6d). Obviously, this result indicates that coordination of the [Mo(DPP)(O)]\(^{\text{II}}\) unit to the Ru-POM significantly enhanced its reactivity as a oxidation catalyst probably due to the large anodic shift of redox potentials of ruthenium ion in complex \(3\) (vide supra). MALDI-TOF-MS measurement suggested that \(3\) could maintain the structure after the oxidation of \(p\)-H in CDCl\(_3\) (see Fig. S1 in ESI).

Next, benzyl alcohol derivatives (\(p\)-nitrobenzyl alcohol (\(p\)-NO\(_2\)), \(p\)-(o)-chlorobenzyl alcohol (\(p\)-(o)-Cl) and \(p\)-(o)-methylbenzyl alcohol (\(p\)-(o)-Me)) were employed as substrates and the conversions from benzyl alcohols to the corresponding benzaldehydes at 60 min are summarized in Table 2.\(^{25}\) The conversion was determined by the integration ratio of the peaks due to the substrates and the products in \(^{1}\)H NMR spectra. The results in Table 2 clearly indicate that the catalytic oxidation reaction showed a significant substituent effect: the electron-withdrawing group accelerates the oxidation reaction while the electron-donating group slows down the reaction. Additionally, when the chloro or the methyl groups was introduced at the ortho-position of \(p\)-H, remarkable retardation of the substrate consumption was observed (Fig. 7), suggesting the existence of strong steric effect of the \(o\)-substituents.

### Table 1: Redox potentials of \(1\), \(2\) and \(3\) in CH\(_2\)Cl\(_2\).\(^{\ast}\)

<table>
<thead>
<tr>
<th>compound</th>
<th>(\text{Mo}^{\text{IV}}/\text{Mo}^{\text{II}})</th>
<th>(\text{Por}^{\text{II}}/\text{Por}^{\text{I}})</th>
<th>(\text{Por}^{\text{III}}/\text{Por}^{\text{II}})</th>
<th>(\text{Ru}^{\text{III}}/\text{Ru}^{\text{II}})</th>
<th>(\text{Ru}^{\text{II}}/\text{Ru}^{\text{I}})</th>
<th>(\text{POM}^{\text{IV}}/\text{POM}^{\text{III}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>-0.46</td>
<td>0.76</td>
<td>1.12</td>
<td>-1.57</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(2)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.07</td>
<td>0.86</td>
<td>irreversible</td>
</tr>
<tr>
<td>(3)</td>
<td>-0.44</td>
<td>0.73</td>
<td>1.15</td>
<td>irreversible</td>
<td>0.90</td>
<td>1.28</td>
</tr>
</tbody>
</table>

\(^{\ast}\) At room temperature under Ar; 0.1 M TBAPF\(_6\) as an electrolyte. \(^{\text{b}}\) Por\(^{\text{II}}\): DPP\(^{\text{b}}\) ligand. \(^{\text{c}}\) POM\(^{\text{IV}}\): lacunary Keggin-type heteropolyoxometalate.

### Scheme 1

\(\text{X = H, Me, Cl, NO}_2\) in CDCl\(_3\), at RT

\(\text{Y = Me, Cl}\) in CDCl\(_3\), at RT

\(\text{cat., PhIO}\)

### Fig. 6: \(^{1}\)H NMR spectra of the reaction mixtures of benzyl alcohol after 6 h in CDCl\(_3\) ([sub] = 160 mM, [PhIO] = 330 mM, [cat] = 1.6 mM). Each fraction contains (a) no catalyst, (b) complex \(1\), (c) complex \(2\), and (d) assembly \(3\) as a catalyst, respectively.

\(\text{Fig. 7: Time profiles of consumption ([sub]/[sub]o) of benzyl alcohols (substrates) in CDCl}_3\) at room temperature with use of TMS (tetramethylsilane) as an internal standard ([sub] = 160 mM, [PhIO] = 330 mM, [cat] = 1.6 mM). The consumption of each substrate was determined on the basis of the peak integration ratio for benzyl alcohols and TMS in \(^{1}\)H NMR spectra.

Plots of \(-\ln\text{[sub]}\) vs. time for oxidation of \(p\)-H, \(p\)-NO\(_2\), \(p\)-Cl and \(p\)-Me by \(3\) as a catalyst were made as depicted in Fig. 8 to determine the pseudo-first-order rate constants \(k_{\text{obs}}\). The \(k_{\text{obs}}\) values thus determined are also summarized in Table 2. The one-electron oxidation potentials \(E_{\text{oxy}}\) of benzyl alcohols were determined by second harmonic AC voltammetry (SHACV) in CH\(_2\)Cl\(_2\) as summarized in Table 2. As expected, \(p\)-NO\(_2\) showed
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Table 2 Summary of conversions (%) and pseudo-first-order rate constants (s⁻¹) of the catalytic oxidation reactions in CDCl₃, and oxidation potentials (Eox) of benzyl alcohols in CH₂Cl₂

<table>
<thead>
<tr>
<th>substrate</th>
<th>conversion (%)</th>
<th>kobs (s⁻¹)</th>
<th>Eox vs. Fe/Fe⁺, V</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-H</td>
<td>41</td>
<td>1.4 × 10⁻⁴</td>
<td>1.48</td>
</tr>
<tr>
<td>p-NO₂</td>
<td>93</td>
<td>3.5 × 10⁻³</td>
<td>1.72</td>
</tr>
<tr>
<td>p-Cl</td>
<td>77</td>
<td>5.5 × 10⁻⁴</td>
<td>1.54</td>
</tr>
<tr>
<td>o-Cl</td>
<td>2</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>p-Me</td>
<td>19</td>
<td>4.3 × 10⁻⁵</td>
<td>1.38</td>
</tr>
<tr>
<td>o-Me</td>
<td>17</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

Conversions were determined by ¹H NMR spectra in CDCl₃ at 60 min. The oxidation potentials (Eox) of benzyl alcohols were determined by SHACV in CH₂Cl₂ in the presence of TBAPF₆ as a supporting electrolyte under Ar at room temperature. p-H: benzyl alcohol

The highest oxidation potential because of the electron-withdrawing NO₂ group, whereas p-Me exhibited the lowest oxidation potential due to the electron-donating Me group. Because the higher the oxidation potential, the higher is the reactivity (Table 2), electron transfer (ET) from the substrate to the catalyst cannot be involved as the rate-determining step of the catalytic reaction. Electron donating substituents stabilize a positively charged transition state (e.g., in hydride transfer), whereas electron withdrawing substituents stabilize a negatively charged transition state (e.g., in proton transfer). Thus, the increase in the rate constant of the catalytic oxidation of benzyl alcohol derivatives with 3 with increasing the oxidation potentials of benzyl alcohols in Table 2 suggests the formation of a negatively charged transition state rather than a positively charged transition state. Such a substituent effect has often been observed in the catalytic oxidation of para-substituted benzyl alcohol derivatives. Because the acidity of the benzyl hydrogen increases with increasing the oxidation potentials of benzyl alcohols, the acidity of the benzyl hydrogen may be involved in determining the catalytic reactivity presented in Table 2 as discussed below. In addition, a Hammett plot was made for the rate constants listed in Table 2 (see Fig. S2 in ESI). The ρ value was determined to be 1.91 ± 0.31, also indicating that the proton transfer from the benzyl C-H bond to the reactive species should be important in the catalytic oxidation of benzyl alcohol derivatives with 3 and PhIO (vide infra).

As for p-H and p-NO₂, the concentration dependence of kobs was examined as shown in Fig. 9. As a result, the saturation behaviors of kobs at higher concentration of the substrates were observed in both cases. This result indicates that there is a pre-equilibrium to form an adduct between substrate and the catalyst prior to the oxidation reaction. In light of a discussion on the location of the proton in a Keggin-type POM (H₃[PW₁₂O₄₀]·6H₂O), the substrate may bind to μ-oxo bridge neighboring active species (Ru(IV)=O) via hydrogen bond due to the stronger basicity of the μ-oxo bridge. The first-order rate constant (k) and binding constant (K) were determined by curve fitting to be k = (2.3 ± 0.8) × 10⁻⁴ s⁻¹, K = 10 ± 2 M⁻¹ for p-H and k = (4.4 ± 0.3) × 10⁻³ s⁻¹, K = 21 ± 6 M⁻¹ for p-NO₂ based on the following equations:

\[ \text{sub + cat \rightarrow product} \]

\[ k_{obs} = \frac{kK[\text{substrate}]}{1 + K[\text{substrate}]} \]

where K is a binding constant, k is a first-order rate constant, [substrate] is substrate concentration. Thus, p-NO₂ exhibited a larger binding constant reflecting the smaller pK₄ value compared with p-H.

Mechanistic insights into the oxidation reaction

To gain further mechanistic insights into the catalytic oxidation of benzyl alcohol, two kinds of deuterated benzyl alcohols were employed to determine the kinetic isotope effects (KIE, kD/kH), PhCH₂OD and PhCD₂OH. The oxidation reaction of PhCD₂OH (1.6 mM) was performed in CHCl₃ in the presence of CDCl₃ (1.6 mM) and CD₂CN (1.6 mM) as internal standards. The time course of the reaction was monitored by ¹H NMR spectroscopy. As shown in Fig. 10, the KIE value for PhCH₂OD was determined to be kD/kH = 1.0, and that for PhCD₂OH was
determined to be $k_H/k_D = 10$. This indicates that the hydrogen abstraction occurs from the benzyl position of benzyl alcohol rather than the hydroxy position.

Based on the results described above, the catalytic oxidation reaction may proceed as follows: (1) A reactive species, presumably a Ru$^{IV}$=O species, is formed by the reaction of 3 with PhIO. \(^{23}\) (2) The substrate binds to a $\mu$-oxo bridge neighboring the Ru$^{IV}$=O moiety by using hydrogen bonding. (3) Hydrogen abstraction occurs at the benzyl position by the Ru$^{IV}$=O species.

In order to compare the observed substituent effect on the catalytic oxidation of benzyl alcohol derivatives in Table 2 with that on the authentic hydrogen abstraction reaction from benzyl alcohol derivatives, we examined the hydrogen abstraction of benzyl alcohol derivatives by cumyl peroxyl radical (CumOO$^\cdot$).

CumOO$^\cdot$ was generated by photoirradiation in the oxygen-saturated CH$_2$Cl$_2$ solution containing di-tert-butyl peroxide (1.0 M) and cumene (1.0 M) at 183 K. \(^{25}\) The decay of the EPR signal at $g = 2.016$ due to CumOO$^\cdot$ in the presence of benzyl alcohols was monitored (Fig. 11) to determine the rate constants of hydrogen abstraction from benzyl alcohols by CumOO$^\cdot$. The second-order rate constants were determined to be $k = 7.2 \times 10^{-2}$

<table>
<thead>
<tr>
<th>substrate</th>
<th>$k$, M$^{-1}$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p$-NO$_2$</td>
<td>1.4</td>
</tr>
<tr>
<td>$p$-Cl</td>
<td>$8.4 \times 10^{-1}$</td>
</tr>
<tr>
<td>$p$-H</td>
<td>$1.8 \times 10^{-1}$</td>
</tr>
<tr>
<td>$p$-Me</td>
<td>$7.2 \times 10^{-2}$</td>
</tr>
<tr>
<td>$p$-OMe</td>
<td>$2.6 \times 10^{-2}$</td>
</tr>
<tr>
<td>$o$-Me</td>
<td>$&lt; 1 \times 10^{-2}$</td>
</tr>
<tr>
<td>$o$-Cl</td>
<td>$&lt; 1 \times 10^{-2}$</td>
</tr>
</tbody>
</table>

Fig. 12 Dependence of $k_{obs}$ for hydrogen atom abstraction reaction of (a) benzyl alcohol ($p$-H), (b) $p$-nitrobenzyl alcohol ($p$-NO$_2$), (c) $p$-chlorobenzyl alcohol ($p$-Cl), (d) $p$-methylbenzyl alcohol ($p$-Me), (e) $o$-chlorobenzyal alcohol ($o$-Cl), (f) $o$-methylbenzyl alcohol ($o$-Me) and (g) $p$-methoxybenzyl alcohol ($p$-OMe) by cumyl peroxyl radical on concentrations of benzyl alcohols in CH$_2$Cl$_2$ at 183 K.

Fig. 11 EPR spectrum of cumyl peroxyl radical in CH$_2$Cl$_2$ at 183 K generated in the photoirradiation of an oxygen-saturated CH$_2$Cl$_2$ solution containing di-tert-butyl peroxide (1.0 M) and cumene (1.0 M). The asterisk (*) denotes the Mn$^{II}$ marker.
Conclusions
A ruthenium-substituted metalloporphyrin-PO-M complex was prepared, acting as an efficient catalyst for oxidation of benzyl alcohols with PHO as an oxidant in CDC\textsubscript{3} at room temperature. The coordination of the cationic Mo(V)-porphyrin unit is effective not only for the improvement of solubility of POM toward low polar solvent, but also for remarkable enhancement of catalytic activity in the oxidation reactions. Benzyl alcohols were oxidized corresponding benzaldehydes via the formation of a catalyst-substrate adduct probably through intermolecular hydrogen bonding. The hydrogen abstraction occurs at the benzyl position, exhibiting a large KIE. Our strategy will provide a new category of POM-based catalytic oxidation systems with high efficiency.

Acknowledgments
We are grateful to financial support provided by Grants-in-Aid (Nos. 20108010 and 21111501), a Global COE program, "the Global Education and Research Centre for Bio-Environmental Chemistry" from the Japan Society of Promotion of Science (JSPS), a JSPS predoctoral fellowship (20-00804 to A. Y.), and KOSEF/MEST through WCU project (R31-2008-10010-0), Korea.

Notes and references
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60  S.-C. Tsai and J. P. Klinman, Biochemistry, 2001, 40, 2303.
75  Under the catalytic conditions, the formation of benzoic acids from the corresponding aldehydes was observed after 90 min.
120  The EPR signal due to the Ru(II) center disappeared upon addition of PhIO. This suggests the formation of a Ru=O (S = 1) species rather than a Ru(IV)=O (S = 3/2 or 1/2) species.
A ruthenium-substituted Keggin-type polyoxometalate forms a molecular assembly with two saddle-distorted MoV-porphyrin units to perform catalytic oxidation of benzyl alcohols.