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Synthesis and oxidation catalysis of a Ti-substituted phosphotungstate, and identification of the active oxygen species

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Abstract

In this paper, we report the synthesis of a Ti-substituted phosphotungstate, $\text{TBA}_6[\gamma\text{-PW}10\text{O}_{36}]_2\text{Ti}_4(\mu-\text{O})_2(\mu-\text{OH})_4$ (I, TBA = tetra-$n$-butylammonium), and its application to $\text{H}_2\text{O}_2$-based oxidation. Firstly, an organic solvent-soluble dilacunary phosphotungstate precursor, $\text{TBA}_3[\gamma\text{-PW}10\text{O}_{34}(\text{H}_2\text{O})_2]$ (PW10), has been synthesized. By the reaction of PW10 and TiO(acac)$_2$ (acac = acetylacetonate) in an organic medium (acetonitrile), I can be obtained. Compound I possesses a tetranuclear Ti core which can effectively activate $\text{H}_2\text{O}_2$ and show high catalytic performance for several oxidation reactions, such as epoxidation of alkenes, oxygenation of sulfides, oxidative bromination of unsaturated compounds, and the hydroxylation of anisole, giving the corresponding oxidation products with high efficiencies and selectivities. The catalytic performance of I is much superior to those of the previously reported Ti-substituted polyoxometalates. In addition, I is highly durable during the catalysis and can be reused several times with keeping its high catalytic performance. Furthermore, we have successfully isolated the truly catalytically active species for the present I-catalyzed oxidation, $\text{TBA}_6[\gamma\text{-PW}10\text{O}_{36}]_2\text{Ti}_4(\mu-\eta^2:\eta^2\text{-O})_4$ (II), and its anion structure has been determined by X-ray crystallographic analysis. All of the four Ti$_2$-µ-$\eta^2:\eta^2$-peroxo species in II are active for stoichiometric oxidation (without $\text{H}_2\text{O}_2$), and II is included in the catalytic cycle for the I-catalyzed oxidation.
Introduction

Selective oxidation is one of the most prevalent transformations in a broad range of fields, and the oxygenated products, such as epoxides, alcohols, aldehydes, ketones, and carboxylic acids, greatly contribute to the quality of our lives. However, oxidation processes sometimes lead to vast amounts of wastes; for example, dichromate, permanganate, and peracids are still frequently utilized in (super)stoichiometric amounts especially for fine chemicals production. In order to minimize wastes in the laboratory-scale as well as the industrial-scale productions, the antiquated stoichiometric oxidation processes should be replaced with catalytic ones. The choice of oxidants is also very important, and H₂O₂ and O₂ (or air) are regarded as “greener oxidants” because of their high contents of active oxygen species, e.g., 47 wt% in the case of H₂O₂, and co-production of only water. Therefore, the current most important subject of basic researches is to develop reliable catalysts that can activate the greener oxidants and transfer the active oxygen species to various substrates with high efficiency and selectivity.

Up to the present, a number of transition-metal catalysts have been developed for H₂O₂-based oxidation of various substrates. The activation of H₂O₂ by transition-metal catalysts typically proceeds through one-electron (Fenton-like) mechanism, two-electron mechanism, or both. Unlike one-electron mechanism, free-radical intermediates are not involved, competitive non-productive H₂O₂ decomposition are suppressed, and electrophilically activated metal-(hydro)peroxo and/or metal-oxo species are recognized to be formed in two-electron mechanism. Thus, two-electron mechanism is desirable for H₂O₂-based selective oxidation especially for electrophilic oxygen transfer reactions to organic substrates. Generally, Ti, V, Mo, W, and Re in their d⁰ electronic configurations are the principal metals that can catalyze H₂O₂-based oxidation through two-electron mechanism.

Amongst d⁰-metal catalysts for H₂O₂-based oxidation, Ti-based catalysts have extensively been investigated. Since the first report on synthesis and oxidation catalysis of TS-1 (titanium silicalite-1), numerous Ti-containing zeolites have been synthesized by isomorphous substitution
for Si (or Al) in the framework. The tetrahedrally coordinated Ti site in TS-1 is believed to contribute the oxidation catalysis, and Ti(\(\eta^1\)-OOH), Ti(\(\eta^2\)-OOH), and/or Ti(\(\eta^2\)-O\(_2\)) species (with coordination of an alcohol (solvent) or a water molecule to the Ti site) have been postulated as active oxygen species on the basis of both experimental approaches and computational calculations (Fig. 1a). Recently, Katsuki and co-workers have reported the synthesis of bis-\(\mu\)-oxo Ti(salen) and Ti(salan) dimeric complexes and their utilization for enantioselective epoxidation with H\(_2\)O\(_2\). Soon after, they have successfully synthesized a \(\mu\)-oxo-\(\eta^2\):\(\eta^2\)-peroxo Ti(salan) complex by the reaction of the bis-\(\mu\)-oxo complex with H\(_2\)O\(_2\), and its structure has been determined by X-ray crystallographic analysis. Although the \(\mu\)-oxo-\(\mu\)-\(\eta^2\):\(\eta^2\)-peroxo complex is effective for catalytic epoxidation with H\(_2\)O\(_2\), it is completely inactive for stoichiometric epoxidation. Thus, the complex is not a truly catalytically active species but just a “precursor” of active species (Fig. 1b). As stated above, although Ti catalysts are recognized to be effective for H\(_2\)O\(_2\)-based oxidation, the truly catalytically active species as well as the detailed reaction mechanism are still unclear and controversial.

We have engaged in design of polyoxometalate (POM)-based molecular catalysts for a long time. POMs are a large class of metal-oxygen cluster anions, and their properties, such as redox potentials, acidic and basic properties, and solubilities, can finely be tuned by choosing constituent elements and counter cations. In particular, POMs are attractive materials for oxidation catalysts because they are thermally and oxidatively stable, and active site structures can precisely be designed by using lacunary POMs as the “structural motifs”. To date, various kinds of metal-substituted POMs have been synthesized for H\(_2\)O\(_2\)-based oxidation. With regard to Ti-substituted ones, [(\(\gamma\)-SiW\(_{10}\)O\(_{36}\))\(_2\)Ti\(_4\)(\(\mu\)-O\(_2\))(\(\mu\)-OH)\(_4\)]\(^{8-}\), [PW\(_{11}\)TiO\(_{40}\)]\(^{5-}\), [PW\(_{10}\)Ti\(_2\)O\(_{40}\)]\(^{7-}\), [(\(\alpha\)-1,2,3-PW\(_9\)Ti\(_3\)O\(_{37}\))\(_2\)(\(\mu\)-O\(_3\))]\(^{12-}\), [\(\alpha\)-PW\(_{10}\)\{Ti(O\(_2\))\}_2O\(_{58}\)]\(^{7-}\) and [(B-\(\alpha\)-AsW\(_9\)O\(_{33}\))\(_2\){Ti(OH)}\(_2\){WO(H\(_2\)O)}]\(^{8-}\) are the typical examples. Despite these advances, there is still plenty room for improvement in their catalytic activities, and in addition their truly catalytically active species have never been clarified and isolated. A POM with Ti-peroxo species,
[α-1,2,3-P2W15O56{Ti(η²-O2)}3(µ-OH)3]9−, has also been synthesized but this peroxo species is too stable to oxidize substrates.16

In this study, we have synthesized for the first time a Ti-substituted phosphotungstate with a tetranuclear Ti core, TBA6[(γ-PW10O36)2Ti4(µ-O)2(µ-OH)4] (I, TBA = tetra-n-butyrammonium), by the reaction of an organic solvent-soluble divacant lacunary phosphotungstate, TBA3[γ-PW10O34(H2O)2] (PW10), with an appropriate Ti⁴⁺ source (TiO(acac)₂, acac = acetylacetonate) in acetonitrile (CH₃CN). Compound I could act as an efficient reusable catalyst for several H₂O₂-based oxidation reactions, such as epoxidation of alkenes, oxygenation of sulfides, oxidative bromination of unsaturated compounds, and the hydroxylation of anisole. In addition, we have successfully isolated the truly catalytically active species, TBA6[(γ-PW10O36)2Ti4(µ-η²:η²-O2)4] (II), and its anion structure has been determined by X-ray crystallographic analysis (Fig. 1c).

Results and discussion

Synthesis and structural characterization of a titanium-substituted phosphotungstate

Generally, the introduction of metal cations into the vacant sites of lacunary POMs has been performed in aqueous media, and various metal-substituted POMs with unique structures and properties have been synthesized.13–15 However, the synthesis in aqueous media should require strict control of the synthetic conditions, such as pH, temperature, and concentration, and POMs frequently isomerized to unexpected structures.17 In addition, alkali metal cations (counter cations) strongly coordinate to the vacant sites of lacunary POMs, which frequently inhibit the introduction of metal cations into the vacant sites.18 We have recently utilized organic solvent-soluble lacunary POMs, e.g., TBA₄[γ-SiW10O34(H2O)₂] (SiW10),¹⁸ as the precursors and introduced metal cations into their lacunary pockets in organic media.¹⁹ In the synthesis in organic media, the undesirable isomerization of lacunary precursors can be avoided during the metal introduction. We have recently found that the reactivity of metal-substituted POMs with H₂O₂ can be increased by changing the central heteroatoms from Si⁴⁺ to P⁵⁺, leading to the significant improvement of catalytic activities for
electrophilic oxidation; for example, the reaction rate of the epoxidation of allyl acetate by a V-substituted phosphotungstate, \( [\gamma\text{-PW}_{10}\text{O}_{38}\text{V}_2(\mu\text{-OH})_2]^{3-} \), was ca. 16 times larger than that by the silicotungstate analogue \( [\gamma\text{-SiW}_{10}\text{O}_{38}\text{V}_2(\mu\text{-OH})_2]^{4-} \).\(^{20}\) However, until now there are only five examples (V, Mn, Mo, W, and Ru)\(^{21}\) of metal substitution into \( [\gamma\text{-PW}_{10}\text{O}_{36}]^{7-} \) likely owing to the low stability and solubility of \( [\gamma\text{-PW}_{10}\text{O}_{36}]^{7-} \) (typically Cs salt) in aqueous media.

In order to demonstrate the metal substitution in organic media, the organic solvent-soluble \( [\gamma\text{-PW}_{10}\text{O}_{36}]^{7-} \) precursors (e.g., TBA salt) should be required, but they are unprecedented compounds. Therefore, we firstly attempted to synthesize an organic solvent-soluble divacant lacunary phosphotungstate precursor (PW10) by the cation exchange reaction of Cs\(_7[\gamma\text{-PW}_{10}\text{O}_{36}]^{22}\) with TBABr. To avoid undesirable isomerization of the POM framework, the reaction was carefully carried out at low temperature (273 K). The IR spectrum of PW10 showed the bands around 1109–1036, 975–951, and 861–798 cm\(^{-1}\) assignable to \( \nu(P\text{-O}) \), \( \nu(W=O) \), and \( \nu(W=O=W) \), respectively, and these bands were also observed at the similar regions in the case of Cs\(_7[\gamma\text{-PW}_{10}\text{O}_{36}]^{22}\) (Fig. S1a,b). The \( ^{31}\text{P} \) NMR spectrum of PW10 in DMSO-\( d_6 \) showed a single signal at –10.5 ppm (Fig. 2a). The \( ^{183}\text{W} \) NMR spectrum of PW10 in DMSO-\( d_6 \) showed five signals at –105.4, –114.2, –117.3, –136.1, and –168.5 ppm with the respective intensity ratio of 1:1:1:1:1, indicating that PW10 possesses the \( C_2 \) symmetry in the solution-state which is the same as that of the silicotungstate analogue SiW10 (Fig. 3a).\(^{8a}\) The cold-spray ionization mass (CSI-MS) spectrum of PW10 in acetone showed the signal set at \( m/z = 3384 \) with the isotopic distribution which agreed with the pattern calculated for \([\text{TBA}_4(\text{PW}_{10}\text{O}_{34})]^+ \) (Fig. S2a). The elemental analysis data showed the TBA/P/W ratio of 3:1:10. Therefore, the formula of PW10 is possibly \( \text{TBA}_3[\gamma\text{-PW}_{10}\text{O}_{34}(\text{H}_2\text{O})_2] \).

By using PW10 as the precursor, a Ti-substituted phosphotungstate (I) could successfully be synthesized. Compound I could readily be synthesized by just simply mixing the required components of PW10 and a suitable Ti source (TiO(acac)_2, two equivalents with respect to PW10) in CH\(_3\)CN at room temperature. Fortunately, the single crystals of I suitable for X-ray crystallographic analysis were obtained by recrystallization from a mixed solvent of CH\(_3\)CN and ethyl acetate.
(EtOAc), and its structure was successfully determined. The structure of the anion part of I is shown in Fig. 4, and the crystallographic data are summarized in Table S1. An edge-shared oxygen-bridged dinuclear titanium core was introduced into the lacunary pocket of $[\gamma\text{-PW}_{10}\text{O}_{36}]^{7-}$, and two monomer subunits were linked by two Ti−O−Ti fragments. Six TBA cations per I anion could crystallographically be assigned in accord with the elemental analysis data. The bond valence sum (BVS) values of phosphorus (4.96), tungsten (5.98–6.15), and titanium (4.22–4.24) atoms in I indicate that the respective valences are +5, +6, and +4. Therefore, four protons are associated with I anion. The BVS values of O1a and O1b were 1.23 and 1.27, respectively, suggesting that these oxygens are monoprotonated to form the $[\text{Ti}_2(\mu\text{-OH})_2]^{6+}$ core in the subunit. The BVS value of O1c was 2.10, showing that the bridging oxygen atom is $\mu$-O species. The X-ray crystallographic and elemental analysis data show that the formula of I is TBA$_6$[$(\gamma\text{-PW}_{10}\text{O}_{36})_2\text{Ti}_4(\mu\text{-O})_2(\mu\text{-OH})_4$]. The formation of I can be expressed by the following equation [eqn (1)].

$$2\text{TBA}_3[\gamma\text{-PW}_{10}\text{O}_{34}(\text{H}_2\text{O})_2] + 4\text{TiO(acac)}_2 + 2\text{H}_2\text{O} \rightarrow \text{TBA}_6[(\gamma\text{-PW}_{10}\text{O}_{36})_2\text{Ti}_4(\mu\text{-O})_2(\mu\text{-OH})_4] + 8\text{Hacac} \quad (1)$$

The anion structure of I was intrinsically isostructural with those of the previously reported TBA$_8$[$(\gamma\text{-SiW}_{10}\text{O}_{36})_2\text{Ti}_4(\mu\text{-O})_2(\mu\text{-OH})_4$] and K$_8$[$(\gamma\text{-GeW}_{10}\text{O}_{36})_2\text{Ti}_4(\mu\text{-O})_2(\mu\text{-OH})_4$]. The lengths of Ti···P (3.77–3.79 Å) in I were slightly longer than those of Ti···Si (3.61–3.69 Å) in TBA$_8$[$(\gamma\text{-SiW}_{10}\text{O}_{36})_2\text{Ti}_4(\mu\text{-O})_2(\mu\text{-OH})_4$] and Ti···Ge (3.60–3.61 Å) in K$_8$[$(\gamma\text{-GeW}_{10}\text{O}_{36})_2\text{Ti}_4(\mu\text{-O})_2(\mu\text{-OH})_4$].

The $^{31}$P NMR spectrum of I in CD$_3$CN showed a single signal at −11.8 ppm, indicating the presence of I as the single species (Fig. 2b). The $^1$H NMR spectrum of I in CD$_3$CN showed signals assignable to TBA cations (1.01, 1.43, 1.67, and 3.17 ppm) and $\mu$-OH species (7.91 ppm) (Fig. S3).
The $^{183}\text{W}$ NMR spectrum of $\text{I}$ in a mixed solvent of CD$_3$CN and propylene carbonate (PC, 1:1 v/v) showed three signals at –110.6, –112.7, and –115.8 ppm with the respective intensity ratio of 1:2:2 in accord with the $C_{2v}$ symmetry of $\text{I}$ in the solid-state (Fig. 3b). The CSI-MS spectrum of $\text{I}$ in CH$_3$CN showed the two sets of signals centered at $m/z = 3561$ and 3674 assignable to $[\text{TBA}_8\text{H}_4\{(\text{PW}_{10}\text{O}_{36})_2\text{Ti}_4\text{O}_5\}]^{2+}$ and $[\text{TBA}_9\text{H}\{(\text{PW}_{10}\text{O}_{36})_2\text{Ti}_4\text{O}_5\}]^{2+}$, respectively (Fig. S2b). These NMR and CSI-MS spectra agreed well with the crystal structure of $\text{I}$, indicating that the solid-state structure of $\text{I}$ is maintained in the solution-state.

**Catalytic performance for H$_2$O$_2$-based oxidations**

To begin with, the epoxidation of cyclooctene with 30% aqueous H$_2$O$_2$ was carried out as the test reaction (Table 1). Under the present reaction conditions, the epoxidation did not proceed at all in the absence of catalysts (Table 1, entry 1). In the presence of $\text{I}$, cyclooctene was smoothly oxidized at 305 K to give 1,2-epoxycyclooctane in 97% yield based on H$_2$O$_2$ (Table 1, entry 2). When lowering the reaction temperature to 273 K, the epoxidation still significantly proceeded (Table 1, entry 3). Even under the stoichiometric conditions using one equivalent of H$_2$O$_2$ with respect to cyclooctene, 1,2-epoxycyclooctane was obtained in 94% yield (Table 1, entry 4). The amount of $\text{I}$ could be much reduced; even when using 0.1 mol% of $\text{I}$ (with respect to H$_2$O$_2$), 1,2-epoxycyclooctane was produced in 94% yield (Table 1, entry 5). The catalytic activities of the precursors of $\text{I}$ were much lower than that of $\text{I}$; the epoxidation using PW10 and TiO(acac)$_2$ afforded 1,2-epoxycyclooctane in only 12% and 4% yields, respectively (Table 1, entries 6 and 7). As above-mentioned, $\text{I}$ could readily be formed by just mixing PW10 and TiO(acac)$_2$ in CH$_3$CN. Thus, it should be noted that a simple mixture of PW10 and TiO(acac)$_2$ (so-called “in-situ-prepared catalyst”) could be utilized for the epoxidation and that the in-situ-prepared catalyst showed almost the same performance as that of $\text{I}$ (Table 1, entry 8). It would be very advantageous to demonstrate the reactions using such in-situ-prepared catalysts because there is no need to synthesize (isolate) the catalysts separately. Hence, several efficient POM-based in-situ-prepared catalyst systems in aqueous media$^{25}$ as well as
in organic media\textsuperscript{19} have been developed to date.

Up to the present, several Ti-substituted POMs for H\textsubscript{2}O\textsubscript{2}-based oxidation have been reported.\textsuperscript{4} The catalytic performance of I was much superior to those of the previously reported Ti-substituted POMs including our silicotungstate analogue TBA\textsubscript{8}[\gamma-SiW\textsubscript{10}O\textsubscript{36}]\textsubscript{2}Ti\textsubscript{4}(\mu-O)\textsubscript{2}(\mu-OH)\textsubscript{4} (Table S3).\textsuperscript{4} As we expected, the effect of the central heteroatoms was very significant; the reaction rate of I under the conditions described in Fig. S4 was 2.7 mM min\textsuperscript{-1} and ca. 11 times larger than that of TBA\textsubscript{8}[\gamma-SiW\textsubscript{10}O\textsubscript{36}]\textsubscript{2}Ti\textsubscript{4}(\mu-O)\textsubscript{2}(\mu-OH)\textsubscript{4} (0.26 mM min\textsuperscript{-1}). By changing the central heteroatom from Si\textsuperscript{4+} to P\textsuperscript{5+}, the negative charge of the POM anion decreases, and thereby the catalytic activity for electrophilic oxidation is likely improved. This is one possible explanation of the effect of the central heteroatoms, and such effect is also observed in the case of V-substituted POMs.\textsuperscript{20}

During the catalytic oxidation, no degradation of I into smaller molecular weight peroxotungstate species, such as [HPO\textsubscript{4}\{WO(O\textsubscript{2})\textsubscript{2}\}\textsubscript{2}]\textsuperscript{2–} and [PO\textsubscript{4}\{WO(O\textsubscript{2})\textsubscript{2}\}\textsubscript{4}]\textsuperscript{3–}, was observed. When adding an excess amount of diethyl ether to the reaction solution, I dissolved in the solution could spontaneously precipitate out, and thus the used I after the reaction could easily be recovered by simple filtration (precipitation method, ≥90\% recovery). Moreover, the recovered I could be reused at least five times with keeping its high catalytic performance for the same reaction (Fig. 5). It should be noted that the IR, CSI-MS, and \textsuperscript{31}P NMR spectra of the recovered I catalyst even after the fifth reuse experiment were almost the same as those of the as-prepared fresh I, showing the high durability of I (Fig. S1d, S2c, and S5).

Next, the synthetic scope of the present I-catalyzed oxidation system was investigated. In the presence of catalytic amounts of I, epoxidation of alkenes, oxygenation of sulfides, oxidative bromination of unsaturated compounds, and the hydroxylation of anisole with H\textsubscript{2}O\textsubscript{2} efficiently proceeded to give the corresponding oxidation products. As for epoxidation, various kinds of structurally diverse alkenes including cyclic, internal, and terminal ones could be converted into the corresponding epoxides with high selectivities (Table 2). In contrast with porous titanosilicate-based catalysts, the epoxidation of relatively bulky alkenes, e.g., norbornene, cyclooctene and
cyclododecene, efficiently proceeded (Table 2, entries 1–3). A non-activated terminal alkene of 1-octene could also be converted into the corresponding epoxide (Table 2, entry 8). For the epoxidation of cis- and trans-alkenes, the configurations around the C=C were completely retained in the corresponding epoxides (Table 2, entries 5–7), indicating no involvement of free-radical intermediates in the present I-catalyzed epoxidation. In the epoxidation of cis- and trans-2-octenes, the yield of cis-2,3-epoxyoctane was significantly higher than that of trans-2,3-epoxyoctane, while the $\pi$(C=C) HOMO energy of cis-2-octene (−0.342 eV) calculated at the HF/6-311G(d,p) level was almost the same as that of trans-2-octene (−0.343 eV) (Table 2, entries 5 and 6). Moreover, the epoxidation of 3-methyl-1-cyclohexene was highly diastereoselective and afforded the corresponding epoxide with the epoxy ring trans to the methyl group (anti configuration) (Table 2, entry 4). Such stereospecific cis-preferential and diastereoselective anti-preferential epoxidations are not common and likely owing to the steric effect of the active oxygen species generated on POMs.20

The present I-catalyzed oxidation system was also applicable to oxygenation of sulfides (Table 3). The reaction completed within 10 min and afforded the corresponding oxygenated products in ≥90% total yields based on H$_2$O$_2$. The oxygenation of thioanisole and its derivatives with electron-donating as well as electron-withdrawing substituents on the phenyl rings efficiently proceeded (Table 3, entries 1–5). With regard to 4-cyanothioanisole, the reaction exclusively took place at the sulfide group, and no Payne-type reaction occurred at the cyano group (Table 3, entry 5). Not only aryl sulfides but also less reactive alkyl ones could effectively be oxygenated (Table 3, entries 6 and 7). Furthermore, I could efficiently catalyze oxidative bromination of various types of unsaturated compounds such as arenes, alkenes, and alkynes to give the corresponding mono- or dibrominated compounds in high yields, and the selected examples are summarized in Scheme 1. The hydroxylation of anisole could also be accomplished by using the present system and preferentially took place the para-position (Scheme 2). As can be seen from the above-mentioned results, one may recognize the broad synthetic utility of the present I-catalyzed oxidation system.
Identification of active oxygen species

With regard to our previously reported H2O2-based oxidation catalyzed by TBA8[(γ-SiW10O36)2Ti4(µ-O)2(µ-OH)4]4a and TBA4[(γ-XW10O38V2(µ-OH)2] (X = Si (n = 4) or P (n = 3)),20 the Ti4(µ-OOH)(µ-OH) and V2(µ-η2:η2-O2) species have been postulated as the respective active oxygen species on the basis of the spectroscopic, kinetic, and/or computational evidences. However, the isolation of the V2(µ-η2:η2-O2) species and even the detection of the Ti4(µ-OOH)(µ-OH) species have not yet been successful because their concentrations are very low and/or they are not stable enough for isolation and/or detection.

We initially measured the NMR (31P and 183W) and CSI-MS spectra of the in-situ-formed active oxygen species by the reaction of I with H2O2. As above-mentioned, the 31P NMR spectrum of I showed a single signal at –11.8 ppm (Fig. 6a). Upon addition of an excess amount of H2O2 (128 equivalents with respect to I) to the CD3CN solution of I, the 31P NMR signal due to I completely disappeared, and one new signal appeared at –16.7 ppm (Fig. 6b). Upon addition of cyclooctene (128 equivalents with respect to I) to this solution, the signal at –16.7 ppm completely disappeared, and the signal at –11.8 ppm due to I appeared again with the concomitant formation of 1,2-epoxycyclooctane (Fig. 6c). Therefore, the –16.7-ppm signal would be due to the active oxygen species (II) for the epoxidation. The 183W NMR spectrum of I with H2O2 (64 equivalents with respect to I) in a mixed solvent of CD3CN and PC (1:1 v/v) showed six signals at –94.3, –110.2, –112.9, –118.7, –123.2, and –127.2 ppm with the respective intensity ratio of 2:1:2:1:2:2 (Fig. 6f).24 The 183W NMR result indicates that II would possess the C2v or C2h symmetry.

The 31P NMR spectrum of the in-situ-formed II was almost unchanged and no signals of low molecular weight peroxotungstate fragments, such as [HPO4{WO(O2)2}2]2− and [PO4{WO(O2)2}4]3− (typically observed at 2.8 and 4.5 ppm in CD3CN, respectively8c), were observed even after the solution was kept for 24 h at room temperature. These results clearly indicate that II is highly stable and that the decomposition of [γ-PW10O36]7− framework in I does not occur at all even in the presence of excess amounts of H2O2. Due to the stability as well as the relatively higher concentration of II, we
assumed that II can be isolated as the single species.

As we expected, II could readily be isolated by addition of an excess amount of diethyl ether to the CH3CN solution containing I and H2O2 at 273 K. Furthermore, the single crystals of II for X-ray crystallographic analysis were successfully obtained by recrystallization of the isolated II from a mixed solvent of nitroethane (EtNO2) and EtOAc at 278 K. The 31P NMR in CD3CN spectrum of the single crystals was the same as that of the in-situ-formed II (Fig. 6d). The CSI-MS spectrum in CH3CN showed the main set of signals centered at m/z = 3705 assignable to [TBA8{(PW10O36)2Ti4(O2)4}\cdot TBAOH]2+ (Fig. S2d). Because the single crystals of II were quite easily damaged by X-ray irradiation, the diffraction data were carefully collected by continuously changing the irradiation spots at the synchrotron facility (see the Experimental Section in detail). Consequently, we could manage to determine the anion structure of II with four peroxo species. Although highly disordered TBA cations could not crystallographically be assigned, the elemental analysis revealed the presence of six TBA cations per II anion. The anion structure of II is shown in Fig. 7, and the crystallographic data are summarized in Table S1. Two Ti atoms in the lacunary pocket of each [γ-PW10O36]7- subunit were linked by one μ-η2:η2-O2 species, and two monomer subunits were linked by two μ-η2:η2-O2 species, that is, the presence of four Ti2-μ-η2:η2-peroxo species in II. The anion structure of II was C2v symmetry in agreement with the 183W NMR spectrum of the in-situ-formed II (Fig. 6f). The elemental analysis data showed TBA/P/W/Ti ratio of 3:1:10:2. The stoichiometric oxidation of triphenylphosphine with II (10 μmol) gave ca. four equivalents (42 μmol) of triphenylphosphine oxide based on II, showing the presence of four active oxygen species in II. These data indicate that the formula of II is TBA6[(γ-PW10O36)2Ti4(μ-η2:η2-O2)4], and II can be formed by the reaction of I with four equivalents of H2O2 [eqn (2)].

\[
\text{TBA}_6[(\gamma-\text{PW}_{10}\text{O}_{36})_2\text{Ti}_4(\mu-\text{O})_2(\mu-\text{OH})_4] + 4\text{H}_2\text{O}_2 \\
\rightleftharpoons \text{TBA}_6[(\gamma-\text{PW}_{10}\text{O}_{36})_2\text{Ti}_4(\mu-\eta^2:\eta^2-\text{O}_2)_4] + 6\text{H}_2\text{O}
\] (2)
With regard to the $\mu$-oxo-$\mu$-$\eta^2$-$\eta^2$-peroxo Ti(salan) complex reported by Katsuki and co-workers, one $\mu$-$\eta^2$-$\eta^2$-O$_2$ species, and two N atoms and two O atoms in the salan ligand were coordinated to each Ti atom in a pseudo-octahedral arrangement (Fig. 1b), resulting in the coordination number of each Ti atom of seven. On the other hand, two O atoms in POM framework and two $\mu$-$\eta^2$-$\eta^2$-O$_2$ species were coordinated to each Ti atom in a pseudotetrahedral arrangement and there was no bridging $\mu$-O ligand between Ti atoms in the case of II. Thus, the coordination number of each Ti atom in II was six. This is the most significant difference between II and the inactive Katsuki’s complex, and thus we assume that the high catalytic performance of I would be ascribed to the formation of the active pseudotetrahedral Ti peroxo species, in good agreement with the high reactivity of tetrahedral titanium species (within zeolite framework).2,12

Besides the above phosphine oxidation, the stoichiometric epoxidation of cyclooctene and thioanisole with II (4 $\mu$mol) also gave ca. four equivalents of 1,2-epoxycyclooctane (17 $\mu$mol) and the corresponding oxygenated products (methyl phenyl sulfide: 7 $\mu$mol, methyl phenyl sulfone: 5 $\mu$mol), respectively, with respect to II, showing that all of the four Ti$_2$-$\mu$-$\eta^2$-$\eta^2$-peroxo species in II are active for these oxidations. Although to date several compounds with M$_2$-$\mu$-$\eta^2$-$\eta^2$-peroxo species (M = Ti, Zr, Hf, U, etc.) have been synthesized and their structures have been determined, these peroxo species are not active for epoxidation. To the best of our knowledge, II is the first example of the structurally determined M$_2$-$\mu$-$\eta^2$-$\eta^2$-peroxo species which are truly active for epoxidation. The reaction rate (0.043 mM min$^{-1}$) of the “stoichiometric” epoxidation of cyclooctene (0.035 M) with II (0.57 mM) agreed well with that (0.041 mM min$^{-1}$) of the “catalytic” epoxidation of cyclooctene (0.035 M) with H$_2$O$_2$ (0.14 M) by I (0.57 mM) (Fig. S6), indicating that II is the truly active oxygen species and included in the catalytic cycle for the present I-catalyzed oxidation.

**Conclusion**

In this work, we have obtained several important findings for the POM-based catalyst design and the application to H$_2$O$_2$-based oxidation. Firstly, we could synthesize an organic solvent-soluble divacant
lacunary phosphotungstate PW10 for the first time. By the reaction of PW10 and TiO(acac)2 in CH3CN, a novel Ti-substituted phosphotungstate I could readily be synthesized. The synthetic strategy using an organic solvent-soluble lacunary precursor in an organic medium demonstrated herein will be applicable to synthesis of various types of metal-substituted POMs and open up a new avenue for POM chemistry and synthesis. In the presence of I, several H2O2-based oxidation reactions, such as epoxidation of alkenes, oxygenation of sulfides, oxidative bromination of unsaturated compounds, and the hydroxylation of anisole, smoothly proceeded to afford the corresponding oxidation products with high efficiencies and selectivities, and the catalytic performance of I was much superior to those of the previously reported Ti-substituted POMs including our silicotungstate analogue TBA8[(γ-SiW10O36)2Ti4(µ-O)2(µ-OH)4]. Moreover, I was highly durable during the catalysis (no degradation into smaller molecular weight peroxotungstate species) and could be reused several times with keeping its high catalytic performance. The in-situ-prepared catalyst by just mixing PW10 and TiO(acac)2 was also equally effective to I, which would be advantageous for practical applications. Fortunately, we could isolate the truly catalytically active species for the present I-catalyzed H2O2-based oxidation (II), and its structure could successfully be determined by X-ray crystallographic analysis. Compound II possessed four Ti2-µη2:η2-peroxo species, and all of the four peroxo species were active for oxidation. To the best of our knowledge, II is the first example of structurally determined M2-µη2:η2-peroxo species truly active for oxidation, which is included in the catalytic cycle for the present I-catalyzed oxidation. We hope that these findings will lead to new insight into chemistry of active oxygen species.

Experimental section

Materials

TBABr, TiO(acac)2, and EtNO2 were obtained from TCI, and used as received. HNO3, diethyl ether, CH3CN, EtOAc, 30 % H2O2, acetone, PC, methanol, and deuterated solvents (CD3CN and
DMSO-$d_6$) were obtained from KANTO Chemical, and used as received. Substrates were obtained from Sigma-Aldrich, TCI, KANTO Chemical, and Wako Pure Chemical Industries, and purified prior to the use (if necessary).\textsuperscript{27} Cs$_7$[$\gamma$-PW$_{10}$O$_{36}$]$^{22}$ and TBA$_8$[(γ-SiW$_{10}$O$_{36}$)$_2$Ti$_4$(μ-O)$_2$(μ-OH)$_4$]$^{43}$ were synthesized according to the reported procedures. Aqueous 90% H$_2$O$_2$ was prepared by concentration of 30 % H$_2$O$_2$.

**Instruments**

IR spectra were measured on Jasco FT/IR-4100 using KBr or KCl disks. NMR spectra were measured at room temperature on JEOL JNM-EX270 (\textsuperscript{31}P, 109 MHz) or JEOL JNM-ECA500 (\textsuperscript{1}H, 500 MHz; \textsuperscript{31}P, 202 MHz; \textsuperscript{183}W, 20.6 MHz). Chemical shifts (δ) of \textsuperscript{1}H, \textsuperscript{31}P and \textsuperscript{183}W were reported in ppm downfield from internal TMS, external 85 % H$_3$PO$_4$ (in D$_2$O), and external 1 M Na$_2$WO$_4$ (in D$_2$O), respectively. NMR measurements were done in different solvents. The solvent selection is simply the solubility reason. Cold-spray ionization mass (CSI-MS) spectra were recorded on JEOL JMS-T100CS. Typical measurements were as follows: Orifice voltage 135 V for positive ions; concentration 0.1 mM; spray temperature 263 K; ion source at room temperature. ICP-AES analyses were performed on Shimadzu ICPS-8100. Elemental analyses for C, H, and N were performed on Yanaco MT-6. GC analyses were performed on Shimadzu GC-2014 with a flame ionization detector (FID) equipped with a Stabilwax capillary column (internal diameter = 0.25 mm, length = 30 m). GC-MS spectra were measured on Shimadzu GCMS-QP2010 at an ionization voltage 70 eV. HPLC analyses were performed on Shimadzu Prominence system with a UV-vis detector (Shimadzu SPD-20A, 270 nm) equipped with a GL Science Inertsil ODS-3 column (particle size = 5 μm, internal diameter = 4.6 mmφ, length = 250 mm), using a mixed solvent of methanol and water as the eluent (9:1 v/v). The π(C=C) HOMO energies of cis- and trans-2-octenes were calculated at the HF/6-311G(d,p) level with the Gaussian 09 program package.\textsuperscript{28}

**X-ray crystallography**

Diffraction measurements of I were made on Rigaku MicroMax-007 Saturn 724 CCD detector with
graphite monochromated Mo Kα radiation ($\lambda = 0.71069$ Å) at 123 K. The diffraction data of I were collected using CrystalClear.²⁹ Diffraction measurements of II were made on BL1A beamline in KEK Photon Factory (synchrotron facility) with a diffractometer equipped with Dectris Pilatus 2M-F PAD detector ($\lambda = 0.95000$ Å) at 95 K. The diffraction data of II were collected using ugui program. All the data were processed using HKL2000.³⁰ Neutral scattering factors were obtained from the standard source. In the reduction of data, Lorentz and polarization corrections were made. All structures were solved by SHELXS-97 (direct methods) and refined by SHELXH-97.³¹ The structural analysis was performed using CrystalStructure,³² Win-GX,³³ and Yadokari-XG.³⁴ The metal atoms (P, W, and Ti) in I were refined anisotropically. The metal atoms (P, W, and Ti) and oxygen atoms in II were refined anisotropically with SIMU. Some of the bond lengths of II were refined with SADI and DFIX. The highly disordered TBA cations of II could not crystallographically be assigned and were omitted by using SQUEEZE program of PLATON,³⁵ affording much improved analytical results. CCDC-1406336 (I) and CCDC-1406337 (II) contain the supplementary crystallographic data for this manuscript. The data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

**BVS calculations**

The BVS values were calculated by the expression for the variation of the length $r_{ij}$ of a bond between two atoms $i$ and $j$ in observed crystal with valence $V_i$:

$$V_i = \sum_j \exp\left(\frac{r'_{ij} - r_{ij}}{B}\right)$$

where $B$ is constant equal to 0.37 Å, $r'_{ij}$ is bond valence parameter for a given atom pair.³⁶

**Catalytic oxidation**

The catalytic oxidations were carried out in a 15 mL glass tube reactor containing a magnetic stir bar. A typical procedure was as follows: I, substrate, 30% H₂O₂, and CH₃CN were successively placed into the glass tube reactor. The reaction mixture was stirred at 305 K. The yields of products were
determined by GC analysis using an internal standard. All products are known and confirmed by comparison of their GC retention times and/or GC-MS patterns with the authentic samples.

**Stoichiometric oxidation**

The stoichiometric oxidations were carried out in a 15 mL glass tube reactor containing a magnetic stir bar. A typical procedure for the stoichiometric epoxidation of cyclooctene was as follows: Cyclooctene (0.25 mmol) and CH$_3$CN (6.96 mL) were successively placed into a glass tube reactor. After the solution was stirred at 253 K, the reaction was initiated by addition of II (4 µmol). The reaction was periodically monitored by GC. Reaction rates ($R_0$) were determined from the slopes of reaction profiles ([epoxide] versus time) at low conversions of cyclooctene (initial rate method). Finally, ca. four equivalents of 1,2-epoxycyclooctane (17 µmol) were produced. The stoichiometric oxidation of thioanisole was carried out via the same procedure at room temperature, and gave ca. four equivalents of oxygenated products (methy phenyl sulfoxide: 7 µmol, methy phenyl sulfone: 5 µmol). A typical procedure for the stoichiometric oxidation of triphenylphosphine was as follows: triphenylphosphine (0.25 mmol) and CH$_3$CN (4 mL) were successively placed into a glass tube reactor. After the solution was stirred at 305 K, the reaction was initiated by addition of II (10 µmol). The reaction was periodically monitored by HPLC. Finally, ca. four equivalents (42 µmol) of triphenylphosphine oxide were produced.

**Synthesis of PW10**

TBABr (0.67 g, 2.1 mmol) was dissolved in HNO$_3$ (2.6 M, 200 mL) at 273 K. Then, Cs$_7$[$\gamma$-PW$_{10}$O$_{36}$]$\cdot$H$_2$O (2.0 g, 0.59 mmol) was added in a single step, and the resulting solution was stirred for 10 min. The resulting white precipitate of PW10 was collected by filtration, washed with water (100 mL) and diethyl ether (200 mL) to afford analytically pure white powder of PW10 (1.6 g, 84% yield based on Cs$_7$[$\gamma$-PW$_{10}$O$_{36}$], >99% purity). Compound PW10 was stored in a freezer (at 253 K). To prevent the isomerization and/or decomposition of PW10, the vacuum drying and the storage at room temperature should be avoided. Elemental analysis calcd (%) for C$_{48}$H$_{118}$N$_3$O$_{39}$PW$_{10}$
(TBA$_3$[PW$_{10}$O$_{34}$(H$_2$O)$_2$]$\cdot$3H$_2$O): C, 17.84; H, 3.68; N, 1.30; P, 0.96; W, 56.90. Found: C, 17.65; H, 3.53; N, 1.21; P, 0.92; W, 56.50. IR (KBr pellet; 4000–400 cm$^{-1}$): 3429, 2962, 2935, 2874, 1625, 1483, 1381, 1347, 1151, 1109, 1057, 1036, 975, 951, 861, 798, 675, 661, 613, 535, 401 cm$^{-1}$. $^{31}$P NMR (DMSO-$d_6$): $\delta$ –10.5 ppm. $^{183}$W NMR (DMSO-$d_6$): $\delta$ –105.4, –114.2, –117.3, –136.1, –168.5 ppm (the integrated intensity ratio of 1:1:1:1:1). CSI-MS (acetone): $m/z$ = 3384 [TBA$_4$(PW$_{10}$O$_{34}$)]$^+$. 

**Synthesis of compound I**

TiO(acac)$_2$ (0.16 g, 0.62 mmol) was dissolved in CH$_3$CN (20 mL) at room temperature. Then, PW$_{10}$ (1.0 g, 0.31 mmol) was added in a single step, and the resulting solution was stirred for 5 min. After filtration, the solution was added to diethyl ether (200 mL) and the resulting pale yellow precipitate was collected by filtration. The crude compound was purified by recrystallization from a mixed solvent of CH$_3$CN and EtOAc. The solution was kept at room temperature for 24 h to afford pale yellow crystals of I (0.47 g, 45% yield based on PW10). Elemental analysis calcd (%) for C$_{100}$H$_{230}$N$_6$O$_{81}$P$_2$Ti$_4$W$_20$ (TBA$_6$[(PW$_{10}$O$_{36}$)$_2$Ti$_4$O$_2$(OH)$_4$]EtOAc$\cdot$H$_2$O): C, 17.81; H, 3.44; N, 1.25; P, 0.92; Ti, 2.84; W, 54.53. Found: C, 18.25; H, 3.51; N, 1.15; P, 0.98; Ti, 2.53; W, 55.60. IR (KBr pellet; 4000–400 cm$^{-1}$): 3580, 3446, 2962, 2934, 2874, 1732, 1623, 1483, 1379, 1246, 1152, 1070, 1050, 1040, 971, 956, 878, 815, 656, 537, 489, 420 cm$^{-1}$. $^1$H NMR (CD$_3$CN): $\delta$ 7.91 (µ-OH, 4H), 4.06 (EtOAc, 2H), 3.17 (TBA, 48H), 1.97 (EtOAc, 3H), 1.67 (TBA, 48H), 1.43 (TBA, 48H), 1.20 (EtOAc, 3H), 1.01 (TBA, 72H) ppm. $^{31}$P NMR (CD$_3$CN): $\delta$ –11.8 ppm. $^{183}$W NMR (CD$_3$CN/PC (1:1 v/v)): $\delta$ –110.6, –112.7, –115.8 ppm (the integrated intensity ratio of 1:2:2). CSI-MS (CH$_3$CN): $m/z$ = 3561 [TBA$_8$H$_4${(PW$_{10}$O$_{36}$)$_2$Ti$_4$O$_6$}]$^{2+}$, 3674 [TBA$_9$H$_4${(PW$_{10}$O$_{36}$)$_2$Ti$_4$O$_5$}]$^{2+}$, 6880 [TBA$_7$H$_4${(PW$_{10}$O$_{36}$)$_2$Ti$_4$O$_6$}]$^+$. 

**Synthesis of compound II**

Compound I (0.10 g, 0.015 mmol) was dissolved in CH$_3$CN (5 mL) at 273 K. Then, 90% H$_2$O$_2$ (128 equivalents, 1.9 mmol) was added in a single step, and the resulting solution was stirred for 1 h.
After filtration, the solution was added to diethyl ether (50 mL) and the resulting yellow precipitate was collected by filtration, and washed with EtOAc (20 mL). The pure compound II was obtained as yellow powder after dryness (0.072 g, 72% yield based on I). Elemental analysis calcd (%) for C_{100}H_{228}N_{6}O_{84}P_{2}Ti_{4}W_{20} (TBA_{6}[(PW_{10}O_{36})_{2}Ti_{4}(O_{2})_{4}]·EtOAc·2H_{2}O): C, 17.69; H, 3.38; N, 1.24; P, 0.91; Ti, 2.82; W, 54.16. Found: C, 17.10; H, 3.39; N, 1.20; P, 0.89; Ti, 2.81; W, 54.41. IR (KCl pellet; 4000–400 cm⁻¹): 3410, 2960, 2932, 2872, 1624, 1482, 1466, 1379, 1131, 1062, 1041, 972, 955, 879, 816, 759, 524, 460, 422 cm⁻¹. ³¹P NMR (CD₃CN): δ = -16.8 ppm. The pale yellow crystals of II suitable for the X-ray crystallographic analysis were obtained by recrystallization from a mixed solvent of EtNO₂ and EtOAc at 278 K. Elemental analysis calcd (%) for C_{102}H_{233}N_{7}O_{86}P_{2}Ti_{4}W_{20} (TBA_{6}[(PW_{10}O_{36})_{2}Ti_{4}(O_{2})_{4}]·EtNO₂·EtOAc·2H_{2}O): C, 17.85; H, 3.42; N, 1.43; P, 0.90; Ti, 2.79; W, 53.57. Found: C, 17.96; H, 3.44; N, 1.42; P, 0.90; Ti, 2.66; W, 53.36. IR (KCl pellet; 4000–400 cm⁻¹): 3421, 2961, 2933, 2873, 1732, 1624, 1546, 1483, 1379, 1131, 1062, 1040, 971, 955, 880, 818, 759, 524, 459, 424 cm⁻¹. ³¹P NMR (CD₃CN): δ = -16.9 ppm. ¹⁸³W NMR (in situ, CD₃CN/PC (1:1 v/v)): δ = -94.3, -110.2, -112.9, -118.7, -123.2, -127.2 ppm (the integrated intensity ratio of 2:1:2:1:2:2). CSI-MS (CH₃CN): m/z = 3705 (main set of signals) [TBA₈{(PW_{10}O_{36})_{2}Ti_{4}(O_{2})_{4}}·TBAOH]²⁻.

**Acknowledgements**

We thank KEK Photon Factory (Research 2013G640) for the use of the X-ray diffraction instruments (BL1A beamline). This work was supported in part by the Japan Society for the Promotion of Science (JSPS) through its “Funding Program for World-Leading Innovative R&D on Science and Technology (FIRST Program)” and Grants-in-Aid for JSPS Fellows and Scientific Research from the Ministry of Education, Culture, Science, Sports, and Technology of Japan.

**References and notes**

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17 By the reaction of K₈[γ-SiW₁₀O₃₆] with TiOSO₄ in acidic solution (pH = 1.3) at room temperature, a dimeric Ti-substituted γ-Keggin POM, [Ti₄(γ-SiW₁₀O₃₆)₂(µ-O)₂(µ-OH)₄]₈⁻, can be synthesized.⁴ᵃ On the other hand, even using the same starting materials, a tetrameric Ti-substituted POM composed of β-Keggin subunits, [(β-Ti₂SiW₁ₐO₃₉)₄]²⁺, is obtained when


24 Because the solubility of I in CD$_3$CN was below the detection limit of $^{183}$W nuclei, PC was added to dissolve I in the solvent. The $^{31}$P NMR spectrum of I after the $^{183}$W NMR measurement showed a single signal at –11.8 ppm, suggesting that the structure of I was maintained during the $^{183}$W NMR measurement.

25 (a) I. A. Weinstock, E. M. G. Barbuzzi, M. W. Wemple, J. J. Cowan, R. S. Reiner, D. M.


Table 1 Effects of catalysts on epoxidation of cyclooctene with H$_2$O$_2$\textsuperscript{a}

<table>
<thead>
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<th>Entry</th>
<th>Catalyst (μmol)</th>
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<th>Yield (%)</th>
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<td>3</td>
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<td>PW10 (8) + TiO(acac)$_2$ (16)</td>
<td>305</td>
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\textsuperscript{a} Reaction conditions: Cyclooctene (5 mmol), 30% H$_2$O$_2$ (1 mmol), CH$_3$CN (6 mL).

\textsuperscript{b} Cyclooctene (1 mmol). Yields were determined by GC with an internal standard. Yield (%) = epoxide (mol)/initial H$_2$O$_2$ (mol) × 100.
Table 2 Epoxidation of various alkenes with H$_2$O$_2$ catalyzed by I

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<th>Substrate</th>
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<td>8$^c$</td>
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<td>8</td>
<td>54</td>
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</table>

$^a$ Reaction conditions: I (4 µmol), substrate (5 mmol), 30% H$_2$O$_2$ (1 mmol), CH$_3$CN (6 mL), 305 K. $^b$ Substrate: cis/trans = 30/70. $^c$ 323 K. Yields were determined by GC with an internal standard. Yield (%) = epoxide (mol)/initial H$_2$O$_2$ (mol) × 100.
Table 3 Oxygenation of various sulfides with H₂O₂ catalyzed by I

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<tr>
<td>7</td>
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<td>5</td>
<td>55/18</td>
<td>90</td>
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</table>

*a Reaction conditions: I (2 µmol), substrate (1 mmol), 30% H₂O₂ (0.2 mmol), CH₃CN (1 mL), 305 K. Yields were determined by GC with an internal standard. Yield (%) = sulfoxide or sulfone (mol)/initial H₂O₂ (mol) × 100. Total yield (%) = {sulfoxide (mol) + sulfone (mol) × 2}/initial H₂O₂ (mol) × 100.
Fig. 1 (a) One of the postulated active oxygen species formed on TS-1,\(^2\) (b) \(\mu\)-oxo-\(\mu\)-\(\eta^2:\eta^2\) peroxo core in the Katsuki’s Ti(salan) complex,\(^3c\) and (c) tetra-\(\mu\)-\(\eta^2:\eta^2\) peroxo core in II (this work).
Fig. 2 $^{31}$P NMR spectra of (a) PW10 in DMSO-$d_6$ and (b) I in CD$_3$CN.
Fig. 3 $^{183}$W NMR spectra of (a) PW10 in DMSO-$d_6$ and (b) I in CD$_3$CN/PC (1:1 v/v).
**Fig. 4** Polyhedral and ball-and-stick representation of the anion part of I. The \{WO$_6$\} and \{PO$_4$\} units are shown as green octahedra and purple tetrahedra, respectively. Yellow and red spheres show Ti and O atoms, respectively.
Fig. 5 Reuse experiments for the epoxidation of cyclooctene with H₂O₂; the profiles for I (blue diamond), and the first (red circle), second (green triangle), third (yellow square), forth (purple cross), and fifth (blue asterisk) reuse experiments. Reaction conditions: I (4 µmol), cyclooctene (5 mmol), 30% H₂O₂ (1 mmol), CH₃CN (6 mL), 305 K.
Fig. 6 $^{31}$P NMR spectra of (a) I, (b) in-situ-formed II (I + 128H$_2$O$_2$), (c) in-situ-formed II + 128 equivalents of cyclooctene, and (d) isolated single crystals of II in CD$_3$CN; $^{183}$W NMR spectrum of (e) I and (f) in-situ-formed II (I + 64H$_2$O$_2$) in CD$_3$CN/PC (1:1 v/v).
Fig. 7 Polyhedral and ball-and-stick representation of the anion part of II. The \{WO$_6$\} and \{PO$_4$\} units are shown as green octahedra and purple tetrahedra, respectively. Yellow and red spheres show Ti and O atoms, respectively.
Scheme 1 Oxidative bromination of unsaturated compounds with H₂O₂ catalyzed by I. Reaction conditions: I (0.25 µmol), substrate (1 mmol), NaBr (2 mmol), 30% H₂O₂ (1 mmol), AcOH/CH₃CN (2/1 mL), 305 K. [a] NaBr (1 mmol). Yields were determined by GC with an internal standard. Yield (%) = product (mol)/initial H₂O₂ (mol) × 100.
Scheme 2. Hydroxylation of anisole with H$_2$O$_2$ catalyzed by I. Reaction conditions: I (1.25 µmol), anisole (5 mmol), 30% H$_2$O$_2$ (0.1 mmol), CH$_3$CN (2 mL), 333 K, 120 min. Yields were determined by GC with an internal standard. Yield (%) = product (mol)/initial H$_2$O$_2$ (mol) × 100.
Graphical abstract

A Ti-substituted phosphotungstate (I) showed high catalytic performance for several oxidation reactions. The truly catalytically active species was successfully isolated, and its anion structure was determined.