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μ-η^1:η^1-Peroxo-Bridged Dinuclear Peroxotungstate Catalytically Active for Epoxidation of Olefins

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The reaction of the dinuclear peroxotungstate, $[(n\text{-}C_4H_9)_4N]_2[\{WO(O_2)_2\}_2(\mu\text{-}O)]$ (**II**), with H_2O_2 gives the novel μ-η^1:η^1-peroxo-bridging dinuclear tungsten species, $[(n\text{-}C_4H_9)_4N]_2[\{WO(O_2)_2\}_2(\mu\text{-}O_2)]$ (**I**), which has been characterized by X-ray crystallography, elemental analysis, IR, Raman, UV–vis, and ^{183}W NMR. Only **I** is active for the epoxidation of cyclic, internal, and terminal olefins, whereas **II** is inactive for each. The low X_{SO} (X_{SO} = (nucleophilic oxidation)/(total oxidation)) value of **I** (0.18 ± 0.02) in comparison with that of **II** (0.39 ± 0.01) for the stoichiometric oxidation of thianthrene 5-oxide, which is a mechanistic probe for determining the electronic character of an oxidant, reveals that **I** is more electrophilic than **II**. On the basis of the kinetic and spectroscopic results, the catalytic epoxidation proceeds by the reaction of **I** with an olefin to form **II** and the corresponding epoxide followed by the regeneration of **I** by the reaction of **II** with H_2O_2.

Introduction

The transition metal peroxo complexes are of great importance in the fields of structural chemistry, biological chemistry, catalysis, and material science.[1] Recently, the di- to polynuclear metal complexes that contain bridging peroxo groups have attracted much attention due to their remarkable oxygenation activity. For example, the polynuclear d^0-transiton metal complexes containing μ-η^1:η^2-peroxo moieties, bio-inspired Cu-based dinuclear μ-η^2:η^2-peroxo complexes, and the related bis(μ-oxo) species show high activity for oxidation reactions such as oxygen transfer to C=C double bonds and activation of the aromatic and aliphatic C−H bonds.[2,3] By contrast, the (μ-η^1:η^1-peroxo)dimetal complexes are usually inactive for the oxygenation of organic substances, and the formation of inactive species after monooxygenation prevents the regeneration of the μ-η^1:η^1-peroxo species.[4] Accordingly, the catalytically active dimetal complexes containing μ-η^1:η^1-peroxo species have never been reported.

Among d^0-transition metal complexes, tungsten-based oxidation systems with H_2O_2 have attracted much attention because of the high reactivity and inherent poor activity for the decomposition of H_2O_2.[5,6] To date, the μ-η^1:η^1-peroxo bridging dinuclear d^0-transition metal complexes have never been reported, whereas the d^0-transition metal peroxo complexes are among the earliest known and best characterized;[7] for example, there have been reported various X-ray crystal structures of peroxotungstates.[8,9] While the dinuclear peroxotungstate of $[\{WO(O_2)_2(H_2O)\}_2(\mu\text{-}O)]^{2-}$ has been suggested as an intermediate for H_2O_2-based oxidations of amines, alcohols, allylic alcohols, and olefins,[10] the catalyti-

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cally active species has not yet been isolated. In this paper, we report the X-ray crystallographic structures and stoichiometric oxidation activities of the tetra-*n*-butylammonium (TBA) salt derivative of μ-η^1:η^1-peroxo bridging dinuclear tungsten species, $(TBA)_2[\{WO(O_2)_2\}_2(\mu\text{-}O_2)]$ (**I**), formed by the reaction of $(TBA)_2[\{WO(O_2)_2\}_2(\mu\text{-}O)]$ (**II**) with H_2O_2 under nonaqueous conditions. This study provides the first example of μ-η^1:η^1-peroxo d^0-dimetal species catalytically active for the epoxidation of olefins.

Experimental Section

Materials. Acetonitrile (Kanto Chemical, >99.5%) was dried and stored over type 3A molecular sieves. Octenes, benzyl alcohol, and triphenylphosphine were purchased from TCI and purified according to the reported procedure.[11] 2-Buten-1-ol (TCI) and 3-methyl-2-buten-1-ol (Acros Organics) were used without further purification. Deuterated solvents (CD_3CN, $CDCl_3$, and D_2O) were purchased from Aldrich. Tungstic acid (Wako Chemical), tetra-*n*-butylammonium chloride (TCI), and H_2O_2 (Kanto Chemical, 30% aqueous solution) were purchased and used as received. A solution of 96−97% aqueous H_2O_2 was prepared by concentration of 30% aqueous H_2O_2 and analyzed by the $Ce^{3+/4+}$ titration.[12] Thianthrene 5-oxide (SSO) was synthesized by the oxidation of thianthrene (Aldrich) with HNO_3 according to the reported procedure.[13] The compounds *cis*-thianthrene 5,10-dioxide (*cis*-SOSO) and *trans*-thianthrene 5,10-dioxide (*trans*-SOSO) were synthesized by the oxidation of SSO using H_2O_2/HCl, and thianthrene 5,5-dioxide (SSO_2) was synthesized by the oxidation of SSO using $KMnO_4$ as previously reported.[14] Thianthrene 5,5,10-trioxide ($SOSO_2$) was synthesized by the oxidation of SSO_2 catalyzed by $TBA_4[\gamma\text{-}SiW_{10}O_{34}(H_2O)_2]$ with 30% aqueous H_2O_2.[6] The oxidation of SSO_2 was carried out under the following conditions: $TBA_4[\gamma\text{-}SiW_{10}O_{34}(H_2O)_2] = 5$ μmol, $SSO_2 = 100$ μmol, 30% aqueous $H_2O_2 = 150$ μmol, reaction temperature =298 K, and reaction time = 24 h. SSO and the oxidation products were purified by silica gel column chromatography.

Instruments. IR spectra were measured on a Jasco FT/IR-460 spectrometer Plus using KCl disks. Raman spectra were recorded on a Jasco NR-1000 spectrometer with excitation at 532.36 nm using a JUNO 100 green laser (Showa Optronics Co., Ltd.). UV−vis spectra were recorded on a Jasco V-570 spectrometer with a Unisoku thermostatic cell holder (USP-203). NMR spectra were recorded on a JEOL JNM-EX-270 spectrometer (^{1}H, 270.0 MHz; ^{13}C, 67.80 MHz; ^{183}W, 11.20 MHz). Chemical shifts (δ) were reported in ppm downfield from $SiMe_4$ (solvent, $CDCl_3$) for ^{1}H and ^{13}C NMR spectra and Na_2WO_4 (solvent, D_2O) for ^{183}W NMR spectra. Analyses were performed on a Shimadzu GC-17A gas chromatograph with a flame ionization detector equipped with a DB-WAX etr capillary column (internal diameter = 0.25 mm,

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length = 30 m) or on a Shimadzu GC-14B gas chromatograph with a flame ionization detector equipped with a SE-30 packed column. HPLC analyses were performed on Agilent 1100 series with a UV detector using a Capcell PAK MG C18-reverse phase column (5 μm × 3 mmϕ × 250 mm, Shiseido Fine Chemicals).

Synthesis and Characterization of II. The TBA salt derivative of $[\{WO(O_2)_2\}_2(\mu\text{-}O)]^{2-}$ was prepared using the method provided as follows: A suspension of H_2WO_4 (6 g, 24 mmol) in 20% aqueous H_2O_2 (30 mL, 200 mmol) was stirred at 323 K for 60 min until a pale yellow solution was obtained. The solution was cooled to ambient temperature and filtered to remove insoluble materials followed by addition of TBA•Cl (3.3 g, 12 mmol) in a single step. The resulting pale yellow precipitate (3.5 g yield) was collected by filtration and then was washed with H_2O (20 mL) and diethyl ether (100 mL). The dried pale yellow precipitate (1.5 g) was recrystallized in a mixture of acetone/diethyl ether (8:4 mL) that resulted in a mixture of granular crystals and plate like crystals. The plate like crystals were separated and analytically pure **II** was obtained. Yield was 0.2 g (12% based on the pale yellow precipitate). ^{183}W NMR (11.20 MHz, CD_3CN, 263 K, Na_2WO_4): $\delta = -587.5$ ($\Delta\nu_{1/2} = 24.3$ Hz). IR (KCl): 962, 955, 848, 835, 655, 631, 615, 571, 554, 543, and 524 cm^{-1}. Raman: 970, 961, 858, 844, 801, 786, 662, 624, 597, 572, 470, 328, 308, 275, and 259 cm^{-1}. Anal. calcd. (found) for $C_{32}H_{72}N_2O_{11}W_2$ (**II**): C, 37.37 (37.24); H, 7.06 (7.13); N, 2.72 (2.69); W, 35.75 (35.38).

Synthesis and Characterization of I. The TBA salt derivative of $[\{WO(O_2)_2\}_2(\mu\text{-}O_2)]^{2-}$ was prepared by the method provided as follows: A solution of acetonitrile (0.1 mL) containing **II** (24 mg, 23 μmol) and 97% aqueous H_2O_2 (414 μmol, 18 equiv with respect to **II**) was cooled to 277 K. The colorless plate like crystalline solid (**I**) was obtained by vapor diffusion of diethyl ether into the acetonitrile solution. Yield 16 mg (65% based on **II**). IR (KCl): 957, 951, 850, 836, 798, 668, 654, 631, 616, 572, 551, and 508 cm^{-1}. Raman: 973, 958, 856, 841, 805, 747, 634, 586, 568, 554, 511, 302, 264, and 218 cm^{-1}. Anal. calcd. (found) for $C_{32.46}H_{72.69}N_{2.23}O_{12}W_2$ ($(TBA)_2[\{WO(O_2)_2\}_2(\mu\text{-}O_2)](CH_3CN)_{0.23}$): C, 36.99 (36.57); H, 6.95 (6.79); N, 2.96 (2.96); W, 34.88 (34.31).

Procedure for Stoichiometric Oxidation. The oxidation of various organic substrates was carried out in a 30-mL glass vessel containing a magnetic stir bar. All products were identified by the comparison of retention time, mass spectra, and NMR spectra with those of the authentic samples. The carbon balance in each experiment was in the range of 95−100%. A typical procedure for the stoichiometric oxidation is provided as follows: acetonitrile (2 mL), cyclooctene (1 mmol), and an internal standard (naphthalene) were charged in the reaction vessel, and the solution was cooled to 273 K. The reaction was initiated by the addition of **I** or **II** (25 μmol), and the reaction solution was periodically analyzed.

The comparison of the reaction rates for the stoichiometric epoxidation and the catalytic epoxidation was carried out under the following reaction conditions. The reaction rates were determined from the reaction profiles at low yields (<10%). The reaction conditions for the catalytic epoxidation of cyclooctene by **II** were 12 mM **II**, 470 mM cyclooctene, 47 mM 96% aqueous H_2O_2, 2 mL of acetonitrile, and a reaction temperature of 273 K. The reaction conditions for the stoichiometric epoxidation of cyclooctene with **I** were 12 mM **I**, 470 mM cyclooctene, 2 mL of acetonitrile, and a reaction temperature of 273 K.

Estimation of the Rate of the Regeneration of I by the Reaction of II with H_2O_2. The rate of the regeneration of **I** by the reaction of **II** with H_2O_2 at 273 K was estimated by using UV−vis spectroscopy. The spectra were recorded by using a 0.1 mm quartz glass cell. The conditions for the reaction of **II** with H_2O_2 were as follows: 12 mM **II**, 47 mM 96% aqueous H_2O_2, 2 mL of acetonitrile, and a reaction temperature of 273 K. The reaction was initiated by the addition of H_2O_2 and the reaction solution was periodically analyzed.

Procedure for Oxidation of SSO. The oxidation products were quantitatively analyzed by HPLC using a Capcell Pak MG C18-reverse phase column (5 μm × 3 mmϕ × 250 mm, Shiseido Fine Chemicals), $CH_3OH/CH_3CN/H_2O$ (60:15:25) as eluent, a flow rate of 0.4 mL/min, a column temperature of 303 K, and detection at $\lambda = 254$ nm. Retention times were 3.57, 4.69, 4.93, 5.72, 7.73, and 10.7 min for *trans*-SOSO, $SOSO_2$, *cis*-SOSO, SSO_2, SSO, and naphthalene (internal standard), respectively. The reaction conditions (i.e., concentration of substrate, substrate to oxidant ratio, reaction temperature, etc.) were controlled to minimize overoxidation to $SOSO_2$ and then to estimate the true electronic nature of the oxidant.[15] The X_{SO} value [X_{SO} = (nucleophilic oxidation)/(total oxidation)] was calculated according to the following equation reported,[15] $X_{SO} = (SSO_2 + SOSO_2)/(SSO_2 + SOSO + 2SOSO_2)$. The reaction conditions for the stoichiometric oxidation of SSO were a catalyst containing 20 μmol of tungsten (i.e., **I**, 10 μmol; **II**, 10 μmol), 200 μmol of SSO, 5 mL of acetonitrile, and a reaction temperature of 273 K.

Details of X-ray Crystallography. Diffraction measurements were made on a Rigaku AFC-10 Saturn 70 CCD area detector equipped with graphite monochromated Mo Kα radiation (λ = 0.71070 Å). The data for **I** and **II** were collected at 153 K and processed using Crystal Clear[16] and HKL 2000,[17] respectively. An empirical absorption correction was applied. As for **I**, the structure was solved by combination of the direct method (SHELXS-97), Fourier synthesis, and least-square refinement (SHELXH-97)[18] with Win-GX software.[19] All of the non-hydrogen atoms were refined anisotropically and the hydrogen atoms were excluded for the solution. The unit cell contained two kinds of crystallographic independent molecules (molecules **A** and **B** in Figure S4, Supporting Information). Molecule **A** sited on the center of symmetry and molecule **B** involved disordered tungsten and oxygen atoms. As for **II**, the structure was solved by a combination of the direct method (SIR2002),[20] Fourier synthesis (DIRDIF),[21] and least-squares refinement (SHELXL-97)[18] with Crystal Structure 3.6 software.[22] All of the non-hydrogen atoms were refined anisotropically and the hydrogen atoms were refined with the riding model. Detailed crystallographic data for **I** and **II** are summarized in Table 1. Selected bond lengths and angles are shown in Table 2.

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Table 1. Crystallographic Data for **I** and **II**

Compound	**I**	**II**
Formula	$C_{48}N_3O_{18}W_3$	$C_{32}H_{72}N_2O_{11}W_2$
formula weight	1458.06	1028.63
crystal system	*C*2/*c* (No. 15)	*P*2$_1$/*c* (No. 14)
space group	monoclinic	monoclinic
a (Å)	34.5727(3)	10.51870(10)
b (Å)	14.2882(2)	32.8781(4)
c (Å)	30.4695(4)	11.73850(10)
α (deg)	90.0000	90.0000
β (deg)	121.6560(10)	92.7546(7)
γ (deg)	90.0000	90.0000
V (Å^3)	12 811.9(3)	4054.89(7)
Z	8	4
d_{calcd} (g·cm^{-3})	1.512	1.685
μ (cm^{-1})	54.32	57.29
no. of parameters refined	429	425
R	0.062 (for 11 478)[a]	0.0410 (for 10 804 data)[a]
wR	0.211 (for all 17 216 data)	0.164 (for all 11 002 data)

[a] For data with $I > 2.0\sigma(I)$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **I** and **II**

	$[\{WO(O_2)_2\}_2(\mu\text{-}O_2)]^{2-}$ (**I**)		
W1−O1	1.711(6)	W1−O5′	2.432(6)
W1−O2	1.936(7)	O2−O3	1.474(12)
W1−O3	1.928(6)	O4−O5	1.460(8)
W1−O4	1.912(6)	O6−O6′	1.484(15)
W1−O5	1.980(6)	W1−W1′	3.3985(4)
W1−O6	1.977(7)	W1−O6-O6′−W1′	51.3(7)
	$[\{WO(O_2)_2\}_2(\mu\text{-}O)]^{2-}$ (**II**)		
W1−O1	1.711(5)	W1−O11	1.950(4)
W1−O2	1.940(5)	W2−O11	1.943(4)
W1−O3	1.940(4)	W1−O10	2.578(4)
W1−O4	1.946(5)	W2−O5	2.645(5)
W1−O5	1.964(5)	O2−O3	1.504(7)
W2−O6	1.709(5)	O4−O5	1.504(6)
W2−O7	1.928(5)	O7−O8	1.483(8)
W2−O8	1.945(5)	O9−O10	1.515(6)
W2−O9	1.912(5)	W1−W2	3.065(4)
W2−O10	2.002(4)	W1−O11−W2	105.4(2)

Results and Discussion

A crystal of **I** that was suitable for the X-ray structural analysis was obtained by the vapor diffusion of diethyl ether into a CH_3CN solution of **II** and H_2O_2 at 277 K. The anion part of **I** consisted of a μ-η^1:η^1-O_2^{2-} bridging group and two neutral $\{W(=O)(O_2)_2\}$ units, in which seven oxygen atoms were coordinated to the tungsten atom in a distorted pentagonal bipyramidal arrangement (Figure 1a). Although several molecular structures of the (μ-η^1:η^1-peroxo)dimetal complexes for Co,[1a] Mn,[4a] Fe,[4b−4e] Ge,[4f] Rh,[4g] Cu,[4h] Ir,[4i] Pt,[4j−4l] Pd,[4m] and Sn[4n] have been reported, nothing is known of the (μ-η^1:η^1-peroxo)d^0-dimetal complexes. Therefore, **I** is the first structurally determined (μ-η^1:η^1-peroxo)d^0-dimetal complex; the existence of **II** has been proposed[10] and the dinuclear d^0-transition metal complexes containing μ-η^1:η^2-peroxo, μ-η^2:η^2-peroxo, and μ-hydroperoxo groups have been reported.[7−9] There were three kinds of peroxo ligands in **I**: η^2-peroxo (O2−O3), μ-η^1:η^2-peroxo (O4−O5), and μ-η^1:η^1-peroxo (O6−O6′). The O−O bond lengths (1.460−1.484 Å) are typical for peroxo ligands and comparable to those for previously reported peroxotungstates.[1−10] The W1−O6 (1.977 Å) bond length was typical for those of peroxotungstates and there was no significant difference among the W−O(peroxo) distances in **I**.

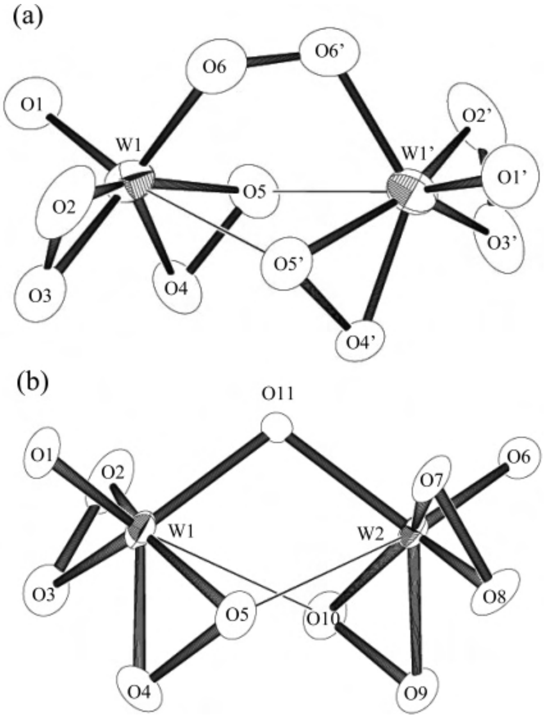


Figure 1. ORTEP drawings of the anion part of (a) **I** and (b) **II** drawn at the 50% probability level.

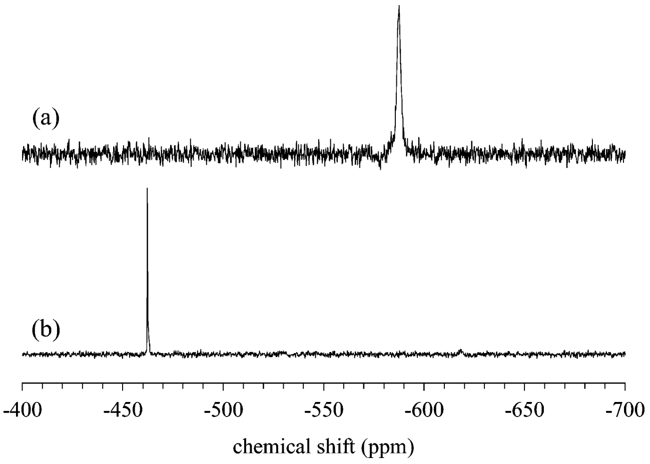
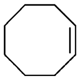
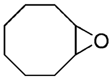
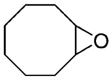
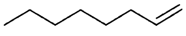
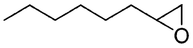
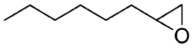
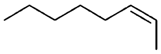
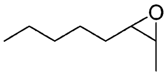
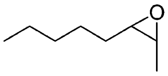
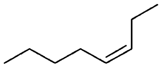
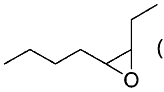
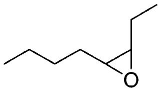
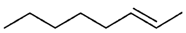
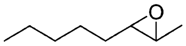
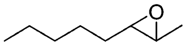
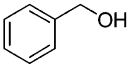
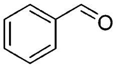
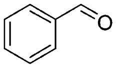
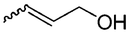
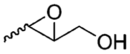
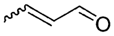
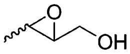
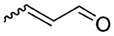
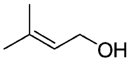
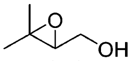
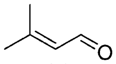
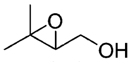
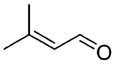
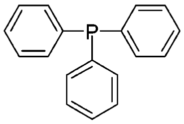
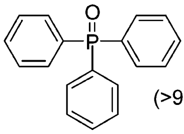
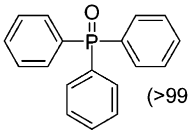


Figure 2. A ^{183}W NMR spectra of (a) **II** and (b) **II** with the addition of 4 equiv of H_2O_2 (96% aqueous solution) with respect to **II**. Conditions include CD_3CN as the solvent, a temperature of 263 K, and a 0.39 M concentration of **II**.

The dinuclear peroxotungstate of **II** was synthesized by the recrystallization of the precipitate obtained from the mixture of tungstic acid, H_2O_2, and TBA·Cl. The X-ray structural analysis of **II** revealed that two aquo ligands of a well-known dinuclear peroxotungstate, $[\{WO(O_2)_2(H_2O)\}_2(\mu\text{-}O)]^{2-}$,[9a] were eliminated as shown in Figure 1b. To the best of our knowledge, **II** is also the first structurally characterized dinuclear species.

The ^{183}W NMR spectrum of **II** in CD_3CN showed one signal at −587.5 ppm ($\Delta\nu_{1/2}$ = 24.3 Hz), which suggests that **II** is a single species (Figure 2a). Upon addition of 4 equiv of H_2O_2 with respect to **II**, one new ^{183}W NMR signal at −462.4 ppm ($\Delta\nu_{1/2}$ = 3.8 Hz) was observed, which is in

Table 3. Reactivities of **I** and **II** for Stoichiometric Oxidation Reactions with Organic Molecules[a]

Entry	Substrate	Time (h)	I		II	
			Yield (%)	Product (Selectivity (%))	Yield (%)	Product (Selectivity (%))
1		42	97	 (>99)	2	 (99)
2[b]		67	91	 (99)	<1	 (99)
3		45	100	 (>99)	2	 (>99)
4		45	94	 (>99)	1	 (>99)
5[c]		75	93	 (>99)	<1	 (>99)
6		<0.2	500	 (>99)	400	 (>99)
7		78	490	 (68)  (32)	390	 (65)  (35)
8		1	500	 (95)  (5)	400	 (98)  (2)
9[d]		<0.2	490	 (>99)	400	 (>99)

[a] Reaction conditions: **I** or **II** (25 μmol), substrate (1 mmol), CH_3CN (2 mL), reaction temperature (273 K). Yield and selectivity were determined by GC (entries 1−6), ^1H NMR (entries 7 and 8), and HPLC (entry 9). Yield (%) = products (mol)/**I** or **II** used (mol) × 100. [b] Substrate (2 mmol), CH_3CN (1 mL). [c] **I** or **II** (50 μmol), substrate (2 mmol), CH_3CN (1 mL). [d] Reaction conditions: **I** or **II** (10 μmol), triphenylphosphine (100 μmol), CH_3CN (2 mL), reaction temperature (273 K).

agreement with the C_2 symmetry of **I** (Figure 2b). The reaction of **II** with concentrated H_2O_2 in CH_3CN facilitated the formation of **I**. On the other hand, the ^{183}W NMR spectrum of $K_2[\{WO(O_2)_2(H_2O)\}_2(\mu\text{-}O)]\cdot 2H_2O$ in D_2O was not changed by the addition of H_2O_2, thus showing that **I** is hardly generated in water.

The reactivities of **I** and **II** for the stoichiometric oxidation reactions with organic molecules were investigated (Table 3). The stoichiometric epoxidation of cyclic, internal, and terminal olefins of cyclo-, *cis*-2-, *cis*-3-, *trans*-2-, and 1-octenes with **I** produced the corresponding epoxides in 97, 100, 94, 93, and 91% yields, respectively (entries 1−5). This suggests that **I** has 1 equiv of active oxygen species for the epoxidation. On the other hand, the stoichiometric epoxidation with **II** hardly proceeded. Triphenylphosphine oxide, benzaldehyde, and epoxy alcohols were produced in 490−500% and 390−400% yields by the reactions of triphenylphosphine, benzyl alcohol, and allylic alcohols with **I** and **II**, respectively (entries 6−9).

The rate of the *stoichiometric* epoxidation of cyclooctene (470 mM) with **I** (12 mM) at 273 K was 8.3 × 10^{-2} mM·min^{-1} and agreed fairly well with that (7.3 × 10^{-2} mM·min^{-1}) of the *catalytic* epoxidation of cyclooctene (470 mM) with H_2O_2 (47 mM) at 273 K by **II** (12 mM). The kinetic studies for the epoxidation of cyclooctene with H_2O_2 catalyzed by **II** showed the first-order dependencies of the reaction rates on the concentrations of **II**, cyclooctene, and H_2O_2 (Figure 3). IR, Raman, and UV−vis spectra of the complex recovered after the stoichiometric epoxidation of cyclooctene with **I** were the same as those of **II** (Figures S1, S2, and S3, Supporting Information). The rate of the regeneration of **I** by the reaction of **II** with H_2O_2 at 273 K was estimated by using UV−vis spectroscopy. The UV−vis spectrum obtained by the subtraction of the spectrum of **II** from that of **I** showed an absorption band at 247 nm (Figure S3, Supporting Information). It has been reported that the peroxotungstates show the characteristic absorption band around 250 nm.[23] The 247 nm absorption band disappeared after the stoichiometric epoxidation of cyclooctene with **I**. Therefore, the 247 nm absorption band is assignable to the peroxotungstate of **I**. The absorbance at 247 nm increased by the reaction of **II** with H_2O_2 (Figure 4). By using the changes in the intensities of the 247 nm

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(23) Aubry, C.; Chottard, G.; Platzer, N.; Brégeault, J.-M.; Thouvenot, R.; Chauveau, F.; Huet, C.; Ledon, H. *Inorg. Chem.* **1991**, *30*, 4409.

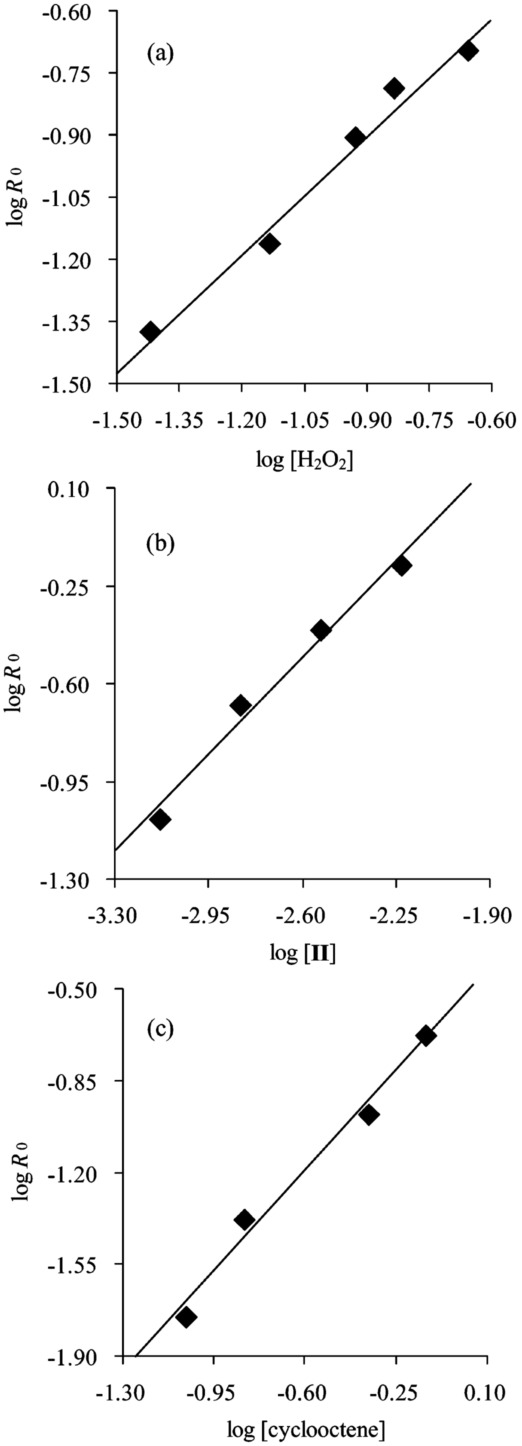


Figure 3. Dependences of the reaction rates on the concentrations of (a) H_2O_2, (b) **II**, and (c) cyclooctene: (a) cyclooctene (0.74 M), **II** (1.47 mM), H_2O_2 (0.04−0.22 M), H_2O (0.98 M), CH_3CN (6 mL), 305 K; (b) cyclooctene (0.737 M), **II** (0.74−5.90 mM), H_2O_2 (0.22 M), H_2O (0.98 M), CH_3CN (6 mL), 305 K; (c) cyclooctene (0.09−0.74 M), **II** (1.47 mM), H_2O_2 (0.22 M), H_2O (0.98 M), CH_3CN (6 mL), 305 K. R_0 (mM·min^{-1}) values were determined from the reaction profiles at low conversions (<10%) of both cyclooctene and H_2O_2. (a) Slope = 0.94 (R^2 = 0.98). (b) Slope = 0.99 (R^2 = 0.98). (c) Slope = 1.10 (R^2 = 0.98).

band, the rate of the regeneration of **I** by the reaction of **II** with H_2O_2 at 273 K was estimated to be more than 4.7 mM·min^{-1} (Figure 4 inset), which is much faster than that of the reaction of **I** and cyclooctene at 273 K. All of these

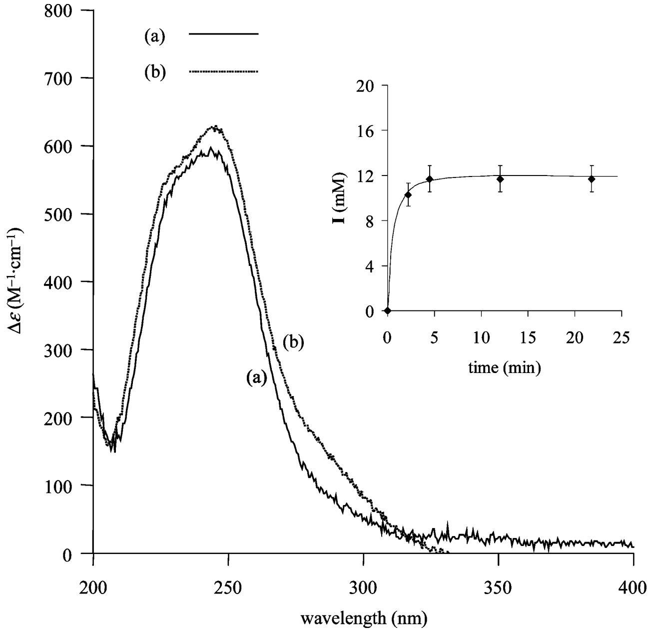


Figure 4. UV−vis spectra obtained by (a) the addition of the spectrum of (d) in Figure S3 (Supporting Information) to that of H_2O_2 (35 mM) and (b) the subtraction of the spectrum of **II** (12 mM) from that of **II** (12 mM) with the addition of H_2O_2 (47 mM) after 4.5 min. Inset: A time course of the concentration of **I** estimated by the absorbance of the reaction solution and the absorption coefficients at 247 nm of **I**, **II**, and H_2O_2.

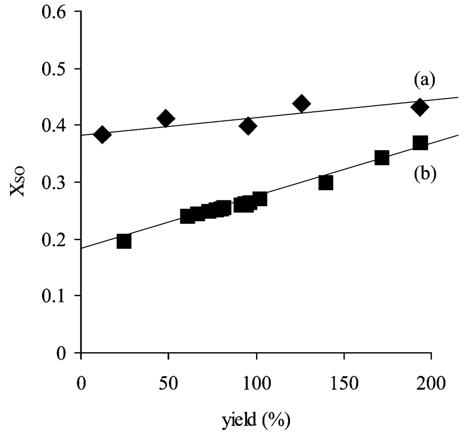
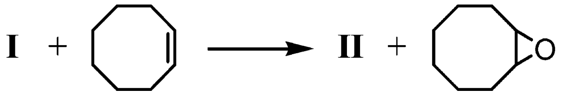


Figure 5. Plots of X_{SO} values against yields for the stoichiometric oxidation of SSO with (a) **II** and (b) **I**. Yield and selectivity were determined by HPLC. Reaction conditions: **I** or **II** (10 μmol), SSO (200 μmol), acetonitrile (5 mL), reaction temperature (273 K). Yield (%) = (SOSO (mol) + SSO_2 (mol) + 2 × $SOSO_2$ (mol))/(**I** or **II** used (mol)) × 100. X_{SO} = (SSO_2 (mol) + $SOSO_2$ (mol))/(SOSO (mol) + SSO_2 (mol) + 2 × $SOSO_2$ (mol)).

results show that the reaction of cyclooctene with **I** (eq 1) is the rate-determining step.



(1)

The electronic characteristics of the active oxygen species of **I** and **II** were examined by using SSO.[24] The X_{SO} values changed slightly as the yields increased (Figure 5). Therefore, the X_{SO} values were determined at low yields (<25%) in order to estimate the true electronic nature of the active

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(24) (a) Adam, W.; Golsch, D. *Chem. Ber.* **1994**, *127*, 1111. (b) Adam, W.; Golsch, D. *J. Org. Chem.* **1997**, *62*, 115.

oxygen species of **I** and **II**. The X_{SO} value for the stoichiometric oxidation of SSO with **I** (0.18 ± 0.02) was lower than that of **II** (0.39 ± 0.01), which suggests that the active oxygen species of **I** is more electrophilic than that of **II**.

Conclusions

In summary, the novel dinuclear peroxotungstate of **I** containing a μ-η^1:η^1-peroxo group was synthesized by the reaction of the dinuclear species (**II)** with H_2O_2 and fully characterized by X-ray crystallography. The stoichiometric epoxidation of olefins with **I** gave quantitative amounts of the corresponding epoxides and **II**. Compound **I** could easily be regenerated by the reaction of **II** with H_2O_2. The catalytic epoxidation proceeded by the reaction of **I** with an olefin to form **II.** The corresponding epoxide followed the regeneration of **I** by the reaction of **II** with H_2O_2.

Acknowledgment. We thank Dr. K. Yamaguchi and Dr. Y. Nakagawa of The University of Tokyo for their helpful discussions. This work was supported by the Core Research for Evolutional Science and Technology (CREST) program of the Japan Science and Technology Agency (JST), the Development in a New Interdisciplinary Field Based on Nanotechnology and Materials Science programs, and a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Science, Sports, and Technology of Japan.

Supporting Information Available: X-ray crystallographic files of **I** and **II** and Figures S1−S4. This material is available free of charge via the Internet at http://pubs.acs.org.

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