Inorg. Chem. **2006**, *45*, 2347−2356

Inorganic Chemistry

Article

Synthesis, Structural Characterization, and Catalytic Performance of Dititanium-Substituted γ-Keggin Silicotungstate

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Received December 23, 2005

A novel titanium-substituted silicotungstate cluster of $[\{\gamma\text{-SiTi}_2W_{10}O_{36}(OH)_2\}_2(\mu\text{-O})_2]^{8-}$ (**1**) is synthesized by the introduction of titanium(IV) ions into a divacant lacunary γ-Keggin-type silicotungstate of $[\gamma\text{-SiW}_{10}O_{36}]^{8-}$. This titanium-substituted polyoxometalate, **1**, exhibits a dimeric structure. One half of the γ-Keggin fragment of **1** contains a dinuclear titanium center bridged by two hydroxo groups, and the resulting $Ti_2(\mu\text{-OH})2$ core connects to the other $Ti_2(\mu\text{-OH})_2$ core of the paired γ-Keggin subunit through Ti–O–Ti linkages. The $Ti_2(\mu\text{-OH})_2$ core of **1** reacts with MeOH to form the corresponding alkoxo derivative, $[\{\gamma\text{-SiTi}_2W_{10}O_{36}(OH)(OMe)\}_2(\mu\text{-O})_2]^{8-}$ (**2**). Two of four hydroxo groups of the $Ti_2(\mu\text{-OH})_2$ cores in **1** are replaced by methoxo groups to give the $Ti_2(\mu\text{-OH})(\mu\text{-OMe})$ core, and the Ti–O–Ti linkages connecting two γ-Keggin subunits are maintained in **2**. The γ-Keggin dititanium-substituted silicotungstate **1** catalyzes mono-oxygenation reactions, such as the epoxidation of olefins and sulfoxidation of sulfides with hydrogen peroxide under mild conditions, while the monotitanium-substituted silicotungstate, $[\alpha\text{-SiTiW}_{11}O_{39}]^{4-}$ (**3**), and the fully occupied silicododecatungstate, $[\gamma\text{-SiW}_{12}O_{40}]^{4-}$, are inactive. The epoxidation with **1** is stereospecific; the configurations around the C═C double bonds of the *cis*- and *trans*-olefins are completely retained in the corresponding epoxides. For the competitive epoxidation of *cis*- and *trans*-2-octenes, the ratio of the formation rate of *cis*-2,3-epoxyoctane to that of the trans isomer (R_{cis}/R_{trans}) is relatively high (21.3) in comparison with those observed for the tungstate catalysts, including $[\gamma\text{-SiW}_{10}O_{34}(H_2O)_2]^{4-}$. The epoxidation of 3-methyl-1-cyclohexene is highly diastereoselective and gives the corresponding epoxide with an anti configuration. The molecular structure of **1** is preserved during the catalysis because the ^{29}Si and ^{183}W NMR spectra of the catalyst recovered after completion of the oxidation are consistent with those of as-prepared compound **1**. All these facts suggest the contribution of rigid nonradical oxidants generated on the multinuclear titanium center of **1**.

Introduction

Metal−oxygen cluster molecules, polyoxometalates (POMs) are attractive compounds for a wide range of chemistry including fundamental coordination chemistry and applied chemistry in catalysis, medicine, and material science because of the controllability of the molecular properties (composition, size, shape, acidity, and redox potential).[1] Recently, the interest in the catalysis of partially metal-substituted heteropolyoxometalates (metal-substituted POMs), which are synthesized by the introduction of substituent metal ions into the vacant site of lacunary POMs, has been growing because of the unique reactivity depending on the composition and structure of the molecules. Dimetal-substituted γ-Keggin

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10.1021/ic052179q CCC: $33.50

POMs containing an edge-shared dinucler $M_2(\mu\text{-}O)_2$ site, $H_x[\gamma\text{-}SiM_2W_{10}O_{40}]^{n-}$ (where M = Mn, Fe, V), exhibit remarkable catalytic activities for hydrocarbon oxidations with *green oxidants* such as hydrogen peroxide and molecular oxygen.[2] These dimetal-substituted POMs are synthesized by the reaction of a divacant silicodecatungstate, $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ (**SiW10**),[3–5] with an appropriate metal source. In some cases, however, the reaction of **SiW10** with first-row transition metal species results in the reorganization of cluster frameworks giving some unexpected compounds.[6] Therefore, the selective syntheses of dimetal-substituted γ-Keggin clusters of various metal derivatives, as well as the studies on their chemical properties including catalytic activities, are still attractive subjects.

Titanium is recognized to be an active element of an oxidation catalyst in both heterogeneous and homogeneous reaction systems. For example, a family of titanosilicates is extensively applied to various oxidation reactions including olefin epoxidation.[7,8] It is proposed that the tetrahedral Ti^{IV} center efficiently activates hydrogen peroxide, although the details of the reaction mechanism, as well as the relationship between the structure of the active site and reactivity, have been unclear so far. Titanium-containing POMs are attractive compounds because of the structural diversity of Ti centers. Several titanium-substituted phosphotungstates, $[PTi_xW_{12-x}O_{40}]^{(3+2x)-}$ ($x = 1, 2$), and their peroxo derivatives are known to catalyze olefin epoxidation.[9] The structures of the Ti centers can be regarded as mononuclear sites (i.e., two titanium ions do not adjacently locate in $[PTi_2W_{10}O_{40}]^{7-}$). Recently, the tetrameric Ti-containing silicotungstate composed of β-Keggin subunits, $[\{\beta\text{-}SiTi_2W_{10}O_{39}\}_4]^{24-}$, has been synthesized from **SiW10**. The molecular structure of this compound is revealed by the single-crystal X-ray analysis, while its catalytic activity has not been reported so far.[10] In this context, the catalysis by various titanium-containing POMs, which are composed of multinuclear Ti sites and the other heteroatoms, should be investigated to reveal the structure-dependent reactivity.

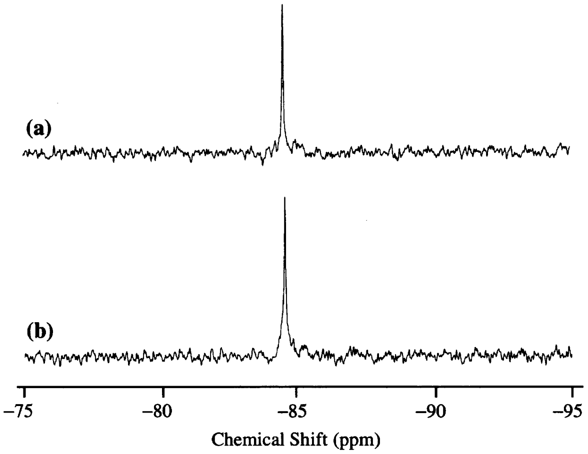

Figure 1. ^{29}Si NMR spectra of (a) as prepared TBA·**1** and (b) TBA·**1** recovered after the use for the epoxidation of cyclooctene. After the completion of the epoxidation, the volume of the reaction mixture was reduced by evaporation. Ether was added to the concentrated solution, and the catalyst precipitated was recovered by the filtration.

In this study, we have synthesized a novel dititanium-substituted γ-Keggin POM, $[\{\gamma\text{-}SiTi_2W_{10}O_{36}(OH)_2\}_2(\mu\text{-}O)_2]^{8-}$ (**1**), containing an edge-shared dinuclear Ti site, and its molecular structure has been successfully determined. The dinuclear titanium core of **1** catalyzes mono-oxygenation reactions, such as epoxidation of olefins and sulfoxidation of sulfides with hydrogen peroxide, as we report herein.

Results and Discussion

Synthesis and Structural Characterization of the Dimer of Silicodititanodecatungstate. The reaction of the potassium salt of **SiW10** with 2 equiv of $Ti(O)(SO_4)$ in acidic aqueous solution at ambient temperature and the successive addition of tetra-*n*-butylammoniumbromide (TBABr) yielded the corresponding tetra-*n*-butylammonium derivative (TBA·**1**) of a desired titanium-substituted silicotungstate. The elemental analysis data indicated the Si/Ti/W ratio was 1:2:10 in TBA·**1**. One ^{29}Si NMR signal was observed at −84.2 ppm (Figure 1a), and the ^{183}W NMR spectrum of TBA·**1** showed three signals at −106.1, −114.0, and −131.7 ppm with an intensity ratio of 1:2:2 (Figure 2a). This structural symmetry of tungsten atoms suggests that the cluster framework of **1** maintains the γ-Keggin structure. The positive ion CSI-MS (cold spray ionization mass spectrometry) spectrum of the MeCN solution of TBA·**1** exhibited a

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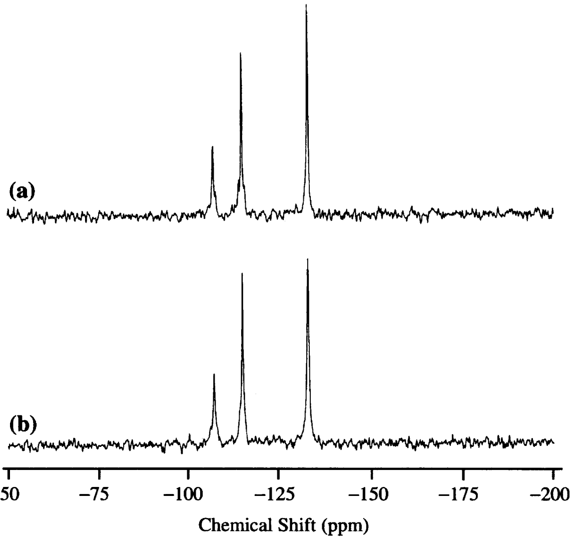


Figure 2. ^{183}W NMR spectra of (a) as prepared TBA·**1** and (b) TBA·**1** recovered after the use for the epoxidation of cyclooctene. After the completion of the epoxidation, the volume of the reaction mixture was reduced by evaporation. Ether was added to the concentrated solution, and the catalyst precipitated was recovered by filtration.

+1-charged ion peak at *m*/*z* 7358 attributed to $\{((C_4H_9)_4N)_9[H_4Si_2Ti_4W_{20}O_{78}]\}^+$ and a +2-charged peak at *m*/*z* 3801 attributed to $\{((C_4H_9)_4N)_{10}[H_4Si_2Ti_4W_{20}O_{78}]\}^{2+}$(Figure S1). Therefore, **1** could be assigned as the dimer of the dititanium-substituted γ-Keggin silicotungstate.

The potassium crown ether clathrate ([K(18-crown-6)]$^+$, CEK) salt derivative of **1** (CEK·**1**) was also synthesized by addition of 18-crown-6 instead of TBABr to the aqueous reaction mixture of **SiW10** with 2 equiv of Ti(O)(SO$_4$). Both TBA and CEK salts were soluble in polar organic solvents, and single crystals of TBA·**1** and CEK·**1** suitable for X-ray analysis were obtained successfully from MeCN/H$_2$O and DMSO, respectively (Table 1). The structural properties of the anion parts (**1**, Figure 3) in both crystals were essentially identical (Table 2).

An edge-shared dinuclear titanium core, $Ti_2(\mu\text{-}O)_2$, was incorporated into the lacunary site of **SiW10**, and the resulting titanium-substituted γ-Keggin POM fragments, $[SiTi_2W_{10}O_{38}]^{4-}$, were dimerized through oxo ligands giving Ti−O−Ti linkages. In other words, a cationic tetranuclear titanium center, Ti_4O_6, was supported by two lacunary γ-Keggin **SiW10** anions. The existence of eight countercations per dimeric cluster molecule implies that the charge of **1** is −8. The bond valence sum values of titanium (3.43−4.55), tungsten (5.68−6.49), and silicon (3.76−3.90) indicate that silicotitanotungstate cluster **1** is composed of Ti(IV), W(VI), and Si(IV) ions. Therefore, four protons are associ-

Table 1. Crystallographic Data for TBA·**1**, CEK·**1**, and CEK·**2**[a]

compound	TBA·**1**·0.5MeCN	CEK·**1**·2DMSO	CEK·**2**
formula	$C_{258}H_{579}O_{156}N_{17}Si_4Ti_8W_{40}$	$C_{100}H_{212}K_8O_{128}S_2Si_2Ti_4W_{20}$	$C_{98}H_{200}K_8O_{126}Si_2Ti_4W_{20}$
fw	14265.94	7764.38	7632.14
cryst syst	*Pna*2$_1$ (No. 33)	*Fddd* (No. 70)	*C*2/*m* (No. 12)
space group	orthorhombic	orthorhombic	monoclinic
a (Å)	29.1660(3)	33.2107(3)	45.4319(7)
b (Å)	38.4971(4)	35.4445(4)	17.8884(4)
c (Å)	37.4046(3)	85.0187(8)	15.8179(3)
α (deg)	90.0000	90.0000	90.0000
β (deg)	90.0000	90.0000	96.3280(8)
γ (deg)	90.0000	90.0000	90.0000
V (Å^3)	41998.1(7)	100078.6(17)	12776.9(4)
Z	4	16	2
d_{calcd} (g cm^{-3})	2.244	2.061	2.036
μ (cm^{-1})	11.132	9.523	9.306
no. of params refined	1166	696	301
R1	0.0444 (for 25900 data)[b]	0.0546 (for 18443 data)[c]	0.0602 (for 9127 data)[c]
wR2[a]	0.1266 (for all 30698 data)	0.0538 (for all 29407 data)	0.0783 (for all 15078 data)

[a] The program packages used for the refinement were SHELXH-97 for TBA·**1** and CrystalStructure for CEK·**1**, and CEK·**2**. [b] For data with $F_0 > 4\sigma(F_0)$. [c] For data with $I > 2\sigma(I)$.

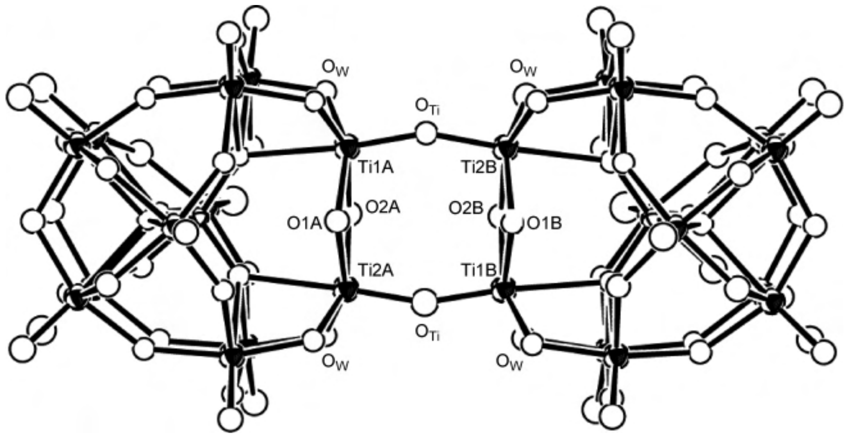


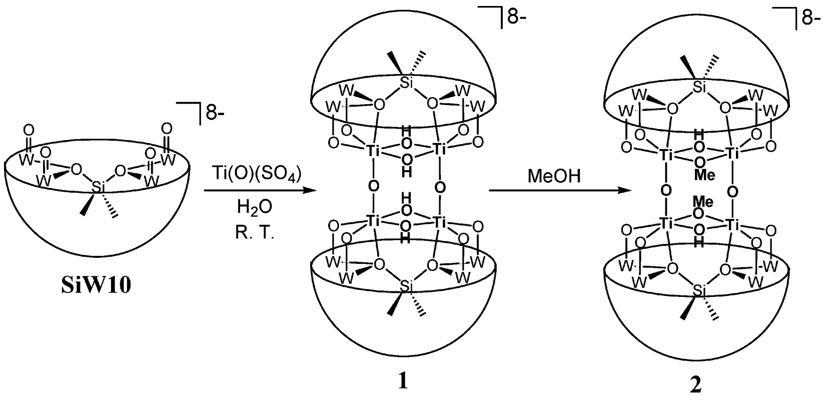
Figure 3. ORTEP drawing of $[\{\gamma\text{-}SiTi_2W_{10}O_{36}(OH)_2\}_2(\mu\text{-}O)_2]^{8-}$ (**1**, TBA derivative) drawn at 30% probability level.

Table 2. Selected Structural Parameters for the Anions **1** and **2** (lengths in Å and angles in deg)

	TBA·**1**[a]			
compound	molecule A	molecule B	CEK·**1**[b]	CEK·**2**[b]
$Ti\cdots Ti_{intra}$	3.146(6), 3.140(11)	3.140(8), 3.151(8)	3.158(3)	3.176(5)
$Ti\cdots Ti_{inter}$	3.518(6), 3.502(6)	3.524(6), 3.523(7)	3.523(3)	3.544(5)
Ti−OR	1.964(17), 2.010(18)	2.009(16), 1.989(18)	1.974(9)	2.009(17)
	2.035(16), 2.000(15)	2.028(15), 1.989(16)	2.008(9)	2.009(19)
	1.969(18), 1.999(16)	2.043(18), 2.013(16)		
	2.035(16), 2.000(15)	1.991(18), 1.990(15)		
$Ti-O_{Ti}$	1.791(16), 1.78(2)	1.798(16), 1.771(18)	1.804(9), 1.807(9)	1.803(5)
	1.779(19), 1.795(16)	1.820(18), 1.788(16)		
$Ti-O_W$ av	1.875, 1.851	1.853, 1.902	1.866	1.869
$Ti-O_{Si}$ av	2.405, 2.369	2.360, 2.338	2.398	2.4151(2)
$W-O_{Si}$ av	2.332, 2.367	2.330, 2.332	2.345	2.348
$W{=}O_{av}$	1.714, 1.697	1.691, 1.694	1.712	1.699
$W-O_{Ti}$ av	1.814, 1.906	1.854, 1.892	1.887	1.884
$W-O_W$ av	1.964, 1.900	1.921, 1.992	1.910	1.923
$Si-O_{av}$	1.653, 1.654	1.623, 1.634	1.626	1.631
Ti−OR−Ti	106.3(8), 100.8(7)	102.1(7), 104.2(7)	106.2(4), 103.5(4)	104.5(12), 104.5(14)
	103.3(7), 103.5(7)	102.8(8), 103.9(7)		
Ti−O−Ti	157.6(10), 159.6(13)	158.7(10), 157.6(11)	154.7(5)	158.8(12)
O_R-Ti-O_R	77.1(7), 75.6(7)	76.9(6), 76.5(7)	75.1(3), 75.0(3)	75.5(9)
	77.3(6), 75.8(7)	75.8(7), 77.5(7)		
$O_{Ti}-Ti-O_R$	98.5(7), 101.9(8)	96.5(7), 99.3(7)	98.8(3), 101.3(3)	99.5(7), 99.6(7)
	97.6(9), 100.0(8)	100.3(7), 100.7(7)	98.8(3), 101.3(3)	
	98.0(8), 99.7(8)	97.6(8), 99.3(7)		
	98.0(7), 100.4(7)	97.8(7), 97.0(7)		
$O_{Ti}-Ti-O_W$	100.4(8), 103.6(7)	100.7(7), 104.3(8)	101.6(4), 101.2(4)	102.4(6), 101.1(6)
	100.8(8), 104.2(8)	102.6(8), 102.1(8)	102.3(4), 101.1(4)	
	101.4(8), 100.5(8)	99.3(7), 103.8(8)		
	102.0(7), 100.9(8)	100.3(8), 101.8(7)		
O_W-Ti-O_W	94.8(7), 96.7(7)	94.5(7), 94.8(7)	94.9(4), 95.1(4)	97.7(7)
	95.0(7), 96.0(8)	95.4(7), 94.9(8)		
O_R-Ti-O_W	90.9(7), 88.6(7)	91.6(7), 89.5(7)	92.1(4), 89.8(4)	89.5(8), 89.3(8)
	92.1(7), 87.6(7)	90.5(7), 89.0(6)		
	92.9(7), 87.9(7)	90.0(7), 91.9(7)		
	91.4(7), 89.2(7)	90.8(7), 90.7(7)		

[a] Molecule A and B are crystallographically independent molecules. [b] Sitting on a crystallographic mirror plane.

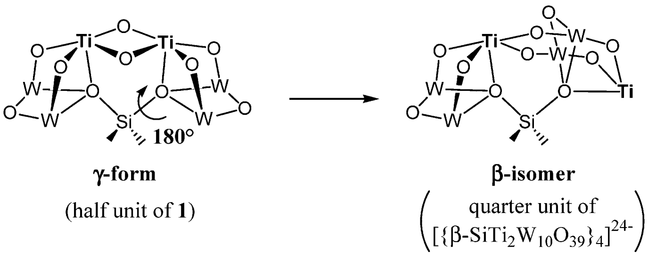
Scheme 1. Formation of **1** and **2**



ated with anionic cluster **1** on the basis of the charge balance. Interestingly, the bond valence sum values of O1 and O2 (1.09−1.34) were clearly lower than those of the other oxygen atoms in the Ti−O−Ti linkages (2.09−2.20). These observations suggest that these oxygen atoms in the edge-shared Ti_2O_2 moieties are protonated. The protonation of the oxo ligands at the edge-shared $Ti_2(\mu\text{-}O)_2$ moiety (i.e., $Ti_2(\mu\text{-}OH)_2$ core) is also suggested by the formation of an alkoxo derivative, **2**, $[\{\gamma\text{-}SiTi_2W_{10}O_{36}(OH)(OMe)\}_2(\mu\text{-}O)_2]^{8-}$ (see later section, Scheme 1). Therefore, the formulation of **1** can be described as $[\{\gamma\text{-}SiTi_2W_{10}O_{36}(OH)_2\}_2(\mu\text{-}O)_2]^{8-}$.

Recently, the tetrameric Ti-containing silicotungstate composed of β-Keggin subunits, $[\{\beta\text{-}SiTi_2W_{10}O_{39}\}_4]^{24-}$, in which two titanium ions separately locate in each β-Keggin fragment, has been synthesized from **SiW10** with a similar procedure to that presented herein except for the synthetic temperature. Kortz and co-workers have suggested that the γ-Keggin silicotitanotungstate component (i.e., half unit of **1**) is an initial intermediate and that the subsequent isomerization under relatively high temperature (353 K) in acidic aqueous solution gives the β-Keggin component of the tetrameric silicotitanotungstate (Scheme 2).[10] To date, several molecular structures of titanium-substituted POMs including the mono-, di-, and trisubstituted α- or β-isomers of Keggin titanotungstates $[XTi_yW_{12-y}O_{40}]^{n-}$ (X = P, Ge; y = 1, 2, 3) have been reported.[11−15] All of these Keggin POMs have

Scheme 2. Isomerization of Ti-containing Keggin POM from the γ-form (**1**) to the β-isomer



dimeric structures except for the monomeric ($[\alpha\text{-}1,5\text{-}PTi_2W_{10}O_{40}]^{7-}$ and $[\alpha\text{-}PTiW_{11}O_{40}]^{5-}$) and tetrameric ($[\{\beta\text{-}SiTi_2W_{10}O_{39}\}_4]^{24-}$) compounds. In contrast with the previously characterized compounds, **1** is the first structurally determined disubstituted γ-isomer of titanotungstate, while the molecular structure is dimeric.

Formation of Methoxo Derivative 2. The addition of an excess amount of MeOH to the MeCN solution of the TBA salt of **1** resulted in the formation of white precipitates of **2**. The ^{183}W NMR spectrum of the DMF solution of the collected white precipitates of **2** exhibited six signals at -102.2, -113.3, -123.8, -127.1, -131.3, and -136.0 ppm with intensities of 1:2:2:2:1:2, while the ^{29}Si NMR spectrum of the same solution showed one signal at -84.5 ppm (Figure S2). These observations suggested that the original C_{2v} symmetry of the γ-Keggin framework of **1** became C_s symmetry in **2**. The same change in the spectral pattern had been observed during the formation of $[\gamma\text{-}SiV_2W_{10}O_{38}(OH)(OMe)]^{4-}$.[16] The positive ion CSI-MS spectrum of the MeCN solution of **2** contained peaks attributed to an alkoxo derivative of **2** (i.e., $[\{\gamma\text{-}SiTi_2W_{10}O_{36}(OH)(OMe)\}_2(\mu\text{-}O)_2]^{8-}$): $\{TBA_9\cdot[\{\gamma\text{-}SiTi_2W_{10}O_{36}(OH)(OMe)\}_2(\mu\text{-}O)_2]\}^+$ (m/z 7387), $\{TBA_8\cdot H\cdot[\{\gamma\text{-}SiTi_2W_{10}O_{36}(OH)(OMe)\}_2(\mu\text{-}O)_2]\}^+$ (m/z 7145), $\{TBA_{10}\cdot[\{\gamma\text{-}SiTi_2W_{10}O_{36}(OH)(OMe)\}_2(\mu\text{-}O)_2]\}^{2+}$ (m/z 3815), and $\{TBA_9\cdot H\cdot[\{\gamma\text{-}SiTi_2W_{10}O_{36}(OH)(OMe)\}_2(\mu\text{-}O)_2]\}^{2+}$ (m/z 3699). Therefore, **2** could be assigned as the dimer of the monomethyl ester derivative of the γ-Keggin silicodititanodecatungstate, and its molecular structure was confirmed by X-ray crystallography of the $[K(18\text{-crown-}6)]^+$ salt derivative (see below).

The single crystal of the alkoxo derivative **2**, $[\{\gamma\text{-}SiTi_2W_{10}O_{36}(OH)(OMe)\}_2(\mu\text{-}O)_2]^{8-}$, was obtained by the recrystallization of CEK·**1** in the presence of MeOH. The overall molecular structure of **2** was similar to that of **1** except for the alkoxy-functionalized sites (Figure 4). The dimeric cluster framework was retained in **2**. The alkoxide groups played a role as the bridging ligands of the edge-shared dinuclear titanium sites, giving the $Ti_2(\mu\text{-}OMe)(\mu\text{-}OH)$ core in each γ-Keggin fragment. The Ti−O−Ti linkages connecting two γ-Keggin subunits were unchanged. The amount of MeOH reacted with **1** was two times larger than that of **1**, supporting the low reactivity of the Ti−O−Ti linkages.

An acid/base titration of TBA·**1** with tetrabutylammoniumhydroxide (TBAOH) in MeCN exhibited a breakpoint at 2 equiv with respect to **1**. This fact suggests that (1) two of the four OH moieties in **1** exhibit Brønsted acidity or that (2) the Lewis acidic Ti centers react with OH^-, resulting in the fission of **1** to form the corresponding monomeric γ-Keggin compounds. The former case (i.e., Brønsted acidity of two OH ligands) is consistent with the formation of **2**; the remaining OH^- ligands are basic enough to react with MeOH, and **2** is formed. Recently, we also revealed that the reaction of the dinuclear $V_2(\mu\text{-}OH)_2$ core of the divanadium-substituted γ-Keggin silicotungstate, $[\gamma\text{-}SiV_2W_{10}O_{38}(OH)_2]^{4-}$, with MeOH yields the corresponding monomethyl ester containing a dinuclear vanadium-μ-hydroxo-μ-alkoxo core, $[\gamma\text{-}SiV_2W_{10}O_{38}(OH)(OMe)]^{4-}$.[16]

Synthesis of Silicotitanoundecatungstate. A monotitanium-substituted Keggin-type silicotungstate, $[\alpha\text{-}H_2SiTiW_{11}O_{40}]^{4-}$ (**3**), was synthesized. Compound **3** was obtained by a method similar to that for the synthesis of the tetra-n-butylammonium salt of phosphotitanoundecatungstate $[\alpha\text{-}PTiW_{11}O_{40}]^{5-}$.[14a] The reaction of the TBA salt of the monovacant α-Keggin-type silicoundecatungstate, $[\alpha\text{-}SiW_{11}O_{39}]^{8-}$, with $TiCl_4$ in MeCN and the successive addition of water yielded the desired compound, **3**, as a white precipitate. The ^{183}W NMR spectrum of a DMSO solution of **3** exhibited six signals with an intensity ratio of 1:2:2:2:2:2, suggesting that **3** has C_s symmetry with the α-Keggin-type undecatungstate. The CSI-MS spectrum of the MeCN/DMSO solution of **3** showed peaks attributed to monotitanium-substituted silicotungstate species $[TBA_5\cdot(SiTiW_{11}O_{39})]^+$ (m/z 3934), $[TBA_5\cdot(SiTiW_{11}O_{39})\cdot MeCN]^+$ (m/z 3975), and $[TBA_5\cdot(SiTiW_{11}O_{39})\cdot DMSO]^+$ (m/z 4015). Our attempts to synthesize analytically pure **3** were not successful with different synthetic routes: the reaction of $K_8[\alpha\text{-}SiW_{11}O_{39}]$ with titanium(IV) compounds such as $Ti(O)(SO_4)$ and $Ti(SO_4)_2$ in water resulted in the formation of non-titanium-containing silicododecatungstate, $[SiW_{12}O_{40}]^{4-}$.

Mono-oxygenation of Olefins and Sulfides Catalyzed by 1. First, the epoxidation of cyclooctene was carried out with TBA salts of di- and monotitanium-substituted silicotungstates **1**, **2**, and **3** and the TBA salt of the fully occupied

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[11] Dititanium-substituted Keggin compound: Nomiya, K.; Takahashi, M.; Widegren, J. A.; Aizawa, T.; Sakai, Y.; Kasuga, N. C. *J. Chem. Soc., Dalton Trans.* **2002**, 3679.

[12] Trititanium-substituted Keggin compounds: (a) Lin, Y.; Weakley, T. J. R.; Rapko, B.; Finke, R. G. *Inorg. Chem.* **1993**, *32*, 5095. (b) Yamase, T.; Ozeki, T.; Sakamoto, H.; Nishiya, S.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 103. (c) Nomiya, K.; Takahashi, M.; Ohsawa, K.; Widegren, J. A. *J. Chem. Soc., Dalton Trans.* **2001**, 2872.

[13] Monosubstituted Keggin compound with dimeric structure: Kholdeeva, O. A.; Maksimov, G. M.; Maksimovskaya, R. I.; Kovaleva, L. A.; Fedotov, M. A.; Grigoriev, V. A.; Hill, C. L. *Inorg. Chem.* **2000**, *39*, 3828.

[14] Titanium-substituted Keggin compounds with monomeric structure: (a) Knoth, W. H.; Domaille, P. J.; Roe, D. C. *Inorg. Chem.* **1983**, *22*, 198. (b) Yamase, T.; Ozeki, T.; Motomura, S. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 1453. (c) Domaille, P. J.; Knoth, W. H. *Inorg. Chem.* **1983**, *22*, 818. (d) Ozeki, T.; Yamase, T. *Acta Crystallogr., Sect. C* **1991**, *47*, 693.

[15] Titanium-substituted Wells−Dawson compounds: (a) Kortz, U.; Hamzeh, S. S.; Nasser, N. A. *Chem.−Eur. J.* **2003**, *9*, 2945. (b) Sakai, Y.; Yoza, K.; Kato, C. N.; Nomiya, K. *Chem.−Eur. J.* **2003**, *9*, 4077. (c) Sakai, Y.; Yoza, K.; Kato, C. N.; Nomiya, K. *Dalton Trans.* **2003**, 3581. (d) Nomiya, K.; Arai, Y.; Shimizu, Y.; Takahashi, M.; Takayama, T.; Weiner, H.; Nagata, T.; Widegren, J. A.; Finke, R. G. *Inorg. Chim. Acta* **2000**, *300−302*, 285.

[16] Nakagawa, Y.; Uehara, K.; Mizuno, N. *Inorg. Chem.* **2005**, *44*, 14. (b) Nakagawa, Y.; Kamata, K.; Kotani, M.; Yamaguchi, K.; Mizuno, N. *Angew. Chem., Int. Ed.* **2005**, *44*, 5136. (c) Nakagawa, Y.; Uehara, K.; Mizuno, N. *Inorg. Chem.* **2005**, *44*, 9068.

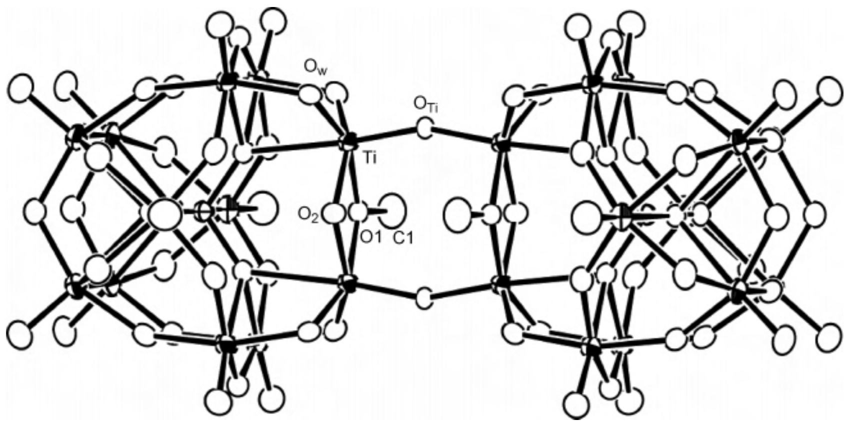

Figure 4. ORTEP drawing of $[\{\gamma\text{-SiTi}_2\text{W}_{10}\text{O}_{36}(\text{OH})(\text{OMe})\}_2(\mu\text{-O})_2]^{8-}$ (**2**, CEK derivative) drawn at 30% probability level.

Table 3. Epoxidation of Cyclooctene with H_2O_2[a]

entry	catalyst	solvent	yield (%)	select (%)
1	TBA·**1**	acetonitrile	98	>99
2	TBA·**2**	acetonitrile	26	>99
3	TBA·**3**	acetonitrile	3	>99
4[b]	$[\gamma\text{-SiW}_{12}\text{O}_{4}0]^{4-}$	acetonitrile	<1	–
5	none	acetonitrile	<1	–
6	TBA·**1**	1,2-dichloroethane	54	>99
7	TBA·**1**	acetone	44	>99
8	TBA·**1**	*N*,*N*-dimethylformamide	2	>99
9[c]	TBA·**1**	acetonitrile	40	>99

[a] Reaction conditions: catalyst (4 μmol), cyclooctene (5 mmol), H_2O_2 (30% aq, 1 mmol), solvent (6 mL), 323 K, 3 h. Yields were determined by GC using an internal standard technique. Yield (%) = cyclooctene oxide (mol)/initial H_2O_2 (mol) × 100. [b] TBA salt of $[\gamma\text{-SiW}_{12}\text{O}_{40}]^{4-}$ was used. [c] Methanol (0.1 mL) was added.

γ-Keggin silicododecatungstate, $[\gamma\text{-SiW}_{12}\text{O}_{40}]^{4-}$ (Table 3). Compound TBA·**1** showed high catalytic activity, and cyclooctene oxide was obtained in a 98% yield (entry 1). The epoxidation did not proceed at all in the absence of the catalyst (entry 5). The monotitanium-substituted compound **3** and nonsubstituted compound $[\gamma\text{-SiW}_{12}\text{O}_{40}]^{4-}$ were inactive under the present conditions (entries 3 and 4). The catalytic activity of methanol monoester of **1** (TBA·**2**, 26% yield) was much lower than that of TBA·**1** (entry 2).

Next, the effects of solvents on the epoxidation of cyclooctene were examined. Among solvents tested, MeCN was the most effective solvent (98% yield, entry 1). In this case, no stoichiometric formation of acetamide to cyclooctene oxide was observed, showing that the present epoxidation does not proceed via a peroxycarboxyimidic acid intermediate formed by the reaction of MeCN and H_2O_2.[17] 1,2-Dichloroethane (54% yield, entry 6) and acetone (44%, entry 7) gave cyclooctene oxide in moderate yield, and *N*,*N*-dimethylformamide was a poor solvent (2%, entry 8). The epoxidation in MeCN was inhibited by the addition of a small amount of methanol (0.1 mL), and the yield of cyclooctene oxide decreased to 40% (entry 9).

Table 4 shows the results of the epoxidation of various olefins in MeCN catalyzed by TBA·**1**. In contrast to porous titanosilicate catalysts, **1** catalyzed the oxygenation of the relatively bulky disubstituted olefins, including cyclic compounds such as cyclooctene and 2-norbornene, with hydrogen peroxide (entries 1 and 2). In the case of a nonactivated aliphatic terminal olefin of 1-octene, the yield of the corresponding epoxide was very low (entry 7). Geraniol was regioselectively epoxidized at the electron-deficient allylic double bond with small amount of the corresponding aldehyde (entry 8).[18] For the epoxidation of *cis*- and *trans*-olefins, the configurations around the C═C double bonds were completely retained in the corresponding epoxides (entries 4−6). Moreover, the epoxidation rate and selectivity were not changed by the addition of free radical trap (e.g., 2,6-di-*tert*-butyl-4-methylphenol and hydroquinone). These results suggest that the free-radical intermediates are not involved in the present epoxidation.

The present system also catalyzed the sulfoxidation as shown in Table 4. Various kinds of sulfides were selectively mono-oxygenated to the corresponding sulfoxides with high selectivity (≥97%) and high efficiency of hydrogen peroxide utilization (≥83%).[19] Not only aryl sulfides but also alkyl sulfides could be converted to the corresponding sulfoxides in excellent yield (entries 14 and 15). In the sulfoxidation of aryl sulfides, the reaction rates were affected by the electronic variation due to the substituents on the aromatic rings: electron-donating substituents on aromatic rings accelerated the reaction rates, while electron-withdrawing ones retarded the rates (entries 9−13).[20] The electronic character of the active oxygen species was examined by the oxidation of thianthrene 5-oxide (SSO).[21] In the present

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(17) Payne, G. B.; Deming, P. H.; Williams, P. H. *J. Org. Chem.* **1961**, *26*, 651. (b) Payne, G. B. *Tetrahedron* **1962**, *18*, 763. (c) Ueno, S.; Yamaguchi, K.; Yoshida, K.; Ebitani, K.; Kaneda, K. *Chem. Commun.* **1998**, 295.

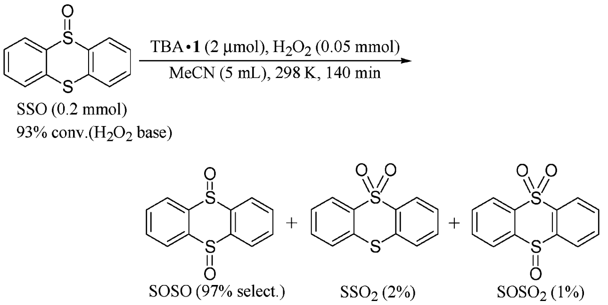
(18) It has been reported in the Ti-β/H_2O_2 system that an allylic alcohol interacts with the oxidant through hydrogen bonding of the hydroxyl group that prefers oxygen transfer to the 2,3-allylic double bond. See: Adam, W.; Corma, A.; Martínez, A.; Mitchell, C. M.; Reddy, T. I.; Renz, M.; Smerz, A. K. *J. Mol. Catal. A* **1997**, *117*, 357.

(19) It was confirmed that no reaction of aryl sulfides (e.g., 1-methoxy-4-(methylthio)benzene), as well as alkyl sulfides (e.g., methyl *n*-octyl sulfide), proceeded under the same conditions *without catalyst*.

(20) The fairly good linearity of the Hammett plots ($\log(k_X/k_H)$ vs σ plots, Figure S3) suggests that the present oxygenation proceeds via a single mechanism. The slope of the linear line gave a Hammett ρ value of −0.81. The negative Hammett ρ value would be the result of the formation of an electrophilic oxidant by the reaction of **2** with hydrogen peroxide.

(21) Adam, W.; Golsch, D. *Chem. Ber.* **1994**, *127*, 1111. (b) Adam, W.; Golsch, D. *J. Org. Chem.* **1997**, *62*, 115. (c) Adam, W.; Mithcell, C. M.; Saha-Möller, C. R.; Selvam, T.; Weichold, O. *J. Mol. Catal. A* **2000**, *154*, 251.

system, the sulfide site of SSO was much more selectively oxidized and the X_{SO} value ((nucleophilic oxidation)/(nucleophilic + electrophilic oxidation) = $(SSO_2 + SOSO_2)/(SSO_2 + SOSO + 2SOSO_2)$) was 0.03 (eq 1). The low X_{SO} value suggests the formation of an electrophilic oxidant on **1**.



(1)

For the competitive epoxidation of *cis*- and *trans*-2-octenes, the ratio of the formation rate of *cis*-2,3-epoxyoctane to that of trans isomer ($= R_{cis}/R_{trans}$) was 21.3. This value is higher than those for the tungstate−hydrogen peroxide systems ($[\gamma\text{-SiW}_{10}O_{34}(H_2O)_2]^{4-}$, 11.5, $NH_2CH_2PO_3H_2/WO_4^{2-}$; 7.3, CPC/$[PW_{12}O_{40}]^{3-}$; 3.7).[4,22] Interestingly, the epoxidation of 3-methyl-1-cyclohexene was highly diastereoselective and gave mainly the corresponding epoxide with the oxirane ring trans to the substituent (anti configuration, entry 3 in Table 2). The ^{29}Si and ^{183}W NMR spectra of the catalyst recovered after completion of the epoxidation were not changed, and the signals from the tungstate compounds, such as $[\alpha\text{-SiW}_{12}O_{40}]^{4-}$, $[\gamma\text{-SiW}_{10}O_{34}(H_2O)_2]^{4-}$, $[\{W({=}O)(O_2)_2(H_2O)\}_2(\mu\text{-}O)]^{2-}$, and $[H_nWO_2(O_2)_2]^{(2-n)-}$, were not observed (Figures 1b and 2b). These results show that the molecular structure of **1** is preserved during the catalysis. In addition, the first-order dependence of the reaction rate on the concentration of TBA·**1** also supports the idea. Therefore, it is likely that the active electrophilic oxygen species formed by the reaction of **1** with hydrogen peroxide is embedded in the rigid polyoxometalate framework, resulting in stereospecificity and diastereoselectivity for the epoxidation.[16b]

As mentioned above, the monotitanium-substituted silicotungstate **3** was completely inactive for the epoxidation under the present conditions, suggesting that the Ti−O−W and Ti−O centers are not the active sites. The fully occupied silicododecatungstate of $[\gamma\text{-SiW}_{12}O_{40}]^{4-}$ was also inactive, suggesting that the tungsten atoms in **1** do not contribute to the epoxidation. In addition, stereospecificity for the epoxidation of *cis*- and *trans*-olefins by **1** was different from those by tungstate catalysts, and there was no formation of tungstate compounds from **1** during the oxidation. These observations suggest that the catalytic reactions proceed on the multinuclear titanium center of **1**. The methoxo derivative **2** was formed by the dehydrative condensation between the hydroxo group in **1** and methanol as mentioned. Therefore, it is likely that the dehydrative condensation between **1** and hydrogen peroxide to form the hydroperoxo complex proceeds.[23] This idea is supported by the fact that the catalytic activity of **2** was much lower than that of **1**.

Conclusion

The novel γ-Keggin silicodititanodecatungstate **1** has been synthesized, and its molecular structure was successfully determined. The edge-shared dinuclear Ti sites are protonated to give $Ti_2(\mu\text{-OH})_2$ cores. The $Ti_2(\mu\text{-OH})_2$ cores of **1** react with MeOH to give the corresponding alkoxo derivative **2**. Compound **1** is found to be an effective homogeneous catalyst for the oxygen transfer reactions of various substrates including olefins and sulfides. The results for the oxidation of SSO and 3-methyl-1-cyclohexene with **1** show the contribution of rigid nonradical electrophilic oxidant(s) generated on the multinuclear titanium center.

Experimental Section

Instruments. IR spectra were measured on a Jasco FT/IR-460 Plus using KBr disks. NMR spectra were recorded at 298 K on a JEOL JNM-EX-270 (^{1}H, 270.0 MHz; ^{13}C, 67.8 MHz; ^{29}Si, 53.45 MHz; ^{183}W, 11.20 MHz) spectrometer. Chemical shifts (δ) of ^{29}Si and ^{183}W were reported in ppm downfield from external $SiMe_4$ (in $CDCl_3$) and Na_2WO_4 (in D_2O). CSI-TOFMS spectra of the polyoxometalates were recorded on a JEOL JMS-T100CS spectrometer. UV−vis spectra were recorded on a JASCO V-570 spectrometer. GC analyses were performed on Shimadzu GC-14B and GC-17A instruments with a flame ionization detector equipped with a TC-WAX or a DB-WAX capillary column (internal diameter = 0.25 mm, length = 30 m) or a SE−30 packed column. GC-MS spectra were recorded on Shimadzu GCMS-QP2010 at an ionization voltage of 70 eV equipped with a DB-WAX capillary column (internal diameter = 0.25 mm, length = 30 m). An acid/base titration was performed by using a TOA DKK HM-30G pH meter with a TOA DKK GST-5721S electrode.

Materials and Methods. MeCN was dried over CaH_2, distilled, and stored under argon. Commercially available reagents (including organic solvents) of the highest grade were used without further purification. The starting materials of the silicotungstates, $K_8[SiW_{10}O_{36}]\cdot 12H_2O$ (K·**SiW10**·H_2O) and $K_8[\alpha\text{-SiW}_{11}O_{39}]\cdot 13H_2O$ (K·**SiW11**·H_2O), were prepared according to the method described in the literature.[3] A 0.1 M $MeCN/H_2O$ solution of tetra-*n*-butylammonium hydroxoide (TBAOH) was prepared by the dilution of 1.0 M aqueous TBAOH (Aldrich).

Synthesis of the Polyoxometalates. Tetra-*n*-butylammonium Salt of $[\{\gamma\text{-SiTi}_2W_{10}O_{36}(OH)_2\}_2(\mu\text{-}O)_2]^{8-}$ (TBA·1). $Ti(O)(SO_4)$ (0.16 g (1.0 mmol)) was dissolved in 20 mL of deionized water, and then the pH of the solution was adjusted to 1.3 with 70% HNO_3. After the resulting suspension was stirred for 3 min at room temperature, $K_8[SiW_{10}O_{36}]\cdot 12H_2O$ (K·**SiW10**·H_2O: 1.5 g (0.5 mmol)) was added in a single step, and the continuous stirring of the reaction mixture produced a clear solution within 15 min. An excess amount of $[(n\text{-}C_4H_9)_4N]Br$ (1.00 g, 3 mmol) was added in a single step. After the white suspension was stirred for 1 h at room temperature, the resulting white precipitate was collected by

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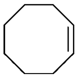
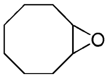
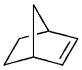
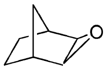
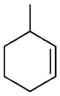
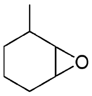
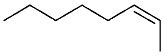
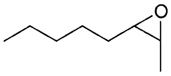
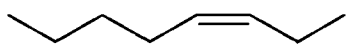
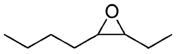
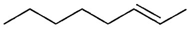
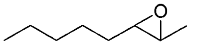
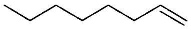
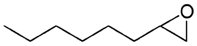
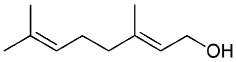
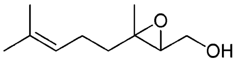
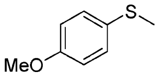
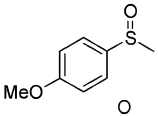
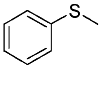
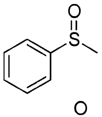
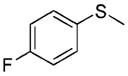
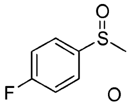
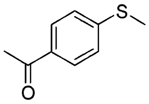
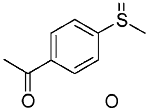
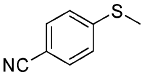
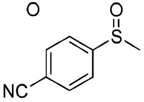
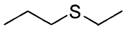
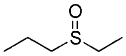
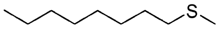
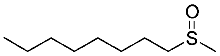
[22] In the case of $[\gamma\text{-1,2-H}_2SiV_2W_{10}O_{40}]^{4-}$ with the $V_2(\mu\text{-OH})_2$ core similar to that with **2**, a very large R_{cis}/R_{trans} value (300) for the competitive epoxidation of *cis*- and *trans*-2-octenes was obtained under the conditions of the low olefin concentration (≤33.3 mM).[16b]

[23] The reaction of the $V_2(\mu\text{-OH})_2$ core in $[\gamma\text{-1,2-H}_2SiV_2W_{10}O_{40}]^{4-}$ with hydrogen peroxide gave the $V_2(\mu\text{-OH})(\mu\text{-OOH})$ species for the epoxidation of olefins as has been reported.[16b] Similarly, the $Ti_2(\mu\text{-OH})_2$ core in **2** would react with hydrogen peroxide to form the $Ti_2(\mu\text{-OH})(\mu\text{-OOH})$ species, according to the following equation: $[\{\gamma\text{-SiW}_{10}Ti_2O_{36}(\mu\text{-OH})_2\}_2(\mu\text{-}O)_2]^{8-} + 2H_2O_2 \rightarrow [\{\gamma\text{-SiW}_{10}Ti_2O_{36}(\mu\text{-OH})(\mu\text{-OOH})\}_2(\mu\text{-}O)_2]^{8-} + 2H_2O$.

Table 4. Oxygenation of Various Olefins and Sulfides with H_2O_2 Catalyzed by TBA·**1**[a]

entry	substrate	product	time (h)	yield (%)	select.(%)
1			3	98	>99
2			10	53	90 (only *exo*)
3			4	64	90 (*syn*/*anti* = 19/81)
4			8	84	98 (only *cis*)
5			10	81	99 (only *cis*)
6			10	12	94 (only *trans*)
7			10	12	91
8			8	91	91[b]
9			1	95	99
10			1.5	83	>99
11			2	84	>99
12			3	92	98
13			3	96	99
14			3	92	98
15			3	84	99

[a] Reaction conditions for epoxidation: TBA·**1** (4 μmol), olefin (5 mmol), H_2O_2 (30% aq, 1 mmol), MeCN (6 mL), 323 K. Reaction conditions for sulfoxidation: TBA·**1** (2 μmol), sulfide (1 mmol), H_2O_2 (30% aq, 0.2 mmol), MeCN (1 mL), 305 K. Yields and selectivities were determined by GC or ^{1}H NMR using an internal standard technique. Yield (%) = epoxide or sulfoxide formed (mol)/initial H_2O_2 (mol) × 100. Select (%) = epoxide or sulfoxide formed (mol)/products formed (mol) × 100. [b] Aldehyde was formed (9% select.).

filtration, and then it was washed with an excess amount of H_2O. After the material was dried, the crude compound was purified by recrystallization from MeCN/H_2O. The solution was kept at 298 K for 24 h to yield the colorless crystals of TBA·**1** (0.64 g, 36% yield). Anal. Calcd for $C_{128}H_{288}O_{78}N_8Si_2Ti_4W_{20}$ ([(n-C_4H_9)$_4$N]$_8$·**1**): C, 21.60; H, 4.14; N, 1.58; Si, 0.79; Ti, 2.69; W, 51.67. Found: C, 21.19; H, 4.18; N, 1.53; Si, 0.74; Ti, 2.60; W, 52.52. IR (KBr, ν): 964, 904, 873, 820, 792, 739, 692, 661, 606, 553, 485, 458 cm^{-1}. UV−vis (MeCN) (ϵ): 252 nm (119 685 M^{-1} cm^{-1}). ^{29}Si NMR (MeCN): δ −84.2. ^{183}W NMR (MeCN): δ −106.1, −114.0, −131.7. CSI-MS (MeCN, spray temperature = 263 K): m/z 7358 ([TBA$_9$·**1**]$^+$), 3801 ([TBA$_{10}$·**1**]$^{2+}$).

[K(18-crown-6)] Salt of [{γ-SiTi$_2$W$_{10}$O$_{36}$(OH)$_2$}$_2$(μ-O)$_2$]$^{8-}$ (CEK·1). Twenty milliliters of aqueous solution of Ti(O)SO$_4$ (0.16 g, 1.0 mmol) was adjusted to pH 1.3. K$_8$[γ-SiW$_{10}$O$_{36}$]·12H_2O (K·**SiW10**, 1.5 g, 0.50 mmol) was added to this solution. The solution was stirred until it became clear; 18-crown-6 (0.81 g, 3.0 mmol) was added, and the solution was stirred for 15 min to form the white yellow precipitate. Filtration and drying under reduced pressure gave the powder of [K(18-crown-6)]$_8$[{γ-SiTi$_2$W$_{10}$O$_{36}$-

$(OH)_2\}_2(\mu\text{-}O)_2]$ (CEK·**1**, 1.07 g, 0.154 mmol) in a 62% yield. The single crystal of CEK·**1** suitable for X-ray crystallography was obtained by slow evaporation of the DMSO solution of CEK·**1**. IR (KBr, ν): 2920, 1473, 1435, 1410, 1388, 1352, 1286, 1251, 1106, 962, 903, 867, 820, 792, 668 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 2.67 (s, CH_2). ^{13}C{H} NMR (DMSO-d_6): δ 69.1 (CH_2). ^{183}W NMR (DMSO-d_6): δ −116.07, −118.37, −129.81. Anal. Calcd for $C_{104}H_{220}O_{130}S_4K_8Si_2Ti_4W_{20}$ ([K(18-crown-6)]$_8$·**1**·4DMSO): C, 15.75; H, 2.80; K, 3.95; Si, 0.71; Ti, 2.42; W, 46.45. Found: C, 15.74; H, 3.15; K, 3.90; Si, 0.71; Ti, 2.46; W, 46.01.

Tetra-*n*-butylammonium Salt of $[\{\gamma\text{-SiTi}_2W_{10}O_{36}(OH)(OMe)\}_2(\mu\text{-}O)_2]^{8-}$ (TBA·2). TBA·**1** (2.0 g, 0.28 mmol) was dissolved in 10 mL MeCN, followed by the addition of 5 mL of MeOH. After the mixture was stirred for 30 min at ambient temperature, the addition of 100 mL of MeOH gave the white precipitate $[TBA]8[\{\gamma\text{-SiTi}_2W_{10}O_{36}(OH)(OMe)\}_2(\mu\text{-}O)_2]$ (TBA·**2**, 1.3 g, 0.18 mmol) in a 65% yield. Anal. Calcd for $C_{130}H_{296}N_8O_{78}Si_2Ti_4W_{20}$ ([(n-$C_4H_9)_4N]_8$·**2**): C, 21.86; H, 4.18; N, 1.57. Found: C, 20.72; H, 4.05; N, 1.49. IR (KBr, ν): 999, 964, 904, 869, 821, 794, 741, 606, 551, 485, 458 cm^{-1}. UV−vis (MeCN) (ϵ): 252 nm (135 347 M^{-1} cm^{-1}). ^{1}H NMR (DMF-d_7): δ 4.60 (s, 6H, CH_3O), 3.53 (TBA, 64H), 1.88 (TBA, 64H), 1.56 (TBA, 64H), 1.08 (TBA, 96H). ^{13}C NMR (DMF-d_7): δ 62.6 (CH_3O), 49.0 (TBA), 23.8 (TBA), 19.7 (TBA), 13.4 (TBA). ^{29}Si NMR (DMF-d_7): δ −84.5. ^{183}W NMR (DMF-d_7): δ −102.2, −113.3, −123.8, −127.1, −131.3, −136.0. CSI-MS (MeCN, spray temperature = 263 K): *m/z* 7387 ([TBA$_9$·**2**]$^+$), 7145 ([TBA$_8$H·**2**]$^+$), 3815 ([TBA$_{10}$·**2**]$^{2+}$), 3699 ([TBA$_9$H·**2**]$^{2+}$).

[K(18-crown-6)] Salt of $[\{\gamma\text{-SiTi}_2W_{10}O_{36}(OH)(OMe)\}_2(\mu\text{-}O)_2]^{8-}$ (CEK·2). CEK·**1** (0.16 g, 23.1 mmol) was dissolved in 1 mL of DMSO, followed by the addition of 1 mL of MeOH. Vapor diffusion of Et_2O gave the white yellow crystalline solid [K(18-crown-6)]$_8[\{\gamma\text{-SiTi}_2W_{10}O_{36}(OH)(OMe)\}_2(\mu\text{-}O)_2]$ (CEK·**2**, 0.06 g, 8.62 mmol) in a 37% yield. IR (KBr): 3522, 2999, 2909, 1473, 1455, 1436, 1403, 1352, 1286, 1251, 1106, 1050, 1022, 998, 962, 902, 865, 819, 791, 708, 658 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 3.52 (s, 96H, CH_2), 3.28 (s, 6H, *Me*). ^{13}C{H} NMR (DMSO-d_6): δ 69.4 (s, CH_2), 40.4 (s, CH_3). Anal. Calcd for $C_{106}H_{224}O_{130}S_4K_8Si_2Ti_4W_{20}$ ([K(18-crown-6)]$_8$·**2**·4DMSO): C, 16.03; H, 2.84; K, 3.94; Si, 0.71; Ti, 2.41; W, 46.28. Found: C, 16.44; H, 3.34; K, 3.59; Si, 0.72; Ti, 2.40; W, 46.17.

Tetra-*n*-butylammonium Salt of $[\alpha\text{-SiW}_{11}O_{39}]^{8-}$ (TBA·SiW11). K·**SiW11**·H_2O (15.9 g, 5 mmol) was quickly dissolved in 1 M AcOH/AcONa buffer solution (200 mL). Then, [(n-$C_4H_9)_4N$]Br (8 g, 25 mmol) was added to the solution in a single step. The resulting white precipitate was collected by filtration and then washed with an excess amount of water (3 L). The crude product was purified twice with the precipitation method, followed by recrystallization to give analytically pure tetra-*n*-butylammonium salt derivative of **SiW11** (37% yield). Anal. Calcd for $C_{64}H_{152}O_{41}N_4SiTiW_{11}$ ([(n-$C_4H_9)_4N]_4H_4$·**SiW11**·$2H_2O$): C, 20.86; H, 4.16; N, 1.52; Si, 0.76; W, 54.89. Found: C, 21.00; H, 4.05; N, 1.60; Si, 0.80; W, 55.32. The UV−vis spectrum (in CH_3CN) showed shoulder bands at 259 nm (ϵ = 33000 M^{-1} cm^{-1}), characteristic of the α-Keggin structure. IR spectrum (KBr): 1005, 963, 956, 910, 800, 737, 547, 533, cm^{-1}. Because of low solubility, the ^{183}W and ^{29}Si NMR spectra of the solution of **TBA**·SiW11 could not be measured.

Tetra-*n*-butylammonium Salt of $[\alpha\text{-H}_2SiTiW_{11}O_{40}]^{5-}$ (TBA·3). The tetra-*n*-butylammonium salt of the monovacant α-Keggin silicoundecatungstate [(n-$C_4H_9)_4N]_4H_4$·**SiW11**·$2H_2O$ (1.55 g (0.4 mmol)) was dissolved in 50 mL of MeCN, followed by the addition of $TiCl_4$ (66 μL (0.6 mmol)). After the resulting clear pale yellow solution was stirred for 1 h at room temperature, H_2O (200 mL) was added in a single step. The resulting white precipitate was collected by filtration and then washed with an excess amount of H_2O. An analytically pure white powder of TBA$_4$·[α-$H_2SiTiW_{11}O_{40}$] (TBA·**3**) was obtained by the evacuation to dryness at room temperature. Anal. Calcd for $C_{64}H_{146}N_4O_{40}SiTiW_{11}$ ([(n-$C_4H_9)_4N]_4$·**3**): C, 20.72; H, 3.97; N, 1.51; Si, 0.76; Ti, 1.29; W, 54.5. Found: C, 20.72; H, 3.97; N, 1.46; Ti, 1.41, W, 52.8. IR (KBr): 963, 915, 880, 800, 651, 546, 530, 386, 333, cm^{-1}. ^{29}Si NMR (DMSO): δ −84.2. ^{183}W NMR (DMSO): δ −89.5, −100.0, −106.6, −110.2, −117.9, −131.4. CSI-MS (DMSO/MeCN, spray temperature = 263 K): *m/z* 3934 ([TBA$_5$·($SiTiW_{11}O_{39}$)]$^+$), 3975 ([TBA$_5$·($SiTiW_{11}O_{39}$)·MeCN]$^+$), 4015 ([TBA$_5$·($SiTiW_{11}O_{39}$)·DMSO]$^+$).

Acid/Base Titration of TBA·1. TBA·**1** (0.406 g, 57 μmol) was dissolved in MeCN (30 mL). The acid/base titration was performed under argon at room temperature as follows. To this MeCN solution of TBA·**1**, 114 μL of a 0.1 M MeCN/H_2O solution of TBAOH (0.2 equiv of **1**) was added with stirring. The measurement of potential was done when the value was stabilized. These operations were repeated 50 times.

Catalytic Oxidation. The catalytic oxidations were carried out with a glass tube reactor. A typical procedure was as follows: catalyst (4 μmol), MeCN (6 mL), hydrogen peroxide (30% aq, 1 mmol), and olefin (5 mmol) were charged in a glass tube reactor. The reaction was carried out at 323 K. The reaction solution was periodically sampled and analyzed by GC in combination with mass spectroscopy. The products were identified by the comparison of their mass spectra with those of authentic samples. The carbon balance in each experiment was in the range of 95−100%. The hydrogen peroxide remaining after the reaction was analyzed by the Ce$^{4+/3+}$ titration.

X-ray Crystallography. Diffraction measurement was made on a Rigaku AFC-10 Saturn 70 CCD detector with graphite monochromated Mo Kα radiation (λ = 0.71069 Å, 5 kW) at −180 °C. Data were collected and processed using CrystalClear[24] and HKL2000 for Linux software.[25] Neutral scattering factors were obtained from the standard source. In the reduction of data, Lorentz and polarization corrections were made. Structure analysis was performed using the CrystalStructure crystallographic structure-solving program package[26] and Win-GX for Windows software.[27] The structures of CEK·**1** and CEK·**2** were solved by heavy-atom Patterson methods (DIRDIF PATTY)[28] and expanded using Fourier techniques (DIRDIF).[29] In the final cycle of full-matrix least-squares refinement on *F*, the titanium and tungsten oxygen atoms were refined anisotropically. The structure of TBA·**1** was solved by SHELXS-97 (direct method) and SHELXH-97 (Fourier synthesis and least-squares refinement).[30] Titanium and tungsten atoms were

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(24) *CrystalClear* 1.3.5 SP2; Rigaku and Rigaku/MSC: The Woodlands, TX. (b) Pflugrath, J. W. *Acta Crystallogr. D* **1999**, *55*, 1718−1725.

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(26) *CrystalStructure* 3.7.0; Rigaku and Rigaku/MSC: The Woodlands, TX.

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refined anisotropically, and all other atoms, except hydrogen and the highly disordered carbon atoms of 18-crown-6, were refined isotropically.

Acknowledgment. We thank Mr. Y. Sumida and Dr. K. Yonehara (Nippon Shokubai Co., Ltd.) for their help with experiments. This work was supported by the Core Research for Evolutional Science and Technology (CREST) program of the Japan Science and Technology Agency (JST) 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 TBA·**1**, CEK·**1**, and CEK·**2**, Figures S1−S7, and Tables S1−S3. This material is available free of charge via the Internet at http://pubs.acs.org.

IC052179Q