Polyoxometalate Chemistry

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Zinc(II) Containing γ-Keggin Sandwich-Type Silicotungstate: Synthesis in Organic Media and Oxidation Catalysis[**]

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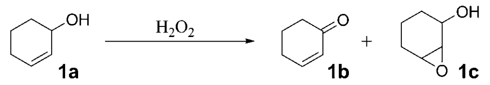
The versatility and accessibility of polyoxometalates (POMs) has led to various applications in the fields of analytical chemistry, medicine, electrochemistry, photochemistry, and catalysis.[1] POMs have especially received much attention in the area of oxidation and acid catalysis.[1] Since the synthesis of the divacant $[\gamma\text{-SiW}_{10}O_{36}]^{8-}$ (SiW10) ion was reported by Tézé and Hervé,[2] a number of monomeric dimetal-substituted POMs has been synthesized with SiW10 as a "structural motif".[3] Also, SiW10 has been utilized as a "macroligand" to encapsulate multinuclear metal–oxygen cluster cores and several POMs built up of two (or more) SiW10 subunits sandwiching multinuclear metal–oxygen cluster cores have been reported.[4] In particular, the interests in the catalysis of these metal-substituted and metal-encapsulating POMs has been increasing because of their unique reactivities that depend on the compositions and structures of their active sites.[1,3,4]

The encapsulation and substitution of multinuclear 3d-metal cations into SiW10 with retention of the γ-Keggin framework(s) have generally been considered to be very difficult.[5,6] It has been reported that SiW10 is easily isomerized and/or decomposed to tri- and tetravacant POMs by the presence of 3d-metal cations in aqueous acidic media.[5] For example, Kortz and co-workers reported that the reaction of the potassium salt of SiW10 (K-SiW10) with 3d-metal cations in aqueous media produced β-Keggin dimer $[\{\beta\text{-SiNi}_2W_{10}O_{36}(OH)_2(OH_2)\}_2]^{12-}$[5a] and α-Keggin dimers $[\{B\text{-}\alpha\text{-SiM}_2W_9O_{34}(OH_2)\}_2]^{12-}$ ($M = Mn^{2+}$, Cu^{2+}, and Zn^{2+})[5b] with isomerization and/or loss of tungsten atoms. Although a series of 3d-metal-substituted γ-Keggin sandwich-type POMs $[\{K(OH_2)\}_2M(OH_2)_2(\gamma\text{-SiW}_{10}O_{35})_2]^{8-}$ ($M = Mn^{2+}$, Co^{2+}, and Ni^{2+}) has been synthesized from K-SiW10 in aqueous media,[6] these POMs have only one 3d-metal cation with respect to two SiW10 subunits. For the formation of $[\{K(OH_2)\}_2M(OH_2)_2(\gamma\text{-SiW}_{10}O_{35})_2]^{8-}$, the role of K^+ ions is very important: Two SiW10 subunits are initially linked through two K^+ ions and the insertion of the 3d-metal cation as a monomeric species from solution then occurs.[6b,7] Therefore, K^+ ions inhibit the formation of multimetal centers.

We have reported that the tetra-*n*-butylammonium (TBA) salt of SiW10 ($TBA_4H_4[\gamma\text{-SiW}_{10}O_{36}]$; TBA-SiW10) can act as an efficient homogeneous catalyst for various kinds of H_2O_2-based oxidations, such as the epoxidation of alkenes,[8a,b] oxygenation of sulfides,[8b] and hydroxylation of organosilanes.[8c] During the course of our investigations, we now found that the effect of metal additives was very significant for the H_2O_2-based oxidations with TBA-SiW10. The oxidation of 2-cyclohexen-1-ol (**1a**) with TBA-SiW10 in acetone preferentially gave the corresponding epoxy alcohol **1c** (Table 1, entry 1).[9] No oxidation occurred with $[Zn(acac)_2]$ (acac = acetylacetonato; Table 1, entry 2). Surprisingly, the epoxidation was completely suppressed and the alcohol oxidation exclusively gave the corresponding enone **1b** in an almost quantitative yield when a simple mixture of TBA-SiW10 and $[Zn(acac)_2]$ was used as the catalyst (Table 1, entry 3).[10] This chemoselectivity is much different from that of reported tungsten-based catalysts including TBA-SiW10 (Table 1, entry 1).[9] The positive-ion cold-spray ionization mass (CSI-MS) spectrum of a mixture of TBA-SiW10 and $[Zn(acac)_2]$ (1:2 molar ratio) in acetone exhibited signals centered at *m*/*z* 7364.7 for a +1 charged species assignable to the $[(TBA)_9H_4Si_2Zn_4W_{20}O_{74}]^+$ ion, and no signals arising from TBA-SiW10 were observed (Figure 1). These results show that TBA-SiW10 reacted with $[Zn(acac)_2]$ in acetone to form a new zinc-containing −8 charged polyanion $[H_4Si_2Zn_4W_{20}O_{74}]^{8-}$, which would catalyze the alcohol oxidation (rather than the epoxidation).

Table 1: Oxidation of 2-cyclohexen-1-ol.[a]



Entry	Catalyst ([mol%])	Yield [%][b]	**1b**/**1c** ratio
1	TBA-SiW10 (0.8)	75	18/82[c]
2	$[Zn(acac)_2]$ (1.6)	No reaction	–
3	TBA-SiW10 (0.8) + $[Zn(acac)_2]$ (1.6)	91	only **1b**

[a] Reaction conditions: Catalyst (0.8–1.6 mol% with respect to **1a**), **1a** (0.5 mmol), 30% aq. H_2O_2 (0.25 mmol), [D$_6$]acetone (1.5 mL), 56 °C, 40 min. The corresponding epoxy ketone was not produced in all cases. [b] Total yield based on H_2O_2 used. Determined by GC and ^1H NMR analyses. [c] The *syn*/*anti* ratio of **1c** was 32/68.

From the above results, we got the idea to synthesize γ-Keggin POM(s) with multinuclear 3d-metal cations: Our

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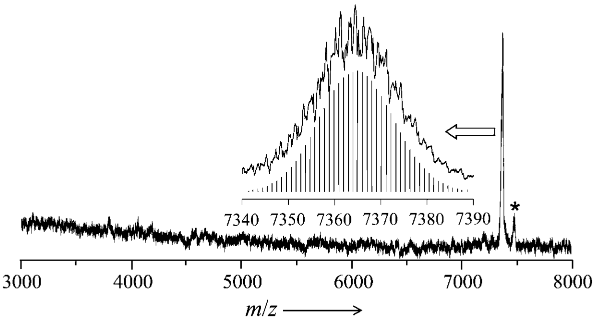


Figure 1. Positive ion CSI-MS spectrum of a mixture of TBA-SiW10 and $Zn(acac)_2$ in acetone. The lines in the inset are the calculated pattern for $[(TBA)_9H_4Si_2Zn_4W_{20}O_{74}]^+$. The asterisk indicates the signals assignable to $[(TBA)_9H_4Si_2Zn_4W_{20}O_{74}(H_2O)_6]^+$.

strategy is to synthesize in organic media[11] and to avoid the use of alkali-metal cations (as counter cations). Herein, we focus on the synthesis of a novel γ-Keggin zinc-containing sandwich-type POM $TBA_8[\{Zn(OH_2)(\mu_3\text{-}OH)\}_2\{Zn(OH_2)_2\}_2\{\gamma\text{-}HSiW_{10}O_{36}\}_2]\cdot 9H_2O$ (TBA-Zn4). The solubility of TBA-SiW10 in various organic solvents, such as acetone, acetonitrile, *N*,*N*-dimethylformamide, and dimethyl sulfoxide, is very high. In TBA-SiW10, four protons are located on the oxo species at the vacant site[8] and it should be possible to exchange these with various metal cations.

Therefore, TBA-SiW10 is an ideal precursor for the synthesis in organic media. Compound TBA-Zn4 could easily be synthesized by simply mixing the required components of TBA-SiW10 and an appropriate zinc source ($[Zn(acac)_2]$)[12] in acetone at room temperature. It was confirmed by the CSI-MS spectroscopy that all of TBA-SiW10 reacted with $[Zn(acac)_2]$ in a few minutes to form TBA-Zn4. Thus, TBA-Zn4 could be obtained in an almost quantitative yield (always >90% yield based on TBA-SiW10, see the Supporting Information).

The molecular structure of TBA-Zn4 could be determined by the X-ray crystallographic analysis (Figure 2a and Supporting Information, Tables S1 and S2).[13] Although various kinds of zinc-containing POMs, such as $[H_2ZnXW_{11}O_{40}]^{n-}$ ($X = P^{5+}$ and Si^{4+}),[14a,b] $[Zn_2(OH_2)_6(WO_2)_2(SbW_9O_{33})_2]^{10-}$,[14c] $[WZnM_2(ZnW_9O_{34})_2]^{n-}$ ($M = Mn^{2+}$, Zn^{2+}, Pd^{2+}, Pt^{2+}, Ru^{3+}, and Rh^{3+}),[14d–f] $[Zn_3(OH_2)_3(AsW_9O_{33})_2]^{12-}$,[14g] $[Zn_4(XW_9O_{34})_2]^{n-}$ ($X = P^{5+}$, Si^{4+}, Ge^{4+}, and Ga^{3+}),[5b,14h] $[(ZnCl)_6(BW_9O_{33})_2]^{12-}$,[14i] $[Zn_4(OH_2)_2(P_2W_{15}O_{56})_2]^{16-}$,[14j] and $[Zn_2As_8V_{12}O_{40}]^{4-}$[14k] have been reported to date, to our knowledge TBA-Zn4 is the first structurally characterized zinc-containing POM with the γ-Keggin structure.

Eight TBA cations per one Zn4 anion could be crystallographically assigned in accord with the result of the elemental analysis (Supporting Information). The bond valence sum (BVS) values of silicon (3.93), tungsten (5.92–6.15), and zinc (1.93–2.02) atoms in TBA-Zn4 indicate that the respective valences are +4, +6, and +2. The BVS value of O1 was 1.23, showing that O1 is μ_3-OH unit bridging three zinc atoms (Zn1, Zn2, and Zn2*). The BVS value of O28 was 1.32, suggesting that H^+ is likely located on the oxygen atom. The data of X-ray analysis, elemental analysis, and thermogravimetry show that the formula of TBA-Zn4 is $TBA_8[\{Zn(OH_2)(\mu_3\text{-}OH)\}_2\{Zn(OH_2)_2\}_2\{\gamma\text{-}HSiW_{10}O_{36}\}_2]\cdot 9H_2O$. The formation of the Zn4 anion can be expressed by Equation (1).

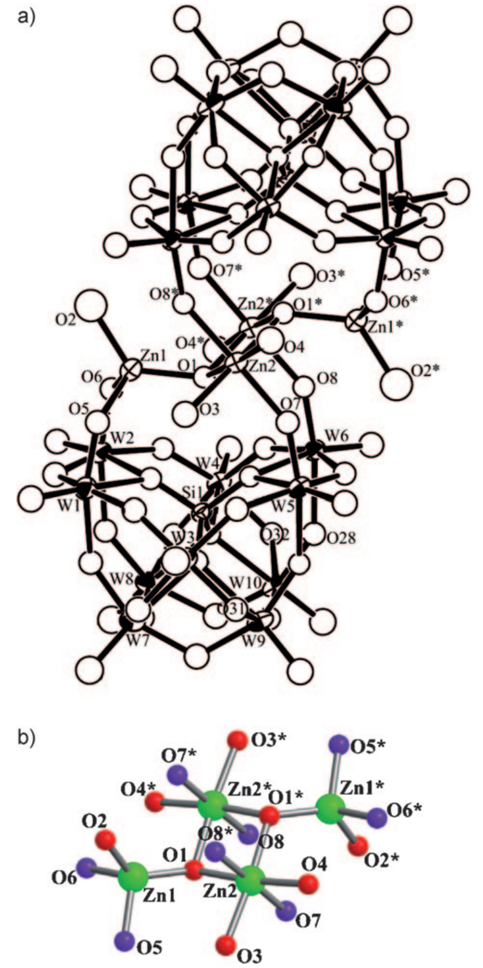


Figure 2. a) ORTEP representation of the anion of TBA-Zn4; thermal ellipsoids set at 50% probability. b) Ball-and-stick representation around the $[\{Zn(OH_2)(\mu_3\text{-}OH)\}_2\{Zn(OH_2)_2\}_2]^{6+}$ core. Green Zn, red O atoms coordinating to Zn, purple O atoms from the SiW10 frameworks.

$$2[\gamma\text{-}SiW_{10}O_{36}]^{8-} + 4\,Zn^{2+} + 8\,H_2O \rightarrow [\{Zn(OH_2)(\mu_3\text{-}OH)\}_2\{Zn(OH_2)_2\}_2\{\gamma\text{-}HSiW_{10}O_{36}\}_2]^{8-} \quad (1)$$

Compound TBA-Zn4 has a tetranuclear zinc–oxygen cluster core $[\{Zn(OH_2)(\mu_3\text{-}OH)\}_2\{Zn(OH_2)_2\}_2]^{6+}$ (Figure 2b) sandwiched between two SiW10 subunits. In the half unit of γ-Keggin $\{\gamma\text{-}SiW_{10}O_{36}Zn_2(OH)(OH_2)_3\}$, two zinc atoms (Zn1 and Zn2) were located "out-of-pocket" of the vacant site in SiW10 and corner sharing. Thus, zinc atoms were coordinated to two terminal oxygen atoms of SiW10 subunits without direct interaction with the internal $\{SiO_4\}$ tetrahedrons. In the tetranuclear zinc–oxygen core, two crystallographically independent zinc atoms were found. The Zn1 atom was tetrahedrally coordinated by a μ_3-OH ligand (O1), an aqua ligand (O2), and two terminal oxygen atoms of one SiW10 subunit (O5 and O6). The Zn2 atom was octahedrally coordinated by two μ_3-OH ligands (O1 and O1*), two aqua ligands (O3 and

O4), and two SiW10 subunits (O7 and O8*). The central Zn2···Zn2* separation was 3.112 Å. The central-to-terminal Zn1···Zn2 and Zn1···Zn2* separations were 3.484 and 3.447 Å, respectively. The μ_3-OH ligands bridged somewhat asymmetrically; the Zn1–O1 bond (1.942(9) Å) was shorter than those of Zn2–O1 (2.095(10) Å) and Zn2–O1* (2.090(9) Å), and the Zn2-O1-Zn2* angle (96.1(4)°) was smaller than those of Zn1-O1-Zn2 (119.2(5)°) and Zn1-O1-Zn2* (117.4(5)°). These bond lengths and angles in the tetranuclear zinc–oxygen cluster core $[\{Zn(OH_2)(\mu_3\text{-}OH)\}_2\{Zn(OH_2)_2\}_2]^{6+}$ were similar to those in reported organozinc complexes with tetranuclear zinc–oxygen cluster cores, such as $[Zn_4(\mu_3\text{-}OH)_2(fa)_3(4,4'\text{-}bpy)_2]$ (fa = fumarate, 4,4′-bpy = 4,4′-bipyridine)[15a] and $[Zn_4(\mu_3\text{-}OH)_2(O_2CPh)_2(pko)_4]$ (pko = di-2-pyridyl ketone oxime)[15b] (Supporting Information, Table S3).

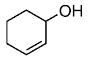
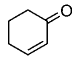
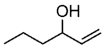
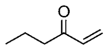
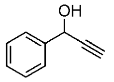
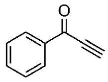
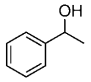
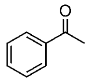
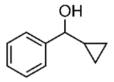
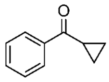
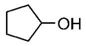
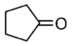
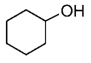
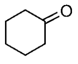
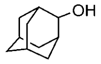
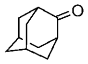
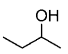
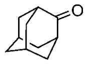
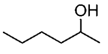
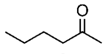
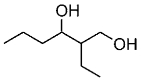
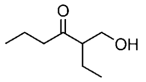
The solid-state ^{29}Si magic-angle spinning (MAS) NMR spectrum of TBA-Zn4 showed a signal at $\delta = -84.2$ ppm (Supporting Information, Figure S1 a). The ^{29}Si NMR spectrum of TBA-Zn4 in a mixed solvent of [D$_6$]acetone and water (10:1, v/v) showed a signal at $\delta = -83.9$ ppm (Supporting Information, Figure S1 b) and the signal position was almost the same as that in the solid-state ^{29}Si MAS NMR spectrum. The ^{183}W NMR spectrum of TBA-Zn4 in the same mixed solvent showed five signals at $\delta = -97.2$, -112.2, -124.7, -144.8, and -169.7 ppm with the respective intensity ratio of 1:1:1:1:1 (Supporting Information, Figure S2). These results show that the solid-state structure of the anion part of TBA-Zn4 is preserved in the solution state.

In the presence of TBA-Zn4, the oxidations of various kinds of secondary alcohols with H_2O_2[16–18] efficiently proceeded to give the corresponding ketones (Table 2).[19] The present system showed high efficiencies of H_2O_2 utilization.[20] For allylic alcohols (**1a** and **2a**), the C–C double bonds remained intact and the alcohol oxidations exclusively proceeded to give the corresponding enones in high yields.[9,21] Notably, a propargylic alcohol (**3a**) could be converted into the corresponding α,β-alkynic ketone.[22] Benzylic alcohols (**4a** and **5a**) were also efficiently oxidized. The oxidation of the radical-clock substrate (**5a**) exclusively produced cyclopropylphenyl ketone. The lack of ring-opened product(s) indicates that free-radical intermediates are not involved in the present alcohol oxidation. The oxidations of cyclic and linear aliphatic alcohols (**6a**–**10a**) efficiently proceeded to afford the corresponding aliphatic ketones. The present TBA-Zn4-catalyzed alcohol oxidation was secondary selective; the oxidation of 1,3-diol (**11a**) selectively took place at the secondary position, affording the corresponding 3-keto alcohol in a high yield. After the oxidation was completed, the catalyst could be retrieved by evaporation of acetone, and addition of an excess amount of diethyl ether. The retrieved catalyst could be reused for the alcohol oxidation; for example, the oxidation of **1a** with the retrieved catalyst under the conditions described in Table 2 selectively gave **1b** in 94 % yield after 60 min.

In acetone, TBA-SiW10 reacts with $[Zn(acac)_2]$ to form TBA-Zn4 within a few minutes. Thus, it is noted that a simple mixture of TBA-SiW10 and $[Zn(acac)_2]$ ("in-situ-prepared catalyst")[10] showed similar activities and chemoselectivities to those of TBA-Zn4 (see the values in the parentheses in Table 2). All these results (including the results in Table 1[9]) suggest that zinc site(s) and/or tungsten site(s) neighboring to zinc site(s) in TBA-Zn4 play an important role in the chemoselective alcohol oxidation.[23]

In conclusion, the novel sandwich-type γ-Keggin zinc-containing POM TBA-Zn4 could easily be synthesized by the reaction of TBA-SiW10 with $[Zn(acac)_2]$ in an organic medium. Compound TBA-Zn4 showed high catalytic performance for the chemoselective oxidation of secondary alcohols even in the presence of alkenic, alkynic, and primary alcoholic

Table 2: Oxidation of various secondary alcohols.[a]

Entry	Substrate		t	Product		Yield [%][b]
1		**1a**	40 min		**1b**	95(91)
2		**2a**	1.5 h		**2b**	91
3		**3a**	1.5 h		**3b**	88(83)
4		**4a**	1.5 h		**4b**	83(88)
5		**5a**	1 h		**5b**	99(99)
6		**6a**	19 h		**6b**	78
7		**7a**	18 h		**7b**	88(86)
8		**8a**	2 h		**8b**	97(89)
9		**9a**	8 h		**9b**	85
10		**10a**	6 h		**10b**	83(70)
11		**11a**[c]	6 h		**11b**	81(64)

[a] Reaction conditions: TBA-Zn4 (0.4 mol% with respect to alcohols), alcohol (0.5 mmol), 30% aq. H_2O_2 (0.25 mmol), acetone or [D$_6$]acetone (1.5 mL), 56°C. [b] Determined by GC and/or ^{1}H NMR spectroscopic analyses and based on H_2O_2 used. The values in parentheses were product yields with the in-situ-prepared catalyst obtained by mixing TBA-SiW10 (0.8 mol%) and $[Zn(acac)_2]$ (1.6 mol%) in situ. [c] A mixture of diastereomers.

functions. Also, the in-situ-prepared catalyst obtained by simply mixing the required components of precursors showed similar catalytic activity and chemoselectivity to those of TBA-Zn4. The strategy demonstrated herein should be very useful for the synthesis of multimetal-substituted POMs and catalytic applications.

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[10] It would be very advantageous for practical applications if the reactions could be carried out with in-situ-prepared catalysts, by simply mixing the required components (even without isolation of truly active catalysts). Although the in-situ-prepared POM-based catalysts in aqueous media with the pH value controlled (actually using synthetic solutions as catalysts) have been reported to be active for aerobic lignin oxidation[10a] and the oxidation of alcohols with H_2O_2,[10b] similar in-situ-prepared catalysts in organic media have not been reported to our knowledge: a) I. A. Weinstock, E. M. G. Barbuzzi, M. W. Wemple, J. J. Cowan, R. S. Reiner, D. M. Sonnen, R. A. Heintz, J. S. Bond, C. L. Hill, *Nature* **2001**, *414*, 191; b) D. Sloboda-Rozner, P. L. Alster, R. Neumann, *J. Am. Chem. Soc.* **2003**, *125*, 5280.

[11] Transition-metal-substituted POMs have usually been synthesized by the reaction of alkali-metal salts of lacunary POMs and the corresponding transition-metal salts in aqueous media. To date, there are only a few reports on the synthesis in organic media. The strategy to use organic media and to control the reactivities of POMs with counter cations demonstrated herein will open up a new avenue for POM chemistry: a) A. M. Khenkin, L. J. W. Shimon, R. Neumann, *Eur. J. Inorg. Chem.* **2001**, 789; b) K. Yamaguchi, N. Mizuno, *New J. Chem.* **2002**, *26*, 972; c) P. Mialane, C. Duboc, J. Marrot, E. Rivière, A. Dolbecq, F. Sécheresse, *Chem. Eur. J.* **2006**, *12*, 1950.

[12] Very recently, Mialane and co-workers reported the synthesis of a sandwich-type POM $Cs_{10}[(\gamma\text{-}SiW_{10}O_{36})_2\{Cr(OH)(OH_2)\}_3]\cdot 17H_2O$ by the reaction of $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ with the trinuclear $[Cr_3(OAc)_7(OH)_2]$ complex in aqueous medium. They mentioned that the choice of the chromium precursor was crucial for the synthesis: J.-D. Compain, P. Mialane, A. Dolbecq, I. M. Mbomekallé, J. Marrot, F. Sécheresse, C. Duboc, E. Rivière, *Inorg. Chem.* **2010**, *49*, 2851.

[13] CCDC-768702 (TBA-Zn4) contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. It was confirmed by IR measurements that TBA-Zn4 was thermally stable upon the heat treatment at least up to 80 °C.

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[16] Owing to increasing environmental concerns, many efforts have been made to develop alcohol oxidation systems using environmentally benign H_2O_2 or O_2 (air) as a sole oxidant: a) R. A. Sheldon, I. W. C. E. Arends, D. Dijisman, *Catal. Today* **2000**, *57*, 157; b) T. Mallat, A. Baiker, *Chem. Rev.* **2004**, *104*, 3037; c) T. Matsumoto, M. Ueno, N. Wang, S. Kobayashi, *Chem. Asian J.* **2008**, *3*, 196.

[17] The aerobic alcohol oxidations are generally carried out at relatively high reaction temperatures.[16] Fine chemicals have various functional groups and their thermal stabilities are generally low. Thus, the oxidations should often be carried out under mild reaction conditions with high functional-group tolerance. In addition, the simplicity of operation is also very important from an economic point of view. For these reasons, H_2O_2 could be the oxidant of choice for alcohol oxidations (especially for fine chemicals): R. A. Sheldon, *J. Chem. Technol. Biotechnol.* **1997**, *68*, 381, and see also ref. [16a].

[18] The TBA-Zn4-catalyzed oxidation of benzyl alcohol under the conditions described in Table 2 gave benzaldehyde and benzoic acid in 87% and 3% yields (for 2.5 h), respectively.

[19] Acetone was not a special solvent; for example, the oxidation of **1a** in acetonitrile gave **1b** in > 99% yield under the same conditions.

[20] Even with an equimolar amount of H_2O_2 with respect to alcohols, the oxidation efficiently proceeded; for example, the TBA-Zn4-catalyzed oxidations of **1a**, **3a**, and **8a** (0.5 mmol) using 1 equivalent of H_2O_2 with respect to alcohols (other conditions were the same as those described in Table 2) gave the corresponding ketones in 99% (for 2 h), 94% (for 3 h), and 93% (for 4.5 h) yields, respectively.

[21] It has been reported that the H_2O_2-based oxidations with metal-substituted POMs (Al^{3+} or Zn^{2+}) show high chemoselectivity to alcoholic functions: a) J. Wang, L. Yan, G. Qian, S. Li, K. Yang, H. Liu, X. Wang, *Tetrahedron* **2007**, *63*, 1832; b) J. Wang, L. Yan, G. Li, X. Wang, Y. Ding, J. Suo, *Tetrahedron Lett.* **2007**, *46*, 7023; c) G. Maayan, R. H. Fish, R. Neumann, *Org. Lett.* **2003**, *5*, 3547.

[22] α,β-Alkynic ketones are very important compounds and have been utilized as precursors for heterocyclic compounds and DNA-cleavage reagents. Although several stoichiometric oxidants such as MnO_2, Swern reagent, and Dess–Martin reagent have been utilized for the oxidation of propargylic alcohols, the catalytic procedures with H_2O_2 or O_2 are quite limited.[16]

[23] The oxidation of **1a** (under the conditions described in Table 1) did not proceed at all in the presence of a mixture of 1) $Na_2WO_4{\cdot}2H_2O$ (8 mol%) and TBABr (6.4 mol%), or 2) $Na_2WO_4{\cdot}2H_2O$ (8 mol%), [Zn(acac)$_2$] (1.6 mol%), and TBABr (6.4 mol%). These results can rule out any contribution to the observed catalysis from tungsten- and/or zinc-based impurities, and the observed catalysis is intrinsically derived from TBA-Zn4.