

Acid–base catalyses by dimeric disilicoicosatungstates and divacant γ -Keggin-type silicodecatungstate parent: Reactivity of the polyoxometalate compounds controlled by step-by-step protonation of lacunary $W=O$ sites

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Abstract

The catalytic properties of disilicoicosatungstates, [$\{\gamma\text{-SiW}_{10}\text{O}_{32}(\text{H}_2\text{O})_2\}_2(\mu\text{-O})_2\}^{4-}$ (**2**) and $[\text{H}(\gamma\text{-SiW}_{10}\text{O}_{32})_2(\mu\text{-O})_4]^{7-}$ (**3**), and their parent divacant γ -Keggin type silicodecatungstate, $[\gamma\text{-SiW}_{10}\text{O}_{34}(\text{H}_2\text{O})_2]^{4-}$ (**1**), toward C–C bond formation reactions have been investigated. The disilicoicosatungstate **2** with aquo ligands exhibits the acidic nature and catalyzes the Mukaiyama-aldol condensation and carbonyl-ene reaction, while **1** and **3** are rather basic and catalyze the Knoevenagel condensation. Therefore, the acid–base properties of a series of lacunary γ -Keggin silicotungstate derivatives **1–3** are clearly different, and the catalyses of **1–3** depend on the molecular structures while **1–3** are composed of a common $[\text{SiW}_{10}\text{O}_{32}]$ fragment.

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1. Introduction

Polyoxometalates (= POMs) are metal–oxygen cluster molecules constructed by the self-assembly of $M\text{-O}/M\text{-OH}$ components [1]. The chemical properties of POMs will be finely controlled by the modification of the molecular structure as well as the composition. On the other hand, however, the structural reorganization (i.e., “isomerization”) of POMs occurs in the solution state depending on the conditions such as temperature, concentration, and pH of the solution. Therefore, POMs show the structural variation and unique properties, and the studies on the syn-

thesis, structural characterization, and chemical properties of novel POMs have been attractive subjects from the viewpoints of the traditional coordination chemistry [2].

POMs are utilized as catalysts because of their acid–base nature and redox properties [3]. For example, Keggin type heteropoly acids, $\text{H}_n[\text{XM}_{12}\text{O}_{40}]$ ($M = \text{Mo(VI)}, \text{W(VI)}$; (n, X) = (3, P), (4, Si); abbreviated as HPAs), are extensively utilized as acid catalysts for various organic transformations because of their strong acidity and the lacks of side reactions of sulfoxidation, chlorination, nitration, *etc.* in comparison with conventional mineral acids [4]. Homogeneous and silica-supported HPA catalysts have been reported to be efficient for the conventional reactions such as hydration of unsaturated bonds, esterification, condensation, *etc.*, and the research interests in the application of HPA catalysts toward fine organic transformations are much growing. To date, a few C–C bond formation reactions such as Diels–Alder reaction, Friedel–Crafts

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acylation, Fries rearrangement of aryl esters, carbonyl-ene reaction, and silylcyanation of ketones have been reported, while some other useful reactions such as Mukaiyama-aldol condensation and Knoevenagel reaction have not been examined so far [5]. In order to expand the scope of applicability to fine reactions and to develop more efficient catalysts, the fundamental studies on the reactivity of various POMs are necessary.

Lacunary polyoxometalates such as $[\text{XM}_9^{\text{VI}}\text{O}_{39}]^{(n+4)-}$ and $[\text{XM}_9^{\text{VI}}\text{O}_{34}]^{(n+6)-}$, which contain the vacant site(s) due to the lack of one or more metal ions from the fully occupied POMs $[\text{XM}_{12}^{\text{VI}}\text{O}_{40}]^{n-}$, are recognized to be the useful precursors for mixed-metal oxide clusters, giant metal clusters, and inorganic–organic hybrid compounds. Especially, the γ -isomer of a divacant Keggin-type silicodecatungstate, $[\text{SiW}_{10}\text{O}_{36}]^{8-}$ (**SiW10**) [6], has been utilized to construct dimetal-substituted clusters such as reactive dinuclear $\text{M}_2(\mu\text{-O})_2$ site-containing POMs [7]. The oxo ligands at the vacant sites (i.e., *cis*- $\text{W}(=\text{O})_2$ components) are basic enough to react with not only metal cations but also H^+ : we have successfully synthesized a protonated silicodecatungstate, $[\gamma\text{-SiW}_{10}\text{O}_{34}(\text{H}_2\text{O})_2]^{4-}$ (**1**), which efficiently catalyzes the olefin epoxidation with H_2O_2 . The single crystal X-ray structural analysis of **1** reveals that two of four oxo ligands located at the vacant sites are protonated selectively to give the aquo ligands [8].

Recently, we have found that the dehydrative condensation of **1** results in the formation of two structurally different disilicoicosatungstates, $[\{\gamma\text{-SiW}_{10}\text{O}_{32}(\text{H}_2\text{O})_2\}_2(\mu\text{-O})_2]^{4-}$ (**2**) and $[(\gamma\text{-SiW}_{10}\text{O}_{32})_2(\mu\text{-O})_4]^{8-}$ (**3'**; mono-protonated form of this compound, $[\text{H}(\gamma\text{-SiW}_{10}\text{O}_{32})_2(\mu\text{-O})_4]^{7-}$, is abbreviated as **3**) [9]. As shown in Scheme 1, the protonation of **1** gives **2**, which has “S-shaped” structure and involves the aquo ligands on the terminal tungsten atoms. On the contrary, the dehydration of **1** resulted in the formation of the “closed-shape” cluster **3'**, which contains neither vacant sites nor terminal aquo ligands. The “S-shaped” cluster **2** can catalyze the Baeyer–Villiger oxidation of cycloalkanones to lactones with H_2O_2 , while **1** and **3** are almost inactive although the compounds **1–3** are composed of a common $[\gamma\text{-SiW}_{10}\text{O}_{32}]$ unit [9]. Such different catalytic performances of **1–3** may arise from the acid or base properties. Herein we apply **1–3** to the C–C bond formation reactions catalyzed by acids or bases and investigate the acid–base properties.

2) and $[(\gamma\text{-SiW}_{10}\text{O}_{32})_2(\mu\text{-O})_4]^{8-}$ (**3'**; mono-protonated form of this compound, $[\text{H}(\gamma\text{-SiW}_{10}\text{O}_{32})_2(\mu\text{-O})_4]^{7-}$, is abbreviated as **3**) [9]. As shown in Scheme 1, the protonation of **1** gives **2**, which has “S-shaped” structure and involves the aquo ligands on the terminal tungsten atoms. On the contrary, the dehydration of **1** resulted in the formation of the “closed-shape” cluster **3'**, which contains neither vacant sites nor terminal aquo ligands. The “S-shaped” cluster **2** can catalyze the Baeyer–Villiger oxidation of cycloalkanones to lactones with H_2O_2 , while **1** and **3** are almost inactive although the compounds **1–3** are composed of a common $[\gamma\text{-SiW}_{10}\text{O}_{32}]$ unit [9]. Such different catalytic performances of **1–3** may arise from the acid or base properties. Herein we apply **1–3** to the C–C bond formation reactions catalyzed by acids or bases and investigate the acid–base properties.

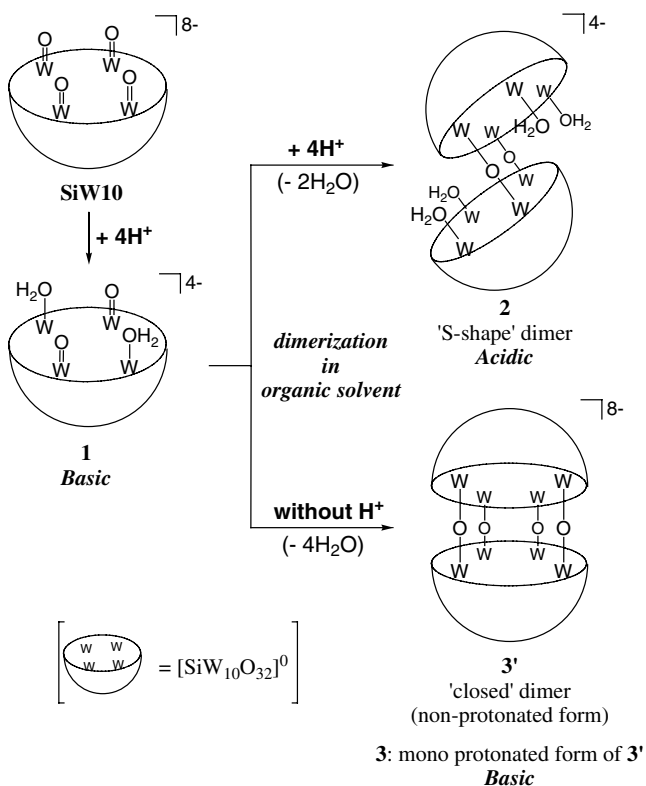
2. Results and discussion

In order to clarify the acid–base properties of a series of lacunary γ -Keggin silicotungstate derivatives **1–3**, the catalytic performances for acid- or/and base-catalyzed C–C bond formation reactions (Mukaiyama-aldol condensation, carbonyl-ene reaction, Diels–Alder reaction, Knoevenagel reaction, and cyanosilylation of ketones) were examined. The catalytic performance of the “S-shaped” dimeric cluster **2** was clearly different from those of the monomeric parent **1** and the “closed-shape” dimer **3**, i.e., **2** worked as an acid catalyst whereas **1** and **3** were rather basic catalysts.

2.1. Acid catalysis of the S-shaped dimer **2**

A crossed-aldol reaction between benzaldehyde and the silyl enol ether of cyclohexenone (namely “Mukaiyama-aldol condensation [10]”) in homogeneous nitromethane solution was efficiently catalyzed by **2**. The main products were trimethylsiloxy derivatives of aldols because the reaction was performed under anhydrous conditions as shown in Table 1 [11]. The TON (= turnover number per molecule; 48) and TOF (= turnover frequency; 4.4 h^{-1}) of **2** were comparable to or higher than those (TON: 3.4–56, TOF: 7.7×10^{-2} – $1.7 \times 10 \text{ h}^{-1}$) of the previously-reported catalysts based on d-block elements [12]. In contrast, the amount of aldol products by **1** was lower than stoichiometric one and **3** was almost inactive under the present conditions. The *syn* to *anti* ratio for **2** was 43:57, and different from that for **1** (75:25). These differences of the catalytic activities and diastereoselectivities among **1–3** suggest the difference of the acid or base properties.

The “S-shape” dimer **2** also catalyzed the intramolecular cyclization of R-(+)-citronellal (i.e., carbonyl-ene reaction [13]), while **1** and **3** were inactive (Table 2) [14]. The main product obtained by **2** was (–)-isopulegol, which is the more valuable intermediate for (–)-menthol. Recently, the same reaction catalyzed by silica-supported $\text{H}_3[\text{PW}_{12}\text{O}_{40}]$ has been reported [5d].

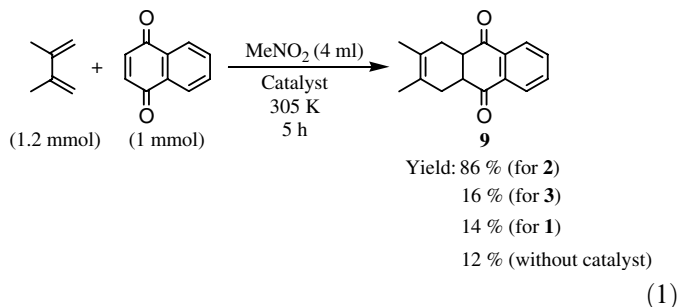


Scheme 1. Formation of disilicoicosatungstates **2** and **3'** from **1**.

Table 1
Catalytic activities for Mukaiyama-aldol reaction.

Catalyst (mol%)	Yield of product (%)		
	4 (<i>syn:anti</i>)	5	6
1 (4.0)	2 (75:25)	Trace	n.d.
2 (2.0)	91 (43:57)	1	4
3 (2.0)	n.d.	Trace	Trace

The Diels–Alder reaction of 2,3-dimethylbutadiene and 1,4-naphthoquinone was also catalyzed by **2**, while **1** and **3** were much less active (comparable to without catalyst) as shown in Eq. (1) (the yields of **9**: 86% for **2**, 16% for **3**, 14% for **1**, 12% for the reaction without catalysts). While **2** worked as an acid catalyst under homogeneous conditions (yield 86%, 5 h, 305 K, MeNO₂ solvent), **2** was less active for same reaction under heterogeneous conditions (yield 20%, 6 h, 305 K, CH₂Cl₂ solvent). In contrast, the crystalline solid of dodecatungstophosphoric acid, H₃[PW₁₂O₄₀], and its derivative supported on silica have been reported to be active for the same reaction under heterogeneous conditions [5a].



2.2. Base catalyses of 1 and 3

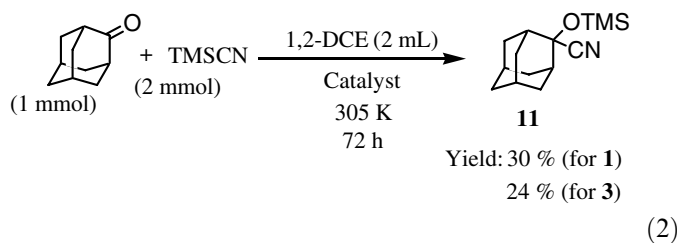
The condensation of benzaldehyde with malononitrile (i.e. “Knoevenagel-type reaction”), is generally considered to be catalyzed by weak bases [15]. In contrast with the order of catalytic activity for Mukaiyama-aldol and carbonyl-ene reaction ($2 \gg 1 \approx 3 \approx 0$), the monomeric cluster **1** and “closed-shape” dimer **3** exhibited high catalytic performance for the present reaction while the “S-shape” cluster **2** was almost inactive (Table 3). Thus, **1** and **3** can abstract protons from the activated methylene moiety.

The catalyses of **1–3** for cyanosilylation of 2-adamantanone with trimethylsilylcyanide (Eq. (2)) were also examined. This reaction is known to be catalyzed both acid and base catalysts [5e]. The base catalysts **1** and **3** exhibited moderate activity (the yields of **11** after 3 days: 30% for **1**, 24% for **3**), while the acid catalyst **2** decomposed during the

Table 2
Catalytic activities for carbonyl-ene reaction.

Catalyst (mol%)	Time (min)	Conversion (%)	Yield of product (%)	
			7 (diastereo selectivity)	8
1 (1.0)	1440	<1	<1	n.d.
2 (0.5)	160	99	84 (1:3:58:38)	4
3 (0.5)	1440	<1	<1	n.d.

reaction. In contrast with the Knoevenagel reaction, **1** and **3** were much less active for the cyanosilylation. This may be related to the basicity and the bulky environment of the basic sites of **1** and **3**.



2.3. Explanation for the acid or base properties of 1–3

The acid catalysis by **2** is likely promoted by (1) the aquo ligand, which works as H⁺ donor (i.e., Brønsted acid), or (2) the coordinatively unsaturated +6-tungsten ion (Lewis acid site) at the lacunary site formed by the dissociation of the coordinated aqua ligand. The diastereoselectivities for both Mukaiyama-aldol and carbonyl-ene reactions are not so high in comparison with those for the epoxidation reactions with hydrogen peroxide by **1**, [γ-SiV₂W₁₀O₃₈(OH)₂]⁴⁻, and [γ-SiT₂W₁₀O₃₆(OH)₂]₂(μ-

Table 3
Catalytic activities for the Knoevenagel reaction

Catalyst (amount, mol%)	Yield of 10 (%)
1 (0.5)	90
2 (0.25)	Trace
3 (0.25)	96

O)₂]⁸⁻, where the sterically hindered active oxygen species were formed [8,16]. The contrast suggests that the present reactions proceed through less hindered intermediates and that **2** works as a Brønsted acid catalyst.

While **1** and **2** retained the “lacunary” sites and the aquo ligands, the catalytic properties were quite different from each other: **1** exhibited rather basic catalysis. From the viewpoint of coordination chemistry, **1** would have amphoteric nature: The oxo ligand(s) at the divacant site works as a base for the dimerization from **1**, and would work as a proton acceptor. On the other hand, the five-coordinated tungsten centers formed by the dissociation of the aquo ligand would bind the oxo ligands of another molecule (i.e., works as an acid for the dimerization process to give **2** and **3**) [9]. Both base catalysts **1** and **3** were efficient for H⁺ abstraction from the less hindered methylene moiety. The basic site in **3** is under investigation.

In conclusion, a series of lacunary γ -Keggin silicotungstate derivatives **1–3**, which were composed of the same [SiW₁₀O₃₂] fragments, catalyzed various C–C bond formation reactions; **2** showed acid catalyses toward Mukaiyama-aldol, carbonyl-ene and Diels–Alder reactions, while **1** and **3** showed base catalyses toward Knoevenagel and cyanosilylation reaction.

3. Experimental section

3.1. Instruments

NMR spectra were recorded at room temperature on a JEOL JNM-EX-270 (¹H: 270 MHz, ¹³C: 67.9 MHz) spectrometer. Chemical shifts (δ) were reported in ppm downfield from internal SiMe₄. Gas chromatographic (GC) analyses were carried out on a Perkin Elmer Autosystem gas chromatograph equipped with a TC-WAX column (30 m, 0.25 mmID, 0.25 μ mdf; GL-Science), and a Shimadzu GC-17A gas chromatograph equipped with a TC-1 column (30 m, 0.25 mmID, 0.25 μ mdf; GL-Science). GC–MS analyses were carried out on a Shimadzu GCMS-QP2010 spectrometer. Liquid chromatographic (LC) analysis was carried out on a Shimadzu HPLC system (pump: LC-10AD, UV-detector: SPD-10A) equipped with Chirapak-AD and Capcellpak C₁₈ columns.

3.2. Materials and methods

The solvents used for the syntheses and catalytic reactions were treated with appropriate drying reagents (nitromethane: MgSO₄, acetonitrile, dichloromethane, and 1,2-dichloroethane: P₂O₅, toluene: Na/benzophenone), distilled, and stored under argon. Benzaldehyde was distilled under reduced pressure in order to remove contaminated benzoic acid, and used immediately after the distillation. 2,3-Dimethylbutadiene was distilled in vacuo prior to use in order to remove hydroquinone (anti-polymerization reagent). The commercially available reagents of the highest grade were used without further

purification. The silicotungstate catalysts **1** [8a], **2** and **3** [9], and the authentic compounds of crossed-aldol reaction products [10a] were prepared according to the reported methods.

3.3. Catalytic reactions

Due to ionic nature of **1–3**, the catalysts were soluble in only polar organic solvent. Especially, the solubility of **2** was quite low, and therefore, nitromethane and acetonitrile were used as solvent for the homogeneous reaction systems. The reaction was carried out in a glass vial with stirring. The Mukaiyama-aldol condensation reactions were carried out as follows: The catalyst containing 25 μ mol of W (i.e., **1**: 2.5 μ mol, **2** and **3**: 1.25 μ mol), solvent (nitromethane: 50 μ L), and substrates (benzaldehyde: 6.4 μ L (62.5 μ mol), 1-trimethylsilyloxycyclohexene: 24.0 μ L (125 μ mol)) were charged in the reaction vial under argon (operated in glove-box). The reaction was carried out at 305 K for 1.5 h. The yield and product selectivity were determined by HPLC, GC, and ¹H NMR analyses. The carbonyl-ene reactions: The catalyst containing 100 μ mol of W (i.e., **1**: 10 μ mol, **2** and **3**: 5.0 μ mol), solvent (dichloromethane: 3.0 mL), and substrates (R-(+)-citronellal: 182 μ L (1.00 mmol)) were charged in the reaction vial. The reaction was carried out at 305 K. The yield and product selectivity were determined by GC, and ¹H and ¹³C NMR analyses. The Diels–Alder reactions: The catalyst containing 100 μ mol of W (i.e., **1**: 10 μ mol, **2** and **3**: 5.0 μ mol), solvent (nitromethane: 4.0 mL), and substrates (2,3-dimethylbutadiene: 135 μ L (1.20 mmol), 1,4-naphthoquinone: 158 mg (1.00 mmol)) were charged in the reaction vial. The reaction was carried out at 305 K for 5 h. The products were assigned by ¹H and ¹³C NMR spectroscopy and the yields were determined by GC analyses. The Knoevenagel-type reactions: The catalyst containing 50 μ mol of tungsten (i.e., **1**: 5.0 μ mol, **2** and **3**: 2.5 μ mol), solvent (acetonitrile: 1.0 mL), and substrates (benzaldehyde: 152 μ L (1.50 μ mol), malononitrile: 62 μ L (1.00 mmol)) were charged in the reaction vial. The reaction was carried out at 305 K for 2.5 h. The yield and product selectivity were determined by GC, and ¹H NMR analyses. The cyanosilylation reactions: the catalyst containing 100 μ mol of W (i.e., **1**: 10 μ mol, **2** and **3**: 5.0 μ mol), solvent (1,2-dichloroethane: 2.0 mL), and substrates (2-adamantanone: 150 mg (1.0 mmol), trimethylsilylcyanide: 279 μ L (2.0 mmol)) were charged in the reaction vial. The reaction was carried out at 305 K for 72 h. The yield and product selectivity were determined by GC, and ¹H and ¹³C NMR analyses.

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