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Isopentatungstate-supported metal carbonyl derivative: synthesis, characterization, and catalytic properties for alkene epoxidation†

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A novel isopentatungstate-supported metal carbonyl derivative $KH[(CH_3)_4N]_3\{[Re(CO)_3]_4[(\mu_2\text{-}OH)(\mu_3\text{-}O)(W_5O_{18})]\}\cdot 6H_2O$ (**1**) has been synthesized and characterized. Compound **1** represents the second example of isopolyoxotungstate-supported metal carbonyl derivative. The catalysis of **1** for alkene epoxidation with H_2O_2 was investigated, and was found to efficiently catalyze the epoxidation of cyclooctene with high conversion (98.9%) and excellent selectivity (99%). Furthermore, the solution behavior of the polyanion **1** was also explored using electrospray ionization mass spectrometry.

Introduction

Polyoxometalates (POMs), anionic metal oxide clusters, have attracted great attention not only due to their remarkable structures and electronic/magnetic properties,[1] but also because of their intriguing applications ranging from catalysis to medicine.[2] POM-based organometallic derivatives have been widely used for the development of materials and catalysts.[3] These inorganic–organic hybrids can enhance the versatility of POMs, thereby leading to a large number of diverse functional POMs with improved properties. Important progress along these lines has been made with organic or organometallic ligands, such as carboxylic acid, alkoxy, organosilicon, organotin, benzyl butyl phthalate and organophosphonates.[4] POM-based metal carbonyl derivatives, as a peculiar class of organometallic oxides,[5] have attracted increasing attention owing to their unique structures and potential catalytic properties.[6] However, compared to other species, POM-based metal carbonyl derivatives were relatively less investigated, mainly because polyanions do not have enough charge density to combine with metal carbonyl groups, along with their poor solubility in the same solvent, their radiation or thermal instability and the expensive prices of metal carbonyl compounds.

At the present time, most of the known clusters are mainly based on mix-addendum type POMs,[7] hetero-POMs,[8] isopolyoxomolybdates,[9] isopolyoxoniobates and isopolyoxotantalates.[10] Table 1 shows the isopolyoxometalate-based metal carbonyl derivatives. Up until now, only one example of an isopolyoxotungstate-based metal carbonyl derivative $\{[H_2W_8O_{30}][M(CO)_3]_2\}^{8-}$ (M = Mn^I and Re^I) was reported by our group in 2011.[11] Furthermore, isopolyoxotungstates show prominent selective catalysis for olefin epoxidation[12] and the catalytic reaction rate can be significantly increased by the incorporation of functionalized ligands.[13] Recently, we reported an organotriphosphonate polyoxotungstate, $[\{(AsW_9O_{33})Zn(H_2O)W_5O_{11}(NCH_2PO_3)_3)\}_2(\mu_2\text{-}O)_2]^{14-}$, and the catalysis for alkene epoxidation with hydrogen peroxide (H_2O_2) as the oxidant was studied.[14]

Table 1 Summary of iso-POMs based on metal carbonyl compounds

Formulas	Ref.
$[(\eta^5\text{-}C_5H_5)Ti(Mo_5O_{18})Mn(CO)_3]^{2-}$	9*a* and *d*
$[Mo_6O_{16}(OCH_3)_2\{HOCH_2C(CH_2O)_3\}_2\{Mn(CO)_3\}_2]^{2-}$	
$[Mo_2O_5(OMe)_5\{M(CO)_3\}_2]^-$ (M = Re, Mn)	9*b*
$[Mo_2O_4(OMe)_6\{Mn(CO)_3\}_2]$	
$[Mo_2O_6(OMe)_4\{Re(CO)_3\}_2]^{2-}$	
$[Mo_2O_4\{RC(CH_2O)_3\}_2\{Mn(CO)_3\}_2]$ (R = Me, CH_2OH)	
$[M(CO)_3(H_2O)\{Mo_5O_{13}(OMe)_4(NO)\}]^{2-}$(M = Mn, Re)	9*c*
$[Na\{Mo_5O_{13}(OMe)_4(NO)\}_2\{Mn(CO)_3\}_2]^{3-}$	
$[Mn(H_2O)_2\{Mo_5O_{16}(OMe)_2\}\{Mn(CO)_3\}_2]^{4-}$	
$[\{H_2Mo_8O_{30}\}\{M(CO)_3\}_2]^{8-}$ (M = Mn^I, Re^I)	9*e*
$[M_6O_{19}\{M'(CO)_3\}_n]^{(8-n)-}$ (M = Nb, Ta; M′ = Mn, Re; *n* = 1, 2)	10
$[\{H_2W_8O_{30}\}\{M(CO)_3\}_2]^{8-}$ (M = Mn, Re)	11

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†Electronic supplementary information (ESI) available: The summary of POM-based carbonyl metal derivatives, the XRPD patterns, IR spectra, TGA and the UV-vis spectrum of **1** (Fig. S1–S6); crystallographic data of **1** (Table S1), bond valence sum calculations of O (Table S2), structural figure (Fig. S7); catalytic properties (Table S3). CCDC 1446505. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6dt00352d

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Herein, we present an example of isopentatungstate-supported four metal carbonyl derivative, $KH[(CH_3)_4N]_3\{[Re(CO)_3]_4[(\mu_2\text{-}OH)(\mu_3\text{-}O)(W_5O_{18})]\}\cdot 6H_2O$ (**1**), which is the second example of an isopolyoxotungstate based metal carbonyl derivative, and has the largest number of metal carbonyl groups. The catalysis of **1** for the conversion of olefin into epoxide with a hydrogen peroxide (H_2O_2) oxidant was studied. Under optimal conditions, cyclohexene was oxidized to the expected 1,2-epoxycyclooctane with high conversion (98.9%) and excellent selectivity (99%). The stability of the cluster was explored using electrospray ionization mass spectrometry (ESI-MS).

Experiment

Instrumentation

All other chemicals were used as purchased without purification. The precursor $K_7Na[HBW_{11}O_{39}]\cdot 13H_2O$ was synthesized as previously described,[15] which was confirmed using FT-IR spectroscopy. A crystallography sample of compound **1** was synthesized using a conventional step-by-step method. The FT-IR spectra were measured on a Bruker VERTEX 70 IR spectrometer using KBr pellets in the range of 4000–500 cm^{-1}. Thermogravimetric (TG) analysis was performed under a N_2 atmosphere using a Mettler-Toledo from 25 to 1000 °C. UV-vis spectra were obtained with a U-4100 spectrometer at room temperature. Elemental analyses (C, H, N) were conducted on a Perkin-Elmer 2400-II CHNS/O analyzer. Inductively coupled plasma (ICP) spectra were obtained on a Perkin-Elmer Optima 2000 ICP-OES spectrometer. X-ray powder diffraction (XPRD) spectral data were recorded on a Bruker AXS D8 Advance diffractometer with Cu Kα radiation in the angular range 2θ = 5–45° at 293 K (Fig. S2†). All electrochemical measurements were performed at room temperature in a standard three-electrode cell connected to a LK98 microcomputer-based electrochemical system. A freshly cleaned glassy carbon disk electrode (3 mm diameter) was used as a working electrode, a platinum wire served as the counter electrode and an Ag/AgCl electrode as the reference electrode. ESI-MS measurement was carried out on an ABSCIEX Triple TOF 4600 mass spectrometer, and the data were collected in the negative mode.

Preparation of $KH[(CH_3)_4N]_3\{[Re(CO)_3]_4[(\mu_2\text{-}OH)(\mu_3\text{-}O)(W_5O_{18})]\}\cdot 6H_2O$

$Re(CO)_5Cl$ (0.135 g, 0.373 mmol) was dissolved in 3 mL of CH_3CN at 70 °C in the dark for 0.5 h, then $K_7Na[HBW_{11}O_{39}]\cdot 13H_2O$ (0.4 g, 0.125 mmol) was dissolved in 10 mL of distilled water and boiled for 15 minutes, then cooled for 15 minutes and added. The solution mixture was heated at 80 °C for 1 h, and orange clear liquid was observed. Additional $(CH_3)_4NCl$ (0.1 g, 1.0 mmol) was added, then cooled and filtrated. The filtrate was allowed to stand at room temperature in the dark for slow evaporation. Yellow block crystals of **1** were isolated after two weeks. Yield: *ca.* 18.81% (based on $Re(CO)_5Cl$). Anal. calcd (found %) for $C_{24}H_{48}KN_3O_{38}Re_4W_5$: C 10.71 (10.84), H 1.87 (1.85), K 1.45 (1.51), N 1.56 (1.56), Re 27.67 (27.87), W 34.15 (35.06). IR (KBr, cm^{-1}): 3036 (w), 2024 (vs), 2006 (vs), 1862 (vs), 1639 (w), 1485 (s), 947 (s), 902 (s), 886 (s), 854 (s), 796 (s), 717 (s), 677 (w), 580 (w), 533 (w).

X-ray crystallography

A yellow block crystal of **1** (dimensions 0.41 mm × 0.18 mm × 0.15 mm) was selected and airproofed in a glass tube. X-ray diffraction intensity data were measured on a Bruker D8 SMART APEX-II CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 296 (2) K. Routine Lorentz and polarization corrections were applied. The absorption correction was based on multiple and symmetry-equivalent reflections in the data set using the SADABS program. The structure was solved by direct methods and refined using full-matrix least squares on F^2. The crystal was kept at 296 (2) K during data collection. Using Olex2,[16] the structure was solved with the ShelXS-1997[17] structure solution program using Direct Methods and refined with the ShelXL[18] refinement package using Least Squares minimisation. No hydrogen atoms associated with the water molecules were located from the difference Fourier map. A summary of the crystal data and structure refinements is listed in Table S1.†

Results and discussion

Synthesis

The preparation of POM-based metal carbonyl derivatives has been a challenge for the following reasons: most polyoxoanions have not enough charge density to combine with metal carbonyl groups; their poor solubility in the same solvent; the radiation or the light-thermal instability of carbonyl; the expensive prices of metal carbonyl compounds. Compound **1** was synthesized by the reaction of $K_7Na[HBW_{11}O_{39}]\cdot 13H_2O$ with tetramethylammonium chloride and $Re(CO)_5Cl$ in a mixed solution ($CH_3CN : H_2O$ = 3 : 10) at 80 °C. Parallel experiments indicate that several factors affect the formation of compound **1**. The optimal pH range of the reaction is from 6.5 to 7.4. For a lower pH (pH < 6.5), the yield was reduced, while for a higher pH (pH > 7.4), no crystal was obtained. Except for the vital factor of pH, the cation also plays an important role in getting the crystal. Compound **1** can not be obtained with the use of potassium chloride, tetrabutylammonium bromide and guanidine hydrochloride. Meanwhile, the molar ratio of CH_3CN/H_2O also reflects the composition of the final products in the synthetic procedure.

Structural description

Single-crystal X-ray diffraction analysis reveals that the compound **1** is monoclinic, which is extended to a two-dimensional (2D) framework connected by $[\{K(H_2O)_2\}_2]^{2+}$ groups *via* terminal oxygen atoms (Fig. 2b). Along the line of the *b*-axis, the polyanions are connected by K–O to form a one-dimensional (1D) chain (Fig. 2a). Compound **1** consists of one $[\{Re(CO)_3\}_4(\mu_2\text{-}OH)(\mu_3\text{-}O)(W_5O_{18})]^{5-}$ (**1a**) unit (Fig. 1b), three

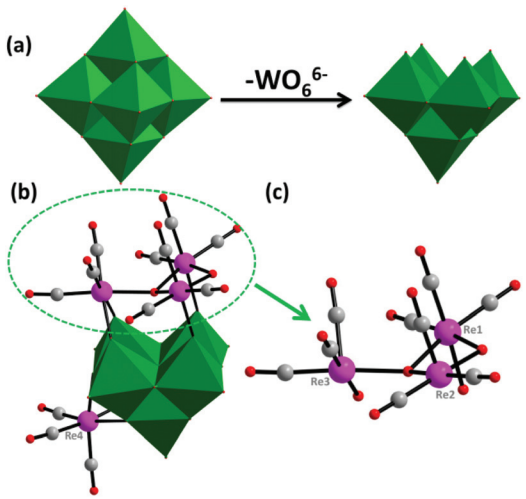

Fig. 1 (a) Polyhedral representation of $[W_6O_{19}]^{2-}$ and $[W_5O_{18}]^{6-}$; WO_6 octahedral, green; (b) ball-and-stick representation of **1a**; (c) ball-and-stick representation of $\{[Re(CO)_3]_4[(\mu_2\text{-}OH)(\mu_3\text{-}O)]\}^+$. Colour code: Re, purple; O, red; C, gray; WO_6, green.

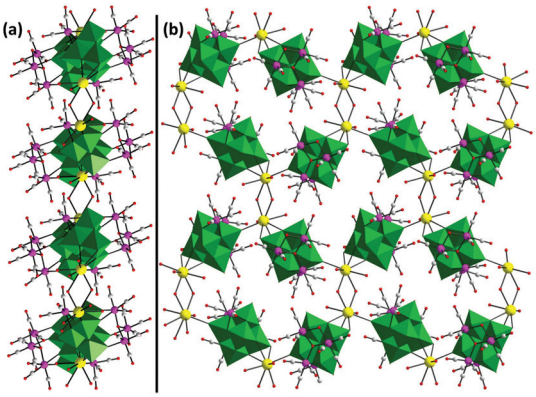

Fig. 2 (a) View of the 1D chain along the *b*-axis; (b) polyhedral/ball-and-stick representation of the 2D layer along the *a*-axis. Colour code: W, green; K, yellow; Re, purple; C, gray; O, red; WO_6 octahedral, green.

$[(CH_3)_4N]^+$ cations, one K^+ cation, one proton and six crystal water molecules. **1a** can be regarded as four metal carbonyl attached to a $[W_5O_{18}]^{6-}$ subunit (Fig. 1a), which is closely related to the Lindqvist hexatungstate structure with one $\{WO_6\}$ octahedron removed from $\{W_6O_{19}\}$. In the structure of **1a**, rhenium atoms can be divided into two categories. The trimetric metal model cluster $\{Re_3\}$ is capped on the $[W_5O_{18}]^{6-}$ subunit through four Re–O–W bonds. The distance of Re1–Re3, Re1–Re2 and Re2–Re3 is 3.849(6), 3.427(6) and 3.845(6) Å, respectively. In addition, the Re4 fragment is linked to the subunit through three Re–O–W bonds.

IR spectra

The IR spectrum of **1** has been recorded between 4000 and 500 cm^{-1} with KBr pellets (Fig. S3†). The IR spectrum of **1** displays strong absorption bands at 947, 902, 886, 854, 796, 717, 677, 580, and 533 cm^{-1}, which are associated with W–O vibrations. And another three strong bands at 2024, 2006, and 1862 cm^{-1} are assigned to CO groups. Compared with that of $Re(CO)_5Cl$ (Fig. S4†), the spectrum of **1** shows some red shift, which may be caused by the metal carbonyl and the anion bond. Moreover, the resonance at 3036 cm^{-1} belongs to –OH and –NH stretching vibrations while the flexural vibrations of –OH and –NH are observed at 1639 and 1485 cm^{-1}, respectively, which shows the existence of water molecules and $(CH_3)_4N^+$. These results are in good agreement with those of the X-ray diffraction structural analysis.

Thermogravimetric analysis

To examine the thermal stability of **1**, thermal gravimetric analysis (TGA) was implemented under a N_2 atmosphere. The TG curve of **1** can be regarded as a two-steps weight loss process, giving a total loss of 29.07% (calcd 29.28%) in the range of 25–1000 °C (Fig. S5†). The first stage from 25–310 °C is ascribed to the loss of six lattice water molecules, and the observed weight loss 3.86% is consistent with the calculated value 4.01%. The second stage with the weight loss of 25.21% may be attributed to the removal of twelve carbonyl units, three tetramethylammonium cations and two protons (in the form of constitutional water molecules), and the sublimation of one ReO_3 (calcd 25.27%).

ESI-MS

ESI-MS is powerful way to determine whether the structural framework is maintained in solution and further infer the nature of the compound present in solution. The negative mode mass spectrum of **1** in acetonitrile is shown in Fig. 3. The spectrum displays three main peaks at 1217.7, 1226.6 and 1235.2, corresponding to the formula of $[KH\{(CH_3)_4N\}\{Re(CO)_3\}_4(\mu_2\text{-}OH)(\mu_3\text{-}O)(W_5O_{18})]^{2-}$, $[KH\{(CH_3)_4N\}\{Re(CO)_3\}_4(\mu_2\text{-}OH)(\mu_3\text{-}O)(W_5O_{18})(H_2O)]^{2-}$ and $[\{(CH_3)_4N\}_2H\{Re(CO)_3\}_4(\mu_2\text{-}OH)(\mu_3\text{-}O)(W_5O_{18})]^{2-}$, respectively. These results suggest that the structure of **1a** in solution is stable.

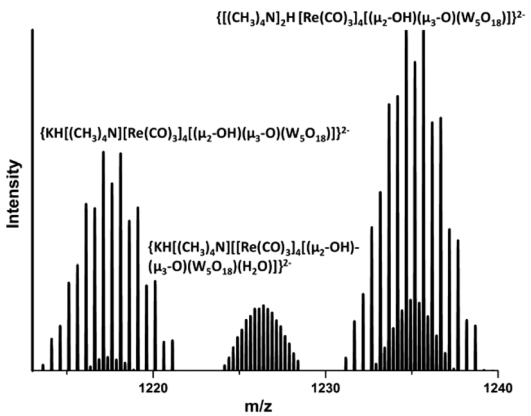

Fig. 3 Negative-ion ESI-MS mass spectrum of **1a** in acetonitile.

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Cyclic voltammetry

In order to investigate the properties of **1** in the mixed solvent CH_3CN–H_2O (1 : 3, volume ratio), the UV-vis spectra were monitored. The UV-vis spectra of **1** are measured in the range of 190–500 nm, and the band at about 270 nm can be attributed to the terminal oxygen to tungsten charge transfer, which suggests the presence of the polyoxoanions.[9e]

As shown in (Fig. S6†), compound **1** remains stable for at least 10 h at room temperature in a dark environment. The electrochemical behaviours of **1** were then explored. Cyclic voltammetric measurements of compound **1** were carried out in the mixed solvents CH_3CN–Na_2SO_4 (0.4 mol L^{-1}) (1 : 3, volume ratio). The electrochemical behaviours are investigated in the potential range of +1.5 to −0.8 V (Fig. 4), and one pair of closely spaced reversible peaks, one irreversible cathodic peak and two irreversible anodic peaks are exhibited for the redox process of the W(VI) atoms and $[Re(CO)_3]^+$ pendants,[19] respectively. As seen in Fig. 4, the two anodic peaks located at +1.180 and +1.094 are attributed to the oxidation of Re(I).[8g] There exists one reversible redox peak (I/I′), whose half-wave potential $E_{1/2} = (E_{pa} + E_{pc})/2 = 0.35$ V, which corresponds to the redox processes of the W^{VI} centres. It is to be noted that there is an additional irreversible cathodic peak which should be assigned to the W atom.[20] As shown in the inset figure, the peak currents are proportional to the scan rates, indicating that the redox processes are probably surface-controlled (E_{pa} and E_{pc} are the values of the anodic and of the cathodic peak potential).

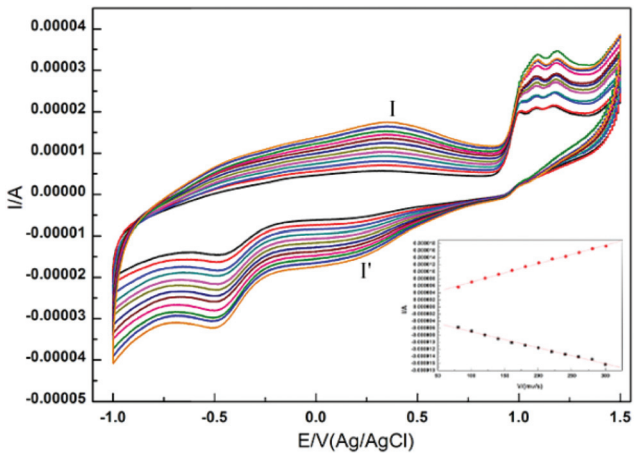


Fig. 4 The CV curves of **1** in the mixed solvent CH_3CN–Na_2SO_4 (0.4 mol L^{-1}) (1 : 3, volume ratio) at different scan rates (from inner to outer: 80, 100, 120, 140, 160, 180, 200, 220, 240, 260, 280, 300 mV s^{-1}). Inset figure: the variation of the peak current intensity for the W^{VI} is proportional to the scan rates from 80 to 300 mV s^{-1} of **1**.

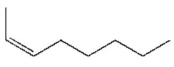
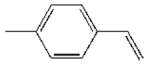
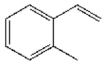
Table 2 Epoxidation of cyclooctene with H_2O_2 [a]

Olefin $\xrightarrow[H_2O_2,\ CH_3CN]{\text{Catalyst 1}}$ Epoxide

Entry	Catalytic (mg)	Substrate	Temp. (°C)	Time (h)	Conv.[b] (%)	Sel. (%)
1	9		25	1	Trace	
2	9		65	1	92.7	99
3	9		70	1	96.3	
4	9		75	0.25	55.3	
5	9		75	0.5	82.3	
6	9		75	0.75	91.6	
7	9		75	1	98.9	
8	6.75		75	1	90.9	
9	4.5		75	1	65.6	

[a] Reaction conditions: catalyst (3.3 μmol, 2.5 μmol, 1.6 μmol); substrate (1 mmol); H_2O_2 (2 mmol); acetonitrile (5 mL). [b] Determined by gas chromatography (GC) analyses based on initial substrate.

Table 3 Epoxidation of alkenes with H_2O_2 [a]

Entry	Catalytic (mg)	Substrate	Temp. (°C)	Time (h)	Conv.[b] (%)	Sel. (%)
1	9		75	1	98.9	99
2	9		75	8	77.5	50.4
3	9		75	8	93.8	70.0
4	9		75	9	73.6	48.4
5	9		75	24	60.0	60.2
6	9		75	19	61.5	41.9
7	9		75	19	43.3	47.0

[a] Reaction conditions: catalyst (3.3 μmol); substrate (1 mmol); H_2O_2 (2 mmol); acetonitrile (5 mL). [b] Determined by gas chromatography (GC) analyses based on initial substrate.

Catalytic properties

Complex **1** was investigated as a homogeneous catalyst in alkene epoxidation with H_2O_2, and demonstrated excellent activity at low catalytic dosage (Tables 2 and 3). Initial experiments were performed using cyclooctene as a model substrate with 2 equiv. of H_2O_2 at room temperature (25 °C). As shown in Table 1, the conversion remarkably changed, which indicated that the reaction time, the catalytic dosage and temperature were the important factors that influence the conversion of epoxide products. A blank experiment without **1** (Table S3†) confirmed that the epoxidation would not occur. In contrast to catalyst **1**, the epoxidation reaction without POM species indicated that the conversion scarcely happened. Therefore, we speculated that the catalytic reaction may be concentrated on the isopolyoxotungstate units. Under optimal conditions (3.3 μmol substrate and 2 mmol H_2O_2), cyclooctene was oxidized to epoxide with 98.9% conversion and 99% selectivity at 75 °C (Table 2, entry 7), respectively. Notably, this reaction is very efficient in terms of oxidant utilization.

The catalytic activities of other olefins like 2,3-dimethyl-2-butene, 1-methyl-1-cyclohexene and cyclohexene, *etc*. were also tested under the same reaction conditions. The results presented in Table 2 demonstrate the variable reactivity of alkene substrates: cyclooctene affords the highest epoxide yields and selectivity, while 2,3-dimethyl-2-butanes and 1-methyl-1-cyclohexene are less reactive corresponding to 93.8% conversion and 70.0% selectivity (Table 3, entry 3) and 77.5% conversion and 50.4% selectivity (Table 3, entry 2), respectively. Next, other substrates such as cyclohexene gave 73.6% conversion and 48.4% selectivity (Table 3, entry 4), *cis*-2-octene gave 60.0% conversion and 60.2% selectivity (Table 3, entry 5), 4-methylphenylene gave 61.5% conversion and 41.9% selectivity (Table 3, entry 6), and 2-methyl styrene gave 43.3% conversion and 47.0% selectivity (Table 3, entry 7), respectively.

Conclusion

In summary, we have synthesized an isopentatungstate-supported metal carbonyl derivative, $KH[(CH_3)_4N]_3\{[Re(CO)_3]_4[(\mu_2\text{-}OH)(\mu_3\text{-}O)(W_5O_{18})]\}\cdot 6H_2O$. It is the second example of an isopolyoxotungstate supported metal carbonyl derivative. Interestingly, it has the largest number of metal carbonyl groups of POM-based metal carbonyl derivatives. Furthermore, compound **1** shows high catalytic activity for the epoxidation of various olefins with hydrogen peroxide. The next work will concentrate on improving the activity and selectivity for alkene epoxidation and the synthesis of novel structural derivatives.

Acknowledgements

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