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COMMUNICATION

A monovacant heteropolytungstate-incorporated trimeric carbonyl rhenium cluster, $[(AsW_{11}O_{39})\{Re(CO)_3\}_3(\mu_3-OH)(\mu_2-OH)]^{6-}$: synthesis, structure and catalytic property

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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An undecatungstoarsenate-supported carbonyl rhenium derivative, $[(AsW_{11}O_{39})\{Re(CO)_3\}_3(\mu_3-OH)(\mu_2-OH)]^{6-}$ (1a**) has been synthesized. Polyoxoanion **1a** consists of one monovacant Keggin structure unit and an unusual trimeric carbonyl rhenium cluster. It exhibits prominent catalytic activity and high selectivity in the cycloaddition of epoxides.**

Polyoxometalates (POMs), a category of amusing functionalized metal oxide clusters, are of great interest due to their structural diversity and attractive applications in medicine, magnetism, electro/photo-chromism and catalysis.^[1] Meanwhile, metal carbonyl unit is also a good multi-functionalized ligand.^[2] Immobilization of activated metal carbonyl units on the bare POMs surface, that is the direct functionalization of POMs, is well-documented and credible, which is expected to be more attractive.^[3]

In this context, POM-based metal carbonyl derivatives (MCDs) have been receiving increasing interest since the first POM-incorporating carbonyl cobalt derivative was reported by Knoth in 1979.^[4] However, most of the previous reports in this field are dominated by plenary isopolyoxometallates.^[5] In comparison, lacunary heteropolytungstates (HPTs) of the Keggin and Wells–Dawson type are excellent ligands allowing for the construction of various metal-oxo assemblies.^[1b] However, the reports on HPTs-supported MCDs are very rare. In 2008, Sadakane et al. communicated the first example of monolacunary HPT-based MCD $[\alpha-SiW_{11}Ru^{II}(CO)]^{6-}$, in which the Ru atom fully occupied the lacunary site of the Keggin framework.^[6] In 2012, our group reported two new complexes, $[(OC)_3Mn(A-\alpha-H_2XW_9O_{34})]^{8-}$ (X = Ge or Si), in which the $[(OC)_3Mn]^+$ group attached the “W₃O₉” cap on the unsaturated polyanion surface *via* three Mn–O–W linkages.^[7] Subsequently, Hill’s group announced another two types of sandwich analogues, $[P_4W_{35}O_{24}\{Re(CO)_3\}_2]^{16-}$ ^[8a] and $[X_2W_{20}O_{70}\{M(CO)_3\}_2]^{12-}$ (X = Sb, Bi and M = Re, Mn)^[8b]. Very recently, they also reported a new tri-rhenium carbonyl cluster based on monolacunary Wells–Dawson type phosphotungstate, $[P_2W_{17}O_{61}\{Re(CO)_3\}_3\{ORb(H_2O)\}(\mu_3-OH)]^{9-}$ ^[8c]. Hitherto, despite some progress, the search for novel POM-based MCD is still a challenge mainly because most polyoxoanions have not enough charge density to combine with metal carbonyl groups,

accompanying with the dissolved incompatibility, the light-thermal instability and the expensive prices of metal carbonyls.^[5b]

Herein, we present the synthesis and structure of an intriguing undecatungstoarsenate-based trimeric rhenium carbonyl cluster, $[(CH_3)_4N]_{13}[H_{11}(AsW_{11}O_{39})_4\{Re(CO)_3\}_3(\mu_3-OH)(\mu_2-OH)] \cdot 23H_2O$ (**1**). We have also discussed the catalytic properties and potential value of POM-based MCDs in the cycloaddition of epoxides for the first time.

Compound **1** was synthesized by reaction of $Re(CO)_5Cl$ and $[(CH_3)_4N]_8[HASW_9O_{34}] \cdot 11H_2O$ (**1b**) in the CH_3CN-H_2O mixed solvent under mild condition [see details in the Supporting Information, Section S1]. It is noteworthy that the trivalent metastable polyanion $[HASW_9O_{34}]^{8-}$ can easily transforms into $[AsW_{11}O_{39}]^{7-}$ configuration in the weak acid environment (pH > 5 nearly).^[9,10] Single crystal X-ray diffraction analysis reveals that compound **1** crystallizes in tetragonal space group $P-42(1)c$. Structure unit of **1** contains four polyoxoanions $[(AsW_{11}O_{39})-Re(CO)_3\}_3(\mu_3-OH)(\mu_2-OH)]^{6-}$ (**1a**), which displays two pertinent features: the presence of monolacunary Keggin fragment; and the presence of the trimeric metal model $\{Re_3\}$ cluster, which is capped on the lacunary site of Keggin fragment through four Re–O–W bonds (Re–O: 2.05(2)–2.219(17) Å), resulting a out-of-pocket motif (Fig. 1a, Fig. S1).

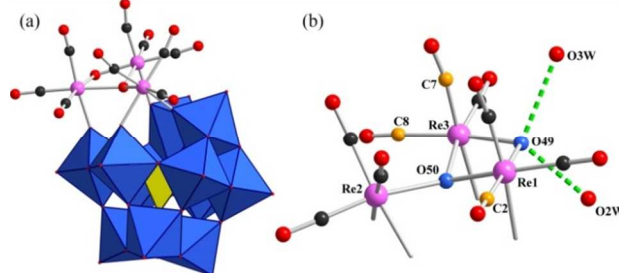


Fig. 1 (a) polyhedral and ball-and-stick representation of polyoxoanion of **1**; (b) ball-and-stick representation of $[(Re(CO)_3)_3(\mu_3-OH)(\mu_2-OH)]^+$. Re, purple; O, red; hydroxyl oxygen atoms, blue; C, dark gray; Activated C, orange; AsO₄, yellow; WO₆, blue.

The suspended $\{Re_3\}$ cluster, Re1 connect Re3 with μ_2 -O49 to form a $[(Re(CO)_3)_2O]$ cluster, simultaneously, $[(Re(CO)_3)_2O]$ cluster and Re3 atoms link together with μ_3 -O50, ultimately forming a

steady-going approximate isosceles triangle (Fig. 1b). The distances between Re1–Re3, Re1–Re2 and Re2–Re3 are 3.413(2), 3.874(2) and 3.856(2) Å, respectively. Moreover, rhenium atoms here can be divided into two categories. On one hand, Re2 centre coordinated with three carbonyl ligands, two terminal oxygen atoms from the mono-lacunary POM and a μ_3 -O50 atom. On the other hand, Re1 and Re3 display similar coordination environment. Each of them is ligated by three carbonyl units, one μ_3 -O50 atom, one μ_2 -O49 atom and one terminal oxygen atom from POM unit, forming a distorted six-coordinated ReO_3C_3 octahedral geometry. Furthermore, the C–O bond lengths range from 1.07(4) to 1.24(4) Å, while the Re–C bond lengths in **1a** range from 1.80(4) to 1.98(4) Å. These bond lengths are consistent with those observed for other Re(I) carbonyl complexes.^[5g,h,8]

It is worth noting that polyoxoanion **1a** resembles structurally the $\{\text{P}_2\text{W}_{17}\text{O}_{61}\{\text{Re}(\text{CO})_3\}_3\}$ cluster of Hill and coworkers.^[8c] Both polyoxoanions **1a** and $\{\text{P}_2\text{W}_{17}\text{O}_{61}\{\text{Re}(\text{CO})_3\}_3\}$ contain one $\{\text{Re}_3\}$ cluster. Relevant data shows some points at strong resemblance between them. Firstly, the bond lengthed (Re1–O50: 2.147(17) Å; Re2–O50: 2.219(17) Å; Re3–O50: 2.196(19) Å) are similar with or even a little longer than those in the $[\{\text{Re}(\text{CO})_3\}_3\{\text{ORb}(\text{H}_2\text{O})\}(\mu_3\text{-OH})]^{+}$ cluster (details given in Table S2). Secondly, the bond valence sum (BVS) calculations^[11] for all the oxygen atoms in **1a** indicate that μ_2 -O49 and μ_3 -O50 are monoprotonated (blue in Fig. 1b, Fig. S3, Table S3). The hydrogen bonds between O50 and the 附近的 bridging oxygen atoms in POM fragment which can facilitate stabilize the structure and transmit electrons (Fig. S2). To the best of our knowledge, it is the only one compound which multinuclear $\{\text{M}(\text{CO})_3\}^{+}$ incorporated into Keggin-type-POM.^[8c]

The BVS calculations show all W atoms and As atom are in the +6 and +5 oxidation states, respectively (Table S4). Furthermore, charge-balance considerations with counter cations suggest that compound **1** contains other eleven protons which may be delocalized in **1a**, and this is common in POM chemistry.^[12] The number of lattice water molecules of the complex was ascertained by TG analysis. Meanwhile, the experimental powder X-ray diffraction (PXRD) pattern is in good agreement with the simulated PXRD pattern based on the results of single-crystal X-ray diffraction, indicating the phase purity of the product (Fig. S4). In addition, the peaks at 2023, 2005 and 1879 cm^{-1} in IR spectrum are attributed to C–O stretching modes, two asymmetric and one symmetric stretching vibration, respectively, while the peaks in the lower wave region (1000–700 cm^{-1}) are characteristic for $[\text{AsW}_{11}\text{O}_{39}]^{7-}$ (Fig. S5).^[13]

The UV–vis spectra of $[(\text{CH}_3)_4\text{N}]_8[\text{HAsW}_9\text{O}_{34}]\cdot 11\text{H}_2\text{O}$, $\text{Re}(\text{CO})_5\text{Cl}$ and **1** are shown in Figure S6. The band at about 251 nm can be attributed to the charge transfer transition $\text{O}_{2p} \rightarrow \text{W}_{5d}$ suggesting the presence of the Keggin polyoxoanions (Fig. S6, black line).^[9] While the absorption band at 311 nm is assigned to $\text{Re}(\text{d}\pi) \rightarrow \text{CO}(\pi^*)$ charge transfer transition (Fig. S6, red line).^[14] On the basis of previous studies, the broad absorption band of **1** in the high visible region is likely belong to charge-transfer from Re canters to POM ligand.^[8a] Furthermore, time-dependent and pH variable of **1** see details in the supporting information.

The CV behaviours of **1** exhibit two pairs of closely spaced reversible and two irreversible redox waves (Fig. S11) which result from the cooperation of the redox process of the W^{VI} atoms and $[\text{Re}(\text{CO})_3]^{+}$ pendants.^[15] The electrocatalytic behaviours of NO_2^{-} and H_2O_2 by **1** are also investigated (Fig. S12–S13). Obviously, there is an irreversible oxidation peak that appears at the positive potential region as the nitrite is added. The parallel CVs of the $\text{CH}_3\text{CN}-\text{Na}_2\text{SO}_4$ (0.4 $\text{mol}\cdot\text{L}^{-1}$) solution containing 0.0–0.5 mM NaNO_2 in the absence of **1** have been done, and the positive peak is confirmed to be NO_2^{-} (Fig. S12). The reduction peak and

corresponding oxidation peak currents of W canters in the negative direction increase dramatically with stepwise addition of nitrite which exhibit well electrocatalytic activity for NaNO_2 , as well as H_2O_2 . In addition, below 300 $\text{mV}\cdot\text{s}^{-1}$, the peak currents are proportional to the root of the scan rates (Fig. S11b), indicating that the redox processes are probably surface-controlled in the range of 50–300 $\text{mV}\cdot\text{s}^{-1}$.^[16]

Scheme 1. Cyclic carbonates synthesis from epoxides and CO_2

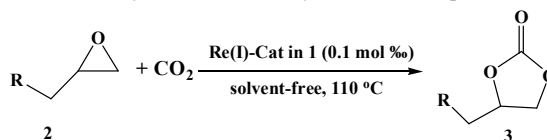


Table 1. Coupling of epoxides with CO_2 catalyzed by **1**

entry	time (h)	CO_2	Yield ^e	TON
1 ^a	24	5.0	72.5%	7250
2 ^a	24	3.0	50.4%	5040
3 ^a	24	1.0	22.4%	2240
4 ^a	12	5.0	40.7%	4070
5 ^b	24	5.0	86.1%	4305
6 ^c	24	5.0	26.6%	—
7 ^d	24	5.0	25.7%	1285

^a R = Cl, reactions were carried out at 110 °C by using 0.1 mol % of **cat.1** in a 25 mL autoclave. ^b R = Cl, 0.2 mol % of **cat.1**. ^c R = Cl, blank experiment. ^d R = H, 0.2 mol % of **cat.1**. ^e GC yield based on **2** used.

Catalysis ability of both $\text{Re}(\text{CO})_5\text{Br}$ and POMs have been studied,^[17,18] but related properties for POM-based MCDs have not report yet. $\text{Re}(\text{CO})_5\text{Br}$ catalytic for coupling of epoxides with CO_2 gave product in 97 % GC yield in the presence of 0.1 mol % amount of catalytic.^[17a] While, good yield (83 %) and excellent selectivity (99 %) was given by (0.1 mol %) POMs-catalytic.^[18a] The potential catalysis property of the combination of both arouses our curiosity.

The catalytic amount is always 0.1 mol % (relative to epoxide). We only take small dosage to promote the reaction as tentative plan, whereas the preliminary trial data suggest that the experimentally fact matches suspect. The cycloaddition of CO_2 to chloromethyloxirane (**2a**) was carried out in a stainless-steel autoclave (25 cm^3 inner volume). When fixing the quantify of **Cat.1** (0.1 mol %), the yield of converting the reagent into 4-chloromethyl-[1,3] dioxolan-2-one (**3a**) is 72.5 % and selectivity overs 99 % in the presence of CO_2 (5.0 MPa) within 24 h at 110 °C (entry 1). The superior TON and TOF values are listed as follows: TON 7250, TOF 302 h^{-1} 0.1 mol% **Cat.1**, and these values are further better than who Hua's group reported (TON 970, TOF 40 h^{-1} , 0.1 mol%, $\text{Re}(\text{CO})_5\text{Br}$).^[17a] And the results indicate that the reaction rate was increased considerably on increasing the CO_2 pressure. Meanwhile, when the primal reaction time was decreased to 12 h, the yield was cut down to 40.7 % (entry 4). While increasing the ratio of **Cat.1** to 0.2 mol % under the same condition, the yield of propylene carbonate remarkably increased to 86.1 %, with the TON of 4305 (entry 5)(Fig. S15). Less than ideal conversion of the low boiling epoxides, for example, propylene oxide (**2b**) was obtained under the same condition.

The catalytic mechanism in the reaction of cycloaddition of epoxides with CO_2 catalyzed by **1** is currently unclear but probably follows that proposed for $\text{Re}(\text{CO})_5\text{Br}$.^[17a] Meanwhile, Hu's group also showed us a postulated reaction mechanism which emphasized the significance of substituted transition metal as active site.^[18a] Crystallographic data may provide conceivable preliminary evidences to speculate the reaction mechanism of the catalytic. Notably, the Re1–C2, Re3–C7 and Re3–C8 bond lengths are about 0.073 Å (on average) longer than other Re–C bonds (mean values:

Re–C 1.857 Å) (Table S2). The hydrogen bonds between protonated μ_3 -O50 and bridging oxygen atoms in POMs as well as μ_2 -O49 and O2W, O3W also drive the catalysis to occur in the {Re3} cluster (Fig. S2). Meanwhile, the crystallographic data of Re2–O50 was about 0.05 Å longer than other Re–O50 bonds, which may also support above hypothesis. The feasible catalytic procedure here may divides into two steps: the undecatungstoarsenate [AsW₁₁O₃₉]⁷⁻ segment first activates the corresponding Re–O–W bond to form an active rhenium centre, which makes CO₂ coordinated to the metal centre easily and then attacks epoxides leading to the formation of propylene carbonate. At the same time, hydrogen bonds between the protonated O49, O50 and the nearby oxygen atoms also induce the catalysis occurs on Re1 and Re3 atoms.^[19]

In conclusion, we present the synthesis of an unprecedented trimeric carbonyl rhenium cluster incorporated into undecatungstoarsenate. Furthermore, compound **1** shows excellent catalytic activity for cycloaddition of epoxy chloropropane, and its potential applications prospect is viewed. In future, we will extend this approach to other metal carbonyl species.

We gratefully acknowledge financial support from the Natural Science Foundation of China, the Natural Science Foundation of Henan Province for financial support.

Notes and references

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† Electronic Supplementary Information (ESI) available: Synthesis and general characterization of compound **1**, crystallographic data and crystal structure figures. CCDC-981546. See DOI: 10.1039/b000000x/

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