Supporting Information

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

Jie Li, Jipeng Guo, Jiage Jia, Pengtao Ma, Dongdi Zhang□, Jingping Wang and Jingyang Niu□

Henan Key Laboratory of Polyoxometalate Chemistry,
Institute of Molecular and Crystal Engineering,
College of Chemistry and Chemical Engineering,
Henan University, Kaifeng 475004, Henan, China,
E-mail: ddzhang@henu.edu.cn, jyniu@henu.edu.cn; Fax: (+86)371-23886876.

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Section 1. Summary of POM-based metal carbonyl compounds

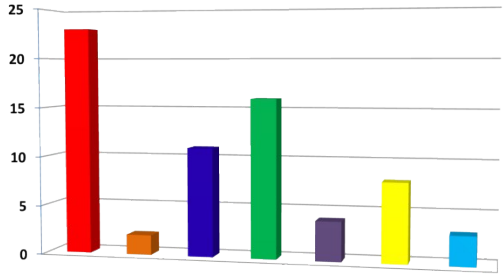

Figure S1. Summary of POMs-based metal carbonyl derivatives. Colour code: heteropolyoxotungstates, red; isopolyoxotungstates, orange; heteropolyoxomolybdates, blue; isopolyoxomolybdates, green; isopolyoxoniobates/isopolyoxotantalates, purple; mix-addendum type, yellow; others, light blue.

Section 2. The XRPD patterns

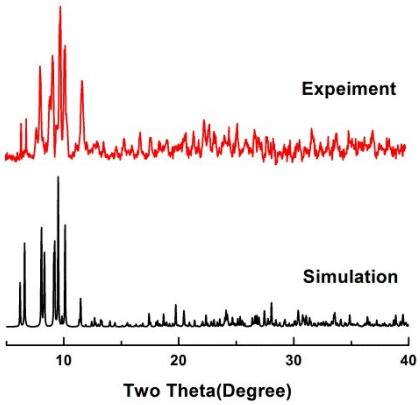

Figure S2. The XPRD patterns of **1**

Section 3. Crystallographic data of 1

Table S1. Crystal data and structure refinement for 1

Empirical formula	$C_{24}H_{50}N_3O_{38}Re_4W_5K$
Formula weight	2691.80
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system	Monoclinic
space group	P2(1)/c
a/[Å]	13.8745(8)
b/[Å]	19.1737(11)
c/[Å]	22.0448(13)
β[°]	105.3700(10)
Z	4
Volume/[Å^3]	5654.7(6)
Calculated density/[g·cm^{-3}]	3.159
μ/[mm^{-1}]	18.820
F(000)	4824

Crystal size	0.41 x 0.18 x 0.15 mm
Theta range for data collection	1.86 to 25.00°
Limiting indices	-16<=h<=16, -22<=k<=16, -26<=l<=26
Reflections collected	28713
Independent reflections	9951 [R(int) = 0.0489]
Completeness to theta = 25.00	99.9 %
Data / restraints / parameters	9951 / 6 / 676
Goodness-of-fit on F^2	1.031
Final R indices [I>2σ(I)]	R1 = 0.0328, wR2 = 0.0715
R indices (all data)	R1 = 0.0444, wR2 = 0.0764
Largest diff. peak and hole/[e·Å^{-3}]	1.313, -1.799

Section 4. The IR spectra of compound 1 and $Re(CO)_5Cl$

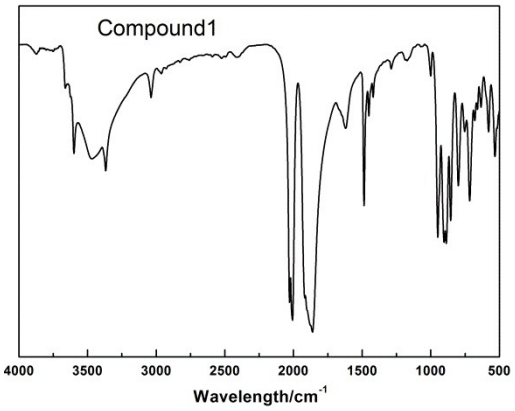

Figure S3. The IR spectrum of compound **1**

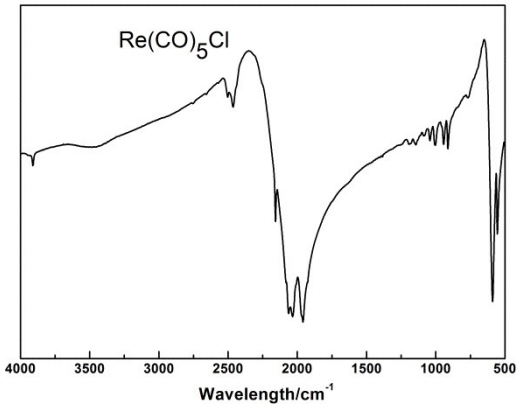

Figure S4. The IR spectrum of $Re(CO)_5Cl$

Section 5. Thermogravimetric analysis of 1

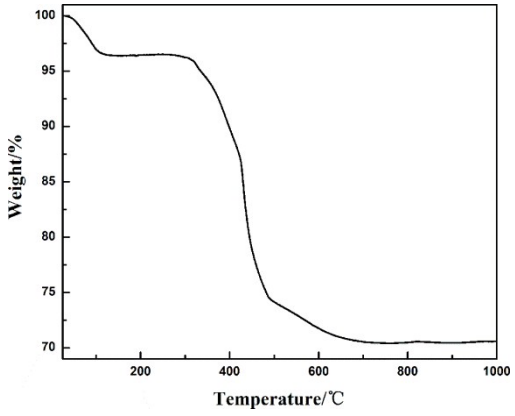

Figure S5. The Thermogravimetric analysis curve of **1**

Section 6. The UV−vis spectrum of 1

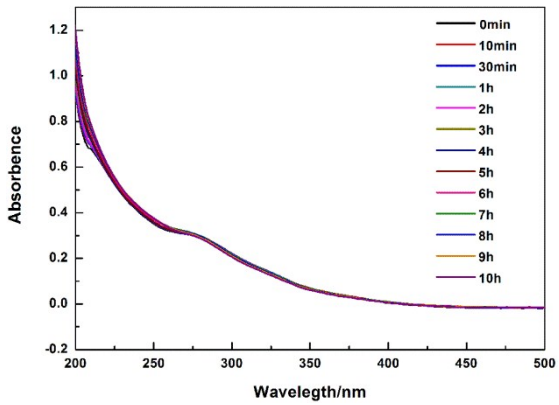

Figure S6. The UV−vis spectrum of **1**

Section 7. Bond valence sum calculations of O

Table S2 Bond valence sum parameters for O atoms on POM fragments in 1

Bond	Bond length	Bond Valence	Valence Sum
O(1)-C(1)	1.157	0.233	Σ(O1) = 1.877
O(2)-C(2)	1.164	0.226	Σ(O2) = 1.842
O(3)-C(3)	1.156	0.234	Σ(O3) = 1.882
O(4)-C(4)	1.154	0.236	Σ(O4) = 1.892
O(5)-C(5)	1.142	0.248	Σ(O5) = 1.954
O(6)-C(6)	1.142	0.248	Σ(O6) = 1.954
O(7)-C(7)	1.143	0.247	Σ(O7) = 1.949
O(8)-C(8)	1.155	0.235	Σ(O8) = 1.887
O(9)-C(9)	1.159	0.231	Σ(O9) = 1.867
O(10)-C(10)	1.142	0.248	Σ(O10) = 1.955
O(11)-C(11)	1.163	0.227	Σ(O11) = 1.847
O(12)-C(12)	1.148	0.242	Σ(O12) = 1.923
O(13)-Re(4)	2.14	-0.17	Σ(O13) = 2.097
O(13)-W(1)	1.993	-0.076	
O(13)-W(2)	2.076	-0.159	
O(14)-W(4)	2.083	-0.166	Σ(O14) = 1.843
O(14)-W(1)	1.848	0.069	
O(15)-W(1)	1.722	0.195	Σ(O15) = 1.694
O(16)-W(3)	2.079	-0.162	Σ(O16) = 1.931
O(16)-W(1)	1.824	0.093	
O(17)-Re(4)	2.179	-0.209	Σ(O17) = 2.056
O(17)-W(5)	2.055	-0.138	
O(17)-W(1)	2	-0.083	
O(18)-W(5)	2.336	-0.419	Σ(O18) =1.593
O(18)-W(4)	2.326	-0.409	
O(18)-W(3)	2.308	-0.391	
O(18)-W(2)	2.37	-0.453	

O(18)-W(1)	2.365	-0.448	
O(19)-W(2)	1.693	0.224	Σ(O19) = 1.832
O(20)-Re(3)	2.133	-0.163	Σ(O20) = 2.080
O(20)-W(2)	1.783	0.134	
O(21)-W(4)	1.938	-0.021	Σ(O21) = 2.053
O(21)-W(2)	1.879	0.038	
O(22)-W(5)	2.029	-0.112	Σ(O22) = 2.082
O(22)-W(2)	2.03	-0.113	
O(22)-Re(4)	2.155	-0.185	
O(23)-W(3)	1.707	0.21	Σ(O23) = 1.764
O(24)-W(3)	1.948	-0.031	Σ(O24) = 2.055
O(24)-W(5)	1.87	0.047	
O(25)-W(3)	1.919	-0.002	Σ(O25) = 1.957
O(25)-W(4)	1.931	-0.014	
O(26)-W(3)	1.777	0.14	Σ(O26) = 2.144
O(26)-Re(2)	2.11	-0.14	
O(27)-W(5)	1.727	0.19	Σ(O27) = 1.671
O(28)-W(4)	1.713	0.204	Σ(O28) = 1.735
O(29)-W(4)	1.777	0.14	Σ(O29) = 2.160
O(29)-Re(1)	2.102	-0.132	
O(30)-Re(3)	2.117	-0.147	Σ(O30) = 2.081
O(30)-W(5)	1.79	0.127	
O(31)-Re(3)	2.196	-0.226	Σ(O31) = 1.640
O(31)-Re(2)	2.201	-0.231	
O(31)-Re(1)	2.184	-0.214	
O(32)-Re(2)	2.147	-0.177	Σ(O32) = 1.251
O(32)-Re(1)	2.14	-0.17	

Section 8. Structural figure

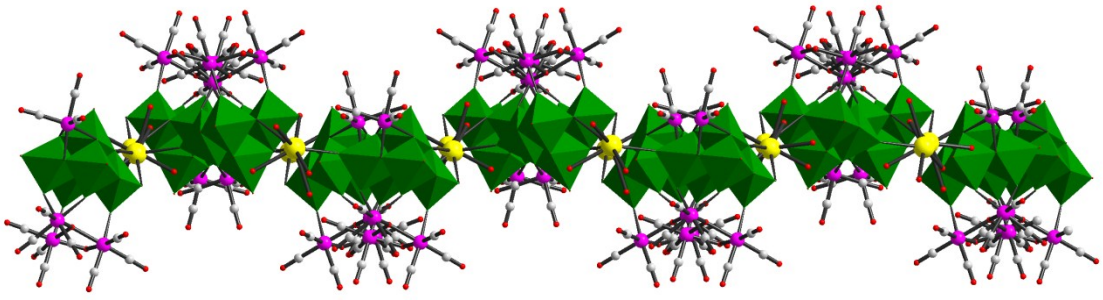

Figure S7. View of the **1** along the *c*-axis. Colour code: W, green; K, yellow; Re, purple; C, gray; O, red; WO_6 octahedral, green.

Section 9 Catalytic properties

Procedures for Catalytic Oxidation.

A glass tube was charged with the catalyst (9.0 mg), substrate (1.0 mmol), 35% H_2O_2 (2.0 mmol), and acetonitrile (5.0 mL) as a typical procedure. The reaction system was maintained at a present temperature with vigorous stirring and the catalyst completely dissolves into the reaction medium. The reaction solution was periodically analyzed by gas chromatography.

Table S3. The catalytic activity of no catalyst and $Re(CO)_5Cl$ compared with catalyst **1**[a]

Entry	Substrate	Catalyst.	Conv. (%)[b]	Sel. (%)
1		—	no reaction	—
2		$Re(CO)_5Cl$	0.3	99
3		catalyst **1**	98.9	99

[a]Reaction conditions: catalyst **1** (3.3 μmol), $Re(CO)_5Cl$ (13.2 μmol), H_2O_2 (2mmol), CH_3CN (5 mL), Temperature (75 ºC). [b]Determined by GC analyses based on initial substrate.