

Supporting Information

Nona-Vacant Keggin-Type Tricarbonyl Rhenium Derivative $\{[PMo_3O_{16}][Re(CO)_3]_4\}^{5-}$ and its Catalytic Performance for CO_2

Cycloaddition Reactions

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Section 1 Experimental Section

1. General Methods and Materials

All chemicals obtained for synthesis were purchased and without further purification. Elemental analyses were operated on a Perkin-Elmer 2400-II CHNS/O analyzer. Inductively coupled plasma atomic emission spectrometry (ICP-AES) analyse was conducted on a Perkin-Elmer Optima 2000 ICP-OES spectrometer. The FT-IR spectra were measured on a KBr pelletson Bruker VERTEX 70 IR spectrometer in the range of 400–4000 cm^{-1} . Thermogravimetric analysis was performed on a Mettler-Toledo TGA/SDTA 851° thermobalance in N_2 flow with a heating rate of 10 $^\circ\text{C min}^{-1}$ from 25 $^\circ\text{C}$ to 800 $^\circ\text{C}$. UV spectra were measured by the Hitachi U-4100 spectrophotometer. GC chromatogram was measured on Bruker 450-GC (FID) instrument, which was equipped with a 30 m column (GsBP-5, 0.25 μm film thickness and 0.25 mm internal diameter).

2. Synthesis of compound 1

$[\text{Re}(\text{CO})_5]\text{Cl}$ (0.18 g, 0.5 mmol) in 5 mL CH_3OH was refluxed in the dark for 1.5 h at 65 $^\circ\text{C}$ (**A**). $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ (0.62 g) was dissolved in 15 mL distilled water, then added $\text{Na}_2\text{HPO}_4\cdot 12\text{H}_2\text{O}$ (0.9 g) and $\text{Mn}(\text{AC})_2\cdot 4\text{H}_2\text{O}$ (0.613 g). The solution was heated for 30 minutes at 80 $^\circ\text{C}$ (**B**). Then the mixed solution was cooled rapidly and filtrated. Furthermore, **A** was added into **B** and the mixed solution was heated at 50 $^\circ\text{C}$ for 30 minutes. Finally, the solution was cooled and filtrated, then the red clear liquid was obtained. $(\text{CH}_3)_4\text{NCl}$ (0.3 g, 2.7 mmol) was added in the red clear liquid. The red liquid was put in the dark place at room temperature for slow evaporation. Then orange-red crystals of **1** were got after some days. Elemental Analysis calcd. (%) for $\text{C}_{12}\text{H}_{23}\text{Mo}_3\text{N}_5\text{O}_{29.5}\text{PRe}_4$ (1772.94 $\text{g}\cdot\text{mol}^{-1}$): C 8.13, H 1.31, N 3.95, P 1.75, Mo 16.23, Re 42.01, found: C 8.26, H 1.20, N 4.02, P 1.82, Mo 16.36, Re 42.31. IR (KBr): $\nu = 3629, 3424, 1997, 1878, 1689, 1486, 1075, 948, 890, 823 \text{ cm}^{-1}$.

3. General procedures for the cycloaddition of CO₂ to epoxides with the co-catalyst of ionic liquid **2**.

Epoxides (5.0 mmol), ionic liquid (70 mg) and compound **1** (0.3 mol %) were well-mixed in an autoclave, then the CO₂ was introduced into the autoclave. The reaction mixtures were stirred at 70 °C for 30 minutes. The autoclave was cooled and the pressure was released after the reaction. Then the autoclave was opened and the reaction mixtures were extracted with ethyl acetate at 70 °C for several times to make sure that the products were entirely moved out. After removal of ethyl acetate completely, the sediments at the bottom of autoclave were recycled.

Section 2 Supplementary crystal data collection

Single crystal X-Ray diffraction: Intensity data of compound **1** were collected on a Bruker APEX-II CCD diffractometer using graphite-monochromated Mo K α radiation ($\lambda = 0.7107\text{\AA}$) at 296 K. The structure was solved by direct methods using the SHELXTL-97 program package¹ and refined by the full-matrix least squares on F². Routine Lorentz and polarization corrections were applied and the absorption correction was performed by using the SADABS program.² Crystal data and structure refinement are shown in **Table S1**. Main bond lengths are shown in **Table S2**. Selected bond angles are summarized in **Table S3**.

Table S1. Crystal data and structure refinement for compound **1**.

Formula	C ₁₂ H ₂₃ Mo ₃ N ₅ O _{29.5} PRE ₄
<i>Mr</i>	1772.94
Crystal system	Monoclinic
Space group	<i>C</i> ₂ / <i>m</i>
<i>a</i> /Å	15.6576(19)
<i>b</i> /Å	19.748(2)
<i>c</i> /Å	18.942(2)
α /°	90
β /°	96.859(2)
γ /°	90
Volume/Å ³	5814.7(12)
<i>Z</i>	4
<i>D</i> _{calcd} , Mg/m ³	2.025
Absorption coefficient/mm ⁻¹	9.013
Reflections collected	14238
Independent reflections	5256
<i>R</i> _{int}	0.0479
Completeness	99.5%
<i>F</i> (000)	3228
Range for data collection	1.90 to 25.00
	-28 ≤ <i>h</i> ≤ 12
Limiting indices	-22 ≤ <i>k</i> ≤ 23
	-22 ≤ <i>l</i> ≤ 21
Goodness-of-fit on <i>F</i> ²	1.034
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	5256/6/282
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0497, <i>wR</i> ₂ = 0.1363
<i>R</i> indices(all data)	<i>R</i> ₁ = 0.0667, <i>wR</i> ₂ = 0.1433
Largest diff. Peak and hole	1.910 and -1.658 e Å ⁻³

$$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|; wR_2 = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$$

Table S2. Main bond lengths (Å) for compound **1**.

Bond	Length	Bond	Length
Mo(1)-O(1)	1.716(8)	P(1)-O(9)	1.498(8)
Mo(1)-O(4)	1.790(6)	P(1)-O(10)	1.530(10)
Mo(1)-O(2)	2.090(6)	P(1)-O(3)	1.581(9)
Mo(1)-O(3)	2.350(7)	Re(1)-C(2)	1.864(16)
Mo(2)-O(5)	1.706(7)	Re(1)-C(1)	1.891(13)
Mo(2)-O(7)	1.788(7)	Re(2)-C(3)	1.854(11)
Mo(2)-O(8)	1.795(6)	Re(2)-C(4)	1.891(15)
Mo(2)-O(2)	2.008(6)	Re(2)-C(5)	1.938(12)
Mo(2)-O(6)	2.226(6)	Re(3)-C(7)	1.810(2)
Mo(2)-O(3)	2.375(5)	Re(3)-C(6)	1.896(14)
Re(1)-O(2)	2.144(6)	Re(2)-O(9)	2.146(7)
Re(1)-O(6)	2.156(9)	Re(3)-O(8)	2.114(7)
Re(2)-O(4)	2.118(6)	Re(3)-O(1)	2.128(11)
Re(2)-O(7)	2.131(8)	C(1)-O(11)	1.165(15)
C(2)-O(12)	1.218(19)	C(5)-O(15)	1.101(14)
C(3)-O(13)	1.196(13)	C(6)-O(16)	1.144(16)
C(4)-O(14)	1.161(15)	C(7)-O(17)	1.290(3)

Table S3. Selected bond angles (°) of compound **1**.

C(2)-Re(1)-C(1)	86.2(5)	C(2)-Re(1)-O(2)	102.0(4)
C(2)-Re(1)-C(1)#1	86.2(5)	C(1)-Re(1)-O(2)	99.6(4)
C(1)-Re(1)-C(1)#1	88.4(9)	C(1)#1-Re(1)-O(2)	168.8(4)
C(2)-Re(1)-O(2)#1	102.0(4)	O(2)#1-Re(1)-O(2)	71.5(3)
C(1)-Re(1)-O(2)#1	168.8(4)	C(2)-Re(1)-O(6)	172.8(6)
C(1)#1-Re(1)-O(2)#1	99.6(4)	C(1)-Re(1)-O(6)	98.9(4)
O(2)-Re(1)-O(6)	72.3(3)	C(5)-Re(2)-O(4)	174.6(4)
C(3)-Re(2)-C(4)	88.0(5)	C(3)-Re(2)-O(7)	95.4(4)
C(3)-Re(2)-C(5)	89.4(5)	C(4)-Re(2)-O(7)	176.3(3)
C(4)-Re(2)-C(5)	87.6(5)	C(5)-Re(2)-O(7)	93.9(4)
C(3)-Re(2)-O(4)	94.2(4)	O(4)-Re(2)-O(7)	81.8(2)
C(4)-Re(2)-O(4)	96.6(4)	C(3)-Re(2)-O(9)	177.4(4)
C(4)-Re(2)-O(9)	93.1(4)	C(6)#1-Re(3)-C(6)	86.8(8)
C(5)-Re(2)-O(9)	93.1(4)	C(7)-Re(3)-O(8)	96.4(5)
O(4)-Re(2)-O(9)	83.3(3)	C(6)#1-Re(3)-O(8)	176.3(5)
O(7)-Re(2)-O(9)	83.5(3)	C(6)-Re(3)-O(8)	93.9(5)
C(7)-Re(3)-C(6)#1	87.3(6)	C(7)-Re(3)-O(8)#1	96.4(5)
C(7)-Re(3)-C(6)	87.3(6)	C(6)#1-Re(3)-O(8)#1	93.9(5)
C(6)-Re(3)-O(8)#1	176.3(5)	C(6)-Re(3)-O(10)	93.4(5)
O(8)-Re(3)-O(8)#1	85.3(4)	O(8)-Re(3)-O(10)	83.0(3)
C(7)-Re(3)-O(10)	179.1(7)	O(8)#1-Re(3)-O(10)	83.0(3)
C(6)#1-Re(3)-O(10)	93.4(5)		

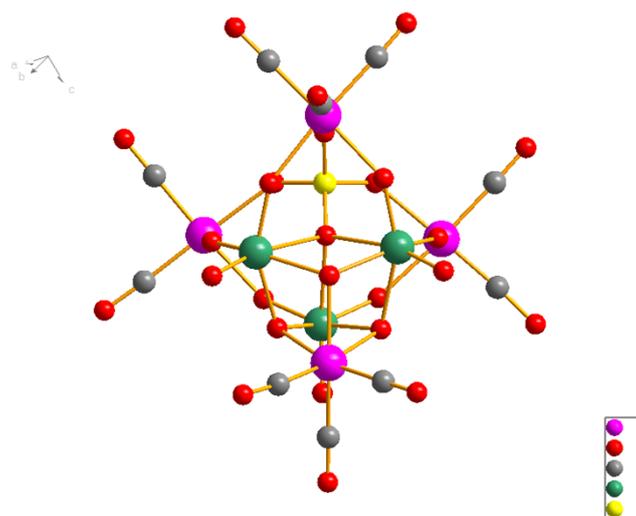


Figure S1. The ball-and-stick representation of polyanion of **1a**.

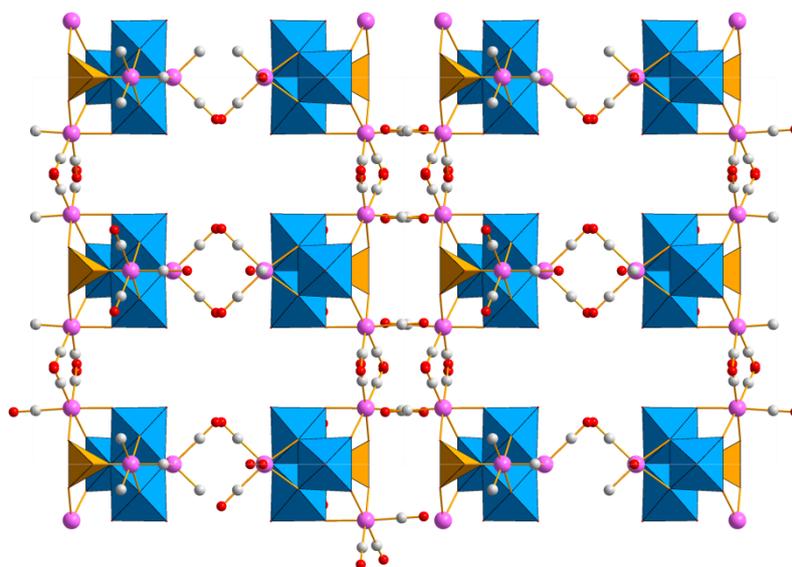


Figure S2. The polyhedral and ball-and-stick representation of **1** along the a direction.

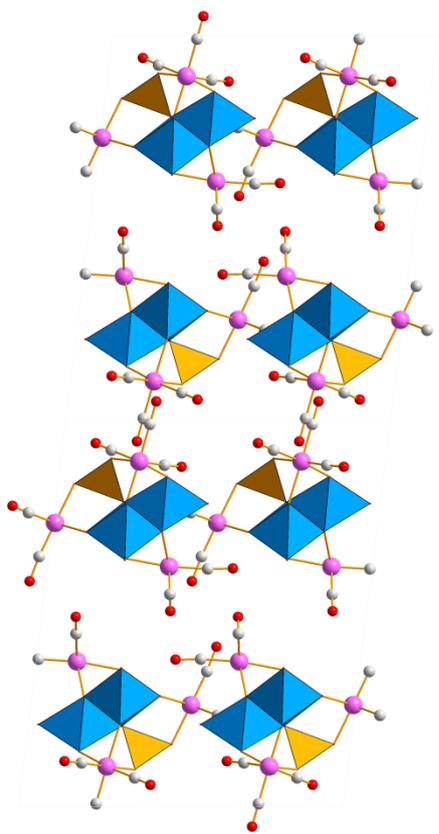


Figure S3.The polyhedral and ball-and-stick representation of **1** along the b direction.

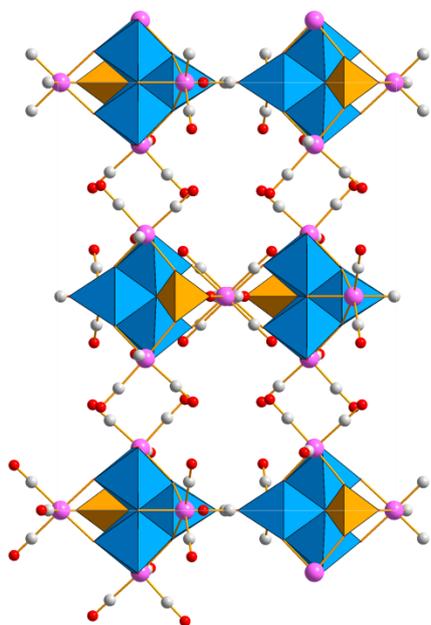


Figure S4.The polyhedral and ball-and-stick representation of **1** along the c direction.

Table S4. The bond valence sum calculations of Mo, P in **1a**.

Bond	Bond length	Bond Valence
Mo(1)-O(1)	1.716	1.675675
Mo(1)-O(4)#1	1.79	1.371927
Mo(1)-O(4)	1.79	1.371927
Mo(1)-O(2)	2.09	0.609818
Mo(1)-O(2)#1	2.09	0.609818
Mo(1)-O(3)	2.35	0.302009
		$\Sigma(\text{Mo1})=5.941$
Mo(2)-O(5)	1.706	1.721581
Mo(2)-O(7)	1.788	1.379363
Mo(2)-O(8)	1.795	1.353512
Mo(2)-O(2)	2.008	0.761113
Mo(2)-O(6)	2.226	0.422248
Mo(2)-O(3)	2.375	0.282277
		$\Sigma(\text{Mo2})=5.920$
P(1)-O(9)#1	1.498	1.379363
P(1)-O(9)	1.498	1.379363
P(1)-O(10)	1.53	1.26508
P(1)-O(3)	1.581	1.102188
		$\Sigma(\text{P1})= 5.126$

Section 3 Additional measurements

3.1 IR spectrum

The IR spectrum of compound **1** shows moderate absorption bands at 1075, 948, 890, 823 cm^{-1} associated with the characteristic stretching vibration of $[\text{PMo}_3\text{O}_{16}]^{9-}$ containing species. Moreover, two strong peaks at 1997 and 1878 cm^{-1} are assigned to one symmetric and one antisymmetric stretching vibration of the CO group respectively. Same bands exist in some C_{3v} metal carbonyl complexes.³ Furthermore, the bands from 3424 to 3629 cm^{-1} are assigned to a series of -OH and -NH stretching vibration, meanwhile, two peaks at 1689 and 1486 cm^{-1} are associated with -OH and -NH flexural vibrations. In conclude, all above indicate that water molecules and NH_4^+ exist in compound **1**. This inference is in good agreement with the results of X-ray diffraction structural analysis.

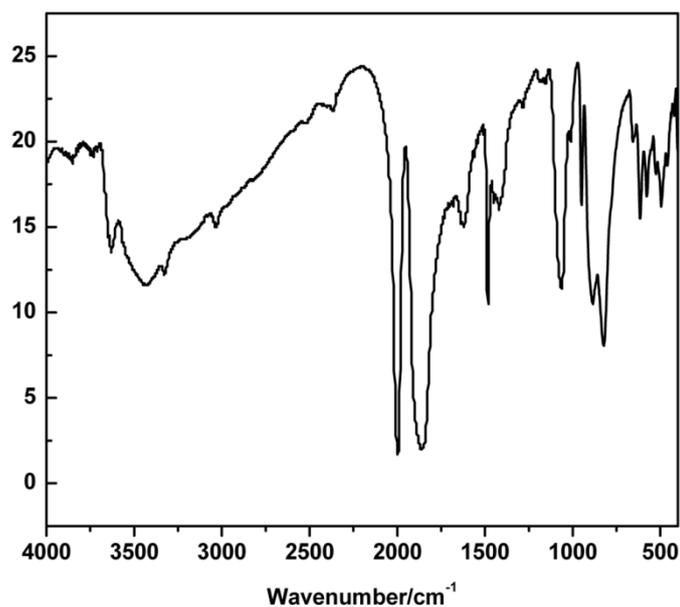


Figure S5. IR spectrum of 1.

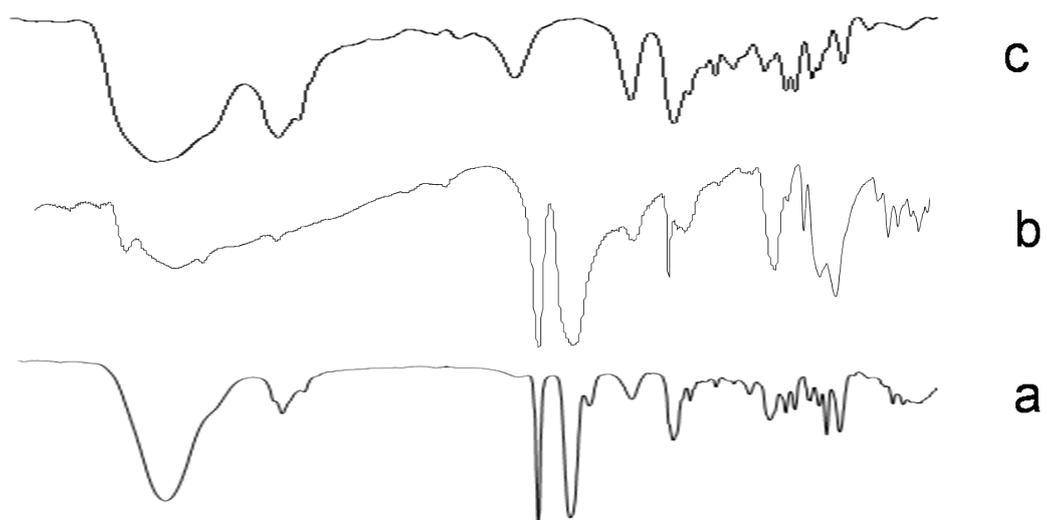


Figure S6. FT-IR spectra of the catalyst system of **1** and **2** (a); catalyst **1** (b); co-catalyst 1-Ethyl-1-methylpyrrolidinium bromide **2** (c).

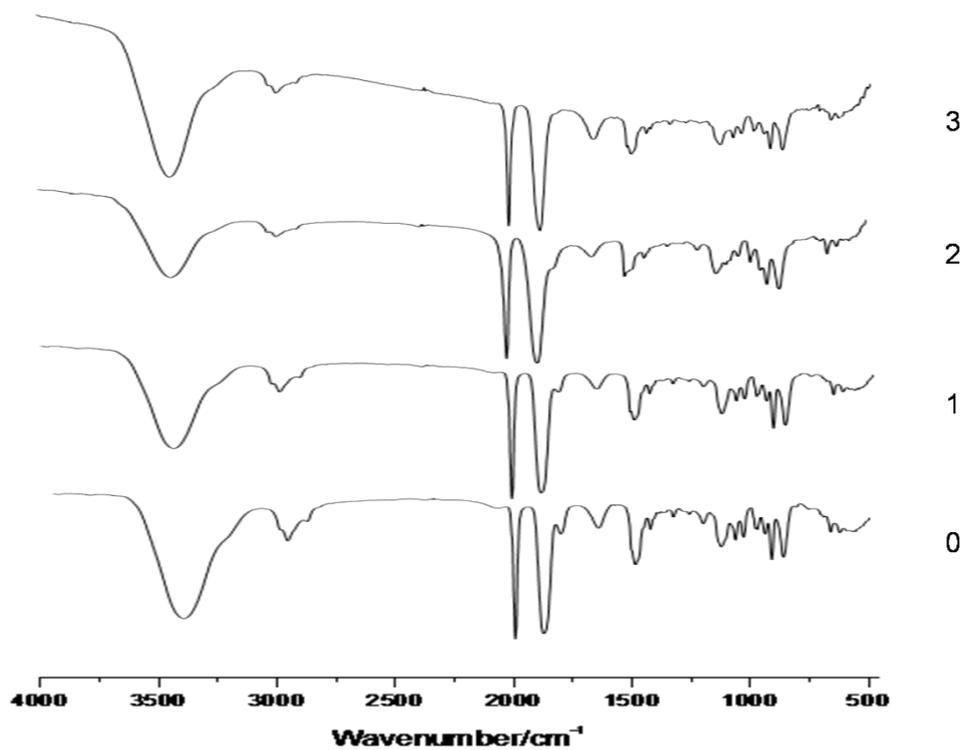


Figure S7. FT-IR spectra of the catalyst system of **1** and **2**: (0) initial, (1) after 1st cycle, (2) after 2nd cycle, (3) after 3rd cycle.

3.2 XRPD patterns

The experimental XRPD pattern of compound **1** is in good agreement with the simulated XRPD pattern, indicating phase purity of compound **1** is good.

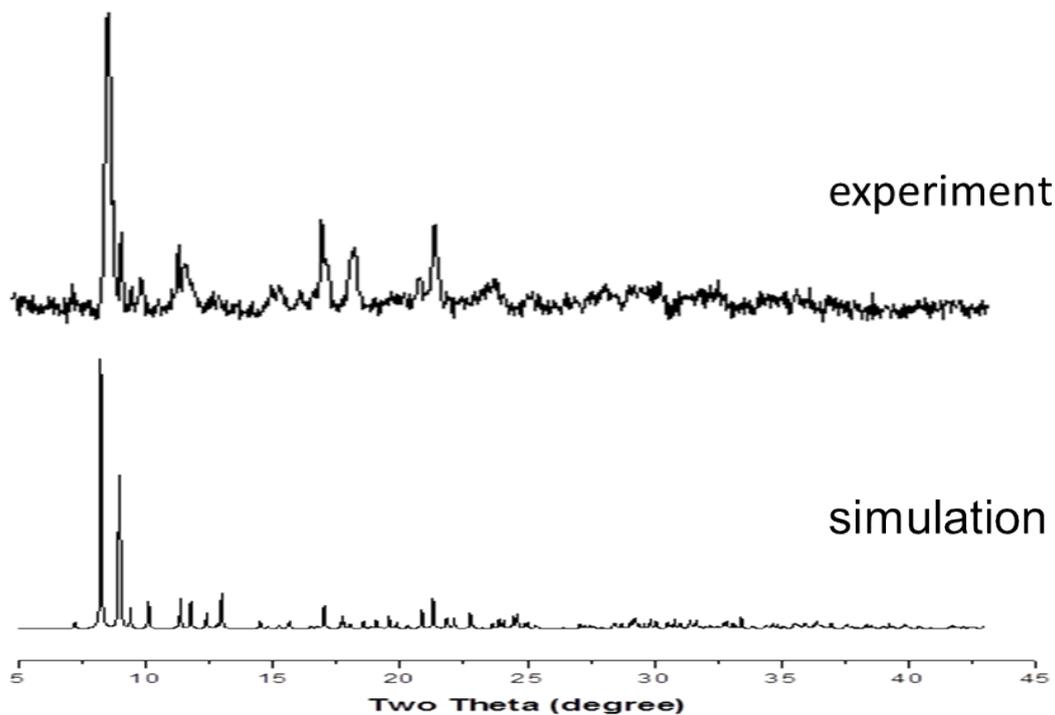


Figure S8. The experimental and simulated XRPD pattern of compound **1**.

3.3 Thermogravimetric analysis

The TG curve of **1** has two stages of weight loss, giving a total loss of 31.43 % (calcd 38.14 %) in the range of 25–1000 °C. The first step from 25–200 °C give the weight loss of 6 % (calcd 6.32 %), which is due to the removal of five NH₃ molecules and one and a half lattice water molecules. The second step with the obvious weight loss of 25.43 % from 200-1000 °C, which is attributed to the removal of twelve carbonyl groups. In the process, the framework of POMs collapsed and P₂O₅ sublimated, which finally left the MoO₃ and Re₂O solid.

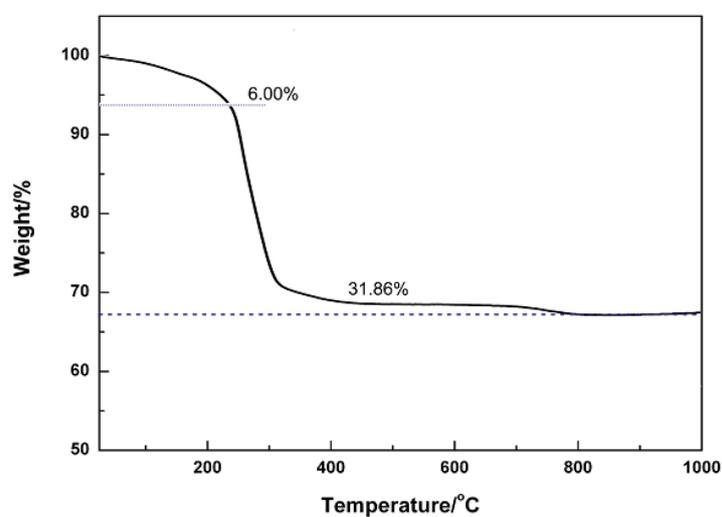


Figure S9. The TG curve of compound **1**.

3.4 Computational methods used

All the calculations were operated at the DFT level by the ADF2008.01 suite of programs. The local density approximation (LDA) was adopted for correlation functional, which was characterized by the functional of Vosko-Wilk-Nusair (VWN) parameterization. In addition, Perdew (BP86) nonlocal corrections and gradients corrections of Beck are employed for the correlation functionals and exchange, respectively. Triple- ξ plus polarization Slater basis sets (TZ2P) was used to characterize the valence electrons of each atom for basis functions. The scalar relativistic effect was explained by the zero-order regular approximation (ZORA), which was adopted in the calculations. Full geometry optimizations were implemented on each structure with the conductor-like screening solvent model (COSMO). Spin-unrestricted calculations were carried out for all the open-shell systems. Frequency analyses were also performed to make sure that it was indeed stable structure.

Section 4 Catalytic properties

Table S5. Catalyst activity of the scaled-up reaction ^a

Entry	Catalyst 1 (mol %)	ionic liquids 2 (mol %)	Substrate 2a (mmol)	Yield (%) ^b
1	0.3	7	5	93.6
2	0.3	7	10	91.3
3	0.3	7	20	92.8

^a Reaction conditions: P=1.0Mpa, T=70°C, t=30min. ^b Determined by GC using Dimethyl phthalate as an internal standard, the selectivity were over 99% in all cases.

Table S6. The catalytic activity of Re(CO)₅Br compared with catalyst **1** ^a

Entry	Catalyst	ionic liquids 2 (mol %)	Substrate 2a (mmol)	Yield (%) ^b
1	1	7	5	93.6
2	Re(CO) ₅ Br	–	5	–
3	Re(CO) ₅ Br	7	5	78.9

^a Reaction conditions: catalyst **1** (0.3 mol %), Re(CO)₅Br (1.2 mol %), P=1.0Mpa, T=70°C, t=30min. ^b Determined by GC using Dimethyl phthalate as an internal standard, the selectivity were over 99% in all cases.

Section 5 References

1. Sheldrick, G. M. SHELXS97: Program for Crystal Structures Solution; University of Göttingen: Göttingen, Germany, **1997**.
2. Sheldrick, G. M. SHELXL-97: Program for Crystal Structures Refinement; University of Göttingen: Göttingen, Germany, **1997**.
3. Besecker, C. J.; Klemperer, W. G. *J. Am. Chem. Soc.* **1980**, *102*, 7598-7600.