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# A nona-vacant Keggin-type tricarbonyl rhenium derivative $\{[PMo_3O_{16}][Re(CO)_3]_4\}^{5-}$ and its catalytic performance for CO<sub>2</sub> cycloaddition reactions<sup>†</sup>

Zhiyuan Huo, Jipeng Guo, Jingkun Lu, Qiaofei Xu, Pengtao Ma, Juan Zhao, Dongdi Zhang, Jingyang Niu<sup>\*</sup> and Jingping Wang<sup>\*</sup>

A nona-vacant Keggin-type tricarbonyl rhenium derivative  $[(NH_4)_5]$ { $[PMo_3O_{16}][Re(CO)_3]_4$ }·1.5H<sub>2</sub>O was obtained and characterized. Its frontier orbitals were computed by density functional theory (DFT) calculations. Furthermore, it could act as a Lewis acid catalyst and promote the conversion of CO<sub>2</sub> to cyclic carbonate under mild reaction conditions with pyrrolidinium bromide as a co-catalyst.

Polyoxometalate (POM)-supported carbonyl metal derivatives, as a category of interesting organometallic oxides,1 have attracted growing attention owing to their rather unique structures and range of fascinating properties.<sup>2</sup> A series of these compounds with their synthetic processes, special structures, and catalytic properties has been reported previously.3-7 However, most of these derivatives are dominated by Lindqvisttype POMs,<sup>3-5</sup> in contrast, Keggin-type POM-supported carbonyl metal derivatives have rarely been reported mainly because Keggin-type polyoxoanions have smaller charge densities to combine with metal carbonyl groups. Recently, an increasing amount of attention has been directed towards rhenium containing POMs due to the attractive catalytic properties of the rhenium atom. Re(1) complexes have been demonstrated to be effective for the transformation of CO<sub>2</sub> and have usually been used as efficient photocatalysts for the reduction of CO2.8 However, their application in the coupling of CO<sub>2</sub> with epoxides to produce cyclic carbonates remains very rare. Hua et al. first described that [Re(CO)<sub>5</sub>Br] could catalyze the synthesis of cyclic carbonates under harsh conditions.9 Subsequently, Wong et al. reported that a tricarbonyl rhenium(I) complex could catalyze

the cycloaddition of CO<sub>2</sub> to epoxides effectively in ionic liquids.<sup>10</sup> Recently, our group reported a POM-based trirhenium carbonyl derivative,  $[(AsW_{11}O_{39})\{Re(CO)_3\}_3(\mu_3\text{-}OH)(\mu_2\text{-}OH)^{6-}$ , which could catalyze the cycloaddition reaction under harsh conditions.<sup>11</sup>

Hence, the need to develop the design of new POMsupported rhenium carbonyl derivatives still remains, as the derivatives may have enhanced catalytic properties toward effective CO<sub>2</sub> conversion. In this paper, we have obtained a nona-vacant Keggin-type tricarbonyl rhenium derivative  $[(NH_4)_5]{[PMO_3O_{16}][Re(CO)_3]_4} \cdot 1.5H_2O$  (1), which has been structurally characterized and computed by density functional theory (DFT). We also investigated the catalytic properties of the derivative in the cycloaddition of CO<sub>2</sub> to epoxides under mild reaction conditions in pyrrolidinium bromide.

Compound 1 was prepared by the reaction of  $(NH_4)_6$ -Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O, Na<sub>2</sub>HPO<sub>4</sub>·12H<sub>2</sub>O, Mn(AC)<sub>2</sub>·4H<sub>2</sub>O and Re(CO)<sub>5</sub>Cl in a CH<sub>3</sub>OH-H<sub>2</sub>O mixed solvent (Section S1, ESI<sup>+</sup>). Single crystal X-ray diffraction analysis reveals that compound 1 crystallizes in the monoclinic space group  $C_2/m$ . Compound 1 consists of a  ${[PMO_3O_{16}][Re(CO)_3]_4}^{5-}$  (1a) unit, five NH<sub>4</sub><sup>+</sup> cations, and one and a half crystal water molecules. Notably, the  $[PMo_3O_{16}]^{9-1}$ fragment presents the highest vacant Keggin-polyoxometalate derivative. It can be considered as a unique fragment by removal of three corner-shared Mo3O10 triads from a saturated Keggin [PM012O40] unit. The POM moiety has twelve terminal oxygen atoms and three µ2-O atoms, providing a large coordination ability for bonding the Re centers of the rhenium carbonyl clusters, and forming the stable structure of  $[PMo_3O_{16}][Re(CO)_3]_4]^{5-}$  (Fig. 1a). The tricarbonyl rhenium units here can be divided into two categories, on one hand, the Re1 atom coordinated with three carbonyl ligands is attached to the  $Mo_3O_{16}$  trimer via three  $\mu_2$ -O atoms, meanwhile, the other two Re2 atoms and the Re3 atom is attached to the terminal oxygen atoms of the Mo<sub>3</sub>O<sub>16</sub> trimer and the PO<sub>4</sub> tetrahedron. Notably, the cubane subunit of {ReMo<sub>3</sub>O<sub>4</sub>} was formed by the Re1 atom and three Mo atoms (Fig. 1b). The bond valence sum (BVS) calculations show that all Mo and P atoms of 1a are in

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: jyniu@henu.edu.cn; jpwang@ henu.edu.cn; Fax: +86 371 23886876

<sup>&</sup>lt;sup>†</sup> Electronic supplementary information (ESI) available: Experimental section, supplementary crystal structure figures, elemental analyses, IR spectrum, XRPD patterns, thermogravimetric analysis, and computational methods. CCDC 1057225. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5ra14201f

the +6 and +5 oxidation states, respectively (Table S4, ESI†). Furthermore, the Re–C bond lengths in **1a** range from 1.81 to 1.938 Å, while the C–O bond lengths range from 1.101 to 1.29 Å (Table S2, ESI†). These bond lengths are consistent with that observed for other Re(1) carbonyl complexes.<sup>6c,7</sup>

As seen in Fig. 2, the DFT calculations prove that the HOMO orbitals are localized on the tricarbonyl rhenium fragment of  $\{[PMO_3O_{16}][Re(CO)_3]_4\}^{5-}$ , in contrast, the LUMO orbitals wholly existing in the [PMo<sub>3</sub>O<sub>16</sub>]<sup>9-</sup> moiety are principally W-O antibonding orbitals. Electrons could transfer easily from the Re atoms to the  $[PMo_3O_{16}]^{9-}$  moiety when the Re atoms are in their excited states, which makes the Re atoms more electropositive. Coincidentally, the bond length (Re2-C5: 1.94 Å; Fig. 1a) is longer than others ( $\approx$  1.86 Å), indicating that the Re2–C5 bond is highly activated and more prone to breaking. Thus, the Re2 atom is proven to be the Lewis acid center when it is in its excited state, since the POM moiety acts as a strong electronwithdrawing group. Exhilaratingly, as reported in the literature recently, there are many binary catalyst systems containing Lewis acid and Lewis base centers that provide good yields for the cycloaddition of CO2 to epoxides.<sup>12</sup> Hence, compound 1 may have good catalytic properties toward the CO<sub>2</sub> cycloaddition reaction. Meanwhile, room-temperature ionic liquids used as co-catalysts are especially beneficial for the transformation of CO<sub>2</sub> because of their high CO<sub>2</sub> solubility, high ion conductivity, negligible vapor pressure and excellent selectivity.13-15 Furthermore, the halide ions in ionic liquids usually act as Lewis base centers that could greatly lower the activation energy barrier of the cycloaddition reaction. In this paper, we use 1-ethyl-1methylpyrrolidinium bromide (2) as the co-catalyst.

The ability of compound **1** to catalyze the synthesis of cyclic carbonates from  $CO_2$  and epoxides with the co-catalyst of ionic liquid **2** was researched. Furthermore, the effects of several reaction parameters on the cycloaddition reaction were studied in detail by using the coupling of chloromethyloxirane (**2a**) with  $CO_2$  to produce 4-chloromethyl-1,3-dioxolan-2-one (**3a**) as a model reaction. In a blank experiment (Table 1, entry 1), ionic liquid **2** itself could convert **2a** into **3a** through a Lewis acid-Lewis base mechanism,<sup>16</sup> though the yield was much lower. However, the yield was remarkably increased to 93.6% by the addition of 0.3 mol% (relative to epoxide) of **1** for 30 minutes



Fig. 1 (a) Polyhedral and ball-and-stick representation of polyanion 1a. (b) Ball-and-stick representation of cubane subunit { $ReMo_3O_4$ }. PO<sub>4</sub>, light orange; WO<sub>6</sub>, light blue.



Fig. 2 Several highest occupied (H = HOMO) and lowest unoccupied (L = LUMO) orbitals of 1a and their orbital energies in eV.

(entry 2). The yield of 3a was slightly affected by the CO<sub>2</sub> pressure in the low pressure range (entries 4 and 5). However, the yield was strongly dependent on the reaction temperature (entries 6-8). The increase of the reaction temperature from 60  $^{\circ}$ C to 65  $^{\circ}$ C resulted in a rapid increase in the yield from 36.8 to 82.7% (entries 6 and 7). On increasing the reaction temperature to 75 °C, 97.8% yield was achieved (entry 8). When compound 1 was replaced by  $[(NH_4)_4]{[MO_8O_{30}H_6][Re(CO)_3]_2} \cdot 14H_2O$  (two Re centers) as the catalyst at the same loading, 80.6% yield was obtained. By contrast, using a [(CH<sub>3</sub>)<sub>4</sub>N]<sub>3</sub>[(OC)<sub>3</sub>Re(H<sub>3</sub>AsMo<sub>9</sub>O<sub>32</sub>)]. 11H<sub>2</sub>O catalyst (just one Re center) at the same loading, only 72.5% yield was achieved. However, no yield was obtained without co-catalyst 2 at 70 °C over 30 minutes (Table 1, entry 13). DFT calculations and the study on the catalytic properties of these POM-based rhenium carbonyl derivatives indicated that the Re centers were regarded as active sites.

Table 1 Effect of the reaction parameters on the coupling of CO<sub>2</sub> and chloromethyloxirane catalyzed by catalyst 1 using ionic liquid 2 as the co-catalyst<sup>a</sup>

Cl	0 2a	+ CO <sub>2</sub> -	Catalyst 1 co-catalyst 2 Cl		O O O O O O O O O O O O O O O O O O O
Entry	Catalyst	$P^{b}$ (MPa)	$T(^{\circ}C)$	Time (min)	Yield <sup>c</sup> (%)
1	_	1.0	70	30	37.2
2	1	1.0	70	30	93.6
3	1	1.0	70	15	46.1
4	1	0.5	70	30	85.9
5	1	1.5	70	30	96.8
6	1	1.0	60	30	36.8
7	1	1.0	65	30	82.7
8	1	1.0	75	30	97.8
$9^d$	1	1.0	70	30	91.5
$10^e$	1	1.0	70	30	88.3
$11^f$	4	1.0	70	30	80.6
$12^g$	5	1.0	70	30	72.5
$13^h$	1	1.0	70	30	_

<sup>*a*</sup> Reaction conditions: catalyst 1 (0.3 mol%), chloromethyloxirane 2a (5 mmol, 390 μL), co-catalyst 2 (7 mol%, 70 mg). <sup>*b*</sup> Initial pressure at room temperature. <sup>*c*</sup> Determined by GC using dimethyl phthalate as an internal standard, the selectivity was over 99% in all cases. <sup>*d*</sup> Yield of the 2nd run in the recycling studies. <sup>*e*</sup> Yield of the 3rd run in the recycling studies. <sup>*f*</sup> Using an  $[(NH_4)_4]{[Mo_8O_30H_6][Re(CO)_3]_2} \cdot 14H_2O$  catalyst (catalyst 4) at the same loading. <sup>*g*</sup> Using a  $[(CH_3)_4N]_3[(OC)_3Re(H_3ASMo_9O_{32})] \cdot 11H_2O$  catalyst (catalyst 5) at the same loading. <sup>*h*</sup> Without ionic liquid 2.

The recyclability of the catalyst system was examined in subsequent reactions. The results showed that it could be recycled at least 3 times with a general decline in yield to 88.3% for the 3rd run (Table 1, entry 10). Furthermore, the IR spectra of the recycled catalyst system were highly similar to that of the fresh one (Fig. S7, ESI<sup>†</sup>), indicating that the catalyst system was stable.

We then focused on further application of the catalyst system's promising catalytic potential. As summarized in Table 2, the catalytic activity of the system depends extremely on the structure of the employed epoxides. Both glycidyl methacrylate (2b) and glycidyl phenyl ether (2c) are highly polar. Glycidyl methacrylate (2b) exhibited an attractive yield of 92.7% at 70 °C for 1 h (Table 2, entry 1) and glycidyl phenyl ether (2c) displayed a good yield of 90.6% (Table 2, entry 2). Styrene oxide (2d) was confirmed as a less-reactive epoxide, with only 63.2% yield achieved in 2 h followed by a slow increase in yield to 87.5% over a further 3 h (Table 2, entry 3 and 4). This may result from the steric hindrance of the phenyl group. However, the aliphatic terminal epoxide 1,2-epoxyhexane (2e), which is relatively nonpolar, showed very sluggish reactivity (Table 2, entry 5 and 6). For low boiling propylene oxide (2f), only 10.8% yield was obtained after 1 h, which is because propylene oxide exists as a gas at 1.0 MPa and 70 °C, most of which then stays in the headspace region of the reaction vessel and hardly participates in the reaction.

In summary, we have reported a nona-vacant Keggin-type tricarbonyl rhenium derivative in this paper. Furthermore, compound **1** shows good catalytic activity for the cycloaddition reaction with co-catalyst ionic liquid **2**. The experimental results and DFT calculations greatly promote the design of more POM-

Table 2 Catalytic cycloaddition of CO<sub>2</sub> (1.0 MPa) and various epoxides at 70  $^\circ\text{C}$  using ionic liquid 2 as the co-catalyst<sup>a</sup>

Entry	Substrate		Time (h)	Product	$\operatorname{Yield}^{b}(\%)$
1		2b	1		92.7
2		2 <b>c</b>	1		90.6
3	<u>0</u>	2d	2	0	63.2
4		2d	3		87.5
5	Q	2e	4	o	43.1
6		2e	9	0-0	91.3
7	Ŏ	2f	1	000	10.8

<sup>*a*</sup> Reaction conditions: catalyst **1** (0.3 mol%), epoxide (5 mmol), ionic liquid **2** (7 mol%, 70 mg). <sup>*b*</sup> Determined by GC using dimethyl phthalate as an internal standard, the selectivity was over 99% in all cases.

supported rhenium carbonyl derivatives with diverse structures and potentially powerful catalytic properties for the cycloaddition reaction.

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