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Nona-Vacant Keggin-Type Tricarbonyl Rhenium Derivative {[PMo₃O₁₆][Re(CO)₃]₄}⁵⁻ and its Catalytic Performance for CO₂ Cycloaddition Reactions

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A nona-vacant Keggin-type tricarbonyl rhenium derivative [(NH₄)₅]{[PMo₃O₁₆][Re(CO)₃]₄}·1.5H₂O was obtained and characterized. Its frontier orbitals were computed by the density functional theory (DFT) calculations. Further, it could act as Lewis acid catalyst and promote the conversion of CO₂ to cyclic carbonate under mild reaction conditions with pyrrolidinium bromide as co-catalyst.

Polyoxometalate (POM)-supported carbonyl metal derivatives, as a category of amusing organometallic oxides,[1] have attracted growing attention owing to their rather unique structures and a range of fascinating properties.[2] A series of these compounds with their synthetic process, special structures, and catalytic properties have been reported previously.[3-7] However, most of these derivatives are dominated by Lindqvist-type POMs,[3-5] in contrast, Keggin-type POM-supported carbonyl metal derivatives have rarely been reported mainly because Keggin-type polyoxoanions have fewer charge density to combine with metal carbonyl groups. Recently, increasing attention has been directed towards rhenium containing POMs due to the attractive catalytic properties of the rhenium atom. Re(I) complexes have been demonstrated to be effective for the transformation of CO₂ and usually been used as efficient photocatalysts for the reduction of CO₂.[8] However, their applications in the coupling of CO₂ with epoxides to produce cyclic carbonates remain very rare. Hua et al. firstly described that [Re(CO)₅Br] could catalyze the synthesis of cyclic carbonate under harsh conditions.[9] Subsequently, Wong et al. reported that the tricarbonyl rhenium(I) complex could catalyze the cycloaddition of CO₂ to epoxides effectively in ionic liquid.[10] Recently, our group reported an POM-based trirhenium carbonyl derivatives, [(AsW₁₁O₃₉){Re(CO)₃}₃(μ₃-OH)(μ₂-OH)]⁶⁻, which could catalyze the

cycloaddition reaction under harsh conditions.[11]

Hence, it still remains to develop the design of new POM-supported rhenium carbonyl derivatives, which may have enhanced catalytic properties toward effective CO₂ conversion. In this paper, we have obtained a nona-vacant Keggin-type tricarbonyl rhenium derivative [(NH₄)₅]{[PMo₃O₁₆][Re(CO)₃]₄}·1.5H₂O (1), which has been structurally characterized and computed by the density functional theory (DFT). We also investigated the catalytic properties of the derivative in the cycloaddition of CO₂ to epoxides under mild reaction conditions in pyrrolidinium bromide.

Compound **1** was prepared by reaction of (NH₄)₆Mo₇O₂₄·4H₂O, Na₂HPO₄·12H₂O, Mn(AC)₂·4H₂O, Re(CO)₅Cl in the CH₃OH−H₂O mixed solvent (Section S1, ESI†). Single crystal X-ray diffraction analysis reveals that compound **1** crystallizes in monoclinic space group C₂/m. Compound **1** consists of an {[PMo₃O₁₆][Re(CO)₃]₄}⁵⁻ (**1a**) unit, five NH₄⁺ cations, one and a half crystal water molecules. Noteworthily, the [PMo₃O₁₆]⁹⁻ 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 [PMo₁₂O₄₀] unit. The POM moiety has twelve terminal oxygen atoms and three μ₂-O atoms, providing fortissimo coordination ability for bonding the Re centers of the rhenium carbonyl clusters, forming the stable structure of {[PMo₃O₁₆][Re(CO)₃]₄}⁵⁻ (Fig. 1a). The tricarbonyl rhenium units here can be divided into two categories, on one hand, Re1 atom coordinated with three carbonyl ligands attached to the Mo₃O₁₆
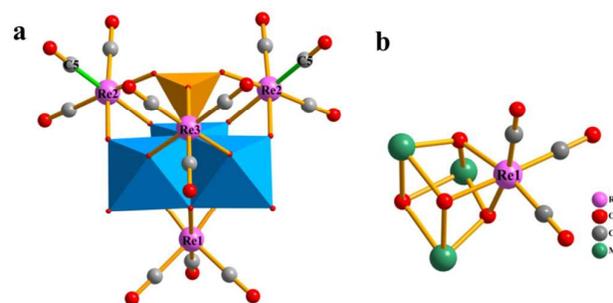
Fig. 1 (a) Polyhedral and ball-and-stick representation of polyanion **1a**. (b) Ball-and-stick representation of cubane subunit {ReMo₃O₄}. PO₄, light orange; WO₆, light blue.

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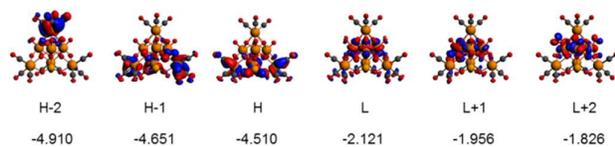
Fig. 2 Several highest occupied (H = HOMO) and lowest unoccupied (L = LUMO) orbitals of **1a** and their orbital energies in [eV].

trimer via three μ_2-O atoms, meanwhile, the other two Re2 atoms and Re3 atom attached to the terminal oxygen atoms of the Mo_3O_{16} trimer and the PO_4 tetrahedron. Notably, the cubane subunit of {$ReMo_3O_4$} was formed by 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 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(I) carbonyl complexes.[6c-7]

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 $[PMo_3O_{16}]^{9-}$ 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. Coincidently, 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 break. Thus, the Re2 atom is proved to be the Lewis acid center when it is in excited states, since the POM moiety acts as a strong electron-withdrawing 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 CO_2 to epoxides.[12] Hence, compound **1** may have good catalytic properties toward the CO_2 cycloaddition reaction. Meanwhile, room-temperature ionic liquids used as co-catalysts are specially beneficial for the transformation of CO_2 because of their high CO_2 solubility, high ion conductivity, negligible vapor pressure and excellent selectivity.[13-15] Furthermore, the halide ions in ionic liquids are usually acted as Lewis base centers that could greatly lower the activation energy barrier of the cycloaddition reaction. In this paper, we use the 1-Ethyl-1-methylpyrrolidinium bromide (**2**) as the co-catalyst.

The ability of compound **1** to catalyze synthesis of cyclic carbonate from CO_2 and epoxides with the co-catalyst of ionic liquid **2** were 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[16], 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 (entry 2). The yield of **3a** was slightly affected by CO_2 pressure in the low pressure range (entries 4 and 5). However, the yield was strongly depended on the reaction

Table 1 Effect of reaction parameters on the coupling of CO_2 and chloromethyloxirane catalyzed by catalyst **1** using ionic liquid **2** as the co-catalyst[a]
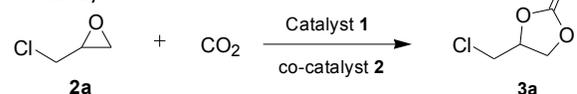
Entry	Catalyst	P (MPa)[b]	T (°C)	Time (min)	Yield (%)[c]
1	–	1.0	70	30	37.2
2	1	1.0	70	30	93.6
3	1	1.0	70	15	46.1
4	1	0.5	70	30	85.9
5	1	1.5	70	30	96.8
6	1	1.0	60	30	36.8
7	1	1.0	65	30	82.7
8	1	1.0	75	30	97.8
9[d]	1	1.0	70	30	91.5
10[e]	1	1.0	70	30	88.3
11[f]	4	1.0	70	30	80.6
12[g]	5	1.0	70	30	72.5
13[h]	1	1.0	70	30	–

[a] Reaction Conditions: catalyst **1** (0.3 mol %), chloromethyloxirane **2a** (5 mmol, 390 μL), co-catalyst **2** (7 mol %, 70 mg). [b] Initial pressure at room temperature. [c] Determined by GC using Dimethyl phthalate as an internal standard, the selectivity were over 99% in all cases. [d] Yield of the 2nd run in the recycling studies. [e] Yield of the 3rd run in the recycling studies. [f] Using an [$(NH_4)_4$]{$[Mo_8O_{30}H_6][Re(CO)_3]_2$}·14$H_2O$ catalyst (catalyst **4**) at the same loading. [g] Using an [$(CH_3)_4N]_3[(OC)_3Re(H_3AsMo_9O_{32})$]·11$H_2O$ catalyst (catalyst **5**) at the same loading. [h] Without ionic liquid **2**.

Table 2 Catalytic cycloaddition of CO_2 (1.0 MPa) and various epoxides at 70°C using ionic liquid **2** as the co-catalyst[a]

Entry	Substrate		Time (h)	Product	Yield (%)[b]
1		**2b**	1		92.7
2		**2c**	1		90.6
3		**2d**	2		63.2
4		**2d**	3		87.5
5		**2e**	4		43.1
6		**2e**	9		91.3
7		**2f**	1		10.8

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

temperature (entries 6–8). The increase of reaction temperature from 60 °C to 65 °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 $[(NH_4)_4]\{[Mo_8O_{30}H_6][Re(CO)_3]_2\}\cdot14H_2O$ (two Re centers) as the catalyst at the same loading, 80.6% yield was obtained. By contrast, using an $[(CH_3)_4N]_3[(OC)_3Re(H_3AsMo_9O_{32})]\cdot11H_2O$ 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 property of these POM-based rhenium carbonyl derivatives indicated that the Re centers were regarded as active sites.

The recyclability of the catalyst system was examined in the subsequent reaction. The results showed that it could be recycled at least 3 times with a general decline in yield to 88.3% at the 3th 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†), 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 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**), relatively non-polar, showed very sluggish reactivity (Table 2, entry 5 and 6). For the low boiling propylene oxide (**2f**), only 10.8 % yield was obtained after 1 h, which is because the 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-supported rhenium carbonyl derivatives with diverse structures and potentially powerful catalytic property for the cycloaddition reaction.

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