Synthesis of Cyclic Carbonates from Carbon Dioxide and Epoxides Catalyzed by a Keggin-Type Polyoxometalate-Supported Rhenium Carbonyl Derivate in Ionic Liquid

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A monovacant Keggin-type polyoxometalate-supported trirhenium carbonyl derivate $[(CH_3)_4N]_5H_{23}[(PW_{11}O_{39})\{Re(CO)_3\}_3(\mu_3\text{-}O)(\mu_2\text{-}OH)]_4 \cdot 24\,H_2O$ was synthesized. It was used as a catalyst for the synthesis of cyclic carbonates from carbon dioxide and epoxides under mild reaction conditions with co-catalyst pyrrolidinium bromide. The catalyst system was recycled 10 times with only a small decline in yield. The catalytic mechanism was hypothesized based on experimental results and the frontier orbitals computed by DFT calculations.

Chemical fixation of CO_2 into useful chemical compounds has attracted great attention in recent years because CO_2 is an attractive and potentially renewable C1 building block in organic synthesis.[1] The cycloaddition of CO_2 to epoxides to produce five-membered cyclic carbonates is one of the most promising strategies because cyclic carbonates can be widely used as precursors for producing polycarbonates, aprotic polar solvents, electrolyte components in lithium batteries, and fine chemical ingredients.[2] Numerous catalysts have been developed for this aim, such as phosphonium salts,[3] transition metal complexes,[4–8] quaternary ammonium salts,[9] alkali metal salts,[10] and functional polymers.[11] However, although the advances are significant, most of these catalysts suffer from low catalyst stability or reactivity, needing high temperatures and/or pressures, and difficulty in recycling. Among the above catalysts, transition metal complexes have emerged as a significant type of catalyst for the coupling of CO_2 with epoxides.[4–8] Surprisingly, transition-metal-substituted polyoxometalates (POMs) were found to have application in catalyzing the synthesis of cyclic carbonate.[5,6] A zinc-substituted polyoxometalate, Na_{12}-$[WZn_3(H_2O)_2(ZnW_9O_{34})_2] \cdot 46\,H_2O$, in conjunction with dimethyl amino pyridine was found to be an efficient catalyst in the cycloaddition reaction.[5] Tetraalkylammonium salts of transition-metal-substituted polyoxometalates, such as $[(n\text{-}C_7H_{15})_4N]_6[\alpha\text{-}SiW_{11}O_{39}Co]$ and $[(n\text{-}C_7H_{15})_4N]_6[\alpha\text{-}SiW_{11}O_{39}Mn]$, could catalyze

the synthesis of cyclic carbonate.[6] In particular, Re^I complexes have proven effective for the transformation of CO_2. Re^I complexes have usually been used as photocatalysts for the reduction of CO_2 to CO.[12] However, their applications in the coupling of CO_2 with epoxides remain very rare. Hua et al. first reported that $[Re(CO)_5Br]$ could be used as an active catalyst in the synthesis of cyclic carbonates under harsh conditions.[7] Recently, a tricarbonyl rhenium(I) complex has been described by Wong et al. that could catalyze the chemical fixation of CO_2 with epoxides in the presence of ionic liquid.[8]

As reported recently, there are plenty of binary catalyst systems containing Lewis acid and base centers that provide good yields under mild reaction conditions for the cycloaddition reaction.[13] Delightfully, Hill et al. demonstrate that the Re atoms are Lewis acid centers if in excited states, as the POM moiety acts as a strong electron-withdrawing group.[14] The potential catalytic properties obtained by the combination of both of these systems greatly arouses our curiosity. Hence, it still remains to develop the design of POM-supported rhenium carbonyl derivatives as catalysts with enhanced properties for CO_2 conversion. It is beneficial for the transformation of CO_2 to use room-temperature ionic liquids as co-catalysts because of their high CO_2 solubility, negligible vapor pressure, high ion conductivity, and excellent selectivity.[15–17] Furthermore, the halide ions in ionic liquids are usually regarded as ideal nucleophiles (Lewis base centers) that can strongly lower the activation energy barrier of the reaction. In this paper, we report a monovacant Keggin-type POM-supported rhenium carbonyl derivate (1) used as an efficient and recyclable catalyst for the CO_2 cycloaddition reaction under mild reaction conditions with 1-ethyl-1-methylpyrrolidinium bromide (2) as the co-catalyst. This catalyst system could circumvent many of the disadvantages described above.

Catalyst 1 was synthesized by reaction of $[Re(CO)_5Cl]$, reaction intermediate **B** in the $CH_3CN–H_2O$ mixed solvent (see Section S1 in the Supporting Information). Each unit lattice of 1 consisted of 4 $[(PW_{11}O_{39})\{Re(CO)_3\}_3(\mu_3\text{-}O)(\mu_2\text{-}OH)]^{7-}$ (**1a**) units, 5 $[(CH_3)_4N]^+$ cations, 27 protons and 54 crystalline water molecules (Figure 1). The crystal structure of **1a** revealed a "cap" model of the trirhenium carbonyl cluster that was combined with $[PW_{11}O_{39}]^{8-}$ (Figure 1a). The POM moiety can be considered as an extremely active tetradentate ligand providing excellent coordination to the Re centers of the trirhenium carbonyl cluster. The trirhenium carbonyl cluster fragment of **1a** is remarkably similar to that reported by Hill et al.[14] The three Re^I centers in $[\{Re(CO)_3\}_3(\mu_3\text{-}O)(\mu_2\text{-}OH)]$ are divided into two cat-

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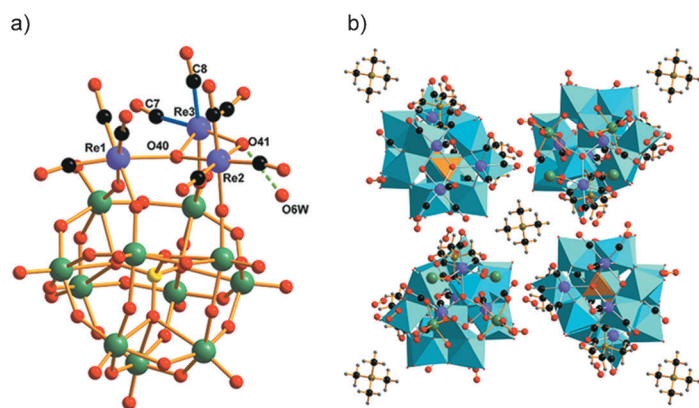Supporting information for this article is available on the WWW under
http://dx.doi.org/10.1002/cctc.201402575.

a)

b)

Figure 1. a) Ball-and-stick representation of polyanion **1a**. b) Polyhedral and ball-and-stick representation of **1** follows the c direction. ●: Re, ●: O, ●: C, ●: P, ●: W, ■: PO$_4$, ■: WO$_6$.

as a nucleophile by accelerating the ring-opening reaction of the epoxide (see Table S2 in the Supporting Information). These results showed that the co-catalyst **2** played a crucial catalytic role.

On testing the recyclability of the catalyst system, the results (see Figure 2) showed that it could be recycled 10 times with a small gradual decline in yield to 80.3 % at the 10th cycle (Table 1, entry 11). Excitingly, the IR spectra of the recovered catalyst systems were almost identical to that of the fresh catalyst system (Figure S9 in the Supporting Information), indicating that the catalyst system was stable.

We then studied further applications of the catalyst system and found it to be applicable to a wide range of epoxides. As shown in Table 2, the catalytic activity of the system depended greatly on the structure of various epoxides. Both epichlorohydrin (**2b**) and gly-

egories. Re2 and Re3 reside in similar coordination environment, each of which is covalently bonded to three carbonyl ligands and O40 and O41, which forms one Re—O—W bond to $[PW_{11}O_{39}]^{8-}$. In comparison, Re1 is bonded to O40, which forms two Re—O—W bonds to the POM moiety. Notably, one proton should be localized on μ_2-O41 according to the bond valence sun calculations[18] of all the oxygen atoms on **1a**. The shortest distance between the protonated O41 and O6W is 2.767 Å, confirming the existence of a hydrogen bond between them (Figure 1a).

The ability of catalyst **1** to catalyze cyclic carbonate synthesis from CO$_2$ and epoxides with co-catalyst ionic liquid **2** were studied. Then the effects of various reaction parameters on the catalytic performance were researched in detail by using the coupling of glycidyl phenyl ether (**2a**) with CO$_2$ to produce 3-phenoxy-1,2-propylene carbonate (**3a**) as a model reaction. We were delighted to discover that catalyst **1** catalyzed the cycloaddition of CO$_2$ with **2a** in conjunction with ionic liquid **2**. In a blank experiment (see Table 1, entry 1), ionic liquid **2** itself could convert the epoxide into **3a** through a Lewis acid–Lewis base mechanism[19] with Br$^-$ as a nucleophile, though the yield was much lower. The yield was increased to 84.3 % by the addition of 0.1 mol % (relative to epoxide) of **1** (entry 2). The outstanding turnover frequency (TOF) of 843 h^{-1} was superior to that of tricarbonyl rhenium(I) complex reported by Wong et al. ($\approx$122 h^{-1}).[8] If addition of **1** was increased incrementally from 0.12 to 0.15 mol %, the yield increased from 91.2 to 96.7 % (entries 3 and 4). The yield of **3a** slightly depended on CO$_2$ pressure in the low pressure range (entries 6 and 7). However, the yield was strongly affected by the reaction temperature (entries 8–10). The increase of reaction temperature from 60 to 65 °C resulted in a rapid increase in the yield from 27.8 to 72.4 % (entries 8 and 9). On increasing the reaction temperature to 75 °C, 97.2 % yield was achieved (entry 10). We then speculated on the catalytic role of co-catalyst **2**. However, no yield was obtained without co-catalyst **2** at 70 °C over 1 h (Table 1, entry 12). If co-catalyst **2** was added incrementally from 4 to 6 mol %, the yield increased from 58.3 to 77.2 % (entries 13 and 14). The Br$^-$ of co-catalyst **2** facilitated the reaction

Table 1. Effect of reaction parameters on the coupling of CO$_2$ and 1,2-epoxy-3-phenoxypropane catalyzed by catalyst **1** with ionic liquid **2** as the co-catalyst.[a]

Entry	1 [mol %]	2 [mol %]	P[b] [MPa]	T [°C]	Yield[c] [%]	TOF[d] [h^{-1}]
1	–	8	1.0	70	34.9	–
2	0.1	8	1.0	70	84.3	843
3	0.12	8	1.0	70	91.2	760
4	0.15	8	1.0	70	96.7	645
5[e]	0.12	8	1.0	70	46.4	773
6	0.12	8	0.5	70	82.9	691
7	0.12	8	1.5	70	95.5	796
8	0.12	8	1.0	60	27.8	232
9	0.12	8	1.0	65	72.4	603
10	0.12	8	1.0	75	97.2	810
11[f]	0.12	8	1.0	70	80.3	669
12[g]	0.1	–	1.0	70	–	–
13	0.12	4	1.0	70	58.3	486
14	0.12	6	1.0	70	77.2	643

[a] Reaction conditions: epoxide (5 mmol, 680 µL), $t = 1$ h. [b] Initial pressure at RT. [c] Determined by GC with dimethyl phthalate as the internal standard; selectivities were over 99 % in all cases. [d] in $[mol_{propylene\ carbonate}\ mol_{catalyst}^{-1}\ h^{-1}]$. [e] $t = 0.5$ h. [f] Yield of the 10th cycle in the recycling studies. [g] Without ionic liquid **2** (Lewis base center).

cidyl methacrylate (**2c**) are highly polar. Epichlorohydrin (**2b**) exhibited the highest activity among the epoxides surveyed. The excellent yield of 94.6 % and high TOF of 1051 h^{-1} were given by using epichlorohydrin at 70 °C for 0.75 h (Table 2, entry 1) and glycidyl methacrylate (**2c**) displayed a good yield of 93.2 % within 1 h (Table 2, entry 2). Styrene oxide (**2d**) was confirmed to be a less-reactive epoxide, with only 65.3 % yield obtained in 2 h followed by an increase in yield to 90.1 % over a further 3 h (Table 2, entries 3 and 4). This probably owed to the steric hindrance of the phenyl group. However, the aliphatic terminal epoxide 1,2-epoxyhexane (**2e**), comparatively non-
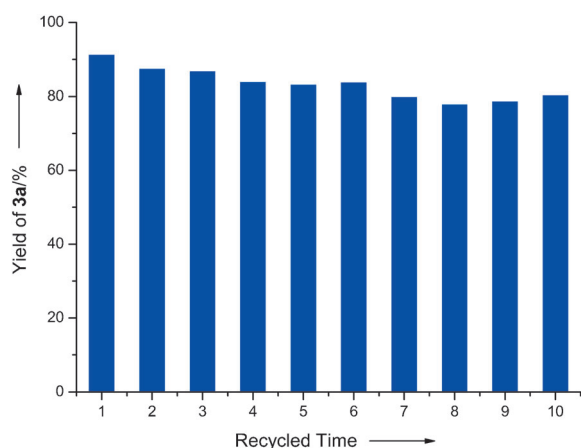
Figure 2. Reuse of the catalyst system. Reaction conditions: 5 mmol **2a**, 0.12 mol% **1**, CO_2 pressure 1.0 MPa, $T = 70\,°C$, $t = 1$ h.

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

Entry	Substrate		t [h]	Product	Yield[b] [%]	TOF[c] [h^{-1}]
1	Cl epoxide	**2b**	0.75	Cl carbonate	94.6	1051
2	methacrylate glycidyl	**2c**	1	methacrylate carbonate	93.2	776
3	styrene oxide		2	phenyl carbonate	65.3	272
4		**2d**	3		90.1	251
5	butyl epoxide		3	butyl carbonate	49.5	137
6		**2e**	8		92.6	96
7	propylene oxide	**2f**	1	propylene carbonate	11.6	97

[a] Reaction conditions: catalyst **1** (0.12 mol%), epoxide (5 mmol), ionic liquid **2** (8 mol%, 80 mg). CO_2 was charged into an autoclave under an initial pressure of 1.0 MPa at RT. [b] Determined by GC with dimethyl phthalate as the internal standard; selectivities were over 99% in all cases. [c] In [mol$_{propylene\ carbonate}$ mol$_{catalyst}^{-1}$ h^{-1}].

hardly participated in the reaction; an analogous result analysis has been described by Wong et al.[8]

Finally, we investigated the reaction mechanism for the cycloaddition of CO_2 to epoxides. The [Re(CO)$_5$Br]-catalyzed mechanism was first proposed by Hua et al.[7] However, the [Re(CO)$_5$Br]-catalyzed reaction occurred under relatively harsh conditions without a halide nucleophile (Lewis base center). Under the conditions described herein, compound **1** was used without co-catalyst to catalyze the cycloaddition reaction and the experimental phenomena were consistent with those described by Hua et al.[7] (see Table S1 in the Supporting Information). This indicated that the reaction mechanism probably followed that proposed for [Re(CO)$_5$Br] under relatively harsh conditions.[7] By comparison, no yield was obtained if **1** was used without co-catalyst at 70 °C for 1 h (Table 1, entry 12), indicating that the [Re(CO)$_5$Br]-catalyzed mechanism was not applicable for our catalyst system under mild reaction conditions. If pyrrolidinium bromide **2** was used as the co-catalyst, we obtained high yield. An analogous result has been described by Kleij et al.[20] indicating that the ring-opening procedure initiated by direct insertion of CO_2 was highly energetically demanding, which suggested that the procedure could only occur under relatively harsh reaction conditions. In contrast, the binary catalyst system for the cycloaddition of CO_2 to epoxides usually combines a Lewis acid center and a halide nucleophile, which can reduce the energy barrier and facilitate subsequent CO_2 insertion.

In this paper, DFT calculations demonstrate that the HOMO orbitals are entirely localized on the trirhenium carbonyl cluster fragment of **1a**, whereas the LUMO orbitals exist wholly in the POM moiety and are principally W—O antibonding orbitals (Figure 3). If the Re centers are in their excited states, electrons can transfer easily from the Re centers to the POM moiety, which makes the Re centers more electropositive. Thus, the Re atoms in excited states are proved to be Lewis acid centers because the POM moiety acts as a strong electron-withdrawing group. An analogous result analysis of DFT calculations has been described by Hill et al.[14]

Excitingly, the formation of a hydrogen bond between the protonated μ_2-O41 and the nearby dissociative crystalline water may activate the corresponding Re—C bond and simultaneously activate the ring-opening reaction of epoxides.[21] Coincidentally, the bond distances (Re3—C7: 2.02; Re3—C8: 1.93 Å; Figure 1a) are longer than others (≈ 1.86 Å), indicating that the Re3—C7 bond is highly activated and more prone to break-

polar, showed sluggish reactivity (Table 2, entries 5 and 6). The propylene oxide (**2f**), as a low boiling epoxide, gave only 11.6% yield after 1 h, which could be because the propylene oxide turned into a gas at 1.0 MPa and 70 °C, most of which then stayed in the upper apex of the reaction vessel and
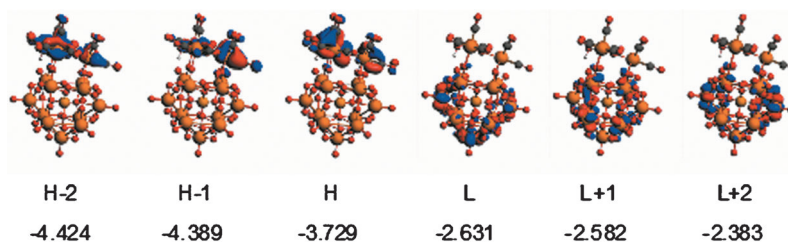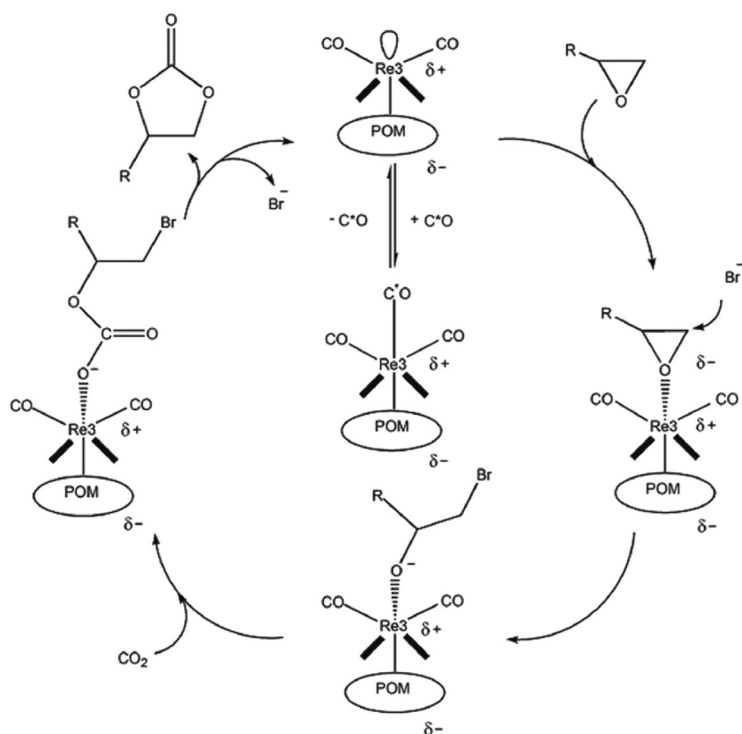

H-2	H-1	H	L	L+1	L+2
-4.424	-4.389	-3.729	-2.631	-2.582	-2.383

Figure 3. Several highest occupied (H = HOMO) and lowest unoccupied (L = LUMO) orbitals of **1a** and their orbital energies in [eV].

Scheme 1. Proposed reaction mechanism for the cycloaddition of CO_2 to epoxides.

age, which gives us crystallographic evidence to further speculate the mechanism of the catalytic reaction. Both of these factors lead to the Re3 center becoming a strong Lewis acid mediator for activating the epoxide. Considering the various kinds of factors mentioned above and the universally recognized mechanisms of the cycloaddition of CO_2 to epoxides,[22, 23] a proposed reaction mechanism is illustrated in Scheme 1. It is suggested that the epoxide is first activated by coordination to the Re3 center, followed by epoxide ring-opening through the nucleophilic attack of Br^-, and the subsequent interaction of the nucleophilic alkoxide intermediate with the electrophilic CO_2 to form the cyclic carbonate. Both the Lewis acidic center (Re3) and the nucleophile (Br^-) have the same importance in this mechanism and the excellent synergistic effects greatly promote the reactions.

In summary, we have reported a Keggin-type polyoxometalate-supported trirhenium carbonyl derivate. Notably, this work features the combination of compound **1** and pyrrolidinium bromide **2** for the formation of cyclic carbonates. The synergistic effects greatly promote the reactions under mild conditions. Significantly, the polyoxometalate moiety plays a particularly positive role in the catalytic reactions. The mechanism proposed is supported by both theoretical and experimental results and provides new insights into the design of more powerful catalyst systems for the cycloaddition reaction.

Experimental Section

Details on the synthetic process of compound **1**, reaction procedures, the recycling process, additional experiments, powder XRD

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