

A ruthenium complex exhibiting high catalytic efficiency for the formation of propylene carbonate from carbon dioxide

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Abstract

A highly efficient catalyst composed of (2,2'-bipy)RuCl₃(CH₃OH) and cetyltrimethylammonium chloride is reported for the first time for the formation of propylene carbonate from carbon dioxide and propylene oxide under mild conditions (75 °C, 3.0 MPa). Nearly 100% selectivity and 100% yield of propylene carbonate was achieved. The catalyst can be easily recovered and reused several times without appreciable loss of catalytic activity, total turn over number reaching 2.04×10^4 after five catalytic recycles with a turnover frequency higher than 1000 h⁻¹. A mechanism for the reaction was proposed.

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Keywords: Propylene carbonate; Propylene oxide; Carbon dioxide; Ruthenium complex

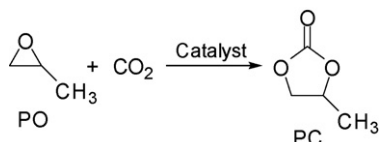
1. Introduction

Since the petroleum resources are limited, there is a growing effort to develop new chemical processes using biorenewable resources. One such resource of particular interest is carbon dioxide that is a nontoxic, nonflammable and naturally abundant C₁ feedstock. However, the thermodynamic stability of carbon dioxide has hampered its use as a reagent for chemical synthesis. To overcome this limitation, great efforts have been made in investigating reactions to activate carbon dioxide as a highly reactive reagent [1,2]. One of the effective routes is the coupling of carbon dioxide with epoxides to synthesize cyclic carbonates, such as ethylene carbonate and propylene carbonate, which are valuable compounds as aprotic polar solvents, electrolytes in secondary batteries, fine chemical intermediates, and starting materials for the synthesis of polymers and engineering plastics. Various catalysts have been found effective for this coupling reaction, such as alkali metal halides, organic bases, metal oxides, zeolite, polymer supported quaternary ammonium salt, ionic liquids, and metal complexes, etc. [3–19].

Although the synthesis of cyclic carbonates from carbon dioxide and epoxides has been known for over 50 years and a great number of works in effective catalyst investigation have been reported, catalytic activity still remain to be improved in getting a higher efficiency [3–5]. Recently, Lu et al. reported the coupling reaction of CO₂ with propylene oxide (PO) to produce optically active propylene carbonate (PC) under mild conditions using a chiral catalyst, SalenCo(III)/*n*-Bu₄NCl with a turnover frequency (TOF, moles of PC produced per mole of catalyst per hour) of 316 h⁻¹ [12]. Kim et al. found that the complex [(2-methylpyridine)₂ZnBr₂] catalyzes the reaction of CO₂ with PO to give PC in a yield of 80% with a TOF of 405 h⁻¹, while the complex [(2,2'-bipyridine)₂ZnBr₂] showed no catalytic activity [13,14]. Man et al. recently reported that a heterobimetallic Ru–Mn complex, [(η⁵-C₅H₅)Ru(CO)(μ-dppm)Mn(CO)₄], catalyzes the reaction of PO with CO₂ to give PC at 100 °C and 4.0 MPa of CO₂ with a turnover number (TON, moles of PC produced per mole of catalyst) of 1490 and a TOF of 37 h⁻¹ [15]. Srivastava et al. found that a composition of Cu(bipy)₂(NO₃)₂(H₂O) with 4-*N,N*-dimethylaminopyridine (DMAP) catalyzes the reaction of CO₂ with PO at 120 °C and 0.69 MPa of CO₂ to give PC with a TON of 772 and a TOF of 193 h⁻¹ [16].

The present paper reports our recent findings in the investigation for highly efficient catalysts for the reactions of carbon

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Scheme 1. Coupling reaction of carbon dioxide with propylene oxide.

dioxide with epoxides. We found that a ruthenium bipyridine complex, [(2,2'-bipy)RuCl₃(CH₃OH)], exhibits very high catalytic activity together with an ammonium salt, cetyltrimethylammonium chloride (CTAC), for the formation of propylene carbonate from carbon dioxide and propylene oxide (Scheme 1). This catalyst gave propylene carbonate with nearly 100% selectivity and 100% yield at a temperature of 75 °C under 3.0 MPa of CO₂, and the catalyst can be reused several times without appreciable loss of catalytic activity and selectivity.

2. Experiments

Propylene oxide was distilled over CaH₂ prior to use. Carbon dioxide of 99.99% purity was used as received. (2,2'-bipy)RuCl₃(CH₃OH) was prepared following a literature procedure [20]. CTAC and other reagents with chemical purity were obtained and used as received.

¹H NMR spectrum was recorded on a Bruker DPX-400 spectrometer. IR spectrum was measured on a Nicolet Protégé 460 infrared spectrophotometer.

The coupling reaction of carbon dioxide with propylene oxide was carried out in a 100 ml stainless steel autoclave equipped with a magnetic stirrer. For a typical reaction process, the catalyst was charged into the reactor, followed by addition of a desired amount of purified propylene oxide using a syringe. Then, the reactor was pressurized to 1.0–4.0 MPa with carbon dioxide and heated to a desired temperature (50–90 °C) with stirring. After 2–6 h of reaction, the autoclave was cooled to room temperature, and the reaction mixture was transferred to a round bottom flask. The product propylene carbonate was obtained as a colorless liquid through distillation under reduced pressure. IR spectrum (neat) showed a typical carbonyl absorption at 1793 cm⁻¹, and ¹H NMR (CDCl₃, TMS, 400 MHz) showed signals at 1.50(d, J = 6.24, 3H, CH₃), 4.04(t, J = 7.82, 1H, CH₂CH), 4.56(t, J = 8.02, 1H, CH₂CH), and 4.82–4.92(m, CH).

For the catalyst recycle process, after the propylene carbonate was removed by distillation, the remaining catalyst was reused for further reaction with a fresh charge of propylene oxide and carbon dioxide through the same procedures as those in the initial reaction described above.

3. Results and discussion

3.1. Optimizing reaction conditions

Since the complex of (2,2'-bipy)RuCl₃(CH₃OH) and CTAC are easily dissolved in a mixture of propylene

Table 1
Effect of the molar ratio of CTAC to (2,2'-bipy)RuCl₃(CH₃OH)^a

Entry	(2,2'-Bipy)RuCl ₃ (CH ₃ OH) (mmol)	CTAC (mmol)	Yield (%) ^b	TON ^c	TOF (h ⁻¹) ^d
1	0.05	0	Trace	–	–
2	0.05	0.02	91	3822	956
3	0.05	0.05	97	4074	1019
4	0.05	0.10	98	4116	1029
5	0	0.10	Trace	–	–

^a PO (15 ml, 0.21 mol); 75 °C; 4 h; 3.0 MPa of CO₂ pressure.

^b Isolated yield.

^c Moles of PC produced per mole of ruthenium complex.

^d Moles of PC produced per mole of ruthenium complex per hour.

Table 2
Effect of reaction time, temperature and pressure^a

Entry	Temperature (°C)	Pressure (MPa)	Time (h)	Yield (%) ^b	TON	TOF (h ⁻¹)
1	75	3.0	2	72	3024	1512
2	75	3.0	3	93	3906	1302
3	75	3.0	4	97	4074	1019
4	75	3.0	6	98	4116	686
5	50	3.0	4	65	2730	683
6	60	3.0	4	86	3612	903
7	70	3.0	4	96	4031	1008
8	80	3.0	4	97	4074	1019
9	90	3.0	4	98	4116	1029
10	75	1.0	4	82	3444	861
11	75	2.0	4	95	3990	996
12	75	4.0	4	97	4074	1019

^a PO, 15 ml, 0.21 mol; (2,2'-bipy)RuCl₃(CH₃OH), 0.05 mmol; CTAC, 0.05 mmol.

^b Isolated yield.

oxide and propylene carbonate, the coupling reaction of carbon dioxide with propylene oxide catalyzed by [(2,2'-bipy)RuCl₃(CH₃OH)/CTAC] does not require an organic co-solvent, and the reaction proceeds in a homogeneous manner.

The molar ratio of CTAC to (2,2'-bipy)RuCl₃(CH₃OH) was found to be a major factor for the catalytic activity. As shown in Table 1, the individual ruthenium complex (2,2'-bipy)RuCl₃(CH₃OH) or CTAC showed no catalytic activity. However, the combination of (2,2'-bipy)RuCl₃(CH₃OH) with CTAC exhibited a significantly high catalytic activity. The yield of propylene carbonate increases with increasing molar ratio of CTAC to (2,2'-bipy)RuCl₃(CH₃OH) in the range between 0 and 1; a further increase in the molar ratio of CTAC gave almost no change in the catalytic activity. Therefore, the suitable molar ratio of CTAC to (2,2'-bipy)RuCl₃(CH₃OH) is 1. The selectivity, which is defined as the molar percentage of PC formed over PO converted, was found nearly 100% in each entry of experiment. ¹H NMR spectroscopy showed that no polymer was formed in any entry of experiment.

Other factors influencing the coupling reaction are given in Table 2. At reaction temperature of 75 °C and CO₂ pressure of 3.0 MPa, the reaction proceeded rapidly within the first 3 h, and the PC yield increased with increasing reaction time. It is important to note that an almost quantitative yield could be achieved in 4 h of reaction time. In other words, a reaction time of 4 h is necessary to complete the propylene oxide conversion.

Reaction temperature gave also an obvious influence on the reaction. Although a moderate PC yield of 65% was obtained even at a lower temperature of 50 °C under CO₂ pressure of 3.0 MPa within 4 h of reaction time, the PC yield increased with increasing reaction temperature and an almost quantitative yield could be achieved at 75 °C. Therefore, increasing the reaction temperature is propitious for the increase in reaction rate.

The reactant mixture consists of both the CO₂-rich gas phase and the liquid phase. The intervention of CO₂-PO complex has been deduced on the basis of appearance of a new absorption band in the UV spectrum of the saturated solution of CO₂ in PO [21]. Hence, carbon dioxide should be soluble in PO, and most of the reaction occurs in the liquid phase. The density and the concentration of PO in the gas phase increase with the temperature increase and the pressure decrease, while the volume of the liquid phase rapidly decreases; the concentration of CO₂ in the liquid phase would be enhanced by increasing the pres-

sure. Probably, this would cause the increase in the PC yield observed with the increase in pressure. But the reaction does not need a higher carbon dioxide pressure; under CO₂ pressure of 1.0 MPa, 82% of PC yield was obtained at 75 °C within 4 h of reaction time. The yield increased as the pressure of CO₂ increased from 1.0 MPa to 3.0 MPa; even higher CO₂ pressure was not necessary for the present reaction studied.

Therefore, we may consider that the optimal conditions for the reaction of carbon dioxide with propylene oxide yielding propylene carbonate catalyzed by [(2,2'-bipy)RuCl₃(CH₃OH)/CTAC] should be 75 °C of reaction temperature, 3.0 MPa of CO₂ pressure, 4 h of reaction time, and the molar ratio of (2,2'-bipy)RuCl₃(CH₃OH) to CTAC should be 1.

As can be seen from Table 3, the results presented above gives higher values of TON and TOF under mild conditions compared with most reported transition metal complex catalysts to date [11–19] for the reaction of CO₂ with PO. Moreover, the present catalyst [(2,2'-bipy)RuCl₃(CH₃OH)/CTAC] has the advantages of being simple in composition, stable in air and easy to be prepared, which is beneficial for industrial application.

3.2. Catalyst recovery and reuse

It is well known that the stability and reusability of a catalyst are two important factors that determine whether it finds practical application in industry. In order to test this characteristic of the present catalyst, a series of catalytic cycles for the coupling reaction of carbon dioxide with propylene oxide was carried out under the optimized reaction conditions. After each run, all volatiles including propylene carbonate and unreacted propylene oxide were distilled off from the reaction mixture, and the remaining catalyst was reused for the succeeding run directly. The results are listed in Table 4, which showed that the catalyst did not present any appreciable loss in either the catalytic activity or the selectivity. After five catalytic recycles, the total TON reached 2.04×10^4 with a TOF higher than 1000 h^{-1} .

3.3. Possible mechanism

It has been proposed that the coupling of carbon dioxide with epoxides to yield cyclic carbonates probably requires the activation through both a Lewis acid and a Lewis base; the former activates the epoxide, while the latter attacks the less sterically

Table 3
Comparison of (2,2'-bipy)RuCl₃(CH₃OH)/CTAC with most reported transition metal complex catalysts for the coupling of PO and CO₂

Catalyst	Pressure (MPa)/temperature (°C)/time (h)	Yield (%)	TON/TOF (h ⁻¹)	Reference
Re(CO) ₅ Br	6.0/110/20	46	460/23	[11]
SalenCo(III)/n-Bu ₄ NCl	0.55/45/1.5	47	474/316	[12]
(2-Methylpyridine) ₂ ZnBr ₂	3.4/100/1	80	405/405	[13,14]
(η ⁵ -C ₅ H ₅)Ru(CO)(μ-dppm)Mn(CO) ₄	4.0/100/45	17	1490/37	[15]
Cu(bipy) ₂ (NO ₃) ₂ (H ₂ O)/DMAP ^a	0.69/120/4	30	772/193	[16]
CoSalen/DMAP	2.1/100/1.5	100	100/67	[17]
CrSalen/DMAP	0.35/75/1.5	100	100/67	[18]
Zn(II) salen-type/Et ₃ N	3.5/100/2	100	100/50	[19]
(2,2'-bipy)RuCl ₃ (CH ₃ OH)/CTAC	3.0/75/4	97	4074/1019	This work

^a DMAP: N,N'-dimethylaminopyridine.

Table 4
Catalyst recycles^a

Entry	Recycle no.	Yield (%) ^b	TON	TOF (h ⁻¹)
1	Fresh	97	4074	1019
2	1	98	4116	1029
3	2	96	4031	1008
4	3	98	4116	1029
5	4	97	4074	1019

^a PO, 15 ml, 0.21 mol; (2,2'-bipy)RuCl₃(CH₃OH), 0.05 mmol; CTAC, 0.05 mmol; 75 °C; 4 h; 3.0 MPa of CO₂ pressure.

^b Isolated yield.

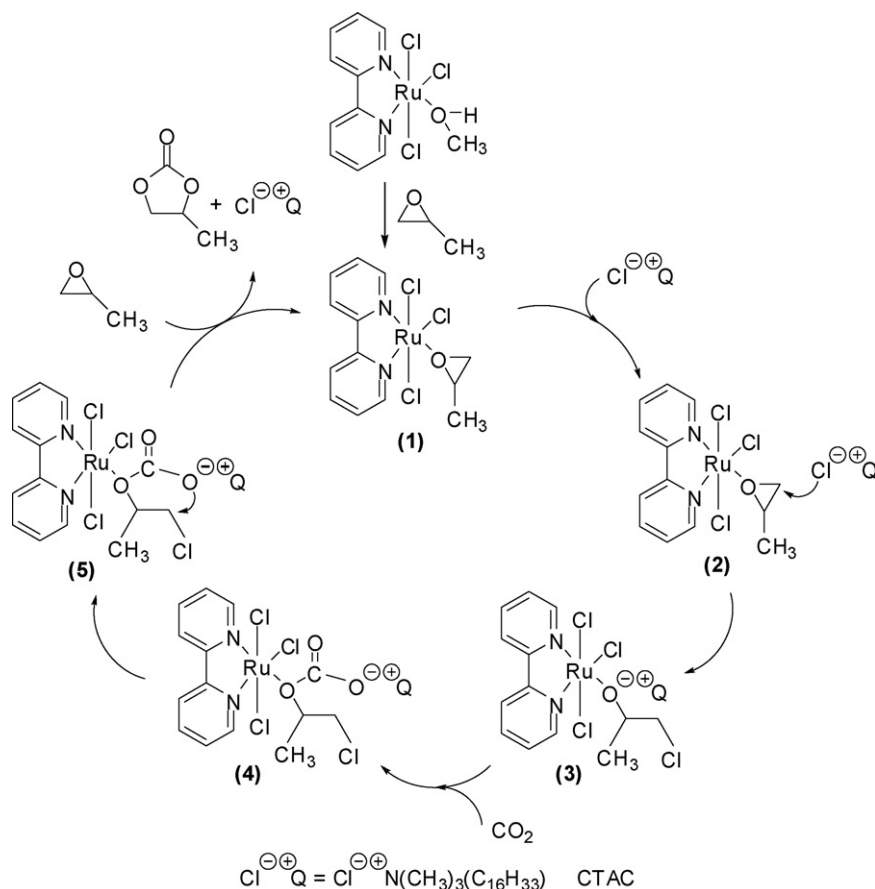
hindered carbon atom to open the epoxide ring. The generated oxy anion species then reacts with CO₂ to give the corresponding cyclic carbonate [4,6,7,12].

The structure of the complex [(2,2'-bipy)RuCl₃(CH₃OH)] has been determined by X-ray diffraction as reported by Eskelinen, in which the ruthenium centre is surrounded by a slightly distorted octahedral coordination environment by three chloride ligands, the bidentate chelating 2,2'-bipyridine ligand and the methanol ligand. The methanol ligand is labile and can be replaced by other neutral ligands [20]. The first crystal structure of a metal epoxide complex has been reported for a ruthenium porphyrin derivative of styrene oxide [22]. The insertion of CO₂ into the metal-oxygen bond to form a metal carbonate species is well established [14,23].

Based on the molecular structure of the complex [(2,2'-bipy)RuCl₃(CH₃OH)] and coupling reaction results, we propose here a possible mechanism for the coupling reaction of propylene oxide and carbon dioxide (Scheme 2).

The reaction is initiated by the ligand exchange of propylene oxide with methanol to form an adduct of ruthenium-epoxide complex (1), which is readily ring-opened by the nucleophilic attack of the highly reactive anions of quaternary ammonium salt; then, a quaternary ammonium salt [CTAC, (CH₃)₃(C₁₆H₃₃)N⁺Cl⁻] attacks the less hindered carbon atom of the coordinated epoxide followed by ring opening, producing an oxy anion species (3). The insertion of CO₂ into the Ru–O bond of (3) would give a ruthenium carbonate active species (4), which eventually produces propylene carbonate by way of intramolecular cyclic elimination.

In the present reaction studied, the complex of (2,2'-bipy)RuCl₃(CH₃OH) should be able to form an adduct of Ru-PO complex (1), but its ability to open the PO ring is not high enough. The addition of a Lewis base (CTAC) is necessary, which performs an important role in facilitating the ring-opened intermediate (3). The cooperation of (2,2'-bipy)RuCl₃(CH₃OH) with CTAC leads to a very efficient catalysis. This point is strongly supported by the observation that in the absence of a Lewis base, the complex of (2,2'-bipy)RuCl₃(CH₃OH) itself is inactive for the coupling reaction of CO₂ and PO. Meanwhile, the fact that an equimolar ratio of CTAC to (2,2'-bipy)RuCl₃(CH₃OH) is appro-



Scheme 2. Proposed mechanism.

priate for the reaction can be well explained by the catalytic mechanism proposed above.

4. Conclusion

A variety of metal-based catalysts have been found active for the coupling of carbon dioxide with epoxides; however, few have exhibited the success based on a ruthenium complex. The combination of (2,2'-bipy)RuCl₃(CH₃OH) with an ammonium salt CTAC exhibits a very high activity and selectivity for the formation of propylene carbonate from carbon dioxide and propylene oxide under mild conditions. TOF higher than 1000 h⁻¹ could be achieved generally and even TOF as high as 1512 h⁻¹ can be achieved at a shorter reaction time. The catalyst can be easily recovered and reused several times without appreciable loss of catalytic activity. After five catalytic recycles, the total TON reached up to 2.04 × 10⁴.

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