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## Short communication

# Hydrogenation of ethylene carbonate catalyzed by lutidine-bridged N-heterocyclic carbene ligands and ruthenium precursors



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## 1. Introduction

The hydrogenation of CO<sub>2</sub> remains a challenge as CO<sub>2</sub> is a thermodynamically stable compound [1,2]. Recently, the hydrogenation of CO<sub>2</sub> derivatives including formates, carbonates, carbamates and urea derivatives has attracted particular attentions, mainly because these hydrogenation processes provide an alternative approach for the indirect transformation of CO<sub>2</sub> [3–5].

Generally, the hydrogenable reactivity of the polar carbonyl groups follows the order of  $RC(O)H > RC(O)R' \gg RC(O)OR' >$  $RC(0)NR_{2}' \implies ROC(0)OR' > ROC(0)NR_{2}' > R_{2}NC(0)NR_{2}'$  [6,7]. Although the hydrogenation of carbonates was difficult to achieve, preliminary progresses still have been made based on homogeneous and heterogeneous catalysts [8-18]. Milstein developed well-defined Ru(II)-PNN complexes for hydrogenation of dimethyl carbonate to methanol under mild conditions [8]. The high catalytic efficiency was attributed to the metal-ligand cooperation by aromatization-dearomatization of pyridine pincer core. Ding reported that Ru(II)-PNP complexes could completely convert ethylene carbonate to glycol and methanol in the presence of KO<sup>t</sup>Bu [10]. The NH moiety of PNP ligand was critically important in facilitating the reduction of C=O bond. Leitner found that Ru/triphos system could efficiently catalyze the hydrogenation of carbonates in the presence of acid additive [11]. In addition, the mechanism of hydrogenation of dimethyl carbonate catalyzed by the Ru(II)-PNN complexes was extensively investigated by density functional theory (DFT) [12-14]. These DFT calculations showed that hydrogenation of carbonates required a lower activation energy

## ABSTRACT

A series of air and moisture-stable lutidine-bridged N-heterocyclic carbene (NHC) ligands and commercial Ru precursors were applied as catalysts for hydrogenation of ethylene carbonate to glycol and methanol. N-Butyl-substituted CNC-pincer ligand **L1** and RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub> catalytic system exhibited the highest catalytic activity with 99% conversion of ethylene carbonate, 92% glycol and 42% methanol yields. The high catalytic activity was attributed to the in-situ formation of Ru-NHC complexes in the presence of base. This facile, stable and efficient catalytic system provided a new method for the indirect conversion of CO<sub>2</sub>.

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barrier than that of CO<sub>2</sub>. Recently, Cu-based heterogeneous catalysts such as CuCr<sub>2</sub>O<sub>4</sub> [15], Cu-SiO<sub>2</sub> [16], Cu/HMS [17] and Cu/CeO<sub>2</sub> [18] were also reported to be efficient for hydrogenation of carbonates and Cu<sup>0</sup> and Cu<sup>+</sup> were proposed as the active sites. However, air-sensitive phosphine ligands were used in these Ru-based complexes and Cu catalyzed reactions need a harsh condition. Thus, it's significant to develop a more stable and facile catalyst for the indirect conversion of CO<sub>2</sub> under milder conditions.

Since the first stable crystalline carbene was isolated and fully characterized by Arduengo [19], increasing scientific attentions have been focused on the diverse N-heterocyclic carbenes (NHCs) chemistry. NHC ligands have strong  $\sigma$ -donor ability and the corresponding metal-NHC complexes are air and moisture stable [20]. Based on these special features, NHCs have been widely applied in various catalytic reactions such as C—C bond coupling, hydrogenation/dehydrogenation and polymerisation [21]. However, these prominent NHCs were rarely used for hydrogenation of carbonates. Herein, for the first time, the lutidine-bridged NHC ligands and commercial Ru precursors were applied to catalyze hydrogenation of ethylene carbonate to glycol and methanol (Scheme 1).

## 2. Experimental

## 2.1. Synthesis of NHC ligands

All the NHC ligands were prepared following the reported procedures with minor modifications in the yields of 83–93% [22] (see Supplementary materials). The structures of NHC ligands were listed in Fig. 1.

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Scheme 1. Hydrogenation of ethylene carbonate by NHC ligand and Ru precursor.

#### 2.2. Typical procedure for hydrogenation of ethylene carbonate

A 50 mL stainless autoclave charged with ethylene carbonate (5 mmol), **L1** (0.1 mmol), RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub> (0.1 mmol), KO<sup>t</sup>Bu (0.5 mmol), and dioxane (10 mL) was purged three times with H<sub>2</sub> and pressurized to 5 MPa then heated to 130 °C. After reaction, the autoclave was cooled down to room temperature and the residual H<sub>2</sub> was vented slowly. The conversion of ethylene carbonate and the yields of glycol and methanol were determined by GC with mesitylene as an internal standard.

#### 3. Results and discussion

3.1. Hydrogenation of ethylene carbonate catalyzed by NHC ligands and Ru precursors

#### 3.1.1. Effects of NHC ligands

Due to the strong electron-donating ability, NHC ligands have been successfully applied to various hydrogenation reactions. Accordingly, a catalytic system composed of NHC ligands and RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub> was developed for hydrogenation of ethylene carbonate (Table 1).

In the presence of NHC ligands or Ru precursors alone, poor catalytic activities were obtained with low conversions of ethylene carbonate (entries 1 and 2). The combination of NHC ligands and RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub> greatly enhanced the catalytic efficiency. Lutidinederived CNC-pincer ligands **L1–L3** gave nearly full conversions (entries 3–5). Particularly, **L1**, which contains n-butyl substituent, provided 99% conversion of ethylene carbonate with glycol and methanol in 92 and 42% yields. The high catalytic activity of CNC-pincer ligands might be ascribed to the metal-ligand cooperation through aromatization-dearomatization of lutidine framework, which facilitated the cleavage of H<sub>2</sub> [23]. In contrast, *m*-xylene-derived CCC-pincer ligand **L4** gave a lower conversion, which also demonstrated the importance of a pyridine linker [24]. Meanwhile, CNN-pincer ligands **L5** and **L6** which



Fig. 1. Structures of NHC ligands.

#### Table 1

Hydrogenation of ethylene carbonate to glycol and methanol catalyzed by various NHC ligands and  $RuHCl(CO)(PPh_3)_3^a$ .

ЛеОН 7 1
7 1
1
2
4
1
6
9
1
0
3
4
3
26
9
2
1
9

 $^a\,$  Ethylene carbonate (5.0 mmol), K0^tBu (0.5 mmol), dioxane (10 mL), H\_2 (5 MPa), 130 °C, 12 h.

<sup>b</sup> 140 °C.

<sup>c</sup> 120 °C.

<sup>d</sup> H<sub>2</sub> 6 MPa.

<sup>e</sup> H<sub>2</sub> 4 MPa.

<sup>f</sup> 48 h.

<sup>g</sup> 6 h.

have a carbene and an amine-donor gave slight lower activities which may be ascribed to the hemilability of amine-donor (entries 7 and 8) [25]. These results showed that bis-NHC also played a significant role in enhancing the catalytic activity. Decreasing the amount of RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub> resulted in lower activities, while increasing the amount of L1 had no significant influence on the catalytic activities (entries 9-11). In order to improve the yield of methanol, other reaction conditions were also investigated. Increasing the temperature or H<sub>2</sub> pressure or prolonging the reaction time did not enhance the yield of methanol. Whereas, the catalytic activities obviously decrease (entries 12–17). 2-Hydroxyethyl formate (<5%), which was an intermediate in hydrogenation of ethylene carbonate [10], was detected by GC-MS after reaction. In addition, CO<sub>2</sub> and CO were also detected in residual gases. The existence of CO<sub>2</sub> could be ascribed to the decomposition of ethylene carbonate. CO was derived from the decarbonylation of ethylene carbonate and hydrogenation of CO<sub>2</sub>. Similar observations were also found in Cu-catalyzed carbonates hydrogenation [15–18]. The existence of these side-products might lead to the relative low yields of methanol.

#### 3.1.2. Effects of Ru precursors

Various commercial Ru precursors were also investigated for hydrogenation of ethylene carbonate in the presence of **L1** (Table 2). Ru precursors which contained tertiary phosphine ligands exhibited high catalytic efficiency with 86–99% conversions (entries 1–3). Particularly,

#### Table 2

Hydrogenation of ethylene carbonate to glycol and methanol catalyzed by various Ru precursors and L1<sup>a</sup>.

Entry	Ru precursors	Conv. (%)	Yield (%)	
			Glycol	MeOH
1	RuHCl(CO)(PPh <sub>3</sub> ) <sub>3</sub>	99	92	42
2	$RuH_2(CO)(PPh_3)_3$	99	84	28
3	$RuCl_2(PPh_3)_3$	86	63	19
4	Ru(acac) <sub>3</sub>	98	85	22
5	RuCl <sub>2</sub> (COD)	53	33	7
6	RuCl <sub>2</sub> (p-cymene)	49	16	4

<sup>a</sup> Ethylene carbonate (5.0 mmol), **L1** (0.1 mmol), Ru precursors (0.1 mmol), KO<sup>t</sup>Bu (0.5 mmol), dioxane (10 mL), H<sub>2</sub> (5 MPa), 130 °C, 12 h.

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