

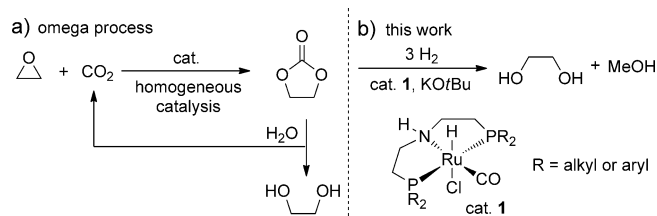
Catalytic Hydrogenation of Cyclic Carbonates: A Practical Approach from CO₂ and Epoxides to Methanol and Diols**

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As an economical, safe and renewable carbon resource, CO₂ turns out to be an attractive C₁ building block for making organic chemicals, materials, and carbohydrates.^[1] From the viewpoint of synthetic chemistry,^[2] the utilization of CO₂ as a feedstock for the production of industrial products may be an option for the recycling of carbon.^[3] On the other hand, the transformation of chemically stable CO₂ represents a grand challenge in exploring new concepts and opportunities for the academic and industrial development of catalytic processes.^[4] The catalytic hydrogenation of CO₂ to produce liquid fuels such as formic acid (HCO₂H)^[5] or methanol^[6] is a promising solution to emerging global energy problems. Methanol, in particular, is not only one of the most versatile and popular chemical commodities in the world, with an estimated global demand of around 48 million metric tons in 2010, but is also considered as the key to weaning the world off oil in the future.^[6e,f] Although the production of methanol has already been industrialized by the hydrogenation of CO with a copper/zinc-based heterogeneous catalyst at high temperatures (250–300 °C) and high pressures (50–100 atm),^[6e,7] the development of a practical catalytic system for the hydrogenation of CO₂ into methanol still remains a challenge, as high activation energy barriers have to be overcome for the cleavage of the C=O bonds of CO₂, albeit with favorable thermodynamics.^[8] Heterogeneous catalysis for the hydrogenation of CO₂ into CH₃OH has been extensively investigated, and Cu/Zn-based multi-component catalyst was found to be highly selective with a long life, but under relatively harsh reaction conditions (250 °C, 50 atm).^[3b,6d] Therefore, the production of methanol from CO₂ by direct hydrogenation under mild conditions is still a great challenge for both academia and industry.^[6a–b,9]

Milstein and coworkers recently developed an indirect approach from CO₂ to methanol through homogeneous

hydrogenation of carbonates or carbamates using pincer-type Ru^{II} catalysts, with the general structure [(PNN)Ru(CO)(H)], under mild conditions.^[10] In particular, the hydrogenation of dimethyl carbonate has established a bridge from CO₂ to methanol,^[11] as dimethyl carbonate can be produced from CO₂ and methanol.^[6e] However, from an economic point of view, this process is less effective in cost, as the starting dimethyl carbonate (US\$ 1000/ton) is much more expensive than the product methanol (US\$ 400/ton). Direct hydrogenation of CO₂ to methanol under homogeneous conditions using either combined Ru^{II} complexes and Lewis acid or a single Ru^{II} complex have also been reported recently by Sanford and Huff,^[12a] and Klankermayer, Leitner, and co-workers, respectively.^[12b] However, the catalytic efficiency of these processes still remain unsatisfactory. Therefore, the development of a new reaction pathway and a practical catalyst system for the production of methanol from CO₂ is in urgent demand. Herein, we report our preliminary results on the use of a type of readily available (PNP)Ru^{II} catalyst (**1**) for the homogeneous hydrogenation of cyclic carbonates from readily available CO₂ and epoxides (Scheme 1 b), to give methanol and the corresponding diols with excellent catalytic efficiency.



Scheme 1. a) Shell omega process for the production of EG, and b) the present approach to produce EG and methanol.

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[**] We thank the NSFC (21121062 and 91127041), the Major Basic Research Development Program of China (2010CB833300), the Science & Technology Commission of Shanghai Municipality, and CAS for financial support of this work. We also thank Prof. Xiao-Bing Lu (Dalian University of Technology) for generously providing a sample of poly(propylene carbonate), and Professors Li-Xin Dai and Pierre Dixneuf for their valuable discussions and comments on this manuscript.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201207781>.

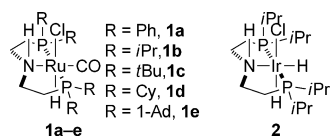
Considering the difficulties in the production of dimethyl carbonate from CO₂, we decided to use ethylene carbonate as the starting material for a hydrogenation study, as the insertion of CO₂ into ethylene oxide to produce ethylene carbonate is thermodynamically favorable and the process has been well developed^[4,9] as the key step in the “omega process” (Scheme 1 a) for the production of ethylene glycol (EG).^[13] On the other hand, pincer complexes have been extensively studied and have proven to be highly active in the catalytic hydrogenation of various amides and esters, as well as the reverse processes.^[14] We initiated our investigation by using pincer-type Ru^{II} complexes as catalysts to check the feasibility of catalyzing the hydrogenation of cyclic carbonates. A preliminary screening of various reaction parameters

for the hydrogenation of 4-methyl-1,3-dioxolan-2-one in the presence of a catalytic amount of Ru^{II} complex **1a**,^[14b] including the solvent, substrate concentration, *t*BuOK concentration, hydrogen pressure, and the reaction temperature, clearly established the feasibility of this catalysis (for details, see the Supporting Information, Tables S1–S5). Subsequently, we examined the catalytic activity of a variety of Ru^{II} and Ir^{III} complexes (**1** and **2**) in the hydrogenation of ethylene carbonate. The reactions were conducted in THF at 140 °C under 50 atm of H₂ in the presence of the catalytic Ru^{II} or Ir^{III} complex and the base *t*BuOK (substrate/catalyst/*t*BuOK = 1000–100 000:1:1), and the results are shown in Table 1.

Table 1: Hydrogenation of ethylene carbonate in the presence of Ru^{II} and Ir^{III} catalysts.^[a]

$\text{ethylene carbonate} + \text{H}_2 \xrightarrow[\text{THF, 140 } ^\circ\text{C}]{\text{1 or 2, KOtBu (50 atm)}} \text{HOCH}_2\text{CH}_2\text{OH} + \text{MeOH} + \text{HCOOMe}$					
Entry	Cat. (mol %)	t [h]	Conv. [%] ^[b]	Yield of EG [%] ^[b]	Yield of MeOH [%] ^[b]
1	1a (0.1)	0.5	> 99	> 99	> 99
2	1b (0.1)	0.5	74	74	45 (18) ^[c]
3	1c (0.1)	0.5	16	15	13
4	1d (0.1)	0.5	76	76	48 (20) ^[c]
5	1e (0.1)	0.5	24	24	22
6	2 (0.1)	1	11	10	1
7	1a (0.05)	1	> 99	> 99	> 99
8	1a (0.02)	10	> 99	> 99	98
9	1a (0.01)	48	> 99	> 99	> 99
10 ^[d]	1a (0.001)	72	89	87	84

[a] Standard reaction conditions: substrate (28.6 mmol), 1 equiv of KOtBu to the Ru^{II} or Ir^{III} complex, THF (20 mL), in a 125 mL autoclave. [b] Determined by GC analysis using *p*-xylene (50 μL) as the internal standard. [c] The data in parentheses are the GC yields of methyl formate (HCOOMe). [d] 60 atm of H₂ was applied.



It was found that at a catalyst loading of 0.1 mol %, Ru^{II} complexes **1a–e** are active for the hydrogenation, simultaneously affording methanol and EG in various yields (entries 1–5), whereas Ir complex **2** is much less effective (entry 6). In the reaction with **1b** and **1d** some amount of methyl formate is also formed along with the expected alcohol products (entries 2 and 4). This is probably due to their lower activity for the hydrogenation of the 2-hydroxyethylformate intermediate, which may undergo a fast ester exchange with methanol to give methyl formate. Among the Ru catalyst series (**1a–e**), complex **1a**, which has a readily available and air-stable *HN*(CH₂CH₂PPh₂)₂ ligand, turned out to be optimal in terms of catalytic performance (entries 2–5 vs. 1).

With the optimized catalyst in hand, we subsequently turned our attention to improving the catalyst turnover numbers (entries 7–10). Complete conversion of the substrate was realized in the presence of 0.05 mol % of **1a** by extending

the reaction time to 1 h, which afforded both methanol and EG in > 99 % yield (entry 7). At a catalyst (**1a**) loading of 0.02 mol %, similar results were obtained in 10 h (entry 8). When the catalyst loading was decreased to 0.01 mol %, the reaction could be completed in 48 h to give methanol and EG in > 99 % yield (entry 9). When the catalyst loading was further decreased to 0.001 mol %, the reaction still proceeded smoothly at 60 atm of H₂ with a 89 % conversion of ethylene carbonate in 72 h, to afford methanol and EG in 84 % and 87 % yields, respectively (with a TON of 87 000 and a TOF of 1200 h^{−1}; entry 10). This result demonstrates the high efficiency and good stability of the catalyst.

The application of the optimized catalyst **1a** was then extended to the hydrogenation of a variety of cyclic carbonates (Table 2). Heating a solution of propylene carbonate (2.92 g, 28.6 mmol) and H₂ (50 atm) with a catalytic amount of complex **1a** (3.4 mg, 0.0057 mmol, 0.02 mol %) at 140 °C in THF (20 mL) in a 125 mL autoclave for 10 h selectively produced methanol and propylene glycol in quantitative yields (entry 1). Under similar conditions, other cyclic carbonates, including 5-membered 1,3-dioxolan-2-ones with one, two, or even four substituents, as well as a six-membered carbonate, can also be efficiently and selectively hydrogenated into methanol and their corresponding diols. The steric hindrance of the substituents at the backbone of cyclic carbonates has a significant impact on the activity of the reaction, as longer reaction time and/or higher catalyst loading are required to reach a complete conversion of sterically more demanding substrates (entries 2–10 vs. 1). The cyclic carbonate with a six-membered ring, 1,3-dioxan-2-one, was also selectively hydrogenated in the presence of 0.05 mol % of **1a** to afford methanol and 1,3-propanediol in quantitative yield (entry 11).

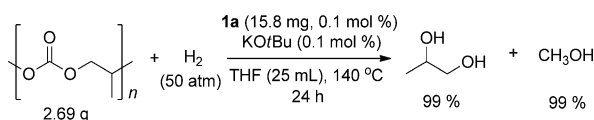
In another unprecedented reaction, complex **1a** was found to catalyze the hydrogenation of polycarbonate into methanol and the corresponding diol, thus realizing a hydrogenative degradation of polycarbonate. As shown in Scheme 2, a sample of poly(propylene carbonate) (PPC; 2.69 g) with a weight-average molecular weight (*M*_w) of 100 698 (*M*_w/*M*_n = 1.77, > 99 % carbonate linkages), which had been prepared by an alternative copolymerization of propylene oxide and CO₂,^[15] was readily depolymerized by hydrogenation in the presence of **1a** (15.8 mg, 0.1 mol %) to afford methanol and 1,2-propyleneglycol in high yields (both 99 %). Therefore, the present catalytic system may provide a potential approach to the use of recovered waste polycarbonate as a resource.

Following the optimized reaction conditions mentioned above, a deuterium-labeling study was carried out by using D₂ instead of H₂ to get insight into the mechanistic aspects of the catalysis. As shown in Scheme 3a, in the **1a**-catalyzed deuteration of ethylene carbonate, methanol is produced with only 87 % deuterium content at the methyl group, as determined by ¹H NMR analysis of its benzoate ester, which indicates a partial transfer of hydrogen atoms from the ethylene backbone of the carbonate to the carbon of methanol. This is also confirmed by a significant deuterium substitution at the carbon atoms of EG (49 % deuteration), which implicates the catalytic activity of complex **1a** in both

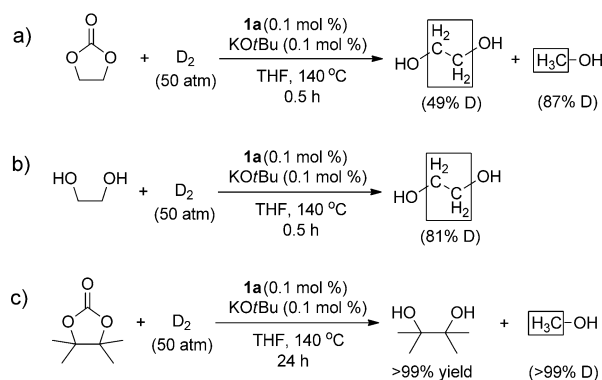
Table 2: Hydrogenation of various cyclic carbonates in the presence of Ru^{II} complex **1a**.^[a]

$\text{R}^1\text{R}^2\text{C}(\text{O})\text{C}(\text{R}^3\text{R}^4)\text{O} + \text{H}_2 \xrightarrow[\text{THF, 140 } ^\circ\text{C}]{\text{1a, KOtBu (50 atm)}} \text{R}^1\text{R}^2\text{C}(\text{OH})\text{C}(\text{R}^3\text{R}^4)\text{OH} + \text{MeOH}$ $n = 0 \text{ or } 1$					
Entry	Substrate	1a [mol %]	<i>t</i> [h]	Yield of diol [%] ^[b]	Yield of MeOH [%] ^[c]
1		0.02	10	99 ^[c]	99
2		0.05	10	96 ^[c]	99
3		0.05	4	99	> 99
4		0.05	4	99	> 99
5		0.05	4	98	> 99
6		0.05	4	99	> 99
7		0.05	4	97	> 99
8		0.05	10	99	98
9		0.05	12	97	> 99
10		0.1	20	96	95
11		0.05	2	99 ^[c]	99

[a] Standard reaction conditions: substrate (28.6 mmol), 1 equiv of KOtBu to **1a**, THF (20 mL), in a 125 mL autoclave. [b] Yield of the isolated diol products, except for entries 1, 2, and 11. [c] Determined by GC analysis using *p*-xylene (50 μ L) as the internal standard.



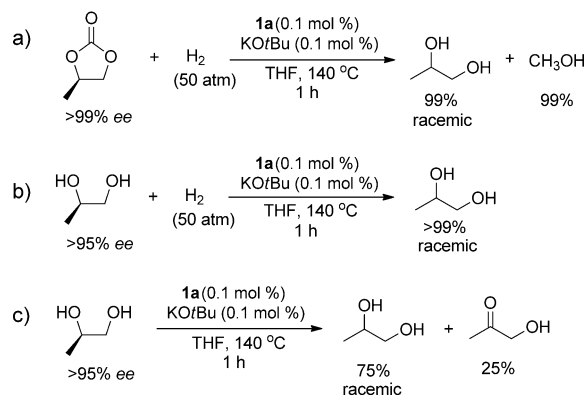
Scheme 2. Hydrogenative depolymerization of PPC.



Scheme 3. Deuterium labeling studies of the hydrogenation.

the dehydrogenation of EG and the hydrogenation of the resultant 2-hydroxyacetaldehyde under the experimental conditions. In fact, the treatment of EG with D₂ (50 atm) in the presence of **1a** (0.1 mol %) and KOtBu (0.1 mol %) at 140 °C for 0.5 h results in the formation of EG with a total of 81% deuterium incorporation at the ethylene carbon atoms (Scheme 3b), thus supporting the above rationale. To prevent D/H exchange in the preparation of deuterated methanol, tetramethyl ethylene carbonate was employed as a substrate instead of ethylene carbonate. As expected, deuterated methanol can be prepared in 99% yield with a >99% deuterium incorporation at the methyl group (Scheme 3c). Therefore, the present catalytic system has provided a facile and practical method for the preparation of deuterated methanol.

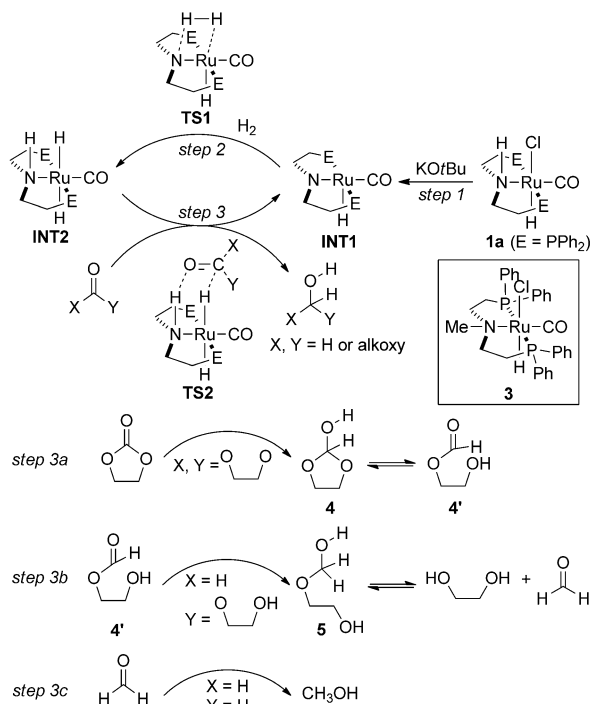
On the other hand, the **1a**-catalyzed hydrogenation of an optically active (>99% *ee*) (*R*)-propylene carbonate under the optimized conditions afforded racemic 1,2-propyleneglycol (Scheme 4a) in addition to methanol, which implies that the initially formed optically active 1,2-propylene glycol might undergo racemization under the experimental conditions, as a result of hydrogenation/dehydrogenation equilibrium under the reaction conditions. In fact, treatment of optically active (*R*)-1,2-propyleneglycol (>95% *ee*) with **1a** (0.1 mol %) and KOtBu (0.1 mol %) in the presence or absence of H₂ (50 atm) at 140 °C for 1 h afforded racemic



Scheme 4. Stereochemistry studies of the hydrogenation.

1,2-propylene glycol (Scheme 4b,c), but with the co-generation of hydroxy acetone (25%) as minor product in the absence of H_2 (Scheme 4c), which further confirms the dual function of **1a** in the dehydrogenation of alcohols and hydrogenation of aldehydes or ketones under basic conditions, and is consistent with the observations in the deuterium-labeling study.

Based on these observations, we proposed the reaction mechanism shown in Scheme 5. First, catalyst **1a** is activated by the elimination of HCl in the presence of a base to afford



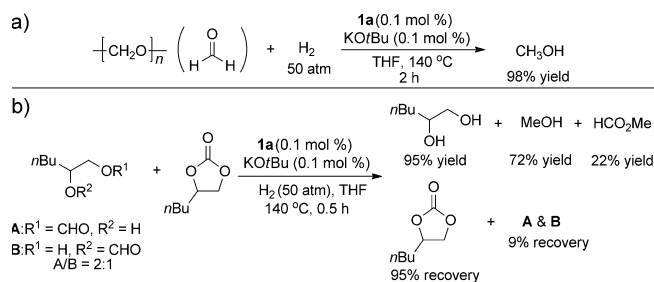
Scheme 5. Proposed mechanism for the (PNP) Ru^{II} -catalyzed hydrogenation of cyclic carbonates.

the $16e^-$ amido Ru complex **INT1** (step 1).^[16] Then, a molecule of H_2 is expected to undergo heterolytic cleavage by reacting with **INT1** via **TS1** to give the $18e^-$ Ru dihydride **INT2** (step 2).^[17] Finally, nucleophilic addition of Ru dihydride **INT2** to the carbonyl group of a carbonate, formate, or formaldehyde gives the corresponding reduced products **4** or **4'** (step 3a), **5** or formaldehyde (step 3b), and methanol (step 3c), respectively, and to regenerate $16e^-$ amido Ru complex **INT1** (step 3),^[16] which enters into the next catalytic cycle. The addition of Ru dihydride **INT2** to the carbonyl group is proposed to proceed by the hydrogen-bonding activation of the carbonyl group in the substrate with the proton of an NH group via a six-membered transition state (**TS2**).

An experiment to clarify the function of NH group in ligand **1** in the catalytic cycle was carried out by examining the catalytic performance of an analogous Ru^{II} complex **3** (Scheme 5), containing the PNP ligand with an *N*-Me group. It was found that no reaction occurs with complex **3** under otherwise identical conditions. The dramatic switch of cata-

lytic activity from the NH-containing catalyst (**1**) to the analogous *N*-Me-derived catalyst **3** indicates that the NH moiety is critically important for the catalytic activity, and that the NH proton should be intimately involved in the catalytic event by cooperation with the metal center, as in the scenarios in many other related catalytic hydrogenation systems.^[14,18]

As shown in Scheme 5, three independent elementary steps (steps 3a–c) related to **INT2** may operate in the overall transformation from ethylene carbonate to methanol and EG. This transformation begins with the initial reduction of ethylene carbonate to 1,3-dioxolan-2-ol (**4**; a lactol form), which stays in an equilibrium with 2-hydroxyethylformate (**4'**) in solution (step 3a), followed by the further reduction of 2-hydroxyethylformate (**4'**) to 2-(hydroxymethoxy)ethanol (**5**) (step 3b), which is a hemiacetal in equilibrium with formaldehyde and glycol. The transformation is finally accomplished by the reduction of formaldehyde to methanol (step 3c). In fact, the direct hydrogenation of paraformaldehyde, which can decompose into formaldehyde in situ through heating, in the presence of **1a** (0.1 mol %) proceeded to completion in THF (2 h) to give methanol in 98% yield (Scheme 6a). This result indicates the feasibility of step 3c in



Scheme 6. Hydrogenation of formaldehyde (a) and a mixture of hydroxyhexyl formates with 1-hexene carbonate (b) catalyzed by **1a**.

the transformation into methanol. On the other hand, the high chemoselectivity for the formation of methanol, even with incomplete conversion of ethylene carbonate (as shown in Table 1, entry 10), implies that the reactivity of the intermediates, such as alkyl formate (**4'**) and formaldehyde, should be much higher than that of the starting ethylene carbonate. To compare the rate of step 3a with that of step 3b (Scheme 5), the hydrogenation of an equimolar mixture of 1-hexene carbonate and hydroxyhexyl formates, containing a 2:1 isomeric mixture of 2-hydroxyhexyl formate (**A**) and 1-hydroxyhexan-2-yl formate (**B**) (both can be viewed as model molecules of **4'**), was carried out in the presence of **1a** (0.1 mol %) at $140^\circ C$ and 50 atm of H_2 with stirring (Scheme 6b). Over 90% conversion of 2-hydroxyhexyl formate and hexane-1,2-diol (95%) with the co-generation of methylformate (22%) was observed in 0.5 h. In contrast, 1-hexene carbonate was largely recovered (95%) without obvious conversion. This experiment suggested that the initial hydrogenation of cyclic carbonate (step 3a) should be the most

difficult one among the sequential hydrogenation steps 3a–c shown in Scheme 5.

In conclusion, we have developed a highly efficient catalytic hydrogenation of cyclic carbonates for the preparation of methanol with the cogeneration of the corresponding diols by using (PNP) Ru^{II} pincer complexes as the catalysts under relatively mild conditions. This process has provided a facile approach for the simultaneous production of two important bulk chemicals, methanol and EG, from ethylene carbonate, which is industrially available by reacting ethylene oxide with CO₂. The coupling of the present catalytic system with the process of ethylene carbonate production in the omega process is expected to establish a new bridge from CO₂ and ethylene oxide to methanol and EG. Apart from the clean production of diol, a big bonus of the present protocol is the efficient chemical utilization of CO₂, which represents a distinct advantage in terms of sustainability over the omega process, which gives back CO₂. Moreover, this catalytic system has also provided a potential process for the utilization of waste poly(propylene carbonate) as a resource to afford 1,2-propylene diol and methanol through hydrogenative depolymerization, and a convenient method for the preparation of deuterated methanol from CO₂ and D₂. A possible catalytic mechanism is proposed, in which the NH moiety of the ligand is demonstrated to be critically important in facilitating the reduction of the carbonate C=O bond through secondary coordination sphere interactions with substrates.

Received: September 26, 2012

Published online: November 14, 2012

Keywords: carbon dioxide · ethylene glycol · hydrogenation · methanol · ruthenium

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