ACS Catalysis

Research Article

pubs.acs.org/acscatalysis

Transfer Hydrogenation of Organic Formates and Cyclic Carbonates: An Alternative Route to Methanol from Carbon Dioxide

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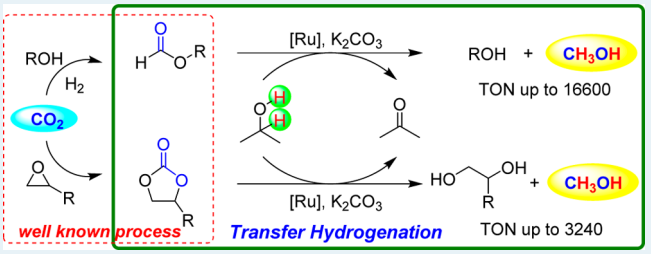
Supporting Information

ABSTRACT: Transfer hydrogenation of organic formates and cyclic carbonates was achieved for the first time using a readily available ruthenium catalyst. Nontoxic and economical 2-propanol was used, both as a solvent and hydrogen source, without the need of using flammable H_2 gas under high pressure. This method provides an indirect strategy to produce methanol from carbon dioxide under mild conditions as well as an operationally simple and environmentally benign way to reduce formates and carbonates.



KEYWORDS: *transfer hydrogenation, methanol production, formyl ester, cyclic carbonate, carbon dioxide*

INTRODUCTION

Transfer hydrogenation (TH) is a highly advanced environmentally benign strategy used for the reduction of organic molecules, which does not require the use of strong and pyrophoric environmentally harmful reducing agents, such as $LiAlH_4$.[1] Furthermore, this reaction proceeds at ambient pressure and in the absence of pressurized, flammable H_2 gas. 2-Propanol, a nontoxic and inexpensive reagent, is commonly used as the hydrogen source in a variety of TH reactions, and significant advances have been achieved in the TH of aldehydes,[2] ketones,[3] imines,[4] and nitriles.[5] However, to the best of our knowledge, TH of formates and carbonates has not yet been reported.

The alkoxy group adjacent to carbonyl carbon makes hydrogenation of esters more difficult than that of ketones due to resonance stabilization.[6] Moreover, two alkoxy groups make carbonates extremely stable. Thus, only a few examples have, so far, been reported for the catalytic hydrogenation of formates and carbonates using H_2 at high pressures.[7] The development of operationally simple and environmentally friendly reduction of formates and carbonates remains a major challenge.

From a different perspective, hydrogenation of formates and carbonates is a highly attractive indirect route to produce methanol from CO_2, a promising solution to worldwide energy problems.[8] Milstein and co-workers reported the generation of methanol through hydrogenation of formates, carbonates, and carbamates using PNN pincer-type Ru(II) catalysts such as complex **5**,[7d] while Ding and co-workers recently reported hydrogenation of cyclic carbonates using complex **1**[9] to produce methanol and diol.[7b] Although both methods produced methanol efficiently, they required high pressures (10−50 atm) of highly flammable H_2 gas. With recently developed highly efficient catalysts for hydrogen transfer reactions (Figure 1),[9] we envisioned that TH of more challenging substrates, such as formates and carbonates, could be achieved. Herein, we report, for the first time, the catalytic TH of formates and carbonates using a readily available Ru catalyst.

RESULTS AND DISCUSSION

To investigate the feasibility of the TH of formates, methyl formate (**7a**) was selected as a benchmark substrate. Conversion of CO_2 to formic acid or alkyl formates has been well reported.[10] Various Ru complexes, known to be good catalysts for hydrogenations or TH reactions, were screened (Table 1). Ru complex **1** was found to be the most efficient catalyst and produced MeOH quantitatively when a catalytic amount of a base such as KO^{t}Bu (entry 1) or K_2CO_3 (entry 2) was used. No reaction took place in the absence of a base (entry 3). Analogous complexes **2** and **3** containing isopropyl (iPr) or cyclohexyl (Cy) groups were less effective (entries 4−5). Complexes **4**[11] and **5**,[7d,12] highly efficient catalysts for hydrogenation of ester derivatives, were not active for the TH reaction (entry 6−7). Complex **6**[4d,13] and other Ru complexes were further screened but failed to reduce the carbonyl group (entries 8−12). Instead, a trans-esterification reaction occurred, producing methanol and isopropyl formate (**7c**).

Having identified complex **1** as the most active catalyst among those tested, we proceeded to examine the catalyst efficiency and substrate scope (Table 2). The reaction worked efficiently even in a gram-scale reaction (1.02 g of **7a**, 94%,

Received: August 4, 2014
Revised: September 3, 2014

   dx.doi.org/10.1021/cs501133m | ACS Catal. 2014, 4, 3630−3636

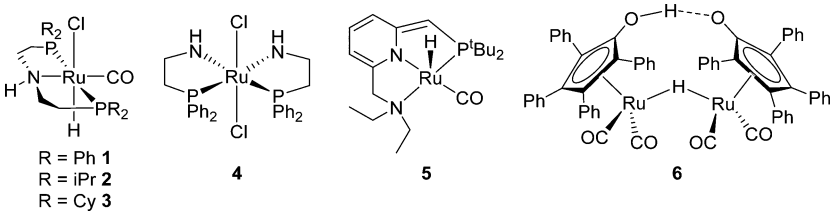
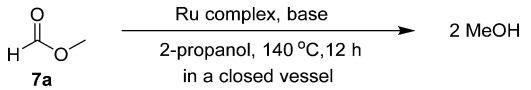


Figure 1. Ru complexes for hydrogen transfer reactions.

Table 1. Transfer Hydrogenation of Methyl Formate[a]



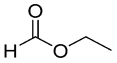
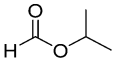
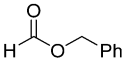
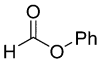
entry	[Ru] (mol %)	base	yield (%)[b]
1	**1** (0.1)	KO^{t}Bu	>99
2	**1** (0.1)	K_2CO_3	>99
3	**1** (0.1)		0
4	**2** (0.1)	K_2CO_3	97
5	**3** (0.1)	K_2CO_3	69
6[c]	**4** (0.5)	KO^{t}Bu	50
7	**5** (0.5)		10
8	**6** (0.5)		21
9[c]	$RuHCl(CO)(PPh_3)_3$ (0.5)	KO^{t}Bu	50
10[c]	$RuH_2(CO)(PPh_3)_3$ (0.5)	KO^{t}Bu	50
11[c]	$RuCl_2(PPh_3)_3$ (0.5)	KO^{t}Bu	49
12[c]	$[Ru(p\text{-cymene})Cl_2]_2$ (0.5), dppb (1.0)	KO^{t}Bu	50
13		KO^{t}Bu	0

[a]Reaction conditions: methyl formate (2.8 mmol, 1.0 equiv), Ru complex (0.1−0.5 mol %), base (same equiv to Ru), isopropanol (20 mL), 140 °C, 12 h in a closed vessel. [b]Determined by GC using *p*-xylene as the internal standard. [c]>99% of isopropyl formate was generated.

entry 2). Reducing the catalyst loading to 0.02 mol % (entry 3) and 0.01 mol % (entry 4) afforded methanol in quantitative yield after 12 and 24 h, respectively. Remarkably, excellent turnover numbers (TONs, 16 600) were achieved with a 50 ppm loading of the catalyst (entry 5). In comparison, Milstein reported hydrogenation of methyl formate with a maximum TON of 4700 with PNN pincer-type Ru(II) catalysts (0.02 mol %) using 50 atm of H_2 gas.[7d] Other alkyl formates such as ethyl, isopropyl, and benzyl formates were also smoothly reduced, producing methanol (entries 6−8). However, phenyl formate was reduced less efficiently (entry 9).

Next, we examined the possibility of TH of cyclic carbonates to produce methanol and the corresponding diol using various ruthenium catalysts (Table 3). Since cyclic carbonates are easily formed by inserting CO_2 into epoxides,[14] TH of cyclic carbonates would be an attractive indirect strategy to produce methanol from CO_2.[7b] Similar to the TH of methyl formate, yields of the reduced product were only moderate when ruthenium complexes **2** and **3** were used (entries 2 and 3). Only trans-esterification occurred quantitatively when other Ru catalysts were used (entries 4−8). To our delight, 4-methyl-1,3-dioxolan-2-one (**8a**) was quantitatively converted to methanol and propylene glycol (**9a**) under our standard conditions (entry 1).

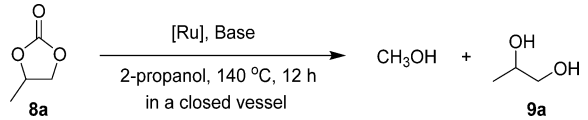
Table 2. Transfer Hydrogenation of Organic Formates[a]

entry	substrate		**1** (mol %)	time (h)	MeOH (%)[b]	TON
1			0.05	3	>99	>1980
2[c]			0.05	24	94	1880
3		**7a**	0.02	12	>99	>4950
4			0.01	24	>99	>9900
5			0.005	48	83	16600
6		**7b**	0.05	3	>99	>1980
7		**7c**	0.05	5	>99	>1980
8		**7d**	0.1	12	94	940
9		**7e**	0.1	12	34	340

[a]Reaction conditions: **7** (5.6 mmol, 1.0 equiv), **1**, K_2CO_3 (same equiv to **1**), 2-propanol (20 mL), 140 °C in a closed vessel. [b]Determined by GC using *p*-xylene as the internal standard. [c]**7a** (17.0 mmol, 1.02 g, 1.0 equiv)

dx.doi.org/10.1021/cs501133m | *ACS Catal.* 2014, 4, 3630−3636

Table 3. Transfer Hydrogenation of 4-Methyl-1,3-dioxolan-2-one (8a) with Various Catalysts[a]



entry	[Ru] (mol %)	MeOH (%)	diol (%)[b]
1[c]	**1** (0.1)	>99	>99
2[c]	**2** (0.1)	60	>99
3[c]	**3** (0.1)	31	>99
4	**4** (0.5)	0	99
5	**5** (0.5)	0	97
6	**6** (0.5)	0	99
7	$RuHCl(CO)(PPh_3)_3$ (0.5)	0	98
8	$RuH_2(CO)(PPh_3)_3$ (0.5)	0	87
9	$[Ru(cymene)Cl_2]_2$ (0.5), dppb (1.0)	0	trace

[a]Reaction conditions: propylene carbonate (2.8 mmol, 1.0 equiv), Ru complex, KO^{t}Bu (0.5 mol %), 2-propanol (20 mL), 140 °C, 12 h. [b]GC Yield using *p*-xylene as the internal standard. [c]K_2CO_3 (0.1 mol %).

Various cyclic carbonates were subsequently subjected to the TH conditions catalyzed by complex **1** (Table 4). Catalytic loadings as low as 0.025% were enough to reduce **8a** in very good yield (entry 4). A further reduction to 0.01% led to a significant decrease in the yield of methanol (51%); however, a higher amount of 1,2-propanediol (**9a**) was obtained with diisopropylcarbonate (**8h**) due to trans-esterification with 2-propanol (entry 5). Ethylene carbonate (**8b**) was easily reduced with 0.1% of the catalyst in a short time (entry 6). Ethyl, butyl, and phenyl substituted cyclic carbonates were also efficiently reduced to afford methanol in excellent yields (entries 7−9). When 4-vinyl-1,3-dioxolan-2-one (**8f**) was subjected to the catalytic TH reaction conditions, reduction also occurred at the olefin group, and 1,2-butanediol (**9c**) was obtained in excellent yield along with methanol (entry 10). Unfortunately, the scope of the reaction could not be extended to linear carbonates such as diethyl carbonate (entry 11).

The mechanism for the complex **1** catalyzed hydrogenation and dehydrogenation reactions has been well studied (Scheme 1).[7b,9a] The 16 e$^-$ amido Ru complex (**1a**), generated from the base-assisted elimination of HCl from complex **1**, is easily transformed to the 18 e$^-$ Ru-dihydride complex (**1b**) either using H_2 at high pressure or a nontertiary alcohol. Complex **1b** can then reversibly liberate H_2 or add to the carbonyl group of carbonates or esters (**TS**).[15]

Using excess amount of 2-propanol as a solvent, an increase of pressure in the reaction tube was observed (~3 bar), due to the generation of H_2 gas.[9g,16] When carbonates were reduced in an open vessel, only small amounts of methanol were obtained (~25%); this indicates that the existence of in situ generated H_2 gas is critical for the efficient reduction of carbonates. This observation led us to question whether the catalytically active species **1b** was continuously generated with the evolved H_2 gas through an outersphere-type mechanism. To address the question, deuterium-labeled 2-propanol $(CD_3)_2CDOD$ was used as the solvent in the presence of external H_2 gas (Table 5).[17] When the reaction was carried out without external H_2 gas (entry 1), the reduction of ethylene carbonate yielded 89% of methanol with hydrogen exchange (H/D 2:98). Furthermore, when nondeuterated methanol and ethylene glycol were submitted to the reaction conditions in 2-propanol-d_8, most of the protons were substituted with deuterium (Scheme 2), which suggested that a reversible hydrogenation/dehydrogenation occurred. We next examined the reaction under different pressures and amounts of external H_2 gas (entries 2−7). It was found that the incorporation of deuterium decreased as the ratios of H_2 to 2-propanol-d_8 increased (entries 2−7). These results suggest that the catalytic cycle via **1b** operates reversibly with both evolved H_2 gas and 2-propanol.

To gain insight into the possible reaction pathways, we monitored the reaction intermediates generated in the TH of ethylene carbonate (**8b**) by GC (Figure 2). Initially, a rapid consumption of **8b** along with the formation of 2-hydroxyethyl isopropyl carbonate (**10**) was observed. As time progressed, the concentration of isopropyl formate (**7c**) increased and those of **8b** and **10** decreased. A similar trend was observed when **10** was submitted to the same reaction conditions (Figure 3). Based on these results, we propose possible reaction pathways (Scheme 3). The ring opening of **8b** with 2-propanol is reversible and, because the reduction of linear carbonates is not facile under our reaction conditions (entry 11, Table 4), we believe that the direct hydrogenation of **10** is not a plausible pathway. Thus, we propose the first step to be the hydrogenation of **8b** to form 2-hydroxyethyl formate (**11**). To support it, **11** was submitted to the reaction conditions, and methanol (81%) and **7c** (16%) were formed within 1 h (Scheme 4). Formaldehyde, a proposed intermediate in our reaction mechanism, was also successfully reduced to methanol under our TH conditions like in the case of Ding and co-workers (Scheme 4).[7b]

CONCLUSION

The TH of formyl esters and cyclic carbonates was achieved for the first time in excellent yields using commercially available Ru catalyst and nontoxic and inexpensive 2-propanol, used both as a solvent and hydrogen source. This strategy is an attractive way to produce methanol from CO_2 indirectly, because formyl esters and cyclic carbonates are easily obtained from CO_2. Our methodology is operationally simple and replaces the use of highly flammable H_2 gas under high pressure.

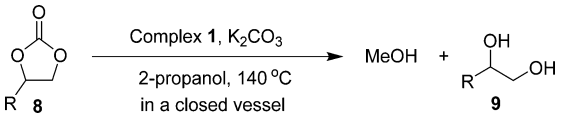
EXPERIMENTAL SECTION

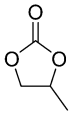
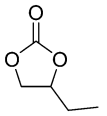
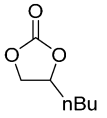
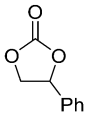
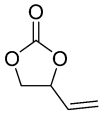
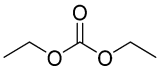
General Method. Unless otherwise noted, all reactions were carried out using standard Schlenk techniques or in an argon-filled glovebox. All transfer hydrogenation reactions were carried out in an oven-dried pressure tolerating vessel under an argon atmosphere. Ru complexes **2** and **3**,[7b] 4-butyl-1,3-dioxolan-2-one (**8d**),[18] 4-phenyl-1,3-dioxolan-2-one (**8e**),[18] and 2-hydroxyethyl isopropyl carbonate (**10**)[19] were prepared according to the literature procedures. Unless otherwise noted, all reagents were obtained from commercial suppliers and used as received. Analytical TLC was performed on a Merck 60 F254 silica gel plate (0.25 mm thickness). Column chromatography was performed on Merck 60 silica gel (230−400 mesh). NMR spectra were recorded on a Bruker DPX-300 (300 MHz) spectrometer. Tetramethysilane was used as a reference, and the chemical shifts were reported in parts per million and the coupling constant in hertz. GC analyses were carried out on an Agilent 7890A gas chromatograph using a DB-624 UI column (60 m × 0.32 mm × 1.80 μm).

General Procedure for Transfer Hydrogenation of Organic Formates. A pressure tolerating reaction vessel was charged with complex **1** (0.0056 mmol, 3.4 mg), K_2CO_3 or KO^{t}Bu (0.0056 mmol), 2-propanol (20 mL), and methyl

dx.doi.org/10.1021/cs501133m | ACS Catal. 2014, 4, 3630−3636

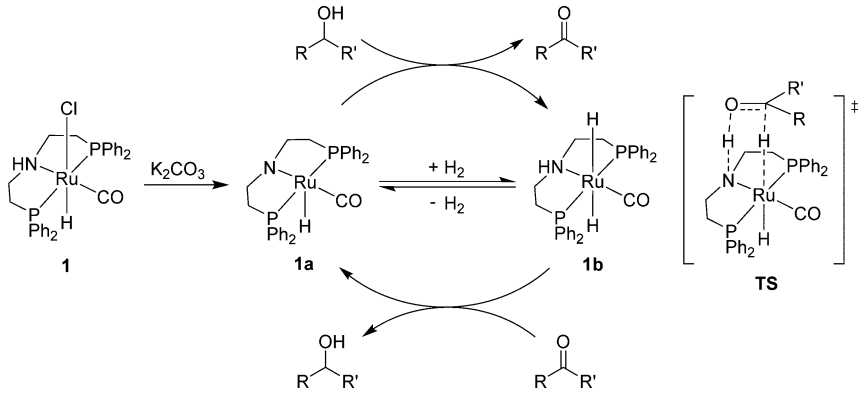
Table 4. Transfer Hydrogenation of Organic Carbonates[a]



entry	substrate		1 (mol %)	time (h)	MeOH (%)[b]	Diol (%)
1		**8a**	0.2	1	>99	>99[b]
2			0.1	2	>99	>99[b]
3			0.05	5	>99	>99[b]
4			0.025	48	81	>99[b]
5			0.01	48	51	81[b]
6		**8b**	0.1	3	91	91[c]
7		**8c**	0.1	12	94	94[c]
8		**8d**	0.1	6	>99	97[c]
9		**8e**	0.1	6	93	95[c]
10		**8f**	0.2	12	>99	96[c,d]
11		**8g**	0.1	12	6	-

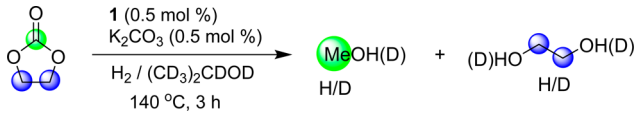
[a]Reaction conditions: **8** (2.8 mmol, 1.0 equiv), **1**, K_2CO_3 (same equiv to **1**), 2-propanol (20 mL), 140 °C, 12 h in a closed vessel. [b]Determined by GC using *p*-xylene as the internal standard. [c]Isolated yield. [d]1,2-butanediol

Scheme 1. Generation of Ru-hydrides from Complex 1



dx.doi.org/10.1021/cs501133m | ACS Catal. 2014, 4, 3630−3636

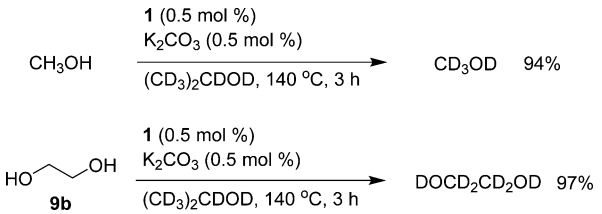
Table 5. Degree of Deuterium Incorporation in Reduction of Ethylene Carbonate[a]



entry	H_2 (bar)	H_2/propanol-d_8[b]	MeOH (%, H/D)	diol (%, H/D)
1	0		89 (2:98)	>99 (2:98)
2	3	10:90	90 (8:92)	>99 (7:93)
3[c]	3	19:81	80 (21:79)	91 (28:72)
4	9	25:75	93 (21:79)	>99 (23:77)
5[c]	9	41:59	89 (37:63)	>99 (47:53)
6	35	56:44	98 (54:46)	>99 (62:48)
7[c]	35	73:27	91 (64:36)	>99 (72:28)

[a]Reaction conditions: **8b** (0.7 mmol, 1.0 equiv), **1** (0.5 mol %), K_2CO_3 (0.5 mol %), 2-propanol-d_8 (5 mL), 140 °C, 3 h in a closed vessel. [b]Molar ratio. [c]**8b** (0.14 mmol), 2-propanol-d_8 (1 mL).

Scheme 2. Deuteration of 1,2-Ethanediol and Methanol



formate (**7a**; 5.6 mmol, 336 mg) in an argon-filled glovebox. The vessel was heated to 140 °C (bath temperature), and after the reaction, it was cooled down to 0 °C for 1.5 h. The generated H_2 was released carefully in a hood. The yield of methanol was analyzed by GC using *p*-xylene as the internal standard.

General Procedure for Transfer Hydrogenation of Cyclic Carbonates. A pressure tolerating reaction vessel was charged with complex **1** (0.0028 mmol, 1.7 mg), K_2CO_3 (0.0028 mmol, 0.39 mg), 2-propanol (20 mL), and cyclic carbonates (2.8 mmol) in a glovebox. The vessel was heated to 140 °C (bath temperature), and after the reaction, it was cooled down to 0 °C for 1.5 h. The generated H_2 was released carefully in a hood. The yield of methanol was analyzed by GC using *p*-xylene as the internal standard. Corresponding diols were purified by flash column chromatography using CH_2Cl_2/MeOH as an eluent. The products were identified by ^{1}H NMR spectral comparison with literature data.

Deuterium Incorporation Study for the TH Reaction of 1,3-Dioxolan-2-one. A stainless steel autoclave was charged with complex **1** (0.5 mol %), K_2CO_3 (0.5 mol %), 2-propanol-d_8 (5 or 1 mL), and 1,3-dioxolan-2-one (**8b**; 0.7 or 0.14 mmol) in a glovebox. The reaction vessel was purged three times with H_2 and finally pressurized with H_2 to 3, 9, or 35 bar. The vessel was heated to 140 °C (bath temperature) for 3 h, and after the reaction, it was cooled down to 0 °C for 1.5 h. The residual H_2 was released carefully in a hood. Overall yields (nondeuterated and deuterated) of methanol and 1,2-ethanediol were analyzed by GC using *p*-xylene as the internal standard, and yields of nondeuterated methanol and 1,2-ethanediol were measured by ^{1}H NMR spectroscopy (Figures S1 and S2).

Deuteration of 1,2-Ethanediol and Methanol with 2-Propanol-d_8. A pressure tolerating reaction vessel was charged with complex **1** (0.5 mol %), K_2CO_3 (0.5 mol %), 2-propanol-d_8 (5 mL), and 1,2-ethanediol (**9b**) or methanol (0.7 mmol) in a glovebox. The vessel was heated to 140 °C (bath temperature) for 3 h, and after the reaction, it was cooled down to 0 °C for 1.5 h. The residual H_2 was released carefully in a hood. Overall yields (nondeuterated and deuterated) of methanol and 1,2-ethanediol were analyzed by GC using *p*-xylene (1.4 mmol) as the internal standard, and yields of nondeuterated methanol and 1,2-ethanediol were measured by ^{1}H NMR spectroscopy (Figure S3).

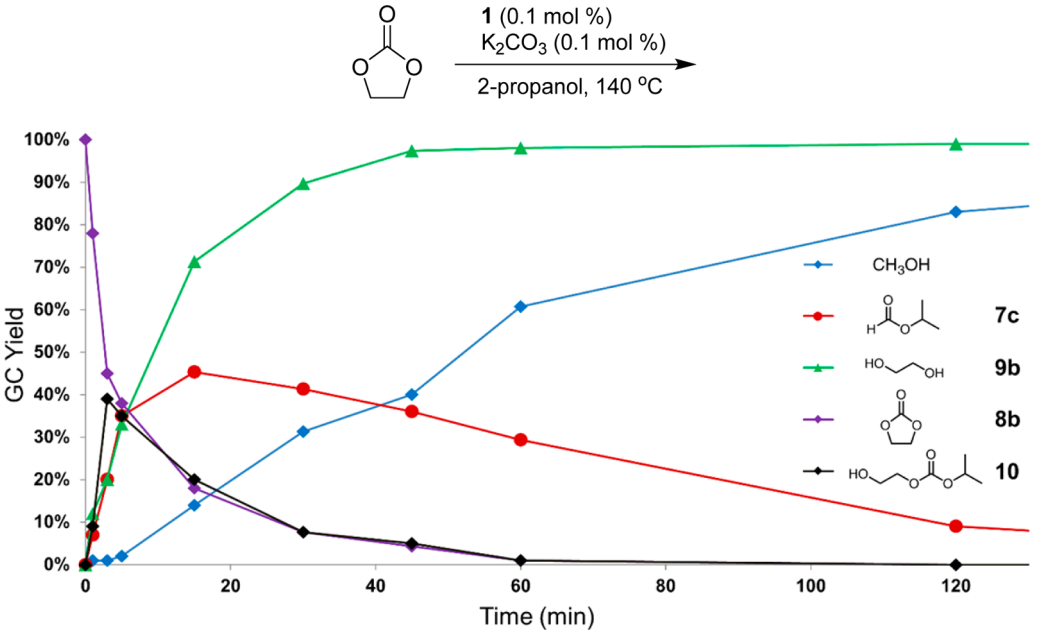


Figure 2. Reaction profile for transfer hydrogenation of ethylene carbonate.

dx.doi.org/10.1021/cs501133m | ACS Catal. 2014, 4, 3630−3636

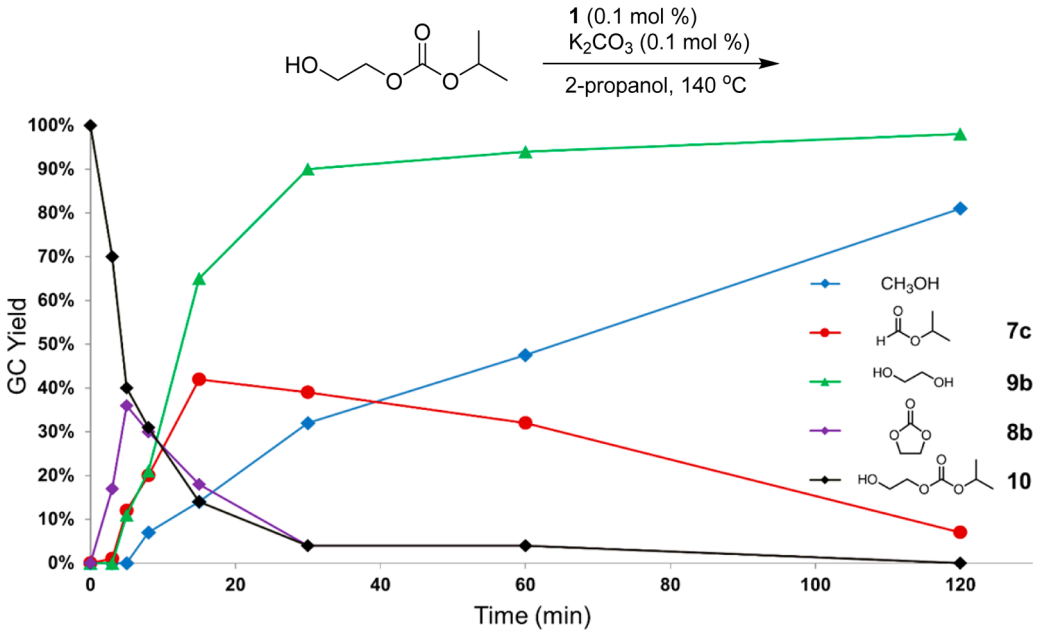
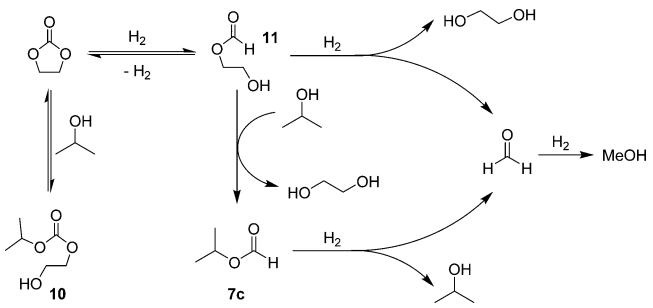
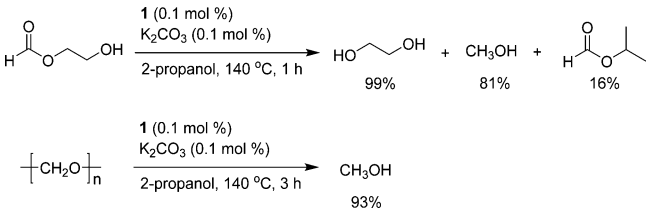


Figure 3. Reaction profile for transfer hydrogenation of 2-hydroxyethyl isopropyl carbonate.

Scheme 3. Proposed Mechanism



Scheme 4. Transfer Hydrogenation of Intermediates



■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures and spectral data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the Korea CCS R&D Center (NRF-2014M1A8A1049347), the Science Research Center Program (NRF-2014R1A5A1011165, Center for New Directions in Organic Synthesis), and the Fostering Core Leaders of the Future Basic Science Program (NRF-2014H1A8A1021111, for S.H.K.) through the National Research Foundation funded by the Korean government.

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