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Re(CO)$_5$Br-Catalyzed Coupling of Epoxides with CO$_2$ Affording Cyclic Carbonates under Solvent-Free Conditions

Jia-Li Jiang, Feixue Gao, Ruimao Hua,* and
Xianqing Qiu

*Department of Chemistry, Tsinghua University,
Key Laboratory of Organic Optoelectronics & Molecular
Engineering of Ministry of Education,
Beijing 100084, China*

ruimao@mail.tsinghua.edu.cn

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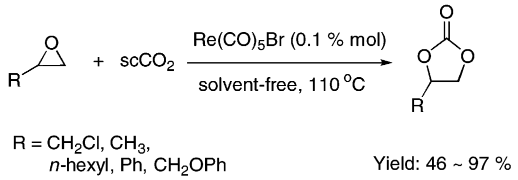
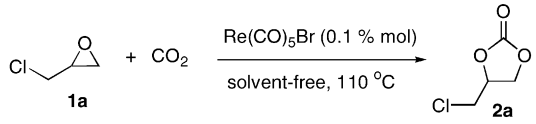


In the presence of a catalytic amount of Re(CO)$_5$Br, the coupling of epoxides with supercritical CO$_2$ without an organic solvent at 110 °C has afforded cyclic carbonates in good to excellent yields.

Catalytic transformation of CO$_2$ into useful organic compounds has received intense attention from the viewpoints of carbon source in industry and environmental problems.[1] The coupling of CO$_2$ with epoxides affording the cyclic carbonates is one of the most extensively studied reactions of the chemical fixation of CO$_2$, because cyclic carbonates not only have been used as polar aprotic solvents but also are valuable intermediates for organic synthesis[2] and polymer synthesis.[3] Although a variety of efficient catalyst systems have been reported,[1b,4] there are only a few reports of transition-metal-catalyzed the coupling of CO$_2$ with epoxides.[1b,5] Furthermore, all these transition-metal-catalyzed procedures were performed either in organic solvent or under oxygen-free conditions. Therefore, development of the new transition-metal catalyst system for activation of CO$_2$ is still one of the most interesting and challenging topics in both organometallic chemistry and C$_1$ chemistry.[6]

TABLE 1. CO$_2$ Pressure Effects in the Coupling of 1a with CO$_2$ Catalyzed by Re(CO)$_5$Br[a]



entry	CO$_2$ (MPa)[b]	time (h)	yield (%)[c]
1	1.0	24	36
2	2.0	24	65
3	3.0	24	74
4	4.0	24	82
5	5.5	3	47
6	5.5	6	61
7	5.5	12	85
8	5.5	24	97

[a] Reactions were carried out at 110 °C by using 10.0 mmol of **1a** and 0.01 mmol of Re(CO)$_5$Br in a 25 mL autoclave. [b] Initial pressure at ambient temperature. [c] GC yield based on **1a** used.

Recently, we have reported the first example of an efficient, early transition-metal complex Re(CO)$_5$Br-catalyzed addition of carboxylic acids to terminal alkynes to afford the alkenyl esters in an air atmosphere.[7] In continuation of our studies on the application of low-valent rhenium complexes as catalysts in catalytic organic syntheses, in this paper, we report our new results of Re(CO)$_5$Br-catalyzed activation of CO$_2$ in the coupling of epoxides with CO$_2$ to give cyclic carbonates under solvent-free conditions.

The reactions were carried out in an autoclave at 110 °C with stirring in the presence of 0.1 mol % (relative to epoxide) rhenium complexes. CO$_2$ was pressurized directly to the autoclave under an air atmosphere at ambient temperature.

Table 1 includes the results of CO$_2$ pressure effects on the yield of 4-chloromethyl-[1,3]dioxolan-2-one **2a** from the reaction of chloromethyloxirane **1a** with CO$_2$. It is apparent from Table 1 that the yield of cyclic carbonate **2a** was increased considerably on increasing the CO$_2$ pressure. Thus, **2a** was obtained in a range of 36−82%

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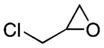
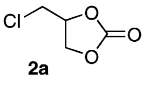
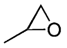
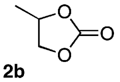
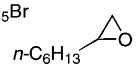
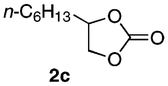
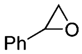
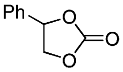
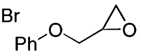
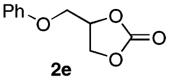
TABLE 2. Rhenium(I)-Catalyzed Coupling of Epoxides with CO_2[a]

entry	catalyst	epoxide	conv. (%)[b]	carbonate **2**	yield (%)[b]	TON[c]
1	$Re(CO)_5Cl$	 **1a**	75	 **2a**	71	710
2	$CpRe(CO)_3$	**1a**	93	**2a**	91	910
3	$Re_2(CO)_{10}$	**1a**	12	**2a**	9	90
4	$Re(CO)_5Br$	 **1b**	50	 **2b**	46	460
5	$Re(CO)_5Br$	 **1c**	80	 **2c**	76	760
6	$Re(CO)_5Br$	 **1d**	90	 **2d**	85	850
7	$Re(CO)_5Br$	 **1e**	97	 **2e**	96	960

[a] Reactions were carried out at 110 °C by using 10.0 mmol of **1** and 0.01 mmol of $Re(CO)_5Br$ in a 25 mL autoclave for 20 h under an initial pressure of 6.0 MPa. [b] Determined by GC based on **1** used. [c] TON = turnover number: moles of carbonate product per mole of catalyst.

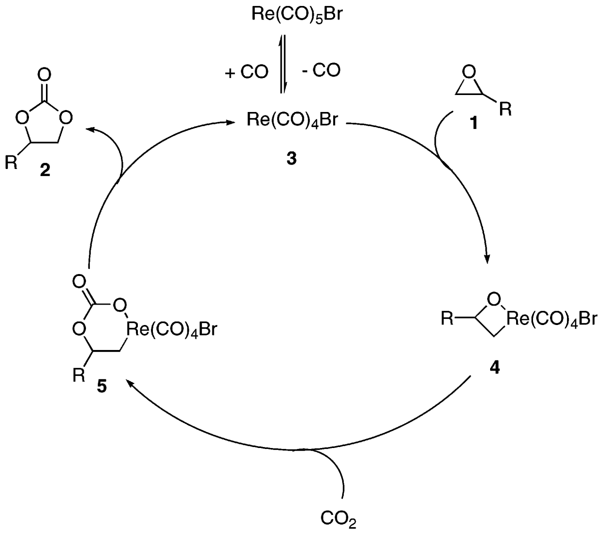
yields under the initial CO_2 pressure of 1.0−4.0 MPa at 110 °C for 24 h (entries 1−4). When the initial pressure was increased to 5.5 MPa, the yield of **2a** was 47% after only 3 h and 97% after 24 h. In these cases, the CO_2 pressure at 110 °C was up to ca. 7.5 MPa, namely, the reactions proceeded under supercritical CO_2 ($scCO_2$) conditions,[8] and the best yield of **2a** could be achieved under such reaction conditions. These results indicated that the reaction rate could be accelerated dramatically under supercritical CO_2 conditions.

The catalytic activities of several other rhenium complexes have been compared for the coupling of **1a** with $scCO_2$. These reactions were performed under 6.0 MPa of initial pressure of CO_2 and at 110 °C for 20 h.

Compared to $Re(CO)_5Br$, $Re(CO)_5Cl$ showed somewhat low catalytic activity to give **2a** in 71% GC yield (Table 2, entry 1). $CpRe(CO)_3$ catalyzed the same coupling to afford **2a** in high yield (Table 2, entry 2). However, under the same reaction conditions, the zerovalent complex $Re_2(CO)_{10}$ catalyzed the reaction to give **2a** in only 9% GC yield (Table 2, entry 3).

The coupling reactions of other epoxides with $scCO_2$ in the presence of $Re(CO)_5Br$ have also been investigated. As shown in Table 2, the catalytic activity of $Re(CO)_5Br$ depends greatly on the structure of employed epoxides. Although the high yield of **2a** could be achieved in the coupling of **1a** with CO_2 (Table 1, entry 8), the coupling of methyloxirane **1b** with CO_2 gave 4-methyl-[1,3]-dioxolan-2-one **2b** in only moderate yield (46% GC yield) (entry 4), while the reaction of hexyloxirane **1c** with CO_2 produced 4-hexyl-[1, 3]dioxolan-2-one **2c** in 76% GC yield. The formation of **2b** in only moderate yield might partly be due to the low boiling point (34 °C) of **1b**. Furthermore, the coupling reaction of an aryl-substituted epoxide, phenyloxirane **1d**, with CO_2 afforded 4-phenyl-[1,3]dioxolan-2-one **2d** in 85% GC yield. A functional group of the aryl ether-bearing epoxide, phenoxymethyloxirane **1e**, showed higher reactivity, affording 4-phenoxymethyl-[1,3]dioxolan-2-one **2e** in 96% GC yield.

SCHEME 1. Proposed Mechanism for $Re(CO)_5Br$-Catalyzed Coupling of Epoxides with CO_2



However, it should be noted that under the same reaction conditions, the coupling of disubstituted epoxides, such as cyclohexene oxide, *trans*-2,3-epoxybutane and 2,2-dimethyloxirane with CO_2 gave only a trace amount of coupling products (<5%). In the cases where cyclohexene oxide and *trans*-2,3-epoxybutane were used, both starting materials could be recovered (>90%). However, in the case where 2, 2-dimethyloxirane was employed, the reaction gave a mixture of dimers of 2,2-dimethyloxirane confirmed by GC-MS (ca. 50%). These results indicated that $Re(CO)_5Br$ showed good catalytic activity for the coupling of CO_2 with terminal epoxides only.

A possible mechanism for the present $Re(CO)_5Br$-catalyzed coupling of epoxides with CO_2 has been proposed as shown in Scheme 1. This proposal is closely related to that of an Ni-catalyzed version of the same reaction.[9] It involves the formation of 16-electron intermediate **3** via the decarbonylation of $Re(CO)_5Br$,[10] the oxidative addition of C−O bond of epoxides to **3** to give oxorhenium intermediate **4**,[11] insertion of CO_2 into the Re−O bond, and finally reductive elimination of C−O bond from **5** to produce cyclic carbonate **2** and regenerate **3**.[12]

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[8] A supercritical fluid is a substance above its critical temperature and critical pressure. The critical temperature and critical pressure of CO_2 are 31.0 °C and 7.38 MPa, respectively.

[9] De Pasquale, R. J. *J. Chem. Soc., Chem. Commun.* **1973**, 157−158.

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In conlusion, we have developed an efficient, simple catalyst system for Re(CO)$_5$Br-catalyzed coupling of epoxides with scCO$_2$ to give cyclic carbonates in good to excellent yields under solvent-free conditions.

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Supporting Information Available: Text describing experimental details and the charts of ^{1}H and ^{13}C NMR of **2a**−**e**. This material is available free of charge via the Internet at http://pubs.acs.org.

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