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

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1. Experimental Section

Re(CO)$_5$Br, Re(CO)$_5$Cl, CpRe(CO)$_3$ and Re$_2$(CO)$_{10}$ were commercial complexes from Strem. All products are known compounds, which were identified by $^1$H, $^{13}$C NMR spectra and GCMS. $^1$H and $^{13}$C NMR spectra were recorded on a JOEL JNM-ECA 300 spectrometer at 300 MHz and 75 MHz, respectively. $^1$H and $^{13}$C NMR chemical shifts (δ) were referenced to internal solvent resonances.

A typical experiment for the synthesis of 4-chloromethyl-[1, 3]dioxolan-2-one 2a (Table 1, entry 8): Chloromethyloxirane 1a (10.0 mmol) and Re(CO)$_5$Br (0.01 mmol) were charged in a 25 mL-autoclave, and then CO$_2$ was introduced at an initial pressure of 5.5
MPa at room temperature. The autoclave was heated at 110 °C with stirring for 24 h. After
the autoclave was cooled to room temperature, CO₂ was released slowly. To the reaction
mixture, 3.0 mmol of mesitylene as an internal standard material for GC analysis was added
with stirring. Analysis of the resulting mixture by GC and GC-MS revealed that the
conversion of 1a was 100 %, 2a was formed in 97 % GC yield. 2a was obtained in 93 % as
an isolated yield by Kugelrohr distillation.

2a ~ e were known compounds and identified by ¹H, ¹³C NMR and GC-MS.

2. The charts of ¹H and ¹³C NMR of 2a ~ e