Electronic Supplementary Information

Synthesis and structure of bismuth compounds bearing a sulfur-bridged bis(phenolato) ligand and their catalytic application to solvent-free synthesis of propylene carbonate from CO$_2$ and propylene oxide

Shuang-Feng Yin,† and Shigeru Shimada*

National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba Central 5, 1–1–1 Higashi, Tsukuba, Ibaraki 305–8565 (Japan). Fax: (+81) 29-861-4511; Tel: (+81) 29-861-4511; E-mail: s-shimada@aist.go.jp

† Present address: College of Chemistry and Chemical Engineering, Hunan University, Changsha 410082, P.R. China.

General. All weighing manipulations of air-sensitive materials were carried out in a glovebox filled with nitrogen. 2,2’-thiobis(6-tert-butyl-4-methylphenol) was prepared according to the literature procedure.$^1$ Anhydrous MeOH, THF and toluene were purchased from Kanto Chemical and used as received. Propylene oxide (Kanto Chemical) and CDCl$_3$ (CIL) were distilled from CaH$_2$. C$_6$D$_6$ (CIL) was distilled from Na/benzophenone ketyl. CO$_2$ was dried by passing through 4A molecular sieves in a glass tube. $^1$H and $^{13}$C spectra were recorded on Jeol LA500 spectrometer. Chemical Shifts are given in ppm using an external reference (tetramethylsilane (0 ppm) for $^1$H and $^{13}$C), and coupling constants were reported in hertz. GC-MS analysis was conducted on Shimadzu QP-5000 spectrometer.

General procedure for the coupling reaction of propylene oxide (PO) with CO$_2$. The coupling reaction of PO with CO$_2$ was conducted in a 400 ml glass flask equipped with a vacuum-tight valve. Compound 2a or 2b (0.024 mmol) and an iodide co-catalyst (0.112 mmol) were added to the flask, followed by evacuation to remove nitrogen in the flask. Then the flask was charged by 1 atm CO$_2$, and propylene oxide (1.60 mL, 23 mmol) was introduced into the flask by a syringe. After the reaction mixture was vigorously stirred at room temperature for 12 h, 1 atm CO$_2$ was again introduced to balance the CO$_2$ pressure. The mixture was further stirred for 12 h (total 24 h) and then analyzed by $^1$H NMR and GC-MS spectroscopies. The PO conversion and the PC yield were estimated by $^1$H NMR spectroscopy.

References: