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Synthesis of Novel Organobismuth Complexes Bearing a Sulfur-bridged Biphenolate Ligand and Their Catalytic Application to CO_2 Cycloaddition with Propylene Epoxide

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Abstract: Novel organobismuth complexes bearing a sulfur-bridged biphenolate ligand were synthesized and characterized. They show high catalytic activity and selectivity for the solvent-free synthesis of propylene carbonate from CO_2 cycloaddition with propylene oxide in the presence of iodide nucleophilic reagents.

Key words: Organobismuth complex; Carbon dioxide; Propylene oxide; Propylene carbonate; Cycloaddition reaction
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The utilization of carbon dioxide as a feedstock for the production of organic substances is a topic of considerable current research for economical and environmental reasons[1~3]. One of the most promising routines is the cycloaddition of CO_2 with propylene epoxide (PO) into propylene carbonate (PC), since PC is an excellent aprotic polar solvent and has many applications, such as electrolytes in lithium battery, as intermediates for producing polycarbonates, dimethyl carbonate and other fine chemicals[4~5]. Several heterogeneous and homogeneous catalysts were reported for this coupling reaction, including metal oxides[6], smectite[7], zeolite[8], transition metal complexes[9~14], alkali metal halides[15~16], ionic liquids[5, 17~19] and so on[1~5]. Most of the reported catalysts showed catalytic activity under pressurized CO_2 and above rt. Few report involves in conducting this cycloaddition reaction at rt and 0.1 MPa CO_2 using the following catalysts: MXn/Lewis base (base: PPh_3; M = Al, Mo, Fe)[11], tetra-t-butylphthalocyaninatoaluminum salt[12~13], and mixture of alkali metal compound and crown ether[16]. However, their catalytic activity is very low (TOF < 6 h^{-1}). Much effort is being made to develop more efficient catalysts for this coupling reaction in view of the so-called "Green Chemistry" and "Sustainable Development" concepts.

We are interested in synthesis and application of new organobismuth compounds because Bi is known to be low-level toxic element and relatively cheap. An extensive survey of the literatures reveals that very few reports are related to the use of organobismuth complex as catalyst and there is no report on Bi complex as catalyst for this cycoaddition reaction[20]. Recent researches showed some organobismuth compounds are potential attractive candidate for environmentally benign reagents and catalysts in organic synthesis. It was found

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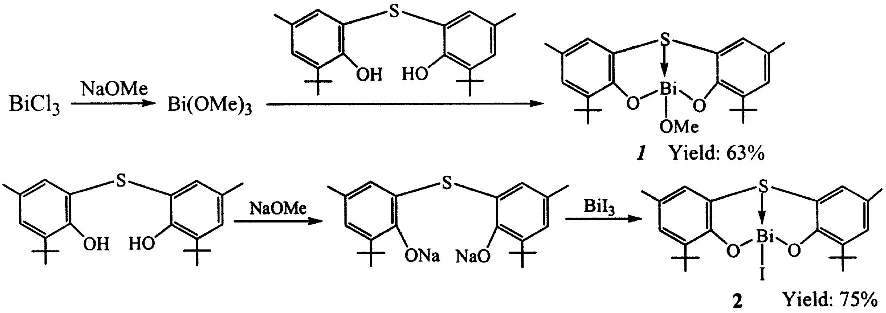
that transition metal complexes having a salen ligand show high catalytic activity for the cycloaddition reaction of CO_2 with epoxides[10, 14]. These results stimulate us to develop novel organobismuth complexes bearing a salen-like ligand (S-bridged diphenolate) and to examine their catalytic activity for solvent-free synthesis of PC from the cycloaddition of CO_2 with PO at room temperature and 0.1 MPa CO_2.

As shown in Scheme 1, organobismuth compound **1** was synthesized by the reaction of bismuth trimethoxide with the ligand precursor at room temperature. It was yellowish and its isolated yield was 63%. Organobismuth compound **2** was obtained from the reaction of Na biphenolate with BiI_3. Compound **2** had the same color as compound **1**, and its isolated yield was 75%. The chemical composition and molecular structure of these two compounds were determined by elemental analysis, ^1H NMR, ^{13}C NMR, and precise mass spectrometry. In order to measure their thermal stability, these compounds were dissolved into toluene-d_8 in a sealed NMR tube and heated at 140 ℃ for 5 h, respectively. However, no change was observed before and after the heating, suggesting these two compounds are stable. Due to the special electronic configuration of Bi, most of Bi dialkoxides are generally unstable at rt and can easily be converted into trialkylbismuth and dialkylbismuth monoalkoxide[20]. Therefore, it can be deduced that special coordination between Bi and S exists in these two compounds, which plays an important role in stabilization of their structure. Similar coordination was found in a phosphonium salt[21].



Scheme 1

Table 1 lists results on the cycloaddition of CO_2 with PO.

No PC was detected after the mixtures of PO and organobismuth

Table 1 Results on Bi complexes-catalyzed cycloaddition of CO_2 with PO[a]

Entry	Catalyst[b]	Reaction Results[c]			
		X_{PO} (%)	S_{PC} (%)	Y_{PC} (%)	TOF_{pc} (h^{-1})
1	$PhMe_3PI$ (0.056)	0	0	0	0
2	Bu_4NI (0.056)	0	0	0	0
3	**1** (0.028) + Ph_4PI (0.056)	79.1	100	79.1	27
4	**1** (0.028) + Et_4NI (0.056)	69.6	100	69.6	24
5	**2** (0.028) + Ph_4PI (0.056)	83.7	100	83.7	29
6	**2** (0.028) + Et_4NI (0.056)	67.5	100	67.5	23
7	**2** (0.014) + Ph_4PI (0.056)	44.4	100	44.4	30
8	**2** (0.035) + Ph_4PI (0.056)	100	100	100	27

[a] The reactions were conducted in 400 mL cone-shaped flask. PO was bought from Aldrich Company and dried by CaH_2; CO_2 was dried by molecular sieve. Initial CO_2 pressure 0.1 MPa, PO 23 mmol, room temperature (23 ~ 25 ℃), 24 h [b] The number after catalysts in the bracket represent their amounts (mmol). [c] X_{PO}: PO conversion, S_{PC}: PC selectivity; Y_{PC}: PC yield; PO conversion and PC selectivity were estimated by comparing the ratio of PC to PO in the ^1H NMR spectrum of the reaction mixture. TOF: Moles of PC produced per mole of Bi compound catalyst per hour

compounds were stirred at rt for 24 under 0.1 MPa CO_2. It has been reported that transition metal complexes bearing salen ligand showed catalytic activities toward the CO_2 cycloaddition reaction when nucleophilic reagents (e.g., I^-) were used as co-catalyst[14]. The novel organobismuth compounds were tested for this coupling reaction in the presence of different iodides including Ph_4PI and Et_4NI. For comparison, the iodides themselves were also examined under the same reaction and showed no catalytic activity towards this reaction at room temperature. One can see from Table 1 that the presence of the iodide salts remarkably improved the catalytic activity of these organobismuth compounds. Especially, the PC selectivity is 100% for all the bi-component catalysts. Generally speaking, side reactions easily take place when the coupling reaction temperature is lower than 80 ℃. Additionally, compound **2** is superior to compound **1** for this cycloaddition reaction. We deduced that I^- in the complex **2** play a role in accelerating ring opening of propylene epoxide. Then the effect of the molar ratio of compound **2** to Ph_4PI was also examined while PO/Ph_4PI molar ratio was fixed at 410. It is clear that the PO conversion and PC yield increased with the increment of **2**/Ph_4PI molar ratio while the change of TOF followed the opposite tendency. Both of PO conversion and PC yield reached 100% at the molar ratio of **2**/Ph_4PI = 0.035/0.056. To the best of our knowledge, these catalysts composed of the novel organobismuth compounds and iodide nucleophilic reagents are the most active catalysts for CO_2 cycloaddition with PO at room temperature under atmospheric CO_2.

Experimental section:

1 Complex catalyst synthesis

a. $C_{23}H_{31}BiO_3S$ (**1**): To NaOMe (2.977 g, 55.5 mmol, 3.06 eq.) in 50 mL MeOH was quickly added $BiCl_3$ (5.7187g, 18.1 mmol, 1 eq.) at 0°C under N_2 flow protection. After the stirring proceeded 0.5 h, 2,2′-thiobis (4-methyl-6-tert-butylphenol) (6.5021g, 18.1 mmol) was added to the reaction mixture. The reaction solution was kept at 0°C for 1 h and warmed to 25 ℃ naturally. The solvent was removed by evacuation and isolation by toluene extraction gave yield of 6.8 g (63%). ^{1}H NMR ($CDCl_3$, 499.1 MHz): δ 1.39 (18H, s), 2.29 (6H, s), 4.54 (3H, s), 7.07 (2H, s), 7.28 (2H, s). ^{13}C NMR ($CDCl_3$, 125.4 MHz): δ 20.35 (CH_3), 29.78 ($C(CH_3)$), 35.19 (C(CH_3), 121.87, 127.67, 129.69, 134.39, 142.46 (CS), 160.75 ($C(O)$). ^{13}C NMR (THF-d_8, 125.4 MHz): δ 20.49 (CH_3), 30.38 ($C(CH_3)$), 35.76 (C(CH_3), 123.54 ($C(S)$), 126.85, 129.79, 135.04, 142.75, 162.80 (CO). Calc. for $C_{23}H_{31}BiO_3S$: C, 46.31; H, 5.24; Found: C, 46.64; H, 5.26 (Averaged). HRMS Calcd for $C_{23}H_{31}BiO_3S$: 596.1798. Found: 596.1835.

b. $C_{22}H_{28}BiIO_2S$ (**2**): To NaOMe (0.2701 g, 5 mmol, 2.0 eq.) in 20 mL THF was added diphenol ligand precursor (0.8963g, 2.5 mmol) at rt. After being stirred at 25 ℃ for 5 h, the mixture was cooled to 0 ℃ and then transferred to BiI_3 (1.4742g, 2.5 mmol, 1 eq.) dissolved in 20 mL THF at 0 ℃ within 10 min. The reaction solution was agitated at 0 ℃ for 1 h and warmed to 25 ℃ naturally. The organobismuth iodide complex was extracted by toluene and dried to give yield of 1.3 g (75%). ^{1}H NMR (C_6D_6, 499.1 MHz): δ 1.59 (18H, s), 2.09 (6H, s), 7.04 (2H, d, J = 2.0), 7.24 (2H, d, J = 1.5). ^{13}C NMR ($CDCl_3$, 125.4 MHz): δ 20.35 (CH_3), 30.04 ($C(CH_3)$), 35.56 (C(CH_3)), 122.95, 129.17, 130.55, 133.90, 145.13 (CS), 158.19 (CO). Calc. for $C_{22}H_{28}BiIO_2S$: C, 38.16; H, 4.08; I, 18.33; Found: C, 38.15; H, 4.02 (Averaged). HRMS Calcd for $C_{22}H_{28}BiIO_2S$: 692.0658. Found: 692.0629.

2 Propylene carbonate

^{1}H NMR ($CDCl_3$, 499.1 MHz): δ1.51 (3H, d, J = 6.0), 4.04 (1H, t, J = 8.0), 4.57 (1H, t, J = 8.0), 4,84 ~ 4,91 (1H, m). ^{13}C NMR ($CDCl_3$, 125.4 MHz): δ 19.3, 70.8, 73.9, 155.3 (C=O).

In conclusion, we obtained two novel organobismuth complexes bearing a S-bridged diphenolate ligand. These complexes are thermally stable and show high catalytic activity towards the cycloaddition reaction of CO_2 with PO in the presence of nucleophilic reagents as co-catalyst. Further work is underway to disclose the reaction mechanism and to improve their catalytic activity by optimizing co-catalyst and reaction conditions.

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含桥式硫原子双酚盐配体的有机铋配合物的合成及其对 CO_2 和环氧丙烷环加成反应催化性能的研究

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摘 要：合成分析了含有桥式硫原子二酚盐配体的新型有机铋配合物，并发现它们在亲核试剂（I^-）存在下对 CO_2 和环氧丙烷环加成反应合成碳酸丙烯酯表现出很高的催化活性和选择性.

关键词：有机配合物；二氧化碳；环氧丙烷；碳酸丙烯酯；环加成反应