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# Synthesis and Structure of Binuclear O/S-Bridged Organobismuth Complexes and Their Cooperative Catalytic Effect on CO<sub>2</sub> Fixation

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In the synthesis of binuclear organobismuth complexes (1-6) through treatment of organobismuth chlorides with NaOH or Na<sub>2</sub>S·9H<sub>2</sub>O, the two 5,6,7,12-tetrahydrodibenz [*c*,*f*]-[1,5]azabismocine frameworks are cross-linked by either a sulfur or an oxygen atom. The complexes (1-6) show high catalytic efficiency in the synthesis of cyclic carbonates from 2-(chloromethyl)oxirane and CO<sub>2</sub>. Compared with their precursor chlorides (7-9), methoxide 10 and methanethioate 11 which are mononuclear organobismuth complexes, the binuclear or-

### Introduction

Bimetallic catalysis is commonly observed in metalloenzyme activities Scientific activities have been devoted to constructing bimetallic systems to mimic such actions.<sup>[1-3]</sup> The chemical fixation and transformation of CO<sub>2</sub> represents a typical example.<sup>[2]</sup> To achieve cooperative action similar to that of metalloenzymes, the two metal atoms have to be suitably arranged in ligand systems.<sup>[3]</sup> Bismuth is a stable heavy element that is free of toxicity and radioactivity. With emphasis on "green chemistry" and "sustainable development", it is of prime significance to investigate the potential uses of novel air-stable binuclear organobismuth complexes.<sup>[4–6]</sup> However, the utilization of this kind of bimetallic complexes in catalysis and organic synthesis is rarely reported, especially in the cases of CO<sub>2</sub> fixation and transformation.<sup>[4]</sup> For instance, there are only a few examples of binuclear organobismuth complexes reported for CO<sub>2</sub> fixation.<sup>[4]</sup> A typical complex is a binuclear organobismuth oxide (cat. 1, Scheme 1; LBi-O-BiL,  $L = RN(CH_2C_6H_4)_2$ , R = tBu) that can react with CO<sub>2</sub> to form a bismuth carbonate species.<sup>[4e]</sup> To the best of our knowledge, there is no report on the utilization of binuclear organobismuth complexes as catalysts for the CO<sub>2</sub> transformation to useful chemicals. This is partly due to 1) the instability of the Bi-C/Bi bond or Bi-E-Bi (E=O, S,Br, etc.) bridge,<sup>[4,5]</sup> 2) weak Lewis acidity of the poorly exposed bismuth centre,<sup>[6]</sup> and 3) cooperative action of the two metal atoms that cannot be successfully achieved owing to poor design of the ligand system.<sup>[1-3]</sup>

Herein, we report the first example of air-stable binuclear organobismuth sulfides used as the catalysts in  $CO_2$  transformation where the two bismuth atoms exhibiting effective cooperative action. ganobismuth complexes show higher cooperative catalytic effect. However, the complexes with an oxygen bridge (1-3) are not stable in air and lose their catalytic efficiency because of hydrolysis or CO<sub>2</sub> adsorption (forming organobismuth carbonates in the latter case). Nonetheless, the binuclear organobismuth complexes (4-6) with a sulfur bridge are highly stable in air and can be applied in the synthesis of cyclic carbonates (with the co-presence of Bu<sub>4</sub>NI) across various kinds of epoxides, thus exhibiting satisfactory efficiency and selectivity.

### **Results and Discussion**

In view of the recent interest in "100% atom-economical" synthesis of cyclic carbonates through CO<sub>2</sub> insertion into epoxides,<sup>[7]</sup> we primarily investigated the catalytic efficiency of the binuclear organobismuth oxides in the interaction of CO<sub>2</sub> with epoxides (Scheme 1). Despite the fact that binuclear organobismuth oxide 1 has a framework similar to that of bimetallic salen complexes, which exhibited high catalytic efficiency towards the reaction,<sup>[2,8]</sup> complex **1** shows no catalytic activity when 2-methyloxirane is adopted as the substrate (Scheme 1, Route A). Surprisingly, when 2-(chloromethyl)oxirane is adopted as the substrate, cyclic carbonates are obtained almost quantitatively (Scheme 1, Route B; Table 1, entries 1-3). Furthermore, when Bu<sub>4</sub>NI was used as a co-catalyst (0.1 mol% based on epoxide), CO<sub>2</sub> insertion into 2-methyloxirane was achieved in a quantitative manner (Scheme 1, Route C). In contrast to those of the monomeric organobismuth chlorides (Table 1, entries 7-9), methoxide (Table 1, entry 10) and methane thiolate (Table 1,

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Scheme 1. Selective insertion of CO $_2$  into epoxides catalyzed by Cat. 1 with or without co-catalyst Bu\_NI.

entry 11), these findings strongly suggest that binuclear organobismuth oxide shows cooperative action and is highly efficient for the synthesis of cyclic carbonates from epoxides and  $CO_2$ .

However, the binuclear organobismuth oxides **1–3** are moisture and  $CO_2$  sensitive, and the rigorous conditions required limits their utilization in catalysis. For practical application in organic synthesis, it is better for a catalyst to be air-stable.<sup>[6,9]</sup> Interestingly, when the bridging atom is changed from an oxygen to a sulfur atom (Scheme 2), the binuclear organobismuth sulfides LBi-S-BiL (**4–6**) are air-stable. The compounds remain as dry crystals or powder (slightly yellow in color) for more than one year under ambient conditions. These sulfurbridged binuclear organobismuth complexes represent a rare class of complexes which are air-stable.<sup>[4d, 5e]</sup>

The procedure for generating complexes 4-6 is similar to that of binuclear organobismuth oxide (1-3),<sup>[4e]</sup> and the complexes were quantitatively prepared by the treatment of 5,6,7,12-tetrahydrodibenz[c,f][1,5]azabismocine chloride derivatives  $(\textbf{7-9})^{\text{[6d]}}$  with sodium sulfide. The products were characterized and their structure confirmed by  $^1\text{H}$  and  $^{13}\text{C}\,\text{NMR}$  and elemental analyses. Single crystals of 4-6 suitable for X-ray diffraction were grown from a solution in toluene/n-hexane (CH<sub>2</sub>Cl<sub>2</sub>/n-hexane for 4). The ORTEP drawings of 4-6 are shown in Figure 1 and the selected bond lengths and angles are listed in Table 2. It is clear that the 5,6,7,12-tetrahydrodibenz-[c,f][1,5]azabismocine framework of complexes 4-6 is bridged by a sulfur atom. The sulfur atom occupies a vacant site left by the bismuth centre; the trigonal-bipyramidal coordination geometry with nitrogen and sulfur atoms in the apical positions and carbon atoms in the equatorial positions is equatorially distorted. The Bi1-N1 distance of 4-6 (2.739(4) Å for 4, 2.710(3) Å for 5, and 2.759(6) Å for 6) is longer than that of the corresponding precursors 7-9 (2.568(3) Å for 7, 2.517(4) Å for 8, and 2.607(5) Å for 9), thus clearly indicating the weakened nitrogen-to-bismuth coordination in 4-6 when the sulfur atom **FULL PAPERS** 

 Table 1. Optimization of reaction condition in cyclic carbonate synthesis from 2-(chloromethyl)oxirane and CO<sub>2</sub>.

	25 mmoi			∽Cl	
Entry	Cat. (mol%)	<i>t</i> [h]	<i>T</i> [°C]	Yield [%]	Sel. [%]
1	1 (0.5)	8	140	99.6	99.8
2	<b>2</b> (0.5)	8	140	quant.	100
3	<b>3</b> (0.5)	8	140	97.3	98.1
4	<b>4</b> (0.5)	8	140	99.4	99.7
5	<b>5</b> (0.5)	8	140	94.3	98.3
6	<b>6</b> (0.5)	8	140	65.8	98.0
7	7 (1.0)	8	140	25.9	97.7
8	<b>8</b> (1.0)	8	140	41.3	98.3
9	<b>9</b> (1.0)	8	140	5.9	96.9
10	<b>10</b> (1.0)	8	140	32.5	98.3
11	<b>11</b> (1.0)	8	140	14.7	92.6
12 <sup>[b]</sup>	-	8	140	3.7	98.2
13	<b>4</b> (0.5)	6	140	99.3	99.7
14	<b>4</b> (0.5)	5	140	92.6	99.5
15	<b>4</b> (0.5)	4	140	79.8	99.8
16	<b>4</b> (0.3)	8	140	61.3	99.5
17	<b>4</b> (0.1)	8	140	10.3	99.1
18	<b>4</b> (0.5)	8	150	99.1	99.3
19	<b>4</b> (0.5)	8	130	97.3	99.8
20	<b>4</b> (0.5)	8	120	90.6	99.8
21 <sup>[c]</sup>	<b>4</b> (0.5)	8	140	2.2	99.6
22 <sup>[d]</sup>	<b>4</b> (0.5)	8	140	99.6	99.6
23 <sup>[e]</sup>	- (0.1)	8	140	2.2	99.6

[a] Reaction conditions: 2-(chloromethyl)oxirane (2 mL, 25 mmol), initial  $CO_2$  pressure was 3.0 MPa, yield determined by GC analysis. [b] Control experiment. [c] The substrate was 2-methyloxirane, without the co-catalyst Bu<sub>4</sub>NI. [d] The substrate was 2-(chloromethyl)oxirane, with the co-catalyst Bu<sub>4</sub>NI (0.1 mol%). [e] The substrate was 2-methyloxirane, and only Bu<sub>4</sub>NI was used as the catalyst.



Scheme 2. Synthetic routes of organobismuth complexes 1–11.

is adopted for bridging. The results also imply that the bismuth centre is exposed more efficiently than that of their precursors **7–9**. The Bi1–S1 distance of **4–6** (2.589(2) Å for **4**, 2.601(3) Å for **5**, and 2.585(6) Å for **6**) is longer than the Bi1–O1

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**Figure 1.** ORTEP plots of **4–6** with thermal ellipsoid drawn at 50% probability. Hydrogen atoms are omitted for clarity.

Table 2. Bond lengths and angles of 4–6 in comparison with 1.								
Bond length [Å]	1 <sup>[a]</sup>	4	5	6				
Bi1–N1 Bi1–Bi1A <sup>(b,c)</sup> Bi1–E1 <sup>(d)</sup>	2.737(6) ≈4.108 2.062(6)	2.739(4) ≈3.759 2.589(2)	2.710(3) ≈3.639 2.601(1)	2.759(6) 3.708(6) 2.585(2)				
Angle [°]								
Bi1-E1-Bi1A <sup>(d)</sup> N1-Bi1-E1 <sup>(d)</sup> Ph-Ph <sup>[c]</sup>	162.9(3) 159.15(9) ≈94.95	93.07(6) 157.37(9) ≈105.87	88.76(4) 158.27(7) ≈99.91	91.93(6) 160.5(1) ≈93.04				
[a] Complex 1 is from reference [4e], $E = S$ or O. [b] Bismuth atom distance. [c] Calculated by Mercury 1.4 (CCDC).								

distance of 1 (2.077(6) Å)<sup>[4e]</sup> and shorter than the Bi1–S1 distance of cationic organobismuth complexes (2.692(3)–2.845(4 Å).<sup>[6a–c]</sup> The Bi1-S1-Bi1A angle of **4–6** (93.07(6)° for **4**, 88.76(4)° for **5**, and 91.93(6)° for **6**) is obviously smaller than the Bi1-O1-Bi1A angle of **1** (162.9(3)°), thus making the two bismuth atoms of **4–6** (Bi1–Bi1A distance, about 3.759 Å for **4**, 3.639 Å for **5**, and 3.708(6) Å for **6**) closer to each other in comparison to the case in **1** (Bi1–Bi1A distance of 4.108 Å), and significantly shorter than that of the sum of van der Waals radii for two Bi atoms [ $\Sigma$ rvdW(Bi,Bi) 4.80 Å].<sup>[4b]</sup> Nonetheless, the distance between the two bismuth atoms of **4–6** is larger than

that of a covalent single Bi–Bi bond  $(3.092(6)-3.2092(8))^{[5f]}$  and Bi–Bi bond  $(3.0648(2))^{[5g]}$ , thus implying that the distance between the two bismuth atoms is appropriate for maintaining suitable stability of the bimetallic complexes. In addition, the five atoms that are linked together, N1-Bi1-S1-Bi1A-N1A, are almost in the same plane (distortion angle  $< 0.5^{\circ}$ ) that bisects the butterfly-shaped tetrahydrodibenz[*c*,*f*][1,5]azabismocine framework.

It can be seen that the four butterfly-shaped phenyl planes of 4-6 have cis geometry and the two bismuth atoms are available for cooperative action. The nitrogen substituents of 4-6 are positioned close to the bismuth centers, thereby protecting the Bi-C bond and Bi-S-Bi bridge from infringers such as water and CO<sub>2</sub>. Notably, there should be an optimum state of nitrogen substituents for protection action so that the bismuth centers are kept exposed. In comparison to those groups (Ph) with a rigid plane and electron-withdrawing ability, the nitrogen substituents with flexible and electron-donating groups (tBu and Cy, Cy=cyclohexyl) linked to the nitrogen atom shows positive steric and electronic effects on the bismuth atoms, consequently enhancing the exposure and Lewis acidity of the bismuth atoms. Furthermore, a small substituent unit (small tBu) is better than a big one (bulky Cy) in terms of bismuth exposure (see the space-filling plots of 4-6 in Figure 2). In other words, using a sulfur atom for bridging and varying the nitrogen substituent, one can regulate the state suitability as well as the ligand system of the bismuth centers to mimic those of the natural metalloenzymes.

The cooperative action of the binuclear centers was examined for the synthesis of cyclic carbonates from epoxides and  $CO_2$ . First, we applied complexes **4–6** in the synthesis of cyclic carbonate from 2-(chloromethyl)oxirane and  $CO_2$  (Table 1). We found that most of the complexes showed catalytic efficiency (Table 1, entries 1–3; yield up to 99.4%, selectivity up to 99.7%). In terms of catalytic efficiency, the nitrogen substituent



Figure 2. Space-filling plots of complexes 4–6: (left): side view; (right): top view.

with a flexible and electron-donating group (tBu, 4; Cy, 5) is superior to that with a rigid and electron-withdrawing group (Ph, 6). The results indicate that through simple modification of the nitrogen substituent in the main framework of bimetallic organobismuth complexes, one can tune the catalytic activity. It should be noted that when an epoxide compound without chloride, such as 2-methyloxirane, is adopted as the substrate, the co-presence of binuclear organobismuth complex 4 and co-catalyst Bu₄NI is required (Table 1, entries 21-23), thus denoting that the two species play a synergistic role. Sakakura et al. pointed out that a reaction temperature of around 150 °C would be more desirable from a practical viewpoint, because the cycloaddition reactions are highly exothermic, and effective heat removal is fundamental for saving energy.<sup>[10]</sup> Based on such an understanding, we found that the optimum conditions for the interaction are: 0.5 mol% 4, epoxide (25 mmol) with CO<sub>2</sub> (initial pressure 3.0 MPa) at 140 °C for 8 hours with or without co-catalyst Bu<sub>4</sub>NI (0.1 mol% based on epoxide).

Table 3, entries 1–6 show the performance data of **3** under the optimized conditions across a diversity of epoxide derivatives. In most of the cases, the catalyst is highly effective. As shown in Table 3, entries 2 and 7, without the co-catalyst of Bu<sub>4</sub>NI, 2-methyloxirane conversion is low (2.3%). In contrast, when Bu<sub>4</sub>NI was added, there is 99.7% CO<sub>2</sub> insertion to the epoxide. Based on the X-ray structures of **4–6**, we propose that the role of the binuclear organobismuth complexes may be similar to that of the bimetallic Salen(AI) complex reported by North and Pasquale<sup>[2a]</sup> Further investigations are still underway in our laboratory.

Table 3. Synthesis of cyclic carbonates from CO <sub>2</sub> and various epoxides.								
$R^{2}$ $R^{1}$ $\frac{Cat. 4 (0.5 \text{ mol}\%), Bu_{4}\text{NI} (0.1 \text{ mol}\%)}{3 \text{ MPa CO}_{2}, 140 \text{ °C}, 8 \text{ h}}$ $R^{2}$ $R^{1}$								
Entry	R <sup>1</sup>	R <sup>2</sup>	Conv. [%]	Yield [%]				
1	Н	Н	100	98.2				
2	CH₃	Н	99.7	99.7				
3 <sup>[b]</sup>	CH₂CI	Н	100	99.8				
4 <sup>[c]</sup>	CH₃	CH₃	76.2	76.0				
5 <sup>[d]</sup>	Ph	Н	99.5	99.5				
6 <sup>[c]</sup>	-CH <sub>2</sub> (CH <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub> -		62.1	99.3				
7 <sup>[b]</sup>	CH₃	Н	2.3	2.3				
[a] Reaction conditions: 2-(chloromethyl)oxirane (2 mL), initial CO <sub>2</sub> pressure was 3.0 MPa, 4 (0.5 mol %), 8 h, 140 °C. [b] Without co-catalyst Bu <sub>4</sub> NI.								

[c] Catalyst loading of 4 was 1.0 mol %. [d] Reaction time was 12 h.

### Conclusion

In summary, a series of organobismuth complexes 1–11 were synthesized and structurally characterized. As a result of the cooperative action of the two bismuth atoms of sulfur-bridged binuclear organobismuth complexes 4–6, these compounds showed high catalytic efficiency towards the synthesis of cyclic carbonates from  $CO_2$  and epoxides, especially the complex 4. It is expected that complex 4 will find broad catalytic applications in organic synthesis.

## **Experimental Section**

### General

The chemicals were purchased from Aldrich. Co., Ltd. and used as received unless otherwise indicated. The NMR spectra were recorded at 25 °C using an INOVA-400 MHz (Varian) instrument calibrated using tetramethylsilane (Me<sub>4</sub>Si) as an internal standard. Elemental analysis was performed using a VARIO EL III (Germany). The XRD results for complexes 3-5 and 11 were obtained in Hong Kong Baptist University using a Smart 1000 X-ray diffractometer with CCD area detector.<sup>[11]</sup> In all cases, the diffraction data were collected using graphite monochromated  $\text{Mo}_{\text{K}\alpha}$  radiation ( $\lambda\!=\!0.71073$  Å). The collected frames were processed with the software SAINT +<sup>[12]</sup> and an absorption correction (SADABS) was applied to the collected reflections. The structure was solved by direct method (SHELXTL)<sup>[13]</sup> in conjunction with standard difference Fourier techniques and subsequently refined by full-matrix least-squares analyses on  $F^{2,[14]}$ Hydrogen atoms were generated in their idealized positions and all nonhydrogen atoms were refined anisotropically.

#### Synthesis of air-sensitive binuclear oxygen-bridged organobismuth complexes of LBi-O-BiL (1-3)

The complexes [(*R*)N(CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>Bi]<sub>2</sub>O (1, R=tBu; 2, R=Cy; 3, R=Ph) and (*R*)N(CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>BiEMe (10, E=O; 11, E=S) were synthesized according to the method developed by Yin et al.<sup>[4e,f]</sup> Aqueous NaOH (1.00 M, 160 mL, 160 mmol) was added to a solution of azabismocine chloride **7** (8.00 g, 16.1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (200 mL) at RT under nitrogen. The reaction mixture was stirred at RT for 15 h. The organic layer was separated, washed with water (3×150 mL) and dried over Na<sub>2</sub>SO<sub>4</sub>. Removal of the solvent under vacuum afforded quantitative generation of a mixture of organobismuth hydroxide and organobismuth oxide **1** (7.60 g). Recrystallization of the mixture from toluene afforded oxide **1**.

[{**tBuN(CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>Bi**<sub>2</sub>O] (1): <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta$  = 8.50 (dd, *J* = 7.3 Hz, 4H; ArH), 7.34 (dt, *J* = 7.3 Hz, 4H; ArH), 7.26 (d, *J* = 7.0 Hz, 4H; ArH), 7.16 (dt, *J* = 7.5 Hz, 4H; ArH), 4.27 (d, *J* = 15.2 Hz, 4H; CH<sub>2</sub>), 3.87 (d, *J* = 15.2 Hz, 4H; CH<sub>2</sub>), 1.21 ppm (s, 18H; tBu); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta$  = 171.50 (ArC), 150.07(ArC), 135.54(ArC), 128.70 (ArC), 127.19 (ArC), 127.05 (ArC), 58.04 (tBuC), 57.85 (CH<sub>2</sub>), 27.30 ppm (CH<sub>3</sub>); elemental analysis (%) calcd for C<sub>36</sub>H<sub>42</sub>Bi<sub>2</sub>N<sub>2</sub>O-C<sub>7</sub>H<sub>8</sub>: C 50.20, H 4.90, N 2.72; found: C 50.27, H 4.75, N 2.77.

[**(CyN(CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>Bi**<sub>3</sub>**20**] **(2)**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,TMS):  $\delta$  = 8.32 (d, *J* = 7.6 Hz, 4 H; ArH), 7.34 (td, *J* = 7.6, 1.6 Hz, 4 H; ArH), 7.14–7.22 (m, 8 H; ArH), 3.90 (d, *J* = 15.2 Hz, 4 H; CH<sub>2</sub>), 3.77 (d, *J* = 15.2 Hz, 4 H; CH<sub>2</sub>), 2.61 (t, *J* = 8.0 Hz, 2 H; CyH), 1.80 (d, *J* = 10.0 Hz, 4 H; CyH), 1.68 (d, *J* = 11.6 Hz, 4 H; CyH), 1.55 (d, *J* = 12.4 Hz, 2 H; CyH), 1.08–1.23 (m, 8 H; CyH), 1.00 ppm (t, *J* = 12.0 Hz, 2 H; CyH), 1.08–1.23 (m, 8 H; CyH), 1.00 ppm (t, *J* = 12.0 Hz, 2 H; CyH), 13C NMR (100 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  = 170.87 (ArC), 149.73 (ArC), 137.86 (ArC), 130.02 (ArC), 127.70 (ArC), 127.48 (ArC), 64.90 (PhCH<sub>2</sub>), 64.54 (PhCH<sub>2</sub>), 60.43 (CyC), 30.51 (CyC), 25.75 (CyC), 25.58 ppm (CyC); elemental analysis (%) calcd. for C<sub>40</sub>H<sub>46</sub>Bi<sub>2</sub>N<sub>2</sub>O: C 48.59, H 4.69, N 2.83; found: C 48.47, H 4.82, N 2.74.

[{**PhN(CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>Bi**<sub>2</sub>**O**] (3): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  = 8.33 (d, *J* = 7.0 Hz, 4H; ArH), 7.36 (t, *J* = 7.0 Hz, 4H; ArH), 7.31 (d, *J* = 7.0 Hz, 4H; ArH), 7.12 (d, *J* = 7.0 Hz, 4H; ArH), 7.15 (t, *J* = 7.0 Hz, 4H; ArH), 7.02 (d, *J* = 10.5 Hz, 4H; ArH), 6.88 (t, *J* = 7.0 Hz, 2H; ArH), 4.66 (d, *J* = 14.5 Hz, 4H; ArCH<sub>2</sub>), 4.33 ppm (d, *J* = 14.5 Hz, 4H; ArCH<sub>2</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  = 172.41 (ArC), 149.03

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(ArC), 147.02 (ArC), 137.81 (ArC), 134.91 (ArC), 130.82 (ArC), 130.34 (ArC), 129.61 (ArC), 129.50 (ArC), 128.17 (ArC), 128.08 (ArC), 127.79 (ArC), 123.24 (ArC), 118.61 (ArC), 118.06 (ArC), 62.76 (ArCH<sub>2</sub>), 61.31 ppm (ArCH<sub>2</sub>); elemental analysis (%) calcd. for  $C_{40}H_{34}Bi_2N_2O$ : C 49.19, H 3.51, N 2.87; found: C 48.97, H 3.64, N 2.66.

#### Synthesis of air-stable binuclear sulfur-bridged organobismuth complexes of LBi-S-BiL (4-6)

A solution of Na<sub>2</sub>S·9H<sub>2</sub>O (2.402 g, 10.0 mmol) in H<sub>2</sub>O (10 mL) was added to a solution of **7** (0.456 g, 1.0 mmol) in toluene (20 mL). After the mixture was stirred at 25 °C for 15 h, it settled into two layers. After separation (in air), the organic layer was mixed with *n*hexane (1.0 mL) and the resulting solution was kept at 25 °C for 24 h for the generation of colorless crystals (538 mg, 99%). Single crystals suitable for X-ray diffraction were grown from a solution in toluene/*n*-hexane (90:10).

[**{tBuN(CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>Bi}<sub>2</sub>S] (4)**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): δ = 8.98 (d, J = 7.2 Hz, 2 H; ArH), 7.26 (m, 2 H; Ph), 7.18 (t, J = 5.2 Hz, 4 H; Ph), 4.42 (d, J = 14.8 Hz, 2 H; PhCH<sub>2</sub>), 3.83 (d, J = 14.8 Hz, 2 H; PhCH<sub>2</sub>), 1.16 (s, 9 H; tBu); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS): δ = 150.99, 141.80, 139.80, 129.96, 128.26, 128.03, 59.10, 58.18, 27.60. elemental analysis (%) calc. for C<sub>36</sub>H<sub>42</sub>Bi<sub>2</sub>N<sub>2</sub>S: C 45.38, H 4.44, N 2.94; found: C 45.40, H 4.40, N 2.93. Crystal data for 4-CH<sub>2</sub>Cl<sub>2</sub>: C<sub>37</sub>H<sub>44</sub>Bi<sub>2</sub>Cl<sub>2</sub>N<sub>2</sub>S; *M*<sub>r</sub> = 1037.66; Monoclinic; space group C2/c; *a* = 17.131(1) Å, *b* = 15.2797(9) Å, *c* = 16.2750(9) Å; β = 120.826(1)°; *V* = 3658.1(4) Å<sup>3</sup>; *T* = 173(2) K; *Z* = 4; Reflections collected/unique, 10487/4351, *R*<sub>int</sub> = 0.031; Final *R* indices [*I* > 2*σ*(*I*)], *R*<sub>1</sub> = 0.041, *wR*<sub>2</sub> = 0.118; *R* indices (all data), *R*<sub>1</sub> = 0.0447, *wR*<sub>2</sub> = 0.116. GOF = 1.06.

[{(Cy)N(CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>Bi}<sub>2</sub>S] (5): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS):  $\delta = 9.03$ (d, J=7.2 Hz, 2H; ArH), 7.32-7.36 (dt, J=7.6, 2.4 Hz, 2H; ArH), 7.16-7.27 (m, 4H; ArH), 4.12 (d, J=14.8 Hz, 2H; CH<sub>2</sub> of PhCH<sub>2</sub>), 3.94 (d, J=14.8 Hz, 2 H; CH<sub>2</sub> of PhCH<sub>2</sub>), 2.71–2.79 (tt, J=11.6, 2.8 Hz, 1 H; CH<sub>2</sub> of Cy), 1.98 (d, J=12.8 Hz, 2H; CH<sub>2</sub> of Cy), 1.79 (d, J=12.8 Hz, 2H; CH<sub>2</sub> of Cy), 1.61 (d, J=12.4 Hz, 1H; CH<sub>2</sub> of Cy), 1.29-1.38 (dq, J = 12.4 Hz, 2H; CH<sub>2</sub> of Cy), 1.15–1.24 (q, J = 12.4 Hz, 2H; CH<sub>2</sub> of Cy), 1.08 (t, J=12.8, 12.4 Hz, 1 H; CH of Cy); <sup>13</sup>C NMR (100 MHz,  $CDCl_3$ , TMS):  $\delta = 158.47$ , 148.15, 139.39, 129.97, 127.29, 127.25, 63.01, 57.90, 29.78, 25.94; elemental analysis (%) calcd. for C<sub>40</sub>H<sub>46</sub>Bi<sub>2</sub>N<sub>2</sub>S: C 47.81, H 4.61, N 2.79; found: C 47.85, H 4.63, N 2.75. Crystal data for 5·PhCH<sub>3</sub>:  $C_{47}H_{54}Bi_2N_2S$ ;  $M_r = 1096.94$ ; Monoclinic; space group C2/c; a = 18.063(1) Å, b = 18.443(1) Å, c = 15.345(1) Å;  $\beta = 125.407(1)^{\circ}$ ; V = 4166.5(6) Å<sup>3</sup>; T = 173(2) K; Z = 4; Reflections collected/unique, 12963/5054,  $R_{int} = 0.028$ ; Final R indices  $[I > 2\sigma(I)]$ ,  $R_1 = 0.0023$ ,  $wR_2 = 0.050$ ; R indices (all data),  $R_1 = 0.0386$ ,  $wR_2 = 0.050$ 0.0458. GOF = 1.062.

[{**PhN(CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>Bi**<sub>3</sub>**C**] (6): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): δ = 8.94– 8.96 (dd, *J* = 7.6, 1.2 Hz, 2H; ArH), 7.40–7.44 (m, 2H; ArH), 7.30–7.36 (m, 4H; ArH), 7.19–7.25 (m, 2H; ArH), 7.08 (d, *J* = 8.0 Hz, 2H; ArH), 6.94 (t, *J* = 7.6 Hz, 1H; ArH), 4.74 (d, *J* = 15.2 Hz, 2H; ArCH<sub>2</sub>), 4.43 ppm (d, *J* = 15.2 Hz, 2H; ArCH<sub>2</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS): δ = 158.67 (ArC), 149.15 (ArC), 146.22 (ArC), 139.29 (ArC), 130.70 (ArC), 129.23 (ArC), 127.74 (ArC), 127.59 (ArC), 122.20 (ArC), 117.60 (ArC), 60.11 ppm (ArC); elemental analysis (%) calcd. for  $C_{40}H_{34}Bi_2N_2S$ : C 48.39, H 3.45, N 2.82; found: C 49.23, H 3.54, N 2.83. Crystal data for **6**:  $C_{40}H_{34}Bi_2N_2S$ ; *M*<sub>r</sub> = 992.71; Triclinic; space group *P*<sub>i</sub>; *a* = 9.971(2) Å, *b* = 12.428 (2) Å, *c* = 15.189 (3) Å; *a* = 97.002 (3) deg; β = 99.712 (3)°, γ = 112.165 (3)°; *V* = 1682.2 (5) Å<sup>3</sup>; *T* = 173(2) K; *Z* = 2; Reflections collected/unique, 8443/5729, *R<sub>int</sub>* = 0.040; Final *R*  indices  $[l > 2\sigma(l)]$ ,  $R_1 = 0.042$ ,  $wR_2 = 0.111$ ; R indices (all data),  $R_1 = 0.0484$ ,  $wR_2 = 0.1069$ . GOF = 1.03.

#### Synthesis of air-stable organobismuth chlorides 7-9

The precursors [(R)N(CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>BiCl] (7, R = tBu; 8, R = Cy; 9, R = Ph) of complexes [{(R)N(CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>B]<sub>2</sub>S] (4, R = tBu; 5, R = Cy; 6, R = Ph) were prepared according to the procedure described in the literature.<sup>[6d]</sup> A solution of *N*,*N*-bis(2-bromobenzyl)-2-methylpropan-2amine (41.1 g, 100.0 mmol) in Et<sub>2</sub>O (300 mL) was added to solution of *n*BuLi (2.5  $\mu$  in hexane, 81.6 mL, 204.0 mmol) at -60 °C. The mixture was gradually warmed to RT over 3 h. The mixture was then added to a mixture of  $BiCl_3$  (31.4 g, 102.0 mmol) in  $Et_2O$  (400 mL) at -80°C. The resulting mixture was stirred overnight, during which the temperature was allowed to rise gradually to RT. The solvent was removed under vacuum and the residue was subject to extraction with toluene/brine (2  $\ensuremath{\mathsf{M}}$  NH\_4Cl; 250 mL  $\times$  3), and the insoluble material was removed by filtration. The organic layer was washed with deionized  $H_2O$  (450 mL $\times$ 3) and dried over anhydrous MgSO<sub>4</sub>. The solvent was removed under reduced pressure to leave brownish yellow oil. The residue was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/nhexane (90:10) to give compound 7 in the form of colorless crystals (43.06 g, 87%).

[tBuN(CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>BiCl] (7): m.p. 265–266 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  = 8.63 (d, J=7.2 Hz, 2H; ArH), 7.48 (t, J=7.6 Hz, 2H, ArH), 7.40 (d, J=7.2 Hz, 2H, ArH), 7.32 (d, J=7.6 Hz, 2H, ArH), 4.50 (d, J=15.2 Hz, 2H; ArCH<sub>2</sub>), 4.11 (d, J=15.2 Hz, 2H; ArCH<sub>2</sub>), 1.32 ppm (s, 9H, tBu); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  = 170.73 (ArC), 151.00 (ArC), 138.27 (ArC), 130.73 (ArC), 128.17 (ArC), 127.34 (ArC), 60.20 (ArCH<sub>2</sub>), 60.00 (tBuC), 27.67 ppm (CH<sub>3</sub>); elemental analysis (%) calcd. for C<sub>18</sub>H<sub>21</sub>BiClN: C 43.60, H 4.27, N 2.83; found: C 43.73, H 4.14, N 2.91.

[**CyN(CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>BiCI] (8)**: m.p. 266–269 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  = 8.62 (d, *J* = 7.6 Hz, 2H; ArH), 7.39–7.48 (m, 4H; ArH), 7.31 (t, *J* = 7.6 Hz, 2H; ArH), 4.36 (d, *J* = 15.2 Hz, 2H; ArCH<sub>2</sub>), 4.15 (d, *J* = 15.2 Hz, 2H; ArCH<sub>2</sub>), 2.92 (t, *J* = 11.6 Hz, 1H; CyH), 1.99 (d, *J* = 11.6 Hz, 2H; CyH), 1.84 (d, *J* = 12.8 Hz, 2H; CyH), 1.63 (d, *J* = 12.8 Hz, 1H; CyH); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  = 170.85 (ArC), 149.69 (ArC), 138.15 (ArC), 130.80 (ArC), 128.05 (ArC), 127.63 (ArC), 64.81 (ArCH<sub>2</sub>), 60.67 (CyN), 30.69 (CyC), 25.65 (CyC), 25.48 ppm (CyC); elemental analysis (%) calcd. for C<sub>20</sub>H<sub>23</sub>BiClN: C 46.03, H 4.44, N 2.68; found: C 45.99, H 4.48, N 2.67.

[PhN(CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>BiCI] (9): m.p. 257–259 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  = 8.60 (d, *J* = 7.2 Hz, 2H; ArH), 7.51 (t, *J* = 8.0 Hz, 4H, ArH), 7.44 (d, *J* = 7.2 Hz, 2H; ArH), 7.31 (t, *J* = 7.2 Hz, 1H; ArH), 6.65 (t, *J* = 7.2 Hz, 2H; ArH), 6.47 (d, *J* = 7.6 Hz, 2H; ArH), 4.76 (d, *J* = 14.8 Hz, 2H; ArCH<sub>2</sub>), 4.52 ppm (d, *J* = 14.8 Hz, 2H; ArCH<sub>2</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  = 172.66 (ArC), 147.47 (ArC), 146.98 (ArC), 137.43 (ArC), 130.66 (ArC), 128.79 (ArC), 127.33 (ArC), 127.13 (ArC), 124.06 (ArC), 118.06 (ArC), 62.27 ppm (ArCH<sub>2</sub>); elemental analysis (%) calcd. for C<sub>20</sub>H<sub>17</sub>BiClN: C 46.57, H 3.32, N 2.72; found: C 46.49, H 3.36, N 2.62.

#### Synthesis of organobismuth complex 10

A mixture of oxide **1** was prepared as described above starting from chloride **7** (3.00 g, 6.05 mmol). The resulting mixture was dissolved in methanol (100 mL) and stirred for 2 days at RT under nitrogen. Then the solvent was removed under reduced pressure

and the resulting solid was recrystallized from  $CH_2Cl_2/n$ -hexane (90:10) to give methoxide complex **10** as colorless crystals.

[tBuN(CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>BiOMe] (10): <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  = 8.14 (dd, J = 1.1, 7.5 Hz, 2 H; ArH), 7.42 (dt, J = 0.9, 7.3 Hz, 2 H; ArH), 7.29 (dd, J = 0.6, 7.6 Hz, 2 H; ArH), 7.21 (dt, J = 1.3, 7.4 Hz, 2 H; ArH), 4.30 (d, J = 15.2 Hz, 2 H; ArCH<sub>2</sub>), 4.24 (s, 3 H, OCH<sub>3</sub>), 3.89 (d, J = 15.2 Hz, 2 H; ArCH<sub>2</sub>), 4.24 (s, 3 H, OCH<sub>3</sub>), 3.89 (d, J = 15.2 Hz, 2 H; ArCH<sub>2</sub>), 1.24 ppm (s, 9 H, tBu); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  = 171.17 (ArC), 150.13 (ArC), 135.66 (ArC), 129.47 (ArC), 127.66 (ArC), 127.60 (ArC), 58.63 (ArCH<sub>2</sub>), 58.60 (ArCH<sub>2</sub>), 56.40 (tBuC), 27.43 ppm (CH<sub>3</sub>); elemental analysis (%) calcd. for C<sub>19</sub>H<sub>24</sub>BiNO: C 46.44, H 4.92, N 2.85; found: C 46.35, H 4.77, N 2.66.

#### Synthesis of organobismuth complex 11

The organobismuth chloride **7** (2 mmol, 0.99 g) was treated with NaSMe (100 mmol) in THF (30 mL) and stirred for 24 h at RT under nitrogen. The solvent was removed under reduced pressure and the resulting solid was dissolved with toluene, washed with water, dried with Na<sub>2</sub>SO<sub>4</sub>, and evaporated, the residue was recrystallized from benzene/*n*-hexane (90:10) to give complex **11** as colorless crystals.

**[tBuN(CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>BiSMe] (11):** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  = 8.59 (d, *J*=7.2 Hz, 2H; ArH), 7.32–7.37 (m, 2H; ArH), 7.27–7.29 (m, 4H; ArH), 4.32 (d, *J*=13.2 Hz, 2H; ArCH<sub>2</sub>), 3.92 (d, *J*=13.6 Hz, 2H; ArCH<sub>2</sub>), 2.65 (s, 3H, SCH<sub>3</sub>), 1.26 ppm (s, 9H, tBu); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  = 151.94 (ArC), 149.65 (ArC), 138.95 (ArC), 130.10 (ArC), 127.78 (ArC), 127.48 (ArC), 58.55 (ArCH<sub>2</sub>), 57.92 (ArCH<sub>2</sub>), 27.46 (tBu), 10.99 ppm (SMe); elemental analysis (%) calcd. for C<sub>19</sub>H<sub>24</sub>BiNS: C 44.97, H 4.77, N 2.76; found: C 44.90, H 4.79, N 2.78. Crystal data for **11**: C<sub>19</sub>H<sub>24</sub>BiNS, *M<sub>r</sub>*=507.43; Monoclinic, *P*21/*c*; *a* = 11.7670 (10) Å, *b* = 10.3890 (9) Å, *c*=15.0885 (13) Å, *β*=92.894 (2)°; *V*=1842.2 (3) Å<sup>3</sup>; *T*=293 (2) K; *Z*=4; Reflections collected/unique, 10954/3630; *R*<sub>int</sub>=0.038, Final *R* indices [*I* > *2σ*(*I*)], *R*<sub>1</sub>=0.032, *wR*<sub>2</sub>= 0.079,; *R* indices (all data), *R*<sub>1</sub>=0.038, *wR*<sub>2</sub>= 0.076. GOF = 1.073.

# Typical procedure for $\mathrm{CO}_2$ chemical fixation to cyclic carbonates

The reactions were carried out in high-pressure stainless-steel autoclaves (30 mL) equipped with a magnetic bar. In a typical reaction, the reactor was charged with an appropriate amount of catalyst, epoxide, and biphenyl (as internal standard for GC analysis). Then the reactor was fed with CO<sub>2</sub> to a desired pressure, the autoclave with its contents was heated to a designated temperature and stirred for a designated period of time. Then the reactor was cooled to 0°C in an ice/water bath, and the remaining CO<sub>2</sub> was released using an aspirator and absorbed in an aqueous solution saturated with K<sub>2</sub>CO<sub>3</sub>. The resulting product mixture was analyzed by GC-MS using an Agilent 6890-5973 MSD GC-MS spectrometer and by <sup>1</sup>H NMR spectroscopy using an INOVA 400 MHz NMR spectrometer with TMS as internal standard. All the products were quantitatively analyzed using an Agilent 6890N gas chromatograph equipped with a FID and Rtx-wax capillary column (30 m $\times$ 0.25 mm  $\times$  0.25  $\mu$ m); analysis method: the internal standard method, analysis conditions: injector temperature 250°C, detector temperature 250°C, the oven temperature was programmed (maintained at 40°C for 2 min, heated (15°Cmin<sup>-1</sup>) to 220°C and maintained 10 min). All <sup>1</sup>H NMR data of desired products were confirmed using the spectroscopic database for organic compounds SDBS.

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