

Efficient Fixation of Carbon Dioxide by Hypervalent Organobismuth Oxide, Hydroxide, and Alkoxide**

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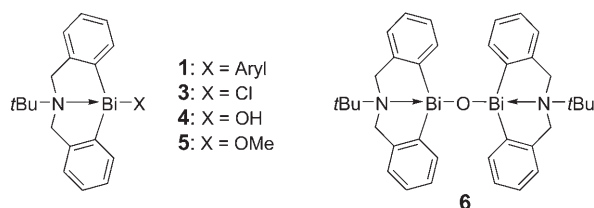
Chemical fixation of CO₂ attracts increasing interests because 1) reduction of the atmospheric concentration of CO₂, a greenhouse gas, is an issue of great current concern, 2) CO₂ is an inexpensive and potentially useful C1 feedstock for industrial production of various chemicals, and 3) fixation of atmospheric CO₂ is an important biological process.^[1,2] A number of metal compounds are known to react with CO₂ and will be key compounds for catalytic transformation and separation of CO₂.^[3] Herein, we report efficient reversible and irreversible fixation of CO₂ (including atmospheric CO₂) by organobismuth oxides, hydroxides, and alkoxides. Although inorganic Bi₂O₃ is known to react with CO₂,^[4] fixation of CO₂ with molecular bismuth compounds containing Bi–O bonds has not been reported until very recently.^[5,6]

We have reported that 12-aryl-5,6,7,12-tetrahydrodibenz[c,f][1,5]azabismocines **1** are useful reagents for cross-coupling reactions.^[7,8] The 5,6,7,12-tetrahydrodibenz[c,f][1,5]azabismocine framework is highly stable as a diorganobismuth fragment and, therefore, is suitable for the study of

diorganobismuth compounds bearing various heteroatom groups on the bismuth atom. Since structural and reactivity studies of diorganobismuth(III) hydroxides,^[5,9] oxides,^[5,9,10] and alkoxides^[9,11] are limited, we examined the synthesis of such compounds with the 5,6,7,12-tetrahydrodibenz[c,f]-[1,5]azabismocine framework. In analogy to the synthesis of {(2,4,6-Me₃C₆H₂)₂Bi}₂O **2**,^[10d] bismuth chloride **3** was treated with aqueous sodium hydroxide solution, and subsequent recrystallization of the crude product from toluene under nitrogen exclusively afforded bismuth oxide **6**. However, analysis of the crude reaction mixture by NMR spectroscopy showed the presence of bismuth hydroxide **4** in addition to the oxide **6**. Hydroxide **4** easily loses water to form **6**; azeotropic removal of water by simple evacuation of a mixture of **4** and **6** in toluene almost completely converted **4** into **6**. In turn, oxide **6** is completely converted into hydroxide **4** by the addition of water to a [D₈]toluene solution of **6**. Although oxide **6** has lower solubility than **4** and preferentially crystallizes from a mixture of **4** and **6**, single crystals of **4** suitable for X-ray analysis were obtained by recrystallization from a moist ether solution. The structures of **4** and **6** were unambiguously confirmed by single crystal X-ray analysis.^[12,13]

Attempted recrystallization of oxide **6** in air did not afford crystals of **6** but unexpectedly produced crystals of bismuth carbonate **7** (Scheme 1). A separate experiment monitored by ¹H NMR spectroscopy showed that vigorous stirring of a toluene solution of **6** in air at room temperature for 4.5 h quantitatively converted **6** into **7**. When an anhydrous CH₂Cl₂ solution of **6** was exposed to CO₂ (1 atm), the same reaction immediately took place to give **7** quantitatively. The same carbonate was also obtained by using hydroxide **4** instead of **6**. The CO₂ fixation by **6** (or **4**) is irreversible at room temperature. Carbonate **7** is stable, and no dissociation of CO₂ was observed in solution or under vacuum at room temperature. However, removal of solvent from the C₆D₆ solution of **7** and further heating of the resulting solid under vacuum at 100 °C for 10 h caused partial dissociation of CO₂ (ca. 30%) to regenerate oxide **6**.

Bismuth methoxide **5**, which can be prepared almost quantitatively by the reaction of **4** or **6** with excess MeOH,^[12,13] is sensitive to water and, on exposure to air,



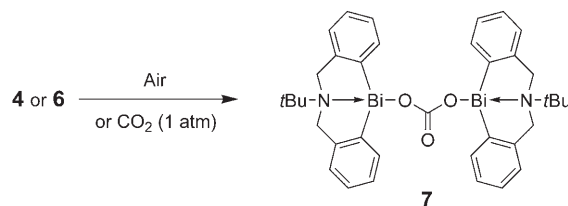
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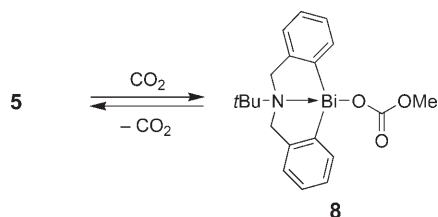
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Scheme 1. Reaction of **4** or **6** with CO₂.

underwent hydrolysis and subsequent reaction with CO₂ to form a mixture of **4**, **6**, and **7**. On the other hand, **5** immediately reacted with dry CO₂ (1 atm) in MeOH, CH₂Cl₂, or toluene to form bismuth methyl carbonate **8** nearly quantitatively (Scheme 2, Figure 1a and b). The



Scheme 2. Reversible reaction of **5** with CO₂.

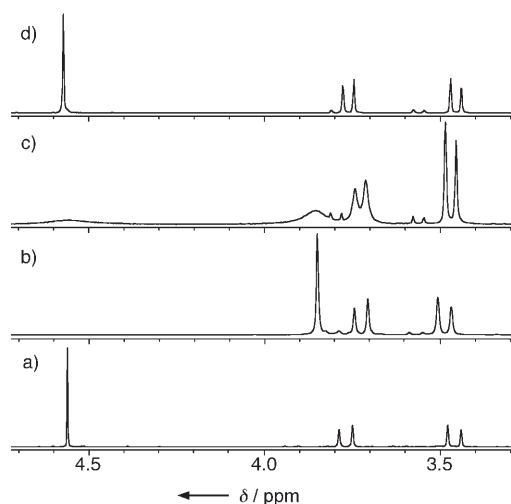


Figure 1. ¹H NMR spectra ($\delta = 3.3\text{--}4.7$ ppm) in [D₈]toluene showing methoxy and methylene signals. a) **5**. b) **5** + CO₂ (1 atm) produced **8**. c) Isolated **8** was dissolved in [D₈]toluene under nitrogen. d) NMR sample for (c) was evacuated to remove the solvent. Then the residue was dissolved in [D₈]toluene.

fixation of CO₂ by methoxide **5** is reversible. Dissolution of isolated **8** in [D₈]toluene in a sealed NMR tube resulted in partial dissociation of CO₂ to show broad signals corresponding to **5** and **8** (Figure 1c). Complete dissociation of CO₂ from **8** took place by evacuation of the NMR sample to mainly regenerate methoxide **5** (Figure 1d).

The formation of **7** may proceed by the substitution reaction of **6** (or **4**) with carbonic acid formed by the reaction of CO₂ and water. Similarly, **8** may be formed by the reaction of **5** with methyl carbonic acid generated from CO₂ and MeOH;^[14] the latter can be initially produced by the reaction of **5** with a trace amount of water in the reaction mixture. Another possibility is the direct insertion of CO₂ into Bi–O bonds.

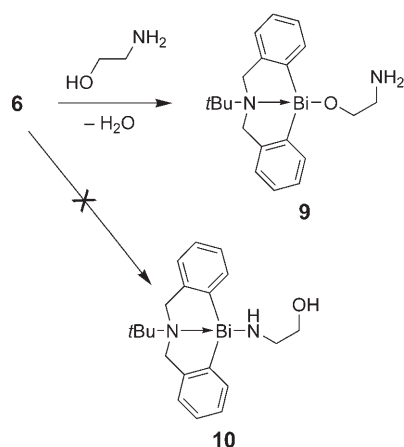
To discern the importance of the hypervalent structure for CO₂ fixation by bismuth compounds, we examined the reaction of {(2,4,6-Me₃C₆H₂)₂Bi₂O} **2**^[10d] with CO₂. Overnight stirring of a toluene solution of **2** in air did not provide a CO₂-fixation product, but rather most **2** remained unchanged. On the other hand, the ¹H NMR spectrum of **2** under 1.4 atm CO₂

in [D₈]toluene showed that most of the signals of **2** were converted into very broad signals; removal of CO₂ under vacuum led to recovery of the signals of **2**.^[13] Although attempts to obtain a single crystal of the CO₂-fixation product failed, a small amount of white powder was obtained when saturated hexane, ether, ethyl acetate, or THF solution of **2** was exposed to 1.5 atm CO₂. The IR spectrum of the powder showed strong bands at 1458 and 1323 cm^{−1}, suggesting the formation of a bismuth carbonate.^[13] These results suggest that oxide **2** can react reversibly with CO₂, and the resulting bismuth carbonate is less stable than **7**. The hypervalent structure probably contributes to the higher stability of bismuth carbonates.

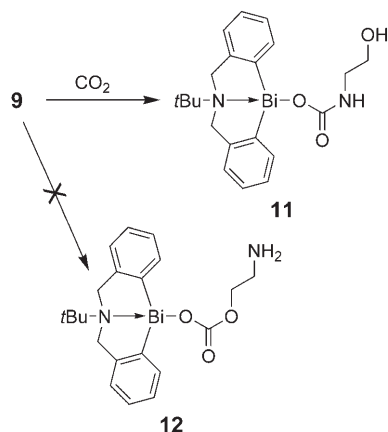
Bismuth displays low toxicity, and its compounds are attracting increasing interest as potential alternatives to toxic materials. For example, bismuth compounds are used as low-toxicity alternatives to tin catalysts for polymer synthesis.^[15] Organotin compounds are also used as catalysts for CO₂ conversion into organic carbonates^[16] and oxazolidinones^[17] by the reaction with alcohols and aminoalcohols, respectively. Therefore, we investigated the possible application of **6** as a catalyst for 2-oxazolidinone synthesis by the reaction of 2-aminoethanol with CO₂.^[17] When an *N*-methylpyrrolidone (NMP) solution of 2-aminoethanol under CO₂ (1 atm) was heated at 170°C for 16 h in the presence of 5 mol% **6**, approximately 5% (determined by ¹H NMR spectroscopy) 2-oxazolidinone was formed, while only a trace (less than 0.5%) 2-oxazolidinone was detected without **6** under the same conditions. This result shows an apparent positive effect of **6** for 2-oxazolidinone formation, although the activity of **6** was not very high. After the reaction, only one bismuth species was observed by ¹H NMR spectrum of the reaction mixture with a small amount of black deposit, showing partial decomposition (less than 14%) of the bismuth compound. On the other hand, bismuth oxide **2** completely decomposed under the same reaction conditions and did not show any positive effect on 2-oxazolidinone formation.

To determine the structure of the new bismuth species formed from **6** in the above reaction, stoichiometric reaction of **6** with 2-aminoethanol and CO₂ was examined. The reaction of **6** with 2-aminoethanol selectively afforded alkoxide **9** but not amide **10** (Scheme 3). Unexpectedly, alkoxide **9** was converted into carbamate **11** in high yield but not to carbonate **12** by the reaction with 1 atm CO₂ (Scheme 4). Comparison of the ¹H NMR spectra of **11** and of the reaction mixture of the above catalytic reaction confirmed that the bismuth species in the reaction mixture is the carbamate **11**. Formation of **11** from **9** may proceed by an intramolecular substitution reaction of a carbamic acid intermediate (LBi–OCH₂CH₂NHCO₂H), which can be formed by the reaction of the free amino group of **9** with CO₂.^[18]

The structures of **7–9** and **11** were unambiguously determined by single-crystal X-ray diffraction (Figures 2–5).^[12] As reported, the Bi–N coordination bonds in 5,6,7,12-tetrahydridibenz[*c,f*][1,5]azabismocenes change length in response to the electronic nature of the bismuth atom.^[7,19] The Bi–N bonds in carbonates **7** (2.610(3) and 2.634(3) Å) and **8** (2.548(3) Å) and in carbamate **11** (2.591(2) Å) are



Scheme 3. Reaction of oxide **6** with 2-aminoethanol.



Scheme 4. Reaction of **9** with CO_2 .

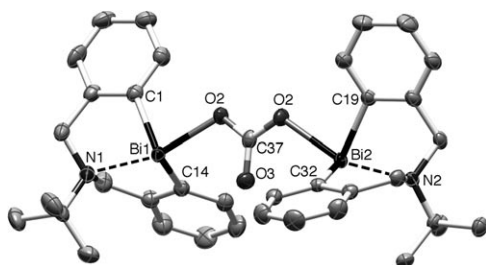


Figure 2. A thermal ellipsoid plot (50% probability level) of **7**. Hydrogen atoms are omitted for clarity.

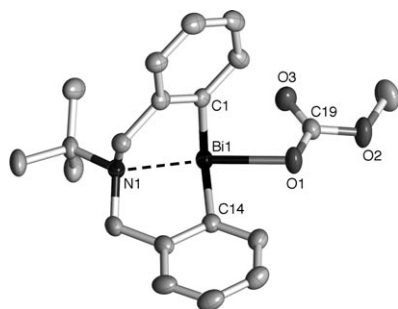


Figure 3. A thermal ellipsoid plot (50% probability level) of **8**. Hydrogen atoms are omitted for clarity.

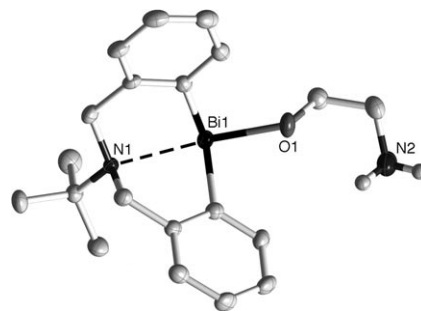


Figure 4. A thermal ellipsoid plot (50% probability level) of **9**. Hydrogen atoms on the carbon atoms are omitted for clarity.

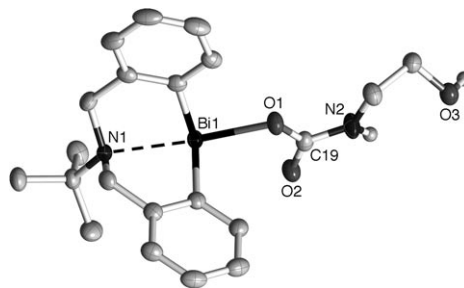


Figure 5. A thermal ellipsoid plot (50% probability level) of **11**. Hydrogen atoms on the carbon atoms are omitted for clarity.

shorter than those in hydroxide **4** (average 2.691(4) Å), alkoxides **5** (2.730(4) Å) and **9** (2.687(2) Å), and oxide **6** (average 2.747(6) Å), in accordance with the expectation. In turn, Bi–O bonds in **7** (2.253(2) Å), **8** (2.303(3) Å), and **11** (2.278(2) Å) are longer than those in **4** (2.170(4) Å), **5** (2.170(4) Å), **9** (2.175(2) Å), and **6** (2.077(6) Å).

The current findings show that bismuth compounds are potentially useful materials for CO_2 conversion into useful chemicals as well as for CO_2 capture and separation.

Experimental Section

7: Oxide **6** (100 mg) in toluene (7 mL) was vigorously stirred in air at room temperature for 4.5 h. After removal of solvent under vacuum, the residual material was analyzed by ^1H NMR spectroscopy to show quantitative formation of carbonate **7**. Recrystallization of the product from a mixture of CH_2Cl_2 and toluene afforded colorless crystals containing CH_2Cl_2 and toluene ($\text{7/CH}_2\text{Cl}_2/\text{toluene} = 4:4:1$ by integration of the ^1H NMR spectrum). ^1H NMR (499.1 MHz, CDCl_3): $\delta = 1.29$ (18H, s), 4.03 (4H, d, $J = 15.2$ Hz), 4.43 (4H, d, $J = 15.2$ Hz), 7.22 (4H, t, $J = 7.3$ Hz), 7.34 (4H, d, $J = 7.6$ Hz), 7.40 (4H, t, $J = 7.3$ Hz), 8.43 ppm (4H, d, $J = 7.3$ Hz); ^{13}C NMR (125 MHz, CDCl_3): $\delta = 27.41$, 59.21, 59.72, 127.30, 127.46, 129.78, 137.70, 151.05, 166.88, 176.70 ppm. IR (KBr): $\tilde{\nu} = 1555$ (s), 1287 cm^{-1} (vs). Elemental analysis calcd (%) for $\text{C}_{37}\text{H}_{42}\text{Bi}_2\text{N}_2\text{O}_3 \cdot \text{C}_2\text{H}_2\text{Cl}_2 \cdot 1/4 \text{C}_7\text{H}_8$: C 43.85, H 4.26, N 2.57; found: C 44.03, H 4.07, N 2.38.

8: Introduction of CO_2 (1 atm) to a methanol (13 mL) solution of **5** (440 mg, 0.896 mmol) immediately produced **8** as a colorless precipitate, which was separated by filtration, washed with methanol, and dried under vacuum (455 mg, 95%). ^1H NMR (499.1 MHz, CDCl_3 , under CO_2 atmosphere): $\delta = 1.31$ (9H, s), 3.80 (3H, s), 4.11 (2H, d, $J = 15.5$ Hz), 4.50 (2H, d, $J = 15.2$ Hz), 7.26 (2H, t, $J = 7.5$ Hz), 7.39 (2H, d, $J = 7.5$ Hz), 7.46 (2H, t, $J = 7.5$ Hz), 8.18 ppm (2H, d, $J = 7.3$ Hz); ^{13}C NMR (125 MHz, CDCl_3 , under CO_2 atmos-

phere): $\delta = 27.54, 54.24, 59.94, 60.43, 127.60, 128.00, 130.32, 137.13, 151.26, 160.24, 176.45$ ppm. IR (KBr): $\tilde{\nu} = 1638$ (s), 1623 (s), 1305 cm^{-1} (vs). Elemental analysis calcd for $\text{C}_{20}\text{H}_{24}\text{BiNO}_3$: C 44.87, H 4.52, N 2.62; found: C 44.97, H 4.47, N 2.48.

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