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CO_2 Fixation

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

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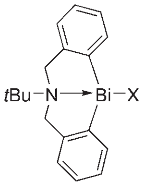
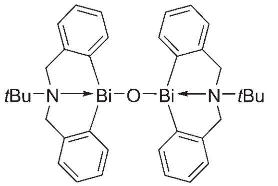
Chemical fixation of CO_2 attracts increasing interests because 1) reduction of the atmospheric concentration of CO_2, a greenhouse gas, is an issue of great current concern, 2) CO_2 is an inexpensive and potentially useful C1 feedstock for industrial production of various chemicals, and 3) fixation of atmospheric CO_2 is an important biological process.[1,2] A number of metal compounds are known to react with CO_2 and will be key compounds for catalytic transformation and separation of CO_2.[3] Herein, we report efficient reversible and irreversible fixation of CO_2 (including atmospheric CO_2) by organobismuth oxides, hydroxides, and alkoxides. Although inorganic Bi_2O_3 is known to react with CO_2,[4] fixation of CO_2 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 $\{(2,4,6\text{-}Me_3C_6H_2)_2Bi\}_2O$ **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 $[D_8]$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]



1: X = Aryl
3: X = Cl
4: X = OH
5: X = OMe



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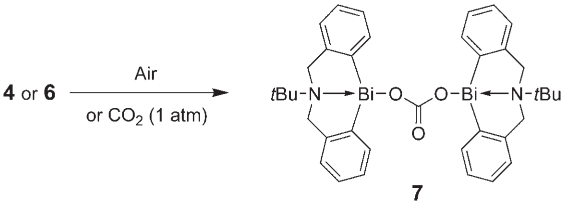
Attempted recrystallization of oxide **6** in air did not afford crystals of **6** but unexpectedly produced crystals of bismuth carbonate **7** (Scheme 1). A separate experiment monitored by ^1H NMR spectroscopy showed that vigorous stirring of a toluene solution of **6** in air at room temperature for 4.5 h quantitatively converted **6** into **7**. When an anhydrous CH_2Cl_2 solution of **6** was exposed to CO_2 (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 CO_2 fixation by **6** (or **4**) is irreversible at room temperature. Carbonate **7** is stable, and no dissociation of CO_2 was observed in solution or under vacuum at room temperature. However, removal of solvent from the C_6D_6 solution of **7** and further heating of the resulting solid under vacuum at 100 °C for 10 h caused partial dissociation of CO_2 (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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Scheme 1. Reaction of **4** or **6** with CO_2.

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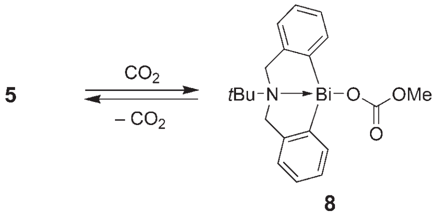
underwent hydrolysis and subsequent reaction with CO_2 to form a mixture of **4**, **6**, and **7**. On the other hand, **5** immediately reacted with dry CO_2 (1 atm) in MeOH, CH_2Cl_2, or toluene to form bismuth methyl carbonate **8** nearly quantitatively (Scheme 2, Figure 1 a and b). The fixation of CO_2 by methoxide **5** is reversible. Dissolution of isolated **8** in [D$_8$]toluene in a sealed NMR tube resulted in partial dissociation of CO_2 to show broad signals corresponding to **5** and **8** (Figure 1 c). Complete dissociation of CO_2 from **8** took place by evacuation of the NMR sample to mainly regenerate methoxide **5** (Figure 1 d).



Scheme 2. Reversible reaction of **5** with CO_2.

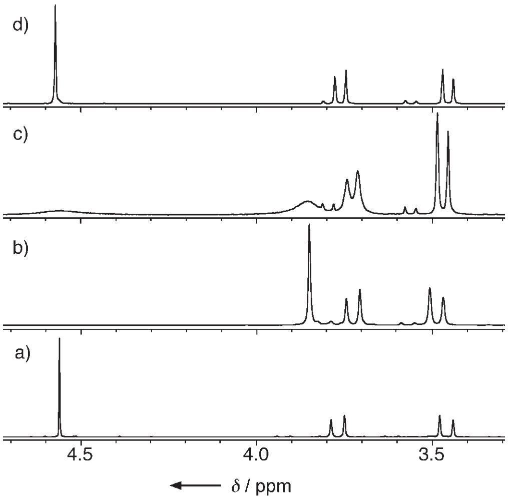


Figure 1. ^{1}H NMR spectra ($\delta = 3.3$–4.7 ppm) in [D$_8$]toluene showing methoxy and methylene signals. a) **5**. b) **5** + CO_2 (1 atm) produced **8**. c) Isolated **8** was dissolved in [D$_8$]toluene under nitrogen. d) NMR sample for (c) was evacuated to remove the solvent. Then the residue was dissolved in [D$_8$]toluene.

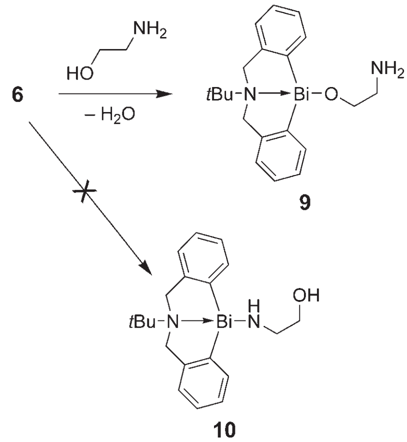
The formation of **7** may proceed by the substitution reaction of **6** (or **4**) with carbonic acid formed by the reaction of CO_2 and water. Similarly, **8** may be formed by the reaction of **5** with methyl carbonic acid generated from CO_2 and MeOH;[14] the latter can be initially produced by the reaction of **5** with a trace amount of water in the reaction mixture. Another possibility is the direct insertion of CO_2 into Bi–O bonds.

To discern the importance of the hypervalent structure for CO_2 fixation by bismuth compounds, we examined the reaction of $\{(2,4,6\text{-}Me_3C_6H_2)_2Bi\}_2O$ **2**[10d] with CO_2. Overnight stirring of a toluene solution of **2** in air did not provide a CO_2-fixation product, but rather most **2** remained unchanged. On the other hand, the ^{1}H NMR spectrum of **2** under 1.4 atm CO_2 in [D$_8$]toluene showed that most of the signals of **2** were converted into very broad signals; removal of CO_2 under vacuum led to recovery of the signals of **2**.[13] Although attempts to obtain a single crystal of the CO_2-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 CO_2. 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 CO_2, and the resulting bismuth carbonate is less stable than **7**. The hypervalent structure probably contributes to the higher stability of bismuth carbonates.

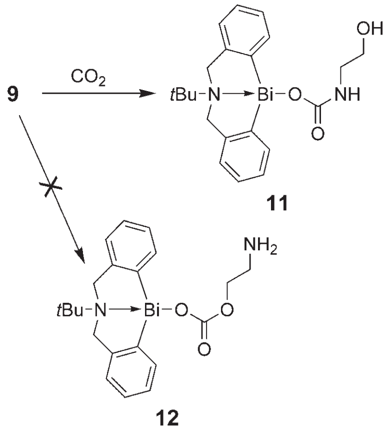
Bismuth displays low toxicity, and its compounds are attracting increasing interest as potential alternatives to toxic materials. For example, bismuth compounds are used as low-toxicity alternatives to tin catalysts for polymer synthesis.[15] Organotin compounds are also used as catalysts for CO_2 conversion 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 CO_2.[17] When an *N*-methylpyrrolidone (NMP) solution of 2-aminoethanol under CO_2 (1 atm) was heated at 170 °C for 16 h in the presence of 5 mol % **6**, approximately 5 % (determined by ^{1}H 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 ^{1}H 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 CO_2 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 CO_2 (Scheme 4). Comparison of the ^{1}H 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 ($LBi{-}OCH_2CH_2NHCO_2H$), which can be formed by the reaction of the free amino group of **9** with CO_2.[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-tetrahydrodibenz[c,f][1,5]azabismocines 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.

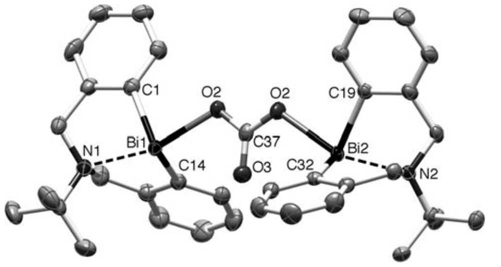


Figure 2. A thermal ellipsoid plot (50% probability level) of **7**. Hydrogen atoms are omitted for clarity.

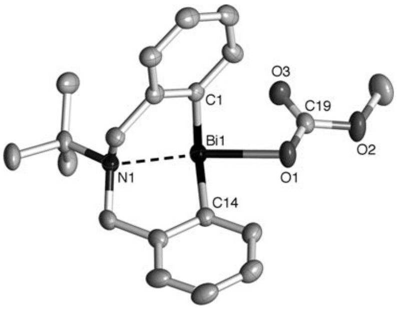


Figure 3. A thermal ellipsoid plot (50% probability level) of **8**. Hydrogen atoms are omitted for clarity.

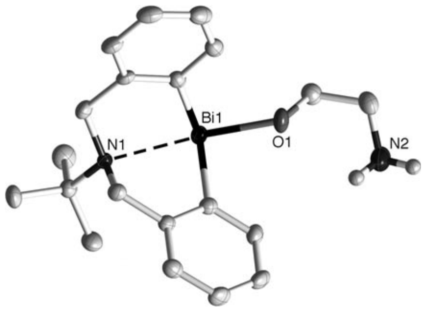


Figure 4. A thermal ellipsoid plot (50% probability level) of **9**. Hydrogen atoms on the carbon atoms are omitted for clarity.

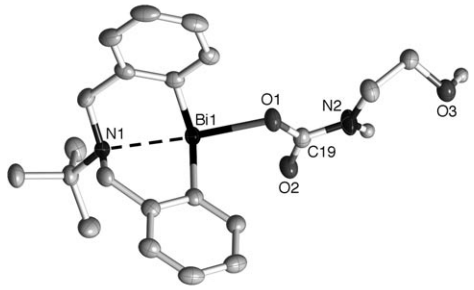


Figure 5. A thermal ellipsoid plot (50% probability level) of **11**. Hydrogen atoms on the carbon atoms are omitted for clarity.

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 ^{1}H 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 (**7**/CH_2Cl_2/toluene = 4:4:1 by integration of the ^{1}H NMR spectrum). ^{1}H 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 $C_{37}H_{42}Bi_2N_2O_3 \cdot C_2H_2Cl_2 \cdot 1/4\,C_7H_8$: 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%). ^{1}H 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 atmosphere): $\delta = 27.54$, 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 $C_{20}H_{24}BiNO_3$: C 44.87, H 4.52, N 2.62; found: C 44.97, H 4.47, N 2.48.

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[12] Crystal data for **4**: $4(C_{18}H_{22}BiNO)\cdot C_4H_{10}O$, $M_r = 1983.56$, triclinic, space group $P\bar{1}$, $a = 9.9844(5)$, $b = 17.7322(8)$, $c = 20.2299(10)$ Å, $\alpha = 88.582(1)$, $\beta = 88.703(1)$, $\gamma = 80.617(1)°$, $V = 3532.0(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.865$ g cm^{-3}, $T = 153(2)$ K, $\mu(Mo_{K\alpha}) = 9.969$ mm^{-1}; 20561 reflections measured, 14800 unique, $R_{int} = 0.019$; $R_1 = 0.0289$ [$I > 2\sigma(I)$] and $wR_2 = 0.0737$ (all data). Crystal data for **5**: $C_{19}H_{24}BiNO$, $M_r = 491.39$, monoclinic, space group $P2_1/c$, $a = 11.089(3)$, $b = 10.557(3)$, $c = 14.600(3)$ Å, $\beta = 90.531(19)°$, $V = 1709.1(8)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.909$ g cm^{-3}, $T = 173(2)$ K, $\mu(Mo_{K\alpha}) = 10.299$ mm^{-1}; 4116 reflections measured, 3920 unique, $R_{int} = 0.026$; $R_1 = 0.0308$ [$I > 2\sigma(I)$] and $wR_2 = 0.0708$ (all data). Crystal data for **6**: $C_{36}H_{42}Bi_2N_2O\cdot C_7H_8$, $M_r = 1028.84$, monoclinic, space group $P2_1/n$, $a = 16.868(5)$, $b = 8.104(6)$, $c = 28.171(3)$ Å, $\beta = 92.1(5)°$, $V = 3848(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.776$ g cm^{-3}, $T = 193(2)$ K, $\mu(Mo_{K\alpha}) = 9.151$ mm^{-1}; 9085 reflections measured, 8789 unique, $R_{int} = 0.012$; $R_1 = 0.0477$ [$I > 2\sigma(I)$] and $wR_2 = 0.0935$ (all data). Crystal data for **7**: $C_{37}H_{42}Bi_2N_2O_3\cdot C_7H_8$, $M_r = 1072.85$, monoclinic, space group $P2_1/c$, $a = 12.3009(8)$, $b = 20.6819(13)$, $c = 15.4808(10)$ Å, $\beta = 95.042(1)°$, $V = 3923.2(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.816$ g cm^{-3}, $T = 153(2)$ K, $\mu(Mo_{K\alpha}) = 8.984$ mm^{-1}; 23239 reflections measured, 8756 unique, $R_{int} = 0.025$; $R_1 = 0.0234$ [$I > 2\sigma(I)$] and $wR_2 = 0.0539$ (all data). Crystal data for **8**: $C_{20}H_{24}BiNO_3$, $M_r = 535.39$, monoclinic, space group $P2_1/n$, $a = 10.2368(12)$, $b = 11.4479(11)$, $c = 16.3306(15)$ Å, $\beta = 97.944(8)°$, $V = 1895.4(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.876$ g cm^{-3}, $T = 173(2)$ K, $\mu(Mo_{K\alpha}) = 9.303$ mm^{-1}; 4492 reflections measured, 4344 unique, $R_{int} = 0.028$; $R_1 = 0.0283$ [$I > 2\sigma(I)$] and $wR_2 = 0.0561$ (all data). Crystal data for **9**: $C_{20}H_{27}BiN_2O$, $M_r = 520.43$, monoclinic, space group $C2/c$, $a = 16.9971(10)$, $b = 12.7741(7)$, $c = 17.5083(10)$ Å, $\beta = 100.6760(10)°$, $V = 3735.6(4)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.851$ g cm^{-3}, $T = 153(2)$ K, $\mu(Mo_{K\alpha}) = 9.431$ mm^{-1}; 11075 reflections measured, 4025 unique, $R_{int} = 0.020$; $R_1 = 0.0196$ [$I > 2\sigma(I)$] and $wR_2 = 0.0429$ (all data). Crystal data for **11**: $C_{21}H_{27}BiN_2O_3$, $M_r = 564.44$, monoclinic, space group $C2/c$, $a = 22.6103(13)$, $b = 13.9382(8)$, $c = 14.7762(9)$ Å, $\beta = 120.9460(10)°$, $V = 3993.8(4)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.877$ g cm^{-3}, $T = 153(2)$ K, $\mu(Mo_{K\alpha}) = 8.837$ mm^{-1}; 11929 reflections measured, 4414 unique, $R_{int} = 0.024$; $R_1 = 0.0214$ [$I > 2\sigma(I)$] and $wR_2 = 0.0493$ (all data). Thermal ellipsoid plots of **4**, **5**, and **6** and brief information on the X-ray crystallography are shown in the Supporting Information. CCDC 678643 (**4**), 678644 (**5**), 678645 (**6**), 678646 (**7**), 678647 (**8**), 687250 (**9**) and 687251 (**11**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[13] See the Supporting Information.

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