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Organoantimony and organobismuth complexes for CO_2 fixation

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The utilization of organoantimony (bismuth) complexes in CO_2 fixation is reviewed in this article. The efficient synthesis of cyclic carbonates from CO_2 and epoxides over an organoantimony (V) catalyst was first reported in 1979. After that, several organoantimony (V) complexes were found active for CO_2 fixation. In 2009, an organoantimony (III) complex was reported as effective CO_2 absorbent and it is the only example of this kind. The study of organobismuth complexes for CO_2 fixation started in 2008, and the achievements are: (i) when organobismuth oxides, hydroxides and methoxides are used as CO_2 absorbents, they are converted to carbonates, and the organobismuth carbonates can be renewed as organobismuth oxides; (ii) organobismuth complexes can be used as catalysts to transform CO_2 into epoxides as cyclic carbonates at room temperature in the presence of a co-catalyst such as LiI and Bu_4NI; (iii) there is the development of bimetallic organobismuth complexes that show cooperative catalytic action; (iv) there is the physical fixation of CO_2 by inorganic-organic bismuth complexes; and (v) CO_2 insertion into the Bi-C bond of an organobismuth complex is disclosed. Most of the above catalytic systems can be considered as "electrophile-nucleophile". In general, the synthesis of cyclic carbonates from CO_2 and epoxides catalyzed by an organoantimony (bismuth) complex follows the mechanism: the complex first reacts with CO_2 to form an organometallic carbonate, then the carbonate reacts with an epoxide with ring-opening by a base (e.g.,*n*-Bu_4NI).

1. Introduction

1.1 CO_2 challenge and opportunity

Atmospheric CO_2 is at its highest level ever recorded, currently amounting to around 390 ppm by volume (590 ppm by mass).[1] The absolute mass of atmospheric CO_2 amounts to an alarming value of 3×10^{15} tons. It is estimated that human activities currently produce an additional 1.3×10^{10} tons of CO_2 per year. The impacts of further increase of atmospheric CO_2 on world climate and oceans could be severe as well as uncontrollable. Nonetheless, despite the notorious image, CO_2 can be the ultimate C1 feedstock. As far as the chemical fixation of CO_2 is concerned, there are significant developments in the past decades. It appears that the capture of CO_2 at source (e.g., at the power plants that use coal as fuel) is a suitable strategy for the mitigation of greenhouse effect.[2-5] For such a goal, effective substrates are needed as absorbents. It is of economic significance if valuable chemicals such as cyclic carbonates can be synthesized in the course of fixing CO_2.[6-14]

1.2 Special properties of CO_2[9, 15-17]

The CO_2 molecule is linear, showing C−O distances of 1.16 Å. Although overall nonpolar, CO_2 contains polar bonds due to the difference in electronegativity between C and O. Its electronic structure is best represented as $O^{-\delta}–C^{+2\delta}–O^{-\delta}$, disclosing susceptibility to nucleophilic attack at the carbon and electrophilic attack at the oxygen atoms. Reactions of CO_2 in biological systems tend to be a combination of nucleophilic and electrophilic interactions. Without the combined interactions, powerful electrophiles or nucleophiles are needed to initiate a CO_2 reaction. With an ionization potential of 13.78 eV, CO_2 is nonbasic and interacts only weakly with Brønsted and Lewis acids. It is considered that the major obstacle preventing efficient conversion of CO_2 into useful chemicals is the lack of appropriate catalysts.[18-27]

1.3 CO_2 fixation with organometallic complexes

Recently, there are reports on the use of transition metal (e.g., Ni,[28-31] Rh,[32] Ir, Fe, Cu, Re, and Co) complexes,[33-40] for CO_2 transformation. Potentially, the use of them could result in better utilization of CO_2 in chemical industry as well as having certain existing processes replaced by ones that are more energy-benign. In real practice, these complexes are not applicable because under mild conditions they do not perform satisfactorily when CO_2 association or dissociation is a matter of concern. For the activation of CO_2 with homogeneous molecular catalysts, there are three major mechanistic steps: (i) CO_2 coordination with the metal or ligand of catalyst, (ii) CO_2 reaction with neighboring ligands, and (iii) release of product and the restoration of catalyst.[41-45]

1.4 Organoantimony and organobismuth complexes for CO_2 fixation

Organobismuth and organoantimony complexes have been investigated for chemical fixation of CO_2 since 1979. Bismuth and antimony are Group 15 elements. The former is known to be nontoxic and noncarcinogenic while the latter is a boundary element showing metal as well as non-metal features. The compounds of both metals are studied because of their versatile roles (acting as reaction reagents, oxidizing agents, catalysts, and medicine).[46-57] In the past decade, there have been researches on novel cationic organobismuth and organoantimony complexes. We present herein representative results of using this kind of material as absorbents for CO_2 capture and/or as catalysts for cycloaddition of CO_2 to epoxides.

2. CO_2 fixation using organoantimony complexes

2.1 Organoantimony(V) complexes

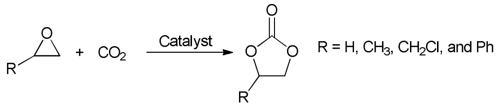
The chemical fixation of CO_2 using organoantimony complexes as catalysts was first reported by Matsuda et al. in 1979.[58] They used pentavalent organoantimony compounds to catalyze the reaction between CO_2 and a number of epoxides (Table 1).[59] In all cases, the corresponding cyclic carbonates are generated in almost quantitative amounts.

It was observed that the catalysts with halogen atoms and phenyl substituents are more active than those without halogen atoms and with methyl substituent. The complexes halogenated with bromine are more active than those with chlorine. The catalytic activities of the complexes decrease in the order of **1b > 1d >1e >1a, 1c, 1f** >>the trivalent compounds (**1g, 1h, 1i**). The catalysts **1b-e** can be recovered from the crude products in good yields. It was reported that catalysts **1a** and **1f** cannot be recovered, and the corresponding crude products are light brown and light yellow in color. Such phenomena could be a result of catalyst instability. As reflected by the time of reaction, the epoxides (R) show reactivity that follows the order of CH_3> Ph >H > CH_2Cl.

Using tetraphenyistibonium halides (Ph_4SbCI and Ph_4SbBr] as catalysts for the hydration of ethylene oxide in the presence of CO_2 or ethylene carbonate at 120 °C, Matsuda et al. gained better control of product distribution.[60] With a small excess of water in the reaction system, ethylene glycol is generated as the predominant product. When the molar ratio of water to ethylene oxide is 1 or less than 1, the stibonium halides selectively give diethylene glycol as the major product.

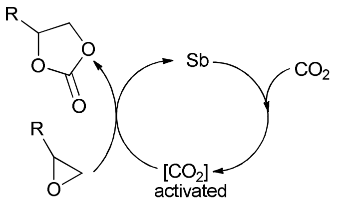
As proposed by Matsuda et al., the catalytic mechanism can be described as shown in Scheme 1. Basically, there is the coordination of epoxide with the Sb atom followed by interaction with CO_2.[59] In the reaction with styrene oxide, polystyrene oxide is formed as by-product (up to a yield of ca. 10%). It is noted that the catalytic activities of organoantimony compounds are superior to those of organotin compounds despite the Lewis acid strength of Sn being stronger than that of Sb.[59] In the case of organoantimony complexes, effects such as reaction acceleration due to preheating and polymerization of epoxides as inferred by epoxide-antimony coordination are not observed. In addition, there is no obvious change of IR and ^1H NMR spectra upon the mixing of epoxides with the Sb catalysts (1 mol% of catalyst in epoxide solution). All the facts point to the absence of epoxide-zinc coordination. It is hence reasonable to consider that the activation of CO_2 follows the cyclic mechanism shown in Scheme 1.

Table 1 Reaction of CO_2 with epoxides catalyzed by pentavalent organoantimony compounds[a] [59]



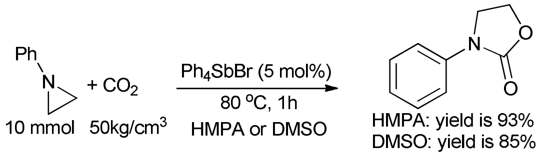
Catalysts	Epoxides(R)	Temp.(°C)	Time (min)	Yield (%)[b]
Ph_5Sb (**1a**)	H	120	330	82
	CH_3	120	130	87
Ph_4SbBr (**1b**)	H	120	12	96
	CH_3	120	8	92[c]
		100	20	98[c]
		60	120	93[c]
	CH_2Cl	120	24	97
	Ph	120	16	91[d]
Ph_3SbBr_2 (**1c**)	H	120	38	95
	CH_3	120	16	97[c]
		100	50	92[c]
		60	390	97[c]
	CH_2Cl	120	80	94
	Ph	120	24	82[e]
Ph_3SbCl_2 (**1d**)	H	120	180	99
		100	480	96
	CH_3	120	150	96[c]
Me_3SbBr_2 (**1e**)	H	120	15	72
		100	40	79
	CH_3	120	60	94[c]
		100	150	91[c]
Ph_3SbO (**1f**)	CH_3	120	120	94
Ph_3Sb (**1g**)	CH_3	120	360	7
Ph_2SbCl (**1h**)	CH_3	120	360	5
$SbCl_3$ (**1i**)	CH_3	120	360	4

[a] Reaction conditions: Epoxides, 0.1 mole; CO_2, 0.2 mole (50 kg/cm^2); Catalysts, 0.001mole. [b] Based on epoxides. [c] Catalysts were recovered. [d] Trace of poly(styrene oxide) was obtained besides the carbonate. [e] Poly(styrene oxide) was obtained in ca. 10% yield besides the carbonate.



Scheme 1 Possible mechanism of the reaction of CO_2 with epoxides catalyzed by pentavalent organoantimony compounds.[59]

It was also reported that Ph_4SbBr is an effective catalyst for the synthesis of 3-phenyloxazolidin-2-one from CO_2 and 1-phenylaziridines. At 80 °C in polar aprotic solvents such as hexamethylphosphoramide (HMPA) and dimethyl sulfoxide (DMSO), the yield is up to 93% and 85%, respectively (Scheme 2).[61]

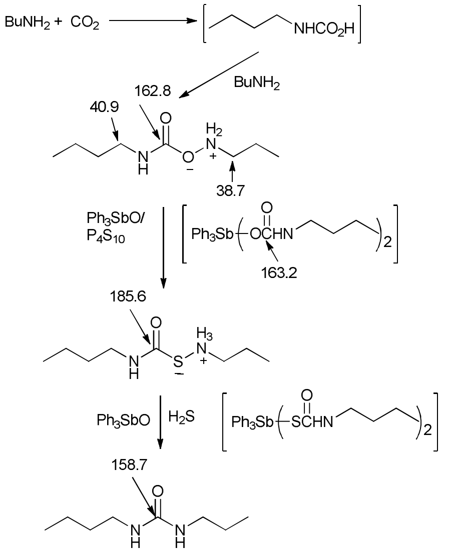


Scheme 2 Reaction of carbon dioxide with 1-phenylaziridine catalyzed by organoantimony compound Ph_4SbBr

In 1992, Nomura et al. reported an efficient catalytic system that involves the combined use of tetraphosphorus decasulfide (P_4S_{10}) and triphenylstibine oxide (Ph_3SbO, **1f**) for the synthesis of urea through amine carbonylation with CO_2.[62] In the Ph_3SbO/P_4S_{10} system, 1,3-dialkylurea (RNHCONHR, where R = Bu, i-Bu, s-Bu, t-Bu, allyl, Ph) and tetramethylurea were successfully synthesized from the corresponding amines at 80 °C and 4.9 MPa initial CO_2 pressure. Based on the results of ^{13}C NMR monitoring, it was concluded that the course of reaction involves the successive thiolation of carbamic acid to intermediate antimony carbamate species, followed by the aminolysis of carbamothioic acid to the final product (Scheme 3). Similarly, cyclic ureas can be synthesized through the carbonylation of diamines ($RNHCH_2CH_2NHR'$, where R, R'= H, H; Me, H; Ph, H; $HOCH_2CH_2$, H; $HOCHMeCH_2$, H; Me, Me) (Table 2). Using the Ph_3SbO/P_4S_{10} catalyst system, trisubstituted ureas such as l-butyl-3,3-diethylurea can be generated through the selective cocarbonylation of butylamine and diethylamine.

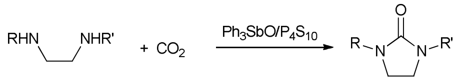
Lermontov et al. reported that the Ph_3SbF_2 complex is a highly efficient catalyst for the synthesis of cyclic carbonates from epoxides and CO_2 in HMPA at 180 °C, giving 100% yield in 5.5 h.[63] They proposed that an efficient catalyst for this kind of reaction should be able to behave as a weak acid (for electrophilic activation of the oxirane ring) as well as a weak base (for nucleophilic activation of CO_2). It is understandable because a strong acid means fast polymerization of oxirane and a strong base means irreversible binding of CO_2. They proposed that β-fluoroalkoxide resulting from electrophilic opening of the oxirane ring (eq. (1)) serves as a base. To check this proposal, they carried out the reaction of propylene oxide with Ph_3SbF_2 in the absence of CO_2, and detected fluoroalkoxide anions by ^{19}F NMR spectroscopy (eq. (2)). In addition, the fluorocarbonate anion resulting from the reaction of fluoride with CO_2 (Eq. (3)) could also serve as a base. However, they did not observe any absorption band of FCOO- in the IR spectrum of a mixture of CsF, HMPA, and CO_2; the result, nonetheless, does not exclude the possible formation of FCOO- under the adopted reaction conditions, viz. 140-180°C and 70-100 atm CO_2 pressure.

The results of Lermontov et al. showed that the catalytic mechanism of Ph_3SbF_2 is different from that of Ph_4SbBr proposed by Nomura et al.[62] The former involves CO_2 activation by the organoantimony complex, followed by interaction with epoxide. As for the latter, it is epoxide that is first activated followed by interaction with CO_2.



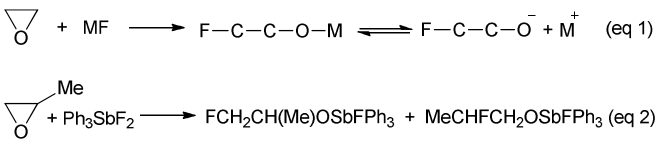
Scheme 3 Synthesis of urea from amine and carbon dioxide (Chemical shifts is $\delta(^{13}C$ NMR)).[62]

Table 2 Synthesis of cyclic urea from diamines and carbon dioxide[a62]



R	R'	Temp.(°C)	Time (h)	Yield (%)[b]
H	H	150	12	85
		150	24	0[c]
		80	24	17
Me	H	120	12	60
Ph	H	100	24	40
$HOCH_2CH_2$-	H	60	24	95
$HOCH(CH_3)CH_2$-	H	120	24	54
Me	Me	120	24	75

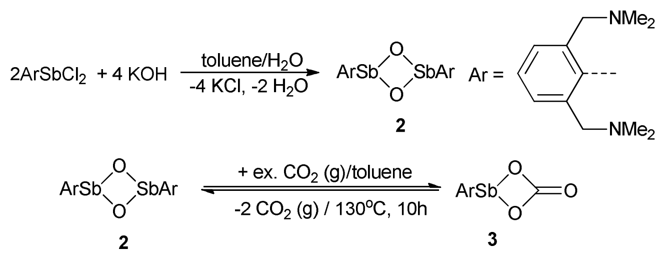
[a] Reaction conditions: diamine/Ph_3SbO/P_4S_{10} = 20/1.0/2.0 mmol, benzene 20 mL, CO_2 4.9 MPa. [b]Isolated yields. [c]Absence of the catalyst system.



$CO_2 + F^- \rightleftharpoons FCOO^-$ (eq 3)

2.2 Organoantimony(III) complexes

In 2009, Dostál et al. reported for the first time the chemical fixation of CO_2 over a trivalent organoantimony(III) complex, showing clear evidence of CO_2 insertion.[64] The dimeric organoantimony(III) oxide $(ArSbO)_2$ ((Ar) NCN chelating ligand C_6H_3-2,6-$(CH_2NMe_2)_2$) was obtained by reacting $ArSbCl_2$ with KOH (Scheme 4). The oxide bonds with CO_2 to form air-stable monomeric carbonate $ArSbCO_3$. In turn, CO_2 can be released by heating the carbonate at 130 °C for $(ArSbO)_2$ recovery (Scheme 4).



Scheme 4 Preparation of $(ArSbO)_2$ (**2**) and reversible fixation of carbon dioxide by **2** to form $ArSbCO_3$ (**3**).[64]

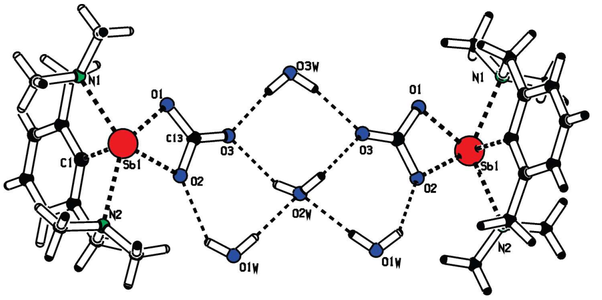


Fig. 1 PLUTON plot showing hydrogen bonding in **3**. Selected O • • • H−O contacts (Å) and angles (deg) characterizing respective hydrogen bonding: O(3) • • • H−O(3w)) 2.829(5), 166.8; O(3) • • • H−O(2w)) 2.773(5), 123.4; O(2) • • • H−O(1w)) 2.969(5), 133.2;O(2w)−H−O(1w)) 2.833(6), 175.9.[64] (Image reproduced from ref. 64 with permission from the ACS)

image reproduced from ref. 46,47 and 91 with permission of Elsevier).

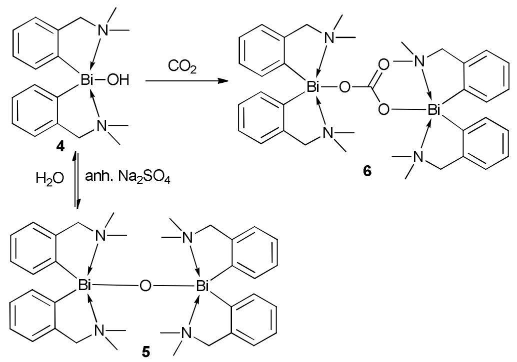
The molecular structure of $(ArSbO)_2$ **3** was unambiguously determined by X-ray analysis (Fig. 1). Single crystals of **3** were obtained through slow evaporation of CH_2Cl_2 from a $(ArSbO)_2/CH_2Cl_2$ solution. The $(ArSbO)_2$ compound was obtained as a solvate with two molecules of water. Despite the use of dried solvents and under an atmosphere of pure argon, it was not possible to obtain anhydrous $(ArSbO)_2$ single crystals. The interesting feature of the molecular structure of **3** is the coordination of the carbonate moiety as a terminal ligand in a chelating fashion.

3. CO_2 fixation using organobismuth complexes

3.1 Organobismuth complexes as CO_2 absorbent

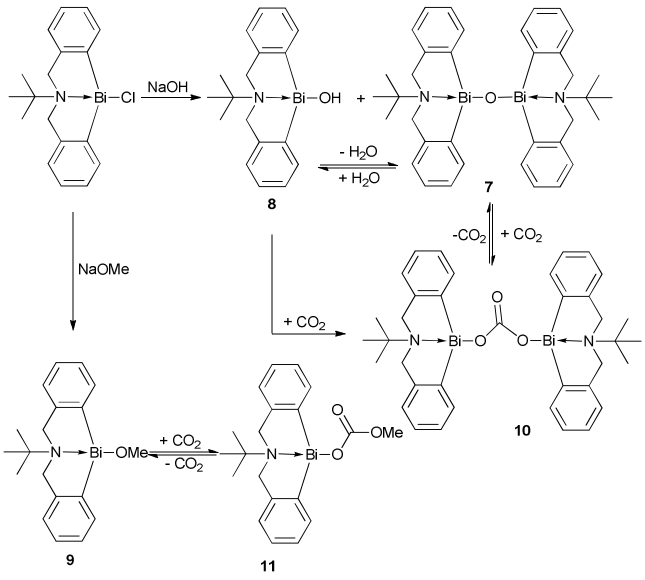
Compared to the use of organoantimony complexes, the use of organobismuth complexes for chemical fixation of CO_2 is rare. For efficient interaction with CO_2, the metal can either be a Lewis base, showing π-type interaction with one of the C=O bonds of CO_2, or be a Lewis acid (or an oxophile) interacting with an oxygen atom of CO_2. The use of organobismuth complex containing Bi-O bond for CO_2 fixation was only reported recently.

In 2008, Breunig et al. firstly reported that exposure of a diethyl ether or a toluene solution of hypervalent diarylbismuth hydroxide $[2\text{-}(Me_2NCH_2)C_6H_4]_2BiOH$ (**4**) as well as that of the corresponding oxide $[(2\text{-}(Me_2NCH_2)C_6H_4)_2Bi]_2O$ (**5**) to air led to CO_2 adsorption and the formation of carbonate $[(2\text{-}(Me_2NCH_2)C_6H_4)_2Bi]_2CO_3$(**6**) (Scheme 5).[65] However, the authors did not mention whether carbonate **6** could be transferred back to hydroxide **4** or oxide **5** or not.



Scheme 5 Chemical fixation of CO_2 with hypervalent organobismuth(III) hydroxide (**4**) and oxide (**5**) to carbonate (**6**) with the pendant arm ligand of $2\text{-}(Me_2NCH_2)C_6H_4$.[65]

Later in the same year, Shimada and co-workers reported another kind of hypervalent organobismuth complexes with a 5,6,7,12-tetrahydrodibenz[*c,f*][*1,5*]azabismocine framework.[66] The synthesis of organobismuth oxide (**7**), hydroxide (**8**) and alkoxide (**9**) are shown in Scheme 6.



Scheme 6 Chemical fixation of CO_2 with hypervalent organobismuth(III) oxide (**7**), hydroxide (**8**), and alkoxide (**9**) to carbonate (**10**) and methyl carbonate (**11**) with a 5,6,7,12-tetrahydrodibenz[*c,f*][*1,5*]azabismocine framework.[66]

The bismuth oxide **7** can be obtained by treating the bismuth chloride with aqueous sodium hydroxide. Analogous to the result of Breunig et al.,[65] bismuth hydroxide **8** readily loses a water molecule to form oxide **7**. In turn, oxide **7** can be completely converted back to hydroxide **8** by the inclusion of a water molecule. When a toluene solution of **8** is vigorously stirred in air at room temperature (RT) for 4.5 h, there is quantitative conversion of **7** to bismuth carbonate **9** (Scheme 6). Also, when an anhydrous CH_2Cl_2 solution of **7** or **8** is exposed to CO_2 (1 atm), a quantitative amount of **10** is obtained readily. The thermal ellipsoid plot of **10** is shown in Fig. 2. It is noted that carbonate **10** is thermally rather stable, and in CH_2Cl_2 or under vacuum at RT, there is no decomposition of carbonate **10**. Partial dissociation of carbonate **10** (ca. 30%) and quantitative regeneration of oxide **7** was observed when **10** was heated under vacuum at 100°C for 10 h. For effective utilization of compounds **8** and **7**, it is critical for them to show association as well as dissociation ability with CO_2. Since it is possible to regenerate compounds **7** and **8** after CO_2 absorption, the two are potential candidates for CO_2 capture. It is observed that bismuth methoxide **9** in methanol, CH_2Cl_2, or toluene readily reacts with dry CO_2 (1 atm) to form bismuth methyl carbonate **11**, and the process is reversible (Fig. 3). Because methoxide **9** is sensitive to water, it is subject to hydrolysis and undergoes the subsequent reaction in the presence of water.

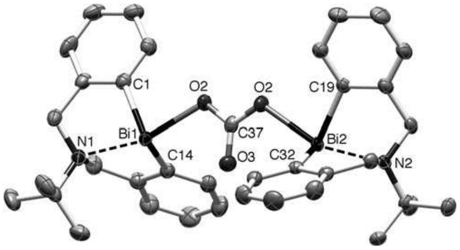


Fig. 2 A thermal ellipsoid plot (50% probability level) of **10**. Hydrogen atoms are omitted for clarity.[66] (Image reproduced from ref. 66 with permission from the Wiley)

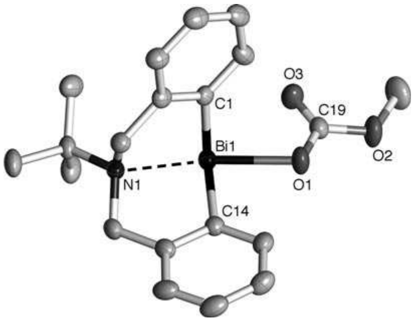


Fig. 3 A thermal ellipsoid plot (50% probability level) of **11**. Hydrogen atoms are omitted for clarity.[66] (Image reproduced from ref. 66 with permission from the Wiley)

3.2 Organobismuth complexes as CO_2-fixation catalysts

Yin et al. investigated the possible application of **7** as a catalyst for 2-oxazolidinone synthesis through the fixing of CO_2 into 2-aminoethanol.[66] 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% **7**, approximately 5% (determined by ^{1}H NMR spectroscopy) of 2-oxazolidinone was formed, whereas there was only a trace (less than 0.5%) of 2-oxazolidinone detected in the absence of **7** under the same conditions. Despite the low activity of **7**, it is considered that the presence of **7** has positive effect on the formation of 2-oxazolidinone. After the reaction, there is a small amount of black deposit in the reaction mixture. The ^{1}H NMR spectrum of the reaction solution after the reaction shows only one kind of bismuth species. The results suggest partial decomposition (less than 14%) of the bismuth compound. On the other hand, there was complete decomposition of bismuth oxide [((2,4,6-$Me_3C_6H_2)_2Bi)_2O$] under the same reaction conditions, and the bismuth oxide did not show any positive effect on 2-oxazolidinone formation.

Later, Yin and Shimada synthesized two new bismuth compounds (**12** and **13**) bearing a sulfur-bridged bis(phenolato) ligand. They found that these complexes could be used in the solvent-free synthesis of propylene carbonate from CO_2 and propylene oxide in the presence of LiI.[67]

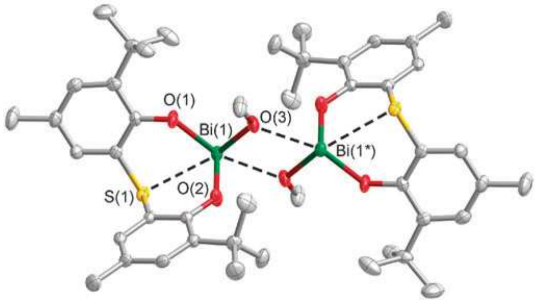


Fig. 4 A thermal ellipsoid plot of compound **12** (50% probability level). Hydrogen atoms on the carbon atoms are omitted for clarity. [67] (Image reproduced from ref. 67 with permission from the RSC)

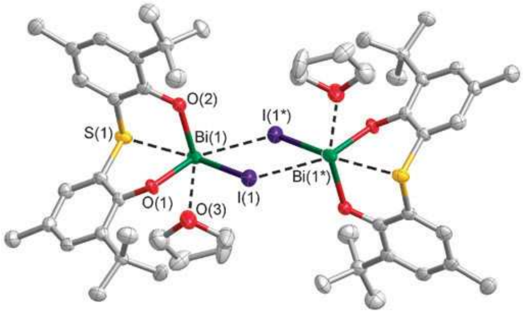


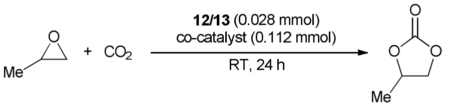
Fig. 5 A thermal ellipsoid plot of compound **13** (50% probability level). Hydrogen atoms on the carbon atoms are omitted for clarity.[67] (Image reproduced from ref. 67 with permission from the RSC)

Figs. 4 and 5 show the molecular structures of **12** and **13**, respectively. In the solid state, **12** and **13** form dimers through intermolecular Bi-O and Bi-I interactions. The Bi atom in **12** is five-coordinate 12-Bi-5, and its geometry can be described as highly distorted square pyramidal, while that in **13** is six-coordinate 14-Bi-6 having a tetrahydrofuran (THF) molecule as an additional ligand, and its geometry is distorted octahedral. These structural features clearly show the Lewis-acid nature of the bismuth centers of **12** and**13**, and are in contrast to those of the trivalent phosphorus compounds bearing 2, 20-thiobis-(phenolato) ligands.

Results of initial attempts of using **7** or **10** as catalyst for the synthesis of propylene carbonate (PC) from propylene oxide (PO) and CO_2 showed that these compounds are catalytically active. Nonetheless, bismuth methoxide **12** (catalyst loading = 0.24 mol%) shows low catalytic activity, giving a GC yield of only 29% in 10.5 h at 120°C with initial CO_2 pressure of 35 atm.

However, in the presence of an iodide salt as co-catalyst, compound **12** exhibits remarkable catalytic activity even under mild reaction conditions. As shown in Table 3, compound **13** is slightly superior to **12** in catalytic performance. The combined use of **13** and LiI results in nearly quantitative yield within 24 h (Table 3, entry 11, yield 98%). The catalytic activity of **13** is much higher than those (at RT and 1 atm CO_2) reported by Ratzenhofer and Kisch.[68] With ^1H NMR monitoring, it was found that the reaction of **12** with CO_2 does not proceed with the formation of a bismuth carbonate. In the solution, the monomers and dimers of **12** are at equilibrium, having composition depending on solvent polarity. In the case of **13**, the compound exists mostly as monomers even in a C_6D_6 solution. It is deduced that both **12** and **13** act as monomeric Lewis acid catalysts, and their mechanistic action is similar to that of the commonly proposed acid-base or electrophile-nucleophile bifunctional mechanism.[20] Hence the high efficiency of the catalyst systems can be attributed to the hypervalent structures of **12** and **13**. The intramolecular coordination of the sulfur atom to the bismuth atom is extremely flexible, and the flexibility enables the adjustment of Lewis acidity of the bismuth atom. The outcome is facile exchange of product and reactant.

Table 3 PC synthesis from PO and CO_2 catalyzed by **12** (or **13**)/iodide catalyst system[a67]

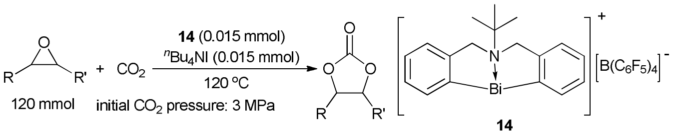


Entry	Catalyst	Conversion.(%)[b]	PC Yield (%)[b]
1	**12**	0	0
2	**13**	0	0
3	Me_3PhPI	0	0
4	**13** + Me_3PhPI	76	76
5	Bu_4NI	0	0
6	**13** + Bu_4NI	77	77
7	NaI	14	14
8	**13** + NaI	91	91
9	LiI	26	26
10	**12** + LiI	92	92
11	**13** + LiI	98	98

[a]The coupling reaction was conducted in a glass flask. The product was analyzed by NMR and GC-MS spectroscopies. [b] The conversion and the PC yield were estimated by ^1H NMR spectroscopy.

To achieve high and efficient conversion of CO_2 into valuable chemicals, and to exploit new applications of organobismuth compounds, Yin et al. developed another efficient catalytic system for the synthesis of cyclic carbonate from epoxide and CO_2.[69] They studied for the first time the cationic organobismuthcomplex (**14**) with the 5,6,7,12-tetrahydrodibenz[*c,f*][*1,5*]azabismocine framework for the transformation of CO_2 into epoxide as cyclic carbonates, using terminal epoxides as substrates and tetrabutylammonium halide as co-catalyst under mild conditions (Table 4). It is a solvent-free system and the catalyst exhibits high activity and selectivity for the coupling reaction of CO_2 with a wide range of terminal epoxides. The selectivity to propylene carbonates could reach 100%, and the maximum turnover frequency was up to 7800 h^{-1} at 120°C and 3 MPa initial CO_2 pressure when tetrabutylammonium iodide (1:1) was used as co-catalyst (entry 1). Moreover, the catalyst is environment-benign, resistant to air and water, and can be readily reused and recycled without any loss of activity (Fig. 6). In other words, the catalyst has great potential for industrial application.

Table 4 Coupling of CO_2 with terminal epoxides catalyzed by cationic organobismuth complex (**14**) + $^nBu_4NI$[a69]



Entry	R	R'	Conv.(%)[d]	Sel.(%)[d]	TOF (h^{-1})[d]
1	Me	H	97.5	>99.0	7800
2	Et	H	92.3	>99.0	7384
3	Bu	H	86.2	>99.0	6896
4	$ClCH_2$	H	90.7	>99.0	7256
5[b]	Ph	H	87.9	>99.0	5274
6[c]	$-CH_2(CH_2)_2CH_2-$		90.3	>99.0	2408

[a] Reaction conditions: epoxide, 120 mmol; Bi compound (**14**), 0.015 mmol; Bu4NI, 0.015 mmol; initial CO_2 pressure, 3.0 MPa; 120°C. [b] Reaction time, 80 min. [c] Reaction time, 3 h. [d] GC analysis, Conv.: epoxide conversion; Sel.: cyclic carbonate selectivity; TOF: moles of epoxide converted per mole of Bi per hour.

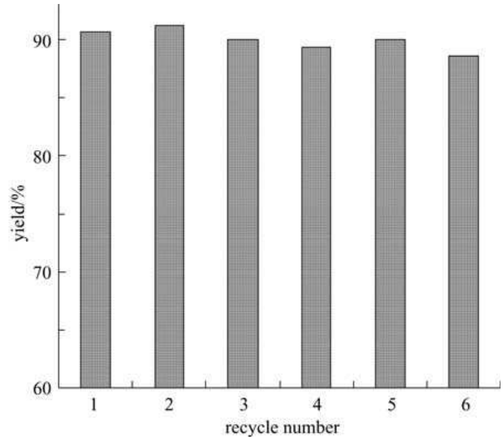
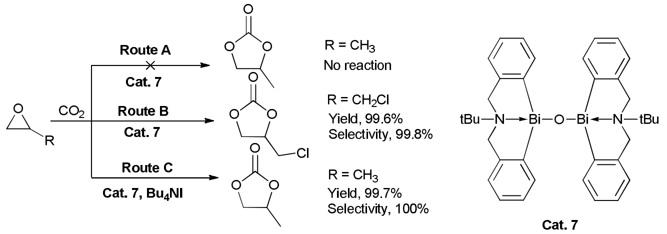


Fig. 6 Catalyst recycling using epoxy chloropropane as substrate. For each cycle: epoxy chloropropane, 120 mmol; Bi compound (**14**), 0.015 mmol; Bu_4NI, 0.015 mmol; CO_2 pressure, 3 MPa; 120°C; 1 h[69] (Image reproduced from ref. 69 with permission from the Springer)

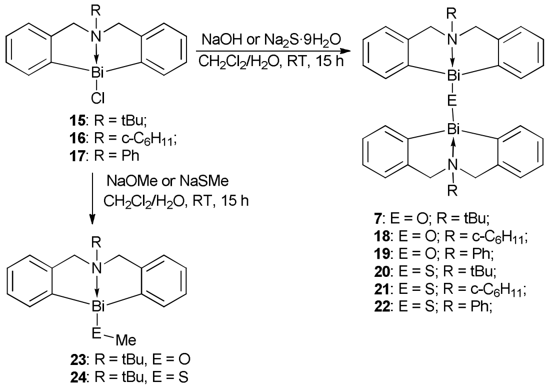
Encouraged by the results, Yin et al. incorporated $^nBu_4NI$ into binuclear organobismuth oxide complex **7** to generate a bifunctional Lewis acid-base system that shows cooperative catalytic effect for CO_2 fixation (Scheme 6).[70] Despite binuclear organobismuth oxide (**7**) having a framework similar to that of bimetallic Salen(Al) (complexes known to be catalytically highly efficient towards the reaction),[71] complex **7** shows no catalytic activity when 2-methyloxirane is adopted as substrate (Scheme 7, *Route A*). Nonetheless, when 2-

(chloromethyl)oxirane is adopted as substrate, cyclic carbonates are obtained almost quantitatively (Scheme 7, *Route B*). Furthermore, when Bu_4NI is used as co-catalyst (0.1 mol% based on epoxide), CO_2 insertion into 2-methyloxirane occurs in a quantitative manner (Scheme 7, *Route C*). In contrast to the results of monomeric organobismuth chlorides, methoxide and methanethiolate, the findings of binuclear organobismuth oxide shows cooperative action that enables high efficiency in the synthesis of cyclic carbonates from epoxides and CO_2.



Scheme 7 Selective insertion of CO_2 into epoxides catalyzed by Cat. **7**(0.5 mol%) with or without co-catalyst Bu_4NI (0.1 mol%).[70]

However, the binuclear organobismuth oxides **7**, **18-19** are sensitive to moisture and CO_2, and the rigorous requirements for manipulation limit their utilization. For practical application in organic synthesis, a catalyst is better to be air-stable.[49] Interestingly when the bridging atom is changed from oxygen to sulfur (Scheme 8), the binuclear organobismuth sulfides LBi-S-BiL (**20-22**) are air-stable. The compounds could remain as dry crystals or powder (slightly yellow in color) for more than one year in ambient environment. These sulfur-bridged binuclear organobismuth complexes represent a rare class of complexes that are air-stable.



Scheme 8 Synthetic routes of organobismuth complexes **7,18-24**[70]

The crystal structures of **20-22** freshly obtained after recrystallization in toluene/hexane (CH_2Cl_2/hexane for **20**) were determined by X-ray analysis. As shown in Fig. 7, the 5,6,7,12-tetrahydrodibenz[*c,f*][*1,5*]azabismocine framework of complexes **20-22** is bridged by a sulfur atom that occupies a vacant site of the bismuth centre. In the equatorially distorted trigonal bipyramidal geometry, the nitrogen and sulfur atoms occupy the apical positions whereas the carbon atoms occupy the equatorial positions. With sulfur bridging, the bismuth centre is exposed more efficiently than that of their precursors, making the two bismuth atoms of **20-22** closer to each other in comparison to the case of **7**. Nonetheless, the distance between the two bismuth atoms of **20-22** is larger than that of a covalent Bi-Bi single bond (3.092(6)-3.2092(8))[72] and Bi=Bi double bond (3.0648(2)).[73] This can be considered as a favorable parameter for maintaining suitable stability of the bimetallic complexes. In addition, the five linked atoms N(1)-Bi(1)-S(1)-Bi(1A)-N(1A) are almost in the same plane (angle distortion < 0.5°) with the plane bisecting the butterfly-shaped tetrahydrodibenz[*c,f*][*1,5*]azabismocine framework. One can see that the butterfly-shaped phenyl planes of **20-22** are *cis*-geometrically located to make the two bismuth atoms available for cooperative action. The *N*-substituents of **20-22** are positioned close to the bismuth centers, protecting the Bi-C bond and Bi-S-Bi bridge from infringers such as water and CO_2. Hence, by using sulfur atom for bridging and varying the *N*-substituent, one can regulate the state suitability as well as the ligands of the bismuth centers to mimic those of natural metalloenzymes.

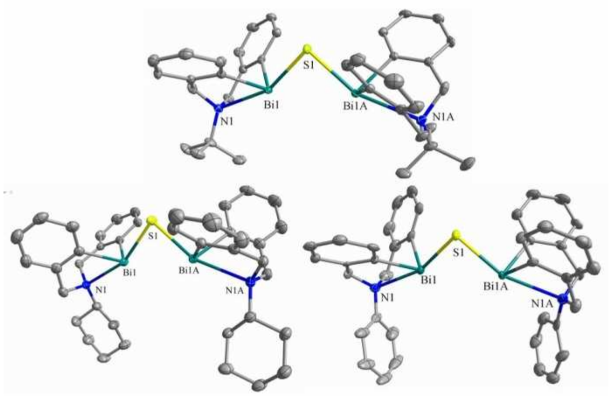
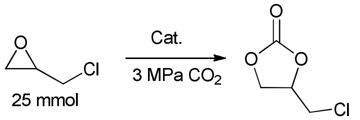


Fig. 7 Thermal ellipsoid plots (50% probability level) of **20** (top)**, 21** (bottom left)**, 22** (bottom right). Hydrogen atoms on the carbon atoms are omitted for clarity.[70] (Image reproduced from ref. 70 with permission from the RSC)

Table 5 Optimization of reaction condition in cyclic carbonate synthesis from 2-(chloromethyl)oxirane and CO_2[a70]

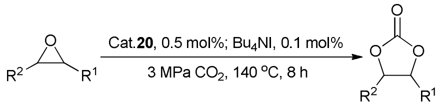


Entry	Cat. (mol%)	Time (h)	Temp. (°C)	Yield (%)	Sel. (%)
1	**7** (0.5)	8	140	99.6	99.8
2	**18**(0.5)	8	140	100	100.0
3	**19** (0.5)	8	140	97.3	98.1
4	**20** (0.5)	8	140	99.4	99.7
5	**21** (0.5)	8	140	94.3	98.3
6	**22** (0.5)	8	140	65.8	98.0
7	**15**(1.0)	8	140	25.9	97.7
8	**16** (1.0)	8	140	41.3	98.3
9	**17** (1.0)	8	140	5.9	96.9
10	**23** (1.0)	8	140	32.5	98.3
11	**24** (1.0)	8	140	14.7	92.6
12[b]	--	8	140	3.7	98.2

[a] Reaction conditions: 2-(chloromethyl)oxirane, 2 mL (25 mmol); initial CO_2 pressure, 3.0 MPa, GC yield. [b] Blank experiment.

To examine the cooperative action of the binuclear bismuth centers, complexes **7**, **18-22** were examined for the synthesis of cyclic carbonates from epoxides and CO_2 (Table 5), and their performance are compared with those of mononuclear organobismuth complexes **15-17** and **23-24**. One can see that most of them show good catalytic efficiency (entries 1-6, GC yield up to 100%). In terms of catalytic efficiency and air-stability, the *N*-substituent with flexible and electron-donating group (*t*Bu, **20**; Cy, **21**) is superior to organobismuth oxides (**7**, **18-19**) (entries 1-3) as well as to those with rigid and electron-withdrawing group (Ph, **22**) (entries 4-6). In contrast to the mononuclear organobismuth complexes (entries 7-11), the binuclear organobismuth complexes show a significant cooperative effect on CO_2 transformation. Without a catalyst, the product yield is only 3.7% (entry 12). The results indicate that by simple modification of the *N*-substituent and the bridging atom in the main framework of bimetallic organobismuth complexes, one can tune catalytic activity as well as achieving air-stability.

Table 6 Synthesis of cyclic carbonates from CO_2 and epoxides[a70]



Entry	R^1	R^2	Conv. (%)	Yield (%)
1	H	H	100.0	98.2
2	CH_3	H	99.7	99.7
3[b]	CH_2Cl	H	100.0	99.8
4[c]	CH_3	CH_3	76.2	76.0
5[d]	Ph	H	99.5	99.5
6[c]	$-CH_2(CH_2)_2CH_2-$	62.3	62.1	99.3
7[b]	CH_3	H	2.3	2.3

[a] Reaction conditions: 2-(chloromethyl)oxirane, 2 mL; initial CO_2 pressure 3.0 MPa, Cat. **20**, 0.5 mol%, 8 h, 140 °C. [b] Without co-catalyst Bu_4NI. [c] Catalyst loading of **20** was 1.0 mol%. [d] 12 h.

The catalytic performance of **20** was also investigated under optimized conditions across a diversity of epoxides (Table 6). In most of the cases, including 2-phenyloxirane and 7-oxabicyclo[4.1.0]heptane of large steric hindrance, the catalyst is highly effective (entries 1-6). The co-presence of Bu_4NI is favorable for CO_2 insertion into the non-halide epoxides (entries 2 and 7).

3.3 Bi-Fe bimetallic complexes for CO_2 fixation

In addition to the organobismuthcomplexes with 5,6,7,12-tetrahydrodibenz[c,f][1,5]azabismocine framework, there are other organobismuth complexes that are catalytically active for CO_2 fixation. It was reported by Wójciket al. that the reaction of $Fe_2(CO)_9$ with $Bi(OSiMe_2tBu)_3$ would result in the formation of soluble $[(CO)_4FeBi(OSiMe_2{}^tBu)]_2$ (**25**) in moderate yield (Fig. 8). Complexes $[(CO)_4FeBi(O^tBu)]_n$ (**26**) and $[(CO)_3FeBi_3(O^tBu)_4(OCO(O^tBu))]_2$ (**27**) were obtained when $Bi(O^tBu)_3$ was used as starting material (Fig. 9).[74] During the reaction of diiron nonacarbonyl with bismuth tert-butoxide, complex **27** was released upon the insertion of CO_2 into a Bi-O^tBu bond. The compounds were characterized by IR and ^1H NMR spectroscopy as well as thermo-gravimetric analysis. Additionally, the molecular structures of compounds **25** and **27** were elucidated by single crystal X-ray diffraction. The core structure of $[(CO)_4FeBi(OSiMe_2{}^tBu)]_2$ (**25**) is a four-membered Bi_2Fe_2 ring. As for **27**, the compound is composed of two cores of tetrahedral $FeBi_3$ clusters that dimerise via the bridging of -$OCO(O^tBu)$ ligands. Analysis of the TGA residues by powder X-ray diffraction revealed that compound **26** is the best precursor for the generation of multi-ferroic $BiFeO_3$ among the compounds studied, despite the detection of $Bi_{25}FeO_{39}$ as minor impurity.

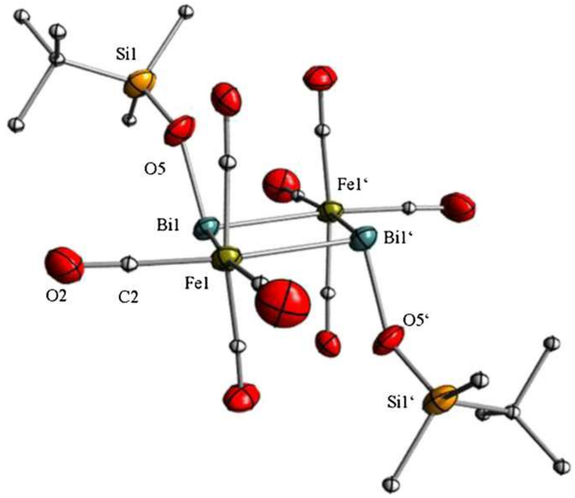


Fig. 8 ORTEP diagram (50% probability level) of the molecular structure of $[(CO)_4FeBi(OSiMe_2{}^tBu)]_2$ (**25**), H atoms are omitted for clarity.[74] (Image reproduced from ref. 74 with permission from the Elesvier)

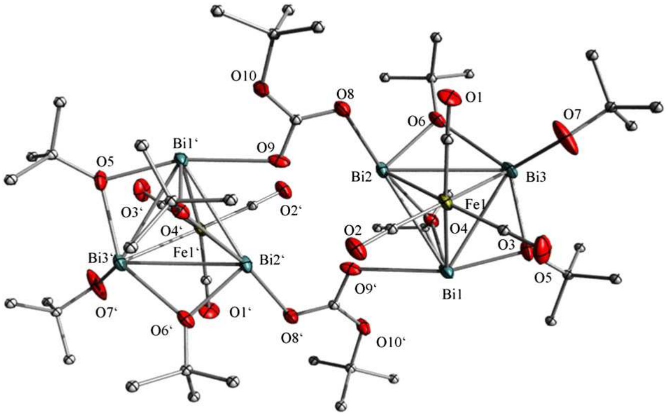
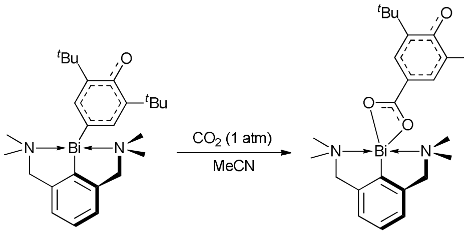


Fig. 9 ORTEP diagram (50% probability level) of the molecular structure of $[(CO)_3FeBi_3(O^tBu)_4(OCO(O^tBu))]_2$ (**27**), H atoms are omitted forclarity.[74] (Image reproduced from ref. 74 with permission from the Elesvier)

3.4 CO_2 insertion into Bi-C bond of an organobismuth complex

Just recently, Kindra et al. demonstrated yet another example of CO_2 insertion into Bi-C bonds of bismuth NCN pincer complex bearing an oxyaryl dianionic ligand $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]Bi(C_6H_2\text{-}{}^tBu_2O)$.[75] The reactivity of the unusual oxyaryl dianionic ligand, $(C_6H_2{}^tBu_2\text{-}3,5\text{-}O\text{-}4)^{2-}$, in the Bi^{3+} NCN pincer complex $Ar'Bi(C_6H_2{}^tBu_2\text{-}3,5\text{-}O\text{-}4)$ (**28**) [Ar′ =

$2,6-(Me_2NCH_2)_2C_6H_3$], was explored with substrates and electrophiles of small molecules. The first insertion reaction of CO_2 into Bi−C bond was observed over this oxyaryl dianionic ligand complex (Scheme 9). The reactions generate new dianions that have quinoidal character similar to that of the oxyaryl dianionic ligand in **28**. The oxyarylcarboxy dianionic ligand in $Ar'Bi[O_2C(C_6H_2{}^tBu_2\text{-}3\text{-}5\text{-}O\text{-}4)\text{-}\kappa^2O,O']$ (**29**) was identified by X-ray crystallography (Fig. 10).



28 **29**

Scheme 9. Insertion of CO_2 into the Bi-C bond of bismuth NCN pincer complex of oxyaryl dianionic ligand $[2,6-(Me_2NCH_2)_2C_6H_3]Bi(C_6H_2\text{-}{}^tBu_2O)$.[75]

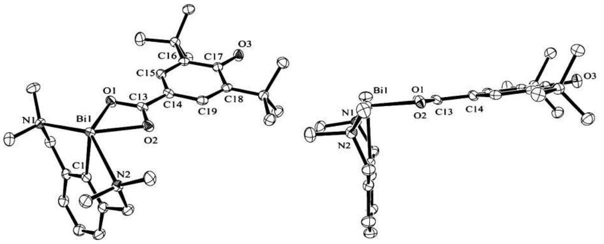


Fig. 10 ORTEP representation of $Ar'\ Bi[O_2C(C_6H_2{}^tBu_2\text{-}3\text{-}5\text{-}O\text{-}4)\text{-}\kappa_2O,O']$ (**29**), from two different perspectives, with thermal ellipsoids drawn at t probability. Hydrogen atoms are omitted for clarity.[75] (Image reproduced from ref. 75 with permission from the ACS)

3.5 Physical fixation of CO_2 with bismuth-organic frameworks

Cheetham's group[76] reported two other bismuth complexes with metal-organic frameworks. They are inorganic-organic bismuth $[LiBi(2,6\text{-}pdc)_3(H_2O)]\cdot 2(dma)$ (**30**) and $Li_5Bi(2,6\text{-}pdc)_4(H_2O)_2$ (**31**) with four Li^+ cations per formula (where dma = dimethyl ammonium cation, dmf = dimethylformamide, and 2,6-pdc = pyridine 2,6-carboxylate). They were synthesized as efficient absorbents for CO_2 absorption. The amount of CO_2 that can be taken up by compound **31** is up to 140 cc g^{-1} (~6 mmol g^{-1}).

4. Summary

Organoantimony(bismuth) complexes have been used as absorbents and catalysts for CO_2 fixation, giving organometallic carbonates and cyclic carbonates as products, respectively. The physical fixation of CO_2 by inorganic-organic bismuth complexes and CO_2 insertion into a Bi-C bond are new. Since 1979, efficient catalysts based on organoantimony (bismuth) have been developed, and most of them are electrophile-nucleophile or Lewis acid/Lewis base systems. The plausible catalytic mechanism involves the reaction of CO_2 with a organoantimony(bismuth) catalyst to form an organometallic carbonate. With the opening of epoxide by a base such as $^nBu_4NI$, the organometallic carbonate reacts with the epoxide to give the cyclic carbonate. The organoantimony and organobismuth complexes have bright prospects in the field of CO_2 fixation. Further work with organoantimony(bismuth) complexes as CO_2 absorbent or catalyst should be focused on the following aspects: (i) simple and cheap CO_2 absorbents whose CO_2 association or dissociation is fast and efficient under mild condition, should be developed; (ii) air-stable, thermo-stable, recyclable, high Lewis acidic organoantimony(bismuth) complexes catalyst is still highly desirable; (iii) highly efficient synthetic method for the useful chemicals from CO_2, such as polycyclic carbonate, dimethyl carbonate, and dimethyl ether is still not well established, especially in the industrial scale; (iv) the related catalytic mechanism for the generation of cyclic carbonates is unclear, lacking of direct evidence, such as NMR and X-ray evidence; and (v) the reactivity of the C-M bond with CO_2 or other small molecules will be another challenge.

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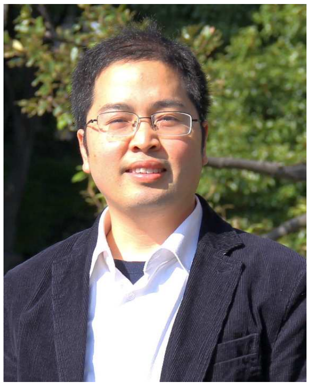
Biography

Yi Chen was born in Hunan Province, China. She received her B.Sc. degree in Hunan Normal University in 1996, and received Master Degree in Hunan University of Chinese Medicine in 2003. From 1996 to present, she worked as lecturer and later associate professor (2006) in Hunan University of Chinese Medicine. At present, she is a visiting researcher with Prof. S.F. Yin. Her main research interest includes basic research of the cardiovascular and cerebrovascular diseases and organbismuth medicine.



Renhua Qiu was born in Hunan Province, China. He received B.Sc. degree in Hunan Normal University in 2004, and received Ph.D. in Hunan University in 2011 under the co-supervision of Professors Shuang-Feng Yin and Xinhua Xu. He was a research assistant (2010) with Prof. C.-T. Au in HKBU and visiting researcher (2011) with Dr. L.-B. Han in AIST (Japan). From 2009 to present, he worked as assistant researcher and later assistant professor (2011) in Hunan University. At present, he is visiting Osaka University (Japan) as a JSPS fellow (2012) with Prof. N. Kambe. Dr. Qiu's main research interest includes organometallic chemistry, Lewis acid catalysis, and C-H bond activation.

Xinhua Xu was born in Hunan Province, China. He received his Master Degree in Hunan Normal University in 1991, and received Ph.D. in Zhejiang University with Prof. Xian Huang in 1998. He did postdoctoral research in Nankai University from 1998 to 2000 with Prof. Ruyu Chen. From 2000 to present, he worked as associate professor and later full professor (2006) in Hunan University. In 2002, he visited Japan as a visiting researcher with Prof. J. Otera. Prof. Xu's main research interest includes organometallic chemistry, heteroatom chemistry, and homogeneous catalysis.

Chak-Tong Au was born in Hong Kong. In 1981, he received Ph.D. in the University of Bradford, UK. From 1980 to 1986, he did research in the University College, Cardiff, Wales. In 1986, he joined Xiamen University, China as associate professor and was promoted to professor in 1987. From 1990 to present, he worked as lecturer and later full professor in Hong Kong Baptist University. He was awarded D.Sc. degree by the University of Liverpool in 2003. Prof. Au has published over 400 papers in areas of heterogeneous catalysis and novel materials. At present, he serves as an editor of Applied Catalysis A: General.

Shuang-Feng Yin was born in Hunan Province, China. He received Ph.D. in Tsinghua University in 2003. He had postdoctoral research with Prof. C.-T. Au from 2002 to 2004 in HKBU. From 2004 to present, he worked as lecturer and later full professor (2006) in Hunan University. From 2004 to 2006, he visited Japan as a JSPS fellow with Dr. S. Shimada. Prof. Yin's main research interest includes organometallic chemistry, CO_2 chemistry, catalysis, new energy, and nanomaterial.

Notes and references

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Organoantimony and organobismuth complexes for CO_2 fixation

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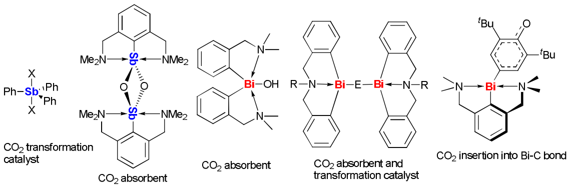

The utilization of organoantimony and organobismuth complexes in CO_2 fixation is reviewed in this article.