Isolation of a Pyridinium Alkoxy Ion Bridged Dimeric Zinc Complex for the Coupling Reactions of CO_2 and Epoxides**

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The synthesis of cyclic carbonates by metal-catalyzed coupling reactions of carbon dioxide and epoxides has attracted much attention with regard to the utilization of carbon dioxide, a gas responsible for global warming.[1, 2] Among the various catalysts and catalyst systems so far reported,[3–5] the use of transition metal based catalysts in conjunction with Lewis bases such as amines or phosphanes has proved to be a highly active combination for promoting the coupling reactions.[6] Zinc(II) complexes have also been applied as catalysts, owing to their high activity in the cyclization and copolymerization of carbon dioxide and epoxides.[7] However, despite extensive studies on the reaction mechanism,[8] potential intermediates, which could clarify the reaction pathway to the formation of cyclic carbonates, have never been structurally characterized or isolated. Accordingly, discussion about these intermediates has usually been speculative.

To understand the reaction pathway more definitely and to elucidate the promoting role of the Lewis base, we have conducted mechanistic studies on the coupling reactions in the presence of a well-defined, soluble catalyst, $[L_2ZnBr_2]$[9](**1a**: L = pyridine; **1b**: L = 2-methylpyridine; **1c**: L = 2,6-dimethylpyridine; **1d**: L = 2-chloropyridine). Here we disclose the first isolation and characterization of the pyridinium alkoxy ion bridged zinc complexes $[Zn_2Br_4(\mu\text{-}OCHRCH_2{-}NC_5H_5)_2]$ (**2a**: R = H, **2b**: R = CH_3), which clearly demonstrate the role of the Lewis base in the coupling reactions of carbon dioxide and epoxides.

Treatment of $[(C_5H_5N)_2ZnBr_2]$ (**1a**) with ten equivalents of ethylene oxide or propylene oxide in CH_2Cl_2 for 10 h at room temperature resulted in a relatively air-stable white precipitate, **2a** or **2b**, respectively, which was characterized by elemental analysis as well as by ^1H and ^{13}C NMR spectroscopy. The ambiguous spectroscopic data of the white precipitates led us to carry out a single-crystal X-ray diffraction study to elucidate the structure of **2**. To our surprise, the X-ray study reveals **2b** to be an addition product with two pyridinium adducts bridging two electrophilic metal centers (Figure 1).[10]

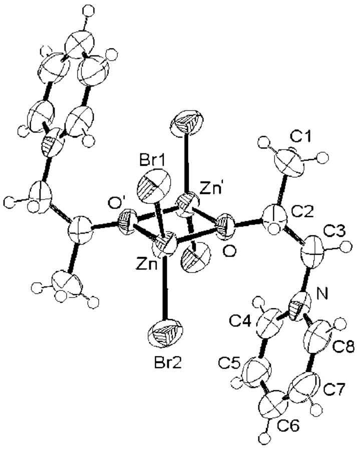

Figure 1. X-ray crystal structure of **2b**. Selected bond lengths [Å] and angles [°]: Zn-O′ 1.956(5), Zn-O 1.971(5), Zn-Zn′ 2.9420(19), N-C3 1.477(12), C2-C3 1.493(13); O′-Zn-O 83.0(2), O′-Zn-Br2 121.94(16), O-Zn-Br2 112.57(16), O′-Zn-Br1 113.08(16), O-Zn-Br1 112.52(16), Br2-Zn-Br1 110.86(6), C2-O-Zn′ 137.7(6), C2-O-Zn 121.1(6), Zn′-O-Zn 97.0(2), O-C2-C3 110.4(8), C2-C3-N 113.4(8).

The Zn–O bond lengths of 1.956 and 1.971 Å in **2b** are comparable to those found in previously reported cadmium and zinc phenoxide complexes (1.864–2.170 Å).[11–13] The structure of **2b** reveals various important aspects of zinc-catalyzed coupling reactions of epoxides and CO_2 such as ligand (pyridine) dissociation, coordination of the epoxide, and ring opening of the coordinated epoxide by a Lewis base (dissociated pyridine) through C–N bond formation. Ring opening of the epoxide occurs exclusively at the less sterically hindered carbon atom.

The insertion of CO_2 into the metal–oxygen bond of terminal alkoxides or phenoxides is well known,[14, 15] but CO_2 insertion into bridging phenoxide or alkoxides has not been established. The rapid interaction of CO_2 with **2b** was confirmed by ^1H and ^{13}C NMR studies (Figure 2). Upon introduction of $^{13}CO_2$ into an NMR tube containing **2b** in $[D_6]$DMSO, a new set of broad resonances appears in the ^1H NMR spectrum, which is likely associated with pyridinium ions in a carbonate species. The ^{13}C NMR spectrum also shows a characteristic carbonate resonance at $\delta = 170$ (peak labeled with*in Figure 2D), confirming the formation of a zinc–carbonate species.[14, 15]

The activities of various zinc complexes containing pyridine or substituted pyridine ligands have been tested for the coupling reactions between CO_2 and epoxides. Table 1 shows that the reactions of alkylene oxides and carbon dioxide in the presence of **1** produce alkylene carbonate in high yield. The catalyst system consisting of $ZnBr_2$ and pyridine exhibits similar activity to **1a**. However, $ZnBr_2$ alone is not able to catalyze the reaction, demonstrating the important role of pyridine.

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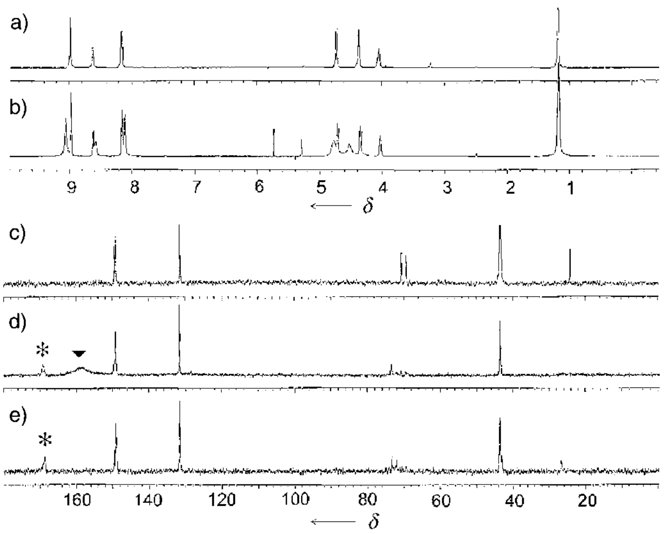


Figure 2. ^1H NMR spectrum of **2b** in a) [D$_6$]DMSO and b) $^{13}CO_2$-saturated [D$_6$]DMSO. ^{13}C NMR spectra of **2b** in c) [D$_6$]DMSO, d) $^{13}CO_2$-saturated [D$_6$]DMSO (*: carbonate, ▼: free dissolved $^{13}CO_2$), and e) after evacuation of the sample in (d).

Table 1. Activities of various catalysts for the coupling reactions of CO_2 and epoxides.[a]

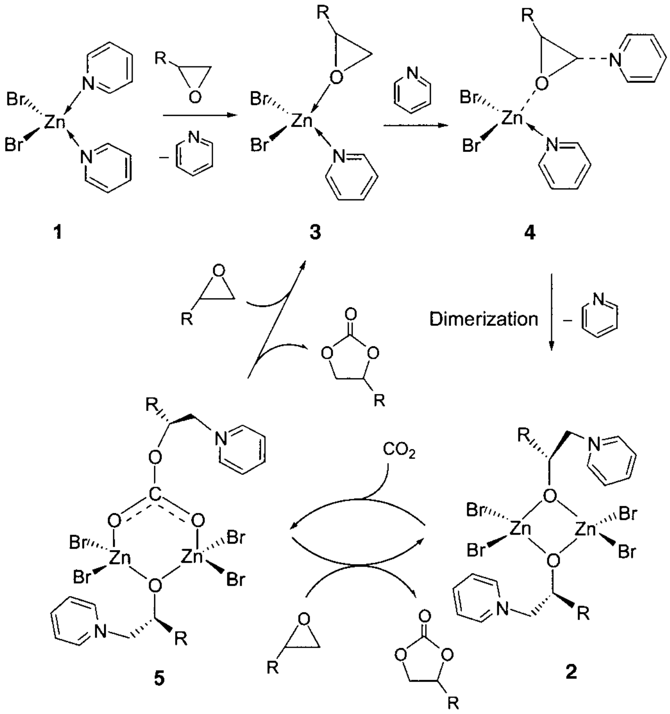
Catalyst	Promoter	Epoxide	Yield [%]	TOF[b] [h^{-1}]
$ZnBr_2$	–	EO	–[c]	–[c]
–	Py	EO	–[c]	–[c]
$ZnBr_2$[d]	Py	EO	76	775
1a	–	EO	83	851
1a	–	PO	8	40
2b	–	PO	47	237
1b	–	PO	80	405
1c	–	PO	62	315
1d	–	PO	≈1	≈5

[a] Conditions: $T = 100\,^\circ C$, $p(CO_2) = 3.4$ MPa, reaction time 1 h; molar ratios: EO/catalyst = 1000, PO/catalyst = 500. [b] TOF = turnover frequency. [c] No reaction. [d] Molar ratio: Py/Zn = 2. EO = ethylene oxide, PO = propylene oxide, Py = pyridine.

Substitution at the 2- or 2,6-positions of the pyridine ligand has a striking effect on the catalytic activity for the coupling reaction between CO_2 and propylene oxide. The catalyst containing pyridine ligands substituted with electron-donating methyl groups (**1b** or **1c**) surprisingly exhibits higher activity than **1a**. In contrast, the catalyst containing an electron-withdrawing chlorine atom at the 2-position of the pyridine ligands (**1d**) shows little catalytic activity. The basicity of the pyridine ligand is believed to play an important role in the ring opening of the coordinated epoxide and in the stabilization of the resulting pyridinium alkoxy ligand.

Interestingly, the activity of **2b** is considerably higher than that of **1a**, indicating the presence of an induction period for the formation of **2b** from **1a**. Surprisingly, complex **2b** retains its integrity even after the coupling reaction of propylene oxide and CO_2 is performed at 100 °C under 3.4 MPa of CO_2 for 1 h.[16] These experimental results strongly suggest that complex **2b** itself is an active species rather than an intermediate. However, the possibility that **2b** exists as a monomeric species under experimental conditions cannot be excluded.

From the activity tests and the mechanistic studies described above, a reasonable mechanism for the coupling reaction of epoxide and CO_2 can be proposed (Scheme 1). Coordination of epoxide with replacement of the pyridine ligands is likely to occur first. Nucleophilic attack of the dissociated pyridine on the less sterically hindered carbon atom of the coordinated epoxide and subsequent dimerization of the resulting pyridinium alkoxy ion lead to the formation of **2**. The insertion of CO_2 into the Zn–O bond of **2** would give a carbonate-bridged intermediate **5**. The coordination of an additional epoxide to **5** followed by the elimination of cyclic carbonate can generate **2**. Rapid insertion of carbon dioxide followed by cyclization would generate cyclic carbonate and complex **2** or **3**.



Scheme 1. Proposed mechanism for the coupling reaction of CO_2 and epoxide in the presence of **1a** (R = H, CH_3).

Efforts to tune the catalytic properties of complexes **1** and **2** by modifying the ligand set as well as detailed mechanistic studies are in progress.

Experimental Section

2: General procedure: A solution of **1** (2.6 mmol) in CH_2Cl_2 (30 mL) was treated with the appropriate epoxide (26 mmol) in a 60-mL high-pressure glass reactor and then stored at room temperature for 10 h. The solution was filtered and dried under vacuum to give a relatively air-stable white solid. Crystals of **2b** were directly obtained from the reaction mixture. Crystals started to grow as the reaction proceeded.

2a: Yield: 96 %; elemental analysis calcd for $C_{14}H_{18}Br_4N_2Zn_2$ (%): C 25.29, H 2.71, N 4.21, Br 48.11, Zn 19.68; found: C 25.00, H 2.65, N 4.19, Br 47.98, Zn 19.51; ^1H NMR (600 MHz, [D$_6$]DMSO, 25 °C): $\delta = 3.90$ (t, ^3J(H,H) = 4.8 Hz, 2H; CH_2), 4.71 (t, ^3J(H,H) = 4.8 Hz, 2H; CH_2), 8.20 (t, ^3J(H,H) = 6.6 Hz, 2H; C_5H_5N), 8.66 (t, ^3J(H,H) = 6.6 Hz, 1H; C_5H_5N), 9.05 (d, ^3J(H,H) = 6.6 Hz, 2H; C_5H_5N).

2b: Yield: 98%; elemental analysis calcd for $C_{16}H_{22}Br_4N_2Zn_2$ (%): C 27.73, H 3.18, N 4.04, Br 46.16, Zn 18.89; found: C 27.59, H 3.09, N 3.98, Br 45.50, Zn 18.83; ^{1}H NMR (600 MHz, [D$_6$]DMSO, 25°C): $\delta = 1.16$ (d, ^3J(H,H) = 1.6 Hz, 3H; CH$_3$), 4.04 (m, 1H,CH), 4.35(dd, ^3J(H,H) = 12.6 Hz, ^2J(H,H) = 3.0 Hz, 1H; CH$_2$), 4.71(dd, ^3J(H,H) = 12.6 Hz, ^2J(H,H) = 8.4 Hz, 1H; CH$_2$), 8.16 (t, ^3J(H,H) = 6.6 Hz, 2H; C_5H_5N), 8.62 (t, ^3J(H,H) = 6.6 Hz, 1H; C_5H_5N), 8.97 (d, ^3J(H,H) = 6.6 Hz, 2H; C_5H_5N).

Catalysis reaction: All the coupling reactions were conducted in a 100-mL stainless-steel bomb equipped with a magnet bar and an electrical heater. The reactor was charged with the appropriate catalyst and epoxide, and pressurized with CO_2 (≈ 1.4 MPa). The bomb was then heated to a specified temperature with the addition of CO_2 (up to 3.4 MPa) from a reservoir tank to maintain a specified pressure. After the reaction, the bomb was cooled to room temperature and the remaining epoxide was removed. The product mixtures were analyzed by GC, HPLC, and GC-MS. Solid catalyst mixtures were characterized by NMR spectroscopy.

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[10] Data for the crystal structure analyses were measured on a CAD-4 diffractometer. **2b**: monoclinic, $P2(1)/c$, $a = 8.8690(10)$, $b = 10.615(2)$, $c = 13.229(3)$ Å, $\alpha = 90.02(2)$, $\beta = 104.15(2)$, $\gamma = 90.020(10)°$, $V = 1207.6(4)$ Å^3, $Z = 4$, $R1 = 0.0481$, $wR^2 = 0.1110$ ($I > 2\sigma I$); $R1 = 0.0505$, $wR^2 = 0.1126$ (all data). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-148670. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
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[16] See the Supporting Information for the ^{1}H NMR spectrum of the reaction mixture.

Rational Construction of Chiral Octanuclear Metallacycles Consisting of Octahedral Co^{III}, Square-Planar Pd^{II}, and Linear Au^{I} or Ag^{I} Ions**

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While self-assembly of organic molecules assisted by metal ions has attracted much interest in the field of supermolecular chemistry,[1] our research interest has been directed to assembly of octahedral metal complexes with simple thiolate ligands, such as 2-aminoethanethiolate (aet) and L-cysteinate (L-cys). It has been shown that the assembly of these types of complexes can be achieved by facile reactions with a variety of metal ions, which utilize the binding ability of a coordinated thiolato sulfur atom toward a second metal ion.[2–7] For example, a number of trinuclear $[M'\{M(aet)_3\}_2]^{n+}$ ($M' = Fe^{III}$, Co^{III}, Ni^{II}),[4] pentanuclear $[M'_3\{M(aet)_3\}_2]^{n+}$ ($M' = Ag^{I}$, Hg^{II}),[5] and octanuclear $[M'_4O\{M(aet)_3\}_4]^{6+}$ ($M' = Co^{II}$, Zn^{II}) complexes,[6] in which two or four equivalents of *fac*(*S*)-$[M(aet)_3]$ ($M = Co^{III}$, Rh^{III}, Ir^{III}) are assembled by forming sulfur-bridged structures with octahedral, linear, or tetrahedral metal ions, have been prepared and their unique stereochemical and spectroscopic properties have been clarified. In these polynuclear structures, all the three thiolato sulfur atoms in each *fac*(*S*)-$[M(aet)_3]$ unit bridge two metal centers and thus, further assembly of these polynuclear complexes assisted by additional metal ions would not be promising. In this context, it is desirable to prepare sulfur-bridged polynuclear complexes, in which thiolato sulfur atoms are still available for bridging, in order to expand the assembly chemistry based on thiolato metal complexes. One way to do this is to introduce a four-coordinate metal ion, such as $M' = Pd^{II}$, Pt^{II}, at the center of the linear trinuclear structure in $[M'\{M(aet)_3\}_2]^{2+}$. While the reaction of *fac*(*S*)-$[Co(aet)_3]$ with $[PdCl_4]^{2-}$ in a 1:1 ratio produced a sulfur-bridged $Co^{III}_2Pd^{II}_3$ pentanuclear complex, $[Pd_2\{Pd(aet)_2\}\{Co(aet)_3\}_2]^{4+}$, in which all of the eight thiolato sulfur atoms from two *fac*(*S*)-$[Co(aet)_3]$ and one *cis*(*S*)-$[Pd(aet)_2]$ units are bound to two square-planar Pd^{II} ions,[7g] we found that the corresponding 2:1 reaction under milder conditions gives the desired trinuclear complex $[Pd\{Co(aet)_3\}_2]^{2+}$, $[\mathbf{1}]^{2+}$, which readily

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