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Novel, recyclable supramolecular metal complexes for the synthesis of cyclic carbonates from epoxides and CO_2 under solvent-free conditions

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ABSTRACT

A series of novel Zn, Cu, Fe supramolecular complexes were designed and synthesized. The structures of these compounds have been confirmed by IR, NMR, EA and X-ray crystallography. The complexes in combination with tetrabutylammonium bromide were studied as a binary catalyst system for CO_2-fixation in the context of organic carbonate formation under solventless condition. The effects of various co-catalysts, co-catalyst concentration, reaction temperature, CO_2 pressure, reaction time, various substituents on ligand and centre metal of complexes have been investigated systematically. The binary catalyst system also showed broad substrate scope of epoxide. The catalysts can be easily recovered and reused without significant loss of activity and selectivity. Comparison of different two-component dinuclear metal complexes catalysts reported by other scientists showed that the dinuclear metal complexes reported herein were competitive with most catalysts currently available. On the basis of the experimental results, the mechanism for the reaction was proposed.

1. Introduction

Nowadays, carbon dioxide (CO_2) has become the major man-made greenhouse gas, which could lead to disaster, such as desertification of land, Arctic ice disappearing, sea level rising, and so on [1]. On the other hand, its nontoxic, nonflammable, inexpensive, and large atmospheric abundance makes it a viable alternative to other depleting substances [2]. From an environmental chemical standpoint, CO_2 is an invaluable chemical resource because of its recovery property as a by-product of many industrial processes and its capability to replace toxic chemicals in various synthetic processes [3]. As a consequence, the chemical fixation of CO_2 is attracting interest to reduce the concentration of CO_2 in the atmosphere recently [4].

An important way of CO_2 fixation is its reaction with epoxides which can be controlled to produce either cyclic carbonates [5] or polycarbonates [6]. Polycarbonates have gained considerable momentum as replacements for petrochemically derived polymers. Cyclic carbonates have numerous applications such as electrolytes for lithium ion batteries [7], polar aprotic solvents [8] and chemical intermediates for drug synthesis [9].

The cycloaddition between epoxides and CO_2 is generally carried out by various homogeneous and heterogeneous catalysts, including metalloporphyrins complexes [10], metal complexes [11], metal oxides [12], molecular sieves [13], metal-organic frameworks [14], Lewis acids or bases [15], ion-exchange resins [16], nanoparticles [17], ionic liquid [18], functionalized polymers [19], biopolymer-supported catalys [20] and so on. Among these catalysts, metal complexes have been of significant interest due to their easy-to-synthetize and excellent stability against moisture and air [21]. Because of the potential advantages than mononuclear complexes as catalysts, binuclear or multinuclear complexes have attracted considerable attention among these metal complexes [22].

Supramolecular catalysts offer chemists precise spatial control over chemical transformations [23]. The allosteric supramolecular catalyst with active sites could be opened and closed by effecting

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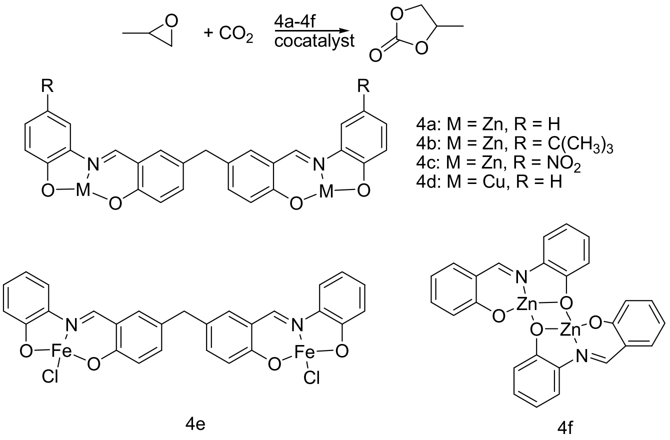

Scheme 1. Cycloaddition of PO and CO_2 to give PC and novel binuclear supramolecular Zn, Cu, Fe complexes 4a–4e and dimer zinc catalyst 4f used in this study.

chemistry at one or more distal sites within the structure. This, in turn, could modulate the catalytic activity of the complex [24]. Although many catalyst systems had been designed, synthesized and used for the coupling reaction of epoxides and CO_2, there are few literature reports about the application of supramolecular catalyst reported in this area to the best of our knowledge [25].

In this work, three hexadentate ligands containing two sets of ONO donor atoms have been designed and synthesized. These ligands were reacted with metal salts to prepare six new dinuclear metal supramolecular complexes in moderate yields. The catalytic performance of the supramolecular catalysts has been systematically investigated for the coupling reaction of epoxides and CO_2, the results indicated that the combination of metal complex with two bimetallic cores and tetrabutylammonium bromide formed an exceptionally active catalyst system for the synthesis of cyclic carbonates from terminal epoxides under mild solvent-free conditions (Scheme 1). Furthermore, the insoluble nature of the complexes in the reactants and products made separation of catalysts much easier, which also leads to 6 times catalyst recyclability without any significant loss of reactivity. Additionally, a proposed mechanism was given.

2. Experimental section

2.1. Chemicals and analytical methods

The detailed information of the materials used in present work is listed in Table 1. The epoxides were distilled from CaH_2 before use.

NMR spectra was recorded on a Bruker Al–400 MHz instrument using trimethylsilane (TMS) as an internal standard. IR spectra was recorded on a Perkin-Elmer 2000 FT-IR spectrometer. Elemental analysis was conducted on a PE 2400 series II CHNSO elemental analyser. Melting point was obtained from X-4-type digital micromelting point apparatus. X-ray diffraction studies were performed on a Bruker-APEX diffractometer equipped with a CCD area detector, MoKa-radiation ($\lambda = 0.71073$ Å), and a graphite monochromator. All spectra were recorded at room temperature. All the known compounds were identified by comparison of their physical and spectral data with those in previous reports.

2.2. Synthesis of ligands and complexes

The synthesis procedure of ligands and complexes was shown in Scheme 2. for comparision, a one-active zinc centre conplex 4f and its coresponding ligand 3f were also designed and synthesized as shown in Scheme 2.

Table 1
Provenance and mass fraction purity of the materials.

Materials	Mass fraction purity	CAS	Provenance
2-Amino-1-hydroxybenzene	0.98	95-55-6	Shanghai Darui Finechemical Co., Ltd
2-Amino-4-t-butylphenol	0.98	1199-46-8	Shanghai Darui Finechemical Co., Ltd
2-Amino-4-nitrophenol	0.98	99-57-0	Shanghai Darui Finechemical Co., Ltd
Propylene oxide	0.99	16088-62-3	Shanghai Darui Finechemical Co., Ltd
1,2-Epoxyethylbenzene	0.99	96-09-3	Shanghai Darui Finechemical Co., Ltd
Epichlorohydrin	0.99	106-89-8	Shanghai Darui Finechemical Co., Ltd
Carbon dioxide	0.9999	124-38-9	Sichuan Tianyi Science & Technology Co., Ltd
Nitrogen	0.9999	7727-37-9	Sichuan Tianyi Science & Technology Co., Ltd
Salicylaldehyde	0.99	90-02-8	J&K Chemica Co
1,2-Epoxyhexane	0.99	1436-34-6	J&K Chemica Co
Glycidyl isopropyl ether	0.99	4016-14-2	J&K Chemica Co
Isobutylene oxide	0.97	558-30-5	J&K Chemica Co
Calcium hydride	0.97	7789-78-8	J&K Chemica Co
Chloroform-d	99.8atom%D	865-49-6	J&K Chemica Co
Tetra-n-butylammonium briomide	0.99	1643-19-2	Tianjin Bodi Chemical Engineering Co., Ltd
Tetra-n-butylammonium iodide	0.99	311-28-4	Tianjin Bodi Chemical Engineering Co., Ltd
Tetra-n-butylammonium chloride	0.99	1112-67-0	Tianjin Bodi Chemical Engineering Co., Ltd
Potassium iodide	0.985	7681-11-0	Tianjin Standard Science & Technology Co., Ltd
Dimethyl sulfoxide-d6	0.9999	2206-27-1	Tianjin Standard Science & Technology Co., Ltd
Pyridine-d5	99.5atom%D	7291-22-7	Deuterium Laboratory Peking University Dabei Sinopharm Chemical Reagent Co., Ltd
Paraformaldehyde	0.94	30525-89-4	Sinopharm Chemical Reagent Co., Ltd
Pyridine	A. R. grade	110-86-1	Sinopharm Chemical Reagent Co., Ltd
Ethyl ether	A. R. grade	60-29-7	Sinopharm Chemical Reagent Co., Ltd
Methanol	A. R. grade	67-56-1	Sinopharm Chemical Reagent Co., Ltd
Acetone	A. R. grade	67-64-1	Sinopharm Chemical Reagent Co., Ltd
Tetrahydrofuran	A. R. grade	109-99-0	Sinopharm Chemical Reagent Co., Ltd
Ethanol	A. R. grade	64-17-5	Sinopharm Chemical Reagent Co., Ltd
Petroleumether	A. R. grade	64742-49-0	Sinopharm Chemical Reagent Co., Ltd
Ethyl acetate	A. R. grade	141-78-6	Sinopharm Chemical Reagent Co., Ltd
Dichloromethane	A. R. grade	75-09-2	Sinopharm Chemical Reagent Co., Ltd