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A New Type of Lewis Acid–Base Bifunctional M(salphen) (M = Zn, Cu and Ni) Catalysts for CO_2 Fixation

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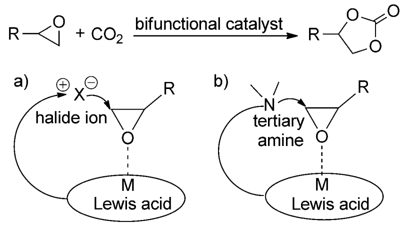
A new type of Lewis acid–base bifunctional M(salphen) complexes ($M = Zn^{II}$, Cu^{II}, and Ni^{II}) pending two *N*-methylhomopiperazine groups as nucleophiles were prepared by a one-pot method. The Zn(salphen) complexes proved to be efficient and recyclable homogeneous catalysts towards the solvent-free synthesis of cyclic carbonates from epoxides and CO_2 in the absence of a co-catalyst. The catalysts can be easily recovered and five times reused without significant loss of activity and selectivity.



Scheme 1. Cooperative activation of epoxide with bifunctional catalysts.

The utilization of carbon dioxide (CO_2) as a renewable C_1 feedstock for the synthesis of value added chemicals currently receives considerable attention.[1] However, the exceptional kinetically and thermodynamically stability of CO_2 is a major drawback regarding its economic use as reactant. Many procedures have been developed towards the easy and economical chemical fixation of CO_2. Among them, the catalytic cycloaddition of CO_2 with epoxides to form cyclic carbonates, which are used as electrolytes in lithium-ion batteries, raw materials for polycarbonate, and polar aprotic solvents, is one of the most promising environment-friendly reactions for the large-scale conversion of CO_2.[2] To date, various homogeneous catalytic systems, including alkali metal halides,[3] metallosalen,[2c,4] metalloporphyrins,[5] and metal-free catalyst,[6] and various heterogeneous catalytic systems, including ion-exchange resins,[7] and quaternary ammonium or phosphonium supported on carbon nanotube or functional polymers,[8] and metallosalen based metal-organic frameworks,[9] have been developed to promote this transformation.

Prominent among these are a variety of metallosalen complexes because of their ease of synthesis, while varying the steric and electronic properties about the metal centers. Over the past decades, many successful examples of metallosalen catalysts that have been developed for the preparation of cyclic carbonates include both binary[4d–l] and bifunctional systems,[4a–c] with the latter category being less developed as a probable result of the more synthetically demanding characteristics of bifunctional catalysts preparation. Nonetheless, bifunctionality (as shown in Scheme 1 a, a Lewis acid (metal center) and a halide anion X^- (nucleophile) are required) has proven to be highly useful in various cases to create more powerful catalyst mediators. For instance, Kleij and co-workers have developed a bifunctional Zn(salpyr) [salpyr = *N*,*N*′-bis(salicylidene)-3,4-pyridinediamine] catalyst that can be alkylated at the pyridyl-N atom, providing a complex with a built-in nucleophile (either I or Br).[4a] The catalysis data support the synergistic effect of the Lewis acidic site and the halide anion nucleophile resulting in markedly improved catalytic behavior compared with a system that lacks a Lewis acid activator. Alternatively, a bifunctional Al(salen) in conjunction with intramolecular quaternary ammonium salts as cocatalysts, has also been recently prepared and successfully applied in regioselective ring opening of three-membered heterocyclic compounds (epoxides or N-substituted aziridines) in coupling reactions with CO_2, affording the corresponding five-membered cyclic products with complete configuration retention at the methine carbon.[4b]

In addition to common halide anion nucleophiles, previously Shi and co-workers reported that a binary system involving an organic base, triethylamine used as nucleophile and binaphthyladiamion M(salen)-type complexes can efficiently catalyze reactions of epoxides with CO_2, and they proposed a Lewis acid and Lewis base cocatalyzed mechanism by isotope-labeling experiments.[4l] Combined these results and our interests in creating bifunctional (rather than binary) catalyst systems that could be prepared in a few steps from readily available materials, herein we present a new type of bifunctional single-component M-salphen [salphen = *N*,*N*′-bis(salicyladehyde-*o*-phenylenediamine)] catalysts system (Scheme 1 b) that involves tertiary amine moiety as Lewis base and metal center as Lewis acid within one structure, and examine their catalytic activity for the cycloaddition of CO_2 and various epoxides. This structural design increases the stability of catalysts compared with the ionic bifunctional systems, therefore enhances their recycling performance.

As shown in Scheme 2, via one-pot method, a series of M(salphen) ($Mn = Zn^{II}$, Cu^{II}, and Ni^{II}) catalysts with electron-donating group (**1 a**–**1 c**) and electron-withdrawing group (**1 d**–**1 e**) were synthesized and characterized by IR spectroscopy, and mass spectrometry, as well as by elemental analysis (for

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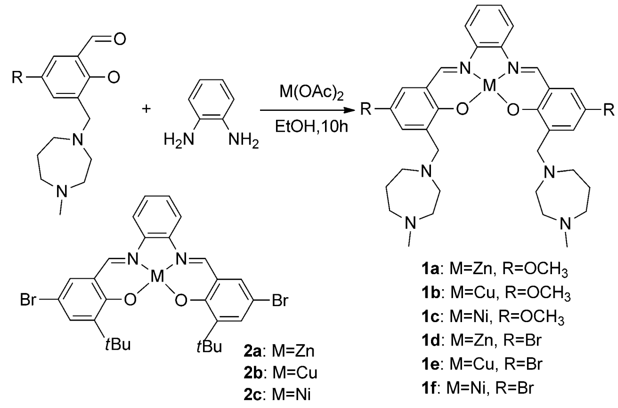


Scheme 2. Synthesis of complexes **1 a**–**1 f** and the structures of **2 a**–**2 c**.

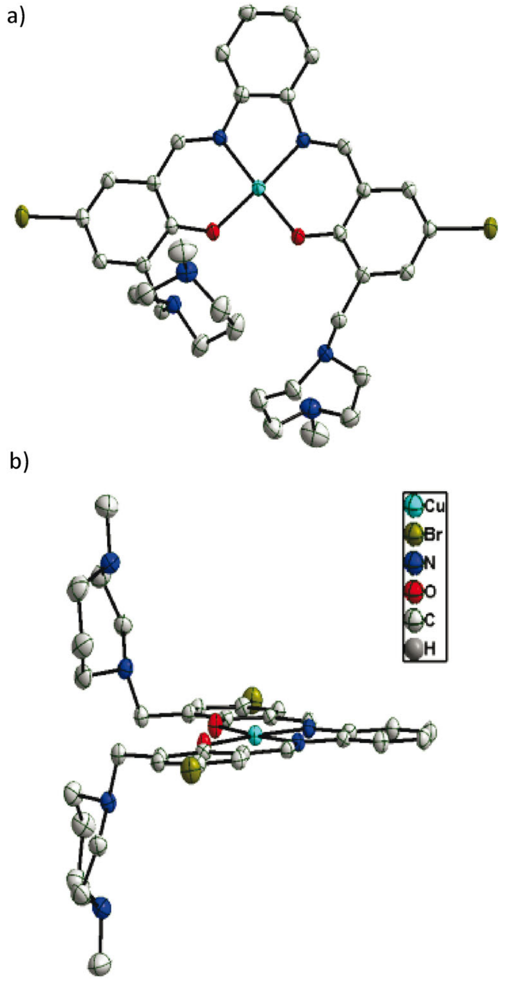


Figure 1. X-ray single crystal structure of **1 e**. Thermal ellipsoids for the non-hydrogen atoms are drawn at the 30 % probability level. All hydrogen atoms are omitted for clarity. a) View down crystallographic *c* axis. b) View down crystallographic *a* axis.

further details see the Supporting Information). These selected divalent metal ions have been proven to be useful in cyclic carbonate synthesis.[2c] Single crystal X-ray diffraction analyses for **1 e** reveal that the central Cu^{II} ion coordinated in a nearly square-planar geometry with two nitrogen atoms and two oxygen atoms from the deprotonated salphen ligand and the seven-membered *N*-methylhomopiperazine adopts a ship-shape conformation locating above and below the salphen plane (Figure 1), as we expected that the coordinatively unsaturated metal center can activate the epoxides ring, meanwhile the tertiary amine of *N*-methylhomopiperazine attacks the less-hindered carbon atom of the coordinated epoxide.

The activity of various catalysts was tested at 100 °C and 2 MPa of CO_2 pressure using the cycloaddition reaction of propylene oxide (PO) with CO_2 with 1 mol % catalyst loading. The yield and selectivity were determined by using gas chromatography (GC), and in all examined cases, the selectivity for five-membered cyclic propylene carbonate (PC) was higher than 99 %. Firstly, we found that the PC could be obtained in excellent yields in the presence of Zn^{II} salphen complexes (Table 1, entries 1 and 4), whereas moderate and lower yields were achieved in the presence of Cu^{II} and Ni^{II} salphen complexes under the same conditions, respectively. This is in accordance with that Zn^{II} ion in salphen complexes shows increased Lewis-acid behavior as a result of the constrained geometry imposed by the ligand scaffold.[4i,10] It should be note that the introduction of electron-withdrawing group (Br) in the both phenyl sides of the salphen ligand scaffold turned out to give almost the same activity (Table 1, entries 1–6). Hence, the catalytic activity of this kind of catalyst is closely related with the metal center not the electronic effect of ligand; a recent study also reported that the catalyst containing a zinc ion was the most active for CO_2 coupling with epoxide owing to its high activity.[4e] For a better understanding of the role of the tertiary amine moieties in seven-membered *N*-methylhomopiperazine, the control complexes **2 a**–**2 c** without *N*-methylhomopiperazine were also prepared for comparison (Scheme 2). If only **2 a**–**2 c** or *N*-methylhomopiperazine was used as catalyst, no reaction occurred (entries 7–10), illustrating that the coexistence of organic base and M(salphen) is essential to promote this reaction. On the contrary, the binary catalyst system of **2 a**–**2 c** and *N*-methylhomopiperazine in a molar ratio of 1/2 also gave PC in moderate yields under the same conditions (entries 11–13). The rationale behind this is the ability of these Lewis acidic complexes to self-dimerize and thus make the coordination of the substrate to the metal catalytic center a competitive process. An accurate study on Zn(salphen) self-assembly has been previously reported and shows that the extent of its strength is dependent on the location and combination of the aromatic ring substituents.[11] However, as expected in our catalysts **1 a**–**1 f**, two bulky *N*-methylhomopiperazine locating above and below the salphen plane (Figure 1 b) not only inhibit the intermolecular self-assembly behavior, but also provide efficient organic base nucleophile into one structure. On the basis of the above results, we suggest that the Lewis base and Lewis acid of **1 a** (or **1 d**) work together to open the epoxy ring and then react with CO_2 to give PC via a ring-opening and recyclization process, and therefore the conclusion should be that bifunctionality pays off as there is higher conversion. This is not the same mechanism in the reported binary catalytic systems composed of binaphthyladiamion M(salen)-type complexes and triethylamine.[4l] Importantly, PC can be easily separated from **1 a** (or

Table 1. Results of the cycloaddition reaction of propylene oxide (PO) with CO_2 in the presence of various catalysts.[a]

Entry	Catalyst	T [°C]	t [h]	Yield[b] [%]
1	**1a**	100	4	92
2	**1b**	100	4	68
3	**1c**	100	4	27
4	**1d**	100	4	90
5	**1e**	100	4	70
6	**1f**	100	4	32
7	**2a**	100	4	<5
8	**2b**	100	4	<5
9	**2c**	100	4	<5
10	base[c]	100	4	<5
11	**2a**+base[c]	100	4	65
12	**2b**+base[c]	100	4	45
13	**2c**+base[c]	100	4	22
14	**1a**	100	1	26
15	**1a**	100	2	65
16	**1a**	25	4	0
17	**1a**	80	4	56
18[d]	**1a**	100	4	52
19[d]	**1a**	100	12	65
20[e]	**1a**	100	3	83
21[e]	**1d**	100	3	78

[a] General reaction conditions: 10 mL stainless-steel autoclave, PO (10 mmol), catalyst (0.1 mmol), CO_2 pressure (2 MPa), [b] The yields were determined by GC with an internal standard. [c] Base is *N*-methylhomopiperazine, [d] The CO_2 pressure is 1 MPa, [e] The catalyst after being used five times.

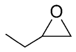
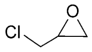
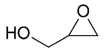
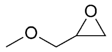
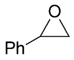
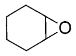
1d) with diethyl ether. While using **2a** and *N*-methylhomopiperazine as co-catalysts, PC can be only separated by distillation, owing to the good solubility of *N*-methylhomopiperazine in the solution of PC. This is a highly energetic process because of the high boiling point of PC and, therefore, has a negative effect on the carbon footprint of the reaction. Consequently, **1a** (or **1d**) offers the possibility of a sustainable system for the chemical fixation of CO_2.

The reaction time, reaction temperature and CO_2 pressure are important factors for the yields of PC. In a short reaction period of only 1 h at 100 °C, for example, PC is obtained in only 26% (entries 14). When reaction time was extended to 8 h, a yield of 95% is reached, a very small amount of increase of the yield compared to that in the reaction time of 4 h. Then the influence of the temperature on the conversion was also investigated. By reducing the temperature from 100 to 80 °C, the yield of PO decreased drastically from 92 to 56% (entries 17), and no reaction could take place at room temperature (entries 16). In addition, the yield of PC decreased as CO_2 pressure decreased from 2 to 1 MPa (entries 18), even increasing this reaction time to 12 h, only 65% of PC was obtained (entries 19). It is known that lower CO_2 pressure could reduce the solubilization effect of CO_2 in the solution of PO; in turn, the yield was decreased.[12] The catalyst loading was not explored in our experiments because of the easy recyclability of **1a** (or **1d**). Finally, the best reaction conditions involve the **1a** (or **1d**) (1 mol%) at 100 °C under a high pressure of CO_2 (2 MPa) for 4 h.

Besides the catalyst activity, the sustainability and recycling potential are also decisive criteria for possible large-scale application. Therefore, recyclability studies of **1a** (or **1d**) were performed to evaluate the sustainability of the catalyst. After each run, **1a** (or **1d**) could easily be precipitated from the PC solution by the addition of diethyl ether. After filtration, another batch of PO was added and the next catalytic run was started. The results of the recycling experiments showed no obvious decrease in activity of the catalyst after being used five times (entries 20 and 21). Furthermore, the catalyst recovered from the catalytic reaction exhibited the almost same chemical composition as the freshly prepared **1a** (or **1d**), unambiguously supporting the stability of the catalyst during the catalytic reactions.

Under optimized reaction conditions, we next examined the chemical fixation reaction of the other epoxides with CO_2 using **1a** and **1d**, respectively. The results are summarized in Table 2. It is very clear that, electron-withdrawing and electron-donating terminal epoxides can be converted to the corresponding cyclic carbonates in good yields. In all experiments, cyclic carbonates are the sole products. The very good conversions of epichlorohydrin and glycidol (Table 2, entries 5–8) can be explained by the electron-withdrawing substituents.[13] These substituents result in facilitated nucleophilic attack of the *N*-methylhomopiperazine during the ring opening of the epoxide. Unfortunately, the internal epoxide, cyclohexene oxide, which is known to undergo cycloaddition with CO_2 poorly, is converted to the corresponding cyclic carbonate with a yield of 35 and 30% by catalyst **1a** and **1d** (entries 11 and 12), respectively, presumably due to the high steric hindrance.[6a]

Table 2. Reactions of other epoxides with CO_2 catalyzed by **1a** and **1d**.[a]

Entry	Epoxide	Catalyst	Yield[b] [%]
1		**1a**	85
2		**1d**	84
3		**1a**	99
4		**1d**	98
5		**1a**	96
6		**1d**	92
7		**1a**	78
8		**1d**	73
9		**1a**	75
10		**1d**	76
11		**1a**	35
12		**1d**	30

[a] Reaction conditions: epoxide (10 mmol), catalyst (0.1 mmol), CO_2 pressure (2 MPa), reaction temperature (100 °C), reaction time (4 h). [b] The yields were determined by GC with an internal standard.

In conclusion, we explored a new bifunctional Zn(salphen) catalysts with an organic base *N*-methylhomopiperazine as nucleophile for the production of cyclic carbonates from CO_2 and epoxides. The notable features of our protocol include the use of an abundant, non-toxic metal (Zn) and the ease of synthesis of the bifunctional catalysts compared with previous ionic bifunctional systems. More importantly, the catalysts used in this catalytic system are extremely stable and can be recycled at least five times and their activity is almost unchanged. Efforts are underway to elucidate the mechanistic details of the reaction and explore the catalytic activities of other trivalent metal complexes with this bifunctional ligand.

Experimental Section

General catalytic procedure: A 10 mL stainless steel reactor was added with catalyst (0.1 mmol) and a magnetic stirring bar. Then the epoxide (10.0 mmol) was added and the steel reactor was charged under a constant pressure of CO_2 (2 MPa) for 1 min and heated to the desired temperature. After reaction completion, the reactor was cooled down to 0 °C and the excess CO_2 was released carefully. The reaction mixture was collected by adding 5 mL of chloroform and a sample was taken for GC analysis (using 1,3,5-trimethylbenzene as an internal standard) to determine yield and selectivity.

For recycling studies of catalyst **1 a** (or **1 d**), propylene carbonate was separated from the catalyst by adding ether. The catalyst precipitates was recovered by centrifugation. Afterwards, the catalyst was dried at 50 °C for 6 h in vacuo. By adding the same amount of epoxide (10.0 mmol), the next catalytic run was started.

Acknowledgements

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Keywords: CO_2 fixation · cyclic carbonate · homogeneous catalysis · salphen · zinc

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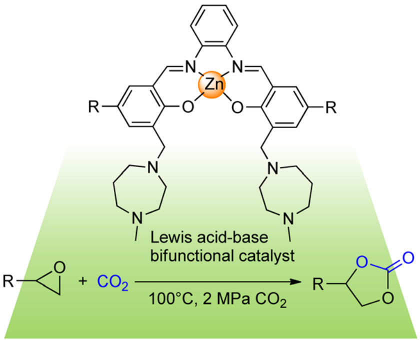
COMMUNICATIONS

Bifunctional catalysts: A new type of Lewis acid–base bifunctional Zn(salphen) catalysts with an organic base, *N*-methylhomopiperazine, as a nucleophile were prepared by a one-pot method and successfully applied in the production of cyclic carbonates from CO_2 and epoxides. The catalysts used in this catalytic system are extremely stable and can be recycled at least five times and their activity is almost unchanged.



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