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# Phosphine-bound zinc halide complexes for the coupling reaction of ethylene oxide and carbon dioxide

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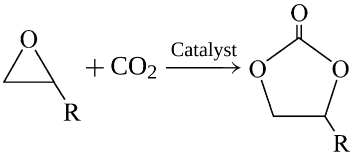
## Abstract

Phosphine adducts of zinc(II) halides, $ZnX_2L_2$ (X = Cl, Br, I; L = $PMe_2Ph$, $PEt_3$, $PBu_3$, $PPh_3$, $PCy_3$), prepared by the reaction of $ZnX_2$ with two equivalents of corresponding phosphines, showed high activities for the coupling reaction of $CO_2$ and ethylene oxide to produce ethylene carbonate. The catalytic activity of $ZnX_2L_2$ was hardly affected by the nucleophilicity of the phosphine ligands, with the exception of $ZnX_2(PCy_3)_2$, but depended strongly on the nature of halide ligands. An active species containing ethoxyphosphonium ligands, $Zn_3Br_6[\mu\text{-}OCH_2CH_2\text{-}P(C_6H_5)_3]_3$, was isolated and characterized by X-ray crystallography, elemental analysis, and NMR spectroscopy. The mechanistic pathway for the formation of active species and cyclic carbonates is discussed.

*Keywords:* Zinc halide; Ethylene oxide; Carbon dioxide; Ethylene carbonate

## 1. Introduction

The synthesis of five-membered cyclic carbonates by the coupling of alkylene oxides with carbon dioxide is attracting increasing interest because of the enlarged application of cyclic carbonates and to the growing concern about the utilization of carbon dioxide [1–4]



Accordingly, there is a substantial body of literature on catalyst development and the mechanism of the coupling reactions [5–7]. The use of transition-metal halides with *tert*-alkyl ammonium halide or alkali metal halides has been shown to be a highly active combination for promoting coupling reactions, in which the halide ligands act as nucleophiles [8–12]. The reactivity pattern of these catalytic systems suggests that an epoxide is coordinated to the halogenated metal anion species formed in situ. The resulting coordinated epoxide is transformed into a haloalkoxy metal species by the nucleophilic attack of a halide ion on the halogenated metal anion species [10,11]. Insertion of $CO_2$ into the metal-oxygen bond of the haloalkoxy metal species leads to a linear halocarbonate, which in turn produces a cyclic carbonate by the intramolecular substitution of halide [13]. The catalytic systems, composed of transition-metal halide ($AlCl_3$, $NiCl_2$, $MoCl_5$) and a Lewis base, have also been employed in the production of cyclic carbonates [14].

Recently we have demonstrated that the catalyst with the general formula $ZnX_2Py_2$ (Py, pyridine or substituted pyridine; X = Cl, Br) is effective in coupling reactions of alkylene oxides and $CO_2$ [15–17]. Problems associated with

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the catalysis in the presence of $ZnX_2Py_2$ are the colorization of the product mixtures and the contamination of cyclic carbonates with various impurities. The cause of the color instability has not been ascertained, but it is suggested that at least some instability is due to the presence of small amounts of nitrogen compounds originating from the catalyst.

During the course of our work on the development of high-performance catalysts, we found that the phosphine adducts of zinc halide catalysts ($ZnX_2L_2$, where L = phosphine and X = Cl, Br) are more active than the pyridine analogues for the coupling of ethylene oxide and $CO_2$. Furthermore, coloration of the product mixture was not observed with phosphine-bound zinc catalysts.

We report in detail on the syntheses and reactivities of a series of zinc halide complexes containing phosphine ligands and a mechanistic investigation of the coupling of ethylene oxide and $CO_2$.

## 2. Experimental

### 2.1. Chemicals

The catalysts were prepared in an inert atmosphere unless otherwise stated (see supplementary material). The solvents were freshly distilled before use according to the published procedure. Ethylene oxide was purchased from Honam Petrochemical Co. and $CO_2$ from Sin Yang Gas. Co.; they were used without further purification. All of the other chemicals, including phosphines, phosphates, zinc halides, and ethylene carbonate, were obtained from Aldrich Chemical Co. and used as received.

### 2.2. Coupling reactions

All of the coupling reactions were conducted in a 200-ml stainless-steel reactor equipped with a magnetic bar and an electric heater. The reactor was charged with an appropriate catalyst and ethylene oxide and pressurized with $CO_2$ ($\approx$ 1.4 MPa). The reactor was then heated to a specified reaction temperature, and $CO_2$ was added from a reservoir tank to maintain a constant pressure. After completion of the reaction, the reactor was cooled to room temperature, and the remaining ethylene oxide was removed by means of an aspirator. The product mixture was analyzed by gas chromatography with a Hewlett Packard 6890 equipped with a flame-ionized detector and a DB-wax column (30 m × 0.32 mm × 0.25 µm) and by mass spectrometry (Hewlett Packard 6890-5973 GC-MSD).

## 3. Results and discussion

The catalytic activities of various zinc complexes containing tertiary phosphine ligands were evaluated for the coupling reaction of ethylene oxide with $CO_2$ at 100 °C for 1 h; the yields and turnover frequencies (TOFs) are listed in Table 1.

Table 1
Catalytic activities of various catalysts in the coupling reaction of $CO_2$ and ethylene oxide (EO)[a]

| Entry | Catalyst | Yield[b] (%) |
|---|---|---|
| 1 | $ZnBr_2$ | 0 |
| 2 | $PPh_3$ | 0 |
| 3[c] | $ZnBr_2/PPh_3$ | 78 |
| 4 | $ZnCl_2(PPh_3)_2$ | 3 |
| 5 | $ZnBr_2(PPh_3)_2$ | 78 |
| 6 | $ZnI_2(PPh_3)_2$ | 37 |
| 7 | $ZnBr_2(PMe_2Ph)_2$ | 82 |
| 8 | $ZnBr_2(PEt_3)_2$ | 79 |
| 9 | $ZnBr_2(PBu_3)_2$ | 77 |
| 10 | $ZnBr_2(PCy_3)_2$ | 43 |
| 11 | $ZnBr_2(CH_2PPh_2)_2$ | 51 |
| 12 | $Zn_3Br_6[\mu\text{-}OCH_2CH_2\text{-}P(C_6H_5)_3]_3$ | 76 |
| 13 | $ZnBr_2/P(OPh)_3$ | < 0.1 |
| 14 | $ZnBr_2/P(O)Ph_3$ | < 0.1 |
| 15 | $ZnBr_2(C_5H_5N)_2$ | 46 |

[a] Reactions were carried out for 1 h at 100 °C and 3.4 MPa. The molar ratio of EO to zinc was set at 2000.
[b] GC yield.
[c] Molar ratio of $ZnBr_2/PPh_3 = 1/2$.

Table 1 shows that zinc bromide and triphenylphosphine were inactive for the coupling reaction when used alone. However, the combination of zinc bromide and triphenylphosphine resulted in surprisingly high activity (entry 3). This result strongly suggests that two active sites, Lewis acidic and Lewis basic sites, are necessary for the coupling reaction to proceed. In a separate experiment, we observed that $ZnBr_2(PPh_3)_2$ is formed in situ during the early phase of the coupling reaction performed in the presence of zinc bromide and triphenylphosphine. To confirm that $ZnBr_2(PPh_3)_2$ is an active catalyst for the coupling reaction, the activity of $ZnBr_2(PPh_3)_2$ was compared with that of the catalytic system composed of triphenylphosphine and $ZnBr_2$. As expected, the activity of $ZnBr_2(PPh_3)_2$ was similar to that of the system consisting of triphenylphosphine and $ZnBr_2$. It is noteworthy that the activity of $ZnBr_2(PPh_3)_2$ is about 1.7 times higher than that of pyridine analogue, $ZnBr_2(C_5H_5N)_2$ (entry 5, 15). Other phosphine complexes ($ZnBr_2L_2$, where L = $PMe_2Ph$, $PEt_3$, $PBu_3$) also showed high activities similar to that of $ZnBr_2(PPh_3)_2$, with the exception of $ZnBr_2(PCy_3)_2$.

The lower activity of $ZnBr_2(PCy_3)_2$ is surprising, because the tricyclohexylphosphine ($PCy_3$) ligand has a strong basicity ($pK_a = 9.7$), which is an important factor in the ring-opening of ethylene oxide. In a previous report on the coupling reaction with $ZnBr_2Py_2$, it was proposed that the first step in the coupling reaction is the dissociation of a pyridine ligand followed by the coordination of ethylene oxide to the zinc center and the subsequent nucleophilic attack of the carbon atom of the coordinated epoxide by the dissociated pyridine [15–17]. Likewise, it is assumed that the first step in the coupling reaction with $ZnX_2L_2$ (L = phosphine, X = Cl, Br, I) is the dissociation of a phosphine ligand. However, dissociation of the phosphine ligand would be more difficult for the complex bearing strongly basic phosphine ligands such as $PCy_3$ because such ligands tend to form stronger bonds with a Lewis acidic zinc center. This probably explains why the $ZnBr_2(PCy_3)_2$ complex exhibited a lower activity than the other phosphine complexes. Another possible explanation is that the nucleophilic attack on the coordinated ethylene oxide is somewhat restricted by the bulkiness of the tricyclohexylphosphine ligand. The importance of the ligand dissociation is more clearly shown by the lower catalytic activity of $ZnBr_2$(diphos). The diphenylphosphinoethane (diphos, $PPh_2CH_2CH_2PPh_2$) ligand tends to form strong Zn–P bonds through chelation, thereby hindering the creation of a vacant site for the coordination of ethylene oxide.

In contrast to phosphine complexes, zinc halide complexes containing phosphite or phosphine oxide ligands showed very low activities, suggesting that ligand nucleophilicity is important in the ring-opening of ethylene oxide (entry 13, 14).

The effect of the halide ligand on the coupling of ethylene oxide and carbon dioxide was also investigated with $ZnX_2(PPh_3)_2$ (X = Cl, Br, I). Table 1 (entry 4–6) shows that the catalyst bearing bromide ligands had the highest activity, with a TOF of 1559. With respect to the alkali-metal halide-catalyzed coupling reaction, it is generally agreed that the halide ligand acts as a nucleophile to ring-open the epoxide; the activity therefore increases with increasing nucleophilicity of the halide ligand. However, in the case of $ZnX_2(PPh_3)_2$, the nucleophilicity of halide ligands is probably not a major factor in determining the catalytic activity, because $ZnI_2(PPh_3)_2$, which has more nucleophilic iodide ligands, has a much lower activity than $ZnBr_2(PPh_3)_2$, which bears fewer nucleophilic bromide ligands. The halide ligands seem to play a role only in controlling the dissociation of phosphine ligands.

Fig. 1 shows the effects of temperature and pressure on the coupling reaction of ethylene oxide and $CO_2$. The yields of ethylene carbonate increased sharply with increasing temperature (60–120 °C), but the effect of $CO_2$ pressure was moderate.

The effect of the molar ratio of ethylene oxide/Zn was also investigated at 100 °C in the presence of $ZnBr_2(PPh_3)_2$ (Fig. 2). The yields decreased continuously with increasing molar ratio (above 1000), and the TOF ($h^{-1}$) increased with increasing molar ratio up to 3000, but drastically decreased thereafter, suggesting that there is an optimal molar ratio. The much lower yield and the TOF at a molar ratio of 4000 cannot be fully explained at the moment; the main reason for this is probably the lower catalyst concentration, which retards the interaction of the catalyst and the ethylene oxide and/or $CO_2$.

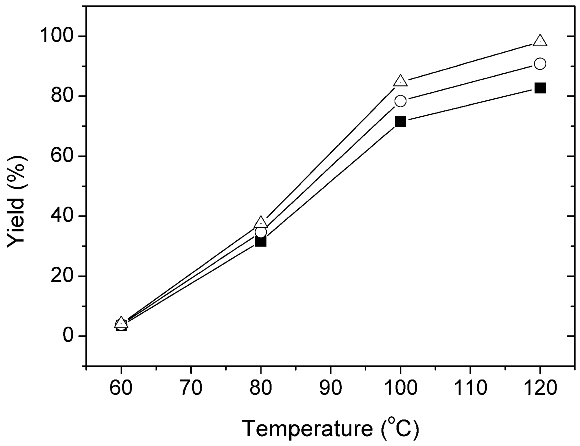


Fig. 1. Effects of temperature and pressure on the coupling reaction of $CO_2$ and ethylene oxide (■, 2.8 MPa; ○, 3.4 MPa; △, 4.8 MPa). Reactions were carried out for 1 h using $ZnBr_2(PPh_3)_2$ as a catalyst. The molar ratio of ethylene oxide to catalyst was set at 2000.

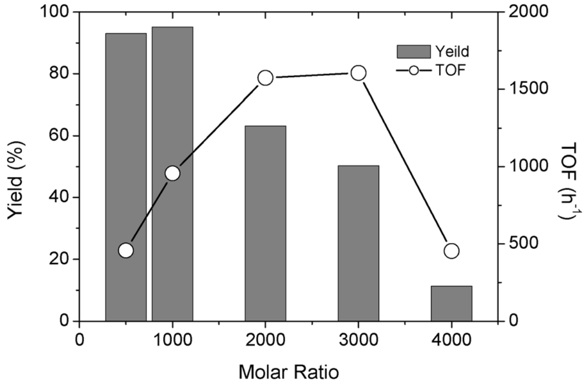


Fig. 2. Effect of the molar ratio of ethylene oxide and $ZnBr_2(PPh_3)_2$. Reactions were carried out for 1 h at 100 °C and 3.4 MPa.

An active species was isolated from the coupling reaction of ethylene oxide with $CO_2$ in the presence of $ZnBr_2(PPh_3)_2$. The characterization of the active species by means of single-crystal X-ray diffraction analysis was unsuccessful because of the disorder in the crystal system. Nevertheless, the incomplete X-ray structure clearly shows that the active species is a trimeric zinc complex containing three bridging ethoxyphosphonium ligands (see supplementary material). The trimeric structure of the active species is further supported by the X-ray crystallographic characterization of the similar complex ($Zn_3Br_6(\mu\text{-}OCH_2CH_2\text{-}NC_5H_5)_3$) obtained from the reaction of $ZnBr_2Py_2$ with ethylene oxide [15].

To confirm the formation of the active species containing the ethylene oxide moiety, a $^{31}P$ NMR experiment was conducted in $CD_2Cl_2$. As shown in Fig. 3b, the $^{31}P$ NMR spectrum of $ZnBr_2(PPh_3)_2$ has a singlet at −12.2 ppm. The single resonance indicates that the two triphenylphosphine ligands are equivalent. The $^{31}P$ NMR spectrum of the reaction mixture of $ZnBr_2(PPh_3)_2$ and ethylene oxide shows new singlets at 18.4 and −6.3 ppm (Fig. 3d). The peak at 18.4 ppm is assigned to the active species containing the ethylene oxide moiety, $Zn_3Br_6[\mu\text{-}OCH_2CH_2\text{-}P(C_6H_5)_3]_3$ (Fig. 3c), and the resonance at −6.3 ppm corresponds to the free triphenylphosphine (Fig. 3a). These NMR spectral results clearly

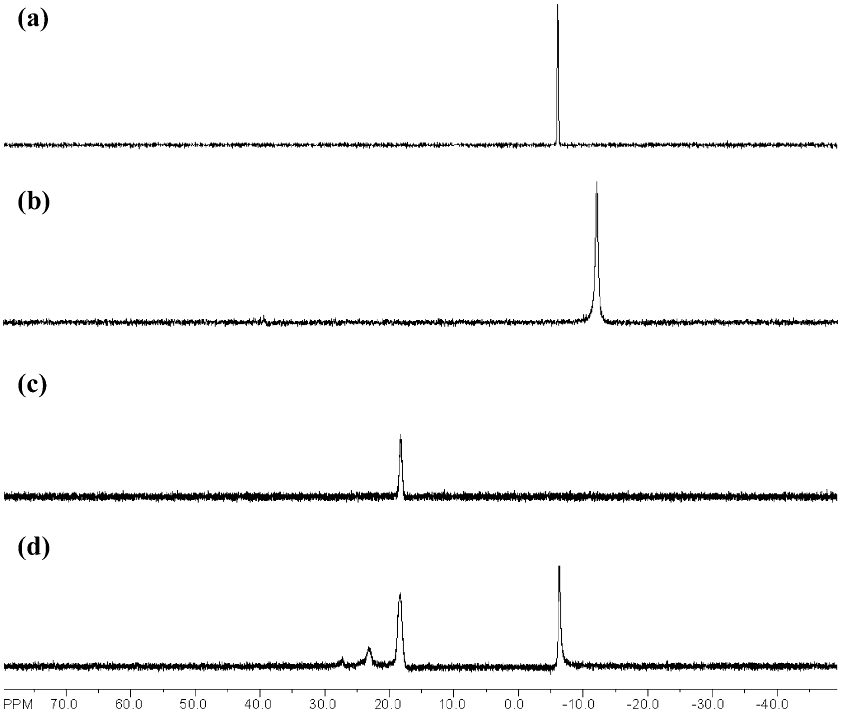
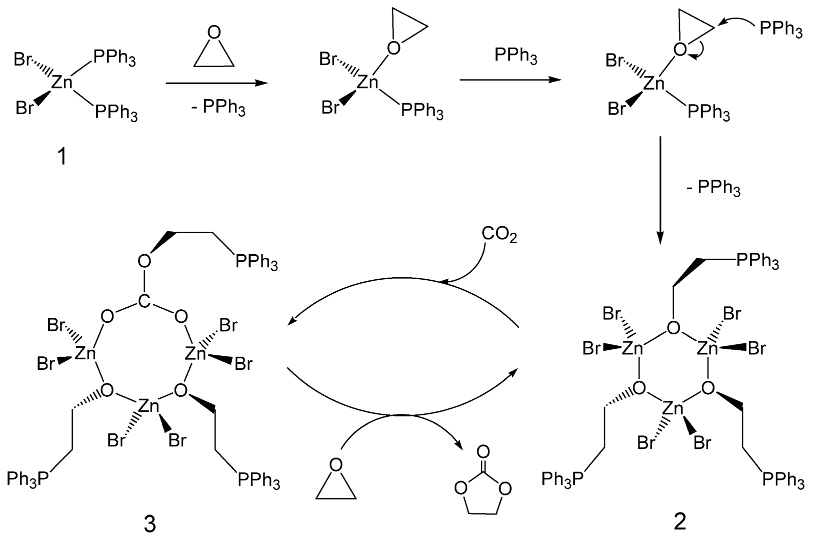


Fig. 3. $^{31}P$ NMR spectra: (a) free $PPh_3$ in $CD_2Cl_2$, (b) $ZnBr_2(PPh_3)_2$ in $CD_2Cl_2$, (c) $Zn_3Br_6[\mu\text{-}OCH_2CH_2\text{-}P(C_6H_5)_3]_3$ in $CD_2Cl_2$, (d) $ZnBr_2(PPh_3)_2$ + ethylene oxide in $CD_2Cl_2$.



Scheme 1. Plausible pathway for the formation of ethylene carbonate in the presence of $ZnBr_2(PPh_3)_2$.

demonstrate that the active species is formed through the dissociation of triphenylphosphine ligands. The most interesting feature in the NMR spectrum of the active species is that the resonance associated with $PPh_3$ is a singlet and far downshifted with respect to that of $PPh_3$ in $ZnBr_2(PPh_3)_2$, implying that both triphenylphosphine ligands in $ZnBr_2(PPh_3)_2$ are no longer bonded to the zinc center. The origin of the peak at 23.1 ppm is not clear, but it seems that the peak is associated with an intermediate species formed from the interaction of the active species with ethylene oxide or free phosphine.

A plausible catalytic cycle is depicted in Scheme 1. Coordination of ethylene oxide with the replacement of a triphenylphosphine ligand is likely to occur first. Nucleophilic attack of the dissociated triphenylphosphine on the carbon atom of the coordinated ethylene oxide and subsequent trimerization of the resulting ethoxyphosphonium species would lead to the formation of species **2**. Insertion of $CO_2$ into the zinc–oxygen bond of **2** would give a carbonato ligand-bridged species **3**, which in turn interacts with an additional ethylene oxide to produce ethylene carbonate along with the generation of species **2**.

## 4. Conclusions

The coupling reaction of ethylene oxide and carbon dioxide to produce ethylene carbonate was conducted in the presence of the catalyst, $ZnX_2L_2$ (L = substituted phosphine; X = Cl, Br, I). The effects of phosphine and halide ligands on the catalytic activity were investigated. The catalytic activity was not significantly affected by substitution on the phosphine ligands but was highly dependent on the nature of the halide ligands. An active zinc species was isolated from the reaction of $Zn(PPh_3)_2Br_2$ with ethylene oxide and was characterized as a trimeric zinc complex bridged by ethoxyphosphonium ligands, which strongly suggests that ethylene oxide is attacked by the phosphine ligand, not by the halide ligand.

## Supplementary material

The online version of this article contains additional supplementary material.

Please visit DOI:10.1016/j.jcat.2005.01.033.

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