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## Article

# Transformation of carbon dioxide into valuable chemicals over bifunctional metallosalen catalysts bearing quaternary phosphonium salts



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## ABSTRACT

The chemical transformation of CO<sub>2</sub> under mild conditions remains a great challenge because of its exceptional kinetic and thermodynamic stability. Two important reactions in the transformation of CO<sub>2</sub> are the *N*-formylation reaction of amines using hydrosilanes and CO<sub>2</sub>, and the cycloaddition of CO<sub>2</sub> to epoxides. Here, we report the high efficiency of bifunctional metallosalen complexes bearing quaternary phosphonium salts in catalyzing both of these reactions under solvent-free, mild conditions without the need for co-catalysts. The catalysts' bifunctionality is attributed to an intramolecular cooperative process between the metal center and the halogen anion. Depending on the reaction, this activates CO<sub>2</sub> by permitting either the synergistic activation of Si–H bond via metal–hydrogen coordinative bond (M–H) or the dual activation of epoxide via metal–oxygen coordinative bond (M–O). The one-component catalysts are also shown to be easily recovered and reused five times without significant loss of activity or selectivity. The current results are combined with previous work in the area to propose the relevant reaction mechanisms.

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## 1. Introduction

The development of green chemistry and atom economy approaches and the fact that carbon dioxide (CO<sub>2</sub>) is an inexpensive, highly abundant and renewable C1 building block, have caused the chemical fixation of CO<sub>2</sub> to produce high-added-value chemicals to attract much interest in recent years [1]. A particularly common example is the cycloaddition reaction between CO<sub>2</sub> and epoxides to synthesize cyclic car-

bonates. This reaction may be facilitated by numerous catalytic systems, including alkali metal halides [2], quaternary onium salts [3], ionic liquids (ILs) [4–6], metal complexes [7], metal oxides [8], metal-organic frameworks (MOFs) [9,10], and porous organic polymers (POPs) [11,12]. Another promising reaction with CO<sub>2</sub>—its reduction to formamides using amines and hydrosilanes [13]—has also been developed using various catalysts, including organic bases [14], inorganic salts [15,16], strong polar solvents [17], ILs [18], metal complexes [19], and

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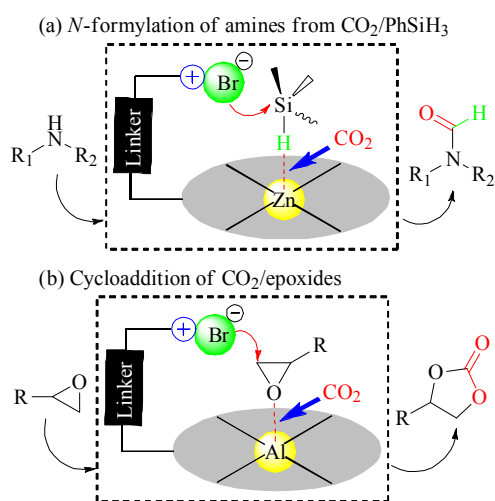
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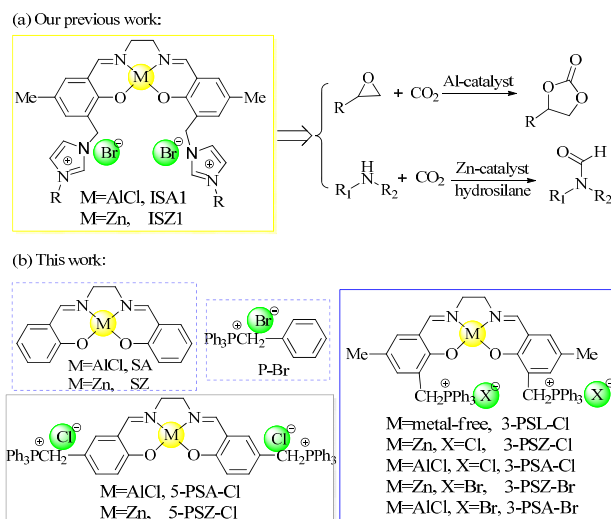
*N*-heterocyclic carbenes [20]. Recently, our group reported that one-component Al(salen) complexes with additional imidazolium-based IL moieties catalyzed the CO<sub>2</sub>/epoxide cycloaddition reaction under ambient conditions [21,22]. Additionally, the IL-functionalized Zn(salen) analogues have been shown to promote the CO<sub>2</sub>-based *N*-formylation reaction of organic amines to yield formamide derivatives when reacted with hydrosilanes [23].

Analysis of the homogeneous catalytic systems above that involve CO<sub>2</sub> (Scheme 1) revealed a dual activation at the metal center (Lewis acid) and at the halogen anion (nucleophile) which may explain the high efficiency [24]. It is possible for the intramolecular cooperative effect to either activate the Si–H bond within hydrosilane through a metal–hydrogen coordinative bond (M–H), or to activate the epoxide through a metal–oxygen coordinative bond (M–O). The highly active intermediates (Zn–H or Al–O species) may make the CO<sub>2</sub> insertion more favorable, thereby facilitating the activation of CO<sub>2</sub>. However, when using traditional quaternary ammonium salts as synthetic units instead of imidazolium-based ILs, low catalytic activity was observed, probably because of the poor solubility exhibited by the simple synthetic method when using ethylenediamine as a feedstock [21,23]. Thus, drawing on other work reported in this area [25,26], we envisioned that bifunctional catalysts bearing quaternary phosphonium salts could exhibit better catalytic performance on account of their superior solubility and stability.

Herein, quaternary phosphonium salts were successfully introduced into the framework of a salen ligand at the 3,3'- and 5,5'-positions as shown in Scheme 2. After metalation with ZnEt<sub>2</sub> or AlEt<sub>2</sub>Cl, the Zn-based catalysts (denoted as 5-PSZ-Cl, 3-PSZ-Cl and 3-PSZ-Br) we describe the novel demonstration of their use as bifunctional catalysts to catalyze the CO<sub>2</sub>-based *N*-formylation of amines with hydrosilanes. Meanwhile, the Al-based complexes (denoted as 5-PSA-Cl, 3-PSA-Cl and 3-PSA-Br) are shown to promote the CO<sub>2</sub>/epoxide cycloaddition reaction at ambient conditions. Accordingly, such efficient intramolecular cooperative catalysis indicates that CO<sub>2</sub> can be



**Scheme 1.** The dual activation of the metal center and the halogen anion.



**Scheme 2.** Bifunctional catalysts developed in (a) previous and (b) the current work.

transformed under mild conditions. The bifunctional metallo-salen catalysts are shown to be very active, highly selective, stable, and easily recycled by manipulating the solvent. A kinetic analysis is also carried out to investigate the reaction mechanism and help understand larger scale development of these bifunctional catalysts that are useful for converting CO<sub>2</sub>.

## 2. Experimental

Propylene oxide, styrene oxide, epichlorohydrin, epibromohydrin, allyl glycidyl ether, *n*-butyl glycidyl ether, *iso*-propyl glycidyl ether, glycidyl methacrylate, cyclohexene oxide, *N*-methylaniline, 4-methoxy-*N*-methylaniline, 4-chloro-*N*-methylaniline, morpholine, diethylamine, 4-methylpiperidine, 4-phenylpiperidine, diphenylsilane, and poly(methylhydrosiloxane) were obtained from J&K Scientific Ltd. Phenylsilane was purchased from Energy Chemical Ltd. The corresponding bifunctional catalysts were synthesized according to procedures detailed in our previous work [21–23,27].

The reaction was carried out in a 10-mL stainless steel autoclave which was coupled with a magnetic stirrer. In a typical experiment for the *N*-formylation of amines with CO<sub>2</sub> and hydrosilanes, *N*-methylaniline, the catalyst 3-PSZ-Br (or other catalysts when performing comparisons), and phenylsilane were added into the reactor. Subsequently, CO<sub>2</sub> was charged into the reactor until the pressure reached 0.5 MPa and the reactor was then heated by an oil bath to 40 °C while being stirred continuously. After the reaction, the autoclave was quickly cooled to 0 °C and depressurized to atmospheric pressure [14]. The cycloaddition reactions with epoxides and CO<sub>2</sub> were carried out in a similar fashion. Conversions and yields were determined using naphthalene or biphenyl as the internal standard and measured by a gas chromatograph (GC2010, Shimadzu Corporation, Japan) equipped with a capillary column (Rtx-5, 30 m × 0.32 mm × 0.25 μm) and a flame ionization detector (FID). The structure and the purity of the corresponding products were identified by <sup>1</sup>H NMR, <sup>13</sup>C NMR, and GC-MS

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