# Synthesis of Cyclic Carbonates from $CO_2$ and Epoxides with Metal-containing Deep Eutectic Solvents

by

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# ABSTRACT

In the introductory chapter, a brief overview of the chemistry of ionic liquids is presented. Ionic liquids have been a very popular alternative reaction media in recent decades because of their very low vapor pressure and non-flammability compared to conventional organic solvents. Ionic liquids have also been widely used in chemical synthesis and catalysis. A deep eutectic solvent (DES) is an ionic solvent which is easily prepared, air/moisture insensitive and frequently environmentally benign. Physical properties of the DES depend on the ratio of the two components from which it is prepared. DESs containing metals can be prepared and some have been used in catalytic reactions. Carbon dioxide utilization is important for sustainable development. At the end of Chapter 1, the use of ionic liquids and metal complexes in the catalytic synthesis of cyclic carbonates from carbon dioxide and epoxides is introduced.

Six metal-containing DESs were synthesized from choline chloride (ChCl) and $MCl_x \cdot yH_2O$ where M = Co (x = 2, y = 6), Cr (x = 3, y = 6), Ni (x = 2, y = 6), Cu (x = 2, y = 2), Fe (x = 3, y = 0), Mn (x = 2, y = 4). Physical properties of the DESs were studied by TGA and DSC. The solubility of the Co(II) DES was also tested. These results are presented in Chapter 2.

In Chapter 3, the metal-containing DESs catalyzed coupling reactions of $CO_2$ and styrene oxide to produce styrene carbonate under solvent-free conditions are described. ^{1}H NMR and GC-MS were used to confirm product formation and the resulted indicated that a high level of selectivity was achieved in this reaction. The effects of reaction

parameters like temperature, $CO_2$ pressure, reaction time and DESs of different ratios were investigated.

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# List of Symbols, Nomenclature or Abbreviations

acac          Acetylacetonate

BMIm          1-butyl-3-methylimidazolium

ChCl          Choline chloride

CHO           Cyclohexene oxide

DCM           Dichloromethane

DES           Deep eutectic solvent

DMAP          4-dimethylaminopyridine

DSC           Differential scanning calorimetry

EMIm          1-ethyl-3-methylimidazolium

$E_T^N$       Normalized Reichardt's parameter

eq.           Equivalent

FAB           Fast atom bombardment

GC-MS         Gas chromatography-mass spectrometry

HBD           Hydrogen bond donor

| 5-HMF | 5-hydroxymethyl-furfural |
|---|---|
| IL | Ionic liquid |
| Imes | 1,3-bis(2,4,6-trimethylphenyl)imidazolium |
| MNP | Magnetic nanoparticle |
| m.p. | Melting point |
| MS | Mass spectrometry |
| MTO | Methyltrioxorhenium |
| NMI | N-methylimidazole |
| NMR | Nuclear magnetic resonance |
| OMIm | 1-octyl-3-methylimidazolium |
| $^-$OTs | $p$-CH$_3$C$_6$H$_4$SO$_3$$^-$ |
| P | Pressure |
| PO | Propylene oxide |
| PPNCl | Bis(triphenylphosphoranylidene)ammonium chloride |
| R. T. | Room temperature |

| | |
|---|---|
| RTIL | Room temperature ionic liquid |
| SO | Styrene oxide |
| SC | Styrene carbonate |
| T | Temperature |
| TBA | Tetrabutylammonium |
| TEA | Tetraethylammonium |
| $T_f$ | Freezing point |
| THF | Tetrahydrofuran |
| $T_m$ | Melting point |
| TMA | Tetramethylammonium |
| TOF | Turnover frequency |
| TON | Turnover number |
| TGA | Thermal gravimetric analysis |
| UHP | Urea hydrogen peroxide |

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# Chapter 1 Introduction

## 1.1 Room temperature ionic liquids (RTILs)

Application of alternative solvents has always been important in green chemistry, since traditional organic solvents have many disadvantages.[1] Disadvantages of traditional solvents include high vapor pressure, high flammability and toxicity. Due to their very low vapor pressure and non-flammability, room temperature ionic liquids (RTILs) are good alternatives for organic solvents in chemical processes including extractions and reactions.

RTILs are defined as salts with melting points below 100 °C. Although the first RTIL was discovered in 1914, the majority of studies were accomplished in recent decades.[2-4] RTILs are generally made from large, asymmetric ions. Both cations and anions or at least one of them are often organic. Figure 1-1 shows some of the ions commonly used in RTILs.
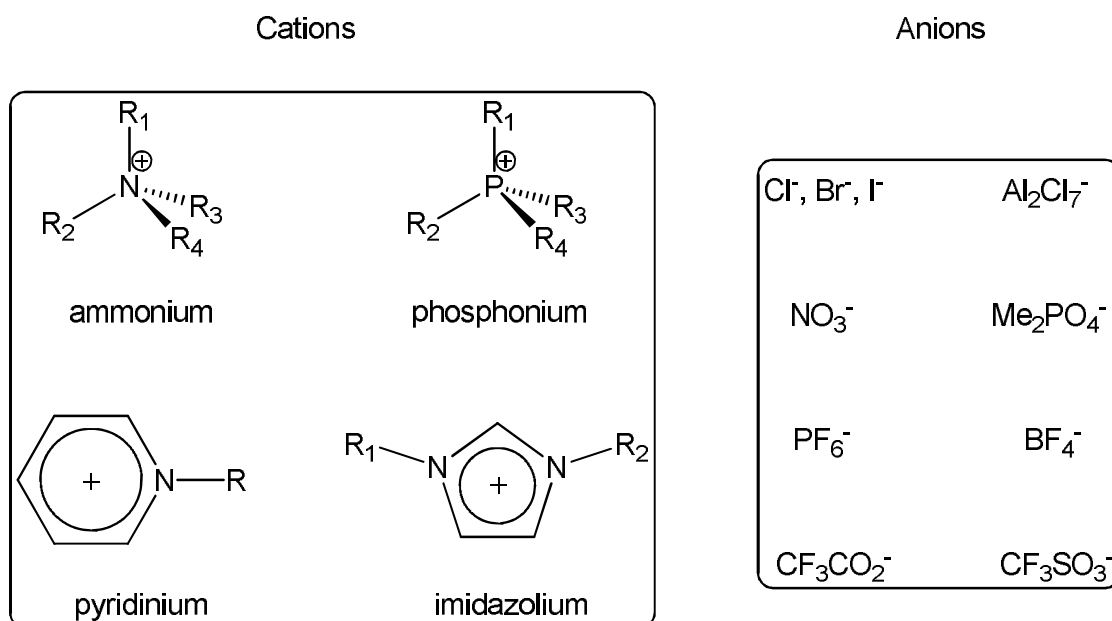
Cations

Anions



**Figure 1-1 Some of the cations and anions commonly used to prepare room temperature ionic liquids (RTILs).**

The most common synthetic approach to prepare a RTIL is quite simple. Figure 1-2 shows the synthesis of [BMIm]PF$_6$ (BMIm = 1-butyl-3-methylimidazolium). At first, chlorobutane is reacted with *N*-methylimidazole to provide [BMIm]Cl. Then the anion can be exchanged if desired. The most effective way to perform the first step is under solvent-free conditions using microwave irradiation to heat the reaction mixture.[5] However, to ensure the purity of RTILs, reagents used in its synthesis should have high purity. For example, in the preparation of [BMIm]Cl, it is essential to distill both of the precursor reagents before use. After the synthesis step, removal of salt by-products by washing with other solvents is often required and can be problematic because of mutual solubility of the by-products and ILs in many solvents. All these procedures lead to

additional costs and a reduction in the green credentials of these solvents, as indicated by an increase in the E-factor which is given by the ratio of waste produced compared to product produced (kg waste/kg product).
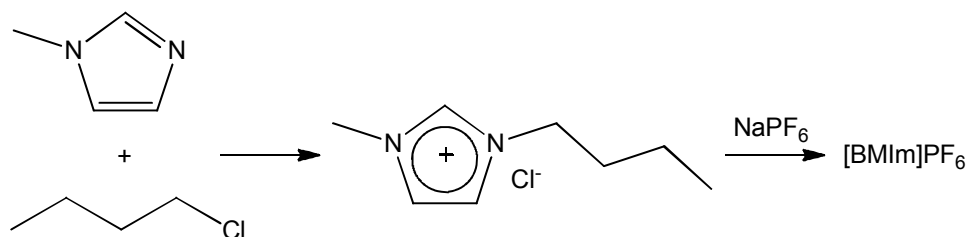


**Figure 1-2 Synthesis of [BMIm]Cl and [BMIm]PF$_6$.**

The polarities of RTILs are often high since they are made of ions. From the recent scientific literature, it is found that the polarities of common RTILs are close to those of alcohols. For example, [BMIm]PF$_6$ has a $E^N_T$ value of 0.667 while that of ethanol is 0.654.[6] The polarity of a RTIL can affect their solvating power and miscibility. In general, solid salts are very soluble in RTILs but other solids have limited solubility. Many RTILs are miscible with water and polar organic solvents. However, some RTILs like [BMIm][PF$_6$] are miscible with DCM and THF but immiscible with water.[7] Such RTILs are termed hydrophobic. Based on the solvating power and miscibility of RTILs with other solvents, RTILs have been widely used as extraction media, including extraction and separation of metal ions, organic molecules, biomolecules and gases.[3, 8]

RTILs have also been used widely in chemical synthesis.[9] In the past decade, over 3000 papers on the application of RTILs for synthesis and catalysis have been published.[4] In organic synthesis (Figure 1-3 and Figure 1-4), RTILs are not only used as solvents, but

have also played the role of catalyst.[4] Of particular importance to this thesis, a number of reactions involving $CO_2$ as a reactant have been performed in RTILs and high conversions and yields have been obtained.
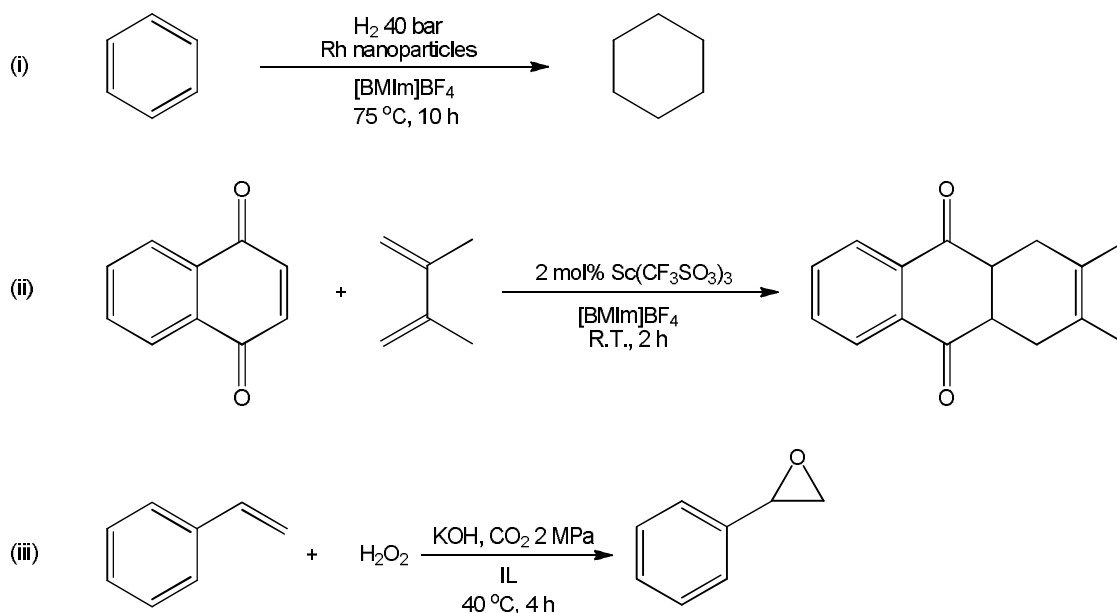


**Figure 1-3 Some examples of organic reactions in RTILs.**

In a hydrogenation reaction Figure 1-3 (i), benzene was selectively fully hydrogenated to cyclohexane with a conversion of 96%.[10] The catalyst was rhodium nanoparticles protected by IL-like copolymers, which were also synthesized in [BMIm]BF$_4$ by reduction of RhCl$_3$ with poly[(N-vinyl-2-pyrrolidone)-co-(1-vinyl-3-butylimidazolium chloride)]. The products could be easily separated without being contaminated by the catalyst.

RTILs have also been used in Diels-Alder reactions. In reaction Figure 1-3 (ii) a quantitative yield could be obtained in 2 h with Sc(CF$_3$SO$_3$)$_3$ as the catalyst and

[BMIm]BF$_4$ as the solvent.[11] The reaction without the triflate catalyst gave a yield of 42% in 6 h demonstrating that the IL itself could catalyze this reaction. A change of ionic liquid to [BMIm]PF$_6$ or [EMIm][CF$_3$COO] did not have a noticeable effect on the yield and may suggest that perhaps the acidic imidazolium cation is responsible for catalysis in the absence of the Lewis acidic metal triflate. The product could be easily extracted from the RTIL using diethyl ether and the ionic liquid could be recovered and reused for six catalytic cycles without significant changes in yield.

In an epoxidation reaction, Figure 1-3 (iii), styrene could be converted to styrene oxide under 2 MPa of CO$_2$ at 40 °C after 4 h.[12] The conversion of styrene and the yield of styrene oxide could reach 95% and 69%, respectively, using [BMIm]BF$_4$. HCO$_4^-$ [peroxymonocarbonate anion, HOOC(=O)O$^-$] produced from CO$_2$ and H$_2$O$_2$ acted as the oxidant in this reaction. Different RTILs gave different conversions for this reaction. [BMIm]BF$_4$ and [BMIm]Cl were miscible with the aqueous H$_2$O$_2$ solution used, so enough HCO$_4^-$ was produced in the ionic liquid and high conversions were obtained. H$_2$O$_2$(aq) was immiscible in [BMIm]PF$_6$, so almost no styrene oxide was produced in this RTIL. This reaction is particularly interesting in the context of this thesis, since in Chapter 3 the reactions of styrene oxide and carbon dioxide using IL catalysts are described.  In the future, it might be possible to combine epoxidation reactions of alkenes with subsequent carboxylation of the resulting epoxide product in a single pot reaction using IL catalysts.
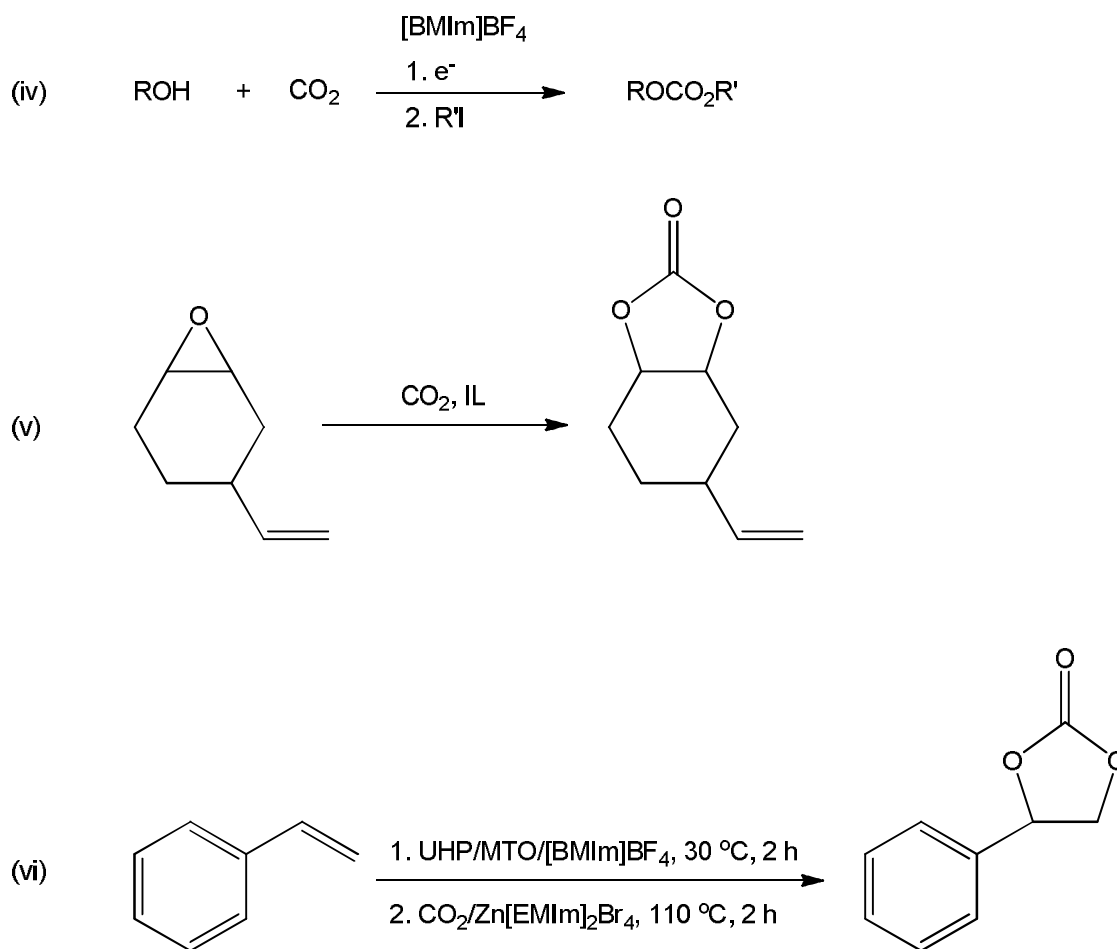
**Figure 1-4 Some examples of organic reactions using $CO_2$ as a feedstock in RTILs.**

RTILs have been widely used in electrochemistry due to their high ionic conductivity and wide electrochemical potential window. In reaction Figure 1-4 (iv) [BMIm]BF$_4$ was used in the synthesis of organic carbonates as a solvent and electrolyte.[13] The first step was electrolysis in [BMIm]BF$_4$ with a continuous flow of 1 bar $CO_2$ until $1.0$ F mol$^{-1}$ of charge was passed. Alcohols were then added and stirred for 1 h. Finally, CH$_3$I or C$_2$H$_5$I was added as the alkylating agent and after stirring at 55 °C for 5 h, carbonates were produced. Primary and secondary alcohols gave good product yields but

tertiary alcohols and phenols were not reactive. The yield also decreased when the alcohol chain length increased. Using methanol in a series of reactions, the reaction parameters were investigated. Optimum conditions involved using Cu as a cathode material with a working potential of −1.8 V (compared to a Ag/AgI electrode), with 0.124 mol L$^{-1}$ alcohol at 55 °C. These conditions were both mild and safe. No organic solvents, no catalysts or any other additional supporting electrolytes were used. The ionic liquid could be recycled five times by removing the alcohols and other products through distillation. The yields of products with the first and second use of IL were around 70% and around 50% with the other three times of use. In this reaction, the radical anion $CO_2^{\bullet-}$ was formed by $CO_2$ reduction and then reacted with the alcohol and alkylating agent.

Reaction (v) in Figure 1-4 shows the synthesis of a cyclic carbonate from vinyl cyclohexene oxide and $CO_2$ with a RTIL acting as a catalyst.[14] In this reaction, RTILs containing 1-alkyl-3-methylimidazolium cations with different alkyl groups (ethyl, butyl, hexyl, octyl) and different anions (Cl$^-$, BF$_4^-$, PF$_6^-$) were investigated. It was found that bulkier cations and more nucleophilic anions increased the activity of the catalyst. With bulkier cations, the distance between cation and anion is longer, which decreased the electrostatic interaction and made the anion more nucleophilic and more reactive towards the epoxide ring. Under 1.07 MPa initial $CO_2$ pressure and 160 °C, after 6 h the reaction could reach a conversion of 51.1% with [OMIm]Cl (OMIm = 1-octyl-3-methylimidazolium). Adding zinc halide as co-catalyst increased the conversion because it provided both a Lewis acid (Zn catalytic sites) and additional nucleophilic anions (F$^-$, Cl$^-$, Br$^-$).

Since RTILs can dissolve many metal catalysts, it is possible to perform several reactions in one container with multiple, sequential steps to give a more environmentally friendly synthesis. Reaction (vi) in Figure 1-4 shows a one-pot multistep synthetic process for the preparation of styrene carbonate from styrene.[15] In this synthesis, the first step was an epoxidation step. With MTO (methyltrioxorhenium) as the catalyst, UHP (urea hydrogen peroxide) as the oxidant and $[BMIm]BF_4$ as the solvent, styrene could be oxidized to styrene oxide with a conversion of 94.8%. In the $CO_2$ coupling step, $Zn[EMIm]_2Br_4$ was added as the catalyst and, with 3 MPa of $CO_2$, styrene carbonate could be obtained with a yield of 83%. The $[BMIm]BF_4$ used in this reaction could also be recycled by extraction with water and $CH_2Cl_2$ and reused in the synthesis.

## 1.2 Deep eutectic solvents (DESs)

As discussed above, in recent decades, room temperature ionic liquids (RTILs) have attracted considerable attention from the scientific community. Owing to their low vapor pressures and high boiling points, RTILs can be easily recycled and qualified as green solvents. However, ILs with high purity are also required since impurities, even in trace amounts, affect their physical properties. Several reports point out the hazardous toxicity and the very poor biodegradability of many ILs.[16, 17] Long alkyl chains on the cations often lead to high toxicity and poor biodegradability. Introducing an ester group in the side chain can improve biodegradability of ILs. The anions play a limited role in the biodegradability of these salts but contribute to the overall toxicity of RTILs. Anions used in ILs are often toxic (e.g. $(CF_3SO_2)_2N^-$).

To overcome the high price and toxicity of ILs, a new generation of solvent, named Deep Eutectic Solvent (DES), has emerged at the beginning of this century.[18] A eutectic mixture is defined as a mixture of different compounds or elements of a certain composition that melts at a lower temperature than that of any other mixtures from the components including the metal alloy.

A DES is a substance with a melting point much lower than either of the individual components from which it is prepared. One of the most widely used components in preparing DESs is choline chloride (ChCl, Figure 1-5). ChCl is a very cheap, biodegradable and non-toxic quaternary ammonium salt which can be either extracted from biomass or readily synthesized from ethylene oxide, hydrochloric acid, and trimethylamine through an atom economic process. Together with hydrogen bond donors such as urea or metal halides, ChCl can rapidly form a eutectic mixture, which is cheap and can be non-toxic.[19]
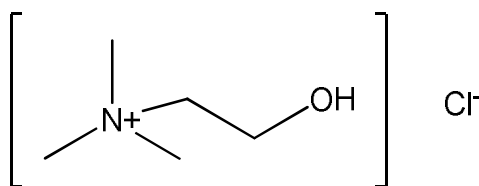


**Figure 1-5 Formula of choline chloride (ChCl).**

Although most DESs are made from ChCl as an ionic species, DESs cannot be considered as ionic liquids because (1) DESs are not composed only of ions but are mixtures of ionic and molecular species and (2) they can also be obtained from non-ionic

species. DESs have been grouped into four types depending on the components used to their preparation (see Table 1-1).

**Table 1-1 Classes of eutectic solvents.**

| | |
|---|---|
| Type I | metal salt + organic salt (e.g. $ZnCl_2$ + choline chloride) |
| Type II | metal salt hydrate + organic salt (e.g. $CoCl_2 \cdot 6H_2O$ + choline chloride) |
| Type III | organic salt + hydrogen bond donor (e.g. choline chloride + urea) |
| Type IV | metal salt (hydrate) + hydrogen bond donor (e.g. $ZnCl_2$ + urea) |

### 1.2.1    Synthesis of DESs

The typical way to make a DES is to simply mix the two components at a specific mole ratio and heat for a certain period of time to obtain a clear solution.[20-22] No purification is required and the synthesis proceeds with 100% atom economy. Figure 1-6 shows some organic salts and hydrogen bond donors often used in DES synthesis. The eutectic composition and properties for different DESs vary depending on the two components and the ratio in which they are combined.
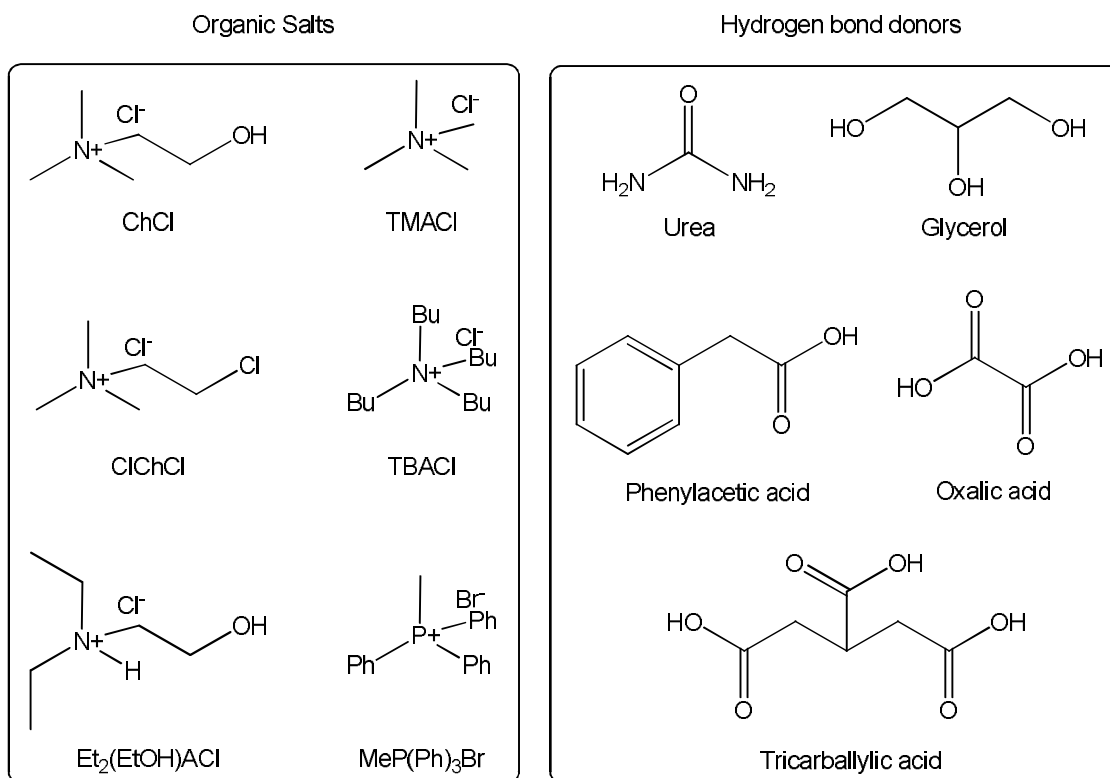
**Figure 1-6 Typical organic salts and hydrogen bond donors used in DES synthesis.**

Type I and Type II DESs, which are similar to traditional RTILs, contain large organic cations (e.g. $Ch^+$) and metal complex anions (e.g. $[Zn_2Cl_5]^-$).[21, 23] For Type IV DESs, metal-containing complex anions have been detected alongside metal-containing cations (e.g. $[ZnCl(urea)]^+$).[19] In Type III DESs, hydrogen bonds between anions of the organic salts and the hydrogen bond donors (HBDs) cause the lowering of the melting point.

Type II DESs cannot be formed through mixing anhydrous metal halides and water with organic salts, which suggests that water molecules behave as ligands in the DES and must be coordinated prior to synthesis, and that this kind of DES is not an

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aqueous solution. The DES formed by ChCl and $CrCl_3 \cdot 6H_2O$ is a dark green liquid at room temperature and changes colour to purple at 65-70 °C suggesting that the coordination sphere around the chromium center has changed.

## 1.2.2   Properties of DESs

### 1.2.2.1   Freezing point ($T_f$)

The freezing point ($T_f$) of a DES is much lower than that for any of the individual components. For Type III DESs, it is due to the hydrogen bond between the halide anions and HBDs. The lowest $T_f$ occurs at the eutectic composition which is often for a ChCl/HBD mixture a ratio of 1:2. For example, ChCl/urea mixtures with different ratios of 1:1, 1:2 and 1:3 have $T_f$ >50 °C, 12 °C and >50 °C respectively.[24]

Table 1-2 shows $T_f$ of Type III DESs. With urea as the HBD, the lowest $T_f$ occurs at a ChCl/HBD ratio of 1:2. Through fast atom bombardment mass spectrometry (FAB-MS), it was found that [Cl(urea)]⁻ and [Cl(urea)₂]⁻ existed in the DES.[24] The ratio is the same with glycerol. For normal carboxylic acids such as phenylacetic acid, the ratio of ChCl/HBD is still 1:2. However, for dicarboxylic acids, the ratio is 1:1 and is 2:1 for tricarboxylic acids. In the oxalic acid DES, a [Cl(oxalic acid)]⁻ anion may exist with two hydrogen bonds in the complex ion, or the oxalic acid may bridge with the neighboring Cl⁻ to create a larger anion.[20]

The ChCl/glycerol DES is liquid at room temperature, which is not surprising as glycerol has a $T_m$ of just 17.8 °C. For the 2,2,2-trifluoroacetamide containing DES, the $T_m$

is quite low presumably because of the presence of the trifluoromethyl group, which has a strong ability to form hydrogen bonds with the Cl⁻ anion.

**Table 1-2 Freezing points (T$_f$) of Type III DESs and comparison with the T$_m$: melting point of the pure HBD.**

| HBD | ChCl : HBD (molar ratio) | T$_m$/°C | T$_f$/°C | Ref. |
|---|---|---|---|---|
| Urea | 1 : 2 | 134 | 12 | [24] |
| Glycerol | 1 : 2 | 17.8 | -40 | [25, 26] |
| Phenylacetic acid | 1 : 2 | 77 | 25 | [20] |
| Oxalic acid | 1 : 1 | 190 | 34 | [20] |
| Tricarboxylic acid | 2 : 1 | 159 | 90 | [20] |
| 2,2,2-Trifluoroacetomide | 1 : 2.5 | 72 | -45 | [27] |
| Imidazole | 3 : 7 | 89 | 56 | [28] |
| Xylitol | 1 : 1 | 96 | Liquid at RT | [29] |

The T$_f$ of Type III DES also depends on the nature of the organic salts. In Table 1-3, DESs obtained from different ammonium salts with urea (1:2 molar ratio) show varying T$_f$, ranging from 1 °C to 113 °C. With only anions changing, the T$_f$ decreases in the order F⁻ > NO$_3^-$ > Cl⁻ > BF$_4^-$, suggesting the order of the hydrogen bond strength plays a strong role in governing the resulting T$_f$. A [Me$_3$NCH$_2$CH$_2$Cl]Cl/urea DES shows a similar T$_f$ (15 °C) compared to ChCl/urea DES (12 °C), while the T$_f$ of TEABr/urea DES

is significantly higher (113 °C). [Et$_2$NH(CH$_2$CH$_2$OH)]Cl and MeP(Ph)$_3$Br both form DESs with glycerol and these have T$_f$s below room temperature.

**Table 1-3 Freezing point (T$_f$) of other Type III DESs.**

| Organic salts | HBD | Salt : HBD (molar ratio) | T$_f$/°C | Ref. |
|---|---|---|---|---|
| ChF | Urea | 1 : 2 | 1 | 24 |
| ChNO$_3$ | Urea | 1 : 2 | 4 | 24 |
| ChBF$_4$ | Urea | 1 : 2 | 67 | 24 |
| [Me$_3$NCH$_2$CH$_2$Cl]Cl | Urea | 1 : 2 | 15 | 24 |
| TEABr | Urea | 1 : 2 | 113 | 24 |
| MeP(Ph)$_3$Br | Glycerol | 1 : 3 | -5.5 | 30 |
| [Et$_2$NH(CH$_2$CH$_2$OH)]Cl | Glycerol | 1 : 2 | -1 | 31 |

Table 1-4 shows a list of DESs synthesized from organic salts and metal salts or hydrated metal salts. With ZnCl$_2$, ChCl DES has a lower T$_f$ than TMACl and MeNEt$_3$Cl. The DES formed from ZnBr$_2$ and ChCl contains two anions (bromide and chloride), which leads to a higher T$_f$ than a single anion containing DES. In the ZnCl$_2$ DES, three anions were detected via FAB-MS, which are [ZnCl$_3$]$^-$, [Zn$_2$Cl$_5$]$^-$ and [Zn$_3$Cl$_7$]$^-$. This mass spectrometric study also provided some insight into the eutectic composition. The [Zn$_2$Cl$_5$]$^-$ anion is larger than [ZnCl$_3$]$^-$. The larger anion will have a lower charge density, so the electrostatic interactions between Ch$^+$ and [Zn$_2$Cl$_5$]$^-$ will be weaker. The amount of [Zn$_2$Cl$_5$]$^-$ in a 1:2 ratio DES is more than that in the 1:1 ratio DES, so the resulting

melting point is lower. For the DES with more $ZnCl_2$, the concentration of $[Zn_3Cl_7]^-$ increases while the melting point also increases, which is likely due to the greater molar mass of $[Zn_3Cl_7]^-$. Therefore, there is a balance between the size of the anion and its charge density. Low-charge density results in a lowering of $T_f$. Increased size of the anion results in an increase in dispersion forces, which results in an increase in $T_f$. For a Sn-containing DES, the lowest $T_f$ occured at a ChCl/$SnCl_2$ ratio of 1:2.5 because $SnCl_2$ is a weaker Lewis acid than $ZnCl_2$. Hence, more $SnCl_2$ is required to push the equilibrium to generate more $[Sn_2Cl_5]^-$. Interestingly, in contrast to many other metal-containing DESs, a DES containing chromium can only be synthesized from hydrated salts and its melting point is below room temperature.[22]

**Table 1-4 Freezing point ($T_f$) of Type I and II DESs and a comparison with the melting point ($T_m$) of the metal salt.**

| Organic salts | Metal salts | Organic salt : Metal salt | $T_m$/°C | $T_f$/°C | Ref. |
|---|---|---|---|---|---|
| TMACl | $ZnCl_2$ | 1 : 2 | 283 | >200 | [23] |
| MeNEt$_3$Cl | $ZnCl_2$ | 1 : 2 | 283 | 53-55 | [23] |
| ChCl | $ZnCl_2$ | 1 : 2 | 283 | 23-25 | [23] |
| ChCl | $SnCl_2$ | 1 : 2.5 | 246 | 43-45 | [23] |
| ChCl | $FeCl_3$ | 1 : 2 | 306 | 65 | [21] |
| ChCl | $ZnBr_2$ | 1 : 2 | 394 | 38 | [21] |
| ChCl | $CrCl_3·6H_2O$ | 1 : 2 | 83 | 14 | [22] |

Table 1-5 shows a list of Type IV DESs, which can be formed from a limited number of HBDs and metal salts according to Abbott and co-workers.[19] The complex is not formed through a hydrogen bond but a coordinate-covalent bond between donors and the metal center. In the urea DES, both cations and anions containing metals were detected through FAB-MS studies, including $[ZnCl]^+$, $[ZnCl(urea)]^+$, $[ZnCl(urea)_2]^+$, $[ZnCl(urea)_3]^+$, $[ZnCl_3]^-$, $[Zn_2Cl_5]^-$ and $[Zn_3Cl_7]^-$.

**Table 1-5 Freezing point ($T_f$) of Type IV DESs and a comparison with the melting point ($T_m$) of the pure HBD.**

| HBD | HBD : $ZnCl_2$ (molar ratio) | $T_m/°C$ | $T_f/°C$ | Ref. |
|---|---|---|---|---|
| Urea | 3.5 : 1 | 134 | 9 | [19] |
| Acetamide | 4 : 1 | 78 | -16 | [19] |
| Ethylene glycol | 4 : 1 | 13 | -30 | [19] |

### 1.2.2.2  Density

Density is an important physical property for solvents and densities of Type III and Type IV DESs have been studied. Some data are shown in Table 1-6. For most of these DESs, the densities are higher than that of water. Different components and the ratio of the two components all affect the densities of DESs. For example, the density of ChCl/glycerol DES increases when more glycerol is added to the DES. For Type III DESs, the densities are lower than that of the pure HBDs (urea: 1.32 and glycerol 1.26 g

cm$^{-3}$). However, the trend is opposite for Type IV DESs, for the ZnCl$_2$/urea DES the density is 1.63 g cm$^{-3}$.[19]

**Table 1-6 Densities of some Type III and Type IV DESs.**

| Salts | HBD | Salt : HBD (molar ratio) | Density (g cm$^{-3}$) | Ref. |
|-------|-----|--------------------------|-----------------------|------|
| ChCl | Urea | 1 : 2 | 1.25 | [32, 33] |
| ChCl | Glycerol | 1 : 1 | 1.16 | [30] |
| ChCl | Glycerol | 1 : 2 | 1.18 | [25, 34] |
| ChCl | Glycerol | 1 : 3 | 1.20 | [34] |
| MeP(Ph)$_3$Br | Glycerol | 1 : 2 | 1.31 | [30] |
| ZnCl$_2$ | Urea | 1 : 3.5 | 1.63 | [19] |

### 1.2.2.3 Viscosity and ionic conductivity

Most DESs have high viscosities (>100 cP), since the interactions between ions and molecules in the solvents are quite powerful. For Type I and II DESs, electrostatic interactions between the cations and anions are the dominant intermolecular forces; and for Type III and IV DESs, the interactions are mainly hydrogen bonding between the two components. Also, the large ion size and small void volume of DESs lead to a lower mobility of the component species, which may increase the viscosities.[34] The viscosities are related to the two components (as outlined above) and also to the temperature with which, as with all solvents, viscosity generally decreases with an increase in temperature.

For most DESs, the viscosity decreases when the temperature increases.[19-22, 24, 25] The viscosity can also be lowered by using smaller cations and fluorinated HBDs.

Most DESs have poor conductivity at room temperature due to their high viscosity. The viscosity decreases when the temperature increases, therefore, the conductivity increases too.

### 1.2.2.4 Polarity

The polarity of DESs is high. For example, the ChCl/glycerol DES with a 1:2 ratio has a $E^N_T$ value of 0.860, which is between that of methanol and water. The polarity increases when the ChCl percentage in the DES increases.

### 1.2.2.5 Dissolution in DESs

It has been shown that $CO_2$ is soluble in DESs prepared from ChCl and urea.[35] The solubility of $CO_2$ is related to the pressure, temperature and the ratio of the two components. The solubility increases as the pressure increases and the temperature decreases. The ChCl/urea (1:2) DES has the strongest solvating power for $CO_2$ compared to other ratios.

The DESs can also dissolve many kinds of compounds[36] including: inorganic salts (e.g. LiCl > 2.5 mol $L^{-1}$, AgCl = 0.66 mol $L^{-1}$), aromatic acids (e.g. benzoic acid = 0.82 mol $L^{-1}$) and amino acids (e.g. D-alanine = 0.38 mol $L^{-1}$), which are all soluble in the ChCl/urea (1:2) DES at 50 °C. More interestingly, many metal oxides are also soluble in

different DESs. For example, $Fe_3O_4$ is more soluble in the ChCl/oxalic acid (1:1) DES than in the ChCl/phenylpropionic acid (1:2) DES, while CuO exhibits the opposite trend in solubility. The solubility of metal oxides in these solvents can potentially be used in the recovery of certain metals from their ores and other metallurgical applications.[36]

### 1.2.3   Applications of DESs

Similar to ILs, DESs have been used in electrochemistry. The ChCl/urea DES can be used as an electrolyte for electrodeposition of metals such as Ni and Zn.[37, 38] DESs can also be used as solvents for electrochemical reactions and for electropolishing.

Various reactions with DESs as catalysts or solvents have been reported in recent years. Most of them involved Type I and Type III DESs as the reaction media since the DESs are cheap, non-toxic and recyclable.
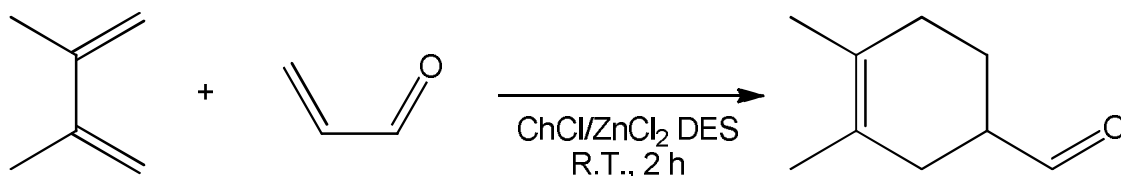


**Scheme 1-1 Diels-Alder reaction in the ChCl/ZnCl$_2$ DES.**

Two Type I DESs (ChCl/ZnCl$_2$ DES and ChCl/SnCl$_2$ DES) were found to be efficient catalysts for Diels-Alder reactions.[39] Scheme 1-1 shows one Diels-Alder reaction in the ChCl/ZnCl$_2$ DES. At room temperature, after stirring for 8 min to 5 h, yields of 90% or more could be achieved for a range of dienes and dienophiles with the ChCl/ZnCl$_2$

DES. The DES acted as both solvent and catalyst. It could dissolve dienophiles and was also a Lewis acid catalyst. Tin-containing DESs are less Lewis acidic, so the catalytic activity was reduced compared with the zinc-analog and the reaction time needed for a similar yield was 20 h to 24 h. The products could be easily pipetted from the top of the DES and the DES could be recycled by washing with hexane. Adding an equivalent amount of water to that of the metal ions did not affect the yield, showing this reaction was moisture stable.
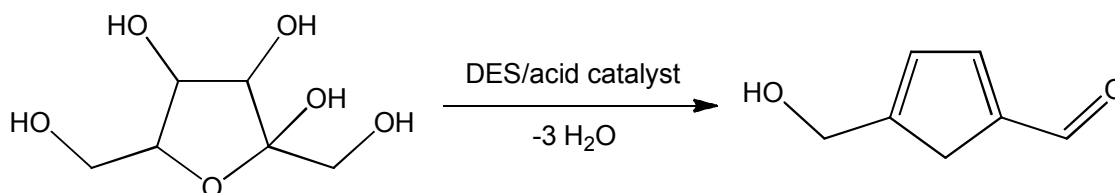


**Scheme 1-2 Dehydration of fructose in DESs.**

DESs have also been used in the dehydration of fructose to 5-hydroxymethyl-furfural (5-HMF), which is a valuable renewable chemical building block. This acid-catalyzed dehydration has been performed in imidazolium-based ILs, which are unfortunately expensive and toxic.[40] DESs are cheaper and safer with similar properties to ILs, thus drawing more attention. In 2009, Koenig and co-workers reported the dehydration of fructose to 5-HMF in ChCl/urea DES.[41] As shown in 错误!未找到引用源。, with an added acid catalyst ($CrCl_2$, $CrCl_3$, $FeCl_3$ or $AlCl_3$), 5-HMF was obtained with low yields (<30%). They next developed a new process using a ChCl/fructose (2:3) DES directly. This DES had a melting point of 70 °C. With an acid catalyst, 5-HMF was

obtained in 40-60% yield. Other carbohydrates (e.g. glucose, sucrose and inulin) could also form DESs with ChCl and could be converted to 5-HMF under the same conditions.
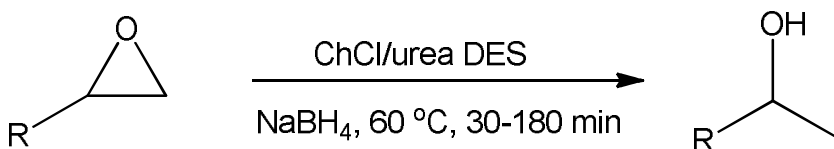


**Scheme 1-3 Reduction of epoxides in ChCl/urea DES.**

Ghafuri and co-workers reported the reduction of carbonyl compounds (e.g. benzaldehyde, cyclohexanone, 4-heptanone) and epoxides (e.g. propylene oxide, styrene oxide, glycidyl phenyl ether) by 2 eq. of $NaBH_4$ in ChCl/urea DES with high yields (75-99%).[42] For carbonyl compounds, the reaction only took 5 min at room temperature. For epoxides, the temperature was 60 °C and the reaction time was 30 to 180 min (Scheme 1-3). Only secondary alcohols could be obtained from epoxides, with the exception of styrene oxide (8% of the product was 2-phenylethanol), indicating this reaction was generally chemoselective.
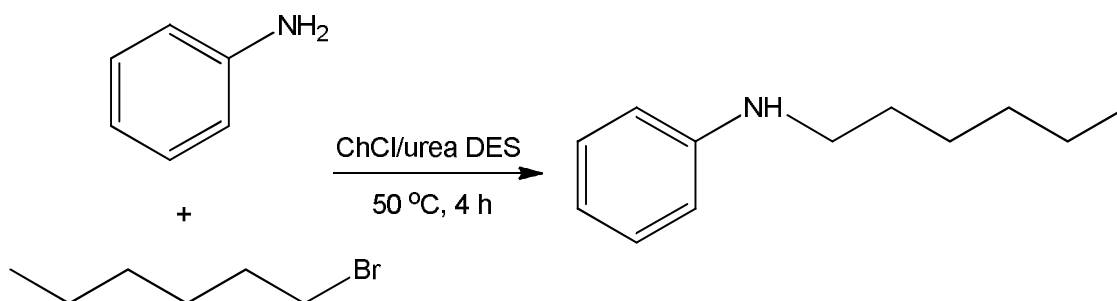
**Scheme 1-4 Mono-*N*-alkylation of aniline with hexyl bromide in the ChCl/urea DES.**

The ChCl/urea DES could also be used as the catalyst and solvent for the mono-*N*-alkylation of aromatic amines (Scheme 1-4).[43] After a 4 h reaction of aniline and hexyl bromide at 50 °C, hexyl aniline could be obtained with a yield of 78%. The ChCl/glycerol DES could also be used in this reaction giving a yield of 65% after 8 h. This method was also tested with a range of aromatic amines and alkyl bromides with a 70-89% yield. The products were extracted with ethyl acetate and the DES could be recycled and reused 5 times without noticeable decrease in yield.

## 1.3 Coupling reaction of epoxides and $CO_2$

The traditional way for preparing organic carbonates uses phosgene or carbon monoxide as the $C_1$ feedstock.[44-49] However, phosgene is toxic and corrosive while carbon monoxide is toxic and flammable. Comparably, $CO_2$ is a widely available, non-toxic and abundant feedstock.[50-52]

In 1969, Inoue claimed that $CO_2$ could be used as the $C_1$ feedstock in the coupling reaction of propylene oxide and $CO_2$ to produce polypropylene carbonate.[53] A catalyst system based on a 1:1 $Et_2Zn/H_2O$ mixture was used and a low TOF (0.12 $h^{-1}$) was achieved at 80 °C and 50 bar. From then on, a large variety of catalyst systems have been developed to catalyze this coupling reaction, including many ionic liquids, onium salts, metal- salen complexes, metal halides,[54, 55] metal oxides,[56, 57] organocatalysts,[58, 59] and many metal complexes (e.g. Al,[60] Co,[61] Ru,[62] Pd,[63] Re,[64] and Bi[65]). Ionic liquids, onium salts and metal- salen complexes catalyst systems will be discussed in this chapter.

Through the 100% atom economical coupling reaction shown in Scheme 1-5, polycarbonates or cyclic carbonates can be obtained under different conditions. Cyclic carbonates are often obtained at high temperature (above 100 °C) and relatively low pressure (1-10 bar), while polycarbonates are produced at lower temperatures and higher pressures, since cyclic carbonates are more thermally stable than polycarbonates. Both polycarbonates and cyclic carbonates have many important industrial applications. Polycarbonates are environmentally friendly packaging materials which can be used to make mobile phones, bottles, lenses and data storage discs.[66, 67] On the other hand, cyclic carbonates are also widely used as polar solvents (e.g. in degreasers or to dissolve the electrolyte in lithium ion batteries) and intermediates for further synthesis. [68]
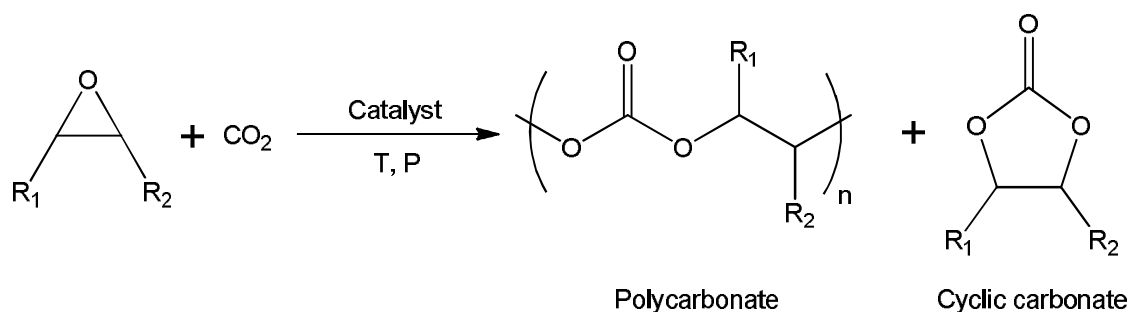
**Scheme 1-5 Coupling reaction between epoxides and $CO_2$.**

### 1.3.1    Coupling reactions catalyzed by cobalt complexes

Many metal salen complexes are effective catalysts for the coupling reaction of $CO_2$ and epoxides.[69-75] Lu *et al.* reported a Co(II) salen complex (Figure 1-7) for the synthesis of ethylene carbonate.[76] With this Co(II) salen complex and one equivalent TBAB, a TOF of 1320 $h^{-1}$ could be obtained at 110 °C and 160 bar.
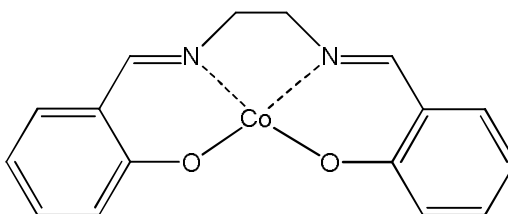


**Figure 1-7 A Co(II) salen complex for the synthesis of ethylene carbonate.**

In a subsequent study, Lu and co-workers described a solid-supported Co(II) salen system (Figure 1-8) for continuous synthesis of ethylene carbonate under supercritical $CO_2$ conditions (110 °C, 123 bar). A TOF of 111 $h^{-1}$ and 86% conversion were obtained.
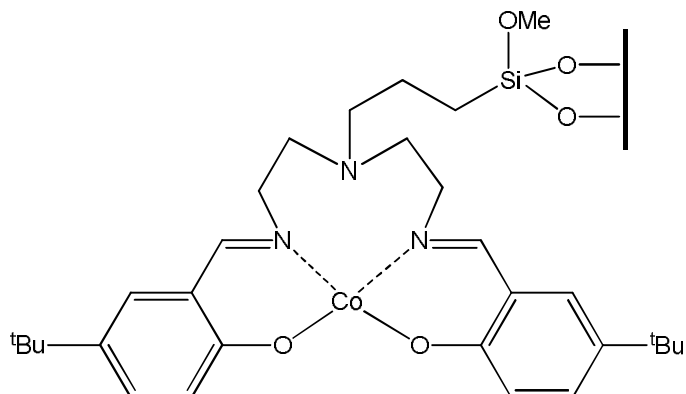
**Figure 1-8 A solid-supported Co(II) salen system for carbon dioxide activation.**

In another paper from Lu's group, two Co(III) salen complexes (Figure 1-9) were reported for the synthesis of propylene carbonate.[77] The binary catalyst system based on the Co(III)(salen)$O_2$CCCl$_3$ complex and TBAB exhibited a TOF of 245 h$^{-1}$ at room temperature and 15 bar $CO_2$. The product was obtained with 50% enantiomeric excess. Replacing TBAB with TBACl gave better enantioselectivity, but the catalytic activity was reduced. Replacing the Co(III)(salen)$O_2$CCCl$_3$ complex with Co(III)(salen)OTs gave 70% enantiomeric excess at 0 °C, but the TOF dropped to 27 h$^{-1}$.

X = O$_2$CCCl$_3$, OTs, Cl
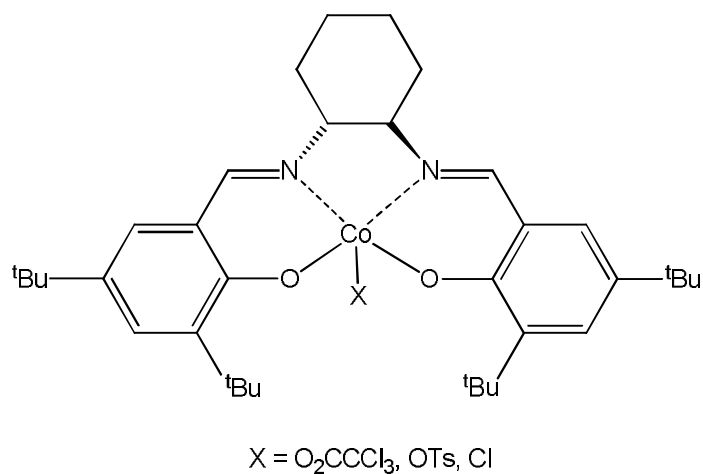
**Figure 1-9 Three Co(III) salen complexes with varying X groups from the groups of Lu and Paddock.**

Paddock and co-workers reported another binary catalyst system based on Co(III)(salen)Cl (Figure 1-9) and DMAP for the synthesis of propylene carbonate.[78] A TOF of 1200 h$^{-1}$ could be obtained at 100 °C, 10 bar.

A co-catalyst was often required for these metal salen complexes catalyst systems. The proposed mechanism for coupling is described in Figure 1-10. The steps in the mechanism are (1) coordination of the epoxide to the metal center, (2) nucleophilic attack of an anion or Lewis base at the epoxide ring, which yields a metal-alkoxide fragment, (3) coordination of $CO_2$ with the metal and attack of the alkoxide at the central carbon of the $CO_2$, (4) backbiting or intramolecular ring-closure to yield the product and reform the catalyst.
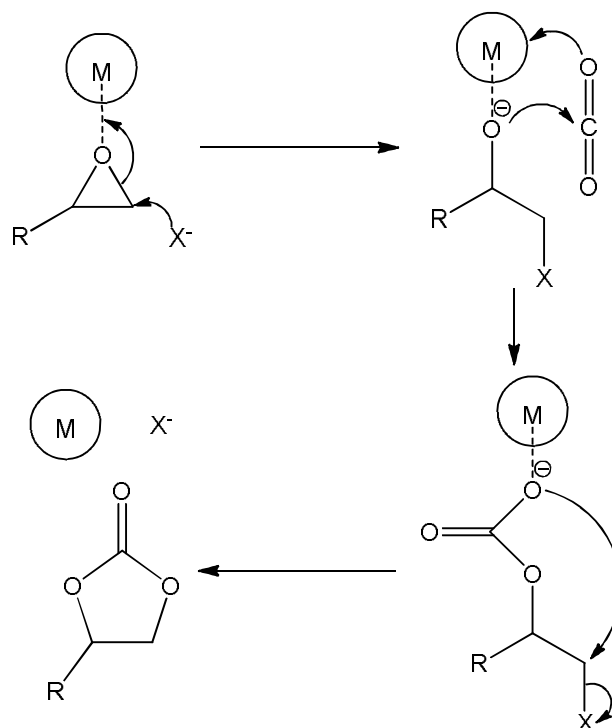
**Figure 1-10 Proposed mechanism for the cyclic carbonate formation catalyzed by metal complexes.**

### 1.3.2  Coupling reactions catalyzed by onium salts

In 2002, TBAB (Figure 1-11) was reported to be an effective catalyst for the synthesis of styrene carbonate from styrene oxide and $CO_2$. An 83% yield of product was obtained at 120 °C and 1 bar with a TOF of 1.3 $h^{-1}$.[79] It was also reported recently in 2011 that, with TBAB, a 96% yield of styrene carbonate could be obtained at 100 °C and 21 bar with a TOF of 15 $h^{-1}$ in dimethyl carbonate. Many other terminal epoxides were also tested. A 98% yield of propylene carbonate could be obtained at the same conditions with a TOF of 39 $h^{-1}$.[80] In another paper in 2012, a 56% yield of propylene carbonate was

obtained at 100 °C, 30 bar and TBAB with a TOF of 28 h$^{-1}$. In this work, the experimental data showed that the activity of the anions increased in the order of I$^{-}$ < Br$^{-}$ < Cl$^{-}$ with the same cation, and was related to the stronger nucleophilicity and the smaller steric hindrance of Cl$^{-}$ versus Br$^{-}$ and I$^{-}$.[81]
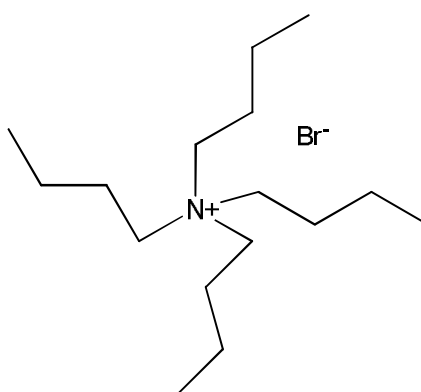


**Figure 1-11 Structure of tetrabutylammonium bromide (TBAB).**

In 2008, Park and co-workers studied the coupling reaction of butyl glycidyl ether and $CO_2$ with tetraalkylammonium salts and found that the catalytic activity of the tetraalkylammonium salts improved as the length of the alkyl group increased. The effect of the anions was also investigated and Cl$^{-}$ proved to be the most effective. Thus, tetrahexylammonium chloride was the most effective salt studied, giving a 81% conversion at 100 °C and 9 bar with a TOF of 2.7 h$^{-1}$.[82]

Many binary catalyst systems based on metal salts and onium salts have been investigated. A catalyst system based on $ZnCl_2$ and TBAI was found to be efficient for the synthesis of many terminal carbonates. A TOF of 143 h$^{-1}$ for propylene carbonate was obtained at room temperature and atmospheric pressure.[83] In 2009, Repo and co-workers

reported a catalyst system based on Co(II) halides and three onium salts for the syntheses of many terminal carbonates.[84] Among all the combinations studied, CoCl$_2$/PPNCl (错误! 未找到引用源。) was the most efficient one, giving a TOF of 2314 h$^{-1}$ for propylene oxide at 120 °C and 10 bar. Imes (TOF = 2174 h$^{-1}$) and TBACl (2223 h$^{-1}$) provided slightly reduced activities under the same conditions. As in other studies discussed above, changing the anion of TBACl to Br$^-$ or I$^-$ reduced the catalytic activity. Other Co(II) salts (bromide and acetate) were also tested, giving lower TOF than CoCl$_2$. Styrene oxide could also be converted with high TOF (1031 h$^{-1}$) while cyclohexene oxide was transformed with much lower activity (TOF = 42 h$^{-1}$). In all reactions, 0.025% mol Co(II) salt and 0.1% onium salt were used in 0.5 mL DCM. The mechanism was proposed to be similar to that shown in Figure 1-10.

TBAX: X = Cl, Br, I

PPNCl

ImesCl
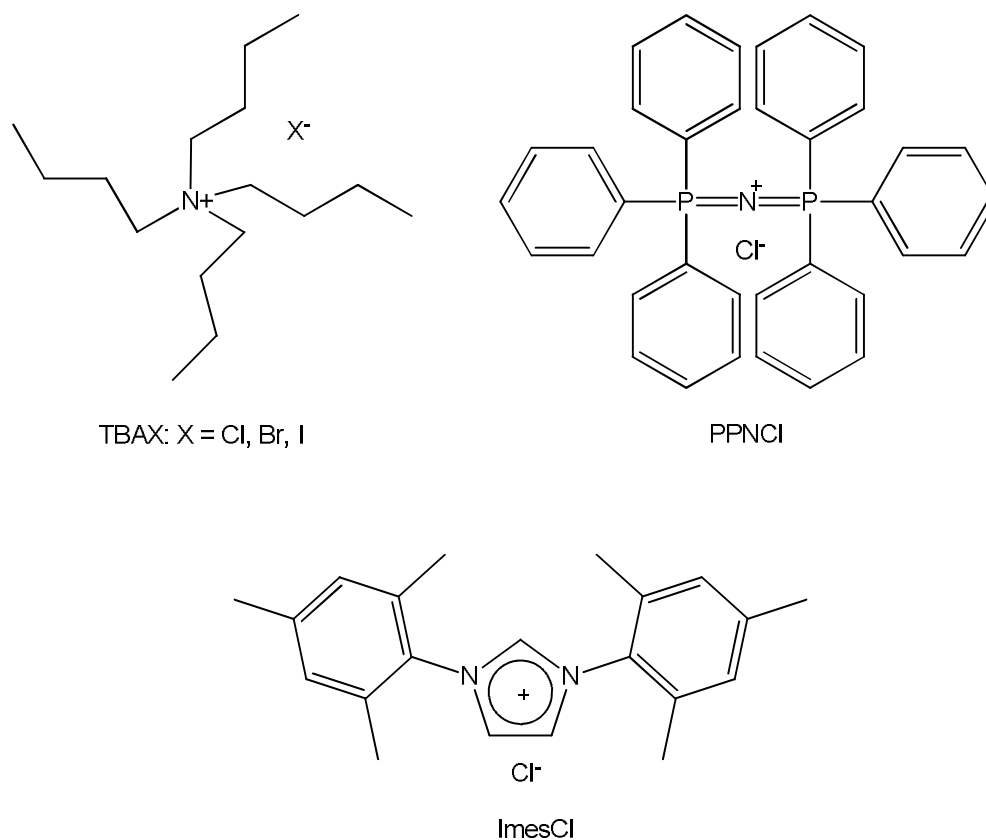
**Figure 1-12 Onium salts in the binary catalyst systems for cyclic carbonate formation reported by Repo and co-workers in 2009.**

### 1.3.3   Coupling reactions catalyzed by ionic liquids

Using an ionic liquid as the catalyst in coupling reactions of epoxides and $CO_2$ was first reported by Peng and Deng in 2001.[85] A quantitative yield of propylene carbonate was obtained in the reaction catalyzed by [BMIm]$BF_4$ at 110 °C and 25 bar with a TOF of 6.6 $h^{-1}$. Many other ILs with different cations and anions were also tested. The activity was shown to decrease in the order imidazolium > pyridinium and $BF_4^-$ > $Cl^-$ > $PF_6^-$.

In 2003, Kim and co-workers investigated the role of Lewis acid species such as $ZnBr_2$ with an IL as the catalyst and obtained higher yields for the cyclic carbonate synthesis.[86] Xia and colleagues tested more combinations of zinc salts with [BMIm]X (X = Cl, Br, $BF_4$, $PF_6$) for the addition of $CO_2$ to propylene oxide.[87] The best results were obtained using a catalytic system of $ZnBr_2$ and [BMIm]Br at 100 °C and 15 bar which gave a 98% yield and a TOF of 5580 $h^{-1}$. Many other terminal epoxides were also tested including styrene oxide and cyclohexene oxide. Most of them gave high yields except cyclohexene oxide.

In 2010, He and co-workers described a range of Lewis basic ionic liquids for the synthesis of cyclic carbonate.[88] They found that one IL, namely 1,8-diazabicyclo[5.4.0]undec-7-enium chloride ([HDBU]Cl, Figure 1-13), gave quantitative yields of product. The process was performed at low pressure without any solvent. The catalyst could be recycled over five times without appreciable loss of catalytic activity.
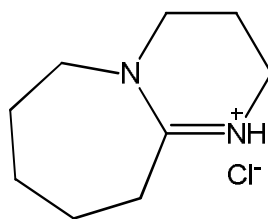


**Figure 1-13 A Lewis basic IL catalyst, [HDBU]Cl.**

Hydroxyl-functionalized ionic liquids for cyclic carbonate synthesis were reported by Sun *et al.* in 2008. In this paper, 1-(2-hydroxyethyl), 3-methylimidazolium bromide ([HEMIm]Br) was the most active one, giving a 99% yield under mild conditions.[89] In a

very recent paper, another kind of hydroxyl-functionalized ionic liquid, 1-butyl, 2-hydroxymethyl, 3-methylimidazolium bromide ([BHMMIm]Br, Figure 1-14), was shown to be very active with 20-30% higher yields achieved as compared to unfunctionalized (non-hydroxyl-containing) analogues. The ionic liquid was base stable and could be recycled six times without loss of catalytic activity.[90]
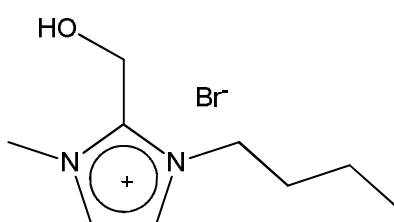


**Figure 1-14 A hydroxyl-functionalized IL catalyst, [BHMMIm]Br.**

Betaine-based catalysts (Figure 1-15) have been studied for cycloaddition reactions.[91] They could be made from natural sources and the catalytic activity was comparable with choline chloride as a catalyst for the synthesis of propylene carbonate. The reactions were performed under 80 bar carbon dioxide with the iodide salt, [Me$_3$NCH$_2$COOH]I, having the highest activity. All the betaine-based catalysts were recyclable and showed little loss in activity upon re-use.

$X = Cl, Br, I, BF_4, PF_6$
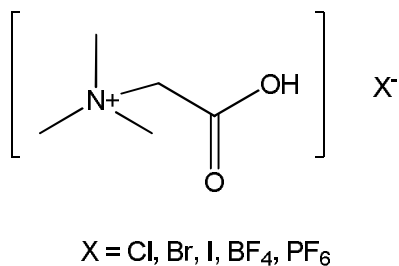
**Figure 1-15 Betaine-based IL catalyst, [Me₃NCH₂COOH]X.**

Zwitterionic materials containing no halide ions have been used as bifunctional organocatalysts in cycloaddition reactions.[92] A range of zwitterions were studied and 3-(trimethylammonio)phenolate was found to be the most effective with 99% yield of propylene carbonate being obtained at 120 °C and 10 bar. Interestingly, a carbonate zwitterion could be formed with $CO_2$ and it could be used as a synthon to form cyclic carbonates upon reaction with one equivalent of epoxide. Therefore, the authors speculated that this carbonate is an intermediate in the catalytic cycle.
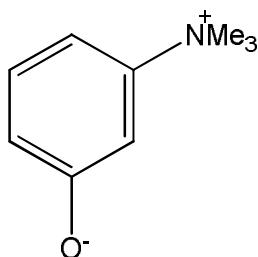


**Figure 1-16 Bifunctional ammonium betaine catalyst, 3-(trimethylammonio)phenolate.**

Many solid-supported ionic liquid catalysts have been studied for cycloaddition reactions. Both inorganic (silica, magnetic nanoparticles, alumina) and organic (polymer

and biopolymer) supports have been tested to see which worked best. Some of these are shown in Figure 1-17. In (i), a silica-supported IL, Si-CIL-Br is shown. High yields (>90%) of product could be obtained at 110 °C, 16 bar in 5 h for most epoxides including styrene oxide and propylene oxide.[93] In (ii), a magnetic nanoparticle-supported IL catalyst, MNP-1 is shown. A 93% yield of styrene carbonate could be achieved at 140 °C and 10 bar in 12 h. In (iii), a hydroxyl IL grafted onto cross-linked divinylbenzene polymer (PDVB-HEIMBr) is shown. A 99% yield of styrene carbonate could be achieved at 140 °C and 20 bar in 4 h. In all cases, moderate (non-ambient) pressures of carbon dioxide and temperatures greater than 100 °C were required to achieve good yields in a reasonable time frame.
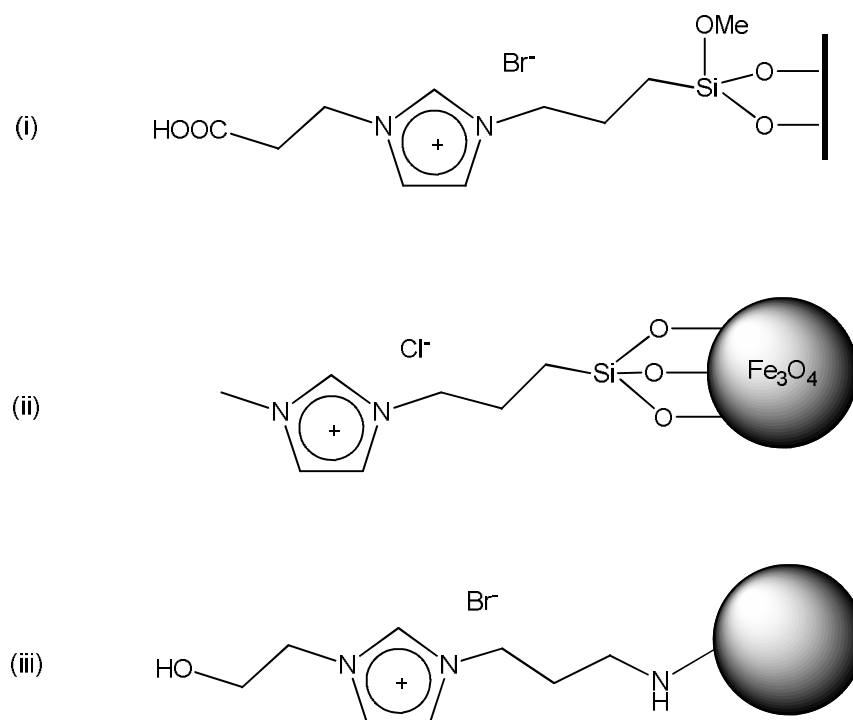
**Figure 1-17 Examples of supported ionic liquid catalysts for cyclic carbonate formation: (i) Silica supported carboxyl containing IL, Si-CIL-Br. (ii) Magnetic nanoparticle supported IL catalyst, MNP-1. (iii) Polymer supported IL, PDVB-HEImBr.**

Given the precedent in the scientific literature for the excellent reactivity of onium salt catalysts and ionic liquid catalysts in $CO_2$ activation, the aim of this thesis was to prepare metal-containing ILs or DESs and to study their behavior towards cyclic carbonate production from carbon dioxide.

Within the research performed and reported herein, coupling reactions of $CO_2$ and epoxides were performed in a steel vessel at various pressures and temperatures with the goal of producing either polycarbonates or cyclic carbonates. Reactions of this type are

known to be very temperature dependent and some catalysts produce polymer at low temperature ($< 60$ $^{\circ}$C) and cyclic carbonate at high temperature ($> 80$ $^{\circ}$C). Herein, results that demonstrate Co(II) DES is an effective catalyst for cyclic styrene carbonate synthesis are described. Also, results for the same reaction using other $3d$ transition metal-containing DESs are presented.

# Chapter 2  Study of DESs

## 2.1    Introduction

As mentioned in Chapter 1, DESs are a new class of ionic solvent that are greener than traditional ILs in terms of their toxicity, biodegradability and life cycle. [16, 17] In our study, DESs containing metal complexes were synthesized from ChCl and metal salts. Ratios of the two components, melting points and solubilities of different DESs were also studied in order to determine whether such properties could be correlated with catalytic activity. The catalytic activity of these DESs in carbon dioxide cycloaddition reactions is presented in Chapter 3.

## 2.2    Results and discussion

## 2.2.1    Synthesis of DESs

$CrCl_3·6H_2O$, $CoCl_2·6H_2O$, $MnCl_2·4H_2O$, $FeCl_3$, $NiCl_2·6H_2O$ and $CuCl_2·2H_2O$ were chosen to react with ChCl to form DESs. The ratio of $MCl_x·yH_2O$ or $MCl_x$ to ChCl used was 2 to 1. After heating to between 80 and 120 °C, ionic liquids of different colors were obtained from the colorless ChCl and the colored transition metal salt which are both solids initially. However, it should be noted that, upon standing at room temperature for a period of hours or days (depending on the nature of M), the liquids solidified or phase separated. Therefore, the DESs were used in further studies shortly after preparation in order to make sure they were homogeneous liquids.

### 2.2.2 Thermal studies and melting points

TGA and DSC were used in thermal studies of the DESs in this thesis. From DSC plots melting points were determined. In Abbott's group, the freezing point for each ionic liquid was ascertained by the lack of viscous flow of the meniscus.[22]
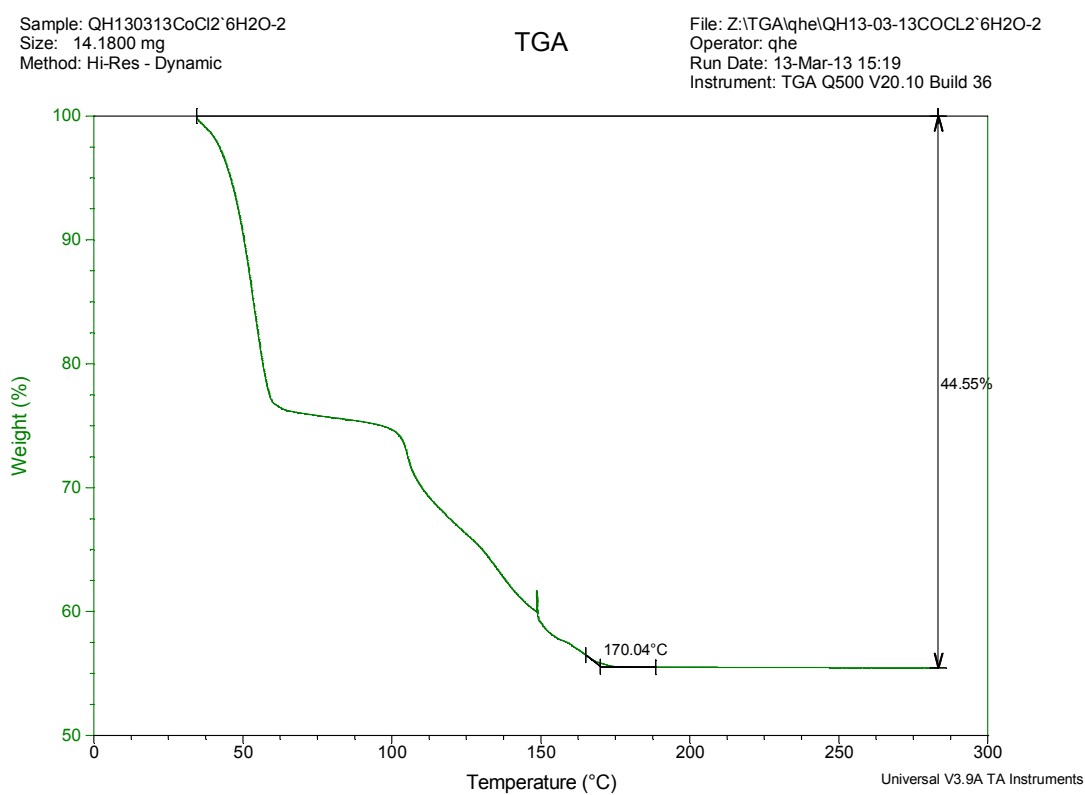


**Figure 2-1 TGA plot for CoCl$_2$·6H$_2$O (one component of a DES in this thesis).**

Sample: QH13-03-05DES07
Size: 17.3080 mg
Method: Ramp

TGA

File: Z:\TGA\qhe\QH13-03-05DES07
Operator: qhe
Run Date: 05-Mar-13 15:44
Instrument: TGA Q500 V20.10 Build 36
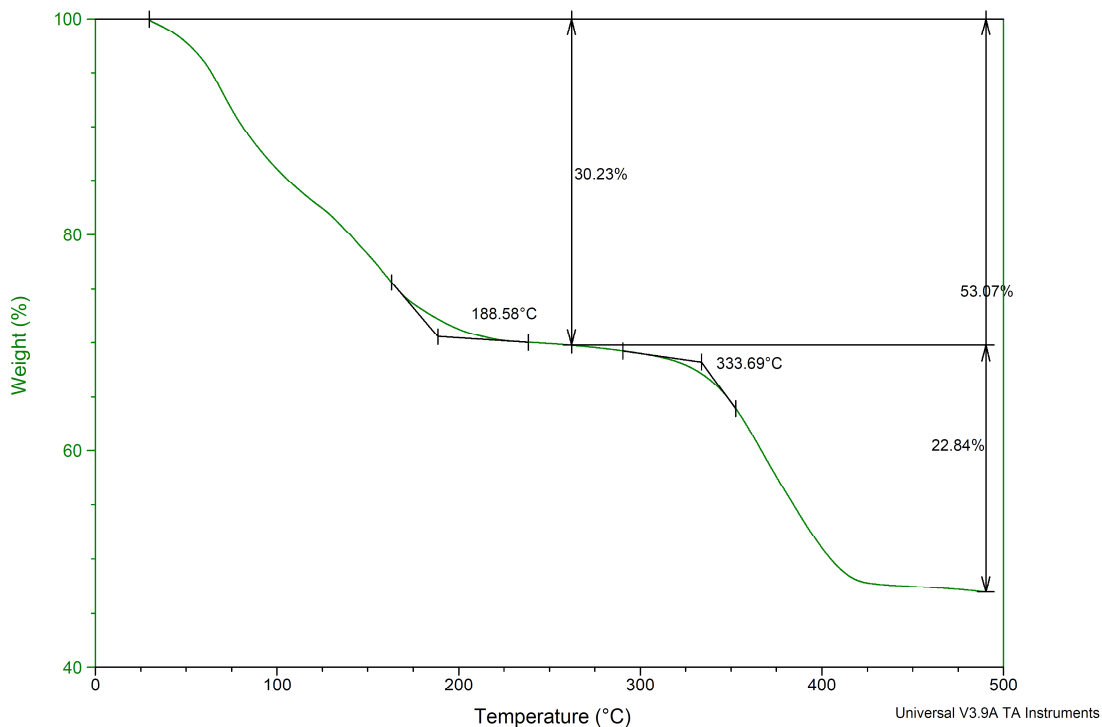
**Figure 2-2 TGA plot for 1:2 ChCl/CoCl$_2$·6H$_2$O DES.**

In Figure 2-1, CoCl$_2$·6H$_2$O loses all 6 water molecules between 30-171 °C. In Figure 2-2, the Co(II) DES loses all 6 water molecules between 30-189 °C, which is a wider temperature range than for the metal salt precursor (CoCl$_2$·6H$_2$O) used. This shows that the presence of ChCl affects the coordination sphere around the cobalt center. After loss of water, the DES loses ChCl between 334-412 °C.

According to DSC data, most of the DESs have melting points slightly higher than room temperature (30-60 °C). Ni(II) DES had the lowest melting point, while Fe(III) DES had the highest melting point.

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DESs with different ratios of ChCl to $CoCl_2 \cdot 6H_2O$ should have different melting points. However, the melting points measured by DSC showed no significant differences, as shown in Table 2-1. All melting points were around 40 °C. The lowest melting point of the three was for the ratio of 1:2, and this DES is the most homogenous one by visual inspection. Compared to Abbott's work, the melting points of Co(II) DESs presented here should be more accurate because, in their work, they synthesized many DESs but only measured the melting points of Cr(III) DESs by visual inspection which is prone to human error.[22]

**Table 2-1 Melting points of ChCl/$CoCl_2 \cdot 6H_2O$ mixtures.**

| Mole ratio of ChCl:$CoCl_2 \cdot 6H_2O$ | Melting Point (°C) |
| --- | --- |
| 1:1 | 42 |
| 1:2 | 40 |
| 1:3 | 42 |

### 2.2.3 Solubility of Co(II) DES

The Co(II) DES (1:2 ChCl:Co) is soluble in water, acetone, methanol, ethanol and acetonitrile and is insoluble in ethyl ether, ethyl acetate, hexane, toluene and dichloromethane, as shown in Table 2-2. The solubility of the DES depends on both components, as ChCl is insoluble in acetone but the DES is soluble. Since ChCl and

CoCl$_2$·6H$_2$O are both ionic compounds, it is not surprising that the DES is more soluble in polar solvents (e.g. acetonitrile) than non-polar ones (e.g. hexane).

**Table 2-2 Solubility of ChCl, CoCl$_2$·6H$_2$O and 1:2 ChCl/Co DES.**

|  | ChCl | CoCl$_2$·6H$_2$O | DES |
|---|---|---|---|
| Water | <1min | <1min | <1min |
| Acetone | — | <1min | <1min[a] |
| Ethanol | <1min | <1min | <1min |
| Acetonitrile | <1min[b] | <1min | <1min |
| Ethyl ether | — | — | — |
| Ethyl acetate | — | — | — |
| Hexane | — | — | — |
| Toluene | — | — | — |
| Dichloromethane | — | — | — |

Time required (at room temperature) to dissolve 50 mg of compound in 5.00 mL of each respective solvent. This corresponds to a concentration of 10 mg/mL. Entries marked as '—' were not soluble after 24 hours. [a] The DES dissolved quickly but some crystals remained. [b] At most 10 mg of ChCl can dissolve in 5 mL of acetonitrile.

## 2.3   Experimental

### 2.3.1   General information

Choline chloride (ChCl) (98+%), chromium(III) chloride hexahydrate (98%) and nickel(II) chloride hexahydrate (98%) were purchased from Alfa-Aesar. Cobalt(II) chloride hexahydrate (99%) was supplied by BDH Chemicals. Manganese(II) chloride tetrahydrate (98+%), anhydrous iron(III) chloride (98%), and copper(II) chloride dihydrate (99+%) were purchased from Strem Chemicals.

### 2.3.2   General procedure for DES synthesis

A mixture of the metal halide (hydrate) and ChCl in the desired molar ratio (from 2:1 to 1:2) was heated to between 80 and 120 °C with gentle stirring until a clear liquid formed. This procedure is taken from the work of Abbot and co-workers.[22]

### 2.3.3   TGA and DSC

TGA method: A TA instruments Q 500 was used in this work. For $CoCl_2 \cdot 6H_2O$, a method of Hi-Res with a heating speed of 20 °C/min to 300 °C was used. For the Co(II) DES and other mixtures, the method was Ramp, with a heating speed of 20 °C/min to 500 °C.

DSC method: A Mettler Toledo DSC 1 instrument was used in this work. The method was dynamic with a heating speed of 10 °C/min from 25 °C to 75 °C.

## 2.4 Conclusion

Metal-containing DESs were easily made following a literature procedure.[22] In the work presented in this thesis, six different $3d$ metal salts were chosen to react with ChCl to prepare DESs. Through thermal study of the Co(II) DES, it was shown that the DES with a 2:1 ratio of $CoCl_2 \cdot 6H_2O$ to ChCl had the lowest melting point. Also, the solubility of the Co(II) DES was tested with many solvents for further reactivity studies. As expected, these ionic materials were easily dissolved in polar solvents such as alcohols, but were insoluble in non-polar solvents.

# Chapter 3  Synthesis of Cyclic Carbonates Using Metal-containing DESs as Catalysts

## 3.1  Introduction

As outlined in Chapter 1, Section 1.3, onium salts often show excellent reactivity in cycloaddition reactions of $CO_2$ and epoxides, and metal salts enhance this reactivity. In Repo's work, the catalyst system of $CoCl_2$ and TBACl was used.[84] Ionic liquid catalysts, such as betaine-based IL catalysts, also show good activity.[91] Therefore, the reactivity of metal-containing eutectics in reactions of carbon dioxide was investigated. Co(II) DES was first studied. Three variables (Scheme 3-1) were optimized in this work: catalyst (its identity and loading), pressure (P) and temperature (T). Also, the effect of running the reaction without solvent compared with using acetonitrile was studied. On that note, it is important that the DES showed good solubility in acetonitrile (Chapter 2, section 2.2.3).
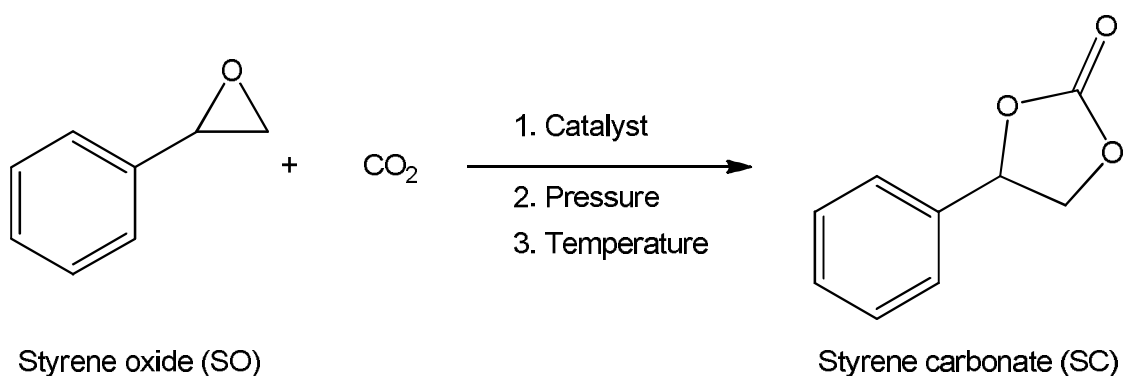


**Scheme 3-1 General scheme for the coupling reaction of $CO_2$ and styrene oxide (SO) to form styrene carbonate.**

Other commonly studied epoxides (propylene oxide, PO and cyclohexene oxide, CHO) in $CO_2$ cycloaddition reactions were also investigated briefly. Finally, a reactivity study of other $3d$-transition metal DESs as catalysts in the reaction of $CO_2$ with SO was undertaken.

## 3.2 Results and discussion

### 3.2.1 Synthesis of styrene carbonate catalyzed by Co(II) DES

Results for control studies and reactions with different catalysts are shown in Table 3-1. Entries 1 and 2 show the poor activity of the individual components ($CoCl_2 \cdot 6H_2O$ or ChCl) of the DES towards the synthesis of styrene carbonate. With very low conversion of SO, it seems that neither $CoCl_2 \cdot 6H_2O$ nor ChCl catalyzes the coupling reaction, while the Co(II) DES performs the reaction well. In entries 3 and 4, two different Co(II) DESs were tested. The two DESs were made from different ratios of the two components, but in reactions the loadings of Co(II) were equal, affording different conversions but the same TOFs (per mol Co per h).

**Table 3-1 Results of control reactions and initial Co(II) catalyzed reactions for styrene carbonate synthesis.**

| Entry | Catalyst | Conv. (%). | TOF ($h^{-1}$) |
|:-----:|:--------:|:----------:|:--------------:|
| 1 | $CoCl_2 \cdot 6H_2O$ | 4 | 0.2 |
| 2 | ChCl | 4 | 0.2 |
| 3 | $ChCl:CoCl_2 \cdot 6H_2O$, 1:2 | 93 | 4.7 |
| 4 | $ChCl:CoCl_2 \cdot 6H_2O$, 1:1 | 53 | 4.8 |

Reaction conditions: $P_{CO_2}$ = 10 bar, T = 90 °C, t = 24 h. TOF = moles of styrene carbonate produced per mole of Co(II) per hour or per mole ChCl in the case of entry 2.

Table 3-2 shows results obtained with the aim of optimizing pressure, solvent and time for Co(II) catalyzed reactions. In going from entry 1 to 2, the pressure was reduced from 40 bar to 10 bar, while the conversion remained the same. This shows the coupling reaction can be performed under milder conditions and, in the later research, 10 bar $CO_2$ was used for all reactions. In entries 1 and 2, acetonitrile was added to dissolve the catalyst. In entry 3, no solvent was added; however, the % conversion and TOF were not affected. Therefore, all remaining reactions were performed under solvent-free conditions. Co(II) DES is insoluble in epoxides, so in reactions (other than entries 1 and 2) the process is heterogeneously catalyzed. The resulting product phase was a green solution and, after filtration through a short silica column, a yellow liquid was obtained, while some blue compound remained on top of the silica. This result shows that the Co(II) DES

is slightly soluble in the styrene carbonate but it can be removed by passing the mixture over a silica column.

**Table 3-2 Optimization of reaction conditions (solvent, pressure and time) for $CO_2$/SO cycloaddition reactions catalyzed by Co(II) DES.**

| Entry | Co : SO | P (bar) | t (h) | Conv. (%). | TOF ($h^{-1}$) |
|-------|---------|---------|-------|-----------|----------------|
| 1[a]  | 1 : 131 | 40      | 24    | >99       | 5.5            |
| 2[a]  | 1 : 144 | 10      | 24    | >99       | 6.0            |
| 3     | 1 : 137 | 10      | 24    | >99       | 5.7            |
| 4     | 1 : 121 | 10      | 16    | 88        | 6.7            |
| 5     | 1 : 131 | 10      | 7     | 49        | 9.2            |
| 6     | 1 : 127 | 10      | 4     | 25        | 8.0            |

T = 100 °C for all entries, 1:2 ChCl/Co DES. [a] 1.1 mL acetonitrile was used to dissolve catalyst.

Table 3-3 shows results for the optimization of temperature and time for this reaction. As expected, conversion rose as temperature increased. If entries 1, 2, 3 and 4 are compared, as T increases from 60-100 °C, the conversion increases from 5% to 99%. This is shown graphically in Figure 3-2. If entries 4, 6 and 8 are compared, it is clear that at the same temperature, the longer the time, the better the conversion.

**Table 3-3 Optimization of temperature and time for $CO_2$/SO cycloaddition catalyzed by Co(II) DES.**

| Entry | Co : SO | T (°C) | t (h) | Conv. (%). | TOF ($h^{-1}$) |
|-------|---------|--------|-------|------------|----------------|
| 1 | 1 : 132 | 60 | 24 | 5 | 0.28 |
| 2 | 1 : 127 | 80 | 24 | 38 | 2.0 |
| 3 | 1 : 121 | 90 | 24 | 93 | 4.7 |
| 4 | 1 : 137 | 100 | 24 | >99 | 5.7 |
| 5 | 1 : 150 | 90 | 16 | 56 | 5.2 |
| 6 | 1 : 121 | 100 | 16 | 88 | 6.7 |
| 7 | 1 : 134 | 120 | 16 | >99 | 8.2 |
| 8 | 1 : 127 | 100 | 4 | 25 | 8.0 |
| 9 | 1 : 146 | 120 | 4 | 47 | 17 |
| 10[a] | 1 : 99 | 140 | 4 | 71 | 18 |
| 11[a] | 1 : 121 | 160 | 4 | 97 | 26 |

$P_{CO_2}$ = 10 bar for all entries, 1:2 ChCl/Co DES. [a] In entry 10 and 11, reactions were performed in a 100 mL reactor instead of the 300 mL reactor.

(a)
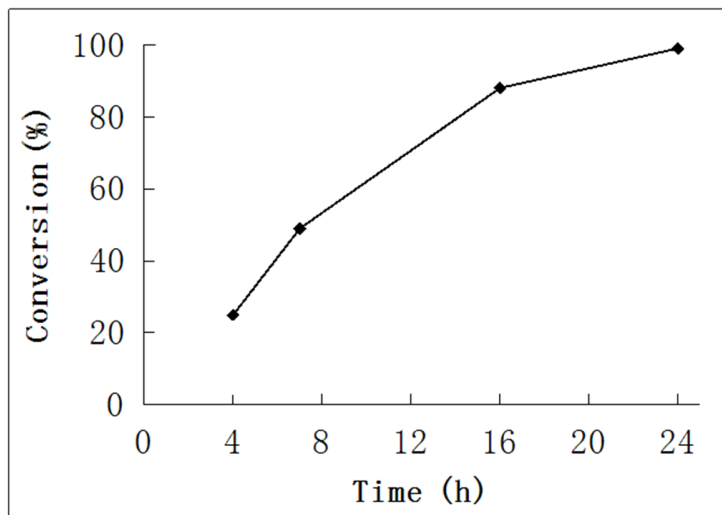


(b)
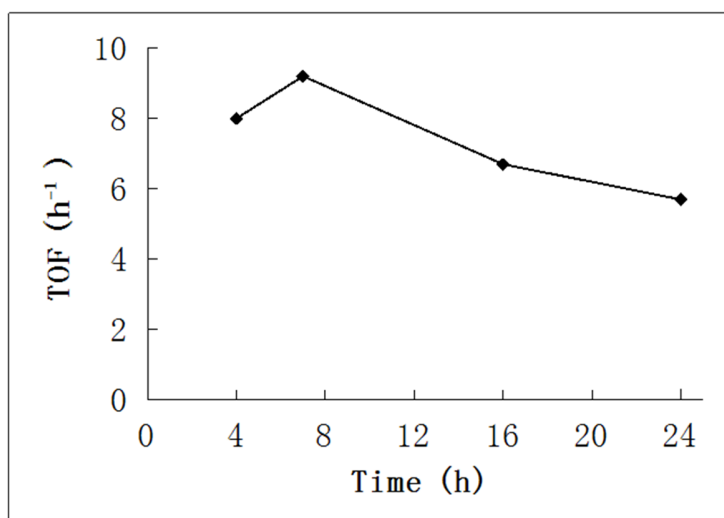


**Figure 3-1 Plots of SO conversion and TOF vs. time for styrene carbonate synthesis.**

**($P_{CO_2}$ = 10 bar, T = 100 °C, 1:2 ChCl/Co DES).**

(a)
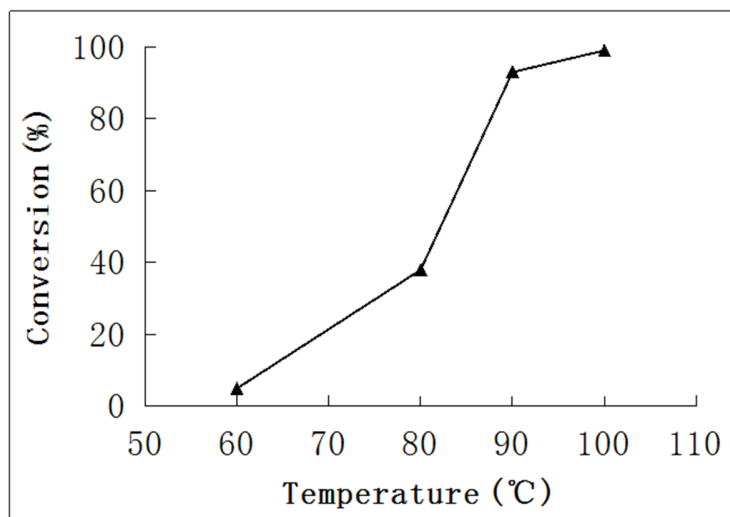


(b)
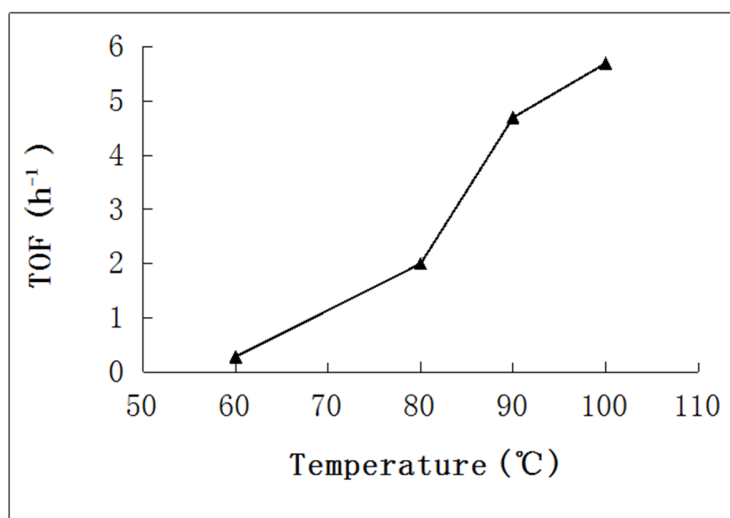


**Figure 3-2 Plots of SO conversion and TOF vs. temperature for styrene carbonate synthesis. ($P_{CO_2}$ = 10 bar, t = 24 h, 1:2 ChCl/Co DES).**

Figure 3-1 shows the effect of reaction time on styrene carbonate synthesis under the following conditions: $P_{CO_2}$ = 10 bar, T = 90 °C, 1:2 ChCl/Co DES. At 100 °C, styrene oxide conversion gradually rose as reaction time was increased and 100% conversion was achieved after 24 h, but TOF peaked at 7 h. Therefore, although conversion was maximized at 24 h, per unit time, the catalyst is being more productive than this maximum time indicates. A high TOF is a sign of a very productive catalyst. Therefore, as TOF decreases at longer reaction times, this suggests that the catalyst might be decomposing over long reaction times or that the reaction rate is strongly dependent on epoxide concentration. Therefore, as the epoxide is used up at longer reaction times, the rate of reaction decreases significantly.

Figure 3-2 shows the temperature effects under the following conditions: $P_{CO_2}$ = 10 bar, t = 24 h, 1:2 ChCl/Co DES. After 24 h reaction, only the reaction at 100 °C achieved 100% conversion and conversion dropped rapidly when temperature was decreased. At 60 °C, little styrene oxide was converted to styrene carbonate and TOF was also significantly reduced. The coupling reaction is clearly more productive at higher temperatures and reaction times can be reduced substantially at temperatures above 100 °C. For example, Table 3-3, entry 11 (160 °C, 4 h) also gave near quantitative conversion of styrene oxide (97%).

The low melting point of Co(II) DES means that the catalyst remains in the liquid phase during reactions. As the catalyst is insoluble in SO, the catalysis is heterogeneous. Therefore, maximizing the contact between the catalyst and the reagents is important. The rate of reaction will increase if the surface area of the catalyst liquid film is increased.

Therefore, reactions performed under identical conditions but in a 100 mL reactor (diameter approx. 5 cm) achieved lower conversions than reactions performed in a 300 mL reactor (diameter approx. 8 cm). Also, as the viscosity of DESs is known to be lower at higher temperatures, a much thinner film of catalyst will be present in a large reactor at higher temperature than a small reactor at low temperature.

Table 3-4 shows the effect of catalyst loading on styrene oxide conversion. When the ratio of Co:SO reaches 1:160, the catalyst amount is sufficient to achieve near quantitative conversion under the conditions stated. Higher loadings of catalyst did not increase the conversion significantly.

**Table 3-4 Optimization of the styrene oxide (substrate) to cobalt molar ratio for styrene carbonate synthesis.**

| Entry | Co : SO | Conv. (%) |
|-------|---------|-----------|
| 1 | 1 : 300 | 75 |
| 2 | 1 : 160 | 97 |
| 3 | 1 : 120 | 97 |

Reaction conditions: $P_{CO_2}$ = 10 bar, T = 160 °C, t = 4 h, 1:2 ChCl/Co DES. All reactions were performed in the 100 mL reactor.

### 3.2.2 Attempted coupling reactions of $CO_2$ and other epoxides using Co(II) DES as a catalyst

Other epoxides were also tested with the Co(II) DES as shown in Table 3-5. Generally propylene oxide (PO) has the highest reactivity towards carbon dioxide cycloaddition with SO being more challenging to react and cyclohexene oxide (CHO) being a very difficult substrate to convert.[84, 94] As these reactions were performed near the beginning of this research, the temperature for the reactions of PO or CHO was low, so it is possible that conversion might be achieved at higher temperatures. When samples from the reactions detailed in Table 3-5 were analyzed, the only compound identified was unreacted epoxide.

**Table 3-5 Attempted coupling reactions of $CO_2$ with other epoxides using Co(II) DES as the catalyst.**

| Entry | Substrate | Co : epoxide | P (bar) | T (°C) | t (h) | Conv. (%) |
|-------|-----------|--------------|---------|--------|-------|-----------|
| 1 | PO | 1 : 267 | 10 | 90 | 24 | n.d. |
| 2 | CHO | 1 : 103 | 40 | 60 | 24 | n.d. |
| 3 | CHO | 1 : 183 | 10 | 100 | 24 | n.d. |

1:2 ChCl/Co DES. n.d. = not detected

### 3.2.3　Characterization of styrene carbonate

The selectivity of the coupling reactions was nearly 100% in all cases (i.e. no polymer, alcohols or other products were detected) as determined by NMR spectroscopy. In $^1$H NMR spectra, only peaks of SC were detected and no peaks of byproducts were seen such as polycarbonates or homopolymer of SO.
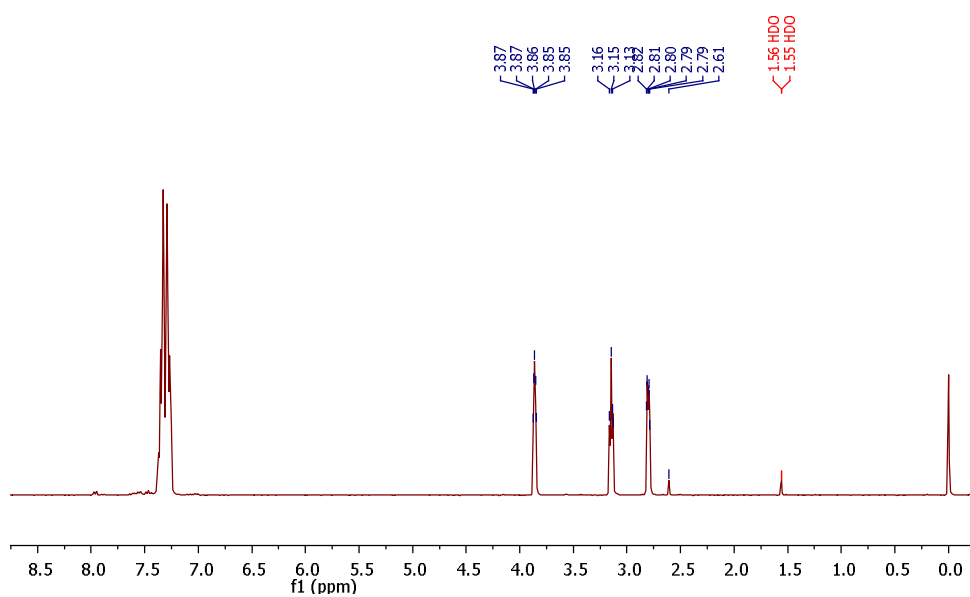


**Figure 3-3 $^1$H NMR spectrum of SO in CDCl$_3$.**
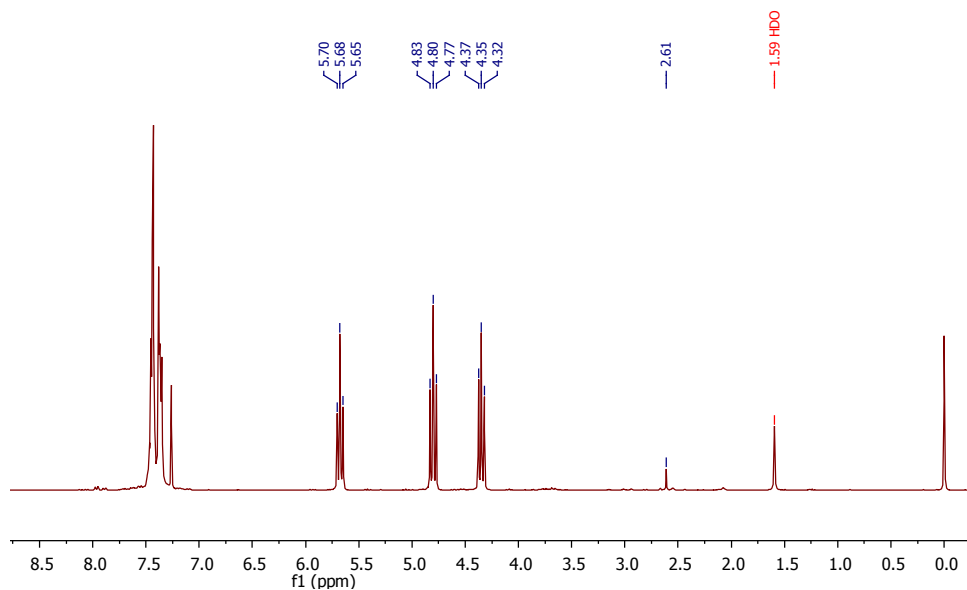
**Figure 3-4 $^1$H NMR spectrum of Entry 3 of Table 3-2 in CDCl$_3$.**

Figure 3-3 shows the $^1$H NMR spectrum of styrene oxide. Figure 3-4 shows the $^1$H NMR spectrum of the reaction mixture from entry 3 in Table 3-2. In the $^1$H NMR spectra for both SO and SC, six H peaks were detected related to the six H atoms (Figure 3-5) in either the substrate or product. The non-aromatic hydrogen peaks of H 4 (3.86 ppm), H 5 (3.15 ppm) and H 6 (2.80 ppm) from SO and H 4' (5.68 ppm), H 5' (4.80 ppm) and H 6' (4.35 ppm) from SC shift most significantly. Therefore, conversion was calculated from the integration of these six peaks.
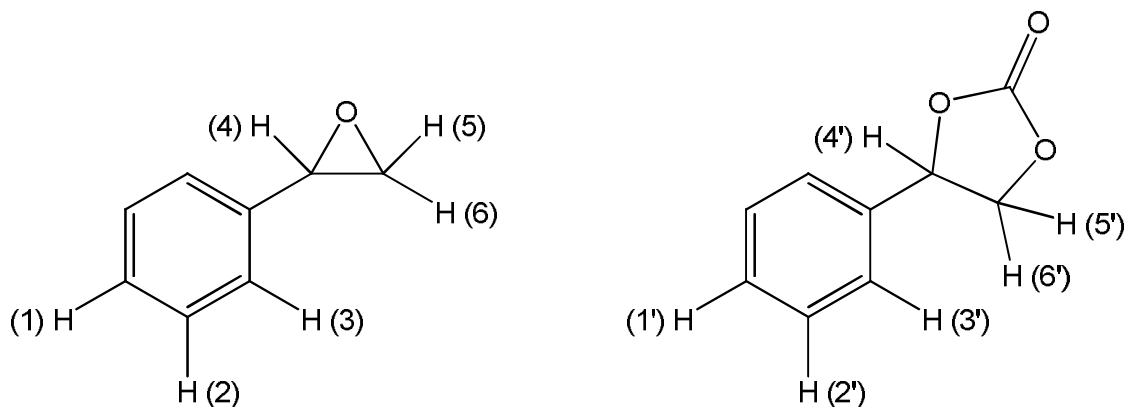
**Figure 3-5 Structures of styrene oxide and styrene carbonate, and labeling scheme for protons in NMR spectra.**

The product of entry 1 in Table 3-2 is a green liquid and was purified by flash chromatography with ethyl acetate and hexane as solvents. The melting point of the purified styrene carbonate measured by DSC apparatus was 55-57 °C, which is similar to that from the scientific literature (55-56 °C). [95]

Figure 3-6 shows the mass spectrum of styrene carbonate from entry 1 in Table 3-2 (EI 70 eV, range 40-170 m/z shown). The peak at *m/z* 164 corresponds to the molecular ion peak for the cyclic styrene carbonate molecule, which further confirmed the structure of product. The peaks at *m/z* 90 and *m/z* 78 are tentatively assigned to a tropylium ion minus one hydrogen radical, and a phenyl ion plus one hydrogen radical, which might be formed in the mass spectrometer.
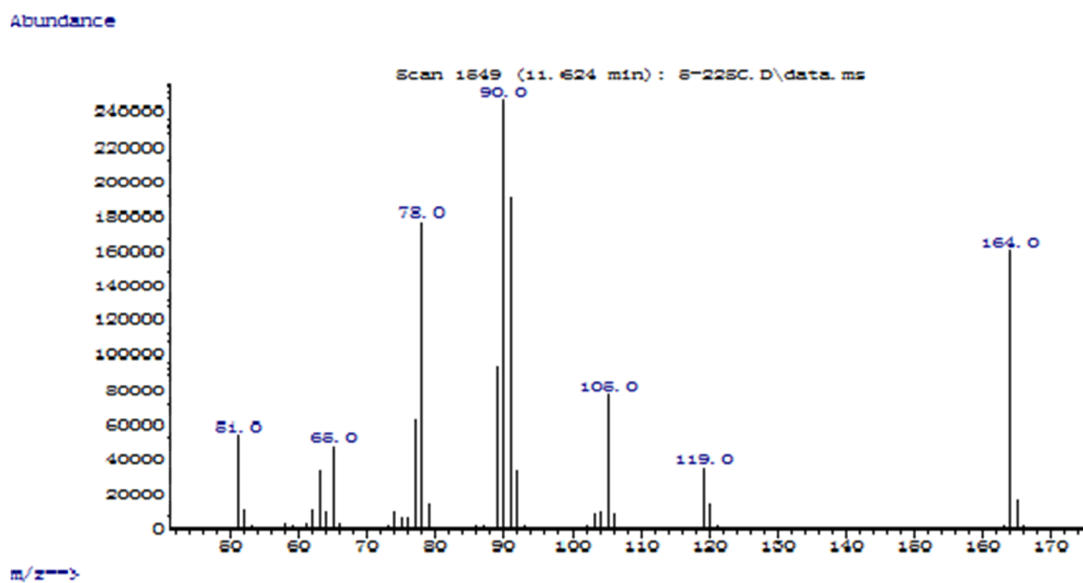
**Figure 3-6 Mass spectrum (EI-MS) of purified styrene carbonate from entry 1 in Table 3-2.**

### 3.2.4  Reaction catalyzed by other DESs.

After the optimization of the reaction conditions, other $3d$ transition metal-containing DESs were used to catalyze the synthesis of styrene carbonate. Table 3-6 shows a list of the reactions performed with different DESs. All the reactions were performed with freshly made DESs in the 100 mL Parr reactor.

**Table 3-6 Styrene carbonate synthesis catalyzed by metal-containing DESs.**

| Metal | T (°C) | Yield. (Conv.) | TON |
|---|---|---|---|
| Co(II) | 160 | 96% (97%) | 134 |
| Cr(III) | 160 | 99% (>99%) | 139 |
| Ni(II) | 160 | 91% (94%) | 127 |
| Mn(II) | 160 | 85% (87%) | 119 |
| Cu(II) | 160 | 35% (38%) | 49 |
| Fe(III) | 160 | 94% (95%) | 132 |
| Fe(III) | 120 | 58% (59%) | 81 |

Reaction conditions: $P_{CO2}$ = 10 bar, t = 4 h, 1:2 ChCl/Metal DES, Metal:SO = 1:140.

Since Cr(III) complexes are often good catalysts for carbonate synthesis, the >99% conversion is not a surprising result. Since iron salts are abundant and non-toxic, it was pleasing to see that Fe(III) system also gave very good conversion comparable with the Co(II) system. The iron-catalyzed reaction was repeated at a lower temperature, which gave a lower conversion, telling us that high temperatures are needed to maintain higher TOF for these systems. The one exception in terms of activity was the Cu(II) system but this cannot be due to an inherent lack of reactivity for Cu(II) in such reactions. A recent paper has described the use of monometallic and trimetallic Cu(II) Schiff base complexes in the production of cyclic carbonates.[96] For SO, the trimetallic complex could achieve TON >3000. At this stage, a good reason for this low reactivity has not been found but

may be due to the viscosity of the DES or another physical phenomenon. Other researchers have looked at series of catalysts with different metal ions (supported on silica and for acac complexes) for cycloaddition reactions.[97, 98] In both of these prior studies Ni(II) salts gave the best result, which is related to the Lewis acidity of the metal ions. However, in our hands Cr(III) exhibited superior reactivity, which we assign to the less viscous nature of this particular DES. The reactions are heterogeneous and Cr(III) DES can form a thinner, higher surface area film within the reactor compared with the other DESs. Further studies are needed to confirm this conclusion and to understand the lower reactivity of the Cu(II) DES.

Data for reactions using other metal-containing catalyst systems for carbon dioxide/epoxide coupling reactions are shown in Table 3-7 for comparison. The TOF for the DES systems in this thesis are comparable with the $ChCl/ZnBr_2$ system and ChCl/urea/molecular sieves system. However, such catalysts are disappointing when compared with the $TBACl/CoCl_2$ system from Repo's work, which achieve TON of more than 1000. This means that the onium salt used in such reactions is critically important, as the main difference between the studies in this thesis and that work is the use of ChCl herein. ChCl alone has also been reported to have moderate activity for cycloaddition reactions at higher temperatures and pressures compared to the control reactions in this thesis (Table 3-1) where little to no reactivity was observed.

**Table 3-7 Selected catalyst and reaction data for cycloaddition reactions for comparison with metal-containing DESs.**

| Catalyst | Reaction conditions | Yield (Conv.) | TON | Ref |
|---|---|---|---|---|
| ChCl | PO:Cat 40:1 | 83% | 33 | [91] |
| | 140 °C, 80 bar, 8 h | | | |
| (MeHNCH$_2$COOH)I | SO:Cat 46.5:1, | 79% (80%) | 36.7 | [99] |
| | 120 °C, 12 bar, 2 h | | | |
| ChCl/Urea/molecular sieves (6.7 nm) | SO:Cat 100:1, SO:CO$_2$ 1:1.67 | 95% | 95 | [100] |
| | 110 °C, 5 h | | | |
| ChCl/ZnBr$_2$ | SO:ChCl:Zn 100:1:0.2 | 98% | 490 | [94] |
| | 110 °C, 15 bar, 12 h | | | |
| TBACl/CoCl$_2$ | SO:TBACl:Co 2000:4:1 | n.r. | 1031 | [84] |
| | 120 °C, 10 bar, 1h, 0.5 mL DCM | | | |
| Co(acac)$_2$ | SO:Et$_4$NBr:Co 100:1:1 | 60% | 60 | [98] |
| | 50 °C, 50 bar, 4.5 h | | | |
| Ni(acac)$_2$ | SO: Et$_4$NBr:Ni 100:1:1 | 97% | 97 | [98] |
| | 50 °C, 50 bar, 4.5 h | | | |

n.r. = not reported

## 3.3 Experimental

### 3.3.1 General information

Styrene oxide (SO) (97%), propylene oxide (PO) (99%) and cyclohexene oxide (CHO) (98%) were purchased from Sigma-Aldrich. SO and PO were directly used without purification. CHO was purified through vacuum distillation. Acetonitrile (HPLC grade) was purchased from Caledon Laboratories. The DESs were used within 6 h of their preparation.

### 3.3.2 General procedure for cyclic carbonate synthesis

The reactions were carried out in a 300 mL or 100 mL stainless steel Parr reactor with an overhead mechanical stirrer. In a typical reaction set-up, the catalyst (DES) and epoxide were loaded into the vessel and then the vessel purged with $CO_2$ several times. The reactor was then pressurized with the appropriate amount of $CO_2$ and heated to the desired temperature. After the required reaction time, the reactor was cooled in an ice bath and vented. The contents were removed, filtered through a short silica column and analyzed by NMR spectroscopy and GC-MS.

### 3.3.3   NMR and GC-MS

NMR procedure: A Bruker 300 MHz NMR spectrometer was used. The solvent was chloroform-d and spectra were referenced to the residual protons of this solvent. Spectra were collected at 25 °C.

GC-MS method: The products were analyzed using an Agilent Technologies 7890 GC with 5975 MSD. 1 μL of sample (dissolved in diethyl ether or ethyl acetate) was injected through a 7683B Series Injector using a split mode of 50%. The GC separation was done using a DB5 column at a flow rate of 1 mL/min He 99.999%. The oven temperature was programmed as follows: 60 °C (hold for 3 min), 15 °C/min$^{-1}$ to 270 °C, hold at final temperature for 5 min. For the first 3.50 min, the eluent was routed away from the mass detector. The products were detected using a 5975C VLMSD with Triple-Axis Detector (EI 70 eV, scan range 50-500 mz, continuous scan mode, T = 150 °C (quad), 230 °C (source) and 250 °C (transfer line), repeller 29 V, ion focus 80 V).

### 3.4   Conclusions

ChCl/urea DES and ChCl/MCl$_x$ DES have been reported to be efficient catalyst for various reactions (Chapter 1, Section 1.2.3). In this work, DESs synthesized from choline chloride and metal chloride hydrates were used to catalyze the coupling reaction of $CO_2$ and styrene oxide. The reaction was performed with different metal-containing DESs. Under the optimized conditions (T = 160 °C , P$_{CO2}$ = 10 bar, t = 4 h), Co(II), Cr(III), Ni(II), Fe(III) DESs showed the highest catalytic activity for this coupling reaction with conversions of over 90%. The reaction with the Mn(II) DES achieved a

lower conversion of 87%, while Cu(II) afforded the lowest conversion. It is proposed that the reactivity of these DESs is related to their viscosity, as the Cr(III) DES was the least viscous and achieved the highest conversion levels possibly due to the high surface/contact area. Co(II) DES was chosen to optimize the reaction conditions due to previous research using cobalt catalysts in the Kerton group.[101] The presence of solvent, catalyst (its identity and loading), pressure (P) and temperature (T) were varied in order to determine the effect of each parameter. It became apparent through these studies that solvent was not needed, high pressures were not required (10 bar was sufficient) and the most significant factor was the temperature at which reactions were performed.

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