Cyclic Carbonates Synthesis via Catalytic Cycloaddition of Carbon Dioxide and Epoxides using Sustainable Metal-based Catalysts and Organocatalytic Systems

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Academic Dissertation

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Abstract

The conversion of carbon dioxide (CO_2), an abundant renewable carbon reagent, into cyclic carbonate is of academic and industrial interest. Cyclic carbonate serve as green solvent and have some outstanding properties such as a high boiling point and low toxicity. Titanium and iron would be attractive metal candidates as benign and efficient alternative to other metal catalysis for CO_2 conversion to cyclic carbonate, due combination of low toxicity and high Lewis acidity.

In the present work the coupling reactions of carbon dioxide with epoxides to produce five-membered cyclic carbonates (propylene, 1-hexene, cyclohexene, styrene, and epichlorohydrin carbonates) were efficiently catalyzed either by sustainable metal-based catalysts of: (1) titanium alkoxide complexes/tetrabutylammonium salts; (2) Schiff base iron(III) complexes/onium salts; (3) bifunctional imidazole-Schiff base iron(III) complex; and (4) metal-free systems consisting of a simple, preferably primary or secondary, amines and halides with organic or inorganic cations (such as tetrabutylammonium or lithium chloride, bromide or iodide). Reactivity of the four above-mentioned catalytic systems was further studied and compared in the coupling reactions. Three possible reaction pathways for catalyzed CO_2/epoxide coupling reaction have been proposed. Route I begins with coordination of an epoxide molecule to the Lewis acidic Ti- or Fe- center, the nucleophilic halide-ion ring opens the epoxide to afford an alkoxide intermediate; CO_2 insertion into the M-O bond, followed by ring closure yields the product. Route II, imidazole-Schiff base Fe(III) molecule serve as Lewis acid for epoxide activation and simultaneously as counter ion for the nucleophile to start ring opening of the epoxide. In route III, the Lewis basic amine activates the CO_2 by forming the carbamate molecule and the halide-ion ring opens the epoxide; and then coupling of epoxide with CO_2; ring closure gives the cyclic carbonate. The first and fourth systems were found to be efficient catalysts for the coupling reactions of CO_2 with neat epoxides. The iron(III) catalysts are required to be dissolved in proper solvents to afford the corresponding cyclic carbonates in moderate to high yields.

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'I dedicate this work to my Mother, Jamilah, whose endless love and prayer inspired me in this life. It was her support, and encouragement that helped me to go through this stage successfully. To my brother, Ahmad, and to my durable daughters Layan & Lilian who brought the truth meaning of love to my world'

List of Original Publications

This thesis is based on the following publications cited in the text with Roman numbers.

I. F. Al-Qaisi, E. Streng, A. Tsarev, M. Nieger and T. Repo, Titanium Alkoxide Complexes as Catalysts for the Synthesis of Cyclic Carbonates from carbon Dioxide and Epoxides, *European Journal of Inorganic Chemistry,* **2015**, 5363–5367.

II. F. Al-Qaisi, N. Genjang, M. Nieger and T. Repo, Synthesis, Structure and Catalytic Activity of Bis(phenoxyiminato)Iron(III) Complexes in Coupling Reaction of CO_2 and Epoxides, *Inorganica Chemica Acta,* **2016**, 442, 81-85.

III. F. Al-Qaisi, M. Nieger, M. Kemell and T. Repo, Catalysis of Cycloaddition of Carbon Dioxide and Epoxide using a Bifunctional Schiff base Iron(III) Catalyst, *ChemistrySelect*, **2016**, 3, 545–548.

IV. F. Al-Qaisi, K. Chernichenko, A. Tsarev, A. Abu-Surrah and T. Repo, Kinetics and Mechanistic Insight into Synthesis of Cyclic Carbonates from CO_2 and Epoxides by Cooperative Amine-Halide Catalysis. Submitted.

Scope of the Thesis

The following literature review provides a broad perspective of the concepts presented by the papers included in the thesis. Discussing of CO_2 chemistry followed by background about cyclic carbonate synthesis in industry and their functions, particular five-membered cyclic carbonates based on phosgene production, and the effective catalytic methods have been used to synthesize cyclic carbonate from carbon dioxide and epoxide.

The aim of the thesis is to evaluate catalysis as an environmentally benign alternative to the conventional chemical processes for cyclic carbonate synthesis via CO_2 fixation with features making them suitable as replacements for currently available toxic methods. Furthermore, the value-driven nature of this research is underpinned by the abundance, low cost, optimum atom economy, and environmental features underlying the use of carbon dioxide as a C-1 feedstock.

This thesis is based on the following publications,

Paper I presented synthesis of new titanium(IV) alkoxide complexes and also demonstrated their effective use as catalysts in the synthesis of a wide range of cyclic organic carbonates derived from carbon dioxide and terminal epoxides.

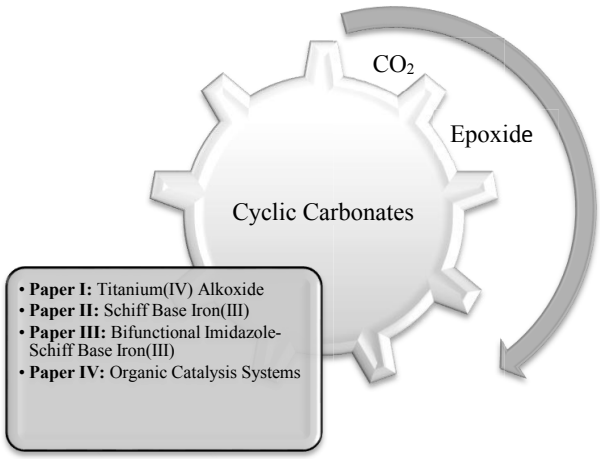
The low toxicity and price of iron makes this metal an extremely interesting candidate as the basis of new catalytic systems; therefore, this fact promoted the production of **Paper II** and **III.**

Paper II was presented as a detailed study of the reaction of the epoxides and CO_2 catalysed by new Schiff base iron(III) complexes, in which we have been able to achieve dramatic improvements compared to the previously-reported systems, both in terms of much higher activity and of full control of the selectivity towards the cyclic product.

Paper III was focused on the development of an effective method of cyclic carbonate synthesis from carbon dioxide and selected epoxides with the use of bifunctional Schiff base Fe(III) catalysts involving the imidazole unit. The scope of the research included the synthesis of catalysts, as well as performing a reaction of obtaining cyclic carbonates in order to select an effective and stable system suitable for practical application.

The results of these three papers promoted the development of **Paper IV** in order to develop a more environmentally benign (metal and solvent free) method for synthesis of cyclic carbonates.

Paper IV was focused on the employment of a series of commercially available amines with halide salts as catalytic systems for cyclic carbonate synthesis from CO_2 and epoxides, and the reaction parameters were studied under solvent and metal free conditions. In addition, kinetic studies were performed to further understand the mechanism of the coupling reaction.



List of Abbreviations

CHO	Cyclohexene Oxide
CPO	Cyclopentene Oxide
CS	Chitosan
DBU	1,8-Diazabicycloundec-7-ene
DCM	Dichloromethane
DMAP	4-Dimethylaminopyridin
DMF	Dimethylformamide
ECH	Epichlorohydrin
ee	enantiomeric excess
HO	1-Hexene Oxide
IL	Ionic Liquid
LA	Lewis acid
LB	Lewis base
M	Metal
PC	Propylene Carbonate
PO	Propylene Oxide
PPC	Poly(Propylene Carbonate)
RT	Room Temperature
SO	Styrene Oxide
TBAB	Tertrabutylammonium bromide
TBD	1,5,7-Triazabicyclo[4.4.0]dec-5-ene
TS	Transition state

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1 Introduction

Since petroleum resources are predicted to be exhausted within the next century at the current rate of consumption,[1] there is a growing effort to develop new chemical processes using bio-renewable resources.[2] One such resource of particular interest is CO_2, a nontoxic, nonflammable, and naturally-abundant.[3]

1.1 Carbon Dioxide

Carbon dioxide is one of the gases in our atmosphere, which is uniformly distributed over the earth's surface at a concentration of about 400 ppm.[4] Commercially, CO_2 has also found growing application as a technological fluid in several industrial sectors such as a refrigerant (dry ice is solid CO_2), in beverage carbonation, in fire extinguishers, and for air conditioning. It is also employed in cleaning fluid, as a solvent for reactions, as a solvent for nano-particle production, and in separation techniques and water treatment, as well as in the food and agro-chemical industries (packaging, additive to beverages, fumigant).[5] Most commercial carbon dioxide is recovered as a by-product of other processes, such as the production of ethanol by fermentation and the manufacture of ammonia. Some CO_2 is obtained from the combustion of coke or other carbon-containing fuels (**Scheme 1.1**).

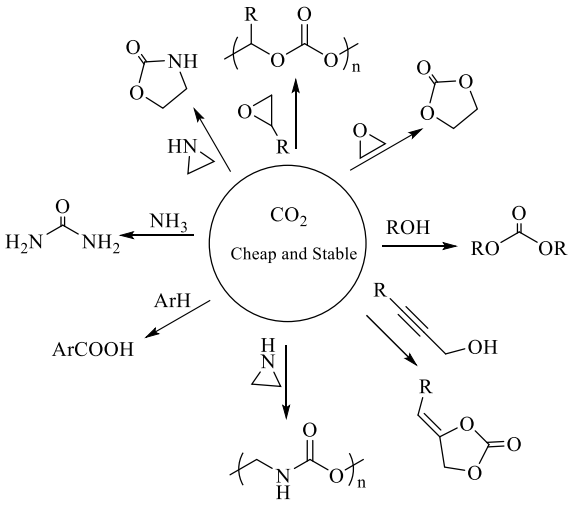
$$C(coke) + O_2(g) \rightarrow CO_2(g)$$

Scheme 1.1. CO_2 from coke combustion.

Carbon dioxide is released into our atmosphere when carbon-containing fossil fuels such as oil, natural gas, and coal are burned in air. As a result of the tremendous world-wide consumption of such fossil fuels, the amount of CO_2 in the atmosphere has increased over the past century, and is now rising at a rate of about 2 ppm per year.[6] Major changes in global climate could result from a continued increase in CO_2 concentration.

Taking such environmental considerations into account, the chemical utilization of excess CO_2 is an important topic. Carbon dioxide is considered to be a renewable source of carbon but conversely, it is inert (CO_2 is the most stable form of oxidized carbon compounds) and hard to activate. To overcome the high energy barrier, the electrophilicity of the carbonyl carbon should be enhanced and the electron density on the catalyst should also be increased.[7] In order to use carbon dioxide in a more benign and practical manner, efficient transformations with less activated substrates under mild conditions must be developed. Obviously, reactions of CO_2 that require a high-energy input are not benign because in general this energy leads also to formation of CO_2.

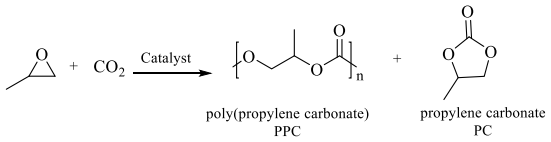
The utilization of carbon dioxide as a source of carbon in synthetic chemistry has been a practice exploited at the industrial level since the second half of the 20th century for the synthesis of urea[8] and salicylic acid.[9] CO_2 has also long been used for making inorganic carbonates and pigments. A renewed interest in the industrial utilization of CO_2 as a source of carbon arose after the 1973 oil crisis.



Scheme 1.2. Representative examples using CO_2 as C1 building block in organic synthesis.[10]

Carbon dioxide reacts with hydrogen, alcohols, acetals, methanol, epoxides, amines, carbon–carbon unsaturated compounds, and other reagents in supercritical carbon dioxide or in other solvents in the presence of catalysts. The products of these reactions are formic acid, formic acid esters, formamides, dimethyl carbonate,

alkylene carbonates, carbamic acid esters, lactones, carboxylic acids, cyclic carbonate, polycarbonate (bisphenol-based engineering polymer), aliphatic polycarbonates, and other compounds (**Scheme 1.2**).[10] One of the more successful processes for CO_2 utilization for material synthesis is the catalytic production of cyclic carbonates and polycarbonates from epoxides,[11] which has also been industrialized (**Scheme 1.3**).[12,13] Incorporation of CO_2 into carbonates is a potentially significant transformation for the decrease of carbon dioxide level in the atmosphere.



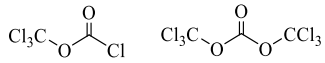
Scheme 1.3. Coupling reaction of CO_2 with epoxide.

1.2 Cyclic Carbonate

Synthesis of cyclic carbonate has been commercialized and is industrially important; example of industrial important carbonares, dimethyl carbonate (DMC), diphenyl carbonate (DPC), ethylene carbonate (EC) and propylene carbonate (PC). Cyclic carbonates can be used as electrolytes in lithium ion batteries.[14] Five- and six-membered cyclic carbonates are excellent aprotic polar solvents which are used extensively as intermediates in the production of fine chemicals such as plastics, and pharmaceutical materials.[15] Furthermore, cyclic carbonates are important raw materials for polyurethane synthesis,[16] and as alternatives to phosgene or dimethyl sulfate for methylation reactions.

Although phosgene remains the most commonly-used reagent for the industrial and academic synthesis of cyclic carbonate, some other reagents have been developed with similar reactivity but less toxicity and which are easier to handle. This family of alternative reagents contains trichloromethyl chloroformate (diphosgene)[17] and bis-(trichloromethyl)carbonate (triphosgene)[18] (**Scheme 1.4**). The advantages of these two phosgene alternatives is that at ambient temperature they are liquid and solid respectively and only generate phosgene *in situ* once activated. The alternative route

that excludes phosgene from the process is attractive as cyclic carbonate synthesis has 100% atom efficiency.[19]



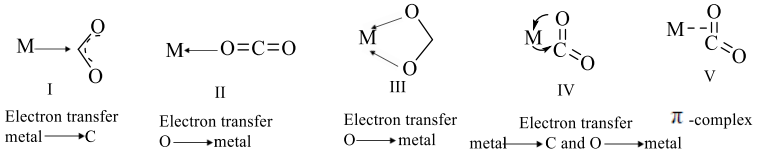
Scheme 1.4. Structures of phosgene derivatives.

The production of five-membered cyclic carbonates from CO_2 has been industrialized since the 1950s. The history of coupling CO_2 with epoxide has been known since 1969 when Inoue *et al.* combined $ZnEt_2$, water, CO_2, and propylene oxide (PO) to yield a small quantity of polymeric material.[20] The subsequent investigations in this area were frequently frustrated by low catalytic activities and competitve formation of polycarbonates and/or undesired by-products, such as high degrees of ether linkages in the polymer chains. Furthermore, many systems that show polymer formation with the cyclohexene oxide (CHO)/CO_2 system, only yield cyclic carbonate or show no conversion at all with PO/CO_2 as monomers. A wide range of catalysts have been explored for the generation of cyclic carbonates using CO_2. The most effective of these were found to be organometallic and salen complexes,[21] metal oxides,[22] alkali metal salts,[23] supported phase catalysts,[24] phosphines,[25] quaternary onium salts,[26] ionic liquids,[27] and metal organic frameworks.[28]

1.3 Cyclic Carbonate Synthesis Catalyzed by Metal Complexes

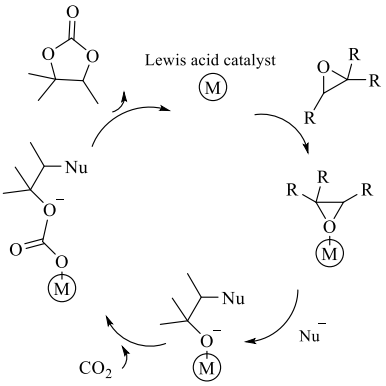
An insightful understanding of the detailed organometallic chemistry of CO_2 is of great importance for the further design of the catalytic processes. In fact, the coordanation mode between transition metal centres and CO_2 has been investigated intensively via stoichiometric experimental studies.[29] As shown in **Scheme 1.5**, CO_2 has multiple reactive sites: the carbon atom is an electrophilic Lewis acid centre and the oxygen atoms act as a weak nucleophilic Lewis base. In its ground state, carbon dioxide possesses two equivalent C-O bonds that could both coordinate to a transition metal centre. As a result, a series of transition metal CO_2 complexes are known.[30] If a metal centre reacts with one molecule of CO_2, there are five different chelating modes possible. More specifically, complex **I** with an M-C bond is sometimes termed as a metallacarboxylate. Electron-rich metal centres are more feasible to form these types

of complexes via electron transfer from metal centre to carbon atom. Adduct **II** (end-on type) seems less plausible due to the weak interaction between the lone pair of only one oxygen atom and the metal centre. Meanwhile, complex **III** should be more stable, since CO_2 acts as a bidentate ligand with two oxygen atoms. In this case, a more electron-deficient metal centre is favoured for the electron transfer from oxygen atom to transition metal. A combination of the two above-mentioned electron transfer processed affords the three-membered metallacycle complex **IV**. Moreover, the side-on-bonding π-complex **V** can also be formed in a similar spatial arrangement of atoms through the coordination of the C-O double bond to the central metal. On the basis of these different coordination and activation modes, well-designed transition metal catalysts are able to promote the reactivity and also control the selectivity of CO_2 fixation reactions in the organic synthesis. This promising research area still has many novelties to be discovered.



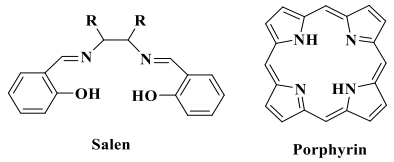
Scheme 1.5. Coordination modes of CO_2 with transition metals.[10]

Accordingly, the most plausible proposed mechanism for epoxide/cyclic carbonate chemical fixation reaction of CO_2 that the system is cocatalyzed by a Lewis base and Lewis acid (complex). The Lewis base and Lewis acid work together to open the epoxy ring and then react with CO_2 to give the corresponding cyclic carbonate via a ringopening and recyclization process (**Scheme 1.6**). Previous reports also suggest the parallel requirement of both Lewis base activation of the CO_2 and Lewis acid activation of the epoxide.[31]



Scheme 1.6. Key steps for the coupling of CO_2 and epoxide to yield cyclic carbonate.[31]

Many new methodologies for cyclic carbonate synthesis from CO_2/epoxide coupling have been developed. In particular, the fixation of the CO_2 by different metal-based ligands.[9] The two most active catalyst families are based on the series of bis(salicylaldiminato)-metal complexes and tetra-dentate metal complexes. Catalysis based on (salen)-metal complexes have seen significant progress. Salen-metal catalysts originally evolved from the metal porphyrinate catalysts (**Scheme 1.7**).



Scheme 1.7. Structure of salen vs porphyrinate based ligands.

Porphyrin-based catalysts represent a powerful catalytic system for CO_2 coupling with epoxide. These catalysts are characterized by planar geometry, which is beneficial for the coordination of terminal epoxides. Moreover, they can be used for the development of bifunctional molecular catalysts to evaluate the effect of the type of central metal atom and of the embedded co-catalyst. The most noticeable example is the work of Sakai *et al.*[32] Initially, utilizing bifunctional metalloporphyrin complexes containing both a Lewis acid (LA) centre and nucleophilic peripherical pendants (1:4 LA/cocat site ratio, 1-hexene oxide (HO) as substrate) within the same molecular structure (**1, Scheme 1.8**), they have measured one of the highest TONs for homogeneous metal-based catalysts. In particular, a TON of 103,000 (after t = 24 h) and initial TOF of 12,000 h^{-1} were observed, obtained after careful optimization of the porphyrin

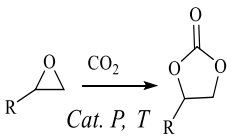
structure in terms of the type of the Lewis acidic metal centre and nucleophilic co-catalyst. To further enhance the catalytic activity of these bifunctional Mg(II) porphyrin systems, a Mg(II) porphyrin complex ligated to eight tetraalkylammonium bromide groups (i.e., a 1:8 LA/cocat site ratio) was prepared.[31b] Consequently, owing to the increased number of anionic nucleophilic centres tightly coordinated to the cationic catalyst molecule, higher TONs were achieved in 24 h (TON = 138,000) and an increased initial TOF of 19,000 h^{-1} (conditions: cat =0.0005 mol. %, CO_2 (17 bar), T = 120 °C). For these bifunctional Mg(porphyrin)-based catalysts, the authors suggested a cooperative effect of embedding the nucleophilic moiety (Br) and the Lewis acidic metal centre in a tight coordination sphere, leading to a simultaneous epoxide activation/nucleophile attack. It was indeed observed that by increasing the number of nucleophilic centres associated through ionic interactions to the same porphyrin framework, the measured TONs and TOFs were higher. The maximum TOF observed for the trinuclear Mg(porphyrin) complex was 46,000 h^{-1}, and the maximum TON was 220,000 (0.0003 mol. % 11, 72 h, 120 °C) with a normalized TOF/Mg centre of 15,333 h^{-1}. The same study was extended to less Lewis acidic Zn(II)porphyrin-based catalysts.[33] Although the bifunctional Zn(II) catalysts demonstrate somewhat lower initial activity than the corresponding Mg(II)porphyrin, they have been shown to be more robust at higher temperature. The trinuclear Zn(II)-based catalytic system was active for 5 days, displaying a TON of 310,000 and an average TOF of 2580 h^{-1} (conditions: cat = 0.0003 mol. %, CO_2 (17 bar), T = 120 °C). Its robustness was further proved by employing this catalyst for t = 5 days at T = 160 °C, observing no appreciable catalyst decomposition, whereas under the same experimental condition. The trinuclear Mg-based catalyst decomposed.

1.3.1 Salen Catalysts

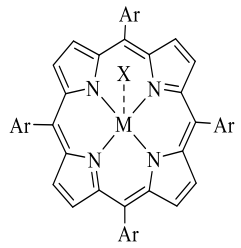
Typically, salen complex offers following advantages: 1) salen and salphen ligands are easily synthesized in contrast to porphyrins, allowing for large-scale synthesis and potential commercial applications; 2) the modular construction of salen/salphen from diamines and salicyladehydes enables easily tuning of steric and electronic properties, by ad hoc structure modifications; the possibility of direct inclusion of a nucleophilic co-catalyst, variation in the type of active metal centre, and formation of mono- and

multinuclear catalysts. In particular, several salen-based complexes of Cr, Mn, Co, Al, and Zn have been found to be remarkably efficient catalysts for this conversion.[34]

The utilization of salen complexes was inspired by Jacobsen's success with their application in asymmetrically ring-opening reactions of epoxides (**2, Scheme 1.8**).[35] Mechanistically, Jacobsen showed that the key reaction step is the formation of a chromium–alkoxide bond through a bimetallic initiation process. Subsequently, if CO_2 could insert into this type of bond, the utilization of (salen)Cr^{III} complexes as a cycloaddition or copolymerization catalyst would be reasonable. As a continuation of employing the advantages of replacing the porphyrin unit by salen, Paddock and Nguyen [36] changed the coordination environment around the Cr(III) porphyrin complex prepared by Kruper *et al*.[37] by using a salen ligand for the same reasons mentioned above. The variation of the diamine backbone resulted in a prominent change of the catalytic activity. This catalytic system can operate efficiently at relatively low CO_2 pressure (8 bar) and temperature (100 ºC). In 2002, Lu and He reported utilizing various metal–salen complexes in conjunction with a quaternary ammonium or phosphonium salt as co-catalyst for the coupling of CO_2 and ethylene oxide to afford cyclic ethylene carbonate.[38] Although the work was primarily focused on salen Al(III)X catalysts, comparative studies were carried out using a series of other metal–salen complexes, such as Mg-, Cr-, Co-, Ni-, Cu-, Zn-Salen, towards the reaction.



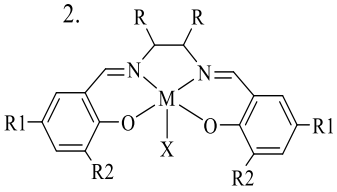
1.



Metaloporphyrine catalysts

M=Al^{III}, X= OMe, Ar= Ph
Inoue *et al.*, 1983
M= Co^{III}, X= OTs, Ar= Ph
CO_2(7 bar), 20 ^oC, up to 930 TON, 93%
Jug *et al.*, 2007
M=Mg^{II}, Ar= 3-O$(CH_3)_6$N-Bu_2Br-, Ph
CO_2 (17 bar), 120 ^oC up to 103,000 TON
12 000 h^{-1} TOF, 83% yield
Sakai *et al.*, 2012
M= Zn^{II}, CO_2 (17 bar), 120 ^oC up to 310 000 TON
2580 h^{-1} TOF
Ema *et al.*, 2015

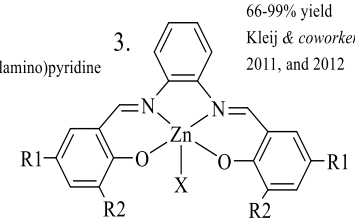
2.



Salen catalysts

M=Cr^{III}, X= Cl, R1,R2=*t*Bu
Jacobsen *et al.*, 2000
M=Cr^{III}, X= Cl
CO_2 (8 bar), 100 ^oC, (4-methylamino)pyridine
up to 916 TON
Nguyen *et al.*, 2001
M=Al^{III}, X=CL, R1,R2=*t*Bu
Lu and He, 2002
M= Zn^{II}, R2=tBu
CO_2(2 bar), 25 ^oC, Bu_4NI
up to 86%yield
Kleij *& coworkers*, 2011
M= Al, X= Cl, R1= imidazolium-based ionic liquid moieties
CO_2 (10 bar), 100 ^oC, up to 90% yeild
Hongbing *et al.*, 2014

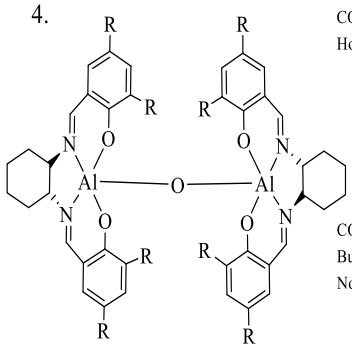
3.



Salphen catalysts

CO_2(1-10 bar), 25-45 ^oC
66-99% yield
Kleij *& coworkers*, 2010, 2011, and 2012

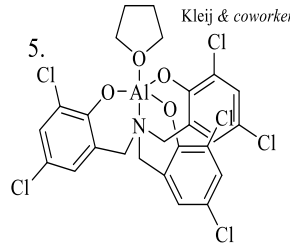
4.



Bimetalic aluminum(salen) catalyst

CO_2 (1bar), 25 ^oC
Bu_4NBr, up to 850 TON
North *& coworkers*, 2010

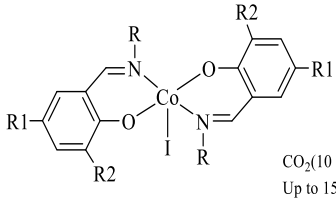
5.



Aminotriphenolate catalyst

CO_2(10 bar), 90 ^oC, Bu_4NI
Up to 112,000TON,
36,000 per hour TOF
Kleij *& coworkers*, 2013

6.

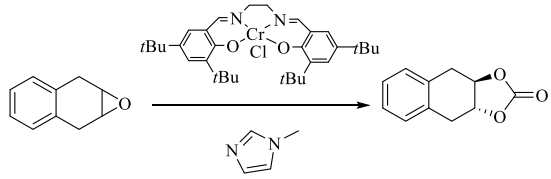


Schiff base catalyst

CO_2(10 bar), 145 ^oC, 2 h, Bu_4NBr
Up to 1500TON
Repo *& coworkers*, 2009

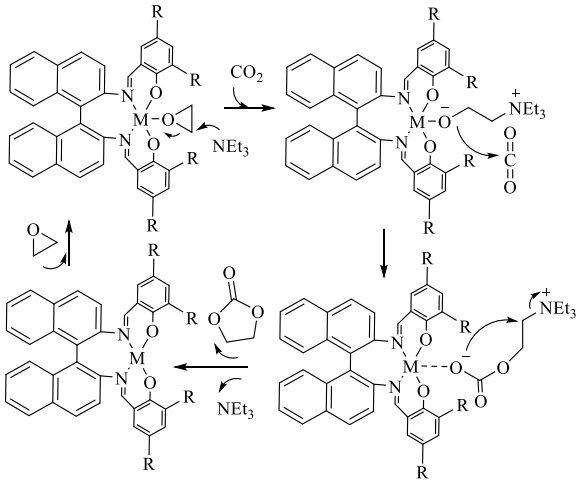
Scheme 1.8. Established catalysts and reaction conditions for the catalytic production of cyclic carbonate.

Darensbourg *et al*. used a simplified Cr salen catalyst system, in conjunction with N-methylimidazole co-catalyst, to couple 2,3-epoxy-1,2,3,4-tetrahydronaphthalene and CO_2 (55 bar, 80 °C, **Scheme 1.9**). Unfortunately, coupling of this epoxide was particularly slow. From monitoring the reaction via *in situ* IR, the authors found the reaction produced equal amounts of polycarbonate copolymer and cyclic carbonate. Nevertheless, after prolonged reaction times (24 h), the cyclic carbonate became the major product and was isolated with a 20% yield.[39] These results led Shi and coworkers[40] to explore other Cu(II), Zn(II), and Co(II) salen-type complexes (**Scheme 1.10**) as potential catalysts for the reaction of epoxides and CO_2. Similar to the Cr-based systems prepared by the Nguyen and Darensbourg laboratories, these salen catalysts also require the addition of an amine-base co-catalyst, specifically NEt_3 (20 mol. %), to ensure complete conversion to the carbonate (89-100% yields) at 100 °C and 34.5 bar of CO_2. Using an enantiopure Cu salen catalyst, low levels of selectivity (3-5% ee) were obtained in the reaction between propylene oxide and CO_2. More recently, they found that a variety of Schiff bases in the absence of transition metal efficiently catalyzed the coupling reaction of CO_2 and epoxides.

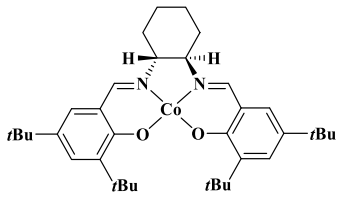


Scheme 1.9. Darensbourg's simplified Cr salen catalyst system.

Interestingly, Darensbourg and Moncada found that (1R,2R)-(-)-1,2-cyclohexanediamino-N,N-bis(3,5-di-tert-butylsalicylidene) cobalt(II)) (**Scheme 1.11**)[41] in the presence of an anion initiator, e.g. bromide, is a very effective catalytic system for the coupling of oxetane and carbon dioxide, to provide the corresponding polycarbonate with minimal amount of ether linkages. The mechanism of the coupling of oxetane and carbon dioxide has been studied by *in situ* infrared spectroscopy, where the first formed product is trimethylene carbonate (TMC). TMC is formed by a backbiting mechanism following ring-opening of oxetane by the anion initiator, subsequent to CO_2 insertion into the cobalt-oxygen bond.



Scheme 1.10. Cu(II), Zn(II), and Co(II) salen-type complexes of Shi's group and their proposed mechanism.



Scheme 1.11. Darensbourg's (salen)Co(II) complex.

North *et al.* reported communicated a dinuclear μ-oxo-bridged Al(salen) complex catalytically active at room temperature and atmospheric pressure of CO_2 for the formation of cyclic carbonates from terminal aliphatic and aromatic epoxides (**4, Scheme 1.8)**. The improved catalytic activity observed when compared with monometallic salen complexes has been ascribed to the presence of two neighbouring metal centres capable of simultaneous activation of both oxirane and CO_2 by promoting an intramolecular nucleophilic attack of the alkoxide to the carbon atom of the activated CO_2 molecule.[42] Furthermore, several salen Al complexes functionalized by polyether-based imidazolium ionic liquieds (ILs) have been first prepared and act as catalysts for the cycloaddition reaction of CO_2 and various epoxides to provide cyclic carbonate at 10 bar of CO_2 and 100 ºC. The salen aluminum complexes proved to be efficient and recyclable homogeneous catalysts towards the organic solvent-free synthesis of cyclic carbonates from epoxides and CO_2 in the absence of a co-catalyst. The catalysts presented excellent "CO_2 capture" capability due to the molecules

containing polyether chains and the metal aluminum center, in which >90% yield of cyclic carbonate could be obtained under mild conditions.[43]

1.3.2 Salphen Catalysts

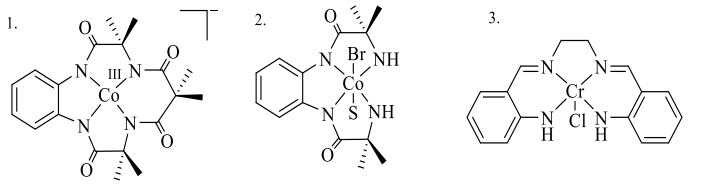
On the other hand there are few examples reported of salphen catalysts, thereafter shortly, Kleij's group reported on a mononuclear Zn(salphen) complex (**3, Scheme 1.8**) active toward CO_2 coupling with terminal epoxides under moderate CO_2 pressures ($p(CO_2)$ = 2 to 10 bar) and mild operating temperatures (T= 25 to 45 °C).[44] The high activity of the Zn(salphen) complex was ascribed to its constrained geometry imposed by the ligand scaffold, which imparts increased Lewis acid character to the catalytically active Zn ion. Moreover, the presence of bulky substituents (R = *t*Bu) in the ortho positions of the two iminiphenol donors prevents undesired dimerization and, thus, inactivation of the Zn(salphen) catalyst.[45] Although efficient, these Zn(salphen) systems suffer some limitations, requiring relatively high catalyst loadings (2.5 mol. %) and a scope limited to terminal epoxides.

1.3.3 N_4-Ligand Based Catalysts

The fourth active catalysis was based on tetradentat ligand. Ghosh *et al*. reported a cobalt-tetraamidomacrocyclic complex (**1, Scheme 1.12**) as a new catalyst for the synthesis of aromatic and aliphatic cyclic carbonates in excellent yields, high selectivity, and fast reaction rates.[46] Structurally, the catalyst resembles porphyrin or salen complexes but has four deprotonated N atoms which act as strong donor ligands to coordinate to Co(III) ion. They inferred that the catalyst would provide the following advantageous characteristics: (a) much more robustness than any salen complexes, especially hydrolytic stability; (b) possesses planar four coordinate geometry (as revealed by the crystal structure of the cobalt complex), and thus leaves two axial positions still available for binding, a crucial feature for allowing the docking of epoxide on the Lewis acidic metal center and facilitate the reaction with carbon dioxide; (c) can easily be synthesized; (d) is uncreative towards oxygen and moisture, and thus can be handled without any specialized equipment, and (e) shows no agglomeration (unlike metal phthalocyanine or porphyrin complexes) and has flexible

solubility including in many epoxides. The same group later reported that bisamino-bisamide Co(III) complex (**2, Scheme 1.12**) was also active toward the formation of cyclic carbonate from internal epoxides. Although the reported scope is limited to a few cyclic scaffolds and the operating temperature is rather high (150 °C), they were able to obtain cyclooctene carbonate in high yield.[47] This can be considered as the first example of cyclooctene carbonate synthesis via direct CO_2 coupling.

Similarly, chromium complexes with N_4-donor Schiff base ligands (**3, Scheme 1.12**) were also found to be active catalysts for the cycloaddition of CO_2 to styrene oxide (conversions up to 92%) affording cyclic styrene carbonate (up to 68% yield). Cationic catalysts gave higher conversions than the neutral ones, and the addition of tetrabutyl ammonium halides increased both the conversion and cyclic carbonate selectivity up to 100% when using dichloromethane as solvent.[48]



CO_2(20bar), 120 °C, 3h
up to 296 h^{-1} TOF
Ghosh *et al.*, 2010

CO_2(20bar), 150 °C, 5h, S= CH_3CN
up to 83% yield
Ramidi *et al.*, 2013

CO_2(20bar), 100 °C, 18h
up to 92% yield
Cuesta-Aluja *et al.*, 2014

Scheme 1.12. Structure of Complexes based on N_4-ligands.

1.3.4 Aminophenolate Catalysts

The fifth active catalysts are known as new class of accessible aminophenolate catalysts, characterized by high activity combined with a wide substrate scope and functional group tolerance. Different from the salen/salphene based systems, aminophenolate catalysts likely allow for more sterically congested substrates to be coordinated/activated and converted into their respective cyclic carbonate. Particularly, in the case of a binary catalyst, the presence of fewer donor atoms in the plane of the metal would be beneficial for sterically more congested substrates and more easily accommodate an incoming nucleophile approaching the substrate and

entering the coordination sphere of the metal. Aminophenolate catalysts have shown to be more active toward internal epoxides conversion than salen- and salphen-based catalysts.

The Kleij group developed novel homogeneous catalytic systems based on Lewis acidic and abundant metals, reporting on a new class of accessible Al(III)amino(triphenolate) catalysts (**5, Scheme 1.8)**. These catalysts were evaluated by comparison with previously-reported catalysts using 1-hexene oxide as a benchmark substrate under mild conditions (T = 30 °C, CO_2 (10 bar), t = 2 h).[49] When compared with Al(III)-(aminotrisphenolate) catalyst, both the bimetallic Al(III)salen[43] and the Zn(salphen)[45] complex proved to be less effective, observing roughly half of the activity of the Al complex in Al(III)-(aminotrisphenolate) catalyst when employed under similar experimental conditions.[50] This example actually reports one of the very few benchmarking experiments performed under similar reaction conditions and application of an identical reactor set up, allowing for a direct comparison among the catalytic efficiencies of various catalyst structures in the formation of cyclic carbonate.

Previously, our group reported the use of simplified catalytic system based on $CoCl_2/Bu_4NCl$, which was reported to be efficient and selective for synthesis of propylene carbonate (up to 2314 TON).[51] The work was inspired from the unbridged iminophenolate-ligated Co(III)I complexes activated by either DMAP or tertrabutylammonium bromide (TBAB) co-catalysts: the complexes are effective and selective catalysts (up to 1500 TON) (**6, Scheme 1.8)**.[52]

1.3.5 Cyclic Carbonate Synthesis Catalyzed by Iron Complexes

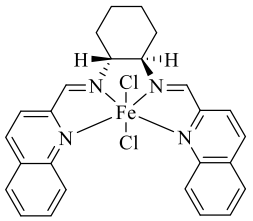
Although iron is environmentally benign and an attractive alternative for other transition metals, reports on iron based catalysts in cyclic carbonate synthesis are rare. Reported examples of divalent iron complexes are [*trans*-*N*,*N*-bis(quinolin-2-ylmethyl)cyclohexane-1,2-diamine]Fe(II)chloride[53] (**1, Scheme 1.13**) and [N,N-bis-2-pyridinylmethylene-cyclohexane-1,2- diamine]Fe(II)chloride[54] (**2, Scheme 1.13**), which catalyze propylene carbonate synthesis along with TBAB. Interestingly, comparison of reactivity between iron(II) and iron(III) complexes having a same

tetradentate Schiff base ligand shows higher activity for iron(III) (**3, Scheme 1.13**).[55] The more active iron(III) system demonstrates a high activity without co-catalysts with long time reaction. Williams and co-workers developed a novel dinuclear iron catalyst mainly aimed for polycarbonate synthesis. Remarkably, this catalyst can also produce cyclic carbonates even at RT and 1 atm CO_2 pressure, although with cost of TOF values (**7, Scheme 1.13**).[56] This differs from the dinuclear Al(III)salen system developed by North and co-workers: this Fe catalyst required only 1 equiv of nucleophilic co-catalyst to achieve quantitative cyclic carbonate formation under these conditions.

Kleij and co-workers have shown that differently substituted Fe(III)amino(trisphenolate) catalysts were active for the conversion of 2,3-epoxybutane (2,3-dimethyloxirane) to the corresponding cyclic carbonate (**4, Scheme 1.13**).[57] In an attempt to broaden the scope of these Fe(III)amino(trisphenolate) catalysts, the same group reported on the conversion of different internal epoxides to the corresponding cyclic carbonate using **5**[58] in scheme 1.13. Despite the relatively low pressure of CO_2 applied, in all cases, moderate to good yields were observed (yield: 39 − 69%, TBAB = 0.5 mol. %, T = 85 °C, CO_2 (2 bar), t = 18 h).

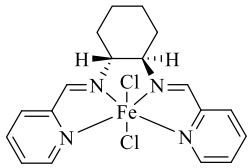
Another interesting example was described by Rieger *et al.*,[59] who developed a dinuclear Fe(III) complex coordinated by dithioether-triphenolate-based ligands (**6, Scheme 1.13**), relying on the soft donor properties of sulfur ligands to increase the Lewis acidity of the metal centres in comparison with catalysts based on N and O ligands, which have been extensively described in the literature. These labile Fe−S bonds facilitate the coordination of the epoxide to the hard Fe(III) metal centres, promoting the formation of cyclic carbonate by a subsequent ring-opening step of the coordinated substrate by the nucleophilic co-catalyst; thus, by combining this binuclear Fe(III) complex with TBAB as a nucleophilic additive, an active catalytic system for the conversion of propylene oxide to the corresponding cyclic carbonate could be developed with an observed TOF value of 580 h^{-1}.

1.



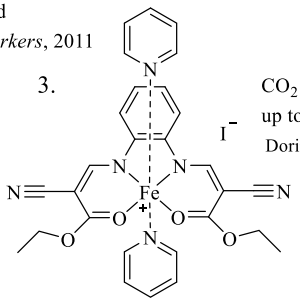
CO_2 (2bar), 100 °C, 2h, Bu_4NBr
up to 80% yield
Rieger *& coworkers*, 2011

2.



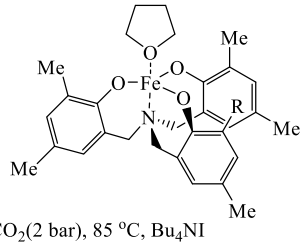
CO_2 (40 bar), 100 °C, 4h, Bu_4NBr
up to 12% yield with TOF= 30 h^{-1}
Wang *& coworkers*, 2014

3.



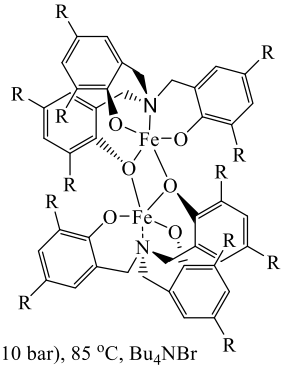
CO_2 (50 bar), 80 °C, 20 h,
up to 99% yeild with TON= 495
Doring *& coworkers, 2013*

4.



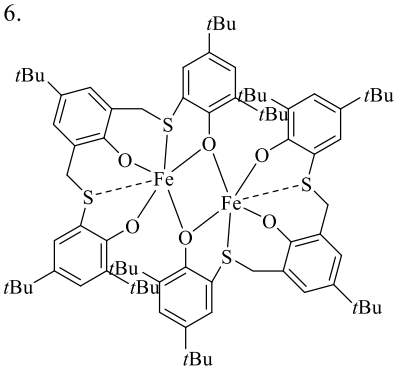
CO_2(2 bar), 85 °C, Bu_4NI
Up to 67% yield
Kleij *& coworkers*, 2012

5.



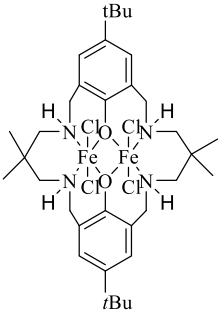
CO_2(10 bar), 85 °C, Bu_4NBr
Up to 83% yield
Kleij *& coworkers*, 2012

6.



CO_2 (20 bar), 100 °C, 6h, Bu_4NBr
TOF up to 580 h^{-1}
Rieger *& coworkers*, 2015

7.



CO_2 (1 bar), 25 °C, 2h, PPN
TOF up to 18 h^{-1}
Williams *& coworkers*, 2011

Scheme 1.13. Iron complexes which activate cyclic carbonate formation.

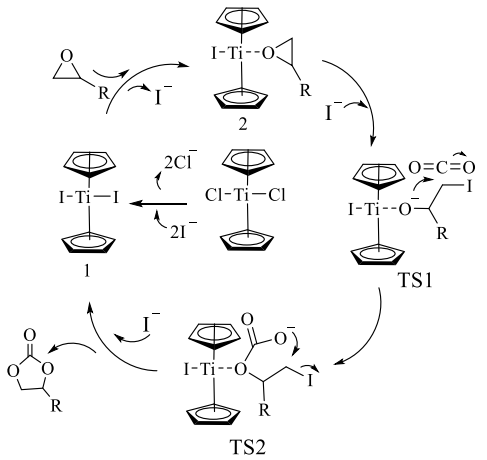
1.3.6 Cyclic Carbonate Synthesis Catalyzed by Titanium Complexes

Titanium would be an attractive metal candidate due to its combination of low toxicity and high Lewis acidity. However, there are only three reports on titanium complexes in catalytic synthesis of cyclic carbonates, including Cp_2TiCl_2 with a Lewis base,[60] the catalysts composed of titanocene dichloride (Cp_2TiCl_2), and tetrabutylammonium bromide. Up to 98% isolated yield of propylene carbonate was reported from a 15 minute reaction in pyridine at 150 °C and 12 bar carbon dioxide pressure using 1 mol. % of catalyst and co-catalyst in THF as a solvent. A crucial effect is that the solubility of Cp_2TiCl_2 is various in different solvents at the reaction temperature of 150 °C. On the other hand, the reaction runs very slowly under solvent-free conditions because of the poor solubility of catalyst in PO. Moreover, the same catalyst along with KI,[61] under the same reaction conditions as previously reported, activate cyclic carbonate synthesis with the same efficiency (up to 98% yield within 4 h). In their proposed mechanism (**Scheme 1.14**), the catalytic cycle, Cp_2TiCl_2 and 2 equiv. KI interchanged I^- with Cl^- in Cp_2TiCl_2 to form catalyst intermediate **1** and KCl first, due to the solubility order was KI > KBr > KCl in polar reagents, then the epoxide was activated by coordinating to the Lewis acidic centre in **1** to generate the reaction intermediate **2**, which was attacked by I^- from the catalyst intermediate **1** to produce the transition state 1 (**TS1**). Transition state 2 (**TS2**) was obtained when the carbon dioxide was attacked by O^- in TS1, which was causing insertion of CO_2 to lead to the corresponding cyclic carbonate. Both Lewis acidic centre (Ti) and Lewis base centre (I^-) have the same importance during the coupling reaction proceeding in this mechanism. From **Scheme 1.14**, we can see that 2 equiv. of KI of Cp_2TiCl_2 was needed to form catalyst intermediate **1** and reaction intermediate **2** in order to ensure the coupling reaction of epoxides and CO_2 to produce the corresponding cyclic carbonate.

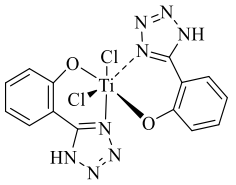
Go *et al.* described an interesting system based on a tetrazole ligand.[62] Although a series of titanium complexes (C_5H_5)*L*$TiCl_2$, *L*$TiCl_3$(THF) and L_2TiCl_2 where *L* is 5-(2- hydroxo-phenyl)tetrazole were reported, the bis-tetrazole complex was shown to be the most active catalyst (**Scheme 1.15**), giving propylene carbonate with 86%

conversion in 4.5 hours using 0.1 mol.% of catalyst and tetrabutylammonium iodide co-catalyst at 75 °C and 22 bar CO_2. No other substrates were studied.

Titanium is also used in a different form for catalysis with titanosilicate molecular sieves. These are very attractive heterogeneous catalysts as they are commercially available, inexpensive, and recyclable. Srivastava *et al.* demonstrated the use of titanium silicate molecular sieves in the coupling of epoxides with carbon dioxide and showed a 77% conversion of propylene oxide to propylene carbonate with high selectivity (88%) in the absence of solvent (100 mg molecular sieves, 0.0072 mmol DMAP as co-catalyst, 18 mmol epoxide, 6.9 bar, 6 hours at 120 °C).[63] Doskocil has also used titanosilicate molecular sieves for this reaction,[64] however the focus of this work was on the interaction of the carbon dioxide with the ion-exchanged ETS-10 sieves rather than preparatory chemistry and only modest yields were achieved (< 15%).



Scheme 1.14. Proposed mechanism for cycloaddition of CO_2 to epoxides catalyzed by titanocene dichloride.[61]



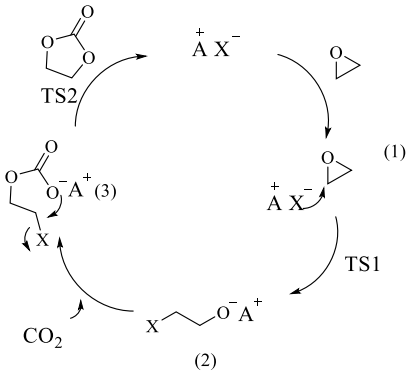
Scheme 1.15. Structure of tetrazole based Ti-complex.

1.4 Cyclic Carbonate Synthesis Catalyzed by Organo-Catalyst Systems

The recent challenges in cyclic carbonate synthesis have focused on limiting the use of inorganic catalysts or replacing them with new, environmentally benign free metal media in a view to develop green chemical synthesis.[65] In addition, the organo catalytic reactions can be carried out under air and the catalysts are usually inexpensive and stable.[66]

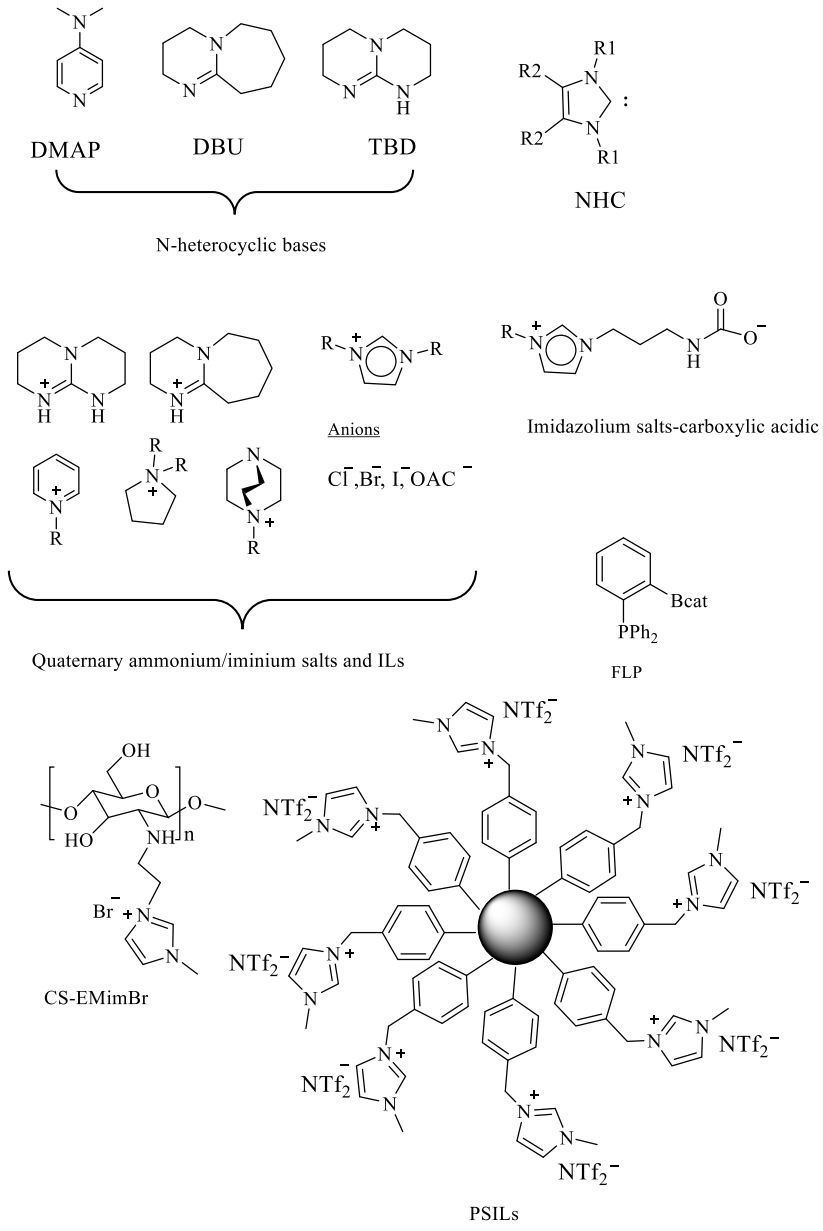
Up to now, the reported organo-catalysts active in CO_2 conversion catalysis can be roughly divided into three distinct categories (**Scheme 1.17**)[67]: (1) nitrogen-based heterocycles (including organic bases and N-heterocyclic carbenes, NHCs); (2) organic salts, molten salts, and ionic liquids (ILs); and (3) (poly)phenolic and poly-alcohol compounds.

Until recently, most reports[67,68] have proposed a mechanism similar to Calo's mechanism (**Scheme 1.16**).[69] This involves nucleophilic attack of the anion at the least-hindered carbon on the epoxide (transition state 1; **TS1**), carbon dioxide addition (**3**), intramolecular cyclization, and reformation of the anion (**TS2**). Cyclization has been proposed to be preferred rather than polymer formation, owing to the thermodynamic stability of five-membered cyclic carbonates. Intermediate **2** apparently lies high in energy, since the opposite ring closing of chlorohydrins into epoxides is readily processed in basic conditions. Presumably, for this reason, some authors suggested stabilization of **2** by hydrogen bonding[70] or other non-covalent interactions from the solvent or co-catalyst.



Scheme 1.16. The proposed mechanism for fixation of CO_2 with epoxide.[71]

Recently, research interest in task-specific ionic liquids has increased strongly because these materials can be designed for specific applications in diverse areas, ranging from synthetic and catalytic chemistry to biotechnology, electrochemistry, and materials science by introducing certain functional groups into the cation or/and anion of traditional ionic liquids.[72] Among these, imidazolium salts that contain carboxylic acidic groups have attracted much attention because they offer the new possibility of developing environmentally-friendly acidic catalysts. This is due to a combination of the advantages of liquid acids and solid acids, that is, uniform acid sites, stability in water and air, ease of separation, and reusability.[73] Furthermore the amino-functional imidazolium ionic liquid was found to be an effective catalyst for the synthesis of cyclic carbonates from carbon dioxide and epoxides under mild conditions without any co-solvent. Furthermore, the catalytic system can be reused at least nine times without a noticeable decrease in activity and selectivity.[74]



Scheme 1.17. Organocatalysts employed for CO_2-epoxide coupling reaction.

Han and co-workers made an attempt to use carboxylic acid groups in functionalized ammonium salts for the synthesis of cyclic carbonates from CO_2 and epoxide.[75] The co-existence of a hydrogen-bond donor (-CO_2H), ammonium cation, and halide anion led to a synergy effect, promoting the reaction. However, the activity of the catalysts was still unsatisfactory, and further effects of the carboxylic-acid group structure on the activities of these betaine-based salts were not investigated.

In addition, the immobilization of a catalyst and reagents on a variety of polymeric supports is attracting considerable attention under the heading of ‘‘green chemistry’’ in both industrial and laboratory chemical processes due to the ease of handling and recycling and the unique microenvironment formed by the reactants within the polymeric support.[76] Park *et al*. successfully developed ionic liquids immobilized onto a structurally modified polyethylene glycol (PEG) through the reaction of imidazolium salt with PEG- succinic acid. In the synthesis of cyclic carbonate from allyl glycidyl ether (AGE) and carbon dioxide, the immobilized ionic liquid on PEG showed good catalytic activity without the use of any solvent. Ionic liquids with a smaller alkyl chain structure and with smaller anion exhibited better reactivity for the synthesis of allyl glycidyl carbonate (AGC), probably due to the less significant steric hindrance.[77] More recently, in 2014, multilayered covalently-supported ionic liquid phase (mlc-SILP) materials were synthesized using a protocol involving covalent grafting of bis-vinylimidazolium salts on a thiol-functionalized silica support and cross-linking between the bis-vinylimidazolium units. The mlc-SILP materials are active heterogeneous catalysts for the reaction of carbon dioxide with various epoxides to yield cyclic carbonates.[78] On the other hand, various tailor-made imidazolium based ionic liquids (ILs) covalently immobilized on polymeric support were (denoted as PSIL) applied in the cycloaddition of CO_2 into epoxides. Imidazolium ($C_3H_5N_2^+$) and various counter anions such as Cl^-, Br^-, BF_4^-, PF_6^-, and NTf_2^-, were selected to construct less coordinating cations with anions in PSILs (yield: 91, T = 100 °C, CO_2 (8 bar), t = 8 h).[79]

As one of the most abundant natural biopolymers, chitosan (CS) has excellent properties such as biocompatibility, biodegradability, non-toxicity, and good adsorption properties.[80] These qualities stem from its highly regular structure: β-(1, 4) linked D-glucosamine repeating units with three reactive groups (**Scheme 1.17**). CS

has broad potential in the design of advanced materials,[81] and can be chemically or physically modified easily as an excellent catalyst support material.[82] Zhang *et al.* synthesized CS chemically supported 1-ethyl-3-methyl imidazolium halide catalysts for cyclic-carbonate synthesis starting from epoxide and CO_2, in which CS could play bi-functional roles in promoting the reaction: the hydrogen-bond assisted ring-opening of epoxide and the nucleophilic tertiary-nitrogen-induced activation of CO_2.[83] CS-grafted quarternary phosphonium IL and its application in the synthesis of cyclic carbonates were also reported by Dai *et al.* in 2014.[84] The catalyst exhibits good catalytic activity and selectivity, even in the absence of co-catalyst and solvent. Moreover, the catalyst can be easily recovered by filtration and reused up to 5 times without showing any significant loss of activity. It is envisaged that the catalyst is suitable for large-scale production of cyclic carbonates.

More simple organic systems have been developed. For example, DMF was found as an efficient organic catalyst for the coupling of epichlorohydrin with CO_2 (yield > 99%, 110 ºC and 50 bar of CO_2 for 20 h),[85] In addition, Kozak *et al.* reported the development and detailed mechanistic investigation of a novel and continuous-flow catalytic system for cycloaddition transformation that requires only catalytic quantities of feedstock chemicals, bromine itself or a combination of N-bromosuccinimide (NBS) and benzoyl peroxide (BPO) in DMF, the efficient conversion of epoxides and CO_2 to cyclic carbonates that were present,[86] and N-methyltetrahydropyrimidine was illustrated to catalyze gas transfer of CO_2 to medium solution to react with n-butyl glycidyl ether to produce cyclic carbonate.[87] Moreover, inorganic halides with or without Lewis basic co-catalysts were reported to catalyze the addition of CO_2 to epoxides.[88] Lithium chloride, bromide, and iodide were evaluated as the inorganic co-catalysts, and showed good synergism with Lewis base catalysts.[89] In addition, direct CO_2 activation has also been achieved with frustrated Lewis pairs (FLPs), i.e. molecular systems incorporating Lewis acid and Lewis base functions which cannot interact directly due to their steric constraints and/or backbone rigidity.[90] FLPs can be catalytically active towards CO_2 coupling to epoxides.[91]

Other employed and effective organic catalysts include 4-dimethylamino-pyridine (DMAP) and amidine- and guanidine-derived superbases. Given the differences in the

Lewis basic strength, the catalytic role of these two classes of compounds is quite different. DMAP has proven to be an efficient homogeneous[92] and heterogeneous[93] catalyst for the synthesis of cyclic carbonates from epoxides, even though high operating temperatures (120 °C) and relatively high CO_2 pressure (17– 40 bar) were required; however, in the presence of Lewis acid co-catalysts such as phenols, this dual catalytic system showed a good catalytic activity for the preparation of cyclic carbonates from epoxides.[94]

On the other hand, organic superbases such as DBU, TBD, and N-methyl TBD (MTBD) have been extensively employed as catalysts for CO_2-coupling reactions.[95] Different terminal and internal epoxides were converted to the corresponding cyclic carbonates with good to excellent yields (60 – 98%) and high chemo-selectivities (90 – 98%), although the reaction conditions were quite harsh (T = 140 °C, CO_2 (50 bar)).

However, the development of catalyst systems for the coupling reaction of epoxides and CO_2, at temperatures below 100 ºC, and low pressures, for shorter time reaction, with readily available, inexpensive nontoxic reagents, suitable for the conversion of long-chain epoxides is still an attractive topic.[96]

2 Results and Discussion

2.1 Experimental

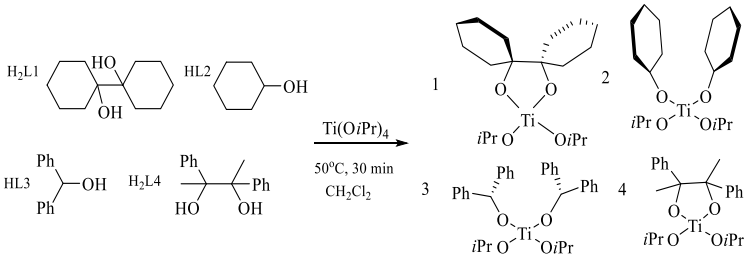
Moisture complexes were synthesized under an inert atmosphere using Schlenk techniques. Chemicals were purchased from Sigma Aldrich and used without further purification. Carbon dioxide was purchased from AGA with 99.9% purity.

Elemental analyses were performed using an EA 1110 CHNS-OCE instrument. IR and UV-vis spectra were collected with a Perkin Elmer Spectrometer and a Hewlett Packard 8453 spectrophotometer, respectively. Thermal gravimetric analysis (TGA) was carried out using Mettler TGA850. EI-mass spectrometers were run with JEOL JMS-SX 102 mass spectrometer (ion voltage 70 eV). ^{1}H NMR spectra were obtained using a 300 MHz Bruker instrument. The spectra were collected at 25 ºC, and chemical shifts were reported in ppm relative to TMS as an external standard.
Detailed experimental procedures can be found in the papers **I-IV**.

2.2 Ligands and Complexes Synthesis

2.2.1 Titanium Complexes Synthesis

The synthesis route for titanium complexes are outlined in **Scheme 2.1.** The synthesized complexes are light yellow solid powders at room temperature.



Scheme 2.1. Synthesis of titanium alkoxide complexes, and their proposed structure.

IR-analyses of the complexes indicate the presence of the ligands (**Figure 2.1**). A slight shift of ligand peak (νC-H) and (νC-C) were observed, and the absence of the alcohol band also verifies the complexation. The coordination reactions were also followed by UV/Vis spectroscopy. A sharp peak in the visible region due to the coordination of ligand was observed. Complexes **1** and **3** showed peaks at 369 and 368 nm, respectively, compared to the corresponding ligands which showed an absorption peak respectively at 281 and 273 nm. Moreover EI-mass spectrometry of the complexes were measured for maximum decomposition temperature 500 °C. Complexes' fragments peaks could be seen clearly, for example complex **1** analysis spectrum gives a peak at 362 at retention times= 7.49 min which refers to the calculated molecular weight of the complex (362.3 g/mol), and the fragments for the chelating ligand without the O*i*Pr group can be detected at retention time= 8.85 with molecular weight= 244 g/mol.

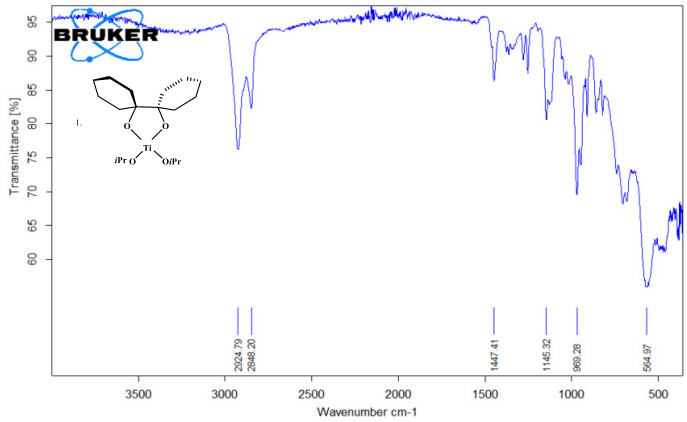


Figure 2.1. IR spectrum of complex.

NMR Spectroscopy

^{1}H NMR spectra of the isolated compounds indicate that the desired alcohol exchange reaction has taken place cleanly and verify the structures depicted in **Scheme 2.1**. In all complexes, isopropoxide groups appear as a narrow doublet, underlining the free rotation and similarity of the present isopropoxide ligands (**Figure 2.2**).

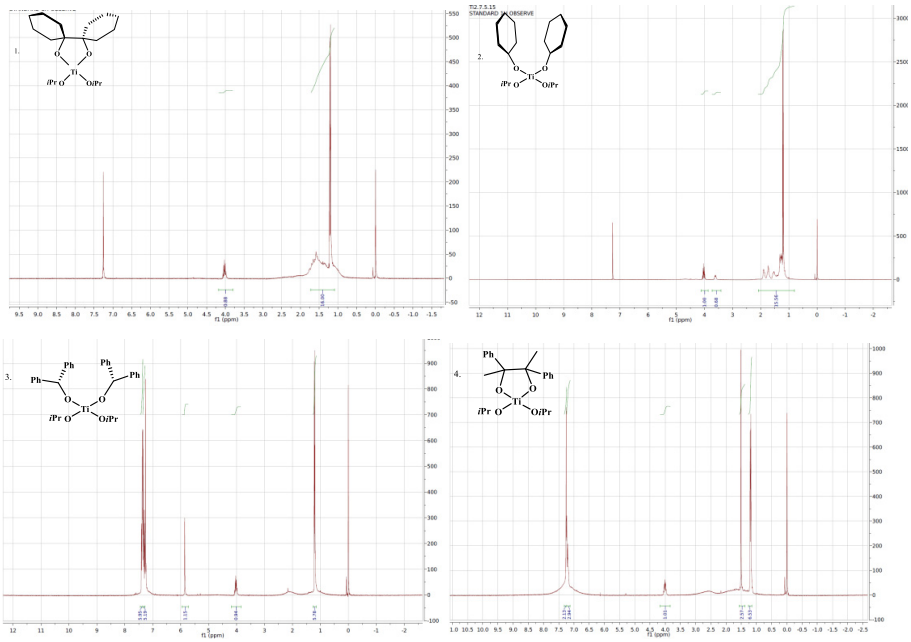


Figure 2.2. NMR spectra for titanium complexes.

In order to confirm the molecular structure and elucidate the metal−ligand bonding in these titanium complexes, single crystal X-ray diffraction study for **1** was performed. The crystals were grown from a saturated dichloromethane solution. The X-ray structure is shown in **Figure 2.3**. In solid-state, the structure of the complex is a dimer, including a Ti_2O_2 core bridging through one of the oxygen atoms of the **L1**. The geometry around each titanium is distorted square pyramidal, with the metal centre pentacoordinated by two O atoms from two isopropoxide groups and two bridging O atoms of two **L1** ligands and by one O atoms from **L1** ligand (Ti1-Ti2 distance is 3.2480(4) Å). It is worth noting that complex **1** adopts a cis geometrical configuration with the adjacent oxygen atoms from two −O*i*Pr groups in the distorted square pyramidal coordination.

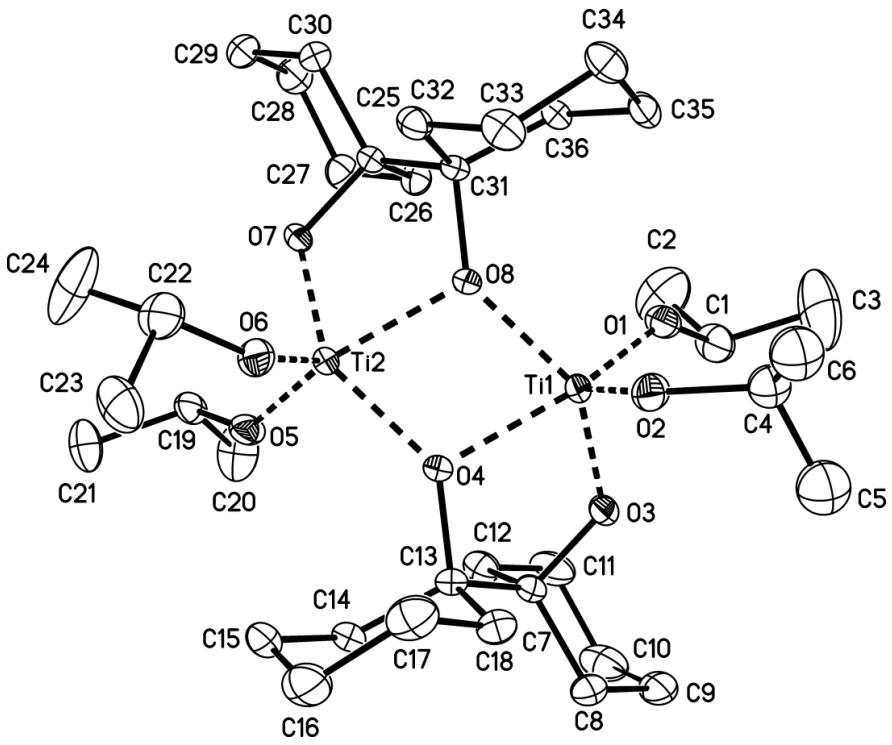


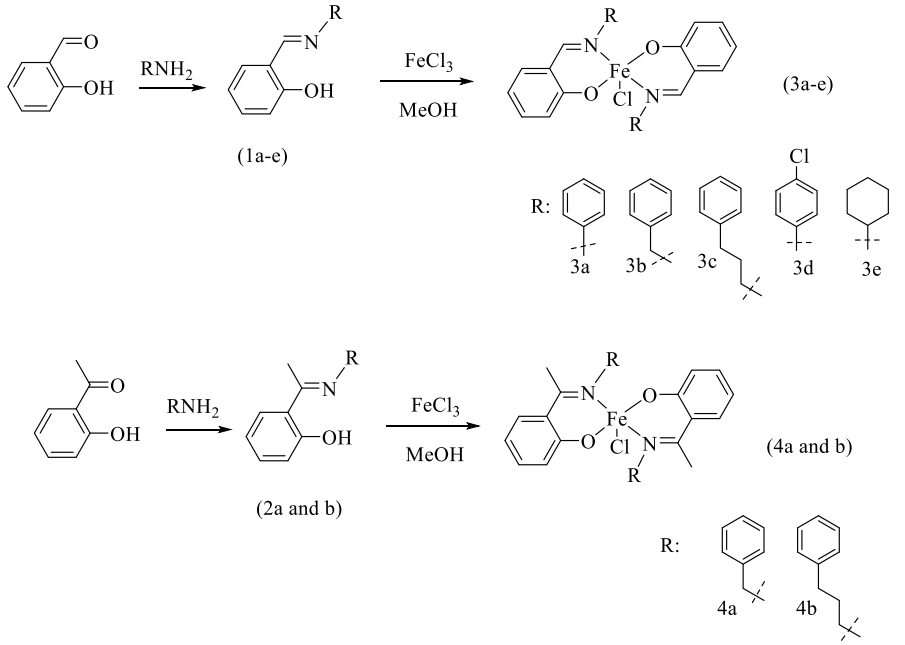
Figure 2.3. Crystal structure for Ti ([1,2'-bi(cyclohexane)]-1,2'-bis(olate))(O*i*Pr)$_2$ (H-atoms and minor disordered part omitted for clarity, displacement parameters are drawn at 50% probability level).

2.2.2 Synthesis of Iron Complexes and their Ligand Precursors

Ligand precursors, phenoxyaldimines **(1a-1e)** and phenoxyketimines **(2a-2b),** were synthesized by a Schiff base condensation reaction between salicylaldehyde or *o*-hydroxyacetophenone and amine in the presence of catalytic amount of formic acid (**Scheme 2.2**). The condensation reactions were followed by IR spectroscopy wherein disappearance of the carbonyl band and the appearance of a new band between 1618 cm^{-1} -1642 cm^{-1} is indication of the imine formation. The isolated ligand precursors were characterized by ^{1}H NMR, IR-, and UV-Vis spectroscopy.

The iron complexes **3a-e** and **4a-b** were synthesized in high yields by treatment of the corresponding ligand precursors with anhydrous $FeCl_3$. The complexes are hygroscopic and isolated under argon using Schlenk techniques.

In IR spectra a slight shift of the imine bonds (ν(C=N)) was observed indicating complexation. For example, imine bands in complexes **3a** and **3d** are observed at 1634 and 1637 cm^{-1} respectively, whereas in the corresponding ligand precursors **1a** and **1d** the band appears at 1614 and 1608 cm^{-1}.



Scheme 2.2. Synthesis of phenoxyaldimines (**1a-e**) and phenoxyketimines (**2a** and **b**) via Schiff base condensation reaction starting from salicylaldehyde or *o*-hydroxyacetophenone and amine.

Thermal Gravimetric Analysis (TGA)

The complexes were characterized by thermal gravimetric analysis (TGA) (**Table 2.1**). According to TGA measurements, all complexes show thermal stability up to 400 ºC. The loss of weight between temperatures of 100 ºC - 200 ºC could be attributed to the loss of water. The presence of significant amounts of water was observed; for instance **4b (Scheme 2.2)** complex contains around two H_2O molecules. Table 2.1 shows these weight losses calculated as contents of water molecules. Some complexes like **3c**, showed very small weight loss at 105 ºC indicating low humidity water content in this complex. Elemental analysis showed that complexes contain few molecules of water and metal-ligands ratio was found to be equal to 1 to 2. Therefore, a penta-

coordinate arrangement around the metal centre can be assumed. Furthermore, EI-MS measurement supports the TGA measurement and proved the coordination of ligand to metal and existence of water molecules in the complexes, for example EIMs for 4b show peak of water content and peaks related to complex fragmentation: 18(100, H_2O); 91(100, FeCl); 239(90, L); 329(30, FeCl-L); 567(10, M^+).

Table 2.1. Thermogravimetric water analysis for iron complexes.

	3b	3c	3e	4a	4b
% of weight loss	10.6	1.6	7.3	8.22	6.5
weight loss (mg)	0.54	0.09	0.32	0.74	0.55
Temperature (˚C)	149	105	118	134	123
mole of H_2O to mole of complex	3	0.5	2	2.5	2

NMR Spectroscopy

^{1}H NMR spectra for bis(phenoxyiminato) chloride iron(III) complexes were measured in $CDCl_3$. The difficulty in getting well-resolved NMR spectra was due to the paramagnetic nature of Fe(III) nucleus. Some information on imine and phenolic proton were obtained from the spectra (**Figure 2.4**). Phenolic proton appeared between 4.0 to 4.6 ppm for ligands but was not seen in complex spectra. This indicated the involvement of phenolic –OH in complexation for all complexes. In ligands, imine proton appeared between 8.2 to 8.4 ppm. The NMR spectra for complexes, for example spectrum of **3e** in scheme 2.2, showed two peaks for imine protons as independent singlet appearing at around 10 ppm and 11 ppm. This splitting is in agreement with imine protons placed *trans* to each other with respect to the metal centre. The *trans* position is evident from the crystallography structure obtained for **3c; Scheme 2.2**. This agreement between the NMR spectrum and the X-ray structure of **3c** could indicate that the other complexes, whose X-ray structures are not available could have the same geometry.

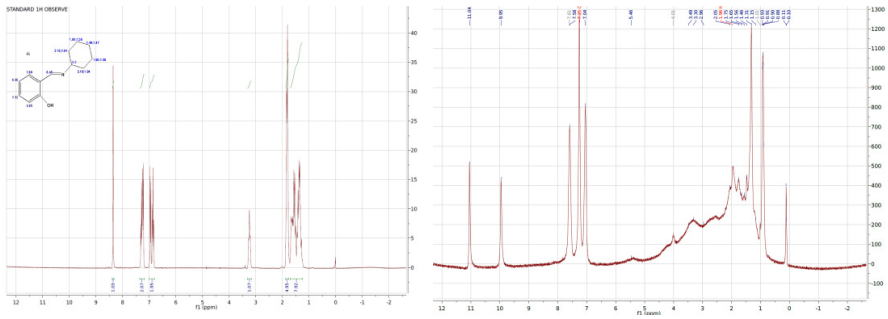


Figure 2.4. Comparison of the NMR spectra between **3e** complex and its ligand precursor **1e**.

Crystals suitable for X-ray analysis were obtained for **3c** from saturated methanol solution (**Figure 2.5**). The X-ray structure consists of two phenoxyaldimine ligands and a chloride coordinated to the iron(III) centre giving a distorted square-pyramid geometry with crystallographic C_2-symmetry.

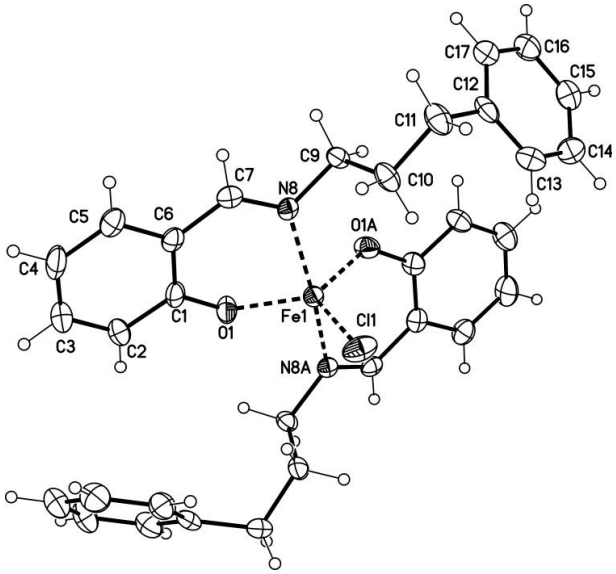
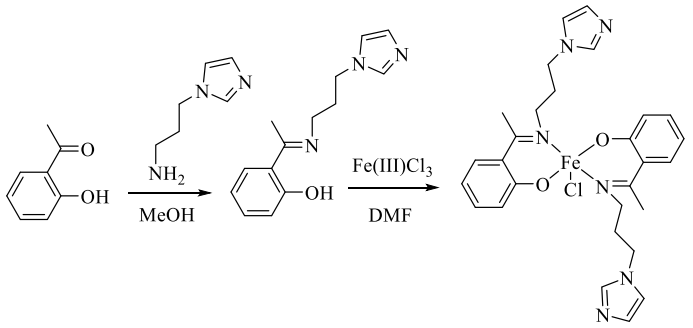


Figure 2.5. Crystal structure for **3c** wherein two phenoxyaldimine ligands occupying the plane and having the imine nitrogens *trans* to each other and Cl^- takes the apical position (displacement parameters are drawn at 50% probability level).

2.2.3 Synthesis of Imidazole-Schiff Base Iron(III) and the Ligand Precursor.

The Schiff base Fe(III) complex was synthesized in high yields by a treatment of anhydrous $FeCl_3$ with two equivalents of N-methylsalicylidene-1-(3-aminopropyl)imidazole in DMF (**Scheme 2.3**). Crystals suitable for X-ray analysis

were obtained for N-methylsalicylidene-1-(3-aminopropyl)imidazole from saturated methanol solution (**Figure 2.6**). The isolated complex is air-stable and was characterized by various techniques.



Scheme 2.3. Synthesis of N-methylsalicylidene-1-(3-aminopropyl)imidazole via a Schiff base condensation reaction. Iron(III) complex was prepared by treating the corresponding ligand precursor with $Fe(III)Cl_3$.

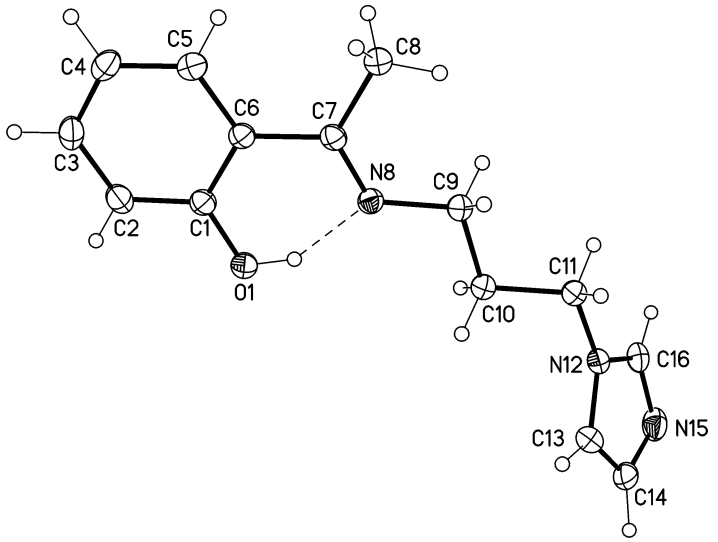


Figure 2.6. Crystal structure for N-methylsalicylidene-1-(3-aminopropyl)imidazole.

2.3 Catalytic Reactivity

2.3.1 Activation of CO_2 and Epoxides Coupling by Titanium Alkoxide Catalysts

The isolated complexes were utilized as catalysts for the coupling reaction between epoxides and CO_2. Our initial studies showed that **1** successfully catalyzes the coupling of CO_2 and propylene oxide (PO) in neat condition with the presence of (4-dimethylamino)pyridine (DMAP), affording full conversion at 120 °C, 15 bar CO_2 pressure, in 3 hours. No coupling reaction was observed in the absence of DMAP, while DMAP by itself failed to catalyze the reaction.

The reactivity of some commercial available titanium complexes for synthesis of PC were also studied, such as titanium(IV) (triethanolaminato)isopropoxide (5) and titanium(IV) phthalocyanine dichloride (6). Complex 5 along with DMAP gave 35 mol. % PC at 120 °C, 15 bar CO_2, but 6 failed to activate the system because of increasing steric hindrance.

Co-catalysts have a significant role in the coupling reaction. From the co-catalysts examined (LiBr, LiI, Bu_4NBr, Bu_4NI, Bu_4NCl, imidazole, morpholine, cyclohexylamine, butylamine, benzylamine and DMAP), tetrabutyl ammonium halides and DMAP were the most effective (**Figure 2.7**). From the onium salts, bromide and iodide analogues were more active than those of chloride, both giving 99% conversions in 3 h reactions. The order reactivity is the same as their order of nucleophilicity and is linked presumably to ring opening of epoxide, and function of the anion as a good leaving group during the ring closing step (**Table 2.2**).[I]

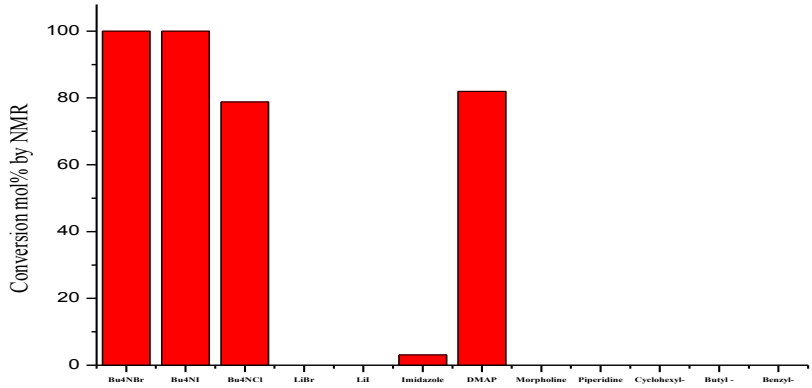


Figure 2.7. Conversions (% measured by NMR) of coupling reactions between carbon dioxide and propylene oxide with the use of **1** catalyst and different co-catalysts. Reaction conditions: 100 °C, 15 bar of CO_2, 3 h; **1** = 1 mol. %, co-catalyst= 1 mol. %, and 2.1 mL propylene oxide.

Table 2.2. Conversions (%, measured by ^{1}H NMR) for 1-4/TBAB catalyzed coupling reactions between different epoxides and CO_2. [a]

Cat.	Epoxide						
	Propylene oxide	Epichlorohydrin	1-Hexene oxide		Styrene oxide		Cyclohexene oxide
	3h	3h	5h	10h	5h	10h	20h
-	18	20	6	11	4	9	5
1	>99	>99	41	81	66	79	41
2	56	72	46	77	56	52	29
3	>99	>99	49	79	48	83	31
4	75	89	68	92	70	96	38

[a] Reaction conditions: 100 ºC, 15 bar CO_2; catalyst = 1 mol. %, TBAB= 1 mol. %, and 2.1 mL epoxide.

Proposed Reaction Mechanism

From the kinetic measurement (**Figure 2.8**), a second-order dependence on the catalyst concentration (starting with values crossbonding with monomer unit), and first order dependence on the co-catalysts concentration were observed, and suggesting that per each cycle one titanium metal centre work, which mean one titanium molecule was proposed to serve as Lewis acid for epoxide activation in each

cycle. (**Scheme 2.4**). We propose that the starting Ti-metal in this system fulfills the role of activating the epoxide (**2**), and the second Ti-metal ion activates CO_2. Then Br^- can attack the activated epoxide (**3**), followed by CO_2 insertion (**4**), and then eventually yield the cyclic carbonate product.

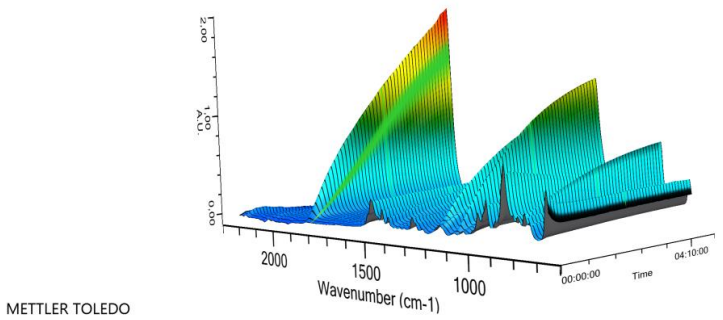
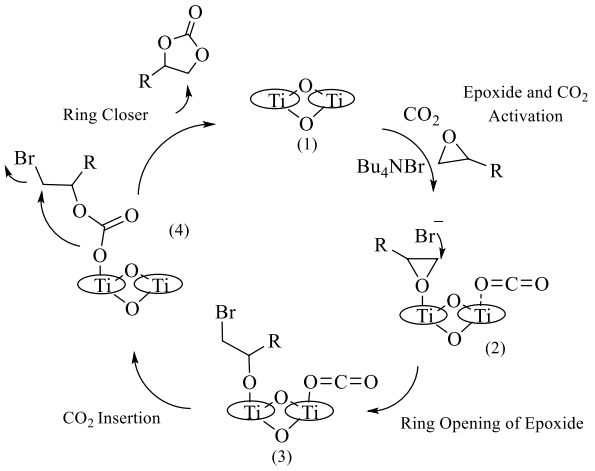


Figure 2.8. Three-dimensional stack plot for the 1-hexene oxide/CO_2 coupling reaction utilizing catalyst system. Reaction condition: 100 °C and 10 bar of CO_2. Performed the kinetic study *in situ* FTIR spectroscopy with a probe fitted to a modified stainless steel reactor.



Scheme 2.4. Proposed mechanism for Ti-alkoxide catalysis the coupling reaction.

2.3.2 *Activation of CO_2 and Epoxides Coupling by Bis(Phenoxyiminato)Iron(III) Catalysts*

Complexes **3a**, **3d**, **4a**, and **4b** showed the highest catalytic activity among the iron complexes tested when Bu_4PBr was used as a co-catalyst (**Table 2.3**). [II]

Table 2.3. Conversions (%, measured by ^1H NMR) of coupling reactions between carbon dioxide and PO using iron catalysts in the presence of DMAP, Bu_4PBr, and Bu_4NCO_3.[a]

Catalyst (0.01 mmol)	Co-catalyst (0.04 mmol)		
	DMAP	Bu_4PBr	Bu_4NCO_3
3a	47	75	39
3b	53	41	44
3c	45	47	43
3d	72	81	50
3e	44	33	48
4a	79	82	40
4b	79	83	40

[a] Reaction conditions: 24 h, 120 ºC, 12.5 bar of CO_2; and 16 mmol PO.

The complex **4b** with Bu_4PBr were chosen as catalysts for coupling of epoxides and CO_2 (**Table 2.4**). The coupling reactions are clearly influenced by the nature of the solvent employed and the highest activities were obtained in DMF, dioxin, and toluene. Of the series of solvents, DMF is the most polar and most likely able to support polar transition states during epoxide ring-opening and ring-closing steps after CO_2 insertion to the Fe-O bond. In fact, DMF alone can catalyze the coupling reaction of epoxides with CO_2 under harsh conditions (110 ºC and 50 bar of CO_2 for 20 h).[84]

The catalysts showed good productivity and selectivity for cyclic carbonate synthesis. The catalysts can be generally applied, yielding propylene, 1-hexene, styrene, and cyclohexene carbonates.

Table 2.4. Conversions (%, measured by ^{1}H NMR) of coupling reactions between carbon dioxide and different epoxides using catalyst **4b** in the presence of Bu_4PBr. [a]

Solvent	Time (hour)	Epoxide			
		Propylene oxide	1-Hexene oxide	Styrene oxide	Cyclohexene oxide
DMF	7	78	64	70	22
	4	-	62	66	16
	2	69	40	46	0
1,4-Dioxane	7	89	66	83	13
	4	-	60	53	7
	2	52	31	28	0
Toluene	7	89	62	67	17
	4	-	46	62	6
	2	49	22	52	7

[a] Reaction conditions: 145 ºC, 10 bar CO_2; 0.02 mmol of **4b**, 0.08 mmol of Bu_4PBr, 0.5 mL solvent, and 16 mmol epoxide.

2.3.3 Activation of CO_2 and Epoxides Coupling by bis(N-methylsalicylidene-1-(3-aminopropyl)imidazole)iron(III)chloride catalyst

Considering the ligand structure and the function of the Lewis base in epoxide and CO_2 coupling, an efficient bifunctional bis-(N-methylsalicylidene-1-(3-aminopropyl)imidazole)iron(III)chloride catalyst containing Lewis base unit (imidazole) is described for cyclic carbonates synthesis from epoxides and CO_2 (**Table 2.5**).[III]

Interestingly, the catalytic studies showed that bifunctional Fe(III) catalyst, with a Lewis acidic iron centre and Lewis basic imidazoles, is able to activate the coupling reaction of propylene oxide (PO) and CO_2 without an additional co-catalyst. The coupling reaction occurs in various solvents (**Table 2.5**, entries 7-10), however, running the reaction in dichloromethane (DCM) gave the highest yield of propylene carbonate (PC). Solvent–free reactions were also attempted, but no reaction was observed. Presumably, this is because of the poor solubility of catalyst into PO (**Table 2.5**, entry 2). However, with the addition of small amount of polar solvent the catalyst is solubilized and the system turns efficiently active.

Table 2.5. Effect of reaction parameters on the PO-CO_2 coupling catalyzed by iron catalyst.

Entry	Catalyst (mmol)	Solvent (0.5 mL)	TBAB mmol	CO_2 (bar)	Temp.	Time (h)	TON	TOF (h^{-1})
1	-	-	0.3	10	100	4	15	4
2	0.036	-	-	10	100	4	-	-
3	0.036	-	0.3	10	100	3	525	175
4	0.036	DCM	0.3	10	100	3	550	183
5	0.036	DMF	-	15	70	17	432	25
6	0.036	DCM	-	15	70	17	475	28
7	0.10	DMF	-	10	100	4	159	40
8	0.10	Acetonitrile	-	10	100	4	-	-
9	0.10	PC	-	10	100	4	208	52
10	0.10	DCM	-	10	100	4	225	56
11	0.10	DCM	-	10	100	3	147	49
12	0.10	-	0.3	15	25	20	43	2.15

Proposed Reaction Mechanism

Out of the kinetic study (**Figure 2.9**), a first-order dependence on the catalyst concentration was observed (**Figure 2.10**), suggesting a monomolecular mechanism (**Scheme 2.5**). As reported that *N*-heterocyclic compounds played the role of activating CO_2 to form organic base-CO_2 carbamate salt with excess amounts of CO_2.[97] We propose that Schiff base Fe(III) molecule serves as a Lewis acid for epoxide activation **(2)** and simultaneously imidazole activates CO_2 and generates carbamate anion trough the electron donation from the imidazole. The carbamate will then ring open the coordinated epoxide (**3**, CO_2/ epoxide coupling), and following intramolecular ring closing releases a cyclic carbonate and recovers the catalytic system. On the other hand, when TBAB is added as a cocatalyst, bromide instead of carbamate anion can act as a nucleophile and promotes, therefore, the oxirane ring opening and this significantly enhances the catalytic process.[II] A monomolecular mechanism was proposed in the bis(phenoxyiminato)Co(III)X-mediated CO_2/epoxide coupling in the presence of a nucleophilic co-catalyst.[98]

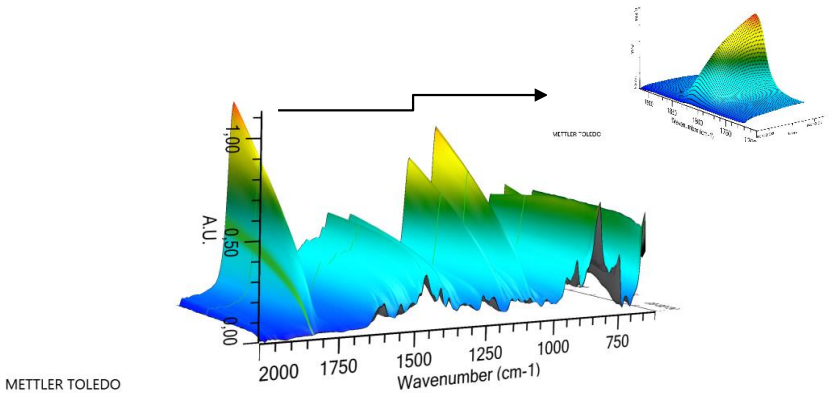


Figure 2.9. Three-dimensional stack plot for the 1-hexene oxide/CO_2 coupling reaction utilizing iron(III) catalyst system.

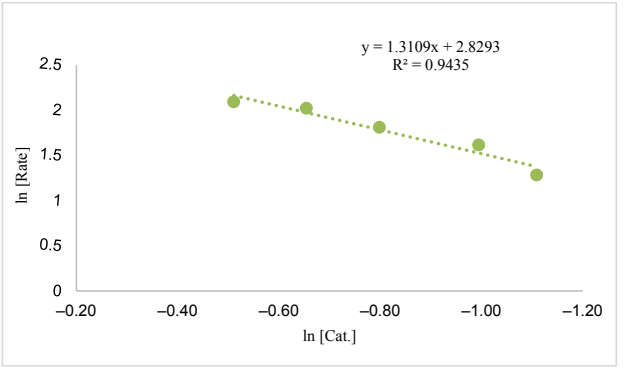
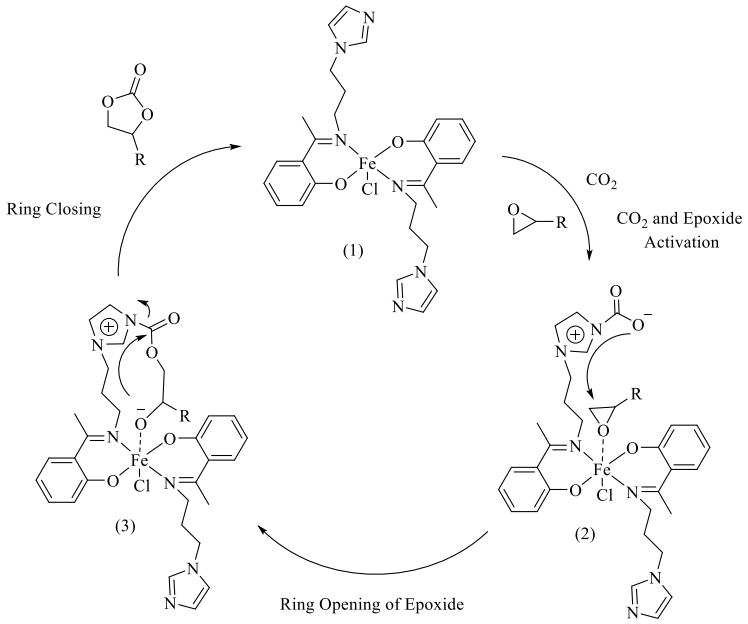


Figure 2.10. Logarithmic plot of initial rate versus concentration of iron catalyst. Slop = n ≈ 1.



Scheme 2.5. Proposed intramolecular mechanism for the epoxide-CO_2 coupling reaction.

In summary, we have developed an efficient catalyst for the cycloaddition of CO_2 to epichlorohydrin, and propylene oxide. The fixation of CO_2 by epoxides can be carried out using bifunctional imidazole-Schiff base iron(III) as catalyst. High conversions with good selectivity towards cyclic carbonates were achieved using this catalytic system under mild conditions.

2.3.4 Activation of CO_2 and Epoxides Coupling by Organo-Catalysts

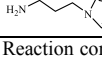
The metal-free coupling reaction between carbon dioxide and various epoxides was catalyzed by several, simple and commercially available amines or heterocyclic compounds like imidazole with tertrabuthylammonium bromide (**Table 2.6**).[IV]

In the row of studied amines, primary and secondary amines demonstrate higher activity than the tertiary amines. This is, presumably, related to different stability of the respective carbamate salts.[99] Primary and secondary amines react reversibly with carbon dioxide and form a weak adduct, which can easily release it back to the solution media under the reaction conditions.[100] Tertiary amines in turn are capable to bind CO_2 efficiently and the corresponding carbamates are much more stable than those with

secondary and primary amines. Accordingly, with tertiary amines the effective concentration of the carbon dioxide in media is relatively smaller but the stability also reflects poorer yields in carbonate synthesis. Steric and electronic effects in amine also play a significant role. For example, steric hindrance near a nitrogen atom, as in the case of 2,2,6,6-tetramethylpiperidine, dramatically diminishes the conversion in comparison with a less crowded analogous, piperidine. This tendency is especially observed when low CO_2 pressure and temperature were used. From an electronic point of view, it is found that aniline gives low reactivity comparing with the more basic cyclohexyl amine. Based on the result in **Table 2.6**, it can be concluded that a wide variety of simple and commercially available amines catalyze the coupling between carbon dioxide and propylene oxide. The best results were observed for aliphatic primary and secondary amines with reduced steric crowd.

In addition, as imidazole showed highest activity with TBAB, the synthesis of propylene carbonates by imidazole derivative (*N*-heterocyclic compounds) and TBAB was investigated further. The high reactivities of imidazole and 1-(3-Aminopropyl)imidazole comparing to *N*-methylimidazole prove the existence of inductive effects in the molecular structures of *N*-heterocyclic compounds resulted in the ability of the compounds to form carbamate salt with CO_2. The order of this ability among all is (1) ≥ (5)> (6)> (4)> (3)> (2) (**Table 2.6**) theoretically. It was seen that the activity order of the above bases was in strict accordance with the established pKa. This indicated that the basicity of the *N*-heterocyclic compounds has an important factor indeed.

Table 2.6. Conversions (% measured by ^{1}H NMR) of coupling reactions between carbon dioxide and propylene oxide in the presence of different amines and salts. [a]

N-base	Salts	Neat		Propylene carbonate (as a solvent)	
		80 ºC	120 ºC	80 ºC	120 ºC
-	Bu_4NI	12	20	-	27
	Bu_4NBr	15	23	-	26
	Bu_4NCl	4	10	-	17
	LiI	0	0	8	13
	LiBr	0	0	9	16
	LiCl	0	0	-	5
Imidazole (1)	Bu_4NI	52	89	-	65
	Bu_4NBr	66	81	-	78
	Bu_4NCl	15	50	-	55
	LiI	75	98	75	95
	LiBr	10	60	50	83
	LiCl	2	11	-	32
Morpholine	Bu_4NI	53	64	-	53
	Bu_4NBr	57	61	-	75
	Bu_4NCl	52	68	-	55
	LiI	15	30	59	75
	LiBr	2	71	48	75
	LiCl	0	27	-	27
Benzylamine	Bu_4NI	55	64	-	60
	Bu_4NBr	62	67	-	76
	Bu_4NCl	32	65	-	53
	LiI	3	20	54	56
	LiBr	1	18	56	63
	LiCl	0	4	-	22
Cyclohexylamine	Bu_4NI	60	66	-	65
	Bu_4NBr	62	53	-	67
	Bu_4NCl	36	72	-	60
	LiI	10	10	64	48
	LiBr	5	26	52	57
	LiCl	0	3	-	28
Butylamine	Bu_4NI	58	66	-	63
	Bu_4NBr	60	51	-	57
	Bu_4NCl	42	71	-	52
	LiI	3	13	60	62
	LiBr	1	33	53	97
	LiCl	0	2	-	21
Piperidine	Bu_4NI	44	66	-	53
	Bu_4NBr	58	62	-	58
	Bu_4NCl	57	64	-	45
	LiI	43	70	57	91
	LiBr	>99	97	>99	>99
	LiCl	5	11	-	38
 (2)	Bu_4NBr	22	51		
 (3)	Bu_4NBr	23	63		
 (4)	Bu_4NBr	43	70		
 (5)	Bu_4NBr	62	80		
 (6)	Bu_4NBr	51	75		

[a] Reaction conditions: Reaction time 5 h, 5 bar; 1.5 mol. % of amine, 1 mol. % of salt and 30 mmol propylene oxide.

Kinetic Study

To compare the kinetic difference of catalyst systems for the coupling reaction of CO_2 and epoxides, we first performed the kinetic study *in situ* FTIR spectroscopy with a probe fitted to a modified stainless steel reactor. In order to better understand the influence of the different catalyst system on the catalytic activity and selectivity for cyclic carbonate formation, kinetic experiments were conducted for the coupling of 1-hexene oxide with CO_2, using (A) imidazole/TBAB in neat, (B) imidazole/LiBr in propylene carbonate, and (C) imidazole/TBAB in propylene carbonate (**Figure 2.11**). Firstly, all the kinetic curves, similarly to the PO-CO_2 coupling, were almost linear on the 0.25 – 2 h time scale, evidencing for the zero order of the reaction for HO. Only the progress of the reaction with the system A carried out at 120 °C was accompanied by minor retardation. Secondly, we observed non-linear dependence of lnk_{obs} from 1/T (**Figure 2.12**).

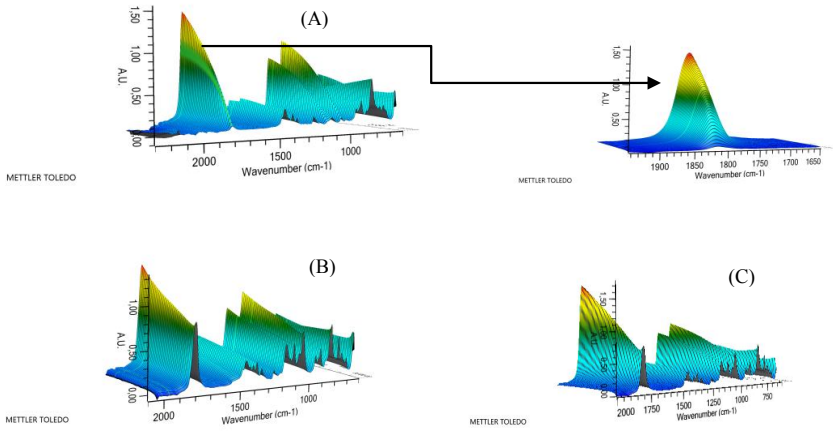


Figure 2.11. Three-dimensional stack plots for the HO-CO_2 coupling reactions utilizing catalyst systems. Reaction condition: 100 °C and 10 bar of CO_2. The intense absorbance for the asymmetric ν(C=O) vibration of cyclic carbonates appears at ~1800 cm^{-1}.

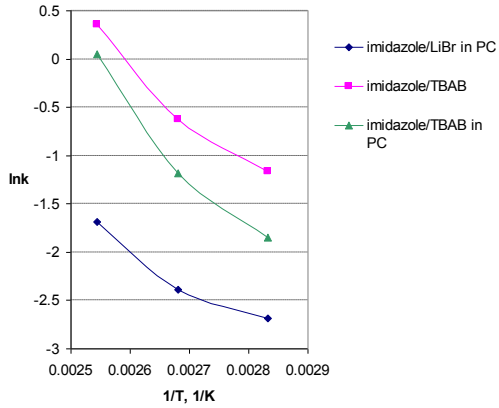
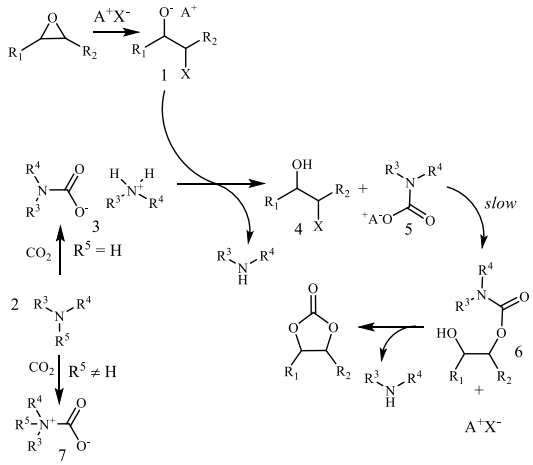


Figure 2.12. Arrhenius plots for the observed rate constants for the imidazole-halide-catalyzed addition of CO_2 to HO carried out at 80 °C, 100 °C, and 120 °C.

Proposed Reaction Mechanism

Based on the experimental results, we proposed a plausible mechanism of cooperative amine-halide catalysis (**Scheme 2.6**). The reaction of secondary and primary amines with CO_2 provide carbamate salts **3**, whereas tertiary amines give zwitterionic species **7**. Carbamate salt **3** neutralizes **1** completely rather than forms a hydrogen bond. As a result, an epoxide, an amine, CO_2, and a halide salt rapidly produce a pair of chlorohydrin **4** and carbamate **5**. The nucleophilic attack of **5** substituting X in **4** is presumably the slowest step of the catalytic cycle. The electron donation from the N atom should compensate the electron-withdrawing character of the carbonyl group and enhance nucleophilicity of **5**. Rapid formation of **4** and **5** and their subsequent slow reaction agrees well with the first order of the catalytic process for each of the co-catalysts and low sensitivity to the pressure of CO_2. We also suggest that the ring closing of **6** can be a slow process competing with the reaction between **4** and **5**. Different temperature dependence of these two stages might result in observed non-linear dependence of $\ln k_{obs}$ from 1/T. It should be noted, that non-protogenic tertiary amines cannot catalyze the reaction in the way described.



Scheme 2.6. Proposed mechanism for the coupling reaction catalyzed by metal-free system.

Conclusions

In the past 5 years, the area of synthesis and development of more-sophisticated cyclic carbonate scaffolds has developed tremendously, as testified by the contents of this thesis' literature review articles. Efforts have been made to increase the reactivity of the applied catalytic systems, providing very high TOFs and impressively high TONs. Obviously, catalytic systems that are able to combine robustness, recyclability, cost-effectiveness, and very high reactivity/selectivity features would serve as privileged systems within the area of cyclic carbonates synthesis from CO_2 and epoxides. Moreover, the employment of more environmentally friendly alternatives to potentially toxic metals such as chromium (if oxidized to Cr(VI)), coupled with mild reaction conditions, and the avoidance of polluting co-solvents is still a chemical challenge with room for improvement.

The present work describes the utilization of four environmentally friendly catalyst systems for CO_2-epoxide couplings: three of them are sustainable metal-based catalysts and one is organocatalysis. The metal-based catalysts were titanium(IV) alkoxide, Schiff base iron(III), and imidazole-Schiff base iron(III), whereas the metal-free catalyst was based on simple amines combined with onium or lithium salts as a green alternative to CO_2 conversion catalysis.

Ti(IV)alkoxide/TBAB is a highly efficient catalyst in the cycloaddition of CO_2 to various epoxides. It is an air stable, easily synthesized, cheap, non-toxic catalyst system, which is free of co-solvent and can tolerate multiple substrates. In addition, the mechanism for the coupling reaction was also discussed, which could explain the reaction results satisfactorily.

Schiff base iron(III) complex catalysts also have exhibited significant catalytic activities for the synthesis of carbonates via the cycloaddition of epoxides and CO_2. The iron catalysts in combination with tetrabutylphosphonium salt as a co-catalyst provided a highly efficient synthesis of propylene carbonate with 1029 TON value, and the catalysts could also be applied to the cycloaddition of various epoxides with CO_2 to prepare the corresponding cyclic carbonates. Later we modified the Schiff base iron(III) complex by starting with precursor ligand having imidazole as Lewis base.

The complex has been shown to be an efficient catalyst for the virtually ambient formation of organic carbonates using terminal epoxides and carbon dioxide as principal reagents at low catalyst loadings. The kinetic study resulted in a first-order reaction of catalyst concentration, suggesting an intramolecular activation mechanism. Since titanium and iron are a green alternative to toxic central metals like chromium, these catalytic systems may exhibit great potential in industrial applications.

The metal-free catalyst system, which is amine/salt, is an efficient, simple, and cheap catalytic system for the coupling reaction of CO_2 and epoxides to generate the five-membered cyclic carbonates under mild conditions without any co-solvents. Under the optimized reaction conditions, >99% PO conversion could be achieved at 80 ºC, 5 bar of CO_2, and 5 h. The catalytic system was also applicable to other terminal epoxides with good yield of cyclic carbonates. The work reported has the potential to improve the catalytic efficiency and reduce cost of products for larger applications.

Although the four catalytic systems can be used for the conversion of CO_2 and epoxides into cyclic carbonates, a direct comparison and evaluation is difficult. In nearly every case, different reaction conditions are applied, which have, to some extent, tremendous effects on the catalytic performance. Thus, the introduction of benchmark reaction conditions would be useful for an accurate evaluation of the overall catalytic performance. Ideally, benchmark reaction conditions should be based on a low temperature and low CO_2 pressure process with simultaneously short reaction time. Moreover, using readily available, inexpensive nontoxic reagents. These criteria must reduce the carbon footprint as much as possible to meet sustainable CO_2 conversion conditions, including easy catalyst recycling. In particular metal-free catalyst systems exhibit high activity and provide further opportunities for improvement.

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