Catalytic Activation of small molecules with metal complexes: CO_2 and O_2

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Academic Dissertation

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Abstract:

Catalytic transformation of carbon dioxide into useful organic compounds has attracted much attention due to its economic and environmental benefits. In addition, other reasons are also taken into account, such as the possible utilization of CO_2 as a renewable source chemical and the growing concern of the greenhouse effect. CO_2 is an abundant, cheap, and safe C_1 building block in organic synthesis. However, due to the inert nature of CO_2, efficient catalytic processes of its chemical fixation remain a significant challenge. In this work, we have studied a possible pathway for practical utilization of CO_2. The reaction of CO_2 with epoxides giving cyclic carbonates, has been investigated. New catalyst systems based on cobalt capable of catalyzing the chemical transformation of carbon dioxide are described in detail.

Oxygen is a cheap, readily available and environmentally friendly natural oxidant. The catalytic activation of molecular oxygen has great potential in a variety of applications. Catalysis and reactions, which are based on molecular oxygen, can also be considered to be ecologically benign processes. Moreover, catalytic reactions in water are highly desirable in terms of green chemistry. In this context, our purpose was to develop an environmentally friendly catalytic systems, suitable for oxidation of alcohols with molecular oxygen in water solution. In this part of the work, efficient catalysts, based on copper complexes have been synthesized and studied in the presence of TEMPO for the oxidation of benzyl and aliphatic alcohols with molecular oxygen in aqueous and nonaqueous medium.

Preface

This work has been carried out at the laboratory of Inorganic Chemistry at the University of Helsinki. Financial support of FORTUM foundation for ‘Carbon dioxide activation’ project and of the University of Helsinki is gratefully acknowledged.

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Contents

List of Original Publications

This thesis is based on the following publications

I. Facile synthesis of cyclic carbonates from CO_2 and epoxides with cobalt(II) /onium salt based. By Ahlam Sibaouih, Paul Ryan, Markku Leskelä and Timo Repo. Appl. Catal. A: Gen. (2009), 365, 194–198.

II. Efficient coupling of CO_2 and epoxides with bis(phenoxyiminato)cobalt(III) /Lewis base catalysts. By Ahlam Sibaouih, Paul Ryan, Kirill V. Axenov, Markku R. Sundberg , Markku Leskelä and Timo Repo. J. Mol. Catal. A: Chem. (2009) 312, 87–91

III. Aerobic oxidation of benzylic alcohols in water by 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)/copper(II) 2-*N*-arylpyrrolecarbaldimino complexes. By Paweł J. Figiel, Ahlam Sibaouih, Jahir Uddin Ahmad, Martin Nieger, Minna T. Räisänen, Markku Leskelä and Timo Repo. Adv. Synth. Catal. (2009) 351, 2625–2632

IV. Efficient copper based-catalysts for oxidation of benzylic alcohols in aqueous solutions by molecular oxygen. By Ahlam Sibaouih, afnan al hunaiti, Markku Leskelä and Timo Repo.

V. Aerobic oxidation of primary alcohols by copper based-catalysts and 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) in air. Ahlam Sibaouih, afnan al hunaiti, Markku Leskelä and Timo Repo.

The publications are referred to in the text by their roman numerals.

Abbreviations

Bu_4NBr	Tetrabutylammonium bromide
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DMAP	Dimethyl amino pyridine
HOMO	Highest Occupied Molecular Orbital
I	Iodine
Imes	1,3-Bis(2,4,6-trimethylphenyl)imidazolium chloride
Ipres	1,3-Bis(2,6-diisopropylphenyl)imidazolium chloride
NEt_3	Triethylamine
PC	Propylene carbonate
PO	Propylene oxide
PPNCl	Bis(triphenylphosphoranylidene) ammonium chloride
TBABr	Tetrabutylammonium bromide
TBACl	Tetrabutylammonium chloride
TBAI	Tetrabutylammoniumiodine
TEMPO	2,2,6,6-Tetramethylpiperidine-1-oxyl
TOF	Turnover frequencies
LUMO	Lowest Unoccupied Molecular Orbital
IL	Ionic Liquid
NMI	N-methyl imidazole
Bpy	Bipyridine
DMF	Dimethyl formamide

I- Catalytic activation of carbon dioxide

1 Introduction

With the growing concern about the environmental impact of chemical transformations, the chemical fixation of carbon dioxide has attracted great attention as a potential carbon source in industrial chemical processes.[1, 2] Carbon dioxide is generally considered as a green, environmentally benign solvent and reactant that is cheap, renewable and non-toxic.[3] Application of carbon dioxide in organic synthesis could result in economical and/or efficient routes to existing products. Moreover, the production of chemicals from CO_2 could lead to new organic materials in an environmentally friendly approach. However, being a stable molecule, carbon dioxide requires a considerable amount of energy or a suitable catalyst to transform CO_2 into desired products.

In this work, catalytic routes to carbon dioxide activation were studied using various substrates, employing copper -based catalysts. Synthesis and comprehensive characterization of catalyst precursors were an important part of this work. As a result, herein the development of efficient catalytic systems for transforming CO_2 into valuable products is reported. The underlying mechanisms and processes involved in the catalytic reactions of CO_2 with epoxides, mediated by copper-based catalyst are investigated. These studies serve to provide further understanding of the interactions between substrate, catalyst and CO_2 during catalytic reactions. Such knowledge is exceedingly important to aid the establishment of new highly efficient catalytic systems in the future.

2 Background

2.1 Carbon Dioxide

2.1.1 Properties

The carbon dioxide molecule is linear and contains 16 valence electrons. Although it contains two polarized C–O bonds, due to its linear configuration, the CO_2 molecule does not have a dipole moment. The vectors associated with charge separation in the C–O bonds are equal in intensity and opposite in direction. (Figure 1)

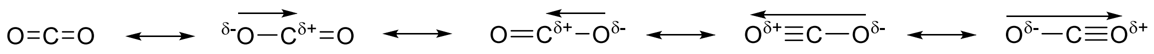


Figure 1. Resonance structure of CO_2

However, CO_2 maintains all the characteristics of a species containing polarized bonds, with electron donor and acceptor sites. The carbon atom is electrophilic, while the oxygen atoms are nucleophilic. It is noteworthy that the electrophilicity of the carbon atom dominates over the nucleophilicity of each of the oxygen atoms, so CO_2 commonly behaves as an electrophile.

2.1.2 Reactivity

Activation of the relatively inert CO_2 molecule and its conversion into organic products has attracted researchers for many years. Carbon dioxide is considered as one of the most thermodynamically stable molecules. The stability of CO_2 has generated the common belief that it is not reactive and thus transformation requires an energy input that renders the use of CO_2 for the synthesis of chemicals inconvenient. The chemical inertness of CO_2 is important with respect to oxidants such as O_2. There are a number of reactions, in which there is no need for an external energy supply, because the co-reagent provides enough energy to facilitate chemical fixation of CO_2 at room temperature or lower. The reactions of CO_2 with epoxides, amines or olefins could be mentioned here as examples.

In general, the reactions of CO_2 can be classified into two categories, according to the required Gibbs energy:

- The processes, in which the CO_2 molecule incorporates without changes into a substrate, do not require any external energy input. These are reactions leading to carbamates, ureas, isocyanates and carbonates.[4, 5]
- Reduction of CO_2 requires a considerable amount of energy, which could be provided via direct heat, electric current or irradiation. Examples are the formation of formate anions, formaldehyde, carbon monoxide, methanol and methane. [6, 7]

Both types of reaction requires a suitable catalyst, which is in most cases a metal coordinated system.

2.1.3 Coordination modes

After the discovery of the first transition metal-CO_2 complex[8,9], emphasis has been placed on studies of CO_2 coordination chemistry, with the aim of discovering new catalysts for chemical utilization of CO_2. In terms of coordination between CO_2 and metal center, the CO_2 molecule exhibits several distinct modes that display specific electronic properties (Figure 2). The carbon atom (maximum of LUMO electron density) has a Lewis acid character and can be described as an electrophilic center, whereas the oxygens (maximums of HOMO electron density) are nucleophilic centers and weak Lewis bases. It is worth noting that most CO_2 catalytic reactions require a simultaneous acid – base activation, with the carbon atom and one of the oxygen atoms involved in the interaction with the metal. The two double C=O bonds contain π electrons that can interact with d electrons of transition metals. When the LUMO orbitals of CO_2 are occupied (via electron transfer), the lowest energy state corresponds to a bent geometry. So, any interaction of carbon dioxide with a metal will induce a loss of linearity.

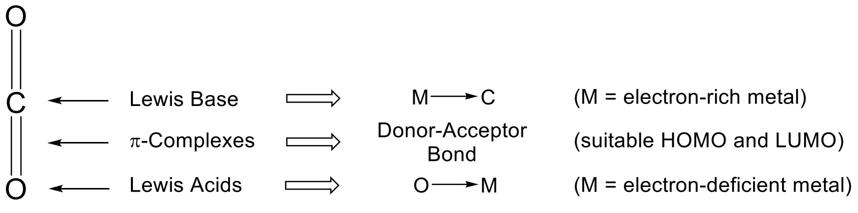


Figure 2. Type of metal and electronic properties of CO_2 dependance in metal-CO_2 bond.

There are different modes of CO_2 coordination to single metal center (Figure 3).

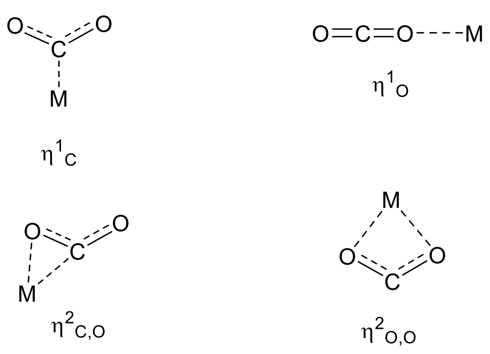
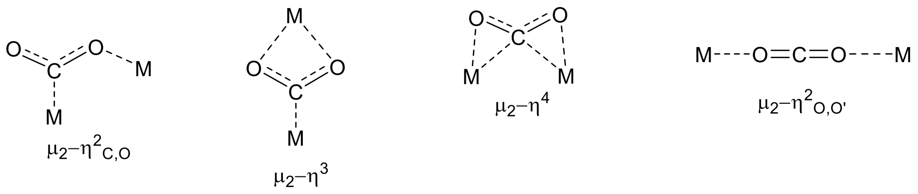
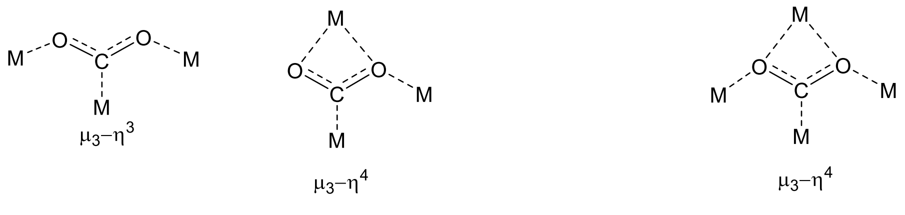


Figure 3: the CO_2 coordination modes to single metal center

Beside CO_2 can also act as a bridging ligand in bi- or polynuclear metal complexes (Figure 4).[10,11] In these coordination modes, a variety of chemical transformations, including insertion, dimerization and disproportionation reactions, became possible, giving a considerable number of transition metals derivatives.[12, 13, 14, 15]



dinuclear complexes



trinuclear complexes

tetranuclear complexes

Figure 4. the CO_2 coordination modes to two and three metals centers

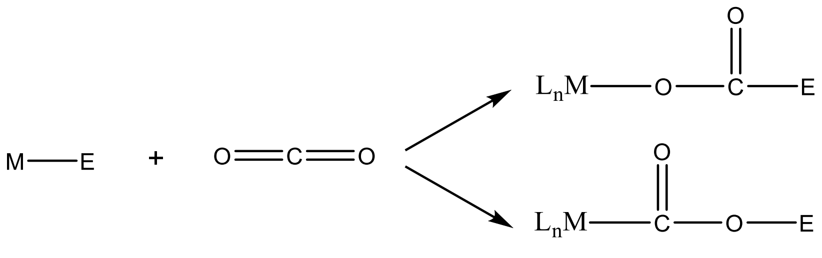
2.2 Conversion of carbon dioxide via metal complex

The binding of CO_2 to a metal centre generally leads to “activation” of the CO_2 molecule, and few reactions of coordinated CO_2 are known.[16,17] However, activation by coordination is not a necessary prerequisite for catalytic conversion of carbon dioxide to useful chemicals. The metal complexes may sometimes behave as stable forms of activated carbon dioxide.[18,19] However, the relationship between the structural and electronic properties of these complexes and their catalytic activity and chemical reactivity is not yet well understood.

The nature of the ligands and their substitution pattern affects the lability of the metal-CO_2 bonding. Apparent differences in the mode and strength of CO_2 binding is correlated with the catalytic activity of the complex. Ideally, metal–CO_2/epoxide bonding should neither be too strong nor too weak so that careful fine tuning of the ligand system facilitates the development of a highly active catalyst.

The activation of CO_2 by coordination to a transition-metal center lowers the activation energy required for further reactions involving the CO_2 molecule. Consequently, the rates of these processes increase, as in most cases the activation of CO_2 is the rate-determining step. The coordination of CO_2 makes it possible to convert this inert molecule with suitable reactants into useful products.

The insertion of CO_2 into a preformed metal–element (M–E) bond is of great industrial importance. Many stoichiometric and most catalytic reactions involving CO_2 activation proceed via formal insertion of CO_2 into highly reactive M–E bonds (E=element) with the formation of new C–E bonds. There are seven types of CO_2 insertion reactions reported so far, i.e. the insertion of CO_2 into the M–E bond (where E= C, H, N, O, P, Si or other metal). Two possible products could be obtained from the insertion of CO_2 into the M–E bond (Scheme 1).



Scheme 1. Insertion of CO_2 into metal-element bond (M-E)

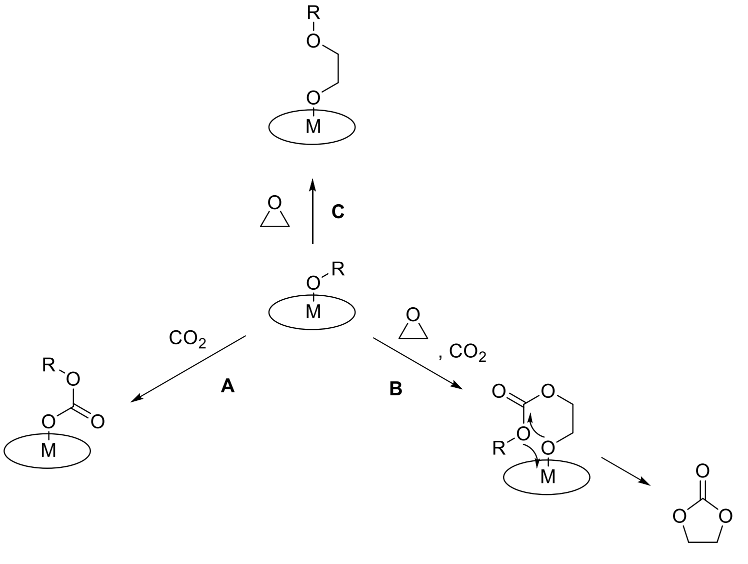
These reactions might not necessarily require strong coordination of CO_2 as in stable complexes, but are generally initiated by nucleophilic attack of E at the Lewis acidic carbon atom of CO_2. Weak interaction between the metal and the lone pairs of one oxygen atom of CO_2 may play a role in supporting the insertion process. There are several publications on the insertion of CO_2 into the M–E bond in the literature.[20,21,22]

The other route for the conversion of CO_2 into organic products is the simultaneous oxidative coupling of CO_2 and an unsaturated compound at a transition metal centre. CO_2 undergoes oxidative coupling reactions with an unsaturated substrate X=Y at a metal centre M to form the metallacycle. The unsaturated compound X=Y can be a hydrocarbon (alkynes, alkenes…), imine or aldehyde. The predominant transition metal complexes which mediate the coupling of CO_2 with unsaturated substrates are electron-rich and low valent metal complexes mainly Ni(0) and Pd(0), but some other transition metals such as Ti, Mo, Fe and Pt are also reactive.[23, 24, 25, 26]

2.3 Catalytic preparation of cyclic carbonate

Cyclic carbonates are widely used as aprotic polar solvents, fine chemical intermediates, sources for polymers and plastics, and ingredients for pharmaceutical in biomedical applications.[27, 28, 29]

When CO_2 and an epoxide are catalytically coupled, three different mechanisms are possible, leading to three different types of product (Scheme 2).[30] After initial coordination of the substrate to the catalyst, formation of a polycarbonate linkage can occur (pathway A) or a consecutive epoxide enchainment to afford a polyether linkage (pathway C). The other alternative is the formation of a cyclic carbonate by cyclization (pathway B). The cyclic carbonate can also be obtained from the decomposition of polycarbonate by a back-biting mechanism.[31]



Scheme 2. The three possible pathways after the coupling of CO_2 and epoxide.
M: metal center, R: polymer chain

According to the reported works on catalytic coupling of CO_2 and epoxides, polycarbonate and cyclic carbonates are formed in two simultaneous concurrent processes.[32, 33] As depicted in the diagram below (Figure 5), the activation energies for formation of polycarbonate or cyclic carbonate from propylene oxide are different.[31, 33] The activation barrier of cyclization between CO_2 and an epoxide is higher than that of linear polymerization.

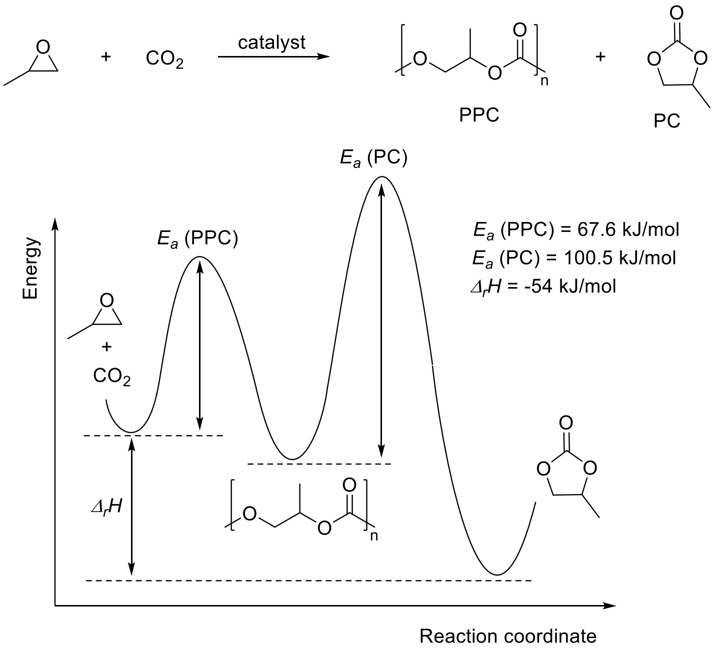
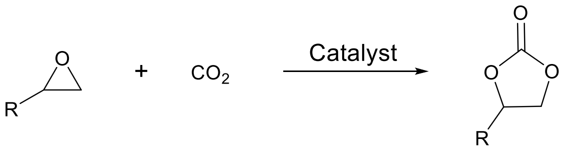


Figure 5. Activation energy diagram for formation of polycarbonate or cyclic carbonate from propylene oxide and CO_2. PPC : poly(propylene) carbonate; PC : propylene carbonate; E_a: energie d'activation .

The selectivity of the coupling reaction depends on different factors, such as the nature of the substrate, the concentration of epoxide, the structure of catalyst, the type and the load of co-catalyst, additives or the reaction pressure and temperature. It is known that high temperatures favor the formation of cyclic carbonates. With stronger Lewis acid catalysts, the formation of cyclic carbonates is usually significantly more relevant.[34] However, when the coupling of CO_2 and epoxides takes place, the occurrence of one specific mechanism is not always exclusive, and therefore to optimize and modulate the production of a specific product (cyclic carbonate), the understanding of the mechanistic details surrounding these reactions is of crucial importance. On this reaction, only formation of cyclic carbonate is discussed (Scheme 3). The coupling reaction of CO_2 and an epoxide selectively leading to cyclic carbonate product will be henceforth referred to as ‘‘cycloaddition reaction’’.



Scheme 3. Cycloaddition reaction of CO_2 and epoxides
R: alkyl or halide

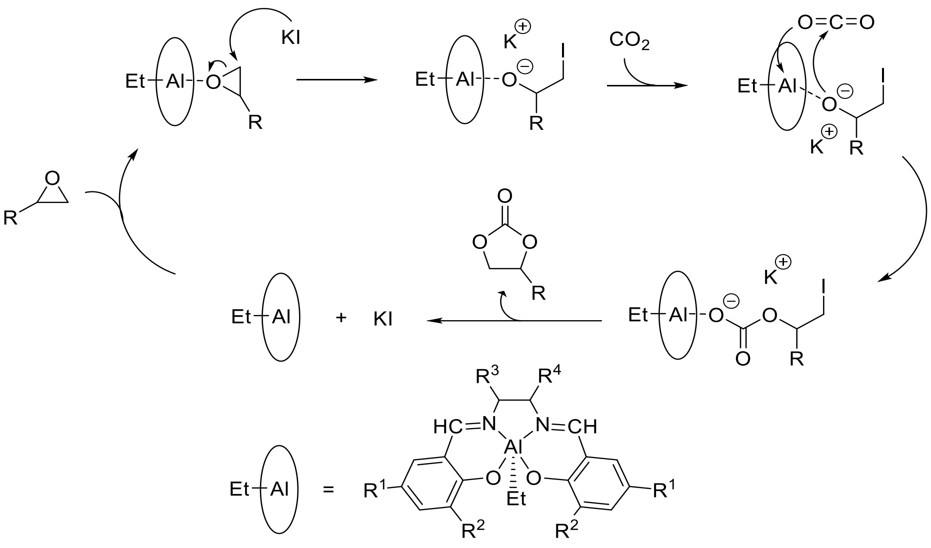
The cycloaddition reaction of CO_2 and epoxides, is usually promoted by bifunctional catalytic systems containing both Lewis-acid and base groups. A wide range of organic and organometallic compounds are well suited for this purpose, such as main group metal halides, metal complexes, transition metal systems, metal oxides, ammonium salts, supported bases, phosphines, ionic liquids.[35, 36, 37, 38] Both homogeneous and heterogeneous catalytic systems can provide selectivity and with high yields of cyclic carbonate products. However, homogeneous catalysts generally have higher catalytic activity and selectivity, and their properties are more easily tuned by modification of ligand. In this respect, the development of homogeneous catalysts based on salen complexes, onium salts, metal halides are discussed in the following sections.

2.3.1 Catalysts based on salen complexes

Salen complexes are very active and selective catalysts for the formation of cyclic carbonates from carbon dioxide and epoxides. There are reports in the literature describing catalytic behaviour of salen or salen-like complexes of aluminium, cobalt, chromium, manganese, zinc, ruthernium and copper, which are used to synthesize cyclic carbonates.[39,40,41,42,43] The majority of these catalysts can afford both polycarbonates and cyclic carbonates. The structure of the salen ligand can be tuned to favor the selective formation of the desired product. Substitution pattern of aromatic rings, axial substituents and/or the diamine backbone proved to be important parameters for the design of an efficient catalyst. As an example, the presence of electron-donating groups on the backbone favors the production of cyclic carbonate with respect to polycarbonate. Most metal complexes are only effective in combination with a nucleophilic cocatalyst, such as a Lewis base or a quaternary ammonium salt. Control experiments without cocatalyst display greatly reduced or completely suppressed yields of cyclic carbonate.[44,45] Various reports on the formation of cyclic carbonates have contributed to show that Lewis base activation of CO_2 and Lewis acid activation of the epoxide are crucial steps.[44, 46]

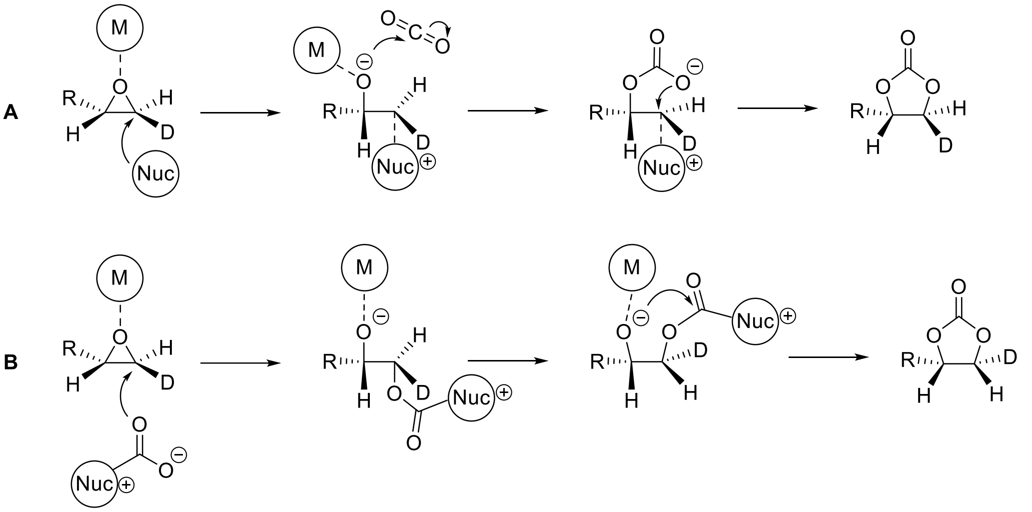
Several mechanisms have been proposed in the literature, explaining the catalytic behavior of salen-type catalysts in the coupling reaction between carbon dioxide and epoxides. While it is generally accepted that the metal salen catalyst activates epoxide by coordination, the role of the cocatalyst differs significantly among proposed mechanisms.

The commonly proposed mechanism starts by initial activation of an epoxide substrate by coordination to metal salen catalyst.[47,48,49,50] A subsequent nucleophilic attack by Lewis base co-catalyst to the least hindered side of epoxide gives a metal-alkoxy intermediate (Scheme 4). The CO_2 molecule inserts into metal-oxygen bond, producing a linear carbonate anion. Subsequent intramolecular attack of the carbonate group leads to the formation of the cyclic product with liberation of the Lewis base cocatalyst. Such a mechanism has been proposed for salen Al and Cu catalysts. [39,41]



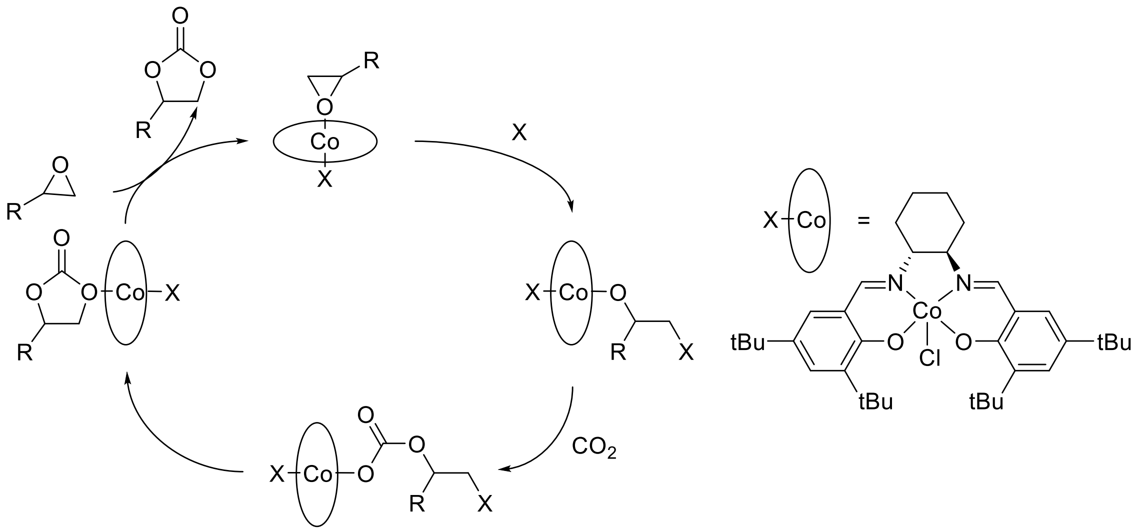
Scheme 4. Reaction mechanism for the cycloaddition reaction of epoxide and CO_2 catalysed by aluminium salen complex. R= CH_3, R^1= R^2=R^3=R^4= H. [39]

In the case of co-catalysts containing basic amines, such as DMAP, trialkyl amine, it is possible that nucleophilic amine reacts with CO_2, giving a $R_2NCO_2^-$ intermediate, which then opens the epoxy ring which has been activated by a Lewis acid (Path B, Scheme 5). In order to clarify the reaction mechanism, labeling studies have been carried out.[39,41] In these experiments, epoxides, *trans*-substituted with deuterium, were synthesized and reacted with carbon dioxide. According to the conventionally proposed pathway (A, Scheme 5), retention of the epoxide framework configuration should be observed in the product, while activation of carbon dioxide by a nucleophilic co-catalyst should lead to an inversion of the configuration in the product (Path B, Scheme 5). Since the inversion product has never been observed, it has been proposed that the path A is the actual mechanism.[39,41]



Scheme 5. Reaction mechanism for formation of cyclic carbonate from CO_2 and deuturated epoxide
R: C_4H_9, M: binaphthyldiamino salen-type Zn or Cu complexes, Nuc: Et_3N [39,41]

An alternative mechanism involves coordination of both a Lewis base and epoxide with the salen catalyst (Scheme 6) [51] Here, the Lewis base serves two roles. It opens the epoxide ring and coordinates with the metal salen complex to facilitate the insertion of carbon dioxide into epoxide. This is the reason, why two equivalents of the Lewis base are usually found to be optimal. According to the suggested catalytic cycle (Scheme 6), a further increase in the concentration of a base should slow down the reaction, due to arising competition between the base and the epoxides for coordination to the metal. A deactivation pathway may also happen, in which a large fraction of the base binds with carbon dioxide at high pressures, preventing the coordination of the base with the metal salen complex.

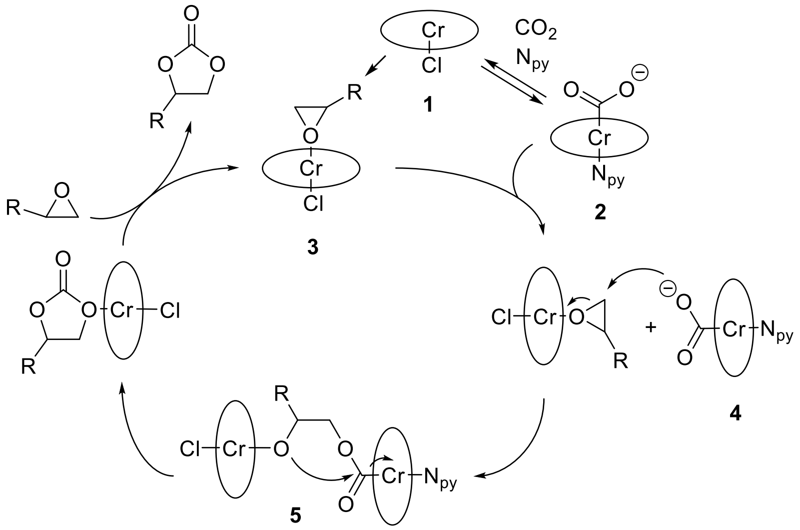


Scheme 6. Reaction mechanism for the cycloaddition reaction of epoxide and CO_2 catalysed by cobalt salen complex and DMAP. R: CH_3, X: Cl^- or DMAP [51]

Lately, it has been suggested that the coordination of Lewis base co-catalyst with the metal salen is in fact not required for catalytic process.[52] In order to prove this hypothesis, both the salen catalyst and the Lewis base were introduced into the reaction bound to two different solid supports, thus making the direct contact between the salen complex and cocatalyst difficult. Based on the conventional mechanism (Scheme 6), this should lead to a dramatic decrease in the catalytic activity and yield of cyclic carbonate. However, the activity of the catalyst was only partially suppressed, indicating that the interactions between salen complex and a Lewis base are not critical for the catalyst.

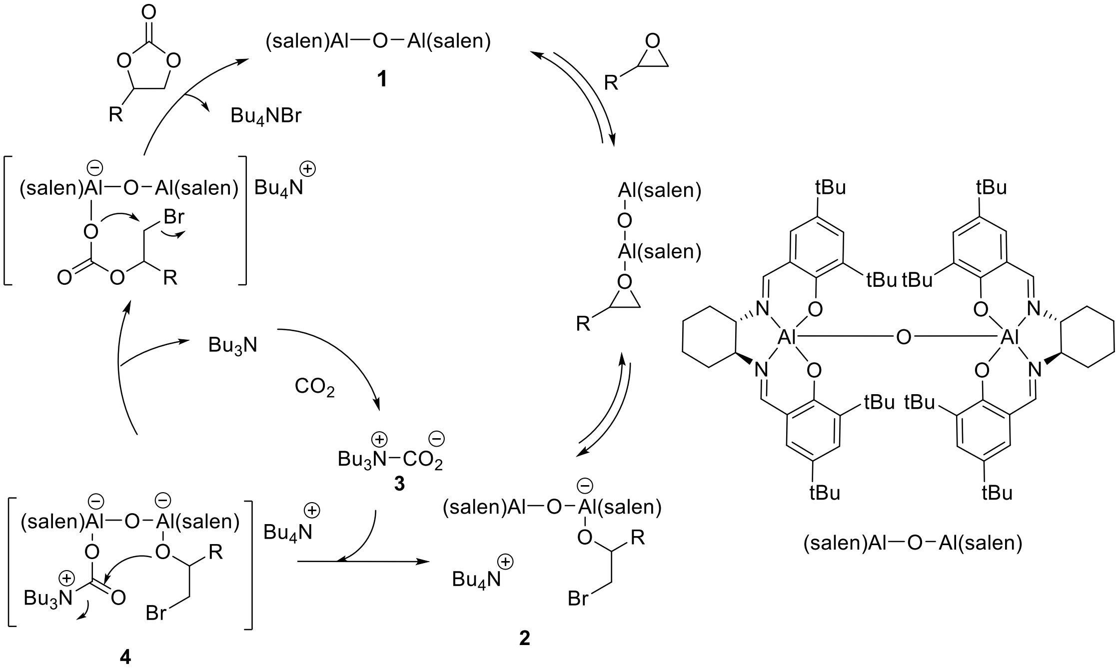
Jacobsen *et al.* have discovered that nucleophilic ring opening of epoxides catalyzed by chromium(III) complexes depends on both the electrophilic epoxide and the incoming nucleophile[53] which requires a mechanism different to those discussed above. In order to solve this problem, Paddock *et al.* proposed a cooperative bimetallic mechanism involving two different metal species activating both an epoxide and CO_2.[45] In their catalytic system, the original (salen)CrCl complex fulfilled the role of activating the epoxide.[45] The DMAP co-catalyst was necessary for creating the more electron-rich Cr(III) center by formation of the (salen)Cr(III)-DMAP complex. This DMAP-complex simultaneously coordinates with CO_2, donating electron density from the metal center to CO_2 ligand (Complex **4**, scheme 7).

Complex **4** can then attack the activated epoxide complex **3** at the least sterically hindered carbon, leading to the formation of the dimeric intermediate **5**, and then the cyclic carbonate product (Scheme 7). The same mechanism was proposed for Cu-salen complexes using DMAP as the nucleophile.[54] This mechanism appears to be in direct opposition to the labeling studies supporting a conventional reaction pathway, presented above (Scheme 5). Also, no reason was given as to why a cocatalyst would not also coordinate with the salen complex activating an epoxide substrate. In this mechanism, the increase in DMAP concentration or CO_2 pressure would lead to a preferred formation of **4** at the expense of **3**, thereby reducing the reaction rate.



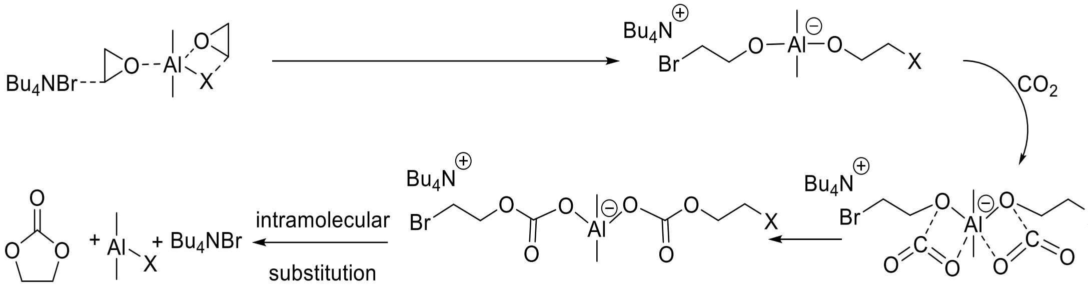
Scheme 7. Reaction mechanism for the cycloaddition reaction of epoxide and CO_2 catalysed by chromium salen complex and DMAP. R: alkyl, N_{PY}: DMAP [45]

For bimetallic $[Al(salen)]_2O$ complexes, a mechanism different from that of monomeric salen Al was suggested (Scheme 8).[42,55,56] In bimetallic catalysis, one aluminum center of a salen catalyst coordinates with an epoxide ring, which is subsequently ring-opened by a Br^- anion from the quaternary ammonium cocatalyst (Scheme 8).[42,56] A second molecule of ammonium salt decomposes into trialkylamine, which coordinates with carbon dioxide to form a carbamate salt **3**. This process is reversible. The carbamate salt **3** binds with another free Al center of the coordinated bimetallic salen complex **2**, giving species **4**. The complex **4** contains both a coordinated alkoxide and a carbamate species bearing an ammonium moiety as a good leaving group. By intramolecular attack of the aluminum-bound alkoxy nucleophile to the carbonyl group of the coordinated carbamate, trialkylamine leaves with the formation of a linear carbonate species. Subsequent cyclization regenerates the Br^- anion and gives the cyclic carbonate product (Scheme 8).[56] Bimetallic composition of the aluminum salen complex may not be required for production of cyclic carbonate, however it considerably enhances the activity of the catalyst.



Scheme 8. Reaction mechanism of cyclic carbonate from epoxide and CO_2 catalysed by bimetallic $[Al(salen)]_2O$ complexes and DMAP. R: alkyl [56]

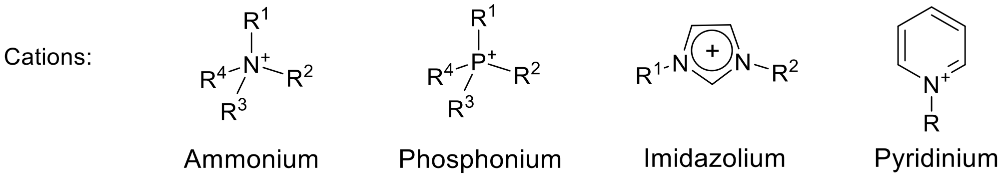
Although other reaction mechanisms have been reported,[57,58,59,60] the reaction schemes outlined here are the most commonly proposed for CO_2-epoxide coupling reactions, catalyzed by salen complexes. For aluminum complexes, it has been proposed by Lu et al. that CO_2 is activated by concerted coordination of a C=O group to an Al-alkoxy intermediate (Scheme 9).[57] It resulted in the insertion of CO_2 into Al–O bond to form linear carbonate species, which were transformed into cyclic ethylene carbonate by intramolecular nucleophilic substitution.[57] In more general approach, multiple reaction pathways can occur simultaneously, with one or more predominating under used reaction conditions. Nevertheless, close examination of these proposed conventional mechanisms could still prove useful in designing of highly active, efficient and selective catalytic systems.



Scheme 9. The possible formation mechanism of ethylene carbonate from sc-CO$_2$ /ethylene oxide mixture in the presence of SalenAlX/n-Bu$_4$NBr binary catalyst. X: [57]

2.3.2 Ionic Liquids in CO$_2$-Epoxide Cycloaddition Reaction: catalyst and cocatalyst.

During the last decades, lot of attention has been given to the application of ionic liquids (ILs) as catalysts, additives, new ligands, and/or solvents in the cycloaddition reaction of CO$_2$ and epoxide for synthesis of cyclic carbonates.[61,62,63,64,65] Carbon dioxide can be easily dissolved into ILs phase, which in turn makes the reaction of CO$_2$ possible and suitable.[66,67,68] In fact, ILs have been reported as one of most efficient media for the cycloaddition reaction of CO$_2$ and epoxide. In addition, the supercritical CO$_2$ mixed with ILs forms a biphasic system, which proved to be selective and efficient media for cyclic carbonate synthesis. The typically used ionic liquids are salts of quaternary ammonium, phosphonium, imidazolium, pyridinium cations with inorganic counterions (Figure 6). The physical and chemical properties of the ionic liquids including their melting points depend on both the nature of the cation and the anion.[69]



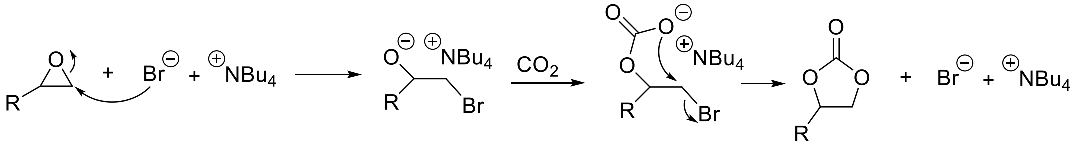
Anions: BF$_4^-$, PF$_6^-$, X$^-$ (X$^-$ = Cl$^-$, Br$^-$, I$^-$), NO$_3^-$, CF$_3$SO$_3^-$, PhSO$_3^-$

Figure 6.The most used ionic liquids in the cycloaddition reaction of epoxide and CO$_2$

The application of ionic liquids as solvents improves the catalytic activity of metal complexes and accelerates the speed of the reaction in comparison with conventional organic solvents. Presumably, ionic liquids promote the formation and/or stabilization of polar or ionic intermediates. The reaction rate depends on the nucleophilicity of the counteranion as well as the structure of the cation in the ionic liquid.[70,71,72] In particular, the ability to liberate halide species or the stability of the reaction intermediates mainly depends on the structure of onium cation.

For example, tetraalkylammonium halides are employed as solvents and catalysts. Epoxides are dissolved in molten tetraalkylammonium salts bearing halide counterions and converted into cyclic carbonates under atmospheric pressure of CO_2.[72] 1-*n*-Butyl-3-methylimidazolium and *n*-butylpyridinium salts are most active catalysts, displaying almost 100% selectivity towards cyclic carbonates.[73,74]

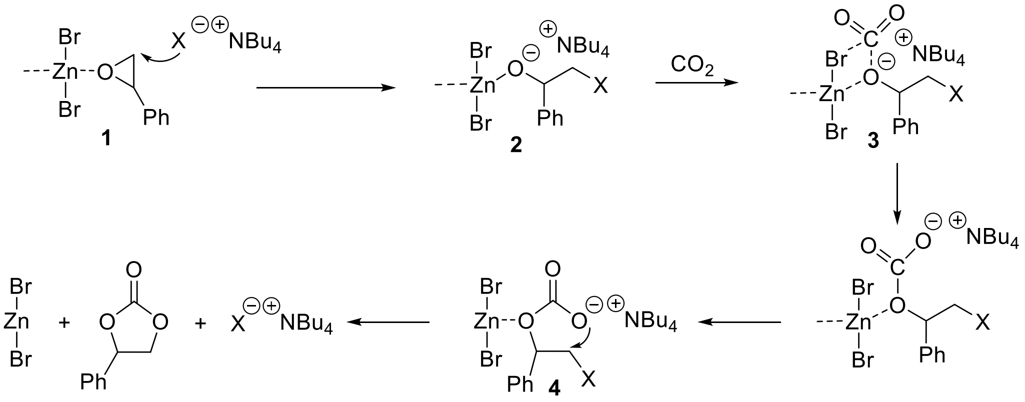
The reaction mechanism of catalysis by ILs operates similarly as it was described for Bu_4NBr. It has been proposed that nucleophilic halide counteranion opens an epoxide cycle with formation of ammonium alkoxide species (Scheme 10). Subsequent insertion of CO_2 and cyclization lead to a cyclic carbonate product and regenerate the ILs catalyst.



Scheme 10. Reaction mechanism of Bu_4NBr in the formation of cyclic carbonate.
R: H, alkyl or halide [72]

The combination of a Lewis acid with an ionic liquid exhibited a marked increase in catalytic activity towards cyclic carbonate.[45,55,75,76,77] Several metal halides were tested. A mixture of ionic liquids and zinc salts showed the best results even with the least reactive substrates, such as styrene and cyclohexyl oxides.[78,79,80,81] Metal halides alone are inactive for the cyclization. As suggested, the increased activity of these bicomponent systems, compared with the pure ionic liquid, might be a result of the cooperative influence from both the Lewis acid cocatalyst and nucleophilic halide anion. There are several proposed reaction mechanisms of the coupling cyclization with metal halide-ionic liquid binary catalytic systems. All of these mechanisms are mostly agreed with the requirement that the presence of both Lewis base and Lewis acid are needed for the activation of CO_2 and epoxide substrate, respectively. According to the literature, zinc halide/onium salt systems operate by another pathway.

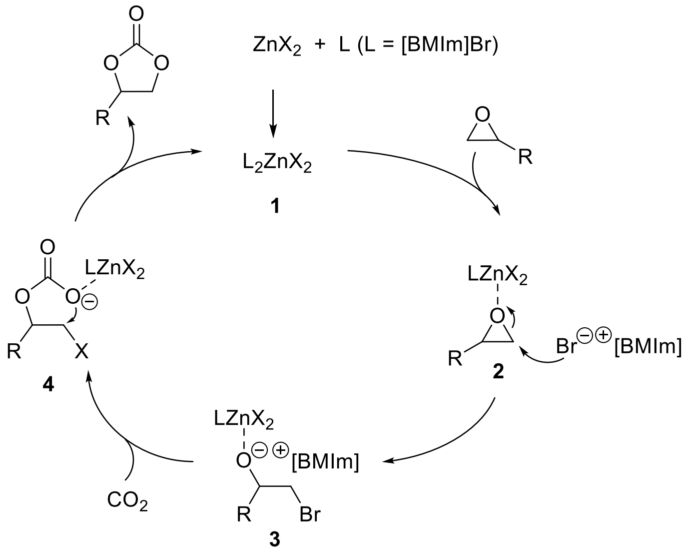
In the generally proposed mechanism for the cycloaddition of CO_2 and epoxide, the epoxide substrate is activated by a coordination of a Lewis acidic ZnX_2 catalyst via the zinc metal center.[77] Then, a halide anion of the onium co-catalyst attacks the less hindered carbon atom of the coordinated epoxide, leading to a ring opening (Scheme 11). The produced alkoxy species are stabilized by coordination with the zinc Lewis acid catalyst. The insertion of CO_2 into a Zn-O bond of the alkoxy intermediate **2** is facilitated by initial interactions between the carbon atom of CO_2 with oxygen and halide atoms of the alkoxyintermediate **3** (Scheme 11). The formed species **4** generates cyclic carbonate product and ZnX_2/onium catalyst is released.[77]



Scheme 11. Reaction mechanism for the formation of cyclic carbonate catalyzed by $ZnBr_2/NBu_4X$. X: Cl^-, Br^- or I^-.[77]

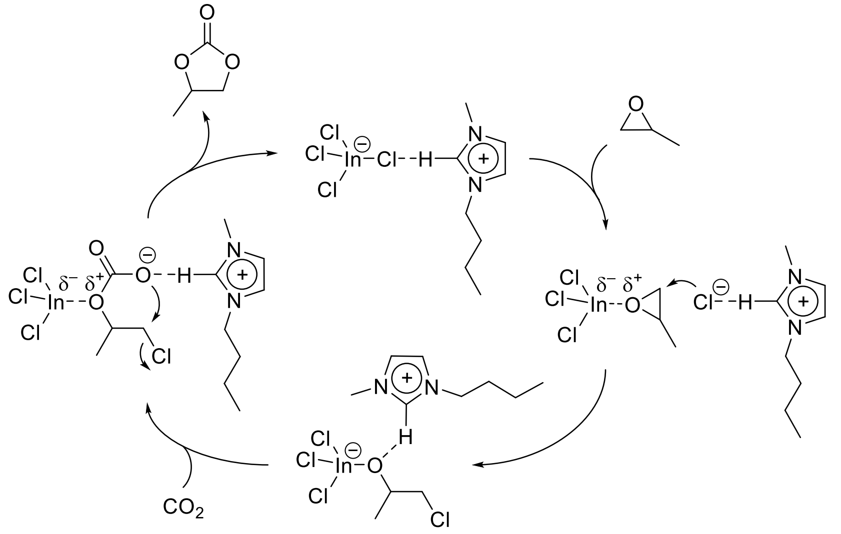
Depending on the onium salt type and the ratio cocatalyst/catalyst, new catalytic species are generated. In contrary to the previous mechanism (Scheme 11), the onium cocatalyst binds as a ligand to ZnX_2 to give a L_2ZnX_2 complex (Scheme 12).[46] In the catalytic system ZnX_2/[BMIm]Br (BMIm = 1-butyl-3-methylimadazolium), the coordination of L group to zinc metal center is taking place through 2-H of imidazolium ring. The resulted L_2ZnX_2 complex coordinates with the epoxide by replacing one of the ligands. At the same time, a nucleophilic attack of the onium halide cocatalyst occurs on the less sterically hindered carbon atom of the coordinated epoxide with formation of the active Zn-alkoxy species **3**. The insertion of CO_2

into the Zn–O bond of **3** provides zinc carbonate **4**, which finally converts into the cyclic carbonate.[46]



Scheme 12. Reaction mechanism for the formation of cyclic carbonate catalyzed by $ZnCl_2$/[BMIm]Br. [46]

Another group has reported that the reaction of 1-alkyl-3-methylimidazolium halides with zinc halides produces a bis(1-alkyl-3-methylimidazolium) tetrahalozincate complexes ($[Alk\text{-}Im]_2^+[ZnX_2Y_2]^{2-}$), which are highly active.[82,83] Their dissociation gives a halide anion, which subsequently attacks the epoxide. The catalytic activity of imidazolium tetrahalozincate species is greatly influenced by the nature of halide groups bonded to the zinc center. The activity increased with increasing nucleophilicity of the halide ligands. Similar to this system, Kim et al reported imidazolium-$[InCl_4]^-$, where the H-bonding between imidazolium cation and tetrahaloindate anion was observed.[71] This H-bonding interaction has been found to be an important factor affecting the catalytic activity of imidazolium halide/InX_3 system in CO_2-epoxide coupling. According to NMR studies, the H-bonding occurs through interactions between the halide ion and hydrogen atom in the position 2 of the imidazolium cation. This property renders the dissociation of halide ion from indate(III) ion and the coordination of epoxide much easier, thus facilitating the activation of coordinated epoxide and via ring-opening formation haloalkoxy species, which are also stabilized by the H-bonding interactions (Scheme 13).



Scheme 13. Reaction mechanism for the formation of propylene carbonate catalyzed by $[C_4mim][InCl_4]$.[71]

3 Experimental

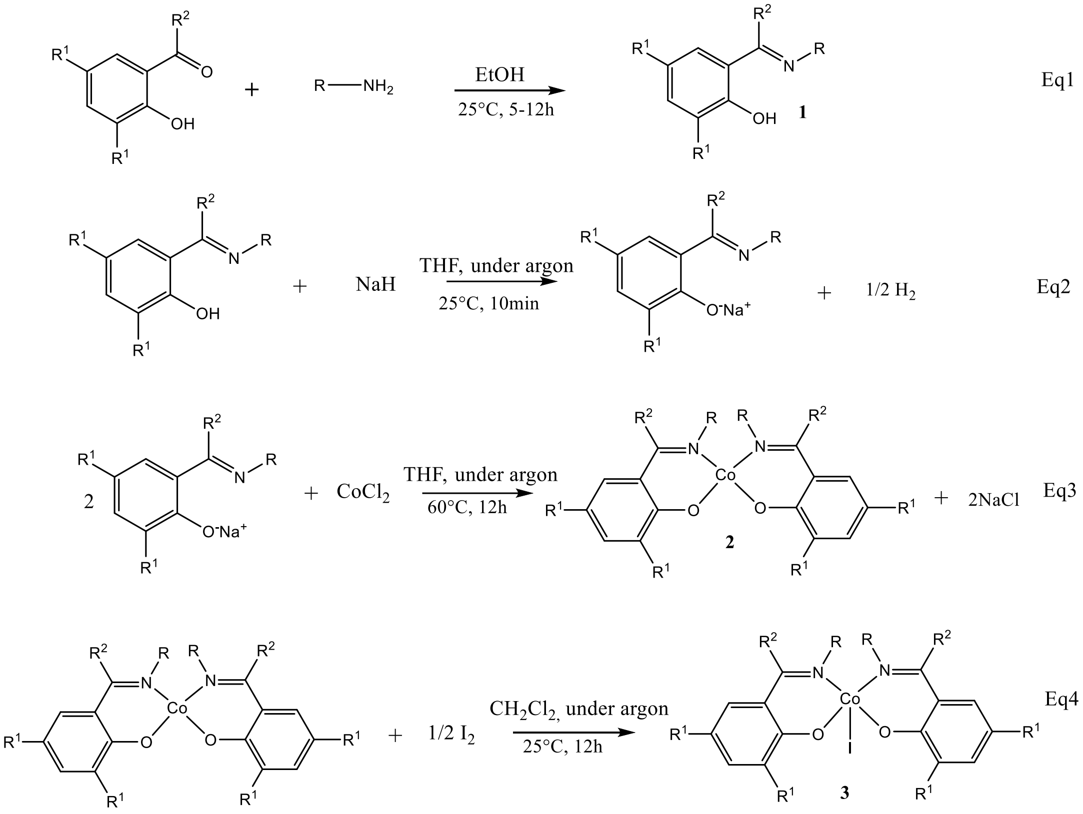
In our experiments, we have developed two catalytic systems active in coupling CO_2 and epoxides. In the beginning of our work, the CoX_2 catalysts were studied in the combination with various onium salts used as cocatalysts. Most components were commercially available, while 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride and 1,3-bis(2,6-diisopropylphenyl) imidazolium chloride were prepared according to literature procedures.[84,85,86] In further experiments, new catalytic systems based on an unbridged bis(phenoxyiminato) Co(III) framework has been designed. In that case, either DMAP or $Bu_4N^+Br^-$ were served as active components to promote the catalytic reaction as cocatalyst.

Catalytic experiments were carried out in a 100 ml steel autoclave equipped with a glass liner and a magnetic stirring bar. In a typical reaction set-up, the catalyst (0.01 mmol), dichloromethane (0.5 ml), epoxide (40 mmol), and onium salt (0.04 mmol) were loaded into the glass liner. The reactor was then pressurized with the appropriate amount of CO_2 (10 bar) and heated to the desired temperature (120-145°C). After the required reaction time (1 h), the reactor was cooled in an ice bath and degassed. Prior to GC analysis, the reaction solution was diluted and an external reference standard (acetophenone) was added. A sample from the reaction solution was then taken and analyzed using a gas chromatograph (Agilent 6890N). The product formation and distribution was verified with a mass spectrometer connected to GC (Agilent 5973).

4 Results and discussion

4.1 Synthesis

The phenoxyimino ligands **1a-1k** were prepared via a series of simple condensation reaction between primary amines and either salicylaldehyde or 2'-hydroxyacetophenone in ethanol (Eq1, Scheme 14). For synthesis of Co(II) complexes, an appropriate ligand was dissolved in dry THF and deprotonated by NaH in THF under argon (Eq2, Scheme 14). A solution of the obtained phenoxyiminato Na-salt was treated with $CoCl_2$ heating to 60 °C and stirring for 12 h under argon (Eq3, Scheme 14). After necessary work up and purification, Co(II) complexes **2a**-**2k** were isolated in pure state with good yields. Prepared Co(II) derivatives **2a-2k** have been oxidized in the presence of I_2 into the corresponding phenoxyiminato Co(III) iodides **3a**-**3k** (Eq4, Scheme 14). An excess of iodine was removed by prolonged drying of obtained products under high vacuum. Characterization of the complexes and experimental details are fully described in the experimental part of the attached original publication II



a, R = Ph-, R^1 = H, R^2 = H

b, R = p-$(CH_3)C_6H_4$-, R^1 = H, R^2 = H

c, R = p-$(Cl)C_6H_4$-, R^1 = H, R^2 = H

d, R = $C_6H_5CH_2$-, R^1 = H, R^2 = CH_3

e, R = $C_6H_5CH_2$-, R^1 = H, R^2 = H

f, R = p-$(F)C_6H_4CH_2$-, R^1 = H, R^2 = H

g, R = $C_6H_5CH_2CH_2$-, R^1 = H, R^2 = CH_3

h, R = $C_6H_5CH_2CH_2$-, R^1 = H, R^2 =H

i, R = $C_6H_5CH_2CH_2$-, R^1 = *t*-Bu, R^2 = H

k, R = $C_6H_5CH_2$-, R^1 = t-Bu, R^2= H

l, R = p-$(F)C_6H_4CH_2$-, R^1=t-Bu, R^2 = H

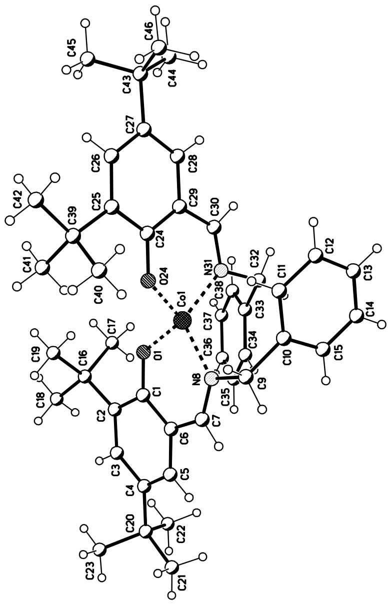
m, R = $(CH_3)_2CH_2$-, R^1 = t-Bu, R^2= H

Scheme 14. Syntheses steps of phenoxyiminato Co(III) iodides

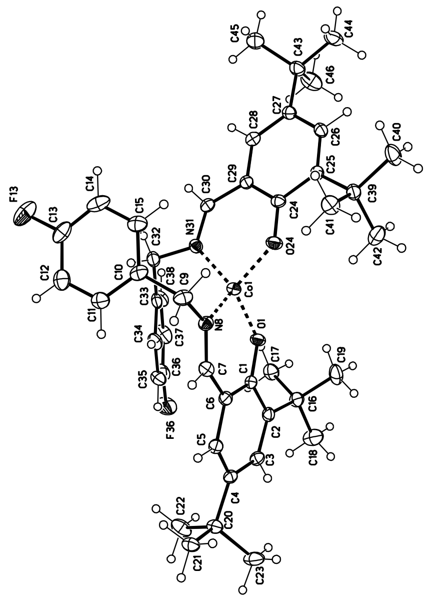
4.2 Structures

Crystal structures of complexes **2k**, **2l** and **2m** are shown in Figure 7. Suitable crystals for X-ray analysis were obtained by slow diffusion of THF into concentrated hexane solutions of the complexes. For the complexes **2k** and **2l**, X-ray crystallography has revealed that the Schiff base ligands are coordinating in a bidentate fashion with the cobalt center. In the molecule, two ligands are bounded with one cobalt center. The molecular geometry around the metal centre can be described as distorted tetrahedral. Nitrogen atoms from the ligand framework adopted a *cis* arrangement. In **2k** and **2l**, the N-Co bond lengths are fairly similar. The same applies to all Co–O bonds, which do not change much among the two complexes. Six bond angles, O(1)-Co(1)-O(24), O(1)-Co(1)-N(31), O(24)-Co(1)-N(31), O(1)-Co(1)-N(8), O(24)-Co(1)-N(8), N(31)-Co(1)-N(8), vary to some extent from each other. For example in the complex **2l**, the above angles are 118.73°, 121.47°, 94.96°, 95.95°, 109.07° and 117.62°, respectively. The distortion from the ideal tetrahedral geometry is greater for the three complexes **2k**, **2l** and **2m**. This can be seen when comparing the N(31)–Co(1)–N(8) bond angles. For complex **2k**, this angle is 121.02°, for complex **2m** is 119,67° while in **2l** corresponding angle is 117.62°. This difference appears most likely due the bulkiness of the ispropyl and the phenyl groups. In addition, the presence of the highly polarized fluoroaryl-substituents in the complex **2l** has reduced the distortion comparing to the complex **2k**.

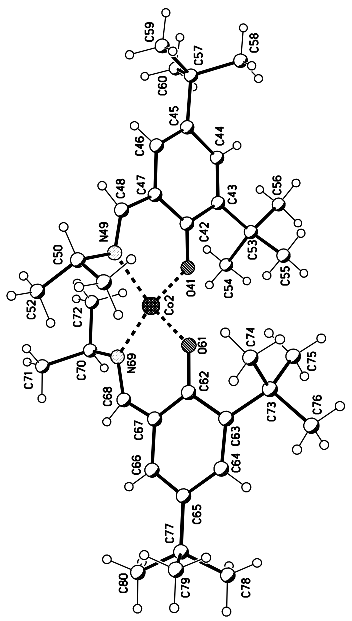
The Complex **4e** was synthesized by the reaction of the complex **2e** with two equivalents of DMAP in THF. Similarly to the above described complexes, suitable crystal for X-ray analysis was obtained by slow diffusion of THF into concentrated hexane solutions of the complexes. The crystal structure of complexes **4e** is shown in Figure 6. The X-ray crystal structure displays that in the complex **4e** the ligands are arranged around the metal center in an octahedral coordination geometry, in which two Shiff base (N-O donors) are bound to the metal atom in the basal plane and two DMAP groups (N donors) are placed at axial positions of the coordination octahedron. The Co-N (DMAP) bonds are rather elongated compared with the ones between the Co center and Shiff base imino-nitrogens. The bond lengths of Co–N, Co(1)-N(8), Co(1)-N(16) are 2.1239(11) and 2.2065(10) Å respectively. Slight distortions of octahedral coordination in **4e** are detected by deviations in the bond angles between the apical and basal donor atoms.



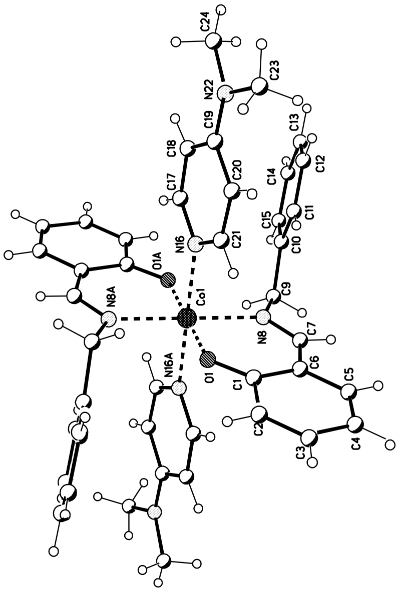
Co(II) Complex **2K**



Co(II) Complex **2l**



*Co(II) Complex **2m***



Co(II) Complex **4e**

Figure 1. Crystal structures of complexes **2k**, **2l**, **2m** and **4e**

4.3 Calculated structures

According to performed quantum chemistry calculations, the coordination sphere in unbridged bis(phenoxyiminato) Co(III) complexes have distorted square pyramidal geometry, wherein iodide lies in the main plane and one of the oxygens from the phenoxy groups occupies the apical position (Figure 8). In another words, both phenoxyimino ligands are placed in planes, which are perpendicular to each other. This differs from bridged salen-type complexes, where the ligand adopts the thermodynamically more favored planar configuration.

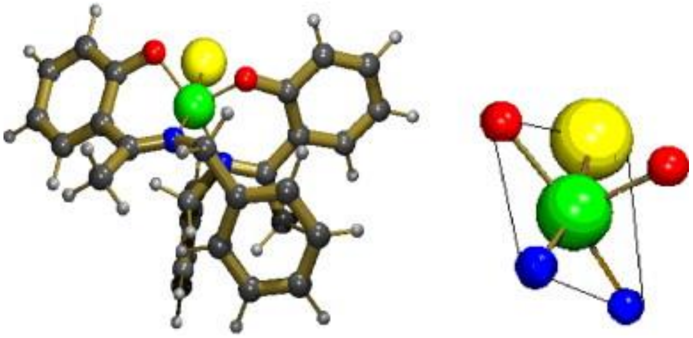


Figure 2. Calculated structure of bis(salicylaldiminato) complex 4 (left) shows a distorted square pyramidal coordination geometry for Co(III) (right).

4.4 Activation of CO_2 with Co(II)/onium Salt Systems

A combination of transition metal halides with Lewis bases has been shown to be a highly active system for promoting the coupling reaction of CO_2 and epoxides toward cyclic carbonates. Kirsh at al. have first observed that $ZnCl_2$, $FeCl_3$, $CoCl_2$ and other metal halides in the presence of phosphines or quaternary salts catalyze the coupling of propylene oxide and CO_2 to form propylene carbonate.[87] In this work, efficient selective and simple catalytic systems based on Co(II) salts/onium salts were studied.

4.4.1 Effects of onium salt and Co^{2+} sources

The reaction of propylene oxide with CO_2 was conducted at 120°C for 1h. Co(II) compounds without onium cocatalysts do not catalyze the coupling of CO_2 with epoxides, while onium salts alone display moderate catalytic activity in this process. The addition of Co(II) derivatives to onium salts have increased largely the conversion of propylene oxide to propylene carbonate (Table 1). To have a better insight into the effect and the role of the cocatalysts, the activities of various onium salts including phosphonium, imidazolium and ammonium halides were evaluated (See Figure 9).

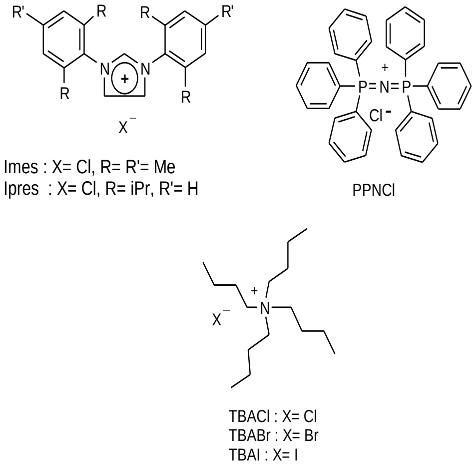


Figure 3. The studied onium salt

The bis(triphenylphosphoranylidene) ammonium chloride (6, PPNCl), showed the highest activities with recorded turnover frequencies (TOFs) up to 2300 (Table 1). The anion and the cations in the onium salt have a marked influence on the reaction rate. By changing the anion in tetrabutyl ammonium salts, Cl^- was found to be more advantageous than Br^- and both of them considerably better than I^-. Anions from the onium cocatalyst seems to provide a nucleophilic attack on the activated epoxide substrate and the effectiveness of chloride anions might arise from its nucleophilicity. Among the imidazolium salts, sterically more demanding 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (Ipres) generated a markedly less active binary catalyst than its methyl substituted analogue Imes. These facts show that the onium cation is involved into the reaction. It could stabilize leaving group upon an intramolecular attack in the linear carbonate intermediate (see below) or it can coordinate with Co(II) catalyst, facilitating its reactivity.

The importance of the coordinated anion in Co(II) salts were also investigated by testing various Co^{2+} sources. $CoCl_2$ was most active compound in the row $CoCl_2$ > $CoBr_2$ > $Co(OAc)_2$. It is worth to note that Lewis acidity decreases in same order. The function of Co(II) catalyst is to coordinate with an epoxide substrate. This leads to the polarization of an epoxide ring and its activation toward subsequent nucleophilic attack. Coordination of most

Lewis acidic $CoCl_2$ should provide strongest influence on the chemical activity of propylene oxide, and this was in fact observed.

Table 1. Catalytic activity of different cobalt and onium salts in propylene oxide and CO_2 reaction

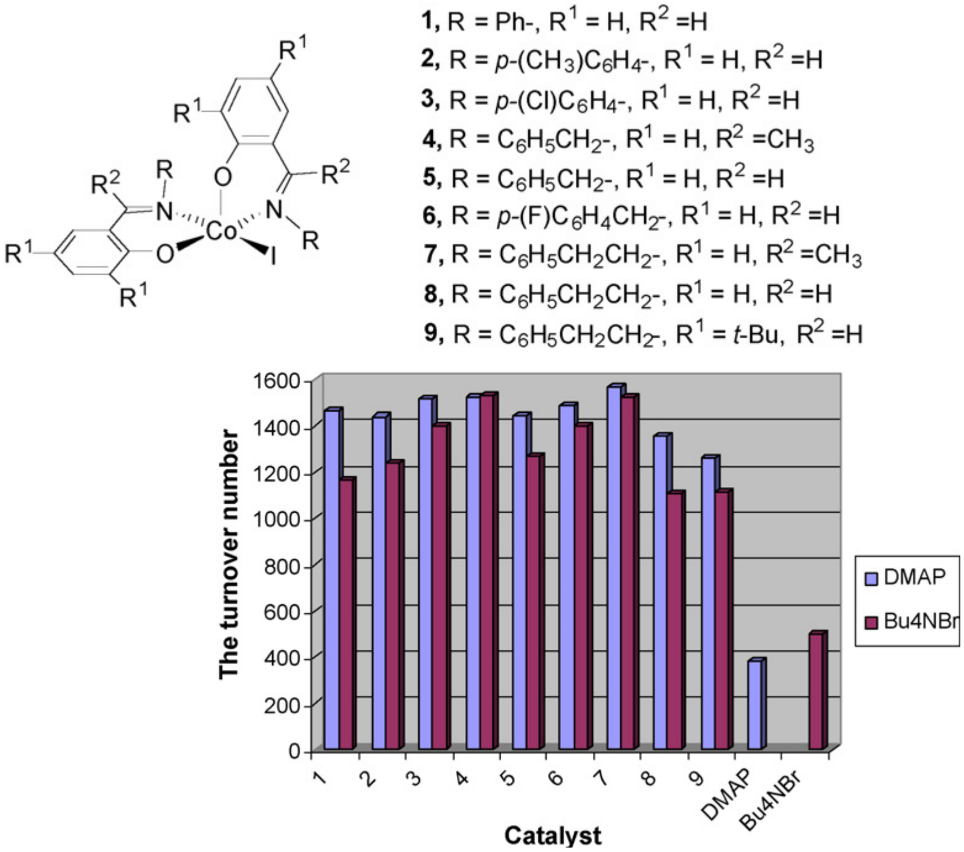
Entry	Co(II) source	Onium Salt	TOF^b
1	$CoCl_2$	TBABr	1568
2	$CoCl_2$	TBACl	2223
3	$CoCl_2$	TBAI	638
4	$CoCl_2$	Imes	2174
5	$CoCl_2$	Ipres	1135
6	$CoCl_2$	PPNCl	2314
7	$CoBr_2$	Imes	1814
8	$CoBr_2$	TBACl	1949
9	$CoBr_2$	PPNCl	1812
10	$CoOAc_2$	Imes	1502
11	$CoOAc_2$	TBACl	1145
12	$CoOAc_2$	PPNCl	1650

Reaction condition, catalyst (0.01 mmol), CH_2Cl_2 (0.5 ml), propylene oxide (40 mmol) and onium salt (0.04 mmol),120°C, 10 bars, 1 h

4.5 Cobalt (III)/Lewis bases catalyst systems

In general, Shiff base complexes of transition metals are active catalysts for huge variety of reactions. As an example, the Co(III), Cr(III) and Al(III) salen complexes were found to be highly efficient catalysts for the preparation of cyclic carbonates or/and polycarbonates.[39,54] In this respect, a series of Co(III) bis(aldiminato) and bis(ketiminato) complexes were synthesized (see above). Although resembling the salen type complexes, unbridged bis(phenoxyiminato) cobalt complexes have not been so far reported for the activation of CO_2.

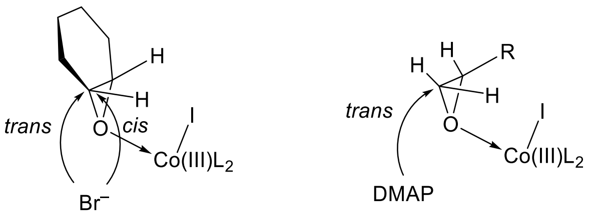
The unbridged bis(phenoxyiminato) Co(III) complexes in combination with tetrabutyl ammonium bromide (Bu_4NBr) or dimethylamino pyridine (DMAP) were studied for the coupling of CO_2 and *n*-hexyl oxide to form the corresponding cyclic carbonate. The Bu_4NBr and DMAP alone can also catalyze the coupling of CO_2 and epoxides, but their activities remained moderate in the absence of cobalt complexes. Both catalyst systems showed high catalytic activity and selectivity. Turnover numbers of up to 1500 were recorded. The catalysts (**4** and **7)** bearing the bis(ketiminato) ligands without tert-butyl substituents were slightly more active than the aldiminato complexes (Figure 10). In general, differences in the ligand substitution pattern of unbridged bis(phenoxyiminato) complexes did not have a great effect on catalytic activity on the DMAP catalyst system. This means that the coordination sphere in these unbridged catalyst precursors facilitates the efficient coupling reaction and the nature and size of ligand substituents in this series have only a minor influence on the course of the reaction. In addition, the solid structure obtained from complex **4e** reveals that DMAP coordination to cobalt center changes the coordination configuration of phenoxyimino ligands. The tetrahedral geometry of complex **4e**, where the phenoxyimino ligands lay on the same plane, resembles salen type structure of bis(phenoxyiminato) Co(III)×2 DMAP complex. This means that similar catalytic behavior can be expected in CO_2 activation reactions, mediated by bis(phenoxyiminato) Co(III) and salen type complexes.



1, R = Ph-, R^1 = H, R^2 =H
2, R = *p*-$(CH_3)C_6H_4$-, R^1 = H, R^2 =H
3, R = *p*-$(Cl)C_6H_4$-, R^1 = H, R^2 =H
4, R = $C_6H_5CH_2$-, R^1 = H, R^2 =CH_3
5, R = $C_6H_5CH_2$-, R^1 = H, R^2 =H
6, R = *p*-$(F)C_6H_4CH_2$-, R^1 = H, R^2 =H
7, R = $C_6H_5CH_2CH_2$-, R^1 = H, R^2 =CH_3
8, R = $C_6H_5CH_2CH_2$-, R^1 = H, R^2 =H
9, R = $C_6H_5CH_2CH_2$-, R^1 = *t*-Bu, R^2 =H

Figure 4. Catalytic activity of unbridged bis(phenoxyiminato) cobalt(III) complexes 1–9. Reaction condition,CO_2 10 bar , Co(III) 0.1 mol%, cocatalyst 0.6 mol%, CH_2Cl_2 0.5ml and n-hexyl oxide 2ml 1660 equiv

In addition to n-hexyl oxide, a range of terminal and cyclic epoxides were studied with complex **4** /DMAP and complex **4** /Bu_4NBr catalytic systems (see article II). The productivity of the Co(III)/BuN^+Br^- system was considerably higher than of that with DMAP, used instead. This could presumably be connected with higher mobility and nucleophilicity of a negatively charged Br^- anion, compared with relatively large and neutral DMAP molecules. The important role of the cocatalyst seems to be, among other functions, opening of the epoxide ring via nucleophilic attack on the least hindered carbon atom (Figure 11). Most probably, the function of the Lewis acidic Co(III) complex is activation of the epoxide ring via coordination with the epoxide oxygen atom, analogously to $CoCl_2$ species (see above). Due to the small steric size of the Br^- anion, it could be proposed that its nucleophilic attack on the nonplanar coordinated Co-epoxide species occurred with equal probability either from side of Co(III) complex (*cis*-attack) or from the other side of the ring (*trans*-attack) (Figure 11). Conversely, it could be suggested that large the DMAP nucleophile preferentially attacks the substrate from *trans*-side of the epoxide ring. For the cyclopentyl and cyclohexyl epoxides, this side is blocked by cycloalkyl ring. For these substrates the opening of the epoxide cycle, mediated by DMAP cocatalyst, appears to be energetically disfavored, leading to low catalytic activity of Co(III)/DMAP systems for these cyclopentyl and cyclohexyl epoxides .

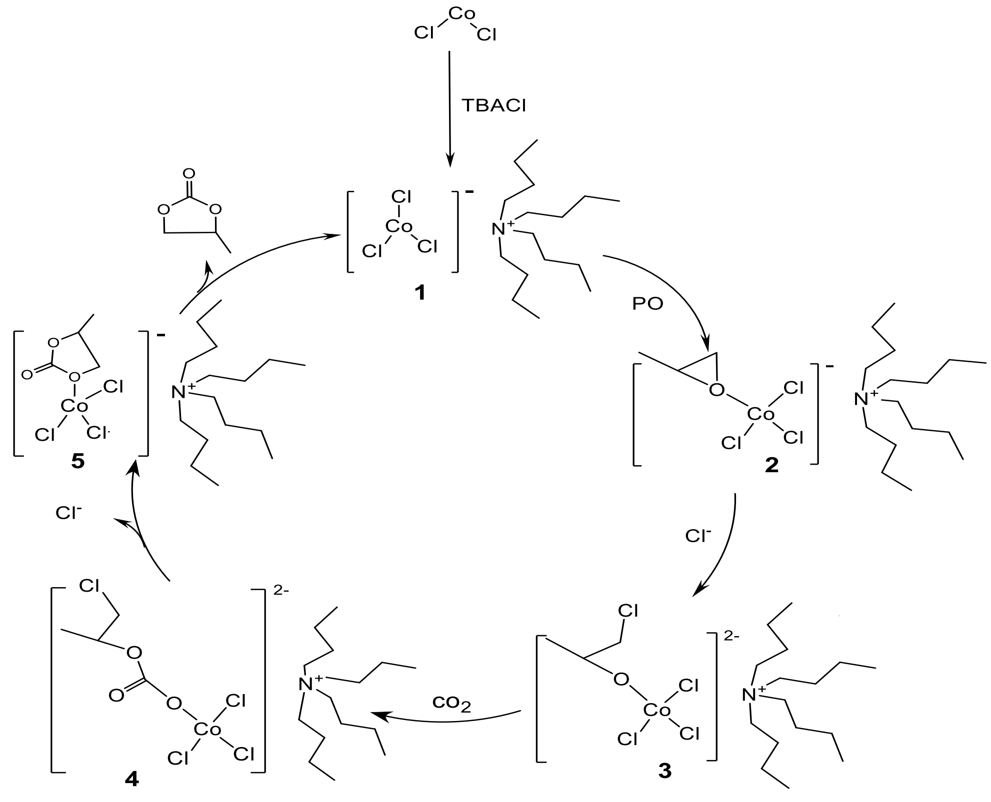


for Br^- - *cis* and *trans*   for DMAP - only *trans*

Figure 11. The possible Br^- and DMAP attacks routes on the activated epoxide

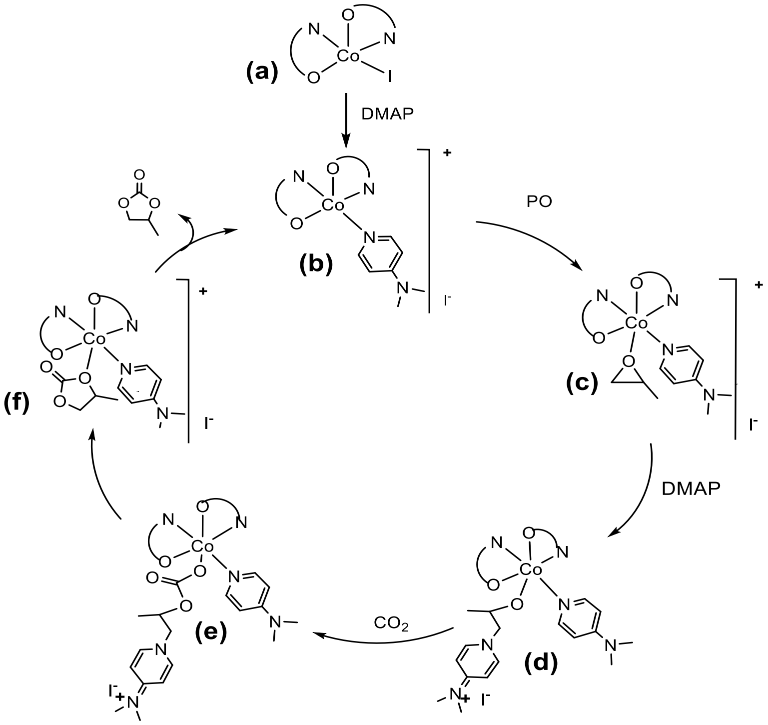
4.6 Mechanism of CO_2-epoxide coupling mediated by cobalt catalysts

In order to get an insight into the catalytic processes occurring with bis(phenoxyiminato) Co(III)/DMAP and $CoCl_2$/TBACl systems, they have been studied by electrospray ionization - mass spectrometry (ESI-MS). Upon treatment of $CoCl_2$ with TBACl, a new ion pair, $[TBA]^+[CoCl_3]$-, is formed. The corresponding anion, $CoCl_3^-$, has been detected in negative mode ESI-MS. From the reaction solution, another peak was observed and identified in the negative ESI-MS mode: $[CoCl_3 \cdot PO \cdot CO_2]^-$. These observable stable species are most probably a resting state of the catalyst and could be described as carbonate moiety coordinated with $CoCl_3^-$ group $[Co.PC]^-$ (Species 5). Formation of this complex in the reaction solution can be explained by the suggested mechanism shown on Scheme 13. According to this mechanism, generated $[CoCl_3]^-$ anion coordinates with propylene oxide via the Lewis acidic cobalt center to form the cobalt-epoxide complex **2**. A nucleophilic chloride anion from the external molecule of TBACl cocatalyst subsequently attacks the less hindered carbon atom of the Co-bound epoxide. This leads to the opening of epoxide ring and formation of reactive Co-alkoxy species **3**. This reaction pathway is supported by the fact that two equivalents of TBACl cocatalyst are required to obtain high yields of the cyclic carbonate product. The Co-alkoxy species **3** readily reacts with CO_2, leading to a linear Co-carbonate species **4**, which forms the cyclic product by intramolecular attack of the carbonate group (Scheme 15). The $[TBA]^+[CoCl_3]^-$ pair and Cl^- are recovered on this step, starting next catalytic cycle.



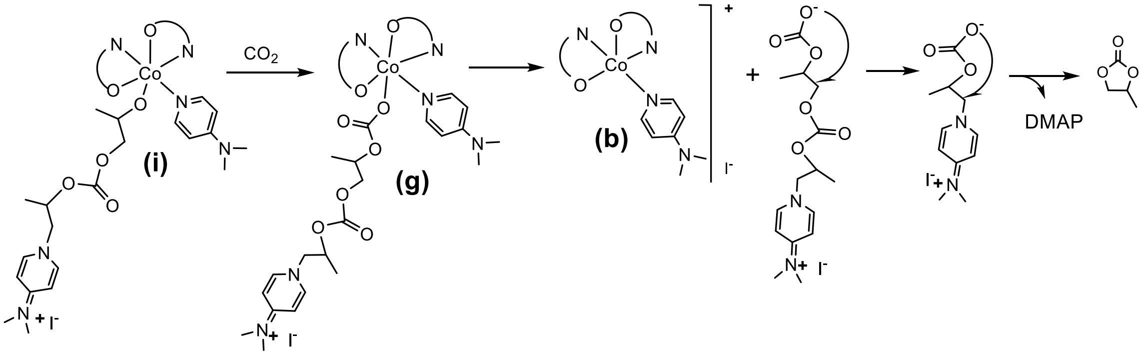
Scheme 15. The proposed reaction mechanism for $CoCl_2$/TBACl catalyst .

A solution of bis(phenoxyiminato) Co(III) complex **8** /DMAP catalytic system was treated with propylene oxide and maintained for 1 h under 10 bar of CO_2. The ESI-MS measurements revealed that the resulting solution contained, beside cyclic carbonate and the initial cobalt complex, various cobalt(III) cations, including [**8**+DMAP-I]$^+$ (**b**), [**8**+DMAP+PO-I]$^+$ (**c**), [**8**+2×DMAP+PO+CO_2-I]$^+$ (**e**), [**8**+DMAP+PO+CO_2-I]$^+$ **(f)**. These complexes were identified using high-resolution ESI-MS mode. The results show that under applied conditions the initial Co complex **8** may coordinate either one dimethylamino pyridine (DMAP) molecule (complex b) or propylene oxide (PO) together with DMAP (complex **c**), which led presumably to the dissociation of Co–I bond and shift of the iodide ion into outer coordination sphere. Activated by coordination with Co-center, epoxide substrate becomes susceptible to nucleophilic attack from an external DMAP molecule, giving the reactive Co-alkoxy species **d** (Scheme 16). Unfortunately, the species **(d)** were undetectable by ESI-MS. Insertion of CO_2 into the Co-alkoxide bond affords the carbonate intermediate complex **(e)**. Subsequent intramolecular cyclization of linear carbonate generates species **(f)**. Dissociation of the complex **f** provides free propylene carbonate and regenerates the catalytic species **(b)**.



Scheme 16. Proposed reaction mechanism for bis(phenoxyiminato) Co(III)/DMAP catalyst in PO/CO_2 cycloaddition reaction. PO: propylene oxide

Intriguingly, Co-complexes other than **a**-**f** were also identified. The presence of [**e**+PO] (**i**), [**e**+PO+CO_2] (**g**) were clear fingerprints that processes other than direct epoxide-CO_2 coupling occured during the reaction. The cyclic carbonate can be formed also from reversible depolymerisation of the growing linear polycarbonate chain by backbiting reaction. The nucleophilic carbonate end groups attack the nearest alkoxy carbon in the chain. During this process, the polymer chain may be either free or coordinated to the metal center (Scheme 17).



Scheme 17. Formation of propylene carbonate by depolymerisation

5 Summary

Due to its low cost, low toxicity and chemical stability, carbon dioxide is attracting growing attention as a potential source of organic compounds for industrial and scientific applications. Towards this end, numerous catalytic systems for the activation of CO_2 have been proposed. In the present work, we investigated phenoxyimino based metal complexes and combinations of onium salts with alkali carbonate bases for their catalytic activity towards chemical transformations with CO_2. We have found that unbridged phenoxyimino Co complexes in the presence of the DMAP base efficiently catalyze the coupling of CO_2 with epoxides under relatively mild conditions. This reaction selectively provides cyclic carbonates (important reagents and solvents for organic synthesis) with high yields. Moreover, new catalytic systems, consisting of cheap and nontoxic $CoCl_2$ together with onium salts display good catalytic activity for the same reaction. Although both catalytic systems operate by different mechanisms, high conversion rates and selectivity have been observed during the studies.

In all of the reported studies we have shown that cheap and simple, yet efficient catalysts can be synthesized and used for chemical transformation of CO_2. A variety of important organic reagents can be obtained by these reactions with high yields and selectivity. It is anticipated that such work will play a vital role in paving the way for further improvements in the cost and efficiency of catalytic systems for future use in industrial and scientific applications.

II- Oxidation of alcohols in water mediated by oxygen

1. Introduction

Selective oxidation of alcohols to the corresponding aldehydes and ketones is reaction of prime importance for organic synthesis. Various types of oxidation reagents have been described, providing carbonyl compounds from alcohols. [88] Traditionally, oxidation of alcohols is performed with stoichiometric amounts of inorganic oxidants, notably chromium(VI) reagents.[89,90] These oxidants are not only expensive, but also generate copious amounts of toxic heavy-metal waste. Abundant oxygen sources, such as dioxygen itself or hydrogen peroxide, can potentially be used as the stoichiometric oxidants in developing ecologically friendly protocols. The role of dioxygen in the oxidation reactions, particularly in catalytic oxidation of alcohol with copper/Tempo catalyst varies depending on the catalyst system. Its presence in the reaction assures the regeneration of the active species and extends the longevity of the catalyst. Oxygen can be reduced by four electrons and transformed into metal oxides (O^{2-}), hydroxides (OH^-) or water (H_2O). Usually, such reactions proceed irreversibly by cleavage of an oxygen-oxygen bond. In copper based catalysts, oxygen oxidizes Cu(I) to C(II) or regenerate TEMPO from TEMPOH in case TEMPO is present.

Many catalytic homogeneous systems which are active in oxygen-mediated oxidation are based on palladium, copper, or ruthenium compounds.[91,92,93,94] Moreover, the oxidation is often carried out in environmentally unfriendly solvents. Chlorinated hydrocarbons, toluene and acetonitrile are used as a typical reaction medium. As a consequence, new green technologies including a choice of reagents and solvents, are in high demand. If oxidation could be performed in water instead, it would be a considerably safer, cheaper, and more environmentally friendly method than many of the processes, which are used today. Despite many advantages of water as a reaction solvent, only few catalytic systems have been shown so far to operate in water.[95,96,97] Development of catalysts that are not only stable but also completely soluble in water is highly desirable.

In this part, we summarize the recent development in catalytic oxidation of alcohols with copper complexes with and without TEMPO including systems operating in water media. Mechanistic insights on copper/TEMPO catalyzed aerobic alcohol oxidation are reported.

2. Background

2.1. Copper Complexes as Catalysts for Oxidation of Alcohols

Various studies have been devoted to oxidation of alcohols to their corresponding aldehydes or ketones, using transition metal catalysts, mainly copper, cobalt, palladium and ruthenium, alone or in combination with stable nitroxyl free radicals.[98,99,100] Copper seems an appropriate metal for the catalytic oxidation of alcohols with O_2 since it is present in nature as the catalytic centre in a variety of enzymes (e.g. galactose oxidase) that catalyze this conversion. With copper catalysts, reversible oxidation is commonly provided by exploiting the Cu^{2+}/Cu^{+} couple. Cu(III) species are very rare exceptions as only a few copper(III) complexes have been isolated and their reactivity has been studied to a lesser extent, when compared with Cu(II) and Cu(I) derivatives.

In 1984, Semmelhack reported the first practical Cu-catalyzed aerobic oxidation of alcohols, using Cu in combination with the stable nitroxyl radical TEMPO (2,2,6,6-tetramethyl-1-piperidine-N-oxyl) in DMF as solvent;[101] However, this system was efficient only for activated primary alcohols. Markó and co-workers pioneered much in this field and in their initial report, a combination of CuCl (5 mol%), phenanthroline (5 mol%) and di-tert butylazodicarboxylate, DBAD (5 mol%) allowed oxidation of alcohols with great tolerance of other functional groups.[100,102,103] However, this system required the presence of 2 equivalents of a base (K_2CO_3) and was not consistent for the oxidation of primary aliphatic alcohols. Recently, Stahl et al. reported a new (bpy)Cu^{I}/TEMPO system which enabled, in the presence of NMI as the base and in CH_3CN as solvent, an efficient and selective aerobic oxidation of a broad scope of primary and secondary alcohols, excellent functional group tolerance and exquisite selectivities for 1° over 2° alcohols, allowing selective oxidation of diols without the need of protecting groups.[104,105,106]

Table 2. Selected examples from reported active catalysts systems for aerobic alcohol oxidation

Authors	Catalyst system	Substrate	Solvent	Temperature Pressure	Time (h)	Activity
Semmelhack [101]	CuCl/TEMPO	Activated and aliphatic primary alcohol	DMF	25°C/ bubbled O_2	4	94% yield
Sheldon [107,108]	bpy/$CuBr_2$/TEMPO/KO^tBu	Activated primary alcohol	CH_3CN/H_2O (2/1)	25°C/ ambient air	2.5	100% conversion
Koskinen [109]	bpy/$Cu(OTf)_2$/TEMPO/NMI or (DBU)	Activated and aliphatic primary alcohol	CH_3CN	25°C/ O_2 (ballon)	0.7	100% Conversion
Stahl[104]	bpy/CuOTf/TEMPO/NMI	Activated, aliphatic primary and secondary alcohols	CH_3CN	27°C/ 1atm O_2 or ambient air	3h	95% yield

2.2. Copper based Catalysts for Oxidation of Alcohols in water

Most of reported copper catalysts for oxidation of alcohols operate only in organic solvents. In general, the copper complexes are not all stable when water is present in the reaction media, whether as a solvent or as a co-product. Water can promote or cause the deactivation of the metal catalysts by competing with the substrate and/or intermediates for vacant coordination sites on the active metal catalysts. Only a few complexes are known to be catalytically active in water. In order to overcome the intolerance of Cu complexes to water, few catalysts were developed for the oxidation of alcohols in aqueous media.[110,111]Most popular water-soluble catalysts were developed for the oxidation of alcohols in water/organic solvent media. In this context, for example Sheldon and coworkers showed that $CuBr_2$ and TEMPO in the presence of 2,2′- bipyridine (bpy) as a ligand for Cu led to the oxidation of several primary alcohols with no overoxidation to carboxylic acids. The advantage of this very mild procedure was that excellent conversions were obtained with air (instead of pure oxygen) at room temperature.

Few copper catalyst systems have been reported using water as the only solvent, and dioxygen as the oxidant. In an alkaline water solution, our group has reported some of these catalysts namely copper complexes based on diamine type ligands such as N,N,N',N'-tetramethyl ethylenediamine (TMEDA), 9,10-diaminephenanthrene (DAPHEN), and 1,2-diaminocyclohexane (DACH) and on diimine type ligands such as 1,10-phenanthroline (phen) or bypirydine (bipy).[99,112] Although, these systems operate at 10bars and 80°C, they oxidize efficiently both the benzylic primary and secondary alcohols.

Other types of water-soluble catalysts for oxidation of alcohol involve the use of a suitable ligand with a hydrophilic functionality. In most cases such a ligand can be obtained by attaching a water-solubilizing group, e.g. a sulfonato or carboxylato group. The challenge with this type of system is the reversible tuning of the acid–base properties of the catalyst, which can enhance the activity/selectivity towards a certain product and/or reversibly change the hydrophilicity. Apart from their main catalytic function, these catalysts serve to maintain the pH within a certain range (i.e. possessing buffer properties). Accordingly, Pombeiro et al have developed a new water-soluble copper(II) complexes with functionalized azo derivatives of β-diketones (ADBs), which contain sites for possible pH regulation properties, in particular sulfo and amino groups. This catalyst oxidized benzylic alcohols giving moderate to good yields of benzylic aldehydes.[113]

Table 3. Selected examples from reported active catalysts systems for alcohol oxidation in water media

	Catalyst system	Substrate	Solvent	Temperature Pressure	Time h	activity
Sheldon[107]	bpy/$CuBr_2$/TEMPO/KO^{t}Bu	Activated and aliphatic primary alcohol	CH_3CN/H_2O (2/1)	25°C/ 1atm air	2.5	100% conversion
Repo[99,112]	phen/$CuSO_4$/TEMPO/NaOH	Activated primary alcohol	H_2O	80°C/ 10bars O_2	5	100% conversion
Pombeiro[113]	ADBs-Cu^{II}/TEMPO/K_2CO_3	Activated primary alcohol	H_2O	80°C/ 1atm air	6	68% yield

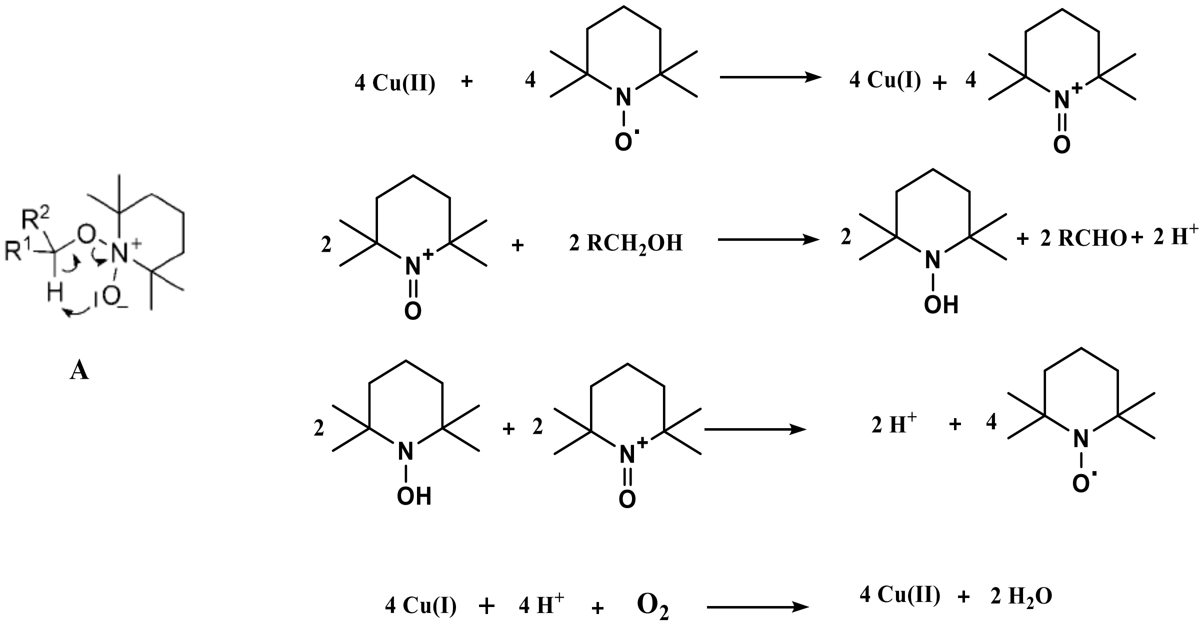
2.3. Mechanistic insight for TEMPO-Cu Catalysts Systems in Oxidation of Alcohol

There are many reports on the aerobic oxidation of alcohols using TEMPO and transition metals. In this regard, copper has been studied most intensively. The roles of TEMPO and copper in the reaction vary depending on the catalytic system. Copper may act as catalyst and TEMPO as an oxidant and vice versa. The reaction mechanisms of alcohol oxidation catalyzed by Cu^{II}-TEMPO may occur via different pathways. The catalytic cycle consists of two parts, namely, alcohol oxidation and TEMPO regeneration. For the alcohol oxidation, two mechanisms were proposed, i.e., Semmelhack's[101] mechanism (oxoammonium cation as the oxidant) and Sheldon's mechanism[107] (copper-centered oxidative dehydrogenation of the alcohol). Additionally, Koskinen et al[109] have proposed an alternative mechanism which supports the presence of an oxo intermediate species in the course of the reaction.

During the oxidation reaction, the TEMPOH is formed from TEMPO radical where its regeneration an important step to complete the catalytic cycle. Although the mechanistic part related to this step is not well developed, few reports investigated it via density functional theory (DFT) calculations[114] and studied the pH-dependency of TEMPO regeneration.

2.3.1. Semmelhack's mechanism

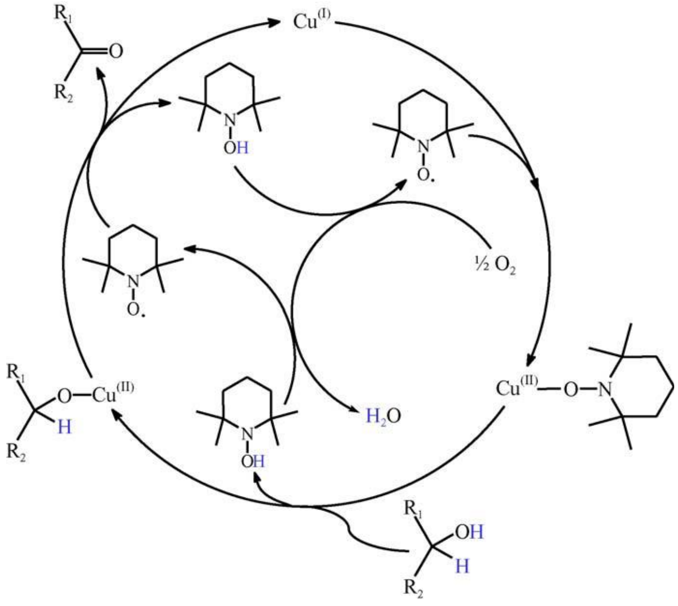
Two decades ago Semmelhack and coworkers reported the use of TEMPO in combination with cuprous chloride (CuCl) as a catalyst for the aerobic oxidation of benzylic and allylic alcohols.[101] They proposed a different role for the TEMPO in the catalytic cycle. Initially the TEMPO radical is oxidized to the oxoammonium ion by Cu(II) complex; then the oxoammonium ion serves as the catalytic oxidant and oxidizes the alcohol substrate via possible ionic transition state A to the corresponding carbonyl compound. During oxidation of alcohols, the oxoammonium ion itself is reduced to hydroxylamine; The oxidation of hydroxylamine with oxoammonium ion gives two TEMPO radicals which are again oxidized by Cu(II) to two oxoammonium ions. The Cu(II) is regenerated by the oxidation of Cu(I) with primary oxidant, oxygen, producing water as a byproduct which completes the catalytic cycle. The catalytic cycle is shown in Scheme 18. Aerobic oxidations with the copper-dependant enzyme laccase and TEMPO were suggested to follow this mechanism. This catalytic system allows smooth oxidation of a large variety of alcohols including aliphatic ones.



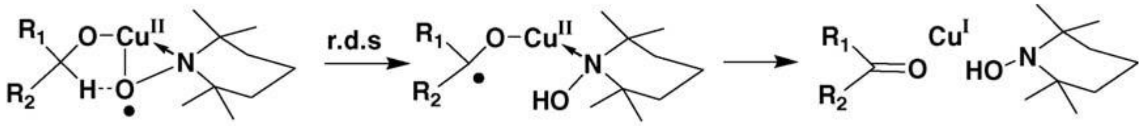
Scheme 18. Semmelhack mechanism for CuCl/TEMPO-catalyzed oxidation of alcohols[101]

2.3.2. Sheldon’s mechanism

Based on the results with the Ru/TEMPO system[115], Sheldon group have suspected that the Cu/TEMPO may involve a copper-centred oxidative dehydrogenation of the alcohol rather than an oxoammonium cation as the oxidant. Then they reinvestigated the mechanism of the original Semmelhack procedure by subjecting the Cu/TEMPO to the same mechanistic studies as with Ru/TEMPO system.[116] The results of stoichiometric experiments under anaerobic conditions, Hammett correlations and kinetic isotope effect studies showed a similar pattern to those with the Ru/TEMPO system, i.e., they are inconsistent with a mechanism involving an oxoammonium species as the active oxidant. Hence, they proposed the mechanism shown in Scheme 19 for Cu/TEMPO-catalyzed aerobic oxidation of alcohols. The active Cu(II)-species is generated via a one-electron oxidation of Cu(I) by TEMPO. Alkoxy replacement, followed by coordination of a second molecule of TEMPO affords the desired carbonyl compound, Cu(I) and TEMPOH. More precisely the key oxidation step involves intramolecular hydrogen abstraction within an alkoxycopper(II)/TEMPO complex, in which the TEMPO is coordinated in a η2 fashion, analogous to that in previously reported copper(II)-TEMPO complexes (Scheme 20).[116] This generates a coordinated ketyl radical anion and TEMPOH. Subsequently, inner sphere electron transfer affords Cu(I) and the carbonyl product (alternatively, these two steps could be a concerted process). Finally, TEMPOH is reoxidized to TEMPO by oxygen. This mechanism resembles that proposed for the aerobic oxidation of alcohols catalyzed by the copper-dependent enzyme, galactose oxidase, and mimics thereof. Finally, TEMPOH is reoxidized to TEMPO by oxygen.

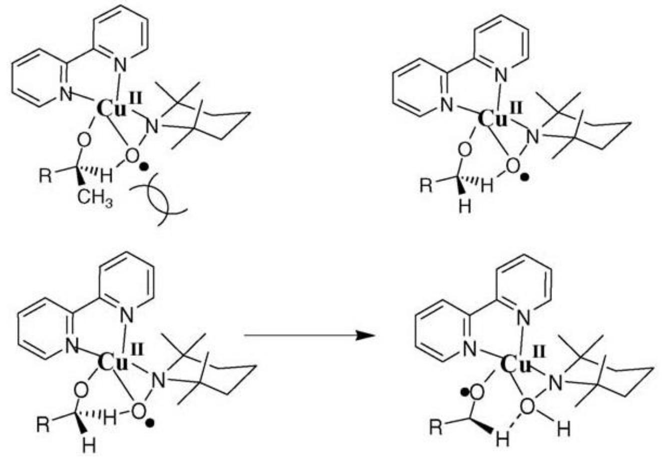


Scheme 19.Scheldon's proposed oxidation mechanism.[116]



Scheme 1: Postulated concerted mechanism for the β-hydrogen abstraction during oxidation of alcohols with TEMPO

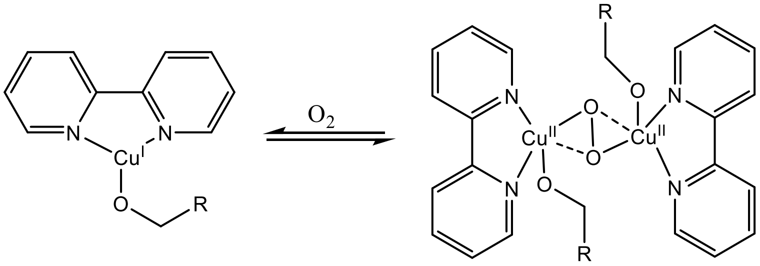
Later on, Sheldon’s group developed a new catalytic system using CuBr$_2$(2,2’-bipyridine)/TEMPO. In the presence of a base it catalyzes the aerobic oxidation of primary alcohols to aldehydes at room temperature. [117] This system showed a remarkable chemoselectivity for a primary versus secondary alcohol moiety. The lack of reactivity in secondary alcohol was explained on the basis of steric hindrance by the alkyl (methyl) group in the intramolecular hydrogen abstraction by the coordinated TEMPO ligand as depicted in Scheme 21. In addition, in the case of primary alcohols the second β-hydrogen atom can form a hydrogen bond with the oxygen atom of coordinated TEMPOH, thereby stabilizing the coordinated ketyl radical intermediate.



Scheme 21. Possible explanations for the lack of reactivity of secondary alcohols proposed by sheldon's group

2.3.3. Reaction mechanism via oxo-copper intermediates.

Contrary to the previous reported Copper–TEMPO systems which are considered to be mimetic to monocopper enzyme galactose oxidase (GO), Koskinen et al have envisioned an alternative mechanism involving the formation of different species, a binuclear oxo-copper complex as intermediates. The later is derived from a monomeric species in the presence of molecular oxygen (Scheme 22).

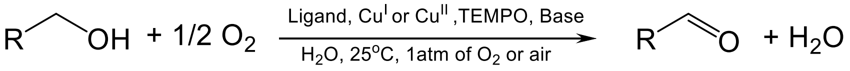


Scheme 22. Koskinen's proposed binuclear copper(II) complex

Recently Stahl‘s group have investigated closely the mechanism of Semmelhack’s[101] , Sheldon’s[107,116] and koskinen’s[109] catalyst systems beside his catalyst Cu^{I}OTf/bpy/NMI/TEMPO[104] in aerobic alcohol oxidation by in situ infrared spectroscopic studies of the reaction kinetics, together with electron paramagnetic resonance and UV-visible spectroscopic analysis of the reaction mixture. [118]The results of the investigation reveal that the rate acceleration observed with the use of a Cu^{I} source arises from *in situ* formation of a hydroxide base that promotes the key L_nCu^{II}-alkoxide intermediate. And when the Cu^{II} sources are employed, a suitable strong base must be used to deprotonate the alcohol to form Cu^{II}-alkoxide species. The overall mechanism of Cu^{I}OTf/bpy/NMI/TEMPO consists of two stage: (1) “catalyst oxidation” in which Cu^{I} and TEMPOH are oxidized By O_2 via a binuclear Cu_2O_2 intermediate and (2) “substrate oxidation” mediated by Cu^{II} and TEMPO radical via Cu^{II} – alkoxide intermediate. The study provides clear insights into the factors that differentiate the reactivity of benzylic and aliphatic alcohols. The reactivity of aliphatic alcohols is hindered relative to benzylic alcohols by the higher pKa of the hydroxyl group and the stonger α-C-H bond. Accordingly these factors contribute to a change in the identity of the catalyst resting state and the turnover-limiting step in the catalytic reaction: a Cu^{I} resting state prevails in the oxidation of the benzylic alcohol while a mixed Cu^{I}/Cu^{II} resting state is present during the oxidation of the less reactive aliphatics alcohols.

3. Results and Discussions

The aim of this work was the design and development of new copper catalysts for the aerobic oxidation of benzylic alcohols to aldehydes (Scheme 23). The main criterion for selection of an efficient catalytic system suitable for further detailed studies was their ability to provide high selectivity in oxidation reaction, carried out in aqueous medium with oxygen as the terminal oxidant.



Scheme 23. oxidation of alcohol to the corresponding aldehyde.

3.1 Ligands

Looking for replacements of classical bipyridine, phenanthroline and salen type ligands in catalytic systems, our attention was focused on imine scaffolds, such as 2-pyrrolecarbaldimine, phenoxyiminatopyridine, phenoxyiminatoquinoline, phenoxyiminato-amine and pyrrole-iminatopyridine ligands. These systems have a structure, which is intermediate between bipyridines and phenoxyimines, the latter being a substructure of classical salen-type frameworks. Although transition metal complexes of these monoanionic imine-based ligands have been known since the 1920s[119] and these chelates share common structural features with porphyrins, their catalytic properties have not been so far extensively studied. As one more advantage, the synthesis of these ligands is simple. In the bidentate 2-pyrrolecarbaldimine series, the ligands and the complexes can be formed by a simple 'one- pot' condensation reaction between pyrrole-2-carbaldehyde and the appropriate aniline derivative in the presence of a selected transition metal salt.[120] This reaction can even be carried out in water, which expands the scope of the reactions and underlines the inherent stability of the Cu(II) complexes.[121] Groups with electron-withdrawing and electron donating properties, as well as sterically bulky substituants were introduced into the ligand core, giving a broad variety of ligand structures. (Figure 12).

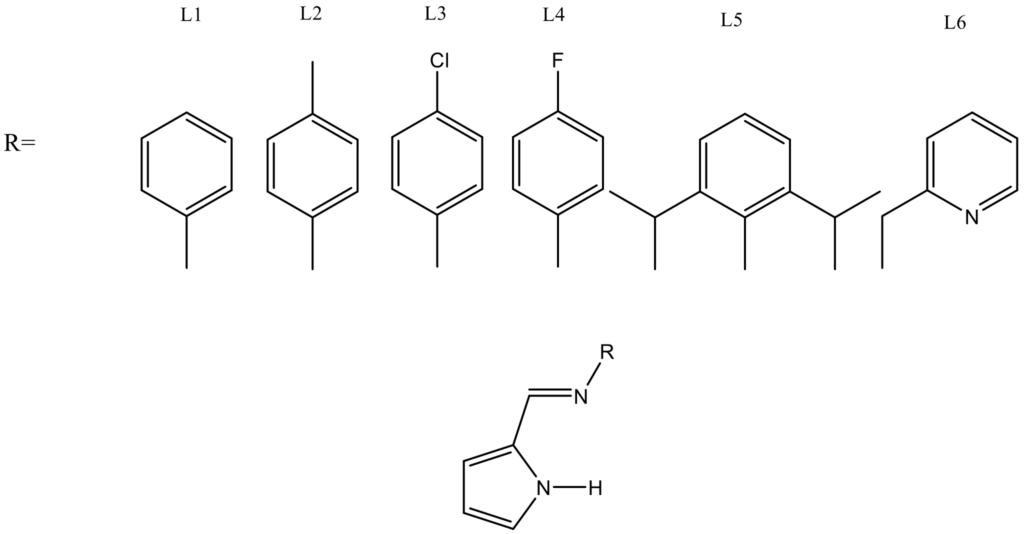
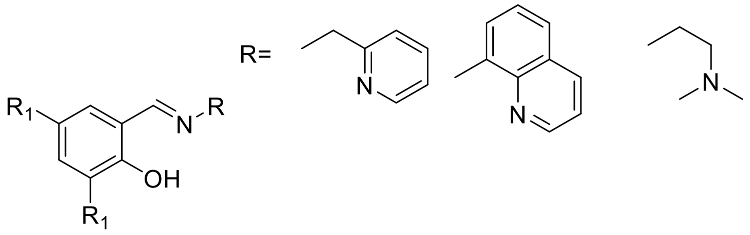


Figure 12. List of pyrrolecarbaldimine and pyrrole-iminatopyridine ligands

Tridentate structures were obtained through a classical imine condensation reaction in methanol between corresponding aldehyde and amines groups at room temperature. (Figure 13)



R_1=H	1a	2a	3a
R_1=Cl	1b	2b	3b
R_1=CH$(CH_3)_3$	1c	2c	3c

Figure 13. List of phenoxyiminoalkyl ligands

Similarly, the furane-based carbodimines (F1, F3) and the furryliminatopyridine (F2) were synthesized by reaction of furfuraldehyde with aniline derivatives and 2-pyridinemethaneamine respectively (Figure 14). These ligands in contrary to the previously listed are entirely neutral in term of coordination to metal center.

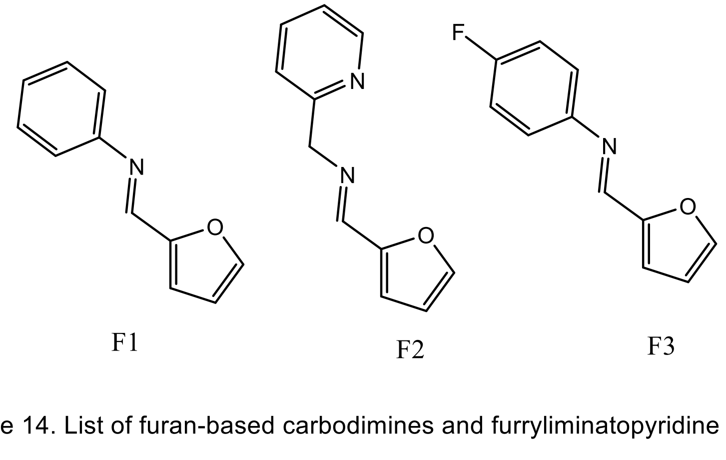
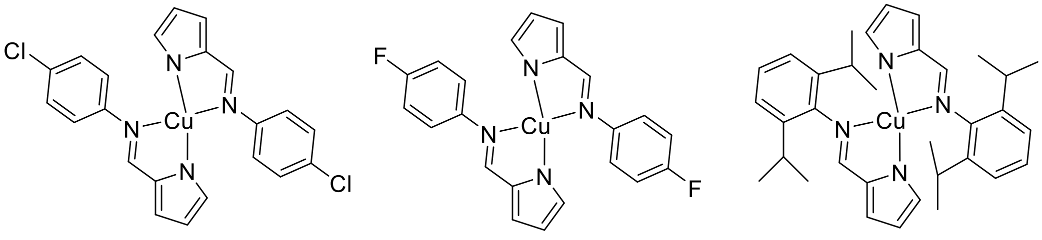


Figure 14. List of furan-based carbodimines and furryliminatopyridine ligands

3.2 - Synthesis of Cu- complexes

A variety of Cu-complexes have been obtained, which contain electron donating, electron-withdrawing or bulky steric groups in the vicinity of imine nitrogen. Complexes were synthesized by an addition of $CuSO_4$ to methanol solution of the appropriate ligand at room temperature. The complexes were characterized by elementary analysis and mass spectroscopy. To obtain detailed information about the bonding and coordination geometry, crystals suitable for structure determination by X-ray diffraction were grown from bilayered solvent systems by a slow evaporation method (See article III and figure 15). 2-*N*-arylpyrrolecarbaldiminato copper(II) complexes were synthesized by addition of aqueous solution of $CuSO_4$ to methanolic solution of 2-*N*-arylpyrrolecarbldiminate ligands .



Cu3 **Cu4** **Cu5**

Figure 15. List of the complexes to which crystal structures were obtained

3.3 Oxidation of alcohols experiment

Oxidation reactions were carried out in 25-mL, two-necked, round-bottom flasks equipped with condenser and connected to a balloon filled with O_2. Whereas, the experiments at atmospheric air pressure were carried out in test tube. In the *in situ* oxidation K_2CO_3 and $CuSO_4$ were mixed followed by an addition of TEMPO and the appropriate ligand. In the oxidation experiments with copper(II) complexes, an adequate amount of the complex was used. Reagents were stirred for 30-60 min prior to the addition of substrate for complex formation and pressure stabilization. The required reaction temperature was achieved using an oil bath. Reaction mixtures after the oxidation reaction were neutralized by 1M HCl, and then extracted by 10 mL of EtOAc. The organic phase was used for chromatographic analyses.

3.4 Oxidation of alcohols by Cu-complexes

Oxidation of benzyl alcohol was chosen as a model reaction to study the oxidation potential of the *in situ* and pre-made complexes. The reaction was carried out in alkaline water solutions using O_2 as the end oxidant. In the case of 2-N-arylpyrrolecarbaldiminato copper systems, both bases NaOH and K_2CO_3 have an equally beneficial influence on the catalytic activity. In phenoxyiminopyridine copper systems, K_2CO_3 gave surprisingly better results over NaOH. Therefore, K_2CO_3 was chosen for further studies, and the overall pH of the reaction mixture remains moderate. The role of the base is probably to activate the alcohol substrate by deprotonation. The resulting alcoholate group coordinates to the copper species, which facilitates further oxidation. In furfuryl copper(I) catalyst system, the used organic base methylimidazole (NMI) might coordinate to metal center as a ligand.

At harch conditions (80°C and 10 bars of O_2) all our copper systems have similar activity to the previously reported phenanthroline-based catalyst. However, contrary to already reported systems, they turned out to have also marked catalytic activity under atmospheric O_2 pressure and room temperature. In addition, the presence of TEMPO is essential to achieve high conversions of the substrate.

3.4.1 2-N-arylpyrrolecarbaldimino copper(II)

The oxidation reaction with *in situ* and pre-made 2-*N*-arylpyrrolecarbaldimino copper (II) complexes Cu1-Cu5 catalyst precursors was simultaneously followed by GC and dioxygen uptake measurements (article III). The *in situ* prepared 2-N-arylpyrrolecarbodimino Cu(II) catalysts provide highly efficient oxidation reactions, comparable to those catalyzed by the pre-made complexes (Table 4). With regard to the catalytic activity, the ligand substitutents in the phenyl ring had a substantial influence. The phenyl substituted complex Cu1 displayed moderate catalytic efficiency (45% conversion). The presence of either electron donating and electron withdrawing groups improve activity of the catalytic system, although in the case of electronegative substituents the observed effect is much more pronounced (Table 4). Whereas, in with the complex **2**, bearing *p*-methyl groups, the conversion reached 74%, the *p*-Cl and F substituted complexes **3** and **4**, respectively, showed very high productivity (up to 95% conversion). Complex 5 with the bulky 2,6-diisopropyl-substituted ligand is barely reactive (Figure 15). Presumably, this was due to steric interactions caused by the bulky ligand surrounding around the catalytically active copper (II) center.

Table 4. Oxidation of benzyl alcohol in water, mediated by TEMPO and copper (II) 2-N-aryl-pyrrolecarbaldimine complexes.

Run	Catalytic system	Conversion GC (%)	Total O_2 uptake (mmol)
1	Cu1	45	0.66
2	Cu2	74	0.91
3	Cu3	95	1.12
4	Cu4	99	1.20
5	Cu5	6	0.13
6	$CuSO_4$+**L1**	91	0.95
7	$CuSO_4$+**L2**	89	0.96
8	$CuSO_4$+**L3**	94	1.08
9	$CuSO_4$+**L4**	100	1.17
10	$CuSO_4$+**L5**	3	0.05
11[a]	$CuSO_4$+**L1**	2	0.08
12	$CuSO_4$	<1	0.02

Reaction conditions: :$CuSO_4$/Ligand : 1/2; 3 mmol of benzyl alcohol, 0.15 mmol of TEMPO, 0.03 mmol of $Cu(L)_2$, 80 °C, 1 atm O_2, 2 h, 0.1 M K_2CO_3 [a] Reaction without TEMPO.

Despite similar catalytic behavior of *in situ* and pre-made catalyst, they displayed significant differences in kinetics of the reaction (Figures 16 and 17). All *in situ* catalysts were rapidly activated and oxidations proceed with fairly similar rates, the halogenated ones remaining slightly more active. Interestingly, all pre-made and *in situ* systems are highly selective (>99%) according to GC-MS analyses.

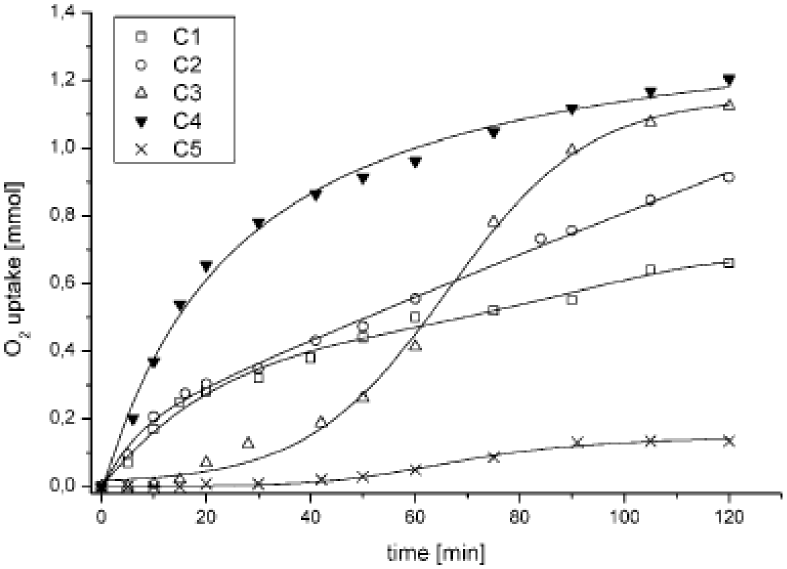


Figure 5. The activity of complexes 1–5 in the aerobic oxidation of benzyl alcohol

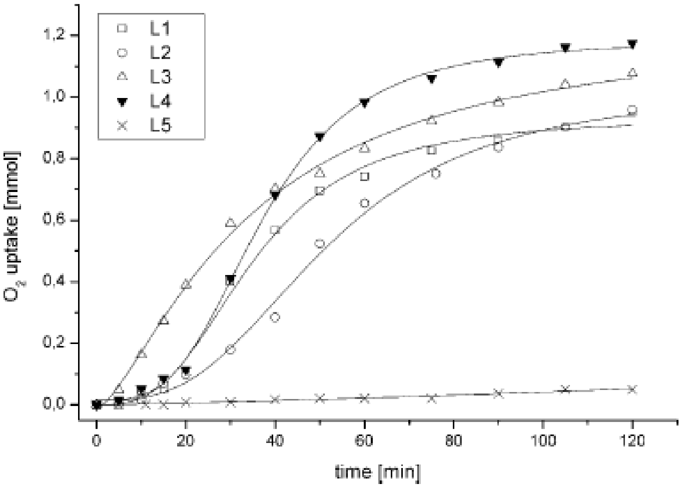


Figure 6. The activity of in situ prepared Cu(II) 2-N-arylpyrrolecarbaldimino complexes in the aerobic of benzyl alcohol.

The catalyst system with ligand L4 which gave the best activity compared to its analogues have been further studied at room temperature. The conversion of benzyl alcohol to benzyl aldehyde is relatively high. The system was investigated at different catalyst Cu/TEMPO ratio. The ratio 2:3 of Cu/TEMPO gave better result with 99% Conversion of benzyl alcohol. The use of air as oxidant at prolonged reaction time (5h) gave a moderate result due to the low concentration of molecular oxygen in it. When acetonitrile (CH_3CN) / water solvent mixture is used as reaction media, the activity drops by half in contrary to Sheldon catalyst copper(II) systems.[107] accordingly, the 2-N-arylpyrrolecarbaldimino copper(II) complexes operate efficiently only in aqueous media.

Table 5. The aerobic oxidation of benzyl alcohol to banzaldehyde with the catalyst Cu^{II} / ligand 4

Run	[Cu] Mol%	TEMPO Mol%	Time (h)	Oxidant	Solvent	Conversion GC (%)
1	1	5	3	O_2	H_20	96
2	2	2	3	O_2	H_20	92
3	2	3	3	O_2	H_20	99
4[a]	2	3	3	O_2	H_20	36
5	2	3	2	O_2	H_20	83
6	2	3	1	O_2	H_20	37
7	2	3	5	air	H_20	20
8[b]	1	5	3	O_2	H_20/CH_3CN	51
9[c]	1	5	3	O_2	H_20/CH_3CN	20

Conditions: $CuSO_4$ / L4: 1:2 , 3 mmol of substrate, 0.1M K_2CO_3 for,[a]Without base;
[b] solvent ratio H_2O/CH_3CN : 2/1; [c] solvent ratio H_2O/CH_3CN : 1/2.

3.4.2 Pyrroliminopyridine copper (II) catalyst

Similarly to 2-N-arylpyrrolecarbaldimino copper(II) catalyst system pyrroliminopyridine (L6) system operates efficiently and equally at high and room temperature. Oxidations were carried out in water with a 2 mol% load of catalyst, and a 2 mol% load of TEMPO. Benzyl alcohol is quantitatively oxidized at those conditions within 2-5h. In addition the reaction was very selective, as any products of overoxidation were not detected. Subsequently, air been tested as oxidant. An increase of temperature from 25°C to 80°C, results in no improvement of conversion from 18% to 16% (Table 6; runs 7 and 8). Nevertheless, the elevated concentration of dioxygen appear to be very important, since 1 atm of pure oxygen is enough to achieve a quantitave conversion up to 95% (vs. 18% with 1 atm of air) after 5 h reaction time (Table 6; runs 4 and 7).

Table 6. The aerobic oxidation of benzyl alcohol to banzaldehyde with the catalyst Cu^{II} / pyrroliminopyridine ligand

Run	[Cu] Mol%	TEMPO Mol%	Time (h)	Temperature (ºC)	Oxidant	Conversion GC (%)	Selectivity (%)
1	2	2	2	80	O_2	99	>99
2[a]	2	2	2	80	O_2	33	>99
3	1	5	2	80	O_2	96	>99
4	2	2	5	25	O_2	95	>99
5	1	5	5	25	O_2	98	>99
6	2,5	5	2	25	O_2	93	>99
7	2	2	5	25	air	18	>99
8	2	2	2	80	air	16	>99

Conditions: 3 mmol of substrate, 2 mol% of TEMPO, 2 mol% of $CuSO_4$ and 2 mol% of ligand, 0.05M K_2CO_3, 1atm of oxidant , [a] without base

3.4.3 Phenoxyiminoalkyl copper complexes

The phenoxyiminoalkyl ligands (Figure 11) rapidly coordinate with copper sulfate forming the corresponding copper complexes. The ligands contain electron- donating or electron-withdrawing groups attached to phenoxyiminato framework. On an imino side, these complexes beared pyridine, alkyl amine or rigid quinoline substituents. The catalytic oxidation of benzyl alcohol was studied with *in situ* and pre-made Cu complexes (manuscript IV). From the series of the tested ligands, the compounds **1c a**nd **3c** containing an electron- donating substituent were the most active in situ complexes (Figure 18). All the ligand with quinoline group displayed low activity which can be due to steric effects. For most of ligands, an introduction of electron-donating group into phenoxy-iminato framework led to the increased catalytic activity. The presence of flexible imino substituent provided analogous positive effect on activity of the catalyst. The flexibility of the ligand appeared to be an important factor to increase the activity of the catalyst. Based on these results the ligands 1c and 3c were selected for further studies.

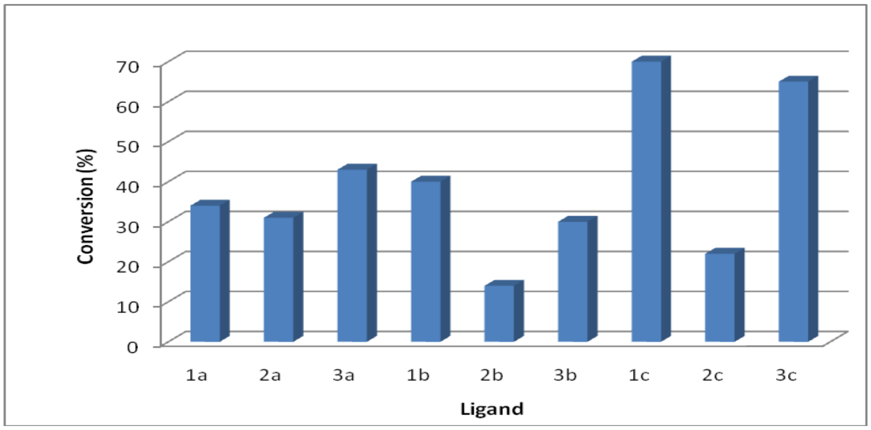


Figure 7. Oxidation of benzyl alcohol with in situ- Phenoxyiminoalkyl copper complexes
Reaction condition: 3 mmol benzyl alcohol, $CuSO_4$ and ligand (0.03 mmol, 1 mol%), TEMPO (0.15 mmol, 5mol%), 10 bars of O_2, 80 °C, 1 h, 3 ml of K_2CO_3 (0,25 M).

Applying prolonged reaction times, the *in situ* and the pre-made catalysts made from ligand 1c and 3c oxidized benzyl alcohol efficiently under 1atm oxygen pressure with high selectivity. Noteworthy, the *in situ* Cu/1c catalyst is highly reactive also at room temperature. However, at mild conditions, reaction required longer reaction time to achieve almost quantitative conversion. (Table7)

Table 7. The oxidation of benzyl alcohol to benzaldehyde with the catalyst Cu^{II} / ligand 1c and Cu^{II} /ligand 3c in aqueous media

Run	Catalyst system	Temperature (°C)	Time (/h)	Conversion (%)	Yield (%)	Selectivity (%)
1	$CuSO_4$/ 1c	80	2	70	67	>99
2	$CuSO_4$/ 1c	80	3	98	95	>99
3	$CuSO_4$/ 1c	25	3	65	60	>99
4	$CuSO_4$/ 1c	25	6	99	95	>99
5	CuS1c	80	3	96	93	>99
6	$CuSO_4$/ 3c	80	3	86	84	>99
7	$CuSO_4$/3c	80	4	99	96	>99
8	CuS3c	80	3	82	80	>99

Reaction conditions: 3 mmol of alcohol, $CuSO_4$ and ligand (0.03 mmol, 1 mol%), **CuS1c** and **CuS3c** (0.015 mmol, 0.5 mol%), TEMPO (0.15 mmol, 5mol%), 1atm of O_2, 80°C, 3 ml of K_2CO_3 (0.1M);

3.4.1 The furane-based iminoalkyl and iminopyridine copper(I) complexes

The discussed above new pyrroleiminopyridine and phenoxyiminoalkyl Cu(II)/TEMPO catalyst systems enables efficient aerobic oxidation of benzylic and allylic alcohols in water media. However, these complexes represent the overall limitation of the applied reaction mechanism and are not able to provide oxidation of very weakly acidic aliphatic alcohols (see detailed consideration of the reaction mechanism below). Recently, Stahl and coworkers published new Cu(I) systems, which overcome the limitations in the structure of substrates.[104] In their reaction setup, the rate determining step was not deprotonation of substrate (as in a typical Cu(II) setup), but oxidation of coordinated alkoholate anion, (see detailed mechanistic) discussion below. In order to mimic the Stahl catalysts and expand the scope of our iminopyridine ligands, we synthesized neutral iminopyridines F1, F2 and F3, where charged pyrrole or phenoxo parts were replaced with neutral furane moiety. First, these new ligands in the presence of Cu(II) salts were tested for the oxidation of benzyl alcohol at room temperature in water media. In the atmosphere of pure oxygen, the new catalyst systems showed moderate activity. The addition of acetonitrile to water improved a little the conversion of benzyl aldehyde, from 22% to 30 (Table 8). These preliminary results showed that furane-based copper complexes could catalyze oxidation of benzylic alcohols, but their catalytic behavior had to be improved. In the further step, components of the reaction setup were replaced accordingly to the work of Stahl *et al.*: Cu(II) salts with Cu(I) sources, oxygen with air, water with acetonitrile, K_2CO_3 with coordinating NMI (N-methylimidazol) base. These changes resulted in a remarkable boost for catalytic activity and expanding the scope of the reaction to alkyl alcohols (Table 10). In these new reaction conditions, generated *in situ* furane-based Cu(I)-iminopyridine complexes provided excellent catalytic activity regarding oxidation of wide range of alcoholic substrates.

Table 8. Aerobic oxidation of benzyl and octanol alcohols with copper and furane based ligands

Run	catalyst	[Cu] Mol%	TEMPO Mol%	Substrate	Base	Time (h)	Oxidant	Solvent	Conversion GC (%)
1	$CuSO_4$/F1	2	2	benzylalcohol	K_2CO_3	5	O_2	H_2O	64
2	$CuSO_4$/F3	2	2	benzylalcohol	K_2CO_3	5	O_2	H_2O	66
3	$CuSO_4$/F2	2	2	benzylalcohol	K_2CO_3	5	O_2	H_2O	46
4	$CuSO_4$/F1	2	2	benzylalcohol	K_2CO_3	5	air	H_2O	22
5	$CuSO_4$/F1	2	2	benzylalcohol	K_2CO_3	5	air	H_2O/CH_3CN	30
6	$CuSO_4$/F3	2	2	benzylalcohol	K_2CO_3	5	air	H_20	34
7	$CuSO_4$/F2	2	2	benzylalcohol	K_2CO_3	5	air	H_20	29
8	CuOTf/F1	5	5	benzylalcohol	NMI	2	air	CH3CN	100
9	CuOTf/F3	5	5	benzylalcohol	NMI	2	air	CH3CN	100
10	CuOTf /F2	5	5	benzylalcohol	NMI	2	air	CH3CN	96
11	CuBr/F3	5	5	benzylalcohol	NMI	1	air	CH_3CN	94
12	CuCl/F3	5	5	benzylalcohol	NMI	1	air	CH_3CN	97
13	CuI/F3	5	5	benzylalcohol	NMI	1	air	CH_3CN	77
14	CuOTf/F1	5	5	Octanol	NMI	22	air	CH_3CN	90
15	CuOTf /F3	5	5	Octanol	NMI	22	air	CH_3CN	94
16	CuOTf /F2	5	5	Octanol	NMI	22	air	CH_3CN	35

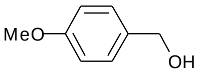
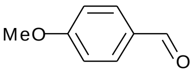
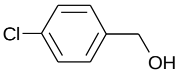
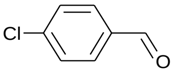
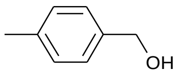
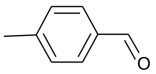
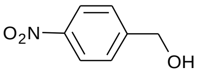
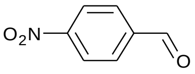
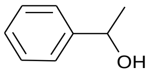
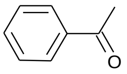
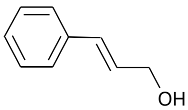
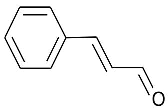
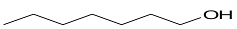
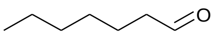
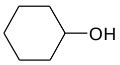
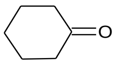
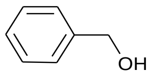
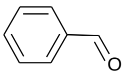
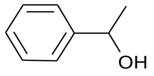
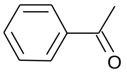
Reaction condition: Temperature 25°C, base NMI in acetonitrile or K_2CO_3 in water

3.5 Substrate Scope

In order to expand the scope of the aerobic oxidation, we performed aerobic oxidations of various alcoholic substrates for three catalyst systems. The results from two catalysts in water media are summarized in table 9 and the result from acetonitrile media are in table 10

Benzyl alcohol was almost quantitatively and selectively converted to benzaldehyde in a high yield (Table 9). Oxidation of electron-rich and electron neutral benzyl alcohols was faster and more efficient than those of electron-deficient ones (Table 9). In the presence of electron-withdrawing groups, the intermediate aryl radical is stabilized via extended delocalization of an unpaired electron over the substituted aryl framework. Consequently, formation of relatively stable radical intermediates decreases the ability of the alcohol substrate to oxidize. The conversions of primary benzylic and allylic alcohols to the corresponding carbonyl compounds were faster and more efficient. Compared to the rest, aliphatic alcohols reacted more slowly. The selectivity towards oxidation of benzylic and allylic alcohols is consistent with their weaker Cα-H bond strengths in comparison with those in aliphatic alcohols. No reactivity was observed for secondary aliphatic alcohol. This might be of great importance in synthetic organic chemistry, as possible way of selective reactions, when several alcoholic functions (primary and secondary) are present in the same molecule. Moreover, the conversion of secondary benzylic alcohol was slower than the primary benzylic alcohols, which might be attributed to the steric hindrance at the α-substituent.

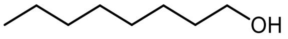
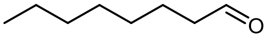
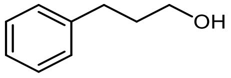
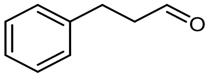
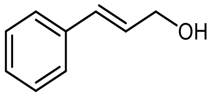
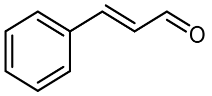
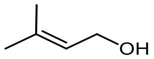
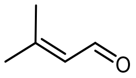
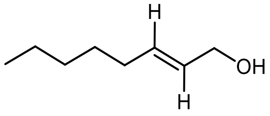
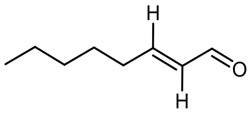
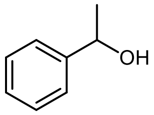
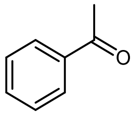
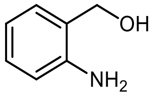
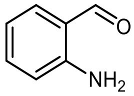
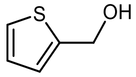
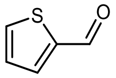
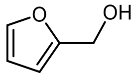
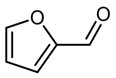
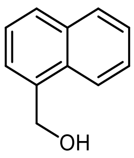
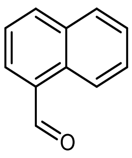
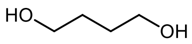
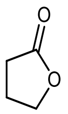
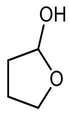
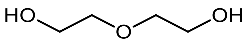
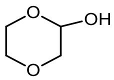
Table 9. Aerobic oxidations of various alcoholic substrates in aqueous media with Cu^{II} /the ligands pyrroliminopyridine (L6) and the ligand p-fluoroaryliminopyrrole (L4)

Run	Substrate	Product	Time (/h)	Conversion (%) Cu/L6	Conversion (%) Cu/L4
1			5 / 3	92	94
2			5 / 3	89	92
3			5 / 3	86	90
4			5 / 3	50	70
5			12	13	11
6			5	88	95
7			12	3	traces
8			12	-	-
9			3	70	91
	+				
			5	4	5

Reaction condition : Room temperature, 1atm of O_2 [in balloon], 0.05M K_2CO_3, 3 mmol of substrate, 2 mol% of TEMPO, 2 mol% of $CuSO_4$ and 2 mol% of ligand

To assess the potential scope of the *in situ* furane based copper(I) complex /TEMPO catalyst system, the oxidation of series benzylic, allylic, aliphatic and propargylic alcohols were examined; Good to excellent conversions were obtained. Functionalized alcohols also undergo facile oxidation to the corresponding aldehydes. Alcohols with oxygen– and sulfur containing heterocycles, as well as alcohols with an unprotected aniline undergo efficient oxidation with excellent conversions. Some alcohols (Table 10; runs 6 and 12) did not reach completion within 12h at ambient temperature, might require higher temperature or prolonged reaction time.

Table 10. Aerobic oxidation of different substrates of alcohols with Cu^{I}/ ligand F3

Run	Substrate	Product	Time (h)	Conversion (%)
1			22	95
2			5	50
3			2	100
4			2	100
5			2	100
6			12	36
7			2	100
8			2	100
9			2	100
10			2	100
11		 	12	58 30
12			12	36

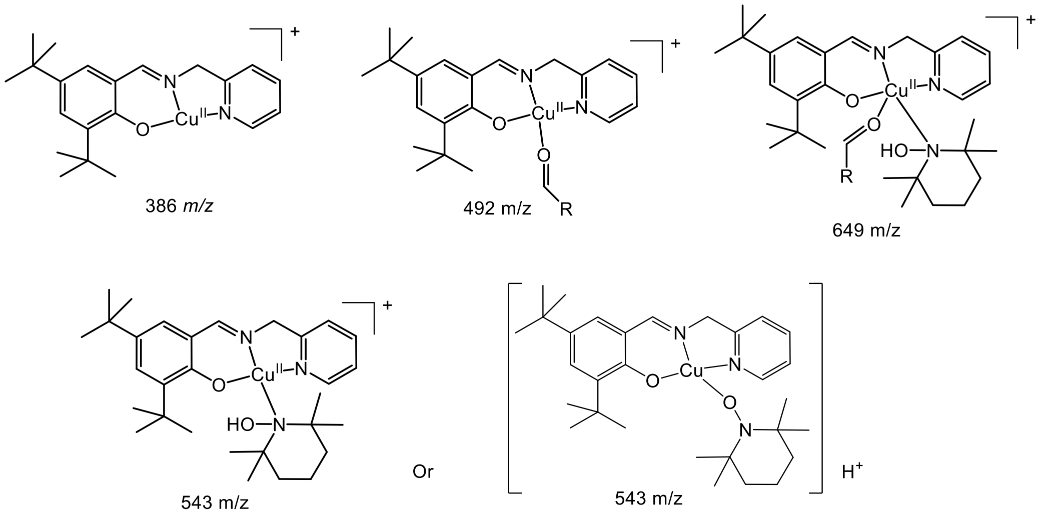
Reaction condition : Room temperature, open air , NMI , 1 mmol of substrate, 5 mol% of TEMPO, 5 mol% of $CuSO_4$ and 5 mol% of ligand , base NMI 5 mol%.

3.6 Reaction mechanism

The electrospray ionisation - mass spectrometry (ESI-MS) is an attractive analytic method for the characterization of organometallic compounds. This relatively soft ionization method provides a great possibility to investigate directly the metals complexes and the reaction intermediates species if detectible. The remarkable ability of electrospray to transfer ionic species from a sample solution to the gas phase was found useful to investigate the composition of reaction mixture. In order to have an insight to the catalytic process, actual reaction mixtures from each studied catalytic system was subjected to (ESI-MS). The samples from the reaction mixture were diluted with the appropriate solvent. They contained the Cu complex, base, TEMPO, benzyl alcohol and exposed to oxygen.

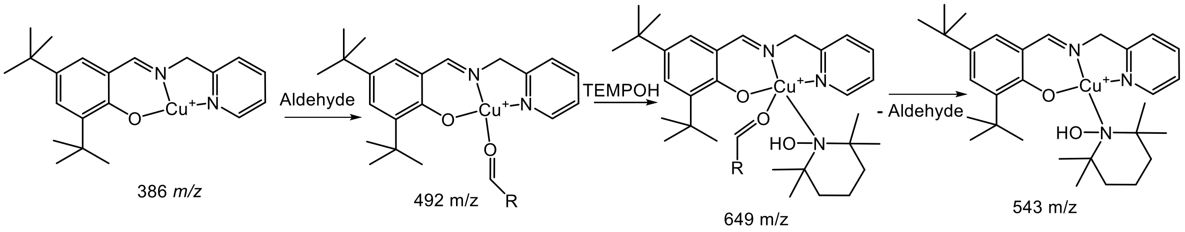
For 2-N-arylpyrrolecarbaldimino copper(II) catalyst, the combination of ESI-MS and UV-visible measurements showed the presence of Cu^{I} and Cu^{II} species. Copper complex with only one ligand and increasing amounts of the carbonate adducts with potassium, sodium and hydrogen cations, were observed in ESI-MS besides the dominating peak patterns of potassium carbonate clusters. Such peak pattern was common during the electrospray ionization measurements. Accordingly, the ligand-complex dissociation generates two coordination sites to Cu^{II} metal center. Subsequently, the deprotonated alcohol substrate might coordinate to generate LCu^{II}-alkoxide species. This step seems to be important in the oxidation reaction.The oxidation results above show higher activity for the p-Cl and the p-F substituted complexes compared to those bearing phenyl and p-Me substituents. Considering the ligand dissociation in alkaline solutions as a key transformation to generate the catalytic active species, the differences in catalytic activity can be rationalized. Electron-withdrawing p-F and p-Cl substituents in Cu3 and Cu4 weaken the coordination of the imine moiety to the Cu center and thus should promote the ligand dissociation and their catalytic activity. For, the mechanistic reaction of this catalyst system resembles the one with the phenoxyiminopyridine copper(II) system(see the mechanism proposal of phenoxyiminopyridine copper(II)).

The phenoxyiminopyridine copper(II), the pyrroliminopyridine copper(II) and the 2-N-arylpyrrolecarbaldimino copper(II) in the presence of TEMPO operating in alkaline aqueous media are similar catalyst system in term of activity and the configuration of the ligand; all of them might have the same mechanism. Only the phenoxyiminopyridine copper catalyst system will be discussed and the reaction mechanism will be generated on the rest (manuscript IV). The measured mass spectrum revealed several peaks related to the *in situ* formed phenoxyiminopyridine copper (II) complexes. The major peaks in the solution were at 386, 492, 543, 649 m/z, which corresponded to the copper cations $[LCu]^+$, $[LCu+TEMPOH]^+$, $[LCu+TEMPOH+RCHO]^+$, $[LCu+RCHO]^+$, respectively. Identities of those peaks were verified by the high-resolution mode (Scheme 24).



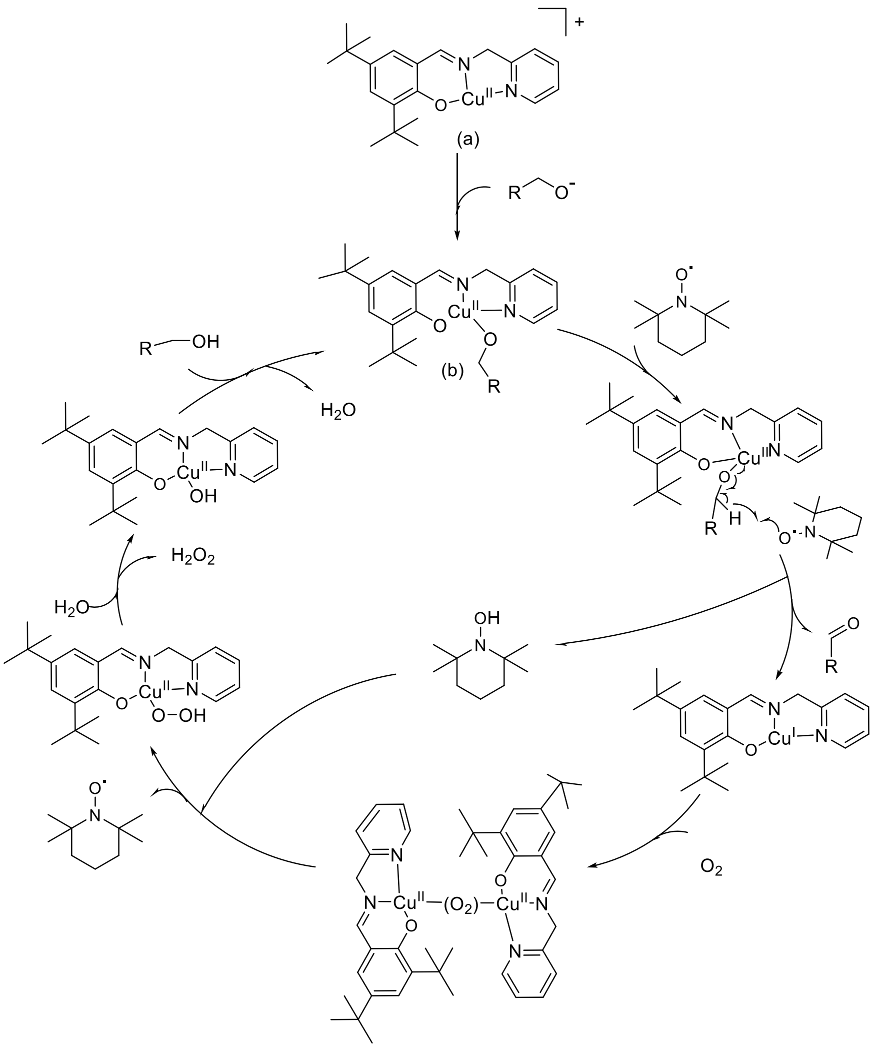
Scheme 24. The identified complexes by ESI-MS

The detected species by ESI–MS are not necessarily actives catalyst species and might be only species in resting state. But their presence can be explained. In the reaction mixture, there is among other components, the complex Cu^{II}, the formed aldehyde and TEMPOH. The aldehyde and TEMPOH coordinate to metal center in Cu^{II} complex to generate the detected species (Scheme 25).



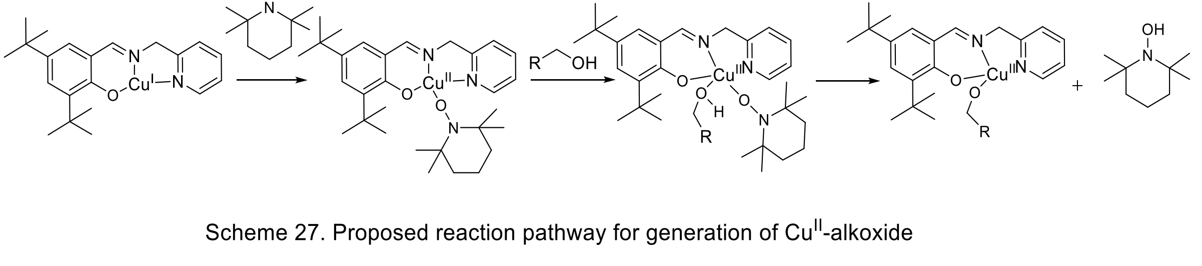
Scheme 25. Proposed pathway with the detected species by ESI-MS

The catalytic oxidation can proceed with similar mechanism as previously proposed for other Cu^{II}/TEMPO catalysts in some extent. The majority of the proposed reaction mechanism were studied in organic solvent generally acetonitrile which is not our case. In alkaline condition, the benzyl alcohol is deprotonated and the resulting alcoholate coordinates to the Cu^{II} center to form Cu^{II}-alkoxide species. Then TEMPO approaches this species and abstracts H-atom en α-C–H alkoxide moiety to form TEMPOH and the corresponding aldehyde. The resulting Cu^{I} complex is oxidized by molecular dioxygen to provid a peroxo-bridged binuclear Cu^{II} species Cu_2O_2. The formed copper species Cu_2O_2 oxidized TEMPOH to TEMPO and generates Cu^{I} and Cu^{II}-OOH species. The Cu^{II}-OOH complex reacts with water to form Cu^{II}-OH and hydrogen peroxide H_2O_2. Under the reaction condition, H_2O_2 decomposes to H_2O and O_2. The Cu^{II}-OH reacts with benzyl alcohol to generate back the Cu^{II}-alkoxide complex. (See scheme 26)



Scheme 26. Proposed mechanism for oxidation of benzyl alcohol to benzyl aldehyde with phenoxyiminopyridine copper (II) and TEMPO in aqueous media

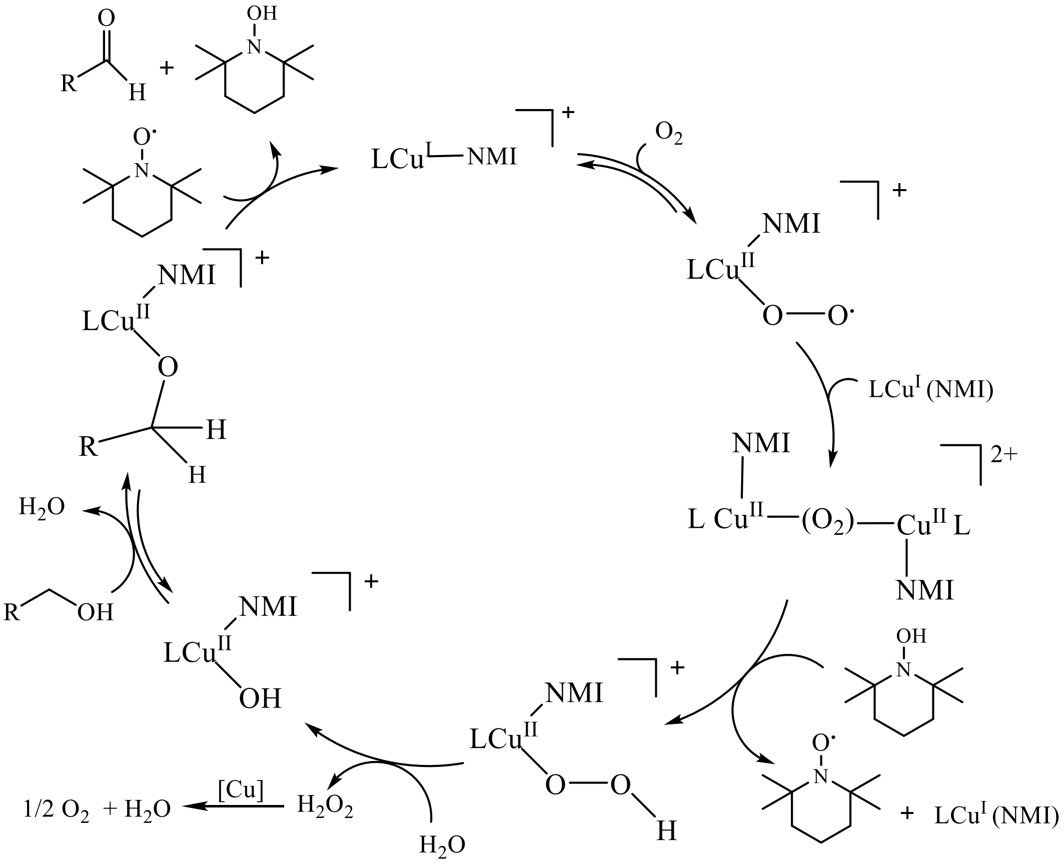
The Cu^{II}-alkoxide species might be also generated by different reaction pathway; the formed Cu^{I} species in the reaction is oxidized with TEMPO to generate Cu^{II}-TEMPO adduct complex. An alcohol substrate coordination to Cu^{II}-TEMPO leads to intramolecular proton abstraction by TEMPO and forms Cu^{II}-alkoxide and TEMPOH (Scheme 27).



Scheme 27. Proposed reaction pathway for generation of Cu^{II}-alkoxide

The limitation of the substrate is not consistent with an oxoammonium mechanism since oxoammonium cations are known to have a broad scope, including the facile oxidation of secondary aliphatic alcohols.

As mentioned earlier the *in situ* furane based copper (I)/TEMPO/NMI is similar to Stahl catalyst system (Scheme 28). The Cu^{I} salt coordinates to the ligand and to methylimidazol (NMI) to form the complex $[LCu^{I}(NMI)]^{+}$.The resulting complex reacts with O_2 to affords a Cu^{II} –superoxide species, followed by reaction with a second complex Cu^{I} center to generate a peroxo-bridged binuclear Cu^{II} species Cu_2O_2. The structure of the Cu_2O_2 is not known. The Cu_2O_2 species oxidize TEMPOH to TEMPO via H-atom transfer, forming a Cu^{II}–OOH species and a Cu^{I} as byproducts. Cu_2O_2–mediated abstraction of a hydrogen atom from O–H bonds, including TEMPO-H, to afford oxyl radicals is known. The oxidation of Cu^{I} to Cu^{II} by O_2 does not require TEMPOH; however TEMPOH is required to achieve kinetically competent rate. At the start of the reaction, when no TEMPOH is available, the alcohol substrate might react with the Cu_2O_2 species to afford Cu^{II}–OOH and Cu-OCH_2R species. Subsequent reaction of Cu^{II}–OOH intermediate with water (or the alcohol substrate) will release H_2O_2 and affords Cu^{II}–OH (or Cu^{II}–OCH_2R) species. H_2O_2 undergoes rapid disproportionation under the catalytic conditions. H_2O_2 disproportionation by Cu^{I} complex has reported previously. Then H_2O_2 is not viable oxidant for this reaction and would not accumulate, if formed as a byproduct of the reaction. The alcohol substrate is oxidized by Cu^{II} species and TEMPO. It proceeds via preequilibrium formation of a Cu^{II}–alkoxide, followed by H-atom abstraction by TEMPO.
Formation of the aldehyde from Cu^{II}-alkoxide intermediate consists of a two–electron / one–proton process in which Cu^{II} and TEMPO work in concert. Stahl‘s kinetic data were consistent with a bimolecular reaction between TEMPO and Cu^{II}–alkoxide, which contrasts previous mechanistic proposals that invoke H-atom abstraction from TEMPO–Cu^{II} adduct.



Scheme 28. Proposed reaction mechanism for aerobic oxidation of alcohol to aldehyde with *in situ* formed furan-based copper (I) in acetonitrile

The oxidation of aliphatic alcohols were a veritable challenge for Cu/TEMPO and related catalyst systems in water media. Aliphatic alcohols have O–H bonds with pK_a values ~ 2 units higher than those of benzylic alcohols, a property that will significantly hinder formation of the Cu–alkoxide intermediate. Moreover, their α-C–H bonds are 8- 10kcal mol^{-1} stronger than those of benzylic alcohols ($E_{\alpha\text{-C–H aliphatic}}$ ~93 kcal mol^{-1}; $E_{\alpha\text{-C–H benzylic}}$ ~83-85 kcal mol^{-1}). The more challenging oxidation of aliphatic alcohols is manifested in the differences between the catalytic rate laws for the two kind of substrates benzylic and aliphatic. With benzyl alcohol, the substrate oxidation steps are sufficiently facile that the rate is controlled exclusively by the oxidation of Cu^{I} by O_2. In the oxidation of aliphatic alcohol, two steps contribute to the turnover rate: the formation of Cu^{II}–alkoxide (deprotonation of aliphatic alcohol with the base in water media) and the abstraction of H-atom by TEMPO. The energy bond of O–H in

TEMPO–H is only ~ 71 kcal mol^{-1} which is considerably lower than the energy bond α-C–H of the alcohol substrate. Thus, the α-C–H bond must be significantly weakened upon formation of the Cu^{II}–alkoxide.

The development of our catalyst systems highlighted the high chemoselectivity for primary over secondary alcohols. This selectivity most likely reflects strong steric effects on the bimolecular reaction between TEMPO and the Cu^{II}–alkoxide; however, the slightly higher pK_a of secondary alcohols also should contribute to the difference in reactivity (ΔpK_a(2°-1°)~ 1).

4 SUMMARY

Oxidation of alcohols into aldehydes and ketones is an important process for preparative organic chemistry and industrial applications. Among used oxidants, oxygen is an abundant, cheap and environmentally friendly reagent. In the present part of work, we studied aerobic oxidation of benzylic and aliphatic alcohols by oxygen in the presence of a Cu-complexes and TEMPO. It was discovered that Cu-complexes having pyrrole-imine, phenoxy-imine or furane-imine ligands exhibit high catalytic activity for these reactions. In the presence of the TEMPO cocatalyst and an alkali carbonate base or organic base, a series of benzylic, allylic and aliphatic alcohols were transformed into corresponding aldehyde products with high conversion values.

Depending on the copper/TEMPO catalyst system in term of copper oxidation state, type of base and the solvent, the reaction mechanism is different with the common step as the formation of LCu^{II}-OH species which serve as actual catalytic species.

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